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# ***Koopmans' theorems, the Hartree-Fock-Roothaan method, UHF/RHF and projected HF, successes & failures of Hartree-Fock***

## ***References***

- [Physics of Atoms and Molecules, Second Edition](#), B.H. Bransden and C.J. Joachain
- [Methods of Electronic structure calculations: From molecules to solids](#), M. Springborg
- [Quantum Chemistry](#), D. A. McQuarrie

# Recalling the Hartree-Fock equations

- Recall the Fock operator in the Hartree-Fock equations:

$$\hat{F}\phi_k = \varepsilon_k\phi_k.$$

The summation here is over the  
the number of electrons  
(# of occupied orbitals)

$$\hat{F} = \hat{h}_1 + \sum_{i=1}^N (\hat{J}_i - \hat{K}_i)$$

$$\hat{J}_i\phi_k(\vec{x}_1) = \int \frac{|\phi_i(\vec{x}_2)|^2}{|\vec{x}_2 - \vec{x}_1|} d\vec{x}_2\phi_k(\vec{x}_1)$$

$$\hat{K}_i\phi_k(\vec{x}_1) = \int \frac{\phi_i^*(\vec{x}_2)\hat{P}_{12}[\phi_i(\vec{x}_2)\phi_k(\vec{x}_1)]}{|\vec{x}_2 - \vec{x}_1|} d\vec{x}_2.$$

- The Hartree-Fock equations need to be **solved self-consistently**.

# Total electronic energy

- Solving the Hartree--Fock equations leads to more than  $N$  orbitals. Which of these should we choose to occupy?
- We will choose the  $N$  orbitals to be occupied that belong to the lowest eigenvalues  $\varepsilon_k$  (ground state).
- This is reasonable based on the so-called Koopmans' theorem to be discussed here.
- Recall from the derivation in our last lecture that the total electronic energy

$E_{HF} = \langle \Phi | H_e | \Phi \rangle$  is given as:

$$\langle \Phi | \hat{H}_e | \Phi \rangle = \sum_{i=1}^N \langle \phi_i | \hat{h}_1 | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^N [\langle \phi_i \phi_j | \hat{h}_2 | \phi_i \phi_j \rangle - \langle \phi_j \phi_i | \hat{h}_2 | \phi_i \phi_j \rangle]$$

- Alternatively, we can compute  $E_{HF}$  using the Hartree-Fock equations as it will be shown next.

# A useful expression for $\varepsilon_k$

- Starting from the Hartree-Fock equations can show that:

$$\langle \phi_k | \hat{F} | \phi_k \rangle = \varepsilon_k \langle \phi_k | \phi_k \rangle$$

- Recall the Fock operator  $\hat{F} = \hat{h}_1 + \sum_{i=1}^N (\hat{J}_i - \hat{K}_i)$  and the expressions for the Coulombian and exchange operators:

$$\hat{J}_i \phi_k(\vec{x}_1) = \int \frac{|\phi_i(\vec{x}_2)|^2}{|\vec{x}_2 - \vec{x}_1|} d\vec{x}_2 \phi_k(\vec{x}_1) \quad \hat{K}_i \phi_k(\vec{x}_1) = \int \frac{\phi_i^*(\vec{x}_2) \hat{P}_{12}[\phi_i(\vec{x}_2) \phi_k(\vec{x}_1)]}{|\vec{x}_2 - \vec{x}_1|} d\vec{x}_2.$$

- With simple substitution in the first equation and using the normalization of the orbitals, you can easily show that

$$\varepsilon_k = \langle \phi_k | \hat{F} | \phi_k \rangle = \langle \phi_k | \hat{h}_1 | \phi_k \rangle + \sum_{l=1}^N [\langle \phi_k \phi_l | \hat{h}_2 | \phi_k \phi_l \rangle - \langle \phi_l \phi_k | \hat{h}_2 | \phi_k \phi_l \rangle]$$

$\hat{h}_2(\vec{r}_i, \vec{r}_j) = \frac{1}{|\vec{r}_i - \vec{r}_j|} = \hat{h}_2(\vec{r}_j, \vec{r}_i)$

# Total electronic energy

$$\varepsilon_k = \langle \phi_k | \hat{F} | \phi_k \rangle = \langle \phi_k | \hat{h}_1 | \phi_k \rangle + \sum_{l=1}^N [\langle \phi_k \phi_l | \hat{h}_2 | \phi_k \phi_l \rangle - \langle \phi_l \phi_k | \hat{h}_2 | \phi_k \phi_l \rangle]$$

- This equation is valid independently if the  $k^{\text{th}}$  orbital is occupied ( $k < N$ ) or not ( $k > N$ ).
- From the above expression with summation, we can compute the following:

$$\sum_{k=1}^N \varepsilon_k = \sum_{k=1}^N \langle \phi_k | \hat{h}_1 | \phi_k \rangle + \sum_{k,l=1}^N [\langle \phi_k \phi_l | \hat{h}_2 | \phi_k \phi_l \rangle - \langle \phi_l \phi_k | \hat{h}_2 | \phi_k \phi_l \rangle]$$

# Total electronic energy

- Comparison of the following two equations:

$$\sum_{k=1}^N \varepsilon_k = \sum_{k=1}^N \langle \phi_k | \hat{h}_1 | \phi_k \rangle + \sum_{k,l=1}^N [\langle \phi_k \phi_l | \hat{h}_2 | \phi_k \phi_l \rangle - \langle \phi_l \phi_k | \hat{h}_2 | \phi_k \phi_l \rangle]$$

$$\langle \Phi | \hat{H}_e | \Phi \rangle = \sum_{i=1}^N \langle \phi_i | \hat{h}_1 | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^N [\langle \phi_i \phi_j | \hat{h}_2 | \phi_i \phi_j \rangle - \langle \phi_j \phi_i | \hat{h}_2 | \phi_i \phi_j \rangle].$$

leads to the following for the electronic energy:

$$\begin{aligned} E_{\text{HF}} &= \sum_{k=1}^N \varepsilon_k - \frac{1}{2} \sum_{k,l=1}^N [\langle \phi_k \phi_l | \hat{h}_2 | \phi_k \phi_l \rangle - \langle \phi_l \phi_k | \hat{h}_2 | \phi_k \phi_l \rangle] \\ &= \sum_k \varepsilon_k - \sum_k \langle \phi_k | \frac{1}{2} (J - K) | \phi_k \rangle \end{aligned}$$

The sums here are over all occupied levels

- The eigenvalues  $\varepsilon_k$  appear like individual orbital energies whose sum gives one large contribution to the total electronic energy but which has to be modified by a double-counting term due to electron-electron interactions.

# Koopmans' theorems

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- These theorems (to be derived from the Hartree-Fock equations) have to do with the calculations of the **ionization energy** and **electron affinity**.
- Ionization energy -- the energy that you need to spend to remove an electron from an atom.
- Electron affinity -- the energy that you gain when an atom captures an extra electron.

How do you calculate these two quantities?

- Let us take the case of the Fe atom. The ionization energy is given by the difference of the Hartree-Fock energy with 26 electrons and the Hartree-Fock energy solution with 25 electrons.
- Similarly the affinity will be the difference between the calculations with 27 and 26 electron calculations.

# Koopmans' theorems

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- You can actually do both calculations (of ionization energy and electron affinity) in one calculation if you make the hypothesis that your single particle electrons do not change in the process (**frozen orbital approximation**).
- If you assume that in going from 26 to 25 electrons, the shape of the orbitals of electron 1, electron 2, etc. do not change, then you can prove that **the difference between the system with 26 electrons and the system with 25 electrons, is given by the eigenvalue of the 26<sup>th</sup> electron.**
- A single calculation gives you an estimate of ionization energies and electron affinities.



# Koopmans' theorems

- Consider a system of  $N$  electrons for which the Hartree-Fock equations were solved. As mentioned before, more than  $N$  orbitals will be found. Koopmans compared the total electronic energy for this system with that obtained by either removing one of the electrons from a given orbital or adding one electron to a given orbital. He found that

$$E_{\text{HF}}(N - 1) - E_{\text{HF}}(N) \simeq -\varepsilon_n$$

We assume here that an electron of the  $n^{\text{th}}$  orbital has been removed.

$$E_{\text{HF}}(N + 1) - E_{\text{HF}}(N) \simeq \varepsilon_m$$

We assume here that an electron has been added to the  $m^{\text{th}}$  orbital.

- In the eqs. above, it is assumed that the  $n^{\text{th}}$  orbital was occupied and the  $m^{\text{th}}$  empty for the  $N$ -electron system, respectively.
- Finally,  $E_{\text{HF}}(M)$  is the total electronic energy for the  $M$ -electron system.

# Proof of Koopmans' theorems

- To prove Koopmans' theorems we proceed as follows:

$$E_{HF}(N) = \sum_{i=1}^N \langle \phi_i | \hat{h}_1 | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^N [\langle \phi_i \phi_j | \hat{h}_2 | \phi_i \phi_j \rangle - \langle \phi_j \phi_i | \hat{h}_2 | \phi_i \phi_j \rangle]$$

- Let us remove an electron from the  $n^{\text{th}}$  occupied orbital. Using the above, we can write:

$$\begin{aligned} E_{HF}(N-1) - E_{HF}(N) &= \sum_{\substack{i=1 \\ i \neq n}}^N \langle \phi_i | \hat{h}_1 | \phi_i \rangle + \frac{1}{2} \sum_{\substack{i,j=1 \\ i,j \neq n}}^N [\langle \phi_i \phi_j | \hat{h}_2 | \phi_i \phi_j \rangle - \langle \phi_j \phi_i | \hat{h}_2 | \phi_i \phi_j \rangle] \\ &\quad - \sum_{i=1}^N \langle \phi_i | \hat{h}_1 | \phi_i \rangle - \frac{1}{2} \sum_{i,j=1}^N [\langle \phi_i \phi_j | \hat{h}_2 | \phi_i \phi_j \rangle - \langle \phi_j \phi_i | \hat{h}_2 | \phi_i \phi_j \rangle] \end{aligned}$$

# Proof of Koopmans' theorems

➤ Simplifying gives (remember an electron is removed from the  $n^{\text{th}}$  orbital):

$$\begin{aligned} E_{\text{HF}}(N-1) - E_{\text{HF}}(N) &= -\langle \phi_n | \hat{h}_1 | \phi_n \rangle - \frac{1}{2} \sum_{\substack{j=1 \\ j \neq n}}^N [\langle \phi_n \phi_j | \hat{h}_2 | \phi_n \phi_j \rangle - \langle \phi_j \phi_n | \hat{h}_2 | \phi_n \phi_j \rangle] \\ &\quad - \frac{1}{2} \sum_{\substack{i=1 \\ i \neq n}}^N [\langle \phi_i \phi_n | \hat{h}_2 | \phi_i \phi_n \rangle - \langle \phi_n \phi_i | \hat{h}_2 | \phi_i \phi_n \rangle] \\ &= -\langle \phi_n | \hat{h}_1 | \phi_n \rangle - \sum_{\substack{j=1 \\ j \neq n}}^N [\langle \phi_n \phi_j | \hat{h}_2 | \phi_n \phi_j \rangle - \langle \phi_j \phi_n | \hat{h}_2 | \phi_n \phi_j \rangle] \\ &= -\langle \phi_n | \hat{h}_1 | \phi_n \rangle - \sum_{j=1}^N [\langle \phi_n \phi_j | \hat{h}_2 | \phi_n \phi_j \rangle - \langle \phi_j \phi_n | \hat{h}_2 | \phi_n \phi_j \rangle] \\ &= -\varepsilon_n, \quad (\text{we already proved this earlier}) \end{aligned}$$

# Koopmans' theorems

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- Koopmans' theorem allows interpreting the eigenvalues  $\varepsilon_k$  of the Hartree-Fock equations as orbital energies that are related to "electronic transition energies".
- It further provides a good argument for occupying the  $N$  orbitals of the  $N$  lowest eigenvalues  $\varepsilon_k$  in solving the Hartree-Fock equations.

# The Hartree-Fock-Roothaan method

- Solving the Hartree-Fock equations  $\hat{F}\phi_k = \varepsilon_k\phi_k$  requires computing the real eigenvalues  $\varepsilon_k$  and the orbitals  $\phi_k$  in every point in space as well as its spin-dependence.

- Roothaan suggested an approximation of the Slater determinant wavefunction:

$$\Phi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{x}_1) & \phi_2(\vec{x}_1) & \dots & \phi_N(\vec{x}_1) \\ \phi_1(\vec{x}_2) & \phi_2(\vec{x}_2) & \dots & \phi_N(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\vec{x}_N) & \phi_2(\vec{x}_N) & \dots & \phi_N(\vec{x}_N) \end{vmatrix} \\ \equiv |\phi_1, \phi_2, \dots, \phi_N|.$$

- Recall that the single electron orbitals were computed from the minimization of:

$$F = \langle \Phi | \hat{H}_e | \Phi \rangle - \sum_{i,j} \lambda_{ij} [\langle \phi_i | \phi_j \rangle - \delta_{i,j}]$$

# The Hartree-Fock-Roothaan method

- Roothaan expanded the orbitals in a FIXED basis  $\phi_l$  (plane waves  $e^{ik \cdot r}$ , Slater functions  $e^{-\beta r}$ , Gaussians  $e^{-\beta r^2}$ , etc.):

$$\psi_l(\vec{x}) = \sum_{p=1}^{N_b} \chi_p(\vec{x}) c_{pl}$$

- Now only the coefficients  $c_{pl}$  are unknown. We will insert this approximation in our variational principle and we will do the minimization with respect to  $c_{pl}$ :

$$F = \langle \Phi | \hat{H}_e | \Phi \rangle - \sum_{i,j} \lambda_{ij} [\langle \phi_i | \phi_j \rangle - \delta_{i,j}]$$
$$F = \sum_{i=1}^N \langle \phi_i | \hat{h}_1 | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^N [\langle \phi_i \phi_j | \hat{h}_2 | \phi_i \phi_j \rangle - \langle \phi_j \phi_i | \hat{h}_2 | \phi_i \phi_j \rangle]$$
$$- \sum_{i,j=1}^N \lambda_{ij} [\langle \phi_i | \phi_j \rangle - \delta_{i,j}]$$

# The Hartree-Fock-Roothaan method

► We finally obtain:

$$F = \sum_{i=1}^N \sum_{m,n=1}^{N_b} c_{mi}^* c_{ni} \langle \chi_m | \hat{h}_1 | \chi_n \rangle$$
$$+ \frac{1}{2} \sum_{i,j=1}^N \sum_{m,n,q,r=1}^{N_b} c_{mi}^* c_{ni} c_{qj}^* c_{rj} [\langle \chi_m \chi_q | \hat{h}_2 | \chi_n \chi_r \rangle - \langle \chi_q \chi_m | \hat{h}_2 | \chi_n \chi_r \rangle]$$
$$- \sum_{i,j=1}^N \lambda_{ij} \left[ \sum_{m,n=1}^{N_b} c_{mi}^* c_{nj} \langle \chi_m | \chi_n \rangle - \delta_{i,j} \right]$$

► We then enforce:  $\delta F = 0$

$$\frac{\partial F}{\partial c_{pl}} = \frac{\partial F}{\partial c_{pl}^*} = 0. \quad C_{pl} \text{ is the coefficient of the } l^{\text{th}} \text{ orbital to the } p^{\text{th}} \text{ function.}$$

# The Hartree-Fock-Roothaan method

- The following final equations are obtained:

$$\sum_{m=1}^{N_b} c_{mi}^* \langle \chi_m | \hat{h}_1 | \chi_p \rangle + \sum_{i=1}^N \sum_{m,n,q=1}^{N_b} c_{mi}^* c_{ni}^* c_{qi} [\langle \chi_m \chi_n | \hat{h}_2 | \chi_p \chi_q \rangle - \langle \chi_n \chi_m | \hat{h}_2 | \chi_p \chi_q \rangle] - \sum_{i=1}^N \lambda_{li} \sum_{m=1}^{N_b} c_{mi}^* \langle \chi_m | \chi_p \rangle = 0$$

and

$$\sum_{m=1}^{N_b} c_{ml} \langle \chi_m | \hat{h}_1 | \chi_p \rangle + \sum_{i=1}^N \sum_{m,n,q=1}^{N_b} c_{ml} c_{ni} c_{qi}^* [\langle \chi_p \chi_q | \hat{h}_2 | \chi_m \chi_n \rangle - \langle \chi_q \chi_p | \hat{h}_2 | \chi_m \chi_n \rangle] - \sum_{i=1}^N \lambda_{il} \sum_{m=1}^{N_b} c_{mi} \langle \chi_p | \chi_m \rangle = 0.$$

- The Lagrange multipliers form a Hermitian matrix (thus the two equations are complex conjugate of each other). We choose the orbitals such that:

$$\lambda_{ij} = \varepsilon_i \delta_{i,j}.$$



# The Hartree-Fock-Roothaan equations

$$\sum_{m=1}^{N_b} \left\{ \langle \chi_p | \hat{h}_1 | \chi_m \rangle + \sum_{i=1}^N \sum_{n,q=1}^{N_b} c_{ni} c_{qi}^* [\langle \chi_p \chi_q | \hat{h}_2 | \chi_m \chi_n \rangle - \langle \chi_q \chi_p | \hat{h}_2 | \chi_m \chi_n \rangle] \right\} c_{mi}$$

$$= \varepsilon_l \sum_{m=1}^{N_b} \langle \chi_p | \chi_m \rangle c_{mi}$$

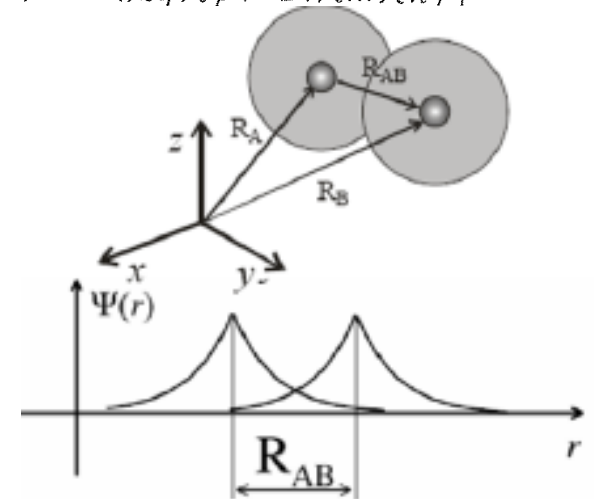
Generalized eigenvalue problem

$$\underline{\underline{F}} \cdot \underline{\underline{C}}_l = \varepsilon_l \cdot \underline{\underline{O}} \cdot \underline{\underline{C}}_l,$$

$$F_{pm} = \langle \chi_p | \hat{h}_1 | \chi_m \rangle + \sum_{i=1}^N \sum_{n,q=1}^{N_b} c_{ni} c_{qi}^* [\langle \chi_p \chi_q | \hat{h}_2 | \chi_m \chi_n \rangle - \langle \chi_q \chi_p | \hat{h}_2 | \chi_m \chi_n \rangle]$$

$$O_{pm} = \langle \chi_p | \chi_m \rangle.$$

- Many real space basis functions are non-orthogonal leading to an overlap as shown in the sketch for atomic basis functions.



# ***The Hartree-Fock-Roothaan equations***

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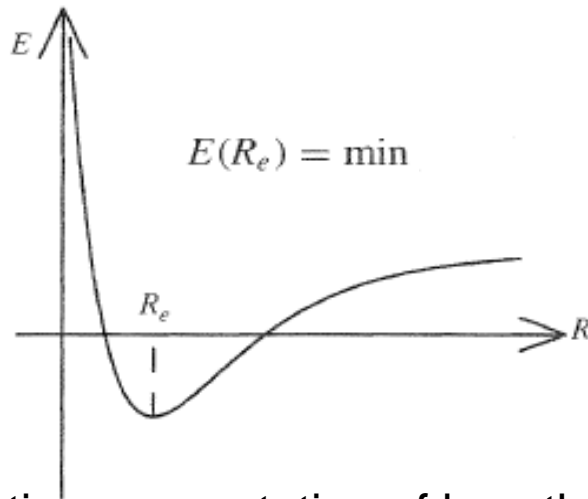
- Instead of determining an infinite number of values (the values of all occupied orbitals in all position-space and spin points), the Roothaan approach simplifies the problem to that of determining only a finite number of parameters.
- Increasing the set of basis functions gives you a better approximation.
- However, the accuracy will never be better than that of the original Hartree-Fock approximation.

We will next review some typical (but old) results of the Hartree-Fock approach

# Total energy

$$E(\vec{X}) = \frac{1}{2} \sum_{k_1 \neq k_2=1}^M \frac{Z_{k_1} Z_{k_2}}{|\vec{R}_{k_1} - \vec{R}_{k_2}|} + E_e(\vec{X})$$

- Here the electronic energy is the H-F energy:  $E_e = E_{\text{HF}}$ .



Schematic representation of how the total energy depends on the bond length for a diatomic molecule

- $R_e$  is in most cases accurately given within the Hartree-Fock approximation.
- There are cases (e.g. transition-metal atoms) where severe errors occur since correlation effects become important.

# Hartree-Fock Calculations vs. Experimental Data

- The eigenvalues  $\epsilon_i$  of the Hartree-Fock approximation are called **orbital energies**. According to Koopmans' theorem the orbital energies are approximations for the ionization energy of an electron from the  $i^{\text{th}}$  orbital  $\phi_i$ . The accuracy of Koopmans' approximation rests upon the assumption that the removal of an electron from the  $i^{\text{th}}$  orbital does not affect the other  $N - 1$  orbitals. Under that approximation,

$$E^+ - E = \text{IE} = -\epsilon_i$$

where  $E$  and  $E^+$  are the Hartree-Fock energies of the neutral atom and the positive ion, respectively.

Comparison of Hartree-Fock Orbital Energies  
with Experimental Data of  $\text{Cu}^+$  (Energies Are in Atomic Units)

Orbital	Ionization energy	
	Hartree-Fock	X-ray value
1s	658.4	661.4
2s	82.3	81.0
2p	71.8	68.9
3s	10.6	8.9
3p	7.3	5.7
3d	1.6	0.4

[From D. McQuarrie](#)

# Correlation energy and Hartree-Fock

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- In the variational principle if we make the wave function more and more flexible, the accuracy of Hartree-Fock can become better and better.
- As we will see, we can write the wavefunction as the sum of multiple determinants thus improving the accuracy of Hartree-Fock.
- Hartree-Fock in principle can be improved indefinitely. We will learn that while density functional theory (DFT) performs better and scales at the 3<sup>rd</sup> power of the size it can't be improved in any systematic way.
- The Hartree-Fock energy is always going to be higher than the true ground state energy of our system. What is called **the correlation energy is the difference between the true energy of your system and the Hartree-Fock energy.**
- When we talk about **correlation energy we refer to the energy that is not captured by a Hartree-Fock approach.**

# ***Ionization energies with Hartree-Fock***

Ionization energies (eV) of Ne and Ar obtained from neutral atom orbital energies (Koopmans' theorem) and by subtracting the Hartree-Fock energy of the neutral atom from the Hartree-Fock energy of the approximate state of the positive ion.

<i>Ionization energies</i>					
	<i>Orbital occupancy</i>	<i>Ion</i>	<i>Koopmans' theorem</i>	<i>Direct Hartree-Fock calculations</i>	<i>Experiment</i>
1s hole	$1s^2s^22p^6$	Ne <sup>+</sup>	891.7	868.6	870.3
2s hole	$1s^22s2p^6$	Ne <sup>+</sup>	52.5	49.3	48.5
2p hole	$1s^22s^22p^5$	Ne <sup>+</sup>	23.1	19.8	21.6
1s hole	$1s^2s^22p^63s^23p^6$	Ar <sup>+</sup>	3227.4	3195.2	3206.3
2s hole	$1s^22s2p^63s^23p^6$	Ar <sup>+</sup>	335.3	324.8	—
2p hole	$1s^22s^22p^53s^23p^6$	Ar <sup>+</sup>	260.4	248.9	248.5
3s hole	$1s^22s^22p^63s3p^6$	Ar <sup>+</sup>	34.8	33.2	29.2
3p hole	$1s^22s^22p^63s^23p^5$	Ar <sup>+</sup>	16.1	14.8	15.8

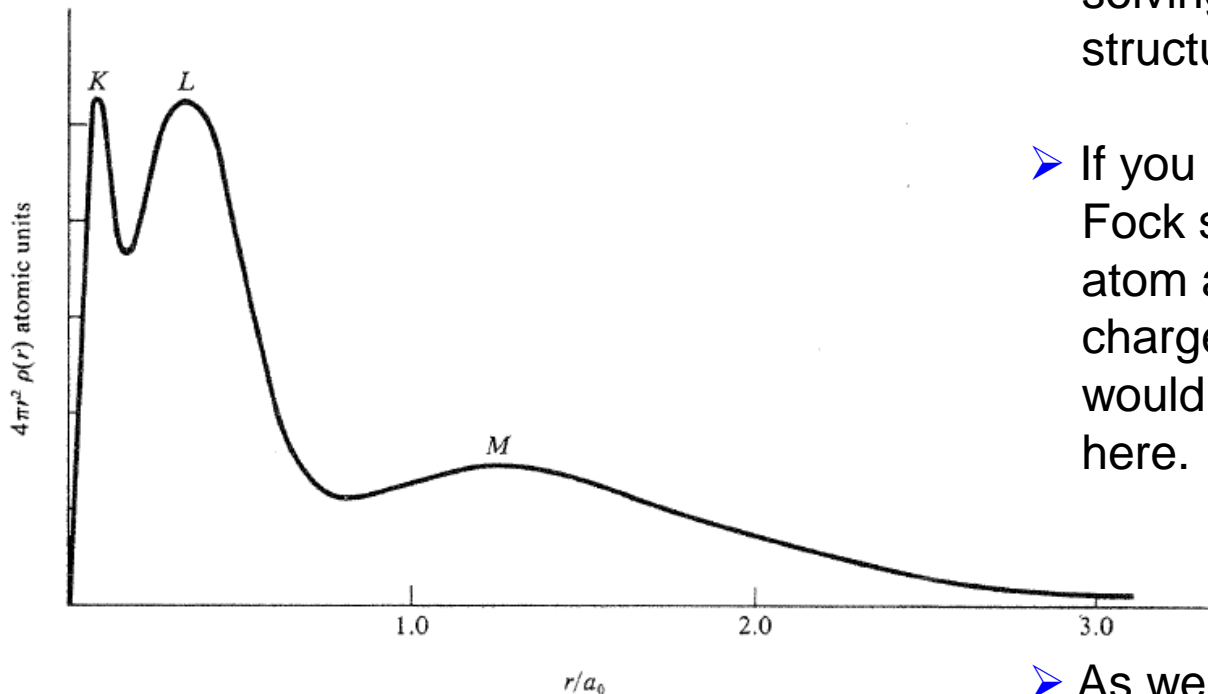
From D. MacQuarrie

# ***Ionization potentials and electron affinities***

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- According to Koopman's theorem, the orbital energies  $\varepsilon_k$  can be related to the ionization potentials and electron affinities.
- The results obtained are not in good agreement with experiments because the Koopmans' theorem neglects effects related to the fact that the **orbitals will change when the number of electrons is changed (relaxation effects)**.

# Hartree-Fock and the periodic table



The distribution of electronic charge in an argon atom as a function of the distance from the nucleus  
(from [D. McQuarrie](#))

- Using Hartree-Fock, one could start solving atoms and recover the shell structure of atoms.
- If you would obtain the Hartree-Fock solution for e.g. an Argon atom and then plot the overall charge density of the system then it would start to look like the figure here.
- As we move from the center outwards it would clearly show the fundamentals of the periodic table nature of things. That is it would show 1s shell and then it would show a 2s and a 2p shell, etc.



# Hartree-Fock and the periodic table

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- **The periodic table itself is not the truth picture of electrons -- it's just a Hartree-Fock picture of electrons.**
- In principle, you shouldn't be able to talk about single particle orbitals 1s, 2s because if you have e.g. an Fe atom, you have many body wave function that is an overall function of all the electrons. It is only when you enter into an Hartree-Fock picture that you can have a well defined concept of a single orbital for an electron and of the energy for that electron.

**The periodic table is nothing else  
than the Hartree-Fock solution for  
the atoms**

# Dissociation energy and harmonic frequencies

$$D_e = E(A) + E(B) - E(AB) = E(\infty) - E(R_e).$$

- Often the calculation of  $D_e$  is less accurate than that of  $R_e$ .
- Harmonic frequencies can be easily approximated:

$$E(R) \simeq E(R_e) + \frac{k}{2}(R - R_e)^2, \quad k = \left. \frac{d^2E}{dR^2} \right|_{R=R_e}, \quad \hbar\omega = \hbar\sqrt{\frac{k}{\mu}}$$

where the reduced mass of the two nuclei is defined:  $\mu = \frac{M_A M_B}{M_A + M_B}$

# ***Dissociation energy and harmonic frequencies***

System	X-H bond length		H-X-H bond angle	
	Theory	Experiment	Theory	Experiment
H <sub>2</sub>	0.730	0.742		
CH <sub>3</sub>	1.072	1.079	120.0	120.0
CH <sub>4</sub>	1.082	1.085	109.5	109.5
NH <sub>2</sub>	1.015	1.024	108.6	103.4
NH <sub>3</sub>	0.991	1.012	116.1	106.7
OH	0.967	0.971		
H <sub>2</sub> O	0.948	0.957	111.5	104.5
HF	0.921	0.917		

Lengths in Angstroms and angles in degrees for small molecules  
(from [Daudel et al., 1983](#)).

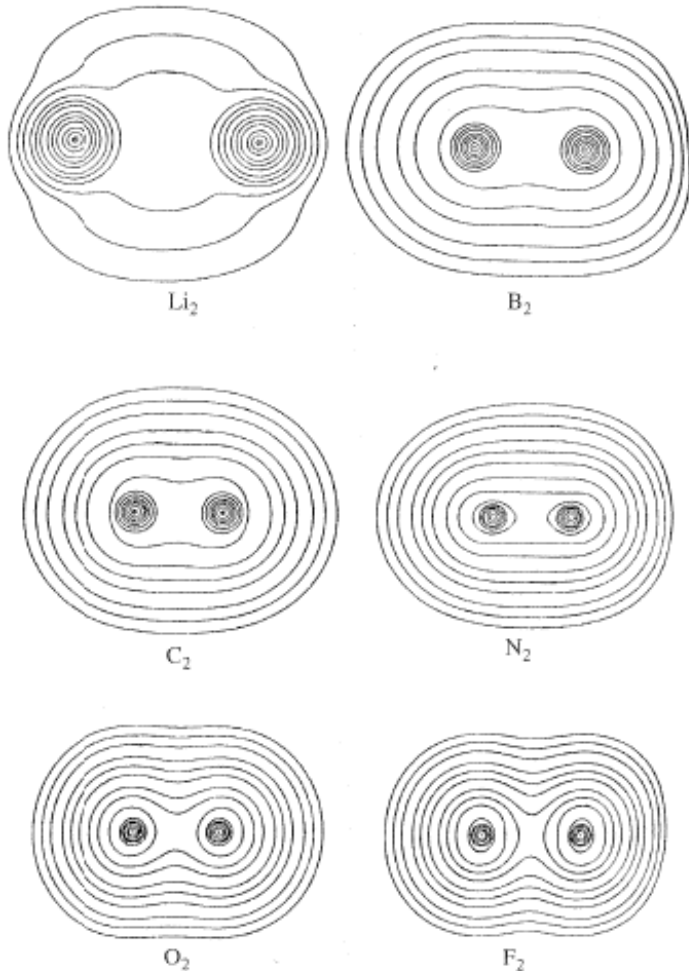
# Vibrational frequencies

System	Theory	Experiment
H <sub>2</sub>	4644	4405
CH <sub>3</sub>	3321	3184
	3125	3002
	1470	1383
	776	580
CH <sub>4</sub>	3372	3019
	3226	2917
	1718	1534
	1533	1306
NH <sub>2</sub>	3676	3220
	3554	3173
	1651	1499
NH <sub>3</sub>	3985	3444
	3781	3336
	1814	1627
	597	950
OH	3955	3735
H <sub>2</sub> O	4143	3756
	3987	3657
	1678	1595
HF	4150	4138

The frequencies  
with H-F  
are overestimated

Vibrational frequencies for small molecules  
in cm<sup>-1</sup> (from [Daudel et al., 1983](#)).

# Electron densities

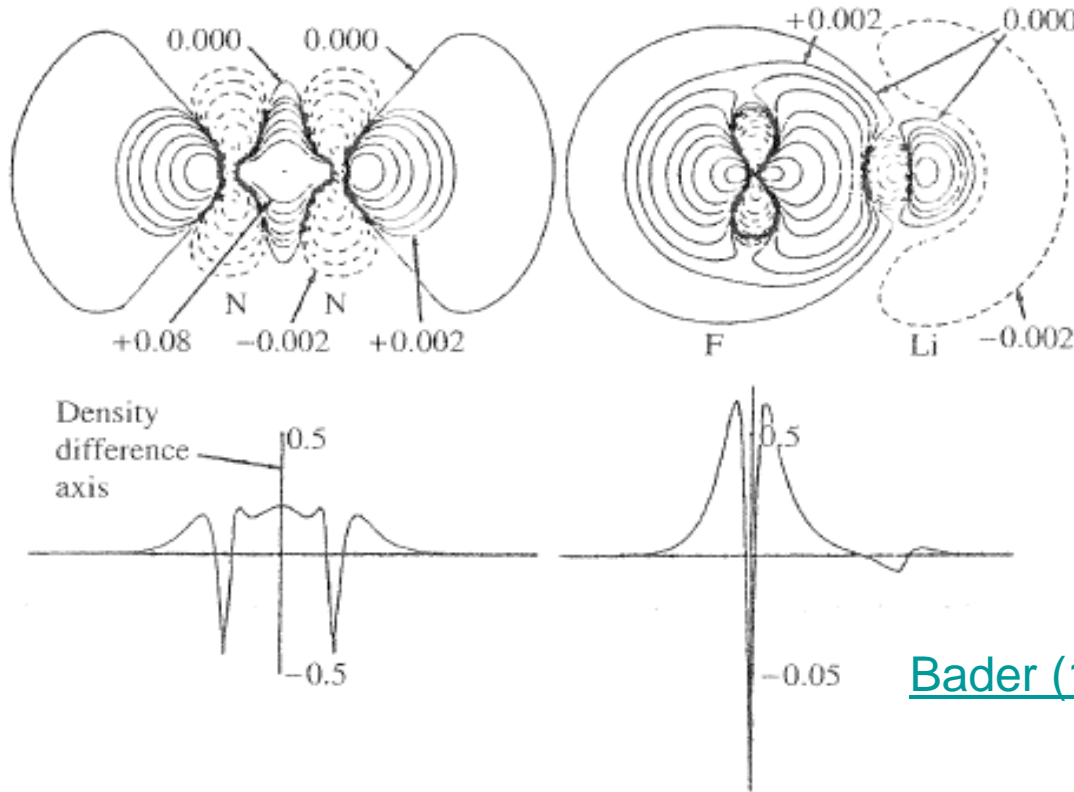


$$\rho(\vec{r}) = \sum_{i=1}^N |\phi_i(\vec{r})|^2$$

- The electron densities computed are structure-less. They resemble the densities of superposed atoms.
- The chemical bonds are hardly visible.

From [R. F.W. Bader](#)

# Electron difference density



$$\Delta\rho(\vec{r}) =$$

$$\rho(\vec{r}) - \sum_{m=1}^M \rho_{\text{atom } m}(\vec{r} - \vec{R}_m)$$

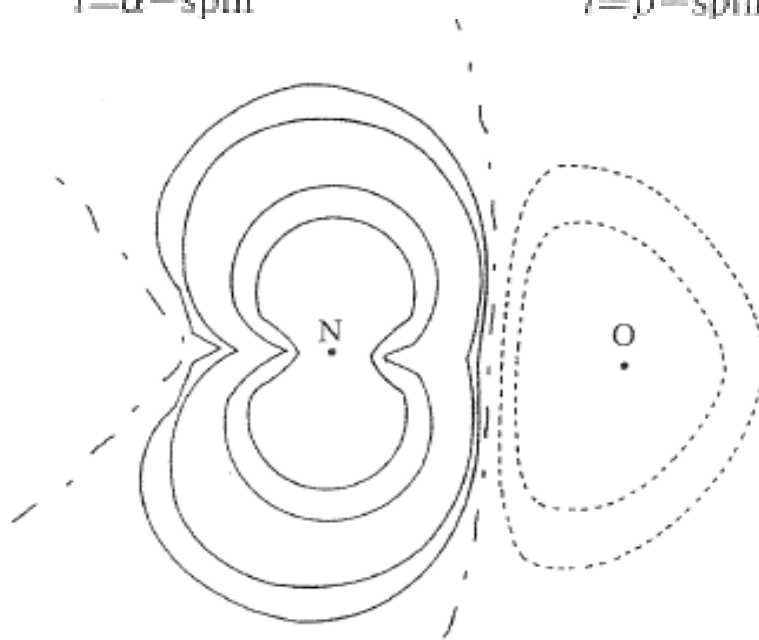
[Bader \(1970\)](#)

- We usually compare the total density with that of the superposed atomic densities (i.e. the sum of the densities of the isolated atoms placed at the positions where the nuclei are for the system of interest).

# Spin density

- The spin density is the difference of the electron density for the electrons with an  $\alpha$  spin minus that of the electrons with a  $\beta$  spin:

$$\rho_s(\vec{r}) = \frac{1}{2} \sum_{i=\alpha\text{-spin}} |\phi_i(\vec{r})|^2 - \frac{1}{2} \sum_{i=\beta\text{-spin}} |\phi_i(\vec{r})|^2$$



NO molecule ([Daudel et al. 1983](#))

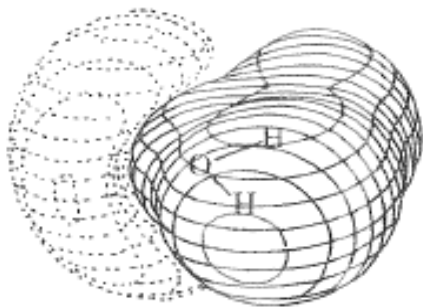
# Total dipole moment, the electrostatic potential

- The **total dipole moment of a molecule** is the sum of the dipole moment of the nuclei plus that of the electrons.

$$\mu_y = \sum_{m=1}^M Z_m Y_m - \sum_{i=1}^N \langle \phi_i | y | \phi_i \rangle$$

- The total electrostatic potential is given as:

$$V(\vec{r}) = \sum_{m=1}^M \frac{Z_m}{|\vec{R}_m - \vec{r}|} - \sum_{i=1}^N \int \frac{|\phi_i(\vec{s})|^2}{|\vec{s} - \vec{r}|} d\vec{s}$$



Electrostatic potentials for H<sub>2</sub>O  
([Daudel et al., 1983](#))

- The potential gives some ideas about where a charged particle would attack in a chemical reaction.
- A positive ion will feel attracted to the regions of negative potential, and vice versa.

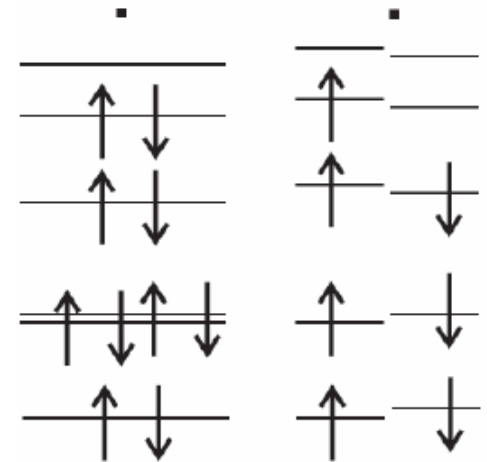


# Restricted and Unrestricted Hartree-Fock

- To describe an electron, we do not only describe what the distribution of its wave function is in space but we also specify what is the spin of the electron.
- For an even number of electrons and total spin  $S=0$  (**closed shell**), the spatial orbitals are the same for spins up and down:

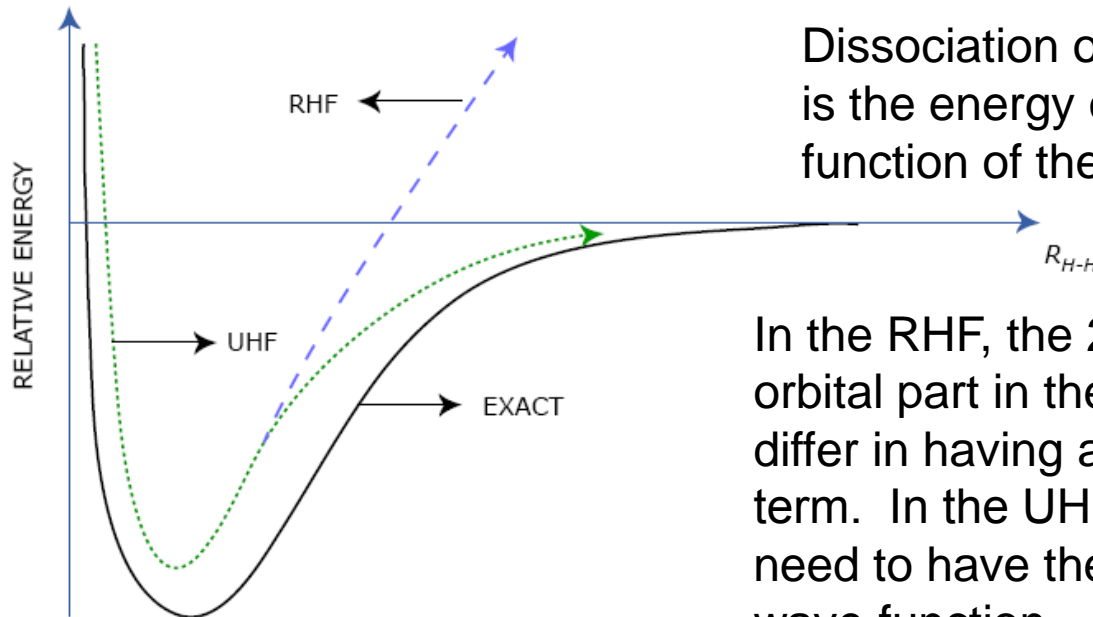
$$\{\psi_{2k-1}(r, \sigma), \psi_{2k}(r, \sigma)\} = \{\phi_k(r)\alpha(\sigma), \phi_k(r)\beta(\sigma)\} \quad \text{closed shell} \quad \text{open shell}$$

- If the number of electrons with spin up and spin down is different (odd number of electrons), then we have an **open shell system**.
- In open shell systems, electrons with different spins move in different fields created by the other electrons.
- **In restricted Hartree-Fock**, an electron of spin-up and an electron of spin-down will have the same spatial part of the wave function. Their wave functions still differ since they describe an electron with spin-up and an electron with spin-down.



# Restricted and Unrestricted Hartree-Fock

- You should actually make your wave function more flexible: an electron with a spin-up and an electron with a spin-down even if they are very close in energy can have 2 wave functions in which the space part differs. This is an **unrestricted Hartree-Fock solution which will always give you a lower energy than a restricted solution.**



Dissociation of a H-molecule. Shown is the energy of 2 H-atoms as a function of the nuclear distance.

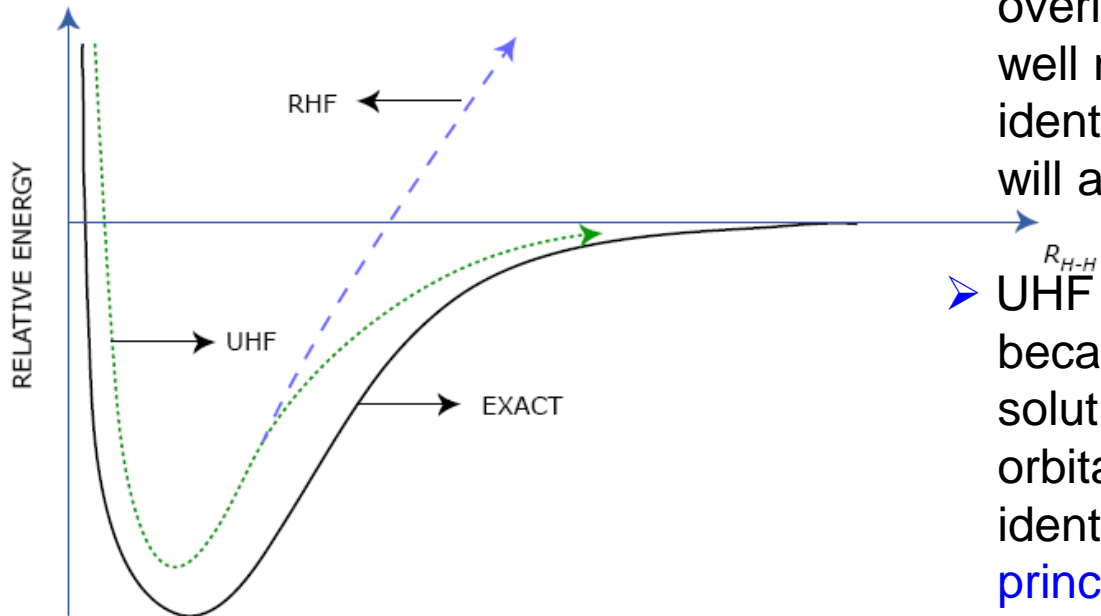
In the RHF, the 2 electrons have the same orbital part in the wave function, they just differ in having a spin-up and a spin-down term. In the UHF, the 2 electrons don't need to have the same orbital part for the wave function.

[From MIT 3.320](#)

Both RHF and UHF formulations do very well close to the equilibrium point

# Restricted and Unrestricted Hartree-Fock

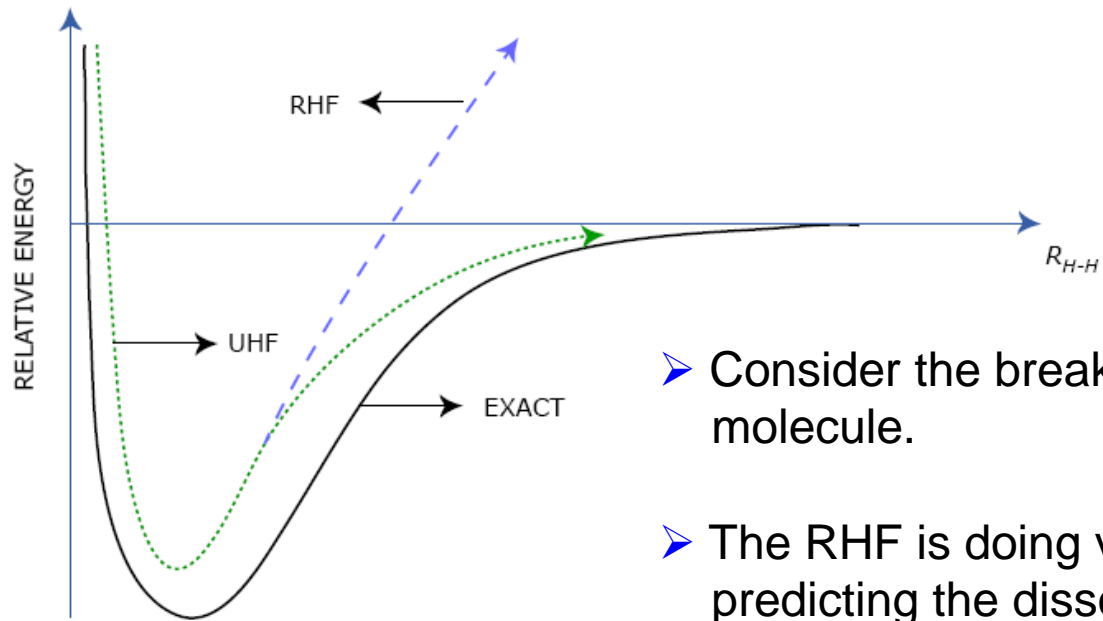
- The restricted Hartree-Fock (RHF) is not doing well in predicting the dissociation energy.



From MIT 3.320

- The two 1s orbitals are covalently overlapping and so RHF does very well near equilibrium. It is basically identical to UHF but formally UHF will always be lower than RHF.
- UHF contains the restricted solution because in order to have a restricted solution you just need to have the orbital part for the 2 electrons to be identical. Recall from the variational principle that the more flexibility you introduce in your trial wave function the lower the ground energy will be.

# Restricted and Unrestricted Hartree-Fock



From MIT 3.320

- Consider the breaking of the H-molecule.
- The RHF is doing very poorly in predicting the dissociation energy. The UHF does very well.
- **To correct this, you will need a wave-function that has an additional determinant to account for anti-bonding states**

# The total spin of the $N$ -electron system

- The total spin of the  $N$ -electron system is a quantity that can be used in evaluating the quality of a given approximate wavefunction.
- It can also be used in restricting the approximate  $N$ -electron wavefunction.
- Let us consider the square of the **total spin operator**:

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2,$$

Each term is a  
sum of single-electron  
contributions

where

$$\hat{S}_x = \sum_{i=1}^N \hat{s}_{i,x} \quad \hat{S}_y = \sum_{i=1}^N \hat{s}_{i,y} \quad \hat{S}_z = \sum_{i=1}^N \hat{s}_{i,z}$$

- You may already have seen in your Quantum Mechanics class the **ladder operators** (which do not commute):

$$\hat{S}_+ = \hat{S}_x + i\hat{S}_y \quad \hat{S}_- = \hat{S}_x - i\hat{S}_y$$

# The total spin of the $N$ -electron system

➤ Consider a spin eigenstate  $\theta_{SM}$  for which:

$$\hat{S}^2 \theta_{S,M} = S(S+1) \theta_{S,M}$$

$$\hat{S}_z \theta_{S,M} = M \theta_{S,M}$$

➤ You can then show that:

$$\hat{S}_+ \theta_{S,M} = [(S+M+1)(S-M)]^{1/2} \theta_{S,M+1}$$

$$\hat{S}_- \theta_{S,M} = [(S-M+1)(S+M)]^{1/2} \theta_{S,M-1}$$

➤ Thus the operators:  $\hat{S}_+ = \hat{S}_x + i\hat{S}_y$  and  $\hat{S}_- = \hat{S}_x - i\hat{S}_y$ .

change the  $z$  component by  $+1$  or  $-1$ , respectively but keep the same total spin.

➤ With these operators, we have:

$$\hat{S}^2 = \hat{S}_+ \hat{S}_- - \hat{S}_z + \hat{S}_z^2 = \hat{S}_- \hat{S}_+ + \hat{S}_z + \hat{S}_z^2$$

# Explicit spin dependence of the wavefunction

- We now include the spin dependence in the Slater determinant:

$$\Phi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{x}_1) & \phi_2(\vec{x}_1) & \dots & \phi_N(\vec{x}_1) \\ \phi_1(\vec{x}_2) & \phi_2(\vec{x}_2) & \dots & \phi_N(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\vec{x}_N) & \phi_2(\vec{x}_N) & \dots & \phi_N(\vec{x}_N) \end{vmatrix} \\ \equiv |\phi_1, \phi_2, \dots, \phi_N|$$

- Assume that we have  $n$  orbitals with  $\alpha$  spin and  $m$  orbitals ( $n+m=N$ ) with  $\beta$  spin:

$$\Phi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = |\phi_1^+ \alpha, \phi_2^+ \alpha, \dots, \phi_n^+ \alpha, \phi_1^- \beta, \phi_2^- \beta, \dots, \phi_m^- \beta, |.$$

- The functions  $\phi_i^+$  and  $\phi_j^-$  depend *only* on position-space coordinates (i.e., no spin dependence), and **we allow for the orbitals of different spins to be different** (hence, the superscripts + and -).

# Spin dependence of the wavefunction

- The exact  $N$ -electron wave function is an eigenfunction to  $\hat{S}^2$  and  $\hat{S}_z$ .
- Is this also the case with the approximate (Slater determinant) wavefunction?

$$\Phi = \frac{1}{\sqrt{N!}} \sum_{i=1}^{N!} (-1)^{P(i)} \phi_1^+(\vec{r}_{i_1})\alpha(i_1)\phi_2^+(\vec{r}_{i_2})\alpha(i_2)\cdots\phi_n^+(\vec{r}_{i_n})\alpha(i_n) \\ \times \phi_1^-(\vec{r}_{i_{n+1}})\beta(i_{n+1})\phi_2^-(\vec{r}_{i_{n+2}})\beta(i_{n+2})\cdots\phi_m^-(\vec{r}_{i_N})\beta(i_N),$$

- Each term contains both all functions and all electron coordinates as arguments exactly once.
- When  $\hat{S}_z$  acts on a single term in the sum in the Eq. above, it returns this sum multiplied by  $1/2$  for each  $\alpha$  spin and by  $-1/2$  for each  $\beta$  spin. This gives a total factor of  $(n - m)/2$  for any term:  $\hat{S}_z \Phi = \frac{n - m}{2} \Phi$ .  
(recall we have  $n$  electrons with spin up and  $m$  electrons with spin down and the operators are sum of the corresponding operators for all electrons).



# Spin dependence of the wavefunction

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- Thus the Slater determinant is an eigenfunction of  $\hat{S}_z$  regardless of the form of the orbitals

$$\hat{S}_z \Phi = \frac{n - m}{2} \Phi$$

- Unfortunately  $\Phi$  is not necessarily an eigenfunction for the  $\hat{S}^2$  operator.

# Spin dependence of the wavefunction

- Consider the case  $n=m=1$  (two electrons):

$$\Phi = \frac{1}{\sqrt{2}} [\phi_1^+(\vec{r}_1)\alpha(1)\phi_1^-(\vec{r}_2)\beta(2) - \phi_1^+(\vec{r}_2)\alpha(2)\phi_1^-(\vec{r}_1)\beta(1)]$$

- Since  $\Phi$  is an eigenfunction of  $\hat{S}_z$  (with an eigenvalue zero,  $n-m=0$ ), it is also an eigenvalue of  $\hat{S}_z^2$ .

- But for  $\hat{S}_+$ , we find:

$$\hat{S}_+\Phi = [\hat{s}_{1,+} + \hat{s}_{2,+}]\Phi$$

$$= \hat{s}_{1,+} \frac{1}{\sqrt{2}} [\phi_1^+(\vec{r}_1)\alpha(1)\phi_1^-(\vec{r}_2)\beta(2) - \phi_1^+(\vec{r}_2)\alpha(2)\phi_1^-(\vec{r}_1)\beta(1)]$$

$$+ \hat{s}_{2,+} \frac{1}{\sqrt{2}} [\phi_1^+(\vec{r}_1)\alpha(1)\phi_1^-(\vec{r}_2)\beta(2) - \phi_1^+(\vec{r}_2)\alpha(2)\phi_1^-(\vec{r}_1)\beta(1)]$$

$$= \frac{1}{\sqrt{2}} [-\phi_1^+(\vec{r}_2)\alpha(2)\phi_1^-(\vec{r}_1)\alpha(1) + \phi_1^+(\vec{r}_1)\alpha(1)\phi_1^-(\vec{r}_2)\alpha(2)]$$

Here, we have used

$$\hat{s}_+\alpha = 0$$

$$\hat{s}_+\beta = \alpha$$

$$\hat{s}_-\alpha = \beta$$

$$\hat{s}_-\beta = 0.$$

# Spin dependence of the wavefunction

➤ We next apply  $\hat{S}_-$  to the earlier expression to obtain:

$$\begin{aligned}
 \hat{S}_- \hat{S}_+ \Phi &= \hat{S}_- \frac{1}{\sqrt{2}} [-\phi_1^+(\vec{r}_2)\alpha(2)\phi_1^-(\vec{r}_1)\alpha(1) + \phi_1^+(\vec{r}_1)\alpha(1)\phi_1^-(\vec{r}_2)\alpha(2)] \\
 &= [\hat{s}_{1,-} + \hat{s}_{2,-}] \frac{1}{\sqrt{2}} [-\phi_1^+(\vec{r}_2)\alpha(2)\phi_1^-(\vec{r}_1)\alpha(1) + \phi_1^+(\vec{r}_1)\alpha(1)\phi_1^-(\vec{r}_2)\alpha(2)] \\
 &= \hat{s}_{1,-} \frac{1}{\sqrt{2}} [-\phi_1^+(\vec{r}_2)\alpha(2)\phi_1^-(\vec{r}_1)\alpha(1) + \phi_1^+(\vec{r}_1)\alpha(1)\phi_1^-(\vec{r}_2)\alpha(2)] \\
 &\quad + \hat{s}_{2,-} \frac{1}{\sqrt{2}} [-\phi_1^+(\vec{r}_2)\alpha(2)\phi_1^-(\vec{r}_1)\alpha(1) + \phi_1^+(\vec{r}_1)\alpha(1)\phi_1^-(\vec{r}_2)\alpha(2)] \\
 &= \frac{1}{\sqrt{2}} [-\phi_1^+(\vec{r}_2)\alpha(2)\phi_1^-(\vec{r}_1)\beta(1) + \phi_1^+(\vec{r}_1)\beta(1)\phi_1^-(\vec{r}_2)\alpha(2)] \\
 &\quad + \frac{1}{\sqrt{2}} [-\phi_1^+(\vec{r}_2)\beta(2)\phi_1^-(\vec{r}_1)\alpha(1) + \phi_1^+(\vec{r}_1)\alpha(1)\phi_1^-(\vec{r}_2)\beta(2)] \\
 &= \frac{1}{\sqrt{2}} [-\phi_1^+(\vec{r}_2)\alpha(2)\phi_1^-(\vec{r}_1)\beta(1) + \phi_1^+(\vec{r}_1)\beta(1)\phi_1^-(\vec{r}_2)\alpha(2) \\
 &\quad - \phi_1^+(\vec{r}_2)\beta(2)\phi_1^-(\vec{r}_1)\alpha(1) + \phi_1^+(\vec{r}_1)\alpha(1)\phi_1^-(\vec{r}_2)\beta(2)]
 \end{aligned}$$

Here, we have used

$$\hat{s}_+\alpha = 0$$

$$\hat{s}_+\beta = \alpha$$

$$\hat{s}_-\alpha = \beta$$

$$\hat{s}_-\beta = 0.$$

# The projected Hartree-Fock method

- However, we already know that:

$$\hat{S}^2 = \hat{S}_+ \hat{S}_- - \hat{S}_z + \hat{S}_z^2 = \hat{S}_- \hat{S}_+ + \hat{S}_z + \hat{S}_z^2.$$

- With  $\hat{S}_z \Phi = 0$ , we conclude that  $\hat{S}_- \hat{S}_+ \Phi = \hat{S}^2 \Phi$ . Now recall that:

$$\hat{S}_- \hat{S}_+ \Phi = \frac{1}{\sqrt{2}} [-\phi_1^+(\vec{r}_2)\alpha(2)\phi_1^-(\vec{r}_1)\beta(1) + \phi_1^+(\vec{r}_1)\beta(1)\phi_1^-(\vec{r}_2)\alpha(2) - \phi_1^+(\vec{r}_2)\beta(2)\phi_1^-(\vec{r}_1)\alpha(1) + \phi_1^+(\vec{r}_1)\alpha(1)\phi_1^-(\vec{r}_2)\beta(2)]$$

- Thus  $\Phi$  can be an eigenfunction of  $\hat{S}^2$  only if:  $\phi_1^+ = \phi_1^-$ . In this case,

$$\hat{S}^2 \Phi = \frac{1}{\sqrt{2}} [-\phi_1^+(\vec{r}_2)\beta(2)\phi_1^-(\vec{r}_1)\alpha(1) + \phi_1^+(\vec{r}_1)\alpha(1)\phi_1^-(\vec{r}_2)\beta(2)] = \Phi \text{ (we should actually remove the + and - scripts here)}$$

- In the general case with  $n=m$  ( $=N/2$ ), one can show that  $\Phi$  is an eigenfunction of

$$\hat{S}^2 \text{ if the condition above is applied for all orbitals.}$$

- In this case, the Hartree-Fock-Roothan equations can be simplified by using the fact that the  $\alpha$  and  $\beta$  functions are orthonormal and by performing all 'spin integrations' and summations.

# Simplified Hartree-Fock-Roothaan equations

- Recall our original Hartree-Fock-Roothaan equation becomes:

$$\sum_{m=1}^{N_b} \left\{ \langle \chi_p | \hat{h}_1 | \chi_m \rangle + \sum_{i=1}^N \sum_{n,q=1}^{N_b} c_{ni} c_{qi}^* [\langle \chi_p \chi_q | \hat{h}_2 | \chi_m \chi_n \rangle - \langle \chi_q \chi_p | \hat{h}_2 | \chi_m \chi_n \rangle] \right\} c_{ml}$$
$$= \varepsilon_l \sum_{m=1}^{N_b} \langle \chi_p | \chi_m \rangle c_{ml}$$

- They now take the form:

$$\sum_{m=1}^{N_b} \left\{ \langle \chi_p | \hat{h}_1 | \chi_m \rangle + \sum_{i=1}^{N/2} \sum_{n,q=1}^{N_b} c_{ni} c_{qi}^* [2 \langle \chi_p \chi_q | \hat{h}_2 | \chi_m \chi_n \rangle - \langle \chi_q \chi_p | \hat{h}_2 | \chi_m \chi_n \rangle] \right\} c_{ml}$$

- The  $N_b$  functions here depend only on position.
- **The summations over the  $N$  orbitals have been replaced by ones over the  $N/2$  different position-space functions.**

$$= \varepsilon_l \sum_{m=1}^{N_b} \langle \chi_p | \chi_m \rangle c_{ml}$$

# Projected Hartree-Fock

- Recall that *any* Hermitian, linear operator  $\hat{A}$  defines a complete set of orthonormal functions  $f_i$  through

$$\hat{A}f_i = a_i f_i, \quad (f_i | f_j) = \delta_{i,j}.$$

- Completeness here implies that *any* other function  $g$  can be expanded like

$$g = \sum c_i f_i, \quad c_i = (f_i | g)$$

- We then have:

$$\hat{A}g = \hat{A} \left[ \sum_i c_i f_i \right] = \sum_i c_i \hat{A}f_i = \sum_i c_i a_i f_i \neq \text{cst} \cdot g.$$

- Apply this to the operator  $\hat{S}^2$  with  $g$  the Slater determinant.  
**The equation above states that the Slater determinant is NOT an eigenvector of  $\hat{S}^2$**

# Projected Hartree-Fock

- Let us define the following projection operator:  $\hat{P}_k = |f_k\rangle\langle f_k|$ .

and assume that:  $f_i = f_i(\vec{x})$  and  $g = g(\vec{x})$

$$\hat{P}_k g(\vec{x}) = f_k(\vec{x}) \int f_k^*(\vec{y}) g(\vec{y}) d\vec{y} = c_k f_k(\vec{x}).$$

- Thus  $\hat{P}_k g(\vec{x})$  returns a constant times an eigenvector of  $\hat{A}$ . -- in essence

$\hat{P}_k g(\vec{x})$  (for any  $g$ ) is also an eigenfunction of  $\hat{A}$ . (more precise the same eigenfunction that was used to define the projection operator)!

- We can now apply this technique to the wavefunction  $\Phi$ :

$$\begin{aligned} \Phi = & \frac{1}{\sqrt{N!}} \sum_{i=1}^{N!} (-1)^{P(i)} \phi_1^+(\vec{r}_{i_1}) \alpha(i_1) \phi_2^+(\vec{r}_{i_2}) \alpha(i_2) \cdots \phi_n^+(\vec{r}_{i_n}) \alpha(i_n) \\ & \times \phi_1^-(\vec{r}_{i_{n+1}}) \beta(i_{n+1}) \phi_2^-(\vec{r}_{i_{n+2}}) \beta(i_{n+2}) \cdots \phi_m^-(\vec{r}_{i_N}) \beta(i_N), \end{aligned}$$

# Projected Hartree-Fock: An example

- We consider the following example:

$$\Phi = \frac{1}{\sqrt{2}} [\phi_1^+(\vec{r}_1)\alpha(1)\phi_1^-(\vec{r}_1)\beta(2) - \phi_1^+(\vec{r}_1)\alpha(2)\phi_1^-(\vec{r}_1)\beta(1)]$$

- You can show that the spin function

$$\theta = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

is an eigenfunction of  $\hat{S}^2$ .

$$\hat{S}^2\theta = 2\theta = 1 \cdot (1 + 1)\theta \equiv S(S + 1)\theta.$$



# Projected Hartree-Fock: An example

$$\Phi = \frac{1}{\sqrt{2}} [\phi_1^+(\vec{r}_1)\alpha(1)\phi_1^-(\vec{r}_1)\beta(2) - \phi_1^+(\vec{r}_1)\alpha(2)\phi_1^-(\vec{r}_1)\beta(1)].$$

$$\theta = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

- We need to form  $\hat{P}_k \Phi$ , where  $\hat{P}_k = |\theta\rangle\langle\theta|$
- We multiply  $\Phi$  with  $\theta^*$  and integrate (i.e. sum over the  $\alpha$  and  $\beta$  spin functions for both electrons) to finally obtain:

$$\frac{1}{\sqrt{2}} [\phi_1^+(\vec{r}_1)\phi_1^-(\vec{r}_2) - \phi_1^+(\vec{r}_1)\phi_1^-(\vec{r}_2)]$$

- We now multiply by  $\theta$  to obtain the following:

$$\frac{1}{\sqrt{2}} [\phi_1^+(\vec{r}_1)\phi_1^-(\vec{r}_2) - \phi_1^+(\vec{r}_1)\phi_1^-(\vec{r}_2)] \times \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

# Projected Hartree-Fock

---

- Simplifying the earlier equation leads to:

$$\begin{aligned} & \frac{1}{2} [\phi_1^+(\vec{r}_1)\alpha(1)\phi_1^-(\vec{r}_2)\beta(2) - \phi_1^+(\vec{r}_2)\alpha(2)\phi_1^-(\vec{r}_1)\beta(1)] \\ & + \frac{1}{2} [\phi_1^+(\vec{r}_1)\beta(1)\phi_1^-(\vec{r}_2)\alpha(2) - \phi_1^+(\vec{r}_2)\beta(2)\phi_1^-(\vec{r}_1)\alpha(1)] \end{aligned}$$

- **This is not any more a single Slater determinant but the sum of two determinants!**
- It is however an eigenfunction of  $\hat{S}^2$ .
- In general normalization of this eigenfunction is needed.

# Projected and extended Hartree-Fock

---

- There are now two different ways of applying this technique.
  - One can perform an unrestricted (standard) Hartree-Fock calculation (i.e., ignore the problem related to  $\hat{S}^2$  and **after** having obtained the self-consistent solutions to the Hartree-Fock-Roothaan equations, perform the projection. This is the so-called **projected Hartree-Fock method**.
  - Alternatively, at each step of the calculation one perform the projection during the iterative process of solving the Hartree-Fock-Roothaan equations. This leads to the so-called **extended Hartree-Fock method**.
- Neither approach is optimal, and one should apply methods that include correlation effects.

# What is missing in Hartree-Fock?

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➤ What is missing in Hartree-Fock is correlation.

## ➤ Dynamic correlation

Recall in the case of He, the 2 interacting electrons like to keep each other instantaneously as far away apart as possible. However, we tend to put electrons too close to each other because we have one electron interacting with the average field of the other (mean field solution). **There are a lot of configurations in which the 2 electrons are too close to each other, that raises the energy of the system (e.g. HF overestimates the energy).**

## ➤ Static correlation

Those have to do more with the fact that **a single determinant solution doesn't have the flexibility that you need and this was the case e.g. of the breaking of the H-molecule.** You really want in breaking apart the molecule to have a 2 determinants kind of flexibility with **both bonding and anti-bonding combinations.**

# ***Multiple determinants – using excited orbitals***

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- We will need to consider a wave function that is a combination of determinants with different coefficients in which the determinants have been constructed with a number of orbitals that **include also excited orbitals**.
- This would increase the variational flexibility of your problem (**configurational interaction**). We will come back to this in a forthcoming lecture.

The more flexible you become in your wave function, the closer you get to the right solution but at an enormous price (scaling of  $N^7$ ).