

Advanced Quantum Mechanics & Spectroscopy (CHEM 7520)

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Week 7-8: Advanced electronic structure theory

VI. RESTRICTED HARTREE-FOCK THEORY (RHF) FOR CLOSED-SHELL MOLECULES

1) Previously, we derived equations of Hartree-Fock theory in terms of the spin-orbitals $|\psi_i\rangle$. These equations are general, they can be applied to closed-shell molecules (all electrons are paired) and open-shell molecules (some electrons are unpaired). Before we discuss how the Hartree-Fock equations are solved in practice, we will introduce one simplification: we will assume that the molecule of interest is closed-shell. In this case, the Hartree-Fock equations can be fully expressed in terms of the spatial orbitals.

2) We have already derived equations for closed-shell molecules within the Hartree approximation. Since the Hartree energy expression includes the one-electron and the Coulomb two-electron terms that appear in the Hartree-Fock energy expression, we can reuse the results of our derivation.

$$E_{\text{HF}} = E_{\text{H}} - \sum_{i>j} \langle ij | ji \rangle \quad (1)$$

As before, we assume that N is the (even) number of electrons and that the first N spin-orbitals are occupied. Half of the electrons will occupy the first $N/2$ spatial orbitals with spin α and the other half will occupy $N/2$ spatial orbitals with spin β . Using the convention

$$|\psi_{2i-1}(1)\rangle = |\phi_i(1)\rangle |\alpha(1)\rangle \quad (2)$$

$$|\psi_{2i}(1)\rangle = |\phi_i(1)\rangle |\beta(1)\rangle \quad i = 1, \dots, N/2 \quad (3)$$

the Hartree energy of a closed-shell molecule can be written as:

$$E_{\text{H}} = 2 \sum_i^{N/2} \langle \phi_i | \hat{h} | \phi_i \rangle + 4 \sum_{i>j}^{N/2} \langle \phi_i \phi_j | \frac{1}{r_{12}} | \phi_i \phi_j \rangle \quad (4)$$

We now consider the exchange term. As for the Coulomb term, there are four types of exchange integrals corresponding to different combinations of spin labels. For the $\langle 2i2j|2j2i \rangle$ and $\langle (2i-1)(2j-1)|(2j-1)(2i-1) \rangle$ types, we get:

$$\begin{aligned}\langle 2i2j|2j2i \rangle &= \int \phi_i^*(1)\beta^*(1)\phi_j^*(2)\beta^*(2)\frac{1}{r_{12}}\phi_j(1)\beta(1)\phi_i(2)\beta(2) d1 d2 \\ &= \langle \phi_i\phi_j|\frac{1}{r_{12}}|\phi_j\phi_i \rangle = \langle (2i-1)(2j-1)|(2j-1)(2i-1) \rangle\end{aligned}\quad (5)$$

For the $\langle (2i-1)2j|2j(2i-1) \rangle$ type, we get:

$$\begin{aligned}\langle (2i-1)2j|2j(2i-1) \rangle &= \int \phi_i^*(1)\alpha^*(1)\phi_j^*(2)\beta^*(2)\frac{1}{r_{12}}\phi_j(1)\beta(1)\phi_i(2)\alpha(2) d1 d2 \\ &= 0\end{aligned}\quad (6)$$

Similarly,

$$\langle 2i(2j-1)|(2j-1)2i \rangle = 0\quad (7)$$

Thus, the closed-shell Hartree-Fock energy can be written as:

$$\begin{aligned}E_{\text{HF}} &= E_{\text{H}} - 2 \sum_{i>j}^{N/2} \langle \phi_i\phi_j|\frac{1}{r_{12}}|\phi_j\phi_i \rangle \\ &= 2 \sum_i^{N/2} \langle \phi_i|\hat{h}|\phi_i \rangle + \sum_{i>j}^{N/2} (4 \langle \phi_i\phi_j|\frac{1}{r_{12}}|\phi_i\phi_j \rangle - 2 \langle \phi_i\phi_j|\frac{1}{r_{12}}|\phi_j\phi_i \rangle) \\ &= 2 \sum_i^{N/2} \langle i|\hat{h}|i \rangle + \sum_{i>j}^{N/2} (4 \langle ij|ij \rangle - 2 \langle ij|ji \rangle)\end{aligned}\quad (8)$$

$$= 2 \sum_i^{N/2} \langle i|\hat{h}|i \rangle + \sum_{ij}^{N/2} (2 \langle ij|ij \rangle - \langle ij|ji \rangle)\quad (9)$$

where in the last two steps we redefined the one- and two-electron integrals in terms of the spatial orbitals ($\langle i|\hat{h}|i \rangle = \langle \phi_i|\hat{h}|\phi_i \rangle$ and $\langle ij|kl \rangle = \langle \phi_i\phi_j|\frac{1}{r_{12}}|\phi_k\phi_l \rangle$). Following a similar derivation, the elements of the Fock matrix can be expressed in the spatial orbital basis as follows:

$$f_{ij} = \langle i|\hat{h}|j \rangle + \sum_k^{N/2} (2 \langle ik|jk \rangle - \langle ik|kj \rangle)\quad (10)$$

3) Solving the Hartree-Fock equations in the basis of spatial orbitals allows to greatly reduce the computational cost. If K is the number of spin-orbitals, the number of spatial orbitals is just $K/2$. While the total number of two-electron integrals in the spin-orbital basis is K^4 , there are only $K^4/8$ two-electron integrals in the spatial-orbital basis. In our derivation we took advantage of the fact that in closed-shell molecules the spin-orbitals with spins α and β are constrained (or restricted) to have the same spatial orbitals. For this reason, this formulation of the Hartree-Fock theory is called the *restricted Hartree-Fock theory* (RHF).

VII. RESTRICTED HARTREE-FOCK THEORY IN THE ATOMIC ORBITAL BASIS

1) The Hartree-Fock equations can be solved by representing the orbitals on a three-dimensional real-space grid where each grid point contains information about the value of the orbital at a given position in space. To compute the integrals (e.g., $\langle i|\hat{h}|j\rangle$ or $\langle ij|kl\rangle$), the orbitals can be integrated numerically. However, a much more common and efficient way to solve the Hartree-Fock equations is to express the orbitals as linear combinations of the atom-centered basis functions (so-called “**atomic orbitals**”):

$$|\phi_i\rangle = \sum_{\mu}^n C_{\mu}^i |\chi_{\mu}\rangle \quad (11)$$

where n is the total number of atomic orbitals. Note that we will use Greek letters μ, ν, \dots to index the atomic orbitals.

2) In the simplest case, each basis function $|\chi_{\mu}\rangle$ can be represented as a single Gaussian-type function defined in the Cartesian space (so-called **Gaussian-type orbital**, GTO):

$$|\chi_{\mu}^{\text{GTO}}(r)\rangle = N_c x^k y^l z^m e^{-\alpha_{\mu} r^2} \quad (12)$$

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 k, l, m 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):

$$|\chi_\mu(r)\rangle = \sum_{\nu} c_{\nu} |\chi_{\nu}^{\text{GTO}}(r)\rangle \quad (13)$$

This allows to reduce the number of integrals that need to be evaluated during a computation without sacrificing the accuracy. We will discuss the basis sets in more detail later.

3) In the atomic-orbital formulation of the Hartree-Fock theory, the problem of finding the optimal orbitals $|\phi_i\rangle$ is reduced to the problem of finding the best C_{μ}^i coefficients that minimize the Hartree-Fock energy for 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), which corresponds to the best (in the variational sense) Hartree-Fock wavefunction.

4) We can now use Eq. (11) to formulate the equations of the RHF theory in the atomic orbital basis. First, we consider expression for the energy:

$$\begin{aligned} E &= 2 \sum_i^{N/2} \langle i | \hat{h} | i \rangle + \sum_{ij}^{N/2} (2 \langle ij | ij \rangle - \langle ij | ji \rangle) \\ &= 2 \sum_i^{N/2} \sum_{\mu\nu}^n C_{\mu}^{i*} C_{\nu}^i \langle \mu | \hat{h} | \nu \rangle + \sum_{ij}^{N/2} \sum_{\mu\nu\rho\sigma}^n C_{\mu}^{i*} C_{\nu}^{j*} C_{\rho}^i C_{\sigma}^j (2 \langle \mu\nu | \rho\sigma \rangle - \langle \mu\nu | \sigma\rho \rangle) \\ &= 2 \sum_{\mu\nu}^n D_{\mu\nu} \langle \mu | \hat{h} | \nu \rangle + \sum_{\mu\nu\rho\sigma}^n D_{\mu\rho} D_{\nu\sigma} (2 \langle \mu\nu | \rho\sigma \rangle - \langle \mu\nu | \sigma\rho \rangle) \end{aligned} \quad (14)$$

where $\langle \mu | \hat{h} | \nu \rangle \equiv \langle \chi_{\mu} | \hat{h} | \chi_{\nu} \rangle$, $\langle \mu\nu | \rho\sigma \rangle \equiv \langle \chi_{\mu} \chi_{\nu} | \frac{1}{r_{12}} | \chi_{\rho} \chi_{\sigma} \rangle$, and we defined the **density matrix \mathbf{D}** that can be expressed in terms of the orbital coefficients as:

$$D_{\mu\nu} = \sum_i^{N/2} C_{\mu}^{i*} C_{\nu}^i \quad (15)$$

5) We see that the energy in Eq. (14) 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., about the orbitals) is now included in the density matrix. This demonstrates an important advantage of solving the Hartree-Fock equations in the atomic-orbital basis: as the molecular orbitals change during

the SCF iterations, only the density matrix changes, while the atomic-orbital one- and two-electron integrals do not. As a result, the one- and two-electron integrals can be computed only once (usually, before the start of the SCF iterations) and stored in memory for later use, which significantly reduces the computational cost of the Hartree-Fock theory.

6) Let us now turn our attention to the Hartree-Fock equations. Starting with these equations in the spatial-orbital basis, we obtain:

$$\begin{aligned} \hat{f}|\phi_i\rangle &= \varepsilon_i|\phi_i\rangle \\ \sum_{\mu}^n \langle v|\hat{f}|\mu\rangle C_{\mu}^i &= \varepsilon_i \sum_{\mu}^n \langle v|\mu\rangle C_{\mu}^i = \varepsilon_i \sum_{\mu}^n S_{v\mu} C_{\mu}^i \end{aligned} \quad (16)$$

where we multiplied by $\langle\chi_v|$ on the left and defined the **overlap matrix** $S_{\mu\nu} = \langle\mu|\nu\rangle$. In the matrix form, Eq. (16) can be written as:

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon} \quad (17)$$

where $\boldsymbol{\varepsilon}$ 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:

$$F_{\mu\nu} = \langle\mu|\hat{h}|\nu\rangle + \sum_{\rho\sigma}^n D_{\rho\sigma} (2\langle\mu\rho|\nu\sigma\rangle - \langle\mu\rho|\sigma\nu\rangle) \quad (18)$$

7) We note that while in the spin- or spatial-orbital basis solving the Hartree-Fock equations involves diagonalizing the Fock matrix, 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. (17). In other words, Eq. (17) is no longer a simple eigenvalue problem, it is a *generalized eigenvalue problem*. Nevertheless, we can still solve Eq. (17) rather efficiently using a simple mathematical technique.

8) First, we construct an auxiliary matrix: the inverse square-root overlap matrix ($\mathbf{S}^{-1/2}$). 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 \mathbf{S} matrix eigenvectors:

$$\sum_{\mu\nu} U_{\mu\mu'} S_{\mu\nu} U_{\nu\nu'} = s_{\mu'} \delta_{\mu'\nu'}$$

$$(S^{-1/2})_{\mu\nu} = \sum_{\mu'} U_{\mu\mu'} \frac{1}{\sqrt{s_{\mu'}}} U_{\nu\mu'} \quad (19)$$

Multiplying both sides of Eq. (17) by $S^{-1/2}$ from the left, we obtain:

$$\begin{aligned} S^{-1/2} \mathbf{F} S^{-1/2} S^{1/2} \mathbf{C} &= S^{-1/2} \mathbf{S} \mathbf{C} \boldsymbol{\epsilon} \\ \tilde{\mathbf{F}} \tilde{\mathbf{C}} &= \tilde{\mathbf{C}} \boldsymbol{\epsilon} \end{aligned} \quad (20)$$

9) Eq. (20) suggests that the generalized eigenvalue problem (17) can be converted to a standard eigenvalue problem with the modified (transformed) Fock matrix:

$$\tilde{\mathbf{F}} = S^{-1/2} \mathbf{F} S^{-1/2} \quad (21)$$

We can solve Eq. (20) 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:

$$\tilde{\mathbf{C}} = S^{1/2} \mathbf{C} \quad (22)$$

Thus, in order to obtain the orbital coefficients \mathbf{C} , we first construct the $\tilde{\mathbf{F}}$ matrix, diagonalize it, and then compute $\mathbf{C} = S^{-1/2} \tilde{\mathbf{C}}$.

10) The procedure that we used to solve the generalized eigenvalue problem in Eq. (20) 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 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.

11) We can now summarize the general procedure for solving the RHF equations and computing the RHF energy using the atomic orbital basis. In short, here are the key steps of the self-consistent field (SCF) optimization:

- (a) Given the atomic-orbital basis set, compute the one- and two-electron integrals in this basis.
- (b) Using the overlap matrix \mathbf{S} , form the $S^{-1/2}$ matrix according to Eq. (19).

- (c) Form the initial (guess) Fock matrix according to Eq. (18), but neglecting the contribution from the two-electron integrals.
- (d) Using the initial Fock matrix, solve the generalized eigenvalue problem as shown in Eq. (20) and compute the initial (guess) orbitals as $\mathbf{C} = \mathbf{S}^{-1/2} \tilde{\mathbf{C}}$.
- (e) Form the density matrix (Eq. (15)).
- (f) Form the new Fock matrix including the contribution from the two-electron integrals (Eq. (18)).
- (g) Compute the Hartree-Fock energy. Note that the energy expression (14) can be expressed in terms of the Fock matrix elements:

$$E = \sum_{\mu\nu}^n D_{\mu\nu} (\langle \mu | \hat{h} | \nu \rangle + F_{\mu\nu}) \quad (23)$$

- (h) Using the new Fock matrix, solve the generalized eigenvalue problem as shown in Eq. (20) and compute the new orbitals as $\mathbf{C} = \mathbf{S}^{-1/2} \tilde{\mathbf{C}}$.
- (i) Form the new density matrix (Eq. (15)).
- (j) Check convergence. If the change in the energy and the RMS of the density matrix elements ($\Delta_{rms} = \sqrt{\sum_{\mu\nu} (D_{\mu\nu}^{new} - D_{\mu\nu}^{old})^2}$) is less than the predefined threshold, the SCF optimization is finished. If not, go back to step (f).