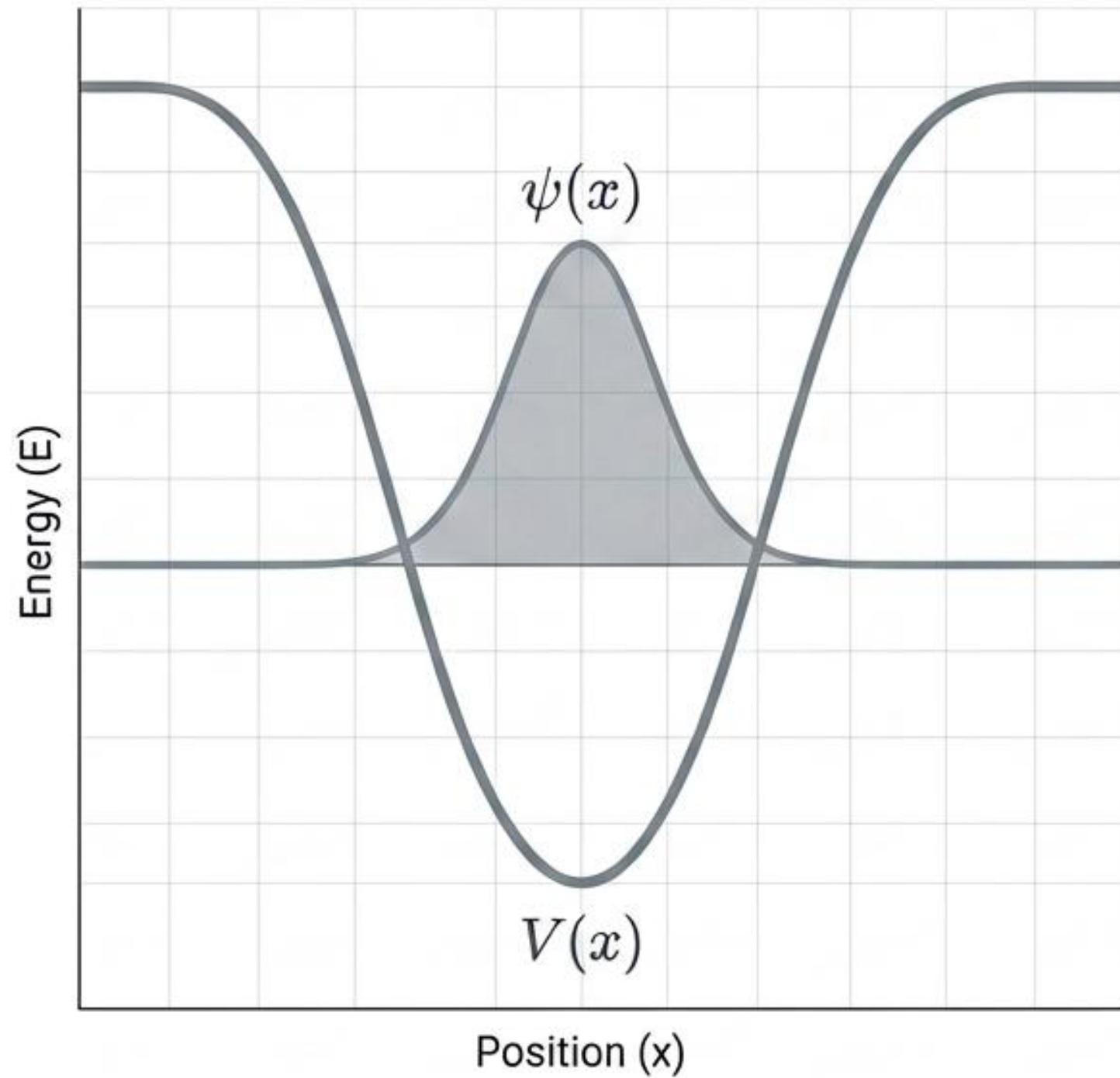


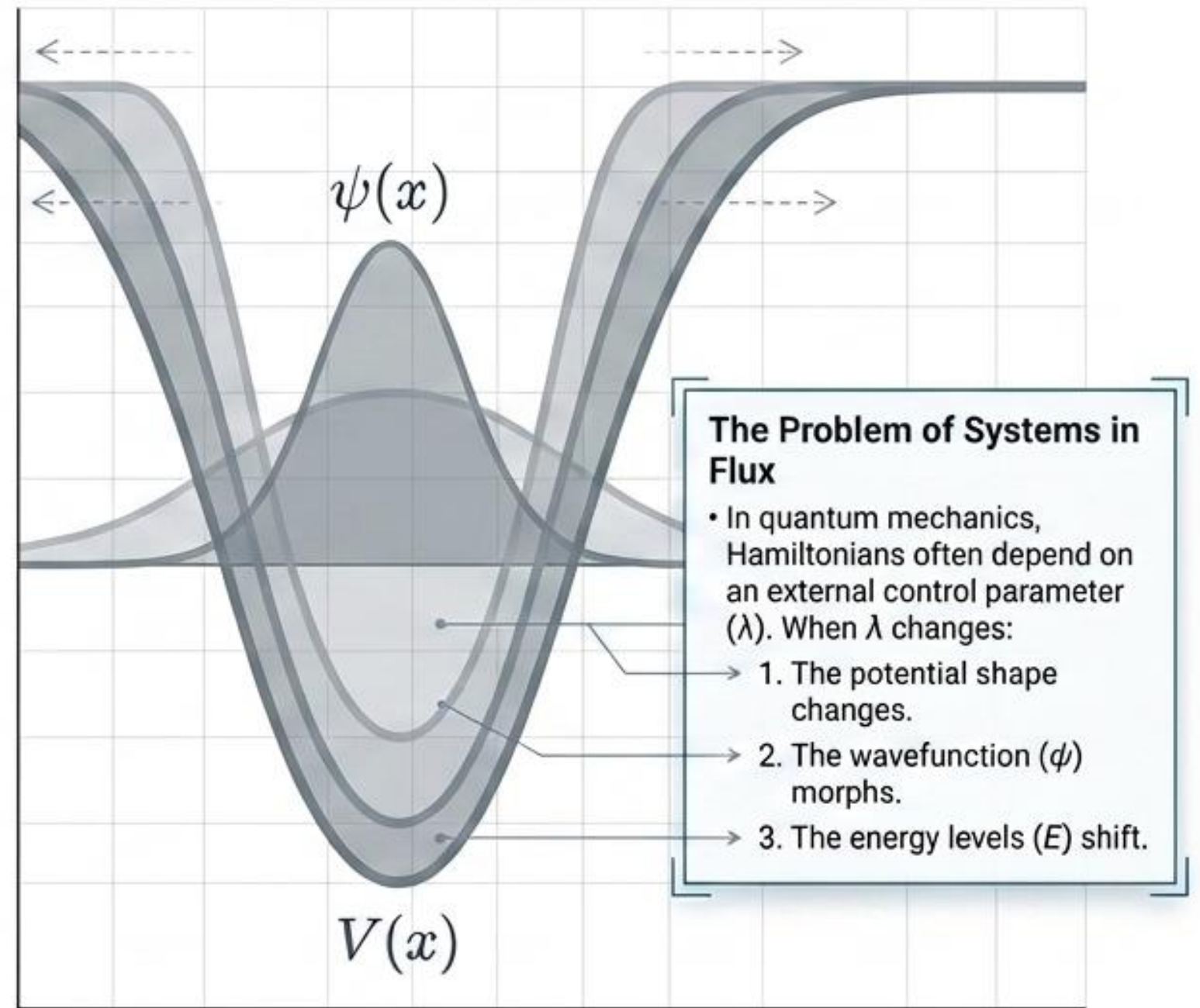
The Hellmann–Feynman Theorem

How Quantum Energy Changes with External Parameters

STATIC SYSTEM



DYNAMIC SYSTEM



How can we calculate the change in energy when the system itself changes?

Anatomy of a Parameter-Dependent Hamiltonian

$$H(\lambda) = \frac{p^2}{2m} + V(x, \lambda)$$

Hamiltonian (System Energy)

Kinetic Energy

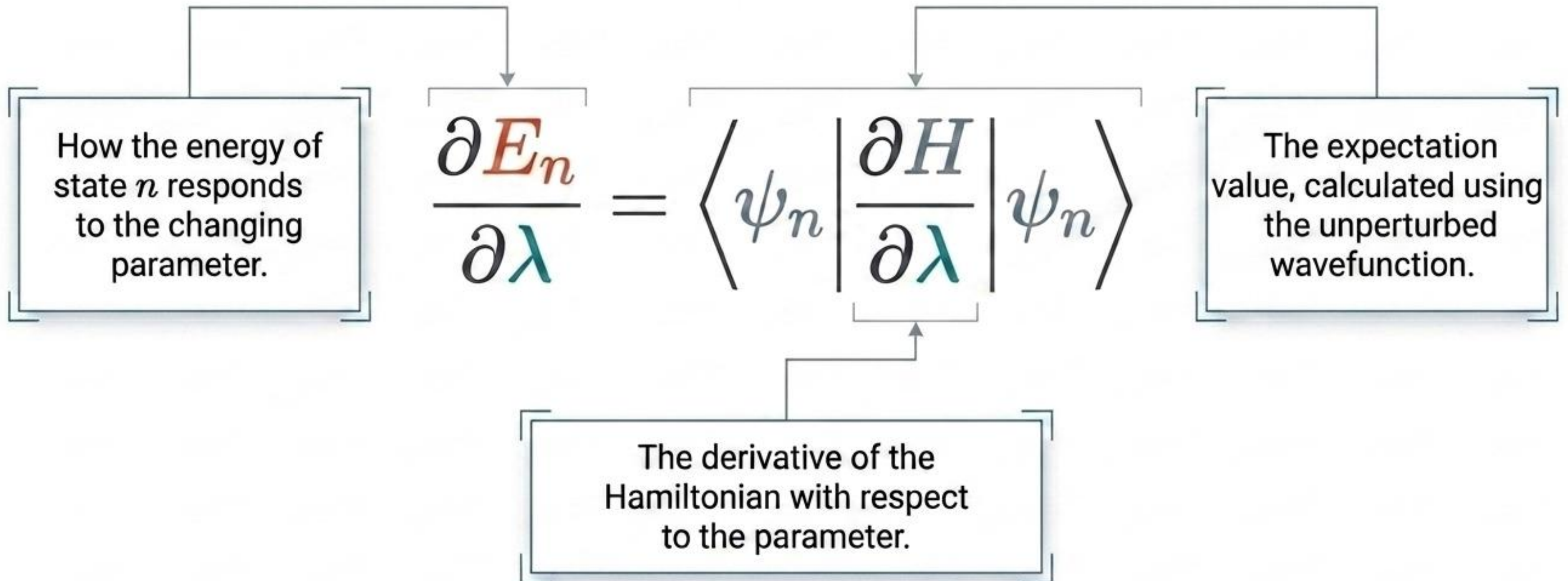
Potential Energy (Environment)

EXTERNAL PARAMETER (CONTROL)

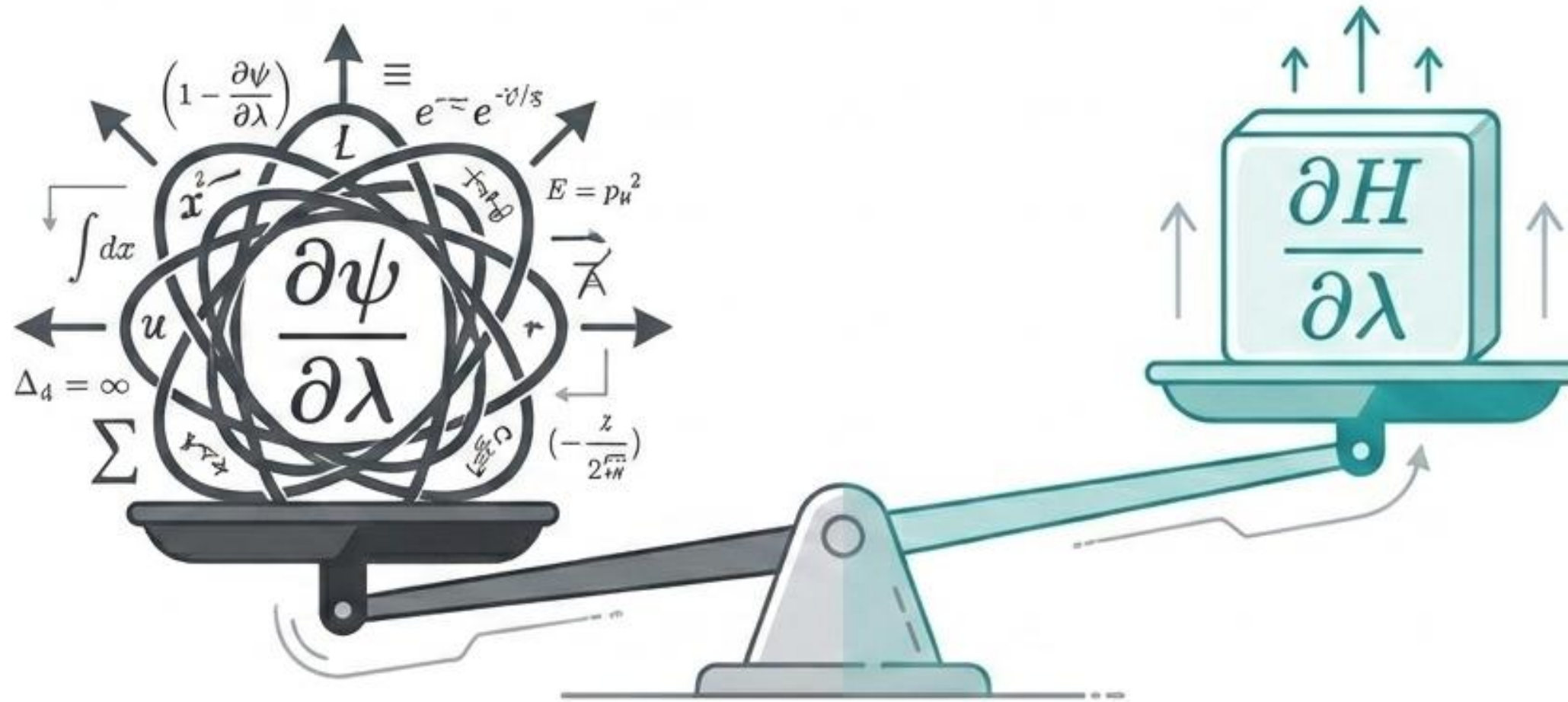
A parameter-dependent Hamiltonian changes when an external control is tuned.
It alters the system's environment, not the particle's state.



The Hellmann–Feynman Theorem



The Shortcut Through Quantum Space



Directly differentiating a complex wavefunction is mathematically arduous. The genius of the theorem is that it proves we only need to differentiate the Hamiltonian. The wavefunction itself remains untouched.

The theorem provides a direct mathematical shortcut to calculate energy shifts without solving the Schrödinger equation all over again.

The Proof in Three Steps

The Expectation Value

$$E = \langle \psi | H(\lambda) | \psi \rangle$$

Apply the Chain Rule

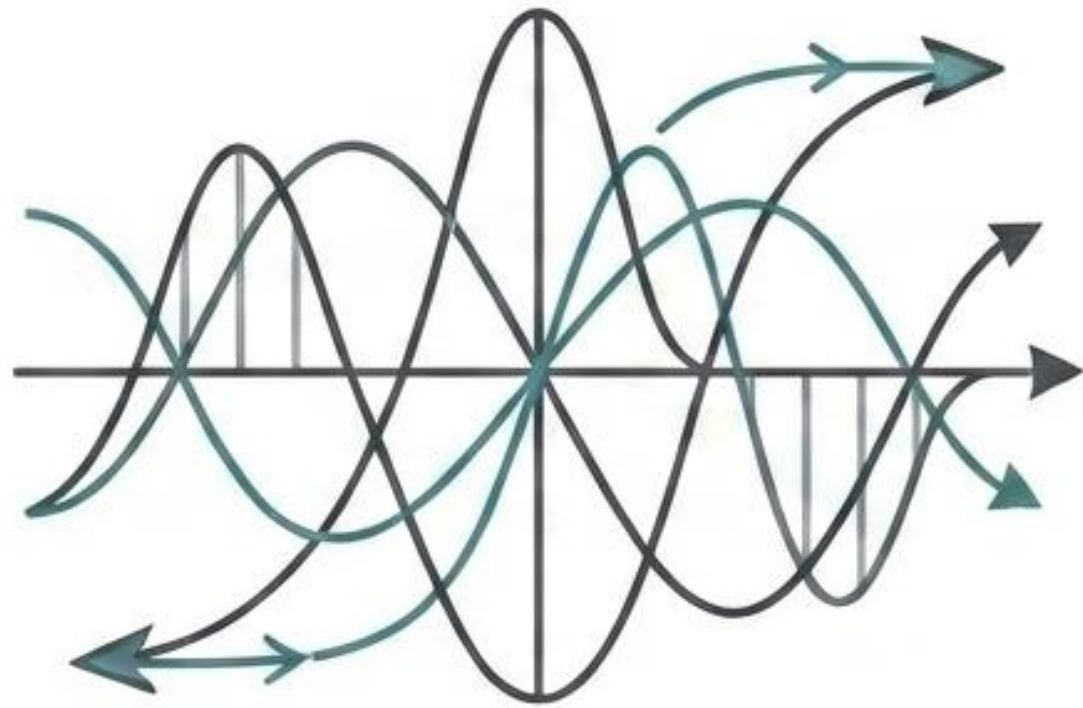
$$\frac{dE}{d\lambda} = \left\langle \frac{d\psi}{d\lambda} | H | \psi \right\rangle + \left\langle \psi | \frac{\partial H}{\partial \lambda} | \psi \right\rangle + \left\langle \psi | H | \frac{d\psi}{d\lambda} \right\rangle$$

Cancellation Magic

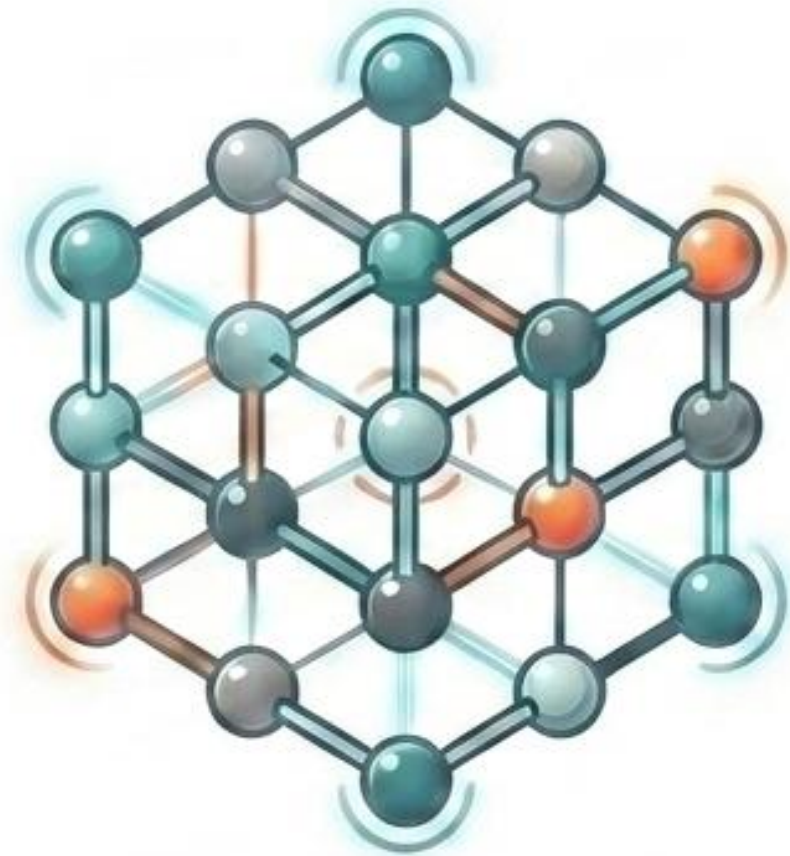
Because $H|\psi\rangle = E|\psi\rangle$ and the wavefunction is normalized ($\langle \psi | \psi \rangle = 1$), the first and third terms sum to exactly zero: $E \frac{d}{d\lambda} \langle \psi | \psi \rangle = 0$.

$$\frac{dE}{d\lambda} = \left\langle \psi | \frac{\partial H}{\partial \lambda} | \psi \right\rangle$$

From Theory to Practice

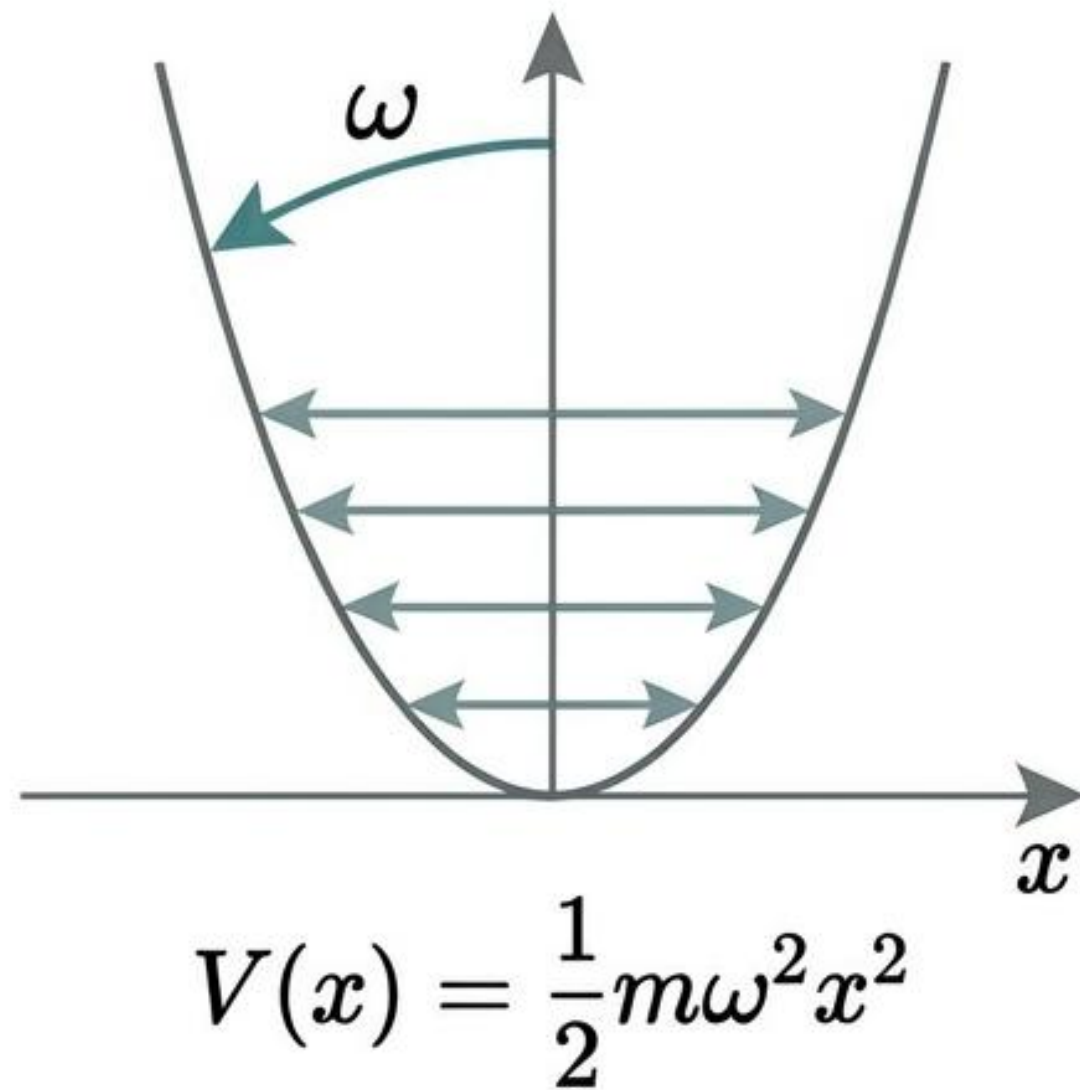


Application 1: Quantum Harmonic Oscillator.
(Proving mathematical efficiency).



Application 2: Molecular Forces.
(Proving real-world chemical relevance).

Application 1: The Quantum Harmonic Oscillator



- The Hamiltonian:

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

- The Target Parameter:

$$\lambda = \omega \text{ (Oscillator frequency)}$$

- Known Energy Levels:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

Extracting Expectation Values

Differentiate the Hamiltonian

$$\frac{\partial H}{\partial \omega} = m\omega x^2$$

Differentiate the Energy

$$\frac{dE_n}{d\omega} = \left(n + \frac{1}{2}\right)\hbar$$

Apply Hellmann-Feynman:

$$\left(n + \frac{1}{2}\right)\hbar = \langle \psi_n | m\omega x^2 | \psi_n \rangle$$

$$\langle x^2 \rangle = \frac{(n + 1/2)\hbar}{m\omega}$$

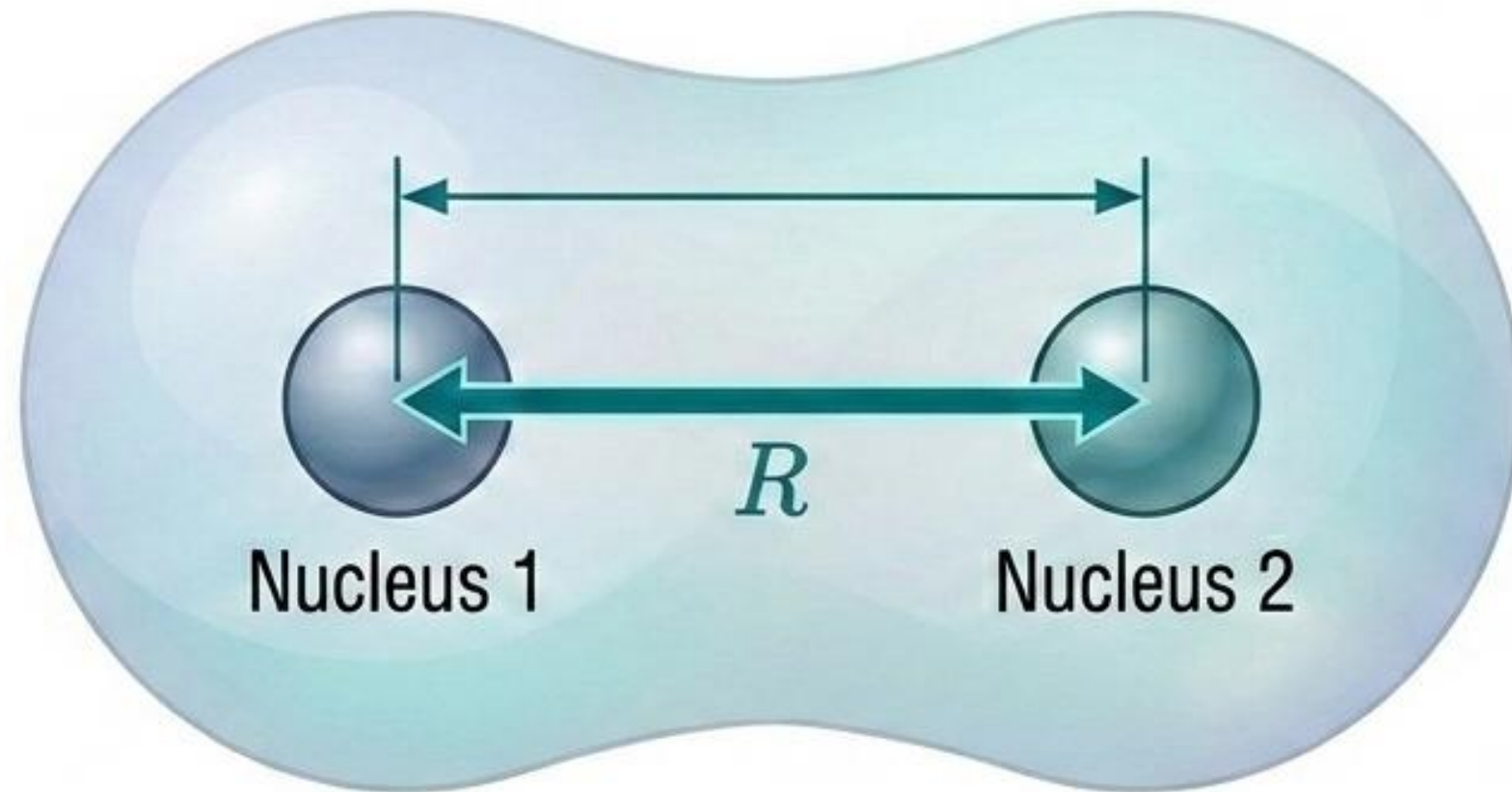
The Physics Payoff



The theorem enables us to calculate complex expectation values with high efficiency.

We bypassed pages of complex spatial integration by executing a single, basic algebraic derivative.

Application 2: Molecular Forces



- **The Setup:** In quantum chemistry, total molecular energy depends on the precise position of the atomic nuclei.
- **The Parameter:** $\lambda = R$ (Nuclear distance)
- **The Physics:** The physical force (F) acting on the nuclei is simply the negative spatial derivative of the energy: $F = -\frac{dE}{dR}$.

Connecting Derivatives to Measurable Forces

$$F = -\left\langle \psi \left| \frac{\partial H}{\partial R} \right| \psi \right\rangle$$

Instead of differentiating astronomically complex molecular wavefunctions (a computationally crippling task), we easily differentiate the Hamiltonian to reveal the exact physical force pushing or pulling the nuclei.

The Hellmann-Feynman Advantage

Brute Force Method

Hellmann-Feynman Method

The Goal

Find how energy changes

Find how energy changes

The Process

Solve full Schrödinger equation from scratch

Take a simple derivative of the Hamiltonian

The Math

Complex spatial integration

Straightforward algebraic differentiation

New Wavefunction Needed?

YES
(Recalculate entirely)

NO (Use the existing unperturbed state)

Conclusion

The theorem elegantly connects energy changes, expectation values, and physical forces through a single, unified mathematical rule.

When a quantum system changes slightly, the Hellmann–Feynman theorem tells us exactly how its energy responds—without ever requiring us to solve the entire Schrödinger equation all over again.