Variation Method

Variation principle

$\frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} \geq E_0$, where ϕ is any well-behaved function that satisfies the boundary conditions of the problem. This is because the wavefunction ϕ can be expanded in the basis set of the eigenfunctions of the problem, i.e. $\phi = \sum_k a_k \psi_k$

We can choose the trial wavefunction such that it depends upon some parameters α, β, γ ...These are the variational parameters. $E_\phi(\alpha, \beta, \gamma \ldots) \geq E_0$. Vary them to minimize the value of E_ϕ.

He atom

$$\hat{H} = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{12}}$$

$$\hat{H} = \hat{H}_H(1) + \hat{H}_H(2) + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{12}}$$

$\hat{H}_H(j)$ is the Hamiltonian operator for a single electron around a He nucleus

$$\hat{H}_H(j)\psi_H(r_j, \theta_j, \phi_j) = E_j \psi_H(r_j, \theta_j, \phi_j)\psi_H(r_j, \theta_j, \phi_j) \qquad j = 1 \text{ and } 2$$

$$E_j = -\frac{Z^2 m_e e^4}{32\pi^2 \varepsilon_0^2 \hbar^2 n_j^2}$$

Using $Z = 2$, GS energy $= 8E_j = 4\,\frac{m_e e^4}{16\,\pi^2 \varepsilon_0^2 \hbar^2 n_j^2} = 4 \text{ Hartree} = 108.8 \text{ eV}$

Experimental value is -2.9033 Hartree. Horrible!!

Ignoring the interelectronic repulsion term, the Hamiltonian is separable and the GS wavefunction is

$$\phi_0(\boldsymbol{r_1}, \boldsymbol{r_2}) = \psi(\boldsymbol{r_1})\psi(\boldsymbol{r_2})$$

$$\psi_{1s}(\boldsymbol{r_j}) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr_j/a_0} \qquad a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$$

Now use Z as a variational parameter. Evaluate,

$$E(Z) = \int \phi_0(\boldsymbol{r_1}, \boldsymbol{r_2}) \hat{H} \phi_0(\boldsymbol{r_1}, \boldsymbol{r_2})\, d\boldsymbol{r_1} d\boldsymbol{r_2}$$

To get,

$$E(Z) = \frac{m_e e^4}{16\pi^2 \varepsilon_0^2 \hbar^2}\left(Z^2 - \frac{27}{8}Z\right) = \left(Z^2 - \frac{27}{8}Z\right) \text{ Hartree}$$

Minimize E w.r.t. Z,

$$E_{min} = -\left(\frac{27}{16}\right)^2 = -2.8477 \text{ Hartree}$$

Most accurate calculation -2.9037 Hartree

Perturbation Method

Perturbation theory

$\hat{H}$ is the Hamiltonian of the problem at hand, $\hat{H}\psi = E\psi$. Find $\hat{H}^{(0)}$ – a fully solvable Hamiltonian that is very close to the problem at hand, i.e.

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$$

Here, $\hat{H}^{(1)}$ is a small deviation, a disturbance or a perturbation to the fully solvable problem whose Hamiltonian is $\hat{H}^{(0)}$.

So,

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

is something we can solve exactly.

Let the solution of the Schrodinger equation $\hat{H}\psi = E\psi$ be written as

$$\psi_n = \psi_n^{(0)} + \psi_n^{(1)} + \psi_n^{(2)} + \cdots$$

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \cdots$$

Then,

$$E_n^{(1)} = \int \psi_n^{(0)*}\hat{H}^{(1)}\psi_n^{(0)}\, d\tau$$

gives the first order correction to energy.

First order correction to the wavefunction,

$$\psi_n^{(1)} = \sum_{m\neq n} \frac{\int \psi_m^{(0)^*}\hat{H}^{(1)}\psi_n^{(0)}\, d\tau}{E_n^{(0)} - E_m^{(0)}}\psi_m^{(0)}$$

Example: Anharmonic Oscillator

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

$$\psi_v^{(0)}(x) = \left[\left(\frac{\alpha}{\pi}\right)^{1/2}\left(\frac{1}{2^v v!}\right)\right]^{1/2} H_v\left(\alpha^{1/2}x\right)e^{-\alpha x^2/2}$$

$$E_v^{(0)} = \left(v + \frac{1}{2}\right) h\nu \quad v = 0,1,2, \ldots$$

$$H^{(1)} = \frac{1}{6}\gamma x^3 + \frac{1}{24} b x^4$$

$$E^{(1)} = \int_{-\infty}^{\infty} \psi^{(0)}(x)^* \hat{H}^{(1)} \psi^{(0)}(x)\, dx$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/2} \left[\frac{\gamma}{6} \int_{-\infty}^{\infty} x^3 e^{-\alpha x^2} dx + \frac{b}{24} \int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} dx\right]$$

$$= \frac{b}{12} \left(\frac{\alpha}{\pi}\right)^{1/2} \int_0^{\infty} x^4 e^{-\alpha x^2} dx$$

$$= \frac{b}{32\alpha^2}$$

$$= \frac{\hbar^2 b}{32k\mu}$$

$$E = E^{(0)} + E^{(1)} = \frac{h\nu}{2} + \frac{\hbar^2 b}{32k\mu}$$