Chapter 6 | Green's Functions

A. INTRODUCTION

Having now seen how methods that are based upon stationary-state N-electron wavefunctions can be used to compute state energies and other physical properties, we turn to examine a class of so-called response functions or Green's functions (GFs) (Linderberg and Öhrn, 1973), which permit a direct calculation of transition properties. For example, the one-particle GF (electron propagator) yields ionization potentials and electron affinities, whereas the two particle GF (polarization propagator) provides us information about electronic excitation energies and oscillator strengths, which then can be used to calculate many other observables (e.g., polarizabilities and spin–spin coupling constants). The general definition of a GF belonging to the reference state $|0\rangle$ is given as

$$\langle\langle A(t); B\rangle\rangle = \mp\frac{i}{\hbar}\,\theta(t)\langle 0|A(t)B|0\rangle + \frac{i}{\hbar}\,\theta(-t)\langle 0|BA(t)|0\rangle \tag{6.1}$$

where $\theta(t)$ is the Heaviside step function

$$\theta(t) = \{1, t > 0; 0, t < 0\} \tag{6.2}$$

and A and B are arbitrary operators in the second quantization form. $A(t)$ is the Heisenberg representation of A,

$$A(t) = \exp(iHt/\hbar)A\exp(-iHt/\hbar) \tag{6.3}$$

and B is the Heisenberg operator at $t = 0$. If the operators A and B contain an even number of creation or annihilation operators (e.g., r^+s, or r^+t^+su) the plus sign is used in Eq. (6.1). For operators A and B having an odd number of such operators (e.g., $A = r^+$ or r^+t^+u, and $B = r$ or rut^+) the minus sign is used. The reasons for these choices are made clear below.

To understand the physical content of such GFs, we introduce between the $A(t)$ and B operators in Eq. (6.1) a resolution of the identity involving a complete set of eigenstates $|n\rangle$. By inserting these resolutions and assuming that the states $|n\rangle$ are eigenfunctions of H, we obtain

$$\begin{aligned}\langle\langle A(t);B\rangle\rangle = {} & \mp\frac{i}{\hbar}\,\theta(t)\sum_n \langle 0|A|n\rangle\langle n|B|0\rangle \exp\left[i\frac{t}{\hbar}(E_0-E_n)\right] \\ & +\frac{i}{\hbar}\,\theta(-t)\sum_n \langle 0|B|n\rangle\langle n|A|0\rangle \exp\left[i\frac{t}{\hbar}(E_n-E_0)\right] \qquad (6.4)\end{aligned}$$

The Fourier transform of $\langle\langle A(t)B\rangle\rangle$, is given as

$$\langle\langle A;B\rangle\rangle_E = \int_{-\infty}^{\infty} dt\,\langle\langle A(t);B\rangle\rangle \exp(iEt/\hbar) \qquad (6.5)$$

If we straightforwardly insert Eq. (6.4) into Eq. (6.5) we encounter improper integrals. For example, the first term of Eq. (6.4) gives an improper integral of the type

$$\int_0^{\infty} dt \exp\left[i\frac{t}{\hbar}(E_0-E_n+E)\right]$$

To overcome this problem we may define the Fourier transform to include a convergence factor $\exp(-|t|\eta)$, where η is a small, real, positive quantity. After the integration is performed, we can then take the limit $\eta \to 0_+$ (Mattuck, 1967). The Fourier transform of the GF may then be expressed as

$$\langle\langle A;B\rangle\rangle_E = \lim_{\eta\to 0_+}\sum_n \frac{\pm\langle 0|A|n\rangle\langle n|B|0\rangle}{E_0-E_n+E+i\eta} + \sum_n \frac{\langle 0|B|n\rangle\langle n|A|0\rangle}{E_n-E_0+E-i\eta} \qquad (6.6)$$

A physical interpretation of the GF may now be obtained by considering the content of Eq. (6.6). If A and B are number conserving (i.e., they both contain equal numbers of creation and annihilation operators) then the states $|n\rangle$ must contain the same number of electrons as the reference state $|0\rangle$ to give a nonvanishing GF. However, if A contains, for example, one more creation operator than annihilation operator, then $|n\rangle$ must contain $N \pm 1$ electrons (notice that the fact that the second-quantized H is independent of N is now becoming convenient). From the frequency spectrum of $\langle\langle A;B\rangle\rangle_E$ it is clear that the GF contains information about energy differences. If A and B are of the one-particle excitation form r^+s, then poles of Eq. (6.6) occur at the energy differences $E_n - E_0$ referring to electronic excitation energies. The residues give the overlap amplitudes $\langle 0|A|n\rangle\langle n|B|0\rangle$, which, for example, express the electric dipole transition probabilities when A and B refer to the electronic dipole moment operator. If A is of the form r^+ (so that B is an annihilation operator s), then the energy differences arising in Eq. (6.6) fall into two classes. The first factor, which has $\langle 0|r^+|n\rangle\langle n|s|0\rangle$ as its amplitude, clearly has to do with ionization potentials $E_0^N - E_n^{N-1}$. The second factor, involving amplitudes $\langle 0|s|n\rangle\langle n|r^+|0\rangle$, relates to electron affinities $E_n^{N+1} - E_0^N$.

The time derivative of Eq. (6.1) may be written as

$$\begin{aligned} i\hbar \frac{d}{dt} \langle\langle A(t); B\rangle\rangle &= \delta(t)\langle 0|\pm A(t)B + BA(t)|0\rangle + \langle\langle [A(t), H]B\rangle\rangle \\ &= \delta(t)\langle 0|BA \pm AB|0\rangle + \langle\langle [A(t), H]B\rangle\rangle \end{aligned} \tag{6.7}$$

where we have used the facts that $A(t)$ satisfies the Heisenberg equation of motion

$$i\hbar \frac{d}{dt} A(t) = [A(t), H] \tag{6.8}$$

and that the Heaviside function is the integral of the Dirac δ-function

$$\theta(t) = \int_{-\infty}^{t} \delta(\tau)\, d\tau \tag{6.9}$$

The Fourier transform of Eq. (6.7) then becomes [the definition of the Fourier transform of the GF always contains the $\exp(-\eta|t|)$ convergence factor, although henceforth we do not explicitly express this fact]

$$E\langle\langle A; B\rangle\rangle_E = \langle 0|BA \pm AB|0\rangle + \langle\langle [A, H]; B\rangle\rangle_E \tag{6.10}$$

As we see later, this result will prove useful in interrelating GFs when A and B refer to the position and momentum operator, respectively.

Although the above spectral representation of $\langle\langle A; B\rangle\rangle_E$ in Eq. (6.6) displays the content of its frequency dependence and amplitudes, this equation is not actually used to compute $\langle\langle A; B\rangle\rangle_E$. To do so would involve computing, by stationary-state methods described in earlier chapters, the energies and wavefunctions $|0\rangle$, E_0, $|n\rangle$, and E_n. The philosophy of the GF method is to avoid doing all of these state calculations by obtaining an equation that can be solved directly for $\langle\langle A; B\rangle\rangle_E$. In this manner one then attempts to obtain an object ($\langle\langle A; B\rangle\rangle_E$) that contains (through its poles and residues) state difference information directly.

B. SUPEROPERATOR ALGEBRA

1. Superoperator Resolvent

To demonstrate how one goes about finding an equation that permits $\langle\langle A; B\rangle\rangle_E$ to be directly computed, let us return to Eq. (6.1) and rewrite the time dependence of $A(t)$ as

$$\begin{aligned} A(t) &\equiv \exp\left(\frac{it}{\hbar}H\right)A\exp\left(-\frac{it}{\hbar}H\right) \\ &= A + \frac{it}{\hbar}[H, A] + \frac{1}{2!}\left(\frac{it}{\hbar}\right)^2[H,[H,A]] \\ &\quad + \frac{1}{3!}\left(\frac{it}{\hbar}\right)^3[H,[H,[H,A]]] + \cdots \\ &\equiv \exp\left(\frac{it}{\hbar}\hat{H}\right)A \end{aligned} \tag{6.11}$$

where the so-called superoperator $\hat{H}$ (Pickup and Goscinski, 1973) is defined by

$$\hat{H}A \equiv [H, A] \tag{6.12}$$

In terms of this superoperator, $\langle\langle A(t); B\rangle\rangle$ can be expressed as

$$\begin{aligned} \langle\langle A(t); B\rangle\rangle = &\mp\frac{i}{\hbar}\theta(t)\langle 0|\left(\exp\left(\frac{i}{\hbar}t\hat{H}\right)A\right)B|0\rangle \\ &+ \frac{i}{\hbar}\theta(-t)\langle 0|B\exp\left(\frac{i}{\hbar}t\hat{H}\right)A|0\rangle \end{aligned} \tag{6.13}$$

[notice that the extra parentheses are needed in the first term on the right-hand side of Eq. (6.13) to ensure that $\hat{H}$ only operates on A]. The Fourier transform can now be carried out to yield

$$\langle\langle A; B\rangle\rangle_E = \pm\langle 0|((E\hat{1} + \hat{H})^{-1}A)B|0\rangle + \langle 0|B(E\hat{1} + \hat{H})^{-1}A|0\rangle \tag{6.14}$$

where the unit superoperator is defined by

$$\hat{1}A \equiv A \tag{6.15}$$

It is conventional to combine the two terms present on the right-hand side of Eq. (6.14) into a single factor by introducing the so-called superoperator binary product. This product, between two operators C and D, is defined as

$$(C|D) \equiv \langle 0|C^+D|0\rangle \pm \langle 0|DC^+|0\rangle \tag{6.16}$$

with the plus sign pertaining to cases when C and D contain odd numbers of creation or annihilation operators (e.g., r^+s^+t or u). With this definition, the above GF can be written as

$$\langle\langle A; B\rangle\rangle_E = (B^+|(E\hat{1} + \hat{H})^{-1}|A) \tag{6.17}$$

In writing $\langle\langle A;B\rangle\rangle_E$ in this way, we say that we have expressed the GF as a superoperator matrix element of the superoperator resolvent $(E\hat{1} + \hat{H})^{-1}$.

2. Complete Sets of Operators

The tools needed for evaluating the above matrix elements of the superoperator resolvent are based upon the idea of operators (of the same "type" as A and B^+) forming complete sets (Manne, 1977; Dalgaard, 1979). For example, if A and B^+ are number-conserving operators (e.g., r^+s), then the set of operators ($\alpha > \beta > \gamma > \cdots ; p > q > r > \cdots$)

$$\{\mathbf{h}\} = \{1, p^+\alpha, p^+q^+\beta\alpha, p^+q^+r^+\gamma\beta\alpha, \ldots\} \tag{6.18}$$

when operating on an N-electron ket corresponding to a single determinant in which $\phi_\alpha, \phi_\beta, \phi_\gamma, \ldots$ are "occupied" and $\phi_p, \phi_q, \phi_r, \ldots$ are not occupied, forms a complete set of N-electron kets. Similarly ($\alpha > \beta > \gamma > \cdots ; p > q > r > \cdots$)

$$\{\mathbf{h}\} = \{r^+, r^+p^+\alpha, r^+p^+q^+\alpha\beta, \ldots\} \tag{6.19}$$

and

$$\{\mathbf{h}\} = \{\alpha, \alpha\beta r^+, \alpha\beta\gamma r^+s^+ \ldots\} \tag{6.20}$$

form, respectively, complete sets of $(N \pm 1)$-electron kets when operating on the above "reference ket". Manne and Dalgaard have shown that the above sets of operators form complete sets of N- and $(N \pm 1)$-electron kets even when operating on a multiconfigurational reference state $|0\rangle$ as long as the reference ket (which defines $\alpha, \beta, \gamma, \ldots ; p, q, r, \ldots$) is not orthogonal to $|0\rangle$.

The above results having to do with completeness of operator manifolds permit us to write a resolution of the identity as

$$1 = \sum_{kl} h_k|0\rangle\langle 0|\mathbf{h}^+\mathbf{h}|0\rangle_{kl}^{-1}\langle 0|h_l^+ \tag{6.21}$$

where the set $\{h_k\}$ is any of the above three sets of operator manifolds and $\langle 0|\mathbf{h}^+\mathbf{h}|0\rangle_{kl}^{-1}$ is the k, l element of the inverse of the matrix having elements $\langle 0|h_k^+h_l|0\rangle$. The completeness relation mentioned above cannot be used in a straightforward manner in manipulations having to do with the superoperator resolvent because the superoperator binary product appearing in $\langle\langle A;B\rangle\rangle_E$ is more complicated than the scalar product occurring in Eq. (6.21). The complete set of operators for N- and $(N \pm 1)$-electron kets may, however, be used to generate a resolution of the identity that can be used within the superoperator binary product. The completeness relation for a superoperator binary product may be written as

$$\hat{1} = |\mathbf{T}^+)(\mathbf{T}^+|\mathbf{T}^+)^{-1}(\mathbf{T}^+| = \sum_{kl} |T_k^+)(\mathbf{T}^+|\mathbf{T}^+)_{kl}^{-1}(T_l^+| \tag{6.22}$$

where $\mathbf{T}^+$ for one-electron creation or annihilation operators A and B^+ becomes ($\alpha > \beta > \gamma > \cdots ; p > q > r > \cdots$) (Dalgaard, 1979)

$$\begin{aligned}\{\mathbf{T}^+\} &= \{\mathbf{T}_1^+ ; \mathbf{T}_3^+ ; \mathbf{T}_5^+ ; \ldots\} \\ &= \{p^+, \alpha^+ ; p^+q^+\alpha, \alpha^+\beta^+p ; p^+q^+r^+\alpha\beta, \alpha^+\beta^+\gamma^+pq ; \ldots\} \end{aligned} \tag{6.23}$$

For number-conserving operators A and B^+, $\{\mathbf{T}^+\}$ becomes

$$\{\mathbf{T}^+\} = \{\mathbf{T}_2^+ ; \mathbf{T}_4^+ ; \ldots\} = \{p^+\alpha, \alpha^+p ; p^+q^+\alpha\beta ; \alpha^+\beta^+pq, \ldots\} \tag{6.24}$$

To better appreciate the meaning of Eq. (6.22), we write in detail some elements of the "overlap" matrix $(T_k^+ \mid T_l^+)$ for the one-electron addition operator case (recall the definition of the "occupied" and "unoccupied" orbitals, ϕ_α, ϕ_r)

$$(\alpha^+ \mid p^+) = \langle 0|\alpha p^+ + p^+\alpha|0\rangle = \delta_{\alpha p} = 0 \tag{6.25}$$

$$\begin{aligned}(\alpha^+ \mid p^+q^+\beta) &= \langle 0|\alpha p^+q^+\beta + p^+q^+\beta\alpha|0\rangle \\ &= \langle 0|p^+q^+\alpha\beta + p^+q^+\beta\alpha|0\rangle = 0\end{aligned} \tag{6.26}$$

$$\begin{aligned}(r^+ \mid p^+q^+\alpha) &= \langle 0|rp^+q^+\alpha + p^+q^+\alpha r|0\rangle \\ &= \delta_{rp}\langle 0|q^+\alpha|0\rangle - \delta_{rq}\langle 0|p^+\alpha|0\rangle .\end{aligned} \tag{6.27}$$

It is clear from the above equations that, in the superoperator binary product, each of the operators contributes both to the $(N + 1)$- and to the $(N - 1)$-electron aspects of the problem. For example, in writing the binary product $(r^+ \mid p^+q^+\alpha)$, we find $\langle 0|r$, which refers to the adjoint of an $(N + 1)$-electron ket, while $r|0\rangle$ becomes an $(N - 1)$-electron ket.

3. The Superoperator Resolvent

In summary, the idea of a complete set of operators has been extended to the superoperator binary product so as to introduce the powerful concept of a completeness relation. This completeness relation can now be exploited to derive an equation that permits $\langle\langle A; B\rangle\rangle_E$ to be expressed in a computationally more useful form (Simons, 1976). We begin by writing the identity

$$(\mathbf{T}^+ \mid \mathbf{T}^+) = (\mathbf{T}^+|(E\hat{I} + \hat{H})(E\hat{I} + \hat{H})^{-1}|\mathbf{T}^+) \tag{6.28}$$

which, by inserting the resolution of the identity in Eq. (6.22), becomes

$$(\mathbf{T}^+ \mid \mathbf{T}^+) = (\mathbf{T}^+|E\hat{I} + \hat{H}|\mathbf{T}^+)(\mathbf{T}^+ \mid \mathbf{T}^+)^{-1}(\mathbf{T}^+|(E\hat{I} + \hat{H})^{-1}|\mathbf{T}^+) \tag{6.29}$$

This equation can be arranged to yield

$$(\mathbf{T}^+|(E\hat{I} + \hat{H})^{-1}|\mathbf{T}^+) = (\mathbf{T}^+|\mathbf{T}^+)(\mathbf{T}^+|E\hat{I} + \hat{H}|\mathbf{T}^+)^{-1}(\mathbf{T}^+ \mid \mathbf{T}^+) \tag{6.30}$$

The operators B^+ and A, which define the desired GF in Eq. (6.17), when operating on $|0\rangle$, can be expanded in terms of the set $\{\mathbf{T}^+\}$ operating on $|0\rangle$:

$$A|0\rangle = \mathbf{T}^+|0\rangle(\mathbf{T}^+|\mathbf{T}^+)^{-1}(\mathbf{T}^+|A) \tag{6.31}$$

and the GF in Eq. (6.17) may thus, using Eqs. (6.30) and (6.31), be written as

$$\begin{aligned}\langle\langle A;B\rangle\rangle_E &= (B^+|(E\hat{1} + \hat{H})^{-1}|A) \\ &= (B^+|\mathbf{T}^+)(\mathbf{T}^+|\mathbf{T}^+)^{-1}(\mathbf{T}^+|(E\hat{1} - \hat{H})^{-1}|\mathbf{T}^+)(\mathbf{T}^+|\mathbf{T}^+)^{-1}(\mathbf{T}^+|A) \\ &= (B^+|\mathbf{T}^+)(\mathbf{T}^+|E\hat{1} + \hat{H}|\mathbf{T}^+)^{-1}(\mathbf{T}^+|A)\end{aligned} \tag{6.32}$$

Equation (6.32) constitutes the working equation for deriving approximate forms for the GF. Notice that the original GF, which involved the matrix representative of an inverse superoperator $(E\hat{1} + \hat{H})^{-1}$, has been expressed in terms of the elements $(B^+|T_k^+)$, $(T_l^+|A)$, the "overlap" $(T_k^+|T_l^+)$, and matrix elements of the superoperator Hamiltonian $(T_k^+|\hat{H}|T_l^+)$. These latter two matrices are analogous to the expressions that give ordinary resolvent matrix elements in terms of configuration interaction Hamiltonian matrix elements and configuration overlaps.

4. Pole and Residue Analysis

From Eq. (6.32), which expresses the desired GF, it is clear that the pole structure (values of E at which $\langle\langle A;B\rangle\rangle_E$ has poles) is determined entirely by the matrix $(\mathbf{T}^+|E\hat{1} + \hat{H}|\mathbf{T}^+)^{-1}$. This matrix has poles when $\det[(\mathbf{T}^+|E\hat{1} + \hat{H}|\mathbf{T}^+)]$ vanishes. Thus, the problem of finding the poles of $\langle\langle A;B\rangle\rangle_E$, which give ionization or excitation energies, can be solved by examining the superoperator generalized eigenvalue problem

$$\sum_l (T_k^+|\hat{H}|T_l^+)U_{lj} = -E_j \sum_l (T_k^+|T_l^+)U_{lj} \tag{6.33}$$

which in matrix notation may be written as

$$\hat{\mathsf{H}}\mathbf{U}_j = -\mathsf{E}_j\mathsf{S}\mathbf{U}_j \tag{6.34}$$

The poles of $\langle\langle A;B\rangle\rangle_E$ occur thus at the eigenvalues $E = E_j$ of Eq. (6.33) and the eigenvectors enter in the evaluation of the corresponding residues. To illustrate how the residues can be determined, we rewrite the GF in Eq. (6.32) so as to be in spectral form, assuming that $\hat{\mathsf{H}}$ is hermitian and that S is positive definite (this is not always the case as we discuss in Section 6.E.2.a). Premultiplying Eq. (6.34) by $\mathsf{S}^{-1/2}$ gives

$$(\mathsf{S}^{-1/2}\hat{\mathsf{H}}\mathsf{S}^{-1/2})(\mathsf{S}^{1/2}\mathbf{U}_j) = -E_j(\mathsf{S}^{1/2}\mathbf{U}_j) \tag{6.35}$$

The vectors $\mathbf{V}_j = \mathsf{S}^{1/2}U_j$ are ordinary eigenvectors of $\mathsf{H}' \equiv \mathsf{S}^{-1/2}\hat{\mathsf{H}}\mathsf{S}^{-1/2}$, and therefore H' can be expressed in spectral form as

$$\hat{\mathsf{H}}' = \sum_j \mathbf{V}_j(-E_j)\mathbf{V}_j^+ \tag{6.36}$$

Because the $\mathbf{V}_j$ are eigenvectors of a hermitian matrix (H'), they form a unitary matrix (V), which diagonalizes H'. Thus, one can write the resolvent matrix as

$$\begin{aligned}(E\hat{\mathsf{S}} + \hat{\mathsf{H}})^{-1} &= \mathsf{S}^{-1/2}(E\hat{1} + \hat{\mathsf{H}}')^{-1}\mathsf{S}^{-1/2} = \mathsf{S}^{-1/2}\mathsf{V}(E\hat{1} - \mathsf{E})^{-1}\mathsf{V}^+S^{-1/2} \\ &= \mathsf{U}(E\hat{1} - \mathsf{E})^{-1}\mathsf{U}^+ \end{aligned} \tag{6.37}$$

where the diagonal matrix E contains the eigenvalues E_j.

By using Eq. (6.37), the expression for $\langle\langle A;B\rangle\rangle_E$ given in Eq. (6.32) can be rewritten in a form that clearly displays its pole and residue structure:

$$\langle\langle A;B\rangle\rangle_E = (B^+|\mathbf{T}^+)\mathsf{U}(E\hat{1} - \mathsf{E})^{-1}\mathsf{U}^+(\mathbf{T}^+|A) \tag{6.38}$$

Thus, the residue at pole E_j is given by

$$\sum_{k,l}(B^+|T_k^+)U_{kj}U_{jl}^+(T_l^+|A) \tag{6.39}$$

C. APPROXIMATION METHODS

1. Operator Manifold Truncation

Although the above equations, in principle, permit one to find the poles and residues of any GF (defined by the choice of B^+ and A), it is never really possible to employ a complete set of operators $\{\mathbf{T}_k^+\}$. Therefore, one is faced both with making some physically motivated choice of a finite number of such $\{\mathbf{T}_k^+\}$ operators and with choosing a reasonably accurate reference wavefunction $|0\rangle$. Clearly the choice of $|0\rangle$ dictates which excitation or ionization energies one obtains from the poles of $\langle\langle A;B\rangle\rangle_E$. The choice of B^+ and A determine whether one is interested in single-particle excited states ($A = i^+j$), primary ionization potentials ($A = j$), or shake-up ionization potentials ($A = ijk^+$). For example, by using as $|0\rangle$ the $2s^2$ configuration and $A = j^+$, one can obtain ionization energies to the $2s^22p$ or $2s^1$ and other anion and cation states; with $A = m^+\alpha$, the $2snp$ excited states may be reached. The truncation of the complete operator set $\{\mathbf{T}_k^+\}$ then determines, together with the approximation made to get $|0\rangle$, the accuracy to which the resultant poles of $\langle\langle A;B\rangle\rangle_E$ describe the excitation or ionization energies and their corresponding residues. Choices of $\{\mathbf{T}^+\}$ must, of course, take into consideration the space and spin symmetry of the states generated by $\mathbf{T}^+|0\rangle$. As a result, the inherent symmetry of each

$\mathbf{T}^+$ must be coupled to that of $|0\rangle$ to give pure symmetry excited or ionic states. Because the reasons for making specific choices of A and B^+ are rather clear, we now focus on explaining the strategies for choosing $|0\rangle$ and truncations of $\{\mathbf{T}_k^+\}$. In the following sections and in our treatment of the polarization propagator, we consider two different approaches for attacking this problem. The first is based on a perturbation analysis while the second is based on selecting a multiconfiguration reference state and an appropriate projection manifold.

2. Order Analysis

The most widely used, and historically older, approach involves perturbation analysis of the GF using RSPT to obtain elements of $(\mathbf{T}^+|E\hat{1} + \hat{H}|\mathbf{T}^+)$ and $(B^+|\mathbf{T}^+)(\mathbf{T}^+|A)$ correct through a chosen order (order is then assumed to be related to accuracy). By decomposing the electronic Hamiltonian H and the reference wavefunction $|0\rangle$ in perturbation series

$$H = H^0 + V \tag{6.40}$$

$$|0\rangle = |0^0\rangle + |0^1\rangle + |0^2\rangle + \cdots \tag{6.41}$$

one then attempts to evaluate $(T_k^+|E\hat{1} + \hat{H}|T_l^+)$ to sufficiently high order to guarantee that the poles of primary interest are obtained accurately through a chosen order. If one is also interested in calculating residues that are accurate through some order, then the chosen operator manifold and reference state $|0\rangle$ must be taken to sufficient size and order to guarantee this. We return to the problem on how to choose $\{\mathbf{T}^+\}$ so as to determine primary poles and residues accurate through a chosen order in Section 6.C.4.

3. Hermiticity Questions

Earlier in this chapter, we noted that the question of the hermiticity of $(T_k^+|\hat{H}|T_l^+)$ had to be examined in individual cases (i.e., it was not automatically valid). When a perturbation expansion is used to determine the reference state, we may more explicitly state the conditions under which the matrix is hermitian by examining the difference between the (kl)th and the complex conjugate of the (lk)th element of the superoperator Hamiltonian. When this difference

$$(T_k^+|\hat{H}|T_l^+) - (T_l^+|\hat{H}|T_k^+)^* = \langle 0|[[T_l^+, T_k], H]|0\rangle \tag{6.42}$$

is equal to zero, the superoperator Hamiltonian is hermitian.

When the reference state $|0\rangle$ is determined through a certain order n in RSPT, $(|0\rangle_n = \sum_{i=0}^{n} |0^i\rangle)$ the Schrödinger equation is solved through the same order:

$$H|0\rangle_n = E_n|0\rangle_n + 0(n+1) \tag{6.43}$$

where $E_n = \sum_{i=0}^{n} E^{(i)}$. Inserting (6.43) into (6.42) then states that Eq. (6.42) is zero through order n and that, as a result, the superoperator Hamiltonian matrix is hermitian through that same order. This theorem is quite useful for two reasons. First, it guarantees that the superoperator Hamiltonian matrix will have no accidental or spurious nonhermitian terms if it is properly calculated. Second, it is often easier to compute $(T_k^+|\hat{H}|T_l^+)$ than $(T_l^+|\hat{H}|T_k^+)$ (e.g., $(p^+q^+\alpha|\hat{H}|r^+)$ is easier than $(r^+|\hat{H}|p^+q^+\alpha)$ because the latter elements require that the Hamiltonian be commuted with $p^+q^+\alpha$). Thus, we can choose to calculate the "easier" matrix elements and to then obtain the others through hermiticity (i.e., by equating the complex conjugate of the former to the latter).

4. Operator Space Partitioning

We next go into more detail concerning the explicit evaluation of $\langle\langle A; B\rangle\rangle_E$ for $A = k^+$, $B^+ = l^+$ [referred to as the electron propagator (EP) or one-particle GF] and for $A = k^+l$, $B = i^+j$ [referred to as the polarization propagator (PP) or two-particle GF]. However, it remains for us to show one more approximation step that is often employed in searching for the poles of $(E\mathsf{S} + \hat{\mathsf{H}})^{-1}$ in Eq. (6.37). Because, according to Eq. (6.38), all elements of this inverse matrix possess poles at all of the E_j, it is possible to search for the desired poles by computing a single element or a submatrix of $(E\mathsf{S} + \hat{\mathsf{H}})^{-1}$. That is, if the operator manifold is partitioned into, say, two classes $\{\mathbf{T}_k^+\} = \{\mathbf{T}_a^+\} + \{\mathbf{T}_b^+\}$, then because $(E\mathsf{S} + \hat{\mathsf{H}})$ blocks into four submatrices

$$(E\mathsf{S} + \hat{\mathsf{H}}) = \begin{pmatrix} E\mathsf{S}_{aa} + \hat{\mathsf{H}}_{aa} & E\mathsf{S}_{ab} + \hat{\mathsf{H}}_{ab} \\ E\mathsf{S}_{ba} + \hat{\mathsf{H}}_{ba} & E\mathsf{S}_{bb} + \hat{\mathsf{H}}_{bb} \end{pmatrix} \tag{6.44}$$

one can solve for any element(s) of $(E\mathsf{S} + \hat{\mathsf{H}})^{-1}$ in terms of the above four submatrices. For example, it is easily shown that

$$(E\mathsf{S} + \hat{\mathsf{H}})_{aa}^{-1} = [(E\mathsf{S}_{aa} + \hat{\mathsf{H}}_{aa}) - (E\mathsf{S}_{ab} + \hat{\mathsf{H}}_{ab})(E\mathsf{S}_{bb} + \hat{\mathsf{H}}_{bb})^{-1}(E\mathsf{S}_{ba} + \hat{\mathsf{H}}_{ba})]^{-1} \tag{6.45}$$

Even if the space $\{\mathbf{T}_a^+\}$ includes a single element, if treated properly and to all orders, Eq. (6.45) will yield all the poles of $(E\mathsf{S} + \hat{\mathsf{H}})^{-1}$.

It is, of course, natural to wonder both why one would be interested in so partitioning $(E\mathsf{S} + \hat{\mathsf{H}})^{-1}$ and what this has to do with an approximation scheme for calculating $\langle\langle A; B\rangle\rangle_E$. It often turns out that if the sets $\{\mathbf{T}_a^+\}$ and $\{T_b^+\}$ are chosen properly, all the "off-diagonal" elements $(E\mathsf{S}_{ab} + \hat{\mathsf{H}}_{ab})$

(and hence $E\mathsf{S}_{ba} + \hat{\mathsf{H}}_{ba}$) contain only terms that are of first or higher order, whereas ($E\mathsf{S}_{aa} + \hat{\mathsf{H}}_{aa}$) contains zeroth- and (perhaps) higher-order terms. If, therefore, one restricts the search for poles to energy ranges in which $(E\mathsf{S}_{bb} + \hat{\mathsf{H}}_{bb})^{-1}$ is not close to being singular, then the term $(E\mathsf{S}_{ab} + \hat{\mathsf{H}}_{ab})(E\mathsf{S}_{bb} + \hat{\mathsf{H}}_{bb})^{-1}$ $(E\mathsf{S}_{ba} + \hat{\mathsf{H}}_{ba})$ can be assumed to be of second or higher order. This restriction of the energy search range is often motivated by knowledge that the zeroth-order poles of $(E\mathsf{S}_{aa} + \hat{\mathsf{H}}_{aa})^{-1}$ are good approximations (e.g., through Koopmans' theorem for the IP) to the desired poles. If one is interested in calculating poles that are accurate to, say, second order, then the second- and higher-order pieces of $(E\mathsf{S}_{ab} + \hat{\mathsf{H}}_{ab})$ and the first- and higher-order pieces of $(E\mathsf{S}_{bb} + \hat{\mathsf{H}}_{bb})^{-1}$ can be neglected. In this way, one is often able to greatly simplify the calculation of certain poles of $\langle\langle A;B\rangle\rangle_E$ [those far from the singularities of $(E\mathsf{S}_{bb} + \hat{\mathsf{H}}_{bb})$ in the above example].

Given a choice of $\{\mathbf{T}_a^+\}$ and $\{\mathbf{T}_b^+\}$ that permits a pole (say E_j) of $\langle\langle A;B\rangle\rangle_E$ to be evaluated through a certain order, it still remains to examine whether the same partitioning will yield residues, which are given in Eq. (6.39), accurate to some chosen order. Thus, if $(\mathbf{B}^+|\mathbf{T}_a^+)$ and $(\mathbf{T}_a^+|A)$ are of zeroth and higher order, whereas $(B^+|\mathbf{T}_b^+)$ and $(\mathbf{T}_b^+|A)$ are of first and higher order, it is convenient to so partition $\{\mathbf{T}_k^+\}$ since the contributions to the desired residues can more easily be order analyzed. This point is made more clear when analyzing the residues of the polarization propagator in Section 6.E.4.

5. Nonperturbative Approaches

The perturbation theory approach to computing approximations to $\langle\langle A;B\rangle\rangle_E$ has been widely used with significant success. However, its fundamental premise (that U is "small") is known to break down under circumstances that are relatively widely appreciated (e.g., for $X^1\Sigma_g H_2$ at large internuclear distance, the contribution of the $1\sigma_u^2$ configuration can not be accurately represented by RSPT). For this reason, researchers have begun to explore the possibility of systematically calculating GFs in which the reference state $|0\rangle$ is taken to be of the MCSCF form. The MCSCF nature of $|0\rangle$ turns out to be very convenient in a GF analysis because the GBT results in hermiticity of certain blocks of the $(\mathbf{T}_k^+|\hat{H}|\mathbf{T}_l^+)$ matrix.

The primary formal difficulty that arises in implementing such MCSCF-based GFs has to do with developing systematic procedures for truncating (and perhaps partitioning) the $\{\mathbf{T}_k^+\}$ operator space. Because we have now lost the concept of order, we must turn to some other criterion for choosing an appropriate operator manifold. In the few developments of the MCSCF-based electron (Banerjee *et al.*, 1978) and polarization propagators (Yeager and Jørgensen, 1979; Dalgaard, 1980) that have been made to date, the

$\{\mathbf{T}_k^+\}$ manifold was chosen by examining the functions $\mathbf{T}_k^+|0\rangle$ and $\mathbf{T}_k|0\rangle$, which result from the application of the $\mathbf{T}_k^+$ operators to $|0\rangle$ as they occur in the superoperator binary product. Decisions were then made to guarantee that these functions contained all of the dominant singly and doubly excited configurations needed to yield proper orbital relaxation and electron correlation (or bond-breaking) effects, respectively. For example, the operator manifold $\{\mathbf{T}_k^+\} = \{r^+s, s^+r, r > s; |n\rangle\langle 0|, |0\rangle\langle n|\}$ has been used to express an MCSCF-based PP. The state projectors $|n\rangle\langle 0|$ and $|0\rangle\langle n|$ can be viewed, when they act on $|0\rangle$, as compact representations of the set of $\{\mathbf{T}_k^+\}$ operators given in Eq. (6.24). It is thus possible to choose another set of operators than the one of Eq. (6.24) to describe accurately the poles and residues of the PP. The decision to choose one truncation of $\{\mathbf{T}_k^+\}$ over the other is usually based upon considerations involving the dimension of the resulting $(\mathbf{T}^+|\hat{H}|\mathbf{T}^+)$ matrix and the ease of calculation of the requisite superoperator matrix elements. The first choice described above (involving the state projectors $|n\rangle\langle 0|, |0\rangle\langle n|$) seems to be especially promising because, as Dalgaard has demonstrated, this set of operators yields a PP whose poles and residues automatically guarantee equality between electric dipole transition moments computed within either the so-called length or velocity representations. This is especially convenient because one then has a continuous range [from the single-configuration time-dependent Hartree–Fock (TDHF) or random-phase approximation (RPA) through the present MCSCF case to the full CI] of PP approximations all of which preserve their length/velocity equivalence. Another reason for choosing the above set of operators for use as $\{\mathbf{T}_k^+\}$ lies in the fact that the resultant $(\mathbf{T}_k^+|\hat{H}|\mathbf{T}_l^+)$ matrix elements are no different than those arising in the original MCSCF calculation of $|0\rangle$ [e.g., $(r^+s|H||n\rangle\langle 0|)$ arises in $\langle 0|[\lambda,[H,S]]|0\rangle$ of Eq. (2.24)]. Also, if one were to consider the effect of an external one-electron perturbation on the MCSCF state $|0\rangle$, one would find the same operators $\{r^+s, s^+r, |n\rangle\langle 0|, |0\rangle\langle n|\}$ appearing naturally in the response of $|0\rangle$ to the external perturbation, as in coupled multiconfigurational HF.

6. Discussion

Because of the high research activity level on how to use an MCSCF reference in the GFs (EP and PP), it is not presently clear how to optimally choose truncated sets of $\{\mathbf{T}_k^+\}$ operators. It is likely that many workers will carry out test calculations involving many choices of the pertinent operator manifolds before this situation is improved. Moreover, questions concerning when and how to partition the resulting $(\mathbf{T}_k^+|\hat{H}|\mathbf{T}_l^+)$ matrix so as to reduce the dimension of the matrix whose poles are to be found remain unanswered for the case of an MCSCF reference function. Again, what is missing is some concept of order (or size or importance) in terms of which to make decisions about how to partition the operator manifold. It is our opinion that significant progress will be made on these important questions within the near future and that, as a result, MCSCF-based GF methods will become common tools in the quantum chemist's library.

Having given an introduction to the fundamental properties of GFs and to the techniques that are used to obtain GFs whose poles and residues are accurate to a chosen precision, we now move on to consider the commonly used EPs and PPs in some detail. We should mention that the resulting working equations arising in the EP and PP cases have also been derived through the so-called equations-of-motion (EOM) formalism (Schaefer and Miller, 1977, Chapter 9). This EOM formalism focuses on setting up the superoperator generalized eigenvalue problem of Eq. (6.33) and, as a result, is equivalent to the propagator development here. We do not enter into a closer discussion of the EOM development here because, for the EP and PP treated below, this tool offers no new insight or convenience.

D. THE ELECTRON PROPAGATOR

If we choose the A and B^+ operators to be of the one-electron addition form (r^+, s^+), then the GF $\langle\langle A; B\rangle\rangle_E$ is known as the EP:

$$\langle\langle r^+; s\rangle\rangle_E = (s^+|(E\hat{1} + \hat{H})^{-1}|r^+) \equiv G_{sr}(E) \tag{6.46}$$

This choice of A and B^+ is made because we are interested in studying primary ionization events [ionization potentials (Cederbaum, 1973; Pickup and Goscinski, 1973; Doll and Reinhardt, 1972; Purvis and Öhrn, 1974) and electron affinities (Simons and Smith, 1973; Jørgensen and Simons, 1975)], which may be reasonably described through acting with a single-electron operator (r^+ or r) on the reference state $|0\rangle$. To obtain computationally useful expressions for $G_{rs}(E)$ specific choices must be made for the reference state $|0\rangle$ and for the operator manifold $\{\mathbf{T}^+\}$ in Eq. (6.32). We describe a few of the most commonly employed choices of these quantities and the resulting GF.

1. Koopmans' Theorem

The simplest approximation to the EP is obtained by taking the reference state to be a single configuration HF wavefunction and the projection manifold to be

$$\{\mathbf{T}^+\} = \{\mathbf{T}_1^+\} = \{\boldsymbol{\alpha}, \mathbf{p}^+\} \tag{6.47}$$

The EP in Eq. (6.32) then reads

$$G_{sr} = ((s^+|\boldsymbol{\alpha}^+)(s^+|\mathbf{p}^+))\begin{pmatrix} (\boldsymbol{\alpha}^+|E\hat{1} + \hat{H}|\boldsymbol{\alpha}^+) & (\mathbf{p}^+|E\hat{1} + \hat{H}|\boldsymbol{\alpha}^+) \\ (\mathbf{p}^+|E\hat{1} + \hat{H}|\boldsymbol{\alpha}^+) & (\mathbf{p}^+|E\hat{1} + \hat{H}|\mathbf{p}^+ \end{pmatrix}^{-1}\begin{pmatrix} (\boldsymbol{\alpha}^+|r^+) \\ (\mathbf{p}^+|r^+) \end{pmatrix} \tag{6.48}$$

The matrix elements appearing in Eq. (6.48) can easily be evaluated because of the single-determinant nature of $|0\rangle$:

$$(s^+|m^+) = \langle 0|[s, m^+]_+|0\rangle = \delta_{sm} \tag{6.49}$$

$$(s^+|\beta^+) = \delta_{s\beta} \tag{6.50}$$

$$\begin{aligned}(\beta^+|E\hat{1} + \hat{H}|\gamma^+) &= \delta_{\beta\gamma}E + \langle 0|[\beta,[H,\gamma^+]]_+|0\rangle \\ &= E\delta_{\beta\gamma} + h_{\beta\gamma} + \sum_{kt}\langle\beta k||\gamma t\rangle\langle 0|k^+ t|0\rangle \\ &= (E + \varepsilon_\gamma)\delta_{\beta\gamma}\end{aligned} \tag{6.51}$$

$$(m^+|E\hat{1} + \hat{H}|n^+) = (E + \varepsilon_m)\delta_{mn} \tag{6.52}$$

$$(m^+|E\hat{1} + \hat{H}|\alpha^+) = 0 \tag{6.53}$$

Here $\{\varepsilon_i\}$ denotes HF orbital energies. Using these results, Eq. (6.48) may be expressed as

$$G_{sr} = \sum_m \frac{\delta_{sm}\delta_{rm}}{E + \varepsilon_s} + \sum_\gamma \frac{\delta_{s\gamma}\delta_{r\gamma}}{E + \varepsilon_s} \tag{6.54}$$

By comparing the spectral representation of the GF in Eq. (6.6) with Eqs. (6.48) and (6.54) we see that the pole of Eq. (6.54) at $E = -\varepsilon_m$ represents an approximation to the electron affinity, while the pole at $E = -\varepsilon_\gamma$ corresponds to an ionization potential. The residue (the square of the transition amplitude) at $E = -\varepsilon_m$ is $\delta_{sm}\delta_{rm}$, while the residue at $E = -\varepsilon_\gamma$ is $\delta_{s\gamma}\delta_{r\gamma}$. All transition amplitudes corresponding to primary ionization events thus become equal to unity at this level of approximation. The above result expresses the EP analog of Koopmans' theorem. To go beyond Koopmans' theorem, better choices must be made for the reference state and operator manifold.

2. Rayleigh–Schrödinger Order Analysis

As discussed in Section A, RSPT has been widely used to develop systematic approximations to $\mathsf{G}(E)$. Here the unperturbed Hamiltonian H^0 is taken to be the HF Hamiltonian [Eq. (3.34)] and the orthonormal basis spin-orbitals are HF spin-orbitals having orbital energies ε_i:

$$H^0 = \sum_j \varepsilon_j j^+ j \tag{6.55}$$

The reference function $|0\rangle$ can be expressed, as in Chapter 3, as a perturbation series in powers of the residual electron–electron interaction. The EP is then used to describe the primary ionization events consistent through a certain order by expanding the reference state in powers of the fluctuation potential and by choosing the projection manifold of Eq. (6.23) to be sufficently large, the meaning of which will be discussed later. In this section, we show how to determine the primary ionization events consistent through zeroth, first, second, and third order. To do so, it proves sufficient to consider the truncated manifold

$$\{\mathbf{T}^+\} = \{\mathbf{T}_1^+ ; \mathbf{T}_3^+\}. \tag{6.56}$$

This conclusion is by no means obvious but should become clear shortly. One must, in principle, examine the interaction between $\mathbf{T}_1^+$, $\mathbf{T}_3^+$ and the $\mathbf{T}_5^+$, $\mathbf{T}_7^+$, etc., operators to conclude that these higher operators have no effect on the poles describing the primary ionization event through third order (Redmon *et al.*, 1975).

With the above choice of the projection manifold, the EP of Eq. (6.32) takes the form

$$G_{sr}(E) = ((s^+|\mathbf{T}_1^+)(s^+|\mathbf{T}_3^+))\begin{pmatrix} \mathsf{A} & \mathsf{C} \\ \mathsf{C}^\mathrm{T} & \mathsf{M} \end{pmatrix}^{-1}\begin{pmatrix} (\mathbf{T}_1^+|r^+) \\ (\mathbf{T}_3^+|r^+) \end{pmatrix} \tag{6.57}$$

where the matrices in Eq. (6.57) are defined as

$$\mathsf{A} = (\mathbf{T}_1^+|E\hat{1} + \hat{H}|\mathbf{T}_1^+) \tag{6.58}$$

$$\mathsf{C} = (\mathbf{T}_3^+|E\hat{1} + \hat{H}|\mathbf{T}_1^+) \tag{6.59}$$

$$\mathsf{M} = (\mathbf{T}_3^+|E\hat{1} + \hat{H}|\mathbf{T}_3^+) \tag{6.60}$$

The poles of the GF are determined entirely by the inverse matrix of Eq. (6.57). Since our interest is in describing the primary ionization events, we partition the inverse matrix as in Eqs. (6.44) and (6.45) with $\mathbf{T}_a^+ = \mathbf{T}_1^+$, and $\mathbf{T}_b^+ = \mathbf{T}_3^+$. We then determine the poles that describe the primary ionization events from the partitioned form of the inverse matrix

$$\mathsf{P}^{-1}(E) = (\mathsf{A} - \mathsf{C}^\mathrm{T}\mathsf{M}^{-1}\mathsf{C})^{-1} \tag{6.61}$$

By using $H = H^0 + U$ [see Eqs. (3.34) and (3.35)] and $|0\rangle = |0^0\rangle + |0^1\rangle + \ldots$, we may carry out a detailed order analysis of each of the four matrices A, ~~B,~~ C, and M. For example, we write A as

$$\mathsf{A} = \sum_{i=0}^{\infty} \mathsf{A}_i \tag{6.62}$$

where the label i indicates the order of the contributions to the A matrix.

Below we show all the contributions to the matrix A through third order:

$$(\mathsf{A}_0)_{jk} = E\langle 0^0|[j,k^+]_+|0^0\rangle + \langle 0^0|[j,[H^0,k^+]]_+|0^0\rangle = (E+\varepsilon_j)\delta_{kj} \tag{6.63}$$

$$\mathsf{A}_1 = \mathsf{A}_2 = 0 \tag{6.64}$$

$$\begin{aligned}(\mathsf{A}_3)_{jk} &= \langle 0^1|[j,[U,k^+]]_+|0^1\rangle + \langle 0^2|[j,[U,k^+]_+|0^0\rangle \\ &\quad + \langle 0^0|[j,[U,k^+]]_+|0^2\rangle = \sum_{il}\langle ji||kl\rangle\left(\sum_{\substack{\alpha>\beta\\ p}} K^{pi}_{\alpha\beta}K^{pl}_{\alpha\beta} - \sum_{\substack{q>p\\ \alpha}} K^{pq}_{\alpha l}K^{pq}_{\alpha i}\right) \\ &\quad + \sum_{p\delta}(\langle j\delta||kp\rangle + \langle jp||k\delta\rangle)K^{p}_{\delta}\end{aligned} \tag{6.65}$$

where the perturbation theory correlation coefficients are given in Eqs. (3.53) and (3.55). It should be noticed that both A_1 and A_2 are identically zero. This fact will be shown to lead to the conclusion that the Koopmans' theorem approximation to $\mathsf{G}(E)$ is accurate through first order. We also list below all of the matrix elements of the C and M matrices, which are required to evaluate $\mathsf{P}(E)$, and hence to obtain poles of $\mathsf{G}(E)$, through third order:

$$\mathsf{C}_0 = 0 \tag{6.66}$$

$$(\mathsf{C}_1)_{pq\alpha,j} = \langle 0^0|[\alpha^+qp,[U,j^+]]_+|0^0\rangle = \langle pq||j\alpha\rangle \tag{6.67}$$

$$(\mathsf{C}_1)_{\alpha\beta m,j} = -\langle\alpha\beta||jm\rangle \tag{6.68}$$

$$(\mathsf{C}_2)_{pq\alpha,j} = \tfrac{1}{2}\sum_{\gamma\delta}\langle i\alpha||\delta\gamma\rangle K^{qp}_{\delta\gamma} + \sum_{\gamma m}[\langle im||\gamma p\rangle K^{qm}_{\alpha\gamma} - \langle im||\gamma q\rangle K^{pm}_{\alpha\gamma}] \tag{6.69}$$

$$(\mathsf{C}_2)_{\alpha\beta m,j} = -\tfrac{1}{2}\sum_{pq}\langle im||pq\rangle K^{pq}_{\alpha\beta} + \sum_{\gamma p}[\langle i\gamma||p\alpha\rangle K^{mp}_{\beta\gamma} - \langle i\gamma||p\beta\rangle K^{mp}_{\alpha\gamma}] \tag{6.70}$$

$$(\mathsf{M}_0)_{nm\alpha,qp\beta} = \delta_{nq}\delta_{mp}\delta_{\alpha\beta}(E+\varepsilon_n+\varepsilon_m-\varepsilon_\alpha) \tag{6.71}$$

$$(\mathsf{M}_0)_{\delta\gamma p,\alpha\beta q} = \delta_{\delta\alpha}\delta_{\gamma\beta}\delta_{pq}(E+\varepsilon_\delta+\varepsilon_\gamma-\varepsilon_p) \tag{6.72}$$

$$(\mathsf{M}_0)_{nm\alpha,\gamma\delta p} = 0 \tag{6.73}$$

$$\begin{aligned}(\mathsf{M}_1)_{nm\alpha,qp\beta} &= -\delta_{qn}\langle m\beta||p\alpha\rangle - \delta_{pm}\langle n\beta||q\alpha\rangle \\ &\quad + \delta_{qm}\langle n\beta||p\alpha\rangle + \delta_{\alpha\beta}\langle mn||pq\rangle + \delta_{pn}\langle m\beta||q\alpha\rangle\end{aligned} \tag{6.74}$$

$$\begin{aligned}(\mathsf{M}_1)_{\delta\gamma p,\alpha\beta q} &= \delta_{\gamma\beta}\langle\delta q||\alpha p\rangle + \delta_{\delta\alpha}\langle\gamma q||\beta p\rangle \\ &\quad - \delta_{\gamma\alpha}\langle\delta q||\beta p\rangle + \delta_{pq}\langle\delta\gamma||\beta\alpha\rangle - \delta_{\delta\beta}\langle\gamma q||\alpha p\rangle\end{aligned} \tag{6.75}$$

$$(\mathsf{M}_1)_{nm\alpha,\delta\gamma p} = 0 \tag{6.76}$$

a. *Pole Structure through Second Order*

The poles of the EP consistent through zeroth order are determined by including all zeroth-order terms in $\mathsf{P}(E)$ [Eq. (6.61)]. Since C contains no zeroth-order contributions, we find that

$$\mathsf{P}_0(E) = \mathsf{A}_0 \tag{6.77}$$

which is the Koopmans' theorem result once again. A determination of $\mathsf{P}(E)$ through first order would not contain any more terms than are already in A_0 since $\mathsf{A}_1 = 0$ and $\mathsf{C}_0 = 0$. The lowest-order correction to A_0 given by $\mathsf{C}^\mathsf{T}\mathsf{M}^{-1}\mathsf{C}$ occurs in second order. In reaching this conclusion, we used the fact that the order of a term that is a product of several matrices is determined by adding up the individual orders of the matrices appearing in the term. The term $\mathsf{C}_0^\mathsf{T}\mathsf{M}_0^{-1}\mathsf{C}_1$ would thus have been of first order if C_0 had not vanished. An EP that contains only the A_0 matrix is identical to the EP obtained in Section 6.D.1 and results in Koopmans' theorem–level estimates of electron affinities and ionization potentials. The success of using Koopmans' theorem to assign peaks in photoelectron spectra relies on the fact that corrections to Koopmans' theorem first appear in second order.

Proceeding now to compute all terms in Eq. (6.61) through second order, we find

$$\mathsf{P}_2(E) = \mathsf{A}_0 - \mathsf{C}_1^\mathsf{T}\mathsf{M}_0^{-1}\mathsf{C}_1 \tag{6.78}$$

since $\mathsf{A}_2 = 0$. In all of the matrices in $\mathsf{P}_2(E)$, only the zeroth-order part of the reference state $|0^0\rangle$ contributes, as can be seen by examining Eqs. (6.66)–(6.76). Inserting the expressions for the individual matrix elements of C_1 and M_0 given in Eqs. (6.67), (6.68), (6.71)–(6.73) into Eq. (6.78) gives explicit expressions for the elements of $\mathsf{P}_2(E)$:

$$\begin{aligned}[\mathsf{P}_2(E)]_{jk} = (E + \varepsilon_j)\delta_{jk} &- \sum_{\substack{p>q\\ \alpha}} \frac{\langle j\alpha||pq\rangle\langle pq||k\alpha\rangle}{E - \varepsilon_\alpha + \varepsilon_p + \varepsilon_q} \\ &- \sum_{\substack{p\\ \alpha>\beta}} \frac{\langle jp||\alpha\beta\rangle\langle\alpha\beta||kp\rangle}{E + \varepsilon_\alpha + \varepsilon_\beta - \varepsilon_p}\end{aligned} \tag{6.79}$$

Such second-order EPs have been used (Doll and Reinhardt, 1972; Purvis and Öhrn, 1974) to compute atomic and molecular ionization potentials, electron affinities, and even electron–atom shape resonance positions and lifetimes with some success. Based upon the experience gained to date, however, we cannot expect the accuracy of this approach to be better than ±0.5 eV, even for systems that are described reasonably well by a single-configuration reference function. Often, this numerical accuracy is not satisfactory and hence the above formalism must be advanced to higher order (or replaced by another development that does not depend upon the Rayleigh–Schrödinger order concept). An example of such a second-order EP calculation is given in Problem 6.1.

b. Physical Interpretation

The physical interpretation of terms arising in $\mathsf{C}_1^\mathsf{T}\mathsf{M}_0^{-1}\mathsf{C}_1$ in terms of orbital relaxation and electron pair correlation effects has been carried out by several workers. To give some feeling for the physical content of the terms in $(\mathsf{P}_2)_{ij}$, we examine the diagonal $i = j = t$ term, which would be expected to be the dominant contributor in the case of adding an electron to spin-orbital ϕ_t. Then, through second order, from Eq. (6.79) we have

$$(P_2)_{tt} = \varepsilon_t + E + \sum_{\alpha > \beta, m} \frac{|\langle tm \| \alpha\beta \rangle|^2}{\varepsilon_m + \varepsilon_t - \varepsilon_\alpha - \varepsilon_\beta} - \sum_{q \neq t; \alpha} \frac{|\langle t\alpha \| tq \rangle|^2}{\varepsilon_q - \varepsilon_\alpha} - \sum_{\substack{p > q \neq t \\ \alpha}} \frac{|\langle t\alpha \| pq \rangle|^2}{\varepsilon_p + \varepsilon_q - \varepsilon_t - \varepsilon_\alpha} \tag{6.80}$$

Clearly this term will vanish (G will have a pole) near $E = -\varepsilon_t$, which is the Koopmans' theorem estimate. The correction to Koopmans' theorem expressed in the three sums occurring above can be given physical meaning in the following manner. The second sum gives the orbital relaxation contribution to the ion–neutral energy difference. By expanding the HF orbitals of the ion in terms of those of the neutral and then computing the ion's energy with these orbitals correct through second order one could derive this term within a wavefunction picture (Pickup and Goscinski, 1973). The fact that this sum has an orbital energy denominator involving only a single orbital excitation energy $(\varepsilon_q - \varepsilon_\alpha)$ has to do with the fact that, in a configuration interaction language, this term arises from single spin-orbital excitations $(\phi_\alpha \rightarrow \phi_q)$. The numerator $|\langle t\alpha \| tq \rangle|^2$ can be identified as the square of the perturbation matrix element coupling orbitals ϕ_α and ϕ_q. The perturbation is the coulomb and exchange potential caused by the electron that has been added into ϕ_t. The third sum in Eq. (6.80) gives the approximate correlation energy of an electron in ϕ_t with the remaining N electrons (in ϕ_α) and hence has to do with double excitations $(\phi_t\phi_\alpha \rightarrow \phi_p\phi_q)$, which would arise in a CI description of such pair correlations. Finally, the first sum describes the changes in the correlation energies between pairs of orbitals ϕ_α, ϕ_β due to the fact that spin-orbital ϕ_t is occupied in the ion (and hence unavailable for correlating ϕ_α and ϕ_β), but was not occupied in the neutral parent molecule.

c. *Third-Order Analysis of Pole Structure*

To obtain the expression for $\mathsf{P}(E)$ that contains all terms through third order (Simons and Smith, 1973; Jørgensen and Simons, 1975; Cederbaum, 1973), we introduce the matrices given explicitly in Eqs. (6.63)–(6.76) into Eq. (6.61) and neglect the fourth-order terms. This allows us to write Eq. (6.61) as

$$\mathsf{P}(E) = \mathsf{A}_0 + \mathsf{A}_3 - \mathsf{C}_1^{\mathsf{T}}(\mathsf{M}_0 + \mathsf{M}_1)^{-1}\mathsf{C}_1 - \mathsf{C}_1^{\mathsf{T}}(\mathsf{M}_0 + \mathsf{M}_1)^{-1}\mathsf{C}_2 - \mathsf{C}_2^{\mathsf{T}}(\mathsf{M}_0 + \mathsf{M}_1)^{-1}\mathsf{C}_1 \tag{6.81}$$

The inverse matrix $(\mathsf{M}_0 + \mathsf{M}_1)^{-1}$ can further be decomposed into orders by performing the expansion

$$(\mathsf{M}_0 + \mathsf{M}_1)^{-1} = \mathsf{M}_0^{-1} - \mathsf{M}_0^{-1}\mathsf{M}_1\mathsf{M}_0^{-1} + \mathsf{M}_0^{-1}\mathsf{M}_1\mathsf{M}_0^{-1}\mathsf{M}_1\mathsf{M}_0^{-1} + \cdots \tag{6.82}$$

which can be used in Eq. (6.81) to identify the terms to keep through third order:

$$\mathsf{P}_3(E) = \mathsf{A}_0 + \mathsf{A}_3 - \mathsf{C}_1^{\mathsf{T}}\mathsf{M}_0^{-1}\mathsf{C}_1 + \mathsf{C}_1^{\mathsf{T}}\mathsf{M}_0^{-1}\mathsf{M}_1\mathsf{M}_0^{-1}\mathsf{C}_1 \\ - \mathsf{C}_1^{\mathsf{T}}\mathsf{M}_0^{-1}\mathsf{C}_2 - \mathsf{C}_2^{\mathsf{T}}\mathsf{M}_0^{-1}\mathsf{C}_1 \tag{6.83}$$

At this third-order level of approximation, the EP has been successfully applied to a large number of inorganic and organic molecules. The ionization potentials (Von Niessen, *et al.*, 1979) and electron affinities (Simons, 1977) thus obtained are usually reliable to within ±0.3 eV.

d. Diagrammatic Analysis

The derivation of the EP consistent through a certain order may alternatively be performed in a way very similar to that used in MBPT to express the state energy and wavefunction. As in MBPT, the result is expressed in terms of a set of diagrams. In this section we give the results of performing such a diagrammic perturbation analysis of the EP. The contribution to $\mathsf{P}(E)$ beyond the $(E + \varepsilon_i)\delta_{ij}$ is, in the diagrammatic analysis, referred to as the self-energy or optical potential matrix $\Sigma(E)$. The self-energy matrix $\Sigma(E)$ in a given order n is expressed in terms of a set of Hugenholtz diagrams. The diagrams, which enter in order n, are determined by applying the rules in Table I of Chapter 3, with rule 3 modified such that when one is connecting lines each diagram has to have one incoming and one outgoing line. The translation of a Hugenholtz diagram into an algebraic expression is, as in MBPT, performed by translating the Hugenholtz diagram into one of its equivalent Brandow diagrams (Fig. 6.1; see Section 3.G). The algebraic expression for the Brandow GF diagram is obtained by applying the rules of Table II of Chapter 3 with rule 3 modified such that an energy parameter equal to $(-1)^h E$ is added to each factor in the denominator $\sum_\alpha \varepsilon_\alpha - \sum_p \varepsilon_p$ if

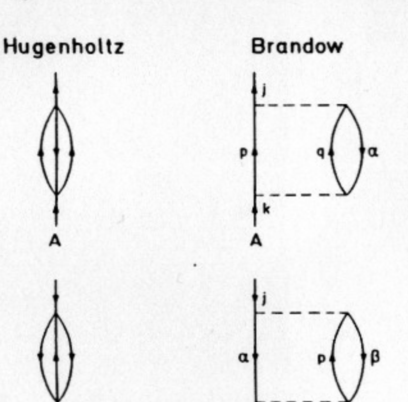

FIG. 6.1. All Hugenholtz and Brandow second-order self-energy diagrams.

the sum of the number of internal hole and particle lines is an odd integer. Here h is the number of internal hole lines in the diagram. Lines are counted as internal only if they lie between the vertices from which the GF's two free lines originate. If the GF's two free lines start at the same point, only those hole lines that exist horizontal to this point are counted. For example, diagrams A and C of Fig. 6.2 contain one and zero internal line, respectively. Diagram G of Fig. 6.2 has one internal hole line and thus each denominator would get a $-E$ factor added in.

If H^0 is taken to be the HF Hamiltonian, then, as in MBPT, all diagrams containing the loop structure ≻o cancel with the corresponding diagrams having the potential symbol ×—< in the same location. No first-order diagrams then enter in the diagrammatic perturbation analysis. In second order only the two diagrams displayed in Fig. 6.1 enter. To obtain some experience in applying the rules in Table II of Chapter 3, we list the analytical expressions for these two diagrams:

$$A = \sum_{\substack{pq\\ \alpha}} (\tfrac{1}{2})^1 (-1)^{1+1} \frac{\langle j\alpha || pq\rangle \langle pq || k\alpha\rangle}{-E + \varepsilon_\alpha - \varepsilon_p - \varepsilon_q} \tag{6.84}$$

$$B = \sum_{\substack{\alpha\beta\\ p}} (\tfrac{1}{2})^1 (-1)^{2+1} \frac{\langle \alpha\beta || jp\rangle \langle kp || \alpha\beta\rangle}{E + \varepsilon_\alpha + \varepsilon_\beta - \varepsilon_p} \tag{6.85}$$

The second-order contribution to the EP given above is, of course, identical to the one derived in Eq. (6.79).

In Fig. 6.2, we list the nonvanishing third-order self-energy diagrams. These may, of course, also be identified with corresponding terms of the

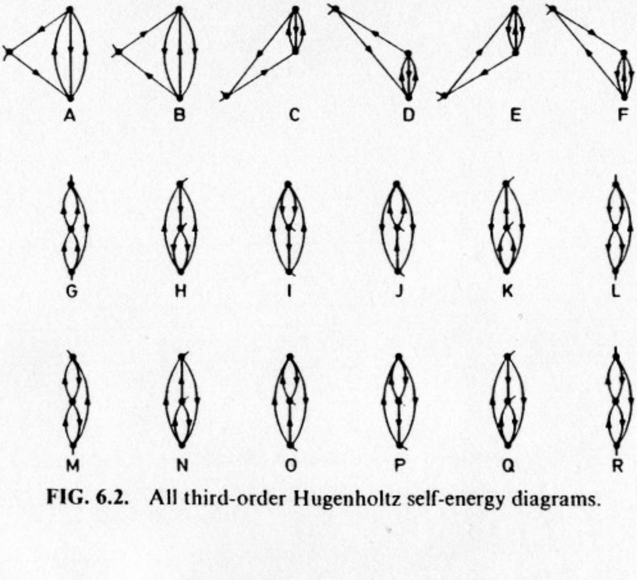

FIG. 6.2. All third-order Hugenholtz self-energy diagrams.

third-order expression of $\mathsf{P}_3(E)$ in Eq. (6.83). The sum of diagrams A and B represents the first two terms of A_3 in Eq. (6.65), while diagrams C–F may be identified as orginating from the last term of Eq. (6.65). The term $\mathsf{C}_1^{\mathsf{T}}\mathsf{M}_0^{-1}\mathsf{M}_1\mathsf{M}_0^{-1}\mathsf{C}_1$ gives rise to G, L, M, and R, while H–K and N–Q may be shown to originate from $\mathsf{C}_2^{\mathsf{T}}\mathsf{M}_0^{-1}\mathsf{C}_1$ and $\mathsf{C}_1^{\mathsf{T}}\mathsf{M}_0^{-1}\mathsf{C}_2$. The analytical third-order expression thus gives a compact representation of the diagrams in Fig. 6.2.

E. THE POLARIZATION PROPAGATOR

1. Introduction

If we choose the operators A and B^+ both to be the electric dipole moment operator $\mathbf{r}$, then the spectral representation of the resulting GF reads

$$\langle\langle \mathbf{r};\mathbf{r}\rangle\rangle_E = \lim_{\eta\to 0}\sum_m \left\{-\frac{\langle 0|\mathbf{r}|m\rangle\langle m|\mathbf{r}|0\rangle}{E - E_m + E_0 + i\eta} + \frac{\langle 0|\mathbf{r}|m\rangle\langle m|\mathbf{r}|0\rangle}{E + E_m - E_0 - i\eta}\right\} \tag{6.86}$$

The residue at the pole $E = \pm(E_m - E_0)$ contains the transition dipole matrix element between the states $|0\rangle$ and $|m\rangle$,

$$\langle 0|\mathbf{r}|m\rangle = \sum_{js}(\mathbf{r})_{js}\langle 0|j^+ s|m\rangle \tag{6.87}$$

where

$$(\mathbf{r})_{js} \equiv \langle \phi_j|\mathbf{r}|\phi_s\rangle \tag{6.88}$$

Since $\mathbf{r}$ is a number-conserving operator, the reference state $|0\rangle$ and the state $|m\rangle$ must contain the same number N of electrons. The poles of this so-called polarization propagator (PP) thus occur at the excitation energies $E = \pm(E_m - E_0)$ of the system described by $|0\rangle$, while the corresponding residues give the squares of the electric dipole transition moments $|\langle 0|\mathbf{r}|m\rangle|^2$.

The real part of the above GF may be expressed by combining terms over a common denominator as

$$Re\langle\langle \mathbf{r};\mathbf{r}\rangle\rangle_E = -\sum_m \frac{2(E_m - E_0)|\langle 0|\mathbf{r}|m\rangle|^2}{E^2 - (E_m - E_0)^2} \tag{6.89}$$

which is identical to the conventional expression for the frequency-dependent polarizability tensor (the frequency being represented by E).

To get some experience in using the PP to express second-order frequency-dependent and -independent properties and to indicate some problems that may appear when using the PP in finite basis set calculations, we now derive alternative but formally equivalent expressions for the frequency-dependent polarizability. We may employ Eq. (6.10) to reexpress the propagator $\langle\langle \mathbf{r};\mathbf{r}\rangle\rangle_E$ as

$$E\langle\langle \mathbf{r};\mathbf{r}\rangle\rangle_E = \langle 0|[\mathbf{r},\mathbf{r}]|0\rangle + \langle\langle [\mathbf{r},H];\mathbf{r}\rangle\rangle_E = i\langle\langle \mathbf{p};\mathbf{r}\rangle\rangle_E \tag{6.90}$$

where we have used (in a.u.)

$$[\mathbf{r},H] = i\mathbf{p} \tag{6.91}$$

For $E \neq 0, iE^{-1}\langle\langle \mathbf{p};\mathbf{r}\rangle\rangle_E$ may alternatively be used to calculate the frequency-dependent polarizability. Near $E = 0$, however, we expect $iE^{-1}\langle\langle \mathbf{p};\mathbf{r}\rangle\rangle_E$ (which should, in principle, equal $\langle\langle \mathbf{r};\mathbf{r}\rangle\rangle_E$) to have difficulty in finite-basis-set calculations because of the explicit appearance of the E^{-1} factor. That is, unless $\langle\langle \mathbf{p};\mathbf{r}\rangle\rangle_E$, as a calculated function of E, is proportional to E near $E = 0$, one might obtain incorrect behavior of $iE^{-1}\langle\langle \mathbf{p};\mathbf{r}\rangle\rangle_E$ here.

Applying Eq. (6.10) once more to Eq. (6.90) gives

$$E\langle\langle \mathbf{p};\mathbf{r}\rangle\rangle_E = \langle 0|[\mathbf{p},\mathbf{r}]|0\rangle + \langle\langle \mathbf{p};[H,\mathbf{r}]\rangle\rangle_E = \langle 0|[\mathbf{p},\mathbf{r}]|0\rangle - i\langle\langle \mathbf{p};\mathbf{p}\rangle\rangle_E \tag{6.92}$$

Using the second-quantized forms for **p** and **r**, we can explicitly calculate the commutator in Eq. (6.92) as

$$\begin{aligned}[\mathbf{p},\mathbf{r}] &= \sum_{ijkl} (\mathbf{p})_{ij}(\mathbf{r})_{kl}(\delta_{jk}i^+l - \delta_{il}k^+j) \\ &= \sum_{jl} [(\mathbf{pr})_{jl} - (\mathbf{rp})_{jl}]j^+l \\ &= -i\sum_{jl} \mathbf{I}_{jl}j^+l \end{aligned} \tag{6.93}$$

where **I** is the unit tensor operator whose elements are $\mathbf{I}_{jl} = \delta_{jl}\mathbf{I}$, and

$$(\mathbf{I})^{xx} = (\mathbf{I})^{yy} = (\mathbf{I})^{zz} = 1, \qquad (\mathbf{I})^{xy} = (\mathbf{I})^{xz} = (\mathbf{I})^{yz} = 0 \tag{6.94}$$

Clearly Eq. (6.93) is valid only if the basis set is complete so that we can write $(\mathbf{pr})_{jl} - (\mathbf{rp})_{jl} = (\mathbf{pr} - \mathbf{rp})_{jl} = -i\delta_{jl}\mathbf{I}$. We may now rewrite Eq. (6.92) to obtain one further expression for the frequency-dependent polarizability

$$\langle\langle \mathbf{r};\mathbf{r}\rangle\rangle_E = \frac{1}{E^2}(N\mathbf{I} + \langle\langle \mathbf{p};\mathbf{p}\rangle\rangle_E) \tag{6.95}$$

where the number N of electrons in $|0\rangle$ arises by evaluating $\mathbf{I}\sum_j \langle 0|j^+j|0\rangle$. As with $i\langle\langle \mathbf{p}_j\mathbf{r}\rangle\rangle_E E^{-1}$, finite-basis-set calculations of this form for the polarizability through the propagator $\langle\langle \mathbf{p};\mathbf{p}\rangle\rangle_E$ would be expected to have difficulty near $E = 0$ because the small-E portion of $\langle\langle \mathbf{p},\mathbf{p}\rangle\rangle_E$, which should exactly cancel the $N\mathbf{I}$ factor may, in a finite basis, not lead to exact cancellation.

We have now discussed how frequency-dependent polarizabilities can be obtained directly from the PP once a closed algebraic equation for $\langle\langle \mathbf{r};\mathbf{r}\rangle\rangle_E$ is found. Other second-order properties can equally well be determined by replacing A and B^+ with other one-electron operators (e.g., the dominant term in the indirect nuclear spin–spin coupling constant results when A and B^+ are taken to be the Fermi contact Hamiltonian).

In the following, we concentrate on how approximate closed expressions may be obtained for the $\langle\langle \mathbf{r};\mathbf{r}\rangle\rangle_E$ form of the polarization propagator. From our treatment of the PP it should become clear how to determine other second-order properties corresponding to other choices for A and B^+.

2. The Single-Configuration TDHF Approximation

In a simple and very commonly used approximation to the PP, the reference state $|0\rangle$ is chosen to be a single-configuration (but not necessarily single determinant) HF wavefunction. The operator manifold $\{\mathbf{T}^+\}$ then is taken as the set of particle–hole excitation and deexcitation operators used for optimizing the reference state:

$$\mathbf{T}^+ = \{\mathbf{T}_2^+\} = \{\mathbf{Q}^+, \mathbf{Q}\} = \{m^+\alpha, \alpha^+ m; m \quad \alpha\} \tag{6.96}$$

With these choices, the propagator takes the form (as expressed in Eq. (6.32)]

$$\langle\langle \mathbf{r};\mathbf{r}\rangle\rangle_E = ((\mathbf{r}|\mathbf{Q}^+)(\mathbf{r}|\mathbf{Q}))\begin{pmatrix} (\mathbf{Q}^+|E\hat{1}+\hat{H}|\mathbf{Q}^+) & (\mathbf{Q}^+|E\hat{1}+\hat{H}|\mathbf{Q}) \\ (\mathbf{Q}|E\hat{1}+\hat{H}|\mathbf{Q}^+) & (\mathbf{Q}|E\hat{1}+\hat{H}|\mathbf{Q}) \end{pmatrix}^{-1}\begin{pmatrix} (\mathbf{Q}^+|\mathbf{r}) \\ (\mathbf{Q}|\mathbf{r}) \end{pmatrix} \tag{6.97}$$

Since the one-particle density matrix is diagonal for the chosen HF reference state, we have

$$(\mathbf{Q}|\mathbf{Q}^+) = (\mathbf{Q}^+|\mathbf{Q}) = \{\langle 0[s^+\beta, r^+\alpha]|0\rangle\} = \{0\} \tag{6.98}$$

and

$$S_{r\alpha,s\beta} \equiv (\mathbf{Q}^+|\mathbf{Q}^+)_{r\alpha,s\beta} = \langle 0|[\alpha^+ r, s^+\beta]|0\rangle = \delta_{rs}\delta_{\alpha\beta}(\nu_\alpha - \nu_r) \tag{6.99}$$

and similarly

$$(\mathbf{r}|\mathbf{Q}^+)_{s\beta} = (\nu_\beta - \nu_s)(\mathbf{r})_{\beta s} \tag{6.100}$$

where ν_k is the occupancy of spin-orbital ϕ_k. Equation (6.97) may be written in more compact notation as

$$\langle\langle \mathbf{r};\mathbf{r}\rangle\rangle_E = ((\mathbf{r}|\mathbf{Q}^+)(\mathbf{r}|\mathbf{Q}))\begin{pmatrix} \mathsf{S}E + \mathsf{A}_{11} & \mathsf{B}_{11} \\ \mathsf{B}_{11} & -\mathsf{S}E + \mathsf{A}_{11} \end{pmatrix}^{-1}\begin{pmatrix} (\mathbf{Q}^+|\mathbf{r}) \\ (\mathbf{Q}|\mathbf{r}) \end{pmatrix} \tag{6.101}$$

where the matrices A_{11} and B_{11} are identical to those defined in connection with the MCSCF orbital optimization in Eqs. (2.29) and (2.30) except that $|0\rangle$ is taken here to be the single-configuration HF function. These matrix elements are evaluated explicitly in Problem 5.2 and used in Problem 6.2 to carry out a PP calculation.

Equation (6.101) is said to express the time-dependent Hartree–Fock (TDHF) or the random phase approximation (RPA) to the PP (Jørgensen, 1975). The TDHF (or RPA) approximation has been derived in a variety of ways, each of which tends to stress a certain aspect or point of view. In the following, we examine the physical content of the TDHF approximation and try to point out various consequences of using it for calculating the frequency-dependent polarizability, oscillator strengths, and excitation energies.

a Pole and Residue Analysis

We now demonstrate how the TDHF propagator may be transformed to a spectral form similar to the one appearing in Eq. (6.6). The poles of Eq. (6.101) can be determined through solving the nonhermitian eigenvalue problem

$$\begin{pmatrix} \mathsf{A}_{11} & \mathsf{B}_{11} \\ \mathsf{B}_{11} & \mathsf{A}_{11} \end{pmatrix} \begin{pmatrix} \mathbf{Z} \\ \mathbf{Y} \end{pmatrix} = E \begin{pmatrix} \mathsf{S} & 0 \\ 0 & -\mathsf{S} \end{pmatrix} \begin{pmatrix} \mathbf{Z} \\ \mathbf{Y} \end{pmatrix} \tag{6.102}$$

whose dimension is the sum of both the number of nonredundant particle–hole and hole–particle operators. The solution of Eq. (6.102) may alternatively be obtained through performing a series of transformations involving matrices of only the dimension of the particle–hole operators (Linderberg and Öhrn, 1977; Jørgensen, Olsen, and Yeager, 1981). To achieve this reduction in the matrix dimension, we first write Eq. (6.102) in component form as

$$\mathsf{A}_{11}\mathbf{Z} + \mathsf{B}_{11}\mathbf{Y} = E\mathsf{S}\mathbf{Z} \tag{6.103}$$

$$\mathsf{B}_{11}\mathbf{Z} + \mathsf{A}_{11}\mathbf{Y} = -E\mathsf{S}\mathbf{Y} \tag{6.104}$$

Successively adding and subtracting the above two equations gives

$$(\mathsf{A}_{11} + \mathsf{B}_{11})(\mathbf{Z} + \mathbf{Y}) = E\mathsf{S}(\mathbf{Z} - \mathbf{Y}) \tag{6.105}$$

$$(\mathsf{A}_{11} - \mathsf{B}_{11})(\mathbf{Z} - \mathbf{Y}) = E\mathsf{S}(\mathbf{Z} + \mathbf{Y}) \tag{6.106}$$

Equation (6.105) may then be rearranged,

$$\mathbf{Z} + \mathbf{Y} = E(\mathsf{A}_{11} + \mathsf{B}_{11})^{-1}\mathsf{S}(\mathbf{Z} - \mathbf{Y}) \tag{6.107}$$

and inserted into Eq. (6.106) to give

$$\mathsf{S}^{-1}(\mathsf{A}_{11} + \mathsf{B}_{11})\mathsf{S}^{-1}(\mathsf{A}_{11} - \mathsf{B}_{11})(\mathbf{Z} - \mathbf{Y}) = E^2(\mathbf{Z} - \mathbf{Y}) \tag{6.108}$$

The eigenvalues of Eq. (6.102) are thus determined by the nonhermitian eigenvalue problem given in Eq. (6.108) for E^2. If $\mathsf{A}_{11} - \mathsf{B}_{11}$ is positive definite, we can form the $(\mathsf{A}_{11} - \mathsf{B}_{11})^{1/2}$ matrix and premultiply Eq. (6.108) with $(\mathsf{A}_{11}-\mathsf{B}_{11})^{1/2}$, thereby achieving the hermitian eigenvalue problem

$$\begin{aligned}&(\mathsf{A}_{11}-\mathsf{B}_{11})^{1/2}\mathsf{S}^{-1}(\mathsf{A}_{11}+\mathsf{B}_{11})\mathsf{S}^{-1}(\mathsf{A}_{11}-\mathsf{B}_{11})^{1/2}(\mathsf{A}_{11}-\mathsf{B}_{11})^{1/2}(\mathbf{Z}-\mathbf{Y})\\&\quad=E^2(\mathsf{A}_{11}-\mathsf{B}_{11})^{1/2}(\mathbf{Z}-\mathbf{Y})\end{aligned}\tag{6.109}$$

which has eigenvalues E^2 and eigenvectors equal to $(\mathsf{A}_{11}-\mathsf{B}_{11})^{1/2}(\mathbf{Z}-\mathbf{Y})$. The eigenvalues of the nonhermitian eigenvalue problem in Eq. (6.102) can thus be determined from a hermitian eigenvalue problem of only the dimension of the particle–hole operators. When S is singular or nearly singular, it may be useful to solve Eq. (6.108) or (6.109) using the inverse eigenvalue equations with eigenvalues $1/E^2$. Equation (6.108) then becomes

$$(\mathsf{A}_{11}-\mathsf{B}_{11})^{-1}\mathsf{S}(\mathsf{A}_{11}+\mathsf{B}_{11})^{-1}\mathsf{S}(\mathbf{Z}-\mathbf{Y})=(1/E^2)(\mathbf{Z}-\mathbf{Y})\tag{6.110}$$

To interpret how transition moments are determined within the TDHF approximation, we continue transforming the propagator to its spectral form. We use the eigenvalues and eigenvectors of Eq. (6.108) together with Eq. (6.107) to determine the Z and Y matrices. Equation (6.102) implies that if the set $\left(\begin{smallmatrix}\mathsf{Z}\\\mathsf{Y}\end{smallmatrix}\right)$ are eigenvectors corresponding to the eigenvalues ω, then $\left(\begin{smallmatrix}\mathsf{Y}\\\mathsf{Z}\end{smallmatrix}\right)$ are eigenvectors with $-\omega$ eigenvalues. This allows us to write Eq. (6.102) in a form that displays its positive and negative eigenvalue spectrum

$$\begin{pmatrix}\mathsf{A}_{11}&\mathsf{B}_{11}\\\mathsf{B}_{11}&\mathsf{A}_{11}\end{pmatrix}\begin{pmatrix}\mathsf{Z}&\mathsf{Y}\\\mathsf{Y}&\mathsf{Z}\end{pmatrix}=\begin{pmatrix}\mathsf{S}&0\\0&-\mathsf{S}\end{pmatrix}\begin{pmatrix}\mathsf{Z}&\mathsf{Y}\\\mathsf{Y}&\mathsf{Z}\end{pmatrix}\begin{pmatrix}\omega&0\\0&-\omega\end{pmatrix}\tag{6.111}$$

or alternatively as

$$\begin{pmatrix}E\mathsf{S}+\mathsf{A}_{11}&\mathsf{B}_{11}\\\mathsf{B}_{11}&-E\mathsf{S}+\mathsf{A}_{11}\end{pmatrix}\begin{pmatrix}\mathsf{Z}&\mathsf{Y}\\\mathsf{Y}&\mathsf{Z}\end{pmatrix}=\begin{pmatrix}\mathsf{S}&0\\0&-\mathsf{S}\end{pmatrix}\begin{pmatrix}\mathsf{Z}&\mathsf{Y}\\\mathsf{Y}&\mathsf{Z}\end{pmatrix}\begin{pmatrix}E\mathsf{1}+\omega&0\\0&E\mathsf{1}-\omega\end{pmatrix}\tag{6.112}$$

Because of the appearance of the metric matrix $\left(\begin{smallmatrix}\mathsf{S}&0\\0&-\mathsf{S}\end{smallmatrix}\right)$ in Eq. (6.102) the $\left(\begin{smallmatrix}\mathsf{Z}\\\mathsf{Y}\end{smallmatrix}\right)$ eigenvectors may be normalized according to

$$(\mathbf{Z},\mathbf{Y})_\lambda\begin{pmatrix}\mathsf{S}&0\\0&-\mathsf{S}\end{pmatrix}\begin{pmatrix}\mathbf{Z}\\\mathbf{Y}\end{pmatrix}_\mu=\delta_{\lambda\mu}\tag{6.113}$$

To obtain a spectral representation of the propagator that contains a unit metric, one must transform the set of particle–hole and hole–particle operators to the representation where they give a diagonal metric with unit elements. This transformation is carried out using the excitation operators defined below:

$$\mathbf{0}^{+}=\mathbf{Q}^{+}\mathsf{Z}+\mathbf{Q}\mathsf{Y}\tag{6.114}$$

$$\mathbf{0}=\mathbf{Q}^{+}\mathsf{Y}^{+}+\mathbf{Q}\mathsf{Z}^{+}\tag{6.115}$$

For example, it is straightforward to show using Eqs. (6.98), (6.99), and (6.113) that

$$(\mathbf{0}^+|\mathbf{0}^+) = (\mathsf{Z}^+, \mathsf{Y}^+)\begin{pmatrix} \mathsf{S} & 0 \\ 0 & -\mathsf{S} \end{pmatrix}\begin{pmatrix} \mathsf{Z} \\ \mathsf{Y} \end{pmatrix} = 1 \tag{6.116}$$

This condition then implies that the full metric matrix involving these new excitation operators becomes

$$\begin{pmatrix} (\mathbf{0}^+|\mathbf{0}^+) & (\mathbf{0}|\mathbf{0}^+) \\ (\mathbf{0}^+|\mathbf{0}) & (\mathbf{0}|\mathbf{0}) \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} \mathsf{Z}^+ & \mathsf{Y}^+ \\ \mathsf{Y}^+ & \mathsf{Z}^+ \end{pmatrix}\begin{pmatrix} \mathsf{S} & 0 \\ 0 & -\mathsf{S} \end{pmatrix}\begin{pmatrix} \mathsf{Z} & \mathsf{Y} \\ \mathsf{Y} & \mathsf{Z} \end{pmatrix} \tag{6.117}$$

The spectral form of the propagator is then obtained by taking the inverse of Eq. (6.112), premultiplying with $\left(\begin{smallmatrix} \mathsf{Z} & \mathsf{Y} \\ \mathsf{Y} & \mathsf{Z} \end{smallmatrix}\right)$, and using Eq. (6.117):

$$\begin{aligned} &\begin{pmatrix} E\mathsf{S} + \mathsf{A}_{11} & \mathsf{B}_{11} \\ \mathsf{B}_{11} & -E\mathsf{S} + \mathsf{A}_{11} \end{pmatrix}^{-1} \\ &\qquad = \begin{pmatrix} \mathsf{Z} & \mathsf{Y} \\ \mathsf{Y} & \mathsf{Z} \end{pmatrix}\begin{pmatrix} E\mathsf{1} + \boldsymbol{\omega} & 0 \\ 0 & E\mathsf{1} - \boldsymbol{\omega} \end{pmatrix}^{-1}\begin{pmatrix} \mathsf{Z}^+ & \mathsf{Y}^+ \\ -\mathsf{Y}^+ & -\mathsf{Z}^+ \end{pmatrix} \end{aligned} \tag{6.118}$$

Introducing Eq. (6.118) into Eq. (6.101) finally allows us to write the propagator in spectral form

$$\langle\langle \mathbf{r}; \mathbf{r} \rangle\rangle_E = \sum_\lambda |(\mathbf{r}|0_\lambda^+)|^2 \left[-\frac{1}{E - \omega_\lambda} + \frac{1}{E + \omega_\lambda} \right] \tag{6.119}$$

A comparison of Eq. (6.119) and the spectral representation of the propagator given in Eq. (6.86) shows that the pole at $E = \omega_\lambda$ corresponds to a total energy difference $E_\lambda - E_0$. The pole at $E = -\omega_\lambda$ corresponds to the same total energy difference $E_\lambda - E_0$, and the propagator therefore is an even function in the excitation energy $E_\lambda - E_0$. The pole at $E = \omega_\lambda$ has a residue of $-|(\mathbf{r}|0_\lambda^+)|^2$, which using Eq. (6.6) may be identified as $-|\langle 0|\mathbf{r}|\lambda\rangle|^2$. The pole at $E = -\omega_\lambda$ has the residue $|(\mathbf{r}|0_\lambda^+)|^2$, which is equal to $|\langle 0|\mathbf{r}|\lambda\rangle|^2$. The transition moments $\langle 0|\mathbf{r}|n\rangle$ may thus be determined from the residue at either of the poles $E = \pm\omega_\lambda$. It should be noted that the above development allows $E_\lambda - E_0$ to be either positive or negative corresponding to excitation energies from ground or excited states. However, in applications where $|0\rangle$ refers to an excited state, Eq. (6.108) must be used to determine the excitation energies, because $\mathsf{A} - \mathsf{B}$ is not then positive definite.

b. The Stability Condition

If imaginary or negative roots are encountered when solving the non-hermitian eigenvalue problem in Eq. (6.108), the RPA approximation is said to have an instability. If $\mathsf{A}_{11} - \mathsf{B}_{11}$ is positive definite, instabilities are not encountered if the matrix $(\mathsf{A}_{11} - \mathsf{B}_{11})^{1/2}\mathsf{S}^{-1}(\mathsf{A}_{11} + \mathsf{B}_{11})\mathsf{S}^{-1}(\mathsf{A}_{11} - \mathsf{B}_{11})^{1/2}$ in Eq. (6.109) is positive definite; that is, if

$$\mathbf{X}(\mathsf{A}_{11} - \mathsf{B}_{11})^{1/2}\mathsf{S}^{-1}(\mathsf{A}_{11} + \mathsf{B}_{11})\mathsf{S}^{-1}(\mathsf{A}_{11} - \mathsf{B}_{11})^{1/2}\mathbf{X}^{\mathrm{T}} > 0 \quad (6.120)$$

for any vector satisfying $|\mathbf{X}| > 0$. Defining the vector

$$\mathbf{Y} = \mathbf{X}(\mathsf{A}_{11} - \mathsf{B}_{11})^{1/2}\mathsf{S}^{-1} \quad (6.121)$$

we may write Eq. (6.120) as

$$\mathbf{Y}(\mathsf{A}_{11} + \mathsf{B}_{11})\mathbf{Y}^{\mathrm{T}} > 0 \quad (6.122)$$

which says that $\mathsf{A}_{11} + \mathsf{B}_{11}$ has to be positive definite to ensure that Eq. (6.120) is fulfilled. Thus if $\mathsf{A}_{11} - \mathsf{B}_{11}$ is positive definite and $\mathsf{A}_{11} + \mathsf{B}_{11}$ is not, then an RPA instability will be encountered. Although it is not obvious from the previous derivation of the solution to the RPA problem, it may be shown by transforming the RPA eigenvalue problem to an equation similar to Eq. (6.108) (but with $\mathsf{Z} + \mathsf{Y}$ occurring as the eigenvector) that if $\mathsf{A}_{11} + \mathsf{B}_{11}$ is positive definite, then an RPA instability is encountered if $\mathsf{A}_{11} - \mathsf{B}_{11}$ is not positive definite. Hence if both $\mathsf{A}_{11} \pm \mathsf{B}_{11}$ are positive definite, instabilities are not encountered in the RPA approximation. If both $\mathsf{A}_{11} \pm \mathsf{B}_{11}$ are nonpositive definite, an explicit solution of Eq. (6.108) has to be determined before it be clear whether an instability is encountered. If $\mathsf{A}_{11} \pm \mathsf{B}_{11}$ are both non–positive-definite, negative excitation energies $(E_\lambda - E_0)$ are obtained in TDHF approximations. Such negative excitation energies may correspond to excitations from higher to lower "excited" states.

As was demonstrated in Chapter 2, the curvature of the energy hypersurface at a stationary point corresponding to the reference state $|0\rangle$ is governed by the same $\mathsf{A}_{11} - \mathsf{B}_{11}$ matrix [Eq. (2.80)] as occurs here in the TDHF. Hence, if the HF wavefunction corresponds to a local energy minimum, $\mathsf{A}_{11} - \mathsf{B}_{11}$ would be positive definite. In our derivation of the energy optimization conditions as given in Chapter 2, we restricted our orbital variations to involve only real variational parameters (i.e., we assumed real spin-orbitals). If we had instead examined the variations in the energy resulting from purely imaginary orbital variational parameters, the second derivative of the total energy would involve the matrix $\mathsf{A}_{11} + \mathsf{B}_{11}$. Hence, the conditions that $\mathsf{A}_{11} \pm \mathsf{B}_{11}$ be positive definite must be met if the HF reference state is to represent a local energy minimum both with respect to real and imaginary orbital variations. Therefore, imaginary excitation energies arise in RPA if one of the matrices $\mathsf{A}_{11} \pm \mathsf{B}_{11}$ is non–positive-definite and the other is positive definite. If negative excitation energies are obtained in the RPA approximation both $\mathsf{A}_{11} \pm \mathsf{B}_{11}$ are non–positive-definite and the reference state $|0\rangle$ then represents a saddle point on the energy hypersurface.

c. Connection with Coupled Hartee–Fock Theory

Having defined the TDHF problem and having shown how excitation energies and oscillator strengths are determined, we now demonstrate that the above TDHF propagator reduces, for $E = 0$, to the equation obtained in Chapter 5 for the second-order response property as expressed in the coupled Hartree–Fock (CHF) approach. For $E = 0$, the TDHF polarization propagator given in Eq. (6.101) becomes

$$\langle\langle \mathbf{r};\mathbf{r}\rangle\rangle_{E=0} = ((\mathbf{r}|\mathbf{Q}^{+})(\mathbf{r}|\mathbf{Q}))\begin{pmatrix} \mathsf{A}_{11} & \mathsf{B}_{11} \\ \mathsf{B}_{11} & \mathsf{A}_{11} \end{pmatrix}^{-1}\begin{pmatrix} (\mathbf{Q}^{+}|\mathbf{r}) \\ (\mathbf{Q}|\mathbf{r}) \end{pmatrix} \tag{6.123}$$

Inserting unit matrices in the form

$$\mathsf{UU}^{+} = 1 \tag{6.124}$$

where

$$\mathsf{U} \equiv \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \tag{6.125}$$

before and after the above inverse matrix, allows us to express the inverse matrix as

$$\begin{pmatrix} \mathsf{A}_{11} & \mathsf{B}_{11} \\ \mathsf{B}_{11} & \mathsf{A}_{11} \end{pmatrix}^{-1} = \mathsf{U}\begin{pmatrix} \mathsf{A}_{11} + \mathsf{B}_{11} & 0 \\ 0 & \mathsf{A}_{11} - \mathsf{B}_{11} \end{pmatrix}^{-1}\mathsf{U}^{+} \tag{6.126}$$

Because the dipole operator $\mathbf{r}$ is real, the elementary definition of the superoperator scalar product given in Eq. (6.16) can be used to write

$$(\mathbf{r}|\mathbf{Q}) = -(\mathbf{r}|\mathbf{Q}^{+}) \tag{6.127}$$

which, together with Eq. (6.126), allows us to rewrite Eq. (6.123) as

$$\langle\langle \mathbf{r};\mathbf{r}\rangle\rangle_{E=0} = 2(\mathbf{r}|\mathbf{Q})(\mathsf{A}_{11} - \mathsf{B}_{11})^{-1}(\mathbf{Q}|\mathbf{r}) \tag{6.128}$$

Comparing this expression to that of the CHF approach [Eq. (5.16)] shows that these two ways of writing the frequency-independent polarizability are indeed identical.

d. Equivalence of Length and Velocity Oscillator Strengths

Another important and attractive feature of the TDHF approximation (and its MC extension described below) is that the oscillator strengths computed within the dipole length and dipole velocity approximations become formally equivalent, provided that a complete basis is used in the calculation. From Eq. (6.119) it is clear that the transition moments in the dipole velocity approximation would given by

$$(\mathbf{p}|0_\lambda^+) = \langle 0|[\mathbf{p}, 0_\lambda^+]|0\rangle \tag{6.129}$$

which from Eq. (6.91) is equivalent to

$$-i\langle 0|[[\mathbf{r}, H], 0_\lambda^+]|0\rangle \tag{6.130}$$

Using the matrix identity of Eq. (6.42) together with the BT theorem in the form

$$\langle 0|[[\mathbf{r}, 0_\lambda^+], H]|0\rangle = 0 \tag{6.131}$$

we can express the above as

$$(\boldsymbol{p}|0_\lambda^+) \;\; = -i\langle 0|[\mathbf{r}, [H, 0_\lambda^+]]|0\rangle = -i\boldsymbol{r}\langle 0|[\mathbf{Q}^+ + \mathbf{Q}, [H, 0_\lambda^+]]|0\rangle \tag{6.132}$$

where $\boldsymbol{r}$ denotes a row vector that contains the particle–hole matrix elements $(\boldsymbol{r})_{m\alpha}$. Equation (6.132) may be rewritten, using the definitions of 0_λ^+ [Eq. (6.114)] and the A_{11} and B_{11} matrices, as

$$(\boldsymbol{p}|0_\lambda^+) = -i(\boldsymbol{r}, \boldsymbol{r})\begin{pmatrix} \mathsf{A}_{11} & \mathsf{B}_{11} \\ \mathsf{B}_{11} & \mathsf{A}_{11} \end{pmatrix}\begin{pmatrix} \mathbf{Z} \\ \mathbf{Y} \end{pmatrix}_\lambda = -\omega_\lambda i(\boldsymbol{r}, \boldsymbol{r})\begin{pmatrix} \mathsf{S} & 0 \\ 0 & -\mathsf{S} \end{pmatrix}\begin{pmatrix} \mathbf{Z} \\ \mathbf{Y} \end{pmatrix}_\lambda \tag{6.133}$$

The last equality sign follows from the eigenvalue relation Eq. (6.102). Since

$$((\mathbf{r}|\mathbf{Q}^+)(\mathbf{r}|\mathbf{Q})) = (\boldsymbol{r}, \boldsymbol{r})\begin{pmatrix} \mathsf{S} & 0 \\ 0 & -\mathsf{S} \end{pmatrix} \tag{6.134}$$

we may finally rewrite Eq. (6.133) as

$$(\mathbf{p}|0_\lambda^+) = -i\omega_\lambda((\mathbf{r}|\mathbf{Q}^+)(\mathbf{r}|\mathbf{Q}))\begin{pmatrix} \mathbf{Z} \\ \mathbf{Y} \end{pmatrix}_\lambda = -i\omega_\lambda(\mathbf{r}|0_\lambda^+) \tag{6.135}$$

where the last step follows from the definition of the excitation operator in Eq. (6.114). Equation (6.135) states that oscillator strengths calculated in the dipole length and in the dipole velocity approximation become identical provided that the commutator relation in Eq. (6.91) is valid. Violation of the commutation relation [Eq. (6.91)] occurs when a finite basis is used in the calculation.

The TDHF approximation thus has three very characteristic features that make it especially useful as a means for calculating excitation energies and oscillator strengths. In ground-state calculations it indicates via imaginary excitation frequencies if the ground state is not stable under the type of one-electron perturbation given by the choice of A and B^+. A singlet instability is thus encountered if A and B^+ are chosen to be the dipole operator, whereas triplet instabilities are obtained if A and B^+ are chosen to be, for example, the Fermi contact Hamiltonian. Second, when the energy parameter $\boldsymbol{E}$ is set equal to zero, one obtains the same expression for the second-order properties in the TDHF method as in the CHF approach. Finally, the oscillator strengths calculated within the dipole length and the dipole velocity approximations are formally equivalent. These attractive features are unique to such an approximate theory.

3. The Multiconfigurational Extension of TDHF

In many calculations on highly correlated or open-shell molecules, it turns out that a single-configuration reference state description of $|0\rangle$ is inadequate even if optimized orbitals are used to describe $|0\rangle$. If the excitation operators of interest belong to the totally symmetric irreducible representation of the Hamiltonian's point group, the results obtained are normally better than if one attempts to calculate properties whose operators are not totally symmetric (e.g., triplet operators). It is well recognized, for example, that the singlet excitation energies for a closed-shell molecule, are described relatively well (to about 10% accuracy) within the TDHF approximation, while the description of the triplet excitation energies is very poor. In fact, triplet instabilities are often encountered when using the above TDHF method.

Approximations that go beyond the simple TDHF approximation are therefore needed. We consider two such approaches here. The second method outlined below is based on a RSPT analysis in which reference state $|0\rangle$ is expanded in powers of the residual electronic interaction [given by U in Eq. (3.35)] and the projection manifold $\{\mathbf{T}^+\}$ is chosen to be large enough to guarantee that all terms in the PP are determined consistent through second order. In light of this order analysis, it will be seen that the TDHF approximation corresponds to the approximation that is consistent through first order in the electronic repulsion. Before presenting this RSPT treatment, we address another approximation that goes beyond the single-configuration TDHF approximation. This extension, which is based upon an MCSCF description of the reference state $|0\rangle$, has the same three useful characteristics mentioned above in describing the single-configuration-based TDHF description. The multiconfigurational time-dependent Hartree–Fock (MCTDHF) approximation thus provides a formalism in which oscillator strengths in the dipole length and velocity approximation remain equivalent as one ranges continuously through (MCTDHF) from a single-configuration description (TDHF) all the way to the full-CI limit.

a. Choice of Reference Function and Operator Manifold

Having now motivated the consideration of more sophisticated reference states, let us develop the above-mentioned approximation in some detail. In the MCTDHF approach (Yeager and Jørgensen, 1979; Dalgaard, 1980) an MCSCF wavefunction is used as the reference state. The projection manifold $\{\mathbf{T}^+\}$ is then chosen to be the same nonredundant (see Section 2.B.7) set of orbital and configuration space excitation [Eq. (2.26)] and deexcitation operators that were used for optimizing the MCSCF reference state

$$\{\mathbf{T}^+\} = \{\mathbf{Q}^+, \mathbf{R}^+, \mathbf{Q}, \mathbf{R}\} \tag{6.136}$$

b. *Hermiticity Problem*

This choice of $|0\rangle$ and $\{\mathbf{T}^+\}$ then permits $\langle\langle \mathbf{r}; \mathbf{r}\rangle\rangle_E$ to be written in a form analogous to that given in Eq. (6.97). In computing the requisite matrix elements, one notices that the elements giving the coupling between orbital and configuration space operators do not obey hermiticity:

$$(\mathbf{Q}^+|\hat{H}|R_n^+) - (R_n^+|\hat{H}|\mathbf{Q}^+)^* = \langle 0|H\mathbf{Q}|n\rangle - E_0\langle 0|\mathbf{Q}|n\rangle \neq 0 \tag{6.137}$$

In the limit where one has in $|0\rangle$ an exact eigenstate

$$H|0\rangle = E_0|0\rangle \tag{6.138}$$

the last two terms in Eq. (6.137) cancel, and the matrix representative of $\hat{H}$ within the $\{\mathbf{T}^+\}$ basis consequently becomes hermitian. Therefore, we are certain that this nonhermitian aspect of the problem is an artifact (i.e., it arises because we do not have an exact $|0\rangle$). To force the matrix to be hermitian even for approximate choices of $|0\rangle$, we equate $(Q^+|H|R^+)$ with $(R^+|H|Q^+)^*$. That is, we simply require the superoperator Hamiltonian to operate on the orbital space (Q^+, Q) when the coupling elements are evaluated. This choice yields a propagator that for $E = 0$ gives the same result for second-order properties as obtained in the coupled multiconfiguration HF approach. An added advantage of this order of operations is that the oscillator strengths in the dipole length and in the dipole velocity approximations become formally equivalent. If we had chosen an alternative means of imposing hermiticity on the matrix, such would not be the case.

c. *Spectral Representation of the Propagator*

Inserting the projection manifold defined in Eq. (6.136) into Eq. (6.32) gives

$$\langle\langle \mathbf{r}; \mathbf{r}\rangle\rangle_E = [(\mathbf{r}|\mathbf{Q}^+)(\mathbf{r}|\mathbf{R}^+)(\mathbf{r}|\mathbf{Q})(\mathbf{r}|\mathbf{R})] \times \left(E\begin{pmatrix} \mathsf{S} & \boldsymbol{\Delta} \\ -\boldsymbol{\Delta} & -\mathsf{S} \end{pmatrix} + \begin{pmatrix} \mathsf{A} & \mathsf{B} \\ \mathsf{B} & \mathsf{A} \end{pmatrix}\right)^{-1} \begin{pmatrix} (\mathbf{Q}^+|\mathbf{r}) \\ (\mathbf{R}^+|\mathbf{r}) \\ (\mathbf{Q}|\mathbf{r}) \\ (\mathbf{R}|\mathbf{r}) \end{pmatrix} \tag{6.139}$$

where

$$\mathsf{S} = \begin{pmatrix} \langle 0|[Q, Q^+]|0\rangle & \langle 0|[Q, R^+]|0\rangle \\ \langle 0|[R, Q^+]|0\rangle & \langle 0|[R, R^+]|0\rangle \end{pmatrix} \tag{6.140}$$

$$\mathbf{\Delta} = \begin{pmatrix} \langle 0|[Q, Q]|0\rangle & \langle 0|[Q, R]|0\rangle \\ \langle 0|[R, Q]|0\rangle & \langle 0|[R, R]|0\rangle \end{pmatrix} \tag{6.141}$$

and $\mathsf{S}^+ = \mathsf{S}^*$ and $\mathbf{\Delta}^+ = -\mathbf{\Delta}^*$. The elements of, for example, $\langle 0|[Q, R^+]|0\rangle$ are given by

$$\langle 0|[s^+r, |n\rangle\langle 0|]|0\rangle = \langle 0|s^+r|n\rangle \tag{6.142}$$

$$\langle 0|[R_n^+, R_m]|0\rangle = \langle 0|[|n\rangle\langle 0|, |0\rangle\langle m|]|0\rangle = -\langle m|n\rangle = -\delta_{mn} \tag{6.143}$$

The A and B matrices are identical to those defined in Eqs. (2.29) and (2.30) and more explicitly written out in (2.42) and (2.44). Of course, now the reference function $|0\rangle$ is the MCSCF state; in the TDHF approximation it was the single-configuration SCF state. In Problem 5.3, the A and B matrices are evaluated for a single molecular ion, and in Problem 6.3 the data are used to perform an MCTDHF calculation on that system.

Because the metric in the MCTDHF approximation [Eqs. (6.140) and (6.141)] has a more general form than the one in the TDHF approximation [Eqs. (6.98) and (6.99)] some minor modifications are required in the procedure described in Section E.2.a. to get the propagator into spectral form.

By carrying out transformations of the MTDHF eigenvalue problem, similar to that done in Eqs. (6.102)–(6.108), we obtain the result analogous to Eq. (6.107) (Jørgensen *et al.*, 1981)

$$\mathbf{Z} + \mathbf{Y} = E(\mathsf{A} + \mathsf{B})^{-1}(\mathsf{S} - \mathbf{\Delta})(\mathbf{Z} - \mathbf{Y}) \tag{6.144}$$

to Eq. (6.108)

$$(\mathsf{S} - \mathbf{\Delta})^{-1}(\mathsf{A} + \mathsf{B})(\mathsf{S} + \mathbf{\Delta})^{-1}(\mathsf{A} - \mathsf{B})(\mathbf{Z} - \mathbf{Y}) = E^2(\mathbf{Z} - \mathbf{Y}) \tag{6.145}$$

and to Eq. (6.109)

$$\begin{aligned}(\mathsf{A} - \mathsf{B})^{1/2}(\mathsf{S} - \mathbf{\Delta})^{-1}(\mathsf{A} + \mathsf{B})(\mathsf{S} + \mathbf{\Delta})^{-1}(\mathsf{A} - \mathsf{B})^{1/2}(\mathsf{A} - \mathsf{B})^{1/2}(\mathbf{Z} - \mathbf{Y}) \\ = E^2(\mathsf{A} - \mathsf{B})^{1/2}(\mathbf{Z} - \mathbf{Y})\end{aligned} \tag{6.146}$$

Using these equations, a spectral representation may easily be derived as was done in the single-configuration case in Eqs. (6.109)–(6.119).

d. Special Characteristics of the MCTDHF Propagator

The MCSCF reference state represents a stationary point on the energy hypersurface. If imaginary excitation energies are encountered, for example, in an MCTDHF ground-state calculation, the minimum point is not stable (does not correspond to a local minimum) under the type of (spatial or spin symmetry) one-electron perturbations described by the operators A and B^+. Also, as in the single-configuration TDHF, the frequency-independent polarizability obtained in the MCTDHF approximation becomes identical to that resulting from the multiconfiguration coupled HF approach. The proof of this equivalence follows exactly the same lines as for the single-configuration case; we refer to that proof for further details [see Eqs. (6.123)–(6.128)]. The essential points of the proof are as follows. For $E = 0$, Eq. (6.139) reduces to

$$\langle\langle \mathbf{r}; \mathbf{r} \rangle\rangle_{E=0} = [(\mathbf{r}|\mathbf{Q}^+)(\mathbf{r}|\mathbf{R}^+)(\mathbf{r}|\mathbf{Q})(\mathbf{r}|\mathbf{R})] \begin{pmatrix} \mathsf{A} & \mathsf{B} \\ \mathsf{B} & \mathsf{A} \end{pmatrix}^{-1} \begin{pmatrix} (\mathbf{Q}^+|\mathbf{r}) \\ (\mathbf{R}^+|\mathbf{r}) \\ (\mathbf{Q}|\mathbf{r}) \\ (\mathbf{R}|\mathbf{r}) \end{pmatrix} \tag{6.147}$$

By next inserting the unit matrix of Eq. (6.124) before and after the above inverse matrix and then using Eq. (6.127), we can write the frequency-independent polarizability in the form

$$\langle\langle \mathbf{r}; \mathbf{r} \rangle\rangle_{E=0} = 2[(\mathbf{r}|\mathbf{Q})(\mathbf{r}|\mathbf{R})](\mathsf{A} - \mathsf{B})^{-1} \begin{pmatrix} (\mathbf{Q}|\mathbf{r}) \\ (\mathbf{R}|\mathbf{r}) \end{pmatrix} \tag{6.148}$$

which is identical to the expression obtained in the multiconfiguration coupled HF calculation of Eq. (5.15). It has further been proven by Dalgaard (1980) that the oscillator strength calculated within the dipole length and dipole velocity approximations become identical if a complete basis is used in the MCTDHF calculation. A proof that follows lines very similar to the ones given in Section E.d for a single-configuration case has been given (Albertsen *et al.*, 1980).

The MCTDHF approximation thus has the same characteristics as the single-configuration-based TDHF approximation. We therefore have the possibility of determining approximate state vectors that, at any level of approximation, show these characteristics as the number of configurations included in the MCSCF reference state is increased from the single-configuration case through the full-CI limit. Initial calculations using the MCTDHF approximation have yielded very promising results. We now move to describing an extension of the TDHF approximation that is based on perturbation theory.

4. Rayleigh–Schrödinger Analysis

The perturbation extension of the TDHF method is obtained by developing systematic approximations to the PP that are consistent through a certain order in the perturbation (Oddershede, 1978). These approximations are based upon expanding the reference state $|0\rangle$ in powers of the residual electron–electron interaction as defined in RSPT [see Eq. (3.14)] and by choosing the projection manifolds $\{\mathbf{T}_k^+\}$ to be sufficiently "large" to ensure that the resulting matrix elements of the PP propagator are consistent through the desired order.

In the EP case, our goal was to determine the primary poles (the ionization potentials and electron affinities involving low-energy ionization of the parent molecule) through second or third order. In the analogous PP calculations, the primary poles correspond to those possessing dominant particle–hole nature; we attempt to determine these poles through a chosen order. Because the residues at a given pole contain information about the transion amplitudes for the given type of excitation, perturbation methods may also be employed to evaluate these residues through a specified order. Further, since the PP expresses the reference states' frequency-dependent polarizabilities, this response quantity may also be calculated consistent through the desired order by using a PP consistent through that order.

a. Choice of Operator Space

As the unperturbed Hamiltonian, we choose the same HF Hamiltonian as was employed in the above EP development, and we use a basis set of real orthonormal spin-orbitals. We develop an approximation to the PP that yields the primary excitation energies and the corresponding transition moments (and the frequency-dependent polarizability) consistent through second order in the residual electronic repulsion (Nielsen *et al.*, 1980). To determine the poles belonging to the principal excitation energies, the corresponding transition moments, and the frequency-dependent polarizability through second order, it proves sufficient to consider the truncated projection manifold

$$\{\mathbf{T}^+\} = \{\mathbf{T}_2^+ ; \mathbf{T}_4^+\} \tag{6.149}$$

This conclusion is by no means obvious. One must, in principle, examine the effects of $\mathbf{T}_6^+$, $\mathbf{T}_8^+$, etc. on the matrix elements $(\mathbf{T}^+|\hat{H}|\mathbf{T}^+)$, $(B^+|\mathbf{T}^+)$, $(\mathbf{T}^+|A)$, and $(\mathbf{T}^+|\mathbf{T}^+)$ to conclude that these higher operators can have no effect, through second order, on the computed poles and residues of the PP (Oddershede and Jørgensen, 1977).

b. Pole and Residue Structure of the Propagator

With the above choice of the operator projection manifold, the PP propagator [Eq. (6.32)] becomes

$$\langle\langle \mathbf{r};\mathbf{r}\rangle\rangle_E = [(\mathbf{r}|\mathbf{T}_2^+)(\mathbf{r}|\mathbf{T}_4^+)]\begin{pmatrix}(\mathbf{T}_2^+|E\hat{I}+\hat{H}|\mathbf{T}_2^+) & (\mathbf{T}_2^+|E\hat{I}+\hat{H}|\mathbf{T}_4^+)\\ (\mathbf{T}_4^+|E\hat{I}+\hat{H}|\mathbf{T}_2^+) & (\mathbf{T}_4^+|E\hat{I}+\hat{H}|\mathbf{T}_4^+)\end{pmatrix}^{-1}\begin{pmatrix}(\mathbf{T}_2^+|\mathbf{r})\\ (\mathbf{T}_4^+|\mathbf{r})\end{pmatrix} \tag{6.150}$$

Introducing the shorthand notation

$$\mathsf{M}_{ij} = (\mathbf{T}_i^+|E\hat{I} + \hat{H}|\mathbf{T}_j^+) \tag{6.151}$$

we may partition the inverse matrix of Eq. (6.150), as was done in the EP, to yield

$$\begin{aligned}&\begin{pmatrix}\mathsf{M}_{22} & \mathsf{M}_{24}\\ \mathsf{M}_{42} & \mathsf{M}_{44}\end{pmatrix}^{-1}\\ &\quad=\begin{pmatrix}(\mathsf{M}_{22}-\mathsf{M}_{24}\mathsf{M}_{44}^{-1}\mathsf{M}_{42})^{-1} & -(\mathsf{M}_{22}-\mathsf{M}_{24}\mathsf{M}_{44}^{-1}\mathsf{M}_{42})^{-1}\mathsf{M}_{24}\mathsf{M}_{44}^{-1}\\ (-\mathsf{M}_{44}^{-1}\mathsf{M}_{42}(\mathsf{M}_{22} & \mathsf{M}_{44}^{-1}+\mathsf{M}_{44}^{-1}\mathsf{M}_{42}(\mathsf{M}_{22}\\ \quad-\mathsf{M}_{24}^{-1}\mathsf{M}_{44}^{-1}\mathsf{M}_{42})^{-1} & \quad-\mathsf{M}_{24}\mathsf{M}_{44}^{-1}\mathsf{M}_{42})^{-1}\mathsf{M}_{24}\mathsf{M}_{44}^{-1}\end{pmatrix} \quad \checkmark\end{aligned} \tag{6.152}$$

By substituting the inverse matrix into Eq. (6.150) and multiplying out the factors we obtain

$$\begin{aligned}\langle\!\langle\mathbf{r};\mathbf{r}\rangle\!\rangle_E &= [(\mathbf{r}|\mathbf{T}_2^+)-(\mathbf{r}|\mathbf{T}_4^+)\mathsf{M}_{44}^{-1}\mathsf{M}_{42}]\mathsf{P}^{-1}(E)[(\mathbf{T}_2^+|\mathbf{r})-\mathsf{M}_{24}\mathsf{M}_{44}^{-1}(\mathbf{T}_4^+|\mathbf{r})]\\ &\quad+(\mathbf{r}|\mathbf{T}_4^+)\mathsf{M}_{44}^{-1}(\mathbf{T}_4^+|\mathbf{r})\\ &\equiv \mathsf{W}_2(E)+\mathsf{W}_4(E)\end{aligned} \tag{6.153}$$

where

$$\mathsf{P}(E) = \mathsf{M}_{22} - \mathsf{M}_{24}\mathsf{M}_{44}^{-1}\mathsf{M}_{42} \tag{6.154}$$

The principal poles of the propagator occur at the eigenvalues of $\mathsf{P}(E)$. Therefore, to obtain these poles consistent through second order, we require $\mathsf{P}(E)$ to be determined consistent through that same order. To compute the transition amplitudes consistent through second order requires that the quantity $\mathbf{F}(E)$ defined by

$$\mathbf{F}(E) \equiv [(\mathbf{r}|\mathbf{T}_2^+) - (\mathbf{r}|\mathbf{T}_4^+)\mathsf{M}_{44}^{-1}\mathsf{M}_{42}] \tag{6.155}$$

which contains zeroth- and higher-order factors, also be evaluated consistent through second order. Finally, if the frequency-dependent polarizability is to be calculated through second order, both $\mathsf{W}_2(E)$ and the $\mathsf{W}_4(E)$ should be computed through that order. Let us now analyze in more detail which of the above matrices have to be evaluated explicitly through which order to guarantee that the above quantities are calculated consistent through second order.

c. *Second-Order Analysis of Pole Structure*

We consider initially the calculation of the excitation energies that are determined as poles of $\mathsf{P}^{-1}(E)$ [Eq. (6.154)]. After introducing the individual components $\mathbf{Q}, \mathbf{Q}^+, \mathbf{Q}^+\mathbf{Q}^+$, and $\mathbf{QQ}$, we may carry out an order analysis of the individual matrices appearing in $\mathsf{P}(E)$. We consider initially the matrix M_{22}, which is expected to be the dominant contributor to P.

$$\mathsf{M}_{22} = \begin{pmatrix} E(\mathbf{Q}^+|\mathbf{Q}^+) + (\mathbf{Q}^+|\hat{H}|\mathbf{Q}^+) & (\mathbf{Q}^+|\hat{H}|\mathbf{Q}) \\ (\mathbf{Q}|\hat{H}|\mathbf{Q}^+) & -E(\mathbf{Q}|\mathbf{Q}) + (\mathbf{Q}|\hat{H}|\mathbf{Q}) \end{pmatrix}$$

$$\equiv \begin{pmatrix} E\mathsf{S} + \mathsf{A} & \mathsf{B} \\ \mathsf{B} & -E\mathsf{S} + \mathsf{A} \end{pmatrix} \tag{6.156}$$

where

$$\mathsf{S} = (\mathbf{Q}^+|\mathbf{Q}^+) \tag{6.157}$$

$$\mathsf{A} = (\mathbf{Q}^+|\hat{H}|\mathbf{Q}^+) \tag{6.158}$$

$$\mathsf{B} = (\mathbf{Q}^+|\hat{H}|\mathbf{Q}) \tag{6.159}$$

and where we have used the fact that

$$(\mathbf{Q}^+|\mathbf{Q})_{m\gamma,n\delta} = \langle 0|[\gamma^+ m, \delta^+ n]|0\rangle = 0 \tag{6.160}$$

is identically zero through any order. This M_{22} is the same matrix that occurred in the earlier TDHF treatment of the PP except that now $|0\rangle$ represents an RSPT expansion of the reference state. As an example of how to carry out the order analysis, we consider the S and A matrices:

$$\begin{aligned} S_{m\alpha,n\beta} &= \langle 0|[\alpha^+ m, n^+\beta]|0\rangle \\ &= \langle {}^0 0|[\alpha^+ m, n^+\beta]|0^0\rangle + \langle {}^1 0|[\alpha^+ m, n^+\beta]|0^1\rangle + O(3) \\ &= (S_0)_{m\alpha,n\beta} + (S_2)_{m\alpha,n\beta} + \cdots \end{aligned} \tag{6.161}$$

where

$$(S_0)_{m\alpha,n\beta} = \delta_{mn}\delta_{\alpha\beta} \tag{6.162}$$

$$(S_2)_{m\alpha,n\beta} = \tfrac{1}{2}\delta_{mn} \sum_{\substack{pq \\ \gamma}} K^{pq}_{\alpha\gamma} K^{pq}_{\beta\gamma} - \tfrac{1}{2}\delta_{\alpha\beta} \sum_{\substack{p \\ \gamma\delta}} K^{mp}_{\gamma\delta} K^{np}_{\gamma\delta} \tag{6.163}$$

and, as in the EP analysis, the superscripts on $|0^0\rangle$, $|0^1\rangle$, etc. denote the orders of these terms. No first-order terms thus appear in S because $|0^1\rangle$ contains only doubly excited configurations. The elements of A are given by

$$\begin{aligned} A_{m\alpha,n\beta} &= \langle 0|[\alpha^+ m, [H, n^+\beta]]|0\rangle \\ &= \langle {}^0 0|[\alpha^+ m, [H_0, n^+\beta]]|0^0\rangle + \langle {}^0 0|[\alpha^+ m, [U, n^+\beta]]|0^0\rangle \\ &\quad + \langle {}^0 0|[\alpha^+ m, [U, n^+\beta]]|0^1\rangle + \langle {}^1 0|[\alpha^+ m, [H_0, n^+\beta]]|0^1\rangle + O(3) \end{aligned} \tag{6.164}$$

In the A matrix zeroth-, first-, and second-order terms appear. The A_0, A_1, and A_2 matrices are given by

$$(\mathsf{A}_0)_{m\alpha,n\beta} = (\varepsilon_m - \varepsilon_\beta)\delta_{mn}\delta_{\alpha\beta} \tag{6.165}$$

$$(\mathsf{A}_1)_{m\alpha,n\beta} = \langle \beta m || n\alpha \rangle \tag{6.166}$$

$$\begin{aligned}(\mathsf{A}_2)_{m\alpha,n\beta} = {} & \tfrac{1}{2}\delta_{\alpha\beta} \sum_{\pi\gamma q} \langle \pi\gamma || qn \rangle K^{mq}_{\pi\gamma} - \tfrac{1}{2}\delta_{mn} \sum_{\pi q p} \langle \beta\pi || qp \rangle K^{qp}_{\alpha\pi} \\ & + (S_2)_{m\alpha,n\beta}(\varepsilon_n - \varepsilon_\beta)\end{aligned} \tag{6.167}$$

The B matrix may similarly be shown to contain only first- and second-order terms $\mathsf{B} = \mathsf{B}_{1+2}$. The B_1 matrix is given in Problem 5.2 and

$$\begin{aligned}(\mathsf{B}_2)_{m\alpha,n\beta} = {} & -\sum_{q\pi} \{\langle \beta q || \pi m \rangle K^{qn}_{\pi\alpha} + \langle \alpha q || \pi n \rangle K^{mq}_{\beta\pi}\} \\ & - \tfrac{1}{2} \sum_{pq} \langle pq || nm \rangle K^{pq}_{\beta\alpha} - \tfrac{1}{2} \sum_{\pi\delta} \langle \alpha\beta || \pi\delta \rangle K^{mn}_{\pi\delta}\end{aligned} \tag{6.168}$$

In the term $\mathsf{M}_{24}\mathsf{M}_{44}^{-1}\mathsf{M}_{42}$, the M_{42} matrix contains no zeroth-order terms and since $\mathsf{M}_{24}^{\mathsf{T}} = \mathsf{M}_{42}$, we only need keep M_{42} through first order and M_{44} through zeroth order to obtain

$$\mathsf{M}_{24}\mathsf{M}_{44}^{-1}\mathsf{M}_{42} \tag{6.169}$$

through second order. The nonvanishing parts of the matrices M_{42} and M_{44} become

$$\begin{aligned}(C_1)_{nm\beta\alpha,p\gamma} &= \langle 0^0 | [\alpha^+ \beta^+ mn, [U, p^+ \gamma]] | 0^0 \rangle \\ &= \delta_{mp}\langle \gamma n || \alpha\beta \rangle - \delta_{np}\langle \gamma m || \alpha\beta \rangle \\ &\quad + \delta_{\alpha\gamma}\langle mn || \beta p \rangle - \delta_{\beta\gamma}\langle mn || \alpha p \rangle\end{aligned} \tag{6.170}$$

$$\begin{aligned}(D_0)_{nm\beta\alpha,pq\gamma\delta} &= E \bullet \langle 0^0 | [\alpha^+ \beta^+ mn, p^+ q^+ \gamma\delta] | 0^0 \rangle \\ &\quad + \langle 0^0 | [\alpha^+ \beta^+ mn, [H_0, p^+ q^+ \gamma\delta]] | 0^0 \rangle \\ &= (E + \varepsilon_\alpha + \varepsilon_\beta - \varepsilon_m - \varepsilon_n)\delta_{np}\delta_{mq}\delta_{\beta\gamma}\delta_{\alpha\delta}\end{aligned} \tag{6.171}$$

$$(D_0)_{\alpha\beta mn,\delta\gamma qp} = (-E + \varepsilon_\alpha + \varepsilon_\beta - \varepsilon_m - \varepsilon_n)\delta_{np}\delta_{mq}\delta_{\beta\gamma}\delta_{\alpha\delta} \tag{6.172}$$

The excitation energies as computed through second order may thus be obtained as poles of

$$\mathsf{P}^{-1}(E) = \begin{pmatrix} \begin{matrix}[E\mathsf{S}_{0+2} + \mathsf{A}_{0+1+2} \\ -\mathsf{C}_1^{\mathsf{T}}\mathsf{D}_0^{-1}\mathsf{C}_1]\end{matrix} & \mathsf{B}_{1+2} \\ \mathsf{B}_{1+2} & \begin{matrix}[-E\mathsf{S}_{0+2} + \mathsf{A}_{0+1+2} \\ -\mathsf{C}_1^{\mathsf{T}}\mathsf{D}_0^{-1}\mathsf{C}_1]\end{matrix} \end{pmatrix}^{-1} \tag{6.173}$$

We should also note that Eq. (6.173), when used to determine the excitation energies consistent only through first order, reduces to the inverse matrix occurring in the TDHF approximation described in Section E.2.

d. Second-Order Analysis of Transition Moments

When the excitation energies are determined through second order we might also wish to determine the corresponding transition moments consistent through the same order. This would require us to evaluate the eigenvectors of $\mathsf{P}^{-1}(E)$ and to further evaluate $\mathbf{F}(E)$ of Eq. (6.155) consistent through second order. Because the eigenvectors of $\mathsf{P}(E)$ become energy dependent, specialized techniques are required to determine the transition moments (Oddershede *et al.*, 1977).

To determine $\mathbf{F}(E)$ consistent through second order, we introduce the individual components of $\mathbf{Q}^+$, $\mathbf{Q}$, etc., which then permits the first component [see Eq. (6.155)] of $\mathbf{F}(E)$ to be expressed as

$$\begin{aligned}(\mathbf{r}|\mathbf{Q}^+) = \langle {}^{0}0|[\mathbf{r},\mathbf{Q}^+]|0^0\rangle + \langle {}^{1}0|[\mathbf{r},\mathbf{Q}^+]|0^1\rangle \\ + \langle {}^{2}0|[\mathbf{r},\mathbf{Q}^+]|0^0\rangle + \langle {}^{0}0|[\mathbf{r},\mathbf{Q}^+]|0^2\rangle + O(3) \qquad (6.174)\end{aligned}$$

which contains zeroth- and second-order contributions. The values of $(\mathbf{r}|\mathbf{Q}^+)_0$ are given in Eq. (6.100). The only $|0^2\rangle$ terms that contribute to $(\mathbf{r}|\mathbf{Q}^+)_2$ are those which contain singly excited configurations relative to $|0^0\rangle$. The matrix $(\mathbf{r}|\mathbf{Q}^+\mathbf{Q}^+)$ has no zeroth-order elements; thus from the expression for $\mathbf{F}(E)$, it is obvious (because M_{42} is of at least first order) that only the first-order elements of $(\mathbf{r}|\mathbf{Q}^+\mathbf{Q}^+)$ can contribute. Explicit expressions for $(\mathbf{r}|\mathbf{Q}^+)_2$ and $(\mathbf{r}|\mathbf{Q}^+\mathbf{Q}^+)_1$ have been obtained (Nielsen *et al.*, 1980). The expression for $\mathbf{F}(E)$ consistent through second order may then be written as

$$\mathbf{F}(E) = \{(\mathbf{r}|\mathbf{Q}^+)_{0+2} - (\mathbf{r}|\mathbf{Q}^+\mathbf{Q}^+)_1\mathsf{D}_0^{-1}\mathsf{C}_1, (\mathbf{r}|\mathbf{Q})_{0+2} - (\mathbf{r}|\mathbf{Q}\mathbf{Q})_1\mathsf{D}_0^{-1}\mathsf{C}_1\} \qquad (6.175)$$

which may be used to calculate the transition moments correct through second order. If we wish to calculate the transition moments correct only through first order, $\mathbf{F}(E)$ reduces to $\{(\mathbf{r}|\mathbf{Q}^+)_0, (\mathbf{r}|\mathbf{Q})_0\}$, which is identical to the expression for $\mathbf{F}(E)$ used in the TDHF approximation. Therefore, we again see that in the TDHF approximation, both the excitation energies and the transition moments are calculated correct through first order.

e. Frequency-Dependent Polarizability

To obtain the frequency-dependent polarizability correct through second order requires that the $\mathsf{W}_2(E)$ be evaluated consistent through second order as described previously and further that $\mathsf{W}_4(E)$ be calculated through second order. By introducing the individual compnents $\mathbf{Q}^+\mathbf{Q}^+$ and $\mathbf{Q}\mathbf{Q}$ we can reduce $\mathsf{W}_4(E)$ to

$$\mathsf{W}_4(E) = (\mathbf{r}|\mathbf{Q}^+\mathbf{Q}^+)_1\mathsf{D}_0^{-1}(\mathbf{Q}^+\mathbf{Q}^+|\mathbf{r})_1 + (\mathbf{r}|\mathbf{Q}\mathbf{Q})_1\mathsf{D}_0^{-1}(\mathbf{Q}\mathbf{Q}|\mathbf{r})_1 \quad (6.176)$$

Since $\mathsf{W}_4(E)$ contains no first-order terms, the frequency-dependent polarizability is thus determined consistent through first order in the TDHF approximation [which contains no analog to $\mathsf{W}_4(E)$].

f. Diagrammatic Analysis

We have previously shown how the results of MBPT and the perturbative analysis of the EP may be interpreted in terms of a set of diagrams. The perturbative analysis of the PP may be given a similar interpretation. We sketch in the following how the diagrammatic analysis of the PP propagator may be carried out. Initially, we limit ourselves to considering how the TDHF approximation may be understood in terms of diagrams. We consider the TDHF PP approximation in the SCF spin-orbital basis, where it reads

$$\langle\langle \mathbf{r};\mathbf{r}\rangle\rangle_E = [(\mathbf{r}|\mathbf{Q}^+)(\mathbf{r}|\mathbf{Q})]\begin{pmatrix} E\mathsf{1} + \mathsf{A}_0 + \mathsf{A}_1 & \mathsf{B}_1 \\ \mathsf{B}_1 & -E\mathsf{1} + \mathsf{A}_0 + \mathsf{A}_1 \end{pmatrix}^{-1}\begin{pmatrix} (\mathbf{Q}^+|\mathbf{r}) \\ (\mathbf{Q}|\mathbf{r}) \end{pmatrix} \quad (6.177)$$

which is identical to Eq. (6.101). The poles of the inverse matrix appearing in Eq. (6.177) may be determined from a partitioned form of the inverse matrix with $\mathbf{T}_a^+ + \mathbf{T}_b^+$ of Section C.4 equal to $\mathbf{Q}^+ + \mathbf{Q}$. The analog of Eq. (6.45) then becomes

$$\mathsf{P}^{-1}(E) = [E\mathsf{1} + \mathsf{A}_0 + \mathsf{A}_1 - \mathsf{B}_1(-E\mathsf{1} + \mathsf{A}_0 + \mathsf{A}_1)^{-1}\mathsf{B}_1]^{-1} \quad (6.178)$$

$\mathsf{P}(E)$ may be given a diagrammatic interpretation by expanding the inverse matrix as

$$\begin{aligned}(-E\mathsf{1}+\mathsf{A}_0+\mathsf{A}_1)^{-1} &= (-E\mathsf{1}+\mathsf{A}_0)^{-1} - (-E\mathsf{1}+\mathsf{A}_0)^{-1}\mathsf{A}_1(-E\mathsf{1}+\mathsf{A}_0)^{-1} \\ &\quad + (-E\mathsf{1}+\mathsf{A}_0)^{-1}\mathsf{A}_1(-E\mathsf{1}+\mathsf{A}_0)^{-1}\mathsf{A}_1(-E\mathsf{1}+\mathsf{A}_0)^{-1} + \cdots \end{aligned} \quad (6.179)$$

We then obtain

$$\begin{aligned}\mathsf{P}(E) &= E\mathsf{1} + \mathsf{A}_0 + \mathsf{A}_1 - \mathsf{B}_1(-E\mathsf{1} + \mathsf{A}_0)^{-1}\mathsf{B}_1 \\ &\quad + \mathsf{B}_1(-E\mathsf{1} + \mathsf{A}_0)^{-1}\mathsf{A}_1(-E\mathsf{1} + \mathsf{A}_0)^{-1}\mathsf{B}_1 - \cdots \end{aligned} \quad (6.180)$$

In Fig. 6.3 we have displayed the diagrammatic representation of Eq. (6.180) in terms of Hugenholtz diagrams. Using the rules in Table II of Chapter 3 for interpreting diagrams with the modifications to rule 3 similar to those discussed in Section 6.D.2.d, we may interpret the A_1 matrix as giving rise

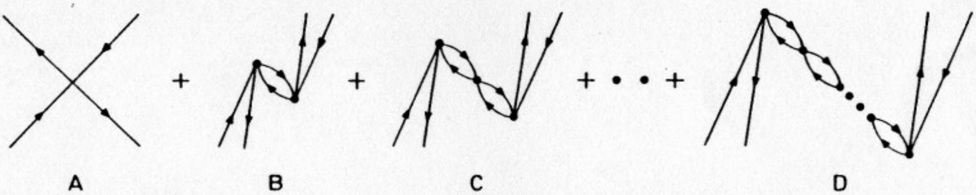

FIG. 6.3. The RPA diagram series, which can be summed to infinite order.

to diagram A in Fig. 6.3. The fourth, fifth, etc. terms in Eq. (6.180) may similarly be interpreted as giving rise to diagrams B, C, etc. in Fig. 6.3. The TDHF approximation to the PP propagator thus corresponds to summing the infinite series of diagrams represented in Fig. 6.3. We emphasize that an explicit summation of this whole series of diagrams is obtained when poles of the PP are determined as described in Section E.2.

A propagator that determines the poles consistently through second order is determined from a partitioned form of Eq. (6.173) to be

$$\mathsf{P}_2(E) = E\mathsf{1} + \mathsf{A}_{0+1+2} - \mathsf{C}_1^{\mathsf{T}}\mathsf{D}_0^{-1}\mathsf{C}_1 - \mathsf{B}_1(-E\mathsf{1} + \mathsf{A}_0)^{-1}\mathsf{B}_1 \qquad (6.181)$$

All terms of order higher than two have been neglected in Eq. (6.181). In Fig. 6.4 we have displayed all the second-order PP diagrams. The A_2 matrix gives rise to diagrams A and B in Fig. 6.4, whereas the term $-\mathsf{C}^{\mathsf{T}}\mathsf{D}_0^{-1}\mathsf{C}_1$ gives diagrams C through H. The last term in Eq. (6.181) corresponds to diagram I in Fig. 6.4. This diagram is the second diagram in the above described TDHF series. We again stress that a determination of the poles of the PP that contain all diagrams through second order [Eq. (6.181)] differs from the approximation we derived in Section E.4.c, which contained all matrices of the PP through second order. A diagrammatric interpretation of this group of matrices would further contain many series of diagrams that would be summed to infinite order. One of these series would be the TDHF series given in Fig. 6.3. We do not go further into the diagrammatic

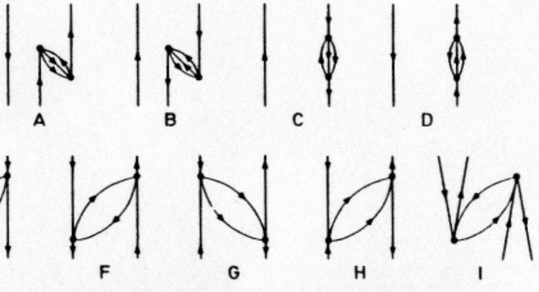

Fig. 6.4. All Hugenholtz second-order PP diagrams.

interpretation of the PP here; rather we refer the reader to the more comprehensive discussion given in the literature (Oddershede and Jørgensen, 1977).

PROBLEMS

6.1

1. Use the formulas for the second-order matrix $\mathsf{P}_2(E)$ appearing in Eq. (6.79) to express the 2×2 matrix relevant to evaluating the ionization potential and electron affinities of the minimal-basis HeH^+ problem.

2. Using the SCF orbital energies and two-electron integrals given in Problem 2.1, insert numerical values for the requisite integrals and orbital energies to express each of the elements of the 2×2 matrix $\mathsf{P}_2(E)$ as functions of E.

3. Use the approximation $(\mathsf{P}_2)_{11} = 0$ to compute the value of E at which the primary ionization potential of HeH^+ would be expected. This is done by using the Koopmans' theorem estimate in the denominators occurring in the self-energy terms and then solving for the "corrected" value of E.

4. Use the approximation $(\mathsf{P}_2)_{22} = 0$ to compute the value of E at which the primary electron affinity of HeH^+ would be expected.

5. Are the values of E found in questions 3 and 4 the only values of E that make $(\mathsf{P}_2)_{11}$ or $(\mathsf{P}_2)_{22}$ vanish?

6.2 Carry out a TDHF calculation for HeH^+, using the minimal basis data of Problem 2.1. The SCF calculation was carried out in Problem 2.1, and the matrix elements necessary for carrying out the TDHF calculation are given in Problem 5.2.

1. Determine the excitation energies and transition moments in the TDHF approximation.

2. Determine the frequency dependent polarizability tensor for $E = 0$ and for $E = 0.1$ a.u.

6.3 Carry out an MCTDHF calculation for HeH^+ that has an MCSCF reference state containing the configurations $1\sigma^2$ and $2\sigma^2$ and that uses the data of Problem 2.1. The MCSCF calculation was carried out in Problem 2.6, and most of the matrix elements necessary for carrying out the MCTDHF calculation are given in Problem 5.3.

1. Determine the excitation energies and transition moments in the MCTDHF approximation.

2. Compare the excitation energies and transition moments obtained here with the results of the full-CI calculation of Problem 5.1. Why are the two sets of results identical?

3. Determine the frequency-dependent polarizability tensor for $E = 0$ and for $E = 0.1$ a.u. in the the MCTDHF approximation. Compare the

MCTDHF polarizability with the coupled multiconfiguration HF result of Problem 5.3 and the full-CI result in Problem 5.1. Why do these three results agree?

SOLUTIONS

6.1

1. Because we have a closed-shell reference state, one can compute $(\mathsf{P}_2)_{ij}$ for i and j having $m_s = \pm 1/2$. The terms having spins $i = \alpha$, $j = \beta$, vanish since $|0\rangle$ is an eigenfunction of S_z. Let us take i and j to be α spin:

$$(\mathsf{P}_2)_{ij} = \delta_{ij}(E + \varepsilon_i) - \sum_{\substack{m<n\\ \gamma}} \frac{\langle i\gamma||mn\rangle\langle mn||j\gamma\rangle}{\varepsilon_m + \varepsilon_n - \varepsilon_\gamma + E} - \sum_{\substack{\gamma<\delta\\ m}} \frac{\langle im||\gamma\delta\rangle\langle\gamma\delta||jm\rangle}{\varepsilon_\gamma + \varepsilon_\delta - \varepsilon_m + E}$$

Because HeH$^+$ has only one occupied orbital, the second sum above must have $\gamma = 1\sigma\alpha$, $\delta = 1\sigma\beta$, and (because i is α spin) $m = 2\sigma\beta$. Likewise, the first sum must have $m = 2\sigma\alpha$, $n = 2\sigma\beta$, and hence $\gamma = 1\sigma\beta$. Therefore,

$$(\mathsf{P}_2)_{ij} = \delta_{ij}(E + \varepsilon_i) - \frac{\langle i1|22\rangle\langle 22|j1\rangle}{2\varepsilon_2 - \varepsilon_1 + E} - \frac{\langle i2|11\rangle\langle 11|j2\rangle}{2\varepsilon_1 - \varepsilon_2 + E}$$

2. $$(\mathsf{P}_2)_{11} = E - 1.6562 - \frac{0.0159}{1.1984 + E} - \frac{0.0382}{-3.0835 + E}$$

$$(\mathsf{P}_2)_{22} = E - 0.2289 - \frac{0.00002}{1.1984 + E} - \frac{0.0159}{-3.0835 + E}$$

$$(\mathsf{P}_2)_{12} = (\mathsf{P}_2)_{21} = + \frac{0.0006}{1.1984 + E} + \frac{0.0246}{-3.0835 + E}$$

3. $$(\mathsf{P}_2)_{11} \cong 0, \qquad E = 1.6562 + \frac{0.0159}{1.1984 + 1.6562} + \frac{0.0382}{1.6562 - 3.0835}$$

$$= 1.6350$$

This iteration process could then be continued by using this value of E to form a new $(\mathsf{P}_2)_{11}$ from which a new E could be obtained.

4. $$(\mathsf{P}_2)_{22} \cong 0, \qquad E = 0.2289 + \frac{0.00002}{1.1984 + 0.2289} + \frac{0.0159}{0.2289 - 3.0835}$$

$$= 0.2233$$

5. No. Shake-up ionizations occur near $E = \varepsilon_1 - 2\varepsilon_2$ and $E = \varepsilon_2 - 2\varepsilon_1$. These arise due to the E dependence of the denominators in the above self-energy terms.

6.2

1. The singlet excitation operator $2_\alpha^+ 1_\alpha + 2_\beta^+ 1_\beta$ gives rise to the overlap

$$S_{21,21} = (2_\alpha^+ 1_\alpha + 2_\beta^+ 1_\beta | 2_\alpha^+ 1_\alpha + 2_\beta^+ 1_\beta) = 2.00$$

because of the closed-shell reference state. For these excitation operators, the A and B matrix elements given in Problem 5.2 become

$$(A_{11})_{21,21} = 2.1464, \qquad (B_{11})_{21,21} = -0.2522$$

The nonvanishing matrix element of **r** in Problem 5.2 is

$$\langle 0|z(2_\alpha^+ 1_\alpha + 2_\alpha^+ 1_\alpha)|0\rangle = 2\langle 2|z|1\rangle = 1.0884$$

The TDHF excitation energy obtained from Eq. (6.109) is

$$E_1 = 1.0657$$

and the corresponding eigenvector is

$$Z = 0.7083, \qquad Y = 0.0418, \qquad (z|0_{12}^+) = 1.0884(0.7083 - 0.0418) = 0.7255$$

2. The nonvanishing components of the polarizability tensor are

$$\langle\langle z; z\rangle\rangle_{E=0} = 0.9878 = \frac{2|(z|0_{12}^+)|^2}{E_1}$$

$$\langle\langle z; z\rangle\rangle_{E=0.1} = 0.9965 = 2\,\frac{|(z|0_{12}^+)|^2 E_1}{E_1^2 - (0.1)^2}$$

6.3

1. From Solution 5.3 we can form the elements of the 2 × 2 S matrix

$$S_{21,21} = (2_\alpha^+ 1_\alpha + 2_\beta^+ 1_\beta | 2_\alpha^+ 1_\alpha + 2_\beta^+ 1_\beta) = \langle 0|1_\alpha^+ 1_\alpha + 1_\beta^+ 1_\beta - 2_\alpha^+ 2_\alpha - 2_\beta^+ 2_\beta|0\rangle$$

Using the density matrices of Solution 5.3, we find

$$\begin{aligned}
S_{21,21} &= 2(0.9968) - 2(0.0033) = 1.9870\\
S_{21,|1\rangle} &= (2_\alpha^+ 1_\alpha + 2_\beta^+ 1_\beta | |n\rangle\langle 0|) = \langle 0|(1_\alpha^+ 2_\alpha + 1_\beta^+ 2_\beta)|1\rangle\langle 0|0\rangle = 0\\
S_{|1\rangle,|1\rangle} &= (|1\rangle\langle 0| \,|\, |1\rangle\langle 0|) = 1.0000
\end{aligned}$$

$$\mathsf{A} - \mathsf{B} = \begin{pmatrix} 2.4251 & 0.4248 \\ 0.4248 & 2.2643 \end{pmatrix}$$

$$(\mathsf{A} - \mathsf{B})^{1/2} = \begin{pmatrix} 1.5510 & 0.1393 \\ 0.1393 & 1.4983 \end{pmatrix}, \qquad (\mathsf{A} - \mathsf{B})^{-1/2} = \begin{pmatrix} 0.6501 & -0.0604 \\ -0.0604 & 0.6731 \end{pmatrix}$$

$$\mathsf{S} = \begin{pmatrix} 1.9870 & 0.0 \\ 0.0 & 1.0000 \end{pmatrix}$$

From Eq. (6.109) we know that we need $(\mathsf{A}-\mathsf{B})^{1/2}\mathsf{S}^{-1}(\mathsf{A}+\mathsf{B})\mathsf{S}^{-1}(\mathsf{A}-\mathsf{B})^{1/2}$ to find the E^2 eigenvalues:

$$(\mathsf{A}-\mathsf{B})^{1/2}\mathsf{S}^{-1}=\begin{pmatrix}0.7806 & 0.1393\\ 0.0701 & 1.4983\end{pmatrix},\qquad \mathsf{S}^{-1}(\mathsf{A}-\mathsf{B})^{1/2}=\begin{pmatrix}0.7806 & 0.0701\\ 0.1393 & 1.4983\end{pmatrix}$$

Then

$$(\mathsf{A}-\mathsf{B})^{1/2}\mathsf{S}^{-1}(\mathsf{A}+\mathsf{B})\mathsf{S}^{-1}(\mathsf{A}-\mathsf{B})^{1/2}=\begin{pmatrix}1.2998 & 1.0247\\ 1.0247 & 5.1724\end{pmatrix}$$

The two eigenvalues are $E^2 = 1.0454$ and $E^2 = 5.4266$, and the corresponding eigenvectors are $(0.9705, -0.2410)$ and $(0.2410, 0.9705)$. The excitation energies are $E = 1.0225$ and 2.3295; $(\mathbf{Z}-\mathbf{Y})$ is obtained for each state, according to Eq. (6.109) as

$$(\mathbf{Z}-\mathbf{Y})_1=(\mathsf{A}-\mathsf{B})^{-1/2}\begin{pmatrix}0.9705\\ -0.2410\end{pmatrix}=\begin{pmatrix}0.6455\\ -0.2208\end{pmatrix}$$

$$(\mathbf{Z}-\mathbf{Y})_2=(\mathsf{A}-\mathsf{B})^{-1/2}\begin{pmatrix}0.2410\\ 0.9705\end{pmatrix}=\begin{pmatrix}0.0981\\ 0.6386\end{pmatrix}$$

The $(\mathbf{Z}+\mathbf{Y})$ for each state can then be obtained from

$$(\mathbf{Z}+\mathbf{Y})=E(\mathsf{A}+\mathsf{B})^{-1}\mathsf{S}(\mathbf{Z}-\mathbf{Y})$$

or from

$$E^{-1}\mathsf{S}^{-1}(\mathsf{A}-\mathsf{B})(\mathbf{Z}-\mathbf{Y})$$

to yield

$$(\mathbf{Z}+\mathbf{Y})_1=\begin{pmatrix}0.7242\\ -0.2209\end{pmatrix},\qquad (\mathbf{Z}+\mathbf{Y})_2=\begin{pmatrix}0.1100\\ 0.6388\end{pmatrix}$$

Solving for $\mathbf{Z}$ and $\mathbf{Y}$ for each state and then renormalizing $(\mathbf{Z},\mathbf{Y})$ for each state such that

$$(\mathbf{Z}\mathbf{Y})\begin{pmatrix}\mathsf{S} & 0\\ 0 & -\mathsf{S}\end{pmatrix}\begin{pmatrix}\mathbf{Z}\\ \mathbf{Y}\end{pmatrix}=1=\mathbf{ZSZ}-\mathbf{YSY}$$

we obtain

$$\mathbf{Z}_1=\begin{pmatrix}0.6926\\ -0.2233\end{pmatrix},\qquad \mathbf{Y}_1=\begin{pmatrix}0.0397\\ -0.0001\end{pmatrix}$$

$$\mathbf{Z}_2=\begin{pmatrix}0.1596\\ 0.9747\end{pmatrix},\qquad \mathbf{Y}_2=\begin{pmatrix}0.0092\\ 0.0002\end{pmatrix}$$

The desired transition moments are given by $(\mathbf{r}|0^+)$, with

$$0^+ = \mathbf{Z}(Q^+_{21,}|1\rangle\langle 0|) + \mathbf{Y}(Q_{21,}|0\rangle\langle 1|)$$

The data of Solution 5.3 tell us that

$$\begin{aligned}(\mathbf{r}|Q^+_{21}) &= 1.1076 = -(\mathbf{r}|Q_{21})\\ (\mathbf{r}||n\rangle\langle 0|) &= -0.1551 = -(\mathbf{r}||0\rangle\langle n|)\end{aligned}$$

and so

$$\begin{aligned}(\mathbf{r}|0^+_1) &= (0.6926, -0.2233)\begin{pmatrix}1.1076\\ -0.1551\end{pmatrix} - (0.0397, -0.0001)\begin{pmatrix}1.1076\\ -0.1551\end{pmatrix}\\ &= 0.7578\end{aligned}$$

Likewise,

$$(\mathbf{r}|0^+_2) = 0.0146$$

2. The full-CI calculation gave excitation energies of 1.0225 and 2.3295. which is exactly what we get here. The CI transition moments are 0.7578 and 0.0144, which are almost identical to ours. The MCSCF reference state is identical to the full-CI wavefunction even though it contains only the $1\sigma^2$ and $2\sigma^2$ configuration. This is true because the orbitals used in the MCSCF wave function are optimized orbitals. The projection manifold operating on $|0\rangle$ then yields two more linearly independent functions, which, taken together with $|0\rangle$, form a three-dimensional space capable of describing the results of the full 3×3 CI problem. We thus have both the exact reference state and a complete projection manifold $\{T^+\}$, and the MCTDHF calculation therefore is able to reproduce the full-CI result of Problem 5.1.

3. $\alpha_{zz} = 2 \sum_{j=1}^{2} |(z|0^+_j)|^2(E_j^2 - E^2)^{-1}E_j$

$$E = 0.0, \qquad \alpha_{zz} = 2\left[\frac{0.7578^2}{1.0225} + \frac{0.0146^2}{2.3295}\right] = 1.1234$$

$$E = 0.1, \qquad \alpha_{zz} = 2\left[\frac{0.7578^2(1.0225)}{1.0454 - 0.01} + \frac{0.0146^2(2.3295)}{5.4266 - 0.01}\right] = 1.1344$$

All three calculations have the potential of giving the full-CI result as discussed in question 2.

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