

Hartree-Fock methods

D.R. Hartree
(1897-1958)
Cambridge, UK



V.A. Fock
(1898–1974)
Leningrad, Russia

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
- [3.320 Atomistic Computer Modeling of Materials](#), Spring 2005, Notes by Prof. N. Marzari

Independent particle (Hartree) model

We will discuss in a systematic manner electronic structure methods starting with Hartree-Fock methods, one of the cornerstones of quantum chemistry (1920)

- We start with **the idea of Hartree** in dealing with the many body electron problem.

Independent particle model (Hartree): each electron moves in an effective potential, representing the attraction of the nuclei and the average effect of the repulsive interactions of the other electrons.

- This average repulsion is the **electrostatic repulsion of the average charge density of all other electrons.**
- Note that the same approach comes up in many other problems where we deal with a large number of interacting bodies (e.g. sensors and sensor networks).
- Here we do not consider what each electron instantly does but what each electron would do **in a field that on average represents what all the other electrons would be doing!**

Mean field approximation

- In this approach we do not try to find the solution that instantaneously knows about what each particle does but we try to find the solution for each particle interacting electrostatically with the average charge distribution of all other particles, *i.e. interacting with an average distribution of all other particles.*
- This is the concept of the **Mean Field Effective Potential**.
- The Hartree solution will lead to a **Schrödinger equation in which we are trying to solve the problem of one single electron at a time** where that electron feels the average electrostatic charge distribution of all the other electrons.

The matrix formulation of the Schrödinger equation

- We have chosen a basis set $\{\phi\}$ in which we expand the ground state wave function ($\{\phi\}$ could be localized Gaussians, sines or cosines of different wavelengths, etc.)

$$|\psi\rangle = \sum_{n=1,k} c_n |\varphi_n\rangle \quad \{|\varphi_n\rangle\} \text{ k orthogonal functions}$$

- Once $\{\phi\}$ is chosen, solving the Schrödinger equation (e.g. finding the eigenvalues and the corresponding eigenvectors) becomes a linear algebra problem.

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r}) \quad \Leftrightarrow \quad \hat{H}|\psi\rangle = E|\psi\rangle$$

$$\langle\varphi_m|\hat{H}|\psi\rangle = E\langle\varphi_m|\psi\rangle$$

$$\sum_{n=1,k} c_n \langle\varphi_m|\hat{H}|\varphi_n\rangle = Ec_m$$

The matrix formulation of the Schrödinger equation

- We arrive at the following computationally tractable eigenvalue problem:

$$\sum_{n=1,k} c_n \langle \varphi_m | \hat{H} | \varphi_n \rangle = E c_m$$

$$\sum_{n=1,k} H_{mn} c_n = E c_m$$

$$\begin{pmatrix} H_{11} & \dots & H_{1k} \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ H_{k1} & \dots & H_{kk} \end{pmatrix} \cdot \begin{pmatrix} c_1 \\ \cdot \\ \cdot \\ \cdot \\ c_k \end{pmatrix} = E \begin{pmatrix} c_1 \\ \cdot \\ \cdot \\ \cdot \\ c_k \end{pmatrix}$$

Reminder of the variational principle

$$E[\Phi] = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

- The other very useful principle is the variational principle.
- We have already shown that: $E[\Phi] \geq E_0$ for any approximation Φ of the ground state wavefunction.
- If $E[\Phi] = E_0$, then Φ is the ground state wavefunction and vice-versa.
- The expectation value of the Hamiltonian divided by a normalization factor takes arbitrary functions as an input and provides a number that is always greater or equal to the ground state (i.e. $E[\Phi]$ is a functional).
- One can try several trial ground state wavefunctions and select the one that gives the lowest value for $E[\Phi]$.

The interacting electron Schrödinger equation

- The problem of many interacting electrons increases its complexity very quickly. Here is the case of 2-electron system (Helium, 2 protons, 2 electrons)

$$\left[-\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right] \psi(\vec{r}_1, \vec{r}_2) = E_{el} \psi(\vec{r}_1, \vec{r}_2)$$

- Or the simpler case of one atom with many electrons

$$\left[-\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_i \sum_{j>i} \frac{1}{|\vec{r}_i - \vec{r}_j|} \right] \psi(\vec{r}_1, \dots, \vec{r}_n) = E_{el} \psi(\vec{r}_1, \dots, \vec{r}_n)$$

- The Hamiltonian for this problem is as follows:

$$\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{e-e} + \hat{V}_{N-N} + \hat{V}_{e-N}$$

The Hamiltonian

$$\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{e-e} + \hat{V}_{N-N} + \hat{V}_{e-N}$$

We can identify the following terms in the Schrödinger equation

- Quantum kinetic energy: $\hat{T}_e = -\frac{1}{2} \sum_i \nabla_i^2$
- Electron-electron interactions (two-body term): $\hat{V}_{e-e} = \sum_i \sum_{j>i} \frac{1}{|\vec{r}_i - \vec{r}_j|}$
- Nucleus-electron interactions $\hat{V}_{e-N} = \sum_i \left[\sum_I V(\vec{R}_I - \vec{r}_i) \right]$
- Quantum kinetic energy of the nucleus \hat{T}_N
- Electrostatic nucleus-nucleus interaction \hat{V}_{N-N}

Complexity of the many-electron Schrödinger equation

- For a nucleus with N -electrons orbiting around, we have a wave function that is the combined amplitude of N different spatial variables.
- For example, for an Iron atom (26 electrons), the wave function will be a combined amplitude of 78 coordinates!! If we discretize each coordinate with 10 values we will have a total of 10^{78} unknowns.
- Recall that the Schrödinger equation contains **two-body terms** (that depend on the simultaneous position of two electrons) and **one-body terms** that act on only one electron at a time (quantum kinetic energy and nucleus-electron attraction terms).
- The many-body Schrödinger equation becomes overly complex and that is where variational methods come to play a role!!

Recall the Born-Oppenheimer approximation

- As discussed in an earlier lecture, we work with the electronic Schrödinger equation (in Hartree units) based on the Born-Oppenheimer or adiabatic approximations

$$\left[-\sum_{i=1}^N \frac{1}{2} \nabla_{\vec{r}_i}^2 + \frac{1}{2} \sum_{i_1 \neq i_2=1}^N \frac{1}{|\vec{r}_{i_1} - \vec{r}_{i_2}|} - \sum_{k=1}^M \sum_{i=1}^N \frac{Z_k}{|\vec{R}_k - \vec{r}_i|} \right] \Psi_e(\vec{x}) = E_e \cdot \Psi_e(\vec{x}).$$

- We will often not use the subscript e in the ground state energy E_e but you always need to remember that this **is not the total energy of our system!**

$$E = \frac{1}{2} \sum_{k_1 \neq k_2=1}^M \frac{1}{4\pi\epsilon_0} \frac{Z_{k_1} Z_{k_2} e^2}{|\vec{R}_{k_1} - \vec{R}_{k_2}|} + E_e(\vec{X})$$

The Hartree approximation: single orbitals

- The Hartree equations can be obtained from the variational principle, once the search is restricted to the **many-body wavefunctions that are written as the product of single orbitals (i.e. we are working with independent electrons)**

$$\psi(\vec{r}_1, \dots, \vec{r}_n) = \varphi_1(\vec{r}_1) \varphi_2(\vec{r}_2) \cdots \varphi_n(\vec{r}_n)$$

- Single particle orbitals implies e.g. that varying r_1 will change the amplitude of the wave function independently from what happens to $r_2 \dots r_n$. **These have all become independent variables.**
- This approximation of course does not capture the complexity of all the possible N -body wavefunctions.

The Hartree method

- Hartree introduced this approximation in the variational principle.
- The difference from earlier treatments of the variational principle (where we had a trial function with some parameters) is that we now need to vary the shapes of the single particle orbitals.
- **We will need to derive the differential equations that each of these orbitals ϕ_1 to ϕ_N must satisfy so that the overall expectation value of the energy is minimum for a wave function written in this restricted form of a product of single particle orbitals.**
- The derivation will be reviewed in the next lecture.
- Instead of dealing with one single N -body Schrödinger equation (many-body wave function), we obtain a set of N different differential equations each one being a differential equation for only a single particle wave function.
- The problem still remains very complex: For the earlier example of the iron-atom, we will arrive at 26 equations each of them in 3D.

The Hartree equation

- The Hartree equation surprisingly looks like a Schrödinger equation for one electron

$$\left[-\frac{1}{2} \nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) + \sum_{j \neq i} \int |\varphi_j(\vec{r}_j)|^2 \frac{1}{|\vec{r}_j - \vec{r}_i|} d\vec{r}_j \right] \varphi_i(\vec{r}_i) = \varepsilon \varphi_i(\vec{r}_i)$$

- Note all the terms in the Hamiltonian: the quantum kinetic energy term for the i^{th} electron, the attractive potential felt from the nucleus, and the two-term electrostatic repulsion felt from all other electrons.

The Hartree equations

$$\left[-\frac{1}{2} \nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) + \sum_{j \neq i} \int |\varphi_j(\vec{r}_j)|^2 \frac{1}{|\vec{r}_j - \vec{r}_i|} d\vec{r}_j \right] \varphi_i(\vec{r}_i) = \varepsilon \varphi_i(\vec{r}_i)$$

- This is like a Schrödinger equation for one electron.
- There is the quantum kinetic energy term for this electron $-\frac{1}{2} \nabla_i^2$
- There is the interaction between this single electron with the Coulombic distribution of nuclei

$$\sum_I V(\vec{R}_I - \vec{r}_i)$$

The Hartree equations

$$\left[-\frac{1}{2} \nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) + \sum_{j \neq i} \int |\varphi_j(\vec{r}_j)|^2 \frac{1}{|\vec{r}_j - \vec{r}_i|} d\vec{r}_j \right] \varphi_i(\vec{r}_i) = \varepsilon \varphi_i(\vec{r}_i)$$

- The last term (“**the Hartree term**”) is the Coulombic repulsion electron i is feeling from all other electrons.

$$\sum_{j \neq i} \int |\varphi_j(\vec{r}_j)|^2 \frac{1}{|\vec{r}_j - \vec{r}_i|} d\vec{r}_j$$

- The **Coulombic repulsion** is between the electron i and the charge density distribution of every other (different from i) electron j .
- The many-body Schrödinger equation has now become a series of **single particle equations**.
- We have a **mean field interaction** between electrons since electron i does not instantaneously need to know what each of the other electrons does.

The Hartree equations: self-consistency

$$\left[-\frac{1}{2} \nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) + \sum_{j \neq i} \int |\varphi_j(\vec{r}_j)|^2 \frac{1}{|\vec{r}_j - \vec{r}_i|} d\vec{r}_j \right] \varphi_i(\vec{r}_i) = \varepsilon \varphi_i(\vec{r}_i)$$

- For the case of Iron-atom for example, 26 differential equations need to be solved simultaneously (using an iterative process).
- To solve for ϕ_i , we will need to know the Hartree term which involves the wave functions of the other electrons. The concept of **self-consistency** and iterative solution is thus always present in all the electronic structure calculations.

The Hartree equations: self-consistency

$$\left[-\frac{1}{2} \nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) + \sum_{j \neq i} \int |\varphi_j(\vec{r}_j)|^2 \frac{1}{|\vec{r}_j - \vec{r}_i|} d\vec{r}_j \right] \varphi_i(\vec{r}_i) = \varepsilon \varphi_i(\vec{r}_i)$$

Example: Self-consistency for the Iron-atom

- (1) Start with a guess for the 26 orbitals.
- (2) Then construct the charge density of every electron and so we can construct what will be the operator acting on each one of the ϕ_i .
- (3) We can then solve the differential eqs to find what are the ground states of each of these 26 differential eqs.
- (4) With those ground states we can construct again a charge density of each electron. Then we have a new Hartree operator and we can solve the differential eqs. again and we keep iterating until what we obtain is a Hartree operator in each differential equation that does not change anymore. We now have a set of **self-consistent orbitals**.

Iterations to self consistency

- Start with an initial guess for the orbitals
- Construct all the operators in the Hamiltonian
- Solve the single-particle Schrödinger equations (compute the ground state)
- With the newly computed set of single-particle orbitals, update the Hartree operators
- Solve again and continue until convergence

Iterations to self consistency

- In practice, one does not want to construct the Hartree operator at every iteration.
- It may be advantageous to modify a little bit the previous charge densities to then move in the direction of the new charge density to be calculated.
- In essence, one tries to minimize the change in the operators from one iteration to the other.
- **The Hartree equations are coupled integral-differential equations.**

Hartree equations for the He atom

- Let us approximate the wave function for the He atom as follows:

$$\Psi(r_1, r_2) = \phi_1(r_1)\phi_2(r_2)$$

- Applying the variational approach with this trial wave function, we can show that the (real) orbitals (s-states) ϕ_1 and ϕ_2 are defined by:

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + \int \frac{|\phi_2(r_2)|^2}{r_{12}} dV_2 \right] \phi_1(r_1) = E_1\phi_1(r_1),$$

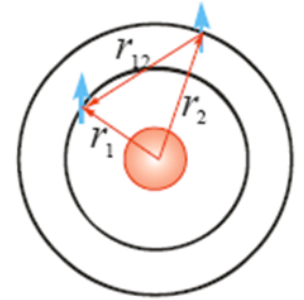
$$\left[-\frac{1}{2}\nabla_2^2 - \frac{2}{r_2} + \int \frac{|\phi_1(r_1)|^2}{r_{12}} dV_1 \right] \phi_2(r_2) = E_2\phi_2(r_2)$$

- These equations are solved self-consistently. The electronic energy $E = \langle \Psi | H \Psi \rangle$ is

$$E = \iint \phi_2(r_2)\phi_1(r_1) \left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \right] \phi_1(r_1)\phi_2(r_2) dV_2 dV_1$$

- Combining the above 3 equations, you can see immediately that:

$$E = E_1 + E_2 - \iint \frac{1}{r_{12}} |\phi_1(r_1)|^2 |\phi_2(r_2)|^2 dV_1 dV_2$$



What is missing in the Hartree equations?

- They do not include correlation
- The wavefunction is not antisymmetric
- It does not remove the (n,l) -accidental degeneracy of the hydrogenoid atom

Correlation

- We are missing information on what is happening instantaneously to all the electrons. This is a very fundamental effect called **correlation**.
- Let us consider the case of the He (2 electrons). We have two Hartree eqs, and in each of them, **one electron fills an average electrostatic repulsion from the other electron**.
- Thus each electron is attracted to the nucleus and is repelled by a spherically symmetric average charge distribution.
- In reality, **electrons instantaneously try to keep themselves as far apart as possible**. In a simplified manner you can think that electron 1 and electron 2 repulse each other and try to orbit the nucleus as much as possible in opposite phases.

Correlation

- This **instantaneous (dynamic) correlation** -- that the wave functions try to keep the electrons as far away as possible -- is lost in the Hartree equations because what we have is one electron interacting with the average position of the other electrons.
- The overall solution of the Hartree equations tends to have **too much electrostatic repulsion between electrons** and thus why ultimately **the energy of the Hartree wave function is higher than the true solution**.
- What we need in the Hartree equations is electron correlation -- electrons trying to keep each other as mush apart as possible.
- In the Hartree solution you have lost the possibility of having instantaneous non-symmetric distribution -- this is what we call correlation.

Antisymmetry of the wavefunction

- ▶ The Hartree wave function does not satisfy a fundamental rule for the wave function -- is not anti-symmetric.
- ▶ A set of indistinguishable fermions has a wavefunction that is antisymmetric by exchange.

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_j, \dots, \vec{r}_k, \dots, \vec{r}_n) = -\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_k, \dots, \vec{r}_j, \dots, \vec{r}_n)$$

- ▶ Note electrons are fermions (half integer spin). For bosons (integer spin), the wave function is symmetric by exchange.
- ▶ There is one more source of error in the estimate of the energy. It does not remove the accidental degeneracy – the fact that there is the same energy for electrons with the same principal quantum number n and the same angular momentum number l .

Antisymmetry of the wavefunction

- You can satisfy the symmetry requirement if instead of taking the product of n -orbitals you take the sum of the product of n -orbitals where you interchange the variables in all the possible ways putting a + or a – sign in front depending on how much interchanges you have.
- For e.g. if you have two electrons and thus two orbitals a and b – the Hartree solution which will be $a(1) b(2)$, i.e. the product of the a -orbital function of the r_1 and the b -orbital function of the r_2 . What we can do is to take instead

$$a(1) b(2) - b(1) a(2)$$

- Our wave function now changes sign when we exchange 1 and 2. **This is a trial wave function that has built in anti-symmetry constraint for exchange particles.** This can be generalized to the case of n -particles –using a determinant! That’s the idea of the Hartree-Fock method.

Slater determinant

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_\alpha(\vec{r}_1) & \varphi_\beta(\vec{r}_1) & \cdots & \varphi_\nu(\vec{r}_1) \\ \varphi_\alpha(\vec{r}_2) & \varphi_\beta(\vec{r}_2) & \cdots & \varphi_\nu(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_\alpha(\vec{r}_n) & \varphi_\beta(\vec{r}_n) & \cdots & \varphi_\nu(\vec{r}_n) \end{vmatrix}$$

- An antisymmetric wave function is constructed via a Slater determinant of the individual orbitals (instead of just a product in the Hartree approach)
- We will show at the end of this handout that **when we plug this into the variational principle we arrive at a single Schrödinger like equation – integral differential equation –that looks like the Hartree equation with an additional (exchange) term.**
- For two electrons in quantum states p_1 and p_2 , compare the wave function for the Hartree and Hartree-Fock methods:

$$\text{Hartree Fock: } \Psi(r_1, r_2) = \frac{1}{\sqrt{2}} [\phi_{p_1}(r_1)\phi_{p_2}(r_2) - \phi_{p_2}(r_1)\phi_{p_1}(r_2)] \quad \text{Hartree: } \Psi(r_1, r_2) = \phi_{p_1}(r_1)\phi_{p_2}(r_2)$$

Final Hartree-Fock equation

Working with the variational principle and the Slater determinant approximation for the many-body wave function, we finally arrive at (proof in a following lecture):

$$\begin{aligned} \psi(\vec{r}_1, \dots, \vec{r}_n) = \|\text{Slater}\| \\ \left[-\frac{1}{2} \nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) \right] \varphi_\lambda(\vec{r}_i) + \\ \left[\sum_\mu \int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\mu(\vec{r}_j) d\vec{r}_j \right] \varphi_\lambda(\vec{r}_i) - \\ \sum_\mu \left[\int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\lambda(\vec{r}_j) d\vec{r}_j \right] \varphi_\mu(\vec{r}_i) = \varepsilon \varphi_\lambda(\vec{r}_i) \end{aligned}$$

Terms in the Hartree-Fock operator

- As in the Hartree equations, we have the **quantum kinetic energy** for that

$$\text{electron } \lambda : -\frac{1}{2} \nabla_i^2$$

- We still have the interaction between that electron and the collection of **attracting Coulombic potentials**:

$$\sum_I V(\vec{R}_I - \vec{r}_i)$$

- We still have the Hartree electrostatic term in which the electron λ interacts with the

charge density $\varphi_\mu^*(\vec{r}_j) \varphi_\mu(\vec{r}_j)$ of **every** electron μ :

$$\left[\sum_\mu \int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\mu(\vec{r}_j) d\vec{r}_j \right]$$

- Our new term with a minus sign comes out from the anti-symmetry requirement of the wavefunction

$$\sum_\mu \left[\int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\lambda(\vec{r}_j) d\vec{r}_j \right] \varphi_\mu(\vec{r}_i)$$

Exchange term in Hartree-Fock

$$\sum_{\mu} \left[\int \varphi_{\mu}^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_{\lambda}(\vec{r}_j) d\vec{r}_j \right] \varphi_{\mu}(\vec{r}_i)$$

- This rather exotic operator has the λ -orbital that we are acting inside the integral. This operator comes exclusively by the antisymmetry requirement of the wave function.
- There is another fundamental distinction between the Hartree and the Hartree-Fock equations: This sum on the following term is over ALL μ .

$$\left[\sum_{\mu} \int \varphi_{\mu}^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_{\mu}(\vec{r}_j) d\vec{r}_j \right] \varphi_{\lambda}(\vec{r}_i)$$

- In the Hartree equation, this sum was running over all the electrons except the one that we were considering. Recall the Hartree eqs:

$$\left[-\frac{1}{2} \nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) + \sum_{j \neq i} \int |\varphi_j(\vec{r}_j)|^2 \frac{1}{|\vec{r}_j - \vec{r}_i|} d\vec{r}_j \right] \varphi_i(\vec{r}_i) = \varepsilon \varphi_i(\vec{r}_i)$$

Self-interaction and exchange

- Thus in the Hartree-Fock eqs, the sum over μ is running on all the possible electrons (**it includes self-interaction**).
- Suppose that for example you were working on the H-atom (1 electron). Let us see what happens first with the Hartree equations.
- In the Hartree equations, there is no exchange term and there would be also no Hartree term because what you have is a sum over all the other electrons but there are no other electrons! We thus recover the single particle Schrödinger equation for the H-atom.

Self-interaction and exchange

- In the Hartree-Fock equation for the H-atom, you have an unphysical self-interaction, that is you have electron 1 interacting with itself (more precisely interacting with itself in a non-local way through its own charge distribution).

$$\left[\sum_{\mu} \int \varphi_{\mu}^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_{\mu}(\vec{r}_j) d\vec{r}_j \right] \varphi_{\lambda}(\vec{r}_i)$$

- Fortunately, in the Hartree-Fock equations there the exchange term shown above (with a minus sign) which cancels exactly for the H-atom the self-interacting term.

$$\sum_{\mu} \left[\int \varphi_{\mu}^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_{\lambda}(\vec{r}_j) d\vec{r}_j \right] \varphi_{\mu}(\vec{r}_i)$$

Self-interaction

- **Thus the Hartree-Fock theory is self-interaction corrected.**

An electron does not interact with itself.

- Other approaches that we will discuss later like density functional theory (DFT) do not satisfy this property. Many problems with DFT have are due to this self-interaction problem.
- Consider for example the case when an electron transitions from a shared bond to a localized bond. Because of the self-interaction problem, DFT would provide wrong energies but this will not be the case in Hartree-Fock.

Hartree-Fock eqs. vs. Hartree eqs.

- In the Hartree-Fock equation, the Hartree operator acting on the single particle orbitals does not depend on which orbital you are looking at because here you have a sum over all the states. Thus the Hartree-Fock equations have the same operator.

$$\left[-\frac{1}{2} \nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) \right] \varphi_\lambda(\vec{r}_i) + \left[\sum_\mu \int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\mu(\vec{r}_j) d\vec{r}_j \right] \varphi_\lambda(\vec{r}_i) - \sum_\mu \left[\int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\lambda(\vec{r}_j) d\vec{r}_j \right] \varphi_\mu(\vec{r}_i) = \varepsilon \varphi_\lambda(\vec{r}_i)$$

- In the Hartree equation, in the Hartree term the sum would exclude the electron itself. Thus the Hartree equations are more complex to solve because the operator changes depending on which electron is acting.

$$\left[-\frac{1}{2} \nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) + \sum_{j \neq i} \int |\varphi_j(\vec{r}_j)|^2 \frac{1}{|\vec{r}_j - \vec{r}_i|} d\vec{r}_j \right] \varphi_i(\vec{r}_i) = \varepsilon \varphi_i(\vec{r}_i)$$

Scaling of the Hartree-Fock equations

- In the Hartree-Fock equation, the main cost is in computing the integrals.

What is the scaling cost of the Hartree-Fock equations? How does the cost of the problem change when we double the size of the system?

- **Hartree-Fock scales to the 4th power of the size of the system.** Thus why we cannot study anything beyond a few molecules with Hartree-Fock. Other methods are needed to investigate clusters of atoms, solids, surfaces/interfaces, DNA, etc.
- Next we will provide a derivation of the Hartree-Fock equations that can be skipped from those not interested on it. We do not give the derivation of the Hartree eqs as that is following the same steps as for the Hartree-Fock equations. The textbooks by Springborg and Bransden & Joachain can be consulted for more details.