Chapter 3 | Perturbation Theory

A. INTRODUCTION

As an alternative to the variational approaches described in Chapter 2, we may use perturbative approaches to solve the Schrödinger equation. Our purpose in this chapter is not to survey the many developments and applications that have been made of perturbation methods. Rather we attempt to cast the most familiar perturbation theory (Rayleigh-Schrödinger, RSPT) in the language of second quantization and then demonstrate how this tool can be used to compute state energies and wavefunctions. In Chapter 5 we extend this treatment to property average values and secondorder response properties. We also illustrate some of the strengths and weaknesses of RSPT by comparing it with other perturbative and nonperturbative methods.

To begin, let us assume that the total electronic Hamiltonian H is decomposed into two pieces

$$H = H^0 + U \tag{3.1}$$

the former of which is assumed to be "larger" in a sense that will be clarified shortly. We also assume that we have available the complete set of eigenstates of H^0 (including the continuum, in principle)

$$H^{0}|k^{0}\rangle = E_{k}^{0}|k^{0}\rangle \tag{3.2}$$

This latter assumption often places substantial practical restrictions on the forms of H^0 that are possible. For example, choosing H^0 to be the *N*-electron Fock operator (or its second-quantized equivalent) would be quite reasonable because the $|k^0\rangle$ are then the usual Slater determinantal wavefunctions, which one is often actually able to obtain to reasonably high precision. On the other hand, choosing H^0 to include some factors (e.g., r_{ij}^{-1}) of the interelectronic distance is probably not practical because one cannot usually

obtain the eigenstates $\{|j^0\rangle\}$ to high precision. Of course, the physical context and requisite accuracy relevant to each specific problem must ultimately dictate how one can most effectively split H into $H^0 + U$.

B. DERIVATION OF GENERAL ENERGY AND WAVEFUNCTION EXPRESSIONS

Given the above decomposition of H, we now express the Schrödinger equation

$$H|j\rangle = E_j|j\rangle \tag{3.3}$$

as (March et al., 1967)

$$(\mathscr{E} - H^0)|j\rangle = (\mathscr{E} - E_j + U)|j\rangle \tag{3.4}$$

where the energy parameter \mathscr{E} , which has simply been added and subtracted, will be used shortly to define different kinds of perturbation theories. The normalization of the exact state $|j\rangle$ will now be chosen such that $|j\rangle$ has unit projection along its zeroth-order component $|j^0\rangle$

 $|j^{0}\rangle\langle j^{0}|j\rangle = |j^{0}\rangle \tag{3.5}$

The total wavefunction $|j\rangle$ can now be written in terms of the projector Q,

$$Q \equiv 1 - |j^{0}\rangle\langle j^{0}|$$
$$|j\rangle = |j^{0}\rangle + Q|j\rangle$$
(3.6)

as

Making use of the fact that $H^0Q = QH^0$, which is easily seen to be valid from definition of Q, we can operate on Eq. (3.4) with the projector Q to obtain a closed expression for $Q|j\rangle$:

$$\langle \mathcal{Q} | j \rangle = \langle \mathcal{Q} | j \rangle = \langle \mathcal{E} - H^0 \rangle^{-1} \mathcal{Q} (\mathcal{E} - E_j + U) | j \rangle$$
(3.7)

The factor of Q, which when applied to Eq. (3.4) gave Eq. (3.7), is needed because the resolvent $(\mathscr{E} - H^0)^{-1}$ is singular at $\mathscr{E} = E_j^0$. The presence of Qguarantees that $(\mathscr{E} - H^0)^{-1}$ never operates on a state $(|j^0\rangle)$ that would cause a singularity at this value of E_j^0 . Clearly $(\mathscr{E} - H^0)^{-1}$ is singular at other values of \mathscr{E} ($\mathscr{E} = E_k^0, k \neq j$) but we need not be concerned with these singularities as long as the parameter \mathscr{E} is held in the neighborhood of E_j^0 and away from the other E_k^0 . This would, of course, be difficult to achieve in systems such as metals, which possess many closely spaced (nearly degenerate) energy levels. Equation (3.7) is then inserted into Eq. (3.6) to yield the

integral equation

$$|j\rangle = |j^0\rangle + (\mathscr{E} - H^0)^{-1}Q(\mathscr{E} - E_j + U)|j\rangle$$
(3.8)

If Eq. (3.8) is iterated, one obtains an order-by-order expansion of the wavefunction

$$|j\rangle = \sum_{n=0}^{\infty} \left[(\mathscr{E} - H^0)^{-1} Q (\mathscr{E} - E_j + U) \right]^n |j^0\rangle$$
(3.9)

Multiplying Eq. (3.3) on the left by $\langle j^0 |$ we get

$$E_j = E_j^0 + \langle j^0 | U | j \rangle \tag{3.10}$$

which then may be used to obtain a perturbative expansion of the energy in the perturbation U:

$$E_{j} - E_{j}^{0} = \sum_{n=0}^{\infty} \langle j^{0} | U[(\mathscr{E} - H^{0})^{-1}Q(\mathscr{E} - E_{j} + U)]^{n} | j^{0} \rangle$$
(3.11)

We now consider two especially relevant choices of the, in principle, arbitrary parameter \mathscr{E} . If \mathscr{E} is taken to be equal to E_j , then the above perturbation series describe the Brillouin-Wigner approximations to $|j\rangle$ and E_j . The choice $\mathscr{E} = E_j^0$ yields the Rayleigh-Schrödinger perturbation series.

To express any of the above perturbation expansions in terms of creation and annihilation operators, we simply write $|j^0\rangle$, H^0 , and U in the secondquantized manner. The zeroth-order Hamiltonian is virtually always taken to be a one-electron operator

$$H^{0} = \sum_{k,l} \langle \phi_{k} | H^{0} | \phi_{l} \rangle k^{+} l$$
(3.12)

involving a one-electron potential V,

$$H^{0} = -\frac{1}{2}\nabla^{2} - \sum_{a} Z_{a} |\mathbf{r} - \mathbf{R}_{a}|^{-1} + V$$
(3.13)

With this choice, the perturbation U becomes

$$U = \frac{1}{4} \sum_{ijkl} \langle ij||kl\rangle i^+ j^+ lk - \sum_{ij} \langle i|V|j\rangle i^+ j$$
(3.14)

If the spin-orbitals $\{\phi_k\}$ are chosen to diagonalize H^0 ,

$$H^{0} = \sum_{k} \langle \phi_{k} | H^{0} | \phi_{k} \rangle k^{+} k \equiv \sum_{k} \varepsilon_{k} k^{+} k$$
(3.15)

then the zeroth-order wavefunctions $\{|j^0\rangle\}$ are simply N-electron Slater determinants (or their second-quantized equivalent) involving these same

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C. Size Consistency Problem in the Energy

spin orbitals $\{\phi_k\}$. This choice of H^0 is especially convenient because the resolvent $(\mathscr{E} - H^0)^{-1}$ becomes diagonal (and hence easy to treat) within this representation.

To gain some experience in the evaluation of perturbation contributions to $|j\rangle$ and E_j and to motivate an analysis of a fundamental weakness of the Buillouin-Wigner perturbation theory (BWPT), let us now consider a few examples. First, we evaluate the first-order correction to the energy that arises from the n = 0 term in Eq. (3.11):

$$E_{j}^{(1)} = \langle j^{0}|U|j^{0}\rangle = \frac{1}{4}\sum_{ijkl}\langle j^{0}|i^{+}j^{+}lk|j^{0}\rangle\langle ij||kl\rangle - \sum_{kl}\langle j^{0}|k^{+}l|j^{0}\rangle\langle k|V|l\rangle$$

$$(3.16)$$

which by straightforward application of Slater-Condon-like rules to compute the above density matrices, yields

$$E_{j}^{(1)} = \frac{1}{2} \sum_{\mu, \nu \in j_{0}} \langle \mu \nu | | \mu \nu \rangle - \sum_{\mu \in j_{0}} \langle \mu | V | \mu \rangle.$$
(3.17)

Note that because $E_j^{(1)}$ contains no reference to the parameter \mathscr{E} , RSPT and BWPT have identical first-order energies.

C. SIZE CONSISTENCY PROBLEM IN THE ENERGY

Next, we consider the second-order energy and, in particular, we examine $E_j^{(2)}$ for a system consisting of two noninteracting subsystems (a and b). For this case, the Hamiltonian H separates into

$$H = H_a^0 + U_a + H_b^0 + U_b \tag{3.18}$$

and the zeroth-order states become (antisymmetric) product states (recall that $|j^0\rangle$ labels our specific state of interest whereas $|k^0\rangle$ labels the other states):

$$|j^{0}\rangle = |j_{a}^{0}j_{b}^{0}\rangle, \{|k^{0}\rangle\} = \{|k_{a}^{0}j_{b}^{0}\rangle, |j_{a}^{0}k_{b}^{0}\rangle, |k_{a}^{0}k_{b}^{0}\rangle\}$$
(3.19)

The second-order energy expression from Eq. (3.11) reduces, using $Q|j^0\rangle = 0$, to

$$E_{j}^{(2)} = \langle j^{0} | U(\mathscr{E} - H^{0})^{-1} Q U | j^{0} \rangle$$
(3.20)

Expressing Q in the conventional sum-over-states manner gives

$$Q \equiv 1 - |j^0\rangle\langle j^0| = \sum_{k^0 \neq j^0} |k^0\rangle\langle k^0|$$
(3.21)

and Eq. (3.20) becomes

$$E_{j}^{(2)} = \sum_{k^{0} \neq j^{0}} \langle j^{0} | U | k^{0} \rangle \langle k^{0} | U | j^{0} \rangle / (\mathscr{E} - E_{k}^{0})$$
(3.22)

Now, introducing the fact that we are dealing with two noninteracting subsystems [through Eqs. (3.18) and (3.19)] and breaking the sum over k^0 into three sums corresponding to the partitioning of $|k^0\rangle$ given in Eq. (3.19), we obtain

$$E_{j}^{(2)} = \sum_{k_{a}^{0}} \frac{|\langle j_{a}^{0} j_{b}^{0} | U_{a} + U_{b} | k_{a}^{0} j_{b}^{0} \rangle|^{2}}{\mathscr{E} - E_{j_{b}}^{0} - E_{k_{a}}^{0}} + \sum_{k_{b}^{0}} \frac{|\langle j_{a}^{0} j_{b}^{0} | U_{a} + U_{b} | j_{a}^{0} k_{b}^{0} \rangle|^{2}}{\mathscr{E} - E_{j_{a}}^{0} - E_{k_{b}}^{0}} + \sum_{k_{b}^{0}, k_{b}^{0}} \frac{|\langle j_{a}^{0} j_{b}^{0} | U_{a} + U_{b} | k_{a}^{0} k_{b}^{0} \rangle|^{2}}{\mathscr{E} - E_{k_{a}}^{0} - E_{k_{b}}^{0}}$$
(3.23)

Using the orthonormality of the spin-orbitals and the fact that the systems are noninteracting permits the simplification of the above matrix elements. For example,

$$\langle j_{a}^{0} j_{b}^{0} | U_{a} + U_{b} | k_{a}^{0} j_{b}^{0} \rangle = \langle j_{a}^{0} | U_{a} | k_{a}^{0} \rangle, \qquad \langle j_{a}^{0} j_{b}^{0} | U_{a} + U_{b} | k_{a}^{0} k_{b}^{0} \rangle = 0 \quad (3.24)$$

Thus, we finally obtain

$$E_{j}^{(2)} = \sum_{k_{a}^{0}} \frac{|\langle j_{a}^{0} | U_{a} | k_{a}^{0} \rangle|^{2}}{\mathscr{E} - E_{j_{b}}^{0} - E_{k_{a}}^{0}} + \sum_{k_{b}^{0}} \frac{|\langle j_{b}^{0} | U_{b} | k_{b}^{0} \rangle|^{2}}{\mathscr{E} - E_{j_{a}}^{0} - E_{k_{b}}^{0}}$$
(3.25)

Notice that this total second-order energy is not, in general, a sum of the second-order energies of the two separated species because of the appearance of the E_{jb}^0 and E_{ja}^0 terms in the denominators. We therefore say that the general (i.e., with arbitrary \mathscr{E}) perturbation theory energy is not size consistent (Pople *et al.*, 1977). However, if \mathscr{E} is chosen, as in RSPT, equal to $\mathscr{E} = E_j^0 = E_{ja}^0 + E_{jb}^0$, then we indeed obtain a perfectly size-consistent result:

$$E_j^{(2)} = E_{ja}^{(2)} + E_{jb}^{(2)}$$
(3.26)

It is clear that the first-order energy expression $\langle j^0 | U | j^0 \rangle$ is also size consistent. Because this size consistency property is important, especially if we are interested in using perturbation methods to study molecular fragmentation, the use of RSPT must be favored over BWPT ($\mathscr{E} = E_j$) or any other perturbation theory derived from alternative choices of \mathscr{E} .

Even if we now decided to use only RSPT to compute $|j\rangle$ and E_j , another potential difficulty arises when we consider the third- (and higher-) order energies

$$E_{j}^{(3)} = \langle j^{0} | UQ(E_{j}^{0} - H^{0})^{-1} UQ(E_{j}^{0} - H^{0})^{-1} U | j^{0} \rangle - E_{j}^{(1)} \langle j^{0} | UQ(E_{j}^{0} - H^{0})^{-2} U | j^{0} \rangle$$
(3.27)

Because $E_j^{(1)}$ is an extensive property (i.e., size consistent), we should expect possible size inconsistency from the last term in $E_j^{(3)}$ if the (second-order) factor in front of $E_j^{(1)}$ is also extensive; $E_j^{(3)}$ would then contain terms that are proportional to the square of the system's size (for identical noninteracting subsystems). Let us now look at this situation more closely. By introducing the spectral representation of the projector Q given in Eq. (3.21), $E_j^{(3)}$ can be written as

$$E_{j}^{(3)} = \sum_{k^{0}, l^{0}} \frac{\langle j^{0} | U | k^{0} \rangle \langle k^{0} | U | l^{0} \rangle \langle l^{0} | U | j^{0} \rangle}{(E_{j}^{0} - E_{k}^{0})(E_{j}^{0} - E_{l}^{0})} - \langle j^{0} | U | j^{0} \rangle \sum_{k^{0}} \frac{\langle j^{0} | U | k^{0} \rangle \langle k^{0} | U | j^{0} \rangle}{(E_{j}^{0} - E_{k}^{0})^{2}}$$
(3.28)

It is now important to demonstrate that the $k^0 = l^0$ terms appearing in the first sum above exactly cancel the size-inconsistent terms in the second factor. This cancellation can be brought about by combining these terms as

$$\Delta = \sum_{k^{0}} \frac{|\langle j^{0} | U | k^{0} \rangle|^{2}}{(E_{j}^{0} - E_{k}^{0})^{2}} \left[\langle k^{0} | U | k^{0} \rangle - \langle j^{0} | U | j^{0} \rangle \right]$$
(3.29)

Now, if we consider Δ for the special case of two noninteracting subsystems (analogous to what was done above for $E_j^{(2)}$), we see that the terms $\langle k^0|U|k^0 \rangle - \langle j^0|U|j^0 \rangle$ decompose, under partitioning of k^0 [as in Eq. (3.19)], into

$$\langle j_a^0 k_b^0 | U_a + U_b | j_a^0 k_b^0 \rangle - \langle j_a^0 j_b^0 | U_b | j_a^0 j_b^0 \rangle = \langle k_b^0 | U_b | k_b^0 \rangle - \langle j_b^0 | U_b | j_b^0 \rangle$$
(3.30)

(notice that reference to system a has disappeared here) and

$$\langle k_a^0 j_b^0 | U_a + U_b | k_a^0 j_b^0 \rangle - \langle j_a^0 j_b^0 | U_a | j_a^0 j_b^0 \rangle = \langle k_a^0 | U_a | k_a^0 \rangle - \langle j_a^0 | U_a | j_a^0 \rangle.$$
(3.31)

(reference to system b has disappeared here).

The states $\{|k_a^0k_b^0\rangle\}$ give no contributions because the first factor in Eq. (3.29) $\langle j^0|U|k^0\rangle$ becomes identically zero for these states. This then permits Δ to be written as a sum of terms referring totally to system *a*:

$$\Delta_{a} = \sum_{k_{a}^{0}} \frac{|\langle j_{a}^{0} | U_{a} | k_{a}^{0} \rangle|^{2}}{(E_{j_{a}}^{0} - E_{k_{a}}^{0})^{2}} \left[\langle k_{a}^{0} | U_{a} | k_{a}^{0} \rangle - \langle j_{a}^{0} | U_{a} | j_{a}^{0} \rangle \right]$$
(3.32)

and an analogous expression for Δ_b . Hence Δ is size consistent even though each of the two terms arising in it [see Eq. (3.29)] are not. When $k^0 \neq l^0$ the first term in Eq. (3.28) may also be shown to be size consistent and $E_j^{(3)}$ therefore is size consistent. RSPT energies are in general size consistent even though substantial regrouping of terms as in $E_j^{(3)}$ may be necessary before it can be realized. If one wishes to use RSPT to perform ab initio quantum-chemical calculations that yield size-consistent energies, then care must be taken in computing the factors that contribute to any given $E_j^{(n)}$. For example, if $E_j^{(3)}$ were calculated as in Eq. (3.28), limitations of numerical precision might not give rise to the exact cancellation of size-inconsistent terms, which we know should occur. This would certainly be the case for an extended system (for which the size-inconsistent terms would dominate). In addition, it is unpleasant to have a formalism in which such improper terms arise in the first place. It is therefore natural to attempt to develop approaches to implementing RSPT in which the size-inconsistent factors are never even computed. Such an approach has been developed and is commonly referred to as many-body perturbation theory (MBPT). The method of implementing MBPT is discussed once we have completed the present treatment of RSPT.

D. MØLLER-PLESSET PERTURBATION THEORY FOR ENERGY

A very common choice of the potential V used to define H^0 as in Eq. (3.13) is the HF potential

$$V = \sum_{k,l} \sum_{\mu \in j^0} \langle k\mu | | l\mu \rangle k^+ l$$
(3.33)

where the sum over μ runs over those spin-orbitals that are occupied in the specific zeroth-order state (the Slater determinant $|j^0\rangle$) whose perturbation we are examining. The unperturbed Hamiltonian H^0 is then given in terms of the HF orbital energies as

$$H^{0} = \sum_{k} \varepsilon_{k} k^{+} k \tag{3.34}$$

With the above choice of H^0 now made, the perturbation U becomes

$$U = \frac{1}{4} \sum_{ijkl} \langle ij| |kl\rangle i^{+}j^{+}lk - \sum_{k,l} \sum_{\mu \in j_{0}} \langle k\mu| |l\mu\rangle k^{+}l \qquad (3.35)$$

These choices of H^0 and U, when used in RSPT, give rise to what is commonly called (Pople *et al.*, 1977) Møller–Plesset perturbation theory (MPPT) and the expression for $E_i^{(1)}$ reduces to the familiar form

$$E_{j}^{(1)} = -\frac{1}{2} \sum_{\mu,\nu \in j_{0}} \langle \mu \nu | | \mu \nu \rangle \qquad (3.36)$$

The RSPT expression for $E_j^{(2)}$ can also be expressed in terms of orbital energies and two-electron integrals. The kets $|k^0\rangle$ appearing in Eq. (3.22) for

 $E_j^{(2)}$ refer to kets that are singly, doubly, etc. excited relative to the reference ket $|j^0\rangle$. Because of the BT, $\langle j^0|U|k^0\rangle$ vanishes when $|k^0\rangle$ is a singly excited ket. Kets $|k^0\rangle$ that are triply excited and higher also give no contribution to $\langle j^0|U|k^0\rangle$. Hence, $E_j^{(2)}$ as given in Eq. (3.22) would contain only contributions from the doubly excited kets,

$$\langle j^{0} | Ur^{+}s^{+}\beta\alpha | j^{0} \rangle = \langle \alpha\beta | | rs \rangle$$
(3.37)

and therefore

$$E_{j}^{(2)} = -\sum_{\substack{\alpha < \beta \\ r < s}} \frac{|\langle \alpha \beta | | rs \rangle|^{2}}{\varepsilon_{r} + \varepsilon_{s} - \varepsilon_{\alpha} - \varepsilon_{\beta}}$$
(3.38)

To obtain more insight into the structure of the size-consistent and -inconsistent terms, we derive an explicit expression for the quantity Δ appearing in Eq. (3.29) within MPPT. Realizing that only the doubly excited determinants $|k^0\rangle$ contribute in Eq. (3.29) because of the BT, we obtain

$$\Delta = \sum_{\substack{m \le n \\ \alpha \le \beta}} \frac{|\langle \alpha \beta | | mn \rangle|^2}{(\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_m - \varepsilon_n)^2} \left[\langle \alpha_{\alpha\beta}^{mn} | U | \alpha_{\beta\beta}^{mn} \rangle - \langle j^0 | U | j^0 \rangle \right]$$
(3.39)

where

$$\binom{mn}{\alpha\beta} \equiv m^+ n^+ \beta \alpha |j^0\rangle \tag{3.40}$$

The expectation value difference contained in the square brackets can be expressed in terms of elementary two-electron integrals and, since U = W - V, HF potential matrix elements as

$$\sum_{\substack{\gamma \in j^{0} \\ \gamma \neq \alpha, \beta}} \left[\langle m\gamma | |m\gamma \rangle + \langle n\gamma | |n\gamma \rangle - \langle \alpha\gamma | |\alpha\gamma \rangle - \langle \beta\gamma | |\beta\gamma \rangle \right] + \langle mn | |mn \rangle - \langle \alpha\beta | |\alpha\beta \rangle$$

$$-\langle m|V|m\rangle - \langle n|V|n\rangle + \langle \alpha|V|\alpha\rangle + \langle \beta|V|\beta\rangle$$
(3.41)

By then introducing the explicit form of V given in Eq. (3.33) this expression can be reduced to

$$\langle mn | |mn \rangle + \langle \alpha \beta | | \alpha \beta \rangle - (1 + P_{mn})(1 + P_{\alpha \beta}) \langle m\alpha | | n\beta \rangle$$
 (3.42)

where P_{mn} means interchanging the indices *m* and *n*. Upon inserting this into Eq. (3.39) one obtains

$$\Delta = \sum_{\substack{m < n \\ \alpha < \beta}} \frac{|\langle \alpha \beta | | mn \rangle|^2}{(\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_m - \varepsilon_n)^2} \left[\langle mn | | mn \rangle + \langle \alpha \beta | | \alpha \beta \rangle - (1 + P_{mn})(1 + P_{\alpha \beta}) \langle m\alpha | | n\beta \rangle \right]$$
(3.43)

The expression for Δ given in Eq. (3.39) may be written as a product of two independent disjoint sums since part of the first term $\langle \frac{mn}{\alpha\beta} | U | \frac{mn}{\alpha\beta} \rangle$ and the whole second term $\langle j^0 | U | j^0 \rangle$ in the square bracket consists of a sum that is independent of the sum m < n and $\alpha < \beta$. Equation (3.39) thus contains a product of two disjoint terms. When the terms in the square brackets are collected together in a different manner, Eq. (3.39) reduces to Eq. (3.43), which cannot be divided up into disjoint sums. The expression for Δ given in Eq. (3.43) is thus linked. It is the linked nature of the size-consistent terms that is used in MBPT to assure that size-consistent terms alone will appear in the many-body perturbation expressions for the electronic energy and other state properties.

E. THE PERTURBED WAVEFUNCTION

Having now carried out some detailed analysis of the RSPT expression for E_j , let us turn to the perturbative corrections to the wavefunction $|j\rangle$. The first-order RSPT wavefunction is, according to Eq. (3.9),

$$|j^{(1)}\rangle = (E_j^0 - H^0)^{-1}Q(E_j^0 - E_j + U)|j^0\rangle$$
(3.44)

which, because $Q|j^0\rangle = 0$, reduces to

$$|j^{(1)}\rangle = (E_j^0 - H^0)^{-1} Q U |j^0\rangle$$
 (3.45)

By inserting the spectral representation of Q [Eq. (3.21)], we obtain

$$|j^{(1)}\rangle = \sum_{k^{0} \neq j^{0}} \frac{\langle k^{0} | U | j^{0} \rangle}{E_{j}^{0} - E_{k}^{0}} | k^{0} \rangle$$
(3.46)

As we did above for the energy, it is instructive to analyze $|j^{(1)}\rangle$ when it pertains to two noninteracting subsystems (a and b). For this special case, the sum in Eq. (3.46) separates into terms pertaining to each of the isolated systems:

$$|j^{(1)}\rangle = -\sum_{k_{a}^{0}} \frac{\langle k_{a}^{0} | U_{a} | j_{a}^{0} \rangle}{E_{k_{a}}^{0} - E_{j_{a}}^{0}} | k_{a}^{0} j_{b}^{0} \rangle - \sum_{k_{b}^{0}} \frac{\langle k_{b}^{0} | U_{b} | j_{b}^{0} \rangle}{E_{k_{b}}^{0} - E_{j_{b}}^{0}} | j_{a}^{0} k_{b}^{0} \rangle$$
(3.47)

Thus, we see that, through first order, the wavefunction $|j\rangle$ contains only terms of the form $|j_a^0 j_b^0\rangle$, $|j_a^0 k_b^0\rangle$, and $|k_a^0 j_b^0\rangle$; terms such as $|k_a^0 k_b^0\rangle$ are not present. One might have expected that, for two noninteracting subsystems, the total wavefunction should be a (antisymmetric) product of the wavefunctions for each subsystem and that terms like $|k_a^0 k_b^0\rangle$ would, thus, be

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present. The RSPT first-order wavefunction certainly does not possess this product-separable property.

It is natural to ask how the RSPT can have the physically consistent property that its energy is extensive whereas its wavefunction does not reduce to a product form for noninteracting systems. The answer has to do with the manner in which the total energy E_i is computed in perturbation theory:

$$E_j = \langle j^0 | H | j \rangle \tag{3.48}$$

In contrast, the total energy is obtained, in variational approaches, by evaluating the expectation value

$$E_{j} = \langle j | H | j \rangle / \langle j | j \rangle \tag{3.49}$$

Because of the structure of the matrix element appearing in Eq. (3.48) it is not possible for terms such as $|k_a^0k_b^0\rangle$ to contribute directly to the RSPT expressions for E_j even though these factors are certainly contained in the exact wavefunction $|j\rangle$ (they will occur as higher order RSPT wavefunction corrections). That is,

$$\langle j_a^0 j_b^0 | H | k_a^0 k_b^0 \rangle \equiv \langle j_a^0 j_b^0 | H_a^0 + H_b^0 + U_a + U_b | k_a^0 k_b^0 \rangle = 0$$
(3.50)

In a sense then, the first-order RSPT wavefunction contains faults (absence of $|k_a^0 k_b^0\rangle$) that do not adversely affect its ability to yield, through

$$E_j^{(2)} = \langle j^0 | U | j^{(1)} \rangle \tag{3.51}$$

a size-consistent second-order energy. The same form of the wavefunction $(|j\rangle \cong |j^0\rangle + |j^{(1)}\rangle)$ when used in the expectation value [Eq. (3.49)] would not yield a size-consistent result; one would have to add on the $|k_a^0 k_b^0\rangle$ terms to generate size consistency in the expectation value. This implies that in a CI or MCSCF calculation one must use these disjoint excitations $|k_a^0 k_b^0\rangle$ (e.g., $|\sigma_u^2 \sigma_u^2\rangle$ for two H₂ molecules) in order to guarantee that the expectation value formula for the energy is size consistent. This necessity that one include, in a CI study of a composite system, excitation levels (in Slater determinants) that are higher than those included for the individual constituent fragments is a problem of the CI and MCSCF methods.

F. MØLLER-PLESSET WAVEFUNCTION

If the unperturbed Hamiltonian H^0 is taken to be the HF Hamiltonian, the first-order MPPT wavefunction [Eq. (3.46)] can be expressed in terms of the doubly excited kets $r^+s^+\beta\alpha|j^0\rangle$ (again BT makes the contributions due to

singly excited kets vanish):

$$|j^{(1)}\rangle = \sum_{\substack{\alpha < \beta \\ r < s}} K_{\alpha\beta}^{rs} r^+ s^+ \beta \alpha |j^0\rangle$$
(3.52)

where

$$K_{\alpha\beta}^{rs} = -\frac{\langle rs | \alpha\beta \rangle}{\varepsilon_r + \varepsilon_s - \varepsilon_\alpha - \varepsilon_\beta}$$
(3.53)

The explicit expression for the second-order wavefunction for this (HF) H^0 case contains singly, doubly, triply, and quadruply excited kets

$$|j^{(2)}\rangle = \sum_{r,\alpha} K_{\alpha}^{r} r^{+} \alpha |j^{0}\rangle + \sum_{\substack{\alpha < \beta \\ r < s}} K_{\alpha\beta}^{rs} r^{+} s^{+} \beta \alpha |j^{0}\rangle + \sum_{\substack{\alpha < \beta < \gamma \\ r < s < t}} K_{\alpha\beta\gamma}^{rst} r^{+} s^{+} t^{+} \gamma \beta \alpha |j^{0}\rangle + \sum_{\substack{\alpha < \beta < \gamma < \delta \\ r < s < t < u}} K_{\alpha\beta\gamma\delta}^{rstu} r^{+} s^{+} t^{+} u^{+} \delta \gamma \beta \alpha |j^{0}\rangle$$
(3.54)

where, for example,

$$K_{\alpha}^{r} = \frac{1}{2} \left(\sum_{\substack{mn \\ \gamma}} \frac{\langle r\gamma | |mn\rangle \langle mn| |\gamma\alpha\rangle}{(\varepsilon_{\alpha} - \varepsilon_{r})(\varepsilon_{\gamma} + \varepsilon_{\alpha} - \varepsilon_{n} - \varepsilon_{m})} + \sum_{\substack{m \\ \gamma\beta}} \frac{\langle \beta\gamma | |\alpham\rangle \langle mr| |\gamma\beta\rangle}{(\varepsilon_{\alpha} - \varepsilon_{r})(\varepsilon_{\gamma} + \varepsilon_{\beta} - \varepsilon_{r} - \varepsilon_{m})} \right)$$
(3.55)

G. MANY-BODY PERTURBATION THEORY

Having now completed our treatment of RSPT, let us return to the problem of finding a mechanism for explicitly computing, in any given order, only those terms in $E_j^{(n)}$ or $|j^{(n)}\rangle$ that are size consistent. Recall that RSPT, as normally expressed, contains size-inconsistent terms that cancel when grouped together properly, but that nevertheless appear in the formal RSPT expression. Recall also that the size-inconsistent terms could be characterized by a factorization into products of two or more terms that did not share common summation indices. In MBPT, the formal cancellation of sizeinconsistent terms in RSPT is carried out explicitly (Brueckner, 1955a,b; Bartlett and Silver, 1975; Kelly, 1969; Löwdin, 1968; Brandow, 1977). Formally, we may thus write $E_i^{(3)}$ as

$$E_{j}^{(3)}(\text{RSPT}) = \langle j^{0} | UQ(E_{j}^{0} - H^{0})^{-1} U(E_{j}^{0} - H^{0})^{-1} QU | j^{0} \rangle$$

- $E_{j}^{(1)} \langle j^{0} | UQ(E_{j}^{0} - H^{0})^{-2} U | j^{0} \rangle$
$$\equiv \langle j^{0} | U(E_{j}^{0} - H^{0})^{-1} U(E_{j}^{0} - H^{0})^{-1} U | j^{0} \rangle_{L} = E_{j}^{(3)}(\text{MBPT}) \quad (3.56)$$

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or $E_i^{(n)}$ in general, using Eq. (3.11), as

$$E_{j}^{(n)} = \langle j^{0} | U \{ (E_{j}^{0} - H^{0})^{-1} Q U \}^{n} | j^{0} \rangle_{L}$$
(3.57)

The subscript L indicates that only the size-consistent terms in that expression are included. The term involving $E_i^{(1)}$ in Eq. (3.56) give rise to purely size-inconsistent terms. In MBPT, the size-consistent terms are said to be linked, while the size-inconsistent terms are referred to as unlinked. If all of the unlinked terms were trivial to identify, such as the second term in $E_{i}^{(3)}$ (RSPT), one could merely exclude them. However, as we demonstrated earlier, there are also unlinked contributions in the first term in $E_i^{(3)}(RSPT)$ that cancel those in the second term and that are not easily identified. It is the strength of MBPT that it allows us directly to identify all the linked terms of RSPT. The derivation that shows how to identify the size-consistent or linked terms is rather tedious and is described in detail in many textbooks (March et al., 1967; Raimes, 1972; Linderberg and Ohrn, 1973). We do not carry out that derivation but simply familiarize the reader with the language of MBPT and report the results of the derivation. The implementation of the MBPT method for evaluating only the linked contributions to $E_i^{(n)}$ is commonly given in terms of a set of diagrams, the numerical values of which are the desired size-consistent components. We use the so-called Hugenholtz diagram rules to determine the number of diagrams, which enter in a given order (n) in the perturbation. In Table I, we report the rules for constructing these diagrams and in Fig. 3.1, the Hugenholtz energy diagrams that enter up through second order are displayed. The translation of the Hugenholtz diagrams into algebraic expressions is commonly performed by translating the Hugenholtz diagram into one of its equivalent Brandow diagrams (Brandow, 1977). The algebraic expression for the Hugenholtz diagram is then obtained by applying the rules given in Table II to the Brandow diagram.

Table I

Rules for Constructing All Hugenholtz Diagrams for a Given Order n

- 1. Represent each of the two-electron interactions (W) with a dot having two incoming and two outgoing lines (e.g., X) and each of the one-electron terms (-V) with a solid line having one endpoint at which one line is entering and one leaving (e.g., Y) ($H = H_0 + W V$).
- 2. To a given order n in the perturbation, write all possible ways (on a time axis) of drawing m (m = 0, 1, ..., n) dots and n m solid lines with one endpoint.
- 3. Connect the lines entering and leaving a dot and a solid line with one endpoint in all possible different ways such that the resulting diagrams are linked. A linked diagram cannot be pulled apart into two separate diagrams without cutting lines. An example of an unlinked diagram is given in Fig. 3.3A.





A Hugenholtz diagram is translated into one of its equivalent Brandow diagrams when the dots (which represent the two-electron interaction) are extended into dashed lines, where one arrow is entering and one leaving at both end points of the dashed line, e.g., $A \rightarrow 4$. The Hugenholtz diagram in Fig. 3.2, may, for example, be translated into one of the eight Brandow diagrams given in Fig. 3.2. At first glance, these eight diagrams look very different, but when applying the rules in Table II, their algebraic expressions become identical. To illustrate this and to get some experience in applying the rules in Table II, we evaluate Brandow diagrams A and E

G. Many-Body Perturbation Theory

Table II

Rules for Evaluating Brandow Diagrams.

- Label the diagram with general "hole" (α, β, γ, ...) (down arrow) and "particle" (m, n, p, ...) (up arrow) indices. A line that starts and ends at the same interaction is labeled with a hole index. An example of the labeling is given in Fig. 3.2A,E.
- The numerator of the diagram contains products of the one-electron integrals (if any) and the antisymmetrized two-electron integrals. The indices of the one- and two-electron integrals are assigned according to the rule

$$\langle out | -V | in \rangle$$

(left-out, right-out |left-in, right-in)

Examples:

p a x	~	$\langle p -V \alpha\rangle$
P Vag VB	~	$\langle pq \alpha \beta \rangle$
pVa_{q	~	<pq ar></pq ar>

- 3. The denominator corresponding to a given diagram is obtained by taking a factor equal to the sum of the hole orbital energies minus the sum of the particle orbital energies for each horizontal cut the eye draws between successive pairs of either dotted or solid lines. These n 1 individual factors are then multiplied to form the denominator.
- 4. Multiply the diagram by $(\frac{1}{2})^n$, where *n* is the number of "equivalent pairs" of lines. Two lines form an equivalent pair if they both begin at the same interaction, both end at the same interaction, and both go in the same direction (e.g., Fig. 3.1C has two pairs, Fig. 3.3A has one pair, and Fig. 3.2A-H has no pairs).
- 5. Multiply each numerator by (-1)^{I+h}, where h is the number of hole lines in the diagram and I the number of closed loops. A closed loop is formed when one can trace from one endpoint of an interaction along the direction of an arrow and end up back at the same point without ever having to cross an interaction (dashed) line (Fig. 3.3A contains three loops, Fig. 3.2C contains two loops, and Fig. 3.2B has one loop).

Brandow

6. Sum over all particle and hole states that occur in the diagram.

Hugenholtz



FIG. 3.2. Translation of a third-order Hugenholtz diagram into corresponding Brandow diagrams.

in Fig. 3.2. We obtain, using the labeling of particle and hole lines given in the figure

$$A = \sum_{\substack{\alpha\beta\gamma \\ mnp}} (-1)^{3+3} \frac{\langle \alpha\gamma | |mp \rangle \langle \beta m | |n\alpha \rangle \langle np | |\beta\gamma \rangle}{(\varepsilon_{\alpha} + \varepsilon_{\gamma} - \varepsilon_{m} - \varepsilon_{p})(\varepsilon_{\beta} + \varepsilon_{\gamma} - \varepsilon_{n} - \varepsilon_{p})}$$
(3.58)

Diagram A contains three hole lines and three closed loops. Diagram E may, in a similar way, be expressed as

$$E = \sum_{\substack{\alpha\beta\gamma\\mnp}} (-1)^{2+3} \frac{\langle \alpha\gamma | |mp\rangle \langle \beta m | |\alpha n\rangle \langle np | |\beta\gamma\rangle}{(\varepsilon_{\alpha} + \varepsilon_{\gamma} - \varepsilon_{m} - \varepsilon_{p})(\varepsilon_{\beta} + \varepsilon_{\gamma} - \varepsilon_{n} - \varepsilon_{p})}$$
(3.59)

since E contains two closed loops. Interchanging α and *n* in the second electronic interaction in E gives a minus sign and A and E thus become identical.

The reason for including only the linked diagrams in the expression for $E_j^{(n)}$ is further clarified by examining the value of an unlinked diagram, e.g., the one given in Fig. 3.3A:

$$\mathbf{A} = (-1)^{1+1} \sum_{\mu p} \langle p | V | \mu \rangle \langle \mu | V | p \rangle_{\frac{1}{2}}^{1} (-1)^{2+2} \sum_{\alpha \beta} \langle \alpha \beta | | \alpha \beta \rangle$$
(3.60)

Because, for two noninteracting subsystems, both of the disjoint sums occurring in Eq. (3.60) are size consistent (i.e., proportional to the size of the system), the product would not be size consistent. Hence, unlinked diagrams correspond directly to non-size-consistent factors, which should not be included.

If H^0 is taken to be the HF Hamiltonian, so that $V = V_{\rm HF}$ of Eq. (3.33), then certain simplifications occur. In particular, all diagrams containing the loop structure ∞ cancel with corresponding diagrams having the potential symbol $\rightarrow \star$ in the same location except in first order. For example, diagrams B and C of Fig. 3.3 cancel since the value of diagram C is

$$C = \frac{1}{2}(-1)^{2+2} \sum_{\substack{\alpha\beta \\ mnp}} \frac{\langle mp | | \alpha\beta \rangle \langle \alpha\beta | | np \rangle (-\langle n | V_{HF} | m \rangle)}{(\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_{p} - \varepsilon_{n})(\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_{p} - \varepsilon_{m})}$$
(3.61)

which, because

$$\langle n|V_{\rm HF}|m\rangle = \sum_{\mu} \langle n\mu||m\mu\rangle$$
 (3.62)



FIG. 3.3. Diagram A is unlinked and diagrams B and C demonstrate the cancellation of the Fock potential.

is equal to (but opposite in sign from) diagram B:

$$\mathbf{B} = \frac{1}{2} (-1)^{3+3} \sum_{\substack{\alpha \beta \mu \\ mnp}} \frac{\langle mp | | \alpha \beta \rangle \langle n\mu | | m\mu \rangle \langle \alpha \beta | | np \rangle}{(\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_{p} - \varepsilon_{n})(\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_{p} - \varepsilon_{m})}$$
(3.63)

Because of the cancellation of \mathcal{R} and \mathcal{A}^{*} that occurs in all orders beyond first, we need only consider diagrams A, B, and C in Fig. 3.1 to determine the energy consistent through second order when $V = V_{\text{HF}}$.

The first-order diagrams shown in Fig. 3.1A,B combine as follows:

$$A + B = \frac{1}{2}(-1)^{2+2} \sum_{\alpha\beta} \langle \alpha\beta | |\alpha\beta \rangle + (-1)^{1+1} \sum_{\alpha} (-) \langle \alpha | V_{\rm HF} | \alpha \rangle$$
$$= -\frac{1}{2} \sum_{\alpha\beta} \langle \alpha\beta | |\alpha\beta \rangle \qquad (3.64)$$

The second-order contribution may be written as

$$C = \sum_{\substack{\alpha\beta\\rs}} (\frac{1}{2})^2 (-1)^{2+2} \frac{\langle \alpha\beta | |rs \rangle \langle rs | |\alpha\beta \rangle}{\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_r - \varepsilon_s}$$
(3.65)

Both the first- and the second-order contributions are, of course, identical to the RSPT expression for $E_j^{(1)}$ and $E_j^{(2)}$ given in Eqs. (3.36) and (3.38), respectively.

In the application of MBPT to certain physical problems, it has been noticed that special families of diagrams seem to make important contributions to the energy in all orders. Attempts have been made to identify such diagrams and then to evaluate their energy contributions in a manner that permits these terms to be algebraically summed through all orders. One example of such a family of diagrams is shown in Fig. 3.4. We can apply the rules for Brandow diagrams given in Table II to each of these diagrams to obtain

$$(\mathbf{A}) = (\frac{1}{2})^2 \sum_{\substack{\alpha\beta \\ \alpha\beta}} (-1)^{2+2} \frac{\langle \alpha\beta | |rs \rangle \langle rs | |\alpha\beta \rangle}{\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_{r} - \varepsilon_{s}}$$
(3.66)

$$(\mathbf{B}) = (\frac{1}{2})^2 \sum_{\substack{\alpha\beta\\ r}} (-1)^{2+4} \frac{\langle \alpha\beta | |rs \rangle \langle \alpha\beta | |\alpha\beta \rangle \langle rs | |\alpha\beta \rangle}{(\epsilon_{\alpha} + \epsilon_{\beta} - \epsilon_{r} - \epsilon_{s})^{2}}$$
(3.67)

$$(C) = (\frac{1}{2})^2 \sum_{\substack{\alpha\beta \\ rs}} (-1)^{2+6} \frac{\langle \alpha\beta | |rs \rangle \langle \alpha\beta | |\alpha\beta \rangle^2 \langle rs | |\alpha\beta \rangle}{(\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_r - \varepsilon_s)^3}.$$
(3.68)



FIG. 3.4. A sequence of diagrams that can be summed to infinite order.

It should be clear that expression for higher-order diagrams analogous to Fig. 3.4A but with one or more additional interaction lines connecting α and β would involve higher powers of $\langle \alpha \beta | | \alpha \beta \rangle (\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_{r} - \varepsilon_{s})^{-1}$. Therefore, the series represented by the sum of Fig. 3.4A–C is an easily summed geometric series of the form $y + yx + yx^{2} + yx^{3} + \cdots$. The result of summing this series is to yield

$$\frac{(\frac{1}{2})^2}{r_s} \sum_{\substack{\alpha\beta \\ r_s}} \langle \alpha\beta | | r_s \rangle \langle r_s | | \alpha\beta \rangle (\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_r - \varepsilon_s)^{-1} [1 - \langle \alpha\beta | | \alpha\beta \rangle (\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_r - \varepsilon_s)^{-1}]^{-1}$$
(3.69)

which can be rearranged to read

$$\frac{1}{4} \sum_{\alpha\beta \atop rs} \langle \alpha\beta | |rs \rangle \langle rs | |\alpha\beta \rangle (\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_{r} - \varepsilon_{s} - \langle \alpha\beta | |\alpha\beta \rangle)^{-1}$$
(3.70)

We see that the result of summing the class of diagrams given in Fig. 3.4 is to generate an expression that is identical to the value of Fig. 3.4A except for the "denominator shift" of $-\langle \alpha \beta | | \alpha \beta \rangle$.

In addition to expressing E_j in terms of diagrams, we may write the perturbation corrections to $|j\rangle$ in this language. A few first- and second-order Brandow wavefunction diagrams are shown in Figs. 3.5. The rules for evaluating these diagrams are similar to those for the energy except in two ways. First, in counting the number of hole lines to determine the sign $(-1)^h$, the external hole lines are not included. Second, each free external line has associated with it an excitation operator and an orbital energy term. For example, the value of diagram D in Fig. 3.5 is

$$\mathbf{D} = \frac{1}{2} (-1)^{1+2} \sum_{\substack{pq \\ \alpha\beta\gamma}} \frac{\langle pq | |\alpha\beta\rangle \langle \alpha\beta| |\gammaq\rangle}{(\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_{p} - \varepsilon_{q})(\varepsilon_{\gamma} - \varepsilon_{p})} p^{+} \gamma | 0^{0} \rangle$$
(3.71)

As was the case for diagram contributions to E_j , the factors $> and > \rightarrow$ that occur in equivalent locations, for example, in Figs. 3.5A,B, exactly cancel when V is V_{HF} . The cancellation in Fig. 3.5A,B is the diagrammatic expression of the BT; that is, the first-or > r wavefunction contains no singly excited configurations.

The kind of perturbation theories (RSPT and MBPT, in particular) described above have proven to be useful quantum-chemical tools. However, these methods are expected to fail whenever the perturbation (the electronic



FIG. 3.5. All first- (A-C) and one (D) second-order wavefunction diagrams.

Problems

fluctuation potential if H^0 is the HF Hamiltonian) is not small or if the system under study is not well described in terms of a single Slater determinant. This would be the case, for example, when one or more of the states $|k^{0}\rangle$ is energetically close to $|j^{0}\rangle$ (i.e., $E_{j}^{0} - E_{k}^{0}$ is small). This arises often when one breaks chemical bonds. Also, it is often not possible to describe a system in terms of a single determinant whose spin-orbital occupation is held constant throughout a large position of nuclear configuration space [e.g., LiH $(1\sigma^2 2\sigma^2)$ gives improper dissociation into ionic states at large R]. For these reasons, there has been recent research activity aimed at developing MBPT for a multiconfigurational reference state, but such tools are not yet commonly available. Thus although MBPT is indeed a size-consistent theory in that it yields total energies proportional to the size of the system for a collection of noninteracting subsystems, it still may suffer from the improper dissociation problem common to most single-configuration-based theories. Size consistency and proper dissociation are different characteristics. The question of proper dissociation has to do with whether the wavefunction contains configurations that can yield proper dissociation products and whether the method used to compute the amplitudes of these configurations (e.g., CI, MBPT, MCSCF) can be trusted to be accurate as dissociation occurs. The MBPT may indeed contain the $1\sigma^2 2\sigma 3\sigma$ configuration needed to dissociate LiH, but the amplitude of this configuration (which dominates at large R) cannot be obtained from an MBPT calculation based upon using the $1\sigma^2 2\sigma^2$ configuration as $|0^0\rangle$ unless a very high correlation level is considered. Hence although MBPT would vield a size-consistent energy for two or more noninteracting LiH molecules (each at their equilibrium bond lengths) it fails to describe even one LiH molecule at large bond lengths.

PROBLEMS

3.1 Using the orbital energies and two-electron integrals found in Problem 2.1, carry out a RSPT calculation of the first-order wavefunction $|1\sigma^2\rangle^{(1)}$ and the second-order energy $E^{(2)}$ for the case in which the zeroth-order wavefunction is taken to be the $1\sigma^2$ Slater determinant.

1. Show that the first-order wavefunction is given by

$$|1\sigma^{2}\rangle^{(1)} = -0.0442|2\sigma^{2}\rangle$$

2. Why does the $|1\sigma 2\sigma\rangle$ configuration not enter into the first-order wavefunction?

3. Normalize the resultant wavefunction that contains zeroth- plus first-order parts and compare it to the wavefunction obtained in the two-configuration CI study of Problem 2.3.

4. Show that the second-order RSPT correlation energy of HeH⁺ is given by -0.0056 a.u. How does this compare with the correlation energy obtained from the two-configuration CI calculation?

5. Show that the second-order RSPT energy of a collection of n noninteracting HeH⁺ ions reduces to n times the correlation energy of one such ion.

3.2 Using MBPT, determine the third-order contribution to the correlation energy for the HeH $^+$.

1. Write all Hugenholtz diagrams that contribute in third order when the perturbation U = -V + W consists of the electronic repulsion W and a one-electron perturbation V.

In the following, assume now that $V = V_{HF}$.

2. Which of the diagrams of question 1 cancel?

3. Write the algebraic expression for the diagrams in question 2 that did not cancel.

The third-order contribution to the correlation energy for the HeH⁺ of Problem 2.1 can now be determined, using the HF orbital energies and the one- and two-electron integrals in the HF basis that is determined there.

4. Determine the third-order contribution to the correlation energy for the HeH^+ system.

5. Compare the third-order contribution with the second-order contributions determined in Problem 3.1 and the full CI correlation energy.

SOLUTIONS

3.1

1.
$$|j^{(1)}\rangle = -\sum_{\substack{\alpha < \beta \\ \alpha < \sigma}} \frac{\langle rs | |\alpha\beta\rangle}{\varepsilon_r + \varepsilon_s - \varepsilon_\alpha - \varepsilon_\beta} r^+ s^+ \beta \alpha | j^0 \rangle$$

In our case $\alpha = 1\sigma\alpha$, $\beta = 1\sigma\beta$, $r = 2\sigma\alpha$, $s = 2\sigma\beta$:

$$|1\sigma^{2(1)}\rangle = -\frac{\langle 22|11\rangle}{2(\epsilon_2 - \epsilon_1)} |2\sigma^2\rangle = -\frac{0.1261}{2[-0.2289 + 1.6562]} |2\sigma^2\rangle$$

= -0.0442|2\sigma^2\>

2. The BT gives $\langle 1\sigma^2 | H | 1\sigma 2\sigma \rangle = 0$; hence the $|1\sigma 2\sigma \rangle$ configuration does not enter into the first-order wavefunction.

3. $|0\rangle \cong |1\sigma^2\rangle - 0.0442|2\sigma^2\rangle$. To normalize, we divide by $[1 + (0.0442)^2]^{1/2} = 1.0010$:

$$|0\rangle = 0.9990 |1\sigma^2\rangle - 0.0441 |2\sigma^2\rangle$$

Solutions

In the CI, we got

$$|0\rangle \cong 0.9984 |1\sigma^{2}\rangle - 0.0556 |2\sigma^{2}\rangle$$
4. $E^{(2)} = -\frac{|\langle 22|11\rangle|^{2}}{2(\varepsilon_{2} - \varepsilon_{1})} = -\frac{(0.1261)^{2}}{2[-0.2289 + 1.6562]}$
 $= -0.0056$ a.u.

From the two CI energy, compared to the SCF energy $\langle 1\sigma^2 | H | 1\sigma^2 \rangle$, the correlation energy is -4.2790 - (-4.2720) = -0.0070 a.u.

5. $E^{(2)}$ is generally given by

$$\sum_{\substack{\alpha < \beta \\ m < p}} \frac{|\langle mp | |\alpha\beta\rangle|^2}{\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_m - \varepsilon_p}$$

For *n* noninteracting HeH⁺ ions, the integrals $\langle mp | | \alpha \beta \rangle$ involving orbitals on different ions vanish. Thus all four orbitals in $\langle mp | | \alpha \beta \rangle$ must be on the same ion. Hence

$$E^{(2)} = \sum_{A=1} \left(\sum_{\substack{\alpha < \beta \\ m < p}} \frac{|\langle mp | | \alpha\beta \rangle|^2}{\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_m - \varepsilon_p} \right)_{\text{on } A}$$

where A runs over the n HeH⁺ ions.

3.2

1. See Fig. 3.6, where the Hugenholtz diagrams are displayed.

2. Diagrams D1-X1 cancel with diagrams D2-X2 such that D1 cancels D2, E1 cancels E2, etc.

3. The Hugenholtz diagrams in Fig. 3.6A-C are translated into the corresponding Brandow diagrams in Fig. 3.7A-C, respectively. Each of these diagrams is then evaluated according to the rules to give

$$A = \sum_{\substack{mnpq \\ \alpha\beta}} \frac{1}{8} \frac{\langle \alpha\beta | |mn \rangle \langle mn| |pq \rangle \langle pq| |\alpha\beta \rangle}{(\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_{m} - \varepsilon_{n})(\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_{p} - \varepsilon_{q})}$$
$$B = \sum_{\substack{\alpha\beta\gamma\delta \\ mn}} \frac{1}{8} \frac{\langle \alpha\beta | |mn \rangle \langle \gamma\delta | |\alpha\beta \rangle \langle mn| |\gamma\delta \rangle}{(\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_{m} - \varepsilon_{n})(\varepsilon_{\gamma} + \varepsilon_{\delta} - \varepsilon_{m} - \varepsilon_{n})}$$
$$C = \sum_{\substack{\alpha\beta\gamma\delta \\ mn}} \frac{\langle \alpha\gamma | |mp \rangle \langle \betam| |n\alpha \rangle \langle np| |\beta\gamma \rangle}{(\varepsilon_{\alpha} + \varepsilon_{\gamma} - \varepsilon_{m} - \varepsilon_{p})(\varepsilon_{\beta} + \varepsilon_{\gamma} - \varepsilon_{n} - \varepsilon_{p})}$$

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References

4.
$$A = \frac{\langle 11|22 \rangle \langle 22|22 \rangle \langle 22|11 \rangle}{4(\varepsilon_1 - \varepsilon_2)^2} = 0.0012$$
$$B = \frac{\langle 11|22 \rangle \langle 11|11 \rangle \langle 22|11 \rangle}{4(\varepsilon_1 - \varepsilon_2)^2} = 0.0019$$
$$C = \frac{\langle 11|22 \rangle \langle 22|11 \rangle (\langle 12|21 \rangle - 2\langle 12|12 \rangle)}{2(\varepsilon_1 - \varepsilon_2)^2} = -0.0042$$

A + B + C = -0.0011

5. Second order, -0.0056; second + third order, -0.0067; full CI -0.0072.

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