

A. CLASSES OF PROPERTIES

Given wavefunctions belonging to one or more states that are obtained from an MCSCF, HF, CI, RSPT, or CC calculation, one is often interested in subsequently using these wavefunctions to compute physical properties of the system other than the total electronic energy. Below we discuss how the three distinct classes of properties—expectation values, transition properties, and response properties—may be evaluated, and we show also how stationary points on the potential energy surface may be determined using a quadratically convergent procedure.

1. Expectation Values

State average values such as dipole and quadrupole moments and electron spin densities are usually evaluated as expectation values of their corresponding quantum-mechanical operators. For example, the electronic contribution to the dipole moment operator is

$$\mathbf{r} = \sum_{i,j} e \langle \phi_i | \mathbf{r} | \phi_j \rangle i^+ j \quad (5.1)$$

and the electronic contribution to the dipole moment of state $|0\rangle$ thus becomes $-\langle 0 | \mathbf{r} | 0 \rangle$. In evaluating expectation values, we must be careful that the wavefunction being used is of sufficiently high quality to permit accurate results. For example, in computing the expectation value of the electronic contributions to the dipole moment beyond the SCF level, it is important to include singly excited configurations in the CI or MCSCF wavefunction. A perturbation analysis of the order in which singly excited, doubly excited, etc. configurations enter in the calculation of the dipole moment makes this statement easily understood. The first-order RSPT function, which includes only doubly excited configurations (relative to the single determinantal zeroth-order

function $|0^0\rangle$), yields a dipole moment average value that differs from $\langle 0^0|r|0^0\rangle$ only in second order since $\langle 0^0|r|_{\alpha\beta}^{rs}\rangle$ vanishes as a result of the fact that r is a one-electron operator. As both the singly and doubly excited states contribute in second order, it becomes equally important to include both singly and doubly excited configurations in the calculation. This observation demonstrates the point that those configurations that are optimal for describing the total electronic energy may not be adequate for obtaining accurate expectation values. This conclusion is now generally accepted as applying to all types (MCSCF, CI, HF, CC) of wavefunctions and is important to keep in mind when choosing which configurations to employ in any calculation.

Within the class of expectation values, we might also include calculations of electronic excitation and ionization energies as differences in individual state energies. The excitation and ionization energies are small numbers compared to the individual state total energies. For this reason, alternative procedures have been developed that can be employed to directly calculate such excitation (and ionization) energies as well as their corresponding oscillator strengths and that avoid the difficulties that might appear when subtracting two large numbers the difference of which is a small number. These direct evaluation techniques are based upon the so-called Green's function (GF) methods described in Chapter 6. The energy differences obtained either from a GF or by subtracting two wavefunction expectation values no longer have the upper bound property that individual state energies possess. Thus, there is no fundamental reason to insist that excitation energies be calculated as differences between state expectation values each of which are upper bounds to two state energies.

2. Transition Properties

The second class of quantities in which one is likely to be interested we refer to as transition properties. They include, for example, the electric dipole transition moment $\langle 0|r|n\rangle$ between stationary states $|0\rangle$ and $|n\rangle$. The primary difficulty in evaluating such transition moments has to do with treating the overlap between nonorthogonal orbitals that arises in computing $\langle 0|i^+j|n\rangle$. That is, unless $|n\rangle$ and $|0\rangle$ are both expressed as linear combinations of determinants involving a common set of orthonormal spin-orbitals, the determinants in $|n\rangle$ will not be orthogonal to those in $|0\rangle$. Rather than being an exceptionally rare situation, this is actually the most likely case. For example, MCSCF calculations or INO-CI calculations on two electronic states of a molecule invariably result in different optimal (MCSCF or INO) orbitals for the two states. Although these nonorthogonality problems do indeed make the evaluation of transition properties quite difficult, it is still possible to compute the requisite overlap matrices and thereby obtain the

desired quantity. However, this formidable difficulty provides strong motivation for us to treat the evaluation of transition moments through the GF framework as described in Chapter 6. Suffice it to say for now that these GF methods are designed to yield both transition moments and electronic energy differences directly rather than as matrix elements and energy differences of two separate states.

3. Response Properties

In addition to expectation values and transition moments, we have a third class of important physical properties, which we refer to as second-order response properties. To develop some understanding for the meaning of and theoretical methods for studying these responses, let us investigate the response of a state $|0\rangle$ corresponding to H to an external time-independent one-electron perturbation (αH_1)

$$H \rightarrow H + \alpha H_1 \quad (5.2)$$

Such perturbations could, for example, include electric field ($\alpha = \mathcal{E}$) effects or nuclear coordinate displacements. The total electronic energy in the presence of the perturbation becomes a function of α and may (for small α) be expanded in a power series

$$E(\alpha) = \langle \tilde{0} | H + \alpha H_1 | \tilde{0} \rangle = E_0 - \alpha E_1 - \frac{1}{2} \alpha^2 E_2 - \frac{1}{6} \alpha^3 E_3 - \frac{1}{24} \alpha^4 E_4 \dots \quad (5.3)$$

The terms that are nonlinear in α arise because the state wavefunction $|\tilde{0}\rangle$ depends on α (i.e., the state has responded to αH_1 , which gives rise to the name "response property"). When, for example, αH_1 represents a static electric field ($\alpha H_1 = \mathcal{E} \cdot \mathbf{r}$), E_1 yields the permanent electric dipole moment (μ) of the unperturbed state $|0\rangle$, E_2 gives this state's polarizability (α), and E_3, E_4 , etc. yield successively higher hyperpolarizabilities (β, γ , etc.).

a. Finite-Field Approach

One way of determining the first- and second-order response properties would be to calculate the total electronic energy of the system with αH_1 present (using the CI, HF, RSPT, MCSCF, or CC method) for several small values of α and to then attempt to fit these computed $E(\alpha)$ values to the series given in Eq. (5.3). This numerical procedure is usually referred to as the finite-field method. As an alternative to performing a least-squares fit to Eq. (5.3) one may, by judiciously choosing the values of the field at which $E(\alpha)$ is computed, employ versions of Eq. (5.3) that contain only odd or even powers of α [$E_{\pm} = E(\alpha) \pm E(-\alpha)$]. Furthermore, by combining computed values of $E_{\pm}(\alpha)$ and $E_{\pm}(2\alpha)$, one can selectively remove higher (odd or even) powers of α from the resultant equation. For example, by using $-\frac{2}{3}E_{-}(\alpha) + \frac{1}{12}E_{-}(2\alpha)$ one obtains $E_1\alpha + O(\alpha^5)$ since the $E_3\alpha^3$ was cancelled by taking the

proper $(-\frac{2}{3}, \frac{1}{12})$ combination of $E_-(\alpha)$ and $E_-(2\alpha)$. Alternatively, using $E_+(\alpha)$ and $E_+(2\alpha)$ one can obtain

$$-\frac{4}{3}E_+(\alpha) + \frac{1}{12}E_+(2\alpha) + \frac{5}{2}E_0 + O(\alpha^6) = \alpha^2 E_2 \quad (5.4)$$

Again, notice the cancellation of the power of α two higher than the power occurring in the property being evaluated. These finite-difference fits (Bartlett and Purvis, 1979) of Eq. (5.3) to calculated values of $E(\alpha)$ then permit one to obtain the dipole moment μ from E_1 and the polarizability from E_2 .

Although the numerical procedure outlined above may permit one to efficiently and precisely extract from computed energy values $[E(\alpha)]$ the desired response properties, it by no means guarantees the accuracy of these properties. The accuracy of the computed response properties is determined by the quality of the wavefunction $|\tilde{0}\rangle$ used to evaluate $E(\alpha)$. It is not at all straightforward to choose an atomic basis set that permits the orthonormal molecular orbitals appearing in $|\tilde{0}\rangle$ to properly polarize in the presence of the field. Furthermore, it is difficult to choose a set of configurations for use in constructing $|\tilde{0}\rangle$ that is certain to yield the same accuracy in the computed $E(\alpha)$ values for all values of the field strengths α . Because of these difficulties, it is important to look for alternative methods for computing response properties. In Section B, we outline an analytical approach to this problem that does not involve fitting values of the energy that are computed at finite values of the applied-field strength.

b. Analytical Approach

As an alternative that does not suffer from these difficulties, analytical expressions for the response properties may be derived. If we are able to obtain a closed-form expression for the response of a state wavefunction $|0\rangle$ to the presence of the "field" αH_1 ,

$$|\tilde{0}\rangle = A^{-1/2}[|0\rangle + \alpha|0^1\rangle + \alpha^2|0^2\rangle + \dots] \quad (5.5)$$

(A is a normalization constant), then this result can be used in Eq. (5.3) to express the Hamiltonian expectation value $\langle\tilde{0}|H + \alpha H_1|\tilde{0}\rangle$ as a power series in α , upon which the desired second-order response is identified as the multiplier of α^2 . Of course, for each specific choice of the form of $|0\rangle$ (i.e., MCSCF, CI, RSPT, CC) the prescription for evaluating Eq. (5.5) is different; the basic approach is, however, identical for all such wavefunctions.

B. MCSCF TREATMENT OF RESPONSE

To illustrate the analytical approach, let us consider how an MCSCF wavefunction would respond to a one-electron external perturbation of the form

$$H \rightarrow H + \alpha H_1 + \alpha^2 H_2 \quad (5.6)$$

The total energy of the system in the presence of the external field may be written as

$$\begin{aligned}
 E(\alpha, \lambda, S) &= \langle 0 | \exp(-iS) \exp(-i\lambda)(H + \alpha H_1 + \alpha^2 H_2) \exp(i\lambda) \exp(iS) | 0 \rangle \\
 &= \langle 0 | H + \alpha H_1 + \alpha^2 H_2 | 0 \rangle - i \langle 0 | [S + \lambda, H + \alpha H_1] | 0 \rangle \\
 &\quad + \frac{1}{2} \langle 0 | [S, [H, S]] | 0 \rangle + \frac{1}{2} \langle 0 | [\lambda, [H, \lambda]] | 0 \rangle \\
 &\quad + \langle 0 | [S, [H, \lambda]] | 0 \rangle + \dots
 \end{aligned} \tag{5.7}$$

The values of \mathbf{P} and $\boldsymbol{\kappa}$ appearing in S and λ , respectively, may be expanded as power series in α :

$$S = S^{(0)} + \alpha S^{(1)} + \alpha^2 S^{(2)} + \dots \tag{5.8}$$

$$\lambda = \lambda^{(0)} + \alpha \lambda^{(1)} + \alpha^2 \lambda^{(2)} + \dots \tag{5.9}$$

Since the λ and S operators are determined by making the total energy expression in Eq. (5.7) stationary, the zeroth-order terms that appear in Eqs. (5.8) and (5.9) become zero because the state $|0\rangle$ was optimized in the absence of the one-electron perturbation. The terms $-i \langle 0 | [\lambda^{(1)} + S^{(1)}, H] | 0 \rangle$, which are of first order in α , and $-i \langle 0 | [\lambda^{(2)} + S^{(2)}, H] | 0 \rangle$, which are of second order, vanish because of the GBT. Hence, in Eq. (5.7) all of the terms remaining should be viewed as containing $\lambda^{(1)}$ and $S^{(1)}$ since we are only keeping terms up through α^2 in our energy expansion.

Using Eqs. (2.29) and (2.30), we may express the above total energy in a form similar to the one given in Eq. (2.25):

$$\begin{aligned}
 E(\alpha, \lambda, S) &= E(0, 0, 0) + \alpha \langle 0 | H_1 | 0 \rangle + \alpha^2 \langle 0 | H_2 | 0 \rangle \\
 &\quad - \alpha 2(\boldsymbol{\kappa} \mathbf{P}) \begin{pmatrix} \mathbf{F} \\ \mathbf{G} \end{pmatrix} + (\boldsymbol{\kappa} \mathbf{P})(\mathbf{A} - \mathbf{B}) \begin{pmatrix} \boldsymbol{\kappa} \\ \mathbf{P} \end{pmatrix} + \dots
 \end{aligned} \tag{5.10}$$

where the matrices \mathbf{F} and \mathbf{G} are defined as

$$\mathbf{F} = \langle 0 | [Q, H_1] | 0 \rangle \tag{5.11}$$

$$\mathbf{G} = \langle 0 | [R, H_1] | 0 \rangle \tag{5.12}$$

and Q and R are given in Eq. (2.26).

Since the total energy must be stationary in the presence of the external perturbation, we may determine $\boldsymbol{\kappa}$ and \mathbf{P} from Eq. (5.10). Neglecting third- and higher-order terms, we obtain by differentiating with respect to $\boldsymbol{\kappa}$ and \mathbf{P}

$$-2\alpha \begin{pmatrix} \mathbf{F} \\ \mathbf{G} \end{pmatrix} + 2(\mathbf{A} - \mathbf{B}) \begin{pmatrix} \boldsymbol{\kappa} \\ \mathbf{P} \end{pmatrix} = 0 \tag{5.13}$$

which may be written as

$$\begin{pmatrix} \boldsymbol{\kappa} \\ \mathbf{P} \end{pmatrix} = \alpha(\mathbf{A} - \mathbf{B})^{-1} \begin{pmatrix} \mathbf{F} \\ \mathbf{G} \end{pmatrix} \tag{5.14}$$

Note that the $A - B$ matrix is evaluated from Eqs. (2.29) and (2.30) and does not contain H_1 or H_2 . Using Eq. (5.14) to eliminate κ and \mathbf{P} in Eq. (5.10), we obtain an expansion of the total energy as a function of α :

$$E(\alpha) = \langle 0|H|0\rangle + \alpha\langle 0|H_1|0\rangle + \alpha^2\langle 0|H_2|0\rangle - \alpha^2(\mathbf{F}\mathbf{G})(\mathbf{A} - \mathbf{B})^{-1}\begin{pmatrix} \mathbf{F} \\ \mathbf{G} \end{pmatrix} + O(\alpha^3) \quad (5.15)$$

Notice that in this MCSCF result, the multiplier of α is equal to the expectation value of the perturbation operator H_1 . We have thus obtained an analytical expression from which to determine the desired first- and second-order response properties. This analytical approach for determining the second-order properties is referred to as the coupled multiconfiguration Hartree-Fock (CMCHF) approach (Dalgaard and Jørgensen, 1978).

If only one configuration is used for expanding the reference state $|0\rangle$ the above development can still be used to give

$$E(\alpha) = \langle 0|H|0\rangle + \alpha\langle 0|H_1|0\rangle + \alpha^2\langle 0|H_2|0\rangle - \alpha^2\mathbf{F}(\mathbf{A}_{11} - \mathbf{B}_{11})^{-1}\mathbf{F} + O(\alpha^3) \quad (5.16)$$

where \mathbf{A}_{11} and \mathbf{B}_{11} are defined in Eqs. (2.29) and (2.30). This approximation to second-order properties has been denoted the coupled Hartree-Fock (CHF) method.

C. CI RESPONSE PROPERTIES

In a CI approach to this same problem, the variation of the reference state is described through variations in the configuration expansion coefficients. These variations may be described either by the $\exp(iS)$ operator or through the linear variational parameters C_{g0} . Because orbital variations are not considered in such a CI calculation, first- and second-order properties may be easily determined from Eq. (5.15) by neglecting all terms that involve the orbital optimization parameter κ :

$$E(\alpha) = \langle 0|H|0\rangle + \alpha\langle 0|H_1|0\rangle - \alpha^2\mathbf{G}\mathbf{A}_{22}^{-1}\mathbf{G} + O(\alpha^3) + \alpha^2\langle 0|H_2|0\rangle \quad (5.17)$$

where

$$\mathbf{G}_n = \langle n|H_1|0\rangle \quad (5.18)$$

and

$$(\mathbf{A}_{22})_{mn} = \langle m|H|n\rangle - \delta_{mn}\langle 0|H|0\rangle \quad (5.19)$$

The matrix \mathbf{A}_{22} contains the CI matrix involving all states $|n\rangle$ except the reference state $|0\rangle$. Carrying out a CI calculation (with H not including αH_1) within this orthogonal complement space would lead to the following famil-

iar expression for the second-order property:

$$\mathbf{GA}_{22}^{-1}\mathbf{G} = \sum_{n \neq 0} |\langle 0|H_1|n\rangle|^2 (E_n - E_0)^{-1} \quad (5.20)$$

However, this diagonalization of $\langle n|H|m\rangle$ is not necessary; Eq. (5.17) still gives the CI approximation to the desired second-order property. It should be noted that the second-order properties obtained from Eq. (5.20) simulate a finite-field CI calculation where the same orbitals are used to obtain the total energy at various strengths of the field. Hence, it is appropriate to take $\boldsymbol{\kappa} = \mathbf{0}$ in deriving Eq. (5.20) because the orbitals used have not been determined in the presence of the external field.

A finite-field CI calculation in which the orthonormal orbitals used to construct $|0\rangle$ are determined via an SCF calculation in the presence of the applied field could not easily be described in the analytical framework given here. Taking $\boldsymbol{\kappa} = \mathbf{0}$ is not appropriate because the orbitals are "optimized" with the field present. However, the orbitals are determined from a single-configuration (SCF) calculation rather than through the simultaneous optimization of $\boldsymbol{\kappa}$ and \mathbf{P} for a multiconfiguration wavefunction. Hence a significant disadvantage of such a finite-field CI method is that it can not easily be directly connected with the analytical response equation given earlier.

D. THE HELLMANN-FEYNMAN THEOREM

It follows from the above MCSCF-based derivation that the Hellmann-Feynman theorem is fulfilled both for SCF and MCSCF wavefunctions since Eq. (5.15) yields, upon differentiation with respect to α ,

$$\left. \frac{dE(\alpha)}{d\alpha} \right|_{\alpha=0} = \langle 0|H_1|0\rangle \quad (5.21)$$

It should, however, be pointed out that this result is a consequence of the fact that the SCF and MCSCF wavefunctions $|0\rangle$ have been optimized with respect to all variational parameters in $|0\rangle$ and that $\lambda^{(0)}$ and $S^{(0)}$ in Eqs. (5.8) and (5.9) therefore vanish. If the orbital optimization is carried out using a limited number of the total set of variational parameters in $|0\rangle$, the expansions in Eqs. (5.8) and (5.9) contain zeroth-order elements. The expansion of the total energy $E(\alpha)$ would then contain first-order terms in α beyond $\langle 0|H_1|0\rangle$ and the Hellmann-Feynman theorem would therefore not be fulfilled. This is the case in a limited CI calculation where the orbital variations are not considered explicitly [Eq. (5.9) contains zeroth-order terms]. Of course, the Hellmann-Feynman theorem is fulfilled in the full CI limit, where the orbital optimization parameters are redundant.

THE COUPLED-CLUSTER RESPONSE PROPERTIES

The above described linear-response approach to calculating first- and second-order properties can also be applied within the CC and RSPT frameworks. In the former (Monkhorst, 1977) theory we consider the CC working equations for a Hamiltonian to which a one-electron perturbation αH_1 has been added:

$$H(\alpha) = H + \alpha H_1 \quad (5.22)$$

$$\exp[-T(\alpha)]H(\alpha)\exp[T(\alpha)]|0^0\rangle = E(\alpha)|0^0\rangle \quad (5.23)$$

Neglecting the variations in the orbitals when the field is applied, the equation for E and the cluster amplitudes $t_{\alpha\beta}^{rs}\dots$,

$$\langle 0^0 | \exp[-T(\alpha)]H(\alpha)\exp[T(\alpha)]|0^0\rangle = E(\alpha) \quad (5.24)$$

and

$$\langle t_{\alpha\beta}^{rs}\dots | \exp[-T(\alpha)]H(\alpha)\exp[T(\alpha)]|0^0\rangle = 0 \quad (5.25)$$

can be expanded in powers of the field α once the cluster operators $T(\alpha)$ and $E(\alpha)$ are so expanded:

$$T(\alpha) = T^0 + \alpha T^{(1)} + \alpha^2 T^{(2)} + \dots \quad (5.26)$$

$$E(\alpha) = E^0 + \alpha E^{(1)} + \alpha^2 E^{(2)} + \dots \quad (5.27)$$

The resultant first- and second-order equations read

$$E^{(1)} = \langle 0^0 | \exp(-T^0)\{H_1 + [H, T^{(1)}]\} \exp(T^0)|0^0\rangle \quad (5.28)$$

$$0 = \langle t_{\alpha\beta}^{rs}\dots | \exp(-T^0)\{H_1 + [H, T^{(1)}]\} \exp(T^0)|0^0\rangle \quad (5.29)$$

and

$$E^{(2)} = \langle 0^0 | \exp(-T^0)\{[H_1, T^{(1)}] + \frac{1}{2}[[H, T^{(1)}], T^{(1)}] + [H, T^{(2)}]\} \exp(T^0)|0^0\rangle \quad (5.30)$$

$$0 = \langle t_{\alpha\beta}^{rs}\dots | \exp(-T^0)\{[H_1, T^{(1)}] + \frac{1}{2}[[H, T^{(1)}], T^{(1)}] + [H, T^{(2)}]\} \exp(T^0)|0^0\rangle \quad (5.31)$$

respectively. The zeroth-order (in α) equations are, of course, nothing but the original CC equations in the absence of αH_1 . We assume that we have already solved these equations. It is probably most reasonable to choose $T^{(1)}$ and $T^{(2)}$ to contain the operators $r^+ s^+ \dots \alpha \beta \dots$, which are of no higher cluster size than those in T^0 (e.g., $T^0 = T_1 + T_2$ is quite likely to be chosen for physical and practical reasons).

The above first-order equation for $T^{(1)}$ [Eq. (5.29)] expresses a set of linear algebraic equations for the cluster amplitudes in $T^{(1)}$, which can be written

in matrix form as

$$D\mathbf{t}^{(1)} = \mathbf{H}_1 \quad (5.32)$$

where the elements of \mathbf{H}_1 and D , respectively, are

$$-\langle \alpha\beta \dots | \exp(-T^0) H_1 \exp(T^0) | 0^0 \rangle, \\ \langle \alpha\beta \dots | \exp(-T^0) [H, p^+ q^+ \dots \gamma\delta \dots] \exp(T^0) | 0^0 \rangle$$

In principle, D and \mathbf{H}_1 can be computed in terms of the known (unperturbed) cluster amplitudes and integrals involving the H_1 operator. The second-order equation that determines $T^{(2)}$ can also be expressed as a set of linear algebraic equations

$$D\mathbf{t}^{(2)} = \mathbf{C} \quad (5.33)$$

where D was given above and \mathbf{C} has elements

$$-\langle \alpha\beta \dots | \exp(-T^0) \{ [H_1, T^{(1)}] + \frac{1}{2} [[H, T^{(1)}], T^{(1)}] \} \exp(T^0) | 0^0 \rangle$$

Clearly, the evaluation of \mathbf{C} requires that Eq. (5.32) first be solved for $T^{(1)}$. Then given $T^{(1)}$ and $T^{(2)}$, Eqs. (5.28) and (5.30) can be used to obtain the desired first- and second-order response properties as $E^{(1)}$ and $E^{(2)}$, respectively. We should point out that the term $T^{(2)}$ arising in this CC development has no analog in the MCSCF treatment given earlier. The absence of such quadratic terms in the MCSCF analog arises because, even if the energy expression given in Eq. (5.7) contained the term $-i\langle 0 | [S^{(2)} + \lambda^{(2)}, H] | 0 \rangle$, it would vanish by the GBT. In the CC treatment of $E^{(2)}$ one needs both $T^{(1)}$ and $T^{(2)}$ because the CC wavefunction does not obey a GBT. We should also mention that, unlike the analogous result for the MCSCF response properties, the CC linear response energy $E^{(1)}$ is not simply equal to the average value of H_1 . The term $\langle 0^0 | \exp(-T^0) [H, T^{(1)}] \exp(T^0) | 0^0 \rangle$ has no counterpart in the MCSCF expression for $E^{(1)}$. In the event that the CC unperturbed energy $\langle 0^0 | \exp(-T^0) H \exp(T^0) | 0^0 \rangle$ were stationary with respect to variations in T , this term would vanish.

F. PERTURBATIVE CALCULATION OF RESPONSE PROPERTIES

The RSPT or MBPT approach to computing response properties for atomic and molecular system is, in principle, straightforward (Kelly, 1969; Barlett and Silver, 1975). The perturbed Hamiltonian $H + \alpha H_1$ is decomposed into an unperturbed part H^0 , which is most commonly taken to be a HF Hamiltonian, and a perturbation that contains both αH_1 and $(H - H^0)$:

$$H(\alpha) = H^0 + \alpha H_1 + H - H^0 \quad (5.34)$$

Then RSPT or MBPT is employed, as discussed in Chapter 3, to calculate perturbation corrections to the system energy. However, the terms $E_j^{(n)}$ are no longer simply grouped together according to their order in the total perturbation $\alpha H_1 + (H - H^0)$ but rather they are regrouped and labeled by two order indices $E_j^{(n,m)}$, which tell their separate orders in αH_1 and $(H - H^0)$, respectively. This additional decomposition is introduced because it is not practical to formulate a perturbation theory of the system's response to αH_1 in terms of the exact eigenstates of the full H .

The desired first- and second-order response properties of the state $|j\rangle$ are calculated by summing $E_j^{(1,m)}$ and $E_j^{(2,m)}$, respectively, over the index m labeling order in $H - H^0$:

$$E^{(1)} = \sum_{m=0}^{\infty} E_j^{(1,m)} \quad (5.35)$$

$$E^{(2)} = \sum_{m=0}^{\infty} E_j^{(2,m)} \quad (5.36)$$

For practical reasons related to difficulty and expense in evaluating the higher-order contributions to $E_j^{(1,m)}$ and $E_j^{(2,m)}$, the index m is usually limited to rather small values.

Either the algebraic methods of RSPT or the diagrammatic methods of MBPT can be used to evaluate $E_j^{(1,m)}$ and $E_j^{(2,m)}$, as described in Chapter 3 in terms of the usual orbital energies, two-electron integrals, and one-electron integrals involving H_1 ($\langle \phi_r | H_1 | \phi_s \rangle$). Because both forms of perturbation theory yield energies that are size consistent, the evaluation of response properties as $E^{(1)}$ and $E^{(2)}$ guarantees that these properties will also be size consistent. As an example of how second-order properties may be evaluated, we display in Fig. 5.1 for a set of HF orbitals all of the zeroth- and first-order (in electron interaction) diagrams appropriate to a second-order response property whose perturbation operator [αH_1 of Eq. (5.2)] is denoted by a square figure. The evaluation of each of these diagrams is treated in the

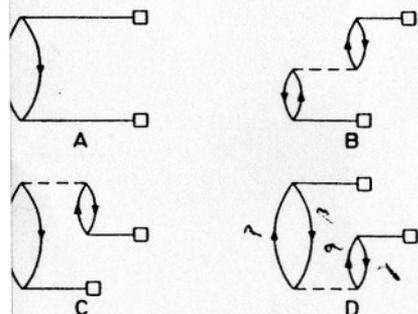


FIG. 5.1. All zeroth- and first-order diagrams for a second-order response property.

manner described in Table II of Chapter 3 with the matrix elements of the (one-electron) perturbation αH_1 being treated as the one-electron operator V . For example, the value of diagram D in Fig. 5.1 is given by

$$D = (-1)^{2+2} \sum_{\substack{pq \\ \gamma\beta}} \frac{\langle \beta | \alpha H_1 | p \rangle \langle pq | | \beta \gamma \rangle \langle \gamma | \alpha H_1 | q \rangle}{(\epsilon_\gamma + \epsilon_\beta - \epsilon_p - \epsilon_q)(\epsilon_\beta - \epsilon_\gamma)} \quad (5.37)$$

The evaluation of all the diagrams in Fig. 5.1 would thus give the desired second-order property consistent through first order in electronic interaction.

G. MOLECULAR GRADIENTS AND FORCE CONSTANTS

The determination of minima and saddle points on the potential-energy surface of a molecule plays an important role (Schaefer and Miller, 1977, Chapter 4) in describing the electronic structure and chemical reactivity of molecules. In this section, we show how such stationary points on a molecule's potential energy surface may be found by using an approach similar to that employed in Section 5.B. We first consider how the electronic Hamiltonian changes when the nuclear positions are changed from an initial set of positions, \mathbf{R}_A^0 to \mathbf{R}_A , i.e., $\mathbf{R}_A \rightarrow \mathbf{R}_A^0 + \mathbf{u}_A$. The electron-nuclear interaction is the only term in the Hamiltonian that depends explicitly on the nuclear position. Performing a Taylor expansion of this potential about the point \mathbf{R}_A^0 , we obtain

$$|\mathbf{r} - \mathbf{R}_A|^{-1} = |\mathbf{r} - \mathbf{R}_A^0 - \mathbf{u}_A|^{-1} = |\mathbf{r} - \mathbf{R}_A^0|^{-1} - (\mathbf{u}_A \cdot \nabla) |\mathbf{r} - \mathbf{R}_A^0|^{-1} + \frac{1}{2} (\mathbf{u}_A \cdot \nabla)^2 |\mathbf{r} - \mathbf{R}_A^0|^{-1} + O(\mathbf{u}_A^3) \quad (5.38)$$

We may thus identify the changes in the electronic Hamiltonian through second order in the nuclear displacements (\mathbf{u}_A) as

$$V_1 = \sum_{\substack{A \\ ts}} + Z_A \langle \phi_t | [(\mathbf{u}_A \cdot \nabla) |\mathbf{r} - \mathbf{R}_A^0|^{-1}] | \phi_s \rangle t^+ s \quad (5.39)$$

$$V_2 = \sum_{\substack{A \\ ts}} - \frac{1}{2} Z_A \langle \phi_t | (\mathbf{u}_A \cdot \nabla)^2 |\mathbf{r} - \mathbf{R}_A^0|^{-1} | \phi_s \rangle t^+ s \quad (5.40)$$

Here, V_1 clearly represents the forces on the electrons due to the nuclear displacement, whereas V_2 describes electric-field gradient terms induced by movement of the nuclei. A stationary point on the potential energy surface occurs when the average value of the first-order term is zero:

$$\langle 0 | V_1 | 0 \rangle = 0 \quad (5.41)$$

As demonstrated below, stationary points on the potential-energy surface may be determined in a quadratically convergent procedure using an analytical expression for the total energy that is accurate through second order in the nuclear displacement, and a Newton-Raphson procedure to determine the step length of the nuclear displacement. We now develop a procedure for carrying out such gradient calculations when $|0\rangle$ refers to a MCSCF wavefunction. Since the changes in the electronic Hamiltonian are determined in Eqs. (5.39) and (5.40) through second order in the nuclear displacement, an analytical expression of the total energy through second order in the nuclear displacement may be determined from the coupled multiconfiguration HF expression for the total energy given in Eq. (5.15) since αH_1 is identified as V_1 and $\alpha^2 H_2$ as V_2 . The first-order term $\alpha \langle 0|H_1|0\rangle$ in Eq. (5.15) may be written as

$$\langle 0|V_1|0\rangle = \sum_A \mathbf{u}_A \cdot \mathbf{V}_{1A} \quad (5.42)$$

where the cartesian components of the force vector for displacement of nucleus A are

$$\mathbf{V}_{1A} = (V_{1A}^x, V_{1A}^y, V_{1A}^z) \quad (5.43)$$

with

$$V_{1A}^i = \sum_{ts} Z_A \langle \phi_t | \left[\frac{\partial}{\partial i} |\mathbf{r} - \mathbf{R}_A^0|^{-1} \right] | \phi_s \rangle \langle 0|t^+ s|0\rangle, \quad i = x, y, z \quad (5.44)$$

The second-order term $\alpha^2 \langle 0|H_2|0\rangle$ becomes

$$\langle 0|V_2|0\rangle = \sum_A \mathbf{u}_A \cdot \mathbf{V}_{2A} \cdot \mathbf{u}_A \quad (5.45)$$

where \mathbf{V}_{2A} is a tensor operator, the components of which are defined as

$$V_{2A}^{ij} = \sum_{ts} -\frac{1}{2} Z_A \langle \phi_t | \left[\frac{\partial^2}{\partial i \partial j} |\mathbf{r} - \mathbf{R}_A^0|^{-1} \right] | \phi_s \rangle \langle 0|t^+ s|0\rangle, \quad i, j = x, y, z \quad (5.46)$$

The matrix $\alpha \mathbf{F}$ given in Eq. (5.11) may similarly be written as

$$\alpha \mathbf{F} = \sum_A \mathbf{u}_A \cdot \mathbf{F}_A \quad (5.47)$$

where

$$\mathbf{F}_A^i = \sum_{ts} Z_A \langle \phi_t | \left[\frac{\partial}{\partial i} |\mathbf{r} - \mathbf{R}_A^0|^{-1} \right] | \phi_s \rangle \langle 0|[Q, t^+ s]|0\rangle, \quad i = x, y, z \quad (5.48)$$

and an analogous expression can be written for the $\alpha \mathbf{G}$ matrix of Eq. (5.12).

The last term of Eq. (5.15) therefore can be written as

$$\sum_{AB} \mathbf{u}_A \cdot \mathbf{D}_{AB} \mathbf{u}_B \quad (5.49)$$

where the tensor operator \mathbf{D}_{AB} is defined through its components as

$$D_{AB}^{ij} = (\mathbf{F}_A^i \mathbf{G}_A^j)(\mathbf{A} - \mathbf{B})^{-1} \begin{pmatrix} \mathbf{F}_B^i \\ \mathbf{G}_B^j \end{pmatrix}, \quad i, j = x, y, z \quad (5.50)$$

The total energy that contains all terms through second order in the nuclear displacement may thus be expressed as

$$E(\mathbf{u}) = \langle 0|H|0\rangle + \sum_A \mathbf{u}_A \cdot \mathbf{V}_{1A} + \sum_{AB} \mathbf{u}_A \cdot \mathbf{M}_{AB} \cdot \mathbf{u}_B \quad (5.51)$$

where

$$\mathbf{M}_{AB} = \mathbf{V}_{2A} \delta_{AB} - \mathbf{D}_{AB} \quad (5.52)$$

is the force constant matrix. This expression contains Hellmann–Feynman force terms in \mathbf{V}_{1A} , field gradient terms in \mathbf{V}_{2A} , as well as terms in \mathbf{D}_{AB} that describe how the MCSCF orbitals and CI coefficients respond to displacements of the nuclei. A stationary point on the molecular potential energy surface is determined when $\delta E(\mathbf{u}) = 0$. Neglecting third- and higher-order terms in the energy function given in Eq. (5.51) and differentiating with respect to \mathbf{u} thus gives

$$\mathbf{V}_1 + 2\mathbf{M}\mathbf{u} = 0 \quad (5.53)$$

where \mathbf{V}_1 and \mathbf{u} are column vectors containing the elements $V_{1A}^x, V_{1A}^y, V_{1A}^z, V_{1B}^x, \dots$ and $u_A^x, u_A^y, u_A^z, u_B^x, \dots$, respectively. The elements of the matrix \mathbf{M} are defined as the components of the tensor operator \mathbf{M}_{AB} in Eq. (5.52):

$$(\mathbf{M})_{Ai, Bj} \equiv M_{AB}^{ij}, \quad i, j = x, y, z \quad (5.54)$$

The nuclear displacements are thus given as

$$\mathbf{u} = -\frac{1}{2}\mathbf{M}^{-1}\mathbf{V}_1 \quad (5.55)$$

In the above derivation we have assumed that the atomic orbital basis employed in forming the MCSCF orbitals was complete. This assumption allowed us to write [in Eqs. (5.39) and (5.40)] the Hamiltonian both at \mathbf{R}_A^0 and $\mathbf{R}_A^0 + \mathbf{u}_A$ in terms of the MCSCF orbitals, which were obtained from an MCSCF calculation performed at the “starting” geometry \mathbf{R}_A^0 . In most molecular calculations, limited basis sets are used and the basis therefore depends on the nuclear positions. This dependence was not considered in the above derivation although it may be quite important depending on the basis set used in any particular calculation. Let us now assume that we shall attempt to describe the potential energy surface of a molecule by using an atomic orbital basis that is attached to the atomic nuclei and that thus moves with the nuclei. The above described formalism will be useful in locating the desired stationary points on the potential surface if both the first and second derivatives (with respect to nuclear displacement) of the dominant basis

orbitals can be expanded in this basis. This can be seen by considering that the coulomb potential $|\mathbf{r} - \mathbf{R}_A|^{-1}$ of Eq. (5.38), when integrated over an electronic charge density $\rho(\mathbf{r})$, yields an interaction energy that can be expanded in powers of $\mathbf{u}_A \equiv \mathbf{R}_A - \mathbf{R}_A^0$ either by expanding $|\mathbf{r} - \mathbf{R}_A|^{-1}$ as in Eq. (5.38) or by expanding the charge density $\rho(\mathbf{r} - \mathbf{u}_A)$. The expansion of this charge density then gives rise to the derivatives of the atomic basis orbitals. This criterion—that the first and second derivatives of the important basis functions can be expanded in the same basis—may, of course, in principle never be met. For practical purposes we can, however, fulfill the criterion if the basis consists of a set of gaussian functions. We know that the nuclear displacement derivative of a gaussian function just is another gaussian with one higher angular momentum value. Thus by including such gaussian basis functions of higher angular momentum in the original basis, we could guarantee that the derivatives of the important gaussian atomic orbitals will indeed be described within our finite basis. If the derivatives of the basis functions cannot be expanded in the basis, the fulfillment of Eq. (5.41) may not lead to an accurate stationary point. As an alternative to including in the atomic orbital basis sufficient flexibility to describe the first and second derivatives of the more important basis functions, one can explicitly evaluate derivatives of the one- and two-electron integrals (Thomsen and Swanstrøm, 1973). Suppose, for example, that s , p , and d atomic orbitals were used in a calculation on CH_2 . Even if only the s and p orbitals were important in describing the orbitals having nonnegligible occupation numbers, one would have to include full sets of d and f orbitals in the basis to guarantee that the second derivatives of the s and p functions could be described. As a result, many two-electron integrals involving d and f functions would have to be computed over the atomic orbital basis. On the other hand, this can be avoided by calculating only the first and second derivatives of the integrals over the s and p orbitals. These derivatives would then involve a very restricted subset of integrals containing d and f functions. For example, the second derivative of $\langle pp|pp \rangle$ would involve $\langle pp|pf \rangle$ and $\langle pp|dd \rangle$ integrals; integrals such as $\langle dd|dd \rangle$ or $\langle dd|fp \rangle$ or $\langle ff|ff \rangle$ could not arise. The smaller number of difficult integrals arising in approaches that explicitly evaluate integral derivatives rather than those using very large basis sets has made these integral derivative schemes more commonly used in state-of-the-art calculations.

PROBLEMS

5.1 Determine the excitation energies and transition moments for HeH^+ using the full CI calculation for HeH^+ again making use of SCF data of Problem 2.1. The nonvanishing matrix elements of the dipole operator

$\mathbf{r}(x, y, z)$ in the atomic basis are

$$\langle 1s_{\text{H}}|z|1s_{\text{He}}\rangle = 0.2854, \quad \langle 1s_{\text{H}}|z|1s_{\text{H}}\rangle = 1.4$$

1. Determine the matrix elements of \mathbf{r} in the SCF orbital basis.

In Problem 2.4, a full CI calculation was carried out on HeH^+ in the SCF orbital basis.

2. Use the results of Problem 2.4 to determine the excitation energies and transition moments from the ground state to the two excited singlet states of HeH^+ .

3. Determine the frequency-independent polarizability and the frequency-dependent polarizability at a frequency $E = 0.1$ a.u. for HeH^+ .

5.2 Carry out a coupled Hartree-Fock (CHF) calculation of the frequency-independent polarizability tensor for the closed-shell HeH^+ system. To achieve this goal, follow the steps given below.

1. Show that

$$\langle 0|[\mathbf{r}, m_{\alpha}^+ \alpha_{\alpha} + m_{\beta}^+ \alpha_{\beta}]|0\rangle = 2\langle \phi_{\alpha}|\mathbf{r}|\phi_m\rangle$$

2. Use the A_{11} and B_{11} matrix elements derived in Problem 2.2 to show that the A_{11} and B_{11} matrix elements in a CHF calculation may be written as

$$\begin{aligned} (A_{11})_{n\beta, m\alpha} &= \langle 0|[\beta_{\alpha}^+ n_{\alpha} + \beta_{\beta}^+ n_{\beta}, H, m_{\alpha}^+ \alpha_{\alpha} + m_{\beta}^+ \alpha_{\beta}]|0\rangle \\ &= 2((\epsilon_m - \epsilon_{\alpha})\delta_{mn}\delta_{\alpha\beta} + 2\langle n\alpha|\beta m\rangle - \langle n\alpha|m\beta\rangle) \\ (B_{11})_{n\beta, m\alpha} &= \langle 0|[n_{\alpha}^+ \alpha_{\alpha} + n_{\beta}^+ \beta_{\beta}, H, m_{\alpha}^+ \alpha_{\alpha} + m_{\beta}^+ \alpha_{\beta}]|0\rangle \\ &= 2\langle mn|\beta\alpha\rangle - 2\langle mn|\alpha\beta\rangle \end{aligned}$$

To obtain these results you must use the definition of the Fock potential given in Eq. (2.92) and assume that the orbitals are HF orbitals.

Now carry out the CHF calculation on HeH^+ , using the single zeta Slater basis and the SCF data given in Problem 2.1. The nonvanishing matrix elements of $\mathbf{r}(x, y, z)$ in the SCF basis are given in Solution 5.1, part 1.

3. Evaluate the matrix elements of \mathbf{r} , which enter into the CHF calculation.

4. Evaluate the A_{11} and B_{11} matrix elements.

5. Determine the frequency-independent polarizability tensor in the CHF approximation for HeH^+ .

5.3 Carry out a CMCHF calculation of the frequency-independent polarizability tensor.

1. Show that

$$\langle 0|[\mathbf{r}, p_{\alpha}^+ q_{\alpha} + p_{\beta}^+ q_{\beta}]|0\rangle = \sum_s \{ \mathbf{r}_{sp} \langle 0|s_{\alpha}^+ q_{\alpha} + s_{\beta}^+ q_{\beta}|0\rangle - \mathbf{r}_{qs} \langle 0|p_{\alpha}^+ s_{\alpha} + p_{\beta}^+ s_{\beta}|0\rangle \}$$

2. Show that

$$\langle 0|[\mathbf{r}, 1n]\langle 0||0\rangle = \sum_{pq} \mathbf{r}_{pq} \langle 0|p_{\alpha}^+ q_{\alpha} + p_{\beta}^+ q_{\beta}|n\rangle$$

3. Indicate the simplifications that occur in the formulas for the A and B matrix elements in Eqs. (2.29) and (2.30), when converged MCSCF orbitals are used for evaluating the A and B matrices.

Now carry out the CMCHF calculation of the frequency-independent polarizability tensor for HeH^+ , using the minimum basis given in Problem 2.1. The multiconfiguration reference state includes the two configurations $1\sigma^2$ and $2\sigma^2$. A MCSCF calculation using these two configurations was carried out in Problem 2.6. The one- and two-electron integrals in the MCSCF basis are given below:

$$\begin{aligned} \langle 1|h|1\rangle &= -2.6119, & \langle 2|h|2\rangle &= -1.3193, & \langle 1|h|2\rangle &= 0.2078 \\ \langle 11|11\rangle &= 0.9521, & \langle 12|12\rangle &= 0.6100, & \langle 12|11\rangle &= -0.1963 \\ \langle 11|22\rangle &= 0.1298, & \langle 22|21\rangle &= -0.0069, & \langle 22|22\rangle &= 0.6161, \end{aligned}$$

where 1 and 2 denote the 1σ and 2σ orbitals, respectively, which are

$$1\sigma = 0.8920 1s_{\text{He}} + 0.1701 1s_{\text{H}}, \quad 2\sigma = -0.8410 1s_{\text{He}} + 1.2140 1s_{\text{H}}$$

The MCSCF states are

$$\begin{aligned} |0\rangle &= 0.9984|1\sigma^2\rangle - 0.0574|2\sigma^2\rangle, & E_0 &= -2.8506 \\ |1\rangle &= 0.0574|1\sigma^2\rangle + 0.9984|2\sigma^2\rangle, & E_1 &= -0.5863 \end{aligned}$$

4. Calculate the nonvanishing one- and two-electron density and transition density matrix elements of the form

$$\langle i|r^+s^+tu|0\rangle, \quad \langle i|r^+s|0\rangle, \quad \langle 0|r^+s|i\rangle, \quad i = |0\rangle, |1\rangle$$

The matrix elements of r in the atomic basis are given in Problem 5.1.

5. Calculate the matrix elements of r in the MCSCF basis.

6. Calculate the numerical values of matrix elements given in questions 1 and 2.

7. Determine the A and B matrix elements.

8. Determine the frequency-independent polarizability tensor in the CMCHF approximation.

SOLUTIONS

5.1

$$\begin{aligned} 1. \quad \langle 1|z|1\rangle &= 2(0.9000)(0.1584)(0.2854) + (0.1584)^2(1.4) = 0.1165 \\ \langle 2|z|2\rangle &= 2(-0.8324)(1.2156)(0.2854) + (1.2156)^2(1.4) = 1.4911 \\ \langle 1|z|2\rangle &= [(0.9000)(1.2156) - (0.8324)(0.1584)]0.2854 \\ &\quad + (0.1584)(1.2156)(1.4) = 0.5442 \end{aligned}$$

2. Excitation energies are $4.2792 - 3.2567 = 1.0225$ and $4.2792 - 1.9497 = 2.3295$. Transition moments:

$$\langle 1\sigma^2|z|1\sigma^2\rangle = 2\langle 1|z|1\rangle, \quad \langle 2\sigma^2|z|2\sigma^2\rangle = 2\langle 2|z|2\rangle, \quad \langle 1\sigma^2|z|2\sigma^2\rangle = 0$$

$$\langle 1\sigma 2\sigma|z|1\sigma 2\sigma\rangle = \langle 1|z|1\rangle + \langle 2|z|2\rangle, \quad \langle 1\sigma^2|z|1\sigma 2\sigma\rangle = \frac{2}{\sqrt{2}}\langle 1|z|2\rangle,$$

$$\langle 2\sigma^2|z|1\sigma 2\sigma\rangle = \frac{2}{\sqrt{2}}\langle 2|z|1\rangle.$$

Therefore

$$\begin{aligned} \langle 0|z|1\rangle &= (0.9982)(-0.0261)2(0.1165) + (-0.0573)(-0.2098)2(1.4911) \\ &\quad + (0.0143)(0.9772)(0.1165 + 1.4911) + [(0.9982)(0.9772) \\ &\quad + (0.0143)(-0.0261) + (-0.0573)(0.9772) \\ &\quad + (-0.2098)(0.0143)]\left(\frac{0.5442}{\sqrt{2}}\right)2 \\ &= 0.7578 \end{aligned}$$

$$\begin{aligned} \langle 0|z|2\rangle &= (0.9982)(0.0530)2(0.1165) + (-0.0573)(0.9761)2(1.4911) \\ &\quad - (0.0143)(0.2109)(0.1165 + 1.4911) + [(0.9982)(0.2109) \\ &\quad + (0.0143)(0.0530) + (-0.0573)(0.2109) \\ &\quad + (0.0143)(0.9761)]\left(\frac{0.5442}{\sqrt{2}}\right)2 \\ &= 0.0144 \end{aligned}$$

$$3. \quad \alpha_{zz}(E) = 2 \sum_{n=1,2} \frac{|\langle 0|z|n\rangle|^2(E_n - E_0)}{(E_n - E_0)^2 - E}$$

$$E = 0, \quad \alpha_{zz} = 2 \left[\frac{0.5742}{1.0225} + \frac{0.0002}{2.3295} \right] = 1.1233$$

$$E = 0.1, \quad \alpha_{zz} = 2 \left[\frac{(0.5742)(1.0225)}{1.0456 - 0.01} + \frac{(0.0002)(2.3295)}{5.4266 - 0.01} \right] = 1.1342$$

5.2

$$\begin{aligned} 1. \quad \langle 0|[\mathbf{r}, m_\alpha^+ \alpha_\alpha + m_\beta^+ \alpha_\beta]|0\rangle &= \sum_{pq} \langle \phi_p|\mathbf{r}|\phi_q\rangle \langle 0|[p^+ q, m_\alpha^+ \alpha_\alpha + m_\beta^+ \alpha_\beta]|0\rangle \\ &= \sum_{pq} \langle \phi_p|\mathbf{r}|\phi_q\rangle \langle 0|p^+ \alpha_\alpha \delta_{m_\alpha q} - m_\alpha^+ q \delta_{p\alpha_\alpha} \\ &\quad + p^+ \alpha_\beta \delta_{q m_\beta} - m_\beta^+ q \delta_{p\alpha_\beta}|0\rangle \\ &= 2\langle \phi_\alpha|\mathbf{r}|\phi_m\rangle \end{aligned}$$

2. The definition of the Fock potential in Eq. (2.92) results in the following definition of the orbital energies

$$h_{rs} + \sum_{\gamma} (2\langle r\gamma | s\gamma \rangle - \langle r\gamma | \gamma s \rangle) = \delta_{rs} \epsilon_r$$

and the A_{11} matrix element in Problem 2.2 therefore may be rewritten as

$$(A_{11})_{n\beta, m\alpha} = 2[(-\epsilon_{\alpha} + \epsilon_m)\delta_{\alpha\beta}\delta_{mn} + 2\langle n\alpha | \beta m \rangle - \langle n\alpha | m\beta \rangle]$$

3. Let 1 and 2 denote 1σ and 2σ , respectively. As was shown in Problem 5.1 $\langle 1|z|2 \rangle = 0.5442$. Hence

$$\langle 0|z(2\alpha^+ 1_{\alpha} + 2\beta^+ 1_{\beta})|0 \rangle = 2(0.5442)$$

$$4. (A_{11})_{21, 21} = 2(\epsilon_2 - \epsilon_1 + 2\langle 21 | 12 \rangle - \langle 21 | 21 \rangle) = 2.1464,$$

$$(B_{11})_{21, 21} = 2(\langle 22 | 11 \rangle - 2\langle 22 | 11 \rangle) = -0.2522$$

5. Only the zz component of the polarizability tensor is nonvanishing. This component becomes $2 \cdot 4 \cdot 0.5442^2 / (2.1464 + 0.2522) = 0.9878$.

5.3

1. Using $\mathbf{r} = \sum_{st} \mathbf{r}_{st}(s_{\alpha}^+ t_{\alpha} + s_{\beta}^+ t_{\beta})$ we obtain

$$\langle 0 | [\mathbf{r}, p_{\alpha}^+ q_{\alpha} + p_{\beta}^+ q_{\beta}] | 0 \rangle = \sum_{st} \mathbf{r}_{ts} \langle 0 | [t_{\alpha}^+ s_{\alpha} + t_{\beta}^+ s_{\beta}, p_{\alpha}^+ q_{\alpha} + p_{\beta}^+ q_{\beta}] | 0 \rangle$$

Performing the commutations then leads immediately to the result asked for.

$$2. \langle 0 | [\mathbf{r}, |n \rangle \langle 0|] | 0 \rangle = \langle 0 | \mathbf{r} | n \rangle = \sum_{pq} \mathbf{r}_{pq} \langle 0 | p_{\alpha}^+ q_{\alpha} + p_{\beta}^+ q_{\beta} | n \rangle$$

3. The A_{11} and B_{11} matrices in Eqs. (2.29) and (2.30) can, when convergence is reached and the GBT is obeyed, be evaluated directly using Eq. (2.42), which does contain the double commutator form.

4.	$\langle i = \langle 0 $	$\langle i = \langle 1 $
	$\langle i 1_{\alpha}^+ 1_{\alpha} 0 \rangle$	0.9968 0.0573
	$\langle i 2_{\alpha}^+ 2_{\alpha} 0 \rangle$	0.0033 -0.0573
	$\langle i 1_{\alpha}^+ 1_{\beta}^+ 1_{\beta} 1_{\alpha} 0 \rangle$	0.9968 0.0573
	$\langle i 1_{\alpha}^+ 1_{\beta}^+ 2_{\beta} 2_{\alpha} 0 \rangle$	-0.0573 -0.0033
	$\langle i 2_{\alpha}^+ 2_{\beta}^+ 1_{\beta} 1_{\alpha} 0 \rangle$	-0.0573 0.9968
	$\langle i 2_{\alpha}^+ 2_{\beta}^+ 2_{\beta} 2_{\alpha} 0 \rangle$	0.0033 -0.0573

We also have $\langle 0 | 1_{\alpha}^+ 1_{\alpha} | 1 \rangle = 0.0573$, $\langle 0 | 2_{\alpha}^+ 2_{\alpha} | 1 \rangle = -0.0573$. See text below Solution 2.6, question 1.

$$5. z_{11} = 0.1271, z_{22} = 1.4805, z_{12} = 0.5574.$$

$$6. \langle 0 | [z, 2_{\alpha}^+ 1_{\alpha} + 2_{\beta}^+ 1_{\beta}] | 0 \rangle = 2z_{12} \{ \langle 0 | 1_{\alpha}^+ 1_{\alpha} - 2_{\alpha}^+ 2_{\alpha} | 0 \rangle \} = 1.1076$$

$$\langle 0 | [z, |1 \rangle \langle 0|] | 0 \rangle = 2z_{11} \langle 0 | 1_{\alpha}^+ 1_{\alpha} | 1 \rangle + 2z_{22} \langle 0 | 2_{\alpha}^+ 2_{\alpha} | 1 \rangle = -0.1551$$

7. Formulas for the A and B matrix element are derived in Solution 2.6, question 2:

$$A = \begin{pmatrix} 2.1756 & 0.4018 \\ 0.4018 & 2.2643 \end{pmatrix}, \quad B = \begin{pmatrix} -0.2495 & -0.0230 \\ -0.0230 & 0 \end{pmatrix}$$

$$8. (A - B)^{-1} = \begin{pmatrix} 0.4264 & -0.0800 \\ -0.0800 & 0.4566 \end{pmatrix}$$

The zz component of the frequency-independent polarizability becomes

$$\alpha_{zz} = 2(1.1076, -0.1551) \begin{pmatrix} 0.4264 & -0.0800 \\ -0.0800 & 0.4566 \end{pmatrix} \begin{pmatrix} 1.1076 \\ -0.1551 \end{pmatrix} = 1.1232$$

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