multi-electron systems

Multi-electron systems are not solvable exactly*, as we have discussed. What happens as we go from the hydrogen case to a multiple particle, interacting system?
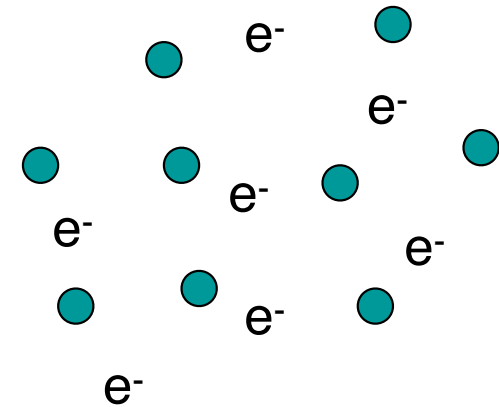
Given a collection of nuclei and electrons in some arrangement, what does the Hamiltonian look like?

Let R_1, …., R_N = positions of the N nuclei

eZ_1, …., eZ_N = charge of the N nuclei

M_1, …, M_N = masses of the nuclei

r_1,…, r_n = positions of the n electrons

Now, our wave function is more complicated

$$\Psi(r) \implies \Psi(R_1,...,R_N,r_1,...,r_n)$$

* at least, not in any finite amount of time or resource.

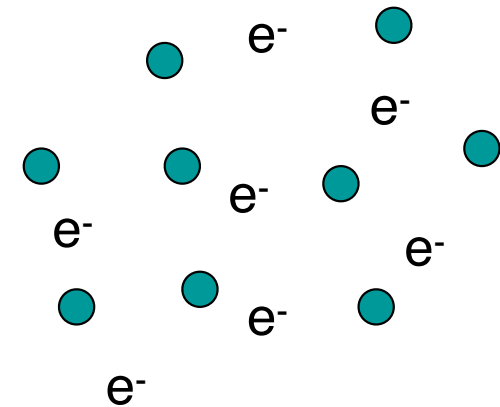Elif Ertekin | ertekin@illinois.edu | Mechanical Science and Engineering

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The Hamiltonian looks like:

$$\hat{H} = \sum_{j=1}^{N}\left(-\frac{\hbar^2}{2M_j}\right)\nabla_{R_j}^2 + \frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N}\frac{Z_iZ_je^2}{|R_i-R_j|} + \sum_{j=1}^{n}\left(-\frac{\hbar^2}{2m}\right)\nabla_{r_j}^2 + \frac{1}{2}\sum_{j=1}^{n}\sum_{i=1}^{n}\frac{e^2}{|r_i-r_j|} - \sum_{j=1}^{N}\sum_{i=1}^{n}\frac{Z_je^2}{|r_i-R_j|}$$

And our eigenvalue problem looks like:

$$\hat{H}\Psi(R_1,...,R_N,r_1,...,r_n) = \varepsilon\Psi(R_1,...,R_N,r_1,...,r_n)$$

In general, we really cannot solve this. We need to make some approximations first. These are related in particular into decoupling the system of interacting particles.

approximations

- No relativity
  - we have already assumed this, as we are not solving the Dirac equation

- Born-Oppenheimer Approximation
  - the nuclei are stationary with fixed ion positions R
  - i.e., we fix the positions R, and then determine the reduced wavefunction for the electrons
  - By doing this and scanning over all possible configurations R, we can find the global minimum for the energy
  - In reality, we need not scan - we can shift the ions in the directions that further minimize the energy

$$\hat{H}\left(\{R_i\}\right)\Psi\left(r_1,...,r_n\right) = \varepsilon\Psi\left(r_1,...,r_n\right)$$

-

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Born-Oppenheimer

A proton is 1836 times heavier than an electron. So, to a good approximation, the electrons can adjust "instantaneously" to changes in the positions of the nuclei.

Thus, the electronic wavefunction depends only on the positions of the nuclei and not on their momenta.

The total energy (as well as wavefunction) can be divided into a nuclear part and an electronic part.

Dynamics simulations are still possible, but for each arrangement of the nuclei the Schrödinger equation is solved for the electrons in the field of the nuclei.

many body Schrodinger equation
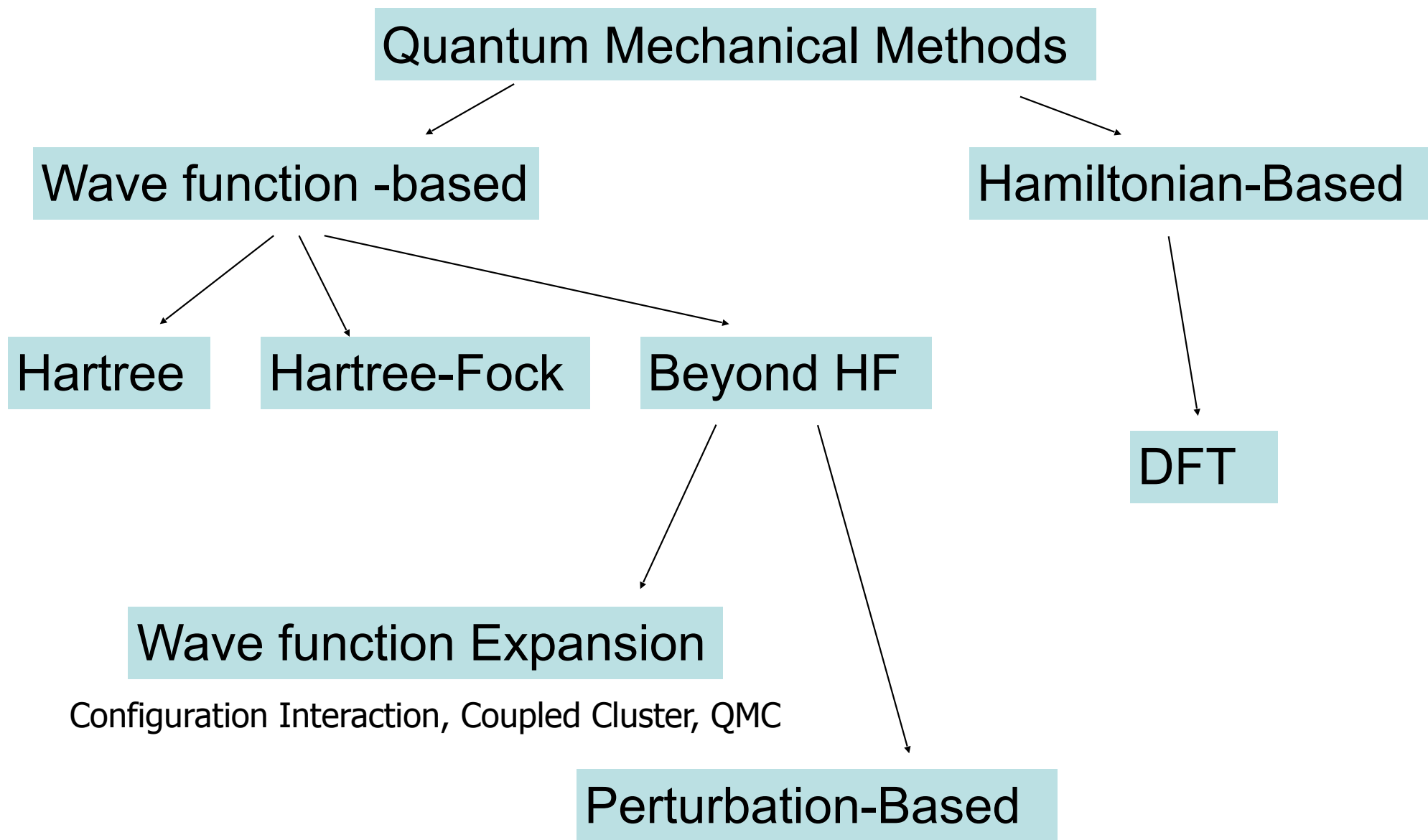
All of these approximations leave us with:

$$H\psi(r_1,...,r_n) = E\psi(r_1,...,r_n)$$

$$\widehat{H} = -\frac{1}{2}\nabla^2 - \sum\frac{Z_n}{r_{e-n}} + \sum\frac{1}{r_{e-e}}$$

Non-interacting part

Contains an Electron-Electron Distance!

This part is "easy". If we only had these two terms, the electrons would be non-interacting and the solution for the wave function actually would be separable.

In reality, the electrons do interact with each other. This existence of this term makes the actual solution not separable in fact.

methods

Quantum Mechanical Methods

Wave function -based

Hamiltonian-Based

Hartree

Hartree-Fock

Beyond HF

DFT

Wave function Expansion

Configuration Interaction, Coupled Cluster, QMC

Perturbation-Based

Wave function based methods

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typical solution approach

As a simple guess, one may try to write the wave function as a product of orbitals:

$$\Psi(1,2,...N) = \varphi_1(1)\varphi_2(2)...\varphi_N(N)$$

Here are are assuming we can write the many-particle wave function simply as a product of single particle states (orbitals) for each electron.

That is, we are assuming a separable solution. We know the actual wave function is not separable, but we can see how close we can get by considering only separable solutions.

This guess for the solution is called the Hartree product, and while it's a good start, it is not acceptable. This is because the wave function is not antisymmetric: exchanging pairs of electrons does not give the negative of the wave function.

A very important conclusion of the Hartree product description is that the probability of finding an electron at a particular point in space is independent of the probability of finding any other electronic at that point in space.

Thus, the motions of electrons in this description are uncorrelated.

Slater determinant

The simplest way to fix the antisymmetry issue is to write a wave function as a Slater determinant.

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \cdots & \varphi_N(1) \\ \varphi_1(2) & \varphi_2(2) & \cdots & \varphi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(N) & \varphi_2(N) & \cdots & \varphi_N(N) \end{vmatrix}$$

This formalism guarantees antisymmetry since exchanging any two rows of a determinant leads to a change in sign (and represents the process of exchanging two electrons).

As a nice bonus, the Slater determinant also guarantees that no two electrons can occupy the same orbital (Pauli tells us this) since that corresponds to two rows being identical.

This is the Hartree-Fock guess for the wave function.

LCAO

Even using a Slater determinant as a guess for the form of the wave function, we usually need to expand the molecular orbitals φ_i using some basis set.

In many quantum mechanical calculations, each molecular orbital is expressed as a linear combination of atomic orbitals (the "LCAO" approach).

In this approximation, each molecular orbital is written as a summation:

$$\varphi_i = \sum_{\mu=1}^{K} c_{\mu i} \phi_\mu$$

For example, in an LCAO picture of the H_2 molecule, there are 2 electrons of opposite spin occupying a spatial orbital $\sigma = (1s_A + 1s_B)$.

Basis Sets for Atomic Orbitals

Basis sets are usually composed of atomic functions. Why?

"Slater type" orbitals are exponential in form and are solutions to the radial part of the simple Hydrogen atomic orbital picture.

However, Slater orbitals are never used because it takes too long to numerically evaluate exponentials, and the multi-center integrals are very difficult to solve.

Instead, what is almost exclusively done is to use Gaussian functions, of the form $\exp(-ar^2)$. If a is large, the function does not spread out very far, while if a is small it gives a large spread.

Since the product of two Gaussians can be represented by a third Gaussian, the two-electron integrals become much simpler to evaluate.

One disadvantage, though, is that a Gaussian doesn't look quite like what we want. That is, it is not a perfect representation of an isolated atomic orbital. Usually we live with this error.

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Hartree-Fock - Variational Approach

So we have decided to use a Slater determinant for the form of the wave function, and we have decided to use a linear combination of atomic orbitals as the basis set for the single particle states.

But even so, we still need a way to find the best representation of the wave function within this constrained space.There is a criterion we can use to discern whether one proposed wave function is "better" than another.

The variational theorem is one mechanism - it states that the energy calculated from an approximation to the true wave function will always be greater than the true energy.

Thus, the better the wave function, the lower the energy. At a minimum, the first derivative of the energy will be zero.

The Hartree-Fock equations simply impose this condition on the expression for the energy, given a form of the wave function of the Slater determinant, and also given a constraint that the orbitals remain orthonormal.

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calculating the energy

$$E = \frac{\int \Psi^* H \Psi d\mathbf{r}}{\int \Psi^* \Psi d\mathbf{r}}$$

The energy calculation is as simple as evaluating these integrals…

Ok, well it's not all that simple, but after a bit of math, one can generalize its calculation to a set of 1-electron and 2-electron integrals.

Most integrals are zero, although there still remain a very large number to evaluate.

The Coulomb and "exchange" integrals are usually the most time-consuming.

What's the exchange interaction? Is it classical?

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