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
7. MPn, MCSCF, CI, CC, DFT
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How does one determine the spin-orbitals ϕ_J and then how does one determine the CI coefficients C_J for various methods?

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:

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

This reduces the HF calculation to a matrix eigenvalue equation

$$\Sigma_{\mu=1,M} <\chi_\nu |h_e| \chi_\mu> C_{J,\mu} = \varepsilon_J\, \Sigma_{\mu=1,M} <\chi_\nu|\chi_\mu> C_{J,\mu}$$

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

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

$$\langle\chi_\nu|\, h_e|\,\chi_\mu\rangle = \langle\chi_\nu|\, -\hbar^2/2m\, \nabla^2\, |\chi_\mu\rangle + \Sigma_A\langle\chi_\nu|\, -Z_A e^2/|r-R_A|\, |\chi_\mu\rangle$$

$$+ \Sigma_{\eta,\kappa}\, \Sigma_{K=occ}\, C_{K,\eta}\, C_{K,\gamma}\, [\langle\chi_\nu(r)\,\chi_\eta(r')\,|(e^2/|r-r'|)\,|\,\chi_\mu(r)\,\chi_\gamma(r')\rangle$$

$$-\langle\chi_\nu(r)\,\chi_\eta(r')\,|(e^2/|r-r'|)\,|\,\chi_\gamma(r)\,\chi_\mu(r')\rangle]$$

and the overlap integrals: $S_{\nu,\mu} = \langle\chi_\nu|\chi_\mu\rangle$.

The nuclear repulsion energy $\Sigma_{A<B} Z_Z Z_B e^2/|\mathbf{R}_A-\mathbf{R}_B|$ is included but it is often not explicitly displayed.

The quantity $\gamma_{\eta,\kappa} = \Sigma_{K=occ}\, C_{K,\eta}\, C_{K,\gamma}$ 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 MxM 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:

$$F_{\mu,\nu} =$$

$$<\chi_\nu|\, h_e|\, \chi_\mu> = <\chi_\nu|\, -\hbar^2/2m\, \nabla^2\, |\chi_\mu> + \Sigma_A <\chi_\nu|\, -Z_A e^2/|r-R_A|\, |\chi_\mu>$$

$$+ \Sigma_{\eta,\kappa} \Sigma_{K=occ}\, C_{K,\eta}\, C_{K,\gamma}\, [<\chi_\nu(r)\, \chi_\eta(r')\, |(e^2/|r-r'|)\, |\, \chi_\mu(r)\, \chi_\gamma(r')>$$

$$-<\chi_\nu(r)\, \chi_\eta(r')\, |(e^2/|r-r'|)\, |\, \chi_\gamma(r)\, \chi_\mu(r')>],$$

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 K=1, ..N $\{C_{K,\mu}\}$ coefficients of the occupied spin-orbitals.

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

$$\langle\chi_\nu| -\hbar^2/2m\ \nabla^2 |\chi_\mu\rangle + \Sigma_A\langle\chi_\nu| -Z_A e^2/|r-R_A|\ |\chi_\mu\rangle$$

$$+ \Sigma_{\eta,\kappa}\Sigma_{K=occ}\ C_{K,\eta}\ C_{K,\gamma}\ [\langle\chi_\nu(r)\ \chi_\eta(r')\ |(e^2/|r-r'|)\ |\ \chi_\mu(r)\ \chi_\gamma(r')\rangle$$

$$-\ \langle\chi_\nu(r)\ \chi_\eta(r')\ |(e^2/|r-r'|)\ |\ \chi_\gamma(r)\ \chi_\mu(r')\rangle]$$

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

Which N?

$$\Sigma_\mu \langle\chi_\nu\ |h_e|\ \chi_\mu\rangle\ C_{J,\mu} = \varepsilon_J\ \Sigma_\mu \langle\chi_\nu|\chi_\mu\rangle\ C_{J,\mu}$$

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.

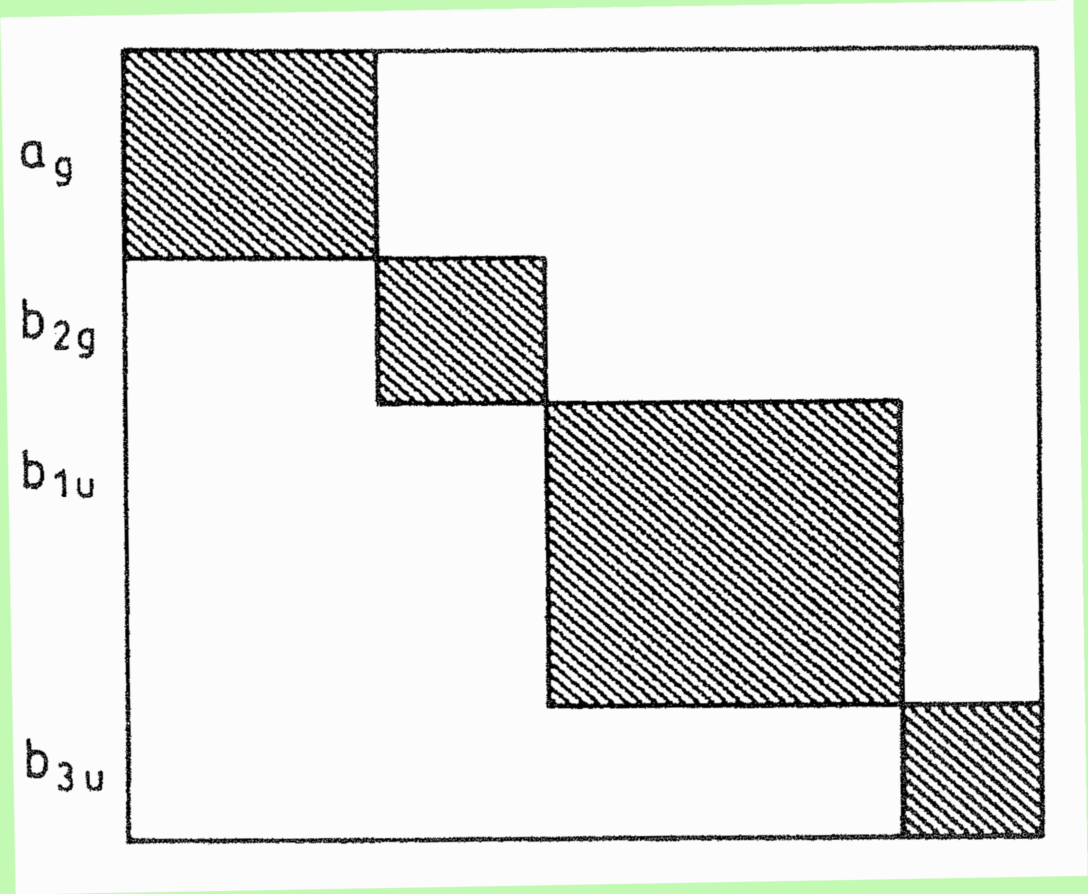
This iterative solution is continued until the $C_{K,\mu}$ coefficients used in one iteration are identical to those obtained in the next solution of the Fock matrix.

One has then achieved self-consistency.

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

$$\chi'_\nu(\mathbf{r}|\mathbf{R}) = \Sigma_{\mu=1,M}\, \chi_\mu(\mathbf{r}|\mathbf{R})\, d^{\text{symmetry}}_{\nu,\mu}$$

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.



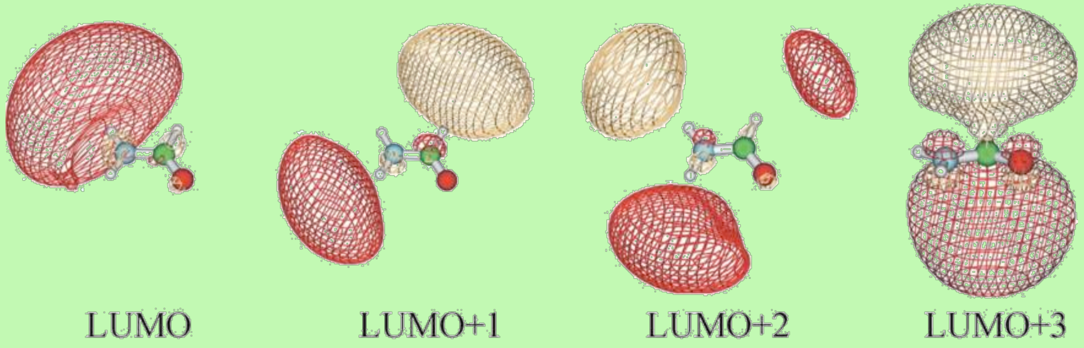
It is crucial to understand that it is by “guessing” the initial values of the LCAO-MO coefficients of the N occupied spin-orbitals that one specifies for which electronic state the HF-SCF spin-orbitals are to be obtained.

That is, one inputs the $C_{K,\mu}$ coefficients of the N occupied spin-orbitals, then an MxM 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.

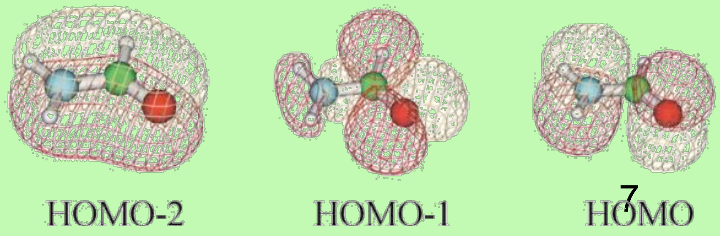
One has to be very careful (often by visually examining the HF orbitals) that the spin-orbitals one wants occupied for the electronic state of interest are those included in the list of occupied spin-orbitals in each iteration of the SCF process. This is especially critical when studying excited states 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

$$<\chi_\nu| h_e| \chi_\mu> = <\chi_\nu| -\hbar^2/2m \nabla^2 |\chi_\mu> + \Sigma_A <\chi_\nu| -Z_A e^2/|r-R_A| |\chi_\mu>$$

$$+ \Sigma_{\eta,\kappa}\Sigma_K C_{K,\eta} C_{K,\gamma} [<\chi_\nu(r) \chi_\eta(r') |(e^2/|r-r'|) | \chi_\mu(r) \chi_\gamma(r')>$$

$$- <\chi_\nu(r) \chi_\eta(r') |(e^2/|r-r'|) | \chi_\gamma(r) \chi_\mu(r')>].$$

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:

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

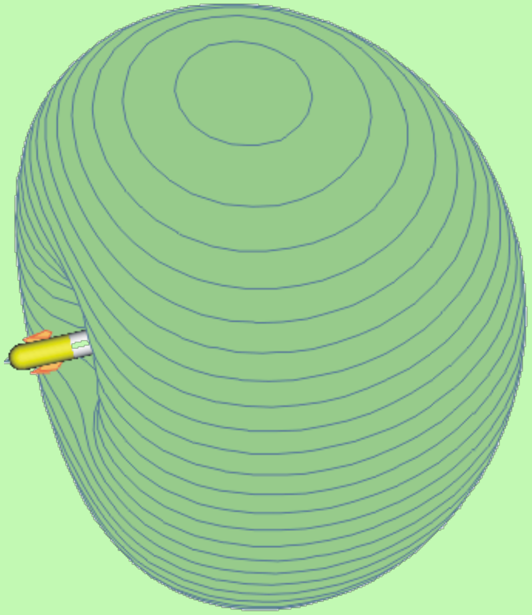
appearing in this density matrix runs over N of the occupied spin-orbitals.

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 $2p_y\alpha$.

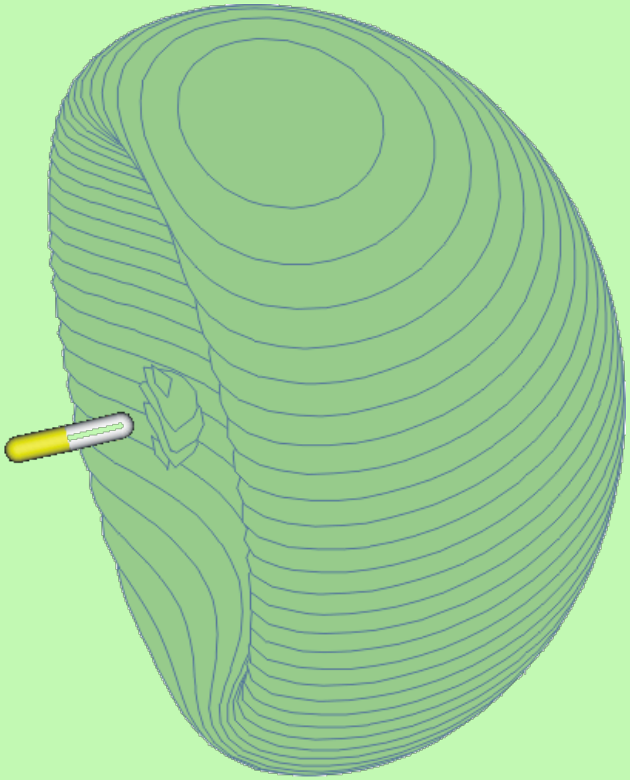
On the other hand, when solving for spin-orbitals of *β type*, there will be Coulomb integrals for K = $1s\alpha$, $1s\beta$, $2s\alpha$, $2s\beta$, $2p_z\alpha$, and $2p_y\alpha$. But exchange contributions only for K = $1s\beta$ and $2s\beta$.

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

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



ε = – 0.01219 Hartrees



ε = + 0.10228 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 φα φ'β spin-orbital product is a mixture of S = 0 and S =1.