Variational Method

Estimating an upper bound for the ground state energy of a system

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Background*

Let Ψ be any normalized wavefunction, then by completeness:

$$\psi = \sum_n c_n \psi_n, \text{ where } H\psi_n = E_n \psi_n \text{ and } 1 = \langle \psi | \psi \rangle = \sum_n |c_n|^2$$

The expectation value of the Hamiltonian derived with our wave function is then:

$$\langle H \rangle = \langle \sum_m c_m \psi_m | H \sum_n c_n \psi_n \rangle = \sum_{mn} c_m^* E_n c_n \delta_{mn} = \sum_n E_n |c_n|^2$$

And since the ground state is, by definition, the lowest energy state:

$$\langle H \rangle \geq E_{gs} \sum_n |c_n|^2 = E_{gs}$$

*_Introduction to Quantum Mechanics_, 2ed., Griffiths, David J. 2005

Strategy

The variational *method* is a algorithmic process that can be broken into 4 simple steps.

1. If not provided, choose an appropriate normalized trial wave function Ψ with an adjustable parameter β that scales the position variable; e.g. $\psi = Ae^{-\beta x^2}$ for a harmonic oscillator problem. The closer the trial wave function is to the actual wavefunction the closer the estimate will be to the actual energy.
2. Substitute the wavefunction into the appropriate Hamiltonian and solve for the expectation energy as a function of the parameter⟨H(β)⟩.
3. Minimize ⟨H(β)⟩and solve for β; that is, solve $\frac{\partial \langle H \rangle}{\partial \beta} = 0$
4. Substitute β back into ⟨H⟩and you have found the upper bound energy.

Example*

a) Use the variational method to estimate the ground state energy of a 1-dimensional harmonic oscillator using the trial wave functions

$$\psi = \frac{1}{1 + \beta x^2} \qquad \text{and} \qquad \psi = \frac{1}{(1 + \beta x^2)^3}$$

where $\beta > 0$.

b) Compare the results with the actual ground state energy of a 1D harmonic oscillator and show that one wave function gives a closer result than the other. Why does one trial wave function give a better estimate? Plot the functions and analyze.

*https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Quantum_Tutorials_(Rioux)/Approximate_Quantum__Mechanical_Methods/433%3A_Variation_Method_for_the_Harmonic_Oscillator

Solution (First Trial Wave Function)

1) Is the wave function normalized? Nope. So we start by normalizing.

$$\int_{-\infty}^{\infty} \frac{A^2}{(1+\beta x^2)^2}\,dx = 1 \qquad \text{gives} \qquad A^2 = \frac{2\sqrt{\beta}}{\pi}$$

2) Substitute the wave function into the Hamiltonian (for a 1D harmonic oscillator) and integrate to find the expectation value

$$\langle H\rangle = \int_{-\infty}^{\infty} \psi^* H \psi\, dx = \int_{-\infty}^{\infty} \frac{A}{1+\beta x^2}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2\right)\frac{A}{1+\beta x^2}\,dx = \frac{\hbar^2\beta}{4m} + \frac{m\omega^2}{2\beta}$$

3) Minimize: $\dfrac{\partial\langle H\rangle}{\partial\beta} = 0$ gives $\beta = \sqrt{2}\dfrac{m\omega}{\hbar}$

4) Substituting back into ⟨H⟩ gives energy

$$\langle H\rangle = E = \frac{\hbar\omega}{\sqrt{2}} = 0.707\hbar\omega$$

Solution (Second Trial Wave Function)

1) Find normalization constant (Use your favorite integration software)

$$\int_{-\infty}^{\infty} \frac{A^2}{(1+\beta x^2)^6} = 1 \qquad A^2 = \frac{256\sqrt{\beta}}{63\pi}$$

2) Setting all the constants equal to 1. And, again, following the algorithm and using your favorite integration software.

$$\langle H \rangle = \int_{-\infty}^{\infty} \psi^* H \psi dx = \int_{-\infty}^{\infty} \frac{A^2}{(1+\beta x^2)^3} \left(-\frac{1}{2}\frac{\partial^2}{\partial x^2}\frac{1}{(1+\beta x^2)^3} + \frac{1}{2}\frac{1}{(1+\beta x^2)^3} \right) dx$$

$$\langle H \rangle = \frac{33}{28}\beta + \frac{1}{18\beta} \longrightarrow \frac{\partial \langle H \rangle}{\partial \beta} = \frac{33}{28} - \frac{1}{18\beta^2} = 0 \longrightarrow \beta_0 = \frac{\sqrt{462}}{99}$$

$$E = 0.511766\hbar\omega$$ Compare to: $$E_0 = 0.5\hbar\omega$$

How do the trial wave functions compare?

TRIAL WAVE FUNCTION	UPPER BOUND ON THE GROUND STATE ENERGY	ERROR WITH RESPECT TO E=0.5ħω
$\psi = \frac{A}{(1+\beta x^2)}$	0.707	41.42%
$\psi = \frac{A}{(1+\beta x^2)^2}$	0.529	5.83%
$\psi = \frac{A}{(1+\beta x^2)^3}$	0.512	2.35%

Why does one trial wave function give a better estimate?