CHAPTER FIVE

PAIR AND COUPLED-PAIR THEORIES

We saw in Chapter 4 that configuration interaction (CI) using only doubly excited states (DCI) predicts that the correlation energy of N noninteracting minimal basis H_2 molecules is proportional to $N^{1/2}$ as N becomes large. Because the energy of a macroscopic system is an extensive thermodynamic property, it must be proportional to the number of particles; thus DCI is not a satisfactory procedure for treating large systems. For example, the correlation energy per atom of a crystal obtained using DCI is zero! It is clear that to describe correlation in infinite systems one must use methods that yield energies that are proportional to the number of particles. Even for finite systems, it is desirable to use approximations which give results that can be meaningfully compared for molecules of different size. For example, when studying the dissociation of a molecule one should use a method which is equally good, in a certain sense, for the intact molecule and the resulting fragments. Approximations, which have the property that the calculated energies vary linearly with the number of particles as the size of the system increases, are said to be *size consistent*. In the special case of a supermolecule formed from N closed-shell noninteracting "monomers," a size-consistent scheme yields a supermolecule energy which is just N times the monomer energy.

Although size consistency seems like a modest requirement, all forms of CI except full CI, which is of course exact, do not have this property. In this chapter we consider pair and coupled-pair theories, which are size consistent, and in the next chapter we discuss a form of perturbation theory, which also has this property. The price one pays for size consistency is that unlike DCI, pair and perturbation theories are not variational and the total electronic energy obtained using them can be lower than the true energy. For example, pair theory can give, in certain cases, as much as 120% of the correlation energy.

In Section 5.1 we describe the independent electron pair approximation (IEPA). We use an approach that leads quickly to the computational formalism but which may give the misleading impression that IEPA is an approximation to DCI. After showing what is involved in performing pair calculations, we will return to the physical basis of the formalism and show that in fact both IEPA and DCI are different approximations to *full* CI. In Subsection 5.1.1 we describe a deficiency of the IEPA, not shared by DCI or the perturbation theory of Chapter 6 namely, that the IEPA is not invariant under unitary transformations of degenerate molecular orbitals. In Subsection 5.1.2 we present some numerical results which show that while the IEPA is reasonably accurate for small atoms, it has serious deficiencies when applied to larger molecules.

In Section 5.2 we consider how to go beyond the IEPA by incorporating coupling between different pairs of electrons. We will discuss the coupled pair many-electron theory (CPMET) which is also called the coupled-cluster approximation (CCA). We then describe a number of simplifications to this rather sophisticated approach; in particular, we consider the coupled electron pair approximation (CEPA). Finally, in Subsection 5.2.4 we present some numerical applications of coupled-pair theories.

Since coupled pair theories are important but somewhat complicated, in Section 5.3 we discuss, as a pedagogical device, the use of these methods to calculate the energy of an N-electron system described by a Hamiltonian containing only single particle interactions. This problem can easily be solved exactly in an elementary way. However, by seeing how "high-powered" approaches work in a simple context, we will be able to gain insight into the nature of these approximations. In particular, the relationship between different many-electron theories will become clear. As a concrete application of many-electron formalisms (CI, IEPA, CEPA, etc.) to a system described by a one-electron Hamiltonian, we consider the resonance energy of cyclic polyenes within the framework of Hückel theory in Subsection 5.3.2. Our purpose here is not to advocate the use of Hückel theory or the use of many-electron methods to obtain the resonance energy. Rather, we wish to exploit the analogy between the resonance energy and the correlation energy and provide an analytically tractable model which can be used to illustrate some of the computational aspects of various many-electron approaches.

5.1 THE INDEPENDENT ELECTRON PAIR APPROXIMATION (IEPA)

We have seen in the last chapter that the correlation energy obtained from the intermediate normalized (i.e., $\langle\Phi_0|\Psi_0\rangle = 1$) full CI wave function formed by making all possible spin orbital excitations from the HF determinant is

$$E_{\text{corr}} = \sum_{a<b} \sum_{r<s} c_{ab}^{rs} \langle \Psi_0 | \mathscr{H} | \Psi_{ab}^{rs} \rangle = \frac{1}{4} \sum_{ab} \sum_{rs} c_{ab}^{rs} \langle \Psi_0 | \mathscr{H} | \Psi_{ab}^{rs} \rangle \tag{5.1}$$

where c_{ab}^{rs} are the variationally determined coefficients of the doubly excited determinants in the full CI wave function. Recall that the coefficients of single excitations are absent because of Brillouin's theorem, while triple and higher excitations do not appear because the Hamiltonian contains at most two-particle interactions. This expression suggests that we write the total correlation energy as a sum of contributions from each occupied pair of spin orbitals,

$$E_{\text{corr}} = \sum_{a<b} e_{ab} \tag{5.2}$$

with

$$e_{ab} = \sum_{r<s} c_{ab}^{rs} \langle \Psi_0 | \mathscr{H} | \Psi_{ab}^{rs} \rangle \tag{5.3}$$

where e_{ab} is the correlation energy resulting from the interaction of the pair of electrons which, in the Hartree-Fock approximation, occupy spin orbitals χ_a and χ_b. Although the above decomposition is exact, it is also deceptive since we need the full CI wave function to obtain the coefficients c_{ab}^{rs}. Thus for an N-electron system, we must consider all the electrons to calculate exactly e_{ab} for the ab pair. Can we devise a scheme for approximating the pair energy of each pair of electrons independently of other pairs? If so, then in effect we could approximately reduce an N-electron problem to $N(N-1)/2$ two-electron problems. The independent electron pair approximation (IEPA) is such a scheme. The IEPA was introduced in quantum chemistry, independently, by O. Sinanoğlu[1] and R. K. Nesbet.[2] These authors used different terminology and formulations, but their final results are essentially equivalent. Sinanoğlu called his theory the Many-Electron Theory (MET) while Nesbet used the name Bethe-Goldstone Theory. In addition, for reasons which will become apparent shortly, the IEPA has been referred to as "pair-at-a-time" CI.

How can we calculate the correlation energy associated with a pair of electrons in spin orbitals a and b (i.e., the pair energy e_{ab})? The simplest approach is to forget about the remaining $N-2$ electrons (i.e., leave them in their HF spin orbitals) and let only the electrons in spin orbitals a and b correlate by exciting them into the virtual orbitals. We construct a correlated wave function for the pair ab, denoted by $|\Psi_{ab}\rangle$, by allowing the HF wave function to interact with determinants formed by exciting only this pair. If for the sake of simplicity we ignore single excitations (which as we have seen in the last chapter have little effect on the correlation energy), the *pair function* $|\Psi_{ab}\rangle$ is

$$|\Psi_{ab}\rangle = |\Psi_0\rangle + \sum_{r<s} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle \tag{5.4}$$

where, as usual, we use intermediate normalization. The energy of this wave function, E_{ab}, is just the sum of the HF energy and the pair correlation energy,

$$E_{ab} = \langle\Psi_0|\mathscr{H}|\Psi_0\rangle + e_{ab} = E_0 + e_{ab} \tag{5.5}$$

Thus the energy of this wave function is below the HF energy by the pair correlation energy. To obtain the best possible energy for the above pair-function, we use the linear variation method. Thus we construct the matrix representation of the Hamiltonian in the subspace spanned by $|\Psi_0\rangle$ and all double excitations involving χ_a and χ_b and then find the lowest eigenvalue of this matrix. Equivalently, we substitute the expansion for $|\Psi_{ab}\rangle$ into

$$\mathscr{H}|\Psi_{ab}\rangle = E_{ab}|\Psi_{ab}\rangle \tag{5.6}$$

to obtain

$$\mathscr{H}\left(|\Psi_0\rangle + \sum_{t<u} c_{ab}^{tu}|\Psi_{ab}^{tu}\rangle\right) = E_{ab}\left(|\Psi_0\rangle + \sum_{t<u} c_{ab}^{tu}|\Psi_{ab}^{tu}\rangle\right) \tag{5.7}$$

We then multiply this equation successively by $\langle\Psi_0|$ and $\langle\Psi_{ab}^{rs}|$ to obtain

$$E_0 + \sum_{t<u} c_{ab}^{tu}\langle\Psi_0|\mathscr{H}|\Psi_{ab}^{tu}\rangle = E_{ab} \tag{5.8a}$$

and

$$\langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_0\rangle + \sum_{t<u} \langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_{ab}^{tu}\rangle c_{ab}^{tu} = E_{ab}c_{ab}^{rs} \tag{5.8b}$$

Using Eq. (5.5), these equations become

$$\sum_{t<u} c_{ab}^{tu}\langle\Psi_0|\mathscr{H}|\Psi_{ab}^{tu}\rangle = e_{ab} \tag{5.9a}$$

and

$$\langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_0\rangle + \sum_{t<u} \langle\Psi_{ab}^{rs}|\mathscr{H} - E_0|\Psi_{ab}^{tu}\rangle c_{ab}^{tu} = e_{ab}c_{ab}^{rs} \tag{5.9b}$$

Finally, one can rewrite these equations in matrix form by defining

$$(\mathbf{D}_{ab})_{rs,tu} = \langle\Psi_{ab}^{rs}|\mathscr{H} - E_0|\Psi_{ab}^{tu}\rangle \tag{5.10a}$$

$$(\mathbf{B}_{ab})_{rs} = \langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_0\rangle \tag{5.10b}$$

$$(\mathbf{c}_{ab})_{rs} = c_{ab}^{rs} \tag{5.10c}$$

so that Eqs. (5.9a) and (5.9b) are equivalent to

$$\begin{pmatrix} 0 & \mathbf{B}_{ab}^\dagger \\ \mathbf{B}_{ab} & \mathbf{D}_{ab} \end{pmatrix}\begin{pmatrix} 1 \\ \mathbf{c}_{ab} \end{pmatrix} = e_{ab}\begin{pmatrix} 1 \\ \mathbf{c}_{ab} \end{pmatrix} \tag{5.11}$$

This matrix eigenvalue problem is solved for each of the $N(N-1)/2$ pairs of occupied electrons. The total correlation energy is then obtained by adding up the respective pair energies,

$$E_{\text{corr}}(\text{IEPA}) = \sum_{a<b} e_{ab} \tag{5.12}$$

Although each pair energy e_{ab} is obtained by doing a variational, CI-type calculation, the sum of the pair energies is not necessarily above the exact correlation energy. The individual pair CI matrices are much smaller than the DCI matrix and one never has to calculate matrix elements of the type $\langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_{cd}^{tu}\rangle$ which couple the pairs *ab* and *cd*. The IEPA is computationally equivalent to doing DCI for each pair separately; thus, it is sometimes called "pair-at-a-time" CI. This terminology and the fact that the IEPA is computationally simpler than DCI would appear to suggest that the IEPA is an approximation to DCI. However, this is misleading and as we will see in the next section, where we consider how to incorporate coupling between different pairs, it is more appropriate to view the IEPA as an approximation to full CI which is different from DCI.

Before we give a simple illustration of pair theory, we consider some approximations to the pair equations in order to make contact with perturbation theory. If in Eq. (5.9b) we neglect coupling between excited determinants (i.e., we keep only the term $t = r$ and $u = s$ in the summation), we have

$$\langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_0\rangle + \langle\Psi_{ab}^{rs}|\mathscr{H} - E_0|\Psi_{ab}^{rs}\rangle c_{ab}^{rs} = e_{ab}c_{ab}^{rs} \tag{5.13}$$

If we solve this equation for c_{ab}^{rs} and substitute it into Eq. (5.9a), we obtain

$$e_{ab} = -\sum_{r<s} \frac{|\langle\Psi_0|\mathscr{H}|\Psi_{ab}^{rs}\rangle|^2}{\langle\Psi_{ab}^{rs}|\mathscr{H} - E_0|\Psi_{ab}^{rs}\rangle - e_{ab}} \tag{5.14}$$

Since e_{ab} is small compared with the difference between the energies of the HF and doubly excited states, it can be set equal to zero in the denominator, so that we have

$$e_{ab}^{\text{EN}} = -\sum_{r<s} \frac{|\langle\Psi_0|\mathscr{H}|\Psi_{ab}^{rs}\rangle|^2}{\langle\Psi_{ab}^{rs}|\mathscr{H} - E_0|\Psi_{ab}^{rs}\rangle} \tag{5.15}$$

Since the correlation energy obtained using this approximation to the pair energies,

$$E_{\text{corr}}(\text{EN}) = \sum_{a<b} e_{ab}^{\text{EN}} \tag{5.16}$$

was derived by Epstein and Nesbet, e_{ab}^{EN} is called the Epstein-Nesbet pair correlation energy. Since the total correlation energy using Epstein-Nesbet pairs, with large basis sets, overestimates the correlation energy even more than pair theory, it is only occasionally discussed in this book. Finally, if we further approximate the energy difference between $|\Psi_0\rangle$ and $|\Psi_{ab}^{rs}\rangle$ by differences in HF orbital energies,

$$\langle\Psi_{ab}^{rs}|\mathscr{H} - E_0|\Psi_{ab}^{rs}\rangle \cong \varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b \tag{5.17}$$

then we obtain

$$e_{ab}^{\mathrm{FO}} = \sum_{r<s} \frac{|\langle\Psi_0|\mathscr{H}|\Psi_{ab}^{rs}\rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \tag{5.18}$$

which is called the first-order pair energy and is the simplest possible approximation to pair theory. The correlation energy obtained using first-order pairs is

$$E_{\mathrm{corr}}(\mathrm{FO}) = \sum_{a<b}\sum_{r<s} \frac{|\langle\Psi_0|\mathscr{H}|\Psi_{ab}^{rs}\rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} = \sum_{a<b}\sum_{r<s} \frac{|\langle ab||rs\rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \tag{5.19}$$

As we will see in the next chapter, this expression is identical to the first correction to the HF energy obtained within the framework of many-body perturbation theory (i.e., it is the second-order energy). Thus the simplest form of perturbation theory immediately leads to a form of pair theory.

Exercise 5.1 The application of pair theory to minimal basis H_2 is trivial since we are dealing with a two-electron system for which the IEPA is exact, i.e., it gives the full CI result obtained in the last chapter, viz.

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

where (see Eq. (4.20))

$$\Delta = (\varepsilon_2 - \varepsilon_1) + \tfrac{1}{2}(J_{11} + J_{22} - 4J_{12} + 2K_{12})$$

a. Calculate the correlation energy using first-order pairs. Remember that the summations in Eq. (5.19) go over spin orbitals (i.e., $a = 1, \bar{1}$ and $r = 2, \bar{2}$). Show that

$$^1E_{\mathrm{corr}}(\mathrm{FO}) = \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}.$$

b. Approximate Δ in the exact correlation energy by $\varepsilon_2 - \varepsilon_1$ and recover the first-order pair correlation energy by expanding the exact answer to first order using the relation $(1 + x)^{1/2} \simeq 1 + x/2$.

As a simple illustration of pair theory we calculate the correlation energy of a dimer consisting of two noninteracting minimal basis H_2 molecules. Since H_2 contains only two electrons, pair theory is identical to full CI and hence is exact for the monomer. Recall that we label the occupied and virtual orbitals of the ith monomer as 1_i and 2_i, respectively, and that, since the monomers are noninteracting, all two-electron integrals containing orbitals from different subunits are zero. Since the dimer has the configuration

$(1_1)^2(1_2)^2$, we need to find six pair correlation energies, i.e., $e_{1_1\bar{1}_1}$, $e_{1_1 1_2}$, $e_{1_1\bar{1}_2}$, $e_{\bar{1}_1 1_2}$, $e_{\bar{1}_1\bar{1}_2}$, and $e_{1_2\bar{1}_2}$. However, only two of these six pair energies are nonzero namely, $e_{1_1\bar{1}_1}$ and $e_{1_2\bar{1}_2}$. To see this, consider the mixing of a doubly excited state in which a pair, say $(1_i, \bar{1}_j)$ is excited into the virtual orbitals 2_k and $\bar{2}_l$, with the HF ground state

$$\langle\Psi_0|\mathscr{H}|\Psi_{1_i\bar{1}_j}^{2_k\bar{2}_l}\rangle = \langle 1_i\bar{1}_j||2_k\bar{2}_l\rangle$$
$$= \begin{cases} \langle 11|22\rangle = K_{12} & \text{if } i = j = k = l \\ 0 & \text{otherwise} \end{cases} \tag{5.20}$$

Since this matrix element is zero unless both electrons are located within a given subunit and unless they are excited to the virtual orbitals of the same subunits, the pair function for $(1_i, \bar{1}_i)$, is

$$|\Psi_{1_i\bar{1}_i}\rangle = |\Psi_0\rangle + c_{1_i\bar{1}_i}^{2_i\bar{2}_i}|\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\rangle \tag{5.21}$$

The corresponding pair equations obtained from Eqs. (5.9a) and (5.9b) are

$$K_{12}c_{1_i\bar{1}_i}^{2_i\bar{2}_i} = e_{1_i\bar{1}_i} \tag{5.22a}$$

$$K_{12} + 2\Delta c_{1_i\bar{1}_i}^{2_i\bar{2}_i} = e_{1_i\bar{1}_i}c_{1_i\bar{1}_i}^{2_i\bar{2}_i} \tag{5.22b}$$

where $2\Delta = 2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12}$. These equations are identical to the full CI equations of a single minimal basis H_2 molecule (see Eqs. (4.19a) and (4.21)). Thus $e_{1_1\bar{1}_1} = e_{1_2\bar{1}_2} = {}^1E_{\text{corr}}$ where ${}^1E_{\text{corr}}$ is the exact correlation energy of a single H_2 molecule. Then the total correlation energy in the IEPA for the dimer is

$${}^2E_{\text{corr}}(\text{IEPA}) = e_{1_1\bar{1}_1} + e_{1_2\bar{1}_2} = 2\,{}^1E_{\text{corr}} \tag{5.23}$$

so that it is twice the exact correlation energy of the monomer. The above discussion can immediately be extended to show that the IEPA correlation energy of N independent H_2 molecules is N times the correlation energy of the monomer. Thus we see that the IEPA is size consistent as stated previously. Since IEPA is exact while DCI fails badly for this model, one cannot really consider the IEPA to be an approximation to DCI.

Exercise 5.2 Derive Eqs. (5.22a) and (5.22b).

Exercise 5.3 Calculate the total first-order pair correlation energy for the dimer using Eq. (5.19) and show that it is twice the result obtained in Exercise 5.1.

5.1.1 Invariance under Unitary Transformations: An Example

In spite of the fact that the IEPA is not variational, it has an advantage over DCI in that it is size consistent. Unlike DCI and many-body perturbation theory (discussed in Chapter 6) the IEPA has the distinct disadvantage of not being invariant to unitary transformations of the occupied spin orbitals in the HF determinant. As we have seen in Chapter 3, if we transform the occupied spin orbitals $\{\chi_a\}$ among themselves, $|\Psi_0\rangle$ will not change; however, the total correlation energy obtained using the IEPA will be different. Since the canonical HF orbitals are unique, apart from degeneracies, the IEPA using nondegenerate orbitals does give a unique correlation energy. In the case of degeneracies, however, an arbitrary mixing of degenerate orbitals can occur in the SCF calculation. The particular linear combination obtained can be a function, for example, of the iteration step at which it was decided to terminate the procedure. The fact that the sum of pair correlation energies is not invariant to this very arbitrary mixing is particularly distressing.

We now investigate this invariance problem with our minimal basis model of two noninteracting H_2 molecules. The following example also provides us with an opportunity to introduce the concept of *spin-adapted pair correlation* energies. Up to this point we have considered *spin-orbital* pair energies. For example, in a 4-electron system with ψ_1 and ψ_2 doubly occupied, we must calculate six spin-orbital pair energies, i.e., $e_{1\bar{1}}$, $e_{\bar{1}2}$, $e_{1\bar{2}}$, $e_{\bar{1}\bar{2}}$, e_{12}, and $e_{2\bar{2}}$. However, not all of the corresponding spin-orbital pair functions are eigenfunctions of $\mathscr{S}^2$. In particular, Ψ_{12}, $\Psi_{1\bar{2}}$, $\Psi_{\bar{1}2}$, and $\Psi_{\bar{1}\bar{2}}$ are not pure spin states. The idea behind spin-adapted pair theory is simply to use only pair functions which are eigenfunctions of $\mathscr{S}^2$. In general, the correlation energy calculated from spin-orbital or spin-adapted pair energies differs, as will be shown by our example.

For two independent H_2 molecules using molecular orbitals *localized* on the two monomers, (i.e., $1_1, 2_1, 1_2, 2_2$) we have seen that the IEPA gives the exact result for the correlation energy of the dimer. We now repeat our analysis using a set of equivalent *delocalized* molecular orbitals. Since orbitals 1_1 and 1_2 as well as 2_1 and 2_2 are degenerate, we can take an arbitrary linear combination of them and retain the same HF description. In particular we consider the completely delocalized orbitals,

$$a = 2^{-1/2}(1_1 + 1_2) \qquad \underset{\cdot}{+} \quad \underset{\cdot}{+} \qquad \underset{\cdot}{+} \quad \underset{\cdot}{+} \quad (g) \tag{5.24a}$$

$$b = 2^{-1/2}(1_1 - 1_2) \qquad \underset{\cdot}{+} \quad \underset{\cdot}{+} \qquad \underset{\cdot}{-} \quad \underset{\cdot}{-} \quad (u) \tag{5.24b}$$

$$r = 2^{-1/2}(2_1 - 2_2) \qquad \underset{\cdot}{+} \quad \underset{\cdot}{-} \qquad \underset{\cdot}{-} \quad \underset{\cdot}{+} \quad (g) \tag{5.24c}$$

$$s = 2^{-1/2}(2_1 + 2_2) \qquad \underset{\cdot}{+} \quad \underset{\cdot}{-} \qquad \underset{\cdot}{+} \quad \underset{\cdot}{-} \quad (u) \tag{5.24d}$$

The pluses and minuses indicate the sign of the atomic basis functions in the LCAO description of the four orbitals. Note that a and r are of gerade symmetry while b and s are of ungerade symmetry. The HF wave function in terms of these delocalized orbitals is

$$|\Psi_0\rangle = |a\bar{a}b\bar{b}\rangle \tag{5.25}$$

This wave function is identical to $|1_1\bar{1}_1 1_2\bar{1}_2\rangle$, which is a reflection of the fact that the HF wave function is invariant to a unitary transformation of the occupied orbitals.

Exercise 5.4 Show that $|a\bar{a}b\bar{b}\rangle = |1_1\bar{1}_1 1_2\bar{1}_2\rangle$. *Hint:* use Eq. (1.40) repeatedly. Eq. (1.40) for Slater determinants is

$$|\chi_1\chi_2\cdots\left(\sum_k c_k\chi'_k\right)\cdots\chi_N\rangle = \sum_k c_k|\chi_1\chi_2\cdots\chi'_k\cdots\chi_N\rangle$$

Using the expansions in Eqs. (5.24) one can show that the two-electron integrals over the delocalized orbitals are

$$(aa|aa) = (aa|bb) = (bb|bb) = (ab|ab) = \tfrac{1}{2}J_{11} \tag{5.26a}$$

$$(rr|rr) = (rr|ss) = (ss|ss) = (rs|rs) = \tfrac{1}{2}J_{22} \tag{5.26b}$$

$$(rr|aa) = (ss|aa) = (rr|bb) = (ss|bb) = (ab|rs) = \tfrac{1}{2}J_{12} \tag{5.26c}$$

$$(ra|ra) = (sb|sb) = (rb|rb) = (sa|sa) = (ra|sb) = (rb|sa) = \tfrac{1}{2}K_{12} \tag{5.26d}$$

and the orbital energies are $\varepsilon_a = \varepsilon_b = \varepsilon_1$ and $\varepsilon_r = \varepsilon_s = \varepsilon_2$.

We now find the six spin-orbital correlation energies: $e_{a\bar{a}}$, e_{ab}, $e_{a\bar{b}}$, $e_{\bar{a}b}$, $e_{\bar{a}\bar{b}}$, $e_{b\bar{b}}$. First consider the pair $a\bar{a}$. Since $|\Psi_0\rangle$ is of gerade symmetry and is an eigenfunction of $\mathscr{S}_z$ with eigenvalue zero (i.e. $M_S = 0$), only doubly excited determinants of gerade symmetry having equal numbers of spin up and spin down electrons, interact with $|\Psi_0\rangle$. Therefore the required pair function is

$$|\Psi_{a\bar{a}}\rangle = |\Psi_0\rangle + c_1|\Psi_{a\bar{a}}^{r\bar{r}}\rangle + c_2|\Psi_{a\bar{a}}^{s\bar{s}}\rangle \tag{5.27}$$

Since

$$\langle\Psi_0|\mathscr{H}|\Psi_{a\bar{a}}^{r\bar{r}}\rangle = \langle a\bar{a}||r\bar{r}\rangle = (ar|ar) = (ra|ra) = \tfrac{1}{2}K_{12} \tag{5.28a}$$

$$\langle\Psi_0|\mathscr{H}|\Psi_{a\bar{a}}^{s\bar{s}}\rangle = \langle a\bar{a}||s\bar{s}\rangle = (as|as) = (sa|sa) = \tfrac{1}{2}K_{12} \tag{5.28b}$$

it is convenient to use symmetric and antisymmetric combinations of these functions (i.e., $2^{-1/2}(|\Psi_{a\bar{a}}^{r\bar{r}}\rangle \pm |\Psi_{a\bar{a}}^{s\bar{s}}\rangle)$) so that only the plus combination mixes with the ground state. Introducing a new notation for this plus combination

$$|\Psi_{a\bar{a}}^{**}\rangle = 2^{-1/2}(|\Psi_{a\bar{a}}^{r\bar{r}}\rangle + |\Psi_{a\bar{a}}^{s\bar{s}}\rangle) \tag{5.29}$$

we can write the $a\bar{a}$ pair function as

$$|\Psi_{a\bar{a}}\rangle = |\Psi_0\rangle + c|\Psi_{a\bar{a}}^{**}\rangle \tag{5.30}$$

The required matrix elements are

$$\langle\Psi_0|\mathscr{H}|\Psi_{a\bar{a}}^{**}\rangle = 2^{-1/2}K_{12} \tag{5.31a}$$

$$\langle\Psi_{a\bar{a}}^{**}|\mathscr{H} - E_0|\Psi_{a\bar{a}}^{**}\rangle = 2(\varepsilon_2 - \varepsilon_1) + J_{22} + \tfrac{1}{2}(J_{11} - 4J_{12} + 2K_{12}) \equiv 2\Delta' \tag{5.31b}$$

Exercise 5.5 Derive Eqs. (5.31a) and (5.31b).

The equations which determine the pair energy are (see Eqs. (5.9a,b)).

$$e_{a\bar{a}} = 2^{-1/2}K_{12}c \tag{5.32a}$$

$$2^{-1/2}K_{12} + 2\Delta'c = e_{a\bar{a}}c \tag{5.32b}$$

By eliminating c from these equations and solving the resulting quadratic equation for $e_{a\bar{a}}$ we find

$$e_{a\bar{a}} = \Delta' - ((\Delta')^2 + K_{12}^2/2)^{1/2} \tag{5.33}$$

Because of the high symmetry of this problem, as manifested by the relationship between the two-electron integrals in Eqs. (5.26), it follows that $e_{b\bar{b}} = e_{a\bar{a}}$. We now show that $e_{ab} = e_{\bar{a}\bar{b}} = 0$. To see this, consider the pair function for the $\bar{a}\bar{b}$ pair. Since only double excitations of gerade symmetry and $M_S = 0$ need be considered, we have

$$|\Psi_{\bar{a}\bar{b}}\rangle = |\Psi_0\rangle + c_1|\Psi_{\bar{a}\bar{b}}^{\bar{r}\bar{s}}\rangle \tag{5.34}$$

However, this double excitation does not mix with $|\Psi_0\rangle$,

$$\langle\Psi_0|\mathscr{H}|\Psi_{\bar{a}\bar{b}}^{\bar{r}\bar{s}}\rangle = \langle\bar{a}\bar{b}||\bar{r}\bar{s}\rangle = (ar|bs) - (as|br) = 0 \tag{5.35}$$

and thus the pair correlation energy of the $\bar{a}\bar{b}$ pair is zero. The argument for the ab pair is the same. This result has an interesting physical interpretation. Since correlation between electrons with the same spin is included in the HF approximation (Fermi hole), pair theory does not give any additional correlation. While it is not true in general that pair energies of electrons with the same spin are zero, they are smaller than the other pair energies.

Finally, we must find $e_{a\bar{b}}$ and $e_{\bar{a}b}$. Proceeding in the same way as for the $a\bar{a}$ pair (i.e., eliminating double excitations of the wrong symmetry and then constructing ± linear combinations) the $a\bar{b}$ pair function becomes

$$|\Psi_{a\bar{b}}\rangle = |\Psi_0\rangle + c|\Psi_{a\bar{b}}^{**}\rangle \tag{5.36}$$

where

$$|\Psi_{a\bar{b}}^{**}\rangle = 2^{-1/2}(|\Psi_{a\bar{b}}^{r\bar{s}}\rangle + |\Psi_{a\bar{b}}^{s\bar{r}}\rangle) \tag{5.37}$$

The $\bar{a}b$ function is obtained by interchanging a and b. Now it can be shown that the equations which determine the $a\bar{b}$ pair are identical to Eqs. (5.32) so that the pair correlation energies for the $a\bar{b}$ and $a\bar{a}$ pair are the same. Thus the total pair correlation energy for the dimer using delocalized orbitals is

$$\begin{aligned} {}^2E_{\text{corr}}(\text{IEPA}(D)) &= e_{a\bar a} + e_{b\bar b} + e_{ab} + e_{a\bar b} + e_{\bar a b} + e_{\bar a\bar b} \\ &= 4e_{a\bar a} \\ &= 4(\Delta' - ((\Delta')^2 + K_{12}^2/2)^{1/2}) \end{aligned} \tag{5.38}$$

This is to be compared to the result obtained using *localized* orbitals.

$$ {}^2E_{\text{corr}}(\text{IEPA}(L)) = 2(\Delta - (\Delta^2 + K_{12}^2)^{1/2}) \tag{5.39}$$

which is exact for the model. It is clear that the two expressions are different, and using the minimal STO-3G basis set two-electron integrals in Appendix D for $R = 1.4$ a.u., we find

$$ {}^2E_{\text{corr}}(\text{exact}) = {}^2E_{\text{corr}}(\text{IEPA}(L)) = -0.0411 \text{ a.u.}$$

$$ {}^2E_{\text{corr}}(\text{IEPA}(D)) = -0.0275 \text{ a.u.}$$

so that there is almost a factor of 2 difference between the two results! In real systems, the situation is not quite so bad, and the results obtained using localized and delocalized molecular orbitals, although different, are closer. For example, Bender and Davidson[3] have found for boron hydride, using a large basis set of Slater orbitals, that with canonical SCF orbitals the IEPA correlation energy is −0.141, a.u., while with localized orbitals it is −0.139 a.u..

Exercise 5.6 Show that $e_{a\bar b} = e_{\bar a b} = e_{a\bar a}$.

Exercise 5.7 Show that DCI is invariant to unitary transformations for the above model.

a. The DCI wave function is

$$|\Psi_{\text{DCI}}\rangle = |\Psi_0\rangle + c_1|\Psi_{a\bar a}^{**}\rangle + c_2|\Psi_{b\bar b}^{**}\rangle + c_3|\Psi_{a\bar b}^{**}\rangle + c_4|\Psi_{\bar a b}^{**}\rangle$$

Show that the corresponding eigenvalue problem which determines the DCI correlation energy of the dimer (${}^2E_{\text{corr}}(\text{DCI})$) is

$$\begin{pmatrix} 0 & 2^{-1/2}K_{12} & 2^{-1/2}K_{12} & 2^{-1/2}K_{12} & 2^{-1/2}K_{12} \\ 2^{-1/2}K_{12} & 2\Delta' & \frac{1}{2}J_{11} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} \\ 2^{-1/2}K_{12} & \frac{1}{2}J_{11} & 2\Delta' & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} \\ 2^{-1/2}K_{12} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} & 2\Delta' & \frac{1}{2}J_{11} \\ 2^{-1/2}K_{12} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}J_{11} & 2\Delta' \end{pmatrix} \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix}$$

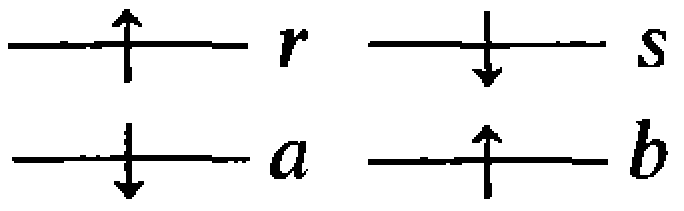
$$= {}^2E_{\text{corr}}(\text{DCI}) \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix}$$

b. Show that $c_1 = c_2 = c_3 = c_4 = c$ and then solve the equations to show

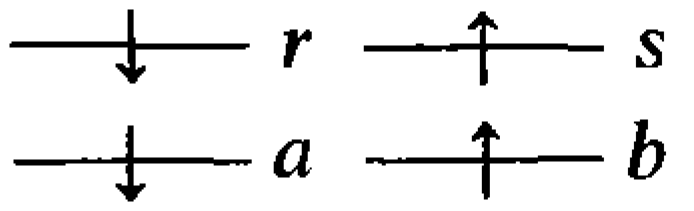
$$ {}^2E_{\text{corr}}(\text{DCI}) = \Delta - (\Delta^2 + 2K_{12}^2)^{1/2} $$

which is the same result as found in the last chapter (see Eq. (4.60)).

The pair functions $|\Psi_{a\bar{b}}\rangle$ and $|\Psi_{\bar{a}b}\rangle$ are not pure singlet wave functions. For example, as can be seen from Eq. (5.37), the doubly excited states in the pair function $\Psi_{a\bar{b}}^{**}$ are $|r\bar{a}b\bar{s}\rangle$ and $|s\bar{a}b\bar{r}\rangle$, which correspond to



and



respectively. Recall (see Table 2.7) that there are two linearly independent singlet spin functions arising from the configuration $(a)^1(b)^1(r)^1(s)^1$ namely, $|{}^A\Psi_{ab}^{rs}\rangle$ and $|{}^B\Psi_{ab}^{rs}\rangle$. The matrix elements we require for our discussion are in Table 4.1. Using these results, along with the integrals in Eqs. (5.26), it follows that

$$ \langle\Psi_0|\mathscr{H}|{}^A\Psi_{ab}^{rs}\rangle = \langle{}^B\Psi_{ab}^{rs}|\mathscr{H}|{}^A\Psi_{ab}^{rs}\rangle = 0 \tag{5.40} $$

and hence we only need consider $|{}^B\Psi_{ab}^{rs}\rangle$ in constructing the spin-adapted pair function for the *ab* pair,

$$ |{}^1\Psi_{ab}\rangle = |\Psi_0\rangle + c|{}^B\Psi_{ab}^{rs}\rangle \tag{5.41} $$

The required matrix elements are

$$ \langle\Psi_0|\mathscr{H}|{}^B\Psi_{ab}^{rs}\rangle = K_{12} \tag{5.42a} $$

$$ \langle{}^B\Psi_{ab}^{rs}|\mathscr{H} - E_0|{}^B\Psi_{ab}^{rs}\rangle = 2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 2J_{12} + K_{12} = 2\Delta'' \tag{5.42b} $$

the corresponding pair equations are

$$ e_{ab}^{\text{singlet}} = K_{12}c \tag{5.43a} $$

$$ K_{12} + 2\Delta''c = e_{ab}^{\text{singlet}}c \tag{5.43b} $$

Solving these in the standard way, we find

$$ e_{ab}^{\text{singlet}} = \Delta'' - ((\Delta'')^2 + K_{12}^2)^{1/2} \tag{5.44} $$

Since the pair functions for the $a\bar{a}$ and $b\bar{b}$ pairs are pure singlets the total correlation energy for the dimer using spin-adapted pairs is

$$ \begin{aligned} {}^2E_{\text{corr}}^{\text{singlet}}(\text{IEPA}(D)) &= e_{a\bar{a}} + e_{b\bar{b}} + e_{ab}^{\text{singlet}} \\ &= 2(\Delta' - ((\Delta')^2 + K_{12}^2/2)^{1/2}) + (\Delta'' - ((\Delta'')^2 + K_{12}^2)^{1/2}) \end{aligned} \tag{5.45} $$

With the STO-3G minimal basis set, the above correlation energy is -0.0258 a.u. as compared to -0.0275 a.u. obtained using spin-orbital pairs. Thus pair theory is not only variant to unitary transformations of degenerate HF orbitals, but also gives different answers depending on whether one uses spin-orbital or spin-adapted pair functions.

It is interesting to note, however, that the simplest form of pair theory, namely, first-order pairs (see Eq. (5.19)), *is* invariant to unitary transformations of degenerate orbitals. To see this, we approximate $\Delta' = \Delta'' = \varepsilon_2 - \varepsilon_1$ in Eqs. (5.38) and (5.45),

$$^2E_{\text{corr}}(\text{IEPA}(D)) = 4\left((\varepsilon_2 - \varepsilon_1) - (\varepsilon_2 - \varepsilon_1)\left(1 + \frac{K_{12}^2}{2(\varepsilon_2 - \varepsilon_1)^2}\right)^{1/2}\right)$$

$$^2E_{\text{corr}}^{\text{singlet}}(\text{IEPA}(D)) = 2\left((\varepsilon_2 - \varepsilon_1) - (\varepsilon_2 - \varepsilon_1)\left(1 + \frac{K_{12}^2}{2(\varepsilon_2 - \varepsilon_1)^2}\right)^{1/2}\right) + \left((\varepsilon_2 - \varepsilon_1) - (\varepsilon_2 - \varepsilon_1)\left(1 + \frac{K_{12}^2}{(\varepsilon_2 - \varepsilon_1)^2}\right)^{1/2}\right)$$

Notice we have factored $(\varepsilon_2 - \varepsilon_1)$ out of the square roots. Expanding the square roots using $(1 + x)^{1/2} = 1 + x/2$, we find

$$^2E_{\text{corr}}(\text{FO}(D)) = 4\left(\frac{-K_{12}^2}{4(\varepsilon_2 - \varepsilon_1)}\right) = 2\left(\frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}\right) \tag{5.46a}$$

and

$$^2E_{\text{corr}}^{\text{singlet}}(\text{FO}(D)) = 2\left(\frac{-K_{12}^2}{4(\varepsilon_2 - \varepsilon_1)}\right) + \left(\frac{-K_{12}^2}{2(\varepsilon_2 - \varepsilon_1)}\right) = 2\left(\frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}\right) \tag{5.46b}$$

These results are equal to the total first-order pair correlation energy, obtained in Exercise 5.3, for the dimer using localized orbitals. The total first-order pair correlation energy is identical to the second-order many-body perturbation result for the correlation energy (see Chapter 6). The above results are a reflection of the fact that many-body perturbation theory is invariant to unitary transformations of degenerate orbitals.

Finally, we have seen that using localized orbitals, the IEPA applied to a dimer of noninteracting minimal basis H_2 molecules gives twice the exact energy of the monomer. However, using delocalized orbitals, the energy of the dimer is no longer twice the monomer energy because of the invariance problem. This appears to contradict our statement that IEPA is size consistent; however, the essential requirement for size consistency is the linear variation of the correlation energy with the number of particles. Thus while the energy of N H_2 molecules calculated within the IEPA may not be N times the exact energy of H_2, it will be proportional to N as N becomes large rather than $N^{1/2}$ as with DCI.

Exercise 5.8 Show directly from Eq. (5.19) using delocalized orbitals and the two-electron integrals in Eq. (5.26) that the total first-order pair correlation energy (which is the same as the many-body second-order perturbation energy) of the dimer is given by Eq. (5.46).

Exercise 5.9 Show that the total correlation energy obtained using Epstein-Nesbet pairs is not invariant to unitary transformations.

a. Show, using localized orbitals, that

$$^{2}E_{\text{corr}}(\text{EN}(L)) = -\frac{K_{12}^{2}}{\Delta}.$$

b. Show, using delocalized spin-orbital pairs, that

$$^{2}E_{\text{corr}}(\text{EN}(D)) = -\frac{K_{12}^{2}}{\Delta'}.$$

c. Show, using delocalized spin-adapted pairs, that

$$^{2}E_{\text{corr}}^{\text{singlet}}(\text{EN}(D)) = -\frac{K_{12}^{2}}{2\Delta'} - \frac{K_{12}^{2}}{2\Delta''}.$$

d. Using the STO-3G integrals for H_2 in Appendix D compare the numerical values of the above expressions at $R = 1.4$ a.u.

Exercise 5.10 The DCI wave function for the H_2 dimer using spin-adapted configurations is

$$|\Psi_{\text{DCI}}\rangle = |\Psi_0\rangle + c_1|\Psi_{a\bar{a}}^{**}\rangle + c_2|\Psi_{b\bar{b}}^{**}\rangle + c_3|^{B}\Psi_{ab}^{rs}\rangle$$

Show that the corresponding DCI eigenvalue problem is

$$\begin{pmatrix} 0 & 2^{-1/2}K_{12} & 2^{-1/2}K_{12} & K_{12} \\ 2^{-1/2}K_{12} & 2\Delta' & \frac{1}{2}J_{11} & 2^{-1/2}(K_{12} - 2J_{12}) \\ 2^{-1/2}K_{12} & \frac{1}{2}J_{11} & 2\Delta' & 2^{-1/2}(K_{12} - 2J_{12}) \\ K_{12} & 2^{-1/2}(K_{12} - 2J_{12}) & 2^{-1/2}(K_{12} - 2J_{12}) & 2\Delta'' \end{pmatrix}$$

$$\times \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \end{pmatrix} = {}^{2}E_{\text{corr}}(\text{DCI}) \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \end{pmatrix}$$

and then solve the resulting equations to show that

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

5.1.2 Some Illustrative Calculations

An impressive success of the IEPA is its prediction of the ground state energy of the beryllium atom. The spin-orbital pair correlation energies obtained by

Table 5.1 Spin-orbital pair correlation energies (a.u.) of Be[a]

Pair	Correlation energies
$(1s, \overline{1s})$	-0.0418
$(1s, 2s)$	-0.0008
$(1s, \overline{2s})$	-0.0021
$(\overline{1s}, 2s)$	-0.0021
$(\overline{1s}, \overline{2s})$	-0.0008
$(2s, \overline{2s})$	-0.0454
Total pair energy	-0.0930
Exact correlation energy	-0.094

[a] R. K. Nesbet, *Phys. Rev.* **155:** 51 (1967).

Nesbet using a large Slater basis set containing *s*, *p*, *d*, and *f* orbitals are shown in Table 5.1. The total IEPA correlation energy is 98.9% of the exact correlation energy. It is estimated that if *g*, *h*, *i*, . . . orbitals were to be included in the basis, the IEPA would give very close to 100% of the exact correlation energy. Of course, because IEPA is not variational, it is possible to obtain over 100%. The individual pair correlation energies listed in Table 5.1 show some interesting trends. The largest values are for pairs with opposite spin in the same orbital (e.g., $(1s, \overline{1s})$) and the smallest are for pairs with parallel spins (e.g., $(1s, 2s)$ or $(\overline{1s}, \overline{2s})$). This is a reflection of the fact that the HF approximation does in fact correlate electrons with the same spin (the Fermi hole); its major defect is that it allows electrons of different spin to be in the same place.

For larger atoms, the IEPA works less well. Using a very large basis containing *s*, *p*, *d*, *f*, *g*, *h*, and *i* orbitals, Nesbet, Barr, and Davidson[4] obtained a correlation energy for neon of 107% of the exact result. Since their basis was still not complete, they estimate that the IEPA gives about 110% of the exact correlation energy. The IEPA appears to be even poorer for molecules. For example, Langhoff and Davidson[5] studied N_2 using a moderately large Gaussian basis set. It was estimated that if full CI were to be performed in this basis one would obtain a correlation energy of -0.35 a.u. They performed an essentially complete DCI calculation, which gave -0.324 a.u. for the correlation energy. This result is necessarily less than the basis set correlation energy. The IEPA, on the other hand, gave a correlation energy of -0.412 a.u., which is 18% larger than the estimated exact result. With larger basis sets, giving 80 or 90% of the exact correlation energy, it is likely that the IEPA is even worse. Thus to obtain a really accurate approximation for the correlation energy one has to improve upon the IEPA. This can be done by incorporating coupling between pairs as will be discussed in the next section.

5.2 COUPLED-PAIR THEORIES

In this section we will extend the IEPA to incorporate coupling between different pairs *ab* and *cd*. Although DCI does include such coupling, since one needs matrix elements of the type $\langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_{cd}^{tu}\rangle$, DCI is not size consistent. Because full CI is the exact, but computationally prohibitive, solution to the many-electron problem, it seems reasonable to begin our search for a size-consistent extension of the IEPA by considering the full CI equations and seeing if we can find a novel approximation to them. For the sake of simplicity, we ignore the presence of single, triple, etc. excitations; thus, the intermediate normalized full CI wave function is

$$|\Phi_0\rangle = |\Psi_0\rangle + \sum_{\substack{a<b\\ r<s}} c_{ab}^{rs}|\Psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c<d\\ r<s<t<u}} c_{abcd}^{rstu}|\Psi_{abcd}^{rstu}\rangle + \cdots \tag{5.47}$$

where the dots represent hextuple etc. excitations. As we have seen in the last chapter, to determine the variational energy of this wave function, we substitute it into

$$(\mathscr{H} - E_0)|\Phi_0\rangle = E_{\mathrm{corr}}|\Phi_0\rangle$$

and then successively multiply by $\langle\Psi_0|$, $\langle\Psi_{ab}^{rs}|$, $\langle\Psi_{abcd}^{rstu}|$, etc. to obtain the following set of coupled equations

$$\sum_{\substack{c<d\\ t<u}} \langle\Psi_0|\mathscr{H}|\Psi_{cd}^{tu}\rangle c_{cd}^{tu} = E_{\mathrm{corr}} \tag{5.48a}$$

$$\langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_0\rangle + \sum_{\substack{c<d\\ t<u}} \langle\Psi_{ab}^{rs}|\mathscr{H} - E_0|\Psi_{cd}^{tu}\rangle c_{cd}^{tu}$$
$$+ \sum_{\substack{c<d\\ t<u}} \langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_{abcd}^{rstu}\rangle c_{abcd}^{rstu} = E_{\mathrm{corr}} c_{ab}^{rs} \tag{5.48b}$$

and so on. For example, the next equation involves the coefficients of the quadruples and the hextuples. Note that in writing the matrix element between doubles and quadruples we incorporated the fact that matrix elements between determinants which differ by more than 2 spin orbitals are zero. The above equations form a hierarchy in which the correlation energy depends on the coefficients of the doubles, but the equation for these coefficients involves the coefficients of the quadruples and so on. Clearly, to make progress, we must terminate or decouple this hierarchy. The simplest procedure is to set c_{abcd}^{rstu} equal to zero, obtaining a closed set of equations involving only the coefficients of the doubles. The resulting equations are identical to the DCI equations, which can be derived by starting with a CI wave function containing only double excitations and then using the linear variation method. Is there an alternate and perhaps less drastic way to decouple the hierarchy?

5.2.1 The Coupled-Cluster Approximation (CCA)

If we could express the coefficients of the quadruples as some function of the doubles coefficients, then we would obtain a closed set of equations. In Chapter 4 we found an indication of how this might be done. The full CI wave function for two noninteracting minimal basis H_2 molecules is

$$\begin{aligned}|\Phi_0\rangle &= |1_1\bar{1}_1 1_2\bar{1}_2\rangle + c_{1_1\bar{1}_1}^{2_1\bar{2}_1}|2_1\bar{2}_1 1_2\bar{1}_2\rangle + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}|1_1\bar{1}_1 2_2\bar{2}_2\rangle \\ &\quad + c_{1_1\bar{1}_1 1_2\bar{1}_2}^{2_1\bar{2}_1 2_2\bar{2}_2}|2_1\bar{2}_1 2_2\bar{2}_2\rangle \qquad (5.49)\end{aligned}$$

In Exercise 4.12 we found that

$$c_{1_1\bar{1}_1 1_2\bar{1}_2}^{2_1\bar{2}_1 2_2\bar{2}_2} = (c_{1_1\bar{1}_1}^{2_1\bar{2}_1})(c_{1_2\bar{1}_2}^{2_2\bar{2}_2}) \qquad (5.50)$$

That is, the coefficient of the quadruple excitation is just the product of the coefficients of the two double excitations. This result can be readily understood without our previous algebraic manipulations. The two H_2 molecules are separated by infinity so that, for all intents and purposes, we can ignore the requirement that the total wave function be antisymmetric with respect to the interchange of electrons which belong to different H_2 molecules. Thus since two H_2 molecules are independent, we can write the exact wave function of the dimer as a product of the exact wave functions of the monomers,

$$\begin{aligned}|\Phi_0\rangle &= [|1_1\bar{1}_1\rangle + c_{1_1\bar{1}_1}^{2_1\bar{2}_1}|2_1\bar{2}_1\rangle][|1_2\bar{1}_2\rangle + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}|2_2\bar{2}_2\rangle] \\ &= |1_1\bar{1}_1\rangle|1_2\bar{1}_2\rangle + c_{1_1\bar{1}_1}^{2_1\bar{2}_1}|2_1\bar{2}_1\rangle|1_2\bar{1}_2\rangle + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}|1_1\bar{1}_1\rangle|2_2\bar{2}_2\rangle \\ &\quad + c_{1_1\bar{1}_1}^{2_1\bar{2}_1}c_{1_2\bar{1}_2}^{2_2\bar{2}_2}|2_1\bar{2}_1\rangle|2_2\bar{2}_2\rangle \qquad (5.51)\end{aligned}$$

Comparing this equation with Eq. (5.49), note that (aside from antisymmetry) for the two functions to be identical the coefficients of the doubles and quadruples must be related by Eq. (5.50). In this simple four-electron model system, the two pairs of electrons are independent and the coefficient of the quadruply excited configuration in the full CI wave function is exactly equal to the product of the coefficients of the double excitations.

In a real many-electron system two pairs of electrons ab and cd are, of course, not independent. However, since the IEPA works fairly well, it seems reasonable to *approximate* the coefficients of the quadruples as products of the coefficients of the doubles. Thus we write symbolically

$$c_{abcd}^{rstu} \cong c_{ab}^{rs} * c_{cd}^{tu} \qquad (5.52)$$

The reason why c_{abcd}^{rstu} is not simply the product of c_{ab}^{rs} and c_{cd}^{tu} can be understood as follows. We can obtain a quadruply excited configuration in which electrons in spin orbitals $abcd$ are excited to $rstu$ in many ways. For example, not only can we excite $\begin{matrix} a \to r \\ b \to s \end{matrix}$ and $\begin{matrix} d \to u \\ c \to t \end{matrix}$ but we can excite $\begin{matrix} a \to r \\ b \to t \end{matrix}$ and $\begin{matrix} d \to u \\ c \to s \end{matrix}$. In the first case, if $|\Psi_0\rangle$ is $|\cdots abcd \cdots\rangle$, we would obtain a quadruply excited determinant $|\cdots rstu \cdots\rangle$ while in the second case we would get $|\cdots rtsu \cdots\rangle$. These determinants represent the same quadruply excited state but have different signs (i.e., $|\cdots rtsu \cdots\rangle = -|\cdots rstu \cdots\rangle$). Thus we could represent c_{abcd}^{rstu} either as $c_{ab}^{rs}c_{cd}^{tu}$ or $-c_{ab}^{rt}c_{cd}^{su}$. Unfortunately, there are 18 distinct ways we can get a particular quadruple excitation from independent double excitations and c_{abcd}^{rstu} is the sum of all possible products of such double excitation coefficients. The rather formidable result is

$$\begin{aligned} c_{abcd}^{rstu} \cong c_{ab}^{rs} * c_{cd}^{tu} &= c_{ab}^{rs}c_{cd}^{tu} - \langle c_{ab}^{rs} * c_{cd}^{tu}\rangle \\ &= c_{ab}^{rs}c_{cd}^{tu} - c_{ac}^{rs}c_{bd}^{tu} + c_{ad}^{rs}c_{bc}^{tu} - c_{ab}^{rt}c_{cd}^{su} + c_{ac}^{rt}c_{bd}^{su} - c_{ad}^{rt}c_{bc}^{su} \\ &\quad + c_{ab}^{ru}c_{cd}^{st} - c_{ac}^{ru}c_{bd}^{st} + c_{ad}^{ru}c_{bc}^{st} + c_{ab}^{tu}c_{cd}^{rs} - c_{ac}^{tu}c_{bd}^{rs} + c_{ad}^{tu}c_{bc}^{rs} \\ &\quad - c_{ab}^{su}c_{cd}^{rt} + c_{ac}^{su}c_{bd}^{rt} - c_{ad}^{su}c_{bc}^{rt} + c_{ab}^{st}c_{cd}^{ru} - c_{ac}^{st}c_{bd}^{ru} + c_{ad}^{st}c_{bc}^{ru} \end{aligned} \tag{5.53}$$

The signs in front of the various terms are a result of the antisymmetry property of Slater determinants as explained above. Substituting this expression into Eq. (5.48b), we have

$$\begin{aligned} &\langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_0\rangle + \sum_{\substack{c<d\\t<u}} \langle\Psi_{ab}^{rs}|\mathscr{H} - E_0|\Psi_{cd}^{tu}\rangle c_{cd}^{tu} \\ &\quad + \sum_{\substack{c<d\\t<u}} \langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_{abcd}^{rstu}\rangle(c_{ab}^{rs} * c_{cd}^{tu}) = \left(\sum_{\substack{c<d\\t<u}} \langle\Psi_0|\mathscr{H}|\Psi_{cd}^{tu}\rangle c_{cd}^{tu}\right) c_{ab}^{rs} \end{aligned} \tag{5.54}$$

where we explicitly used the result in Eq. (5.48a) for E_{corr}. Now

$$\langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_{abcd}^{rstu}\rangle = \langle\Psi_0|\mathscr{H}|\Psi_{cd}^{tu}\rangle$$

when $ab \neq cd$ and $rs \neq tu$. Since $c_{ab}^{rs} * c_{cd}^{tu}$ vanishes when $ab = cd$ and $rs = tu$, Eq. (5.54) becomes

$$\begin{aligned} &\langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_0\rangle + \sum_{\substack{c<d\\t<u}} \langle\Psi_{ab}^{rs}|\mathscr{H} - E_0|\Psi_{cd}^{tu}\rangle c_{cd}^{tu} - \sum_{\substack{c<d\\t<u}} \langle\Psi_0|\mathscr{H}|\Psi_{cd}^{tu}\rangle\langle c_{ab}^{rs} * c_{cd}^{tu}\rangle \\ &\quad + \sum_{\substack{c<d\\t<u}} \langle\Psi_0|\mathscr{H}|\Psi_{cd}^{tu}\rangle c_{ab}^{rs}c_{cd}^{tu} = \left(\sum_{\substack{c<d\\t<u}} \langle\Psi_0|\mathscr{H}|\Psi_{cd}^{tu}\rangle c_{cd}^{tu}\right) c_{ab}^{rs} \end{aligned}$$

where we have used the definition $c_{ab}^{rs} * c_{cd}^{tu} = c_{ab}^{rs}c_{cd}^{tu} - \langle c_{ab}^{rs} * c_{cd}^{tu}\rangle$ (see Eq. (5.53)). Note that the expression on the right-hand side cancels with a term on the left-hand side, to give

$$\langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_0\rangle + \sum_{\substack{c<d\\t<u}} \langle\Psi_{ab}^{rs}|\mathscr{H} - E_0|\Psi_{cd}^{tu}\rangle c_{cd}^{tu} - \sum_{\substack{c<d\\t<u}} \langle\Psi_0|\mathscr{H}|\Psi_{cd}^{tu}\rangle\langle c_{ab}^{rs} * c_{cd}^{tu}\rangle = 0 \tag{5.55}$$

This equation, along with the definition of the symbol $\langle c_{ab}^{rs} * c_{cd}^{tu}\rangle$ given in Eq. (5.53), and the expression for the correlation energy in Eq. (5.48a) are the equations of Coupled-Pair Many-Electron Theory (CPMET), which is also called the Coupled-Cluster Approximation (CCA). We shall use the latter name throughout this book. In quantum chemistry the CCA is associated with the names of J. Čižek and J. Paldus[6] who first derived these equations and studied their properties. The casting of Eq. (5.55) into a computationally convenient form involves fairly laborious manipulations. It should be remembered that we have neglected single excitations in obtaining the CCA equations. The CCA including only double excitations has been called CCD (coupled-clusters doubles) to distinguish it from more general versions of the theory that also incorporate single (CCSD) and higher excitations. Since such extensions are not considered here we will continue to use the acronym CCA.

We now briefly discuss various aspects of CCA. One of the interesting features of this formalism is that Eq. (5.55) does not explicitly contain the correlation energy. Moreover, since it contains products of the doubles coefficients, it is *nonlinear*. Thus, unlike CI, the correlation energy within the CCA cannot be obtained by simple matrix diagonalization. The CCA, although quite complicated, has many attractive properties. Although it incorporates coupling between different pairs just as DCI (i.e., it contains matrix elements of the form $\langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_{cd}^{tu}\rangle$) it is, in contrast to DCI, size consistent. Moreover, it does not suffer from the invariance problems of the IEPA (i.e., it is invariant to unitary transformations of degenerate orbitals). However, it is still not a variational scheme; that is, it is possible to obtain more than 100% of the exact correlation energy using the CCA.

After applying the CCA to the problem of N independent minimal basis H_2 molecules, we will briefly reconsider the ideas behind this formalism from a more fundamental point of view.

Consider a supermolecule consisting of N noninteracting minimal basis H_2 molecules. In this system, there are N double excitations of the form $|\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\rangle$ $i = 1, \ldots, N$. Since all the H_2 monomers are identical, all the coefficients of these doubles are equal. Denoting these coefficients by c, and since $\langle\Psi_0|\mathscr{H}|\Psi_{1_i 1_i}^{2_i 2_i}\rangle = K_{12}$ for all i, Eq. (5.48a) becomes

$$^{N}E_{\text{corr}} = NcK_{12} \tag{5.56}$$

A given double excitation $|\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}\rangle$ will mix with $N-1$ quadruple excitations of the type $|\Psi_{1_i\bar{1}_i 1_j\bar{1}_j}^{2_i\bar{2}_i 2_j\bar{2}_j}\rangle j \neq i$. The matrix element between the double and quadruple excitations is again just K_{12}

$$\langle\Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i}|\mathscr{H}|\Psi_{1_i\bar{1}_i 1_j\bar{1}_j}^{2_i\bar{2}_i 2_j\bar{2}_j}\rangle = \langle\Psi_0|\mathscr{H}|\Psi_{1_j\bar{1}_j}^{2_j\bar{2}_j}\rangle = K_{12} \qquad i \neq j$$

If we write the coefficient of this quadruple excitation as $c_{1_i\bar{1}_i}^{2_i\bar{2}_i}c_{1_j\bar{1}_j}^{2_j\bar{2}_j} = c^2$, Eq. (5.54) becomes

$$K_{12} + 2\Delta c + (N-1)K_{12}c^2 = {}^{N}E_{\text{corr}}c = (NcK_{12})c \tag{5.57}$$

The factor $(N-1)$ appears in front of $K_{12}c^2$ since there are $N-1$ quadruple excitations that mix with a given double excitation. Note that $NK_{12}c^2$ cancels, and we can rewrite Eq. (5.57) as

$$K_{12} + 2\Delta c - K_{12}c^2 = 0 \tag{5.58}$$

Solving this equation for c, we find

$$c = \frac{\Delta - (\Delta^2 + K_{12}^2)^{1/2}}{K_{12}} \tag{5.59}$$

so that the correlation energy in Eq. (5.56) becomes

$$^N E_{\text{corr}}(\text{CCA}) = N(\Delta - (\Delta^2 + K_{12}^2)^{1/2}) \tag{5.60}$$

which is just N times the exact correlation energy of a single H_2 molecule. Thus the CCA, unlike DCI, is exact for our model problem. Recall that DQCI is not exact for $N > 2$. Thus by approximating the coefficients of the quadruples by the square of the coefficient of the doubles we did much more that just approximate DQCI. We have in fact implicitly approximated the coefficient of the hextuples as the cube of the coefficients of the doubles and so on. The reason CCA gave the exact answer for our idealized model is because in our model the coefficient of *all* higher (hextuple, octuple, etc) excitations are *exactly* equal to products of the coefficients of the double excitations. This aspect of CCA is brought out clearly using a more fundamental point of view (which is how historically CCA arose) discussed in the next subsection. This section uses some second quantization notation and may be skipped without loss of continuity.

5.2.2 The Cluster Expansion of the Wave Function

Recall that, using second quantization, a doubly excited determinant $|\Psi_{ab}^{rs}\rangle$ can be written as

$$|\Psi_{ab}^{rs}\rangle = a_r^\dagger a_s^\dagger a_b a_a |\Psi_0\rangle$$

where a_a, a_b remove occupied spin orbital from the HF determinant and $a_r^\dagger$, $a_s^\dagger$ replace these by unoccupied spin orbitals. Thus the doubly excited CI wave function can be written as

$$|\Psi_{\text{DCI}}\rangle = \left(1 + \frac{1}{4}\sum_{abrs} c_{ab}^{rs} a_r^\dagger a_s^\dagger a_b a_a\right)|\Psi_0\rangle$$

We now introduce a wave function, which not only contains double excitations but also quadruples, hextuples, etc. excitations in such a way that the coefficients of the $2n$th-tuple excitations are approximated by products of n doubly excited coefficients. Such a wave function $|\Phi_{\text{CCA}}\rangle$, can be written as

$$|\Phi_{\text{CCA}}\rangle = \exp(\mathscr{T}_2)|\Psi_0\rangle \tag{5.61a}$$

where

$$\mathscr{T}_2 = \frac{1}{4} \sum_{abrs} c_{ab}^{rs} a_r^\dagger a_s^\dagger a_b a_a \tag{5.61b}$$

This is called the cluster form of the wave function. To get some feeling for it, we expand the exponential as $\exp(x) = 1 + x + \frac{1}{2}x^2 + \cdots$ to obtain

$$\begin{aligned} |\Phi_{\mathrm{CCA}}\rangle &= \left(1 + \frac{1}{4} \sum_{abrs} c_{ab}^{rs} a_r^\dagger a_s^\dagger a_b a_a + \frac{1}{32} \sum_{\substack{abcd \\ rstu}} c_{ab}^{rs} c_{cd}^{tu} a_r^\dagger a_s^\dagger a_b a_a a_t^\dagger a_u^\dagger a_d a_c + \cdots \right) |\Psi_0\rangle \\ &= |\Psi_0\rangle + \frac{1}{4} \sum_{abrs} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \frac{1}{32} \sum_{\substack{abcd \\ rstu}} c_{ab}^{rs} c_{cd}^{tu} |\Psi_{abcd}^{rstu}\rangle + \cdots \end{aligned}$$

which, after somewhat lengthy manipulations, can be written as

$$|\Phi_{\mathrm{CCA}}\rangle = |\Psi_0\rangle + \sum_{\substack{a<b \\ r<s}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c<d \\ r<s<t<u}} c_{ab}^{rs} * c_{cd}^{tu} |\Psi_{abcd}^{rstu}\rangle + \cdots \tag{5.62}$$

where $c_{ab}^{rs} * c_{cd}^{tu}$ is our shorthand notation for the sum of the 18 products of doubly excited coefficients in Eq. (5.53). Thus this form of the wave function has the feature that higher excitations are products of double excitations.

An alternate, but equivalent, derivation of CCA can be given using the wave function $|\Phi_{\mathrm{CCA}}\rangle$ in Eq. (5.62). By substituting $|\Phi_{\mathrm{CCA}}\rangle$ into the Schrödinger equation

$$(\mathscr{H} - E_0) |\Phi_{\mathrm{CCA}}\rangle = E_{\mathrm{corr}} |\Phi_{\mathrm{CCA}}\rangle$$

and then successively multiplying by $\langle\Psi_0|$, and $\langle\Psi_{ab}^{rs}|$ one can show that the resulting equations are identical to our previous Eqs. (5.48a) and (5.55), since the matrix element between $\langle\Psi_{ab}^{rs}|$ and any hextuple excitation is zero. The above theory can be generalized to incorporate the effect of single and/or triple and higher excitations. For example, single excitations can be included by replacing $\mathscr{T}_2$ in Eq. (5.61a) by $\mathscr{T}_1 + \mathscr{T}_2$, where

$$\mathscr{T}_1 = \sum_{ra} c_a^r a_r^\dagger a_a$$

To distinguish various extensions, the theory using only double excitations (i.e., $\mathscr{T}_2$) is commonly called CCD, while the acronym CCSD is used when both single and double excitations are included (i.e., $\mathscr{T}_1 + \mathscr{T}_2$).

Exercise 5.11 Show that the wave function two independent H_2 molecules in Eqs. (5.49) and (5.50) can be written as

$$|\Phi\rangle = \exp(c_{1_1\bar{1}_1}^{2_1\bar{2}_1} a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1} a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2} a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2} a_{1_2}) |1_1\bar{1}_1 1_2\bar{1}_2\rangle$$

5.2.3 Linear CCA and the Coupled-Electron Pair Approximation (CEPA)

Although CCA is an excellent approximation, it is rather demanding from the computational standpoint. The final equations of CCA have a complicated algebraic structure and can be approximated in numerous ways. In this subsection we consider two possibilities that are most often encountered in the literature. The simplest possible approximation is to set $\langle c_{ab}^{rs} * c_{cd}^{tu}\rangle$ equal to zero in Eq. (5.55) to obtain

$$\langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_0\rangle + \sum_{\substack{c<d\\t<u}} \langle\Psi_{ab}^{rs}|\mathscr{H} - E_0|\Psi_{cd}^{tu}\rangle c_{cd}^{tu} = 0 \tag{5.63a}$$

This along with the usual expression for the correlation energy

$$E_{\text{corr}} = \sum_{\substack{c<d\\t<u}} \langle\Psi_0|\mathscr{H}|\Psi_{cd}^{tu}\rangle c_{cd}^{tu} \tag{5.63b}$$

constitute what is called *linear* CCA (L-CCA). Note that we have eliminated the nonlinear terms *after* the cancellation involving the correlation energy was performed. If we would have simply set $c_{ab}^{rs} * c_{cd}^{tu}$ equal to zero, we would have obtained the usual DCI equations.

Introducing the matrix notation

$$(\mathbf{B}^\dagger)_{rasb} = \langle\Psi_0|\mathscr{H}|\Psi_{ab}^{rs}\rangle$$

$$(\mathbf{D})_{rasb,\,tcud} = \langle\Psi_{ab}^{rs}|\mathscr{H} - E_0|\Psi_{cd}^{tu}\rangle$$

$$(\mathbf{c})_{rasb} = c_{ab}^{rs}$$

Eqs. (5.63a, b) become

$$\mathbf{B} + \mathbf{D}\mathbf{c} = 0 \tag{5.64a}$$

$$E_{\text{corr}} = \mathbf{B}^\dagger\mathbf{c} \tag{5.64b}$$

Solving Eq. (5.64a) for c and substituting the result into Eq. (5.64b), we have

$$E_{\text{corr}} = -\mathbf{B}^\dagger(\mathbf{D})^{-1}\mathbf{B} \tag{5.65}$$

which is a convenient form for the correlation energy in linear CCA. It is interesting to compare this with an expression for the DCI correlation energy obtained in the last chapter (see Eq. (4.30a)),

$$E_{\text{corr}} = -\mathbf{B}^\dagger(\mathbf{D} - E_{\text{corr}}\mathbf{1})^{-1}\mathbf{B} \tag{5.66}$$

Recall that one way of finding the DCI correlation energy is to solve Eq. (5.66) iteratively (i.e., begin by setting $E_{\text{corr}} = 0$ on the right-hand side, find E'_{corr} and use this to find E''_{corr} and so on until convergence is found). Thus Eq. (5.65) appears to be an approximation to DCI. This is, however, misleading because the linear CCA, although no longer variational, is size consistent. This approximation is identical to the infinite-order doubly excited many-body perturbation theory (D-MBPT(∞)) of Bartlett and coworkers[7] which was originally derived by diagrammatic summation techniques (see Subsection 6.7.3).

Exercise 5.12

a. Show that if the matrix $\mathbf{D}$ is approximated by its diagonal elements, the L-CCA correlation energy is identical to the result obtained using Epstein-Nesbet pairs (i.e., Eqs. (5.15) and (5.16)).

b. Show that linear CCA is invariant under unitary transformations for the problem of two independent H_2 molecules. First show that for this model the correlation energy of the dimer using localized orbitals is the same as that obtained in Exercise 5.9a. Then show using delocalized spin orbitals that, in contrast to the results of Exercise 5.9, one gets the same correlation energy. You will find the DCI matrix given in Exercise 5.7 useful.

We now consider a different approximation to CCA, originally proposed and implemented by W. Meyer[8] called the Coupled Electron Pair Approximation (CEPA). We begin again with the CCA equation (5.55). Instead of ignoring all the terms involving $\langle c_{ab}^{rs} * c_{cd}^{tu}\rangle$ we retain those where $c = a$ and $d = b$. Thus we have

$$\langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_0\rangle + \sum_{\substack{c<d\\t<u}} \langle\Psi_{ab}^{rs}|\mathscr{H} - E_0|\Psi_{cd}^{tu}\rangle c_{cd}^{tu} = \sum_{t<u} \langle\Psi_0|\mathscr{H}|\Psi_{ab}^{tu}\rangle\langle c_{ab}^{rs} * c_{ab}^{tu}\rangle \tag{5.67a}$$

From Eq. (5.53), which defines $\langle c_{ab}^{rs} * c_{cd}^{tu}\rangle$, it follows that

$$\langle c_{ab}^{rs} * c_{ab}^{tu}\rangle = c_{ab}^{rs}c_{ab}^{tu}$$

where we have used the fact that a coefficient like c_{ab}^{rs} is antisymmetric in the occupied or unoccupied indices (e.g., $c_{ab}^{rs} = -c_{ba}^{rs} = -c_{ab}^{sr}$). Substituting this into Eq. (5.67a) we have

$$\langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_0\rangle + \sum_{\substack{c<d\\t<u}} \langle\Psi_{ab}^{rs}|\mathscr{H} - E_0|\Psi_{cd}^{tu}\rangle c_{cd}^{tu} = \left(\sum_{t<u} \langle\Psi_0|\mathscr{H}|\Psi_{ab}^{tu}\rangle c_{ab}^{tu}\right) c_{ab}^{rs} \tag{5.67b}$$

Recognizing that the sum in parentheses is the expression for the pair energy e_{ab} (see Eq. (5.9a))

$$e_{ab} = \sum_{t<u} \langle\Psi_0|\mathscr{H}|\Psi_{ab}^{tu}\rangle c_{ab}^{tu} \tag{5.68a}$$

Eq. (5.67b) becomes

$$\langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_0\rangle + \sum_{\substack{c<d\\t<u}} \langle\Psi_{ab}^{rs}|\mathscr{H} - E_0|\Psi_{cd}^{tu}\rangle c_{cd}^{tu} = e_{ab}c_{ab}^{rs} \tag{5.68b}$$

The CEPA correlation energy is given by

$$E_{\text{corr}} = \sum_{a<b} e_{ab} \tag{5.68c}$$

These are the equations of CEPA. Note that they are very similar to both the IEPA and DCI equations. If e_{ab} in Eq. (5.68b) were replaced by the total correlation energy, we would obtain the DCI equation (See Eq. (4.26b)). On the other hand, if the summation over $c < d$ were approximated by a single term (i.e., $c = a$, $d = b$) we would recover the IEPA result given in Eq. (5.9b). CEPA includes coupling between pairs ab and cd, unlike the IEPA, yet it remains size consistent, unlike DCI. Note that computationally, because the equation which determines e_{ab} contains the coefficients of other pairs (c_{cd}^{tu}), the equations in CEPA must be solved iteratively. The major advantage of CEPA over CCA is that it is much simpler computationally. The price one has to pay is (among others) that CEPA is no longer invariant to unitary transformations as is CCA. However, it appears to be more nearly invariant than the IEPA.

As an illustration of the above formalism we calculate the CEPA correlation energy of our dimer of two noninteracting H_2 molecules using both localized and delocalized orbitals. Since with localized orbitals there is no coupling between different pairs in this model (i.e., $\langle \Psi_{1_i \bar{1}_i}^{2_i \bar{2}_i} | \mathscr{H} | \Psi_{1_j \bar{1}_j}^{2_j \bar{2}_j} \rangle = 0$ when $i \neq j$) CEPA and IEPA are the same. Using delocalized orbitals, the situation is different. The CCA is exact in this case since it is invariant to unitary transformations, while CEPA is not. However, as we will see CEPA works much better than the IEPA. Since CEPA can formally be obtained from the DCI equations by merely replacing E_{corr} by the appropriate pair correlation energies, we immediately get from the result given in Exercise 5.7

$$^2E_{\text{corr}} = 2^{-1/2}K_{12}(c_1 + c_2 + c_3 + c_4) = e_{a\bar{a}} + e_{b\bar{b}} + e_{a\bar{b}} + e_{\bar{a}b}$$

$$2^{-1/2}K_{12} + 2\Delta' c_1 + \tfrac{1}{2}J_{11}c_2 + (\tfrac{1}{2}K_{12} - J_{12})c_3 + (\tfrac{1}{2}K_{12} - J_{12})c_4 = e_{a\bar{a}}c_1$$

and similar equations for $e_{b\bar{b}}$, $e_{a\bar{b}}$, $e_{\bar{a}b}$. From the symmetry of the equations, it follows that $c_1 = c_2 = c_3 = c_4 = c$ and thus all four pair energies are equal. Hence

$$^2E_{\text{corr}} = 4e = 4(2^{-1/2}K_{12}c) \tag{5.69a}$$

$$2^{-1/2}K_{12} + (2\Delta' + \tfrac{1}{2}J_{11} + K_{12} - 2J_{12})c = ec \tag{5.69b}$$

Recognizing the quantity in parentheses in Eq. (5.69b) as 2Δ (see Eqs. (4.20) and (5.31b)) we have

$$2^{-1/2}K_{12} + 2\Delta c = ec$$

Multiplying this equation by $2^{-1/2}K_{12}$ and using Eq. (5.69a), we obtain

$$K_{12}^2/2 + 2\Delta e = e^2 \tag{5.70}$$

Solving the quadratic equation for e and then using Eq. (5.69a), we finally have

$$ {}^2E_{\text{corr}}(\text{CEPA}(D)) = 4(\Delta - (\Delta^2 + K_{12}^2/2)^{1/2}) \tag{5.71} $$

Note that this is not equal to the exact correlation energy (i.e., $2(\Delta - (\Delta^2 + K_{12}^2)^{1/2})$) of the dimer. However, using the STO-3G minimal basis H_2 integrals, in Appendix D, ${}^2E_{\text{corr}}(\text{CEPA}(D)) = -0.0414$ a.u. as compared to the exact value of -0.0411 a.u. Thus CEPA is nearly invariant for this problem.

Before considering some applications of coupled-pair theories, it is appropriate to summarize the formal relationship of these theories among themselves and with DCI (see Table 5.2). It can be seen that DCI, L-CCA, and CEPA are rather similar from the computational point of view. Formally, L-CCA can be obtained from DCI by setting $E_{\text{corr}} = 0$, while by setting $E_{\text{corr}} = e_{ab}$ one obtains CEPA. One must be careful not to be mislead by this formal similarity. It might appear that L-CCA is in fact an approximation to DCI. This is not the case; L-CCA is size consistent in contrast to DCI. A better point of view is that all these schemes are different approximations to full CI. DCI is variational but is not size consistent. L-CCA, CEPA, and CCA are not variational but are size consistent. Among the three coupled-pair theories, the CCA is expected to be the best. As we have seen, the L-CCA can be obtained from the CCA by setting $\langle c_{ab}^{rs} * c_{cd}^{tu} \rangle = 0$ while to obtain CEPA, one makes an apparently less drastic approximation. However, it turns out that while L-CCA is invariant to unitary transformations of degenerate orbitals, CEPA is not. On the other hand, it is difficult to argue, on first principles without numerical applications, that L-CCA should work better than CEPA when applied to a variety of molecules.

Table 5.2 The formal relationship between DCI and various coupled-pair theories

$$E_{\text{corr}} = \sum_{a<b} e_{ab} \qquad e_{ab} = \sum_{r<s} \langle \Psi_0 | \mathscr{H} | \Psi_{ab}^{rs} \rangle c_{ab}^{rs}$$

$$\langle \Psi_{ab}^{rs} | \mathscr{H} | \Psi_0 \rangle + \sum_{\substack{c<d \\ t<u}} \langle \Psi_{ab}^{rs} | \mathscr{H} - E_0 | \Psi_{cd}^{tu} \rangle c_{cd}^{tu} = X$$

Method	X
DCI	$E_{\text{corr}} c_{ab}^{rs}$
L-CCA	0
CEPA	$e_{ab} c_{ab}^{rs}$
CCA	$\sum_{\substack{c<d \\ t<u}} \langle \Psi_0 \| \mathscr{H} \| \Psi_{cd}^{tu} \rangle \langle c_{ab}^{rs} * c_{cd}^{tu} \rangle$

These comments emphasize that one must be careful in evaluating various approximation schemes. The consequence of an approximation is often more subtle than it appears at first glance.

5.2.4 Some Illustrative Calculations

In this section we present results for the correlation energy and equilibrium geometry of H_2O obtained with a near-HF one-electron basis (the 39-STO basis described in Chapter 4) via DCI, IEPA, L-CCA, and CCA. Meyer and his coworkers have studied potential energy surfaces, ionization potentials, dipole moments, and polarizabilities of a variety of molecules using CEPA. Some of their impressive results are contained in a review by Meyer.[9]

The correlation energies of H_2O obtained via a variety of many-electron theories within the same one-electron basis are shown in Table 5.3. These results must be compared with the exact basis set correlation energy (-0.296 a.u.), which is different from the exact correlation energy (-0.37 a.u.) because the one-electron basis is incomplete. Otherwise one would obtain the erroneous conclusion that of all the methods, the IEPA works the best. It is, in fact, the worst; it overestimates the correlation energy by 13%. We note that the correlation energies obtained via the L-CCA and CCA are close to each other and to the exact result. Both are superior to SDCI. The closeness of the L-CCA and CCA is somewhat surprizing because the L-CCA involved an apparently drastic approximation to CCA.

In Table 5.4 we present the calculated equilibrium geometries and two force constants obtained using the above methods. It can be seen that

Table 5.3 Correlation energies (a.u.) of H_2O at the experimental geometry calculated with the 39-STO basis described in Chapter 4

	E_{corr}
SDCI[a]	-0.2756
IEPA[a]	-0.3274
L-CCA[b]	-0.2908
CCA[b]	-0.2862
Estimated full CI	-0.296 ± 0.001
Exact	-0.37

[a] B. J. Rosenberg and I. Shavitt, *J. Chem. Phys* 63: 2162 (1975).

[b] R. J. Bartlett, I. Shavitt, and G D Purvis, *J. Chem. Phys.* 71: 281 (1979).

Table 5.4 Equilibrium geometry and some force constants of H_2O calculated with the 39-STO basis described in Chapter 4

	SCF[a]	SDCI[a]	L-CCA[b]	CCA[b]	Experiment
R_e(a.u.)	1.776	1.800	1.810	1.806	1.809
θ_e	106.1	104.9°	104.6°	104.7°	104.5°
f_{RR}	9.79	8.88	8.51	8.67	8.45
$f_{\theta\theta}$	0.88	0.81	0.80	0.80	0.76

[a] B. J. Rosenberg, W. C. Ermler, and I. Shavitt, *J. Chem. Phys.* **65**: 4072 (1976).

[b] R. J. Bartlett, I. Shavitt, and G. D. Purvis, *J. Chem. Phys.* **71**: 281 (1979). These references contain a large number of additional force constants.

L-CCA and CCA represent a significant improvement over SDCI, which is in turn significantly better than SCF. When compared to experiment, the L-CCA appears to be slightly better than the CCA! However, one should not jump to the conclusion that the L-CCA is a better approximation. After all, the one-electron basis is clearly not complete and we do not know the equilibrium geometry of H_2O that would be obtained if a full CI were to be performed in this basis. On the other hand, it is possible that the L-CCA accidently accounts for the effect of single and triple excitations absent in the CCA so that the L-CCA results are really closer to the exact values in the basis. These considerations highlight the need to apply approximation schemes to a variety of molecules, using basis sets of increasing sophistication, before drawing conclusions as to the superiority of one method over another.

5.3 MANY-ELECTRON THEORIES WITH SINGLE PARTICLE HAMILTONIANS

We have encountered a variety of techniques (CI, IEPA, CCA, CEPA) for calculating the correlation energy of a many-electron system, and in Chapter 6 we will discuss still another approach based on perturbation theory. The complexity of these formalisms and of the many-electron problem itself is the result of the two-particle nature of the coulomb repulsion between electrons. If the Hamiltonian contained only single particle interactions, there would be no need for sophisticated many-electron theories since we could solve the problem exactly simply by diagonalizing the Hamiltonian in a basis of one-electron functions (i.e., the orbital picture would be exact). Nevertheless, it is instructive to apply the formalism of many-electron theories to an N-electron problem described by a Hamiltonian that contains only single particle interactions. By seeing how these sophisticated techniques work in such a simple context, insight into the nature of these approaches can be gained. As we shall see here and in the next chapter, when one approaches a many-electron system with only single particle interactions, using the formalism of many-electron theories, one obtains equations that are almost completely analogous, yet much simpler, than those encountered previously. In particular, the nature of the approximations and the relationship between different approaches becomes especially transparent. Moreover, the calculations can be done analytically but still contain many of the features of *ab initio* calculations. This section is a rather long diversion and may be skipped without loss of continuity. Only the second half of Section 6.3 depends on some of the results obtained here.

We begin by posing the problem and solving it exactly in an elementary way. Suppose we have a N-electron system described by the Hamiltonian

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{V} = \sum_i h_0(i) + \sum_i v(i) \tag{5.72}$$

To obtain a zeroth-order description we assume that the perturbation $\mathscr{V}$ is negligible, and find the eigenfunctions and eigenvalues of the N-electron Hamiltonian $\mathscr{H}_0$. Since $\mathscr{H}_0$ contains only single-particle interactions, we proceed as follows. First, we find the complete orthonormal set of spin orbitals $\{\chi_i^{(0)}\}$, which are eigenfunctions of h_0

$$h_0\chi_i^{(0)} = \varepsilon_i^{(0)}\chi_i^{(0)} \tag{5.73}$$

The ground state wave function, $|\Psi_0\rangle$, is then a Slater determinant constructed from the N spin orbitals with the lowest energies. As usual, we label occupied spin orbitals by $a, b, \ldots$ and the unoccupied spin orbitals by $r, s, \ldots$. Thus we have

$$|\Psi_0\rangle = |\chi_1^{(0)} \cdots \chi_a^{(0)} \cdots \chi_N^{(0)}\rangle \tag{5.74}$$

This wave function is an eigenfunction of $\mathscr{H}_0$

$$\mathscr{H}_0|\Psi_0\rangle = \sum_a \varepsilon_a^{(0)}|\Psi_0\rangle \tag{5.75}$$

with an eigenvalue equal to the sum of the occupied spin orbital energies. The approximate ground state energy of the system, in the presence of $\mathscr{V}$ is

$$E_0 = \langle\Psi_0|\mathscr{H}|\Psi_0\rangle = \sum_a \varepsilon_a^{(0)} + \sum_a \langle a|v|a\rangle = \sum_a \varepsilon_a^{(0)} + \sum_a v_{aa} \tag{5.76}$$

so that the total energy is not simply the sum of orbital energies. Note the analogy to the HF energy of a real system having two-particle interactions.

The excited determinants formed from the spin orbitals $\{\chi_i^{(0)}\}$, i.e., $|\Psi_a^r\rangle$, $|\Psi_{ab}^{rs}\rangle$, etc., form a complete set of N-electron basis functions. Thus the exact wave function, $|\Phi_0\rangle$, of the N-electron system can be expressed as a linear combination of these as

$$|\Phi_0\rangle = |\Psi_0\rangle + \sum_{ra} c_a^r|\Psi_a^r\rangle + \sum_{\substack{a<b\\r<s}} c_{ab}^{rs}|\Psi_{ab}^{rs}\rangle + \cdots \tag{5.77}$$

where we have used, as usual, intermediate normalization (i.e., $\langle\Psi_0|\Phi_0\rangle = 1$). The exact ground state energy, $\mathscr{E}_0$, can be obtained by diagonalizing $\mathscr{H}$ in the basis of N-electron functions (i.e., using (5.77) and the linear variation method).

However, there is a much simpler way of finding $\mathscr{E}_0$. Since the total Hamiltonian $\mathscr{H}$ is, just like $\mathscr{H}_0$, a sum of single-particle interactions, we can find a set of spin orbitals $\{\chi_i\}$, which are eigenfunctions of $h_0 + v$

$$(h_0 + v)\chi_i = \varepsilon_i\chi_i \tag{5.78}$$

Then the exact ground state wave function is just a Slater determinant constructed from the N exact spin orbitals with the lowest energies

$$|\Phi_0\rangle = |\chi_1 \cdots \chi_a \cdots \chi_N\rangle \tag{5.79}$$

Since this wave function is an eigenfunction of the total Hamiltonian $\mathscr{H}$

$$\mathscr{H}|\Phi_0\rangle = \sum_a \varepsilon_a|\Phi_0\rangle \tag{5.80}$$

with an eigenvalue equal to the sum of the N lowest spin orbital energies, the exact ground state energy is

$$\mathscr{E}_0 = \langle\Phi_0|\mathscr{H}|\Phi_0\rangle = \sum_a \varepsilon_a \tag{5.81}$$

Clearly, the two procedures 1) diagonalizing $\mathscr{H}$ in the basis of N-electron functions formed from the eigenfunctions of h_0 and 2) diagonalizing $h_0 + v$ and adding up the N lowest spin orbital energies must give identical ground state energies. It is equally clear that method (2) is much easier. As a pedagogical device, we will approach the problem the hard way using N-electron functions. In analogy to the correlation energy, we define the *relaxation energy* of our system as the difference between the exact energy and the energy of $|\Psi_0\rangle$,

$$E_R = \mathscr{E}_0 - E_0 \tag{5.82}$$

Our objective will be to calculate E_R using many-electron formalisms.

First, let us calculate the relaxation energy simply by solving the eigenvalue problem for $h_0 + v$,

$$(h_0 + v)|\chi\rangle = \varepsilon|\chi\rangle \tag{5.83}$$

in the basis $\{|\chi_i^{(0)}\rangle\}$. We expand $|\chi\rangle$ as

$$|\chi\rangle = \sum_i |\chi_i^{(0)}\rangle c_i = \sum_b |\chi_b^{(0)}\rangle c_b + \sum_s |\chi_s^{(0)}\rangle c_s \tag{5.84}$$

Note that we have divided the sum over all zeroth-order spin orbitals into the sum of the first N occupied ones and the rest. Substituting this expansion into Eq. (5.83) and then multiplying by $\langle\chi_a^{(0)}|$ and $\langle\chi_r^{(0)}|$ we find

$$\sum_b \langle\chi_a^{(0)}|h_0 + v|\chi_b^{(0)}\rangle c_b + \sum_s \langle\chi_a^{(0)}|v|\chi_s^{(0)}\rangle c_s = \varepsilon c_a \tag{5.85a}$$

$$\sum_b \langle\chi_r^{(0)}|v|\chi_b^{(0)}\rangle c_b + \sum_s \langle\chi_r^{(0)}|h_0 + v|\chi_s^{(0)}\rangle c_s = \varepsilon c_r \tag{5.85b}$$

or equivalently

$$\sum_b (\varepsilon_a^{(0)}\delta_{ab} + v_{ab})c_b + \sum_s v_{as}c_s = \varepsilon c_a \tag{5.86a}$$

$$\sum_b v_{rb}c_b + \sum_s (\varepsilon_r^{(0)}\delta_{rs} + v_{rs})c_s = \varepsilon c_r \tag{5.86b}$$

To rewrite these equations in matrix notation, we introduce an $N \times N$ matrix $\mathbf{H}_{AA}$ with elements

$$(\mathbf{H}_{AA})_{ab} = \varepsilon_a^{(0)}\delta_{ab} + v_{ab} \tag{5.87a}$$

Similarly, if we define

$$(\mathbf{H}_{BB})_{rs} = \varepsilon_r^{(0)}\delta_{rs} + v_{rs} \tag{5.87b}$$

$$(\mathbf{H}_{AB})_{as} = v_{as} \tag{5.87c}$$

$$(\mathbf{H}_{BA})_{rb} = v_{rb} \tag{5.87d}$$

Eqs. (5.86a,b) become

$$\begin{pmatrix} \mathbf{H}_{AA} & \mathbf{H}_{AB} \\ \mathbf{H}_{BA} & \mathbf{H}_{BB} \end{pmatrix} \begin{pmatrix} \mathbf{c}_A \\ \mathbf{c}_B \end{pmatrix} = \varepsilon \begin{pmatrix} \mathbf{c}_A \\ \mathbf{c}_B \end{pmatrix} \tag{5.88}$$

Note that $\mathbf{H}_{AA}$ is a square matrix with dimensionality equal to the number of occupied orbitals while the dimensionality of $\mathbf{H}_{BB}$ is equal to the number of unoccupied spin orbitals.

To obtain the exact energy, $\mathscr{E}_0$, we must solve this eigenvalue problem and add up the N eigenvalues with the lowest energies. To make this more explicit we let

$$\mathbf{U} = \begin{pmatrix} \mathbf{U}_{AA} & \mathbf{U}_{AB} \\ \mathbf{U}_{BA} & \mathbf{U}_{BB} \end{pmatrix}$$

be the unitary transformation, which diagonalizes the Hamiltonian matrix in Eq. (5.88),

$$\begin{pmatrix} \mathbf{H}_{AA} & \mathbf{H}_{AB} \\ \mathbf{H}_{BA} & \mathbf{H}_{BB} \end{pmatrix} \begin{pmatrix} \mathbf{U}_{AA} & \mathbf{U}_{AB} \\ \mathbf{U}_{BA} & \mathbf{U}_{BB} \end{pmatrix} = \begin{pmatrix} \mathbf{U}_{AA} & \mathbf{U}_{AB} \\ \mathbf{U}_{BA} & \mathbf{U}_{BB} \end{pmatrix} \begin{pmatrix} \boldsymbol{\varepsilon}_A & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\varepsilon}_B \end{pmatrix} \tag{5.89}$$

where $\boldsymbol{\varepsilon}_A$ is a diagonal matrix containing the N lowest eigenvalues. Then the exact energy is

$$\mathscr{E}_0 = \operatorname{tr} \boldsymbol{\varepsilon}_A \tag{5.90}$$

Note that we have defined the matrix $\mathbf{H}_{AA}$ in such a way that the sum of its diagonal elements is equal to E_0. Thus the relaxation energy can be written in the compact form

$$E_R = \mathscr{E}_0 - E_0 = \mathscr{E}_0 - \left(\sum_a \varepsilon_a^{(0)} + v_{aa}\right) = \operatorname{tr}(\boldsymbol{\varepsilon}_A - \mathbf{H}_{AA}) \tag{5.91}$$

Finally, using the unitary matrix $\mathbf{U}$ one can express the exact orbitals $|\chi_i\rangle$ in terms of the zeroth-order orbitals $|\chi_i^{(0)}\rangle$. Since the ith column of $\mathbf{U}$ contains the coefficients of the ith eigenvector, the exact occupied orbitals can be written as

$$|\chi_a\rangle = \sum_b |\chi_b^{(0)}\rangle(\mathbf{U}_{AA})_{ba} + \sum_r |\chi_r^{(0)}\rangle(\mathbf{U}_{BA})_{ra} \qquad a = 1, 2, \ldots, N \tag{5.92}$$

A similar relation holds for the exact unoccupied orbitals.

For future reference we now reformulate the above theory in a way which might appear unfamiliar at first glance but on closer inspection will turn out to be a generalization of the procedure we have used many times to find the lowest eigenvalue of a matrix. We are now interested in finding the sum of the N lowest eigenvalues. The matrix eigenvalue problem in Eq. (5.89) is equivalent to four equations, two of which are

$$\mathbf{H}_{AA}\mathbf{U}_{AA} + \mathbf{H}_{AB}\mathbf{U}_{BA} = \mathbf{U}_{AA}\boldsymbol{\varepsilon}_A \tag{5.93a}$$

$$\mathbf{H}_{BA}\mathbf{U}_{AA} + \mathbf{H}_{BB}\mathbf{U}_{BA} = \mathbf{U}_{BA}\boldsymbol{\varepsilon}_A \tag{5.93b}$$

Multiplying the first of these by $\mathbf{U}_{AA}^{-1}$ on the right we have

$$\mathbf{H}_{AA} + \mathbf{H}_{AB}\mathbf{U}_{BA}\mathbf{U}_{AA}^{-1} = \mathbf{U}_{AA}\boldsymbol{\varepsilon}_A\mathbf{U}_{AA}^{-1} \tag{5.94}$$

Taking the trace of both sides of this equation and using the fact that $\operatorname{tr}\mathbf{AB} = \operatorname{tr}\mathbf{BA}$ we have

$$\operatorname{tr}\mathbf{H}_{AA} + \operatorname{tr}\mathbf{H}_{AB}\mathbf{U}_{BA}\mathbf{U}_{AA}^{-1} = \operatorname{tr}\mathbf{U}_{AA}\boldsymbol{\varepsilon}_A\mathbf{U}_{AA}^{-1} = \operatorname{tr}\boldsymbol{\varepsilon}_A\mathbf{U}_{AA}^{-1}\mathbf{U}_{AA} = \operatorname{tr}\boldsymbol{\varepsilon}_A$$

Using this identity and defining

$$\mathbf{C}_{BA} = \mathbf{U}_{BA}\mathbf{U}_{AA}^{-1} \tag{5.95}$$

we can rewrite the relaxation energy as

$$E_R = \operatorname{tr}(\boldsymbol{\varepsilon}_A - \mathbf{H}_{AA}) = \operatorname{tr}\mathbf{H}_{AB}\mathbf{C}_{BA} \tag{5.96}$$

Now let us find the equation which determines $\mathbf{C}_{BA}$. To do this, multiply Eq. (5.94) by $\mathbf{U}_{BA}\mathbf{U}_{AA}^{-1}$ on the left to obtain

$$\mathbf{U}_{BA}\mathbf{U}_{AA}^{-1}\mathbf{H}_{AA} + \mathbf{U}_{BA}\mathbf{U}_{AA}^{-1}\mathbf{H}_{AB}\mathbf{U}_{BA}\mathbf{U}_{AA}^{-1} = \mathbf{U}_{BA}\boldsymbol{\varepsilon}_A\mathbf{U}_{AA}^{-1} \tag{5.97a}$$

Then multiply Eq. (5.93b) by $\mathbf{U}_{AA}^{-1}$ on the right to obtain

$$\mathbf{H}_{BA} + \mathbf{H}_{BB}\mathbf{U}_{BA}\mathbf{U}_{AA}^{-1} = \mathbf{U}_{BA}\boldsymbol{\varepsilon}_A\mathbf{U}_{AA}^{-1} \tag{5.97b}$$

Substracting these two equations and using the definition of $\mathbf{C}_{BA}$ in Eq. (5.95) we finally have

$$\mathbf{H}_{BA} + \mathbf{H}_{BB}\mathbf{C}_{BA} - \mathbf{C}_{BA}\mathbf{H}_{AA} - \mathbf{C}_{BA}\mathbf{H}_{AB}\mathbf{C}_{BA} = 0 \tag{5.98}$$

This relation together with Eq. (5.96) completely determine the relaxation energy. Note that Eq. (5.98) is nonlinear (i.e., it has a quadratic dependence on the matrix $\mathbf{C}_{BA}$) and therefore must be solved iteratively. Finally, we translate these equations back into a form containing the zeroth-order orbital energies and matrix elements of the perturbation. If we define

$$(\mathbf{C}_{BA})_{ra} = C_{ra} \tag{5.99}$$

then we can rewrite Eq. (5.96) as

$$E_R = \operatorname{tr} \mathbf{H}_{AB}\mathbf{C}_{BA} = \sum_{bs} (\mathbf{H}_{AB})_{bs}(\mathbf{C}_{BA})_{sb} = \sum_{bs} v_{bs}C_{sb} \tag{5.100}$$

where we have used Eq. (5.87). Similarly, the *ra* element of the matrix equation (5.98) is

$$(\mathbf{H}_{BA})_{ra} + \sum_{s} (\mathbf{H}_{BB})_{rs}(\mathbf{C}_{BA})_{sa} - \sum_{b} (\mathbf{C}_{BA})_{rb}(\mathbf{H}_{AA})_{ba} - \sum_{bs} (\mathbf{C}_{BA})_{rb}(\mathbf{H}_{AB})_{bs}(\mathbf{C}_{BA})_{sa} = 0$$

which upon using the definitions in Eq. (5.87) becomes

$$v_{ra} + \sum_{s} (\varepsilon_r^{(0)}\delta_{rs} + v_{rs})C_{sa} - \sum_{b} C_{rb}(\varepsilon_a^{(0)}\delta_{ab} + v_{ba}) - \sum_{bs} C_{rb}v_{bs}C_{sa} = 0 \tag{5.101}$$

If this equation is solved for the C_{ra}'s, then the exact relaxation energy can be found from Eq. (5.100).

In the past when we considered eigenvalue problems we were usually interested in only the lowest eigenvalue. For the problem at hand we need the N lowest eigenvalues. The above procedure is just a generalization of our standard approach to finding the lowest eigenvalue. To see this, suppose $\mathbf{H}_{AA}$ is a 1×1 matrix and that the entire matrix is $M \times M$. In this case Eq. (5.96) simplifies to

$$E_R = \varepsilon_1 - H_{11} = \sum_{i=2}^{M} H_{1i}C_{i1} \tag{5.102}$$

and Eq. (5.98) becomes

$$H_{i1} + \sum_{j=2}^{M} H_{ij}C_{j1} - C_{i1}H_{11} - C_{i1}\sum_{j=2}^{M} H_{1j}C_{j1} = 0 \qquad i = 2, 3, \ldots, M \tag{5.103}$$

Setting $C_{i1} = c_i$ and using Eq. (5.102) in Eq. (5.103) we have

$$H_{i1} + \sum_{j=2}^{M} (H_{ij} - H_{11}\delta_{ij})c_j = E_R c_i \tag{5.104}$$

Equations (5.102) and (5.104) are equivalent to the matrix equation

$$\begin{pmatrix} 0 & H_{12} & \cdots & H_{1M} \\ H_{21} & H_{22}-H_{11} & \cdots & H_{2M} \\ \vdots & \vdots & & \vdots \\ H_{M1} & H_{M2} & \cdots & H_{MM}-H_{11} \end{pmatrix} \begin{pmatrix} 1 \\ c_2 \\ \vdots \\ c_M \end{pmatrix} = E_R \begin{pmatrix} 1 \\ c_2 \\ \vdots \\ c_M \end{pmatrix} = (\varepsilon_1 - H_{11}) \begin{pmatrix} 1 \\ c_2 \\ \vdots \\ c_M \end{pmatrix}$$

which is precisely the equation we would start with if we were after the lowest eigenvalue.

Exercise 5.13 For the 2 × 2 matrix

$$\begin{pmatrix} \mathbf{H}_{AA} & \mathbf{H}_{AB} \\ \mathbf{H}_{BA} & \mathbf{H}_{BB} \end{pmatrix} \equiv \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \qquad \begin{matrix} H_{11} < H_{22} \\ H_{12} > 0 \end{matrix}$$

Equation (5.96) simplifies to

$$E_R = \varepsilon_1 - H_{11} = H_{12}C$$

and Eq. (5.98) is

$$H_{21} + H_{22}C - CH_{11} - C^2H_{12} = 0$$

Solve this quadratic equation for the lowest C and then show that ε_1 thus obtained is the lowest eigenvalue of the matrix.

5.3.1 The Relaxation Energy via CI, IEPA, CEPA, and CCA

Many-electron methods use N-electron wave functions (i.e., Slater determinants). For example, to perform a full CI calculation one must diagonalize the N-electron Hamiltonian in a basis of N-electron functions formed by making all possible excitations from a reference function, $|\Psi_0\rangle$. Formally, one can proceed in the identical manner irrespective of whether the Hamiltonian contains one or two-particle interactions or both. Of course there are considerable simplifications in the case that the N-electron Hamiltonian has only single particle interactions. In particular, the evaluation of the required matrix elements is easy, and the final equations have a much simpler structure. Recall that in a real many-electron system the correlation energy can be written in terms of the coefficients of the doubly excited determinants in the full CI wave function. As we shall see, because of the one-particle nature of the Hamiltonian, the relaxation energy can be expressed in terms of the coefficients of single excitations. Thus, in this section, single excitations play the same role as double excitations do in real many-body systems. Moreover, double excitations here are analogous to quadruple excitations in previous sections. In particular, when we consider the analogue of CCA for our model problem, we will need to express the coefficient of the doubles in terms of products of the coefficients of the singles. This is much simpler; instead of a messy 18-term result (see Eq. (5.53)) we will have a simple two term expression. Finally, when the Hamiltonian only contains single particle interactions, the analogues of pair theories are just "particle" theories. For example, instead of writing the correlation energy as a sum of independently calculated pair energies, e_{ab}, we will express the relaxation energy as a sum of "particle" energies, e_a. We can retain the various acronyms used for pair and coupled-pair theories if we simply change the meaning of the P's.

We now calculate the relaxation energy using the various many-electron approaches.

1. Full CI. The intermediate normalized full CI wave function is given in Eq. (5.77)

$$|\Phi_0\rangle = |\Psi_0\rangle + \sum_{sb} c_b^s|\Psi_b^s\rangle + \sum_{\substack{b<c \\ s<t}} c_{bc}^{st}|\Psi_{bc}^{st}\rangle + \cdots \tag{5.105}$$

To obtain the full CI equations, we substitute the above expansion for $|\Phi_0\rangle$ into

$$(\mathscr{H} - E_0)|\Phi_0\rangle = (\mathscr{H}_0 + \mathscr{V} - E_0)|\Phi_0\rangle = (\mathscr{E}_0 - E_0)|\Phi_0\rangle = E_R|\Phi_0\rangle \tag{5.106}$$

and then successively multiply by $\langle\Psi_0|$, $\langle\Psi_a^r|$, $\langle\Psi_{ab}^{rs}|$, and so on, remembering that the matrix element of a Hamiltonian containing single particle interactions vanishes when the determinants differ by more than *one* spin orbital. In this way we find

$$\sum_{bs} \langle\Psi_0|\mathscr{H}|\Psi_b^s\rangle c_b^s = E_R \tag{5.107a}$$

$$\langle\Psi_a^r|\mathscr{H}|\Psi_0\rangle + \sum_{bs} \langle\Psi_a^r|\mathscr{H} - E_0|\Psi_b^s\rangle c_b^s + \sum_{bs} \langle\Psi_a^r|\mathscr{H}|\Psi_{ab}^{rs}\rangle c_{ab}^{rs} = E_R c_a^r \tag{5.107b}$$

and so on (i.e., the next equation in this hierarchy involves the coefficients of the doubles and triples).

Exercise 5.14 Show that

a. $\langle\Psi_0|\mathscr{H}|\Psi_b^s\rangle = v_{bs}$.

b. $\langle\Psi_a^r|\mathscr{H}|\Psi_0\rangle = v_{ra}$.

c. $\langle\Psi_a^r|\mathscr{H} - E_0|\Psi_b^s\rangle = 0$ if $a \neq b \quad r \neq s$

$= v_{rs}$ if $a = b \quad r \neq s$

$= -v_{ba}$ if $a \neq b \quad r = s$

$= \varepsilon_r^{(0)} + v_{rr} - \varepsilon_a^{(0)} - v_{aa}$ if $a = b \quad r = s$.

d. $\langle\Psi_a^r|\mathscr{H}|\Psi_{ab}^{rs}\rangle = v_{bs}$ if $a \neq b \quad r \neq s$

$= 0$ otherwise.

Using the matrix elements found in Exercise 5.14, Eqs. (5.107a, b) become

$$\sum_{bs} v_{bs} c_b^s = E_R \tag{5.108a}$$

$$v_{ra} + \sum_s (\varepsilon_r^{(0)} \delta_{rs} + v_{rs}) c_a^s - \sum_b (\varepsilon_a^{(0)} \delta_{ab} + v_{ba}) c_b^r + \sum_{\substack{b \neq a \\ s \neq r}} v_{bs} c_{ab}^{rs} = E_R c_a^r \tag{5.108b}$$

and so on. We now consider various approximations to full CI.

2. SCI. The analogue of truncating the CI expansion for the correlation energy at double excitations is to use only single excitations for the relaxation energy. This amounts to setting $c_{ab}^{rs} = 0$ in Eq. (5.108b),

$$v_{ra} + \sum_s (\varepsilon_r^{(0)} \delta_{rs} + v_{rs}) c_a^s - \sum_b (\varepsilon_a^{(0)} \delta_{ab} + v_{ba}) c_b^r = E_R c_a^r \tag{5.109}$$

This along with Eq. (5.108a) for the relaxation energy completely specify the simplest form of truncated CI.

3. IEPA. Since our Hamiltonian contains only single particle interactions, we must devise an independent "particle" theory. In analogy to pair theory we define a "particle" function

$$|\Psi_a\rangle = |\Psi_0\rangle + \sum_s c_a^s |\Psi_a^s\rangle \tag{5.110}$$

with a variational energy equal to $E_0 + e_a$. The relaxation energy then is approximated by a sum of "particle" energies as

$$E_R = \sum_a e_a \tag{5.111}$$

To find e_a, we substitute the expansion for the "particle" function into

$$(\mathscr{H} - E_0)|\Psi_a\rangle = e_a |\Psi_a\rangle \tag{5.112}$$

and then multiply successively by $\langle\Psi_0|$ and $\langle\Psi_a^r|$. Using the matrix elements in Exercise 5.14, we obtain

$$\sum_r v_{ar} c_a^r = e_a \tag{5.113a}$$

$$v_{ra} + \sum_s (\varepsilon_r^{(0)} \delta_{rs} + v_{rs}) c_a^s - (\varepsilon_a^{(0)} + v_{aa}) c_a^r = e_a c_a^r \tag{5.113b}$$

which are the required equations. Note that they can be formally obtained from the SCI equations by restricting the summation over b to one term (i.e., $b = a$, this corresponds to neglecting "particle-particle" interactions) and replacing E_R by e_a.

4. CCA. As we have seen in Section 5.2, the idea of this method, as applied to a real many-particle system, is to truncate the full CI hierarchy by approximating the coefficients of the quadruples as sums of products of the coefficients of the doubles. Here we express the coefficients of the doubles as sums of products of the coefficients of the singles. There are two independent ways in which we can obtain the double excitation Ψ_{ab}^{rs}: 1) we can excite $a \rightarrow r$ and then $b \rightarrow s$ to get $|\cdots rs \cdots\rangle$ and 2) we can excite $a \rightarrow s$ and then $b \rightarrow r$ to get $|\cdots sr \cdots\rangle$. Because the second determinant is the negative of the first, we can represent c_{ab}^{rs} either as $c_a^r c_b^s$ or $-c_a^s c_b^r$. In analogy to Eq. (5.53), we can write

$$c_{ab}^{rs} = c_a^r c_b^s - c_a^s c_b^r \tag{5.114}$$

Substituting this into Eq. (5.108b) with the expression for E_R in Eq. (5.108a) we have

$$v_{ra} + \sum_s (\varepsilon_r^{(0)}\delta_{rs} + v_{rs})c_a^s - \sum_b (\varepsilon_a^{(0)}\delta_{ab} + v_{ba})c_b^r + \sum_{bs} v_{bs}c_a^r c_b^s - \sum_{bs} v_{bs}c_a^s c_b^r = \left(\sum_{bs} v_{bs}c_b^s\right)c_a^r$$

Note that we need not worry about the restriction $b \neq a$ and $s \neq r$ since the expression for c_{ab}^{rs} in Eq. (5.114) vanishes when $b = a$ or $r = s$. Cancelling the common term on the right and left-hand sides, we finally have

$$v_{ra} + \sum_s (\varepsilon_r^{(0)}\delta_{rs} + v_{rs})c_a^s - \sum_b (\varepsilon_a^{(0)}\delta_{ab} + v_{ba})c_b^r - \sum_{bs} c_b^r v_{bs} c_a^s = 0 \tag{5.115}$$

Note that this equation is nonlinear and does not explicitly contain the relaxation energy. Before we discuss its properties, we consider two approximations to CCA.

5. L-CCA. The simplest approximation is to linearize Eq. (5.115) by setting the term which is a quadratic function of the coefficients equal to zero, i.e.,

$$v_{ra} + \sum_s (\varepsilon_r^{(0)}\delta_{rs} + v_{rs})c_a^s - \sum_b (\varepsilon_a^{(0)}\delta_{ab} + v_{ba})c_b^r = 0 \tag{5.116}$$

This is called the linear approximation to CCA.

6. CEPA. Finally, we consider the analogue of the coupled-electron pair approximation. Here instead of throwing away the quadratic term, we approximate it as follows. First note that

$$\sum_{bs} c_b^r v_{bs} c_a^s = \sum_s c_a^r v_{as} c_a^s + \sum_{\substack{b \neq a \\ s}} c_b^r v_{bs} c_a^s$$

and then ignoring the $b \neq a$ terms, we obtain

$$\sum_{bs} c_b^r v_{bs} c_a^s \cong c_a^r \sum_s v_{as} c_a^s = e_a c_a^r$$

Finally, using this in Eq. (5.115), we have

$$v_{ra} + \sum_s (\varepsilon_r^{(0)}\delta_{rs} + v_{rs})c_a^s - \sum_b (\varepsilon_a^{(0)}\delta_{ab} + v_{ba})c_b^r = e_a c_a^r \tag{5.117}$$

which is the required equation.

Table 5.5 Equations for the relaxation energy in many-electron theories

$$E_R = \sum_a e_a \qquad e_a = \sum_r v_{ar} c_a^r$$

SCI:	$v_{ra} + \sum_s (\varepsilon_r^{(0)} \delta_{rs} + v_{rs}) c_a^s - \sum_b (\varepsilon_a^{(0)} \delta_{ab} + v_{ba}) c_b^r = E_R c_a^r$
IEPA:	$v_{ra} + \sum_s (\varepsilon_r^{(0)} \delta_{rs} + v_{rs}) c_a^s - (\varepsilon_a^{(0)} + v_{aa}) c_a^r = e_a c_a^r$
L-CCA:	$v_{ra} + \sum_s (\varepsilon_r^{(0)} \delta_{rs} + v_{rs}) c_a^s - \sum_b (\varepsilon_a^{(0)} \delta_{ab} + v_{ba}) c_b^r = 0$
CEPA:	$v_{ra} + \sum_s (\varepsilon_r^{(0)} \delta_{rs} + v_{rs}) c_a^s - \sum_b (\varepsilon_a^{(0)} \delta_{ab} + v_{ba}) c_b^r = e_a c_a^r$
CCA:	$v_{ra} + \sum_s (\varepsilon_r^{(0)} \delta_{rs} + v_{rs}) c_a^s - \sum_b (\varepsilon_a^{(0)} \delta_{ab} + v_{ba}) c_b^r = \sum_{bs} c_b^r v_{bs} c_a^s$

In Table 5.5 we summarize the various results obtained so far. Although the structure of these equations is considerably simpler than the corresponding ones for a real many-body system, the insights concerning the interrelations among the various approaches gained from a perusal of this table are generally valid. In particular, note that 1) CEPA can formally be obtained from SCI by replacing the total relaxation energy E_R by e_a; 2) IEPA can be obtained from CEPA by ignoring the coupling between different "particles," i.e., setting $v_{ab} \to v_{aa} \delta_{ab}$; 3) L-CCA can be obtained from SCI by setting $E_R = 0$ or from CEPA by putting $e_a = 0$. It is important to remember that just because a method can be obtained from another by setting something to zero does not mean that it is inferior. Table 5.5 also shows that all methods except CCA are closely related from the computational point of view. In the next section we will apply the various formalisms to a simple model problem where the exact answer for the relaxation energy is known.

First, let us consider the CCA equations more closely. If we set

$$c_a^r = C_{ra}$$

in Eqs. (5.108a) and (5.115) we see that they are identical to Eqs. (5.100) and (5.101), which determine the exact relaxation energy. Thus CCA is exact for an N-electron system with only single particle interactions! It is gratifying that among all the many-electron theories we have considered at least one is exact when applied to a problem where the orbital picture is exact. This must mean that the approximation used in deriving the CCA equations from the exact full CI ones, i.e.,

$$c_{ab}^{rs} = c_a^r c_b^s - c_a^s c_b^r$$

is really not an approximation in the present context, but an exact relation.

This relation can be mathematically proved using the property of determinants given in Eq. (1.40) and the fact that the exact wave function $|\Phi_0\rangle$ is a single determinant. Recall that (see Eq. (5.79))

$$|\Phi_0\rangle = |\chi_1 \cdots \chi_a \cdots \chi_N\rangle \tag{5.118}$$

and that the exact orbitals $|\chi_a\rangle$ can be expressed as linear combinations of the zeroth-order orbitals $|\chi_i^{(0)}\rangle$ as (see Eq. (5.92))

$$|\chi_a\rangle = \sum_b |\chi_b^{(0)}\rangle(\mathbf{U}_{AA})_{ba} + \sum_r |\chi_r^{(0)}\rangle(\mathbf{U}_{BA})_{ra} \tag{5.119}$$

If we substitute the above expansion for the occupied orbitals into Eq. (5.118) and make repeated use of Eq. (1.40), it can be shown that the exact wave function is

$$|\Phi_0\rangle = |\mathbf{U}_{AA}|\left(|\Psi_0\rangle + \sum_{ar} c_a^r|\Psi_a^r\rangle + \sum_{\substack{a<b\\ r<s}} c_{ab}^{rs}|\Psi_{ab}^{rs}\rangle + \cdots\right) \tag{5.120a}$$

where the coefficients c_a^r are given by

$$c_a^r = (\mathbf{U}_{BA}\mathbf{U}_{AA}^{-1})_{ra} \tag{5.120b}$$

and

$$c_{ab}^{rs} = c_a^r c_b^s - c_a^s c_b^r \tag{5.120c}$$

In an analogous way, coefficients of the higher excitations can be expressed as sums of products of the singles coefficients. Note that for relation (5.120c) to hold, we must use the intermediate normalized form of $|\Phi_0\rangle$. Let us illustrate the above with an example. Suppose we have a two-electron problem (i.e., $|\Phi_0\rangle = |\chi_1\chi_2\rangle$) and

$$|\chi_1\rangle = |\chi_1^{(0)}\rangle + a_3|\chi_3^{(0)}\rangle + a_4|\chi_4^{(0)}\rangle \tag{5.121a}$$

$$|\chi_2\rangle = |\chi_2^{(0)}\rangle + b_3|\chi_3^{(0)}\rangle + b_4|\chi_4^{(0)}\rangle \tag{5.121b}$$

Then by repeated applications of Eq. (1.40) one can show that

$$\begin{aligned}|\Phi_0\rangle &= |\chi_1^{(0)}\chi_2^{(0)}\rangle + b_3|\chi_1^{(0)}\chi_3^{(0)}\rangle + b_4|\chi_1^{(0)}\chi_4^{(0)}\rangle \\ &\quad + a_3|\chi_3^{(0)}\chi_2^{(0)}\rangle + a_4|\chi_4^{(0)}\chi_2^{(0)}\rangle + (a_3b_4 - a_4b_3)|\chi_3^{(0)}\chi_4^{(0)}\rangle \\ &= |\Psi_0\rangle + b_3|\Psi_2^3\rangle + b_4|\Psi_2^4\rangle + a_3|\Psi_1^3\rangle + a_4|\Psi_1^4\rangle \\ &\quad + (a_3b_4 - a_4b_3)|\Psi_{12}^{34}\rangle\end{aligned} \tag{5.122}$$

It is then clear that

$$c_{12}^{34} = (a_3b_4 - a_4b_3) = c_1^3c_2^4 - c_1^4c_2^3 \tag{5.123}$$

as we claimed.

Exercise 5.15 Repeat the above analysis using

$$|\chi_1\rangle = a_1|\chi_1^{(0)}\rangle + a_2|\chi_2^{(0)}\rangle + a_3|\chi_3^{(0)}\rangle + a_4|\chi_4^{(0)}\rangle$$

$$|\chi_2\rangle = b_1|\chi_1^{(0)}\rangle + b_2|\chi_2^{(0)}\rangle + b_3|\chi_3^{(0)}\rangle + b_4|\chi_4^{(0)}\rangle$$

instead of Eqs. (5.121a, b).

a. By repeated use of Eq. (1.40) show that

$$\begin{aligned}|\Phi_0\rangle &= (a_1b_2 - b_1a_2)|\chi_1^{(0)}\chi_2^{(0)}\rangle + (a_1b_3 - b_1a_3)|\chi_1^{(0)}\chi_3^{(0)}\rangle \\ &\quad + (a_1b_4 - b_1a_4)|\chi_1^{(0)}\chi_4^{(0)}\rangle + (a_3b_2 - b_3a_2)|\chi_3^{(0)}\chi_2^{(0)}\rangle \\ &\quad + (a_4b_2 - b_4a_2)|\chi_4^{(0)}\chi_2^{(0)}\rangle + (a_3b_4 - b_3a_4)|\chi_3^{(0)}\chi_4^{(0)}\rangle\end{aligned}$$

Intermediate normalize this wave function by dividing the right-hand side by $a_1b_2 - b_1a_2$ and then explicitly verify that Eq. (5.123) is satisfied.

b. To make contact with the general formalism, note that

$$\mathbf{U}_{AA} = \begin{pmatrix} a_1 & b_1 \\ a_2 & b_2 \end{pmatrix} \quad \text{and} \quad \mathbf{U}_{BA} = \begin{pmatrix} a_3 & b_3 \\ a_4 & b_4 \end{pmatrix}$$

Note that $|\mathbf{U}_{AA}| = a_1b_2 - b_1a_2$ as required to make Eq. (5.120a) consistent with the result obtained in part (a). Use the result of Exercise 1.4(f) to evaluate $\mathbf{U}_{AA}^{-1}$ and then verify the general result given in Eq. (5.120b) by calculating

$$(\mathbf{U}_{BA}\mathbf{U}_{AA}^{-1})_{11} = c_1^3$$

and showing that it is identical to the coefficient of $|\chi_3^{(0)}\chi_2^{(0)}\rangle$ obtained in part (a).

5.3.2 The Resonance Energy of Polyenes in Hückel Theory

We now consider an interesting application of the various many-electron approaches just discussed. We will use them to calculate the resonance energy of a cyclic polyene with an even number of carbon atoms ($N = 2n$) within the framework of Hückel theory, and then compare the predicted results with the exact value of this quantity. The *resonance energy* is defined as the difference between the exact energy of the polyene (as obtained by diagonalizing the Hückel matrix and adding up to the occupied orbital energies) and the energy of n localized and noninteracting double bonds or ethylenic units. Since Hückel theory is a one-particle theory (i.e., the effective Hamiltonian does not contain two-particle interactions), the resonance energy is analogous to the relaxation energy previously defined.

To introduce notation, we briefly review the application of Hückel theory to a cyclic polyene with $N = 2n$ carbon atoms. Each carbon atom contributes one electron to the π system of the molecule. The total Hamiltonian is approximated as a sum of one-particle terms as

$$\mathscr{H} = \sum_{i=1}^{N} h_{\text{eff}}(i) \tag{5.124}$$

where h_{eff} is completely specified by its matrix elements between an orthonormal set of atomic orbitals ($\langle\phi_\mu|\phi_\nu\rangle = \delta_{\mu\nu}$, $\mu, \nu = 1, \ldots, N$) as

$$\begin{aligned}(\mathbf{H})_{\mu\nu} = H_{\mu\nu} = \langle\phi_\mu|h_{\text{eff}}|\phi_\nu\rangle &= \alpha \qquad \text{if } \nu = \mu \\ &= \beta \qquad \text{if } \nu = \mu \pm 1 \\ &= 0 \qquad \text{otherwise}\end{aligned} \tag{5.125}$$

Both the parameters α and β are negative. Note that in this model only nearest-neighbor (or "bonded") carbon atoms interact. We seek a set of molecular orbitals, $|\psi_i\rangle$, $i = 1, \ldots, N$, which are eigenfunctions of h_{eff}

$$h_{\text{eff}}|\psi_i\rangle = \varepsilon_i|\psi_i\rangle \tag{5.126}$$

If we expand $|\psi_i\rangle$ as a linear combination of atomic orbitals as

$$|\psi_i\rangle = \sum_{\mu} C_{\mu i}|\phi_\mu\rangle \qquad i = 1, 2, \ldots, N \tag{5.127}$$

and use the linear variational principle, we are lead to the matrix eigenvalue problem

$$\mathbf{HC} = \mathbf{C}\boldsymbol{\varepsilon} \tag{5.128}$$

where the matrix elements of the Hückel matrix, **H**, are given in Eq. (5.125). Since the n molecular orbitals with smallest orbital energies are doubly occupied, the total Hückel energy is

$$\mathscr{E}_0 = 2\sum_{i=1}^{n} \varepsilon_i = 2\sum_{a}^{N/2} \varepsilon_a \tag{5.129}$$

The exact wave function of the system is

$$|\Phi_0\rangle = |\psi_1\bar{\psi}_1 \cdots \psi_a\bar{\psi}_a \cdots \psi_n\bar{\psi}_n\rangle \tag{5.130}$$

where the spin orbitals are obtained by multiplying the spatial orbitals by a spin function corresponding to spin up (no bar) or spin down (bar).

For the case of cyclic polyenes $(\text{CH})_N$, the Hückel problem is analytically soluble.[10] The orbital energies are

$$\varepsilon_i = \alpha + 2\beta \cos(\pi i/n) \qquad i = 0, \pm 1, \pm 2, \ldots, \pm(n-1), n \tag{5.131}$$

Polyenes with $N = 4\nu + 2$, $\nu = 1, 2, \ldots$ carbon atoms have closed-shell electronic configurations. In this case, the exact ground state energy is

$$\begin{aligned}\mathscr{E}_0 &= 2\sum_{i=-\nu}^{\nu} \varepsilon_i = 2\sum_{i=-\nu}^{\nu} \alpha + 4\beta \sum_{i=-\nu}^{\nu} \cos\left(\frac{\pi i}{2\nu+1}\right) \\ &= N\alpha + 4\beta/\sin(\pi/N) \qquad (5.132)\end{aligned}$$

For example, for benzene ($N = 6$, n = 3, $\nu = 1$) the ground state energy is $6\alpha + 8\beta$.

Exercise 5.16 Set up the Hückel matrix for benzene and find its eigenvalues. Remember that if the carbon atoms are labeled clockwise from 1 to 6, then atoms 1 and 6 are nearest neighbors. Show that the six eigenvalues are identical to those given by Eq. (5.131). Find the total energy and compare it with the result given by Eq. (5.132).

We now turn to the localized description of polyenes. As the zeroth-order approximation, we assume that the polyene consists of n noninteracting double bonds or ethylenic units. To obtain the energy corresponding to this description we note that the Hückel matrix for ethylene is

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}$$

with eigenvalues and eigenfunctions

$$\varepsilon_1^{(0)} = \alpha + \beta \qquad |1\rangle = 2^{-1/2}(|\phi_1\rangle + |\phi_2\rangle) \qquad (5.133a)$$

$$\varepsilon_{1^*}^{(0)} = \alpha - \beta \qquad |1^*\rangle = 2^{-1/2}(|\phi_1\rangle - |\phi_2\rangle) \qquad (5.133b)$$

where $|1\rangle$ is the bonding orbital, while $|1^*\rangle$ is the antibonding orbital. Since an ethylenic unit has two electrons, its energy is $2\alpha + 2\beta$. Therefore, the energy of n noninteracting units is

$$E_0 = n(2\alpha + 2\beta) = N\alpha + N\beta \qquad (5.134)$$

The difference between the exact energy of the polyene and this approximate localized energy is the resonance energy. Using Eqs. (5.132) and (5.134), we have

$$E_R = \mathscr{E}_0 - E_0 = \beta(4/\sin(\pi/N) - N) \qquad (5.135)$$

For benzene, this expression gives $E_R = 2\beta$. In the limit that the number of carbons becomes large ($N \to \infty$) (since sin(x) ≈ x for small x) the resonance energy approaches

$$\lim_{N\to\infty} E_R = N\beta(4/\pi - 1) = 0.2732N\beta \qquad (5.136)$$

Since β is negative, the resonance energy, just like the correlation energy of a real many-electron system, is negative. Moreover, it is proportional to the number of particles as these become large. Therefore, only a size consistent approach is suitable for the calculation of the resonance energy of large polyenes.

To make contact with the various many-electron approaches to the relaxation energy, we define the set of occupied ($|i\rangle$) and unoccupied ($|i^*\rangle$) ethylenic orbitals as

$$|i\rangle = 2^{-1/2}(|\phi_{2i-1}\rangle + |\phi_{2i}\rangle) \qquad i = 1, 2, \ldots, n \tag{5.137a}$$

$$|i^*\rangle = 2^{-1/2}(|\phi_{2i-1}\rangle - |\phi_{2i}\rangle) \tag{5.137b}$$

Using these localized orbitals, the wave function corresponding to our zeroth-order description is

$$|\Psi_0\rangle = |1\bar{1}2\bar{2}\cdots n\bar{n}\rangle \tag{5.138}$$

Since the atomic orbitals are orthonormal (i.e., $\langle\phi_\mu|\phi_\nu\rangle = \delta_{\mu\nu}$), it follows that

$$\langle i|j\rangle = \langle i^*|j^*\rangle = \delta_{ij} \tag{5.139a}$$

$$\langle i|j^*\rangle = 0 \tag{5.139b}$$

Using the matrix elements given in Eq. (5.125), it can be shown that the nonzero matrix elements of h_{eff} in the localized basis are

$$\langle i|h_{\text{eff}}|i\rangle = \alpha + \beta = \varepsilon_i^{(0)} \tag{5.140a}$$

$$\langle i^*|h_{\text{eff}}|i^*\rangle = \alpha - \beta = \varepsilon_{i^*}^{(0)} \tag{5.140b}$$

$$\langle i|h_{\text{eff}}|i \pm 1\rangle = \beta/2 \tag{5.140c}$$

$$\langle i^*|h_{\text{eff}}|(i \pm 1)^*\rangle = -\beta/2 \tag{5.140d}$$

$$\langle i|h_{\text{eff}}|(i \pm 1)^*\rangle = \langle (i \mp 1)|h_{\text{eff}}|i^*\rangle = \pm\beta/2 \tag{5.140e}$$

Exercise 5.17 Verify Eqs. (5.139) and (5.140).

Finally to make contact with the general formalism previously given, we partition h_{eff} as

$$h_{\text{eff}} = h_0 + v \tag{5.141}$$

where h_0 is defined so that the localized bonding and antibonding orbitals are its eigenfunctions

$$h_0|i\rangle = (\alpha + \beta)|i\rangle = \varepsilon_i^{(0)}|i\rangle \tag{5.142a}$$

$$h_0|i^*\rangle = (\alpha - \beta)|i^*\rangle = \varepsilon_{i^*}^{(0)}|i^*\rangle \tag{5.142b}$$

Since the localized orbitals are orthonormal (see Eq. (5.139)), it follows from Eq. (5.140) that the nonzero matrix elements of the perturbation v are

$$\langle i|v|i \pm 1\rangle = \langle i|v|(i+1)^*\rangle = \langle i^*|v|i-1\rangle = \beta/2 \qquad i = 1, 2, \ldots, n \tag{5.143a}$$

$$\langle i^*|v|(i \pm 1)^*\rangle = \langle i|v|(i-1)^*\rangle = \langle i^*|v|i+1\rangle = -\beta/2 \tag{5.143b}$$

In using the above matrix elements, it is important to remember that because of the cyclic nature of the problem $|n+1\rangle = |1\rangle$ and $|0\rangle = |n\rangle$. As a consistency check, let us calculate $E_0 = \langle\Psi_0|\mathscr{H}|\Psi_0\rangle$ using the definition of $|\Psi_0\rangle$ in Eq. (5.138) and the above matrix elements.

$$\begin{aligned} E_0 &= \sum_{i=1}^{n} [\langle i|h_0|i\rangle + \langle\bar{i}|h_0|\bar{i}\rangle] + [\langle i|v|i\rangle + \langle\bar{i}|v|\bar{i}\rangle] \\ &= \sum_{i=1}^{n} [(\alpha+\beta) + (\alpha+\beta)] = N\alpha + N\beta \end{aligned}$$

where we have used the fact that $\langle i|v|i\rangle$ and $\langle\bar{i}|v|\bar{i}\rangle$ are zero. Note that this result for E_0 agrees with that obtained in Eq. (5.134).

We are now ready to use the various many-electron theories to calculate the resonance energy. We restrict ourselves to benzene and leave the extension to larger systems to the exercises. We begin with the IEPA because it is the easiest. Since benzene has six occupied spin orbitals, we need to calculate six "particle" energies e_1, $e_{\bar{1}}$, e_2, $e_{\bar{2}}$, e_3, and $e_{\bar{3}}$. Since all localized bonds are equivalent, all these pair energies are equal to, say, e_1 so that

$$E_R = 6e_1 \tag{5.144}$$

To calculate e_1 we consider the "particle" function $|\Psi_1\rangle$ obtained by mixing the ground state wave function $|\Psi_0\rangle$ with single excitations obtained by promoting the electron in orbital $|1\rangle$ to all possible virtual orbitals,

$$|\Psi_1\rangle = |\Psi_0\rangle + c_1|\Psi_1^{1*}\rangle + c_2|\Psi_1^{2*}\rangle + c_3|\Psi_1^{3*}\rangle \tag{5.145}$$

We did not include excitations involving spin-flips (e.g., $|\Psi_1^{\overline{2*}}\rangle$) because these do not mix with $|\Psi_0\rangle$. Now consider the matrix elements

$$\begin{aligned} \langle\Psi_0|\mathscr{H}|\Psi_1^{1*}\rangle &= \langle 1|h_0|1*\rangle + \langle 1|v|1*\rangle = 0 \\ \langle\Psi_0|\mathscr{H}|\Psi_1^{2*}\rangle &= \langle 1|h_0|2*\rangle + \langle 1|v|2*\rangle = \beta/2 \\ \langle\Psi_0|\mathscr{H}|\Psi_1^{3*}\rangle &= \langle 1|h_0|3*\rangle + \langle 1|v|3*\rangle = -\beta/2 \end{aligned}$$

where we have used Eqs. (5.142) and (5.143). Note that $|\Psi_1^{1*}\rangle$ does not interact with $|\Psi_0\rangle$, so we need not consider it further. Moreover, since the other two excitations have matrix elements that are negatives of each other, we consider the normalized linear combinations $2^{-1/2}(|\Psi_1^{2*}\rangle \pm |\Psi_1^{3*}\rangle)$. The plus combination does not mix with $|\Psi_0\rangle$. Introducing a new notation for the minus combination

$$|{}^{*}_{1}\rangle = 2^{-1/2}(|\Psi_1^{2*}\rangle - |\Psi_1^{3*}\rangle)$$

or in general

$$|{}^{*}_{i}\rangle = 2^{-1/2}(|\Psi_i^{(i+1)*}\rangle - |\Psi_i^{(i-1)*}\rangle) \tag{5.146}$$

we can write the "particle" function $|\Psi_1\rangle$ as

$$|\Psi_1\rangle = |\Psi_0\rangle + c|{}^{*}_{1}\rangle \tag{5.147}$$

The corresponding "particle" equations are

$$c\langle\Psi_0|\mathscr{H}|{}^{*}_{1}\rangle = e_1 \tag{5.148a}$$

$$\langle{}^{*}_{1}|\mathscr{H}|\Psi_0\rangle + \langle{}^{*}_{1}|\mathscr{H} - E_0|{}^{*}_{1}\rangle c = e_1 c \tag{5.148b}$$

The required matrix elements are

$$\langle\Psi_0|\mathscr{H}|{}^{*}_{1}\rangle = 2^{-1/2}\beta \tag{5.149a}$$

$$\langle{}^{*}_{1}|\mathscr{H} - E_0|{}^{*}_{1}\rangle = -\tfrac{3}{2}\beta \tag{5.149b}$$

Substituting these into Eq. (5.148) and solving these in the usual way, we find

$$e_1 = \beta\left(\frac{(17)^{1/2} - 3}{4}\right)$$

so that

$$E_R(\mathrm{IEPA}) = 6e_1 = 1.685\beta \tag{5.150}$$

which is to be compared with the exact value of 2β (i.e., the IEPA gives 84% of the exact result).

Exercise 5.18 Evaluate the matrix elements given in Eq. (5.149) and fill in the remaining steps leading to Eq. (5.150).

Exercise 5.19 a) Extend the above analysis to calculate the IEPA resonance energy for a cyclic polyene with $N = 2n$ $(N > 6)$ carbon atoms. As before, argue that all "particle" energies are the same so that

$$E_R = Ne_1$$

Consider only single excitations that mix with $|\Psi_0\rangle$. Show that the "particle" function $|\Psi_1\rangle$ is

$$|\Psi_1\rangle = |\Psi_0\rangle + c|{}^{*}_{1}\rangle$$

where $|{}^{*}_{1}\rangle$ is obtained from Eq. (5.146),

$$|{}^{*}_{1}\rangle = 2^{-1/2}(|\Psi_1^{2^*}\rangle - |\Psi_1^{n^*}\rangle)$$

Now show that

$$\langle\Psi_0|\mathscr{H}|{}^{*}_{1}\rangle = 2^{-1/2}\beta$$

as before, but that here

$$\langle{}^{*}_{1}|\mathscr{H} - E_0|{}^{*}_{1}\rangle = -2\beta.$$

instead of the result in Eq. (5.149b). Why the difference? Finally, solve the resulting "particle" equations to show that

$$E_R(\text{IEPA}) = N((3/2)^{1/2} - 1)\beta = 0.2247N\beta.$$

Note that the IEPA is indeed size consistent and that in the limit of large N it gives 82% of the exact resonance energy.

b) The above result is not really exact within the IEPA. The reason for this is that there exist single excitations involving orbital $|1\rangle$ that do not mix with $|\Psi_0\rangle$ but do mix with $|{}^{*}_{1}\rangle$ and thus have some effect on the "particle" energy e_1. These excitations are analogous to single excitations in CI for a real many-particle system in the sense that although single excitations do not mix with the HF wave function because of Brillouin's theorem, they do mix indirectly through the double excitations. Investigate the effect of such excitations for the case $N = 10$. Show that the exact "particle" function $|\Psi_1\rangle$ is

$$|\Psi_1\rangle = |\Psi_0\rangle + c_1|{}^{*}_{1}\rangle + c_3|\Psi_1^{3*}\rangle + c_4|\Psi_1^{4*}\rangle$$

Now show that

$$\begin{aligned}
\langle\Psi_0|\mathscr{H}|\Psi_1^{3*}\rangle &= \langle\Psi_0|\mathscr{H}|\Psi_1^{4*}\rangle = 0\\
\langle\Psi_1^{3*}|\mathscr{H} - E_0|\Psi_1^{3*}\rangle &= \langle\Psi_1^{4*}|\mathscr{H} - E_0|\Psi_1^{4*}\rangle = -2\beta\\
\langle\Psi_1^{3*}|\mathscr{H}|\Psi_1^{4*}\rangle &= -\beta/2\\
\langle{}^{*}_{1}|\mathscr{H}|\Psi_1^{3*}\rangle &= -\beta/2^{3/2}\\
\langle{}^{*}_{1}|\mathscr{H}|\Psi_1^{4*}\rangle &= \beta/2^{3/2}
\end{aligned}$$

Finally, show from the resulting "particle" equations that e_1 is the solution of

$$4e_1^3 + 14\beta e_1^2 + 9\beta^2 e_1 - 3\beta^3 = 0$$

This cubic equation can be solved to yield $e_1 = 0.2387\beta$ so that the exact IEPA resonance energy for $N = 10$ is 2.387β, which is to be compared with the approximate result of 2.247β obtained in part (a), so that there is a 6% difference. The exact resonance energy found from Eq. (5.135) is 2.944β for this case.

We now consider the use of singly excited CI to calculate the resonance energy of benzene. The SCI wave function is

$$|\Psi_{\text{SCI}}\rangle = |\Psi_0\rangle + \sum_{i=1}^{3} c_i|{}^{*}_{i}\rangle + \sum_{i=1}^{3} \bar{c}_i|{}^{\bar{*}}_{\bar{i}}\rangle \tag{5.151}$$

where $|{}^{*}_{i}\rangle$ is defined in Eq. (5.146); $|{}^{\bar{*}}_{\bar{i}}\rangle$ is simply the corresponding wave function involving a spin orbital with spin down. Because of the symmetry of benzene, it follows that $c_1 = c_2 = c_3 = \bar{c}_1 = \bar{c}_2 = \bar{c}_3 = c$. Furthermore, the required matrix elements, when $i = 1, 2, 3$

$$\langle \overset{*}{i} | \mathscr{H} | \Psi_0 \rangle = 2^{-1/2}\beta \qquad (5.152a)$$

$$\langle \overset{*}{i} | \mathscr{H} - E_0 | \overset{*}{i} \rangle = -\tfrac{3}{2}\beta \qquad (5.152b)$$

$$\langle \overset{*}{1} | \mathscr{H} | \overset{*}{2} \rangle = \langle \overset{*}{1} | \mathscr{H} | \overset{*}{3} \rangle = \langle \overset{*}{2} | \mathscr{H} | \overset{*}{3} \rangle = \beta/4 \qquad (5.152c)$$

are readily evaluated. The matrix elements for the "barred" states are identical and $\langle \overset{*}{i} | \mathscr{H} | \overset{\bar{*}}{\bar{j}} \rangle = 0$ for all i and j. Proceeding in the standard way, the SCI equations can be shown to be

$$E_R(\mathrm{SCI}) = 6(2^{-1/2}c\beta) \qquad (5.153a)$$

$$2^{-1/2}\beta - \beta c = E_R(\mathrm{SCI})c \qquad (5.153b)$$

Solving these for $E_R(\mathrm{SCI})$ we find

$$E_R(\mathrm{SCI}) = ((13)^{1/2} - 1)\beta/2 = 1.303\beta \qquad (5.154)$$

which is to be compared with the exact value of 2β for the resonance energy. Thus SCI gives only 65% of the correct answer. Moreover, as will be seen in Exercise 5.21, this theory is not size consistent, and it predicts that the resonance energy of a cyclic polyene is proportional to $N^{1/2}$ as the number of carbons increase. This result is quite analogous to the case of N noninteracting H_2 molecules, where the correlation energy obtained using DCI also has the same incorrect N-dependence.

Exercise 5.20 Verify Eq. (5.152c), derive Eq. (5.153a,b), and solve them to obtain the result shown in Eq. (5.154).

Exercise 5.21 Extend the above analysis to calculate the SCI resonance energy for a cyclic polyene with $N = 2n$ ($N > 6$) carbon atoms. If we restrict ourselves to only those configurations which interact with $|\Psi_0\rangle$, then the appropriate generalization of Eq. (5.151) is

$$|\Psi_{\mathrm{SCI}}\rangle = |\Psi_0\rangle + \sum_{i=1}^{n} c_i |\overset{*}{i}\rangle + \sum_{i=1}^{n} \bar{c}_i |\overset{\bar{*}}{\bar{i}}\rangle$$

As discussed in Exercise 5.19b, this is not the complete SCI wave function because there exist additional singly excited configurations which, although they do not mix with $|\Psi_0\rangle$, they do mix with $|\overset{*}{i}\rangle$. The omission of these does not affect our qualitative conclusions. Show that the required matrix elements are

$$\langle \Psi_0 | \mathscr{H} | \overset{*}{i} \rangle = 2^{-1/2}\beta$$

$$\langle \overset{*}{i} | \mathscr{H} - E_0 | \overset{*}{j} \rangle = (-2\beta)\delta_{ij}$$

Why are Eqs. (5.152b) and (5.152c) different? Using these matrix elements, show that the SCI equations are

$$E_R(\text{SCI}) = Nc\beta 2^{-1/2}$$

$$2^{-1/2}\beta - 2c\beta = E_R(\text{SCI})c$$

Finally, solve them to obtain

$$\text{E}_R(\text{SCI}) = ((1 + N/2)^{1/2} - 1)\beta$$

which is proportional to $N^{1/2}$ as N becomes large.

Finally, we consider the various coupled-"particle" theories. There is no need to do a CCA calculation because we have already proved in general that it gives the exact relaxation energy. To obtain the L-CCA and the CEPA equations, we use the formal relationship of these methods to SCI which was brought out by Table 5.5. Thus we can obtain the L-CCA equations by formally setting $E_R(\text{SCI})$ equal to zero in Eq. (5.153b). Hence

$$E_R(\text{L-CCA}) = 6c\beta 2^{-1/2} \tag{5.155a}$$

$$2^{-1/2}\beta - \beta c = 0 \tag{5.155b}$$

Solving the second equation for c and substituting the result into the first, we find

$$E_R(\text{L-CCA}) = 3\beta \tag{5.156}$$

which grossly overestimates the exact resonance energy.

The CEPA equations are formally obtained from the SCI equations by replacing $E_R(\text{SCI})$ in Eq. (5.153b) by the particle energy e. Thus we have

$$E_R(\text{CEPA}) = 6e \tag{5.157a}$$

$$e = c\beta 2^{-1/2} \tag{5.157b}$$

$$2^{-1/2}\beta - \beta c = ec \tag{5.157c}$$

Eliminating c from Eqs. (5.157b, c), we obtain the following quadratic equation for e

$$2e^2 - 2e\beta - \beta^2 = 0 \tag{5.158}$$

Solving this for e and substituting it into Eq. (5.157a), we have

$$E_R(\text{CEPA}) = 3(3^{1/2} - 1)\beta = 2.196\beta \tag{5.159}$$

Thus CEPA gives a respectable approximation to the resonance energy of benzene.

The results obtained by the various many-electron approaches are summarized in Table 5.6. It can be seen that, aside from CCA, which is

Table 5.6 Resonance energy of benzene

Exact	2β	Percent of exact
SCI	1.303β	65
IEPA	1.685β	84
CCA	2β	100
L-CCA	3β	150
CEPA	2.196β	110

exact, CEPA works the best. It should be emphasized that one should not draw any conclusions about the validity or accuracy of these methods when applied to a real many-particle problem from this table. For example, for a six-electron system, DCI in a large basis set certainly gives more than 65% of the correlation energy. In some sense the calculation of the resonance energy in this model is more demanding than the calculation of the correlation energy. We certainly do not mean that it is computationally more difficult but merely that our zeroth-order description here is worse than is the HF description for a real many-electron system. In benzene all the six nearest-neighbor atoms interact equivalently (i.e., the matrix elements between adjacent carbons are all equal to β). In the localized description we assume that the resonance integral is β between atoms 1 and 2, 3 and 4, and 5 and 6, but is zero between 2 and 3, 4 and 5, and 6 and 1. Thus our zeroth-order picture is poor, and a general approach like CI does not work very well then truncated at the lowest nontrivial level. Of course, the CCA takes full advantage of the fact that the Hamiltonian contains only single particle interactions and, hence, is exact no matter how poor the starting point.

NOTES

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FURTHER READING

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