Introduction to the Self-Consistent Field Method

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1 Schrödinger equation

In quantum chemistry we seek for approximate solutions of the non-relativistic time-independent Schrödinger equation:

$$\hat{H}\Psi = E\Psi \ . \tag{1}$$

The Hamiltonian operator $\hat{H}$ is defined (in atomic units) as:

$$\begin{aligned} \hat{H} = & -\frac{1}{2}\sum_{i}^{n}\nabla_i^2 - \frac{1}{2}\sum_{A}^{N}\frac{1}{M_A}\nabla_A^2 \\ & -\sum_{i}^{n}\sum_{A}^{N}\frac{Z_A}{r_{iA}} + \sum_{i>j}^{n}\frac{1}{r_{ij}} + \sum_{A>B}^{N}\frac{Z_A Z_B}{R_{AB}} \ , \end{aligned} \tag{2}$$

where the indices i run over the total number of electrons (n), indices A, B run over the total number of nuclei (N), M_A is the mass of the nucleus A, Z_A is the nuclear charge, R_{AB} is the distance between two nuclei, r_{iA} is the electron-nuclear distance, and r_{ij} is the distance between two electrons. The first two terms of Eq. (2) describe the kinetic energy of the electrons and nuclei, while the last three terms describe the potential energy of the electron-nuclear, electron-electron, and nuclear-nuclear interaction.

If Ψ is the true (exact) ground-state wavefunction, then the equation (1) yields the exact energy E. We can express the differential equation (1) in the integral form:

$$E = \int \Psi^* \hat{H} \Psi \, \mathrm{d}\tau \ , \tag{3}$$

where the energy E is obtained by integrating over the coordinates of all electrons and nuclei, which we label as τ. Using the Dirac's bra-ket notation, Eq. (1) can be rewritten as:

$$E = \langle \Psi | \hat{H} | \Psi \rangle \ . \tag{4}$$

In Eqs. (3) and (4), we assumed that the wavefunction is normalized, i.e.:

$$\langle \Psi | \Psi \rangle = \int \Psi^* \, \Psi \, \mathrm{d}\tau = 1 \ . \tag{5}$$

2 Born-Oppenheimer Approximation

In Eq. (4), the wavefunction $|\Psi\rangle$ depends on the coordinates of all electrons and nuclei in a molecule. We can take advantage of the fact that the nuclei are much heavier than the electrons and, thus, assume that the electrons are moving in the field of the fixed nuclei. Within this approximation (also known as the Born-Oppenheimer approximation), the second term of Eq. (2) (the kinetic energy of the nuclei) can be neglected and the last term of Eq. (2) (the internuclear repulsion) can be considered to be constant. The energy expression takes the form:

$$E = E_{elec} + E_{nuc} = \langle \Psi_{elec} | \hat{H}_{elec} | \Psi_{elec} \rangle + \sum_{A>B}^{N} \frac{Z_A Z_B}{R_{AB}} \ . \tag{6}$$

The first term of Eq. (6) is the solution of the electronic Schrödinger equation

$$\hat{H}_{elec} \, |\Psi_{elec}\rangle = E_{elec} \, |\Psi_{elec}\rangle \ , \tag{7}$$

where $|\Psi_{elec}\rangle$ is the wavefunction that depends only on the coordinates of the electrons and the electronic Hamiltonian is defined as:

$$\begin{aligned} \hat{H}_{elec} &= -\frac{1}{2} \sum_{i}^{n} \nabla_i^2 - \sum_{i}^{n} \sum_{A}^{N} \frac{Z_A}{r_{iA}} + \sum_{i>j}^{n} \frac{1}{r_{ij}} \\ &= \sum_{i}^{n} \hat{h}_i + \sum_{i>j}^{n} \frac{1}{r_{ij}} \ . \end{aligned} \tag{8}$$

In Eq. (8), we defined the one-electron operator

$$\hat{h}_i = -\frac{1}{2} \nabla_i^2 - \sum_{A}^{N} \frac{Z_A}{r_{iA}} \ , \tag{9}$$

which is often referred to as the core Hamiltonian.

From now on, we will always assume that we work in the framework of the Born-Oppenheimer approximation and define $\hat{H} \equiv \hat{H}_{elec}$ and $|\Psi\rangle \equiv |\Psi_{elec}\rangle$ for brevity.

3 Variational method

The electronic Schrödinger equation (7) yields the exact ground-state energy ($E = E_0$) provided that $|\Psi\rangle$ is the exact ground-state electronic wavefunction. Let's consider an approximate wavefunction $|\tilde{\Psi}\rangle$. In this case, we can write the energy as an expectation value:

$$\tilde{E} = \frac{\langle\tilde{\Psi}|\hat{H}|\tilde{\Psi}\rangle}{\langle\tilde{\Psi}|\tilde{\Psi}\rangle} \ . \tag{10}$$

We can show that the expectation value (10) may approach but never be lower than the exact ground state energy E_0 of the system:

$$\tilde{E} \geq E_0 \ . \tag{11}$$

Eq. (11) is known as the variational principle. It becomes an equality if and only if $|\tilde{\Psi}\rangle$ is the exact ground-state wavefunction.

To prove that, we will use the fact that the Hamiltonian $\hat{H}$ is Hermitian and, therefore, its eigenfunctions form a complete and orthonormal set of basis functions, which we will denote as $|\Phi_I\rangle$. This orthonormal set can be used to represent any wavefunction $|\tilde{\Psi}\rangle$ as a linear combination:

$$|\tilde{\Psi}\rangle = \sum_I C_I \, |\Phi_I\rangle \ \ , \tag{12}$$

where

$$\hat{H} \, |\Phi_I\rangle = E_I \, |\Phi_I\rangle \ \ , \tag{13}$$

$$\sum_I \ C_I^* C_I \ = \ 1 \ . \tag{14}$$

Then, for the expectation value (10) we obtain:

$$\tilde{E} = \sum_{IJ} C_I^* C_J \, \langle\Phi_I|\hat{H}|\Phi_J\rangle = \sum_I C_I^* C_I E_I \ , \tag{15}$$

where we used the fact the the eigenfunctions $|\Phi_I\rangle$ are orthonormal. We can now subtract the exact ground-state energy from both sides of Eq. (15):

$$\tilde{E} - E_0 = \sum_I C_I^* C_I (E_I - E_0) \ . \tag{16}$$

Note that each term in the summation on the r.h.s. of Eq. (16) is either zero or positive, since $E_I \geq E_0$. Thus, we can conclude that

$$\tilde{E} - E_0 \geq 0 \ , \tag{17}$$

which proves that Eq. (11) is true.

The *variational principle* states that the energy expectation value is a rigorous upper bound to the exact ground state energy. The essential problem in the *variational method* is to find a wavefunction, which gives the *lowest possible* value of $\tilde{E}$. For this purpose, the *variational condition*

$$\delta\tilde{E} = 0 \tag{18}$$

is usually employed. If the chosen wavefunction is a good approximation to the exact wavefunction, it is possible to approach the exact energy very closely by enforcing the variational condition (18). In general, the more variational parameters is included in the variational wavefunction, the closer the exact energy can be approached as these variables are optimized.

4 Hartree-Fock approximation

The main problem of quantum chemistry is finding approximate solutions to the electronic Schrödinger equation. Central to this problem for systems with many electrons is the Hartree-Fock approximation. It has played an important role in the development of modern quantum chemistry and our theoretical understanding of chemistry in general. In addition, it usually constitutes the first step towards more accurate approximations.

In the Hartree-Fock approximation, the electronic wavefunction is expressed as the antisymmetrized product of the one-electron basis functions $\psi_i(x_i)$ (so-called *spin-orbitals*):

$$|\Psi(x_1, \ldots, x_n)\rangle \approx |\Psi_{\mathrm{HF}}\rangle = \hat{\mathcal{A}}(x_1, \ldots, x_n) \prod_i^n \psi_i(x_i) \ , \tag{19}$$

where x_i denotes the spin and spatial coordinates of the ith electron. The antisymmetrizer operator $\hat{\mathcal{A}}(x_1, \ldots, x_n)$ is used to ensure that the resulting many-electron wavefunction is antisymmetric with respect to the permutation of any pair of the electrons (thus, satisfies the Pauli exclusion principle).

Each spin-orbital $\psi(x_i)$ can be expressed as a product of two functions:

$$\psi(x_i) = \phi(i)\,\sigma(i) \ , \tag{20}$$

where $\phi(i)$ is the *spatial orbital*, which depends only on the spatial coordinates of the ith electron, and $\sigma(i)$ is the *spin function*, which denotes the spin (we use $\sigma(i) = \alpha(i)$ for the spin-up electron and $\sigma(i) = \beta(i)$ for the spin-down electron). The spin-orbitals satisfy the orthonormality condition:

$$\langle \psi_i | \psi_j \rangle = S_{ij} = \delta_{ij} \ , \tag{21}$$

where δ_{ij} is the Kronecker delta:

$$\delta_{ij} \ = \ \begin{cases} 1 & for\ i \ = \ j \\ 0 & for\ i \ \neq \ j \ . \end{cases} \tag{22}$$

The same orthonormality condition applies to the spatial orbitals and the spin functions.

Now, let's consider an example of the Hartree-Fock wavefunction for a system with two electrons. We will assume that both electrons occupy the same spatial orbital (ϕ_1) with opposite spins (as in the ground electronic state of a hydrogen molecule or a helium atom). Thus, we can express the electronic wavefunction as:

$$\begin{aligned} |\Psi_{\mathrm{HF}}(x_1, x_2)\rangle &= \hat{\mathcal{A}}(x_1, x_2)\psi_1(x_1)\psi_2(x_2) \\ &= \frac{1}{\sqrt{2}}[\psi_1(x_1)\psi_2(x_2) - \psi_1(x_2)\psi_2(x_1)] \\ &= \frac{1}{\sqrt{2}}[\phi_1(1)\alpha(1)\phi_1(2)\beta(2) - \phi_1(2)\alpha(2)\phi_1(1)\beta(1)] \ . \end{aligned} \tag{23}$$

In Eq. (23), the prefactor $\frac{1}{\sqrt{2}}$ is necessary to satisfy the normalization condition $\langle \Psi_{\mathrm{HF}} | \Psi_{\mathrm{HF}} \rangle = 1$ (this prefactor can be included in the definition of the operator $\hat{\mathcal{A}}(x_1, \ldots, x_n)$). We can see that the above wavefunction satisfies the Pauli principle, i.e. it is antisymmetric with respect to the interchange of the two electrons ($|\Psi_{\mathrm{HF}}(x_1, x_2)\rangle = -\,|\Psi_{\mathrm{HF}}(x_2, x_1)\rangle$). We also observe that if we put two electrons in the same spatial orbital with the parallel spins the resulting wavefunction will be zero, which is a consequence of the Pauli principle.

For a system with more than two electrons, the Hartree-Fock wavefunction can be written in the form similar to Eq. (23), but the resulting expression will be quite lengthy, as it will include more terms and longer products of spin-orbitals. We can write the wavefunction in a more compact form if we realize that Eq. (19) is the definition of the determinant:

$$|\Psi_{\text{HF}}\rangle \;=\; \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \dots & \psi_{n-1}(1) & \psi_n(1) \\ \psi_1(2) & \psi_2(2) & \dots & \psi_{n-1}(2) & \psi_n(2) \\ \dots & \dots & \dots & \dots & \dots \\ \psi_1(n) & \psi_2(n) & \dots & \psi_{n-1}(n) & \psi_n(n) \end{vmatrix} \;, \qquad (24)$$

where we used a shorthand notation for the electron coordinates ($\psi_i(k) \equiv \psi_i(x_k)$). The wavefunction in Eq. (24) is known as the *Slater determinant.* We can easily verify that Eq. (24) reduces to Eq. (23) for the two-electron system that we considered as an example. Interestingly, Eq. (24) demonstrates one of the postulates of quantum mechanics: each electron is associated with every orbital, i.e. electrons are *indistinguishable.* Since a determinant is uniquely defined by its diagonal (e.g., the product of the occupied orbitals in Eq. (24)), we can represent the wavefunction more compactly as $|\Psi_{\text{HF}}\rangle = |\psi_1\psi_2\dots\psi_{n-1}\psi_n\rangle$. In this notation, the normalization prefactor is implied.

5 Hartree-Fock energy

Now that we have defined the Hartree-Fock wavefunction, it is time to solve the Schrödinger equation. Using Eq. (6), we can write the electronic energy of the system as:

$$E_{elec} \approx E_{\text{HF}} = \langle\Psi_{\text{HF}}|\hat{H}_{elec}|\Psi_{\text{HF}}\rangle \;. \qquad (25)$$

Note that in the above equation the integration is performed over the coordinates of all n electrons, but the Hamiltonian $\hat{H}_{elec}$ contains terms that depend on at most two electrons at a time (see Eq. (8)). Using the fact that the wavefunction $|\Psi_{\text{HF}}\rangle$ can be represented in terms of the products of the spin-orbitals and that the spin-orbitals are orthonormal (Eq. (21)), the n-electron integral in Eq. (25) can be reduced down to a sum of the one- and two-electron integrals. The energy expression takes the following form:

$$E_{\text{HF}} = \sum_{i}^{n} \langle i|\hat{h}|i\rangle + \frac{1}{2}\sum_{ij}^{n} \langle ij||ij\rangle \;, \qquad (26)$$

where $\langle i|\hat{h}|i\rangle$ are the integrals over the one-electron terms of the Hamiltonian

$$\langle i|\hat{h}|i\rangle = \int \psi_i^*(1)\hat{h}_1\psi_i(1)\,\mathrm{d}\tau_1 \tag{27}$$

and $\langle ij||ij\rangle$ are the integrals over the two-electron repulsion operator:

$$\langle ij||ij\rangle = \langle ij|ij\rangle - \langle ij|ji\rangle \ , \tag{28}$$

$$\langle ij|ij\rangle = \int \psi_i^*(1)\psi_j^*(2)\frac{1}{r_{12}}\psi_i(1)\psi_j(2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \ . \tag{29}$$

Note that the double vertical bar in $\langle ij||ij\rangle$ implies that the two-electron integral is *antisymmetrized*, i.e. $\langle ij||ij\rangle = -\langle ij||ji\rangle$. In general, the two-electron integrals have the following symmetry properties:

$$\begin{aligned}\langle pq||rs\rangle &= -\langle pq||sr\rangle = -\langle qp||rs\rangle = \langle qp||sr\rangle \\ &= \langle rs||pq\rangle = -\langle sr||pq\rangle = -\langle rs||qp\rangle = \langle sr||qp\rangle \ ,\end{aligned} \tag{30}$$

$$\begin{aligned}\langle pq|rs\rangle &= \langle rq|ps\rangle = \langle ps|rq\rangle = \langle rs|pq\rangle \\ &= \langle qp|sr\rangle = \langle qr|sp\rangle = \langle sp|qr\rangle = \langle sr|qp\rangle \ .\end{aligned} \tag{31}$$

The notation used for the two-electron integrals in Eqs. (28) to (31) is called the Physicists' notation. In some literature, the Chemists' notation is used where the two-electron integrals are represented as $(pq|rs)$. There exists a simple relationship between the two types of notation:

$$(pq|rs) = \int \psi_p^*(1)\psi_q(1)\frac{1}{r_{12}}\psi_r^*(2)\psi_s(2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 = \langle pr|qs\rangle \ . \tag{32}$$

6 Hartree-Fock equations

Eq. (26) states that the Hartree-Fock energy can be evaluated using the spin-orbitals $|\psi_i\rangle$. But how do we determine $|\psi_i\rangle$? According to the variational principle (Section 3), the best approximation to the exact wavefunction is given by the Hartree-Fock wavefunction that has the lowest energy. Thus, we will seek for the spin-orbitals that minimize the Hartree-Fock energy. An important condition is that the spin-orbitals should remain orthonormal during the minimization. We can perform such constrained minimization by using the Lagrange's method of undetermined multipliers, where we construct a functional that has the form of the Hartree-Fock energy augmented by the orthonormality constraint:

$$\mathcal{L} = E_{\mathrm{HF}} - \sum_{ij}^{n} \epsilon_{ij}(S_{ij} - \delta_{ij}) \ . \tag{33}$$

In Eq. (33), ϵ_{ij} are the Lagrange multipliers and S_{ij} is the overlap between the two spin-orbitals (Eq. (21)). Setting the variation $\delta\mathcal{L} = 0$, we arrive at the equations that prescribe how to obtain the spin-orbitals that minimize the Hartree-Fock energy:

$$\hat{f}\,|\psi_i\rangle = \epsilon_i\,|\psi_i\rangle \ . \tag{34}$$

Thus, the optimal spin-orbitals must be the eigenfunctions of the one-electron operator $\hat{f}$ called *the Fock operator*:

$$\hat{f}(1) = \hat{h}(1) + \sum_{j}^{n}(\hat{J}_j(1) - \hat{K}_j(1)) \ , \tag{35}$$

where $\hat{J}_j$ and $\hat{K}_j$ are *the Coulomb and exchange operators*, respectively. The Coulomb operator is defined as:

$$\hat{J}_j(1) = \int \psi_j^*(2)\psi_j(2)\frac{1}{r_{12}}\,\mathrm{d}\tau_2 \ , \tag{36}$$

while the exchange operator can be defined in terms of its action on a spin-orbital $|\psi_i\rangle$:

$$\hat{K}_j(1)\psi_i(1) = \int \psi_j^*(2)\psi_i(2)\frac{1}{r_{12}}\,\mathrm{d}\tau_2\,\psi_j(1) \ . \tag{37}$$

Note that although the spin-orbitals $|\psi_i\rangle$ must be the eigenfunctions of the Fock operator, the Fock operator itself depends on the spin-orbitals $|\psi_i\rangle$ via the operators $\hat{J}_j$ and $\hat{K}_j$. This demonstrates the *self-consistent* nature of the Hartree-Fock equations: changing the spin-orbitals leads to a modified Fock operator, which gives rise to a new set of spin-orbitals as its eigenfunctions. In practice, the Hartree-Fock equations are solved by starting with an initial set of spin-orbitals $|\psi_i\rangle$ (also known as the guess) and optimizing the spin-orbitals by updating the Fock operator and solving Eq. (34) at every iteration. This process is called the *self-consistent field* method (SCF).

The Hartree-Fock equations can be solved efficiently if we formulate Eq. (34) in the matrix form. Multiplying both sides of Eq. (34) by $\langle\psi_j|$, we obtain:

$$f_{ji} = \langle\psi_j|\hat{f}|\psi_i\rangle = \epsilon_i\delta_{ij} \ , \tag{38}$$

Thus, the spin-orbitals can be obtained by diagonalizing the Fock operator matrix f_{ij}, which can be expressed in terms of the one- and two-electron integrals as:

$$f_{ij} = \langle i|\hat{h}|j\rangle + \sum_k^n \langle ik||jk\rangle \ . \tag{39}$$

The eigenvalues of the Fock matrix ϵ_i are called *the orbital energies.*

7 Hartree-Fock theory in the atomic orbital basis

The Hartree-Fock equations can be solved by representing the spin-orbitals on a grid and integrating over them numerically. However, a much more common and efficient way to solve Eq. (34) is to express the spin-orbitals as a linear combination of the Gaussian-type atom-centered basis functions (so-called “atomic orbitals”):

$$|\psi_i\rangle \ = \ \sum_\mu^N \ C_\mu^i \, |\chi_\mu\rangle \ , \tag{40}$$

where N is the total number of atomic orbitals. [Note that in Eq. (40) we do not include the spin function (Eq. (20)) that is necessary to make sure that the spin-orbitals of different spin are orthogonal. However, as long as the coefficients C_μ^i satisfy the orthogonality requirement, the spin function can be omitted. See Section 8 for more details.] In the simplest case, each basis function $|\chi_\mu\rangle$ is represented as a single Gaussian-type function in the Cartesian space (so-called Gaussian-type orbital, GTO):

$$|\chi_\mu^{\mathrm{GTO}}(r)\rangle = N_c \, x^l y^m z^n e^{-\alpha_\mu r^2} \ , \tag{41}$$

where $r = \sqrt{x^2 + y^2 + z^2}$, N_c is the normalization coefficient, α_μ is the parameter that defines the shape of the basis function's radial distribution, and the exponents l, m, n are related to the projection of the basis function's angular momentum. In practice, the atomic orbitals $|\chi_\mu\rangle$ are usually expressed in terms of the linear combination of GTO's with fixed coefficients (so-called *contracted* GTO):

$$|\chi_\mu(r)\rangle = \sum_\nu c_\nu \, |\chi_\nu^{\mathrm{GTO}}(r)\rangle \ . \tag{42}$$

This allows to reduce the number of integrals that need to be evaluated during a computation without significantly loosing accuracy.

In the atomic-orbital formulation, the problem of finding the optimal spin-orbitals is reduced to the problem of finding the best C_μ^i coefficients that minimize the Hartree-Fock energy in a specified basis set. As we increase the size of the basis set N, the energy obtained at the end of the SCF optimization will approach the lowest possible Hartree-Fock energy (so-called Hartree-Fock basis set limit).

We can now use Eq. (40) to formulate the Hartree-Fock equations in the atomic orbital basis. First, we consider expression for the energy:

$$\begin{aligned} E_{\mathrm{HF}} &= \sum_{\mu\nu}^{N} \sum_{i}^{n} C_\mu^{i*} C_\nu^{i} \, \langle \mu | \hat{h} | \nu \rangle + \frac{1}{2} \sum_{\mu\nu\rho\sigma}^{N} \sum_{ij}^{n} C_\mu^{i*} C_\nu^{j*} C_\rho^{i} C_\sigma^{j} \, \langle \mu\nu || \rho\sigma \rangle \\ &= \sum_{\mu\nu}^{N} D_{\mu\nu} \, \langle \mu | \hat{h} | \nu \rangle + \frac{1}{2} \sum_{\mu\nu\rho\sigma}^{N} D_{\mu\rho} D_{\nu\sigma} \, \langle \mu\nu || \rho\sigma \rangle \ , \end{aligned} \tag{43}$$

where $\langle \mu | \hat{h} | \nu \rangle \equiv \langle \chi_\mu | \hat{h} | \chi_\nu \rangle$, $\langle \mu\nu || \rho\sigma \rangle \equiv \langle \chi_\mu \chi_\nu || \chi_\rho \chi_\sigma \rangle$, and we defined the *density matrix* $D_{\mu\nu}$ that can be expressed in terms of the orbital coefficients:

$$D_{\mu\nu} = \sum_{i}^{n} C_\mu^{i*} C_\nu^{i} \ . \tag{44}$$

Note that Eq. (43) is now expressed in terms of the one- and two-electron integrals in the atomic-orbital basis and all of the information about the Hartree-Fock wavefunction (i.e., spin-orbitals) is now included in the density matrix. This demonstrates an important advantage of working in the atomic-orbital formulation: as the molecular orbitals change during the SCF optimization, only the density matrix changes, while the molecular integrals do not. As a result, the one- and two-electron integrals can be computed only once (e.g., at the beginning of a computation) and stored in memory for later use, which significantly reduces the cost of computing the Hartree-Fock energy.

Let us now turn our attention to the Hartree-Fock equations. Starting with Eq. (38) and multiplying by $\langle \chi_\nu |$ on the left, we obtain:

$$\sum_{\mu}^{N} \langle \nu | \hat{f} | \mu \rangle \, C_\mu^i = \epsilon_i \sum_{\mu}^{N} \langle \nu | \mu \rangle \, C_\mu^i = \epsilon_i \sum_{\mu}^{N} S_{\nu\mu} C_\mu^i \ . \tag{45}$$

In the matrix form, Eq. (45) can be written as:

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\epsilon} \ , \tag{46}$$

where $\boldsymbol{\epsilon}$ is a diagonal matrix of the orbital energies. The atomic-orbital basis Fock matrix $F_{\mu\nu} = \langle \mu | \hat{f} | \nu \rangle$ has the following form:

$$F_{\mu\nu} = \langle \mu | \hat{h} | \nu \rangle + \sum_{\rho\sigma}^{N} \langle \mu\rho || \nu\sigma \rangle \, D_{\rho\sigma} \ . \tag{47}$$

(It is a good exercise to verify this equation by starting with Eq. (39)). Note that while in the spin-orbital basis solving the Hartree-Fock equations reduces to diagonalizing the Fock matrix (Eq. (38)), in the atomic orbital basis it is not that straightforward due to the fact that the basis functions $|\chi_\mu\rangle$ are in general non-orthogonal, which leads to the appearance of the overlap matrix $\mathbf{S}$ in Eq. (46). In other words, Eq. (46) is no longer a simple eigenvalue problem, it is a *generalized eigenvalue problem*. Nevertheless, we can still solve Eq. (46) rather efficiently using a few mathematical tricks. First, we construct two auxiliary matrices: the square-root overlap matrix ($\mathbf{S^{1/2}}$) and its inverse ($\mathbf{S^{-1/2}}$). The $\mathbf{S^{-1/2}}$ matrix is defined such that $\mathbf{S^{-1/2}}\,\mathbf{S^{-1/2}} = \mathbf{S^{-1}}$ and can be computed by diagonalizing the $\mathbf{S}$ matrix, taking the inverse square root of its eigenvalues, and transforming back using the eigenvectors:

$$\begin{aligned} \sum_{\mu\nu} U_{\mu\mu'} S_{\mu\nu} U_{\nu\nu'} &= s_{\mu'} \delta_{\mu'\nu'} \ , \\ (S^{-1/2})_{\mu\nu} &= \sum_{\mu'} U_{\mu\mu'} \frac{1}{\sqrt{s_{\mu'}}} U_{\nu\mu'} \ . \end{aligned} \tag{48}$$

If we multiply both sides of Eq. (46) by $\mathbf{S^{-1/2}}$ from the left, we obtain:

$$\begin{aligned} \mathbf{S^{-1/2}}\,\mathbf{F}\,\mathbf{S^{-1/2}}\,\mathbf{S^{1/2}}\,\mathbf{C} &= \mathbf{S^{-1/2}}\,\mathbf{S}\,\mathbf{C}\,\boldsymbol{\epsilon} \ , \\ \tilde{\mathbf{F}}\,\tilde{\mathbf{C}} &= \tilde{\mathbf{C}}\,\boldsymbol{\epsilon} \ . \end{aligned} \tag{49}$$

Eq. (49) suggests that the generalized eigenvalue problem (46) can be converted into a standard eigenvalue problem with the modified (transformed) Fock matrix:

$$\tilde{\mathbf{F}} = \mathbf{S}^{-1/2}\,\mathbf{F}\,\mathbf{S}^{-1/2}\ . \tag{50}$$

We can solve Eq. (49) by diagonalizing the $\tilde{\mathbf{F}}$ matrix. Note that $\mathbf{F}$ and $\tilde{\mathbf{F}}$ have the same eigenvalues $\boldsymbol{\epsilon}$, but their eigenvectors are different and are related to each other as:

$$\tilde{\mathbf{C}} = \mathbf{S}^{1/2}\,\mathbf{C}\ . \tag{51}$$

Thus, in order to obtain the orbital coefficients $\mathbf{C}$, we first construct the $\tilde{\mathbf{F}}$ matrix, diagonalize it, and then compute $\mathbf{C} = \mathbf{S}^{-1/2}\,\tilde{\mathbf{C}}$. The procedure that we used to solve the generalized eigenvalue problem in Eq. (49) is known as the *symmetric orthogonalization*, it was first used in quantum chemistry by Löwdin. As the name of this method suggests, it is based on the transformation of the non-orthogonal atomic orbitals $|\chi_\mu\rangle$ to the the orthogonal basis $|\tilde{\chi}_{\mu'}\rangle = \sum_\mu |\chi_\mu\rangle\,(S^{-1/2})_{\mu\mu'}$ where the eigenvalue problem can be solved by diagonalizing the symmetric matrix $\tilde{\mathbf{F}}$. In fact, it is easy to verify that in the basis of $|\tilde{\chi}_{\mu'}\rangle$ the overlap matrix is the identity matrix.

The above equations summarize the general procedure for solving the Hartree-Fock equations and computing the energy in the atomic orbital basis. In short, here are the key steps of the self-consistent field (SCF) optimization:

1. Given the basis set, compute the one- and two-electron integrals in the atomic orbital basis.
2. Using the overlap matrix $\mathbf{S}$, form the $\mathbf{S}^{-1/2}$ matrix according to Eq. (48).
3. Form the initial (guess) Fock matrix according to Eq. (47), but neglecting the contribution from the two-electron integrals.
4. Using the initial Fock matrix, solve the generalized eigenvalue problem as shown in Eq. (49) and compute the initial orbitals as $\mathbf{C} = \mathbf{S}^{-1/2}\,\tilde{\mathbf{C}}$.
5. Form the density matrix (Eq. (44)).
6. Form the new Fock matrix including the contribution from the two-electron integrals (Eq. (47)).

7. Compute the Hartree-Fock energy. Note that the energy expression (43) can be expressed in terms of the Fock matrix elements:

$$E_{\mathrm{HF}} = \frac{1}{2} \sum_{\mu\nu}^{N} D_{\mu\nu} (\langle \mu | \hat{h} | \nu \rangle + F_{\mu\nu}) \ . \tag{52}$$

8. Using the new Fock matrix, solve the generalized eigenvalue problem as shown in Eq. (49) and compute the new orbitals as $\mathbf{C} = \mathbf{S}^{-1/2}\, \tilde{\mathbf{C}}$.
9. Form the new density matrix (Eq. (44)).
10. Check convergence. If the change in the energy and the RMS of the density matrix elements ($\Delta_{rms} = \sqrt{\sum_{\mu\nu} (D^{new}_{\mu\nu} - D^{old}_{\mu\nu})^2}$) is less than the predefined threshold, the SCF optimization is finished. If not, go back to step 6.

8 Restricted Hartree-Fock theory (RHF) for closed-shell molecules

In the previous section, we discussed how the Hartree-Fock equations can be solved efficiently by expressing the spin-orbitals as the linear combination of the atomic orbitals. As the number of the atomic orbitals increases and the number of the C^i_μ coefficients in Eq. (40) grows, solving the Hartree-Fock equations becomes more expensive computationally. In this section, we will briefly discuss how we can reduce the cost of solving the Hartree-Fock equations for molecules with closed electronic shells (all electrons are paired).

First, we recall that the spin-orbitals $|\psi(x_i)\rangle$ are the functions of the spatial and spin coordinates of the electrons and that they can be expressed as $|\psi(x_i)\rangle = |\phi(i)\rangle\, |\sigma(i)\rangle$, where $|\phi(i)\rangle$ is the spatial orbital and $|\sigma(i)\rangle$ is the spin function (we use $|\sigma(i)\rangle = |\alpha(i)\rangle$ for the spin-up electron and $|\sigma(i)\rangle = |\beta(i)\rangle$ for the spin-down electron). Thus, every spin-orbital $|\psi_i\rangle$ can be assigned a particular spin and labeled by the corresponding spin function (either α or β). If we expand $|\psi_i\rangle$ using Eq. (40), solving the Hartree-Fock equations would require finding the orbital coefficients C^i_μ for every spin-orbital independently of its spin, even if some of the spin-orbitals with opposite spins share the same spatial orbital $|\phi(i)\rangle$. This situation is common in closed-shell molecules, where every α spin-orbital shares the same spatial orbital with one of the

β spin-orbitals (i.e., all electrons are paired). We can take advantage of that by *restricting* the α spin-orbitals to have the same orbital coefficients C^i_μ as the β spin-orbitals, thus, reducing the number of the independent variables in the Hartree-Fock equations by a factor of two. In this case, the Hartree-Fock equations can be formulated entirely in terms of the spatial orbitals by integrating over the spin coordinates of the electrons. Using the orthonormality of the spin functions ($\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1$, $\langle\alpha|\beta\rangle = 0$), the Hartree-Fock energy expression can be written as:

$$E_{\mathrm{HF}} = 2\sum_{i}^{n/2} \langle i|\hat{h}|i\rangle + \sum_{ij}^{n/2}(2\,\langle ij|ij\rangle - \langle ij|ji\rangle) \ , \tag{53}$$

where the indices i and j now refer to the spatial orbitals $|\phi_i\rangle$ and $|\phi_j\rangle$, the one- and two-electron integrals are defined in terms of the spatial orbitals [$\langle i|\hat{h}|i\rangle \equiv \langle\phi_i(1)|\hat{h}|\phi_i(1)\rangle$, $\langle ij|ij\rangle = \langle\phi_i(1)\phi_j(2)|\phi_i(1)\phi_j(2)\rangle$], and the summations run over the number of doubly occupied orbitals ($n/2$). In the atomic-orbital basis, Eq. (53) takes the form:

$$E_{\mathrm{HF}} = 2\sum_{\mu\nu}^{N} D_{\mu\nu}\,\langle\mu|\hat{h}|\nu\rangle + \sum_{\mu\nu\rho\sigma}^{N} D_{\mu\rho}D_{\nu\sigma}(2\,\langle\mu\nu|\rho\sigma\rangle - \langle\mu\nu|\sigma\rho\rangle) \ , \tag{54}$$

where $D_{\mu\nu}$ is the spinless (or spatial-orbital) density matrix:

$$D_{\mu\nu} = \sum_{i}^{n/2} C^{i*}_{\mu} C^{i}_{\nu} \ . \tag{55}$$

The Fock operator can be written as:

$$f_{ij} = \langle i|\hat{h}|j\rangle + \sum_{k}^{n/2}(2\,\langle ik|jk\rangle - \langle ik|kj\rangle) \ , \tag{56}$$

while in the atomic orbital basis it has the following form:

$$F_{\mu\nu} = \langle\mu|\hat{h}|\nu\rangle + \sum_{\rho\sigma}^{N} D_{\rho\sigma}(2\,\langle\mu\rho|\nu\sigma\rangle - \langle\mu\rho|\sigma\nu\rangle) \ . \tag{57}$$

Using Eq. (57), the Hartree-Fock energy can be written as:

$$E_{\mathrm{HF}} = \sum_{\mu\nu}^{N} D_{\mu\nu}(\langle\mu|\hat{h}|\nu\rangle + F_{\mu\nu}) \ . \tag{58}$$