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Isaiah Shavitt and Rodney J. Bartlett
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Introduction

1.1 Scope

The book focuses primarily on many-body (or better, many-electron) methods for electron correlation. These include *Rayleigh–Schrödinger perturbation theory (RSPT)*, particularly in its diagrammatic representation (referred to as *many-body perturbation theory*, or *MBPT*), and *coupled-cluster (CC)* theory; their relationship to *configuration interaction (CI)* is included. Further extensions address properties other than the energy, and also excited states and multireference CC and MBPT methods.

The many-body algebraic and diagrammatic methods used in electronic structure theory have their origin in quantum field theory and in the study of nuclear matter and nuclear structure. The second-quantization formalism was first introduced in a treatment of quantized fields by Dirac (1927) and was extended to fermion systems by Jordan and Klein (1927) and by Jordan and Wigner (1928). This formalism is particularly useful in field theory, in scattering problems and in the study of infinite systems because it easily handles problems involving infinite, indefinite or variable numbers of particles. The diagrammatic approach was introduced into field theory by Feynman (1949a,b) and applied to many-body systems by Hugenholtz (1957) and by Goldstone (1957). Many-body perturbation theory and its linked-diagram formalism were first introduced by Brueckner and Levinson (1955) and by Brueckner (1955), and were formalized by Goldstone (1957). Other important contributions to the methodology, first in field theory and then in the theory of nuclear structure, are due to Dyson (1949a,b), Wick (1950), Hubbard (1957, 1958a,b) and Frantz and Mills (1960). Applications to the electronic structure of atoms and molecules began with the work of Kelly (1963, 1964a,b, 1968), and molecular applications using finite analytical basis sets appeared in the work of Bartlett and Silver (1974a,b).

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More complete accounts of the history of these methods have been given by Lindgren and Morrison (1986) and by Lindgren (1998).

The coupled-cluster method also has origins in nuclear structure theory, with the seminal papers of Coester (1958) and Coester and Kümmel (1960). It was introduced to electronic structure theory and formalized by Čížek (1966, 1969) and Čížek and Paldus (1971). A historical account of its origins and development was given by Paldus (2005).

Additional references to the development and extensions of the many-body methods are given in the relevant chapters.

The rest of this chapter provides some background material, including a brief discussion of the independent-particle model and the configuration-interaction method. We discuss the limitations of these methods and the need for the perturbation-theoretical and many-body methods that form the subject of the rest of this book. We also provide a preliminary introduction to the cluster ideas that form the basis of coupled-cluster theory. Readers in need of a more extensive introduction are referred to the excellent book by Szabo and Ostlund (1982).

A detailed exposition of formal perturbation theory is given in Chapter 2. A number of different derivations and approaches are included in this exposition in order to provide a broad foundation for the terminology and techniques employed in this field. The many-body technique of second quantization is introduced in Chapter 3, and the diagrammatic representation is described in Chapter 4. The application of the many-body and diagrammatic techniques to perturbation theory is described in Chapter 5, and this is followed by proof of the crucial linked-diagram theorem in Chapter 6 and a discussion of some practical aspects of many-body perturbation-theory calculations in Chapter 7. Open-shell and quasidegenerate perturbation theory is presented in Chapter 8. Coupled-cluster theory is discussed in Chapters 9 and 10, again including several forms of the derivations in order to provide better understanding. The calculation of properties in the coupled-cluster method is described in Chapter 11. Several additional aspects of coupled-cluster theory are discussed in Chapter 12, and the equation-of-motion (EOM) coupled-cluster method for excited-state calculations is described in Chapter 13. Finally, multireference coupled-cluster methods are presented in Chapter 14.

1.2 Conventions and notation

Throughout this book we use atomic units, setting $m = e = \hbar = 1$ where m and $-e$ are the mass and charge of the electron and $\hbar = h/2\pi$ is Planck's

Table 1.1. *Terminology for excitation levels*

Level	Symbol	Name	Alternative
1	S	singles	mono-excited
2	D	doubles	bi-excited
3	T	triples	tri-excited
4	Q	quadruples	tetra-excited
5	P	pentuples	penta-excited
6	H	hextuples	hexa-excited

constant. As is customary in quantum chemistry, these constants are omitted from the expressions in this book but their implied presence is needed for proper dimensionality.

With a few exceptions, lower-case letters ($a, b, \ldots, \phi, \psi, \ldots$, etc.) are used for one- and two-particle entities, and upper-case letters ($A, B, \ldots, \Phi, \Psi, \ldots$, etc.) are used for many-particle entities. Operators are designated by a caret over a roman letter ($\hat{a}, \hat{\imath}, \hat{F}, \hat{H}$, etc.), by a script upper-case letter ($\mathcal{H}, \mathcal{P}$, etc.) or by an Greek upper-case letter (Λ, Ω, etc.). Vectors and matrices are represented by boldface lower- and upper-case letters, respectively.

The acronyms used to specify excitation-level combinations included in the different computational models have evolved, first in configuration interaction (CI) and then in coupled-cluster (CC) theory, using a mixture of English, Greek and Latin roots, in view of the need to provide a unique initial letter for each level, as listed in Table 1.1. For example, a CI calculation that includes all single, double and triple excitations is described as CISDT. The fourth column in Table 1.1 lists some alternative excitation-level names that have been used.

1.3 The independent-particle approximation

In this section we briefly summarize several aspects of the procedures used to obtain starting approximations for correlated molecular electronic structure calculations. For more complete discussions and detailed derivations the reader is referred to other sources, such as Szabo and Ostlund (1982) or standard textbooks.

Most electronic structure calculations begin with a relatively simple approximation based on the independent-particle model. The wave function

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for such a model is a single Slater determinant (SD),

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \cdots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & \cdots & \psi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(N) & \psi_2(N) & \cdots & \psi_N(N) \end{vmatrix} = \mathcal{A}\psi_1\psi_2\ldots\psi_N, \tag{1.1}$$

where $\psi_i(\mu)$ is a spinorbital, a function of the space and spin coordinates of the μth electron (typically a product of a spatial orbital and a spin function), and $\mathcal{A}$ is the antisymmetrizer. The most commonly used independent-particle model is the *Hartree–Fock (HF)* or *self-consistent field (SCF)* wave function,† in which the spinorbitals are varied to minimize the energy expectation value of the single-determinant wave function. The minimization can be achieved by solving a set of coupled one-electron eigenvalue equations for the spinorbitals,

$$\hat{f}\psi_i = \varepsilon_i\psi_i\,, \tag{1.2}$$

in which the Fock operator $\hat{f}$ depends on all the spinorbitals (this dependence is given explicitly later in this section). Iterative procedures are required to obtain consistency between the spinorbitals used to define $\hat{f}$ and the spinorbitals obtained as its eigenfunctions.

Because a determinant is invariant to unitary transformations of its columns or rows, the SD wave function (1.1) is invariant under unitary transformations of the occupied spinorbitals $\{\psi_i, i = 1, 2, \ldots, N\}$ among themselves. Therefore, any unitary transformation of the occupied spinorbitals provides an alternative representation of the *same SD wave function.* The particular representation of the wave function in which the spinorbitals are solutions of (1.2), i.e., are eigenfunctions of $\hat{f}$ (so that the matrix representation of $\hat{f}$ in terms of these spinorbitals is diagonal, $\langle\psi_i|\hat{f}|\psi_j\rangle = \varepsilon_i\delta_{ij}$), is called the *canonical HF wave function*; the corresponding spinorbitals (including

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† It was common to distinguish between the original type of *Hartree–Fock* solution, which achieves the absolute minimum of the energy of an SD wave function (1.1) with respect to any variation of the spinorbitals (subject only to appropriate restrictions in the restricted HF case) and usually require numerical (finite difference) methods of solution as employed by Hartree and others for atomic wave functions, and the *self-consistent field* form (also known as *Hartree–Fock–Roothaan* or *matrix Hartree–Fock*), in which the spinorbitals are expanded in a basis set and the lowest energy solution within the space generated by that basis set is sought. This second approach converts the operator eigenvalue equation (1.2) to a matrix eigenvalue equation for the eigenvectors of expansion coefficients. The HF solution is thus the limiting result (the *HF limit*) of the self-consistent field procedure as the basis set approaches completeness. In current usage, however, the distinction has unfortunately been lost, and the terms Hartree–Fock and self-consistent field are used interchangeably, both commonly referring to the basis-set expansion approach. We shall follow this practice in this book.

the unoccupied or *virtual* spinorbitals obtained as additional eigenfunctions of $\hat{f}$ that are not used in the SD wave function) are the *canonical spinorbitals*. All other representations of the HF solution are called *noncanonical* and produce a block-diagonal matrix representation of $\hat{f}$ with two internally non-diagonal blocks representing the occupied and virtual spinorbital spaces, respectively. The orbital energies ε_i, which are the eigenfunctions of $\hat{f}$, are invariant under unitary transformations but are associated one-to-one with the canonical spinorbitals only.

The degree of freedom provided by the invariance of the HF wave function under unitary transformations of the occupied spinorbitals (and, separately, of the unoccupied spinorbitals) is sometimes used to transform the spinorbitals to a localized form, in which the individual spinorbitals are localized to the regions of individual atoms or bonds. Such localized forms of the solution often offer advantages of simpler interpretation and provide a basis for more compact descriptions of correlated wave functions.

Several variants of the Hartree–Fock approach are in common use; these are defined by the restrictions, if any, that are placed on the spinorbitals $\{\psi_i\}$. In the usual form of the *unrestricted Hartree–Fock (UHF)* model there are no restrictions other than that each spinorbital is a product of a spatial orbital and a spin-up (α) or spin-down (β) spin function. This form is often used for open-shell states and sometimes for the description of bond dissociation. The most common restriction constrains pairs of spinorbitals to share the same spatial orbital, leading to the *restricted Hartree–Fock (RHF)* model in which each spatial orbital can accommodate at most two electrons. The RHF model is most commonly used for closed-shell molecules near their equilibrium geometry. When applied to open-shell cases, in which one or more spinorbitals are unpaired, it is often referred to as *restricted open-shell Hartree–Fock (ROHF)*. For closed-shell molecules near their equilibrium geometry the UHF and RHF solutions are generally equivalent and produce the same set of doubly occupied spatial orbitals.†

Independently of whether spin restrictions are used, restrictions can be placed on the symmetry properties of the spatial orbitals requiring them to belong to irreducible representations (*irreps*) of the point group of the molecule. Such restrictions can often cause difficulties in the descriptions of potential-energy surfaces, when symmetry-restricted solutions at high-symmetry points may be higher in energy than symmetry-unrestricted solutions at the same points (a phenomenon referred to as *symmetry breaking*)

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† Except where stated explicitly otherwise, the treatment in this book is in terms of unrestricted spinorbitals, and the terms orbitals and Hartree–Fock (or SCF) generally refer to spinorbitals and UHF.

and thus do not connect continuously with the solutions for distorted (lower-symmetry) structures.

In most cases, a Hartree–Fock solution provides an excellent initial approximation for the electronic wave function and energy of a molecular system, often accounting for more than 99% of the total electronic energy and 95% of the wave function. Nevertheless, because the energy differences of interest in chemical and spectroscopic processes are a fraction of one percent of the total electronic energy and because the accuracy of the HF model tends to vary considerably between different structures and different electronic states, this model does not usually provide adequately accurate solutions by itself. In most cases, though, it provides a satisfactory zero-order solution that can then be used as the starting point for the *post-Hartree–Fock* methods discussed in this book. There are however cases in which HF does not provide an adequate zero-order function; these are due primarily to near degeneracies between several Slater-determinantal contributions to the wave function. In such cases a multideterminantal ("multiconfigurational") function can provide a better zero-order wave function. The *multiconfigurational Hartree–Fock (MCHF)* model, also referred to as *multiconfigurational SCF (MCSCF)*, can be particularly effective in providing good zero-order solutions in such cases, but the use of such multiconfigurational zero-order functions requires *multireference* methods in the post-HF stage and introduces additional complications for the many-body methods that are the principal topic of this book.

It is instructive to consider an alternative derivation of the Hartree–Fock model that provides physical insight into the reasons for its success and introduces some important concepts. We shall do this in terms of the unrestricted model, because of its generality and its relatively simple notation. Instead of invoking the variational principle and minimizing the energy of a single-determinant wave function with respect to the spinorbitals, the same Fock equation (1.2) can be obtained by a physically motivated argument.

The difficulty in the solution of the electronic Schrödinger equation is principally due to the interelectron repulsion terms $1/r_{\mu\nu}$ in the Hamiltonian. Those terms couple the motions of the different electrons and prevent separation of the equation into individual one-electron equations. It is therefore natural to seek an approximate solution in which the instantaneous interelectron interaction terms are replaced by averaged interactions, describing the motion of each electron in the time-averaged field of the other electrons. The averaged interaction energy of an electron in spinorbital ψ_i, when the total electron distribution is described by the single-SD wave function (1.1), is obtained as

$$\begin{aligned} \langle \psi_i | \hat{u} | \psi_i \rangle &= \sum_{j\ (j \neq i)}^{N} \left\langle \psi_i(1)\psi_j(2) \middle| \frac{1}{r_{12}} \middle| \psi_i(1)\psi_j(2) - \psi_j(1)\psi_i(2) \right\rangle \\ &= \sum_{j=1}^{N} \langle \psi_i(1) | \hat{J}_j - \hat{K}_j | \psi_i(1) \rangle\,, \end{aligned} \tag{1.3}$$

where the restriction on the summation in the first line can be ignored because of the cancellation between the first (*Coulomb* or *direct*) term and the second (*exchange*) term when $i = j$. The *Coulomb* and *exchange operators* are defined by

$$\begin{aligned} \hat{J}_i(1)\phi(1) &= \left\langle \psi_i(2) \middle| \frac{1}{r_{12}} \middle| \psi_i(2) \right\rangle_2 \phi(1)\,, \\ \hat{K}_i(1)\phi(1) &= \left\langle \psi_i(2) \middle| \frac{1}{r_{12}} \middle| \phi(2) \right\rangle_2 \psi_i(1)\,, \end{aligned} \tag{1.4}$$

the integration being over the coordinates of electron 2 only. With the replacement of the instantaneous electron repulsion by the average form, the Schrödinger equation becomes separable, the equation for each electron takes the form (1.2) and the Fock operator is given by

$$\hat{f} = \hat{h} + \sum_{i=1}^{N} (\hat{J}_i - \hat{K}_i)\,, \tag{1.5}$$

where $\hat{h}$ is the one-electron operator in the Hamiltonian. Because of the cancellation of the Coulomb and exchange terms in (1.3) when $i = j$, and thus the removal of the restriction on the summation, the Fock operators for all the spinorbitals are equal and we have only one eigenvalue equation for the spinorbitals, with the different spinorbitals obtained as different eigenfunctions of that operator. The iterative and coupled nature of the equations is due to the dependence of the Coulomb and exchange operators on all the occupied orbitals.

The average-interaction approach leads to exactly the same equations as the energy-minimization approach and serves to provide a physical rationale for the Hartree–Fock model. It also provides the basis for defining the concept of *electron correlation*, as discussed in the next section.

1.4 Electron correlation

The purpose of all many-body methods is to describe *electron correlation*, defined as representing the difference between the Hartree–Fock description

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of the electronic wave function and the exact solution of the nonrelativistic time-independent Schrödinger equation (Löwdin 1959, Kutzelnigg 2003). (Note that this definition is not necessarily unique, because of the different types of Hartree–Fock model that can be used as the reference point.) We are interested in the correlation correction to the energy, called the *correlation energy*,

$$\Delta E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}} \tag{1.6}$$

(where E_{HF} implies the exact solution of the Hartree–Fock problem, i.e., in an infinite, complete, basis set), and also in the correction to the wave function,

$$\Psi_{\text{exact}} = \Phi_{\text{HF}} + \chi_{\text{corr}} \, , \tag{1.7}$$

which determines the electron density and all other properties of molecules.

The naming of the correlation correction reflects the fact that the Hartree–Fock model describes the motion of the electrons in the average field of the other electrons, neglecting the instantaneous correlation in the motions of the electrons due to their mutual repulsion. However, this dynamic effect is not the only type of error in the Hartree–Fock model. In many cases, especially for excited states and other open-shell states and even for ground-state closed-shell molecules when bonds are stretched to near breaking (if the RHF model is used as the reference), near degeneracies between single-configuration descriptions cause the single-configuration Hartree–Fock model to be deficient even as a zero-order approximation for the wave function and energy. Therefore we distinguish between the two components of the correlation effect: *dynamic correlation*, reflecting the instantaneous correlation in electron motions due to their mutual repulsion, and *nondynamic correlation*, reflecting the effect of near degeneracies and other substantial inadequacies of the single-configuration model. While it is difficult to provide a quantitative separation between these two components of the correlation error, the understanding provided by these concepts is important in designing methods for obtaining satisfactory solutions of the Schrödinger equation.

The two components of the correlation error respond best to two different types of treatment. Nondynamic correlation is handled most efficiently by using a multiconfigurational zero-order description such as multiconfigurational SCF (MCSCF). Dynamical correlation is handled efficiently by the perturbation methods and coupled cluster approaches described in the rest of this book. Unfortunately, unlike the situation in the configuration interaction model, the *multireference* extension of the perturbation and coupled-

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cluster models is quite difficult, and general methods for this type of approach are still not widely available. Nevertheless, single-reference coupled-cluster theory, when carried to a high enough level, has proved to be capable of overcoming the nondynamic correlation problem to a considerable extent.

1.5 Configuration interaction

The simplest approach to treating electron correlation is by the *configuration-interaction (CI)* method. If we start with the *self-consistent field (SCF)* wave function and orbitals (the Hartree–Fock solution limited to the space spanned by a given basis set), we can write the CI expansion of an N-electron wave function in the (unnormalized) form

$$\Psi = \Phi_{\mathrm{SCF}} + \sum_{i,a} C_i^a \Phi_i^a + \sum_{i<j,\, a<b} C_{ij}^{ab} \Phi_{ij}^{ab} + \cdots \qquad \text{(up to } N \text{ excitations)}, \tag{1.8}$$

where Φ_i^a is a *singly excited* configuration in which an occupied orbital ϕ_i of the SCF wave function has been replaced by a virtual orbital ϕ_a (an orbital not occupied in the SCF function, which can also be chosen to be an eigenfunction of the Fock operator, $\hat{f}\phi_a = \varepsilon_a \phi_a$), Φ_{ij}^{ab} is a *double-excitation* configuration etc.

If m is the number of SCF occupied orbitals and n is the number of virtual orbitals ($m + n$ equals the number of basis functions) then the number of k-fold excited configurations is $O(m^k n^k)$ (as long as $k \ll m$). This number grows very rapidly with k, so that a complete solution is impractical and the CI expansion needs to be truncated. Usually the truncation is made after the double-excitation level, producing CISD, i.e. CI with single (S) and double (D) excitations. Because Φ_{SCF} is (usually) a reasonable starting approximation to Ψ and because the Hamiltonian $\hat{H}$ has no more than two-electron operators (so that $\langle \Phi_{\mathrm{SCF}} | \hat{H} | \Phi_{ij\ldots}^{ab\ldots} \rangle = 0$ for higher than double excitations), this represents a reasonable approximation in most cases.

The contribution of single excitations to a CI expansion (1.8) based on an SCF function (unrestricted or closed-shell restricted) as the initial term is quite small. This is due to the *Brillouin theorem*, which states that the Hamiltonian matrix element between the SCF function and a single excitation vanishes,

$$\langle \Phi_{\mathrm{SCF}} | \hat{H} | \Phi_i^a \rangle = 0\,. \tag{1.9}$$

This theorem holds for both canonical and noncanonical forms of the SCF function and is a consequence of the block-diagonal nature of the Fock operator $\hat{f}$ (Section 1.3) given by $f_{ia} = \langle \Phi_{\mathrm{SCF}} | \hat{H} | \Phi_i^a \rangle = 0$ (see Chapter 3). As a

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consequence of the Brillouin theorem, a CI expansion with single excitations only (CIS) based on an unrestricted or closed-shell restricted SCF function provides no improvement over SCF. It is only through the interaction of the single excitations with the doubles (and, to a much smaller extent, triples) that the singles acquire nonzero coefficients C_i^a in the expansion. These arguments do not apply to the restricted open-shell SCF (ROHF) case, for which the $\hat{f}$ matrix is not block diagonal, the Brillouin theorem does not hold, and a CIS wave function can provide a useful improvement over SCF.

The contribution of single excitations to the CI expansion (as well as to perturbation expansions and coupled-cluster wave functions) can be eliminated completely by a suitable transformation of the orbitals. Such a transformation involves some mixing of occupied and virtual orbitals and therefore the initial term in the transformed expansion is no longer exactly equivalent to the SCF function. The resulting orbitals are called *Brueckner orbitals* and can be obtained by an iterative procedure in which, in each iteration, pairs of occupied and virtual orbitals are mixed to eliminate the corresponding single-excitation contributions in first order. This process must be applied to an expansion that includes at least double excitations, because it is the interaction of the single excitations with the doubles that is responsible for almost all of the contribution of the single excitations to the expansion.

Natural orbitals (NOs) are very similar to Brueckner orbitals; they are obtained by transforming the orbitals so as to diagonalize the one-particle density matrix of the correlated wave function. For two-electron systems, the natural orbitals are the same as the Brueckner orbitals, making it relatively easy to eliminate single excitations from correlated two-electron wave functions. In natural-orbital-based expansions for systems of more than two electrons the contribution of single excitations tends to be very small, in fact much smaller than even the small contributions in the SCF case.

The exact solution, within the given basis set, is obtained by using all terms of the CI expansion, up to N excitations. This is called *full CI* and is invariant under any linear transformation of the orbitals.

1.6 Motivation

The motivation for studying perturbation theory (PT) and other many-body (MB) techniques comes from the following principal sources.

1. Unlike truncated CI, most PT formulations provide properly *extensive* descriptions. These concepts are discussed in Section 1.7; briefly,