

So.

$$\hat{H}_{\text{tot}} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} \quad (2)$$

These terms are in atomic units.

where $m = \hbar = e^2 = 1$

The electron-nuclear interaction, also called the external potential and written

as $\hat{V}_{eN} = \hat{V}_{\text{ext}}$.

Then equ (2) will be

$$\hat{H}_{\text{tot}} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{\text{ext}} \quad (3)$$

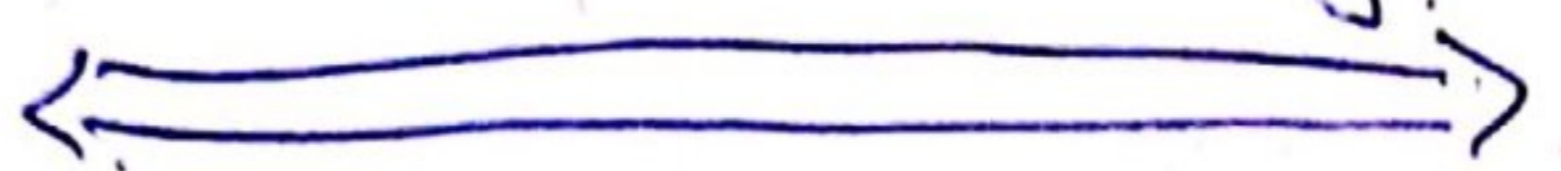
It is important to note that the kinetic and the electron-electron interaction terms in our Hamiltonian (equ (3)) depend only on a many-electron system and not on a many-proton system, where the strong nuclear force would play a central role. Specific information about the system (specifying the nuclei and their positions) is entirely described by \hat{V}_{ext} .

The Hamiltonian obtained after applying the Born-Oppenheimer approximation is much simpler than the original, but still too difficult to solve.

There are several methods to reduce equ. (3) to an approximate but in suitable form. A very important one is the Hartree-Fock method. It is frequently used in quantum chemistry because it performs very well for atoms and molecules, however, it is less accurate for solids (neglecting the electronic correlation, e.g.)

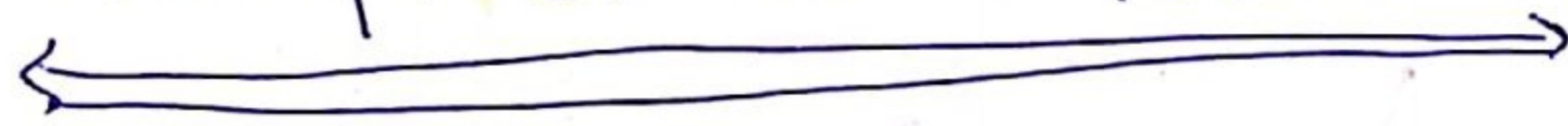
The other one is the Density functional theory, which is a more powerful and also more accurate method than the Hartree-Fock method.

Hartree Theory



Hartree theory is a wavefunction approach in order to solve the quantum many body problems. Let start with the brief overview over wavefunction methods.

Wavefunctions Methods



wavefunction approaches are based on Ritz variational principle:

$$E_0 \leq \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle}$$

where E_0 is the ground state energy of the system and H is the Hamiltonian and $\langle \phi |$ and $|\phi \rangle$ are the bra and ket joint eigenstates.

The Variational Principles :-

We solve the time-independent Schrödinger wave equation, which is

$$\hat{H}\psi = E\psi,$$

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V$$

for free particles. $V = 0$.

$$H = -\frac{\hbar^2}{2m} \nabla^2$$

Known as time-independent Hamiltonian. Let ψ be the trial normalized solution to the above eigenvalue equation. Thus, the variational principle states, quite simply, that the ground state energy E_0 is always less than or equal to expectation value of \hat{H} calculated with trial wavefunction i.e.

$$E_0 \leq \langle \psi | \hat{H} | \psi \rangle$$

Thus by varying ψ until the expectation value of \hat{H} is minimized, we can obtain

an approximation to the wavefunction and energy of the ground state: i.e.

Let us prove the variational principle. Suppose that the ψ_n and the E_n are true eigenstates and eigenvalues of \hat{H} ,

$$H \psi_n = E_n \psi_n$$

Furthermore, let

$$E_0 < E_1 < E_2 < \dots, \quad \text{--- (A)}$$

so that ψ_0 is the ground state, ψ_1 is the first excited state, ... we assume that the ψ_n are the orthonormal, so we can write in this form

$$\langle \psi_n | \psi_m \rangle = \delta_{nm}$$

The normalized trial wavefunction ψ is properly normalized the has the following form

$$\psi = \sum_n c_n \psi_n$$

where c_n is the normalization constant. and where

$$\sum_n |c_n|^2 = 1 \quad \checkmark \text{--- (B)}$$

Now, the expectation value of H , calculated with Ψ , takes the form

$$\langle \Psi | H | \Psi \rangle = \left\langle \sum_n C_n \Psi_n | H | \sum_m C_m \Psi_m \right\rangle$$

$$= \sum_{n,m} \int C_n^* C_m \Psi_n^* H \Psi_m dx$$

$$= \sum_{n,m} C_n^* C_m \int \Psi_n^* H \Psi_m dx$$

$$= \sum_n \underbrace{|C_n|^2}_{n=m} \int \Psi_n^* H \Psi_n dx$$

$$= \sum_n |C_n|^2 \int \Psi_n^* H \Psi_n dx$$

$$= \sum_n |C_n|^2 E_n$$

$$\langle \Psi | H | \Psi \rangle = \sum_n |C_n|^2 E_n \quad \text{--- (1)}$$

Therefore, we can write as $n=0$ and higher values of n .

$$\langle \Psi | H | \Psi \rangle = |C_0|^2 E_0 + \sum_{n>0} |C_n|^2 E_n \quad \text{--- (2)}$$

Then, from (*) eqn; we can write

$$|C_0|^2 + \sum_{n>0} |C_n|^2 = 1$$