

WAVE FUNCTION THEORY

For a single particle we have:

h-hat = -1/2 D^2 + V(z), V(z) = external potential

h-hat psi_alpha = E_alpha psi_alpha, psi_alpha = psi_alpha sigma(z) = psi_alpha(z, sigma)

Single-particle wave functions are usually normalized, so that |psi_alpha(z, sigma)|^2 d^3z represents the probability of finding a particle at z in state alpha, with spin sigma.

int_space |psi_alpha(z, sigma)|^2 d^3z = 1 = <psi|psi>, space is the space where any wave function is defined.

If I consider more than one particle, and I add an interaction term, my Hamiltonian looks like:

H-hat = -1/2 sum_{i=1}^n D_i^2 + sum_{i=1}^n V(z_i) + 1/2 sum_i sum_{j != i} 1/|z_i - z_j| = T-hat + V_ext + V_int

The solution of my interacting problem is a function of all spins and coordinates. (2)

$$\hat{H} \psi_n(\underline{r}_1, \sigma_1, \dots, \underline{r}_N, \sigma_N) = E_n \psi_n(\underline{r}_1, \sigma_1, \dots, \underline{r}_N, \sigma_N)$$

k is a quantum number; Since the electrons are fermions, the wave-function has to be anti-symmetric upon permutation of 2 particles; for example.

$$\psi_k(\underline{r}_1, \sigma_1, \underline{r}_2, \sigma_2, \dots, \underline{r}_N, \sigma_N) = -\psi_k(\underline{r}_2, \sigma_2, \underline{r}_1, \sigma_1, \dots, \underline{r}_N, \sigma_N)$$

Particles are indistinguishable \Rightarrow there are $N!$ equivalent permutations of the indexes, which correspond to one particle in $\underline{r}_1(\sigma_1), \underline{r}_2(\sigma_2), \dots, \underline{r}_N(\sigma_N)$; they all have the same $|\psi|^2$.

$N! |\psi(\underline{r}_1, \sigma_1, \dots, \underline{r}_N, \sigma_N)|^2 d^3r_1 \dots d^3r_N$ is the probability of finding one particle in $d^3r_1 \dots d^3r_N$

$$\Rightarrow \langle \psi | \psi \rangle = 1 \text{ can be rewritten as: } \frac{1}{N!} \sum_{\sigma_1, \dots, \sigma_N} \int d^3r_1 \dots \int d^3r_N \quad N! |\psi(\underline{r}_1, \sigma_1, \dots, \underline{r}_N, \sigma_N)|^2 = 1$$

From this definition, we derive that of the electronic density (with the correct normalization factor).

We have:

$$n_{\sigma}(\underline{z}) = \frac{1}{(N-1)!} \sum_{\sigma_2 \dots \sigma_N} \int d^3r_2 \dots \int d^3r_N N! |\psi(\underline{z}, \sigma_1, \dots, \underline{z}_N \sigma_N)|^2 = N \sum_{\sigma_2 \dots \sigma_N} \int d^3r_2 \dots d^3r_N |\psi(\underline{z}, \sigma_1, \dots, \underline{z}_N \sigma_N)|^2$$

It is clear that:

$$\sum_{\sigma} \int n_{\sigma}(\underline{z}) d^3r = N$$

If there are many electrons, two ^{or more} electrons can occupy the same point in space; this is why $n_{\sigma}(\underline{z})$ integrates to N and not to 1 (it is not a probability).

Furthermore, the average of the external potential is:

PROOF

$$\langle \hat{V}_{ext} \rangle = \langle \psi | \sum_{i=1}^N V(\underline{z}_i) | \psi \rangle = \sum_{\sigma_1 \dots \sigma_N} \int d^3r_1 \int d^3r_2 \dots d^3r_N V(\underline{z}_1) |\psi(\underline{z}_1, \sigma_1, \dots, \underline{z}_N \sigma_N)|^2 +$$

$$+ \dots + \sum_{\sigma_1 \dots \sigma_N} \int d^3r_1 \dots \int d^3r_N V(\underline{z}_N) |\psi(\underline{z}_1 \sigma_1, \dots, \underline{z}_N \sigma_N)|^2 = N \sum_{\sigma_1} \int d^3r_1 \left[\sum_{\sigma_2, \dots, \sigma_N} \int d^3r_2 \dots d^3r_N |\psi(\underline{z}_1, \sigma_1, \dots, \underline{z}_N \sigma_N)|^2 \right]$$

$$\times V(\underline{z}_1) =$$

$$= \sum_{\sigma_1} \int n_{\sigma_1}(\underline{z}_1) V(\underline{z}_1)$$

$$= \int d^3r n(\underline{z}) V(\underline{z}) = \langle \hat{V}_{ext} \rangle$$

Simple case (non-interacting electrons) : $\hat{V}_{ee} = \emptyset$

$$\Rightarrow \hat{H} = \hat{H}^{(0)} = \sum_{i=1}^N \left[-\frac{1}{2} \nabla_i^2 + v(\underline{z}_i) \right]$$

$$\hat{H}^{(0)} \Phi^{(0)} = E^{(0)} \Phi^{(0)}$$

We know that $\Phi^{(0)}$ can be written as an antisymmetrized product of single-particle wave functions (Slater determinant):

$$\Phi^{(0)} = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \psi_{a_1}(P_1) \psi_{a_2}(P_2) \dots \psi_{a_n}(P_n)$$

$P =$ order of the permutation

$$E^{(0)} = \sum_i \epsilon_{a_i} = \epsilon_{a_1} + \epsilon_{a_2} + \dots + \epsilon_{a_n}$$

E_x : Ground-state of non-interacting He molecule $N=2$

$$\psi_1(\underline{z}, \sigma) = \psi_{1s}(\underline{z}) |\uparrow\rangle$$

$$\psi_2(\underline{z}, \sigma) = \psi_{1s}(\underline{z}) |\downarrow\rangle$$

$$\Phi^{(0)}(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(\underline{z}_1, \sigma_1) & \psi_2(\underline{z}_1, \sigma_1) \\ \psi_1(\underline{z}_2, \sigma_2) & \psi_2(\underline{z}_2, \sigma_2) \end{vmatrix} =$$

$$\Phi^{(0)}(1,2) = \frac{1}{\sqrt{2}} \left[\psi_1(z_1, \sigma_1) \psi_2(z_2, \sigma_2) - \psi_2(z_1, \sigma_1) \psi_1(z_2, \sigma_2) \right] =$$

$$= \frac{1}{\sqrt{2}} \psi_{1s}(z_1) \psi_{1s}(z_2) \left[|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle \right]$$

ANTISYMMETRIC SINGLET

Using WAVEFUNCTIONS, we can rewrite the Schrödinger's equation with the VARIATIONAL

PRINCIPLE:

$$\delta \left\{ \langle \psi | \hat{H} | \psi \rangle / \langle \psi | \psi \rangle \right\} = 0$$

The function ψ which MINIMIZES this expression is the ground-state wavefunction ψ_0 (and $\langle \psi_0 | H | \psi_0 \rangle = E_0$ is the corresponding energy).

In practice, one always tries to minimize this expression over a subset of wavefunctions:

- ⇒ SINGLE SLATER determinant: Hartree-Fock
- ⇒ More than one Slater determinant: Configurational Interaction (CI)
- ⇒ Variational Monte Carlo (more sophisticated): Slater determinant \times Jastrow factor.

WAVEFUNCTION
METHODS