Chapter 37
Variational Method in quantum mechanics

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37.1 Theory

We attempt to guess the ground state energy E_0 by considering a "trial ket", $|\psi_0\rangle$, which tries to imitate the true ground-state ket $|\varphi_0\rangle$. We define

$$\overline{H} = \frac{\langle\psi_0|\hat{H}|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle} \qquad (1)$$

((**Thoerem**))

$$\overline{H} = \frac{\langle\psi_0|\hat{H}|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle} \geq E_0$$

We can obtain an upper bound to E_0 by considering various kinds of $|\psi_0\rangle$.

((**Proof**))

$$|\psi_0\rangle = \sum_n |\varphi_n\rangle\langle\varphi_n|\psi_0\rangle$$

where $|\varphi_n\rangle$ is an exact energy eigenstate of $\hat{H}$

$$\hat{H}|\varphi_n\rangle = E_n|\varphi_n\rangle$$

$$\overline{H} = \frac{\langle\psi_0|\hat{H}\sum_n|\varphi_n\rangle\langle\varphi_n|\psi_0\rangle}{\sum_n|\langle\varphi_n|\psi_0\rangle|^2} = \frac{\sum_n E_n|\langle\varphi_n|\psi_0\rangle|^2}{\sum_n|\langle\varphi_n|\psi_0\rangle|^2}$$

$$= E_0 + \frac{\sum_n (E_n - E_0)|\langle\varphi_n|\psi_0\rangle|^2}{\sum_n|\langle\varphi_n|\psi_0\rangle|^2} \geq E_0$$

The equality sign in Eq.(1) holds only if $|\psi_0\rangle$ coincides exactly with $|\varphi_0\rangle$.

Another method to state the theorem is to assert that $\overline{H}$ is stationary with respect to the variation

$$|\psi_0\rangle = |\psi_0(\lambda_1, \lambda_2, \lambda_3, ..., \lambda_n)\rangle$$

with λ_1, λ_2, λ_3, ..., λ_n are parameters.

$$\frac{\partial \overline{H}}{\partial \lambda_1} = 0, \frac{\partial \overline{H}}{\partial \lambda_2} = 0, \frac{\partial \overline{H}}{\partial \lambda_3} = 0, ..., \frac{\partial \overline{H}}{\partial \lambda_n} = 0 .$$

37.2 Example-1

Wave function for the ground state of the hydrogen

$$\psi_0(r) = e^{-r/a}$$

where a is a parameter.

$$H = \frac{1}{2m}\mathbf{p}^2 - \frac{e^2}{r} = \frac{1}{2m}(p_r^2 + \frac{\mathbf{L}^2}{r^2}) - \frac{e^2}{r}$$

with

$$p_r = \frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r} r ,$$

Since $\mathbf{L}^2 \psi_0 = 0$, we have

$$H\psi_0 = [\frac{1}{2m}(p_r^2 + \frac{\mathbf{L}^2}{r^2}) - \frac{e^2}{r}]\psi_0 = [\frac{1}{2m}p_r^2 - \frac{e^2}{r}]\psi_0 = \frac{-\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi_0) - \frac{e^2}{r}\psi_0$$
$$= \frac{-\hbar^2}{2m}[\psi_0'' + \frac{2}{r}\psi_0'] - \frac{e^2}{r}\psi_0 = \frac{-\hbar^2}{2m}(\frac{1}{a^2} - \frac{2}{ar})\psi_0 - \frac{e^2}{r}\psi_0$$

$$\overline{H} = \frac{\langle\psi_0|\hat{H}|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle}$$

$$\langle\psi_0|\hat{H}|\psi_0\rangle = \int \psi_0{}^*(\mathbf{r}) H \psi_0(\mathbf{r}) d\mathbf{r} = \int_0^\infty \left(\frac{-\hbar^2}{2ma^2} + \frac{\hbar^2}{mar} - \frac{e^2}{r}\right) e^{-2r/a} (4\pi r^2 dr)$$

$$= 4\pi \int_0^\infty \left(\frac{-\hbar^2}{2ma^2} r^2 + \frac{\hbar^2}{ma} r - e^2 r\right) e^{-2r/a} dr) = 4\pi \frac{a(-2ae^2 m + \hbar^2)}{8m}$$

$$\langle\psi_0|\psi_0\rangle = \int |\psi_0(\mathbf{r})|^2 d\mathbf{r} = \int_0^\infty e^{-2r/a} 4\pi r^2 dr = 4\pi \frac{a^3}{4}$$

Note that

$$\int_0^\infty e^{-\alpha r} r^n dr = \frac{n!}{\alpha^{n+1}}$$

Then we have

$$\overline{H} = \frac{\hbar^2}{2ma^2} - \frac{e^2}{a}$$

$$\frac{\partial \overline{H}}{\partial a} = \frac{\hbar^2}{2m}\left(-\frac{2a}{a^4}\right) + \frac{e^2}{a^2} = 0$$

or

$$a_0 = \frac{\hbar^2}{me^2} \qquad \text{(Bohr radius)}$$

Therefore

$$\tilde{\psi}_0(r) = e^{-r/a_0}$$

$$\overline{H} = -\frac{e^2}{2a_0},$$

which is correct ground state energy.

37.3 Example-2: Simple harmonics

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2} m\omega_0{}^2 x^2$$

We assume that

$$\psi_0(x) = e^{-\alpha x^2}$$

where α>0 (even function).

$$\overline{H} = \frac{\langle \psi_0 | \hat{H} | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle}$$

$$\langle \psi_0 | \psi_0 \rangle = \int |\psi_0(x)|^2 dx = \int_{-\infty}^{\infty} e^{-2\alpha x^2} dx = \sqrt{\frac{\pi}{2\alpha}}$$

$$\begin{aligned}
\langle \psi_0 | \hat{H} | \psi_0 \rangle &= \int \psi_0^{*}(x) H \psi_0(x) dx \\
&= \int_{-\infty}^{\infty} e^{-\alpha x^2} \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2} m \omega_0^{\,2} x^2\right) e^{-\alpha x^2} dx \\
&= \int_{-\infty}^{\infty} e^{-2\alpha x^2} \frac{1}{2m} [m^2 x^2 \omega^2 + 2\alpha \hbar^2 (1 - 2\alpha x^2)] dx = \sqrt{\frac{\pi}{2}} \frac{(m^2\omega^2 + 4\alpha^2\hbar^2)}{8m\alpha^{3/2}}
\end{aligned}$$

Then we have

$$\overline{H} = \frac{m^2\omega^2 + 4\alpha^2\hbar^2}{8m\alpha}$$

$$\frac{\partial \overline{H}}{\partial \alpha} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha^2} = 0$$

or

$$\alpha = \alpha_0 = \frac{m\omega}{2\hbar}$$

$$\tilde{\psi}_0(x) = e^{-\frac{m\omega}{2\hbar}x^2}$$

$$\overline{H}(\alpha_0) = \frac{1}{2}\hbar\omega_0$$

37.4 Example-III Sakurai

The ground state of one-dimensional harmonics

Trial function

$$\langle x|\tilde{0}\rangle = e^{-\beta|x|} \qquad (\beta>0).$$

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0{}^2x^2$$

$$\langle\tilde{0}|\tilde{0}\rangle = 2\int_0^\infty e^{-2\beta x}dx = \frac{1}{\beta}$$

$$\overline{H} = \frac{\langle\tilde{0}|\hat{H}|\tilde{0}\rangle}{\langle\tilde{0}|\tilde{0}\rangle}$$

$$I = \langle\tilde{0}|\hat{H}|\tilde{0}\rangle = \int_{-\infty}^{\infty} e^{-\beta|x|}(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0{}^2x^2)e^{-\beta|x|}dx$$

or

$$I = \int_{-\infty}^{-\varepsilon} e^{\beta x}(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0{}^2x^2)e^{\beta x}dx$$
$$+\int_{\varepsilon}^{\infty} e^{-\beta x}(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0{}^2x^2)e^{-\beta x}dx + \int_{-\varepsilon}^{\varepsilon} e^{-\beta|x|}(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0{}^2x^2)e^{-\beta|x|}dx$$

In the first term of *I*, we put *x*' = -*x*

$$\int_{\infty}^{\varepsilon}(-\frac{\hbar^2}{2m}\beta^2 + \frac{1}{2}m\omega_0{}^2x'^2)e^{-2\beta x'}(-1)dx' = \int_{\varepsilon}^{\infty}(-\frac{\hbar^2}{2m}\beta^2 + \frac{1}{2}m\omega_0{}^2x^2)e^{-2\beta x}dx$$

Then

$$I = 2\int_{\varepsilon}^{\infty}(-\frac{\hbar^2}{2m}\beta^2 + \frac{1}{2}m\omega_0{}^2x^2)e^{-2\beta x}dx + \int_{-\varepsilon}^{\varepsilon} e^{-\beta|x|}(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0{}^2x^2)e^{-\beta|x|}dx$$

in the limit of $\varepsilon\to 0$.

Noting that

$$\int_0^\infty x^2e^{-ax} = \frac{2}{a^3}$$

I is calculated as

$$I=-\frac{\hbar^2}{2m}\beta+\frac{m\omega_0{}^2}{4\beta^3}+\int_{-\varepsilon}^{\varepsilon}e^{-\beta|x|}(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}m\omega_0{}^2x^2)e^{-\beta|x|}dx$$

We now consider the second term

$$f(x)=e^{-\beta|x|}$$

This function $f(x)$ is continuous at x = 0, but df/dx is discontinuous at x = 0.

df/dx=-β exp(-βx) for x>0 and β exp(βx) for x<0.

$$I_2=\int_{-\varepsilon}^{\varepsilon}e^{-\beta|x|}(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}m\omega_0{}^2x^2)e^{-\beta|x|}dx=-\frac{\hbar^2}{2m}\int_{-\varepsilon}^{\varepsilon}f(x)\frac{d^2f(x)}{dx^2}dx$$

Note that (df/dx)^2 is continuous at x = 0.

$$\int_{-\varepsilon}^{\varepsilon}f(x)\frac{d^2f(x)}{dx^2}dx=[f(x)\frac{df(x)}{dx}]_{-e}^{\varepsilon}-\int_{-\varepsilon}^{\varepsilon}[\frac{df(x)}{dx}]^2dx=f(0)[\frac{df(x)}{dx}|_{x=\varepsilon}-\frac{df(x)}{dx}|_{x=-\varepsilon}]=-2\beta$$

Then we have

$$I_2=\frac{\hbar^2\beta}{m}$$

or

$$I=-\frac{\hbar^2}{2m}\beta+\frac{m\omega_0{}^2}{4\beta^3}+\frac{\hbar^2\beta}{m}=\frac{\hbar^2}{2m}\beta+\frac{m\omega_0{}^2}{4\beta^3}$$

$$\overline{H}=\frac{I}{(1/\beta)}=\beta(\frac{\hbar^2}{2m}\beta+\frac{m\omega_0{}^2}{4\beta^3})=\frac{\hbar^2}{2m}\beta^2+\frac{m\omega_0{}^2}{4\beta^2}\geq 2\sqrt{\frac{\hbar^2}{2m}\beta^2\frac{m\omega_0{}^2}{4\beta^2}}=\frac{1}{\sqrt{2}}\hbar\omega_0$$

The equality is valid when

$$\beta^4=\frac{m^2\omega_0{}^2}{2\hbar^2}$$