

Chapter 2

Hartree–Fock Method

2.1 Hartree Method

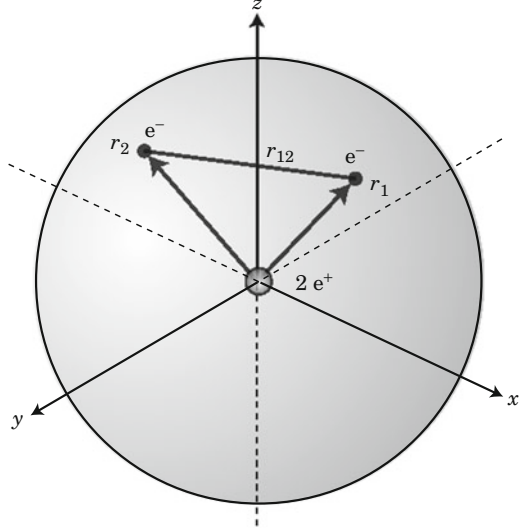
For atoms other than the hydrogen atom, as treated in Sect. 1.9, we can obtain the quantum states of electronic motions in theory by constructing the Hamiltonian operators in a similar fashion and solving the Schrödinger equation. However, when we actually solve the Schrödinger equation for these atoms, we are faced with a serious problem: the *three-body problem*. That is, the state of motion cannot be solved analytically for systems in which three or more distinct masses interact. This three-body problem is not unique to quantum mechanics but is a classic problem in analytical physics. As described in Sect. 1.3, Poincaré proved that there are very few classical mechanics problems for which the equations of motions can be solved analytically. This is due to the three-body problem. Poincaré addressed this three-body problem in classical mechanics with the idea that only periodical solutions can be solved by the least (stationary)-action principle (Ekeland 2009). On the other hand, Hartree suggested an idea to solve the three-body problem for atoms containing multiple electrons.

In 1928, 2 years after the Schrödinger equation was published, Hartree proposed a method solving this equation for multiple-electron systems, based on fundamental physical principles: the *Hartree method* (Hartree 1928). Let us consider the electronic motion of a helium atom (Fig. 2.1). The Hamiltonian operator of this atom is given as

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + V_{\text{ne}}(\mathbf{r}_1) + V_{\text{ne}}(\mathbf{r}_2) + V_{\text{ee}}(\mathbf{r}_1, \mathbf{r}_2), \quad (2.1)$$

where \mathbf{r}_n is the position vector of the n -th electron and ∇_n is the gradient vector operator for the n -th electron. On the right-hand side of Eq. (2.1), the first two terms are kinetic energy operators, and the next two terms are nuclear-electron electrostatic interaction potentials. These are one-electron terms collectively called *one-electron operators*. On the other hand, the last term is an electron–electron

Fig. 2.1 Electrons in a helium atom, where \mathbf{r}_i is the coordinate vector of the i -th electron, r_{12} is the distance between two electrons, and e^- and e^+ are negative and positive charges



electrostatic interaction potential called a *two-electron operator*. Notice that *atomic units* are used in this equation for the first time. Atomic units are a convenient system of units usually used in electronic property calculations. In this system, the *electron mass* m_e , *electron charge* e , *reduced Planck constant* $\hbar = h/2\pi$, and *Coulomb force constant* $1/(4\pi\epsilon_0)$ are assumed to be 1. Henceforth, let us consider the mechanics in atomic units for in order to reduce the complexity. In Eq. (2.1), potentials V_{ne} and V_{ee} are written as

$$V_{ne}(\mathbf{r}) = -\frac{2}{r} \quad (2.2)$$

and

$$V_{ee}(\mathbf{r}_{12}) = \frac{1}{r_{12}}, \quad (2.3)$$

where $r = |\mathbf{r}|$ and $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$. That is, Hartree assumed that each electron moves in the averaged potential of the electrostatic interactions with surrounding electrons and suggested the *independent electron approximation* which approximates the averaged potential as an effective potential V_{eff} . For this approximation, the Hamiltonian operator is divided into terms for the different electrons, as follows:

$$\begin{aligned} \hat{H} &= \left[-\frac{\nabla_1^2}{2} + V_{ne}(r_1) + V_{\text{eff}}(\mathbf{r}_1) \right] + \left[-\frac{\nabla_2^2}{2} + V_{ne}(r_2) + V_{\text{eff}}(\mathbf{r}_2) \right] \\ &= \hat{h}(\mathbf{r}_1) + \hat{h}(\mathbf{r}_2), \end{aligned} \quad (2.4)$$

where $h(\mathbf{r}_i)$ is the Hamiltonian operator for the i -th electron. In this Hamiltonian operator, the wavefunction is represented as the product of different electronic motion wavefunctions,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2). \quad (2.5)$$

In this case, the expectation value of the Hamiltonian operator is given as

$$\begin{aligned} E &= \frac{\int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \Psi^*(\mathbf{r}_1, \mathbf{r}_2) \hat{H} \Psi(\mathbf{r}_1, \mathbf{r}_2)}{\int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \Psi^*(\mathbf{r}_1, \mathbf{r}_2) \Psi(\mathbf{r}_1, \mathbf{r}_2)} \\ &= \frac{\sum_{i=1}^2 \int d^3\mathbf{r}_i \phi_i^*(\mathbf{r}_i) \hat{h}(\mathbf{r}_i) \phi_i(\mathbf{r}_i)}{\sum_{i=1}^2 \int d^3\mathbf{r}_i \phi_i^*(\mathbf{r}_i) \phi_i(\mathbf{r}_i)}. \end{aligned} \quad (2.6)$$

With the variational method, the Schrödinger equation for obtaining the set of one-electron wavefunctions $\{\phi_i\}$, which makes this expectation value stationary, is represented as

$$\hat{h}(\mathbf{r}_i) \phi_i(\mathbf{r}_i) = \epsilon_i \phi_i(\mathbf{r}_i). \quad (2.7)$$

Since the eigenvalue of Eq.(2.7), ϵ_i , is interpreted as the eigenenergy for the motion of the i -th electron, the total wavefunction can be obtained by solving the eigenequation for each electron. This one-electron wavefunction ϕ_i and the corresponding eigenenergy ϵ_i are later called the *orbital* and *orbital energy*, respectively. This equation also indicates that the total eigenenergy is the sum of the orbital energies corresponding to different electronic motions,

$$\hat{H} \Psi = (\epsilon_1 + \epsilon_2) \phi_1 \phi_2 = \epsilon \Psi. \quad (2.8)$$

This theory is called the Hartree method.

Although the effective potential is replaced with a virtual potential in Eq.(2.4), this does not necessarily require such a replacement. The effective potential corresponding to the wavefunction in Eq.(2.5) is derived as

$$V_{\text{eff}}(\mathbf{r}_i) = \sum_j \int d^3\mathbf{r}_j \frac{|\phi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (2.9)$$

The above discussion is applicable to the theory using this potential, because the motions of electrons are independent for this potential. In general, a theory using a potential derived with no semiempirical parameters is called an *ab initio theory* (“ab initio” means “from the beginning” in Latin). Solving this ab initio Hartree equation is not as straightforward as it might appear at first glance, because the effective potential in Eq.(2.9) is represented by the wavefunctions of other electronic motions. That is, Eq.(2.7) is a nonlinear equation in which the operator

depends on the solution of this equation. Hartree incorporated the *self-consistent field (SCF) method* to solve this equation. For the SCF method, further details are described in Sect. 2.4. This ab initio Hartree method reproduces the shapes of atomic orbitals reasonably close to those of state-of-the-art theories that take into account electron correlation, as mentioned later. However, it was found that the energies given by this method are too inaccurate to be used in the analyses of chemical reactions and properties. It becomes clear that the inaccurate energies are mainly attributed to the neglect of electron–electron exchange interactions (see Sect. 2.3).

2.2 Molecular Orbital Theory

What motional states do electrons have in molecules? Let us consider the case of the hydrogen molecule (Fig. 2.2). With the Hartree method, the Hamiltonian operator for the hydrogen molecule is given by

$$\hat{H} = \hat{h}(\mathbf{r}_1) + \hat{h}(\mathbf{r}_2) + V_{\text{nn}}(R_{\text{AB}}), \quad (2.10)$$

where R_{AB} is the distance between two atomic nuclei, A and B. Neglecting nuclear motions is one of the most important and convenient approximations in considering the electronic motions in molecules. Since even the lightest atomic nucleus, hydrogen, is 1836 times heavier than the electron, electrons are considered to move overwhelmingly faster than nuclei do. Actually, the kinetic energy of the nucleus has already been neglected when electronic motions are considered in Eq. (2.1). The approximation neglecting atomic nuclear motions to consider electronic motions is called the *adiabatic approximation*, based on the interpretation that the absence

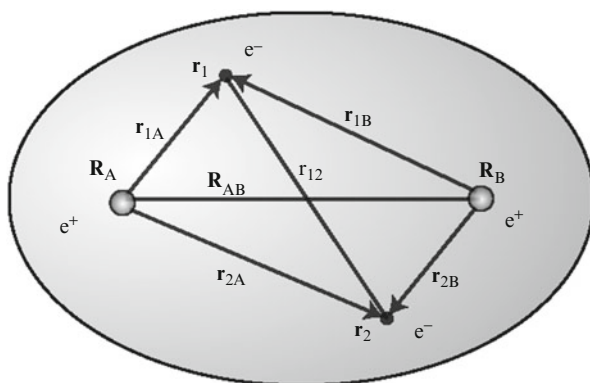


Fig. 2.2 Electrons in hydrogen molecule, where \mathbf{R}_I is the coordinate vector of the I -th nuclear, r_{iI} is the distance between the i -th electron and I -th nuclear, and R_{AB} is the distance between nuclei A and B

of atomic nuclear motion means that there is no heat energy interchange with the outside environment, or also as the *Born–Oppenheimer approximation*, capping the names of the developers (Born and Oppenheimer 1927). This approximation is so efficient that it hardly affects the chemical properties of electronic ground states. Therefore, this approximation is used by default in quantum chemical calculations. With this adiabatic approximation, since the nuclear–nuclear interactions V_{nn} can be neglected, Eq. (2.10) becomes

$$\hat{H} = \hat{h}(\mathbf{r}_1) + \hat{h}(\mathbf{r}_2), \quad (2.11)$$

which appears similar to the Hamiltonian of the helium atom. However, the equation is more difficult to solve than it appears, because the hydrogen molecule has two atomic nuclei. Actually, the position vectors of the electrons must be considered for each atomic nucleus, although these are represented as \mathbf{r}_n in Eq. (2.11).

To solve this problem, the concept of the *molecular orbital* was introduced. The concept of the molecular orbital was used by Hund for the first time to explain the electronic states of molecules (Hund 1926). Mulliken summarized this concept in English, which helped to hasten its introduction to the world at large (Mulliken 1927). He is also the one who coined the term “orbital” in 1932 to indicate its similarity to an orbit. In 1929, Lennard–Jones suggested an ansatz (educated guess) that molecular eigenfunctions are representable as the linear combination of atomic eigenfunctions, which became the basis of the linear combination of atomic orbitals–molecular orbital (LCAO–MO) approximation for describing molecular orbitals in terms of the atomic orbitals (Lennard–Jones 1929). Coulson reported the variational calculation results of the hydrogen molecule using the LCAO–MO approximation for the first time (Coulson 1938). This was the first usage of *molecular orbital theory*.

Based on the LCAO–MO approximation, the molecular orbital of the hydrogen molecule is written as

$$\phi = C_1\chi_1 + C_2\chi_2, \quad (2.12)$$

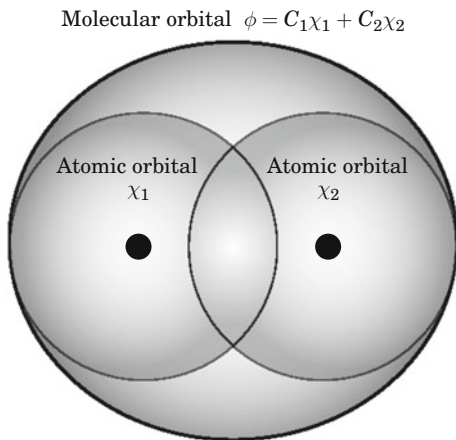
as shown in Fig. 2.3, where χ_I is the atomic orbital centered on the I -th atomic nucleus, and C_I is the corresponding molecular orbital coefficient. In Eq. (2.12), the atomic orbitals and molecular orbital coefficients are assumed to be real. Substituting this molecular orbital ϕ into Eq. (2.6) gives

$$\epsilon = \frac{C_1^2 h_{11} + C_2^2 h_{22} + 2C_1 C_2 h_{12}}{C_1^2 + C_2^2 + 2C_1 C_2 S_{12}}, \quad (2.13)$$

where h_{ij} and S_{12} are given by

$$h_{ij} = \int d^3\mathbf{r} \chi_i \hat{h} \chi_j < 0 \quad (2.14)$$

Fig. 2.3 Molecular orbital of the hydrogen molecule, ϕ , composed of the atomic orbitals of hydrogen atoms, χ_1 and χ_2 , for the LCAO–MO approximation



and

$$S_{12} = \int d^3\mathbf{r} \chi_1 \chi_2 > 0, \quad (2.15)$$

and ϵ indicates the molecular orbital energy. Since the coefficients C_1 and C_2 minimizing this ϵ are determined by

$$\partial\epsilon/\partial C_1 = \partial\epsilon/\partial C_2 = 0, \quad (2.16)$$

Eq. (2.13) gives

$$(h_{11} - \epsilon)C_1 + (h_{12} - \epsilon S_{12})C_2 = 0, \quad (2.17)$$

and

$$(h_{12} - \epsilon S_{12})C_1 + (h_{22} - \epsilon)C_2 = 0. \quad (2.18)$$

The solutions for these equations, except for the case of $C_1 = C_2 = 0$, are obtained by

$$\begin{vmatrix} h_{11} - \epsilon & h_{12} - \epsilon S_{12} \\ h_{12} - \epsilon S_{12} & h_{22} - \epsilon \end{vmatrix} = 0. \quad (2.19)$$

By solving this equation, the orbital energies of the hydrogen molecule are given by

$$\epsilon_{\pm} = \frac{h_{11} \pm h_{12}}{1 \pm S_{12}} \quad (2.20)$$

and the corresponding normalized molecular orbitals are

$$\phi_{\pm} = \frac{\chi_1 \pm \chi_2}{\sqrt{2 \pm 2S_{12}}}. \quad (2.21)$$

For the orbital energies, ϵ_+ is supposed to have a lower energy, because S_{12} and h_{12} are generally given as $0 < S_{12} \ll 1$ and $h_{12} \approx S_{12}(h_{11} + h_{22})/2 < 0$. The electron occupancy of the molecular orbitals obeys the *Pauli exclusion principle* (Pauli 1925). This principle indicates that the electron has *spin* as the fourth quantum number, and no two electrons can have the identical set of quantum numbers simultaneously. For a hydrogen molecule containing only two electrons, opposite-spin electrons occupy the molecular orbital ϕ_+ . Therefore, the wavefunction for the hydrogen molecule is given by the

$$\Phi = \phi_+(\mathbf{r}_1)\phi_+(\mathbf{r}_2) \quad (2.22)$$

$$= \frac{1}{2 + 2S_{12}} \{\chi_1(\mathbf{r}_1) + \chi_2(\mathbf{r}_1)\} \{\chi_1(\mathbf{r}_2) + \chi_2(\mathbf{r}_2)\}. \quad (2.23)$$

The total electronic energy of the hydrogen molecule is calculated as

$$E = 2\epsilon_+ = \frac{2(h_{11} + h_{12})}{1 + S_{12}}. \quad (2.24)$$

Notice that this is based not on the ab initio method but on the original Hartree method. With the ab initio method, the double-counted electron–electron Coulomb interaction must be removed from the total energy. In this way, the electronic states of molecules can be calculated using the LCAO–MO approximation.

As described above, the binding energy of the hydrogen molecule equals the orbital energy. However, *the analysis of binding energies based on orbital energies is applicable only to the limited case in which only two electrons are involved in the bond, like the hydrogen molecule*. Discussing other types of binding energies requires consideration of the energy contributions from other orbitals. For instance, it is generally difficult to evaluate molecular bond strength from the energetic stabilities of molecular orbital energies before and after reactions. In most cases, there is no clear relation between orbital and binding energies. However, this does not negate the value of the conceptual reaction analysis using molecular orbital images. *Since molecular orbitals have a relatively small dependence of the shapes on the type of calculation method, these are assumed to be correct in most cases, if the calculated system is not so large*. It is therefore possible to obtain information on reaction sites and reactivities of molecules from electron distributions given by molecular orbitals, as seen in the analysis on the Frontier orbital theory (Fukui et al. 1952). Note, however, that since orbital energies significantly depend on the calculation method, as described in Sect. 7, the order of the orbital energy levels are easily changed, especially if there are virtual orbitals.

2.3 Slater Determinant

In 1926, Heisenberg and Dirac independently proposed that *the wavefunction of electronic motions must be antisymmetric* (the sign of the wavefunction becomes opposite for the exchange of electrons) *to satisfy the Pauli exclusion principle naturally and therefore should be represented as a determinant* (Heisenberg 1926; Dirac 1926). The new electron–electron interaction resulting from the antisymmetrization is called the *exchange interaction*. Slater constructed a general method for solving the Schrödinger equation based on the normalized determinant representing the antisymmetrized wavefunction (Slater 1929). In this study, the *exchange integral* was also suggested for the first time.

Let us consider the exchange of electrons by taking the helium atom as an example. The Hamiltonian operator in Eq. (2.1) does not change by exchanging the coordinates of two electrons:

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2) = \hat{H}(\mathbf{r}_2, \mathbf{r}_1). \quad (2.25)$$

Since this leads to

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2)\Psi(\mathbf{r}_2, \mathbf{r}_1) = E\Psi(\mathbf{r}_2, \mathbf{r}_1), \quad (2.26)$$

it is easily proven that the Hamiltonian operator is commutative with the exchange operator replacing the positions of two electrons \hat{P}_{12} , as follows:

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2)\hat{P}_{12}\Psi(\mathbf{r}_1, \mathbf{r}_2) = \hat{P}_{12}\hat{H}(\mathbf{r}_1, \mathbf{r}_2)\Psi(\mathbf{r}_1, \mathbf{r}_2), \quad (2.27)$$

i.e.,

$$[\hat{H}, \hat{P}_{12}]\Psi = (\hat{H}\hat{P}_{12} - \hat{P}_{12}\hat{H})\Psi = 0. \quad (2.28)$$

This indicates that the Hamiltonian and exchange operators have simultaneous eigenstates. Moreover, $\hat{P}_{12}^2 = 1$ is found by considering that the positions of two electrons are reverted by two exchanges. This leads to the eigenvalues of \hat{P}_{12} being ± 1 . Therefore, there are two different wavefunctions for the exchange operator \hat{P}_{12} : the symmetric wavefunction corresponding to the $+1$ eigenvalue,

$$\Psi^{(S)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \{\Psi(\mathbf{r}_1, \mathbf{r}_2) + \Psi(\mathbf{r}_2, \mathbf{r}_1)\}, \quad (2.29)$$

and the antisymmetric wavefunction corresponding to the -1 eigenvalue,

$$\Psi^{(A)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \{\Psi(\mathbf{r}_1, \mathbf{r}_2) - \Psi(\mathbf{r}_2, \mathbf{r}_1)\} = -\Psi^{(A)}(\mathbf{r}_2, \mathbf{r}_1), \quad (2.30)$$

where $1/\sqrt{2}$ is the normalization constant.

Next, let us consider the Hartree wavefunction in Eq. (2.5). The symmetric and antisymmetric wavefunctions are given by

$$\Psi^{(S)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \{ \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1) \} \quad (2.31)$$

and

$$\Psi^{(A)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \{ \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1) \}, \quad (2.32)$$

respectively. In these wavefunctions, only the antisymmetric wavefunction satisfies the Pauli exclusion principle. This is because wavefunctions must be zero for the case in which the same electron occupies the same orbital, i.e. $\mathbf{r}_1 = \mathbf{r}_2$. As a result, *electronic motions always have antisymmetric wavefunctions*. The antisymmetric wavefunction in Eq. (2.32) can be written as a determinant,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) \\ \phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) \end{vmatrix}. \quad (2.33)$$

For the case of three or greater electrons, the antisymmetric wavefunction can be described in a determinant form,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \dots & \phi_1(\mathbf{r}_N) \\ \phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) & \dots & \phi_2(\mathbf{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(\mathbf{r}_1) & \phi_N(\mathbf{r}_2) & \dots & \phi_N(\mathbf{r}_N) \end{vmatrix} \quad (2.34)$$

$$= \frac{1}{\sqrt{N!}} \det |\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \cdots \phi_N(\mathbf{r}_N)|. \quad (2.35)$$

This determinant is called the *Slater determinant* (Slater 1929).

2.4 Hartree–Fock Method

In 1930, Fock applied the Slater determinant to the Hartree method and proposed the *Hartree–Fock method*, which is one of the core theories in quantum chemistry (Fock 1930). Slater also suggested the same method independently in the same year (Slater 1930).

For simplicity, let us consider closed-shell systems, in which n orbitals are occupied by electrons two by two. The Slater determinants for closed-shell systems are given by defining orbitals as functions of the spatial and spin coordinates, as follows:

$$\begin{aligned} \Phi(\{\mathbf{r}, \boldsymbol{\sigma}\}) \\ = \frac{1}{\sqrt{(2n)!}} \det |\phi_1(\mathbf{r}_1, \alpha) \phi_1(\mathbf{r}_2, \beta) \cdots \phi_n(\mathbf{r}_{2n-1}, \alpha) \phi_n(\mathbf{r}_{2n}, \beta)|, \end{aligned} \quad (2.36)$$

where $\{\mathbf{r}, \boldsymbol{\sigma}\} = \{\mathbf{r}_1 \boldsymbol{\sigma}_1, \dots, \mathbf{r}_{2n} \boldsymbol{\sigma}_{2n}\}$. The expectation value of the corresponding Hamiltonian operator is written instead of Eq. (2.6) as

$$\begin{aligned} E = \frac{1}{(2n)!} \int d^3\{\mathbf{r}\} d\{\boldsymbol{\sigma}\} \det |\phi_1^*(\mathbf{r}_1, \alpha) \cdots \phi_n^*(\mathbf{r}_{2n}, \beta)| \hat{H} \\ \times \det |\phi_1(\mathbf{r}_1, \alpha) \cdots \phi_n(\mathbf{r}_{2n}, \beta)|, \end{aligned} \quad (2.37)$$

where $d^3\{\mathbf{r}\} = d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_{2n}$ and $d\{\boldsymbol{\sigma}\} = d\boldsymbol{\sigma}_1 \cdots d\boldsymbol{\sigma}_{2n}$. Since electrons are indistinguishable, the integrals for the one-electron operator (*one-electron integrals*) are $2n$ -tuplicate, and the integrals for the two-electron operator (*two-electron integrals*) are $\{2n(2n-1)/2\}$ -tuplicate. Therefore, the expectation value is transformed to

$$\begin{aligned} E &= \frac{1}{(2n)!} \int d^3\{\mathbf{r}\} d\{\boldsymbol{\sigma}\} \det |\phi_1^*(\mathbf{r}_1, \alpha) \cdots \phi_n^*(\mathbf{r}_{2n}, \beta)| \hat{H} \\ &\quad \times \det |\phi_1(\mathbf{r}_1, \alpha) \cdots \phi_n(\mathbf{r}_{2n}, \beta)| \\ &= \frac{1}{(2n-1)!} \int d^3\{\mathbf{r}\} d\{\boldsymbol{\sigma}\} \det |\phi_1^*(\mathbf{r}_1, \alpha) \cdots \phi_n^*(\mathbf{r}_{2n}, \beta)| \\ &\quad \times \left(-\frac{\nabla^2}{2} + V_{\text{ne}} \right) \det |\phi_1(\mathbf{r}_1, \alpha) \cdots \phi_n(\mathbf{r}_{2n}, \beta)| \\ &\quad + \frac{1}{2(2n-2)!} \int d^3\{\mathbf{r}\} d\{\boldsymbol{\sigma}\} \det |\phi_1^*(\mathbf{r}_1, \alpha) \cdots \phi_n^*(\mathbf{r}_{2n}, \beta)| \frac{1}{r_{12}} \\ &\quad \times \det |\phi_1(\mathbf{r}_1, \alpha) \cdots \phi_n(\mathbf{r}_{2n}, \beta)|. \end{aligned} \quad (2.39)$$

The one-electron integrals in the first term of the right-hand side of Eq. (2.39) are $(2n-1)!$ -tuplicate under the following conditions:

$$\int d^3\mathbf{r}_\lambda d\boldsymbol{\sigma} \phi_k^*(\mathbf{r}_\lambda, \sigma) \phi_l(\mathbf{r}_\lambda, \sigma) = \delta_{kl} \quad (2.40)$$

and

$$\int d^3\mathbf{r}_\lambda d\boldsymbol{\sigma} \phi_k^*(\mathbf{r}_\lambda, \sigma) \phi_l(\mathbf{r}_\lambda, \sigma') \neq \sigma = 0. \quad (2.41)$$

Since the same spatial orbitals are used for α and β spins, the one-electron integrals are described without concern for spins as

$$\begin{aligned}
(\text{One-electron integrals}) &= 2 \sum_i^n \int d^3\mathbf{r} \phi_i^*(\mathbf{r}) \left\{ -\frac{1}{2} \nabla^2 + V_{\text{ne}}(\mathbf{r}) \right\} \phi_i(\mathbf{r}) \\
&= 2 \sum_i^n h_i.
\end{aligned} \tag{2.42}$$

Note that ϕ_k is switched from a spin orbital $\phi_k(\mathbf{r}, \sigma)$ to a spatial orbital $\phi_k(\mathbf{r})$. For the two-electron integrals of the second term in Eq. (2.39), it is not necessary to take spin into consideration for the combinations of different spin terms, which equal zero under the same conditions, similarly to the one-electron integrals. On the other hand, for the spatial terms, the combinations of exchanging two electrons remain besides those of the same spatial terms. These combinations are $(n-2)!$ -tuplicate. The two-electron integrals are summarized as

$$(\text{Two-electron integrals}) = \sum_{i,j}^n (2J_{ij} - K_{ij}), \tag{2.43}$$

where J_{ij} and K_{ij} are

$$J_{ij} = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) = \langle ij | ij \rangle \tag{2.44}$$

and

$$K_{ij} = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_j(\mathbf{r}_1) \phi_i(\mathbf{r}_2) = \langle ij | ji \rangle. \tag{2.45}$$

Attaching the stationary condition for the minimal variation of orbital ϕ_i ($\phi_i \rightarrow \phi_i + \delta\phi_i$), $\delta E / \delta\phi_i = 0$, to the expectation value of the Hamiltonian operator containing one- and two-electron integrals, we obtain

$$\left\{ h_i + \sum_j^n (2\hat{J}_j - \hat{K}_j) \right\} \phi_i = \sum_j \phi_j \epsilon_{ji} \tag{2.46}$$

$$\left\{ h_i^* + \sum_j^n (2\hat{J}_j^* - \hat{K}_j^*) \right\} \phi_i^* = \sum_j \phi_j^* \epsilon_{ji}^* \tag{2.47}$$

from the variational principle. In Eqs. (2.46) and (2.47), \hat{J}_j and \hat{K}_j are called *Coulomb operator* and *exchange operator*, respectively, which are defined as

$$\hat{J}_j(\mathbf{r}_1) \phi_i(\mathbf{r}_1) = \int d^3\mathbf{r}_2 \phi_j^*(\mathbf{r}_2) \phi_j(\mathbf{r}_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_1) \tag{2.48}$$

and

$$\hat{K}_j(\mathbf{r}_1)\phi_i(\mathbf{r}_1) = \int d^3\mathbf{r}_2 \phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_2) \frac{1}{r_{12}}\phi_j(\mathbf{r}_1). \quad (2.49)$$

Note that the meaningful Hamiltonian operator is a Hermitian operator, giving real eigenenergies,

$$\epsilon_{ji} = \epsilon_{ij}^*. \quad (2.50)$$

This indicates that Eq. (2.47) is the complex conjugate of Eq. (2.46). Provided that the Fock matrix is defined as

$$\hat{F} = \hat{h} + \sum_j^n \left(2\hat{J}_j - \hat{K}_j \right), \quad (2.51)$$

the one-electron equation is derived as

$$\hat{F}\phi_i = \epsilon_i\phi_i. \quad (2.52)$$

Equation (2.52) is called the *Hartree–Fock equation*, and the operator \hat{F} is called the *Fock operator*.

Using Eq. (2.52), the orbital energy ϵ_i is represented as

$$\epsilon_i = \int d^3\mathbf{r}_1 \phi_i^*(\mathbf{r}_1) \hat{F}\phi_i(\mathbf{r}_1) \quad (2.53)$$

$$= h_i + \sum_j^n (2J_{ij} - K_{ij}). \quad (2.54)$$

By this orbital energy, the total electron energy is written as

$$E = 2 \sum_i^n \epsilon_i - \sum_{i,j}^n (2J_{ij} - K_{ij}) \quad (2.55)$$

$$= \sum_i^n (\epsilon_i + h_i). \quad (2.56)$$

Note that the total electron energy is not identical to the sum of the two orbital energies, because the latter doubly counts the electron–electron interactions. The total energy is calculated by adding the nucleus–nucleus repulsion energies to the total electron energy,

$$E_{\text{total}} = E + \sum_{A \neq B} \frac{Z_A Z_B}{R_{AB}}. \quad (2.57)$$

Since the Hartree–Fock equation is a nonlinear equation, similarly to the Hartree equation, it is usually solved by the SCF method. The Hartree–Fock SCF method is carried out via the following process:

1. Set up the information on the calculated molecular system (nuclear coordinates, nuclear charges, and number of electrons) and initial reference molecular orbitals $\{\phi_i^0\}$.
2. Calculate the two-electron operators of the Fock operator in Eq. (2.51) using the reference orbitals.
3. Solve Eq. (2.52) with the calculated Fock operator.
4. Compare the given molecular orbitals with the reference orbitals to determine if these orbitals are the eigenfunctions of this equation. The given orbitals are taken as the eigenfunctions if the differences of all the given orbitals to the corresponding reference orbitals are less than a given threshold value. If the orbitals have differences greater than the threshold, return to step 2 with the given orbitals as initial orbitals.

In general, the Hartree–Fock method indicates this SCF-based method. Despite the simplicity of the procedure, it soon became clear that solving this equation is not-trivial for usual molecular electronic systems. The Hartree–Fock equation essentially cannot be solved for molecules without computers. Actually, solving the Hartree–Fock equation for molecules had to await the appearance of general-purpose computers.

2.5 Roothaan Method

The preparation for computer-based science began following the practical use of computers represented by the appearance of commercial computers in 1950. In the following year (1951), Roothaan, an IBM researcher, developed a method for solving the Hartree–Fock equation on a computer, which is called the *Roothaan method* (Roothaan 1951). Since Hall independently suggested this method in the same year (Hall 1951), this is also called Roothaan–Hall method. This method is based on the character of von Neumann-type computer architecture, which efficiently performs matrix operations. A year earlier (1950), the *Gaussian-type basis function* was suggested by Boys (Boys 1950). Using the contracted nature of the Gaussian basis functions (see Sect. 2.6), the Roothaan method dramatically reduced the computational time of the Hartree–Fock calculations to realize the electronic state calculations of general molecules. After the development of this method, quantum chemistry began to make progress that tracked the growth of computer power.

Based on the LCAO–MO approximation given in Sect. 2.2, molecular orbitals $\{\phi_i\}$ can be expanded as

$$\phi_i(\mathbf{r}) = \sum_{p=1}^{n_{\text{AO}}} \chi_p(\mathbf{r}) C_{pi}, \quad (2.58)$$

where n_{AO} is the number of atomic orbitals. The expansion coefficient C_{pi} is called the *molecular orbital (MO) coefficient*. Although $\{\chi_p\}$ is essentially the set of atomic orbitals, it is more efficient and general to use basis functions modeling atomic orbitals (For basis sets, see Sect. 2.6). Using the expansion of molecular orbitals, the Hartree–Fock equation is transformed to a matrix equation,

$$\mathbf{F}\mathbf{C}_i = \epsilon_i \mathbf{S}\mathbf{C}_i, \quad (2.59)$$

where the elements of matrix \mathbf{F} and \mathbf{S} are given as

$$\begin{aligned} F_{pq} &= \int d^3\mathbf{r} \chi_p^*(\mathbf{r}) \hat{F} \chi_q(\mathbf{r}) \\ &= \int d^3\mathbf{r} \chi_p^*(\mathbf{r}) \hat{h} \chi_q(\mathbf{r}) + \sum_{j=1}^n \int d^3\mathbf{r} \chi_p^*(\mathbf{r}) (2\hat{J}_j - \hat{K}_j) \chi_q(\mathbf{r}) \\ &= h_{pq} + \sum_{r,s=1}^{n_{\text{basis}}} P_{sr} \left(\langle pr|qs \rangle - \frac{1}{2} \langle pr|sq \rangle \right), \end{aligned} \quad (2.60)$$

$$S_{pq} = \int d^3\mathbf{r} \chi_p^*(\mathbf{r}) \chi_q(\mathbf{r}). \quad (2.61)$$

In these equations, n_{basis} is the number of basis functions, and the integrals h_{pq} , $\langle pr|qs \rangle$ and $\langle pr|sq \rangle$ indicate

$$h_{pq} = \int d^3\mathbf{r} \chi_p^*(\mathbf{r}) \left\{ -\frac{1}{2} \nabla_r^2 + V_{\text{ne}}(\mathbf{r}) \right\} \chi_q(\mathbf{r}), \quad (2.62)$$

$$\langle pr|qs \rangle = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \chi_p^*(\mathbf{r}_1) \chi_r^*(\mathbf{r}_2) \frac{1}{r_{12}} \chi_q(\mathbf{r}_1) \chi_s(\mathbf{r}_2), \quad (2.63)$$

$$\langle pr|sq \rangle = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \chi_p^*(\mathbf{r}_1) \chi_r^*(\mathbf{r}_2) \frac{1}{r_{12}} \chi_s(\mathbf{r}_1) \chi_q(\mathbf{r}_2). \quad (2.64)$$

P_{pq} is called the *density matrix*, which is defined using molecular orbital coefficients as

$$P_{pq} = 2 \sum_{j=1}^n C_{pj} C_{qj}^*. \quad (2.65)$$

The density matrix was first introduced by von Neumann (von Neumann 1927) and Landau (Landau 1927) independently to describe the quantum mechanical natures

of statistical systems. The diagonal term of the density matrix in Eq. (2.65), P_{pp} , indicates the existence probability of an electron in the p -th molecular orbital.

For Eq. (2.59), the condition

$$|\mathbf{F} - \epsilon_i \mathbf{S}| = 0 \quad (2.66)$$

is required to make the coefficient matrix \mathbf{C}_i give nonzero solutions. To solve Eq. (2.66), a transformation is usually used for Eq. (2.59). That is, the Fock matrix \mathbf{F} is transformed to give matrix \mathbf{F}' satisfying

$$|\mathbf{F}' - \epsilon_i \mathbf{E}| = 0, \quad (2.67)$$

where \mathbf{E} is the unit matrix. By this transformation, Eq. (2.66) is easily solved by simply diagonalizing matrix \mathbf{F}' . The simplest way to give Eq. (2.67) is orthonormalizing basis sets beforehand. Provided that basis sets giving the unit matrix \mathbf{E} for the overlap matrix \mathbf{S} would be used, Eq. (2.66) is easily solved only by diagonalizing the Fock matrix. Such a basis set transformation is actually employed in many quantum chemistry calculation programs.

For using orthonormalized basis sets, the Roothaan equation is solved by the SCF method as follows:

1. Set up the information for the calculated molecular system (nuclear coordinates, nuclear charges, and number of electrons) and the orthonormalized basis set, $\{\chi_p\}$.
2. Calculate one- and two-electron integrals: h_{pq} , $\langle pr|qs\rangle$ and $\langle pr|sq\rangle$.
3. Determine the density matrix \mathbf{P} with the initial molecular orbital coefficient, $\{\mathbf{C}_i\}$.
4. Compute the Fock matrix \mathbf{F} in Eq. (2.60).
5. Diagonalize \mathbf{F} to obtain the molecular orbital coefficients, $\{\mathbf{C}'_i\}$, and orbital energies, $\{\epsilon_i\}$.
6. Update the density matrix, \mathbf{P}' , with the new molecular orbital coefficients, $\{\mathbf{C}'_i\}$.
7. Compare the given density matrix, \mathbf{P}' , with the previous one, \mathbf{P} , and halt the SCF process, regarding it as convergent if the difference between these density matrices is less than a given threshold value. If the difference is greater than the threshold value, return to step 4 and continue with the calculation.

This SCF calculation lowers the total electronic energy by the unitary transformation of molecular orbitals. Therefore, this can be taken as a process relaxing molecular orbitals.

Using the density matrix \mathbf{P} , the Fock matrix \mathbf{F} , and the one-electron integral, the total electronic energy can be calculated by Eqs. (2.54) and (2.57) as

$$E = \frac{1}{2} \sum_{p,q=1}^{n_{\text{basis}}} P_{pq} (h_{pq} + F_{pq}). \quad (2.68)$$

2.6 Basis Function

In the previous section, the Roothaan method was introduced as a method for speeding up the Hartree–Fock calculation by expanding molecular orbitals with a basis set. The accuracy and computational time of the Roothaan calculations depend on the quality and number of basis functions, respectively. Therefore, it is necessary for reproducing accurate chemical reactions and properties to choose basis functions that give highly accurate molecular orbitals with a minimum number of functions.

The most frequently used basis function is the Gaussian-type function in quantum chemistry calculations. This is due to the following *product rule of Gaussian-type functions* (Szabo and Ostlund 1996).

$$\begin{aligned} & \exp(-\alpha|\mathbf{r} - \mathbf{R}_A|^2) \exp(-\beta|\mathbf{r} - \mathbf{R}_B|^2) \\ &= \left[\frac{2\alpha\beta}{(\alpha + \beta)\pi} \right]^{3/4} \exp\left(-\frac{\alpha\beta}{\alpha + \beta}|\mathbf{R}_A - \mathbf{R}_B|^2\right) \exp[-(\alpha + \beta)|\mathbf{r} - \mathbf{R}_C|^2], \quad (2.69) \end{aligned}$$

$$\mathbf{R}_C = \frac{\alpha}{\alpha + \beta}\mathbf{R}_A + \frac{\beta}{\alpha + \beta}\mathbf{R}_B, \quad (2.70)$$

where \mathbf{R}_A is the coordinate vector of nucleus A. Based on this rule, the product of Gaussian-type functions is given by a Gaussian-type function centered on a different point, and this drastically speeds up the two-electron integral calculations. However, as shown in the wavefunction of the hydrogen atom (Eq. (1.80)), actual atomic orbitals are close to the Slater-type function, $\exp(-\zeta r)$. It is therefore unfavorable to use Gaussian-type functions as they are. To solve this problem, the *contracted Gaussian-type basis function*, which is a linear combination of Gaussian-type functions, was proposed by Boys (Boys 1950):

$$\chi_p(\mathbf{r} - \mathbf{R}_A) = \sum_{\mu} c_{\mu p} \exp(-\alpha_{\mu p}|\mathbf{r} - \mathbf{R}_A|^2). \quad (2.71)$$

In this equation, the original Gaussian-type functions are called *primitive functions* to distinguish them from the contracted ones. The primitive functions are specified only by the orbital exponent, $\alpha_{\mu p}$, contracted coefficient, $c_{\mu p}$, and coordinate vector of the center of the function, \mathbf{R}_A . By using these contracted Gaussian-type functions as basis functions, it was expected that highly accurate results could be obtained with far fewer basis functions.

Different from the contracted Gaussian-type basis functions mentioned later, primitive functions usually have a standardized form to save the effort of developing a different computational program for each basis function. The primitive functions corresponding to s, p, d, and f atomic orbitals are represented analogically to the spherical harmonic functions (see Sect. 1.8) as

s function : $\exp(-\alpha r^2)$,

p function : $(x, y, z) \exp(-\alpha r^2)$,

d function : $(x^2, y^2, z^2, xy, yz, zx) \exp(-\alpha r^2)$,

f function : $(x^3, y^3, z^3, x^2y, x^2z, xy^2, y^2z, yz^2, xz^2, xyz) \exp(-\alpha r^2)$, (2.72)

respectively. Note that the numbers of linear independent d and f functions are essentially five and seven, respectively. Therefore, these primitive functions are generally combined for d and f orbitals to provide linear independent functions: $x^2 - y^2$ function is formed for d orbitals and $x^2z - y^2z$, $3x^2y - y^3$ and $3xy^2 - x^3$ functions are formed for f orbitals.

For contracted Gaussian-type basis functions, various types of functions have been suggested. The following are several major Gaussian-type basis functions (for further details, see, e.g., [\(Jensen 2006\)](#)):

- *Minimal basis functions* (e.g. STO-LG) contain only minimal required contracted functions for each atom. For example, since electrons occupy atomic orbitals up to the 2p orbital in the carbon atom, five contracted Gaussian-type functions corresponding to 1s, 2s, 2p_x, 2p_y, and 2p_z orbitals are necessary at the minimum. The minimal basis functions approximating Slater-type orbitals (STO) corresponding to atomic orbitals with L primitive functions are called *STO-LG basis functions*.
- *Split valence basis functions* (e.g. 6-31G, 6-311G, DZ, TZ, and DZV) use one type of contracted Gaussian-type function for core orbitals and multiple contracted functions for valence orbitals. In most molecules, valence orbitals mainly contribute to chemical bonds, while core orbitals hardly participate in the bonds. It is therefore reasonable to use many basis functions for valence orbitals to calculate electronic states accurately while conserving the total number of basis functions. In this type of basis function, *Pople-type basis functions*, including the 6-31G basis, are included. “6-31” indicates the extent of the contraction and split, in which “6” means the use of contracted basis functions of 6 primitive functions for core orbitals and “31” means the use of doubly-split basis functions combining contracted basis functions of 3 primitive functions with one uncontracted basis function for valence orbitals. “6-311G” uses triply-split basis functions for valence orbitals. In this type of basis function, the *Dunning–Huzinaga-type* and *Ahlrichs-type basis functions* are also included: Dunning–Huzinaga-type functions are described as “DZ,” “TZ,” and “QZ” for doubly-, triply-, and quadruply-split functions for valence orbitals, while the Ahlrichs-type are similarly written as “DZV,” “TZV,” and “QZV.”
- *Polarization function-supplemented basis functions* (e.g. 6-31G*, 6-31G(d), DZp, cc-pVXZ, and cc-pCVXZ) add *polarization functions* to incorporate the anisotropic nature of molecular orbitals originating from chemical bonds. Polarization functions usually have higher angular momenta than the highest angular momenta of the atomic orbitals that mainly make up the molecular

orbitals. In the Pople-type basis functions, the inclusion of polarization functions is represented by an asterisk “*” such as “6-31G*.” For a single asterisk “*,” one polarization function is added for all atoms except hydrogen atoms, while for a double asterisk “**,” one p orbital function is also added to each hydrogen atom. Recently, the form of polarization function is often written explicitly, for example, “6-31G(d)” (for this basis function, a d orbital function is added). In the case of the Dunning–Huzinaga-type basis functions, polarization functions are represented by “p,” for example, “DZp” for a single polarization function and “TZ2p” for double polarization functions. Recent highly accurate calculations frequently use *correlation consistent basis functions*. Dunning et al. developed these basis functions to create the remaining functions so that they produce electron correlations equivalently when they are included in the valence orbitals, such as the 4d and 4f orbitals. These basis functions are represented as “cc-pVXZ” (X=D, T, Q, 5, 6,...). Furthermore, there are “cc-pCVXZ” basis functions, which take into account the electron correlations of the core orbitals by adding s and p orbital functions.

- *Diffuse-function-augmented basis functions* (e.g. 6-311+G(d), 6-311++G(2df, 2pd), and aug-cc-pVXZ) employ *diffuse functions* to take weakly bound electrons into consideration. In particular, these diffuse functions are requisite in the calculations of the anions and excited states of small molecules. Adding diffuse functions is shown by a plus “+” in Pople-type basis functions. “6-311+G(d)” augments sp diffuse functions mixing s and p orbitals for all atoms except hydrogen atoms, and “6-311++G(2df, 2pd)” adds two d and one f diffuse functions for all atoms except hydrogen and two p and one d orbital functions for hydrogen in addition. For correlation consistent basis functions, augmenting diffuse functions is represented by “aug-” at the head of the names and one diffuse function is added to each angular momentum type of basis function. In the “aug-cc-pVDZ” function, containing up to d orbital functions, diffuse functions are added to s through d orbital functions one by one.
- *Effective core potential (ECP) basis functions* (e.g. LanL2DZ and Stuttgart-ECP) approximate core orbitals, which hardly affect reactions and properties in most systems, as effective potentials were introduced to drastically reduce the number of basis functions. In particular, for the fourth-period atoms or later, ECP basis functions are used in most cases, except for the reactions and properties in which core electrons participate, and have given highly accurate results. The most widely used ECP is the *relativistic ECP (RECP)*, incorporating the relativistic effects of the core electrons: The best known ECP basis functions are LanL2DZ, of Los Alamos National Laboratory (USA), and the Stuttgart relativistic small core (STRSC) and large core (STRLC) ECP basis functions (Germany). Among others, there are the *ab initio model potential (AIMP)* basis functions, which were developed to reproduce the ab initio potentials of core orbitals with nodes in order to consider the indirect effects of core electrons.

These are the most frequently used basis functions in quantum chemistry calculations. Of course, there are various basis functions in addition to the above, and some functions have been confirmed to be efficient, especially in calculations

for specific systems. Although the accuracies and reliabilities of calculated results clearly depend on the basis functions used, it is usually hard to answer the question which basis set should be used for specific systems. The only way to choose basis functions is to contrast their features.

It is worthwhile to note that although only Gaussian-type basis functions have so far been explained, they are not the only option in quantum chemistry calculations. Actually, Slater-type basis functions, which reproduce the shapes of orbitals more accurately, as mentioned above, are used in, e.g., the Amsterdam Density Functional (ADF) program, in which numerical integral calculations are carried out with Slater-type functions.

Finally, let us examine *basis set superposition error (BSSE)*, which Gaussian-type basis functions generally produce. This error is attributed to the artificial stabilization energy coming from the overlap of nonorthogonal basis functions. Therefore, this error has the effect of making atoms approaching closer to each other. The attracting force from this error is called the *Pulay force* (Pulay 1969). To remove this error, the *counterpoise method* (van Duijneveldt et al. 1994) is frequently used: For example, if system AB is calculated with $a + b$ basis functions, the counterpoise method estimates the BSSE as

$$\Delta E = E_A^{a+b} + E_B^{a+b} + E_A^a + E_B^b, \quad (2.73)$$

and subtracts this ΔE from the total energy. In this equation, E_A^{a+b} indicates the energy of system A calculated with both a and b basis functions. It is well known that BSSE is severe in calculating weak bonds. For example, *van der Waals bonds cannot be reproduced correctly without a BSSE correction* (see Sect. 6.3). However, since the overlap of basis functions is natural in chemical bonds, it is difficult to specify the BSSE in chemical bond calculations. The BSSE is therefore neglected in most calculations involving reactions and properties.

2.7 Coulomb and Exchange Integral Calculations

The Coulomb and exchange integral calculations of the Hartree–Fock equation are usually the rate-determining processes in Hartree–Fock calculations. As seen in Eqs. (2.63) and (2.64), the two-electron integrals called the two-electron repulsion integrals are represented with basis functions and have double integrations in terms of electronic position vectors in three-dimensional space coordinates. These two-electron repulsion integrals are given in the fourth order of basis functions. Since this indicates that the number of integrals drastically increases with the number of basis functions, the integral calculations rapidly approach a limitation on the number of electrons, unless the order is decreased. Fortunately, the two-electron integrals contain many that are non-contributing or duplicate. It is therefore necessary to eliminate these integrals for efficient integral calculations.

In the field of quantum chemistry, many algorithms have been developed to improve the efficiency of the two-electron integral calculations over the years. One of the most frequently used algorithms is the screening based on the *Schwartz* (K.H.A. Schwartz) *inequality* (1888). That is, based on the inequality,

$$\left| \int d^3\mathbf{r} \chi_p^*(\mathbf{r}) \chi_q(\mathbf{r}) \right|^2 \leq \int d^3\mathbf{r} |\chi_p(\mathbf{r})|^2 \cdot \int d^3\mathbf{r} |\chi_q(\mathbf{r})|^2, \quad (2.74)$$

negligible integrals can be screened out by calculating only the integrals of the squared basis functions. Moreover, various sophisticated algorithms have been suggested for the two-electron repulsion integral calculations. Recent major algorithms combine various existing algorithms: the Obara–Saika recursive algorithm (Obara and Saika 1986) for less-contracted Gaussian-type basis functions, the Rys polynomial algorithm (Dupuis et al. 1976) for large angular momentum basis functions, the Pople–Hehre axis-switching algorithm (Pople and Hehre 1978) for more-contracted basis functions, and so forth. The major example is the PRISM algorithm (Gill and Pople 1991), which is used in Gaussian09 and other programs. By using these algorithms, the order of the two-electron repulsion integral calculations can be decreased to the second to third order for the number of basis functions. However, the calculations of large systems require further decrease of the order.

Coulomb interactions are not quantum mechanical interactions but classical mechanical interactions between charges. Therefore, established techniques for increasing efficiency in classical mechanics are available in Coulomb integral calculations. So far, various techniques for classical mechanical systems have been applied to the Coulomb integral calculations to reduce the computational order. One of the major techniques is the *fast multipole method* (FMM) (Greengard and Rokhlin 1987), which has been used to compute the gravity between stars scattered through an astronomical body. FMM distinguishes long-range electron–electron interactions and calculates these interactions by the multipole method and other short-range electron–electron interactions by the usual method. For FMM, there are different methods for distinguishing long-range interactions and expanding multipoles (White et al. 1994). Another major technique for Coulomb integral calculations is the use of the *Poisson equation* (Becke and Dickson 1988; Delley 1996; Manby et al. 2001),

$$\int d^3\mathbf{r}' \frac{\nabla^2 \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = -4\pi\rho(\mathbf{r}), \quad (2.75)$$

where ρ is the *total electron density* defined by

$$\rho(\mathbf{r}) = 2 \sum_i^n |\phi_i(\mathbf{r})|^2. \quad (2.76)$$

In this equation, the Coulomb integral can be transformed into a single integral by replacing the basis functions with the Laplacian of the auxiliary density basis functions $\{\nabla^2 \xi_a\}$. The Coulomb integral is transformed for the combinations of the auxiliary density basis functions as

$$\begin{aligned} J_{ab} &= \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{|\nabla_1^2 \xi_a(\mathbf{r}_1)| |\nabla_2^2 \xi_b(\mathbf{r}_2)|}{r_{12}} \\ &= -4\pi \int d^3\mathbf{r} \xi_a(\mathbf{r}) \nabla^2 \xi_b(\mathbf{r}), \end{aligned} \quad (2.77)$$

and for the mixed basis functions with the usual basis functions $\{\chi_p\}$ as

$$\begin{aligned} J_{ap} &= \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{|\nabla_1^2 \xi_a(\mathbf{r}_1)| |\chi_p(\mathbf{r}_2)|}{r_{12}} \\ &= -4\pi \int d^3\mathbf{r} \xi_a(\mathbf{r}) \chi_p(\mathbf{r}). \end{aligned} \quad (2.78)$$

The auxiliary density basis functions $\{\xi_a\}$ are arbitrary electron density basis functions that are smaller than the basis functions $\{\chi_p\}$, spanning the model electron density,

$$\tilde{\rho}(\mathbf{r}) = \sum_a c_a \xi_a(\mathbf{r}), \quad (2.79)$$

and determines coefficient $\{c_a\}$ by minimizing

$$\Delta = \frac{1}{2} \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{|\rho(\mathbf{r}_1) - \tilde{\rho}(\mathbf{r}_1)| |\rho(\mathbf{r}_2) - \tilde{\rho}(\mathbf{r}_2)|}{r_{12}}. \quad (2.80)$$

This technique is called *electron density fitting* and is employed in the DMol program (Delley 1990). Methods combining the FMM and Poisson methods have also been suggested (Watson et al. 2008). By using these techniques, the order of the Coulomb integral calculations approaches the first order for the number of basis functions. This order can be taken as the order of the electron number N , because the number of basis functions is nearly proportional to the number of electrons. A method that makes a computational process approach the first order of the calculated system is generally called a *linear-scaling method* or *Order- N method*. In the Hartree–Fock method, most linear-scaling methods are proposed for Coulomb integral calculations.

Exchange interactions are purely quantum-mechanical interactions, acting even on distant electrons. Due to these interactions, total electronic energies are lowered, stabilizing electronic states. *A significant proportion of the exchange interactions is taken up by the self-interactions of the electrons themselves.* Exchange self-interactions correspond to the K_{ii} terms in Eq. (2.45) and cancel out with J_{ii} terms,

as shown in Eq. (2.43). Consequently, these exchange self-interactions remove the Coulomb potential of one electron. *Exchange interactions increase the overlap of orbitals to produce attractions between orbitals.* As a result, these attractions lead to the delocalization of the electron distribution, which causes the long-range nature of the exchange interactions. Exchange interactions also enhance the quantum nature of electronic states and significantly contribute to the chemical reactions and properties of molecules. Therefore, it is difficult to discuss chemistry even qualitatively without taking exchange interactions into consideration. Similarly to Coulomb integral calculations, various types of linear-scaling methods have been suggested for exchange integral calculations: e.g., the near-field exchange (NFX) method (Burant et al. 1996), based on FMM, and the order- N exchange (ONX) method (Schwegler et al. 1997a), which assumes the exponential decay of the electron density for regions far from given nuclei. However, it has been reported that both methods cannot achieve the linear scaling of exchange integral calculations except for linearly extended long-chain systems. This may be attributed to *the long-range nature of exchange interactions* (Schwegler et al. 1997b) and *the non-classical nature of long-range exchange interactions*.

2.8 Unrestricted Hartree–Fock Method

Thus far, the spin-independent forms of the various calculation methods have been described without clear notification, despite these forms being available only in the electronic state calculations for closed-shell molecules, in which electrons occupy molecular orbitals two by two. To take open-shell molecules containing unpaired electrons into consideration, spin orbitals should be explicitly considered. As a simple method for calculating the electronic states of open-shell molecules, Pople and Nesbet developed the *unrestricted Hartree–Fock (UHF) method* (Pople and Nesbet 1954), which independently deals with the spatial orbitals for α and β spins, in 1954.

In the UHF method, the Hartree–Fock equation in Eq. (2.52) is transformed into simultaneous equations for α - and β -spin electrons,

$$\hat{F}_\alpha \phi_{i\alpha} = \epsilon_{i\alpha} \phi_{i\alpha}, \quad (2.81)$$

and

$$\hat{F}_\beta \phi_{i\beta} = \epsilon_{i\beta} \phi_{i\beta}. \quad (2.82)$$

The spin-dependent Fock operator is given as

$$\hat{F}_\sigma = \hat{h}_\sigma + \sum_j^{n_\sigma} \left(\hat{J}_{j\sigma} - \hat{K}_{j\sigma} \right) + \sum_j^{n_{\sigma'}} \hat{J}_{j\sigma'}, \quad (2.83)$$

where n_σ is the number of σ -spin electrons and $\sigma' \neq \sigma$. Note that each electron has Coulomb interactions but no exchange interactions with opposite-spin electrons. The spin-dependent Coulomb operator $\hat{J}_{j\sigma}$ and exchange operator $\hat{K}_{j\sigma}$ in Eq. (2.83) are defined as

$$\hat{J}_{j\sigma}(\mathbf{r}_1)\phi_{i\sigma}(\mathbf{r}_1) = \int d^3\mathbf{r}_2 \phi_{j\sigma}^*(\mathbf{r}_2)\phi_{j\sigma}(\mathbf{r}_2) \frac{1}{r_{12}} \phi_{i\sigma}(\mathbf{r}_1), \quad (2.84)$$

and

$$\hat{K}_{j\sigma}(\mathbf{r}_1)\phi_{i\sigma}(\mathbf{r}_1) = \int d^3\mathbf{r}_2 \phi_{j\sigma}^*(\mathbf{r}_2)\phi_{i\sigma}(\mathbf{r}_2) \frac{1}{r_{12}} \phi_{j\sigma}(\mathbf{r}_1). \quad (2.85)$$

These equations are called the *UHF equation* or the *Pople–Nesbet equation* (Pople and Nesbet 1954). From the beginning, these equations have the form of the Roothaan method given by simultaneous equations,

$$\mathbf{F}_\alpha \mathbf{C}_{i\alpha} = \epsilon_{i\alpha} \mathbf{S} \mathbf{C}_{i\alpha}, \quad (2.86)$$

and

$$\mathbf{F}_\beta \mathbf{C}_{i\beta} = \epsilon_{i\beta} \mathbf{S} \mathbf{C}_{i\beta}, \quad (2.87)$$

where the spin-dependent Fock operator \mathbf{F}^σ and overlap matrix \mathbf{S}^σ are given as

$$F_{pq\sigma} = h_{pq\sigma} + \sum_{r,s=1}^{n_{\text{basis}}} P_{sr\sigma} (\langle pr|qs \rangle - \langle pr|sq \rangle) + \sum_{r,s=1}^{n_{\text{basis}}} P_{pq\sigma'} \langle pr|qs \rangle, \quad (2.88)$$

and

$$S_{pq\sigma} = \int d^3\mathbf{r} \chi_{p\sigma}^*(\mathbf{r}) \chi_{q\sigma}(\mathbf{r}). \quad (2.89)$$

Although the solution method of this equation is similar to that of the Roothaan method for closed-shell molecules, it includes pairs of Fock matrices, their diagonalizations, and density matrices for the α - and β -spins.

UHF calculations consequently give different spatial orbitals for α - and β -spins. This causes a problem in that UHF wavefunctions are often not eigenfunctions for the square of the total spin operator, $\hat{\mathbf{S}}^2$. The total spin operator $\hat{\mathbf{S}}$ is the sum of the spin angular momentum operators of the constituent electrons, $\hat{\mathbf{s}}$, and is written as

$$\hat{\mathbf{S}} = (\hat{S}_x, \hat{S}_y, \hat{S}_z) = \sum_i^N \hat{\mathbf{s}}_i. \quad (2.90)$$

Defining the spin functions of molecular orbital ϕ_i as α_i and β_i , the spin angular momentum operator, $\hat{\mathbf{s}} = (\hat{s}_x, \hat{s}_y, \hat{s}_z)$, gives

$$\hat{s}_z \begin{pmatrix} \alpha_i \\ \beta_i \end{pmatrix} = \frac{1}{2} \begin{pmatrix} \alpha_i \\ -\beta_i \end{pmatrix}, \quad \hat{s}_x \begin{pmatrix} \alpha_i \\ \beta_i \end{pmatrix} = \frac{1}{2} \begin{pmatrix} \beta_i \\ \alpha_i \end{pmatrix}, \quad \hat{s}_y \begin{pmatrix} \alpha_i \\ \beta_i \end{pmatrix} = \frac{i}{2} \begin{pmatrix} \beta_i \\ -\alpha_i \end{pmatrix}, \quad (2.91)$$

and

$$\hat{s}^2 \begin{pmatrix} \alpha_i \\ \beta_i \end{pmatrix} = (\hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2) \begin{pmatrix} \alpha_i \\ \beta_i \end{pmatrix} = \frac{3}{4} \begin{pmatrix} \alpha_i \\ \beta_i \end{pmatrix}. \quad (2.92)$$

Therefore, spin functions are the eigenfunctions of \hat{s}^2 and \hat{s}_z^2 . Since the nonrelativistic Hamiltonian operator generally does not explicitly depend on spins, it is commutative with the \hat{s}^2 and \hat{s}_z operators. This indicates that the *total wavefunctions including the spatial functions, Ψ , are the eigenfunctions of \hat{s}^2 and \hat{s}_z^2* . Therefore, it is easily proven that the Hamiltonian operator is commutative with the square of total spin operator, $\hat{\mathbf{S}}^2$, and the z -component of the total spin operator, \hat{S}_z , and consequently, wavefunctions satisfy

$$\hat{\mathbf{S}}^2 \Psi = \left(\sum_{i,j}^N \hat{\mathbf{s}}_i \cdot \hat{\mathbf{s}}_j \right) \Psi = \left(\frac{N_\alpha - N_\beta}{2} \right) \left(\frac{N_\alpha - N_\beta}{2} + 1 \right) \Psi, \quad (2.93)$$

and

$$\hat{S}_z \Psi = \left(\sum_i^N \hat{s}_z \right) \Psi = \left(\frac{N_\alpha - N_\beta}{2} \right) \Psi, \quad (2.94)$$

where N_σ is the number of σ -spin electrons in molecules. Since the total number of spins is preserved, UHF wavefunctions satisfy Eq. (2.94) to be the eigenfunctions of \hat{S}_z . However, since the spatial functions of the UHF wavefunctions are different for spins, the spins for the same number of molecular orbitals do not cancel out, violating Eq. (2.93). Therefore, the *UHF wavefunctions are generally not eigenfunctions of $\hat{\mathbf{S}}^2$* . Actually, for UHF wavefunctions, the expectation value of the $\hat{\mathbf{S}}^2$ operator is proven to be (Szabo and Ostlund 1996)

$$\begin{aligned} \langle \hat{\mathbf{S}}^2 \rangle_{\text{UHF}} &= \left(\frac{N_\alpha - N_\beta}{2} \right) \left(\frac{N_\alpha - N_\beta}{2} + 1 \right) + N_\beta \\ &\quad - \sum_{i,j}^N \left| \int d^3\mathbf{r} \phi_{i\alpha}^*(\mathbf{r}) \phi_{j\beta}(\mathbf{r}) \right|^2. \end{aligned} \quad (2.95)$$

2.9 Electronic States of Atoms

The electronic configurations in atoms can be explained qualitatively by the Hartree–Fock wavefunctions to some extent. Since atoms are spherically symmetric, potentials are also taken as spherically symmetric. Therefore, similarly to the wavefunction of the hydrogen atom in Eq. (1.78), the angular functions of the atomic wavefunctions are spherical harmonics. On the other hand, the radial functions are different from those for the hydrogen atom, because the degeneracy for the azimuthal quantum number l is resolved due to the appearance of the interelectronic potential, V_{ee} . However, as anticipated from the fact that the eigenenergy of the hydrogen atom in Eq. (1.82) depends only on main quantum number n , the energy differences between the motional states of different l are much smaller than those of different n for relatively light atoms. There are, therefore, possible motional states for natural the numbers l ($l \leq n - 1$) in ascending n number. For the azimuthal quantum number l , the radial functions are represented as s, p, d, f, g, h, These radial functions are also degenerate for the magnetic quantum number m , which is an integer $-l \leq m \leq l$. In this way, the electronic motional states, i.e., atomic orbitals, with (n, l, m) quantum numbers are determined as 1s, 2s, 2p ($2p_{-1}$, $2p_0$, $2p_{+1}$), 3s, 3p ($3p_{-1}$, $3p_0$, $3p_{+1}$), 3d ($3d_{-2}$, $3d_{-1}$, $3d_0$, $3d_{+1}$, $3d_{+2}$),

How are electrons distributed to these atomic orbitals? The atomic electron configurations are summarized in Tables 2.1–2.3. Electrons occupy the energetically lowest atomic orbitals two by two in closed-shell atoms such as the rare gases. However, it is not so simple in open-shell atoms. As a practical explanation, *Hund's rule* (Hund 1925a,b) is available. This rule consists of the following two rules:

- In electron configurations with the same main and azimuthal quantum numbers, the highest total spin configuration is the most stable.
- In the highest total spin configurations, the highest angular momentum configuration is the most stable.

For example, the electron configuration of the carbon atom is $(1s)^2(2s)^2(2p)^2$, obeying Hund's rule for the assignment of two electrons to the outermost 2p orbitals. That is, 2p orbitals are occupied by two α -spin electrons to maximize the total spin and $2p_{+1}$ and $2p_0$ orbitals are occupied to maximize the total angular momentum. Exchange interactions are the underlying cause for the first rule that the highest total spin configuration is the most stable. The second rule that the highest angular momentum configuration is the most stable is due to Coulomb interactions, which are minimized by allocating electrons close to the equatorial planes of atoms, where electrons are farthest from each other. Actually, atomic ground-state configurations cannot essentially be given by the Hartree method, but can be reproduced by the Hartree–Fock method containing exchange interactions to some extent. Note, however, that electron configurations containing open-shell core orbitals such as those of rare earth atoms cannot be provided without considering electron correlation, as described in the next chapter.

Table 2.1 Electronic configurations of atoms up to krypton

Period	Atomic number	Element	K	L		M			N				O		Ground state
			1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	
1	1	H	1												$^2S_{1/2}$
	2	He	2												1S_0
2	3	Li	2	1											$^2S_{1/2}$
	4	Be	2	2											1S_0
	5	B	2	2	1										$^2P_{1/2}$
	6	C	2	2	2										3P_0
	7	N	2	2	3										$^4S_{3/2}$
	8	O	2	2	4										3P_2
	9	F	2	2	5										$^2P_{3/2}$
	10	Ne	2	2	6										1S_0
3	11	Na	2	2	6	1									$^2S_{1/2}$
	12	Mg	2	2	6	2									1S_0
	13	Al	2	2	6	2	1								$^2P_{1/2}$
	14	Si	2	2	6	2	2								3P_0
	15	P	2	2	6	2	3								$^4S_{3/2}$
	16	S	2	2	6	2	4								3P_2
	17	Cl	2	2	6	2	5								$^2P_{3/2}$
	18	Ar	2	2	6	2	6								1S_0
4	19	K	2	2	6	2	6		1						$^2S_{1/2}$
	20	Ca	2	2	6	2	6		2						1S_0
	21	Sc	2	2	6	2	6	1	2						$^2D_{3/2}$
	22	Ti	2	2	6	2	6	2	2						3F_2
	23	V	2	2	6	2	6	3	2						$^4F_{3/2}$
	24	Cr	2	2	6	2	6	5	1						7S_3
	25	Mn	2	2	6	2	6	5	2						$^6S_{5/2}$
	26	Fe	2	2	6	2	6	6	2						5D_4
	27	Co	2	2	6	2	6	7	2						$^4F_{9/2}$
	28	Ni	2	2	6	2	6	8	2						3F_4
	29	Cu	2	2	6	2	6	10	1						$^2S_{1/2}$
	30	Zn	2	2	6	2	6	10	2						1S_0
	31	Ga	2	2	6	2	6	10	2	1					$^2P_{1/2}$
	32	Ge	2	2	6	2	6	10	2	2					3P_0
	33	As	2	2	6	2	6	10	2	3					$^4S_{3/2}$
	34	Se	2	2	6	2	6	10	2	4					3P_2
	35	Br	2	2	6	2	6	10	2	5					$^2P_{3/2}$
	36	Kr	2	2	6	2	6	10	2	6					1S_0

In addition, there is a third, complementary rule:

- The configuration with the lowest total angular momentum (total spin + total orbital angular momentum) is the most stable for atoms containing less-than-half occupied outermost orbitals, and the configuration with the highest total angular momentum is the most stable for those containing greater-than-half occupied outermost orbitals.

Table 2.2 Electronic configurations of atoms from rubidium to lutetium

Period	Atomic number	Element	K 1s - N 4p	N		O				P				Ground state
				4d	4f	5s	5p	5d	5f	6s	6p	6d	6f	
5	37	Rb	[Kr]			1								$^2S_{1/2}$
	38	Sr	[Kr]			2								1S_0
	39	Y	[Kr]	1		2								$^2D_{3/2}$
	40	Zr	[Kr]	2		2								3F_2
	41	Nb	[Kr]	4		1								$^6D_{1/2}$
	42	Mo	[Kr]	5		1								7S_3
	43	Tc	[Kr]	6		1								$^6S_{5/2}$
	44	Ru	[Kr]	7		1								5F_5
	45	Rh	[Kr]	8		1								$^4F_{9/2}$
	46	Pd	[Kr]	10										1S_0
	47	Ag	[Kr]	10		1								$^2P_{1/2}$
	48	Cd	[Kr]	10		2								3P_0
	49	In	[Kr]	10		2	1							$^4S_{3/2}$
	50	Sn	[Kr]	10		2	2							3P_2
	51	Sb	[Kr]	10		2	3							$^2P_{3/2}$
	52	Te	[Kr]	10		2	4							1S_0
	53	I	[Kr]	10		2	5							$^2S_{1/2}$
	54	Xe	[Kr]	10		2	6							1S_0
6	55	Cs	[Kr]	10		2	6			1				$^2D_{3/2}$
	56	Ba	[Kr]	10		2	6			2				3H_4
	57	La	[Kr]	10		2	6	1		2				4I
	58	Ce	[Kr]	10	2	2	6			2				5I_4
	59	Pr	[Kr]	10	3	2	6			2				6H
	60	Nd	[Kr]	10	4	2	6			2				7F_0
	61	Pm	[Kr]	10	5	2	6			2				$^8S_{7/2}$
	62	Sm	[Kr]	10	6	2	6			2				9D_2
	63	Eu	[Kr]	10	7	2	6			2				$^6H_{15/2}$
	64	Gd	[Kr]	10	7	2	6	1		2				5I
	65	Tb	[Kr]	10	9	2	6			2				4I
	66	Dy	[Kr]	10	10	2	6			2				3H_4
	67	Ho	[Kr]	10	11	2	6			2				$^2F_{7/2}$
	68	Er	[Kr]	10	12	2	6			2				1S_0
	69	Tm	[Kr]	10	13	2	6			2				$^2D_{3/2}$
	70	Yb	[Kr]	10	14	2	6			2				3F_2
	71	Lu	[Kr]	10	14	2	6	1		2				$^4F_{3/2}$

“[Kr]” indicates the electron configuration of krypton

This rule is based on *spin-orbit interactions*, which are based on relativistic effects (see Sect. 6.4). For example, let us compare the electron configurations of silicon and sulfur atoms. Since the outermost 3p orbitals are occupied by two and four electrons in silicon and sulfur atoms, respectively, the silicon atom, containing less-than-half occupancy, has a 3P_0 ground state with the minimum zero total angular

Table 2.3 Electronic configurations of atoms from hafnium to rutherfordium

Period	Atomic number	Element	K 1s - N 4p	N		O				P				Q		Ground state
				4d	4f	5s	5p	5d	5f	6s	6p	6d	6f	7s	7p	
6	72	Hf	[Kr]	10	14	2	6	2		2						5D_0
	73	Ta	[Kr]	10	14	2	6	3		2						$^6S_{5/2}$
	74	W	[Kr]	10	14	2	6	4		2						5D_4
	75	Re	[Kr]	10	14	2	6	5		2						$^4F_{9/2}$
	76	Os	[Kr]	10	14	2	6	6		2						3D_3
	77	Ir	[Kr]	10	14	2	6	7		2						$^2S_{1/2}$
	78	Pt	[Kr]	10	14	2	6	9		1						1S_0
	79	Au	[Kr]	10	14	2	6	10		1						$^2P_{1/2}$
	80	Hg	[Kr]	10	14	2	6	10		2						3P_0
	81	Tl	[Kr]	10	14	2	6	10		2	1					$^4S_{3/2}$
	82	Pb	[Kr]	10	14	2	6	10		2	2					3P_2
	83	Bi	[Kr]	10	14	2	6	10		2	3					$^2P_{3/2}$
	84	Po	[Kr]	10	14	2	6	10		2	4					1S_0
	85	At	[Kr]	10	14	2	6	10		2	5					$^2S_{1/2}$
	86	Rn	[Kr]	10	14	2	6	10		2	6					1S_0
7	87	Fr	[Kr]	10	14	2	6	10		2	6			1		$^2D_{3/2}$
	88	Ra	[Kr]	10	14	2	6	10		2	6			2		3F_2
	89	Ac	[Kr]	10	14	2	6	10		2	6	1		2		$^2D_{3/2}$
	90	Th	[Kr]	10	14	2	6	10		2	6	2		2		$^3F^a$
	91	Pa	[Kr]	10	14	2	6	10	2	2	6	1		2		$^4K^a$
	92	U	[Kr]	10	14	2	6	10	3	2	6	1		2		$^5L^a$
	93	Np	[Kr]	10	14	2	6	10	4	2	6	1		2		$^6L^a$
	94	Pu	[Kr]	10	14	2	6	10	5	2	6	1		2		$^7K^a$
	95	Am	[Kr]	10	14	2	6	10	7	2	6			2		$^8S^a$
	96	Cm	[Kr]	10	14	2	6	10	7	2	6	1		2		$^9D^a$
	97	Bk	[Kr]	10	14	2	6	10	8	2	6	1		2		$^8H^a$
	98	Cf	[Kr]	10	14	2	6	10	10	2	6			2		$^5I^a$
	99	Es	[Kr]	10	14	2	6	10	11	2	6			2		$^4I^a$
	100	Fm	[Kr]	10	14	2	6	10	12	2	6			2		$^3H^a$
	101	Md	[Kr]	10	14	2	6	10	12	2	6	1		2		$^4K^a$
	102	No	[Kr]	10	14	2	6	10	14	2	6			2		$^1S^a$
	103	Lr	[Kr]	10	14	2	6	10	14	2	6			2	1	$^2D^a$
	104	Rf	[Kr]	10	14	2	6	10	14	2	6	2		2		$^3F_2^a$

Ground states designated by “*a*” (Küchle et al. 1994) and “*b*” (Eliav et al. 1995) are the most stable electronic states, and their electron configurations in relativistic full-electron calculations. “[Kr]” indicates the electron configuration of krypton

momentum and the sulfur atom, containing greater-than-half occupancy, has a 3P_2 ground state with the maximum two total angular momentum. It is required to include the relativistic spin–orbit interactions to reproduce these ground states.

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