

From Electrons to Materials Properties

Density Functional Theory for Engineers and Materials Scientists

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Chapter IV

Hartree-Fock Theory and Correlation

Integrating the spin

When considering electrons, we have to deal with spin. Each electron can have a spin eigenvalue of $s = \pm \frac{1}{2}$, with corresponding wavefunctions for α spin (aka up spin) and β spin (aka down spin). Spin eigenfunctions are orthonormal, i.e.

$$(1) \quad \langle s_i | s_j \rangle = \delta_{ij}$$

And they are multiplicative with the spatial wavefunctions, i.e.

$$(2) \quad |\phi(i)\omega(s)\rangle = |\phi(i)\rangle|\omega(s)\rangle$$

This directly yields the integrals

$$(3) \quad \langle is | jt \rangle = \langle i | j \rangle \langle s | t \rangle = \delta_{ij} \delta_{st}$$

With this knowledge, let us check the integrals appearing in our molecular Hamiltonian:

$$(4) \quad \langle i\alpha | \hat{h} | j\alpha \rangle = \langle i | \hat{h} | j \rangle \langle \alpha | \alpha \rangle = h_{ij} \delta_{ij}$$

$$(5) \quad \langle i\beta | \hat{h} | j\beta \rangle = \langle i | \hat{h} | j \rangle \langle \beta | \beta \rangle = h_{ij} \delta_{ij}$$

$$(6) \quad \langle i\alpha | \hat{h} | j\beta \rangle = \langle i | \hat{h} | j \rangle \langle \alpha | \beta \rangle = 0$$

$$(7) \quad \langle i\beta | \hat{h} | j\alpha \rangle = \langle i | \hat{h} | j \rangle \langle \beta | \alpha \rangle = 0$$

The one-electron operator only survives if the spin is the same on both basis functions.

$$(8) \quad \langle i\alpha j\alpha | \hat{J} | i\alpha j\alpha \rangle = \langle ij | \hat{J} | ij \rangle \langle \alpha\alpha | \alpha\alpha \rangle = \langle ij | \hat{J} | ij \rangle \langle \alpha | \alpha \rangle \langle \alpha | \alpha \rangle = J_{ij}$$

$$(9) \quad \langle i\alpha j\beta | \hat{J} | i\alpha j\beta \rangle = \langle ij | \hat{J} | ij \rangle \langle \alpha\beta | \alpha\beta \rangle = \langle ij | \hat{J} | ij \rangle \langle \alpha | \alpha \rangle \langle \beta | \beta \rangle = J_{ij}$$

The Coulomb operator survives regardless of the spins of electrons i and j .

$$(10) \quad \langle i\alpha j\alpha | \hat{K} | i\alpha j\alpha \rangle = \langle ij | \hat{J} | ji \rangle \langle \alpha\alpha | \alpha\alpha \rangle = \langle ij | \hat{J} | ji \rangle \langle \alpha | \alpha \rangle \langle \alpha | \alpha \rangle = K_{ij}$$

$$(11) \quad \langle i\alpha j\beta | \hat{K} | i\alpha j\beta \rangle = \langle ij | \hat{J} | ji \rangle \langle \alpha\beta | \beta\alpha \rangle = \langle ij | \hat{J} | ji \rangle \langle \alpha | \beta \rangle \langle \beta | \alpha \rangle = 0$$

The exchange operator only survives if both electrons have the same spin.

Integrated over all possibilities, we obtain (with an even number of electrons and the same number of electrons for each spin)

$$(12) \quad \sum_{i>j} \langle ij || ij \rangle = J - \frac{1}{2} K$$

$$(8) \quad \langle i\alpha j\alpha | \hat{J} | i\alpha j\alpha \rangle = \langle ij | \hat{J} | ij \rangle \langle \alpha\alpha | \alpha\alpha \rangle = \langle ij | \hat{J} | ij \rangle \langle \alpha | \alpha \rangle \langle \alpha | \alpha \rangle = J_{ij}$$

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The Fock Operator and basis sets

The Fock operator

$$(13) \quad \hat{F} = \hat{h} + \hat{J} - \hat{K}$$

yields one-electron wavefunctions for N electrons (in $N/2$ doubly occupied spatial orbitals) within a Schrödinger-like approach as

$$(14) \quad \hat{F}|i\rangle = \hat{h}|i\rangle + \sum_{j=1}^{N/2} (2\hat{J}_j - \hat{K}_j)|i\rangle = \epsilon_i|i\rangle$$

Now if we use any basis expansion in the form

$$(15) \quad |m\rangle = \sum_i c_{im}|i\rangle$$

our equation becomes

$$(16) \quad \hat{F}|m\rangle = \sum_i \hat{F}c_{im}|i\rangle = \epsilon_m \sum_i c_{im}|i\rangle$$

With the overlap matrix

$$(17) \quad S_{ij} = \langle i|j \rangle$$

we obtain the matrix equation

$$(18) \quad \mathbf{FC} = \mathbf{SCE}$$

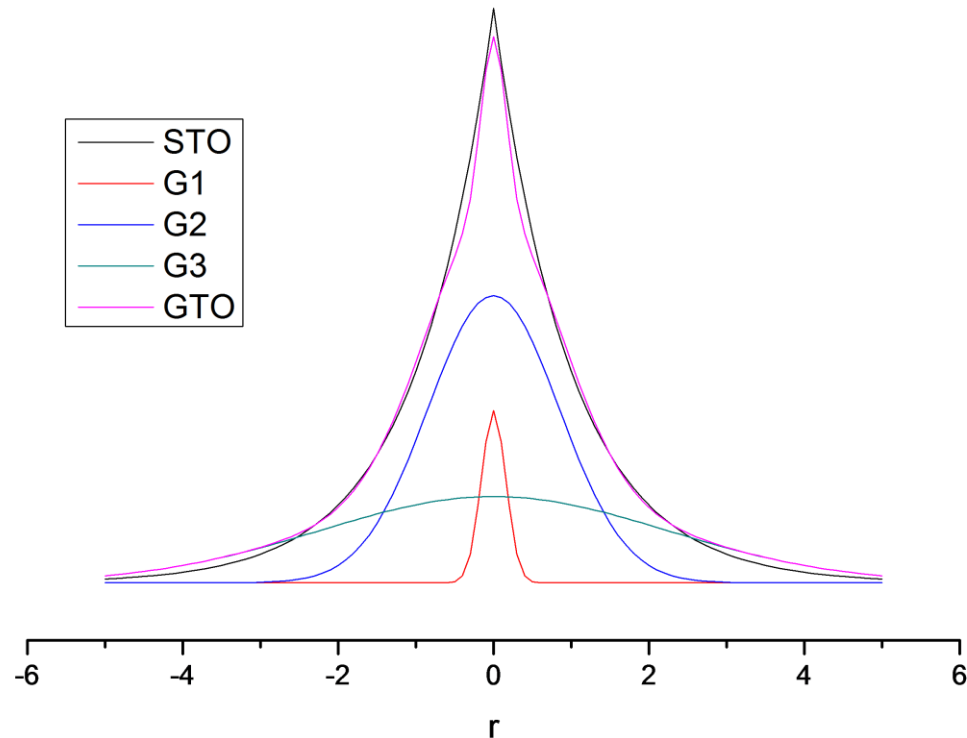
The only problem we have is that it is an iterative procedure. How can we solve this iteratively, with minimal computer time?

The Hartree-Fock algorithm (Roothaan-Hall method)

- i) Set up the atomic information (positions of nuclei, charges of nuclei, number of electrons, basis set)
- ii) Compute $\langle i|\hat{h}|j\rangle$, $\langle ij|\hat{J}|kl\rangle$ and $\langle ij|\hat{K}|kl\rangle$, $\langle i|j\rangle$
- iii) Determine density matrix $\mathbf{P} = 2\mathbf{C}^T\mathbf{C}$
- iv) Compute \mathbf{F}
- v) Diagonalize \mathbf{E} so that $\mathbf{F}' = \text{diag}(\mathbf{F})$, and obtain new coefficients \mathbf{C}' as eigenvectors
- vi) Update $\mathbf{P}' = 2\mathbf{C}'^T\mathbf{C}'$
- vii) Compare if $(\mathbf{P}' - \mathbf{P}) < \text{accuracy}$; if yes, go to viii), else go to iv)
- viii) Compute observables

Basis sets

Now we can work within different basis sets. The original, hydrogen-like basis is problematic, as we have a cusp in the center of the basis function. It is not continuous in this point. However, we can fit a set of Gaussian functions to this Slater-type function



Now all we need to do is optimize the expansion coefficients of the Gaussian basis (primitive Gaussians). However, not all expansion coefficients need to be optimized. Especially for inner-shell orbitals, we can optimize them once and then keep them constant, so that later on this ensemble is only scaled by a single expansion coefficient. We call such orbitals contracted Gaussians, and we write the contraction like

$$(19) \quad 10s4p3d1f \rightarrow 6s3p2d1f$$

This means that 10 primitive Gaussians of s-type character are contracted into 6 contracted Gaussian-type orbitals (CGTOs), 4 of p-type character into 3 CGTOs, 3 of d-type character into 2 CGTOs, and the f-type character is described by a single primitive Gaussian.

Furthermore, we can add more diffuse Gaussian-type orbitals (GTOs) to help describe Rydberg states or strongly excited states, and we typically add polarization functions.

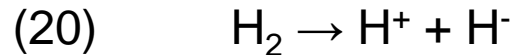
A polarization function is a function of higher angular momentum (quantum number l) than the respective orbital. It is typically a diffuse function as well. This changes the symmetry of the density distribution in the orbital, hence it makes it appear as if it is facing a polarizing force. This helps minimizing the basis for a valid description of chemical bonds.

Another advantage of GTOs is that the product of two Gaussians is another Gaussian. This helps to solve integrals.

In condensed phase, especially in solids, we are facing periodic boundary conditions. The good news is that we can still use a GTO basis for this, as we can apply FFTs, and the Fourier transform of a Gaussian is a just another Gaussian. Unfortunately, especially in solids we face an electronic band structure, which is delocalized, and GTOs are localized by nature. The solution is to use plane waves, hence sine (or cosine) functions.

Finally, we have to take care of a change of sign if we permute two electrons. This tells us that we can only formulate our wavefunction as a determinant of basis functions, and not as a product.

Now let us have a look at the disadvantages of Hartree-Fock. If we want to dissociate H_2 , we face the problem that we are in a closed-shell formalism. Each orbital can only have either two or zero electrons. This means that we can only formulate our dissociation as



This yields a totally wrong dissociation curve. Even if we try an unrestricted approach, where both electrons are treated separately, we face the wrong behavior, as we still freeze their spin. Now, an easy way to overcome this is to apply a linear combination. In our minimal basis H_2 this would yield a wavefunction

$$(21) \quad \begin{aligned} \psi(r) &= A\psi_{\sigma}(r) \pm B\psi_{\sigma^*}(r) \\ &= \frac{A}{\sqrt{2}}(\phi_{1s}(r_1) + \phi_{1s}(r_2)) \pm \frac{B}{\sqrt{2}}(\phi_{1s}(r_1) - \phi_{1s}(r_2)) \end{aligned}$$

We are facing two different effects:

- A) Close to the minimum, Hartree-Fock yields the correct physical behavior. This state is determined by the dynamic correlation of electrons, i.e. Coulomb and exchange.
- B) Far away from the minimum, Hartree-Fock fails. Only a multi-determinant wavefunctions yields correct results. We have a dependence on the distance between the nuclei, hence we call it static correlation. Hartree-Fock methods cannot describe static correlation.

Obviously, if we are trying to solve the problem of static correlation as we did for minimal basis H_2 , the general problem scales as $\frac{2S+1}{n+1} \binom{n+1}{\frac{N}{2}-S} \binom{n+1}{\frac{N}{2}+S+1}$ with total spin S , N correlated electrons and n correlated orbitals. It is written in the well-known binomial form $\binom{m}{k} = \frac{m!}{k!(m-k)!}$, which shows that things can easily get out of control already for small systems.

Density Functional Theory (DFT)

Now let us consider that we do not have to look at individual electrons. Can the electronic density be sufficient to solve our problem?

Let us consider that there exists a density $\rho(\mathbf{r})$ describing a system, so that with a given potential energy V_1 we obtain

$$(22) \quad E_1 = \langle 1 | \hat{H}_1 | 1 \rangle = \int d\mathbf{r} V_1(\mathbf{r}) \rho(\mathbf{r}) + \langle 1 | \hat{T} + \hat{U} | 1 \rangle$$

If we now have a second potential V_2 with proper eigenfunction we obtain from variational theory

$$(23) \quad \begin{aligned} E_1 &< \langle 2 | \hat{H}_1 | 2 \rangle = \langle 2 | \hat{H}_2 | 2 \rangle - \langle 2 | \hat{H}_1 - \hat{H}_2 | 2 \rangle \\ &= E_2 + \int d\mathbf{r} (V_1(\mathbf{r}) - V_2(\mathbf{r})) \rho(\mathbf{r}) \end{aligned}$$

Analogously, we obtain

$$(24) \quad E_2 < \langle 1 | \hat{H}_2 | 1 \rangle = E_1 + \int d\mathbf{r} (V_2(\mathbf{r}) - V_1(\mathbf{r})) \rho(\mathbf{r})$$

The combination of eqs. 23 and 24 yields

$$(25) \quad E_1 + E_2 < E_1 + E_2$$

This means that the density of a system is unique to this system, hence we obtain a complete description of any system if we know the density.

Now all we need to do is derive the correct electronic density for any system...

Kohn and Sham suggested the following. As we know that our density is

$$(26) \quad \rho(\mathbf{r}) = |\psi^2(\mathbf{r})|$$

We can use this and approximate our density iteratively from orbital wavefunctions

$$(27) \quad \left(-\frac{1}{2} \nabla^2 + v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}[\rho(\mathbf{r})] \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

This reduces our problem to finding the correct exchange-correlation functional $v_{xc}[\rho(\mathbf{r})]$.