

THE VARIATIONAL PRINCIPLE IN QUANTUM MECHANICS

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 7.1.

Shankar, R. (1994), *Principles of Quantum Mechanics*, Plenum Press. Section 5.2, Exercise 5.2.2a.

We've used the calculus of variations to derive the geodesic equation in general relativity, but a similar approach can be used in quantum mechanics to get an upper bound on the ground state energy for a given hamiltonian. The technique rests on the following theorem:

Theorem. *If ψ is any normalized function and H is a hamiltonian, then the ground state energy E_0 of this hamiltonian has an upper bound given by*

$$(1) \quad \boxed{E_0 \leq \langle \psi | H | \psi \rangle \equiv \langle H \rangle}$$

Although we don't know the eigenfunctions or eigenvalues of H , we do know that the eigenfunctions satisfy $H\psi_n = E_n\psi_n$ and form a complete orthonormal set, so we can expand ψ in terms of them:

$$(2) \quad \psi = \sum_n c_n \psi_n$$

Therefore

$$(3) \quad \langle \psi | H | \psi \rangle = \sum_{n,m} c_m^* c_n \langle \psi_m | H | \psi_n \rangle$$

$$(4) \quad = \sum_{n,m} c_m^* c_n E_n \langle \psi_m | \psi_n \rangle$$

$$(5) \quad = \sum_n |c_n|^2 E_n$$

Since $E_n \geq E_0$ for all n , we get

$$(6) \quad \langle \psi | H | \psi \rangle \geq E_0 \sum_n |c_n|^2 = E_0$$

This theorem is usually applied by choosing the function ψ such that it depends on one or more parameters which can then be varied to find the minimum value for $\langle H \rangle$.

Example 1. We'll use a Gaussian trial function to get an upper bound on the ground state energy for the potential

$$(7) \quad V(x) = \alpha|x|$$

The trial function is

$$(8) \quad \psi = Ae^{-bx^2}$$

The parameter A is determined by normalization:

$$(9) \quad |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} dx = 1$$

$$(10) \quad A = \left(\frac{2b}{\pi}\right)^{1/4}$$

We get

$$(11) \quad \langle H \rangle = \sqrt{\frac{2b}{\pi}} \int_{-\infty}^{\infty} \left[-\frac{\hbar^2}{2m} e^{-bx^2} \frac{d^2}{dx^2} (e^{-bx^2}) + e^{-2bx^2} \alpha|x| \right] dx$$

The integrand is an even function of x , so this is equivalent to

$$(12) \quad \langle H \rangle = 2\sqrt{\frac{2b}{\pi}} \int_0^{\infty} \left[-\frac{\hbar^2}{2m} e^{-bx^2} \frac{d^2}{dx^2} (e^{-bx^2}) + e^{-2bx^2} \alpha x \right] dx$$

$$(13) \quad = \frac{1}{2\sqrt{2\pi m}} \left(\hbar^2 b \sqrt{2\pi} + \frac{2\alpha m}{\sqrt{b}} \right)$$

where we did the integral using Maple.

We want to vary the parameter b to find the minimum of this expression, so we take the derivative and set it to zero:

$$(14) \quad \frac{d\langle H \rangle}{db} = \frac{1}{2\sqrt{2\pi m}} \left(\hbar^2 \sqrt{2\pi} - \frac{\alpha m}{b^{3/2}} \right) = 0$$

$$(15) \quad b = \frac{(\alpha m)^{2/3}}{(2\pi)^{1/3} \hbar^{4/3}}$$

This gives the upper bound on E_0 as

$$(16) \quad E_0 \leq \frac{3(2\alpha\hbar)^{2/3}}{4(\pi m)^{1/3}}$$

Example 2. Now we'll use the potential

$$(17) \quad V(x) = \alpha x^4$$

Doing the calculations yields (since the potential is again an even function):

$$(18) \quad \langle H \rangle = 2\sqrt{\frac{2b}{\pi}} \int_0^\infty \left[-\frac{\hbar^2}{2m} e^{-bx^2} \frac{d^2}{dx^2} (e^{-bx^2}) + e^{-2bx^2} \alpha x^4 \right] dx$$

$$(19) \quad = \frac{1}{16} \frac{8\hbar^2 b^3 + 3\alpha m}{b^2 m}$$

$$(20) \quad = \frac{\hbar^2 b}{2m} + \frac{3\alpha}{16b^2}$$

Finding the parameter value that minimizes $\langle H \rangle$ we get

$$(21) \quad \frac{d\langle H \rangle}{db} = \frac{\hbar^2}{2m} - \frac{3\alpha}{8b^3} = 0$$

$$(22) \quad b = \frac{(6\alpha m)^{1/3}}{2\hbar^{2/3}}$$

$$(23) \quad E_0 \leq \frac{3}{8} \left(\frac{6\hbar^4 \alpha}{m^2} \right)^{1/3}$$

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