

- b. For benzene, show that the diagrammatic result for the fourth-order energy agrees with the independently calculated result found in Exercise 6.6.

6.5 PERTURBATION EXPANSION OF THE CORRELATION ENERGY

In this section, we consider the problem of improving the Hartree-Fock energy of an N -electron system by means of perturbation theory. In other words, we wish to obtain a perturbation expansion for the correlation energy. We partition the Hamiltonian as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V} \quad (6.58)$$

where \mathcal{H}_0 is the Hartree-Fock Hamiltonian,

$$\mathcal{H}_0 = \sum_i f(i) = \sum_i [h(i) + v^{\text{HF}}(i)] \quad (6.59)$$

and

$$\mathcal{V} = \sum_{i<j} r_{ij}^{-1} - \mathcal{V}^{\text{HF}} = \sum_{i<j} r_{ij}^{-1} - \sum_i v^{\text{HF}}(i) \quad (6.60)$$

The use of the above partitioning of the Hamiltonian, along with the general expressions of RS perturbation theory, is sometimes called Møller-Plesset perturbation theory.

In this section, we will use the physicists' notation for two-electron integrals rather than the chemists' notation, which we used extensively in Chapter 3. We do this not out of perversity or even laziness but because almost all the literature in this area uses this notation, and we believe that one should develop equal facility with both notations. Recall that in the physicists' notation

$$\int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) = \langle ij|kl \rangle \quad (6.61)$$

It is important to remember that i and k label the spin orbitals which are functions of the coordinates of electron-one while j and l refer to spin orbitals which depend on the coordinates of electron-two, i.e.,

$$\langle \overbrace{ij}^{\downarrow} | \overbrace{kl}^{\downarrow} \rangle$$

Recall that the antisymmetrized two-electron integral is defined as

$$\langle ij||kl \rangle = \langle ij|kl \rangle - \langle ij|lk \rangle \quad (6.62)$$

Using this notation, we have

$$\left\langle \Psi_0 \left| \sum_{i < j} r_{ij}^{-1} \right| \Psi_{ab}^{rs} \right\rangle = \langle ab || rs \rangle \quad (6.63)$$

and

$$v^{\text{HF}}(1)\chi_j(\mathbf{x}_1) = \sum_b \langle b | r_{12}^{-1} | b \rangle \chi_j(\mathbf{x}_1) - \sum_b \langle b | r_{12}^{-1} | j \rangle \chi_b(\mathbf{x}_1) \quad (6.64)$$

Thus

$$\langle i | v^{\text{HF}} | j \rangle = v_{ij}^{\text{HF}} = \sum_b \langle ib | jb \rangle - \langle ib | bj \rangle = \sum_b \langle ib || jb \rangle \quad (6.65)$$

The Hartree-Fock wave function $|\Psi_0\rangle$ is an eigenfunction of \mathcal{H}_0 ,

$$\mathcal{H}_0 |\Psi_0\rangle = E_0^{(0)} |\Psi_0\rangle \quad (6.66)$$

with the eigenvalue

$$E_0^{(0)} = \sum_a \varepsilon_a \quad (6.67)$$

which is just the zeroth-order perturbation energy. The first-order energy is

$$\begin{aligned} E_0^{(1)} &= \langle \Psi_0 | \mathcal{V} | \Psi_0 \rangle \\ &= \langle \Psi_0 | \sum_{i < j} r_{ij}^{-1} | \Psi_0 \rangle - \langle \Psi_0 | \sum_i v^{\text{HF}}(i) | \Psi_0 \rangle \\ &= \frac{1}{2} \sum_{ab} \langle ab || ab \rangle - \sum_a \langle a | v^{\text{HF}} | a \rangle \\ &= -\frac{1}{2} \sum_{ab} \langle ab || ab \rangle \end{aligned} \quad (6.68)$$

The Hartree-Fock energy is the sum of the zeroth and first-order energies,

$$E_0 = E_0^{(0)} + E_0^{(1)} = \sum_a \varepsilon_a - \frac{1}{2} \sum_{ab} \langle ab || ab \rangle \quad (6.69)$$

Thus the first correction to the Hartree-Fock energy occurs in the second order of perturbation theory.

The general result for the second-order energy, derived in Section 6.1, is

$$E_0^{(2)} = \sum_n' \frac{|\langle 0 | \mathcal{V} | n \rangle|^2}{E_0^{(0)} - E_n^{(0)}} \quad (6.70)$$

where the summation runs over all but the ground state of the system. Clearly, we take $|0\rangle = |\Psi_0\rangle$ but what about $|n\rangle$? These states cannot be single excitations since

$$\begin{aligned} \langle \Psi_0 | \mathcal{V} | \Psi_a^r \rangle &= \langle \Psi_0 | \mathcal{H} - \mathcal{H}_0 | \Psi_a^r \rangle \\ &= \langle \Psi_0 | \mathcal{H} | \Psi_a^r \rangle - f_{ar} = 0 \end{aligned}$$

The first term vanishes because of Brillouin's theorem and the second because the spin orbitals are eigenfunctions of the Fock operator. In addition, triply excited states do not mix with $|\Psi_0\rangle$ because of the two-particle nature of the perturbation. Therefore, we are left with double excitations of the form $|\Psi_{ab}^{rs}\rangle$. Since

$$\mathcal{H}_0|\Psi_{ab}^{rs}\rangle = (E_0^{(0)} - (\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s))|\Psi_{ab}^{rs}\rangle$$

and because we can sum over all possible double excitations by summing over all a and all b greater than a and over all r and all s greater than r , the second-order energy is

$$E_0^{(2)} = \sum_{\substack{a < b \\ r < s}} \frac{|\langle \Psi_0 | \sum_{i < j} r_{ij}^{-1} |\Psi_{ab}^{rs}\rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} = \sum_{\substack{a < b \\ r < s}} \frac{|\langle ab || rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \quad (6.71)$$

Note that the second-order energy can be expressed as a sum of contributions from each pair of electrons in occupied orbitals,

$$E_0^{(2)} = \sum_{a < b} e_{ab}^{\text{FO}}$$

where

$$e_{ab}^{\text{FO}} = \sum_{r < s} \frac{|\langle ab || rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

We have seen in Chapter 5 that e_{ab}^{FO} is the first-order pair energy. Thus at the level of first-order pairs, pair theory gives the same correlation energy as second-order perturbation theory.

The expression for the second-order energy can be transformed into a number of other useful forms. Since the quantity being summed is symmetric in a and b and r and s , and vanishes when $a = b$ or $r = s$, we can write

$$E_0^{(2)} = \frac{1}{4} \sum_{abrs} \frac{|\langle ab || rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \quad (6.72)$$

Furthermore, in terms of regular two-electron integrals, the second-order energy is

$$E_0^{(2)} = \frac{1}{2} \sum_{abrs} \frac{\langle ab || rs \rangle \langle rs || ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \frac{1}{2} \sum_{abrs} \frac{\langle ab || rs \rangle \langle rs || ba \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \quad (6.73)$$

Finally, for a closed-shell system, the second-order energy can be written in terms of sums over spatial orbitals as

$$E_0^{(2)} = 2 \sum_{abrs} \frac{\langle ab || rs \rangle \langle rs || ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \sum_{abrs} \frac{\langle ab || rs \rangle \langle rs || ba \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \quad (6.74)$$

Exercise 6.8 Derive Eqs. (6.73) and (6.74) starting with Eq. (6.72).

In a similar, but much more laborious way, starting with Eq. (6.15) it can be shown that the third-order energy is

$$\begin{aligned}
 E_0^{(3)} = & \frac{1}{8} \sum_{abcdrs} \frac{\langle ab||rs\rangle\langle cd||ab\rangle\langle rs||cd\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)(\varepsilon_c + \varepsilon_d - \varepsilon_r - \varepsilon_s)} \\
 & + \frac{1}{8} \sum_{abrstu} \frac{\langle ab||rs\rangle\langle rs||tu\rangle\langle tu||ab\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)(\varepsilon_a + \varepsilon_b - \varepsilon_t - \varepsilon_u)} \\
 & + \sum_{abcrst} \frac{\langle ab||rs\rangle\langle cs||tb\rangle\langle rt||ac\rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)(\varepsilon_a + \varepsilon_c - \varepsilon_r - \varepsilon_t)} \quad (6.75)
 \end{aligned}$$

As an illustration of the above formalism, we now calculate the second and third-order energies of minimal basis H_2 . In Chapter 4, we showed that the exact correlation energy of H_2 in the minimal basis set is

$$E_{\text{corr}} = \Delta - (\Delta^2 + K_{12}^2)^{1/2} \quad (6.76)$$

where

$$\begin{aligned}
 2\Delta &= 2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12} \\
 &= 2(\varepsilon_2 - \varepsilon_1) + \langle 11|11\rangle + \langle 22|22\rangle - 4\langle 12|12\rangle + 2\langle 11|22\rangle
 \end{aligned}$$

If we expand the expression for the correlation energy in a Taylor series in the two-electron integrals up to third order, we find

$$E_{\text{corr}} = E_0^{(2)} + E_0^{(3)} + \dots$$

where

$$E_0^{(2)} = \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)} \quad (6.77)$$

and

$$E_0^{(3)} = \frac{K_{12}^2(J_{11} + J_{22} - 4J_{12} + 2K_{12})}{4(\varepsilon_1 - \varepsilon_2)^2} \quad (6.78)$$

We will now show that the second-order energy in Eq. (6.77) is a special case of the general expression given by Eq. (6.74). Since we have but a single hole orbital, $a = b = 1$. Similarly, $r = s = 2$ so that Eq. (6.74) becomes

$$\begin{aligned}
 E_0^{(2)} &= 2 \frac{\langle 11|22\rangle\langle 22|11\rangle}{2(\varepsilon_1 - \varepsilon_2)} - \frac{\langle 11|22\rangle\langle 22|11\rangle}{2(\varepsilon_1 - \varepsilon_2)} \\
 &= \frac{|\langle 11|22\rangle|^2}{2(\varepsilon_1 - \varepsilon_2)} = \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}
 \end{aligned}$$

In Section 6.7.2, we will show that the general expression for the third-order energy, given in Eq. (6.75), can be used to obtain the result given in Eqs. (6.78).

Exercise 6.9 Derive Eqs. (6.77) and (6.78) from (6.76).

6.6 THE N -DEPENDENCE OF THE RS PERTURBATION EXPANSION

In the introduction to this chapter, we mentioned that Brueckner was the first to investigate the applicability of the RS perturbation expansion of infinite (macroscopic) systems. He was able to show, by a careful examination of the algebraic expressions that appear in various orders, that $E_0^{(n)}$ for $n = 0, 1, \dots, 6$ was indeed proportional to the number of particles. He was, however, unable to prove this in general (i.e., for $n = 7, 8, \dots, \infty$). Here we present a simple illustration of Brueckner's analysis. In Subsection 6.7.2 we shall discuss Goldstone's linked cluster theorem which, using a diagrammatic representation of RS perturbation theory, is proof of Brueckner's conjecture that RS perturbation theory is satisfactory in all orders. We consider a supermolecule consisting of N noninteracting minimal basis H_2 molecules. We will show, using the general expressions derived in Section 6.1, that the first-, second-, and third-order energies of the supermolecule are simply N times the corresponding results for a single molecule. This is precisely the model we used to show, in Chapter 4, that the DCI result for the correlation energy was proportional to $N^{1/2}$ in the limit of large N . Recall that we label the orbitals of the supermolecule as:

$$\begin{array}{ccccccc} \frac{2_1}{1_1} & \frac{2_2}{1_2} & \frac{2_3}{1_3} & \dots & \frac{2_N}{1_N} & \varepsilon_2 & \\ & & & & & \varepsilon_1 & \end{array}$$

and that all two-electron integrals involving orbitals from different units are zero. The Hartree-Fock wave function for this system is

$$|\Psi_0\rangle = |1_1\bar{1}_1 1_2\bar{1}_2 \cdots 1_N\bar{1}_N\rangle \quad (6.79)$$

If \mathcal{H}_0 is the Hartree-Fock Hamiltonian as in the previous section, the zeroth- and first-order energies are

$$E_0^{(0)} = \langle \Psi_0 | \mathcal{H}_0 | \Psi_0 \rangle = 2 \sum_{i=1}^N \langle 1_i | f | 1_i \rangle = 2N\varepsilon_1 \quad (6.80a)$$

and

$$E_0^{(1)} = \langle \Psi_0 | \mathcal{V} | \Psi_0 \rangle = - \sum_{i=1}^N \langle 1_i 1_i | 1_i 1_i \rangle = -NJ_{11} \quad (6.80b)$$

The Hartree-Fock energy of the supermolecule,

$$E_0 = \langle \Psi_0 | \mathcal{H}_0 + \mathcal{V} | \Psi_0 \rangle = E_0^{(0)} + E_0^{(1)} = N(2\varepsilon_1 - J_{11}) \quad (6.81)$$

is indeed simply N times the Hartree-Fock energy of one subunit. The general expression for the second-order energy (Eq. (6.12)) is

$$E_0^{(2)} = \sum_n' \frac{|\langle 0|\mathcal{V}|n\rangle|^2}{E_0^{(0)} - E_n^{(0)}} \quad (6.82)$$

Clearly, $|0\rangle = |\Psi_0\rangle$ and the state $|n\rangle$ must be a double excitation of the type $|\Psi_{1,1}^{2,\bar{2}}\rangle$. For these excitations

$$E_0^{(0)} - E_n^{(0)} = 2(\varepsilon_1 - \varepsilon_2) \quad (6.83a)$$

$$\langle \Psi_0|\mathcal{V}|\Psi_{1,1}^{2,\bar{2}}\rangle = \langle 1_i\bar{1}_i|2_i\bar{2}_i\rangle - \langle 1_i\bar{1}_i|\bar{2}_i2_i\rangle = \langle 11|22\rangle = K_{12} \quad (6.83b)$$

and the summation over n can be replaced by a summation over i , so that

$$E_0^{(2)} = \sum_{i=1}^N \frac{|\langle \Psi_0|\mathcal{V}|\Psi_{1,1}^{2,\bar{2}}\rangle|^2}{2(\varepsilon_1 - \varepsilon_2)} = \frac{NK_{12}^2}{2(\varepsilon_1 - \varepsilon_2)} \quad (6.84)$$

which again is just N times the second-order energy of one unit.

The general expression for the third-order energy (Eq. (6.15)) is

$$E_0^{(3)} = A_0^{(3)} + B_0^{(3)} \quad (6.85)$$

where

$$A_0^{(3)} = \sum_n' \sum_m' \frac{\langle 0|\mathcal{V}|n\rangle \langle n|\mathcal{V}|m\rangle \langle m|\mathcal{V}|0\rangle}{(E_0^{(0)} - E_n^{(0)})(E_0^{(0)} - E_m^{(0)})} \quad (6.86)$$

and

$$B_0^{(3)} = -E_0^{(1)} \sum_n' \frac{|\langle 0|\mathcal{V}|n\rangle|^2}{(E_0^{(0)} - E_n^{(0)})^2} \quad (6.87)$$

At first glance, the third-order energy does not appear to have the correct N dependence, since $B_0^{(3)}$ is proportional to N^2 :

$$B_0^{(3)} = -(-NJ_{11}) \sum_{i=1}^N \frac{K_{12}^2}{(2\varepsilon_1 - 2\varepsilon_2)^2} = \frac{N^2 J_{11} K_{12}^2}{4(\varepsilon_1 - \varepsilon_2)^2} \quad (6.88)$$

where we have used Eqs. (6.80b) and (6.83a,b). If the third-order energy is to be proportional to N , this term must be cancelled by a part of $A_0^{(3)}$. This is just the type of cancellation that Brueckner found, as discussed in the introduction to this chapter. Let us now examine $A_0^{(3)}$ more closely. It is clear that both $|n\rangle$ and $|m\rangle$ must be states of the type $|\Psi_{1,1}^{2,\bar{2}}\rangle$ so that

$$A_0^{(3)} = \sum_{i=1}^N \frac{\langle \Psi_{1,1}^{2,\bar{2}}|\mathcal{V}|\Psi_{1,1}^{2,\bar{2}}\rangle K_{12}^2}{4(\varepsilon_1 - \varepsilon_2)^2} \quad (6.89)$$

where only the diagonal element remains since two-electron integrals

involving different units are zero. It can be shown that

$$\begin{aligned}\langle \Psi_{1,1}^{2,\bar{2}} | \mathcal{V} | \Psi_{1,1}^{2,\bar{2}} \rangle &= \langle \Psi_{1,1}^{2,\bar{2}} | \mathcal{H} - \mathcal{H}_0 | \Psi_{1,1}^{2,\bar{2}} \rangle \\ &= -NJ_{11} + J_{11} + J_{22} - 4J_{12} + 2K_{12}\end{aligned}\quad (6.90)$$

so we have

$$A_0^{(3)} = -\frac{N^2 J_{11} K_{12}^2}{4(\varepsilon_1 - \varepsilon_2)^2} + \frac{NK_{12}^2(J_{11} + J_{22} - 4J_{12} + 2K_{12})}{4(\varepsilon_1 - \varepsilon_2)^2}\quad (6.91)$$

Thus the N^2 terms do indeed cancel, leaving us with

$$E_0^{(3)} = A_0^{(3)} + B_0^{(3)} = \frac{NK_{12}^2(J_{11} + J_{22} - 4J_{12} + 2K_{12})}{4(\varepsilon_1 - \varepsilon_2)^2}\quad (6.92)$$

As with $E_0^{(1)}$ and $E_0^{(2)}$, this is just N times the third-order energy of a single H_2 molecule (Eq. (6.78)). Recall that Eq. (6.78) was obtained by expanding the exact correlation energy within the basis in a Taylor series, so that the equivalence of the expressions derived in different ways provides a consistency check. Although this example is by no means a proof, we hope it will inspire some confidence in the statement that RS perturbation theory—in contrast to DCI—yields an approximation to the correlation energy which is size consistent (i.e., has the correct N -dependence).

Exercise 6.10 Derive Eqs. (6.80b) and (6.90).

*6.7 DIAGRAMMATIC REPRESENTATION OF THE PERTURBATION EXPANSION OF THE CORRELATION ENERGY

We now introduce a diagrammatic representation of the n th-order energy. Our zeroth-order wave function is taken to be the Hartree-Fock function. Although it is possible to derive a perturbation expansion starting with any single determinantal wave function, the Hartree-Fock description is the most convenient starting point because of Brillouin's theorem. The fact that single excitations do not mix with the Hartree-Fock ground state considerably simplifies the structure of the perturbation expansion. The rules we give for constructing the diagrams will be correct only for Hartree-Fock perturbation theory. Although we will not "derive" the rules for constructing and evaluating the diagrams, we hope that the formalism will appear as a "natural" generalization of our previous results.

6.7.1 Hugenholtz Diagrams

As before, we represent an interaction by a dot and a hole or a particle state by a line with an arrow pointing down or up, respectively. Looking back to

systems that are characterized by degenerate or nearly degenerate electronic configurations. For such systems, MCSCF wave functions and multireference CI wave functions are better suited.

When the Hartree–Fock description is reasonably accurate – as for the stable water molecule – the restricted CCSD model appears to provide a satisfactory representation of the FCI wave function. Although less accurate than CCSDT, it represents a useful compromise between accuracy and cost and can be routinely applied to relatively large molecular systems in a black-box manner. The excellent performance of the CCSDT model is quite remarkable but its cost is so high that it is applicable only to small systems. For most purposes, however, the CCSDT model may be replaced by the CCSD(T) model at little or no loss of accuracy, making it possible to carry out highly accurate calculations on systems containing up to ten atoms.

5.8 Perturbation theory

When the Hartree–Fock wave function provides a reasonably accurate description of the electronic structure, it is tempting to try and improve on it by the application of perturbation theory. Indeed, this approach to the correlation problem has been quite successful in quantum chemistry – in particular, in the form of Møller–Plesset perturbation theory, to which we now turn our attention.

5.8.1 MØLLER–PLESSET PERTURBATION THEORY

In *Møller–Plesset perturbation theory (MPPT)*, the electronic Hamiltonian \hat{H} in (5.1.2) is partitioned as

$$\hat{H} = \hat{f} + \hat{\Phi} + h_{\text{nuc}} \quad (5.8.1)$$

where \hat{f} is the *Fock operator* (5.4.4) of Section 5.4.2, $\hat{\Phi}$ the *fluctuation potential* and h_{nuc} the nuclear–nuclear term. The fluctuation potential represents the difference between the true two-electron Coulomb potential \hat{g} of the Hamiltonian operator (5.1.2) and the effective one-electron Fock potential \hat{V} of the Fock operator (5.4.5):

$$\hat{\Phi} = \hat{H} - \hat{f} - h_{\text{nuc}} = \hat{g} - \hat{V} \quad (5.8.2)$$

In MPPT, the Fock operator represents the zero-order operator and the fluctuation potential the perturbation. The zero-order electronic state is represented by the Hartree–Fock state in the canonical representation

$$\hat{f}|\text{HF}\rangle = \sum_I \varepsilon_I |\text{HF}\rangle \quad (5.8.3)$$

where the summation is over the occupied spin orbitals. The excited zero-order states are spanned by all single, double and higher excitations $|\mu\rangle$ with respect to the Hartree–Fock state.

Applying the standard machinery of perturbation theory, we obtain to second order in the perturbation

$$E_{\text{MP}}^{(0)} = \langle \text{HF} | \hat{f} | \text{HF} \rangle = \sum_I \varepsilon_I \quad (5.8.4)$$

$$E_{\text{MP}}^{(1)} = \langle \text{HF} | \hat{\Phi} | \text{HF} \rangle \quad (5.8.5)$$

$$E_{\text{MP}}^{(2)} = - \sum_{A>B, I>J} \frac{|g_{AIBJ} - g_{AJBI}|^2}{\varepsilon_A + \varepsilon_B - \varepsilon_I - \varepsilon_J} \quad (5.8.6)$$

in the spin-orbital basis. Thus, the Hartree–Fock energy is equal to the sum of the zero- and first-order corrections

$$E_{\text{HF}} = E_{\text{MP}}^{(0)} + E_{\text{MP}}^{(1)} + h_{\text{nuc}} = \langle \text{HF} | \hat{H} | \text{HF} \rangle \quad (5.8.7)$$

and, by adding the second-order correction, we obtain the *second-order Møller–Plesset energy*

$$E_{\text{MP2}} = E_{\text{MP}}^{(0)} + E_{\text{MP}}^{(1)} + E_{\text{MP}}^{(2)} + h_{\text{nuc}} = E_{\text{HF}} - \sum_{A>B, I>J} \frac{|g_{AIBJ} - g_{AJBI}|^2}{\epsilon_A + \epsilon_B - \epsilon_I - \epsilon_J} \quad (5.8.8)$$

The MP2 model represents a highly successful approach to the correlation problem in quantum chemistry, providing a surprisingly accurate, size-extensive correction at low cost. Higher-order corrections may be derived as well. The MP3 and MP4 corrections, in particular, have found widespread use but represent less successful compromises between cost and accuracy than does the MP2 correction. For a detailed exposition of perturbation theory, we refer to Chapter 14.

5.8.2 THE GROUND STATE OF THE WATER MOLECULE

Let us consider the application of Møller–Plesset theory to the calculation of the dissociation curve of the water molecule. In Figure 5.19, we have plotted the cc-pVDZ potential-energy curves of the restricted and unrestricted Møller–Plesset models at the MP2, MP3 and MP4 levels. Close to the equilibrium geometry, the restricted MP2 energy represents a significant improvement on the Hartree–Fock energy. Referring to the CI energy curves in Figure 5.16, we find that the MP2 energy compares favourably with that of the more expensive CISD wave function, in particular when we recall that the MP2 correlation correction is size-extensive. The comparison with coupled-cluster theory in Figure 5.18 is less favourable.

The restricted Møller–Plesset description of the dissociation process is improved as we go to higher orders in perturbation theory, in particular at the MP4 level. However, as for all methods based on the dominance of a single electronic configuration, the description deteriorates as the OH bonds are stretched, although the MP4 curve is quite satisfactory for bond distances up to $3.5a_0$. For sufficiently large distances, the restricted potential-energy curves diverge at all levels of theory.

The performance of the unrestricted Møller–Plesset theory is perhaps somewhat surprising: even though the unrestricted theory performs well in the dissociation limit, its performance in the intermediate region is altogether unsatisfactory. Thus, the hump apparent in the coupled-cluster dissociation curve in Figure 5.18 is now much more prominent and persists even at the MP4 level. In addition, a kink has appeared where the restricted and unrestricted curves separate. Clearly, unrestricted Møller–Plesset perturbation theory does not provide a uniform description of the dissociation process and does not appear to be an appropriate tool for the study of such processes.

5.8.3 CONVERGENCE OF THE MØLLER–PLESSET PERTURBATION SERIES

Like any perturbation method, the Møller–Plesset series does not converge unconditionally. In Table 5.12, we have listed the restricted Møller–Plesset energies up to order 15 at R_{ref} and $2R_{\text{ref}}$. Although the series converges at the equilibrium bond distance, the convergence is less obvious at $2R_{\text{ref}}$. Clearly, at some point along the dissociation curve, the dominance of the RHF determinant is sufficiently eroded to destroy the convergence completely, although the exact location for the onset of the divergence would be difficult to pinpoint. For a discussion of convergence in Møller–Plesset theory, we refer to Section 14.5.

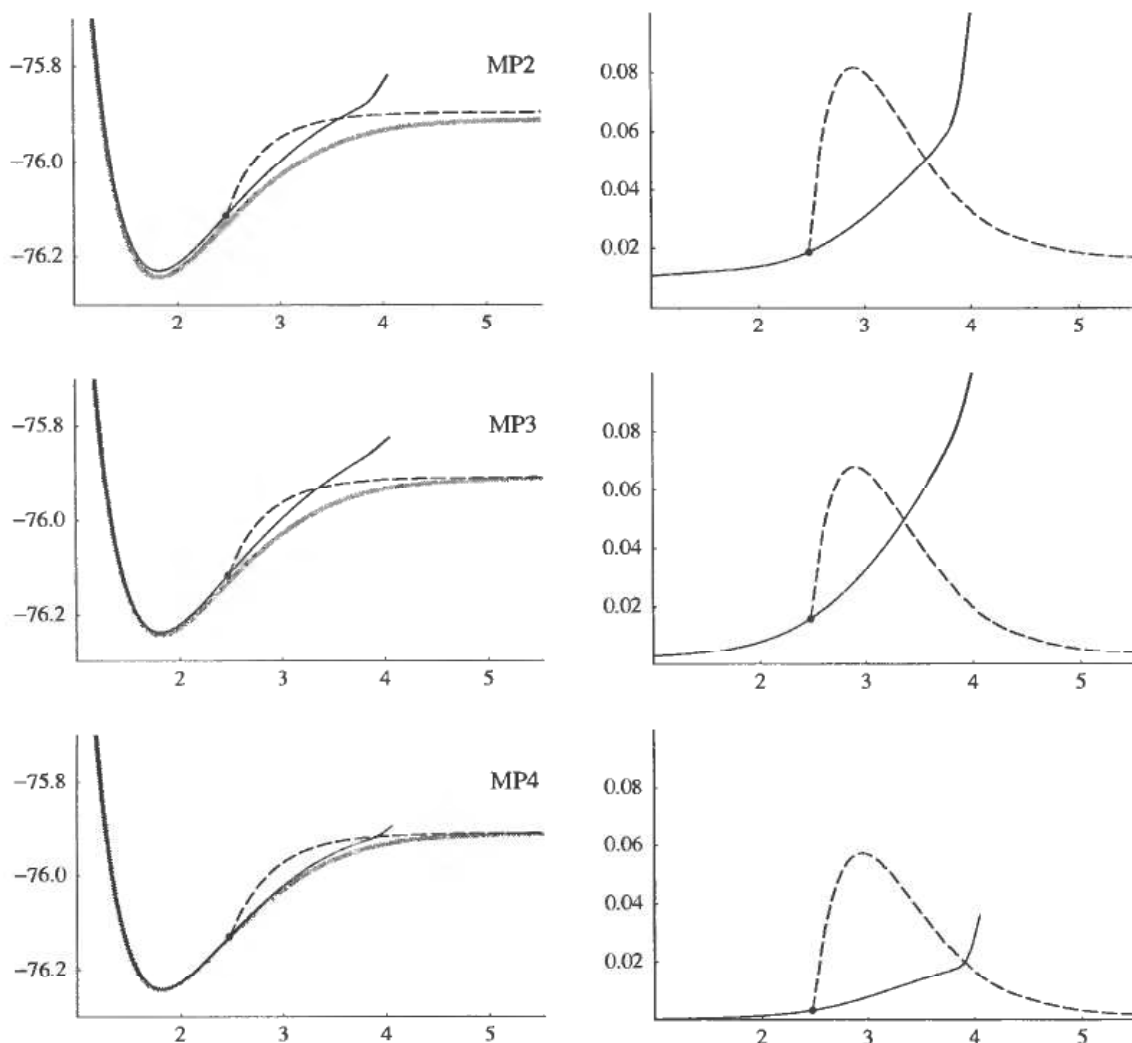


Fig. 5.19. The Møller–Plesset dissociation curves of the C_{2v} water molecule in the cc-pVDZ basis (atomic units) for a fixed HOH bond angle of 110.565° . In the two uppermost figures, we have on the left plotted the restricted MP2 dissociation curve (full black line), the unrestricted MP2 curve (dashed black line) and the FCI curve (grey line); on the right, we have plotted the corresponding differences between the MP2 and FCI energies. In the middle and lower figures, we have made similar plots for the MP3 and MP4 models.

As a minor point of interest, we note that the Møller–Plesset energy in Table 5.12 occasionally falls below that of the FCI wave function. This behaviour should not surprise us since the Møller–Plesset energy (like the coupled-cluster energy) is not variational. Indeed, we have already seen in Figure 5.19 that the unrestricted Møller–Plesset energy may be higher than the corresponding restricted energy, which would never happen for a variational wave function.

5.8.4 THE GROUND STATE OF THE HYDROGEN MOLECULE

As another illustration of the performance and, in particular, the conditional convergence of the Møller–Plesset series, we have in Figure 5.20 plotted the restricted MP2, MP3, MP4 and MP50 dissociation curves for the hydrogen molecule in the cc-pVQZ basis. For comparison, we have also plotted the FCI and RHF dissociation curves in the same basis.

Table 5.12 The differences ($E_{\text{MP}n} - E_{\text{FCI}}$) between the restricted cc-pVDZ Møller–Plesset energies and the FCI energy (in E_h) of the C_{2v} water molecule at the OH separations R_{ref} and $2R_{\text{ref}}$. The HOH bond angle is fixed at 110.565° and $R_{\text{ref}} = 1.84345a_0$

	$R = R_{\text{ref}}$	$R = 2R_{\text{ref}}$
RHF	0.217822	0.363954
MP2	0.013131	0.054730
MP3	0.006439	0.069096
MP4	0.001069	0.016046
MP5	0.000511	0.016686
MP6	0.000130	0.004300
MP7	0.000067	0.000626
MP8	0.000014	-0.000475
MP9	0.000011	-0.002065
MP10	-0.000001	-0.001652
MP11	-0.000002	-0.001332
MP12	0.000000	-0.001130
MP13	0.000000	-0.000523
MP14	0.000000	-0.000397
MP15	0.000000	-0.000146

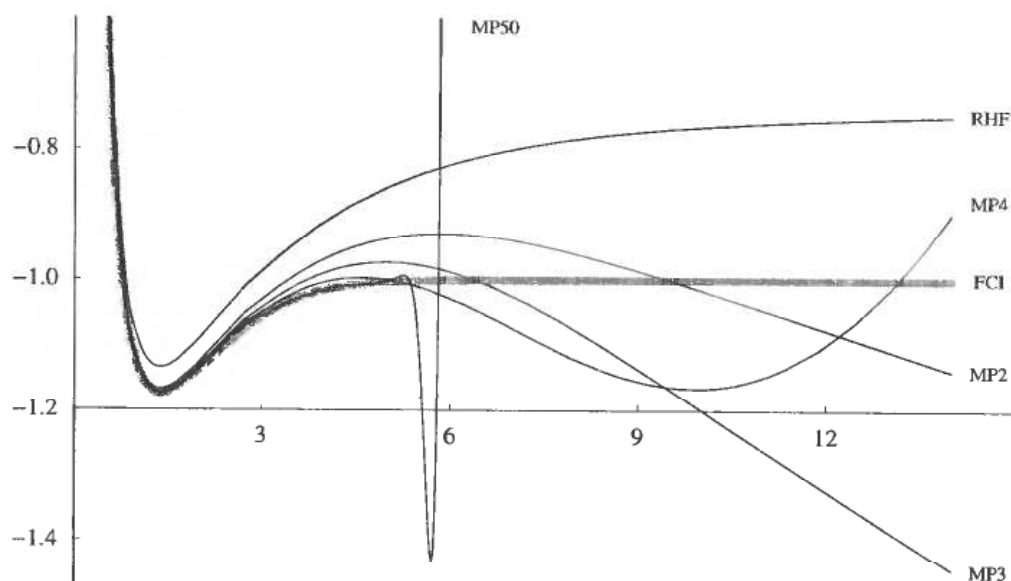


Fig. 5.20. The cc-pVQZ potential-energy curves of the hydrogen molecule at the FCI, RHF, MP2, MP3, MP4 and MP50 levels (atomic units). The oscillations in the MP50 potential-energy curve for bond lengths beyond $6a_0$ are not shown.

For bond distances shorter than $5a_0$, the perturbation series converges and MPPT provides excellent representations of the FCI curve, particularly for distances shorter than $3a_0$. At $5-6a_0$, however, the MPPT convergence is disrupted, as seen from the pathological behaviour of the MP50 curve. Also, the lower-order curves behave in an unphysical manner for long bond distances, although in a less spectacular fashion. Thus, the MP2, MP3 and MP4 curves bend downwards

and intersect the FCI curve at the internuclear separations of 9.5, 6.4 and $5.2a_0$, respectively. At a separation of $13.2a_0$, the MP4 curve rises above the FCI curve again.

5.8.5 FINAL COMMENTS

Møller–Plesset perturbation theory represents a useful approach to the calculation of size-extensive correlation energies for systems dominated by a single electronic configuration. The MP2 model, in particular, represents a successful compromise between computational cost and accuracy. Higher-order corrections may also be calculated, but it should be emphasized that the Møller–Plesset series does not converge unconditionally.

The application of Møller–Plesset theory is limited to systems dominated by a single configuration, making the theory ill suited to the study of near-degeneracy problems. Also, since Møller–Plesset theory is based on the Hartree–Fock description, it is not well suited to the study of excited electronic states. For such problems, *multiconfigurational perturbation theory* has been developed, based on the dominance of an active reference space. Multiconfigurational perturbation theory is discussed in Chapter 14, as part of a detailed exposition of perturbation methods in electronic-structure theory.

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Further reading

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Exercises

EXERCISE 5.1

Calculate the overlap integral

$$S = \int 1_{SA}(\mathbf{r})1_{SB}(\mathbf{r}) \, d\mathbf{r} \quad (5E.1.1)$$