Non-relativistic time-dependent Schroedinger equation

$$H|\Phi> = i\hbar \frac{\partial |\Phi>}{\partial t}$$

Evolution of a system with time

Non-relativistic time-independent Schroedinger equation

Hamiltonian operator for a system of nuclei and electrons

$$H|\Phi >= E|\Phi >$$

Hamiltonian operator for a system of nuclei and electrons

the operator for the **kinetic** energy of the electrons

Number of electrons

Number of nuclei

the operator for the **kinetic** energy of the nuclei

the operator for the **repulsion** energy between electrons

the operator for the **repulsion** energy between nuclei

$$H = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{A=1}^{M} \frac{\hbar^2}{2M'_A}\nabla_A^2 + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{Z_A e}{4\pi\epsilon_0 r_{iA}} + \sum_{A=1}^{M}\sum_{B>A}^{M} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$

Distance between the *i*th and *j*th electron

the operator for the **attraction** energy between electrons and nuclei

Distance between the *i*th electron and *A*th nucleus

Distance between the *A*th and *B*th nucleus

Hamiltonian operator for a system of nuclei and electrons in Atomic Units

$$H = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M} \frac{1}{2M_A}\nabla_A^2$$

$$+\sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{r_{AB}}$$

the operator for the **kinetic** energy of the electrons

Number of electrons

Number of nuclei

the operator for the **kinetic** energy of the nuclei

the operator for the **repulsion** energy between electrons

the operator for the **repulsion** energy between nuclei

Distance between the *i*th and *j*th electron

Distance between the *i*th electron and *A*th nucleus

the operator for the **attraction** energy between electrons and nuclei

Distance between the *A*th and *B*th nucleus

Schroedinger equation solution

Hydrogen atom and hydrogenic atoms
(H, He^{+}, Li^{2+}, ..., U^{91+})
--> EXACT SOLUTION
wave-function --> coordinates of a single electron

He, Hydrogen molecule, H_2^{+}
--> APPROXIMATED SOLUTION
wave-function --> coordinates of all electrons
many-body system

Born-Oppenheimer Approximation

Nuclei, being so much heavier than electrons, move relatively slowly and may be treated as stationary while the electrons move in their field.

$$H_{elec} = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}} - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{Z_A}{r_{iA}}$$

$$H_{elec}\Phi_{elec} = E_{elec}\Phi_{elec}$$

$$E_{tot} = E_{elec} + \sum_{A=1}^{M}\sum_{B>A}^{M} \frac{Z_A Z_B}{r_{AB}}$$

$$\Phi_{elec} = \Phi_{elec}(\{\mathbf{r}_i\}; \{\mathbf{r}_A\})$$

explicit dependence on the electron coordinates

parametric dependence on the nuclear coordinates

Variational principle

According to the variation principle for the ground state $|\Phi_0>$, the energy of an approximate wave function $|\tilde{\Phi}>$ is always higher.

$$H|\Phi_0> = E_0|\Phi_0>$$

$$E_{\tilde{\Phi}} = \frac{\int \tilde{\Phi}^* H \tilde{\Phi} d\tau}{\int \tilde{\Phi}^* \tilde{\Phi} d\tau}$$

$$E_0 = \frac{\int \Phi_0^* H \Phi_0 d\tau}{\int \Phi_0^* \Phi_0 d\tau}$$

$$E_{\tilde{\Phi}} \geq E_0$$

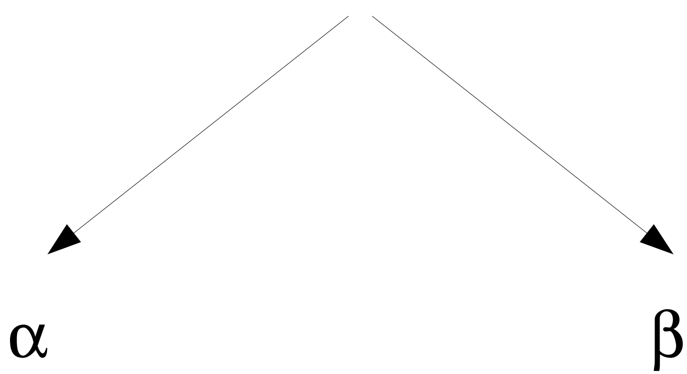
Thus one measure of the quality of a wave function is its energy:

The lower the energy, the better the wave function.

Spin

To complete describe an electron is necessary to specify its *spin*.

$$\mathbf{x} = \{\mathbf{r}, \omega\}$$



Pauli principle

No more than two electrons may occupy any given orbital and, if two do occupy one orbital, then their spin must be paired.

General statement:

When the label of any two identical fermions (electrons) are exchanged, the total wavefunction changes sign.

$$\Phi(x_1, \ldots, x_i, \ldots, x_j, \ldots, x_N) = -\,\Phi(x_1, \ldots, x_j, \ldots, x_i, \ldots, x_N)$$

Hartree-Fock method I

$$\Psi = \psi_{i,\alpha}(\mathbf{r_1})\psi_{i,\beta}(\mathbf{r_2})\psi_{j,\alpha}(\mathbf{r_3})\psi_{j,\beta}(\mathbf{r_4})...\psi_{k,\alpha}(\mathbf{r_{N-1}})\psi_{k,\beta}(\mathbf{r_N})$$

Molecular orbital

$$\Psi = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_{i,\alpha}(\mathbf{r_1})\psi_{i,\beta}(\mathbf{r_1})...\psi_{k,\beta}(\mathbf{r_1}) \\ \psi_{i,\alpha}(\mathbf{r_2})\psi_{i,\beta}(\mathbf{r_2})...\psi_{k,\beta}(\mathbf{r_2}) \\ ... \quad\quad ... \quad\quad\quad ... \\ \psi_{i,\alpha}(\mathbf{r_N})\psi_{i,\beta}(\mathbf{r_N})...\psi_{k,\beta}(\mathbf{r_N}) \end{vmatrix}$$

Hartree-Fock method II

$$f(i)\psi_{i,\alpha}(\mathbf{r}_1) = \epsilon\psi_{i,\alpha}(\mathbf{r}_1)$$

$$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + v^{HF}(i)$$

the average potential experienced by the *i*th electron due to the presence of the other electrons

The essence of HF approximation is to replace the complicated many-electron problem by a one-electron-problem.