

Q&A Lecture 7

How well is the trial wavefunction that consists of the single-electron wavefunctions in practice? Is there another typical form of wavefunction used when electron-electron interactions are strong?

The single-electron states can be constructed using different types of functions, typically based on orbitals and their linear combinations but not only. Depending on the structure and level of complexity of these functions, the accuracy varies and can be quite good. When interactions are relevant, the form is adapted to account - for example for correlation effects. A full description of Hartree and Hartree-Fock methods and of families of trial wavefunctions can be found in the book Modern Quantum Chemistry by Szabo and Ostund.

Could you just precisely explain how we do the algorithm to solve the Hartree model system. I am not sure to have understood how to pass from the i th step to the $(i+1)$ th step.

We start from a "guess" for the solutions and use it to compute the two mean field terms in the equations for the two single electron states (i.e. we assume a form for the two single electron states and we use it ONLY to compute the integral of the interaction term). With these mean field terms, we can obtain a solution for the system of variational equations for the states. This concludes the first iteration. For the second, we take the solution of the first iteration and we use it to compute again the two mean field terms. Then we repeat to converge.

I did not understand very well, from the point of view of assumptions and algorithms, the difference between the Hartree method alone and the Hartree-Fock method, could you enlighten me on this point?

The methods differ in the choice of the trial state. For Hartree we assume a simple product state, for Hartree-Fock we use a Slater determinant to incorporate the physical requirement that the total state of a system of electrons must be antisymmetric in the exchange of particles labels. The algorithm for the solution of the variational equations is essentially the same, but for Hartree-Fock the process is more costly due to the more complex shape of the trial state. H-F is, however, more accurate because it embeds more physics.

What are the advantages/disadvantages of Hartree-Fock compared to other methods such as perturbation theory?

Easier to apply numerically and larger convergence radius.

Are the coefficients automatically normalized or do we apply constrained minimization?

Constrained minimization must be applied (not done in class for simplicity).

When we take the interaction between two electrons into account, why can we assume the trial state as the tensor product of two pure states? Can there be any entanglement between the two electrons? For example, if the two electrons can not be in the ground states simultaneously, then the ground state of the whole system should be like

$\frac{1}{\sqrt{2}}(|\text{ket}\{0\}\text{ket}\{1\} + |\text{ket}\{1\}\text{ket}\{0\})$, which can not be expressed by a tensor product state. I'm not sure whether this example is correct.

The Hartree states do not include information about indistinguishability. The Hartree-Fock states (i.e. using the Slater determinant of a matrix whose entries are single electrons states) do. The Hartree-Fock states are antisymmetric and include entanglement.

We use the Hartree approximation that assumes the particles of the system evolve independently in an average interaction field from the rest of the system. This allows us to write the total wavefunction as a product of the wavefunctions of the two electrons. This results in two separable equations when we minimize our functional. How do we check what's a "satisfying" solution for us?

The evolutions are not independent, they are coupled via the mean field. The writing of the trial state as a product is AN ASSUMPTION not a consequence of the mean field. The equations are not separable, they are connected via the interaction term. If you mean in the iterative scheme, we stop the cycle when two successive iterations give values of the energies whose difference is smaller than a predefined threshold (say 10^{-8}).

Is the self-consistent method more/less prone to local minima? Do we have local minima in such methods where the solutions do not change much but are not truly the optimum? Would it occur if, instead of the ground state, we reached a higher excited state?

The issue of local minima is not particularly serious in this type of calculations. To be honest, in the field it is usually "assumed" that the minimization is to a global minimum and experience shows that the values of the energy obtained variationally are ok. Landing on an excited state is unlikely (and can be prevented). In particular, the first excited state is orthogonal to the ground state and one can impose, e.g., symmetry restrictions on the trial state that ensure that it is not compatible with it.

If two electrons are assumed not to interact, why do we use the sum of tensor products instead of the sum of each electron's Hamiltonian?

When we "expand" the system to account for the presence of the two electrons, we need a representation of the Hamiltonian and of the state that can represent this expanded space. A state, and an operator, must be able to represent operations in which both electrons are engaged. We construct the Hamiltonian as the tensor product of operators that act in the expanded state. Note that the tensor products always involve operators that live in the two different spaces ($H_1 \otimes I_2$ and vice versa) and then we sum these products. If we were to use only the sum of Hamiltonian of single electrons, we would have an inconsistency when trying to apply the total Hamiltonian to a state that represents both electrons (as a tensor product).

Are the integrals that contain W (mean field integrals) functions or functionals?

The integrals are part of the equation that we obtain when we take the functional derivative with respect to one of the single electron trial states. As such (like all first functional derivatives) they are a functional (in this case of the two single electrons trial states) AND a function of the point at which we take the functional derivative (i.e. the label of the coordinate index at the "denominator" in the functional derivative).

As mean field theory uses an average interaction between particles, is this method applicable to systems containing 3 or more particles? Would the self-consistent process still converge? And does the error in this method increase as more particles are added and the interaction term becomes more significant?

The method is applicable to systems containing any number of particles. For an N particles system, in the variational equations for each particle, the mean field part will contain an integral over the “other” $N-1$ particles. For the special and important case of Coulomb interactions, in which particles interact via a two-body potential, there will be a sum of terms like the one we have seen in class - each involving one of the “other” $N-1$ particles. The error does not increase with the number of particles (but the operations needed in the SCF become more costly). The key is the strength of the (sum of the) interaction(s): the stronger the less accurate the variational based on a tensor product structure.

Before doing the derivation of $\langle \psi | H | \psi \rangle$ we said that we assume the interaction between the electrons is small but I'm not sure to see where we used that assumption.

I think that the statement was more of a comment, the point being that if we start from a product form - i.e. a form that is correct in the absence of interaction - we expect it to lead to a reasonable variational approximation of the solution of the interacting problem when the interaction is small. The SCF will usually converge also for “large” interactions, but the number of iterations needed will be large and the obtained energy will be considerably larger than the exact ground state energy.

In the case where we have multiple N electrons, we will then have N equations, which each depend on $N-1$ other terms. Does it become possible to solve these equations this way anymore?

Yes, in fact I believe that Edrick has discussed (for the Hartree-Fock form of the trial function) the case of N electrons.

The question that I had is about the convergence of this method. Is it possible that the trial states that are chosen in the beginning (Hartree states) do not converge to the desired states yielding minimum energy? P. ex in a system with strong electronic interactions where the Hartree states would be too far from the actual state of the system? Or is there a theorem stating that this method always converges?

The convergence of the method can be studied using the so-called fixed point theorem. There are indeed situations in which the method can fail to converge, but the convergence conditions are “gentle” enough that this is quite rare. Convergence can, of course, always be verified numerically and in case of failure the situation is usually improved by refining the form of the initial guess for the single electron states.

If 2 or more electrons occupy the same orbital, are their states ($|\psi_i\rangle$ and $|\chi_i\rangle$, for example) still orthonormal?

If by orbital you mean only the coordinate-dependent part of the state (i.e. with no spin) and by state the full state (i.e. with the spin) then yes: the full states are still orthogonal because they will have different z components of the spin. If by orbital you mean the full state, then the two electrons cannot be in such a situation due to the Pauli principle.

In which cases would we want to use the Hartree approximation when we can use the Hartree Fock method instead? Also, when we solve for the spin-orbital solutions, do we need to consider the spin and the spatial wavefunction separately or not?

Nowadays, the Hartree method is not really used, while Hartree-Fock is. It is, however, important for historical reasons and as a stepping stone towards HF. Not sure what you mean by separately: the total state considers both spatial and spin.