

Péter R. Surján

Second Quantized Approach to Quantum Chemistry

An Elementary Introduction



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With 11 Figures

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To my wife Zsuzsa
and to my parents

Foreword

The aim of this book is to give a simple, short, and elementary introduction to the second quantized formalism as applied to a many-electron system. It is intended for those, mainly chemists, who are familiar with traditional quantum chemistry but have not yet become acquainted with second quantization. The treatment is, in part, based on a series of seminars held by the author on the subject. It has been realized that many quantum chemists either interested in theory or in applications, being educated as chemists and not as physicists, have never devoted themselves to taking a course on the second quantized approach. Most available textbooks on this topic are not very easy to follow for those who are not trained in theory, or they are not detailed enough to offer a comprehensive treatment. At the same time there are several papers in quantum chemical literature which take advantage of using second quantization, and it would be worthwhile if those papers were accessible for a wider reading public. For this reason, it is intended in this survey to review the basic formalism of second quantization, and to treat some selected chapters of quantum chemistry in this language. Most derivations will be carried out in a detailed manner, so the reader need not accept gaps to understand the result. Due to space limitations, however, the whole of quantum chemistry is not translated into second quantized language; the treatment is kept as short as possible so as not to deter the reader by a voluminous book, while the material presented here is fully sufficient to completely understand the approach. This allows everyone to continue his/her studies alone or by more advanced textbooks, some of which will be referred to at the appropriate places.

Again to save space, some other related methods such as Green's function formalism or the diagrammatic perturbation theory, which are usually treated with second quantization on an equal footing, are not presented here. Merely the second quantized approach (particle number representation) will be elaborately discussed. However, a short review of some recent developments partly connected to the author's own work is included to illustrate the value and actuality of second quantization.

A limited number of problems (exercises) is also included to help the reader to gain more experience in the formalism; the solutions are given at the end of the book. The text is detailed enough to make the inclusion of a larger number of problems unnecessary.

Only the most important basic references are given, with the exception of the last few sections which contain more references since they discuss recent developments.

The author is convinced that second quantization is the simplest approach to the many-electron problem, and it should be available not only for physicists but for every chemist engaged in quantum chemistry. If this does not come about from the present treatment, it is the fault of the presentation and not of the second quantized approach.

Budapest, April 1989

Péter R. Surján

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List of Symbols

\hat{A}	Operator of observable A	S	Overlap matrix
a_i^+, i^+	Creation operator	\vec{S}	Spin operator
a_i, i^-	Annihilation operator	\vec{s}_i	One-electron spin operator
C_{in}	MO expansion coefficient	\hat{W}	Perturbation operator
E	Electronic energy	Z_a	Atomic number
\hat{F}	Fockian	Γ	Second-order density matrix
\hat{h}	One-electron Hamiltonian	Δ	Laplacian
\hat{H}	Hamiltonian	α, β	Spin functions
\hat{I}	Unity operator	γ	Electron repulsion integral
J	Exchange parameter	ε_i	Orbital energy
M	Number of orbitals	χ_μ	One-electron function (AO)
n_i	Occupation number	ϕ_i, ψ_i	One-electron function (MO)
\hat{N}_i	Occupation number operator	ϕ, ψ	Many-electron wave function
N	Number of electrons	σ	Spin label
\hat{N}	Particle number operator	$\langle \hat{A} \rangle$	Expectation value of \hat{A}
N	Normalization factor	$ vac\rangle$	Vacuum state
P	First-order density matrix	$ HF\rangle$	Fermi vacuum
\hat{Q}	Quasiparticle commutator	$[A,B]_+$	Anticommutator
r_i	Electron coordinate	$[A,B]_-$	Commutator
R	Spin density matrix		

1 Introduction

1.1 Importance of Second Quantization

In the many-electron problem, one is focused on solving the Schrödinger equation which for stationary states Ψ reads:

$$\hat{H}\Psi = E\Psi \quad (1.1)$$

where \hat{H} is the many-electron Hamiltonian which in the non-relativistic case, under the Born-Oppenheimer approximation, for N electrons and M atoms reads:

$$\hat{H} = -\frac{1}{2} \sum_i^N \Delta_i - \sum_a^M \sum_i^N \frac{Z_a}{|r_i - r_a|} + \sum_{i>j}^N \frac{1}{r_{ij}}. \quad (1.2)$$

In Eq. (1.1) E is the electronic energy, while Ψ is the many-electron wave function. In Eq. (1.2) atomic units have been used ($\hbar = e = m_e = 1$) with usual notations for the kinetic energy operator of the i -th electron ($-\frac{1}{2}\Delta_i$), atomic number Z_a , the coordinates r_i and r_a , and the electronic coordinate difference $r_{ij} = |r_i - r_j|$.

In the general case, approximate solutions to Eq. (1.1) can be obtained only. The main goal of quantum chemistry, and some fields of solid state physics as well, is to develop approximate theories suitable to solve the Schrödinger equation [Eq. (1.1)] for many-electron systems. Many approaches have been developed, which are equivalent in the sense that they yield the same numerical result at the same level of approximation. For a particular problem, however, they are not equivalent in the sense that one can be significantly simpler than the other one.

Among possible approaches, the so-called second quantization plays an important role. The ultimate goal of the second quantized approach to the many-electron problem is to offer a formalism which is substantially simpler than the traditional one in many cases. As a matter of fact, most difficulties of the traditional or “first quantized” approach arises from the Pauli principle which requires the wave function Ψ of Eq. (1.1) to be antisymmetric in the electronic variables. This is an additional requirement which does not result from the Schrödinger equation and requires a special formalism: the using of Slater determinants for constructing appropriate solutions to Eq. (1.1). The Slater determinant is not a very pictorial mathematical entity, and the evaluation of matrix elements over determinantal wave functions makes the “first quantized” quantum chemistry somewhat complicated for beginners. In the second quantized

approach any wave function is automatically antisymmetric, and one need not be concerned with determinants. The antisymmetry problem is converted into an extremely simple algebra of creation and annihilation operators.

Another useful feature of the second quantized formalism is that the second quantized representant of the Hamiltonian (and any other physical observable) is independent of the number of electrons, N , in contrast to the first quantized form of the Hamiltonian, Eq. (1.2). Thus, chemical systems containing different numbers of electrons, for example, can be described by one and the same (or very similar) Hamiltonian.

A third, but not negligible importance of second quantization is that this approach inherently deals with one-electron functions, although the theory is not restricted to one-electron methods. The occupancies of one-electron orbitals are the basic quantities one is dealing with in second quantization. This is a very descriptive picture which is in the mind of every chemist who tries to understand something about the electronic structure of molecules.

Finally, among many advantages of using second quantization, it is to be mentioned that this approach represents a convenient treatment of the finite basis approximation which is used in practically all quantum-chemical calculations. This is the only point where a criticism to the generality of the second quantized approach may apply, because the existence of a one-electron basis set is inherently assumed. In our opinion, however, this feature should be considered as a practical advantage since it reflects the present-day approach to quantum chemistry. So, second quantization offers a valuable tool to understand and analyze quantum-chemical problems in a given basis set. The size of the underlying basis set is not restricted, however. In principle it can be complete, but this is not required by the formalism itself. In other words, second quantization offers one the possibility to write down, and to deal with, the model Hamiltonians describing molecules in the actual finite basis set. More precisely, the second quantized Hamiltonian is equivalent to the *projection of the exact Hamiltonian* to the space spanned by the finite basis set in question.

The name “second quantization” comes from the quantum field theory, where the usual wave function is considered as a field operator (this is the “second” quantization), and the creation/annihilation operators are introduced by expanding these field operators in terms of one-electron functions (see, e.g. Linderberg & Öhrn 1973). We do not follow this approach, however, because second quantization for many-electron systems can be introduced in a simpler manner.

1.2 The One-electron Model

Before getting started with second quantization it appears to be useful to summarize some important features of the usual “first quantized” theory. As it was already noted, the following treatment of second quantization is intended

for those, mainly chemists or students, who are already familiar with the basic problems of quantum mechanics and quantum chemistry. For this reason the whole of traditional quantum-mechanical formalism is not presented here. Rather, the most important points are listed and some definitions are given as a recapitulation and as a collection of our notations which will be used throughout. If anybody finds the things below completely unfamiliar he or she is referred to standard quantum chemistry textbooks.

The basic concept of standard many-electron theory is that of the Slater determinant:

$$D = \mathcal{N} \begin{vmatrix} \phi_1(1) & \phi_2(1) \dots \phi_N(1) \\ \phi_1(2) & \phi_2(2) \dots \phi_N(2) \\ \vdots & \vdots \\ \phi_1(N) & \phi_2(N) \dots \phi_N(N) \end{vmatrix} \quad (1.3)$$

where \mathcal{N} is a normalization factor, $\phi_i(k)$ is the i -th one-electron function depending on the coordinates of electron k . The ϕ_i can possess 0 or 1 electrons with spin either α or β . It is also called spinorbital, to be distinguished from an orbital which can be doubly occupied by electrons of opposite spins.

Owing to the mathematical properties of determinants, D is antisymmetric in the coordinates of electrons. This fulfills the Pauli principle for electrons. Note that in general the Pauli principle requires the wave function to be symmetric in the variables of particles of integer spin (called *bosons*) and antisymmetric for particles of half-integer spin (called *fermions*) such as electrons, for example.

The determinant of Eq. (1.3) can be conveniently abbreviated as:

$$D = |\phi_1(1) \ \phi_2(2) \ \dots \ \phi_N(N)|. \quad (1.3a)$$

Any wave function of a many-electron system which is composed of one-electron functions, should be a linear combination of Slater determinants to fulfill the Pauli principle.

Matrix elements of physical observables are to be calculated over such determinantal wave functions. The rules for the values of matrix elements of different operators between two determinants, D_1 and D_2 :

$$O_{12} = \langle D_1 | \hat{O} | D_2 \rangle \quad (1.4)$$

are called the Slater rules (Slater, 1931). The Slater rules apply only if the one-electron functions constituting the determinants form an orthonormal set. Otherwise one should consult with the more general Löwdin rules (Löwdin 1955).

The matrix element in Eq. (1.4) is called a bracket. Accordingly, $\langle D_1 |$ is called a *bra*-function or *bra*-vector, while $| D_2 \rangle$ is the *ket*-vector. A large body of quantum chemistry can also be developed by using the abstract form of *bra*- and *ket*-vectors, and in fact, there is some similarity between this formalism and that of second quantization. This point will be discussed in Sect. 8 in some detail.

The best wave function which can be written down as a single Slater determinant is the Hartree-Fock wave function. It is built up from the Hartree-Fock orbitals ϕ_i which are eigenfunctions of the Fockian \hat{F} :

$$\hat{F}\phi_i = \varepsilon_i \phi_i. \quad (1.5)$$

These orbitals minimize the total energy $E = \langle D | H | D \rangle$. In a finite basis set representation, the molecular orbitals (MOs) are expanded in terms of known basis orbitals χ_μ as:

$$\phi_i = \sum_{\mu} C_{i\mu} \chi_{\mu} \quad (1.6)$$

and the Fockian has the matrix elements (Roothaan 1951):

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda,\sigma} P_{\lambda\sigma} \{ (\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu) \} \quad (1.7)$$

in terms of spinorbitals. Here:

$$P_{\lambda\sigma} = \sum_i^{\text{(occ)}} C_{i\lambda} C_{i\sigma}^* \quad (1.8)$$

is the so-called density matrix (the asterisk refers to the complex conjugate, the label i runs over the occupied molecular spinorbitals):

$$h_{\mu\nu} = \langle \mu | -\frac{1}{2} \Delta - \sum_a \frac{Z_a}{|r - r_a|} | \nu \rangle \quad (1.9)$$

is the core Hamiltonian containing kinetic energy and electron-nuclear attraction, while:

$$(\mu\nu|\lambda\sigma) = \int \int \chi_{\mu}(1) \chi_{\nu}(1) r_{12}^{-1} \chi_{\lambda}(2) \chi_{\sigma}(2) dV_1 dV_2 \quad (1.10)$$

is a two-electron repulsion integral written down in the (11|12) convention. (The notation for the integral convention specifies the no. of electrons for orbitals μ , ν , λ , and σ , respectively.) In many cases the [12|12] convention is used which is defined by:

$$[ij|kl] = (ik|jl). \quad (1.11)$$

To simplify the formulae, one often introduces the double-bar notation:

$$[ij||kl] = [ij|kl] - [ij|lk]. \quad (1.12)$$

In what follows the second quantized formulation of quantum chemistry will be introduced. This requires to study the following issues:

- (i) Second quantized form of *wave functions*. This will be described in Sect. 2, along with the evaluation of some necessary basic formalistic aspects.
- (ii) Second quantized form of *operators*. This will be treated in Sects. 3 and 4.

(iii) Rules for evaluating *matrix elements* of second quantized operators between second quantized wave functions. Sects. 5 and 6 will be devoted to this issue.

Having performed the development as described by these there points we may really claim that a representation of quantum mechanics is found. In fact, the whole of quantum chemistry can be formulated in this representation. A cross section of this theory is presented herein.

2 The Concept of Creation and Annihilation Operators

This section is devoted to describe the second quantized representation of simple wave functions. To begin with, we introduce some general concepts characteristic to the theory of second quantization.

2.1 The Vacuum State

We introduce first the concept of the vacuum state. The vacuum state is simply an abstract state which is empty. That is, it contains no electron. It is denoted by:

$$|\text{vac}\rangle \tag{2.1}$$

if it is considered as a ket-vector, or by:

$$\langle \text{vac}| \tag{2.2}$$

if it is a bra-vector. Two mathematical properties are required:

(i) the vacuum state is normalized to unity, i.e.:

$$\langle \text{vac} | \text{vac} \rangle = 1 \tag{2.3}$$

(ii) The vacuum state is orthogonal to any other state.

The concept of the vacuum state seems to be rather abstract, and in fact, it is. One often asks whether the vacuum state has any physical meaning or significance. The answer is no: the vacuum state does not describe any real physical system. It is merely an abstract mathematical entity which will turn to be useful throughout the following development. In general, one must realize that only expectation values may have any real physical significance in quantum theory; the rest is just mathematics.

2.2 Creating Electrons

Let us turn now to the representation of electronic wave functions. We study first the orbitals of a single electron.

Assume the existence of a set of one-electron spinorbitals $\{\phi_i\}_{i=1}^n$. In principle, this set can be complete but this is not required by the second quantized formalism.

The fact that the spinorbital ϕ_k is occupied by an electron will be denoted as:

$$|k\rangle = a_k^+ |\text{vac}\rangle. \quad (2.4)$$

We say that the (abstract) operator a_k^+ has created an electron on the vacuum state, in state ϕ_k . So one has the correspondence:

$$\phi_k(1) \leftrightarrow a_k^+ |\text{vac}\rangle. \quad (2.5)$$

It is to be emphasized that this is not an equation, but merely a correspondence between the wave function of electron number 1 and its second quantized counterpart. Operator a_k^+ is called a creation operator.

If one has two electrons numbered as 1 and 2 which occupy the orbitals ϕ_i and ϕ_k , our “first quantized” wave function is a Slater determinant:

$$\Phi(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_i(1) & \phi_k(1) \\ \phi_i(2) & \phi_k(2) \end{vmatrix}. \quad (2.6)$$

The same entry is denoted in the second quantized notation as:

$$|ik\rangle = a_i^+ a_k^+ |\text{vac}\rangle. \quad (2.7)$$

In words, an electron is created on the vacuum in state $|k\rangle$, then another one in state $|i\rangle$. One has the correspondence:

$$\Phi(1, 2) \leftrightarrow a_i^+ a_k^+ |\text{vac}\rangle. \quad (2.8)$$

The creation operators must have a very important mathematical property as a consequence of the Pauli principle. Namely, $\Phi(1, 2)$ is an antisymmetric function (determinant):

$$\Phi(2, 1) = -\Phi(1, 2). \quad (2.9)$$

To maintain the correspondence given in Eq. (2.8) one has to require:

$$a_k^+ a_i^+ |\text{vac}\rangle = -a_i^+ a_k^+ |\text{vac}\rangle. \quad (2.10)$$

Thus the order how the abstract creation operators act is very important. The antisymmetry requirement of Eq. (2.10) can be fulfilled by demanding the following property:

$$a_k^+ a_i^+ = -a_i^+ a_k^+$$

or:

$$a_k^+ a_i^+ + a_i^+ a_k^+ = 0. \quad (2.11)$$

In words, the creation operators anticommute.¹ Equation (2.11) is nothing but the second quantized representation of the Pauli principle for electrons. The

¹The *commutator* of two operators a and b is defined in mathematics as $ab - ba$. The *anticommutator* is $ab + ba$.

antisymmetry of the wave function Φ is manifested in the anticommuting property of these abstract operators.

The anticommutator is commonly abbreviated by:

$$a_i^+ a_k^+ + a_k^+ a_i^+ = [a_i^+, a_k^+]_+. \quad (2.12)$$

The subscript ‘+’ after the bracket indicates the *anticommutator*. The wavy bracket is also sometimes used as a notation for an anticommutator: $\{a_i^+, a_k^+\}$.

It may be helpful to note that the form of the Pauli principle given by Eq. (2.11) is valid not only for electrons, but for any fermions having half-integer spin. For Bose particles (bosons), however, which bear an integer spin, the Pauli principle requires the wave function to be symmetric. In that case there is no negative sign in Eqs. (2.9) and (2.10), and instead of Eq. (2.11) we have:

$$a_k^+ a_i^+ - a_i^+ a_k^+ = 0 \quad (\text{for bosons}). \quad (2.13)$$

Equations (2.11) and (2.13) can be given compactly using the notation introduced in Eq. (2.12):

$$a_k^+ a_i^+ \pm a_i^+ a_k^+ \equiv [a_k^+, a_i^+]_{\pm} = 0 \quad (2.14)$$

where the “+” sign is valid for fermions while the “−” sign holds for bosons. Equation (2.14) is the second quantized representation of the general Pauli principle.

Further on in this treatment, with the exception of Sect. 16, we shall consider fermions (electrons) only, so the creation operators will anticommute.

Equation (2.11) has an important consequence. Namely, if $i = k$, one gets:

$$a_i^+ a_k^+ = 0. \quad (2.15)$$

So, if one tries to create two electrons on one and the same spinorbital, one gets zero: the corresponding wave function would vanish. This is just the pictorial formulation of the Pauli principle: at most, one electron can occupy one spinorbital.

Notations for creation operators

Before proceeding further, it appears to be useful to list here some other notations commonly used for a creation operator a_k^+ .

- (i) If a_k^+ creates an electron on the spinorbital ϕ_k , this can also be denoted as ϕ_k^+ . This Longuet-Higgins notation (Longuet-Higgins 1966), is very useful if one works with different sets of orbitals at the same time, because it permits one to distinguish between ϕ_k^+ which creates an electron on spinorbital ϕ_k , and ψ_k which creates one on ψ_k .
- (ii) Different sets of orbitals are often indicated by choosing different letters for the creation operators without referring directly to the orbitals in question. For example, one may write a_k^+ , b_k^+ , c_k^+ , etc.
- (iii) If there is no need for the above distinction, that is the set of one-electron functions onto which the electrons are created is unique, the creation opera-

tor a_k^+ can be denoted simply by k^+ (Jørgensen and Simons 1981). With this simplified notation, the two-electron determinant form of Eq. (2.7) becomes:

$$|ik\rangle = i^+ k^+ |vac\rangle.$$

2.3 Particle Number Representation

Let us turn now to the problem of creating more than two particles: consider a many-electron one-determinantal wave function in its second quantized representation. As is easily seen from the previous example for the two-electron case, a many-electron one-determinantal wave function is constructed by successive application of creation operators on the vacuum state. It will be useful though to consider this problem from a somewhat different point of view.

First of all, the short-hand notations $|k\rangle$ and $|ik\rangle$ used above in Eqs. (2.4) and (2.7) merit some discussion. Consider an abstract wave function, a ket, for example, of the following form:

$$|n_1, n_2, \dots, n_M\rangle. \quad (2.16)$$

This wave function can describe a state (configuration) containing at most M electrons. The quantities n_i are simply *occupation numbers*, that is, n_i is equal to zero if orbital i is empty, while it is equal to 1 if there is an electron on the i -th spinorbital.

This way of specifying one-determinantal wave functions is called the *particle number representation*. The state where every occupation number is zero contains no particles, so it is just the vacuum state:

$$|0, 0, \dots, 0\rangle = |vac\rangle. \quad (2.17)$$

The wave function denoted previously by $|k\rangle$ in Eq. (3.4) can be written in the particle number representation as:

$$|k\rangle = a_k^+ |0, 0, \dots, 0\rangle = |0, 0, \dots, 0, 1, 0, \dots, 0\rangle \quad (2.18)$$

where figure 1 is at the k -th place.

The two-electron wave function $|ik\rangle$ of Eq. (3.7) can be given similarly as:

$$|ik\rangle = a_i^+ a_k^+ |0, 0, \dots, 0\rangle = \pm |0, \overset{i}{\dots}, 0, 1, 0, \dots, 0, \overset{k}{1}, 0, \dots, 0\rangle \quad (2.19)$$

where we have figure 1 at the i -th and at the k -th positions, respectively. Here, in accordance with the antisymmetry of the state $|ik\rangle$ and with the anticommutator in Eq. (2.11), the negative sign occurs if column k precedes column i requiring a transposition $i \leftrightarrow k$.

The particle number representation is conceptually very important because, strictly speaking, the abstract wave functions given in this representation serve as the *carrier space* of the second quantized creation operators. In other words, the creation operators act on the particle-number represented wave functions,

and they simple change the values of the occupation numbers n_k . Namely, if $n_k = 0$, the action of operator a_k^+ results in $n_k = 1$, in accordance with Eq. (2.18). If we had already $n_k = 1$, the action of operator a_k^+ results in zero indicating that one spinorbital cannot be filled by two electrons. Note that, according to the Pauli principle, transposition of two rows of the particle number represented wave function involves a sign change:

$$\begin{array}{c} \overset{1}{\textcircled{1}} \quad \overset{2}{\textcircled{2}} \quad \overset{3}{\textcircled{3}} \\ |\mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3, \dots\rangle \end{array} = - \begin{array}{c} \overset{2}{\textcircled{2}} \quad \overset{1}{\textcircled{1}} \quad \overset{3}{\textcircled{3}} \\ |\mathbf{n}_2, \mathbf{n}_1, \mathbf{n}_3, \dots\rangle \end{array}.$$

Now, creating an N-electron wave function Ψ in which spinorbitals $\psi_1, \psi_2, \dots, \psi_N$ are occupied, one writes:

$$\Psi(1, 2, \dots, N) \leftrightarrow a_N^+ \dots a_2^+ a_1^+ |\text{vac}\rangle. \quad (2.20)$$

This wave function is physically equivalent to a Slater determinant of N orbitals. The proper antisymmetry is ensured by the anticommutation relation of Eq. (2.11) for the creation operators. The simplicity of this representation is manifested in that it is not necessary to worry about properties of determinants, one never needs to write out a determinant explicitly, and, for example, one doesn't have to worry about the normalization of a determinant. (Later we shall see that the wave function of Eq. (2.20) is automatically properly normalized if the underlying one-electron functions form an orthonormal set.) We shall draw many advantages from these features in the course of the following development.

Problem 2.1

Put down the second quantized forms and the particle number representations of the following wave functions:

$$(i) D = \frac{1}{\sqrt{2}} [\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)]$$

$$(ii) \Psi = \frac{1}{\sqrt{6}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \phi_3(1) \\ \phi_1(2) & \phi_2(2) & \phi_3(2) \\ \phi_1(3) & \phi_2(3) & \phi_3(3) \end{vmatrix}$$

$$(iii) \Phi = C_1 \begin{vmatrix} \phi_1(1) & \phi_2(1) \\ \phi_1(2) & \phi_2(2) \end{vmatrix} + C_2 \begin{vmatrix} \phi_1(1) & \psi_2(1) \\ \phi_1(2) & \psi_2(2) \end{vmatrix}$$

2.4 Annihilating Electrons

Besides of creation operators, the second quantized formalism also requires to the use of formal operators which remove (annihilate) electrons.

Consider first a one-electron system. An annihilation operator a_i is defined so that it removes the electron from spinorbital ψ_i if the latter was occupied:

$$a_i|i\rangle = |\text{vac}\rangle, \quad (2.21)$$

but results in zero if ψ_i was empty:

$$a_i|\text{vac}\rangle = 0. \quad (2.22)$$

This last equation expresses that one cannot annihilate an electron from the vacuum state.

Equation (2.21) can also be written as:

$$a_i a_i^+ |\text{vac}\rangle = |\text{vac}\rangle. \quad (2.23)$$

That is, an electron is created on the vacuum in the state ψ_i by a_i^+ , then it is annihilated by the operator a_i and the result is again the vacuum state.

One has to be careful when allowing an annihilation operator to act on a multi-electron state. In the case of a two-electron state, for example, one may write:

$$a_i a_i^+ a_k^+ |\text{vac}\rangle = a_k^+ |\text{vac}\rangle \quad (2.24)$$

by definition. However, owing to the commutation relation of Eq. (2.11) expressing the antisymmetry of the wave function:

$$a_i^+ a_k^+ |\text{vac}\rangle,$$

we may write:

$$\begin{aligned} a_i a_k^+ a_i^+ |\text{vac}\rangle &= -a_i a_i^+ a_k^+ |\text{vac}\rangle \\ &= -a_k^+ |\text{vac}\rangle \end{aligned} \quad (2.25)$$

for $i \neq k$. So, by definition, a_i annihilates simply the electron on the orbital i if it stands immediately after a_i^+ or, naturally, if an even number of transpositions is required to bring the string of creation operators into such a form. If, however, an odd number of transposition is required, a_i annihilates the electron but multiplies the wave function by -1 as seen from Eq. (2.25). This rule of sign is very important, thus we give here some concrete examples:

$$a_3 a_3^+ a_2^+ a_1^+ |\text{vac}\rangle = a_2^+ a_1^+ |\text{vac}\rangle \quad (2.26a)$$

(perfect order: plus sign);

$$\begin{aligned} a_3 a_2^+ a_1^+ a_3^+ |\text{vac}\rangle &= -a_3 a_2^+ a_3^+ a_1^+ |\text{vac}\rangle \\ &= a_3 a_3^+ a_2^+ a_1^+ |\text{vac}\rangle \\ &= a_2^+ a_1^+ |\text{vac}\rangle \end{aligned} \quad (2.26b)$$

(even transposition: plus sign); and:

$$\begin{aligned} a_3 a_2^+ a_3^+ a_1^+ |\text{vac}\rangle &= -a_3 a_3^+ a_2^+ a_1^+ |\text{vac}\rangle \\ &= -a_2^+ a_1^+ |\text{vac}\rangle \end{aligned} \quad (2.26c)$$

(odd transposition: minus sign).

This rule of establishing the sign of such expressions will be used throughout the following development.

Using the language of particle number representation, one can say that if a_i acts on a determinant for which $n_i = 1$, then the result is $n_i = 0$, but if $n_i = 0$ originally, the resulting wave function vanishes. In the former case the wave function changes its sign if an odd number of transpositions are required to bring the wave function into a form where n_i is given at the first column.

It is to be emphasized that the above definition holds for the true annihilation operators independently of the choice for the one-electron functions. However, no connection has yet been specified between a_k^+ and a_k . For example, it was not mentioned that operator a_k^+ were the adjoint of a_k . This point will be clarified later (cf. Sect. 2.6).

Problem 2.2

Evaluate the wave function determined by

$$a_i a_k^+ a_j^+ |vac\rangle$$

Notations for annihilation operators

Similarly to the case of creation operators, the annihilation operators can be denoted in several ways. They have been denoted so far by the most frequently used symbol a_i . Of course, any other letter (b_i , c_i , etc.) could have been equally well used. If one wants to refer explicitly to the orbitals ψ_i , χ_i , etc. in question, the Longuet-Higgins notation ψ_i^- , χ_i^- , etc. can be used, analogously to ψ_i^+ , χ_i^+ denoting creation operators. In this notation the ‘ $-$ ’ superscript symbolizes the annihilation. Finally, the simple short-hand notation i^- can also be useful to simplify the form of complicated mathematical equations.

In summarizing, the following forms

$$a_i a_i^+ = \psi_i^- \psi_i^+ = i^- i^+$$

may have the same meaning.

2.5 Commutator Relation between Creation and Annihilation Operators

Application of the second quantized formalism in quantum chemistry is merely an application of simple algebraic rules followed by creation and annihilation operators. We have already been acquainted with one rule of this kind: the anti-commutator relation for creation operators of Eq. (2.11). The mutual commutator properties of creation and annihilation operators will be studied below. Again, the ‘true’ annihilation operators will be considered as introduced above leaving open the question how a_k is related to a_k^+ .

Consider an N-electron one-determinantal wave function Ψ in the particle number representation:

$$\Psi = |n_1, n_2, \dots, n_N\rangle. \quad (2.27)$$

Let us rearrange this wave function so that two selected orbitals, say i and k (with $i \neq k$) form the first two columns:

$$\Psi = \pm |n_i, n_k, n_1, \dots, n_N\rangle \quad (2.28)$$

where the sign is + or - according to the parity of the interchanges we did in rearranging the wave function.² Let us study now the following expression:

$$a_i a_k^+ |n_i, n_k, n_1, \dots, n_N\rangle. \quad (2.29)$$

According to the rules given above, this expression vanishes if either $n_k = 1$ (because no more electron can be created), or if $n_i = 0$ (because no electron can be annihilated from an empty orbital). So one must have $n_k = 0$ and $n_i = 1$ otherwise Eq. (2.29) vanishes. In this case, indicating only the orbitals i and k , the wave function may be abbreviated as $|i\rangle$, and Eq. (2.29) becomes:

$$a_i a_k^+ |i\rangle = a_i |ki\rangle = -a_i |ik\rangle = -|k\rangle. \quad (2.30)$$

Here the negative sign occurs upon the transposition:

$$|ik\rangle = -|ki\rangle.$$

That is, operator $a_i a_k^+$ moves an electron from orbital i to orbital k , and the wave function is multiplied by (-1) .

Consider now the effect of these operators in the reverse order:

$$a_k^+ a_i |n_i, n_k, n_1, \dots, n_N\rangle. \quad (2.31)$$

This expression vanishes under the same conditions as Eq. (2.29) does. If it survives, one gets:

$$a_k^+ a_i |i\rangle = a_k^+ |\text{vac}\rangle = |k\rangle. \quad (2.32)$$

So we got the same result as above in Eq. (2.30) but of opposite sign.³ Addition of Eq. (3.30) to Eq. (2.32) results in:

$$[a_i a_k^+ + a_k^+ a_i] |n_1, n_2, \dots, n_N\rangle = 0 \quad (2.33)$$

for an arbitrary determinant $|n_1, n_2, \dots, n_N\rangle$. The result will be zero either because Eqs. (2.30) and (2.32) cancel each other, or both vanish individually. The fulfillment of Eq. (2.33) for arbitrary n_1, n_2, \dots, n_N is possible only if:

$$a_i a_k^+ + a_k^+ a_i = 0 \quad (\text{for } i \neq k). \quad (2.34)$$

² In writing down Eq. (2.28) we assumed that i, k is neither 1 nor N , but this can be done without any loss of generality.

³ Again, the operator string $a_k^+ a_i$ moved an electron initially on orbital i to orbital k . Accordingly, such operator strings are often called *shift operators*.

That is, if the orbitals i and k are different, the creation operator a_k^+ anticommutes with the annihilation operator a_i .

In order to establish the commutation rule between a_i and a_i^+ , consider again a general determinant of form of Eq. (2.27), and study the effect of operators $a_i^+ a_i$ and $a_i a_i^+$, respectively. One finds:

$$\begin{aligned} a_i^+ a_i |n_1, n_2, \dots, n_k\rangle &= 0 && \text{if } n_i = 0; \\ &= |n_1, n_2, \dots, n_N\rangle && \text{if } n_i = 1 \end{aligned} \quad (2.35)$$

while

$$\begin{aligned} a_i a_i^+ |n_1, n_2, \dots, n_N\rangle &= |n_1, n_2, \dots, n_N\rangle && \text{if } n_i = 0; \\ &= 0 && \text{if } n_i = 1. \end{aligned} \quad (2.36)$$

Adding these latter two equations one gets:

$$[a_i^+ a_i + a_i a_i^+] |n_1, n_2, \dots, n_N\rangle = |n_1, n_2, \dots, n_N\rangle \quad (2.37)$$

in any case. Again, since the occupation numbers n_1, n_2, \dots, n_N are arbitrary, we obtain

$$[a_i^+ a_i + a_i a_i^+] = 1 \quad (2.38)$$

which tells us that the anticommutator of the creation operator a_i^+ and the annihilation operator a_i is the unity operator.⁴

Collecting Eqs. (2.34) and (2.38) we may write:

$$a_i a_k^+ + a_k^+ a_i = \delta_{ik}. \quad (2.39)$$

This very important result gives the anticommutator relation between creation and annihilation operators.

2.6 The Adjoint Relation—Role of Orthogonality of One-Particle States

As emphasized above, we did not specify so far any direct connection between the creation operators a_i^+ and the annihilation operators a_i . The only property required for a_i was that it should annihilate the effect of a_i^+ in the sense:

$$a_k a_i^+ |\text{vac}\rangle = \delta_{ik} |\text{vac}\rangle. \quad (2.40)$$

Now we shall show that operator a_i is the adjoint of operator a_i^+ provided that the underlying one-electron functions are orthonormal.

⁴The notation for the unity operator in Eq. (2.38) is symbolic: figure 1 is not a *number* here, but an *operator* which acts on the same carrier space as the second quantized operators do.

Consider the binary product of two such functions (i.e., two orthogonal functions created by operators a_i^+ and a_k^+):

$$\langle i|k \rangle = \delta_{ik} \quad (2.41)$$

and evaluate it using second quantization. One has:

$$|k\rangle = a_k^+ |\text{vac}\rangle, \quad (2.42)$$

and, taking the adjoint:

$$\langle i| = \langle \text{vac}|(a_i^+)^{\dagger} \quad (2.43)$$

where the dagger (\dagger) indicates the hermitian conjugate (or adjoint) of the operator. Taking now the binary product of Eqs. (2.42) and (2.43), one gets:

$$\langle \text{vac}|(a_i^+)^{\dagger} a_k^+ |\text{vac}\rangle = \delta_{ik}. \quad (2.44)$$

Comparing this result to Eq. (2.40), it is seen that $(a_i^+)^{\dagger}$ is the true annihilation operator, i.e.:

$$a_i = (a_i^+)^{\dagger} \quad (2.45)$$

for the case of orthonormal spinorbitals. The role of the orthogonality is crucial here; it was utilized in Eq. (2.41). The above result is very important because it permits one to construct *bra*-functions from *ket*-functions by taking simply the adjoint. For example, if:

$$|\Psi\rangle = a_N^+ \dots a_2^+ a_1^+ |\text{vac}\rangle \quad (2.46a)$$

then, if Eq. (2.45) holds, one may write⁵:

$$\langle \Psi | = \langle \text{vac}| a_1 a_2 \dots a_N. \quad (2.46b)$$

The relation between a_k^+ and a_k is more complicated if the underlying set of one-electron spinorbitals is not orthogonal:

$$\langle i|k \rangle = S_{ik} \quad (2.47)$$

S being the overlap (or metric) matrix. Writing this in second quantization, i.e., using Eqs. (2.42) and (2.43), one finds:

$$\langle \text{vac}|(a_i^+)^{\dagger} a_k^+ |\text{vac}\rangle = S_{ik}.$$

In this case there is an interference between a_k^+ and $(a_i^+)^{\dagger}$, even if i is different from k , and the adjoints of creation operators can no longer be considered as true annihilation operators. For this reason, they do not obey the same anti-commutation law, Eq. (2.39), as the true annihilation operators do.⁶ This case

⁵ Notice the reverse order of creation operators in Eq. (2.46b) as compared to Eq. (2.46a). This is a consequence of the rule $(ab)^{\dagger} = b^{\dagger}a^{\dagger}$ known in mathematics.

⁶ More precisely, if $S_{ii} = 1$, that is, if the orbitals are normalized to unity, $(a_i^+)^{\dagger}$ annihilates the effect of a_i^+ even in the nonorthogonal case. The main problem is that $(a_i^+)^{\dagger \dagger}$ annihilates also a component of a_k^+ if $S_{ik} \neq 0$ for $i = k$.

will be treated in more detail in Sect. 13: we shall derive the commutation rule between a_i^+ and $(a_k^+)^{\dagger}$, and we shall show how to construct the true annihilation operators in the case of non-orthogonal one-electron states. Now and further on in Sects. 3–12 we consider the orthonormal case where Eqs. (2.45) and (2.46) hold true.

2.7 Summary of the Properties of Creation and Annihilation Operators

At this point let's recall all important results of the previous sections on the properties of creation/annihilation operators in the case of orthogonal one-electron functions. The present section may thus serve as a “reference manual” for the basic rules.

(i) Algebraic properties

Anticommutators reflecting the Pauli principle:

$$a_i^+ a_k^+ + a_k^+ a_i^+ \equiv [a_i^+, a_k^+]_+ = 0 \quad (2.48a)$$

$$a_i a_k + a_k a_i \equiv [a_i, a_k]_+ = 0 \quad (2.48b)$$

$$a_i^+ a_k + a_k a_i^+ \equiv [a_i^+, a_k]_+ = \delta_{ik}. \quad (2.48c)$$

The properties of the vacuum state:

$$\langle \text{vac} | \text{vac} \rangle = 1 \quad (2.49)$$

$$a_k | \text{vac} \rangle = 0 \quad (2.50a)$$

$$\langle \text{vac} | a_k^+ = 0. \quad (2.50b)$$

The adjoint relation:

$$a_k = (a_k^+)^{\dagger}. \quad (2.51)$$

Note that Eq. (2.48b) follows from Eq. (2.48a) as a consequence of Eq. (2.51). Similarly, Eq. (2.50b) follows from Eq. (2.50a). Note also that all the above properties, with the exception of the adjoint relation of Eq. (2.51), hold for the true annihilation operators even in the nonorthogonal case.

(ii) Wave function correspondence

One-electron orbitals:

$$\text{kets: } |\psi_i\rangle \Leftrightarrow a_i^+ | \text{vac} \rangle \quad (2.52a)$$

$$\text{bras: } \langle \psi_i | \Leftrightarrow \langle \text{vac} | a_i. \quad (2.52b)$$

N-electron determinants:

$$\text{kets: } |\Phi\rangle \Leftrightarrow a_N^+ \dots a_2^+ a_1^+ | \text{vac} \rangle \quad (2.53a)$$

$$\text{bras: } \langle \Phi | \Leftrightarrow \langle \text{vac} | a_1 a_2 \dots a_N. \quad (2.53\text{b})$$

Similarly, the linear combination of determinants Φ_K can be written as:

$$\text{kets: } |\Psi\rangle = \sum_K C_K |\Phi_K\rangle \Leftrightarrow \sum_K C_K [a_{K_N}^+ \dots a_{K_2}^+ a_{K_1}^+] |\text{vac}\rangle \quad (2.54\text{a})$$

$$\text{bras: } \langle \Psi | = \sum_K C_K \langle \Phi_K | \Leftrightarrow \sum_K C_K \langle \text{vac} | [a_{K_1} a_{K_2} \dots a_{K_N}] \quad (2.54\text{b})$$

where K denotes the configuration in which orbitals K_1, K_2 , and K_N are occupied. The expressions for the *bra*-functions are obtained by taking the adjoints of the corresponding ket-expressions. They are valid only if the one-electron orbitals are orthonormalized.

We emphasize again that the symbol “ \Leftrightarrow ” does not mean equality in the mathematical sense because of the different Hilbert spaces considered. The wave function Φ on the left-hand side of Eq. (2.53) is represented in the L_2 function space (or, in the l_2 space in the case of a finite basis), while the second quantized wave function on the right-hand side of Eq. (2.53) makes use of the particle number representation. In a given basis, however, there is a one-to-one correspondence between the two representations. This permits one to apply the above correspondences [Eqs. (2.52)–(2.54)] to rewrite any “first quantized” wave function to the second quantized language or vice versa.

3 Particle Number Operators

Second quantization provides an operator whose eigenvalues are just the number of electrons in a given state. To see this, consider first the operator:

$$\hat{N}_i = a_i^+ a_i. \quad (3.1)$$

If this operator acts on any one-determinantal wave function of the form¹:

$$\Psi = |n_1, n_2, \dots, n_i, \dots, n_M\rangle \quad (3.2)$$

the result will depend on the value of the occupation number n_i . Namely, if $n_i = 0$, the result is zero due to a_i which cannot annihilate from an empty orbital. If, however, $n_i = 1$, the electron annihilated by a_i is recreated by a_i^+ , thus Ψ remains unchanged. Both cases can be summarized as:

$$\begin{aligned} \hat{N}_i \Psi &= a_i^+ a_i |n_1, n_2, \dots, n_i, \dots, n_M\rangle \\ &= n_i |n_1, n_2, \dots, n_i, \dots, n_M\rangle \\ &= n_i \Psi. \end{aligned} \quad (3.3)$$

Note that no sign change may occur, because even if an odd number of transpositions is required to destroy the electron on orbital i , the same number of transposition is necessary to recreate it. So one can write:

$$\hat{N}_i \Psi = n_i \Psi. \quad (3.4)$$

That is, any one-determinantal wave function Ψ is an eigenfunction of operator \hat{N}_i with the eigenvalue n_i . Operator \hat{N}_i is said to be an occupation number operator.

Consider now the operator:

$$\hat{N} = \sum_{i=1}^M \hat{N}_i = \sum_{i=1}^M a_i^+ a_i \quad (3.5)$$

where the summation is performed over all one-electron states. Investigating the effect of this operator \hat{N} on the one-determinantal wave function Ψ defined by Eq. (3.2) one finds:

¹ It is very important here that the creation and annihilation operators present in \hat{N}_i refer to the same set of one-electron orbitals as those the determinant is built from. This will always be assumed if the contrary is not mentioned.

$$\begin{aligned}
 \hat{N}\Psi &= \sum_i a_i^+ a_i |n_1, n_2, \dots, n_i, \dots, n_M\rangle \\
 &= \sum_i n_i |n_1, n_2, \dots, n_i, \dots, n_M\rangle \\
 &= \sum_i n_i \Psi
 \end{aligned} \tag{3.6}$$

That is

$$\hat{N}\Psi = N\Psi \tag{3.7}$$

where the number N denotes the total number of electrons in the system:

$$N = \sum_{i=1}^M n_i. \tag{3.8}$$

We have found that the eigenvalue of operator \hat{N} is the total number of electrons in the system under consideration. Single determinantal wave functions are eigenfunctions of \hat{N} . This operator is called the particle number operator; namely, it is the operator of the total number of electrons in the system.

Some properties of the particle number operators are worth studying. One may ask what happens if \hat{N} acts on a wave function which cannot be described by a single determinant. For the sake of simplicity, let us study first the case when operator \hat{N}_i acts on a wave function which is a linear combination of two determinants:

$$\hat{N}_i \Psi = \hat{N}_i \{C_1 \Psi_1 + C_2 \Psi_2\} \tag{3.9}$$

where Ψ_1 and Ψ_2 are single determinantal wave functions, while C_1 and C_2 are linear combination coefficients. The two determinants Ψ_1 and Ψ_2 may differ in the occupancy of their orbitals. Evaluating Eq. (3.9) according to Eq. (3.4) one gets:

$$\hat{N}_i \Psi = C_1 n_{i1} \Psi_1 + C_2 n_{i2} \Psi_2 \tag{3.10}$$

where n_{i1} and n_{i2} are the occupation numbers of orbital i in the determinants Ψ_1 and Ψ_2 , respectively. Their value is either 0 or 1. Suppose $n_{i2} = 0$ for example. Then one has:

$$\hat{N}_i \Psi = C_1 n_{i1} \Psi_1. \tag{3.11}$$

That is, operator \hat{N}_i selected (or projected) out that component of Ψ where orbital i was occupied.

Another interesting result is found when the action of \hat{N}_i is repeated. By virtue of Eq. (3.10) we get:

$$\begin{aligned}
 \hat{N}_i \hat{N}_i \Psi &= \hat{N}_i (C_1 n_{i1} \Psi_1 + C_2 n_{i2} \Psi_2) \\
 &= C_1 n_{i1} \hat{N}_i \Psi_1 + C_2 n_{i2} \hat{N}_i \Psi_2 \\
 &= C_1 (n_{i1})^2 \Psi_1 + C_2 (n_{i2})^2 \Psi_2 \\
 &= C_1 n_{i1} \Psi_1 + C_2 n_{i2} \Psi_2.
 \end{aligned} \tag{3.12}$$

This latter equality is true because n_{ii} is either 1 or 0, thus $(n_{ii})^2 = n_{ii}$, and similarly for n_{i2} . We have found that the effect of \hat{N}_i^2 is just the same as that of \hat{N}_i . In the operator sense one may write:

$$\hat{N}_i^2 = \hat{N}_i. \quad (3.13)$$

We see that operator N_i is *idempotent*.²

This idempotency property of particle number operators holds also in the more general case. Consider a many-electron multideterminantal wave function of the form:

$$\Psi = \sum_K C_K \Psi_K \quad (3.14)$$

where Ψ_K are various determinants, while C_K are linear combination coefficients.³ Let us study the effect of operator \hat{N}_i on this wave function:

$$\hat{N}_i \Psi = \sum_K n_{Ki} C_K \Psi_K \quad (3.15)$$

where n_{Ki} is the occupancy of the i -th orbital in the determinant Ψ_K . This number is again either 1 or 0. Restricting the summation only over those determinants where orbital i is occupied, one writes:

$$\hat{N} \Psi = \sum_K^{\text{occ}(i)} C_K \Psi_K \quad (3.16)$$

with obvious notations. We see that operator \hat{N}_i again projected out that component of Ψ , where orbital i was occupied. Such operators are called *projection operators* or *projectors*.

The reader may easily investigate the idempotency property of \hat{N}_i for this general case. It will turn out that the operator \hat{N}_i is indeed idempotent for any multideterminantal wave function.

The situation is not much more complicated for the particle number operator \hat{N} corresponding to the total number of electrons. We have seen that single determinants are eigenfunctions of this operator with the eigenvalues of the total number of electrons N . Let us now study the way in which it acts on a multideterminantal wave function of the type given by Eq. (3.14):

$$\begin{aligned} \hat{N} \Psi &= \sum_K C_K \hat{N} \Psi_K = \sum_K C_K \sum_{i=1}^M \hat{N}_i \Psi_K \\ &= \sum_K C_K \sum_{i=1}^M n_{ik} \Psi_K \\ &= \sum_K C_K N \Psi_K = N \Psi \end{aligned} \quad (3.17)$$

² An operator \hat{O} is idempotent over a domain \mathcal{D} if $\hat{O}^2 \Psi = \hat{O} \Psi$ for any $\Psi \in \mathcal{D}$.

³ Such coefficients may result from a configuration interaction (CI) or multiconfiguration SCF (MC-SCF) calculation, for example.

provided that exactly N orbitals are occupied in all determinants, that is:

$$\sum_{i=1}^M n_{ik} = N \text{ for all } k.$$

Any multideterminantal N -electron wave function is also an eigenfunction of the operator of the total number of electrons \hat{N} . Operator \hat{N} has an interesting property:

$$\begin{aligned}\hat{N}^2\Psi &= \hat{N} \left\{ N \sum_k C_k \Psi_k \right\} \\ &= N^2 \sum_k C_k \Psi_k.\end{aligned}\tag{3.18}$$

That is:

$$\hat{N}^2\Psi = \hat{N}N\Psi = (N^2)\Psi\tag{3.19}$$

for any Ψ which is an eigenfunction of \hat{N} with the eigenvalue of the total number of particles N . Consequently, \hat{N} is idempotent up to a constant factor, which can also be expressed as the renormalized particle number operator:

$$\frac{1}{N} \hat{N}$$

which is idempotent. This is a trivial consequence of the eigenvalue relationship of Eq. (3.17)

Problem 3.1

Show that two occupation number operators \hat{N}_i and \hat{N}_k commute.

Besides of their conceptual importance, particle number operators introduced above are useful in the calculus of second quantization. They will be applied throughout this book at the appropriate places.

4 Second Quantized Representation of Quantum-Mechanical Operators

4.1 General

We are already familiar with the second quantized form of wave functions. In this section the second quantized form of various quantum-mechanical operators is going to be established. Then we shall be in a position to undertake any quantum-mechanical analysis in this representation.

In principle, there are two equivalent ways for introducing operators in second quantization. The first is a more physical approach; one may (in fact, one must) demand that the expectation value of any observable be the same in the second and the first quantized formalisms. Textbooks on second quantization usually choose this way (see, e.g. Szabó & Oslund 1982, and references therein). Here we shall proceed in a more formal manner, which, however, permits us to construct the second quantized operators, not only to introduce them heuristically.

Consider a wave function Φ and an operator \hat{A} . If \hat{A} acts on Φ , one gets a transformed function which is denoted by Ψ :

$$\Psi = \hat{A}\Phi. \quad (4.1)$$

Using second quantization, the correspondences of Φ and Ψ are known in that representation, cf. (Eqs. 2.52–54). Let Φ^+ and Ψ^+ denote the second quantized counterparts of Φ and Ψ , respectively. We are interested in the second quantized form of the operator \hat{A} , which is denoted by \hat{A}^\pm for the moment. The relation between these quantities can be represented by the following chart:

$$\begin{array}{ccc} \Phi & \xrightarrow{\hspace{1cm}} & \Phi^+ \\ \downarrow \hat{A} & & \downarrow \hat{A}^\pm \\ \Psi & \xrightarrow{\hspace{1cm}} & \Psi^+ \end{array} \quad (4.2)$$

Here the vertical arrows (\downarrow) indicate the mapping by the operator \hat{A} while the horizontal arrows (\rightarrow) denote the second quantized representation.

Accordingly, \hat{A} being the mathematical quantity which maps Φ to Ψ , \hat{A}^\pm is defined as the mathematical object which maps Φ^+ to Ψ^+ . This definition is the key to construct the second quantized representant of operator \hat{A} in various cases.

4.2 One-Electron Operators

For the sake of simplicity, consider first a special case which is rarely of actual interest: the second quantized representation of an operator acting on the coordinates of a single electron. (Actually, this example is relevant only if there is only one electron in the system. Although somewhat artificial, this case is so simple that it enables comprehension of the basic ideas of how to find the second quantized representation of quantum-mechanical operators.)

Let ϕ_i be the wave function of an electron in state i , and assume the existence of an orthonormal set $\{\phi_k\}_{k=1}^M$. If operator \hat{A} acts on ϕ_i , one writes:

$$\hat{A}\phi_i = \psi_i. \quad (4.3)$$

The same expression can be written down in second quantization as:

$$\hat{A}^\pm \phi_i^\pm |vac\rangle = \psi_i^\pm |vac\rangle \quad (4.4)$$

(recall the “Longuet-Higgins notation” introduced in Sect. 2 for creation operators.) We know \hat{A} , and ask which operator maps ϕ_i^\pm to ψ_i^\pm ? To get this operator, let us expand the transformed function ψ_i in terms of the set $\{\phi_k\}$:

$$\psi_i = \sum_k C_{ik} \phi_k. \quad (4.5)$$

Alternatively, using second quantization, the same writes:

$$\psi_i^\pm = \sum_k C_{ik} \phi_k^\pm. \quad (4.6)$$

Determine first the expansion coefficients C_{ik} . This can be done by following the standard theory of vector spaces. Combining Eqs. (4.3) and (4.5) gives:

$$\hat{A}\phi_i = \sum_k C_{ik} \phi_k. \quad (4.7)$$

Multiplying this equation by ϕ_l from the left and taking the binary (scalar) product one gets:

$$\langle \phi_l | \hat{A} | \phi_i \rangle = \sum_k C_{ik} \langle \phi_l | \phi_k \rangle. \quad (4.8)$$

Utilizing now the orthonormality of the set $\{\phi_i\}$ this result reduces to:

$$\langle \phi_l | \hat{A} | \phi_i \rangle = C_{il}. \quad (4.9)$$

The expansion coefficients C_{il} were found to be equal to the matrix element of operator \hat{A} , A_{li} .

Combining Eqs. (4.4) and (4.6) leads to:

$$\hat{A}^\pm \phi_i^\pm = \sum_k C_{ik} \phi_k^\pm. \quad (4.10)$$

One may write formally:

$$\hat{A}^\pm \phi_i^+ \phi_i^- = \sum_k C_{ik} \phi_k^+ \phi_i^-. \quad (4.11)$$

Summing up over all one-particle states i (that is, over all basis functions) one gets:

$$\hat{A}^\pm \sum_i \phi_i^+ \phi_i^- = \sum_{i,k} C_{ik} \phi_k^+ \phi_i^- \quad (4.12)$$

where on the left-hand side we have the particle number operator \hat{N} introduced in Sect. 3. Dealing with a one-electron system, when operator \hat{N} acts on an occupied state, it has the eigenvalue of 1, as learned in the previous section. So in this case \hat{N} acts as the unity operator, thus it may be omitted. One gets:

$$\hat{A}^\pm = \sum_{k,i} A_{ki} \phi_k^+ \phi_i^- \quad (4.13)$$

where Eq. (4.9) is utilized with the usual short-hand notation for the matrix element $A_{ki} = \langle \phi_k | \hat{A} | \phi_i \rangle$. Equation (4.13) gives the second quantized representation of the one-electron operator \hat{A} :

$$\hat{A} \leftrightarrow \sum_{i,k} A_{ki} \phi_k^+ \phi_i^- . \quad (4.14)$$

It can be hardly overemphasized that Eq. (4.14) is only a correspondence and not an equation. For example, our mapping $\hat{A}\phi_i = \psi_i$ in first quantization holds independently of the occupation of the orbitals, while $\sum_{ki} A_{ki} \phi_k^+ \phi_i^-$ results in zero if acting on an empty orbital. However, what is required physically is only the equality of both sides of Eq. (4.14) when taking their expectation values by some wave function:

$$\langle \hat{A} \rangle = \sum_{i,k} A_{ki} \langle \phi_k^+ \phi_i^- \rangle . \quad (4.15)$$

It is an interesting exercise to show that Eq. (4.15) is indeed satisfied. Let us calculate the expectation value of Eq. (4.14) with some ϕ_i . For the left-hand side we have:

$$\langle \hat{A} \rangle = \langle \phi_i | \hat{A} | \phi_i \rangle = A_{ii} \quad (4.16)$$

while for the right-hand side [cf. Eqs. (2.52)]:

$$\sum_{ki} A_{ki} \langle \text{vac} | \phi_i^- \phi_k^+ \phi_i^- \phi_k^+ | \text{vac} \rangle . \quad (4.17)$$

This was obtained by using the wave function correspondence:

$$|\phi_i\rangle \leftrightarrow \phi_i^+ |\text{vac}\rangle \quad (4.18a)$$

and its adjoint relation:

$$\langle \phi_i | \leftrightarrow \langle \text{vac} | \phi_i^- . \quad (4.18b)$$

The evaluation of the matrix element in Eq. (4.17) is very simple. It is immediately seen that $i = l$, otherwise ϕ_i^- could not annihilate, and also that $l = k$, for the similar reason. (We shall get more experience in evaluating such matrix elements in Sect. 5.) So, both k and i equals l , thus performing the summation in Eq. (4.17) gives us A_{ll} . This is the same result as that of Eq. (4.16).

After the above demonstration, we turn to the more realistic case, when there is more than one electron in the system. Then, a typical operator \hat{A} is represented by a sum of one-electron operators:

$$\hat{A} = \sum_{n=1}^N \hat{A}_n \quad (4.19)$$

where \hat{A}_n affects the coordinates of electron n , and the summation label n runs over all electrons in the system. Some important examples for quantum-mechanical operators of this type are:

(i) the operator of the kinetic energy of electrons \hat{T} , in atomic units:

$$\hat{T} = -\frac{1}{2} \sum_n \Delta_n$$

(ii) the electron-nuclear attraction operator \hat{V} :

$$\hat{V} = -\sum_{a,n} Z_a / |\mathbf{r}_a - \mathbf{r}_n|$$

or

(iii) the dipole moment operator:

$$\hat{\mu} = \sum_n \hat{\mu}_n.$$

We shall show now that the second quantized representation of such operators is also given by Eq. (4.14). To begin with, let Φ be a Slater determinant of an N -electron system which is transformed to determinant Ψ by operator \hat{A} :

$$\Psi = \hat{A}\Phi. \quad (4.20)$$

Writing out operator \hat{A} and the determinant Φ (the latter being built up from one-electron orbitals ϕ_i) we get:

$$\Psi = \sum_{n=1}^N \hat{A}_n |\phi_1 \phi_2 \dots \phi_n \dots \phi_N|. \quad (4.21)$$

Since operator \hat{A}_n acts on the orbital of electron n , $\hat{A}_n \phi_n$ may be expanded in terms of the set $\{\phi_i\}$:

$$\Psi = \hat{A}\Phi = \sum_{n=1}^N \sum_l C_{nl} |\phi_1 \phi_2 \dots \phi_l \dots \phi_N|. \quad (4.22)$$

Again, the expansion coefficients $C_{nl} = A_{ln}$ are introduced [cf. Eq. (4.9)]; the function ϕ_l stands at the place¹ of ϕ_n . Writing this equation in the second quantized form:

$$\hat{A}^\pm \phi_N^+ \dots \phi_n^+ \dots \phi_2^+ \phi_1^+ |vac\rangle = \sum_{n=1}^N \sum_l A_{ln} \phi_N^+ \dots \phi_l^+ \dots \phi_2^+ \phi_1^+ |vac\rangle \quad (4.23)$$

¹ Strictly speaking, one has to utilize in Eq. (4.22) that operator A commutes with the antisymmetrizer.

where at the right-hand side ϕ_i stands in the place of ϕ_n . It is easy to show now that the (4.14) form of \hat{A}^\pm obeys this equation. Substituting:

$$\hat{A}^\pm = \sum_{l,n} A_{ln} \phi_l^\pm \phi_n^\mp$$

we get for the left-hand side:

$$\sum_{l,n} A_{ln} \phi_l^\pm \phi_n^- \phi_N^+ \dots \phi_n^+ \phi_2^+ \phi_1^+ |vac\rangle \quad (4.24)$$

we see that n must be an element of the set $\{1, 2, \dots, N\}$ otherwise ϕ_n^- could not annihilate. This is in accordance with the summation restriction at the right-hand side of Eq. (4.23). So one may write Eq. (4.24) as²:

$$\sum_l \sum_{n=1}^N A_{ln} \phi_l^\pm \phi_n^- \phi_N^+ \dots \phi_n^+ \dots \phi_2^+ \phi_1^+ |vac\rangle \quad (4.25)$$

which, using the anticommutation rules of Eq. (2.48), can be rearranged by an even number of transpositions (i.e., without change of sign) as:

$$\begin{aligned} & \sum_l \sum_{n=1}^N A_{ln} \phi_N^+ \dots \phi_l^+ \phi_n^- \phi_n^+ \dots \phi_2^+ \phi_1^+ |vac\rangle \\ &= \sum_l \sum_{n=1}^N A_{ln} \phi_N^+ \dots \phi_l^+ \dots \phi_2^+ \phi_1^+ |vac\rangle \end{aligned} \quad (4.26)$$

the ϕ_l^+ standing at the n -th position. Thus we got exactly the right-hand side of Eq. (4.23), so the proof is completed.³ Therefore, the second quantized representation of sums of one-particle operators can be given as:

$$\sum_n \hat{A}_n \leftrightarrow \sum_{i,k} A_{ik} \phi_i^+ \phi_k^- . \quad (4.27)$$

This result is independent of the number of electrons in the system. Of course, one should show that the physical requirement for the expectation values:

$$\left\langle \sum_n \hat{A}_n \right\rangle = \sum_{i,k} A_{ik} \langle \phi_i^+ \phi_k^- \rangle$$

holds. The reader may try to prove this theorem following the derivation given above for the single-electron case. Later we shall evaluate this expectation value for some wave functions (see Sect. 5).

4.3 Two-Electron Operators

Another class of quantum-mechanical operators, which is also of extreme importance in quantum chemistry, consists of operators affecting the coordinates of two electrons. Mostly the sum of such operators over all electron pairs

² If $n = 1$, or $n = N$ than ϕ_n^+ coincides with ϕ_1^+ or ϕ_N^+ which is not repeated twice, of course.

³ We considered only one-determinantal wave functions but the result of Eq. (4.27) holds for multideterminantal wave functions (linear combination of determinants) as well.

are needed:

$$\hat{A} = \sum_{i < j}^N \hat{A}_{ij}. \quad (4.28)$$

The most important example for an operator of this type is the electron repulsion operator:

$$\hat{V}_e = \sum_{i < j}^N 1/r_{ij}$$

[cf. the Hamiltonian of Eq. (1.2)].

To determine the second quantized representation of such two-electron operators one may follow the same line as in Sect. 4.2.

Consider the effect of operator \hat{A} on the determinant of orbitals ϕ_i :

$$\sum_{i < j}^N \hat{A}_{ij} |\phi_1 \phi_2 \dots \phi_N| = \sum_{i < j}^N |\phi_1 \dots \psi_i \dots \psi_j \dots \phi_N| \quad (4.29)$$

where ψ_i and ψ_j are some transformed functions, which may be expanded over the original set $\{\phi_i\}$:

$$\sum_{i < j}^N \hat{A}_{ij} |\phi_1 \phi_2 \dots \phi_N| = \sum_{i < j}^N \sum_{k,l} C_{ij,kl} |\phi_1 \dots \phi_k \dots \phi_l \dots \phi_N|. \quad (4.30)$$

As known from the first quantized theory, the expansion coefficients are given by⁴:

$$C_{ij,kl} = [kl|ij] = \int \int \phi_k(1) \phi_l(2) \hat{A}_{12} \phi_i(1) \phi_j(2) d\tau_1 d\tau_2 \quad (4.31)$$

provided that the transformed determinant differs from the original one in two spinorbitals, i.e., $k, l \neq i, j$. For simplicity, we shall consider this case; coincidences between k, l and i, j can easily be investigated separately.

The second quantized counterpart of Eq. (4.30) is written as:

$$\begin{aligned} & \sum_{i < j}^N \hat{A}_{ij}^+ \phi_1^+ \phi_2^+ \dots \phi_i^+ \dots \phi_j^+ \dots \phi_N^+ \\ &= \sum_{i < j}^N \sum_{k,l} [kl|ij] \phi_1^+ \dots \phi_k^+ \dots \phi_l^+ \dots \phi_N^+ |vac\rangle \end{aligned} \quad (4.32)$$

where at the right-hand side ϕ_k^+ and ϕ_l^+ stand at the i -th and j -th positions, instead of ϕ_i^+ and ϕ_j^+ , respectively.

Accordingly, the effect of the two-electron operator \hat{A}_{ij}^\pm consists of substituting the orbital pair ϕ_i, ϕ_j by some linear combination of ϕ_k, ϕ_l . This can be achieved by an operator of the following type:

$$\sum_{i < j}^N \hat{A}_{ij}^\pm = \sum_{i < j}^N \sum_{k,l} A_{ij,kl} \phi_k^+ \phi_l^+ \phi_i^- \phi_j^- \quad (4.33)$$

⁴The validity of Eq. (4.31) can easily be checked by multiplying Eq. (4.30) with the appropriate determinant from the left, integrating, and applying the Slater rules.

To prove this, and to find the coefficients $A_{ij,kl}$, Eq. (4.33) is to be substituted into Eq. (4.32):

$$\begin{aligned} & \sum_{i < j} \sum_{k,l} A_{ij,kl} \phi_k^+ \phi_l^+ \phi_i^- \phi_j^- \phi_1^+ \phi_2^+ \dots \phi_N^+ |vac\rangle \\ &= \sum_{i < j} \sum_{k,l} [kl|ij] \phi_k^+ \phi_l^+ \dots \phi_k^+ \dots \phi_i^+ \dots \phi_N^+ |vac\rangle \end{aligned} \quad (4.34)$$

where on the right-hand side k and l stand at the i-th and the j-th positions, respectively.

Analyzing the left-hand side, it is seen that i and j should be elements of the set $\{1, 2, \dots, N\}$, otherwise ϕ_i^- or ϕ_j^- could not annihilate. Therefore, the summation restrictions are the same on both sides of this equation. On the left-hand side, two electrons are annihilated from orbitals ϕ_i and ϕ_j by operators ϕ_i^- and ϕ_j^- , but two electrons are created by ϕ_k^+ and ϕ_l^+ . It is easy to see that an odd number of transpositions is required to bring the operator string on the left-hand side to the same form as that of the string at the right, thus a minus sign is obtained:

$$\begin{aligned} & \phi_k^+ \phi_l^+ \phi_i^- \phi_j^- \phi_1^+ \dots \phi_i^+ \dots \phi_j^+ \dots \phi_N^+ |vac\rangle \\ &= -\phi_1^+ \dots \phi_k^+ \dots \phi_l^+ \dots \phi_N^+ |vac\rangle. \end{aligned} \quad (4.35)$$

This can mostly readily be seen by performing the transposition⁵ $\phi_i^- \phi_l^+ = -\phi_l^+ \phi_i^-$ ($i \neq l$) on the left-hand side, which gives a minus sign. Then the strings $\phi_k^+ \phi_i^-$ and $\phi_l^+ \phi_j^+$ can be moved to the appropriate places without any further change in sign, since a pair of fermion operators is moved together.

Using this result, the comparison of the two sides of Eq. (4.34) gives:

$$A_{ij,kl} = -[kl|ij] \quad (4.36)$$

thus operator \hat{A} , in the second quantized form of Eq. (4.33) is given by:

$$\sum_{i < j} \hat{A}_{ij} = - \sum_{i < j} \sum_{k,l} [kl|ij] \phi_k^+ \phi_l^+ \phi_i^- \phi_j^- . \quad (4.37)$$

This result is quite general; one may show that it holds also if the indices k or l coincide with i or j. To bring Eq. (4.37) into a more compact form, eliminate the $i < j$ restriction by introducing a factor of $1/2$, and the minus sign by interchanging ϕ_i^- and ϕ_j^- . The final result is:

$$\sum_{i < j} \hat{A}_{ij} \leftrightarrow \frac{1}{2} \sum_{kl,ij} [kl|ij] \phi_k^+ \phi_l^+ \phi_i^- \phi_j^- . \quad (4.38)$$

This is the second quantized form of two-electron operators. It has been obtained by studying the effect of such operators on a one-determinantal wave function, but it is easy to generalize the above considerations for arbitrary multi-determinantal wave functions as well.

⁵ As noted above, the $i = l$ case should be considered separately.

Equations (4.27) and (4.38) enable us to represent any one- or two-electron operator in quantum chemistry. We know already the representation of the wave functions according to Eqs. (2.52)–(2.54), and also the basic algebraic properties Eqs. (2.48)–(2.50) for the creation and annihilation operators. This is practically all one needs to know in order to undertake any elementary analysis in quantum chemistry using the language of second quantization.

4.4 The Second Quantized Form of the Born-Oppenheimer Hamiltonian

The Born-Oppenheimer electronic Hamiltonian introduced in Eq. (1.2) consists of two parts: the first one is a sum of one-electron operators, the second one is a sum of two-electron operators:

$$H = \sum_{i=1}^N h_i + \sum_{i < j} \frac{1}{r_{ij}}. \quad (4.39)$$

The one-electron part contains the kinetic energy and the nuclear-electron attraction, while the two-electron part is due to the electron-electron repulsion. The corresponding matrix elements, $h_{\mu\nu}$ and $[\mu\nu|\lambda\sigma]$, have been introduced by Eqs. (1.9)–(1.11).

In Sect. 4.1 we have learned how to convert the one-electron part into the second quantized form [cf. Eq. (4.27)]. Similiary, the representation of the two-electron part is given by Eq. (4.38) of Sect. 4.2. Thus, the Hamiltonian in the second quantized form can be written down immediately as:

$$H = \sum_{\mu,\nu} h_{\mu\nu} a_\mu^\dagger a_\nu + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} [\mu\nu|\lambda\sigma] a_\mu^\dagger a_\nu^\dagger a_\sigma a_\lambda. \quad (4.40)$$

Here, the Greek labels refer to an arbitrary orthonormalized basis set. Note that the labels σ and λ appear in a reverse order in the operator string as compared to that in the integral list. This is not a misprint, but a consequence of the eliminated negative sign in Eq. (4.37).

It is to be strongly emphasized again that the Hamiltonian as given by Eq. (4.40) is not *equal* to the usual many-electron Coulombic Hamiltonian which was given in Eq. (1.2). The latter is defined over the L_2 space and has rather complicated mathematical properties; it is not bounded, for example (Löwdin 1988). The second quantized Hamiltonian of Eq. (4.40) is, in some sense, much simpler. Its domain is given by the domain of creation and annihilation operators whose carrier space is the very pictorial particle number representation. This simplification is achieved by introducing the space of the one-electron functions $\{\phi_k\}_{k=1}^M$, where M can be any positive number. If M is infinitely large, the set $\{\phi_k\}$ can be complete, and in this limit (and only in this one) the eigensolutions of the second and first quantized Hamiltonians of Eqs. (4.40) and (4.2) are identical. If M is finite, the orbital space is necessarily incomplete and, very

probably, it does not contain the exact eigenvector of the Hamiltonian of Eq. (1.2). In this case of the second quantized Hamiltonian can be interpreted as the projection of the exact one to a finite subspace spanned by the basis orbitals. This point will be discussed in more detail in Sect. 8. Here we note only that this is very important from the point of view of practical quantum chemistry, where almost exclusively finite basis expansions are used.

Another essential difference between the first and second quantized Hamiltonian is the following one. It is clear that the first quantized Hamiltonian of Eq. (1.2) depends explicitly on the number of electrons in the system: this number N appears as the upper limit of the electronic summation labels. Even in the absence of the change of external potential, if an electron is approaching or leaving our system, we have to deal with different Hamiltonians. On the other hand, the second quantized Hamiltonian of Eq. (4.40) is clearly independent of the number of electrons: it is determined simply by the list of one- and two-electron integrals. The second quantized Hamiltonian is the same for an atom and for its positive or negative ions for example; these systems are different eigenstates of the same Hamiltonian. In the second quantized representation the dependence on the number of particles is shifted from the Hamiltonian to the wave functions. This feature is very useful in studying ionization energies, electron affinities, and it has also considerable advantage in solid state theory where the number of electrons in the system is infinite, as well as in quantum field theory where the number of particles is not necessarily constant. These latter points, being out of the scope of this book, will not be investigated (see, e.g. Landau & Lifsic 1965, 1980; Linderberg & Öhrn 1973; Paul 1982).

We are already familiar with the second quantized wave functions and operators. In what follows we shall study how to work with them. First, it appears to be worthwhile to check an important property, the Hermiticity of quantum mechanical operators.

4.5 Hermiticity of Second Quantized Operators

As is well known, in the quantum mechanics physical observables correspond to Hermitian operators, that is:

$$\hat{A} = \hat{A}^\dagger \tag{4.41}$$

for any physical operator \hat{A} . In this section we study how this relationship is manifested for the second quantized form of the same operator which naturally must also be Hermitian. Although the treatment below is quite trivial, it may be useful to gain some practice in using second quantized operators.

It follows simply from Eq. (4.41) that the matrix elements of such an operator form a Hermitian matrix⁶:

⁶ Remember that the Hermitian conjugate of a matrix is the transpose of the complex conjugate matrix.

$$A_{\mu\nu} = (A^\dagger)_{\mu\nu} = A_{\nu\mu}^* \quad (4.42)$$

where the asterisk indicates the complex conjugate. In most cases one is dealing with real quantities, thus taking the complex conjugate is irrelevant. In such a case the matrix representation of a Hermitian operator is symmetric:

$$A_{\mu\nu} = A_{\nu\mu}. \quad (4.43)$$

Accordingly, the list of one-electron integrals of the Hamiltonian $h_{\mu\nu}$ of Eq. (4.40) form a symmetric matrix.

The symmetry of the two-electron integral list is two-fold. On the one hand, it is based on the fact that renumbering electrons 1 and 2 in Eq. (4.31) does not change the value of the integral. That is:

$$[\mu\nu|\lambda\sigma] = [\nu\mu|\sigma\lambda]. \quad (4.44)$$

On the other hand, it is based on the Hermiticity of the two-electron operator $1/r_{12}$, which, in the case of real orbitals, results in the Hermitian symmetry:

$$[\mu\nu|\lambda\sigma] = [\lambda\nu|\mu\sigma] \quad (4.45a)$$

and

$$[\mu\nu|\lambda\sigma] = [\mu\sigma|\lambda\nu]. \quad (4.45b)$$

Any combination of the above symmetry rules is possible, of course. Note again that the symmetries given by Eqs. (4.43) and (4.45) hold only if the orbitals are real, otherwise one should take the complex conjugates. For complex orbitals, one has Eq. (4.42) instead of (Eq. 4.43), while instead of Eq. (4.45) one gets:

$$[\mu\nu|\lambda\sigma] = [\lambda\sigma|\mu\nu]^*. \quad (4.46)$$

The second quantized forms of quantum mechanical operators should also be Hermitian. This can be proven explicitly by using the above symmetry properties of the integral list and the Hermitian conjugate properties of the creation and annihilation operators discussed in Sect. 2.6.

Consider first the case of a one-electron operator. The one-electron part of the Hamiltonian will be chosen as an example. Taking its Hermitian conjugate:

$$\hat{h}^\dagger = \left[\sum_{\mu,\nu} h_{\mu\nu} a_\mu^+ a_\nu \right]^\dagger = \sum_{\mu,\nu} h_{\mu\nu}^* a_\nu^+ a_\mu. \quad (4.47)$$

Here the general mathematical rules are utilized for taking the Hermitian conjugate⁷, and the fact that the creation and annihilation operators are the Hermitian conjugates of each other [cf. Eq. (2.45)]. Using the symmetry rule of Eq. (4.42) one gets:

$$\hat{h}^\dagger = \sum_{\mu,\nu} h_{\nu\mu} a_\nu^+ a_\mu = \sum_{\mu,\nu} h_{\mu\nu} a_\mu^+ a_\nu = \hat{h}$$

⁷ Remember that Hermitian conjugation results in a reverse order of an operator product: $(AB)^\dagger = B^\dagger A^\dagger$.

where an interchange of the summation indices μ and v is performed recovering in this manner the original form of the second quantized one-electron Hamiltonian, which is now proved to be Hermitian.

The Hermiticity of the two-electron part of the Hamiltonian (or that of any other two-particle operator) can also be proven along the same lines:

$$\begin{aligned}\hat{V}^\dagger &= \frac{1}{2} \sum_{\mu\nu\lambda\sigma} [\mu\nu|\lambda\sigma]^* a_\lambda^+ a_\sigma^+ a_v a_\mu \\ &= \frac{1}{2} \sum_{\mu\nu\lambda\sigma} [\lambda\sigma|\mu\nu] a_\lambda^+ a_\sigma^+ a_v a_\mu = \frac{1}{2} \sum_{\mu\nu\lambda\sigma} [\mu\nu|\lambda\sigma] a_\mu^+ a_v^+ a_\sigma a_\lambda = \hat{V}\end{aligned}$$

where we utilized first Eq. (4.46) than the interchange of indices $\sigma \leftrightarrow v$ and $\mu \leftrightarrow \lambda$ was applied. This shows that the second quantized form of the two-electron part of the Hamiltonian is also Hermitian. This result, together with the Hermiticity of the one-electron part, proves the Hermiticity of the total Born-Oppenheimer Hamiltonian. The same results apply, of course, for the second quantized forms of any other one- or two-electron Hermitian operators.

5 Evaluation of Matrix Elements

5.1 Basic Matrix Elements

Physically measurable quantities in quantum mechanics are associated with expectation values or matrix elements of the corresponding operators. It is therefore of fundamental importance to elaborate efficient methods for the calculation of such matrix elements. One of the most attractive features of the second quantized approach is its simplicity in evaluating matrix elements. To appreciate this, one must get some practice in the formalism.

Consider first the matrix element of the operator string $a_v^+ a_\lambda$ between orbitals $\langle \mu |$ and $|\sigma \rangle$:

$$\langle \mu | a_v^+ a_\lambda | \sigma \rangle = \langle \text{vac} | a_\mu a_v^+ a_\lambda a_\sigma^+ | \text{vac} \rangle \quad (5.1)$$

where the wave function correspondence for the *bra*- and *ket*-vectors (Sect. 2) is utilized. For the evaluation of the matrix element at the right-handside, the most straightforward method is to apply successive transpositions using the anticommutation rules of Eq. (2.48). Here the goal is to move annihilation operators to the *ket*-vacuum, or creation operators to the *bra*-vacuum, because the corresponding terms will vanish [cf. Eqs. (2.50)]. For Eq. (5.1) one gets:

$$\begin{aligned} \langle \text{vac} | a_\mu a_v^+ a_\lambda a_\sigma^+ | \text{vac} \rangle &= \langle \text{vac} | (\delta_{\mu v} - a_v^+ a_\mu)(\delta_{\lambda \sigma} - a_\sigma^+ a_\lambda) | \text{vac} \rangle \\ &= \delta_{\mu v} \delta_{\lambda \sigma} \langle \text{vac} | \text{vac} \rangle = \delta_{\mu v} \delta_{\lambda \sigma}, \end{aligned} \quad (5.2)$$

because all other terms vanish.

It is possible to obtain this result by an even simpler consideration:

$$\langle \text{vac} | \underline{a}_\mu \underline{a}_v^+ \underline{a}_\lambda \underline{a}_\sigma^+ | \text{vac} \rangle = \delta_{\mu v} \delta_{\lambda \sigma}. \quad (5.3)$$

The horizontal bars $\underline{}$ indicate that the index μ must coincide with v otherwise a_v cannot annihilate. Similarly, λ must coincide with σ .

As a next example consider the expression:

$$\langle \text{vac} | a_\mu a_v a_\lambda^+ a_\sigma^+ | \text{vac} \rangle. \quad (5.4)$$

The evaluation is simple. The transposition $v \leftrightarrow \lambda$ results in an expression for which the result is already known from the previous example:

$$\begin{aligned} \langle \text{vac} | a_\mu a_v a_\lambda^+ a_\sigma^+ | \text{vac} \rangle &= \langle \text{vac} | a_\mu (\delta_{v\lambda} - a_\lambda^+ a_v) a_\sigma^+ | \text{vac} \rangle \\ &= \langle \text{vac} | \underline{a}_\mu \underline{a}_\sigma^+ | \text{vac} \rangle \delta_{\mu\lambda} - \langle \text{vac} | \underline{a}_\mu \underline{a}_\lambda^+ \underline{a}_v \underline{a}_\sigma^+ | \text{vac} \rangle \\ &= \delta_{\mu\sigma} \delta_{v\lambda} - \delta_{\mu\lambda} \delta_{v\sigma} \end{aligned} \quad (5.5)$$

where Eq. (5.3) is applied. This derivation can also be done in a more automatic manner. Since the pair of annihilation operators in Eq. (5.4) should coincide with the pair of creation operators, one has only two possibilities:

$$\text{either } \langle \text{vac} | \overline{a_\mu a_v} \overline{a_\lambda^+ a_\sigma^+} | \text{vac} \rangle = \delta_{v\lambda} \delta_{\mu\sigma} \quad (5.6a)$$

$$\text{or } \langle \text{vac} | \overline{a_\mu a_v} \overline{a_\lambda^+ a_\sigma^+} | \text{vac} \rangle = -\delta_{\mu\lambda} \delta_{v\sigma}. \quad (5.6b)$$

(Bars placed below or above the operators denote the same thing: the coincidence of the indicated labels.) In Eq. (5.6b) the negative sign appears because an odd number of transpositions (namely, one) is required to reorder the string as $\overline{a_\mu a_\lambda^+} \overline{a_v a_\sigma^+}$. Since both Eqs. (5.6a) and (5.6b) are possible, the result for the matrix element is their sum, the result found under Eq. (5.5).

In the general case, evaluating the matrix element of any string of creation and annihilation operators, one should consider all possible pairing of annihilation and creation operators, and by successive application of transpositions¹ one should try to bring the expression into the following form (note the order of operators):

$$\langle \text{vac} | \overline{a_\mu a_\lambda^+} \dots \overline{a_\lambda a_\sigma^+} \overline{a_\epsilon a_\eta^+} | \text{vac} \rangle = \delta_{\mu\nu} \dots \delta_{\lambda\sigma} \delta_{\epsilon\eta}. \quad (5.7)$$

This is possible in as many ways as there are terms for the matrix element. The sign of each term is given by the parity of the required transpositions.

In counting all possible pairings, one has to take into account that $a_\lambda | \text{vac} \rangle = 0$ and similarity $\langle \text{vac} | a_\lambda^+ = 0$. It follows that, e.g.:

$$\dots a_\lambda a_\sigma^+ | \text{vac} \rangle = \dots | \text{vac} \rangle \delta_{\lambda\sigma}$$

where the dots symbolize an arbitrary string of creation/annihilation operators. This is the reason why the pairing:

$$\langle \text{vac} | \overline{a_\mu a_v^+} \overline{a_\lambda a_\sigma^+} | \text{vac} \rangle$$

in Eq. (5.3) is not possible, since λ must coincide with σ . The indicated pairing in Eq. (5.7) is the only possible one for the same reason.

If it is not possible to bring our expression into the form of Eq. (5.7), the value for the matrix element is zero. It is clear, for example, that the result is zero if the number of creation and annihilation operators is not the same.

The general rules for the evaluation of matrix elements can be formulated in a more strict manner. They are contained in the so-called Wick's theorem which we will not use directly in its original formulation (Wick 1950). The algebraic properties of creation and annihilation operators given by Eqs. (2.48–50), or the above rules based on these properties, give sufficient information to evaluate any matrix element we need. For some further reading, we refer to the more advanced

¹ Transposition of two operators should always be done according to the relevant commutation rules.

monographs and reviews (Paul 1982 p. 126, Raimes 1972, Cižek, 1966, 1969, Paldus and Cižek 1975).

Problem 5.1

Determine the signs of the matrix elements

- (i) $\langle \text{vac} | a_1 a_2 a_3 a_3^\dagger a_2^\dagger a_1^\dagger | \text{vac} \rangle$
 - (ii) $\langle \text{vac} | a_3 a_2 a_1 a_3^\dagger a_2^\dagger a_1^\dagger | \text{vac} \rangle$
 - (iii) $\langle \text{vac} | a_3 a_4 a_3^\dagger a_4^\dagger a_1 a_2 a_2^\dagger a_1^\dagger | \text{vac} \rangle$
-
-

Problem 5.2

$$\langle \text{vac} | \mu^- v^- \rho^- \lambda^+ \sigma^+ \tau^+ | \text{vac} \rangle$$

Problem 5.3

Show that the cyclic permutation of indices μ, v, ρ or that of λ, σ, τ in Problem 5.2 does not affect the value of the matrix element.

5.2 Concept of the Fermi Vacuum

In this section we shall introduce the very useful concept of the *Fermi vacuum*, which makes the evaluation of certain types of matrix elements much easier. As a matter of fact, many (if not most) quantum-chemical considerations and methods are based on the Hartree-Fock single determinantal wave function which serves also as a zeroth-order wave function (“reference state”) in guessing more accurate wave functions as well. For this reason, one is often interested in evaluating expectation values with respect to Hartree-Fock-type wave functions. The evaluation of such expressions will be analyzed below in some detail.

To begin with, consider the matrix element of the operator string $a_i^\dagger a_k$ between a Hartree-Fock wave function, i.e. determinant, built up from orbitals $\Psi_1 \Psi_2 \dots \Psi_N$. Assume $i, k \in \{1, 2, \dots, N\}$. We have then:

$$\langle a_i^\dagger a_k \rangle = \langle \text{vac} | a_1 a_2 \dots a_N a_i^\dagger a_k a_N^\dagger \dots a_2^\dagger a_1^\dagger | \text{vac} \rangle. \quad (5.8)$$

To determine all possible pairings, or to move the strings to the left seems to be rather complicated. However, the annihilation operator a_l , $l \in \{1, 2, \dots, N\}$, can always be moved just before a_l^\dagger if $l \neq i$ and $l \neq k$ by an even number of successive

transpositions, without changing the sign. Thus, if $i \neq k$, one gets²:

$$\begin{aligned}\langle a_i^+ a_k \rangle &= \langle \text{vac} | a_i a_k a_i^+ a_k a_i^+ a_k^+ a_N a_N^+ \dots a_1 a_1^+ | \text{vac} \rangle \\ &= \langle \text{vac} | a_i a_k a_i^+ a_k a_i^+ a_k^+ | \text{vac} \rangle \quad (i \neq k).\end{aligned}\quad (5.9)$$

This latter expression is easy to evaluate: the result is zero (notice, for example, that two electrons are being created on orbital ψ_i which is impossible). Thus one has:

$$\langle a_i^+ a_k \rangle = 0 \quad \text{if } i \neq k. \quad (5.10)$$

If, however, $i = k$:

$$\langle a_i^+ a_i \rangle = \langle \text{vac} | a_1 \dots a_i \dots a_N a_i^+ a_i a_N^+ \dots a_1^+ \dots a_1^+ | \text{vac} \rangle. \quad (5.11)$$

Here again, the operator a_l for $l \neq i$ can be moved by an even number of transpositions right after a_i^+ , and since $i \in \{1, 2, \dots, N\}$ one is left with:

$$\langle a_i^+ a_i \rangle = \langle \text{vac} | a_i a_i^+ a_i a_i^+ | \text{vac} \rangle = \langle \text{vac} | \text{vac} \rangle = 1. \quad (5.12)$$

Combining the results of Eqs. (5.10) and (5.12), one may write:

$$\langle a_i^+ a_k \rangle = \delta_{ik} \quad \text{if } k \in \{1, 2, \dots, N\}. \quad (5.13)$$

The result is zero, of course, if $k \notin \{1, 2, \dots, N\}$ because a_k cannot then annihilate.

Derivations of the above type can be made much simpler by introducing the *Fermi vacuum*. Consider the expectation value of some operator \hat{A} with a Hartree-Fock-type wave function:

$$\langle \hat{A} \rangle = \sum_{\mu, \nu, \dots} A_{\mu\nu} \dots \langle \text{vac} | a_1 a_2 \dots a_N [a_{\mu}^+ \dots] a_N^+ \dots a_2^+ a_1^+ | \text{vac} \rangle. \quad (5.14)$$

Inside the square bracket is a string of creation/annihilation operators corresponding to operator \hat{A} . This string altogether cannot annihilate any of the operators $a_N^+ \dots a_2^+ a_1^+$, otherwise the result will be zero when acting with $a_1 a_2 \dots a_N$ which try to annihilate again. Similarly, the string of operator \hat{A} cannot create an electron on orbitals other than $\psi_N \dots \psi_2 \psi_1$, because that electron would not be annihilated by the string $a_1 a_2 \dots a_N$. Accordingly, the operator string in the square bracket of Eq. (5.14) must not modify the Hartree-Fock-like function represented by the operators $a_N^+ \dots a_2^+ a_1^+$. In other words, that string of creation and annihilation operators must be “self-annihilating” in order to recover the same Hartree-Fock-like state after its action. Any electron created by this string should be annihilated, and any electron once annihilated should be created again. Therefore, introducing the notation:

$$|\text{HF}\rangle = a_N^+ \dots a_2^+ a_1^+ | \text{vac} \rangle \quad (5.15a)$$

and its adjoint:

$$\langle \text{HF}| = \langle \text{vac} | a_1 a_2 \dots a_N \quad (5.15b)$$

² Assume again that $i, k \neq 1, N$; otherwise Eq. (5.9) is to be modified accordingly.

we may say that the vectors $|HF\rangle$ and $\langle HF|$ can be considered as a new vacuum state. The expression for the expectation value in Eq. (5.14) can be written as:

$$\langle \hat{A} \rangle = \sum_{\mu\nu\dots} A_{\mu\nu\dots} \langle HF | \underbrace{[string]}_{\text{self-annihilating}} | HF \rangle. \quad (5.16)$$

The expectation value of the string is reduced now to a matrix element between the new vacuum state. It can be evaluated similar to the case for the true vacuum: most rules introduced in the previous section may be applied. An essential difference, however, is that the annihilation is not forbidden from $|HF\rangle$, in contrast to the true vacuum. That is, it is possible to create a hole in $|HF\rangle$. For example, while:

$$\begin{aligned} a_i^\dagger a_i |\text{vac}\rangle &= 0, \\ a_i^\dagger a_i |HF\rangle &= n_i |HF\rangle \end{aligned} \quad (5.17)$$

n_i being the occupation number of orbital ψ_i in $|HF\rangle$. This expresses also that the result will still be zero if the operator string tries to annihilate an electron which was not created in $|HF\rangle$. This new vacuum state is introduced only to help us in evaluating matrix elements over determinantal wave functions, and its must thoroughly be distinguished from the true vacuum $|\text{vac}\rangle$. The $|HF\rangle$ is usually referred to as the *Fermi vacuum*.

It may be useful to spend some space here to clarify this terminology. In physics, the Fermi level is an often-used term; this corresponds roughly to the energy of the HOMO (highest occupied molecular orbital) in the chemists' terminology. The ensemble of the occupied orbitals is essentially the Fermi sea. The term 'Fermi vacuum' corresponds to this philosophy: the *ket* $|HF\rangle$ contains the set of the creation operators of the occupied orbitals while the *bra* $\langle HF|$ is built of the set of annihilation operators referring to the occupied orbitals. Some authors use a similar expression for the true vacuum state (the term 'Fermion vacuum', for example) from which this $|HF\rangle$ must be thoroughly distinguished because the former simply refers to the fact that electrons (fermions) are dealt with and has nothing to do with the Fermi sea of occupied levels.

The following examples permit the reader to get some practice with the use of the *Fermi vacuum*. It is easy to see that $|HF\rangle$ is normalized:

$$\langle HF | HF \rangle = \langle \text{vac} | \overbrace{a_1 a_2 \dots a_N a_1^\dagger \dots a_2^\dagger a_N^\dagger}^{} | \text{vac} \rangle = \langle \text{vac} | \text{vac} \rangle = 1. \quad (5.18)$$

Our previous consideration for the matrix element of $a_i^\dagger a_k$ now simplifies to:

$$\langle a_i^\dagger a_k \rangle_{HF} = \langle HF | \overbrace{a_i^\dagger a_k}^{} | HF \rangle = n_k \delta_{ik} \quad (5.19)$$

which is unity if k is occupied in $|HF\rangle$, and zero otherwise.

The appearance of the occupation numbers is the only difference one has to keep in mind when evaluating the expectation value of an operator string with respect to the *Fermi vacuum*. Checking the occupancies may be too time-consuming; however, by introducing a simple trick the whole process can be

automated. This trick consists of introducing the hole operators b_i^+ , b_i by the following definition (Cizek 1966, 1969):

$$b_i^+ = \begin{cases} a_i^+ & \text{if } n_i = 0 \\ a_i & \text{if } n_i = 1 \end{cases} \quad (5.20)$$

and

$$b_i = \begin{cases} a_i & \text{if } n_i = 0 \\ a_i^+ & \text{if } n_i = 1 \end{cases}. \quad (5.21)$$

In words, for virtual orbitals the holes operators b_i^+ , b_i act exactly in the same manner as the particle operators a_i^+ , a_i do, while their role is reversed for occupied orbitals. Operator b_i^+ creates an electron in the virtual space, while it annihilates an electron in the Fermi see. This is equivalent to saying that it creates a hole in $|HF\rangle$. Similarly, operator b_i creates an electron in $|HF\rangle$, while it annihilates one in the virtual subspace. This “particle-hole formalism” is in analogy with that of quantum field theory where, for instance, the holes correspond to positrons while the particles are electrons.

Problem 5.4

Show that operators b_i^+ , b_k obey the same anticommutation rules as operators a_i^+ , a_k do.

It is now a trivial task to show that the following equations hold for the hole operators:

$$\langle HF | b_i^+ b_k | HF \rangle = 0 \quad (5.22)$$

for any i and k , while:

$$\langle HF | b_i b_k^+ | HF \rangle = \delta_{ik} \quad (5.23)$$

independently of the occupation of orbital i . The information on the occupancy of the corresponding orbitals is now hidden in the definition of operators b_i^+ , b_k . The proof of Eqs. (5.22) and (5.23) is simple: it follows from the substitution of the definitions in Eqs. (5.20) and (5.21) and checking both the occupied and virtual cases separately. In the following development we shall not utilize this particle-hole formalism but the original particle operators will be used throughout.

It is to be emphasized that $|HF\rangle$ behaves as the *Fermi vacuum* only for those strings of creation and annihilation operators which refer to the same orbitals as those constituting the determinant $|HF\rangle$. More precisely, the orbitals corresponding to the operator string, and those present in $|HF\rangle$, are required to form an orthonormalized set altogether. Specifically speaking, a_i^+ (a_i) in Eq. (5.19) should create (annihilate) an electron on a molecular orbitals, and not an atomic orbital, for example. This is required because otherwise the

anticommutation rules would be violated. “Mixed” anticommutators such as $[\psi_i^+, \chi_\mu^-]_+$ which contain fermion operators corresponding to two different sets of orbitals will be discussed in Sect. 7.1.

Problem 5.5

Determine the expectation value

$$\langle \text{vac} | \psi_3^- \psi_2^- \psi_1^- \psi_\mu^+ \psi_\nu^+ \psi_\sigma^- \psi_\lambda^- \psi_1^+ \psi_2^+ \psi_3^+ | \text{vac} \rangle$$

Problem 5.6

Show that the Fermi vacuum is orthogonal to a singly excited state Ψ_1 , i.e.,

$$\langle \text{HF} | \Psi_1 \rangle = 0$$

In what follows the concept of the *Fermi vacuum* will be utilized in many derivations and the reader will see how powerful it is.

6 Advantages of Second Quantization—Illustrative Examples

6.1 General

Throughout the previous sections we become acquainted with the basic notations and rules of second quantization. It is time now to utilize the benefits of this formalism. In this section the usefulness of the second quantized approach will be illustrated from the practical point of view on a few selected simple examples. In fact, this formalism can only be appreciated by those who really use it in practice. It is hoped that the following development and examples will help the reader to appreciate the beauty and power of this formalism and to give him/her the possibility to apply it in his/her work. Before turning to the concrete examples, some general remarks are made in order to put the second quantized formalism to its proper place. Some of the following remarks have already been noted before, but it appears to be useful to collect here the most important points.

Advantages of second quantization are both conceptual and practical. The conceptual benefits concern the following features of the many-electron theory:

- (i) In the second quantized form of the Hamiltonian there is no explicit reference to the number of electrons of the system, N . This is an advantage in quantum field theory of systems with variable particle numbers, or in solid-state physics where one has an infinite number of electrons. In quantum chemistry, this feature is important, e.g., in studying ionization processes: the ion and the neutral molecule (or atom) can be described by one and the same Hamiltonian. The wave functions of ions and neutral systems can be considered as different states of the same Hamiltonian, provided that the same set of one-electron basis functions is used. This feature will be utilized, e.g., in Sect. 10.2 discussing particle-hole symmetry, and it also permits one to derive appropriate expressions for ionization potentials (Pickup & Goscinski 1973; Öhrn & Born 1981; Paul 1982; Oddershede 1987).
- (ii) The antisymmetry of the many-electron wave function is automatically ensured by second quantization due to the anticommutation properties of creation/annihilation operators.
- (iii) It is possible to introduce a partitioning of the total Hamiltonian by a classification of the one-electron basis orbitals, i.e., of the list of one- and two-electron integrals in a given basis set. Thus, the second quantized Hamiltonian is well suited for studying interacting subsystems. We shall utilize this property in Sects. 15–16.

(iv) There are also some features of the many-electron problem which would be difficult to understand without second quantization. The inherent connection between the N-electron problem and the unitary group can be cited as an example (cf. Sect. 17.2).

Practical benefits of second quantization are consequences of the above conceptual advantages. For the forthcoming simple introduction, the above point (ii) is the most important one. This allows us to understand and derive many formulae and theorems of quantum chemistry in a very simple manner.

6.2 Overlap of Two Determinants

Matrix elements between determinantal wave functions can be evaluated by the so-called Slater (or Slater-Condon) rules. We shall not derive the Slater rules in general, but in some particular cases the first and second quantization-based derivations will be compared.

Consider the overlap:

$$S_{KL} = \langle \Phi_K | \Phi_L \rangle \quad (6.1)$$

where Φ_K and Φ_L are two determinants constructed by orthonormalized one-electron functions:

$$\Phi_K = |\phi_{K_1}, \phi_{K_2}, \dots, \phi_{K_N}| \quad (6.2a)$$

$$\Phi_L = |\phi_{L_1}, \phi_{L_2}, \dots, \phi_{L_N}|. \quad (6.2b)$$

Evaluation of S_{KL} in the framework of the “first quantized” procedure proceeds along the following lines. Substituting the determinants of Eq. (6.2) into Eq. (6.1), one writes:

$$S_{KL} = \left\langle \frac{1}{\sqrt{N!}} \sum_P (-1)^P \phi_{K_1}(P_1) \dots \phi_{K_N}(P_N) \middle| \frac{1}{\sqrt{N!}} \right. \\ \left. \times \sum_Q (-1)^Q \phi_{L_1}(Q_1) \dots \phi_{L_N}(Q_N) \right\rangle. \quad (6.3)$$

An analysis of this expression makes clear that it should vanish if there is no perfect coincidence of the MOs in the *bra*- and the *ket*-functions. So the two determinants should be the same:

$$S_{KL} = S_{KK} \delta_{KL}. \quad (6.4)$$

The quantity S_{KK} can be evaluated as follows:

$$S_{KK} = \frac{1}{N!} \sum_{PQ} (-1)^{P+Q} \langle \hat{P} \phi_1(1) \dots \phi_N(N) | \hat{Q} \phi_1(1) \dots \phi_N(N) \rangle. \quad (6.5)$$

where \hat{P} and \hat{Q} denote the appropriate permutation operators. We can observe

that if the two permutations \hat{P} and \hat{Q} are not exactly the same, due to the orthogonality of the set $\{\phi_i\}$, the corresponding term vanishes upon integration. Therefore:

$$S_{KK} = \frac{1}{N!} \sum_{\mathbf{P}} \langle \hat{P} \phi_1(1) \dots \phi_N(N) | \hat{P} \phi_1(1) \dots \phi_N(N) \rangle. \quad (6.6)$$

In Eq. (6.6), the value of the bracket is just 1 for any permutation, provided provided that the orbitals ϕ_i are normalized. Since the total number of permutations is $N!$, one gets:

$$S_{KK} = \frac{1}{N!} \sum_{\mathbf{P}} 1 = \frac{N!}{N!} = 1. \quad (6.7)$$

Thus one concludes:

$$S_{KL} = \delta_{KL} \quad (6.8)$$

which is the well-known result.

Let us see now how this finding is obtained in second quantization. We have:

$$S_{KL} = \langle \text{vac} | a_{K_1} a_{K_2} \dots a_{K_N} a_{L_N}^+ \dots a_{L_2}^+ a_{L_1}^+ | \text{vac} \rangle. \quad (6.9)$$

If the set $\{K_1, K_2, \dots, K_N\}$ is not the same as the set $\{L_1, L_2, \dots, L_N\}$, one gets zero, since any a_{K_i} which does not have its pair $a_{K_i}^+$ cannot annihilate. We thus discovered Eq. (7.4). If the two sets are the same, one has:

$$\begin{aligned} S_{KK} &= \langle \text{vac} | a_{K_1} a_{K_2} \dots a_{K_N} a_{K_N}^+ \dots a_{K_2}^+ a_{K_1}^+ | \text{vac} \rangle \\ &= \langle \text{HF} | \text{HF} \rangle = 1 \end{aligned} \quad (6.10)$$

as noted also at Eq. (5.18). Thus Eq. (6.8) is recovered. This latter consideration is apparently simpler, more transparent and more automatic, than that based on determinants and permutations.¹

6.3 Hückel Energy Expression

As a next example, consider the expectation value of a one-electron Hamiltonian \hat{H} as calculated by a one-determinantal wave function built up from the molecular spinorbitals which diagonalize \hat{H} :

$$\hat{H} = \sum_n \hat{h}_n \leftrightarrow \sum_{\mu\nu} h_{\mu\nu} a_\mu^+ a_\nu = \sum_i \varepsilon_i a_i^+ a_i \quad (6.11)$$

where $h_{\mu\nu}$ is the matrix of the Hamiltonian in the basis of atomic orbitals while ε_i are the eigenvalues of matrix h , i.e., the orbital energies. We are interested in

¹ Being familiar with the formalism of permutations or the properties of the antisymmetrizer operator, one may simplify the first quantized derivation, too. Nevertheless, the second quantization-based consideration remains the simplest.

obtaining the expression for the energy as the expectation value:

$$E = \langle \Psi | H | \Psi \rangle \quad (6.12)$$

where Ψ is an N-electron determinant built up from orbitals ψ_i . Let us first recall how this expression is evaluated by classical means, that is, via the Slater-Condon rules. Expanding the determinants:

$$E = \frac{1}{N!} \sum_{PQ} (-1)^{P+Q} \langle \hat{P}\psi_1(1) \dots \psi_N(N) | \sum_n \hat{h}_n | \hat{Q}\psi_1(1) \dots \psi_N(N) \rangle. \quad (6.13)$$

Observing that the sum over electrons (n) can be taken outside the bracket, and the bracket gives identical results for every n, one can write:

$$E = \frac{1}{N!} \sum_{PQ} (-1)^{P+Q} N \langle \hat{P}\psi_1(1) \dots \psi_N(N) | \hat{h}_1 | \hat{Q}\psi_1(1) \dots \psi_N(N) \rangle. \quad (6.14)$$

Integration over the coordinates of electrons 2, 3, ..., N results in zero unless electrons 2, 3, ..., N are on the same orbital for the permutations \hat{P} and \hat{Q} . Therefore, electron 1 should also be on the same orbital in the *bra*- and in the *ket*-function. That is, the two permutations \hat{P} and \hat{Q} are identical. We get:

$$E = \frac{N}{N!} \sum_P \langle \hat{P}\psi_1(1) \dots \psi_N(N) | \hat{h}_1 | \hat{P}\psi_1(1) \dots \psi_N(N) \rangle. \quad (6.15)$$

Analysing this permutation \hat{P} , it turns out that, assuming electron 1 is assigned to a particular orbital ψ_i , the remaining $(N - 1)$ electrons can be permuted among the remaining $(N - 1)$ orbitals in $(N - 1)!$ ways. When \hat{P} runs over all permutations, electron 1 runs over all orbitals ψ_i , so one may write:

$$\begin{aligned} E &= \frac{1}{(N - 1)!} \sum_i (N - 1)! \langle \psi_i(1) | \hat{h}_1 | \psi_i(1) \rangle \\ &= \sum_i \langle \psi_i(1) | \hat{h}_1 | \psi_i(1) \rangle = \sum_i \epsilon_i. \end{aligned} \quad (6.16)$$

This result is very simple, though the way it is obtained is less simple.² Now consider the same derivation using the second quantized language:

$$\begin{aligned} E &= \langle \text{vac} | a_1 a_2 \dots a_N \sum_i \epsilon_i a_i^+ a_i a_N^+ \dots a_2^+ a_1^+ | \text{vac} \rangle \\ &= \sum_i \epsilon_i \langle \text{vac} | a_1 a_2 \dots a_N a_i^+ a_i a_N^+ \dots a_2^+ a_1^+ | \text{vac} \rangle \\ &= \sum_i \epsilon_i \langle \text{HF} | a_i^+ a_i | \text{HF} \rangle = \sum_i \epsilon_i n_i \\ &= \sum_i^{\text{occ}} \epsilon_i \end{aligned} \quad (6.17)$$

²This derivation can also be made somewhat simpler introducing the concept of the antisymmetrizer operator and utilizing its properties that it is Hermitian and commutes with the Hamiltonian.

where the *Fermi vacuum* is introduced with i indicating an occupied orbital. (The same restriction, of course, applies for Eq. (6.16) where i runs over all electrons.) Thus the same result is obtained. No further comments are necessary to emphasize the advantage of this latter derivation.

6.4 Interaction of Two Electrons

Consider two electrons, one on orbital ψ_1 , and another one on orbital ψ_2 . The repulsion energy of these two electrons is given by:

$$\Delta E = \langle \Psi | \frac{1}{r_{12}} | \Psi \rangle \quad (6.18)$$

where Ψ is a 2-by-2 determinant:

$$\begin{aligned} \Psi &= \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(1) & \psi_1(2) \\ \psi_2(1) & \psi_2(2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} [\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)]. \end{aligned} \quad (6.19)$$

To evaluate ΔE in the traditional way, one may substitute Eq. (6.19) into (6.18):

$$\begin{aligned} \Delta E &= \frac{1}{2} \left[\langle \psi_1(1)\psi_2(2) | \frac{1}{r_{12}} | \psi_1(1)\psi_2(2) \rangle \right. \\ &\quad - \langle \psi_1(1)\psi_2(2) | \frac{1}{r_{12}} | \psi_2(1)\psi_1(2) \rangle \\ &\quad - \langle \psi_2(1)\psi_1(2) | \frac{1}{r_{12}} | \psi_1(1)\psi_2(2) \rangle \\ &\quad \left. + \langle \psi_2(1)\psi_1(2) | \frac{1}{r_{12}} | \psi_2(1)\psi_1(2) \rangle \right]. \end{aligned} \quad (6.20)$$

Renumbering electrons 1 and 2 in the last two terms, one can observe that the two positive and the two negative terms are identical, respectively:

$$\begin{aligned} \Delta E &= \langle \psi_1(1)\psi_2(2) | \frac{1}{r_{12}} | \psi_1(1)\psi_2(2) \rangle - \langle \psi_1(1)\psi_2(2) | \frac{1}{r_{12}} | \psi_2(1)\psi_1(2) \rangle \\ &= [12|12] - [12|21] \end{aligned} \quad (6.21)$$

where the usual notation for the two-electron integrals is introduced. The two terms in Eq. (6.21) are called Coulomb and exchange interactions, respectively.

Let us do the same derivation using second quantization. The interaction operator is a two-electron operator, thus it takes the form:

$$\frac{1}{r_{12}} = \sum_{i < j} \frac{1}{r_{ij}} = \frac{1}{2} \sum_{ijkl} [ij|kl] a_i^+ a_j^+ a_l a_k. \quad (6.22)$$

The expectation value of this expression is:

$$\begin{aligned} \Delta E &= \frac{1}{2} \sum_{ijkl} [ij|kl] \langle HF | a_i^+ a_j^+ a_l a_k | HF \rangle \\ &\text{either } \overbrace{\quad\quad\quad}^{+} (+ \text{ sign}) \\ &\text{or } \overbrace{\quad\quad\quad}^{-} (- \text{ sign}) \\ &= \frac{1}{2} \sum_{ijkl}^{\text{occ}} [ij|kl] (\delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk}) \\ &= \frac{1}{2} \sum_{ij}^{\text{occ}} ([ij|ij] - [ij|ji]). \end{aligned} \quad (6.23)$$

This result is quite general; it is valid for any number of orbitals. In our particular case, the labels i and j are either 1 or 2, thus we get the same result as in Eq. (6.21):

$$\Delta E = [12|12] - [12|21]. \quad (6.24)$$

If the number of orbitals increases, the first quantized derivation presented above becomes more and more involved. As the size of the determinant increases, one should apply the general Slater-Condon rules, or “rederive” them similarly as was done for the Hückel energy expression (Sect. 6.4). On the other hand, the general result of Eq. (6.23) is valid for any number of electrons and orbitals.

Beside the above three examples, there are many formulae which are much easier to obtain by the second quantized technique. The interested reader may exercise in trying to rederive some other well-known results of quantum chemistry.

Problem 6.1

Compare the first and second quantized derivations of the matrix element $\langle \Phi_K | \sum_{i < j} \hat{g}_{ij} | \Phi_L \rangle$ where \hat{g} is a two-electron operator while Φ_K and Φ_L are two determinants.

Hint: Distinguish between the cases when the two determinants differ in 0, 1, 2, 3 or more spinorbitals.

7 Density Matrices

Let us now proceed further in the formalism, studying a more general and automatic way of calculating expectation values. The appropriate tools are offered by density matrices.

7.1 First-Order Density Matrix

Consider an orthonormalized basis set $\{\chi_\mu\}$ associated with the creation/annihilation operators χ_μ^+/χ_μ^- in the Longuet-Higgins notations (cf. Sect. 2). Let \hat{A} be a one-electron operator:

$$\hat{A} = \sum_{\mu, v} A_{\mu v} \chi_\mu^+ \chi_v^-, \quad (7.1)$$

and let us study its expectation value:

$$\langle \hat{A} \rangle = \langle \Psi | \hat{A} | \Psi \rangle. \quad (7.2)$$

Assume that Ψ is an N-electron one-determinantal wave function which is constructed from orbitals ψ_i :

$$|\Psi\rangle = \psi_N^+ \dots \psi_2^+ \psi_1^+ |\text{vac}\rangle = |\text{HF}\rangle \quad (7.3)$$

where $|\text{HF}\rangle$ symbolizes the *Fermi vacuum* (cf. Sect. 5.2). Using Eqs. (7.1) and (7.3), the expectation value in Eq. (7.2) takes the form:

$$\langle \hat{A} \rangle = \sum_{\mu, v} A_{\mu v} \langle \text{HF} | \chi_\mu^+ \chi_v^- | \text{HF} \rangle. \quad (7.4)$$

We introduce the following notation:

$$P_{v\mu} = \langle \text{HF} | \chi_\mu^+ \chi_v^- | \text{HF} \rangle \quad (7.5)$$

and write Eq. (7.4) as:

$$\langle \hat{A} \rangle = \sum_{\mu, v} A_{\mu v} P_{v\mu} = \text{Tr}(AP). \quad (7.6)$$

Matrix P is called the first-order density matrix which is represented now in the basis set $\{\chi_\mu\}$. Before evaluating its elements, the following remarks are relevant:

- (i) The result of Eq. (7.6) is quite general: it has the same form even for multi-determinantal wave functions provided that the density matrix elements are defined as:

$$P_{\nu\mu} = \langle \chi_{\mu}^{+} \chi_{\nu}^{-} \rangle \quad (7.7)$$

which is the expectation value with respect to the actual wave function. However, the orthogonality of the set $\{\chi_{\mu}\}$ is very important; for the non-orthogonal case refer to Sect. 13.

- (ii) It should be emphasized that $|HF\rangle$ does not behave as a vacuum state for χ^+, χ^- because it is built up from a different set of one-electron functions ψ_i [see remark after Eq. (5.23)]. Namely, $\{\chi_{\mu}\}$ is an arbitrary set of orthonormal one-electron spinorbitals, while the ψ_i -s in $|HF\rangle$ are the molecular orbitals constructing the determinant. For this reason, the $P_{\nu\mu}$ in Eq. (7.5) is not equal to $\delta_{\nu\mu}$.
- (iii) Nondiagonal density matrices may also result if using molecular orbitals ψ_i as a basis set, in replacement of the set $\{\chi_{\mu}\}$, but dealing with multideterminantal wave functions. In this case, however, one can always turn to a new basis set by diagonalizing the first-order density matrix. The resulting spinorbitals are called Löwdin's natural spinorbitals (Löwdin 1955).

To evaluate $P_{\nu\mu}$ for the one-determinantal case, the relation between orbitals ψ_i and χ_{μ} should be written down explicitly. Both sets being orthonormalized, they are connected by a unitary transformation:

$$\psi_i = \sum_{\mu} C_{i\mu} \chi_{\mu}. \quad (7.8)$$

To be less abstract, one may say that $\{\chi_{\mu}\}$ is a set of orthonormalized atomic orbitals (AOs), while $\{\psi_i\}$ is the set of orthonormalized molecular orbitals (MOs). $C_{i\mu}$ are then the MO expansion coefficients. Eq. (7.8) can be written in the matrix notation as:

$$\psi = C\chi. \quad (7.9)$$

Since C is a unitary matrix, its inverse equals to its adjoint, thus one may write:

$$\chi = C^{-1}\psi = C^{\dagger}\psi. \quad (7.10)$$

Alternatively, in components we have:

$$\chi_{\mu} = \sum_i C_{i\mu}^* \psi_i. \quad (7.11)$$

Equation (6.11) defines also the connection between the corresponding creation and annihilation operators:

$$\chi_{\mu}^{+} = \sum_i C_{i\mu}^* \psi_i^{+} \quad (7.12a)$$

$$\chi_{\mu}^{-} = \sum_i C_{i\mu} \psi_i^{-}. \quad (7.12b)$$

Although real orbitals are dealt with, in this section asterisks will be put at the relevant places to indicate complex conjugation, making the formulae a bit more transparent. The above formulae permit us to express our operator string in Eq.

(7.5) in terms of the creation/annihilation operators ψ^+/ψ^- for which $|\text{HF}\rangle$ does behave as the true Fermi vacuum. Inserting Eqs. (7.12) into (7.5) one gets:

$$\begin{aligned} P_{v\mu} &= \sum_{ik} C_{i\mu}^* C_{kv} \langle \text{HF} | \overline{\psi_i^+ \psi_k^-} | \text{HF} \rangle \\ &= \sum_{ik} C_{i\mu}^* C_{kv} n_i \delta_{ik} = \sum_i n_i C_{i\mu}^* C_{iv} \\ &= \sum_i^{\text{occ}} C_{i\mu}^* C_{iv}. \end{aligned} \quad (7.13)$$

This result for the density matrix elements is well known from the SCF theory.¹

The same expression can also be derived directly from Eq. (7.5), by establishing the specific commutation rules between the MO and AO operators. Substitution of the MO expansion of Eq. (7.8) into the commutators yields:

$$[\psi_i^+, \chi_\mu^+]_- = \sum_v C_{iv}^* [\chi_v^+, \chi_\mu^+]_- = 0 \quad (7.14a)$$

$$[\psi_i^-, \chi_\mu^-]_- = \sum_v C_{iv} [\chi_v^-, \chi_\mu^-]_- = 0 \quad (7.14b)$$

$$[\psi_i^+, \chi_\mu^-]_- = \sum_v C_{iv}^* [\chi_v^+, \chi_\mu^-]_- = \sum_v C_{iv}^* \delta_{v\mu} = C_{i\mu}^* \quad (7.14c)$$

$$[\psi_i^-, \chi_\mu^+]_- = \sum_v C_{iv} [\chi_v^-, \chi_\mu^+]_- = \sum_v C_{iv} \delta_{v\mu} = C_{i\mu}. \quad (7.14d)$$

Application of these commutation rules in evaluating Eq. (7.5) gives us Eq. (7.13). The derivation presented previously is simpler, however.

We may wonder how the first-order density matrix may appear with respect to $|\text{HF}\rangle$ in the MO basis. Simply:

$$P_{ji} = \langle \psi_i^+ \psi_j^- \rangle = \langle \text{HF} | \psi_i^+ \psi_j^- | \text{HF} \rangle = n_i \delta_{ij}. \quad (7.15)$$

That is, P_{ij} forms a diagonal matrix with the occupation numbers as eigenvalues.

Two properties of the first-order density matrix are worth mentioning. First, it has the Hermitian symmetry:

$$P_{\mu\nu} = P_{v\mu}$$

which can be easily seen by taking the adjoint of the defining relation in Eq. (7.7). Second, one may easily evaluate the trace of P :

$$\text{Tr } P = \sum_\mu P_{\mu\mu} = \sum_\mu \langle \chi_\mu^+ \chi_\mu^- \rangle = \sum_\mu n_\mu = N \quad (7.16)$$

where n_μ is the “occupation number” of orbital χ_μ , and N is the total number of electrons.

¹ In fact, the same expression for the $P_{v\mu}$ is used also in the ab-initio SCF theory where the basis set $\{\chi_\mu\}$ is usually not orthogonal. In that case, however, $P_{v\mu}$ is not the expectation value of $\langle \chi_\mu^+ \chi_v^- \rangle$, so it is not the LCAO representant of the first-order density matrix. For more details see Sect. 13.

Problem 7.1

Derive the expression for the first-order density matrix in terms of MOs with respect to the following two-determinantal wave function $\Psi = C_0|HF\rangle + C_2\Psi_b^+\psi_a^+\psi_j^-\psi_i^-|HF\rangle$ where i, j and a, b refer to occupied and empty levels in $|HF\rangle$, respectively.

7.2 Second-Order Density Matrix

Studying the expectation value of a two-electron operator \hat{A} :

$$\hat{A} = \frac{1}{2} \sum_{\mu\nu\lambda\sigma} A_{\mu\nu\lambda\sigma} \chi_\mu^+ \chi_\nu^+ \chi_\sigma^- \chi_\lambda^-$$

leads to the natural definition of the second-order density matrix. Introducing the following notation:

$$\Gamma_{\lambda\sigma\mu\nu} = \langle \chi_\mu^+ \chi_\nu^+ \chi_\sigma^- \chi_\lambda^- \rangle \quad (7.17)$$

the expectation value of the two-electron operator \hat{A} can be written as:

$$\langle \hat{A} \rangle = \frac{1}{2} \sum_{\mu\nu\lambda\sigma} A_{\mu\nu\lambda\sigma} \Gamma_{\lambda\sigma\mu\nu}. \quad (7.18)$$

The four-index matrix Γ is called the second-order density matrix represented in the basis $\{\chi_\mu\}$. The expression for $\Gamma_{\lambda\sigma\mu\nu}$ may be very complicated in the general case, but it takes an especially simple form with a single-determinantal wave function:

$$\Gamma_{\lambda\sigma\mu\nu} = \langle HF | \chi_\mu^+ \chi_\nu^+ \chi_\sigma^- \chi_\lambda^- | HF \rangle. \quad (7.19)$$

To determine this expectation value for the case of a one-determinantal wave function one may proceed exactly in the same manner as in Sect. 7.1. That is, the AO operators are expressed in terms of the MO operators. Substituting Eq. (7.12) into Eq. (7.19) one gets:

$$\begin{aligned} \Gamma_{\lambda\sigma\mu\nu} &= \sum_{ijkl} C_{k\sigma} C_{l\lambda} C_{i\mu}^* C_{j\nu}^* \langle HF | \psi_i^+ \psi_j^+ \psi_k^- \psi_l^- | HF \rangle \\ &= \sum_{ijkl} C_{k\sigma} C_{l\lambda} C_{i\mu}^* C_{j\nu}^* [\delta_{il} \delta_{jk} - \delta_{ik} \delta_{jl}] n_k n_l \\ &= \sum_{ij}^{\text{occ}} C_{j\sigma} C_{i\lambda} C_{i\mu}^* C_{j\nu}^* - \sum_{ij}^{\text{occ}} C_{i\sigma} C_{j\lambda} C_{i\mu}^* C_{j\nu}^* \\ &= P_{\lambda\mu} P_{\sigma\nu} - P_{\sigma\mu} P_{\lambda\nu}. \end{aligned} \quad (7.20)$$

Here, use has been made of our former experience for evaluating the matrix element, cf. Eq. (6.23), and of Eq. (7.13), the definition of $P_{\nu\mu}$. We obtained the important result that the second-order density matrix elements $\Gamma_{\lambda\sigma\mu\nu}$ can be

expressed in terms of the first-order density matrix elements $P_{\nu\mu}$. This holds only for one-determinantal wave functions, however.

According to Eq. (7.20), the second-order density matrix corresponding to a one-determinantal wave function consists of two parts. When Γ is expressed in terms of P , these two parts differ only in the order of the indices. The first term can be called the Coulomb part, while the second one is the exchange part. This nomenclature is justified because the latter term appears as a consequence of the antisymmetry of the wave function which is reflected by the anticommutation rules in this formalism.

The symmetry properties of the second-order density matrix are easy to establish. First, its Hermitian symmetry follows from the definition of Eq. (7.17) and from the adjoint relation:

$$\Gamma_{\mu\nu\lambda\sigma} = \langle \lambda^+ \sigma^+ v^- \mu^- \rangle = \langle \mu^+ v^+ \sigma^- \lambda^- \rangle = \Gamma_{\lambda\sigma\mu\nu} \quad (7.21)$$

where the short-hand notation is used for the fermion operators. Next, the antisymmetry properties follow also from the definition:

$$\begin{aligned} \Gamma_{\lambda\sigma\mu\nu} &= \langle \mu^+ v^+ \sigma^- \lambda^- \rangle = -\langle \mu^+ v^+ \lambda^- \sigma^- \rangle = -\Gamma_{\sigma\lambda\mu\nu} \\ &= -\langle v^+ \mu^+ \sigma^- \lambda^- \rangle = -\Gamma_{\lambda\sigma\nu\mu} \\ &= \langle v^+ \mu^+ \lambda^- \sigma^- \rangle = \Gamma_{\sigma\lambda\nu\mu}. \end{aligned} \quad (7.22)$$

As a consequence of these antisymmetry properties, the corresponding diagonal elements are zero. In particular:

$$\Gamma_{\mu\mu\lambda\sigma} = \Gamma_{\mu\nu\lambda\lambda} = 0 \quad (7.23)$$

which reflects simply the Pauli principle.

It is useful to check also the trace of Γ . Being a two-electron quantity, its trace is calculated as:

$$\text{Tr } \Gamma = \sum_{\mu, \nu} \Gamma_{\mu\nu\mu\nu}. \quad (7.24)$$

Substituting the definition of Γ and applying the anticommutation rules one may write:

$$\begin{aligned} \text{Tr } \Gamma &= \sum_{\mu, \nu} \langle \mu^+ v^+ v^- \mu^- \rangle = -\sum_{\mu, \nu} \langle \mu^+ v^+ \mu^- v^- \rangle \\ &= -\sum_{\mu, \nu} (\delta_{\mu\nu} \langle \mu^+ v^- \rangle - \langle \mu^+ \mu^- v^+ v^- \rangle) \\ &= -\sum_{\mu} P_{\mu\mu} + \sum_{\mu, \nu} n_{\mu} n_{\nu} = N^2 - N = 2 \binom{N}{2}. \end{aligned} \quad (7.25)$$

This result is a special case of a general sum rule for density matrices.²

² For the p -th-order density matrix one can prove that $\text{Tr } \Gamma^{(p)} = p! \binom{N}{p}$. Density matrices are often normalized in a different manner so that $\text{Tr } \Gamma^{(p)} = \binom{N}{p}$.

A more complete treatment of density matrices (without applying second quantization) can be found in the classical papers by Löwdin (1955) and McWeeny (1960).

7.3 Hartree-Fock Energy Expression

By means of the first- and second-order density matrices introduced above it is a trivial task to derive the expression of the electronic energy in the Hartree-Fock theory. The goal is simply to evaluate the expectation value of the Hamiltonian \hat{H} , which in the second quantized formalism is given by Eq. (4.40):

$$\begin{aligned} E &= \langle \hat{H} \rangle = \langle HF | \hat{H} | HF \rangle \\ &= \sum_{\mu, v} h_{\mu v} \langle HF | \chi_{\mu}^{+} \chi_{v}^{-} | HF \rangle \\ &\quad + \frac{1}{2} \sum_{\mu v \lambda \sigma} [\mu v | \lambda \sigma] \langle HF | \chi_{\mu}^{+} \chi_{v}^{+} \chi_{\sigma}^{-} \chi_{\lambda}^{-} | HF \rangle \\ &= \sum_{\mu, v} h_{\mu v} P_{v\mu} + \frac{1}{2} \sum_{\mu v \lambda \sigma} [\mu v | \lambda \sigma] \Gamma_{\lambda \sigma \mu v}. \end{aligned} \quad (7.26)$$

Expressing the second-order density matrix in terms of the first-order one via Eq. (7.20) one obtains:

$$E = \sum_{\mu, v} h_{\mu v} P_{v\mu} + \frac{1}{2} \sum_{\mu v \lambda \sigma} [\mu v | \lambda \sigma] (P_{\lambda \mu} P_{\sigma v} - P_{\sigma \mu} P_{\lambda v}). \quad (7.27)$$

To bring this result into a more familiar form, we may interchange the indices v and λ in the first term, and apply the interchanges $v \leftrightarrow \sigma$ than $\sigma \leftrightarrow \lambda$ in the second term of the two-electron part. We get:

$$E = \sum_{\mu, v} h_{\mu v} P_{v\mu} + \frac{1}{2} \sum_{\mu v \lambda \sigma} P_{v\mu} P_{\sigma \lambda} \{ [\mu \lambda | v \sigma] - [\mu \lambda | \sigma v] \}. \quad (7.28)$$

This energy expression consists of three terms: the one-electron term, the Coulomb-energy term and the exchange term, respectively. Although transparent, it is not very suitable for actual computation of the electronic energy since one should deal with the long list of two-electron integrals $[\mu \lambda | v \sigma]$, the manipulation of which is rather time consuming. However, we recall that the Fock matrix elements are defined as:

$$F_{\mu v} = h_{\mu v} + \sum_{\lambda \sigma} P_{\sigma \lambda} \{ [\mu \lambda | v \sigma] - [\mu \lambda | \sigma v] \}. \quad (7.29)$$

Combining Eqs. (7.28) and (7.29) one gets:

$$E = \frac{1}{2} \sum_{\mu, v} (h_{\mu v} + F_{\mu v}) P_{v\mu} \quad (7.30)$$

which is more suitable for computation provided that the $F_{\mu\nu}$ matrix elements are available.

A pictorial interpretation of the Hartree-Fock energy is obtained by writing this latter expression in terms of molecular orbitals. Then, cf. Eq. (7.15), we have:

$$P_{ij} = n_i \delta_{ij} \quad (7.31)$$

while

$$F_{ij} = \varepsilon_i \delta_{ij} \quad (7.32)$$

where ε_i are the orbital energies. Inserting Eqs. (7.31) and (7.32) into the analog of Eq. (7.30) written down for the MO basis we get:

$$E = \frac{1}{2} \sum_i (h_{ii} + \varepsilon_i). \quad (7.33)$$

That is, the Hartree-Fock electronic energy is the arithmetic mean of the sum of the MO energies and the pure one-electron energy. The latter quantity clearly does not take into account electron-electron interaction, while the sum of orbital energies contains the electron-electron repulsion energy twice.

8 Connection to “Bra and Ket” Formalism

This section is devoted to point out some formal similarities between the second quantized representation and the so-called “bra and ket” formalism introduced into quantum theory originally by Dirac (1958). A short summary can be found in Löwdin (1985). Although we will not refer to the details of bra-ket formalism in the rest of the book, we feel that the brief comparison below may be useful, offering a deeper understanding of second quantization. Bra and ket functions have already been introduced in Sect. 1 and they have been utilized throughout, but a more detailed discussion is justified by its relevance to the second quantized formalism.

For the sake of simplicity, let us discuss a one-electron system. Consider a set of orthonormalized functions $\{\phi_i\}_{i=1}^M$. *Bra*- and *ket*-functions, respectively, are defined by their binary (or scalar) product, called a bracket:

$$\langle i|k\rangle = \int \phi_i^*(x)\phi_k(x) dx = \delta_{ik} \quad (8.1)$$

for any orthonormal set. This simple notation turns out to be very useful if we accept that $\langle i|$ or $|k\rangle$ can be symbolically taken as independent of an actual bracket. Then the spinorbital ϕ_i is represented either by the vector $\langle i|$ or by the vector $|i\rangle$, depending on whether it enters the *bra*- or the *ket*-part of a matrix element. The *bra*-functions are understood to carry the complex conjugation if this is relevant.

Let us investigate, for example, the quantity:

$$\hat{Q}^i = |i\rangle \langle i|. \quad (8.2)$$

We can consider \hat{Q}^i as an operator which is defined by its action on a *ket*-function:

$$\hat{Q}^i |k\rangle = |i\rangle \langle i|k\rangle = \delta_{ik}|i\rangle. \quad (8.3)$$

This operator \hat{Q}^i has the matrix elements:

$$\hat{Q}_{ik}^i = \langle l|\hat{Q}^i|k\rangle = \langle l|i\rangle \langle i|k\rangle = \delta_{li}\delta_{ik}. \quad (8.4)$$

It is easy to see that \hat{Q}^i is a projector. If an arbitrary one-electron function ψ is expanded in terms of the basis functions $\{\phi_k\}$ as:

$$|\psi\rangle = \sum_k C_k |k\rangle \quad (8.5)$$

for *kets*, then the effect of \hat{Q}^i on this wave function is:

$$\hat{Q}^i |\psi\rangle = \sum_k C_k |i\rangle \langle i|k\rangle = C_i |i\rangle. \quad (8.6)$$

Thus, \hat{Q}^i projected out the i -th component of ψ . The idempotency of \hat{Q}^i is also obvious:

$$(\hat{Q}^i)^2 |\psi\rangle = \hat{Q}^i C_i |i\rangle = C_i |i\rangle \langle i|i\rangle = C_i |i\rangle = \hat{Q}^i |\psi\rangle \quad (8.7)$$

for arbitrary ψ , thus:

$$(\hat{Q}^i)^2 = \hat{Q}^i$$

in the operator sense. We can easily verify that operator:

$$\hat{I} = \sum_i |i\rangle \langle i| \quad (8.8)$$

is the unity operator over the space of one-electron orbitals in the sense that:

$$\hat{I} |\psi\rangle = |\psi\rangle \quad (8.9)$$

for arbitrary ψ having the expansion of Eq. (8.5). Substitution of Eqs. (8.8) and (8.5) into Eq. (8.9) yields:

$$\hat{I} |\psi\rangle = \sum_{i,k} C_k |i\rangle \langle i|k\rangle = \sum_k C_k |k\rangle = |\psi\rangle$$

which verifies the statement of Eq. (8.9). The decomposition of Eq. (8.8) is usually called the *resolution of identity*. Consider now the quantity:

$$\hat{E} = \sum_i E_i |i\rangle \langle i|.$$

It is easy to show that \hat{E} is an operator with eigenvalues E_i and eigenvectors $|k\rangle$:

$$\hat{E} |k\rangle = \sum_i E_i |i\rangle \langle i|k\rangle = E_k |k\rangle.$$

This result can be used to put down the *bra-ket* representation of an operator through its spectral resolution. Let \hat{H} be a Hermitian operator with eigenvalues E_i and eigenfunctions $|\psi_i\rangle$. Then:

$$\hat{H} = \sum_i E_i |\psi_i\rangle \langle \psi_i| \quad (8.10)$$

is the spectral resolution of the Hamiltonian \hat{H} . The eigenfunctions $|\psi_i\rangle$ can be expanded in our basis set $\{\phi_k\}$ as:

$$|\psi_i\rangle = \sum_k C_{ik} |k\rangle \quad (8.11a)$$

for *ket*-functions, or:

$$\langle \psi_i | = \sum_k C_{ik}^* \langle k | \quad (8.11b)$$

for *bra*-functions. The expansion coefficients obey the matrix eigenvalue equation:

$$\sum_q H_{pq} C_{iq} = E_i C_{ip} \quad (8.12)$$

where the matrix elements H_{pq} are defined as:

$$H_{pq} = \sum_i E_i \langle p|\psi_i\rangle \langle \psi_i|q\rangle,$$

which, using Eq. (8.11) becomes:

$$H_{pq} = \sum_{ikl} E_i C_{ik} C_{il}^* \langle p|k\rangle \langle l|q\rangle = \sum_i E_i C_{ip} C_{iq}^*. \quad (8.13)$$

Substituting the expansions of Eq. (8.11) into Eq. (8.10) the following expression is obtained for operator \hat{H} :

$$\hat{H} = \sum_i E_i \sum_{k,l} C_{ik} C_{il}^* |k\rangle \langle l|$$

which, using the result of Eq. (8.13) reduces to:

$$\hat{H} = \sum_{k,l} H_{kl} |k\rangle \langle l|. \quad (8.14)$$

This is the offdiagonal representation of a one-electron operator in the *bra-ket* formalism. A unitary transformation of the underlying vector space, which brings the matrix of elements H_{kl} to a diagonal form, results in the spectral resolution of \hat{H} given by Eq. (8.10).

The formal similarities between the above treatment and the second quantized approach are obvious. The last result of Eq. (8.14) resembles very much to the second quantized representation of a one-electron operator, cf. Eq. (4.27), and the second quantized counterparts of all previous formulae can easily be identified. The correspondences that have been obtained so far are collected in Table 8.1. This shows that creation operators are analogs of ket functions, while annihilation operators correspond to *bra*-functions. The eigenprojector $|i\rangle \langle i|$ plays a similar role as the particle number operator $\hat{N}_i = a_i^\dagger a_i$ does. The resolution of identity is analogous to the operator of the total number of particles. The

Table 8.1. Formal connection between the bra-ket formalism and second quantization

Bra-ket formalism	Second quantization
$ i\rangle$	a_i^\dagger
$\langle i $	a_i
$\langle i i\rangle$	$\langle \text{vac} a_i a_i^\dagger \text{vac}\rangle$
$ i\rangle\langle i $	$\hat{N}_i = a_i^\dagger a_i$
$\hat{I} = \sum_i i\rangle\langle i $	$\hat{N} = \sum_i a_i^\dagger a_i$
(resolution of the identity)	(particle number operator)
$\hat{H} = \sum_i E_i i\rangle\langle i $	$\hat{H} = \sum_i E_i a_i^\dagger a_i$
(spectral resolution)	(diagonalized form of second quantized operators)
$\hat{H} = \sum_{k,l} H_{kl} k\rangle\langle l $	$\hat{H} = \sum_{k,l} H_{kl} a_k^\dagger a_l$
(offdiagonal resolution)	(second quantized representation of one-electron operators)

spectral resolution of an operator is practically the same as the second quantized representation of an operator in a basis where the matrix elements of this operator form a diagonal matrix. The offdiagonal resolution corresponds the general second quantized form.

The projection property of operator $|i\rangle\langle i|$, cf. Eq. (9.7), can be used to better understand this bra-ket formalism as well as the second quantized representation. Consider the operator:

$$\hat{P} = \sum_{i=1}^M |i\rangle\langle i| \quad (8.15)$$

which is clearly a projector to a finite M-dimensional subspace. Let us project the one-electron Hamiltonian \hat{H} to this subspace:

$$\hat{H}_s = \hat{P}\hat{H}\hat{P}. \quad (8.16)$$

Substituting Eq. (8.15) we may write:

$$\hat{H}_s = \sum_{i,k=1}^M |i\rangle\langle i| H |k\rangle\langle k| = \sum_{i,k=1}^M H_{ik} |i\rangle\langle k| \quad (8.17)$$

thus we obtain a result similar to Eq. (8.14). This suggests that the representation of the Hamiltonian in the *bra-ket* formalism is equivalent to projecting it onto the space spanned by the underlying basis orbitals. If the number of basis functions, M, in Eq. (8.15) goes to infinity, this set may be complete, but the projection property of operator \hat{P} (which is equal to the unity operator \hat{I} of Eq. (8.8) in this case) still remains relevant. As a matter of fact, the original Hamiltonian \hat{H} is defined over the Hilbert space of square-integrable functions (L_2 space), while the *bra-ket* representation is done in the space of abstract “bras” and “kets” which form a linear vector space. Operator \hat{I} of Eq. (8.8) serves as the unity operator within this vector space, and when acting on different wave functions, it projects them onto this space. Thus, the representation by operator \hat{I} as a projector:

$$\hat{H}' = \hat{I}\hat{H}\hat{I} = \sum_{i,k} |i\rangle\langle i| \hat{H} |k\rangle\langle k| = \sum_{i,k} H_{ik} |i\rangle\langle k| \quad (8.18)$$

leads to the *bra-ket* representation of \hat{H} .

Taking advantage of the above-established connection between the bra-ket formalism and second quantization, one may claim that the second quantized form of quantum-mechanical operators can be considered as the projection of the operator onto the space constructed by the underlying one-electron orbitals.

Projecting the Hamiltonian and other quantum-mechanical operators onto a finite basis sets has serious consequences, even if the basis is large. It can be shown that certain quantum-mechanical rules *eo ipso* cannot be represented in finite basis. This leads to serious inconsistencies inherent in practical quantum chemistry where the basis set is finite in nearly all calculations. One such example is given by the Heisenberg commutation rule between the coordinate operator \hat{q} and the canonically conjugated momentum operator \hat{p} :

$$\hat{p}\hat{q} - \hat{q}\hat{p} = \frac{\hbar}{i} N \hat{I} \quad (8.19)$$

where \hat{I} is the operator of the unity and N is the number of electrons. Let us assume that we have a finite basis of dimension M , then \hat{p} and \hat{q} are represented by their second quantized forms:

$$\hat{p} = \sum_{\mu, v} p_{\mu v} a_{\mu}^{+} a_v \quad (8.20a)$$

$$\hat{q} = \sum_{\mu, v} q_{\mu v} a_{\mu}^{+} a_v \quad (8.20b)$$

where the coefficients $p_{\mu v}$ and $q_{\mu v}$ form M by M matrices. The unity operator is represented by:

$$\hat{I} = \sum_{\mu, v} \delta_{\mu v} a_{\mu}^{+} a_v = \sum_{\mu} a_{\mu}^{+} a_{\mu}. \quad (8.21)$$

Substituting these expressions into the Heisenberg commutation rule of Eq. (8.19) we obtain:

$$\sum_{\mu, v, \lambda} (p_{\mu \lambda} q_{\lambda v} - q_{\mu \lambda} p_{\lambda v}) a_{\mu}^{+} a_v = \frac{\hbar}{i} \sum_{\mu} a_{\mu}^{+} a_{\mu}. \quad (8.22)$$

Taking the expectation value of this equation we find:

$$\sum_{\mu, v, \lambda} (p_{\mu \lambda} q_{\lambda v} - q_{\mu \lambda} p_{\lambda v}) P_{v \mu} = \frac{\hbar}{i} \sum_{\mu} P_{\mu \mu} = \frac{\hbar}{i} N \quad (8.23)$$

This equation can be valid only if matrices p and q obey the commutation rule:

$$\sum_{\lambda} (p_{\mu \lambda} q_{\lambda v} - q_{\mu \lambda} p_{\lambda v}) = \frac{\hbar}{i} \delta_{\mu v} \quad (8.24)$$

which is not possible in finite basis.¹ What is our mistake? There is none, just that we applied an incomplete, finite basis. Improving gradually the basis set this situation does not change, even if some of the physical properties, e.g., the energy, have nearly converged. (Usually, the energy converges nicely with increasing the basis size because of its variational property: addition of any new basis function decreases the energy. The same does not hold for other physical properties which do not necessarily improve if a larger basis set is used.) The solution of the paradoxon showed by Eq. (8.24) is possible only in a really complete basis, where a careful analysis of the domains of operators \hat{p} and \hat{q} is necessary.²

Difficulties have also been encountered with other quantum mechanical commutation rules. As known, two physical observables are simultaneously measurable only if their operators commute. The simplest example is the x and

¹ Finite basis involves that Eq. (8.24) leads to a contradiction: If we take the trace of Eq. (8.24), and utilize the mathematical property of the traces as $\text{Tr}(pq - qp) = 0$, we get

$0 = \frac{\hbar}{i} M.$

y component of the position operator for which one must have:

$$\hat{x}\hat{y} - \hat{y}\hat{x} = 0. \quad (8.25)$$

Usually, this is also violated in a finite basis. Violation of the Heisenberg equation of motion for electrons:

$$\hat{p} = \hat{q} = \frac{\hbar}{i} [\hat{r}, \hat{H}] \quad (8.26)$$

has been studied in quantum chemistry in great detail because this rule is important to ensure the equivalence of the so-called “dipole length” and “dipole velocity” formalisms in the calculation of ordinary and rotatory intensities of electronic transitions (Chen 1964, Hansen & Bouman 1977). Without discussing this problem, we note that even if the wave function is sophisticated enough to obey Eq. (8.26), the finite basis expansion always leads to violations of this rule.

Besides the apparent similarities, Table 8.1 illustrates also the obvious formal differences between bras and kets and their second quantized counterparts. Namely, the corresponding symbols are mathematically very different. The *bra* and *ket* vectors are elements of a linear vector space over which quantum-mechanical operators are defined, while the creation and annihilation operators are defined over the abstract space of particle number represented wave functions serving as their carrier space. This carrier space leads to the concept of the vacuum state, which has no analog in the *bra-ket* formalism. Moreover, an essential difference is that the effect of second quantized operators depends on the occupancies of the one-electron levels in the wave function, since no annihilation is possible from an empty level and no electron can be created on an occupied spinorbital. At the same time, the occupancies of orbitals play no role in evaluating bra and ket expressions. Of course, both formalisms yield identical results after calculating the values of matrix elements.

The points discussed above stand for one-electron operators. Generalization of the *bra-ket* formalism for many-electron systems is possible, but somewhat complicated, mainly because of the antisymmetry requirement for many-electron wave functions. The unique preference of second quantization is its natural simplicity in treating many-electron problems.

² The domains of these two operators are not the same (though they have a common part everywhere dense in the L_2 space) thus $\text{Tr } \hat{p}\hat{q} \neq \text{Tr } \hat{q}\hat{p}$.

9 Using Spatial Orbitals

In many applications, especially for programming purposes, it is very important to rewrite theoretical expressions containing spinorbitals in terms of spatial orbitals. This is imperative for the sake of effective computation, since the number of spinorbitals is twice as large as the number of spatial orbitals. If the computational procedure manipulates with the full list of two-electron integrals, the time requirement of the calculation is proportional at least to the fourth power of the number of basis functions. Consequently, if the programming would be done in terms of spinorbitals, this would lead to a $2^4 = 64$ -times longer run. The situation is usually worse, since the time requirement of a quantum chemical calculation including the approximate treatment of electron correlation is proportional to the (at least) 6th power of the number of orbitals.

In this section we give some examples how one can rewrite spinorbital expressions in a simple manner. The basis of this transcription is that any integration over spinorbitals contains also summation over spin functions.

Consider first the expectation value of a one-electron operator \hat{A} :

$$\langle \hat{A} \rangle = \sum_{\mu, v} \langle \mu | \hat{A} | v \rangle P_{v\mu} \quad (9.1)$$

where the Greek indices refer to spinorbitals. Any spinorbital μ consist of a spatial part m and a spin part denoted σ_m :

$$\mu = \{m, \sigma_m\}. \quad (9.2)$$

The spin part σ_m can be either α and β . Formally, any summation over spinorbitals can therefore be rewritten as:

$$\sum_{\mu} = \sum_m \sum_{\sigma_m} \quad (9.3)$$

Using this formal identity, the expectation value in Eq. (9.1) becomes:

$$\langle \hat{A} \rangle = \sum_{m, n} \sum_{\sigma_m, \sigma_n} \langle m, \sigma_m | \hat{A} | n, \sigma_n \rangle P_{n,m}^{\sigma_n \sigma_m}. \quad (9.4)$$

The next step is to eliminate the spin functions from this result. This can be done by performing the integration over spin functions. Assuming that operator \hat{A} is spin independent, one has:

$$\langle A \rangle = \sum_{m, n} \sum_{\sigma_m, \sigma_n} \langle m | \hat{A} | n \rangle \langle \sigma_m | \sigma_n \rangle P_{n,m}^{\sigma_n \sigma_m}. \quad (9.5)$$

Due to the orthogonality of spin functions, integration over spin gives:

$$\langle \sigma_m | \sigma_n \rangle = \delta_{\sigma_m, \sigma_n}. \quad (9.6)$$

Substituting this condition into Eq. (9.5) we are left with:

$$\begin{aligned} \langle \hat{A} \rangle &= \sum_{m,n} \langle m | \hat{A} | n \rangle \sum_{\sigma_m} P_{n,m}^{\sigma_m \sigma_m} \\ &= \sum_{m,n} \langle m | \hat{A} | n \rangle (P_{n,m}^{\alpha\alpha} + P_{n,m}^{\beta\beta}). \end{aligned} \quad (9.7)$$

Let us introduce the spinless density matrix P referring to the spatial orbitals as:

$$P_{nm} = P_{nm}^{\alpha\alpha} + P_{nm}^{\beta\beta}. \quad (9.8)$$

With this notation one may write the expectation value of a spinless one-electron operator as:

$$\langle A \rangle = \sum_{m,n} \langle m | \hat{A} | n \rangle P_{nm}. \quad (9.9)$$

The forms of Eqs. (9.1) and (9.9) are similar; the essential difference is that the latter is expressed over spatial orbitals thus it involves a summation over a much lesser number of terms. To be more specific, since the number of spinorbitals is twice as large as that of the corresponding spatial functions, the number of terms in Eq. (9.1) is four times more as compared to those in Eq. (9.9).

For the next example, let us rewrite the Hartree-Fock energy expression (cf. Sect. 7.3) in terms of spatial orbitals. The problem for the one-electron part has been solved above. Let us be concerned with the two-electron part $E^{(2)}$:

$$\begin{aligned} E^{(2)} &= \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{v\mu} P_{\sigma\lambda} [\mu\lambda | v\sigma] - \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{v\mu} P_{\sigma\lambda} [\mu\lambda | \sigma v] \\ &= E_C^{(2)} + E_X^{(2)} \end{aligned}$$

where $E_C^{(2)}$ denotes the Coulomb term while $E_X^{(2)}$ refers to exchange. These two terms can be manipulated in a similar manner, though the results will be slightly different. Consider first the Coulomb term:

$$\begin{aligned} E_C^{(2)} &= \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{v\mu} P_{\sigma\lambda} [\mu\lambda | v\sigma] \\ &= \frac{1}{2} \sum_{mnls} \sum_{\sigma_m \sigma_n \sigma_l \sigma_s} P_{nm}^{\sigma_m \sigma_m} P_{sl}^{\sigma_l \sigma_l} \left[\begin{array}{c|c} \sigma_m \sigma_l & \sigma_n \sigma_s \\ ml & ns \end{array} \right] \end{aligned} \quad (9.10)$$

where the notations for the spatial orbitals are introduced as $\mu = \{m, \sigma_m\}$, $\lambda = \{l, \sigma_l\}$, etc., and the spin labels in the two electron integrals are written above the corresponding spatial index. The same convention is used for the indices of the density matrix. The integration over spin in the two-electron integrals can easily be performed:

$$\left[\begin{array}{c|c} \sigma_m \sigma_l & \sigma_n \sigma_s \\ ml & ns \end{array} \right] = [ml | ns] \delta_{\sigma_m \sigma_n} \delta_{\sigma_l \sigma_s}. \quad (9.11)$$

Substituting this expression into the Coulomb term Eq. (9.10) one gets:

$$\begin{aligned} E_C^{(2)} &= \frac{1}{2} \sum_{mnls} \sum_{\sigma_m \sigma_l} P_{nm}^{\sigma_m \sigma_m} P_{sl}^{\sigma_l \sigma_l} [ml|ns] \\ &= \frac{1}{2} \sum_{mnls} (P_{nm}^{\alpha\alpha} + P_{nm}^{\beta\beta}) (P_{sl}^{\alpha\alpha} + P_{sl}^{\beta\beta}) [ml|ns] \\ &= \frac{1}{2} \sum_{mnls} P_{nm} P_{sl} [ml|ns] \end{aligned} \quad (9.12)$$

where the spin-free density matrices were introduced according to Eq. (9.8).

The derivation for the exchange term of $E_X^{(2)}$ is analogous:

$$\begin{aligned} E_X^{(2)} &= -\frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{v\mu} P_{\sigma\lambda} [\mu\lambda|\sigma v] \\ &= -\frac{1}{2} \sum_{mnls} \sum_{\sigma_m \sigma_n \sigma_l \sigma_s} P_{nm}^{\sigma_n \sigma_m} P_{sl}^{\sigma_s \sigma_l} [ml|sn] \delta_{\sigma_m \sigma_s} \delta_{\sigma_l \sigma_n} \\ &= -\frac{1}{2} \sum_{mnls} \sum_{\sigma_m \sigma_l} P_{nm}^{\sigma_l \sigma_m} P_{sl}^{\sigma_m \sigma_l} [ml|sn]. \end{aligned} \quad (9.13)$$

We can take into account that, by the definition of the density matrix Eq. (7.5), its two index must refer to the same spin:

$$P_{nm}^{\sigma_l \sigma_m} = P_{sl}^{\sigma_m \sigma_m} \delta_{\sigma_m \sigma_l}, \quad (9.14)$$

thus for the exchange energy one gets:

$$\begin{aligned} E_X^{(2)} &= -\frac{1}{2} \sum_{mnls} \sum_{\sigma_m} P_{nm}^{\sigma_m \sigma_m} P_{sl}^{\sigma_m \sigma_m} [ml|sn] \\ &= -\frac{1}{2} \sum_{mnls} (P_{nm}^{\alpha\alpha} P_{sl}^{\alpha\alpha} + P_{nm}^{\beta\beta} P_{sl}^{\beta\beta}) [ml|sn]. \end{aligned} \quad (9.15)$$

To eliminate the explicit reference to spin functions, the *spin density* matrix may be defined as:

$$R_{nm} = P_{nm}^{\alpha\alpha} - P_{nm}^{\beta\beta}. \quad (9.16)$$

With this notation the $P^{\alpha\alpha}$ and $P^{\beta\beta}$ matrices can be expressed as:

$$P_{nm}^{\alpha\alpha} = (P_{nm} + R_{nm})/2 \quad (9.17)$$

$$P_{nm}^{\beta\beta} = (P_{nm} - R_{nm})/2. \quad (9.18)$$

Substituting these relations into the exchange term Eq. (9.15) one obtains:

$$\begin{aligned} E_X^{(2)} &= -\frac{1}{8} \sum_{mnls} \{(P_{nm} + R_{nm})(P_{sl} + R_{sl}) \\ &\quad + (P_{nm} - R_{nm})(P_{sl} - R_{sl})\} [ml|sn]. \end{aligned} \quad (9.19)$$

This expression becomes much simpler if the system under consideration has a closed-shell singlet electronic structure. Under this condition the probabilities for finding an electron with spin α and β are equal, thus:

$$P_{nm}^{\alpha\alpha} = P_{nm}^{\beta\beta}. \quad (9.20)$$

That is:

$$R_{nm} = P_{nm}^{\alpha\alpha} - P_{nm}^{\beta\beta} = 0, \quad (9.21)$$

and the exchange term reduces to:

$$E_X^{(2)} = -\frac{1}{4} \sum_{mnls} P_{nm} P_{sl} [ml|sn]. \quad (9.22)$$

Collecting now all terms which enter the energy expression, that is Eqs. (9.12), (9.22), and the one-electron part based on Eq. (9.9), we get for the Hartree-Fock energy of a closed-shell state in terms of spatial orbitals:

$$E = \sum_{m,n} h_{mn} P_{nm} + \frac{1}{2} \sum_{mnls} P_{nm} P_{sl} \left([ml|ns] - \frac{1}{2} [ml|sn] \right). \quad (9.23)$$

Note that if using spatial orbitals the exchange integrals enter the energy expression with a factor of 1/2 relative to the Coulombic part.

The energy expression of Eq. (9.23) can be written in terms of the Hartree-Fock molecular orbitals which diagonalize the density matrix P [cf. Eq. (7.15)]. The diagonal elements are the occupation numbers (n_i) of the spatial orbitals which can be 0, 1, or 2. For a restricted HF wave function in a closed-shell state $n_i = 0$ or 2, that is a level is either empty or doubly filled.¹ That is, each summation containing density matrix elements P_{ij} can be written as:

$$\sum_{i,j} P_{ij} \rightarrow 2 \sum_i^{\text{occ}}.$$

By virtue of this transformation, Eq. (9.23) in terms of MOs becomes:

$$E = 2 \sum_i^{\text{occ}} h_{ii} + \sum_{i,k}^{\text{occ}} (2[ik|ik] - [ik|ki]). \quad (9.24)$$

The Fockian can also be introduced into the spatial energy expression of Eq. (9.23) by defining it over spatial orbitals as²:

$$F_{mn} = h_{mn} + \sum_{l,s} P_{sl} \left([ml|ns] - \frac{1}{2} [ml|sn] \right) \quad (9.25)$$

which is analogous to the spinorbital expression of Eq. (7.29). Combining Eqs. (9.23) and (9.25) one gets:

¹ Such states are automatically singlets.

² This definition is consistent to rewriting the spinorbital expression of the Fock matrix, and introducing the spatial density matrix Eq. (9.8).

$$E = \frac{1}{2} \sum_{m,n} (h_{mn} + F_{mn}) P_{nm} \quad (9.26)$$

which is analogous to Eq. (7.30). The summation here, as it was already emphasized, runs over only a lesser number of orbitals than in Eq. (7.30).

In term of MOs, Eq. (9.26) writes:

$$E = \sum_i^{\text{occ}} (h_{ii} + F_{ii}) = \sum_i^{\text{occ}} (h_{ii} + \varepsilon_i) \quad (9.27)$$

which is the analog of Eq. (7.33) in terms of spatial orbitals. Note the absence of the factor of 1/2.

On the basis of the experience gained in transcribing expectation values to spatial orbitals, it is very simple to put down second quantized operators in spatial form. For a one-electron operator we have:

$$\hat{A} = \sum_{\mu,\nu} A_{\mu\nu} a_{\mu}^+ a_{\nu} = \sum_{m,n} \sum_{\sigma_m \sigma_n} A_{mn} \delta_{\sigma_m \sigma_n} a_{m\sigma_m}^+ a_{n\sigma_n} \quad (9.28)$$

where the Kronecker δ results from the integration over spin functions in the matrix element $A_{\mu\nu}$. We get:

$$\hat{A} = \sum_{m,n} A_{mn} \sum_{\sigma} a_{m\sigma}^+ a_{n\sigma}. \quad (9.29)$$

A similar formula may be obtained for a two-electron operator. Accordingly, the second quantized Hamiltonian in terms of spatial orbitals becomes:

$$\hat{H} = \sum_{m,n} h_{mn} \sum_{\sigma} a_{m\sigma}^+ a_{n\sigma} + \frac{1}{2} \sum_{mnls} [mn|ls] \sum_{\sigma_1 \sigma_2} a_{m\sigma_1}^+ a_{n\sigma_2}^+ a_{s\sigma_2} a_{l\sigma_1}. \quad (9.30)$$

It is important to observe that the spin labels are not eliminated from the second quantized form of the Hamiltonian. They do not appear in the list of the integrals, however, which corresponds to the fact that the first quantized Hamiltonian is spin-independent and permits one to use the spin-free formalism. But it is essential to realize that creation and annihilation operators cannot be specified merely for spatial orbitals.

If one wants to specify the Hartree-Fock determinantal wave function in terms of spatial molecular orbitals ψ_i , one may write:

$$|\Psi_{HF}\rangle = \psi_{1\alpha}^+ \psi_{1\beta}^+ \psi_{2\alpha}^+ \psi_{2\beta}^+ \dots \psi_{(N/2)\alpha}^+ \psi_{(N/2)\beta}^+ |vac\rangle \quad (9.31)$$

for a closed-shell state of $N/2$ doubly occupied MOs. Note that spin labels are not eliminated, since the Pauli principle requires antisymmetry in terms of one-electron spinorbitals.

In many applications it is useful to have a more general recipe for rewriting integrals over spinorbitals to those over spatial ones. Let us see, for instance, the product of three two-electron integrals:

$$[\mu\nu|\lambda\sigma][\lambda\sigma|\kappa\rho][\kappa\rho|\mu\nu] \quad (9.32a)$$

and assume that summation over all indices is performed. (Such types of expres-

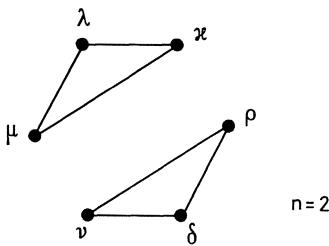


Fig. 9.1. Simple graphical tool for spin integration in Eq. (9.32). The dots indicate spinorbitals over which summation is performed. The bars connecting dots show the coincidence of the corresponding labels resulting from integration over spin; n is the number of disjunct graphs in the resulting diagram

sions frequently occur in perturbation theory.) In terms of spatial orbitals one writes:

$$[mn|ls][ls|kr][kr|mn]\delta_{\sigma_m\sigma_l}\delta_{\sigma_n\sigma_s}\delta_{\sigma_i\sigma_k}\delta_{\sigma_i\sigma_r}\delta_{\sigma_k\sigma_m}\delta_{\sigma_i\sigma_n} \quad (9.32b)$$

where the Kronecker δ -s come from integration over spin. Taking into account the six Kronecker δ -s, from the six original spin labels we are left with two independent ones, thus summation over spin results in a factor of 4. This consideration can be formulated in a quite general manner. Having an expression in which summation is performed over a certain number of spinorbitals, we arrange the symbols of orbitals as dots around a circle. Now, if some of the spin labels must coincide due to integration over spin, we connect the two corresponding dots. So each line on the diagram reflects a Kronecker δ resulting from spin integration. In this manner the number of independent spin labels will be equal to n , where the diagram decouples into n disjunct graphs. The summation over spin results in a factor of 2^n , since any independent summation label brings a factor of 2. As an illustration, the graph for Eqs. (9.32) is given in Fig. 9.1.

Problem 9.1

Apply the above simple diagrammatic rule to establish the weighting factor for the spatial equivalent of the following spinorbital expressions:

- $\sum [\mu\nu|\lambda\sigma][\lambda\sigma|\mu\nu]$
- $\sum [\mu\nu|\lambda\sigma][\lambda\sigma|\nu\mu]$
- $\sum [\mu\nu|\lambda\sigma][\lambda\sigma|\mu\nu]h_{\mu\nu}$

where the summation is performed over all indices.

At the end of this section, we put down the expressions for the basic anti-commutator rules in terms of spatial orbitals. Based on Eq. (9.2), they obviously read as:

$$[a_{m\sigma_m}^+, a_{n\sigma_n}] = \delta_{mn}\delta_{\sigma_m\sigma_n} \quad (9.33)$$

while:

$$[a_{m\sigma_m}^+, a_{n\sigma_n}^+] = [a_{m\sigma_m}, a_{n\sigma_n}] = 0. \quad (9.34)$$

Transcription of formulae from spinorbitals to spatial ones may be quite complicated in the general case, especially if one cannot use the simplifications permitted by a closed-shell configuration and the Restricted Hartree-Fock (RHF) wave function. In most cases, it is still a simpler task to perform a derivation in terms of spinorbitals, and translate the results afterwards: carrying the spin labels throughout the derivation may complicate the whole story tremendously.

In any case, such transcriptions can be done along the lines presented above. Later on in this book we shall get some practice in rewriting formulae derived in terms of spinorbitals to those in terms of spatial ones.

10 Some Model Hamiltonians in Second Quantized Form

This section is devoted to give an overview on the second quantized forms of various model Hamiltonians used extensively in the everyday practice of quantum chemistry and theoretical solid-state physics. In many scientific publications different quantum chemical models and approximations are introduced or defined by means of the second quantized approach. These models might be as simple as the Hückel model, for example. Quite often no specific features of second quantization are utilized, but this formalism is used as a convenient language to define various model Hamiltonians.¹ It seems to be useful therefore to review the most frequently applied model Hamiltonians. For further reading we refer to the brief monograph by Del Re et al. (1980). A simple description of the semiempirical schemes discussed below, not using second quantization, can be found in Náray et al. (1987).

10.1 π -electron Hamiltonians

10.1.1 Hückel level

We start with discussing the simplest case, the Hückel scheme. This model has been introduced into quantum chemistry a long time ago (Hückel 1930), and practically it still represents the only possibility to obtain (at least semi-quantitative) information about extended π -electron systems containing several dozens (or hundreds) of atoms (Kertész & Surján 1981, Surján & Kuzmany 1986).

The essence of this model is as follows. If the system lies in the xy plane², the underlying basis set consists of the $2p_z$ atomic orbitals of the atoms, that is, each atom contributes by a single orbital of symmetry π . The model remains strictly in the one-electron scheme, which means that it does not take into account any electron-electron interaction explicitly. Consequently, the Hückel Hamiltonian has the form of a one-electron Hamiltonian:

$$\hat{H} = \sum_{\mu, \nu} h_{\mu\nu} a_{\mu}^+ a_{\nu}. \quad (10.1)$$

¹ This is most often the case in the solid state literature.

² In its original formulation, the Hückel model, as any π -electron scheme, is applicable only for planar systems.

As discussed in the previous section, in terms of spatial orbitals this Hamiltonian writes:

$$\hat{H} = \sum_{m,n} \sum_{\sigma} h_{mn} a_{m\sigma}^+ a_{n\sigma}. \quad (10.2)$$

Here the labels m and n run over all $2p_z$ orbitals of the system. The matrix elements h_{nm} in the Hückel model are not evaluated by integration, but are parametrized empirically. The diagonal elements h_{mm} are the so-called Hückel α -parameters (α_m), and the off-diagonal elements h_{nm} , ($n \neq m$) have nonzero values only if the sites n and m are first neighbors in the chemical sense. This first-neighbor approximation is a characteristic feature of the Hückel model, and as it will be discussed later, it has some particular significance. The nonvanishing h_{nm} ($m \neq n$) matrix elements are the so-called β integrals:

$$\hat{H} = \sum_m \alpha_m \sum_{\sigma} a_{m\sigma}^+ a_{m\sigma} + \sum_{m,n}^{\text{(first neighbours)}} \beta_{mn} \sum_{\sigma} a_{m\sigma}^+ a_{n\sigma}. \quad (10.3)$$

The β_{nm} values are also called resonance or hopping integrals. Since the first neighbors are bonds, we may write:

$$\hat{H} = \sum_m \alpha_m \sum_{\sigma} a_{m\sigma}^+ a_{m\sigma} + \sum_i \beta_i \sum_{\sigma} (a_{i_1\sigma}^+ a_{i_2\sigma} + a_{i_2\sigma}^+ a_{i_1\sigma}). \quad (10.4)$$

Here the label i runs over all the bonds of the system connecting atoms i_1 and i_2 . The notation β_i stands for $\beta_{i_1 i_2}$ and it is utilized that:

$$\beta_{i_1 i_2} = \beta_{i_2 i_1} = \beta_i.$$

(Note that in Eq. (10.3) all bonds are counted twice; for instance, if atoms 2 and 3 are first neighbors, both β_{23} and β_{32} contribute.)

It is usual to write Eq. (10.4) in a simpler form by realizing that the Hermitian conjugate of the operator string:

$$a_{i_1\sigma}^+ a_{i_2\sigma}$$

is just:

$$a_{i_2\sigma}^+ a_{i_1\sigma}.$$

Using this, the Hückel Hamiltonian takes the form:

$$\hat{H} = \sum_m \alpha_m \sum_{\sigma} a_{m\sigma}^+ a_{m\sigma} + \sum_i \beta_i \sum_{\sigma} (a_{i_1\sigma}^+ a_{i_2\sigma} + \text{h.c.}) \quad (10.5)$$

where h.c. means ‘Hermitian conjugate’. This way of writing the Hamiltonian is very convenient because it reflects explicitly the Hermitian nature of the Hamiltonian.

In many applications of the Hückel method one does not consider hetero-atoms, that is, all atoms are carbons, for example. Then all α_m -s are equal and, as a first approximation, all β_i are equal, too. This fact greatly simplifies the Hamiltonian of Eq. (10.5), which reduces to:

$$\hat{H} = \alpha \sum_m \sum_{\sigma} a_{m\sigma}^+ a_{m\sigma} + \beta \sum_i \sum_{\sigma} (a_{i_1\sigma}^+ a_{i_2\sigma} + \text{h.c.}) \quad (10.6)$$

Moreover, the origin of the energy scale can always be chosen so that $\alpha = 0$, and the energy unit can be taken equal to β . Then we have:

$$H = \sum_i \sum_{\sigma} (a_{i_1\sigma}^+ a_{i_2\sigma} + \text{h.c.}) \quad (10.7)$$

which is indeed a very simple Hamiltonian since no integrals are present. There are no parameters of this Hamiltonian. It merely reflects the molecular topology, or better, the molecular graph (Graovac et al. 1977; Trinajstic 1983): the structure of bonds which connect neighboring atoms. This simple theory gives the information how far the molecular topology alone determines the electronic structure.

It appears to be useful to stop here for a while and discuss the usefulness and limitations of the Hückel Hamiltonian. Of course, one cannot expect that fine details of the electronic structure will be reflected by this primitive approach. Nevertheless, there are many characteristics of the Hückel model (not only the computational feasibility) which keeps it in the state-of-art especially in the field of solid-state physics. Since the Hamiltonian of Eq. (10.7) is the simplest one describing a π -electron system, it is often useful and informative to check whether the physical or chemical effect under study could be explained by this model. If yes, and a qualitative explanation is sufficient, there is no need to go to more sophisticated schemes which complicate the interpretation of the results. One has to keep in mind, however, that there are several real π -electron effects which cannot be described by Hückel-type Hamiltonians of the above forms. These are connected to any of the two main shortcomings of the Hückel model for π electrons: (i) the lack of explicit electron-electron interaction; and (ii) the insensitivity of the Hamiltonian to the geometrical arrangement of the atoms. As an example for (i), the energy levels of the system are obtained simply by diagonalizing the Hamiltonian of Eq. (10.7). That is, they do not depend on the number of electrons present in the system: if the basis set of AOs is not changed, removing or putting an electron to an orbital does not change the levels for other electrons in the Hückel model, which is far from being true in more sophisticated one-electron models which take into account electron-electron interactions self-consistently.

Some advantage of the Hückel model is manifested in the possibility to write down the Hamiltonian for special systems explicitly, and to solve the model analytically in some cases. (Analytical solutions, if possible to find, are preferred to numerical ones since the former give a much better insight and permit to draw more general conclusions.)

Let us specify the Hückel Hamiltonian for some important special cases.

A system is called one-dimensional if its atoms form a chain, i.e., there is no branching in the molecular graph. As noted above, the Hückel Hamiltonian is insensitive to the geometrical arrangement, thus a geometrically bent or twisted system, in principle, can be considered as (quasi)one-dimensional. Under this condition, numbering the atoms in the chain consecutively from one end to

the other, the Hamiltonian of Eq. (10.5) reduces to:

$$H^{1D} = \sum_m \alpha_m \sum_{\sigma} a_{m\sigma}^+ a_{m\sigma} + \sum_m \beta_m \sum_{\sigma} (a_{m,\sigma}^+ a_{m+1,\sigma} + \text{h.c.}) \quad (10.8)$$

Here the label m runs over all atoms in the chain and β_m is a short-hand notation for $\beta_{m,m+1} = \beta_{m+1,m}$ denoting the hopping integral between the neighboring atoms m and $m + 1$. Equation (10.8) can be simplified analogously to Eqs. (10.6) and (10.7) if α and β are uniform constants.

Several extensions of this Hamiltonian have been proposed to treat one-dimensional systems. Their typical philosophy is the following. In practice, one often deals with a particular physical system and one is usually interested in a particular physical property. Then, if the system under study is too complicated to be studied by a general Hamiltonian, one may develop specific model Hamiltonians which can only describe the given system with the desired properties. This type of modelling is very common in theoretical solid-state physics, and has often lead to a fruitful interplay between theory and experiment.

An interesting specific model Hamiltonian was proposed by Longuet-Higgins and Salem (1959) for the polyacetylene chain denoted as $(CH)_x$. This system consists of alternating double ($C = C$) and single ($C - C$) bonds in a one-dimensional chain of carbon atoms. Due to conjugation, however, the CC bonds are not purely single or double, but the bond orders are functions of the corresponding bond distances which vary along the chain. The aim of the theory is just to describe this conjugation and establish a connection between conjugation and various physical properties.

To describe this system, Longuet-Higgins and Salem proposed the following model Hamiltonian:

$$H^{LS} = \sum_{n,\sigma} \beta_n [a_{n,\sigma}^+ a_{n+1,\sigma} + \text{h.c.}] + \sum_n f_n(r_n) \quad (10.9)$$

where the resonance integral β_n for the $C \cdots C$ bond n is not an a priori constant, as it were in the standard Hückel theory, but it is expressed as an exponential function of the corresponding bond length r_n :

$$\beta_n = -A e^{-ar_n} \quad (10.10)$$

where the empirical constants A and a are parameters of the Hamiltonian. The function $f_n(r_n)$ is an empirical potential for the σ skeleton to describe the stretching of the σ component of the $C \cdots C$ bond n . Due to its fully empirical nature, the function f_n is not represented by a second quantized operator, but it appears simply as a constant in the π -electron Hamiltonian. It is parametrized to ensure that Coulson's linear bond length—bond order relationship (Coulson 1970) is satisfied. Using this model, one can optimize the bond lengths along the chain by minimizing the energy functional $\langle \Psi | H^{LS} | \Psi \rangle$, and one can study many interesting phenomena showed by polyacetylene (Kertész & Surján 1981). Recently, a slightly extended version of the Longuet-Higgins Hamiltonian was proposed (Surján & Kuzmany 1986):

$$\hat{H} = \sum_{n,\sigma} \alpha_n a_{n\sigma}^+ a_{n\sigma} + \sum_{n,\sigma} \beta_n \cos \phi_n [a_{n,\sigma}^+ a_{n+1,\sigma} + \text{h.c.}] + \sum_n f_n(r_n) \quad (10.11)$$

where the parameters α_n are devoted to describe local impurities (heteroatoms, substitutions, etc.) at the site n in the spirit of the Hückel model, while the factor $\cos \phi_n$ at the resonance integral permits one to study the effect of a cleavage of conjugation at the bond n which may result, e.g., from twisting the chain by an angle of ϕ_n around this bond.

For polyacetylene, many authors apply the so-called SSH Hamiltonian introduced by Su, Schrieffer, and Heeger (1980), which is an alternative to the Longuet-Higgins model. The difference is only in the handling of the σ core potential function f_n and in the parametrization of the model.

10.1.2 The Hubbard Model

The simplest possibility to switch on the mutual interaction between π -electrons is given by the Hubbard scheme. This model takes into account only the most dominant effect of electron-electron interaction: the so-called on-site repulsion. This means that if there is an electron on the site ($2p_z$ orbital) m, putting an additional electron on this site involves a significant increase in energy as a consequence of the Coulomb repulsion. The on-site repulsion can be incorporated into the π -electron Hamiltonian by adding a two-electron term corresponding to each site:

$$H^{\text{HUBBARD}} = \sum_{nm\sigma} h_{nm} a_{n\sigma}^+ a_{m\sigma} + \frac{1}{2} \sum_{\sigma_1\sigma_2} \gamma_n a_{n\sigma_1}^+ a_{n\sigma_2}^+ a_{n\sigma_2} a_{n\sigma_1} \quad (10.12)$$

where γ_n is the on-site repulsion parameter at atom n. This form of the Hamiltonian can be deduced from the more general Hamiltonian by keeping only the very diagonal elements of the electron repulsion integral matrix:

$$\gamma_n = [nn|nn].$$

The second summation label for the spin, σ_2 , is redundant since it must be different from σ_1 otherwise $a_{n\sigma_1}$ and $a_{n\sigma_2}$ would coincide. Thus, the Hubbard Hamiltonian can be rewritten as:

$$H^{\text{HUBBARD}} = \sum_{nm,\sigma} h_{nm} a_{n\sigma}^+ a_{m\sigma} + \frac{1}{2} \sum_{n\bar{\sigma}} \gamma_n a_{n\sigma}^+ a_{n\bar{\sigma}}^+ a_{n\bar{\sigma}} a_{n\sigma} \quad (10.13)$$

where $\bar{\sigma}$ denotes the dual spinfunction³ to σ .

The two-electron part of the Hubbard Hamiltonian can be brought into a simpler form by realizing that the density operators:

$$\hat{N}_{n\sigma} = a_{n\sigma}^+ a_{n\sigma} \quad (10.14)$$

can be introduced in a natural manner. To do this, one has to apply the

³That is, $\bar{\sigma} = \beta$ if $\sigma = \alpha$ and $\bar{\sigma} = \alpha$ if $\sigma = \beta$.

commutator rules and move the operator $a_{n\sigma}$ left, to the place right after $a_{n\sigma}^+$. The transposition of $a_{n\bar{\sigma}}$ and $a_{n\sigma}$ simply changes the sign of the two-electron term, and the same holds for the transposition of $a_{n\sigma}^+$ and $a_{n\bar{\sigma}}$ because of the differences of their spin labels. Accordingly:

$$H^{\text{HUBBARD}} = \sum_{nm,\sigma} h_{nm} a_{n\sigma}^+ a_{m\sigma} + \frac{1}{2} \sum_{n\sigma} \gamma_n a_{n\sigma}^+ a_{n\sigma} a_{n\bar{\sigma}}^+ a_{n\bar{\sigma}}. \quad (10.15)$$

By introducing now the particle number operator of Eq. (10.14) this Hamiltonian takes the form:

$$H^{\text{HUBBARD}} = \sum_{nm,\sigma} h_{nm} a_{n\sigma}^+ a_{m\sigma} + \frac{1}{2} \sum_n \gamma_n \sum_{\sigma} \hat{N}_{n\sigma} \hat{N}_{n\bar{\sigma}}. \quad (10.16)$$

The summation over the spin label σ in the two-electron term can be eliminated since $\hat{N}_{n\alpha}$ and $\hat{N}_{n\beta}$ commute:

$$\begin{aligned} H^{\text{HUBBARD}} &= \sum_{nm,\sigma} h_{nm} a_{n\sigma}^+ a_{m\sigma} + \frac{1}{2} \sum_n \gamma_n (\hat{N}_{n\alpha} \hat{N}_{n\beta} + \hat{N}_{n\beta} \hat{N}_{n\alpha}) \\ &= \sum_{nm,\sigma} h_{nm} a_{n\sigma}^+ a_{m\sigma} + \sum_n \gamma_n \hat{N}_{n\alpha} \hat{N}_{n\beta}. \end{aligned} \quad (10.17)$$

The last term is usually written as:

$$\sum_n \gamma_n \hat{N}_{n\uparrow} \hat{N}_{n\downarrow}.$$

The one-electron part of the Hubbard Hamiltonian is mostly simplified in the same manner as in the Hückel model, cf. Eqs. (10.5 – 10.7). Having a homogenous system, the on-site repulsion parameters γ_n can also be taken equal. This uniform value is often denoted by U , and within this condition the Hubbard Hamiltonian takes the form:

$$H^{\text{HUBBARD}} = \sum_{i,\sigma} (a_{i_1,\sigma}^+ a_{i_2,\sigma} + \text{h.c.}) + U \sum_n \hat{N}_{n\alpha} \hat{N}_{n\beta} \quad (10.18)$$

where the label i runs over all bonds connecting atoms i_1 and i_2 , while n runs over all atoms (sites) of the system. The on-site repulsion integral U is the only parameter of this model. The adjustment of the Hubbard model described by this Hamiltonian to a particular π -electron system is possible by selecting an appropriate value for this parameter. Differences between optimally selected values are usually interpreted as changes in the importance of electron-electron repulsion (Baeriswyl 1987).

While the solution of the Hückel model is mathematically very simple (it consists of the diagonalization of the matrix of the one-electron integrals h_{nm}), the diagonalization of the Hubbard Hamiltonian is not always straightforward (Whaley & Falicov 1987). One-determinantal wave functions can be calculated analogously to the Hartree-Fock theory by an iterative procedure; this corresponds to averaging the two-electron term. Such wave functions are only approximations to the exact solution of the Hubbard Hamiltonian whose exact eigenfunctions can be expressed only as linear combinations of determinants.

10.1.3 The Pariser-Parr Pople (PPP) Model

The PPP model introduced by Pariser and Parr (1953) and Pople (1953) can be considered as a generalization of the Hubbard model. In the PPP Hamiltonian not only “on-site” repulsion but two-center two-electron interactions are also considered:

$$H^{\text{PPP}} = \sum_{nm,\sigma} h_{nm} a_{n\sigma}^\dagger a_{m\sigma} + \frac{1}{2} \sum_{nm} \sum_{\sigma_1 \sigma_2} \gamma_{nm} a_{n\sigma_1}^\dagger a_{m\sigma_2}^\dagger a_{m\sigma_2} a_{n\sigma_1} \quad (11.19)$$

where the diagonal elements of γ_{nn} are the on-site repulsion parameters which are present even in the Hubbard model, while γ_{nm} is a Coulomb repulsion integral between sites n and m. This Hamiltonian can be deduced from the most-general π -electron Hamiltonian by keeping only the two-electron integrals of type:

$$\gamma_{nm} = [nm|nm]$$

which are often called Coulomb-type integrals.⁴ In most parametrization, only first-neighbor γ_{nm} integrals are kept, which are either approximated simply as:

$$\gamma_{nm} = 1/R_{nm} \quad (10.20)$$

(in atomic units, R_{nm} being the distance between sites n and m), or they are parametrized by some empirical formulae through the on-site repulsion parameters γ_{nn} . The two most often used formulas are:

(i) the Mataga-Nishimoto approximation:

$$\gamma_{nm} = \frac{1}{R_{nm} + 2/(\gamma_{nn} + \gamma_{mm})} \quad (10.21)$$

(ii) and the Ohno-formula:

$$\gamma_{nm} = \frac{1}{\sqrt{R_{nm}^2 + 4/(\gamma_{nn} + \gamma_{mm})^2}}. \quad (10.22)$$

The two-electron part of the PPP Hamiltonian can be expressed in terms of the particle number operators similarly to the Hubbard case. Applying the relevant anticommutation rules one may write H^{PPP} as:

⁴ We note in this respect that there is a frequent confusion in the nomenclature for Coulomb integrals. The reason is that two completely different things are denoted by this term. The first one is the sum of integrals which appear in the Coulomb part of the HF energy expression for example, cf. Eq. (7.28). The second thing is the special integral of type $[nm|nm]$. This is denoted as Coulomb-type in order to distinguish it from the exchange-type integral $[nm|mn]$. But it is very important to realize that both Coulomb and exchange type integrals enter the Coulombic part of the energy (or Fockian). Both enter also the exchange part of the energy as defined in Eq. (7.28).

$$\begin{aligned} H^{PPP} = & \sum_{nm,\sigma} h_{nm} a_{n\sigma}^+ a_{m\sigma} \\ & + \frac{1}{2} \sum_{nm} \sum_{\sigma_1 \sigma_2} \gamma_{nm} [a_{n\sigma_1}^+ a_{n\sigma_1} a_{m\sigma_2}^+ a_{m\sigma_2} - \delta_{nm} \delta_{\sigma_1 \sigma_2} a_{n\sigma_1}^+ a_{m\sigma_2}] \end{aligned} \quad (10.23)$$

which reduces to

$$\begin{aligned} H^{PPP} = & \sum_{nm,\sigma} h_{nm} a_{n\sigma}^+ a_{m\sigma} + \frac{1}{2} \sum_{nm} \sum_{\sigma_1 \sigma_2} \gamma_{nm} \hat{N}_{n\sigma_1} \hat{N}_{m\sigma_2} \\ & - \frac{1}{2} \sum_n \sum_\sigma \gamma_{nn} \hat{N}_{n\sigma}. \end{aligned} \quad (10.24)$$

The PPP method has been extensively used in quantum chemistry to study the electronic structure of planar π -electron systems some years ago, when more sophisticated semiempirical all-valence electron models or ab initio methods were not available. Recently, the PPP model received considerable attention in solid state physics (see, e.g. Soos & Ramasesha 1984; Ramasesha & Soos 1984a, b), where, due to the size of the systems under study, it represents perhaps the most advanced general computational method taking into account electron-electron interaction explicitly.⁵

The PPP Hamiltonian is usually not solved exactly—this would be rather time consuming in most cases—but it is solved at the SCF level under the Hartree-Fock approximation. If desirable, these SCF PPP wave functions can be improved by the configuration interaction (CI) method. The full CI solution⁶ which corresponds to an exact diagonalization of the PPP Hamiltonian of Eqs. (10.9) or (10.24) has also been calculated in some cases numerically (Mayer 1980).

10.2 Particle-Hole Symmetry

A π -electron model is necessarily oversimplified because, among other reasons, it lies upon the so-called $\sigma - \pi$ separation. This means that the π electrons are described by an effective model Hamiltonian as discussed in the previous sections while the effect of the σ electrons (σ core) is taken into account only by modifying the matrix elements of the effective Hamiltonian for the π electrons. Another drastic simplification is the first-neighbor approximation discussed also in the previous sections. These approximations may considerably limit the power of the

⁵ Note that if the translational symmetry of the system is perfect, one can use the full integral list in the given basis set (ab initio scheme) performing a band calculation. In this case, however, no effects violating the strict periodicity (geometry distorsions, impurities, etc.) can be taken into account.

⁶ A CI calculation is called “full CI” if it takes into account all possible configurations within the given basis set. Accordingly, the full CI wave function is an eigenfunction of the second quantized Hamiltonian.

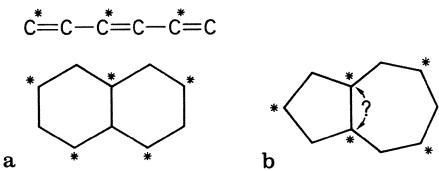


Fig. 10.1a, b. Examples for alternant (a) and non-alternant (b) hydrocarbons

model, but, on the other hand, they may result in special symmetries of the model Hamiltonian which help one to interpret and classify calculational as well as experimental results.

Needless to say that realistic systems do not follow such symmetries exactly: these are to be considered as approximate symmetries in this sense. Real systems and more sophisticated Hamiltonians obey the approximate symmetries only to the extent the approximations inherent in the model are valid. The approximate symmetry is, however, an exact symmetry of the model Hamiltonian.

A very important approximate symmetry for a specific class of π electron system is the so-called particle-hole symmetry which will be discussed below in some detail. This is a symmetry generally of alternant hydrocarbons (vide infra). In order to understand the origin and the importance of this symmetry we have to discuss what do we mean here on "particles" and "holes", and the class of alternant hydrocarbons has to be specified.

Hydrocarbons are compounds composed only of carbon and hydrogen atoms. The systems considered here should be planar in order to exhibit the typical properties characteristic to a delocalized π -electron system. Under this condition the hydrogen atoms lie in the plane thus they contribute only to the system of σ electrons, if their electronic structure is described merely by s-type atomic orbitals. The π -electron system is formed only by the $2p_z$ orbitals and the corresponding electrons of the carbon atoms, thus only the latter ones are to be discussed.

Alternant hydrocarbons form a special class of hydrocarbons in which the carbon atoms can be sorted into two groups so that neighboring carbons always belong to different groups. A chain obviously meets this criterion, and rings formed by an even number of atoms will also do. Clearly, alternant hydrocarbons cannot contain odd-numbered rings by definition. Some examples for alternant and non-alternant hydrocarbons are shown in Fig. 10.1.

Alternant hydrocarbons exhibit certain symmetry properties which are reflected by the special arrangement of their orbital energy levels and the specific form of their molecular orbitals. These special properties are often referred to as the pair-theorem⁷ or, using the terminology of physics, it is called the particle-hole symmetry. It holds under the first-neighbor approximation in the π -electron system. In the name of this symmetry, the term 'particle' refers simply to the electrons of the molecule. We say that the occupied levels are filled with particles,

⁷To be distinguished from Löwdin's pairing theorem for the mutual orthogonalization of two orbital subsets.

while the empty levels are said to be filled with ‘holes’. The operator a_i^+ create particles, and operators a_i annihilate particles. This is equivalent to saying that the annihilation operators a_i create holes, while the creation operators a_i^+ annihilate the holes.

To express this terminology in mathematical terms we introduce the notations⁸:

$$b_i^+ = a_i \quad (10.25a)$$

and

$$b_i = a_i^+. \quad (10.25b)$$

The operators b_i^+ (b_i) are the creation (annihilation) operators for holes. Shortly, they are called hole operators. The commutation properties of the hole operators b_i^+, b_i are obviously identical to those of the particle operators a_i^+ and a_i .

The particle-hole transformation of Eq. (10.25) appears to be rather formal but we shall see its advantages below. Let us first study the symmetry of the second quantized Hamiltonian of alternant hydrocarbons under the particle-hole transformation.

For simplicity, we begin the discussion at the Hückel level. Then the Hamiltonian for an alternant hydrocarbon, in terms of spatial orbitals reads [cf. Eq. (10.3)]:

$$\begin{aligned} \hat{H} &= \sum_{mn\sigma} \beta_{mn} a_{m\sigma}^+ a_{n\sigma} \\ &= \sum_{mn^*\sigma} \beta_{mn^*} a_{m\sigma}^+ a_{n^*\sigma} + \sum_{m^*n\sigma} \beta_{m^*n} a_{m^*\sigma}^+ a_{n\sigma}. \end{aligned} \quad (10.26)$$

Here we utilized that all α parameters (diagonal elements of the Hückel matrix) are zero, and, as a consequence of the first-neighbor approximation, the surviving β integrals must connect sites belonging to different groups. As usual, one of the groups is denoted by an asterisk. Application of an $m \leftrightarrow n$ interchange of the summation labels in the last term of Eq. (10.26) yields:

$$\hat{H} = \sum_{mn^*\sigma} \beta_{mn^*} a_{m\sigma}^+ a_{n^*\sigma} + \sum_{n^*m\sigma} \beta_{n^*m} a_{n^*\sigma}^+ a_{m\sigma}. \quad (10.27)$$

Utilizing the symmetry of the β matrix one gets:

$$\begin{aligned} \hat{H} &= \sum_{mn^*\sigma} \beta_{mn^*} [a_{m\sigma}^+ a_{n^*\sigma} + a_{n^*\sigma}^+ a_{m\sigma}] \\ &= \sum_{mn^*\sigma} \beta_{mn^*} [a_{m\sigma}^+ a_{n^*\sigma} + h.c.] \end{aligned} \quad (10.28)$$

“h.c.” indicating the Hermitian conjugate.

Let us apply now the particle-hole transformation to this Hamiltonian. The transformation consists of substituting the particle operators a_i^+, a_i by the corre-

⁸Note that the hole operators introduced in this section are different from those in Sect. 5, since the definition of the latter depends on the occupancy of the orbital which they are acting on. No such trick is utilized here.

sponding hole operators b_i^+ , b_i in each string. Denoting the transformed Hamiltonian by \hat{H}' one may write:

$$\hat{H}' = \sum_{mn*\sigma} \beta_{mn*} [b_{m\sigma}^+ b_{n*\sigma} + \text{h.c.}] \quad (10.29)$$

Rewriting this Hamiltonian using the original particle operators by Eqs. (10.25):

$$\hat{H}' = \sum_{mn*\sigma} \beta_{mn*} [a_{m\sigma} a_{n*\sigma}^+ + \text{h.c.}] \quad (10.30)$$

Application of the anticommutation rule for the two particle operators gives a minus sign (the system being alternant, $m \neq n^*$):

$$\hat{H}' = - \sum_{mn*\sigma} \beta_{mn*} [a_{n*\sigma}^+ a_{m\sigma} + \text{h.c.}] \quad (10.31)$$

Finally, comparing the Hamiltonians of Eqs. (10.28) and (10.31) we find:

$$\hat{H}' = -\hat{H} \quad (10.32)$$

That is, the Hückel Hamiltonian of alternant hydrocarbons simply changes its sign under the particle-hole transformation. Consequently, the spectrum of \hat{H}' and \hat{H} should be the mirror image of each other. Now we apply a simple “trick” to show that the spectrum of \hat{H} is invariant to the particle-hole transformation. Without changing any expectation value, that is, without any physical consequence, the *sign* of any basis orbital⁹ can be changed. Let us change the sign of each “starred” orbital. This involves a sign change of all resonance integrals because $\beta_{mn*} = \langle m | \hat{H} | n^* \rangle$ is an odd function of $|n^*\rangle$. Let the creation/annihilation operators over the new basis set be denoted by the letter c. The original Hamiltonian in the new basis is therefore:

$$\hat{H} = \sum_{mn*\sigma} (-\beta_{mn*}) [c_{m\sigma}^+ c_{n*\sigma} + \text{h.c.}] \sim \hat{H}' \quad (10.33)$$

where the particle-hole transformed Hamiltonian \hat{H}' is formally recovered, cf. Eq. (10.31). We have found that the particle hole transformation is equivalent to changing the sign of all starred basis functions. The operator \hat{H}' acts in the space of the original basis functions exactly in the same manner as the Hamiltonian \hat{H} does in the modified space. Since the two spaces are physically completely equivalent, the spectrum of \hat{H} and \hat{H}' should be identical.

Earlier it was found that the two spectra are the mirror images of each other. These two requirements are possible only if the energy levels of \hat{H} and \hat{H}' lie symmetrically below and above the zero level (Fig. 10.2). The orbitals appear in pairs of positive and negative energy justifying to call this statement the ‘pair-theorem’. If the system is neutral, the levels of negative energy are doubly filled in the ground state, while the positive levels are empty; then the orbitals appear in occupied-virtual pairs. It follows also that if an alternant hydrocarbon consists of an odd number of atoms, there should be a zero energy level in the spectrum

⁹The sign of an orbital (or any wave function) is completely arbitrary—it is just a phase factor.

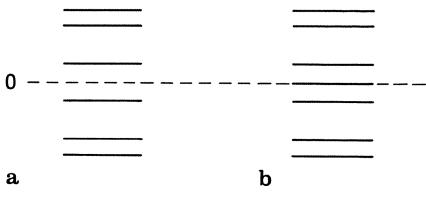


Fig. 10.2a, b. Characteristic spectra of alternant hydrocarbons possessing particle-hole symmetry and having an even (a) or odd (b) number of sites

("midgap state"). The Hückel molecular orbitals (eigenvectors of \hat{H}) should also be invariant under the particle-hole transformation up to an irrelevant phase factor.

The alternant nature of the system, together with the first-neighbor approximation, have been extensively utilized in the above demonstration; it is obvious that these are necessary conditions for the fulfillment of the particle-hole symmetry. The fact that the system is a hydrocarbon was used only in the sense that all α parameters have a common value thus they could be eliminated from the Hamiltonian by an appropriate shift of the energy origin. The presence of a heteroatom with a different α destroys the particle-hole symmetry. However, the system need not be a hydrocarbon in the strict sense, silicon or other atoms would also qualify provided they form a π -electron system in a planar arrangement.

We may ask whether this simple property of alternant hydrocarbons could be generalized to more sophisticated levels, or it is restricted to the Hückel scheme. As will be shown below, electron correlation effects do not necessarily destroy the particle-hole symmetry: it survives even in the PPP model. (Since the Hubbard model is a special case of the PPP model, the Hubbard Hamiltonian has also particle-hole symmetry). The thorough treatment of this problem was given by McLahlan (1961). We shall present here a simplified discussion based on the excellent review article by Longuet-Higgins (1966). Though the following derivation is a bit more involved, the reader may gain some more practice in manipulating second quantized operators by checking the next few pages. One may also jump and leave out this section, however.

According to Eq. (10.19), the PPP Hamiltonian can be written as:

$$H^{PPP} = \sum_{nm} \left[h_{nm} \sum_{\sigma} a_{n\sigma}^+ a_{m\sigma} + \frac{1}{2} \gamma_{nm} \sum_{\sigma_1 \sigma_2} a_{n\sigma_1}^+ a_{m\sigma_2}^+ a_{m\sigma_2} a_{n\sigma_1} \right] \quad (10.34)$$

where n and m are first neighbors. Note that the one-electron integrals are not simple resonance integrals, but describe also the electron-core attraction. For alternant hydrocarbons this Hamiltonian reduces to:

$$\begin{aligned} H^{PPP} = & \sum_{k,\sigma} \left(h_{kk} a_{k\sigma}^+ a_{k\sigma} + \frac{1}{2} \gamma_{kk} a_{k\sigma}^+ a_{k\bar{\sigma}}^+ a_{k\bar{\sigma}} a_{k\sigma} \right) \\ & + \sum_{nm*} h_{nm*} \sum_{\sigma} (a_{n\sigma}^+ a_{m*\sigma} + h.c.) \\ & + \frac{1}{2} \sum_{nm*} \gamma_{nm*} \sum_{\sigma_1 \sigma_2} (a_{n\sigma_1}^+ a_{m*\sigma_2}^+ a_{m*\sigma_2} a_{n\sigma_1} + h.c.) \end{aligned} \quad (10.35)$$

where similar manipulations are made as for the Hückel case [cf. Eqs. (10.26–28)], except that the diagonal integrals h_{kk} and γ_{kk} are kept now to describe electron-nuclear attraction and on-site repulsion, respectively. The label k runs over both the starred and unstarred atoms, while the indices n and m^* are used to distinguish the two subsets. The label σ indicates a spin function as before, while $\bar{\sigma}$ is used for the dual spin function (opposite to σ). The alternant character of the system is utilized in Eq. (10.35) as all off diagonal matrix elements connect sites of different classes (“starred” or “unstarred”) as a consequence of the first-neighbor approximation.

Application of the particle-hole transformation on the Hamiltonian of Eq. (10.35) yields:

$$\begin{aligned}\hat{H}'^{PPP} = & \sum_{k,\sigma} \left(h_{kk} a_{k\sigma} a_{k\sigma}^+ + \frac{1}{2} \gamma_{kk} a_{k\sigma} a_{k\bar{\sigma}} a_{k\bar{\sigma}}^+ a_{k\sigma}^+ \right) \\ & + \sum_{nm^*} h_{nm^*} \sum_{\sigma} (a_{n\sigma} a_{m^*\sigma}^+ + \text{h.c.}) \\ & + \frac{1}{2} \sum_{nm^*} \gamma_{nm^*} \sum_{\sigma_1 \sigma_2} (a_{n\sigma_1} a_{m^*\sigma_2} a_{m^*\sigma_2}^+ a_{n\sigma_1}^+ + \text{h.c.}).\end{aligned}\quad (10.36)$$

The operator strings can be reordered applying the fermion anticommutation rules. The result is:

$$\begin{aligned}\hat{H}'^{PPP} = & \sum_{k,\sigma} (h_{kk} [1 - a_{k\sigma}^+ a_{k\sigma}] \\ & + \frac{1}{2} \gamma_{kk} [1 - a_{k\sigma}^+ a_{k\sigma}] [1 - a_{k\bar{\sigma}}^+ a_{k\bar{\sigma}}]) \\ & - \sum_{nm^*} h_{nm^*} \sum_{\sigma} (a_{m^*\sigma}^+ a_{n\sigma} + \text{h.c.}) \\ & + \frac{1}{2} \sum_{nm^*} \gamma_{nm^*} \sum_{\sigma_1 \sigma_2} (a_{n\sigma_1}^+ a_{m^*\sigma_2}^+ a_{m^*\sigma_2} a_{n\sigma_1} + \text{h.c.}) \\ & + \frac{1}{2} \sum_{nm^*} \gamma_{nm^*} \sum_{\sigma_1 \sigma_2} (1 - a_{m^*\sigma_2}^+ a_{m^*\sigma_2} - a_{n\sigma_1}^+ a_{n\sigma_1} + \text{h.c.}).\end{aligned}\quad (10.37)$$

Now we apply the same trick as previously in the Hückel case: we change the phase of each starred orbital. The diagonal integrals h_{kk} and γ_{kk} are clearly not affected by this change, since they contain either 0 or 2 starred orbitals. Two two-electron integrals $\gamma_{nm^*} = [nm^*|nm^*]$ are also not affected for the same reason. The sign of the offdiagonal one-electron matrix elements, however, will be reversed. Writing Eq. (10.37) in the new basis set, and using the letter c for the corresponding creation/annihilation operators, one gets:

$$\begin{aligned}
\hat{H}'^{\text{PPP}} = & \sum_{\mathbf{k}, \sigma} (h_{\mathbf{kk}} [1 - c_{\mathbf{k}\sigma}^+ c_{\mathbf{k}\sigma}]) \\
& + \frac{1}{2} \gamma_{\mathbf{kk}} [1 - c_{\mathbf{k}\sigma}^+ c_{\mathbf{k}\sigma}] [1 - c_{\mathbf{k}\bar{\sigma}}^+ c_{\mathbf{k}\bar{\sigma}}] \\
& + \sum_{\mathbf{nm}^*} h_{\mathbf{nm}^*} \sum_{\sigma} (c_{\mathbf{m}^*\sigma}^+ c_{\mathbf{n}\sigma} + \text{h.c.}) \\
& + \frac{1}{2} \sum_{\mathbf{nm}^*} \gamma_{\mathbf{nm}^*} \sum_{\sigma_1 \sigma_2} (c_{\mathbf{n}\sigma_1}^+ c_{\mathbf{m}^*\sigma_1}^+ c_{\mathbf{m}^*\sigma_2} c_{\mathbf{n}\sigma_1} + \text{h.c.}) \\
& + \frac{1}{2} \sum_{\mathbf{nm}^*} \gamma_{\mathbf{nm}^*} \sum_{\sigma_1 \sigma_2} (1 - c_{\mathbf{m}^*\sigma_1}^+ c_{\mathbf{m}^*\sigma_2} - c_{\mathbf{n}\sigma_1}^+ c_{\mathbf{n}\sigma_1} + \text{h.c.}). \tag{10.38}
\end{aligned}$$

This Hamiltonian can be rearranged by simple algebraic manipulation to the following form:

$$\begin{aligned}
\hat{H}'^{\text{PPP}} = & \sum_{\mathbf{k}, \sigma} (h_{\mathbf{kk}} c_{\mathbf{k}\sigma}^+ c_{\mathbf{k}\sigma} + \frac{1}{2} \gamma_{\mathbf{kk}} c_{\mathbf{k}\sigma}^+ c_{\mathbf{k}\bar{\sigma}}^+ c_{\mathbf{k}\bar{\sigma}} c_{\mathbf{k}\sigma}) \\
& + \sum_{\mathbf{nm}^*} h_{\mathbf{nm}^*} \sum_{\sigma} (c_{\mathbf{m}^*\sigma}^+ c_{\mathbf{n}\sigma} + \text{h.c.}) \\
& + \frac{1}{2} \sum_{\mathbf{nm}^*} \gamma_{\mathbf{nm}^*} \sum_{\sigma_1 \sigma_2} (c_{\mathbf{n}\sigma_1}^+ c_{\mathbf{m}^*\sigma_1}^+ c_{\mathbf{m}^*\sigma_2} c_{\mathbf{n}\sigma_1} + \text{h.c.}) \\
& + \frac{1}{2} \sum_{\mathbf{nm}^*} \gamma_{\mathbf{nm}^*} \sum_{\sigma_1 \sigma_2} (1 - c_{\mathbf{m}^*\sigma_1}^+ c_{\mathbf{m}^*\sigma_2} - c_{\mathbf{n}\sigma_1}^+ c_{\mathbf{n}\sigma_1} + \text{h.c.}) \\
& + \sum_{\mathbf{k}, \sigma} (h_{\mathbf{kk}} + \frac{1}{2} \gamma_{\mathbf{kk}}) [1 - 2c_{\mathbf{k}\sigma}^+ c_{\mathbf{k}\sigma}] \tag{10.39}
\end{aligned}$$

where the first three lines have exactly the same form as the original PPP Hamiltonian, while the last two lines represent the difference. We see that $\hat{H}' = \hat{H}$ does not hold under the PPP approximation, it was valid only at the Hückel level. However, the particle-hole symmetry still survives in the following sense. The last two lines of Eq. (10.39), representing the difference (\hat{D}) between the original and the transformed Hamiltonians, can be rewritten as:

$$\hat{D} = \sum_{\mathbf{k}} \left[h_{\mathbf{kk}} + \frac{1}{2} \gamma_{\mathbf{kk}} + \sum_{\mathbf{l} \neq \mathbf{k}} \gamma_{\mathbf{kl}} \right] \sum_{\sigma} (1 - 2c_{\mathbf{k}\sigma}^+ c_{\mathbf{k}\sigma}). \tag{10.40}$$

Remember now that operators $c_{\mathbf{k}\sigma}^+$, $c_{\mathbf{k}\sigma}$ refer to holes rather than electrons. The particle number operator $\hat{N}_{\mathbf{k}}$ of Eq. (3.1) can be expressed in terms of hole operators as:

$$\hat{N}_{\mathbf{k}} = \sum_{\sigma} a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}\sigma} = \sum_{\sigma} (1 - a_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma}^+) = \sum_{\sigma} (1 - c_{\mathbf{k}\sigma}^+ c_{\mathbf{k}\sigma}). \tag{10.41}$$

Substituting this into Eq. (10.40):

$$\hat{D} = \sum_{\mathbf{k}} \left[h_{\mathbf{kk}} + \frac{1}{2} \gamma_{\mathbf{kk}} + \sum_{\mathbf{l} \neq \mathbf{k}} \gamma_{\mathbf{kl}} \right] 2(\hat{N}_{\mathbf{k}} - 1). \tag{10.42}$$

Now we have to realize that the term in the square bracket is constant if there is no heteroatom in the system. This is true because in the PPP method the h_{kk} core integral is parametrized as:

$$h_{kk} = -I_k - \sum_{l \neq k} \gamma_{kl}$$

where I_k is the ionization potential of the atom on site k , and the offdiagonal γ integrals account for the core-electron attraction. Since in the absence of heteroatoms I_k and γ_{kk} are constants, one may write:

$$\hat{D} = 2\mathcal{C} \sum_k (\hat{N}_k - 1) \quad (10.43)$$

where the constant \mathcal{C} denotes the square bracket of Eq. (10.42). This is the difference between the original and the particle-hole transformed PPP Hamiltonians. The expectation value of \hat{D} is very easy to evaluate, since:

$$\left\langle \sum_k (\hat{N}_k - 1) \right\rangle = \sum_k \langle \hat{N}_k \rangle - M = N - M$$

where N is the total number of electrons in the system (trace of \hat{N}) and M is the number of basis functions. Dealing with hydrocarbons, each atom or site contributes to the total charge by the core charge + 1, thus $N-M$ is just the net charge (Q) of the molecule. Consequently:

$$\langle \hat{D} \rangle = 2\mathcal{C}Q. \quad (10.44)$$

It follows that, if $Q = 0$, the expectation values of \hat{H} and \hat{H}' are the same: the energy is invariant to the particle-hole transformation. Moreover, many-electron states of the corresponding positive and negative ions of the molecule are in a one-to-one correspondance, their energy difference is determined by $2\mathcal{C}Q$. The corresponding ‘electron affinities’ and ‘ionization potentials’ have the same absolute value. These are the most important consequences of the particle-hole symmetry of the PPP Hamiltonian for alternant hydrocarbons. Unfortunately, this symmetry cannot be generalized to more sophisticated Hamiltonians which will be discussed in the forthcoming sections.

10.3 All-Valence-Electron Hamiltonians

In describing non-planar and/or saturated systems, the σ - π separation cannot be maintained and a merely π -electron theory cannot be justified. In most cases the treatment of inner shells is still separable from that of the valence shell to a certain degree of approximation. This leads to the so-called all-valence-electron methods. One may either construct a pseudopotential accounting for the effect of the inner-shell electrons on the valence shell, or simply consider a model where each nucleus is replaced by a core having a positive charge of:

$$Z_c = Z - n_c$$

where Z is the atomic number and n_c is the number of inner-shell (core) electrons. This is equivalent to saying that the core electrons are simply compressed into the nuclei.

This latter model is extensively utilized by semiempirical schemes such as the Compete Neglect of Differential Overlap (CNDO), Intermediate Neglect of Differential Overlap (INDO), Neglect of Diatomic Differential Overlap (NDDO), etc. methods (called NDO-family, Pople & Beveridge 1970) which represent the quantum chemical tools for studying the electronic structure of larger molecules which are not available for ab initio calculations. We shall not discuss the details of the parametrization of these schemes. The aim of this section is merely to put down the second quantized Hamiltonians of the most frequently used semi-empirical methods of this type.¹⁰

The simplest NDO scheme is the CNDO method which fully utilizes the Zero Differential Overlap (ZDO) approximation for the two-electron integrals. The ZDO condition means that we neglect all two-electron integrals in which the differential overlap of two different basis functions is present:

$$[nm|ls] = [nm|nm]\delta_{nl}\delta_{ms} \quad (10.45)$$

for the spatial orbitals. Although it is clear that the CNDO Hamiltonian can be considered as the generalization of \hat{H}^{PPP} to the all-valence-electron level, it is most straightforward to derive it from the full Hamiltonian of the usual form:

$$\hat{H} = \sum_{nms} h_{nm} a_{n\sigma}^+ a_{m\sigma} + \frac{1}{2} \sum_{nm} \sum_{\sigma_1 \sigma_2} [nm|ls] a_{n\sigma_1}^+ a_{m\sigma_2}^+ a_{s\sigma_2} a_{l\sigma_1}$$

where the summation labels n , m , l , and s run over all (spatial) valence orbitals which are assumed to form an orthonormal set. Introducing the ZDO condition given in Eq. (10.45) one finds:

$$H^{CNDO} = \sum_{nms} h_{nm} a_{n\sigma}^+ a_{m\sigma} + \frac{1}{2} \sum_{nm} \sum_{\sigma_1 \sigma_2} [nm|nm] a_{n\sigma_1}^+ a_{m\sigma_2}^+ a_{m\sigma_2} a_{n\sigma_1}. \quad (10.46)$$

The structure of this Hamiltonian is exactly the same as that of the PPP model, the only essential difference is that here the underlying basis set consists of the valence AOs and not only of $2p_z$ orbitals. The formal similarity of the CNDO and the PPP Hamiltonians involves that the former can be manipulated in the same manner as in Sect. 10.1.3. The result is:

$$\begin{aligned} H^{CNDO} &= \sum_{nms} h_{nm} a_{n\sigma}^+ a_{m\sigma} + \frac{1}{2} \sum_{nm} \sum_{\sigma_1 \sigma_2} \gamma_{nm} \hat{N}_{n\sigma_1} \hat{N}_{m\sigma_2} - \frac{1}{2} \sum_n \sum_{\sigma} \gamma_{nn} \hat{N}_{n\sigma} \\ &= \sum_{nms} h_{nm} a_{n\sigma}^+ a_{m\sigma} + \frac{1}{2} \sum_{nm} \gamma_{nm} \hat{N}_n \hat{N}_m - \frac{1}{2} \sum_n \gamma_{nn} \hat{N}_n \end{aligned} \quad (10.47)$$

where the spatial particle number operators:

¹⁰Note that the Extended Hückel theory (EHT) which deals also with valence electrons only will be discussed in Section 14, since it is represented in a nonorthogonal basis.

$$\hat{N}_n = \sum_{\sigma} \hat{N}_{n\sigma}$$

are introduced.

In spite of the formal similarities, the parametrization of the PPP and the CNDO Hamiltonians are quite different. In particular, the CNDO model is not restricted to the first-neighbor approximation. For this reason the particle-hole symmetry does not apply for H^{CNDO} .

Various NDO schemes differ from CNDO in that they do not utilize fully the ZDO approximation. These schemes are discussed in the book by Pople and Beveridge (1970). In the “intermediate neglect of differential overlap” (INDO) model the differential overlaps between orbitals on the same atom are kept in one-center two-electron integrals, while the “neglect of diatomic differential overlap” (NDDO) model neglects only diatomic differential overlaps in any two-electron integral.

Let us put down the INDO Hamiltonian in a second quantized form. To this end the two-electron integrals are partitioned to monocentric and bicentric ones. In the monocentric part we keep all integrals, while in the rest of the integral list we use the ZDO condition:

$$\begin{aligned} H^{INDO} = & \sum_{nm\sigma} h_{nm} a_{n\sigma}^+ a_{m\sigma} + \frac{1}{2} \sum_A \sum_{nm|ls}^{(A)} \sum_{\sigma_1\sigma_2} [nm|ls] a_{n\sigma_1}^+ a_{m\sigma_2}^+ a_{s\sigma_2} a_{l\sigma_1} \\ & + \frac{1}{2} \sum'_{m,n} [mn|mn] \sum_{\sigma_1\sigma_2} \hat{N}_{m\sigma_1} \hat{N}_{n\sigma_2} \end{aligned} \quad (10.48)$$

where the summation index A runs over all atoms, while the prime on the second summation indicates that m and n belong to different atoms. The last term in Eq. (10.48) is in analogy with the corresponding term of H^{CNDO} , but the diagonal term present in Eq. (10.47) is missing from Eq. (10.48) since it is contained in the monocentric term.

The significance of the second term of Eq. (10.48) is worth mentioning. It is clear that it cannot be expressed through the particle number operators, in contrast to the CNDO-type terms in which the spatial particle number operators can be introduced. As a consequence, the CNDO model cannot distinguish between states of the same electronic structure but different spin. Such distinction is possible in INDO due to the presence of the second term of Eq. (10.48). This is a necessary prerequisite in studying spin-dependent phenomena such as ESR spectra.

We do not put down here the second quantized form of the NDDO Hamiltonian; the interested reader may do this along the same lines as H^{CNDO} or H^{INDO} were derived.

Various levels of NDO methods correspond to second quantized Hamiltonians which differ from each other only in the list of integrals defining the model Hamiltonian. This feature calls the attention to one of the important advantages of the second quantized formalism, namely, that it permits one to put down the model Hamiltonians corresponding to various approximate quantum chemical

schemes. One has to be careful, however. The model Hamiltonian of the NDO schemes discussed above, for example, have their structure in the above forms only if they are written down in the basis set of atomic orbitals. The full Hamiltonian is invariant against unitary transformations on the basis set (cf. Sect. 17.2), but the ZDO condition is not invariant. For example, transforming the list of two-electron integrals from the AO basis to the MO basis by means of the MO expansion coefficients C_{im} one gets:

$$[ij|kl] = \sum_{mnrs} C_{im} C_{jn} C_{kr} C_{ls} [mn|rs]$$

\uparrow
MO
integrals

\uparrow
AO
integrals

(10.49)

If the ZDO condition is introduced in the AO basis we have:

$$[ij|kl] = \sum_{mn} C_{im} C_{jn} C_{km} C_{ln} \gamma_{mn} \quad (10.50)$$

with $\gamma_{mn} = [mn|mn]$. Note that though the transformation of the two-electron integrals is considerably simplified, the ZDO condition does not hold for the MO integrals. This means that an NDO Hamiltonian in the MO basis has exactly the same structure as an “exact” non-ZDO Hamiltonian in the same (valence) basis. They differ merely in the values of the integrals. For this reason, post-Hartree-Fock calculations within an NDO scheme (which usually imply the transformation of the integrals into the MO basis) are almost as complicated as an ab-initio calculation.¹¹ This is one of the reasons that in modern quantum chemistry the main attention is paid towards ab-initio schemes as far as they are computationally feasible.

10.4 The Hartree-Fock Hamiltonian

The Hartree-Fock model leads to an effective one-electron Hamiltonian, called the Fockian \hat{F} . The second quantized representation of the Fockian has that same form as any other one-electron operator. In the basis of orthogonalized spin-orbitals $\{\chi_\mu\}$ one can write:

$$\hat{F} = \sum_{\mu, \nu} F_{\mu\nu} \chi_\mu^+ \chi_\nu^- \quad (10.51)$$

where $F_{\mu\nu}$ are the elements of the Fock matrix. Solution of the Hartree-Fock equations involves the diagonalization of the Fock matrix. The eigenvalues of the Fockian are the orbital energies ϵ_i . Thus, Eq. (10.51) after diagonalization

¹¹ This statement does not hold for the simpler π -electron models such as the Hubbard scheme where analytical solutions are possible to find in some cases.

takes the form:

$$\hat{F} = \sum_i \epsilon_i \psi_i^+ \psi_i^- \quad (10.52)$$

where ψ refers to molecular spinorbitals. The Fockian is usually applied in many-electron theory in this latter form—it is seen that it is defined by the orbital energies unequivocally. Note that in Eq. (10.52) the summation label i extends over all molecular orbitals, including virtual ones. Equation (10.52) is somewhat formal because the orbital energies are not known a priori, they result from the diagonalization of the Fock matrix. The latter is not known before completing a Hartree-Fock calculation, since the matrix elements of the Fockian are to be determined self-consistently.

The expression for the matrix elements $F_{\mu\nu}$ can be derived in the second quantized formalism in an elegant manner. This derivation relies on the physical picture behind the Hartree-Fock approximation. As known, in this model the electrons interact only in an averaged manner, so correlational effects are excluded. To derive such an averaged operator, we start again with the usual Hamiltonian:

$$\hat{H} = \sum_{\mu\nu} h_{\mu\nu} \chi_\mu^+ \chi_\nu^- + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} [\mu\nu|\lambda\sigma] \chi_\mu^+ \chi_\nu^+ \chi_\sigma^- \chi_\lambda^- .$$

The first term is of one-electron nature by itself, thus it does not represent any problem: the $h_{\mu\nu}$ integrals will enter the Fockian as they are. On the other hand, the two-electron term requires an averaging. Mathematically speaking, the averaging means the substitution of the two-electron operator string $\chi_\mu^- \chi_\nu^+ \chi_\sigma^- \chi_\lambda^-$ by an appropriate one-electron string multiplied by some density matrix elements. That is, while the fully averaged (expectation) value of this string is:

$$\langle \chi_\mu^+ \chi_\nu^+ \chi_\sigma^- \chi_\lambda^- \rangle = P_{\mu\lambda} P_{\nu\sigma} - P_{\mu\sigma} P_{\nu\lambda},$$

we define a “partial average” as:

$$(\chi_\mu^+ \chi_\nu^+ \chi_\sigma^- \chi_\lambda^-) = P_{\nu\sigma} \chi_\mu^+ \chi_\lambda^- - P_{\nu\lambda} \chi_\mu^+ \chi_\sigma^- + P_{\mu\lambda} \chi_\nu^+ \chi_\sigma^- - P_{\mu\sigma} \chi_\nu^+ \chi_\lambda^- \quad (10.53)$$

where all possible combinations are taken into account to pick up a one-electron string from the two-electron string of the left-hand side. (Note that the expectation value of Eq. (10.53) differs from the full average value of the two-electron string by a factor of two. This is intentional and will be explained below.) Substitution of Eq. (10.53) into the Hamiltonian yields the Fockian:

$$\begin{aligned} \hat{H} \rightarrow \hat{F} = & \sum_{\mu\nu} h_{\mu\nu} \chi_\mu^+ \chi_\nu^- + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} [\mu\nu|\lambda\sigma] \\ & \times (P_{\nu\sigma} \chi_\mu^+ \chi_\lambda^- - P_{\nu\lambda} \chi_\mu^+ \chi_\sigma^- + P_{\mu\lambda} \chi_\nu^+ \chi_\sigma^- - P_{\mu\sigma} \chi_\nu^+ \chi_\lambda^-). \end{aligned}$$

We may bring this expression into a more transparent form by appropriate interchanges of summation indices in order to have the operator string $\chi_\mu^+ \chi_\nu^-$ in all terms. In particular, this requires a $\nu \leftrightarrow \lambda$ interchange in the first term, a $\nu \leftrightarrow \sigma$

interchange at the second term, etc. Utilizing the symmetry properties of the two-electron integrals and that of the first-order density matrix P , the two terms of identical sign will turn out to be identical and finally the following result is obtained:

$$\begin{aligned}\hat{F} &= \sum_{\mu\nu} \left[h_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} ([\mu\lambda|\nu\sigma] - [\mu\lambda|\sigma\nu]) \right] \chi_{\mu}^{+} \chi_{\nu}^{-} \\ &= \sum_{\mu\nu} F_{\mu\nu} \chi_{\mu}^{+} \chi_{\nu}^{-}.\end{aligned}\quad (10.54)$$

Here the Fock matrix is introduced as:

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} ([\mu\lambda|\nu\sigma] - [\mu\lambda|\sigma\nu]) \quad (10.55)$$

by which the well-known result is recovered. Clearly, this Fockian describes an averaged electron-electron repulsion. For each electron the interaction with all other electrons is accounted for, since it moves in the field of all other ones. This has the consequence that running over all electrons one counts the number of pairs and the electron-electron interaction twice. This typical feature of the HF method (and any other effective interaction theories) results that the sum of orbital energies is not the Hartree-Fock energy. This was the reason to introduce the factor of 2 in the partial averaging given in Eq. (10.53).

It is convenient to have the Fockian in terms of spatial orbitals. The situation is simple in the closed-shell case where each orbital is required to be either doubly occupied or empty according to the restricted Hartree-Fock (RHF) method. Then, the spatial density matrix is given by Eq. (9.8), and the transcription of Eq. (10.55) can be performed in the usual manner. We find that the spatial Fock matrix is independent of spin:

$$F_{mn} = h_{mn} + \sum_{l,s} P_{ls} \left([ml|ns] - \frac{1}{2} [ml|sn] \right). \quad (10.56)$$

In this case, according to Eqs. (9.29), the Fock operator is clearly:

$$\hat{F} = \sum_{m,n} F_{mn} \sum_{\sigma} \chi_{m\sigma}^{+} \chi_{n\sigma}^{-}. \quad (10.57)$$

In the MO basis this expression reduces to:

$$\hat{F} = \sum_i \varepsilon_i \sum_{\sigma} \psi_{i\sigma}^{+} \psi_{i\sigma}^{-}$$

where the orbital energies ε_i are the eigenvalues of the spatial Fock matrix.

The situation is more complicated if the restriction of double occupancy is dropped. Here we discuss the unrestricted Hartree-Fock (UHF) method in some detail. In this case one has different density matrices for the α and β electrons, P^{α} and P^{β} , respectively. As a consequence, one has also different Fockians for the α and β electrons: F^{α} and F^{β} . The expressions of their matrix elements can be derived from Eq. (10.55) by performing the integration over spin functions:

$$F_{mn}^{\alpha} = h_{mn} + \sum_{ls} (P_{ls}^{\alpha}[ml|ns] + P_{ls}^{\beta}[ml|ns] - P_{ls}^{\alpha}[ml|sn]).$$

Note that in the exchange part (last term) the summation over spin resulted in a single term since the spin of the orbital pair (l, s) must be the same as that of the pair (m, n). It is apparent that the spatial density matrix can be introduced only in the Coulomb term:

$$F_{mn}^{\alpha} = h_{mn} + \sum_{ls} (P_{ls}[ml|ns] - P_{ls}^{\alpha}[ml|sn]). \quad (10.58a)$$

The analogous result holds for the β electrons:

$$F_{mn}^{\beta} = h_{mn} + \sum_{ls} (P_{ls}[ml|ns] - P_{ls}^{\beta}[ml|sn]). \quad (10.58b)$$

If P^{α} were equal to P^{β} , Eq. (10.58) would be reduced to the RHF Fock matrix of Eq. (10.56).

The second quantized form of the Fockian in the UHF case is obtained by performing the summation over spin in Eq. (10.51) in the usual way, but taking into account that the Fock matrix is spin dependent according to Eq. (10.58):

$$\hat{F}^{UHF} = \sum_{mn} \sum_{\sigma} F_{mn}^{\sigma} \chi_{m\sigma}^{+} \chi_{n\sigma}^{-}. \quad (10.59)$$

In the UHF method one diagonalizes both F^{α} and F^{β} self-consistently, that is in the MO basis the Fockian is given by:

$$\hat{F}^{UHF} = \sum_i \sum_{\sigma} \epsilon_{i,\sigma} \psi_{i\sigma}^{+} \psi_{i\sigma}^{-}.$$

The spin dependency of the UHF Fockian and the corresponding eigenvectors has the unfortunate consequence that the resulting many-electron wave function is usually not a pure spin state, rather a mixture of states of different spin multiplicities. The state of a definite multiplicity can be selected by the appropriate spin-projection operator. The thorough investigation of this problem results in the spin-projected extended Hartree-Fock equations (Mayer 1980).

11 The Brillouin Theorem

Let Ψ_G be the Hartree-Fock ground-state wave function and Ψ_E a singly excited state which differs from Ψ_G by substituting an occupied spinorbital by a virtual one. Then the following statement holds (Brillouin theorem):

$$H_{GE} = \langle \Psi_G | H | \Psi_E \rangle = 0. \quad (11.1)$$

In words, singly excited states do not interact with the HF ground state: the corresponding matrix element of the Hamiltonian is zero. This famous theorem (Brillouin 1933) plays an important role in the Hartree-Fock theory as well as in more sophisticated methods based on a Hartree-Fock reference state. It can be shown that Eq. (11.1) is a necessary and sufficient condition for Ψ_G to be the exact Hartree-Fock wave function, and, in fact, the most general derivation of the Hartree-Fock equations is possible through the Brillouin theorem which can be proved directly from the variation principle (Mayer 1971, 1973, 1974). We shall not prove here the complete equivalence of the Hartree-Fock equations and Eq. (11.1), it will be shown only that the Brillouin theorem is fulfilled for the Hartree-Fock wave function. The proof will make use of second quantization which helps us to evaluate the matrix element easily. To this goal, Eq. (11.1) should be rewritten in the second quantized notation. The ground state is simply represented the Fermi vacuum:

$$\langle \Psi_G | = \langle HF |$$

for the *bra*-function. Since Ψ_E is a singly excited wave function, it can be derived from Ψ_G by annihilating an electron on a molecular spinorbital (ρ) and re-creating it onto another one (τ^*):

$$|\Psi_E\rangle = a_{\tau^*}^\dagger a_\rho |HF\rangle \quad (11.2)$$

for the *ket*-function, where the asterisk indicates that τ^* labels a virtual orbital. This excited state wave function is a single determinant. However, it is not a pure spin state, but a mixture of singlet and triplet states. We will not consider spin adaptation here because it is irrelevant for the proof of the Brillouin theorem.

Substitution of the singly excited determinant of Eq. (11.2) and the second quantized form of the Hamiltonian into the left-hand side of Eq. (11.1) yields:

$$\begin{aligned} H_{GE} &= \sum_{\mu\nu} h_{\mu\nu} \langle HF | a_\mu^\dagger a_\nu a_{\tau^*}^\dagger a_\rho | HF \rangle \\ &\quad + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} [\mu\nu|\lambda\sigma] \langle HF | a_\mu^\dagger a_\nu^\dagger a_\sigma a_\lambda a_{\tau^*}^\dagger a_\rho | HF \rangle. \end{aligned} \quad (11.3)$$

We have to evaluate now the matrix elements which is a rather simple task. The matrix element of the one-electron part is trivial:

$$\langle HF | a_\mu^+ a_v a_{\tau^*}^* a_\rho^- | HF \rangle = \delta_{\mu v} \delta_{\tau^* \rho} + \delta_{\mu \rho} \delta_{v \tau^*} = \delta_{\mu \rho} \delta_{v \tau^*}$$

either



or



(11.4)

Note that both terms enter with positive sign since no transposition is required. However, the first term is zero because τ^* is a virtual orbital while ρ is an occupied one therefore they cannot coincide. So we are left with a single term at the right-hand side. The matrix element of the two-electron term in Eq. (11.3) is determined by the following possible pairings:

$$\langle HF | \underbrace{\mu^+ v^+}_{\boxed{\mu v}} \sigma^- \lambda^- \tau^{*+} \rho^- | HF \rangle = 0 \quad (11.5a)$$

$$\langle HF | \underbrace{\mu^+ v^+}_{\boxed{\mu v}} \overline{\sigma^- \lambda^-} \tau^{*+} \rho^- | HF \rangle = 0 \quad (11.5b)$$

$$\langle HF | \underbrace{\mu^+ v^+}_{\boxed{\mu v}} \sigma^- \lambda^- \tau^{*+} \rho^- | HF \rangle = n_\sigma \delta_{\mu \rho} \delta_{v \sigma} \delta_{\lambda \tau^*} \quad (11.5c)$$

$$\langle HF | \underbrace{\mu^+ v^+}_{\boxed{\mu v}} \overline{\sigma^- \lambda^-} \tau^{*+} \rho^- | HF \rangle = -n_\sigma \delta_{\mu \sigma} \delta_{v \rho} \delta_{\lambda \tau^*} \quad (11.5d)$$

$$\langle HF | \underbrace{\mu^+ v^+}_{\boxed{\mu v}} \overline{\sigma^- \lambda^-} \tau^{*+} \rho^- | HF \rangle = -n_\lambda \delta_{\mu \rho} \delta_{v \lambda} \delta_{\sigma \tau^*} \quad (11.5e)$$

$$\langle HF | \underbrace{\mu^+ v^+}_{\boxed{\mu v}} \sigma^- \lambda^- \tau^{*+} \rho^- | HF \rangle = n_\lambda \delta_{\mu \lambda} \delta_{v \rho} \delta_{\sigma \tau^*}. \quad (11.5f)$$

Here we switched to the short-hand notation for the creation/annihilation operators. The first two terms are zero again because the occupied ρ cannot be equal to the virtual τ^* . The remaining four terms give contributions to the matrix element which, substituting also the one-electron expression from Eq. (11.4), becomes:

$$\begin{aligned} H_{GE} = & \sum_{\mu v} h_{\mu v} \delta_{\mu \rho} \delta_{v \tau^*} \\ & + \frac{1}{2} \sum_{\mu v \lambda \sigma} [\mu v | \lambda \sigma] \{ n_\sigma \delta_{\mu \rho} \delta_{v \sigma} \delta_{\lambda \tau^*} - n_\sigma \delta_{\mu \sigma} \delta_{v \rho} \delta_{\lambda \tau^*} \\ & + n_\lambda \delta_{\mu \lambda} \delta_{v \rho} \delta_{\sigma \tau^*} - n_\lambda \delta_{\mu \rho} \delta_{v \lambda} \delta_{\sigma \tau^*} \}. \end{aligned} \quad (11.6)$$

Performing the summations and interchanging the appropriate summation labels one gets:

$$\begin{aligned}
 H_{GE} &= h_{\rho\tau^*} + \frac{1}{2} \sum_v^{\text{occ}} [\rho v | \tau^* v] - \frac{1}{2} \sum_\mu^{\text{occ}} [\mu \rho | \tau^* \mu] \\
 &\quad + \frac{1}{2} \sum_\mu^{\text{occ}} [\mu \rho | \mu \tau^*] + \frac{1}{2} \sum_v^{\text{occ}} [\rho v | v \tau^*] \\
 &= h_{\rho\tau^*} + \sum_\mu^{\text{occ}} \{[\rho \mu | \tau^* \mu] - [\rho \mu | \mu \tau^*]\} = F_{\rho\tau^*}
 \end{aligned} \tag{11.7}$$

where the symmetry properties of the two-electron integrals are utilized and finally we recovered the matrix element of the Fockian between the occupied orbital ρ and the virtual orbital τ^* [cf. Eq. (7.15) and the definition of the Fock matrix, Eq. (1.7)]. Since \hat{F} is diagonal in terms of canonical MOs, $F_{\rho\tau^*}$ is zero, which proves the Brillouin theorem. The result of Eq. (11.7) can also be obtained from Slater's rules which verifies the present derivation.

One may observe that the diagonality of the Fock matrix is not required by the Brillouin theorem: it is sufficient that \hat{F} be block-diagonal so that no matrix elements between occupied and virtual orbitals be different from zero. The matrix elements in the occupied-occupied block, as well as those in the virtual-virtual block, need not be eliminated to satisfy the Brillouin condition. As known from the first quantized theory, the Brillouin theorem is equivalent to the general Hartree-Fock equations. Consequently, the above finding implies that exact Hartree-Fock orbitals do not necessarily diagonalize the Fockian. As a matter of fact, the Hartree-Fock MOs can be subjected to any non-singular linear transformation among the occupied orbitals without affecting the occupied-virtual block of the Fock matrix, that is keeping $F_{\rho\tau^*}$ zero. Any transformation can be performed within the virtual subspace, too. These transformations are illustrated schematically on Fig. 11.1.

The transformed orbitals do not obey the usual, canonical Hartree-Fock equations:

$$\hat{F}\Psi_v = \varepsilon_v\Psi_v. \tag{11.8}$$

Their equations can be derived in the following manner. Consider a linear transformation of the occupied orbitals:

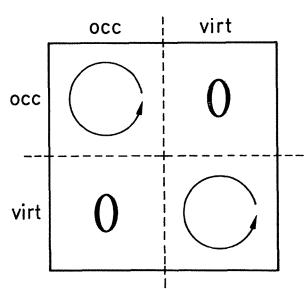


Fig. 11.1. The structure of the Fock matrix satisfying the general Hartree-Fock equations. The curly arrows indicate arbitrary unitary transformations within the indicated block

$$\phi_\lambda = \sum_v^{\text{occ}} L_{\lambda v} \psi_v, \quad (11.9a)$$

and the inverse transformation:

$$\psi_v = \sum_\lambda^{\text{occ}} L_{v\lambda}^{-1} \phi_\lambda. \quad (11.9b)$$

Substituting this transformation into Eq. (11.8), we get:

$$\sum_\lambda^{\text{occ}} L_{v\lambda}^{-1} \hat{F} \phi_\lambda = \epsilon_v \sum_\lambda^{\text{occ}} L_{v\lambda}^{-1} \phi_\lambda. \quad (11.10a)$$

That is:

$$\hat{F} \phi_\mu = \sum_{\lambda, v}^{\text{occ}} L_{\mu v} \epsilon_v L_{v\lambda}^{-1} \phi_\lambda. \quad (11.10b)$$

Introducing the full ϵ matrix by the definition:

$$\epsilon_{\mu\lambda} = \sum_v L_{\mu v} \epsilon_v L_{v\lambda}^{-1}. \quad (11.11)$$

Eq. (11.10b) becomes:

$$\hat{F} \phi_\mu = \sum_v^{\text{occ}} \epsilon_{\mu\lambda} \phi_\lambda \quad (11.12)$$

which is the general form of the Hartree-Fock equations for occupied orbitals. This result is very important because it permits one to gain a deeper insight into the Hartree-Fock model. As seen above, the Brillouin theorem requires only the occupied-virtual block of the Fock matrix to be zero. This demand is satisfied by Eq. (11.12) which describes the transformation of an occupied MO to a new orbital by the Fock operator. This transformed orbital, $\hat{F} \phi_\mu$, however, can be completely expanded within the occupied subspace. In other words, the Fockian does not bring out an occupied MO from the occupied subspace. Mathematically, the occupied subspace is an invariant subspace of the Fockian.

These considerations call our attention that individual molecular orbitals have no direct physical significance in a many-electron system.¹ It is merely the occupied subspace which has physical meaning in the Hartree-Fock theory. Any transformation among occupied MOs is permitted without affecting the validity of the Brillouin condition, the value of the ground-state energy, or that of any physical observable obtained as an expectation value by the Hartree-Fock wave function.

The invariance of the Hartree-Fock wave function to unitary transformations² can also be checked explicitly. In the first quantized theory the mathematical

¹ This statement is true for the ground state. For excited or ionized states the significance of the canonical MOs is to be emphasized, cf. Koopmans theorem.

² A unitary transformation of the orbitals preserves the orthogonality of the MOs. The Brillouin theorem permits one to consider not only unitary transformations, but any non-singular linear transformation, too. In the latter case the transformed MOs will not be orthogonal to each other, but Eq. (11.12) still holds.

properties of determinants should be used to show this invariance. Here we present the proof using second quantization.

Since any unitary transformation can be constructed from successive 2 by 2 rotations, it is sufficient to show that:

$$|\text{HF}\rangle = \hat{U}_{ik} |\text{HF}\rangle \quad (11.13)$$

where \hat{U}_{ik} is a 2 by 2 rotation affecting the occupied MOs i and k . The transformation \hat{U} can be given in matrix form, assuming real quantities throughout, as:

$$U_{ik} = \begin{bmatrix} \cos \phi & \sin \phi \\ -\sin \phi & \cos \phi \end{bmatrix} \quad (11.14)$$

where ϕ is the “angle” of the rotation. Writing Eq. (11.13) in terms of spinorbitals explicitly:

$$\psi_1^+ \dots \psi_i^+ \dots \psi_k^+ \dots \psi_n^+ |\text{vac}\rangle = \psi_1^+ \dots \psi_i^+ \dots \psi_k'^+ \dots \psi_N^+ |\text{vac}\rangle \quad (11.15)$$

where:

$$\psi_i'^+ = \cos \phi \psi_i^+ + \sin \phi \psi_k^+ \quad (11.16a)$$

$$\psi_k'^+ = -\sin \phi \psi_i^+ + \cos \phi \psi_k^+. \quad (11.16b)$$

Substitution of these rotations into the right-hand side of Eq. (11.15) results in:

$$\begin{aligned} \psi_1^+ \dots (\cos \phi \psi_i^+ + \sin \phi \psi_k^+) \dots (-\sin \phi \psi_i^+ + \cos \phi \psi_k^+) \dots \psi_N^+ |\text{vac}\rangle \\ = -\cos \phi \sin \phi \psi_1^+ \dots \psi_i^+ \dots \psi_i^+ \dots \psi_N^+ |\text{vac}\rangle \\ + \cos^2 \phi \psi_1^+ \dots \psi_i^+ \dots \psi_k^+ \dots \psi_N^+ |\text{vac}\rangle \\ - \sin^2 \phi \psi_1^+ \dots \psi_k^+ \dots \psi_i^+ \dots \psi_N^+ |\text{vac}\rangle \\ + \sin \phi \cos \phi \psi_1^+ \dots \psi_k^+ \dots \psi_k^+ \dots \psi_N^+ |\text{vac}\rangle. \end{aligned} \quad (11.17)$$

Here, the first and last term vanish because ψ_i^+ and ψ_k^+ , respectively, are present in them twice. The transposition of operators ψ_i^+ and ψ_k^+ in the third term yields a negative sign thus Eq. (11.17) reduces to:

$$(\cos^2 \phi + \sin^2 \phi) \psi_1^+ \dots \psi_i^+ \dots \psi_k^+ \dots \psi_N^+ |\text{vac}\rangle = |\text{HF}\rangle \quad (11.18)$$

which is just the left-hand side of Eqs. (11.13) or (11.15). Thus, the invariance of $|\text{HF}\rangle$ to unitary transformations is proven.

The transformational freedom of the occupied MOs gives the possibility to localize them into certain regions of space leading to MOs with a shape corresponding to classical chemical expectations (bonds, lone pairs, etc.). Several localization criteria have been proposed which define particular unitary transformations. We do not discuss this issue here since it is not directly related to second quantization. The interested reader is referred to the book of Chalvet et al. (1975) and the review of Surján (1989).

By the above considerations we have seen that the antisymmetry of the Hartree-Fock wave function results in a transformational degree of freedom for the MOs. As it was discussed previously, this is consistent with the condition $F_{pt^*} = 0$ which is the expanded form of the Brillouin theorem. The latter has a particular significance also in post-Hartree-Fock calculations. This property will be utilized in the next section.

12 Many-Body Perturbation Theory

The second quantized formalism is perhaps most extensively utilized in the field of perturbation theory of many-electron systems. This is due to the tedious derivations necessary to arrive at feasible working formulae, especially at the higher orders of PT. This topic has a quite rich literature, including books (Raimes 1972, Mattuck 1976, Jørgensen & Simons 1981, Szabó & Ostlund 1982, Wilson 1984, 1987), reviews (Paldus & Cižek 1975) as well as timely scientific papers (see, e.g. Kutzelnigg 1984, Urban et al. 1984, Sæbo and Pulay 1988, Cullen 1988, Kapuy et al., 1987) the latter indicating that this field is being actively cultivated. In the spirit of the present treatment, we shall not address the most advanced problems of many-body perturbation theory (MBPT). Rather, the forthcoming chapter offers a simple introduction permitting one to pick up the basis ideas of MBPT. In particular, we shall derive the second-order Møller-Plesset formula for the correlation energy.

Some general remarks on the perturbation theory and the many-body approach are now in order. Let us review first the essence of the nondegenerate Rayleigh-Schrödinger perturbation theory.¹ Consider the time-independent Schrödinger equation for the ground state:

$$\hat{H}\Psi = E\Psi. \quad (12.1)$$

Finding solutions to this equation is, in most cases, a difficult task. Assume, however, that the Hamiltonian consists of two Hermitian parts:

$$\hat{H} = \hat{H}^{(0)} + \hat{W} \quad (12.2)$$

where solutions to the eigenvalue problem for $\hat{H}^{(0)}$:

$$\hat{H}^{(0)}\Psi_K^{(0)} = E_K^{(0)}\Psi_K^{(0)} \quad (12.3)$$

are manageable for all states ($K = 0, 1, 2, \dots$). The $\hat{H}^{(0)}$ is called the zeroth-order Hamiltonian while \hat{W} is a perturbation. Equation (12.2) specifies a partition of the Hamiltonian. If the perturbation is assumed to be small, the zeroth-order solutions $\Psi_K^{(0)}$ and $E_K^{(0)}$ approximate the exact solutions Ψ_K and E_K to an

¹ Among different perturbation theories, the Rayleigh-Schrödinger theory is distinguished in quantum chemistry, because it gives us *size-extensive* results. This means that the energy of two non-interacting subsystem is equal to the sum of the energies of the individual fragments. This property resembles the extensivity concept in thermodynamics (cf. Kutzelnigg 1977, Čarsky & Urban 1980). One often speaks also about *size-consistency* including the proper behavior of the wave function in dissociation processes.

acceptable accuracy. The zeroth-order approximation can be improved by taking into account the effect of \hat{W} in the following manner. If the set $\{\Psi_K^{(0)}\}$ is complete, the exact wave function Ψ can be expanded in the Fourier series:

$$\Psi = \sum_K C_K \Psi_K^{(0)}. \quad (12.4)$$

Accordingly, the complete set of zeroth-order eigenfunctions is assumed to be known. The coefficient at the zeroth-order ground state in Eq. (12.4) is often chosen as $C_0 = 1$ which can be achieved by an appropriate renormalization² of Ψ . By this choice, Eq. (12.4) becomes:

$$\Psi = \Psi_0^{(0)} + \sum_{K \neq 0} C_K \Psi_K^{(0)}. \quad (12.5)$$

This is the so-called intermediate normalization which can also be expressed as:

$$\langle \Psi | \Psi_0^{(0)} \rangle = 1 \quad (12.6)$$

The validity of Eq. (12.6) can be seen from Eq. (12.5) by multiplying with $\Psi_0^{(0)}$ from the right, integrating, and assuming the orthonormality of the zeroth-order set:

$$\langle \Psi_K^{(0)} | \Psi_L^{(0)} \rangle = \delta_{KL}. \quad (12.7)$$

This latter condition is satisfied if the zeroth-order Hamiltonian is Hermitian. If the zeroth-order wave function $\Psi_0^{(0)}$ is a good approximation to Ψ , the coefficients C_K in Eq. (12.5) are expected to be small and can be expanded in a perturbation series:

$$C_K = \sum_{\lambda=1}^{\infty} C_K^{(\lambda)} \quad (12.8)$$

where $C_K^{(\lambda)}$ is a λ th-order contribution to C_K . Similarly, the exact energy E can be expanded in a perturbation series as:

$$E_K = E_K^{(0)} + E_K^{(1)} + E_K^{(2)} + \dots \quad (12.9)$$

The aim of perturbation theory is to derive expressions for $C_K^{(\lambda)}$ and $E_K^{(\lambda)}$. Substituting the above expansions into the Schrödinger equation of Eq. (12.1), one gets explicit formulae for these unknown quantities. We report here only the following final results for energy corrections in the ground state:

$$E_0^{(1)} = \langle \Psi_0^{(0)} | \hat{W} | \Psi_0^{(0)} \rangle = W_{00} \quad (12.10a)$$

$$E_0^{(2)} = - \sum_{K \neq 0} \frac{\langle \Psi_0^{(0)} | \hat{W} | \Psi_K^{(0)} \rangle \langle \Psi_K^{(0)} | \hat{W} | \Psi_0^{(0)} \rangle}{E_K^{(0)} - E_0^{(0)}} = - \sum_{K \neq 0} \frac{W_{0K} W_{K0}}{E_K^{(0)} - E_0^{(0)}} \quad (12.10b)$$

$$E_0^{(3)} = \sum_{K,L} \frac{W_{0K} W_{KL} W_{L0}}{(E_K^{(0)} - E_0^{(0)})(E_L^{(0)} - E_0^{(0)})} - W_{00} \sum_{K \neq 0} \frac{W_{0K} W_{K0}}{(E_K^{(0)} - E_0^{(0)})^2}. \quad (12.10c)$$

² Renormalization [Eq. (12.5)] is not possible when $C_0 = 0$ in Eq. (12.4), that is, the exact eigenfunction has no component on $\Psi_0^{(0)}$. We say in this case that the zeroth-order approximation is singularly wrong.

These are standard results of the time-independent nondegenerate perturbation theory³ which are presented in every quantum mechanical textbook. The term ‘nondegenerate’ refers to the zeroth-order spectrum where degenerate levels would lead to singularities in the perturbation expressions, cf. Eqs. (12.10).

The second- and third-order results can be alternatively written in the following equivalent form:

$$E_0^{(2)} = \langle \Psi_0^{(0)} | \hat{W} \hat{Q} \hat{W} | \Psi_0^{(0)} \rangle \quad (12.11a)$$

$$E_0^{(3)} = \langle \Psi_0^{(0)} | \hat{W} \hat{Q} \hat{W} \hat{Q} \hat{W} | \Psi_0^{(0)} \rangle - W_{00} \langle \Psi_0^{(0)} | \hat{W} \hat{Q} \hat{W} | \Psi_0^{(0)} \rangle \quad (12.11b)$$

where:

$$\hat{Q} = - \sum_{K \neq 0} \frac{|\Psi_K^{(0)}\rangle \langle \Psi_K^{(0)}|}{E_K^{(0)} - E_0^{(0)}} \quad (12.11c)$$

is the so-called reduced resolvent.

The role of the many-body theory is to evaluate the above expressions containing many-electron wave functions in terms of orbital contributions. The matrix elements should be expressed in terms of integrals over one-electron functions. In course of the quantum-chemical application, the following points should be clarified:

- (i) Specification of the Hamiltonian
- (ii) Choice for $H^{(0)}$
- (iii) Solution of the 0th order Schrödinger equation
- (iv) Evaluation of the matrix elements W_{LK} .

Ad (i): The nonrelativistic Born-Oppenheimer many-body Hamiltonian projected to a given basis set can be most conveniently specified by the usual second quantized form. For convenience, the underlying basis set is assumed to be orthonormalized; MBPT calculations are usually performed in the MO basis which meets this criterion.

Ad (ii): The choice of the zeroth-order Hamiltonian is arbitrary, any Hermitian operator would do in principle. In practice, one wishes to chose $\hat{H}^{(0)}$ as close to \hat{H} as possible in order to obtain favorable convergence properties of the perturbation series. On the other hand, $\hat{H}^{(0)}$ should be as simple as possible, since one should be able to diagonalize it and obtain its complete set of eigenfunctions. A practical balance between these two conflicting requirements is to choose $\hat{H}^{(0)}$ as the Fock operator:

$$\hat{H}^{(0)} = \hat{F} = \sum_i \epsilon_i \psi_i^+ \psi_i^- \quad (12.12)$$

in terms of molecular spinorbitals ψ_i and orbital energies ϵ_i . By this choice, the perturbation operator \hat{W} describes the electron correlation (the error of

³ Eqs. (12.10–11) are valid only if the Schrödinger equation is linear, i.e., the Hamiltonian is independent of Ψ . This holds for isolated systems. For the generalization of the standard RS-PT to the nonlinear case see Surján & Ángyán (1983)

the Hartree-Fock approach) and the aim of the perturbation calculation is to improve the HF energy towards the exact solution of the Schrödinger equation in the same basis set. This is the so-called Møller-Plesset partitioning.⁴ As to the accuracy of the Hartree-Fock method, this varies from system to system (Čarsky & Urban 1980). If the molecule can be reasonably well described by a single determinant, the Hartree-Fock method represents an acceptable approximation in most cases.

This means that usually more than 99% of the total energy is accounted for.⁵ There are cases when the Hartree-Fock model is not suitable for describing the system. This is usually connected to the degeneracy (or near-degeneracy) of the ground- and excited states. If an RHF wave function is used, degeneracy occurs, e.g., during dissociation or bond fission processes, or upon twisting the molecule around a double bond. Clearly, the restriction of double occupancy cannot be maintained in the study of such processes leading to open-shell products. In these cases the RHF model cannot even be used as a suitable reference state for perturbational or limited configuration interaction calculations. It seems, for instance, from Eqs. (12.10) that if $E_K^{(0)}$ and $E_0^{(0)}$ tend to be degenerate, the corresponding term diverges.⁶ In these cases, an UHF calculation may be performed which possess asymptotically good dissociation properties⁷, and the PT can be based on the UHF reference state (unrestricted Møller-Plesset, UMP). Alternatively (and preferably), one may choose a multi-configurational reference state.

Ad (iii): Accepting the partition described by Eq. (13.12), the solution of the zeroth-order equation involves the solution of the Hartree-Fock problem. We have to specify the ground states and excited many-electron states explicitly. The ground state is simply the Fermi vacuum:

$$\Psi_0^{(0)} = \psi_1^+ \psi_2^+ \dots \psi_N^+ |vac\rangle = |\text{HF}\rangle. \quad (12.13)$$

The excited states can be classified according to the number of electrons to be excited. Singly excited states are given by:

$$\Psi_K^{(0)} = \psi_k^+ \psi_i^- |\text{HF}\rangle \quad (12.14)$$

where K labels the $i \rightarrow k^*$ excitation. Equation (12.14) expresses that an electron is annihilated from spinorbital ψ_i and it is inserted into ψ_k^* , the latter being one of the virtual levels.

⁴The correlation energy can be calculated perturbatively also in the Epstein-Nesbet partitioning in which the zeroth order is defined by the diagonal elements of the CI matrix.

⁵It is to be emphasized however, that this is not yet the “chemical accuracy”: the error in the Hartree-Fock energy is usually larger than the energy changes observed by experimentalists. Consequently, the Hartree-Fock calculation is chemically meaningful only if the correlation energy is conserved in the chemical process under study.

⁶Modified perturbation theories in which this singularity is eliminated have also been proposed (Cioslowski 1987)

⁷UHF potential curves quantitatively are not accurate enough: they are often deformed which is caused by the different spin contamination at different parts of the curve.

Problem 12.1

Check the mutual orthogonality of the singly excited states defined by Eq. (12.14).

A doubly excited state is given by the following expression:

$$\Psi_K^{(0)} = \psi_{i^*}^+ \psi_{k^*}^+ \psi_j^- \psi_i^- |HF\rangle \quad (12.15)$$

where $K = \begin{cases} i \rightarrow k^* \\ j \rightarrow l^* \end{cases}$. All doubly excited states are counted if $i < j$ and $k^* < l^*$.

The order of the virtual creation operators (as well as that of the occupied annihilation operators) is indifferent here since it defines simply the sign of the excited-state wave function. Analogously, a p-fold excited state can be specified as:

$$\Psi_K^{(0)} = \psi_{K_p}^+ \dots \psi_{K_1}^+ \psi_{K_p}^- \dots \psi_{K_1}^- |HF\rangle. \quad (12.16)$$

Ad (iv): Evaluation of the W_{LK} matrix elements can be performed according to the second quantization rules as described in Sect. 5.

Let us see now the PT formulae for the lowest orders.

(0) At the zeroth order, one has from Eqs. (12.3), (12.12) and (12.13):

$$\begin{aligned} H^{(0)} \Psi_0^{(0)} &= \hat{F} |HF\rangle = \sum_i \epsilon_i \psi_i^+ \psi_i^- \psi_1^+ \dots \psi_N^+ |vac\rangle \\ &= \sum_i \epsilon_i n_i \psi_1^+ \dots \psi_N^+ |vac\rangle \\ &= \sum_i^{\text{occ}} \epsilon_i |HF\rangle. \end{aligned} \quad (12.17)$$

That is, the *Fermi vacuum* is the zeroth order eigenfunction in the ground state. The corresponding eigenvalue is the sum of the energies of the occupied orbitals, and not the Hartree-Fock energy.

(1) The first order contribution is given by Eq. (12.10a):

$$E^{(1)} = \langle HF | \hat{W} | HF \rangle.$$

It follows that the energy to the first order will be:

$$\begin{aligned} E &= E^{(0)} + E^{(1)} = \langle HF | \hat{H}^{(0)} | HF \rangle + \langle HF | \hat{W} | HF \rangle \\ &= \langle HF | \hat{H}^{(0)} + \hat{W} | HF \rangle = \langle HF | \hat{H} | HF \rangle = E_{HF} \end{aligned} \quad (12.18)$$

which is the expectation value of the full Hamiltonian with the Hartree-Fock wave function, the Hartree-Fock electronic energy. The relevant expression has been derived in Sect. 7.3. We see that, using the Møller-Plesset partitioning, the first order of perturbation theory corrects the sum of orbital energies to the true HF energy.

(2) In deriving the second-order result, the explicit form of the perturbation operator \hat{W} should be specified. Using the short-hand notation for the creation/

annihilation operators, one may write:

$$\hat{W} = \hat{H} - \hat{H}^{(0)} = \sum_{ik} h_{ik} i^+ k^- + \frac{1}{2} \sum_{ijkl} [ij|kl] i^+ j^+ l^- k^- - \sum_i \varepsilon_i i^+ i^- \quad (12.19)$$

To evaluate the second order formula, the only matrix element we need⁸ is W_{0K} , since the second-order energy correction, Eq. (12.10b), can also be written as:

$$E^{(2)} = -\sum |W_{0K}|^2 / (E_K^{(0)} - E_0^{(0)}) \quad (12.20)$$

where K labels an excited state. In principle, it can be a p-fold excited state with $p = 1, 2, 3, \dots$. However, it is easy to show only $p = 2$ contributes to W_{0K} . Let us check first the role of singly excited states. From the Brillouin theorem we know that the full Hamiltonian does not have such a matrix element:

$$H_{0K} = \langle \Psi_0^{(0)} | \hat{H} | \Psi_K^{(0)} \rangle = 0,$$

that is,

$$\begin{aligned} \langle \Psi_0^{(0)} | \hat{H}^{(0)} + W | \Psi_K^{(0)} \rangle &= E_K \langle \Psi_0^{(0)} | \Psi_K^{(0)} \rangle + \langle \Psi_0^{(0)} | \hat{W} | \Psi_K^{(0)} \rangle \\ &= W_{0K} = 0 \end{aligned} \quad (12.21)$$

where the zeroth-order Schrödinger equation [Eq. (12.3)] and the orthogonality of the zeroth-order states are utilized. It follows that $W_{0K} = 0$ if K is a singly excited state.

Consider now a p-fold excitation for $p \geq 3$. Here we make use of the fact that the perturbation operator \hat{W} contains at most two-electron terms, cf. Eq. (12.19). For this reason the matrix element W_{0K} has the following structure:

$$W_{0K} = \sum \dots \langle HF | i^+ j^+ l^- k^- K_{p*}^+ \dots K_{2*}^+ K_{1*}^+ K_p^- \dots K_2^- K_1^- | HF \rangle$$

where Eq. (12.16) is substituted and again the short-hand notation for the operators is used. Trivially, this expression vanishes for $p > 2$. This can be seen, e.g., by counting the virtual creation and annihilation operators whose number should be the same in order to get a nonzero matrix element. In the above expression, there are p virtuals created upon excitation, while at most two can be annihilated by l^- and k^- . Thus, at least $p - 2$ virtuals remain which make the matrix element zero for $p \geq 3$.

Summarizing, only doubly excited states contribute to the matrix element W_{0K} , thus only they enter the second-order formula Eq. (12.20). With this result, the matrix element of W_{0K} can easily be evaluated. A doubly excited state is specified as:

$$|\Psi_K^{(0)}\rangle = s^{*+} r^{*+} q^- p^- |HF\rangle.$$

First, we find that one-electron part of \hat{W} given by Eq. (12.19) cannot contribute since any matrix element of type:

$$\langle HF | i^+ k^- s^{*+} r^{*+} q^- p^- | HF \rangle$$

⁸Since \hat{W} is Hermitian, $W_{0K} = W_{K0}$.

vanishes due to the uncompensated virtuals (two of them are created while at most one is annihilated by k^-). The same argument applies to the last term of Eq. (12.19) containing the HF orbital energies. Thus, we are concerned only with the two-electron part of \hat{W} , and the matrix element of Eq. (12.19) becomes:

$$W_{OK} = \frac{1}{2} \sum_{ijkl} [ij|kl] \langle HF | i^+ j^+ l^- k^- s^{*+} r^{*+} q^- p^- | HF \rangle. \quad (12.22)$$

The expectation value of the operator string sandwiched by the *Fermi vacuum* can be evaluated in several manner. The simplest way is to realize that $l^- k^-$ must annihilate the virtuals $s^{*+} r^{*+}$, and $i^+ j^+$ must re-create $q^- p^-$. Collecting all possible pairings we get:

$$\langle HF | i^+ j^+ l^- k^- s^{*+} r^{*+} q^- p^- | HF \rangle = (\delta_{ks^*} \delta_{lr^*} - \delta_{kr^*} \delta_{ls^*}) (\delta_{jq} \delta_{ip} - \delta_{iq} \delta_{jp}).$$

Substituting this result into Eq. (12.22) the following expression is obtained for the matrix element:

$$W_{OK} = \frac{1}{2} \{ [pq|s^*r^*] - [pq|r^*s^*] - [qp|s^*r^*] + [qp|r^*s^*] \},$$

which, utilizing the symmetry of the two-electron integrals, reduces to:

$$W_{OK} = [pq|s^*r^*] - [pq|r^*s^*] = [pq \parallel s^*r^*] \quad (12.23)$$

where the usual notation is introduced for the antisymmetrized integral, see Eq. (1.12).

The excitation energy in the denominator of the second-order formula is determined by the change in the sum of orbital energies due to the change in the occupancy of the orbitals upon excitation:

$$E_K^{(0)} - E_0^{(0)} = \sum_i n_i^K \epsilon_i - \sum_i n_i^0 \epsilon_i = \epsilon_r^* + \epsilon_s^* - \epsilon_p - \epsilon_q \quad (12.24)$$

where n_i^K is the occupation number of orbital i when the molecule is in state K . Substituting Eqs. (12.23) and (12.24) into Eq. (12.20) we find:

$$E^{(2)} = - \sum'_{pqrs^*} \frac{|[pq \parallel s^*r^*]|^2}{\epsilon_r^* + \epsilon_s^* - \epsilon_p - \epsilon_q} \quad (12.25)$$

where the summation over the doubly excited state K has been substituted by the summation over the orbitals involved in the two-electron excitation.⁹ Equation (12.25) is the second-order Møller-Plesset formula for the correlation energy in terms of spinorbitals.

⁹ The prime on the summation in Eq. (12.25) indicates the restrictions $p < q$ and $r^* < s^*$ which avoid the double counting of excited states, see Eq. (12.15). For $p = q$ or $r^* = s^*$ the numerator vanishes anyway, c.f. Eq. (12.23).

Problem 12.2

Show that the following formula is equivalent to Eq. (12.25):

$$E^{(2)} = -2 \sum'_{pqr^*s^*} \frac{[pq|r^*s^*]([pq|r^*s^*] - [pq|s^*r^*])}{\varepsilon_{r^*} + \varepsilon_{s^*} - \varepsilon_p - \varepsilon_q}. \quad (12.26)$$

Hint: Utilize the symmetry properties of the two-electron integrals.

It might be useful to rewrite the obtained expression for the correlation energy in terms of spatial orbitals; this will result in a formula suitable for computer programming. We do this on the basis of Eq. (12.26) for the closed-shell case. Since the denominator is immaterial in this respect, we focus our attention to the numerator. Using the corresponding capitals to denote spatial orbitals, the first term becomes:

$$[pq|r^*s^*][pq|r^*s^*] = [PQ|R^*S^*][PQ|R^*S^*]\delta_{\sigma_p\sigma_r}\delta_{\sigma_q\sigma_s}. \quad (12.27)$$

Summation over spin indices σ_p , σ_q , σ_{r^*} , and σ_{s^*} , two of them being independent due to the coincidence expressed by the above Kronecker delta, gives a factor of 4. For the exchange term all spin labels should coincide since:

$$\begin{aligned} & [pq|r^*s^*][pq|s^*r^*] \\ &= [PQ|R^*S^*][PQ|S^*R^*]\delta_{\sigma_p\sigma_r}\delta_{\sigma_q\sigma_{s^*}}\delta_{\sigma_p\sigma_{s^*}}\delta_{\sigma_q\sigma_{r^*}}. \end{aligned} \quad (12.28)$$

Summation over spin labels gives a factor of 2, since there is only one independent label. Thus, the second-order Møller-Plesset formula for the correlation energy can be given in terms of spatial orbitals as:

$$E^{(2)} = -4 \sum'_{PQR^*S^*} \frac{[PQ|R^*S^*](2[PQ|R^*S^*] - [PQ|S^*R^*])}{\varepsilon_{R^*} + \varepsilon_{S^*} - \varepsilon_p - \varepsilon_Q}. \quad (12.29)$$

The above consideration for finding the numerical factor in front of integrals over spatial orbitals can be done more automatically using the simple graphical tool as discussed in Sect. 9. The relevant graphs for Eqs. (12.27) and (12.28) are given in Fig. 12.1. Clearly, they bring the factors of 4 and 2, respectively.

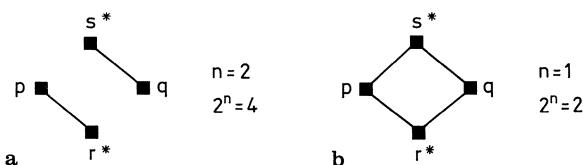


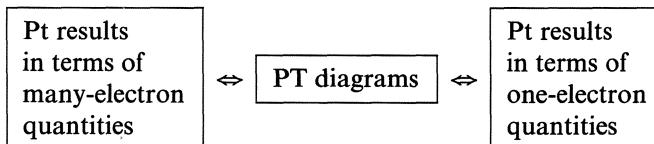
Fig. 12.1a, b. Spin integration in Eqs. (12.27) (a) and (12.28) (b)

Problem 12.3

Derive the third-order contribution to the correlation energy in terms of spinorbitals.

Derivation of higher order perturbation formulae, in principle, can be done along the same lines as we did for the second order. Due to the increasing complexity of derivations and of the resulting formulae with increasing order, special diagrammatic methods have been developed which serve as efficient book-keeping techniques in the manipulation of PT expressions. The diagrammatic PT can be learned from several books and reviews; the monograph by Szabó and Ostlund (1982) as well as that of Čarsky and Urban (1980) are suggested for beginners. The latter gives a short summary of the essence of diagrammatic PT, while the former offers a more detailed but easy-to-follow treatment. For further reading, see e.g. Jørgensen and Simons (1981). In what follows, the basic idea of the diagrammatic representation of MBPT will be explained for the second-order Hugenholtz diagram representing the spinorbital expression of Eq. (12.25).

The basic idea of diagrammatic PT is the following one. The structure of the general PT formulae expressed in terms of many-electron wave functions [Eqs. (12.11)] determines unequivocally the structure of the corresponding orbital expressions. A one-to-one mapping can be established between general PT results and diagrams, as well as between diagrams and orbital expressions:



Once this connection has been established, the PT diagrams can be constructed directly, following their own rules, and can easily be converted into orbital forms. Hence, they serve as efficient tools in deriving orbital expressions, especially at higher orders where the direct route is not really feasible.

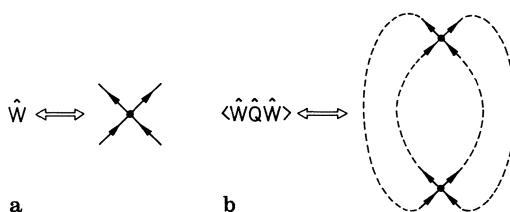


Fig. 12.2a, b. Diagrammatic derivation of the second-order contribution of the correlation energy. **a** representation of the interaction operator; **b** linking of two operators

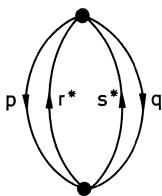


Fig. 12.3. The second-order diagram

The construction of the second-order diagram is illustrated in Fig. 12.2. First, the diagrammatic representation of a two-electron operator \hat{W} presented. Such an operator corresponds to a dot with two outgoing and two ingoing lines. This is shown in Fig. 12.2a. The second-order PT formula to be represented is Eq. (12.11a), in which two \hat{W} operators are present. Accordingly, one has to put down two dots (Fig. 12.2b). The two dots can be oriented either vertically or horizontally; here we use the vertical orientation. As shown, the lines on the two dots should be connected so that the diagram is completely linked. The resulting graph can be arranged in an attractive manner (Fig. 12.3).

Conversion of the second-order diagram to the orbital expression can be done as follows. The lines with downward arrows are labelled by indices of occupied orbitals, while lines with upward arrows bear virtual labels. A set of labels defines a matrix element of \hat{W} ; more precisely, an antisymmetrized integral $[pq||s^*r^*]$. Summation is performed over all indices. The diagram is understood to carry the overall sign, the relevant energy denominator, and a factor of $1/2^n$ where n is the number of equivalent pairs of lines which enter/leave the same vertex. For the second-order diagram in Fig. 12.3, n is equal to 2, thus one has a factor of $1/4$ which substitutes the summation restrictions $p < q$ and $r^* < s^*$ in Eq. (12.25).

Representation of the third-order formula (12.11b) requires to put down three different dots oriented vertically corresponding to the three \hat{W} operators in Eq. (12.11b). Connecting of the lines entering and leaving the vertices in all possible manner we find the three graphs shown in Fig. 12.4. These diagrams represent the third-order corrections to the correlation energy.

Besides of Hugenholtz diagrams, one may also use different graphical representations of perturbation expressions which can help one in rewriting the formulae in terms of spatial orbitals. The latter rules are essentially generalizations of the simple graphical tool introduced in Sect. 9.

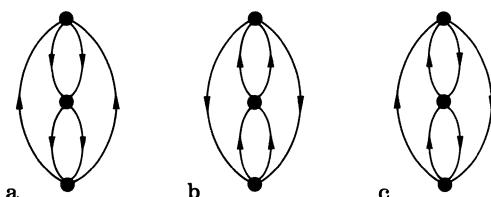


Fig. 12.4. Diagrammatic representation of the third-order contribution of the correlation energy (cf. Problem 12.2.)

13 Second Quantization for Nonorthogonal Orbitals

In the preceding treatment we became familiar with the basic notions of second quantization. By this section we begin to discuss less standard chapters of this theory. These subjects are not as widely documented in the literature, therefore the interested reader should consult mostly with original papers rather than books, though review articles are available in some cases.

An important generalization of the second quantized formalism is the extension to the case of a nonorthogonal basis set. Such an extension is inevitable if one is aiming to develop a theory within the original AO basis, or if one is studying the interaction between different molecules whose wave functions (or MOs) mutually overlap. In what follows we shall review this theory in detail, since, up to our knowledge, no such review has yet been published.

As this matter is in a close relationship with the usual nonorthogonality problem, it is not surprising that one of the first pioneers of the field was Löwdin (personal communication). In the early review by Longuet-Higgins (1966) the basic commutator relations for the nonorthogonal case are mentioned. Other inventors of this formalism were Moshinsky and Seligman (1971) who developed a consistent theory of second quantization in the nonorthogonal case along with an application to the unitary group approach as applied to the problem of nuclei. Later, Kvasnička (1977) developed a formal theory as applied to quantum-chemical problems; his approach is based on a mapping to an ideal space which is essentially a Löwdin-orthogonalized basis set. Mayer (1983) applied a bi-orthogonal formulation in his second-quantization-based “Chemical Hamiltonian Approach”. Recently, Ng and Newman (1985) used a similar formalism to develop an MBPT in nonorthogonal basis. We shall not review the above-cited papers in detail, but rather a general treatment will be given, to our intention, in an easy-to-follow manner.

13.1 Anticommutation Rules

The essential feature of the orthogonality of the underlying basis orbitals with respect to second quantization is the adjoint relation:

$$(a_i^+)^{\dagger} = a_i \quad (13.1)$$

where a_i is the true annihilation operator satisfying the anticommutation rule:

$$[a_i^+, a_k]_+ = \delta_{ik}. \quad (13.2)$$

Both of these equations have their own significance. The adjoint relation is essential when putting down the second quantized correspondances of *bra*-vectors, cf. Eq. (2.53). The anticommutation rule is important in dealing with matrix elements where one often has to transpose creation and annihilation operators.

As seen in Sect. 2.6, Eqs. (13.1) and (13.2) hold simultaneously only if the underlying orbital set is orthogonal:

$$\langle i|k \rangle = \delta_{ik}. \quad (13.3)$$

Violation of Eq. (13.3) leads to the violation of either Eq. (13.1) or Eq. (13.2).

Accordingly, the second quantized formalism can be generalized to the non-orthogonal case in two alternative manners: one may keep either the adjoint relation of Eq. (13.1) or the simple anticommutation rule of Eq. (13.2). In the former case the commutation rules become more complicated, while in the latter case the annihilation operators will not be the adjoints of the corresponding creation operators.

Let us first look at the generalization of the anticommutation rules if we accept Eq. (13.1). For the sake of forthcoming distinctions, the creation operators creating electrons on a nonorthogonal set of spinorbitals $\{\chi\}$ will be denoted by:

$$\chi_k^+$$

(cf. the Longuet-Higgins notations, Sect. 2.2). The nonorthogonality of the set $\{\chi\}$ is given as:

$$\langle \chi_i | \chi_k \rangle = S_{ik} \neq \delta_{ik} \quad (13.4)$$

where S is the overlap (or metric) matrix.

To derive the commutation rule for operators χ_i^+ and their adjoints:

$$\chi_i^- = (\chi_i^+)^{\dagger},$$

we assume the existence of a second, orthonormalized basis set of spinorbitals. This auxiliary set is introduced just for the sake of the derivation and there is no need to orthogonalize the orbitals explicitly. Let us denote the orthogonalized functions by ψ_i . They can be obtained from the overlapping set by Löwdin's symmetric orthogonalization procedure¹:

$$\psi_i = \sum_l S_{il}^{-1/2} \chi_l \quad (13.5)$$

where $S^{-1/2}$ is the inverse square root of the overlap matrix S . Substitution of Eq. (13.5) into Eq. (13.3) and utilization of Eq. (13.4) proves the orthogonality of the orbitals $\{\psi\}$, which are usually called Löwdin orbitals.

Since the set $\{\psi\}$ is orthonormalized, second quantization can be developed in terms of its elements in the usual manner. We know, for instance, that the

¹ One may choose any other orthogonalization procedure as well (Schmidt, canonical, etc. orthogonalization); in this case the resulting orthonormal set is related to the set $\{\psi\}$ by a unitary transformation.

following anticommutation rules hold:

$$\psi_i^+ \psi_k^+ + \psi_k^+ \psi_i^+ = 0 \quad (13.6a)$$

$$\psi_i^- \psi_k^- + \psi_k^- \psi_i^- = 0 \quad (13.6b)$$

$$\psi_i^+ \psi_k^- + \psi_k^- \psi_i^+ = \delta_{ik} \quad (13.6c)$$

where ψ_i^+ / ψ_i^- are creation/annihilation operators in the Löwdin basis. Clearly, the inverse transformation of the Löwdin orthogonalization of Eq. (13.5) is given by:

$$\chi_i = \sum_i S_{ii}^{1/2} \psi_i. \quad (13.7)$$

The same transformations hold for the corresponding creation/annihilation operators:

$$\psi_i^+ = \sum_l S_{il}^{-1/2} \chi_l^+, \quad \psi_i^- = \sum_l S_{il}^{-1/2} \chi_l^- \quad (13.8a)$$

$$\chi_l^+ = \sum_i S_{ii}^{1/2} \psi_i^+ \quad \chi_l^- = \sum_i S_{ii}^{1/2} \psi_i^-. \quad (13.8b)$$

The commutation rules for operators over the nonorthogonal set $\{\chi\}$ can be derived in a straightforward manner by substituting this inverse transformation and utilizing the commutation rules in the Löwdin basis:

$$[\chi_l^+, \chi_n^+]_+ = \sum_{ik} S_{il}^{1/2} S_{kn}^{1/2} [\psi_i^+, \psi_k^+]_+ = 0. \quad (13.9a)$$

Similarly:

$$[\chi_l^-, \chi_n^-]_+ = 0. \quad (13.9b)$$

While:

$$[\chi_l^+, \chi_n^-]_+ = \sum_{ik} S_{il}^{1/2} S_{nk}^{1/2} [\psi_i^+, \psi_k^-]_+ = \sum_{ik} S_{il}^{1/2} S_{nk}^{1/2} \delta_{ik}$$

performing the summation one finds:

$$[\chi_l^+, \chi_n^-]_+ = S_{nl}. \quad (13.9c)$$

Thus, we see that the anticommuting character of the creation operators χ^+ , as well as that of their adjoints χ^- , remain true in a nonorthogonal basis set, but the mutual commutation rule between χ^+ and χ^- is replaced by Eq. (13.9c).

The consequences of Eq. (13.9) are so serious that operators χ^- can no longer be considered as true annihilation operators with respect to operators χ^+ . We cannot transpose an annihilation and a creation operator even if they have different labels, which leads to serious complications in evaluating matrix elements. The first thing one may observe is that a determinant of the usual form:

$$|D\rangle = \chi_N^+ \dots \chi_2^+ \chi_1^+ |vac\rangle \quad (13.10)$$

is not normalized:

$$\langle D|D\rangle = \langle \text{vac} | \chi_1^- \chi_2^- \dots \chi_N^- \chi_N^+ \dots \chi_2^+ \chi_1^+ | \text{vac} \rangle \neq 1. \quad (13.11)$$

This can be most easily seen on a two-by-two example:

$$\begin{aligned} \langle D|D\rangle &= \langle \text{vac} | \chi_1^- \chi_2^- \chi_2^+ \chi_1^+ | \text{vac} \rangle \\ &= S_{22} \langle \text{vac} | \chi_1^- \chi_1^+ | \text{vac} \rangle - \langle \text{vac} | \chi_1^- \chi_2^+ \chi_2^- \chi_1^+ | \text{vac} \rangle \\ &= S_{22} S_{11} - \langle \text{vac} | (S_{12} - \chi_2^+ \chi_1^-)(S_{21} - \chi_1^+ \chi_2^-) | \text{vac} \rangle \\ &= S_{22} S_{11} - S_{12} S_{21} \neq 1 \end{aligned} \quad (13.12)$$

where we applied the anticommutation rule of Eq. (13.9c) and used that χ^- acting on the vacuum results in zero even in the nonorthogonal case. (This is obvious since the χ^- operators are linear combinations of the ψ^- ones, cf. Eq. (13.8b), and all ψ^- have this property.)

Problem 13.1

Evaluate the normalization factor for the N-electron determinant given in Eq. (13.10).

Similar difficulties are encountered for calculating any other matrix elements in a nonorthogonal basis: neither of the rules discussed in Sect. 5 are applicable. The consistent analysis of this problem leads to the rederivation of the so-called Löwdin rules (1955) for such matrix elements. Application of these rules is rather laborious and computationally time-consuming in most cases. Instead of checking all such rules, let us turn back to another possible generalization of the second quantized formalism for nonorthogonal orbitals, where we drop the adjoint relation while keeping the original anticommutation rule.

Let us start again by introducing the creation operators χ_i^+ for the non-orthogonal basis. The annihilation operators, however, will not be taken as the adjoints of χ^+ , but they will be defined to obey the usual anticommutation rules. To avoid any confusion, they are denoted by $\tilde{\chi}_k^-$:

$$[\chi_i^+, \tilde{\chi}_k^-]_+ = \delta_{ik} \quad (13.13)$$

by definition. The relation between operators $\tilde{\chi}_k^-$ and χ_k^- is easy to find. Assume that the formers are linear combinations of the latter ones:

$$\tilde{\chi}_k^- = \sum_l L_{kl} \chi_l^- . \quad (13.14)$$

Substitution of this expression into Eq. (13.13) gives:

$$[\chi_i^+, \tilde{\chi}_k^-]_+ = \sum_l L_{kl} [\chi_i^+, \chi_l^-] = \sum_l L_{kl} S_{li} = \delta_{ik}$$

from which we see that $L = S^{-1}$, that is:

$$\tilde{\chi}_k^- = \sum_l S_{kl}^{-1} \chi_l^- . \quad (13.15)$$

We conclude that the true annihilation operators $\tilde{\chi}_k^-$ are related to the adjoints of the creation operators by a transformation with the inverse of the overlap matrix.² Since operators $\tilde{\chi}_k^-$ are linear combinations of $\chi_k^- - s$, their anti-commuting properties:

$$[\tilde{\chi}_k^-, \tilde{\chi}_k^-]_+ = 0 \quad (13.16)$$

are clearly maintained.

Application of operators $\tilde{\chi}_k^-$ is advantageous since we can use any results derived for the orthogonal case which are based on the anticommutation rule of Eq. (13.13). On the other hand, this story represents a typical example for the law of “the conservation of the difficulty”. As a matter of fact, in the absence of the adjoint relation, the construction of bra wave functions may be troublesome. It is possible only by means of the inverse transformation:

$$\chi_k^- = \sum_l S_{kl} \tilde{\chi}_k^- . \quad (13.17)$$

Let us check again the normalization of a two-electron determinant as an example:

$$\langle D|D \rangle = \langle \text{vac} | \chi_1^- \chi_2^- \chi_2^+ \chi_1^+ | \text{vac} \rangle .$$

Expanding operators χ_1^- and χ_2^- via Eq. (13.17) one writes:

$$\begin{aligned} \langle D|D \rangle &= \sum_{lm} S_{1l} S_{2m} \langle \text{vac} | \tilde{\chi}_1^- \tilde{\chi}_m^- \chi_2^+ \chi_1^+ | \text{vac} \rangle \\ &= \sum_{lm} S_{1l} S_{2m} (\delta_{m2} \delta_{l1} - \delta_{m1} \delta_{l2}) \\ &= S_{11} S_{22} - S_{12} S_{21} \end{aligned} \quad (13.18)$$

where the expectation value is evaluated as usual, which is permitted by the proper anticommutation rules of Eq. (13.13). Notice that the same expressions are recovered as under Eq. (13.12), indicating that the two methods are completely equivalent as far as the final result is concerned.

Problem 13.2

Derive the normalization of an N-electron determinant using operators $\tilde{\chi}_k^-$.

We have to emphasize that the significance of operators $\tilde{\chi}_k^-$ is that they are the true annihilation operators related to $\chi^+ - s$ in a nonorthogonal basis, as expressed by the anticommutation rule of Eq. (13.13). The nonorthogonality of the basis orbitals is manifested in Eq. (13.15) specifying the connection between $\tilde{\chi}_k^-$ (annihilation operators) and χ_k^- (adjoints of χ_k^+).

² It has to be supposed that the matrix S is invertable, that is, there is no linear dependency in the basis set.

One can say that operators $\tilde{\chi}_k^-$ are related to a bi-orthogonal set with respect to χ_k^- . Given a set of nonorthogonal functions $\{\chi_k\}$, the bi-orthogonal (or reciprocal) functions are defined by

$$\langle \tilde{\chi}_i | \chi_k \rangle = \delta_{ik}. \quad (13.19)$$

This equation is satisfied if:

$$\tilde{\chi}_i = \sum_l S_{li}^{-1} \chi_l \quad (13.20)$$

where S^{-1} is the inverse of the overlap matrix. Such bi-orthogonal vectors are regularly applied in solid-state physics (reciprocal lattice vectors) as well as in field theories (co- and contravariant coordinates). Their mathematical properties have been reviewed by Lathouwers (1976), and they were applied in quantum chemistry by several authors. Their advantages in second quantization will be further utilized below.

13.2 The Hamiltonian in Nonorthogonal Representations

In order to find the second quantized Hamiltonian in a nonorthogonal representation, we proceed in a similar manner as we did in finding the anticommutation rules of Eq. (13.9). That is, we introduce again an auxiliary orthonormal set $\{\psi\}$ for which the result is known:

$$\hat{H} = \sum_{ik} h_{ik} \psi_i^+ \psi_k^- + \frac{1}{2} \sum_{ijkl} [ij|kl] \psi_i^+ \psi_j^+ \psi_l^- \psi_k^-. \quad (13.21)$$

Afterwards, the transformations of Eqs. (13.8) are substituted:

$$\begin{aligned} \hat{H} &= \sum_{ik} h_{ik} S_{pi}^{-1/2} S_{qk}^{-1/2} \chi_p^+ \chi_q^- \\ &+ \frac{1}{2} \sum_{ijkl} [ij|kl] S_{pi}^{-1/2} S_{qj}^{-1/2} S_{lr}^{-1/2} S_{ks}^{-1/2} \chi_p^+ \chi_q^+ \chi_r^- \chi_s^-. \end{aligned} \quad (13.22)$$

This form of the Hamiltonian is not very useful since the integral list refers to the auxiliary basis set. Let us transform it back to the original basis:

$$\begin{aligned} h_{ik} &= \langle \psi_i | h | \psi_k \rangle = \sum_{ab} S_{ia}^{-1/2} S_{bk}^{-1/2} \langle \chi_a | h | \chi_b \rangle \\ &= \sum_{ab} S_{ia}^{-1/2} h_{ab} S_{bk}^{-1/2} \end{aligned} \quad (13.23a)$$

and similarly for two-electron integrals:

$$[ij|kl] = \sum_{abcd} S_{ia}^{-1/2} S_{jb}^{-1/2} [ab|cd] S_{ck}^{-1/2} S_{dl}^{-1/2}. \quad (13.23b)$$

Substitution of Eq. (13.23) into Eq. (13.22) results in a considerable simplification.

tion. Summation over indices i, k (one-electron term) and i, j, k, l (two-electron term) can be performed leading to the appearance of the S^{-1} matrix, since, for example:

$$\sum_i S_{pi}^{-1/2} S_{ia}^{-1/2} = S_{pa}^{-1}.$$

By doing so, the Hamiltonian of Eq. (13.22) takes the form:

$$\begin{aligned} \hat{H} = & \sum_{pqab} S_{pa}^{-1} h_{ab} S_{qb}^{-1} \chi_p^+ \chi_q^- \\ & + \frac{1}{2} \sum_{\substack{pqrs \\ abcd}} S_{pa}^{-1} S_{qb}^{-1} [ab|cd] S_{cs}^{-1} S_{dr}^{-1} \chi_p^+ \chi_q^+ \chi_r^- \chi_s^- \end{aligned} \quad (13.24)$$

where all indices refer to the nonorthogonal basis. Consequently, Eq. (13.24) can be considered as the second quantized representation of the Hamiltonian in an overlapping basis set. It appears to be quite complicated, since it contains as much as eight summation indices, and the second quantized operators follow the unfavorable anticommutation rule of Eq. (13.9).

Several equivalent forms of this Hamiltonian can be put down by performing the summation over some indices of S^{-1} . A convenient form is obtained, for instance, when transforming all *bra*-indices of the integrals as well as all annihilation operators to the reciprocal space:

$$\hat{H} = \sum_{pb} h_{pb} \chi_p^+ \tilde{\chi}_b^- + \frac{1}{2} \sum_{pqcd} [\tilde{p}\tilde{q}|cd] \chi_p^+ \chi_q^+ \tilde{\chi}_d^- \tilde{\chi}_c^- \quad (13.25)$$

where the annihilation operators $\tilde{\chi}^-$ are introduced following Eq. (13.15), and the *bra*-transforms are defined as:

$$h_{pb} = \sum_a S_{pa}^{-1} h_{ab} \quad (13.26a)$$

and:

$$[\tilde{p}\tilde{q}|cd] = \sum_{ab} S_{pa}^{-1} S_{qb}^{-1} [ab|cd]. \quad (13.26b)$$

The Hamiltonian of Eq. (13.25) is formally very similar to the second quantized representation in an orthogonal basis, cf. Eq. (13.21). In fact, it can be manipulated in a similar manner since the anticommutation rules of Eq. (13.13) hold. An essential difference is that the integral list in Eq. (13.25) is not symmetric:

$$h_{pb} \neq h_{bp} \quad (13.27a)$$

and:

$$[\tilde{p}\tilde{q}|cd] \neq [\tilde{c}\tilde{d}|pq]. \quad (13.27b)$$

The total Hamiltonian is still Hermitian, of course. This is possible because $\tilde{\chi}_p^-$ is not the adjoint of χ_p^+ . One has to be careful, however, when considering partitionings of Eq. (13.25), since individual terms of this Hamiltonian are not Hermitian.

An alternative form of the Hamiltonian results if we keep all integrals untransformed, but the creation operators are also transformed to the reciprocal space:

$$\hat{H} = \sum_{ab} h_{ab} \tilde{\chi}_a^+ \tilde{\chi}_b^- + \frac{1}{2} \sum_{abcd} [ab|cd] \tilde{\chi}_a^+ \tilde{\chi}_b^+ \tilde{\chi}_d^- \tilde{\chi}_c^- . \quad (13.28)$$

Problem 13.3

Find the commutation rules between $\tilde{\chi}_i^-$ and $\tilde{\chi}_k^+$, and show that $\tilde{\chi}_k^-$ is the adjoint of $\tilde{\chi}_k^+$.

This form of the Hamiltonian has the disadvantage that the relevant commutation rules are complicated, while the advantages are that (i) each term of Eq. (13.28) is Hermitian and (ii) all integrals refer to the original basis set. Further, Eq. (13.28) is well suited to specify the energy expression:

$$E = \langle H \rangle = \sum_{ab} h_{ab} P_{ba} + \frac{1}{2} \sum_{abcd} [ab|cd] \Gamma_{cdab} \quad (13.29)$$

where:

$$P_{ba} = \langle \tilde{\chi}_a^+ \tilde{\chi}_b^- \rangle \quad (13.30a)$$

and:

$$\Gamma_{cdab} = \langle \tilde{\chi}_a^+ \tilde{\chi}_b^+ \tilde{\chi}_d^- \tilde{\chi}_c^- \rangle \quad (13.30b)$$

are the representations of the first- and second-order density matrices, respectively.

We have to note here that the properties of matrix P are different from those in an orthogonal representation. While in the latter case its trace gives the number of electrons, in a non-orthogonal basis we find:

$$\text{Tr}(PS) = N. \quad (13.31)$$

This can easily be verified:

$$\begin{aligned} \text{Tr}(PS) &= \sum_{\mu\nu} P_{\mu\nu} S_{\nu\mu} = \sum_{\mu\nu} \langle \tilde{\chi}_v^+ \tilde{\chi}_\mu^- \rangle S_{\nu\mu} = \sum_{\mu\nu\lambda} S_{\lambda v}^{-1} \langle \tilde{\chi}_\lambda^+ \tilde{\chi}_\mu^- \rangle S_{\nu\mu} \\ &= \sum_\mu \langle \tilde{\chi}_\mu^+ \tilde{\chi}_\mu^- \rangle = \sum_\mu n_\mu = N. \end{aligned} \quad (13.32)$$

Here we utilized the fact that the mixed use of direct-space creation operators and reciprocal space annihilation operators permits us to use the same algebra which would be valid for the orthogonal case, as follows from the proper commutation rules of Eq. (13.13).

A third possible form of the Hamiltonian arises if the bi-orthogonal transformation is carried out for all integral labels, but the fermion operators χ^+ and χ^- remain untransformed:

$$\hat{H} = \sum_{pq} h_{\tilde{p}\tilde{q}} \chi_p^+ \chi_q^- + \frac{1}{2} \sum_{pqrs} [\tilde{p}\tilde{q}|\tilde{s}\tilde{r}] \chi_p^+ \chi_q^+ \chi_r^- \chi_s^- . \quad (13.33)$$

The transformed integral list is symmetric, but the associated commutation rules are unfavorable. This form of the Hamiltonian has little value.

Finally, we may put down the fourth possible form of \hat{H} in which the *ket*-indices of the integrals are transformed together with the creation operators:

$$\hat{H} = \sum_{aq} h_{aq} \tilde{\chi}_a^+ \chi_q^- + \frac{1}{2} \sum_{abrs} [ab|\tilde{s}\tilde{r}] \tilde{\chi}_a^+ \tilde{\chi}_b^+ \chi_r^- \chi_s^- \quad (13.34)$$

which has a rather similar significance as Eq. (13.25), since the integral list is unsymmetric while the fermion operators properly anticommute.

The above four forms of the Hamiltonian, Eqs. (13.25), (13.28), (13.33), and (13.34), are equivalent, but require a different algebra to deal with the integrals and the fermion operators. In many ways, the mixed form of Eq. (13.25) is the most useful one, where the creation operators χ^+ refer to the direct space and the $\tilde{\chi}^-$ operators are defined as the true annihilators. In what follows we shall mainly use this form and sometimes that of Eq. (13.28).

13.3 Extended Hückel Theory

The extended Hückel theory, EHT, developed originally by Hoffmann (1963), is a semiempirical method which can be considered as the generalization of the Hückel π -electron theory to the all-valence-electron level. Since the model includes explicitly the overlap between AOs, it serves as a good exercise to nonorthogonal second quantization. The problems associated with the overlapping basis prevented us from discussing this method in Sect. 10.3 among all-valence-electron schemes. Having introduced second quantization for non-orthogonal orbitals, we are in a position to specify the EHT Hamiltonian. Since it is a one-electron Hamiltonian, it can be written as:

$$\hat{H}^{EHT} = \sum_{\mu\nu} h_{\tilde{\mu}\tilde{\nu}} \chi_\mu^+ \tilde{\chi}_\nu^- = \sum_{\mu\nu\lambda} S_{\mu\lambda}^{-1} h_{\lambda\nu} \chi_\mu^+ \tilde{\chi}_\nu^- \quad (13.35)$$

where the tildes ($\tilde{}$) refer to the reciprocal space. The summation labels run over all atomic spinorbitals in the valence shell. In terms of spatial orbitals the same can be written as:

$$\hat{H}^{EHT} = \sum_{mn} h_{\tilde{m}\tilde{n}} \sum_{\sigma} \chi_{m\sigma}^+ \tilde{\chi}_{n\sigma}^- = \sum_{mnl} S_{ml}^{-1} h_{ln} \sum_{\sigma} \chi_{m\sigma}^+ \tilde{\chi}_{n\sigma}^- . \quad (13.36)$$

The EHT Hamiltonian is defined by the h_{ln} one-electron integrals and the S_{ml} overlap matrix. The former ones are parametrized as:

$$h_{ln} = \begin{cases} \alpha_n & \text{if } l = n \\ \frac{1}{2} \mathcal{K}(\alpha_l + \alpha_n) S_{ln} & \text{if } l \neq n \end{cases} \quad (13.37)$$

where α_n are empirical ionization potentials corresponding to the AO χ_n , while \mathcal{K} is an empirical constant in the range $1 < \mathcal{K} < 2$ (usually, $\mathcal{K} = 1.75$).

The deviation of \mathcal{K} from unity is important. Let us assume that we have a system of identical atoms so that all α_n parameters have a uniform value α . Then, if \mathcal{K} were equal to 1, the h_{ln} integrals in Eq. (13.37) would reduce as:

$$h_{ln} = \alpha S_{ln}$$

for any l, n . Consequently, the EHT Hamiltonian would read:

$$H^{\text{EHT}} = \alpha \sum_{mnl} S_{ml}^{-1} S_{ln} \sum_{\sigma} \chi_{m\sigma}^+ \tilde{\chi}_{n\sigma}^- = \alpha \sum_{m\sigma} \chi_{m\sigma}^+ \tilde{\chi}_{m\sigma}^-.$$

Clearly, this is a very bad model since any determinant of form:

$$\chi_1^+ \chi_2^+ \dots \chi_N^+ |vac\rangle$$

is an eigenfunction of H^{EHT} which can be shown using the commutation rules. This means that no interaction can be described by this Hamiltonian.

On the other hand, the usual extended Hückel Hamiltonian in a careful parametrization is capable of describing many aspects of interorbital interactions, and it represents a standard tool of applied quantum chemistry (Fernández-Alonso 1976, Hoffmann 1982, Náray et al. 1987).

Diagonalization of the EHT Hamiltonian of Eq. (13.36) involves the diagonalization of the unsymmetric matrix of integrals h_{mn} :

$$\sum_n h_{mn} C_{Kn} = \varepsilon_K C_{Km} \quad (13.38)$$

where the coefficient C_{Kn} gives the n -th component of the K -th right eigenvector of the nonsymmetric Hamiltonian matrix. It is usual to bring Eq. (13.38) to another form by writing out the bi-orthogonal transformation explicitly:

$$\sum_{np} S_{mp}^{-1} h_{pn} C_{Kn} = \varepsilon_K C_{Km}$$

which, alternatively, can be written as:

$$\sum_n h_{qn} C_{Kn} = \varepsilon_K \sum_m S_{qm} C_{Km}. \quad (13.39)$$

This is the standard form of the matrix eigenvalue problem written in a non-orthogonal metric. The coefficients C_{Kn} are normalized as:

$$\sum_{qm} C_{Kq} S_{qm} C_{Lm} = \delta_{KL}. \quad (13.40)$$

The diagonalized Hamiltonian is written in terms of MOs as:

$$H^{\text{EHT}} = \sum_K \varepsilon_K \psi_K^+ \psi_K^- \quad (13.41)$$

where the MO creation and annihilation operators are defined as:

$$\psi_{K\sigma}^+ = \sum_m C_{Km} \chi_{m\sigma}^+ \quad (13.42a)$$

and:

$$\Psi_{K\sigma}^- = \sum_q C_{Kq} \chi_{q\sigma}^- = \sum_{qn} C_{Kq} S_{qn} \tilde{\chi}_{n\sigma}^- \quad (13.42b)$$

Problem 13.4

Prove the validity of Eq. (1.3.41) using Eqs. (13.38–42).

The one-electron molecular spinorbitals are eigenfunctions of H^{EHT} .

The commutation rules of the MO fermion operators can be calculated from Eq. (13.42):

$$[\Psi_K^+, \Psi_L^-] = \sum_{mq} C_{Km} C_{Lq} [\chi_m^+, \chi_q^-] = \sum_{mq} C_{Km} C_{Lq} S_{mq} = \delta_{KL} \quad (13.43)$$

where the normalization condition of Eq. (13.40) was used. We see that the MO operators properly anticommute. This is quite natural since the Hamiltonian being Hermitian, its eigenvectors form an orthonormal set whether or not they are expanded in a nonorthogonal metric. The N-electron eigenfunctions of the EHT Hamiltonian are usual determinants, which can be most easily checked in terms of spinorbitals:

$$\begin{aligned} H^{EHT}\Psi &= \sum_K \varepsilon_K \Psi_K^+ \Psi_K^- \Psi_N^+ \dots \Psi_2^+ \Psi_1^+ |vac\rangle \\ &= \sum_K \varepsilon_K \Psi_K^+ \Psi_K^- |HF\rangle = \sum_K \varepsilon_K n_K |HF\rangle = E\Psi \end{aligned} \quad (13.44)$$

where:

$$E = \sum_K \varepsilon_K n_K \quad (13.45)$$

is the total energy in the EHT approximation.

In Sects. 14.3, 15, and 16 we shall benefit from the exercise we got in handling overlap effects. In the rest of the book we shall deal with usual orthogonal expansions.

14 Second Quantization and the Hellmann-Feynman Theorem

14.1 General

In the preceding chapters we have seen the advantages of the second quantized approach rather from the formalistic point of view. Here we take another stand-point and show an example where second quantization involves a somewhat different interpretation of the results. The example will be somewhat peculiar (Surján et al. 1988): we shall study the significance of the Hellmann-Feynman theorem in evaluating the first derivatives of the energy, which is topical in the field of optimizing molecular geometries, exponents of basis orbitals, etc.

As known from quantum mechanics, the Hellmann-Feynman theorem states:

$$\frac{\partial E}{\partial R} = \langle \Psi | \frac{\partial \hat{H}}{\partial R} | \Psi \rangle \quad (14.1)$$

if

$$\hat{H}\Psi = E\Psi. \quad (14.2)$$

Here, R is any parameter of the Hamiltonian (Hellmann 1937, Feynman 1939). Equation (14.1) is often written in form of an arbitrary variation as:

$$\delta E = \langle \Psi | \delta \hat{H} | \Psi \rangle \quad (14.1')$$

where δ represents an infinitesimal change. Equation (14.2) is a sufficient though not necessary condition for Eq. (14.1): the Hellmann-Feynman theorem is satisfied not only for the exact wave function (eigenfunction of \hat{H}), but also for certain variational wave functions. The true Hartree-Fock wave function represents such an example. The Hartree-Fock equations, however, are very difficult to solve exactly; this would involve either a fully numerical solution or an expansion in a complete basis. Wave functions resulting from a truncated basis Hartree-Fock calculation violate the Hellmann-Feynman theorem. The same holds for a full-CI solution of \hat{H} in a finite basis.

It is of some interest to consider whether there is a possibility to find a theoretical formalism permitting one to extend the applicability of the Hellmann-Feynman theorem to such cases. In what follows we shall take advantage of the second quantized formalism to investigate this point. In this framework one has a model Hamiltonian for which quantum-chemical wave functions expanded in a finite orbital basis obey a formal Hellmann-Feynman theorem.

This holds in all cases when the usual Hellmann-Feynman theorem is violated only just due to the finiteness of the basis.

In order to understand the significance of second quantization in the validity of the Hellmann-Feynman theorem, the following points have to be considered. As it was first emphasized by Pulay (1969), in the case of approximate wave functions Ψ^A which violate the Hellmann-Feynman theorem for some reason, the so-called ‘wave function forces’ may give considerable contributions to the total variance of the energy¹:

$$\delta E = \langle \Psi^A | \delta \hat{H} | \Psi^A \rangle + \langle \delta \Psi^A | \hat{H} | \Psi^A \rangle + \langle \Psi^A | \hat{H} | \delta \Psi^A \rangle \quad (14.3)$$

the superscript ‘A’ referring to the term ‘approximate’. (The conditions $\langle \Psi^A | \Psi^A \rangle = 1$ and $\langle \Psi^A | \delta \Psi^A \rangle = 0$ have been assumed). The first term can be called the Hellmann-Feynman force, while the two latter terms are the wave function forces. If \hat{H} is the usual Hamiltonian, the finite basis expansion does not allow us to use Eq. (14.1); instead the gradients have to be evaluated by using the more complicated Eq. (14.3). This is the case even if we work with a variational wave function which satisfies the Hellmann-Feynman theorem in a complete basis.

The appearance of wave-function forces in the expression of δE is a big change. Consider, for instance, the variation of the energy as a function of a nuclear coordinate. Using the first quantized Hamiltonian and the Hellmann-Feynman theorem, it is clear that only the electron-nuclear attraction operator V_{en} has a contribution:

$$\frac{\partial H}{\partial R} = \frac{\partial}{\partial R} [T_{kin} - V_{en} + V_{ee}] = -\frac{\partial}{\partial R} V_{en}$$

since both the kinetic energy (T_{kin}) and the electron-electron repulsion (V_{ee}) operators are independent of the nuclear coordinates. Derivatives of $\langle T_{kin} \rangle$ and $\langle V_{ee} \rangle$ appear in the expression for δE only if one has to consider also the wave-function forces in Eq. (14.3).

The situation is quite different in the second quantized formalism. In this framework the Hamiltonian is defined by the list of one- and two-electron integrals over basis orbitals, and any such integrals (including those of kinetic energy and electron repulsion) may depend on nuclear coordinates. Accordingly, the derivation of the second quantized Hamiltonian involves also the derivation of the kinetic energy as well as the two-electron integrals. This is not the consequence of the wave function here, but an effect included into the model Hamiltonian. On the other hand, no variation of the wave function emerges directly from the variation of the basis orbitals. The second quantized wave function is an algebraic entity; cf. the occupation number representation where one deals with figures of 0 and 1 and there is no room for any geometrical change.

¹ This terminology comes from the fact that $-\partial E / \partial R_a$ is the force acting on atom a pushing it towards the equilibrium position if R_a is its position coordinate.

If the creation and annihilation operators anticommute properly, they change the occupation numbers in an abstract Hilbert space of particle number representation which can be considered the same even if the physical orbitals do move (change). For this reason the true fermion operators need not be varied either. Their algebraic properties are determined by the relevant commutation rules, which are also independent of the physical properties of the system or of the nature of the basis orbitals. These anticommutation properties of the operators are the same after and before the variation.

We can understand this point more clearly with the example of a full CI wave function expanded in the finite basis. As mentioned above, the finite basis approximation prevents us from using the Hellmann-Feynman theorem of Eq. (14.1). However, the full CI wave function is an exact eigenfunction of the second quantized model Hamiltonian, for which a formal Hellmann-Feynman theorem is satisfied. Consequently, the second quantized form of the Hamiltonian serves as an appropriate model-Hamiltonian H^M for which the Hellmann-Feynman theorem formally holds as:

$$\delta E = \langle \Psi^A | \delta \hat{H}^M | \Psi^A \rangle \quad (14.4)$$

for the exact eigenvectors of the model Hamiltonian H^M , as well as for any variational wave function which would fulfill the usual Hellmann-Feynman theorem of Eq. (14.1) in a complete basis.

In the next section we are going to present a simple derivation of energy gradients for the case of a finite basis set by using the formal Hellmann-Feynman theorem of Eq. (14.4) with H^M being the second quantized Hamiltonian.

It is to be emphasized that for any given wave function the result of the following derivation should be identical with the gradient formula obtained by the usual technique. (The latter is commonly carried out by the explicit variation of the energy expression.) Nonetheless, the present derivation technique corresponds to an alternative view on the problem of energy derivatives: all the changes of the orbitals are transferred to those of the Hamiltonian.

14.2 Variation of Energy—Orthogonal Basis Set

The second quantized Hamiltonian in an orthogonal basis is given as usual:

$$\hat{H} = \sum_{\mu\nu} h_{\mu\nu} \psi_\mu^+ \psi_\nu^- + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} [\mu\nu|\lambda\sigma] \psi_\mu^+ \psi_\nu^+ \psi_\sigma^- \psi_\lambda^- . \quad (14.5)$$

Based on the previous discussion, variation of this Hamiltonian results:

$$\delta \hat{H} = \sum_{\mu\nu} \delta h_{\mu\nu} \psi_\mu^+ \psi_\nu^- + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \delta [\mu\nu|\lambda\sigma] \psi_\mu^+ \psi_\nu^+ \psi_\sigma^- \psi_\lambda^- \quad (14.6)$$

where $\delta h_{\mu\nu}$ and $\delta [\mu\nu|\lambda\sigma]$ are the variations of the one- and two-electron integrals. Using the formal Hellmann-Feynman theorem of Eq. (14.4), the variation of

the energy becomes:

$$\begin{aligned}\delta E &= \langle \Psi | \delta H | \Psi \rangle \\ &= \sum_{\mu\nu} \delta h_{\mu\nu} \langle \psi_\mu^+ \psi_\nu^- \rangle + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \delta[\mu\nu|\lambda\sigma] \langle \psi_\mu^+ \psi_\nu^+ \psi_\sigma^- \psi_\lambda^- \rangle \\ &= \sum_{\mu\nu} \delta h_{\mu\nu} P_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \delta[\mu\nu|\lambda\sigma] \Gamma_{\sigma\lambda\mu\nu}\end{aligned}\quad (14.7)$$

where P and Γ are the usual first- and second-order density matrices. Equation (14.7) gives us the gradient formula in an orthogonal basis set. It is valid in the MO basis, and in the AO basis if the overlap of the AOs is neglected (cf. NDO methods, Sect. 10.3) or if the AOs are explicitly orthogonalized, for example, by Löwdin's procedure. In this latter case, it might be useful to put down the expression for δE in the original nonorthogonal basis. This can be done either by an explicit transformation of Eq. (14.7), or by rederiving δE by using the non-orthogonal basis set from the beginning. This latter derivation will be presented in the next section.

14.3 Variation of Energy—Nonorthogonal Basis Set

In an overlapping basis of spinorbitals, the Hamiltonian can be put down in the following form [cf. Eq. (13.25)]:

$$H^M = \sum_{\mu\nu} h_{\tilde{\mu}\tilde{\nu}} \chi_\mu^+ \tilde{\chi}_\nu^- + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} [\tilde{\mu}\tilde{\nu}|\lambda\sigma] \chi_\mu^+ \chi_\nu^+ \tilde{\chi}_\sigma^- \tilde{\chi}_\lambda^- . \quad (14.8)$$

It is essential now to use this form of the second quantized Hamiltonian which is expressed over the true fermion operators obeying the anticommutation relations of Eqs. (13.13). The use of Eqs. (13.28) or (13.33) for the Hamiltonian would complicate the following treatment since the appearance of the overlap matrix in the commutation rules would destroy the purely algebraic character of the creation/annihilation operators. The proper anticommutation rules permit us to consider χ_μ^+ and $\tilde{\chi}_\nu^-$ as abstract operators creating and annihilating electrons, respectively. Accordingly, taking the variation of Eq. (14.8) we get:

$$\delta H^M = \sum_{\mu\nu} \delta h_{\tilde{\mu}\tilde{\nu}} \chi_\mu^+ \tilde{\chi}_\nu^- + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \delta[\tilde{\mu}\tilde{\nu}|\lambda\sigma] \chi_\mu^+ \chi_\nu^+ \tilde{\chi}_\sigma^- \tilde{\chi}_\lambda^- . \quad (14.9)$$

Substitution of δH^M into the formal Hellmann-Feynman theorem of Eq. (14.4) gives the variation of the electronic energy as the expectation value:

$$\delta E^M = \sum_{\mu\nu} \delta h_{\tilde{\mu}\tilde{\nu}} \langle \chi_\mu^+ \tilde{\chi}_\nu^- \rangle + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \delta[\tilde{\mu}\tilde{\nu}|\lambda\sigma] \langle \chi_\mu^+ \chi_\nu^+ \tilde{\chi}_\sigma^- \tilde{\chi}_\lambda^- \rangle . \quad (14.10)$$

In order to bring this formula into a more transparent form, two problems have

to be solved. First, the expectation values of creation/annihilation operators should be expressed in terms of the usual first- and second-order density matrices, P and Γ , respectively. This can be done as follows:

$$\langle \chi_\mu^+ \tilde{\chi}_v^- \rangle = \sum_\lambda S_{\lambda\mu} \langle \tilde{\chi}_\lambda^+ \tilde{\chi}_v^- \rangle = \sum_\lambda P_{v\lambda} S_{\lambda\mu}$$

where the first-order density matrix elements are introduced according to Eq. (13.30). A similar transformation can be used to introduce the second-order density matrix Γ . Thus we may write:

$$\langle \chi_\mu^+ \tilde{\chi}_v^- \rangle = \sum_\lambda P_{v\lambda} S_{\lambda\mu}, \quad (14.11a)$$

$$\langle \chi_\mu^+ \chi_v^+ \tilde{\chi}_\sigma^- \tilde{\chi}_\lambda^- \rangle = \sum_{\eta\tau} \Gamma_{\sigma\lambda\eta\tau} S_{\eta\mu} S_{\tau v}. \quad (14.11b)$$

Second, the variation of the integrals in Eq. (14.10) should be evaluated by taking into account the S^{-1} transformation in their *bra*-indices. This is easier to do in matrix notations. For the one-electron integrals we get:

$$\delta(S^{-1}h) = \delta S^{-1}h + S^{-1}\delta h \quad (14.12)$$

where δS^{-1} is the variation of the inverse of the overlap matrix which can be obtained from varying the relation:

$$SS^{-1} = 1$$

as:

$$\delta SS^{-1} + S\delta S^{-1} = 0, \quad (14.13)$$

that is:

$$\delta S^{-1} = -S^{-1}\delta SS^{-1}. \quad (14.14)$$

In components Eq. (14.12) is written as:

$$\delta h_{\mu\nu} = \sum_\eta [\delta S_{\mu\eta}^{-1} h_{\eta\nu} + S_{\mu\eta}^{-1} \delta h_{\eta\nu}] \quad (14.15)$$

where:

$$\delta S_{\mu\eta}^{-1} = -\sum_{\tau\rho} S_{\mu\tau}^{-1} \delta S_{\tau\rho} S_{\rho\eta}^{-1}. \quad (14.16)$$

Similarly, for the variation of the S^{-1} -transformed two-electron integrals one gets:

$$\begin{aligned} \delta[\tilde{\mu}\tilde{\nu}|\lambda\sigma] &= \sum_{\eta\tau} (\delta S_{\mu\eta}^{-1} S_{\nu\tau}^{-1} [\eta\tau|\lambda\sigma] + S_{\mu\eta}^{-1} \delta S_{\nu\tau}^{-1} [\eta\tau|\lambda\sigma] \\ &\quad + S_{\mu\eta}^{-1} S_{\nu\tau}^{-1} \delta[\eta\tau|\lambda\sigma]). \end{aligned} \quad (14.17)$$

Thus the problem is reduced to the variation of original AO integrals $\delta S_{\mu\nu}$, $\delta h_{\mu\nu}$, and $\delta[\mu\nu|\lambda\sigma]$ which can be evaluated analytically. With the results of Eqs. (14.14–17), Eq. (14.10) for the first-order variation of the energy becomes, after simple manipulations:

$$\begin{aligned}
\delta E = & - \sum_{\mu\nu\lambda\sigma} \delta S_{\mu\nu} S_{\nu\lambda}^{-1} h_{\lambda\sigma} P_{\sigma\mu} + \sum_{\mu\nu} \delta h_{\mu\nu} P_{\nu\mu} \\
& - \frac{1}{2} \sum_{\mu\nu\lambda\sigma\rho\tau} \delta S_{\mu\nu} S_{\nu\lambda}^{-1} [\lambda\sigma|\rho\tau] \Gamma_{\rho\mu\sigma} \\
& - \frac{1}{2} \sum_{\mu\nu\lambda\sigma\rho\tau} \delta S_{\mu\nu} S_{\nu\lambda}^{-1} [\sigma\lambda|\rho\tau] \Gamma_{\rho\mu\sigma} \\
& + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \delta [\mu\nu|\lambda\sigma] \Gamma_{\sigma\lambda\mu\nu}.
\end{aligned} \tag{14.18}$$

14.4 Special Case: The SCF Gradient Formula

The above gradient formula of Eq. (14.18) has been obtained by assuming that the wave function in question satisfies the formal Hellmann-Feynman theorem of Eq. (14.4) with respect to the second quantized Hamiltonian in the given basis set. Gradient formulae for diverse variational wave functions can be obtained as special cases of the general result of Eq. (14.18). In what follows we shall demonstrate how the familiar SCF gradient formula (Pulay 1969, Fletcher 1970, Pople et al. 1979) can be obtained from Eq. (14.18). The one-determinantal nature of the SCF wave function allows us to introduce some simplifications. Namely, as it was shown in Sect. 7.2:

$$\Gamma_{\sigma\lambda\mu\nu} = P_{\sigma\nu} P_{\lambda\mu} - P_{\sigma\mu} P_{\lambda\nu} \tag{14.19}$$

for the SCF wave function, which allows us to rearrange Eq. (14.18) to the simple form:

$$\begin{aligned}
\delta E = & \sum_{\mu\nu} \delta h_{\mu\nu} P_{\nu\mu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \delta [\mu\nu|\lambda\sigma] (P_{\lambda\mu} P_{\sigma\nu} - P_{\lambda\nu} P_{\sigma\mu}) \\
& - \sum_{\mu\nu\lambda\sigma} F_{\mu\nu} P_{\nu\lambda} \delta S_{\lambda\sigma} S_{\sigma\mu}^{-1}
\end{aligned}$$

where the usual Fockian F is introduced. Using Eq. (1.8) for the single-determinantal density matrix P and the SCF condition Eq. (1.5), the last term can be rewritten as:

$$- \sum_{\mu\nu} \sum_i^{\text{occ}} \epsilon_i C_{i\mu} C_{i\nu}^* \delta S_{\nu\mu} \tag{14.20}$$

with ϵ_i being the orbital energy. Introducing the energy-weighted density matrix W as:

$$W_{\mu\nu} = \sum_i^{\text{occ}} \epsilon_i C_{i\mu} C_{i\nu}^* \tag{14.21}$$

the SCF gradient formula takes the form:

$$\delta E = \sum_{\mu\nu} \delta h_{\mu\nu} P_{\nu\mu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \delta[\mu\nu|\lambda\sigma] (P_{\lambda\mu} P_{\sigma\nu} - P_{\lambda\nu} P_{\sigma\mu}) - \sum_{\mu\nu} W_{\mu\nu} \delta S_{\nu\mu} \quad (14.22)$$

which is exactly the result given by Fletcher (1970) or Pople et al. (1979). The first two terms describe the variation of the electronic energy due to the change in the one- and two-electron integrals, while the last term accounts for the overlap effects.

Similarly, specifying the first- and second-order density matrices P and Γ in Eq. (14.18), one can obtain the actual gradient formulae for other types of variational wave functions as well.

In this section we have presented a new derivation scheme for gradient formulae for all types of variational wave functions which violate the Hellmann-Feynman theorem only as a consequence of using an incomplete basis set.² We have pointed out that if the second quantized Hamiltonian is applied, the Hellmann-Feynman theorem formally holds even in a finite basis, and the first derivatives of the energy can be obtained without considering wave function forces explicitly. On this ground, we derived a unified gradient formula from which the known results can be recovered in every special case. This has been demonstrated for the case of the Hartree-Fock wave function.

The role of second quantization in this field is neither to contribute directly to practical gradient evaluations nor to give gradient formulae which cannot be derived by another means. The significance of this presentation is rather to offer an alternative and unifying view of energy derivatives, eliminating the concept of the wave function force for a rather wide class of variational functions used in quantum chemistry. The effects which lead to the wave function forces in the usual approach are included in the second quantized Hamiltonian. The two approaches are, therefore, completely equivalent and represent alternative possibilities to treat the problem.

² Some wave functions (truncated CI, for example) violate the Hellmann-Feynman theorem even in a complete basis. In this case the application of second quantization does not help.

15 Intermolecular Interactions

In the previous chapter we have seen an example where second quantization provided us a different interpretation of the same result. In this section we shall consider a case where second quantization contributes also to understanding the physics of the problem. The questions we shall treat here arise when considering the interaction between two many-electron systems.¹

Several theories for describing the interaction between two molecules were elaborated (Hirschfelder 1967, Musher & Amos 1967, Van der Avoird 1967, Amos & Musher 1967, Salem 1968, Daudey et al. 1974b, Bachler et al. 1975, Pullman 1978, Claverie 1978, Adams & Polymeropoulos 1978, 1980, Sadlej 1980, Hayes & Stone 1983, Power & Thirunamachandran 1985, Surján et al. 1985b, Van Lenthe et al. 1987, etc.) but the problem has not been solved in a satisfactory manner. The main aim of such theories is to find a good estimation for the interaction energy which is defined by:

$$\Delta E = E^{AB} - E^A - E^B. \quad (15.1)$$

Here E^A and E^B are the exact energies of the two individual molecules A and B when they are isolated, while E^{AB} is the exact energy of the supersystem (molecular complex, for example).² Theoretically, these quantities can be obtained from the exact solution of the Schrödinger equation for the corresponding systems. (We remain within the nonrelativistic Born-Oppenheimer model.) This requires the definition of the Hamiltonians \hat{H}^A , \hat{H}^B and \hat{H}^{AB} , and one feels challenged to handle these Hamiltonians in a common (e.g., perturbational) scheme. This point is not at all trivial especially if approximate model Hamiltonians are used. In what follows we shall consider this issue emphasizing the points where the second quantized approach can help to clarify the situation.

15.1 The Operator of Interaction

The problem of intermolecular interactions can be approached from two sides: the physical process under study is considered either as a fusion of monomers A and B to form a complex: $A + B \rightarrow AB$, or as the fission of the super-

¹ We restrict the following investigations to the case of two interacting systems.

² Thermodynamical aspects of the problem are not discussed here.

molecule into two pieces: $\text{AB} \rightarrow \text{A} + \text{B}$. Using the picture of fusion, the first step is to construct a zeroth-order Hamiltonian $\hat{H}^{(0)}$ from the isolated system Hamiltonians:

$$\hat{H}^{(0)} = \hat{H}^{\text{A}} + \hat{H}^{\text{B}}. \quad (15.2)$$

Operator $\hat{H}^{(0)}$ describes a hypothetical supersystem in which both constituents are present but do not interact. Though Eq. (15.2) is cited most usually, it is rather loosely written, since \hat{H}^{A} and \hat{H}^{B} are Hamiltonians of different systems and they are defined over different Hilbert spaces \mathcal{H}^{A} and \mathcal{H}^{B} , respectively. With more rigor, $H^{(0)}$ should be written as a sum of two effective operators:

$$\hat{H}^{(0)} = \hat{H}_{\text{eff}}^{\text{A}} + \hat{H}_{\text{eff}}^{\text{B}} \quad (15.3a)$$

where $\hat{H}_{\text{eff}}^{\text{A}}$ and $\hat{H}_{\text{eff}}^{\text{B}}$ are defined by the *direct products*:

$$\hat{H}_{\text{eff}}^{\text{A}} = \hat{H}^{\text{A}} \otimes \hat{I}^{\text{B}}, \quad \hat{H}_{\text{eff}}^{\text{B}} = \hat{I}^{\text{A}} \otimes \hat{H}^{\text{B}} \quad (15.3b)$$

\hat{I}^{A} and \hat{I}^{B} representing the unity operators in the Hilbert spaces \mathcal{H}^{A} and \mathcal{H}^{B} . Operator $H^{(0)}$ is defined over the direct product space of the two Hilbert spaces \mathcal{H}^{A} and \mathcal{H}^{B} .

The next step is to switch on the interaction between A and B. The interaction Hamiltonian \hat{W} connects the dynamical variables of the two systems. It should be chosen so that the perturbed Hamiltonian be equal to the Hamiltonian of the supersystem:

$$\hat{H}^{\text{AB}} = \hat{H}^{(0)} + \hat{W}. \quad (15.4)$$

Inadequacy of Eq. (15.2) can be illustrated by second quantization. Introducing a complete set of one-electron functions, a naive application of the results of Sect. 4 would lead to the following representations:

$$\hat{H}^{\text{A}} \simeq \sum_{ik} T_{ik} i^+ k^- + \sum_{ik} U_{ik}^{\text{A}} i^+ k^- + \frac{1}{2} \sum_{ijkl} [ij|kl] i^+ j^+ l^- k^- \quad (15.5a)$$

$$\hat{H}^{\text{B}} \simeq \sum_{ik} T_{ik} i^+ k^- + \sum_{ik} U_{ik}^{\text{B}} i^+ k^- + \frac{1}{2} \sum_{ijkl} [ij|kl] i^+ j^+ l^- k^- \quad (15.5b)$$

$$\hat{H}^{\text{AB}} \simeq \sum_{ik} T_{ik} i^+ k^- + \sum_{ik} U_{ik}^{\text{AB}} i^+ k^- + \frac{1}{2} \sum_{ijkl} [ij|kl] i^+ j^+ l^- k^- \quad (15.5c)$$

where T stands for the kinetic energy, while U^{A} , U^{B} , and U^{AB} are attractive potentials from nuclei of systems A, B, and AB, respectively. Subtracting Eqs. (15.5a) and (15.5b) from Eq. (15.5c), which would be the recipe to form an interaction Hamiltonian $\hat{W} = \hat{H}^{\text{AB}} - \hat{H}^{\text{A}} - \hat{H}^{\text{B}}$, leads to a completely improper expression with negative kinetic energy and electron repulsion terms. The error is that second quantized Hamiltonians must not be added or subtracted from each other if they refer to a different system. One has to be extremely careful if dealing with second quantized Hamiltonians for physically different systems; it

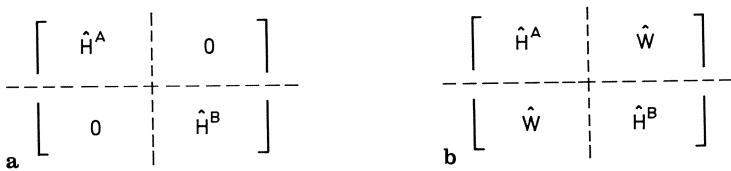


Fig. 15.1a, b. Schematic view of the the direct sum of two Hamiltonians \hat{H}^A and \hat{H}^B without (a) and with (b) interaction

is not justified to use the same fermion operators³ for systems A, B, and AB in Eqs. (15.5).

The appropriate definition of $\hat{H}^{(0)}$ and \hat{W} in the second quantized representation is entirely different from Eqs. (15.3), too. Using a different set of fermion operators for systems A and B involves that one has a different set of orbitals assigned to these subsystems. The noninteracting supersystem Hamiltonian is given by the *direct sum* of the isolated Hamiltonians:

$$\hat{H}^{(0)} = \hat{H}^A \oplus \hat{H}^B \quad (15.2')$$

which is illustrated in Fig. 15.1.

Let us put down the interaction Hamiltonian in the conventional form. In the L_2 space, one usually writes⁴:

$$\hat{H}^{AB} = \sum_i T_i - \sum_{ia} \frac{Z_a}{R_{ia}} + \sum_{i>j} \frac{1}{R_{ij}} \quad (15.6a)$$

where the labels i and j run over all electrons in the system AB. For the Hamiltonian of system A, one has:

$$\hat{H}^A = \sum_{i \in A} T_i - \sum_{\substack{i \in A \\ a \in A}} \frac{Z_a}{R_{ia}} + \sum_{\substack{i > j \\ (i, j \in A)}} \frac{1}{R_{ij}} \quad (15.6b)$$

and analogously for \hat{H}^B . The interaction operator is usually written as the difference:

$$\hat{W} = \hat{H}^{AB} - \hat{H}^A - \hat{H}^B = - \sum_{\substack{i \in A \\ a \in B}} \frac{Z_a}{R_{ia}} - \sum_{\substack{i \in B \\ a \in A}} \frac{Z_a}{R_{ia}} + \sum_{\substack{i \in A \\ j \in B}} \frac{1}{R_{ij}}. \quad (15.7)$$

Notice that the kinetic energy has dropped out. This interaction operator is

³If systems A and B are really isolated, their dynamical variables are independent and the corresponding fermion operators commute. Such a second-quantized formalism was used by Chang and Weinstein (1978).

⁴Throughout this section we do not carry the nuclear-nuclear repulsion which represent only a constant term of the Hamiltonian and is immaterial with respect to the present considerations.

commonly applied, but in the L_2 representation it is by far no strict. It involves a partition of the electrons: each electron is assigned either to A or to B as expressed by the symbol $i \in A$ or $i \in B$. Since electrons are indistinguishable, such a distinction is not permitted by the basic principles of quantum mechanics.⁵ So strictly speaking, the form of Eq. (15.7) of the interaction operator should be considered only as a model of the interaction, though there is no question that it is a good model. It is based on the picture that the interaction between A and B emerges from the Coulomb potential of particles localized on A or B. The localization of electrons is the point which can be questioned theoretically.

The problem is perhaps better studied in the fission picture, where we consider the dissociation of the complex into molecules A and B. Here the goal is to find a *partition* of the total Hamiltonian to a noninteracting part and a perturbation \hat{W} :

$$\hat{H}^{AB} = \hat{H}^{(0)} + \hat{W}.$$

The fission process $AB \rightarrow A + B$ can be described as a physical dissociation leading to the potential curve $E(R)$ where R is an appropriately chosen distance parameter⁶ between A and B. At any R , the distances between nuclei of A and those in B are kept rigid while intersystem distances vary with R . Consequently, the Hamiltonian of the supersystem depends on R parametrically:

$$\hat{H}^{AB} = \hat{H}^{AB}(R). \quad (15.8)$$

A zeroth-order Hamiltonian describing noninteracting sub-systems can be defined as:

$$\hat{H}^{(0)} = \lim_{R \rightarrow \infty} \hat{H}^{AB}(R). \quad (15.9)$$

Clearly, $\hat{H}^{(0)}$ describes the dissociated species.⁷ It is important that $\hat{H}^{(0)}$ and \hat{H}^{AB} are defined over the *same* Hilbert spaces. No classification of the electrons during the dissociation process is done, and no artificial ‘localization’ of electrons is introduced. If it turns out, by solving the Schrödinger equation at various R values, that a given number of electrons follow the dissociating nuclei, this will be reflected by the factorization of the wave function $\Psi(R)$ of the supersystem at the $R \rightarrow \infty$ limit. Physically this means that the electronic coordinates in the Hamiltonian $\hat{H}^{AB}(R)$ are all dynamical variables at any R , and \hat{H}^{AB} depends on R only through the nuclear-electron attraction potential:

⁵ No such problem is encountered with the partition of nuclei expressed by the symbols $a \in A$, as far as one works within the Born-Oppenheimer model. When considering the electronic Schrödinger equation, nuclei are not treated as quantum particles, their role is merely to give rise an external potential for electrons.

⁶ The relative orientation of A and B may also change but it is immaterial here.

⁷ There are some approximate methods in quantum chemistry which suffer from the so-called size inconsistency error: The eigenvalue of the dissociated Hamiltonian of Eq. (16.9) is not equal to the sum of the solutions of the two independent Hamiltonians. A typical wave function of this type is that of a truncated CI calculation. Size consistent wave functions are preferred for the study of intermolecular interactions.

$$U(R) = \sum_i U_i(R) = - \sum_i \sum_a Z_a / |R_i - R_a| \quad (15.10)$$

where the coordinates of the nuclei R_a are present. Keeping this in mind, the limit in Eq. (15.9) can be carried out as:

$$\hat{H}^{(0)} = \hat{H}(\infty) = \sum_i T_i + \sum_i U_i(\infty) + \sum_{i < j} 1/R_{ij}. \quad (15.11)$$

In this picture, the interaction operator is given by:

$$\begin{aligned} \hat{W} &= \hat{H}(R) - \hat{H}(\infty) = \sum_i [U_i(R) - U_i(\infty)] \\ &= - \sum_i \sum_a Z_a \left[\frac{1}{|R_i - R_a^0|} - \frac{1}{|R_i - R_a^\infty|} \right] \end{aligned} \quad (15.12)$$

where R^0 refers to the nuclear coordinates in the dimer while R^∞ stands for those in the dissociated geometry.⁸ This operator consists of one-electron terms only, and it is entirely different from that in Eq. (15.7). Thus the paradox is found that either one has the somewhat unusual⁹ result of Eq. (15.12) or, in order to get the more familiar form for W , one has to introduce a classification of electrons—a procedure unfounded on quantum-mechanical grounds.

This paradox can be resolved by turning to second quantization where the basic structure of the formalism ensures that no artificial classification of electrons is possible or necessary. We shall investigate under which conditions one arrives at Eq. (15.7) or Eq. (15.12), using a second quantized many-body Hamiltonian.

The aim is to determine a partition of the supersystem Hamiltonian which is given by

$$\hat{H}^{AB} = \sum_{ik} T_{ik} \psi_i^+ \psi_k^- + \sum_{ik} U_{ik}^{AB} \psi_i^+ \psi_k^- + \frac{1}{2} \sum_{ijkl} [ij|kl] \psi_i^+ \psi_j^+ \psi_l^- \psi_k^-. \quad (15.13)$$

This Hamiltonian depends on R of Eq. (15.9) through the list of integrals. At this point, two possibilities for selecting the one-electron basis functions are to be investigated:

- (i) The underlying basis set is fixed, that is, the location of the basis functions ψ does not change with R .
- (ii) The basis orbitals are classified whether they belong to A or B, and they follow their subsystems upon dissociation (“orbital following”).

Case (i) is meaningful only if the basis $\{\psi\}$ is complete in the rigorous mathematical sense, since the wave function of a far-lying system can be expanded only

⁸To avoid any conceptual difficulty with handling infinite distances, one always can think of a finite but very large value for R .

⁹To point out that Eq. (15.12) is indeed unusual, it is sufficient to note that we did not get any two-electron operator which is commonly used to describe, e.g., dispersion effects associated with intersystem electron correlation.

in this case. This is hard to realize practically. The disadvantage of case (ii) is that the basis changes with R which may lead to serious errors (vide infra).

Check first the interaction operator in scheme (i). It is very simple to evaluate the Hamiltonian for the dissociated system from Eq. (15.9). Since the orbitals do not move with R , only the nuclear-electron attraction integrals U_{ik}^{AB} change:

$$\hat{H}^{(0)} = \sum_{ik} T_{ik} \psi_i^+ \psi_k^- + \sum_{ik} U_{ik}^{AB}(\infty) \psi_i^+ \psi_k^- + \frac{1}{2} \sum_{ijkl} [ij|kl] \psi_i^+ \psi_j^+ \psi_l^- \psi_k^-. \quad (15.14)$$

Accordingly, for the interaction operator one gets:

$$\hat{W} = \hat{H}^{AB} - \hat{H}^{(0)} = \sum_{ik} \left[U_{ik}^{AB}(R) - \sum_{ik} U_{ik}^{AB}(\infty) \right] \psi_i^+ \psi_k^-. \quad (15.15)$$

The kinetic energy terms are dropped, as expected, but the somewhat surprising result is found again that the electron-electron repulsion terms disappeared, too. This result is equivalent to that of Eq. (15.12).

The second quantized derivation is very informative because it tells us that a complete set of spatially fixed one-electron basis functions is necessary to derive such an interaction operator. Hence, one cannot expect the \hat{W} of Eq. (15.15) to be a suitable perturbation operator in practical cases.¹⁰

It remains to be seen whether the usual form of the interaction operator, Eq. (15.7), leads to correct results despite of the apparent inconsistency caused by the artificial distinction between electrons. This can be checked by writing it in the orbital form, which can be compared directly to the result of a more realistic second quantized derivation. We shall consider below the partitioning of the second quantized Hamiltonian to a zeroth-order and a perturbation part, the latter being identified with the interaction between molecules A and B, and check under which conditions this many-body derivation yields results analogous to Eq. (15.7). The realistic case of orbital following (vide supra) will be studied, when each basis function is uniquely assigned either to A and to B.¹¹ This assignment will be denoted as $i \in A$ or $i \in B$.

For simplicity, let us assume first that overlap effects can be neglected, and the orbitals are orthogonal. Then the Hamiltonian of the supersystem is given

¹⁰ This situation is quite analogous to the role of Hellmann-Feynman theorem in gradient evaluations (cf. Sect. 14). In a complete basis the Hellmann-Feynman theorem is satisfied, and the energy derivatives with respect to nuclear coordinates come only from the nuclear-electron attraction operator. This case corresponds to Eq. (15.12). If the basis set is incomplete, the original Hellmann-Feynman theorem is violated, and the changes of the electron repulsion integrals should also be taken into account (wave function forces). This is analogous to Eq. (15.7). Using a set of spatially fixed basis functions in Sect. 14, only electron-nuclear attraction integrals would have been changed and the usual Hellmann-Feynman force would have been recovered there by the second quantized derivation. Derivatives of the kinetic energy and electron-electron repulsion integrals appeared there only as a consequence of the orbital following.

¹¹ This is, by the way, a shortcoming of this picture, since in principle one could use basis functions centred between A and B, in addition to those centred on them.

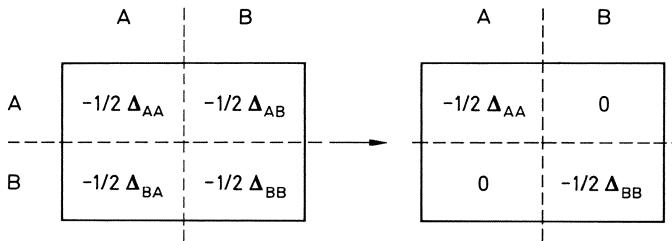


Fig. 15.2. Offdiagonal blocks of the kinetic energy matrix give rise to interaction in the orbital scheme

by Eq. (15.5c). By partitioning the orbitals according to the molecules they belong to, this Hamiltonian decouples to¹²:

$$\hat{H}^{AB} = \hat{H}^A + \hat{H}^B + \hat{W} \quad (15.16)$$

where:

$$\hat{H}^A = \sum_{ik \in A} (T_{ik} + U_{ik}^A) \psi_i^+ \psi_k^- + \frac{1}{2} \sum_{ijkl \in A} [ij|kl] \psi_i^+ \psi_j^+ \psi_l^- \psi_k^- \quad (15.17a)$$

$$\hat{H}^B = \sum_{ik \in B} (T_{ik} + U_{ik}^B) \psi_i^+ \psi_k^- + \frac{1}{2} \sum_{ijkl \in B} [ij|kl] \psi_i^+ \psi_j^+ \psi_l^- \psi_k^- \quad (15.17b)$$

$$\begin{aligned} \hat{W} = & \sum_{\substack{i \in A \\ k \in B}} (T_{ik} + U_{ik}^{AB}) \psi_i^+ \psi_k^- + \sum_{\substack{i \in B \\ k \in A}} (T_{ik} + U_{ik}^{AB}) \psi_i^+ \psi_k^- \\ & + \sum_{ik \in A} U_{ik}^B \psi_i^+ \psi_k^- + \sum_{ik \in B} U_{ik}^A \psi_i^+ \psi_k^- + \left\{ \begin{array}{l} \text{two-electron} \\ \text{terms} \end{array} \right\}. \end{aligned} \quad (15.17c)$$

It is seen that off-diagonal blocks of the kinetic energy matrix have appeared in the perturbation. While it is a natural consequence of the orbital partitioning (Fig. 15.2), this result is not consistent with the usual L_2 -space form of \hat{W} , Eq. (15.7), since the latter does not contain kinetic energy integrals at all. The appearance of U_{ik}^{AB} , $i \in A$, $k \in B$ -type integrals in Eq. (15.17c) is also somewhat spurious, while the last two one-electron terms have clear physical significance: they describe the electron-nuclear attraction between the systems A and B. So we have found that the second quantized interaction operators neither in the rigid basis [Eq. (15.12)], nor in the orbital following case [Eq. (15.17)] confirm the usual model Hamiltonian of Eq. (15.7).

This situation can be further analyzed on the basis of a typical shortcoming of using infinite bases leading to an effect called basis set superposition error, BSSE (Kestner 1968, Mayer 1983, Van Lenthe et al. 1987). As a consequence of the orbital following principle, the underlying basis set changes with R upon

¹² In this partitioning, H^A and H^B are not the isolated molecule Hamiltonians due to the orthogonalization of the basis. This will not affect the following conclusion, however.

dissociation. This change is manifested in the dependence of the overlap, one- and two-electron integrals on R , and it leads to a conceptual difficulty in the interpretation of the potential curve $E(R)$. One may argue that it is not justified to compare two energies, say $E(R_1)$ and $E(R_2)$, since they are obtained from approximate calculations in two different basis set. This point is often stressed on the example of the interaction energy:

$$\Delta E = E(R) - E(\infty) = E_{AB} - E_A - E_B. \quad (15.18)$$

Since the basis set for the dimer is the superposition of the basis sets for A and B, the E_{AB} value is calculated in a larger (i.e., more flexible) basis than E_A or E_B . This will probably result in an extra improvement of E_{AB} thus in an overestimation of the interaction energy. In other terms, the basis functions centered on B also improve the description of system A in the dimer and vice versa, which is, however, not a true effect of interaction but an artefact of using incomplete basis sets.

Several procedures have been proposed to avoid, or at least moderate, this effect (Boys & Bernardi 1970, Daudey et al. 1974b, Mayer 1983). The problem stimulated a lot of controversy (see, e.g. Gutowski et al. 1986, Collins & Gallup 1986)—we shall not jump into this jungle here, since no unique scheme has yet been accepted. Most schemes imply an *a posteriori* adjustment of the interaction energy. For the present purpose, that is in order to derive an expression for the interaction operator, we shall take advantage of the *a priori* analysis of Mayer (1983) followed in his Chemical Hamiltonian Approach (CHA).

One of the key ideas in CHA is the analysis of certain two-center matrix elements. We shall consider this point only on the example of the kinetic energy integrals which represent an essential discrepancy between the forms of Eqs. (15.15) and (15.17) of the interaction operator. Other types of matrix elements can be investigated mutatis mutandis. Consider an intersystem matrix element:

$$T_{jk} = \langle \psi_j | \hat{T} | \psi_k \rangle \quad j \in B, k \in A. \quad (15.19)$$

Operator \hat{T} transforms the function ψ_k , $k \in A$, to a new function which is expanded as¹³:

$$\hat{T}|\psi_k\rangle = \sum_{l \in A} T_{kl} |\psi_l\rangle + \{BSSE\}. \quad (15.20)$$

That is, we expanded the transformed function only within the subspace A; such expansion would be used in the isolated problem of molecule A. In the supersystem AB, the transformed function $T|\psi_l\rangle$ would have components also on the basis orbitals of B, but these result merely from the extension of the basis set. If the basis on A were to be complete, no such components would have to be considered. Since such matrix elements do not enter the intrasystem problem, a balanced description of the supersystem emerges if one neglects these com-

¹³The basis orbitals centred on the same system are assumed orthogonal, so one has to deal only with intermolecular overlap integrals. This does not represent any restriction from the conceptual point of view while makes the analysis much simpler.

ponents even in the problem of AB, considering them as a source of BSSE. Dropping of the BSSE terms and substituting Eq. (15.20) into Eq. (15.19), an “integral approximation” results:

$$T_{jk} = \sum_{l \in A} S_{jl} T_{lk}, \quad j \in B, k \in A, \quad (15.21)$$

where the intermolecular matrix element T_{jk} is expressed in terms of intramolecular matrix elements T_{lk} and intermolecular overlaps S_{jl} .¹⁴

The kinetic energy part of the supersystem Hamiltonian in terms of the original non-orthogonal basis reads, cf. Eq. (13.25):

$$\hat{T} = \sum_{ijk} S_{ij}^{-1} T_{jk} \psi_i^+ \tilde{\psi}_k^- \quad (15.22)$$

where the bi-orthogonal transformation of the integrals is written out to show overlap effects explicitly. Let us check how this term is reduced by substituting the “BSSE-free” integrals of Eq. (15.21). Operator \hat{T} can be decomposed as:

$$\hat{T} = \sum_{ij} \sum_{k \in A} S_{ij}^{-1} T_{jk} \psi_i^+ \tilde{\psi}_k^- + \sum_{ij} \sum_{k \in B} S_{ij}^{-1} T_{jk} \psi_i^+ \tilde{\psi}_k^- . \quad (15.23)$$

Substituting Eq. (15.21) into the first term, its counterpart (resulting from an $A \leftrightarrow B$ interchange) into the second term, one finds:

$$\begin{aligned} \hat{T} &= \sum_{ij} \sum_{kl \in A} S_{ij}^{-1} S_{jl} T_{lk} \psi_i^+ \tilde{\psi}_k^- + \sum_{ij} \sum_{kl \in B} S_{ij}^{-1} S_{jl} T_{lk} \psi_i^+ \tilde{\psi}_k^- \\ &= \sum_{ik \in A} T_{ik} \psi_i^+ \tilde{\psi}_k^- + \sum_{ik \in B} T_{ik} \psi_i^+ \tilde{\psi}_k^- = T^A + T^B. \end{aligned} \quad (15.24)$$

The two latter terms can be identified with the kinetic energy operators of systems A and B.

Using BSSE-free matrix elements, the kinetic energy is completely separated into intramolecular contributions, and no interaction part occurs—a result consistent to the model Hamiltonian of Eq. (15.7). Performing a similar analysis on the supermolecule Hamiltonian of Eq. (15.13), substituting “BSSE-free” integrals at every relevant places, one finds that:

$$\hat{H} = \hat{H}^A + \hat{H}^B + \hat{W} + \{\text{BSSE}\} \quad (15.25)$$

where \hat{H}^A and \hat{H}^B are defined by:

$$\hat{H}^A = \sum_{ik \in A} (T_{ik} + U_{ik}^A) \psi_i^+ \tilde{\psi}_k^- + \frac{1}{2} \sum_{ijkl \in A} [ij|kl] \psi_i^+ \psi_j^+ \tilde{\psi}_l^- \tilde{\psi}_k^- \quad (15.26a)$$

$$\hat{H}^B = \sum_{ik \in B} (T_{ik} + U_{ik}^B) \psi_i^+ \tilde{\psi}_k^- + \frac{1}{2} \sum_{ijkl \in B} [ij|kl] \psi_i^+ \psi_j^+ \tilde{\psi}_l^- \tilde{\psi}_k^- . \quad (15.26b)$$

These operators are the effective Hamiltonians of the isolated systems written in the dimer basis. For the interaction operator, the following result is obtained

¹⁴ An analogous integral approximation was proposed by Ruedenberg (1951) for two-electron integrals.

(Mayer 1983, Surján et al. 1985b):

$$\begin{aligned}\hat{W} = & \sum_{i \in B} \sum_{kl} S_{kl}^{-1} U_{li}^A \psi_k^+ \tilde{\psi}_i^- + \sum_{i \in A} \sum_{kl} S_{kl}^{-1} U_{li}^B \psi_k^+ \tilde{\psi}_i^- \\ & + \sum_{k \in A} \sum_{mn} S_{im}^{-1} S_{jn}^{-1} [mn|kl] \psi_i^+ \psi_j^+ \tilde{\psi}_i^- \tilde{\psi}_k^-\end{aligned}\quad (15.27)$$

which is claimed to be a BSSE-free many-body operator for intermolecular interactions. Different terms of the above expression describing electron-nuclear attraction and electron-electron repulsion, respectively, can be related to those of the L_2 -space Hamiltonian of Eq. (15.7). We can see, however, that the overlap has complicated the result significantly; we could not get rid the S^{-1} matrix elements in \hat{W} , for example, which may lead to numerically unstable results for large, nearly overcomplete basis sets.¹⁵ Individual operators in Eq. (15.25) are not Hermitian which reflects also overlap effects.

Let us summarize now the considerations of this section. We have discussed four different formulae for the operator of the interaction of two molecules: Eqs. (15.7), (15.12), (15.17c), and (15.27). They can be commented as follows.

- (i) The most common partition of the supermolecule Hamiltonian into the Hamiltonian of individual molecules and an interaction part, Eq. (15.7), is unacceptable if one takes quantum mechanics rigorously, since it involves distinction between electrons.
- (ii) A more consistent interaction operator, Eq. (15.12), involves only the partition of the nuclei. It contains only the change in one-electron matrix elements, thus it has a substantially simpler form.
- (iii) Using methods which involve orbital expansion, this latter interaction Hamiltonian is relevant only if the basis set is strictly complete so a one-center expansion is permitted.
- (iv) In truncated basis models the partition of the dimer Hamiltonian is done by means of a partition of the basis orbitals. Then, off-diagonal blocks of the kinetic energy, etc. integrals give also rise to interaction, thus the picture is entirely different from the L_2 space model (i).
- (v) An a priori analysis of the basis set superposition problem eliminates all such spurious interaction and leads to a \hat{W} which is consistent to model (i). Neither the zeroth-order part nor the perturbation \hat{W} are Hermitian in this formalism, and one has to deal with a bi-orthogonal transformation of the integrals in \hat{W} .

¹⁵ We would like to point out in this respect that elimination of the S^{-1} matrix does not solve the problem of instability in a (nearly) redundant basis. Given a set of orthogonal vectors C expanded in the overlapping basis, one has in matrix form $CSC^\dagger = 1$, from which $S^{-1} = C^\dagger C$. This shows that if S^{-1} is not well defined in a redundant basis, the same holds for the expansion coefficients either.

Apparently, there is room for further research in this field. In the next section we shall review some many-body perturbation theories for intermolecular interactions which make use of one of the interaction operators discussed above.

15.2 Symmetry-Adapted Perturbation Theory

In the present context, the term ‘symmetry’ refers to the permutational symmetry of electrons, that is to the Pauli principle. This problem plays a central role in perturbation theories of intermolecular interactions since the antisymmetry of the perturbed wave functions has to be ensured. The symmetry-adapted PT is called also as ‘exchange-PT’, because the antisymmetry results exchange interactions between molecules A and B. Several formulations of the exchange-PT have been developed (Van der Avoird, 1967, Amos & Musher 1967, Hirschfelder 1967, Murrel & Shaw 1967, Salewicz & Jeziorski 1979) which will not be discussed in detail. In the spirit of the present treatment, we shall focus on the application of second quantization to this problem. This formalism *eo ipso* guarantees the proper antisymmetry of any wave function expressed in terms of anticommuting fermion operators, thus the symmetry adaptation is done automatically and it does not require any further discussion.

Various formulations of the second quantization-based perturbation theories of intermolecular interactions differ in the partitioning of the Hamiltonian, in the way of handling the intermolecular overlap, and in the amount of BSSE exhibited by the PT formulae. These three questions are closely related.

An interesting many-body approach was developed by Basilevsky and Berenfeld (1972) and by Kvasnicka et al. (1974). These authors turned to a Löwdin-orthogonalized basis and wrote the dimer Hamiltonian as:

$$\hat{H}^{AB} = \sum_{ik} h_{ik} \psi_i^+ \psi_k^- + \frac{1}{2} \sum_{ijkl} [ij|kl] \psi_i^+ \psi_j^+ \psi_l^- \psi_k^- \quad (15.28)$$

where the integrals are explicitly transformed to the Löwdin basis set:

$$h_{ik} = \sum_{ab} S_{ia}^{-1/2} h_{ab} S_{bk}^{-1/2} \quad (15.29a)$$

$$[ij|kl] = \sum_{abcd} S_{ia}^{-1/2} S_{jb}^{-1/2} [ab|cd] S_{ck}^{-1/2} S_{dl}^{-1/2} \quad (15.29b)$$

where the labels a, b, ... refer to the original overlapping basis. The fermion operators ψ_i^+ , ψ_k^- refer also to the Löwdin basis, thus they obey the proper anticommutation rules:

$$[\psi_i^+, \psi_k^-] = \delta_{ik}. \quad (15.30)$$

The original orbitals ψ_a , ψ_b , ... are chosen to be the MOs of the separated molecules, and they are identified as $a \in A$ or $a \in B$. The orthogonalization procedure mixes the orbitals of the two fragments, thus distinctions like $i \in A$ don't make much sense. However, the integrals $S_{ia}^{-1/2}$, h_{ik} , $[ij|kl]$ all depend

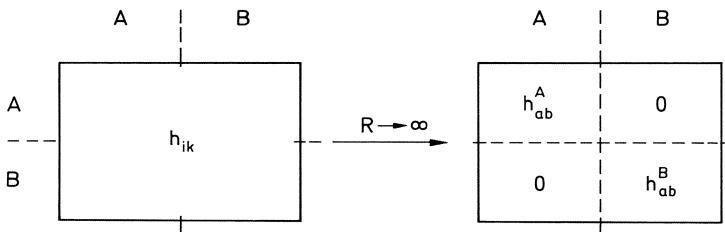


Fig. 15.3. Change in the block structure of one-electron integrals in Löwdin basis upon $R \rightarrow \infty$. The labels a, b refer to the original overlapping basis set, while i, k denote Löwdin-orthogonalized orbitals. The two bases are in a one-to-one correspondence

on R , the distance parameter between A and B. This leads to an R dependence of the Hamiltonian of Eq. (15.28), and a zeroth-order Hamiltonian can be defined as:

$$\hat{H}^{(0)} = \lim_{R \rightarrow \infty} \hat{H}(R).$$

Provided that the MOs are chosen orthogonal on each molecule, the overlap matrix S tends to the unit matrix in the $R \rightarrow \infty$ limit. Matrix $S^{-1/2}$ reduces to the unit matrix, too. Matrices of integrals h_{ik} and $[ij|kl]$ will also tend to the direct sums of the untransformed matrices (see Fig. 15.3). Consequently, the limiting value $\hat{H}^{(0)}$ will be decoupled as:

$$\hat{H}^{(0)} = \hat{H}^A \oplus \hat{H}^B \quad (15.31)$$

where the operators \hat{H}^A and \hat{H}^B are defined in Eqs. (15.17). Note that the anticommutation rules of Eq. (15.30) are valid at any R , including the limiting case $R \rightarrow \infty$ when ψ_i^+ and ψ_k^- reduce to the untransformed operators ψ_a^+ and ψ_b^- . At the zeroth order, the Hamiltonian \hat{H}^{AB} is approximated by the $\hat{H}^{(0)}$ of Eq. (15.31), and the remainder of this approximation gives rise to the perturbation:

$$\hat{H}^{AB} = \hat{H}^{(0)} + \hat{W}. \quad (15.32)$$

The interaction operator can be given explicitly as:

$$\hat{W} = \sum_{ik} (h_{ik} - h_{ik}^0) \psi_i^+ \psi_k^- + \frac{1}{2} \sum_{ijkl} ([ij|kl] - [ij|kl]^0) \psi_i^+ \psi_j^+ \psi_l^- \psi_k^- \quad (15.33)$$

where h_{ik}^0 and $[ij|kl]^0$ denote the limiting values of the integrals at $R \rightarrow \infty$.

Evaluation of the zeroth-order wave functions and energies requires the solution of the zeroth-order Schrödinger equation:

$$\hat{H}^{(0)} \Psi_K^{(0)} = E_K^{(0)} \Psi_K^{(0)} \quad (15.34)$$

which, due to Eq. (15.31), reduces to:

$$\hat{H}^A \Psi_m^A = E_m^A \Psi_m^A, \quad \hat{H}^B \Psi_m^B = E_m^B \Psi_m^B. \quad (15.35)$$

An exact (full CI) solution of these equations is rarely feasible. It may be convenient

to substitute Eqs. (15.35) by the corresponding Hartree-Fock problems:

$$\hat{F}^A \psi_i^A = \varepsilon_i^A \psi_i^A, \quad \hat{F}^B \psi_i^B = \varepsilon_i^B \psi_i^B \quad (15.36)$$

with the Fockians defined as:

$$\hat{F}^A = \sum_{i \in A}^{\text{occ}} \varepsilon_i^A \psi_i^+ \psi_i^-, \quad \hat{F}^B = \sum_{i \in B}^{\text{occ}} \varepsilon_i^B \psi_i^+ \psi_i^-. \quad (15.37)$$

The many-electron functions and energies are written as:

$$\Psi^A = \psi_{AN_A}^+ \dots \psi_{A2}^+ \psi_{A1}^- |vac\rangle \quad (15.38a)$$

$$\Psi^B = \psi_{BN_B}^+ \dots \psi_{B2}^+ \psi_{B1}^- |vac\rangle \quad (15.38b)$$

$$E^A = \sum_{i \in A}^{\text{occ}} \varepsilon_i, \quad E^B = \sum_{i \in B}^{\text{occ}} \varepsilon_i. \quad (15.39)$$

The zeroth-order, properly antisymmetric wave function is defined as:

$$\Psi^{(0)} = \psi_{AN_A}^+ \dots \psi_{A2}^+ \psi_{A1}^- \psi_{BN_B}^+ \dots \psi_{B2}^+ \psi_{B1}^- |vac\rangle \quad (15.40)$$

which for the zeroth-order Hamiltonian:

$$\hat{H}^{(0)} = \hat{F}^A + \hat{F}^B \quad (15.41)$$

leads to the zeroth-order energy:

$$E^{(0)} = E^A + E^B = \sum_{i \in A \cup B}^{\text{occ}} \varepsilon_i. \quad (15.42)$$

The perturbation theory is now completely defined, and low-order contributions can be derived in the standard manner.

Problem 15.1

Evaluate the first- and second-order contributions to the interaction energy

$$\Delta E^{(1)} = W_{00}, \quad \Delta E^{(2)} = \sum_K W_{0K}^2 / (E_K - E_0)$$

for the interaction operator of Eq. (15.33) using the Møller-Plesset like partitioning defined by Eqs. (15.36–42).

Hint: Proceed in the same manner as for the correlation energy in Sect. 12.

Since the zeroth-order equations are solved only in the Hartree-Fock approximation, the perturbation corrections account not only for intermolecular interactions, but for the intramolecular correlation energy as well. These two effects cannot be separated in the Löwdin basis set, but one may subtract the contributions of those $[ij|kl]^0$ integrals which result in local correlation.

The PT sketched above keeps antisymmetrizing the wave functions even in the $R \rightarrow \infty$ limit. This feature is different from the method by Chang and Weinstein (1978) who used a different set of fermion operators for A and for B,

and assumed a commutation relationship (and not anticommutation) between them. This is a large change in the algebra but it makes no difference in physics in the absence of any interaction (matrix element) between A and B at $R \rightarrow \infty$. At finite distances the commutator relation implies that a simple product of the monomer wave functions is used as a basis set. For this reason no exchange effects appear and the only intermolecular interaction which can be taken into account by this formalism is the Coulombic one.¹⁶

A shortcoming of the exchange perturbation theories discussed above is that the resulting interaction energies suffer from basis set superposition error. To moderate this effect in a similar scheme, Daudey et al. (1974b) proposed to drop all contributions from ΔE which involve an occupied \rightarrow virtual transition from A to B (or vice versa) which result only in an improvement of the description of A by the virtual orbitals of B; thus they are typical representatives of BSSE. This method is essentially equivalent to re-adjusting the monomer energies by extending the monomer basis to include the virtual orbitals of the other monomer. This procedure is called as the “virtuals only” counterpoise scheme, and it was recently strongly criticized (Van Lenthe et al. 1987) because it underestimates BSSE significantly.

It may be of some interest to check whether the BSSE-free interaction operator of Eq. (15.27) could be used to solve this problem. This project was carried out in our laboratory (Surján et al. 1985b, Surján & Poirier 1986). To utilize the full power of this interaction operator, we did not turn to a Löwdin basis, but applied a non-Hermitian perturbation theory similar to the former work by Kochanski and Gouyet (1975).

The following Hamiltonian has been chosen:

$$\hat{H}^{AB} = \hat{H}^{(0)} + \hat{W} = \hat{F}^A + \hat{F}^B + \hat{W} \quad (15.43)$$

where:

$$F^A = \sum_{i \in A}^{\text{occ}} \varepsilon_i^A \psi_i^+ \tilde{\psi}_i^-, \quad F^B = \sum_{i \in B}^{\text{occ}} \varepsilon_i^B \psi_i^+ \tilde{\psi}_i^- \quad (15.44)$$

with ψ and $\tilde{\psi}$ obeying Eq. (13.13). The perturbation operator is given by Eq. (15.27). As shown by Eq. (15.43), the effect of intramolecular correlation is neglected. This is justified up to the second order of PT where no interference between local correlation and intermolecular interaction takes place.

Since neither $\hat{H}^{(0)}$ nor \hat{W} are Hermitian, one had to apply a non-symmetric generalization of the Rayleigh-Schrödinger PT (Surján et al. 1985a, 1985b). The relevant formulae are collected below.

The zeroth-order Schrödinger equation is given by Eq. (15.34). The eigenfunctions of $\hat{H}^{(0)}$ from the right, $\Psi^{(0)}$, are direct-space wave functions which are

¹⁶ Chang and Weinstein (1978) used an extra correction to describe overlap effects resulting from the antisymmetry of the zeroth order wave function. This correction is not incorporated into the many body formalism, and it is essentially equivalent to a Taylor expansion of matrix S^{-1} keeping only the leading terms.

antisymmetrized products of the MOs of individual molecules. The $\hat{H}^{(0)}$ being non-Hermitian, the zeroth-order set of many-electron functions is not orthogonal. One can construct a bi-orthogonal set as:

$$\langle \tilde{\Psi}^{(0)} | = \langle \text{vac} | \tilde{\Psi}_{A1}^- \tilde{\Psi}_{A2}^- \dots \tilde{\Psi}_{AN_A}^- \tilde{\Psi}_{B1}^- \tilde{\Psi}_{B2}^- \dots \tilde{\Psi}_{BN_B}^- . \quad (15.45)$$

The proper anticommutation rules between MOs ψ and $\tilde{\psi}$ ensure that the set of all possible many electron functions $\langle \tilde{\Psi}_K^{(0)} |$, which are generated by all possible configurations of type of Eq. (15.45), is bi-orthogonal to the set of direct-space many-electron functions $|\Psi_L^{(0)}\rangle$:

$$\langle \tilde{\Psi}_K^{(0)} | \Psi_L^{(0)} \rangle = \delta_{KL}. \quad (15.46)$$

The PT corrections turn out to be:

$$E_0^{(1)} = \langle \tilde{\Psi}_0^{(0)} | \hat{W} | \Psi_0^{(0)} \rangle \quad (15.47a)$$

$$E_0^{(2)} = - \sum_K \frac{\langle \tilde{\Psi}_0^{(0)} | \hat{W} | \Psi_K^{(0)} \rangle \langle \tilde{\Psi}_K^{(0)} | \hat{W} | \Psi_0^{(0)} \rangle}{E_K^{(0)} - E_0^{(0)}} \quad (15.47b)$$

which are straightforward generalizations of the usual PT formulae. Substituting Eqs. (15.27) and (15.45–46) into Eq. (15.47) and evaluating the matrix elements by means of standard rules, the following results are obtained:

$$E_0^{(1)} = \sum_{i \in B} \langle \tilde{\Psi}_i | U^A | \Psi_i \rangle + \sum_{i \in A} \langle \tilde{\Psi}_i | U^B | \Psi_i \rangle + \sum_{\substack{i \in A \\ k \in B}} [\tilde{\Psi}_i \tilde{\Psi}_k | \Psi_i \Psi_k] \quad (15.48)$$

and for the second order:

$$E_0^{(2)} = E_{\text{pol}}^{(2)}(A) + E_{\text{pol}}^{(2)}(B) + E_{\text{del}}^{(2)}(A \rightarrow B) + E_{\text{del}}^{(2)}(B \rightarrow A) + E_{\text{disp}}^{(2)} \quad (15.49)$$

where:

$$E_{\text{pol}}^{(2)}(A) = - \sum_{\substack{i \in A \\ j^* \in A}} \frac{\left(\sum_{k \in B} [\tilde{i}\tilde{k} | j^*k] + U_{ij^*}^B \right) \left(\sum_{k \in B} [j^*\tilde{k} | ik] + U_{j^*i}^B \right)}{\varepsilon_{j^*}^A - \varepsilon_i^A} \quad (15.50a)$$

and:

$$E_{\text{del}}^{(2)}(A \rightarrow B) = - \sum_{\substack{i \in A \\ j^* \in B}} \frac{\left(\sum_{k \in A} [\tilde{i}\tilde{k} | j^*k] + U_{ij^*}^A \right) \left(\sum_{k \in B} [j^*\tilde{k} | ik] + U_{j^*i}^B \right)}{\varepsilon_{j^*}^B - \varepsilon_i^A} \quad (15.50b)$$

while:

$$E_{\text{disp}}^{(2)} = - \sum_{\substack{i, k, j^*, l^* \\ \{i, j^* \in A \\ k, l^* \in B\}}} \frac{[\tilde{i}\tilde{k} | j^*l^*] [\tilde{j}^*\tilde{l}^* | ik]}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_k - \varepsilon_i} \quad (15.50c)$$

with obvious notations, the asterisk indicating virtual orbitals. The terms ($B \rightarrow A$) can be obtained from Eqs. (15.50) by interchanging A and B .

The above formulae are essentially the same as those obtained by Kochanski and Gouyet (1975) on the basis of the L_2 space model Hamiltonian of Eq. (15.7). This illustrates that the BSSE-free many-body operator (15.27) and the first quantized model Hamiltonian of Eq. (15.7) have a similar significance. We emphasize again that no intermolecular matrix element of the kinetic energy gives rise to interaction in either cases.

Assuming convergency of the PT series, the above formulae converge to the exact interaction energy at infinite order. However, low-order contributions do not give reliable results in all cases. At small intermolecular distances the PT series may also diverge. Solution of this problem requires another partition of the Hamiltonian.

16 Quasiparticle Transformations

Second quantized operators create and annihilate particles. Depending on the interpretation of these operators, the corresponding particles may have classical analogs or may not. Throughout the previous treatment we have dealt with electrons which are considered as true “physical” particles. In this section we shall discuss certain combinations of electron creation and annihilation operators which are said to create “quasiparticles”.

Properties of the condensed matter are often described in terms of *elementary excitations*. Various physical quantities (energy, momentum, etc.) can be assigned to these excitations which justifies to consider them as quasiparticles (Landau et al. 1980). Though these quasiparticles carry some physical information, they cannot be identified with the real particles (electrons, atoms, molecules) of the system. Discussion of the physics of quasiparticles is out of the scope of the present book. Mathematical description of quasiparticles is inherently connected to second quantization; this point will be considered below.

In a broad sense, a quasiparticle transformation consists of an arbitrary transformation of the creation/annihilation operators and it is usually introduced for mathematical convenience. In most applications, the transformations involve one-particle operators, but sometimes two-particle combinations are useful, too. Such transformations will be briefly reviewed in Sects. 16.1 and 16.2, respectively, while in Sect. 16.3 an application to the latter will be presented.

16.1 One-Particle Transformations

Consider a set of creation and annihilation operators a_k^+ and a_k . The most general linear transformation of these operators can be written as:

$$\begin{aligned} b_i^+ &= \sum_k (A_{ik} a_k^+ + B_{ik} a_k) \\ b_i &= \sum_k (A_{ik} a_k + B_{ik} a_k^+) \end{aligned} \tag{16.1}$$

where the transformed operators b_i^+ and b_i create and annihilate the “quasiparticles”. Various types of quasiparticle transformations are obtained by various restrictions on the linear combination coefficients A and B. (In this section these coefficients are supposed to be real).

Assume that the original operators a_k^+ , a_k obey the usual fermion anti-commutation rules:

$$[a_k, a_i]_+ = [a_k^+, a_i^+]_+ = 0$$

$$[a_k^+, a_i]_+ = \delta_{ki}.$$

The transformation of Eq. (16.1) is said to be *canonical* if the same rules are maintained for the transformed operators:

$$\begin{aligned} [b_k, b_i]_+ &= [b_k^+, b_i^+]_+ = 0 \\ [b_k^+, b_i]_+ &= \delta_{ki}. \end{aligned} \tag{16.2}$$

These equations give some conditions for the transformation coefficients A and B which can be obtained by substituting Eq. (16.1) into Eq. (16.2):

$$\sum_j (A_{ij}B_{kj} + B_{ij}A_{kj}) = 0 \tag{16.3a}$$

$$\sum_j (A_{ij}A_{kj} + B_{ij}B_{kj}) = \delta_{ik}. \tag{16.3b}$$

These are the conditions for the quasiparticle transformation to be a canonical transformation. Some special cases of such transformations we have seen previously. If, for example, $B_{ik} = 0$, one has:

$$\begin{aligned} b_i^+ &= \sum_k A_{ik}a_k^+ \\ b_i &= \sum_k A_{ik}a_k \end{aligned} \tag{16.4}$$

and the canonical nature of the transformation requires:

$$\sum_j A_{ij}A_{kj} = \delta_{ik}. \tag{16.5}$$

The transformation of Eq. (16.4) is not really a quasiparticle transformation, since it just reflects a transformation of the underlying orbital space: If a_i^+ creates an electron on orbital χ_i , than b_i^+ creates one on $\chi'_i = \sum_k A_{ik}\chi_k$. The canonical condition of Eq. (16.5) means that the transformation matrix A is unitary. In Sect. 13 we have also seen non-unitary basis set transformations of the form of Eq. (16.4), for which Eq. (16.5) does not hold, and which do not leave the anticommutation rules invariant.

Another special case of the general quasiparticle transformation is when the coefficients $A_{ik} = 0$. This corresponds to interchanging the creation and annihilation operators. The canonical conditions of Eq. (16.3) then require matrix B to be unitary. With B being the unit matrix, this is the particle-hole transformation we have considered in Sect. 10.2.

Mixing of the above two limiting cases can sometimes be useful, too. One of the most important quasiparticle transformations of this type is the so-called Bogoliubov transformation applied in the standard theory of superfluidity and superconductivity. These theories are out of the scope of this book but we shall make an exception below to explain the merit of the Bogoliubov transformation (Landau et al. 1980).

A microscopic system of a large number of interacting particles is called a quantum fluid. In the theory of quantum fluids one deals with quasiparticles which are identified with the elementary excitations of the system.

Let us check first the case when the quasiparticles under study are spinless, thus they follow Bose statistics:

$$\begin{aligned} [a_p, a_{p'}]_- &= [a_p^+, a_{p'}^+]_- = 0 \\ [a_p^+, a_{p'}]_- &= \delta_{pp'}. \end{aligned} \quad (16.6)$$

Assume that the momentum p of the quasiparticles is the only relevant quantum number, and consider the following model Hamiltonian:

$$H = \sum_p \frac{p^2}{2m} a_p^+ a_p + g \sum_p (a_p a_{-p} + a_p^+ a_{-p}^+ + 2a_p^+ a_p) \quad (16.7)$$

where m is the effective mass of the quasiparticles. This Hamiltonian can be derived from the usual many-body Hamiltonian in the weakly interacting limit assuming that there is no external field and the dominant interaction is between quasiparticles with opposite momentum (Landau et al. 1980). The coupling parameter g characterizes the strength of the interaction. It is seen that this Hamiltonian is not expressed in terms of operators conserving the particle number, since the number of creation and annihilation operators is not equal in each term. This is possible because we are dealing with a Bose fluid.

Let us introduce now the following transformation of operators a_p^+ , a_p :

$$\begin{aligned} a_p &= u_p b_p + v_p b_{-p}^+ \\ a_p^+ &= u_p b_p^+ + v_p b_{-p}. \end{aligned} \quad (16.8)$$

This is called the Bogoliubov transformation. To maintain the commutation rules of Eq. (16.6) for operators $b_p^+ b_p$ the coefficients should obey the condition:

$$u_p^2 - v_p^2 = 1. \quad (16.9)$$

With Eq. (16.9), the Bogoliubov transformation is canonical. Substituting Eq. (16.8) into the model Hamiltonian of Eq. (16.7), one finds:

$$\begin{aligned} H &= H^0 + \sum_p \epsilon_p b_p^+ b_p \\ &\quad + \sum_p \left[\left(2g + \frac{p^2}{2m} \right) u_p v_p + g(u_p^2 + v_p^2) \right] (b_p^+ b_{-p}^+ + b_p b_{-p}) \end{aligned} \quad (16.10)$$

where H^0 is a constant term. The free parameters of the transformation, u_p and v_p , can be chosen to eliminate the nondiagonal term (the one inside the square bracket) in Eq. (16.10). Then the Hamiltonian becomes:

$$H = H^0 + \sum_p \epsilon_p b_p^+ b_p \quad (16.11)$$

where:

$$\epsilon_p = \sqrt{\frac{2p^2}{m}g + \frac{p^4}{2m^2}}.$$

We can see that the Bogoliubov transformation diagonalized the model Hamiltonian of Eq. (16.7) exactly.

As a next example we consider a Fermi fluid or electron gas. The creation/annihilation operators obey anticommutation rules. Let us investigate the following model Hamiltonian:

$$H = \sum_{p\sigma} \epsilon_p a_{p\sigma}^+ a_{p\sigma} + g \sum_{pp'} a_{p'\uparrow}^+ a_{p'\downarrow}^+ a_{-p\downarrow} a_{p\uparrow} \quad (16.12)$$

where σ is the spin label and the parameter g is interpreted as the coupling constant for the electron-electron interaction. Namely, it describes the interaction of electrons of opposite spins (\uparrow and \downarrow) and opposite momenta (p and $-p$). This Hamiltonian resembles formally to the Hubbard Hamiltonian (see Sect. 10.1), since the electron-electron interaction is characterized by a single coupling constant. The difference is that here the interaction between electrons in states p and $-p$ are considered instead of an on-site repulsion. For negative g values this Hamiltonian describes a superconducting system, which can be described within the Bardeen-Cooper-Schrieffer (BCS) theory (Bardeen et al. 1957).

Following Bogoliubov, we consider the quasiparticle transformation:

$$\begin{aligned} b_{p\downarrow} &= u_p a_{p\downarrow} + v_p a_{-p\uparrow} \\ b_{p\uparrow} &= u_p a_{p\uparrow} + v_p a_{-p\downarrow}. \end{aligned} \quad (16.13)$$

The adjoints of these equations give $b_{p\downarrow}^+$ and $b_{p\uparrow}^+$, respectively. The transformation is canonical if:

$$u_p^2 + v_p^2 = 1. \quad (16.14)$$

The inverse transformation is readily obtained as:

$$\begin{aligned} a_{p\downarrow} &= u_p b_{p\downarrow} + v_p b_{-p\uparrow}^+ \\ a_{p\uparrow} &= u_p b_{p\uparrow} + v_p b_{-p\downarrow}^+. \end{aligned} \quad (16.15)$$

The problem of this interacting Fermi gas is more complicated than the weakly interacting Bose system treated previously, and the Bogoliubov transformation of Eqs. (16.13–15) does not diagonalize the Hamiltonian of Eq. (16.12) exactly. Let us still transform this Hamiltonian by expressing it in terms of operators b , b^+ . The result is:

$$\begin{aligned} H &= 2 \sum_p \epsilon_p v_p^2 + \sum_p \epsilon_p (u_p^2 - v_p^2) (b_{p\uparrow}^+ b_{p\uparrow} + b_{p\downarrow}^+ b_{p\downarrow}) \\ &\quad + 2 \sum_p \epsilon_p u_p v_p (b_{p\uparrow}^+ b_{-p\downarrow}^+ + b_{-p\downarrow} b_{p\uparrow}) + g \sum_{pp'} B_{p'}^+ B_p \end{aligned} \quad (16.16)$$

where:

$$B_p = u_p^2 b_{-p\downarrow} b_{p\uparrow} - v_p^2 b_{p\uparrow}^+ b_{-p\downarrow}^+ + u_p v_p (b_{-p\downarrow} b_{-p\downarrow}^+ - b_{p\uparrow}^+ b_{p\uparrow}).$$

Let us assume now that the system under study is built up by bound pairs of

quasiparticles of opposite spin and momentum:

$$C_p^+ = b_{p\uparrow}^+ b_{-p\downarrow}^+. \quad (16.17)$$

Evaluating the energy as the expectation value of Eq. (16.16) by a wave function constructed from such pairs, only the diagonal elements enter the energy formula which will be:

$$E = 2 \sum_p \varepsilon_p v_p^2 + \sum_p \varepsilon_p (u_p^2 - v_p^2) (n_{p\uparrow} + n_{p\downarrow}) - g \left[\sum_p u_p v_p (1 - n_{p\uparrow} - n_{p\downarrow}) \right]^2$$

where $n_{p\sigma}$ is the occupation number. The unknown parameters of the Bogoliubov transformation, u_p and v_p , can be determined by minimizing this energy at fixed occupation numbers taking into account the normalization condition of Eq. (16.14). The result is:

$$u_p^2 = \frac{1}{2} \left[1 + \frac{\varepsilon_p}{\sqrt{\varepsilon_p^2 + \Delta^2}} \right]$$

$$v_p^2 = \frac{1}{2} \left[1 - \frac{\varepsilon_p}{\sqrt{\varepsilon_p^2 + \Delta^2}} \right]$$

where Δ is determined by the implicit equation:

$$1 = \frac{g}{2} \sum_p \frac{1 - n_{p\uparrow} - n_{p\downarrow}}{\sqrt{\varepsilon_p^2 + \Delta^2}}.$$

The analysis of the physical meaning of these results leads to an explanation of low-temperature superconductivity, but we stop the treatment here having reached the aim to show how the Bogoliubov quasiparticle transformation of Eq. (16.13) resulted in a useful energy formula.

An interesting feature of Eq. (16.17) is worth mentioning. It is seen that two fermion operators are collected in this equation to form a pair of zero resulting spin. Such pairs are called Cooper pairs in the theory of superconductivity. Equation (16.17) can also be considered as a quasiparticle transformation which is, however, very different from the single-particle transformations we have seen previously. Two-electron quasiparticle transformations will be introduced in the next section in a somewhat different context.

16.2 Two-Particle Transformations

Nonlinear quasiparticle transformations involving a product of two creation operators can be called two-particle transformations. The form of two-particle transformations we shall consider here is given as:

$$\psi_i^+ = \sum_{\mu > \nu} C_{\mu\nu}^i a_\mu^+ a_\nu^+ \quad (16.18a)$$

$$\psi_i^- = \sum_{\mu > v} C_{\mu v}^i a_v a_\mu \quad (16.18b)$$

where a_μ^+ , a_μ create/annihilate electrons. The summation restriction $\mu > v$ is introduced to avoid the double counting of electron pairs; the $\mu = v$ case need not be considered due to the fermion anticommutation rules. The quasiparticle transformations of Eq. (16.18) are useful because they can describe different electron pair methods on an equal footing. Several authors have considered such types of transformations from diverse viewpoints (Girardeau 1963, 1971, 1980; Kvasnička 1982, 1984; Takahashi & Fukutome 1983). This topic is also referred to as second quantization for composite particles. Here some basic features of such transformations will be summarized while the next section will discuss an application.

It is essential to investigate the algebraic properties of operators ψ_i^+ , ψ_i^- which are defined by their commutation rules. The first thing we realize is that:

$$\psi_i^+ \psi_k^+ - \psi_k^+ \psi_i^+ = \sum_{\substack{\mu > v \\ \lambda > \sigma}} C_{\mu v}^i C_{\lambda \sigma}^k [a_\mu^+ a_v^+ a_\lambda^+ a_\sigma^+ - a_\lambda^+ a_\sigma^+ a_\mu^+ a_v^+] = 0.$$

That is:

$$[\psi_i^+, \psi_k^+]_- = 0 \quad (16.19a)$$

and similarly:

$$[\psi_i^-, \psi_k^-]_- = 0. \quad (16.19b)$$

The operators ψ^+ (and ψ^-) commute and they describe Bose-like quasiparticles. This is quite natural since transposition of such composite quasiparticles involves the simultaneous transposition of two electrons, thus the sign is always unchanged.

The situation is far more complicated for the commutation rules between ψ^- and ψ^+ :

$$[\psi_i^-, \psi_k^+]_- = \hat{Q}_{ik}. \quad (16.20)$$

Substituting the expansion of the quasiparticles, one gets:

$$\hat{Q}_{ik} = \sum_{\substack{\mu > v \\ \lambda > \sigma}} C_{\mu v}^i C_{\lambda \sigma}^k [a_v a_\mu, a_\lambda^+ a_\sigma^+]_-.$$

Evaluation of the commutator gives us, after some appropriate interchange of the summation labels:

$$\hat{Q}_{ik} = \sum_{\mu > v} C_{\mu v}^i C_{\mu v}^k + \sum_{\mu \neq \lambda} C_{\mu v}^i C_{\mu \lambda}^k a_v^+ a_\lambda \quad (16.21)$$

where we have introduced the convention:

$$C_{\mu v}^i = -C_{\mu v}^i \quad (\mu > v). \quad (16.22)$$

We can see from Eq. (16.21) that the commutation rules of Eq. (16.20) are indeed complicated. The presence of operators \hat{Q}_{ik} prevents us from developing an

efficient theory for the quasiparticles, since the evaluation of any matrix element is extremely complicated. The situation is entirely different from that of non-unitary one-electron transformations which lead to second quantization for nonorthogonal orbitals (Sect. 13). The commutator in the latter case is a scalar quantity, while \hat{Q}_{ik} is an operator. One cannot get rid of \hat{Q}_{ik} by an orthogonalization or bi-orthogonal transformation. This reflects that the quasiparticles are *composite*.¹

One can, however, impose certain conditions on the coefficients $C_{\mu\nu}^i$ resulting in a simpler form of the quasi-particle commutator \hat{Q}_{ik} . First, the requirement that the two-electron wave functions created by ψ_i^+ form an orthonormal set requires:

$$\delta_{ik} = \langle \text{vac} | \psi_i^- \psi_k^+ | \text{vac} \rangle = \sum_{\substack{\mu > v \\ \lambda > \sigma}} C_{\mu\nu}^i C_{\lambda\sigma}^k \langle \text{vac} | \underbrace{\nu^- \mu^- \lambda^+ \sigma^+}_{\text{pairing}} | \text{vac} \rangle.$$

In evaluating the matrix element only the indicated pairing is compatible the summation restriction thus one gets:

$$\sum_{\mu > v} C_{\mu\nu}^i C_{\mu\nu}^k = \delta_{ik}. \quad (16.23)$$

This is called the *weak orthogonality* condition; note that the summation is performed over both labels μ and v . Under this condition the quasiparticle commutator writes:

$$\hat{Q}_{ik} = \delta_{ik} + \sum_{\mu\nu\lambda} C_{\mu\nu}^i C_{\mu\lambda}^k a_v^+ a_\lambda. \quad (16.24)$$

This form of \hat{Q}_{ik} is not substantially simpler because we could not eliminate the offdiagonal terms. One may require also the so-called *strong orthogonality* condition²:

$$\sum_{\mu} C_{\mu\nu}^i C_{\mu\lambda}^k = 0 \quad \text{for } i \neq k \text{ and for any } v, \lambda. \quad (16.25)$$

Note that the summation is performed only over one index. Under strong orthogonality \hat{Q}_{ik} reduces to:

$$\hat{Q}_{ik} = \delta_{ik} \left[1 + \sum_{\mu\nu\lambda} C_{\mu\nu}^i C_{\mu\lambda}^k a_v^+ a_\lambda \right] \quad (16.26)$$

which represents an essential simplification. To illustrate this, let us check the normalization of the many-electron wave function:

$$\Psi = \psi_1^+ \psi_2^+ \dots \psi_N^+ | \text{vac} \rangle. \quad (16.27)$$

It becomes:

¹ For elementary bosons $[\psi_i^-, \psi_k^+] = \delta_{ik}$.

² In first quantized notations, strong orthogonality is expressed as $\int \psi_i(\vec{r}_1, \vec{r}_2) \psi_k(\vec{r}_1, \vec{r}_2) \times d\vec{r}_1 = 0$ for $i \neq k$. This reduces to Eq. (16.25) if expanding the geminals $\psi(\vec{r}_1, \vec{r}_2)$ as in Eq. (16.18).

$$\langle \Psi | \Psi \rangle = \langle \text{vac} | \psi_N^- \dots \psi_2^- \psi_1^- \psi_1^+ \psi_2^+ \dots \psi_N^+ | \text{vac} \rangle$$

where the quasiparticle operators obey the commutation rules of Eq. (16.20). If \hat{Q}_{ik} is determined by the general formulae of Eqs. (16.21) or (16.24), evaluation of this matrix element is extremely difficult, since we cannot transpose, e.g., ψ_1^- and ψ_2^+ . If the strong orthogonality condition of Eq. (16.25) is fulfilled, the operator string can be reordered as:

$$\langle \Psi | \Psi \rangle = \langle \text{vac} | \psi_N^- \psi_N^+ \dots \psi_2^- \psi_2^+ \psi_1^- \psi_1^+ | \text{vac} \rangle$$

which can easily be evaluated as:

$$\psi_1^- \psi_1^+ | \text{vac} \rangle = \psi_1^+ \psi_1^- | \text{vac} \rangle + \hat{Q}_{11} | \text{vac} \rangle = | \text{vac} \rangle.$$

Because in general³:

$$\hat{Q}_{ii} | \text{vac} \rangle = | \text{vac} \rangle.$$

We find that:

$$\langle \Psi | \Psi \rangle = \langle \text{vac} | \text{vac} \rangle = 1,$$

thus the wave function of Eq. (16.27) is normalized to unity. Any other matrix elements containing the composite particle operators ψ^+ , ψ^- can be evaluated in a similar manner provided that the strong orthogonality condition is imposed. The energy expression can also be derived in this case as the expectation value of the Hamiltonian with Eq. (16.27).

The coefficients $C_{\mu\nu}^i$ determine the internal structure of the composite Bose-like quasiparticles created by ψ_i^+ . If these coefficients are determined variationally subject to Eq. (16.25), the wave function of Eq. (16.27) is called the antisymmetrized product of strongly orthogonal geminals (APSG) (Hurley et al. 1953, Ahlrichs & Kutzelnigg 1968). The term ‘geminal’ refers to the two-electron function (“biorbital”) created by ψ_i^+ . The APSG wave function represents a fairly accurate description of the molecular electronic structure including a significant amount of electron correlation. In the second quantized picture, each geminal is identified to a Bose-like quasiparticle composed of two electrons. The non-elementary nature of these quasiparticles is manifested in the complicated form of the commutator \hat{Q}_{ik} . The point is that \hat{Q}_{ik} is a matrix of *operators* and not simply a matrix of numbers as it would be in the case of non-unitary one-particle transformation discussed in Sect. 16.1.

³ It is interesting to note that with respect to acting on the vacuum state, \hat{Q}_{ik} behaves as the unity operator in the sense:

$$\hat{Q}_{ik} | \text{vac} \rangle = \delta_{ik} | \text{vac} \rangle$$

even in the weakly orthogonal case. This is trivial since the terms of \hat{Q}_{ik} differing from δ_{ik} end with annihilation operator.

16.3 A Theory of the Local Chemical Bond

We have seen in the previous section that the strong orthogonality condition represents a remarkable simplification in the mathematical structure of the quasiparticle operators. Strong orthogonality can be ensured either as an auxiliary condition to a variational procedure, as it is done in APSG models, or directly, by constructing ab ovo strongly orthogonal geminals. The simplest way to this latter scheme is to restrict the expansion of the quasiparticles on mutually disjunct subspaces:

$$\psi_i^+ = \sum_{\substack{\mu, v \in i \\ (\mu > v)}} C_{\mu v}^i a_\mu^+ a_v^+ \quad (16.28)$$

In other words, the basis set and the corresponding fermion operators are partitioned into different subspaces and the expansion coefficients are strictly localized on one of these subspaces. The wave function:

$$\Psi_{AP-SLG} = \psi_1^+ \psi_2^+ \dots \psi_N^+ |vac\rangle \quad (16.29)$$

which describes a system of $2N$ electrons can be called the antisymmetrized product of *strictly localized geminals*. The quasiparticle transformation of Eq. (16.28) offers a convenient tool to study certain properties of the local two-electron chemical bond (Surján 1984, 1989; Surján et al. 1985a). In what follows we shall review this many-body theory in some detail.

Assume the existence of a local subset of basis orbitals assigned to each two-electron chemical bond of the molecule. Such basis orbitals can be constructed from local atomic hybrids or off-centered bond functions, for example. We do not discuss the actual choice of the basis set here supposing only that each basis function is uniquely assigned to one of the chemical bonds of the molecule. The term ‘chemical bond’ is used here in a broad sense: it refers to two-center bonds as well as other two-electron fragments (inner shells, lone pairs) of the system.

The most general local wave function for the bond i , expanded in the corresponding subset, is given by Eq. (16.28), in which a_μ^+ is a creation operator creating an electron on the basis orbital χ_μ , $\mu \in i$. In order to derive the local equations for determining the optimum values of the expansion coefficients $C_{\mu v}^i$, we have to analyze the structure of the Hamiltonian. The analysis should be performed in terms of the basis orbitals χ_μ which form a nonorthogonal set. Hence, the Hamiltonian is written as:

$$H = \sum_{\mu v} h_{\mu v} a_\mu^+ \tilde{a}_v + \frac{1}{2} \sum_{\mu v \lambda \sigma} [\tilde{\mu} \tilde{v} | \lambda \sigma] a_\mu^+ a_v^+ \tilde{a}_\sigma \tilde{a}_\lambda \quad (16.30)$$

where the annihilation operators \tilde{a}_v refer to the reciprocal space and obey the true fermion anticommutation rules (cf. Sect. 13). The integrals are also transformed in their *bra*-indices.

Since each basis function χ_μ is assigned to a particular bond, any summation over basis orbitals can be formally substituted by a summation over bonds i and

over orbitals centered on the bond i:

$$\sum_{\mu} \equiv \sum_i \sum_{\mu \in i}. \quad (16.31)$$

This leads to the partitioning of the Hamiltonian:

$$H = \sum_i H^i + \sum'_{ij} H^{ij} + \sum'_{ijk} H^{ijk} + \sum'_{ikjl} H^{ikjl} \quad (16.32)$$

where the primes on the summations indicate that no indices coincide. The operator H^i is a one-bond Hamiltonian in which the summation labels run only within the i-th subspace:

$$H^i = \sum_{\mu \nu \in i} h_{\tilde{\mu} \nu} a_{\mu}^{+} \tilde{a}_{\nu} + \frac{1}{2} \sum_{\mu \nu \lambda \sigma \in i} [\tilde{\mu} \tilde{\nu} | \lambda \sigma] a_{\mu}^{+} a_{\nu}^{+} \tilde{a}_{\sigma} \tilde{a}_{\lambda}. \quad (16.33)$$

This operator is considered as the Hamiltonian for the bond i. Apart from overlap effects reflected by the biorthogonal integral list, it describes an isolated bond. The next three terms of the total Hamiltonian in Eq. (16.32) describe interbond interactions. The expressions of these interaction Hamiltonians can be obtained by the partitioning of the summation labels according to Eq. (16.31). The pairwise interaction operator H^{ij} after simple algebraic manipulations can be given in the following compact form:

$$\begin{aligned} H^{ij} = & \sum_{\mu \in i} \sum_{\nu \in j} h_{\tilde{\mu} \nu} a_{\mu}^{+} \tilde{a}_{\nu} + \sum_{\mu \lambda \in i} \sum_{\sigma \in j} [\tilde{\mu} \tilde{\nu} | \lambda \sigma] a_{\mu}^{+} a_{\nu}^{+} \tilde{a}_{\sigma} \tilde{a}_{\lambda} \\ & + \sum_{\mu \lambda \sigma \in i} \sum_{\nu \in j} [\tilde{\mu} \tilde{\nu} | \lambda \sigma] a_{\mu}^{+} a_{\nu}^{+} \tilde{a}_{\sigma} \tilde{a}_{\lambda} \\ & + \sum_{\mu \lambda \in i} \sum_{\nu \sigma \in j} \{[\tilde{\mu} \tilde{\nu} | \lambda \sigma] - [\tilde{\mu} \tilde{\nu} | \sigma \lambda]\} a_{\mu}^{+} a_{\nu}^{+} \tilde{a}_{\sigma} \tilde{a}_{\lambda} \\ & + \frac{1}{2} \sum_{\mu \nu \in i} \sum_{\lambda \sigma \in j} [\tilde{\mu} \tilde{\nu} | \lambda \sigma] a_{\mu}^{+} a_{\nu}^{+} \tilde{a}_{\sigma} \tilde{a}_{\lambda}. \end{aligned} \quad (16.34)$$

Different terms of H^{ij} have simple physical meaning. In the first term $a_{\mu}^{+} \tilde{a}_{\nu}$ annihilates an electron in the bond j and creates one on the bond i, hence it describes a $j \rightarrow i$ electron delocalization. The next two terms have similar meaning. The fourth term has a different significance: its operator string, $a_{\mu}^{+} a_{\nu}^{+} \tilde{a}_{\sigma} \tilde{a}_{\lambda}$ conserves the number of electrons on both bonds i and j, thus it describes the interbond Coulomb and exchange interaction and dispersion. Finally, the last term describes a simultaneous transfer of two electrons which is expected to be of smaller importance as compared to the previous effects.

Expressions for the three- and four-body operators H^{ijk} and H^{ikjl} are available (Surján, 1984), but we do not put them down here since they exhibit a smaller influence. Indeed, they do not enter the working formulae of a low-order perturbation treatment.

Let us study now the formal aspects of the quasiparticle transformation of Eq. (16.28). The quasiparticle annihilation operators are defined by:

$$\tilde{\Psi}_i^- = \sum_{\substack{\mu, v \in i \\ (\mu < v)}} C_{\mu v}^i \tilde{a}_v \tilde{a}_\mu. \quad (16.35)$$

Operators $\psi_i^+(\tilde{\Psi}_i^-)$ create (annihilate) the wave function of the bond i on the vacuum state. We may say that they create (annihilate) a composite particle identified with a two-electron bond. Local chemical bonds of a molecule can be viewed as quasiparticles whose internal structure is defined by the expansion coefficients $C_{\mu v}^i$.

Let us recall the computational properties of these quasi-boson operators:

$$[\psi_i^+, \psi_j^+]_- = [\tilde{\Psi}_i^-, \tilde{\Psi}_j^-]_- = 0 \quad (16.36a)$$

and, owing to the strong orthogonality ensured by the strict localization:

$$[\tilde{\Psi}_i^-, \psi_j^+]_- = \hat{Q}_i \delta_{ik} \quad (16.36b)$$

where the operator \hat{Q}_i is defined by the square bracket of Eq. (16.26) restricting the summation indices on bond i . As seen in the previous section, the presence of operator \hat{Q}_i in the commutator equations does not result in any complications, because the commutator of Eq. (16.36b) is diagonal in the indices i and k .

It is clear from the definitions of ψ_i^+ and $\tilde{\Psi}_i^-$ that they are not the adjoints of each other if \tilde{a}_μ is not the adjoint of a_μ^+ owing to the nonorthogonality of the basis set. Evaluation of the usual expectation values of type $\langle \Psi | H | \Psi \rangle$, etc. is therefore very complicated. However, one may define the counterpart of the AP-SLG wave function of Eq. (16.29) in the reciprocal space as:

$$\langle \tilde{\Psi} | = \langle \text{vac} | \tilde{\Psi}_N^- \dots \tilde{\Psi}_2^- \tilde{\Psi}_1^-, \quad (16.37)$$

and define our energy functional by the following generalized Rayleigh quotient:

$$E = \frac{\langle \tilde{\Psi} | H | \Psi \rangle}{\langle \tilde{\Psi} | \Psi \rangle}. \quad (16.38)$$

Evaluation of matrix elements of type of Eq. (16.38) can be done exactly in the same manner as in the orthogonal case. All formal rules of second quantization remain valid. For example, application of the commutation rules in Eq. (16.36) gives us immediately:

$$\langle \tilde{\Psi} | \Psi \rangle = \langle \text{vac} | \tilde{\Psi}_N^- \dots \tilde{\Psi}_2^- \tilde{\Psi}_1^- \psi_1^+ \psi_2^+ \dots \psi_N^+ | \text{vac} \rangle = 1.$$

This means that the wave function $|\Psi\rangle$, though not normalized, is ‘binormalized’ to unity. The energy functional of Eq. (16.38) has the value of the exact energy only in the limiting case if Ψ is an exact eigenfunction of H . Using approximate wave functions, Eq. (16.37) corresponds to the method of moments (Preuß 1958, Szondy & Szondy 1966, Boys 1969, Hegyi et al. 1971) rather than to the variational method. Further on, when for the sake of brevity we shall write ‘expectation value’, this will be understood as the generalized matrix element of Eq. (16.38).

Let us study first the matrix element of the one-bond Hamiltonian H^i :

$$\begin{aligned}\langle \tilde{\Psi} | H^i | \Psi \rangle &= \langle \text{vac} | \tilde{\Psi}_i^- H^i \Psi_i^+ | \text{vac} \rangle \\ &= \sum_{\mu\nu \in i} h_{\mu\nu} P_{\nu\mu}^i + \frac{1}{2} \sum_{\mu\nu\lambda\sigma \in i} [\tilde{\mu}\tilde{\nu} | \lambda\sigma] \Gamma_{\lambda\sigma\mu\nu}^i\end{aligned}\quad (16.39)$$

where P^i and Γ^i are the analogs of the first- and second-order density matrices for the bond i . They are defined as the (generalized) expectation values of the corresponding operator strings:

$$P_{\nu\mu}^i = \langle \text{vac} | \tilde{\Psi}_i^- a_\mu^+ \tilde{a}_\nu \Psi_i^+ | \text{vac} \rangle = \sum_{\lambda \in i} C_{\mu\lambda}^i C_{\nu\lambda}^i \quad (16.40a)$$

$$\Gamma_{\lambda\sigma\mu\nu}^i = \langle \text{vac} | \tilde{\Psi}_i^- a_\mu^+ a_\nu^+ \tilde{a}_\sigma \tilde{a}_\lambda \Psi_i^+ | \text{vac} \rangle = C_{\mu\lambda}^i C_{\nu\sigma}^i \quad (16.40b)$$

where the matrix elements have been evaluated by substituting the expansion of SLGs and applying the usual fermion anticommutation rules.

The chemical bonds of a molecule are not isolated, but they are in the electrostatic field of each other—an effect which can be accounted for even in strictly localized models (Malrieu 1977). This can be done by defining the effective bond Hamiltonians $H^{i(\text{eff})}$ analogously to the group function theory (McWeeny 1959, Mehler 1977, 1981). The effective Hamiltonians will be used to write the local Schrödinger equations for each bond, which determine the expansion coefficients of the SLGs:

$$H^{i(\text{eff})} \Psi_i^+ | \text{vac} \rangle = E_i \Psi_i^+ | \text{vac} \rangle \quad (i = 1, 2, \dots, N). \quad (16.41)$$

The effective Hamiltonian is constructed by incorporating the average value of H^{ij} to form an effective one-body core $h^{i(\text{eff})}$ (for the relevant formulae see Surján 1984, Surján et al. 1985a).

At the zeroth order one may neglect the interbond overlap effects. This involves the neglect of the biorthogonal transformation of the integral list which will give first-order contributions to the total energy (vide infra). Intrabond overlap effects can be handled by appropriate local orthogonalization. Thus, the final form of the effective Hamiltonian of the bond i becomes:

$$H^{i(\text{eff})} = \sum_{\mu\nu \in i} h_{\mu\nu}^{i(\text{eff})} a_\mu^+ \tilde{a}_\nu + \sum_{\mu\nu\lambda\sigma \in i} [\mu\nu | \lambda\sigma] a_\mu^+ a_\nu^+ \tilde{a}_\sigma \tilde{a}_\lambda. \quad (16.42)$$

The wave function and the effective energy of the bond i are obtained as the “full CI” solution of the local Schrödinger equation [Eq. (16.41)] in the corresponding local basis set. Due to the interbond electrostatic interactions, these local equations are coupled and have to be solved iteratively. The total electronic energy of the system is not simply the sum of effective bond energies, but the latter has to be corrected for a double counting of intrabond electron repulsion described by the effective core. The difference between the biorthogonal and the direct two-electron integral list will also enter the energy formula as a first-order correction. The final energy expression for the AP-SLG wave function takes the form:

$$\begin{aligned}
 E_{\text{SLG}} = & \sum_{i=1}^N E_i - \frac{1}{2} \sum_{i \neq j} \sum_{\mu\nu \in i} \sum_{\lambda\sigma \in j} P_{\mu\nu}^i P_{\lambda\sigma}^j ([\mu\lambda|\nu\sigma] - [\mu\lambda|\sigma\nu]) \\
 & + \sum_{i=1}^N \sum_{\mu\nu \in i} (h_{\bar{\mu}\bar{\nu}} - h_{\mu\nu}) P_{\nu\mu}^i \\
 & + \sum_{i=1}^N \sum_{\mu\nu\lambda\sigma \in i} ([\tilde{\mu}\tilde{\nu}|\lambda\sigma] - [\mu\nu|\lambda\sigma]) \Gamma_{\lambda\sigma\mu\nu}^i
 \end{aligned} \tag{16.43}$$

with the density matrices defined by Eqs. (16.40). This formula gives only a crude approximation to the exact electronic energy as a consequence of the strict localization of the geminals. Still, this zeroth-order method can be useful in some cases, because it is very simple and represents a fairly correlated description taking into account the so-called “left-right” intrabond correlation. As a consequence, it yields qualitatively correct potential curves for the fission of single bonds (Surján et al. 1985a, Poirier & Surján 1987). Treatment of dissociation of multiple bonds is possible in a similar framework (England 1982, England et al. 1984). Further, assuming proper hybridization, this description provides us the best possible local representation of chemical bonds, thus the shortcomings of the SLG wave function reflect the limitations of the localized bond models in the given basis set.

Accuracy of the SLG approximation can be improved by perturbation theory. Second quantization provides us a powerful tool in developing a many-body theory suitable to derive interbond delocalization and correlation effects. The first question concerns the partitioning of the Hamiltonian to a zeroth-order part and perturbation. Using a straightforward generalization of the Møller-Plesset (1934) partitioning, the zeroth-order Hamiltonian is chosen as the sum of the effective intrabond Hamiltonians:

$$H^0 = \sum_{i=1}^n H^{i(\text{eff})}. \tag{16.44}$$

The perturbation operator W is defined as the difference between the exact Hamiltonian and H^0 :

$$W = H - H^0. \tag{16.45}$$

If the zeroth-order solution of the problem provides a good approximation, one expects that low-order PT contributions will be sufficient to consider. In this case, not all the terms of the perturbation operator W will contribute to the energy formula. For example, only two-bond terms will enter the second-order energy expression.

The zeroth-order Hamiltonian H^0 is not Hermitian, since the creation and annihilation operators are not the adjoints of each other. Owing to this non-Hermiticity various eigenstates of H^0 do not form an orthonormal set. This is the same situation we were faced with in the intermolecular PT using the biorthogonal formulation (cf. Sect. 15), thus we have to apply here the same formulae for energy corrections, Eqs. (15.47). Application of these PT formulas

requires the construction of direct and reciprocal space-excited wave functions which are biorthogonal to each other. The excited states can be distinguished according to the number of electrons excited, and according to the number of bonds involved in the transition. Thus the following representations are adequate:

$$\begin{aligned} |\Psi_K^0\rangle_{\text{pol}} &= \psi_i^{+q}\tilde{\psi}_i^-|\Psi_0^0\rangle \\ |\Psi_K^0\rangle_{\text{del}} &= \psi_j^{+(3)q}\psi_i^{+(1)p}\tilde{\psi}_j^-\tilde{\psi}_i^-|\Psi_0^0\rangle \\ |\Psi_K^0\rangle_{\text{disp}} &= \psi_j^{+q}\psi_i^{+p}\tilde{\psi}_j^-\tilde{\psi}_i^-|\Psi_0^0\rangle \end{aligned} \quad (16.46a)$$

where $|\Psi_0^0\rangle$ is the zeroth-order AP-SLG ground-state wave function, q and p are the local quantum numbers for the excited states of the bonds and K labels the corresponding molecular excitation. The subscripts ‘pol’, ‘del’, and ‘disp’ indicate the nature of the excited state (polarization, delocalization or dispersion). The biorthogonal bra-function counterparts of these formulae are readily seen to be:

$$\begin{aligned} \langle\Psi_K^0|_{\text{pol}} &= \langle\Psi_0^0|\psi_i^+\tilde{\psi}_i^- \\ \langle\Psi_K^0|_{\text{del}} &= \langle\Psi_0^0|\psi_i^+\psi_j^+\tilde{\psi}_i^{-(1)p}\tilde{\psi}_j^{-(0)q} \\ \langle\Psi_K^0|_{\text{disp}} &= \langle\Psi_0^0|\psi_i^+\psi_j^+\tilde{\psi}_i^-p\tilde{\psi}_j^-q. \end{aligned} \quad (16.46b)$$

The one- and three-electron states $\psi^{+(1)p}$ and $\psi^{+(3)q}$ are expanded analogously to Eq. (16.28):

$$\psi^{+(1)q} = \sum_{\mu \in i} C_{\mu}^{iq} a_{\mu}^+ \quad (16.47a)$$

and:

$$\psi^{+(3)p} = \sum_{\mu\nu\lambda \in i} C_{\mu\nu\lambda}^{ip} a_{\mu}^+ a_{\nu}^+ a_{\lambda}^+ \quad (16.47b)$$

both of them are Fermion operators, describing a system of an odd number of electrons. The coefficients C_{μ}^{iq} and $C_{\mu\nu\lambda}^{ip}$ can be obtained by solving local one- and three-electron Schrödinger equations for each bond.

Substituting the above representation of various excited states into the general PT results, and evaluating the matrix elements by the usual rules of the second quantized algebra, we get the relevant PT corrections to the energy. The first-order results have already been included in the SLG energy formula given in Eq. (16.43). At the second order, we get corrections due to (i) the overlap effects neglected at the zeroth order; (ii) delocalization between different bonds; and (iii) interbond dispersion:

$$\Delta E_{ov} = - \sum_i \sum_q^{\text{singlets}} \frac{S_{OK}^i S_{KO}^i}{E_i^q - E_i^o} \quad (16.48a)$$

$$\Delta E_{\text{deloc}} = - \sum_{ij} \sum_{pq}^{\text{doublets}} \frac{W_{OK}^{\text{del}} W_{KO}^{\text{del}}}{E_i^p + E_j^q - E_i^o - E_j^o} \quad (16.48b)$$

$$\Delta E^{\text{disp}} = - \sum_{\substack{ij \\ (i < j)}} \sum_{pq}^{M_s=0} \frac{\left| \sum_{hk \in j} \sum_{er \in i} \left([he|kr] - \frac{1}{2} [he|rk] \right) P_{hk}^{ip} P_{er}^{iq} \right|^2}{E_i^p + E_j^q - E_i^o - E_j^o} \\ - \frac{1}{4} \sum_{j < i} M_s^{p,q} = \pm 1; M_s^p + M_s^q = 0 \frac{\left| \sum_{hk \in j} \sum_{er \in i} [\tilde{h}\tilde{e}|rk] P_{hk}^{ip} P_{er}^{iq} \right|^2}{E_i^p + E_j^q - E_i^o - E_j^o} \quad (16.48c)$$

with obvious notations for the S_z quantum numbers M_s . In these equations the energy E_i^q is the eigenvalue of the effective Hamiltonian of the bond i corresponding to state q (cf. Møller-Plesset partitioning). The elements of the matrix S^i result from the neglect of the biorthogonal transformation at the zeroth order:

$$S_{OK}^i = \sum_{m,n \in i} (h_{mn} - h_{mn}) P_{nm}^{iq} + \frac{1}{2} \sum_{mnrs \in i} ([\tilde{m}\tilde{n}|rs] - [mn|rs]) C_{mn}^{io} C_{rs}^{iq} \quad (16.49)$$

where m, n, r , and s label the spatial basis orbitals and P^{iq} is the spatial first-order transition density matrix of bond i which is defined as:

$$P_{nm}^{iq} = \sum_{\sigma} P_{n\sigma, m\sigma}^{iq} \equiv \sum_{\sigma} P_{\mu\nu}^{iq} = \sum_{\sigma} \langle \text{vac} | \tilde{\psi}_i^- a_{\mu}^+ a_{\nu} \psi_i^+ | \text{vac} \rangle \\ = \sum_{\lambda \in i} \sum_{\sigma} C_{\mu\lambda}^{io} C_{\nu\lambda}^{iq} \quad (16.50)$$

Here σ is the spin label (either α or β), $\mu = \{mc\}$ is a spin orbital, and the SLG expansion coefficients $C_{\mu\nu}^{iq}$ were defined previously. The S_{OK} matrix elements appearing also in Eq. (16.48a) can be given analogously. The matrix elements of the delocalization operator can be expressed as:

$$W_{OK}^{\text{del}} = 2 \sum_{mn \in i} \sum_{rst \in j} h_{mr}^{\text{eff}} c_n^{ip} c_{rts}^{jq} c_{mn}^{io} c_{ts}^{jo} \\ - 2 \sum_{hek \in i} \sum_{rts \in j} [\tilde{h}\tilde{e}|kr] c_k^{ip} c_{he}^{io} c_{rts}^{jq} c_{ts}^{jo} \\ + 2 \sum_{hkr \in j} \sum_{ef \in i} [\tilde{h}\tilde{e}|kr] c_f^{ip} c_{ef}^{iq} c_{hs}^{j} (c_{krs}^{jq} - c_{rsk}^{jq}). \quad (16.51)$$

The above equations are the working formulae for the perturbation calculation of interbond interaction in the present scheme. Although they may appear to be complicated, they are computable with a rather small effort. The working integral list is obtained by a local four-index hybridization transformation and a global two-index transformation to the biorthogonal set. Only one- and two-bond integrals are required with the exception of the two-bond effective core in which certain types of three-bond integrals appear. Anyway, only a small portion of the whole integral list should be transformed and manipulated. On the other hand, since the zeroth-order results are already fairly correlated, the second-order PT contributions should give very accurate results. Numerical checking of these second-order formulae has not been accomplished yet, however.

In this section we aimed to overview a theory for the representation of local two-electron chemical bonds in a many-electron system. The above ideas became well known in the past few decades and several effective computational and interpretative schemes have been developed and applied on these grounds (see Surján 1989). The best known achievement is that of the PCILO method (Diner et al. 1969, Malrieu 1977) which was elaborated under semiempirical schemes though some ab initio PCILO calculations were also published (Daudey et al. 1974a, Otto & Ladik 1982). The basic idea of PCILO is to start from a fully localized SCF reference state and approach the exact solution by means of perturbation theory.

The limitations of this localized approach are obvious. Beside the fact that there are systems where a localized treatment is not adequate at all, the above theories are based on the assumption that the wave functions of different chemical fragments are expanded in disjunct subspaces of basis orbitals. This assumption is very advantageous practically, since it makes the mathematical formalism feasible and the computational strategy effective. Conceptually, however, it reflects a limitation of such type of theories.

One may hope that ab initio local approaches such as the SLG + PT treatment discussed in this chapter will represent a useful alternative to more standard delocalized methods. In some applications, the evaluation of higher-order terms of PT might be necessary. Assuming the convergence of the PT series, it approaches the same final result as other methods do. Computationally, the localized treatment is superior to standard techniques, and it represents practically the only possibility to perform sophisticated quantum-chemical calculations for extended but not strictly periodic systems. The significance of this perspective is evident in the field of molecules of biological interest.

17 Miscallenous Topics Related to Second Quantization

In this section we shall marginally discuss two selected topics of quantum chemistry emphasizing the points where second quantization is useful. First in Sect. 17.1 the second quantized representation of spin operators will be introduced and they will be applied to construct a model Hamiltonian. Section 17.2 will explain the connection between second quantization and the unitary group approach.

17.1 Spin Operators and Spin Hamiltonians

Though the idea of spin Hamiltonians as useful model Hamiltonians is quite old (Heisenberg 1926, 1928; Dirac 1929), they receive at present considerable interest in quantum chemistry and solid state physics (Malrieu et al. 1985, Sanchez-Marin et al. 1987). The basic point is to express the many-electron Hamiltonian in terms of spin operators which can be done if one is not interested in the spatial distribution of electrons. Using the language of the old valence bond method, this corresponds to the neglect of all ionic terms of the wave function, using merely the so-called covalent terms. Under this condition any wave function can be characterized by the distributions of spins, and one expects that the corresponding model Hamiltonian can be expressed through spin operators.

To see this, we begin with collecting some basic relations for spin operators. The spin has a vector-operator with three components:

$$\vec{S} = (S_x, S_y, S_z). \quad (17.1)$$

One usually defines the non-Hermitian combinations:

$$S^+ = S_x + iS_y \quad (17.2a)$$

$$S^- = S_x - iS_y. \quad (17.2b)$$

With respect to their action on the basic spin functions α and β , these operators are defined as:

$$S_z\alpha = \frac{1}{2}\alpha \quad (17.3a)$$

$$S_z\beta = -\frac{1}{2}\beta \quad (17.3b)$$

and

$$\begin{aligned} S^+ \alpha &= 0 & S^- \alpha &= \beta \\ S^+ \beta &= \alpha & S^- \beta &= 0. \end{aligned} \quad (17.4)$$

Since α and β are often referred to as spin up (\uparrow) and spin down (\downarrow) states, S^+ and S^- are called spin raising and lowering operators, respectively. Looking at Eqs. (17.4) one gets the impression that there is some analogy between creation/annihilation operators and the spin operators S^+/S^- . To work out the connection between spin operators and second quantization, one has to analyze some points in more detail. The spin operators obey the following commutation rules:

$$[S_x, S_y] = iS_z \quad (17.5)$$

and two other relations obtained by cyclic permutation of indices (x, y, z). Different components of spin do not commute, therefore they do not possess common eigenfunctions. Physical states are usually characterized by the eigenvalues of S_z and S^2 where:

$$S^2 = S_x^2 + S_y^2 + S_z^2 = S^+ S^- + S_z^2 - S_z = S^- S^+ + S_z^2 + S_z \quad (17.6)$$

which can easily be verified upon substitution of Eq. (17.2) and using the commutator of Eq. (17.5)

In a many-electron system one defines the sum of one-electron spin operators as:

$$S_z = \sum_{i=1}^N s_z(i) \quad (17.7a)$$

$$S^\pm = \sum_{i=1}^N s^\pm(i) \quad (17.7b)$$

while the S^2 operator can be expressed again by Eq. (17.6). As follows directly from Eqs. (17.5) and (17.6), operator S^2 commutes with S_z , so they have a common set of eigenfunctions. Further, if the Hamiltonian is spin independent (non-relativistic case), it commutes with both S^2 and S_z . Hence, eigenfunctions of the Hamiltonian are eigenfunctions of these spin operators, too. In constructing approximate wave functions, great care has to be taken to ensure this spin symmetry. For a good survey of the construction and use of spin functions, the reader is referred to the excellent monograph by Pauncz (1979).

Let us determine the second quantized representation of the above spin operators. (For more details, see Jørgensen and Simons 1981). Consider first S_z which is a sum of one-electron operators; thus, in terms of spin orbitals we can write:

$$S_z = \sum_{\mu\nu} \langle \mu | S_z | \nu \rangle a_\mu^+ a_\nu. \quad (17.8)$$

A more compact formula may be obtained by writing out the spatial- and spin-part of spin orbitals as $\mu = m\sigma$ ($\sigma = \alpha$ or β):

$$\begin{aligned} S_z &= \sum_{mn} \sum_{\sigma_1 \sigma_2} \langle m\sigma_1 | s_z | n\sigma_2 \rangle a_{m\sigma_1}^+ a_{n\sigma_2} \\ &= \sum_{mn} \langle m | n \rangle \sum_{\sigma_1 \sigma_2} \langle \sigma_1 | s_z | \sigma_2 \rangle a_{m\sigma_1}^+ a_{n\sigma_2}. \end{aligned}$$

Here we used the fact that the spin operator acts only on the spin functions. Orthogonalizing the spatial orbitals leads to:

$$S_z = \sum_{\sigma_1 \sigma_2} \langle \sigma_1 | s_z | \sigma_2 \rangle \sum_m a_{m\sigma_1}^+ a_{m\sigma_2}.$$

Using Eq. (17.3) and the orthogonality of the basis spin functions, we get for the Pauli spin matrix:

$$\langle \sigma_1 | s_z | \sigma_2 \rangle = \pm \frac{1}{2} \delta_{\sigma_1 \sigma_2}$$

where the sign is + for α (\uparrow) and - for β (\downarrow) states. Finally:

$$S_z = \frac{1}{2} \sum_m (a_{m\uparrow}^+ a_{m\uparrow} - a_{m\downarrow}^+ a_{m\downarrow}). \quad (17.9)$$

This is the second quantized form of the S_z operator. Introducing the particle number operators for α and β spin [cf. Sects. 3 and 9], Eq. (17.9) can be written as:

$$S_z = \frac{1}{2} (\hat{N}_\uparrow - \hat{N}_\downarrow).$$

Problem 17.1

Show that $[H, S_z] = 0$ using Eq. (17.9) and the second quantized form of the Hamiltonian.

Similar considerations can be invoked to find the representation of the raising and lowering spin operators:

$$\begin{aligned} S^+ &= \sum_{\mu\nu} \langle \mu | s^+ | \nu \rangle a_\mu^+ a_\nu = \sum_{\sigma_1 \sigma_2} \langle \sigma_1 | s^+ | \sigma_2 \rangle \sum_m a_{m\sigma_1}^+ a_{m\sigma_2} \\ &= \sum_m a_{m\uparrow}^+ a_{m\downarrow} \end{aligned} \quad (17.10)$$

where we used Eq. (17.4). In the same manner we find:

$$S^- = \sum_m a_{m\downarrow}^+ a_{m\uparrow}. \quad (17.11)$$

Problem 17.2

Show that (i) $[S^+, S_z] = -S^+$; (ii) $[S^-, S_z] = S^-$ using the second quantized form of these spin operators.

Having obtained the second quantized representation of fundamental spin operators, one may ask under what conditions can the second quantized Hamiltonian be expressed in terms of spin operators. These considerations serve as efficient tools for deriving model Hamiltonians.

One of the most important spin Hamiltonian was introduced by van Vleck (1932) and Dirac (1929) to describe magnetic systems:

$$\hat{H} = H^0 - 2 \sum_{i < j} J_{ij} \vec{s}_i \cdot \vec{s}_j \quad (17.12)$$

where H^0 is a constant while J_{ij} are called exchange parameters. The summation runs over all electrons. This Hamiltonian describes the model of magnetism studied by Heisenberg (1926, 1928), thus it is usually referred to as the Heisenberg Hamiltonian. The electrons in the Heisenberg model are supposed to be localized on different sites, and the J_{ij} integrals are kept only for neighboring sites. If all such integrals are assumed to have a uniform value, we have:

$$\hat{H} = H^0 - 2J \sum_{i < j} \vec{s}_i \cdot \vec{s}_j \quad (17.13)$$

which describes a ferromagnetic system for $J > 0$ and an antiferromagnetic one for $J < 0$.

Following Anderson (1963), the model Hamiltonian of Eq. (17.12) can be deduced easily by using second quantization. Let us consider a simple model for a system of N electrons described within a basis set of N orthonormal spatial orbitals. Each electron is assumed to be localized on one orbital (site). The many-body Hamiltonian of this model is:

$$H = \sum_{m,n=1}^N h_{mn} \sum_{\sigma} a_{m\sigma}^+ a_{n\sigma} + \frac{1}{2} \sum_{mnpr=1}^N [mn|pr] \sum_{\sigma_1 \sigma_2} a_{m\sigma_1}^+ a_{n\sigma_2}^+ a_{r\sigma_2} a_{p\sigma_1}. \quad (17.14)$$

In Anderson's model there is one electron on each site whose spin is either α or β . This can be expressed as:

$$\hat{N}_{n\uparrow} + \hat{N}_{n\downarrow} = 1. \quad (17.15)$$

Or, by using the definition of particle number operators:

$$a_{n\uparrow}^+ a_{n\uparrow} + a_{n\downarrow}^+ a_{n\downarrow} = 1. \quad (17.16)$$

We introduce the following spin operators:

$$\hat{s}_n^z = \frac{1}{2} (\hat{N}_{n\uparrow} - \hat{N}_{n\downarrow}) \quad (17.17a)$$

$$\hat{s}_n^+ = a_{n\uparrow}^+ a_{n\downarrow} \quad (17.17b)$$

$$\hat{s}_n^- = a_{n\downarrow}^+ a_{n\uparrow}. \quad (17.17c)$$

Clearly, the relations to Eqs. (17.9), (17.10), and (17.11) are given by:

$$\hat{S}_z = \sum_{n=1}^N s_n^z, \quad S^{\pm} = \sum_{n=1}^N s_n^{\pm}. \quad (17.18)$$

The one-electron part of the Hamiltonian can be approximated by keeping only diagonal elements h_{mm} . This corresponds to the neglect of charge transfer terms of type $a_m^+ a_n^-$ ($m \neq n$) which is consistent to the localization of electrons at the sites. Then the one-electron part H^1 reduces to:

$$H^1 = \sum_n h_{nn} (a_{n\uparrow}^+ a_{n\uparrow} + a_{n\downarrow}^+ a_{n\downarrow}) = \sum_n h_{nn} = \text{Tr } h \quad (17.19)$$

where Eq. (17.16) is used. Hence, in this simple model, H^1 contributes to the energy by a constant which is equal to the trace of matrix h .

Let us analyze the interaction part of the Hamiltonian of Eq. (17.14) denoted by H^2 . Neglecting again the charge transfer terms, we write:

$$\begin{aligned} H^2 &= \frac{1}{2} \sum_{mnpr} [mn|pr] \sum_{\sigma_1 \sigma_2} a_{m\sigma_1}^+ a_{n\sigma_2}^+ a_{r\sigma_2} a_{p\sigma_1} \{\delta_{mp} \delta_{nr} + \delta_{mr} \delta_{np}\} \\ &= \frac{1}{2} \sum_{mn} [mn|mn] \sum_{\sigma_1 \sigma_2} a_{m\sigma_1}^+ a_{n\sigma_2}^+ a_{n\sigma_2} a_{m\sigma_1} \\ &\quad + \frac{1}{2} \sum_{mn} [mn|nm] \sum_{\sigma_1 \sigma_2} a_{m\sigma_1}^+ a_{n\sigma_2}^+ a_{m\sigma_2} a_{n\sigma_1} \end{aligned} \quad (17.20)$$

where the Kronecker δ -s express the absence of charge transfer. At the first term on the right-hand side, the operator string can be expressed in terms of particle number operators:

$$H^2 = \frac{1}{2} \sum_{m \neq n} [mn|mn] \left(\sum_{\sigma_2} \hat{N}_{m\sigma_1} \right) \left(\sum_{\sigma_2} \hat{N}_{n\sigma_2} \right) + \hat{V} \quad (17.21)$$

where V denotes the second (exchange) term of H^2 in Eq. (17.20). Using the localization condition of Eq. (17.15), the first (Coulomb-like) term becomes a constant and we have the following simplified Hamiltonian:

$$\hat{H} = C + \hat{V} \quad (17.22)$$

where the value of the constant C is determined from Eqs. (17.19) and (17.21):

$$C = \sum_m h_{mm} + \frac{1}{2} \sum_{mn} [mn|mn] \quad (17.23)$$

while \hat{V} is the exchange Hamiltonian:

$$\hat{V} = \frac{1}{2} \sum_{m \neq n} [mn|nm] \sum_{\sigma_1 \sigma_2} a_{m\sigma_1}^+ a_{n\sigma_2}^+ a_{m\sigma_2} a_{n\sigma_1}. \quad (17.24)$$

The $m = n$ case can be excluded since one cannot annihilate two electrons form an orbital. Using the second quantized form of spin operators, this exchange Hamiltonian can be expressed as:

$$\hat{V} = -\frac{1}{2} \sum_{m \neq n} J_{mn} (s_m^+ s_n^- + s_m^- s_n^+ + \hat{N}_{m\uparrow} \hat{N}_{n\uparrow} + \hat{N}_{m\downarrow} \hat{N}_{n\downarrow}) \quad (17.25)$$

where the exchange integral:

$$J_{mn} = [mn|nm]$$

is introduced.¹ This result can be further transformed by using the identity:

$$s_m^+ s_n^- + s_n^- s_m^+ = 2 \vec{s}_m \cdot \vec{s}_n - 2 s_m^z s_n^z,$$

by which one obtains:

$$\hat{V} = - \sum_{m \neq n} J_{mn} \vec{s}_m \cdot \vec{s}_n - \frac{1}{2} \sum_{m \neq n} J_{mn} [N_{m\uparrow} \hat{N}_{n\uparrow} + \hat{N}_{m\downarrow} \hat{N}_{n\downarrow} - 2 s_m^z s_n^z].$$

The terms in square brackets can be simplified by substituting the s^z spin operator from Eq. (17.17a). In fact, by using Eq. (17.15) these terms reduce to a constant of 1/2. Finally one finds:

$$\hat{V} = - \sum_{m \neq n} J_{mn} \left(\vec{s}_m \cdot \vec{s}_n + \frac{1}{4} \right) \quad (17.26)$$

while the total Hamiltonian is:

$$H = H^0 - \sum_{m \neq n} J_{mn} \vec{s}_m \cdot \vec{s}_n \quad (17.27)$$

with:

$$H^0 = \sum_m h_{mm} + \sum_{m < n} \left([mn|mn] - \frac{1}{2} [mn|nm] \right).$$

The derivation of the Heisenberg spin Hamiltonian of Eq. (17.12) is thus completed.

Heisenberg Hamiltonians are most useful in studying magnetic phenomena. Since the exchange parameters J_{mn} in the above-studied model are all positive numbers, the spin Hamiltonian of Eq. (17.27) favors parallel spin states; thus it describes a model of ferromagnetism. A different model, leading to negative J values corresponding to an antiferromagnetic coupling has also been studied by Anderson (1963). Mayer and Angelov (1984, 1985) discussed antiferromagnetic systems in detail. Recently, Malrieu and coworkers (Malrieu et al. 1985, Said et al. 1984, Sanchez-Marin et al. 1987) applied Heisenberg-type Hamiltonians in a series of papers to treat ground- and excited-state properties of molecular systems.

In order to establish a connection between the Heisenberg Hamiltonian and conventional molecular Hamiltonians, Coope (1967) had an opposite look on this problem. He applied a nonlinear transformation of the spin operators in the Heisenberg Hamiltonian leading a creation/annihilation operators obeying true fermion anticommutation rules. He showed that the transformed Hamiltonian resembled very much the PPP Hamiltonian of the system.

¹ To avoid any confusion, we note that capital J is widely used to denote exchange integrals in the solid state literature, in contrast to the usual quantum-chemical notation where K denotes the exchange while J stands for Coulomb integrals.

17.2 Unitary Group Approach

Among post-Hartree-Fock calculations, one of the most widely applied method is the configuration interaction (CI) technique. A central problem in CI is to elaborate an efficient way for evaluating the matrix elements of the Hamiltonian between (preferably spin adapted) configurations. An indeed successful method for constructing such matrix elements is offered by the unitary group approach. Besides of original expositions (Paldus 1974, 1976; Shavitt 1977, 1978; Hegarty & Robb 1979), several review articles or book chapters (Pauncz 1979, Hinze 1981, Matsen and Pauncz 1986) are available on this subject. Here we shall point out merely the connection between second quantization and the unitary group.

First of all, we show that the second quantized many-body Hamiltonian is invariant against a unitary transformation of the orbital basis. The proof is trivial; we work it out on the example of the one-electron part of the Hamiltonian. Given a set of orthonormalized functions $\{\chi_\mu\}$, the one-electron Hamiltonian is written as:

$$H^1 = \sum_{\mu\nu} \langle \chi_\mu | \hat{h} | \chi_\nu \rangle \chi_\mu^+ \chi_\nu^- . \quad (17.28)$$

Consider the unitary transformation:

$$\chi_\mu = \sum_i U_{i\mu} \phi_i . \quad (17.29)$$

The fermion operators are clearly transformed as:

$$\chi_\mu^+ = \sum_i U_{i\mu} \phi_i^+ \quad (17.30a)$$

$$\chi_\mu^- = \sum_i U_{i\mu}^* \phi_i^- = \sum_i U_{\mu i}^\dagger \phi_i^- \quad (17.30b)$$

where the asterisk (*) denotes complex conjugation while the dagger (\dagger) stands for adjoint.² Substitution of this transformation into the Hamiltonian of Eq. (17.28) leads to:

$$H^1 = \sum_{\mu\nu} \sum_{ijkl} U_{\mu i}^\dagger U_{j\nu} U_{k\mu} U_{l\nu}^\dagger \langle \phi_i | \hat{h} | \phi_j \rangle \phi_k^+ \phi_l^-$$

which, summing up over indices μ and ν reduces to:

$$H^1 = \sum_{ij} \langle \phi_i | \hat{h} | \phi_j \rangle \phi_i^+ \phi_j^- .$$

This is the same form as that of untransformed Hamiltonian of Eq. (17.28), which means that H^1 is invariant against the transformation U .

² U_{kl}^\dagger is a short-hand notation for $(U^\dagger)_{kl}$

Problem 17.3

Prove that the two-electron part of the second quantized Hamiltonian is also invariant to the unitary transformation of Eqs. (17.29–30).

As shown in Sect. 16, the fermion anticommutation rules are also invariant, thus unitary transformations are “canonical”.

It can be seen easily that the unitary transformation described by $n \times n$ unitary matrices U form a group. This holds because:

- (1) The product of two unitary matrices is also a unitary matrix;
- (2) The unit element of the group is given by the unit matrix δ_{ik} which is itself unitary;
- (3) The inverse of a unitary matrix U always exists and it is given by U^\dagger ;
- (4) The associativity holds since $U_1(U_2U_3) \equiv (U_1U_2)U_3$ for the matrix multiplication.

These are the defining conditions for a set to be a group. The set of n by n unitary matrices is called the unitary group $U(n)$. The mathematical theory of the unitary group and its representations is well elaborated (Hamermesh 1962; Gelfand & Tsetlin 1967). The important concept of the so-called infinitesimal generators of $U(n)$ will be discussed below with less rigor.

The elements of the unitary group are continuous functions of a certain number of parameters. The number of independent parameters for $U(n)$ is n^2 . This can be seen by writing matrix U in the exponential form:

$$U = e^{iA} \quad (17.31)$$

where A is a complex Hermitian matrix³ which has n^2 independent elements⁴. One can say that the complex $n \times n$ Hermitian matrices A generate the unitary matrices via Eq. (17.31). The infinitesimal generators of a group are defined as the derivatives of the group elements with respect to the independent parameters, at the parameter values corresponding to the unit element. Clearly, one has n^2 such infinitesimal generators for $U(n)$. Matrix A can be formally expressed in terms of the basic matrix unit e_{jk} as:

$$A = \sum_{jk} A_{jk} e_{jk} \quad (17.32)$$

where the numbers A_{jk} are the elements of matrix A while e_{jk} is a matrix having all zero elements except that in the j -th row and k -th column which is 1. The

³ Any such matrix is clearly unitary since $U^\dagger = e^{-iA} = U^{-1}$.

⁴ This is trivial because $A \equiv \text{Re}(A) + i \text{Im}(A)$; in order to A be Hermitian $\text{Re}(A)$ must be symmetric thus having $n(n + 1)/2$ independent elements, while $\text{Im}(A)$ must be anti-symmetric possessing $n(n - 1)/2$ independent elements which is n^2 altogether.

complex numbers A_{jk} (for which $A_{kj} = A_{jk}^*$) are the independent parameters of the unitary matrices. When all $A_{rs} = 0$, one gets the unit matrix, hence the infinitesimal generators of $U(n)$ are derived from the formula:

$$E_{rs} = -i \frac{\partial U}{\partial A_{rs}} \Big|_{A_{jk}=0}$$

where U stands for a general element of the group $U(n)$. Using Eqs. (17.31) and (17.32) one gets:

$$E_{rs} = -i \frac{\partial}{\partial A_{rs}} \left(i \sum_{jk} A_{jk} e_{jk} \right) = e_{rs}.$$

One can see that the basic matrix units can be considered as the infinitesimal generators of the unitary group. A more precise derivation is done by considering a set of one-parameter subgroups of $U(n)$ (see, e.g. Pauncz 1979).

From their definition, it follows easily that the basic matrix units e_{mn} , hence the infinitesimal generators E_{mn} too, obey the following commutation rules:

$$[E_{mn}, E_{rs}] = \delta_{rn} E_{ms} - \delta_{ms} E_{rn}. \quad (17.33)$$

That is, the infinitesimal generators of $U(n)$ form a closed set for the commutation as an operation. One says they follow a *Lie algebra*.

We shall show now that the second quantized Hamiltonian can be expressed in terms of certain operators which follow the same Lie-algebraic structure. Let us start with the Hamiltonian written down in terms of spatial orbitals:

$$\hat{H} = \sum_{mn} \sum_{\sigma} h_{mn} a_{m\sigma}^+ a_{n\sigma} - \frac{1}{2} \sum_{mnrs} \sum_{\sigma_1 \sigma_2} [mn|rs] a_{m\sigma_1}^+ a_{n\sigma_2}^+ a_{r\sigma_1} a_{s\sigma_2}. \quad (17.34)$$

Introducing a transposition in the two-electron operator string one may write:

$$\begin{aligned} \hat{H} = & \sum_{mn} \sum_{\sigma} h_{mn} a_{m\sigma}^+ a_{n\sigma} \\ & + \frac{1}{2} \sum_{mnrs} \sum_{\sigma_1 \sigma_2} [mn|rs] (a_{m\sigma_1}^+ a_{r\sigma_1} a_{n\sigma_2}^+ a_{s\sigma_2} - \delta_{rn} \delta_{\sigma_1 \sigma_2} a_{m\sigma_1}^+ a_{s\sigma_2}). \end{aligned}$$

Let us introduce now the following notation:

$$\hat{E}_{mn} = \sum_{\sigma} a_{m\sigma}^+ a_{n\sigma} \quad (17.35)$$

which gives us a spinless shift-operator having the property:

$$\hat{E}_{mn}^\dagger = \sum_{\sigma} a_{n\sigma}^+ a_{m\sigma} = \hat{E}_{nm}.$$

The Hamiltonian can be expressed in terms of these operators as:

$$\hat{H} = \sum_{mn} h_{mn} \hat{E}_{mn} + \frac{1}{2} \sum_{mnrs} [mn|rs] (\hat{E}_{mr} \hat{E}_{ns} - \delta_{rn} \hat{E}_{ms}). \quad (17.36)$$

It is easy to check the commutation properties of the shift operators:

$$\hat{E}_{mn} \hat{E}_{rs} = \sum_{\sigma_1 \sigma_2} a_{m\sigma_1}^+ a_{n\sigma_1} a_{r\sigma_2}^+ a_{s\sigma_2} \quad (17.37)$$

while:

$$\begin{aligned} \hat{E}_{rs} \hat{E}_{mn} &= \sum_{\sigma_1 \sigma_2} a_{r\sigma_2}^+ a_{s\sigma_2} a_{m\sigma_1}^+ a_{n\sigma_1} \\ &= \sum_{\sigma_1 \sigma_2} (a_{m\sigma_1}^+ a_{n\sigma_1} a_{r\sigma_2}^+ a_{s\sigma_2} + \delta_{\sigma_1 \sigma_2} (\delta_{ms} a_{r\sigma_2}^+ a_{n\sigma_1} - \delta_{nr} a_{m\sigma_1}^+ a_{s\sigma_2})). \end{aligned}$$

Substituting this equation from Eq. (17.37) one finds:

$$\begin{aligned} [\hat{E}_{mn}, \hat{E}_{rs}] &= \sum_{\sigma} (-a_{r\sigma}^+ a_{n\sigma} \delta_{ms} + a_{m\sigma}^+ a_{s\sigma} \delta_{nr}) \\ &= \delta_{nr} \hat{E}_{ms} - \delta_{ms} \hat{E}_{rn} \end{aligned}$$

which is exactly the same rule as that in Eq. (17.33). This result shows the inherent connection between the theory of the unitary group and the many-body problem.

A very useful achievement in group theory is that the representation matrices of the infinitesimal generators E_{mn} are available for the irreducible representations of the unitary group. We have seen that the unitary group is a symmetry group of the second quantized Hamiltonian, thus the irreducible representations determine appropriate basis vectors. Matrix elements of the Hamiltonian entering, e.g., the CI problem are therefore preferably calculated in the basis of the irreducible representations of the unitary group. All the more so, because this choice also takes care of spin adaptation automatically reflecting the intimate connection of the unitary group approach with spin-free quantum chemistry (Matsen et al. 1977, Wormer & Paldus 1979, Pauncz 1979, Matsen & Nelin 1981).

The matrix elements of the Hamiltonian of Eq. (17.36) between states $\langle K |$ and $| L \rangle$ are given by:

$$\begin{aligned} \hat{H}_{KL} &= \sum_m h_{mn} \langle K | \hat{E}_{mn} | L \rangle \\ &+ \frac{1}{2} \sum_{mnrs} [mn|rs] \left\{ \sum_j \langle K | \hat{E}_{mr} | J \rangle \langle J | \hat{E}_{ns} | L \rangle - \delta_{rn} \langle K | \hat{E}_{ms} | L \rangle \right\}. \end{aligned}$$

Evaluation of the coupling constants $\langle K | E_{mn} | L \rangle$ is done by a purely algebraic procedure using the representation theory of the unitary group. The irreducible representations are determined by the number of electrons and spin quantum numbers, while the rest of quantum chemistry enters the problem through the list of integrals h_{mn} and $[mn|rs]$. For some recent publications in this field see, e.g. Gould & Chandler (1984), Pickup & Mukhopadhyay (1984), Karwowski et al. (1986), Lin & Cao (1987).

18 Problem Solutions

Problem 2.1

- (i) The wave function in question is just a two-electron Slater determinant with the proper normalization factor of $1/\sqrt{N!} = 1/\sqrt{2}$. Thus, in the second quantized notation:

$$D = a_2^+ a_1^+ |vac\rangle$$

or in the particle number representation:

$$D = \overset{1}{\underset{2}{|}} \underset{0}{\dots} 0 \rangle.$$

- (ii) Wave function Ψ is a three-electron Slater determinant for which the normalization factor is $1/\sqrt{N!} = 1/\sqrt{6}$. Thus:

$$\Psi = a_3^+ a_2^+ a_1^+ |vac\rangle$$

or:

$$\Psi = \overset{1}{\underset{2}{\underset{3}{|}}} \underset{0}{\dots} 0 \rangle.$$

- (iii) Wave function Φ is a linear combination of determinants. The coefficients C_1 and C_2 contain also the normalization factors, thus:

$$\begin{aligned}\Phi &= \sqrt{2}C_1\varphi_2^+\varphi_1^+|vac\rangle + \sqrt{2}C_2\psi_2^+\varphi_1^+|vac\rangle \\ &= \sqrt{2}(C_1\varphi_2^+ + C_2\psi_2^+)\varphi_1^+|vac\rangle\end{aligned}$$

where it was convenient to use the Longuet-Higgins notations. Owing to the use of different sets of orbitals, the notation of particle number representation is not very descriptive.

Problem 2.2

We have to distinguish the various cases of coincidences among indices i, j , and k .

- (a) If $k = j$, the result is zero since two electrons cannot be created on the same spinorbital.
(b) For $k \neq j$, we have the following case:
(b.1) $i \neq k$ and $i \neq j$: the result is zero since a_i cannot annihilate.
(b.2) $i \neq k$ and $i = j$:

$$a_i a_k^+ a_i^+ |vac\rangle = -a_k^+ a_i a_i^+ |vac\rangle = -a_k^+ |vac\rangle \rightarrow -|k\rangle.$$

(b.3) $i = k$ and $i \neq j$:

$$a_i a_k^+ a_i^+ |vac\rangle = a_i^+ a_i a_k^+ |vac\rangle = a_j^+ |vac\rangle \rightarrow |j\rangle.$$

Problem 3.1

This is trivial if $i = k$, since any operator commutes with itself. If $i \neq k$, one can write:

$$[\hat{N}_i, \hat{N}_k] = [a_i^+ a_i a_k^+ a_k - a_k^+ a_k a_i^+ a_i] = 0,$$

since the second term can be brought to the form of the first term by an even number of transpositions. It follows also that:

$$[\hat{N}_i, \hat{N}] = \sum_i [\hat{N}_i, \hat{N}] = 0$$

for the operator of the total number of particles \hat{N} .

Problem 5.1

Our task is very simple since all strings can be brought to the standard form of Eq. (5.7) by simple transpositions. The sign of the expression is determined by the parity of the transposition.

- (i) $a_1 a_2 a_3 a_3^+ a_2^+ a_1^+ = a_1 a_3^+ a_3 a_2 a_2^+ a_1^+ = a_3 a_3^+ a_2 a_2^+ a_1 a_1^+$, where we did even number of transpositions. The resulting sign is therefore +, the value of the matrix element is 1.
- (ii) Here two transpositions are required to bring the operator string into the form of the string in (i), namely, to shift a_1 to the beginning of the string. Thus, the resulting sign is again +.
- (iii) $a_3 a_4 a_3^+ a_4^+ a_1 a_2 a_2^+ a_1^+ = -a_3 a_3^+ a_4 a_4^+ a_2 a_2^+ a_1 a_1^+$ because of the odd number of transpositions. The resulting sign is -, the expectation value of the string is -1.

Problem 5.2

The matrix element is zero if any of the creation operators λ^+ , σ^+ and τ^+ coincides with another one. The same holds for the annihilation operators μ^- , v^- , and ρ^- , too. If all these indices are different, we should investigate the possible coincidences between the creation and annihilation operators. We have the following pairings:

$$\langle vac | \underbrace{\mu^- v^- \rho^-}_{\text{pair}} \lambda^+ \sigma^+ \tau^+ | vac \rangle \quad (\text{sign: } +)$$

$$\langle vac | \underbrace{\mu^- v^- \rho^-}_{\text{pair}} \lambda^+ \sigma^+ \tau^+ | vac \rangle \quad (\text{sign: } -)$$

$$\langle vac | \underbrace{\mu^- v^- \rho^-}_{\text{pair}} \lambda^+ \sigma^+ \tau^+ | vac \rangle \quad (\text{sign: } -)$$

$$\langle \text{vac} | \mu^- v^- \rho^- \lambda^+ \sigma^+ \tau^+ | \text{vac} \rangle \quad (\text{sign: } +)$$

$$\langle \text{vac} | \mu^- v^- \rho^- \lambda^+ \sigma^+ \tau^+ | \text{vac} \rangle \quad (\text{sign: } +)$$

$$\langle \text{vac} | \mu^- v^- \rho^- \lambda^+ \sigma^+ \tau^+ | \text{vac} \rangle \quad (\text{sign: } -).$$

It is obvious that an even number of transpositions are required in the 1st, 4th, and 5th terms to bring the to the form of Eq. (5.7) which can be evaluated directly. An odd number of transpositions are required in the rest of terms. This determines the sign of each term. Accordingly, the value of the matrix elements will be:

$$\begin{aligned} \langle \text{vac} | \mu^- v^- \rho^- \lambda^+ \sigma^+ \tau^+ | \text{vac} \rangle &= \delta_{\mu\tau} \delta_{v\sigma} \delta_{\rho\lambda} - \delta_{\mu\sigma} \delta_{v\tau} \delta_{\rho\lambda} \\ &\quad - \delta_{\mu\tau} \delta_{v\lambda} \delta_{\rho\sigma} + \delta_{\mu\lambda} \delta_{v\tau} \delta_{\rho\sigma} \\ &\quad + \delta_{\mu\tau} \delta_{v\sigma} \delta_{\rho\lambda} - \delta_{\mu\sigma} \delta_{v\tau} \delta_{\rho\lambda}. \end{aligned}$$

As a rule of thumb, we may notice that the sign of each term is determined by the parity of the number of crossings of the lines connecting the creation and annihilation operators.

Problem 5.3

The proof is trivial. Consider a cyclic permutation of the annihilation operators, for example:

$$(\mu^- v^- \rho^-) \rightarrow (v^- \rho^- \mu^-) \equiv -(v^- \mu^- \rho^-) \equiv +(\mu^- v^- \rho^-).$$

The same holds for the string of creation operators ($\lambda^+ \sigma^+ \tau^+$), too. In general, this result is always true if the string consists of an odd number of anticommuting operators. If we have an even number of anticommutation operators, a cyclic permutation will change its sign.

Problem 5.4

Let us investigate first the commutator $[b_i^+, b_k^+]$. Trivially, this is zero if $i \neq k$. If $i = k$, we have:

$$[b_i^+, b_i^+] = \begin{cases} [a_i^+, a_i^+] = 0 & \text{if } i \text{ is virtual} \\ [a_i, a_i] = 0 & \text{if } i \text{ is occupied.} \end{cases}$$

We conclude:

$$[b_i^+, b_k^+] = 0.$$

The same applies to the commutator:

$$[b_i, b_k] = 0.$$

Check now $[b_i^+, b_k]$. Again, it clearly vanishes if $i \neq k$. For the diagonal case we

can write:

$$[b_i^+, b_i] = \begin{cases} [a_i^+, a_i] = 1 & \text{if } i \text{ is virtual} \\ [a_i, a_i^+] = 1 & \text{if } i \text{ is occupied.} \end{cases}$$

Summarizing:

$$[b_i^+, b_k] = \delta_{ik}, \quad \text{Q.E.D.}$$

Problem 5.5

This is rather tedious unless one introduces the Fermi vacuum as:

$$\begin{aligned} \langle HF | &= \langle vac | \psi_3^- \psi_2^- \psi_1^- \\ | HF \rangle &= \psi_1^+ \psi_2^+ \psi_3^+ | vac \rangle. \end{aligned}$$

By which the matrix element can be written as:

$$\langle HF | \psi_\mu^+ \psi_\nu^+ \psi_\sigma^- \psi_\lambda^- | HF \rangle = n_\sigma n_\lambda (\delta_{\mu\lambda} \delta_{\nu\sigma} - \delta_{\mu\sigma} \delta_{\nu\lambda})$$

where $n_\sigma = 1$ if $\sigma \in \{1, 2, 3\}$ and $n_\sigma = 0$ otherwise.

Problem 5.6

A singly excited state $|\Psi_1\rangle$ is obtained from $|HF\rangle$ by annihilating an electron on an occupied orbital and creating one on a virtual level:

$$|\Psi_1\rangle = a_{k^*}^+ a_i |HF\rangle$$

which describes the $i \rightarrow k^*$ excitation (note that it is not a pure spin state). The condition of orthogonality:

$$\langle HF | \Psi_1 \rangle = \langle HF | a_{k^*}^+ a_i | HF \rangle = 0$$

is trivially fulfilled, since $k^* \neq i$.

Problem 6.1

This results leading to the corresponding Slater rules are well known. Here, the second quantized derivation will be worked out in some detail.

(i) If $\Phi_K = \Phi_L$, one has:

$$\begin{aligned} \langle \Phi_K | \sum_{i < j} \hat{g}_{ij} | \phi_L \rangle &= \frac{1}{2} \sum_{\mu\nu\lambda\sigma} g_{\mu\nu\lambda\sigma} \langle \Phi_K | \mu^+ \nu^+ \sigma^- \lambda^- | \Phi_L \rangle \\ &= \frac{1}{2} \sum_{\mu\nu\lambda\sigma} (g_{\mu\nu\mu\nu} - g_{\mu\nu\nu\mu}) \end{aligned}$$

where $g_{\mu\nu\lambda\sigma}$ stands for the matrix element of the two-electron operator [cf. Eqs. (1.10–11)].

(ii) If $\Phi_K = \Phi_L$ differ in one spinorbital, the latter can be rewritten as:

$$|\Psi_L\rangle = \rho^+ \tau^- |\Phi_K\rangle$$

where orbital τ is substituted by ρ . Then:

$$\begin{aligned}\langle \Phi_K | \sum_{i < j} \hat{g}_{ij} | \phi_L \rangle &= \frac{1}{2} \sum_{\mu\nu\lambda\sigma} g_{\mu\nu\lambda\sigma} \langle \Phi_K | \mu^+ v^+ \sigma^- \lambda^- \rho^+ \tau^- | \Phi_K \rangle \\ &= \frac{1}{2} \sum_{\mu\nu\lambda\sigma} g_{\mu\nu\lambda\sigma} [\delta_{\lambda\rho} (\delta_{v\sigma} \delta_{\mu\tau} - \delta_{v\tau} \delta_{\mu\sigma}) \\ &\quad - \delta_{\sigma\rho} (\delta_{v\lambda} \delta_{\mu\tau} - \delta_{v\tau} \delta_{\mu\lambda})] \\ &= \sum_{\mu} [g_{\mu\tau\mu\rho} - g_{\mu\tau\rho\mu}]\end{aligned}$$

where the symmetry property $g_{\mu\nu\lambda\sigma} = g_{\nu\mu\sigma\lambda}$ is utilized.

(iii) If $\Phi_K = \Phi_L$ differ in two spinorbitals, one may write:

$$|\Psi_L\rangle = \rho^+ \eta^+ \tau^- \vartheta^- |\Phi_K\rangle$$

where the labels ρ, η, τ , and ϑ do not coincide. The matrix element is given by:

$$\langle \Phi_K | \sum_{i < j} \hat{g}_{ij} | \phi_L \rangle = \frac{1}{2} \sum_{\mu\nu\lambda\sigma} g_{\mu\nu\lambda\sigma} \langle \Phi_K | \mu^+ v^+ \sigma^- \lambda^- \rho^+ \eta^+ \tau^- \vartheta^- | \Phi_K \rangle.$$

Collecting all possible pairings, this expression reduces to:

$$\begin{aligned}\langle \Phi_K | \sum_{i < j} \hat{g}_{ij} | \phi_L \rangle &= \frac{1}{2} (g_{\vartheta\tau\rho\eta} - g_{\tau\vartheta\rho\eta} - g_{\vartheta\tau\eta\rho} + g_{\tau\vartheta\eta\rho}) \\ &= g_{\vartheta\tau\rho\eta} - g_{\vartheta\tau\eta\rho}.\end{aligned}$$

(iv) Finally, if $\Phi_K = \Phi_L$ differ in three or more spinorbitals, the result is zero because the two annihilation operators of \hat{g} (σ^- and λ^-) cannot compensate three or more creation operators expressing the difference between Φ_K and Φ_L .

Problem 7.1

Elements of the first-order density matrix are defined as:

$$P_{v\mu} = \langle \Psi | \mu^+ v^- | \Psi \rangle.$$

Substituting Ψ :

$$\begin{aligned}P_{v\mu} &= C_0^2 \langle HF | \mu^+ v^- | HF \rangle \\ &\quad + C_0 C_2 \langle HF | \mu^+ v^- b^+ a^+ j^- i^- | HF \rangle \\ &\quad + C_2 C_0 \langle HF | i^+ j^+ a^- b^- \mu^+ v^- | HF \rangle \\ &\quad + C_2^2 \langle HF | i^+ j^+ a^- b^- \mu^+ v^- b^+ a^+ j^- i^- | HF \rangle.\end{aligned}$$

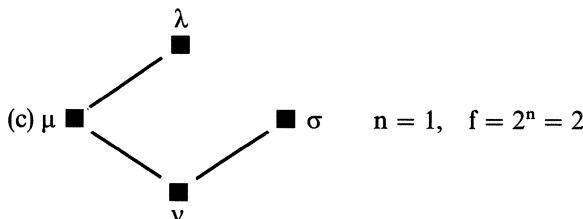
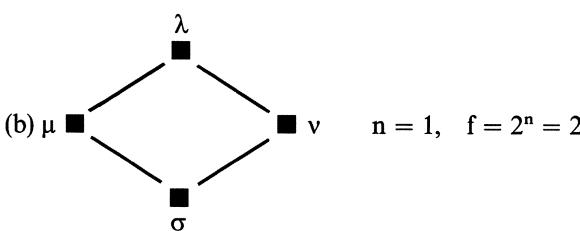
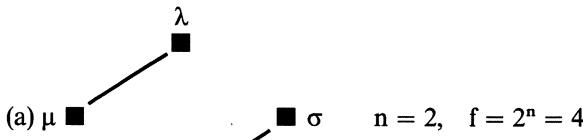
The second term is clearly zero since two virtuals are created (a^+ and b^+) while at most one can be annihilated by v^- . For a similar reason, the third term is zero, too. Collecting all possible pairings in the first and the last terms, a straightforward algebra gives:

$$P_{\mu\nu} = \delta_{\mu\nu} [n_v(C_0^2 + C_2^2(1 - \delta_{vi})(1 - \delta_{vj})) + C_2^2(\delta_{va} + \delta_{vb})].$$

Here n_v is 1 if v is occupied in $|HF\rangle$ and zero otherwise. Note that matrix P remained diagonal, that is the MOs in question are natural orbitals for this simple two-configurational wave function Ψ . This property does not hold if a linear combination of doubly excited configurations is considered.

Problem 9.1

In each case, four dots are put down representing indices μ, v, λ, σ . Connecting the indices of spin coincidences, we get



where f is the corresponding weighting factor.

Problem 12.1

Let Ψ_K^o and Ψ_L^o be two singly excited states, with $K = j \rightarrow l^*$ and $L = i \rightarrow k^*$. It is to be shown that:

$$\langle \Psi_K^o | \Psi_L^o \rangle = \delta_{KL}.$$

Indeed:

$$\langle \Psi_K^o | \Psi_L^o \rangle = \langle HF | \overbrace{\psi_j^+ \psi_{l^*}^- \psi_{k^*}^+ \psi_i^-}^{[]} | HF \rangle = \delta_{ij} \delta_{k^* l^*} = \delta_{KL} \quad Q.E.D.$$

Orthogonality of $\langle HF |$ and $|\Psi_K^o \rangle$ can be shown in the same manner.

Problem 12.2

The numerator of Eq. (12.25) is written as:

$$\begin{aligned} |[pq||sr]|^2 &= [pq||sr][pq||sr] \\ &= ([pq|sr] - [pq|rs])([pq|sr] - [pq|rs]) \\ &= [pq|sr][pq|sr] - [pq|rs][pq|sr] \\ &\quad - [pq|sr][pq|rs] + [pq|rs][pq|rs]. \end{aligned}$$

Substituting this into Eq. (12.25) and applying an interchange of the summation labels $r \leftrightarrow s$ in the first term gives Eq. (12.26).

Problem 12.3

As seems from Eq. (12.10c), calculation of $E^{(3)}$ involves the evaluation of the quantities W_{OK} , W_{KL} , and W_{LO} where O labels the ground state (*Fermi vacuum*) while K and L denote excited states. The latter can be, in principle, singly, doubly, triply, etc. excited configurations, relative to $|HF\rangle$. Evaluation of W_{OK} was done in the text when calculation $E^{(2)}$; it was shown that only doubly excited states contribute. In $E^{(3)}$ both W_{OK} and W_{LO} are present, thus the matrix element of the new type, W_{KL} , should also be calculated only between doubly excited states. Let:

$$\begin{aligned} K &= \begin{cases} i \rightarrow p^* \\ j \rightarrow q^* \end{cases} \\ L &= \begin{cases} k \rightarrow r^* \\ l \rightarrow s^* \end{cases} \end{aligned}$$

be two doubly excited states, then W_{KL} is written as:

$$W_{KL} = \langle HF | i^+ j^+ p^{*-} q^{*-} \hat{W} s^{*+} r^{*+} l^- k^- | HF \rangle.$$

In the perturbing operator \hat{W} only the two-electron term contributes, since the matrix elements of one-electron terms are zero. The two-electron term \hat{W}_2 can be rewritten in a more compact manner as:

$$\hat{W}_2 = \frac{1}{2} \sum_{\mu\nu\lambda\sigma} [\mu\nu|\lambda\sigma] \mu^+ v^+ \sigma^- \lambda^- \equiv \sum_{\substack{\mu \leq v \\ \lambda < \sigma}} [\mu\nu|\lambda\sigma] \mu^+ v^+ \sigma^- \lambda^-.$$

This can easily be verified by decoupling the summation according to the restrictions $\mu < v$, $\mu > v$, $\lambda < \sigma$, $\lambda > \sigma$, by the appropriate interchange of the summation labels and utilizing antisymmetry. This form of \hat{W}_2 is useful because it leads to immediately to antisymmetrized integrals. Substituting \hat{W}_2 , the matrix element W_{KL} can be evaluated by collecting all possible pairings in the operator string. Details of this derivation are not reported here; the reader may do this by applying the rules given in the text and may show that the final result for $E^{(3)}$ is:

$$E^{(3)} = E_A^{(3)} + E_B^{(3)} + E_C^{(3)}$$

where

$$\begin{aligned} E_A^{(3)} &= \sum_{\substack{abc \\ rst}} \frac{(2[ab|rs] - [ab|sr])(2[bc|st] - [bs|ct])(2[ac|rt] - [ac|tr]) - 3[ab|sr][bs|ct][ac|tr]}{(\epsilon_r + \epsilon_s - \epsilon_a - \epsilon_b)(\epsilon_r + \epsilon_t - \epsilon_a - \epsilon_c)} \\ E_B^{(3)} &= \sum_{\substack{ab \\ rsut}} \frac{[ab|rs][rs|tu](2[ab|tu] - [ab|ut])}{(\epsilon_r + \epsilon_s - \epsilon_a - \epsilon_b)(\epsilon_t + \epsilon_u - \epsilon_a - \epsilon_b)} \\ E_C^{(3)} &= \sum_{\substack{abcd \\ rs}} \frac{[ab|rs][ab|cd](2[cd|rs] - [dc|rs])}{(\epsilon_r + \epsilon_s - \epsilon_a - \epsilon_b)(\epsilon_r + \epsilon_s - \epsilon_c - \epsilon_d)} \end{aligned}$$

in terms of spatial orbitals. Here a, b, c and d label occupied orbitals while r, s, t and u stand for virtual ones. This result is consistent to that derived by means of the diagrammatic technique.

Problem 13.1

The square norm is written as:

$$\mathcal{N}^2 = \langle \text{vac} | \psi_1^- \psi_2^- \dots \psi_N^- \psi_N^+ \dots \psi_2^+ \psi_1^+ | \text{vac} \rangle$$

where:

$$\psi_i^- \psi_k^+ + \psi_k^+ \psi_i^- = S_{ik}.$$

Performing an interchange of ψ_N^- and ψ_N^+ we get:

$$\mathcal{N}^2 = S_{NN} D_{NN} - \langle \text{vac} | \psi_1^- \psi_2^- \dots \psi_{N-1}^- \psi_N^+ \psi_N^- \psi_{N-1}^+ \dots \psi_2^+ \psi_1^+ | \text{vac} \rangle$$

where D_{NN} denotes the overlap of two determinants in which ψ_N is absent. Transposing now ψ_N^- and ψ_{N-1}^+ in the second term one gets:

$$\begin{aligned} \mathcal{N}^2 &= S_{NN} D_{NN} - S_{N,N-1} D_{N,N-1} \\ &\quad + \langle \text{vac} | \psi_1^- \psi_2^- \dots \psi_{N-1}^- \psi_N^+ \psi_{N-1}^+ \psi_N^- \psi_{N-2}^+ \dots \psi_2^+ \psi_1^+ | \text{vac} \rangle \end{aligned}$$

where $D_{N,N-1}$ is the overlap of two determinants in which ψ_N is absent from the *bra* and ψ_{N-1} is absent from the *ket*. Continuing the process moving ψ_N^- to the left one finds:

$$\mathcal{N}^2 = S_{NN} D_{NN} - S_{N,N-1} D_{N,N-1} + S_{N,N-2} D_{N,N-2} - \dots + S_{N,1} D_{N,1}.$$

This equation resembles to the expansion of a determinant around its last row. Indeed:

$$\mathcal{N}^2 = \det|S| = \begin{vmatrix} S_{11} & S_{12} & \dots & S_{1N} \\ \vdots & & & \\ S_{N1} & S_{N2} & \dots & S_{NN} \end{vmatrix}.$$

This was shown explicitly for the two-electron case in the text and it can be verified by induction for the general case using the previous equation.

Problem 13.2

The square norm is written as:

$$\begin{aligned} \mathcal{N}^2 &= \langle \text{vac} | \chi_1^- \chi_2^- \dots \chi_N^- \chi_N^+ \dots \chi_2^+ \chi_1^+ | \text{vac} \rangle \\ &= \sum_{i_1 i_2 \dots i_N} S_{i_1, 1} S_{i_2, 2} \dots S_{i_N, N} \langle \text{vac} | \tilde{\chi}_{i_1}^- \tilde{\chi}_{i_2}^- \dots \tilde{\chi}_{i_N}^- \chi_N^+ \dots \chi_2^+ \chi_1^+ | \text{vac} \rangle \end{aligned}$$

where the annihilation operators have been transformed to their biorthogonal counterparts by the overlap matrix. The set $\{i_1 i_2 \dots i_N\}$ should be an even (or odd) permutation of $\{1, 2, \dots, N\}$ to get nonzero result, 1 (or -1), in the matrix element. One can write:

$$\mathcal{N}^2 = \sum_P (-1)^P S_{p_1, 1} S_{p_2, 2} \dots S_{p_N, N} = \det|S|$$

which is the same result as that found in Problem 13.1.

Problem 13.3

a) The commutator is evaluated as:

$$[\tilde{\chi}_i^-, \tilde{\chi}_k^+] = \sum_l S_{li}^{-1} [\chi_l^-, \tilde{\chi}_k^+] = \sum_l S_{li}^{-1} \delta_{kl} = S_{ik}^{-1}.$$

b) The adjoint of $\tilde{\chi}_k^-$ can be obtained by taking the adjoint of the corresponding definition:

$$(\tilde{\chi}_k^-)^\dagger = \sum_l (S_{kl}^{-1} \chi_l^-)^\dagger = \sum_l S_{lk}^{-1} (\chi_l^-)^\dagger = \sum_l S_{lk}^{-1} \chi_l^+ = \tilde{\chi}_k^+$$

which was to be shown.

Problem 13.4

Multiplying Eq. (13.38) by C_{pk}^{-1} from the left and summing over all k one finds:

$$h_{mp} = \sum_k \varepsilon_k C_{km} C_{pk}^{-1}.$$

Using the normalization condition Eq. (13.40), this can be rearranged as:

$$h_{mp} = \sum_{kn} \varepsilon_k C_{km} S_{pn} C_{kn}$$

which is the formula for the spectral resolution in matrix form within a non-orthogonal metrics. Substituting this result into the Hamiltonian of Eq. (13.35), one gets:

$$H^{EHT} = \sum_{mp} h_{mp} \sum_{\sigma} \chi_{m\sigma}^+ \tilde{\chi}_{p\sigma}^- = \sum_k \varepsilon_k \sum_{mpn} C_{km} S_{pn} C_{kn} \sum_{\sigma} \chi_{m\sigma}^+ \tilde{\chi}_{p\sigma}^-.$$

Realizing here the expansions of Eq. (13.42) one gets directly Eq. (13.41), Q.E.D.

Problem 15.1

It is convenient to introduce the notations:

$$\delta h_{ik} = h_{ik} - h_{ik}^0$$

$$\delta [ij|kl] = [ij|kl] - [ij|kl]^0$$

[cf. Eq. (15.33)]. The first-order contribution to the interaction energy is given by:

$$\begin{aligned} W_{00} &= \langle \Psi^0 | \hat{W} | \Psi^0 \rangle = \langle HF | \sum_{ik} \delta h_{ik} i^+ k^- | HF \rangle \\ &\quad + \frac{1}{2} \sum_{ijkl} \delta[ij|kl] \langle HF | i^+ j^+ l^- k^- | HF \rangle \\ &= \sum_i^{\text{occ}} \delta h_{ii} + \frac{1}{2} \sum_{ij}^{\text{occ}} (\delta[ij|ij] - \delta[ij|ji]). \end{aligned}$$

The second-order contribution, using the results of Sect. 12 mutatis mutandis, can be expressed as:

$$E^{(2)} = - \sum_{ijk \neq l*} \frac{|\delta[ij||kl]|^2}{\varepsilon_{k*} + \varepsilon_{l*} - \varepsilon_i - \varepsilon_j}.$$

Problem 17.1

Check first the one-electron term of the Hamiltonian. It is convenient to express it in terms of spatial orbitals as:

$$\hat{H} = \sum_{pq} h_{pq} \sum_{\sigma} a_{p\sigma}^+ a_{q\sigma}^-.$$

The spin operator S_z is given by:

$$\hat{S}_z = \frac{1}{2} \sum_m (a_{m\uparrow}^+ a_{m\uparrow}^- - a_{m\downarrow}^+ a_{m\downarrow}^-).$$

The commutator of these two operators can be evaluated in a straightforward manner by means of the commutation rules of the fermion operators a_i^+ , a_k :

$$[\hat{H}, \hat{S}_z] = \frac{1}{2} \sum_{mpq} h_{pq} \sum_{\sigma} ([a_{p\sigma}^+ a_{q\sigma}^-, a_{m\uparrow}^+ a_{m\uparrow}^-] - [a_{p\sigma}^+ a_{q\sigma}^-, a_{m\downarrow}^+ a_{m\downarrow}^-]).$$

In the first term $\sigma = \uparrow$ otherwise the commutator is zero, while $\sigma = \downarrow$ in the second commutator for the same reason. Thus:

$$[\hat{H}, \hat{S}_z] = \frac{1}{2} \sum_{mpq} h_{pq} ([a_{p\uparrow}^+ a_{q\uparrow}^-, a_{m\uparrow}^+ a_{m\uparrow}^-] - [a_{p\downarrow}^+ a_{q\downarrow}^-, a_{m\downarrow}^+ a_{m\downarrow}^-]).$$

A trivial algebra gives, however, that both commutators at the right-hand side are zero; switching to the short-hand notation and suppressing spin labels:

$$\begin{aligned} [p^+ q^-, m^+ m^-] &= p^+ q^- m^+ m^- - m^+ m^- p^+ q^- \\ &= p^+ q^- m^+ m^- - (\delta_{mp} m^+ q^- - \delta_{mq} p^+ m^- + p^+ q^- m^+ m^-) \\ &= 0. \end{aligned}$$

Problem 17.2

This is a trivial exercise by substituting the operators:

$$S^+ = a_\uparrow^\dagger a_\downarrow$$

$$S^- = a_\downarrow^\dagger a_\uparrow$$

and

$$S_z = \frac{1}{2}(n_\uparrow - n_\downarrow)$$

into the relevant commutators. Check here case (i):

$$\begin{aligned} [S^+, S_z] &= \frac{1}{2}[a_\uparrow^\dagger a_\downarrow, n_\uparrow] - \frac{1}{2}[a_\uparrow^\dagger a_\downarrow, n_\downarrow] \\ &= \frac{1}{2}[a_\uparrow^\dagger a_\downarrow, a_\uparrow^\dagger a_\uparrow] - \frac{1}{2}[a_\uparrow^\dagger a_\downarrow, a_\downarrow^\dagger a_\downarrow] \\ &= \frac{1}{2}a_\uparrow^\dagger a_\downarrow a_\uparrow^\dagger a_\uparrow - \frac{1}{2}a_\uparrow^\dagger a_\uparrow a_\uparrow^\dagger a_\downarrow - \frac{1}{2}a_\uparrow^\dagger a_\downarrow a_\downarrow^\dagger a_\downarrow - \frac{1}{2}a_\downarrow^\dagger a_\downarrow a_\uparrow^\dagger a_\downarrow. \end{aligned}$$

Here, the first term is obviously zero since two electrons of spin \uparrow cannot be created on the same orbital. The last term is zero, too, due to the presence of two $a_\downarrow - s$. One may write:

$$[S^+, S_z] = -\frac{1}{2}(a_\uparrow^\dagger a_\uparrow a_\uparrow^\dagger a_\downarrow + a_\uparrow^\dagger a_\downarrow a_\downarrow^\dagger a_\downarrow).$$

In the first term $a_\uparrow^\dagger a_\uparrow = n_\uparrow$ can safely be omitted since, standing after a_\uparrow^\dagger , it cannot change the value of any matrix element. Similarly, the product $a_\downarrow^\dagger a_\downarrow = n_\downarrow$ can be dropped from the last term since it is followed by a_\downarrow . Finally one gets:

$$[S^+, S_z] = -a_\uparrow^\dagger a_\downarrow = -S^+.$$

Case (ii) can be proved in the same manner.

Problem 17.3

Write the Hamiltonian in the usual form:

$$H^2 = \frac{1}{2} \sum_{\mu\nu\lambda\sigma} [\mu\nu|\lambda\sigma] \chi_\mu^+ \chi_\nu^+ \chi_\sigma^- \chi_\lambda^-$$

and substitute the unitary transformation of Eqs. (17.29–30):

$$H^2 = \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \sum_{ijkl} U_{\mu i}^+ U_{\nu j}^+ U_{k\lambda} U_{l\sigma} U_{p\mu} U_{q\nu} U_{r\sigma}^+ U_{s\lambda}^+ [ij|kl] \phi_p^+ \phi_q^+ \phi_r^- \phi_s^-.$$

Summing up over indices μ , v , λ , and σ and utilizing the unitary nature of the transformation ($UU^\dagger = 1$), one finds:

$$H^2 = \frac{1}{2} \sum_{ijkl} [ij|kl] \phi_i^+ \phi_j^+ \phi_l^- \phi_k^-$$

That is, the Hamiltonian is recovered in the same form.

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I. Gutman, Kragujevac, Yugoslavia; O. E. Polansky,
Mülheim a. d. Ruhr, FRG

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The present book is an attempt to outline some, certainly not all, mathematical aspects of modern organic chemistry. The mathematical concepts of organic chemistry as graph theory, group theory, and topology as well as their numerous interrelations are presented in a concise and simple, but mathematically rigorous fashion. Thus, this book emphasizes for the first time the concepts of mathematical chemistry – new branch of science that is being formed in our own times.

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