Variational method

1 Variational principle

Requirement for the applicability of the variational principle: the Hamiltonian is bounded from below. It means that exists a lowest eigenvalue of the Hamiltonian. Examples for bounded systems: harmonic oscillator, Hydrogen atom. Examples for non-bounded systems: charged particle in uniform electric field, free particle.

$$H|\varphi_n\rangle = E_n|\varphi_n\rangle \ , \quad E_0 < E_1 \le E_2 \cdots \le E_n$$

Statement: $\langle\psi|H|\psi\rangle \ge E_0$

$$|\psi\rangle = \sum_n c_n|\varphi_n\rangle \ , \qquad \sum_n |c_n|^2 = 1$$
$$\langle\psi|H|\psi\rangle = \sum_{n,m} c_n^* c_m \langle\varphi_n|H|\varphi_m\rangle = \sum_n |c_n|^2 E_n \ge \sum_n |c_n|^2 E_0 = E_0$$

2 Application of the variational principle:

2.1 Schrödinger equation

Suppose the Hamiltonian of the problem is bounded from below. We are looking for a state of the Hilbert space which minimize the energy with the requirement that it is normalized. The functional which should be minimize is the following:

$$F[\psi] = \langle\psi|H|\psi\rangle + \lambda(1 - \langle\psi|\psi\rangle)$$

At the minimum the first order variation of the functional with respect of ψ^* should disappear for each $\delta\psi^*$:

$$\delta F = \langle\psi + \delta\psi|H|\psi\rangle + \lambda\langle\psi + \delta\psi|\psi\rangle - \langle\psi|H|\psi\rangle + \lambda(1 - \langle\psi|\psi\rangle = \langle\delta\psi|H|\psi\rangle - \lambda\langle\delta\psi|\psi\rangle = \langle\delta\psi|(H-\lambda)|\psi\rangle = 0$$

We get the time independent Schrödinger equation:

$$H|\psi\rangle = \lambda|\psi\rangle$$

3 Ritz variational method

$\psi(\mathbf{r}, \{\alpha_i\})$ is a function of a set of parameters $\{\alpha_i\}$. In order to find a variational solution the following expression should be minimized:

$$F(\{\alpha_i\}) = \frac{\langle\psi(\{\alpha_i\})|H|\psi(\{\alpha_i\})\rangle}{\langle\psi(\{\alpha_i\})|\psi(\{\alpha_i\})\rangle}$$
$$\frac{\partial F}{\partial\alpha_i} = 0$$

An example: harmonic oscillator in coordinate representation

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

The probe function is $\psi(r,\alpha) = e^{-\alpha x^2}$.

$$\langle\psi|\psi\rangle = \int_{-\infty}^{\infty} e^{-2\alpha x^2}dx = \sqrt{\frac{\pi}{2\alpha}}$$

$$\frac{d}{dx}e^{-\alpha x^2} = -2\alpha x e^{-\alpha x^2}\ , \qquad \frac{d^2}{dx^2}e^{-\alpha x^2} = (-2\alpha + 4\alpha x^2)e^{-\alpha x^2}$$
$$\langle\psi|H|\psi\rangle = \int_{-\infty}^{\infty}\left(-\frac{\hbar^2}{2m}(-2\alpha+4\alpha x^2)+\frac{1}{2}m\omega^2x^2\right)e^{-2\alpha x^2}dx = \frac{\hbar^2}{m}\alpha\int_{-\infty}^{\infty}e^{-2\alpha x^2}dx + \left(\frac{1}{2}m\omega^2 - \frac{2\hbar^2\alpha^2}{m}\right)\int_{-\infty}^{\infty}x^2e^{-2\alpha x^2}dx$$

$$\int_{-\infty}^{\infty}x^2e^{-2\alpha x^2}dx = -\frac{1}{4\alpha}xe^{-2\alpha x^2}\Big|_{-\infty}^{\infty} + \frac{1}{4\alpha}\int_{-\infty}^{\infty}e^{-2\alpha x^2}dx = \frac{1}{4\alpha}\int_{-\infty}^{\infty}e^{-2\alpha x^2}dx$$

$$E(\alpha) = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\hbar^2}{m}\alpha + \left(\frac{1}{2}m\omega^2 - \frac{2\hbar^2\alpha^2}{m}\right)\frac{1}{4\alpha} = \frac{\hbar^2}{2m}\alpha + \frac{1}{8}m\omega^2\frac{1}{\alpha}$$
$$\frac{dE}{d\alpha} = \frac{\hbar^2}{2m} - \frac{1}{8}m\omega^2\frac{1}{\alpha^2} = 0\ , \qquad \alpha = \frac{m\omega}{2\hbar}\ , \qquad E = \frac{1}{2}\hbar\omega$$

4 Problem: Ground state of a Hydrogen atom

Schrödinger equation:

$$\left(-\frac{\hbar^2}{2m}\Delta - ke^2\frac{1}{r}\right)\psi = E\psi$$

Introducing the length scale a_0 and the energy scale: $E_0 = \frac{ke^2}{a_0}$, where k is the Coulomb constant, e is the elementary charge, the Schrödinger equation can be written as:

$$(-\frac{a_0}{ke^2}\frac{\hbar^2}{2m}\Delta - \frac{a_0}{r})\psi = \frac{E}{E_0}\psi$$

Applying the new length scale $\tilde{r} = \frac{r}{a_0}$ the Schrödinger equation can be rewritten as

$$(-\frac{a_0}{ke^2}\frac{\hbar^2}{2ma_0^2}\tilde{\Delta} - \frac{1}{\tilde{r}})\psi(\tilde{r}) = \frac{E}{E_0}\psi(\tilde{r})$$

$$a_0 = \frac{\hbar^2}{ke^2m}$$
$$(-\frac{1}{2}\Delta - \frac{1}{r})\psi = E\psi\ ,$$

where $\tilde{}$ is omitted. Schrödinger equation:

$$H = -\frac{1}{2}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{1}{r}$$

Probe function: $\psi = e^{-\alpha r}$. Give an estimate of the ground state energy and ground state wave-function using the Ritz variational principle! Compare them to the exact solution!