THE VARIATIONAL PRINCIPLE: YET ANOTHER EXAMPLE

The basic idea is very simple: since the ground state minimizes the energy of a system, the expectation value of the Hamiltonian on a generic state is necessarily larger than (or equal to) the ground state energy:

$$E_{gs} \leq \langle \psi | H | \psi \rangle$$

where ψ is my guess at the ground state wavefunction. More interestingly, we can make ψ depend on some parameter $\lambda_1, \lambda_2, \lambda_3, \ldots$. Since the expression above shall be valid for any ψ, we can minimize it as a function of the λ_i parameters, thus obtaining a better estimate of E_{gs}.
In practice, we write a <u>normalized</u> wavefunction $\psi(\vec{r}, \lambda_1, \lambda_2 \ldots)$ and then require:

$$\frac{\partial}{\partial \lambda_i} \langle \psi(\vec{r}, \lambda_1, \lambda_2, \ldots) | H | \psi(\vec{r}, \lambda_1, \lambda_2, \ldots) \rangle = 0$$

for all λ_i parameters. Let us note that there is <u>no way</u> to tell how close the minimized $\langle \psi | H | \psi \rangle$ is to E_{gs}, the true ground state energy.

It is useful to make the λ_i parameters correspond to a physically motivated quantity, such as an effective charge, the width of a wavefunction, the distance between two nuclei in a molecule.

Let us study the problem of a particle of mass m subject to a potential $V(x) = -\alpha\, \delta(x)$ (a Dirac δ function).

<u>Exact solution</u>:

$$\psi_{gs}(x) = \sqrt{\frac{m\alpha}{\hbar}}\ \exp(-m\alpha |x| / \hbar^2)$$

$$E_{gs} = -m\alpha^2 / 2\hbar^2$$

Let us guess a solution in the form of a Gaussian wavefunction:

$$\psi(x,b)=\left(\frac{2b}{\pi}\right)^{1/4}e^{-bx^2}$$

b tells us how wide the wavefunction is in the real space (the larger b, the narrower $\psi \Longrightarrow$ the larger the uncertainty on the particle's momentum, hence the larger the expectation value of the particle's kinetic energy!).

$\psi(x,b)$ must be normalized to unity: $\langle\psi(x,b)|\psi(x,b)\rangle=1$

The Hamiltonian is simple:

$$H=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}-\alpha\,\delta(x)=T+V$$

Let us calculate the expectation values:

$$\langle T\rangle=-\frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\left(\frac{2b}{\pi}\right)^{1/2}e^{-bx^2}\frac{\partial^2}{\partial x^2}\left(e^{-bx^2}\right)=$$

$$=-\frac{\hbar^2}{2m}\left(\frac{2b}{\pi}\right)^{1/2}\int_{-\infty}^{\infty}e^{-bx^2}\left(-2be^{-bx^2}+4b^2x^2e^{-bx^2}\right)=$$

$$=-\frac{\hbar^2}{2m}\cancel{\left(\frac{2b}{\pi}\right)^{1/2}}\cdot(-2b)\cdot\cancel{\left(\frac{\pi}{2b}\right)^{1/2}}+\left(-\frac{\hbar^2}{2m}\right)\left(\frac{\cancel{2b}}{\cancel{\pi}}\right)^{1/2}\cdot(\cancel{4}b^{\cancel{2}})\cdot\frac{\sqrt{\cancel{2\pi}}}{\cancel{8}}\cdot\frac{1}{\cancel{b^{3/2}}}$$

$$=\frac{\hbar^2 b}{m}-\frac{\hbar^2 b}{2m}=\boxed{\frac{\hbar^2 b}{2m}=\langle T\rangle}$$

$$\boxed{\langle V\rangle=}-\alpha\int_{-\infty}^{\infty}\left(\frac{2b}{\pi}\right)^{1/2}e^{-2bx^2}\delta(x)\boxed{=-\left(\frac{2b\alpha^2}{\pi}\right)^{1/2}}$$

Then:

$$\langle H\rangle=\frac{\hbar^2 b}{2m}-\left(\frac{2b\alpha^2}{\pi}\right)^{1/2}\Longrightarrow\frac{\partial\langle H\rangle}{\partial b}=\frac{\hbar^2}{2m}-\frac{1}{2}\cdot\left(\frac{2\alpha^2}{\pi}\right)^{1/2}\cdot b^{-\frac{1}{2}}$$

Finally:

$$\frac{\partial \langle H \rangle}{\partial b} = 0 \implies b = \frac{2}{\pi} \frac{\mu^2 \alpha^2}{\hbar^4}$$

Correspondingly:

$$\langle H \rangle = -\frac{1}{\pi} \frac{m\alpha^2}{\hbar^2} \geq -\frac{1}{2} \frac{\mu\alpha^2}{\hbar^2} \quad \text{exact solution!}$$

Crucial notes:

1) the Hamiltonian <u>cannot</u> be modified. One can rearrange its pieces, and make it more explicit how expectation values depend on the λ_i parameters used to model the guessed wavefunction ψ (e.g.: He atom and Z: we wrote $-\frac{2}{r} = -\frac{Z}{r} + \frac{Z-2}{r}$!), but the Hamiltonian itself <u>cannot</u> depend on λ_i: we are allowed to modify only our guessed ψ

2) when making ψ depend on λ_i parameters, do not forget to normalize ψ:

$$\langle \psi(\lambda_i) | \psi(\lambda_i) \rangle = 1$$

the normalization constant may depend on λ_i, and that dependency is important!