Chapter 6
Wave Function Methods

Abstract A hierarchy of the *Self-Consistent Field* (SCF) theories of the molecular electronic structure is surveyed. First, the rudiments of the *Hartree* approach using the trial wave function in the form of the product of the occupied Molecular Orbitals (MO) describing independent one-electron states and providing the reference in defining the electron *exchange-correlation* effects are given. The *Hartree–Fock* (HF) method adopting the Slater determinant (antisymmetrized product) as the variational wave function, which constitutes a natural reference for determining the electron *Coulomb correlation* effects, and its analytical implementation in the finite basis set of AO, called SCF LCAO MO theory, are summarized. The Koopmans theorem is discussed and the concepts of Slater's *transition state* (TS) in electronic excitations and of the *local pseudopotential* of Phillips and Kleinman (PK) are introduced. Typical errors in SCF calculations are identified and the electron correlation problem is formulated in terms of the conditional two-electron densities and the associated correlation holes, the sum-rules of which are examined. Alternative *Configuration Interaction* (CI) strategies for determining the *static* and/or *dynamic* Coulomb correlation effects, formally based upon the MO expansion theorem for molecular electronic states, are reviewed. Both the *Single-Reference* (SR) SCF (HF) and *Multireference* (MR) SCF (MR SCF) or Multiconfigurational (MC) SCF (MC SCF) and the *Complete-Active-Space* (CAS) SCF (CAS SCF) wave functions can be used to generate the excited configurations to be included in the subsequent CI expansion, giving rise to SR CI and MR CI approaches, respectively. Several *single*- and *multi* reference CI methods are identified, including the alternative variants using either the *full* CI (FCI) or a limited expansion in terms of the *single* (S), *double* (D), *triple* (T), *quadruple* (Q), and in general *n-tuple* electron excitations from the HF/SCF or MR SCF wave functions, e.g., the *variational* SR techniques: CID, CISD, CISTQ, etc. The *size*-consistency and *size*-extensivity requirements of such approximate variational treatments are commented upon and the problem of choosing an effective orbital set for subsequent CI calculations is addressed. The reduced density matrices are introduced and the associated concepts of the correlated one- and two-electron functions, called the *Natural Orbitals* (NO) and *Natural Geminals* (NG),

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respectively, are defined together with their pseudoapproximations in the limited CI approaches.

The simplest variant of the *Many-Body Perturbation Theory* (MBPT), the *Møller–Plesset* (MP) theory, is examined and the Brillouin and McDonald theorems are formulated. A hierarchy of expressions for the electron correlation energy and CI coefficients in the intermediate-normalization representation is derived. The CI theories of the correlated electronic pairs are summarized, including several *separated*-pair approximations, e.g. the *Independent Electron Pair Approximation* (IEPA), and that using the *Antisymmetrized Product of Strongly Orthogonal Gemminals* (APSG), as well as selected *coupled*-pair approaches, e.g., the *Coupled Electron Pair Approximation* (CEPA), the related *Coupled-Pair Many Electron Theory* (CPMET), and the *Coupled Cluster* (CC) approximation. The second-quantization formalism of the electron correlation theory, in terms of the electron *creation* and *annihilation operators* or their local field analogs, acting in the molecular *Fock space* is introduced and the associated representations of the one- and two-electron terms in the molecular electronic Hamiltonian are examined. The cluster expansion of *many*-electron wave functions is introduced and the simplest case of the CC method is examined.

This overview of the standard ab initio MO theories is then followed by the elements of the *chemical* quantum theory of molecular systems provided by the modern *Valence Bond* (VB) methods originating from the classical *Heitler–London* (HL) treatment of the hydrogen molecule. The origins of the theory and a variety of the covalent and ionic VB structures constructed directly from the valence-shell AO's of constituent atoms, are traditionally presented using the illustrative case of H_2. The importance of the electron pairing and of the VB exchange integral in terms of AO for the interpretation of the origins of the chemical bonding is emphasized, various physical factors shaping the optimum orbitals are examined, and the associated estimates of the bonding energy of H_2 are summarized. The equivalence of the VB and CID theories in the *minimum basis* description of the hydrogen molecule is demonstrated and the AO-expansion theorem is formulated, which provides a formal basis for the VB treatments of general molecular systems. The semilocalized AO's of Coulson and Fischer are introduced. They are shown to absorb in the covalent HL-type function the effects due to ionic resonant structures. The *Perfect Pairing Approximation* (PPA) of the *Generalized VB* (GVB) approach of Goddard et al., corresponding to a single (dominant) Lewis structure, is introduced and the use of Rumer diagrams in selection of the linearly independent (canonical) set of VB structures from a multitude of admissible spin couplings in a molecule is illustrated for the π-electron systems in butadiene and benzene. Finally, a brief summary of the modern ab initio VB methods is given. Both *single*- and *many*-reference techniques of determining the optimized orbitals are surveyed. The former include the GVB method using both the *Perfect-Pairing* (PP) wave function (GVB-PP) and the *Spin-Coupled* (SC) algorithm, which makes no prior assumptions about the dominant spin-coupling pattern. Both schemes can be subsequently improved by adding the (nonorthogonal) CI stage, e.g., within the *Correlation Consistent* CI (CCCI) extension of GVB approach and the SCVB generalization of the SC method. The MR VB theories, using different orbitals for different structures, e.g., the *Resonating* GVB (RGVB) or *Breathing Orbital* VB (BOVB) variants, are introduced; they are essential to adequately describe some molecular states in terms of the *broken* symmetry VB functions.

6.1 Self-Consistent Field Theories

First variational theories of electronic structure of the N-electron atomic or molecular system described by the electronic Hamiltonian (5.69) have used as trial wave functions either the product of SO (5.61), describing the independent (distinguishable) spinless particles, or the Slater determinant (5.64), describing the exchange-correlated (indistinguishable) fermions. The former approach marks the *Hartree* theory (Hartree 1928), historically first quantum mechanical approach to *many*-electron systems, which still serves as the reference for defining the overall (Coulomb + Fermi) electron correlation effects, while the latter approach gives rise to the *Hartree–Fock* (HF) theory (Fock 1930; Froese-Fischer 1977), which constitutes the reference in extracting the Coulomb correlation energy. The analytical (Ritz) realization of the HF method, originally proposed by Roothaan and Hall, is known as SCF MO theory. In this section, we provide a short overview of the basic elements of these theories, including the relevant Euler equations for the optimum orbitals and, in the final part, the rudiments of the PK pseudopotential theory.

6.1.1 Hartree Method

The expectation value of the electronic Hamiltonian in the product state (5.61) defined by the N-lowest (singly occupied) SO $\{\psi_i(\boldsymbol{q}_i) = \psi_i(i) = \varphi_i(\boldsymbol{r}_i)\zeta_i(\sigma_i)\}$, with the spatial parts $\{\varphi_i(\boldsymbol{r})\} \equiv \boldsymbol{\varphi}(\boldsymbol{r})$ defining the associated (orthonormal) MO,

$$\langle\varphi_i|\varphi_j\rangle \equiv \langle i|j\rangle = \int \varphi_i^*(\boldsymbol{r})\,\varphi_j(\boldsymbol{r})\,d\boldsymbol{r} = \delta_{i,j}, \tag{6.1}$$

and electronic spin states $\{\zeta_i(\sigma_i) \in [\alpha_i(\sigma_i), \beta_i(\sigma_i)]\}$, can be expressed in terms of the corresponding one- and two-electron integrals (5.73)–(5.75)]:

$$\begin{aligned}\langle E^e(N)\rangle_\Psi &= \langle\Psi(N)\,|\hat{\mathrm{H}}^e(N)|\Psi(N)\rangle = \left\langle \prod_{k=1}^{N}\psi_k(k)\left|\sum_{i=1}^{N}\hat{\mathrm{h}}(i)+\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}g(i,j)\right|\prod_{l=1}^{N}\psi_l(l)\right\rangle\\ &=\sum_{i=1}^{N}\langle\psi_i(i)|\hat{\mathrm{h}}(i)|\psi_i(i)\rangle\prod_{k\neq i}\langle\psi_k(k)\,|\,\psi_k(k)\rangle\\ &\quad+\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\langle\psi_i(i)\psi_j(j)|g(i,j)|\psi_i(i)\psi_j(j)\rangle\prod_{k\neq(i,j)}\langle\psi_k(k)\,|\,\psi_k(k)\rangle\\ &=\sum_{i=1}^{N}\bar{h}_{i,i}[\psi_i]+\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\bar{J}_{i,j}[\psi_i,\psi_j]\equiv E_{\mathrm{H}}[\boldsymbol{\psi}]\\ &=\sum_{i=1}^{N}h_{i,i}[\varphi_i]+\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}(1-\delta_{i,j})J_{i,j}[\varphi_i,\varphi_j]\equiv E_{\mathrm{H}}[\boldsymbol{\varphi}].\end{aligned}\tag{6.2}$$

Again, due to the normalization of spin functions (5.79), the integrals in terms of SO $\boldsymbol{\psi}(\boldsymbol{q})$ are equal to those in terms of their spatial functions (MO) [see (5.78) and (5.80)]: $\bar{h}_{i,i}[\psi_i] = h_{i,i}[\varphi_i]$ and $\bar{J}_{i,j}[\psi_i,\psi_j] = J_{i,j}[\varphi_i,\varphi_j]$. For example, for $N = 2p$, i.e., p doubly occupied orbitals $\{\varphi_i(\boldsymbol{r}_i),\ i = 1, 2, \ldots, p\}$ of the spin-restricted approximation [compare (5.66)],

$$\Psi(N) = \varphi_1^+(\boldsymbol{r}_1)\varphi_1^-(\boldsymbol{r}_2)\varphi_2^+(\boldsymbol{r}_3)\varphi_2^-(\boldsymbol{r}_4)\ \ldots\ \varphi_p^+(\boldsymbol{r}_{N-1})\varphi_p^-(\boldsymbol{r}_N),\tag{6.3}$$

one finds [compare (5.81)]:

$$E_{\mathrm{H}}[\boldsymbol{\varphi}] = 2\sum_{i=1}^{p}h_{i,i}[\varphi_i]+\sum_{i=1}^{p}\sum_{j=1}^{p}(2-\delta_{i,j})J_{i,j}[\varphi_i,\varphi_j].\tag{6.4}$$

In accordance with the variational principle of quantum mechanics, the optimum Hartree (H) orbitals $\boldsymbol{\varphi}_{\mathrm{H}}$ have to minimize the auxiliary energy functional including the Lagrange terms associated with conditions of their orthonormality,

$$\delta\left\{E_{\mathrm{H}}[\boldsymbol{\varphi}']-\sum_{i=1}^{p}\sum_{j=1}^{p}\lambda_{k,l}\left(\langle\varphi_i'\mid\varphi_j'\rangle-\delta_{i,j}\right)\right\}\Big|_{\boldsymbol{\varphi}_{\mathrm{H}}}\equiv\delta\mathcal{E}_{\mathrm{H}}[\boldsymbol{\varphi}_{\mathrm{H}};\boldsymbol{\lambda}]=0,\tag{6.5}$$

where $\boldsymbol{\lambda} = \{\lambda_{i,j}\}$ groups the Lagrangian multipliers enforcing these constraints. Examining the complex conjugate of the preceding equation then reveals that $\lambda_{i,j}^*$ enforces the subsidiary condition $\langle\varphi_j'|\varphi_i'\rangle = \delta_{j,i}$, and hence $\lambda_{i,j}^* = \lambda_{j,i}$, or $\boldsymbol{\lambda} = \boldsymbol{\lambda}^\dagger$. Thus, the Lagrangian multipliers define the Hermitian matrix which can be diagonalized in the unitary transformation: $\mathbf{U}^\dagger\boldsymbol{\lambda}\mathbf{U} = \boldsymbol{\varepsilon}_{\mathrm{H}} = \{\varepsilon_i\delta_{i,j}\}$, $\mathbf{U}^\dagger\mathbf{U} = \mathbf{U}\mathbf{U}^\dagger = \mathbf{I}$. In this representation of the *canonical* orbitals $\boldsymbol{\varphi}_{\mathrm{H}} = \boldsymbol{\varphi}'\mathbf{U} = \{\varphi_k\}$, the variation principle of (6.5) reads:

$$\delta\{E_{\mathrm{H}}[\boldsymbol{\varphi}] - \sum_{k=1}^{p} \varepsilon_k \langle \varphi_k \mid \varphi_k \rangle\} \equiv \delta\boldsymbol{\mathcal{E}}_{\mathrm{H}}[\boldsymbol{\varphi}_{\mathrm{H}}; \boldsymbol{\varepsilon}_{\mathrm{H}}] = 0. \tag{6.6}$$

We also recall at this point that for generally complex orbitals the variations $\delta\boldsymbol{\varphi}^*$ and $\delta\boldsymbol{\varphi}$ ultimately represent the independent displacements of the real and imaginary parts of MO (see also Sect. 5.1.2). Moreover, due to the Hermitian character of the electronic Hamiltonian the corresponding Euler equations for the optimum shapes of MO resulting from these two variations must be identical. Therefore, in what follows we assume that in taking the variation of $\boldsymbol{\mathcal{E}}_{\mathrm{H}}[\boldsymbol{\varphi}; \boldsymbol{\varepsilon}_{\mathrm{H}}]$, to derive equations to be satisfied by the optimum orbitals, the complex-conjugate orbitals are being infinitesimally modified: $\boldsymbol{\varphi}^* \rightarrow \boldsymbol{\varphi}^* + \delta\boldsymbol{\varphi}^*$.

The integral $J_{k,l}[\varphi_k, \varphi_l]$ [see (5.78)] in the average electronic energy of (6.4) in the canonical representation $\boldsymbol{\varphi}_{\mathrm{H}}$ stands for the average Coulomb repulsion between one electron in state φ_k and another electron in state φ_l,

$$\begin{aligned} J_{k,l}[\varphi_k, \varphi_l] &= \int\!\!\int |\varphi_k(1)|^2 \frac{1}{r_{1,2}} |\varphi_l(2)|^2 d\boldsymbol{r}_1 d\boldsymbol{r}_2 = \int\!\!\int \rho_k(1) \frac{1}{r_{1,2}} \rho_l(2) d\boldsymbol{r}_1 d\boldsymbol{r}_2 \\ &\equiv \langle k(1)l(2)|g|k(1)l(2)\rangle_{1,2} \\ &= \int \varphi_k^*(1) \left[\int \varphi_l^*(2) \frac{1}{r_{1,2}} \varphi_l(2)\, d\boldsymbol{r}_2\right] \varphi_k(1)\, d\boldsymbol{r}_1 = \int \rho_k(1) \left[\int \frac{\rho_l(2)}{r_{1,2}}\, d\boldsymbol{r}_2\right] d\boldsymbol{r}_1 \\ &\equiv \langle k(1)|\hat{\mathrm{J}}_l(1)|k(1)\rangle_1. \end{aligned} \tag{6.7}$$

In the preceding equation we have introduced the (multiplicative) *Coulomb operator* $\hat{\mathrm{J}}_l(1)$, which measures the average electrostatic potential in the position of electron "1" due to the probability distribution $\rho_l = |\varphi_l|^2$ of electron "2." Obviously, interchanging the orbital indices or electronic labels, which only name the integration variables of the definite integrals, has no effect on the value of the integral itself:

$$J_{k,l}[\varphi_k, \varphi_l] = \langle k(1)|\hat{\mathrm{J}}_l(1)|k(1)\rangle_1 = \langle l(1)|\hat{\mathrm{J}}_k(1)|l(1)\rangle_1 = J_{l,k}[\varphi_l, \varphi_k]. \tag{6.8}$$

The stationary condition of (6.6), that the variation $\delta\boldsymbol{\mathcal{E}}_{\mathrm{H}}[\boldsymbol{\varphi}; \boldsymbol{\varepsilon}_{\mathrm{H}}]$ linear in $\delta\boldsymbol{\varphi}^*$ vanishes for the optimum canonical orbitals $\boldsymbol{\varphi} = \boldsymbol{\varphi}_{\mathrm{H}}$, marks the local extremum of this MO functional:

$$\sum_{k=1}^{N} \langle \delta k(1)|\hat{\mathrm{h}}(1) + \sum_{l=1}^{N} (1 - \delta_{k,l})\hat{\mathrm{J}}_l(1) - \varepsilon_k|k(1)\rangle_1 = 0. \tag{6.9}$$

Since variations $\{\langle\delta\varphi_k|\}$ are arbitrary, this equation can be satisfied only when

$$\{[\hat{\mathrm{h}}(1) + \sum_{l=1}^{N} (1 - \delta_{k,l})\hat{\mathrm{J}}_l(1)] - \varepsilon_k\}|k(1)\rangle \equiv \{\hat{\mathrm{F}}_{\mathrm{H}}(1) - \varepsilon_k\}|k(1)\rangle = 0, \tag{6.10}$$

where we have defined the effective one-electron Hamiltonian $\hat{\mathrm{F}}_{\mathrm{H}}(1)$ of the Hartree method. Its eigenvalue problem,

$$\hat{\mathrm{F}}_{\mathrm{H}}(1)\,\varphi_k(1) = \varepsilon_k\,\varphi_k(1), \qquad k = 1, 2, \ldots, N, \tag{6.11}$$

thus determines the optimum canonical orbitals $\boldsymbol{\varphi}_{\mathrm{H}} = \{\varphi_k\}$, which define the best approximation of the system electronic wave function in the family of N-electron functions delineated by the variational product of (5.61).

It also follows from this effective one-electron Schrödinger equation that the Lagrangian multiplier

$$\begin{aligned}\varepsilon_k = \langle\varphi_k|\hat{\mathrm{F}}_{\mathrm{H}}|\varphi_k\rangle &= \langle k(1)|[\hat{\mathrm{h}}(1) + \sum_{l=1}^{N}(1-\delta_{k,l})\hat{\mathrm{J}}_l(1)|k(1)\rangle_1\\ &= h_{k,k}[\varphi_k] + \sum_{l=1}^{N}(1-\delta_{k,l})J_{k,l}[\varphi_k,\varphi_l]\end{aligned} \tag{6.12}$$

measures the corresponding *orbital energy* of an electron occupying kth MO, moving in the effective external potential

$$V_{\mathrm{H}}(\boldsymbol{r}) = v(\boldsymbol{r}) + \sum_{l=1}^{N}(1-\delta_{k,l})\hat{\mathrm{J}}_l(1) \equiv v(\boldsymbol{r}) + v_{\mathrm{H}}(\boldsymbol{r}), \tag{6.13}$$

which combines the external potential $v(\boldsymbol{r})$ due to the system nuclei and the resultant *electrostatic potential* (ESP) $v_{\mathrm{H}}(\boldsymbol{r}) = v_{\mathrm{H}}[\boldsymbol{r};\,\boldsymbol{\varphi}_{\mathrm{H}}]$ generated by the remaining electrons, averaged over their instantaneous positions.

Since the Hartree effective Hamiltonian depends upon the MO themselves, $\hat{\mathrm{F}}_{\mathrm{H}} = \hat{\mathrm{F}}_{\mathrm{H}}[\boldsymbol{\varphi}_{\mathrm{H}}]$, the Hartree equations (6.11) have to be solved iteratively by using the optimum orbitals $\boldsymbol{\varphi}_{\mathrm{H}}^{(n)}$ from the previous iteration to define the next approximation of the Hartree operator, $\hat{\mathrm{F}}_{\mathrm{H}}\left[\boldsymbol{\varphi}_{\mathrm{H}}^{(n)}\right]$, which generates better orbitals $\boldsymbol{\varphi}_{\mathrm{H}}^{(n+1)}$, etc.,

$$\ldots \to \boldsymbol{\varphi}_{\mathrm{H}}^{(n)}\Big\} \to \Big\{\hat{\mathrm{F}}_{\mathrm{H}}\left[\boldsymbol{\varphi}_{\mathrm{H}}^{(n)}\right] \to \boldsymbol{\varphi}_{\mathrm{H}}^{(n+1)}\Big\} \to \Big\{\hat{\mathrm{F}}_{\mathrm{H}}\left[\boldsymbol{\varphi}_{\mathrm{H}}^{(n+1)}\right] \to \ldots,$$

until the field of electronic interactions is *self-consistent*, $v_{\mathrm{H}}\left[\boldsymbol{r};\,\boldsymbol{\varphi}_{\mathrm{H}}^{(m+1)}\right] \cong v_{\mathrm{H}}\left[\boldsymbol{r};\boldsymbol{\varphi}_{\mathrm{H}}^{(m)}\right]$, or $\boldsymbol{\varphi}_{\mathrm{H}}^{(m+1)} \cong \boldsymbol{\varphi}_{\mathrm{H}}^{(m)}$, to within the assumed tolerance threshold.

The average electronic energy in the *Hartree limit* (Hl), for an infinite variational flexibility of orbitals $\boldsymbol{\varphi}_{\mathrm{Hl}}$ in the product function describing the independent, spinless particles, $E_{\mathrm{Hl}} = E_{\mathrm{Hl}}[\boldsymbol{\varphi}_{\mathrm{Hl}}]$, then determines the reference for extracting the overall electron correlation energy. In the next section we shall examine the related *Hartree–Fock* (HF) approximation, using the Slater determinant as variational wave function, thus describing the *exchange*-correlated fermions. Clearly, the optimum canonical Hartree–Fock orbitals $\boldsymbol{\varphi}_{\mathrm{HF}}$, already reflecting the exchange correlation between electrons, will slightly differ from their corresponding Hartree analogs $\boldsymbol{\varphi}_{\mathrm{H}}$, but these two sets strongly resemble one another: $\boldsymbol{\varphi}_{\mathrm{H}} \cong \boldsymbol{\varphi}_{\mathrm{HF}}$.

6.1.2 Hartree–Fock Theory

For the determinantal variational wave function, the average electronic energy is given by the known functional of the (orthonormal) occupied SO $\boldsymbol{\psi}$ (see Sect. 5.4):

$$\langle E^e[\boldsymbol{\psi}]\rangle_{\Psi_A} = \sum_{i=1}^{N} \bar{h}_{i,i}[\psi_i] + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left(\bar{J}_{i,j}[\psi_i,\psi_j] - \bar{K}_{i,j}[\psi_i,\psi_j]\right) \equiv E_{\mathrm{HF}}[\boldsymbol{\psi}], \tag{6.14}$$

where the exchange integral $\bar{K}_{i,j}[\psi_i,\psi_j] = K_{i,j}[\varphi_i,\varphi_j]\delta_{\zeta_i,\zeta_j}$ of (5.77) identically vanishes when the two SO involve different spin states of the two electrons. The best variational approximation of the system ground state is thus obtained by the optimum SO which minimize this average electronic energy subject to the orthonormality constraints of MO [see (6.5)]:

$$\delta\left\{E_{\mathrm{HF}}[\boldsymbol{\psi}] - \sum_{i=1}^{p}\sum_{j=1}^{p} v_{k,l}\Big(\langle\psi_i \mid \psi_j\rangle - \delta_{i,j}\Big)\right\} \equiv \delta\mathcal{E}_{\mathrm{HF}}[\boldsymbol{\psi};\boldsymbol{v}] = 0. \tag{6.15}$$

For simplicity, in what follows the closed-shell configuration of (5.66) is assumed, for which [see (5.81)]

$$E_{\mathrm{HF}}[\boldsymbol{\psi}] = E_{\mathrm{HF}}[\boldsymbol{\varphi}] = 2\sum_{i=1}^{p} h_{i,i}[\varphi_i] + \sum_{i=1}^{p}\sum_{j=1}^{p}\left(2J_{i,j}[\varphi_i,\varphi_j] - K_{i,j}[\varphi_i,\varphi_j]\right). \tag{6.16}$$

Turning now to the canonical representation of HF orbitals, $\boldsymbol{\varphi}_{\mathrm{HF}} = \boldsymbol{\varphi}\mathbf{U} = \{\phi_k\}$, in which the matrix of Lagrangian multipliers enforcing the orthonormality constraints becomes diagonal, $\mathbf{U}^{\dagger}\boldsymbol{v}\mathbf{U} = \mathbf{e} = \{e_i\delta_{i,j}\}$, $\mathbf{U}^{\dagger}\mathbf{U} = \mathbf{U}\mathbf{U}^{\dagger} = \mathbf{I}$, the relevant variational principle becomes:

$$\delta\left\{E_{\mathrm{HF}}[\boldsymbol{\varphi}_{\mathrm{HF}}] - \sum_{k=1}^{p} e_k(\langle\phi_k \mid \phi_k\rangle\right\} \equiv \delta\mathcal{E}_{\mathrm{HF}}[\boldsymbol{\varphi}_{\mathrm{HF}};\mathbf{e}] = 0. \tag{6.17}$$

Again, to facilitate a compact expression for the linear variation of the system electronic energy corresponding to the variation $\delta\boldsymbol{\varphi}^{*}_{\mathrm{HF}}$ of the complex-conjugate orbitals one formally expresses the exchange integral as the expectation value of the effective *exchange operator* [compare (6.7)] defined by the following result of its action on the one-electron function $f(\boldsymbol{r}_1) \equiv f(1)$:

$$\hat{\mathrm{K}}_l(1)f(1) \equiv \left(\int \phi_l^*(2)\frac{1}{r_{1,2}}f(2)d\boldsymbol{r}_2\right)\phi_l(1). \tag{6.18}$$

It follows from this definition that this integral operator exchanges two electrons in the product of the nonconjugate orbitals, $\phi_l(2)f(1) \to \phi_l(1)f(2)$, which explains its name. The exchange integral can be then expressed as the expectation value:

$$\begin{aligned} K_{k,l}[\phi_k,\phi_l] &= \iint \phi_k^*(1)\phi_l^*(2)\frac{1}{r_{1,2}}\phi_l(1)\phi_k(2)\,d\boldsymbol{r}_1 d\boldsymbol{r}_2 = \langle k(1)l(2)|g(1,2)|l(1)k(2)\rangle_{1,2} \\ &= \langle k(1)|\hat{\mathrm{K}}_l(1)|k(1)\rangle_1 = \langle l(1)|\hat{\mathrm{K}}_k(1)|l(1)\rangle_1. \end{aligned} \tag{6.19}$$

Finally, calculating the variation $\delta\boldsymbol{\mathcal{E}}_{\mathrm{HF}}[\boldsymbol{\varphi}_{\mathrm{HF}};\mathbf{e}]$ corresponding to $\delta\boldsymbol{\varphi}_{\mathrm{HF}}^*$ gives the following condition for the local extremum of the auxiliary functional of (6.17),

$$\sum_{k=1}^{p}\langle\delta k(1)|\hat{\mathrm{h}}(1)+\sum_{l=1}^{p}[2\hat{\mathrm{J}}_l(1)-\hat{\mathrm{K}}_l(1)]-e_k|k(1)\rangle = 0. \tag{6.20}$$

For arbitrary variations of MO it can be satisfied only when

$$\begin{aligned} &\left\{[\hat{\mathrm{h}}(1)+\sum_{l=1}^{p}[2\hat{\mathrm{J}}_l(1)-\hat{\mathrm{K}}_l(1)]\right\}\phi_k(1) \equiv \hat{\mathrm{F}}(1)\,\phi_k(1) = e_k\phi_k(1), \\ &k = 1, 2, \ldots, p. \end{aligned} \tag{6.21}$$

Again, since the effective *Fock operator*

$$\begin{aligned} \hat{\mathrm{F}}(\boldsymbol{r}) &= -\frac{1}{2}\Delta + v(\boldsymbol{r}) + \sum_{l=1}^{p}[2\hat{\mathrm{J}}_l(\boldsymbol{r})-\hat{\mathrm{K}}_l(\boldsymbol{r})]\} \equiv \hat{\mathrm{h}}(\boldsymbol{r})+\hat{\mathrm{J}}(\boldsymbol{r})-\hat{\mathrm{K}}(\boldsymbol{r}) \\ &\equiv -\frac{1}{2}\Delta + [v(\boldsymbol{r})+v_{\mathrm{HF}}(\boldsymbol{r})] \equiv -\frac{1}{2}\Delta + V_{\mathrm{HF}}(\boldsymbol{r}), \end{aligned} \tag{6.22}$$

depends on the orbitals it is supposed to determine, $\hat{\mathrm{F}} = \hat{\mathrm{F}}[\boldsymbol{\varphi}_{\mathrm{HF}}]$, one has to solve the above HF equations iteratively:

$$\ldots \to \boldsymbol{\varphi}_{\mathrm{HF}}^{(n)}\Big\} \to \Big\{\hat{\mathrm{F}}\Big[\boldsymbol{\varphi}_{\mathrm{HF}}^{(n)}\Big] \to \boldsymbol{\varphi}_{\mathrm{HF}}^{(n+1)}\Big\} \to \Big\{\hat{\mathrm{F}}\Big[\boldsymbol{\varphi}_{\mathrm{HF}}^{(n+1)}\Big] \to \ldots,$$

until one reaches the *self-consistent field* (SCF) of the two-electron contribution $v_{\mathrm{HF}}(\boldsymbol{r})$ to the effective external potential $V_{\mathrm{HF}}(\boldsymbol{r})$, called the Coulomb-exchange potential:

$$v_{\mathrm{HF}}\Big[\boldsymbol{r};\boldsymbol{\varphi}_{\mathrm{HF}}^{(m+1)}\Big] \cong v_{\mathrm{HF}}\Big[\boldsymbol{r};\boldsymbol{\varphi}_{\mathrm{HF}}^{(m)}\Big] \quad \text{or} \quad \boldsymbol{\varphi}_{\mathrm{HF}}^{(m+1)} \cong \boldsymbol{\varphi}_{\mathrm{HF}}^{(m)}.$$

The physical meaning of the diagonal Lagrangian multiplier e_k is again revealed by multiplying (6.21) from the left by $\phi_k^*(1)$ and integrating over positions of electron "1":

$$\begin{aligned} e_k &= \langle \phi_k|\hat{\mathrm{F}}|\phi_k\rangle = \langle k(1)|\left[\hat{\mathrm{h}}(1) + \sum_{l=1}^{p}\left[2\hat{\mathrm{J}}_l(1) - \hat{\mathrm{K}}_l(1)\right]\right]|k(1)\rangle_1 \\ &= h_{k,k}[\phi_k] + \sum_{l=1}^{p}\left(2J_{k,l}[\phi_k,\phi_l] - K_{k,l}[\phi_k,\phi_l]\right). \end{aligned} \tag{6.23}$$

This orbital energy of kth MO in HF theory thus combines the corresponding kinetic and nuclear attraction energies, given by the expectation value of the one-electron operator $\hat{\mathrm{h}}(1)$, and the effective Coulomb-exchange interactions with all remaining electrons. It should be observed that in (6.23) the *self*-interaction of the electron with itself is exactly eliminated by the identity $J_{k,k} = K_{k,k}$, whereas in (6.12) it is removed by the Kronecker-delta factor.

The *Koopmans theorem* links the approximate estimate of the system ionization potentials I_k, the energy required to remove the electron occupying ϕ_k,

$$I_k^{\mathrm{HF}} = E_k^+[\boldsymbol{\varphi}^+] - E^0[\boldsymbol{\varphi}^0], \tag{6.24a}$$

with the orbital energy e_k; here $\boldsymbol{\varphi}^+$ denotes the optimum MO of the HF method occupied in the *cation* X_k^+, the $(N-1)$-electron system in state $|\phi_1^+\phi_1^- \ldots\ \phi_k^+ \ldots \phi_p^+\phi_p^-|$, and $\boldsymbol{\varphi}^0$ groups the optimum MO of the *neutral* N-electron system X^0 in state $\left|\phi_1^+\phi_1^- \ldots\ \phi_k^+\phi_k^- \ldots\ \phi_p^+\phi_p^-\right|$. By assuming that the HF MO $\boldsymbol{\varphi}^0$ of the neutral system X^0 are to a good approximation preserved after ionization, $\boldsymbol{\varphi}^+ \approx \boldsymbol{\varphi}^0$, i.e., neglecting the *orbital relaxation* accompanying the ionization process, one can express the electronic energy $E_k^+[\boldsymbol{\varphi}^0]$ of the resulting cation in terms of the same one- and two-electron integrals $\{h_{k,k}[\phi_k^0]\}$, $\{J_{k,l}[\phi_k^0,\phi_l^0]\}$, and $\{K_{k,l}[\phi_k^0,\phi_l^0]\}$ as those used for expressing the energy $E^0[\boldsymbol{\varphi}^0]$ of the neutral system. Their difference then approximates the HF ionization potential of (6.24a):

$$I_k^{\mathrm{HF}} \approx E_k^+[\boldsymbol{\varphi}^0] - E^0[\boldsymbol{\varphi}^0] \equiv \Delta E_k\left(\Delta\boldsymbol{n}_k;\boldsymbol{\varphi}^0\right) = -e_k[\boldsymbol{\varphi}^0], \tag{6.24b}$$

where $\boldsymbol{n} = \{n_k\}$ groups the MO occupation numbers and $\Delta\boldsymbol{n}_k = (0, \ldots, \Delta n_k = -1, 0, \ldots, 0)$ reflects a removal of the electron occupying ϕ_k.

It should be observed that since in this ionization process a change in the occupation number of ϕ_k, $\Delta n_k = -1$, the above formulation of the Koopmans theorem can be also interpreted as the *finite*-difference approximation of the energy derivative with respect to the system occupation number of ϕ_k, or the overall number of electrons, $dN = dn_k$,

$$\partial\Delta E_k\left(\Delta\boldsymbol{n}_k;\boldsymbol{\varphi}^0\right)/\partial n_k \approx \Delta E_k\left(\Delta\boldsymbol{n}_k;\boldsymbol{\varphi}^0\right)/\Delta n_k = e_k. \tag{6.25}$$

Thus, the canonical orbital energy approximately measures the slope of the electronic energy with respect to the MO occupation number.

In addition to the Coulomb correlation neglected in the orbital approximation of the HF theory, the Koopmans theorem does not account for the orbital relaxation. Fortunately, there is a substantial cancelation of these errors in electron removal process, since the magnitude of correlation energy increases monotonically with a growing number of electrons. Thus, the sum of a diminished correlation and the (neglected) orbital relaxation energy in the cation roughly reproduces a larger correlation error in the neutral system. The orbital relaxation error gradually disappears in large systems, for large N, when the removal of a single electron causes a relatively minor perturbation of the whole system. In such cases, the change in the Coulomb correlation of electrons is also relatively small. Accordingly, these errors become relatively large in the two-electron systems, e.g., the helium atom and hydrogen molecule. This cancelation of the orbital relaxation and electron Coulomb correlation errors in the electron removal processes explains a surprisingly good performance of Koopmans' theorem in the closed-shell systems. It also provides a physical justification for calling the canonical MO of HF method the *spectroscopic orbitals*.

The molecular electron density [see (3.7)] is the sum of the corresponding MO contributions:

$$\begin{aligned}\rho(\boldsymbol{r}) &= \sum_{k=1}^{N} |\phi_k(\boldsymbol{r})|^2 = \sum_{k=1}^{N} \rho_k(\boldsymbol{r}) \\ &= \sum_{\sigma=\uparrow,\downarrow} \left[\sum_{l=1}^{N_\sigma} |\phi_{l\sigma}(\boldsymbol{r})|^2 \right] = \sum_{\sigma=\uparrow,\downarrow} \left[\sum_{l=1}^{N_\sigma} \rho_{l\sigma}(\boldsymbol{r}) \right] \equiv \sum_{\sigma=\uparrow,\downarrow} \rho_\sigma(\boldsymbol{r}), \qquad (6.26)\end{aligned}$$

where $\phi_{l\sigma}(\boldsymbol{r})$ denotes lth orbital describing the electron with the spin orientation $\sigma = \uparrow, \downarrow$, $\rho_\sigma(\boldsymbol{r})$ stands for the corresponding spin density (3.9), and $N_\sigma = \int \rho_\sigma(\boldsymbol{r}) d\boldsymbol{r}$ is the overall number of electrons with spin σ,

$$\sum_{\sigma=\uparrow,\downarrow} N_\sigma = N.$$

Compared with the system *promolecule* M^0, the hypothetical combination of all constituent (free) atoms in their molecular positions, it exhibits an accumulation of the electronic probability density in the bonding regions of the molecule M, between the nuclei of the bonded AIM. The promolecular reference can be used to extract the effects due to the bond formation, e.g., in form of the *density difference* function

$$\Delta\rho(\boldsymbol{r}) = \rho(\boldsymbol{r}) - \rho^0(\boldsymbol{r}), \qquad (6.27)$$

where ρ^0 denotes the promolecular electron density.

The delocalized (canonical) MO, which reflect the molecular geometry, have been widely used in physical interpretations of the bonding patterns of molecular systems, their structural preferences, and in rationalizing diverse phenomena of electronic spectroscopy. They are also successfully applied in diagnosing trends in chemical reactivity, particularly in organic chemistry. The most important in these applications are the *Frontier Orbitals* (FO), including the *Highest Occupied* MO (HOMO) and the *Lowest Unoccupied* MO (LUMO). The former roughly determines how the energetically most accessible (first) *ionization* process, the electron *removal* to the system environment when the system acts as the chemical *base* (electron donor), affects its electron distribution, whereas the latter gives an approximate representation of the charge redistribution accompanying the electron *addition* to the system in molecular complexes or in the *electron affinity* phenomena when the system acts as the chemical *acid* (electron acceptor).

The normalized responses of the molecular electron density to an addition/removal of a single electron are known as the *Fukui function* (FF) descriptors (Parr and Yang 1984). It follows from these intuitive considerations that they are dominated by the topology of the corresponding FO densities. In the *donor–acceptor* interactions between molecules the FO of both reactants also play a crucial role in shaping their reactivity preferences.

To conclude this section, we observe that the HF equations for the optimum shapes of orbitals can be also derived through the functional derivatives of Sect. 2.8. As we have observed in Sect. 6.1.1, there are two groups of independent functions to be optimized when determining the extremum of the auxiliary energy functionals of (6.14) and (6.16), $\boldsymbol{\varphi}_{\mathrm{HF}} = \{\phi_l\}$ and $\boldsymbol{\varphi}^*_{\mathrm{HF}} = \left\{\phi^*_k\right\}$, since they are linearly related to independent components $\mathrm{Re}(\boldsymbol{\varphi}_{\mathrm{HF}})$ and $\mathrm{Im}(\boldsymbol{\varphi}_{\mathrm{HF}})$ of the (complex) canonical orbitals. This calls for the separate optimizations of $\boldsymbol{\varphi}^*_{\mathrm{HF}}$ and $\boldsymbol{\varphi}_{\mathrm{HF}}$, each giving the same set of equations for the optimum solutions. It can be easily verified that the vanishing functional derivative of the auxiliary functional of (6.17), $\mathcal{E}_{\mathrm{HF}}[\boldsymbol{\varphi}_{\mathrm{HF}};\, \mathbf{e}] = \mathcal{E}_{\mathrm{HF}}\left[\boldsymbol{\varphi}^*_{\mathrm{HF}},\, \boldsymbol{\varphi}_{\mathrm{HF}};\, \mathbf{e}\right]$, with respect to, say, ϕ^*_k, directly gives the HF equation for this MO:

$$\begin{aligned}
\delta\mathcal{E}_{\mathrm{HF}}\left[\boldsymbol{\varphi}^*_{\mathrm{HF}}, \boldsymbol{\varphi}_{\mathrm{HF}}; \mathbf{e}\right]/\delta\phi^*_k(\boldsymbol{r}) &= \delta E_{\mathrm{HF}}\left[\boldsymbol{\varphi}^*_{\mathrm{HF}}, \boldsymbol{\varphi}_{\mathrm{HF}}; \mathbf{e}\right]/\delta\phi^*_k(\boldsymbol{r}) - e_k\delta\langle\phi_k|\phi_k\rangle/\delta\phi^*_k(\boldsymbol{r}) \\
&= \hat{\mathrm{h}}(\boldsymbol{r})\phi_k(\boldsymbol{r}) + \sum_{l=1}^{N}\left(\hat{\mathrm{J}}_l(\boldsymbol{r}) - \hat{\mathrm{K}}_l(\boldsymbol{r})\right)\,\phi_k(\boldsymbol{r}) - e_k\phi_k(\boldsymbol{r}) \\
&\equiv [\hat{\mathrm{h}}(\boldsymbol{r}) + \hat{\mathrm{J}}(\boldsymbol{r}) - \hat{\mathrm{K}}(\boldsymbol{r})]\phi_k(\boldsymbol{r}) - e_k\phi_k(\boldsymbol{r}) \\
&= \hat{\mathrm{F}}(\boldsymbol{r})\phi_k(\boldsymbol{r}) - e_k\phi_k(\boldsymbol{r}) = 0.
\end{aligned} \tag{6.28}$$

In the ground state of the N-electron system, only N lowest SO are occupied, with the remaining higher (empty) SO determining the system *virtual* orbitals. The latter have no physical meaning, since they do not contribute to the self-consistent field of electronic interactions and to expectation values of physical properties of the molecule. Thus, the ground state virtual orbitals become "physical", when they are fully or partly occupied, e.g., in the electronically excited states or in the CI description of the ground state. Notice that when one uses the LUMO as a probe in the electron-absorbing phenomena, one mentally populates this orbital in the intermolecular interactions with at least a fraction of an electron, thus making it physically meaningful in reactivity descriptions.

6.1.3 Transition-State Concept

The HF equations (6.21) can be compactly written in terms of the system electron density $\rho(\boldsymbol{r})$ (6.26) and the spin components $\{\gamma_\sigma(\boldsymbol{r},\boldsymbol{r}')\}$ of the overall (spinless) one-electron *density matrix*:

$$\gamma(\boldsymbol{r},\boldsymbol{r}') = \sum_{k=1}^{N} \phi_k(\boldsymbol{r})\phi_k^*(\boldsymbol{r}') = \sum_{\sigma=\uparrow,\downarrow} \left[\sum_{l=1}^{N_\sigma} \phi_{l\sigma}(\boldsymbol{r})\phi_{l\sigma}^*(\boldsymbol{r}')\right] = \sum_{\sigma=\uparrow,\downarrow} \gamma_\sigma(\boldsymbol{r},\boldsymbol{r}'). \tag{6.29}$$

Indeed, a straightforward transformation of HF equations for the optimum orbitals of spin σ gives:

$$\begin{aligned}
&\left[\hat{\mathrm{h}}(\boldsymbol{r}) + \sum_{\sigma=\uparrow,\downarrow}\sum_{l=1}^{N\sigma} \hat{\mathrm{J}}_{l\sigma}(\boldsymbol{r})\right]\phi_{l\sigma}(\boldsymbol{r}) - \sum_{l=1}^{N\sigma} \hat{\mathrm{K}}_{l\sigma}(\boldsymbol{r})\,\phi_{l\sigma}(\boldsymbol{r})\\
&\quad\equiv [\hat{\mathrm{h}}(\boldsymbol{r}) + \hat{\mathrm{J}}(\boldsymbol{r}) - \hat{\mathrm{K}}_\sigma(\boldsymbol{r})]\phi_{l\sigma}(\boldsymbol{r})\\
&\quad= \left(-\frac{\nabla^2}{2} + v(\boldsymbol{r}) + \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}'\right)\phi_{l\sigma}(\boldsymbol{r}) - \int \frac{\gamma_\sigma(\boldsymbol{r},\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\phi_{l\sigma}(\boldsymbol{r}')\,d\boldsymbol{r}' = e_{l\sigma}\phi_{l\sigma}(\boldsymbol{r}),\\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\sigma = \uparrow,\downarrow\,.
\end{aligned} \tag{6.30}$$

Any set of N occupied orthonormal orbitals $\{\phi_{l\sigma}\}$ that satisfy these equations makes the total energy stationary. The energy expression (6.14) refers to the special case of the ground state (full) occupation pattern of N lowest orbitals, $\boldsymbol{n}_{g.s,} = [(1,1, \ldots, 1,)\ 0, 0, \ldots] = \{n_{l\sigma}\}$, of the whole (infinite) set of orbitals $\boldsymbol{\varphi}_{\mathrm{HF}} = [(\phi_1, \phi_2, \ldots, \phi_N), \phi_{N+1}, \phi_{N+2}, \ldots] = \{\phi_{l\sigma}\}$, arranged in such a way that $e_1 \le e_2 \le e_3 \le \ldots$, including the infinite set of *virtual* SO $\{\phi_{N+1}, \phi_{N+2}, \ldots\}$, which are not occupied in the ground-state configuration. Hence, for any fixed vector $\boldsymbol{n}$ of electron occupations obtained via the associated electron excitations from the ground state occupied to virtual subspaces, with

$$\begin{aligned}
&\sum_{k=1}^{\infty} n_k = \sum_{\sigma=\uparrow,\downarrow}\sum_{l=1}^{\infty} n_{l,\sigma} = \sum_{\sigma=\uparrow,\downarrow} N_\sigma = N,\\
&\rho^{(\boldsymbol{n})}(\boldsymbol{r}) = \sum_{k=1}^{\infty} n_k\left|\phi_k^{(\boldsymbol{n})}(\boldsymbol{r})\right|^2 \equiv \sum_{k=1}^{\infty} n_k\rho_k^{(\boldsymbol{n})}(\boldsymbol{r}) = \sum_{\sigma=\uparrow,\downarrow}\left[\sum_{l=1}^{\infty} n_{l\sigma}\left|\phi_{i\sigma}^{(\boldsymbol{n})}(\boldsymbol{r})\right|^2\right] = \sum_{\sigma=\uparrow,\downarrow} \rho_\sigma^{(\boldsymbol{n})}(\boldsymbol{r}),\\
&\gamma^{(\boldsymbol{n})}(\boldsymbol{r},\boldsymbol{r}') = \sum_{k=1}^{\infty} n_k\phi_k^{(\boldsymbol{n})}(\boldsymbol{r})\phi_k^{(\boldsymbol{n})*}(\boldsymbol{r}') \equiv \sum_{k=1}^{\infty} n_k\gamma_k^{(\boldsymbol{n})}(\boldsymbol{r},\boldsymbol{r}')\\
&\qquad= \sum_{\sigma=\uparrow,\downarrow}\left[\sum_{l=1}^{\infty} n_{l\sigma}\phi_{l\sigma}^{(\boldsymbol{n})}(\boldsymbol{r})\phi_{l\sigma}^{(\boldsymbol{n})*}(\boldsymbol{r}')\right] = \sum_{\sigma=\uparrow,\downarrow} \gamma_\sigma^{(\boldsymbol{n})}(\boldsymbol{r},\boldsymbol{r}'),
\end{aligned} \tag{6.31}$$

the HF electronic energy is given by the following expression in terms of the self-consistent canonical orbitals for the specified electron occupation vector $\boldsymbol{n}$, $\boldsymbol{\varphi}^{(\boldsymbol{n})} = \left\{\phi_k^{(\boldsymbol{n})} = \phi_{l\sigma}^{(\boldsymbol{n})}\right\}$, the associated electron density $\rho^{(\boldsymbol{n})}(\boldsymbol{r})$, spin densities $\{\rho_\sigma^{(\boldsymbol{n})}(\boldsymbol{r})\}$, and spin density matrices $\{\gamma_\sigma^{(\boldsymbol{n})}(\boldsymbol{r},\boldsymbol{r}')\}$:

$$\begin{aligned} E_{\mathrm{HF}}(\boldsymbol{n}) &= -\frac{1}{2}\sum_{k=1}^{\infty} n_k \int \phi_k^{(\boldsymbol{n})*}(\boldsymbol{r})\,\Delta\,\phi_k^{(\boldsymbol{n})}(\boldsymbol{r})\,d\boldsymbol{r} + \int \rho^{(\boldsymbol{n})}(\boldsymbol{r})\,v(\boldsymbol{r})\,d\boldsymbol{r} \\ &\quad + \frac{1}{2}\int\!\!\int \frac{\rho^{(\boldsymbol{n})}(\boldsymbol{r})\rho^{(\boldsymbol{n})}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,d\boldsymbol{r}\,d\boldsymbol{r}' - \frac{1}{2}\sum_{\sigma=\uparrow,\downarrow}\int\!\!\int \frac{\gamma_\sigma^{(\boldsymbol{n})}(\boldsymbol{r},\boldsymbol{r}')\gamma_\sigma^{(\boldsymbol{n})}(\boldsymbol{r}',\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}\,d\boldsymbol{r}\,d\boldsymbol{r}'. \end{aligned} \tag{6.32}$$

In the ordinary *ground state* (g.s.) HF calculations in each iterative step only the orbitals with N-lowest energies are used to form the Slater determinant, but one is by no means restricted to this choice: any occupation vector for which the procedure converges will determine the self-consistent solutions defining the determinantal approximation of an *excited state* (e.s.) of the N-electron system under consideration. It should be stressed, however, that the Slater determinants corresponding to different occupation vectors are not orthogonal, since they represent eigenfunctions of different Fock operators, with their effective electron interactions being defined by different sets of canonical MO. For the same reason the optimum, self-consistent orbitals in different electron configurations are not identical: $\phi_k^{(\boldsymbol{n})} \neq \phi_k^{(\boldsymbol{n}')}$.

The generalized self-consistent HF energy of (6.32), with the fully relaxed orbitals for the assumed occupation vector $\boldsymbol{n} = \{n_k \equiv n_{k\sigma}\}$, thus becomes a function of the continuous occupation variables $\{0 \le n_k \le 1\}$. As first shown by Slater the partial derivative of this function with respect to the orbital occupation gives exactly its orbital energy for the assumed occupation vector [compare the approximate Koopmans' relation of (6.25)]:

$$\begin{aligned} \left.\frac{\partial E_{\mathrm{HF}}(\boldsymbol{n})}{\partial n_k}\right|_{\boldsymbol{n}} &= e_k(\boldsymbol{n}) = \left.\frac{\partial E_{\mathrm{HF}}(\boldsymbol{n})}{\partial n_{k\sigma}}\right|_{\boldsymbol{n}} = e_{k\sigma}(\boldsymbol{n}) \\ &= -\frac{1}{2}\int \phi_k^{(\boldsymbol{n})*}(\boldsymbol{r})\,\Delta\,\phi_k^{(\boldsymbol{n})}(\boldsymbol{r})\,d\boldsymbol{r} + \int \rho_k^{(\boldsymbol{n})}(\boldsymbol{r})\,v(\boldsymbol{r})\,d\boldsymbol{r} \\ &\quad + \int\!\!\int \frac{\rho_k^{(\boldsymbol{n})}(\boldsymbol{r})\rho^{(\boldsymbol{n})}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,d\boldsymbol{r}\,d\boldsymbol{r}' - \int\!\!\int \frac{\gamma_{k\sigma}^{(\boldsymbol{n})}(\boldsymbol{r},\boldsymbol{r}')\gamma_\sigma^{(\boldsymbol{n})}(\boldsymbol{r}',\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}\,d\boldsymbol{r}\,d\boldsymbol{r}'. \end{aligned} \tag{6.33}$$

This relation has been subsequently rediscovered and somewhat extended by Janak (1978) in the framework of KS DFT.

It is tempting to use two independent SCF calculations, for the ground state occupations $\boldsymbol{n}_{g.s.} = \boldsymbol{n}_0$ and the *singly* excited electron configuration $\boldsymbol{n}_{e.s.} = \boldsymbol{n}_{p\to q}$ corresponding to an electron transfer from the ground state occupied orbital ϕ_p to ground state virtual orbital ϕ_q, to calculate the approximate excitation energy as the difference of the corresponding total electronic energies,

$$\Delta E_{p\to q} \approx E_{\mathrm{HF}}(\boldsymbol{n}_{p\to q}) - E_{\mathrm{HF}}(\boldsymbol{n}_0), \tag{6.34}$$

where:

$$\begin{aligned}\Psi_{g.s.}(N) &= \det(\phi_1, \ldots, \phi_{p-1}, \phi_p, \phi_{p+1}, \ldots, \phi_N) \equiv \Psi_0(N),\\ \Psi_{e.s.}(N) &= \det(\phi_1, \ldots, \phi_{p-1}, \phi_{p+1}, \ldots, \phi_N, \phi_q) = \Psi_{p\to q}(N) \equiv \Psi_p^q(N).\end{aligned} \tag{6.35}$$

However, besides requiring two separate SCF calculations, this recipe is not sound numerically, since the two states are not orthogonal anyway and it determines the small quantity of the excitation energy as difference of two approximate large numbers.

Slater's (1974) concept of the *transition state* (TS) allows one to determine the approximate $p \longrightarrow q$ excitation energy in a *single* SCF calculation as the difference of orbital energies (small numbers) for the hypothetical system exhibiting the half occupations of the two MO involved in the $p \longrightarrow q$ transition and the full occupations of the remaining orbitals defining the Slater determinant $\Psi_{p\to q}(N)$ in (6.35):

$$\boldsymbol{n}_{\mathrm{TS}} = \begin{bmatrix} \phi: & 1 & \ldots & p-1 & p & p+1 & \ldots & N & q \\ n_\phi: & 1 & \ldots & 1 & 1/2 & 1 & \ldots & 1 & 1/2 \end{bmatrix}. \tag{6.36}$$

The electron density of TS is thus given by the following expression,

$$\rho_{\mathrm{TS}}(\boldsymbol{r}) = \sum_{l\neq p}^{N} |\phi_l(\boldsymbol{r})|^2 + \frac{1}{2}\left[|\phi_p(\boldsymbol{r})|^2 + |\phi_q(\boldsymbol{r})|^2\right] = \frac{1}{2}[\rho_0(\boldsymbol{r}) + \rho_{p\to q}(\boldsymbol{r})], \tag{6.37}$$

where $\rho_0(\boldsymbol{r})$ and $\rho_{p\to q}(\boldsymbol{r})$ denote the electron densities in the ground and excited states, respectively.

Therefore, $\rho_{\mathrm{TS}}(\boldsymbol{r})$ does not correspond to a single Slater determinant. Indeed, it represents the ensemble average (see Sect. 3.3.4) of the electron densities in the initial and final electronic states of this electron excitation [see (6.35)], corresponding to the density operator (3.60a)

$$\hat{\mathrm{D}}_{\mathrm{TS}} = |\Psi_0\rangle \frac{1}{2} \langle\Psi_0| + |\Psi_{p\to q}\rangle \frac{1}{2} \langle\Psi_{p\to q}|. \tag{6.38}$$

Slater's TS thus represents an ensemble, i.e., the statistical mixture of two electronic states, and not the pure (single) quantum mechanical state.

Since this concept invokes the continuous orbital occupations of orbitals p and q, which are involved in this electron transfer, linked by the closure relation $n_p + n_q = 1$ or $-\delta n_p = \delta n_q = \delta n = 1/2$, one can expand the HF energies in the initial and final electronic states involved in this electron excitation as the corresponding power series in the associated TS vector of displacements in the orbital occupations,

$$\begin{aligned}\delta \boldsymbol{n}_{\mathrm{TS}} &= \boldsymbol{n}_{\mathrm{TS}} - \boldsymbol{n}_0 \\ &= \begin{bmatrix} \phi: & 1 & \ldots & p-1 & p & p+1 & \ldots & N & q \\ \delta n_\phi: & 0 & \ldots & 0 & -1/2 & 0 & \ldots & 0 & +1/2 \end{bmatrix},\end{aligned} \tag{6.39}$$

with $\boldsymbol{n}_0 = \boldsymbol{n}_{\mathrm{TS}} - \delta \boldsymbol{n}_{\mathrm{TS}}$ and $\boldsymbol{n}_{p\to q} = \boldsymbol{n}_{\mathrm{TS}} + \delta \boldsymbol{n}_{\mathrm{TS}}$. Thus, expanding the electronic energies of these two states around the TS configuration $\boldsymbol{n}_{\mathrm{TS}}$ generates the following Taylor series expressions for these two self-consistent energies:

$$\begin{aligned} E_{\mathrm{HF}}(\boldsymbol{n}_0) &= E_{\mathrm{HF}}(\boldsymbol{n}_{\mathrm{TS}} - \delta\boldsymbol{n}_{\mathrm{TS}}) = E_{\mathrm{HF}}(\boldsymbol{n}_{\mathrm{TS}}) - \delta n \left(\left.\frac{\partial E_{\mathrm{HF}}}{\partial n_q}\right|_{\boldsymbol{n}_{\mathrm{TS}}} - \left.\frac{\partial E_{\mathrm{HF}}}{\partial n_p}\right|_{\boldsymbol{n}_{\mathrm{TS}}} \right) \\ &\quad + \frac{(\delta n)^2}{2} \left\{ \left.\frac{\partial^2 E_{\mathrm{HF}}}{\partial n_p^2}\right|_{\boldsymbol{n}_{\mathrm{TS}}} - 2\left.\frac{\partial^2 E_{\mathrm{HF}}}{\partial n_p \partial n_q}\right|_{\boldsymbol{n}_{\mathrm{TS}}} + \left.\frac{\partial^2 E_{\mathrm{HF}}}{\partial n_q^2}\right|_{\boldsymbol{n}_{\mathrm{TS}}} \right\} + \ldots, \\ E_{\mathrm{HF}}(\boldsymbol{n}_{p\to q}) &= E_{\mathrm{HF}}(\boldsymbol{n}_{\mathrm{TS}} + \delta\boldsymbol{n}_{\mathrm{TS}}) = E_{\mathrm{HF}}(\boldsymbol{n}_{\mathrm{TS}}) + \delta n \left(\left.\frac{\partial E_{\mathrm{HF}}}{\partial n_q}\right|_{\boldsymbol{n}_{\mathrm{TS}}} - \left.\frac{\partial E_{\mathrm{HF}}}{\partial n_p}\right|_{\boldsymbol{n}_{\mathrm{TS}}} \right) \\ &\quad + \frac{(\delta n)^2}{2} \left\{ \left.\frac{\partial^2 E_{\mathrm{HF}}}{\partial n_p^2}\right|_{\boldsymbol{n}_{\mathrm{TS}}} - 2\left.\frac{\partial^2 E_{\mathrm{HF}}}{\partial n_p \partial n_q}\right|_{\boldsymbol{n}_{\mathrm{TS}}} + \left.\frac{\partial^2 E_{\mathrm{HF}}}{\partial n_q^2}\right|_{\boldsymbol{n}_{\mathrm{TS}}} \right\} + \ldots, \end{aligned} \tag{6.40}$$

A subsequent subtraction of these expansions and use of (6.33) finally give:

$$\begin{aligned} \Delta E_{p\to q} &= E_{\mathrm{HF}}(\boldsymbol{n}_{p\to q}) - E_{\mathrm{HF}}(\boldsymbol{n}_0) = \left.\frac{\partial E_{\mathrm{HF}}}{\partial n_q}\right|_{\boldsymbol{n}_{\mathrm{TS}}} - \left.\frac{\partial E_{\mathrm{HF}}}{\partial n_p}\right|_{\boldsymbol{n}_{\mathrm{TS}}} + O(\delta \boldsymbol{n}_{\mathrm{TS}}^3) \\ &= e_q(\boldsymbol{n}_{\mathrm{TS}}) - e_p(\boldsymbol{n}_{\mathrm{TS}}) + O(\delta \boldsymbol{n}_{\mathrm{TS}}^3). \end{aligned} \tag{6.41}$$

To summarize, the $p \to q$ excitation energy can be estimated, neglecting very small terms of order $\delta \boldsymbol{n}_{\mathrm{TS}}^3$, as the difference of energies of two orbitals involved in the transition, obtained from a single SCF calculation for the TS occupations $\boldsymbol{n}_{\mathrm{TS}}$ of (6.36).

6.1.4 Analytical Realization of Hall and Roothaan

In atoms, for which the angular parts of AO are given by the spherical harmonics, the radial self-consistent field can be determined numerically. However, in all molecular applications the analytical realization of the HF method, which adopts the Ritz variant of the variational method (Sect. 5.1.2) to determine the optimum MO approximated as linear combinations (LC) of the fixed *basis set* of the AO functions. For example, the canonical AO of the system constituent AIM are selected as basis functions in the LCAO MO approach, or some arbitrary functions selected for reasons of numerical convenience, e.g., the exponential *Slater-type orbitals* (STO) or *Gaussian-type orbitals* (GTO), are used to expand MO in the associated LCSTO (e.g., Harris 1967; Clementi and Roetti 1974) and LCGTO (e.g., Shavitt 1963; Boys 1968; Pople 1976; Dunning and Hay 1977; Huzinaga et al. 1984; Poirier et al. 1985) calculations, respectively. The former,

$$s_{s,\alpha}^{l,m}(\boldsymbol{r}_\alpha) = N\exp(-\zeta_s r_\alpha)\,Y_l^m(\theta,\varphi), \tag{6.42a}$$

where N stands for the normalization constant, $\boldsymbol{r}_a = \boldsymbol{r} - \boldsymbol{R}_a = x_\alpha \boldsymbol{i} + y_\alpha \boldsymbol{j} + z_\alpha \boldsymbol{k} = (r_a, \theta, \varphi)$ is the position vector of an electron relative to the atomic nucleus α in the fixed position $\boldsymbol{R}_\alpha = X_\alpha \boldsymbol{i} + Y_\alpha \boldsymbol{j} + Z_\alpha \boldsymbol{k}$ (BO approximation), provide more compact expansions, since they exhibit generally correct analytical properties at both $r_\alpha \to 0$ (cusp at nucleus) and $r_\alpha \to \infty$ (exponential decay). The latter,

$$g_{s,\alpha}^{k,l,m}(\boldsymbol{r}_\alpha) \equiv N x_\alpha^k y_\alpha^l z_\alpha^m \exp(-\mu_s r_\alpha^2), \tag{6.42b}$$

exhibit incorrect behavior in both these limits, so that several GTO are required to adequately represent a single STO. However, GTO give rise to analytical expressions for the crucial (muticenter) electron repulsion integrals, for which Slater orbitals require a time-consuming numerical integration. For this reason the SCF LCGTO MO calculations dominate all molecular applications of the HF theory. This Hall–Roothaan analytical realization is customarily denoted as the SCF method.

Thus, in the SCF LCAO MO approach, the fixed set of basis functions of the Ritz method, $\boldsymbol{\chi} = (\chi_1, \chi_2, \ldots, \chi_w)$, represents the AO of constituent AIM, themselves represented as combinations of either the primitive GTO centered on atomic nuclei or their formal *contractions* combining subsets of primitive GTO, defined to limit the computational effort and maximize the variation flexibility of MO. The basis functions available in standard programs for molecular calculations range from the *minimum set*, of AO occupied in the ground states of all constituent (free) atoms, to *extended basis sets*, including the *split valence* contractions of the valence shell orbitals and some *polarization functions* corresponding to higher values of the orbital quantum number l, compared with those characterizing the AO functions of the minimum set. Such extended bases generate the required variety of both the radial (μ) and angular exponents (k, l, m) of the primitive GTO (6.42b), thus allowing for the radial expansion/contraction of bonded atoms in the molecular environment and their angular deformations (polarizations) in presence of the remaining AIM. It should be emphasized that in each of these variants several GTO-expansions of each AO/SO can be selected, which adds to the range of the basis set options available in modern software systems of the ab initio calculations (e.g., GAMESS, GAUSSIAN).

The HF orbitals are thus expanded in the adopted basis set $\boldsymbol{\chi}$, $\boldsymbol{\varphi}_{\mathrm{HF}} = \boldsymbol{\chi}\mathbf{C}$, which also determines the associated *overlap matrix* $\mathbf{S} = \langle\boldsymbol{\chi}|\boldsymbol{\chi}\rangle = \{S_{s,t} = \langle\chi_s|\chi_t\rangle\}$, defining the metric tensor of this function space. In accordance with the development of

Sect. 5.1.2, in order to formulate the relevant *secular equations* for the optimum LCAO MO coefficients $\mathbf{C} = \{C_{s,k}\}$ one also requires the *energy* (*Fock*) *matrix* $\mathbf{F} = \langle \boldsymbol{\chi}|\hat{\mathrm{F}}|\boldsymbol{\chi}\rangle = \{F_{s,t} = \langle \chi_s|\hat{\mathrm{F}}|\chi_t\rangle\}$, the basis set representation of the Fock operator [(6.22) and (6.28)], which defines the effective one-electron Hamiltonian of the HF method. For the closed-shell configuration of (5.66) expressing the matrix element $F_{s,t}$ in terms of the elementary one- and two-electron integrals in the chosen AO basis set,

$$\begin{aligned}&\{h_{s,t} = \langle \chi_s(1)|\hat{\mathrm{h}}(1)|\chi_t(1)\rangle_1\} \quad \text{and}\\ &\quad \left\{(st|uv) \equiv \langle \chi_s(1)\chi_u(2)|g(1,2)|\chi_t(1)\chi_v(2)\rangle_{1,2}\right\},\end{aligned} \tag{6.43}$$

then gives:

$$\begin{aligned}F_{s,t} &= \langle \chi_s(1)|\hat{\mathrm{h}}(1)|\chi_t(1)\rangle_1 + \sum_{k=1}^{p} \langle \chi_s(1)|2\hat{\mathrm{J}}_k(1) - \hat{\mathrm{K}}_k(1)|\chi_t(1)\rangle_1\\ &= h_{s,t} + \sum_{u=1}^{w}\sum_{v=1}^{w}\left(2\sum_{k=1}^{p} C_{v,k}C^*_{u,k}\right)\left[(st|uv) - \frac{1}{2}(sv|ut)\right]\\ &\equiv h_{s,t} + \sum_{u=1}^{w}\sum_{v=1}^{w} P_{v,u}(st \parallel uv).\end{aligned} \tag{6.44}$$

In the preceding equation we have introduced the elements of the *charge and-bond-order* (CBO, density) matrix,

$$\mathbf{P}(\mathbf{C}_o) = \{P_{v,u}\} = 2\mathbf{C}_o\mathbf{C}_o^{\dagger} = \mathbf{C}\mathbf{n}\mathbf{C}^{\dagger}, \tag{6.45}$$

where the rectangular ($w \times p$) matrix $\mathbf{C}_o$ groups the expansion coefficients of the p (doubly) *occupied* MO, i.e., the first p columns of $\mathbf{C} = (\mathbf{C}_o, \mathbf{C}_v)$ with the remaining columns $\mathbf{C}_v$ corresponding to the virtual (empty) MO, and the diagonal matrix of MO occupations $\mathbf{n} = \{n_k\delta_{k,l}\}$ with $n_k = 2$ for occupied MO and $n_k = 0$ for virtual MO in the *spin-restricted* HF (RHF) theory. They are the only component of the Fock matrix $\mathbf{F}(\mathbf{C}_o) = \mathbf{F}(\mathbf{P})$, which changes from one iteration to another, while the overlap matrix and the elementary integrals of (6.43) are calculated once at the beginning of the SCF procedure and used in all iterations to construct the current Fock matrix $\mathbf{F}(\mathbf{C}^{(k)}) = \mathbf{F}(\mathbf{P}^{(k)})$.

We also recall that in the basis set of the Löwdin orthogonalized functions (see Sect. 5.1.2),

$$\tilde{\boldsymbol{\chi}} = \boldsymbol{\chi}\mathbf{S}^{-1/2},\quad \boldsymbol{\varphi}_{\mathrm{HF}} = (\boldsymbol{\chi}\mathbf{S}^{-1/2})\,\mathbf{U} = \tilde{\boldsymbol{\chi}}\mathbf{U},\quad \mathbf{U} = \langle \tilde{\boldsymbol{\chi}}|\boldsymbol{\varphi}_{\mathrm{HF}}\rangle,\quad \mathbf{U}\mathbf{U}^{\dagger} = \mathbf{U}^{\dagger}\mathbf{U} = \mathbf{I}, \tag{6.46}$$

the transformed Fock matrix $\tilde{\mathrm{F}} = \langle \tilde{\boldsymbol{\chi}}|\hat{\mathrm{F}}|\tilde{\boldsymbol{\chi}}\rangle = \mathbf{S}^{-1/2}\mathbf{F}\mathbf{S}^{-1/2}$ defines the eigenvalue problem for determining the optimum (canonical) HF solutions in the form of the diagonalization of $\tilde{\mathbf{F}}$ in the unitary transformation $\mathbf{U}$ [see (5.37)]:

$$\mathbf{U}^{\dagger}\tilde{\mathbf{F}}\mathbf{U} = \mathbf{e} = (e_k \delta_{k,l}), \qquad \mathbf{C} = \mathbf{S}^{-1/2}\mathbf{U}. \tag{6.47}$$

Therefore, in each iteration the new Fock matrix is constructed using the CBO matrix obtained in the previous iteration; it is then transformed to the orthogonal representation and diagonalized, to determine the next approximation of the LCAO MO coefficients and hence also of the CBO matrix, the orbital energies, etc. The time-determining step in the SCF calculations is the calculation of all electron-repulsion integrals $\{(st|uv)\}$, the number of which dramatically increases with the dimension of the basis set. It scales like $O(N^4)$ with the number of electrons.

It also follows from the preceding equation that

$$\begin{aligned}\mathbf{P} = \mathbf{C}\mathbf{n}\mathbf{C}^{\dagger} &= (\mathbf{S}^{-1/2}\mathbf{U})\ \mathbf{n}\ (\mathbf{U}^{\dagger}\mathbf{S}^{-1/2}) \\ &= \mathbf{S}^{-1/2}\langle\tilde{\boldsymbol{\chi}}|\boldsymbol{\varphi}_{\mathrm{HF}}\rangle\ \mathbf{n}\ \langle\boldsymbol{\varphi}_{\mathrm{HF}}|\tilde{\boldsymbol{\chi}}\rangle\mathbf{S}^{-1/2} = \mathbf{S}^{-1}\langle\boldsymbol{\chi}|\boldsymbol{\varphi}_{\mathrm{HF}}\rangle\ \mathbf{n}\ \langle\boldsymbol{\varphi}_{\mathrm{HF}}|\boldsymbol{\chi}\rangle\mathbf{S}^{-1} \\ &= 2\mathbf{S}^{-1}\langle\boldsymbol{\chi}|\boldsymbol{\varphi}_o\rangle\langle\boldsymbol{\varphi}_o|\boldsymbol{\chi}\rangle\mathbf{S}^{-1} = 2\mathbf{S}^{-1}\left\langle\boldsymbol{\chi}|\hat{\mathrm{P}}^{o}_{\boldsymbol{\varphi}}|\boldsymbol{\chi}\right\rangle\mathbf{S}^{-1}.\end{aligned} \tag{6.48}$$

Thus, for the orthogonalized AO basis set, when $\mathbf{S} = \mathbf{S}^{-1/2} = \mathbf{S}^{-1} = \mathbf{I}$, the CBO matrix constitutes the AO representation of the projector into the *bonding subspace* consisting of all (doubly) occupied MO $\boldsymbol{\varphi}_o$ or the (singly) occupied SO $\{\boldsymbol{\varphi}_{o,\sigma}\}$ for both spin orientations of an electron:

$$\hat{\mathrm{P}}^{o}_{\boldsymbol{\varphi}} = |\boldsymbol{\varphi}_{\mathrm{o}}\rangle\langle\boldsymbol{\varphi}_o| = \sum\nolimits_{\sigma}|\boldsymbol{\varphi}_{o,\sigma}\rangle\langle\boldsymbol{\varphi}_{o,\sigma}| = \hat{\mathrm{P}}^{\alpha}_{\boldsymbol{\varphi}} + \hat{\mathrm{P}}^{\beta}_{\boldsymbol{\varphi}}.$$

6.1.5 Local Pseudopotential

The pseudopotentials, representing in the valence-only calculations the presence of atomic cores which practically do not participate in the bond-forming/breaking processes, have been introduced in Sect. 5.6. Here, we present the PK idea of the *local* pseudopotential (Phillips and Kleinman 1960), for the simplest case of the $N = n + 1$ electron system with a single valence electron occupying the normalized *pseudoorbital* ψ, nonorthogonal to the core orbitals, moving in the effective field due to the nuclei and n *inner*-shell electrons occupying the normalized and mutually orthogonal orbitals $\boldsymbol{\varphi}_c = (\varphi_1, \varphi_2, \ldots, \varphi_n)$, $\langle\varphi_i|\varphi_j\rangle = \delta_{i,j}$.

We first observe that the "frozen" core scenario calls for the Schmidt orthogonalization (Sect. 3.3.2) of the *outer*-shell pseudoorbital describing the valence electron with respect to all *inner*-shell orbitals $\boldsymbol{\varphi}_c$, which does not affect these "frozen" reference states. This way of making the core (closed) shells being "felt" by the valence electrons has also been used by Herring (1940) within the *Orthogonalized Plane Wave* (OPW) method for determining the wave function of valence electrons in crystals. Following Phillips and Kleinman we Schmidt-orthogonalize the pseudoorbital [see (3.45b)] into the new valence electron state:

$$\varphi = \mathcal{N}\left[\psi - \sum_{i=1}^{n}\varphi_i\langle\varphi_i\,|\,\psi\rangle\right] \equiv \mathcal{N}\left[\psi - \sum_{i=1}^{n}\varphi_i\alpha_i\right],\ \mathcal{N} = \left(1 - \sum_{i=1}^{n}|\alpha_i|^2\right)^{-1/2}. \quad (6.49)$$

In the framework of HF theory, the (orthogonal) canonical MO $\boldsymbol{\varphi} = (\boldsymbol{\varphi}_c, \varphi \equiv \varphi_{n+1})$ satisfy the Fock equations (6.21), $\hat{\mathrm{F}}\varphi_i = e_i\varphi_i, \quad i = 1, 2, \ldots, n+1$, with $e \equiv e_{n+1}$ denoting the orbital energy of the valence electron. It should be observed that in action of the Fock operator on the valence orbital φ the Coulomb and exchange operators due to φ exactly cancel each other, since $\hat{\mathrm{J}}_\varphi\varphi = \hat{\mathrm{K}}_\varphi\varphi$, and hence

$$\hat{\mathrm{F}}[\boldsymbol{\varphi}]\varphi = \hat{\mathrm{h}}\varphi + \sum_{i=1}^{n}(\hat{\mathrm{J}}_i - \hat{\mathrm{K}}_i)\varphi = \hat{\mathrm{F}}[\boldsymbol{\varphi}_c]\varphi. \quad (6.50)$$

Therefore, inserting (6.49) into the eigenvalue problem for the canonical valence MO, $\hat{\mathrm{F}}\varphi = e\varphi$, gives the equivalent (effective) Schrödinger equation for the pseudoorbital ψ,

$$\{\hat{\mathrm{F}}[\boldsymbol{\varphi}_c] + V_p\}\,\psi = e\psi, \quad (6.51)$$

including the local pseudopotential

$$V_p(\boldsymbol{r}) = \sum_{i=1}^{n}\frac{\alpha_i(e - e_i)\varphi_i(\boldsymbol{r})}{\psi(\boldsymbol{r})}. \quad (6.52)$$

Thus, the valence shell electron can be rigorously described by the (non-orthogonal to the core) pseudoorbital, provided that the effective potential V_{HF} of (6.22) will be supplemented with the pseudopotential V_p, which replaces the valence-core orthogonality requirement, thus making the presence of the inner shell electrons felt by the valence electron. This ab initio formulation can be extended into a general case of many valence electrons, including the correlated treatment of both the inner and outer electrons (Szasz 1985).

The equivalence of both descriptions is also directly seen when one compares the associated Slater determinants: det($\varphi_1, \varphi_2, \ldots, \varphi_n, \varphi$) and det($\varphi_1, \varphi_2, \ldots, \varphi_n, \psi$). Indeed, since ψ in the second determinant constitutes the linear combination of functions defining the first determinant (6.49) it then directly follows from the known invariance properties of determinants that both these functions in fact determine the same state of all $N = n + 1$ electrons.

6.2 Beyond HF Theory: Electron Coulomb Correlation

The HF theory, which can be also formulated in the relativistic version, exactly accounts for the exchange (x) correlation between the spin-like electrons, i.e., that part of the interdependence between the particle instantaneous positions, which originates from the Fermi statistics. However, since the product function of the truly independent particle approximation constitutes the source of the Slater determinant of (5.64), by acting on it with the antisymmetrizer Â, the HF method totally neglects the Coulomb (c) correlation between all electrons, due to a finite electronic charge. Since the spin-like, statistically correlated electrons already "avoid" each other in the determinantal wave function, the Pauli principle of the wave-function antisymmetry effectively accounts also for a large portion of their Coulomb correlation. Hence, the largest error of this missing correlation effect can be expected to originate from electrons exhibiting the opposite spin orientations, which remain statistically uncorrelated at the HF level, e.g., from electron pairs occupying the same spatial orbitals in the spin-*Restricted* HF (RHF) approach.

In atoms one distinguishes both the *radial* and *angular* correlation effects. The former has already been observed in the spin-*Unrestricted* HF (UHF), variational treatment of helium atom (Sect. 5.5.2). Namely, when one electron occupied the more compact spherical (1*s*) orbital φ_2 ($\zeta_2 = 2.18$), distributed closer to the nucleus, the other electron preferred to occupy a more diffused orbital φ_1 ($\zeta_1 = 1.19$), exhibiting a larger average distance from the nucleus. Therefore these two spin-paired electrons, which are not correlated by the Fermi statistics, indeed exhibit a distinct effect of avoiding each other radially, due to their mutual Coulomb repulsion. This effect explains the observed lowering of the total UHF electronic energy, $E_0^{\mathrm{UHF}} = -2.876$ a.u., compared with the corresponding RHF energy level, $E_0^{\mathrm{RHF}} = -2.848$ a.u., where both electrons are constrained to occupy the same AO: $\varphi_1 = \varphi_2 = \varphi$ ($\zeta = 1.69$).

However, the exact value of the ground state energy in He, $E_0 = -2.904$ a.u., indicates that if we neglect a very small relativistic correction, $|\Delta E_{rel.}| = 0.0001$ a.u., there still remains a substantial angular correlation, which has not been accounted in the above *spherical* UHF approach. Indeed, due to the mutual repulsion the two electrons at their fixed radial distances should prefer the opposite positions relative to the nucleus. This effect can be accounted for when one lifts the spherical, 1*s*-type constraints [(5.90) and (5.98)] of the two AO φ_1 and φ_2, which define the spatial part (5.104),

$$\Phi^{\mathrm{UHF}}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{\sqrt{2}}[\varphi_1(\boldsymbol{r}_1)\varphi_2(\boldsymbol{r}_2) + \varphi_1(\boldsymbol{r}_2)\varphi_2(\boldsymbol{r}_1)], \tag{6.53}$$

of the singlet UHF wave function (5.103). For example, one can approximate these orbitals by the mutually orthogonal *sp*-type hybrids along the z axis:

$$h_z = \mathcal{N}_1(\varphi_1 + Cp_z), \quad h_{-z} = \mathcal{N}_2(\varphi_2 - Cp_z), \quad p_z = \mathcal{N}_z z \exp(-\zeta r), \tag{6.54}$$

where $\mathcal{N}_1$, $\mathcal{N}_2$, and $\mathcal{N}_z$ stand for the corresponding normalization constants. One observes that the symmetric combination of the associated product functions, $h_z(\boldsymbol{r}_1)h_{-z}(\boldsymbol{r}_2) + h_z(\boldsymbol{r}_2)h_{-z}(\boldsymbol{r}_1)$, then contains the previous (spherical) $\Phi^{\mathrm{UHF}}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ function of (6.53) and the $\left[p_z^2\right]$ configuration, $p_z(1)p_z(2)$.

However, in order to keep the helium atom spherically symmetrical, we have to treat the three axes of the coordinate system on equal footing, which calls for the following trial function of the UHF approximation, extended by the *Configuration Interaction* (CI) between the ground state electron configuration $[\varphi_1\varphi_2]$ and the doubly excited configurations $(\varphi_1\varphi_2) \rightarrow (p^2) = \left\{ \left[p_x^2\right] + \left[p_y^2\right] + \left[p_z^2\right] \right\}$, in which the two electrons occupy the ground-state–virtual $2p$ orbitals,

$$\begin{aligned}\Phi^{\mathrm{UHF/CI}}(\boldsymbol{r}_1,\boldsymbol{r}_2) &= \mathcal{N}\left\{\Phi^{\mathrm{UHF}}(\boldsymbol{r}_1,\boldsymbol{r}_2) - \frac{2C^2}{3}[p_x(\boldsymbol{r}_1)p_x(\boldsymbol{r}_2) + p_y(\boldsymbol{r}_1)p_y(\boldsymbol{r}_2) + p_z(\boldsymbol{r}_1)p_z(\boldsymbol{r}_2)]\right\}\\ &= \mathcal{N}\left\{\Phi^{\mathrm{UHF}}[1s,1s'] - \frac{2C^2}{3}\left(\Phi\left[p_x^2\right] + \Phi\left[p_y^2\right] + \Phi\left[p_z^2\right]\right)\right\},\end{aligned} \tag{6.55}$$

where $\mathcal{N}$ denotes the overall normalization factor, containing only two variational parameters: the linear coefficient C and the nonlinear exponent ζ of $2p$ orbitals.

This angularly correlated wave function gives the best variational estimate of the ground state energy $E_0^{\mathrm{UHF/CI}} = -2.895\,\mathrm{a.u.}$ Therefore, this relatively simple trial wave function is already capable of accounting for almost 80% of the Coulomb correlation energy: $(2.862 - 2.895)/(2.862 - 2.904) = 0.79$, where we have used the known energy level in the RHF *limit*, $E_0^{\mathrm{RHFL}} = -2.862\,\mathrm{a.u.}$, representing the energy estimate for the "saturated," very large basis set, which practically generates the full variational flexibility of the atomic orbital.

This example suggests a systematic way for including the Coulomb correlation through CI. One first creates the orthonormal excited configurations by replacing in the HF Slater determinant the selected ground state occupied SO by the equinumerous list of the ground state virtual SO (see the Slater–Condon rules of Sect. 5.4), and then mixes them with the ground state determinant in the variational wave function of the CI theory, which combines the N-electron wave functions for the ground and excited configurations, all of them derived from the fixed set of the optimum orbitals determined in a single (ground state) SCF calculation. For example, in the RHF approach to helium atom, for which $\varphi_1 = \varphi_2 = \varphi = 1s$, the radial correlation effect in He can be introduced to the ground-state HF wave function $\Phi^{\mathrm{RHF}}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \varphi(\boldsymbol{r}_1)\varphi(\boldsymbol{r}_2) \equiv \Phi[1s^2]$ by mixing it with the doubly excited function $\Phi[2s^2] = \phi(\boldsymbol{r}_1)\phi(\boldsymbol{r}_2)$, $\phi = 2s$, resulting from the excitation of the spin-paired electrons occupying $1s$ orbital into the virtual $2s$ state: $(\varphi^+,\varphi^-) \rightarrow (\phi^+,\phi^-)$. Furthermore, to account for the angular correlation, one should also include the doubly excited configurations $\Phi\left[p_i^2\right]$, $i = x, y, z$, $(\varphi^+,\varphi^-) \rightarrow (p_i^+,p_i^-)$:

$$\Phi^{\mathrm{RHF/CI}} = \mathcal{N}'\left\{\Phi[1s^2] + C_1\Phi[2s^2] + C_2\left(\Phi[p_x^2] + \Phi[p_y^2] + \Phi[p_z^2]\right)\right\}. \tag{6.56}$$

The RHF approach often fails to properly describe the dissociation of chemical bonds, e.g., in H_2 or F_2. This so-called *static* (near-degeneracy) *correlation* error can be corrected by an inclusion in the $\Phi^{\mathrm{RHF/CI}}$ wave function of the excited configuration $\Phi\left[\sigma_u^2\right]$, obtained by exciting two valence electrons occupying the bonding σ_g MO in $\Phi_0^{\mathrm{RHF}} = \Phi\left[\sigma_g^2\right]$ to the antibonding MO σ_u, nearly degenerated with σ_g at very large internuclear separations: $\left(\sigma_g^+, \sigma_g^-\right) \to \left(\sigma_u^+, \sigma_u^-\right)$.

The formal basis for expanding the exact wave function of N electrons in terms of Slater determinants involving all SO, both the ground state occupied and virtual, comes from the so-called *expansion theorem* of quantum theory, which forms the basis for several methods in computational quantum chemistry. When the basis set of one-electron functions $\boldsymbol{\chi}(\boldsymbol{r})$ of the SCF MO method is nearly complete, the associated (orthonormal) MO, $\boldsymbol{\varphi}(\boldsymbol{r}) = \boldsymbol{\chi}(\boldsymbol{r})\mathbf{C}$, determine a practically complete set of SO in the RHF theory, $\{\psi_k(\boldsymbol{r},\sigma)\} = \{\boldsymbol{\varphi}(\boldsymbol{r})\alpha(\sigma), \boldsymbol{\varphi}(\boldsymbol{r})\beta(\sigma)\} = \{\psi_k(\boldsymbol{q})\}$, in terms of which any one-electron wave function can be expanded. For example, for the exact quantum state of a single electron, one obtains the familiar expansion:

$$\Psi(1) = \sum\nolimits_k c_k\, \psi_k(1), \quad c_k = \int \psi_k^*(\boldsymbol{q}_1)\Psi(\boldsymbol{q}_1)\, d\boldsymbol{q}_1 \equiv \langle \psi_k(1)|\Psi(1)\rangle_1 \tag{6.57}$$

The same procedure can be repeated for expanding the exact state of two electrons,

$$\begin{aligned} \Psi(1,2) &= \sum\nolimits_k c_k(2)\, \psi_k(1), \\ c_k(2) &= \int \psi_k^*(\boldsymbol{q}_1)\Psi(\boldsymbol{q}_1,\boldsymbol{q}_2)\, d\boldsymbol{q}_1 \equiv \langle \psi_k(1)|\Psi(1,2)\rangle_1, \end{aligned} \tag{6.58}$$

followed by the expansion of the coefficient function

$$c_k(2) = \sum\nolimits_l d_{k,l}\, \psi_l(2), \quad d_{k,l} = \int \psi_l^*(\boldsymbol{q}_2)c_k(\boldsymbol{q}_2)\, d\boldsymbol{q}_2 \equiv \langle \psi_l(2)|c_k(2)\rangle_2. \tag{6.59}$$

Substituting (6.59) into (6.58) finally gives:

$$\Psi(1,2) = \sum\nolimits_k \sum\nolimits_l d_{k,l}\psi_k(1)\psi_l(2), \tag{6.60}$$

with the proper exchange symmetry for fermions subsequently enforced by the antisymmetrizer $\hat{\mathrm{A}}$ of (5.64):

$$\Psi_A(1,2) = \sum\nolimits_k \sum\nolimits_l d_{k,l}\hat{\mathrm{A}}\{\psi_k(1)\,\psi_l(2)\} = \sum\nolimits_k \sum\nolimits_l d_{k,l}\det(\psi_k\ \psi_l). \tag{6.61}$$

The two-electron wave function can be thus exactly expanded in terms of two-electron Slater determinants constructed from the complete set of SO, thus giving credence to the CI expansion of the exact quantum state in He or H_2.

This expansion procedure can be straightforwardly extended to a general N-electron case:

$$\begin{aligned}\Psi_A(1,2,\ldots,N) &= \sum_{k_1}\sum_{k_2}\cdots\sum_{k_N} d_{k_1,k_2,\ldots,k_N}\hat{\mathrm{A}}\{\psi_{k_1}(1)\,\psi_{k_2}(2)\ \ldots\ \psi_{k_N}(N)\}\\ &= \sum_{k_1}\sum_{k_2}\cdots\sum_{k_N} d_{k_1,k_2,\ldots,k_N}\det\{\psi_{k_1}\psi_{k_2}\ \ldots\ \psi_{k_N}\}.\end{aligned} \tag{6.62}$$

Therefore, the exact state of N-electron systems can be always expanded as linear combination of Slater determinants of N electrons built from the complete set of SO. There is no guarantee, though, that such an expansion is fast convergent. Indeed, much of the effort in the formal CI theory (Löwdin 1959; Shavitt 1977) has been devoted to improve a generally slow convergence of this determinantal expansion.

6.2.1 Errors in SCF MO Calculations

Although the effects neglected in the HF approximation amount to a very small fraction (of the order of 1%) of the system total electronic energy, they may be crucial for even qualitatively correct prediction of the energy differences of chemical interest, e.g., energies of the ionization, dissociation, activation, and isomerization processes or conformational barriers. Indeed, this relatively minute correlation error often results in incorrect conclusions regarding dissociation energies, electronic spectra, and energy differences on PES. Such applications of the quantum theory call for the *chemical accuracy*, of the order of 1 kcal/mole $\approx$ 1.6 m Hartree, which escapes the approximations present in the SCF method. Fortunately, the theory systematic errors cancel in some energy differences, so that even at this low level of the theory one obtains quite satisfactory predictions of many molecular properties, e.g., selected conformational barriers, structural parameters (bond lengths and angles), and molecular bonding patterns. Indeed, one encounters quite frequent examples, where small basis sets and modest studies can provide important chemical insights.

In this section we identify the main sources of errors in SCF method, which effectively limit a range of its adequate applications. As shown in Fig. 6.1, the analytical SCF method using a finite number of basis functions exhibits the *basis set* error, relative to the *HF limit* (HFl) corresponding to the complete (infinite) basis set, i.e., the full variational flexibility of the function space in the Ritz method: $\Delta E_{basis} = E_{\mathrm{HFl}} - E_{\mathrm{SCF}} < 0$. In general, the *minimum basis set*, consisting of AO occupied in the ground states of constituent (free) atoms, has several interpretative advantages and generates the most physical net charges of bonded atoms predicted from Mulliken's populational analysis (Mulliken 1935, 1955, 1962). However, this small basis set often favors some conformations of molecular systems, thus introducing a nonsystematic errors in predicted energy barriers. Splitting the valence AO into the independent *short*- and *long*-range contractions in the *extended*

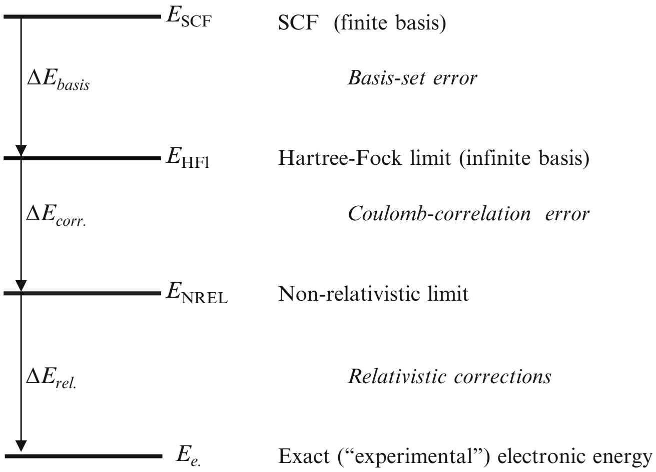


Fig. 6.1 Main sources of errors in SCF MO calculations

basis set properly describes the radial polarization of bonded atoms, while an additional inclusion of polarization functions allows for their angular adjustments in the molecular framework.

The *basis set superposition* error can also falsify the interaction energies between molecules at finite distances, since the basis functions of one reactant improves the quality of the basis function of the other reactant. To minimize this effect in the predicted interaction energy, given by the difference between the energy of the molecular complex ("supermolecule") and the sum of energies of both molecular reactants, the *counterpoise correction* of Boys and Bernardi (1970) is applied in estimating the reference energy of the two separated molecules, by using the full molecular basis set of both reactants when determining the energy of both the interacting and nearly separate reactants.

As we have already remarked in the preceding section, the other important source of error in the SCF calculations is the neglected correlation between electrons, due to their finite electric charges. This *Coulomb correlation* error, $\Delta E_{corr.} = E_{\mathrm{NREL}} - E_{\mathrm{HFl}} < 0$, is to a good approximation constant, when one compares the energies of conformations preserving the number of electronic pairs, and even more so, when the number of neighboring pairs of electrons is conserved. The main Coulomb correlation error is due to the spin-paired electrons confined to the same space occupied by the localized MO. Therefore, by preserving the number of such strongly correlated electronic pairs, one roughly preserves the overall correlation error, which then cancels out in the energy difference as the method systematic deviation. Good examples are provided by the inversion of ammonia and the "free" rotation around a single (σ) C–C bond in ethane, for which the number of the electronic pairs occupying the localized MO is the same at each stage of the conformation change.

This correlation error manifests itself strongly, when the pair-number criterion is not satisfied, e.g., in the electron ionization/attachment processes and the bond-breaking phenomena, e.g., in the bond dissociation or the "hindered" internal rotation in ethylene. It should be also observed that the RHF theory cannot explain the stability of F_2 molecule, giving the negative sign of the predicted bond dissociation energy. This is because it neglects the *dynamic* (avoidance) Coulomb correlation between the congested electronic pairs in the valence shell and fails to properly describe the *Separated Atoms Limit* (SAL), $F^0 + F^0$, giving instead a mixture of the SAL and the *ion* pair $F^+ + F^-$ state. The same *static* correlation deficiency of the RHF variant is observed in its description of the H_2 dissociation.

Finally, the *relativistic corrections*, not covered by this book, are defined as the difference between the exact (experimental) value of the electronic energy and that in the nonrelativistic limit (NREL): $\Delta E_{rel.} = E_e - E_{\mathrm{NREL}} < 0$. It combines several small energy contributions originating from the week interactions missing in the Coulombic molecular Hamiltonian of (5.51), e.g. *spin–orbit* or *spin–spin* interactions, of great importance for both the fine structure of atomic spectra and NMR and ESR experiments, the dependence of the particle mass on its speed, etc. They all require the relativistic formulation of quantum theory, in the form of the Dirac equation of state or the Pauli approximation to the Breit equation, which constitutes an approximate generalization of the Dirac equation to *many*-electron systems. The relativistic generalization of the SCF theory is known as the Dirac–Hartree–Fock (DHF) approach. Clearly, various terms in the Breit–Pauli Hamiltonian, which naturally follow from the relativistic extension of the quantum theory, can be also applied as perturbations to the nonrelativistic energy operator, and the standard perturbation theory can be then used to determine the associated corrections to the system energy.

In atoms the average correlation error per electron, $\Delta e_{corr.} = \Delta E_{corr.}/N$, stays roughly preserved with N: $\Delta e_{corr.} \approx -0.05$ a.u. The magnitude of the overall relativistic correction increases with the atomic number. For example in helium atom $|\Delta E_{rel.}(Z = 2)| = 0.0001$ a.u. $<<$ $|\Delta E_{corr.}(Z = 2)| = 0.0420$ a.u., but starting from silicon atom it exceeds the correlation energy: $|\Delta E_{rel.}(Z = 14)| = 0.584$ a.u. $>$ $|\Delta E_{corr.}| = 0.494$ a.u. In most energy differences in chemistry, e.g., in conformational energy barriers, the relativistic energy is less important, since it is dominated by the *inner*-shell electrons of atomic cores, which remain practically unaffected by the bond-forming/breaking processes taking place in the valence shell. Therefore, neglecting the relativistic terms has only a minor effect on the energetical descriptors of bond dissociations or conformational changes. For example, the relativistic correction to the dissociation energy of F_2, $D_e = 0.062$ a.u., has been estimated as $\Delta D_{e,rel.} = 0.001$ a.u. Similarly, for the dissociation of NaCl, $D_e = 0.16$ a.u., the relativistic correction $\Delta D_{e,rel.} = 0.002$ a.u. is much below the correlation error $\Delta D_{e,corr.} = 0.04$ a.u. However, the relativistic effects may strongly influence other physical properties of atoms and molecules, e.g., the bonding energies of the core electrons and atomic radii and bond lengths, particularly in systems containing heavy atoms.

6.2.2 Static and Dynamic Correlation

The spatial RHF wave function for the ground state of $H_2 = H_A$–H_B, $\Phi_0^{\mathrm{RHF}}(A-B) = \phi_b(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_2)$, in which the spin-paired electrons occupy the bonding MO, $\phi_b = \sigma_g = N_b(1s_A + 1s_B)$, $N_b = (2 + 2\langle 1s_A|1s_B\rangle)^{-1/2}$, is not capable of a proper description of the dissociation into separated atoms, H_A + H_B, described by the spatial wave function $\Phi_0^{atom.}(\infty) = \left(1/\sqrt{2}\right)\,[1s_A(\boldsymbol{r}_1)1s_B(\boldsymbol{r}_2) + 1s_A(\boldsymbol{r}_2)1s_B(\boldsymbol{r}_1)]$. Indeed, expressing the occupied MO in terms of both AO gives in the SAL:

$$\begin{aligned}\Phi_0^{\mathrm{RHF}}(A-B) &= \frac{1}{2}\{[1s_A(\boldsymbol{r}_1)1s_B(\boldsymbol{r}_2) + 1s_A(\boldsymbol{r}_2)1s_B(\boldsymbol{r}_1)] + [1s_A(\boldsymbol{r}_1)1s_A(\boldsymbol{r}_2) \\ &\quad + 1s_B(\boldsymbol{r}_1)1s_B(\boldsymbol{r}_2)]\} = \frac{1}{\sqrt{2}}[\Phi_0^{atom.}(\infty) + \Phi_0^{ion.}(\infty)]. \qquad (6.63)\end{aligned}$$

It follows from this limiting RHF wave function that it describes the equal mixture of the dissociation into atoms, represented by $\Phi_0^{atom.}(\infty)$, and into ionic pair: $(H_A^- + H_B^+)$ or $(H_B^- + H_A^+)$, represented by $\Phi_0^{ion.}(\infty)$, thus giving $E_0^{\mathrm{RHF}}(\infty)$ distinctly above $E_0(\infty) = -1$ a.u. The UHF approximation, which already includes a fraction of the Coulomb correlation, correctly predicts the dissociation into atoms in this limit.

The crucial configuration, which remedies this shortcoming of the RHF treatment in the improved CI wave function is the *double* excitation to the antibonding MO $\phi_a = \sigma_u = N_a(1s_A - 1s_B), N_b = [2 - 2\langle 1s_A|1s_B\rangle]^{-1/2}$:

$$\Phi_0^{\mathrm{CI}}(A-B) = C_1^{\mathrm{CI}}\left|\overset{+}{\phi_b}\ \overset{-}{\phi_b}\right| + C_2^{\mathrm{CI}}\left|\overset{+}{\phi_a}\ \overset{-}{\phi_a}\right|. \qquad (6.64)$$

In fact, at large internuclear distances, the HF configuration $\left|\phi_b^+\phi_b^-\right|$ and the *doubly* excited state $\left|\phi_a^+\phi_a^-\right|$ become degenerate, thus exhibiting comparable participation in this CI combination. Therefore, inclusion of both these functions in the CI expansion appears to be crucial for the correct description of the dissociation of this covalent bond. At shorter bond lengths $R \approx R_e$, where the equilibrium internuclear distance $R_e \cong 1.4$ a.u., this degeneracy is removed and hence $\left|C_1^{\mathrm{CI}}\right| \approx 1$ and $\left|C_2^{\mathrm{CI}}\right| \approx 0$, which explains a good description of the hydrogen molecule already in the RHF approximation.

This long-range, near-degeneracy Coulomb correlation is called *static*, since it is more related to the symmetry requirement of the wave function, rather than the instantaneous interaction between electrons. It calls for the inclusion of the missing $\left|\phi_a^+\phi_a^-\right|$ configuration in addition to the RHF determinant $\left|\phi_b^+\phi_b^-\right|$. This static correlation error introduces a substantial deviation of the bonding energy,

$$\Delta E_{bond}(R_e) = E_e(R_e) - E_e(\infty) \equiv -D_e < 0, \qquad (6.65)$$

overestimated relative to $E_e^{\mathrm{RHF}}(\infty)$ dissociation limit by about 6.4 eV, compared with the experimental value reproduced exactly by the theoretical calculations of Kołos and Wolniewicz (KW) (1964, 1965, 1968): $\Delta E_{bond}^{exp.}(R_e^{exp.} = 1.4006) = \Delta E_{bond}^{\mathrm{KW}}(R_e^{\mathrm{KW}} = 1.4006) = -0.1745\,\mathrm{a.u.}$ This error of the RHF wave function is already drastically reduced at the minimum CI level of (6.64), in which this energy difference is underestimated by only 1 eV. The CI expansion involving 28 most important excited configurations gives still better prediction: $\Delta E_{bond}^{\mathrm{CI(28)}}(1.40) = -0.1672\,\mathrm{a.u.}$ The bonding energy predicted in the HFL, $\Delta E_{bond}^{\mathrm{HFL}}(1.40) = -0.1336\,\mathrm{a.u.}$, allows one to estimate the overall Coulomb correlation error in H_2 for $\Delta E_{rel.}^{bond} \cong 0$ at about $\Delta E_{corr.}^{bond} \cong -0.041\,\mathrm{a.u.} = -\,1.116\,\mathrm{eV}$.

The concept of the *dynamical* correlation refers to the instantaneous avoidance of electrons due to a strong Coulomb repulsion between them in atoms and molecules, thus resulting in their tendency to assume positions, which maximize the instantaneous distances between them. This dynamical effect gives rise to both the radial and angular correlation effects in atoms, which we have discussed before. To account for this phenomenon rather extensive CI has to be included in the ab initio (*first* principle) calculations. This dynamic correlation error is crucial for the adequate determination of the atomic electron affinities measured by the difference between the energy of the neutral atom X(0) and its anion X(−1): $A_{\mathrm{X}} = E_{\mathrm{X(0)}} - E_{\mathrm{X}\,(-1)}$. For example, the HF prediction for oxygen, $A_{\mathrm{O}}^{\mathrm{HF}} = -0.54\,\mathrm{eV}$ (!), is qualitatively incorrect, predicting the neutral atom to be more stable than the anion; the experimental value $A_{\mathrm{O}}^{\mathrm{exp.}} = 1.46\,\mathrm{eV}$ can be reproduced only by the trial wave functions of both species using large CI expansions.

The dynamical correlation also explains the failure of the SCF method to predict the stability of the F_2 molecule, $\Delta E_{bond}^{\mathrm{SCF}}\,(F_2) = 1.37\,\mathrm{eV}$(!), the result qualitatively incorrect compared with $\Delta E_{bond}^{\mathrm{exp.}}\,(F_2) = -1.68\,\mathrm{eV}$. The reason for this failure is the dynamical correlation between the electrons of the *lone*-pairs on both atoms and the *bonding* pair of electrons. Only using the multideterminant trial function and the extended basis sets including all orbitals up to $g(l = 4)$ AO, one can reproduce theoretically this experimental value with the chemical accuracy.

Large dynamical correlation error should be also present in all multiple bonded molecules, e.g., in N_2: $D_e^{\mathrm{RHF}}\,(N_2) = 5.3\,\mathrm{eV}$, compared with $D_e^{exp.}\,(N_2) = 9.9\,\mathrm{eV}$. Again, using the extended basis set (to g-functions) and the adequate level of CI required for the correct description of the dissociation into atoms, and reoptimization of orbitals in the CI formalism within the so-called *multiconfiguration SCF* (MC SCF or MR SCF) procedure gives the satisfactory value of the dissociation energy:$D_e^{\mathrm{MCSCF}}\,(N_2) = 9.8\,\mathrm{eV}$. The minimum level of CI, to account for the dynamical correlation between the outer electrons involved in the metal–ligand chemical bonds, is generally required also in complexes of the transitional metal ions, since the coordination bonds in these compounds involve different shells of the central atom: nd, $(n + 1)s$, and $(n + 1)p$.

The variational determinantal function(s), for which the orbitals determining the subsequent CI expansion are optimized in the relevant SCF procedure, determine the so-called *reference functions*. This set includes either a single Slater determinant, e.g., in the standard HF method for the *closed*-shell states, called the *single-reference* (SR) SCF, or several determinants, e.g., in the HF approach to the *open*-shell states or in MC SCF method, in which the MO are optimized for the CID-type combination of Slater determinants, including the ground state configuration and the most important *double* excitations from it. The latter approach can be thus called the *multi-reference* (MR) *SCF* (MR SCF) or *multiconfigurational SCF* (MC SCF) technique. Accordingly, the CI expansions of the Coulomb-correlated wave functions can be also classified as either SR CI, when they originate from the SR SCF orbitals, and MR CI, when the MR SCF orbitals are used to generate the excited configurations (Shavitt 1977).

The MR approaches are crucial for the correct description of the open-shell states to generate the correct *orbital* and *spin* symmetry of the trial wave function, in view of the degeneracy of orbitals and the alternative spin orientations of electrons in the open shells. In the MR variant, in which the ground state orbitals are optimized for a combination of several Slater determinants $\{\Phi_i^0\}$, $\Phi_0^{\mathrm{MCSCF}} = \sum_i C_{i,0}^{\mathrm{MCSCF}} \Phi_i^0$, the excited configurations derived from one determinant may repeat the configurations generated from another determinant, so that a careful selection of the *independent* configurations is required. One of the popular variants of the MC SCF method is the *Complete Active Space* SCF (CAS SCF) technique (Roos and Siegbahn 1977). In this CI method the reference set $\{\Phi_i^0\}$ contains all configurations involving the complete set of orbitals active (populated) at each stage of the chemical reaction under consideration, thus determining the subset of the *active* MO in this process, i.e., exhibiting *fractional* electron occupations. The remaining part of the fully occupied MO determines the subset of the reaction *inactive orbitals* of the CAS SCF wave function. One also delineates within some appropriately chosen "energy window" the *external orbitals*, the excitation to which should be vital to represent the most important changes in the Coulomb correlation between electrons. The independent excited configurations originating from all occupied MO, active and inactive, to these external MO are then used in the associated (limited) MR CI expansion.

The number n_c of all configurations in the given basis set grows dramatically with the basis set size $w > N$, which also marks the number of all MO determined at the SCF stage giving rise to $2w$ SO. The former is thus equal to the number of alternative choices of N occupied SO from the overall set of $2w$ functions, given by the familiar combinatorial formula

$$n_c = \binom{2w}{N} = \frac{(2w)!}{N!(2w-N)!}. \tag{6.66}$$

For example, already for rather small system containing only $N = 10$ electrons, say water molecule, and 14 SO derived from its 7 (*doubly* occupied) MO obtained in the minimum basis set, $w = 7$, one obtains $n_c = 1{,}001$, while the moderately extended, *split* valence basis, for $w = 13$ MO, i.e., 26 SO, generates $n_c = 5\,311\,735$ configurations. Therefore, the *Full* CI (FCI) calculations, involving all admissible excitations in the adopted basis set, are possible only for small molecules. The limited CI realizations of the method assume the excited configurations in the given energy window around the HOMO and LUMO (Fig. 6.2) and require rather stringent selection of the most important configurations, probed using standard perturbational techniques.

One also realizes that a direct diagonalization of the CI Hamiltonian matrix,

$$\mathbf{H}^{\mathrm{CI}} = \left\{ \langle \Phi_s(N) | \hat{\mathrm{H}}^e(N) | \Phi_t(N) \rangle = H^{\mathrm{CI}}_{s,t} \right\},$$

is impossible, due to a limited size of the operational memory of contemporary digital computers. The special, sometimes ingenious algorithms for extracting CI eigenvectors and eigenvalues for a small number of the lowest electronic states have been designed to achieve this goal when millions of configurations are included in the limited CI expansion (Shavitt 1977; Roos and Siegbahn 1977).

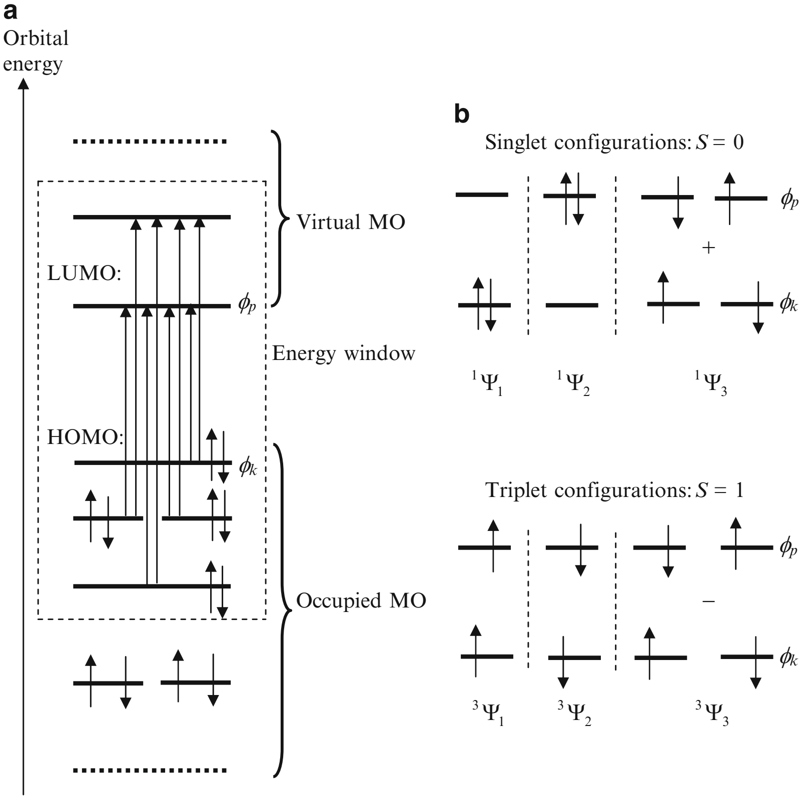
However, cutting the value of the excitation energy and a variety/multiplicity of excitations included in the variational CI theory using the chosen subset of configurations introduces the so-called *size consistency* error into the predicted interaction energies, which has to be properly compensated for. The alternative Møller–Plesset (MP) theory (Møller and Plessett 1934), in which the limited CI coefficients are determined from PT, is free from this shortcoming. We shall discuss such typical CI approaches in detail in other sections of this chapter, limiting the present discussion to a general survey of problems encountered in practical realizations of such advanced numerical procedures.

In general, a single Slater determinant does not exhibit the proper spatial and spin symmetry required of an adequate description of spectroscopic states. The CI wave functions $\Psi^{\mathrm{CI}}_{S,M_S}$ should correspond to the sharply specified length and the projection of the resultant spin $\boldsymbol{S}$, satisfying the associated eigenvalue problems for the overall spin of N electrons:

$$\begin{aligned} &\hat{\mathrm{S}}^2 \Psi^{\mathrm{CI}}_{S,M_S} = S(S+1)\hbar^2 \Psi^{\mathrm{CI}}_{S,M_S}, \quad \hat{\mathrm{S}}_z \Psi^{\mathrm{CI}}_{S,M_S} = M_S \hbar \Psi^{\mathrm{CI}}_{S,M_S}, \\ &M_S = -S, -S+1, \ldots, S-1, S. \end{aligned} \tag{6.67}$$

Therefore, the CI expansion of the given spin state should be limited to configurations exhibiting the same spin characteristics, given by the appropriate combinations of determinantal functions. This severely limits the "length" of the expansion itself but requires advanced algorithms for generating such *spin-adapted* configurations. Examples of such spin-adapted configurations generated by the FO are shown in Fig. 6.2.

For the Coulomb (spin-independent) Hamiltonian, the $(2S+1)$ states corresponding to different values of the (orientation) quantum number M_S for to the specified value of the (length) spin quantum number S, are degenerate so it suffices to consider a single state, say $\Psi^{\mathrm{CI}}_{S,S}$, to determine the corresponding energy.



Singlet configurations, $S = M_S = 0$:

$$^1\Psi_1 = \left|\phi_k^+\phi_k^-\right| = \phi_k(\boldsymbol{r}_1)\phi_k(\boldsymbol{r}_2)\frac{1}{\sqrt{2}}[\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)] \equiv \Phi_k^S(\boldsymbol{r}_1,\boldsymbol{r}_2)\ U_{0,0}(\sigma_1,\sigma_2)$$

$$^1\Psi_2 = \left|\phi_p^+\phi_p^-\right| = \phi_p(\boldsymbol{r}_1)\phi_p(\boldsymbol{r}_2)U_{0,0}(\sigma_1,\sigma_2) \equiv \Phi_p^S(\boldsymbol{r}_1,\boldsymbol{r}_2)U_{0,0}(\sigma_1,\sigma_2)$$

$$^1\Psi_3 = \frac{1}{\sqrt{2}}\{\left|\phi_k^+\phi_p^-\right| + \left|\phi_p^+\phi_k^-\right|\} = \frac{1}{\sqrt{2}}[\phi_k(\boldsymbol{r}_1)\phi_p(\boldsymbol{r}_2) + \phi_p(\boldsymbol{r}_1)\phi_k(\boldsymbol{r}_2)]\,U_{0,0}(\sigma_1,\sigma_2)$$
$$\equiv \Phi_{k,p}^S(\boldsymbol{r}_1,\boldsymbol{r}_2)\ U_{0,0}(\sigma_1,\sigma_2)$$

Triplet configurations, $S = 1$, $M_S = (-1, 0, 1)$:

$$^3\Psi_1 = \left|\phi_k^+\phi_p^+\right| = \frac{1}{\sqrt{2}}[\phi_k(\boldsymbol{r}_1)\phi_p(\boldsymbol{r}_2) - \phi_p(\boldsymbol{r}_1)\phi_k(\boldsymbol{r}_2)]\alpha(\sigma_1)\alpha(\sigma_2) \equiv \Phi_{k,p}^A(\boldsymbol{r}_1,\boldsymbol{r}_2)\ U_{1,1}(\sigma_1,\sigma_2)$$

$$^3\Psi_1 = \left|\phi_k^-\phi_p^-\right| = \Phi_{k,p}^A(\boldsymbol{r}_1,\boldsymbol{r}_2)\beta(\sigma_1)\beta(\sigma_2) \equiv \Phi_{k,p}^A(\boldsymbol{r}_1,\boldsymbol{r}_2)\ U_{1,-1}(\sigma_1,\sigma_2)$$

$$^3\Psi_3 = \frac{1}{\sqrt{2}}\{\left|\phi_k^+\phi_p^-\right| - \left|\phi_p^+\phi_k^-\right|\} = \Phi_{k,p}^A(\boldsymbol{r}_1,\boldsymbol{r}_2)\frac{1}{\sqrt{2}}[\alpha(\sigma_1)\beta(\sigma_2) + \beta(\sigma_1)\alpha(\sigma_2)]$$
$$\equiv \Phi_{k,p}^A(\boldsymbol{r}_1,\boldsymbol{r}_2)\ U_{1,0}(\sigma_1,\sigma_2)$$

Fig. 6.2 Energy window determining the range of electron excitations in the limited CI approaches (Panel *a*) and the singlet/triplet configurations involving excitations between the Frontier MO: HOMO → LUMO (Panel *b*)

This additionally limits the number of the spin-adapted configurations, which have to be considered explicitly in order to extract the spectroscopic energy levels.

One similarly uses the spatial symmetry to limit the length of the CI expansion. More specifically, only configurations of the same symmetry type can mix, with the subsets of the (space-spin)-adapted configurations of the same symmetry type determining the nonvanishing diagonal blocks of $\mathbf{H}^{\mathrm{CI}}$, with the *off*-diagonal blocks corresponding to two subsets of different symmetries identically vanishing. Thus, each subset can be considered separately, which radically lowers the number of secular equations to be solved simultaneously by the diagonalization of the associated diagonal block of the CI energy matrix.

Finally, an extra reduction of the configuration number results from using the perturbation theory in determining how effective a given configuration really is in improving the electronic state of interest. This preliminary exploration allows one to remove inefficient excitations and focus solely on those, which strongly couple to the state to be determined. Indeed, in addition to the spin and spatial symmetry restrictions one can directly probe the importance of the current configuration Φ_s in the CI expansion of the ground state wave function, $\Psi_0^{\mathrm{CI}}(N) = \sum_s C_{s,0}^{\mathrm{CI}} \Phi_s(N)$, using the *first*-order estimates from the Ryleigh–Schrödinger PT (5.12):

$$C_{s,0}^{\mathrm{CI}(1)} = H_{s,0}^{\mathrm{CI}} / \left(H_{0,0}^{\mathrm{CI}} - H_{s,s}^{\mathrm{CI}} \right), \tag{6.68}$$

giving rise to the *second*-order (correlation energy) contribution [see (5.16)]:

$$\Delta E_{s,0}^{(2)} = \left| H_{s,0}^{\mathrm{CI}} \right|^2 / \left(H_{0,0}^{\mathrm{CI}} - H_{s,s}^{\mathrm{CI}} \right). \tag{6.69}$$

Both these probes are inversely proportional to the excitation energy measured by the denominator in these expressions. Therefore, by appropriate choice of the energy window for such excitations one can a priori eliminate configurations that most likely generate a minor energy lowering, in advance of the diagonalization step of the $\mathbf{H}^{\mathrm{CI}}$ block grouping only the most important configurations.

It should be also observed that the traditional routines for the diagonalization of $\mathbf{H}^{\mathrm{CI}}$ can be applied only to relatively short and medium CI expansions, e.g., in MC SCF method, while mixing millions of configurations calls for special algorithmic solutions often dictated by the "architectural" designs of the computers themselves (see: Shavitt 1977). For example, the *integral-driven* technique of Roos (Roos 1972; Roos and Siegbahn 1977), called the *direct CI*, maximizes the effects of a single, time-consuming readout of a large number of two-electron integrals from the external memory device to the operational memory of the computer. This is achieved by simultaneously determining the integral contributions to all currently needed elements of the energy matrix. In fact, the full Hamiltonian matrix $\mathbf{H}^{\mathrm{CI}}$, required to determine simultaneously all eigenvectors, is never generated in this procedure. Instead, each eigenvector of interest is determined separately and this reduced problem requires the knowledge of only a small part of $\mathbf{H}^{\mathrm{CI}}$.

6.2.3 Correlation Holes

The essence of the correlation phenomenon lies in an interdependence between the instantaneous, relative positions of electrons. It can be quantified in terms of the corresponding simultaneous (or conditional) density or probability distributions of two electrons, which we have introduced in Sect. 3.1. We first observe that for the *independent* (*ind.*) distributions of the two *distinguishable* electrons, say electron "1" located at $\boldsymbol{r}$ occupying the orbital φ_1, and the electron "2" at $\boldsymbol{r}'$ occupying the orbital φ_2, the simultaneous two-electron probability $p_2^{ind.}(\boldsymbol{r},\boldsymbol{r}') = p_1(\boldsymbol{r})p_2(\boldsymbol{r}')$, where $p_1(\boldsymbol{r}) = |\varphi_1(\boldsymbol{r})|^2$ and $p_2(\boldsymbol{r}) = |\varphi_2(\boldsymbol{r})|^2$. Hence, the conditional probability density of detecting the "*dependent*" electron 2 at $\boldsymbol{r}'$, when the "*reference*" electron 1 is known to be located at $\boldsymbol{r}$, then reads:

$$p^{ind.}(\boldsymbol{r}'|\boldsymbol{r}) = p_2^{ind.}(\boldsymbol{r},\boldsymbol{r}')/p_1(\boldsymbol{r}) = p_2(\boldsymbol{r}'), \qquad \int p^{ind.}(\boldsymbol{r}'|\boldsymbol{r})\, d\boldsymbol{r}' = 1. \tag{6.70a}$$

Similar result follows when one treats two particles in this hypothetical $N = 2$ electron system as *indistinguishable*. The overall one-electron distributions,

$$p(\boldsymbol{r}) = [p_1(\boldsymbol{r}) + p_2(\boldsymbol{r})]/2 = \rho(\boldsymbol{r})/2, \qquad \int p(\boldsymbol{r})\, d\boldsymbol{r} = 1, \quad \int \rho(\boldsymbol{r})\, d\boldsymbol{r} = 2,$$

then generate the simultaneous probability/density of two electrons:

$$p_2^{ind.}(\boldsymbol{r},\boldsymbol{r}') = p(\boldsymbol{r})p(\boldsymbol{r}') = \rho(\boldsymbol{r})\rho(\boldsymbol{r}')/4 = \rho_2^{ind.}(\boldsymbol{r},\boldsymbol{r}')/2,$$
$$\int\!\!\int p_2^{ind.}(\boldsymbol{r},\boldsymbol{r}')\; d\boldsymbol{r}\, d\boldsymbol{r}' = 1, \qquad \int\!\!\int \rho_2^{ind.}(\boldsymbol{r},\boldsymbol{r}')\; d\boldsymbol{r}\, d\boldsymbol{r}' = 2,$$

and the associated conditional distributions of detecting one (dependent) electron at $\boldsymbol{r}'$ when another (reference) electron is at $\boldsymbol{r}$:

$$p^{ind.}(\boldsymbol{r}'|\boldsymbol{r}) = p_2^{ind.}(\boldsymbol{r},\boldsymbol{r}')/p(\boldsymbol{r}) = p(\boldsymbol{r}'), \qquad \int p^{ind.}(\boldsymbol{r}'|\boldsymbol{r})\, d\boldsymbol{r}' = 1;$$
$$\rho^{ind.}(\boldsymbol{r}'|\boldsymbol{r}) = \rho_2^{ind.}(\boldsymbol{r},\boldsymbol{r}')/\rho(\boldsymbol{r}) = \rho(\boldsymbol{r}')/2, \quad \int \rho^{ind.}(\boldsymbol{r}'|\boldsymbol{r})\, d\boldsymbol{r}' = 1. \tag{6.70b}$$

This independent conditional probability/density provides the reference against which the *exchange*- and/or *Coulomb*-correlated distributions are compared in order to extract the displacements ("*holes*") due to the two-electron correlation.

For a general N-electron system in the Hartree approximation of Sect. 6.1.1, one obtains the following expression for the one- and two-electron densities [see (3.7) and (3.10)]:

$$\begin{aligned}
\rho^{\mathrm{H}}(\boldsymbol{r}) &= \langle\Psi(N)|\hat{\rho}(\boldsymbol{r})|\Psi(N)\rangle = \sum_{k=1}^{N}|\varphi_k(\boldsymbol{r})|^2,\\
\rho_2^{\mathrm{H}}(\boldsymbol{r},\boldsymbol{r}') &= \langle\Psi(N)|\hat{\rho}_2(\boldsymbol{r},\boldsymbol{r}')|\Psi(N)\rangle\\
&= \rho^{\mathrm{H}}(\boldsymbol{r})\left[\rho^{\mathrm{H}}(\boldsymbol{r}') - \frac{1}{\rho^{\mathrm{H}}(\boldsymbol{r})}\sum_{k=1}^{N}|\varphi_k(\boldsymbol{r})|^2|\varphi_k(\boldsymbol{r}')|^2\right]\\
&\equiv \rho^{\mathrm{H}}(\boldsymbol{r})\rho^{\mathrm{H}}(\boldsymbol{r}'|\boldsymbol{r}) \equiv \rho^{\mathrm{H}}(\boldsymbol{r})\left[\rho^{\mathrm{H}}(\boldsymbol{r}') + h_{\mathrm{H}}^{\mathrm{SI}}(\boldsymbol{r}'|\boldsymbol{r})\right]. \qquad (6.71)
\end{aligned}$$

It thus follows from the above expression that the Hartree method of Sect. 6.1.1 involves the *self-interaction* (SI) *hole*:

$$h_{\mathrm{H}}^{\mathrm{SI}}(\boldsymbol{r}'|\boldsymbol{r}) = -\frac{1}{\rho^{\mathrm{H}}(\boldsymbol{r})}\sum_{k=1}^{N}|\varphi_k(\boldsymbol{r})|^2|\varphi_k(\boldsymbol{r}')|^2, \qquad (6.72)$$

by which the Hartree conditional probability, $\rho^{\mathrm{H}}(\boldsymbol{r}'|\boldsymbol{r}) = \rho_2^{\mathrm{H}}(\boldsymbol{r},\boldsymbol{r}')/\rho^{\mathrm{H}}(\boldsymbol{r})$, differs from the product reference value $\rho^{ind.}(\boldsymbol{r}'|\boldsymbol{r}) = \rho^{\mathrm{H}}(\boldsymbol{r}')$, which marks the truly independent (SI-contaminated) distributions of two electrons. One also observes that the integration of the SI-hole over positions of the dependent electron gives:

$$\int h_{\mathrm{H}}^{\mathrm{SI}}(\boldsymbol{r}'|\boldsymbol{r})\, d\boldsymbol{r}' = -\frac{1}{\rho^{\mathrm{H}}(\boldsymbol{r})}\sum_{k=1}^{N}|\varphi_k(\boldsymbol{r})|^2\langle\varphi_k|\varphi_k\rangle = -1. \qquad (6.73)$$

Therefore, in this approximation, the SI-hole density effectively eliminates one dependent electron from the surroundings of the reference electron.

Moreover, using (3.15) one expresses the electron repulsion energy in the Hartree method in terms of the classical interaction between independent charge distributions and the self-repulsion correction term involving the SI-hole:

$$\begin{aligned}
V_{e,e}^{\mathrm{H}}(N) &= \frac{1}{2}\int\!\!\int\frac{\rho_2^{\mathrm{H}}(\boldsymbol{r},\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}\,d\boldsymbol{r}' = \frac{1}{2}\int\!\!\int\frac{\rho^{\mathrm{H}}(\boldsymbol{r})\rho^{\mathrm{H}}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}\,d\boldsymbol{r}' + \frac{1}{2}\int\!\!\int\frac{\rho^{\mathrm{H}}(\boldsymbol{r})h_{\mathrm{H}}^{\mathrm{SI}}(\boldsymbol{r}'|\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}\,d\boldsymbol{r}'\\
&= J[\rho^{\mathrm{H}}] + E_{\mathrm{SI}}[\rho^{\mathrm{H}}, h^{\mathrm{SI}}] = \frac{1}{2}\sum_{k=1}^{N}\sum_{l=1}^{N}J_{k,l} - \frac{1}{2}\sum_{k=1}^{N}J_{k,k}.
\end{aligned} \qquad (6.74)$$

It is seen to be given by the difference between the classical Coulomb repulsion energy of the electronic charge density ρ^{H}, $J[\rho^{\mathrm{H}}]$, and the SI-correction term $E_{\mathrm{SI}}[\rho^{\mathrm{H}}, h^{\mathrm{SI}}]$ representing the interaction between this charge distribution and the SI-hole. It should be also observed that this expression exactly reproduces the two-electron part of the energy expectation value of (6.2).

Next, let us examine the corresponding hole concept in HF theory, in which the state function satisfies Pauli's antisymmetrization postulate. The relevant electron distributions now read:

$$\begin{aligned}
\rho^{\mathrm{HF}}(\boldsymbol{r}) &= \langle \Psi_A(N)|\hat{\rho}(\boldsymbol{r})|\Psi_A(N)\rangle = \sum_{k=1}^{N} |\,\phi_k(\boldsymbol{r})|^2, \\
\rho_2^{\mathrm{HF}}(\boldsymbol{r},\boldsymbol{r}') &= \langle \Psi_A(N)|\hat{\rho}_2(\boldsymbol{r},\boldsymbol{r}')|\Psi_A(N)\rangle \\
&= \rho^{\mathrm{HF}}(\boldsymbol{r})\left\{\rho^{\mathrm{HF}}(\boldsymbol{r}') - \frac{1}{\rho^{\mathrm{HF}}(\boldsymbol{r})}\sum_{k=1}^{N}\sum_{l=1}^{N}\left[\phi_k^*(\boldsymbol{r})\phi_l(\boldsymbol{r})\right]\left[\phi_l^*(\boldsymbol{r}')\phi_k(\boldsymbol{r}')\right]\right\} \\
&\equiv \rho^{\mathrm{HF}}(\boldsymbol{r})\rho^{\mathrm{HF}}(\boldsymbol{r}'|\boldsymbol{r}) \equiv \rho^{\mathrm{HF}}(\boldsymbol{r})\left[\rho^{\mathrm{HF}}(\boldsymbol{r}') + h_x(\boldsymbol{r}'|\boldsymbol{r})\right].
\end{aligned} \tag{6.75}$$

Again, the HF conditional density $\rho^{\mathrm{HF}}(\boldsymbol{r}'|\boldsymbol{r}) = \rho_2^{\mathrm{HF}}(\boldsymbol{r},\boldsymbol{r}')/\rho^{\mathrm{HF}}(\boldsymbol{r})$ differs from the associated reference $\rho^{\mathrm{HF}}(\boldsymbol{r}')$ of the independent distribution, which does not eliminate SI, by the *exchange* (Fermi) *hole*:

$$h_x(\boldsymbol{r}'|\boldsymbol{r}) = -\frac{1}{\rho^{\mathrm{HF}}(\boldsymbol{r})}\sum_{k=1}^{N}\sum_{l=1}^{N}\left[\phi_k^*(\boldsymbol{r})\phi_l(\boldsymbol{r})\right]\left[\phi_l^*(\boldsymbol{r}')\phi_k(\boldsymbol{r}')\right]. \tag{6.76}$$

Its integration over positions of the dependent electron again gives:

$$\begin{aligned}
\int h_x(\boldsymbol{r}'|\boldsymbol{r})\,d\boldsymbol{r}' &= -\frac{1}{\rho^{\mathrm{HF}}(\boldsymbol{r})}\sum_{k=1}^{N}\sum_{l=1}^{N}\left[\phi_k^*(\boldsymbol{r})\phi_l(\boldsymbol{r})\right]\langle\phi_l \mid \phi_k\rangle \\
&= -\frac{1}{\rho^{\mathrm{HF}}(\boldsymbol{r})}\sum_{k=1}^{N}\left|\phi_k^*(\boldsymbol{r})\right|^2 = -1,
\end{aligned} \tag{6.77}$$

where we have recognized the orthonormality relations $\langle\phi_l|\phi_k\rangle = \delta_{l,k}$.

The above expression for the two-electron density in this approximation thus gives the following partition of the electron repulsion energy:

$$\begin{aligned}
V_{e,e}^{\mathrm{HF}}(N) &= \frac{1}{2}\int\int\frac{\rho_2^{\mathrm{HF}}(\boldsymbol{r},\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}\,d\boldsymbol{r}' \\
&= \frac{1}{2}\int\int\frac{\rho^{\mathrm{HF}}(\boldsymbol{r})\rho^{\mathrm{HF}}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}\,d\boldsymbol{r}' + \frac{1}{2}\int\int\frac{\rho^{\mathrm{HF}}(\boldsymbol{r})h_x(\boldsymbol{r}'|\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}\,d\boldsymbol{r}' \\
&= J[\rho^{\mathrm{HF}}] + E_x[\rho^{\mathrm{HF}}, h_x] = \frac{1}{2}\sum_{k=1}^{N}\sum_{l=1}^{N}J_{k,l} - \frac{1}{2}\sum_{k=1}^{N}\sum_{l=1}^{N}K_{k,l}.
\end{aligned} \tag{6.78}$$

The second term $E_x[\rho^{\mathrm{HF}}, h_x]$, called the *exchange energy*, which corrects the classical energy $J[\rho^{\mathrm{HF}}]$ for the Fermi correlation effects, also removes the *self*-interaction since $J_{k,k} = K_{k,k}$. Indeed, by separating in the exchange hole of (6.76), the orbital-diagonal, SI-part from the remaining interorbital (IOE), *exchange* contribution,

$$\begin{aligned} h_x(\boldsymbol{r}'|\boldsymbol{r}) &= -\frac{1}{\rho^{\mathrm{HF}}(\boldsymbol{r})}\left\{\sum_{k=1}^{N}|\phi_k(\boldsymbol{r})|^2|\phi_k(\boldsymbol{r}')|^2 + \sum_{k,l\neq k}\left[\phi_k^*(\boldsymbol{r})\phi_l(\boldsymbol{r})\right]\left[\phi_l^*(\boldsymbol{r}')\phi_k(\boldsymbol{r}')\right]\right\} \\ &\equiv h_{\mathrm{HF}}^{\mathrm{SI}}(\boldsymbol{r}'|\boldsymbol{r}) + h_{\mathrm{HF}}^{\mathrm{IOE}}(\boldsymbol{r}'|\boldsymbol{r}), \end{aligned} \tag{6.79}$$

the exchange energy in (6.78) can be partitioned into the intraorbital SI- correction, and the IOE energy, respectively:

$$\begin{aligned} E_x[\rho^{\mathrm{HF}}, h_x] &= \frac{1}{2}\int\!\!\int \frac{\rho^{\mathrm{HF}}(\boldsymbol{r})h_{\mathrm{HF}}^{\mathrm{SI}}(\boldsymbol{r}'|\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}\,d\boldsymbol{r}' + \frac{1}{2}\int\!\!\int \frac{\rho^{\mathrm{HF}}(\boldsymbol{r})h_{\mathrm{HF}}^{\mathrm{IOE}}(\boldsymbol{r}'|\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}\,d\boldsymbol{r}' \\ &\equiv E_{\mathrm{SI}}\left[\rho^{\mathrm{HF}}, h_{\mathrm{HF}}^{\mathrm{SI}}\right] + E_{\mathrm{IOE}}\left[\rho^{\mathrm{HF}}, h_{\mathrm{HF}}^{\mathrm{IOE}}\right] = -\frac{1}{2}\sum_{k=1}^{N} J_{k,k}^{\mathrm{HF}} - \sum_{k=1}^{N-1}\sum_{l=k+1}^{N} K_{k,l}. \end{aligned} \tag{6.80}$$

One similarly introduces the concept of the resultant *exchange-correlation* (*xc*) hole, combining changes in the conditional two-electron density due to both the Fermi and Coulomb correlations,

$$h_{xc}(\boldsymbol{r}'|\boldsymbol{r}) = h_x(\boldsymbol{r}'|\boldsymbol{r}) + h_c(\boldsymbol{r}'|\boldsymbol{r}). \tag{6.81}$$

It determines the displacements of the fully correlated two-electron density, e.g., that determined from CI calculations, relative to the independent electron reference:

$$\begin{aligned} \rho_2^{\mathrm{CI}}(\boldsymbol{r},\boldsymbol{r}') &= \left\langle \Psi^{\mathrm{CI}}(N)\middle|\hat{\rho}_2(\boldsymbol{r},\boldsymbol{r}')\middle|\Psi^{\mathrm{CI}}(N)\right\rangle \\ &\equiv \rho^{\mathrm{CI}}(\boldsymbol{r})\rho^{\mathrm{CI}}(\boldsymbol{r}'|\boldsymbol{r}) \equiv \rho^{\mathrm{CI}}(\boldsymbol{r})\left[\rho^{\mathrm{CI}}(\boldsymbol{r}') + h_{xc}^{\mathrm{CI}}(\boldsymbol{r}'|\boldsymbol{r})\right], \end{aligned} \tag{6.82}$$

where $\rho^{\mathrm{CI}}(\boldsymbol{r}) = \left\langle \Psi^{\mathrm{CI}}(N)\middle|\hat{\rho}(\boldsymbol{r})\middle|\Psi^{\mathrm{CI}}(N)\right\rangle$ is the electron density in state $\Psi^{\mathrm{CI}}(N)$.

It follows from the normalization of $\rho_2^{\mathrm{CI}}(\boldsymbol{r},\boldsymbol{r}')$[see (3.10)],

$$\int\!\!\int \rho_2^{\mathrm{CI}}(\boldsymbol{r},\boldsymbol{r}')\,d\boldsymbol{r}\,d\boldsymbol{r}' = N(N-1) = N^2 + \int \rho^{\mathrm{CI}}(\boldsymbol{r})\left[\int h_{xc}^{\mathrm{CI}}(\boldsymbol{r}'|\boldsymbol{r})\,d\boldsymbol{r}'\right]d\boldsymbol{r}, \tag{6.83}$$

that this equation can be satisfied only when the integral in square brackets gives

$$\int h_{xc}^{\mathrm{CI}}(\boldsymbol{r}'|\boldsymbol{r})\,d\boldsymbol{r}' = -1. \tag{6.84}$$

Therefore, since the $h_{xc}(\boldsymbol{r}'|\boldsymbol{r})$ satisfies the same sum rule as its exchange contribution (6.77), the corresponding "normalization" of the Coulomb hole requires:

$$\int h_c(\boldsymbol{r}'|\boldsymbol{r})\,d\boldsymbol{r}' = 0. \tag{6.85}$$

The corresponding expression for the electron repulsion energy then reads:

$$\begin{aligned} V_{e,e}^{\mathrm{CI}}(N) &= \frac{1}{2}\int\int \frac{\rho_2^{\mathrm{CI}}(\boldsymbol{r},\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,d\boldsymbol{r}\,d\boldsymbol{r}' = \frac{1}{2}\int\int \frac{\rho^{\mathrm{CI}}(\boldsymbol{r})\rho^{\mathrm{CI}}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,d\boldsymbol{r}\,d\boldsymbol{r}' \\ &+ \frac{1}{2}\int\int \frac{\rho^{\mathrm{CI}}(\boldsymbol{r})h_{xc}^{\mathrm{CI}}(\boldsymbol{r}'|\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}\,d\boldsymbol{r}\,d\boldsymbol{r}' = J[\rho^{\mathrm{CI}}] + E_{xc}^{e,e}\left[\rho^{\mathrm{CI}}, h_{xc}^{\mathrm{CI}}\right], \end{aligned} \tag{6.86}$$

where $E_{xc}^{e,e}\left[\rho^{\mathrm{CI}}, h_{xc}^{\mathrm{CI}}\right]$ stands for the exchange-correlation contribution to the repulsion energy between electrons, expressed as functional of the resultant correlation hole.

It should be observed that this energy component is in fact determined by the *spherically averaged hole*. Define the relative separation between the reference and dependent electrons in the local spherical coordinate system centered at $\boldsymbol{r}$: $\boldsymbol{u} = \boldsymbol{r}' - \boldsymbol{r} = (u, \theta_{\boldsymbol{u}}, \varphi_{\boldsymbol{u}}) \equiv (u, \Omega_{\boldsymbol{u}})$, and introduce the spherically averaged hole:

$$h_{xc}^{\mathrm{CI}}(u|\boldsymbol{r}) = \frac{1}{4\pi}\int h_{xc}^{\mathrm{CI}}(\boldsymbol{r}+\boldsymbol{u}|\boldsymbol{r})\,d\Omega_{\boldsymbol{u}}. \tag{6.87}$$

The functional $E_{xc}^{e,e}\left[\rho^{\mathrm{CI}}, h_{xc}^{\mathrm{CI}}\right]$ of (6.86) can be then transformed into the associated functional of $h_{xc}^{\mathrm{CI}}(u|\boldsymbol{r})$:

$$\begin{aligned} E_{xc}^{e,e}\left[\rho^{\mathrm{CI}}, h_{xc}^{\mathrm{CI}}\right] &= \frac{1}{2}\int\int \frac{\rho^{\mathrm{CI}}(\boldsymbol{r})h_{xc}^{\mathrm{CI}}(\boldsymbol{r}+\boldsymbol{u}|\boldsymbol{r})}{|\boldsymbol{u}|}\,d\boldsymbol{r}\,d\boldsymbol{u} \\ &= 2\pi\int_0^\infty u\int \rho^{\mathrm{CI}}(\boldsymbol{r})\,h_{xc}^{\mathrm{CI}}(u|\boldsymbol{r})\,d\boldsymbol{r}\,du. \end{aligned} \tag{6.88}$$

The spin-resolved correlation hole can be expressed in terms of the elementary spin-dependent contributions:

$$h_{xc}^{\mathrm{CI}}(\boldsymbol{q}'|\boldsymbol{q}) = h_x^{\mathrm{CI}}(\boldsymbol{q}'|\boldsymbol{q}) + h_c^{\mathrm{CI}}(\boldsymbol{q}'|\boldsymbol{q}) \equiv h_{xc}^{\sigma,\sigma'}(\boldsymbol{r}'|\boldsymbol{r}) = h_x^{\sigma,\sigma'}(\boldsymbol{r}'|\boldsymbol{r}) + h_c^{\sigma,\sigma'}(\boldsymbol{r}'|\boldsymbol{r}), \tag{6.89}$$

where $h_x^{\sigma,\sigma'}(\boldsymbol{r}'|\boldsymbol{r}) = h_x^{\sigma,\sigma}(\boldsymbol{r}'|\boldsymbol{r})\delta_{\sigma,\sigma'}$. They define the corresponding spin contributions to the two-electron density [see (3.11)]:

$$\begin{aligned} \rho_2^{\mathrm{CI}}(\boldsymbol{q},\boldsymbol{q}') &= \left\langle \Psi^{\mathrm{CI}}(N)\middle|\hat{\mathrm{p}}_2(\boldsymbol{q},\boldsymbol{q}')\middle|\Psi^{\mathrm{CI}}(N)\right\rangle \\ &= \rho^{\mathrm{CI}}(\boldsymbol{q})\rho^{\mathrm{CI}}(\boldsymbol{q}'|\boldsymbol{q}) \equiv \rho^{\mathrm{CI}}(\boldsymbol{q})\left[\rho^{\mathrm{CI}}(\boldsymbol{q}') + h_{xc}^{\mathrm{CI}}(\boldsymbol{q}'|\boldsymbol{q})\right] \\ &\equiv \rho_2^{\sigma,\sigma'}(\boldsymbol{r},\boldsymbol{r}') = \rho^{\sigma}(\boldsymbol{r})\rho^{\sigma,\sigma'}(\boldsymbol{r}'|\boldsymbol{r}) \equiv \rho^{\sigma}(\boldsymbol{r})\left[\rho^{\sigma'}(\boldsymbol{r}') + h_{xc}^{\sigma,\sigma'}(\boldsymbol{r}'|\boldsymbol{r})\right], \end{aligned} \tag{6.90}$$

with the correlated spin density (3.9):

$$\rho^{\mathrm{CI}}(\boldsymbol{q}) = \langle \Psi^{\mathrm{CI}}(N)|\hat{\rho}(\boldsymbol{q})|\Psi^{\mathrm{CI}}(N)\rangle \equiv \rho^{\sigma}(\boldsymbol{r}), \quad \int \rho^{\sigma}(\boldsymbol{r})\,d\boldsymbol{r} = N^{\sigma}, \quad \sum\nolimits_{\sigma} N_{\sigma} = N. \tag{6.91}$$

It then follows from the alternative expressions for $\rho_2^{\mathrm{CI}}(\boldsymbol{r},\boldsymbol{r}')$,

$$\begin{aligned}\rho_2^{\mathrm{CI}}(\boldsymbol{r},\boldsymbol{r}') &= \rho^{\mathrm{CI}}(\boldsymbol{r})\left[\rho^{\mathrm{CI}}(\boldsymbol{r}') + h_{xc}^{\mathrm{CI}}(\boldsymbol{r}'|\boldsymbol{r})\right] = \sum_{\sigma}\sum_{\sigma'} \rho_2^{\sigma,\sigma'}(\boldsymbol{r},\boldsymbol{r}') \\ &= \sum_{\sigma}\sum_{\sigma'} \rho^{\sigma}(\boldsymbol{r})\left[\rho^{\sigma'}(\boldsymbol{r}') + h_{xc}^{\sigma,\sigma'}(\boldsymbol{r}'|\boldsymbol{r})\right] \\ &= \rho^{\mathrm{CI}}(\boldsymbol{r})\rho^{\mathrm{CI}}(\boldsymbol{r}') + \sum_{\sigma}\sum_{\sigma'} \rho^{\sigma}(\boldsymbol{r}) h_{xc}^{\sigma,\sigma'}(\boldsymbol{r}'|\boldsymbol{r}),\end{aligned} \tag{6.92}$$

that the spinless hole is given by the following combination of the spin-resolved components:

$$h_{xc}^{\mathrm{CI}}(\boldsymbol{r}'|\boldsymbol{r}) = \sum_{\sigma}\sum_{\sigma'} \frac{\rho^{\sigma}(\boldsymbol{r})}{\rho^{\mathrm{CI}}(\boldsymbol{r})} h_{xc}^{\sigma,\sigma'}(\boldsymbol{r}'|\boldsymbol{r}). \tag{6.93}$$

The relevant sum rules for the *exchange* spin holes read:

$$\begin{aligned}&\int h_{x}^{\sigma,\sigma'}(\boldsymbol{r}'|\boldsymbol{r})\,d\boldsymbol{r}' = \int h_{xc}^{\sigma,\sigma'}(\boldsymbol{r}'|\boldsymbol{r})\,d\boldsymbol{r}' = -\delta_{\sigma,\sigma'} \quad \text{or} \\ &\sum_{\sigma'}\int h_{xc}^{\sigma,\sigma'}(\boldsymbol{r}'|\boldsymbol{r})\,d\boldsymbol{r}' = \int h_{xc}^{\mathrm{CI}}(\boldsymbol{q}'|\boldsymbol{q})\,d\boldsymbol{q}' = \sum_{\sigma'}\int h_{x}^{\sigma,\sigma'}(\boldsymbol{r}'|\boldsymbol{r})\,d\boldsymbol{r}' = \int h_{x}^{\mathrm{CI}}(\boldsymbol{q}'|\boldsymbol{q})\,d\boldsymbol{q}' = -1,\end{aligned} \tag{6.94}$$

while the overall normalization of the *correlation* spin holes requires:

$$\sum_{\sigma'}\int h_{c}^{\sigma,\sigma'}(\boldsymbol{r}'|\boldsymbol{r})\,d\boldsymbol{r}' = \int h_{c}^{\mathrm{CI}}(\boldsymbol{q}'|\boldsymbol{q})\,d\boldsymbol{q}' = 0. \tag{6.95}$$

Moreover, since the *pair* density $\rho_2(\boldsymbol{q},\boldsymbol{q}')$ is symmetrical with respect to exchanging the spin-position coordinates of two (indistinguishable) electrons, $\rho_2(\boldsymbol{q},\boldsymbol{q}') = \rho_2(\boldsymbol{q}',\boldsymbol{q})$ this invariance property must be also reflected by its hole contributions:

$$\rho(\boldsymbol{q})h_{\lambda}(\boldsymbol{q}'|\boldsymbol{q}) = \rho(\boldsymbol{q}')h_{\lambda}(\boldsymbol{q}|\boldsymbol{q}') \quad \text{or} \quad \rho^{\sigma}(\boldsymbol{r})h_{\lambda}^{\sigma,\sigma'}(\boldsymbol{r}'|\boldsymbol{r}) = \rho^{\sigma'}(\boldsymbol{r}')h_{\lambda}^{\sigma',\sigma}(\boldsymbol{r}|\boldsymbol{r}'), \quad \lambda = xc, x, c. \tag{6.96}$$

The hole distribution $h(\boldsymbol{r}'|\boldsymbol{r}) = \rho_2(\boldsymbol{r},\boldsymbol{r}')/\rho(\boldsymbol{r})$ introduces a nonsymmetrical treatment of the “reference” electron at $\boldsymbol{r}$ and the “dependent” electron at $\boldsymbol{r}'$. Alternatively, one can use the *pair correlation function*,

$$f(\boldsymbol{r},\boldsymbol{r}') = \rho_2(\boldsymbol{r},\boldsymbol{r}')/[\rho(\boldsymbol{r})\rho(\boldsymbol{r}')], \tag{6.97}$$

in which both electrons are treated symmetrically. Hence, from the equality $\rho_2(\boldsymbol{r},\boldsymbol{r}') = f(\boldsymbol{r},\boldsymbol{r}')\rho(\boldsymbol{r})\rho(\boldsymbol{r}') = \rho(\boldsymbol{r})[\rho(\boldsymbol{r}') + h(\boldsymbol{r}'|\boldsymbol{r})]$, one finds:

$$h(\boldsymbol{r}'|\boldsymbol{r}) = \rho(\boldsymbol{r}')[f(\boldsymbol{r},\boldsymbol{r}') - 1] \quad \text{or} \quad f(\boldsymbol{r},\boldsymbol{r}') = 1 + h(\boldsymbol{r}'|\boldsymbol{r})/\rho(\boldsymbol{r}'). \tag{6.98}$$

The spherically averaged *pair* correlation function reads:

$$f(\boldsymbol{r},u) = \frac{1}{4\pi}\int f(\boldsymbol{r},\boldsymbol{r}+\boldsymbol{u})\,d\Omega_{\boldsymbol{u}}. \tag{6.99}$$

In terms of the corresponding spin-resolved distributions,

$$\begin{aligned} f_{xc}(\boldsymbol{q},\boldsymbol{q}') &= \frac{\rho_2(\boldsymbol{q},\boldsymbol{q}')}{\rho(\boldsymbol{q})\rho(\boldsymbol{q}')} \equiv f_{xc}^{\sigma,\sigma'}(\boldsymbol{r},\boldsymbol{r}') = \frac{\rho_2^{\sigma,\sigma'}(\boldsymbol{r},\boldsymbol{r}')}{\rho^{\sigma}(\boldsymbol{r})\rho^{\sigma'}(\boldsymbol{r}')} \\ &= f_x(\boldsymbol{q},\boldsymbol{q}') + f_c(\boldsymbol{q},\boldsymbol{q}') \equiv f_x^{\sigma,\sigma'}(\boldsymbol{r},\boldsymbol{r}') + f_c^{\sigma,\sigma'}(\boldsymbol{r},\boldsymbol{r}'), \end{aligned} \tag{6.100}$$

the spinless *pair* correlation function of (6.97) then reads:

$$f(\boldsymbol{r},\boldsymbol{r}') = \sum_{\sigma}\sum_{\sigma'}\frac{1}{\rho(\boldsymbol{r})}\rho_2^{\sigma,\sigma'}(\boldsymbol{r},\boldsymbol{r}')\frac{1}{\rho(\boldsymbol{r}')} = \sum_{\sigma}\sum_{\sigma'}\frac{\rho^{\sigma}(\boldsymbol{r})}{\rho(\boldsymbol{r})}f^{\sigma,\sigma'}(\boldsymbol{r},\boldsymbol{r}')\frac{\rho^{\sigma'}(\boldsymbol{r}')}{\rho(\boldsymbol{r}')}. \tag{6.101}$$

As shown by Kato (1957) the Coulomb interaction between the two electrons implies in the near coalescence limit $\boldsymbol{r}' \to \boldsymbol{r}$, or $u \to 0$, the condition of the so-called *correlation cusp*:

$$f'(\boldsymbol{r},\boldsymbol{r}) \equiv \left.\frac{\partial f(\boldsymbol{r},u)}{\partial u}\right|_{u=0} = f(\boldsymbol{r},\boldsymbol{r}). \tag{6.102}$$

This condition supplements the *nuclear cusp* relation, for the coalescence of electron and the nucleus, when $\boldsymbol{r}_\alpha = \boldsymbol{r} - \boldsymbol{R}_\alpha = (r_\alpha, \Omega_\alpha) \to 0$, where $\boldsymbol{R}_\alpha$ stands for the position of nucleus α, exhibiting the electric charge Z_α (a.u.), formulated in terms of the spherically averaged electron density

$$\rho(r_\alpha) = \frac{1}{4\pi}\int \rho(\boldsymbol{r}_\alpha)\,d\Omega_\alpha, \tag{6.103}$$

$$\rho'(r_\alpha \to 0) \equiv \left.\frac{\partial \rho(r_\alpha)}{\partial r_\alpha}\right|_{r_\alpha=0} = -2Z\rho(r_\alpha = 0). \tag{6.104}$$

Consider, for example, the ground state of the hydrogen-like atom (4.62), for which the spherically symmetrical density $\rho(r) = (Z^3/\pi)\exp(-2Zr)$ and hence

$$\rho'(r \to 0) \equiv \left.\frac{\partial \rho(r)}{\partial r}\right|_{r=0} = -2Z\rho(r=0) = -\frac{2Z^4}{\pi}. \quad (6.105)$$

In terms of the spin components of the exchange and correlation distribution functions, the correlation cusp reads:

$$f_x{}'[(\boldsymbol{r}, \sigma), (\boldsymbol{r}, \sigma')] = 0, \quad f_c{}'[(\boldsymbol{r}, \sigma), (\boldsymbol{r}, \sigma')] = (1 - \delta_{\sigma,\sigma'}) f_c[(\boldsymbol{r}, \sigma), (\boldsymbol{r}, \sigma')]. \quad (6.106)$$

Thus, it is the Coulomb correlation between electrons which constitutes the exclusive origin of the correlation cusp of the *pair* correlation function. Indeed, it directly follows from the Pauli antisymmetrization principle that the *near*-coalescence events of two electrons with the parallel spins are excluded, thus giving rise to the vanishing cusp in the exchange contributions to the pair correlation function. Moreover, the nonvanishing cusp is seen to appear only for electrons exhibiting the antiparallel spins. This is also in accord with the above implications of the exclusion principle, since as a result of the requirements of the Fermi statistics the *near*-coalescence of two electrons with identical spins cannot occur due to the exchange correlation.

6.3 Configuration Interaction Techniques

In Sect. 6.2. we have hinted upon a systematic way to include the effects of the Coulomb correlation in the variational N-electron wave function by mixing the HF determinant with the excited configurations obtained by replacing a single or several HF SO by orbitals which remain unoccupied in the ground state. The formal basis for such beyond-HF, SR CI approach was also given in the form of the associated expansion theorem: any N-electron state can be expanded as a combination of all Slater determinants, which can be formed by distributing N electrons among different subsets of the complete basis of SO. Therefore, the FCI scheme in principle offers the exact description of all stationary states of molecular systems, should the set of AO in SCF calculations be large enough to generate a nearly complete basis of MO.

Such *first* principle (ab initio) theories using the CI expansion of *many*-electron wave functions can be developed in both the perturbational and variational formulations. The former methods fall into the category of the *Many-Body Perturbation Theory* (MBPT) (Møller and Plessett 1934; Mattuck 1976; Szabo and Ostlund 1982), while the latter methods are classified as the *Configuration Interaction* (CI) theories (Löwdin 1959; Shavitt 1977). The MBPT variants were shown by Brueckner and Goldstone, using the diagrammatic representation of Feynmann, to be size consistent at any order of the truncation (e.g., Brandow 1967; Freed 1971; Manne 1977; Bartlett 1981, Paldus and Čižek 1975). Both these approaches, at least in principle, are capable to deliver the calculated values of the physical observables to any desired accuracy. We shall briefly summarize in this section some of the most popular variational realizations of the CI techniques, which use a limited CI expansion, truncated due to numerical difficulties involved in the FCI scheme (see Sect. 6.2.2). The necessity to use a limited variety of electron excitations immediately arises, when one intends to apply these methods to large molecules of interest in the contemporary chemistry. For an overview of the wave function techniques of tackling the Coulomb correlation problem the reader is also referred to monographs by Szabo and Ostlund (1982), Christoffersen (1989), and McWeeny (1989).

The SR CI approach relies on the expansion of the current nth electronic state of interest, $\Psi_n^{\mathrm{CI}}(N)$, $n = 0, 1, 2, \ldots$, in terms of the system orthonormal configurations $\{\Phi_s(N),\ s = 1, 2, \ldots, n_c\}$ [see (6.66)],

$$\Psi_n^{\mathrm{CI}}(N) = \sum_{s=1}^{n_c} \Phi_s(N) C_{s,n}^{\mathrm{CI}}, \quad \langle \Phi_s \mid \Phi_t \rangle = S_{s,t}^{\mathrm{CI}} = \delta_{s,t}, \tag{6.107}$$

grouping in the FCI scheme all n_c antisymmetrized products (Slater determinants) $\{\Phi_s(N) = \det[\boldsymbol{\varphi}_s(N)\}$ of alternative choices of N one-electron functions (SO), $\{\boldsymbol{\varphi}_s(N) = (\phi_{1,s}, \phi_{2,s}, \ldots, \phi_{N,s}\}$, from the whole set of w canonical MO, $\boldsymbol{\varphi} = \{\phi_1, \phi_2, \ldots, \phi_w\}$, determined in the SCF MO calculations in the basis set of the same size, $\boldsymbol{\varphi} = \boldsymbol{\chi}\mathbf{C}$, $\boldsymbol{\chi} = \{\chi_1, \chi_2, \ldots, \chi_w\}$ (6.66).

This expansion may also involve appropriate linear combinations of these determinants, the eigenfunctions of $\hat{\mathrm{S}}^2$ and $\hat{\mathrm{S}}_z$ [see (6.67) and Fig. 6.2] or functions of the specified spatial symmetry type. Indeed, the true configuration functions of the appropriate spatial and spin symmetries in general require linear combinations of several Slater determinants (see, e.g., Fig. 6.2). Therefore, it is only for simplicity of presentation that we call single determinants of (6.109) and (6.110) as "configurations."

The elementary Slater determinants of the excited configurations can be envisaged as resulting from the appropriate electron excitations from the ground state determinant of the HF method,

$$\begin{aligned}\Phi_1(N) &\equiv \Psi_0^{\mathrm{HF}}(N) = |\phi_{1,1}, \phi_{2,1} \ldots, \phi_{N,1}| = \det[\boldsymbol{\varphi}_1(N)] \\ &= |\phi_1, \phi_2, \ldots, \phi_N|,\end{aligned} \tag{6.108}$$

by replacing a subset of the occupied SO in Φ_1, $\boldsymbol{\varphi}^{occd.} = \boldsymbol{\varphi}_1 = \{\phi_k\}$, by an equally numerous subset of the virtual SO, absent in Φ_1, $\boldsymbol{\varphi}^{virt.} = \{\phi_{N+1}, \phi_{N+2}, \ldots, \phi_w\} = \{\phi_p\}$. Thus, in the *singly* excited ($k \rightarrow p$) configuration Φ_k^p, the occupied SO ϕ_k has been replaced by the virtual SOϕ_p in the list of the occupied one-electron states:

$$\Phi_k^p = \det|\phi_1, \phi_2, \ldots, \phi_{k-1}, \phi_{k+1}, \ldots, \phi_N, \phi_p| \equiv \Phi[k \rightarrow p]. \tag{6.109}$$

Accordingly, in the *doubly* excited configuration $\Phi_{k<l}^{p<q} = \Phi[(k,l) \rightarrow (p,q)]$, the indicated pair of SO has been replaced, $(\phi_k, \phi_l) \rightarrow \{\phi_p, \phi_q)$,

$$\Phi_{k<l}^{p<q} = \det|\phi_1, \phi_2, \ldots, \phi_{k-1}, \phi_{k+1}, \ldots, \phi_{l-1}, \phi_{l+1}, \ldots, \phi_N, \phi_p, \phi_q|. \qquad (6.110)$$

Extension to the *triple*, *quadruple*, and higher excitations is obvious. In this notation the CI expansion of (6.62) and (6.107) reads:

$$\Psi_n^{\mathrm{CI}} = C_0(n)\Psi_0^{\mathrm{HF}} + \sum_{k}^{occd.}\sum_{p}^{virt.} C_k^p(n)\,\Phi_k^p + \sum_{k<l}^{occd.}\sum_{p<q}^{virt.} C_{k,l}^{p,q}(n)\,\Phi_{k,l}^{p,q}$$
$$+ \sum_{k<l<m}^{occd.} \quad \sum_{p<q<r}^{virt.} C_{k,l,m}^{p,q,r}(n)\,\Phi_{k,l,m}^{p,q,r} + \ldots \qquad (6.111)$$

The optimum (linear) variational parameters of the CI method, $\mathbf{C}^{\mathrm{CI}} = \left\{C_{s,t}^{\mathrm{CI}} \equiv C_s(t)\right\}$, which determine the unknown molecular states $\boldsymbol{\Psi}^{\mathrm{CI}} = \boldsymbol{\Phi}\mathbf{C}^{\mathrm{CI}} = \{\Psi_n\}$ in the (orthonormal) basis of the N-electron configuration functions $\boldsymbol{\Phi} = \{\Phi_s(N)\}$, $\mathbf{S}^{\mathrm{CI}} = \left\{S_{s,t}^{\mathrm{CI}}\right\} = \mathbf{I}^{\mathrm{CI}}$, and the associated energies $\mathbf{E}^{\mathrm{CI}} = \left\{E_n^{\mathrm{CI}}\delta_{n,m}\right\}$ are thus determined by the corresponding secular equations of the Ritz method (5.37), $\mathbf{H}^{\mathrm{CI}}\mathbf{C}^{\mathrm{CI}} = \mathbf{C}^{\mathrm{CI}}\mathbf{E}^{\mathrm{CI}}$, or

$$\mathbf{E}^{\mathrm{CI}} = (\mathbf{C}^{\mathrm{CI}})^{\dagger}\mathbf{H}^{\mathrm{CI}}\mathbf{C}^{\mathrm{CI}}, \qquad (\mathbf{C}^{\mathrm{CI}})^{\dagger}\mathbf{C}^{\mathrm{CI}} = \mathbf{I}^{\mathrm{CI}}. \qquad (6.112)$$

They are solved by the diagonalization of the energy matrix:

$$\mathbf{H}^{\mathrm{CI}} = \left\{\langle\Phi_s(N)|\hat{\mathrm{H}}^e(N)|\Phi_t(N)\rangle = H_{s,t}^{\mathrm{CI}}\right\} \qquad (6.113)$$

in the unitary transformation $\mathbf{C}^{\mathrm{CI}}$. Thus, the typical limited-CI calculations in principle consist of determining the set of the orthonormal MO, evaluating integrals in this MO basis, selecting the most important configurations, generating the energy matrix in the adopted configuration basis and solving the secular equations to determine energy levels and the associated wave functions.

The *MacDonald theorem* (see, e.g., Hylleraas and Undheim 1930; MacDonald, 1933; Shull and Löwdin 1958) of the linear variational method states that the ordered (nondegenerate) CI eigenvalues, $E_1^{\mathrm{CI}} < E_2^{\mathrm{CI}} < \ldots < E_{n_c}^{\mathrm{CI}}$, provide the upper bounds to the corresponding exact values of the electronic energy in the molecular ground and excited states, $\{E_n^e\} = \left(E_1^e < E_2^e < \ldots < E_{n_c}^e\right)$:

$$E_n^{\mathrm{CI}} \geq E_n^e, \quad n = 1, \ldots, n_c. \qquad (6.114)$$

It also proves that more refined calculations, with successively enlarged basis set of excited configurations, continue to improve these energy estimates:

$$E_n^{\mathrm{CI}}(n_c) \geq E_n^{\mathrm{CI}}(n_c+1) \geq E_n^{\mathrm{CI}}(n_c+2)\ldots \geq E_n^e, \qquad (6.115)$$

where $E_n^{\mathrm{CI}}(n_c)$ denotes the energy level from the CI expansion in terms of n_c configurations.

6.3.1 Special Variants of Limited CI

It directly follows from the *closed*-shell HF equations (6.21) and the Slater–Condon rule (5.85) that the matrix elements of $\mathbf{H}^{\mathrm{CI}}$ coupling the ground state (6.108) with the *singly* excited configurations $\left\{\Phi_k^p\right\}$ identically vanish:

$$\begin{aligned}\langle\Phi_1|\hat{\mathrm{H}}^e\left|\Phi_k^p\right\rangle &= H_{1,k\to p}^{\mathrm{CI}}\\ &= \langle k|\,\hat{\mathrm{h}}\,|p\rangle + \sum_{j=1}^{N}\langle kj|\,g\,|pj-jp\rangle = \langle k|\,\hat{\mathrm{F}}\,|p\rangle = e_p\langle k\mid p\rangle = 0.\end{aligned} \quad (6.116)$$

It indicates that the *singly*-excited configurations alone cannot improve the *closed*-shell HF wave function. This statement, also known as the *Brillouin theorem* (Brillouin 1933, 1934), is no longer satisfied for the *open*-shell ground state.

However, since by the Slater–Condon rules the *single* excitations directly couple to the *double* and *triple* excitations, their presence is generally required and beneficiary, when these higher excitations are also included in the CI expansion [see, e.g., (6.111)]. Nevertheless, the Brillouin theorem indicates the *indirect*, secondary role played by the *single* excitations in representing the ground state Coulomb correlation, when the HF (closed-shell) ground state is used as the reference function, compared with the *direct*, primary role played by the dominating *double* excitations.

Therefore, in determining the Coulomb correlation effects in such molecular ground state, the limited CI approaches must take into account at least double excitations. For example, the CI-*Doubles* (CID) scheme, intended to remedy limitations of HF theory in the ground state applications, uses the variational wave function in the form of the linear combination of the HF determinant and the *doubly* excited configurations:

$$\Psi_0^{\mathrm{CID}} = C_0\Psi_0^{\mathrm{HF}} + \sum_{k<l}^{occd.}\sum_{p<q}^{virt.} C_{k,l}^{p,q}\,\Phi_{k,l}^{p,q}. \quad (6.117)$$

In the CI expansions of excited states, which are dominated by some excited configuration derived from Ψ_0^{HF}, the *singly* excited configurations directly influence the wave function thus being equally important as *double* excitations in the approximate representations of such states. This is the reason why the other popular variant, called CI-(*Singles* and *Doubles*) (CISD) of the limited CI expansion, additionally includes the single excitations in the variational wave function:

$$\Psi_n^{\mathrm{CISD}} = C_0(n)\Psi_0^{\mathrm{HF}} + \sum_{k}^{occd.}\sum_{p}^{virt.} C_k^p(n)\,\Phi_k^p + \sum_{k<l}^{occd.}\sum_{p<q}^{virt.} C_{k,l}^{p,q}(n)\,\Phi_{k,l}^{p,q}, \quad n=0,1,\ldots \quad (6.118)$$

In the SR CI approaches, the optimum SO are calculated only once, at the preceding HF stage, with the CI coefficients (linear variational parameters) being subsequently determined for the fixed ("frozen") MO basis, including both the HF occupied and virtual MO. This approach gives rise to a relatively slow convergence of such a *linear* CI representation of the electron correlation effects. It can be improved decisively by allowing the shapes of orbitals, which determine the configuration functions, to adjust to the current form of the CI wave function, with MO being optimized at each iteration simultaneously with the CI coefficients themselves. Such a generalized MC SCF (or MR SCF) technique, which is usually applied to the ground state problems, adopts the CID trial function of (6.117) which guarantees the correct description of the alternative bond-forming/bond-breaking phenomena, with the MO used in all configurations treated as optimized entities in the generalized iteration scheme of the MC SCF process combining the orbital optimization (SCF) and CI stages:

$$\begin{aligned} \ldots \to \left[\mathrm{SCF}_{(k)}\left(\mathbf{C}^{(\mathrm{CI})}_{(k-1)}\right) \to \boldsymbol{\varphi}_{(k)}\right] &\to \left[\mathrm{CI}_{(k)}(\boldsymbol{\varphi}_{(k)}) \to \mathbf{C}^{(\mathrm{CI})}_{(k)}\right] \\ \to \left[\mathrm{SCF}_{(k+1)}\left(\mathbf{C}^{(\mathrm{CI})}_{(k)}\right) \to \boldsymbol{\varphi}_{(k+1)}\right] &\to \ldots \end{aligned}$$

Here $\mathbf{C}^{(\mathrm{CI})}_{(k)}$ and $\boldsymbol{\varphi}_{(k)}$ denote the optimum CI coefficients and MO of the kth iteration of such self-consistent optimization process. At its SCF stage, the current shapes of orbitals, i.e., the LCAO MO coefficients, are being determined, using the optimum CI coefficients from the previous iteration, and then the next approximation of $\mathbf{C}^{\mathrm{CI}}$ is generated at the CI stage, using the modified MO obtained from the preceding SCF procedure. The first, SCF stage uses the appropriately generalized HF equations to determine the MO coefficients, while the CI stage involves solving the secular equations (6.112) for the CI coefficients. The Fock operator in the MC SCF method depends on the effective occupancies of orbitals in the CID configurations, thus explicitly depending on the CI coefficients themselves. This full optimization of the CID wave function, which minimizes the electronic energy, is carried out until both the shapes of MO and the CI coefficients in the next iteration agree with those of the preceding iteration, thus determining the doubly self-consistent CI state, in both CI coefficients and MO shapes.

These variational, limited CI approaches suffer from severe *size*-consistency and *size*-extensivity problems. The former concept of the method adequacy deals with the requirement that its estimate of the energy of the system consisting of two infinitely distant (noninteracting) subsystems, say [He + He], must be equal to the sum of energies of the separate subsystems calculated by the same method: $E^e[\mathrm{He} + \mathrm{He}] = 2E^e[\mathrm{He}]$. In other words, the energy of the "dimer" composed of two noninteracting monomers must be twice the energy of the "monomer" and hence the energy of the system being dissociated into subsystems reaches in the limit of their infinite separation the sum of energies of the separate subsystems.

This requirement is satisfied by HF theory: the HF energy of a supermolecule composed of two noninteracting closed-shell subsystems is just the sum of the subsystem HF energies. Unfortunately, at the CI level of theory, this intuitively obvious postulate of the energy additivity is satisfied only by the *full*-CI approach, being violated by all variational methods using a *limited* CI expansion. To illustrate the problem, we observe that the CISD applied to each separate part generates the triple (T) and quadruple (Q) excitations of the system as a whole, since the wave function of the combined system (*supermolecule*) is then given by the product of the subsystem wave functions. Therefore, the configurations appearing at the CISD treatment of fragments are included only at the different CISDTQ levels of the theory for the whole molecule. This indicates that the dimer wave function truncated at CID level does not have sufficient flexibility to generate twice the CID energy of the monomer, thus confirming that this truncated CI scheme does not have the property of size consistency. In principle, no form of limited CI is size consistent. However, CI scheme including quadruple excitations has been shown to be approximately size consistent for small molecules.

To remedy this problem Davidson (Davidson 1974; Langhoff and Davidson 1974) has suggested the following corrected estimate of the ground state correlation energy:

$$\Delta E_{corr.} = \left(1 - C_0^2\right)\Delta E_{corr.}^{\mathrm{CISD}}, \tag{6.119}$$

where $\Delta E_{corr.}^{\mathrm{CISD}}$ stands for its CISD value and C_0^2 determines the participation of Ψ_0^{HF} configuration in the normalized expansion of (6.118). The projected correlation energies per electronic pair were observed to stay remarkably constant, at ~0.042 a.u. (≈1.14 eV).

The related notion of *size* extensivity, which first arose in the nuclear and solid state physics, refers to the method scaling with the number of correlated particles. Indeed, the appropriate scaling of the atomic results to an infinite system is required before the results obtained for an isolated atom can be used in a description of a solid containing an infinite number of atoms. This requirement refers to increasing the size of the "continuous" system, while keeping the particle density constant, e.g., that of the *free* electron gas. When the size of the system is doubled under such constraint, the total energy must be also doubled, thus being proportional to the number of particles N. In other words, the correlation energy per particle should be independent of N.

Thus, in the molecular scenario, the concept of extensivity does not apply to a single atom or molecule. This requirement represents a valid property, however, when the system consisting of many (*weakly* interacting or noninteracting) replicas of a molecule ("monomers"), e.g., H_2, are considered. Then the system energy represents to a good approximation the extensive property, and hence the correlation energy per electron should be expected to be conserved. For example, the HF energy of a crystal is proportional to the number N of constituent molecules, although it is not simply N times the energy of an isolated molecule. We further observe that the MBPT approaches, which we shall discuss in the next section, are both the size consistent and size extensive. The MR-SCF and MR-CI procedures also give rise to an approximate fulfillment of these requirements already at the CISD level.

To conclude this short overview of the limited-CI techniques, we also mention the problem of the most effective orbitals for the CI studies, which will be tackled in the subsequent section. Let us only observe here that the occupied HF orbitals are each determined in an effective field of $N - 1$ electrons, while the corresponding virtual orbitals are determined in an effective field of all N electrons. As a result the *low*-energy virtual MO are generally more diffused, especially in large basis sets, than their filled counterparts. This discrepancy causes a generally low effectiveness of the virtual MO when used as *correlation orbitals*, giving rise to generally slow convergence of the associated CI representation of the correlated wave functions.

Clearly, it would be physically more proper if the correlation virtual orbitals would also "feel" an $N - 1$ electron potential, since the optimum orbitals for correlation purposes should be located in the same regions of space as the electrons whose motion they intend to correlate. One partial solution to this problem is to use the orbitals determined in the MC SCF (small CI) problem, for setting up the MR CI matrix problem, dimension of which is much larger than that of the MC SCF calculation. Indeed, the major orbital relaxation effects would then be already accounted for in the following CI stage. In Sect. 6.3.3 we shall introduce the concept of *natural orbitals*, which give rise to the fastest convergence of the CI expansion and generate a significant physical insight into both the most important correlation mechanisms and the nature of the chemical bond.

6.3.2 Perturbational Theory of Møller and Plesset

The variational bounds for the system total electronic energy are of little value when one calculates the energy differences in which chemistry abounds. For this purpose it is essential to eliminate such nonsystematic errors as a lack of *size* consistency/extensivity and the *Basis Set Superposition Error* (BSSE), which may falsify the predicted structural preferences and reactivity trends, even qualitatively. Since for the solid state physicists, interested in systems of infinite size, the elimination of the former was essential, they have developed MBPT approaches (Brueckner 1955; Brueckner et al. 1955; Brueckner and Levinson 1955; Goldstone 1957; Kelly 1969) or Coupled Cluster (CC) theory (Coester 1958; Coester and Kümmel 1960; Kümmel 1969; Paldus and Čižek 1975), which use the standard Rayleigh–Schrödinger PT coupled with powerful diagrammatic techniques to extract Coulomb correlation corrections from the known HF solutions (Brandow 1967; Freed 1971; Manne 1977; Bartlett 1981; Paldus and Čižek 1975; Čižek and Paldus 1980; Szabo and Ostlund 1982). This theory is wholly satisfactory for molecular structures in the vicinity of the equilibrium geometry, but at present does not provide a useful tool for calculations of the complete PES of chemical reactions.

Such perturbation theory approaches are free from the *size*-consistency problem in all orders of PT. Indeed, let us recall that the FCI scheme, which can be regarded as the *infinite*-order PT, is also free from this problem. In the perturbational treatment this can be the case only when each of n-order corrections also exhibits this property. As also shown by Goldstone, the *finite*-order perturbational estimates of the correlation energy are also size extensive, exhibiting the linear increase with the number of electrons for systems consisting a large number of weakly interacting atoms or molecules: $\Delta E_{corr.}(N) \propto N$, which thus makes them particularly suitable and attractive for applications to infinite systems. This result is due to the exact cancelation in this version of PT of the so-called *unlinked* cluster contributions that are not N-proportional.

We shall now briefly examine the simplest formulation of MBPT proposed by Møller and Plessett (1934), called the MP theory, in which the *zeroth*-order Hamiltonian of N electrons is defined by the sum of the effective Fock operators (6.22) for each electron:

$$\hat{\mathrm{H}}_0^{\mathrm{MP}}(N) = \sum_{i=1}^{N} \hat{\mathrm{F}}(i), \quad \hat{\mathrm{F}}(i) = -\frac{1}{2}\Delta_i + V_{\mathrm{HF}}(\boldsymbol{r}_i), \quad \hat{\mathrm{F}}(\boldsymbol{r})\,\phi_k(\boldsymbol{r}) = e_k\,\phi_k(\boldsymbol{r}). \tag{6.120}$$

This choice of the unperturbed Hamiltonian for the correlation problem is indeed justified by the fact that the configurations appearing in the CI expansion of (6.107) and (6.111) are themselves eigenfunctions of this operator:

$$\hat{\mathrm{H}}_0^{\mathrm{MP}}(N)\Phi_s(N) = \left(\sum_{k=1}^{occd[s]} e_k\right)\Phi_s(N) \equiv E_s^{(0)}\Phi_s(N), \qquad s = 1,\ 2,\ \ldots \tag{6.121}$$

with the eigenvalue $E_s^{(0)}$ given by the sum of orbital energies of all occupied SO in $\Phi_s(N)$. Thus, the lowest eigenvalue corresponding to the HF ground state (6.108) is different from the corresponding HF energy [see (6.14) and (6.23)]:

$$E_0^{\mathrm{HF}} = E_1^{(0)} - \frac{1}{2}\sum_{k=1}^{N}\sum_{l=1}^{N}\{\bar{J}_{k,l} - \bar{K}_{k,l}\}, \tag{6.122}$$

due to a double counting of the electron repulsion terms in $E_1^{(0)}$.

The N-electron perturbation in MP approach, called the correlation (fluctuation) operator, is defined as the difference between the electronic Hamiltonian and this unperturbed effective Hamiltonian of the independent-particle (HF) model:

$$\hat{\mathrm{h}}^{corr.}(N) = \hat{\mathrm{H}}^{e}(N) - \hat{\mathrm{H}}_0^{\mathrm{MP}}(N) = \sum_{i<j}\frac{1}{r_{i,j}} - \sum_{i} V_{\mathrm{HF}}(i). \tag{6.123}$$

Indeed, this correlation operator carries only that part of the interelectronic interactions which has not been included in the averaged (effective) interactions of the resultant potential $V_{\mathrm{HF}}(\boldsymbol{r})$ combining the Coulomb and exchange operators defining the Fock operator.

For simplicity let us assume that we are interested in the Coulomb correlation correction to the (*closed*-shell) ground state of the system, $s = 1$ [see (6.108)].

In accordance with the Rayleigh-Schrödinger theory of Sect. 5.1.1, the consecutive correlation corrections to the unperturbed eigenvalue $E_1^{(0)} = \sum_{k=1}^{N} e_k$, and the associated eigenfunction Φ_1 (6.108), determine the corresponding ground state solutions of the perturbed (correlated) Hamiltonian

$$\hat{\mathrm{H}}_{\lambda}^{\mathrm{MP}}(N) = \hat{\mathrm{H}}_{0}^{\mathrm{MP}}(N) + \lambda \hat{\mathrm{h}}^{corr.}(N), \tag{6.124}$$

where $\hat{\mathrm{H}}_{\lambda=0}^{\mathrm{MP}}(N) = \hat{\mathrm{H}}_{0}^{\mathrm{MP}}(N)$ and $\hat{\mathrm{H}}_{\lambda=1}^{\mathrm{MP}}(N) = \hat{\mathrm{H}}^{e}(N)$:

$$\begin{aligned} E_\lambda = \sum_{j=0}^{\infty} \lambda^j E_1^{(j)} &\equiv E_1^{(0)} + \Delta E_1^{(1)} + \Delta E_1^{(2)} + \ldots \\ &= E_0^{\mathrm{HF}} + \Delta E_0^{\mathrm{HF}(1)} + \Delta E_0^{\mathrm{HF}(2)} + \ldots \end{aligned} \tag{6.125}$$

$$\Psi_\lambda = \sum_{i=0}^{\infty} \lambda^i \Psi_0^{(i)} = \Phi_1 + \Delta\Phi_1^{(1)} + \Delta\Phi_1^{(2)} + \ldots = \Psi_0^{\mathrm{HF}} + \Delta\Psi_0^{\mathrm{HF}(1)} + \Delta\Psi_0^{\mathrm{HF}(2)} + \ldots \tag{6.126}$$

The *first*-order energy correction [see (5.11)] corrects $E_1^{(0)}$ to E_0^{HF},

$$\begin{aligned} E_1^{(0)} + \Delta E_1^{(1)} = E_1^{(0)} + \langle \Phi_1 | \hat{\mathrm{h}}^{corr.} | \Phi_1 \rangle &= \left\langle \Psi_0^{\mathrm{HF}} \middle| \hat{\mathrm{H}}_0^{\mathrm{MP}} \middle| \Psi_0^{\mathrm{HF}} \right\rangle + \left\langle \Psi_0^{\mathrm{HF}} \middle| \hat{\mathrm{H}}^{e} - \hat{\mathrm{H}}_0^{\mathrm{MP}} \middle| \Psi_0^{\mathrm{HF}} \right\rangle \\ &= \left\langle \Psi_0^{\mathrm{HF}} \middle| \hat{\mathrm{H}}^{e} \middle| \Psi_0^{\mathrm{HF}} \right\rangle = E_0^{\mathrm{HF}}, \end{aligned} \tag{6.127}$$

thus removing the double counting of the electron repulsion terms in $E_1^{(0)}$. Therefore, it is the *second*-order term which represents the most important part of the Coulomb correlation energy. A reference to (5.16) indicates that it is determined by the *first*-order correction to $\Phi_1 = \Psi_0^{\mathrm{HF}}$:

$$\Delta\Psi_0^{\mathrm{HF}(1)} = \sum_{s\neq 1} \frac{\langle \Phi_s | \hat{\mathrm{h}}^{corr.} | \Phi_1 \rangle}{E_1^{(0)} - E_s^{(0)}} \Phi_s \equiv \sum_{s\neq 1} \frac{h_{s,1}^{corr.}}{E_1^{(0)} - E_s^{(0)}} \Phi_s = \sum_{s\neq 1} C_{s,1}^{(1)} \Phi_s. \tag{6.128}$$

It also follows from the orthogonality relations between configurations, $\langle \Phi_s \mid \Phi_t \rangle = \delta_{s,t}$, that the *off*-diagonal matrix elements ($s \neq t$) of the correlation operator, coupling different configurations, are identical with the corresponding elements of the energy matrix $\mathbf{H}^{\mathrm{CI}}$ representing the electronic Hamiltonian in the CI method:

$$\langle \Phi_s | \hat{\mathrm{h}}^{corr.} | \Phi_t \rangle = \langle \Phi_s | \hat{\mathrm{H}}^{e} - \hat{\mathrm{H}}_0^{\mathrm{MP}} | \Phi_t \rangle = H_{s,t}^{\mathrm{CI}} - E_t^{(0)} \langle \Phi_s \mid \Phi_t \rangle = H_{s,t}^{\mathrm{CI}}. \tag{6.129}$$

Therefore, in accordance with the Slater–Condon rules, there is no correlation coupling between this ground state reference configuration and the excited configurations exhibiting higher than double excitations: *Triple* (T), *Quadruple* (Q), etc. Moreover, the Brillouin theorem states that there is no direct coupling between the (closed-shell) ground state and the *Singly* (S) excited configurations, so that the expansion of (6.126) determining the MP2 scheme is then limited only to *Doubly* (D) excited configurations [see (6.117)]:

$$\Delta\Psi_0^{\mathrm{HF}(1)} = \sum_{s\in \mathrm{D}} C_{s,1}^{(1)}\Phi_s = \sum_{k<l}^{occd.}\sum_{p<q}^{virt.} C_{k,l}^{p,q}\Phi_{k,l}^{p,q}, \tag{6.130}$$

with the perturbational expression for the expansion coefficients [see (5.86)]:

$$C_{s,l}^{(1)} = \frac{H_{s,1}^{\mathrm{CI}}}{E_1^{(0)} - E_s^{(0)}} = C_{k,l}^{p,q}\, \frac{\langle kl|g|pq - qp\rangle}{e_k + e_l - e_p - e_q}. \tag{6.131}$$

One thus obtains for the *second*-order correlation energy in this MP2 variant of the perturbational CI method [see (5.16)]:

$$\begin{aligned}\Delta E_0^{\mathrm{HF}(2)} &= \left\langle \Psi_0^{\mathrm{HF}}\middle|\hat{\mathrm{H}}^e - \hat{\mathrm{H}}_0^{\mathrm{MP}}\middle|\Delta\Psi_0^{\mathrm{HF}(1)}\right\rangle = \left\langle \Psi_0^{\mathrm{HF}}\middle|\hat{\mathrm{H}}^e\middle|\Delta\Psi_0^{\mathrm{HF}(1)}\right\rangle - E_1^{(0)}\left\langle \Psi_0^{\mathrm{HF}}\middle|\Delta\Psi_0^{\mathrm{HF}(1)}\right\rangle \\ &= \left\langle \Psi_0^{\mathrm{HF}}\middle|\hat{\mathrm{H}}^e\middle|\Delta\Psi_0^{\mathrm{HF}(1)}\right\rangle,\end{aligned} \tag{6.132}$$

since the correction of (6.130), involving the excited configurations orthogonal to the ground state, must be also orthogonal to the latter. Substituting (6.129)–(6.131) into preceding equation finally gives:

$$\Delta E_0^{\mathrm{HF}(2)} = \sum_{k<l}^{occd.}\left(\sum_{p<q}^{virt.} \frac{|\langle kl|g|pq - qp\rangle|^2}{e_k + e_l - e_p - e_q}\right) \equiv \sum_{k<l}^{occd.} e_{k,l}^{\mathrm{MP2}} \equiv \Delta E_{corr.}^{\mathrm{MP2}}. \tag{6.133}$$

Therefore, this *second*-order correlation energy combines the additive contributions from all electronic pairs of the HF-occupied MO, which define the two-electron *clusters* $\{(k,l)\}$. For this reason, the MP2 method can be classified as corresponding within the PT approach to the *Independent Electron Pair Approximation* (IEPA) of Sect. 6.4.2, since only independent pairs give rise to *additive* energy contributions.

Obviously, by using the standard expressions from PT one could similarly determine the *higher* order contributions to the overall Coulomb correlation energy. Next in importance is the *third*-order correction $\Delta E_0^{\mathrm{HF}(3)}$, determined within the MP3 variant. It results from (5.6) for $p = 3$, projected onto $|n^{(0)}\rangle$, which gives $\Delta E_n^{(3)} = \left\langle n^{(0)}\middle|\hat{\mathrm{h}}\middle|\Delta n^{(2)}\right\rangle$, where the *second*-order correction to the wave function is given by (5.17). For example, for H_2O one finds the following percentages of the correlation energy recovered by different orders of MBPT, $\Delta E_0^{\mathrm{HF}(2)} = 97.7$ and

$\Delta E_0^{\mathrm{HF}(3)} = 1.5$, while in BH_3 the *higher*-order term appears to be relatively more significant: $\Delta E_0^{\mathrm{HF}(2)} = 80.0$ and $\Delta E_0^{\mathrm{HF}(3)} = 16.5$.

6.3.3 Density Matrices and Natural Orbitals

The spin position representation of the Hermitian operator of the projection onto the quantum state of N electrons, $\hat{\mathrm{P}}_{\Psi(N)} = |\Psi(N)\rangle\langle\Psi(N)|$(see Chap. 2), defines the N-particle *density matrix* (Löwdin 1955a, b; Coleman 1963, 1981; Coleman and Erdahl 1968; Davidson 1976):

$$\begin{aligned}&\hat{\Gamma}(\boldsymbol{q}_1, \boldsymbol{q}_2, \ \ldots, \ \boldsymbol{q}_N; \boldsymbol{q}_1{}', \boldsymbol{q}_2{}', \ \ldots, \ \boldsymbol{q}_N{}') \equiv \hat{\Gamma}(\mathcal{Q}^N ; \mathcal{Q}'^N)\\ &= \left\langle \mathcal{Q}^N \middle| \Psi(N)\right\rangle\left\langle \Psi(N) \middle| \mathcal{Q}'^N \right\rangle = \Psi(\mathcal{Q}^N)\Psi^*(\mathcal{Q}'^N).\end{aligned} \tag{6.134}$$

This continuous matrix represents the kernel of the associated operator $\hat{\Gamma}$ acting in the molecular Hilbert space:

$$\begin{aligned}\left\langle \mathcal{Q}^N \middle| \hat{\Gamma}\Phi \right\rangle &= \int \left\langle \mathcal{Q}^N \middle| \hat{\Gamma} \middle| \mathcal{Q}'^N \right\rangle \left\langle \mathcal{Q}'^N \middle| \Phi \right\rangle d\mathcal{Q}'^N = \int \hat{\Gamma}(\mathcal{Q}^N ; \mathcal{Q}'^N)\Phi(\mathcal{Q}'^N)\ d\mathcal{Q}'^N\\ &= \left\langle \mathcal{Q}^N \middle| \Psi \right\rangle \langle \Psi | \Phi \rangle = \Psi(\mathcal{Q}^N)\langle \Psi \mid \Phi \rangle,\end{aligned} \tag{6.135}$$

and carries the same (complete) information about the system state as does the wave function itself. One observes that its diagonal part, for $\mathcal{Q}^N = \mathcal{Q}'^N$, determines the N-particle probability of (3.4), $\hat{\Gamma}(\mathcal{Q}^N ; \mathcal{Q}^N) = p(\mathcal{Q}^N)$, so that

$$\mathrm{tr}\ \hat{\Gamma} = \int p(\mathcal{Q}^N)\, d\mathcal{Q}^N = 1 \tag{6.136}$$

and the *pure* state expectation value of the observable $\hat{\mathrm{A}}$ can be brought into the form similar to the *ensemble* average expression of (3.60a) (3.60b):

$$\langle A \rangle = \langle \Psi | \hat{\mathrm{A}} | \Psi \rangle = \iint \left\langle \mathcal{Q}^N \middle| \hat{\mathrm{A}} \middle| \mathcal{Q}'^N \right\rangle \Psi(\mathcal{Q}'^N)\Psi^*(\mathcal{Q}^N)\ d\mathcal{Q}^N d\mathcal{Q}'^N = \mathrm{tr}(\hat{\mathrm{A}}\hat{\Gamma}). \tag{6.137}$$

As we have already observed in Sect. 3.3.4, the density operator characterization of molecular systems becomes necessary when the system is in the *mixed* quantum state, which cannot be represented by a single vector in the Hilbert space or the associated wave function; it represents the statistical mixture of several quantum states. For the system to be in the *pure* quantum state, it is necessary and sufficient for its density operator to be idempotent, $\hat{\Gamma}^2 = \hat{\Gamma}$. This condition expresses the idempotency of the associate state projector $\hat{\mathrm{P}}_{\Psi(N)}$. In the Schrödinger picture of Quantum Mechanics the time evolution of this pure state density operator is given by (3.101).

The spin-independent electronic Hamiltonian of (5.51) and (5.69) is seen to involve the symmetric combinations of either one- or two-electron terms and the system wave function is antisymmetric with respect to exchanges of the subjective labels attributed to electrons. As we have already observed in Sect. 5.4, one can thus select as representative interactions of the indistinguishable electrons the one-electron energies of electron "1" and two electron repulsion energy between electrons "1" and "2." Therefore, when calculating the expectation values of all one- and two-electron interactions one can take the partial trace (integrate) over the remaining particle variables, equal in the primed and unprimed sets, in the generalized products appearing in the expectation value and matrix element expressions:

$$\begin{gathered} \Psi(\boldsymbol{Q}^N)\Psi^*(\boldsymbol{Q}'^N)\big|_{\boldsymbol{q}_2=\boldsymbol{q}_2',\boldsymbol{q}_3=\boldsymbol{q}_3',\ldots,\,\boldsymbol{q}_N=\boldsymbol{q}_N'} \quad \text{and} \\ \Psi(\boldsymbol{Q}^N)\Psi^*(\boldsymbol{Q}'^N)\big|_{\boldsymbol{q}_3=\boldsymbol{q}_3',\boldsymbol{q}_4=\boldsymbol{q}_4',\ldots,\,\boldsymbol{q}_N=\boldsymbol{q}_N'}, \end{gathered} \tag{6.138}$$

respectively. This simplification was the basic motivation of Löwdin (1955a, b) when he introduced the concept of the *reduced density matrix* of order *p*:

$$\begin{aligned} &\hat{\gamma}_p(\boldsymbol{q}_1,\boldsymbol{q}_2,\ \ldots,\boldsymbol{q}_p;\boldsymbol{q}_1',\boldsymbol{q}_2',\ \ldots,\boldsymbol{q}_p') \\ &\quad= \binom{N}{p}\ \mathrm{tr}\,\hat{\Gamma}(\boldsymbol{q}_1,\boldsymbol{q}_2,\ \ldots,\boldsymbol{q}_N;\boldsymbol{q}_1',\boldsymbol{q}_2',\ \ldots,\boldsymbol{q}_N')\big|_{\boldsymbol{q}_{p+1},\boldsymbol{q}_{p+2},\ \ldots,\boldsymbol{q}_N} \\ &\quad= \binom{N}{p}\int \Psi(\boldsymbol{q}_1,\ \ldots,\boldsymbol{q}_p,\boldsymbol{q}_{p+1},\ \ldots,\boldsymbol{q}_N)\Psi^*(\boldsymbol{q}_1',\ \ldots,\boldsymbol{q}_p',\boldsymbol{q}_{p+1},\ \ldots,\boldsymbol{q}_N) \\ &\qquad\times d\boldsymbol{q}_{p+1}d\boldsymbol{q}_{p+2}\ \ldots\ d\boldsymbol{q}_N, \end{aligned} \tag{6.139a}$$

where $\binom{N}{p}$ stands for the binomial coefficient [see (3.12) and (6.66)].

For example, the *first*-order reduced density matrix, or the *1-matrix* for short, reads:

$$\hat{\gamma}_1(\boldsymbol{q}_1;\boldsymbol{q}_1') = N\int \Psi(\boldsymbol{q}_1,\ \boldsymbol{q}_2,\ \ldots,\boldsymbol{q}_N)\Psi^*(\boldsymbol{q}_1',\ \boldsymbol{q}_2,\ \ldots,\boldsymbol{q}_N)\ d\boldsymbol{q}_2\ \ldots\ d\boldsymbol{q}_N. \tag{6.140a}$$

Its diagonal part thus represents the spin density of the system electrons (3.9): $\rho(\boldsymbol{q}) = \rho(\boldsymbol{r},\sigma) = \hat{\gamma}_1(\boldsymbol{q};\boldsymbol{q})$, which implies the associated normalization:

$$\mathrm{tr}\,\hat{\gamma}_1(\boldsymbol{q}_1;\boldsymbol{q}_1') = \int \hat{\gamma}_1(\boldsymbol{q}_1;\boldsymbol{q}_1)\,d\boldsymbol{q}_1 = N. \tag{6.141a}$$

One similarly obtains the *second*-order reduced density matrix (or *2-matrix*):

$$\hat{\gamma}_2(\boldsymbol{q}_1,\boldsymbol{q}_2;\boldsymbol{q}_1{}',\boldsymbol{q}_2{}') = \binom{N}{2}\int \Psi(\boldsymbol{q}_1,\ \boldsymbol{q}_2,\boldsymbol{q}_3,\ \dots\ ,\boldsymbol{q}_N) \\ \times\ \Psi^*(\boldsymbol{q}_1{}',\ \boldsymbol{q}_2{}',\boldsymbol{q}_3,\ \dots\ ,\boldsymbol{q}_N)\ d\boldsymbol{q}_3\ \dots\ d\boldsymbol{q}_N, \qquad (6.142)$$

the *pair* diagonal element of which now represents the *pair* spin density [see (3.12)],

$$\hat{\gamma}_2(\boldsymbol{q},\boldsymbol{q}';\boldsymbol{q},\boldsymbol{q}') = \Gamma(\boldsymbol{q},\boldsymbol{q}') = \int \Psi^*(\mathbb{Q}^N)\hat{\Gamma}(\boldsymbol{q},\boldsymbol{q}')\Psi(\mathbb{Q}^N)\,d\mathbb{Q}^N, \\ \hat{\Gamma}(\boldsymbol{q},\boldsymbol{q}') = \sum_{k=1}^{N-1}\sum_{l=k+1}^{N}\delta(\boldsymbol{q}_k-\boldsymbol{q})\delta(\boldsymbol{q}_l-\boldsymbol{q}'). \qquad (6.143)$$

This implies the associated normalization of the 2-matrix:

$$\mathrm{tr}\,\hat{\gamma}_2(\boldsymbol{q}_1,\boldsymbol{q}_2;\boldsymbol{q}_1{}',\boldsymbol{q}_2{}') = \iint \hat{\gamma}_2(\boldsymbol{q}_1,\boldsymbol{q}_2;\boldsymbol{q}_1,\boldsymbol{q}_2)\,d\boldsymbol{q}_1 d\boldsymbol{q}_2 = N(N-1)/2 = \binom{N}{2}. \qquad (6.144)$$

The expectation value of the sum of all one-electron operators in $\hat{\mathcal{F}} = \sum_{i=1}^{N}\hat{\mathrm{h}}(i)$ [see (5.69)–(5.71)] now reads:

$$\left\langle \Psi \mid \hat{\mathcal{F}} \middle| \Psi \right\rangle = \mathrm{tr}\,(\hat{\mathcal{F}}\,\hat{\Gamma}) = \mathrm{tr}\,(\hat{\mathrm{h}}\,\hat{\gamma}_1) = \int \hat{\mathrm{h}}(\boldsymbol{q}_1)\,\hat{\gamma}_1(\boldsymbol{q}_1;\boldsymbol{q}_1{}')|_{\boldsymbol{q}_1=\boldsymbol{q}_1{}'}\,d\boldsymbol{q}_1. \qquad (6.145)$$

For the expectation value of the two-electron energy one similarly obtains:

$$\left\langle \Psi \mid \hat{\mathcal{G}} \middle| \Psi \right\rangle = \mathrm{tr}\,(\hat{\mathcal{G}}\,\hat{\Gamma}) = \mathrm{tr}(g\,\hat{\gamma}_2) \\ = \iint g(\boldsymbol{q}_1,\boldsymbol{q}_2)\,\hat{\gamma}_2(\boldsymbol{q}_1,\boldsymbol{q}_2;\boldsymbol{q}_1{}',\boldsymbol{q}_2{}')|_{\boldsymbol{q}_1=\boldsymbol{q}_1{}',\boldsymbol{q}_2=\boldsymbol{q}_2{}'}\,d\boldsymbol{q}_1 d\boldsymbol{q}_2. \qquad (6.146)$$

Since operators $\hat{\mathrm{h}}$ and g are both spin independent these expressions can be further simplified in terms of the reduced *spinless* density matrices, obtained by summations over the spin variables of the spin-dependent analogs:

$$\begin{aligned} \hat{\rho}_1(\boldsymbol{r}_1;\boldsymbol{r}_1{}') &= \int \hat{\gamma}_1(\boldsymbol{r}_1,\sigma_1;\boldsymbol{r}_1{}',\sigma_1)\,d\sigma_1 \equiv \sum_{\sigma_1}\hat{\gamma}_1(\boldsymbol{r}_1,\sigma_1;\boldsymbol{r}_1{}',\sigma_1) = \mathrm{tr}\,\hat{\gamma}_1(\boldsymbol{q}_1;\boldsymbol{q}_1{}')|_{\sigma_1} \\ &= \hat{\gamma}_1(\boldsymbol{r}_1,\alpha;\boldsymbol{r}_1{}',\alpha) + \hat{\gamma}_1(\boldsymbol{r}_1,\beta;\boldsymbol{r}_1{}',\beta) \equiv \hat{\rho}_1^{\alpha;\alpha}(\boldsymbol{r};\boldsymbol{r}') + \hat{\rho}_1^{\beta;\beta}(\boldsymbol{r};\boldsymbol{r}'), \\ \hat{\rho}_2(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_1{}',\boldsymbol{r}_2{}') &= \iint \hat{\gamma}_2(\boldsymbol{r}_1,\sigma_1,\boldsymbol{r}_2,\sigma_2;\boldsymbol{r}_1{}',\sigma_1,\boldsymbol{r}_2{}',\sigma_2)\,d\sigma_1 d\sigma_2 \\ &\equiv \sum_{\sigma_1}\sum_{\sigma_2}\hat{\gamma}_2(\boldsymbol{r}_1,\sigma_1,\boldsymbol{r}_2,\sigma_2;\boldsymbol{r}_1{}',\sigma_1,\boldsymbol{r}_2{}',\sigma_2) = \mathrm{tr}\,\hat{\gamma}_2(\boldsymbol{q}_1,\boldsymbol{q}_2;\boldsymbol{q}_1{}',\boldsymbol{q}_2{}')|_{\sigma_1,\sigma_2} \\ &\equiv \hat{\rho}_2^{\alpha\alpha;\alpha\alpha}(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_1{}',\boldsymbol{r}_2{}') + \hat{\rho}_2^{\alpha\beta;\alpha\beta}(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_1{}',\boldsymbol{r}_2{}') + \hat{\rho}_2^{\beta\alpha;\beta\alpha}(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_1{}',\boldsymbol{r}_2{}') \\ &\quad + \hat{\rho}_2^{\beta\beta;\beta\beta}(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_1{}',\boldsymbol{r}_2{}'). \end{aligned} \qquad (6.147)$$

Their diagonal elements respectively represent the electron density (3.7) and *pair* density (3.12):

$$\rho(\boldsymbol{r}) = \hat{\rho}_1(\boldsymbol{r};\boldsymbol{r}) \qquad \text{and} \qquad \Gamma(\boldsymbol{r},\boldsymbol{r}') = \hat{\rho}_2(\boldsymbol{r},\boldsymbol{r}';\boldsymbol{r},\boldsymbol{r}'), \tag{6.148}$$

thus giving rise to the associated normalizations:

$$\begin{aligned} \operatorname{tr} \hat{\rho}_1(\boldsymbol{r}_1;\boldsymbol{r}_1{}') &= \int \hat{\rho}_1(\boldsymbol{r};\boldsymbol{r})\, d\boldsymbol{r} = N, \\ \operatorname{tr} \hat{\rho}_2(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_1{}',\boldsymbol{r}_2{}') &= \int\!\!\int \hat{\rho}_2(\boldsymbol{r},\boldsymbol{r}';\boldsymbol{r},\boldsymbol{r}')\, d\boldsymbol{r}\, d\boldsymbol{r}' = N(N-1)/2. \end{aligned} \tag{6.149}$$

The spinless expression for the expectation value of the system electronic energy thus reads:

$$\begin{aligned} E^e[\hat{\rho}_1,\hat{\rho}_2] = \int [-\frac{1}{2}\Delta_{\boldsymbol{r}}\, \hat{\rho}_1(\boldsymbol{r};\boldsymbol{r}')|_{\boldsymbol{r}=\boldsymbol{r}'}\, d\boldsymbol{r} + \int v(\boldsymbol{r})\rho(\boldsymbol{r})\, d\boldsymbol{r} \\ + \int\!\!\int \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\Gamma(\boldsymbol{r},\boldsymbol{r}')\, d\boldsymbol{r}\, d\boldsymbol{r}'. \end{aligned} \tag{6.150}$$

The reduced density matrices define kernels of the Hermitian, positive semi-definite operators:

$$\begin{aligned} &\hat{\gamma}_1(\boldsymbol{q}_1;\boldsymbol{q}_1{}') = \hat{\gamma}_1^*(\boldsymbol{q}_1{}';\boldsymbol{q}_1), && \hat{\gamma}_1(\boldsymbol{q}_1;\boldsymbol{q}_1) \geq 0; \\ &\hat{\gamma}_2(\boldsymbol{q}_1,\boldsymbol{q}_2;\boldsymbol{q}_1{}',\boldsymbol{q}_2{}') = \hat{\gamma}_2^*(\boldsymbol{q}_1{}',\boldsymbol{q}_2{}';\boldsymbol{q}_1,\boldsymbol{q}_2), && \hat{\gamma}_2(\boldsymbol{q}_1,\boldsymbol{q}_2;\boldsymbol{q}_1,\boldsymbol{q}_2) \geq 0. \end{aligned} \tag{6.151}$$

The antisymmetry of the wave function also implies that the reduced densities change their sign on exchange of any two primed or two unprimed particle indices:

$$\begin{aligned} \hat{\gamma}_2(\boldsymbol{q}_1,\boldsymbol{q}_2;\boldsymbol{q}_1{}',\boldsymbol{q}_2{}') &= -\hat{\gamma}_2(\boldsymbol{q}_2,\boldsymbol{q}_1;\boldsymbol{q}_1{}',\boldsymbol{q}_2{}') = -\hat{\gamma}_2(\boldsymbol{q}_1,\boldsymbol{q}_2;\boldsymbol{q}_2{}',\boldsymbol{q}_1{}') \\ &= \hat{\gamma}_2(\boldsymbol{q}_2,\boldsymbol{q}_1;\boldsymbol{q}_2{}',\boldsymbol{q}_1{}'). \end{aligned} \tag{6.152}$$

Of particular interest in the electron correlation theory are the eigenvalue problems of $\hat{\gamma}_1$ and $\hat{\gamma}_2$:

$$\int \hat{\gamma}_1(\boldsymbol{q};\boldsymbol{q}')\, \psi_i(\boldsymbol{q}')d\boldsymbol{q}' = n_i^{\mathrm{NO}}\psi_i(\boldsymbol{q}), \tag{6.153}$$

$$\int\!\!\int \hat{\gamma}_2(\boldsymbol{q}_1,\boldsymbol{q}_2;\boldsymbol{q}_1{}',\boldsymbol{q}_2{}')\, G_j(\boldsymbol{q}_1{}',\boldsymbol{q}_2{}')\, d\boldsymbol{q}_1{}'d\boldsymbol{q}_2{}' = \nu_j^{\mathrm{NG}}G_j(\boldsymbol{q}_1,\boldsymbol{q}_2). \tag{6.154}$$

The eigenfunctions $\{\psi_i\}$ of $\hat{\gamma}_1$ are called the *Natural Orbitals* (NO) (Löwdin 1955a, b; Löwdin and Shull 1956; Carlson and Keller 1961; Davidson 1969, 1972a, b, 1976;

Bingel and Kutzelnigg 1970), with the corresponding eigenvalues measuring their effective occupations in Ψ: $\left\{0 \leq n_i^{\mathrm{NO}} \leq 1\right\}$. The corresponding two-electron (antisymmetric) eigenfunctions of $\hat{\gamma}_2$, $\{G_j(\boldsymbol{q}_1, \boldsymbol{q}_2) = -G_j(\boldsymbol{q}_2, \boldsymbol{q}_1)\}$, determine the system *natural geminals* (NG), with the eigenvalues $\left\{\nu_j^{\mathrm{NG}}\right\}$ again reflecting their effective occupations.

It should be observed that these two density matrices assume the most compact (diagonal) representations in terms of their respective eigenfunctions:

$$\begin{aligned}
\hat{\gamma}_1 &= \sum_i n_i^{\mathrm{NO}} |\psi_i\rangle\langle\psi_i| \equiv |\boldsymbol{\psi}^{\mathrm{NO}}\rangle \mathbf{n}^{\mathrm{NO}} \langle\boldsymbol{\psi}^{\mathrm{NO}}|,\\
\mathbf{n}^{\mathrm{NO}} &= \{n_i^{\mathrm{NO}} \delta_{i,j}\},\ |\boldsymbol{\psi}^{\mathrm{NO}}\rangle = \{|\psi_i\rangle\},\ \text{or}\\
\hat{\gamma}_1(\boldsymbol{r}_1; \boldsymbol{r}_1') &= \langle \boldsymbol{r}_1|\hat{\gamma}_1|\boldsymbol{r}_1'\rangle = \sum_i n_i^{\mathrm{NO}} \langle \boldsymbol{r}_1|\psi_i\rangle\langle\psi_i|\boldsymbol{r}_1'\rangle = \sum_i n_i^{\mathrm{NO}}\, \psi_i(\boldsymbol{r}_1)\, \psi_i^*(\boldsymbol{r}_1');
\end{aligned} \tag{6.155}$$

$$\begin{aligned}
\hat{\gamma}_2 &= \sum_j \nu_j |G_j\rangle\langle G_j| \equiv |\boldsymbol{G}^{\mathrm{NG}}\rangle \boldsymbol{\nu}^{\mathrm{NG}} \langle \boldsymbol{G}^{\mathrm{NG}}|,\\
\boldsymbol{\nu}^{\mathrm{NG}} &= \{\nu_i^{\mathrm{NG}} \delta_{i,j}\},\ |\boldsymbol{G}^{\mathrm{NG}}\rangle = \{|G_j\rangle\},\ \text{or}\\
\hat{\gamma}_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2') &= \langle \boldsymbol{r}_1, \boldsymbol{r}_2|\hat{\gamma}_2|\boldsymbol{r}_1', \boldsymbol{r}_2'\rangle = \sum_j \nu_j^{\mathrm{NG}} \langle \boldsymbol{r}_1, \boldsymbol{r}_2|G_j\rangle\langle G_j|\boldsymbol{r}_1', \boldsymbol{r}_2'\rangle\\
&= \sum_j \nu_j^{\mathrm{NG}}\, G_j(\boldsymbol{r}_1, \boldsymbol{r}_2)\, G_j^*(\boldsymbol{r}_1', \boldsymbol{r}_2').
\end{aligned} \tag{6.156}$$

Expanding NO in the AO basis functions $\boldsymbol{\chi} = \{\chi_s\}$, $\boldsymbol{\psi}^{\mathrm{NO}} = \boldsymbol{\chi}\mathbf{D} = \{\psi_i\}$ (the row vector), gives the following expression for the 1-matrix [compare (6.45)]:

$$\begin{aligned}
\hat{\gamma}_1(\boldsymbol{r}_1; \boldsymbol{r}_1') &= \langle \boldsymbol{r}_1|\boldsymbol{\psi}^{\mathrm{NO}}\rangle \mathbf{n}^{\mathrm{NO}} \langle \boldsymbol{\psi}^{\mathrm{NO}}|\boldsymbol{r}_1'\rangle = \boldsymbol{\psi}^{\mathrm{NO}}(\boldsymbol{r}_1)\mathbf{n}^{\mathrm{NO}}\boldsymbol{\psi}^{\mathrm{NO}\dagger}(\boldsymbol{r}_1')\\
&= \boldsymbol{\chi}(\boldsymbol{r}_1)[\mathbf{D}\mathbf{n}^{\mathrm{NO}}\mathbf{D}^\dagger]\boldsymbol{\chi}^\dagger(\boldsymbol{r}_1') = \boldsymbol{\chi}(\boldsymbol{r}_1)\mathbf{P}^{\mathrm{NO}}(\mathbf{D})\boldsymbol{\chi}^\dagger(\boldsymbol{r}_1'),
\end{aligned} \tag{6.157}$$

where we have grouped the NO occupations as diagonal elements of the square matrix $\mathbf{n}^{\mathrm{NO}} = \left\{n_i^{\mathrm{NO}}\ \delta_{i,i'}\right\}$, while $\boldsymbol{\chi}^\dagger = \left\{\chi_s^*\right\}^{\mathrm{T}}$ and $\boldsymbol{\psi}^{\mathrm{NO}\dagger} = \left\{\psi_i^*\right\}^{\mathrm{T}}$ denote the associated column vectors. Therefore, the NO CBO matrix in the AO representation,

$$\mathbf{P}^{\mathrm{NO}}(\mathbf{D}) = \left\{P_{s,t}^{\mathrm{NO}} = \sum_i^{\mathrm{NO}} D_{s,i} n_i^{\mathrm{NO}} D_{t,i}^*\right\}, \tag{6.158}$$

determines the 1–matrix in terms of basis functions $\boldsymbol{\chi}$.

The corresponding AO expansion of NG,

$$\begin{aligned}
\boldsymbol{G}^{\mathrm{NG}}(\boldsymbol{r}_1, \boldsymbol{r}_2) &= \{G_j(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{s,t}^{\mathrm{AO}} \chi_s(\boldsymbol{r}_1)\chi_t(\boldsymbol{r}_2)\, A_{s,t;j}\\
&\equiv \sum_{s,t}^{\mathrm{AO}} \Omega_{s,t}(\boldsymbol{r}_1, \boldsymbol{r}_2) A_{s,t;j}\} \equiv \boldsymbol{\Omega}(\boldsymbol{r}_1, \boldsymbol{r}_2)\mathbf{A},
\end{aligned} \tag{6.159}$$

gives the following expression for the 2-matrix:

$$\begin{aligned}\hat{\gamma}_2(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_1{}',\boldsymbol{r}_2{}') &= \langle \boldsymbol{r}_1,\boldsymbol{r}_2|\boldsymbol{G}^{\mathrm{NG}}\rangle \boldsymbol{\nu}^{\mathrm{NG}}\langle \boldsymbol{G}^{\mathrm{NG}}|\boldsymbol{r}_1{}',\boldsymbol{r}_2{}'\rangle = \boldsymbol{G}^{\mathrm{NG}}(\boldsymbol{r}_1,\boldsymbol{r}_2)\boldsymbol{\nu}^{\mathrm{NG}}\boldsymbol{G}^{\mathrm{NG}\dagger}(\boldsymbol{r}_1{}',\boldsymbol{r}_2{}')\\ &= \boldsymbol{\Omega}(\boldsymbol{r}_1,\boldsymbol{r}_2)[\mathbf{A}\boldsymbol{\nu}^{\mathrm{NG}}\mathbf{A}^{\dagger}]\boldsymbol{\Omega}^{\dagger}(\boldsymbol{r}_1{}',\boldsymbol{r}_2{}') = \boldsymbol{\Omega}(\boldsymbol{r}_1,\boldsymbol{r}_2)\,\mathbf{P}^{\mathrm{NG}}(\mathbf{A})\,\boldsymbol{\Omega}^{\dagger}(\boldsymbol{r}_1{}',\boldsymbol{r}_2{}'),\end{aligned} \tag{6.160}$$

where $\boldsymbol{\nu}^{\mathrm{NG}} = \left\{ \nu_j^{\mathrm{NG}}\delta_{j,j'} \right\}$. Again, the corresponding NG CBO matrix

$$\mathbf{P}^{\mathrm{NG}}(\mathbf{A}) = \left\{ P^{\mathrm{NG}}_{s,t;u,v} = \sum_{j}^{\mathrm{NG}} A_{s,t;j}\,\nu_j^{\mathrm{NG}} A^*_{u,v;j} \right\} \tag{6.161}$$

defines the 2-matrix in the AO representation.

The density matrices for the HF wave function, given by a single Slater determinant (5.64), defined by the optimum HF SO $\boldsymbol{\psi} = \{\psi_i\}$, assume particularly simple forms (Löwdin 1955b). The 1-matrix in this approximation reads,

$$\hat{\gamma}_1^{\mathrm{HF}}(\boldsymbol{q}_1;\boldsymbol{q}_1{}') = \sum_{i=1}^{N} \psi_i(\boldsymbol{q}_1)\,\psi_i^*(\boldsymbol{q}_1{}'), \tag{6.140b}$$

while the *second*-order reduced density matrix is given by the following determinant of 1-matrices:

$$\begin{aligned}\hat{\gamma}_2^{\mathrm{HF}}(\boldsymbol{q}_1,\boldsymbol{q}_2;\boldsymbol{q}_1{}',\boldsymbol{q}_2{}') &= \frac{1}{2}\begin{vmatrix} \hat{\gamma}_1^{\mathrm{HF}}(\boldsymbol{q}_1;\boldsymbol{q}_1{}') & \hat{\gamma}_1^{\mathrm{HF}}(\boldsymbol{q}_1;\boldsymbol{q}_2{}') \\ \hat{\gamma}_1^{\mathrm{HF}}(\boldsymbol{q}_2;\boldsymbol{q}_1{}') & \hat{\gamma}_1^{\mathrm{HF}}(\boldsymbol{q}_2;\boldsymbol{q}_2{}') \end{vmatrix}\\ &= \frac{1}{2}[\hat{\gamma}_1^{\mathrm{HF}}(\boldsymbol{q}_1;\boldsymbol{q}_1{}')\hat{\gamma}_1^{\mathrm{HF}}(\boldsymbol{q}_2;\boldsymbol{q}_2{}') - \hat{\gamma}_1^{\mathrm{HF}}(\boldsymbol{q}_2;\boldsymbol{q}_1{}')\hat{\gamma}_1^{\mathrm{HF}}(\boldsymbol{q}_1;\boldsymbol{q}_2{}')].\end{aligned} \tag{6.141b}$$

As also shown by Löwdin (1955b), this prescription can be extended into a general reduced density matrix of (6.139a) in HF approximation:

$$\hat{\gamma}_p^{\mathrm{HF}}(\boldsymbol{q}_1,\boldsymbol{q}_2,\ldots,\boldsymbol{q}_p;\boldsymbol{q}_1{}',\boldsymbol{q}_2{}',\ldots,\boldsymbol{q}_p{}') = \frac{1}{p!}\begin{vmatrix} \hat{\gamma}_1^{\mathrm{HF}}(\boldsymbol{q}_1;\boldsymbol{q}_1{}') & \hat{\gamma}_1^{\mathrm{HF}}(\boldsymbol{q}_1;\boldsymbol{q}_2{}') & \cdots & \hat{\gamma}_1^{\mathrm{HF}}(\boldsymbol{q}_1;\boldsymbol{q}_p{}') \\ \hat{\gamma}_1^{\mathrm{HF}}(\boldsymbol{q}_2;\boldsymbol{q}_1{}') & \hat{\gamma}_1^{\mathrm{HF}}(\boldsymbol{q}_2;\boldsymbol{q}_2{}') & \cdots & \hat{\gamma}_1^{\mathrm{HF}}(\boldsymbol{q}_2;\boldsymbol{q}_p{}') \\ \cdots & \cdots & \cdots & \cdots \\ \hat{\gamma}_1^{\mathrm{HF}}(\boldsymbol{q}_p;\boldsymbol{q}_1{}') & \hat{\gamma}_1^{\mathrm{HF}}(\boldsymbol{q}_p;\boldsymbol{q}_2{}') & \cdots & \hat{\gamma}_1^{\mathrm{HF}}(\boldsymbol{q}_p;\boldsymbol{q}_p{}') \end{vmatrix}. \tag{6.139b}$$

There is a number of analytical arguments and a growing numerical evidence for small molecules that the convergence of the CI expansion is greatly enhanced by the use of NO. In other words, the correlation energy recovery is greater for the NO-based CI treatment, compared with that using the canonical SCF MO, at the same length of expansion (Shavitt et al. 1976). This analysis of wave functions is basis-set independent and allows one to compare any set of approximate wave functions. There are also conceptual advantages associated with the NO representation. It has been found to provide almost universal patterns of the orbital shapes and occupations for diverse wave functions obtained using widely different basis sets and CI expansions (Davidson 1972b). The observed "invariance" of the NO occupation numbers to choices of the basis set and the length of the CI expansion, respectively, suggests some "universality" of the NO description of atoms and molecules. The NO analysis emphasizes the strongly, near-unity populated HF-like NO and generates the weakly populated *correlation orbitals*, which represent the independent modes of the electron Coulomb correlation in molecular systems, the relative importance of which can be inferred from the corresponding orbital occupations. For example, in He the first correlation NO introduces the angular ("*left–right*")-type correlation, while the second correlation orbital brings in the ("*in–out*")-effect of the radial correlation. The NO analysis has also been widely used to study the nature of the chemical bond and the adequacy of the HF description in the bond-breaking – bond-forming processes (e.g., Shull 1959; Hagstrom and Shull 1963).

Thus, the NO play a significant role as both means for improving the CI convergence and in obtaining the physical insight and understanding of approximate wave functions. However, since NO are determined by "retrospective" analysis of an already known CI wave function, their construction in advance of the CI calculations can be only an approximate one, e.g., in an iterative procedure of determining the so-called *pseudo* NO (PNO). It usually consists of using the SCF virtuals in a limited-CI study, diagonalizing the resulting 1-matrix, which determines the first-approximation PNO, using them as a basis for an improved CI expansion, from which the second-approximation PNO are constructed, etc. Such iterative process is carried out until self-consistency is attained within the adopted level of electron excitations, when the subsequent iterations do not appreciably modify the PNO shapes and occupations.

6.4 Electron Pair Theories

As we have concluded from (6.133), the MP2 theory in fact represents the *perturbational* IEPA approximation (Sinanoĝlu 1964; Nesbet 1965; Szabo and Ostlund 1982) giving rise to the additive contributions to the system Coulomb correlation energy due to each occupied MO-pair of electrons. Clearly, a similar perspective can be also adopted within the *variational* method of determining approximate wave functions of molecular systems. Since the Coulomb correlation effect should be the strongest in pairs of electrons exhibiting opposite spins and occupying the same MO, the simplest formulation of such a variational approach should involve the antisymmetrized product of the electron pair functions, called *geminals*, the name first coined by Shull (1959) to distinguish these two-electron (group) functions from their one-electron analogs – the orbitals. In this *separated pair* approach, each MO-pair of electrons is correlated internally, but the interpair correlation is neglected. This missing part of the Coulomb correlation is accounted for in the more sophisticated *Coupled Electronic Pair Approximation* (CEPA) (Meyer 1977), *Coupled Pair Many Electron Theory* (CPMET) or *Coupled Cluster Approximation* (CCA) (Bartlett 1981, 1989, 1995, 2000; Kucharski and Bartlett 1986; Čižek 1966, 1969; Paldus and Čižek 1973, 1975; Hurley 1976; Kutzelnigg 1977; Čižek and Paldus 1980; Jørgensen and Simons 1981; Szabo and Ostlund 1982), which use appropriate simplifications of the whole hierarchy of the CI equations. As expected, the inclusion of interpair correlation improves accuracy at the expense of the computational complexity and clarity of interpretation. Of similar character is the *Generalized Valence Bond* (GVB) approach of Goddard and collaborators (Goddard III 1967; Goddard III and Ladner 1971; Hunt et al. 1972; Goddard III et al. 1973; Moss and Goddard III 1975; Bobrowicz and Goddard III 1977; Goddard III and Harding 1978), which represents another electron pair generalization of the classical VB theory of Heitler and London.

The *geminal* method can be also viewed as a logical next step in the wave function factorization following the *orbital* approximation. It represents a particular case of the *group* wave functions, describing specific molecular fragments, in which each constituent subsystem is first considered as a separate entity and subsequently their mutual interaction is accounted for, e.g., in the perturbative or self-consistent way. It should be observed that such a general line of thinking also lies behind the separation between the inner and valence shells, the σ and π electrons in aromatic systems, etc. The use of electronic pairs as fundamental structural entities in the limited-CI theories is very much in line with the intuitive chemical thinking. Indeed, the concepts of the bonding pairs in valence shell, as well as the lone pairs of both the valence or inner shells, have been very successful in the early, qualitative theories of electronic structure. Hence, their explicit recognition in the modern beyond-HF calculations brings an additional, chemical insight into the mechanism of the electron Coulomb correlation and represents an element of continuity in the development of such ideas in the theory of chemistry (Pauling 1949; Hurley et al. 1953; Parks and Parr 1958, 1960; Karplus and Grant 1959; McWeeny and Ohno 1960; McWeeny 1989).

One could also include in this category Moffitt's (1951) method of *Atoms-in-Molecules* (AIM) and its subsequent extension involving *deformed* AIM (Arai 1957, 1960; Ellison 1965; Ellison and Wu 1967, 1968; Ellison and Slezak 1969), as well as the *Diatomics-in-Molecules* (DIM) theory (Kuntz 1979; Tully 1977, 1980) and its generalization in the form of the *Molecules-in-Molecules* (MIM) approach, which involves groups of electrons of larger parts of the whole molecular system. All these approaches have played an important role in modeling the molecular PES for the dynamical calculations, e.g., in developing the familiar *London–Eyring–Polanyi–Sato* (LEPS) (e.g.: Hirst 1985; Murrell et al. 1984; Murrell and Bosanac 1989), *Bond-Energy – Bond-Order* (BEBO) (Johnston and Parr 1963) and DIM energy surfaces for the reactive scattering calculations.

6.4.1 Electron Pairs on Strongly Orthogonal Geminals

Following the orbital approximation of the HF theory, marking the separated electrons approach, we now assume the related form of the variational wave function of, say, $N = 2p$ electrons in terms of the separated electronic pairs [compare (5.66)] given by the antisymmetrized product of two-electron functions (geminals) $\{G_j(1, 2)\}$:

$$\Psi_A^G(1, 2, \ldots, N) = \hat{\mathrm{A}}'\{G_1(1, 2)\, G_2(3, 4) \ldots G_p(N-1, N)\}; \tag{6.162}$$

here $\hat{\mathrm{A}}'$ stands for the partial antisymmetrizer exchanging electrons between different geminals.

These normalized two-electron functions,

$$\iint |G_j(1, 2)|^2\, d\boldsymbol{q}_1 d\boldsymbol{q}_2 = \langle G_j(1, 2) \mid G_j(1, 2)\rangle_{1,2} = 1, \tag{6.163}$$

have to be also mutually orthogonal:

$$\iint G_i^*(1, 2) G_j(1, 2)\, d\boldsymbol{q}_1 d\boldsymbol{q}_2 = \langle G_i(1, 2) \mid G_j(1, 2)\rangle_{1,2} = 0, \quad i \neq j. \tag{6.164}$$

However, to simplify the expression for the expectation value of the electronic energy and hence also the resulting Euler equations of the variational method using this trial function, the *strong orthogonality* condition is imposed on the optimum geminals:

$$\int G_i^*(1, 2) G_j(1, 2) d\boldsymbol{q}_1 = \langle G_i(1, 2) \mid G_j(1, 2)\rangle_1 = 0, \quad \text{for any } \boldsymbol{q}_2. \tag{6.165}$$

Notice that this requirement automatically implies the ordinary orthogonality of (6.164). The trial wave function of (6.162) is then referred to as the *Antisymmetrized Product of Strongly Orthogonal Geminals* (APSG).

In each (antisymmetric) two-electron state, $G_j(1, 2) = -G_j(2, 1)$, representing the spin-paired electrons in the singlet spin eigenstate of (6.67) (see Fig. 6.2), one can also separate its spatial and spin parts [see (5.103)]:

$$\begin{aligned} G_j(\boldsymbol{q}_1, \boldsymbol{q}_2) \equiv G_j(1, 2) &= \Phi_j(\boldsymbol{r}_1, \boldsymbol{r}_2) \frac{1}{\sqrt{2}} [\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)] \\ &\equiv \Phi_j(1, 2)\, U_{0,0}(1, 2). \end{aligned} \tag{6.166}$$

Therefore, since the singlet spin factor of each geminal in APSG of (6.162) is also antisymmetric, $U_{0,0}(1, 2) = -U_{0,0}(2, 1)$, the spatial factors must be symmetric functions of two electrons, $\Phi_j(1, 2) = \Phi_j(2, 1)$, in order to satisfy the Pauli antisymmetrization requirement for these two (spin-paired) fermions.

Let us now examine the corresponding expression for the expectation value of the electronic Hamiltonian in such a trial state [see (5.69)–(5.71)]:

$$\langle E^e\rangle_{\Psi_A^G} = \left\langle\Psi_A^G\middle|\hat{\mathrm{H}}^e\middle|\Psi_A^G\right\rangle = \left\langle\Psi_A^G\middle|\hat{\mathcal{F}}\middle|\Psi_A^G\right\rangle + \left\langle\Psi_A^G\middle|\hat{\mathcal{G}}\middle|\Psi_A^G\right\rangle \equiv \langle\mathcal{F}\rangle_{\Psi_A^G} + \langle\mathcal{G}\rangle_{\Psi_A^G}. \tag{6.167}$$

Due to the strong orthogonality relations between the two-electron functions, the one-electron operator $\hat{\mathrm{h}}(1)$[(5.69) and (5.70)] can only couple the electron in the same geminal of Ψ_A^{G*} and Ψ_A^G. One thus finds the following expression for the overall one-electron contribution to the electronic energy:

$$\langle\mathcal{F}\rangle_{\Psi_A^G} = 2\sum_{j=1}^{p}\left\langle\Phi_j(1,\,2)\middle|\hat{\mathrm{h}}(1)\middle|\Phi_j(1,\,2)\right\rangle_{1,2}. \tag{6.168}$$

The two-electron repulsion $g(1,2) = 1/r_{1,2}$ couples both the pairs of particles on the same and different geminals of Ψ_A^{G*} and Ψ_A^G. Thus, using again the orthonormality relations and summing over electron spin orientations gives:

$$\begin{aligned}\langle\mathcal{G}\rangle_{\Psi_A^G} =& \sum_{j=1}^{p}\left\langle\Phi_j(1,2)\middle|g(1,2)\middle|\Phi_j(1,2)\right\rangle_{1,2}\\ &+\sum_{i=1}^{p-1}\sum_{j=i+1}^{p}2\Big(2\left\langle\Phi_i(1,2)\Phi_j(3,4)\middle|g(1,3)\middle|\Phi_i(1,2)\Phi_j(3,4)-\Phi_i(3,2)\Phi_j(1,4)\right\rangle_{1,2,3,4}\Big).\end{aligned} \tag{6.169}$$

The strong orthogonality condition (6.165) can be automatically satisfied when one uses different (mutually orthogonal) subspaces $\{\psi_{l,j}\}$ of NO to represent different geminals, i.e., when the total (complete) space of the orthonormal orbitals $\boldsymbol{\psi} = \{\psi_s\}$ is partitioned into the exclusive subsets $\{\boldsymbol{\psi}_j = \{\psi_{l,j}\}\}$ for representing jth geminal, $\boldsymbol{\psi} = (\boldsymbol{\psi}_1,\,\boldsymbol{\psi}_2,\,\ldots,\,\boldsymbol{\psi}_p)$,

$$\begin{aligned}&\{\psi_s\} = (\{\psi_{l,1}\},\{\psi_{l,2}\},\ldots,\{\psi_{l,p}\}), \quad \{\psi_{l,j}\} = \left(\psi_{1,j},\psi_{2,j},\ldots,\psi_{w_j,j}\right),\\ &\left\langle\psi_{l,j}\middle|\psi_{k,i}\right\rangle = \delta_{l,k}\delta_{j,i},\\ &\Phi_j(1,\,2) = \sum_{k=1}^{w_j} b_{k,j}\psi_{k,j}(1)\psi_{k,j}(2), \qquad j = 1,2,\,\ldots,p.\end{aligned} \tag{6.170}$$

The normalization of geminals thus implies the following relation to be satisfied by unknown expansion coefficients $\{b_{k,j}\}$ related to NO occupations $\left\{n_{k,j} = b_{k,j}^2\right\}$:

$$\sum_{k=1}^{w_j} b_{k,j}^2 = \sum_{k=1}^{w_j} n_{k,j} = 1. \tag{6.171}$$

In order to justify this NO expansion consider a general spatial two-electron function $\Phi(1,\,2)$, symmetric in the antisymmetric (singlet) spin state, e.g., that describing the ground state in He or H_2. It can be expressed in the complete basis set of the orthonormal (real) MO, $\boldsymbol{\varphi} = (\varphi_1, \varphi_2, \ldots, \varphi_w)$, using the symmetrized CI expansion of (6.60):

$$\begin{aligned}\Phi(1,\,2) &= \sum_{k=1}^{w}\sum_{l=1}^{w} d_{k,l}\frac{1}{2}[\varphi_k(1)\varphi_l(2) + \varphi_l(1)\varphi_k(2)] \\ &= \frac{1}{2}[\boldsymbol{\varphi}(1)\,\mathbf{d}\,\boldsymbol{\varphi}^{\mathrm{T}}(2) + \boldsymbol{\varphi}(2)\,\mathbf{d}\,\boldsymbol{\varphi}^{\mathrm{T}}(1)].\end{aligned} \tag{6.172}$$

It gives rise to the following spinless 1-matrix of (6.157):

$$\begin{aligned}\hat{\gamma}_1(\boldsymbol{r}_1;\boldsymbol{r}_1{}') &= 2\sum_{k=1}^{w}\sum_{k'=1}^{w}\varphi_k(\boldsymbol{r}_1)\left[\sum_{l=1}^{w} d_{k,l}d_{k',l}\right]\varphi_{k'}(\boldsymbol{r}_1{}') \\ &\equiv 2\sum_{k=1}^{w}\sum_{k'=1}^{w}\varphi_k(\boldsymbol{r}_1)\,\gamma_{k,k'}^{\mathrm{MO}}\,\varphi_{k'}(\boldsymbol{r}_1{}') \equiv \sum_{k=1}^{w}\sum_{k'=1}^{w}\varphi_k(\boldsymbol{r}_1)\,P_{k,k'}^{\mathrm{MO}}(\mathbf{d})\,\varphi_{k'}^{*}(\boldsymbol{r}_1{}'),\end{aligned} \tag{6.173}$$

where the CBO matrix $\mathbf{P}^{\mathrm{MO}}(\mathbf{d}) = 2\mathbf{d}\mathbf{d}^{\mathrm{T}} = 2\boldsymbol{\gamma}^{\mathrm{MO}}$.

The NO $\boldsymbol{\psi} = \boldsymbol{\varphi}\mathbf{U}$ are then determined by the orthogonal transformation $\mathbf{U}$ which diagonalizes the CBO matrix $\boldsymbol{\gamma}^{\mathrm{MO}}$:

$$\begin{aligned}\mathbf{U}^{\mathrm{T}}\boldsymbol{\gamma}^{\mathrm{MO}}\mathbf{U} &= \mathbf{U}^{\mathrm{T}}\mathbf{d}\mathbf{d}^{\mathrm{T}}\mathbf{U} = (\mathbf{U}^{\mathrm{T}}\mathbf{d}\mathbf{U})(\mathbf{U}^{\mathrm{T}}\mathbf{d}^{\mathrm{T}}\mathbf{U}) = (\mathbf{U}^{\mathrm{T}}\mathbf{d}\mathbf{U})(\mathbf{U}^{\mathrm{T}}\mathbf{d}\mathbf{U})^{\mathrm{T}} \\ &\equiv \mathbf{c}\mathbf{c}^{\mathrm{T}} = \left\{c_\alpha^2\delta_{\alpha,\beta} = n_\alpha\delta_{\alpha,\beta}\right\};\end{aligned} \tag{6.174}$$

and hence $c_\alpha = \pm\sqrt{n_\alpha}$. Finally, substituting the inverse transformation $\boldsymbol{\psi}\mathbf{U}^{\mathrm{T}} = \boldsymbol{\varphi}$ into (6.172) gives the equivalent, more compact natural expansion of the spatial two-electron wave function (geminal):

$$\Phi(1,2) = \frac{1}{2}[\boldsymbol{\psi}(1)(\mathbf{U}^{\mathrm{T}}\mathbf{d}\mathbf{U})\,\boldsymbol{\psi}^{\mathrm{T}}(2) + \boldsymbol{\psi}(2)(\mathbf{U}^{\mathrm{T}}\mathbf{d}\mathbf{U})\,\boldsymbol{\psi}^{\mathrm{T}}(1)] = \sum_{\alpha=1}^{w} c_\alpha\,\psi_\alpha(1)\,\psi_\alpha(2). \tag{6.175}$$

For example, Shull and colleagues (Shull 1960, 1962, 1964; Hagstrom and Shull 1963; Shull and Prosser 1964; Anex and Shull 1964; Christoffersen and Shull 1968; Christoffersen 1989a, b) have argued that the chemical bond in H_2 (one-geminal system) is already well described by the two-term natural expansion

$$\begin{aligned}\Phi(1,\,2) &= c_1\,\psi_1(1)\,\psi_1(2) + c_2\,\psi_2(1)\,\psi_2(2) \\ &= \sqrt{n_1}\,\psi_1(1)\,\psi_1(2) - \sqrt{n_2}\,\psi_2(1)\,\psi_2(2)\,,\end{aligned} \tag{6.176}$$

where $n_1 + n_2 \cong 1$. Indeed, in this highly symmetric (homonuclear) diatomic the two dominating NO basically represent the bonding and antibonding MO, so that the two terms in the preceding equation represent the HF ground and doubly excited MO configurations, respectively, generated in the minimum basis set of two $1s$ orbitals contributed by the two constituent atoms. Therefore, the above wave function in fact corresponds to the minimum CID approximation required to correctly describe the dissociation of the molecule into atoms, which is variationally equivalent to the *Heitler–London* (HL) description of the classical VB theory.

Therefore, in the NO representation of geminals (6.170) the average energy functional of (6.167)–(6.169) becomes the associated function of the NO occupations $\{n_{k,j}\}$ determining the CI expansion coefficients $\left\{b_{k,j} = \pm\sqrt{n_{k,j}}\right\}$, and the functional of the shapes of NO themselves. The latter can be subsequently expressed in terms of the appropriate AO basis, with only the expansion coefficients being optimized, as in the SCF MO method. It should be stressed, however, that the effective energy operators are generally different for each NO, being not invariant to the unitary transformation of the basis set, so that the *off*-diagonal Lagrange multipliers enforcing the orthonormality of NO cannot be easily eliminated. This greatly complicates finding the optimum solutions in practical applications of the method.

The four-electron (heteronuclear) diatomic LiH involves the *inner*-shell (nonbonding) and the *valence*-shell (bonding) geminals. The former represents practically unchanged atomic inner shell of Li, while the dominating NO of the latter exhibits typical effects of the intraatom radial and angular promotion, due to $2s \rightarrow 2p$ and $2s \rightarrow 3s$ effective excitations in Li, as well as the interatom AO mixing generating the covalent (electron delocalization) bond component. The Coulomb correlation energy recovery was about 80%, giving rise to the calculated magnitude of the binding energy, 2.3 eV, which compares favorably with the experimental estimate of 2.52 eV. However, the *strong*-orthogonality constraint has been shown to be a reason for rather poor description of the σ *lone* pair geminal in NH (four- geminal system), since the mainly $2p$ NO has been used to describe the bonding geminal, thus being unavailable for the *lone* pair geminal. Also, the accumulation of four electronic pairs on N gives rise to a strong intergeminal Coulomb correlation, which is missing in this separated pair approach.

One finally observes that the APSG approximation within the separated electron pair method represents a variant of the coupled variational procedure of the MC SCF theory, in which both the shapes of orbitals and CI coefficients are being simultaneously optimized. The quality of the CI expansion determining the reference function is now determined by the length of the NO basis set used to represent the strongly orthogonal geminals.

6.4.2 Independent Electron Pair Approximation

For reasons of simplicity in what follows we shall focus on the Coulomb correlation in the molecular (closed-shell) ground state. The corresponding CI expansion of the exact (unnormalized) ground state function $\bar{\Psi}_0$,

$$\hat{\mathrm{H}}^e\bar{\Psi}_0 = E_0^e\bar{\Psi}_0,$$

where E_0^e denotes the exact electronic energy in the NREL limit (Fig. 6.1), is represented by the CI expansion in the so called *intermediate* normalization representation, for $C_0 \equiv 1$ (e.g., Szabo and Ostlund 1982),

$$\bar{\Psi}_0 = \bar{\Psi}_0^{\mathrm{CI}} \equiv \Psi_0^{\mathrm{HF}} + \sum_{k}^{occd.} \sum_{p}^{virt.} \bar{C}_k^p \, \Phi_k^p + \sum_{k<l}^{occd.} \sum_{p<q}^{virt.} \bar{C}_{k,l}^{p,q} \, \Phi_{k,l}^{p,q} + \sum_{k<l<m}^{occd.} \sum_{p<q<r}^{virt.} \bar{C}_{k,l,m}^{p,q,r} \, \Phi_{k,l,m}^{p,q,r} + \ldots; \qquad (6.177)$$

here Ψ_0^{HF} stands for the fully optimized Slater determinant of the HF theory, giving rise to the HF energy $E_0^{\mathrm{HF}} = \langle \Psi_0^{\mathrm{HF}} | \hat{\mathrm{H}}^e | \Psi_0^{\mathrm{HF}} \rangle$.

Therefore, it directly follows from the definition of the Coulomb correlation energy, $\Delta E_{corr.} = E_0^e - E_0^{\mathrm{HF}}$, that

$$\left(\hat{\mathrm{H}}^e - E_0^{\mathrm{HF}}\right) \bar{\Psi}_0 = \Delta E_{corr.} \bar{\Psi}_0. \qquad (6.178)$$

Multiplying from the left by $\left(\Psi_0^{\mathrm{HF}}\right)^*$ and integrating over the position-spin variables of all electrons then gives the following expression for the correlation energy:

$$\left\langle \Psi_0^{\mathrm{HF}} \right| \left(\hat{\mathrm{H}}^e - E_0^{\mathrm{HF}}\right) \left| \bar{\Psi}_0 \right\rangle = \Delta E_{corr.}. \qquad (6.179)$$

This expression can be further simplified using the Brillouin theorem (6.116) and the Slater–Condon rule of (5.87):

$$\begin{aligned} \left\langle \Psi_0^{\mathrm{HF}} \right| \left(\hat{\mathrm{H}}^e - E_0^{\mathrm{HF}}\right) \left| \bar{\Psi}_0 \right\rangle &= \sum_{k<l}^{occd.} \sum_{p<q}^{virt.} \bar{C}_{k,l}^{p,q} \left\langle \Psi_0^{\mathrm{HF}} \right| \left(\hat{\mathrm{H}}^e - E_0^{\mathrm{HF}}\right) \left| \Phi_{k,l}^{p,q} \right\rangle \\ &= \sum_{k<l}^{occd.} \sum_{p<q}^{virt.} \bar{C}_{k,l}^{p,q} \left\langle \Psi_0^{\mathrm{HF}} \right| \hat{\mathrm{H}}^e \left| \Phi_{k,l}^{p,q} \right\rangle \equiv \sum_{k<l}^{occd.} e_{k,l} = \Delta E_{corr.}. \end{aligned} \qquad (6.180)$$

The preceding equation again emphasizes the dominating role of the *doubly* excited configurations in correcting the HF wave function for the Coulomb correlation effects, and it formally expresses the overall correlation energy as the sum of contributions from all electronic pairs identified by labels $\{k < l\}$ of the occupied SO in the (ground-state) HF determinant, which is analogous to the MP2 expression of (6.133).

In the *Independent Electron Pair Approximation* (IEPA) one uses the variational method to determine the correlation energies $\left\{ e_{k,l}^{\mathrm{IEPA}} \right\}$ due to each separate electron pair $k < l$, when the contributions to the correlation energy from the remaining electrons are ignored. For this given electron pair, one thus defines the CID-type correlated wave function in the intermediate normalization representation:

$$\bar{\Psi}_{k,l}^{\mathrm{IEPA}} = \Psi_0^{\mathrm{HF}} + \sum_{p<q}^{virt.} \bar{C}_{p,q}^{\mathrm{IEPA}} \Phi_{k,l}^{p,q}, \tag{6.181}$$

and determines the optimum CI coefficients by minimizing the expectation value of the electronic Hamiltonian:

$$\begin{aligned} E_{k,l}^{\mathrm{IEPA}} &= \left\langle \bar{\Psi}_{k,l}^{\mathrm{IEPA}} \middle| \hat{\mathrm{H}}^e \middle| \bar{\Psi}_{k,l}^{\mathrm{IEPA}} \right\rangle / \left\langle \bar{\Psi}_{k,l}^{\mathrm{IEPA}} \middle| \bar{\Psi}_{k,l}^{\mathrm{IEPA}} \right\rangle \\ &\equiv \bar{E}_{k,l}^{\mathrm{IEPA}} / \left\langle \bar{\Psi}_{k,l}^{\mathrm{IEPA}} \middle| \bar{\Psi}_{k,l}^{\mathrm{IEPA}} \right\rangle \equiv \left\langle \Psi_{k,l}^{\mathrm{IEPA}} \middle| \hat{\mathrm{H}}^e \middle| \Psi_{k,l}^{\mathrm{IEPA}} \right\rangle = E_0^{\mathrm{HF}} + e_{k,l}^{\mathrm{IEPA}}, \end{aligned} \tag{6.182}$$

where the normalized pair wave function $\Psi_{k,l}^{\mathrm{IEPA}} = \bar{\Psi}_{k,l}^{\mathrm{IEPA}} / \left\langle \bar{\Psi}_{k,l}^{\mathrm{IEPA}} \mid \bar{\Psi}_{k,l}^{\mathrm{IEPA}} \right\rangle^{1/2}$.

This variational criterion gives the associated eigenvalue problem:

$$\begin{aligned} \frac{\delta \bar{E}_{k,l}^{\mathrm{IEPA}}}{\delta \bar{\Psi}_{k,l}^{\mathrm{IEPA}*}} &= \frac{\delta E_{k,l}^{\mathrm{IEPA}}}{\delta \bar{\Psi}_{k,l}^{\mathrm{IEPA}*}} \left\langle \bar{\Psi}_{k,l}^{\mathrm{IEPA}} \mid \bar{\Psi}_{k,l}^{\mathrm{IEPA}} \right\rangle + E_{k,l}^{\mathrm{IEPA}} \bar{\Psi}_{k,l}^{\mathrm{IEPA}} = E_{k,l}^{\mathrm{IEPA}} \bar{\Psi}_{k,l}^{\mathrm{IEPA}} \\ &= \hat{\mathrm{H}}^e \bar{\Psi}_{k,l}^{\mathrm{IEPA}}, \end{aligned} \tag{6.183}$$

where we have used the variational principle $\delta E_{k,l}^{\mathrm{IEPA}} / \delta \bar{\Psi}_{k,l}^{\mathrm{IEPA}*} = 0$.

By repeating this procedure for all pairs of electrons and summing over such additive energy terms, one then estimates the system overall Coulomb correlation energy in the IEPA approximation:

$$\Delta E_{corr.}^{\mathrm{IEPA}} \cong \sum_{k<l}^{occd.} e_{k,l}^{\mathrm{IEPA}}. \tag{6.184}$$

This method thus uses different wave functions to estimate different contributions to the total correlation energy between independent pairs of electrons and hence the magnitude of such an estimate may exceed that of the exact correlation energy. Since in this treatment, one neglects the correlation coupling between different pairs of electrons, by neglecting the *off*-diagonal elements of the CI energy matrix between *doubly* excited configurations originating from different pairs of occupied orbitals in the HF reference function, $H_{(k,l)\to(p,q);(m,n)\to(p',q')}^{\mathrm{CI}}$ for $(m, n) \neq (k, l)$, this method is simpler than the CID variant, which violates the size consistency requirement. For the same reason the IEPA approach is size-consistent, i.e., the energy of m noninteracting monomers is m times the energy of a single monomer.

The equations for the pair correlation energy and the optimum (ground-state) CI coefficients $\left\{\bar{C}_{k,l}^{p,q}\right\} \equiv \bar{\boldsymbol{C}}^{(k,l)}$(the column vector) directly follow from the intermediate normalization projections of the related eigenvalue equations onto the Ψ_0^{HF} and $\left\{\Phi_{k,l}^{p,q}\right\}$ configurations, respectively [see (6.178)–(6.180)]. It follows from (6.180) that the former gives the expression for the electron pair correlation energy,

$$\left\langle \Psi_0^{\mathrm{HF}} \middle| \hat{\mathrm{H}}^e - E_0^{\mathrm{HF}} \middle| \bar{\Psi}_{k,l}^{\mathrm{IEPA}} \right\rangle = e_{k,l}^{\mathrm{IEPA}} = \sum_{p<q}^{virt.} H_{0,(k,l)\to(p,q)}^{CI} \bar{C}_{k,l}^{p,q}$$
$$\equiv \sum_{p<q}^{virt} (\boldsymbol{A}^{(k,l)})_{p,q} (\boldsymbol{C}^{(k,l)})_{p,q} = \boldsymbol{A}^{(k,l)} \boldsymbol{C}^{(k,l)}, \qquad (6.185)$$

where $\boldsymbol{A}^{(k,l)}$ denotes the row vector. The latter projection and (6.183) generate the additional relation for the expansion coefficients,

$$\left\langle \Phi_{k,l}^{p,q} \middle| \hat{\mathrm{H}}^e - E_0^{\mathrm{HF}} \middle| \bar{\Psi}_{k,l}^{\mathrm{IEPA}} \right\rangle = \left\langle \Phi_{k,l}^{p,q} \middle| \hat{\mathrm{H}}^e \middle| \Psi_0^{\mathrm{HF}} \right\rangle + \sum_{p'<q'}^{virt.} \left\langle \Phi_{k,l}^{p,q} \middle| \hat{\mathrm{H}}^e - E_0^{\mathrm{HF}} \middle| \Phi_{k,l}^{p',q'} \right\rangle \bar{C}_{k,l}^{p',q'}$$
$$= e_{k,l}^{\mathrm{IEPA}} \left\langle \Phi_{k,l}^{p,q} \middle| \bar{\Psi}_{k,l}^{\mathrm{IEPA}} \right\rangle = e_{k,l}^{\mathrm{IEPA}} \bar{C}_{k,l}^{p,q}, \qquad (6.186)$$

or in the matrix notation of (6.185):

$$(\boldsymbol{A}^{(k,l)\dagger})_{p,q} + \sum_{p'<q'}^{virt} (\mathbf{D}^{(k,l)})_{p,q;p',q'} (\boldsymbol{C}^{(k,l)})_{p',q'} = e_{k,l}^{\mathrm{IEPA}} (\boldsymbol{C}^{(k,l)})_{p,q}, \qquad (6.187)$$

where

$$(\mathbf{D}^{(k,l)})_{p,q;p',q'} = \left\langle \Phi_{k,l}^{p,q} \middle| \hat{\mathrm{H}}^e - E_0^{\mathrm{HF}} \middle| \Phi_{k,l}^{p',q'} \right\rangle$$
$$= H_{(k,l)\to(p,q);(k,l)\to(p',q')}^{\mathrm{CI}} - E_0^{\mathrm{HF}} \delta_{p,p'} \delta_{q,q'}. \qquad (6.188)$$

Finally, the coupled matrix equations (6.185) and (6.187),

$$e_{k,l}^{\mathrm{IEPA}} = \boldsymbol{A}^{(k,l)} \bar{\boldsymbol{C}}^{(k,l)} \quad \text{and} \quad \boldsymbol{A}^{(k,l)\dagger} + \mathbf{D}^{(k,l)} \bar{\boldsymbol{C}}^{(k,l)} = e_{k,l}^{\mathrm{IEPA}} \bar{\boldsymbol{C}}^{(k,l)}, \qquad (6.189)$$

which determine the *pair* correlation energies and the associated CI coefficients, can be combined in the following eigenvalue equation:

$$\begin{bmatrix} 0 & \boldsymbol{A}^{(k,l)} \\ \boldsymbol{A}^{(k,l)\dagger} & \mathbf{D}^{(k,l)} \end{bmatrix} \begin{bmatrix} 1 \\ \bar{\boldsymbol{C}}^{(k,l)} \end{bmatrix} \equiv \mathbf{B}^{(k,l)} \begin{bmatrix} 1 \\ \bar{\boldsymbol{C}}^{(k,l)} \end{bmatrix} = e_{k,l}^{\mathrm{IEPA}} \begin{bmatrix} 1 \\ \bar{\boldsymbol{C}}^{(k,l)} \end{bmatrix}. \qquad (6.190)$$

Therefore, the relevant CI coefficients determine the eigenvector of $\mathbf{B}^{(k,l)}$, with the eigenvalue $e_{k,l}^{\mathrm{IEPA}}$ determining the pair correlation energy. In view of the variational principle of (6.183),

$$\min E_{k,l}^{\mathrm{IEPA}} = \min\left(E_0^{\mathrm{HF}} + e_{k,l}^{\mathrm{IEPA}}\right) = \min e_{k,l}^{\mathrm{IEPA}}, \qquad (6.191)$$

one thus diagonalizes the symmetric matrix $\mathbf{B}^{(k,l)}$ and selects the (normalized) eigenvector corresponding to the *lowest* eigenvalue, which determines the optimum value of the *pair* correlation energy. For each pair of the occupied MO in the HF reference state, the associated $\{\mathbf{B}^{(k,l)}\}$ matrices are different, so that there is no variational lower bound to the IEPA overall estimate of the Coulomb (intrapair) correlation energy.

As shown by Ahlrichs et al. (1975a, b) in a series of simple hydrides exhibiting different numbers of the localized bonds and the lone pairs in the valence shell, one finds that the magnitude of the correlation energy of two electrons occupying the nonbonding orbital is lower than the corresponding intrabond contribution. The smaller interorbital correlation energies between bonding and/or nonbonding electrons were found to be of comparable magnitude. In each case, the total estimate of the Coulomb correlation energy exceeded the corresponding CI value, thus confirming the altogether nonvariational aspect of the IEPA method.

6.4.3 Coupled Electron Pair Approximations

In fact the internally correlated electronic pairs repel each other and thus are not fully independent. Therefore, several improvements relative to the IEPA approach have been proposed, which approximately take into account the interpair correlation as well. These *size*-consistent *Coupled Electron Pair Approximations* (CEPA) represent a special case of a more general strategy, called the *Coupled Cluster* (CC) approximation, which we shall introduce in Sect. 6.5. Although all these extensions generally give rise to higher accuracy of the predicted effects of the electron correlation, be it at a severe cost of increased computational complexity and hence a reduced capability of an easy interpretation, the need for further improvement still remains. Such more advanced techniques, however, are generally unsuitable for applications to very large supramolecular systems of the contemporary chemistry/biology and in solid state physics.

The interpair correlation is represented by the *quadruply* (Q) excited configurations from the reference HF wave function, involving excitations of both electrons in each pair. Therefore, to cover these effects the CI expansion of (6.177) should be at least of the CIDQ type:

$$\begin{aligned}\bar{\Psi}_0^{\mathrm{CI}} &\cong \Psi_0^{\mathrm{HF}} + \sum_{k<l}^{occd.} \sum_{p<q}^{virt.} \bar{C}_{k,l}^{p,q}\, \Phi_{k,l}^{p,q} + \sum_{k<l<m<n}^{occd.} \sum_{p<q<r<s}^{virt.} \bar{C}_{k,l,m,n}^{p,q,r,s}\, \Phi_{k,l,m,n}^{p,q,r,s} \\ &\equiv \bar{\Psi}_0^{\mathrm{CIDQ}}. \end{aligned} \tag{6.192}$$

Notice that (6.180), obtained from projecting the eigenvalue problem for the correlation energy (6.178) onto the HF reference state, remains valid also for this extended size of the CI expansion,

$$\left\langle\Psi_0^{\mathrm{HF}}\right|\left(\hat{\mathrm{H}}^e - E_0^{\mathrm{HF}}\right)\left|\bar{\Psi}_0^{\mathrm{CIDQ}}\right\rangle = \sum_{k<l}^{occd.}\sum_{p<q}^{virt.}\bar{C}_{k,l}^{p,q}\left\langle\Psi_0^{\mathrm{HF}}\right|\hat{\mathrm{H}}^e\left|\Phi_{k,l}^{p,q}\right\rangle$$
$$\equiv \sum_{k<l}^{occd.} e_{k,l}^{\mathrm{CIDQ}} = \Delta E_{corr.}^{\mathrm{CIDQ}}. \qquad (6.193)$$

The projection onto the *doubly* excited configuration [compare (6.186)] now gives the following coupled equations for the CI coefficients,

$$\left\langle\Phi_{i,j}^{r,s}\right|\hat{\mathrm{H}}^e - E_0^{\mathrm{HF}}\left|\bar{\Psi}_0^{\mathrm{CIDQ}}\right\rangle = \left\langle\Phi_{i,j}^{r,s}\right|\hat{\mathrm{H}}^e\left|\Psi_0^{\mathrm{HF}}\right\rangle + \sum_{k<l}^{occd.}\sum_{p<q}^{virt.}\left\langle\Phi_{i,j}^{r,s}\right|\hat{\mathrm{H}}^e - E_0^{\mathrm{HF}}\left|\Phi_{k,l}^{p,q}\right\rangle\bar{C}_{k,l}^{p,q}$$
$$+\sum_{m<n}^{occd.}\sum_{t<u}^{virt.}\left\langle\Phi_{i,j}^{r,s}\right|\hat{\mathrm{H}}^e\left|\Phi_{i,j,m,n}^{r,s,t,u}\right\rangle\bar{C}_{i,j,m,n}^{r,s,t,u} = \Delta E_{corr.}^{\mathrm{CIDQ}}\bar{C}_{i,j}^{r,s},$$
$$(6.194)$$

which directly follow from the orthogonality relations between the configuration functions and the Slater–Condon rules for the matrix elements of the electronic Hamiltonian. The preceding equation relates the CI coefficients of the *doubly* excited configurations to those corresponding to the quadruple excitations. The latter reflect the interpair correlation, which has been neglected in the IEPA method.

It should be observed that only the assumption $\left\{\bar{C}_{k,l,m,n}^{p,q,r,s} = 0\right\}$ gives the uncoupled equations of the standard CID approach of Sect. 6.3.1 [see also the matrix notation of (6.185), (6.187) and (6.189)]:

$$\left\langle\Psi_0^{\mathrm{HF}}\right|\left(\hat{\mathrm{H}}^e - E_0^{\mathrm{HF}}\right)\left|\bar{\Psi}_0^{\mathrm{CID}}\right\rangle = \sum_{k<l}^{occd.}\sum_{p<q}^{virt.}\left\langle\Psi_0^{\mathrm{HF}}\right|\hat{\mathrm{H}}^e\left|\Phi_{k,l}^{p,q}\right\rangle\bar{C}_{k,l}^{p,q} \equiv \boldsymbol{A}^{\mathrm{CID}}\bar{\boldsymbol{C}}^{\mathrm{CID}} = \Delta E_{corr.}^{\mathrm{CID}},$$
$$\left\langle\Phi_{k,l}^{p,q}\right|\hat{\mathrm{H}}^e - E_0^{\mathrm{HF}}\left|\bar{\Psi}_0^{\mathrm{CID}}\right\rangle = \left\langle\Phi_{k,l}^{p,q}\right|\hat{\mathrm{H}}^e\left|\Psi_0^{\mathrm{HF}}\right\rangle + \sum_{m<n}^{occd.}\sum_{r<s}^{virt.}\left\langle\Phi_{k,l}^{p,q}\right|\hat{\mathrm{H}}^e - E_0^{\mathrm{HF}}\left|\Phi_{m,n}^{r,s}\right\rangle\bar{C}_{m,n}^{r,s}$$
$$= \Delta E_{corr.}^{\mathrm{CID}}\bar{C}_{k,l}^{p,q},$$
$$(6.195)$$

or in the matrix notation,

$$\boldsymbol{A}^{\mathrm{CID}\dagger} + \mathbf{D}^{\mathrm{CID}}\bar{\boldsymbol{C}}^{\mathrm{CID}} = \Delta E_{corr.}^{\mathrm{CID}}\bar{\boldsymbol{C}}^{\mathrm{CID}}, \qquad (6.196)$$

with the CI energy-difference matrix $\mathbf{D}^{\mathrm{CID}}$ defined in (6.188).

These equations can be again combined into the associated eigenvalue equation for the ground state correlation energy [compare (6.190)]:

$$\begin{bmatrix} 0 & \boldsymbol{A}^{\mathrm{CID}} \\ \boldsymbol{A}^{\mathrm{CID}\dagger} & \mathbf{D}^{\mathrm{CID}} \end{bmatrix}\begin{bmatrix} 1 \\ \bar{\boldsymbol{C}}^{\mathrm{CID}} \end{bmatrix} \equiv \mathbf{B}^{\mathrm{CID}}\begin{bmatrix} 1 \\ \boldsymbol{C}^{\mathrm{CID}} \end{bmatrix} = \Delta E_{corr.}^{\mathrm{CID}}\begin{bmatrix} 1 \\ \bar{\boldsymbol{C}}^{\mathrm{CID}} \end{bmatrix}. \qquad (6.197)$$

Multiplying both sides by the normalization constant of $\bar{\Psi}_0^{\mathrm{CID}}$, equal to C_0^{CID}, and realizing that $\mathbf{B}^{\mathrm{CID}} = \mathbf{H}^{\mathrm{CID}} - E_0^{\mathrm{HF}}\mathbf{I}^{\mathrm{CID}}$ and $\Delta E_{corr.}^{\mathrm{CID}} = E_0^{\mathrm{CID}} - E_0^{\mathrm{HF}}$, one indeed recovers the eigenvalue equation for $\boldsymbol{C}^{\mathrm{CID}\dagger} = C_0^{\mathrm{CID}}[1, \bar{\boldsymbol{C}}^{\mathrm{CID}}]^\dagger$ corresponding to E_0^{CID}:

$$\mathbf{H}^{\mathrm{CID}}\boldsymbol{C}^{\mathrm{CID}} = E_0^{\mathrm{CID}}\boldsymbol{C}^{\mathrm{CID}}. \tag{6.198}$$

Should one include the *Hextuple* (H) excitations in the $\bar{\Psi}_0^{\mathrm{CIDQH}}$ expansion of the ground state wave function, which represent the electron correlation between *three* electronic pairs, the projection of the associated (6.178) onto the *doubly* and *quadruply* excited configurations gives rise to yet another set of coupled equations for the underlying CI coefficients. In this case, the coefficients of *Doubles* and *Quadruples* depend upon the *Hextuple* coefficients, etc. In fact, the CI expansion determines the infinite hierarchy of such coupled equations for determining the CI coefficients corresponding to increasing excitation multiplicities.

However, practical calculations call for terminating this hierarchy at some reasonable level of a limited CI, by using an approximate decoupling scheme, which would unable one to obtain the closed set of these equations, say, for the unknowns $\left\{\bar{C}_{k,l}^{p,q}\right\}$, which determine the pair correlations $\{e_{k,l}\}$. This requires an expression of CI coefficients standing before more highly excited configurations in terms of coefficients associated with lower excitations, e.g., for estimating $\left\{\bar{C}_{i,j,m,n}^{r,s,t,u}\right\}$ in terms of $\left\{\bar{C}_{k,l}^{p,q}\right\}$. Existence of such approximate relationships is indeed suggested by the fact that the dominant Coulomb correlation effects originate from the intrapair correlations, between electrons exhibiting the opposite spin orientations. This implies that the most important *quadruply* excited configurations are given by the products of two double excitations, which give the same overall quadruple excitation. This intuition lies behind specific decoupling schemes generating alternative variants of the CEPA or CC approximations.

For example, let us examine the coupled equations (6.194), which introduce the interpair correlation effects neglected in the IEPA scheme. Consider the representative CI coefficient $\bar{C}_{i,j,m,n}^{r,s,t,u}$ multiplying in (6.192) the function $\Phi_{i,j,m,n}^{r,s,t,u}$, which represents the replacements of the HF-occupied SO, identified by the lower indices $(i < j < m < n)$, by the corresponding HF-virtual SO, labeled by the upper indices $(r < s < t < u)$: $(i \to r,\ j \to s,\ m \to t,\ n \to u)$. We want to identify all double (pair) excitations, the product of which generates the same quadruple excitation, e.g., $\Phi_{i,j}^{r,s}\Phi_{m,n}^{t,u}$.

In fact there are 18 distinct products of such pair excitations, which give rise to the same final state as the selected quadruple excitation $\Phi_{i,j,m,n}^{r,s,t,u}$. One first realizes that there are three distinct assignments of the above four occupied SO to two electron pairs in the initial Slater determinants (we disregard the occupied SO which are not replaced in the excitation), in which the second orbital index in the pair is greater than the first one:

$$\{|i<j\,\text{¦}\,m<n|,\ |i<m\,\text{¦}\,j<n|,\ |i<n\,\text{¦}\,j<m|\}. \qquad \text{(I)}$$

These sets of occupied SO thus exhaust the possible lists of the lower indices of the pair excitations, which may be associated with the quadruple excitation $\Phi^{r,s,t,u}_{i,j,m,n}$. The upper indices of such pair excitations, which determine the final configurations in such excitations of two electronic pairs, are similarly determined by the following six Slater determinants, with the intrapair ordered orbital labels:

$$\{|r<s\,\text{¦}\,t<u|,\ |t<u\,\text{¦}\,r<s|,\ |r<t\,\text{¦}\,s<u|,\ |s<u\,\text{¦}\,r<t|,\ |r<u\,\text{¦}\,s<t|,\ |s<t\,\text{¦}\,r<u|\}. \qquad \text{(II)}$$

Each initial assignment of the list (I) can be combined with each final assignment of the list (II), thus giving rise to 18 products of double excitations. For example, the first determinant of (I) combined with the first determinant of (II) generates the canonically ordered product $\Phi^{r,s}_{i,j}\Phi^{t,u}_{m,n}$ corresponding to the associated product of CI coefficients: $\bar{C}^{r,s}_{i,j}\bar{C}^{t,u}_{m,n}$, etc. Each of these 18 *quadruply* excited configurations can be then transformed into the canonically ordered Slater determinant $|r<s\,\text{¦}\,t<u|$, the first in the list (II), by the corresponding number of exchanges of rows in the Slater determinant of the current configuration, with each single exchange changing the sign of the determinant and hence also the sign of the associated product of CI coefficients. The overall number of such exchanges is given by the sum of replacements required to bring the current list (p, q, v, w) of the upper indices to the canonical list (r, s, t, u) and the number of exchanges which transform the current list of lower indices (a, b, c, d) into the ordered set (i, j, m, n).

Therefore, the CI coefficient $\bar{C}^{r,s,t,u}_{i,j,m,n}$ multiplying the quadruple excitation $\Phi^{r,s,t,u}_{i,j,m,n}$ in (6.192) can be associated with the following combination of products of the CI coefficients of double excitations:

$$\begin{aligned}
\bar{C}^{r,s,t,u}_{i,j,m,n} \approx\ & \bar{C}^{r,s}_{i,j}\bar{C}^{t,u}_{m,n} + \bar{C}^{t,u}_{i,j}\bar{C}^{r,s}_{m,n} - \bar{C}^{r,t}_{i,j}\bar{C}^{s,u}_{m,n} - \bar{C}^{s,u}_{i,j}\bar{C}^{r,t}_{m,n} + \bar{C}^{r,u}_{i,j}\bar{C}^{s,t}_{m,n} + \bar{C}^{s,t}_{i,j}\bar{C}^{r,u}_{m,n} \\
& - \bar{C}^{r,s}_{i,m}\bar{C}^{t,u}_{j,n} - \bar{C}^{t,u}_{i,m}\bar{C}^{r,s}_{j,n} + \bar{C}^{r,t}_{i,m}\bar{C}^{s,u}_{j,n} + \bar{C}^{s,u}_{i,m}\bar{C}^{r,t}_{j,n} - \bar{C}^{r,u}_{i,m}\bar{C}^{s,t}_{j,n} - \bar{C}^{s,t}_{i,m}\bar{C}^{r,u}_{j,n} \\
& + \bar{C}^{r,s}_{i,n}\bar{C}^{t,u}_{j,m} + \bar{C}^{t,u}_{i,n}\bar{C}^{r,s}_{j,m} - \bar{C}^{r,t}_{i,n}\bar{C}^{s,u}_{j,m} - \bar{C}^{s,u}_{i,n}\bar{C}^{r,t}_{j,m} + \bar{C}^{r,u}_{i,n}\bar{C}^{s,t}_{j,m} + \bar{C}^{s,t}_{i,n}\bar{C}^{r,u}_{j,m} \\
\equiv\ & \bar{C}^{r,s}_{i,j}\bar{C}^{t,u}_{m,n} - \left\langle \begin{matrix} rs\ \ tu \\ ij\ \ mn \end{matrix} \right\rangle .
\end{aligned} \tag{6.199}$$

The first three “rows” of the preceding expression are identified by the corresponding determinants in the list (I), while the corresponding “columns” correspond to the associated determinants in the list (II).

Substituting this expression to (6.194) and using (6.193) then gives quadratic equations for the unknowns $\left\{\bar{C}^{p,q}_{k,l}\right\}$:

$$\begin{aligned}
\left\langle \Phi_{i,j}^{r,s} \middle| \hat{\mathrm{H}}^{e} \middle| \Psi_{0}^{\mathrm{HF}} \right\rangle &+ \sum_{k<l}^{occd.} \sum_{p<q}^{virt.} \left\langle \Phi_{i,j}^{r,s} \middle| \hat{\mathrm{H}}^{e} - E_{0}^{\mathrm{HF}} \middle| \Phi_{k,l}^{p,q} \right\rangle \bar{C}_{k,l}^{p,q} \\
&+ \sum_{m<n}^{occd.} \sum_{t<u}^{virt.} \left\langle \Phi_{i,j}^{r,s} \middle| \hat{\mathrm{H}}^{e} \middle| \Phi_{i,j,m,n}^{r,s,t,u} \right\rangle \bar{C}_{i,j,m,n}^{r,s,t,u} \\
&= \sum_{m<n}^{occd.} \sum_{t<u}^{virt.} \left\langle \Psi_{0}^{\mathrm{HF}} \middle| \hat{\mathrm{H}}^{e} \middle| \Phi_{m,n}^{t,u} \right\rangle \bar{C}_{i,j}^{r,s} \bar{C}_{m,n}^{t,u} \\
&= \sum_{m<n}^{occd.} \sum_{t<u}^{virt.} \left\langle \Psi_{0}^{\mathrm{HF}} \middle| \hat{\mathrm{H}}^{e} \middle| \Phi_{m,n}^{t,u} \right\rangle \left(\bar{C}_{i,j,m,n}^{r,s,t,u} + \left\langle \begin{matrix} rs & tu \\ ij & mn \end{matrix} \right\rangle \right),
\end{aligned}$$

or

$$\begin{aligned}
\left\langle \Phi_{i,j}^{r,s} \middle| \hat{\mathrm{H}}^{e} \middle| \Psi_{0}^{\mathrm{HF}} \right\rangle &+ \sum_{k<l}^{occd.} \sum_{p<q}^{virt.} \left\langle \Phi_{i,j}^{r,s} \middle| \hat{\mathrm{H}}^{e} - E_{0}^{\mathrm{HF}} \middle| \Phi_{k,l}^{p,q} \right\rangle \bar{C}_{k,l}^{p,q} \\
&- \sum_{m<n}^{occd.} \sum_{t<u}^{virt.} \left\langle \Psi_{0}^{\mathrm{HF}} \middle| \hat{\mathrm{H}}^{e} \middle| \Phi_{m,n}^{t,u} \right\rangle \left\langle \begin{matrix} rs & tu \\ ij & mn \end{matrix} \right\rangle = 0, \qquad (6.200)
\end{aligned}$$

where we have also used the identity

$$\left\langle \Phi_{i,j}^{r,s} \middle| \hat{\mathrm{H}}^{e} \middle| \Phi_{i,j,m,n}^{r,s,t,u} \right\rangle = \left\langle \Psi_{0}^{\mathrm{HF}} \middle| \hat{\mathrm{H}}^{e} \middle| \Phi_{m,n}^{t,u} \right\rangle = \langle mn | g | tu - ut \rangle, \qquad (6.201)$$

which directly follows from the Slater–Condon rule (5.86).

Such a nonvariational and size-consistent method is known as the *Coupled Pair Many Electron Theory* (CPMET) (Paldus and Čižek 1975; Čižek and Paldus 1980). Determining solutions $\left\{ \bar{C}_{k,l}^{p,q} \right\}$ of (6.200) and using them in (6.193) then gives the correlation energy, which takes into account the effective correlation coupling between different electronic pairs:

$$\Delta E_{corr.}^{\mathrm{CPMET}} \cong \Delta E_{corr.}^{\mathrm{CIDQ}}. \qquad (6.202)$$

A number of approximate schemes derived from this full CPMET treatment have also been proposed (see, e.g., Szabo and Ostlund 1982). The simplest variant of such CC equations is obtained, when one neglects in (6.200) the last term $\left\langle \begin{matrix} rs & tu \\ ij & mn \end{matrix} \right\rangle$ altogether:

$$\left\langle \begin{matrix} rs & tu \\ ij & mn \end{matrix} \right\rangle = 0 \qquad \text{or} \qquad \bar{C}_{i,j,m,n}^{r,s,t,u} \approx \bar{C}_{i,j}^{r,s} \bar{C}_{m,n}^{t,u}. \qquad (6.203)$$

This gives rise to linear equations for the unknowns $\left\{ \bar{C}_{k,l}^{p,q} \right\}$:

$$\left\langle \Phi_{i,j}^{r,s} \middle| \hat{\mathrm{H}}^{e} \middle| \Psi_{0}^{\mathrm{HF}} \right\rangle + \sum_{k<l}^{occd.} \sum_{p<q}^{virt.} \left\langle \Phi_{i,j}^{r,s} \middle| \hat{\mathrm{H}}^{e} - E_{0}^{\mathrm{HF}} \middle| \Phi_{k,l}^{p,q} \right\rangle \bar{C}_{k,l}^{p,q} = 0. \tag{6.204}$$

When substituted in (6.193) they give rise to a nonvariational but size-consistent estimate of the correlation energy: $\Delta E_{corr.}^{\mathrm{CCA}} \approx \Delta E_{corr.}^{\mathrm{CIDQ}}$

In a more accurate CEPA method of Meyer (1977) only the products diagonal in pairs of lower indices in $\left\langle \begin{matrix} rs & tu \\ ij & mn \end{matrix} \right\rangle$ are retained:

$$\left\langle \begin{matrix} rs & tu \\ ij & mn \end{matrix} \right\rangle = \left\langle \begin{matrix} rs & tu \\ ij & ij \end{matrix} \right\rangle \delta_{i,m}\delta_{j,n} = C_{i,j}^{r,s} C_{i,j}^{t,u} \delta_{i,m}\delta_{j,n}. \tag{6.205}$$

This result directly follows from (6.199). Indeed, one observes that all terms in the second row of this equation, corresponding to the lower indices $(i,i,\ j,j)$, must identically vanish since $\bar{C}_{k,k}^{p,q} = 0$ (a given occupied SO can participate only in a single substitution). Moreover, the corresponding terms of the same columns $2 \div 6$ in the first and third row differ in only a single exchange of lower indices, thus exactly canceling each other. The only remaining term is thus given by the first contribution of the third row, $-\bar{C}_{i,j}^{r,s}\bar{C}_{j,i}^{t,u} = \bar{C}_{i,j}^{r,s}\bar{C}_{i,j}^{t,u}$, where we have used the above-mentioned antisymmetry property of the CI coefficients, implied by the same property of the Slater determinants determining the associated configuration functions:

$$\bar{C}_{k,l}^{p,q} = -\bar{C}_{l,k}^{p,q} = -\bar{C}_{k,l}^{q,p}. \tag{6.206}$$

Finally, using the approximation of (6.205) in (6.200) gives the following (quadratic) equations for the unknown CI coefficients $\bar{\boldsymbol{C}}^{\mathrm{CEPA}} = \left\{ \bar{C}_{k,l}^{p,q} \right\}$ of the CEPA variant,

$$\begin{aligned} &\left\langle \Phi_{i,j}^{r,s} \middle| \hat{\mathrm{H}}^{e} \middle| \Psi_{0}^{\mathrm{HF}} \right\rangle + \sum_{k<l}^{occd.} \sum_{p<q}^{virt.} \left\langle \Phi_{i,j}^{r,s} \middle| \hat{\mathrm{H}}^{e} - E_{0}^{\mathrm{HF}} \middle| \Phi_{k,l}^{p,q} \right\rangle \bar{C}_{k,l}^{p,q} \\ &\qquad - \left\{ \sum_{t<u}^{virt.} \left\langle \Psi_{0}^{\mathrm{HF}} \middle| \hat{\mathrm{H}}^{e} \middle| \Phi_{i,j}^{t,u} \right\rangle \bar{C}_{i,j}^{t,u} \right\} \bar{C}_{i,j}^{r,s} = 0, \end{aligned} \tag{6.207}$$

or in terms of the *pair* correlation quantities $\left\{ e_{k,l}^{\mathrm{CIDQ}} \right\}$ defined in (6.193):

$$\left\langle \Phi_{i,j}^{r,s} \middle| \hat{\mathrm{H}}^{e} \middle| \Psi_{0}^{\mathrm{HF}} \right\rangle + \sum_{k<l}^{occd.} \sum_{p<q}^{virt.} \left\langle \Phi_{i,j}^{r,s} \middle| \hat{\mathrm{H}}^{e} - E_{0}^{\mathrm{HF}} \middle| \Phi_{k,l}^{p,q} \right\rangle \bar{C}_{k,l}^{p,q} = e_{i,j}^{\mathrm{CEPA}} \bar{C}_{i,j}^{r,s}. \tag{6.208}$$

These equations must be solved iteratively until the self-consistency is reached. More specifically, the *pair* correlation contributions $\left\{ e_{k,l}^{\mathrm{CEPA}} \left(\bar{\boldsymbol{C}}_{(n-1)}^{\mathrm{CEPA}} \right) \right\}$ obtained from (6.193), the linear functions of the CI coefficients $\bar{\boldsymbol{C}}_{(n-1)}^{\mathrm{CEPA}}$ obtained in the previous iteration of (6.208), must generate the same expansion coefficients in the next iteration of these equations: $\bar{\boldsymbol{C}}_{(n-1)}^{\text{CEPA}} = \bar{\boldsymbol{C}}_{(n)}^{\text{CEPA}}$. This nonvariational method also gives rise to the size-consistent estimate of the overall Coulomb correlation energy in the molecular ground state: $\Delta E_{corr.}^{\text{CEPA}} = \sum_{k<l}^{occd.} e_{k,l}^{\text{CEPA}}$.

In the next section, we shall demonstrate that the CPMET represents a special case of a more general CC strategy, which is based upon the so-called cluster expansion of the correlated wave function of N electrons. In fact CPMET represents the CC approximation for electronic pairs, i.e., the two-electron *clusters*. This formalism is most elegantly formulated in the so-called second-quantization representation of quantum states of N fermions, by using the *creation* and *annihilation* operators acting in the *Fock space* of state vectors representing all admissible occupations of the one-electron states of the HF (orbital) approximation. In this alternative, occupation number formalism the Pauli exclusion principle is safeguarded by the appropriate for fermions algebraic relations of the anticommutation properties of the creation and annihilation operators. It allows one to treat both the *closed* molecules with the fixed number of electrons, $N = N^0$, and the *open* systems with varying (fluctuating) number of electrons. This more general description of electronic quantum states is the main subject of the next section.

6.5 Second-Quantization Representation

The Hilbert space $\mathcal{H}(N)$ of state vectors (or wave functions) of N-particles (see Chaps. 2 and 3) combines the antisymmetric (A) and symmetric (S) subspaces, $\mathcal{H}_A(N)$ and $\mathcal{H}_S(N)$, corresponding to fermions and bosons, respectively: $\mathcal{H}(N) = \mathcal{H}_A(N) + \mathcal{H}_S(N)$. The expansion theorem of Sect. 6.2 demonstrates that the N-electron subspace $\mathcal{H}_A(N)$ is spanned by determinants constructed from the complete set of SO. These N-electron basis functions are thus uniquely identified by different N-conserving occupation patterns of the one-electron functions (see also Sect. 6.1.3).

However, in many applications of the quantum theory it is convenient to refer to a union of the mutually orthogonal Hilbert spaces for all admissible numbers of particles, $N = 0, 1, 2, \ldots$,

$$\begin{aligned}\mathcal{H} &= \mathcal{H}(0) + \mathcal{H}(1) + \ldots = \{\mathcal{H}_A(0) + \mathcal{H}_A(1) + \ldots\} + \{\mathcal{H}_S(0) + \mathcal{H}_S(1) + \ldots\} \\ &\equiv \mathcal{H}_A + \mathcal{H}_S,\end{aligned} \tag{6.209}$$

with the fermion (antisymmetric) subspace $\mathcal{H}_A$ called the *Fock space*. It combines the state vectors for any number of electrons. Here, the $\mathcal{H}_A(0)$ subspace corresponds to the Hilbert space of no electrons, the electronic *vacuum*. This generalized concept of the vector space has originated in the field theory, with "particles," the photons, being "created" or "annihilated" in the emission or absorption processes, respectively.

The generalized state vector of an electronic system in such an enlarged vector space thus exhibits components corresponding to different numbers of electrons:

$$|\Psi_A\rangle = |\Psi_A(0)\rangle + |\Psi_A(1)\rangle + \ldots + |\Psi_A(N)\rangle + \ldots,$$
$$|\Psi_A(N)\rangle = \hat{\mathrm{P}}_A(N)|\Psi_A\rangle,\ \hat{\mathrm{P}}_A(N)\hat{\mathrm{P}}_A(N') = \delta_{N,N'}; \tag{6.210}$$

here, $\hat{\mathrm{P}}_A(N)$ stands for the projector onto $\mathcal{H}_A(N)$, with the scalar product being determined by the overall projection operator onto $\mathcal{H}_A$, $\hat{\mathrm{P}}_A = \sum_N \hat{\mathrm{P}}_A(N)$, the action of which on an arbitrary fermion state $|\Xi_A\rangle \in \mathcal{H}_A$ amounts to the identity operation, $\hat{\mathrm{P}}_A|\Xi_A\rangle = |\Xi_A\rangle$:

$$\langle \Phi_A \mid \Psi_A\rangle = \sum_N \left(\langle \Phi_A|\hat{\mathrm{P}}_A(N)\right)\left(\hat{\mathrm{P}}_A(N)|\Psi_A\rangle\right) = \sum_N \langle \Phi_A(N) \mid \Psi_A(N)\rangle. \tag{6.211}$$

The state vectors in $\mathcal{H}_A$ exhaust both the N conserving and nonconserving patterns of occupations of the complete set of one-electron states. In order to effect changes in the system number of particles the *creation* and *annihilation* (destruction) operators are being introduced in this *second quantization* (occupation number) *representation* of electronic states (see, e.g.: Jørgensen and Simons 1981; Szabo and Ostlund 1982; McWeeny 1989; Surjan 1989). When acting on an N-electron state the former gives rise to a state of $(N + 1)$ electrons, while the action of the latter generates a state of $(N - 1)$ electrons. In what follows we shall apply this formalism in the specific context of the Coulomb correlation in the N-electron molecular/atomic systems. We shall demonstrate that in this elegant formulation of the generalized CI theory of electronic clusters, the crucial stage of determining the matrix elements of the electronic Hamiltonian in the basis set of Slater determinants defining the excited configurations amounts to straightforward algebraic manipulations on the one- and two-electron integrals calculated in the nearly complete basis set of molecular SO.

In this generalized description the fractional-N states appear as ensembles (statistical mixtures) of the integer-N states. This enables one to treat in quantum theory a variety of classical *chemical* problems involving *open* molecules, dealing with the *Charge Transfer* (CT) phenomena, e.g., the fractional or integral electron attachment or withdrawal processes, and the thermodynamic equilibria of the externally open molecular systems, coupled to electron reservoirs.

6.5.1 Fock Space and Creation/Annihilation Operators

A general Slater determinant

$$\Psi_A(N) = |\psi_i\psi_j \ldots \psi_p| \equiv \langle \mathbf{q}|\psi_i\psi_j \ldots \psi_p\rangle \equiv \langle \mathbf{q}|ij\ldots p\rangle \equiv \langle \mathbf{q}|\Psi_A\rangle \tag{6.212}$$

provides the $\mathbf{q} = \{\boldsymbol{q}_l\} = \mathcal{Q}^N$ (position-spin) representation of the N-electron state vector $|\Psi_A(N)\rangle = |\psi_i\, \psi_j, \ldots, \psi_p\rangle \equiv |i\, j \ldots p\rangle$, which is uniquely identified by its selection of the one-electron state vectors $\{|\psi_k\rangle = |k\rangle\}$ or the singly occupied SO: $\{\psi_k(\boldsymbol{q}) = \langle \boldsymbol{q}|k\rangle\}$. Notice that the order in which SO are listed, although immaterial for the direction of the state vector in the molecular Hilbert space, and hence also for the identity of the quantum state itself, does matter for its sign (phase): any exchange of two SO changes the sign of the state-vector and the associated Slater determinant.

Therefore, such an antisymmetric state of N-electrons is uniquely identified by the occupation numbers $\{n_k\}$ (see Sect. 6.1.3) of the complete set of SO: $n_k = 1$ for the occupied and $n_k = 0$ for the unoccupied SO. For example, the occupation vector $|001010\ldots\rangle$ of the two-electron system identifies the state vector $|\psi_3\, \psi_5\rangle$ and hence also the Slater determinant $|\psi_3\psi_5|$. Similarly, the normalized vacuum state, $\langle vac|vac\rangle = 1$, corresponds to the vanishing occupations of all SO: $|vac\rangle = |00\ldots\rangle$. The Fock ($F$) space thus contains all kets $\{|n_1\, n_2 \ldots n_k \ldots\rangle\}$ for any overall number of electrons $N = \sum_k n_k$:

$$|vac\rangle,\ \{|i\rangle\},\ \{|ij\rangle\}, \{|ijk\rangle\},\ \ldots,\ \{|ij\ldots p\rangle\},\ \ldots \tag{6.213}$$

This enlarged basis of the independent state vectors defines the so called *occupation number* representation. It should be observed that kets corresponding to different permutations of the same set of occupied SO determine the same quantum state of N electrons, which can be uniquely identified by the *ordered* (increasing) labels of SO in $|\Psi_A\rangle$.

As we have already remarked above, the transition from $\Psi_A(N) = |i\, j \ldots p| \to \Psi_A(N+1) = |i\, j \ldots pr|$ is effected by the action of the *creation operator* $\hat{a}_r^+$, which creates an additional electron in state $|r\rangle$. Its action in the Fock space is defined in the following way:

$$\hat{a}_r^+|i\, j \ldots p\rangle = \begin{cases} |ij\ldots pr\rangle = (-1)^{v_r}|ij\ldots\, r \ldots\, p\rangle, & r \notin (i,j,\, \ldots\, ,p); \\ 0, & r \in (i,j,\, \ldots\, ,p); \end{cases} \tag{6.214}$$

here v_r stands for the number of SO exchanges required to shift index r of $|ij\ldots pr\rangle$ to its proper position in the ordered set $|ij\ldots\, r \ldots\, p\rangle$. The zero vector results when the SO to be created is already involved in the initial determinant.

A lowering of the number of electrons is similarly effected by the *annihilation operator* $\hat{a}_r^-$ symbolizing the action opposite to that of $\hat{a}_r^+$, i.e., the destruction of an electron in state $|r\rangle$, $(-1)^{v_r}\hat{a}_r^-|ij\ldots\, r \ldots\, p\rangle = \hat{a}_r^-|ij\ldots pr\rangle = |ij\ldots p\rangle$, or:

$$\hat{a}_r^-|i\, j \ldots p\rangle = \begin{cases} (-1)^{v_r}|ij\ldots\ \not{r} \ldots\, p\rangle = |ij\ldots\, p\ \not{r}\rangle, & r \in (i,j,\, \ldots\, ,p); \\ 0, & r \notin (i,j,\, \ldots\, ,p). \end{cases} \tag{6.215}$$

Again, v_r counts the number of orbital exchanges required to move r to the end of the list of SO and $\not{r}$ marks the destroyed SO. The zero vector is seen to result when the SO to be annihilated is not initially present in the determinant.

Therefore, all vectors in the Fock space (6.213) can be derived from the vacuum state by actions of the relevant creation operators,

$$\left\{|i\rangle = \hat{a}_i^+|vac\rangle\right\}, \qquad \left\{|ij\rangle = \hat{a}_j^+|i\rangle = \hat{a}_j^+\,\hat{a}_i^+|vac\rangle\right\},\ \ldots,$$
$$\left\{|ij\ldots p\rangle = \hat{a}_p^+\ldots\hat{a}_j^+\,\hat{a}_i^+|vac\rangle\right\},\ \ldots, \tag{6.216}$$

or traced back to the vacuum state by actions of the corresponding annihilation operators applied in the reverse order:

$$|vac\rangle = \hat{a}_i^-|i\rangle = \hat{a}_i^-\,\hat{a}_j^-|ij\rangle = \ldots = \hat{a}_i^-\,\hat{a}_j^-\ \ldots\ \hat{a}_p^-|ij\ \ldots\ p\rangle. \tag{6.217}$$

One also observes that $\hat{a}_i^+\hat{a}_i^+|vac\rangle = \hat{a}_i^+|i\rangle = \hat{a}_i^-\hat{a}_i^-|i\rangle = \hat{a}_i^-|vac\rangle = 0$.

These relations imply the anticommutation property of Jordan and Wigner for these operators:

$$\begin{aligned}&\hat{a}_j^+\,\hat{a}_i^+|vac\rangle = |ij\rangle = -|ji\rangle = -\hat{a}_i^+\,\hat{a}_j^+|vac\rangle \quad \text{or}\\ &\hat{a}_j^+\,\hat{a}_i^+ + \hat{a}_i^+\,\hat{a}_j^+ \equiv \left[\hat{a}_i^+, \hat{a}_j^+\right]_+ = 0,\end{aligned} \tag{6.218}$$

$$\hat{a}_i^-\,\hat{a}_j^-|ij\rangle = |vac\rangle = -\hat{a}_j^-\,\hat{a}_i^-|ji\rangle \quad \text{or} \quad \hat{a}_i^-\,\hat{a}_j^- + \hat{a}_j^-\,\hat{a}_i^- = \left[\hat{a}_i^-,\,\hat{a}_j^-\right]_+ = 0, \tag{6.219}$$

where $[\hat{A}, \hat{B}]_+ = \hat{A}\hat{B} + \hat{B}\hat{A}$ denotes the anticommutator of two operators. It follows from these equations that in the language of the second quantization formalism these relations reflect the Pauli principle of the antisymmetrization of the fermion wave function.

Next, let us examine the products of the creation and annihilation operators. One can easily verify that the nondiagonal ($s \neq r$) product operator $\hat{a}_s^+\hat{a}_r^-$ replaces the occupied state $|r\rangle$ with the occupied state $|s\rangle$, since the right operator in the product destroys an electron in $|r\rangle$ and the left operator creates in its place an electron in state $|s\rangle$:

$$\begin{aligned}\hat{a}_s^+\,\hat{a}_r^-|ij\ldots r\ldots p\rangle &= (-1)^{v_r}\hat{a}_s^+\,\hat{a}_r^-|ij\ \ldots\ pr\rangle = (-1)^{v_r}\hat{a}_s^+|ij\ \ldots\ p\rangle\\ &= (-1)^{v_r}|ij\ \ldots\ ps\rangle = (-1)^{2v_r}|ij\ \ldots\ s\ \ldots\ p\rangle\\ &= |ij\ \ldots\ s\ \ldots\ p\rangle \equiv |r \to s\rangle.\end{aligned} \tag{6.220}$$

We have observed above that placing the newly created state $|s\rangle$ in the position originally kept by $|r\rangle$ requires the same number of exchanges as that required to move the latter to the end of the original list of the occupied SO. We therefore conclude that the operator $\hat{a}_s^+\hat{a}_r^-$ indeed amounts to a single $r \to s$ excitation. One similarly verifies the action of the product operator with reverse order of the two factors:

$$\begin{aligned}\hat{\mathrm{a}}_r^- \,\hat{\mathrm{a}}_s^+ |ij\ldots r\ldots p\rangle &= \hat{\mathrm{a}}_r^- |ij\ldots r\ldots ps\rangle = (-1)^{v_r+1}\hat{\mathrm{a}}_r^- |ij\ldots psr\rangle \\ &= (-1)^{v_r+1}|ij\ldots ps\rangle. \end{aligned} \tag{6.221}$$

The diagonal ($s = r$) products of such creation and annihilation operators similarly give:

$$\hat{\mathrm{a}}_r^+ \,\hat{\mathrm{a}}_r^- |ij\ldots p\rangle = \begin{cases} |ij\ldots p\rangle, & r \in (i,j,\ldots,p); \\ 0, & r \notin (i,j,\ldots,p); \end{cases} \tag{6.222}$$

$$\hat{\mathrm{a}}_r^- \,\hat{\mathrm{a}}_r^+ |ij\ldots p\rangle = \begin{cases} |ij\ldots p\rangle, & r \notin (i,j,\ldots,p); \\ 0, & r \in (i,j,\ldots,p). \end{cases} \tag{6.223}$$

Hence, (6.220)–(6.223) are also compactly summarized by the following anticommutator identity:

$$\hat{a}_s^+ \,\hat{a}_r^- + \hat{a}_r^- \,\hat{a}_s^+ = \left[\hat{a}_s^+,\, \hat{a}_r^-\right]_+ = \delta_{s,r}. \tag{6.224}$$

Indeed, using these four equations gives for the $r \in (i, j, \ldots, p)$ case:

$$\begin{aligned}&\left[\hat{\mathrm{a}}_s^+,\, \hat{\mathrm{a}}_r^-\right]_+ |ij\ldots r\ldots p\rangle = |ij\ldots s\ldots p\rangle - |ij\ldots s\ldots p\rangle = 0, \\ &\left[\hat{\mathrm{a}}_r^+,\, \hat{\mathrm{a}}_r^-\right]_+ |ij\ldots r\ldots p\rangle = |ij\ldots r\ldots p\rangle, \text{ etc.}\end{aligned}$$

One also observes that the normalization of the state vectors in the Fock space requires:

$$\begin{aligned}\langle ij\ldots p|\left(\hat{\mathrm{a}}_r^+\right)^\dagger \hat{\mathrm{a}}_r^+ |ij\ldots p\rangle = 1,\ \ r \notin (i,j,\ldots,p), \quad &\text{or} \quad \left(\hat{\mathrm{a}}_r^+\right)^\dagger \hat{\mathrm{a}}_r^+ = 1, \\ \langle ij\ldots r\ldots p|\left(\hat{\mathrm{a}}_r^-\right)^\dagger \hat{\mathrm{a}}_r^- |ij\ldots r\ldots p\rangle = 1, \quad &\text{or} \quad \left(\hat{\mathrm{a}}_r^-\right)^\dagger \hat{\mathrm{a}}_r^- = 1.\end{aligned} \tag{6.225}$$

It thus follows from these operator reciprocity relations that:

$$\left(\hat{\mathrm{a}}_r^+\right)^\dagger = \left(\hat{\mathrm{a}}_r^+\right)^{-1} = \hat{\mathrm{a}}_r^- \equiv \hat{\mathrm{a}}_r \qquad \left(\hat{\mathrm{a}}_r^-\right)^\dagger = \left(\hat{\mathrm{a}}_r^-\right)^{-1} = \hat{\mathrm{a}}_r^+ \equiv \hat{\mathrm{a}}_r^\dagger. \tag{6.226}$$

Therefore, the creation operators are Hermitian conjugates of the annihilation operators, and vice versa; as such they are not Hermitian themselves. In the new notation introduced in the preceding equation, the anticommutation relations read:

$$\left[\hat{\mathrm{a}}_r^\dagger,\, \hat{\mathrm{a}}_s^\dagger\right]_+ = \left[\hat{\mathrm{a}}_r,\, \hat{\mathrm{a}}_s\right]_+ = 0 \quad \text{and} \quad \left[\hat{\mathrm{a}}_s^\dagger,\, \hat{\mathrm{a}}_r\right]_+ = \delta_{s,r}. \tag{6.227}$$

The creation and destruction operators in the position-spin representation, called the *field operators* $\hat{\psi}^\dagger(\boldsymbol{q})$ and $\hat{\psi}(\boldsymbol{q})$, introduce the *local* aspect of the electron distribution. They respectively create and destroy one-particle state $|\boldsymbol{q}\rangle = |\boldsymbol{r},\sigma_z\rangle$, the eigenfunction of the operator $\hat{\mathbf{q}} = (\hat{\mathbf{r}}, \hat{\sigma}_z)$ associated with the particle position-spin "coordinates" $\boldsymbol{q} = (\boldsymbol{r}, \sigma_z)$, i.e., the state corresponding to the sharply specified position ($\boldsymbol{r}$) and *spin* orientation (σ_z) of an electron,

$$\hat{\mathbf{r}}|\boldsymbol{q}\rangle = \boldsymbol{r}|\boldsymbol{q}\rangle \quad \text{and} \quad \hat{\sigma}_z|\boldsymbol{q}\rangle = \sigma_z|\boldsymbol{q}\rangle, \tag{6.228}$$

or in the combined short notation: $\hat{\mathbf{q}}|\boldsymbol{q}\rangle = \boldsymbol{q}|\boldsymbol{q}\rangle$. This definition of field operators thus implies:

$$\hat{\psi}^{\dagger}(\boldsymbol{q})|vac\rangle = |\boldsymbol{q}\rangle \quad \text{and} \quad \hat{\psi}(\boldsymbol{q})|\boldsymbol{q}\rangle = |vac\rangle.$$

They satisfy the associated anticommutation relations,

$$\begin{aligned}[\hat{\psi}^{\dagger}(\boldsymbol{q}), \hat{\psi}^{\dagger}(\boldsymbol{q}')]_{+} &= [\hat{\psi}(\boldsymbol{q}), \hat{\psi}(\boldsymbol{q}')]_{+} = 0 \quad \text{and}\\ [\hat{\psi}^{\dagger}(\boldsymbol{q}), \hat{\psi}(\boldsymbol{q}')]_{+} &= \delta(\boldsymbol{q} - \boldsymbol{q}'),\end{aligned} \tag{6.229}$$

which represent the local analogs of those summarized in (6.227).

From the relevant identity (completeness) projections,

$$\int d\boldsymbol{q}|\boldsymbol{q}\rangle\langle\boldsymbol{q}| = \sum_r |r\rangle\langle r| = 1, \tag{6.230}$$

and the associated resolutions of SO in the continuous basis $\{|\boldsymbol{q}\rangle\}$ and of $|\boldsymbol{q}\rangle$ in the discrete SO basis $\{|r\rangle\}$,

$$\begin{aligned}|r\rangle &= \int d\boldsymbol{q}|\boldsymbol{q}\rangle\langle\boldsymbol{q}|r\rangle = \int |\boldsymbol{q}\rangle\ \psi_r(\boldsymbol{q})\, d\boldsymbol{q},\\ |\boldsymbol{q}\rangle &= \sum_r |r\rangle\langle r \mid \boldsymbol{q}\rangle = \sum_r |r\rangle\ \psi_r^*(\boldsymbol{q}),\end{aligned} \tag{6.231}$$

one then arrives at the following relations between the creation/annihilation operators and their (local) field operator analogs:

$$|r\rangle = \hat{a}_r^{\dagger}|vac\rangle = \int d\boldsymbol{q}\, \psi_r(\boldsymbol{q})\, \hat{\psi}^{\dagger}(\boldsymbol{q})|vac\rangle \quad \text{or} \quad \hat{a}_r^{\dagger} = \int d\boldsymbol{q}\ \psi_r(\boldsymbol{q})\, \hat{\psi}^{\dagger}(\boldsymbol{q}), \tag{6.232}$$

$$|\boldsymbol{q}\rangle = \hat{\psi}^{\dagger}(\boldsymbol{q})|vac\rangle = \sum_r \psi_r^*(\boldsymbol{q})\, \hat{a}_r^{\dagger}|vac\rangle \quad \text{or} \quad \hat{\psi}^{\dagger}(\boldsymbol{q}) = \sum_r \psi_r^*(\boldsymbol{q})\, \hat{a}_r^{\dagger}. \tag{6.233}$$

Hence the relations between their adjoints, the associated annihilation operators:

$$\hat{a}_r = \int d\boldsymbol{q}\ \psi_r^*(\boldsymbol{q})\, \hat{\psi}(\boldsymbol{q}) \quad \text{and} \quad \hat{\psi}(\boldsymbol{q}) = \sum_r \psi_r(\boldsymbol{q})\, \hat{a}_r. \tag{6.234}$$

It further follows from (6.222) that kets in the Fock space, $\{|\boldsymbol{n}\rangle\}$, which are identified by the corresponding occupation vector of SO, $\boldsymbol{n} = (n_1, n_2, \ldots, n_r, \ldots)$, are eigenfunctions of the operators $\left\{\hat{\mathrm{a}}_r^+ \, \hat{\mathrm{a}}_r^- = \hat{\mathrm{a}}_r^\dagger \, \hat{\mathrm{a}}_r\right\}$, with the eigenvalues reflecting the SO occupation numbers $\{n_r\}$:

$$\hat{\mathrm{a}}_r^\dagger \hat{\mathrm{a}}_r |\boldsymbol{n}\rangle \equiv \hat{\mathrm{n}}_r^F |\boldsymbol{n}\rangle = n_r |\boldsymbol{n}\rangle, \qquad n_r = \begin{cases} 1, & \text{occupied SO} \\ 0, & \text{unoccupied SO} \end{cases}. \tag{6.235}$$

Therefore, the Hermitian operator $\hat{\mathrm{n}}_r^F = \hat{\mathrm{n}}_r^{F\dagger}$ represents the occupation number of ψ_r. Hence, the Fock space vectors also satisfy the eigenvalue problem for the overall number of electrons N, represented in the second quantization formalism by the Hermitian operator $\hat{\mathrm{N}}^F = \sum_r \hat{\mathrm{n}}_r^F = \sum_r \hat{\mathrm{a}}_r^\dagger \hat{\mathrm{a}}_r$:

$$\hat{\mathrm{N}}^F |\boldsymbol{n}\rangle = \left(\sum\nolimits_r n_r\right) |\boldsymbol{n}\rangle = N |\boldsymbol{n}\rangle. \tag{6.236}$$

Let us now examine how the electronic Hamiltonian [(5.51) and (5.69)] and its one- and two-electron contributions $\hat{\mathrm{h}}(1)$ and $g(1,2)$ are represented in the Fock space. We first observe that using the discrete projection of (6.230) onto the complete space of SO gives:

$$\hat{\mathrm{h}}|i\rangle = \sum_r |r\rangle\langle r|\hat{\mathrm{h}}|i\rangle = \sum_r |r\rangle \bar{h}_{r,i}, \tag{6.237}$$

where $\bar{h}_{r,i}$ denotes the matrix element of $\hat{\mathrm{h}}(1)$ between the indicated SO (5.73). The one-electron part of the molecular N-electron (Coulomb) Hamiltonian is given by the sum of such one-electron operators:

$$\hat{\mathcal{F}}(N) = \sum_i \hat{\mathrm{h}}(i), \tag{6.238}$$

with $\hat{\mathrm{h}}(i)$ acting on the one-electron state describing ith electron. Hence, its action on the Slater determinant gives [see (6.237)]:

$$\hat{\mathcal{F}}(N)\det[\psi_{k_1}(1)\psi_{k_2}(2)\ldots\psi_{k_i}(i)\ldots] = \sum_{k_i}\sum_{k_i'} \det[\psi_{k_1}(1)\,\psi_{k_2}(2)\,\ldots\,\psi_{k_i'}(i)\,\ldots]\bar{h}_{k_i',k_i}. \tag{6.239}$$

Here, relative to the original determinant in the l.h.s., the determinant in the r.h.s. sum involves the substitution of the orbital describing ith electron, $\psi_{k_i} \rightarrow \psi_{k_i'}$, which in the Fock space can be accomplished by the action of the *single*-excitation operator of (6.220) on the original state:

$$\hat{\mathcal{F}}^F |k_1\, k_2\, \ldots\, k_i\, \ldots\rangle = \sum_{k_i}\sum_{k_i'} \hat{a}_{k_i'}^\dagger \hat{a}_{k_i} |k_1\, k_2 \ldots\, k_i\, \ldots\rangle\, \bar{h}_{k_i',\,k_i}. \tag{6.240}$$

Therefore, the *second* quantization form of the (symmetrical) one-electron operator of (6.238) reads:

$$\hat{\mathcal{F}}^F = \sum_r \sum_s \bar{h}_{s,r} \hat{a}_s^\dagger \hat{a}_r. \tag{6.241}$$

It is devoid of any explicit N-dependence, so it applies to both the neutral systems and ions. As we have argued in (6.236), the number of electrons is ultimately recognized by another N-independent operator: $\hat{N}^F = \sum_r \hat{a}_r^\dagger \hat{a}_r$.

One similarly determines the Fock space form of the two-electron operator

$$\hat{\mathcal{G}}(N) = \sum_{i<j} g(i,j). \tag{6.242}$$

We first observe that in the Fock space the *double* excitation $(t,u) \to (r,s)$, consisting of simultaneous replacements of two SO, $\psi_t \to \psi_r$ and $\psi_u \to \psi_s$, is effected by the operator $\hat{a}_r^\dagger \hat{a}_s^\dagger a_u a_t$:

$$\begin{aligned}
\hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_u \hat{a}_t |ij \ldots u \ldots t \ldots p\rangle &= (-1)^{v_t} \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_u \hat{a}_t |ij \ldots u \ldots pt\rangle \\
&= (-1)^{v_t} \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_u |ij \ldots u \ldots p\rangle = (-1)^{v_t+v_u} \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_u |ij \ldots pu\rangle \\
&= (-1)^{v_t+v_u} \hat{a}_r^\dagger \hat{a}_s^\dagger |ij \ldots p\rangle = (-1)^{v_t+v_u} \hat{a}_r^\dagger |ij \ldots ps\rangle \\
&= (-1)^{v_t+2v_u} \hat{a}_r^\dagger |ij \ldots s \ldots p\rangle = (-1)^{v_t+2v_u} |ij \ldots s \ldots pr\rangle \\
&= (-1)^{2v_t+2v_u} |ij \ldots s \ldots r \ldots p\rangle = |ij \ldots s \ldots r \ldots p\rangle \equiv |t \to r, u \to s\rangle.
\end{aligned} \tag{6.243}$$

The complete two-electron basis is spanned by all product functions $\{\psi_k(1)\psi_l(2)\}$ [see (6.60)] or the associated Slater determinants $\{|kl\rangle\}$ in the Fock space: $\sum_{k,l} |kl\rangle\langle kl| = 1$. The action of the (multiplicative) operator coupling the two electrons is then determined by the two-electron integrals in the SO basis set [see (5.75)]:

$$g|tu\rangle = \Sigma_{r,s} |rs\rangle\langle rs|g|tu\rangle = \Sigma_{r,s} |rs\rangle\ (rt|su). \tag{6.244}$$

The corresponding action of the symmetrical operator of (6.242) on the representative vector in the Fock space or the associated Slater determinant then reads:

$$\begin{aligned}
\hat{\mathcal{G}}^F |\ldots k_i \ldots k_j \ldots\rangle \equiv \hat{\mathcal{G}}^F |\ldots u \ldots t \ldots\rangle \\
&= \sum_{t<u} \sum_r \sum_s |\ldots s \ldots r \ldots\rangle \langle sr|g|ut\rangle \\
&\equiv \frac{1}{2} \sum_r \sum_s \sum_t \sum_u |\ldots s \ldots r \ldots\rangle \langle sr|g|ut\rangle \\
&= \frac{1}{2} \sum_r \sum_s \sum_t \sum_u \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_u \hat{a}_t |\ldots u \ldots t \ldots\rangle \langle sr|g|ut\rangle,
\end{aligned} \tag{6.245}$$

and hence

$$\hat{\mathcal{G}}^F = \frac{1}{2}\sum_r\sum_s\sum_t\sum_u \langle sr|g|ut\rangle\, \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_u \hat{a}_t. \tag{6.246}$$

Therefore, the electronic Hamiltonian $\hat{\mathrm{H}}^e(N) = \hat{\mathcal{F}}(N) + \hat{\mathcal{G}}(N)$ assumes the following form in the *second* quantization representation of the Fock space:

$$\hat{\mathrm{H}}^{e,F} = \hat{\mathcal{F}}^F + \hat{\mathcal{G}}^F = \sum_r\sum_s \bar{h}_{s,r}\, \hat{a}_s^\dagger \hat{a}_r + \frac{1}{2}\sum_r\sum_s\sum_t\sum_u \langle sr|g|ut\rangle\, \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_u \hat{a}_t. \tag{6.247}$$

The equivalence of this formalism to the previous expressions derived in Sect. 5.4 using the position-spin representation can be demonstrated by calculating the expectation value of the electronic energy in state $\Psi_A(N) = |\psi_i\, \psi_j \ldots|$ represented by the associated vector $|i\, j\, \ldots\rangle$ in the Fock space. For the average one-electron energy, one indeed recovers (5.74):

$$\begin{aligned}\langle ij\ldots|\hat{\mathcal{F}}^F\,|ij\ldots\rangle &= \sum_r\sum_s \bar{h}_{s,r}\,\langle ij\ldots r\ldots|\hat{a}_s^\dagger\, \hat{a}_r|ij\ldots r\ldots\rangle \\ &= \sum_r\sum_s \bar{h}_{s,r}\,\langle ij\ldots r\ldots|ij\ldots s\ldots\rangle = \sum_r\sum_s \bar{h}_{s,r}\,\delta_{r,s} = \sum_r \bar{h}_{r,r}.\end{aligned} \tag{6.248}$$

The expectation value of the two-electron operator similarly gives

$$\begin{aligned}\langle ij\ldots|\hat{\mathcal{G}}^F\,|ij\ldots\rangle &= \frac{1}{2}\sum_r\sum_s\sum_t\sum_u \langle sr|g|ut\rangle\, \langle ij\ldots u\ldots t\ldots|\, \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_u \hat{a}_t|ij\ldots u\ldots t\ldots\rangle \\ &= \frac{1}{2}\sum_r\sum_s\sum_t\sum_u \langle sr|g|ut\rangle\, \langle ij\ldots u\ldots t\ldots|ij\ldots s\ldots r\ldots\rangle.\end{aligned} \tag{6.249}$$

The mutual projection of the two vectors in the Fock space does not vanish only in two cases: for $(s = u) \wedge (r = t)$, when $\langle ij\ldots u\ldots t\ldots|ij\ldots u\ldots t\ldots\rangle = 1$, and for $(s = t) \wedge (r = u)$, when $\langle ij\ldots u\ldots t\ldots|ij\ldots t\ldots u\ldots\rangle = -\langle ij\ldots u\ldots t\ldots|ij\ldots u\ldots t\ldots\rangle = -1$. This again gives the familiar result of (5.75):

$$\langle ij\ldots|\hat{\mathcal{G}}^F\,|ij\ldots\rangle = \frac{1}{2}\sum_r\sum_s \left[\langle sr|g|sr\rangle - \langle sr|g|rs\rangle\right] = \frac{1}{2}\sum_r\sum_s \left[\bar{J}_{s,r} - \bar{K}_{s,r}\right]. \tag{6.250}$$

It should be further emphasized that the creation operator and its field operator analog act as such only when acting on the *ket*, to their right. Indeed, when acting on the *bra*, to their left, they have the opposite, annihilation meaning, e.g.,

$$\begin{aligned}&\hat{a}_r^\dagger|ij\ldots pr\rangle = 0 \quad \text{but} \\ &\quad \langle ij\ldots pr|\hat{a}_r^\dagger = [\hat{a}_r|ij\ldots pr\rangle]^\dagger = |ij\ldots p\rangle^\dagger = \langle ij\ldots p|.\end{aligned} \tag{6.251}$$

In the position-spin representation, one finds analogous expressions for operators depending upon the continuous/discrete variable $\boldsymbol{q}$. For example, the Fock space representation of the spin density operator $\hat{\rho}(\boldsymbol{q})$ (3.9) is given by the product of the creation and annihilation field operators:

$$\hat{\rho}^F(\boldsymbol{q}) = \hat{\psi}^\dagger(\boldsymbol{q})\ \hat{\psi}(\boldsymbol{q}). \tag{6.252}$$

Indeed, using expressions reported in (6.233) and (6.234, one then recovers the known expression for the spin density in terms of the occupied SO:

$$\begin{aligned}\langle ij\ldots|\hat{\rho}^F(\boldsymbol{q})|ij\ldots\rangle &= \sum_r\sum_s \psi_s^*(\boldsymbol{q})\psi_r(\boldsymbol{q})\,\langle ij\ldots r\ldots|\hat{a}_s^\dagger\ \hat{a}_r|ij\ldots r\ldots\rangle\\ &= \sum_r\sum_s \psi_s^*(\boldsymbol{q})\,\psi_r(\boldsymbol{q})\langle ij\ldots r\ldots|ij\ldots s\ldots\rangle\\ &= \sum_r\sum_s \psi_s^*(\boldsymbol{q})\,\psi_r(\boldsymbol{q})\,\delta_{r,s} = \sum_r |\psi_r(\boldsymbol{q})|^2.\end{aligned} \tag{6.253}$$

The kinetic energy operator in the position-spin representation $\hat{\mathrm{T}}_e(\mathbf{q})$ has the following representation in the Fock space (a.u.):

$$\hat{\mathrm{T}}_e^F(\mathbf{q}) = \int d\boldsymbol{q}\ \hat{\psi}^\dagger(\boldsymbol{q})\left(-\frac{1}{2}\Delta\right)\hat{\psi}(\boldsymbol{q}) = \frac{1}{2}\int d\boldsymbol{q}\nabla\hat{\psi}^\dagger(\boldsymbol{q})\cdot\nabla\hat{\psi}(\boldsymbol{q}). \tag{6.254}$$

Notice the similarity of the preceding expressions for the (*many*-electron) quantum mechanical operators to the corresponding one-electron expectation values in the one-electron state $\varphi(\boldsymbol{q})$:

$$\rho(\boldsymbol{q}) = \varphi^*(\boldsymbol{q})\,\varphi(\boldsymbol{q}) \quad \text{and} \quad T_e[\varphi] = \frac{1}{2}\int d\boldsymbol{q}\,\nabla\varphi^*(\boldsymbol{q})\cdot\nabla\varphi(\boldsymbol{q}),$$

with the field operators of the Fock space in the former replacing the wave functions of the latter. This analogy also holds in the Fock space representation of the probability current operator $\hat{\mathbf{j}}(\boldsymbol{q})$[compare (3.128)]:

$$\hat{\mathbf{j}}^F(\boldsymbol{q}) = \frac{1}{2i}[\hat{\psi}^\dagger(\boldsymbol{q})\ \nabla\hat{\psi}(\boldsymbol{q}) - \hat{\psi}(\boldsymbol{q})\ \nabla\hat{\psi}^\dagger(\boldsymbol{q})]. \tag{6.255}$$

The remaining parts of the electronic Hamiltonian in the coordinate-spin representation read:

$$\begin{aligned}\hat{\mathrm{V}}_{ne}^F &= \int d\boldsymbol{q}\ v(\boldsymbol{q})\ \hat{\psi}^\dagger(\boldsymbol{q})\ \hat{\psi}(\boldsymbol{q}),\\ \hat{\mathrm{V}}_{ee}^F &= \frac{1}{2}\int d\boldsymbol{q}_1\int d\boldsymbol{q}_2\,\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\,\hat{\psi}^\dagger(\boldsymbol{q}_1)\ \hat{\psi}^\dagger(\boldsymbol{q}_2)\ \hat{\psi}(\boldsymbol{q}_2)\ \hat{\psi}(\boldsymbol{q}_1).\end{aligned} \tag{6.256}$$

In this local *second* quantization formalism, the *first*- and *second*-order reduced density matrices are expectation values of the following products of field operators:

$$\hat{\gamma}_1^F(\boldsymbol{q}_1;\boldsymbol{q}_1{}') = \hat{\psi}^\dagger(\boldsymbol{q}_1)\,\hat{\psi}(\boldsymbol{q}_1{}'),$$
$$\hat{\gamma}_2^F(\boldsymbol{q}_1,\boldsymbol{q}_2;\boldsymbol{q}_1{}',\boldsymbol{q}_2{}') = \frac{1}{2}\hat{\psi}^\dagger(\boldsymbol{q}_1)\,\hat{\psi}^\dagger(\boldsymbol{q}_2)\,\hat{\psi}(\boldsymbol{q}_2{}')\,\hat{\psi}(\boldsymbol{q}_1{}'). \tag{6.257}$$

Indeed, the spin density operator of (6.252) is seen to constitute the diagonal part of $\hat{\gamma}_1^F(\boldsymbol{q}_1;\boldsymbol{q}_1{}')$ thus giving rise to the following position-spin representation of the particle number operator of (6.236):

$$\hat{\mathrm{N}}^F = \int d\boldsymbol{q}\;\hat{\rho}^F(\boldsymbol{q}) = \int d\boldsymbol{q}\;\hat{\psi}^\dagger(\boldsymbol{q})\,\hat{\psi}(\boldsymbol{q}). \tag{6.258}$$

The equivalence of this continuous expression and the previously reported discrete operator can be directly verified using the relevant expansions of the field operators [(6.233) and (6.234)]:

$$\hat{\mathrm{N}}^F = \sum_{r,r'} \langle r \mid r' \rangle\,\hat{\mathrm{a}}_r^\dagger \hat{\mathrm{a}}_{r'} = \sum_{r,r'} \delta_{r,r'} \hat{\mathrm{a}}_r^\dagger\,\hat{\mathrm{a}}_{r'} = \sum\nolimits_r \hat{\mathrm{a}}_r^\dagger \hat{\mathrm{a}}_r = \sum\nolimits_r \hat{\mathrm{n}}_r^F, \tag{6.259}$$

where $\hat{\mathrm{n}}_r^F$ stands for the occupation operator of $|r\rangle$.

6.5.2 Cluster Expansion of Electronic States

We have demonstrated in the preceding section that the state vectors of the excited configurations appearing in the CI expansion of the correlated electronic wave functions can be written in the *second* quantization representation as the result of acting on the HF ("vacuum") state $\left|\Psi_0^{\mathrm{HF}}\right\rangle \equiv |vac\rangle = |\ldots,k,l,\ldots,m,\ldots\rangle$ (containing zero excitations) with the corresponding electron excitation operators [see (6.220) and (6.243)]:

$$\left|\Phi_k^p\right\rangle \equiv |k \to p\rangle = \hat{\mathrm{a}}_p^\dagger \hat{\mathrm{a}}_k|vac\rangle, \qquad \left|\Phi_{k,l}^{p,q}\right\rangle \equiv |(k,l) \to (p,q)\rangle = \hat{\mathrm{a}}_p^\dagger \hat{\mathrm{a}}_q^\dagger \hat{\mathrm{a}}_l \hat{\mathrm{a}}_k|vac\rangle,$$
$$\left|\Phi_{k,l,\ldots,m}^{p,q,\ldots,r}\right\rangle \equiv |(k,l,\ldots,m) \to (p,q,\ldots,r)\rangle = \hat{\mathrm{a}}_p^\dagger \hat{\mathrm{a}}_q^\dagger \ldots \hat{\mathrm{a}}_r^\dagger \hat{\mathrm{a}}_m \ldots \hat{\mathrm{a}}_l \hat{\mathrm{a}}_k|vac\rangle, \text{ etc.} \tag{6.260}$$

Therefore, the FCI expansion of the correlated ground state of electrons can be interpreted as the result of acting on the HF vacuum state with the general electron excitation operator $\hat{\mathrm{T}}$, which combines excitations of all multiplicities:

$$\begin{aligned}\left|\Psi_0^{\mathrm{CI}}\right\rangle \equiv C_0\left|\bar{\Psi}_0^{\mathrm{CI}}\right\rangle &= C_0\left(1+\sum_k^{occd.}\sum_p^{virt.}\bar{C}_k^p\,\hat{\mathrm{a}}_p^\dagger\hat{\mathrm{a}}_k+\sum_{k<l}^{occd.}\sum_{p<q}^{virt.}\bar{C}_{k,l}^{p,q}\,\hat{\mathrm{a}}_p^\dagger\hat{\mathrm{a}}_q^\dagger\hat{\mathrm{a}}_l\hat{\mathrm{a}}_k+\ldots\right)|vac\rangle\\ &\equiv C_0\left(1+\sum_k^{occd.}\hat{\mathrm{u}}_k+\sum_{k<l}^{occd.}\hat{\mathrm{u}}_{k,l}+\ldots+\sum_{k<l<\ldots<m}^{occd.}\hat{\mathrm{u}}_{k,l,\ldots,m}+\ldots\right)|vac\rangle\\ &\equiv C_0(1+\hat{\mathrm{T}}_1+\hat{\mathrm{T}}_2+\ldots+\hat{\mathrm{T}}_n+\ldots)\,|vac\rangle\equiv C_0(1+\hat{\mathrm{T}})\,|vac\rangle,\end{aligned}\tag{6.261}$$

where $\hat{\mathrm{u}}_{k,l,\ldots,m}=\sum_{p<q<\ldots<r}^{virt.}\bar{C}_{k,l,\ldots,m}^{p,q,\ldots,r}\,\hat{\mathrm{a}}_p^\dagger\hat{\mathrm{a}}_q^\dagger\ldots\hat{\mathrm{a}}_r^\dagger\hat{\mathrm{a}}_m\ldots\hat{\mathrm{a}}_l\hat{\mathrm{a}}_k$. The cluster operators

$$\hat{\mathrm{T}}_1=\sum_k^{occd.}\hat{\mathrm{u}}_k,\quad \hat{\mathrm{T}}_2=\sum_{k<l}^{occd.}\hat{\mathrm{u}}_{k,l},\quad\ldots,\quad \hat{\mathrm{T}}_n=\sum_{k<l<\ldots<m}^{occd.}\hat{\mathrm{u}}_{k,l,\ldots,m},\quad\ldots\tag{6.262}$$

are said to generate the 1-cluster, 2-cluster, …, n-cluster, …, corrections to the HF (vacuum) state, respectively, through the excitations of single electrons, electronic pairs, …, n-electron clusters, etc.

Consider now the action on the HF vacuum state of the *exponential* electron excitation operator of the CC approximation [see (3.92a,b)],

$$\exp(\hat{\mathrm{T}})=1+\hat{\mathrm{T}}+\frac{1}{2}\hat{\mathrm{T}}^2+\frac{1}{3!}\hat{\mathrm{T}}^3+\ldots,\tag{6.263}$$

$$\begin{aligned}\exp(\hat{\mathrm{T}})\,|\mathrm{vac}\rangle &= \left[1+\hat{\mathrm{T}}_1+\left(\hat{\mathrm{T}}_2+\frac{1}{2}\hat{\mathrm{T}}_1^2\right)+\left(\hat{\mathrm{T}}_3+\hat{\mathrm{T}}_1\hat{\mathrm{T}}_2+\frac{1}{3!}\hat{\mathrm{T}}_1^3\right)\right.\\ &\quad\left.+\left(\hat{\mathrm{T}}_4+\hat{\mathrm{T}}_3\hat{\mathrm{T}}_1+\frac{1}{2}\hat{\mathrm{T}}_2^2+\frac{1}{2}\hat{\mathrm{T}}_2\hat{\mathrm{T}}_1^2+\frac{1}{4!}\hat{\mathrm{T}}_1^4\right)+\ldots\right]|vac\rangle\\ &\equiv(1+\hat{\mathrm{C}}_1+\hat{\mathrm{C}}_2+\hat{\mathrm{C}}_3+\hat{\mathrm{C}}_4+\ldots)\,|vac\rangle\equiv\left|\bar{\Psi}_0^{\mathrm{CC}}\right\rangle.\end{aligned}\tag{6.264}$$

It reveals the structure of the n-tuple excitation operator $\hat{\mathrm{C}}_n$ in the correlated state $\left|\bar{\Psi}_0^{\mathrm{CC}}\right\rangle$ of the CC approximation. Besides $\hat{\mathrm{T}}_n$ this operator is seen to contain also all products of the *lower*-order excitations, originating from smaller excitation clusters, which together give rise to the combined multiplicity n of all such partial excitations.

For example, it follows from this expansion that *quadruple* operator $\hat{\mathrm{C}}_4$ of the CC expansion contains five different cluster excitations. In accordance with the discussion of Sect. 6.4.3, the most important contribution should be expected to originate from the $\hat{\mathrm{T}}_2^2$ term, which represents strong Coulomb correlation interactions between two electronic pairs, e.g., electrons occupying two different MO. The same type of reasoning indicates that the $\hat{\mathrm{T}}_4$ term in this operator is much less important, since it represents Coulomb correlation interactions between four electrons, which are already to a large extent *exchange* correlated. Finally, the $\hat{\mathrm{T}}_1$

contribution to $\hat{C}_4$ can be strongly limited by using the MC SCF reference function in the associated MR-CC method.

6.5.3 Coupled Cluster Method

As argued above, the most important in the cluster expansion of (6.263) are the 2-clusters (electronic pairs) represented by operator $\hat{T}_2$:

$$\hat{T} \cong \hat{T}_2 \equiv \frac{1}{4}\sum_{k<l}^{occd.}\sum_{p<q}^{virt.} t_{k,l}^{p,q}\, \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_l \hat{a}_k, \tag{6.265}$$

where the unknowns $\left\{t_{k,l}^{p,q}\right\}$, called the CC *amplitudes*, represent the renormalized CI coefficients $\left\{\bar{C}_{k,l}^{p,q}\right\}$. This CC-2 approximation is basically equivalent to the CPMET treatment of Sect. 6.4.3.

The relevant equations for determining the coefficients defining the correlated state of the coupled 2-clusters are derived in a way similar to that used to derive the corresponding CPMET equations. One starts with the eigenvalue equation of the electronic Hamiltonian for $\left|\bar{\Psi}_0^{CC}\right\rangle \cong \exp(\hat{T}_2)\,|vac\rangle$,

$$\hat{H}^e \exp(\hat{T}_2)\,|vac\rangle = E_0^e \exp(\hat{T}_2)\,|vac\rangle, \tag{6.266}$$

where $E_0^e = E_0^{HF} + \Delta E_{corr.}^{CC}$. Acting from the left on both sides of the preceding equation with the inverse exponential operator $\exp(-\hat{T}_2)$, $\exp(-\hat{T}_2)\exp(\hat{T}_2) = \exp(0) = 1$, one then arrives at the associated eigenvalue problem of the similarity-transformed electronic Hamiltonian:

$$\exp(-\hat{T}_2)\hat{H}^e \exp(\hat{T}_2)\,|vac\rangle \equiv \hat{H}_2^e|vac\rangle = E_0^e\,|vac\rangle. \tag{6.267}$$

Its projection onto the HF vacuum state gives the familiar expression for the correlated energy of the system ground state [see (6.180) and (6.195)]:

$$\begin{aligned}
E_0^e &= E_0^{HF} + \Delta E_{corr.}^{CC} = \langle vac|\hat{H}_2^e|vac\rangle \\
&= \langle vac|(1 - \hat{T}_2 + \frac{1}{2}\hat{T}_2^2 - \ldots)\hat{H}^e(1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \ldots)|vac\rangle \\
&= \langle vac|\hat{H}^e|vac\rangle + \langle vac|\hat{H}^e\hat{T}_2|vac\rangle \\
&= E_0^{HF} + \sum_{k<l}^{occd.}\sum_{p<q}^{virt.} t_{k,l}^{p,q}\langle vac|\hat{H}^e|(k,l) \to (p,q)\rangle \\
&= E_0^{HF} + \sum_{k<l}^{occd.}\sum_{p<q}^{virt.} t_{k,l}^{p,q}\langle kl|g|pq - qp\rangle = E_0^{HF} + \sum_{k<l}^{occd.} e_{k,l}^{CC}.
\end{aligned} \tag{6.268}$$

Above, we have observed that

$$\langle vac|\hat{\mathrm{T}}_2 = 0, \tag{6.269}$$

since the action of the creation operators of $|p\rangle$ and $|q\rangle$ on the *bra* vacuum vector amounts to annihilation of one-particle states which are not used in the HF determinant [see also (6.251)]. For example,

$$\langle vac|\hat{\mathrm{a}}_p^\dagger \hat{\mathrm{a}}_q^\dagger \hat{\mathrm{a}}_l \hat{\mathrm{a}}_k = \left(\hat{\mathrm{a}}_k^\dagger \hat{\mathrm{a}}_l^\dagger \hat{\mathrm{a}}_q \hat{\mathrm{a}}_p |vac\rangle\right)^\dagger = 0. \tag{6.270}$$

We have also used in (6.268) the Slater–Condon rules of (5.86) and (5.87), which predict the vanishing matrix element $\langle vac|\hat{\mathrm{H}}^e \hat{\mathrm{T}}_2 \hat{\mathrm{T}}_2|vac\rangle$, the ket of which represents the *quadruply* excited configuration relative to the HF vacuum.

As in the electron-pair theories, the equations for the optimum CC amplitudes result from projecting (6.267) into the *doubly* excited states:

$$\langle (kl) \to (p,q)|\hat{\mathrm{H}}_2^e|vac\rangle = E_0^e \langle (kl) \to (p,q) \mid vac\rangle = 0, \tag{6.271}$$

by the orthogonality of configurations. Expanding the exponential operators then gives the following nonvanishing contributions to the matrix element on the l.h.s of the preceding equation,

$$\langle (kl) \to (p,q)|\hat{\mathrm{H}}^e (1 + \hat{\mathrm{T}}_2 + \frac{1}{2}\hat{\mathrm{T}}_2^2) - \hat{\mathrm{T}}_2 \hat{\mathrm{H}}^e (1 + \hat{\mathrm{T}}_2)|vac\rangle = 0, \tag{6.272}$$

which imply the (coupled) quadratic equations for the CC amplitudes.

Since the number of such unknowns is very large, solving these equations is not an easy task. This severely restricts the range of applications of the CC method to at best medium-size molecular systems. The other problem which still awaits a satisfactory solution is the use of the multireference functions, e.g., the ground-states of the *open*-shell systems or the optimum states from the MC SCF method, as the starting point in the cluster expansion.

6.6 Elements of Valence Bond Approach

The *Valence Bond* (VB) theory originates from the classical Heitler and London (HL) (1927) treatment of the hydrogen molecule (see also: London 1928), the first quantum theory of the chemical bond. It has played an extremely important part in the early history of the quantum treatment of the molecular electronic structure, being strongly advocated by Slater and Pauling, later to be dominated by the MO theory of Mulliken, Hund, and Hückel, and made a strong comeback from 1980s onward. An interesting account of the early VB-MO rivalry has recently been given in an excellent primer by Shaik and Hiberty (2004). This theory connects more directly to the classical chemical concepts and offers important insights into the elementary chemical processes, generates the key paradigms of chemistry, such as the bonding electron pair and octet rule, successfully tackles many classical issues in the theory of molecular structure, and conceptualizes the chemical reactivity (e.g., Shaik 1989, Shaik and Hiberty 1991, 1995; Shaik et al. 2001, 2009). Some of its oversimplified implementations in the past have created notable "failures," which gave a false impression and reputation in some circles of the VB theory as representing an obsolete model. A good example of such a problem is the spin multiplicity of the ground state of O_2. Although it is possible to give the VB explanation of why this molecule has a triplet ground state, this reasoning is rather involved in contrast to the very simple and more natural MO explanation.

However, when properly applied, with all its intrinsic nonorthogonalities and the matrix elements of the Hamiltonian properly accounted for, the VB treatment appears as an alternative approach to molecular electronic structure which is fully equivalent to the MO method. The theory quantitative variants, the ab initio VB methods, e.g., *Generalized* VB (GVB) scheme of Goddard and coworkers (Goddard 1967; Goddard and Ladner 1971; Goddard et al. 1973; Goddard and Harding 1978; Rappé and Goddard 1982; see also: Simonetta 1968; Gerratt 1974), provide very efficient computational tools for determining the molecular PES and predicting the outcomes of chemical reactions.

To obtain from a very large calculation the result which agrees with experiment is only part of science. Of equal importance is a convincing, simple, and elegant model of the molecular phenomena, giving the crucial understanding without elaborate calculations. The VB approach, which closely follows the chemical intuition in coupling atomic states in molecules, has been quite successful in providing such a direct insight into many classical problems of the electronic structure. For example, one of the great merits of the VB theory is its visually intuitive wave function, given by the linear combination of the chemically meaningful "structures." The theory gives rise to our present understanding of the competition between the σ and π electrons in aromatic systems (e.g., Shaik et al. 2001; see also Jug and Köster 1990), implies the new, *charge-shift* bonding mechanism (Shaik et al. 2009), and provides qualitative models of chemical reactions (e.g., Epiotis 1978; Shaik and Hiberty 2004) and the VB ideas have been proven very useful in modeling the Born–Oppenheimer energy surfaces for elementary reactive collisions (e.g., Murrell et al. 1984). Several important developments in the straightforward VB theory have also occurred in recent decades, e.g., the Moffitt (1951) theory of AIM with its subsequent refinements (Balint-Kurti and Karplus 1973), the theory of the separated, strongly orthogonal electron pairs (see Sect. 6.4.1) of Hurley et al. (1953), and the general group function model of McWeeny (1989).

The VB strategy for constructing the molecular wave functions uses the quantum states of constituent atoms (fragments), with a strong emphasis on the spin pairing of electrons on the *singly* occupied valence orbitals of AIM as the source of all chemical bonds in the system. This strategy of determining the antisymmetric basis functions for molecular wave functions is thus multideterminant in character. The VB basis set involves all independent N-electron wave-functions, called the VB structures, constructed directly from the valence shell AO of constituent atoms by using the singlet coupling of the spins in the "bonded" electronic pairs, and admitting all possible distributions of spin factors of the unpaired electrons coupled to the specified length and the projection of the resultant spin (6.67). Such functions, however, which represent the admissible spin-pairing patterns of the valence electrons, are not mutually orthogonal. They may even strongly overlap and in general a selection of the independent set of VB structures is not a trivial mathematical problem, requiring the group-theoretic, antisymmetrizing projections for both the spin and spatial functions, as well as special techniques for constructing the spin and spatial parts of the elementary antisymmetric basis functions (e.g., Gerratt 1974).

The simplest way to generate the desired spin functions is to successively couple together the spins according to the rules for adding angular momenta in quantum mechanics, with the totality of such standard spin functions being conventionally visualized in terms of the familiar "branching" diagrams (e.g., Gerratt 1974). This perspective is thus fundamentally different from that used in the HF theory, which aimed at the best one-determinantal representation in terms of the (delocalized) canonical MO represented by LCAO.

6.6.1 Origins of VB Theory

Let us illustrate the basic proposition of HL theory using the classical case of the hydrogen molecule H_a–H_b, with two atoms contributing a single electron each, and the minimum basis set of the atomic functions, $1s_a \equiv a \in H_a$ and $1s_b \equiv b \in H_b$, respectively. There are two independent Slater determinants, which can be created in this minimum AO basis set:

$$\begin{aligned}|a^+b^-| &= \frac{1}{\sqrt{2}}[a(1)b(2)\alpha(1)\beta(2) - b(1)a(2)\beta(1)\alpha(2)],\\ |a^-b^+| &= \frac{1}{\sqrt{2}}[a(1)b(2)\beta(1)\alpha(2) - b(1)a(2)\alpha(1)\beta(2)],\end{aligned} \tag{6.273}$$

from which two combinations, representing proper spin states of two electrons, can be constructed (see Fig. 6.2),

$$\begin{aligned}\Psi_S^{\mathrm{HL}}(1,2) &= \frac{N_S}{\sqrt{2}}[|a^+b^-| - |a^-b^+|] = \frac{N_S}{\sqrt{2}}[|a^+b^-| + |b^+a^-|]\\ &= \left(\frac{N_S}{\sqrt{2}}[a(1)b(2) + b(1)a(2)]\right)\left(\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\right)\\ &\equiv \Phi_g(a—b)U_{0,0}(1,2),\end{aligned} \tag{6.274}$$

$$\begin{aligned}\Psi_T^{\mathrm{HL}}(1,2) &= \frac{N_T}{\sqrt{2}}\left[|a^+b^-| + |a^-b^+|\right] = \frac{N_T}{\sqrt{2}}\left[|a^+b^-| - |b^+a^-|\right]\\ &= \left(\frac{N_T}{\sqrt{2}}[a(1)b(2) - b(1)a(2)]\right)\left(\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]\right)\\ &\equiv \Phi_u(a—b)U_{1,0}(1,2),\end{aligned} \tag{6.275}$$

where the normalizing factors $N_s = \left(1 + S_{a,b}^2\right)^{-1/2}$ and $N_T = \left(1 - S_{a,b}^2\right)^{-1/2}$, $S_{a,b} = \langle a|b\rangle$. Here, $U_{0,0}(1,\ 2)$ and $U_{1,0}(1,\ 2)$ stand for the $M_S = 0$ singlet (S) and triplet (T) spin states, respectively, while the spatial functions $\Phi_g(a—b)$ and $\Phi_u(a—b)$ represent the *even* (g) and *odd* (u) combinations of the two AO product states, which are symmetric and antisymmetric, respectively, with respect to the inversion operation $\hat{\mathrm{i}}$ relative to the bond midpoint, or – equivalently – with respect to the permutation of the two electrons.

It thus follows from the two preceding equations that the two independent orbital products $\{a(1)b(2) \equiv |ab\rangle,\ b(1)a(2) \equiv |ba\rangle\}$ or their combinations in the bonding (g) and antibonding (u) spatial functions $\{\Phi_g(a—b),\ \Phi_u(a—b)\}$, or equivalently the Slater determinants $\{|a^+b^-|,\ |a^-b^+|\}$, form the equivalent bases of the two-electron functions in terms of which the singlet and triplet states of the hydrogen molecule can be expressed in the adopted minimum basis set of AO. Let us examine the corresponding matrix elements of the electronic Hamiltonian (a.u.), with $\boldsymbol{r}_{i\mathrm{X}} = |\boldsymbol{r}_i - \boldsymbol{R}_\mathrm{X}|$, $i \in (1, 2)$, $\mathrm{X} \in (\mathrm{H}_a, \mathrm{H}_b)$, $R = |\boldsymbol{R}_a - \boldsymbol{R}_b|$,

$$\begin{aligned}\hat{\mathrm{H}}_e(1,2) &= \hat{\mathrm{h}}(1) + \hat{\mathrm{h}}(2) + g(1,2) + R^{-1} \equiv \hat{\mathrm{H}}^e(1,2) + R^{-1}\\ &= \left(-\frac{1}{2}\Delta_1 - \frac{1}{r_{1a}}\right) + \left(-\frac{1}{2}\Delta_2 - \frac{1}{r_{2b}}\right) + \left(-\frac{1}{r_{1b}} - \frac{1}{r_{2a}} + \frac{1}{r_{1,2}} + \frac{1}{R}\right)\\ &\equiv \hat{\mathrm{H}}_a(1) + \hat{\mathrm{H}}_b(2) + \hat{\mathrm{H}}_{ab}(1,2),\end{aligned} \tag{6.276}$$

where $\{\hat{\mathrm{H}}_X\}$ denote the atomic Hamiltonians satisfying the eigenvalue equations of the separated atoms, $\hat{\mathrm{H}}_a|a\rangle = -1/2\,|a\rangle$ and $\hat{\mathrm{H}}_b|b\rangle = -1/2\,|b\rangle$, $\hat{\mathrm{H}}_{ab}$ groups the interaction terms between the two atoms, all vanishing in the $R \to \infty$ limit, and the one-electron operator of (5.70) reads:

$$\hat{\mathrm{h}}(i) = -\frac{1}{2}\Delta_i - \frac{1}{r_{ia}} - \frac{1}{r_{ib}} = -\frac{1}{2}\Delta_i + v(i). \tag{6.277}$$

The VB-*Coulomb* (diagonal) matrix elements of the electronic Hamiltonian for the elementary VB structures can be then expressed in terms of the orbital one- and two-electron integrals:

$$\begin{aligned}Q &= \langle ab|\hat{\mathrm{H}}^e|ab\rangle = \langle |a^+b^-||\hat{\mathrm{H}}^e||a^+b^-|\rangle = \langle |a^-b^+||\hat{\mathrm{H}}^e||a^-b^+|\rangle\\ &= \langle a|\hat{\mathrm{h}}|a\rangle + \langle b|\hat{\mathrm{h}}|b\rangle + \langle ab|g|ab\rangle = h_{a,a} + h_{b,b} + J_{a,b} \qquad \text{or}\end{aligned} \tag{6.278}$$

$$\begin{aligned}\langle ab|\hat{\mathrm{H}}_e|ab\rangle &= \langle|a^+b^-||\hat{\mathrm{H}}_e||a^+b^-|\rangle = \langle|a^-b^+||\hat{\mathrm{H}}_e||a^-b^+|\rangle = Q + R^{-1}\\ &= -1 + \langle ab|\hat{\mathrm{H}}_{ab}|ab\rangle \equiv -1 + \mathcal{J}(R),\end{aligned} \tag{6.279}$$

where the expectation value of the interatomic hamiltonian

$$\begin{aligned}\mathcal{J}(R) &= \langle ab|\hat{\mathrm{H}}_{ab}|ab\rangle = \langle|a^+b^-||\hat{\mathrm{H}}_{ab}||a^+b^-|\rangle = \langle|a^-b^+||\hat{\mathrm{H}}_{ab}||a^-b^+|\rangle\\ &= \exp(-2R)(R^{-1} + 5/8 - 3R/4 - R^2/6).\end{aligned} \tag{6.280}$$

The VB *exchange* (nondiagonal) matrix element of the electronic Hamiltonian can be similarly expressed in terms of the AO overlap integral,

$$S_{a,b}(R) = \langle a|b\rangle = \exp(-R)(1 + R + R^2/3), \tag{6.281}$$

the coupling one-electron integral $h_{a,b}$, and the exchange two-electron integral $K_{a,b}$:

$$\begin{aligned}K &= \langle ab|\hat{\mathrm{H}}^e|ba\rangle = \langle|a^+b^-||\hat{\mathrm{H}}^e||b^+a^-|\rangle = \langle|a^-b^+||\hat{\mathrm{H}}^e||b^-a^+|\rangle\\ &= 2S_{a,b}\langle a|\hat{\mathrm{h}}|b\rangle + \langle ab|g|ba\rangle = 2S_{a,b}h_{a,b} + K_{a,b} \qquad \text{or}\end{aligned} \tag{6.282}$$

$$\begin{aligned}\langle ab|\hat{\mathrm{H}}_e|ba\rangle &= \langle|a^+b^-||\hat{\mathrm{H}}_e||b^+a^-|\rangle = -S_{a,b}^2(R) + \langle ab|\hat{\mathrm{H}}_{ab}|ba\rangle\\ &\equiv -S_{a,b}^2(R) + \mathcal{K}(R),\end{aligned} \tag{6.283}$$

where $\mathcal{K}(R)$ represents the spin exchange term of the interatomic Hamiltonian $\hat{\mathrm{H}}_{ab}$.

Finally, for the overlap between the two elementary VB product functions one obtains:

$$\boldsymbol{S}(R) = \langle ab \mid ba\rangle = \langle|a^-b^+| \mid |b^-a^+|\rangle = S_{a,b}^2(R). \tag{6.284}$$

For the equilibrium internuclear distance, one thus finds $S_{a,b}(R_e) = 0.75$ and hence $\boldsymbol{S}(R_e) = 0.56$.

In terms of these matrix elements the expectation values of the electronic energy in the singlet (bonding) state (6.274) and its triplet (antibonding) analog (6.275) of H_2 respectively read:

$$\begin{aligned}\langle E^e\rangle_{\Psi_S^{\mathrm{HL}}} \equiv E^e\left[\Psi_S^{\mathrm{HL}}\right] &= \left\langle\Psi_S^{\mathrm{HL}}\middle|\hat{\mathrm{H}}^e\middle|\Psi_S^{\mathrm{HL}}\right\rangle = \frac{Q+K}{1+\boldsymbol{S}} \qquad \text{or}\\ E_e\left[\Psi_S^{\mathrm{HL}}\right] &= \left\langle\Psi_S^{\mathrm{HL}}\middle|\hat{\mathrm{H}}_e\middle|\Psi_S^{\mathrm{HL}}\right\rangle = -1 + \frac{\mathcal{J}+\mathcal{K}}{1+\boldsymbol{S}},\end{aligned} \tag{6.285}$$

$$\begin{aligned}\langle E^e\rangle_{\Psi_T^{\mathrm{HL}}} \equiv E^e\left[\Psi_T^{\mathrm{HL}}\right] &= \left\langle\Psi_T^{\mathrm{HL}}\middle|\hat{\mathrm{H}}^e\middle|\Psi_T^{\mathrm{HL}}\right\rangle = \frac{Q-K}{1-\boldsymbol{S}} \qquad \text{or}\\ E_e\left[\Psi_T^{\mathrm{HL}}\right] &= \left\langle\Psi_T^{\mathrm{HL}}\middle|\hat{\mathrm{H}}_e\middle|\Psi_T^{\mathrm{HL}}\right\rangle = -1 + \frac{\mathcal{J}-\mathcal{K}}{1-\boldsymbol{S}}.\end{aligned} \tag{6.286}$$

In the two preceding equations, the first expression does not include the nuclear repulsion term, while the second expression explicitly separates the dissociation limit, at $R \to \infty$, $E^e\left[\Psi_S^{\mathrm{HL}}(\infty)\right] = E^e\left[\Psi_T^{\mathrm{HL}}(\infty)\right] = -1$, when $S = \hat{\mathrm{H}}_{ab} = 0$ and hence also $\mathcal{J} = \mathcal{K} = 0$.

Should one neglect the overlap, $S \approx 0$, the electronic energies of the singlet and triplet states of H_2 thus read: $E^e\left[\Psi_S^{\mathrm{HL}}\right] = Q + K$ and $E^e\left[\Psi_T^{\mathrm{HL}}\right] = Q - K$. The energy $Q + R^{-1}$ represents the energy of the separated atoms plus their coulombic interaction and it remains quasiconstant as function of the internuclear distance, from the infinite distance to about the equilibrium distance R_e, showing a shallow minimum near R_e. It corresponds to the energy of the semiclassical state of the two hydrogen atoms, when they are brought together without exchanging their spins. The spin exchange term K describes the nonclassical effect associated with enforcing the proper spin state of two electrons, and it becomes large and negative at the normal interatomic distance, accounting for over 90% of the binding energy of the molecule in the singlet state. In the antibonding triplet state K appears with the opposite sign thus giving rise to an effective repulsion at all distances leading to a spontaneous dissociation of the molecule into two hydrogen atoms.

This explains why in the early quantum theory of the chemical bond the VB energy term associated with the spin exchange between the two AO in the two elementary determinantal states $|a^+b^-|$ and $|a^-b^+|$ has acquired an apparently crucial importance. To quote the Shaik and Hiberty (2004), "*. . .the physical phenomenon responsible for the bond is the exchange of spins between the two AOs, that is the resonance between the two spin arrangements . . .*." However, this diagnosis may be somewhat misleading, since it directly follows from the final expression of (6.282) that only the second term represents the *true* exchange integral $K_{a,b} = \langle a(1)b(2)|g(1,2)|b(1)a(2)\rangle_{1,2} > 0$, involving the *two* electrons and interchange of their variables. Its remaining, dominant contribution, proportional to the overlap of (6.281), $2h_{a,b}S_{a,b}$, is of the one-electron character, $h_{a,b} = \langle a(1)|\hat{\mathrm{h}}(1)|b(1)\rangle_1 = t_{a,b} + v_{a,b} < 0$, including the nondiagonal matrix element of the kinetic energy, $t_{a,b} = \langle a(1)| - ½\Delta_1|b(1)\rangle_1$, representing the nonadditive kinetic energy in AO resolution, and the attraction energy between the nuclei and the overlap charge distribution of the chemical bond, $v_{a,b} = \langle a(1)|v(1)|b(1)\rangle_1$. It is large and negative, completely outweighing the (positive) real exchange integral $K_{a,b}$. Therefore, the VB exchange term K can assume its correct, negative value only when the AO overlap is not neglected. As emphasized by McWeeny (1989), this energy "*. . . effectively disquises the actual factors involved in chemical bonding by indiscriminately mixing together terms representing kinetic energy, electron–nuclear attraction energy and electron-electron repulsion energy . . .*."

Nevertheless, one cannot dismiss altogether the importance of this VB spin exchange term as an important bond increment ("invariant") for a qualitative understanding of the origins of the chemical bond. Indeed, it directly follows from the molecular (BO) virial theorem that formation of the chemical bond involves changes in all energy contributions, both kinetic and potential, attractive and repulsive, of one- and two-electron origin. It thus follows that the above-mentioned mixed character of K, combining different kinetic and potential one- and two-electron energies, cannot be seriously contemplated as a disqualifying feature in a discussion of its potential usefulness in a qualitative understanding/interpretation of the elementary bonding/antibonding effects.

6.6.2 Bond Energies and Ionic Structures

The experimental value of the magnitude of the bonding energy in H_2 (a.u.) (6.65), $-\Delta E_{bond}^{exp.}\left(R_e^{exp.}=1.4006\right)=D_e^{exp.}\left(R_e^{exp.}\right)=0.1745$, is already quite well reproduced in the HL approximation in the minimum basis set of the two $1s$ orbitals of constituent atoms, $D_e^{\mathrm{HL}}\left(R_e^{\mathrm{HL}}=1.64\right)=0.115$. It thus gives a better prediction than the corresponding simple MO function, $D_e^{\mathrm{MO}}\left(R_e^{\mathrm{MO}}=1.57\right)=0.097$, although the predicted equilibrium bond length is much overestimated. The HL function gives the correct atomic dissociation, while the RHF MO approximation predicts the equimixture of the atomic and ionic dissociation products [see (6.63)]. This is because the HL wave function of (6.274) partly accounts for the Coulomb correlation between electrons by representing the state in which the two spin-paired electrons avoid the simultaneous occupancy of the same AO.

Such *ion* pair occupation patterns, of two spin-paired electrons occupying the same AO, generate the elementary *ionic* VB products $\{a(1)a(2)=|aa\rangle\equiv\left[\mathrm{H}_a^-\mathrm{H}_b^+\right]$ and $b(1)b(2)=|bb\rangle\equiv\left[\mathrm{H}_a^+\mathrm{H}_b^-\right]\}$ or equivalently their *even* (g) combination, symmetric with respect to the inversion operation $\hat{\mathrm{i}}$ relative to the bond midpoint, compatible with the spatial symmetry type of the singlet wave function Ψ_S^{HL},

$$\begin{aligned}\Phi_g^{ion.}(a--b)&=\frac{1}{\sqrt{2(1+S_{a,b}^2)}}[a(1)a(2)+b(1)b(2)]\\&=N^{ion.}\left\{\left[\mathrm{H}_a^-\mathrm{H}_b^+\right]+\left[\mathrm{H}_a^+\mathrm{H}_b^-\right]\right\}.\end{aligned}\tag{6.287a}$$

It represents the spatial factor of the associated g-type (singlet) ionic VB structure:

$$\Psi_S^{ion.}(1,2)=\frac{N_S}{\sqrt{2}}\left[|a^+a^-|+|b^+b^-|\right]=\Phi_g^{ion.}(a--b)\,U_{0,0}(1,\,2).\tag{6.287b}$$

Therefore, the Ψ_S^{HL} state represents the *covalent* structure of (6.63), $\Phi_g(a—b)\equiv\Phi_g^{cov.}=\Phi_0^{atom.}$, in which electrons are shared between the two bonded atoms. However, the exact ground state must also partly involve the simultaneous *double* occupancy of the two AO, thus calling for an admixture of the ionic configurations. Indeed, the covalent HL wave function $\Phi_g^{cov.}$ supplemented by the ionic VB structure $\Phi_g^{ion.}$ in the CI-type combination,

$$\Phi_g^{cov.+ion.}\equiv C^{cov.}\Phi_g^{cov.}+C^{ion.}\Phi_g^{ion.},\tag{6.288}$$

can be shown to be equivalent to the CID wave function of the MO theory (see the next section).

It should be emphasized, however, that the covalent and ionic combinations are strongly overlapping,

$$\left\langle \Phi_g^{cov.}(R_e) \,\middle|\, \Phi_g^{ion.}(R_e) \right\rangle = 2S_{a,b}(R_e) \Big/ \left[1 + S_{a,b}^2(R_e)\right] = 0.96, \tag{6.289}$$

so that both states are practically identical and the expansion coefficients in (6.288) have no physical meaning implied by the superposition principle.

In order to extract the really new content $\bar{\Phi}_g^{ion.}$ of $\Phi_g^{ion.}$, which is not already contained in $\Phi_g^{cov.}$, one has to Schmidt orthogonalize the former with respect to the latter [see (3.45a)]:

$$\bar{\Phi}_g^{ion.} = 3.57\Phi_g^{ion.} - 3.43\Phi_g^{cov.}, \tag{6.290}$$

while the inverse transformation reads:

$$\Phi_g^{ion.} = 0.96\,\Phi_g^{cov.} - 0.28\,\bar{\Phi}_g^{ion.}. \tag{6.291}$$

The last equation shows directly that the main ingredient of $\Phi_g^{ion.}$ is already present in $\Phi_g^{cov.}$, so that admixture of this ionic function introduces but little new, independent (orthogonal) component to the system ground state wave function. The variationally optimum VB wave function of (6.288) at $R = R_e$,

$$\Phi_g^{cov.+ion.} = 0.454\ \Phi_g^{cov.} + 0.116\ \Phi_g^{ion.} = 0.998\,\Phi_g^{cov.} + 0.058\,\bar{\Phi}_g^{ion.}, \tag{6.292}$$

thus predicts the 99.7% overall participation of Φ_g^{cov} and only 0.3% of the orthogonal ionic component $\bar{\Phi}_g^{ion.}$, i.e., a practically purely covalent chemical bond. Nevertheless, this slightly (ionically) modified wave function further improves the bonding energy of H_2 but still fails to correct the overestimated equilibrium bond length: $D_e^{\mathrm{HL}/ion.}\left(R_e^{\mathrm{HL}/ion.} = 1.67\right) = 0.119$.

Both MO and VB descriptions can be further improved by scaling the exponents of both 1*s* AO, $\chi_{1s}(r;\ \zeta\ ) = (\zeta^3/\pi)^{1/2}\exp(-\zeta r)$, with the optimum factor ζ, a nonlinear variational parameter, reflecting the effective charge of the atomic nucleus [see (4.62) and (5.98)] in the presence of the unshielded nucleus of the bond partner: $\zeta > 1$. The corresponding predictions then show a decisive improvement in the equilibrium bond length: $D_e^{\mathrm{MO}/\zeta}\left(R_e^{\mathrm{MO}/\zeta} = 1.38\right) = 0.128$, $\zeta^{\mathrm{MO}} = 1.197$; $D_e^{\mathrm{HL}/\zeta}\left(R_e^{\mathrm{HL}/\zeta} = 1.39\right) = 0.139$, $\zeta^{\mathrm{HL}} = 1.166$; $D_e^{\mathrm{HL}/ion./\zeta}\left(R_e^{\mathrm{HL}/ion./\zeta} = 1.43\right) = 0.148$, $\zeta^{\mathrm{HL}/ion.} = 1.193$.

When two atoms approach each other their electron distributions should undergo a cylindrical polarization toward the bonding partner. Therefore, instead of using the spherical AO, one could apply in the VB wave function the optimum (fractional) hybrids $\chi_h = s^x p_z^y$ on both atoms, which are directed along the bond (z) axis:

$$\chi_h(\boldsymbol{r}) = (1 + \mu^2)^{-1/2}[1s(\boldsymbol{r}) + \mu 2p_z(\boldsymbol{r})], \tag{6.293}$$

where the mixing coefficient μ then constitutes additional variational degree of freedom of the molecular wave function. The corresponding predictions read: $D_e^{\mathrm{HL}/h/\zeta}\left(R_e^{\mathrm{HL}/h/\zeta} = 1.42\right) = 0.148, \zeta^{\mathrm{HL}/h} = 1.19$; $D_e^{\mathrm{HL}/ion./h/\zeta}\left(R_e^{\mathrm{HL}/ion./h/\zeta} = 1.41\right) = 0.151$, $\zeta^{\mathrm{HL}/ion./h} = 1.19$.

Clearly, such hybrid AO in the MO approach implies an effective extension of the minimum basis set. Let us compare these best VB results with the associated HFL predictions, obtained for the variationally saturated, "complete" basis set, which fully accounts for both the effective contraction and polarization of atomic electron distributions: $D_e^{\mathrm{HFL}}\left(R_e^{\mathrm{HFL}} = 1.40\right) = 0.134$. This comparison explicitly shows that a substantial portion of the bond energy due to the Coulomb correlation has already been recovered in these simple VB descriptions of the hydrogen molecule.

6.6.3 Comparison with MO Theory and AO Expansion Theorem

Let us now compare the MO and VB wave functions for H_2, obtained in the minimum basis set of two $1s$ orbitals of constituent atoms. The simple RHF description predicts that the two spin-paired electrons occupy the bonding (even) $1\sigma_g$ MO, symmetric with respect to the inversion $\hat{\mathrm{i}}$ with respect to the bond midpoint,

$$\phi_g(\boldsymbol{r}) = N_g[a(\boldsymbol{r}) + b(\boldsymbol{r})], \qquad N_g = [2(1 + S_{a,b}(R)]^{-1/2}, \qquad \hat{\mathrm{i}}\phi_g = \phi_g, \quad (6.294)$$

with the antibonding (odd) $1\sigma_u$ MO, antisymmetric with respect to inversion,

$$\phi_u(\boldsymbol{r}) = N_u[a(\boldsymbol{r}) - b(\boldsymbol{r})], \quad N_u = [2(1 - S_{a,b}(R)]^{-1/2}, \quad \hat{\mathrm{i}}\phi_u = -\phi_u, \quad (6.295)$$

remaining unoccupied in the system ground state configuration.

Hence, the spatial part of the singlet (ground state) wave function in the RHF approximation, when expressed in terms of AO, predicts equimixture of the covalent and ionic VB structures:

$$\begin{aligned}\Phi_0^{\mathrm{RHF}}(1,2) &= N_g^2[a(1) + b(1)][a(2) + b(2)] \\ &= N_g^2\{[a(1)b(2) + b(1)a(2)] + [a(1)a(2) + b(1)b(2)]\} \\ &\equiv \bar{N}_g\left[\Phi_g^{cov.}(1,2) + \Phi_g^{ion.}(1,2)\right], \qquad (6.296)\end{aligned}$$

This explains the wrong dissociation limit of this RHF function for $R \to \infty$ [see (6.63)] and its variational inferiority with respect to the VB wave function of (6.288), in which the relative participation of both components is not fixed, with the equilibrium ratio $C^{ion.}(R_e)/C^{cov.}(R_e) = 0.256$ approaching zero as $R \to \infty$.

The Pauli principle implies that in the singlet (antisymmetric) spin state of two electrons their spatial function must be symmetric with respect to exchanging the positions of electrons. Moreover, by the Brillouin theorem the *singly* excited configuration $\Phi^S_{g,u}(1,2) = 2^{-1/2}[\phi_g(1)\phi_u(2) + \phi_u(1)\phi_g(2)]$(see Fig. 6.2) does not couple directly to the *closed*-shell RHF function. Therefore, the most important Coulomb correlation contribution originates from including in the CI function the doubly excited configuration $\Phi^S_u(1,2) = \phi_u(1)\phi_u(2)$ in the CID-type trial function

$$\begin{aligned}\Phi^{\mathrm{CID}}(1,2) &= C_0\Phi_0^{\mathrm{RHF}}(1,2) + C_u\Phi_u^S(1,2)\\ &= C_0N_g^2[a(1)+b(1)][a(2)+b(2)] + C_uN_u^2[a(1)-b(1)][a(2)-b(2)]\\ &\equiv \lambda_g\left[\Phi_g^{cov.}(1,2) + \Phi_g^{ion.}(1,2)\right] + \lambda_u\left[\Phi_g^{ion.}(1,2) - \Phi_g^{cov.}(1,2)\right]\\ &= (\lambda_g - \lambda_u)\Phi_g^{cov.}(1,2) + (\lambda_g + \lambda_u)\Phi_g^{ion.}(1,2)\\ &\equiv \lambda_{cov.}\Phi_g^{cov.}(1,2) + \lambda_{ion.}\Phi_g^{ion.}(1,2). \end{aligned} \tag{6.297}$$

This CID trial wave function is variationally equivalent to the $\Phi_g^{cov.+ion.}$ state of (6.288) since it also represents a combination of the independent components $\Phi_g^{cov.}$ and $\Phi_g^{ion.}$. Therefore, the amount of the Coulomb correlation of two electrons in the ground state of H_2 recovered by this VB approximation is the same as that generated in the CID approximation using the same (minimum) basis set of AO.

It should be observed that from the expansion theorem of Sect. 6.2 it directly follows that any N-electron function can be expanded in terms of the Slater determinants built from any complete set of the one-electron functions, e.g., the orthonormal SO. Therefore, such state functions should be also represented as combinations of the chemically meaningful elementary VB structures, represented by determinants constructed from the nonorthogonal AO, e.g., the localized canonical or hybridized valence orbitals of constituent atoms, or partly delocalized AO of molecularly promoted AIM, the *group*-MO of molecular fragments, etc.

Let us briefly examine the relevant VB expansion theorem, in which the *atomic* (nonorthogonal) spin orbitals, $\boldsymbol{\chi}(\boldsymbol{r},\sigma) \equiv \boldsymbol{\chi}(\boldsymbol{q}) = \{\boldsymbol{\chi}(\boldsymbol{r})\alpha(\sigma) \equiv \boldsymbol{\chi}^+(\boldsymbol{r}),\ \boldsymbol{\chi}(\boldsymbol{r})\beta(\sigma) \equiv \boldsymbol{\chi}^-(\boldsymbol{r})\}$, constitute the one-electron basis themselves, instead of their *molecular* (orthonormal) SO combinations, $\boldsymbol{\psi}(\boldsymbol{q}) = \boldsymbol{\chi}(\boldsymbol{q})\,\mathbf{C}$, used in the MO expansion of the CI approach. Since AO constitute the normalized, but nonorthogonal basis, $\langle\boldsymbol{\chi}|\boldsymbol{\chi}\rangle = \mathbf{S} \neq \mathbf{I}$, the corresponding completeness projection reads

$$\hat{\mathrm{P}}_{\boldsymbol{\chi}} = |\boldsymbol{\chi}\rangle\mathbf{S}^{-1}\langle\boldsymbol{\chi}| = 1, \tag{6.298}$$

or, in the spin position representation,

$$\begin{aligned}\hat{\mathrm{P}}_{\boldsymbol{\chi}}(\boldsymbol{q},\boldsymbol{q}') &= \langle\boldsymbol{q}|\hat{\mathrm{P}}_{\boldsymbol{\chi}}|\boldsymbol{q}'\rangle = \boldsymbol{\chi}(\boldsymbol{q})\mathbf{S}^{-1}\boldsymbol{\chi}^\dagger(\boldsymbol{q}') = \sum_{k,l}\chi_k(\boldsymbol{q})S^{-1}_{k,l}\chi_l^*(\boldsymbol{q}')\\ &= \langle\boldsymbol{q}\mid\boldsymbol{q}'\rangle = \delta(\boldsymbol{q}'-\boldsymbol{q}). \end{aligned} \tag{6.299}$$

This gives the following AO expansion of any one-electron function $\Psi(\boldsymbol{q})$:

$$\begin{aligned}\Psi(\boldsymbol{q}) \equiv \Psi(1) &= \int d\boldsymbol{q}'\, \hat{\mathrm{P}}_{\boldsymbol{\chi}}(\boldsymbol{q}, \boldsymbol{q}')\Psi(\boldsymbol{q}') \\ &= \boldsymbol{\chi}(\boldsymbol{q})\mathbf{S}^{-1} \int d\boldsymbol{q}'\boldsymbol{\chi}^{\dagger}(\boldsymbol{q}')\Psi(\boldsymbol{q}') \equiv \sum_{k}^{\mathrm{AO}} \chi_k(1)\, D_k, \\ D_k &= \sum_{l}^{\mathrm{AO}} S_{k,l}^{-1} \langle \chi_l \mid \Psi \rangle \equiv \sum_{l}^{\mathrm{AO}} S_{k,l}^{-1} \Psi_l. \end{aligned} \qquad (6.300)$$

One similarly expands any two-electron wave function $\Psi(\boldsymbol{q}_1, \boldsymbol{q}_2) \equiv \Psi(1,2)$:

$$\Psi(1,2) = \sum_{k}^{\mathrm{AO}} \chi_k(1) \sum_{l}^{\mathrm{AO}} S_{k,l}^{-1} \langle \chi_l(1) \mid \Psi(1,2) \rangle_1 \equiv \sum_{k}^{\mathrm{AO}} \chi_k(1) D_k(2), \qquad (6.301)$$

where the subsequent AO expansion of the coefficient function $D_k(2)$ gives:

$$D_k(2) = \sum_{k'}^{\mathrm{AO}} \chi_{k'}(2) \sum_{l'}^{\mathrm{AO}} S_{k',l'}^{-1} \langle \chi_{l'} \mid D_k \rangle \equiv \sum_{k'}^{\mathrm{AO}} D_{k,k'} \chi_{k'}(2). \qquad (6.302)$$

It thus follows from the two preceding equations that

$$\Psi(1,2) = \sum_{k}^{\mathrm{AO}} \sum_{k'}^{\mathrm{AO}} D_{k,k'} \chi_k(1) \chi_{k'}(2), \qquad (6.303)$$

and hence, by acting with the antisymmetrizer Â on both sides of the last equation,

$$\Psi_A(1,2) = \sum_{k}^{\mathrm{AO}} \sum_{k'}^{\mathrm{AO}} D_{k,k'} \det(\chi_k \chi_{k'}). \qquad (6.304)$$

Clearly, one can proceed to expand in this way any antisymmetric wave function of N electrons as a linear combination of Slater determinants built directly from AO, which represent the corresponding VB structures or their components,

$$\begin{aligned}\Psi_A(1,\ 2,\ \ldots,\ N) &= \sum_{k_1}^{\mathrm{AO}} \sum_{k_2}^{\mathrm{AO}} \cdots \sum_{k_N}^{\mathrm{AO}} D_{k_1,k_2,\ldots,k_N} \hat{\mathrm{A}}\{\chi_{k_1}(1)\, \chi_{k_2}(2)\ \ldots\ \chi_{k_N}(N)\} \\ &= \sum_{k_1}^{\mathrm{AO}} \sum_{k_2}^{\mathrm{AO}} \cdots \sum_{k_N}^{\mathrm{AO}} D_{k_1,k_2,\ldots,k_N} \det\big(\chi_{k_1} \chi_{k_2}\ \ldots\ \chi_{k_N}\big). \end{aligned} \qquad (6.305)$$

This AO expansion provides the formal basis for the trial wave functions generated as linear combinations of the N-electron valence structures used in the VB approach.

6.6.4 Semilocalized AO and Extension to Polyatomic Systems

A relatively more complicated combination of the covalent and ionic VB structures of (6.288) can be brought into a simpler HL-like form of (6.274) by replacing the fully localized AO $\{a, b\}$, centered on the corresponding nuclei, by the distorted, strongly overlapping (normalized) orbitals $\{\varphi_a, \varphi_b\}$, both partly delocalized toward the bonding partner, with φ_a strongly resembling a and φ_b representing a b-like orbital:

$$\begin{aligned}\Phi_g^{cov.+ion.}(1,2)\,U_{0,0}(1,2) &\equiv \lambda[a(1)b(2)+b(1)a(2)]+\mu[a(1)a(2)+b(1)b(2)]\}\,U_{0,0}(1,2)\\ &= \lambda\left(\left|a^+b^-\right|-\left|a^-b^+\right|\right)+\mu\left(\left|a^+a^-\right|+\left|b^+b^-\right|\right)\\ &= \mathcal{N}[\varphi_a(1)\varphi_b(2)+\varphi_b(1)\varphi_a(2)]\,U_{0,0}(1,2)\\ &= \mathcal{N}\left[\left|\varphi_a^+\varphi_b^-\right|-\left|\varphi_a^-\varphi_b^+\right|\right]\equiv\Phi^{\mathrm{CF}}(1,2)\,U_{0,0}(1,2)\end{aligned} \tag{6.306}$$

where the normalization factor $\mathcal{N}=[2(1+\langle\varphi_a|\varphi_b\rangle)]^{-1/2}$. These semilocalized, atomic-like one-electron functions of Coulson and Fischer (CF) (1949) are determined by a small AO-mixing parameter ε:

$$\begin{aligned}&\varphi_a=\mathcal{N}_\varphi(a+\varepsilon b),\quad \varphi_b=\mathcal{N}_\varphi(b+\varepsilon a)\},\quad 0<\varepsilon<1,\\ &\mathcal{N}_\varphi=(1+2\varepsilon\,S_{a,b}+\varepsilon^2)^{-1/2}.\end{aligned} \tag{6.307}$$

Substituting these expressions into the effective covalent structure Φ^{CF} indeed gives back the mixture of the covalent and ionic structures in terms of the localized AO:

$$\begin{aligned}\Phi^{\mathrm{CF}}(1,2) &= \mathcal{N}\mathcal{N}_\varphi^2\{(1+\varepsilon^2)[a(1)b(2)+b(1)a(2)]+2\varepsilon[a(1)a(2)+b(1)b(2)]\}\\ &= C^{cov.}\Phi_g^{cov.}+C^{ion.}\Phi_g^{ion.}.\end{aligned} \tag{6.308}$$

This generalized CF representation of the Lewis structure H_a–H_b, embedding the ionic effects in an effective “covalent” structure through the delocalization tails of the semilocalized AO, has been also adopted to polyatomic molecules in the GVB approach, with the semilocalized functions being determined from the variational principle, by minimizing the expectation value of the system electronic energy. These functions are expanded in terms of the localized AO or primitive basis functions centered on the corresponding nuclei, and the optimum AO mixing coefficients are determined by iteratively solving one-electron equations that resemble those of the standard SCF method.

The VB theory is thus closely related to chemist’s idea of molecules consisting of AIM held together by localized bonds, each of them described by the combination of two determinantal wave functions of the type given in (6.306), representing the singlet spin-coupled (shared) valence electrons of the covalent bond in question.

This "chemical" quantum theory also views the molecules as composed of atomic "cores," each including the nucleus and the chemically inactive *inner*-shell electrons, and the chemically active *valence* electrons. The spin coupling of the latter is the main objective of the VB treatment of polyatomic systems, which places great emphasis on the spin pairing of electrons.

The chemical intuition can be used in various ways to simplify the VB representation of molecular wave functions. In the so-called *Perfect Pairing Approximation* (PPA) one takes the Lewis structure of the molecule in the assumed singlet ground state, represents each bond by the HL/CF combination of two determinants, and finally expresses the full molecular wave function as product of all such *bond* functions. Therefore, the molecular wave function describing n bonds present in the Lewis structure will be described by 2^n determinants, displaying the possible 2×2 spin permutations between two singlet-coupled orbitals. Consider, as an illustrative example, the Li_a—Li_b molecule, for which the inner-shell $1s$ electrons of both atoms, listed at the beginning of the relevant Slater determinants belong to atomic cores and remain chemically inactive, with only the (unpaired) $2s$ valence electrons participating in the formation of the σ chemical bond. The corresponding VB structure representing this single chemical bond thus reads:

$$\begin{aligned}\mathrm{Li}_a\text{—}\mathrm{Li}_b &= \left|1s_a^+1s_a^-1s_b^+1s_b^-2s_a^+2s_b^-\right| - \left|1s_a^+1s_a^-1s_b^+1s_b^-2s_a^-2s_b^+\right| \\ &\equiv \left|\ldots\; 2s_a^+2s_b^-\right| - \left|\ldots\; 2s_a^-2s_b^+\right| \equiv \left|\ldots\; \overline{2s_a2s_b}\right|, \qquad (6.309\text{a})\end{aligned}$$

or, by retaining only the chemically active part,

$$\begin{aligned}\mathrm{Li}_a\text{—}\mathrm{Li}_b &= [2s_a(1)2s_b(2) + 2s_b(1)2s_a(2)]\; U_{0,0}(1,2) = \left|\overline{2s_a2s_b}\right| \\ &\equiv (2s_a\text{—}2s_b)\, U_{0,0}. \qquad (6.309\text{b})\end{aligned}$$

For the triple bond in $:\mathrm{N}_a \equiv \mathrm{N}_b:$, with the inactive set of electrons now determined by the *doubly* occupied inner shells ($1s_a$, $1s_b$) and the *lone* pair (lp) $\approx 2sp_z$ hybrids $(2h_a^{lp}, 2h_b^{lp})$, the same approach will involve eight determinants originating from the antisymmetrized product of the covalent/CF valence structures for the three localized bonds: the σ bond resulting from the singlet coupling of two unpaired electrons occupying the bonding $2sp_z$ hybrids of both atoms $(2h_a^{bond.}\text{—}2h_b^{bond.})$ and two π bonds resulting from the singlet coupling of the symmetry compatible pairs of $2p_\pi$ orbitals: ($2p_{xa}$—$2p_{xb}$) and ($2p_{ya}$—$2p_{yb}$). The sign of the corresponding determinant in the VB representation of the system electronic wave function is either "+" or "−", according to whether the number of the interchanges required to generate the current determinant from the chosen PPA "*parent*" determinant, say $|\ldots\; 2h_a^{bond.,+}h_a^{bond.,-}2p_{xa}^+2p_{xb}^-2p_{ya}^+2p_{yb}^-|$, is even or odd. For example, the determinant $|\ldots\; 2h_a^{bond.,+}h_a^{bond.,-}2p_{xa}^-2p_{xb}^+2p_{ya}^+2p_{yb}^-|$, representing a single exchange of spins between $2p_x$ AO relative to the reference determinant, will appear with the negative sign in the VB combination representing the ground state of N_2 in PPA.

There are three admissible sets of the localized singlet couplings between the chemically active electrons, determining the joint VB structures of two individual "bonds" in water molecule H_a—O—H_b, in which the oxygen 1*s* orbital describes the two inner-shell electrons and the two doubly occupied $\approx 2sp^3$ hybrids $\left\{h_{\mathrm{O}}^{lp}\right\}$ determine the state of two *lone* pairs of valence electrons on oxygen,

$$\begin{aligned} &\Phi_A = (2h_a^{bond.}\text{—}a,\ 2h_b^{bond.}\text{—}b), \quad \Phi_B = (2h_a^{bond.}\text{—}2h_b^{bond.},\ a\text{—}b), \\ &\quad \text{and} \quad \Phi_C = (2h_a^{bond.}\text{—}b,\ 2h_b^{bond.}\text{—}a), \end{aligned} \tag{6.310}$$

where $2h_a^{bond.}$ and $2h_b^{bond.}$ stand for the bonding hybrids on oxygen directed toward the corresponding orbitals (*a*, *b*) contributed by the two hydrogen atoms. However, by a straightforward multiplication of the spin factors involved in the underlying Slater determinants one can demonstrate that $\Phi_C = (\Phi_A + \Phi_B)$. Therefore, only the first two sets of VB structures exhibiting two localized bonds are linearly independent (see also Fig. 6.3), so that

$$\Phi^{\mathrm{VB}} = C_A\Phi_A + C_B\Phi_B. \tag{6.311}$$

This ansatz is still further simplified in GVB approach, which uses only the dominant Lewis structure H_a—O—H_b, with the bond couplings being recognized only between the nearest neighbors, $\Phi^{\mathrm{GVB}}(\mathrm{H_2O}) = (f_a^{bond.}\text{—}g_a, f_b^{bond.}\text{—}g_b)$; the generating orbitals on oxygen, $\{f_a^{bond.},\ f_b^{bond.}\}$, and the two hydrogen atoms $\{g_a, g_b\}$ are freely adjusting their shapes in accordance with the variational principle of the minimum electronic energy. The GVB function of methane would similarly involve only the dominant structure of four C—H bonds: $\Phi^{\mathrm{GVB}}(\mathrm{CH_4}) = (f_a\text{—}g_a, f_b\text{—}g_b, f_c\text{—}g_c, f_d\text{—}g_d)$.

The number of admissible spin states of all valence electrons in a general polyelectronic case is very large indeed, but it is effectively limited by selecting the proper eigenfunctions of the resultant spin operators [see (6.67)] and the linearly independent, canonical set of VB structures. The latter task is accomplished by using an appropriate diagrammatic technique, e.g., the Rumer (1932) diagrams (see Figs. 6.3 and 6.4). This technique for selecting the linearly independent set of "canonical" VB structures involves putting the chemically active orbitals on a circle in any a priori order, although interpretation of the results in chemical terms is greatly facilitated by having this ordering as close as possible to the order of orbitals in the molecule. The independent structures are then determined by all valence configurations in which the active orbitals are joint in pairs by noncrossing lines (see Fig. 6.3). The Rumer diagrams for water molecule shown in Fig. 6.3 indeed exclude the Φ_C structure from the canonical set, as being linearly dependent on Φ_A and Φ_B. For the even number *n* of active orbitals the number of ways of drawing ½*n* noncrossing lines between *n* points on a circle is *n*!/[(½*n*)! (½*n* + 1)!] (Barriol 1971). For the water molecule, $n = 4$, one indeed finds 4!/(2!3!) = 2 independent VB structures. For an odd number of orbitals to be paired, one adds a "phantom" orbital, whose contribution is eventually removed.

Next, let us consider the π-bonds in butadiene and benzene. In the former case the first two diagrams of Fig. 6.3 determine the independent valence structures (Φ_a, Φ_b) of Fig. 6.5, while the third diagram determines the linearly dependent structure $\Phi_c = \Phi_b - \Phi_a$. The relevant Rumer diagrams for π-bonds in benzene are shown in Fig. 6.4. The first two diagrams generate the familiar Kekulé structures (Φ_a , Φ_b) of Fig. 6.5, while the remaining diagrams give rise to the Dewar structures (Φ_c, Φ_d, Φ_e) of the same figure, where the associated singly polar structures are also shown.

The chemical intuition can also guide the VB description of chemical changes in terms of the group orbitals, which can be delocalized over the specified molecular fragment(s). Such delocalized one-electron functions can be determined from earlier SCF MO calculations of the separate molecular subsystems, e.g., reactants or their crucial functional groups. This approach allows one to eliminate the explicit description of chemical bonds which remain practically unaffected by the chemical reaction under consideration. For example, in the nucleophilic substitution (S_N2) involving a simultaneous bond-breaking – bond-forming process, $OH^- + CH_3—Cl \rightarrow OH—CH_3 + Cl^-$, the PPA spatial wave function should involve the explicit covalent/CF VB structures of only two bonds, $H_3C—Cl$ and $HO—CH_3$, i.e., four Slater determinants, with the localized MO of the remaining σ bonds, O—H and C—H, and the lone pairs of electrons in the valence shell of oxygen and chlorine forming an effective "core" for the four truly active orbitals in this chemical reaction.

6.6.5 Ab Initio VB Calculations

The *single* structure PPA of molecular wave function, using the strongly overlapping pairs of directed orbitals on individual atoms for each localized chemical bond, invokes the concept of hybrid AO's. In fact, the orbital hybridization arose from efforts to retain the *perfect* pairing picture in interpreting stereochemical situations, which would be ambiguous in terms of the canonical AO's. However, in many situations, in which there are no strong grounds for preferring one valence structure to another, the PPA breaks down, and a mixture

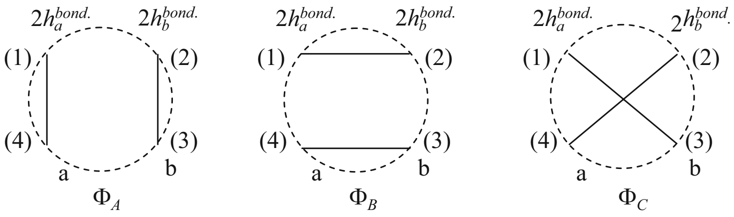


Fig. 6.3 The Rumer diagrams corresponding to the valence structures of water (6.310) and π bonds in butadiene, between $2p_{zi}$, $i = 1, 2, 3, 4$ orbitals (in parentheses) of the carbon atoms (for their consecutive numbering in the π-chain)

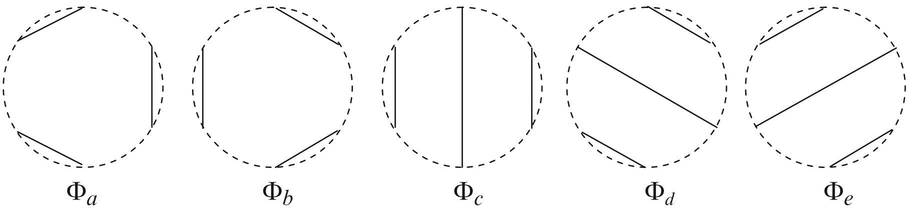


Fig. 6.4 The Rumer diagrams corresponding to the canonical valence structures of π bonds in benzene, between $2p_{zi}$, $i = 1, 2, \ldots, 6$, orbitals of the carbon atoms in the π-ring (distributed consecutively on the perimeter of the circle)

of many VB structures must be used to adequately represent the system wave function. In order to carry out nonempirical VB calculations of comparable accuracy with that of the ab initio SCF MO (CI) theory, it is essential to remove the assumption of the orthonormal orbitals, which is often adopted in qualitative VB considerations, although the calculation of matrix elements is then immensely more difficult. As we have already observed in Sect. 6.6.2, the crude approximation using AO's of the free atoms, without any further adjustment, gives rather poor energies, missing considerable rearrangements these orbitals undergo in a molecule. Therefore, the optimization of the CF orbitals for each chemical bond constitutes another essential requirement of an accurate ab initio VB theory. The perfect-pairing CF representation allows one to determine the HL level of the bond correlation energy in an unbiased variational way. These generalized, orbital-optimized VB methods explore the same variety of *single*- and multiconfigurational approaches, which we have already encountered in the MO theory. For recent surveys of the modern variants of the ab initio VB theories and evaluations of their already remarkable capabilities the reader is referred to the monograph by McWeeny (1989) as well as to reviews by Gerrat (1974) and by Shaik and Hiberty (2004). The following short summary is based upon the latter monographic survey.

The simplest among the *single*-configuration representations is the GVB description of Goddard and coworkers (Goddard 1967; Hunt et al. 1972; Bobrowicz and Goddard 1977; Goddard and Harding 1978) originating from the earlier *separated electron pair* approach of Hurley et al. (1953) (see also Sect. 6.4.1). It is usually based upon the PPA (GVB-PP), by which only a single VB structure of say n valence-pair electron system is generated in the calculation. It is defined in terms of the strongly orthogonal geminals, each describing one particular bond or a single lone electron pair [see also (6.162)], which take the form of the singlet-coupled pair of electrons (in parentheses):

$$\begin{aligned} G_i(1,2) &= \left[\left|\varphi_{i,a}^{+}\varphi_{i,b}^{-}\right| - \left|\varphi_{i,a}^{-}\varphi_{i,b}^{+}\right|\right] \\ &\equiv N_i[\varphi_{i,a}(1)\varphi_{i,b}(2) + \varphi_{i,a}(2)\varphi_{i,b}(1)]U_{0,0}(1,2), \end{aligned} \tag{6.312}$$

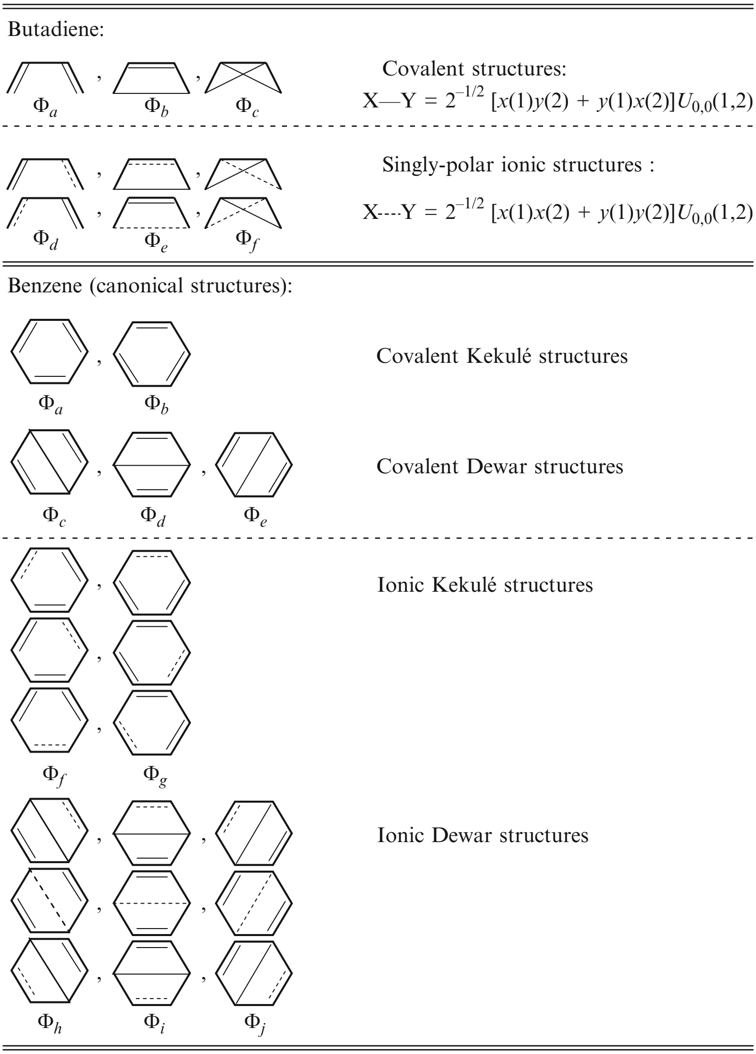


Fig. 6.5 The most important covalent and ionic valence structures of butadiene and benzene; the singly occupied, orthogonalized valence orbitals $2p_\pi$: $x \in$ X and $y \in$ Y are used to form elementary covalent structure, X—Y, and singly polar ionic structure X----Y = $2^{-1/2}(\mathrm{X}^+\mathrm{Y}^- + \mathrm{X}^-\mathrm{Y}^+)$ between the constituent carbon atoms X and Y of the π system, with the singlet spin factor (see Fig. 6.2) $U_{0,0}(\sigma_1, \sigma_2) \equiv U_{0,0}(1,2) = 2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$

$$\Psi_A^{\mathrm{GVB}} = \hat{\mathrm{A}}'\{G_1(1,2)G_2(3,4)\ldots G_n(2n-1,2n)\}\ . \qquad (6.313)$$

Only orbitals within a given geminal pair display a strong overlap, while those associated with different geminals are required to be mutually orthogonal. This constraint, which greatly simplifies the numerical calculations, is not a serious one, since the orbitals of different geminals are not expected to overlap significantly anyway. For further numerical convenience each *open*-shell geminal product of (6.312) is generated from the two *closed*-shell contributions due to orthonormal natural orbitals (NO) ϕ_i and $\bar{\phi}_i$, bonding and antibonding, respectively, obtained by a simple "rotation" of the original orbitals $\varphi_{i,a}$ and $\varphi_{i,b}$:

$$\varphi_{i,a}(1)\varphi_{i,b}(2) + \varphi_{i,a}(2)\varphi_{i,b}(1) \equiv C_i\, \phi_i(1)\, \phi_i(2) + \bar{C}_i\, \bar{\phi}_i(1)\, \bar{\phi}_i(2). \tag{6.314}$$

It can be easily verified that the latter are given by the NO combinations

$$\varphi_{i,a} = \mathcal{N}\,[\phi_i + \kappa\bar{\phi}_i], \quad \varphi_{i,b} = \mathcal{N}\,[\phi_i - \kappa\bar{\phi}_i], \quad \mathcal{N} = (1+\kappa^2)^{-1/2}, \tag{6.315}$$

which give rise to:

$$C_i = 1 + \kappa^2, \qquad \bar{C}_i = \frac{-\kappa^2}{1+\kappa^2}, \qquad \langle \varphi_{i,a} | \varphi_{i,b} \rangle = \frac{1-\kappa^2}{1+\kappa^2}. \tag{6.316}$$

The GVB-PP approach is thus equivalent to the *low*-dimensional MC SCF method, accounting for a part of the nondynamical electron correlation. The PP and strong orthogonality approximations greatly simplify the numerical calculations with no great loss of accuracy in the molecular systems exhibiting clearly separated local bonds. In benzene, however, all electron pairing schemes have to be taken into account to generate a reasonable description of the delocalized π electrons. Inclusion of the full nondynamical correlation would require the CAS SCF calculations, which involve all possible configurations of the *valence*-shell orbitals. As a rule, the GVB method generates a much better agreement with the CAS SCF predictions than the HF theory. However, due to a neglect of the dynamical correlation the GVB bond energies are generally too low. Thus, this *single*-configuration method at best can be regarded as a good starting point for the subsequent Correlation-Consistent CI (CCCI) treatment of Carter and Goddard (1988). For example, this more advanced GVB–CCCI approach has been successfully applied to investigate catalysis by transition metals (Rappé and Goddard 1982) and metallic bonds (McAadon and Goddard 1985, 1987).

A more accurate *single*-configuration VB technique is represented by the Spin-Coupled (SC) approach of Gerratt and coworkers (Cooper et al. 1981, 1987, 1988, 1990a, b; Sironi et al. 2002), which introduces no constraints or preconceptions on the level of the spin coupling, orbital overlaps, and shapes, with all these degrees of freedom of the molecular VB wave function remaining unrestricted in the variational treatment. Therefore, this method represents the ultimate level of accuracy of the *single*-configuration VB wavefunction assuming the fixed orbital occupancies. It provides the unique set of orbitals and measures of a relative importance of alternative spin couplings, which constitute important unbiased chemical descriptors of chemical bonds, thus providing a solid basis for such originally qualitative and intuitive concepts as the valence state of AIM, orbital hybridization, resonance between VB structures, etc.

For example, in the eight spin-coupled orbitals of methane, including four degenerate, symmetry-related (approximately sp^3) hybrids on carbon atom and four degenerate orbitals localized on hydrogen atoms, the PP configuration represents the dominant mode of the spin coupling. The PPA introduces only a minor correlation error to predicted energy, superior to the corresponding HF result, with the SC total energy being very close to the CAS SCF value. In water the method predicts about 20% more p character in the bonding hybrids, compared with those describing the lone pairs on oxygen, in full accord with chemical intuition. In lithium clusters, the interstitial optimum orbitals, localized between two or several nuclei, have been determined. In the π electron system of benzene, the two Kekulé structures have been found to represent the dominant patterns of the spin coupling of electrons occupying slightly distorted p_π AO's, perpendicular to the molecular plane, with the participation of Dewar structures amounting to about 20%.

The single configuration SC description can be further improved by adding the CI involving (nonorthogonal) VB configurations, covalent and ionic, derived from alternative occupations of the optimum (active) orbitals determined at the SC stage. This determines the Spin-Coupled VB (SCVB) variant of the theory. The localized $\sigma \rightarrow \pi$ valence excitations can be then included at the CI stage, with the virtual π orbital being localized in the vicinity of the σ orbital in question.

The most accurate among the ab initio variants are the multiconfigurational VB methods. For example, the VB SCF approach of van Lenthe and Balint-Kurti (1983) can be classified as the MC SCF method in the nonorthogonal AO representation. It uses the trial wave function expressed as the linear combination of the (*fundamental*) VB structures, with both (*occupied*) orbitals and configuration coefficients being simultaneously determined by the variational principle alone. The method is especially suited for studying the resonance stabilization energies, particularly in molecules described by many Lewis structures, and in solving the avoided-crossing problems. The optimized orbitals can be either localized (atomic) or semilocalized (CF) in character, or they may be restricted to specific molecular fragments.

Again the configuration interaction can be used to supplement the VB SCF method with the dynamic correlation effects. Among these post VB SCF treatments the VB CI method of Wu et al. (2001, 2002) using different levels of CI, e.g., VBCIS, VBCISD, VBCISDT, and methods using the *symmetry*-broken wave functions derived from different orbitals for different structures, e.g., Resonating-GVB (RGVB) model of Voter and Goddard (1981a, b) or the Breathing Orbital VB (BOVB and GRVB) schemes of Hiberty and coworkers (Hiberty 1997; Hiberty and Shaik 2002a, b; Hiberty et al. 1992, 1994a, b), appear to be most promising. The virtual orbitals used at the CI stage preserve the interpretability offered by the occupied set defining the fundamental configurations, each having a clear chemical meaning. This is achieved by using the appropriate projection operators to make the *acceptor* virtual orbitals of the electron excitation, receiving electrons from the given subset of the excitation *donor* occupied orbitals of the specified molecular fragment, to be localized in the same molecular fragment, thus describing the same classical VB structure and maximizing the effect of the dynamic correlation correction. Various multiplicities of the electron excitations used at the CI stage of the VB CI treatment can be taken into account, giving rise to the associated limited CI VB variants, VB CIS, VB CISD, etc., which still preserve the interpretability of simple VB methods. The accuracy of VB CISD has been found to be comparable with that of the CCSD and CCSD(T) variants of MO theory.

The MR VB methods are required to adequately describe the molecules, and particularly some radicals, that are naturally described in terms of two or more resonance structures. Care has to be taken to avoid discontinuities observed at a lower level of theory, for which the wave function often exhibits a lower artefactual symmetry of a single VB structure than the nuclear framework itself, due to energy gain resulting from using the optimum orbitals for this structure alone. Therefore, this *symmetry*-breaking effect, resulting from the competition between the resonance and orbital energy stabilization effects, cannot be adequately remedied using a single set of orbitals, optimized within the one-configuration MO or VB theories, since competing resonance structures are associated with the exclusive sets of the optimum orbitals. Within the MO theory Jackels and Davidson (1976) has cured the symmetry-breaking problem in NO_2 by using the *symmetry*-adapted combination of two *symmetry*-broken HF wave functions. The RGVB approach or its generalized (GRVB) version represent the same strategy applied within the VB theory: the symmetry broken GVB wave functions are first determined for each individual resonance structure alone or in the presence of the other structure(s) and then their resonance is determined at the subsequent (nonorthogonal) CI stage. Of similar character is the BOVB method, which focuses on the proper description of both the bond-dissociation phenomena, in which different-orbitals-for-different structures are optimized in the presence of the remaining structures, so that they minimize the energies of each individual valence structure and maximize the stabilization effect due to their mutual resonance (mixing).

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