Ab initio methods: Hartree–Fock

Alston J. Misquitta

Centre for Condensed Matter and Materials Physics
Queen Mary, University of London

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The force-fields (equivalent term: potentials) you have encountered are generally fine, but may sometimes lead to insufficiently precise, or even qualitatively wrong results.

$$V_{\mathrm{LJ}}(r_{ij}) = \frac{A}{r_{ij}^{12}} - \frac{C}{r_{ij}^{6}}$$

$$V_{\mathrm{exp6}}(r_{ij}) = e^{-\alpha(r_{ij}-\rho_{ij})} - \frac{C_6^{ij}}{r_{ij}^{6}} + \frac{q_i q_j}{r_{ij}}$$

- ‘spherical’ atoms
- simple electrostatic models
- ‘static’ potentials

How do we go beyond the limitations of empirical potentials?

Are point-charges good enough?

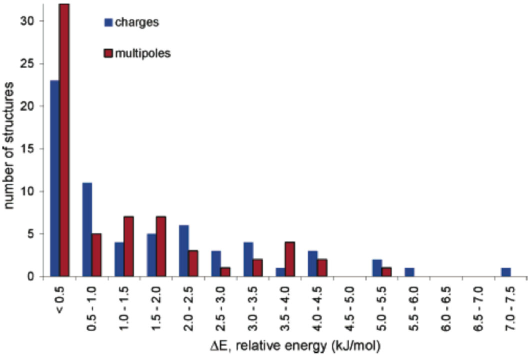
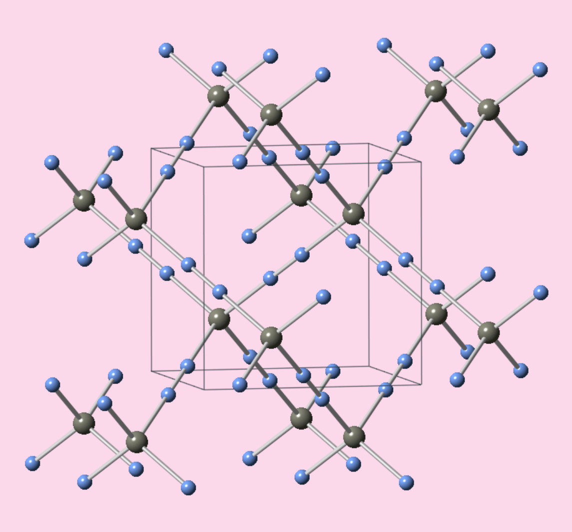
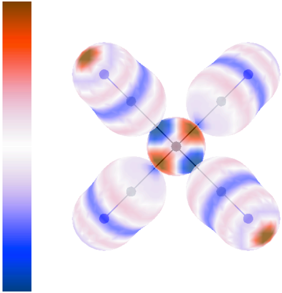


Figure 4. Distributions of ΔE with the atomic point charge and atomic multipole models.

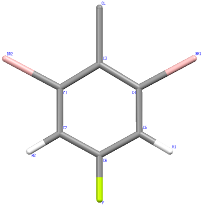
From Day *et al.* (2005).

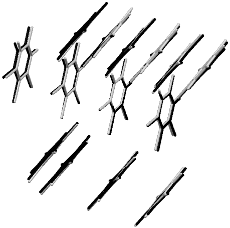
Point charges? Metal-organic frameworks.

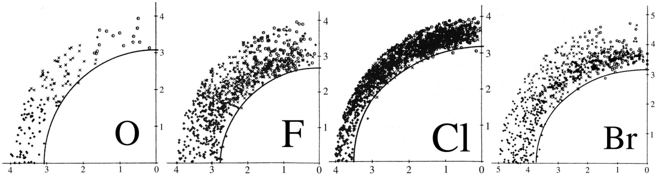




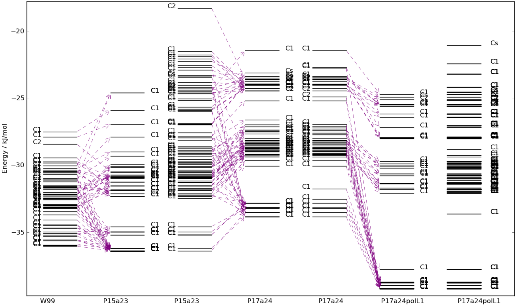
Are atoms spherical? (They aren't!)

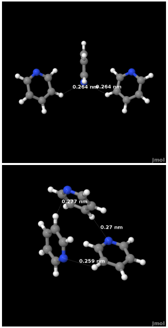


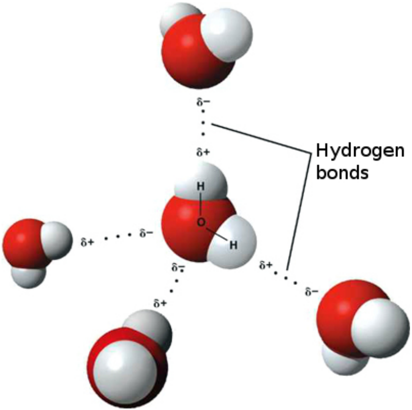




Going beyond static potentials: In systems with strong permanent moments and polarizabilities (water is a good example) the effects of *polarization* can be very important. This introduces a dynamical effect to the potential: it now needs to respond to the *environment*.






δ−
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Hydrogen bonds
H
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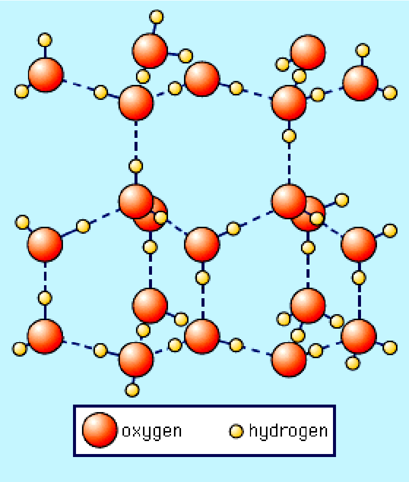
oxygen
hydrogen

So we might want to use *many-body* potentials of the form:

$$
\begin{aligned}
V_{MB}(r_{ij}) = e&^{-\alpha(r_{ij}-\rho_{ij}(\Omega))} \\
&- f_6(\beta r_{ij})\frac{C_6^{ij}}{r_{ij}^6} - f_8(\beta r_{ij})\frac{C_8^{ij}}{r_{ij}^8}\cdots \\
&+ Q^i_{lm} T^{ij}_{lm,l'm'} Q^j_{l'm'} \\
&+ \{\alpha^i_{lm,l'm'}, Q^i_{lm}, \forall i\}
\end{aligned}
$$

Q: Where do we get the data to develop all these extra terms?

Other reasons for *ab initio* data:

- Comformations used by complex molecules
- Bond-making/breaking
- No experimental data available to parameretize potentials in region of phase-space (simulations of matter under extreme or unusual conditions (see next example).
- Complex electronic excitations coupled with dymanics: charge (electron or proton) transfer. Lots of chaps in UCL doing this sort of thing theoretically and a number here in QM studying such processes experimentally.

Matter under extreme conditions: Ab initio random structure searching (AIRSS) of Chris Pickard and Richard Needs.

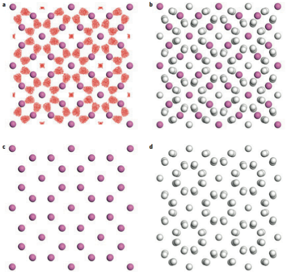

Figure 2 | Host-guest structures. a, The Al16 host-guest structure pictured along the axis of the guest chains, as obtained from density functional theory calculations. The guest atoms are at the centres of the octagonal rings. The red areas show the valence charge density above 65% of its maximum value. **b**, A structure obtained from random structure searching with simple pairwise potentials describing the interactions between 16 'Al' atoms (purple) and 28 'electron' blobs (white). **c**, The positions of the purple 'Al' ions from **b**, which gives a good approximation to the Ba-IV structure. **d**, The white 'electron' blobs from **b**, which give a good approximation to the Rb-IV structure.

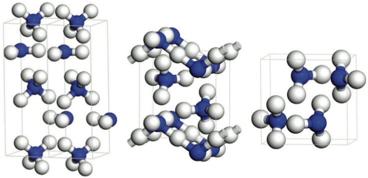

Figure 3 The *Pma*2, *P*2$_1$ / *m* and *Pnma* structures. The white spheres indicate hydrogen atoms and the blue spheres nitrogen atoms. The *Pma*2 structure (shown at 100 GPa) was calculated to be stable in the pressure range 90–331 GPa. It consists of alternate layers of approximately tetrahedral NH_4^+ ions and approximately right-angled NH_2^- ions. The NH_2^- ions are efficiently packed in a square-planar array, with the H atoms pointing towards the N atoms of neighbouring NH_2^- ions. The NH_4^+ ions are arranged in a square-planar array that is commensurate with the NH_2^- layers. The *P*2$_1$ / *m* structure (shown at 300 GPa) is stable in the range 331–440 GPa and consists of buckled NH_4^+ and NH_2^- layers with some symmetric hydrogen bonding between NH_2^- ions. The *Pnma* structure (shown at 450 GPa), calculated to be stable above 440 GPa, is a dense molecular phase. As shown in Fig. 1, this phase is quite competitive with the other molecular phases at low pressures.

Electronic structure methods

- Single-determinant methods: Hartree–Fock (HF), Density functional theory (DFT), Moller-Plesset perturbation theory at various orders (MP2, MP3, MP4,...), Configuration interaction (CI), Coupled-cluster methods (CCSD, CCSD(T), CCSDT,...), Full-configuration interaction (FCI)
- Multi-configutation methods: MCSCF, MRCI, ...
- Plane-wave methods
- Basis sets: STO-3G, 6-31G, 6-31G*, aug-cc-pVDZ, aug-cc-pVTZ, ...
- Programs: Castep, DALTON, NWChem, ADF, Molpro, Gaussian, Onetep, CamCASP, SAPT2008,...

Q: How do we choose the appropriate method/basis/program?

Variational Principle I

Q: How do we solve the Schrödinger equation?

We know how to do this only for a handful of systems:

- Harmonic oscillator
- Hydrogen atom
- Morse oscillator
- Square well

Variational Principle II

The variational principle provides us with a powerful method for solving the Schrödinger equation.

$$E_0 \leq \tilde{E} = \langle \tilde{\Psi} | \mathcal{H} | \tilde{\Psi} \rangle \tag{1}$$

with the normalization condition

$$\langle \tilde{\Psi} | \tilde{\Psi} \rangle = 1. \tag{2}$$

More generally,

$$E_0 \leq \tilde{E} = \frac{\langle \tilde{\Psi} | \mathcal{H} | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle}. \tag{3}$$

Variational Principle III

A reminder of the proof: Expand $\tilde{\Psi}$ in terms of the normalized eigenfunctions of $\mathcal{H}$ (Q: why can this be done?):

$$\tilde{\Psi} = \sum_k c_k \Psi_k. \tag{4}$$

$$\begin{aligned}
\langle \tilde{\Psi} | \mathcal{H} | \tilde{\Psi} \rangle &= \sum_{kl} c_k{}^* c_l \langle \Psi_k | \mathcal{H} | \Psi_l \rangle \\
&= \sum_{kl} c_k{}^* c_l \langle \Psi_k | E_l | \Psi_l \rangle \\
&= \sum_{kl} c_k{}^* c_l E_l \delta_{kl} \\
&= \sum_k |c_k|^2 E_k. \qquad (5)
\end{aligned}$$

$$\begin{aligned}
\langle \tilde{\Psi} | \tilde{\Psi} \rangle &= \sum_{kl} c_k{}^* c_l \langle \Psi_k | \Psi_l \rangle \\
&= \sum_{kl} c_k{}^* c_l \delta_{kl} \\
&= \sum_k |c_k|^2. \qquad (6)
\end{aligned}$$

Variational Principle IV

We get

$$\tilde{E} = \frac{\langle\tilde{\Psi}|\mathcal{H}|\tilde{\Psi}\rangle}{\langle\tilde{\Psi}|\tilde{\Psi}\rangle} = \frac{\sum_k |c_k|^2 E_k}{\sum_k |c_k|^2}. \tag{7}$$

So

$$\begin{aligned}\tilde{E} - E_0 = \frac{\sum_k |c_k|^2 E_k}{\sum_k |c_k|^2} - \frac{\sum_k |c_k|^2 E_0}{\sum_k |c_k|^2} &= \frac{\sum_k |c_k|^2 (E_k - E_0)}{\sum_k |c_k|^2} \\ &\geq 0,\end{aligned} \tag{8}$$

that is, $\tilde{E}$ is an upper-bound to the ground-state energy E_0.

Variational Principle V

Casting the variational principle as a linear equation problem

Consider the relatively straightforward case where $\mathcal{H}$ is a single-electron Hamiltonian:

$$\mathcal{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r}. \tag{9}$$

This is the hydrogen atom Hamiltonian and we all know how to solve it exactly. But this time we are going to find solutions using the variational principle.

Linear combination of basis functions I

Ansatz: Linear combination of basis functions

$$|\tilde{\Psi}\rangle = \sum_{i=1}^{N} c_i |\Phi_i\rangle \tag{10}$$

where the $\{|\Phi_i\rangle\}$ are a *fixed* set of N basis functions. More on the form of these later when we discuss Basis Functions. These basis functions may not be orthogonal (in fact, as we shall see, they won't be). Our goal is to optimize the coefficients $\{c_i\}$ to get an upper bound on the ground state energy.

Linear combination of basis functions II

We can perform the minimization of eq. 1 subject to condition eq. 2 using the method of Lagrange multipliers. Using the Lagrange multiplied E—chosen in anticipation that it will turn our to be the energy—let's define the functional:

$$\begin{aligned}\mathcal{L} &= \langle\tilde{\Psi}|\mathcal{H}|\tilde{\Psi}\rangle - E(\langle\tilde{\Psi}|\tilde{\Psi}\rangle - 1)\\ &= \sum_{ij} c_i^* c_j \langle\Phi_i|\mathcal{H}|\Phi_j\rangle - E\left(\sum_{ij} c_i^* c_j \langle\Phi_i|\Phi_j\rangle - 1\right)\end{aligned}$$

Linear combination of basis functions III

Setting first-order variations in $\mathcal{L}$ to zero we get:

$$\begin{aligned}
0 = \delta\mathcal{L} &= \sum_{ij} \delta c_i^* c_j \langle \Phi_i | \mathcal{H} | \Phi_j \rangle - E \sum_{ij} \delta c_i^* c_j \langle \Phi_i | \Phi_j \rangle \\
&\quad + \sum_{ij} c_i^* \delta c_j \langle \Phi_i | \mathcal{H} | \Phi_j \rangle - E \sum_{ij} c_i^* \delta c_j \langle \Phi_i | \Phi_j \rangle \\
&= \sum_{ij} \delta c_i^* c_j \langle \Phi_i | \mathcal{H} | \Phi_j \rangle - E \sum_{ij} \delta c_i^* c_j \langle \Phi_i | \Phi_j \rangle \\
&\quad + \sum_{ij} c_j^* \delta c_i \langle \Phi_j | \mathcal{H} | \Phi_i \rangle - E \sum_{ij} c_i^* \delta c_i \langle \Phi_j | \Phi_i \rangle
\end{aligned}$$

where we have interchanged dummy indices $i \leftrightarrow j$ in the last step.

Linear combination of basis functions IV

This can be written as

$$0 = \sum_i \delta c_i^* \left[\sum_j H_{ij} c_j - E \sum_j S_{ij} c_j \right] + \mathrm{c.c.} \tag{11}$$

Since the variations in the coefficients $\{\delta c_i^*\}$ and $\{\delta c_i\}$ are independent, the quantity in the square brackets must be zero, so we get

$$\sum_j H_{ij} c_j = E \sum_j S_{ij} c_j \tag{12}$$

or, using a matrix notation:

$$\mathbf{Hc} = E\mathbf{Sc} \tag{13}$$

Solve these linear equations and you have the *solutions* to the problem.

Meaning of eigenvalues I

A few points to note:

- We get as many solutions as the number of functions in the basis set.
- Q: The lowest energy solution is our ground state. But what do the others correspond to?
- The variational principle can be generalized: the other solutions are all upper bounds to the excited states in our system.
- This gives us a good way to calculate excited states too. But use with caution as excited states can require very extensive basis sets.

Hartree–Fock I

Now are need to consider what's to be done for many-electron systems. The Hartree–Fock approximation is the simplest physically correct theory we can use to solve such systems. The idea behind HF theory is simple:

- Expand the many-electron wavefunction in an appropriate basis. This basis has to have the correct symmetry properties—something we have not worried about so far.
- Minimize using the variational principle.

It's really that simple. But the symmetry condition makes it a little complicated and the fact that we are dealing with a many-electron system makes the mathematics harder. Here we will gloss over the details but look only at the main steps in HF theory.

Many electron Hamiltonian I

First of all, we have electrons and nuclei in our general Hamiltonian. The nuclei complicate matters. But we can simplify life by arguing that since the nuclei are nearly 2000 times heavier than the electrons, they can be considered fixed while we solve the electronic Hamiltonian. That is we solve

$$\mathcal{H}_\mathrm{e}\Psi_\mathrm{e} = E_\mathrm{e}\Psi_\mathrm{e} \tag{14}$$

where

$$\mathcal{H}_\mathrm{e} = -\sum_i \frac{1}{2}\nabla_i^2 - \sum_i \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} \tag{15}$$

Many electron Hamiltonian II

to get the wavefunction and energy that will be parametrically dependent on the positions of the nuclei:

$$\begin{aligned} \Psi_{\mathrm{e}} &= \Psi_{\mathrm{e}}(\{r_i\};\{R_\alpha\}) \\ E_{\mathrm{e}} &= E_{\mathrm{e}}(\{R_\alpha\}) \end{aligned}$$

From the latter we get our notion of an energy landscape on which the nuclei move (often assumed to be Classically using Newtons Laws - i.e, Molecular Dynamics).

Many electron Hamiltonian III

There are two cases then the BO approximation is invalid:

- Fast nuclei: The BO condition should not really be stated in terms of the mass ratios of the electrons and nuclei, but rather in terms of the kinetic energy ratios. If nuclei are very fast, they can have kinetic energies comparable with those of the electrons. Example: Radiation damage.
- Level crossing: This is a subtle one. If two electronic energy levels cross (often happens with excited states) then if there is a vibrational mode of appropriate symmetry, the BO approximation breaks down. This is the Jahn–Teller effect where we must consider a coupling of the electronic and nuclear motions.

Many electron basis I

The many-electron basis has two requirements we have not considered so far:

- Spin: We need to consider spin-orbitals rather than just spatial orbitals.
- Antisymmetry: The many electron basis functions cannot simply be products of one-electron spin-orbitals. It must be antisymmetric with respect to electron exchange.

Many electron basis II

The first condition is simple enough to take care of. If we have a spatial orbital $\psi(r)$ we can construct two spin-orbitals:

$$\chi(x) = \begin{cases} \psi(r)\alpha(\omega) \\ \psi(r)\beta(\omega) \end{cases} \tag{16}$$

All wavefunctions will be constructed from these spin-orbitals. We have assumed that there is no difference between the up and down spins states. This *restricted* solution is valid for a closed-shell systems. In general we will want to allow the spatial parts of the two spins to vary independently. This leads to what's known as an *unrestricted* solution. More later.

Many electron basis III

The antisymmetry condition puts restrictions on the kinds of trial wavefunctions we can use. Consider a two-electron case: The following trial wavefunction is not allowed for electrons

$$\Psi^{\mathrm{HP}}(x_1, x_2) = \chi_i(x_1)\chi_j(x_2)$$

This is because $\Psi^{\mathrm{HP}}(x_1, x_2) = \Psi^{\mathrm{HP}}(x_2, x_1)$. I.e., the wavefunction remains invariant on interchanging the electron labels. Such a wavefunction is suitable for bosons and is called the Hartree product (hence, the 'HP' superscript).

Many electron basis IV

To make our trial wavefunction antisymmetric we need it to be of the form:

$$\begin{aligned}\Psi(x_1, x_2) &= \frac{1}{\sqrt{2}}\left(\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2)\right) \\ &= \frac{1}{\sqrt{2}}\begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) \\ \chi_i(x_2) & \chi_j(x_2) \end{vmatrix}\end{aligned}$$

This is called a *Slater determinant*.

Many electron basis V

More generally, for N-electrons the Slater determinant takes the form

$$\Psi(x_1, x_2, \cdots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_k(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \cdots & \chi_k(x_N) \end{vmatrix} \tag{17}$$

$$\equiv |\chi_i \chi_j \cdots \chi_k\rangle \tag{18}$$

where the last equation is short-hand for writing out the determinant.

Hartree–Fock equations I

So now let us describe the ground state of our N-electron system with the BO approximation using a single Slater determinant:

$$\Psi_0(x_1, x_2, \cdots, x_N) = |\chi_1 \chi_2 \cdots \chi_N\rangle \tag{19}$$

The Hartree–Fock approximation to the ground state energy is found by varying the spin-orbitals $\{\chi_i\}$ to minimize the energy:

$$E_0 \leq E^{\mathrm{HF}} = \min \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle \tag{20}$$

subject to the conditions that the spin-orbitals are orthonormal.

Hartree–Fock equations II

As before, but with many more steps, the variational principle leads to the following equations for the spin-orbitals

$$f(i)\chi(x_i) = \epsilon\chi(x_i) \tag{21}$$

where $f(i)$ is an effective operator called the *Fock operator*

$$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} + v^{\mathrm{HF}}(i) \tag{22}$$

where $v^{\mathrm{HF}}(i)$ is the Hartree–Fock *effective* potential that depends on the solutions to the above equations. So we must solve these equations self-consistently: Make a guess for the solutions; construct the potential $v^{\mathrm{HF}}(i)$ from this guess; solve the Fock equations; get new solutions; and repeat till convergence.

Hartree–Fock equations III

What is the structure of the Hartree–Fock potential v^{HF}?

$$v^{\mathrm{HF}}(1)\chi_a(1) = \sum_{b\in\mathrm{occ}} \left(\int dx_2 \frac{|\chi_b(2)|^2}{r_{12}} \chi_a(1) - \int dx_2 \frac{\chi_b^*(2)\chi_a(2)}{r_{12}} \chi_b(1) \right)$$

$$= \sum_{b\in\mathrm{occ}} \int dx_2 \frac{\chi_b^*(2)(1-\mathcal{P}_{12})\chi_b(2)}{r_{12}} \chi_a(1)$$

The first term is a coulomb term: every electron sees the average coulomb potential of all electrons. The second is the exchange term. It lowers the total energy by introducing an *exchange hole*.

More on the exchange hole in a later lecture.

Hartree–Fock equations IV

- Like any Hamiltonian, there are an infinity of solutions to the Fock equations.
- We cannot in general solve for all of these, rather we introduce a basis in which we express the spatial parts of the spin-orbitals $\{\chi_i\}$:

$$\psi_i(r) = \sum_m C_{im}\phi_m(r) \tag{23}$$

- Exactly as before, this leads to a reformulation of the eigenvalue problem as a set of linear equations:

$$\mathbf{FC} = \epsilon\mathbf{SC} \tag{24}$$

  And we solve for the orbitals and orbital energies (the $\{\chi_i\}$ are the HF orbitals and the $\{\epsilon_i\}$ the orbital energies).
- The only complication is the self-consistency bit.

Hartree–Fock equations V

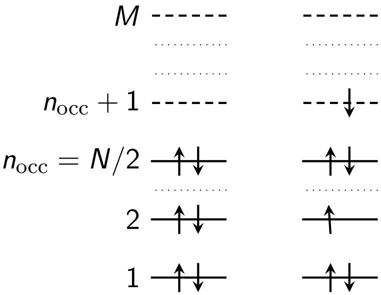

Figure : Left: HF ground state configuration for an N electron close-shell system. There are M basis functions in the spatial basis so we have M orbitals. Right: An example of an excited state configuration.

Hartree–Fock equations VI

Q: What is the Hartree–Fock energy?

$$
\begin{aligned}
E_0^{\mathrm{HF}} &= \sum_{a \in \mathrm{occ}} \epsilon_a \\
&\quad - \frac{1}{2} \sum_{a,b \in \mathrm{occ}} \left[\langle ab | r_{12}^{-1} | ab \rangle - \langle ab | r_{12}^{-1} | ba \rangle \right] \\
&\quad + E_{nn} \\
&= \sum_{a \in \mathrm{occ}} \epsilon_a - \frac{1}{2} \sum_{a,b \in \mathrm{occ}} (J_{ab} - K_{ab}) + E_{nn}
\end{aligned}
$$

where the first term is just the sum over orbital energy eigenvalues, the second term removes a double-counting of the e-e interations and the last is the nuclear-nuclear interaction term.

Hartree–Fock equations VII

The Coulomb integrals are:

$$J_{ab} = \langle ab|r_{12}^{-1}|ab\rangle = \iint \frac{\Psi_a^*(\mathbf{r}_1)\Psi_b^*(\mathbf{r}_2)\Psi_a(\mathbf{r}_1)\Psi_b(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

$$= \iint \frac{|\Psi_a(\mathbf{r}_1)|^2|\Psi_b(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

and the exchange integrals are:

$$K_{ab} = \langle ab|r_{12}^{-1}|ba\rangle = \iint \frac{\Psi_a^*(\mathbf{r}_1)\Psi_b^*(\mathbf{r}_2)\Psi_b(\mathbf{r}_1)\Psi_a(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

Hartree–Fock equations VIII

Physical quantities: The density.

$$\begin{aligned}
\rho(r) &= \sum_{a\in\mathrm{occ}} \chi_a^*(r)\chi_a(r) \\
&= \sum_{a\in\mathrm{occ}} \sum_{m} C_{am}^*\phi_m^*(r) \sum_{n} C_{an}\phi_n(r) \\
&= \sum_{mn} \left[\sum_{a\in\mathrm{occ}} C_{am}^* C_{an} \right] \phi_m^*(r)\phi_n(r) \\
&= \sum_{mn} P_{mn}\phi_m^*(r)\phi_n(r)
\end{aligned}$$

Where P_{mn} is called the *density matrix*. Once we have the charge density we can calculate quantities like the molecular multipoles...

Hartree–Fock equations IX

Koopmans' Theorem
The (vertical) ionization potential for removing an electron from spin-orbital c is the negative of the energy eigenvalue of orbital c:

$$\mathrm{IP} = E_c(N-1) - E_0(N) = -\epsilon_c$$

Likewise, the electron affinity to produce an $N+1$ electron state with additional electron in orbital r is equal to the negative of the orbital energy of that orbital, i.e.,

$$\mathrm{EA} = E_0(N) - E_r(N+1) = -\epsilon_r$$

Summary I

- Why *ab initio*? More realistic description of molecular processes. Unusual experimental conditions: very high pressures, electronic processes like bond-breaking, electron transfer. Premium on accurate predictions.
- Variational Principle Powerful method that underlies all approaches we will use. In combination with expansions in terms of a *basis*. Leads to sets of simultaneous equations.
- Hartree–Fock Born–Oppenheimer approximation. Spin-orbitals. *Antisymmetry* of trial wavefunctions. Single-determinant. Leads to Fock equations which are single-electron equations. Hartree–Fock effective potential: consists of Coulomb and exchange terms. *Potential depends on solutions!* Solve them by introducing an expansion in terms of a basis. Leads to self-consistent linear equations.

Summary II

References:

- Szabo and Ostlund, *Modern Quantum Chemistry*.
- Jorge Kohanoff, *Electronic Structure Calculations for Solids and Molecules*, Cambridge 2006.