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Variation Method

$\int \psi^* \hat{H} \psi \, d\tau \geq E_{ground}$ if ψ is normalized

Prove : $\psi = \sum_n c_n \psi_n \quad \hat{H}\psi_n = E_n \psi_n$

$$\int \psi^* \hat{H} \psi \, d\tau = \int \sum_k a_k^* \psi_k^* \hat{H} \sum_j a_j \psi_j \, d\tau = \int \sum_k a_k^* \psi_k^* \sum_j a_j \hat{H} \psi_j \, d\tau = \int \sum_k a_k^* \psi_k^* \sum_j a_j E_j \psi_j \, d\tau$$

$$= \sum_k \sum_j a_k^* a_j E_j \int \psi_k^* \psi_j \, d\tau = \sum_k \sum_j a_k^* a_j E_j \delta_{kj} = \sum_k a_k^* a_k E_k$$

$$= \sum_k |a_k|^2 E_k$$

$$E_k \geq E_{gs}, \quad |a_k|^2 E_k \geq |a_k|^2 E_{gs}, \quad \sum_k |a_k|^2 E_k \geq \sum_k |a_k|^2 E_{gs} = E_{gs}$$

if ψ is non-normalized, Rayleigh ratio $\dfrac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau} \geq E_{gs}$

Example 1D harmonic oscillator

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2, \quad \text{guess } \psi(x) = Ae^{-bx^2}, \quad A = \left(\frac{2b}{\pi}\right)^{\frac{1}{4}}$$

$$\langle T \rangle = -\frac{\hbar^2}{2m}|A|^2 \int_{-\infty}^{\infty} e^{-bx^2} \frac{d^2}{dx^2} e^{-bx^2} \, dx = \frac{\hbar^2 b}{2m}$$

$$\langle V \rangle = \frac{1}{2}m\omega^2 |A|^2 \int_{-\infty}^{\infty} e^{-bx^2} x^2 \, dx = \frac{m\omega^2}{8b}$$

$$\frac{d}{db}\langle H \rangle = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} = 0, \quad b = \frac{m\omega}{2\hbar}, \quad \langle H \rangle_{min} = \frac{1}{2}\hbar\omega$$

Example 1-D box l $\quad \psi = 0$ when $x=0$, $x=l$

assume $\psi = x(l-x)$ for $0 \leq x \leq l$

$$\int \psi^* \hat{H} \psi \, d\tau = -\frac{\hbar^2}{2m}\int_0^l (lx - x^2)\frac{d^2}{dx^2}(lx - x^2)\, dx = \frac{\hbar^2 l^3}{6m} \quad \text{and} \quad \int \psi^* \psi = \frac{l^5}{30}$$

$$E \leq \frac{5h^2}{4\pi^2 m l^2} = 0.1266515 \frac{h^2}{ml^2} \quad (1.3\% \text{ error})$$

For excited state

$$\int \psi^* \hat{H} \psi \, d\tau \geq E_2 \quad \text{if} \quad \int \psi_1^* \psi \, d\tau = 0 \quad \text{and} \quad \int \psi^* \psi \, d\tau = 1$$

Prove $a_k = \langle \psi_k | \phi \rangle$

$$\int \psi^* \hat{H} \psi \, d\tau = \sum_{n=2}^{\infty} |a_n|^2 E_n \quad \text{and} \quad \int \psi^* \psi \, d\tau = \sum_{n=2}^{\infty} |a_n|^2 = 1$$

for $n \geq 2$, we have $E_n \geq E_2$ and $|a_n|^2 E_n \geq |a_n|^2 E_2$

$$\sum_{n=2}^{\infty} |a_n|^2 E_n \geq \sum_{n=2}^{\infty} |a_n|^2 E_2 = E_2$$

Similarly, $\dfrac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau} \geq E_{n+1}$ if $\int \psi_1^* \psi \, d\tau = \int \psi_2^* \psi \, d\tau = \cdots \int \psi_n^* \psi \, d\tau = 0$

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$\phi = \sum_{j=1}^{n} c_j f_j$ basis function

$\int \phi^* \phi \, d\tau = \int \sum_{j=1}^{n} c_j^* f_j^* \sum_{k=1}^{n} c_k f_k \, d\tau = \sum_{j=1}^{n}\sum_{k=1}^{n} c_j^* c_k \int f_j^* f_k \, d\tau = \sum_{j=1}^{n}\sum_{k=1}^{n} c_j c_k \underline{S_{jk}}$ overlap integral

$\int \phi^* \hat{H} \phi \, d\tau = \int \sum_{j=1}^{n} c_j^* f_j^* \hat{H} \sum_{k=1}^{n} c_k f_k \, d\tau = \sum_{j=1}^{n}\sum_{k=1}^{n} c_j c_k \int f_j^* \hat{H} f_k \, d\tau = \sum_{j=1}^{n}\sum_{k=1}^{n} c_j c_k H_{jk}$

variational integral $E = \dfrac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} = \dfrac{\sum_{j}^{n}\sum_{k}^{n} c_j c_k H_{jk}}{\sum\sum c_j c_k S_{jk}}$, $E \sum_j \sum_k c_j c_k S_{jk} = \sum_j \sum_k c_j c_k H_{jk}$

$\dfrac{\partial E}{\partial c_i} = 0$, $\dfrac{\partial E}{\partial c_i} \sum_j \sum_k c_j c_k S_{jk} + E \underline{\dfrac{\partial}{\partial c_i} \sum_j \sum_k c_j c_k S_{jk}} = \dfrac{\partial}{\partial c_i} \sum_j \sum_k c_j c_k H_{jk}$

$= \sum\sum \dfrac{\partial}{\partial c_i}(c_j c_k) S_{jk}$ $\qquad = \sum\sum c_k \delta_{ij} S_{jk} + \sum\sum c_j \delta_{ik} S_{jk}$

$= \sum\sum \left(c_k \dfrac{\partial c_j}{\partial c_i} + c_j \dfrac{\partial c_k}{\partial c_i}\right) S_{jk}$ $\qquad = \sum c_k S_{ik} + \sum c_j S_{ji}$

$\Rightarrow \dfrac{\partial}{\partial c_i} \sum\sum c_j c_k S_{jk} = \sum c_k S_{ik} + \sum c_j S_{ij} = 2 \sum c_k S_{ik}$, similar $\dfrac{\partial}{\partial c_i} \sum\sum c_j c_k H_{jk} = 2 \sum c_k H_{ik}$

$\Rightarrow 2E \sum c_k S_{ik} = 2 \sum c_k H_{ik}$, $\sum_{k=1}^{n} (H_{ik} - S_{ik} E) c_k = 0$ homogenous equation

for $n = 2$ $\quad (H_{11} - S_{11}E)c_1 + (H_{12} - S_{12}E)c_2 = 0$
$\qquad (H_{21} - S_{21}E)c_1 + (H_{22} - S_{22}E)c_2 = 0$, $\begin{vmatrix} H_{11} - S_{11}E & H_{12} - S_{12}E \\ H_{21} - S_{21}E & H_{22} - S_{22}E \end{vmatrix} = 0$, $\det(H_{ij} - S_{ij}E) = 0$

Example 1-D box

$\phi = c_1 \underbrace{x(l-x)}_{f_1} + c_2 \underbrace{x^2(l-x)^2}_{f_2} + c_3 \underbrace{x(l-x)(\tfrac{1}{2}l - x)}_{f_3} + c_4 \underbrace{x^2(l-x)^2(\tfrac{1}{2}l - x)}_{f_4}$

f_1 f_2 even
f_3 f_4 odd $\Rightarrow$
$S_{13} = S_{31} = 0 \qquad S_{23} = S_{32} = 0$
$S_{14} = S_{41} = 0 \qquad S_{24} = S_{42} = 0$
$H_{13} = H_{31} = 0 \qquad H_{23} = H_{32} = 0$
$H_{14} = H_{41} = 0 \qquad H_{24} = H_{42} = 0$

$$\Rightarrow \begin{vmatrix} H_{11} - S_{11}E & H_{12} - S_{12}E & 0 & 0 \\ H_{21} - S_{21}E & H_{22} - S_{22}E & 0 & 0 \\ 0 & 0 & H_{33} - S_{33}E & H_{34} - S_{34}E \\ 0 & 0 & H_{43} - S_{43}E & H_{44} - S_{44}E \end{vmatrix} = 0$$

$\Rightarrow (H_{11} - S_{11}E)c_1 + (H_{12} - S_{12}E)c_2 = 0 \qquad (H_{33} - S_{33}E)c_3 + (H_{34} - S_{34}E)c_4 = 0$
$\quad (H_{21} - S_{21}E)c_1 + (H_{22} - S_{22}E)c_2 = 0 \qquad (H_{43} - S_{43}E)c_3 + (H_{44} - S_{44}E)c_4 = 0$

$\Downarrow$

$E = \dfrac{\hbar^2}{ml^2}(60 \pm \sqrt{1620})$

$H_{11} = \langle f_1 | \hat{H} | f_1 \rangle = \dfrac{\hbar^2 l^3}{6m}$

$S_{11} = \langle f_1 | f_1 \rangle$
$= \dfrac{l^5}{30}$

$\Rightarrow m^2 l^4 E^2 - 56\, m l^2 \hbar^2 E + 252 \hbar^4 = 0$. $E = \dfrac{\hbar^2}{ml^2}(28 \pm \sqrt{532})$

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