Método variacional

Útil cuando el método perturbativo no es adecuado, ó cuando una solución numérica no es aceptable.

La idea es resolver $\check{H}|\psi\rangle = E|\psi\rangle$

utilizando una fn. de prueba $\psi = \psi(\alpha, \beta, \dots \gamma)$

donde $\alpha, \beta, \dots, \gamma$ son parámetros ajustables del problema

$$E(\psi) = \frac{\langle\psi|\check{H}|\psi\rangle}{\langle\psi|\psi\rangle} = E(\alpha, \beta, \dots, \gamma)$$

y se procede a minimizar $E(\alpha, \beta, \dots, \gamma)$ c/r a $\{\alpha, \beta, \dots, \gamma\}$. El valor hallado, E^* const. una cota superior a la verdadera energía del sistema $\Rightarrow$ útil para estimar la energía del estado fundamental y la autofunción.

Nota: $E(\alpha, \beta, \dots, \gamma) \geq E_0$

Dem: $|\psi\rangle = \sum_n a_n |\phi_n\rangle$ $\rightarrow$ autoestados exactos de H , $H|\phi_n\rangle = E_n|\phi_n\rangle$

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum_{n,m} a_n^* a_m \langle\phi_n|\check{H}|\phi_m\rangle}{\sum_{n,m} a_n^* a_m \langle\phi_n|\phi_m\rangle} = \frac{\sum_n a_n^* a_m E_m \langle\phi_n|\phi_m\rangle}{\sum_{n,m} a_n^* a_m \langle\phi_n|\phi_m\rangle}$$

$$= \frac{\sum_n |a_n|^2 E_n}{\sum_n |a_n|^2} \geqslant \frac{E_0 \sum_n |a_n|^2}{\sum_n |a_n|^2} = E_0$$

$$\therefore \boxed{E \geqslant E_0}$$ indep. del valor de $\{\alpha, \beta, \ldots, \gamma\}$

Procedimiento

(i) Escoger una función de prueba apropiada incluyendo parámetros ajustables $\alpha_1, \alpha_2 \ldots$

$$|\psi_0\rangle = |\psi_0(\alpha_1, \alpha_2, \ldots)\rangle$$

(ii) calcular $$\frac{\langle \psi_0(\alpha_1,\alpha_2 \ldots)|\check{H}|\psi_0(\alpha_1, \alpha_2, \ldots)\rangle}{\langle \psi_0(\alpha_1,\alpha_2 \ldots)|\psi_0(\alpha_1, \alpha_2 \ldots)\rangle} = E_0(\alpha_1, \alpha_2 \ldots)$$

(iii) Hallar el mínimo de $E_0(\alpha_1, \alpha_2, \ldots)$ c/r a $\alpha_1, \alpha_2, \ldots$

$$0 = \frac{\partial E_0(\alpha_1, \alpha_2, \ldots)}{\partial \alpha_i} \qquad i = 1, 2 \ldots$$

(iv) sustituir $(\alpha_{10}, \alpha_{20}, \ldots)$ en $E = E(\{\alpha_i\})$ para obt. un valor aprox. del estado base. El estado fund. será aproximado por $|\psi_0(\alpha_{10}, \alpha_{20} \ldots)\rangle$.

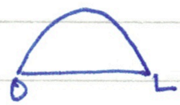
2

Método variacional para el pozo ∞ 1-D

$\psi(x) \doteq 0$ en $x=0$ y $x=L$

En particular $\psi_0(x)$ debe ser par, sin nodos, c/r a $x=L/2$.
La fn. más simple, que satisface los criterios es:

$$\psi_0(x) = Ax(L-x)$$



$$1 = \langle\psi_0|\psi_0\rangle = A^2\int_0^L x^2(L-x)^2\,dx = \frac{A^2L^5}{30} \Rightarrow A = \sqrt{\frac{30}{L^5}}$$

$$\langle\psi_0|\check{H}|\psi_0\rangle = \int_0^L \psi_0(x)\left(\frac{-\hbar^2}{2m}\frac{d^2\psi_0}{dx^2}\right)dx = \frac{+\hbar^2}{2m}\int_0^L\left(\frac{d\psi_0}{dx}\right)^2 dx$$

$$= \int_0^L \left(A(L-x) + Ax(-1)\right)^2 dx = A^2\int_0^L (L-2x)^2\,dx = A^2\int_0^L (L^2-4xL+4x^2)\,dx$$

$$= \frac{A^2 L^3}{3}$$

$$\langle\psi_0|\check{H}|\psi_0\rangle = \frac{\hbar^2}{2m}\cdot\left(\frac{30}{L^5}\right)\cdot\frac{L^3}{3} = \frac{10\hbar^2}{2mL^2}$$

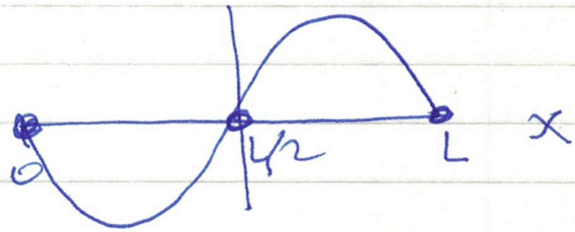
$$E_0 = \frac{\langle\psi_0|\check{H}|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle} = \frac{10\hbar^2}{2mL^2} = \left(\frac{10}{\pi^2}\right)E_{exacto} = 1.01\,E_{exacto}$$

(1% mayor)

Estimación para el 1er estado excitado:

$\psi_1(x)$ debe tener un nodo en $x = L/2$ y ser impar c/r a $x = L/2$. (También, $\psi_1(0) = 0 = \psi_1(L)$)

$$\psi_1(x) = Bx(L-x)\left(x-\frac{L}{2}\right)$$



$$1 = \langle\psi_1(x)|\psi_1(x)\rangle$$
$$= B^2\int_0^L x^2(L-x)^2\left(x-\frac{L}{2}\right)^2 dx = \frac{B^2L^7}{840} \Rightarrow \boxed{B = \sqrt{\frac{840}{L^7}}}$$

$$\langle\psi_1(x)|\hat{H}|\psi_1(x)\rangle = \frac{\hbar^2}{2m}\int_0^L\left(\frac{d\psi_1}{dx}\right)^2 dx = \frac{\hbar^2}{2m}\cdot\frac{L^5}{20}\cdot\frac{840}{L^7} =$$

$$= \frac{21\hbar^2}{mL^2} = \frac{21\times 2}{\pi^2(2^2)}\,\frac{\pi^2\hbar^2}{2mL^2}(2^2) = \left(\frac{21}{2\pi^2}\right)E_2(\text{exacto})$$

$$= 1.064\,E_2(\text{exacto})$$

$\boxed{E_1 = 1.064\,E_2(\text{exacto}).}$ (6.4% mayor)

¿Y los estados excitados?

Una vez hallado E_0 y $|\psi_0\rangle$, podemos estimar E_1 y $|\phi_1\rangle$ mediante un $|\psi_1\rangle \perp |\psi_0\rangle$:

$$\langle \psi_1 | \psi_0 \rangle = 0$$

y se procede a minimizar $E_1(\alpha_1, \alpha_2 \dots)$

$$0 = \frac{\partial}{\partial \alpha_i} \left\{ \frac{\langle \psi_1(\alpha_1, \alpha_2 ..) | \check{H} | \psi_1(\alpha_1, \alpha_2, ...) \rangle}{\langle \psi_1(\alpha_1, \alpha_2 ..) | \psi_1(\alpha_1, \alpha_2 ..) \rangle} \right\}$$

Para evaluar el 2^{do} estado excitado, usamos $|\psi_2(\alpha_1, \alpha_2)\rangle \perp$ a $|\psi_0\rangle$ y a $|\psi_1\rangle$:

$$\langle \psi_2 | \psi_0 \rangle = 0 \,, \quad \langle \psi_2 | \psi_1 \rangle = 0 \,.$$

y se procede como antes.

<u>Ejemplo</u>: Estado base del oscilador armónico.

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

imponiendo $1 = \int |\psi_0(x, \alpha)|^2 \Rightarrow A = (2\alpha/\pi)^{1/4}$

$$\langle \psi_0 | H | \psi_0 \rangle = A^2 \int_{-\infty}^{\infty} e^{-\alpha x^2} \left\{ \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2 \right\} e^{-\alpha x^2} dx$$

$$\frac{d}{dx}\left(e^{-\alpha x^2}\right) = -2\alpha x\, e^{-\alpha x^2}$$

$$\Rightarrow \frac{d^2}{dx^2}\left(e^{-\alpha x^2}\right) = -2\alpha\, e^{-\alpha x^2} + 2\alpha x(+2\alpha x)\, e^{-\alpha x^2} = -2\alpha\, e^{-\alpha x^2}\left(1-2\alpha x^2\right)$$

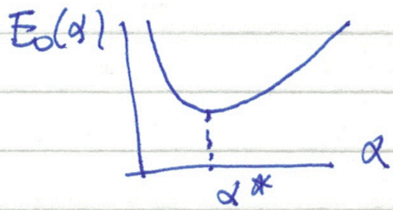
$$E_0(\alpha) = A^2 \int_{-\infty}^{\infty} \frac{+\hbar^2}{2m}(+2\alpha)(1-2\alpha x^2)\, e^{-2\alpha x^2} + \frac{1}{2} m\omega^2 x^2 e^{-2\alpha x^2}\, dx$$

$$= A^2 \frac{\hbar^2 \alpha}{m} \int_{-\infty}^{\infty} e^{-2\alpha x^2}\, dx + A^2\left(\frac{1}{2}m\omega^2 - \frac{2\alpha^2\hbar^2}{m}\right) \underbrace{\int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2}\, dx}_{\frac{\sqrt{\pi}}{2\alpha^{3/2}}}$$

$$\cancel{\sqrt{\frac{2\alpha}{\pi}}} \cdot \frac{\hbar^2\alpha}{m} \cdot \cancel{\frac{\sqrt{\pi}}{\sqrt{2\alpha}}} + \sqrt{\frac{2\alpha}{\pi}}\left(\frac{1}{2}m\omega^2 - \frac{2\hbar^2\alpha^2}{m}\right)\frac{\sqrt{\pi}}{2\alpha^{3/2}\sqrt{2}}$$

$$= \frac{\hbar^2\alpha}{m} + \frac{1}{4\alpha}\left(\frac{1}{2}m\omega^2 - \frac{2\hbar^2\alpha^2}{m}\right) = \frac{\hbar^2}{2m}\alpha + \frac{m\omega^2}{8\alpha}$$

$$E_0(\alpha) = \frac{\hbar^2}{2m}\alpha + \frac{m\omega^2}{8\alpha}$$



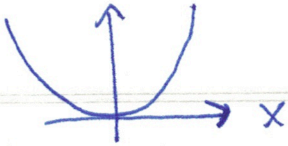
$$0 = \frac{\partial E_0}{\partial \alpha} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha^2} \Rightarrow \boxed{\alpha_0 = \frac{m\omega}{2\hbar}}$$

$$\Rightarrow E_0(\alpha_0) = \frac{\hbar^2}{2m}\cdot\frac{m\omega}{2\hbar} + \frac{m\omega^2\, 2\hbar}{8m\omega} = \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4} = \boxed{\frac{\hbar\omega}{2}}$$

$$\boxed{\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}}} \quad //$$

Coincide con resultados exactos.

1er estado excitado



$\psi_1(\alpha, x)$ debe ser impar, anularse cuando $x \to \pm\infty$, debe tener un sólo nodo, y debe ser $\perp$ a $\psi_0(x, \alpha_0)$.

$$\psi_1(x,\alpha) = B x e^{-\alpha x^2}$$

$$1 = \int_{-\infty}^{\infty} |\psi_1|^2 dx = B^2 \int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx = \frac{B^2 \sqrt{\pi}}{2(2\alpha)^{3/2}}$$

$$\Rightarrow B^2 = \frac{2(2\alpha)^{3/2}}{\pi^{1/2}} = \frac{(32\alpha^3)^{1/2}}{\sqrt{\pi}} \Rightarrow \boxed{B = \left(\frac{32\alpha^3}{\pi}\right)^{1/4}}$$

$$\langle \psi_0 | \psi_1 \rangle = B \cdot \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \underbrace{\int_{-\infty}^{\infty} x e^{-\alpha x^2} e^{-\frac{m\omega}{2\hbar} x^2} dx}_{0 \text{ (por paridad)}}$$

$$E_1(\alpha) = B^2 \int_{-\infty}^{\infty} x e^{-\alpha x^2} \left[\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m\omega^2 x^2 \right] x e^{-\alpha x^2} dx$$

$$\left[\frac{-\hbar^2}{2m}\left(-6\alpha x + (2\alpha)^2 x^3\right) + \frac{1}{2} m\omega^2 x^3 \right] e^{-\alpha x^2}$$

$$B^2 \int_{-\infty}^{\infty} \left(\frac{-\hbar^2}{2m}\left(-6\alpha + (2\alpha)^2 x^2\right) + \frac{m\omega^2}{2} x^2 \right) x^2 e^{-2\alpha x^2} dx$$

$$B^2 \int_{-\infty}^{\infty} \frac{3\hbar^2\alpha}{m} x^2 e^{-2\alpha x^2} dx + B^2 \left(\frac{m\omega^2}{2} - \frac{2\hbar^2\alpha^2}{m} \right) \int_{-\infty}^{\infty} x^4 e^{-2\alpha x^2} dx$$

$$= \frac{3\hbar^2}{2m}\alpha + \frac{3m\omega^2}{8\alpha}$$

$$0 = \frac{\partial E_1}{\partial \alpha}(\alpha) = \frac{3\hbar^2}{2m} - \frac{3m\omega^2}{8\alpha^2} \Rightarrow \boxed{\alpha_0 = \frac{m\omega}{2\hbar}}$$

$$\Rightarrow \boxed{E_1(\alpha_0) = \frac{3}{2}\hbar\omega}$$

$$y \ \boxed{\psi_1(x,\alpha_0) = \left(\frac{4m^3\omega^3}{\pi\hbar^3}\right)^{1/4} x\, e^{-\frac{m\omega}{2\hbar}x^2}}$$

2^do estado excitado

$$\psi_2(x,\alpha,\beta) = C(\beta x^2 - 1)\, e^{-\alpha x^2}$$

(necesitamos al menos 2 parámetros debido a $\perp$ con ψ_0, ψ_1)

ψ_2 es par, posee 2 nodos, y $\to 0$ en $x \to \pm\infty$

$$1 = \langle \psi_2 | \psi_2 \rangle \Rightarrow C = \left(\frac{2\alpha}{\pi}\right)^{1/4}\left(\frac{3\beta^2}{16\alpha^2} - \frac{\beta}{2\alpha} + 1\right)^{-1/2}$$

$0 = \langle \psi_2 | \psi_1 \rangle$ obvio porque ψ_2 = par y ψ_1 = impar

$0 = \langle \psi_2 | \psi_0 \rangle$ implica $\beta = \frac{m\omega}{\hbar} + 2\alpha$

$$E_2(\alpha\beta) = c^2\sqrt{\frac{\pi}{2\alpha}}\left\{\frac{\hbar^2\alpha}{2m} + \frac{\hbar^2\beta}{4m} + \frac{7\hbar^2\beta^2}{32m\alpha} + \frac{15m\beta^2\omega^2}{128\alpha^3} - \frac{3m\beta\omega^2}{16\alpha^2} + \frac{m\omega^2}{8\alpha}\right\}$$

y usando $\beta = \frac{m\omega}{\hbar} + 2\alpha$

$$E_2(\alpha) = \frac{\left(\frac{15\hbar^2\alpha}{m} + \frac{9\hbar\omega}{8} + \frac{7m\omega^2}{16\alpha} + \frac{15m^3\omega^4}{128\hbar^2\alpha^3} + \frac{9m^2\omega^3}{32\hbar\alpha^2}\right)}{\left(\frac{3m^2\omega^2}{16\hbar^2\alpha^2} + \frac{m\omega}{4\hbar\alpha} + \frac{3}{4}\right)}$$

$$0 = \frac{\partial E_2}{\partial\alpha} \Rightarrow \alpha_0 = \frac{m\omega}{2\hbar} \Rightarrow \beta_0 = \frac{2m\omega}{\hbar}$$

$$\Rightarrow E_2(\alpha_0, \beta_0) = \frac{5}{2}\hbar\omega$$

$$\psi_2(\alpha_0, \beta_0, x) = \left(\frac{m\omega}{4\pi\hbar}\right)^{1/4}\left(\frac{2m\omega}{\hbar}x^2 - 1\right)e^{-\frac{m\omega}{2\hbar}x^2}$$

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