

18.1: Optimization of the Energy for a Multiconfiguration Wavefunction

The Energy Expression

The most straightforward way to introduce the concept of optimal molecular orbitals is to consider a trial wavefunction of the form which was introduced earlier in Chapter 9.2. Consider a multi-electron wavefunction of the multiconfigurational form

$$\Psi = \sum_I^M C_I \Phi_I$$

where Φ_I is a space- and spin-adapted configuration state function (CSF) consisting of determinantal wavefunctions of spin-orbitals (ϕ_i):

$$\Phi_I = |\phi_{I1} \phi_{I2} \phi_{I3} \dots \phi_{IN}|.$$

The expectation value of the Hamiltonian with this wavefunction

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

can be expanded as:

$$E = \sum_{I=1}^M \sum_{J=1}^M C_I C_J \langle \Phi_I | \hat{H} | \Phi_J \rangle.$$

The spin- and space-symmetry of the Φ_I SCFs determine the symmetry of the state Ψ whose energy is to be optimized. In this form, it is clear that E is a quadratic function of the C_I amplitudes C_J ; it is a quartic functional of the spin-orbitals because the Slater-Condon rules express each $\langle \Phi_I | \hat{H} | \Phi_J \rangle$ CI matrix element in terms of one- and two-electron integrals $\langle \phi_i | f | \phi_j \rangle$ and $\langle \phi_i \phi_j | g | \phi_k \phi_l \rangle$ over these spin-orbitals.

The Fock and Secular Equations

The **variational** method can be used to optimize the above expectation value expression for the electronic energy (i.e., to make the functional stationary) as a function of the CI coefficients C_J and the LCAO-MO coefficients $\{C_{\nu,i}\}$ that characterize the spin-orbitals. However, in doing so the set of $\{C_{\nu,i}\}$ can not be treated as entirely independent variables. The fact that the spin-orbitals $\{\phi_i\}$ are assumed to be orthonormal imposes a set of constraints on the $\{C_{\nu,i}\}$:

$$\langle \phi_i | \phi_j \rangle = \delta_{i,j} = \sum_{\mu,\nu} C_{\mu,i}^* \langle \chi_\mu | \chi_\nu \rangle C_{\nu,j}$$

These constraints can be enforced within the variational optimization of the energy function mentioned above by introducing a set of Lagrange multipliers $\{\epsilon_{i,j}\}$, one for each constraint condition, and subsequently differentiating

$$E - \sum_{i,j} \epsilon_{i,j} \left[\delta_{i,j} - \sum_{\mu,\nu} C_{\mu,i}^* \langle \chi_\mu | \chi_\nu \rangle C_{\nu,j} \right]$$

with respect to each of the $C_{\nu,i}$ variables.

Upon doing so, the following set of equations is obtained (early references to the derivation of such equations include A. C. Wahl, J. Chem. Phys. 41,2600 (1964) and F. Grein and T. C. Chang, Chem. Phys. Lett. 12, 44 (1971) and R. Shepard, p 63, in Adv. in Chem. Phys. LXIX, K. P. Lawley, Ed., WileyInterscience, New York (1987); the subject is also treated in the textbook **Second Quantization Based Methods in Quantum Chemistry**, P. Jørgensen and J. Simons, Academic Press, New York (1981)):

$$\sum_{J=1}^M H_{I,J} C_J = E C_I \quad (18.1.1)$$

with $I = 1, 2, \dots M$ and

$$F \phi_i = \sum_j \epsilon_{i,j} \phi_j, \quad (18.1.2)$$

where the $\epsilon_{i,j}$ are Lagrange multipliers.

The set of equations in Equation 18.1.1 that govern the $\{C_J\}$ amplitudes are called the **CI-secular equations**. The set of equations in Equation 18.1.2 that determine the LCAO-MO coefficients of the spin-orbitals $\{\phi_j\}$ are called the **Fock equations**. The Fock operator F is given in terms of the one- and two-electron operators in H itself as well as the so-called one- and two-electron density matrices $\gamma_{i,j}$ and $\Gamma_{i,j,k,l}$ which are defined below. These density matrices reflect the averaged occupancies of the various spin orbitals in the CSFs of Ψ . The resultant expression for F is:

$$F\phi_i = \sum_j \gamma_{i,j} h\phi_j + \sum_{j,k,l} \Gamma_{i,j,k,l} J_{k,l}\phi_k,$$

where h is the one-electron component of the Hamiltonian (i.e., the kinetic energy operator and the sum of coulombic attractions to the nuclei). The operator $J_{j,l}$ is defined by:

$$J_{j,l}\phi_k(r) = \int \phi_j^*(r')\phi_l(r') \frac{1}{|r-r'|} d\tau \phi_k(r),$$

where the integration denoted $d\tau'$ is over the spatial and spin coordinates. The so-called spin integration simply means that the α or β spin function associated with ϕ_l must be the same as the α or β spin function associated with ϕ_j or the integral will vanish. This is a consequence of the orthonormality conditions $\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1$, $\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0$

One- and Two- Electron Density Matrices

The density matrices introduced above can most straightforwardly be expressed in terms of the CI amplitudes and the nature of the orbital occupancies in the CSFs of Ψ as follows:

1. $\gamma_{i,i}$ is the sum over all CSFs, in which ϕ_i is occupied, of the square of the CI coefficient of that CSF:

$$\gamma_{i,i} = \sum_I (\text{with } \phi_i \text{ occupied}) C_I^2.$$

2. $\gamma_{i,j}$ is the sum over pairs of CSFs which differ by a single spin-orbital occupancy (i.e., one having ϕ_i occupied where the other has ϕ_j occupied after the two are placed into maximal coincidence-the sign factor (sign) arising from bringing the two to maximal coincidence is attached to the final density matrix element):

$$\gamma_{i,j} = \sum_{I,J} (\text{sign})(\text{with } \phi_i \text{ occupied in } I \text{ where } \phi_j \text{ is in } J) C_I C_J.$$

The two-electron density matrix elements are given in similar fashion:

3. $\Gamma_{i,j,i,j} = \sum_I (\text{with both } \phi_i \text{ and } \phi_j \text{ occupied}) C_I C_I$

4. $\Gamma_{i,j,j,i} = -\sum_I (\text{with both } \phi_i \text{ and } \phi_j \text{ occupied}) C_I C_I = -\Gamma_{i,j,i,j}$ (it can be shown, in general that $\Gamma_{i,j,k,l}$ is odd under exchange of i and j , odd under exchange of k and l and even under $(i,j) \leftrightarrow (k,l)$ exchange; this implies that $\Gamma_{i,j,k,l}$ vanishes if $i = j$ or $k = l$);

5. $\Gamma_{i,j,k,j} = \sum_{I,J} (\text{sign})(\text{with } \phi_j \text{ in both } I \text{ and } J \text{ and } \phi_i \text{ in } I \text{ where } \phi_k \text{ is in } J) C_I C_J$

$$= \Gamma_{j,i,j,k} = -\Gamma_{i,j,j,k} = -\Gamma_{j,i,l,k};$$

6. $\Gamma_{i,j,k,l} = \sum_{I,J} (\text{sign})(\text{with } \phi_i \text{ in } I \text{ where } \phi_k \text{ is in } J \text{ and } \phi_j \text{ in } I \text{ where } \phi_l \text{ is in } J) C_I C_J$

$$= \Gamma_{j,i,l,k} = -\Gamma_{j,i,j,l} = -\Gamma_{i,j,l,k} = \Gamma_{j,i,l,k}.$$

These density matrices are themselves quadratic functions of the CI coefficients and they reflect all of the permutational symmetry of the determinantal functions used in constructing Ψ ; they are a compact representation of all of the Slater-Condon rules as applied to the particular CSFs which appear in Ψ . They contain all information about the spin-orbital occupancy of the CSFs in Ψ . The one- and two- electron integrals $\langle\phi_i|f|\phi_j\rangle$ and $\langle\phi_i\phi_j|g|\phi_k\phi_l\rangle$ contain all of the information about the magnitudes of the kinetic and Coulombic interaction energies.

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