PROPAGATORS IN QUANTUM CHEMISTRY

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Second Edition

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Chapter 1

Introduction

This text has grown out of the monograph *"Propagators in Quantum Chemistry"* by J. Linderberg and Y. Öhrn, Academic Press, London, 1973, which has been out of print for some time. The content is revised to take into account some of the considerable literature in the intervening years by many workers in the field. However, this is not intended as a review of the theory and application of propagators, but rather an attempt to present the theory and the basic approximations in a unified manner with some illustrative applications. The material is presented from our own perspective, and we apologize for any omissions of references to important work in the field.

Propagators gained early prominence in formal many-body theory of fermion systems[1]. Concerns about the elimination of unlinked terms in the perturbation expansions and the associated correct scaling with systems size naturally led to the propagator concept. Treatment of double-time Green's functions (propagators)[2] established that they provide an important and useful link between pure state quantum mechanics at the absolute zero of temperature and quantum statistical mechanics employing ensembles at finite temperature. Condensed matter theory employed the propagator concept to great advantage[3]. Recent advances in computational techniques and power of electronic computers have led to numerous successful applications of approximate propagator theory for so-called quasiparticle calculations in solids [4]. Propagator theory for finite systems led to new ideas in the theory of molecular electronic spectra[5].

Computer codes were developed, and *ab initio* calculations were carried out primarily for a great variety of electronic spectra and properties of molecular systems, in particular, implementing the theory of the electron and the po-

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[1] see P. Nozière, *Theory of Interacting Fermion Systems*, W. A. Benjamin Inc., New York, 1964

[2] see D. N. Zubarev, *Soviet Physics Uspekhi* **3**, 320 (1960)

[3] see L. Hedin and S. Lundqvist, *Solid State Physics* **23**, 1 (1969) and references therein

[4] see W. G. Aulbur, L. Jönsson, and J. W. Wilkins, *Solid State Physics* **54**, 1 (2000)

[5] see Y. Öhrn and J. Linderberg, *Phys Rev.* **139**, A1063 (1965), and J. Linderberg and Y. Öhrn, *Proc. Roy. Soc.* (London) **A285**, 445 (1965); *Chem. Phys. Letters* **1**, 295 (1967)

larization propagators[6]. Also, reviews were written[7], as well as an important monograph by P. Jørgensen and J. Simons[8].

In recent years there has been many applications of the electron and the polarization propagators to a great variety of problems concerned with molecular properties and spectra, demonstrating the importance and usefulness of propagators to the understanding of experimental results. Stationary states, which is the focus of traditional electronic structure theory cannot, strictly speaking, be observed as such through experiments, since every observation involves a probing of the system with some external perturbation. The response of the molecular system to such probing and the associated influence on the probe are directly involved in the measuring process. A theoretical analysis, which focuses on the determination of observable quantities, naturally leads to the study of propagators as a key concept. This view was pioneered by Richard P. Feynman in his path integral approach to quantum mechanics, and propagators are theoretical tools commonly used in physics.

In spite of their demonstrated power and success, propagators are not yet widely accepted tools in theoretical chemistry. This may have to do with the tendency on the part of all but a few quantum chemists to focus almost exclusively on the running of generally available computer codes, which employs traditional and well-worn concepts, and applying them to new chemistry problems. There is also a certain reluctance to struggle with new theoretical concepts, no matter how powerful they may be. There are notable exceptions, however, and particularly the work of J. V. Ortiz shows great promise [9]. He uses the electron propagator to achieve correlated treatments of molecular electronic structure and spectra while still preserving the chemically useful orbital concept. This approach is available for applications through the ubiquitous Gaussian program system.

This text is written with the graduate student or researcher in mind, who is already familiar with atomic and molecular quantum theory and with elementary statistical physics. The choice of topics reflects the personal tastes of the authors. Problems are introduced throughout the text to give the reader an opportunity to work out further details and applications of the theory.

Special thanks go to Dr. Remigio Cabrera-Trujillo who has provided the expertise and help to convert text files from outdated formats to .tex files that can be easily edited and merged into a book format.

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[6] see *e.g.* G. D. Purvis and Y. Öhrn, *J. Chem Phys.* **60**, 4063 (1974); *J. Chem Phys.* **62**, 2045 (1974); L. S. Cederbaum, *Theor. Chim. Acta* **31**, 239 (1973); *Mol. Phys.* **26**, 1405 (1973); J. Simons and W. D. Smith, *J. Chem. Phys.* **58**, 4899 (1973)

[7] see G. Csanak, H. S. Taylor, and R. Yaris, in *Advances in Atomic and Molecular Physics* **7**, 287 (1971), Editors D. R. Bates and I. Esterman; P. Jørgensen, *Annual Reviews of Physical Chemistry*, **26**, 359 (1975); L. S. Cederbaum and W. Domcke, in *Advances in Chemical Physics* **36**, 205 (1977), Editors I. Prigogine and S. A. Rice; J. Oddershede, *Advances in Quantum Chemistry* **11**, 275 (1978); Y. Öhrn and G. Born, *Advances in Quantum Chemistry* **13**, 1 (1981)

[8] P. Jørgensen and J. Simons, *Second Quantization-Based Methods in Quantum Chemistry*, Academic Press, New York, 1981

[9] see, for instance, J. V. Ortiz,*J. Phys. Chem. A* **106**, 5924 (2002), and references therein

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Chapter 2

Differential Equations and Green's Functions

Consider a homogeneous differential equation in one dimension on $a \leq x \leq b$

$$\left[E + \frac{1}{2}\frac{d^2}{dx^2} - V(x)\right]\Phi(x) = 0. \tag{2.1}$$

In the study of stationary states in quantum chemistry, one would normally introduce boundary conditions, as for instance, $\Phi(a) = \Phi(b) = 0$ and solve the resulting eigenvalue problem. Solutions occur only for certain values of $E = \epsilon_n$, so-called eigenvalues, and the corresponding solutions $\Phi_n(x)$ are called eigenfunctions.

Example 1: Particle in a box, *i.e.*,

$$V(x) = \begin{cases} 0 & a < x < b \\ \infty & x \leq a,\ x \geq b, \end{cases} \tag{2.2}$$

and for a = 0, the solutions $\Phi_n(x) = \sqrt{\frac{2}{b}}\sin\frac{n\pi}{b}x$, $\epsilon_n = \frac{\pi^2 n^2}{2b^2}$ are obtained.

Example 2: Harmonic oscillator, *i.e.*,

$$V(x) = \frac{1}{2}kx^2 \qquad \text{and} \qquad a = -\infty, b = +\infty, \tag{2.3}$$

with the solutions $\Phi_n(x) = A\exp\left[-\alpha x^2\right] H_n\left(\sqrt{\alpha}x\right)$, $\epsilon_n = (n+\frac{1}{2})\omega_0$, where $\omega_0 = \sqrt{k}$, $\alpha = \frac{1}{2}\sqrt{k}$, $A = \left[\left(\frac{k^{\frac{1}{2}}}{\pi}\right)^{\frac{1}{2}}\frac{1}{2^n n!}\right]^{\frac{1}{2}}$, and H_n is a *Hermite polynomial* of degree n.

The previous two example solutions were obtained by traditional solution methods, as, for example, a series method. Instead of proceeding in this manner, we consider a general solution of the second-order differential equation (2.1):

$$\Phi_E(x) = A\,u_E(x) + B\,v_E(x), \tag{2.4}$$

where u and v are particular solutions to Eq. (2.1), and the subscript E indicates that the solution applies for all values of that parameter. From now on, the subscript E is dropped.

The particular solutions are chosen such that $u(a) = v(b) = 0$, and the Wronskian is

$$W \equiv W[u,v] = u(x)v^{'}(x) - u^{'}(x)v(x), \tag{2.5}$$

where the single prime is used to denote the first derivative with respect to x. (Similarly the double prime notation is used for the second derivative.) The Wronskian does not depend on x, because $\frac{dW}{dx} = u(x)v^{''}(x) - u^{''}(x)v(x) = 0$, where the property that u and v are particular solutions has been used, *i.e.*,

$$u^{''} = 2[V(x) - E]u \qquad \text{and} \qquad v^{''} = 2[V(x) - E]v\,. \tag{2.6}$$

To solve the inhomogeneous equation corresponding to Eq. (2.1),

$$\left[E + \frac{1}{2}\frac{d^2}{dx^2} - V(x)\right]\Psi(x) = r(x)\,, \tag{2.7}$$

the boundary conditions $\Psi(a) = \Psi(b) = 0$ are used, and Eq. (2.7) is multiplied by $2\,u(x)$. The relations in Eq. (2.6) yield

$$\frac{d}{dx}[u(x)\Psi^{'}(x) - u^{'}(x)\Psi(x)] = 2u(x)r(x)\,, \tag{2.8}$$

which can be directly integrated from a to x to yield

$$u(x)\Psi^{'}(x) - u^{'}(x)\Psi(x) = 2\int_a^x u(x^{'})r(x^{'})dx^{'}\,. \tag{2.9}$$

Similarly

$$v^{'}(x)\Psi(x) - v(x)\Psi^{'}(x) = 2\int_x^b v(x^{'})r(x^{'})dx^{'} \tag{2.10}$$

is obtained.

Eliminating Ψ' between Eqs. (2.9) and (2.10) yields

$$W\Psi(x) = 2[v(x)\int_a^x u(x^{'})r(x^{'})dx^{'} + u(x)\int_x^b v(x^{'})r(x^{'})dx^{'}]\,. \tag{2.11}$$

This can be rewritten using $x_<$ and $x_>$ as the smaller and greater of x and x', respectively,

$$\Psi(x) = \frac{2}{W}\int_a^b u(x_<)v(x_>)r(x^{'})dx^{'} = \int_a^b G(x,x^{'};E)r(x^{'})dx^{'} \tag{2.12}$$

(for $W \neq 0$). Thus, the two independent particular solutions of the homogeneous differential equation (2.1) determines $G(x, x'; E)$, the Green's function, which determines the solution $\Psi(x)$ of the inhomogeneous differential equation (2.7) for arbitrary source function $r(x)$.

If in particular $r(x) = \delta(x - x')$, Eq. (2.12) becomes

$$\begin{aligned} \Psi(x) &= \int_a^b G(x, x''; E) r(x'') dx'' = \\ &= \int_a^b G(x, x''; E) \delta(x'' - x') dx'' = G(x, x'; E) \,. \end{aligned} \tag{2.13}$$

This shows that in particular the Green's function G satisfies the inhomogeneous differential equation

$$\left[E + \frac{1}{2} \frac{d^2}{dx^2} - V(x) \right] G(x, x'; E) = \delta(x - x') \,. \tag{2.14}$$

Example 3: Consider again the particle in a box problem discussed in Example 1. Put $E = \kappa^2/2$, put $a = 0$, and use the particular solutions $u(x) = A \sin(\kappa x)$; $v(x) = B \sin(\kappa(b - x))$ to obtain $W = -AB\kappa \sin(\kappa b)$ and

$$G(x, x'; E) \equiv f(\kappa) = -\frac{2 \sin(\kappa x_<) \sin(\kappa(b - x_>))}{\kappa \sin(\kappa b)} \,. \tag{2.15}$$

Consider κ (and thus E) a complex parameter, and note that $f(\kappa)$ has simple poles at $\kappa = n\pi/b$ for $n = 1, 2, 3 \ldots$. The residue at such a pole is

$$r_n = \lim_{\kappa \to n\pi/b} (\kappa - n\pi/b) f(\kappa) = \frac{2}{n\pi} \sin(\frac{n\pi}{b} x_<) \sin(\frac{n\pi}{b} x_>) \,. \tag{2.16}$$

The following theorem from the theory of meromorphic functions applies:

Theorem: When $f(\kappa)$ has simple poles at $p_1, p_2, \ldots, p_n$ such that $0 < |p_1| \leq |p_2| \leq \ldots \leq |p_n|$, (with residues $r_1, r_2, \cdots, r_n$) the contour(s) C_n, which encloses these poles (and no other poles) has a length $L_n = O(R_n)$ (*e.g.*, a circle $L_n = 2\pi R_n$), and $f(\kappa)$ is bounded on C_n, then as $n \to \infty$ (with $R_n \to \infty$)

$$f(\kappa) = f(0) + \sum_{n=1}^{\infty} r_n \left[\frac{1}{\kappa - p_n} + \frac{1}{p_n} \right] \,. \tag{2.17}$$

In our case this leads to

$$f(\kappa) = f(0) + \sum_{n=-\infty}^{\infty} \frac{2b}{n\pi} \sin(\frac{n\pi}{b} x) \sin(\frac{n\pi}{b} x') \left[\frac{1}{b\kappa - n\pi} + \frac{1}{n\pi} \right] , \tag{2.18}$$

where $n = 0$ is not included in the summation. Combining the terms for positive and negative n values, one can write

$$\begin{aligned} G(x, x'; E) &= G(x, x'; 0) + \sum_{n=1}^{\infty} \frac{2}{b} \sin(\frac{n\pi}{b} x) \sin(\frac{n\pi}{b} x') / [E - \epsilon_n] \\ &+ \sum_{n=1}^{\infty} \frac{2}{b} \sin(\frac{n\pi}{b} x) \sin(\frac{n\pi}{b} x') / \epsilon_n . \end{aligned} \tag{2.19}$$

This means that

$$G(x,x';E)=\sum_{n=1}^{\infty}\frac{2}{b}\sin(\frac{n\pi}{b}x)\sin(\frac{n\pi}{b}x')/[E-\epsilon_n], \tag{2.20}$$

i.e., the Green's function has an expansion in terms of eigenfunctions and eigenvalues of the homogeneous differential equation, and they appear as residues and poles as a consequence of the analytical properties of the Green's function.

Example 4: The analogous treatment for the harmonic oscillator problem in Example 2, proceeds by first making the variable transformation $\xi=2\sqrt{\alpha}x$ and putting $c=-E/\sqrt{k}$, which yields the equation

$$[\frac{d^2}{d\xi^2}-\frac{1}{4}\xi^2-c]\Phi(\xi)=0\,. \tag{2.21}$$

This equation has the *parabolic cylinder functions* as standard solutions. Choose the two particular solutions $u(\xi)=U(c,\xi)$ and $v(\xi)=U(c,-\xi)$, which satisfy the desired boundary conditions at $a=-\infty$, and $b=\infty$, respectively.

The relationship with the "irregular" parabolic cylinder function $V(c,\xi)$, $U(c,-\xi)=\pi V(c,\xi)/\Gamma(c+\frac{1}{2})-\sin(\pi c)U(c,\xi)$ can then be used to evaluate the Wronskian

$$W[U(c,\xi),U(c,-\xi)]=\frac{\pi}{\Gamma(c+\frac{1}{2})}W[U,V]=\frac{\sqrt{2\pi}}{\Gamma(c+\frac{1}{2})}\,. \tag{2.22}$$

The Green's function then becomes $G(\xi,\xi';E)=\sqrt{2/\pi}\,\Gamma(c+\frac{1}{2})U(c,\xi)U(c,-\xi)$.

The *gamma function* $\Gamma(c+1/2)$ is single valued and analytic over the entire complex c-plane except at $c=-n-1/2$ for $n=0,1,2,...$, where it has simple poles with residues $(-1)^n/n!$. The parabolic cylinder functions satisfy

$$U(-n-\frac{1}{2},\xi)=(-1)^nU(-n-\frac{1}{2},-\xi)=2^{-\frac{1}{2}n}\exp[-\frac{1}{4}\xi^2]H_n(\xi/\sqrt{2}) \tag{2.23}$$

making Eq. (2.18) read as

$$\begin{aligned}G(\xi,\xi';E) &= G(\xi,\xi';0)\\ &+ \sum_{n=0}^{\infty}\frac{2^{-n+\frac{1}{2}}(n!)^{-1}\sqrt{\frac{k}{\pi}}\exp[-\frac{1}{4}(\xi^2+\xi'^2)]H_n(\zeta)H_n(\zeta')}{E-(n+\frac{1}{2})\sqrt{k}}\\ &+ \sum_{n=0}^{\infty}\frac{2^{-n+\frac{1}{2}}(n!)^{-1}\sqrt{\frac{k}{\pi}}\exp[-\frac{1}{4}(\xi^2+\xi'^2)]H_n(\zeta)H_n(\zeta')}{(n+\frac{1}{2})\sqrt{k}}\,,\end{aligned} \tag{2.24}$$

with $\zeta=\xi/\sqrt{2}$, and thus

$$G(x,x';E)=\sum_{n=0}^{\infty}\Phi_n(x)\Phi_n(x')/[E-\epsilon_n]\,, \tag{2.25}$$

where Φ_n and ϵ_n are defined in Example 2.

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Chapter 3

Propagators and Second Quantization

The Schrödinger equation for an electron or for N noninteracting electrons is

$$\left[-\frac{1}{2}\nabla^2 + V(\xi)\right]\psi(\xi,t) = i\partial\psi(\xi,t)/\partial t \tag{3.1}$$

with units such that Planck's constant is 2π and the electron mass is 1, and with $\xi = (\vec{r},\zeta)$ being a combined space-spin variable. The wave function or Schrödinger amplitude $\psi(\xi,t)$ can be expressed in an orthonormal basis $\{u_s(\xi)\}$ as

$$\psi(\xi,t) = \sum_r u_r(\xi)a_r(t), \tag{3.2}$$

giving the Schrödinger equation in discrete form

$$i\partial a_s(t)/\partial t - \sum_r h_{sr}a_r(t) = 0\,. \tag{3.3}$$

The notation

$$h_{sr} = \int u_s^*(\xi)\left[-\frac{1}{2}\nabla^2 + V(\xi)\right]u_r(\xi)d\xi \tag{3.4}$$

has been employed.

Let $\mathbf{x}$ be a unitary transformation to energy eigenstates: $\mathbf{x}^\dagger\mathbf{x} = \mathbf{x}\mathbf{x}^\dagger = \mathbf{1}$, $\mathbf{x}^\dagger\mathbf{h}\mathbf{x} = \epsilon$ (diagonal). A formal solution to Eq. (3.3) may be written as

$$a_s(t) = \sum_k x_{sk}\exp[-i\epsilon_k(t-t')]\left(\sum_r x_{kr}^\dagger a_r(t')\right)\,. \tag{3.5}$$

The system may be prepared such that $|a_r(t')|^2 = 1$, and $|a_s(t')|^2 = 0$ for $s \neq r$. Then the quantity

$$|a_s(t)|^2 = |\sum_k x_{sk}\exp[-i\epsilon_k(t-t^{'})]x^{\dagger}_{kr}|^2 \tag{3.6}$$

is the probability for the electron to be "observed" in spin orbital s at time t, when it is known to be in spin orbital r at time t' with unit probability.

Consider a formal scattering process with an electron entering a system of N (noninteracting) electrons at time t' in spin orbital r and being detected leaving the system at time t in spin orbital s. The N-electron system is in its ground state, consisting of the N lowest spin orbitals being occupied. An injected electron has access only to the unoccupied orbitals (Pauli principle), and entering the system at time t', it cannot be observed leaving the system prior to that time, *i.e.*, $t > t'$. Define an associated probability

$$P_{sr}(t,t^{'}) = \begin{cases} |\sum_k x_{sk}(1-f_k)\exp[-i\epsilon_k(t-t^{'})]x^{\dagger}_{kr}|^2 & t > t^{'} \\ 0 & t < t^{'} \end{cases} \tag{3.7}$$

with the occupation numbers $f_k = 1$ or 0 if spin orbital k is occupied or unoccupied, respectively in the N-electron ground state. An electron could, of course, be observed leaving the system in spin orbital s at time $t < t'$ provided it is one of the electrons already present in the N-electron system. The associated probability is defined as

$$\bar{P}_{sr}(t,t^{'}) = \begin{cases} 0 & t > t^{'} \\ |\sum_k x_{sk} f_k \exp[-i\epsilon_k(t-t^{'})]x^{\dagger}_{kr}|^2 & t < t^{'} \end{cases} . \tag{3.8}$$

This leads to the definition of the probability amplitude

$$\begin{aligned} G_{sr}(t,t^{'}) = & -i\theta(t-t')\sum_k x_{sk}(1-f_k)\exp[-i\epsilon_k(t-t^{'})]x^{\dagger}_{kr} \\ & +i\theta(t'-t)\sum_k x_{sk} f_k \exp[-i\epsilon_k(t-t^{'})]x^{\dagger}_{kr}, \end{aligned} \tag{3.9}$$

where the Heaviside step function

$$\theta(t) = \begin{cases} 1 & t > 0 \\ 0 & t < 0, \end{cases} \tag{3.10}$$

such that $|G_{sr}(t,t^{'})|^2$ is the probability of detecting an electron leaving the system in s at time t provided an electron enters in spin orbital r at time t'. The probability amplitude is the *electron propagator* $G_{sr}(t,t^{'})$ and the Green's function of the differential equation (3.3) because it can readily be shown that

$$i\partial G_{sr}/\partial t - \sum_q h_{sq}G_{qr} = \delta_{sr}\delta(t-t^{'}) . \tag{3.11}$$

Here we have used a relationship between the Heaviside step function and the Dirac delta function expressed as

$$\theta(t) = \int_{-\infty}^{t} \delta(\tau)d\tau, \tag{3.12}$$

and also that the delta function satisfies $\delta(-t) = \delta(t)$.

The propagator is discontinuous at $t = t'$ for $s = r$, which is shown by

$$\lim_{d \to +0} [G_{sr}(t, t+d) - G_{sr}(t, t-d)] = i\delta_{sr} \,. \tag{3.13}$$

According to Eq. (3.9), the propagator is a function of the time interval $t - t'$ and the temporal behavior can be studied via the Fourier integral

$$G_{sr}(t - t') = (2\pi)^{-1} \int_{-\infty}^{\infty} dE\, G_{sr}(E) \exp[-iE(t - t')] \,. \tag{3.14}$$

The inverse relation

$$G_{sr}(E) = \int_{-\infty}^{\infty} d(t - t')G_{sr}(t - t') \exp[iE(t - t',)], \tag{3.15}$$

leads to improper integrals of the type

$$\int_{0}^{\infty} dt \exp[i\, t(E - \epsilon_k)] \,, \tag{3.16}$$

which can be dealt with by introducing a convergence factor $\exp[-t\eta]$ and taking the limit $\eta \to +0$ after integration. It follows from Eqs. (3.9) and (3.15) that

$$G_{sr}(E) = \lim_{\eta \to +0} \sum_{k} x_{sk} [\frac{f_k}{E - \epsilon_k - i\eta} + \frac{1 - f_k}{E - \epsilon_k + i\eta}] x^{\dagger}_{kr} \,, \tag{3.17}$$

which allows the definition of $G_{sr}(E)$ for arbitrary complex E, as

$$G_{sr}(E) = \sum_{k} x_{sk} [E - \epsilon_k]^{-1} x^{\dagger}_{kr} \,. \tag{3.18}$$

This expression is a resolvent to the Hamiltonian matrix **h** and satisfies

$$E\, G_{sr}(E) = \delta_{sr} + \sum_{q} h_{sq} G_{qr}(E) \,, \tag{3.19}$$

which can be readily discerned from the identity

$$E[E - \epsilon]^{-1} = 1 + \epsilon[E - \epsilon]^{-1}. \tag{3.20}$$

It may be used in the integral Eq. (3.14) instead of the form Eq. (3.17), provided the integration of the energy variable is performed as a contour integral in the complex E-plane. An appropriate contour is chosen such that it bypasses the singularities at $E = \epsilon_k$ on the real axis. Figure 3.1 displays an acceptable contour for the case that $f_k \geq f_l$ when $\epsilon_k \leq \epsilon_l$.

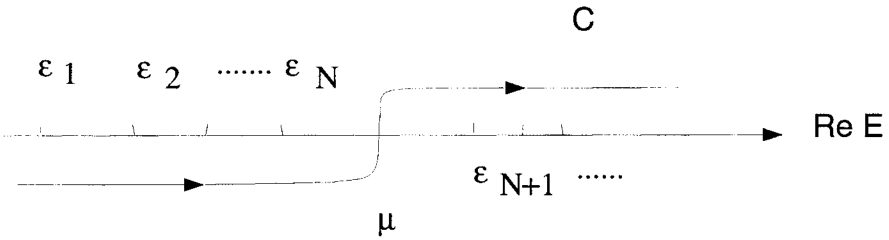

Figure 3.1: Acceptable contour for the case of $f_k > f_l$ and $\epsilon_k < \epsilon_l$.

This corresponds to the ground state of the N-electron system with the condition on the occupation numbers being

$$f_k = \begin{cases} 1, & \epsilon_k < \mu \\ 0, & \epsilon_k > \mu \,. \end{cases} \tag{3.21}$$

A continuous spectrum, showing a cut on the real axis rather than simple poles, can be handled similarly when considered as the limit of a discrete one.

The Fourier transform $G_{sr}(E)$ of the propagator is an analytic function in the complex E-plane, except on the real axis where it can have simple poles and cuts. These correspond to energy eigenvalues of the (single-particle) Hamiltonian $\mathbf{h}$. Consideration of the discontinuity of $G_{sr}(E)$ at the real axis yields the *spectral density function*

$$\begin{aligned} A_{sr}(\epsilon) &= \lim_{\eta\to+0}(i/2\pi)[G_{sr}(\epsilon+i\eta) - G_{sr}(\epsilon-i\eta)] \\ &= \sum_k x_{sk}x^\dagger_{kr}\lim_{\eta\to+0}(\eta/\pi)[(\epsilon-\epsilon_k)^2+\eta^2]^{-1} \\ &= \sum_k x_{sk}x^\dagger_{kr}\delta(\epsilon-\epsilon_k). \end{aligned} \tag{3.22}$$

The Dirac delta function appears here as the limiting function

$$\delta(x) = \lim_{\eta\to+0}(\eta/\pi)[x^2+\eta^2]^{-1}, \tag{3.23}$$

which satisfies all defining criteria for that "function," particularly

$$\int_a^b \delta(x-c)f(x)dx = \begin{cases} f(c), & a<c<b \\ 0, & otherwise. \end{cases} \tag{3.24}$$

It is notable that the knowledge of the spectral density function $A_{sr}(\epsilon)$ suffices to yield $G_{sr}(E)$ in the complex E-plane from the integral

$$G_{sr}(E) = \int_{-\infty}^{+\infty} d\epsilon A_{sr}(\epsilon)/[E-\epsilon]\,. \tag{3.25}$$

Also, the physical properties feasible to obtain from the propagator are calculated once the spectral density function is known. Stationary state properties of an N-electron system are related to the propagator, and in particular, one can write

$$\begin{aligned} N=\sum_k f_k &= -i\lim_{t\to t'-0}\sum_s G_{ss}(t,t') \\ &= (2\pi i)^{-1}\int_C dE\sum_s G_{ss}(E) \\ &= \sum_s\int_{-\infty}^{\mu} d\epsilon A_{ss}(\epsilon)\,. \end{aligned} \tag{3.26}$$

The contour C consists of the one given in Fig. 3.1 plus an infinite semicircle in the upper half of the complex E-plane or in fact any other contour obtainable from it by a deformation that does not bring it through any of the singularities. A particular contour used by Coulson is shown in Fig. 3.2

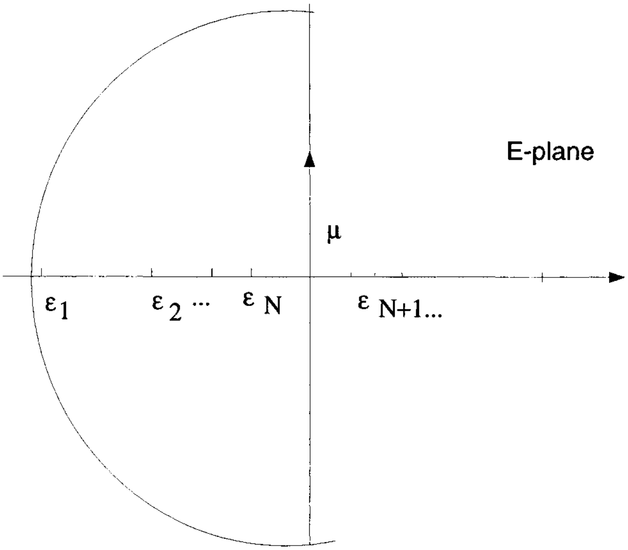

Figure 3.2: Contour used by Coulson (see text).

The total energy can be obtained as

$$\begin{aligned} E_0 &= \sum_k \epsilon_k f_k = \lim_{t\to t'-0} -iG_{ss}(t,t') \\ &= (2\pi i)^{-1}\int_C EdE\sum_s G_{ss}(E) \end{aligned} \tag{3.27}$$

$$= \sum_s \int_{-\infty}^{\mu} \epsilon d\epsilon A_{ss}(\epsilon) \, ,$$

with the same choice of contour as above. Relations such as these are examples of the initial conditions that specify the propagator or Green's function in conjunction with the differential equations. They appear as sum rules for the spectral density function.

In terms of the spin orbital basis $\{u_r(\xi)\}$, we can define the Green's function

$$G(\xi, \xi'; E) = \sum_{r,s} u_r(\xi) G_{rs}(E) u_s^*(\xi), \tag{3.28}$$

and similarly

$$G(\xi, \xi'; t - t') = \sum_{r,s} u_r(\xi) G_{rs}(t - t') u_s^*(\xi). \tag{3.29}$$

From Eq.(3.11), it follows that

$$i\frac{\partial G(\xi, \xi'; t - t')}{\partial t} - [-\frac{1}{2}\nabla^2 + V(\xi)]G(\xi, \xi'; t - t') = \delta(t - t')\delta(\xi - \xi') \tag{3.30}$$

and similarly we can obtain an expression analogous to the Eq.(3.19). Here the delta function $\delta(\xi - \xi')$ comes from

$$\sum_r u_r(\xi) u_r^*(\xi') = \delta(\xi - \xi'), \tag{3.31}$$

which assumes the spin orbital basis to be complete.

Notes and Bibliography

An excellent exposition of the propagator concept and role in quantum mechanics is given by

- R. P. Feynman and A. R. Hibbs, in *Quantum Mechanics and Path Integrals*, McGraw-Hill Book Co., New York, 1965

Several useful results in the theory of matrices, determinants, and resolvents are developed by

- R. Courant and D. Hilbert, in *Methods of Mathematical Physics*, Vol. 1, Interscience Publishers, New York, 1953.

3.1 The Hückel Model

E. Hückel introduced a simple quantum mechanical model for the description of the electronic structure of planar unsaturated molecules with the bonding connectivity as input. This model has been widely used. Although today's computing power and quantum chemistry software available for all chemists have made the assumptions of the Hückel model unnecessarily simplistic, the model is still used to make estimates of molecular energies and has established itself as a useful teaching tool.

Coulson and Longuet-Higgins gave the theory an elegant formulation that readily connects to the propagator theory as discussed above. As the Hamiltonian is independent of electron spin, the discussion can be limited to situations where the labels such as r and s refer to orbitals rather than spin orbitals. Each orbital is associated with a particular atomic site in the molecule, and with one orbital per site there is a one-to-one correspondence between labels and sites.

The resolvent or the Fourier transform of the propagator is used and a matrix notation

$$\mathbf{G}(E) = \{G_{sr}(E)\}, \qquad (s, r = 1, 2, \cdots M) \tag{3.32}$$

is introduced so that one can write

$$(E\mathbf{1} - \mathbf{h})\mathbf{G}(E) = \mathbf{1}\,. \tag{3.33}$$

The secular determinant

$$D(E) = \det\{E\mathbf{1} - \mathbf{h}\} \tag{3.34}$$

is a function of the various Hamiltonian matrix elements h_{sr}, and from the matrix theory expression for the elements of an inverse matrix it follows that

$$G_{sr}(E) = (-1)^{r+s+1} \partial \ln D(E) / \partial h_{rs}\,. \tag{3.35}$$

This formula is valid when all elements h_{sr} are independent, *i.e.*,

$$\partial h_{pq} / \partial h_{rs} = \delta_{rp} \delta_{sq}\,. \tag{3.36}$$

Another result from matrix theory is

$$\mathrm{Tr}\mathbf{G}(E) = \sum_s G_{ss}(E) = \frac{\partial \ln D(E)}{\partial E}\,. \tag{3.37}$$

The simple case of doubly filled orbitals leads to the expressions

$$\begin{aligned} N &= (\pi i)^{-1} \int_C dE \frac{\partial \ln D(E)}{\partial E}, \\ E_0 &= (\pi i)^{-1} \int_C dE \frac{\partial \ln D(E)}{\partial E} E, \end{aligned} \tag{3.38}$$

for the number of electrons and the total energy, respectively.

The particulars of the Hückel model include the following choices of matrix elements:

$$\begin{aligned} h_{rr} &= \alpha_r, \\ h_{rs} &= h_{sr} = \beta_{sr}, \qquad s \neq r, \end{aligned} \tag{3.39}$$

all being real and considered the basic parameters of the model. Furthermore, the off-diagonal elements β_{sr} are zero unless sites s and r are neighbors. The formal electron charge on site s is defined as

$$q_s = \partial E_0/\partial \alpha_s\,, \tag{3.40}$$

which can be equivalently expressed as

$$q_s = (\pi i)^{-1}\int_C dE\, G_{ss}(E) \tag{3.41}$$

readily seen from the above expressions. Similarly, the mobile bond order

$$p_{sr} = \frac{1}{2}\partial E_0/\partial \beta_{sr} \tag{3.42}$$

can be expressed as

$$\begin{aligned} p_{sr} &= (2\pi i)^{-1}\int_C dE\,[G_{sr}(E) + G_{rs}(E)] \\ &= (\pi i)^{-1}\int_C dE\, G_{sr}(E)\,. \end{aligned} \tag{3.43}$$

Higher derivatives of the energy are used in the Hückel model and are called mutual atom-atom, atom-bond, or bond-bond polarizabilities. These quantities are all obtainable from a general second derivative

$$\partial^2 E_0/\partial h_{rs}\partial h_{pq} = (\pi i)^{-1}\int_C dE\, G_{sp}(E)G_{qr}(E)\,, \tag{3.44}$$

where the actual form of the derivative of $\mathbf{G}(E)$ with respect to any parameter comes from the differentiation of Eq. (3.33).

Using the asymptotic form of $D(E)$ for large E-values and the contour integral expression in Eq. (3.38), one can derive the Coulson's energy formula

$$E_0 = \mathrm{Tr}\,\mathbf{h} + \pi^{-1}\int_{-\infty}^{\infty} dy[(\mu + iy)\frac{\partial \ln D(\mu + iy)}{\partial(\mu + iy)} - M]\,. \tag{3.45}$$

The Hückel model for planar unsaturated hydrocarbons introduces the parameter choices

$$\begin{aligned} h_{rr} &= \alpha_r = \alpha = \mu \qquad\qquad (3.46) \\ h_{rs} &= h_{sr} = \begin{cases} \beta_{sr} & \text{for bonded atoms } r \text{ and } s \\ 0 & \text{otherwise,} \end{cases} \end{aligned}$$

leading to the propagator equation

$$(E-\mu)G_{sr}(E)=\delta_{sr}+\sum_{q}\beta_{sq}G_{qr}(E)\,. \tag{3.47}$$

It is straightforward to show that iteration of this equation yields

$$[(E-\mu)^2-\sum_{q}|\beta_{rq}|^2]G_{rr}(E)=(E-\mu)+\sum_{q}\sum_{p\neq r}\beta_{rq}\beta_{qp}G_{pr}(E)\,. \tag{3.48}$$

An approximate treatment where the last term is discarded can be used to calculate the total energy and the bond orders for molecules with all β-parameters equal. The average energy per atom for a graphite layer, for instance, equals $\mu+\beta\sqrt{3}$, which is less than 10% in error in comparison to the accurate value $\mu+1.576\beta$.

Notes and Bibliography

An elegant form of Hückel theory was formulated by:

- C. A. Coulson and H. C. Longuet-Higgins, in a series of papers in *Proc. Roy. Soc.* (London), **A191**, 39; **A192**, 16; **A193**, 447; **A193**, 456 (1947).
- Coulson published his integration method in *Proc. Camb. Phil. Soc.* **40**, 201 (1940).

3.2 Electron Field Operators

In order to discuss interacting electrons, it is often advantageous to introduce electron field operators or *second quantization*, which means that the expansion coefficients $a_s(t)$ of Eq. (3.2) become operators rather than scalars. These operators are non-Hermitian so that also their adjoints $a_s^\dagger(t)$ are needed. These operators are postulated to satisfy the anticommutation relations (at equal times):

$$\begin{aligned}
[a_s(t),a_r(t)]_+ &= a_sa_r+a_ra_s &&= 0\\
[a_s^\dagger(t),a_r^\dagger(t)]_+ &= a_s^\dagger a_r^\dagger+a_r^\dagger a_s^\dagger &&= 0\\
[a_s(t),a_r^\dagger(t)]_+ &= a_sa_r^\dagger+a_r^\dagger a_s &&= \delta_{sr}\,.
\end{aligned} \tag{3.49}$$

This means that the adjoint amplitudes of $\psi(\xi,t)$ are also operators satisfying the anticommutation relations $[\psi(\xi,t),\psi(\xi',t)]_+=[\psi^\dagger(\xi,t),\psi^\dagger(\xi',t)]_+=[\psi(\xi,t),\psi^\dagger(\xi',t)]_+-\delta(\xi-\xi')=0$. For a complete basis, this is compatible with Eq.(3.49).

The energy integral value

$$\int\psi^\dagger(\xi,t)h\psi(\xi,t)d\xi=\sum_{s,r}h_{sr}a_s^\dagger(t)a_r(t)=H_0 \tag{3.50}$$

thus becomes an operator, and the question arises if it will do as a hamiltonian. The question of what kind of vector space the electron field operators a_s and their adjoints should act on has not yet been addressed, but the guide will be the evaluation of quantum mechanical expectation values.

The field operators are time dependent and thus Heisenberg operators, *i.e.*, they satisfy

$$i\partial a_s(t)/\partial t = [a_s, H_0]_- , \tag{3.51}$$

where the right-hand side is the commutator

$$[a_s, H_0]_- = \sum_{q,r} h_{qr}[a_s, a_q^\dagger a_r]_- = \sum_r h_{sr} a_r \tag{3.52}$$

and where the relations in Eq. (3.49) were used. Comparison with Eq. (3.3) shows that the definition of H_0 as the hamiltonian makes sense.

The charge density of electrons is

$$q(\vec{r}) = e \sum_\zeta \psi^\dagger(\xi)\psi(\xi) , \tag{3.53}$$

with the electron charge e and the summation over spin. The time variable is suppressed. The charge density q is also an operator, and an operator Q of total electron charge is obtained by integrating over all space:

$$Q = \int q(\vec{r})d\vec{r} = e \int \psi^\dagger(\xi)\psi(\xi)d\xi = e N_0 , \tag{3.54}$$

where N_0 is the operator for the total number of electrons

$$N_0 = \int \psi^\dagger(\xi)\psi(\xi)d\xi = \sum_s a_s^\dagger a_s = \sum_s n_s . \tag{3.55}$$

N_0 has eigenvalues 0, 1, 2, ..., because the operators $n_s = a_s^\dagger a_s$ commute and are idempotent, *i.e.*, $n_s^2 = n_s$. The eigenstate $|vac\rangle$ corresponding to the eigenvalue 0 is assumed to be non-degenerate, normalized to unity $\langle vac|vac\rangle = 1$, and satisfying the condition

$$a_s|vac\rangle = 0 . \tag{3.56}$$

This also makes $n_s|vac\rangle = 0$, and $N_0|vac\rangle = 0$. The definition $a_r^\dagger|vac\rangle = |r\rangle$ and the basic anticommutation relations in Eq. (3.49) show that

$$N_0|r\rangle = |r\rangle ; \tag{3.57}$$

i.e., $|r\rangle$ is an eigenstate of N_0 corresponding to the eigenvalue 1, which means that it is a one-electron state. Similarly $|rs\rangle = a_r^\dagger a_s^\dagger|vac\rangle$ is a two-electron state, and it is antisymmetric, *i.e.*,

$$N_0|rs\rangle = 2|rs\rangle, \qquad |rs\rangle = -|sr\rangle . \tag{3.58}$$

Note that $\langle rs| = \langle vac|a_s a_r$ and that

$$\langle rs|rs\rangle = \langle vac|vac\rangle = 1\,. \tag{3.59}$$

It is easy to show that $|N\rangle = a^\dagger_{r_1}a^\dagger_{r_2}...a^\dagger_{r_N}|vac\rangle$ is an N-electron state, properly antisymmetric, and with a one-one correspondence to the Slater determinant D such that

$$\begin{aligned} D &= \det\{u_{r_1}(\xi_1)u_{r_2}(\xi_2)...u_{r_N}(\xi_N)\} \\ &= \langle vac|\psi(\xi_N)\psi(\xi_{N-1})...\psi(\xi_1)|N\rangle. \end{aligned} \tag{3.60}$$

It should be noted that $\langle N|N\rangle = 1$ and $\langle N|M\rangle = 0$ for $N \neq M$. In this way, the electron field operators $\{a^\dagger_s\}$ map the N-electron Hilbert space on the $(N+1)$-electron Hilbert space, whereas the $\{a_s\}$ map the N-electron Hilbert space on the $(N$ - $1)$-electron one. This is illustrated by the result $a_r|rs\rangle = |s\rangle$ (note that $a_s|rs\rangle = -|r\rangle$).

Rather than express the hamiltonian H_0 in terms of a general spin orbital basis, one could, of course, choose the diagonal representation

$$\begin{aligned} H_0 = \sum_{s,r} h_{sr}a^\dagger_s a_r &= \sum_k \Big(\sum_s a^\dagger_s x_{sk}\Big)\epsilon_k\Big(\sum_r x^\dagger_{kr}a_r\Big) \\ &= \sum_k \epsilon_k \tilde{a}^\dagger_k \tilde{a}_k\,. \end{aligned} \tag{3.61}$$

Ordering the energies $\epsilon_1 \leq \epsilon_2 \leq ... \leq \epsilon_N \leq ...$, one can write the ground state of the N-electron system as

$$|0\rangle = \tilde{a}^\dagger_1\tilde{a}^\dagger_2...\tilde{a}^\dagger_N|vac\rangle\,. \tag{3.62}$$

The average value

$$\langle 0|H_0|0\rangle = \sum_k \epsilon_k\langle 0|\tilde{a}^\dagger_k\tilde{a}_k|0\rangle = \sum_k f_k\epsilon_k \tag{3.63}$$

is another evidence that our hamiltonian choice is correct. (Note that the occupation number $\langle 0|\tilde{a}^\dagger_k\tilde{a}_k|0\rangle = f_k$ is unity when spin orbital k is occupied in $|0\rangle$ and zero when unoccupied.)

It is now straightforward to show that

$$G_{sr}(t,t') = \begin{cases} -i\langle 0|a_s(t)a^\dagger_r(t')|0\rangle & t > t' \\ i\langle 0|a^\dagger_r(t')a_s(t)|0\rangle & t < t' \end{cases} \tag{3.64}$$

by noting that from Eq. (3.5) that

$$a_s(t) = \sum_k x_{sk}\exp[-i\epsilon_k t]\tilde{a}_k(0)\,, \tag{3.65}$$

and thus

$$\begin{aligned} -i\langle 0|a_s(t)a_r^\dagger(t')|0\rangle &= \sum_{k,k'} x_{sk}\exp[-i\epsilon_k t + i\epsilon_{k'}t'](1-f_k)\langle 0|\tilde{a}_k\tilde{a}_{k'}^\dagger|0\rangle x_{kr}^\dagger \\ &= -i\sum_k x_{sk}(1-f_k)\exp[-i\epsilon_k(t-t')]x_{kr}^\dagger\,. \end{aligned} \tag{3.66}$$

The relation $\tilde{a}_k\tilde{a}_{k'}^\dagger = \delta_{kk'} - \tilde{a}_{k'}^\dagger\tilde{a}_k$ and the identity $\langle 0|\tilde{a}_k f_k = 0$ are used.

Eq. (3.64) is the *defining* expression for the electron propagator or Green's function, and it applies for the case of interacting electrons, with $|0\rangle$ being the ground state of the full hamiltonian including electron interaction.

Problems

1. Prove, in a similar way as in the text, the second part of Eq. (3.64).

3.3 Angular Momentum

Angular momentum is an important example of quantum mechanical operators in terms of electron field operators. The components of the angular momentum vector $\vec{j} = \vec{l} + \vec{s}$ are the generators of the 3-dimensional rotation group. In our units, the operator of orbital angular momentum is

$$\vec{l} = \vec{r}\times\vec{p} = -i\vec{r}\times\vec{\nabla} \tag{3.67}$$

and the operator of spin angular momentum is $\vec{s} = \frac{1}{2}\vec{\sigma}$ in terms of the Pauli spin matrices $\vec{\sigma} = (\sigma_x\ \sigma_y\ \sigma_z)$. The total angular momentum operator of a many-electron system is then obtained as

$$\vec{J} = \int \psi^\dagger(\xi)\vec{j}\psi(\xi)d\xi = \sum_{r,s}\vec{j}_{rs}a_r^\dagger a_s = \vec{L} + \vec{S}\,. \tag{3.68}$$

Many molecular hamiltonians commute with the total spin angular momentum operator, a fact that leads to the consideration of transformation properties of electron field operators under rotations in spin space. Basis functions, natural for such studies, are

$$u_{s\pm\frac{1}{2}}(\xi) = \chi_s(\vec{r})\begin{cases}\alpha(\zeta)\\ \beta(\zeta),\end{cases} \tag{3.69}$$

with α and β eigenvectors of the z-component of $\vec{s}$ and $\{\chi_r(\vec{r})\}$ a set of orthonormal functions. The operator of total spin of a many-electron system is then

$$\vec{S} = \int \psi^\dagger(\xi)\vec{s}\psi(\xi)d\xi = \sum_r \vec{S}_r\,, \tag{3.70}$$

with

$$\vec{S}_r = S_{rx}\vec{e}_x + S_{ry}\vec{e}_y + S_{rz}\vec{e}_z \tag{3.71}$$

and

$$\begin{aligned} S_{rx} &= \frac{1}{2}(a^\dagger_{r+\frac{1}{2}}a_{r-\frac{1}{2}} + a^\dagger_{r-\frac{1}{2}}a_{r+\frac{1}{2}}), \\ S_{ry} &= -i\frac{1}{2}(a^\dagger_{r+\frac{1}{2}}a_{r-\frac{1}{2}} - a^\dagger_{r-\frac{1}{2}}a_{r+\frac{1}{2}}), \\ S_{rz} &= \frac{1}{2}(n_{r+\frac{1}{2}} - n_{r-\frac{1}{2}}). \end{aligned} \tag{3.72}$$

A rotation in spin space about an axis, the magnitude and direction of which can be given by a vector $\vec{\Theta} = (\Theta_x\ \Theta_y\ \Theta_z)$, produces transformed electron field operators

$$\begin{aligned} \tilde{a}^\dagger_{r\nu} &= \exp(i\vec{\Theta}\cdot\vec{S})a^\dagger_{r\nu}\exp(-i\vec{\Theta}\cdot\vec{S}) \\ &= \exp(i\vec{\Theta}\cdot\vec{S}_r)a^\dagger_{r\nu}\exp(-i\vec{\Theta}\cdot\vec{S}_r), \end{aligned} \tag{3.73}$$

where the last line follows because the operators $\vec{\Theta}\cdot\vec{S}_r$ commute. The following commutation relations are readily proven:

$$\begin{aligned} [\vec{\Theta}\cdot\vec{S}_r, a^\dagger_{r\nu}]_- &= \nu\Theta_z a^\dagger_{r\nu} + (\frac{1}{2}\Theta_x + i\nu\Theta_y)a^\dagger_{r-\nu}, \\ [\vec{Q}\cdot\vec{S}_r, [\vec{Q}\cdot\vec{S}_r, a^\dagger_{r\nu}]_-]_- &= (\frac{1}{2}\Theta)^2 a^\dagger_{r\nu}. \end{aligned} \tag{3.74}$$

This leads to the transformed field operators

$$\begin{aligned} \tilde{a}^\dagger_{r\nu} &= a^\dagger_{r\nu} + i[\vec{\Theta}\cdot\vec{S}_r, a^\dagger_{r\nu}]_- - \frac{1}{2}[\vec{\Theta}\cdot\vec{S}_r, [\vec{\Theta}\cdot\vec{S}_r, a^\dagger_{r\nu}]_-]_- + \cdots \\ &= a^\dagger_{r\nu}\cos\frac{1}{2}\Theta + i[\vec{\Theta}\cdot\vec{S}_r, a^\dagger_{r\nu}]_-(\frac{1}{2}\Theta)^{-1}\sin\frac{1}{2}\Theta, \end{aligned} \tag{3.75}$$

where $\Theta = |\vec{\Theta}|$.

Notes and Bibliography

- Second quantization was introduced in the study of many-particle systems in the early days of quantum mechanics by Born, Jordan, Dirac, Fock, and others.
- Those who are intrigued by the mathematical aspects of the field operator algebra are referred to F. A. Berezin, *The Method of Second Quantization*, Academic Press, New York, 1966.
- The transformation properties of field operators is discussed by F. A. Kaempffer in *Concepts in Quantum Mechanics*, Academic Press, New York, 1965.

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Chapter 4

Double-Time Green's Functions

The proper electron interaction hamiltonian is

$$H_{int} = \frac{1}{2} \sum_{r,s,r',s'} (rs|r's')a_r^\dagger a_{r'}^\dagger a_{s'} a_s \tag{4.1}$$

with

$$(rs|r's') = e^2 \int d\xi \int d\xi' u_r^*(\xi) u_s(\xi) |\vec{r} - \vec{r}'|^{-1} u_{r'}^*(\xi') u_{s'}(\xi'). \tag{4.2}$$

This hamiltonian is correct because it gives the correct expectation values. The average value with respect to a two-electron state is $\langle kl|H_{int}|kl\rangle = (kk|ll) - (kl|lk)$ exactly as the result (coulomb minus exchange) of calculating the average of $1/|\vec{r}_1 - \vec{r}_2|$ with respect to a two-electron Slater determinant with the spin orbitals u_k and u_l in "first-quantization". The full electronic hamiltonian can be expressed as

$$H = \sum_{r,s} h_{rs} a_r^\dagger a_s + \frac{1}{2} \sum_{r,s,r',s'} (rs|r's') a_r^\dagger a_{r'}^\dagger a_{s'} a_s \,. \tag{4.3}$$

It is common to use an alternative notation for the electron-electron interaction integrals $\langle rr'|ss'\rangle = (rs|r's')$, *i.e.*, with the complex conjugate spin orbitals, belonging to the $a^\dagger$ operators, on the left. One can introduce the compact notation $\langle rs||tv\rangle = \langle rs|tv\rangle - \langle rs|vt\rangle$ for an "antisymmetric interaction integral" and write

$$H_{int} = \frac{1}{4} \sum_{r,s,r',s'} \langle rr'||ss'\rangle a_r^\dagger a_{r'}^\dagger a_{s'} a_s \,. \tag{4.4}$$

The state $|0\rangle$ is the N-electron ground state (including electron interaction) and satisfies $H|0\rangle = E_0\,(N)\,|0\rangle$. The electron propagator can then be expressed as

$$\begin{aligned} G_{sr}(t,t') &\equiv \langle\langle a_s(t); a_r^\dagger(t')\rangle\rangle \\ &= -i\theta(t-t')\langle 0|a_s(t)a_r^\dagger(t')|0\rangle \\ &+ \; i\theta(t'-t)\langle 0|a_r^\dagger(t')a_s(t)|0\rangle\,, \end{aligned} \tag{4.5}$$

where θ is the Heaviside step function.

Following Zubarev[1], the double bracket notation introduced above is used to define a general double-time Green's function or propagator

$$\begin{aligned} \langle\langle A(t); B(t')\rangle\rangle = &- \; i\theta(t-t')\langle A(t)B(t')\rangle \\ &\pm \; i\theta(t'-t)\langle B(t')A(t)\rangle, \end{aligned} \tag{4.6}$$

where A and B are boson-like or fermion-like dynamical operators, which could, for instance, be formed as sums of products of even or odd numbers of simple electron field operators, respectively. A and B could of course also refer to other particles, *e.g.*, photons. The plus sign of the second term in Eq. (4.6) applies only for the case of *both* A and B being fermion-like.

Double-time Green's functions or propagators are often studied in terms of their Fourier transforms

$$\langle\langle A; B\rangle\rangle_E = \int_{-\infty}^{\infty} \langle\langle A(t); B(t')\rangle\rangle \exp[iE(t-t')]d(t-t'), \tag{4.7}$$

and sometimes the inverse relation is useful,

$$\langle\langle A(t); B(t')\rangle\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty} \langle\langle A; B\rangle\rangle_E \exp[-iE(t-t')]dE\,. \tag{4.8}$$

Such integrals can be made well defined by contour integration in the complex plane and with appropriate convergence factors and limiting procedures, as discussed in the previous chapter.

Formal expansions are considered in terms of energy eigenstates $|n\rangle$ of the many-electron hamiltonian (Eq. (4.3)) and the number operator (Eq. (3.55)):

$$H|n\rangle = E_n\,(M_n)\,|n\rangle, \qquad N_0|n\rangle = M_n|n\rangle\,, \tag{4.9}$$

with $M_n = 0, 1, 2, \ldots$. Again, $|0\rangle$ is the N-electron ground state. Using the fact that A and B are Heisenberg operators, [*i.e.*, $A(t) = e^{iHt}A(0)e^{-iHt}$ and

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[1] Zubarev, *Soviet Phys. Uspekhi* **3**, 320 (1960)

$B(t) = e^{iHt}B(0)e^{-iHt}$], and the completeness of the eigenstates $1 = \sum |n\rangle\langle n|$, we can write

$$\begin{aligned}&\langle\langle A(t); B(t')\rangle\rangle \qquad (4.10)\\ &= \begin{cases} -i\sum_n \langle 0|A|n\rangle\langle n|B|0\rangle \exp[-i(E_n - E_0)(t-t')] & t > t' \\ \pm i\sum_n \langle 0|B|n\rangle\langle n|A|0\rangle \exp[-i(E_0 - E_n)(t-t')] & t < t'. \end{cases}\end{aligned}$$

The identities

$$\begin{aligned}&\lim_{\eta\to+0} \tfrac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\exp[-iE(t-t')]}{E-(E_0-E_n)-i\eta} dE \qquad (4.11)\\ &= \begin{cases} 0 & t > t' \\ i\exp[-i(E_0-E_n)(t-t')] & t < t' \end{cases}\end{aligned}$$

and

$$\begin{aligned}&\lim_{\eta\to+0} \tfrac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\exp[-iE(t-t')]}{E-(E_n-E_0)+i\eta} dE \qquad (4.12)\\ &= \begin{cases} -i\exp[-i(E_n-E_0)(t-t')] & t > t' \\ 0 & t < t' \end{cases}\end{aligned}$$

are then used to write

$$\langle\langle A; B\rangle\rangle_E = \lim_{\eta\to+0} \sum_n [\frac{\langle 0|A|n\rangle\langle n|B|0\rangle}{E - E_n + E_0 + i\eta} \pm \frac{\langle 0|B|n\rangle\langle n|A|0\rangle}{E - E_0 + E_n - i\eta}], \qquad (4.13)$$

for the Fourier transform from Eq. (4.8). This is the so-called spectral (or Lehmann) representation of the propagator.

The identity $E(E-a)^{-1} = 1 + a(E-a)^{-1}$, and the relations

$$\begin{aligned}\langle 0|A|n\rangle(E_n - E_0) &= \langle 0|[A,H]_-|n\rangle \\ \langle n|B|0\rangle(E_n - E_0) &= \langle n|[H,B]_-|0\rangle\,,\end{aligned} \qquad (4.14)$$

can be used to obtain the two equivalent forms of the equation of motion of $\langle\langle A; B\rangle\rangle_E$:

$$\begin{aligned}E\langle\langle A; B\rangle\rangle_E &= \langle [A,B]_\pm\rangle + \langle\langle [A,H]_\pm; B\rangle\rangle_E \\ &= \langle [A,B]_\pm\rangle + \langle\langle A; [H,B]_-\rangle\rangle_E\,. \end{aligned} \qquad (4.15)$$

It is sometimes useful to consider the averages in Eq. (4.6) that define the propagator not to be taken with respect to a pure state $|0\rangle$ but rather with respect to a density operator ρ,

$$\langle AB\rangle = \mathrm{Tr}\left\{\rho AB\right\} , \tag{4.16}$$

which would lead to the expression

$$\begin{aligned}&\langle\langle A;B\rangle\rangle_E \\ &= \lim_{\eta\rightarrow +0}\sum_{n,m}\langle n|A|m\rangle\langle m|B|n\rangle\left[\frac{\rho_n}{E-E_m+E_n+i\eta}\pm\frac{\rho_m}{E-E_m+E_n-i\eta}\right],\end{aligned} \tag{4.17}$$

assuming that the density operator is diagonal in the energy eigenstates, *i.e.*, $\rho_{nm} = \langle n|\rho|m\rangle = \delta_{mn}\rho_n$.

The actual calculation of the propagator naturally involves approximations of various kinds. Approximate treatments of propagators are often handled in terms of the moment expansion

$$\begin{aligned}\langle\langle A;B\rangle\rangle_E &= E^{-1}\langle[A,B]_\pm\rangle + E^{-2}\langle[[A,H]_-B]_\pm\rangle \\ &\quad +E^{-3}\langle[[[A,H]_-,H]_-,B]_\pm\rangle+\cdots \\ &= E^{-1}\langle[A,B]_\pm\rangle + E^{-2}\langle[A,[H,B]_-]_\pm\rangle \\ &\quad +E^{-3}\langle[A,[H,[H,B]_-]_-]_\pm\rangle+\cdots\end{aligned} \tag{4.18}$$

obtained by iterating the equations of motion (4.15). In order to obtain a systematic treatment in terms of matrices, it is often useful to introduce the concept of a linear space of field operators and the notion of superoperators acting on this space. Thus, a basis of field operators $\{X_i\}$, a superoperator hamiltonian $\hat{H}$, and a superoperator identity $\hat{I}$ are introduced, such that $\hat{H}X = [H,X]_-$ and $\hat{I}X = X$. A scalar product $(A|B) = \langle[A^\dagger,B]_\pm\rangle$ is defined for any two operators in the space spanned by $\{X_i\}$. The moment expansion can then be expressed as

$$\begin{aligned}\langle\langle A^\dagger;B\rangle\rangle_E &= E^{-1}(A|B) + E^{-2}(A|\hat{H}B) + E^{-3}(A|\hat{H}^2B)+\cdots \\ &= (A|(E\hat{I}-\hat{H})^{-1}B),\end{aligned} \tag{4.19}$$

where a formal summation has been performed to obtain the superoperator resolvent $(E\hat{I}-\hat{H})^{-1}$.

In the following, it will sometimes be useful to consider the array of all propagators in terms of a suitable basis of field operators

$$\{(X_i|(E\hat{I}-\hat{H})^{-1}X_j)\} = \{G_{ij}(E)\} = \mathbf{G}(E) \tag{4.20}$$

and the notation

$$\begin{aligned} \mathbf{G}(E) &= E^{-1}(\mathbf{X}|\mathbf{X}) + E^{-2}(\mathbf{X}|\hat{H}\mathbf{X}) + E^{-3}(\mathbf{X}|\hat{H}^2\mathbf{X}) + \cdots \\ &= (\mathbf{X}|(E\hat{I} - \hat{H})^{-1}\mathbf{X}) \end{aligned} \tag{4.21}$$

is introduced, where $\mathbf{G}$ is a square matrix and $\mathbf{X}$ is the appropriate row (or column) array of field operators.

The higher moments in the moment expansion of the propagator or the propagator matrix can become quite complicated and approximations are necessary. The simplest approximation that yields useful results proceeds by approximating higher moments as powers of the first moment $\mathbf{F} = (\mathbf{X}|\hat{H}\mathbf{X})$. Denote $\mathbf{S} = (\mathbf{X}|\mathbf{X})$ and obtain the approximation

$$\begin{aligned} \mathbf{G}(E) &\simeq E^{-1}\mathbf{S}[\mathbf{1} + E^{-1}\mathbf{S}^{-1}\mathbf{F} + E^{-2}\mathbf{S}^{-1}\mathbf{F}\mathbf{S}^{-1}\mathbf{F} + \cdots] \\ &= \mathbf{S}(E\mathbf{S} - \mathbf{F})^{-1}\mathbf{S}, \end{aligned} \tag{4.22}$$

where again the geometric progression has been summed. This is called the *geometric approximation.*

Problems

1. Show that the average value of Eq. (4.1) with respect to a two-electron state is $\langle kl|H_{int}|kl\rangle = (kk|ll) - (kl|lk)$, and that it is the same as calculating the average of $1/|\vec{r}_1 - \vec{r}_2|$ with respect to a two-electron Slater determinant with the spin orbitals u_k and u_l in "first-quantization". Also show that the average value of the electron interaction hamiltonian in Eq. (4.1) is zero with respect to a one-electron state, as it should be.

4.1 The Electron Propagator

The electron propagator is obtained when the basis field operators are restricted to the electron field operators $X_i = a_i^\dagger$ and becomes

$$\langle\langle a_i; a_j^\dagger\rangle\rangle_E = (a_i^\dagger|(E\hat{I} - \hat{H})^{-1}a_j^\dagger). \tag{4.23}$$

This propagator is particularly useful in studying single-electron detachment or attachment processes, because it exhibits simple poles in the complex energy plane corresponding to ionization potentials and electron affinities. This can be seen from the expressions $\langle 0|a_i|n\rangle\langle n|a_j^\dagger|0\rangle$ and $\langle 0|a_j^\dagger|n\rangle\langle n|a_i|0\rangle$, the numerators in the energy representation of the propagator as given in expression (4.13). For $|0\rangle$ being an N-electron state these expressions differ from zero only if $|n\rangle$ is either an $(N+1)$-electron or an $(N-1)$-electron state, which means that the electron propagator singularities in the energy plane occur at $E = E_n(N+1) - E_0(N)$ and $E = E_0(N) - E_n(N-1)$.

The elements of the "metric matrix" **S** and the "dynamical matrix" **F** that occur in the geometric approximation are readily calculated from the basic anticommutation relations (Eq. (3.49)) and the hamiltonian as given by Eqs. (4.3) and (4.4). The results are

$$\begin{aligned} S_{ij} &= (a_i^\dagger|a_j^\dagger) = \langle [a_i, a_j^\dagger]_+ \rangle = \delta_{ij} \\ F_{ij} &= (a_i^\dagger|\hat{H}a_j^\dagger) = \langle [a_i, [H, a_j^\dagger]_-]_+ \rangle \\ &= h_{ij} + \sum_{r,s} \langle ir||js \rangle \langle a_r^\dagger a_s \rangle \,. \end{aligned} \tag{4.24}$$

Diagonalization of **F** with the constraint that the first-order reduced density matrix γ (the one-matrix) satisfies $\gamma_{sr} = \langle a_r^\dagger a_s \rangle = \langle n_r \rangle \delta_{sr}$ with occupation numbers $\langle n_r \rangle = 0$ or 1 (*i.e.*, Tr $\gamma = N$ and $\gamma^2 = \gamma$) is done iteratively and converges to a single determinantal SCF approximation for the N-electron ground state corresponding to the appropriate set of occupation numbers.

The unitary transformation **x** then satisfies $\mathbf{x}^\dagger \mathbf{F} \mathbf{x} = \epsilon$, where ϵ is a diagonal matrix so that

$$\langle\langle \mathbf{a}; \mathbf{a}^\dagger \rangle\rangle_E = (\mathbf{a}^\dagger|(E\hat{I} - \hat{H})^{-1}\mathbf{a}^\dagger) \simeq \mathbf{x}(E\mathbf{1} - \epsilon)^{-1}\mathbf{x}^\dagger \tag{4.25}$$

in the geometric approximation. Comparing this expression with the energy representation of the electron propagator

$$\begin{aligned} &\langle\langle a_i; a_j^\dagger \rangle\rangle_E \\ &= \sum_m \left[\frac{\langle 0|a_i|m\rangle\langle m|a_j^\dagger|0\rangle}{E - E_m + E_0 + i\eta} + \frac{\langle 0|a_j^\dagger|m\rangle\langle m|a_i|0\rangle}{E + E_m - E_0 - i\eta}\right] \end{aligned} \tag{4.26}$$

the identifications $E_m\,(N+1) - E_0\,(N) = \epsilon_m$ and $\langle 0|a_i|m\rangle = x_{im}$ ($\langle m|a_j^\dagger|0\rangle = x_{jm}^*$), can be made for spin orbital m unoccupied in the$N$-electron ground state $|0\rangle$, whereas $E_m\,(N-1) - E_0\,(N) = -\epsilon_m$ and $\langle m|a_i|0\rangle = x_{im}$ ($\langle 0|a_j^\dagger|m\rangle = x_{jm}^*$) for spin orbital m occupied in the N-electron ground state.

The unitarity of **x** leads to the following result:

$$\langle m| \sum_j a_j^\dagger x_{jm}|0\rangle = \sum_j x_{jm}^* x_{jm} = 1 \,, \tag{4.27}$$

which means that $\sum_j a_j^\dagger x_{jm}|0\rangle = |m\rangle$. This result introduces the transformed electron field operators

$$\tilde{a}_m = \sum_j a_j x_{jm}^* \qquad \text{and} \qquad \tilde{a}_m^\dagger = \sum_j a_j^\dagger x_{jm} \tag{4.28}$$

corresponding to the SCF spin orbitals, and it inspires the introduction of the basic excitation and de-excitation operators

$$Q_m^\dagger = \begin{cases} \tilde{a}_m^\dagger & \text{for} \quad m \quad \text{unocc.} \\ \tilde{a}_m & \text{for} \quad m \quad \text{occ.} \end{cases}, \quad Q_m = \begin{cases} \tilde{a}_m & \text{for} \quad m \quad \text{unocc.} \\ \tilde{a}_m^\dagger & \text{for} \quad m \quad \text{occ.} \end{cases}$$

The SCF spin orbitals and their corresponding electron field operators are labeled in order of increasing energies ϵ_m, making the N first orbitals occupied in the N-electron ground state

$$|0\rangle = \tilde{a}_1^\dagger \tilde{a}_2^\dagger \cdots \tilde{a}_N^\dagger |vac\rangle . \tag{4.29}$$

This is also the reference state defining the electron propagator in this approximation. It is now straightforward to deduce that

$$\begin{aligned} \langle m|n\rangle &= \langle 0|Q_m Q_n^\dagger|0\rangle = \langle 0|[Q_m, Q_n^\dagger]_+|0\rangle = \delta_{mn}, \\ \langle m|\hat{H}|n\rangle &= \langle 0|Q_m \hat{H} Q_n^\dagger|0\rangle = \langle 0|[Q_m, [H, Q_n^\dagger]_-]_+|0\rangle \\ &= \delta_{mn}\epsilon_m, \end{aligned} \tag{4.30}$$

which is the essence of a *consistent* model, *i.e.*, a model where our only choice is the computational orbital basis and everything else is a consequence of the equations of motion. In Eq (4.30), the fact that $Q_m|0\rangle = 0$ for all m has been used. This so-called *killer* condition for all of the de-excitation operators becomes an essential *consistency* requirement, and it permits us to identify the various stationary states $|m\rangle$ as independent spectroscopic states for electron detachment and attachment processes in this approximation.

The geometric approximation for the electron propagator, as discussed above, is of course the Hartree-Fock approximation (or in a finite basis, the SCF approximation). This approximation can be generalized slightly by using a density operator, which yields the pure state Hartree-Fock propagator as a special case. The grand-canonical density operator $\rho = \exp[-\beta(H_0 - \mu N_0)]/\mathrm{Tr}\{\exp[-\beta(H_0 - \mu N_0)]\}$ is introduced, with $H_0 = \sum_k \epsilon_k n_k$, $N_0 = \sum_k n_k$, $n_k = \tilde{a}_k^\dagger \tilde{a}_k$, and μ the chemical potential. As the so-called occupation number operators n_k are idempotent ($n_k^2 = n_k$) and mutually commute,

$$\rho = \prod_k (1 + \lambda_k n_k)/\mathrm{Tr}\{\prod_k (1 + \lambda_k n_k)\} , \tag{4.31}$$

with $\lambda_k = \exp[-\beta(\epsilon_k - \mu)] - 1$. One should here observe that the Fock space is a direct product of eigenspaces of the operators n_k and that the trace of a direct product of operators is a product of the traces of the individual factors. The eigenstates of n_k are the two states corresponding to spin orbital k empty or filled. The matrix representatives of the operators in this basis are

$$n_k = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}, \; \tilde{a}_k^\dagger = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}, \; \tilde{a}_k = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}, \; 1 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}.$$

This permits the expression

$$\rho = \prod_k \frac{1 + \lambda_k n_k}{2 + \lambda_k}, \tag{4.32}$$

and the occupation numbers are $\langle n_k \rangle = \mathrm{Tr}\{\rho n_k\} = (1 + \lambda_k)/(2 + \lambda_k) = 1/(1 + \exp[\beta(\epsilon_k - \mu)])$, which with $\beta = 1/kT$ (k is Boltzmann's constant and T is the absolute temperature) yields the ordinary Fermi-Dirac distribution. However, the density operator can now be expressed entirely in terms of the occupation numbers without reference to any thermodynamic parameters:

$$\rho = \prod_k [1 - \langle n_k \rangle + (2\langle n_k \rangle - 1) n_k]. \tag{4.33}$$

Comparing the geometric approximation as given by Eq. (4.25) with the energy representation of the electron propagator according to Eq. (4.17)

$$\langle\langle a_s; a_r^\dagger \rangle\rangle_E = \sum_{m,n} \langle n|a_s|m\rangle \langle m|a_r^\dagger|n\rangle \left[\frac{\rho_n}{E - E_m + E_n} + \frac{\rho_m}{E - E_m + E_n}\right],$$

one obtains $x_{sk} x_{rk}^* = \langle n|a_s|m\rangle\langle m|a_r^\dagger|n\rangle\,(\rho_n + \rho_m)$ and $\epsilon_k = E_m - E_n$. It is straightforward to show that for a density operator $\rho = C\exp[-\beta(H_0 - \mu N_0)]$ it holds that $\rho_n/\rho_m = \exp[\beta(E_m - E_n) - \mu(N_m - N_n)] = \exp[\beta(\epsilon_k - \mu)]$, yielding the results

$$\begin{aligned} \rho_m \langle n|a_s|m\rangle\langle m|a_r^\dagger|n\rangle &= x_{sk} x_{rk}^* / [1 + \exp[\beta\,(\epsilon_k - \mu)]] \\ &= x_{sk} x_{rk}^* \langle n_k \rangle \\ \rho_n \langle n|a_s|m\rangle\langle m|a_r^\dagger|n\rangle &= x_{sk} x_{rk}^* \,(1 - \langle n_k \rangle)\,. \end{aligned} \tag{4.34}$$

This means that the electron propagator in the geometric approximation can be given as

$$G_{sr}(E) = \langle\langle a_s; a_r^\dagger \rangle\rangle_E = \sum_k x_{sk} \left[\frac{\langle n_k \rangle}{E - \epsilon_k - i\eta} + \frac{(1 - \langle n_k \rangle)}{E - \epsilon_k + i\eta}\right] x_{kr}^\dagger, \tag{4.35}$$

which is the most general expression consistent with the equation of motion

$$\sum_q (E\delta_{sq} - F_{sq}) G_{qr}(E) = \delta_{sr}. \tag{4.36}$$

The significance of this result is that a set of occupation numbers $\langle n_k \rangle$ can be specified, which could even be fractional numbers between zero and one, defining a density operator as the one in Eq. (4.33). Such a density operator is normalized and internally consistent, *i.e.*, $\mathrm{Tr}\{\rho\} = 1$, and $\mathrm{Tr}\{\rho n_k\} = \langle n_k \rangle$, and permits a self-consistent determination of the singularities (poles) of $G_{sr}(E)$ or the molecular orbital energies ϵ_k and the residues at those poles, or the corresponding molecular orbital coefficients x_{sk}.

Most stable molecular systems have a gap in the electron propagator spectrum because the ionization potential of the $(N+1)$-electron molecular ion is smaller than the one of the N-electron molecule, *i.e.*,

$$\min[E_m(N+1) - E_0(N)] > \max[E_0(N) - E_m(N-1)]\,. \tag{4.37}$$

This means that the "chemical potential" or "Fermi energy" μ may be chosen, such that it lies in the gap. The occupation numbers then satisfy $N = \sum_k \langle n_k \rangle$ for the sum over all k such that $\epsilon_k < \mu$. For open shell systems where there is no gap, the possibility of using noninteger occupation numbers is particularly useful.

The propagator $G_{sr}\,(E)$ is analytical in the complex E-plane except on the real axis (for $\eta = 0$) where it has simple poles. (The exact propagator can also have cuts along the real axis corresponding to the continuum part of the spectrum, but in a finite basis, the approximate propagator has only (simple) poles.) These poles correspond to eigenvalues of the single-particle effective hamiltonian or Fock operator F, with matrix elements F_{ij} as given in Eq. (4.24), which depend on the single particle reduced density matrix with elements $\gamma_{sr} = \langle a_r^\dagger a_s \rangle$. This density matrix can be calculated from the electron propagator as a contour integral in the complex E-plane

$$\gamma_{sr} = \langle a_r^\dagger a_s \rangle = \frac{1}{2\pi i} \int_C G_{sr}(E)dE, \tag{4.38}$$

where the closed contour C consists of the real axis $\mathrm{Re}(E)$ and a semicircle in the upper half-plane (*i.e.*, for $\mathrm{Im}(E) > 0$) such that, when the infinitesimal $\eta > 0$, C encloses the so-called occupied orbital energies. Thus, from the residue theorem,

$$\gamma_{sr} = \sum_m \sum_n \langle m|a_s|n\rangle\langle n|a_r^\dagger|m\rangle\rho_n = \mathrm{Tr}\{\rho a_r^\dagger a_s\} = \langle a_r^\dagger a_s \rangle. \tag{4.39}$$

In this manner, an iterative process can be followed to determine the electron propagator self-consistently in the geometric approximation. This approach represents a slight generalization of the ordinary SCF method for the calculation of molecular spin orbitals and orbital energies.

Problems

1. Show that Eq. (4.36) follows from Eq. (4.15) for the electron propagator in the geometric approximation.

Notes and Bibliography

D. N. Zubarev has written an interesting account of the theory and application of general double-time Green's functions, published in *Soviet Physics Uspekhi* **3**, 320 (1960) (English translation).

4.2 Electrons in a Central Potential

Some of the consequences for the Green's function of a spherically symmetric potential energy are explored. The WKB (Wentzel-Kramers-Brillouin) electron propagator for this case is introduced.

4.2.1 Electron Propagator

The electron propagator

$$\langle\langle\psi(\xi,t);\psi^\dagger(\xi',t')\rangle\rangle = (2\pi)^{-1}\int dE e^{-iE(t-t')}G(\xi,\xi';E) \tag{4.40}$$

for a system with a hamiltonian

$$H = \int d\xi\psi^\dagger(\xi)\left[-\frac{1}{2m}\vec{\nabla}^2 + V(r)\right]\psi(\xi) \tag{4.41}$$

i.e., with a spherically symmetric, spin-independent potential energy, can be represented as

$$G(\xi,\xi';E) = \delta_{\zeta\zeta'}G(\vec{r},\vec{r}';E). \tag{4.42}$$

Only three variables are significant for $G(\vec{r},\vec{r}';E)$ and can be chosen to be $r = |\vec{r}|$, $r' = |\vec{r}'|$ and γ, where $\vec{r}\cdot\vec{r}' = rr'\cos\gamma$.

The electron propagator or Green's function describes an electron scattering from a spherically symmetric center or equivalently from another particle (electron or proton) in the center-of-mass coordinate system. The physics of such a scattering process possesses cylindrical symmetry about the polar axis and is independent of the polar angle ϕ.

The hamiltonian is separable in the variables r and γ, and we obtain the total Green's function as a convolution:

$$G(\vec{r},\vec{r}';E) = (2\pi i)^{-1}\int_C d\lambda D(cos\gamma;\lambda)G_\lambda(r,r';E)/rr', \tag{4.43}$$

with the contour C surrounding the positive real λ -axis in the counterclockwise direction such that no poles of G_λ fall inside the contour. The angular Green's function satisfies the equation

$$\left[\lambda + \partial^2/\partial\gamma^2 + cot\gamma\partial/\partial\gamma\right] D(\cos\gamma; \lambda) = \delta(1 - \cos\gamma), \tag{4.44}$$

and one can show that it has the spectral form

$$D(\cos\gamma; \lambda) = (4\pi)^{-1} \sum_{l=0}^{\infty} \frac{(2l+1)P_l(\cos\gamma)}{\lambda - l(l+1)}, \tag{4.45}$$

in terms of the Legendre polynomials. The radial Green's function satisfies

$$\left[2m(E - V(r)) - \lambda/r^2 + \partial^2/\partial r^2\right] G_\lambda(r, r^{'}; E) = 2m\delta(r - r^{'}) \tag{4.46}$$

and the boundary condition that it vanishes at the origin.

A closed expression for $D(\cos\gamma; \lambda)$ can be obtained from the theory of Legendre functions $P_\nu(\cos\gamma)$, which are solutions to

$$\left[\nu(\nu+1) + \partial^2/\partial\gamma^2 + cot\gamma\partial/\partial\gamma\right] P_\nu(\cos\gamma) = 0. \tag{4.47}$$

Legendre functions for general complex degree ν are not regular for $\gamma = \pi$. Two linearly independent solutions to Eq. (4.47) are $P_\nu(\cos\gamma)$ ($P_\nu(1) = 1$) and $P_\nu(\cos(\pi - \gamma)) = P_\nu(-\cos\gamma)$. The first is regular at the end point $\gamma = 0$ and the second at the end point $\gamma = \pi$ of the interval on which the Legendre functions are defined.

The Green's function

$$D(\cos\gamma; \nu(\nu+1)) \tag{4.48}$$

satisfies Eq. (4.44) for $0 < \gamma \leq \pi$ and is then proportional to $P_\nu(-\cos\gamma)$, since it follows from the spectral form, Eq. (4.45), that it has a finite value at $\gamma = \pi$. The constant of proportionality follows from

$$\begin{aligned} \sum_{l=0}^{\infty} \frac{(-1)^l(2l+1)}{[\nu(\nu+1) - l(l+1)]} &= \sum_{l=0}^{\infty}(-1)^l[\frac{1}{\nu - l} - \frac{1}{\nu + l + 1}] \\ &= \sum_{l=-\infty}^{\infty} \frac{(-1)^l}{\nu - l} = \frac{\pi}{\sin\nu\pi}, \end{aligned} \tag{4.49}$$

where the last step uses the result of expansion of a meromorphic function from Appendix A. Thus,

$$D(\cos\gamma;\nu(\nu+1)) = \frac{1}{4\pi}\frac{\pi}{\sin\nu\pi}P_\nu(-\cos\gamma) \tag{4.50}$$

and the relation between ν and λ is

$$\nu = -\frac{1}{2} \pm (\lambda + \frac{1}{4})^{\frac{1}{2}}. \tag{4.51}$$

The integration in Eq. (4.43) can be changed to involve the variable ν with the contour surrounding the real ν-axis in counterclockwise direction.

Only a few potential energies $V(r)$ admit closed form expressions for the radial Green's function. The Coulomb case

$$V(r) = -e^2Z/r \tag{4.52}$$

has been studied by many and obtained in a variety of representations.

4.2.2 The WKB Propagator

An approximate solution of Eq. (4.46) can be obtained for a general potential energy $V(r)$ by means of the WKB method and expressions derived for a number of quantities. Using Kramers' modification $\lambda = (\nu + \frac{1}{2})^2$ in the differential equation (4.46), one defines the local wave number as

$$p_\nu(r) = \left[2m(E - V(r)) - (\nu + \frac{1}{2})^2/r^2\right]^{\frac{1}{2}}, \tag{4.53}$$

where Im $p_\nu(r) > 0$. The homogeneous equation corresponding to Eq. (4.46) has two linearly independent solutions, which in the WKB approximation are given as

$$\exp[\pm i\int^r p_\nu(s)ds - \frac{1}{2}\ln p_\nu(r)]. \tag{4.54}$$

Comment: The WKB approximation uses a power series in $\hbar$ and since the units chosen here have $\hbar = 1$ it may be useful to briefly outline the essence of the WKB approximation without those units. The solution is expressed as $\exp[iS(r)/\hbar]$ yielding

$$i\hbar S'' - S'^2 + p_\nu^2(r) = 0, \tag{4.55}$$

which with

$$S = S_0 + \hbar S_1 + \ldots \tag{4.56}$$

and equating equal powers of $\hbar$ results in the first two equations

$$\begin{aligned} -S_0'^2 + p_\nu^2(r) &= 0 \\ iS_0'' - 2S_0'S_1' &= 0. \end{aligned} \tag{4.57}$$

The solutions are

$$S_0(r) = \pm \int^r p_\nu(s)ds \tag{4.58}$$

and

$$S_1(r) = \frac{1}{2} i \ln p_\nu(r). \tag{4.59}$$

The Wronskian of the two independent solutions is $2i$ and the Green's function, which should vanish when r or r' equals zero or infinity, is

$$G_\nu(r, r'; E) = (m/i) \exp[i \int_{r_<}^{r_>} p_\nu(s)ds - \frac{1}{2} \ln p_\nu(r) - \frac{1}{2} \ln p_\nu(r')], \tag{4.60}$$

where ν has replaced λ as the label of the radial propagator. The integration limits $r_<$ and $r_>$ denote the smaller and greater of r and r', respectively, and the integration in the exponent thus performed over a positive interval, which together with the choice of branch of the local wave number guarantees the desired boundary conditions.

The Green's function (4.60) has, for real ν, a branch cut along the real E-axis, thus exhibiting a completely continuous spectrum. The spectral density function can be determined as discussed before. The complex energy variable is written as $E = \epsilon + i\eta$ and the real quantity

$$k_\nu(r) = \left| 2m[\epsilon - V(r)] - \frac{(\nu + \frac{1}{2})^2}{r^2} \right|^{\frac{1}{2}} \tag{4.61}$$

defined. When

$$\epsilon < V(r) + \frac{(\nu + \frac{1}{2})^2}{2mr^2}, \tag{4.62}$$

r is said to be in the forbidden region, and then

$$\lim_{\eta \to 0} p_\nu(r) = ik_\nu(r). \tag{4.63}$$

On the other hand, when

$$\epsilon > V(r) + \frac{(\nu + \frac{1}{2})^2}{2mr^2}, \tag{4.64}$$

r is said to be in the allowed region, and

$$\lim_{\eta \to \pm 0} p_\nu(r) = \pm k_\nu(r). \tag{4.65}$$

The spectral density function is obtained as

$$A_\nu(r, r'; \epsilon) = \lim_{\eta \to +0} (i/2\pi)[G_\nu(r, r'; \epsilon + i\eta) - G_\nu(r, r'; \epsilon - i\eta)]. \tag{4.66}$$

Several distinct cases can be recognized depending on whether r and r' are in forbidden or allowed regions and the number of turning points, *i.e.*, zeros of $k_\nu(r)$, lie in the interval (r, r'). Assuming for simplicity that r is less than r', one can distinguish the following cases:

i) r and r' both in forbidden regions and no turning points in (r, r'), then

$$A_\nu(r, r'; \epsilon) = 0. \tag{4.67}$$

ii) r and r' both in forbidden regions and two turning points, $a < b$ in (r, r'), then

$$\begin{aligned} A_\nu(r, r'; \epsilon) &= (m/\pi)[k_\nu(r)k_\nu(r')]^{-\frac{1}{2}} \\ &\times \exp[-\int_r^a k_\nu(s)ds - \int_b^{r'} k_\nu(s)ds] \times \sin[\int_b^b k_\nu(s)ds]. \end{aligned}$$

iii) r in forbidden and r' in allowed region, one turning point, a, in (r, r'), then

$$\begin{aligned} A_\nu(r, r'; \epsilon) &= (m/\pi)[k_\nu(r)k_\nu(r')]^{-\frac{1}{2}} \\ &\times \exp[-\int_r^a k_\nu(s)ds] \times \sin[\int_a^{r'} k_\nu(s)ds + \frac{\pi}{4}]. \end{aligned}$$

iv) r and r' in allowed region, no turning points, $a < b$, in (r, r'), then

$$A_\nu(r, r'; \epsilon) = (m/\pi)[k_\nu(r)k_\nu(r')]^{-\frac{1}{2}} \cos[\int_r^{r'} k_\nu(s)ds]. \tag{4.68}$$

v) r and r' in allowed regions, two turning points in (r, r'), then

$$\begin{aligned} A_\nu(r, r'; \epsilon) &= (m/\pi)[k_\nu(r)k_\nu(r')]^{-\frac{1}{2}} \qquad (4.69) \\ &\times \exp[-\int_a^b k_\nu(s)ds] \times \cos[\int_r^a k_\nu(s)ds + \int_b^{r'} k_\nu(s)ds]. \end{aligned}$$

These formulas can be collected in the form

$$A_\nu(r,r';\epsilon) = (m/\pi)[k_\nu(r)k_\nu(r')]^{-\frac{1}{2}} \exp[-\alpha] \sin\beta, \tag{4.70}$$

where α is the sum of integrals of k_ν over the forbidden regions in (r,r'), and β is the sum of integrals of k_ν over the allowed regions plus $\pi/4$ for each end point in an allowed region.

The spectral density function $A_\nu(r,r';\epsilon)$ is clearly related to the wave functions in the WKB approximation. In particular, in case (iii), it is the product of two connecting solutions across a turning point. The Green's function does not, at this level of approximation, give the Bohr-Sommerfeld quantization condition, but one can note that in case (ii) the spectral density function is the product of the wave functions in the end points of the interval and an amplitude factor, which assumes its extremum value when the quantization condition

$$\int_a^b k_\nu(s)ds = (n+\frac{1}{2})\pi \tag{4.71}$$

holds.

The radial density distribution for real angular momentum ν is given as (see Eq. (4.60))

$$n_\nu(r) = (2\pi i)^{-1} \int_C dEG_\nu(r,r;E) = (2\pi i)^{-1} \int_C dE[m/ip_\nu(r)], \tag{4.72}$$

which is analogous to the expression for electron charge on a site in the Hückel model . Changing the integration variable to p_ν yields

$$\begin{aligned} n_\nu(r) &= -(2\pi)^{-1} \int dp_\nu \\ &= \begin{cases} k_\nu(r)/\pi, & \epsilon = \mu > V(r) + (\nu+\frac{1}{2})^2 r^{-2} \\ 0, & \text{otherwise.} \end{cases} \end{aligned} \tag{4.73}$$

This formula was used by Fermi to obtain the number of electrons in a given angular momentum state in the statistical theory of the atom. One can note that there is an upper bound to the possible angular momentum in that the radial density distribution vanishes when

$$|\nu+\frac{1}{2}| > rk_{-\frac{1}{2}}(r) \tag{4.74}$$

corresponding to r times the maximum linear momentum.

The total density is similarly obtained as

$$\begin{aligned} n(\vec{r}) &= (2\pi i)^{-1} \int_C dE \sum_{\zeta} G(\xi, \xi; E) \\ &= (\pi i)^{-1} \int_C dE \, G(\vec{r}, \vec{r}; E) \\ &= \sum_l (l + \frac{1}{2}) n_l(r)/\pi r^2. \end{aligned} \tag{4.75}$$

The summation over l can be approximated by an integration to yield

$$n(\vec{r}) \simeq -(\pi/3) \int d[n_l(r)]^3 = (\pi/3)[n_{-\frac{1}{2}}(r)]^3, \tag{4.76}$$

where the integration limits for l has been taken as -1/2 and $rk_{-\frac{1}{2}}(r)$. This result permits the parameter μ, which separates the occupied and unoccupied levels to be related to the density, *i.e.*,

$$\mu = V(r) + (2m)^{-1}[3\pi^2 n(\vec{r})]^{\frac{2}{3}}, \tag{4.77}$$

which is the result for an electron gas and reduces to one of the conditions for the statistical model of the atom when μ=0. These results illustrate the role of μ as chemical potential.

The total number of electrons is obtained from the density as

$$N = 4\pi \int n(\vec{r}) r^2 dr \tag{4.78}$$

using Eq. (4.76), which for the case of a Coulomb potential $V(r) = -e^2 Z/r$ yields

$$N = (2/3)[-e^4 Z^2 m/2\mu]^{3/2}. \tag{4.79}$$

Solving for the parameter μ, one obtains

$$\mu = -\frac{1}{2} e^4 Z^2 m [2/3N]^{\frac{2}{3}}, \tag{4.80}$$

which implies that the principal quantum number of the highest occupied level equals the integer part of $[3N/2]^{\frac{1}{3}}$.

Problems

1. Calculate the energy density for the WKB-approximation to the electron propagator as

$$W_\nu(r) = (2\pi i)^{-1} \int_C E dE G_\nu(r, r; E). \tag{4.81}$$

4.3 The Atomic Central Field Problem

Some of the consequences of the spherical symmetry of the hamiltonian of an atomic system for the Green's function are explored in this section. A number of results concerning tensor operators are invoked and the reader are assumed to be familiar with the Wigner $3j$ and $6j$ symbols.

4.3.1 Electron Propagator

It has been shown in Sec. 4.2 that the electron propagator for a spherically symmetric potential can be expressed as a convolution of an angular and a radial factor Green's function. Such a separation is also possible for the case of a many-electron system, when the ensemble used for the definition of the Green's functions is invariant under rotations about the atomic nucleus. The many-electron states appearing in the spectral form of the electron propagator can, in the case of an atom, be characterized by explicit labels of total orbital and electron spin angular momentum quantum numbers. Assuming Russell-Saunders coupling, one writes

$$|n\rangle = |\gamma L M_L S_{M_S}\rangle, \tag{4.82}$$

where γ denotes other possible quantum numbers. The density operator would then have diagonal elements

$$\rho_n = \rho_{\gamma L M_L S M_S} = w(\gamma L S)/[(2L+1)(2S+1)], \tag{4.83}$$

when it commutes with the operators of orbital and spin angular momentum. The electron field operators are expanded in a spin orbital basis $\{u_s(\xi)\}$ with the compound space spin coordinate $\xi = (\vec{r}, \zeta)$ adapted to the spherical symmetry, *i.e.*,

$$u_s(\xi) = R_{nl}(r) Y_{lm}(\theta, \phi) \delta_{\nu\zeta}, \tag{4.84}$$

where Y_{lm} is a spherical harmonic and where the electron spin function is represented as a Kronecker delta ($\nu = \pm\frac{1}{2}$). The spherical harmonics are defined with the phase convention of Condon and Shortley[2], such that

$$Y_{ll}(\theta, \phi) = \left[\frac{(2l+1)!}{4\pi l!^2}\right]^{1/2} \left[-e^{i\phi}\frac{1}{2}\sin\theta\right]^l, \tag{4.85}$$

and

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[2] Condon and Shortley, *The Theory of Atomic Spectra*, Cambridge University Press, 1953

$$Y_{lm}(\theta,\phi) = \left[\frac{(l+m)!}{(l-m)!(2l)!}\right]^{1/2} \left[e^{i\phi}(-\partial/\partial\theta + icot\theta\partial/\partial\phi\right]^{l-m} Y_{ll}(\theta,\phi)). \quad (4.86)$$

The electron field operators are

$$\psi(\xi) = \sum_{n,l,m,\nu} R_{nl}(r)Y_{lm}(\theta,\phi)\delta_{\nu\zeta}a_{nlm\nu}, \quad (4.87)$$

leading to the following expressions for the operators of total (electron) orbital and spin angular momentum,

$$\begin{aligned}
L_+ = L_x + iL_y &= \sum_{n,l,m,\nu} [(l-m)(l+m+1)]^{1/2} a^\dagger_{nlm+1\nu} a_{nlm\nu}, \\
L_- = L_x - iL_y &= \sum_{n,l,m,\nu} [(l+m)(l-m+1)]^{1/2} a^\dagger_{nlm-1\nu} a_{nlm\nu}, \quad (4.88) \\
L_z &= \sum_{n,l,m,} m a^\dagger_{nlm\nu} a_{nlm\nu},
\end{aligned}$$

$$\begin{aligned}
S_+ &= S_x + iS_y = \sum_{n,l,m} a^\dagger_{nlm\frac{1}{2}} a_{nlm-\frac{1}{2}}, \\
S_- &= S_x - iS_y = \sum_{n,l,m} a^\dagger_{nlm-\frac{1}{2}} a_{nlm\frac{1}{2}}, \quad (4.89) \\
S_z &= \frac{1}{2}\sum_{n,l,m} [a^\dagger_{nlm\frac{1}{2}} a_{nlm\frac{1}{2}} - a^\dagger_{nlm-\frac{1}{2}} a_{nlm-\frac{1}{2}}],
\end{aligned}$$

when the radial functions are assumed to be orthonormal, *i.e.*,

$$\int R^*_{nl}(r)R_{n'l}(r)r^2dr = \delta_{nn'}. \quad (4.90)$$

The creation operator is a tensor operator of rank l with respect to the orbital angular momentum and of rank $\frac{1}{2}$ with respect to spin. For instance,

$$[L_+, a^\dagger_{nlm\nu}]_- = [(l-m)(l+m+1)]^{1/2} a^\dagger_{nlm+1\nu} \quad (4.91)$$

and

$$[S_+, a^\dagger_{nlm\nu}]_- = \left[(\frac{1}{2}-\nu)(\frac{1}{2}+\nu+1)\right]^{1/2} a^\dagger_{nlm\nu+1} = \delta_{-\frac{1}{2}\nu} a^\dagger_{nlm\frac{1}{2}}. \quad (4.92)$$

Similar expressions can be derived for the annihilators $a_{nlm\nu}$. It must be recognized that $(-1)^{l-m+\frac{1}{2}-\nu}a_{nlm\nu}$ transforms as $a^{\dagger}_{nl-m-\nu}$.

Matrix elements of the field operator $\psi^{\dagger}(\xi)$ over the many-electron states can now be calculated in terms of reduced matrix elements of the tensor operators $a^{\dagger}_{nlm\nu}$ using the Wigner-Eckart theorem. Explicitly one obtains

$$\begin{aligned}
&\langle\gamma LM_L SM_S|\psi^{\dagger}(\xi)|\gamma' L' M_L' S' M_S'\rangle \\
= &\sum_{n,l,m,\nu} R^*_{nl}(r)Y^*_{lm}(\theta,\phi)\delta_{\nu\varsigma}(-1)^{L-M_L+S-M_S} \qquad (4.93)\\
&\times\begin{pmatrix} L & l & L' \\ -M_L & m & M_L' \end{pmatrix}\begin{pmatrix} S & 1/2 & S' \\ -M_S & \nu & M_S' \end{pmatrix}\langle\gamma LS||a^{\dagger}_{nl}||\gamma' L' S'\rangle.
\end{aligned}$$

Since only the reduced matrix element and the radial function depend on the label n, it is advantageous to define a more general reduced matrix element as

$$\langle\gamma LS||R^{\dagger}_l(r)||\gamma' L' S'\rangle = \sum_n R^*_{nl}(r)\langle\gamma LS||a^{\dagger}_{nl}||\gamma' L' S'\rangle, \qquad (4.94)$$

which is independent of the particular choice of radial basis functions. As a consequence of the transformation properties of $\psi(\xi)$ and $a_{nlm\nu}$, it follows that

$$\begin{aligned}
\langle\gamma' L' S'||R_l(r)||\gamma LS\rangle &= \sum_n R_{nl}(r)\langle\gamma' L' S'||a_{nl}||\gamma LS\rangle \qquad (4.95)\\
&= (-1)^{L'+l-L+S'+\frac{1}{2}-S}\langle\gamma LS||R^{\dagger}_l(r)||\gamma' L' S'\rangle^*.
\end{aligned}$$

In addition to the orbital and spin rotations, one can also consider other symmetry properties. In the case of Russell-Saunders coupling, considerations of parity further limits the possible l values such that only even (odd) values are allowed when γ and γ' have equal (different) parity quantum numbers.

The form of the matrix elements in Eq. (4.93) permits partial summations in the spectral representation of the electron propagator. Thus, one obtains explicitly that

$$\begin{aligned}
&\sum_{M_L,M_L',M_S,M_S'} \langle\gamma' L' M_L' M_S'|\psi(\xi)|\gamma LSM_L M_S\rangle \\
&\times\langle\gamma LM_L M_S|\psi^{\dagger}(\xi')|\gamma' L' S' M_L' M_S'\rangle \\
= &\frac{\delta_{\varsigma\varsigma'}}{8\pi}\sum_l P_l(\cos\Theta)\langle\gamma LS||R^{\dagger}_l(r)||\gamma' L' S'\rangle^* \\
&\times\langle\gamma LS||R^{\dagger}_l(r')||\gamma' L' S'\rangle, \qquad (4.96)
\end{aligned}$$

with

$$\begin{aligned} \cos\Theta &= \sin\theta\sin\theta' \cos(\phi-\phi') + \cos\theta\cos\theta' \\ &= \vec{r}\cdot\vec{r}'/rr', \end{aligned} \tag{4.97}$$

where the orthogonality of the $3j$ symbols and the addition theorem of spherical harmonics have been used. The result for the electron propagator in the case of a spherically symmetric potential can now be employed to write

$$G(\xi,\xi';E) = \delta_{\zeta\zeta'}\sum_l \frac{2l+1}{4\pi}P_l(cos\Theta)G_{l(l+1)}(r,r';E)/rr'. \tag{4.98}$$

Identifying this expression with the spectral form of the electron propagator, for the case of a density operator [Eq. (4.33)] that commutes with the orbital and spin angular momentum operators, and using Eq. (4.96) lead to the result

$$\begin{aligned} G_{l(l+1)}(r,r';E) &= \sum \frac{rr'}{4l+2}\langle\gamma LS||R_l^\dagger(r)||\gamma'L'S'\rangle^* \\ &\quad\times\langle\gamma LS||R_l^\dagger(r')||\gamma'L'S'\rangle \\ &\quad\times\left[\frac{w(\gamma LS)/(2L+1)(2S+1)}{E-E(\gamma'L'S')+E(\gamma LS)-i\eta}\right. \\ &\quad\left.+\frac{w(\gamma'L'S')/(2L'+1)(2S'+1)}{E-E(\gamma'L'S')+E(\gamma LS)+i\eta}\right]. \end{aligned} \tag{4.99}$$

One could compare this expression to that of the radial Green's function for the case of a spherically symmetric potential (noninteracting electrons)

$$G_{l(l+1)}(r,r';E) = \sum_k u_k(r)u_k^*(r')/(E-\epsilon_k), \tag{4.100}$$

with the orthonormal functions $u_k(r)$:

$$\int u_k^*(r)u_{k'}(r)dr = \delta_{kk'}. \tag{4.101}$$

In the case of interacting electrons, the corresponding amplitudes are proportional to $\langle\gamma'L'S'||R_l(r)||\gamma LS\rangle$, which in general are not linearly independent. Instead of considering the general case one could study specific cases. For instance, in the simplest theory of atomic spectra, the many-electron states $|\gamma LM_LSM_S\rangle$ are expressed in terms of configurations with a prescribed number of basis spin orbitals from each occupied subshell (nl). That is, these states are eigenvectors of the subshell number operators

$$N_{nl} = \sum_{m\nu} a^{\dagger}_{nlm\nu} a_{nlm\nu}. \tag{4.102}$$

Let us consider an atomic term (γLS) , corresponding to eigenvalues $N_{nl}(\gamma)$ of the operators N_{nl}, respectively. This atomic term can be thought to arise from a term $(\gamma^{'} L^{'} S^{'})$ of the positive ion by adding an electron to the subshell (nl). Thus,

$$N_{nl}(\gamma) = N_{nl}(\gamma^{'}) + 1 \tag{4.103}$$

for that subshell, while equal in the two terms for all other subshells. In such a case, only one reduced matrix element $\langle \gamma LS || a^{\dagger}_{n'l'} || \gamma^{'} L^{'} S^{'} \rangle$ is different from zero and one can define a coefficient of fractional parentage $(\gamma LS\{|\gamma^{'} L^{'} S^{'})$ through the relation

$$\begin{aligned} & \langle \gamma LS || a^{\dagger}_{nl} || \gamma^{'} L^{'} S^{'} \rangle \\ = \quad & (-1)^{N_{nl}(\gamma)} [N_{nl}(\gamma)(2L+1)(2S+1)]^{1/2} (\gamma LS\{|\gamma^{'} L^{'} S^{'}). \end{aligned} \tag{4.104}$$

The coefficients of fractional parentage satisfy the orthonormality condition

$$\sum_{\gamma', L', S'} (\gamma LS\{|\gamma^{'} L^{'} S^{'})(\gamma^{''} LS\{|\gamma^{'} L^{'} S^{'})^{*} = \delta_{\gamma\gamma''}, \tag{4.105}$$

which follows from the definitions (4.104) and (4.102) and the relation (4.93).

Using this simplest description of atomic spectra, it is straightforward to show that the radial electron propagator of Eq. (4.99) achieves a form similar to that of (4.100) in that the radial amplitudes are orthonormal, but instead of each factor $(E - \epsilon_{nl})^{-1}$ appears a sum of terms $\sum_j c_j (E - \epsilon_j)^{-1}$, where each pole corresponds to a transition from a term (γLS) to another.

A particular simple example of an atomic electron propagator is obtained in the pure state case for a half-filled subshell.

Then all terms have zero weight, except the one with $L = 0$ and $S = l + \frac{1}{2}$. These two quantum numbers specify the term uniquely. The Pauli exclusion principle then gives the selection rule

$$(0, l + \frac{1}{2}\{|\gamma LS) = \delta_{Ll}\delta_{Sl}(0, l + \frac{1}{2}\{|l, l) = \delta_{Ll}\delta_{Sl} \tag{4.106}$$

and

$$(\gamma LS\{|0, l + \frac{1}{2}) = \delta_{Ll}\delta_{Sl}(2l+1)^{-1/2}. \tag{4.107}$$

The final expression for the electron propagator is

$$\langle\langle a_{m\nu}; a^{\dagger}_{m'\nu'}\rangle\rangle_E = \delta_{mm'}\delta_{\nu\nu'}\left(\frac{\frac{1}{2}}{E - E_1 + i\eta} + \frac{\frac{1}{2}}{E - E_2 - i\eta}\right) \tag{4.108}$$

with

$$E_1 = E(l^{2l+1}, 0, l + \frac{1}{2}) - E(l^{2l+2}, l, l) \tag{4.109}$$

and

$$E_2 = E(l^{2l}, l, l) - E(l^{2l+1}, 0, l + \frac{1}{2}). \tag{4.110}$$

An example would be the nitrogen atom with its ^4S ground state term connecting with the anion and cation ^3P terms.

Expressing the electron propagator in terms of the spectral weights $A(\xi, \xi'; s)$, one can write the electron propagator as

$$G(\xi, \xi'; E) = \sum_s \frac{A(\xi, \xi'; s)}{E - \epsilon_s \mp \eta}, \tag{4.111}$$

with

$$\epsilon_s = \begin{cases} E_0(N) - E_s(N-1) & \text{for} \quad \text{Im}E > 0 \\ E_s(N+1) - E_0(N) & \text{for} \quad \text{Im}E < 0 \end{cases}$$

of a spectrum from infinitely negative to infinitely positive values, and which has a gap, the midpoint of which is an energy equal to the negative of the electronegativity on the Mulliken scale. The gap arises because

$$\min[E_s(N+1) - E_0(N)] > \max[E_0(N) - E_s(N-1)], \tag{4.112}$$

which is equivalent to stating that the ionization potential of the (N+1)-electron ion is less than that of the N-electron atom. The negative of the electronegativity, as defined by Mulliken, is the average of these energies, *i.e.*,

$$\begin{aligned} \alpha &= \frac{1}{2}\max[E_0(N) - E_s(N-1)] + \frac{1}{2}\min[E_s(N+1) - E_0(N)] \\ &= -\frac{1}{2}[I(N) + I(N+1)], \end{aligned} \tag{4.113}$$

where $I(N)$ is the energy required to remove an electron from the N-particle system.

The spectral weight can be obtained from the spectral form of the electron propagator as

$$A(\xi,\xi^{'};s) = \sum_{n,m}^{\epsilon_s=E_m-E_n} \langle n|\psi(\xi)|m\rangle\langle m|\psi^{\dagger}(\xi)|n\rangle[\rho_n+\rho_m], \tag{4.114}$$

where the energy selection rule (imposed by the delta function form of the spectral density) limits the summation to a restricted set of states.

The energy spectrum and the spectral weights are directly useful for the determination of atomic properties. For instance, the one-electron reduced density matrix becomes

$$\langle\psi^{\dagger}(\xi^{'})\psi(\xi)\rangle = \sum_{\epsilon_s<\alpha} A(\xi,\xi^{'};s). \tag{4.115}$$

The sumrules

$$N = \int\langle\psi^{\dagger}(\xi)\psi(\xi)\rangle d\xi = \sum_{\epsilon_s<\alpha}\int A(\xi,\xi;s)d\xi \tag{4.116}$$

and

$$\sum_{s} A(\xi,\xi^{'};s) = \langle\psi^{\dagger}(\xi)\psi(\xi)+\psi(\xi)\psi^{\dagger}(\xi)\rangle = \delta(\xi-\xi^{'}), \tag{4.117}$$

follow straightforwardly from the properties of the propagator and the field operators as discussed above.

The transition amplitude

$$\langle\gamma NLM_LSM_S|\psi^{\dagger}(\xi)|\gamma^{'}N^{'}L^{'}M_L^{'}S^{'}M_S^{'}\rangle \tag{4.118}$$

may be interpreted as the complex conjugate of the wavefunction for an electron appended to the state $|\gamma^{'}N^{'}L^{'}M_L^{'}S^{'}M_S^{'}\rangle$ of N' electrons to produce the state $|\gamma NLM_LSM_S\rangle$ of N electrons. The functional form of the angular part of this wavefunction is quite restricted by symmetry, whereas there are no such symmetry restrictions that in general determines the radial part. Approximate calculations of these radial amplitudes for the hydrogen, carbon, and nitrogen atoms are presented at the end of this section. The contribution of such transition amplitudes to the spectral weight matrix is obtained as

$$\begin{aligned} A(\xi,\xi^{'};s) \quad = \quad & \frac{\delta_{\zeta\zeta^{'}}}{8\pi}\sum_{l} P_l(\cos\Theta)\langle\gamma NLS||R_l^{\dagger}(r)||\gamma^{'}N^{'}L^{'}S^{'}\rangle^{*} \\ & \times\langle\gamma NLS||R_l^{\dagger}(r^{'})||\gamma^{'}N^{'}L^{'}S^{'}\rangle \\ & \times[w(\gamma NLS)/(2L+1)(2S+1) \\ & +w(\gamma^{'}N^{'}L^{'}S^{'})/(2L^{'}+1)(2S^{'}+1)], \end{aligned} \tag{4.119}$$

and the amplitudes

$$\langle \gamma NLS \| R_l^\dagger(r') \| \gamma' N' L' S' \rangle \tag{4.120}$$

for $\epsilon_s < \alpha$ determines the charge distribution of the atom in a way analogous to that of the occupied orbitals in the Hartree-Fock approximation.

4.3.2 Hartree-Fock Equations

The Hartree-Fock equations for the case of an atom exhibit sufficiently special features to warrant separate considerations. The form of the spin orbital basis (which can be assumed to be the solutions) is defined in Eq. (4.84), and the density operator is

$$\rho = \prod_k [(1 - \langle n_k \rangle) + (2\langle n_k \rangle - 1) n_k] \tag{4.121}$$

with normalization

$$\mathrm{Tr}\rho = 1, \tag{4.122}$$

and the occupation numbers

$$\mathrm{Tr}\rho n_k = \langle n_k \rangle. \tag{4.123}$$

Requiring the density operator to be invariant under rotations of the coordinate system is equivalent to demanding that the occupation numbers $\langle n_s \rangle = \langle n_{nlm\nu} \rangle$ are independent of m and ν. Denoting the average number of electrons in a subshell by

$$\langle N_{nl} \rangle = q(nl), \tag{4.124}$$

it follows that

$$\langle n_{nlm\nu} \rangle = q(nl)/(4l + 2). \tag{4.125}$$

As is shown in the general discussion of the Hartree-Fock approximation, the relations

$$\langle a_k^\dagger a_l \rangle = \delta_{kl} \langle n_k \rangle \tag{4.126}$$

and

$$\langle a_k^\dagger a_l^\dagger a_m a_n \rangle = \langle n_k \rangle \langle n_l \rangle (\delta_{kn}\delta_{lm} - \delta_{km}\delta_{ln}) \tag{4.127}$$

hold and the average value of the many-electron atomic hamiltonian is

$$\langle H \rangle = \sum_s h_{ss}\langle n_s \rangle + \frac{1}{2}\sum_{s,t}\langle st||st\rangle \langle n_s \rangle \langle n_t \rangle . \tag{4.128}$$

Because of the assumption of a spherically symmetric density operator the matrix elements h_{ss} are independent of m and ν, and one can denote them by

$$I(nl). \tag{4.129}$$

The two-electron integrals are in detail expressed in terms of 3*j*-symbols and Slater integrals R^k as

$$\begin{aligned} &\langle n_1 l_1 m_1 \nu_1, n_3 l_3 m_3 \nu_3 | n_2 l_2 m_2 \nu_2, n_4 l_4 m_4 \nu_4 \rangle \\ = \; & \delta_{\nu_1\nu_2}\delta_{\nu_3\nu_4}(-1)^{-m_1-m_4} \\ & \times \sum_{k,\mu} \begin{pmatrix} l_1 & k & l_2 \\ -m_1 & \mu & m_2 \end{pmatrix} \begin{pmatrix} l_4 & k & l_3 \\ -m_4 & \mu & m_3 \end{pmatrix} \begin{pmatrix} l_1 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_4 & k & l_3 \\ 0 & 0 & 0 \end{pmatrix} \\ & \times \left[(2l_1+1)(2l_2+1)(2l_3+1)(2l_4+1)\right]^{1/2} R^k(n_1l_1, n_3l_3, n_2l_2, n_4l_4). \end{aligned} \tag{4.130}$$

It is obvious from the average Eq. (4.128) that the only integrals $R^k(n_1l_1, n_3l_3, n_2l_2, n_4l_4)$ occurring are those with

$$\begin{aligned} (n_1l_1) &= (n_2l_2) &= (n, l), \\ (n_3l_3) &= (n_4l_4) &= (n'l'), \end{aligned} \tag{4.131}$$

which are denoted

$$F^k(nl, n'l') = \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 |R_{nl}(r_1)|^2 \left(\frac{r_<^k}{r_>^{k+1}}\right) |R_{n'l'}(r_2)|^2, \tag{4.132}$$

and those with

$$\begin{aligned} (n_1l_1) &= (n_4l_4) &= (n, l), \\ (n_2l_2) &= (n_3l_3) &= (n', l'), \end{aligned} \tag{4.133}$$

denoted

$$\begin{aligned} & G^k(nl, n'l') \\ &= \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 R^*_{nl}(r_1) R_{n'l'}(r_1) \left(\frac{r_<^k}{r_>^{k+1}} \right) R^*_{n'l'}(r_2) R_{nl}(r_2). \end{aligned} \tag{4.134}$$

In these expressions, $r_<$ and $r_>$ are the smaller and greater of r_1 and r_2, respectively.

Summations over the magnetic (m) and spin (ν) quantum numbers in the two-electron part of $\langle H \rangle$ yield the average electron-electron interaction parameters

$$V(nl, n'l') = F^0(nl, n'l') - \frac{1}{2} \sum_k \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 G^k(nl, n'l').$$

With the results and notations introduced above, one can express $\langle H \rangle$ as the energy functional

$$\langle H \rangle = \sum_{n,l} I(nl) q(nl) + \frac{1}{2} \sum_{n,l,n',l'} q(nl) q(n'l') V(nl, n'l'). \tag{4.135}$$

By introducing the modified radial functions

$$P_{nl}(r) = r R_{nl}(r) \tag{4.136}$$

(assumed real) and defining the potential functions

$$\begin{aligned} U_k(nl, n'l'; r) &= r^{-k-1} \int_0^r s^k P_{nl}(s) P_{n'l'}(s) ds \\ &\quad + r^k \int_r^\infty s^{-k-1} P_{nl}(s) P_{n'l'}(s) ds, \end{aligned} \tag{4.137}$$

one can form the functional derivative of $\langle H \rangle$ with respect to P_{nl} to obtain

$$\begin{aligned} & \delta \langle H \rangle / \delta P_{nl} \\ = \; & q(nl) \Bigg[-\frac{1}{2} P''_{nl}(r) + \frac{1}{2} l(l+1) r^{-2} P_{nl}(r) - (Z/r) P_{nl}(r) \\ & + \sum_{n',l'} q(n'l') U_0(n'l', n'l'; r) P_{nl}(r) \\ & - \frac{1}{2} \sum_{n',l',k} q(n'l') \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 U_k(n'l', nl; r) P_{n'l'}(r) \Bigg] \\ = \; & q(nl) F_l P_{nl}(r). \end{aligned} \tag{4.138}$$

Atomic units have been used, and F_l is the integro-differential operator of the Hartree-Fock equations that determines the radial factors P_{nl}. The usual way of making stationary an energy functional that includes the orthonormality constraints of these radial factors introduces undetermined multipliers $\epsilon(nl)$. As the definition of F_l introduces the same potential for all P_{nl}, there is no need for off-diagonal undetermined multipliers, and the variation of the energy functional with the constraints yields the equation

$$F_l P_{nl}(r) = \epsilon(nl) P_{nl}(r) \tag{4.139}$$

for the optimal radial functions.

Assuming that this equation has been solved and that these optimal orbitals are used in calculating $\langle H\rangle$, then the partial derivatives with respect to the subshell occupations $q(nl)$ can be studied. One obtains

$$\partial\langle H\rangle/\partial q(nl) = I(nl) + \sum_{n',l'} q(n'l')V(nl,n'l') = \epsilon(nl), \tag{4.140}$$

i.e., the (subshell) orbital energies are obtained as partial derivatives of the total energy. It should be noted that this treatment is carried out in Fock space and that the averaging with the chosen density operator involves a distribution over all possible occupations of the subshell under consideration. For example, one electron in an s-subshell corresponds to $\langle n_s\rangle = \frac{1}{2}$ and the density operator gives rise to a binomial distribution over the configurations s^0, s^1, and s^2, with weights $w(s^0) = 1/4$, $w(s^1) = 2/4$, and $w(s^2) = 1/4$. The total energy is then

$$\langle H\rangle = \sum_k w(s^k)E(s^k), \tag{4.141}$$

with $E(s^k)$ the Slater average of configuration. For the lithium atom, one obtains

$$\begin{aligned}\langle H\rangle &= 2I(1s) + I(2s) + F^0(1s,1s) + 2F^0(1s,2s)\\ &\quad -G^0(1s,2s) + \frac{1}{4}F^0(2s,2s),\end{aligned} \tag{4.142}$$

where the last term represents a certain amount of self-interaction in the open subshell. Positive contributions like this will result in somewhat higher total energies $\langle H\rangle$ than that obtained with a fixed number of electrons. There is no physical significance in this fact alone, but the importance lies in the novel central field obtained and the spin orbitals it defines. Resulting multiplet splittings and one-electron energies are quite reasonable and agreement with experiment quite satisfactory and actually better than what is obtained with conventional

Table 4.1: Comparison of central field calculations for Fe, Co, and Ni atoms. Energies in Hartrees. I: Derived from Eq. (4.135). II: Derived from Slater's average of configuration energy functional (from J. B. Mann)

	$\langle H\rangle$	$\epsilon(3d)$	$\epsilon(4s)$
Fe $3d^6 4s^2$			
I	-1261.304	-0.3474	-0.2718
II	-1262.291	-0.6079	-0.2601
Co $3d^7 4s^2$			
I	-1380.388	-0.4472	-0.2773
II	-1381.309	-0.6531	-0.2686
Ni $3d^8 4s^2$			
I	-1506.069	-0.5531	-0.2825
II	-1506.816	-0.6971	-0.2768

central fields. Comparison of different central field calculations are given in Table 4.1.

Minimization of the expectation value of the energy while keeping the expectation value of the number operator constant leads to the condition $\partial[\langle H\rangle - \mu\langle N_{op}\rangle]/\partial q(nl) \leq 0$, whereas

$$0 \leq q(nl) \leq 4l+2. \tag{4.143}$$

The undetermined multiplier μ appears as the chemical potential in statistical mechanics, and it has a value that separates occupied from unoccupied orbital energy levels. The minimum total energy is obtained when

$$\begin{array}{rcll} q(nl) & = & 4l+2 & \text{for } \epsilon(nl) < \mu, \\ q(nl) & = & 0 & \text{for } \epsilon(nl) > \mu, \\ 0 \leq q(nl) & \leq & 4l+2 & \text{for } \epsilon(nl) = \mu, \end{array} \tag{4.144}$$

and

$$\sum_{n,l} q(nl) = \langle N_{op}\rangle = N. \tag{4.145}$$

These relations are seen to lead to several open subshells only in the case when the corresponding orbital energies are degenerate.

Problems

1. Express $\langle H\rangle$ for the fluorine atom in terms of $I(nl)$, F^k, and G^k integrals.

2. Show that the width of the number operator $N_{op} = \sum_s n_s$ satisfies

$$[\langle (N_{op} - \langle N_{op} \rangle) \rangle^2]^{1/2} = [\sum_s \langle n_s \rangle (1 - \langle n_s \rangle)]^{1/2}, \tag{4.146}$$

when the average is taken with the density operator

$$\rho = \prod_s [1 - \langle n_s \rangle + (2\langle n_s \rangle - 1)\, n_s]. \tag{4.147}$$

4.4 Complex Spectra

The many-electron hamiltonian can be partitioned into an unperturbed part consisting of the Fock operator in diagonal form and a perturbation consisting of modified interaction terms. One can write

$$\begin{aligned} H &= \sum_r \epsilon_r n_r + \sum_{r,s,r',s'} \langle rr' | ss' \rangle [a_r^\dagger a_{r'}^\dagger a_{s'} a_s - a_r^\dagger \langle a_{r'}^\dagger a_{s'} \rangle a_s \\ &- a_{r'}^\dagger \langle a_r^\dagger a_s \rangle a_{s'} + a_r^\dagger \langle a_{r'}^\dagger a_s \rangle a_{s'} + a_{r'}^\dagger \langle a_r^\dagger a_{s'} \rangle a_s]. \end{aligned} \tag{4.148}$$

The perturbation term plays an important role for open shell atoms and ions, as has been shown by Slater. He used first-order perturbation theory, and Russell-Saunders states $|\gamma L M_L S M_S\rangle$ to calculate multiplet energies. Exactly the same treatment can be used with our Fock operator, which is different in the case of open shells from the one derived by the conventional variational treatment. The density operator employed by us leads to averages involving configurations with different numbers of electrons. As this approach can be seen as dealing with an ensemble of atoms and ions and the electron number operator receives a nonzero width, this approach has been named Grand Canonical Hartree-Fock. It has also been applied to the study of molecular absorption spectra. In the Table 4.2 some calculated multiplet separations are given for several atomic systems using the Grand Canonical Hartree-Fock central field with first-order perturbation theory. The agreement with experiment must be judged satisfactory for this type of treatment.

4.5 Single Subshell Approximation

When the discussion is limited to a single open subshell and to perturbations within such a shell, an interesting formulation of the many-electron atomic problem can be achieved that exhibits useful particle-hole symmetry. The summations in the perturbation term of the hamiltonian then run only over electron states $(nlm\nu)$ of the open subshell (nl). This means that the electron repulsion integrals can be expressed as

Table 4.2: Multiplet separations from Grand Canonical Hartree-Fock central field calculations and experiment for some atomic systems in units of cm^{-1}.

ATOM	TERM	CALCULATED	OBSERVED
	^3P	0	0
C I $2p^2$	^1D	10211	10164
	$^1S^*$	17706	21619
	^4S	0	0
N I $2p^3$	^2D	20202	19200
	^2P	26917	28840
	^3P	0	0
O I $2p^4$	^1D	16556	15790
	$^1S^*$	29517	33700
	^3F	0	0
	^1D	9141	8231
Ti III $3d^2$	^3P	11169	10419
	^1G	14354	14156
	^5D	0	0
	^3P	22500	18551
	^3H	20200	19173
	^3F	23200	20411
Fe I $3d^6 4s^2$	^3G	25600	23636
	^1I	30300	28910
	^3D	33200	28953
	^1G	31300	29396
	^1D	30900	34234

$$
\begin{aligned}
&\langle nlm_1\nu_1, nlm_3\nu_3 | nlm_2\nu_2, nlm_4\nu_4\rangle = \delta_{\nu_1\nu_2}\delta_{\nu_3\nu_4}\sum_{k,\mu} F^k(nl,nl)(2l+1)^2 \\
&\times \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} l & k & l \\ -m_1 & \mu & m_2 \end{pmatrix} \begin{pmatrix} l & k & l \\ -m_3 & -\mu & m_4 \end{pmatrix} (-1)^{-m_1-m_3-\mu} \\
= \;& \delta_{\nu_1\nu_2}\delta_{\nu_3\nu_4} \sum_{k,L,M} F^k \,(2l+1)^2 \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{Bmatrix} l & l & k \\ l & l & L \end{Bmatrix} \\
&\times (2L+1)(-1)^L \begin{pmatrix} l & l & L \\ m_1 & m_3 & -M \end{pmatrix} \begin{pmatrix} l & l & L \\ m_2 & m_4 & -M \end{pmatrix},
\end{aligned}
$$

where the last expression follows from the properties of the $3j$ and $6j$ symbols, and where the arguments (nl) of the integrals F^k have been suppressed.

Electron pair annihilation, $\pi(LM_LSM_S)$, and creation, $\pi^\dagger(LM_LSM_S)$, operators can be defined such that $\pi^\dagger$ creates a normalized two-electron state with the specified orbital and spin angular momenta when applied to the vacuum state or to a state where no electrons occupy the spin orbitals of the subshell in question. These operators are given by

$$\begin{aligned}\pi^\dagger(LM_LSM_S) &= (-1)^{M_L+M_S}[(2L+1)(2S+1)/2]^{1/2} \\ &\times \sum_{m,m',\nu,\nu'} \begin{pmatrix} l & l & L \\ m' & m & -M_L \end{pmatrix} \begin{pmatrix} 1/2 & 1/2 & S \\ \nu' & \nu & -M_S \end{pmatrix} a^\dagger_{m'\nu'} a^\dagger_{m\nu}\end{aligned} \tag{4.149}$$

and by the adjoint expression.

It follows from the symmetry properties of the $3j$-symbols and from the anticommutation relations of the electron field operators that the triplet operators do not exist for L even, while the singlet operators exist only for such L.

The hamiltonian in reduced form for the subshell (nl) can be expressed as

$$\begin{aligned} H &= \left[\epsilon(nl) - q(nl)F^0 + \frac{1}{2}q(nl)\sum_k F^k \begin{pmatrix} l & l & k \\ 0 & 0 & 0 \end{pmatrix}^2\right] N_{nl} \\ &\quad + \frac{1}{2}F^0 N_{nl}(N_{nl}-1) \\ &\quad + \sum_{L,M_L,S,M_S} V(L)\pi^\dagger(LM_LSM_S)\pi(LM_LSM_S), \end{aligned} \tag{4.150}$$

where

$$V(L) = \sum_{k\neq 0} F^k (2l+1)^2 \begin{pmatrix} l & l & k \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{Bmatrix} l & l & k \\ l & l & L \end{Bmatrix} (-1)^L$$

are the electron repulsion energies in the pair states with angular momentum quantum number L. The average energy of the electrons in this subshell is

$$\langle H \rangle = \epsilon(nl)q(nl) - \frac{1}{2}q(nl)^2 \left[F^0 - \frac{1}{2}\sum_k F^k \begin{pmatrix} l & l & k \\ 0 & 0 & 0 \end{pmatrix}^2\right],$$

when computed with the density operator in Eq. (4.121).

The introduction of the pair operators allows a simple way to demonstrate that corresponding particle and hole configurations have the same terms and similar energy expressions. This particle-hole symmetry has been known since the early work of Heisenberg. A unitary transformation U is employed, which is expressed in terms of the pair operator $\pi^\dagger = \pi^\dagger\,(0000)$ and its adjoint

such that

$$U = \exp[iS], \tag{4.151}$$

where $S = \left(\gamma\pi + \gamma^*\pi^\dagger\right)$ is Hermitian, with γ an arbitrary complex number. The transformation of an operator A can be expressed as

$$\begin{aligned}\tilde{A} &= UAU^\dagger \\ &= A - i[A,S]_- + (i^2/2!)[[A,S]_-,S]_- \\ &\quad -(i^3/3!)[[[A,S]_-,S]_-,S]_- + \cdots .\end{aligned} \tag{4.152}$$

The commutator

$$[a_{m\nu}, S]_- = (-1)^{l-m+\frac{1}{2}-\nu}\gamma^*(2l+1)^{-1/2}a^\dagger_{-m-\nu} \tag{4.153}$$

then yields the transformed electron field operator

$$\begin{aligned}\tilde{a}_{m\nu} &= a_{m\nu}\cos|\gamma(2l+1)^{-1/2}| \\ &\quad -(-1)^{l-m+\frac{1}{2}-\nu}a^\dagger_{-m-\nu}(i\gamma^*/|\gamma|)\sin|\gamma(2l+1)^{-1/2}|.\end{aligned} \tag{4.154}$$

One can see from this result that a complete particle-hole transformation occurs when

$$|\gamma| = \frac{1}{2}\pi(2l+1)^{1/2}. \tag{4.155}$$

The generators π and $\pi^\dagger$ of the transformation commute with the total orbital and spin angular momenta such that the transformation only connects states with the same quantum numbers (LM_LSM_S). The various operators appearing in the hamiltonian in Eq. (4.150) under a complete particle-hole transformation become

$$\tilde{N}_{nl} = 4l + 2 - N_{nl} \tag{4.156}$$

and

$$\tilde{\pi}^\dagger(LM_LSM_S) = (-1)^{M_L+M_S+1}(i|\gamma|/\gamma)^2\pi(L-M_LS-M_S), \tag{4.157}$$

which means that

$$\begin{aligned}&\sum_{M_L,M_S} \tilde{\pi}^\dagger(LM_LSM_S)\tilde{\pi}(LM_LSM_S) \\ &= \sum_{M_L,M_S} \pi^\dagger(LM_LSM_S)\pi(LM_LSM_S) \\ &\quad + \sum_{M_L,M_S} [\pi(LM_LSM_S), \pi^\dagger(LM_LSM_S)]_-,\end{aligned} \tag{4.158}$$

with the last term equal to

$$(2L+1)(2S+1)[1 - N_{nl}/(2l+1)]. \tag{4.159}$$

This means that apart from a term involving the number operator, the hamiltonian is invariant under the complete particle-hole transformation and the relative energies of the terms of a configuration $(nl)^q$ are the same as those of a configuration $(nl)^{4l+2-q}$.

One can assume generally that the energy parameter $V(0)$ is dominant of all the $V(L)$, and one can investigate the consequences of neglecting all but $V(0)$. If then there are states $|N, g\rangle$ that are characterized by the eigenvalue N of the number operator N_{nl} and by other quantum numbers g, and that satisfy the relation

$$\pi|N, g\rangle = 0, \tag{4.160}$$

it follows that the energy of such states is dependent only upon N. For a given N such a state is written

$$|N, N, g\rangle, \tag{4.161}$$

where the second label in this notation denotes the seniority number. Thus, such a state has the seniority number N. Another set of states may satisfy

$$(\pi)^{f+1}|N, N-2f, g\rangle = 0 \tag{4.162}$$

and are given the seniority number $N - 2f$, where it is implied that

$$(\pi)^f|N, N-2f, g\rangle \neq 0. \tag{4.163}$$

The label g can distinguish between the different eigenstates of the hamiltonian with a common particle number and a common seniority number. One can also define states

$$|N+2f, N, g\rangle = C_{fN}(\pi^\dagger)^f|N, N, g\rangle, \tag{4.164}$$

which are eigenstates of the hamiltonian, and where C_{fN} is the normalization constant, *i.e.*,

$$\begin{aligned} |C_{fN}|^{-2} &= \langle N, N, g|\pi^f(\pi^\dagger)^f|N, N, g\rangle \\ &= \langle N, N, g|\pi^{f-1}[\pi, (\pi^\dagger)^f]_-|N, N, g\rangle \\ &= [f(2l+2-N-f)/(2l+1)]\langle N, N, g|\pi^{f-1}(\pi^\dagger)^{f-1}|N, N, g\rangle \\ &= (f!)^2\binom{2l+1-N}{f}(2l+1)^{-f}. \end{aligned} \tag{4.165}$$

The calculation of the electronic interaction energy in such a state is straightforward:

$$\begin{aligned}
&\langle N+2f, N, g|V(0)\pi^\dagger\pi|N+2f, N, g\rangle \\
=\ &|C_{fN}|^2\langle N, N, g|\pi^f V(0)\pi^\dagger\pi(\pi^\dagger)^f|N, N, g\rangle \\
=\ &V(0)f(2l+2-N-f)/(2l+1). \qquad (4.166)
\end{aligned}$$

Due to the particle-hole symmetry, the range of the parameters N and f can be limited, so that

$$N + 2f \leq 2l + 1, \qquad (4.167)$$

implying that the largest interaction energy occurs for states with the greatest difference between the electron number and the seniority number. Racah, who introduced the seniority concept, found the seniority number to be an almost good quantum number. This fact is borne out in the above analysis, since the neglected terms in the hamiltonian are small. It is clear that the pair creator $\pi^\dagger$ commutes with the orbital and spin angular momentum operators for the electrons and will not change the corresponding quantum numbers for a state. Thus, a general particle-hole transformation will have matrix elements only between states of equal seniority, orbital, and spin angular momentum.

Other two-particle operators can also be expressed in terms of the general pair creators and annihilators. For instance, the total orbital angular momentum is

$$\begin{aligned}
\hat{L}^2 &= l(l+1)N_{nl} + 2l(l+1)(2l+1) \qquad (4.168)\\
&\times \sum(-1)^L \begin{Bmatrix} l & l & 1 \\ l & l & L \end{Bmatrix} \pi^\dagger(LM_LSM_S)\pi(LM_LSM_S),
\end{aligned}$$

and the total spin is

$$\begin{aligned}
\hat{S}^2 &= (3/4)N_{nl} \qquad (4.169)\\
&+ 3\sum(-1)^{S+1} \begin{Bmatrix} 1/2 & 1/2 & 1 \\ 1/2 & 1/2 & S \end{Bmatrix} \pi^\dagger(LM_LSM_S)\pi(LM_LSM_S).
\end{aligned}$$

The number of electron pairs in the subshell is

$$\frac{1}{2}N_{nl}(N_{nl}-1) = \sum \pi^\dagger(LM_LSM_S)\pi(LM_LSM_S).$$

It is in general possible to express any two-particle interactions in terms of these operators with a result analogous to that in Eq. (4.150) with a more general form of $V(L)$ parameters than that given in Eq. (4.151). Such ideas have been explored by Trees, although expressed in different terms from those introduced here.

Problems

1. Introduce a complete set of projectors P_N corresponding to eigenvalues N of the number operator.

   (a) Verify that the realization

$$P_N = \int_0^1 dt \exp[2\pi i t\,(N_{op} - N)] \tag{4.170}$$

   of the projectors satisfy the relations

$$(N_{op} - N)\,P_N = 0,\; P_N^2 = P_N,\; \sum_N P_N = 1. \tag{4.171}$$

   (b) Introduce the density operator [with ρ defined in Eq. (4.121]

$$\rho_N = P_N \rho / \mathrm{Tr} P_N \rho, \tag{4.172}$$

   and show that the average of H is given by

$$\langle H \rangle_N = \sum_{n,l} I(nl) q(nl) + \frac{1}{2} \sum_{n,l,n',l'} Q(nl, n'l') V(nl, n'l'), \tag{4.173}$$

   with $\langle n_{nlm\nu} \rangle_N (4l+2) = q(nl)$ and $\langle n_{nlm\nu} n_{n'l'm'\nu'} \rangle_N (4l+2)(4l'+2) = Q(nl, n'l')$.

Notes and bibliography

- The Wigner $3j$ and $6j$ symbols, their basic properties and their fundamental relations are discussed in a great many different sources.
- The book by E. P Wigner, *Group Theory and its Application to the Quantum Mechanics of Atomic Spectra* (Academic Press, New York, 1959), and the text by B. R. Judd, *Second Quantization and Atomic Spectroscopy* (The Johns Hopkins Press, Baltimore, 1967), provide the necessary material. The latter monograph also discusses the relations between the reduced field operator matrix elements and the coefficients of fractional parentage.
- The basic definitions of the spherical harmonics as well as the details of the atomic central field problem can be found in E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, 1953).
- The atomic Hartree-Fock problem is treated in considerable detail in J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Co., Vol. 1 and Vol. 2, 1960).
- The theory of complex spectra also receives a full treatment in the references mentioned above, but can it even better be studied in the original paper by J. C. Slater, *Phys. Rev.*, **34**, 1293 (1929), and by G. Racah, *Phys. Rev.*, **61**, 186, and **62**, 438 (1942).
- The discussion of the particle-hole symmetry goes back to the early work of W. Heisenberg published in *Ann. Physik*, **10**, 888 (1931).
- Transformation of field operators generated by the totally symmetric pair operators has also been discussed by H. Watanabe in *Operator Methods in Ligand Field Theory* (Prentice-Hall Inc., Englewood Cliffs NJ, 1966), but in a different form from what is done here.

- Racah, in *Phys. Rev.* **63**, 367 (1943) introduced the seniority concept and R. E. Trees in *Phys. Rev.* **83**, 756 (1951), **85**, 382 (1952), and in *J. Opt. Soc. Amer.* **54**, 651 (1964) has presented the single subshell approximation idea.
- The ensemble based Hartree-Fock methods have been treated by S. F. Abdulnur, J. Linderberg, Y. Öhrn, and P. W. Thulstrup in *Phys. Rev.* **A6**, 889 (1972), and by P. Jørgensen and Y. Öhrn in *Phys. Rev.* **A8**, 112 (1973).
- Polarization propagator calculations based on the grand canonical Hartree-Fock orbitals have been performed by P. Jørgensen and Y. Öhrn, in *Chem. Phys. Lett.* **18**, 261 (1973) for triplet-triplet absorption spectra of hydrocarbons.
- Atomic Hartree-Fock calculations for the whole periodic system have been performed by J. B. Mann and are available in Reports Nos. LA-3690/1 from Los Alamos Scientific Laboratory, University of California, New Mexico.

4.6 Approximate Atomic Transition Amplitudes

In this section, a few examples are given of the approximate determination of matrix elements of electron field operators. Atomic units are used throughout.

4.6.1 The Hydrogen Atom

The ground state is degenerate and the corresponding manifold of states are

$$\begin{aligned} |1s,0,0,1/2,1/2\rangle &= a^\dagger_{100\frac{1}{2}}|vac\rangle, \\ |1s,0,0,1/2,-1/2\rangle &= a^\dagger_{100-\frac{1}{2}}|vac\rangle. \end{aligned} \tag{4.174}$$

The amplitudes of interest are

$$\langle 1s,0,0,1/2,-1/2|\psi^\dagger(\xi)|vac\rangle = u^*_{100-\frac{1}{2}}(\xi) \equiv u_{1s\beta}(\xi) \tag{4.175}$$

as defined in Eq. (4.84), with the radial part R_{10} being the exact ground state solution of the radial Schrödinger equation for the hydrogen atom, and

$$\begin{aligned} &\langle (1s)^2,0,0,0,0|\psi^\dagger(\xi)|1s,0,0,1/2,-1/2\rangle \\ = &\int u_{1s\beta}(\xi')\langle (1s)^2,0,0,0,0|\psi^\dagger(\xi)\psi^\dagger(\xi')|vac\rangle d\xi', \end{aligned} \tag{4.176}$$

which can be calculated with an explicit choice of wavefunction for the hydrogen anion. A simple spin singlet wavefunction can be expressed as

$$\begin{aligned} &\langle vac|\psi(\xi')\psi(\xi)|(1s)^2,0,0,0,0\rangle \\ &\propto \exp[-\mu(r+r')]\cosh[\nu(r-r')]\left\{\alpha(\zeta')\beta(\zeta)-\beta(\zeta')\alpha(\zeta)\right\}. \end{aligned} \tag{4.177}$$

This wavefunction has been variationally determined[3] for H^- with the optimal parameter values $\mu = 0.6612$ and $\nu = 0.3780$. One can directly evaluate the amplitude

$$\begin{aligned}&\langle(1s)^2,0,0,0,0|\psi^\dagger(\xi)|1s,0,0,1/2,-1/2\rangle\\&\propto \exp(-\mu r)[(1+\mu+\nu)^{-3}\exp(\nu r)\\&+(1+\mu-\nu)^{-3}\exp(-\nu r)]\alpha^*(\zeta).\end{aligned} \tag{4.178}$$

This amplitude has the normalization integral

$$\int\langle(1s)^2,0,0,0,0|\psi^\dagger(\xi)|1s,0,0,1/2,-1/2\rangle d\xi = 0.695 \tag{4.179}$$

and overlaps the hydrogenic $1s$ orbital to almost 67%, or

$$|\langle(1s)^2,0,0,0,0|a^\dagger_{100\frac{1}{2}}|1s,0,0,1/2,-1/2\rangle|^2 = 0.445\,. \tag{4.180}$$

It is notable that the two largest terms in the sum rule

$$\sum_s \int u^*_{100\frac{1}{2}} A(\xi,\xi';s)u_{100\frac{1}{2}}(\xi')d\xi d\xi' = 1 \tag{4.181}$$

equals 70% of the total value. A closer look at the amplitude (4.178) shows that the component that dominates at large distances from the nucleus has a considerably smaller exponent than that of the other component. This reflects the fact that the probability amplitude for finding an electron far from the nucleus in the hydrogen anion and another in the $1s$ state has an asymptotic functional form corresponding to a wavefunction of an electron with a small binding energy. The numerical value of the asymptotic exponent is $\mu - \nu = 0.2832$ to be compared with the "exact" theoretical value of $(-2m\epsilon_s)^{1/2} = 0.2355$.

4.6.2 The Carbon and Nitrogen Atoms

A quasi-vacuum consisting of the singlet state core

$$|qv\rangle = |(1s)^2(2s)^2,0,0,0,0\rangle \tag{4.182}$$

is introduced and held fixed throughout the calculation. The discussion is limited to the lowest multiplets of the $(2p)$, $(2p)^2$, and $(2p)^3$ configurations.

States of interest can be calculated from approximate wavefunctions, such as

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[3] H. Shull and P.-O. Löwdin, *J. Chem. Phys.* **25**, 1035 (1956)

$$|(2p),1,1,1/2,1/2\rangle = \int u(\xi)\psi^\dagger(\xi)|qv\rangle d\xi, \tag{4.183}$$

with

$$u(\xi) = C(\mu) r \exp(-\mu r) Y_{11}(\theta,\phi)\alpha(\zeta), \tag{4.184}$$

where $C(\mu)$ is a normalization constant. Similarly, for two electrons in the $(2p)^2$ subshell the triplet state

$$|(2p)^2,1,1,1,1\rangle = \int u(\xi_1,\xi_2)\psi^\dagger(\xi_1)\psi^\dagger(\xi_2)|qv\rangle d\xi_1 d\xi_2, \tag{4.185}$$

with

$$\begin{aligned} u(\xi_1,\xi_2) &= C(\mu_1,\mu_2)\left[\sum_{P\in S_2} P r_1 r_2 \exp(-\mu_1 r_1 - \mu_2 r_2)\right] \\ &\quad \times S(1,2)\alpha(\zeta_1)\alpha(\zeta_2), \end{aligned} \tag{4.186}$$

where $C(\mu_1,\mu_2)$ is the normalization constant, $\frac{1}{N!}\sum_{P\in S_N} P$ is the symmetric projector of the permutation group S_N of N electrons, and

$$S(1,2) = \sum_{m_1,m_2} 3^{1/2}\begin{pmatrix} 1 & 1 & 1 \\ m_1 & m_2 & -1 \end{pmatrix} Y_{1m_1}(\theta_1,\phi_1) Y_{1m_2}(\theta_2,\phi_2)$$

is the antisymmetric angular part. For the quartet state of $(2p)^3$, one can write

$$\begin{aligned} &|(2p)^3,0,0,3/2,3/2\rangle \\ &= \int u(\xi_1,\xi_2,\xi_3)\psi^\dagger(\xi_1)\psi^\dagger(\xi_2)\psi^\dagger(\xi_3)|qv\rangle d\xi_1 d\xi_2 d\xi_3, \end{aligned} \tag{4.187}$$

with

$$\begin{aligned} u(\xi_1,\xi_2,\xi_3) &= C(\mu_1,\mu_2,\mu_3) \\ &\quad \times [\sum_{P\in S_3} P r_1 r_2 r_3 \exp(-\mu_1 r_2 - \mu_2 r_2 - \mu_3 r_3)] \\ &\quad \times S(1,2,3)\alpha(\zeta_1)\alpha(\zeta_2)\alpha(\zeta_3), \end{aligned} \tag{4.188}$$

where $C(\mu_1,\mu_2,\mu_3)$ is the normalization, and

$$\begin{aligned} S(1,2,3) &= \sum_{m_1,m_2,m_3} \begin{pmatrix} 1 & 1 & 1 \\ m_1 & m_2 & m_3 \end{pmatrix} \\ &\quad \times Y_{1m_1}(\theta_1,\phi_1)Y_{1m_2}(\theta_2,\phi_2)Y_{1m_3}(\theta_3,\phi_3) \end{aligned} \tag{4.189}$$

is the antisymmetric angular part. It should be noted that the spin and radial parts are symmetric in the electron labels. The exponents can be optimized using the wavefunctions u for the separate ions. Then, defining the modified radial amplitude for the N electron ion as

$$P_N^* = r\langle\gamma NLS||R_l(r)||\gamma' N' L' S'\rangle[N(2L+1)(2S+1)]^{-1/2}, \tag{4.190}$$

the following amplitudes are obtained for carbon:

$$\begin{aligned} P_5(r) &= r^2 5.00546\exp(-1.798r), \\ P_6(r) &= r^2[3.18457\exp(-2.016r) + 0.82624\exp(-1.114r)], \\ P_7(r) &= r^2[0.1549\exp(-0.628r) + 0.5393\exp(-1.191r) \\ &\quad +2.0578\exp(-2.061r)]. \end{aligned} \tag{4.191}$$

In Tables 4.3 and 4.4 the calculated exponents, total energies in Hartrees, and the ionization potential in electronvolts are given.

Table 4.3: **Carbon**

N	4	5	6	7
μ_1	0	1.798	1.114	0.628
μ_2	0	0	2.016	1.191
μ_3	0	0	0	2.061
E_{tot}	-36.33054	-37.26425	-37.67795	-37.70538
IP(calc)	-	25.41	11.26	0.75
IP(exp)	-	24.38	11.26	1.25

Table 4.4: **Nitrogen**

N	4	5	6	7
μ_1	0	2.345	2.644	2.787
μ_2	0	0	1.624	1.732
μ_3	0	0	0	1.220
E_{tot}	-50.90343	-52.73425	-53.86133	-54.39581
IP(calc)	-	49.82	30.67	14.54
IP(exp)	-	47.43	29.61	14.54

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Chapter 5

The Excitation Propagator

The energy representations in Eq. (4.13) or Eq. (4.17) show that the appropriate energy differences corresponding to excitations of the *N*-electron system are obtained from the excitation propagator, *i.e.*, the one with the field operator basis

$$X_i = q_i^\dagger = \tilde{a}_k^\dagger \tilde{a}_l, \qquad \text{for} \qquad \langle n_k \rangle < \langle n_l \rangle, \tag{5.1}$$

where $\langle n_k \rangle = \langle \tilde{a}_k^\dagger \tilde{a}_k \rangle$ and the average is taken over the appropriate reference state or with the appropriate density operator. If the reference would be the Hartree-Fock single-determinantal ground state of Eq. (4.29), the index k refers to unoccupied (or particle) spin orbitals and l to occupied (or hole) spin orbitals, making the operators $q_i^\dagger$ so-called particle-hole operators with the compound index $i = (k,l)$. It should be noted that the adjoint (hole-particle) operators are $q_i = \tilde{a}_l^\dagger \tilde{a}_k$. The matrix propagator to consider has the block structure

$$\begin{aligned} \mathbf{P}(E) &= \begin{bmatrix} \langle\langle \mathbf{q}; \mathbf{q}^\dagger \rangle\rangle_E & \langle\langle \mathbf{q}; \mathbf{q} \rangle\rangle_E \\ \langle\langle \mathbf{q}^\dagger; \mathbf{q}^\dagger \rangle\rangle_E & \langle\langle \mathbf{q}^\dagger; \mathbf{q} \rangle\rangle_E \end{bmatrix} \\ &= \begin{bmatrix} (\mathbf{q}^\dagger|(E\hat{I}-\hat{H})^{-1}\mathbf{q}^\dagger) & (\mathbf{q}^\dagger|(E\hat{I}-\hat{H})^{-1}\mathbf{q}) \\ (\mathbf{q}|(E\hat{I}-\hat{H})^{-1}\mathbf{q}^\dagger) & (\mathbf{q}|(E\hat{I}-\hat{H})^{-1}\mathbf{q}) \end{bmatrix} \\ &\simeq \mathbf{S}(E\mathbf{S}-\mathbf{F})^{-1}\mathbf{S}, \end{aligned} \tag{5.2}$$

where in the last step, the geometric approximation is invoked. Using the basic anticommutation relations of the electron field operators and taking the average with respect to the density operator of Eq. (4.33), which for integer occupation numbers (0 and 1) becomes the single-determinantal pure state of Eq. (4.29), one can easily compute the elements S_{ij} (with $i = (k,l)$ and $j = (k',l')$) of the metric matrix $\mathbf{S}$ (for $\langle n_l \rangle > \langle n_k \rangle$):

$$\begin{aligned} (q_i^\dagger|q_j^\dagger) &= \langle [q_i, q_j^\dagger]_- \rangle = \delta_{kk'}\delta_{ll'}(\langle n_l \rangle - \langle n_k \rangle) = \delta_{ij}\lambda_i, \\ (q_i|q_j) &= \langle [q_i^\dagger, q_j]_- \rangle = \delta_{kk'}\delta_{ll'}(\langle n_k \rangle - \langle n_l \rangle) = -\delta_{ij}\lambda_i, \\ (q_i^\dagger|q_j) &= (q_i|q_j^\dagger) = 0. \end{aligned} \tag{5.3}$$

The dynamical matrix **F** similarly has the elements

$$\begin{aligned} (q_i^\dagger|\hat{H}q_j^\dagger) &= \langle[q_i,[H,q_j^\dagger]_-]_-\rangle = (q_i|\hat{H}q_j)^* = B_{ij}, \\ (q_i^\dagger|\hat{H}q_j) &= \langle[q_i,[H,q_j]_-]_-\rangle = (q_i|\hat{H}q_j^\dagger)^* = C_{ij}, \end{aligned} \tag{5.4}$$

where [1]

$$\begin{aligned} B_{ij} &= (\epsilon_k - \epsilon_l)\lambda_i\delta_{ij} - \lambda_i\lambda_j\langle kl'||k'l\rangle, \\ C_{ij} &= \lambda_i\lambda_j\langle kk'||l'l\rangle. \end{aligned} \tag{5.5}$$

For fractional occupation numbers, the division between occupied and unoccupied spin orbitals gets blurred and one could have a situation where $\langle n_k\rangle = \langle n_l\rangle$. Operators q_i and their adjoints for which this situation occurs are simply excluded from the basis. This avoids a singular metric.

The propagator matrix in block form is

$$\begin{aligned} \mathbf{P}(E) &= \begin{bmatrix} \lambda & 0 \\ 0 & -\lambda \end{bmatrix} \begin{bmatrix} E\lambda - \mathbf{B} & -\mathbf{C} \\ -\mathbf{C}^* & -E\lambda - \mathbf{B}^* \end{bmatrix}^{-1} \begin{bmatrix} \lambda & 0 \\ 0 & -\lambda \end{bmatrix} \\ &= \begin{bmatrix} \lambda^{\frac{1}{2}} & 0 \\ 0 & \lambda^{\frac{1}{2}} \end{bmatrix} \begin{bmatrix} E\mathbf{1} - \bar{\mathbf{B}} & -\bar{\mathbf{C}} \\ -\bar{\mathbf{C}}^* & -E\mathbf{1} - \bar{\mathbf{B}}^* \end{bmatrix}^{-1} \begin{bmatrix} \lambda^{\frac{1}{2}} & 0 \\ 0 & \lambda^{\frac{1}{2}} \end{bmatrix}, \end{aligned} \tag{5.6}$$

where λ is a diagonal matrix and $\bar{\mathbf{B}} = \lambda^{-\frac{1}{2}}\mathbf{B}\lambda^{-\frac{1}{2}}$, and $\bar{\mathbf{C}} = -\lambda^{-\frac{1}{2}}\mathbf{C}\lambda^{-\frac{1}{2}}$. This is the excitation propagator in the Time-Dependent Hartree-Fock (TDHF) or the Random Phase Approximation (RPA). It is known to give imaginary excitation energies for the case that the optimized single-determinantal Hartree-Fock reference state does not correspond to an absolute energy minimum (*i.e.*, has a positive energy Hessian). This is known as instabilities and can in general be cured by choosing a suitable correlated reference state. In the case of $\bar{\mathbf{B}}$ and $\bar{\mathbf{C}}$ real and $\bar{\mathbf{B}} + \bar{\mathbf{C}}$ and $\bar{\mathbf{B}} - \bar{\mathbf{C}}$ positive, one can proceed as follows.

Find a unitary transformation **U** such that

$$(\bar{\mathbf{B}} + \bar{\mathbf{C}})\mathbf{U} = \mathbf{U}\mathbf{X}, \tag{5.7}$$

where **X** is diagonal and positive. Then form the positive matrix

$$\mathbf{W}^2 = \mathbf{X}^{\frac{1}{2}}\mathbf{U}^\dagger(\bar{\mathbf{B}} - \bar{\mathbf{C}})\mathbf{U}\mathbf{X}^{\frac{1}{2}}, \tag{5.8}$$

and find the unitary matrix **V** such that $\mathbf{W}^2\mathbf{V} = \mathbf{V}\mathbf{w}^2$, where $\mathbf{w}^2$ is diagonal and positive. The matrices

$$\mathbf{D} = \mathbf{U}\mathbf{X}^{-\frac{1}{2}}\mathbf{V}\mathbf{w}^{\frac{1}{2}}, \quad \text{and} \quad \mathbf{T} = \mathbf{U}\mathbf{X}^{\frac{1}{2}}\mathbf{V}\mathbf{w}^{-\frac{1}{2}} = (\mathbf{D}^\dagger)^{-1} \tag{5.9}$$

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[1] Note that the C matrix defined in Appendix D is the negative of this C matrix.

are defined and the combinations $\mathbf{Z} = (\mathbf{D}+\mathbf{T})/2$ and $\mathbf{Y} = (\mathbf{D}-\mathbf{T})/2$ formed. The propagator matrix can then be expressed as

$$\begin{aligned}\mathbf{P}(E) &= \begin{bmatrix} \lambda^{\frac{1}{2}} & 0 \\ 0 & \lambda^{\frac{1}{2}} \end{bmatrix}\begin{bmatrix} \mathbf{Z} & \mathbf{Y} \\ \mathbf{Y} & \mathbf{Z} \end{bmatrix}\begin{bmatrix} (E\mathbf{1}-\mathbf{w})^{-1} & 0 \\ 0 & -(E\mathbf{1}+\mathbf{w})^{-1} \end{bmatrix} \\ &\quad\times\begin{bmatrix} \mathbf{Z}^{\dagger} & \mathbf{Y}^{\dagger} \\ \mathbf{Y}^{\dagger} & \mathbf{Z}^{\dagger} \end{bmatrix}\begin{bmatrix} \lambda^{\frac{1}{2}} & 0 \\ 0 & \lambda^{\frac{1}{2}} \end{bmatrix}. \end{aligned} \tag{5.10}$$

Comparing the (m,n) element of $\mathbf{P}$ in the geometric approximation

$$P_{mn}(E) = \sum_k \left[\frac{\lambda_m^{\frac{1}{2}} Z_{mk} Z_{nk}^* \lambda_n^{\frac{1}{2}}}{E - w_k} - \frac{\lambda_m^{\frac{1}{2}} Y_{mk} Y_{nk}^* \lambda_n^{\frac{1}{2}}}{E + w_k} \right] \tag{5.11}$$

with a corresponding element in, say, the $\langle\langle q; q^{\dagger}\rangle\rangle_E$ block of the energy representation of the excitation propagator, the following identifications can be made

$$\begin{aligned} \lambda_m^{\frac{1}{2}} Z_{mk} &= \langle 0|q_m|k\rangle, & \lambda_n^{\frac{1}{2}} Z_{nk}^* &= \langle k|q_n^{\dagger}|0\rangle, \\ \lambda_m^{\frac{1}{2}} Y_{mk} &= \langle k|q_m|0\rangle. & \lambda_n^{\frac{1}{2}} Y_{nk}^* &= \langle 0|q_n^{\dagger}|k\rangle, \\ w_k &= E_k(N) - E_0(N). \end{aligned} \tag{5.12}$$

Since $\mathbf{Z}^{\dagger}\mathbf{Z} - \mathbf{Y}^{\dagger}\mathbf{Y} = \mathbf{1}$, it holds that

$$\langle k| \sum_m \lambda_m^{-\frac{1}{2}} (q_m^{\dagger} Z_{mk} - q_m Y_{mk}^*)|0\rangle = 1, \tag{5.13}$$

and one can conclude that the excitation operator that creates an excited state $|K\rangle$ from the reference state is

$$Q_K^{\dagger} = \sum_{k,l} \lambda_{(k,l)}^{-\frac{1}{2}} (\tilde{a}_k^{\dagger}\tilde{a}_l Z_{(k,l)K} - \tilde{a}_l^{\dagger}\tilde{a}_k Y_{(k,l)K}^*). \tag{5.14}$$

The corresponding de-excitation operators Q_K must also, in this case, satisfy the *killer* condition $Q_K|0\rangle = 0$ for consistency, but for a single-determinantal reference, this is not in general true because $\tilde{a}_k^{\dagger}\tilde{a}_l|0\rangle \neq 0$. The consistency then only obtains when all elements $Y_{(k,l)K} = 0$ or are insignificantly small. This means that all excited states are represented as monoexcited CI states out of a single-determinantal reference. This has been referred to as the Tamm-Dancoff Approximation (TDA). As in general all the Y-elements do not vanish, there is an inconsistency in RPA, which can be addressed in various ways in practice by introducing correlated reference states. Strictly speaking, one cannot within RPA identify the various individual stationary states. There is only a spectral density function.

Problems

1. Show that when **B+C** and **B-C** are positive, the second variation of $\langle H\rangle$ for the single determinantal Hartree-Fock ground state is positive.

5.1 Antisymmetrized Geminal Power

As in general all the Y-coefficients do not vanish one has to assume a more general reference state than the single determinant SCF state. This is the rather well-known problem of finding the consistent reference state for the Random Phase Approximation (RPA). It also means that the field operator basis can be enlarged and can for instance include the N-electron occupation number operators (in this discussion, electron field operators b_i and their adjoints are used referring to a basis of spin orbitals that are the "natural spin orbitals" of the reference state, as will be discussed below, *i.e.*, the spin orbitals that diagonalize the one-matrix)

$$q_{ii} = (b_i^\dagger b_i - \langle b_i^\dagger b_i \rangle)|0\rangle\langle 0|, \tag{5.15}$$

with

$$\langle b_i^\dagger b_i \rangle = \langle n_i \rangle = \langle 0|b_i^\dagger b_i|0\rangle. \tag{5.16}$$

The elements of the metric corresponding to these operators are

$$\begin{aligned} \Lambda_{ij} &= (q_{ii}^\dagger|q_{jj}) = \langle 0|[q_{ii}, q_{jj}^\dagger]_-|0\rangle \\ &= -\langle 0|0\rangle\langle 0|(b_j^\dagger b_j - \langle b_j^\dagger b_j \rangle)(b_i^\dagger b_i - \langle b_i^\dagger b_i \rangle)|0\rangle\langle 0|0\rangle \\ &= -\delta_{ij}\langle n_i \rangle - \langle b_i^\dagger b_j^\dagger b_j b_i \rangle(1-\delta_{ij}) - \langle n_i \rangle\langle n_j \rangle. \end{aligned} \tag{5.17}$$

Similarly,

$$(q_{ii}|q_{jj}) = -\Lambda_{ij}, \quad \text{and} \quad (q_{ii}|q_{jj}^\dagger) = (q_{ii}^\dagger|q_{jj}) = 0. \tag{5.18}$$

The metric matrix elements between operators q_{ii} and the operators $b_k^\dagger b_l$ and their adjoints also vanish.

It has been shown[2] that for an even number of electrons $2N$, the appropriate correlated reference state to consider is

$$|0\rangle = (G^\dagger)^N|vac\rangle, \quad \text{with} \quad G^\dagger = \sum_i g_i b_i^\dagger b_{i+s}^\dagger. \tag{5.19}$$

Such a reference state has been called an antisymmetrized geminal power (AGP). Should the number of electrons be odd $2N+1$, one may construct the appropriate reference state as a generalized antisymmetrized geminal power (GAGP)

$$|0\rangle = (G^\dagger)^m \prod_{k=2m+1}^{2N+1} b_k^\dagger|vac\rangle, \tag{5.20}$$

with k referring to spin orbitals that are orthogonal to the $2s$ spin orbitals that make up the geminal (two-electron function)

$$\begin{aligned} g(1,2) &= \langle vac|\psi(2)\psi(1)G^\dagger|vac\rangle \qquad (5.21) \\ &= \sum_{i=1}^{s} g_i|u_i(1)u_{i+s}(2)\rangle = |g\rangle, \qquad (5.22) \end{aligned}$$

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[2] Linderberg and Öhrn, *Int. J. Quantum Chem.* **11**, 161 (1977), and *ibid* **15**, 343 (1979)

with

$$\psi(1) = \sum_i b_i u_i(1) \quad \text{and} \quad |u_i(1)u_{i+s}(2)\rangle \tag{5.23}$$

being an electron field operator and a Slater determinant, respectively. A GAGP might be useful also for the case of an even number of electrons when a part, say the core, can be given an uncorrelated treatment. In the following, the case of an even number of electrons is explicitly treated with an AGP reference.

The two-matrix of the geminal $|g\rangle$ is simply

$$D^2(g) = |g\rangle\langle g|, \tag{5.24}$$

and the normalization of the geminal coefficients is conveniently chosen as

$$\mathrm{Tr}\{D^2(g)\} = \sum_{i=1}^{s} |g_i|^2 = 1, \tag{5.25}$$

with

$$D^2(g) = \sum_{i=1}^{s}\sum_{j=1}^{s} D^2_{i\; i+s;j\; j+s} |u_i(1)u_{i+s}(2)\rangle\langle u_j(1')u_{j+s}(2')|. \tag{5.26}$$

The one-matrix has eigenvalues n_i (i=1,2,...,2s) displaying at least the double degeneracy

$$n_i = n_{i+s} = |g_i|^2, \quad \text{for} \quad i = 1, 2, .., s, \tag{5.27}$$

simply due to the antisymmetry of the geminal g. Thus, the one-matrix becomes

$$D^1(g) = \sum_{j=1}^{s} n_j [u_j(1)u_j^*(1') + u_{j+s}(1)u_{j+s}(1')] \tag{5.28}$$

with

$$\mathrm{Tr}\{\, D^1(g)\} = 2\sum_{i=1}^{s} |g_i|^2 = 2. \tag{5.29}$$

The AGP wavefunction may be expanded in determinantal components:

$$\begin{aligned} &\langle vac|\psi(N)\psi(N-1)...\psi(1)(G^\dagger)^N|vac\rangle \equiv |g^N\rangle \\ = \;& \sum_{j_1=1}^{s}\sum_{j_2=1}^{s} \cdots \sum_{j_N=1}^{s} g_{j_1} g_{j_2} \cdots g_{j_N} \\ &\times |u_{j_1}(1)u_{j_1+s}(2)...u_{j_N}(2N-1)u_{j_N+s}(2N)\rangle. \end{aligned} \tag{5.30}$$

From this expression, one can see that the AGP can be represented as a leading determinant and all double, quadruple, hexatuple, *e.t.c.*, even nonlinked replacements out of that determinant. The mixing coefficients of these determinants are all functions of the far fewer geminal coefficients g_i. Each mixing coefficient is in fact a product of N out of the total number of s geminal coefficients, and thus a very nonlinear function of the s basic parameters g_i, with s being the total number of orbitals in our basis set. The normalization of the AGP

$$\begin{aligned} \langle g^N | g^N \rangle &= (N!)^2 \sum_{1 \leq j_1} \sum_{1 < j_2 < \dots} \dots \sum_{< j_N \leq s} n_{j_1} n_{j_2} \dots n_{j_N} \\ &= (N!)^2 S_N \end{aligned} \tag{5.31}$$

depends on the symmetric function S_N of order N of the s geminal parameters (occupation numbers) $n_j = |g_j|^2$ for $j = 1, 2, .., s$. The one-matrix $D^1(g^N)$ of the AGP has the same eigenfunctions (the natural spin orbitals of the AGP) as the one matrix $D^1(g)$ of the geminal, but it has different occupation numbers

$$N_i = S_N^{-1} n_i \partial S_N / \partial n_i. \tag{5.32}$$

Thus,

$$D^1(g^N) = \sum_j N_j \{ u_j(1) u_j^*(1') + u_{j+s}(1) u_{j+s}^*(1') \}. \tag{5.33}$$

The number of determinants in the expansion of the AGP, $s!/N!(s-N)!$, grows impressively large as the number of spin orbitals $r = 2s$ increases. For example, when $s = 40$ (*i.e.* a forty orbital basis) and $N = 20$ (a 20-electron system), there are approximately 10^9 configurations. The coefficients of these are of course not free to vary independently, but they are functions of the s variational parameters g_i.

Also the two-matrix has a simple form when the basis is ordered as follows:

$$\{ |u_i u_{i+s}\rangle, \quad 1 \leq i \leq s; \quad |u_i u_j\rangle, \quad 1 \leq i < j \leq 2s \quad \text{and} \quad i + s \neq j \}. \tag{5.34}$$

The two-matrix then has the form

$$\mathbf{D^2}(g^N) = \begin{bmatrix} \mathbf{B} & 0 \\ 0 & \mathbf{T} \end{bmatrix}, \tag{5.35}$$

the so-called "Box and Tail" form where **T** is a diagonal matrix of dimension 2s(s-1), and with the elements

$$\begin{aligned} T_{ij;ij} &= \langle g^N | b_i^\dagger b_j^\dagger b_j b_i | g^N \rangle / \langle g^N | g^N \rangle \qquad (5.36) \\ &= S_N^{-1} n_i n_j \partial^2 S_N / \partial n_i \partial n_j \quad \text{for} \quad 1 \leq i < j \leq 2s, \quad i + s \neq j. \end{aligned}$$

The block **B** is of dimension s and has the off-diagonal elements

$$\begin{aligned} B_{jj+s;kk+s} &= \langle g^N | b_k^\dagger b_{k+s}^\dagger b_{j+s} b_j | g^N \rangle / \langle g^N | g^N \rangle \qquad (5.37) \\ &= S_N^{-1} g_j^* g_k \partial^2 S_{N+1} / \partial n_j \partial n_k \quad \text{for} \quad 1 \leq j \neq k \leq s \end{aligned}$$

and the diagonal elements

$$B_{jj+s;jj+s} = S_N^{-1} n_j \partial S_N / \partial n_j = N_j \quad \text{for} \quad 1 \leq j \leq s. \tag{5.38}$$

The total electronic energy is

$$\begin{aligned} E(g) &= \langle g^N | H | g^N \rangle / \langle g^N | g^N \rangle \\ &= \operatorname{Tr}\left\{\mathbf{hD}^1(g^N)\right\} + \operatorname{Tr}\left\{\mathbf{VD}^2(g^N)\right\}, \end{aligned} \tag{5.39}$$

where

$$h_{ij} = \langle u_i | -\frac{1}{2}\nabla^2 - \sum_k Z_k / |\vec{R}_k - \vec{r}| | u_j \rangle \tag{5.40}$$

are the one-electron integrals with Z_k the atomic number and $\vec{R}_k$ the position vector of nucleus k, while the antisymmetric electron interaction integrals are

$$V_{ij;kl} = \langle ij | kl \rangle - \langle ij | lk \rangle = \langle ij || kl \rangle \tag{5.41}$$

for $1 \leq i < j \leq 2s$ and $1 \leq k < l \leq 2s$.

The total energy of the AGP can then be expressed in terms of these one- and two-electron integrals as

$$\begin{aligned} E(g) &= \sum_{j=1}^{s} N_j \{ h_{jj} + h_{j+sj+s} + \langle jj+s || jj+s \rangle \} \\ &\quad + \sum_{1 \leq j < k \leq s} T_{jk+s;jk+s} \times \{ \langle kj || kj \rangle + \langle kj+s || kj+s \rangle \\ &\quad + \langle k+sj || k+sj \rangle + \langle k+sj+s || k+sj+s \rangle \} \\ &\quad +2 \sum_{1 \leq j < k \leq s} \Re\{ B_{jj+s;kk+s} \langle kk+s || jj+s \rangle \}. \end{aligned} \tag{5.42}$$

In general, the geminal is a linear combination of a spin singlet and a spin triplet function. A restricted version of the AGP that guarantees a spin singlet reference state is obtained when the geminal is restricted to be a singlet function only. This restriction means that u_{i+s} is the conjugate spin orbital to u_i; *i.e.*, it would have the complex conjugate orbital part and opposite spin. The expression for the total energy then simplifies to

$$\begin{aligned} E(g) &= 2\sum_{j=1}^{s} N_j \{ h_{jj} + \frac{1}{2}\langle jj | jj \rangle \} \\ &\quad + \sum_{1 \leq j < k \leq s} T_{jk;jk} \{ 4\langle jk | jk \rangle - \langle jk | kj \rangle \} \\ &\quad +2 \sum_{1 \leq j < k \leq s} \Re\{ B_{jj;kk} \langle kk | jj \rangle \}, \end{aligned} \tag{5.43}$$

after summation over spin. The first two terms in this expression should be compared with the closed shell single-determinantal SCF energy. It has the same general form, but the coefficients N_j and $T_{jk;jk}$ are now quite general fractional numbers. The last term has the appearance of a sum of pair energies.

The field operators

$$\begin{aligned} q^\dagger_{ij+s} &= g_j^* b_i^\dagger b_{j+s} + g_i^* b_j^\dagger b_{i+s} \\ q^\dagger_{i+sj} &= g_j^* b^\dagger_{i+s} b_j + g_i^* b^\dagger_{j+s} b_i \end{aligned} \tag{5.44}$$

$$\begin{aligned} q^\dagger_{ij} &= g_j^* b_i^\dagger b_j - g_i^* b^\dagger_{j+s} b_{i+s} \\ q^\dagger_{i+sj+s} &= g_j^* b^\dagger_{i+s} b_{j+s} - g_i^* b_j^\dagger b_i \end{aligned} \tag{5.45}$$

are introduced for $1 \leq i < j \leq s$ and $n_i \neq n_j$. These operators acting on the AGP yield, for instance,

$$\begin{aligned} q^\dagger_{ij+s} |g^N\rangle &= A b_i^\dagger b_j^\dagger (G^\dagger)^{N-1} |vac\rangle \\ \text{with} \quad A &= S_N^{-1}(n_i - n_j)N. \end{aligned} \tag{5.46}$$

This is so because

$$[q^\dagger_{ij+s}, G^\dagger]_- = (n_i - n_j) b_i^\dagger b_j^\dagger, \tag{5.47}$$

and

$$\begin{aligned} [q^\dagger_{ij+s}, (G^\dagger)^N]_- &= \sum_k (G^\dagger)^{N-k} [q^\dagger_{ij+s}, G^\dagger]_- (G^\dagger)^{k-1} \\ &= N [q^\dagger_{ij+s}, G^\dagger]_- (G^\dagger)^{N-1}. \end{aligned} \tag{5.48}$$

Similar relations for the other operators permit us to write

$$\begin{aligned} q^\dagger_{i+sj} |g^N\rangle &= -A b^\dagger_{i+s} b^\dagger_{j+s} (G^\dagger)^{N-1} |vac\rangle, \\ q^\dagger_{ij} |g^N\rangle &= -A b_i^\dagger b^\dagger_{j+s} (G^\dagger)^{N-1} |vac\rangle, \\ q^\dagger_{i+sj+s} |g^N\rangle &= A b^\dagger_{i+s} b_j^\dagger (G^\dagger)^{N-1} |vac\rangle. \end{aligned} \tag{5.49}$$

All of these states are GAGP's and together with the reference AGP, $|g^N\rangle$, form an orthogonal set of $2N$-electron states. On the other hand, the operators

$$q_{ij+s} = g_j b^\dagger_{j+s} b_i + g_i b^\dagger_{i+s} b_j \tag{5.50}$$

satisfy the relation

$$[q_{ij+s}, G^\dagger]_- = g_j g_i b^\dagger_{j+s} b^\dagger_{i+s} + g_j g_i b^\dagger_{i+s} b^\dagger_{j+s} = 0, \tag{5.51}$$

which means that q_{ij+s} annihilates $|g^N\rangle$. The same holds true for q_{i+sj}, q_{ij}, and q_{i+sj+s}.

The first step in the determination of the propagator is the optimization of the reference $|g^N\rangle$, *i.e.*, the minimization of $E(g)$ with respect to the natural orbitals corresponding to the field operators b_i and with respect to the s geminal coefficients g_i for a given orbital basis set.

With these optimized orbitals and geminal coefficients, the operators are formed and the normalized reference obtained as

$$|g^N\rangle = [S_N(N!)^2]^{-\frac{1}{2}}(G^\dagger)^N|vac\rangle. \tag{5.52}$$

The operators $q^\dagger_{ij+s}$, $q^\dagger_{i+sj}$, $q^\dagger_{ij}$, and $q^\dagger_{i+sj+s}$ for $i < j$ and for $n_i \neq n_j$ are constructed and augmented with the "diagonal" operators

$$\begin{aligned}\hat{q}^\dagger_{ii} &= (b^\dagger_i b_i - \langle b^\dagger_i b_i\rangle)|g^N\rangle\langle g^N| \\ &\quad +(b^\dagger_{i+s} b_{i+s} - \langle b^\dagger_{i+s} b_{i+s}\rangle)|g^N\rangle\langle g^N|,\end{aligned} \tag{5.53}$$

with

$$\langle b^\dagger_i b_i\rangle = \langle g^N|b^\dagger_i b_i|g^N\rangle \quad \text{for} \quad 1 \leq i \leq s. \tag{5.54}$$

Then the metric

$$\mathbf{S} = \begin{bmatrix} \mu & 0 \\ 0 & -\mu \end{bmatrix}, \quad \text{with} \quad \mu = \begin{bmatrix} \Upsilon & 0 \\ 0 & \Lambda \end{bmatrix}, \tag{5.55}$$

is calculated, where Υ is the metric of the "diagonal" operators and Λ is the metric of the "regular" q operators. Although Λ is diagonal Υ is not. A unitary transformation $\mathbf{U}$ is found that diagonalizes Υ, which is a semipositive matrix with at least one zero eigenvalue. This arises from the fact that the number operator for the total number of electrons is spanned by the "diagonal" operators, resulting in a linear relationship between these basis operators. Discarding the zero eigenvalues L_k of

$$\mathbf{L} = \mathbf{U}^\dagger \Upsilon \mathbf{U}, \tag{5.56}$$

the canonically orthonormalized operators

$$q^\dagger_{kk} = (L_k)^{-\frac{1}{2}} \sum_{i=1}^{s} \hat{q}^\dagger_{ii} U_{ik} \quad \text{for} \quad L_k > 0 \tag{5.57}$$

can be obtained.

Using the array of operators

$$\mathbf{q}^\dagger = \{q^\dagger_{ij+s}, q^\dagger_{i+sj}, q^\dagger_{ij}, q^\dagger_{i+sj+s}, q^\dagger_{ii}\} \tag{5.58}$$

and an array of their adjoints, the metric

$$\lambda = \langle g^N|[\mathbf{q}, \mathbf{q}^\dagger]_-|g^N\rangle \tag{5.59}$$

is formed and the dynamical matrices

$$\mathbf{B} = \langle g^N | [\mathbf{q}, [H, \mathbf{q}^\dagger]_-]_- | g^N \rangle \tag{5.60}$$

and

$$\mathbf{C} = \langle g^N | [\mathbf{q}, [H, \mathbf{q}]_-]_- | g^N \rangle \tag{5.61}$$

constructed, where the notation tacitly assumes that the arrays of operators $\mathbf{q}^\dagger$ and $\mathbf{q}$ are in the appropriate column or row format so as to result in square matrices λ, $\mathbf{B}$, and $\mathbf{C}$.

For real orbitals and geminal coefficients g_i, the excitation propagator $P(E)$ is written in the geometric approximations as before, but now with the augmented set of field operators. Considering the block

$$\langle\langle \mathbf{q}; \mathbf{q}^\dagger \rangle\rangle_E \tag{5.62}$$

of the matrix propagator, the element

$$P_{mn}(E) = \sum_k \left[\frac{\lambda_m^{\frac{1}{2}} Z_{mk} Z_{nk}^* \lambda_n^{\frac{1}{2}}}{E - \omega_k} - \frac{\lambda_m^{\frac{1}{2}} Y_{mk} Y_{nk}^* \lambda_n^{\frac{1}{2}}}{E + \omega_k} \right] \tag{5.63}$$

can be identified with the spectral representation to obtain

$$\begin{aligned} \lambda_m^{\frac{1}{2}} Z_{mk} &= \langle 0 | q_m | k \rangle, \quad \lambda_n^{\frac{1}{2}} Z_{nk}^* = \langle k | q_n^+ | 0 \rangle, \\ \lambda_m^{\frac{1}{2}} Y_{mk} &= \langle k | q_m | 0 \rangle, \quad \lambda_n^{\frac{1}{2}} Y_{nk}^* = \langle 0 | q_n^+ | k \rangle, \end{aligned} \tag{5.64}$$

and $\omega_k = E_k - E_0$, with $E_0 = E(g)$.

The field operators q can be transformed so that they produce spin eigenstates when applied to the singlet restricted AGP. Thus, $q_m = q_{lk} + q_{l+sk+s}$ or $q_m = q_{kk}$ for singlets, and $q_m = q_{lk} - q_{l+sk+s}$ and $q_m = q_{lk+s}$, $q_m = q_{l+sk}$ for spin triplets with z-component of spin angular momentum equal 0, 1, and -1, respectively. As $\mathbf{Z}^\dagger\mathbf{Z} - \mathbf{Y}^\dagger\mathbf{Y} = \mathbf{1}$, the relation

$$\langle k | \sum_m \lambda_m^{-\frac{1}{2}} (q_m^\dagger Z_{mk} - q_m Y_{mk}^*) | 0 \rangle = 1 \tag{5.65}$$

holds. Thus, the excitation operator

$$Q_k^\dagger = \sum_m \lambda_m^{-\frac{1}{2}} (q_m^\dagger Z_{mk} - q_m Y_{mk}^*) \tag{5.66}$$

satisfies the relation

$$|k\rangle = Q_k^\dagger |0\rangle. \tag{5.67}$$

But, the de-excitation operators Q_k still do not annihilate the reference unless all Y_{mk} vanish. From the earlier discussion, one can see that this will happen if the matrix **C** is neglected in the propagator expression. This approximation is the so-called AGP-based Tamm-Dancoff Approximation (TDA) and means that the excited states are represented in terms of all single excitations out of the AGP reference. Calculations show that in many cases the **C** matrix elements and the Y-coefficients are several orders of magnitude (10^{-3} – 10^{-6}) smaller with the AGP reference than they are with the single-determinantal SCF reference. The AGP-based TDA then gives the same excitation energies and transition moments as does the AGP-based Random Phase Approximation (RPA), which is obtained when the **C** matrix is included in the propagator. In this sense, the singlet restricted AGP reference is the consistent reference of the excitation propagator in the RPA. There are, however, cases for which the TDA and the RPA give quite different results and the consistency of the approximation is lacking. The use of spin unrestricted AGP reference states should then be studied. This might require spin projections to guarantee pure spin states and would also lead to more complicated field operators.

Several calculations have been reported for the AGP-based polarization propagator applied to atoms and small molecular systems. When the Eq. (5.67) is satisfied, individual stationary excited states can be obtained as excitations from the AGP reference state. Thus, starting from an energy optimized AGP, the vertical excitation (and de-excitation energies, when the AGP is not the ground state) determines potential energy surfaces and wavefunctions for other states. B. Weiner and Y. Öhrn[3] calculate the $X^1\Sigma^+$ ground state of the LiH molecule as an AGP and, with a modest basis, obtains potential energy curves from the polarization propagator also for the $A^1\Sigma^+$, and the $B^1\Pi$ states in excellent agreement with rather elaborate CI (configuration interaction) calculations, which use a considerably larger orbital basis. Electric dipole moments and transition moments (see Fig. 5.2) as a function of internuclear distance for all three states agree very well with the more elaborate wavefunction calculations. E. Sangfelt, R. Roy Chowdhury, B. Weiner, and Y. Öhrn[4], although primarily studying the stability problem, obtain equally satisfactory results for the three lowest $^3\Sigma$ and the lowest $^3\Pi$ state of LiH. Unpublished results also show excellent results for the various transition moments as functions of internuclear distance for this system. Comparisons were made with H. Partridge and S. Langhoff[5] for the singlet states and with K. K. Docken and J. Hinze[6] for the triplet states, and although the total energies are lower for these more elaborate calculations, the overall shapes and splittings of the potential energy curves from the AGP calculations agree within 20 cm^{-1} or better.

Applications to the Li_2 molecule by E. Sangfelt, H. A. Kurtz, N. Elander, and O. Goscinski[7] show equally excellent results employing modest basis sets. Once a potential energy curve is obtained and interpolated, the Schrödinger

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[3] B. Weiner and Y. Öhrn, *J. Phys. Chem.* **91**, 563 (1987)

[4] E. Sangfelt, R. Roy Chowdhury, B. Weiner, and Y. Öhrn, *J. Chem. Phys.* **86**, 4523 (1987)

[5] H. Partridge and S. Langhoff, *J. Chem. Phys.* **74**, 2361 (1981)

[6] K. K. Docken and J. Hinze, *J. Chem. Phys.* **57**, 4928, 4936 (1972)

[7] E. Sangfelt, H. A. Kurtz, N. Elander, and O. Goscinski, *J. Chem. Phys.* **81**, 3976 (1984)

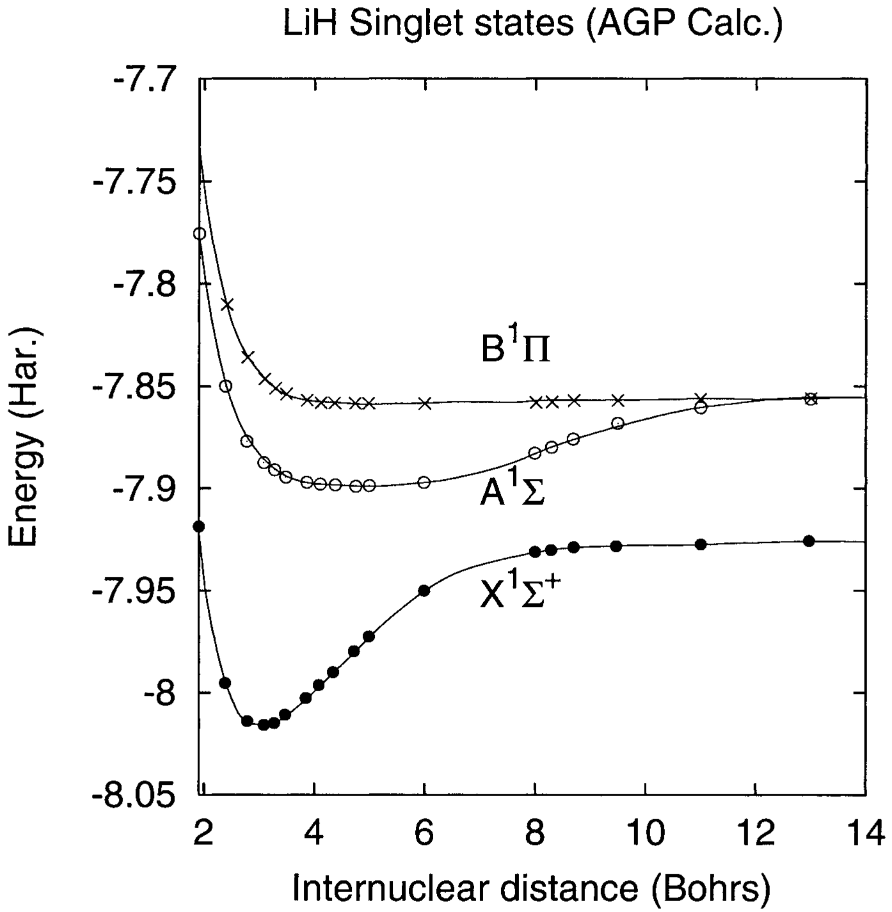

Figure 5.1: AGP potential energy curves for $X^1\Sigma^+$, $A^1\Sigma^+$, and $B^1\Pi$ states of LiH.

equation for nuclear motion can be integrated (for Li_2 regarded as a symmetric top. In this way, spectroscopic constants and vibrational energies are obtained. The eigenenergies in terms of vibrational and rotational quantum numbers ν and J are given as

$$\begin{aligned} E(\nu, J) &= G(\nu) + F_\nu(J), \\ G(\nu) &= \omega_e(\nu + 1/2) - \omega_e x_e(\nu + 1/2)^2, \\ F_\nu(J) &= B_\nu J(J+1), \\ B_\nu &= B_e - \alpha_e(\nu + 1/2). \end{aligned} \tag{5.68}$$

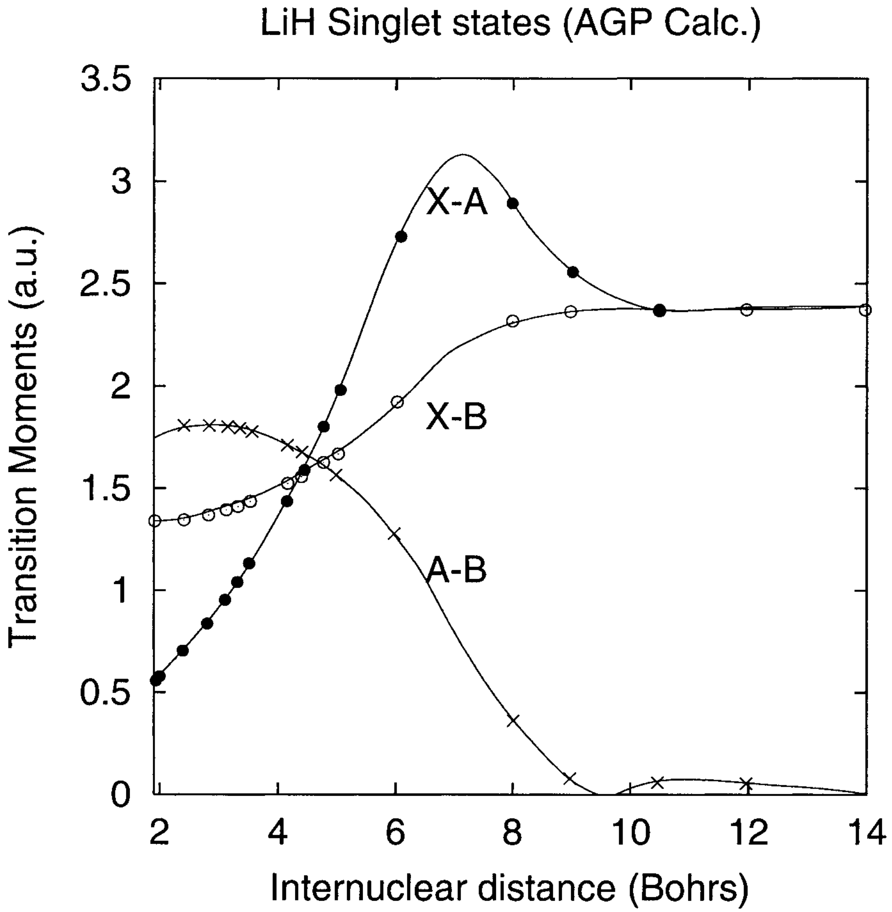

Figure 5.2: Transition moment curves for the $X \leftarrow A$, $X \leftarrow B$, and $A \leftarrow B$ transitions in LiH.

The ω_e and $\omega_e x_e$ values are determined from a fit to the $G(\nu)$ values using the three or four lowest vibrational states. The B_ν values are calculated as $B_\nu = (\hbar/4\pi c\mu)\langle\nu|R^{-2}|\nu\rangle$, where $|\nu\rangle$ is a rotationless vibrational wavefunction and μ is the reduced mass. A straight line fit of the B_ν values yield B_e and α_e. The agreement with experimentally determined spectroscopic constants and with those obtained from quite elaborate configuration interaction calculations is reasonable for the four lowest singlet and three lowest triplet states. The published AGP results contained some mistakes and were later corrected, [8] resulting in vastly improved agreement. In Table 5.1, the corrected AGP spectroscopic

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[8] E. Sangfelt, personal communication

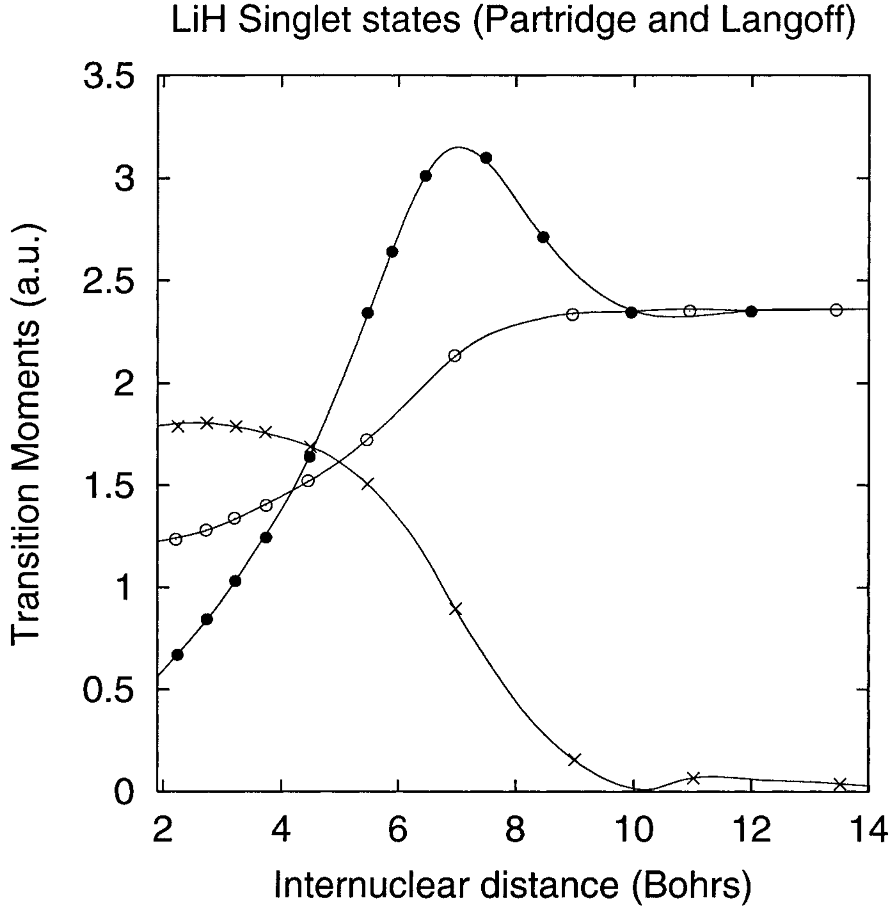

Figure 5.3: Transition moment curves for the $X \leftarrow A$, $X \leftarrow B$, and $A \leftarrow B$ transitions in LiH.

constants for the $X^1\Sigma_g^+$ are compared with experiment.

The corrected $G(\nu)$ values for the eleven lowest vibrational states of the Li_2 ground state are given in Table 5.2.

This excellent performance of the theory is, indeed, very interesting and should be explored further for other systems and with the theory generalized to spin unrestricted AGP's. Most quantum chemistry calculations including the propagator variety usually do not consider situations far removed from the equilibrium ground state geometry, and in general quantum chemistry tends to use rather different methodology to calculate energy dependence on geometry (potential energy surfaces) from that used to calculate spectra (excitation

Table 5.1: Spectroscopic constants for the Li_2 ground state (in cm^{-1} and bohr)

	ω_e	$\omega_e x_e$	B_e	α_e	r_e	D_e	D_0
KO[a]	347.0	3.6	0.66	0.0055	2.696	8297	8120
AGP	352.5	2.66	0.6736	0.00745	2.698	8519	8344
EXP[b]	351.39	2.58	0.6726	0.00702	2.673	8600	8425

a.- KO refers to M. L. Olson and D. D. Konowalow, *Chem. Phys.* **22**, 129 (1977) and D. D. Konowalow and M. L. Olson, *J. Chem. Phys.* **71**, 450 (1979).

b.- EXP refers to results in K. F. Huber and G. Hertzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York, 1979.

Table 5.2: $G(\nu)$ values for the first several vibrational states of the Li_2 ground state

ν	KO[a]	AGP	EXP[b]
0	177.2	174.5	175.0
1	524.0	521.1	521.3
2	860.2	863.3	862.3
3	1189.3	1201.1	1198.0
4	1513.1	1534.0	1528.4
5	1832.4	1861.5	1853.5
6	2147.5	2183.6	2173.1
7	2458.4	2500.5	2487.2
8	2764.5	2811.7	2795.8
9	3065.7	3117.3	3098.7
10	3361.7	3417.3	3395.8

a.- KO refers to M. L. Olson and D. D. Konowalow, *Chem. Phys.* **22**, 129 (1977) and D. D. Konowalow and M. L. Olson, *J. Chem. Phys.* **71**, 450 (1979).

b.- EXP refers to M. Hessel and C. R. Vidal, *J. Chem. Phys.* **70**, 4439 (1979).

energies and transition moments). Starting from a reference AGP state, the polarization propagator seems to offer a way to compute simultaneous potential energy surfaces for ground and a few low-lying excited states. This is so because this procedure seems to exhibit reasonable energy splittings at most molecular geometries and is capable of generating separate stationary electronic state wavefunctions from the energy optimized AGP ground state.

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Chapter 6

Interaction of Radiation and Matter

The general theory of the interaction between electromagnetic radiation and matter lies in the realm of Quantum Electrodynamics, which is well beyond the scope of this text. Thus, our aim in this chapter is to formulate a working description of electromagnetic processes, which permits discussion of various photon scattering and absorption processes on a common footing using propagator theory.

6.1 A Charged Particle in an Electromagnetic Field

A particle with charge e and mass m moving under the influence of an electromagnetic field experiences the force field

$$\vec{F} = e\left[\vec{E} + \frac{1}{c}\vec{v} \times \vec{B}\right], \tag{6.1}$$

where $\vec{v}$ is the velocity of the particle and c is the speed of light in vacuum. The electric field strength $\vec{E}$ and the magnetic field strength $\vec{B}$ can be expressed in terms of the vector potential $\vec{A} = \vec{A}(\vec{r})$ and the scalar potential $\phi(\vec{r})$, where $\vec{r}$ is the position vector of the particle. Note that the dependence on the time parameter t is not explicitly shown, and that $\vec{v} = \dot{\vec{r}} = d\vec{r}/dt$.

Newton's equation of motion yields

$$m\dot{\vec{v}} = \vec{F} = e\left[-\frac{1}{c}\frac{\partial \vec{A}}{\partial t} - \vec{\nabla}\phi + \frac{1}{c}\vec{v} \times (\vec{\nabla} \times \vec{A})\right]. \tag{6.2}$$

This can be rewritten using the result from vector analysis that

$$\vec{v} \times (\vec{\nabla} \times \vec{A}) = \vec{\nabla}(\vec{v} \cdot \vec{A}) - (\vec{v} \cdot \vec{\nabla})\vec{A} \tag{6.3}$$

and the result (using the chain rule of differentiation) that

$$\frac{d\vec{A}}{dt}=\frac{\partial\vec{A}}{\partial t}+\frac{\partial\vec{A}}{\partial x}\dot{x}+\frac{\partial\vec{A}}{\partial y}\dot{y}+\frac{\partial\vec{A}}{\partial z}\dot{z}=\frac{\partial\vec{A}}{\partial t}+(\vec{v}\cdot\vec{\nabla})\vec{A} \tag{6.4}$$

to give

$$\frac{d}{dt}[m\vec{v}+\frac{e}{c}\vec{A}]=\vec{\nabla}[-e\phi+\frac{e}{c}\vec{v}\cdot\vec{A}]. \tag{6.5}$$

Comparing this result to the Lagrange's equation

$$\frac{d}{dt}\left(\frac{\partial L}{\partial\dot{x}}\right)=\frac{\partial L}{\partial x} \tag{6.6}$$

and the analogous ones for the y and z components shows that an appropriate Lagrangian is

$$L=\frac{1}{2}m\vec{v}^2-e\phi+\frac{e}{c}\vec{v}\cdot\vec{A}, \tag{6.7}$$

and, thus, the momentum $\vec{p}=(p_x,p_y,p_z)$ conjugate to $\vec{r}=(x,y,z)$ is

$$\begin{aligned}\vec{p} &= (\partial L/\partial\dot{x},\partial L/\partial\dot{y},\partial L/\partial\dot{z})\\ &= m\vec{v}+\frac{e}{c}\vec{A}.\end{aligned} \tag{6.8}$$

The corresponding hamiltonian is

$$\begin{aligned}H &= \vec{p}\cdot\vec{v}-L=\frac{1}{2}m\vec{v}^2+e\phi\\ &= \frac{1}{2m}\left(\vec{p}-\frac{e}{c}\vec{A}\right)^2+e\phi.\end{aligned} \tag{6.9}$$

In order to derive an expression for the energy of interaction between an intrinsic magnetic moment (as for a particle with nonzero spin angular momentum) and the electromagnetic field, one cannot proceed via classical mechanics as for the charged particle. Rather one proceeds via the relativistic Dirac equation and seeks the nonrelativistic limit[1].

The result is that the energy of interaction between the intrinsic magnetic moment $\vec{\mu}=\beta\vec{\sigma}=\beta(\sigma_x,\sigma_y,\sigma_z)$ of an electron and an electromagnetic field is

$$-\beta\vec{\sigma}\cdot\vec{B}=-\beta\vec{\sigma}\cdot(\vec{\nabla}\times\vec{A}), \tag{6.10}$$

where $\beta=e/2mc$ is the Bohr magneton and $\vec{\sigma}_i$ are the Pauli spin operator components.

The hamiltonian for an electron with charge e and spin $\vec{s}=\frac{1}{2}\vec{\sigma}$ (note that $\hbar$ = 1) in an electromagnetic field then takes the form

$$H=\frac{1}{2m}\left(\vec{p}-\frac{e}{c}\vec{A}\right)^2-e\phi-\beta\vec{\sigma}\cdot(\vec{\nabla}\times\vec{A}), \tag{6.11}$$

in the nonrelativistic limit.

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[1] see, *e.g.*, L. I. Schiff, *Quantum Mechanics*, McGraw-Hill, New York, 1955, p. 329f.

6.2 Quantization of the Radiation Field

A key quantity is the vector potential $\vec{A}(\vec{r},t) \equiv \vec{A}(\vec{r})$, which satisfies a wave equation analogously to the wave equation for the electron field operators $\psi(\xi)$. It is chosen divergence free $\vec{\nabla}\cdot\vec{A}(\vec{r}) = 0$. Invoking zero scalar potential and this choice is usually referred to as the Coulomb gauge.

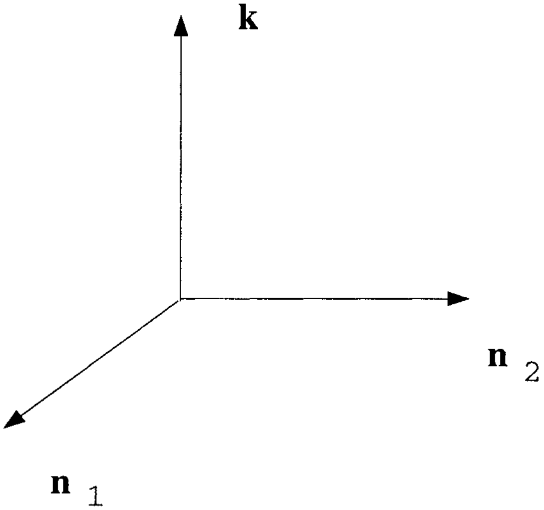

Figure 6.1: The polarization vectors $\vec{n}_1$ and $\vec{n}_2$ and the propagation vector $\vec{k}$ for a right-handed set of axis.

The vector potential is expanded in a complete set of plane waves orthonormalized over a finite volume V:

$$\vec{A}(\vec{r}) = V^{-\frac{1}{2}} \sum_{\vec{k}} \vec{A}(\vec{k}) \exp(i\vec{k}\cdot\vec{r}), \tag{6.12}$$

and thus,

$$\vec{\nabla}\cdot\vec{A}(\vec{r}) = V^{-\frac{1}{2}} \sum_{\vec{k}} \vec{k}\cdot\vec{A}(\vec{k}) \exp(i\vec{k}\cdot\vec{r}) = 0 \tag{6.13}$$

or $\vec{k}\cdot\vec{A}(\vec{k}) = 0$, *i.e.*, $\vec{A}(\vec{k})$ lies in a plane perpendicular to the propagation vector $\vec{k}$. The unit vectors $\vec{n}_1(\vec{k})$ and $\vec{n}_2(\vec{k})$ define two mutually orthogonal polarization directions in this plane. These vectors can be arranged such that $(\vec{n}_1(\vec{k}), \vec{n}_2(\vec{k}), \vec{k})$ form a right-handed set of axes (see Fig. 6.1). The vector potential can then be expressed as

$$\vec{A}(\vec{r}) = V^{-\frac{1}{2}} \sum_{\vec{k},\lambda} A_\lambda(\vec{k}) \vec{n}_\lambda(\vec{k}) \exp(i\vec{k}\cdot\vec{r}), \tag{6.14}$$

which permits us to use the Maxwell's equations to write

$$\begin{aligned}\vec{E}(\vec{r}) &= -\frac{1}{c}\frac{\partial \vec{A}(\vec{r})}{\partial t} \\ &= -\frac{1}{cV^{\frac{1}{2}}}\sum_{\vec{k},\lambda} \dot{A}_\lambda(\vec{k})\vec{n}_\lambda(\vec{k})\exp(i\vec{k}\cdot\vec{r}) \qquad (6.15)\end{aligned}$$

for the electric field, and

$$\begin{aligned}\vec{B}(\vec{r}) &= \vec{\nabla}\times\vec{A}(\vec{r}) \\ &= -iV^{-\frac{1}{2}}\sum_{\vec{k},\lambda}(-1)^\lambda kA_\lambda(\vec{k})\vec{n}_{\lambda\pm1}(\vec{k})\exp(i\vec{k}\cdot\vec{r}) \qquad (6.16)\end{aligned}$$

for the magnetic field. (Units in terms of the esu and emu system are employed.)

The energy of the electromagnetic field is

$$\begin{aligned}H_{ph} &= \frac{1}{8\pi}\int\left[\vec{E}^\dagger(\vec{r})\vec{E}(\vec{r})+\vec{B}^\dagger(\vec{r})\vec{B}(\vec{r})\right]d\vec{r} \\ &= \frac{1}{8\pi c^2}\sum_{\vec{k},\lambda}\left[\dot{A}^\dagger_\lambda(\vec{k})\dot{A}_\lambda(\vec{k})+(kc)^2A^\dagger_\lambda(\vec{k})A_\lambda(\vec{k})\right], \qquad (6.17)\end{aligned}$$

where the classical expression is generalized by anticipating that the electric and magnetic fields are operators. Define the operators

$$\begin{aligned}b_\lambda(\vec{k}) &= \left[i\dot{A}_\lambda(\vec{k})+(kc)A_\lambda(\vec{k})\right](8\pi kc^3)^{-\frac{1}{2}}, \\ b^\dagger_\lambda(-\vec{k}) &= \left[-i\dot{A}^\dagger_\lambda(-\vec{k})+(kc)A^\dagger_\lambda(-\vec{k})\right](8\pi kc^3)^{-\frac{1}{2}}, \qquad (6.18)\end{aligned}$$

and use the relation $A^\dagger_\lambda(\vec{k}) = (-1)^{\lambda+1}A_\lambda(-\vec{k})$, which follows from, say, that the electric field is a Hermitian operator, $\vec{E}^\dagger = \vec{E}$, and that $\vec{n}_\lambda(-\vec{k}) = (-1)^{\lambda+1}\vec{n}_\lambda(\vec{k})$. It then follows that

$$b^\dagger_\lambda(-\vec{k}) = (-1)^{\lambda+1}\left[-i\dot{A}(\vec{k})+(kc)A_\lambda(\vec{k})\right](8\pi kc^3)^{-\frac{1}{2}}. \qquad (6.19)$$

The energy (hamiltonian) can be expressed as

$$H_{ph} = \frac{1}{2}\sum_{\vec{k},\lambda}kc\left[b^\dagger_\lambda(\vec{k})b_\lambda(\vec{k})+b_\lambda(-\vec{k})b^\dagger_\lambda(-\vec{k})\right]. \qquad (6.20)$$

One of Maxwell's equations, $\partial\vec{E}(\vec{r},t)/c\partial t = \vec{\nabla}\times\vec{B}(\vec{r},t)$, permits us to write

$$-\ddot{A}_\lambda(\vec{k}) \equiv -\frac{\partial^2 A_\lambda(\vec{k})}{\partial t^2} = (kc)^2A_\lambda(\vec{k}), \qquad (6.21)$$

and thus $i\partial b_\lambda(\vec{k})/\partial t = [b_\lambda(\vec{k}), H_{ph}]_- = kcb_\lambda(\vec{k})$, where the last equality is consistent with the commutation relations

$$\begin{aligned}[b_\lambda(\vec{k}), b_{\lambda'}(\vec{k}')]_- &= [b^\dagger_\lambda(\vec{k}), b^\dagger_{\lambda'}(\vec{k}')]_- = 0, \\ [b_\lambda(\vec{k}), b^\dagger_{\lambda'}(\vec{k}')]_- &= \delta_{\lambda\lambda'}\delta_{\vec{k}\vec{k}'}. \qquad (6.22)\end{aligned}$$

Analogously to the situation for electrons, the operator $b_\lambda^\dagger(\vec{k})$ applied to the vacuum state produces a state vector of one photon with propagation vector $\vec{k}$ and polarization vector $\vec{n}_\lambda(\vec{k})$. The expression

$$\vec{A}(\vec{r}) = \sum_{\vec{k},\lambda}(2\pi c/kV)^{\frac{1}{2}}\left[b_\lambda(\vec{k}) + (-1)^{\lambda+1}b_\lambda^\dagger(-\vec{k})\right]\vec{n}_\lambda(\vec{k})\exp(i\vec{k}\cdot\vec{r}) \tag{6.23}$$

for the vector potential is easily obtained, where the time variable is suppressed. The hamiltonian can be rewritten using the commutation relations of Eq. (4.28) to read

$$H_{ph} = \sum_{\vec{k},\lambda} kc\left[b_\lambda^\dagger(\vec{k})b_\lambda(\vec{k}) + \frac{1}{2}\right]. \tag{6.24}$$

When the source charges and currents of the photon field are separate (distant) from the electron system under study, the hamiltonian for the interacting electrons and the photon field can be expressed as

$$\begin{aligned} H &= \int \psi^\dagger(\xi)\left[\frac{1}{2m}\left(-i\vec{\nabla} - \frac{e}{c}\vec{A}(\vec{r})\right)^2\right. \\ &\quad \left. -\frac{e}{2mc}\vec{\sigma}\cdot(\vec{\nabla}\times\vec{A}(\vec{r})) + V(\xi)\right]\psi(\xi)d\xi \\ &\quad +\frac{e^2}{2}\int \psi^\dagger(\xi)\psi^\dagger(\xi')\frac{1}{|\vec{r}-\vec{r}'|}\psi(\xi')\psi(\xi)d\xi d\xi' + H_{ph}, \end{aligned} \tag{6.25}$$

where $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ are the Pauli spin operators.

In order to study the equations of motion, the relation

$$[b_\lambda(\vec{k}), H]_- = kcb_\lambda(\vec{k}) - (2\pi/kcV)^{\frac{1}{2}}j_\lambda(\vec{k}) \tag{6.26}$$

is used, where $j_\lambda(\vec{k}) = \vec{n}_\lambda(\vec{k})\cdot\int d\vec{r}\vec{j}(\vec{r})\exp(-i\vec{k}\cdot\vec{r})$ and the current density operator is

$$\begin{aligned} \vec{j}(\vec{r}) &= \frac{e}{2m}\sum_{spin}\left[\left(i\vec{\nabla}\psi^\dagger(\xi)\right)\psi(\xi) - i\psi^\dagger(\xi)\vec{\nabla}\psi(\xi)\right. \\ &\quad \left. -\frac{2e}{c}\psi^\dagger(\xi)\psi(\xi)\vec{A}(\vec{r}) + \vec{\nabla}\times\left(\psi^\dagger(\xi)\vec{\sigma}\psi(\xi)\right)\right]. \end{aligned} \tag{6.27}$$

The propagation of photons through matter is governed by Eq. (6.26) and the corresponding ones for electron operators. Define the photon propagator $D_{\lambda'\lambda}(\vec{k}',\vec{k};E) = \langle\langle b_{\lambda'}(\vec{k}'); b_\lambda^\dagger(\vec{k})\rangle\rangle_E$, which satisfies the equation of motion

$$\begin{aligned} &E\langle\langle b_{\lambda'}(\vec{k}'); b_\lambda^\dagger(\vec{k})\rangle\rangle_E \\ &= \langle[b_{\lambda'}(\vec{k}'), b_\lambda^\dagger(\vec{k})]_-\rangle + \langle\langle[b_{\lambda'}(\vec{k}'), H]_-; b_\lambda^\dagger(\vec{k})\rangle\rangle_E \end{aligned} \tag{6.28}$$

from which it follows, with the help of Eq. (6.26), that

$$\begin{aligned}&(E - k'c)D_{\lambda'\lambda}(\vec{k}', \vec{k}; E)\\&= \delta_{\lambda'\lambda}\delta_{\vec{k}'\vec{k}} - (2\pi/k'cV)^{\frac{1}{2}}\langle\langle j_{\lambda'}(\vec{k}'); b_{\lambda}^{\dagger}(\vec{k})\rangle\rangle_E.\end{aligned} \tag{6.29}$$

Using the second form of the equation of motion (4.15), one obtains

$$\begin{aligned}&(E - kc)\langle\langle j_{\lambda'}(\vec{k}'); b_{\lambda}^{\dagger}(\vec{k})\rangle\rangle_E\\&= \langle[j_{\lambda'}(\vec{k}'), b_{\lambda}^{\dagger}(\vec{k})]_-\rangle - (2\pi/kcV)^{\frac{1}{2}}\langle\langle j_{\lambda'}(\vec{k}'); j_{\lambda}^{\dagger}(\vec{k})\rangle\rangle_E\end{aligned} \tag{6.30}$$

with

$$\langle[j_{\lambda'}(\vec{k}'), b_{\lambda}^{\dagger}(\vec{k})]_-\rangle = -\left(2\pi e^2/m^2kcV\right)^{\frac{1}{2}}\vec{n}_{\lambda'}(\vec{k}')\cdot\vec{n}_{\lambda}(\tilde{k})\tilde{q}(\vec{k}' - \vec{k}), \tag{6.31}$$

where $\tilde{q}(\vec{k}) = \langle\int d\vec{r}q(\vec{r})\exp(-i\vec{k}\cdot\vec{r})\rangle$, *i.e.*, the Fourier transform of the charge density of the matter ground state. In this way the study of photon processes naturally leads to the consideration of the propagator $\langle\langle j_{\lambda'}(\vec{k}'); j_{\lambda}^{\dagger}(\vec{k})\rangle\rangle_E$.

Problems

1. Show that Eq. (6.26) is correct with the definition of the current density operator as given by Eq. (6.27).

6.3 Absorption Spectroscopy

In dealing with dilute systems and not too intense light sources one can eliminate, from the current density operator, the term with the vector potential $\vec{A}(\vec{r})$. This eliminates from consideration multiple scattering processes and inelastic processes. The propagator $\langle\langle j_{\lambda'}(\vec{k}'); j_{\lambda}^{\dagger}(\vec{k})\rangle\rangle_E$ is then approximated with its counterpart derived from the equations of motion of matter (electrons).

Information about photon scattering processes can with advantage be discussed in terms of wave packets. Assume that a wave packet with wave vector $\vec{k}$ polarization λ and energy kc is emitted at time $t = 0$. It takes the wave packet L/c seconds to traverse the system volume V with linear dimensions L.

The probability that the wave packet can be detected with polarization λ' and wave vector $\vec{k}'$ (with the same energy kc) is the square of the amplitude

$$\begin{aligned}\langle b_{\lambda'}(\vec{k}', L/c)b_{\lambda}^{\dagger}(\vec{k}, 0)\rangle &= \frac{i}{2\pi}\int dE\langle\langle b_{\lambda'}(\vec{k}'); b_{\lambda}^{\dagger}(\vec{k})\rangle\rangle_E\exp(-iEL/c)\\&= \exp(-ikL)\left[\delta_{\lambda'\lambda}\delta_{\vec{k}'\vec{k}}\right.\\&\quad -(2\pi iL/kc^2V)\left\{(e/m)\,\tilde{q}(\vec{k}' - \vec{k})\vec{n}_{\lambda'}(\vec{k}')\cdot\vec{n}_{\lambda}(\vec{k})\right.\\&\quad \left.\left.+\ \langle\langle j_{\lambda'}(\vec{k}'); j_{\lambda}^{\dagger}(\vec{k})\rangle\rangle_{kc}\right\}\right],\end{aligned} \tag{6.32}$$

where Eq. (4.8) is used and terms proportional to L retained.

The probability amplitude $\langle b_\lambda(\vec{k}, L/c) b_\lambda^\dagger(\vec{k}, 0)\rangle$ gives direct information on the photon absorption process. Let the specific volume per molecule be the quantization volume V. The probability that a photon (wave packet) can pass through this volume of linear dimension L without being scattered is

$$|\langle b_\lambda(\vec{k}, L/c) b_\lambda^\dagger(\vec{k}, 0)\rangle|^2 = 1 + (4\pi L/kc^2 V)\Im\langle\langle j_\lambda(\vec{k}); j_\lambda^\dagger(\vec{k})\rangle\rangle_{kc}, \tag{6.33}$$

where again terms proportional to L are retained (*i.e.*, terms proportional to $(L/V)^2$ are neglected). The absorption coefficient (extinction coefficient per molecule) is the decrease in probability per unit length:

$$a = -\left(4\pi/kc^2 V\right) \Im\langle\langle j_\lambda(\vec{k}); j_\lambda^\dagger(\vec{k})\rangle\rangle_{kc}. \tag{6.34}$$

This holds for the matter ground state, *i.e.*, excluding emission processes.

When the wavelength of the radiation is much greater than the molecular dimensions $(\vec{k} \cdot \vec{r} << 1)$

$$j_\lambda(\vec{k}) = \vec{n}_\lambda(\vec{k}) \cdot \int \vec{j}(\vec{r}) e^{-i\vec{k}\cdot\vec{r}} d\vec{r} \approx \vec{n}_\lambda(\vec{k}) \cdot \int \vec{j}(\vec{r}) d\vec{r}, \tag{6.35}$$

and if the field-dependent and spin-dependent terms in the current density operator are excluded, the result is

$$\int \vec{j}(\vec{r}) d\vec{r} \simeq (e/m) \int \psi^\dagger(\xi)(-i\vec{\nabla}\psi(\xi)) d\xi = (e/m)\vec{p}. \tag{6.36}$$

Thus, the basic propagator to consider is the (tensor) propagator $\langle\langle \vec{p}; \vec{p}\rangle\rangle_{kc}$, which is related to $\langle\langle \vec{R}; \vec{R}\rangle\rangle_{kc}$ through the relation $[\vec{R}, H]_- = ie\vec{p}/m$, where

$$\vec{R} = \int \vec{r} q(\vec{r}) d\vec{r} = e \int \psi^\dagger(\xi) \vec{r} \psi(\xi) d\xi \tag{6.37}$$

is the so-called polarization operator. One can write

$$a = -(4\pi k/V)\Im\langle\langle R_\lambda; R_\lambda\rangle\rangle_{kc}. \tag{6.38}$$

Put $kc = \omega$ and $\omega_{mn} = E_m - E_n$ and use Eq. (4.17) to write the *polarization propagator* as

$$\langle\langle R_\lambda; R_\lambda\rangle\rangle_\omega = \sum_{m,n} |\langle m|R_\lambda|n\rangle|^2 \rho_n \left[\frac{1}{\omega - \omega_{mn} + i\eta} - \frac{1}{\omega + \omega_{mn} - i\eta}\right] \tag{6.39}$$

so that

$$\begin{aligned} \Im\langle\langle R_\lambda; R_\lambda\rangle\rangle_\omega &= -\sum_{m,n} |\langle m|R_\lambda|n\rangle|^2 \rho_n \pi \left[\delta(\omega - \omega_{mn}) + \delta(\omega + \omega_{mn})\right] \\ &= -\sum_{m,n} |\langle m|R_\lambda|n\rangle|^2 \rho_n S(\omega - \omega_{mn}), \end{aligned} \tag{6.40}$$

where in the second line the second delta function has been dropped (considering only absorption $E_m > E_n$). The shape function S shows a delta function "spike" spectrum. A more realistic extinction function will take into account molecular collisions in a gaseous sample leading to Lorentzian shape functions $S(\omega - \omega_{mn}) = A/((\omega - \omega_{mn})^2 + B)$ or will take into account Doppler broadening leading to Gaussian shapes $S(\omega - \omega_{mn}) = A\exp[-B(\omega - \omega_{mn})^2]$.

Averaging over all molecular orientations, as is appropriate for a gaseous sample, yields[2]

$$\begin{aligned}\langle\langle R_\lambda; R_\lambda\rangle\rangle_\omega &\rightarrow \frac{1}{3}\left[\langle\langle R_x; R_x\rangle\rangle_\omega + \langle\langle R_y; R_y\rangle\rangle_\omega + \langle\langle R_z; R_z\rangle\rangle_\omega\right] \\ &= -\frac{1}{3}\alpha(\omega), \qquad (6.41)\end{aligned}$$

where $\alpha(\omega)$ is the frequency-dependent polarizability. Thus, $a = (4\pi\omega/3cV)\Im\alpha(\omega)$, or for a pure state ($\rho_n = \delta_{n0}$), one obtains

$$a = (4\pi\omega N_0/3c)\sum_m |\langle m|\vec{R}|0\rangle|^2 S(\omega - \omega_{m0}), \qquad (6.42)$$

where $N_0 = 1/V$ is the number of molecules per unit volume in the ground state $|0\rangle$. For a light source frequency close to ω_{m0}, the single term $\{4\pi\omega(N_0 - N_m)/3c\}|\langle m|\vec{R}|0\rangle|^2 S(\omega - \omega_{m0})$ will dominate the contribution to the extinction coefficient, where the effect of induced emission from the state $|m\rangle$ with population N_m is included. The emitted photons are assumed to have propagation vector $\vec{k}$ and will reduce the extinction coefficient by giving photons to the field. When degenerate states are involved, appropriate degeneracy factors must be included.

When a transition is dipole forbidden, *i.e.*, $\langle m|\vec{R}|0\rangle = 0$, say, due to symmetry, then higher terms in the expansion $\exp(-i\vec{k}\cdot\vec{r}) \simeq 1 - i\vec{k}\cdot\vec{r} + \cdots$ become important in the expression for $j_\lambda(\vec{k})$ and lead to so-called magnetic dipole and electric quadrupole transitions.

For electrons,

$$j_\lambda(\vec{k}) = (e/m)\int d\xi\psi^\dagger(\xi)[1 - ikr_k + \cdots](-i\nabla_\lambda\psi(\xi)), \qquad (6.43)$$

where r_k is the component of $\vec{r}$ along $\vec{k}$ and ∇_λ is the component of $\vec{\nabla}$ along $\vec{n}_\lambda(\vec{k})$. The identity

$$\begin{aligned}r_k(-i\nabla_\lambda) &= \frac{1}{2}\left[r_k(-i\nabla_\lambda) - r_\lambda(-i\nabla_k)\right] \\ &\quad + \frac{1}{2}\left[r_k(-i\nabla_\lambda) + r_\lambda(-i\nabla_k)\right] \qquad (6.44)\end{aligned}$$

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[2] $(8\pi)^{-1}\sum_\lambda \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi\langle\langle R_\lambda; R_\lambda\rangle\rangle_\omega$ with, say, $\vec{n}_1(\vec{k}) = (\cos\theta\cos\phi,\ \cos\theta\sin\phi,\ -\sin\theta)$ and $\vec{n}_2(\vec{k}) = (-\sin\phi,\ \cos\phi,\ 0)$, for $\vec{k} = k(\sin\theta\cos\phi,\ \sin\theta\sin\phi,\ \cos\theta)$.

permits us to write

$$j_\lambda(\vec{k}) \simeq (e/m)\left[p_\lambda - (ik/2)(-1)^{\lambda\pm1}l_{\lambda\pm1} - ikT^{(2)}_{\lambda k}\right] \tag{6.45}$$

in terms of the components of electron momentum p_λ, of orbital angular momentum l_λ, and of a tensor operator $T^{(2)}_{\lambda k}$ corresponding to the second term of Eq. (6.44) transforming as spherical harmonics of order two and directly related to the electric quadrupole tensor.

The spin operator part of the current density also causes absorption of electromagnetic energy. The corresponding contribution to $j_\lambda(\vec{k})$ is

$$\begin{aligned}&(e/2m)\int d\xi e^{-i\vec{k}\cdot\vec{r}}\vec{n}_\lambda(\vec{k})\cdot\vec{\nabla}\times(\psi^\dagger(\xi)\vec{\sigma}\psi(\xi))\\ &= (-iek/m)(-1)^{\lambda\pm1}\vec{n}_{\lambda\pm1}(\vec{k})\vec{s},\end{aligned} \tag{6.46}$$

where integration by parts has been used, $\exp(-i\vec{k}\cdot\vec{r}) \simeq 1$, and the operator of total electronic spin $\vec{s}$ introduced .

One can then write quite generally that

$$a = -(4\pi/kc^2V)\Im\langle\langle j_\lambda(\vec{k}); j^\dagger_\lambda(\vec{k})\rangle\rangle_{kc} \tag{6.47}$$

with

$$\begin{aligned} j_\lambda(\vec{k}) \quad \simeq \quad & (e/m)\vec{n}_\lambda(\vec{k})\cdot\vec{p} - ic\vec{k}\times\vec{n}_\lambda(\vec{k})\cdot(e/2mc)(\vec{l}+2\vec{s})\\ & -ikc(e/mc)T^{(2)}_{\lambda k}.\end{aligned} \tag{6.48}$$

This form would be particularly useful for the case of polarized light passing through an anisotropic medium. In many experiments, however, unpolarized light is passing through an isotropic medium as a liquid solution, or a gas. One then averages over all molecular orientations or equivalently over all photon directions, and also over polarizations:

$$\frac{1}{2}\sum_\lambda \frac{1}{4\pi}\int d\Omega. \tag{6.49}$$

One should also remember that when summing over states in the propagator expressions, one is summing over energy eigenstates of $H_{matter} + H_{ph}$, where H_{matter} is the operator of Eq. (4.3). This means that one is summing over states that are products of matter eigenstates and photon eigenstates. When the terms with the vector potential in the expression of the current density operator are excluded in Eq. (6.27), the only effect of the summation over photon eigenstates is a factor in the expression of the absorption coefficient a giving the number of photon states at a particular frequency ω. An expression can be derived for this by considering the photon field in a cubic box of side L. The end result is actually not critically dependent on the shape of the box. The appropriate boundary conditions for standing waves in the box are to demand that the vector potential (and its derivatives) should have the same values at corresponding positions of opposite surfaces of the box.

This means that $k^2 = \frac{4\pi^2}{L^2}(n_x^2+n_y^2+n_z^2)$, since $k_xL = 2\pi n_x$, $k_yL = 2\pi n_y$, and $k_zL = 2\pi n_z$ for the propagation vector $\vec{k} = (k_x, k_y, k_z)$, where $\vec{n} = (n_x, n_y, n_z)$ defines a set of integer lattice points in three dimensions with each point or triplet of integers corresponding to a photon state for a fixed polarization. The number of lattice points (states) per polarization in a frequency range ω to ω+dω can be figured as follows. Note that $k^2c^2 = \omega^2 = \frac{4\pi^2c^2}{L^2}n^2$, *i.e.*, $n = \frac{L}{2\pi c}\omega$, and that the number of lattice points in a solid angle dΩ about $\vec{n}$ (or $\vec{k}$) between n and $n+dn$ is $n^2dnd\Omega = (L/2\pi c)^3\omega^2d\omega d\Omega$. The number of photon states at the frequency ω is then $(V/8\pi^3c^3)\,\omega^2$ for a particular propagation direction and polarization.

Problems

1. Show that $\langle a|r_k\,(-i\nabla_\lambda) + r_\lambda\,(-i\nabla_k)\,|b\rangle = i\omega_{ab}\langle a|r_kr_\lambda|b\rangle$ for two energy eigenfunctions $|a\rangle$ and $|b\rangle$, where $\omega_{ab} = E_a - E_b$ in the units with Planck's constant $= 2\pi$, and electron mass=1. Note the relation to the electric quadrupole moment operator for an electronic system $\int d\vec{r}\vec{r}\vec{r}q(\vec{r})$. Note the dyadic notation $\vec{r}\vec{r}$ for the tensor quantity!

2. Try to carry out the averaging in Eq. (6.49). It can be done using, say, the vectors $\vec{k} = k(\sin\theta\cos\phi,\ \cos\theta)$, $\vec{n}_1(\vec{k}) = (\cos\theta\cos\phi,\ \cos\theta\sin\phi,\ -\sin\theta)$, and $\vec{n}_2(\vec{k}) = (-\sin\phi,\ \cos\phi,\ 0)$ in spherical polar angles.

6.4 RPA Transition Moments

The excitation propagator (particle-hole propagator) at the RPA level of approximation can be expressed as

$$\begin{aligned}\langle\langle q_m; q_n^\dagger\rangle\rangle_E &= \sum_k \left[\frac{\lambda_m^{1/2}Z_{mk}Z_{nk}^*\lambda_n^{1/2}}{E-\omega_k} - \frac{\lambda_m^{1/2}Y_{mk}Y_{nk}^*\lambda_n^{1/2}}{E+\omega_k}\right] \\ &= \sum_k \left[\frac{\langle 0|q_m|k\rangle\langle k|q_n^\dagger|0\rangle}{E-E_k+E_0} - \frac{\langle 0|q_n^\dagger|k\rangle\langle k|q_m|0\rangle}{E-E_0+E_k}\right], \qquad (6.50)\end{aligned}$$

where the appropriate identifications can be made between the RPA expression in the first line and the formal spectral representation in the second. This means that

$$\begin{aligned}\langle 0|q_m|k\rangle &= \lambda_m^{1/2}Z_{mk}, \\ \langle 0|q_n^\dagger|k\rangle &= \lambda_n^{1/2}Y_{nk}, \qquad (6.51)\end{aligned}$$

and, thus,

$$\begin{aligned}\langle k|q_n^\dagger|0\rangle &= \langle 0|q_n|k\rangle^* = Z_{nk}^*\lambda_n^{1/2}, \\ \langle k|q_n|0\rangle &= \langle 0|q_n^\dagger|k\rangle^* = Y_{nk}^*\lambda_n^{1/2}. \qquad (6.52)\end{aligned}$$

The transition energies $\omega_k = E_k - E_0$, *i.e.*, excitation energies out of the reference (ground) state, and their negatives, *i.e.*, de-excitation energies to the ground state, are simple poles of this propagator, and the residues are related to corresponding transition moments.

Consider a general one-electron operator

$$M = \sum_{r,s} M_{rs} a_r^\dagger a_s \tag{6.53}$$

and represent it in the Hartree-Fock basis of spin orbitals. Then

$$\langle 0|M|k\rangle = \sum_m \left\{ M_m \langle 0|q_m|k\rangle + M_m^* \langle 0|q_m^\dagger|k\rangle \right\}, \tag{6.54}$$

where $M_{rs}^* = M_{sr}$ and $q_m = a_r^\dagger a_s$, $q_m^\dagger = a_s^\dagger a_r$ for $\langle n_r\rangle > \langle n_s\rangle$. Remembering the matrices $\mathbf{Z} = \frac{1}{2}[\mathbf{D} + \mathbf{T}]$ and $\mathbf{Y} = \frac{1}{2}[\mathbf{D} - \mathbf{T}]$, one can now write

$$\langle 0|M|k\rangle = \sum_m \left\{ \Re\left\{M_m\right\} \lambda_m^{1/2} D_{mk} + i\Im\left\{M_m\right\} \lambda_m^{1/2} T_{mk} \right\}. \tag{6.55}$$

For real orbitals, the dipole length matrix elements $\langle 0|\vec{r}|k\rangle$ are real, while dipole velocity matrix elements $\langle 0|\vec{p}|k\rangle$ are purely imaginary. This means that

$$\langle 0|\vec{r}|k\rangle = \sum_m \vec{r}_m \lambda_m^{1/2} D_{mk}, \tag{6.56}$$

whereas

$$\langle 0|\vec{p}|k\rangle = \sum_m \vec{p}_m \lambda_m^{1/2} T_{mk}. \tag{6.57}$$

For exact eigenstates of the many-electron hamiltonian, it holds that

$$\begin{aligned} \langle 0|i\vec{p}|k\rangle &= \langle 0|[\vec{r}, H]_-|k\rangle \\ &= (E_k - E_0)\,\langle 0|\vec{r}|k\rangle \\ &= \omega_k \langle 0|\vec{r}|k\rangle, \end{aligned} \tag{6.58}$$

because

$$[\vec{r}, H]_- = [\vec{r}, \vec{p}^2/2]_- = [\vec{r}, \vec{p}]_- \vec{p} = i\vec{p}. \tag{6.59}$$

For the RPA, the relations

$$\begin{aligned} \langle 0|\vec{r}|k\rangle &= \sum_m \vec{r}_m \lambda_m^{1/2} D_{mk} \\ &= \sum_{m,n} \vec{r}_m \lambda_m^{1/2} (\bar{B}_{mn} - \bar{C}_{mn}) T_{nk}/\omega_k \qquad (6.60) \\ &= \sum_{m,n} \vec{r}_m \lambda_m^{1/2} \lambda_m^{-1/2} (B_{mn} + C_{mn}) \lambda_n^{-1/2} T_{nk}/\omega_k \end{aligned}$$

hold, where

$$\begin{aligned} \mathbf{U}\mathbf{x}^{-1/2}\mathbf{V}\omega^{1/2} &= \mathbf{D} = (\bar{\mathbf{B}} - \vec{\mathbf{C}})\mathbf{U}\mathbf{x}^{1/2}\mathbf{V}\omega^{-3/2} \\ &= (\bar{\mathbf{B}} - \vec{\mathbf{C}})\mathbf{T}\omega^{-1} \end{aligned} \tag{6.61}$$

has been used. Further simplifications can be made by using the definitions of the **B** and **C** matrices so that

$$\begin{aligned} \langle 0|\vec{r}|k\rangle &= \sum_{m,n} \vec{r}_m \langle [q_m + q_m^\dagger, [H, q_n^\dagger]_-]_-\rangle \lambda_n^{-1/2} T_{nk}/\omega_k \\ &= \sum_{n} \langle [\vec{r}, [H, q_n^\dagger]_-]_-\rangle \lambda_n^{-1/2} T_{nk}/\omega_k \\ &= \sum_{n} \langle [[\vec{r}, H]_-, q_n^\dagger]_-\rangle \lambda_n^{-1/2} T_{nk}/\omega_k \\ &= \sum_{n} \langle [i\vec{p}, q_n^\dagger]_-\rangle \lambda_n^{-1/2} T_{nk}/\omega_k \\ &= \sum_{m,n} i\vec{p}_m \langle [q_m, q_n^\dagger]_-\rangle \lambda_n^{-1/2} T_{nk}/\omega_k \\ &= \sum_{m} i\vec{p}_m \lambda_m^{1/2} T_{mk}/\omega_k = \langle 0|i\vec{p}|k\rangle/\omega_k. \end{aligned} \tag{6.62}$$

This means that the oscillator strengths of an absorption spectrum calculated within the RPA (in a complete orbital basis) will be identical in the dipole length form

$$f_{0k}^{L} = \frac{2}{3}|\langle 0|\vec{r}|k\rangle|^2 \omega_k \tag{6.63}$$

and in the dipole velocity form

$$f_{0k}^{V} = \frac{2}{3}|\langle 0|\vec{p}|k\rangle|^2/\omega_k. \tag{6.64}$$

6.5 Optical Rotatory Dispersion and Circular Dichroism

The first discovery of optical rotatory power in some materials, *i.e.*, that they have the property to rotate the plane of polarization of linearly polarized light, was made already in the early 1800's. From a macroscopic point of view, one can consider optical rotation as the difference of refraction of left and right circular polarized light[3]. Another effect, circular dichroism, first observed just before the year 1900 is that some materials transform linearly polarized light into elliptically polarized light, simply due to a difference of absorption for the left- and right-hand circularly polarized light. (Linearly polarized light can be

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[3] M. Born, *Optik*, Springer, Berlin, 1930

thought of as made up of two equally weighted components of left and right circularly polarized light.) The quantity that describes this property is called the ellipticity. It is related to optical rotatory power in the same way that ordinary dispersion is related to ordinary absorption. Recall that the absorption coefficient can be written as

$$a = -\left(\frac{4\pi}{kc^2V}\right)\Im\langle\langle j_\lambda(\vec{k}); j_\lambda^\dagger(\vec{k})\rangle\rangle_{kc}, \tag{6.65}$$

or spherically averaged,

$$\bar{a} = \left(\frac{4\pi}{3c^2V}\right)\Im\alpha(kc) \tag{6.66}$$

with

$$\alpha(kc) = -\sum_{a,b}|\langle a|\vec{R}|b\rangle|^2\rho_a\left[\frac{1}{kc - E_{ba} + i\eta} - \frac{1}{kc + E_{ba} - i\eta}\right]. \tag{6.67}$$

Theoretically, the phenomena of optical activity can be described with the tools already developed. A photon (wave packet) with wave vector $\vec{k}$ is scattered from polarization $\vec{n}_1(\vec{k})$ to $\vec{n}_2(\vec{k})$ (and the same energy) with probability amplitude

$$\langle b_2(\vec{k}, L/c)b_1^\dagger(\vec{k}, 0)\rangle = -\exp(-ikL)\left(\frac{2\pi iL}{kc^2V}\right)\langle\langle j_2(\vec{k}); j_1^\dagger(\vec{k})\rangle\rangle_{kc}, \tag{6.68}$$

obtained from Eq. (6.32).

For the case of minimal absorption the photon in the forward direction will have the polarization vector $\vec{n}_1(\vec{k}) - \vec{n}_2(\vec{k})\Phi L$, where

$$\Phi = (2\pi i/kc^2V)\langle\langle j_2(\vec{k}); j_1^\dagger(\vec{k})\rangle\rangle_{kc} \tag{6.69}$$

is the so-called *complex rotatory power.* The polarization direction of a beam of photons will be turned an angle $\Re\Phi$ (the rotatory power) radians per unit length of a medium with $1/V$ molecules per unit volume. Similarly $-\Im\Phi$ is the ellipticity per unit length under these conditions. A connection between the ellipticity and ordinary absorption can be established by observing that the averaged difference of absorption coefficient for left and right circularly polarized light equals the ellipticity. Light entering the eye of an observer is right circularly polarized if its polarization vector is turning in the clockwise direction.

In order to compare this result with the expressions commonly used in the theory of optical rotation[4], the long-wavelength limit is considered, *i.e.*, Eq. (6.45) is used to write

$$\begin{aligned} &\langle\langle j_2(\vec{k}); j_1^\dagger(\vec{k})\rangle\rangle_{kc} \\ &= \left(\frac{e}{m}\right)^2\langle\langle p_2 + ik(\frac{1}{2}l_1 - T_{2k}^{(2)}); p_1 + ik(\frac{1}{2}l_2 + T_{1k}^{(2)})\rangle\rangle_{kc}. \end{aligned} \tag{6.70}$$

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[4] E.U. Condon, *Rev. Modern Phys.* **9**, 432 (1937); Eyring, Walter, and Kimball, *Quantum Chemistry*, Wiley 1944, p. 342

The average over molecular orientations, or equivalently over photon propagation directions, appropriate for gaseous samples or liquid solutions, yields

$$\Phi = -(\pi k e^2/3m^2c^2V)\sum_{\nu}[\langle\langle l_\nu; p_\nu\rangle\rangle_{kc} + \langle\langle p_\nu; l_\nu\rangle\rangle_{kc}], \tag{6.71}$$

where one sums over Cartesian coordinates ν=x,y, and z.

As $kc\langle\langle R_\nu; l_\nu\rangle\rangle_{kc} = (ie/m)\,\langle\langle p_\nu; l_\nu\rangle\rangle_{kc}$ and the angular momentum $\vec{l}$ defines the magnetic dipole moment operator $\vec{M} = (e/2mc)\vec{l}$, it holds that

$$\Phi = (2\pi i k/3V)\sum_{\nu}\left[\langle\langle R_\nu; M_\nu\rangle\rangle_{kc} - \langle\langle M_\nu; R_\nu\rangle\rangle_{kc}\right]. \tag{6.72}$$

Comparing this expression with Eq. (4.17), one finds for the complex rotatory power

$$\begin{aligned}\Phi \;=\;& (8\pi k^2c^2/3cV)\Bigg\{\sum_a \rho_a \sum_b \Im\langle a|\vec{R}|b\rangle\langle b|\vec{M}|a\rangle/[E_{ba}^2 - (kc)^2] \\ &+ \frac{i\pi}{2kc}\sum_a \rho_a(\eta/\pi)\sum_b \Im\langle a|\vec{R}|b\rangle\langle b|\vec{M}|a\rangle \\ &\times\left[\frac{1}{(kc-E_{ba})^2+\eta^2} - \frac{1}{(kc+E_{ba})^2+\eta^2}\right]\Bigg\},\end{aligned} \tag{6.73}$$

where $R_{ab} = \Im\langle a|\vec{R}|b\rangle\langle b|\vec{M}|a\rangle$ is the so-called *rotatory strength.*

It holds that $\sum_b R_{ab} = 0$, *i.e.*, for each state $|a\rangle$, all the rotatory strengths cannot have the same sign. One can, from this, draw the conclusion that optical rotatory dispersion is a small effect in comparison with ordinary dispersion and ellipticity is a small effect in comparison with ordinary absorption. The fact that only electronic transitions give a significant contribution to optical activity and that vibrational or rotational transitions are significantly less important can be understood from the fact that the magnetic moments for nuclei are proportional to the inverse nuclear mass and, thus, several orders of magnitude less than the electronic magnetic moment. From Eq. (6.73) the inverse dependence on E_{ba}^2 follows, making transitions in the visible region much more important than transitions in the far ultraviolet.

Considering absorption involving one particular band involving electronic states a and b, it follows that

$$\frac{\Im\Phi}{\bar{a}} = \frac{R_{ab}}{|\langle a|\vec{R}|b\rangle|^2}, \tag{6.74}$$

showing that measurements of absorption $\bar{a}$ from Eq.(6.66) and ellipticity for a band permits the determination of rotatory strengths from line strengths.

Problems

1. Show that the polarization vectors $\vec{n}_r(\vec{k}) = \Re\big[\{\vec{n}_1(\vec{k}) + i\vec{n}_2(\vec{k})\}e^{i\Re\Phi_r}\big]$ and $\vec{n}_l(\vec{k}) = \Re\big[\{\vec{n}_1(\vec{k}) - i\vec{n}_2(\vec{k})\}e^{i\Re\Phi_l}\big]$ apply to right and left circularly polarized light, respectively.

2. Do the spherical averaging of Eq. (6.71) using the vector representation in spherical polar angles.
3. Consider the rotatory strength and show that fundamental symmetry requirements for a molecule to be optically active are that it possesses neither a center nor a plane of symmetry, and it cannot be superimposed on its mirror image.
4. Demonstrate that the $\Im\Phi$ can be obtained as the rotationally averaged difference of absorption coefficients for left and right circular polarized light.

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Chapter 7

Temperature-Dependent Perturbation Theory

Consider the partition function

$$Z(\beta) = \mathrm{Tr}\ \exp[-\beta(H - \mu N_0)] \tag{7.1}$$

with $\beta = 1/kT$, N_0 the number operator for electrons, and the hamiltonian $H = H_0 + V$ split into an unperturbed part H_0 and a perturbation V. The factorization

$$Z(\beta) = \mathrm{Tr}\{\exp[-\beta(H_0 - \mu N_0)]S(\beta)\} \tag{7.2}$$

is introduced, where the relation $S(\beta) = \exp[\beta(H_0 - \mu N_0)]\exp[-\beta(H - \mu N_0)]$ is used. Correspondingly, the unperturbed partition function

$$Z_0(\beta) = \mathrm{Tr}\exp[-\beta(H_0 - \mu N_0)] \tag{7.3}$$

is defined permitting the expression $Z(\beta) = Z_0(\beta)\langle S(\beta)\rangle_0$, where the average $\langle\cdots\rangle_0$ is formed with the density operator $\rho = Z_0^{-1}(\beta)\exp[-\beta(H_0 - \mu N_0)]$.

Since $S(0) = 1$, it follows that $S(\beta) = 1 + \int_0^\beta(\partial S(\tau)/\partial\tau)d\tau$. Explicit differentiation yields

$$\frac{\partial S(\tau)}{\partial\tau} = -\exp[\tau(H_0 - \mu N_0)]V\exp[-\tau(H_0 - \mu N_0)]S(\tau), \tag{7.4}$$

and the notation $V(\tau) = \exp[\tau(H_0 - \mu N_0)]V\exp[-\tau(H_0 - \mu N_0)]$ can be introduced to write

$$S(\beta) = 1 - \int_0^\beta V(\tau)S(\tau)d\tau. \tag{7.5}$$

One can then write a formal expansion of $\langle S(\beta)\rangle_0$ by iteration of Eq. (7.5):

$$\langle S(\beta)\rangle_0 = 1 + \sum_{n=1}^{\infty}(-1)^n\int_0^\beta d\tau_1\int_0^{\tau_1}d\tau_2\cdots\int_0^{\tau_{n-1}}d\tau_n\langle V(\tau_1)\cdots V(\tau_n)\rangle_0$$

$$= 1+\sum_{n=1}^{\infty}\frac{1}{n!}(-1)^n\int_0^\beta d\tau_1\int_0^\beta d\tau_2\cdots\int_0^\beta d\tau_n\langle T[V(\tau_1)\cdots V(\tau_n)]\rangle_0. \tag{7.6}$$

In the last expression, T means the "τ-ordering" operator which arranges the operators inside the brackets so that the arguments τ_i increase from right to left. If now $V=\lambda V_1+\lambda^2V_2$, one can write in some more detail that

$$\begin{aligned}\langle S(\beta)\rangle_0 &= \sum_{n=0}^{\infty}\sum_{m=0}^{\infty}(-1)^{n+m}\frac{\lambda^{n+2m}}{[n!m!]}\int_0^\beta d\tau_1\cdots\int_0^\beta d\tau_n\int_0^\beta d\tau_{n+1} \\ &\cdots\int_0^\beta d\tau_{n+m}\langle T[V_1(\tau_1)\cdots V_1(\tau_n)V_2(\tau_{n+1})\cdots V_2(\tau_{n+m})]\rangle_0.\end{aligned} \tag{7.7}$$

The free energy, and the unperturbed free energy are defined as $F=-\beta^{-1}$ $\ln Z(\beta)$ and $F_0=-\beta^{-1}\ln Z_0(\beta)$, respectively. This leads to the expression

$$\langle S(\beta)\rangle_0 = Z(\beta)/Z_0(\beta)=\exp[-\beta(F-F_0)]. \tag{7.8}$$

Through first order in V,

$$\langle S(\beta)\rangle_0 = 1-\beta\langle V\rangle_0 \tag{7.9}$$

which can be compared to the expansion of the exponential in Eq. (7.8),

$$\langle S(\beta)\rangle_0 = 1-\beta(F-F_0)+\cdots \tag{7.10}$$

to conclude that through first order in the perturbation V

$$F-F_0=\langle V\rangle_0=\lambda\langle V_1\rangle_0+\lambda^2\langle V_2\rangle_0. \tag{7.11}$$

Similarly, through second order in V

$$F-F_0=\langle V\rangle_0+\frac{\beta}{2}\langle V\rangle_0^2-\frac{1}{2\beta}\int_0^\beta d\tau_1\int_0^\beta d\tau_2\langle T[V(\tau_1)V(\tau_2)]\rangle_0. \tag{7.12}$$

Using Eq. (7.6), one gets, through second order in λ, that

$$F-F_0=\lambda\langle V_1\rangle_0+\lambda^2\left[\langle V_2\rangle_0+\frac{\beta}{2}\langle V_1\rangle_0^2+\frac{1}{2}\Re\langle\langle V_1;V_1\rangle\rangle_{E=0}\right], \tag{7.13}$$

where the result of problem 1 is used in the last term.

A magnetic field $\vec{B}=\vec{\nabla}\times\vec{A}(\vec{r})$ external to our electron system is an important type of perturbation that will result in a total hamiltonian of the form given in Eq. (6.25). The perturbation terms in orders of the vector potential can be identified as

$$\begin{aligned}V_1 &= -\int d\vec{r}\vec{A}(\vec{r})\cdot\vec{j}_0(\vec{r})-\int d\vec{r}\vec{B}(\vec{r})\vec{m}(\vec{r}), \\ V_2 &= (e/m)\int d\vec{r}|\vec{A}(\vec{r})|^2q(\vec{r}),\end{aligned} \tag{7.14}$$

where the gauge is chosen as $\vec{\nabla} \cdot \vec{A}(\vec{r}) = 0$, the charge density is $q(\vec{r}) = e\sum_{spin} \psi^\dagger(\xi)\psi(\xi)$, the electron momentum part of the current density is $\vec{j}_0(\vec{r}) = (e/2m)\sum_{spin}[(i\vec{\nabla}\psi^\dagger(\xi))\psi(\xi) - i\psi^\dagger(\xi)\vec{\nabla}\psi(\xi)] = \frac{e}{m}\vec{p}(\vec{r})$, with $\vec{p}(\vec{r})$ being the electron moment density, and the magnetic moment density is $\vec{m}(\vec{r})$, the electron part of which is $(e/2m)\sum_{spin} \psi^\dagger(\xi)\vec{\sigma}\psi(\xi)$.

The free energy for a nondegenerate ground state for $T = 0$ ($\beta = \infty$) and with the order parameter $\lambda = 1/c$ becomes

$$\begin{aligned} F - F_0 &= \frac{1}{2c^2}\left[2\langle V_2\rangle_0 + \Re\int d\vec{r}\int d\vec{r}'\vec{A}(\vec{r})\langle\langle\vec{j}_0(\vec{r});\vec{j}_0(\vec{r}')\rangle\rangle_{E=0}\vec{A}(\vec{r}')\right. \\ &\qquad \left. +\Re\int d\vec{r}\int d\vec{r}'\vec{B}(\vec{r})\langle\langle\vec{m}(\vec{r});\vec{m}(\vec{r})\rangle\rangle_{E=0}\vec{B}(\vec{r}')\right]. \end{aligned} \tag{7.15}$$

The mixed terms in $\langle\langle V_1; V_1\rangle\rangle_{E=0}$ vanish for this case, because $\vec{j}_0$ is a tensor of rank zero in spin space, while $\vec{m}$ is of rank one. Note that $\langle V_1\rangle_0 = 0$.

Problems

1. Show that $-\frac{1}{2\beta}\int_0^\beta d\tau_1\int_0^\beta d\tau_2\langle T[V_1(\tau_1)V_1(\tau_2)]\rangle_0 = \frac{1}{2}\Re\langle\langle V_1; V_1\rangle\rangle_{E=0}$.

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Chapter 8

Molecules in Magnetic Fields

Nuclear magnetic resonance (NMR) experiments subject a sample to a strong, static homogeneous magnetic field $\vec{B} = (0, 0, B)$ that splits the energy levels of degenerate nuclear spin states. Transitions between these "Zeeman levels" are induced with an oscillating field (*radio frequencies* around 10^{-4} cm^{-1}).

8.1 Nuclear Spins

An atomic nucleus with spin angular momentum $\vec{I}_s$ has magnetic moment $\gamma_s\vec{I}_s$, where $\gamma_s = g_s\beta_N$ is the gyromagnetic ratio, *i.e.*, the *g*-factor of the nucleus times the nuclear magneton ($\beta_N = \frac{|e|\hbar}{2m_p}$); note that the electron charge is e and the proton charge is -e in our notation. This magnetic moment contributes to the magnetic vector potential, as discussed in problem 8.1. The total vector potential then becomes

$$\vec{A}(\vec{r}) = \frac{1}{2}\vec{B} \times \vec{r} + \sum_s \gamma_s(\vec{I}_s \times \vec{r}_s)/r_s^3, \tag{8.1}$$

where $|\vec{r} - \vec{R}_s| = |\vec{r}_s| = r_s$. The total magnetic field is then not only the applied external field $\vec{B}$ but also contains contributions $\vec{\nabla} \times \vec{A}(\vec{r})$ from the nuclear magnetic moments, as shown in one of the problems.

The free energy can now be written in the form

$$F - F_0 = -\frac{1}{2}\vec{B}\underline{\chi}\vec{B} - \sum_s \gamma_s\vec{I}_s(1 - \underline{\sigma}_s)\vec{B} + \frac{1}{2}\sum_{g,h}\vec{I}_g\underline{J}_{gh}\vec{I}_h, \tag{8.2}$$

where $\underline{\chi}$ is the magnetic susceptibility tensor, $\underline{\sigma}_s$ is the magnetic shielding constant tensor for nucleus s, and $\underline{J}_{gh}$ is the nuclear spin-spin coupling (constant) tensor. The convention is used of introducing the $(1 - \underline{\sigma})$ factor to emphasize the shielding of the bare nuclei due to the electrons. One can now set out to study more closely the various contributions to these tensors.

Problems

1. Show that the vector potential from a constant magnetic moment $\vec{\mu}$ is $\vec{A}(\vec{r}) = \vec{\mu} \times \vec{r}/r^3 = \vec{\nabla} \times (\vec{\mu}/r)$.
2. Show that the magnetic field from a vector potential as the one in the previous problem with $\vec{mu} = \gamma_s \vec{I}_s$ is

$$\vec{\nabla} \times \vec{\nabla} \times \sum_s \frac{\gamma_s \vec{I}_s}{r_s} = (8\pi/3) \sum_s \gamma_s \vec{I}_s \delta(\vec{r}_s) + \sum_s \gamma_s \frac{[3(\vec{I}_s \cdot \vec{r}_s)\vec{r}_s - \vec{I}_s r_s^2]}{r_s^5}.$$

8.2 Magnetic Susceptibility

One contribution to the magnetic susceptibility obviously comes from the term $\frac{1}{2c^2} 2\langle V_2 \rangle_0$, which gives the contribution

$$-\frac{e}{4mc^2} \int (x^2 + y^2) \langle q(\vec{r}) \rangle_0 d\vec{r}, \tag{8.3}$$

to the susceptibility tensor, when $\vec{B} = (0, 0, B)$ and $\vec{A}(\vec{r}) = \frac{1}{2}\vec{B} \times \vec{r} = \frac{1}{2}(-By,$ $Bx, 0)$.

Other contributions to the magnetic susceptibility tensor come from the last two terms in Eq. (7.15). From the first of these comes

$$\begin{aligned} &\frac{1}{8c^2} \Re \int d\vec{r} \int d\vec{r}' (\vec{B} \times \vec{r}) \langle\langle \vec{j}_0(\vec{r}); \vec{j}_0(\vec{r}') \rangle\rangle_{E=0} (\vec{B} \times \vec{r}') \\ &= \frac{e^2 B^2}{8c^2 m^2} \Re \langle\langle l_z; l_z \rangle\rangle_{E=0}, \end{aligned} \tag{8.4}$$

which yields the contribution $-\Re\langle\langle \vec{M}; \vec{M} \rangle\rangle_{E=0}$ to the susceptibility, where the relation $\vec{M} = \frac{e}{2mc} \vec{l}$ for the magnetic moment due to electron orbital angular momentum is introduced .

There is no contribution from the last term in Eq. (7.15) for the electron magnetic moment $\frac{e}{m} \vec{s}$, in the case of a nondegenerate electron ground state (a spin singlet state). The nuclear spins will add a term $\sum_s \gamma_s \vec{I}_s$ so that for the general case there is a contribution to the magnetic susceptibility tensor

$$-\Re\langle\langle \vec{M}; \vec{M} \rangle\rangle_{E=0}, \tag{8.5}$$

with

$$\vec{M} = \frac{e}{2mc}(\vec{l} + 2\vec{s}) + \sum_s \gamma_s \vec{I}_s. \tag{8.6}$$

The representation of operators in incomplete basis sets will cause severe problems in maintaining gauge invariance in the calculation of magnetic susceptibilities. It is generally required to use field-dependent basis functions (see the section on magnetic properties) and to refrain from expansions in terms of the order parameter $1/c$ at intermediate steps in the development.

8.3 NMR-Spectra

The last two terms of the free energy in Eq. (8.2) are studied in NMR spectroscopy, and the one linear in the applied field involves the shielding constant tensor $\underline{\sigma}$, which arises from various terms in Eq. (7.15). The origin in shielding calculations is usually put at the nucleus in question (for a discussion of the origin dependence, see the section on magnetic properties).

The term $\langle V_2\rangle_0/c^2$ gives rise to the contribution

$$\begin{aligned} & 2(e/2mc^2)\int d\vec{r}\frac{1}{2}(\vec{B}\times\vec{r})\cdot\frac{\gamma_g\vec{I}_g\times\vec{r}_g}{r_g^3}\langle q(\vec{r})\rangle_0 \\ = \quad & (e\gamma_g/2mc^2)\vec{I}_g\int d\vec{r}\left[\frac{\vec{r}\cdot\vec{r}_g-\vec{r}\vec{r}_g}{r^3}\right]\langle q(\vec{r})\rangle_0\vec{B}, \end{aligned} \tag{8.7}$$

where the dyadic notation $\vec{r}\vec{r}_g$ is used in the tensor and the scalar product is assumed multiplied with the unit tensor. An isotropic sample yields 1/3 of the trace, *i.e.*,

$$\frac{1}{3}(e\gamma_g/2mc^2)\vec{B}\cdot\vec{I}_g\int d\vec{r}(2r^2/r^3)\langle q(\vec{r})\rangle_0. \tag{8.8}$$

Another contribution comes from the next to the last term in Eq. (7.15) and can be expressed as

$$\begin{aligned} & 2(1/2c^2)\Re\int\frac{1}{2}(\vec{B}\times\vec{r})\langle\langle\vec{j}_0(\vec{r});\vec{j}_0(\vec{r}')\rangle\rangle_{E=0}\left(\frac{\gamma\vec{I}\times\vec{r}'}{r'^3}\right)d\vec{r}d\vec{r}' \\ = \quad & -\gamma I_z B_z\frac{1}{c}\Re\int d\vec{r}\left[\langle\langle M_z;j_{0x}(\vec{r})\rangle\rangle_{E=0}\left(\frac{y}{r^3}\right)\right. \\ & \left. -\langle\langle M_z;j_{0y}(\vec{r})\rangle\rangle_{E=0}\left(\frac{x}{r^3}\right)\right]. \end{aligned} \tag{8.9}$$

When averaged over all molecular orientations and combined with the result from Eq. (8.8),

$$\begin{aligned} \sigma_g \quad = \quad & (e/3mc^2)\int d\vec{r}\langle q(\vec{r})\rangle_0/r \\ & -(1/3c)\Re\sum_{\lambda,\mu,\nu}\epsilon_{\lambda\mu\nu}\int d\vec{r}\langle\langle M_\lambda;j_{0\mu}(\vec{r})\rangle\rangle_{E=0}\left(\frac{r_\nu}{r^3}\right) \end{aligned} \tag{8.10}$$

where the notation $r_1 = x$, $r_2 = y$, $r_3 = z$, and the Levy-Cevita tensor $\epsilon_{\lambda\mu\nu}$, which assumes the value 1 for $\lambda\mu\nu$ an even permutation, -1 for $\lambda\mu\nu$ an odd permutation of 123, and 0 for any two of λ, μ, and ν being equal, are used.

8.3.1 Indirect Nuclear Spin-Spin Coupling Constants

The term $\frac{1}{2}\sum_{g,h}\vec{I}_g \underline{J}_{gh}\vec{I}_h$ in the free energy, which gives rise to the fine-structure in NMR spectra, is obtained from a variety of contributions. The term $\frac{1}{c^2}\langle V_2\rangle_0$ in Eq. (7.13) yields the contribution

$$(e/2mc^2)\gamma_g\gamma_h \int \left(\frac{\vec{I}_g \times \vec{r}_g}{r_g^3}\right) \cdot \left(\frac{\vec{I}_h \times \vec{r}_h}{r_h^3}\right) \langle q(\vec{r})\rangle_0 d\vec{r} \tag{8.11}$$

to be summed over g and h. A spherical average appropriate for, say, a liquid solution sample, yields

$$\vec{I}_g \cdot \vec{I}_h (e/3mc^2)\gamma_g\gamma_h \int \langle q(\vec{r})\rangle_0 \left[\frac{\vec{r}_g \cdot \vec{r}_h}{(r_g r_h)^3}\right] d\vec{r}. \tag{8.12}$$

Another contribution comes from the next to the last term in Eq. (7.15) when the nuclear moment part of the vector potential is used. After averaging over molecular orientations, the result is

$$\begin{aligned} &\vec{I}_g \cdot \vec{I}_h (1/6c^2)\gamma_g\gamma_h \\ &\times \Re \sum_{\lambda,\mu,\nu,\rho,\tau} \epsilon_{\lambda\mu\nu}\epsilon_{\lambda\rho\tau} \int d\vec{r}d\vec{r}^{\,'} r_{g\mu} \langle\langle j_{0\nu}(\vec{r}); j_{0\tau}(\vec{r}^{\,'})\rangle\rangle_{E=0} r_{h\rho}/(r_g r_h^{'})^3. \end{aligned} \tag{8.13}$$

The so-called orbital contributions to the nuclear spin-spin coupling constants are then

$$\begin{aligned} J^o_{gh} &= \gamma_g\gamma_h(1/3c^2)\Big[(2e/m)\int d\vec{r}\langle q(\vec{r})\rangle_0 \frac{\vec{r}_g \cdot \vec{r}_h}{(r_g r_h)^3} \\ &+ \Re \sum_{\lambda,\mu,\nu,\rho,\tau} \epsilon_{\lambda\mu\nu}\epsilon_{\lambda\rho\tau} \int d\vec{r}d\vec{r^{'}} r_{g\mu} \langle\langle j_{0\nu}(\vec{r}); j_{0\tau}(\vec{r^{'}})\rangle\rangle_{E=0} r^{'}_{h\rho}/(r_g r^{'}_h)^3\Big]. \end{aligned} \tag{8.14}$$

Note that this means that integrals over operators as l_z/r^3 are needed for the propagator in Eq. (8.14). The diagonal term J^o_{gg} appears to be infinite, a difficulty attributed to the assumption of point dipoles and to the nonrelativistic treatment of the electrons. These terms, however, do not influence the interpretation of the NMR experiments.

Next, the contributions from the last term in Eq. (7.15) are considered with the magnetic field due to the nuclear magnetic moments . When the unperturbed hamiltonian contains no magnetic fields $\langle\langle\vec{m}(\vec{r}); \vec{m}(\vec{r'})\rangle\rangle_{E=0}$ is proportional to the unit tensor. We write

$$\Re\langle\langle m_\nu(\vec{r}); m_{\nu'}(\vec{r'})\rangle\rangle_{E=0} = \delta_{\nu\nu'} U_0(\vec{r}, \vec{r'}). \tag{8.15}$$

The dipole term of the magnetic field then yields

$$\begin{aligned} &\gamma_g\gamma_h \int d\vec{r}\vec{r}^{\,'} \frac{3(\vec{I}_g \cdot \vec{r}_g)\vec{r}_g - \vec{I}_g r_g^2}{r_g^5} \\ &\times U_0(\vec{r}, \vec{r^{'}}) \frac{3(\vec{I}_h \cdot \vec{r^{'}_h})\vec{r^{'}_h} - \vec{I}_h r_h^{'2}}{r_h^{'5}}, \end{aligned} \tag{8.16}$$

which after averaging over molecular orientations gives the dipole contribution to the nuclear spin-spin coupling constants suitable for isotropic samples

$$\begin{aligned} J^d_{gh} &= (\gamma_g\gamma_h/c^2) \\ &\times \int d\vec{r}d\vec{r}^{\,\prime} U_0(\vec{r},\vec{r}^{\,\prime})[3(\vec{r}_g\cdot\vec{r}^{\,\prime}_h)^2-(r_g r^{\prime}_h)^2]/(r_g r^{\prime}_h)^5. \end{aligned} \tag{8.17}$$

This term is finite also for g and h equal [1].

There is also a delta function term in the expression for the magnetic field due to the nuclear spins. The cross terms between the delta function part and the dipolar part vanishes upon spherical averaging, and one is left with the delta function contribution to the nuclear spin-spin coupling constants. This term is called the Fermi contact contribution

$$J^c_{gh} = \gamma_g\gamma_h(8\pi/3c)^2 U_0(\vec{R}_g,\vec{R}_h), \tag{8.18}$$

and in total $J_{gh} = J^o_{gh} + J^d_{gh} + J^c_{gh}$. It has long been assumed that J^c_{gh} is the dominant contribution, and although this seems to be true for protons, recent quantum chemical calculations indicate that the orbital and dipolar terms can be just as important and even dominate for other magnetic nuclei.

Problems

1. Show that $\langle\langle m_\mu\vec{r}); m_\nu(\vec{r}^{\,\prime})\rangle\rangle_{E=0} = \delta_{\mu\nu}U_0(\vec{r}\vec{r}^{\,\prime})$ when the unperturbed hamiltonian contains no magnetic fields.

2. Calculate the NMR spectrum for two protons A and B (spin 1/2) in terms of their shielding constants σ_A and σ_B, the frequency ν=γB, where $\vec{B} = (0,0,B)$ is the applied field, and in terms of the coupling constant J.(See Section 8.12 for help.)

8.4 Magnetic Properties of Molecules

The magnetic moment operator for electrons is $\vec{M} = -\frac{\beta}{\hbar}(\vec{l}+g_e\vec{s})$ with the Bohr magneton and the electron g-value being $\beta = \frac{|e|\hbar}{2m}$, $g_e = 2.0023....$ Usually the electron g-value is put equal to 2. The deviation from that value is due to quantum electrodynamics effects and results in very minor corrections not significant at the level of treatment feasible for molecules.

8.5 Diamagnetic Molecules

Diamagnetic molecules mean singlet ground state molecules. The diamagnetic susceptibility of such molecules has a diamagnetic $\underline{\chi}^d$ and a paramagnetic $\underline{\chi}^p$

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[1] The $g = h$ term has been considered by P. Pyykköö and J. Linderberg in "On Nuclear Pseudoquadrupole Interactions in Lithium Fluoride and Lithium Bromide Molecules," *Chem. Phys. Lett.* **5**, 34 (1970) and is shown to yield a very small effect.

part. The diamagnetic part of the diamagnetic susceptibility tensor can be obtained from

$$\frac{e}{mc^2}\int d\vec{r}|\vec{A}(\vec{r})|^2\langle q(\vec{r})\rangle_0 \tag{8.19}$$

(see Chapter 7 on Temperature Dependent Perturbation Theory) with

$$\vec{A}(\vec{r}) = \frac{1}{2}\vec{B}\times\vec{r} \tag{8.20}$$

and $\vec{B}$ independent of $\vec{r}$. Using the identity

$$(\vec{B}\times\vec{r})\cdot(\vec{B}\times\vec{r}) = (\vec{B}\cdot\vec{B})(\vec{r}\cdot\vec{r}) - (\vec{B}\cdot\vec{r})(\vec{r}\cdot\vec{B}), \tag{8.21}$$

the diamagnetic susceptibility tensor becomes

$$\begin{aligned} \underline{\chi}^d &= -\frac{e}{4mc^2}\int d\vec{r}(\vec{r}\cdot\vec{r} - \vec{r}\,\vec{r})\langle q(\vec{r})\rangle_0 \\ &= -\frac{e^2}{4mc^2}\langle 0|\vec{r}\cdot\vec{r} - \vec{r}\,\vec{r}|0\rangle, \end{aligned} \tag{8.22}$$

where the dyadic notation $\vec{r}\,\vec{r}$ is used for a tensor and where in the second line the notation

$$\vec{r}\cdot\vec{r} - \vec{r}\,\vec{r} = \int d\xi\psi^\dagger(\xi)\psi(\xi)(\vec{r}\cdot\vec{r} - \vec{r}\,\vec{r}) \tag{8.23}$$

for the operator in second quantization is employed. The spherical average for an isotropic sample as a gas or liquid solution, as shown before, becomes

$$\frac{1}{3}\mathrm{Tr}\underline{\chi}^d = -\frac{e}{6mc^2}\int d\vec{r}r^2\langle q(\vec{r})\rangle_0 = -\frac{e^2}{6mc^2}\langle 0|r^2|0\rangle, \tag{8.24}$$

where in the last expression, the operator notation $r^2 = \int d\xi\psi^\dagger(\xi)r^2\psi(\xi)$ again is used.

The paramagnetic part of the magnetic susceptibility for a spin singlet ground state is, as shown before,

$$\underline{\chi}^p = -\Re\langle\langle\vec{M};\vec{M}\rangle\rangle_{E=0} = \frac{2e^2}{4m^2c^2}\sum_{n\neq 0}\frac{\langle 0|\vec{l}|n\rangle\langle n|\vec{l}|0\rangle}{E_n - E_0} \tag{8.25}$$

obtained from the definition of the propagator.

8.6 Units and Magnitude of Magnetic Susceptibilities

The dimensionality of the susceptibility is

$$[\chi] = \frac{[E]}{[B]^2}, \tag{8.26}$$

and in *cgs* units, the magnetic field (actually the magnetic flux density or induction) is measured in Gauss (1 Tesla=10^4 Gauss), which has the dimension (Gauss=$\mathrm{cm}^{-1/2}\ \mathrm{g}^{1/2}\ \mathrm{s}^{-1}$) and χ is obtained in cm^3. For a macroscopic sample that is given per mole, while for single molecule calculations, the relation

$$\chi/cm^3mol^{-1} = \frac{\chi}{N_A a_0(cm)^3}/a.u.\ molecule^{-1} \tag{8.27}$$

can be used, where N_A is Avogadro's number$= 6.0225 \times 10^{23}$ and a_0(cm) is the Bohr radius $= 0.529172 \times 10^{-8}$ cm. This works out such that $\chi/cm^3mol^{-1} = 11.206\chi/a.u.\ molecule^{-1}$. A typical unit used is in terms of parts per million (ppm=10^{-6}).

Table 8.1: Diamagnetic susceptibilities of molecules

Molecule	$\chi/ppm\ cm^3\ mol^{-1}$
CH_3CH_2OH	-33.60
meso-naphtodianthrone	-221.8
glucose	-102.60
NH_3	-18.0
C(graphite)	-6.0
He	-1.88

The applied magnetic field (induction) varies typically from 1-10 Tesla in NMR experiments. Sustained *B*-fields of 50 Tesla (1 T = 1 Wbm^{-2} = 10^4 Gauss)[2] are possible with special magnets [3]. At 32 Tesla the energy density (in SI units) is (μ_0 = vacuum permeability=$4\pi \times 10^{-7}$ N A^{-2})

$$\frac{B^2}{2\mu_0} = \frac{32^2}{8\pi \times 10^{-7}} Jm^{-3} = 4.074 \times 10^8 Jm^{-3}. \tag{8.28}$$

For NH_3 with

$$\begin{aligned} \chi &= -18.0\, ppm\ cm^3\ mol^{-1} \\ &= -18.0 \times 10^{-12}\ m^3\ mol^{-1} \end{aligned} \tag{8.29}$$

the energy becomes

$$\begin{aligned} F - F_0 &= 7.333 \times 10^{-3} J\ mol^{-1} \\ &= 1.218 \times 10^{-26} J\ molecule^{-1} \\ &= 6.1 \times 10^{-4}\ cm^{-1} \\ &= 18 MHz \end{aligned} \tag{8.30}$$

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[2] Note that a Weber is a Voltsecond.

[3] The High Magnetic Field Laboratory in Florida is constantly pushing the limit of higher fields.

i.e., a very small energy.

The diamagnetic contribution $\underline{\chi}^d$ is easy to calculate since it is only a ground state average. Experience shows that it is rather insensitive to electron correlation. The calculated values of $\langle r^2\rangle$ are given in Table 8.2 at the equilibrium geometry for a number of small molecules[4].

Table 8.2: Calculated values of $\langle r^2\rangle$ in a.u.

Molecule	SCF	MRSD-CI
H_2O	19.3968	19.6489
N_2	39.3968	38.9108
NH_3	26.5927	26.7063
HCl	34.1387	34.0287

The paramagnetic contribution $\underline{\chi}^p$ is more demanding to calculate and is a bit more sensitive to electron correlation, although not a great deal. For instance, for ammonia, the RPA (effectively uncorrelated) value is 38.45 ppm a.u., while the Second Order Polarization Propagator Approximation (correlated) yields 38.15 ppm a.u.

8.7 Paramagnetic Molecules

Neglecting the influence of nuclear spins the magnetic susceptibility is

$$\underline{\chi} = -\Re\langle\langle \vec{M}; \vec{M}\rangle\rangle_{E=0} \tag{8.31}$$

with $\vec{M} = \frac{e}{2mc}(\vec{l} + 2\vec{s})$. For the external magnetic field directed along the laboratory z-axis, consider first the diagonal zz-component of the susceptibility tensor. Details are provided only for the case when the splittings of the multiplet levels are considerably less than kT. Other cases follow by similar reasoning.

The propagator expression

$$\langle\langle l_z; l_z\rangle\rangle_{E=0} = \sum_{m,n} |\langle m|l_z|n\rangle|^2 \rho_m \left[\frac{\rho_n/\rho_m}{E_n - E_m} - \frac{1}{E_n - E_m}\right] \tag{8.32}$$

with $\rho_m = e^{\beta(F_0 - E_m + \mu N)}$ and $\beta = 1/kT$. As for $(E_n - E_m) << kT$, it follows that

$$\rho_n/\rho_m = e^{-\beta(E_n - E_m)} \approx 1 - \beta(E_n - E_m) \tag{8.33}$$

and

$$\begin{aligned}\langle\langle l_z; l_z\rangle\rangle_{E=0} &\approx -\beta\sum_{m,n} |\langle m|l_z|n\rangle|^2 \rho_n \\ &= -\langle l_z^2\rangle/kT. \end{aligned} \tag{8.34}$$

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[4] D. Feller, C. M. Boyle, and E. R. Davidson, *J. Chem. Phys.* **86**, 3424 (1987)

Similarly, it is straightforward to obtain

$$\langle\langle s_z; s_z\rangle\rangle_{E=0} = -\langle s_z^2\rangle/kT \tag{8.35}$$

and

$$\langle\langle l_z; s_z\rangle\rangle_{E=0} + \langle\langle s_z; l_z\rangle\rangle_{E=0} = -2\langle l_z s_z\rangle/kT, \tag{8.36}$$

which lead to the result

$$\begin{aligned} \underline{\chi}^p &= -\frac{e^2}{4m^2c^2}\Re\langle\langle l_z + 2s_z; l_z + 2s_z\rangle\rangle_{E=0} \\ &= \frac{e^2}{4m^2c^2}\langle l_z^2 + 4s_z^2 + 4l_z s_z\rangle/kT \\ &= \frac{e^2}{4m^2c^2}\langle (l_z + 2s_z)^2\rangle/kT. \end{aligned} \tag{8.37}$$

For an isotropic sample, the result

$$\chi = \frac{1}{3}(\chi_{zz} + \chi_{yy} + \chi_{xx}) = \frac{e^2}{12m^2c^2}\langle(\vec{l} + 2\vec{s})^2\rangle/kT \tag{8.38}$$

is valid, and should for some reason the orbital angular momentum contribution be negligible (for an orbital non-degenerate state it would be zero), the paramagnetic susceptibility would be

$$\chi = \frac{e^2}{3m^2c^2}\langle\vec{s}^2\rangle/kT = \frac{e^2\hbar^2}{3m^2c^2}S(S+1)/kT, \tag{8.39}$$

where in the last step, the existence of a dominant spin multiplet is assumed. This equation is sometimes referred to as the Langevin-Debye equation.

Examples of paramagnetic molecules in the gas phase are NO at T=293K with a $\chi = 1461$ ppm cm^3 mol^{-1}, NO_2 at $T = 408$K with $\chi = 150$ ppm cm^3 mol^{-1}, and O_2 at $T = 293$K with $\chi = 3449$ ppm cm^3 mol^{-1}.

It is noteworthy that the $1/T$ dependence of the paramagnetic susceptibility agrees with experiment.

8.8 NMR Spectra and Shielding

The spin $\vec{I}_h$ of a magnetic nucleus h gives rise to a (point) magnetic moment

$$\vec{\mu}_h = \frac{|e|}{2m_p}g_h\vec{I}_h = \gamma_h\vec{I}_h, \tag{8.40}$$

where m_p is the proton mass. The $|g_h|$ values range from 0 to 6 depending on the nucleus, and the spin of a magnetic nucleus ranges from 1/2 to 6 ($|\vec{I}(^{50}V)| = 6$) in units of $\hbar$. The nuclear spin and g-value for some common isotopes are given in Table 8.3.

Table 8.3: Nuclear spin and g-value for some common isotopes.

Isotope	I	g	Isotope	I	g
^{1}H	1/2	5.5854	^{29}Si	1/2	-1.1094
^{13}C	1/2	1.4042	^{14}N	1	0.4036
^{15}N	1/2	-0.5660	^{2}H	1	0.8574
^{19}F	1/2	5.2546	^{17}O	5/2	-0.7572
^{31}P	1/2	2.2610	^{10}B	3	0.6001

Consider first the interaction of a *bare* nucleus with an external magnetic field with induction $\vec{B} = (0 \quad 0 \quad B)$:

$$F - F_0 = -\vec{\mu} \cdot \vec{B} = -\gamma B I_z. \tag{8.41}$$

This spin hamiltonian causes a splitting of the $|I, M\rangle$ substates of an energy level (see Fig. 8.1).

The splitting between the energy levels is the same and proportional to B. Another (oscillating) field in the x-direction would induce transitions between the energy levels with selection rules $\Delta M = \pm 1$. In the example of a nucleus with spin 3/2, there are three possible transitions all with energy $h\nu = \gamma B$. One can see from this that for magnetically equivalent protons, one would expect a single line in the NMR spectrum with an intensity roughly proportional to the number of protons.

For a nucleus with spin 1/2, as a proton, there would only be two energy levels and one transition. Inserting the g-value for a proton, the frequency of the absorbed electromagnetic radiation is found to be

$$\nu_H(MHz) = 42.6 B(Tesla). \tag{8.42}$$

The magnitude of B is commonly described by the proton resonance frequency $\nu_H\,(MHz)$ it will cause. Thus, the magnetic flux in a 60 MHz NMR spectrometer is about 1.4 Tesla, while in a 600MHz spectrometer, it is about 14 Tesla.

Due to the presence of electrons, the magnetic field at the nucleus does not equal the applied external field for an atom or molecule, but the nucleus is said to be shielded by the electrons and this is normally expressed as

$$\vec{B}(\vec{R}) = (\underline{1} - \underline{\sigma})\vec{B}, \tag{8.43}$$

where $\underline{\sigma}$ is the shielding tensor, 1/3 the trace of which is called *the nuclear magnetic shielding.* The magnitude of σ (which is dimensionless) is of the order of ppm (10^{-6}) but can vary widely depending on the particular nucleus and its chemical environment.

It is not possible to measure the shielding directly in an NMR experiment, but rather the chemical shift $\delta = \sigma_{ref} - \sigma$, where σ_{ref} is the shielding of the nucleus in some reference compound.

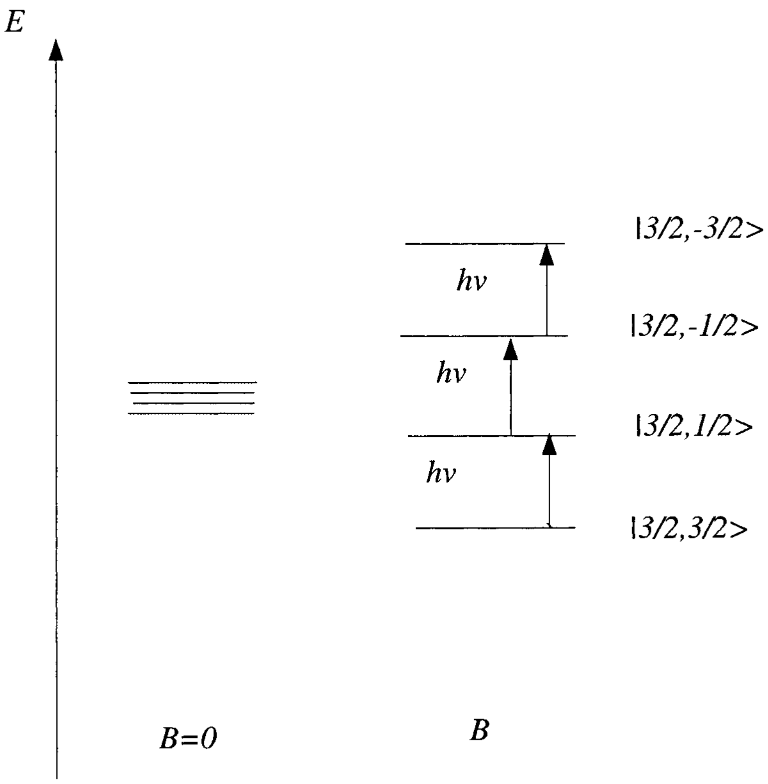

Figure 8.1: The energy levels ($h\nu = \gamma B$)of the spin hamiltonian in Eq.(8.41) for a nuclear state with spin $I = \frac{3}{2}$.

From Section 8.3, expressions for the various contributions to the shielding tensor can be discerned. In particular,

$$\begin{aligned}\underline{\sigma}_g^d &= \frac{e}{2mc^2}\int d\vec{r}[\vec{r}\cdot\vec{r}_g - \vec{r}\,\vec{r}_g]\langle q(\vec{r})\rangle_0/r_g^3 \\ &= \frac{e^2}{2mc^2}\langle 0|\frac{\vec{r}\cdot\vec{r}_g - \vec{r}\,\vec{r}_g}{r_g^3}|0\rangle \end{aligned} \tag{8.44}$$

is called the "diamagnetic" contribution and

$$\begin{aligned}\underline{\sigma}_g^p &= \frac{e^2}{2m^2c^2}\Re\langle\langle\vec{l};\vec{l}_g/r_g^3\rangle\rangle_{E=0} \\ &= \frac{e^2}{2m^2c^2}\sum_{n\neq 0}\frac{\langle 0|\vec{l}|n\rangle\langle n|\vec{l}_g/r_g^3|0\rangle + \langle 0|\vec{l}_g/r_g^3|n\rangle\langle n|\vec{l}|0\rangle}{E_0 - E_n}\end{aligned} \tag{8.45}$$

the "paramagnetic" contribution to the shielding tensor (see Eq. (8.10)). Here the notation

$$\vec{l}_g/r_g^3 = \int d\xi \psi^\dagger(\xi)[(\vec{r}_g \times \vec{p}(\vec{r}))/r_g^3]\psi(\xi) \tag{8.46}$$

is used. The similarities of the two contributions to the shielding tensor with those to the susceptibility tensor are quite striking and are part of the reason for labeling the two contributions to the shielding as diamagnetic and paramagnetic.

8.9 NMR Spectra and Spin-Spin Coupling

More detailed expressions for the indirect nuclear spin-spin coupling constants can be obtained from those already considered. For instance, the so-called diamagnetic orbital part is

$$\begin{aligned} \underline{J^{do}_{gh}} &= \frac{e\gamma_g\gamma_h}{mc^2}\int d\vec{r}\left[\frac{\vec{r}_g\cdot\vec{r}_h - \vec{r}_g\,\vec{r}_h}{r_g^3 r_h^3}\right]\langle q(\vec{r})\rangle_0 \\ &= \frac{e^2\gamma_g\gamma_h}{mc^2}\langle 0|\frac{\vec{r}_g\cdot\vec{r}_h - \vec{r}_g\,\vec{r}_h}{r_g^3 r_h^3}|0\rangle. \end{aligned} \tag{8.47}$$

In the second line, the notation

$$\frac{(\vec{r}_g\cdot\vec{r}_h - \vec{r}_g\,\vec{r}_h)}{r_g^3 r_h^3} = \int d\xi\psi^\dagger(\xi)\psi(\xi)\frac{(\vec{r}_g\cdot\vec{r}_h - \vec{r}_g\,\vec{r}_h)}{r_g^3 r_h^3} \tag{8.48}$$

is used for the operator in second quantization. This type of abbreviated notation is often used, and the reader has to be aware of the context in which an expression is used. Similarly, because

$$\begin{aligned} &\int d\vec{r}\int d\vec{r}'\,(\vec{I}_g\times\vec{r}_g)\cdot\langle\langle\vec{j}_0(\vec{r});\vec{j}_0(\vec{r}'\,)\rangle\rangle_E\cdot(\vec{I}_h\times\vec{r}_h') \\ &= \frac{e^2}{m^2}\int d\vec{r}\int d\vec{r}'\,\vec{I}_g\cdot\langle\langle\vec{l}_g(\vec{r});\vec{l}_h(\vec{r}'\,)\rangle\rangle_E\cdot\vec{I}_h \end{aligned} \tag{8.49}$$

with $\vec{l}_g(\vec{r}) = \vec{r}_g\times\vec{p}(\vec{r})$, it follows that

$$\begin{aligned} \underline{J^{po}_{gh}} &= \gamma_g\gamma_h\frac{e^2}{m^2c^2}\Re\int d\vec{r}\int d\vec{r}'\langle\langle\vec{l}_g(\vec{r})/r_g^3;\vec{l}_h(\vec{r}')/r_h'^3\rangle\rangle_{E=0} \\ &= \gamma_g\gamma_h\frac{e^2}{m^2c^2} \\ &\quad\times\sum_{n\neq 0}\frac{\langle 0|\vec{l}_g/r_g^3|n\rangle\langle n|\vec{l}_h/r_h'^3|0\rangle + \langle 0|\vec{l}_h/r_h'^3|n\rangle\langle n|\vec{l}_g/r_g^3|0\rangle}{E_0 - E_n} \end{aligned} \tag{8.50}$$

for the paramagnetic orbital part, with the notation $\vec{l}_g/r_g^3 = \int d\vec{r}\vec{l}_g(\vec{r})/r_g^3$.

The dipole contribution to the nuclear spin-spin coupling constants in Section 8.3 comes from the more general expression

$$\begin{aligned}
&\int d\vec{r} \int d\vec{r}^{\,\prime}\, \frac{3(\vec{I}_g \cdot \vec{r}_g)\vec{r}_g - \vec{I}_g r_g^2}{r_g^5} \langle\langle \vec{m}(\vec{r}); \vec{m}(\vec{r}^{\,\prime}) \rangle\rangle_E \frac{3(\vec{I}_h \cdot \vec{r}^{\,\prime}_h)\vec{r}^{\,\prime}_h - \vec{I}_h r_h^{\prime 2}}{r_h^{\prime 5}} \\
&= \vec{I}_g \int d\vec{r} \int d\vec{r}^{\,\prime} \qquad\qquad (8.51) \\
&\times \langle\langle 3(\vec{r}_g \cdot \vec{m}(\vec{r}))\frac{\vec{r}_g}{r_g^5} - \frac{\vec{m}(\vec{r})}{r_g^3}; 3(\vec{r}^{\,\prime}_h \cdot \vec{m}(\vec{r}^{\,\prime}))\frac{\vec{r}^{\,\prime}_h}{r_h^{\prime 5}} - \frac{\vec{m}(\vec{r}^{\,\prime})}{r_h^{\prime 3}} \rangle\rangle_E \vec{I}_h,
\end{aligned}$$

where the magnetic moment density is due only to the electron spin, *i.e.*, $\vec{m}(\vec{r}) = \frac{e}{2m} \sum_{spin} \psi^\dagger(\xi)\vec{\sigma}\xi(\chi) = \frac{e}{m}\vec{s}(\vec{r})$. Introducing the notation

$$\vec{S}_g = \int d\vec{r} \left[\frac{3(\vec{r}_g \cdot \vec{s}(\vec{r}))\vec{r}_g - \vec{s}(\vec{r}) r_g^2}{r_g^5} \right] \qquad (8.52)$$

one finds

$$\begin{aligned}
\underline{J}_{gh}^{sd} &= \gamma_g \gamma_h \frac{e^2}{m^2 c^2} && (8.53) \\
&\times \sum_{n=0} \frac{\langle 0|\vec{S}_g|n\rangle\langle n|\vec{S}_h|0\rangle + \langle 0|\vec{S}_h|n\rangle\langle n|\vec{S}_g|0\rangle}{E_0 - E_n} && (8.54)
\end{aligned}$$

for the spin dipole part of the nuclear spin-spin coupling tensor.

There are also the contributions from the delta function part of the field due to the nuclear spins, which give

$$\begin{aligned}
\underline{J}_{gh}^{fc} &= \gamma_g \gamma_h (8\pi e/3mc)^2 \\
&\times \sum_{n\neq 0} \frac{\langle 0|\vec{s}(\vec{R}_g)|n\rangle\langle n|\vec{s}(\vec{R}_h)|0\rangle + \langle 0|\vec{s}(\vec{R}_h)|n\rangle\langle n|\vec{s}(\vec{R}_g)|0\rangle}{E_0 - E_n}, \qquad (8.55)
\end{aligned}$$

the so-called Fermi contact term.

8.10 The Origin Problem

If the origin of the coordinate system, in which the molecular system particles are described, is changed so that the position of the new origin relative the old one is given by a vector $\vec{G}$, one can investigate the origin dependence of the magnetic susceptibility and the shielding tensors.

The electron coordinates change to $\vec{r}_G = \vec{r} - \vec{G}$, the nuclear coordinates to $\vec{R}_{gG} = \vec{R}_g - \vec{G}$, while the electron coordinates $\vec{r}_g$ relative a given nucleus remain the same. This means that the spin-spin coupling tensor is invariant to the change of origin.

From the equation of motion of a (excitation) propagator $\langle\langle A;B\rangle\rangle_E$, it follows that

$$\langle 0|[A,B]_-|0\rangle = \langle\langle [H,A]_-;B\rangle\rangle_{E=0} = \langle\langle A;[B,H]_-\rangle\rangle_{E=0}. \tag{8.56}$$

Consideration of the magnetic susceptibility tensor and the observation that the identity

$$[\vec{a}\times\vec{l},\vec{r}]_- = i\hbar(\vec{r}\cdot\vec{a} - \vec{r}\,\vec{a}) \tag{8.57}$$

holds[5], involving the orbital angular momentum operator, lead to the expression

$$\begin{aligned}\langle 0|\vec{r}\cdot\vec{r} - \vec{r}\,\vec{r}|0\rangle &= \frac{1}{i\hbar}\langle 0|[\vec{r}\times\vec{l},\vec{r}]_-|0\rangle \\ &= \frac{1}{i\hbar}\langle\langle \vec{r}\times\vec{l};[\vec{r},H]_-\rangle\rangle_{E=0}.\end{aligned} \tag{8.58}$$

Using the relation

$$\frac{i\hbar}{m}\vec{p} = [\vec{r},H]_-, \tag{8.59}$$

it follows that

$$\begin{aligned}\underline{\chi}^d &= -\frac{e^2}{4m^2c^2}\Re\langle\langle \vec{r}\times\vec{l};\vec{p}\rangle\rangle_{E=0} \\ \underline{\chi}^p &= -\frac{e^2}{4m^2c^2}\Re\langle\langle \vec{l};\vec{l}\rangle\rangle_{E=0}\end{aligned} \tag{8.60}$$

displaying a great deal of "symmetry"; *i.e.*, (as a mnemonic device) you get from one to the other by "moving" $\vec{r}\times$ from one operator to the other in the propagator expression.

Similarly, putting $\vec{a} = \vec{r}_g/r_g^3$ in Eq. (8.57), one gets (see Eqs.(8.44) and (8.45))

$$\begin{aligned}\underline{\sigma}^d &= \frac{e^2}{2m^2c^2}\Re\langle\langle \vec{r}_g\times\vec{l}/r_g^3;\vec{p}\rangle\rangle_{E=0}, \\ \underline{\sigma}^p &= \frac{e^2}{2m^2c^2}\Re\langle\langle \vec{l}_g/r_g^3;\vec{l}\rangle\rangle_{E=0}.\end{aligned} \tag{8.61}$$

The magnetic susceptibility tensor referred to the displaced origin can be expressed as

$$\begin{aligned}\underline{\chi}^d_G = \underline{\chi}^d &+ \frac{e^2}{4m^2c^2}\Big\{m\langle 0|\vec{r}\cdot\vec{G} - \vec{r}\,\vec{G}|0\rangle + m\langle 0|\vec{G}\cdot\vec{r} - \vec{G}\,\vec{r}|0\rangle \\ &- \langle\langle \vec{G}\times(\vec{G}\times\vec{p});\vec{p}\rangle\rangle_{E=0}\Big\},\end{aligned} \tag{8.62}$$

---

[5] We are here and in the following using the dyad notation, such as $\vec{r}\,\vec{a}$, for nine component tensors, with each component being a product of cartesian components of the vectors.

where taking the real part has temporarily been omitted. The analogous expression for the paramagnetic part becomes

$$\begin{aligned} \underline{\chi}^p_G = \; & \underline{\chi}^p \; + \frac{e^2}{4m^2c^2}\Big\{\langle\langle\vec{l};\vec{G}\times\vec{p}\rangle\rangle_{E=0} + \langle\langle\vec{G}\times\vec{p};\vec{l}\rangle\rangle_{E=0} \\ & - \; \langle\langle\vec{G}\times\vec{p};\vec{G}\times\vec{p}\rangle\rangle_{E=0}\Big\} . \end{aligned} \tag{8.63}$$

Taking the trace of these tensors and focusing first on the terms quadratic in origin displacement yields

$$\begin{aligned} \mathrm{Tr}\langle\langle\vec{G}\times(\vec{G}\times\vec{p});\vec{p}\rangle\rangle_{E=0} &= \mathrm{Tr}\langle\langle(\vec{G}\cdot\vec{p})\vec{G} - (\vec{G}\cdot\vec{G})\vec{p};\vec{p}\rangle\rangle_{E=0} \\ &= \langle\langle\vec{G}\cdot\vec{p};\vec{G}\cdot\vec{p}\rangle\rangle_{E=0} - (\vec{G}\cdot\vec{G})\mathrm{Tr}\langle\langle\vec{p};\vec{p}\rangle\rangle_{E=0} \end{aligned} \tag{8.64}$$

and

$$\mathrm{Tr}\langle\langle\vec{G}\times\vec{p};\vec{G}\times\vec{p}\rangle\rangle_{E=0} = (\vec{G}\cdot\vec{G})\mathrm{Tr}\langle\langle\vec{p};\vec{p}\rangle\rangle_{E=0} - \langle\langle\vec{G}\cdot\vec{p};\vec{G}\cdot\vec{p}\rangle\rangle_{E=0}, \tag{8.65}$$

where in the last equation the trace of the tensor $(\vec{G}\times\vec{p})\;(\vec{G}\times\vec{p})$ is expressed as $(\vec{G}\times\vec{p})\cdot(\vec{G}\times\vec{p})$ and the vector relation $(\vec{a}\times\vec{b})\cdot(\vec{c}\times\vec{d}) = (\vec{a}\cdot\vec{c})(\vec{b}\cdot\vec{d}) - (\vec{a}\cdot\vec{d})(\vec{b}\cdot\vec{c})$ then employed. It follows that the terms quadratic in origin displacement cancel in the expression for the total $\chi = \frac{1}{3}\mathrm{Tr}\left(\underline{\chi}^d + \underline{\chi}^p\right)$, which applies for the case of an isotropic sample.

It is possible to eliminate also the linear origin-dependence of the trace of the susceptibility tensor[6]. This is done by considering

$$\begin{aligned} \langle\langle\vec{l};\vec{G}\times\vec{p}\rangle\rangle_{E=0} &= \langle\langle\vec{G}\times\vec{p};\vec{l}\rangle\rangle_{E=0} \\ &= -m\langle 0|\vec{G}\cdot\vec{r} - \vec{G}\,\vec{r}|0\rangle, \end{aligned} \tag{8.66}$$

provided $(E_0 - E_n)\langle n|\vec{r}|0\rangle = \frac{i\hbar}{m}\langle n|\vec{p}|0\rangle$ (called the off-diagonal hypervirial relation), which holds true in an exact theory and in certain approximations as the RPA, when using a complete orbital basis. Thus, origin dependence can be somewhat controlled in this manner but never completely eliminated.

Analogous treatment of the shielding tensor yields origin independence also for that quantity for an isotropic sample.

The equation for the magnetic shielding constant corresponding to Eqs. (8.62) and (8.63) has an origin dependent term expressible as [see also Eqs. (8.44) and (8.45)]

$$\begin{aligned} \Delta\underline{\sigma}_g(\vec{r}\rightarrow\vec{r}_g) = \; & - \; \frac{e^2}{2m^2c^2}\langle\langle\vec{l}_g/r_g^3;\vec{G}\times\vec{p}\rangle\rangle_{E=0} \\ & - \; \frac{e^2}{2mc^2}\left(\vec{G}\cdot\langle 0|\frac{\vec{r}_g}{r_g^3}|0\rangle - \vec{G}\,\langle 0|\frac{\vec{r}_g}{r_g^3}|0\rangle\right) . \end{aligned} \tag{8.67}$$

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[6] see J. Geertsen, *J. Chem. Phys.* **90**, 4892 (1989)

Convention and convenience put the origin at the center of mass for susceptibility calculations, and at the particular nucleus for shielding constant calculations. The origin dependence is often large and unsettling. There are, however, methods that guarantee origin independence also for calculations in any finite basis. These are the techniques of using so-called field-dependent orbitals or gauge-independent atomic orbitals (GIAO).

8.11 The Gauge Problem

A transformation,

$$\begin{aligned} \vec{A}' &= \vec{A} + \vec{\nabla}\Lambda(\vec{r}, t) \\ \phi' &= \phi + \partial\Lambda(\vec{r}, t)/c\partial t \end{aligned} \tag{8.68}$$

of the vector and scalar potentials is called a gauge transformation. All measured and calculated quantities should be independent of such a transformation, in particular the magnetic and electric fields,

$$\begin{aligned} \vec{B} &= \vec{\nabla} \times \vec{A}, \\ \vec{E} &= -\vec{\nabla}\phi + \partial\vec{A}/c\partial t, \end{aligned} \tag{8.69}$$

remain invariant under such a transformation. (Remember that $\vec{\nabla} \times \vec{\nabla}\Lambda(\vec{r}, t) = 0$.) The corresponding transformation of the state vector (Schrödinger amplitude) must be $\Psi \rightarrow \Psi' = \Psi \exp\left(\frac{ie}{c\hbar}\Lambda\right)$ for the Schrödinger equation with the hamiltonian

$$H = \left(-i\hbar\vec{\nabla} - \frac{e}{c}\vec{A}\right)^2 /2m - e\vec{\sigma} \cdot (\vec{\nabla} \times \vec{A})/2mc - e\phi + V \tag{8.70}$$

to be gauge invariant.

When the origin of our coordinate system is translated by a vector $\vec{G}$, the vector potential of a constant external magnetic field transforms as $\vec{A}' = \frac{1}{2}\vec{B} \times \vec{r}_G = \vec{A} - \frac{1}{2}\vec{B} \times \vec{G}$. It follows that

$$\vec{\nabla}\Lambda = -\frac{1}{2}\vec{B} \times \vec{G} \quad \text{or} \quad \Lambda = -\frac{1}{2}(\vec{B} \times \vec{G}) \cdot \vec{r}, \tag{8.71}$$

which can be written as

$$\Lambda = \frac{1}{2}\vec{G} \cdot (\vec{B} \times \vec{r}) = \vec{G} \cdot \vec{A}. \tag{8.72}$$

Field-dependent basis orbitals as $v_j(\vec{r}, \vec{G}, \vec{B}) = u_j(\vec{r}) \exp(-\frac{ie}{2\hbar c}(\vec{B} \times \vec{G}) \cdot \vec{r})$ should be used, resulting in a similar transformation of the electron field operators. Such field-dependent orbitals would guarantee gauge origin independence even in a finite basis. In this expression, $\vec{G}$ is the position of orbital u_j with respect to an arbitrary origin and the electron coordinate $\vec{r}$ is given in the same coordinate system. Usually the atomic orbitals are centered at the nuclear positions. In such cases, $\vec{R}_g$ takes the place of $\vec{G}$ for the orbital $v_j(\vec{r}, \vec{R}_g, \vec{B})$[7].

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[7] see, e.g., F. London, *J. Phys. Radium* 8, 397 (1937), and R. Ditchfield, *Mol. Phys.* **27**,789 (1974)

8.11.1 Calculation of Magnetic Properties

The nuclear spin-spin coupling constants of $^1H^{19}F$ are given in Table 8.4 [8].

Table 8.4: The nuclear spin-spin coupling constants of $^1H^{19}F$ at equilibrium R = 1.7328 a.u.) in Hertz

Contrib.	RPA	HRPA	SOPPA	CCSDPPA	Exp.
fc	467.3	419.9	338.3	329.4	
sd	-12.4	-6.4	-1.0	-0.6	
po	119.3	164.9	195.7	195.7	
do	-0.1				
total	654.1	578.4	532.9	524.4	529±23

The nuclear spin-spin coupling constants of HD are given in Table 8.5 [9]

Table 8.5: The nuclear spin-spin coupling constants of HD in Hz at equilibrium $R = 1.40$ a.u.

Contrib.	CHF	HRPA	SOPPA	CCSDPPA	Exp.
fc	53.11	42.62	42.60	39.93	
sd	0.57	0.52	0.51	0.49	
po	0.83	0.82	0.83	0.82	
do	-0.33	-0.33	-0.33	-0.33	
total	54.18	43.63	43.61	40.91	42.94± 0.04

Even better agreement with experiment can be obtained by vibrational averaging.

The relative importance of the various contributions to the spin-spin coupling constants varies greatly from system to system, and it appears absolutely necessary to compute them all. In Table 8.6 the results for $^{13}C^{17}O$ at the equilibrium bond distance $R = 2.132$ a.u. are given, as well as vibrationally averaged results[10] in Hertz.

The difference between the HRPA and the SOPPA1 approximations is primarily the inclusion of the so-called 2particle-2hole correction in SOPPA1. It is generally observed that the Fermi contact (fc) contribution exhibits the strongest dependence on internuclear separation.

Nuclear magnetic shielding is hard to calculate, and results without employing field-dependent orbitals are somewhat unpredictable with any method. Table 8.7 shows results for the CO molecule with different methods:

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[8] see J. Geertsen, J. Oddershede, and G. E. Scuseria, *Int. J. Quantum Chem.* **S21**, 475 (1987)

[9] see J. Oddershede, J. Geertsen, and G. E. Scuseria, *J. Phys. Chem.* **92**, 3056 (1988)

[10] J. Geertsen, J. Oddershede, and G. E. Scuseria, *J. Chem. Phys.* **87**, 2138 (1987)

Table 8.6: Spin-spin coupling constants in Hz for $^{13}C^{17}O$ at the equilibrium bond distance $R = 2.132$ a.u.

Contrib.	RPA	HRPA	SOPPA1	SOPPA2	SOPPA vib. avg.	Exp
fc	-8.13	1.53	8.51	7.30	7.93	
sd	-9.26	-2.94	-3.82	-3.97	-3.99	
po	12.24	11.86	15.29	14.80	14.95	
do	0.1	0.1	0.1	0.1	0.1	
total	-5.05	10.55	20.08	18.23	18.99	16.4± 0.1

Table 8.7: Nuclear magnetic shielding for the CO molecule with a variety of methods as discussed in the text.

Method	σ_C/ppm	$\Delta\sigma_C$/ppm	σ_O/ppm	$\Delta\sigma_O$/ppm
RPA	-22.5	439.86	-84.79	743.42
LORG	-22.22	440.12	-84.94	743.64
SOPPA	-15.40	429.88	-73.45	726.40
SOLO	-13.31	413.44	-69.15	719.95
Mixed method	10.2	392.1	-5.8	624.4
Experiment	3.0± 0.9	405± 1.4	-40.1± 17.2	676.1± 26

The gauge origins are the nuclear positions (equilibrium bond distance $R = 2.132$ a.u.). The SOLO method is described by T. D. Bouman and Aa. E. Hansen[11]. LORG is just RPA using local gauge origins. The mixed method is described by S. I. Chan, M. R. Baker, and N. F. Ramsey[12]. A discussion of the experimental results and some calculations can be found in I. Paidarova, J. Komasa, and J. Oddershede[13]. Considerably better agreement with experiments are obtained in that paper for the HCN molecule. The gauge origin dependence of the magnetic shielding tensor is given in Eq. (8.67) and this term can be rotationally averaged to yield 1/3 the trace of the tensor, which are the numbers given in the table above.

The large gauge origin effects are rather unsettling, but what they ought to be can be estimated from experiments on spin rotation constants[14], the details of which are left out of this discussion.

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[11] T. D. Bouman and Aa. E. Hansen, *J. Chem. Phys.* **175**, 292 (1990)

[12] S. I. Chan, M. R. Baker, and N. F. Ramsey, *Phys. Rev.* **136**, 1224 (1964)

[13] I. Paidarova, J. Komasa, and J. Oddershede, *Mol. Phys.* **72**, 559 (1991)

[14] see *Molecular Structure and Dynamics* by W. H. Flygare, Prentice-Hall, Englewood Cliffs, NJ (1978)

8.12 An Elementary Example of NMR Spectra

Consider two spin one-half nuclei with spins $\vec{I}_A$ and $\vec{I}_B$ in an applied field $\vec{B} = (\,0 \quad 0 \quad B\,)$. The free energy expression

$$H_s = F - F_0 = -w(1-\sigma_A)I_{Az} - w(1-\sigma_B)I_{Bz} + J\vec{I}_A \cdot \vec{I}_B, \qquad (8.73)$$

which can now be viewed as an effective spin hamiltonian with the notation $w = \gamma B$. The spin quantum number for a proton is 1/2 in units of $\hbar$. The product basis for the two spins is

$$|\alpha\alpha\rangle,\ |\alpha\beta\rangle,\ |\beta\alpha\rangle,\ |\beta\beta\rangle \qquad (8.74)$$

such that, say, $I_{Az}|\alpha\beta\rangle = \frac{1}{2}|\alpha\beta\rangle$, while $I_{Bz}|\alpha\beta\rangle = -\frac{1}{2}|\alpha\beta\rangle$; *i.e.*, the first position refers to nucleus A and the second to nucleus B. Using the ladder operators, it follows that

$$\vec{I}_A \cdot \vec{I}_B = I_{Az}I_{Bz} + \frac{1}{2}\left(I_{A+}I_{B-} + I_{A-}I_{B+}\right), \qquad (8.75)$$

which readily yields the energy expressions

$$\begin{aligned}
\langle\alpha\alpha|H_s|\alpha\alpha\rangle &= -w + \frac{1}{2}w(\sigma_A + \sigma_B) + J/4 = E_1,\\
\langle\beta\beta|H_s|\beta\beta\rangle &= w - \frac{1}{2}w(\sigma_A + \sigma_B) + J/4 = E_4,\\
\langle\alpha\beta|H_s|\alpha\beta\rangle &= -\frac{1}{2}w(\sigma_B - \sigma_A) - J/4,\\
\langle\beta\alpha|H_s|\beta\alpha\rangle &= \frac{1}{2}w(\sigma_B - \sigma_A) - J/4,\\
\langle\alpha\beta|H_s|\beta\alpha\rangle &= J/2 = \langle\beta\alpha|H_s|\alpha\beta\rangle. \qquad (8.76)
\end{aligned}$$

Solving the 2×2 eigenvalue problem gives

$$\begin{aligned}
E_2 &= -J/4 - \frac{1}{2}\left[J^2 + w^2(\sigma_A - \sigma_B)^2\right]^{1/2} = -J/4 - Q,\\
E_3 &= -J/4 + \frac{1}{2}\left[J^2 + w^2(\sigma_A - \sigma_B)^2\right]^{1/2} = -J/4 + Q. \qquad (8.77)
\end{aligned}$$

In order to draw an energy level diagram, the assumptions $q = \frac{1}{2}w(\sigma_B - \sigma_A) > 0$ and $J > 0$ are used (the sign of J cannot be determined by NMR measurements), and the notation $b = \frac{1}{2}w(\sigma_A + \sigma_B)$ is introduced [see Fig. 8.2].

An oscillating field along the x-axis would induce transitions among these energy levels, the intensities of which would be proportional to $|\langle m|I_{Ax} + I_{Bx}|n\rangle|^2$. Since $I_{Ax} + I_{Bx} = \frac{1}{2}(I_{A+} + I_{A-} + I_{B+} + I_{B-})$, it means that the states $|m\rangle$ and $|n\rangle$ must differ by $+1$ or -1 in the eigenvalues of $I_{Az} + I_{Bz}$ for an allowed transition. This means that the following transitions are allowed $1 \rightarrow 2,\ 1 \rightarrow 3,\ 2 \rightarrow 4,\ 3 \rightarrow 4$. The eigenvectors are

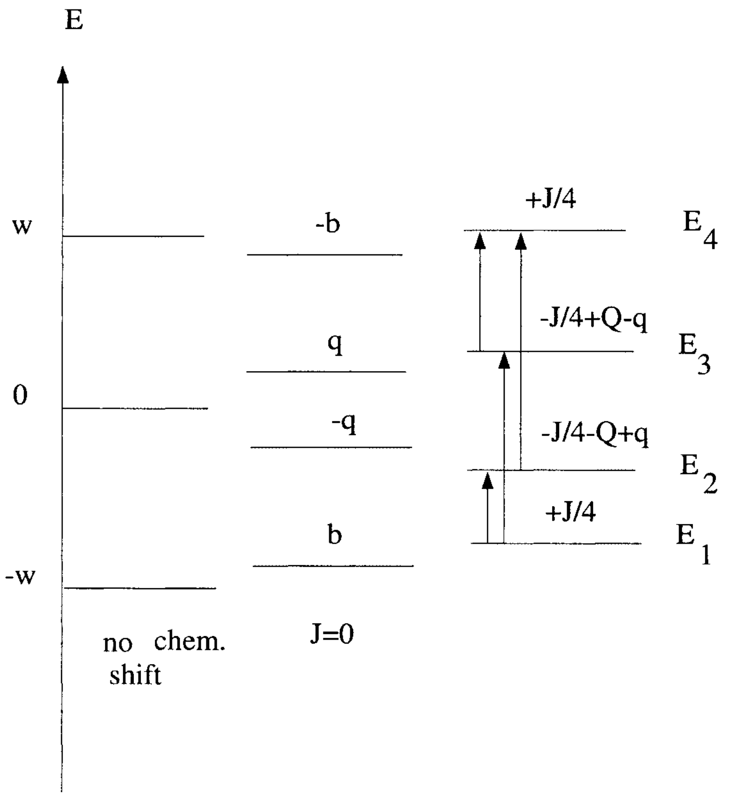

Figure 8.2: Energy levels of the hamiltonian in Eq.(8.73) with $\sigma_A = \sigma_B = 0, J = 0$, with $\sigma_B > \sigma_A \neq 0, J = 0$, and for $\sigma_B > \sigma_A \neq 0, J > 0$.

$$\begin{aligned} |1\rangle &= |\alpha\alpha\rangle, \\ |2\rangle &= |\alpha\beta\rangle \cos\theta - |\beta\alpha\rangle \sin\theta, \\ |3\rangle &= |\alpha\beta\rangle \sin\theta + |\beta\alpha\rangle \cos\theta, \\ |4\rangle &= |\beta\beta\rangle \end{aligned} \tag{8.78}$$

with

$$\tan(2\theta) = J/w(\sigma_B - \sigma_A) \tag{8.79}$$

i.e.,

$$\sin(2\theta) = J/[J^2 + w^2(\sigma_A - \sigma_B)^2]^{1/2}. \tag{8.80}$$

The following spectrum results with $a = w - \frac{1}{2}w(\sigma_A + \sigma_B) = w - b$.

Table 8.8: Transitions, frequencies, and relative intensities corresponding to the spectrum in Fig. 8.3

transition	frequency	relative intensity
$1 \to 2$	$a - J/2 - Q$	$1 - \sin(2\theta)$
$3 \to 4$	$a + J/2 - Q$	$1 + \sin(2\theta)$
$1 \to 3$	$a - J/2 + Q$	$1 + \sin(2\theta)$
$2 \to 4$	$a + J/2 + Q$	$1 - \sin(2\theta)$

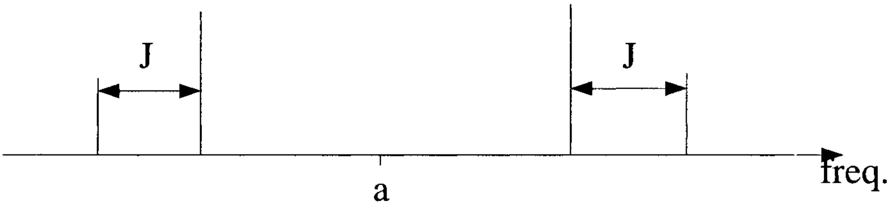

Figure 8.3: Spectrum resulting from the transitions depicted in Fig. 8.2.

1. When $J = 0$ ($\sin 2\theta = 0$), the four lines coalesce into two with equal intensity.
2. When J nonvanishing and $<< q$, there are four lines with almost equal intensity.
3. When σ_A approximately equal to σ_B($\sin 2\theta$ close to 1), the two outer lines will disappear.
4. When the two protons are magnetically equivalent (*i.e.*, $\sigma_A = \sigma_B = \sigma$ and $J_{Ag} = J_{Bg}$ for all nuclei with σ_g different from σ), then the spectrum degenerates to one line.

It is obvious from this example that only relative magnetic shielding for a nucleus is obtainable from an NMR spectrum. One therefore uses reference compounds in order to be able to make comparisons between different compounds for a given nucleus. The compound $(CH_3)_4Si$ (tetramethylsilane) is often used as the reference for proton shielding.

The case 2 above would be with the doublet at higher field corresponding to nucleus A ($\sigma_B > \sigma_A$). Thus, the presence of nucleus A causes the splitting of the B resonance into a doublet and vice versa (see Fig. 8.4). It should also be possible to see that spin-spin coupling between groups in a molecule can cause specific multiplet structures in the NMR spectrum. For instance, the CH_3 group in ethanol (CH_3CH_2OH) (see Fig. 8.5) has three magnetically equivalent protons, and would by itself result in a single line in the spectrum corresponding to a characteristic chemical shift δ_1, but the spin-spin coupling with the protons

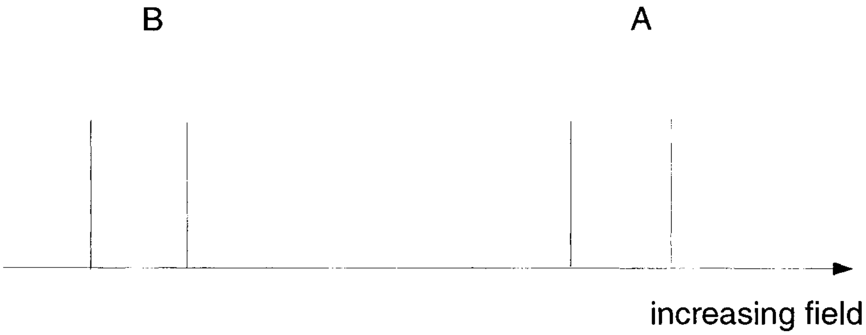

Figure 8.4: Illustration of how proton A causes the splitting of the proton B resonance into a doublet and vice versa.

of the CH_2 group (both having the same chemical shift δ_2) will cause a triplet splitting of the CH_3 line with intensity pattern 1:2:1 (because of the

$$\alpha\alpha,\ \begin{matrix}\alpha\beta\\ \beta\alpha\end{matrix},\beta\beta \tag{8.81}$$

spin distribution). Similarly the single resonance of the CH_2 group will be split into a quartet with intensity pattern 1:3:3:1 by the protons of the CH_3 group because of the spin distribution

$$\alpha\alpha\alpha,\ \begin{matrix}\alpha\alpha\beta\\ \alpha\beta\alpha\\ \beta\alpha\alpha\end{matrix},\ \begin{matrix}\alpha\beta\beta\\ \beta\alpha\beta\\ \beta\beta\alpha\end{matrix},\beta\beta\beta \tag{8.82}$$

and each line is split into a doublet to a small extent, due to the OH proton.

8.13 Paramagnetic Molecules

Consider a molecule with a ground state manifold of states (multiplet) with nonzero spin but orbitally nondegenerate. At sufficiently low temperatures this multiplet is dominating and the density operator

$$\rho = e^{-\beta(H_0-\mu N_0)}/\mathrm{Tr}\{e^{-\beta(H_0-\mu N_0)}\} \tag{8.83}$$

can be expressed as

$$\begin{aligned}\rho &= \sum_n |n\rangle\omega_n\langle n|/\sum_n \omega_n,\\ \omega_n &= \exp[-\beta(E_n-\mu N)]\end{aligned} \tag{8.84}$$

in terms of the unperturbed energy eigenstates. In our case, these states would be

$$|n\rangle = |n,S,M\rangle \tag{8.85}$$

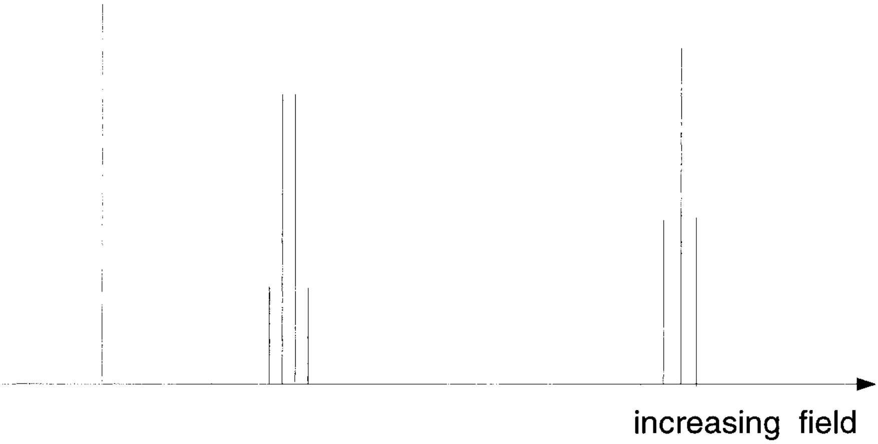

Figure 8.5: Schematic NMR spectrum of ethanol.

in general, with spin quantum numbers S and $M = -S, -S+1, \cdots, S$, while at low temperatures, only the ground state manifold would be involved; *i.e.*,

$$\begin{aligned} |n\rangle &= |0, S, M\rangle, \\ E_n &= E(0, S), \\ \rho &= (2S+1)^{-1} \sum_M |0, S, M\rangle\langle 0, S, M|. \end{aligned} \tag{8.86}$$

The expression for the free energy contains the average of the perturbation

$$V_1 = -\int d\vec{r} \vec{A}(\vec{r}) \cdot \vec{j}_0(\vec{r}) - \int d\vec{r} \vec{B}(\vec{r}) \cdot \vec{m}(\vec{r}). \tag{8.87}$$

The average of the first term over any electronic state is zero because of the electronic momentum operator being odd under inversion. The second term also vanishes, because

$$\begin{aligned} \langle V_1\rangle_o &= (2S+1)^{-1} \sum_M \langle 0, S, M|V_1|0, S, M\rangle \\ &= (2S+1)^{-1} \sum_M \frac{e}{m} \int d\vec{r} B_z(\vec{r}) \langle 0, S, M|s_z|0, S, M\rangle \\ &= 0. \end{aligned} \tag{8.88}$$

This means that the term

$$\frac{1}{2c^2} \Re\langle\langle V_1; V_1\rangle\rangle_{E=0} = \frac{1}{2c^2} \sum_{n,m} |\langle n|V_1|m\rangle|^2 \frac{\rho_n - \rho_m}{E_n - E_m} \tag{8.89}$$

$$= \frac{1}{2c^2} \sum_{M,m} |\langle 0,S,M|V_1|m\rangle|^2 \rho_{0MS} \frac{1-\rho_m/\rho_{0MS}}{E(0S)-E_m}$$

gives the lowest order nonvanishing contribution. The ratio

$$\rho_m/\rho_{0SM} = e^{\beta(E(0S)-E_m)} \approx 1 + \beta(E(0S)-E_m) \qquad (8.90)$$

has in the last step been approximated for the case that $1/\beta = kT >> (E(0S) - E_m)$. This means that

$$\frac{1}{2c^2}\Re\langle\langle V_1; V_1\rangle\rangle_{E=0} = -\frac{\beta}{2c^2}(2S+1)^{-1}\sum_M \langle 0,S,M|V_1^2|0,S,M\rangle. \qquad (8.91)$$

After averaging over molecular orientations, the contribution

$$\chi = \frac{e^2\hbar^2}{3m^2c^2} S(S+1)/kT \qquad (8.92)$$

to the magnetic susceptibility remains.

Contributions to the average $\langle V_1\rangle_0$ could arise from the magnetic field terms coming from the nuclear spins. The aim here is to obtain a spin hamiltonian acting on both nuclear and electronic spin states so one would in general be interested in the terms obtained before summing over electronic spin coordinates to obtain a spin hamiltonian

$$F - F_0 = \vec{I}_g \underline{A} \vec{s} \qquad (8.93)$$

for each nucleus. For the ground state manifold, we would thus be interested in matrix elements

$$\frac{1}{c}\langle 0,S,M|V_1|0,S,M'\rangle. \qquad (8.94)$$

There are two contributions for each nucleus (i) the contact field

$$\vec{B}(\vec{r}) = \frac{8\pi}{3}\gamma_g \vec{I}_g \delta(\vec{r}-\vec{R}_g) \qquad (8.95)$$

and (ii) the dipole field

$$\vec{B}(\vec{r}) = \frac{\gamma_g}{r_g^5}\left[3(\vec{I}_g\cdot\vec{r}_g)\vec{r}_g - \vec{I}_g r_g^2\right]. \qquad (8.96)$$

The dipole field contribution vanishes upon spherical averaging.

The contact field yields the contribution

$$\begin{aligned} -\frac{8\pi}{3c}\gamma_g \vec{I}_g \quad &\cdot \quad \int d\vec{r}\delta(\vec{r}-\vec{R}_g)\langle 0,S,M|\vec{m}(\vec{r})|0,S,M'\rangle \\ &= \langle 0,S,M|\vec{I}_g\cdot\vec{s}|0,S,M'\rangle \\ &\times \left[-\frac{8\pi\gamma_g}{3c}\frac{\langle 0,S||\vec{m}(\vec{R}_g)||0,S\rangle}{\langle 0,S||\vec{s}||0,S\rangle}\right]. \end{aligned} \qquad (8.97)$$

This is so since for tensor operators, it holds that

$$\begin{aligned}&\langle 0,S,M|\vec{I}\cdot\vec{s}|0,S,M\rangle\\ &=\sum_q(-1)^{S-M}I_q\langle 0,S||\vec{s}||0,S\rangle\begin{pmatrix} S & 1 & S\\ -M & -q & M' \end{pmatrix}\end{aligned} \tag{8.98}$$

and a similar expression for $\langle 0,S,M|\vec{I}\cdot\vec{m}(\vec{R}_g)|0,S,M'\rangle$. The properties of the $3j$ symbols means that the right-hand side reduces to one term, *i.e.*, the one for $q=M'-M$.

The expression in the square brackets in Eq.(8.97) is the isotropic part a_g of the $\underline{A}$ tensor used in the interpretation of paramagnetic resonance experiments. This means that

$$a_g=-\frac{8\pi\gamma_g e}{3cm}\langle q(\vec{R}_g)\rangle_o, \tag{8.99}$$

which shows that only orbitals with nonzero amplitude at the nucleus will contribute.

Problems

1. Use the properties of tensor operators to show that

$$a_g=-\left[\frac{8\pi\gamma_g}{3cS(S+1)}\langle\vec{s}\cdot\vec{m}(\vec{R}_g)\rangle_o\right]. \tag{8.100}$$

Notes and Bibliography

- The classic reference on electric and magnetic properties of atoms and molecules is the monograph by J. H. van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, Cambridge, 1932.
- A Carrington and A. D. McLachlan have in their book, *Introduction to Magnetic Resonance*, Harper and Row, 1967, an excellent survey of the relevant parameters.
- The comprehensive volume *Nuclear Moments*, J. Wiley & Sons, New York, 1953, by N. F. Ramsey, thoroughly analyzes the phenomena associated with nuclear spins.
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Chapter 9

The Electron Propagator in Higher Orders

Improved descriptions of single-electron processes require treatments beyond the geometric approximation given by the Hartree-Fock electron propagator in Eq. (4.25). More elaborate approximations of the equation of motion (9.1)

$$E\langle\langle a_s; a_r^\dagger\rangle\rangle_E = \langle[a_s, a_r^\dagger]_+\rangle + \langle\langle a_s; [H, a_r^\dagger]_-\rangle\rangle_E \tag{9.1}$$

may be generated in various ways. The discussion here will be confined to the use of perturbation theory.

Such a treatment can, with advantage, be expressed in terms of the superoperators introduced in Eq. (4.19) and in terms of a basis of field operators. The basis of fermion-like operators $\{X_i\} = \{\tilde{a}_k^\dagger, \tilde{a}_k^\dagger\tilde{a}_l^\dagger\tilde{a}_m, \tilde{a}_k^\dagger\tilde{a}_l^\dagger\tilde{a}_m^\dagger\tilde{a}_n\tilde{a}_p, \cdots\}$ is chosen, such that the electron field operators correspond to the SCF spin orbitals. The field operator space supports a scalar product $(X_i|X_j) = \langle[X_i^\dagger, X_j]_+\rangle = \mathrm{Tr}\{\rho[X_i^\dagger, X_j]_+\}$, where ρ is the density operator defined in Eq. (4.33). The superoperator identity and the superoperator hamiltonian operate on this space of fermion-like field operators and, in particular, $(X_i|\hat{H}X_j) = \langle[X_i^\dagger, [H, X_j]_-]_+\rangle = \mathrm{Tr}\{\rho[X_i^\dagger, [H, X_j]_-]_+\}$.

Perturbation theory starts with a partitioning of the hamiltonian, and thus of the superoperator hamiltonian, into an unperturbed part and a perturbation:

$$\hat{H} = \hat{H}_0 + \hat{V}, \tag{9.2}$$

such that $\hat{H}_0 X = [H_0, X]_-$ and $\hat{V}X = [V, X]_-$, with X being a fermion-like operator and

$$\begin{aligned} H_0 &= \sum_r \epsilon_r \tilde{a}_r^\dagger \tilde{a}_r, \\ V &= \sum_{r,r',s,s'} \langle rr'||ss'\rangle \left[\frac{1}{4}\tilde{a}_r^\dagger\tilde{a}_{r'}^\dagger\tilde{a}_{s'}\tilde{a}_s - \delta_{r's'}\langle n_{r'}\rangle\tilde{a}_r^\dagger\tilde{a}_s\right]. \end{aligned} \tag{9.3}$$

This expression in terms of the SCF spin orbital basis is readily obtained from Eqs. (4.3), (4.4), and (4.24).

The field operator space can be partitioned by the projection operator

$$\hat{O} = \sum_k |\tilde{a}_k^\dagger)(\tilde{a}_k^\dagger| = |\tilde{\mathrm{a}}^\dagger)(\tilde{\mathrm{a}}^\dagger| \tag{9.4}$$

and its complement

$$\hat{P} = \hat{I} - \hat{O}. \tag{9.5}$$

Consider the superoperator resolvent $(E\hat{I} - \vec{H})^{-1}$ and its outer projection

$$\hat{G}(E) = \hat{O}(E\hat{I} - \hat{H})^{-1}\hat{O} \tag{9.6}$$

onto the model subspace of single-electron field operators and note that the electron propagator matrix of Eq. (4.25) can be expressed as

$$\mathbf{G}(E) = (\hat{\mathrm{a}}^\dagger|\hat{G}(E)\hat{\mathrm{a}}^\dagger). \tag{9.7}$$

Implementing the perturbation theory, one obtains

$$\begin{aligned} \hat{G}(E) &= \hat{O}(E\hat{I} - \hat{H}_0 - \hat{V})^{-1}\hat{O} \qquad (9.8) \\ &= \hat{G}_0(E) + \hat{G}_0(E)\hat{V}\hat{G}_0(E) + \hat{G}_0(E)\hat{V}[\hat{G}_0(E) + \hat{T}_0(E)]\hat{V}\hat{G}_0(E) \\ &\quad + \hat{G}_0(E)\hat{V}[\hat{G}_0(E) + \hat{T}_0(E)]\hat{V}[\hat{G}_0(E) + \hat{T}_0(E)]\hat{V}\hat{G}_0(E) + \cdots, \end{aligned}$$

where the identity $(A - B)^{-1} = A^{-1} + A^{-1}B(A - B)^{-1}$ has been iterated with $A = E\hat{I} - \hat{H}_0$ and $B = \hat{V}$. Also, the relations $[\hat{O}, \hat{H}_0]_- = 0$ and $\hat{O}^2 = \hat{O}$ and the notations

$$\begin{aligned} (E\hat{I} - \hat{H}_0)^{-1} &= (E\hat{I} - \hat{H}_0)^{-1}\hat{O} + (E\hat{I} - \hat{H}_0)^{-1}\hat{P} \\ &= \hat{G}_0(E) + \hat{T}_0(E) \qquad (9.9) \end{aligned}$$

are used. The perturbation expansion can be rearranged such that

$$\begin{aligned} \hat{G}(E) &= \hat{G}_0(E) + \hat{G}_0(E)[\hat{V} + \hat{V}\hat{T}_0(E)\hat{V} \\ &+ \hat{V}\hat{T}_0(E)\hat{V}\hat{T}_0(E)\hat{V} + \cdots]\hat{G}(E), \qquad (9.10) \end{aligned}$$

which can be easily checked order by order. The quantity in the square brackets is referred to as the self-energy or mass (super)operator $\hat{\Sigma}$, and

$$\hat{G}(E) = \hat{G}_0(E) + \hat{G}_0(E)\hat{\Sigma}(E)\hat{G}(E), \tag{9.11}$$

which is the so-called Dyson-like equation or just the Dyson equation after the analogous equation in quantum electrodynamics.

The quantities $\hat{G}(E)$, $\hat{G}_0(E)$, $\hat{\Sigma}(E)$, and $\hat{T}_0(E)$ are functions of the superoperators $\hat{I}$, $\hat{H}_0$, and $\hat{V}$. When such superoperator functions operate on the field operator space, they must first be expanded in terms of the superoperators, which are then successively applied. For example, $\hat{T}_0(E)\hat{V}X = [\hat{I}E^{-1} + E^{-2}\hat{H}_0 + E^{-3}\hat{H}_0^2 + \cdots]\hat{P}\hat{V}X$.

The propagator matrix can be formed as

$$\begin{aligned} \mathbf{G}(E) &= (\tilde{\mathbf{a}}^\dagger|\hat{G}(E)\tilde{\mathbf{a}}^\dagger) = (\tilde{\mathbf{a}}^\dagger|\hat{G}_0(E)\tilde{\mathbf{a}}^\dagger) \\ &\quad +(\tilde{\mathbf{a}}^\dagger|\hat{G}_0(E)\tilde{\mathbf{a}}^\dagger)(\tilde{\mathbf{a}}^\dagger|\hat{\Sigma}(E)\tilde{\mathbf{a}}^\dagger)(\tilde{\mathbf{a}}^\dagger|\hat{G}(E)\tilde{\mathbf{a}}^\dagger) \\ &= \mathbf{G}_0(E) + \mathbf{G}_0(E)\mathbf{\Sigma}(E)\mathbf{G}(E). \end{aligned} \tag{9.12}$$

Solving for the electron propagator matrix, one obtains

$$\mathbf{G}(E) = [\mathbf{G}_0^{-1}(E) - \mathbf{\Sigma}(E)]^{-1}. \tag{9.13}$$

Various approximations of $\mathbf{G}$ are defined by their different forms of self-energy Σ, since $\mathbf{G}_0$ is given by the choice of partitioning. Because

$$\hat{H}_0\tilde{a}_j^\dagger = [H_0, \tilde{a}_j^\dagger]_- = \sum_k \epsilon_k[\tilde{a}_k^\dagger\tilde{a}_k, \tilde{a}_j^\dagger]_- = \epsilon_j\tilde{a}_j^\dagger, \tag{9.14}$$

i.e., the simple electron field operators are eigenelements of the unperturbed hamiltonian, and since

$$(\tilde{a}_i^\dagger|\tilde{a}_j^\dagger) = \mathrm{Tr}\left\{\rho[\tilde{a}_i, \tilde{a}_j^\dagger]_+\right\} = \delta_{ij}, \tag{9.15}$$

it holds that

$$G_0(E)_{ij} = (\tilde{a}_i^\dagger|(\hat{I}E - \hat{H}_0)^{-1}\tilde{a}_j^\dagger) = \delta_{ij}(E - \epsilon_i)^{-1}. \tag{9.16}$$

The evaluation of each term in the expansion of the self-energy requires consideration of

$$\begin{aligned} \hat{V}\tilde{a}_j^\dagger = [V, \tilde{a}_j^\dagger]_- &= \frac{1}{4}\sum_{r,r',s,s'} \langle rr'||ss'\rangle[\tilde{a}_r^\dagger\tilde{a}_{r'}^\dagger\tilde{a}_{s'}\tilde{a}_s, \tilde{a}_j^\dagger]_- \\ &\quad - \sum_{r,s,s'} \langle rs'||ss'\rangle\langle n_{s'}\rangle[\tilde{a}_r^\dagger\tilde{a}_s, \tilde{a}_j^\dagger]_- \\ &= \frac{1}{2}\sum_{r,r',s'} \langle rr'||js'\rangle\tilde{a}_r^\dagger\tilde{a}_{r'}^\dagger\tilde{a}_{s'} \\ &\quad - \sum_{r,s'}\langle rs'||js'\rangle\langle n_{s'}\rangle\tilde{a}_r^\dagger. \end{aligned} \tag{9.17}$$

The first-order contribution to the self-energy now becomes

$$\begin{aligned} (\tilde{a}_i^\dagger|\hat{V}\tilde{a}_j^\dagger) &= \frac{1}{2}\sum_{r,r',s'} \langle rr'||js'\rangle\mathrm{Tr}\left\{\rho[\tilde{a}_i, \tilde{a}_r^\dagger\tilde{a}_{r'}^\dagger\tilde{a}_{s'}]_+\right\} \\ &\quad - \sum_{r,s'}\langle rs'||js'\rangle\langle n_{s'}\rangle\mathrm{Tr}\left\{\rho[\tilde{a}_i, \tilde{a}_r^\dagger]_+\right\} \\ &= \sum_{r',s'}\langle ir'||js'\rangle\langle n_{s'}\rangle\delta_{r's'} - \sum_{s'}\langle is'||js'\rangle\langle n_{s'}\rangle = 0, \end{aligned} \tag{9.18}$$

where the result $\mathrm{Tr}\left\{\rho\tilde{a}_r^\dagger\tilde{a}_s\right\} = \delta_{r's'}\langle n_{s'}\rangle$ is used.

The second-order contribution to the self-energy is the lowest order nonvanishing correction to the electron binding energies as given by the orbital energies in the geometric approximation. In order to evaluate this correction term,

$$\hat{T}_0(E)\hat{V}\tilde{a}_j^\dagger = \left(\hat{I}E - \hat{H}_0\right)^{-1}\hat{P}\hat{V}\tilde{a}_j^\dagger = \left(\hat{I}E - \hat{H}_0\right)^{-1}\hat{V}\tilde{a}_j^\dagger \tag{9.19}$$

is considered, where the last term arises because $\hat{P} = \hat{I} - \hat{O}$ and $\hat{O}\hat{V}\tilde{a}_j^\dagger = \sum_k |\tilde{a}_k^\dagger)(\tilde{a}_k^\dagger|\hat{V}\tilde{a}_j^\dagger) = 0$, as shown above. Also, the result

$$\hat{H}_0\tilde{a}_r^\dagger\tilde{a}_{r'}^\dagger\tilde{a}_{s'} = [\hat{H}_0, \tilde{a}_r^\dagger\tilde{a}_{r'}^\dagger\tilde{a}_{s'}]_- = (\epsilon_r + \epsilon_{r'} - \epsilon_{s'})\,\tilde{a}_r^\dagger\tilde{a}_{r'}^\dagger\tilde{a}_{s'} \tag{9.20}$$

is needed such that

$$\begin{aligned}\left(\hat{I}E - \hat{H}_0\right)^{-1}\hat{V}\tilde{a}_j^\dagger &= \left(\hat{I}E - \hat{H}_0\right)^{-1}[V, \tilde{a}_j^\dagger]_- \\ &= \frac{1}{2}\sum_{r,r',s'}\langle rr'||js'\rangle\,(E - \epsilon_r - \epsilon_{r'} + \epsilon_{s'})^{-1}\,\tilde{a}_r^\dagger\tilde{a}_{r'}^\dagger\tilde{a}_{s'} \\ &\quad -\sum_{r,s'}\langle rs'||js'\rangle\langle n_{s'}\rangle\,(E - \epsilon_r)^{-1}\,\tilde{a}_r^\dagger. \end{aligned} \tag{9.21}$$

The second-order correction to the self-energy then becomes

$$\begin{aligned}\Sigma_{ij}^{(2)}(E) &= (\tilde{a}_i^\dagger|\hat{V}\hat{T}_0(E)\hat{V}\tilde{a}_j^\dagger) \\ &= \frac{1}{2}\sum_{r,r',s'}\langle rr'||js'\rangle\,(E - \epsilon_r - \epsilon_{r'} + \epsilon_{s'})^{-1}\,(\tilde{a}_i^\dagger|\hat{V}\tilde{a}_r^\dagger\tilde{a}_{r'}^\dagger\tilde{a}_{s'}) \\ &= \frac{1}{2}\sum_{r,r',s'}\frac{\langle is'||rr'\rangle\langle rr'||js'\rangle N_{rr's'}}{E - \epsilon_r - \epsilon_{r'} + \epsilon_{s'}}, \end{aligned} \tag{9.22}$$

where

$$N_{rr's'} = [\langle n_{s'}\rangle + \langle n_r\rangle\langle n_{r'}\rangle - \langle n_r\rangle\langle n_{s'}\rangle - \langle n_{r'}\rangle\langle n_{s'}\rangle]. \tag{9.23}$$

The evaluation of averages of the commutators and anticommutators arising from $(\tilde{a}_i^\dagger|\hat{V}\tilde{a}_r^\dagger\tilde{a}_{r'}^\dagger\tilde{a}_{s'})$ uses the results

$$\begin{aligned}\mathrm{Tr}\left\{\rho\tilde{a}_r^\dagger\tilde{a}_s\right\} &= \delta_{rs}\langle n_r\rangle, \\ \mathrm{Tr}\left\{\rho\tilde{a}_r^\dagger\tilde{a}_{r'}^\dagger\tilde{a}_{s'}\tilde{a}_s\right\} &= (\delta_{rs}\delta_{r's'} - \delta_{rs'}\delta_{r's})\,\langle n_r\rangle\langle n_{r'}\rangle. \end{aligned} \tag{9.24}$$

In general, the result

$$\mathrm{Tr}\left\{\rho\tilde{a}_{r_1}^\dagger\cdots\tilde{a}_{r_n}^\dagger\tilde{a}_{s_n}\cdots\tilde{a}_{s_1}\right\} = \det\left\{\delta_{r_1s_1}\delta_{r_2s_2}\cdots\delta_{r_ns_n}\right\}\prod_{i=1}^{n}\langle n_{r_i}\rangle \tag{9.25}$$

holds.

For integer occupation numbers (0 and 1), $N_{rr'_{s'}}$ differs from zero only for the two cases

$$\begin{aligned} \langle n_r \rangle &= \langle n_{r'} \rangle = 0,\ \langle n_{s'} \rangle = 1, \\ \text{and} \quad \langle n_r \rangle &= \langle n_{r'} \rangle = 1,\ \langle n_{s'} \rangle = 0, \end{aligned} \tag{9.26}$$

which means that

$$\Sigma_{ij}^{(2)}(E) = \frac{1}{2} \sum_{a,p,q} \frac{\langle ia||pq\rangle\langle pq||ja\rangle}{E + \epsilon_a - \epsilon_p - \epsilon_q} + \frac{1}{2} \sum_{a,b,p} \frac{\langle ip||ab\rangle\langle ab||jp\rangle}{E + \epsilon_p - \epsilon_a - \epsilon_b}, \tag{9.27}$$

where $a,b,...$ denote spin orbitals occupied in the single determinantal reference state, $p,q,...$ denote unoccupied spin orbitals, and $i,j,...$ denote either.

One should note that because the electron propagator matrix elements $G_{ij}(E)$ have simple poles, *i.e.*, become infinite, the inverse of the propagator matrix will have a zero eigenvalue at those energies. Neglect of off-diagonal terms in the self energy gives the form

$$G_{ij}(E) = \delta_{ij} / \left[(E - \epsilon_j)\, \delta_{ij} - \Sigma_{jj}(E) \right]. \tag{9.28}$$

The poles are thus obtained from

$$E = \epsilon_i + \Sigma_{ii}(E), \tag{9.29}$$

where E is an electron binding energy. It can be solved either by iteration or by perturbation methods, *i.e.*, the calculation of $\Sigma_{ii}(\epsilon_i)$ through some definite order of the perturbation V.

The lowest order correction to the so-called Koopmans' theorem, which equates the electron binding energies with spin orbital energies, can then be expressed as

$$E_i \simeq \epsilon_i + \frac{1}{2} \sum_{a,p,q} \frac{\langle ia||pq\rangle\langle pq||ia\rangle}{\epsilon_i + \epsilon_a - \epsilon_p - \epsilon_q} + \frac{1}{2} \sum_{a,b,p} \frac{\langle ip||ab\rangle\langle ab||ip\rangle}{\epsilon_i + \epsilon_p - \epsilon_a - \epsilon_b}, \tag{9.30}$$

where the electron binding energy is labeled by the spin orbital energy. This expression can be further analyzed[1]

$$\begin{aligned} \Sigma_{ii}^{(2)}(\epsilon_i) &= \sum_a \left[\frac{1}{2} \sum_{p,q} \frac{|\langle ia||pq\rangle|^2}{\epsilon_i + \epsilon_a - \epsilon_p - \epsilon_q} \right] + \sum_{a,p} \frac{|\langle ip||ia\rangle|^2}{\epsilon_p - \epsilon_a} \\ &\quad + \frac{1}{2} \sum_{a \neq i, b \neq i, p} \frac{|\langle ip||ab\rangle|^2}{\epsilon_i + \epsilon_p - \epsilon_a - \epsilon_b}, \end{aligned} \tag{9.31}$$

where the expression in the square brackets can be identified as the lowest order pair correlation energy term[2]. The second term is the lowest order orbital

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[1] see, *e.g.*, B. Pickup and O. Goscinski, *Mol. Phys.* **26**, 1013 (1973)

[2] see, *e.g.*, O. Sinanouglu, *Adv. Chem. Phys.* **14**, 237 (1969)

relaxation correction, *i.e.*, the lowest order correction. This means that it is the lowest order correction to the Koopmans' theorem result for, say, an ionization potential, calculated as the difference of two separately optimized total Hartree-Fock (SCF) energies, *i.e.*,

$$E_{HF}(N) - E^{i}_{HF}(N-1) = \epsilon_i + \sum_{a,p} \frac{|\langle ip||ia\rangle|^2}{\epsilon_p - \epsilon_a} + \cdots, \tag{9.32}$$

where $E^{i}_{HF}(N-1)$ is the total Hartree-Fock energy for the hole state with spin orbital i empty.

The third-order contributions to the self-energy can also readily be calculated. These terms lead to fivefold summations and are more cumbersome to compute[3].

Problems

1. Diagram the third-order contributions to the electron propagator self-energy listed in Appendix D.

9.1 Renormalization of the Electron Propagator

The order by order treatment of the self-energy is performed under the tacit assumption that the perturbation expansion converges. In nuclear many-body theory and in the theory of the electron gas model system, one has found that not to be the case. In order to remove the divergencies, it has been found necessary to sum certain types of diagrams to all orders. This practice of summing certain types of diagrams through all orders is often referred to as renormalization. A great variety of renormalization procedures exist, such as propagator, interaction, and vertex renormalizations. What distinguishes such various procedures is mainly the type of diagrams that are being summed. In what follows, we concentrate on some specific forms of renormalizations of the self-energy. The superoperator formalism can be adapted to yield renormalized self-energy expressions corresponding to the summations of specific types of diagrams.

9.1.1 The 2p-h TDA and the Diagonal 2p-h TDA Self-Energy

The self-energy matrix in a spin orbital basis can be expressed as

$$\Sigma(E) = (\mathbf{a}^\dagger|(\hat{V} + \hat{V}T(E)\hat{V})\mathbf{a}^\dagger), \tag{9.33}$$

with

$$\hat{T}(E) = \hat{P}[\alpha\hat{O} + (E\hat{I} - \hat{H}_0)\hat{P} - \hat{P}\hat{V}\hat{P}]^{-1}\hat{P}, \tag{9.34}$$

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[3] see, *e.g.*, G. Born, H.A. Kurtz, and Y. Öhrn, *J. Chem. Phys.*68, 74 (1978)

where $\alpha \neq 0$ is an arbitrary constant, and $\hat{O} = |\mathbf{a}^\dagger)(\mathbf{a}^\dagger|$, $\hat{P} = \hat{I} - \hat{O}$, $\hat{O}^2 = \hat{O}$, $\hat{P}^2 = \hat{P}$, and $\hat{O}\hat{P} = \hat{P}\hat{O} = 0$. Using an SCF reference state and the associated spin orbitals, the self-energy can be expressed as

$$\Sigma(E) = (\mathbf{a}^\dagger|\hat{V}\hat{T}(E)\hat{V}\mathbf{a}^\dagger) \tag{9.35}$$

since $(\mathbf{a}^\dagger|\hat{V}\mathbf{a}^\dagger) = \mathbf{0}$.

The projector for the orthogonal complement to the single-particle space is

$$\hat{P} = |\mathbf{f}^\dagger)(\mathbf{f}^\dagger|, \tag{9.36}$$

with

$$\{\mathbf{f}^\dagger\} = \{a_k^\dagger a_l^\dagger a_m, a_k^\dagger a_l^\dagger a_m^\dagger a_p a_q, \cdots\}. \tag{9.37}$$

Restricting $\{\mathbf{f}^\dagger\}$ to only some simple fermion-like products of electron field operators will generate only certain types of diagrams that can then be summed to all orders. For instance, self-energy diagrams in third order of the "ring" and "ladder" types, which can easily be generalized in any order. It is notable that between consecutive interaction lines, there only occur one hole line and two particle lines or vice versa [see Fig. 9.1].

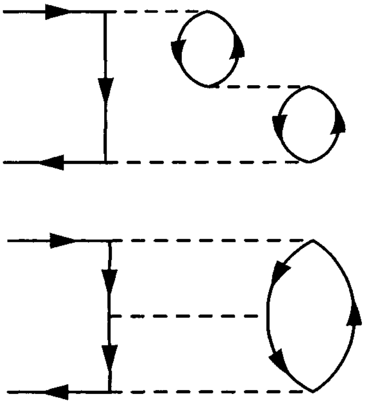

Figure 9.1: RINGS and LADDERS

This suggests that the intermediate virtual states in these perturbation terms are "two particle one hole" (2p-h) or "two holes one particle" (2h-p) excitations out of the reference state. Since the rings and ladders are important contributions to the self-energy, one can assume that restricting the complement space to the operators

$$\{\mathbf{f}^\dagger\} = \{a_p^\dagger a_q^\dagger a_a, a_a^\dagger a_b^\dagger a_p\} \tag{9.38}$$

will be a reasonable approximation.

This particular truncation of the complement space of field operators is internally orthonormal and orthogonal to the single-particle space, *i.e.* $(\mathbf{f}^\dagger|\mathbf{f}^\dagger) = \mathbf{1}$, and $(\mathbf{a}^\dagger|\mathbf{f}^\dagger) = \mathbf{0}$. Thus, while $\hat{P} + \hat{O} \neq \hat{I}$, $\hat{P}^2 = \hat{P}$, and $\hat{O}\hat{P} = \hat{P}\hat{O} = 0$. The superoperator in Eq. (9.34) can be expanded to read

$$\begin{aligned} \hat{T}(E) &= \hat{P}[(\alpha^{-1}\hat{O} + (E\hat{I} - \hat{H}_0)^{-1}\hat{P}) \\ &\quad +(\alpha^{-1}\hat{O} + (E\hat{I} - \hat{H}_0)^{-1}\hat{P})\hat{P}\hat{V}\hat{P}(\alpha^{-1}\hat{O} + (E\hat{I} - \hat{H}_0)^{-1}\hat{P}) \\ &\quad +\cdots]\hat{P} \end{aligned} \tag{9.39}$$

and because

$$\hat{H}_0 f^\dagger_{klm} = \hat{H}_0 a^\dagger_k a^\dagger_l a_m = (\epsilon_k + \epsilon_l - \epsilon_m)\, a^\dagger_k a^\dagger_l a_m \tag{9.40}$$

and

$$(f^\dagger_{klm}|(E\hat{I} - \hat{H}_0)^{-1} f^\dagger_{k'l'm'}) = \frac{\delta_{kk'}\delta_{ll'}\delta_{mm'}}{(E + \epsilon_m - \epsilon_k - \epsilon_l)}, \tag{9.41}$$

which means that

$$(\mathbf{f}^\dagger|(E\hat{I} - \hat{H}_0)^{-1}\mathbf{f}^\dagger) = (\mathbf{f}^\dagger|(E\hat{I} - \hat{H}_0)\mathbf{f}^\dagger)^{-1} \tag{9.42}$$

and that

$$\begin{aligned} \hat{T}(E) &= |\mathbf{f}^\dagger)(\mathbf{f}^\dagger|(E\hat{I} - \hat{H}_0)\mathbf{f}^\dagger)^{-1}(\mathbf{f}^\dagger| \\ &\quad +|\mathbf{f}^\dagger)(\mathbf{f}^\dagger|(E\hat{I} - \hat{H}_0)\mathbf{f}^\dagger)^{-1}(\mathbf{f}^\dagger|\hat{V}\mathbf{f}^\dagger) \\ &\quad \times(\mathbf{f}^\dagger|(E\hat{I} - \hat{H}_0)\mathbf{f}^\dagger)^{-1}(\mathbf{f}^\dagger| + \cdots. \end{aligned} \tag{9.43}$$

This expression can again be summed to read

$$\hat{T}(E) = |\mathbf{f}^\dagger)(\mathbf{f}^\dagger|(E\hat{I} - \hat{H}_0 - \hat{V})\mathbf{f}^\dagger)^{-1}(\mathbf{f}^\dagger|. \tag{9.44}$$

This means that the self-energy matrix becomes

$$\mathbf{\Sigma}(E) = (\mathbf{a}^\dagger|\hat{V}\mathbf{f}^\dagger)(\mathbf{f}^\dagger|(E\hat{I} - \hat{H}_0 - \hat{V})\mathbf{f}^\dagger)^{-1}(\mathbf{f}^\dagger|\hat{V}\mathbf{a}^\dagger) \tag{9.45}$$

and a general matrix element can be evaluated as follows:

$$\begin{aligned} (a^\dagger_a a^\dagger_b a_p|\hat{V} a^\dagger_j) &= \langle 0|[a^\dagger_p a_b a_a, [V, a^\dagger_j]_-]_+|0\rangle \\ &= \sum_{r,r',s'} \langle rr'||js'\rangle \left\{ \frac{1}{2}\langle 0|[a^\dagger_p a_b a_a, a^\dagger_r a^\dagger_{r'} a_{s'}]_+|0\rangle \right. \\ &\quad \left. -\delta_{r's'}\langle n_{r'}\rangle\langle 0|[a^\dagger_p a_b a_a, a^\dagger_r]_+|0\rangle \right\} \\ &= \langle ab||jp\rangle \end{aligned} \tag{9.46}$$

and

$$\begin{aligned} &(a^\dagger_a a^\dagger_b a_p|(E\hat{I} - \hat{H}_0 - \hat{V}) a^\dagger_{a'} a^\dagger_{b'} a_{p'}) \\ &= \delta_{aa'}\delta_{bb'}\delta_{pp'}(E + \epsilon_p - \epsilon_a - \epsilon_b) - \Delta_{abp}, \end{aligned} \tag{9.47}$$

with

$$\begin{aligned} \Delta_{abp} &= (a_a^\dagger a_b^\dagger a_p|\hat{V} a_{a'}^\dagger a_{b'}^\dagger a_{p'}) \\ &= \langle 0|[a_p^\dagger a_b a_a, [\hat{V}, a_{a'}^\dagger a_{b'}^\dagger a_{p'}]_-]_+|0\rangle \\ &= -\frac{1}{2}\langle ab||a'b'\rangle\delta_{pp'} + \langle p'a||pa'\rangle\delta_{bb'} \\ &\quad +\langle p'b||pb'\rangle\delta_{aa'}. \end{aligned} \tag{9.48}$$

Similarly,

$$(a_p^\dagger a_q^\dagger a_a|\hat{V} a_j^\dagger) = \langle pq||ja\rangle \tag{9.49}$$

and

$$\Delta_{pqa} = \frac{1}{2}\langle pq||p'q'\rangle\delta_{aa'} - \langle a'p||p'a\rangle\delta_{qq'} - \langle q'a||qa'\rangle\delta_{pp'}. \tag{9.50}$$

The size of the $\{f_{abp}^\dagger, f_{pqa}^\dagger\}$ subspace is quite large for reasonable basis sets. For N electrons and a spin orbital basis of rank K, there are $(K-N)(K-2)N/2$ elements in the orthogonal complement space. The solution of the Dyson-like equation would require the inversion of a matrix of this dimension for every value of the energy parameter. This approximation of the self-energy first introduced by J. Linderberg and Y. Öhrn,[4], has been discussed by G. D. Purvis III, and Y. Öhrn,[5] and J. Schirmer and L. S. Cederbaum[6]. A simplified version of this approach is the so-called "Diagonal 2p-h TDA", which becomes

$$\begin{aligned} \Sigma_{ij}^{2p-hTDA}(E) &= \frac{1}{2}\sum_{a,b,p} \frac{\langle ip||ab\rangle\langle ab||jp\rangle}{E+\epsilon_p-\epsilon_a-\epsilon_b-\Delta_{abp}} \\ &\quad +\frac{1}{2}\sum_{p,q,a} \frac{\langle ia||pq\rangle\langle pq||ja\rangle}{E+\epsilon_a-\epsilon_p-\epsilon_q-\Delta_{apq}}, \end{aligned} \tag{9.51}$$

where

$$\Delta_{abp} = -\frac{1}{2}\langle ab||ab\rangle + \langle ap||ap\rangle + \langle bp||bp\rangle \tag{9.52}$$

and

$$\Delta_{pqa} = \frac{1}{2}\langle pq||pq\rangle - \langle pa||pa\rangle - \langle qa||qa\rangle. \tag{9.53}$$

9.2 Partitioning and Inner Projections

Starting with the matrix electron propagator in Eq. (9.12), an alternative formulation of approximation can be introduced. One employs an inner projection

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[4] J. Linderberg and Y. Öhrn, *Chem. Phys. Lett.* **1**, 295 (1967)

[5] G. D. Purvis III, and Y. Öhrn, *J. Chem. Phys.* **60**, 4063 (1974)

[6] J. Schirmer and L. S. Cederbaum, *J. Phys.* **B11**, 1889 and 1901 (1978)

manifold[7]

$$\begin{aligned}\{\mathbf{h}\} &= \{\mathbf{h}_1\} \cup \{\mathbf{h}_3\} \cup \{\mathbf{h}_5\} \cup \cdots \\ &= \{a^\dagger, i^\dagger\} \cup \{a^\dagger b^\dagger i, i^\dagger j^\dagger a\} \cup \{a^\dagger b^\dagger c^\dagger ij, i^\dagger j^\dagger k^\dagger ab\} \cup \cdots \qquad (9.54)\end{aligned}$$

from the space of fermion-like operators, where the notation $\{a_r \equiv r\}$ is used for the SCF electron field operators, to write

$$\begin{aligned}\mathbf{G}(E) &= (\mathbf{a}^\dagger|(E\hat{I} - \hat{H})^{-1}\mathbf{a}^\dagger) \\ &= (\mathbf{a}^\dagger|\mathbf{h})(\mathbf{h}|(E\hat{I} - \hat{H})\mathbf{h})^{-1}(\mathbf{h}|\mathbf{a}^\dagger), \qquad (9.55)\end{aligned}$$

which transforms the superoperator inverse to a matrix inverse[8].

It is convenient to use an orthonormal set of inner projection basis elements so that $(\mathbf{h}_i|\mathbf{h}_i) = \mathbf{1}$ and $(\mathbf{h}_i|\mathbf{h}_j) = \mathbf{0}$ for $i \neq j$. A first step in seeking adequate approximation schemes for the electron propagator is a partitioning of the inner projection manifold. When the aim is to obtain a theoretical photoelectron spectrum, it is convenient to choose the partitioning

$$\begin{aligned}\mathbf{h} &= \{\mathbf{h}_1, \mathbf{f}\}, \\ \mathbf{f} &= \{\mathbf{h}_3\} \cup \{\mathbf{h}_5\} \cup \cdots \qquad (9.56)\end{aligned}$$

such that Eq. (9.55) becomes

$$\mathbf{G}(E) = \begin{bmatrix} \mathbf{1} & \mathbf{0} \end{bmatrix} \begin{bmatrix} E\mathbf{1} - (\mathbf{a}^\dagger|\hat{H}\mathbf{a}^\dagger) & -(\mathbf{a}^\dagger|\hat{H}\mathbf{f}) \\ -(\mathbf{f}|\hat{H}\mathbf{a}^\dagger) & E\mathbf{1} - (\mathbf{f}|\hat{H}\mathbf{f}) \end{bmatrix}^{-1} \begin{bmatrix} \mathbf{1} \\ \mathbf{0} \end{bmatrix}. \qquad (9.57)$$

The partitioned form of the inverse matrix yields

$$\begin{aligned}\mathbf{G}^{-1}(E) &= E\mathbf{1} - (\mathbf{a}^\dagger|\hat{H}\mathbf{a}^\dagger) \\ &\quad -(\mathbf{a}^\dagger|\hat{H}\mathbf{f})[E\mathbf{1} - (\mathbf{f}|\hat{H}\mathbf{f})]^{-1}(\mathbf{f}|\hat{H}\mathbf{a}^\dagger) \\ &= (\mathbf{a}^\dagger|(E\hat{I} - \hat{H})\mathbf{a}^\dagger) \qquad (9.58) \\ &\quad +(\mathbf{a}^\dagger|\hat{H}\mathbf{f})(\mathbf{f}|(E\hat{I} - \hat{H})\mathbf{f})^{-1}(\mathbf{f}|\hat{H}\mathbf{a}^\dagger) \\ &= \mathbf{G}_0^{-1}(E) - \Sigma(E),\end{aligned}$$

where the unperturbed propagator and the self-energy term have been defined to show the relation to the so-called Dyson-like equation for the propagator. An untruncated manifold **f** means no approximation, only a reformulation of the propagator equations. In order to arrive at a definite approximation and provide

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[7] see P.-O. Löwdin in *Perturbation Theory and Its Application in Quantum Mechanics*, edited by C. H. Wilcox, Wiley, New York, 1966 and L. T. Redmon, G. D. Purvis, and Y. Öhrn, *J. Chem. Phys.* **63**, 5011 (1975).

[8] Another way to achieve this is to use a nonorthogonal basis of field operators, which in general affords the expansion $|\mathbf{a}^\dagger) = |\mathbf{h})(\mathbf{h}|\mathbf{h})^{-1}(\mathbf{h}|\mathbf{a}^\dagger)$, and if the basis is complete, the resolution of the identity is $|\mathbf{h})(\mathbf{h}|\mathbf{h})^{-1}(\mathbf{h}| = 1$. This permits the identity $(\mathbf{h}|\mathbf{h}) = (\mathbf{h}|A^{-1}A\mathbf{h}) = (\mathbf{h}|A^{-1}\mathbf{h})(\mathbf{h}|\mathbf{h})^{-1}(\mathbf{h}|A\mathbf{h})$, which can be written as $(\mathbf{h}|A^{-1}\mathbf{h}) = (\mathbf{h}|\mathbf{h})(\mathbf{h}|A\mathbf{h})^{-1}(\mathbf{h}|\mathbf{h})$. For $A = E\hat{I} - \hat{H}$, this yields Eq. (9.55).

algorithms for the calculation of the matrix elements defining the propagator, a reference state and a truncation of the inner projection field operator manifold must be chosen.

The Hartree-Fock or SCF single determinantal state $|0\rangle = |HF\rangle$ provides the natural starting point for the choice of reference state at various levels of approximation. Although the electron propagator theory can be fully developed within a perturbation theory framework with only the SCF single determinantal reference state and choice of inner projection manifold, it is desirable to keep a balance between the level of description of the reference state $|0\rangle$ and that of the inner projection manifold $\mathbf{f}$. Such a balance kept through various orders of perturbation theory guarantees hermiticity of the superoperator hamiltonian matrix and the elimination of spurious terms. Starting from a partitioning of the hamiltonian and thus also of the superoperator hamiltonian

$$\begin{aligned} H &= H_0 + \delta H \\ H_0 &= \sum_p \epsilon_p p^\dagger p \\ \delta H &= \sum_{p,q,r,s} \langle pq||rs\rangle [\frac{1}{4} p^\dagger q^\dagger sr - \delta_{qs}\langle n_s\rangle p^\dagger r], \end{aligned} \tag{9.59}$$

the reference state can be expressed in terms of Rayleigh-Schrödinger perturbation theory (RSPT), or coupled-cluster (CC) theory. Also multi-configurational SCF (MCSCF) theory has been implemented for the electron propagator reference state. Here we restrict the discussion to reference states based on RSPT and CC theory.

The hermiticity problem consists of the equation

$$(X|\hat{H}Y) = (Y|\hat{H}X)^* \tag{9.60}$$

not being satisfied for an approximate reference state or more generally for a density operator

$$\rho = \rho_0 + \delta\rho + \delta^2\rho + \cdots + \delta^n\rho \tag{9.61}$$

correct through order n in perturbation theory. The average defining the propagator matrices is then formed as a trace, as discussed in the introduction to double-time Greens functions [see Chapter 4], *i.e.*,

$$\langle\cdots\rangle \equiv \mathrm{Tr}\{\rho\cdots\}. \tag{9.62}$$

Because

$$\begin{aligned} \langle[X^\dagger,[H,Y]_-]_+\rangle &- \langle[Y^\dagger,[H,X]_-]_+\rangle^* = \langle[H,[X^\dagger,Y]_+]_-\rangle \\ &= \mathrm{Tr}\{\rho[H,[X^\dagger,Y]_+]_-\} \\ &= \mathrm{Tr}\{[\rho,H]_-[X^\dagger,Y]_+]_-\} \end{aligned} \tag{9.63}$$

and since

$$[\rho_0, H_0]_- = 0 \tag{9.64}$$

and

$$[\delta^k \rho, H_0]_- + [\delta^{k-1}\rho, \delta H]_- = 0 \tag{9.65}$$

are assumed to hold for $k = 1, 2, \ldots, n$, the error term is of order $n+1$, *i.e.*,

$$(X|\hat{H}Y) - (Y|\hat{H}X)^* = \mathrm{Tr}\{[\delta^n \rho, \delta H]_- [X^\dagger, Y]_+\}. \tag{9.66}$$

The Rayleigh-Schrödinger perturbation expansion for the reference state,

$$|0\rangle_{RSPT} = (1 + K_1 + K_2 + K_3 + \cdots)|HF\rangle, \tag{9.67}$$

is defined by

$$K_1 = \sum_i \sum_a k_i^a a^\dagger i\ , \tag{9.68}$$

$$K_2 = \sum_{i>j} \sum_{a>b} k_{ij}^{ab} a^\dagger i b^\dagger j\ , \tag{9.69}$$

and

$$K_3 = \sum_{i>j>k} \sum_{a>b>c} k_{ijk}^{abc} a^\dagger i b^\dagger j c^\dagger k\ , \tag{9.70}$$

with , in particular

$$k_{ij}^{ab} = \frac{\langle ij||ab\rangle}{D_{ij}^{ab}}\ , \tag{9.71}$$

and

$$k_i^a = \frac{1}{2}\left[\sum_{jbc} \frac{\langle bc||aj\rangle}{D_i^a} k_{ij}^{bc} - \sum_{jkb} \frac{\langle ib||jk\rangle}{D_i^a} k_{jk}^{ab}\right]. \tag{9.72}$$

The denominators are defined as

$$D_i^a = \epsilon_i - \epsilon_a \tag{9.73}$$

and

$$D_{ij}^{ab} = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b. \tag{9.74}$$

The concept of order in the perturbation expansion of the electron propagator ultimately means order in terms of the electron-electron interaction, or equivalently, two-electron integrals. The inclusion of electron correlation through first order in the reference state is achieved with the double excitation terms K_2, whereas the K_1 terms are also needed for second-order corrections.

The coupled-cluster (CC) expression[9] for the reference state

$$|0\rangle_{CC} = e^{T}|HF\rangle \tag{9.75}$$

is defined by

$$T = T_1 + T_2 + T_3 + \ldots + T_N, \tag{9.76}$$

with N being the number of electrons of the system and

$$T_1 = \sum_i \sum_a t_i^a a^\dagger i, \tag{9.77}$$

$$T_2 = \sum_{i>j} \sum_{a>b} t_{ij}^{ab} a^\dagger i b^\dagger j, \tag{9.78}$$

$$T_3 = \sum_{i>j>k} \sum_{a>b>c} t_{ijk}^{abc} a^\dagger i b^\dagger j c^\dagger k, \tag{9.79}$$

and so on.

The T amplitudes contain infinite order contributions to each excitation level from the HF state. Thus, replacing the RSPT K amplitudes with the CC T amplitudes may be considered a renormalization procedure since certain classes of perturbation terms or diagrams are summed to infinite order. This idea was employed in work on both the electron propagator[10] and the excitation propagator[11].

Expansion of the exponential in the CC method gives

$$\begin{aligned} |0\rangle_{CC} &= [1 + T_1 + (T_2 + \frac{1}{2}T_1^2) + \ldots]|HF\rangle \\ &= [1 + \sum_i \sum_a t_i^a a^\dagger i + \sum_{i>j} \sum_{a>b} t_{ij}^{ab} a^\dagger b^\dagger ij \\ &\quad + \frac{1}{2}(\sum_i \sum_a t_i^a a^\dagger i)(\sum_j \sum_b t_j^b b^\dagger j) + \ldots]|HF\rangle\ , \end{aligned} \tag{9.80}$$

where the last term can be rewritten as

$$\begin{aligned} \frac{1}{2}(\sum_i \sum_a t_i^a a^\dagger i)(\sum_j \sum_b t_j^b b^\dagger j) &= \sum_{i>j} \left[(\sum_a t_i^a a^\dagger i)(\sum_b t_j^b b^\dagger j) \right] \\ &= \sum_{i>j} \sum_{a>b} \left[(t_i^a t_j^b a^\dagger i b^\dagger j) + (t_i^b t_j^a b^\dagger i a^\dagger j) \right], \end{aligned} \tag{9.81}$$

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[9] see, *e.g.*, J. Čižek and J. Paldus, *Physica Scripta* **21**, 251 (1980)

[10] see J. V. Ortiz, *Int. J. Quantum Chem.* **S25**, 35 (1991)

[11] see J. Geertsen and J. Oddershede, *J. Chem. Phys.* **85**, 211 (1986)

and, since for the orthonormal basis of SCF spin orbitals,

$$b^\dagger i a^\dagger j = -a^\dagger i b^\dagger j, \tag{9.82}$$

the CC reference state becomes,

$$\begin{aligned} |0\rangle_{CC} &= [1 + T_1 + (T_2 + \frac{1}{2}T_1^2) + \ldots]|HF\rangle \\ &= [1 + \sum_i \sum_a t_i^a a^\dagger i + \sum_{i>j} \sum_{a>b} \tau_{ij}^{ab} a^\dagger i b^\dagger j + \ldots]|HF\rangle, \end{aligned} \tag{9.83}$$

where

$$\tau_{ij}^{ab} = t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a. \tag{9.84}$$

Restricting the coupled-cluster expansion to single and double (CCSD) excitations, *i.e.*,

$$|0\rangle_{CC} \approx |0\rangle_{CCSD} = e^{(T_1+T_2)}|HF\rangle, \tag{9.85}$$

the equations for the T amplitudes can be obtained by inserting the trial function in the Schrödinger equation and form

$$e^{-(T_1+T_2)} H e^{T_1+T_2}|HF\rangle = E|HF\rangle. \tag{9.86}$$

Projecting this expression against $\langle HF|$ yields the CCSD energy. Projecting against a singly excited determinant $\langle HF|i^\dagger a$ yields a vanishing right-hand side and an equation for the T_1 amplitudes:

$$\begin{aligned} D_i^a t_i^a &= \sum_b t_i^b F_{ab} - \sum_j t_j^a F_{ji} + \sum_{jb} t_{ij}^{ab} F_{jb} + \\ &\quad - \sum_{jb} t_j^b \langle ja||ib\rangle - \frac{1}{2} \sum_{ibc} t_{ij}^{bc} \langle ja||bc\rangle \\ &\quad - \frac{1}{2} \sum_{jkb} t_{jk}^{ab} \langle kj||bi\rangle. \end{aligned} \tag{9.87}$$

Similarly, a projection against a doubly excited determinant $\langle HF|j^\dagger b i^\dagger a$ yields an equation for the T_2 amplitudes:

$$\begin{aligned} D_{ij}^{ab} t_{ij}^{ab} &= \langle ij||ab\rangle + P(ab) \sum_c t_{ij}^{ac} \left(F_{bc} - \frac{1}{2} \sum_k t_k^b F_{kc} \right) \\ &\quad - P(ij) \sum_k t_{ik}^{ab} \left(F_{kj} + \frac{1}{2} \sum_c t_j^c F_{kc} \right) \\ &\quad + \frac{1}{2} \sum_{kl} \tau_{kl}^{ab} W_{klij} + \frac{1}{2} \sum_{cd} \tau_{ij}^{cd} W_{abcd} \end{aligned} \tag{9.88}$$

$$+P(ij)P(ab)\sum_{kc}\left(t_{ik}^{ac}W_{kbcj} - t_i^c t_k^a\langle kb||cj\rangle\right)$$
$$+P(ij)\sum_{c} t_i^c\langle ab||cj\rangle - P(ab)\sum_{k} t_k^a\langle kb||ij\rangle,$$

where

$$F_{ab} = \sum_{kc} t_k^c\langle ka||cb\rangle - \frac{1}{2}\sum_{klc}\tilde{\tau}_{kl}^{ac}\langle kl||bc\rangle\ , \tag{9.89}$$

$$F_{ji} = \sum_{ak} t_k^a\langle jk||ia\rangle + \frac{1}{2}\sum_{kab}\tilde{\tau}_{ik}^{ab}\langle jk||ab\rangle\ , \tag{9.90}$$

$$F_{jb} = \sum_{ia} t_i^a\langle ij||ba\rangle\ , \tag{9.91}$$

$$\begin{aligned} W_{klij} &= \langle kl||ij\rangle + P\,(ij)\sum_{a} t_j^a\langle kl||ia\rangle \\ &+ \frac{1}{4}\sum_{ab}\tau_{ij}^{ab}\langle kl||ab\rangle\ , \end{aligned} \tag{9.92}$$

$$\begin{aligned} W_{abcd} &= \langle ab||cd\rangle - P\,(ab)\sum_{i} t_i^b\langle ai||cd\rangle \\ &+\frac{1}{4}\sum_{ij}\tau_{ij}^{ab}\langle ij||cd\rangle\ , \end{aligned} \tag{9.93}$$

and

$$\begin{aligned} W_{kbcj} &= \langle kb||cj\rangle + \sum_{a} t_j^a\langle kb||ca\rangle - \sum_{i} t_i^b\langle ki||cj\rangle + \\ &-\sum_{ia}\left(\frac{1}{2}t_{ji}^{ab} + t_j^a t_i^b\right)\langle ki||ca\rangle\ . \end{aligned} \tag{9.94}$$

The effective two-particle excitation operators τ and $\tilde{\tau}$ are

$$\tau_{ij}^{ab} = t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a \tag{9.95}$$

and

$$\tilde{\tau}_{ij}^{ab} = t_{ij}^{ab} + \frac{1}{2}\left(t_i^a t_j^b - t_i^b t_j^a\right)\ , \tag{9.96}$$

respectively. In the above equation, $P\,(ij)$ and $P(ab)$ denote the permutational interchange operations.

The k coefficients in the RSPT expansion can be obtained from the coupled-cluster *ansatz* through iteration of the T equations. For instance, the first iteration of the T_2 equation gives K_2; that is,

$$k_{ij}^{ab} = t_{ij}^{ab}(1) = \frac{\langle ij||ab\rangle}{D_{ij}^{ab}}, \tag{9.97}$$

which, when applied in the T_1 equation yields

$$k_i^a = t_i^a(1) = \frac{1}{2}\left[\sum_{jbc} \frac{\langle aj||bc\rangle}{D_i^a} t_{ij}^{bc}(1) - \sum_{jkb} \frac{\langle jk||ib\rangle}{D_i^a} t_{jk}^{ab}(1)\right]. \tag{9.98}$$

Consequently, it is possible to write reference states for the electron propagator approach as expansion coefficients of the perturbation theory or as converged T amplitudes from the solution of the coupled-cluster equations.

Also, in comparing the RSPT and CC wave functions, it is clear that

$$\begin{array}{rcl} |0\rangle_{RSPT} = (1+ & K_1 & + K_2 + \ldots)\,|HF\rangle \\ & \Updownarrow & \\ |0\rangle_{CCSD} = (1 + T_1 + (& T_2 & + T_1^2/2) + \ldots)\,|HF\rangle \\ & \Downarrow & \\ CC - EP & \leftrightarrow & RSPT - EP \\ & \Uparrow & \\ t_i^a & \leftrightarrow & k_i^a \\ \tau_{ij}^{ab} & \leftrightarrow & k_{ij}^{ab}. \end{array} \tag{9.99}$$

From the definition of the spectral representation, it follows that the elements of the electron propagator matrix $\mathbf{G}(E)$ become infinite when E equals an electron binding energy. Then, the inverse $\mathbf{G}^{-1}(E)$ has a zero eigenvalue at such an energy. This result can be used to devise iterative methods to find the electron propagator poles and residues at a given level of perturbation expansion.

Truncation of the inner projection operator manifold $\mathbf{f}$ and the use of RSPT for the reference state based on the so-called Möller-Plesset partitioning of the hamiltonian as expressed in Eq. (9.59) facilitates an order analysis of the electron propagator. In particular, the self-energy and consequently properties as, *e.g.*, electron binding energies and the one-electron reduced density matrix can be calculated to a given desired order of electron correlation or electron interaction. Starting from the inverse propagator matrix, as given in Eq. (9.58) and using a shorthand notation, the following expression is obtained:

$$\mathbf{G}^{-1}(E) = \mathbf{R}_{aa}(E) - \mathbf{R}_{af}\mathbf{R}_{ff}^{-1}(E)\mathbf{R}_{fa}, \tag{9.100}$$

where

$$\mathbf{R}_{aa}(E) \;=\; (\mathrm{a}^\dagger|(E\hat{I} - \hat{H})\mathrm{a}^\dagger) = E\mathbf{1} - \mathbf{H}_{aa},$$

$$\begin{aligned}\mathbf{R}_{af} &= (\mathrm{a}^{\dagger}|(E\hat{I}-\hat{H})\mathrm{f}) = -\mathbf{H}_{af}, \\ \mathbf{R}_{fa} &= (\mathrm{f}|(E\hat{I}-\hat{H})\mathrm{a}^{\dagger}) = -\mathbf{H}_{fa} = -\mathbf{H}^{\dagger}_{af}, \\ \mathbf{R}_{fa}(E) &= (\mathrm{f}|(E\hat{I}-\hat{H})\mathrm{f}) = E\mathbf{1} - \mathbf{H}_{ff}.\end{aligned} \tag{9.101}$$

The RSPT expression for the reference state then permits the expansion

$$\mathbf{R}_{af} = -\sum_{i=1}^{n} \mathbf{H}^{(i)}_{af}, \tag{9.102}$$

where the fact that $\mathbf{H}^{(0)}_{af} = \mathbf{0}$ has been used. Together with corresponding expansions for the other matrices, this gives an expression for the inverse electron propagator matrix through order n as

$$\begin{aligned}\mathbf{G}_n^{-1}(E) &= \mathbf{R}^{(0)}_{aa} + \sum_{i=1}^{n} \mathbf{R}^{(i)}_{aa} \\ &- \left[\left(\sum_{i=1}^{n_1} \mathbf{H}^{(i)}_{af}\right)\left(\sum_{i=0}^{n_2} \mathbf{R}^{(i)}_{ff}\right)^{-1}\left(\sum_{i=1}^{n_1} \mathbf{H}^{\dagger(i)}_{af}\right)\right]^{(n)}.\end{aligned} \tag{9.103}$$

The first-order propagator vanishes and the lowest order expressions are obtained by calculating the various matrices to specific orders and by choosing the operator manifold f as follows:

$$\begin{aligned} n &= 2 \Rightarrow n_1 = 1, n_2 = 0; \mathbf{f} = \mathbf{h}_3, \\ n &= 3 \Rightarrow n_1 = 2, n_2 = 1; \mathbf{f} = \mathbf{h}_3, \\ n &= 4 \Rightarrow n_1 = 3, n_2 = 2; \mathbf{f} = \mathbf{h}_3 \cup \mathbf{h}_5, \end{aligned} \tag{9.104}$$

which will be further elaborated in the following sections.

Obviously the inversion of the very large matrix $\mathbf{R}_{ff}(E)$ is one of the difficult problems that has to be addressed. An inversion could be performed by employing a reduced linear equation (RLE) scheme but rapidly becomes impractical with increasing basis sets. A number of approximate treatments have been proposed with varying success. The order concept can be preserved with the identity

$$\begin{aligned}\mathbf{R}^{-1}_{ff}(E) &\equiv \left(\mathbf{R}^{(0)}_{ff} + \sum_{i=1}^{n} \mathbf{R}^{(i)}_{ff}\right)^{-1} \\ &\equiv \left(\mathbf{R}^{(0)}_{ff}\right)^{-1} - \left(\mathbf{R}^{(0)}_{ff}\right)^{-1}\left(\sum_{i=1}^{n} \mathbf{R}^{(i)}_{ff}\right)\left(\mathbf{R}^{(0)}_{ff} + \sum_{i=1}^{n} \mathbf{R}^{(i)}_{ff}\right)^{-1},\end{aligned} \tag{9.105}$$

which can be iterated and truncated.

9.2.1 Method of Solution

The general expression for the element

$$G_{pq}(E) = (a_p|(E\hat{I} - \hat{H})^{-1}a_q) \tag{9.106}$$

of the electron propagator matrix $\mathbf{G}(E)$ is symmetry blocked, where each block is formed by the spin orbital indices p and q belonging to the same irreducible representation of the orbitals. In addition, the electron propagator matrix $\mathbf{G}(E)$ is spin blocked. Therefore, it is sufficient to solve separately the electron propagator equations for each symmetry and spin block pq.

For a given block and energy E, it is possible to construct the matrix

$$\begin{aligned}
\mathbf{W}(E) &= E\mathbf{1} - \mathbf{G}^{-1}(E) \\
&= E\mathbf{1} - (\mathbf{R}_{aa}(E) - \mathbf{H}_{af}\mathbf{R}_{ff}^{-1}(E)\mathbf{H}_{af}^{\dagger}) \\
&= E\mathbf{1} - ((\mathbf{a}^{\dagger}|(E\hat{1} - \hat{H})|\mathbf{a}^{\dagger}) - \mathbf{H}_{af}\mathbf{R}_{ff}^{-1}(E)\mathbf{H}_{af}^{\dagger}) \\
&= E\mathbf{1} - ((E\mathbf{1} - \mathbf{H}_{aa} - \mathbf{H}_{af}\mathbf{R}_{ff}^{-1}(E)\mathbf{H}_{\mathbf{af}}^{\dagger}) \\
&= \mathbf{H}_{aa} + \mathbf{H}_{af}\mathbf{R}_{ff}^{-1}(E)\mathbf{H}_{\mathbf{af}}^{\dagger},
\end{aligned} \tag{9.107}$$

which allows the expression

$$(\mathbf{1}E - \mathbf{W}(E))\mathbf{G}(E) = \mathbf{1}. \tag{9.108}$$

This shows that the diagonalization

$$\begin{aligned}
\mathbf{U}^{\dagger}\mathbf{W}(E)\mathbf{U} = \mathbf{\Lambda}(E) &= \begin{pmatrix} \lambda_1(E) & \cdots & 0 \\ & \ddots & \\ \vdots & \lambda_p(E) & \vdots \\ & & \ddots \\ 0 & \cdots & \lambda_n(E) \end{pmatrix} \\
&= \mathbf{U}^{\dagger}(\mathbf{H}_{aa} + \mathbf{R}_{ab}^{\dagger}\mathbf{R}_{bb}^{-1}(E)\mathbf{R}_{ab})\mathbf{U},
\end{aligned} \tag{9.109}$$

is important, with n being the dimension of the symmetry pq block, and the eigenvalue corresponding to the spin orbital of interest (p) should be the p-th pole (E_p) of the electron propagator matrix. This eigenvalue can be used as the next guess for an iterative search of the p-th pole or used to obtain a guess for a Newton-Raphson procedure. As the derivatives of $\mathbf{W}(\mathbf{E})$ with respect to E can be evaluated analytically, a Newton-Raphson procedure can be efficiently employed to calculate the next guess for E, so that usually, after three or four iterations the difference between the input E and the eigenvalue is less than 10^{-5} Hartree.

Layzer[12] treated such (in general non-Hermitian) eigenvalue problems. When

$$\mathbf{U}_r(E) = \{U_{pr}\}, \qquad p = 1, 2, \cdots, n \tag{9.110}$$

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[12] A. J. Layzer, *Phys. Rev.* **129**, 897 (1963)

is the eigenvector of $\mathbf{W}(E)$ corresponding to the eigenvalue $\lambda_r(E)$ and $\mathbf{U}_r^*(E)$ is the eigenvector of $\mathbf{W}^\dagger$ corresponding to eigenvalue $\lambda_r^*(E)$, the expansion

$$G_{pq}(E) = \sum_r \frac{U_{pr}(E)\, U_{qr}^*(E)}{E - \lambda_r(E)} \tag{9.111}$$

follows. The types of possible solutions have been discussed by G. Csanak, H. S. Taylor, and R. Yaris,[13] and details have been explored by G. D. Purvis and Y. Öhrn[14]. The pole of interest E_r is found when

$$E_r = \lambda_r(E_r) \tag{9.112}$$

and within a finite basis, the E_r are real and discrete. Elementary residue calculus gives

$$\lim_{E \to E_R} \left[(E - E_r)\, G_{pq}(E)\right] = \Gamma_r U_{pr}(E_r)\, U_{qr}^*(E_r), \tag{9.113}$$

where

$$\Gamma_r = \left[1 - \frac{d\lambda_r(E)}{dE}\right]_{E=E_r} \tag{9.114}$$

is the pole strength introduced earlier. The resulting expression

$$G_{pq}(E) = \sum_r \frac{\Gamma_r U_{pr}(E_r) U_{qr}(E_r)}{E - E_r} \tag{9.115}$$

can then be compared with the spectral representation to find

$$\begin{aligned} \langle 0|a_p|r\rangle &= \Gamma_r^{1/2} U_{pr}(E_r(N+1) - E_0(N)), \\ \langle r|a_p|0\rangle &= \Gamma_r^{1/2} U_{pr}(E_0(N) - E_r(N-1)). \end{aligned} \tag{9.116}$$

The Feynman-Dyson amplitudes directly associated with the various electron binding energies are then

$$\chi^{FDA}(\xi) = \sum_p \chi_p(\xi) U_{pr}(E_r)\Gamma_r^{1/2} \tag{9.117}$$

in terms of the canonical molecular SCF spin orbitals.

The relationship of these amplitudes to the electron propagator

$$\begin{aligned} G(\xi, \xi'; E) &= \langle\langle \psi(\xi); \psi^\dagger(\xi')\rangle\rangle_E \\ &= \lim_{\eta \to +0} \sum_r \left[\frac{f_r(\xi) f_r^*(\xi')}{E + E_0(N) - E_r(N+1) + i\eta} \right. \\ &\quad \left. + \frac{g_r(\xi) g_r(\xi')}{E - E_0(N) + E_r(N-1) - i\eta} \right] \end{aligned} \tag{9.118}$$

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[13] G. Csanak, H. S. Taylor, and R. Yaris, *Advances in Atomic and Molecular Physics* **7**, 287 (1971)

[14] G. D. Purvis and Y. Öhrn, *J. Chem. Phys.* **60**, 4063 (1974)

defined in position and spin coordinate space becomes obvious from the expansion

$$\psi(\xi, t) = \sum_p \chi_p(\xi) a_p(t) \tag{9.119}$$

of the fundamental electron field operators $\psi(\xi, t)$ and their adjoints in the basis. The Feynman-Dyson amplitudes then are of two kinds associated with electron attachment processes and with electron detachment processes, respectively

$$\begin{aligned} f_r(\xi) &= \sum_p \chi_p(\xi)\langle 0|a_p|r\rangle = \sum_p \chi_p(\xi) U_{pr}\Gamma_r^{1/2}, \\ g_r(\xi) &= \sum_p \chi_p(\xi)\langle r|a_p|0\rangle = \sum_p \chi_p(\xi) U_{pr}\Gamma_r^{1/2}. \end{aligned} \tag{9.120}$$

9.2.2 A Possible Algorithm

1. choose r
2. get block pq
3. get guess for E_r
4. construct $\mathbf{W}(E) = \mathbf{H}_{aa} + \mathbf{H}_{af}\mathbf{R}_{ff}^{-1}(E_r)\mathbf{H}_{af}^{\dagger}$
5. diagonalize $\mathbf{UW}(E_r) = \lambda(E_r)\mathbf{1}$
6. get the eigenvalue λ_r associated with r
7. set $E_{new}^{(i)} = \lambda_r$
8. get new guess (Newton-Raphson):

$$E_{i+1} = E_i - \mathbf{G}^{-1}(E_i) / \left(\frac{\partial \mathbf{G}^{-1}(E)}{\partial E}\right)_{E=E_i} \tag{9.121}$$

9. $|E_i - E_{i-1}| < 10^{-5}$?
   a. ? yes ⇒ *Pole* $= E_i$
   b. ? no ⇒ go to step 3

9.2.3 Order Analysis of the Propagator Matrices

Second-order electron propagator

In the following, the subscript 1 refers to the $\mathbf{h}_1 = \mathbf{a}^{\dagger}$ part of the field operator manifold and the subscript 3 to the $\mathbf{h}_3$ part and so on. Through second order, the inverse of the electron propagator matrix then becomes

$$\mathbf{G}_{(2)}^{-1}(E) = \mathbf{R}_{11}^{(0)} - \mathbf{H}_{13}^{(1)}\left(\mathbf{R}_{33}^{(0)}(E)\right)^{-1}\left(\mathbf{H}_{13}^{(1)}\right)^{\dagger}, \tag{9.122}$$

where

$$\begin{aligned}
(\mathbf{R}_{11}^{(0)}(E))_{pq} &= (E-\epsilon_p)\delta_{pq}, \\
(\mathbf{H}_{13}^{(1)})_{p,abi} &= \langle pi||ab\rangle, \\
(\mathbf{H}_{13}^{(1)})_{p,ija} &= \langle pa||ij\rangle, \\
(\mathbf{R}_{33}^{(0)}(E))_{abi,cdj} &= (E+\epsilon_i-\epsilon_a-\epsilon_b)\delta_{ac}\delta_{bd}\delta_{ij}, \\
(\mathbf{R}_{33}^{(0)}(E))_{ija,klb} &= (E+\epsilon_a-\epsilon_i-\epsilon_j)\delta_{ik}\delta_{jl}\delta_{ab}.
\end{aligned} \tag{9.123}$$

The second-order self-energy matrix then has the elements

$$\begin{aligned}
(\Sigma^{(2)}(E))_{pq} &= \frac{1}{2}\sum_{i,a,b}\frac{\langle pi||ab\rangle\langle ab||qi\rangle}{E+\epsilon_i-\epsilon_a-\epsilon_b} \qquad (9.124)\\
&+ \frac{1}{2}\sum_{i,j,a}\frac{\langle pa||ij\rangle\langle ij||qa\rangle}{E+\epsilon_a-\epsilon_i-\epsilon_j},
\end{aligned}$$

where the factor of 1/2 comes from the relaxation of the ordered indices.

Third-order electron propagator

A similar treatment through third order yields

$$\begin{aligned}
\mathbf{G}_{(3)}^{-1}(E) &= \mathbf{G}_{(2)}^{-1}(E) \qquad (9.125)\\
&+\mathbf{H}_{11}^{(3)} - \mathbf{H}_{13}^{(1)}(\mathbf{R}_{33}^{(0)}(E))^{-1}\mathbf{H}_{33}^{(1)}(\mathbf{R}_{33}^{(0)}(E))^{-1}(\mathbf{H}_{13}^{(1)})^{\dagger} \\
&-\mathbf{H}_{13}^{(1)}(\mathbf{R}_{33}^{(0)}(E))^{-1}(\mathbf{H}_{13}^{(2)})^{\dagger} - \mathbf{H}_{13}^{(2)}(\mathbf{R}_{33}^{(0)}(E))^{-1}(\mathbf{H}_{13}^{(1)})^{\dagger},
\end{aligned}$$

where

$$\begin{aligned}
(\mathbf{H}_{11}^{(3)})_{pq} &= \sum_{a,b}\langle pa||bq\rangle\kappa_{ab} - \sum_{i,j}\langle pi||qj\rangle\kappa_{ij} \\
&+\sum_{i,a}(1+P(ia))\langle pi||qa\rangle k_i^a,
\end{aligned} \tag{9.126}$$

with

$$\begin{aligned}
\kappa_{ab} &= \sum_c\sum_{i>j} k_{ij}^{ac}k_{ij}^{bc}, \\
\kappa_{ij} &= \sum_l\sum_{a>b} k_{il}^{ab}k_{jl}^{ab}
\end{aligned} \tag{9.127}$$

and where $P(ia)$ is the permutational interchange operation. The second-order matrices are

$$(\mathbf{H}_{13}^{(2)})_{abi,p} = \sum_{m>n}\langle ip||mn\rangle k_{mn}^{ab}$$

$$\begin{aligned} & +(1-P(ab))\sum_{m,c}\langle pc||ma\rangle k^{bc}_{im}, \\ (\mathbf{H}^{(2)}_{13})_{ija,p} &= \sum_{b>c}\langle ap||bc\rangle k^{bc}_{ij} \\ & +(1-P(ij))\sum_{m,c}\langle pm||ci\rangle k^{ac}_{jm}, \end{aligned} \tag{9.128}$$

and the first-order diagonal terms are

$$\begin{aligned} \left(\mathbf{H}^{(1)}_{33}\right)_{abi,cdj} &= \delta_{ij}\langle ab||cd\rangle - \delta_{ac}\langle bj||di\rangle + \delta_{ad}\langle bj||ci\rangle \\ & +\delta_{bc}\langle aj||di\rangle - \delta_{bd}\langle aj||ci\rangle, \\ \left(\mathbf{H}^{(1)}_{33}\right)_{ija,klb} &= \delta_{ab}\langle ij||kl\rangle + \delta_{ik}\langle jb||la\rangle - \delta_{il}\langle jb||ka\rangle \\ & -\delta_{jk}\langle ib||la\rangle + \delta_{jl}\langle ib||ka\rangle. \end{aligned} \tag{9.129}$$

Fourth-order and partial fourth-order electron propagator

Without including the operator manifold $\mathbf{h}_5$, the full fourth-order propagator matrix can be expressed as

$$\begin{aligned} \mathbf{G}^{-1}_{(4)}(E) &= \mathbf{G}^{-1}_{(3)}(E) + \mathbf{H}^{(4)}_{11} - \mathbf{H}^{(2)}_{13}\left(\mathbf{R}^{(0)}_{33}(E)\right)^{-1}\mathbf{H}^{(2)\dagger}_{13} \\ & -\mathbf{H}^{(1)}_{13}\left(\mathbf{R}^{(0)}_{33}(E)\right)^{-1}\mathbf{H}^{(3)\dagger}_{13} - \mathbf{H}^{(3)}_{13}\left(\mathbf{R}^{(0)}_{33}(E)\right)^{-1}\mathbf{H}^{(1)\dagger}_{13} \\ & -\mathbf{H}^{(1)}_{13}\left(\mathbf{R}^{(0)}_{33}(E)\right)^{-1} bfH^{(1)}_{33}\left(\mathbf{R}^{(0)}_{33}(E)\right)^{-1}\mathbf{H}^{(2)\dagger}_{13} \\ & -\mathbf{H}^{(2)}_{13}\left(\mathbf{R}^{(0)}_{33}(E)\right)^{-1}\mathbf{H}^{(1)}_{33}\left(\mathbf{R}^{(0)}_{33}(E)\right)^{-1}\mathbf{H}^{(1)\dagger}_{13} \\ & -\mathbf{H}^{(1)}_{13}\left(\mathbf{R}^{(0)}_{33}(E)\right)^{-1}\mathbf{H}^{(2)}_{33}\left(\mathbf{R}^{(0)}_{33}(E)\right)^{-1}\mathbf{H}^{(1)\dagger}_{13} \\ & -\mathbf{H}^{(1)}_{13}\left(\mathbf{R}^{(0)}_{33}(E)\right)^{-1}\mathbf{H}^{(1)}_{33}\left(\mathbf{R}^{(0)}_{33}(E)\right)^{-1}\mathbf{H}^{(1)}_{33}\left(\mathbf{R}^{(0)}_{33}(E)\right)^{-1}\mathbf{H}^{(1)\dagger}_{13}. \end{aligned} \tag{9.130}$$

It is generally more important to include the contributions from the $\mathbf{h}_5$ manifold before increasing the order of the expansion, and one therefore finds it justifiable to study the electron propagator through what has been coined the "partial fourth-order", where only the terms formed from the matrices already obtained in third order are retained.

9.3 Recipe for Diagrams

We consider the diagramming of a perturbation series and choose the electron propagator self-energy expanded in terms of the electron interaction and expressed in terms of a Hartree-Fock spin orbital basis and the associated orbital energies.

Consider the sum

$$\frac{1}{2}\sum_{a,b}\sum_{p}\frac{\langle ip||ab\rangle\langle ab||jp\rangle}{E+\epsilon_p-\epsilon_a-\epsilon_b}, \tag{9.131}$$

where a and b denote occupied spin orbitals, p unoccupied spin orbitals, and i, j label unspecified Hartree-Fock spin orbitals. The two-electron integrals

$$\langle ip||ab\rangle = \int i^*(1)p^*(2)r_{12}^{-1}(1-P_{12})a(1)b(2)d(1)d(2) \tag{9.132}$$

are antisymmetric, *i.e.*, contain Coulomb minus exchange contributions.

9.3.1 STEP 1

Choose one of the antisymmetric two-electron integrals in Eq. (9.131) (say the second), and draw a line (dashed or wavy) to represent this interaction. In a formal scattering process, the left end of this interaction line represents the point where electron 1 enters and leaves, and the right end where electron 2 enters and leaves [see Fig. 9.2].

Figure 9.2: Interaction line of the integral $\langle a(1)b(2)||j(1)(p(2))\rangle$.

9.3.2 STEP 2

Draw propagation lines with arrows to indicate direction. The labels on the left side of the double bar in the integral notation $\langle a(1)b(2)||j(1)p(2)\rangle$ carry the "star" of complex conjugation, *i.e.*, label the (daggered) creation field operators in the hamiltonian, and stand for "outgoing" or "post-collision" electrons. The first letter (in this case "a") thus labels an outgoing electron, and we draw a solid line with an arrow going out of the left end of the interaction line. When "a," as in this case, also denotes an *occupied* spin orbital, the line goes *downward* in addition to going away from the end of the interaction line. An unoccupied orbital would have the solid line pointed up and away from the interaction line, and a general spin orbital would have the line going out horizontally.

The second label ("b") also stands for an outgoing electron in an occupied orbital, and we draw a solid line for it following the same convention, *i.e.*, down and out from the right end of the interaction line.

The labels on the right of the double bar represent "incoming" or "pre-collision" electrons, and we draw incoming solid lines. If the orbital is occupied, the lines comes down and in; if it is unoccupied, the line comes up and in; and if the orbital is a general one, the line comes in horizontally.

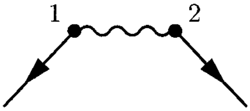

Figure 9.3: Orbitals a(1) and b(2) in $\langle a(1)b(2)||j(1)(p(2)\rangle$ depicted as "down and out" arrows.

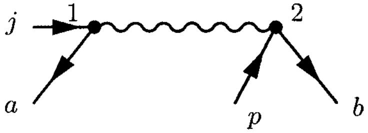

Figure 9.4: Integral $\langle a(1)b(2)||j(1)(p(2)\rangle$.

9.3.3 STEP 3

Decide whether the next interaction line should lie above or below the first interaction line. In our simple example the next interaction is $\langle ip||ab\rangle$. Since a downward line is not permitted to suddenly turn upward of its own (and an upward line suddenly to turn downward), and as $\langle ip||ab\rangle$ contains an incoming downward "a" line, which must be joined to the directed line in the above figure, we conclude that the new interaction line must lie below the first one. If contradictions occur at this stage, you have made a mistake.

Repeat STEP 2 for the second interaction line.

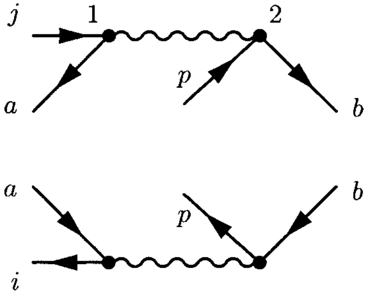

Figure 9.5: Integrals $\langle ab||jp\rangle$ and $\langle ip||ab\rangle$.

9.3.4 STEP 4

Join the solid propagation lines, which have the same label. As the lines are joined, check that each continuous line starting at one interaction and ending at another travels in only one direction.

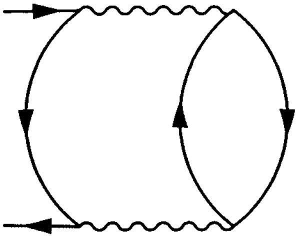

Figure 9.6: The second order diagram corresponding to Eq. (9.131).

9.3.5 REMARKS

The diagrammatic methods are ordinarily used to derive perturbation expressions. Here we have emphasized the converse approach primarily to familiarize ourselves with diagrams.

When a perturbation series cannot be diagrammed, it must be wrong. Diagrammatic analysis provides an *independent* check on the perturbation series. The diagrams used here are the kind discussed by Brandow. They are a combination of Goldstone and Hugenholtz diagrams. One distinguishing feature is the antisymmetrized interactions.

I. Diagrams for the self-energy have two horizontal lines with free ends. Diagrams for the total energy have no lines with free ends. Diagrams for the wavefunction have an even number of lines with free ends all entering from above all interaction lines (Kelly).

II. Include a factor 1/2 for each "equivalent pair" of lines. Two lines form an equivalent pair if they (1) both begin at the same interaction, and (2) both end at the same interaction (*i.e.*, both also go in the same direction).

III. Include an overall sign factor $(-1)^{l+h}$, where l = number of closed loops, and h = number of downgoing (internal) line segments ("hole lines").

IV. The numerator is a product of antisymmetrized two-electron integrals $\langle 12||34\rangle$, (1) "left out," (2) "right out," (3) "left in," (4) "right in," for each interaction line or vertex.

V. Include the energy denominators: the sum of all downgoing line energies minus the sum of all upgoing line energies between consecutive interaction lines constitute one factor; the product of all such factors constitute the denominator. The imaginary line joining the free lines gives the unspecified energy E.

VI. Sum each upgoing line independently over all unoccupied spin orbitals (particle states), and each downgoing line independently over all occupied spin orbitals (hole states).

9.4 Photoelectron Spectra

The calculation of electron binding energies and photoelectron intensities for atomic and molecular systems is a natural problem area for employing the electron propagator. In this section, some prototypical results are given for various levels of treatment. As an example, in the table below, the valence ionization energies for the N_2 molecule at various levels of theory are listed.

Table 9.1: Valence ionization energies (eV) for N_2

State	K.T. limit (a)	Delta SCF (b)	K.T. (c)	G(E) 2nd.ord (d)	G(E) 3rd order (e)	G(E) part. 4th order (f)	Exp. (g)
$3\sigma_g$	17.28	15.97	17.30	14.91	15.69	15.80	15.60
$1\pi_u$	16.74	15.38	16.72	17.23	18.04*	17.09	16.98
$2\sigma_u$	21.17	20.17	21.08	17.55	18.63	18.76	18.78

(a) Koopmans' Theorem (K.T.) results (i.e. orbital energies) from P. E. Cade, K. D. Sales, and A. C. Wahl, *J. Chem. Phys.* **44**, 1973 (1966).

(b) Estimated value from potential energy curves in reference (a).

(c) Hartree-Fock orbital energies with a 22 STO basis G. Purvis and Y. Öhrn, *Int. J. Quantum Chem.* **S11**, 359 (1977).

(d) from G. D. Purvis and Y. Öhrn, *J. Chem. Phys.* **60**, 4063 (1974).

(e) from T.T. Chen, W. D. Smith, and J. Simons, *Chem. Phys. Letters* **26**, 296 (1974); * this result is corrected from the one first given in this reference.

(f) partial fourth-order results from reference (c).

(g) from D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, *Molecular Photoelectron Spectroscopy*, Wiley, New York, 1970.

As can be seen from this example, for a small molecule, one can expect errors of about 1 eV to persist through the third-order treatment of the self-energy. Partial fourth-order theory has been applied with some success to small molecules, although it represents a substantial computational effort. The corrections of the orbital energies through second order tend to overshoot as is the case here. Delta SCF (see Eq.(9.32)) is not particularly good for valence binding energies, although it represents almost the entire correction for core binding energies.

The contributions to the self energy can be classified, as shown, into relaxation and correlation contributions. Performing a delta SCF calculation for a particular electron binding energy would account (by definition) for the entire relaxation contribution. The additional corrections can be labeled as correlation and when calculated through third order gives quite reasonable electron binding energies with typical errors of a few tenths of an electron volt.

Even in second-order theory some predictions may be reliable if only qualitative results suffice. For instance, if only the principal peaks in a photoelectron spectrum are needed, such as in the study of some simple donor-acceptor complexes, as borane (BH_3) with donors such as H_2O and CO.

Monomeric borane has a very short lifetime, but it is a strong Lewis acid and may be stabilized by forming complexes with Lewis bases. BH_3 resembles a transition metal atom in a low oxidation state, in the sense that it can form complexes with, say, carbon monoxide and phosphorous trifluoride having negligible basicity. It has been suggested that the complexes of BH_3 with

CO or PF_3 are formed via a π-type delocalization of the BH_3 e-orbitals into unoccupied CO and PF_3 orbitals. A motivation for the study of systems such as $BH_3 \bullet CO$ and $BH_3 \bullet H_2O$ is that it may provide experience as to the reliability and suitability of the electron propagator as a tool for analyzing PES experiments[15] on heterogeneous catalysis, for instance, CO chemisorption and reactions (methanol synthesis) on low oxidation state d^{10} transition metal oxide surfaces, such as ZnO(10$\bar{1}$0) and CuCl(111). The basis sets are correlated consistent pVDZ, which consist of (9s4p1d/[3s2p1d] for first row elements and (4s1p)/[2s1p] for hydrogen. All structures are optimized at the MBPT[2] level of theory. The results are listed in Table 9.2.

Table 9.2: Optimized geometries at the MBPT[2] level with pVDZ bases. The notation H_s means that the proton lies in the symmetry plane of the C_s point group.

Complex	Point Group	Geometrical Parameter	MBPT[2] /pVDZ	Experimental
$H_3B \bullet CO$	C_{3v}	BC	1.565 Å	1.540 Å
		CO	1.144 Å	1.131 Å
		BH	1.217 Å	1.194 Å
		CBH	103.8°	104.2°
$H_3B \bullet OC$	C_{3v}	BO	2.585 Å	
		CO	1.147 Å	
		BH	1.203 Å	
		OBH	90.9°	
$H_3B \bullet OH_2$	C_s	BO	1.730 Å	
		OH	0.963 Å	
		BH& BH_s	1.214 Å	
		OBH	100.6°	
		OBH_s	103.7°	
H_3B	D_{3h}	BH	1.203 Å	
CO	$C_{\infty v}$	CO	1.147 Å	1.128 Å
H_2O	C_{2v}	OH	0.964 Å	0.958 Å
		HOH	102.0°	104.5°

The photoelectron spectrum with a UV source (UPS) of $H_3B \bullet OH_2$ calculated at the SCF (Koopmans' theorem) and the EP2 levels are compared with experimental results in Table 9.3.

Due to the hydrolysis of diborane, the experimental investigation of the $H_3B \bullet OH_2$ complex is difficult and introduces some uncertainty about whether the observed features in the HeI spectrum really are due to $H_3B \bullet OH_2$ or something else. The agreement between the calculated (EP2) peaks and the UPS spectrum is as expected except for the observed feature at 14.4 eV. This is not consistent with the theoretical result, but before suggesting that this feature

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[15] see R. Longo, B. Champagne, and Y. Öhrn, *Theor. Chim. Acta* **90**, 397 (1995)

Table 9.3: Electron propagator poles at the SCF level (Koopmans) and at the EP2 level are compared with experiment for the $H_3B\bullet OH_2$ complex

Assignment	Koopmans (eV)	EP2 (eV) (Pole Strength)	Experiment UPS (eV)
π(B-H) 7a'	11.3	10.5 (0.93)	9.7
π(B-H) 7a"	11.8	11.1 (0.94)	10.6
σ(B-O) 6a'	15.6	13.5 (0.91)	11.8
n(O) 5a'	16.4	14.2 (0.90)	13.2
n(O) + σ(B-O) 4a'	20.7	18.6 (0.89)	14.4

might not be due to $H_3B\bullet OH_2$, the electron propagator calculations have to be carried to the third or partial fourth order and a larger basis should be used.

Comparison of the Koopmans' theorem and the EP2 results with experiment for the $H_3B\bullet CO$ complex is presented in Table 9.4. Experimental results from T. Pradeep and C. N. R. Rao[16] are used.

Table 9.4: Electron propagator poles at the SCF (Koopmans) level and at the EP2 level compared with experiment for the $H_3B\bullet CO$ complex

Assignment	Koopmans' (eV)	EP2 (eV) (Pole Strength)	Experiment UPS (eV)
2e (B-H)	12.8	11.9 (0.92)	11.9
6a$_1$ (B-C)	15.1	13.9 (0.91)	14.1
1e (C-O)	18.6	17.1 (0.87)	17.0
5a$_1$ (CO)	21.6	18.1 (0.85)	18.5*

* Adiabatic ionization energy

Similar calculations are carried out for the $H_3B\bullet OC$ complex and are reported in Table 9.5.

Table 9.5: Comparison of the electron propagator poles at the SCF (Koopmans) level and at the EP2 level with the same UPS spectrum as in Table 4

Assignment	Koopmans (eV)	EP2 (eV) (Pole strength)	Experiment UPS (eV)
2e (B-H)	13.2	12.6 (0.94)	11.9
6a$_1$ (B-C)	15.3	14.0 (0.92)	14.1
1e (C-O)	17.5	16.3 (0.89)	17.0
5a$_1$ (B-H)	18.7	17.5 (0.92)	
			18.5*
4a$_1$ (C-O)	22.5	19.0 (0.86)	

* Adiabatic ionization energy

There is definitely a better agreement between the calculated and the ob-

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[16] T. Pradeep and C. N. R. Rao, *J. Mol. Struct. (Theochem)* **200**, 339 (1989)

served PES for $H_3B\bullet CO$, than for $H_3B\bullet OC$ indicating the discriminatory power of the electron propagator theory even at this primitive level.

In conclusion, one can again reaffirm what already has been established by many workers in the field, namely, that the propagator theory is an appropriate and practical approach to the interpretation and prediction of spectra. The results presented here also show that in order to contain truly quantitative agreement with experiment, it is necessary to consider electron propagator theory at the third and partial fourth order and to also be able to accommodate larger basis sets.

9.5 Photoionization Cross Sections

The photoionization process involves an absorption of a photon as discussed in Section 6.3 on absorption spectroscopy. Rather than to use the result from that section, the photoionization cross section is discussed in terms of "first-quantization." This will introduce some appreciation for how the electron propagator amplitudes are related to the wavefunctions of the N- ,(N - 1), and (N + 1)-electron systems. The differential cross section for photoionization, *i.e.*, the probability that the system absorbs a photon and makes a transition from the ground state $|N\rangle$ to the excited state $|N,s\rangle$ in the continuum with one electron escaping into solid angle $d\Omega_f$ with wave vector $\vec{k}_f$ (and the rest of the system in a bound state) is[17]

$$\frac{d\sigma_s}{d\Omega_f} = \left(e^2 k_f/2\pi mc|A_0|^2\omega\right) |\langle N,s|\sum_{j=1}^{N} \vec{A}(\vec{r}_j)\cdot\vec{\nabla}_j|N\rangle|^2, \tag{9.133}$$

where $\vec{A}(\vec{r}) = A_0\vec{n}\exp(i\vec{k}\cdot\vec{r})$ is the vector potential of the monochromatic radiation field with polarization vector $\vec{n}$ and $\omega = kc$ is the circular frequency.

The N-electron ground state $|N\rangle$ is represented by the wavefunction $\Phi_0(\xi_1, \xi_2, \cdots \xi_N)$ and the final state $|N,s\rangle$ by the wavefunction $O_{AS}N^{\frac{1}{2}}v(\vec{k}_f,\xi_N)\Phi_s(\xi_1, \xi_2, \cdots \xi_{N-1})$.

Both Φ_0, and Φ_s are assumed to be antisymmetric in the electron indices and $O_{AS} = N^{-1}[1 - \sum_{k=1}^{N-1} P_{kN}]$ with the permutational interchanges P_{kN} guarantees that the final state is antisymmetric in all of the electron indices. This permits us to write

$$\begin{aligned}\langle N,s|\sum_{j=1}^{N}\vec{A}(\vec{r}_j)\cdot\vec{\nabla}_j|N\rangle &= \int v^*(\vec{k}_f,\xi)\vec{A}\cdot\vec{\nabla}g_s(\xi)d\xi \\ &+ \int v^*(\vec{k}_f,\xi)p_s(\xi)d\xi,\end{aligned} \tag{9.134}$$

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[17] see, *e.g.*, H.A. Bethe and E.E. Salpeter *Quantum Mechancis of One- and Two-Electron Atoms*, Academic Press, New York, 1957.

where $g_s(\xi) = N^{\frac{1}{2}} \int \Phi_s^*(\xi_1, \xi_2, \cdots \xi_{N-1}) \Phi_0(\xi_1, \cdots \xi_{N-1}, \xi) d\xi_1 \cdots d\xi_{N-1}$ and

$$\begin{aligned} p_s(\xi) &= (N-1)N^{\frac{1}{2}} \int \Phi_s^*(\xi_1, \xi_2, \cdots \xi_{N-1}) \vec{A}(\vec{r}_1) \\ &\quad \cdot \vec{\nabla}_1 \Phi_0(\xi_1, \cdots \xi_{N-1}, \xi) d\xi_1 \cdots d\xi_{N-1}. \end{aligned} \tag{9.135}$$

The photoelectron amplitude $v(\vec{k}_f, \xi)$ being strongly orthogonal to Φ_0 leads to the conclusion that the second term on the right-hand side of Eq. (9.134) vanishes. This can be accomplished by assuring that $v(\vec{k}_f, \xi)$ is orthogonal to the bound state basis set. This would be the case if the photoelectron amplitude was an orthogonalized plane wave. It can be shown that even when strong orthogonality does not exist, the first term in Eq. (9.134) dominates over the second term for photon energies away from threshold.

In cases as these,

$$\frac{d\sigma_s}{d\Omega_f} = \frac{e^2 k_f}{\pi m c \omega} \left| \int v^*(\vec{k}_f, \vec{r}) e^{i\vec{k}\cdot\vec{r}} \vec{n} \cdot \vec{\nabla} g_s(\vec{r}) d\vec{r} \right|^2 \tag{9.136}$$

where a factor 2 has been introduced for the two possible spins of the ejected electron. Further simplifications are possible when the wavelength of the ionizing radiation is large in comparison with the molecular dimensions. Then $\exp(i\vec{k} \cdot \vec{r}) \simeq 1$, and

$$\frac{d\sigma_s}{d\Omega_f} = \frac{e^2 k_f}{pimc\omega} |\vec{n} \cdot \vec{P}|^2, \tag{9.137}$$

with $\vec{P} = \int v^*(\vec{k}_f, \vec{r}) \vec{\nabla} g_s(\vec{r}) d\vec{r}$. For an isotropic sample, as a gas, the photoionization intensities represent an average over all incident photon directions. Furthermore, if the incident photon is unpolarized, one must average over polarizations:

$$\begin{aligned} \frac{d\sigma_s}{d\Omega_f} &= \frac{e^2 k_f}{\pi m c \omega 8\pi} \int [|\vec{n}_1 \cdot \vec{P}|^2 + |\vec{n}_2 \cdot \vec{P}|^2] d\Omega \\ &= \frac{e^2 k_f}{3\pi c \omega} |\vec{P}|^2. \end{aligned} \tag{9.138}$$

The result needs to be modified when the system is anisotropic or when the radiation is linearly or otherwise polarized.

The evaluation of $|\vec{P}|$ requires knowledge about the photoelectron amplitude. It should, of course, be calculated as a continuum amplitude from the Dyson equation, but for a general molecule that is still a tough problem, and one proceeds by making more or less *ad hoc* choices. The perhaps simplest description of the photoelectron is $v(\vec{k}_f, \vec{r}) = (2\pi)^{-\frac{3}{2}} \exp(i\vec{k}_f \cdot \vec{r})$. This choice of a plane wave is often referred to as the sudden approximation, or the zeroth-order Born approximation. If a primitive atomic orbital basis $\{\Phi_{\alpha j}(\vec{r} - \vec{R}_\alpha)\}$ is used,

$$\vec{P} = \frac{i\vec{k}_f}{(2\pi)^{\frac{3}{2}}} \sum_{\alpha,j} e^{-i\vec{k}_f \cdot \vec{R}_\alpha} c_{\alpha j}^s \int e^{-i\vec{k}_f \cdot \vec{r}} \Phi_{\alpha j}(\vec{r}) d\vec{r}. \tag{9.139}$$

If the detector is swept, one integrates over all photoelectron directions

$$\sigma_s = \left(e^2 k_f / 3\pi m c \omega\right) \int |\vec{P}|^2 d\Omega_f. \tag{9.140}$$

Since $\vec{P}$ involves summation over atomic centers, this expression for σ_s involves both one- and two-center terms.

For linearly polarized light (say in the $\vec{n}_1$ direction and with a plane wave, $v(\vec{k}_f, \vec{r}) = (2\pi)^{-3/2} \exp(i\vec{k}_f \cdot \vec{r})$, it holds that

$$\frac{d\sigma_s}{d\Omega_f} = \frac{e^2 k_f}{8\pi^4 m c \omega} |\vec{n}_1 \cdot \vec{k}_f|^2 \left| \int \exp\left(-i\vec{k}_f \cdot \vec{r}\right) g_s(\vec{r})\, d\vec{r} \right|^2, \tag{9.141}$$

or with $\vec{n}_1 \cdot \vec{k}_f = k_f cos\theta$, one gets a differential cross section of the form $\beta cos^2\theta$. This form does not agree with most experimental findings. However, with the term involving p_s nonzero, or with a photoelectron amplitude being a distorted wave, as for instance an orthogonalized plane wave, one obtains

$$\frac{d\sigma_s}{d\Omega_f} = \alpha + \beta \cos^2 \theta, \tag{9.142}$$

a form that agrees with much experimental data. Normally one controls the angle Θ between the incident photon direction, $\vec{k}$ and the direction $\vec{k}_f$ of the ejected electron. Then

$$\cos^2 \theta = \sin^2 \Theta \cos^2 \Phi \tag{9.143}$$

where the polarization direction $\vec{n}_1$, of course, is in a plane perpendicular to the propagation direction $\vec{k}$. Many experimental setups work with a fixed angle $\Theta = 90°$.

Problems

1. Show that g$_s$ is a Dyson amplitude, *i.e.*, $g_s(\xi) = \sum_i u_i(\xi) \langle N-1, s|a_i|N\rangle$ in terms of the basis spin orbitals.

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Chapter 10

Atomic and Molecular Orbitals

This chapter deals with the discussion and interpretation of approximate molecular electronic structure methods in terms of propagator concepts. Only situations with fixed nuclear frameworks are considered, and the discussion is limited to the description of states that are close in energy to the normal state of the system. We adopt the view that the main features of the electronic structure of such states can be developed in terms of atomic orbital representations of operators and that only valence shell orbitals need be considered.

10.1 Nonorthogonal Basis Sets

The treatment of orbital overlap in conjunction with the use of nonorthogonal basis sets deserves particular attention in treatments in terms of electron field operators. The definition of creation and annihilation operators and their anticommutation rules are basic for this development. Let $\{u_s(\xi)\}$ be a set of atomic spin orbitals used to define the creation operators

$$a_s^\dagger = \int u_s(\xi)\psi^\dagger(\xi)d\xi \tag{10.1}$$

and annihilation operators

$$a_s = \int u_s^*(\xi)\psi(\xi)d\xi. \tag{10.2}$$

The fundamental anticommutation rules

$$\begin{aligned} [\psi(\xi),\psi(\xi')]_+ &= [\psi^\dagger(\xi),\psi^\dagger(\xi')]_+ \\ &= [\psi(\xi),\psi^\dagger(\xi')]_+ - \delta(\xi-\xi') = 0 \end{aligned} \tag{10.3}$$

lead to the relations

$$\begin{aligned} [a_s, a_r]_+ &= [a_s^\dagger, a_r^\dagger]_+ = 0, \\ [a_s, a_r^\dagger]_+ &= \int u_s^*(\xi) u_r(\xi) d\xi = \delta_{sr} + S_{sr}. \end{aligned} \tag{10.4}$$

For an orthonormal basis set, all of the matrix elements S_{sr} equal zero. The basis defines a subspace of the total Hilbert space and a projection operator can be introduced through the kernel

$$D(\xi|\xi') = \sum_{s,r} u_s(\xi)[(\mathbf{1} + \mathbf{S})^{-1}]_{sr} u_r^*(\xi'), \tag{10.5}$$

which defines the components of the electron field operators in approximate electronic structure theory as

$$\begin{aligned} \psi(\xi) \rightarrow \psi_D(\xi) &= \int D(\xi|\xi')\psi(\xi')d\xi' \\ &= \sum_s u_s(\xi) a_s + \sum_{s,r} u_s(\xi) T_{sr} a_r, \end{aligned} \tag{10.6}$$

with $\mathbf{T} = \{T_{sr}\} = (\mathbf{1} + \mathbf{S})^{-1} - \mathbf{1}$. This truncated expansion of an electron field operator is an example of an approximate representation. Such approximations will impose limitations on the general theory, some of which will be discussed in this chapter.

There will also be corresponding approximate representations of the state vectors of interest. It will be assumed that such states can be generated from a common reference state, analogous to the vacuum state. The reference state $|0\rangle$ should have the property that

$$\psi_D(\xi)|0\rangle = 0 \tag{10.7}$$

and need not be specified further. A general state vector $|\Phi\rangle$ can be expressed as

$$|\Phi\rangle = \int d(12...N)\psi_D^\dagger(1)\psi_D^\dagger(2)\cdots\psi_D^\dagger(N)|0\rangle\Phi(12\cdots N) \tag{10.8}$$

or as

$$|\Phi\rangle = \sum a_r^\dagger a_s^\dagger \cdots a_t^\dagger |0\rangle \Phi_{rs\cdots t}, \tag{10.9}$$

where $\Phi(12\cdots N)$ and

$$\Phi_{rs\cdots t} \tag{10.10}$$

are the appropriate amplitudes corresponding to the wave function in a continuous or discrete representation, respectively. The dimension of this state vector space is 2^M, where M is the rank of the spin orbital basis $\{u_s(\xi)\}$.

The problem can now be formulated as one of finding the appropriate mapping from the states of physical interest to the model states given in Eqs. (10.8) and (10.9).

10.2 Green's Function Considerations

The formal structure of the electron propagator of a free atom can provide indications as to the appropriateness of the choice of limited basis set and the associated choice of model hamiltonian. We consider the Green's function

$$G(\xi,\xi^{'};E) = \sum_s \frac{A(\xi,\xi^{'};s)}{E-\epsilon_s \mp \eta}, \tag{10.11}$$

expressed in terms of the spectral weights $A(\xi,\xi^{'};s)$ and the electron attachment and detachment energies

$$\begin{aligned} \epsilon_s &= E_s(N+1) - E_0(N), \\ \epsilon_s &= E_0(N) - E_s(N-1). \end{aligned} \tag{10.12}$$

In the limited basis, the outer projection Green's function

$$\begin{aligned} G_D(\xi,\xi^{'};E) &= \langle\langle \psi_D(\xi); \psi_D^\dagger(\xi^{'})\rangle\rangle_\epsilon \\ &= \int d(12) D(\xi|1) G(1,2;\epsilon) D(2|\xi^{'}), \end{aligned} \tag{10.13}$$

and its corresponding spectral densities $A_D(\xi,\xi^{'};\epsilon)$ are the appropriate quantities. The projected spectral densities obey the sum rule

$$\int d\epsilon A_D(\xi,\xi^{'};\epsilon) = D(\xi|\xi^{'}) \tag{10.14}$$

to be compared with the relation

$$\sum_s A(\xi,\xi^{'};s) = \delta(\xi-\xi^{'}) \tag{10.15}$$

for the exact spectral weights.

For the case of a free atom, the low-lying states can often be described as arising from orbital configurations of the form $[s^{q(s)}p^{q(p)}]$. The limited basis then consists of the eight spin orbitals ($\xi = (\vec{r}, \zeta)$, $\nu = \pm\frac{1}{2}$)

$$\begin{aligned} u_{s\nu}(\xi) &= R_0(r)Y_{00}(\theta,\phi)\delta_{\nu\zeta}, \\ u_{x\nu}(\xi) &= R_1(r)[Y_{1-1}(\theta,\phi) - Y_{11}(\theta,\phi)]\delta_{\nu\zeta}/\sqrt{2}, \\ u_{y\nu}(\xi) &= R_1(r)[Y_{1-1}(\theta,\phi) + Y_{11}(\theta,\phi)]i\delta_{\nu\zeta}/\sqrt{2}, \\ u_{z\nu}(\xi) &= R_1(r)Y_{10}(\theta,\phi)\delta_{\nu\zeta}. \end{aligned} \tag{10.16}$$

The kernel $D(\xi|\xi')$ can then be expressed as

$$\begin{aligned} D(\xi|\xi') &= \delta_{\zeta\zeta'}[R_0(r)R_0^*(r') \\ &\quad +3P_1(\cos\Theta)R_1(r)R_1^*(r')]/4\pi, \end{aligned} \tag{10.17}$$

with

$$\cos\Theta = \vec{r}\cdot\vec{r}'/rr'. \tag{10.18}$$

One can now express the spectral density as

$$\begin{aligned} A_D(\xi,\xi';\epsilon) &= \delta_{\zeta\zeta'}[R_0(r)A_0(\epsilon)R_0^*(r') \\ &\quad +3P_1(\cos\Theta)R_1(r)A_1(\epsilon)R_1^*(r')]/4\pi, \end{aligned} \tag{10.19}$$

where the "orbital densities" $A_0(\epsilon)$ and $A_1(\epsilon)$ both sum to unity.

We have used moment expansions in terms of nested commutators in the determination of propagators, and these concepts are useful also in this context. The notation

$$\begin{aligned} a_r^{(k)} &= [a_r^{(k-1)}, H], \\ a_r^{(0)} &= a_r \end{aligned} \tag{10.20}$$

is introduced. The spectral densities can now be expressed as

$$\begin{aligned} \int d\epsilon\epsilon^k A_0(\epsilon) &= \langle[a_{s\frac{1}{2}}^{(k)}, a_{s\frac{1}{2}}^\dagger]_+\rangle \equiv W_0(k), \\ \int d\epsilon\epsilon^k A_1(\epsilon) &= \langle[a_{x\frac{1}{2}}^{(k)}, a_{x\frac{1}{2}}^\dagger]_+\rangle \equiv W_1(k). \end{aligned} \tag{10.21}$$

In these equations, the expectation value is supposed to be taken over a rotationally invariant ensemble as was used in Chapter 4. The moments $W_l(k)$

will depend on this choice of ensemble, and on the overlap between the radial amplitudes of Eq. (4.95) and the basis functions $R_l(r)$. When it holds, as is often the case, that these overlaps are large only for a few states, one can expect to be able to obtain approximate values for the moments from experimental energy levels by the means of fractional parentage and vector coupling coefficients. Similarly, one may assume moments to be known from calculations on atomic systems. Once known, the moments can be used to establish a model hamiltonian for an atomic valence shell.

A model hamiltonian should have the structure of the full hamiltonian, but could in principle have terms consisting of higher order products of annihilation and creation operators. Here we limit considerations to such operators that contain a one-electron part and an electron-electron interaction part. The number of independent matrix elements can be considerably reduced by symmetry considerations and by requiring compatibility with other operator representatives. It is clear that the form of the spectral density requires that the hamiltonian commutes with the total orbital angular momentum and with various spin operators. These are given in the limited basis as

$$\begin{aligned}\vec{L} = i\vec{e}_x\sum_\nu(a^\dagger_{z\nu}a_{y\nu} - a^\dagger_{y\nu}a_{z\nu}) &+ i\vec{e}_y\sum_\nu(a^\dagger_{x\nu}a_{z\nu} - a^\dagger_{z\nu}a_{x\nu}) \\ &+ i\vec{e}_z\sum_\nu(a^\dagger_{y\nu}a_{x\nu} - a^\dagger_{x\nu}a_{y\nu}) \qquad (10.22)\end{aligned}$$

and

$$\vec{S} = \vec{S}_s + \vec{S}_x + \vec{S}_y + \vec{S}_z, \tag{10.23}$$

with

$$\vec{S}_r = \vec{e}_x S_{rx} + \vec{e}_y S_{ry} + \vec{e}_z S_{rz}, \quad \text{for} \quad r = s, x, y, z \tag{10.24}$$

and

$$\begin{aligned}S_{rx} &= \left(a^\dagger_{r+\frac{1}{2}}a_{r-\frac{1}{2}} + a^\dagger_{r-\frac{1}{2}}a_{r+\frac{1}{2}}\right)/2, \\ S_{ry} &= -i\left(a^\dagger_{r+\frac{1}{2}}a_{r-\frac{1}{2}} - a^\dagger_{r-\frac{1}{2}}a_{r+\frac{1}{2}}\right)/2, \qquad (10.25) \\ S_{rz} &= \left(a^\dagger_{r+\frac{1}{2}}a_{r+\frac{1}{2}} + a^\dagger_{r-\frac{1}{2}}a_{r-\frac{1}{2}}\right)/2.\end{aligned}$$

The only one-electron part that commutes with $\vec{L}$ and $\vec{S}$ is a linear combination of the number operators N_l [see Eq. (4.102)], *i.e.*,

$$\begin{aligned}H &= \alpha_0 N_0 + \alpha_1 N_1 \qquad (10.26) \\ &= \alpha_0\sum_\nu a^\dagger_{s\nu}a_{s\nu} + \alpha_1\sum_\nu\left(a^\dagger_{x\nu}a_{x\nu} + a^\dagger_{y\nu}a_{y\nu} + a^\dagger_{z\nu}a_{z\nu}\right).\end{aligned}$$

Were we to choose this as our model hamiltonian, the coefficients α_l would be identified with the moments $W_l(k)$, which would guarantee that the first moment of the spectral density agrees with the experimentally determined value. This is equivalent to the assumption that α_l is the negative of the orbital electronegativity parameter.

The electron interaction terms are considerably more complicated than the one-electron part. They may be analyzed using the pair creation operators of Eq. (4.149). In Table 10.1 we give them in cartesian form for the limited basis.

Table 10.1: Pair creation operators for a set of *s*- and *p*-operators in cartesian form. Other operators for $S = 1$ can readily be obtained from the ones given using the "step-down" operator such that $[S_-, \pi^\dagger(S, M_S)] = \pi^\dagger(S, M_S)[(S + M_S)(S - M_S + 1)]^{\frac{1}{2}}$

γ	L	M_L	S	M_S	$\pi^\dagger(\gamma L M_L S M_S)$
s^2	0	0	0	0	$a^\dagger_{s\frac{1}{2}} a^\dagger_{s-\frac{1}{2}}$
sp	1	x	0	0	$(a^\dagger_{s\frac{1}{2}} a^\dagger_{x-\frac{1}{2}} - a^\dagger_{s-\frac{1}{2}} a^\dagger_{x\frac{1}{2}})/\sqrt{2}$
sp	1	y	0	0	$(a^\dagger_{s\frac{1}{2}} a^\dagger_{y-\frac{1}{2}} - a^\dagger_{s-\frac{1}{2}} a^\dagger_{y\frac{1}{2}})/\sqrt{2}$
sp	1	z	0	0	$(a^\dagger_{s\frac{1}{2}} a^\dagger_{z-\frac{1}{2}} - a^\dagger_{s-\frac{1}{2}} a^\dagger_{z\frac{1}{2}})/\sqrt{2}$
p^2	0	0	0	0	$(a^\dagger_{x\frac{1}{2}} a^\dagger_{x-\frac{1}{2}} + a^\dagger_{y\frac{1}{2}} a^\dagger_{y-\frac{1}{2}} + a^\dagger_{z\frac{1}{2}} a^\dagger_{z-\frac{1}{2}})/\sqrt{3}$
p^2	2	xy	0	0	$(a^\dagger_{x\frac{1}{2}} a^\dagger_{y-\frac{1}{2}} - a^\dagger_{x-\frac{1}{2}} a^\dagger_{y\frac{1}{2}})/\sqrt{2}$
p^2	2	yz	0	0	$(a^\dagger_{y\frac{1}{2}} a^\dagger_{z-\frac{1}{2}} - a^\dagger_{y-\frac{1}{2}} a^\dagger_{z\frac{1}{2}})/\sqrt{2}$
p^2	2	zx	0	0	$(a^\dagger_{z\frac{1}{2}} a^\dagger_{x-\frac{1}{2}} - a^\dagger_{z-\frac{1}{2}} a^\dagger_{x\frac{1}{2}})/\sqrt{2}$
p^2	2	$x^2 - y^2$	0	0	$(a^\dagger_{x\frac{1}{2}} a^\dagger_{x-\frac{1}{2}} - a^\dagger_{y\frac{1}{2}} a^\dagger_{y-\frac{1}{2}})/\sqrt{2}$
p^2	2	zz	0	0	$(2a^\dagger_{z\frac{1}{2}} a^\dagger_{z-\frac{1}{2}} - a^\dagger_{x\frac{1}{2}} a^\dagger_{x-\frac{1}{2}} + a^\dagger_{y\frac{1}{2}} a^\dagger_{y-\frac{1}{2}})/\sqrt{6}$
sp	1	x	1	1	$a^\dagger_{s\frac{1}{2}} a^\dagger_{x\frac{1}{2}}$
sp	1	y	1	1	$a^\dagger_{s\frac{1}{2}} a^\dagger_{y\frac{1}{2}}$
sp	1	z	1	1	$a^\dagger_{s\frac{1}{2}} a^\dagger_{z\frac{1}{2}}$
p^2	1	x	1	1	$a^\dagger_{y\frac{1}{2}} a^\dagger_{z\frac{1}{2}}$
p^2	1	y	1	1	$a^\dagger_{z\frac{1}{2}} a^\dagger_{x\frac{1}{2}}$
p^2	1	z	1	1	$a^\dagger_{x\frac{1}{2}} a^\dagger_{y\frac{1}{2}}$

As in the subshell hamiltonian in Eq. (4.150), there should be an interaction parameter $V(\gamma LS)$ corresponding to the electron pair operators. The possibility exists to introduce parameters that couple pair states of equal L and S but different γ's. We require that the two-particle part of the hamiltonian commutes with the *parity* operator

Table 10.2: Interaction parameter in terms of Slater-Condon F- and G-integrals

γ	L	S	$V(\gamma LS)$
s^2	0	0	$F^0(s,s)$
sp	1	0	$F^0(s,p)+(1/3)G^1(s,p)$
sp	1	1	$F^0(s,p)-(1/3)G^1(s,p)$
p^2	1	1	$F^0(p,p)-(1/5)F^2(p,p)$
p^2	2	0	$F^0(p,p)+(1/25)F^2(p,p)$
p^2	0	0	$F^0(p,p)+(2/5)F^2(p,p)$
s^2,p^2			$G^1(s,p)/\sqrt{3}$

$$P=\exp(i\pi\sum_l lN_l), \tag{10.27}$$

and this leaves us only one possible extra parameter to be called

$$V(s^2,p^2). \tag{10.28}$$

The interaction hamiltonian then has the form

$$\begin{aligned} H_{int} &= \sum V(\gamma LS)\pi^\dagger(\gamma LM_LSM_S)\pi(\gamma LM_LSM_S) \qquad (10.29)\\ &\quad +V(s^2,p^2)[\pi^\dagger(s^20000)\pi(p^20000)+\pi^\dagger(p^20000)\pi(s^20000)]. \end{aligned}$$

The parameters $V(\gamma LS)$ can be calculated from Slater-Condon F- and G-integrals and are given in Table 10.2.

In general, there could be seven parameters of this kind; however, we note that there are only five independent Slater-Condon parameters.

Accurate atomic energy levels could be determined from a hamiltonian $H+H_{int}$ expressed as in Eqs. (10.26) and (10.29) with the, in general, nine parameters (the seven $V(\gamma LS)$, and α_0 and α_1) at our disposal. Description of transitions between such energy levels requires a representative of the electric dipole moment operator in the chosen basis. We use the form

$$\vec{R}=e\int d\xi\psi_D^\dagger(\xi)\vec{r}\psi_D(\xi) \tag{10.30}$$

and introduce the notation

$$\mu=(e/\sqrt{3})\int drr^3R_0(r)R_1(r) \tag{10.31}$$

to write

$$R_x = \mu \sum_\nu (a^\dagger_{s\nu} a_{x\nu} + a^\dagger_{x\nu} a_{s\nu}), \tag{10.32}$$

and analogous expressions for the other cartesian components of the dipole moment operator. Obviously, these representatives of R_x, R_y, and R_z do not commute with one another, which is a typical result of the truncated basis. Furthermore, the dipole velocity operator commonly obtained via the commutator of $\vec{R}$ with the hamiltonian,*i.e.*,

$$\begin{aligned} \dot{R}_x &= -i[R_x, H + H_{int}] \\ &= -i\mu(\alpha_1 - \alpha_0) \sum_\nu (a^\dagger_{s\nu} a_{x\nu} - a^\dagger_{x\nu} a_{s\nu}) - i[R_x, H_{int}], \end{aligned} \tag{10.33}$$

has a two-particle contribution. The requirement that the dipole velocity operator should be represented as a single-particle operator, as it is in a complete basis, means that

$$[R_x, H_{int}] = 0 \tag{10.34}$$

must be satisfied. In order to accomplish this, we introduce relationships between the free parameters, such that only two independent interaction parameters $V(\gamma LS)$ remain.

A convenient form of the hamiltonian can then be found in terms of $N = N_0 + N_1$ and $\vec{S}$, which both commute with $\vec{R}$. Such a model hamiltonian can be expressed as

$$H_{atom} = \sum_l \alpha_l N_l + \frac{1}{2} K N(N-1) - J(\vec{S}^2 - \frac{3}{4} N), \tag{10.35}$$

with K an average Coulomb-type integral and J an exchange integral. When this hamiltonian is used to derive the moments of Eq. (10.21), we obtain

$$W_l(1) = \alpha_l + K\langle N \rangle - (K - \frac{3}{2} J)\langle N_l \rangle / (4l + 2), \tag{10.36}$$

which depends explicitly on the ensemble used for calculating the average values. The second moments are more involved, but one obtains straightforwardly the

$$\begin{aligned} W_l(2) &= W_l^2 + (K - \frac{3}{2} J)^2 \langle N_l \rangle (4l + 2 - \langle N_l \rangle)(4l+2)^{-2} \\ &\quad + (2K - J) J \langle \vec{S} \cdot \vec{S}_l \rangle (2l+1)^{-1} + J^2 \langle \vec{S}^2 \rangle, \end{aligned} \tag{10.37}$$

with $\vec{S}_0 = \vec{S}_s$ and $\vec{S}_1 = (\vec{S}_x + \vec{S}_y + \vec{S}_z)/3$ (see Eq. (10.24)).

The four parameters in the model hamiltonian may be determined in terms of the four moments $W_l(k)$, $l = 0, 1$; $k = 1, 2$. The detailed calculation of the moments may vary from case to case depending on the number of available energy levels and on which ensemble average is used to determine their relative weights. According to Eq. (4.99), we obtain the moments for a term as

$$\begin{aligned} W_l(\gamma LS, k) &= \sum_{\gamma', L', S'} \omega^k(\gamma' L' S') |\langle \gamma LS || a_l^\dagger || \gamma' L' S' \rangle|^2 \\ &\quad + (-1)^k \sum_{\gamma', L', S'} \omega^k(\gamma' L' S') |\langle \gamma' L' S' || a_l^\dagger || \gamma LS \rangle|^2, \end{aligned} \tag{10.38}$$

with

$$\omega^k(\gamma' L' S') = \frac{[E(\gamma' L' S') - E(\gamma LS)]^k}{(4l+2)(2L+1)(2S+1)}. \tag{10.39}$$

In Table 10.3, we list the weights for the configurations under considerations with the reduced matrix elements of creation operators obtained within the simple orbital picture.

Table 10.3: Weights for the calculation of moments of the spectral densities $A_l(\epsilon)$ for s^2p^n configurations. Note that for such configurations there is a unique spin multiplicity for each L- value

		$\frac{|\langle s^2p^nLS||a_1^\dagger||s^2p^{n-1}L'S'\rangle|^2}{6(2L+1)(2S+1)}$			$\frac{|\langle s^2p^{n+1}L'S'||a_1^\dagger||s^2p^nLS\rangle|^2}{6(2L+1)(2S+1)}$		
n	$L\backslash L'$	0	1	2	0	1	2
0	0	0	0	0	0	1	0
1	1	1/6	0	0	1/18	1/2	5/18
2	0	0	1/3	0	0	2/3	0
2	1	0	1/3	0	2/9	1/6	5/18
2	2	0	1/3	0	0	1/6	1/2
3	0	0	1/2	0	0	1/2	0
3	1	1/9	5/36	1/4	1/9	5/36	1/4
3	2	0	1/4	1/4	0	1/4	1/4
4	0	0	2/3	0	0	1/3	0
4	1	2/9	1/6	5/18	0	1/3	0
5	1	1/18	1/2	5/18	1/6	0	0
6	0	0	1	0	0	0	0

$$\frac{|\langle s^2p^nLS||a_1^\dagger||sp^nLS'\rangle|^2}{2(2L+1)(2S+1)} = \frac{2S'+1}{4S+2}$$

The calculation of the hamiltonian parameters from moments of the spectral density of the electron propagator offers a systematic approach to the general problem of assigning weights in a fitting procedure for energy levels. We notice that when J is neglected in the simple hamiltonian in Eq. (10.35), one recovers the result that the Coulomb parameter γ equals the difference between the ionization energy and the electron affinity of the atom.

10.3 A Simple Model Hamiltonian

Analysis of Green's functions can be useful in seeking to establish model hamiltonians with the property of giving approximately correct propagators, when put in the equations of motion. In this section, we explore a particularly simple model in order to familiarize the reader with various molecular orbital concepts using the terminology of Green's function theory. We employ the Hartree-Fock approximation and seek the molecular Fock operator matrix elements

$$f_{rs} = \langle [[a_r, H_{tot}], a_s^\dagger]_+ \rangle. \tag{10.40}$$

As a guide to this calculation, we consider the limit of separated atoms, for which we may write

$$f_{rs} \rightarrow \delta_{rs} W_r, \tag{10.41}$$

which can be derived from an effective hamiltonian

$$H_{eff} = \sum_r W_r a_r^\dagger a_r, \tag{10.42}$$

expressed in terms of only the first moments $W_r = W_r(1)$ of the atomic spectral density functions. When we assume that this effective hamiltonian also applies at interatomic distances in molecules and when the electron field operators refer to a nonorthogonal basis, Eq. (10.4) applies and we get

$$f_{rs} = \delta_{rs} W_r + S_{rs}(W_r + W_s) + \sum_t S_{rt} W_t S_{ts}. \tag{10.43}$$

This result is similar to the widely used approximations suggested using different arguments by Mulliken and by Wolfsberg and Helmholz. The equation of motion for the Green's function [Eq. (4.15)]

$$E G_{rs}(E) = \delta_{rs} + S_{rs} + W_r G_{rs}(E) + \sum_t S_{rt} W_t G_{ts}(E), \tag{10.44}$$

and in matrix form, this has the solution

$$\mathbf{G}(E) = [E(\mathbf{1} + \mathbf{S})^{-1} - \mathbf{W}]^{-1}, \tag{10.45}$$

where $\mathbf{W}$ is a diagonal matrix of moments.

It is often the case that all the elements W_r are negative, so we can write

$$W_r = -\kappa_r^2, \tag{10.46}$$

where κ_r are the elements of a diagonal positive definite matrix κ. An alternative form may then be given for this approximate electron propagator such that

$$\mathbf{G}(E) = \kappa^{-1}[E\mathbf{1} + \kappa(\mathbf{1} + \mathbf{S})\kappa]^{-1}\kappa(\mathbf{1} + \mathbf{S}). \tag{10.47}$$

This means that the poles of the Green's function, *i.e.*, the molecular orbital energies, are obtained as eigenvalues of a negative definite matrix with elements $-\kappa_r(\delta_{rs} + S_{rs})\kappa_s$. The molecular orbital coefficients can straightforwardly be inferred from the residues at the poles of this spectral representation.

In spite of the very simple assumptions leading to this model, it leads to quite acceptable approximate values for electron binding energies for molecular species when compared with some other approximate approaches. This model has been applied under the name Energy Weighted Maximum Overlap (EWMO) to a number of problems involving photoelectron spectra and to a number of problems in the interpretation of spin resonance experiments.

10.4 Electronic Indices from Green's Functions

The electron propagator can be used to calculate the charge distribution and other electronic indices that are relevant for a discussion of ground state properties of molecules. We will examine in detail the Mulliken population analysis, which attempts to relate charge distributions to a partial occupation of atomic orbitals and valence shells.

The number operator for electrons in a limited basis is obtained from Eq. (10.6) as

$$N_{op} = \sum_r [a_r^\dagger + \sum_s a_s^\dagger T_{sr}]a_r = \sum_r N_r, \tag{10.48}$$

where N_r are the so-called population operators. These operators mutually commute and are idempotent, but not Hermitian. The gross population of spin orbital r is defined by the expectation value

$$N(r) = \langle N_r \rangle = \frac{1}{2\pi i}\int_C dE \sum_s G_{rs}(E)[\delta_{sr} + T_{sr}], \tag{10.49}$$

where we have invoked the definition of the reduced density matrix from Eq. (4.38). When we now use the particular EWMO propagator, we get

$$N(r) = (2\pi i)^{-1}\int_C dE[E\mathbf{1} + \kappa(\mathbf{1} + \mathbf{S})\kappa]_{rr}^{-1}, \tag{10.50}$$

which is the result that would have been obtained for an orthonormal set of orbitals had we chosen the Fock operator matrix elements as

$$-\kappa_r(\delta_{rs} + S_{rs})\kappa_s. \tag{10.51}$$

The gross atomic population, which gives a measure of the formal charge of an atom in a molecule, is defined as the sum over all $N(r)$ for r a spin orbital on the atom under consideration.

The population numbers $N(r)$ are clearly not physical observables in a strict sense, but serve as electronic indices, which may be employed in various ways.

Table 10.4: Electron binding energies (in eV) of the molecules SF_6 (O_h symmetry) and CF_4 (T_d symmetry) calculated in various approximate ways and compared with measured values from photoelectron spectroscopy

Molecule	Symm.	(a)	(b)	(c)	(d)	Exp.
SF_6	e_g	19.4	17.5	17.8	18.1	~ 16
	t_{1u}	19.0	16.8	21.5	18.5	
	t_{1g}	18.2	15.9	22.4	17.9	17.3
	t_{2u}	19.4	16.8	23.1	19.1	18.7
	t_{2g}	22.2	18.8	24.2	21.7	19.9
	t_{1u}	24.7	21.8	29.0	23.5	22.9
	a_{1g}	29.6	26.7	30.8	27.5	27.0
	e_g	45.4	35.6	43.1	41.4	39.3
	t_{1u}	46.9	36.5	50.8	47.4	41.2
	a_{1g}	50.4	39.3	57.0	57.4	44.2
CF_4	t_2		16.2	20.5	18.2	16.1
	t_1		15.3	22.5	18.3	17.4
	e		16.8	23.6	20.5	18.5
	t_2		20.8	28.5	23.5	22.2
	a_1		23.4	29.8	25.9	25.1
	t_2		35.0	48.5	45.7	40.3
	a_1		37.7	55.0	56.3	43.8

(a) Hartree-Fock calculations with Gaussian basis set from U. Gelius, B. Roos, and P. Siegbahn, *Chem. Phys. Lett.* **4**, 471 (1970) as quoted in (b).

(b) "Muffin-tin" potential, one-electron self-consistent calculation, J. W. D. Connolly, and K. H. Johnson, *Chem. Phys. Lett.* **10**, 616 (1971) for SF_6, and J. W. D. Connolly, *Int. J. Quantum Chem.* **S6**, 201 (1972) for CF_4.

(c) CNDO approximation, K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Hedén, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, *ESCA Applied to Free Molecules*, North-Holland Publishing Co., Amsterdam, 1969. This reference also contains the experimental values.

(d) The values are the poles of electron propagator in Eq. (10.47) with W_r taken as the free atom Hartree-Fock orbital energies. Overlap integral are calculated from the corresponding atomic orbitals given by E. Clementi, *Tables of Atomic Functions*, Suppl. to *IBM Journal of Research and Development* **9**, (1965)

For instance, they can be used to estimate the molecular dipole moment in a point charge model with the dipole moment operator approximated as

$$\vec{R} = \sum_s N_s \int d\xi \vec{r} |u_r(\xi)|^2. \tag{10.52}$$

Other electronic indices are the bond orders, which may be correlated with bond distances and bond energies. Their definition in the context of nonorthogonal orbitals has been the subject of much discussion. The simple EWMO model examined here offers a definition of a bond order matrix element as

$$p_{rs} = (2\pi i)^{-1} \int_C dE[E\mathbf{1} + \kappa(\mathbf{1} + \mathbf{S})\kappa]^{-1}_{rs}. \tag{10.53}$$

This is in line with the definition used in Hückel theory.

10.5 Orthogonalized Atomic Orbitals

A variety of models for molecular electronic structure have been developed where the overlap problem has been circumvented by using formally orthogonalized orbital. In a separate chapter, we examine in some detail the Pariser-Parr-Pople model for π-electron systems. In this section, we discuss some of the common general features of such models. The symmetric orthogonalization procedure introduced by Löwdin offers a unique transformation of a set of atomic orbitals to an orthonormal set, where each member has the maximum overlap with a corresponding member of the original set still consistent with orthonormality. The orthogonal set obtained in this fashion is denoted $\{\tilde{u}_s(\xi)\}$, while the original nonorthogonal basis is denoted $\{u_s(\xi)\}$.

We write

$$u_s(\xi) = \sum_t \tilde{u}_t(\xi) c_{ts}, \tag{10.54}$$

with

$$c_{ts} = \int d\xi \tilde{u}^*_t(\xi) u_s(\xi). \tag{10.55}$$

From these relations, it follows that

$$\delta_{rs} + S_{rs} = \sum_t c^*_{tr} c_{ts}. \tag{10.56}$$

A general expression for the expansion coefficients that satisfy this relation can be expressed as

$$c_{ts} = \sum_k Y_{tk}[1 + \lambda_k]^{\frac{1}{2}} X^\dagger_{ks}, \tag{10.57}$$

where $\mathbf{X} = \{X_{sk}\}$ is a unitary matrix satisfying

$$\sum_{r,s} X^\dagger_{kr} S_{rs} X_{sk'} = \lambda_k \delta_{kk'}, \tag{10.58}$$

and where $\mathbf{Y} = \{Y_{rk}\}$ is another unitary matrix, which may be varied. The maximum overlap property between members of the two sets may be formulated in terms of the expression

$$\sum_s \int d\xi |u_s(\xi) - \tilde{u}_s(\xi)|^2 = \sum_s [2 - c_{ss} - c^*_{ss}], \tag{10.59}$$

which should be a minimum when the unitary matrix $\mathbf{Y}$ is varied. The optimum choice is found to be $\mathbf{Y} = \mathbf{X}$, which leads to the result

$$\mathbf{c} = \{c_{ts}\} = (\mathbf{1} + \mathbf{S})^{\frac{1}{2}}. \tag{10.60}$$

According to the definition of the electron field operators in a basis (Eqs. (10.1) and (10.2)), the basis electron field operator transformations are

$$a_s^\dagger = \sum_t \tilde{a}_t^\dagger c_{ts} \tag{10.61}$$

and the corresponding relation for the annihilators. The transformed operators $\tilde{a}_s$ and $\tilde{a}_s^\dagger$ satisfy the appropriate anticommutation relations for an orthonormal basis.

When the orthonormal set $\{\tilde{u}_s(\xi)\}$ is now employed for representations of the hamiltonian and other relevant operators, it is in approximate theories taken as a justification to neglect in a first approximation integrals involving the product density of spin orbitals associated with different atomic centers. This is the so-called Zero Differential Overlap (ZDO) approximation. The charge density operator, for instance, would then become

$$\begin{aligned} q(\vec{r}) = e\sum_{spin} \psi_D^\dagger(\xi)\psi_D(\xi) &= e \sum_{spin,s,t} \tilde{u}_s^*(\xi)\tilde{u}_t(\xi)\tilde{a}_s^\dagger\tilde{a}_t \\ &\simeq \sum_A q_A(\vec{r}), \end{aligned} \tag{10.62}$$

where $q_A(\vec{r})$ is an atomic charge density operator defined as a partial sum over spin orbital s and t, belonging to atom A. Two-center terms are neglected, and the approximation has been termed Neglect of Diatomic Differential Overlap (NDDO).

A more drastic approximation than the NDDO is the Complete Neglect of Differential Overlap (CNDO), where all cross products in Eq. (10.62) are omitted and the atomic charge density operator is simply

$$q_A(\vec{r}) = e\sum_{spin}\sum_{s\epsilon A} |\tilde{u}_s(\xi)|^2\tilde{a}_s^\dagger\tilde{a}_s. \tag{10.63}$$

Both the NDDO and the CNDO assumptions apply only to matrix elements involving the charge density operator. Other arguments have to be used for matrix elements of other operators, such as the kinetic energy and the current density.

The properties of the charge density operator $q_A(\vec{r})$ warrants some additional comments. The incomplete basis set causes the charge density operator at $\vec{r}$ not to commute with the position vector $\vec{r}' \neq \vec{r}$. The CNDO approximation restores this commutation property of the full theory. The cost of this is rather high because then also the dipole moment operator will have a representation where so-called atomic dipoles are neglected. This means that matrix elements of the position operator between orbitals on the same atom are omitted even though these are important for the determination of transition moments, for instance, between *s*- and *p*-orbitals. Furthermore, the form of $q_A(\vec{r})$ should be invariant under unitary transformations among the basis orbitals of atom A. This implies that the CNDO approximation must be used in a form such as

$$q_A(\vec{r}) = e|\tilde{u}_A|^2 \sum_{s\epsilon A} \tilde{a}_s^\dagger \tilde{a}_s = e|\tilde{u}_A|^2 N_A, \tag{10.64}$$

with N_A the number operator for atom A and where $|\tilde{u}_A|^2$ denotes a representative orbital density on atom A. With the CNDO approximation for the charge density operator, the electron interaction term of the hamiltonian becomes

$$H_{int} \simeq \frac{1}{2} \sum \gamma_{AB} N_A (N_B - \delta_{AB}). \tag{10.65}$$

The one-electron terms in the total hamiltonian cannot be expressed only in terms of the charge density and one adopts the general form

$$\sum_{r,s} h_{rs} \tilde{a}_r^\dagger \tilde{a}_s, \tag{10.66}$$

where the off-diagonal elements h_{rs} are proportional to the overlap integral S_{rs}. The remaining diagonal elements h_{rr} are usually chosen such that atomic properties are reproduced when S_{rs}, and thus, the so-called hopping terms h_{rs} are omitted.

We can use the total hamiltonian

$$H = \sum_{r,s} h_{rs} \tilde{a}_r^\dagger \tilde{a}_s + \frac{1}{2} \sum_{A,B} \gamma_{AB} N_A (N_B - \delta_{AB}) \tag{10.67}$$

to obtain the following expression for the Fock operator matrix elements in the basis:

$$f_{rs} = \langle [[\tilde{a}_r, H], \tilde{a}_s^\dagger]_+ \rangle = h_{rs} - \gamma_{AB} \langle \tilde{a}_s^\dagger \tilde{a}_r \rangle + \delta_{sr} \sum_C \gamma_{AC} \langle N_C \rangle \tag{10.68}$$

where spin orbitals r and s are associated with atoms A and B, respectively.

Neglect of off-diagonal elements leads to that the number operators N_A commute with the total hamiltonian and that the bond orders $\langle \tilde{a}_s^\dagger \tilde{a}_r \rangle$ vanish. It also follows that the expectation values $\langle N_C \rangle$ assume integer values that equal the normal number of occupied valence spin orbitals in an isolated atom, *i.e.*, $\langle N_C \rangle \to Z_C$. Identification with the separated atoms limit and comparison with Eq. (10.36) for the diagonal elements of the Fock matrix lead to

$$f_{rr} = \alpha_r + \gamma_{AA}(Z_A - \langle \tilde{a}_r^\dagger \tilde{a}_r \rangle) + \sum_C \gamma_{AC}(\langle N_C \rangle - Z_C). \tag{10.69}$$

From the above discussion, it follows that the construction of parameterized hamiltonians for molecular orbital calculations may lead to certain operator relationships being violated in a limited basis. It is also clear that some of these operator relations can be restored at the expense of introducing various approximations in the evaluation of integrals. Atomic parameters may be derived from consideration of the separated atoms limit, while interatomic parameters are commonly associated with overlap integrals and possibly other functions of the interatomic distance. For instance, it is often assumed that when r is a spin orbital on atom A and s is one on atom B, a suitable form for the hopping term is

$$h_{rs} = \frac{1}{2}(\beta_A + \beta_B) S_{rs}, \tag{10.70}$$

where the β parameters may be determined from comparisons with experimental or theoretical data for selected molecules. The CNDO form in Eq. (10.63) of the one-electron off-diagonal matrix elements leads to the following expression for the many-electron hamiltonian in the CNDO approximation; the CNDO model hamiltonian:

$$\begin{aligned} H(CNDO) &= const. + \sum_s \alpha_s \tilde{a}_s^\dagger \tilde{a}_s + \frac{1}{2}\sum_{r,s} (\beta_A + \beta_B) S_{rs} \tilde{a}_r^\dagger \tilde{a}_s \\ &\quad + \frac{1}{2}\sum_{A,B} \gamma_{AB}(N_A - Z_A)(N_B - Z_B) \\ &\quad + \sum_A \gamma_{AA} N_A (Z_A - \frac{1}{2}). \end{aligned} \tag{10.71}$$

The constant contribution to the hamiltonian is significant only in the sense that it can serve to define an appropriate average value for some reference state.

We saw in connection with the establishment of the atomic model hamiltonian that it commutes with the electric dipole moment operator even if it contains average exchange integrals. Strict application of the CNDO approximation of Eq. (10.63) yield a purely diagonal representation of the dipole moment, but it is the general experience that both transition moments and permanent electric dipole moments have significant contributions from intra-atomic dipole integrals. Thus, one would favor the NDDO approximation over the CNDO. The arguments leading to Eq. (10.34) showed on the other hand that only electron interaction terms constructed from the number operators N_A and spin operators $\vec{S}_A$ could be considered. Based on such arguments, we can put forth a model hamiltonian containing intra- and interatomic exchange integrals J_{AB}, such as

$$H(CNDOX) = H(CNDO) - \sum_{A,B} J_{AB}\vec{S}_A \cdot \vec{S}_B. \qquad (10.72)$$

The interatomic exchange integrals would be zero in any approximation where diatomic differential overlap is neglected, while the intra-atomic exchange is included in the approximation called Intermediate Neglect of Differential Overlap (INDO). The form of hamiltonian in Eq. (10.72) is more restricted than the one which applies for the NDDO approximation. These restrictions are imposed by Eq. (10.34) as soon as the dipole moment operator cannot be expressed in terms of the N_A's only.

Notes and Bibliography

- Many of the arguments and approximations in molecular orbital theory based on linear combinations of atomic orbitals are those of Robert S. Mulliken. In particular, we refer to his review in *J. chim. phys.* **46**, 497 and 675 from 1949.
- The idea of population analysis is put forth in *J. Chem. Phys.* **23**, 1833 (1955).
- Orthogonalized atomic orbitals as they are defined in this chapter were first suggested by P. O. Löwdin in *J. Chem. Phys.* **18**, 365 (1959).
- The NDDO, INDO, and CNDO models are reviewed by J. A. Pople and D. L. Beveridge in *Approximate Molecular Orbital Theory*, McGraw-Hill, 1970.
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  - photoelectron spectra (see J. Spanget-Larsen in *J. Electr. Spectry*, **3**, 369 (1974)),
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Chapter 11

The Pariser-Parr-Pople Model

11.1 Introduction

Propagator or Green's function methods are employed in this chapter to analyze the many-electron problem in planar unsaturated molecules as treated within the Pariser-Parr-Pople (PPP) model. A derivation of the model in many-electron theory serves to demonstrate the nature of the approximations involved. Applications are presented for the case of weakly interacting atoms. A decoupling procedure for Green's functions proposed by the authors is shown capable of yielding a correct description of this case.

Propagators have the advantage of giving direct information about transition energies and amplitudes from a reference state, but like density matrices, they suffer from a lack of simple ways generally to ensure so-called N-representability or correspondence to proper many-electron state vectors. Nevertheless, the propagator approach to semi-empirical many-electron theory appears to have certain advantages over other methods. Such treatment has led to useful relations between matrix elements in the PPP-model [1].

The molecular orbital method is a very flexible and often successful tool for analyzing electronic structure-dependent properties. Its deficiencies are intimately connected with the treatment of superpositions of configurations. In particular, the molecular orbital model is not satisfactory when the overlap between relevant valence orbitals on adjacent atoms is smaller than 1/2. This result was particularly well illustrated by Coulson and Fischer [2] in their well-known study of the hydrogen molecule, and it is relevant for the molecular orbital treatment of π-electron systems, where the typical overlap is in the range 1/3-1/4. Evidence has also been presented for the insufficiency of the PPP-model when

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[1] J. Linderberg, *Chem. Phys. Lett.* **1**, 39 (1967)

[2] C. A. Coulson and I. Fischer, *Philos. Mag.* **303**, 386 (1949)

the overlap exceeds 1/2 [3]. Thus, it appears that the construction of approximate eigenstates to the PPP-hamiltonian using the molecular orbital method requires considerable justification. The instabilities of the normal molecular orbital ground state noticed in the application of the random phase approximation further supports this view. Extensions of the simplest molecular orbital picture to include superposition of configurations have been reported by several authors, and Cizek [4] has given an effective formulation of the problem. However, the drawback of such an approach is the need to perform separate calculations for different states and the difficulty in claiming similar accuracy for separate calculations. The propagator approaches have the advantage that they give direct information on energy differences of sets of states and that the approximations generally yield similar accuracy for all states considered.

An alternative approach to extend the molecular orbital method is offered by the work of Hubbard [5] for the study of narrow energy bands in solids with the aim to study magnetism. The main idea of this work is to analyze the many-electron problem for the case of separated atoms, which means the limit of zero bandwidth.

A separation of intra- and interatomic characteristics is sought. Rather than proceeding with a perturbation theory treatment from the separated atomic limit, which appears to be too complicated for actual applications, we apply a decoupling procedure for the truncation of the chains of propagator equations. This suggests a general technique for systematic decoupling of such equations. The next section casts the derivation of the PPP π-electron approximation in terms of electron field operators. The second section contains an analysis of the separated atom limit. Special attention is given to the definition of elementary excitation operators and the relationship to the Heisenberg spin hamiltonian for the determination of the ground state energy. The third section deals with interatomic terms and the propagator decoupling procedure. In the fourth section, various expectation values needed for the equations of motion are calculated. The proposed scheme is applied in the fifth section to the infinite linear chain.

11.2 Reduction to the Pariser-Parr-Pople Model

In order to derive the PPP-hamiltonian, it is assumed that the nuclear framework of the molecular system is invariant under the point group C_s, which contains the operations of identity and a reflection. This is not always true for all molecules to which the model is applied, and then the magnitude of the perturbation caused by the noninvariant part of the nuclear potential must be examined. The electron field operators $\psi(\xi, t)$ are expressed as the sum of two components, each transforming according to an irreducible representation of C_s,

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[3] I. Fischer-Hjalmars, in *Adv. Quantum Chem.*, P.O. Löwdin, Ed., Academic Press Inc., New York, 1965, Vol. 2, p. 25

[4] J. Cizek, *J. Chem. Phys.* **45**, 4256 (1966)

[5] J. Hubbard, *Proc. Roy. Soc.* (London) **A244**, 199 (1958)

such that

$$\psi(\xi) = \psi(a',\xi) + \psi(a'',\xi). \tag{11.1}$$

The a'- and a''-components are the σ- and π-components, respectively, in the conventional nomenclature.

As the "σ-field" and the "π-field" are orthogonal by symmetry, the total number operator for electrons is simply the sum

$$N_{op} = \int d\xi \psi^\dagger(\xi)\psi(\xi) = N(a') + N(a'') \tag{11.2}$$

of number operators for the two separate fields. The hamiltonian is obtained as a sum of several terms

$$H = H_0 + H_1 + H_2, \tag{11.3}$$

where ($\hbar = 1$)

$$\begin{aligned} H_0 &= \frac{1}{2}e^2 \sum_{g\neq h} Z_g Z_h / |\vec{R}_g - \vec{R}_h|, && (11.4) \\ H_1 &= \int d\xi \psi^\dagger(\xi)[-(1/2m)\nabla^2 - e^2 \sum Z_g/|\vec{r} - \vec{R}_g|]\psi(\xi) && (11.5) \\ &= H_1(a') + H_1(a''), \\ H_2 &= \frac{1}{2}e^2 \int d\xi d\xi' |\vec{r} - \vec{r}'|^{-1} \psi^\dagger(\xi)\psi^\dagger(\xi')\psi(\xi')\psi(\xi) && (11.6) \\ &= H_2(a',a',a',a') + 2H_2(a'',a',a',a'') + 2H_2(a'',a',a'',a') \\ &+ H_2(a',a',a'',a'') + H_2(a'',a'',a',a') + H_2(a'',a'',a'',a''). \end{aligned}$$

The hamiltonian has in this manner been divided into parts that represent in order: the mutual repulsion of nuclei, the kinetic and potential energy of the "σ- and π-fields," the self-interaction of the "σ-field," the coulomb and exchange interactions between the "σ- and π-fields," the energy of transfer of electrons from π to σ and reverse, and finally the self interaction of the "π-field."

Electron transfer between the two "fields," *i.e.*, the fourth and fifth terms of H_2, do not commute with $N(a')$ and $N(a'')$ separately and prevent the number of π-electrons from being a constant of the motion. The omission of these terms is equivalent to the *ansatz* of Lykos and Parr[6]. A perturbation theory argument can be made to show that the effect of this omission is small when the ratio of exchange-like integrals between σ and π orbitals or reverse is small. This approximation appears to be more valid than some others introduced in the following.

A second step considered by Lykos and Parr is the "freezing" of the σ-part. In second quantization, this corresponds to a neglect of the operator nature of $\psi(a',\xi)$ and the replacement of products such as $\psi^\dagger(a',\xi')\psi(a',\xi)$ with their expectation values, assuming that such average values are not dependent on the particulars of the states under consideration. This is a crucial point in the

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[6] P. G. Lykos and R. G. Parr, *J. Chem. Phys.* **24**, 1166 (1956)

establishment of the PPP model and requires special attention. Perturbation theory arguments can be presented that show that the approximation is not severe when the polarizability of the molecular σ-skeleton is small. Particularly interesting in this connection is an experimental study of the optical reflectivity of graphite by Taft and Philipp [7]. It demonstrates convincingly that it is meaningful to consider a separation of a σ- and π-part of the electrons. One would expect this to hold true for most planar unsaturated molecules at least in describing their response to long wavelength optical excitations. The study of Taft and Philipp also demonstrates that the polarizability of the σ-skeleton is not small and that dispersive effects are not important for energies below the $10-16eV$ range. The total effect of the σ-system is to shift the resonance energy of the π-system to lower energy, which is to say that the neglect of dynamical effects of the σ-skeleton can be formally compensated for by a reduction of the electronic interaction within the π-system. Such a reduction or screening can be considered as a dielectric effect from the σ-medium, but the introduction of a simple dielectric factor in the electron repulsion integrals may be too much of a simplification.

Screening of electronic interactions can be qualitatively understood, but hardly subject to numerical estimates. The difficulty arises from the inhomogeneous nature of the medium, since the reduced interaction must be described at distances comparable to chemical bonds. Neither is it sufficient to consider only local effects of screening, nor to screen independently the various wavelengths in the Fourier transform of the coulomb interaction. Hubbard formulated an integral equation for the screened interaction, but only very approximate solutions seems to be feasible. We will demonstrate that some numerical evidence supports the determination of interaction integrals based on screening theory.

The neglect of dynamical effects of the σ-skeleton makes it possible to include the second and third terms of H_2 into $H_1(a'')$ to obtain $H_{core}(a'')$ in the common nomenclature of the model. The first term of H_2 combines with H_0 to a new constant H_0'. The effective hamiltonian for the π-electron system then may be expressed as

$$H(a'') = H_0' + H_{core}(a'') + H_2(a'', a'', a'', a''). \tag{11.7}$$

The precise definition of $H_{core}(a'')$ is

$$\begin{aligned} H_{core}(a'') = &\int d\xi \psi^\dagger(a'',\xi)[-(1/2m)\nabla^2 + V_{core}(\vec{r})]\psi(a'',\xi) \\ &-e^2 \int d\xi d\xi' \psi^\dagger(a'',\xi)\langle\psi^\dagger(a',\xi')\psi(a',\xi)\rangle\psi(a'',\xi')|\vec{r}-\vec{r}'|^{-1} \end{aligned} \tag{11.8}$$

with

$$V_{core}(\vec{r}) = -e^2 \sum Z_g/|\vec{r}-\vec{R}_g| + e^2 \int d\xi' \langle\psi^\dagger(a',\xi')\psi(a',\xi')\rangle|\vec{r}-\vec{r}'|^{-1}. \tag{11.9}$$

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[7] E. A. Taft and H. R. Philipp, *Phys. Rev.* **138**, A197 (1965)

The core potential is the Coulomb potential from the nuclei and the electron density of the a'-system. The exchange potential is represented separately.

It is worth mentioning at this stage that Eq. (11.7) is a complete definition of $H(a'')$ and cannot without extra specifications be given a configuration space representation. The field operators $\psi(a'',\xi)$ contains the supplementary condition that in the configuration space picture of the states there will only be π-orbitals in the wavefunction.

One further step is required to reach the PPP-model, and that is the approximation of linear combinations of atomic orbitals. The field operators are expanded in a set of symmetrically orthonormalized atomic spin orbitals of a'' symmetry. Furthermore, each atomic orbital is associated with a separate atomic center r in the molecule. We write

$$\psi(a'',\xi) = \sum u_{r\nu}(\xi)a_{r\nu}, \tag{11.10}$$

$$a_{r\nu} = \int d\xi u^*_{r\nu}(\xi)\psi(a'',\xi), \tag{11.11}$$

where the operators $a_{r\nu}$ are annihilation operators for electrons in the π-orbital on atom r with spin component ν. The zero differential overlap approximation, which is part of the PPP-model means that the spin orbital product $u_{r\nu}(\xi)u_{s\nu'}(\xi)$ is put equal to zero for $r \neq s$. This leads to

$$\psi^\dagger(a'',\xi)\psi(a'',\xi) = \sum |u_{r\nu}(\xi)|^2 n_{r\nu}, \tag{11.12}$$

where $n_{r\nu} = a^\dagger_{r\nu}a_{r\nu}$ is the occupation number operator for the spin orbital $u_{r\nu}$. The orbital expansions Eq. (11.10) and Eq. (11.12) are inserted in the hamiltonian in Eq. (11.7), resulting in the Pariser-Parr-Pople model hamiltonian

$$H(PPP) = H_0' + \sum \alpha_r n_{r\nu} + {\sum}' \beta_{rs} a^\dagger_{r\nu} a_{s\nu} + \frac{1}{2}{\sum}' \gamma_{rs} n_{r\nu} n_{s\nu'}. \tag{11.13}$$

A prime on the summation sign as usual indicates the omission of diagonal terms. In the PPP-hamiltonian, this means the omission of terms where the operators would correspond to the same spin orbital. Thus, there is neither a term with β_{rr} nor with $n_{r\nu}n_{r\nu}$, but there is one with $n_{r\nu}n_{r-\nu}$. The parameters α_r and β_{rs} are matrix elements of H_{core} between atomic spin orbitals $u_{r\nu}(\xi)$ and $u_{s\nu}(\xi)$, and γ_{rs} is the electron repulsion integral between spin orbital densities $|u_{r\nu'}(\xi)|^2$ and $|u_{s\nu}(\xi)|^2$.

An immediate consequence of the form of $H(PPP)$ in (11.13) is that excitation energies for transitions between states of equal number of π-electrons involve only differences of the α and γ parameters. This can be illustrated by the operator

$$\begin{aligned} \delta H &= \delta\alpha N(a'') + \delta\gamma N(a'')[N(a'') - 1] & (11.14) \\ &= \delta\alpha \sum n_{r\nu} + \frac{1}{2}\delta\gamma {\sum}' n_{r\nu}n_{s\nu'}, \end{aligned}$$

which when added to $H(PPP)$ changes it to an equivalent form where all the α and γ parameters are uniformly increased by $\delta\alpha$ and $\delta\gamma$, respectively. Moreover, δH is a constant within each manifold of eigenstates belonging to a particular eigenvalue of $N(a'')$, which means that energy eigenvalue differences within such a manifold are independent of $\delta\alpha$ and $\delta\gamma$.

The result of the previous paragraph permits us to draw some conclusions regarding the appropriate magnitude of the electron repulsion integrals. According to Hubbard's theory of screening of electronic interactions, the γ_{rs} represents the potential felt at atom r, averaged over $|u_r|^2$, from an electron with charge distribution $|u_s|^2$ and its surrounding polarization field. The results of Taft and Philipp suggest that the polarization is essentially instantaneous on the time-scale of the π-electrons, and should have little effect. This result is reflected in most empirical determinations of these parameters. A modification of the electron repulsion parameters due to dielectric effects influences only one-center and nearest-neighbor integrals. Such changes of the parameter values are noticeable in spectra through the differences of these integrals to second neighbor values. For instance, in the case of the benzene molecule, these differences as given by Simmons[8] in various approximations are generally scaled down by a factor 1/2, which would correspond to a an effective dielectric constant for the σ-medium equal to 2. That compares well with the optical value of 2.5 found by Taft and Philipp. The technique afforded by Hubbard's theory of screening appears more satisfactory than simple perturbation theory arguments. One might suggest that the evaluation of the electron repulsion integrals be based on the assumption that the charge distributions should correspond to a more diffuse atomic π-orbital, which would be computed for a valence state configuration. Obviously, there are some drawbacks to such a procedure, because the nearest-neighbor integrals will increase due to the decrease in localization, and the use of the zero differential overlap approximation will be harder to justify.

11.3 Limit of Separated Atoms

In this section, we examine in some detail the case when the off-diagonal matrix elements of the core operator β_{rs} are small in comparison with the electron repulsion integrals γ_{rr}. This corresponds to the situation of separated atoms, but it should be realized that other matrix elements also depend on the relative positions of the nuclei, both through the core operator and the symmetric orthonormalization procedure of the orbitals used in the expansion Eq. (11.10). In the following, the constant term of $H(PPP)$ is omitted, the third term is considered as a perturbation, while the second and fourth parts constitute the unperturbed hamiltonian for this case.

Thus, in the limit of separated atoms, we write the hamiltonian as

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[8] H. E. Simmons, *J. Chem. Phys.* **40**, 3554 (1964)

$$H_{atoms} = \sum_r H_r + \frac{1}{2}\sum_{r\neq s} \gamma_{rs}(n_{r+} + n_{r-})(n_{s+} + n_{s-}), \quad (11.15)$$

$$H_r = \alpha_r(n_{r+} + n_{r-}) + \gamma_{rr} n_{r+} n_{r-}. \quad (11.16)$$

The only nonvanishing anticommutation relation of the basis field operators is

$$[a_{r\nu}, a^\dagger_{s\nu'}]_+ = \delta_{\nu\nu'}\delta_{rs}, \quad (11.17)$$

which means that all the operators $n_{r\nu}$ commute, and all

$$N_r = n_{r+} + n_{r-} \quad (11.18)$$

mutually commute and commute with H_{atom}.

The unperturbed energy eigenvalues are given in terms of the eigenvalues of the operators N_r, which are simply 0, 1, or 2, meaning that an atom can have zero, one, or two electrons in its π-orbital. The states with one electron in each atomic orbital are degenerate, and in general, a large number of degenerate states corresponds to each unperturbed eigenvalue. Some of these degeneracies can be classified according to the theory of coupling of spin angular momentum.

The operators

$$\begin{aligned} S_{rx} &= \frac{1}{2}[a^\dagger_{r+}a_{r-} + a^\dagger_{r-}a_{r+}], & (11.19)\\ S_{ry} &= \frac{1}{2}i[a^\dagger_{r+}a_{r-} - a^\dagger_{r-}a_{r+}], \\ S_{rz} &= \frac{1}{2}[a^\dagger_{r+}a_{r+} - a^\dagger_{r-}a_{r-}] \end{aligned}$$

satisfy the commutation relations for components of angular momentum, *i.e.*

$$[S_{rx}, S_{ry}]_- = iS_{rz}, x, y, z, \text{cyclic}, \quad (11.20)$$

and the total spin on site r is given by

$$\vec{S}_r^2 = S^2_{rx} + S^2_{ry} + S^2_{rz} = \frac{3}{4}N_r(2 - N_r). \quad (11.21)$$

Within each manifold of states characterized by the eigenvalues of the operators N_r, there will be a unique correspondence between the operators $\vec{S}_r$ and ordinary spin operators and they will be interpreted as spin operators for atoms. The different spin components for an atom are all constants of the motion in the unperturbed case. Spin coupling becomes important when the perturbation terms are introduced.

Before considering spin coupling details, we examine the Heisenberg equation of motion for the electron annihilation operators in the unperturbed case. Hubbard found that the two components $n_{r-\nu}a_{r\nu}$ and $(1 - n_{r-\nu})a_{r\nu}$ of the operator $a_{r\nu}$ develop harmonically in time when the hamiltonian is H_r. We write

$$\begin{aligned} i\frac{d}{dt}(1-n_{r-\nu})a_{r\nu} &= [(1-n_{r-\nu})a_{r\nu}, H_r]_- = \alpha_r(1-n_{r-\nu})a_{r\nu}, && (11.22)\\ i\frac{d}{dt}n_{r-\nu}a_{r\nu} &= [n_{r-\nu}a_{r\nu}, H_r]_- = (\alpha_r+\gamma_{rr})n_{r-\nu}a_{r\nu}. && (11.23) \end{aligned}$$

The solution of (11.23) and (11.23) yields

$$a_{r\nu}(t) = [1 + n_{r-\nu}(0)(\exp(-i\gamma_{rr}t) - 1)]a_{r\nu}(0)\exp -i\alpha_r t, \qquad (11.24)$$

which can also be written as

$$a_{r\nu}(t) = a_{r\nu}(0)\exp[-it(\alpha_r + \gamma_{rr}n_{r-\nu})]. \qquad (11.25)$$

When the total unperturbed hamiltonian is used for the time evolution, we obtain

$$\begin{aligned} a_{r\nu}(t) &= \exp(itH_{atoms})a_{r\nu}(0)\exp(-itH_{atoms}) && (11.26)\\ &= a_{r\nu}(0)\exp[-it(\alpha_r+\gamma_{rr}n_{r-\nu}) + \sum_{s\neq r} N_s]. \end{aligned}$$

The expansion of the exponential operator in Eq. (11.26) gives a product of factors similar to the expression in Eq. (11.24). It follows from Eq. (11.26) that the compound field operators $n_{r-\nu}a_{r\nu}$ and $(1-n_{r-\nu})a_{r\nu}$ are basic for the full treatment within a manifold of states defined by a set of eigenvalues of the operators N_r. They act as operators for elementary excitations for the case of separated atoms.

The algebraic steps presented above can now be applied in the development of a perturbation expansion of the evolution operator in a similar way used by Bulaevskii[9]. We consider only terms of the second order in the perturbation

$$H_{pert} = \sum \beta_{rs}a^\dagger_{r\nu}a_{s\nu}, \qquad (11.27)$$

since there are no first-order energy shifts, and degenerate second-order perturbation theory is required to find the stable zero-order states.

When P is the projection operator on the particular degenerate manifold of eigenstates of H_{atoms} in which we are interested, it can be specified in terms of the eigenvalues q_r of N_r,

$$N_rP = q_rP. \qquad (11.28)$$

The formal charge q_r of electrons on atom r also defines uniquely the unperturbed energy,

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[9] L. N. Bulaevskii, *Zh. Eksp. Teor. Fiz.* **51**, 230 (1966) [*Sov. Phys.- JETP* **24**, 154 (1967)]

$$H_{atoms}P = E_0 P, \tag{11.29}$$

$$E_0 = \sum [\alpha_r q_r + \frac{1}{2}\gamma_{rr} q_r (q_r - 1)] + \frac{1}{2}\sum{}' \gamma_{rs} q_r q_s. \tag{11.30}$$

As the perturbation cannot connect degenerate states within a particular manifold defined by a set of formal charges q_r, we can conclude that

$$PH_{pert}P = 0. \tag{11.31}$$

Schrödinger perturbation theory leads to the study of the second-order reduced hamiltonian, which is given by

$$\begin{aligned} H_{red} &= PH_{pert}[(1-P)/(E_0 - H_{atoms})]H_{pert}P \qquad (11.32) \\ &= \lim_{\delta \to 0} -i \int_{-\infty}^{0} PH_{pert}(0)H_{pert}(t)Pe^{\delta t}dt. \end{aligned}$$

The perturbation operator in the interaction representation is obtained by inserting the expression (11.27) in the form (11.32). The integrand in Eq. (11.32) then assumes the form

$$PH_{pert}(0)H_{pert}(t)P = P\sum_{rs,\nu\nu'} \beta_{rs} a_{r\nu}^{\dagger} a_{s\nu} \beta_{sr} a_{s\nu'}^{\dagger}(t) a_{r\nu'}(t) P. \tag{11.33}$$

In order to simplify this expression, it is useful to define

$$W_r = \alpha_r + \sum_{s \neq r} \gamma_{rs} q_s, \tag{11.34}$$

and to observe that the commutation relation

$$[N_r, a_{r\nu}]_- = -a_{r\nu} \tag{11.35}$$

can be used to obtain

$$\exp[itN_r\gamma_{sr}]a_{r\nu} = a_{r\nu}\exp[it(N_r - 1)\gamma_{sr}]. \tag{11.36}$$

We find after some algebraic manipulation that

$$\begin{aligned} &\sum_{\nu\nu'} Pa_{r\nu}^{\dagger} a_{s\nu} a_{s\nu'}^{\dagger}(t) a_{r\nu'}(t) P \\ =\ & P\{\frac{1}{2} q_r (2 - q_r)(2 - q_s)(1 - q_s)\exp[it(W_s - W_r - \gamma_{sr})] \qquad (11.37) \\ +\ & \frac{1}{2} q_r (q_r - 1)(2 - q_s)(1 - q_s)\exp[it(W_s - W_r - \gamma_{sr} - \gamma_{rr})] \end{aligned}$$

$$
\begin{aligned}
&+ \quad \frac{1}{2}q_r(2-q_r)q_s(2-q_s)\exp\left[it(W_s - W_r + \gamma_{ss} - \gamma_{rs})\right] \\
&+ \quad \frac{1}{2}q_r(q_r-1)q_s(2-q_s)\exp\left[it(W_s - W_r + \gamma_{ss} - \gamma_{sr} - \gamma_{rr})\right] \\
&- \quad 2\vec{S}_r \cdot \vec{S}_s \exp\left[it(W_s - W_r + \gamma_{ss} - \gamma_{rs})\right]\}.
\end{aligned}
$$

The first four terms of the right-hand side of Eq.(11.37) when inserted into Eq. (11.33) give a constant contribution to H_{red} in Eq. (11.32), and we obtain a spin hamiltonian of Heisenberg type

$$H_{red} = \text{constant} - \sum J_{rs}\vec{S}_r \cdot \vec{S}_s, \tag{11.38}$$

with

$$J_{rs} = -|\beta_{rs}|^2[(W_s - W_r + \gamma_{ss} - \gamma_{rs})^{-1} + (W_r - W_s + \gamma_{rr} - \gamma_{sr})^{-1}]. \tag{11.39}$$

A system with identical atoms and with one π-electron per atom will in this approximation behave as a Heisenberg antiferromagnet with the exchange integrals

$$J_{rs} = -2|\beta_{rs}|^2/(\gamma_{rr} - \gamma_{rs}). \tag{11.40}$$

The constant in this case is such that we can write

$$H_{red} = \sum_{rs} J_{rs}(-\frac{1}{4} + \vec{S}_r \cdot \vec{S}_s). \tag{11.41}$$

The above analysis demonstrates the nature of the spectrum of the PPP-hamiltonian when the off-diagonal elements of the core hamiltonian are small. The elementary excitation operators are essentially atomic and correspond to localized processes. There will be families of states that are almost degenerate and that are connected to one another through spin excitations.

11.4 Interacting Atoms

This section deals with the calculation of double-time Green's functions for the study of electron propagation through a system with small interactions between atoms.

The Green's functions of interest are defined with respect to the ground state of the system, and the decoupling procedure for the equations of motion refers to this state. The detailed nature of ground state will ideally be the result of the calculation, but it should be clear from the following that its construction is a complicated matter. However, ground state properties may be calculated without explicit knowledge of the state. Important questions regarding N-representabilty are left unanswered here.

The two types of elementary excitation operators, $n_{r-\nu}a_{r\nu}$ and $(1-n_{r-\nu})a_{r\nu}$, to describe the limit of separated atoms form the basis also for the discussion of interacting atoms. We introduce the particular linear combinations

$$a_{r\nu} = (1 - n_{r-\nu})a_{r\nu} + n_{r-\nu}a_{r\nu} \tag{11.42}$$

and

$$b_{r\nu} = z_r(n_{r-\nu} - \langle n_{r-\nu}\rangle)a_{r\nu}, \tag{11.43}$$

with

$$z_r = \left[\langle n_{r-\nu}\rangle(1 - \langle n_{r-\nu}\rangle)\right]^{-1/2}. \tag{11.44}$$

All expectation values are assumed to be evaluated for a *singlet spin state.* Thinking of the ground state as an expansion of valence bond states, we can see that while $a_{r\nu}$ annihilates an electron on atom r with spin ν, $b_{r\nu}$ has the same effect with a change of relative phase and weights of the structures for which atom r is "ionic" and "covalent".

These operators satisfy the relations

$$\langle [b_{r\nu}, a^\dagger_{s\nu}]_+\rangle = 0 \tag{11.45}$$

and

$$\langle [b_{r\nu}, b^\dagger_{s\nu'}]_+\rangle = \delta_{rs}\delta_{\nu\nu'}. \tag{11.46}$$

The two propagators of interest are the electron propagator

$$G_{rs}(t - t') = \langle\langle a_{r\nu}(t); a^\dagger_{s\nu}(t')\rangle\rangle, \tag{11.47}$$

and the mixed propagator

$$K_{rs}(t - t') = \langle\langle b_{r\nu}(t); a^\dagger_{s\nu}(t')\rangle\rangle. \tag{11.48}$$

Their Fourier transforms

$$G_{rs}(E) = \langle\langle a_{r\nu}; a^\dagger_{s\nu}\rangle\rangle_E = \int G_{rs}(t)e^{iEt}dt, \tag{11.49}$$

and the analogous expression for $K_{rs}(E)$ are used in the calculations and satisfy the equations of motion

$$EG_{rs}(E) = \delta_{rs} + \langle\langle [a_{r\nu}, H]_-; a^\dagger_{s\nu}\rangle\rangle_E \tag{11.50}$$

and

$$EK_{rs}(E) = \langle\langle [b_{r\nu}, H]_-; a^\dagger_{s\nu}\rangle\rangle_E, \tag{11.51}$$

as well as certain initial conditions. The hamiltonian in these equations is the PPP-hamiltonian from Eq.(11.13).

The procedure of decoupling of the equations of motion means to truncate the chain of equations such that the propagators on the right-hand side of Eqs. (11.50) and (11.51) are expressed as linear combinations of only G and K type propagators. This is equivalent to expressing a general fermion field operator X in terms of only a's and b's, *i.e.*,

$$X = \sum (f_{r\nu} a_{r\nu} + I_{r\nu} b_{r\nu}). \tag{11.52}$$

The coefficients $f_{r\nu}$ and $I_{r\nu}$ can be determined from the requirement that the effect of the operator X on the ground state should equal the effect of the expansion on the same. This yields the two equations

$$\begin{aligned} X|0\rangle &= \sum (f_{r\nu} a_{r\nu} + I_{r\nu} b_{r\nu})|0\rangle, & (11.53) \\ \langle 0|X &= \langle 0| \sum (f_{r\nu} a_{r\nu} + I_{r\nu} b_{r\nu}), & (11.54) \end{aligned}$$

which imply that

$$f_{r\nu} = \langle [X, a^\dagger_{r\nu}]_+ \rangle \tag{11.55}$$

and

$$I_{r\nu} = \langle [X, b^\dagger_{r\nu}]_+ \rangle. \tag{11.56}$$

From the Eqs. (11.50) and (11.51), it follows that in the present case, the operator X is either $[a_{r\nu}, H]_-$ or $[b_{r\nu}, H]_-$. Thus, we define the matrix elements

$$\begin{aligned} f_{rs} &= \langle [[a_{r\nu}, H]_-, a^\dagger_{s\nu}]_+ \rangle, & (11.57) \\ I_{rs} &= \langle [[a_{r\nu}, H]_-, b^\dagger_{s\nu}]_+ \rangle, & (11.58) \\ \hat{f}_{rs} &= \langle [[b_{r\nu}, H]_-, b^\dagger_{s\nu}]_+ \rangle. & (11.59) \end{aligned}$$

The approximation defined by this truncation of the propagator equations leads to the following matrix equation:

$$\begin{bmatrix} E\mathbf{1} - \mathbf{f} & -\mathbf{I} \\ -\mathbf{I}^\dagger & E\mathbf{1} - \hat{\mathbf{f}} \end{bmatrix} \begin{bmatrix} \mathbf{G(E)} \\ \mathbf{K(E)} \end{bmatrix} = \begin{bmatrix} \mathbf{1} \\ \mathbf{0} \end{bmatrix}. \tag{11.60}$$

The ordinary molecular orbital approximation according to the Hartree-Fock method is obtained from Eq. (11.60) when the matrix $\mathbf{I}$ is neglected and there is no coupling between the Green's function of type G and type K.

The solution of Eq. (11.60) is achieved by standard methods once the matrix elements are obtained. Their evaluation involves the calculation of expectation values, which can be found when the solution of Eq. (11.60) is available, and we are, thus, faced with a self-consistency requirement, which is similar to but more complex than the corresponding challenge in the Hartree-Fock approximation. In the next section, the calculation of the matrix elements is addressed.

The solution of Eq. (11.60) can be conveniently discussed in terms of the eigensolutions of the homogeneous problem obtained when the right-hand side is replaced by zero. This defines the eigenvalue problem

$$\begin{bmatrix} \mathbf{f} & \mathbf{I} \\ \mathbf{I}^\dagger & \hat{\mathbf{f}} \end{bmatrix} \begin{bmatrix} \mathbf{u_k} \\ \mathbf{v_k} \end{bmatrix} = \epsilon_k \begin{bmatrix} \mathbf{u_k} \\ \mathbf{v_k} \end{bmatrix} \tag{11.61}$$

with the orthonormality condition

$$\mathbf{u}^\dagger_\mathbf{k}\mathbf{u}_{\mathbf{k}'} + \mathbf{v}^\dagger_\mathbf{k}\mathbf{v}_{\mathbf{k}'} = \delta_{\mathbf{k}\mathbf{k}'}. \tag{11.62}$$

The eigenvectors serve to define elementary excitation operators $A_{k\nu}$ as

$$A_{k\nu} = \sum_r (u^\dagger_{kr}a_{r\nu} + v^\dagger_{kr}b_{r\nu}), \tag{11.63}$$

which are a convenient basis, *i.e.*,

$$a_{r\nu} = \sum_k u_{rk}A_{k\nu}, \tag{11.64}$$

$$b_{r\nu} = \sum_k v_{rk}A_{k\nu}, \tag{11.65}$$

and derive their importance from the property that

$$\langle[[A_{k\nu}, H]_-, A^\dagger_{k'\nu'}]_+\rangle = \epsilon_k\delta_{kk'}\delta_{\nu\nu'}, \tag{11.66}$$

and that

$$(E - \epsilon_k)\langle\langle A_{k\nu}; A_{k'\nu}\rangle\rangle_E = \delta_{kk'}. \tag{11.67}$$

Important are also boundary conditions, and we know that the behavior of Green's functions at the poles of their Fourier transforms uniquely determines the various properties of the solution. The only sensible specification with regard to the poles is to require that the inverse Fourier transform is carried out with an integration along the real axis in the complex E-plane as in the contour in Fig. 3.1, *i.e.*, such that all poles to the left of a point μ are circumvented below the axis, while all poles to the right of μ are circumvented above the real axis. As we have seen before, this is equivalent to adding or subtracting an imaginary infinitesimal part when $\epsilon_k - \mu$ is negative or positive, respectively, *i.e.*,

$$\epsilon_k \to \epsilon_k + i\delta\text{sgn}(\mu - \epsilon_k), \delta > 0. \tag{11.68}$$

The choice of the point μ is critical and determined by the condition that the ground state should contain a certain number of electrons. It is not apparent that this number always should be an integer, and we may have to accept states of the type used by Bardeen, Cooper, and Schrieffer in their theory of superconductivity, *i.e.*, a superposition of states with varying number of particles. This difficulty has not occurred in actual applications carried out so far.

The number of electrons in the ground state is given in terms of the propagator as

$$N = \sum_{r\nu} \langle n_{r\nu} \rangle = 2 \sum_{r} \lim_{t \to 0-} -iG_{rr}(t) = 2 \sum_{r} (2\pi i)^{-1} \int_C dE G_{rr}(E). \tag{11.69}$$

The contour C in the complex E-plane encircles the part of the real axis where $E < \mu$. Thus, we get

$$N = 2 \sum_{r} \sum_{(k)} |u_{rk}|^2, \tag{11.70}$$

where the summation over k extends over the values for which $\epsilon_k < \mu$.

This expression does not necessarily yield an integer. However, the deviation from an integer can be analyzed by applying the identity

$$a^\dagger_{r\nu} a_{r\nu} = n_{r\nu} = b^\dagger_{r\nu} b_{r\nu} + (2\langle n_{r-\nu} \rangle - 1) z_r a^\dagger_{r\nu} b_{r\nu}, \tag{11.71}$$

which leads to the expression

$$N = 2 \sum_{r} \sum_{(k)} [|v_{rk}|^2 + (\langle N_r \rangle - 1) z_r u^\dagger_{kr} v_{rk}], \tag{11.72}$$

where we have used the expansions in terms of the excitation operators $A_{k\nu}$ and averaged the number operator over the spin singlet ground state. An alternative result is obtained as the average of this expression and the result in Eq.(11.70),

$$N = \sum_{r} \sum_{(k)} [|u_{rk}|^2 + |v_{rk}|^2 + (\langle N_r \rangle - 1) z_r u^\dagger_{kr} v_{rk}]. \tag{11.73}$$

The case of one electron per atom, $\langle N_r \rangle = 1$, then immediately yields an integer result from the normalization condition (11.62). However, for other cases, this may not be true.

Alternative forms are also available for the calculation of the total ground state energy. The most direct approach is to compute the expectation value of the hamiltonian. Another common technique in the application of Green's functions makes use of the identity

$$\sum_{r\nu} a^\dagger_{r\nu} [a_{r\nu}, H]_- = \sum_{r,s,\nu} (\alpha_r \delta_{rs} + \beta_{rs}) a^\dagger_{r\nu} a_{r\nu} + \sideset{}{'}\sum_{r,s,\nu,\nu'} \gamma_{rs} n_{r\nu} n_{s\nu'}, \tag{11.74}$$

so that

$$\begin{aligned} E_0 &= \langle H \rangle \\ &= (2\pi i)^{-1} \int_C dE \sum_{rs} [(\alpha_r + E)\delta_{rs} + \beta_{rs}] G_{sr}(E) \\ &= \sum_{rs} \sum_{(k)} [(\alpha_r + \epsilon_k)\delta_{rs} + \beta_{rs}] u_{sk} u^\dagger_{kr}. \end{aligned} \tag{11.75}$$

The expression (11.75) is also valid in the Hartree-Fock approximation, where all the v_{kr} vanish. In the more general case, this expression may not agree with the direct calculation of the hamiltonian expectation value. This is a difficulty not uncommon in the application of Green's functions. It should have been avoided by some auxiliary constraint on the decoupling procedure[10].

Inconsistencies in the theory such as the ones discussed above may be considered connected with the lack of preservation of certain formal equivalencies in an approximate theory. An obvious relation that follows from the Hellmann-Feynman theorem is the expression for the bond order as a derivative of the total energy

$$\begin{aligned} p_{sr} = \frac{1}{2}\partial E_0/\partial\beta_{sr} &= \frac{1}{2}\sum_{\nu}\langle a^\dagger_{r\nu}a_{s\nu} + a^\dagger_{s\nu}a_{r\nu}\rangle \qquad (11.76)\\ &= (\pi i)^{-1}\int_C dEG_{sr}(E). \end{aligned}$$

The simultaneous validity of Eqs. (11.75) and (11.76) puts conditions on the relations of various expectation values and thereby on the decoupling procedure. There is no simple way to incorporate these conditions, and it is not given any further considerations in this chapter.

We now investigate the result of Eq. (11.76) with the energy computed with the reduced hamiltonian of Eq. (11.38). The bond order should be computed to order β_{rs}, and the matrix elements of Eq. (11.61) are obtained for the case when all $\langle N_r\rangle = 1$ and all atoms are equivalent as

$$\begin{aligned} f_{rr} &= W + O(\beta^2), && (11.77)\\ f_{rs} &= \beta_{rs} - \frac{1}{2}\gamma_{rs}p_{rs}, && (11.78)\\ I_{rr} &= \frac{1}{2}\gamma_{rr} + O(\beta^2), && (11.79)\\ Irs &= O(\beta^2), && (11.80)\\ \hat{f}_{rr} &= W + O(\beta^2), && (11.81)\\ \hat{f}_{rs} &= \beta_{rs}\langle[[b_{r\nu}, a^\dagger_{r\nu}a_{s\nu} + a^\dagger_{r-\nu}a_{s-\nu} + a^\dagger_{s-\nu}a_{r-\nu}], b^\dagger_{s\nu}]_+\rangle && (11.82)\\ &+ \frac{1}{2}\gamma_{rs}p_{rs} + O(\beta^2). \end{aligned}$$

A straightforward perturbation calculation on Eq. (11.60) produces the Green's function through order β. The contour integral in Eq. (11.76) with the parameter μ chosen equal to W yields

$$p_{rs} = [\hat{f}_{rs} - f_{rs}]/\gamma_{rr}. \qquad (11.83)$$

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[10] See, for instance, the Ward identities in perturbation theory discussed in P. Noziere, *Le problems a N corps*, Dunod Cie, Paris, 1963, p. 243ff.

This is an implicit equation for p_{rs} according to Eqs. (11.78) and (11.83), which can be solved to yield

$$p_{rs} = -[\beta_{rs}/(\gamma_{rr} - \gamma_{rs})][1 - 4\langle \vec{S}_r \cdot \vec{S}_s \rangle], \tag{11.84}$$

when terms of higher order in β are neglected in the evaluation of the expectation value in Eq. (11.83) and spin symmetry is used.

Thus, the correct result is obtained provided the the expectation values of the product of spin operators can be evaluated. This analysis is given in the next section.

11.5 Calculation of Expectation Values

The matrix elements defined in Eqs. (11.58)-(11.59) are evaluated in this section under the assumption that a ground state $|E_0\rangle$ exists such that the Green's functions are determined in the manner described in this chapter. This assumption takes the form

$$\langle A^\dagger_{k\nu} A_{k'\nu'} \rangle = \nu_k \delta_{kk'} \delta_{\nu\nu'}, \tag{11.85}$$

where the "occupation number" ν_k is defined such that

$$\nu_k = \begin{cases} 1 & \text{if} \quad \epsilon_k < \mu \\ 0 & \text{if} \quad \epsilon_k > \mu \end{cases}. \tag{11.86}$$

This implies the property

$$[(1 - \nu_k) A_{k\nu} + \nu_k A^\dagger_{k\nu}] |E_0\rangle = 0. \tag{11.87}$$

The conditions imposed on the ground state by this equation have not been proven to be incompatible, and this property is basic for the following calculations.

All expectation values of concern can be expressed in the form $\langle X^\dagger a_{r\nu} \rangle$, with X a fermion-like annihilation operator. Eq.(11.64) and the property (11.87) are applied to obtain

$$\begin{aligned} \langle X^\dagger a_{r\nu} \rangle &= \sum_k u_{rk} \nu_k \langle X^\dagger A_{k\nu} \rangle = \sum_k u_{rk} \nu_k \langle [X^\dagger, A_{k\nu}]_+ \rangle \\ &= \sum_k \sum_s u_{rk} \nu_k u^\dagger_{ks} \langle [X^\dagger, a_{s\nu}]_+ \rangle \\ &+ \sum_k \sum_s u_{rk} \nu_k v^\dagger_{ks} \langle [X^\dagger, b_{s\nu}]_+ \rangle. \end{aligned} \tag{11.88}$$

We introduce the following notations:

$$\begin{aligned} g_{rs} &= (2\pi i)^{-1}\int_C dE G_{rs}(E) = \sum_k u_{rk}\nu_k u^\dagger_{ks} = g_{sr}, & (11.89)\\ k_{rs} &= (2\pi i)^{-1}\int_C dE K_{rs}(E) = \sum_k v_{rk}\nu_k u^\dagger_{ks}, & (11.90)\end{aligned}$$

which are assumed to be real and for which the ground state is assumed to be nondegenerate. Eq. (11.88) can now be written as

$$\langle X^\dagger a_{r\nu}\rangle = \sum_s g_{rs}\langle [X^\dagger, a_{s\nu}]_+\rangle + \sum_s k^*_{rs}\langle [X^\dagger, b_{s\nu}]_+\rangle. \tag{11.91}$$

This equation is an implicit equation that leads to an equation system for several expectation values. Only when X is a simple fermion or quasi-fermion operator do we get the result that

$$\langle a^\dagger_{s\nu} a_{r\nu}\rangle = g_{rs} \tag{11.92}$$

and

$$\langle b^\dagger_{s\nu} a_{r\nu}\rangle = k^*_{rs}, \tag{11.93}$$

in accordance with the initial value conditions on the Green's functions.

There is a formal exact correspondence between the matrix elements f_{rs} and the Fock operator in the Hartree-Fock approximation, *i.e.*, the expression

$$f_{rs} = \delta_{rs}[\alpha_r + 2\sum_t \gamma_{rt} g_{tt}] + \beta_{rs} - \gamma_{rs} g_{rs} \tag{11.94}$$

holds, but the difference with Hartree-Fock lies in the calculation of the g_{rs}'s.

The elements of the I-matrix are evaluated from the expression

$$I_{rs} = \delta_{rs}\sum_{t\mu} \gamma_{rt} z_r \langle (n_{r-\nu} - g_{rr}) n_{t\mu}\rangle - \gamma_{rs} k^*_{sr}. \tag{11.95}$$

Application of Eq. (11.91) to $\langle (n_{r\nu} - g_{rr}) n_{t\mu}\rangle$ yields a system of equations,

$$\begin{aligned} \langle (n_{r\nu} - g_{rr}) n_{t\mu}\rangle &= \delta_{\nu\mu}[g_{rr}\delta_{rt} - g^2_{rt} - |k_{rt}|^2] \\ &+ k_{tt} z_t \langle (n_{r\nu} - g_{rr}) n_{t-\mu}\rangle, & (11.96)\end{aligned}$$

with the solution

$$\langle (n_{r\nu} - g_{rr})(n_{t\mu} + n_{t-\mu})\rangle = [g_{rr}\delta_{rt} - g^2_{rt} - |k_{rt}|^2]/[1 - k_{tt} z_t]. \tag{11.97}$$

The explicit expression for the matrix element I_{rs} is obtained by inserting this expression into Eq. (11.95), a step we omit here. The matrix elements $\hat{f}_{rs}$ are more complicated, and we first express them in a less compact form obtained from Eq. (11.59) and the definition (11.43) such that

$$\begin{aligned}
\hat{f}_{rs} &= z_r\langle(n_{r-\nu}-g_{rr})[[a_{r\nu},H]_-,b^\dagger_{s\nu}]_+ \\
&+ [n_{r-\nu},H]_-[a_{r\nu},b^\dagger_{s\nu}]_+ + [b^\dagger_{s\nu},[n_{r-\nu},H]_-]_-a_{r\nu}\rangle \\
&= z_r z_s\langle(n_{r-\nu}-g_{rr})(n_{s-\nu}-g_{ss})[[a_{r\nu},H]_-,a^\dagger_{s\nu}]_+ \\
&+ \delta_{rs}[n_{r-\nu},H]_-(n_{r-\nu}-g_{rr}) + a^\dagger_{s\nu}[n_{s-\nu},[n_{r-\nu},H]_-]_-a_{r\nu}\rangle.
\end{aligned} \tag{11.98}$$

It follows that the diagonal elements are

$$\begin{aligned}
\hat{f}_{rr} &= f_{rr} + z_r(1-2g_{rr})I_{rr} + z_r\sum_t(\beta_{rt}k^*_{tr} + k_{rt}\beta_{tr}) \\
&+ z_r^2(2g_{rr}-1)\sum_t g_{rt}\beta_{tr}.
\end{aligned} \tag{11.99}$$

It can be shown that it is self-consistent for the case of an even alternant hydrocarbon molecule to assume that the last three terms in this expression vanish.

Off-diagonal elements can be expressed as

$$\begin{aligned}
\hat{f}_{rs} &= \beta_{rs}z_r z_s\langle(n_{r-\nu}-g_{rr})(n_{s-\nu}-g_{ss}) \\
&+ a^\dagger_{s\nu}a_{s-\nu}a^\dagger_{r-\nu}a_{r\nu} - a^\dagger_{s\nu}a^\dagger_{s-\nu}a_{r-\nu}a_{r\nu} - \gamma_{rs}\langle b^\dagger_{s\nu}b_{r\nu}\rangle.
\end{aligned} \tag{11.100}$$

The average value in the last term is denoted $\hat{g}_{rs}$ and evaluated as

$$\langle b^\dagger_{s\nu}b_{r\nu}\rangle = \sum v_{rk}\nu_k\langle[b^\dagger_{s\nu},A_{k\nu}]_+\rangle = \sum v_{rk}\nu_k v^\dagger_{ks} = \hat{g}_{rs}. \tag{11.101}$$

The average value of the first term is obtained from Eq. (11.96) as

$$\langle(n_{r-\nu}-g_{rr})(n_{s-\nu}-g_{ss})\rangle = [g_{rr}\delta_{rs} - g^2_{rs} - |k_{rs}|^2]/[1-k^2_{ss}z^2_s] \tag{11.102}$$

a form that is not expressed symmetrically in r and s.

Similarly, we find the expressions

$$\langle a^\dagger_{s\nu}a_{s-\nu}a^\dagger_{r-\nu}a_{r\nu}\rangle = [g_{rr}\delta_{rs} - g^2_{rs} - |k_{rs}|^2]/[1+k_{ss}z_s] \tag{11.103}$$

and

$$\langle a^\dagger_{s\nu}a^\dagger_{s-\nu}a_{r-\nu}a_{r\nu}\rangle = [g^2_{rs} - k^{*2}_{rs} + k^*_{rs}g_{sr}z_r(1-2g_{rr})]/[1-k_{ss}z_s]. \tag{11.104}$$

We note that the frequently appearing quantity $k_{ss}z_s$ is a measure of the dispersion of the operator N_s, *i.e.*,

$$k_{ss}z_s = z^2_s\langle(n_{s-\nu}-g_{ss})n_{s\nu}\rangle = \frac{1}{2}z^2_s\langle(N_s-\langle N_s\rangle)^2\rangle - 1. \tag{11.105}$$

In the limit of small interatomic coupling, the denominators in the expressions (11.103) and (11.104) are almost vanishing and the limit needs to be taken with due consideration of the details. A careful analysis reveals that the limit can be expressed in terms of the spin operators $\vec{S}_r$ and $\vec{S}_s$ of atoms r and s, as we have already indicated.

11.6 Application to Linear Chains

A linear chain is here defined as a system with the hamiltonian $H(PPP)$ in Eq. (11.13) for which it is appropriate to assume a periodic arrangement of the atoms. Examples of such a system would be the annulenes.

Hückel theory for the even alternant hydrocarbons leads to the Coulson-Rushbrooke theorem[11] and some other characteristic results shown by McLachlan [12] to be valid also in the Pariser-Parr-Pople model. These are the well-known pairing relations between electronic states of alternant hydrocarbon cat- and anions. This particle-hole symmetry is analogous to the situation discussed in Chapter 4 for electrons and holes in atomic subshells.

For even alternant hydrocarbons, the atomic sites may be divided into two classes (even and odd) such that the atoms belonging to one class have nearest neighbors only of the other. This symmetry property of the PPP-hamiltonian can be readily explored if we write

$$\begin{aligned} H(PPP) = KN_{op} &+ \sum{}' \beta_{rs} a^\dagger_{r\nu} a_{s\nu} + \sum_{r<s} \gamma_{rs}[(N_r-1)(N_s-1)-1] \\ &+ \sum \gamma_{rr}[(n_{r+}-\frac{1}{2})(n_{r-}-\frac{1}{2})-\frac{1}{4}], \end{aligned} \tag{11.106}$$

where $K = \alpha_r + \frac{1}{2}\gamma_{rr} + \sum_{s\neq r} \gamma_{rs}$ is a constant for all atoms r.

Consider the complete particle-hole transformation by the unitary operator $U = \exp(iS)$, where

$$S = S^\dagger = \frac{\pi}{2}\{\sum^{even}(a^\dagger_{r+}a^\dagger_{r-} + a_{r-}a_{r+}) - \sum^{odd}(a^\dagger_{r+}a^\dagger_{r-} + a_{r-}a_{r+})\}. \tag{11.107}$$

From the result in Chapter 3, we obtain the following relations for the transformed field operators $\hat{a} = UaU^\dagger$:

$$\begin{aligned} \hat{a}_{r+} &= -ia^\dagger_{r-} \\ \hat{a}_{r-} &= ia^\dagger_{r+} \end{aligned} \quad \text{for } r \text{ even} \tag{11.108}$$

and

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[11] C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.* **40**, 193 (1940)

[12] A. D. McLachlan, *Mol. Phys.* **2**, 271 (1959)

Table 11.1: Matrix elements for a cyclic alternant hydrocarbon in the Pariser-Parr-Pople model

Matrix elements	r and s both odd or even	r and s not both odd or even
β_{rs}	0	$\neq 0$
$g_{rs}, \hat{g}_{rs}$	$\frac{1}{2}\delta_{rs}$	$\neq 0$
k_{rs}	$\neq 0$	0
f_{rs}	$\mu\delta_{rs}$	$\neq 0$
I_{rs}	$\neq 0$	0
$\hat{f}_{rs}$	$\mu\delta_{rs}$	$\neq 0$

$$\begin{aligned} \hat{a}_{r+} &= i a^{\dagger}_{r-} \\ \hat{a}_{r-} &= -i a^{\dagger}_{r+} \end{aligned} \quad \text{for} \quad r \quad \text{odd}. \tag{11.109}$$

One should note that when only nearest-neighbor interactions are considered for β_{rs} the atomic sites r and s belong to different classes and the associated "bond order" operator product satisfies the relation

$$a^{\dagger}_{r\nu} a_{s\nu} = a^{\dagger}_{s\nu} a_{r\nu}. \tag{11.110}$$

The transformed hamiltonian can then be written as

$$\hat{H}(PPP) = H(PPP) + 2K(n - N_{op}), \tag{11.111}$$

where n is the number of carbon atoms and the parameters β_{rs} are considered to be real, since no magnetic fields are included in this treatment.

The implications of these results for the present study are a number of conditions on the matrix elements g_{rs}, k_{rs}, and $\hat{g}_{rs}$, which we will show to be self-consistent for the case of an alternant hydrocarbon. Table 11.1 lists the effects of the alternant character on the model.

The parameter μ can be chosen equal to the common constant diagonal element of matrices **f** and $\hat{\mathbf{f}}$, since the resulting secular equation (11.60) will show pairing of roots around μ and the number of roots equals twice the number of electrons (cf. Eq. (11.70)). The pairing property can be shown from Eq. (11.61) by using the transformations

$$\begin{aligned} \epsilon_k - \mu &\rightarrow \mu - \epsilon_k, \\ u_{rk} &\rightarrow (-)^r u_{r-k}, \\ v_{rk} &\rightarrow (-)^r v_{r-k}, \end{aligned} \tag{11.112}$$

which can also be used to demonstrate the self-consistency of the solution. An obvious feature of the pairing is the existence of a "gap" in the energy spectrum around μ. This is not an unreasonable result because even the Hartree-Fock approximation yields a small number of states around the middle of the spectrum, in particular, all unrestricted Hartree-Fock procedures give a finite "gap" for nonvanishing interactions in a linear system.

Electronic interaction integrals enter the various matrix elements, but he most significant contribution from them comes in the matrix **I**, particularly in its diagonal elements. Most of the characteristics of the problem are preserved by omitting off-diagonal parts of **I** or equivalently put all two-center integrals γ_{rs} equal to zero. This is not such a crude approximation as it may seem because those integrals occur only in conjunction with small factors everywhere except in the diagonal elements f_{rr}, which anyway are put equal to a reference point on the energy scale. Furthermore, they occur in the nearest-neighbor elements f_{rs} and $\hat{f}_{rs}$ and here they can be accounted for by a "renormalization" of the β-value. In this manner, we can account for the last term in Eq. (11.94). These approximations lead to a significant simplification of the problem, and we are left with the following matrix elements when μ is put to zero.

$$f_{rs} = \begin{cases} \beta & r, s \quad \text{neighbors} \\ 0 & \quad \text{otherwise,} \end{cases} \tag{11.113}$$

$$I_{rs} = I\delta_{rs} = \frac{1}{2}\gamma_{rr}\delta_{rs}, \tag{11.114}$$

and

$$\hat{f}_{rs} = \begin{cases} \lambda\beta & r, s \quad \text{neighbors} \\ 0 & \quad \text{otherwise,} \end{cases} \tag{11.115}$$

where $\lambda = -12g_{rs}^2/(1 - 4k_{ss}^2)$ for r, s neighbors.

Solution of the eigenvalue problem is obtained with the *ansatz*

$$\sqrt{N}u_{rk} = \cos\theta \exp i\phi r, \tag{11.116}$$

$$\sqrt{N}v_{rk} = \sin\theta \exp i\phi r, \tag{11.117}$$

with the boundary conditions for a periodic solution, *i.e.*,

$$u_{rk} = u_{(r+N)k}, \tag{11.118}$$

$$v_{rk} = v_{(r+N)k},$$

which yield the equation system

$$(\epsilon_k - 2\beta\cos\phi)\cos\theta = I\sin\theta, \tag{11.119}$$

$$(\epsilon_k - 2\lambda\beta\cos\phi)\sin\theta = I\cos\theta.$$

From this equation, two branches of eigenvalues arise, which can be seen from the quadratic form

$$(\epsilon_k - 2\beta\cos\phi)(\epsilon_k - 2\lambda\beta\cos\phi) = I^2. \tag{11.120}$$

Using the boundary condition (11.119) and the pairing property (11.113), we obtain

$$\phi = 2\pi k/N \tag{11.121}$$

for positive or negative integers k, and we obtain the roots

$$\epsilon_k = (1+\lambda)\beta\cos(2\pi k/N) + [I^2 + (1-\lambda)^2\beta^2\cos^2(2\pi k/N)]^{\frac{1}{2}}, \tag{11.122}$$

for $k = 0, 1, 2, \cdots, N-1$ and

$$\epsilon_k = -\epsilon_{|k|}, \tag{11.123}$$

for $k = -N, -N+1, \cdots, -2, -1$.

The eigenvectors are determined in terms of the parameters $\theta_k = \theta_k$ from Eq. (11.120), and we can determine the parameter $\lambda = -12g_{rs}^2/(1-4k_{ss}^2)$ self-consistently.

One can derive that

$$\begin{aligned} Ng_{01} &= -\sum_{k=-N}^{-1}\cos^2\theta_k\cos(2\pi k/N) \\ &= -\frac{1}{2}(1-\lambda)(\beta/I)\sum_{k=0}^{N-1)}\cos^2(2\pi k/N) \\ &\times\ [1+(1-\lambda)^2(\beta/I)^2\cos^2(2\pi k/N)]^{-\frac{1}{2}}, \end{aligned} \tag{11.124}$$

which yields the two limiting results

$$\lim_{\beta/I\to 0} g_{01} = -(1-\lambda)(\beta/4I) \tag{11.125}$$

and

$$\lim_{I/\beta\to 0} g_{01} = \sum_{k=0}^{N-1} |\cos(2\pi k/N)|/2N \overset{N\to\infty}{\longrightarrow} = 1/\pi. \tag{11.126}$$

One can also derive that

$$\begin{aligned} Nk_{00} &= \sum_{k=-N}^{-1}\cos\theta_k\sin\theta_k \\ &= -\frac{1}{2}\sum_{k=0}^{N-1}[1+(1-\lambda)^2(\beta/I)^2\cos^2 2\pi k/N)]^{-\frac{1}{2}} \end{aligned} \tag{11.127}$$

Table 11.2: Comparison of calculations of the energy of an infinite linear chain in the limit of $|\beta/I| \ll 1$

Method	$E_0 I/2\beta^2 N$	% of exact value
One-parameter AMO	-0.4053	58.5
Many-parameter AMO	-0.5000	72.1
Eq.(11.76)	-0.6250	90.2
Eq.(11.75)	-0.8594	124
Exact	-0.6931	100

with the limiting values

$$\lim_{\beta/I \to 0} k_{00} = -\frac{1}{2} + \frac{1}{2}(1-\lambda)^2(\beta/I)^2 \tag{11.128}$$

and

$$\lim_{I/\beta \to 0} k_{00} = 0. \tag{11.129}$$

We conclude that for $N \geq 6$ it holds that

$$-\frac{3}{2} < \lambda < -12/\pi^2 = -1.216\ldots \tag{11.130}$$

and that this result is rather insensitive to the ratio β/I. The two branches of the eigenvalue spectrum defined by Eq. (11.120) form a hyperbola when the eigenvalues ϵ_k are plotted against the Hückel energy $2\beta\cos(2\pi k/N)$ with asymptotes, the slopes of which are unity and λ.

In order to compare this treatment of the PPP hamiltonian with known results, the total energy of the linear chain is calculated in the limit of small β. The total energy of the presented Green's function approach is obtained in two ways: from Eq.(11.75) and from the integral of Eq.(11.76). These results are compared to the one- and many-parameter alternant molecular orbital energies[13], and with an exact calculation for the antiferromagnetic chain[14]. We note that Eq. (11.75) gives too low an energy, a result that we interpret as a failure to satisfy the identity (11.74) within the present approximate calculation.

Notes and Bibliography

- The Green's function method applied to the Pariser-Parr-Pople hamiltonian going beyond the Hartree-Fock approximation follows closely the work presented by the authors in 1967 (*Chem. Phys. Lett.* **1**, 295) and in 1968 (*J. Chem. Phys.* **49**, 716).

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[13] R. Pauncz, J. de Heer, and P. -O. Löwdin, *J.Chem. Phys.* **36**, 2247, 2257 (1962)

[14] L. Hulthén, *Arkiv. Mat. Fys. Astr.* **26A**, 11 (1938)

- The original work that has given the name to this model are from 1953 by R. Pariser and R. G. Parr in *J. Chem. Phys.* **21**, 446 and 767, and by J. A. Pople in *Trans. Faraday Soc.* **42**, 1375.
- The Hellmann-Feynman theorem used in developing the formula as a derivative of the total energy has its origin in the work of H. G. A. Hellmann (1937) *Einführung in die Quantenchemie*, Leipzig, page 285, and in the work of R. P. Feynman from 1939 published in *Phys. Rev.* **56**, 340.
- Detailed calculations for the six-membered ring using the approximations presented in this chapter were published by J. Linderberg and E. W. Thulstrup in 1968 in *J. Chem. Phys.* **49**, 710.
- The linear chain problem with a simplified hamiltonian using $\gamma_{rs} = \gamma\delta_{rs}$ has been solved by E. H. Lieb and F. Y. Wu in *Phys. Rev. Lett.* **20**, 1445 (1968).

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Jan Linderberg and Yngve Öhrn

Chapter 12

The Excitation Propagator in Higher Orders

The excitation propagator is of importance for the understanding of electronic excitation spectra, polarizabilities, indirect nuclear spin-spin coupling tensors, and many other quantities. It has been treated in higher order approximations[1] and is capable of yielding predictive results. An approach analogous to the one followed for the electron propagator is quite feasible.

A more accurate treatment of the equation of motion

$$E\langle\langle a_i^\dagger a_j; a_k^\dagger a_l\rangle\rangle_E = \langle [a_i^\dagger a_j, a_k^\dagger a_l]_-\rangle + \langle\langle a_i^\dagger a_j; [H, a_k^\dagger a_l]_-\rangle\rangle_E \tag{12.1}$$

is needed than what is done within the geometric approximation (RPA). The reference state is chosen as a single determinantal SCF state $|0\rangle$ with the SCF spin orbital basis and the associated electron field operators being divided into occupied (labeled by indices *a, b, c, ...*) and unoccupied (labeled by indices *p, q, r, ...*). The superoperator hamiltonian is used again, and a basis of Boson-like operators

$$\begin{aligned} \{X_i\} &= \left\{a_p^\dagger a_a, a_p^\dagger a_a a_q^\dagger a_b, a_p^\dagger a_a a_q^\dagger a_b a_r^\dagger a_c \cdots\right\} \\ &= \left\{q_k^\dagger, q_k^\dagger q_i^\dagger, q_k^\dagger q_i^\dagger q_j^\dagger \cdots\right\} \end{aligned} \tag{12.2}$$

is employed. The hamiltonian is again partitioned into an unperturbed part and a perturbation as

$$\begin{aligned} H_0 &= \sum_i \epsilon_i a_i^\dagger a_i \\ V &= \sum_{i,j,k,l} \langle ij||kl\rangle \left[\frac{1}{4} a_i^\dagger a_j^\dagger a_l a_k - \delta_{jl}\langle n_j\rangle a_i^\dagger a_k\right] \end{aligned} \tag{12.3}$$

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[1] see, *e.g.*, J. Oddershede and P. Jørgensen, *J. Chem. Phys.* **66**, 1541 (1977)

but a different (but equivalent) way is chosen to proceed toward the perturbation expansion than what was done in the case of the electron propagator.

The excitation (matrix) propagator in Eq. (5.2)

$$\mathbf{P}(E) = \left(\begin{pmatrix} \mathbf{q}^\dagger \\ \mathbf{q} \end{pmatrix}\middle|(E\hat{I}-\hat{H})^{-1}(\,\mathbf{q}^\dagger \quad \mathbf{q}\,)\right) \tag{12.4}$$

can now be approximated by introducing a truncated inner projection manifold $\mathbf{h}$ of our field operator space such that

$$\mathbf{P}(E) \approx \left(\begin{pmatrix} \mathbf{q}^\dagger \\ \mathbf{q} \end{pmatrix}\middle|\mathbf{h})(\mathbf{h}|(E\hat{I}-\hat{H})\mathbf{h})^{-1}(\mathbf{h}|(\,\mathbf{q}^\dagger \quad \mathbf{q}\,)\right). \tag{12.5}$$

If the projection manifold spans the entire field operator space, there is no approximation. However, that is not feasible and one proceeds by partitioning the projection manifold so that $\{\mathbf{h}\} = \{(\,\mathbf{q}^\dagger \quad \mathbf{q}\,)\,|\mathbf{f}\}$. Provided $\mathbf{f}$ is orthogonalized against the particle-hole and the hole-particle space, *i.e.*,

$$\begin{aligned} (\mathbf{q}^\dagger|\mathbf{f}) &= \mathbf{0}, \\ (\mathbf{q}|\mathbf{f}) &= \mathbf{0}, \end{aligned} \tag{12.6}$$

one obtains

$$\begin{aligned} \mathbf{P}(E) \approx\ & \left(\begin{pmatrix} \mathbf{q}^\dagger \\ \mathbf{q} \end{pmatrix}\middle|(\,\mathbf{q}^\dagger \quad \mathbf{q}\,)\right)\Bigg\{\left(\begin{pmatrix} \mathbf{q}^\dagger \\ \mathbf{q} \end{pmatrix}\middle|(E\hat{I}-\hat{H})(\,\mathbf{q}^\dagger \quad \mathbf{q}\,)\right) \\ & -\left(\begin{pmatrix} \mathbf{q}^\dagger \\ \mathbf{q} \end{pmatrix}\middle|\hat{H}\mathbf{f})(\mathbf{f}|(E\hat{I}-\hat{H})\mathbf{f})^{-1}(\mathbf{f}|\hat{H}(\,\mathbf{q}^\dagger \quad \mathbf{q}\,)\right)\Bigg\}^{-1} \\ & \times\left(\begin{pmatrix} \mathbf{q}^\dagger \\ \mathbf{q} \end{pmatrix}\middle|(\,\mathbf{q}^\dagger \quad \mathbf{q}\,)\right). \end{aligned} \tag{12.7}$$

The treatment of this expression through third order in electron interaction has been carried through[2]. It is necessary to introduce corrections to the SCF reference state through second order in electron interaction. This is usually accomplished via a Rayleigh-Schrödinger perturbation expansion. When this is done, one needs to also introduce renormalized particle-hole and hole-particle operators, which slightly complicates the formalism.

An explicit treatment of the excitation propagator through *second order in electron interaction* is presented in the following. First the projection manifold is limited to $\{\mathbf{f}\} = \{(\,\mathbf{q}^\dagger\mathbf{q}^\dagger \quad \mathbf{q}\mathbf{q}\,)\}$, and the superoperator

$$\hat{R} = \hat{H} + \hat{H}|\mathbf{f})(\mathbf{f}|(E\hat{I}-\hat{H})\mathbf{f})^{-1}(\mathbf{f}|\hat{H} \tag{12.8}$$

is introduced to write

$$\mathbf{P}(E) = \begin{pmatrix} E\mathbf{1} - (\mathbf{q}^\dagger|\hat{R}\mathbf{q}^\dagger) & (\mathbf{q}^\dagger|\hat{R}\mathbf{q}) \\ (\mathbf{q}|\hat{R}\mathbf{q}^\dagger) & -E\mathbf{1} - (\mathbf{q}|\hat{R}\mathbf{q}) \end{pmatrix}^{-1}. \tag{12.9}$$

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[2] see, *e.g*, J. Oddershede and P. Jørgensen, *J. Chem. Phys.* **66**, 1541 (1977)

As all four blocks of the matrix propagator contain the same information regarding excitation energies and transition moments (as is clear from the spectral representation), one can choose to concentrate on the so-called particle-hole propagator, which satisfies

$$\langle\langle \mathbf{q}; \mathbf{q}^\dagger \rangle\rangle_E^{-1} = E\mathbf{1} - \mathbf{M}(E), \tag{12.10}$$

where $\mathbf{M}(E)$ is the proper particle-hole self-energy or the "irreducible vertex part". The expression

$$\mathbf{M}(E) = (\mathbf{q}^\dagger|\hat{R}\mathbf{q}^\dagger) + (\mathbf{q}^\dagger|\hat{R}\mathbf{q})[E\mathbf{1} + (\mathbf{q}|\hat{R}\mathbf{q})]^{-1}(\mathbf{q}|\hat{R}\mathbf{q}^\dagger) \tag{12.11}$$

can be analyzed through various orders of perturbation theory, where order is defined in terms of the electron interaction. For excitation energies through second order in electron interaction, one has to evaluate $(\mathbf{q}^\dagger|\hat{R}\mathbf{q}^\dagger)$ through second order, while since $(\mathbf{q}^\dagger|\hat{R}\mathbf{q})$ is at least of first order, $(\mathbf{q}|\hat{R}\mathbf{q})$ needs only be evaluated through zeroth order.

The reference state of the propagator needs to be evaluated through first order in electron interaction, which gives

$$|ref\rangle = |0\rangle + |DE\rangle = N(1 + \sum_{\substack{p>q \\ a>b}} \frac{\langle qp||ab\rangle a_p^\dagger a_a a_q^\dagger a_b}{\epsilon_p + \epsilon_q - \epsilon_a - \epsilon_b})|0\rangle. \tag{12.12}$$

First, consider

$$\begin{aligned}(\mathbf{q}^\dagger|\hat{R}\mathbf{q}^\dagger) &= (\mathbf{q}^\dagger|\hat{H}\mathbf{q}^\dagger) \\ &+ (\mathbf{q}^\dagger|\hat{H}\begin{pmatrix} \mathbf{q}^\dagger\mathbf{q}^\dagger & \mathbf{q}\mathbf{q} \end{pmatrix})(\begin{pmatrix} \mathbf{q}^\dagger\mathbf{q}^\dagger \\ \mathbf{q}\mathbf{q} \end{pmatrix}|(E\hat{I} - \hat{H})\begin{pmatrix} \mathbf{q}^\dagger\mathbf{q}^\dagger & \mathbf{q}\mathbf{q} \end{pmatrix})^{-1} \\ &\times (\begin{pmatrix} \mathbf{q}^\dagger\mathbf{q}^\dagger \\ \mathbf{q}\mathbf{q} \end{pmatrix}|\hat{H}\mathbf{q}^\dagger),\end{aligned} \tag{12.13}$$

where several terms can be dropped when limiting the treatment only to low orders. For instance, $(\mathbf{q}\mathbf{q}|\hat{H}\mathbf{q}^\dagger)$ is zero when using the SCF average, and when the first-order correction $|DE\rangle$ is used, these terms are at least of second order. Thus, through second order one would only have to consider

$$(\mathbf{q}^\dagger|\hat{R}\mathbf{q}^\dagger) = \mathbf{B} + \mathbf{a}^T(E\mathbf{1} - \mathbf{A})^{-1}\mathbf{a} \tag{12.14}$$

with

$$\begin{aligned}\mathbf{B} &= (\mathbf{q}^\dagger|\hat{H}\mathbf{q}^\dagger), \qquad \mathbf{a} = (\mathbf{q}^\dagger\mathbf{q}^\dagger|\hat{H}\mathbf{q}^\dagger), \\ \mathbf{A} &= (\mathbf{q}^\dagger\mathbf{q}^\dagger|\hat{H}\mathbf{q}^\dagger\mathbf{q}^\dagger).\end{aligned} \tag{12.15}$$

Similar arguments lead to $\left(\mathbf{q}^\dagger|\hat{R}\mathbf{q}\right) = \mathbf{C} = \left(\mathbf{q}^\dagger|\hat{H}\mathbf{q}\right)$, which starts to contribute in first order.

Through second order, the excitation propagator can then be expressed as

$$\begin{aligned}
\mathbf{P}^{-1}(E) &= \begin{pmatrix} E\mathbf{1}-\mathbf{B} & \mathbf{C} \\ \mathbf{C}^* & -E\mathbf{1}-\mathbf{B}^* \end{pmatrix} \\
&\quad - \begin{pmatrix} \mathbf{a}^T\left(E\mathbf{1}-\mathbf{A}\right)^{-1}\mathbf{a} & \mathbf{0} \\ \mathbf{0} & \mathbf{a}^\dagger(-E\mathbf{1}-\mathbf{A}^*)^{-1}\mathbf{a}^* \end{pmatrix},
\end{aligned} \tag{12.16}$$

where the first matrix is the inverse of the RPA propagator and the second matrix contains the so-called "two-particle two-hole corrections" ($2p$–$2h$-corrections).

One can now evaluate explicit expressions for the elements of these matrices in terms of two-electron integrals over SCF spin orbitals and spin orbital energies. Observing the special nature of the particle-hole and hole-particle operators, one obtains readily

$$\begin{aligned}
B_{qb;pa}(0) &= \langle 0|[a_b^\dagger a_q,[H_0,a_p^\dagger a_a]_-]_-|0\rangle = (\epsilon_p-\epsilon_a)\,\delta_{pq}\delta_{ab}, \\
B_{qb;pa}(1) &= \langle 0|[a_b^\dagger a_q,[V,a_p^\dagger a_a]_-]_-|0\rangle = \langle qa||bp\rangle, \\
B_{qb;pa}(2) &= \langle 0|[a_b^\dagger a_q,[V,a_p^\dagger a_a]_-]_-|DE\rangle \\
&= \frac{\delta_{ab}}{2}\sum_{m,c,d}\frac{\langle qm||cd\rangle\langle cd||mp\rangle}{\epsilon_q+\epsilon_m-\epsilon_a-\epsilon_b} \\
&\quad -\frac{\delta_{pq}}{2}\sum_{m,n,c}\frac{\langle ac||mn\rangle\langle mn||bc\rangle}{\epsilon_q+\epsilon_p-\epsilon_c-\epsilon_b},
\end{aligned} \tag{12.17}$$

for the terms contributing to the B-matrix through second order. For the other matrices, one finds

$$\begin{aligned}
C_{qb;pa}(1) &= \langle 0|[a_q^\dagger a_b,[V,a_p^\dagger a_a]_-]_-|0\rangle = \langle ab||qp\rangle, \\
a_{ndmc;pa}(1) &= \langle 0|[a_c^\dagger a_m a_d^\dagger a_n,[V,a_p^\dagger a_a]_-]_-|0\rangle \\
&= -\delta_{mp}\langle an||cd\rangle + \delta_{np}\langle am||cd\rangle \\
&\quad -\delta_{ca}\langle mn||dp\rangle + \delta_{da}\langle mn||cp\rangle, \\
A_{ndmc;sfre}(0) &= \langle 0|[a_c^\dagger a_m a_d^\dagger a_n,[H_0,a_s^\dagger a_f a_r^\dagger a_e]_-]_-|0\rangle \\
&= (\epsilon_m+\epsilon_n-\epsilon_c-\epsilon_d)\,\delta_{ns}\delta_{mr}\delta_{df}\delta_{ce},
\end{aligned} \tag{12.18}$$

for the terms that contribute through second order.

One can, of course, proceed to higher orders and introduce diagrammatic analysis analogously to what was done for the electron propagator[3]. Calculations beyond second order are yet not feasible for other than the smallest systems. Iterative solutions of

$$E = M_{qb;pa}(E) \tag{12.19}$$

for converged excitation energies can be obtained, although they are costly. Similar considerations to those expressed for the electron propagator apply here[4].

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[3] see, *e.g.*, J. Oddershede and P. Jørgensen, *J. Chem. Phys.* **66**, 1541 (1977)

[4] see, *e.g.*, J. Oddershede, in *Adv. in Quantum Chem.* Vol. **11**, 275 (1978) and references therein for a comprehensive discussion of connections to other methods

12.1 Auger Spectroscopy

Auger spectroscopy prepares a system in a core-hole state by ionizing radiation and measures the kinetic energy of secondary electrons produced when the highly excited core-hole state makes a radiationless transition to a continuum state with two valence-holes and a free electron. The initial photoelectron and the secondary (Auger) electron make this a two-electron detachment process leading to the two-particle two-hole propagator

$$\begin{aligned}\langle\langle \tilde{a}_k \tilde{a}_l ; \tilde{a}_n^\dagger \tilde{a}_m^\dagger \rangle\rangle_E &= \sum_p \left[\frac{\langle 0|\tilde{a}_k \tilde{a}_l|p\rangle\langle p|\tilde{a}_n^\dagger \tilde{a}_m^\dagger|0\rangle}{E - E_p\,(N+2) + E_0\,(N) + i\eta} \right. \\ &\qquad \left. - \frac{\langle 0|\tilde{a}_n^\dagger \tilde{a}_m^\dagger|p\rangle\langle p|\tilde{a}_k \tilde{a}_l|0\rangle}{E - E_0\,(N) + E_p\,(N-2) - i\eta} \right], \qquad (12.20)\end{aligned}$$

which can be expressed in matrix form as

$$\begin{aligned}\mathbf{A}(E) = \langle\langle \tilde{\mathbf{a}}\tilde{\mathbf{a}}; \tilde{\mathbf{a}}^\dagger \tilde{\mathbf{a}}^\dagger \rangle\rangle_E &= (\tilde{\mathbf{a}}^\dagger \tilde{\mathbf{a}}^\dagger | (E\hat{I} - \tilde{H})^{-1} \tilde{\mathbf{a}}^\dagger \tilde{\mathbf{a}}^\dagger) \\ &\simeq \mathbf{S}(E\mathbf{S} - \mathbf{F})^{-1}\mathbf{S}, \qquad (12.21)\end{aligned}$$

where in the last step the geometric approximation is again invoked. A single-determinantal SCF reference state $|0\rangle$ is employed and the indices ordered such that $k < l$ $(m < n)$. It should be noted that in the operator basis $\{X_i\} = \{\tilde{a}_l^\dagger \tilde{a}_k^\dagger\}$, *both* k and l (m and n) are either occupied or unoccupied spin orbitals in the reference state. Should, say, k refer to an occupied spin orbital and l refer to an unoccupied spin orbital (or vice versa), the metric would be singular. This can be seen from

$$S_{ij} = (X_i|X_j) = \langle 0|[\tilde{a}_k \tilde{a}_l, \tilde{a}_n^\dagger \tilde{a}_m^\dagger]_-|0\rangle = \delta_{ln}\delta_{km}\,(1 - \langle n_k\rangle - \langle n_l\rangle)\,, \qquad (12.22)$$

with i and j being the compound indices (k,l), and (m,n), respectively. Such "mixed" field operators are excluded from the basis. The basis field operators are then ordered in such a way that propagator assumes the block form

$$\mathbf{A}(E) = \langle\langle \tilde{\mathbf{a}}\tilde{\mathbf{a}}; \tilde{\mathbf{a}}^\dagger \tilde{\mathbf{a}}^\dagger \rangle\rangle_E = \begin{bmatrix} oo & ou \\ uo & uu \end{bmatrix}, \qquad (12.23)$$

where oo refers to the block with the indices of both $\tilde{a}\tilde{a}$ and $\tilde{a}^\dagger \tilde{a}^\dagger$ corresponding to occupied spin orbitals, and so on.

In the following, the convention is used that a and b refer to occupied and p and q refer to unoccupied spin orbitals. The inverse of the propagator in the geometric approximation can then be expressed as

$$\mathbf{A}^{-1}(E) = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} -E\mathbf{1} - \mathbf{B} & -\mathbf{C} \\ -\bar{\mathbf{C}} & E\mathbf{1} - \mathbf{D} \end{bmatrix} \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}. \qquad (12.24)$$

Using the single-determinantal SCF reference state, one can readily calculate

$$\begin{aligned}B_{ij} = (X_i|\hat{H}X_j) &= \langle 0|[\tilde{a}_a \tilde{a}_b, [H, \tilde{a}_{a'}^\dagger, \tilde{a}_{b'}^\dagger]_-]_-|0\rangle \\ &= -\delta_{aa'}\delta_{bb'}\,(\epsilon_a + \epsilon_b) + \langle ab||a^{'} b^{'}\rangle, \qquad (12.25)\end{aligned}$$

where the hamiltonian in Eq. (9.3) is used. Similarly,

$$\begin{aligned} C_{ij} = (X_i|\hat{H}X_j) &= \langle 0|[\vec{a}_a\tilde{a}_b, [H, \tilde{a}_q^\dagger\tilde{a}_p^\dagger]_-]_-|0\rangle \\ &= -\langle ab||pq\rangle. \end{aligned} \tag{12.26}$$

One should note that the off-diagonal block **C** is rectangular because as a rule the rank of the unoccupied space of spin orbitals exceeds that of the occupied space by a factor of two or more. It is quite easy to show that

$$\begin{aligned} \bar{C}_{ji} = (X_j|\hat{H}X_i) &= \langle 0|[\tilde{a}_p\tilde{a}_q, [H, \tilde{a}_b^\dagger\tilde{a}_a^\dagger]_-]_-|0\rangle \\ &= -\langle pq||ab\rangle = C_{ij}^*, \end{aligned} \tag{12.27}$$

i.e., $\bar{\mathbf{C}} = \mathbf{C}^\dagger$. The diagonal block corresponding to the unoccupied spin orbitals has the elements

$$\begin{aligned} D_{ij} &= \langle 0|[\tilde{a}_p\tilde{a}_q, [H, \tilde{a}_{q'}^\dagger\tilde{a}_{p'}^\dagger]_-]_-|0\rangle \\ &= \delta_{pp'}\delta_{qq'}\,(\epsilon_p + \epsilon_q) + \langle pq||p'q'\rangle. \end{aligned} \tag{12.28}$$

Partitioning can be used so that the various blocks of **A**(E) can be expressed in terms of blocks of its inverse. In particular, for the top diagonal block of **A**(E), which corresponds to the occupied spin orbitals or the "hole states", one obtains

$$\mathbf{A}\,(E)_{oo} = [-\,(E\mathbf{1} - \mathbf{B}) - \mathbf{C}\,(E\mathbf{1} - \mathbf{D})^{-1}\,\mathbf{C}^\dagger]^{-1}. \tag{12.29}$$

This means that a particular diagonal element of this block of the inverse is

$$A^{-1}\,(E)_{ab;ab} = -E - B_{ab;ab} - \sum_{p,q,p',q'} C_{ab;pq}\,(E1 - D)^{-1}_{pq;p'q'}\,C^*_{ab;p'q'}. \tag{12.30}$$

As **A**(E) becomes infinite for E equal to a two-electron binding energy, it holds that the inverse has a zero eigenvalue and an estimate of the E-value is found from Eq. (12.31). Thus,

$$A^{-1}(E)_{ab;ab} = 0, \quad \text{for} \quad E = E_0(N) - E_s(N-2), \tag{12.31}$$

i.e., the negative of a two-electron detachment energy.

The resulting equation for the negative of the two-electron detachment energy can be solved by iteration or by perturbation theory. Through second order in electron interaction,

$$E = \epsilon_a + \epsilon_b - \langle ab||ab\rangle - \sum_{p,q} \frac{|\langle ab||pq\rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_p - \epsilon_q}. \tag{12.32}$$

Although this is an expression for the negative of the energy required to remove two electrons (in spin orbital a and b) from our system, it reveals nothing about the specific process. The Auger process, as has been previously remarked, is an internal conversion or radiationless transition between two states of the same energy. The initial step creates a hole state

$$\tilde{a}_c(0)\,|0\rangle, \tag{12.33}$$

where $\tilde{a}_c(0)$ removes an electron at time 0 out of the core spin orbital c in the N-electron ground state.

This is, of course, a somewhat oversimplified description, since the initial ionization at $t = 0$ produces not only a simple hole state but also has amplitudes corresponding to other processes as "shake-ups" and "shake-offs". In most cases, though, the by far largest amplitude initially obtains for the simple vertical hole state. The initially created hole state might then evolve into

$$\tilde{a}_k^\dagger(\tau)\tilde{a}_a(\tau)\tilde{a}_b(\tau)|0\rangle, \tag{12.34}$$

at time τ, *i.e.*, a state with a free electron in continuum spin orbital k (orthogonal to all the bound state spin orbitals) and with two (valence) holes in spin orbitals a and b of the original N-electron state. In order for the Auger electron to be observed escaping in spin orbital k, this process must be faster than the radiative lifetime of the initial hole state, *i.e.*, typically $\tau < 10^{-9}$ seconds.

The probability amplitude for the radiationless transition of the Auger process then is

$$\langle 0|\tilde{a}_a^\dagger(\tau)\,\tilde{a}_b^\dagger(\tau)\,\tilde{a}_k(\tau)\,\tilde{a}_c(0)\,|0\rangle. \tag{12.35}$$

One can express this probability amplitude in terms of the appropriate propagator as

$$\begin{aligned}&\langle 0|\tilde{a}_a^\dagger(\tau)\tilde{a}_b^\dagger(\tau)\tilde{a}_k(\tau)\tilde{a}_c(0)|0\rangle\\ &= (i/2\pi)\int_{-\infty}^{\infty}\langle\langle\tilde{a}_a^\dagger\tilde{a}_b^\dagger\tilde{a}_k;\tilde{a}_c\rangle\rangle_E\exp(-iE\tau)dE\end{aligned} \tag{12.36}$$

for $\tau > 0$, which follows from the Fourier transform of the double-time Green's function in Eq. (4.8). Since the equation of motion is

$$E\langle\langle\tilde{a}_a^\dagger\tilde{a}_b^\dagger\tilde{a}_k;\tilde{a}_c\rangle\rangle_E = \langle[\tilde{a}_a^\dagger\tilde{a}_b^\dagger\tilde{a}_k,\tilde{a}_c]_+\rangle + \langle\langle\tilde{a}_a^\dagger\tilde{a}_b^\dagger\tilde{a}_k;[H,\tilde{a}_c]_-\rangle\rangle_E, \tag{12.37}$$

it follows from Eqs. (9.14) and (9.17) that

$$\begin{aligned}(E+\epsilon_c)\langle\langle\tilde{a}_a^\dagger\tilde{a}_b^\dagger\tilde{a}_k;\tilde{a}_c\rangle\rangle_E &= \frac{1}{2}\sum_{i,j,l}\langle ic||jl\rangle\langle\langle\tilde{a}_a^\dagger\tilde{a}_b^\dagger\tilde{a}_k;\tilde{a}_i^\dagger\tilde{a}_l\tilde{a}_j\rangle\rangle_E\\ &\quad-\sum_{i,j}\langle ci||ji\rangle\langle n_i\rangle\langle\langle\tilde{a}_a^\dagger\tilde{a}_b^\dagger\tilde{a}_k;\tilde{a}_j\rangle\rangle_E.\end{aligned} \tag{12.38}$$

This looks somewhat complicated, but if one wants only the result through first order in electron interaction, only the first term in the moment expansion of the propagators on the right side of Eq. (12.38) is needed. This means the evaluation of the averages

$$\langle 0|[\tilde{a}_a^\dagger \tilde{a}_b^\dagger \tilde{a}_k, \tilde{a}_i^\dagger \tilde{a}_l \tilde{a}_j]_+|0\rangle = \delta_{ik}\langle n_a\rangle\langle n_b\rangle\left(\delta_{aj}\delta_{bl} - \delta_{al}\delta_{bj}\right) \tag{12.39}$$

and

$$\langle 0|[\tilde{a}_a^\dagger \tilde{a}_b^\dagger \tilde{a}_k, \tilde{a}_j]_+|0\rangle = 0, \tag{12.40}$$

where the natures of the spin orbitals a, b, and k have been used to get the result.

Eq. (12.36) will then read

$$\begin{aligned}&\langle 0|\tilde{a}_a^\dagger(\tau)\,\tilde{a}_b^\dagger(\tau)\,\tilde{a}_k(\tau)\,\tilde{a}_c(0)\,|0\rangle \\ &= (i/2\pi)\int_{-\infty}^{\infty} \frac{\langle kc||ab\rangle e^{-iE\tau}}{E\left(E+\epsilon_c+i\eta\right)}dE,\end{aligned} \tag{12.41}$$

where the infinitesimal $i\eta$ ($\eta > 0$) is added, because the poles of the propagator under the integral sign in Eq. (12.36) that correspond to electron detachment energies lie in the lower complex energy half-plane. Also observe that the propagator has no poles at $E = 0$, so that pole in the above expression is spurious. Thus, one obtains

$$\langle 0|\tilde{a}_a^\dagger(\tau)\tilde{a}_b^\dagger(\tau)\tilde{a}_k(\tau)\tilde{a}_c(0)|0\rangle = \langle kc||ab\rangle e^{i\epsilon_c\tau}/\epsilon_c. \tag{12.42}$$

Assuming the reference state to be a singlet, the final two-(valence)hole state can be either a spin singlet or a triplet. This means that the operator $\tilde{a}_a\tilde{a}_b$ in the basis should be replaced by

$$\left(\tilde{a}_{a\alpha}\tilde{a}_{b\beta} - \tilde{a}_{a\beta}\tilde{a}_{b\alpha}\right)/2^{\frac{1}{2}} \tag{12.43}$$

for the singlet case, where now a and b label orbitals rather than spin orbitals. Similarly, for the triplet case, the operators

$$\begin{aligned}&\left(\tilde{a}_{a\alpha}\tilde{a}_{b\beta} + \tilde{a}_{a\beta}\tilde{a}_{b\alpha}\right)/2^{\frac{1}{2}}, \\ &\tilde{a}_{a\alpha}\tilde{a}_{b\alpha}, \qquad \text{or} \\ &\tilde{a}_{a\beta}\tilde{a}_{b\beta}\end{aligned} \tag{12.44}$$

are used. It is straightforward to show that the probability for the emission of an Auger electron in continuum orbital k then is proportional to the square of the amplitude

$$\left(\langle kc|ab\rangle + \langle kc|ba\rangle\right) \tag{12.45}$$

for the two-(valence)hole singlet, and

$$3^{1/2}\left(\langle kc|ab\rangle - \langle kc|ba\rangle\right) \tag{12.46}$$

for the triplet.

The relation between the (negative of) two-electron binding energies and the Auger spectrum that measures the kinetic energy $\frac{1}{2}k_A^2$ of the Auger electron can be expressed as

$$\frac{1}{2}k_A^2 = constant + (E_0 (N) - E_s (N-2)). \tag{12.47}$$

This is so since $E_c(N-1) = \frac{1}{2}k_A^2 + E_s(N-2)$, where $E_c(N-1)$ is the energy of the initial core-hole state and

$$E_c (N-1) - E_0 (N) = h\nu - \frac{1}{2}k_I^2, \tag{12.48}$$

with $h\nu$ the energy of the ionizing photon and $\frac{1}{2}k_I^2$ the kinetic energy of the initial photoelectron. For a given spectrum, both of these quantities are constant, giving us the desired relation.

Problems

1. Diagonalize the propagator matrix in the geometric approximation and compare with the energy representation of the two-hole two-particle propagator analogously to what was done in the case of the polarization propagator.

Notes and bibliography

- Auger spectroscopy was first introduced by P. Auger in *Compt. rend.* **180**, 65 (1925).

- The book *X-Ray Photoelectron Spectroscopy* in the series *Benchmark Papers in Physical Chemistry and Chemical Physics, v.2* Ed. Thomas A. Carlson, Dowden, Hutchinson & Ross Inc., Stroudsburg, PA, 1978, discusses a few interesting experimental results.

- More elaborate and precise theoretical treatments of molecular Auger processes are presented by H. D. Schulte and L. S. Cederbaum in *Phys. Rev.* **A60**, 2047 (1999), and by E. Pahl, L.S. Cederbaum, and F. Tarantelli in *Phys. Rev.* **A60**, 1070 (1999).

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Chapter 13

Propagators and Chemical Reaction Rate

Chemical reactions and their rates are central to chemical research. The quantum mechanical theory of reaction rates invokes quantum mechanical scattering theory and statistical mechanics. Thus, one considers the propagation of a system from an initial situation to a different one. Expressions for such processes are developed by means of *quasi-stationary nonequilibrium* theory.

Central to the development is an ensemble operator Γ akin to the one considered in the previous chapter and constructed from the appropriate system hamiltonian H of the reacting system and a *bias* operator B. A self-adjoint orthogonal operator B is constructed as the difference between a projector onto the product states and a projector Q_R onto the reactant states, such that

$$B = (1 - Q_R) - Q_R = 1 - 2Q_R. \tag{13.1}$$

Obviously it holds that $B^2 = 1$. A suitable ensemble operator is

$$\Gamma = \exp\left[\beta(F - H + \lambda B)\right], \tag{13.2}$$

where $\beta = 1/kT$, F is the free energy, and λ is the energy bias parameter. A positive value of the bias favors the product subspace of states. The expectation value of B is a measure of the difference in the number of systems present in the product and that present in the reactant states. The bias operator induces a perturbed equilibrium, and to first order in the parameter λ, the change can be calculated by perturbation theory as

$$\langle B \rangle = \langle B \rangle_0 + \frac{\lambda}{\beta}\left[\int_0^\beta d\tau \int_0^\beta d\tau' \langle B(\tau) B \rangle_0 - \beta \langle B \rangle_0^2\right], \tag{13.3}$$

where

$$B(\tau) = e^{\tau H} B e^{-\tau H} \tag{13.4}$$

and the subscript 0 indicates an average over the unperturbed ensemble with $\lambda = 0$. It holds that

$$\langle B\rangle = \langle B\rangle_0 + \frac{\lambda}{2}\int_0^\beta d\tau \int_0^\beta d\tau' \langle T\left[B(\tau)B(\tau')\right]\rangle_c. \tag{13.5}$$

The τ-ordering operator T and the concept of connected terms are used in Chapter 7, and Appendix F.

The expectation value in Eq. (13.3) does not remain constant in time, because the bias operator does not commute with the hamiltonian. A quasi-equilibrium is maintained through an adiabatic switching that turns on the bias via the integral representation

$$\tilde{B} = \eta \int_{-\infty}^{0} dt e^{\eta t} B(it) = B - \int_{-\infty}^{0} dt e^{\eta t} J(it), \tag{13.6}$$

where the flux operator

$$J(it) = -i[B(it), H] \tag{13.7}$$

is introduced. The expectation value of the flux operator gives the rate of change of the expectation value of the bias, *i.e.*,

$$\begin{aligned} \frac{\partial \langle B\rangle}{\partial t} &= \langle J\rangle = \lambda \int_0^\beta d\tau \langle \tilde{B}(\tau) J\rangle_c \\ &= -\lambda \int_0^\beta d\tau \int_{-\infty}^{0} dt e^{\eta t} \langle J(\tau + it) J\rangle_0. \end{aligned} \tag{13.8}$$

Solving for the parameter λ and using Eq. (13.3), the expression

$$\frac{\frac{\partial\langle B\rangle}{\partial t}}{\langle B\rangle_0 - \langle B\rangle} = \frac{\int_0^\beta d\tau \int_{-\infty}^0 dt e^{\eta t}\langle J(\tau + it)J\rangle_0}{\frac{1}{\beta}\int_0^\beta d\tau \int_0^\beta d\tau' \langle T\left[B(\tau)B(\tau')\right]\rangle_c} \tag{13.9}$$

emerges for the reaction rate, where the numerator depends on the flux-flux autocorrelation function, and the denominator expresses the fluctuations in the bias value.

A spectral representation of the flux-flux autocorrelation function takes the form

$$\begin{aligned} &\int_0^\beta d\tau \int_{-\infty}^{0} dt e^{\eta t} \langle J(\tau + it) J\rangle_0 \qquad (13.10) \\ &= \int_0^\beta d\tau \int_{-\infty}^{0} dt \sum_{m,n} e^{(\beta - \tau - it)(F - E_m)} J_{mn} e^{(\tau + it)(F - E_n) + \eta t} J_{nm}. \end{aligned}$$

Continuous spectra are more conveniently accommodated in terms of a spectral density function

$$A_J(x,x';E) = \sum_m J\psi_m(x)\delta(E - E_m)\psi_m^*(x'), \tag{13.11}$$

which expresses the result of the flux operator applied to the propagator spectral density

$$A(x,x';E) = \sum_m \psi_m(x)\delta(E - E_m)\psi_m^*(x'). \tag{13.12}$$

We note that

$$\begin{aligned} & \int_0^\beta d\tau \int_{-\infty}^0 dt e^{(\beta-\tau-it)(F-E)} e^{(\tau+it)(F-E')+\eta t} \\ = \; & \frac{e^{\beta(F-E')} - e^{\beta(F-E)}}{(E-E')(\eta + i(E-E'))} \\ \rightarrow \; & \beta\pi\delta(E'-E)e^{\beta(F-E)}, \end{aligned} \tag{13.13}$$

for $\eta \rightarrow 0$, which means that we can write

$$\begin{aligned} & \int_0^\beta d\tau \int_\infty^0 dt e^{\eta t}\langle J(\tau+it)J\rangle_0 \\ = \; & \beta\pi \int dE dx dx' e^{\beta(F-E)} A_J(x,x';E) A_J(x',x;E) \\ = \; & \beta\pi \sum_{m,n} e^{\beta(F-E_m)} |J_{mn}|^2 \delta(E_m - E_n), \end{aligned} \tag{13.14}$$

where the last expression is sometimes referred to as "a summation over final states and an average over initial ones".

Processes that may be interpreted in terms of a one-dimensional quantum mechanical model offer simplifications of the general expression. The system hamiltonian is specified in terms of a local potential $U(x)$, and a mass M, *i.e.*,

$$H = U(x) - \frac{1}{2M}\frac{d^2}{dx^2}. \tag{13.15}$$

The bias operator is local with the value 1 for the product region, $x > 0$, and the value -1 for the reactant region $x < 0$, or in terms of the Heaviside step function Θ

$$B = B(x) = \Theta(x) - \Theta(-x). \tag{13.16}$$

The flux operator then becomes

$$J = -i[B,H] = -\frac{i}{M}\left\{\delta(x)\frac{d}{dx} - \frac{d}{dx}\delta(x)\right\}, \tag{13.17}$$

and matrix elements have the form

$$\int dx\psi^*(x)J\phi(x) = -\frac{i}{M}\left\{\psi^*(0)\frac{d\phi(0)}{dx} - \frac{d\psi^*(0)}{dx}\phi(0)\right\}. \tag{13.18}$$

For this simple case, we obtain the expression

$$\begin{aligned} &\int\int dx'dxA_J(x,x';E)A_J(x',x;E) \qquad (13.19)\\ = &\left(\frac{4i}{M}\right)^2\left[\frac{dA(0,0;E)}{dx}\frac{dA(0,0;E)}{dx'} - A(0,0;E)\frac{d^2A(0,0;E)}{dxdx'}\right], \end{aligned}$$

which needs to be evaluated.

In Appendix F, we present an application of this approach to the Eckart potential, which is a one-dimensional potential applicable to chemical reaction problems and which yields to analytical solutions.

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Appendix A

Complex Calculus Primer

A complex variable z has a real part x and an imaginary part y and is written $z = x + iy$. Functions $f(z)$ of a complex variable are our concern. Explicit examples are $1/z$, z^2, and $\exp(z)$. Any function of a complex variable can be expressed as

$$f(z) = u(x, y) + iv(x, y), \tag{A.1}$$

where u and v are real functions.

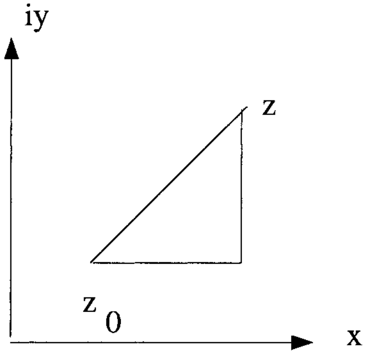

Figure A.1: Complex number plane.

A.1 Continuity

A function $f(z)$ is said to be continuous at $z = z_0$ if given *any* positive number ϵ, one can find a number δ such that $|f(z) - f(z_0)| < \epsilon$ provided that $|z - z_0| < \delta$.

Let $z_0 = x_0 + iy_0$. It then follows that $|u(x,y) - u(x_0,y_0)| \leq |f(z) - f(z_0)| < \epsilon$ if $|z - z_0| < \delta$ *i.e.*, $|x - x_0| < \delta\sqrt{2},\ y - y_0| < \delta/\sqrt{2}$. Hence, if $f(z)$ is continuous, so is $u(x,y)$ and similarly $v(x,y)$. Conversely, it can be shown that if $u(x,y)$ and $v(x,y)$ are continuous, so is $f(z)$.

A.2 Differentiability

If the limit

$$f'(z_0) = \lim_{z \to z_0} \frac{f(z) - f(z_0)}{z - z_0} \tag{A.2}$$

exists, $f(z)$ is said to be differentiable and the limit $f'(z_0)$ is the derivative at $z = z_0$. It is essential to note that this definition asserts that along whatever path z approaches z_0, the ratio in Eq. (A.2) always tends to a limit, and that all paths lead to the same limit.

Using this severe requirement and choosing $z - z_0$ first purely real *i.e.*, $z_0 = x_0 + iy_0$, and $z = x + iy_0$, and then purely imaginary, *i.e.*, $z = x_0 + iy$, one obtains the Cauchy-Riemann equations

$$\frac{du}{dx} = \frac{dv}{dy}, \qquad \frac{dv}{dx} = -\frac{du}{dy} \tag{A.3}$$

for the derivatives of the functions u, and v at $x = x_0$, $y = y_0$, by equating the real and imaginary parts, respectively, of the limits of the ratio in Eq. (A.2) obtained for the two paths.

A.3 Analytic Functions

A function $f(z)$ differentiable in the above sense is said to be analytic at $z = z_0$. The Cauchy-Riemann equations are necessary, but not sufficient for analyticity.

A function is said to be analytic in a region if it is analytic at all points of the region. Analyticity in a region has useful consequences. Examples are $\log(1+z) = z - \frac{z^2}{2} + \frac{z^3}{3} - \cdots$, which is analytic for $|z| < 1$, and $e^z = \sum_{n=0}^{\infty} \frac{z^n}{n!}$, $\cos z = (e^{iz} + e^{-iz})/2$, and $\sin z = (e^{iz} - e^{-iz})/2i$, which are analytic for all finite values of $|z|$.

A.4 Complex Integration

Let AB be an arc C of a curve defined by $x = \phi(t)$; $y = \psi(t)$, where ϕ and ψ are functions of a real parameter t and have continuous derivatives ϕ' and ψ'. The parameter t varies from t_A to t_B when the point (x,y) moves steadily from A to B. Let $f(z) = u(x,y) + iv(x,y)$ be continuous along C.

One proceeds as in the case of real integration by dividing the arc C successively into more intervals $z_m - z_{m-1}$ and considers the infinitesimal limit to be the integral $\int_C f(z)dz$.

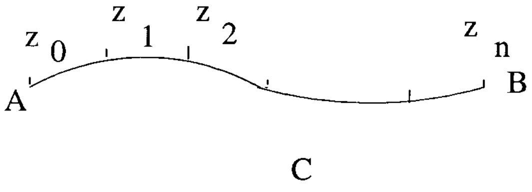

Figure A.2: Arc of a curve in the complex number plane.

Thus, $S_n = \sum_{m=1}^{n} f(\zeta_m)(z_m - z_{m-1})$, where $\zeta_m = \xi_m + i\eta_m$ is a point on C between z_m and z_{m-1}. Also, define $u_m = u(\xi_m, \eta_m)$ and $v_m = v(\xi_m, \eta_m)$ and write

$$S_n = \sum_{m=1}^{n} (u_m + iv_m)(x_m + iy_m - x_{m-1} - iy_{m-1}). \tag{A.4}$$

The expressions

$$\begin{aligned} x_m - x_{m-1} &= \phi(t_m) - \phi(t_{m-1}) = \phi'(\tau_m)(t_m - t_{m-1}), \\ y_m - y_{m-1} &= \psi(t_m) - \psi(t_{m-1}) = \psi'(\bar{\tau}_m)(t_m - t_{m-1}) \end{aligned} \tag{A.5}$$

are introduced, where τ_m and $\bar{\tau}_m$ are points in the closed interval (t_{m-1}, t_m).

Since all functions concerned are (uniformly) continuous, one can find a δ, given ϵ, such that $|u_m \phi'(\tau_m) - u(x_m, y_m)\phi'(t_m)| < \epsilon$ provided $|t_m - t_{m-1}| < \delta$. Since $\sum_{m=1}^{n} \epsilon(t_m - t_{m-1}) = \epsilon(t_B - t_A)$, it follows that as ϵ and δ tend to zero, $\sum_{m=1}^{n} u_m \phi'(\tau_m)(t_m - t_{m-1})$ tends to the same limit as $\sum_{m=1}^{n} u(x_m, y_m)\phi'(t_m)(t_m - t_{m-1})$, which is the integral $\int_{t_A}^{t_B} u(\phi(t), \psi(t))\phi'(t)dt$. Similar arguments can be given for the terms of v and ψ' of Eqs. (A.4) and (A.5) and the limit of the sum S_n becomes the integral

$$\int_C f(z)\,dz = \int_{t_A}^{t_B} (u + iv)\left\{\phi'(t) + i\psi'(t)\right\} dt. \tag{A.6}$$

This has the obvious interpretation as the sum of two real integrals, one of which is multiplied by i.

This complex integral of $f(z)$ along C (generally referred to as the contour) has some obvious properties as can be seen from Eq. (A.6), *e.g.*, $\int_C (f(z) +$

$g(z))dz = \int_C f(z)dz + \int_C g(z)dz$, and $\int_{C_\rightarrow} f(z)dz = -\int_{C_\leftarrow} f(z)dz$. If M is an upper bound for $|f(z)|$ on C and L is the length of C, then $|\int_C f(z)dz| \leq ML$.

Example: Let us calculate the integral $\int_C \frac{dz}{z}$ where the contour C is a circle of radius r centered at the origin (see Fig.A.3).

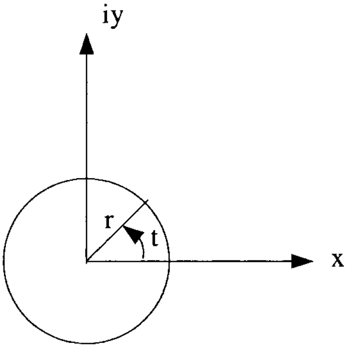

Figure A.3: Integration contour.

It follows that $x = r\cos t = \phi(t)$, $y = r\sin t = \psi(t)$, and $0 \leq t < 2\pi$, while $z = r\exp(it)$, and $\phi'(t) + i\psi'(t) = ri\exp(it)$. Thus,

$$\int_C \frac{dz}{z} = i\int_0^{2\pi} dt = 2\pi i. \tag{A.7}$$

A.5 Cauchy's Theorem

If a function $f(z)$ is analytical and single-valued inside and on a closed contour C, then

$$\int_C f(z)dz = 0. \tag{A.8}$$

This is so because $\int_C f(z)dz = \int_C (udx - vdy) + i\int_C (vdx + udy)$ and the integrands of the two integrals on the right are complete differentials due to Cauchy's equations (*i.e.*, say, if $u = dG/dx$, it follows that $v = -dG/dy$).

A.5.1 Cauchy's Integral

Let $f(z)$ be a function analytic inside and on a closed contour C. Let z be any point inside C. It follows that the function $f(w)/(w - z)$ is analytic on and inside C, except at $w = z$. Hence,

$$\int_C \frac{f(w)}{w-z}dw = \int_\gamma \frac{f(w)}{w-z}dw, \tag{A.9}$$

where γ is any other closed contour inside C that includes $w = z$. Let γ be a circle centered in $w = z$ with radius r. This can be seen by using Eq. (A.8) with a contour Γ (as used in the discussion of the Laurent series) consisting of C and γ and a straight line between them traveled once in each direction.

As $f(w)$ is continuous, r can be made so small that $|f(w) - f(z)| < \epsilon$ on γ. One can then write

$$\int_\gamma \frac{f(w)}{w-z}dw = f(z)\int_\gamma \frac{dw}{w-z} + \int_\gamma \frac{f(w)-f(z)}{w-z}dw. \tag{A.10}$$

From the complex integral in the above Example, it follows that $f(z)\int_C (w-z)^{-1}dw = f(z)2\pi i$ and from the fact that the upper bound of the integrand in the second term on the right of Eq. (A.10) is ϵ/r, and the length of the contour γ is $2\pi r$, one can conclude that $|\int_\gamma (w-z)^{-1}f(w)dw - 2\pi i f(z)| \leq 2\pi\epsilon$, and because the left side is independent of ϵ,

$$f(z) = \frac{1}{2\pi i}\int_C \frac{f(w)}{w-z}dw. \tag{A.11}$$

Any derivative $f^{(n)}(z)$ is also readily obtained as

$$f^{(n)}(z) = \frac{n!}{2\pi i}\int_C \frac{f(w)}{(w-z)^{n+1}}dw. \tag{A.12}$$

A.6 Laurent Series

Let $f(z)$ be analytic in the ring-shaped region between two concentric circles C and C$'$ of radii R and R' and center a, and on the circles themselves. Then $f(z)$ can be expressed as

$$f(z) = \sum_{n=0}^{\infty} a_n(z-a)^n + \sum_{n=1}^{\infty} b_n(z-a)^{-n} \tag{A.13}$$

for $R' < |z-a| < R$.

The contour Γ encloses the ring-shaped region where $f(z)$ is analytic, thus, $f(z) = \frac{1}{2\pi i}\int_\Gamma (w-z)^{-1}f(w)dw$. Since $f(z)$ is single-valued, the two integrals along the radius vector joining the circles cancel and

$$f(z) = \frac{1}{2\pi i}\int_C \frac{f(w)}{w-z}dw - \frac{1}{2\pi i}\int_{C'} \frac{f(w)}{w-z}dw. \tag{A.14}$$

First, consider the integral on C and write

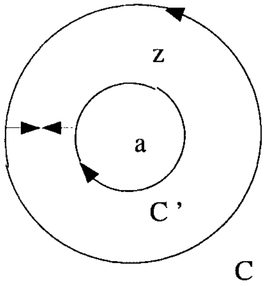

Figure A.4: The contour Γ encloses the ring-shaped region and travels both directions along the radius vector joining the two circles.

$$\begin{aligned}\frac{1}{w-z} &= \frac{1}{w-a}\left[\frac{1}{1-\frac{z-a}{w-a}}\right] = \frac{1}{w-a} + \frac{z-a}{(w-a)^2} \\ &+\cdots+\frac{(z-a)^n}{(w-a)^{n+1}}+\cdots \end{aligned} \tag{A.15}$$

which can be multiplied by $(2\pi i)^{-1}$ and integrated term by term to obtain

$$\frac{1}{2\pi i}\int_C \frac{f(w)}{w-z}dw = \sum_{n=0}^{\infty} a_n (z-a)^n, \tag{A.16}$$

where $a_n = \frac{1}{2\pi i}\int_C (w-a)^{-n-1} f(w)dw$. Note that in general $a_n \neq \frac{f^{(n)}(a)}{n!}$, since $f(z)$ is not necessarily analytic throughout the interior of C.

Considering the integral over C' in Eq. (A.14), one can write

$$\frac{1}{z-w} = \frac{1}{z-a} + \frac{w-a}{(z-a)^2} + \cdots + \frac{(w-a)^n}{(z-a)^{n+1}} + \cdots \tag{A.17}$$

which is uniformly convergent on C', and can be integrated term by term to yield

$$-\frac{1}{2\pi i}\int_{C'} \frac{f(w)}{w-z}dw = \sum_{n=1}^{\infty} b_n (z-a)^{-n}, \tag{A.18}$$

with $b_n = \frac{1}{2\pi i}\int_{C'} (w-a)^{n-1} f(w)dw$. Thus, the Laurent series is obtained.

A.7 Isolated Singularities

When $f(z)$ is analytic at z for $|z-a| < R$ except at $z = a$ then a is an isolated singularity of $f(z)$.

One can then make C' arbitrarily small ($R' \to 0$), and then

$$f(z) = \sum_{n=0}^{\infty} a_n(z-a)^n + \sum_{n=1}^{\infty} b_n(z-a)^{-n}, \tag{A.19}$$

with $0 < |z-a| < R$. Three cases can be distinguished:

(i) All $b_n = 0$: Then $f(z)$ analytic for $|z-a| < R$ except at $z = a$. Example:

$$f(z) = \begin{cases} 1 & z \neq a \\ 0 & z = a \end{cases} \tag{A.20}$$

This is an artificial, noninteresting case.

(ii) A finite number of $b_n \neq 0$:

$$f(z) = \sum_{n=0}^{\infty} a_n(z-a)^n + \sum_{n=1}^{m} b_n(z-a)^{-n}. \tag{A.21}$$

The singularity at $z = a$ is a pole of order m. If $f(z)$ has a pole of order m, then obviously $(z-a)^m f(z)$ is analytic and different from zero at $z = a$. Hence $g(z) = 1/(z-a)^m f(z)$ is analytic and different from zero at $z = a$, and $1/f(z) = (z-a)^m g(z)$ has a zero of order m at $z = a$.

(iii) The series $\sum_{n=1}^{\infty} b_n(z-a)^{-n}$ does not terminate. Then the singularity at $z = a$ is an *essential singularity*. Example: $f(z) = \exp(1/z)$ has an essential singularity at $z = 0$.

A.8 Residue at a Singularity

In the neighborhood of an isolated singularity $z = a$, a single-valued analytic function $f(z)$ may be expanded according to Eq. (A.19). The coefficient b_1 is called the residue of $f(z)$ at $z = a$. It is readily seen that

$$b_1 = \frac{1}{2\pi i} \int_{\gamma} f(z)dz, \tag{A.22}$$

where γ is a circle with center in a and it excludes all other singularities. One can also readily conclude that if the singularity at $z = a$ is a simple pole ($m = 1$), then

$$\lim_{z \to a} (z-a) f(z) = b_1. \tag{A.23}$$

It follows from Cauchy's theorem that if there is a finite number of contours C$_1$, C$_2$, ... ,C$_n$ inside C, and $f(z)$ is analytic in the region between them, then

$$\int_C f(z)dz = \int_{C_1} f(z)dz + \int_{C_2} f(z)dz + \cdots + \int_{C_n} f(z)dz. \tag{A.24}$$

Thus, if $f(z)$ is single-valued, analytic inside and on C except at a finite number of isolated singularities at $z = z_1, z_2, ..., z_n$, with the residues at these points being $r_1, r_2, ..., r_n$, then

$$\int_C f(z)dz = 2\pi i(r_1 + r_2 + \cdots + r_n). \tag{A.25}$$

A.9 Expansion of a Meromorphic Function

A function $f(z)$ is said to be *meromorphic* in a region if it is analytic in the region except at a finite number of poles. Let $f(z)$ only have singularities that are simple poles (except at infinity) at $p_1, p_2, ..., p_n$, $(0 < |p_1| \leq |p_2| \leq \cdots \leq |p_n|)$. Let the residues be $r_1, r_2, ..., r_n$, respectively. Let C_n be a contour that includes $z = p_1, p_2, ..., p_n$, but no other poles. Let the minimum distance R_n of C_n from the origin tend to infinity with n. Let L_n (the length of C_n) be $O(R_n)$, and let $f(z)$ be bounded on C_n. Then

$$f(z) = f(0) + \sum_{n=1}^{\infty} r_n \left[\frac{1}{z - p_n} + \frac{1}{p_n}\right]. \tag{A.26}$$

The proof follows from that

$$\begin{aligned} I &= \frac{1}{2\pi i}\int_{C_n} \frac{f(w)}{w(w-z)}dw \\ &= \sum_{m=1}^{n} \frac{r_m}{p_m(p_m - z)} - \frac{f(0)}{z} + \frac{f(z)}{z} \end{aligned} \tag{A.27}$$

and

$$|I| \leq \frac{L_n}{2\pi R_n(R_n - |z|)} \max_{as\ n\to\infty} |f(z)|_{C_n} \to 0\ . \tag{A.28}$$

Thus,

$$\frac{f(z)}{z} = \frac{f(0)}{z} - \lim_{n\to\infty}\sum_{m=0}^{n} \frac{r_m}{p_m(p_m - z)}, \tag{A.29}$$

or

$$\begin{aligned} f(z) &= f(0) - \sum_{m=1}^{\infty} \frac{r_m z}{p_m(p_m - z)} \\ &= f(0) + \sum_{m=1}^{\infty} r_m \left[\frac{1}{z - p_m} + \frac{1}{p_m}\right]. \end{aligned} \tag{A.30}$$

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Appendix B

First and Second Quantization

Quantum mechanics takes many different guises. For instance, one can use a Hilbert space realization in terms of time-dependent wavefunctions $\Phi\ (\xi_1,\xi_2,\cdots \xi_N;t)$ of an N-particle system, where $\xi = (\vec{r},\zeta)$ is a compound configuration space and spin variable for a particle. Operators acting on this Hilbert space are obtained by making the common identifications $\vec{p} \rightarrow -i\hbar\vec{\nabla}$ for the momentum and $\vec{r} \rightarrow \vec{r}$ for position vector of a particle, which can be referred to as first quantization, producing quantum mechanical operators out of classical expressions. One can equally well use time-dependent field operators (so-called second quantization) $\psi(\xi,t)$ and their adjoints $\psi^\dagger(\xi,t)$ to build Hilbert spaces (or rather Fock spaces) and corresponding quantum mechanical operators. The connection between different formulations must be that they give the same expectation values of operators.

Thus, we have, say, an N-electron operator in first quantization, which is a sum of single-particle operators

$$\hat{A}_1 = \sum_{i=1}^{N} \hat{a}_1(\xi_i). \tag{B.1}$$

An example would be the N-electron kinetic energy operator with $\hat{a}_1(\xi_i) = -\frac{\hbar^2}{2m}\vec{\nabla}_i^2$. The corresponding operator in second quantization is

$$\hat{A}_2 = \int \psi^\dagger(\xi,t)\hat{a}_1(\xi)\psi(\xi,t)d\xi. \tag{B.2}$$

If we introduce a spin orbital basis $\{u_s(\xi)\}$, in which to expand the electron field operators

$$\psi(\xi,t)=\sum_s u_s(\xi)a_s(t), \tag{B.3}$$

we can write

$$\hat{A}_2=\sum_{r,s}\langle r|\hat{a}_1|s\rangle a_r^\dagger a_s, \tag{B.4}$$

where

$$\langle r|\hat{a}_1|s\rangle=\int u_r^*(\xi)\hat{a}_1(\xi)u_s(\xi)d\xi \tag{B.5}$$

is a one-electron integral in the chosen basis.

Similarly one can treat operators made up of pair-operators

$$\hat{B}_1=\frac{1}{2}\sum_{p,q}\hat{b}_1(\xi_p,\xi_q). \tag{B.6}$$

An example would be the operator of electron-electron interaction energy, for which

$$\hat{b}_1(\xi_p,\xi_q)=\frac{e^2}{|\vec{r}_p-\vec{r}_q|}. \tag{B.7}$$

The corresponding operator in second quantization is

$$\begin{aligned}\hat{B}_2 &= \frac{1}{2}\int d\xi\int d\xi'\,\psi^\dagger(\xi,t)\psi^\dagger(\xi',t)\hat{b}_1(\xi,\xi')\psi(\xi',t)\psi(\xi,t)\\ &= \frac{1}{2}\sum_{r,s,r',s'}\langle rr'|ss'\rangle a_r^\dagger a_{r'}^\dagger a_{s'}a_s.\end{aligned} \tag{B.8}$$

An integral operator $\hat{K}$ acts via its kernel $k(\xi,\xi')$ such that

$$\hat{K}f(\xi)=\int k(\xi,\xi')f(\xi')d\xi'. \tag{B.9}$$

An example is the exchange potential energy in the Fock operator, *i.e.*, an integral operator with the kernel

$$k(\xi,\xi')=\frac{e^2\gamma(\xi,\xi')}{|\vec{r}-\vec{r}'|}, \tag{B.10}$$

where

$$\gamma(\xi,\xi^{'}) = \sum_{r,s} u_s(\xi)\langle a_r^{\dagger}a_s\rangle u_r^*(\xi^{'}) \tag{B.11}$$

is the one-particle reduced density matrix in the Hartree-Fock approximation.

In wavefunction form or in terms of first quantization, the one-particle reduced density matrix corresponding to an N-electron state with wavefunction $\Phi(\xi_1,\xi_2,\cdots,\xi_N)$ is defined as

$$\gamma(\xi,\xi^{'}) = N\int \Phi(\xi,\xi_2,\xi_3,\cdots,\xi_N)\Phi^*(\xi^{'},\xi_2,\xi_3,\cdots,\xi_N)d\xi_2\cdots d\xi_N. \tag{B.12}$$

This expression can be rewritten as an expectation value of an integral operator

$$\hat{O} = \sum_{p=1}^{N} \hat{o}(p) \tag{B.13}$$

with the single-particle integral operator $\hat{o}(p)$ having the kernel

$$o(\xi_p,\xi_p^{'}) = \delta(\xi-\xi_p^{'})\delta(\xi_p-\xi^{'}). \tag{B.14}$$

This means that

$$\begin{aligned}
\langle\hat{O}\rangle &= N\langle\hat{o}\rangle \\
&= N\int \Phi^*(\xi_1,\xi_2,\cdots,\xi_N)o(\xi_1,\xi_1^{'})\Phi\left(\xi_1^{'},\xi_2,\cdots,\xi_N\right)d\xi_1^{'}d\xi_1\cdots d\xi_N \\
&= \gamma(\xi,\xi^{'}) = \sum_{r,s} u_s(\xi)\gamma_{sr}u_r^*(\xi^{'}),
\end{aligned} \tag{B.15}$$

where in the first line we have used the symbol $\langle\cdots\rangle$ for the average value, and assumed the wavefunction to be normalized to unity and antisymmetric under permutation of the electron labels. In the last step, an expansion in a spin orbital basis is performed. Let the state vector $|N\rangle$ in second quantization correspond to the wavefunction Φ. Then one can write

$$\begin{aligned}
\gamma(\xi,\xi^{'}) &= \langle N|\int \psi^{\dagger}(\xi_1)\hat{o}(1)\psi(\xi_1)d\xi_1|N\rangle \\
&= \langle N|\int \psi^{\dagger}(\xi_1)o(\xi_1,\xi_1^{'})\psi(\xi_1^{'})d\xi_1^{'}d\xi_1|N\rangle \\
&= \langle N|\psi^{\dagger}(\xi^{'})\psi(\xi)|N\rangle = \sum_{r,s} u_s(\xi)\langle a_r^{\dagger}a_s\rangle u_r^*(\xi^{'})
\end{aligned} \tag{B.16}$$

and one can conclude that the one particle reduced density matrix (one-matrix) in a basis is simply

$$\gamma_{sr} = \langle a_r^\dagger a_s \rangle \tag{B.17}$$

as used before.

Exercise: Use the average of the integral operator $\hat{O} = \frac{1}{2}\sum_p \sum_{q \neq p} \hat{o}(p) \times \hat{o}(q)$ to show that the two-particle reduced density matrix (two-matrix)

$$\begin{aligned} &\Gamma(\xi,\eta;\xi',\eta') \\ &= \frac{N(N-1)}{2}\int \Phi^*(\xi',\eta',\xi_3,\cdots,\xi_N)\Phi(\xi,\eta,\xi_3,\cdots,\xi_N)d\xi_3\cdots d\xi_N \end{aligned} \tag{B.18}$$

in second quantization becomes $\frac{1}{2}\langle N|\psi^\dagger(\xi')\psi^\dagger(\theta')\psi(\theta)\psi(\xi)|N\rangle$.

The single-particle Green's function or electron propagator

$$\begin{aligned} G(\xi,\xi';E) &\equiv \langle\langle \psi(\xi);\psi^\dagger(\xi')\rangle\rangle_E \\ &= \sum_m \left[\frac{\langle N|\psi(\xi)|N+1,m\rangle\langle N+1,m|\psi^\dagger(\xi')|N\rangle}{E - E_m(N+1) + E_0(N) + i\eta}\right. \\ &\quad \left. + \frac{\langle N|\psi^\dagger(\xi')|N-1,m\rangle\langle N-1,m|\psi(\xi)|N\rangle}{E - E_0(N) + E_m(N-1) - i\eta}\right] \\ &= \sum_m \left[\frac{f_m(\xi)f_m^*(\xi')}{E - \epsilon_m + i\eta} + \frac{g_m(\xi)g_m^*(\xi')}{E - \epsilon_m - i\eta}\right] \end{aligned} \tag{B.19}$$

yields the one-particle reduced density matrix

$$\gamma(\xi,\xi') = \frac{1}{2\pi i}\int_C G(\xi,\xi';E)dE, \tag{B.20}$$

where the contour C consists of the real axis $\Re E$ and a semicircle in the upper complex E-plane. We can thus write

$$\gamma(\xi,\xi') = \sum_m g_m(\xi)g_m^*(\xi') \tag{B.21}$$

in terms of the so-called Dyson amplitudes. Using the definition in Eq. (B.12) it is straightforward to show that these Dyson amplitudes in first quantization are

$$g_m(\xi) = \sqrt{N}\int \Phi(\xi,\xi_2,\cdots\xi_N)\Phi_m^*(\xi_2,\cdots\xi_N)d\xi_2\cdots d\xi_N \tag{B.22}$$

i.e., an overlap between the (neutral ground) N-electron state and a particular (positive ion) $(N-1)$-state Φ_m. In the Hartree-Fock approximation with the N-electron ground state described by a single determinant and with the positive ion state the same determinant with a single spin orbital removed, it is obvious that in this Koopmans theorem description, the Dyson amplitude is just the missing spin orbital (*i.e.*, the one out of which an ionization has taken place). At this level of theory, the Dyson amplitudes are orthonormal, something that is not guaranteed in general.

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Appendix C

Stability of Hartree-Fock Solutions

The many-electron Hamiltonian is expressed as

$$H = \sum_{r,s} h_{rs} a_r^\dagger a_s + \frac{1}{2} \sum_{r,r',s,s'} (rs|r's') a_r^\dagger a_{r'}^\dagger a_{s'} a_s, \tag{C.1}$$

where the Mulliken notation is used for the two-electron integrals. The Fock matrix then has the elements

$$F_{rs} = h_{rs} + \sum_{r',s'} \left[(rs|r's') - (rs'|r's) \right] \gamma_{s'r'} \tag{C.2}$$

with $\gamma_{s'r'} = \langle a_{r'}^\dagger a_{s'} \rangle = \mathrm{Tr}\{\rho a_{r'}^\dagger a_{s'}\}$ an element of the 1-matrix, and the single-particle density operator $\rho = \Pi_k[1 - \langle \tilde{n}_k \rangle + (2\langle \tilde{n}_k \rangle - 1)\tilde{n}_k]$. The tilde denotes operators relative the Hartree-Fock spin orbitals, *i.e.*,

$$\tilde{n}_k = \tilde{a}_k^\dagger \tilde{a}_k, \quad \tilde{a}_k = \sum_r a_r x_{rk}^*, \tag{C.3}$$

with $\sum_r x_{rk}^* x_{rl} = \delta_{kl}$ and $\sum_k x_{rk} x_{ks}^* = \delta_{rs}$.

The average value of the Hamiltonian can be expressed in a number of ways

$$\begin{aligned} \langle H \rangle &= \mathrm{Tr}\{\rho H\} \\ &= \sum_{r,s} h_{rs}\gamma_{sr} + \frac{1}{2} \sum_{r,r',s,s'} (rs|r's') \left[\gamma_{sr}\gamma_{s'r'} - \gamma_{sr'}\gamma_{s'r} \right] \\ &= \sum_{r,s} h_{rs}\gamma_{sr} + \frac{1}{2} \sum_{r,r',s,s'} \left[(rs|r's') - (rs'|r's) \right] \gamma_{sr}\gamma_{s'r'} \end{aligned}$$

$$= \frac{1}{2}\sum_{r,s}[h_{rs} + F_{rs}]\gamma_{sr}. \tag{C.4}$$

Note that

$$\begin{aligned}
&\sum_{r,r',s,s'} (rs|r's')\mathrm{Tr}\{\rho a_r^\dagger a_{r'}^\dagger a_{s'} a_s\} \\
&= \sum_{r,r',s,s'} (rs|r's') \sum_{p,q,m,n} x_{rp}^* x_{r'q}^* x_{s'm} x_{sn} \mathrm{Tr}\{\rho \tilde{a}_p^\dagger \tilde{a}_q^\dagger \tilde{a}_m \tilde{a}_n\},
\end{aligned} \tag{C.5}$$

with

$$\begin{aligned}
\mathrm{Tr}\{\rho \tilde{a}_p^\dagger \tilde{a}_q^\dagger \tilde{a}_m \tilde{a}_n\} &= \mathrm{Tr}\{[1 - \langle\tilde{n}_p\rangle + (2\langle\tilde{n}_p\rangle - 1)\tilde{n}_p]\tilde{a}_p^\dagger \tilde{a}_p \delta_{pn}\} \\
&\quad \times \mathrm{Tr}\{[1 - \langle\tilde{n}_q\rangle + (2\langle\tilde{n}_q\rangle - 1)\tilde{n}_q]\tilde{a}_q^\dagger \tilde{a}_q \delta_{qm}\} \\
&\quad - \mathrm{Tr}\{[1 - \langle\tilde{n}_p\rangle + (2\langle\tilde{n}_p\rangle - 1)\tilde{n}_p]\tilde{a}_p^\dagger \tilde{a}_p \delta_{pm}\} \\
&\quad \times \mathrm{Tr}\{[1 - \langle\tilde{n}_q\rangle + (2\langle\tilde{n}_q\rangle - 1)\tilde{n}_q]\tilde{a}_q^\dagger \tilde{a}_q \delta_{qn}\} \\
&= \langle\tilde{n}_p\rangle\langle\tilde{n}_q\rangle[\delta_{pn}\delta_{qm} - \delta_{pm}\delta_{qn}].
\end{aligned} \tag{C.6}$$

Thus,

$$\begin{aligned}
&\sum_{r,r',s,s'} (rs|r's')\mathrm{Tr}\{\rho a_r^\dagger a_{r'}^\dagger a_{s'} a_s\} \\
&= \sum_{r,r',s,s'} (rs|r's')[\langle a_r^\dagger a_s\rangle\langle a_{r'}^\dagger a_{s'}\rangle - \langle a_{r'}^\dagger a_s\rangle\langle a_r^\dagger a_{s'}\rangle]
\end{aligned} \tag{C.7}$$

because

$$\langle a_r^\dagger a_s\rangle = \sum_{k,l} x_{rk}^* \langle\tilde{a}_k^\dagger \tilde{a}_l\rangle x_{sl} = \sum_k x_{sk}\langle\tilde{n}_k\rangle x_{kr}^\dagger \tag{C.8}$$

and because the trace of a direct product is a product of traces.

The first variation of the energy is (for an extremum point)

$$0 = \delta\langle H\rangle = \frac{1}{2}\sum_{r,s}\delta F_{rs}\gamma_{sr} + \frac{1}{2}\sum_{r,s}[h_{rs} + F_{rs}]\delta\gamma_{sr} \tag{C.9}$$

or since

$$\delta F_{rs} = \sum_{r',s'}(rs||r's')\delta\gamma_{s'r'}, \tag{C.10}$$

one can write

$$\delta\langle H\rangle = \mathrm{Tr}\{\mathbf{F}\delta\gamma\}. \tag{C.11}$$

A general unitary transformation of the spin orbital basis, which conserves the factorization property $\langle a_r^\dagger a_{r'}^\dagger a_{s'} a_s\rangle = \gamma_{sr}\gamma_{s'r'} - \gamma_{sr'}\gamma_{s'r}$ and thus the independent particle character of ρ, can be expressed as

$$U = \exp[i\Lambda] = \exp[i\sum_{p,q}\Lambda_{pq}a_p^\dagger a_q] \tag{C.12}$$

with $\Lambda^\dagger = \Lambda$. The transformed density operator can then be given as

$$\begin{aligned} \rho' &= U^\dagger \rho U \\ &= [1 - i\Lambda + (-i\Lambda)^2/2! + \cdots]\rho[1 + i\Lambda + (i\Lambda)^2/2! + \cdots] \\ &= \rho + i[\rho,\Lambda]_- - \frac{1}{2}[[\rho,\Lambda]_-,\Lambda]_- + \cdots. \end{aligned} \tag{C.13}$$

Only infinitesimal transformations are considered, so that

$$\begin{aligned} \delta\gamma_{sr} &= \mathrm{Tr}\{(\rho' - \rho)a_r^\dagger a_s\} = i\mathrm{Tr}\{[\rho,\Lambda]_- a_r^\dagger a_s\} \\ &= i\mathrm{Tr}\{\rho[\Lambda, a_r^\dagger a_s]_-\} = i\{[\gamma,\Lambda]_-\}_{sr} \\ &= i(\langle\tilde{n}_s\rangle - \langle\tilde{n}_r\rangle)\Lambda_{sr}, \end{aligned} \tag{C.14}$$

where in the next-to-last step

$$[\Lambda, a_r^\dagger a_s]_- = \sum_{p,q}\Lambda_{pq}\left(\delta_{rq}a_p^\dagger a_s - \delta_{sp}a_r^\dagger a_q\right) \tag{C.15}$$

is used. In the last step, the result is given in terms of the Hartree-Fock spin orbitals.

The second variation can be written as

$$\begin{aligned} \delta^2\gamma_{sr} &= -\frac{1}{2}\mathrm{Tr}\{[[\rho,\Lambda]_-,\Lambda]_- a_r^\dagger a_s\} \\ &= -\frac{1}{2}\mathrm{Tr}\{\rho[\Lambda,[\Lambda, a_r^\dagger a_s]_-]_-\} \end{aligned} \tag{C.16}$$

where

$$[\Lambda,[\Lambda, a_r^\dagger a_s]_-]_- = \sum_{p,q}(\delta_{rq}[\Lambda, a_p^\dagger a_s]_- - \delta_{sp}[\Lambda, a_r^\dagger a_q]_-)\Lambda_{pq}. \tag{C.17}$$

Thus,

$$\delta^2\gamma_{sr} = -\frac{1}{2}[[\gamma,\Lambda],\Lambda]_{sr} = -(\langle\tilde{n}_s\rangle - \langle\tilde{n}_r\rangle)|\Lambda_{sr}|^2, \tag{C.18}$$

where again, in the last step, the basis is assumed to be the Hartree-Fock spin orbitals.

From Eq. (C.4), the total electronic energy can be written as

$$\langle H\rangle = \sum_{r,s} h_{rs}\gamma_{sr} + \frac{1}{2}\sum_{r,s,r',s'}(rs||r's')\gamma_{sr}\gamma_{s'r'}, \tag{C.19}$$

with the antisymmetric two-electron integrals $(rs||r's') = (rs|r's') - (rs'|r's)$. Assuming that γ^o_{sr} corresponds to a stationary point of the energy and one writes

$$\gamma_{sr} = \gamma^o_{sr} + \delta\gamma_{sr} + \delta^2\gamma_{sr} + \cdots, \tag{C.20}$$

which leads to the expression

$$\begin{aligned}\langle H\rangle &= \langle H\rangle_o + \delta\langle H\rangle + \delta^2\langle H\rangle + \cdots \\ &= \langle H\rangle_o + \sum_{r,s} F_{rs}\delta\gamma_{sr} + \frac{1}{2}\sum_{r,s,r',s'}(rs||r's')\delta\gamma_{sr}\delta\gamma_{s'r'} \\ &\quad + \sum_{r,s} F_{rs}\delta^2\gamma_{sr}\end{aligned} \tag{C.21}$$

through second order. From Eq. (C.14), it follows that

$$\begin{aligned}\delta\langle H\rangle &= \mathrm{Tr}\{\mathbf{F}\delta\gamma\} = i\mathrm{Tr}\{\mathbf{F}[\gamma,\mathbf{\Lambda}]_-\} \\ &= i\mathrm{Tr}\{[\mathbf{F},\gamma]_-\mathbf{\Lambda}\} = 0,\end{aligned} \tag{C.22}$$

where the fact that the matrices γ and $\mathbf{F}$ commute has been used. Thus, the first variation of the energy in the Hartree-Fock approximation vanishes. Further characterization of the stationary point involves the second variation of the energy.

In the Hartree-Fock spin orbitals, *i.e.*, the basis that diagonalizes $\mathbf{F}$ and γ, it holds that $F_{rs} = \epsilon_s\delta_{rs}$, which yields

$$\sum_{r,s} F_{rs}\delta^2\gamma_{sr} = -\sum_{r,s}\epsilon_s(\langle\tilde{n}_s\rangle - \langle\tilde{n}_r\rangle)|\Lambda_{sr}|^2. \tag{C.23}$$

The third term in Eq. (C.21) becomes

$$-\frac{1}{2}\sum_{r,s,r',s'}(rs||r's')(\langle\tilde{n}_s\rangle-\langle\tilde{n}_r\rangle)(\langle\tilde{n}_{s'}\rangle-\langle\tilde{n}_{r'}\rangle)\Lambda_{sr}\Lambda_{s'r'}. \tag{C.24}$$

The Hartree-Fock spin orbitals, which are assumed to be real, can now be separated into particle ones (k) and hole ones (l), such that $\langle\tilde{n}_l\rangle > \langle\tilde{n}_k\rangle$. For a pure single determinantal state, these occupation numbers are simply 1 and 0. Obviously, the spin orbitals with $\langle\tilde{n}_l\rangle = \langle\tilde{n}_k\rangle$ are not contributing. The matrices with elements

$$\begin{aligned} B_{ij} &= \delta_{kk'}\delta_{ll'}(\epsilon_k-\epsilon_l)(\langle\tilde{n}_l\rangle-\langle\tilde{n}_k\rangle) \\ &\quad +(kl||l'k')(\langle\tilde{n}_l\rangle-\langle\tilde{n}_k\rangle)(\langle\tilde{n}_{l'}\rangle-\langle\tilde{n}_{k'}\rangle) \end{aligned} \tag{C.25}$$

and

$$C_{ij} = (kl||k'l')(\langle\tilde{n}_l\rangle-\langle\tilde{n}_k\rangle)(\langle\tilde{n}_{l'}\rangle-\langle\tilde{n}_{k'}\rangle) \tag{C.26}$$

and compound indices $i=(k,l)$ and $j=(k',l')$, can now be used to write

$$\begin{aligned} \delta^2\langle H\rangle &= \frac{1}{2}\sum_{i,j}[\Lambda_i^* B_{ij}\Lambda_j + \Lambda_i B_{ij}\Lambda_j^* \\ &\quad -\Lambda_i^* C_{ij}\Lambda_j^* - \Lambda_i C_{ij}\Lambda_j]. \end{aligned} \tag{C.27}$$

In matrix form, this reads

$$\delta^2\langle H\rangle = \frac{1}{2}\begin{pmatrix} \mathbf{\Lambda}^\dagger & \mathbf{\Lambda}^T \end{pmatrix}\begin{pmatrix} \mathbf{B} & -\mathbf{C} \\ -\mathbf{C} & \mathbf{B} \end{pmatrix}\begin{pmatrix} \mathbf{\Lambda} \\ \mathbf{\Lambda}^* \end{pmatrix}, \tag{C.28}$$

where now the $\mathbf{\Lambda}$ array is a column vector. If one separates the real and imaginary parts of $\mathbf{\Lambda}$, such that $\mathbf{\Lambda} = \mathbf{\Lambda}_1 + i\mathbf{\Lambda}_2$, it follows that

$$\delta^2\langle H\rangle = \mathbf{\Lambda}_1^T(\mathbf{B}-\mathbf{C})\mathbf{\Lambda}_1 + \mathbf{\Lambda}_2^T(\mathbf{B}+\mathbf{C})\mathbf{\Lambda}_2, \tag{C.29}$$

which means that both $(\mathbf{B}-\mathbf{C})$ and $(\mathbf{B}+\mathbf{C})$, since $\mathbf{\Lambda}_1$ and $\mathbf{\Lambda}_2$ are arbitrary, must be positive for a true minimum point.

Notes and Bibliography

- The self-consistent field method was introduced in many-electron quantum mechanics by D. R. Hartree in *Proc. Camb. Phil. Soc.* **24**, 105 (1928), and his ideas spawned an intensive development, particularly by J. C. Slater and V. Fock.
- V. Fock gave a derivation of the basic equations in 1932 using second quantization in *Z. Physik* **75**, 622.

- P. A. M. Dirac formulated the time-dependent version in *Proc. Camb. Phil. Soc.* **26**, 376 (1930).
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Appendix D

Third-Order Self-Energy

The 12 energy-dependent and 6 "constant" terms of the electron propagator self-energy that contribute in third order are listed below. The convention is followed of denoting the spin orbital occupied in the SCF reference state by *a,b,c,...*, and those unoccupied by *p,q,r,...*, while unspecified spin orbitals are denoted by *i,j,...*

$$\begin{aligned}
\Sigma_{ij}^{(3)}(E) \;=\; & \frac{1}{4} \sum_{\substack{a \\ p,q,r,s}} \frac{\langle ia||pq\rangle\langle pq||rs\rangle\langle rs||ja\rangle}{(E+\epsilon_a-\epsilon_r-\epsilon_s)\,(E+\epsilon_a-\epsilon_p-\epsilon_q)} \\
& -\frac{1}{4} \sum_{\substack{p \\ a,b,c,d}} \frac{\langle ip||ab\rangle\langle ab||cd\rangle\langle cd||jp\rangle}{(E+\epsilon_p-\epsilon_c-\epsilon_d)\,(E+\epsilon_p-\epsilon_a-\epsilon_b)} \\
& - \sum_{\substack{a,b \\ p,q,r}} \frac{\langle ib||rq\rangle\langle ra||pb\rangle\langle pq||ja\rangle}{(E+\epsilon_a-\epsilon_p-\epsilon_q)\,(E+\epsilon_a-\epsilon_q-\epsilon_r)} \\
& + \sum_{\substack{a,b,c \\ p,q}} \frac{\langle iq||cb\rangle\langle cp||aq\rangle\langle ab||jp\rangle}{(E+\epsilon_p-\epsilon_a-\epsilon_b)\,(E+\epsilon_q-\epsilon_b-\epsilon_c)} \\
& +\frac{1}{4} \sum_{\substack{a,b,c \\ p,q}} \frac{\langle ic||ab\rangle\langle ab||pq\rangle\langle pq||jc\rangle}{(E+\epsilon_c-\epsilon_p-\epsilon_q)\,(\epsilon_a+\epsilon_b-\epsilon_p-\epsilon_q)} \\
& +\frac{1}{4} \sum_{\substack{a,b,c \\ p,q}} \frac{\langle ia||pq\rangle\langle pq||bc\rangle\langle bc||ja\rangle}{(E+\epsilon_a-\epsilon_p-\epsilon_q)\,(\epsilon_b+\epsilon_c-\epsilon_p-\epsilon_q)}
\end{aligned}$$

$$
\begin{aligned}
&+\frac{1}{4}\sum_{\substack{a,b\\p,q,r}} \frac{\langle ip||ab\rangle\langle ab||qr\rangle\langle qr||jp\rangle}{(E+\epsilon_p-\epsilon_a-\epsilon_b)\,(\epsilon_a+\epsilon_b-\epsilon_q-\epsilon_r)}\\
&+\frac{1}{4}\sum_{\substack{a,b\\p,q,r}} \frac{\langle ip||qr\rangle\langle qr||ab\rangle\langle ab||jp\rangle}{(E+\epsilon_p-\epsilon_a-\epsilon_b)\,(\epsilon_a+\epsilon_b-\epsilon_q-\epsilon_r)}\\
&-\sum_{\substack{a,b\\p,q,r}} \frac{\langle ir||aq\rangle\langle ab||pr\rangle\langle pq||jb\rangle}{(E+\epsilon_b-\epsilon_p-\epsilon_q)\,(\epsilon_a+\epsilon_b-\epsilon_p-\epsilon_r)} \qquad\qquad \text{(D.1)}\\
&-\sum_{\substack{a,b\\p,q,r}} \frac{\langle ib||pr\rangle\langle pq||ab\rangle\langle ar||jq\rangle}{(E+\epsilon_b-\epsilon_p-\epsilon_r)\,(\epsilon_a+\epsilon_b-\epsilon_p-\epsilon_q)}\\
&-\sum_{\substack{a,b,c\\p,q}} \frac{\langle iq||ac\rangle\langle ab||pq\rangle\langle pc||jb\rangle}{(E+\epsilon_q-\epsilon_a-\epsilon_c)\,(\epsilon_a+\epsilon_b-\epsilon_p-\epsilon_q)}\\
&-\sum_{\substack{a,b,c\\p,q}} \frac{\langle ic||qb\rangle\langle qp||ac\rangle\langle ab||jp\rangle}{(E+\epsilon_p-\epsilon_a-\epsilon_b)\,(\epsilon_a+\epsilon_c-\epsilon_p-\epsilon_q)}\\
&+\frac{1}{2}\sum_{\substack{a,b\\p,q,r}} \frac{\langle ir||jp\rangle\langle ab||rq\rangle\langle pq||ab\rangle}{(\epsilon_a+\epsilon_b-\epsilon_p-\epsilon_q)\,(\epsilon_a+\epsilon_b-\epsilon_q-\epsilon_r)}\\
&-\frac{1}{2}\sum_{\substack{a,b,c\\p,q}} \frac{\langle ia||jc\rangle\langle cb||pq\rangle\langle pq||ab\rangle}{(\epsilon_a+\epsilon_b-\epsilon_p-\epsilon_q)\,(\epsilon_b+\epsilon_c-\epsilon_p-\epsilon_q)}\\
&+\frac{1}{2}\sum_{\substack{a,b\\p,q,r}} \frac{\langle ip||ja\rangle\langle ab||qr\rangle\langle qr||pb\rangle}{(\epsilon_a+\epsilon_b-\epsilon_q-\epsilon_r)\,(\epsilon_a-\epsilon_p)}\\
&-\frac{1}{2}\sum_{\substack{a,b,c\\p,q}} \frac{\langle ip||ja\rangle\langle bc||pq\rangle\langle aq||bc\rangle}{(\epsilon_b+\epsilon_c-\epsilon_p-\epsilon_q)\,(\epsilon_a-\epsilon_p)}\\
&+\frac{1}{2}\sum_{\substack{a,b\\p,q,r}} \frac{\langle ia||jr\rangle\langle rb||pq\rangle\langle pq||ab\rangle}{(\epsilon_a+\epsilon_b-\epsilon_p-\epsilon_q)\,(\epsilon_a-\epsilon_r)}
\end{aligned}
$$

$$-\frac{1}{2}\sum_{\substack{a,b,c\\p,q}}\frac{\langle ic||jp\rangle\langle pq||ab\rangle\langle ab||cq\rangle}{(\epsilon_a+\epsilon_b-\epsilon_p-\epsilon_q)\,(\epsilon_c-\epsilon_p)}.$$

Problems

1. Using the diagram rules of Chapter 10, draw the third-order self-energy diagrams that correspond to the above expressions.

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Appendix E

Temperature-Dependent Propagators

E.1 Preliminaries

A diagram technique can be constructed for so-called "temperature Green's functions", which depend on a temperature T, or rather on τ, which varies from 0 to $1/kT$, where k is Boltzmann's constant.

One seeks a perturbation expansion of the partition function

$$Z(\beta) = \text{Tr}\{\exp[-\beta(H - \mu N_0)]\}, \tag{E.1}$$

with $\beta = 1/kT$, H the many-electron Hamiltonian, N_0 the number operator for electrons, and μ a parameter, which may be called the "chemical potential". The trace is taken in Fock space; *i.e.*, the summation is taken over all possible states of the system with a given number of electrons and over all numbers of electrons.

The Hamiltonian is partitioned into a reference or unperturbed part H_0 and a perturbation V as

$$H = H_0 + V \tag{E.2}$$

with

$$H_0 = \sum_k \epsilon_k a_k^\dagger a_k = \sum_k \epsilon_k n_k \tag{E.3}$$

in diagonal form. The number operator in the same basis is

$$N_0 = \sum_k n_k. \tag{E.4}$$

A partition function for the unperturbed system is

$$Z_0(\beta) = \mathrm{Tr}\{\exp[-\beta(H_0 - \mu N_0)]\}, \tag{E.5}$$

and the trace can be taken over a direct product space made up of the eigenstates of the occupation number operators

$$a_k^\dagger a_k = n_k. \tag{E.6}$$

As $n_k^2 = n_k$, it has eigenvalues of 0 and 1 and in the eigenbasis (*i.e.*, two states with spin orbital u_k occupied or unoccupied) has the form

$$n_k = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}. \tag{E.7}$$

The trace over a direct product space is the product of the traces of the factor spaces, such that

$$\begin{aligned} Z_0(\beta) &= \prod_k \mathrm{Tr}\{\exp[-\beta(\epsilon_k - \mu)n_k]\} \\ &= \prod_k [2 + (e^{-\beta(\epsilon_k-\mu)} - 1)]. \end{aligned} \tag{E.8}$$

The unperturbed average of an operator A is defined as

$$\langle A \rangle_0 = \mathrm{Tr}\{e^{-\beta(H_0-\mu N_0)}A\}/Z_0(\beta). \tag{E.9}$$

Define

$$S(\beta) = e^{\beta(H_0-\mu N_0)}e^{-\beta(H-\mu N_0)}; \tag{E.10}$$

then, obviously,

$$\langle S(\beta) \rangle_0 = Z(\beta)/Z_0(\beta). \tag{E.11}$$

Similarly, define

$$S(\tau) = e^{\tau(H_0-\mu N_0)}e^{-\tau(H-\mu N_0)}, \tag{E.12}$$

and form the derivative

$$\begin{aligned}\frac{\partial S(\tau)}{\partial \tau} &= -e^{\tau(H_0-\mu N_0)}Ve^{-\tau(H_0-\mu N_0)}S(\tau) \\ &= -V(\tau)S(\tau), \end{aligned} \tag{E.13}$$

where

$$V(\tau) = e^{\tau(H_0-\mu N_0)}Ve^{-\tau(H_0-\mu N_0)}. \tag{E.14}$$

Obviously

$$\int_0^\beta \frac{\partial S(\tau)}{\partial \tau}d\tau = S(\beta) - S(0) = S(\beta) - 1, \tag{E.15}$$

and thus,

$$S(\beta) = 1 + \int_0^\beta \frac{\partial S(\tau)}{\partial \tau}d\tau = 1 - V(\tau)S(\tau). \tag{E.16}$$

Iteration of this equation straightforwardly yields

$$\begin{aligned}\langle S(\beta)\rangle_0 &= 1 + \sum_{n=1}^{\infty}(-1)^n \int_0^\beta d\tau_1 \int_0^{\tau_1} d\tau_2 \cdots \\ &\quad \int_0^{\tau_{n-1}} d\tau_n \langle V(\tau_1)V(\tau_2)\cdots V(\tau_n)\rangle_0 \\ &= 1 + \sum_{n=1}^{\infty}\frac{(-1)^n}{n!} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \cdots \\ &\quad \int_0^\beta d\tau_n \langle T_\tau[V(\tau_1)V(\tau_2)\cdots V(\tau_n)]\rangle_0, \end{aligned} \tag{E.17}$$

with T_τ the "τ-ordering operator" that orders the operators in the brackets [...] such that the arguments τ_i decreases from left to right and accounts for the necessary sign changes due to the anticommutation rules of Fermion operators. At equal "times" τ operators are put in *normal order*. Thus, one can write

$$S(\tau) = T_\tau \exp[-\int_0^\tau V(\tau')d\tau']. \tag{E.18}$$

E.1.1 Intermezzo

The introduction of the "τ-ordering" operator can be understood from the rather elementary Dirichlet's theorem in calculus. Starting with two functions $F(x)$ and $G(y)$, one forms the integral

$$\int_0^a dx \int_0^a dy F(x)G(y) = \int_0^a dx \int_0^x dy F(x)G(y) + \int_0^a dx \int_x^a dy F(x)G(y), \tag{E.19}$$

where the second term on the right equals

$$\int_0^a dy \int_0^y dx F(x)G(y). \tag{E.20}$$

This can be seen from two figures below that intend to show the two equivalent modes to integrate over the same area.

Figure E.1: Illustration of that $\int_0^a dx \int_x^a dy = \int_0^a dy \int_0^y dx$.

Now a change of integration variable yields

$$\int_0^a dx \int_0^a dy F(x)G(y) = \int_0^a dx \int_0^x dy F(x)G(y) + \int_0^a dx \int_0^x dy F(y)G(x), \tag{E.21}$$

and if $G = F$ is an operator and

$$F(x)F(y) = \pm F(y)F(x) \tag{E.22}$$

and T the x, y-ordering operator, then

$$\int_0^a dx \int_0^a dy T[F(x)F(y)] = \int_0^a dx \int_0^x dy T[F(x)F(y)] + \int_0^a dx \int_0^x dy T[F(y)F(x)], \tag{E.23}$$

or

$$\int_0^a dx \int_0^a dy T[F(x)F(y)] = 2\int_0^a dx \int_0^x dy T[F(x)F(y)], \tag{E.24}$$

where the generalization to arbitrary number of factors F is straightforward.

E.1.2 Electron Field Operators

The electron field operators in analogy with the time-dependent case can now be expressed as

$$\begin{aligned} \bar{\psi}(x,\tau) &= e^{(H-\mu N_0)\tau}\psi(x)e^{-(H-\mu N_0)\tau}, \\ \bar{\psi}^\dagger(x,\tau) &= e^{(H-\mu N_0)\tau}\psi^\dagger(x)e^{-(H-\mu N_0)\tau}, \end{aligned} \tag{E.25}$$

or in the so-called "interaction picture"

$$\begin{aligned} \psi(x,\tau) &= e^{(H_0-\mu N_0)\tau}\psi(x)e^{-(H_0-\mu N_0)\tau} \\ \psi^\dagger(x,\tau) &= e^{(H_0-\mu N_0)\tau}\psi^\dagger(x)e^{-(H_0-\mu N_0)\tau}, \end{aligned} \tag{E.26}$$

where it should be noted that $\psi^\dagger(x,\tau)$ is *not* the adjoint of $\psi(x,\tau)$ in either case.

The electron propagator at finite temperature ($T \neq 0$) is defined as

$$\begin{aligned} & G(x_1,\tau_1;x_2,\tau_2) = G(x_1,x_2;\tau_1-\tau_2) \\ = & \begin{cases} -\mathrm{Tr}\{e^{(F+\mu N_0-H)}\bar{\psi}(x_1,\tau_1)\vec{\psi}^\dagger(x_2,\tau_2)\} & \tau_1 > \tau_2 \\ \ \ \mathrm{Tr}\{e^{(F+\mu N_0-H)}\bar{\psi}^\dagger(x_2,\tau_2)\bar{\psi}(x_1,\tau_1)\} & \tau_1 < \tau_2 \end{cases} \\ = & \begin{cases} G^> & \tau_1 < \tau_2 \\ G^< & \tau_2 < \tau_1, \end{cases} \end{aligned} \tag{E.27}$$

with F the free energy defined by

$$e^{-F\beta} = Z(\beta). \tag{E.28}$$

Remembering that

$$S(\tau) = e^{(H_0-\mu N_0)\tau}e^{-(H-\mu N_0)\tau} \tag{E.29}$$

and, thus,

$$S^{-1}(\tau) = e^{(H-\mu N_0)\tau}e^{-(H_0-\mu N_0)\tau}, \tag{E.30}$$

it follows that

$$\begin{aligned} G^{>} &= -e^{F\beta}\mathrm{Tr}\Big\{e^{-(H_0-\mu N_0)\beta}S(\beta)S^{-1}(\tau_1)e^{(H_0-\mu N_0)\tau_1}\psi(x_1) \\ &\quad \times e^{-(H_0-\mu N_0)\tau_1}S(\tau_1)S^{-1}(\tau_2)e^{(H_0-\mu N_0)\tau_2}\psi^{\dagger}(x_2)e^{-(H_0-\mu N_0)\tau_2}S(\tau_2)\Big\} \\ &= -e^{F\beta}\mathrm{Tr}\Big\{e^{-(H_0-\mu N_0)\beta}S(\beta)S^{-1}(\tau_1)\psi(x_1,\tau_1)S(\tau_1) \qquad \text{(E.31)} \\ &\quad \times S^{-1}(\tau_2)\psi^{\dagger}(x_2,\tau_2)S(\tau_2)\} \, . \end{aligned}$$

Similarly, one can write

$$\begin{aligned} G^{<} &= e^{F\beta}\mathrm{Tr}\Big\{e^{-(H_0-\mu N_0)\beta}S(\beta)S^{-1}(\tau_2)\psi^{\dagger}(x_2,\tau_2)S(\tau_2) \\ &\quad \times S^{-1}(\tau_1)\psi(x_1,\tau_1)S(\tau_1)\} \, . \end{aligned} \qquad \text{(E.32)}$$

Using the properties of T_τ, the electron propagator or Green's function can be expressed as

$$G(x_1,\tau_1;x_2,\tau_2) = -\frac{\langle T_\tau[\psi(x_1,\tau_1)\psi^{\dagger}(x_2,\tau_2)S(\beta)]\rangle_0}{\langle S(\beta)\rangle_0}. \qquad \text{(E.33)}$$

In this expression, the fact has been utilized that

$$e^{-F\beta} = Z(\beta) = Z_0(\beta)\langle S(\beta)\rangle_0. \qquad \text{(E.34)}$$

In terms of a spin orbital basis $\{u_k(x)\}$, the electron field operators in the interaction picture can be expressed as

$$\psi(x,\tau) = \sum_k u_k(x)a_k(\tau) = e^{(H_0-\mu N_0)\tau}\psi(x)e^{-(H_0-\mu N_0)\tau}, \qquad \text{(E.35)}$$

and, thus,

$$a_k(\tau) = e^{(H_0-\mu N_0)\tau}a_k e^{-(H_0-\mu N_0)\tau}. \qquad \text{(E.36)}$$

As

$$e^{\Lambda}ae^{-\Lambda} = a + [\Lambda,a]_- + \frac{1}{2!}[\Lambda,[\Lambda,a]_-]_- + \frac{1}{3!}[\Lambda,[\Lambda,[\Lambda,a]_-]_-]_- \cdots \qquad \text{(E.37)}$$

for $\Lambda = (H_0 - \mu N_0)\,\tau$, and as

$$[\Lambda,a_k]_- = \sum_l (\epsilon_l-\mu)[n_l,a_k]_- = -(\epsilon_k-\mu)\tau a_k, \qquad \text{(E.38)}$$

it follows that

$$a_k(\tau) = a_k e^{-(\epsilon_k-\mu)\tau} \tag{E.39}$$

and

$$\begin{aligned}\psi(x,\tau) &= \sum_k u_k(x) a_k e^{-(\epsilon_k-\mu)\tau}, \\ \psi^\dagger(x,\tau) &= \sum_k u_k^*(x) a_k^\dagger e^{(\epsilon_k-\mu)\tau}.\end{aligned} \tag{E.40}$$

The expression

$$\begin{aligned}g(x\tau, x^{'}\tau^{'}) &\equiv -\langle T_\tau[\psi(x,\tau)\psi^\dagger(x^{'},\tau^{'})]\rangle_0 \qquad \text{(E.41)} \\ &= -\sum_{k,k'} u_k(x) u_{k'}^*(x^{'}) \langle a_k a_{k'}^\dagger\rangle_0 e^{-(\epsilon_k-\mu)\tau} e^{(\epsilon_{k'}-\mu)\tau^{'}} \theta(\tau-\tau^{'}) \\ &\quad + \sum_{k,k'} u_k(x) u_{k'}^*(x^{'}) \langle a_{k'}^\dagger a_k\rangle_0 e^{-(\epsilon_k-\mu)\tau} e^{(\epsilon_{k'}-\mu)\tau^{'}} \theta(\tau^{'}-\tau)\end{aligned}$$

is called a contraction and becomes

$$\begin{aligned}g(x\tau, x^{'}\tau^{'}) &= \sum_k u_k(x) u_k^*(x^{'}) e^{(\tau-\tau^{'})(\epsilon_k-\mu)} \\ &\quad \times \left[\theta(\tau^{'}-\tau)\langle n_k\rangle_0 - \theta(\tau-\tau^{'})\langle 1-n_k\rangle_0\right].\end{aligned} \tag{E.42}$$

This is so, because

$$\begin{aligned}\langle a_{k'}^\dagger a_k\rangle_0 &= \mathrm{Tr}\{e^{-(H_0-\mu N_0)\beta} a_{k'}^\dagger a_k\}/Z_0(\beta) \\ &= \delta_{kk'} \mathrm{Tr}\{\exp[-\sum_l (\epsilon_l-\mu) n_l] n_k]/Z_0(\beta) \\ &= \delta_{kk'} \mathrm{Tr}\{(1+\lambda_k) n_k \prod_{l\neq k} (1+\lambda_l n_l)\}/Z_0(\beta),\end{aligned} \tag{E.43}$$

where $\lambda_l = e^{-(\epsilon_l-\mu)\beta} - 1$. Using Eq. (E.8), one obtains an expression for the occupation numbers $\langle a_k^\dagger a_k\rangle_0 = \langle n_k\rangle_0$ from

$$\begin{aligned}\langle a_{k'}^\dagger a_k\rangle_0 &= \delta_{kk'}\langle n_k\rangle_0, \\ \langle n_k\rangle_0 &= \frac{1+\lambda_k}{2+\lambda_k} = \frac{1}{1+e^{\beta(\epsilon_k-\mu)}}.\end{aligned} \tag{E.44}$$

E.2 Wick's Theorem

An average value of a "τ-ordered" product of field operators can be evaluated as the determinant of a matrix with elements $g(x\tau, x^{'}\tau^{'})$. In particular,

$$\begin{aligned}&(-1)^n \langle T_\tau[\psi(1)\psi(2)\cdots\psi(n)\psi^\dagger(n^{'})\psi^\dagger(n^{'}-1)\cdots\psi^\dagger(1^{'})]\rangle_0 \\ &= \begin{vmatrix} g(1,1^{'}) & g(1,2^{'}) & \cdots & g(1,n^{'}) \\ g(2,1^{'}) & g(2,2^{'}) & \cdots & g(2,n^{'}) \\ \vdots & \vdots & \vdots & \vdots \\ g(n,1^{'}) & g(2,n^{'}) & \cdots & g(n,n^{'}) \end{vmatrix},\end{aligned} \tag{E.45}$$

where the notations

$$\psi(j) = \psi(x_j, \tau_j); \qquad g(i, j^{'}) = g(x_i\tau_i, x_j^{'}\tau_j^{'}) \tag{E.46}$$

have been used.

Proof: The theorem is by definition true for $n = 1$, suggesting that one can proceed by induction. Consider the two relations

$$\langle Xa_k\rangle_0 = \langle a_k^\dagger a_k\rangle_0 \langle [X, a_k]_+\rangle_0 \tag{E.47}$$

and

$$\langle Xa_k^\dagger\rangle_0 = \langle a_k a_k^\dagger\rangle_0 \langle [X, a_k^\dagger]_+\rangle_0, \tag{E.48}$$

where X is any "τ-ordered" product of an odd number of electron field operators.

The first of these relations can be obtained from

$$\begin{aligned}\langle Xa_k\rangle_0 &= \mathrm{Tr}\left\{Xa_k e^{-(H_0-\mu N_0)\beta}\right\}/Z_0(\beta) \\ &= \mathrm{Tr}\left\{Xe^{-(H_0-\mu N_0)\beta} a_k(\beta)\right\}/Z_0(\beta) \\ &= \langle a_k(\beta)X\rangle_0 = \langle a_k X\rangle_0 e^{-(\epsilon_k-\mu)\beta},\end{aligned} \tag{E.49}$$

where the definition

$$a_k(\beta) = e^{(H_0-\mu N_0)} a_k e^{-(H_0-\mu N_0)} = a_k e^{-(\epsilon_k-\mu)\beta} \tag{E.50}$$

has been used. Thus,

$$\begin{aligned}\langle Xa_k\rangle_0 + \langle a_k X\rangle_0 &= \langle [a_k, X]_+\rangle_0 \\ &= \langle Xa_k\rangle_0 \left(1 + e^{(\epsilon_k+\mu)\beta}\right)\end{aligned} \tag{E.51}$$

and

$$\begin{aligned}\langle Xa_k\rangle_0 &= \left(1 + e^{(\epsilon_k-\mu)\beta}\right)^{-1} \langle [X, a_k]_+\rangle_0 \\ &= \langle a_k^\dagger a_k\rangle_0 \langle [X, a_k]_+\rangle_0.\end{aligned} \tag{E.52}$$

The second relation can be shown analogously.

Two separate cases can be distinguished: (*i*) an unprimed variable τ_j and (*ii*) a primed variable τ'_j, respectively, is less than all other τ and τ' variables.

(*i*)

$$\begin{aligned} & (-1)^n \langle T_\tau[\psi(1)\cdots\psi(n)\psi^\dagger(n')\cdots\psi^\dagger(1')]\rangle_0 \\ = \; & (-1)^{n-j}\langle X\psi(j)\rangle_0 = \sum_k u_k(x_j) e^{-(\epsilon_k-\mu)\tau_j}(-1)^{n-j}\langle X a_k\rangle_0, \end{aligned} \tag{E.53}$$

where

$$X = T_\tau[\psi(1)\cdots\psi(j-1)\psi(j+1)\psi^\dagger(n')\cdots\psi^\dagger(1')], \tag{E.54}$$

since bringing $\psi(j)$ to the right means $n-j+n$ interchanges of field operators. Using Eq. (E.47) leads to

$$\begin{aligned} & (-1)^n \langle T_\tau[\psi(1)\cdots\psi(n)\psi^\dagger(n')\cdots\psi^\dagger(1')]\rangle_0 \\ = \; & \sum_k u_k(x_j) e^{-(\epsilon_k-\mu)\tau_j}\langle a_k^\dagger a_k\rangle_0 \langle [X, a_k]_+\rangle_0 \\ = \; & \sum_k u_k(x_j) e^{-(\epsilon_k-\mu)\tau_j}\langle a_k^\dagger a_k\rangle_0 \\ & \times \sum_\nu (-1)^{n-j+\nu-1}[\psi^\dagger(\nu'), a_k]_+\rangle_0 \langle T_\tau[j,\nu']\rangle_0, \end{aligned} \tag{E.55}$$

where $T_\tau[j,\nu']$ is the original ordered product of field operators with $\psi(j)$ and $\psi^\dagger(\nu')$ missing. Again using Eq. (E.47) yields

$$\begin{aligned} & (-1)^n \langle T_\tau[\psi(1)\cdots\psi(n)\psi^\dagger(n')\cdots\psi^\dagger(1')]\rangle_0 \\ = \; & \sum_\nu (-1)^{\nu+j}\langle\psi^\dagger(\nu')\psi(j)\rangle_0 (-1)^{n-1}\langle T_\tau[j,\nu']\rangle_0 \\ = \; & \sum_\nu (-1)^{\nu+j} g(j,\nu')(-1)^{n-1}\langle T_\tau[j,\nu']\rangle_0, \end{aligned} \tag{E.56}$$

which can be viewed as the expansion of the determinant in Eq. (E.45) by the *j*-th row, with

$$(-1)^{\nu+j}(-1)^{n-1}\langle T_\tau[j,\nu']\rangle_0 \tag{E.57}$$

the corresponding minors.

(*ii*) An analogous treatment of this case using Eq. (E.48) yields

$$\begin{aligned}
&(-1)^n\langle T_\tau[\psi(1)\cdots\psi(n)\psi^\dagger(n')\cdots\psi^\dagger(1')]\rangle_0 \\
=\ &\sum_\nu(-1)^{\nu+j}g(\nu,j')(-1)^{n-1}\langle T_\tau[\nu,j']\rangle_0,
\end{aligned} \tag{E.58}$$

which can be viewed as the expansion of the determinant in Eq. (E.45) by the j-th column.

Then if the determinantal form of Eq. (E.45) is correct for $n-1$, it is correct for n, and because it holds true for $n=1$, the induction proof is complete, and Wick's theorem is proven.

E.3 Diagrams

A rational approach to the evaluation of the terms in the series in Eq. (E.17) is to apply the diagrammatic analysis introduced by Feynman for the time-dependent and by Matsubara for the temperature-dependent case. It is in this process that Wick's theorem is crucial.

The electron-electron interaction term in the interaction picture is

$$V(\tau)=\frac{1}{2}\int dx\int dy\, w(x,y)T_\tau[\psi(x,\tau)\psi(y,\tau)\psi^\dagger(y,\tau)\psi^\dagger(x,\tau)] \tag{E.59}$$

and

$$S(\beta)=-T_\tau\exp[-\int_0^\beta V(\tau)d\tau]. \tag{E.60}$$

From Eqs. (E.17) and (E.33), it follows that the first-order correction to G is

$$\begin{aligned}
&-\frac{1}{2\langle S(\beta)\rangle_0}\int_0^\beta d\tau\int dx\int dy\, w(x,y) \\
&\times\langle T_\tau[\psi(x_1,\tau_1)\psi^\dagger(x_2,\tau_2)\psi(x,\tau)\psi(y,\tau)\psi^\dagger(y,\tau)\psi^\dagger(x,\tau)]\rangle_0.
\end{aligned} \tag{E.61}$$

The average of the τ-ordered product of field operators can be reorganized to read

$$\begin{aligned}
&-\langle T_\tau[\psi\psi^\dagger\psi\psi\psi^\dagger\psi^\dagger]\rangle_0 \\
&=-\langle T_\tau[\psi(x_1,\tau_1)\psi(x,\tau)\psi(y,\tau)\psi^\dagger(y,\tau)\psi^\dagger(x,\tau)\psi^\dagger(x_2,\tau_2)]\rangle_0 \\
&=\begin{vmatrix} g(x_1\tau_1,x_2\tau_2) & g(x_1\tau_1,x\tau) & g(x_1\tau_1,y\tau) \\ g(x\tau,x_2\tau_2) & g(x\tau,x\tau) & g(x\tau,y\tau) \\ g(y\tau,x_2\tau_2) & g(y\tau,x\tau) & g(y\tau,y\tau) \end{vmatrix}
\end{aligned} \tag{E.62}$$

according to the properties of T_τ, and Wick's theorem. The integral in Eq. (E.61) after expanding the determinant of contractions can be expressed as

$$
\begin{array}{ll}
(a) & \int dx \int dy \int_0^\beta d\tau\, w(x,y) g(x\tau, x\tau) g(y\tau, y\tau) g(x_1\tau_1, x_2\tau_2), \\
(b) & -\int dx \int dy \int_0^\beta d\tau\, w(x,y) g(x\tau, y\tau) g(y\tau, x\tau) g(x_1\tau_1, x_2\tau_2), \\
(c) & -\int dx \int dy \int_0^\beta d\tau\, w(x,y) g(x_1\tau_1, x\tau) g(x\tau, x_2\tau_2) g(y\tau, y\tau), \\
(d) & \int dx \int dy \int_0^\beta d\tau\, w(x,y) g(x_1\tau_1, x\tau) g(x\tau, y\tau) g(y\tau, x_2\tau_2), \\
(e) & \int dx \int dy \int_0^\beta d\tau\, w(x,y) g(x_1\tau_1, y\tau) g(y\tau, x\tau) g(x\tau, x_2\tau_2), \\
(f) & \int dx \int dy \int_0^\beta d\tau\, w(x,y) g(x_1\tau_1, y\tau) g(y\tau, x_2\tau_2) g(x\tau, x\tau).
\end{array}
\tag{E.63}
$$

The terms (a) through (f) can be diagrammed (see Figure E.2 using the rules of Feynman; *i.e.*, the $(x,\, \tau)$ coordinates are points in the plane, and points in a single contraction are connected by a line with direction ($\psi(x,\tau)$ outgoing arrow and $\psi^\dagger(x,\tau)$ incoming arrow). Points in the symmetric interaction $w(x,y) = w(y,x)$ are connected by a dashed line.

Diagrams (a) and (b) have disconnected parts and are called *disconnected diagrams*, whereas the rest are called *connected diagrams.* Diagrams (c) and (f) are actually the same, because of the symmetry $w(x,y) = w(y,x)$, and so are (d) and (e). Actually if the interaction is written as the antisymmetric form

$$
w(x,y)(1 - P_{xy}), \tag{E.64}
$$

where the interchange operator acts on the left entries in the contractions, all four can be expressed as a single diagram (see Figure E.3) with the dashed interaction line representing a so-called antisymmetric vertex (this corresponds to a coulomb minus exchange integral)

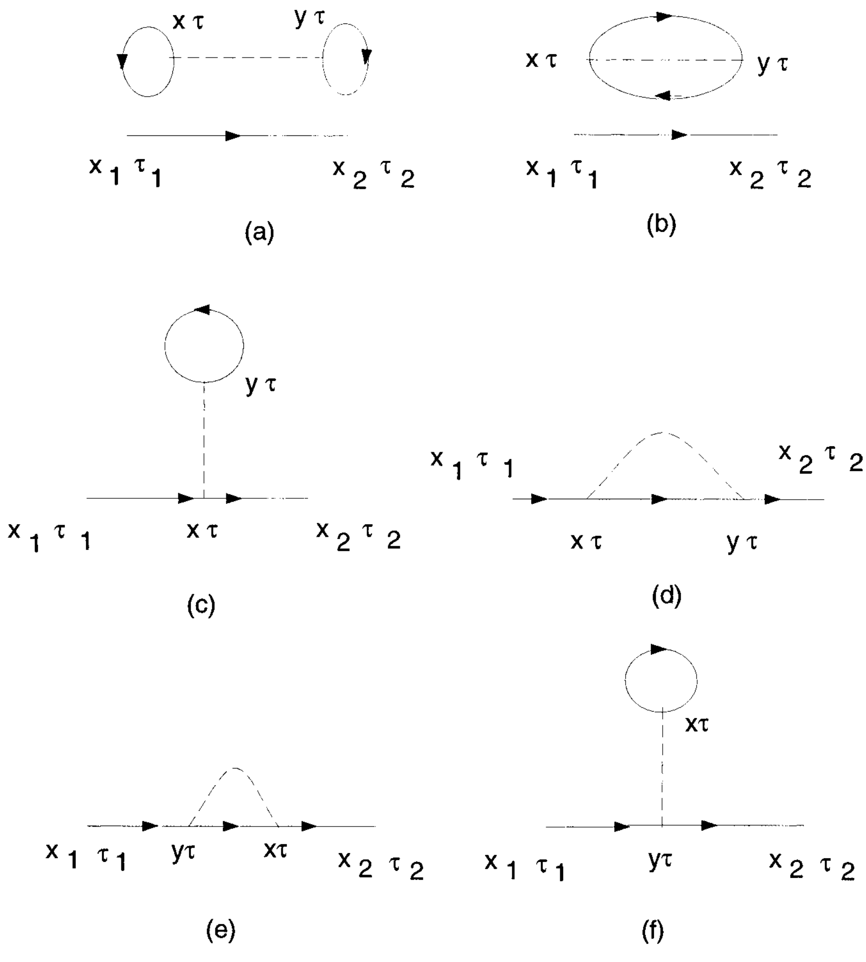
E.3.1 Disconnected Diagrams

Disconnected diagrams consist of two distinguishable parts: (*i*) A factor consisting of all $V(\tau)$ or parts of $V(\tau)$ connected to $\psi(x_1,\tau_1)$ and $\psi^\dagger(x_2,\tau_2)$ and (*ii*) a second factor, which simply is the remainder of the diagram. A general such term can be expressed as

$$
\begin{aligned}
- & \frac{(-1)^n}{n!} \int d\tau_1' d\tau_2' \cdots d\tau_m' \langle T_\tau[\psi(x_1,\tau_1)\psi^\dagger(x_2,\tau_2)V(\tau_1')\cdots V(\tau_m')]\rangle_c \\
\times & \int d\tau_{m+1}' \cdots d\tau_n' \langle T_\tau[V(\tau_{m+1}')\cdots V(\tau_n')]\rangle_0,
\end{aligned}
\tag{E.65}
$$

where $\langle\cdots\rangle_c$ is the connected part of the diagram. Redistribution of the n different τ_i' among the m V's in $\langle\cdots\rangle_c$ and the n - m V's in $\langle\cdots\rangle_0$ merely corresponds to relabeling of the integration variables and gives an identical contribution to G from each such term. There are $n!/m!(n-m)! = \binom{n}{m}$ such arrangements, and the total contribution from such terms then equals

$$-\frac{(-1)^m}{m!}\int d\tau_1' d\tau_2' \cdots d\tau_m' \langle T_\tau[\psi(x_1,\tau_1)\psi^\dagger(x_2,\tau_2)V(\tau_1')\cdots V(\tau_m')]\rangle_c$$



(a) (b) (c) (d) (e) (f)

Figure E.2: Diagram version of the terms in Eq. (E.63).

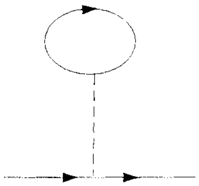


Figure E.3: Single diagram representation of the four diagrams (c), (d), (e), and (f) in Figure E.2 using an antisymmetric vertex.

$$\times \quad \frac{(-1)^{n-m}}{(n-m)!}\int d\tau'_{m+1}\cdots d\tau'_n \langle T_\tau[V(\tau'_{m+1})\cdots V(\tau'_n)]\rangle_0. \tag{E.66}$$

Summing the contributions of those diagrams of all orders that consist of a *particular connected part* and an *arbitrary disconnected part*, *i.e.*,

$$\begin{aligned} &- \frac{(-1)^m}{m!}\int d\tau'_1 d\tau'_2\cdots d\tau'_m \langle T_\tau[\psi(x_1,\tau_1)\psi^\dagger(x_2,\tau_2)V(\tau'_1)\cdots V(\tau'_m)]\rangle_c \\ &\times \langle 1 - \int d\tau'_{m+1}V(\tau'_{m+1}) + \frac{1}{2}\int d\tau'_{m+1}d\tau'_{m+2}T_\tau[V(\tau'_{m+1})V(\tau'_{m+2})]\cdots \\ &+ \frac{(-1)^k}{k!}\int d\tau'_{m+1}\cdots d\tau'_{m+k}T_\tau[V(\tau'_{m+1})\cdots V(\tau'_{m+k})] + \cdots\rangle_0, \end{aligned} \tag{E.67}$$

shows that all terms have a common factor of $\langle S(\beta)\rangle_0$, and thus,

$$\langle T_\tau[\psi(x_1,\tau_1)\psi^\dagger(x_2,\tau_2)S(\beta)]\rangle_0 = \langle T_\tau[\psi(x_1,\tau_1)\psi^\dagger(x_2,\tau_2)]\rangle_c\langle S(\beta)\rangle_0 \tag{E.68}$$

and

$$G(x_1\tau_1;x_2\tau_2) = \langle T_\tau[\psi(x_1,\tau_1)\psi^\dagger(x_2,\tau_2)]\rangle_c. \tag{E.69}$$

E.3.2 Propagator Diagram Rules

1. Form all connected topologically nonequivalent diagrams with $2n$ vertices and two external lines where two solid lines and two dashed lines meet each vertex.
2. Associate a factor $g(x_1\tau_1, x_2\tau_2)$ with each solid line starting in $(x_1\tau_1)$ and ending in $(x_2\tau_2)$.
3. Associate $w(x,y)(1 - P_{xy})$ with each dashed line.
4. Integrate over all internal vertex coordinates $(x_i\tau_i)$, and sum over all internal spin coordinates.

5. Multiply the resulting expression by $(-1)^{n+F}$, where F equals the number of closed Fermion loops.

6. Put $g(x_1\tau, x_2\tau) = \langle\psi^\dagger(x_2)\psi(x_1)\rangle_0$ for equal τ's.

E.3.3 Fourier Transform

Consider the Green's function in Eq. (E.27),

$$G^> = -\mathrm{Tr}\left\{e^{(F+\mu N_0-H)\beta}\bar{\psi}(x_1,\tau_1)\bar{\psi}^\dagger(x_2,\tau_2)\right\}, \qquad \tau_1 < \tau_2, \tag{E.70}$$

and use the definitions in Eq. (E.25) to write

$$\begin{aligned} G^> &= -\mathrm{Tr}\left\{e^{(F+\mu N_0-H)\beta}e^{(H-\mu N_0)\tau}\psi(x_1)e^{-(H-\mu N_0)\tau}\psi^\dagger(x_2)\right\} \\ &\equiv G(x_1, x_2; \tau), \end{aligned} \tag{E.71}$$

where $\tau = \tau_1 - \tau_2$. Similarly,

$$\begin{aligned} G^< &= \mathrm{Tr}\{e^{(F+\mu N_0-H)\beta}\bar{\psi}^\dagger(x_2,\tau_2)\bar{\psi}(x_1,\tau_1)\} \\ &= \mathrm{Tr}\{e^{F\beta}e^{(H-\mu N_0)\tau}\psi(x_1)e^{-(H-\mu N_0)(\tau+\beta)}(\psi^\dagger(x_2)\} \\ &= \mathrm{Tr}\{e^{(F+\mu N_0-H)\beta}e^{(H-\mu N_0)(\tau+\beta)}\psi(x_1)e^{-(H-\mu N_0)(\tau+\beta)}(\psi^\dagger(x_2)\} \\ &\equiv -G(x_1, x_2; \tau+\beta), \end{aligned} \tag{E.72}$$

where $\tau_1 < \tau_2$, and, thus $\tau < 0$, and $0 < \tau + \beta < \beta$. Analogous algebraic manipulations show that

$$\begin{aligned} g(x_1\tau_1, x_2\tau_2) &= -\langle T_\tau[\psi(x_1,\tau_1)\psi^\dagger(x_2,\tau_2)]\rangle_0 \\ &\equiv g(x_1, x_2; \tau) \end{aligned} \tag{E.73}$$

(see also Eq. (E.42)) is a function of τ on the interval $(-\beta, \beta)$, which satisfies the relation

$$g(x_1, x_2; \tau) = -g(x_1, x_2; \tau+\beta) \tag{E.74}$$

for $\tau < 0$.

Expansion in a Fourier series on this interval yields

$$g(x_1, x_2; \tau) = \sum_n g_n(x_1, x_2)e^{-in\pi\tau/\beta}, \tag{E.75}$$

with the coefficients

$$g_n(x_1,x_2) = \frac{1}{2\beta}\int_{-\beta}^{\beta} g(x_1,x_2;\tau)e^{in\pi\tau/\beta}d\tau. \tag{E.76}$$

Using the properties discussed above, one obtains

$$\begin{aligned} g_n(x_1,x_2) &= \frac{1}{2\beta}\left[\int_0^{\beta} g(x_1,x_2;\tau)e^{in\pi\tau/\beta}d\tau + \int_{-\beta}^{0} g(x_1,x_2;\tau)e^{in\pi\tau/\beta}d\tau\right] \\ &= \frac{1}{2\beta}\left[\int_0^{\beta} g(x_1,x_2;\tau)e^{in\pi\tau/\beta}d\tau - \int_0^{\beta} g(x_1,x_2;\tau)e^{in\pi(\tau-\beta)/\beta}d\tau\right] \end{aligned} \tag{E.77}$$

$$= \frac{1}{2\beta}[1-e^{-in\pi}]\int_0^{\beta} g(x_1,x_2;\tau)e^{in\pi\tau/\beta}d\tau \begin{cases} =0, & n=2m \\ \neq 0, & n=2m+1. \end{cases}$$

Using Eq. (E.42), one obtains

$$g_{2m+1}(x_1,x_2) = \frac{1}{\beta}\sum_k u_k(x_1)u_k^*(x_2)/[(\mu-\epsilon_k)+i(2m+1)/\beta\pi]. \tag{E.78}$$

When $T \to 0$, the parameter $\beta \to \infty$ and the Fourier series in Eq. (E.75) becomes an integral. This can be seen from

$$\begin{aligned} &\frac{1}{\beta}\sum_{m=-\infty}^{\infty}\left(\sum_k \frac{u_k(x_1)u_k^*(x_2)}{[\mu-\epsilon_k+i(2m+1)\pi/\beta]}\right)e^{-i(2m+1)\pi\tau/\beta}\Delta m \\ &= \frac{1}{2\pi}\sum_{m=-\infty}^{\infty}\left(\sum_k \frac{u_k(x_1)u_k^*(x_2)}{[\mu-\epsilon_k+i(2m+1)\pi/\beta]}\right)e^{-i(2m+1)\pi\tau/\beta}\Delta(2m+1)\pi/\beta \\ &\to \sum_k u_k(x_1)u_k^*(x_2)\frac{1}{2\pi}\int_{-\infty}^{\infty} dz e^{-iz}[iz+\mu-\epsilon_k]^{-1}. \end{aligned} \tag{E.79}$$

Rewriting the integral with $iz+\mu=\epsilon$ yields

$$g(x_1,x_2;\tau) = \sum_k u_k(x_1)u_k^*(x_2)\frac{1}{2\pi i}\int_{\mu-i\infty}^{\mu+i\infty} d\epsilon\, e^{-(\epsilon-\mu)\tau}/[\epsilon-\epsilon_k] \tag{E.80}$$

and further writing this as

$$g(x_1,x_2;\tau) = (2\pi i)^{-1}\int_{\mu-i\infty}^{\mu+i\infty} d\epsilon\, g(x_1,x_2;\epsilon)e^{-(\epsilon-\mu)\tau} \tag{E.81}$$

shows that a system of noninteracting electrons has the electron propagator with an energy representation

$$g(x_1, x_2; \epsilon) = \sum_k \frac{u_k(x_1)u_k^*(x_2)}{\epsilon - \epsilon_k}. \tag{E.82}$$

The functions $g(x_1, x_2; \tau)$ and $g(x_1, x_2; \epsilon)$ above are connected via a Laplace transform.

Notes and Bibliography

- Diagramatic analysis was introduced by R. P. Feynman in 1949 in *Phys. Rev.* **76**, 769 for the time-dependent case and by T. Matsubara in 1955 in *Progr. Theoret. Phys. (Kyoto)* **14**, 351, for the temperature case.
- Wick's theorem occurs first in a paper by G. C. Wick in *Phys. Rev.* **80**, 268 (1950).
- Analytical properties of propagators, analytical continuation and other relevant procedures for their mathematical treatment are discussed by
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  - J. M. Luttinger and J. C. Ward in *Phys. Rev.* **118**, 1417 (1960) and by
  - W. Parry, and R. Turner in *Reports on Progress in Physics* **27**, 23 (1964).
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- Laplace transforms are discussed in some detail in *Handbook of Mathematical Functions*, Edited by M. Abramovitz and I. A. Stegun, Dover Publications, Inc., New York, 1970, p. 1020.

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Appendix F

The Eckart Potential and its Propagator

Eckart (see references in Notes and Bibliography at the end of this appendix) introduced a one-dimensional, analytically solvable,quantum mechanical model, which is applicable to the study of chemical reactions . The potential is given by

$$U(x) = U(-\infty)\left\{\frac{1}{1+\exp(x/b)} + \frac{\kappa \exp(x/b)}{[1+\exp(x/b)]^2}\right\}, \tag{F.1}$$

where the parameter κ provides the shape of the transition from the initial situation with energy $U(-\infty)$ to the final one with energy $U(\infty) = 0$. A κ-value on the interval $[-1, 1]$ gives a smooth step, while other values yield a barrier or a well in the transition region (see Figure F.1).

The Green's function satisfies the equation ($\hbar = 1$)

$$[E - U(x)]G(x, x'; E) + \frac{1}{2M}\frac{d^2}{dx^2}G(x, x'; E) = \delta(x - x'). \tag{F.2}$$

The introduction of dimensionless independent and dependent variables such that $x = bq$, $E = k^2/2Mb^2$, $G(x, x'; E) = 2Mbg(q, q'; k^2)$, $U(x) = w(q)/2Mb^2$, $a = 2Mb^2U(-\infty)$, and $w(q) = a[1 + \kappa/(1 + e^{-q})]/(1 + e^q)$ results in the equation

$$[k^2 - w(q)]g(q, q'; k^2) + \frac{d^2}{dq^2}g(q, q'; k^2) = \delta(q - q'), \tag{F.3}$$

A solution $u(z)$ to the homogeneous equation corresponding to Eq. (F.3) can conveniently be expressed in terms of the Gauss hypergeometric series $F(z)$ of the auxiliary variable $z = 1/(1 + e^{-q})$. Thus,

$$[k^2 - w(q)]u(z) + \frac{dz}{dq}\frac{d}{dz}\left[\frac{dz}{dq}\frac{du(z)}{dz}\right] = 0, \tag{F.4}$$

with

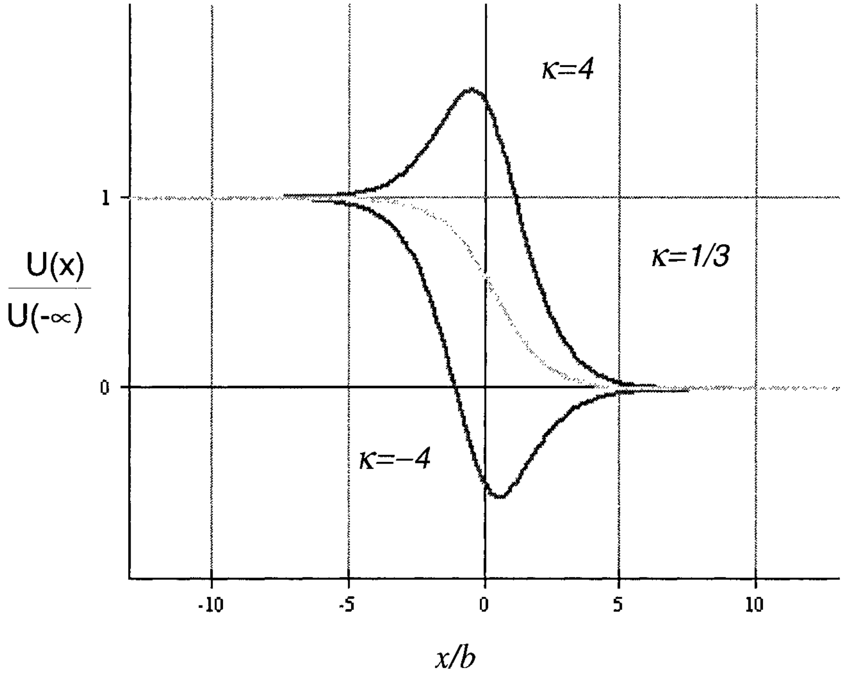

Figure F.1: Eckart potential for three values of the shape parameter, $\kappa = 4, 1/3, -4$.

$$w(q) = a(1-z)(1+\kappa z) \tag{F.5}$$

and

$$\frac{dz}{dq} = (1-z)z. \tag{F.6}$$

A solution has the form

$$u(z) = z^{\sigma}(1-z)^{\tau}F(\frac{1}{2}+\sigma+\tau+\omega, \frac{1}{2}+\sigma+\tau-\omega; 1+2\sigma; z), \tag{F.7}$$

with the parameters of the Gauss hypergeometric series defined as

$$\sigma^2 = a - k^2; \quad \tau^2 = -k^2; \quad \omega^2 = \frac{1}{4} - a\kappa. \tag{F.8}$$

Properties of the Gauss series admits another independent solution of the form

$$v(z) = z^{\sigma}(1-z)^{\tau}F(\frac{1}{2}+\sigma+\tau+\omega, \frac{1}{2}+\sigma+\tau-\omega; 1+2\tau; 1-z). \tag{F.9}$$

The properties of these solutions are such that as q tends to infinity on the negative real axis and z to zero, $u(z)$ tends to $\exp(q\sigma)$. Similarly, as q tends to infinity on the positive real axis and z to 1, $v(z)$ tends to $\exp(-q\tau)$. The Gauss series in $u(z)$ and $v(z)$ are absolutely convergent for $|z| \leq 1$, when the real part of τ and σ, respectively, is negative. The following definitions are useful:

$$\sigma = ik' = i(k^2 - a)^{1/2}, \quad \sigma + \sigma^* < 0, \quad \tau = ik; \tau + \tau^* < 0, \tag{F.10}$$

and introduce the wave numbers k' and k, which are both chosen to lie in the upper half of the complex plane. The two roots to the equation $\omega^2 = \frac{1}{4} \pm a\kappa$ for ω occur in the Gauss series, and the choice of branch is arbitrary.

The two linearly independent solutions to be used to express the propagator can then be written in terms of these new parameters as

$$u(z) = z^{-ik'}(1-z)^{ik}F(\frac{1}{2} - ik' + ik + \omega, \frac{1}{2} - ik' + ik - \omega; 1 - 2ik'; z) \tag{F.11}$$

and

$$v(z) = z^{ik'}(1-z)^{-ik}F(\frac{1}{2} + ik' - ik + \omega, \frac{1}{2} + ik' - ik - \omega; 1 - 2ik; 1 - z). \tag{F.12}$$

The asymptotic behavior of these solutions are such that

$$u(z) \longrightarrow e^{-ik'q}, \quad \text{and} \quad v(z) \longrightarrow \left(\frac{W}{2ik'}\right) e^{ik'q} \tag{F.13}$$

for $q \longrightarrow -\infty$, and $z \longrightarrow 0$, while

$$u(z) \longrightarrow \left(\frac{W}{2ik}\right) e^{-ikq} \quad \text{and} \quad v(z) \longrightarrow e^{ikq} \tag{F.14}$$

for $q \longrightarrow \infty$ and $z \longrightarrow 1$.

The Wronskian W equals

$$\begin{aligned} W(u,v) &= u(z)\frac{dv(z)}{dq} - v(z)\frac{du(z)}{dq} = \frac{dz}{dq}\left(u\frac{dv}{dz} - v\frac{du}{dz}\right) \\ &= -\frac{\Gamma(1-2ik')\Gamma(1-2ik)}{\Gamma(\frac{1}{2} - ik' - ik + \omega)\Gamma(\frac{1}{2} \pm ik' - ik - \omega)}, \\ &= 2ik'F(\frac{1}{2} + ik' - ik + \omega, \frac{1}{2} + ik' - ik + \omega; 1 - 2ik; 1) \\ &= 2ikF(\frac{1}{2} - ik' + ik + \omega, \frac{1}{2} - ik' + ik + \omega; 1 - 2ik'; 1), \end{aligned} \tag{F.15}$$

and, thus, the propagator can be written as

$$g(q,q';k^2) = \frac{u(z_<)v(z_>)}{W(u,v)}, \tag{F.16}$$

according to Eq. (2.12).

The spectral density of the Green's function reflects the discontinuity as the energy parameter crosses the real axis. Complex energy values are considered and the energy plane is cut along the real axis from a least energy value where both regions are open to infinity, *i.e.*, the interval $\{\max[0, U(-\infty)], \infty\}$. Limiting values for k and k' are positive and real when approaching the cut from above and otherwise negative.

The transformation property of the hypergeometric series under wave number sign change is found to be

$$\begin{aligned} & F(\frac{1}{2} + ik' - ik + \omega, \frac{1}{2} + ik' - ik - \omega; 1 - 2ik; 1 - z) \\ = \; & F(\frac{1}{2} + ik' - ik + \omega, \frac{1}{2} + ik' - ik - \omega; 1 + 2ik'; z)\frac{W}{2ik'} \\ + \; & z^{-2ik'}(1-z)^{2ik} \\ \times \; & F(\frac{1}{2} - ik' + ik + \omega, \frac{1}{2} - ik' + ik - \omega; 1 - 2ik'; z)\frac{W\chi}{2ik'}, \end{aligned} \tag{F.17}$$

with the amplitude χ given in terms of ratios of gamma functions as

$$\chi = \frac{\Gamma(\frac{1}{2} - ik' - ik + \omega)\Gamma(\frac{1}{2} - ik' - ik - \omega)\Gamma(2ik')}{\Gamma(\frac{1}{2} + ik' - ik + \omega)\Gamma(\frac{1}{2} + ik' - ik - \omega)\Gamma(-2ik')}. \tag{F.18}$$

It holds, for positive values of k and k', that

$$v(z) = \frac{W(u,v)}{2ik'}\{u^*(z) + u(z)\chi\}, \tag{F.19}$$

and the general form of the spectral density function yields

$$A(x,x';E) = -\frac{2Mb}{\pi}\Im \lim_{\eta\to+0} g(q,q';k^2 + i\eta), \tag{F.20}$$

which reduces to

$$A(x,x';E) = \frac{Mb}{\pi k'}\Re u(z_<)\{u^*(z_>) + u(z_>)\chi\}. \tag{F.21}$$

The derivatives of the spectral density exhibit a discontinuity at equal arguments, which can be seen from

$$\begin{aligned} \frac{\partial z_<}{\partial x} &= \frac{dq}{dx}\frac{dz}{dq}\frac{dz_<}{dz} = \frac{z(1-z)}{b}\Theta(z'-z), \\ \frac{\partial z_>}{\partial x} &= \frac{dq}{dx}\frac{dz}{dq}\frac{dz_>}{dz} = \frac{z(1-z)}{b}\Theta(z-z'), \end{aligned} \tag{F.22}$$

from which follows that

$$\begin{aligned} \frac{\partial A(x,x';E)}{\partial x} &= \frac{Mz(1-z)}{\pi k'}\Theta(z'-z)\Re\frac{du(z)}{dz}\{u^*(z')+u(z')\chi\} \\ &+ \frac{Mz(1-z)}{\pi k'}\Theta(z-z')\Re u(z')\left\{\frac{du^*(z)}{dz}+\frac{du(z)}{dz}\chi\right\}. \end{aligned} \tag{F.23}$$

An equivalent expression holds for the derivative with respect to x', and for the second derivative at the origin, we obtain

$$\frac{\partial^2 A(0,0;E)}{\partial x \partial x'} = \frac{M}{16\pi k' b}\Re\frac{du(\frac{1}{2})}{dz}\{\frac{du^*(\frac{1}{2})}{dz}+\frac{du(\frac{1}{2})}{dz}\chi\}, \tag{F.24}$$

where we note that the δ-function term from the differentiation of the Heaviside step function does not appear after the real part is taken.

The expression in Eq. (13.19) now becomes

$$\begin{aligned} &\int dxdx' A_J(x,x';E)A_J(x',x;E) \\ &= \left(\frac{4i}{M}\right)^2\left[\frac{dA(0,0;E)}{dx}\frac{dA(0,0;E)}{dx'} - A(0,0;E)\frac{d^2A(0,0;E)}{dxdx'}\right] \\ &= \left(\frac{i}{\pi k'}\right)^2\left[\Re(u'\tilde{u})\Re(u\tilde{u}') - \Re(u\tilde{u})\Re(u'\tilde{u}')\right], \end{aligned} \tag{F.25}$$

where in the last expression, the derivatives with respect to z or z' are indicated by primes and the suppressed arguments are $\frac{1}{2}$. We recall the definition of $\tilde{u}$ as

$$\tilde{u} = u^* + u\chi, \tag{F.26}$$

which can be used to obtain the following expression for Eq. (F.25):

$$2\left(\frac{uu'^* - u'u^*}{8\pi i k'}\right)^2\left(1-|\chi|^2\right) = \frac{2}{\pi^2}\left(1-|\chi(E)|^2\right). \tag{F.27}$$

with the energy dependence of the amplitude χ explicitly given. The numerator in the rate expression Eq. (13.9) can now be expressed as

$$\int_0^\beta d\tau \int_{-\infty}^0 dt e^{\eta t}\langle J(\tau+it)J\rangle_0 = \frac{2\beta}{\pi}\int dE e^{\beta(F-E)}\left(1-|\chi(E)|^2\right), \tag{F.28}$$

and it is essentially the energy weighted average transmission coefficient for the Eckart potential. It should be noted that the choice $x=0$ is arbitrary and could be replaced by another value to obtain the identical result.

The transmission coefficient is

$$\begin{aligned} T(E) &\equiv (1 - |\chi(E)|^2) \\ &= 1 - \left| \frac{\Gamma(\frac{1}{2} - ik' - ik + \omega)\Gamma(\frac{1}{2} - ik' - ik - \omega)\Gamma(2ik')}{\Gamma(\frac{1}{2} + ik' - ik + \omega)\Gamma(\frac{1}{2} + ik' - ik - \omega)\Gamma(-2ik')} \right|^2 \\ &= 1 - \frac{\cosh \pi(k' - k + i\omega) \cosh \pi(k' - k - i\omega)}{\cosh \pi(k + k' + i\omega) \cosh \pi(k + k' + i\omega)} \\ &= 2\frac{2sinh2\pi k \sinh 2\pi k'}{\cosh 2\pi(k + k') + \cosh 2\pi i\omega} \end{aligned} \tag{F.29}$$

for a purely imaginary value of ω. The formula holds also for real values as pointed out by Eckart. Both k and k' have to be real and positive and no transmission is allowed unless the kinetic energy is positive in both regions. After substitution, the integral can be expressed as

$$\frac{2\beta}{\pi} \int dE e^{\beta(F-E)} T(E) = \frac{2}{\pi} e^{\beta(F-U(-\infty))} \int_0^1 d\theta T(\theta) \tag{F.30}$$

with

$$\theta = 1 - e^{\beta(U(-\infty)-E)}. \tag{F.31}$$

There are four energy parameters in $T(\theta)$: (i) the potential energy difference between the entrance and exit channels, $U(-\infty)$; (ii) the height of the potential barrier,

$$U_{\text{max}} = U(-\infty)\frac{(\kappa + 1)^2}{4\kappa} = U(-\infty)\left[1 + \frac{(\kappa - 1)^2}{4\kappa}\right]; \tag{F.32}$$

(iii) the width of the barrier $1/2Mb^2$; and (iv) the temperature parameter $1/\beta$. Only ratios of these parameters are significant and we choose the dimensionless quantities a, $h = a\frac{(\kappa+1)^2}{4\kappa}$, and $\tau = \frac{2Mb^2}{\beta}$ as our parameters. It holds that $\omega^2 = \frac{1}{4} \pm (\sqrt{h} + \sqrt{h - a})^2$ Figure F.2 shows how the integrand changes under changes in parameter values.

The similarity between panels A and C shows that it is the height of the barrier above the higher energy channel that is the important parameter and not the energy difference between the two. A similar conclusion derives from panel B, where it is the barrier height in relation to the average kinetic energy in the system that changes. Panel D shows that the thinner barrier admits tunneling at lower energies than does the wider one.

The integral in Eq. (F.30), for a boson or fermion system, takes the form

$$\frac{2\beta}{\pi} \int dE \frac{T(E)}{e^{\beta(E-\mu)} \mp 1} = \frac{2}{\pi} \int d\theta \frac{T(\theta)}{e^{\beta U(-\infty)-\mu)} \mp (1 - \theta)}, \tag{F.33}$$

where the exponential in the denominator dominates so that it may be considered constant.

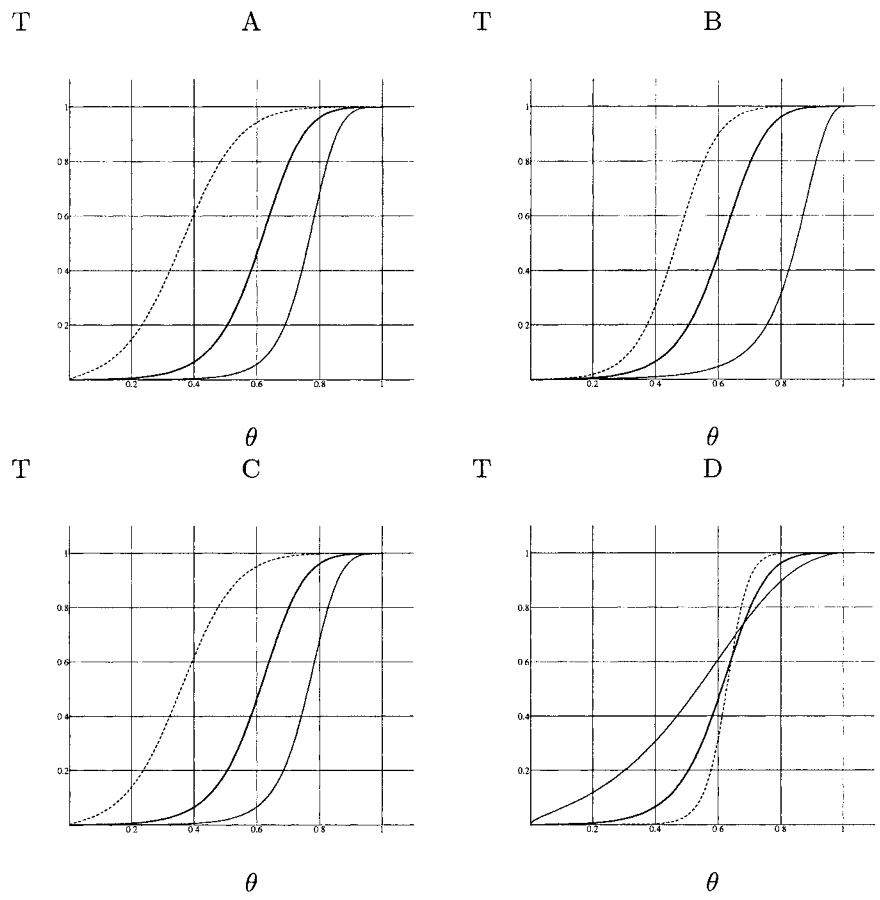

Figure F.2: Illustrations of the transmission coefficient T as a function of the energy-dependent variable θ. The heavy line in all panels shows the form when $a = \tau = h/2 = 1$. Panel A shows in addition the values for $a = 0.5$ and $a = 1.5$. Panel B shows changes with temperature as $\tau = 0.5$ and $\tau = 1.5$. Panel C gives the form for different barrier heights $h = 1.5$ and $h = 2.5$. Panel D indicates changing barrier widths when $a = \tau = h/2 = 0.25$ and $a = \tau = h/2 = 4$.

The denominator in the rate expression Eq. (13.9) is calculated with the relevant Green's functions. Thus,

$$\begin{aligned}\frac{1}{K} &= \frac{1}{2\beta}\int_0^\beta d\tau \int_0^\beta d\tau' \langle T\left[B(\tau)B(\tau')\right]\rangle_c \\ &= \pm\frac{1}{2\beta}\int d\tau d\tau' dx dx' B(x')G(x'\tau', x\tau)B(x)G(x\tau, x'\tau'), \qquad \text{(F.34)}\end{aligned}$$

with the temperature form of the propagator. The upper sign applies to boson systems, while the lower one works for the fermion case.

Using the Fourier representation (see Appendix E for the propagators, we obtain for the boson case the form

$$G(x\tau, x'\tau') = \frac{2Mb}{\beta} \sum_{n=-\infty}^{\infty} g(q, q'; \mu - \frac{2n\pi}{\beta}) \exp\left[\frac{2ni\pi}{\beta}(\tau - \tau')\right], \tag{F.35}$$

whereas for fermions, we write

$$\begin{aligned} &G(x\tau, x'\tau') &\text{(F.36)}\\ &= \frac{2Mb}{\beta} \sum_{n=-\infty}^{\infty} g(q, q'; \mu - \frac{(2n-1)\pi}{\beta}) \exp\left[\frac{(2n-1)i\pi}{\beta}(\tau - \tau')\right]. \end{aligned}$$

Integrals over the τ-variables become summations, and we get

$$\frac{1}{K} = \frac{1}{\beta} \sum_n \left(\frac{2Mb^2}{W}\right)^2 \int_0^1 dz \frac{B(z)u^2(z)}{z(1-z)} \int_z^1 dz' \frac{B(z')v^2(z')}{z'(1-z')}. \tag{F.37}$$

It is implied here that u, v, and W depend on the Fourier summation index n through the complex wave numbers

$$k = \left(2MB^2(\mu - 2ni\pi/\beta)\right)^{1/2} \tag{F.38}$$

and

$$k' = \left(2Mb^2(\mu - U(-\infty) - 2ni\pi/\beta)\right)^{1/2}. \tag{F.39}$$

The integral is obviously divergent when the limits of the interval$[0, 1]$ are implemented. We observe that

$$\int_z^1 \frac{v^2(z')}{z'(1-z')} dz' = \frac{iv^2(z)}{2kz} + \cdots \quad \text{for} \quad |1 - z| \ll 1 \tag{F.40}$$

and

$$\int_z^1 \frac{v^2(z')}{z'(1-z')} dz' = \frac{iv^2(z)}{2k'(1-z)} + \cdots \quad \text{for} \quad |z| \ll 1, \tag{F.41}$$

where the terms that cause singularities are indicated. Limiting the integration to a finite interval $-L < x < L$, we can write

$$\begin{aligned} &\int_\zeta^{1-\zeta} dz \frac{B(z)u^2(z)}{z(1-z)} \int_z^1 dz' \frac{B(z')v^2(z')}{z'(1-z')} \\ \approx\ & \frac{u^2(\zeta)v^2(\zeta)}{2ik'(1-\zeta)^2} \ln(\zeta) + \frac{u^2(1-\zeta)v^2(1-\zeta)}{2ik'(1-\zeta)^2} \ln(\zeta) \\ \approx\ & -\frac{W^2 L}{b} \left[(2ik')^{-3} + (2ik)^{-3}\right] \end{aligned} \tag{F.42}$$

for $\zeta = (1 + \exp(L/b))^{-1}$ and $b \ll L$.

The relation

$$\left(2Mb^2\left(\mu + \frac{2ni\pi}{\beta}\right)\right)^{1/2} = -\left(2Mb^2\left(\mu - \frac{2ni\pi}{\beta}\right)\right)^{1/2^*} = -k^* \tag{F.43}$$

is used to sum over positive integers in the expressions

$$\begin{aligned}\frac{1}{K} &= -\frac{8M^2L}{\beta}\left\{(2i\sqrt{2M\mu'})^{-3} + (2i\sqrt{2M\mu})^{-3}\right.\\ &+ \left.2\Re\sum_{n=1}^{\infty}\left[\left(\frac{b}{2ik'}\right)^3 + \left(\frac{b}{2ik}\right)^3\right]\right\}\\ &= \frac{ML}{\pi}\left\{\frac{\pi}{2\beta|\mu'|\sqrt{2M|\mu'|}} + \frac{\pi}{2\beta|\mu|\sqrt{2M|\mu|}}\right.\\ &- \left.\Re\sum_{n=1}^{\infty}\frac{\partial}{\partial n}\left[\frac{b}{k'} + \frac{b}{k}\right]\right\}.\end{aligned} \tag{F.44}$$

An integral estimate of the infinite sums yields

$$\frac{1}{K} = \frac{\sqrt{2ML^2}}{2\pi}\Re\left[\frac{1}{\sqrt{\mu' - i\eta}} + \frac{1}{\sqrt{\mu - i\eta}} + \frac{\pi\sqrt{|\mu'|}}{2\beta\mu'^2} + \frac{\pi\sqrt{|\mu|}}{2\beta\mu^2}\right] \tag{F.45}$$

for $\mu' = \mu - U(-\infty)$ and $\eta = 2\pi\vartheta/\beta$ with $0 < \vartheta < 1$. Explicitly, for the boson case, we get

$$\begin{aligned}\frac{1}{K} &= \frac{L(2M|\mu'|)^{1/2}}{4\beta\mu'^2} - \frac{L\left(M(\sqrt{\mu'^2 + \eta^2} + \mu')\right)^{1/2}}{2\pi\sqrt{\mu'^2 + \eta^2}}\\ &+ \frac{L(2M|\mu|)^{1/2}}{4\beta\mu^2} - \frac{L\left(M(\sqrt{\mu^2 + \eta^2} + \mu)\right)^{1/2}}{2\pi\sqrt{\mu^2 + \eta^2}}.\end{aligned} \tag{F.46}$$

Appropriate modifications for the fermion case yield the same functional form with a change of sign and no zero frequency term. The η parameter requires careful consideration.

The result for $1/K$ can also be expressed as a derivative of the number of systems with respect to the chemical potential. The number of systems N is written as an integral of the propagator as

$$N = \int_{-\infty}^{\infty} dx G(x\tau, x\tau_+)$$

$$\begin{aligned} &= \frac{2Mb^2}{\beta}\sum_n \int_{-\infty}^{\infty} dq\,[g(q,q;-\infty-2\pi in/\beta) \\ &- g(q,q;\mu-2\pi in/\beta)]\,. \end{aligned} \tag{F.47}$$

The integration approximation of the sum is a contour integration like the one depicted in Fig. 3.2 in Chapter 3, using the so-called Coulson contour, which is an infinite semicircle in the left half-plane and a straight vertical line. The first propagator g in Eq.(F.47), which is evaluated at an infinitely large negative value of the chemical potential, corresponds to the semicircle of the Coulson contour. Change of sign and summation variable is required for the fermion case. A useful rewrite Eq. (F.47) yields

$$N = -\frac{2Mb^2}{\beta}\sum_n \int_{-\infty}^{\infty} dq \int_{-\infty}^{\mu} d\sigma \frac{\partial}{\partial\sigma} g(q,q;\sigma-2\pi in/\beta). \tag{F.48}$$

Limiting the divergent integral over q, as was done above, results in

$$\int_{-L}^{L} dqg(q,q;\sigma 2\pi in/\beta) = \int_{\zeta}^{1-\zeta} dz \frac{u(z)v(z)}{z(1-z)W} = \left(\frac{1}{2ik'}+\frac{1}{2ik}\right)\frac{L}{b}, \tag{F.49}$$

and we can write

$$\begin{aligned} N &= -\frac{2ML}{\beta}\sum_n \int_{-\infty}^{\mu} d\sigma \frac{\partial}{\partial\sigma}\left(\frac{b}{2ik'}+\frac{b}{2ik}\right) \\ &= -\frac{8M^2L}{\beta}\int_{-\infty}^{\mu} d\sigma \sum_{n=-\infty}^{\infty}\left(\left(\frac{b}{2ik'}\right)^3+\left(\frac{b}{2ik}\right)^3\right) \\ &= \int_{-\infty}^{\mu}\frac{d\sigma}{K(\sigma)}, \end{aligned} \tag{F.50}$$

with a generalized notation for K. The final expression for the number of systems is

$$\begin{aligned} N &= \frac{L}{\pi}\left\{\frac{\pi\sqrt{2M|\mu'|}}{2\beta|\mu'|} - \left(M\left(\sqrt{(\mu')^2+\eta^2}+\mu'\right)\right)^{1/2}\right\} \\ &+ \frac{L}{\pi}\left\{\frac{\pi\sqrt{2M|\mu|}}{2\beta|\mu|} - \left(M\left(\sqrt{(\mu^2+\eta^2}+\mu\right)\right)^{1/2}\right\}, \end{aligned} \tag{F.51}$$

for bosons, where $\mu < 0$ and $\mu < U(-\infty)$, and

$$\begin{aligned} N &= \frac{L}{\pi}\left\{\left(M\left(\sqrt{(\mu')^2+\eta^2}+\mu'\right)\right)^{1/2}\right\} \\ &+ \frac{L}{\pi}\left\{\left(M\left(\sqrt{(\mu^2+\eta^2}+\mu\right)\right)^{1/2}\right\} \end{aligned} \tag{F.52}$$

for fermions. The inverse relation between between chemical potential and the density of systems per unit length is not readily expressed.

Notes and Bibliography

In this appendix, a scattering approach is used that can be found in the book *Quantum Chemistry*, John Wiley & Sons, Inc., New York, 1944, p. 311, by H. Eyring, J. Walter, and G. E. Kimball. The mathematical development uses formulas and relations that can be found in the *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, U. S. Department of Commerce, National Bureau of Standards, Applied Mathematics Series, 55, Fourth printing, December 1965, Edited by M. Abramowitz and I. A. Stegun. In particular, the chapter on *Hypergemetric Functions* by F. Oberettinger, p. 555 is useful for the material presented here. The original introduction of the potential can be found in the paper *Phys. Rev.* **35**, 1303 (1930), by C. Eckart. Related treatments of chemical reactions can be found in the book *Nonequilibrium Statistical Thermodynamics* by D. N. Zubarev, Consultant Bureau, London, 1974, in *J. Chem. Phys.* **33**, 281 (1960) by T. Yamamoto, and in *J. Chem. Soc. Faraday Trans.* **93**, 893 (1997) by J. Linderberg.

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