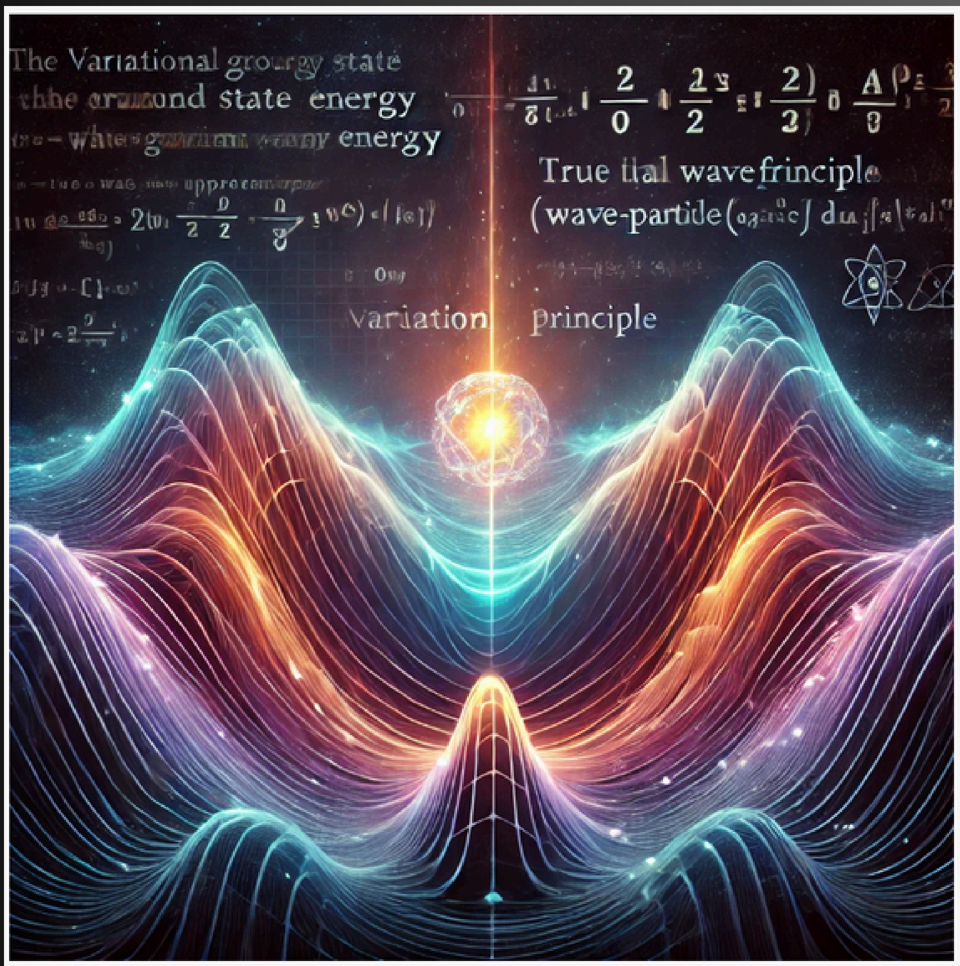
VARIATIONAL PRINCIPLE



GATE-NET-SET

Dr. Nanda Kishore

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Variational Principle

The **Variational principle** is a powerful and widely used technique in quantum mechanics to approximate the ground state energy of a quantum system when the exact solution is not available. It provides an **upper bound for the ground state energy** and is particularly useful for complex systems like atoms, molecules, and quantum field systems.

1 The Basic Idea

The variational principle is based on the Rayleigh-Ritz method, which states that for any trial **wave function** ψ_{trial} , the expectation value of the Hamiltonian provides an upper bound for the true ground state energy E_0 :

$$\boldsymbol{E}_{\text{trial}} = \frac{\left\langle \boldsymbol{\psi}_{\text{trial}} \middle| \hat{\boldsymbol{H}} \middle| \boldsymbol{\psi}_{\text{trial}} \right\rangle}{\left\langle \boldsymbol{\psi}_{\text{trial}} \mid \boldsymbol{\psi}_{\text{trial}} \right\rangle} \geq \boldsymbol{E}_0$$

where:

- $\hat{\boldsymbol{H}}$ is the Hamiltonian of the system,
- $\boldsymbol{E}_0$ is the exact ground state energy,
- $\boldsymbol{\psi}_{\text{trial}}$ is an arbitrary, normalized trial wave function.

The key idea is to choose a trial wave function that is as close as possible to the actual ground state wave function. By minimizing $\boldsymbol{E}_{\text{trial}}$, we obtain an approximation for $\boldsymbol{E}_0$.

2 Mathematical Foundation of the Variational Principle

Given a quantum system described by a Hamiltonian $\hat{H}$ with eigenstates ψ_n and corresponding eigenvalues E_n :

$$\hat{\boldsymbol{H}}\boldsymbol{\psi}_n = \boldsymbol{E}_n\boldsymbol{\psi}_n, \qquad \boldsymbol{n} = \mathbf{0}, \mathbf{1}, \mathbf{2}, \ldots$$

Any normalized trial wave function ψ_{trial} can be expanded in terms of the exact eigen states:

$$\psi_{\text{trial}} = \sum_n c_n \psi_n, \text{ with } \sum_n |c_n|^2 = 1$$

The expectation value of $\hat{H}$ is:

$$E_{\text{trial}} = \left\langle \psi_{\text{trial}} \middle| \hat{H} \middle| \psi_{\text{trial}} \right\rangle = \sum_n |c_n|^2 E_n$$

Since E_0 is the smallest eigenvalue, we obtain:

$$\boldsymbol{E_{\text{trial}} \geq E_0}$$

This inequality proves that the variational energy estimate is always an upper bound to the true ground state energy.

3 Choosing the Trial Wave function

To apply the variational principle effectively, we need a good choice of trial **wave function** ψ_{trial}, which should:

1 **Satisfy Boundary Conditions**: The trial **wave function** should obey the same boundary conditions as the actual **wave function**.

2 **Include Adjustable Parameters**: The trial function should include one or more free parameters that can be optimized to minimize $\boldsymbol{E_{\text{trial}}}$.

3 **Reflect the Symmetry of the System**: It should incorporate the physical features of the problem, such as symmetry and expected behavior at infinity.

A common choice for a trial function is:

$$\boldsymbol{\psi_{\text{trial}}(x) = Ae^{-\alpha x^2}}$$

where α is a variational parameter.

6 Limitations of the Variational Principle

Depends on the Trial Wave function: A poor choice may lead to inaccurate results.

Only Provides an Upper Bound: The method cannot determine excited state energies directly.

Computational Complexity: For large systems, solving variational integrals can be challenging.

Example: Variational Method for the Quantum Harmonic Oscillator

Step 1: Exact Solution for Comparison
The quantum harmonic oscillator has the Hamiltonian:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

The exact ground-state wave function is:

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

and the exact ground-state energy is:

$$E_0 = \frac{1}{2}\hbar\omega$$

Now, let's approximate E_0 using the variational method.

Step 2: Choosing a Trial Wave function
A good trial wave function should resemble the actual ground-state wave function. We choose:

$$\psi_{\text{trial}}(x) = Ae^{-\alpha x^2}$$

where α is the variational parameter to be optimized.

Step 3: Normalize the Trial Wave function
The normalization condition is:

$$\int_{-\infty}^{\infty} \left|\psi_{\text{trial}}(x)\right|^2 dx = 1$$

Substituting $\psi_{\text{trial}}(x)$:

$$A^2 \int_{-\infty}^{\infty} e^{-2\alpha x^2} dx = 1$$

Since the standard Gaussian integral formula:

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$$

applies here with $a = 2\alpha$, we get:

$$A^2 \sqrt{\frac{\pi}{2\alpha}} = 1$$

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Thus, the normalization constant is:

$$A = \left(\frac{2\alpha}{\pi}\right)^{\frac{1}{4}}$$

Step 4: Compute Expectation Value of Energy
The variational estimate for energy is:

$$\boldsymbol{E_{\text{trial}}} = \frac{\left\langle \boldsymbol{\psi_{\text{trial}}} \middle| \boldsymbol{\hat{H}} \middle| \boldsymbol{\psi_{\text{trial}}} \right\rangle}{\left\langle \boldsymbol{\psi_{\text{trial}}} \mid \boldsymbol{\psi_{\text{trial}}} \right\rangle}$$

We evaluate the kinetic and potential energy terms separately.
Kinetic Energy Term
The kinetic energy operator is:

$$\hat{T} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

the expectation value of K.E is :

$$\left\langle \psi_{\text{trial}} \middle| \hat{T} \middle| \psi_{\text{trial}} \right\rangle = \frac{\hbar^2 \alpha}{2m}$$

Potential Energy Term
The potential energy operator is:

$$V(x) = \frac{1}{2} m\omega^2 x^2$$

the expectation value of P.E:

$$\left\langle \psi_{\text{trial}} \middle| \hat{V} \middle| \psi_{\text{trial}} \right\rangle = \frac{m\omega^2}{4\alpha}$$

Thus, the total energy is:

$$\boldsymbol{E_{\text{trial}}(\alpha) = \frac{\hbar^2 \alpha}{2m} + \frac{m\omega^2}{4\alpha}}$$

Step 5: Minimizing the Energy
To find the optimal α, we minimize $E_{\text{trial}}(\alpha)$ by solving:

$$\frac{dE_{\text{trial}}}{d\alpha} = 0$$
$$\frac{\hbar^2}{2m} - \frac{m\omega^2}{4\alpha^2} = 0$$

Solving for α :

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

Substituting into $E_{\text{trial}}(\alpha)$:

$$E_{\text{trial}} = \frac{\hbar^2}{2m} \cdot \frac{m\omega}{2\hbar} + \frac{m\omega^2}{4} \cdot \frac{2\hbar}{m\omega}.$$
$$E_{\text{trial}} = \frac{1}{4}\hbar\omega + \frac{1}{4}\hbar\omega = \frac{1}{2}\hbar\omega.$$

Step 6: Comparing with the Exact Result

- The exact ground-state energy is $E_0 = \frac{1}{2}\hbar\omega$.
- The variational method gives $E_{\text{trial}} = \frac{1}{2}\hbar\omega$.

Since the trial wave function closely resembles the actual ground-state wave function, the variational estimate is exact in this case.

Why is the Variational Method Beneficial?

1 **Provides an Upper Bound**

The variational method ensures:

$$\boldsymbol{E_{\text{trial}} \geq E_0}$$

This helps us find approximate ground-state energies with confidence, knowing we are never underestimating.

2. **Useful for Complex Systems**

For many-body problems like atoms and molecules (e.g., Helium, Lithium), exact solutions are impossible. The variational method allows us to approximate these energies efficiently.

3 Flexible Choice of Trial Wave functions

We can use **wave functions** tailored to the system's physical properties, improving accuracy.

4. Computationally Feasible

Unlike numerical methods (which may be expensive), the variational method provides accurate estimates with simple integrals and algebraic minimization.

5. Basis for Advanced Methods

- Hartree-Fock Theory: Used in quantum chemistry.
- Density Functional Theory (DFT): An extension of the variational principle in condensed matter physics.

The **variational method** is a **powerful tool** in quantum mechanics that provides **accurate approximations** for ground-state energies when exact solutions are difficult. As seen in the quantum harmonic oscillator example, it can yield **exact** results for well-chosen trial functions and offers an upper bound that ensures reliability. The method plays a crucial role in quantum chemistry, condensed matter physics, and nuclear physics.

Move Forward, whatever happens…..

Multiple choice questions

MCQ 1:

The variational principle states that for any trial wave function ψ_{trial},

$$E_{\text{trial}} = \frac{\langle \psi_{\text{trial}} | \hat{H} | \psi_{\text{trial}} \rangle}{\langle \psi_{\text{trial}} | \psi_{\text{trial}} \rangle}$$

is always:

(A) Greater than or equal to the ground-state energy

(B) Less than or equal to the ground-state energy

(C) Exactly equal to the ground-state energy for any trial wave function

(D) Independent of the choice of trial wave function

✓**Answer:** (A) Greater than or equal to the ground-state energy

Explanation: The variational principle guarantees that $E_{\text{trial}} \geq E_0$, ensuring that our estimate is an upper bound.

MCQ 2:

What is the primary criterion for choosing a trial wave function in the variational method?

(A) It must be an eigenfunction of the Hamiltonian

(B) It must be an even function

(C) It must satisfy boundary conditions and normalization

(D) It must be chosen arbitrarily without constraints

Answer: (C) It must satisfy boundary conditions and normalization

Explanation: The trial **wave function** must be normalizable, satisfy the boundary conditions of the problem, and be as close as possible to the true **wave function**.

MCQ 3:

In the variational method, how do we obtain the best possible estimate of the ground-state energy?

(A) By selecting the trial wave function with the highest energy

(B) By minimizing the expectation value of energy with respect to variational parameters

(C) By solving Schrödinger's equation exactly

(D) By using any arbitrary function without optimization

Answer: (B) By minimizing the expectation value of energy with respect to variational parameters **Explanation**: The best estimate is obtained by optimizing variational parameters to minimize E_{trial} .

MCQ 4:

The variational principle is best interpreted as:

(A) A method to find exact energy eigenvalues of all states

(B) A technique that ensures an upper bound on the ground-state energy

(C) A method that applies only to classical systems

(D) A rule that allows us to determine eigenvalues without a Hamiltonian

Answer: (B) A technique that ensures an upper bound on the ground-state energy **Explanation**: The variational principle is an approximation tool for quantum systems, always yielding an upper bound for E_0.

MCQ 5:

Which of the following trial wave functions is most suitable for estimating the ground-state energy of the hydrogen atom?

(A) $\psi_{\text{trial}}(r) = Ae^{-\alpha r}$

(B) $\psi_{\text{trial}}(r) = A\cos(\alpha r)$

(C) $\psi_{\text{trial}}(r) = Ae^{-\alpha r^2}$

(D) $\psi_{\text{trial}}(r) = A\sin(\alpha r)$

✓**Answer**: (A) $\psi_{\text{trial}}(r) = Ae^{-\alpha r}$

Explanation: The exact hydrogen atom ground state has an exponential decay, so choosing a similar trial function leads to an accurate approximation.

MCQ 6:

For a quantum harmonic oscillator, a natural choice of a trial wave function is:

(A) $\psi_{\text{trial}}(x) = Ae^{-\alpha x^2}$

(B) $\psi_{\text{trial}}(x) = A\cos(\alpha x)$

(C) $\psi_{\text{trial}}(x) = Ae^{-\alpha x}$

(D) $\psi_{\text{trial}}(x) = Axe^{-\alpha x^2}$

Answer: (A) $\psi_{\text{trial}}(x) = Ae^{-\alpha x^2}$

Explanation: The ground-state **wave function** of the harmonic oscillator is Gaussian in nature, making this a good variational choice.

MCQ 7:

In a variational calculation, the parameter α in the trial wave function is optimized by:

(A) Solving Schrödinger's equation for α

(B) Setting $\frac{dE_{\text{trial}}}{d\alpha} = 0$

(C) Guessing the best value for α

(D) Choosing α such that E_{trial} is maximized

✓**Answer**: (B) Setting $\frac{dE_{\text{trial}}}{d\alpha} = 0$

Explanation: The variational parameter is optimized by minimizing the energy expectation value.

MCQ 8:

The variational principle is primarily used to approximate:

(A) The ground-state energy only

(B) Both ground and excited-state energies with equal accuracy

(C) Only excited-state energies

(D) Any eigenvalue of the Hamiltonian

Answer: (A) The ground-state energy only

Explanation: The variational principle provides an upper bound for E_0 but does not guarantee accuracy for excited states.

MCQ 9:

The Hartree-Fock method, a fundamental technique in quantum chemistry, is based on:

(A) The Born-Oppenheimer approximation

(B) The exact solution of the Schrödinger equation

(C) The variational principle

(D) The Heisenberg uncertainty principle

Answer: (C) The variational principle

Explanation: Hartree-Fock uses a trial **wave function** with Slater determinants to approximate electron interactions using the variational principle.

MCQ 10:

Which of the following statements about the variational principle is incorrect?

(A) It provides an upper bound for the ground-state energy

(B) It requires a normalized trial wave function

(C) It guarantees an exact solution for any Hamiltonian

(D) It is useful when exact solutions are unavailable

✓**Answer**: (C) It guarantees an exact solution for any Hamiltonian

Explanation: The variational principle does not always give an exact solution-it provides an approximation that depends on the choice of trial **wave function**.