

Electronic Structure Theory

TSTC Session 5



1. Born-Oppenheimer approx.- energy surfaces
2. Mean-field (Hartree-Fock) theory- orbitals
3. Pros and cons of HF- RHF, UHF
4. Beyond HF- why?
5. **First, one usually does HF-how?**
6. Basis sets and notations
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How does one determine the spin-orbitals ϕ_J and then how does one determine the CI coefficients C_J ?

The orbitals are usually determined by first carrying out a **HF calculation**. This is not done (except in rare cases) by solving the HF second order partial differential equations in $3N$ dimensions on a spatial grid but by expanding the ϕ_J in terms of so-called atomic orbital (**AO**) (because they usually are centered on atoms) **basis functions** using the **LCAO-MO** expansion:

$$\phi_J(\mathbf{r}|\mathbf{R}) = \sum_{\mu=1,M} \chi_{\mu}(\mathbf{r}|\mathbf{R}) C_{J,\mu}$$

This reduces the HF calculation to a **matrix eigenvalue equation**

$$\sum_{\mu=1,M} \langle \chi_{\nu} | h_e | \chi_{\mu} \rangle C_{J,\mu} = \epsilon_J \sum_{\mu=1,M} \langle \chi_{\nu} | \chi_{\mu} \rangle C_{J,\mu}$$

Here, h_e is the Fock operator- kinetic, nuclear attraction, J-K and nuclear repulsion

The **Fock-operator** (F or h_e) matrix elements needed to carry out such a calculation are:

$$\begin{aligned} \langle \chi_\nu | h_e | \chi_\mu \rangle = & \langle \chi_\nu | -\hbar^2/2m \nabla^2 | \chi_\mu \rangle + \sum_A \langle \chi_\nu | -Z_A e^2/|r-R_A| | \chi_\mu \rangle \\ & + \sum_{\eta,\kappa} \sum_{K=occ} C_{K,\eta} C_{K,\gamma} [\langle \chi_\nu(r) \chi_\eta(r') | (e^2/|r-r'|) | \chi_\mu(r) \chi_\gamma(r') \rangle \\ & - \langle \chi_\nu(r) \chi_\eta(r') | (e^2/|r-r'|) | \chi_\gamma(r) \chi_\mu(r') \rangle] \end{aligned}$$

and the overlap integrals: $\langle \chi_\nu | \chi_\mu \rangle$.

The nuclear repulsion energy $\sum_{A<B} Z_A Z_B / |\mathbf{R}_A - \mathbf{R}_B|$ is included but it is often not explicitly displayed.

The quantity $\gamma_{\eta,\kappa} = \sum_{K=occ} C_{K,\eta} C_{K,\gamma}$ is called the one-electron **density matrix**

The number of these one- and two electron integrals **scales** with the **basis set size** M as M^2 and M^4 .

The computer effort needed to solve the $M \times M$ eigenvalue problem scales as M^3 .

The sum over K runs over all of the **occupied spin-orbitals** in the state studied.

Recall this makes the occupied orbitals “feel” $N-1$ other electrons, but the virtual orbitals “feel” the N occupied spin-orbitals.

To form the elements of the **MxM Fock matrix**:

$$\begin{aligned}
 F_{\mu,\nu} = & \\
 \langle \chi_\nu | h_e | \chi_\mu \rangle = & \langle \chi_\nu | -\hbar^2/2m \nabla^2 | \chi_\mu \rangle + \sum_A \langle \chi_\nu | -Z_A e^2/|r-R_A| | \chi_\mu \rangle \\
 & + \sum_{\eta,\kappa} \sum_{K=\text{occ}} C_{K,\eta} C_{K,\gamma} [\langle \chi_\nu(r) \chi_\eta(r') | (e^2/|r-r'|) | \chi_\mu(r) \chi_\gamma(r') \rangle \\
 & - \langle \chi_\nu(r) \chi_\eta(r') | (e^2/|r-r'|) | \chi_\gamma(r) \chi_\mu(r') \rangle],
 \end{aligned}$$

one needs to already know the LCAO-MO coefficients $C_{K,\mu}$ for the **occupied** MOs.

A so-called **self-consistent field (SCF)** process is used to address this:

SCF: One guesses (eigenfunctions of the Fock operator with all J and K terms ignored are often used, or coefficients from a calculation carried out at a “nearby geometry” are used) the N $C_{K,\mu}$ coefficients of the occupied spin-orbitals.

The $M \times M$ Fock matrix is then formed using these $C_{K,\mu}$ coefficients:

$$\begin{aligned} & \langle \chi_\nu | -\hbar^2/2m \nabla^2 | \chi_\mu \rangle + \sum_A \langle \chi_\nu | -Z_A e^2/|r-R_A| | \chi_\mu \rangle \\ & + \sum_{\eta, \kappa} \sum_{K=\text{occ}} C_{K,\eta} C_{K,\gamma} [\langle \chi_\nu(r) \chi_\eta(r') | (e^2/|r-r'|) | \chi_\mu(r) \chi_\gamma(r') \rangle \\ & \quad - \langle \chi_\nu(r) \chi_\eta(r') | (e^2/|r-r'|) | \chi_\gamma(r) \chi_\mu(r') \rangle] \end{aligned}$$

The HF equations are solved to obtain M sets of “new” $C_{K,\mu}$ coefficients:

Which N ?

$$\sum_\mu \langle \chi_\nu | h_e | \chi_\mu \rangle C_{J,\mu} = \epsilon_J \sum_\mu \langle \chi_\nu | \chi_\mu \rangle C_{J,\mu}$$

N of these “new” $C_{K,\mu}$ coefficients are used to form a “new” Fock matrix.

The HF equations are solved to obtain M “newer” $C_{K,\mu}$ coefficients.

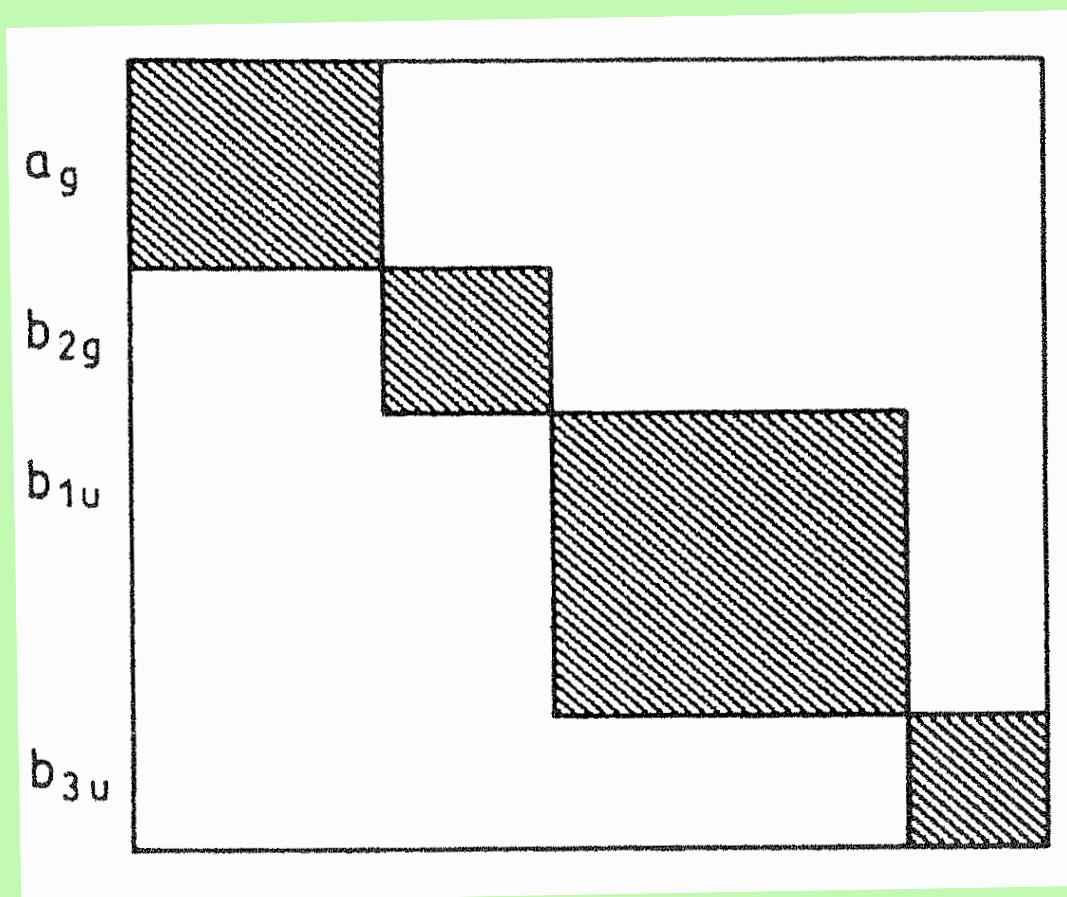
This iterative solution is continued until the $C_{K,\mu}$ coefficients used in one iteration are identical to those obtained in the next solution of the Fock matrix.

One has then achieved self-consistency.

When a molecule has point group **symmetry**, most programs will form symmetry adapted combinations of the basis functions

$$\chi'_v(\mathbf{r}|\mathbf{R}) = \sum_{\mu=1,M} \chi_{\mu}(\mathbf{r}|\mathbf{R}) d_{v,\mu}^{\text{symmetry}}$$

and the HF molecular spin-orbitals will be LCAO-expressed in terms of them. In this case, the **MxM** Fock matrix will be **block-diagonal** as shown below.



It is crucial to understand that it is by “guessing” the initial values of the LCAO-MO coefficients of the N occupied spin-orbitals that one specifies for which electronic state the HF-SCF spin-orbitals are to be obtained.

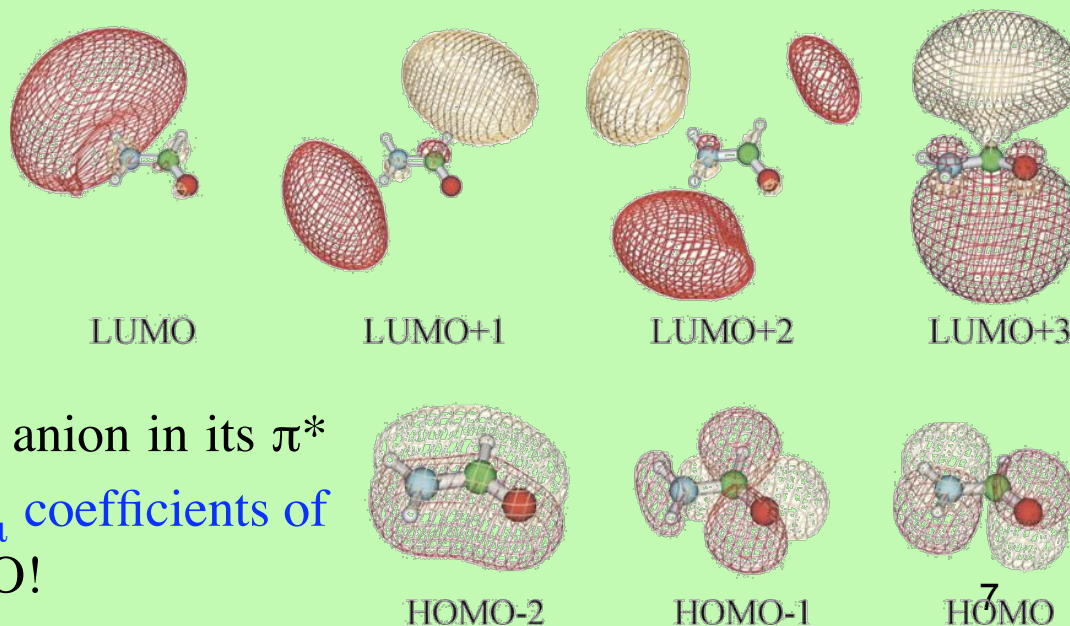
That is, one inputs the $C_{K,\mu}$ coefficients of the N occupied spin-orbitals, then an $M \times M$ Fock matrix is formed and its M eigenvalues ϵ_K and M eigenvectors $C_{K,\mu}$ are obtained.

However, of the M spin-orbitals thus determined, only N are occupied.

One has to be very careful (often by visually examining the HF orbitals) that the spin-orbitals one wants occupied for the electronic state of interest are those included in the list of occupied spin-orbitals in each iteration of the SCF process. This is especially critical when studying excited states where the occupied spin-orbitals are probably not those having the lowest orbital energies ϵ_K . Let's consider an example to illustrate the problem.

Suppose one were interested in studying an **anionic state of formamide** in which the **excess electron occupies** the OCN π^* orbital.

An **SCF calculation** on **neutral formamide** using an *aug-cc-pVDZ* basis set produces the orbitals shown below. The orbital energies for the bonding and non-bonding OCN π MOs (HOMO-2 and HOMO) are -15.4 and -11.5 eV, respectively. The HOMO-1 orbital is a lone pair orbital on the oxygen atom. The **SCF orbital energy** of the lowest unoccupied molecular orbital (**LUMO**) is **+0.72 eV**. However, the **LUMO is not even of π^* symmetry**, nor is the LUMO+1 or the LUMO+2 orbital. The lowest unoccupied orbital of π^* character is the **LUMO+3**, and this orbital has an energy of + 2.6 eV.



So, to study formamide anion in its π^* state, one must “guess” the $C_{K,\mu}$ coefficients of the **LUMO+3** as an occupied MO!

Why UHF Wavefunctions are not eigenfunctions of S^2

$$\begin{aligned} \langle \chi_\nu | h_e | \chi_\mu \rangle &= \langle \chi_\nu | -\hbar^2/2m \nabla^2 | \chi_\mu \rangle + \sum_A \langle \chi_\nu | -Z_A e^2/|r-R_A| | \chi_\mu \rangle \\ &+ \sum_{\eta, \kappa} \sum_K C_{K, \eta} C_{K, \gamma} [\langle \chi_\nu(r) \chi_\eta(r') | (e^2/|r-r'|) | \chi_\mu(r) \chi_\gamma(r') \rangle \\ &- \langle \chi_\nu(r) \chi_\eta(r') | (e^2/|r-r'|) | \chi_\gamma(r) \chi_\mu(r') \rangle]. \end{aligned}$$

Consider **C: $1s^2 2s^2 2p_z \alpha 2p_y \alpha$** 3P

The **matrix elements** of the Fock operator are **different** for an α and a β spin-orbital because the sum:

$$\gamma_{\eta, \kappa} = \sum_K C_{K, \eta} C_{K, \gamma}$$

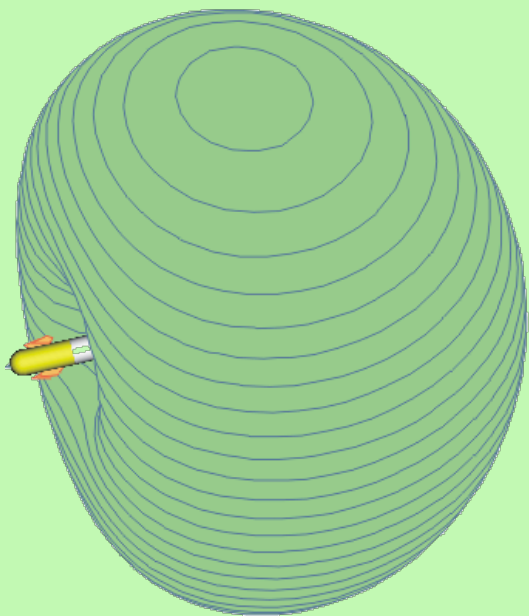
appearing in this density matrix runs over **N** of the occupied spin-orbitals.

When forming matrix elements for **α type orbitals**, there will be Coulomb integrals for $K = 1s\alpha, 1s\beta, 2s\alpha, 2s\beta, 2p_z\alpha$, and $2p_y\alpha$ and exchange integrals for $K = 1s\alpha, 2s\alpha, 2p_z\alpha$, and $2p_y\alpha$.

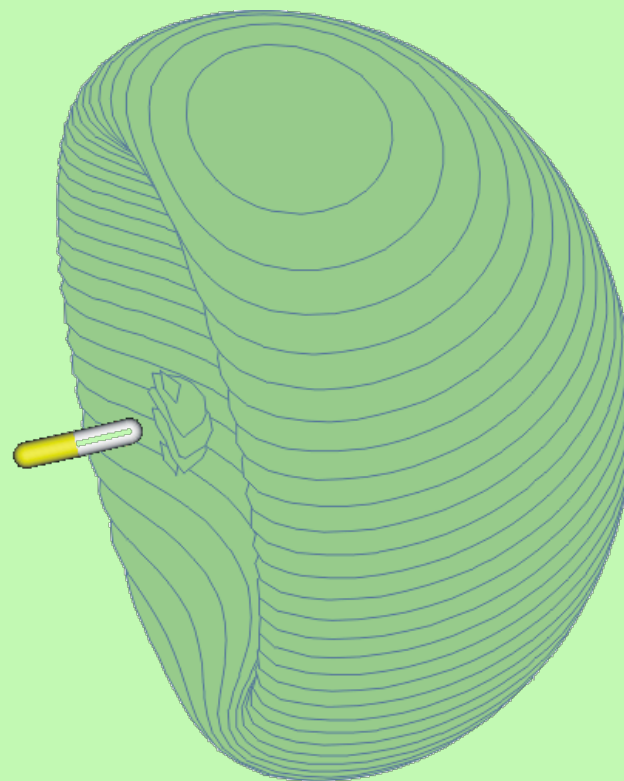
On the other hand, when solving for spin-orbitals of **β type**, there will be Coulomb integrals for $K = 1s\alpha, 1s\beta, 2s\alpha, 2s\beta, 2p_z\alpha$, and $2p_y\alpha$. But exchange contributions only for $K = 1s\beta$ and $2s\beta$.

How much different are the α and β spin-orbitals?

Here are the α (SOMO) and β (LUMO) orbitals of the dipole-bound LiF^-



$$\varepsilon = -0.01219 \text{ Hartrees}$$



$$\varepsilon = +0.10228 \text{ Hartrees}$$

This spin difference means that, even though an **ROHF** wave function

$$| \phi_{1s} \alpha \phi_{1s} \beta \phi_{2s} \alpha \phi_{2s} \beta \phi_{2px} \alpha \phi_{2py} \alpha |$$

is a $M_S = 1$ **triplet** function, the UHF process causes the 1s and 2s spin-orbitals of α and β spin to be different. So, the **UHF** function is really

$$| \phi_{1s} \alpha \phi'_{1s} \beta \phi_{2s} \alpha \phi'_{2s} \beta \phi_{2px} \alpha \phi_{2py} \alpha |$$

Although this function has $M_S = 1$, it is **not a triplet** (because the 1s and 2s spin-orbitals are not coupled together into singlet functions).

Most programs will compute the **expectation value of S^2** (using $S^2 = S_- S_+ + S_Z^2 + \hbar S_Z$)

so one can be aware of how **spin contaminated** the **UHF** function is. The above carbon function should have $S = 1$ (so $S(S+1) = 2$), but it contains components of $S = 1, 2$, and 3 , because each $\phi \alpha \phi' \beta$ spin-orbital product is a mixture of $S = 0$ and $S = 1$.

