Variational Method

In perturbation theory, we begin with a "base" Hamiltonian of which we know the exact stationary states. We define a perturbation and then determine corrections to the energy levels & eigenstates up to some order in a small parameter λ.

The _variational method_ is useful even if we don't know exact solution of a sufficiently similar "unperturbed" Hamiltonian.

Primary use: method for estimating ground state energy. Take any normalized state vector $|\psi\rangle$. You can always produce an over-estimate of ground state energy by taking $\langle H \rangle_\psi$.

Theorem: $E_g \leq \langle \psi | H | \psi \rangle = \langle H \rangle_\psi$.

or equivalently, $E_g \leq \dfrac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \langle H \rangle_\psi$
$\qquad\qquad\qquad\qquad\qquad$ if $|\psi\rangle$ not
$\qquad\qquad\qquad\qquad\qquad$ normalized.

Proof: Assume $\{|k\rangle\}$ are the set of exact energy eigenstates of the Hamiltonian H. $H|k\rangle = E_k|k\rangle$.

Then in this basis expand $|\psi\rangle = \sum\limits_{k=0}^{\infty} |k\rangle\langle k|\psi\rangle$

Assume $|\psi\rangle$ is normalized.

$1 = \langle\psi|\psi\rangle = \left(\sum\limits_{k=0}^{\infty} \langle\psi|k\rangle\langle k|\right)\left(\sum\limits_{\ell=0}^{\infty} |\ell\rangle\langle\ell|\psi\rangle\right)$

$\qquad = \sum\limits_{k}\sum\limits_{\ell} C_k^* C_\ell \langle k|\ell\rangle = \sum\limits_{k} |C_k|^2$

Let's compute

$\langle H\rangle = \langle\psi|H|\psi\rangle = \sum\limits_{k} E_k |C_k|^2$

But the ground state energy $E_g \leq E_k \; \forall \, k$ so

$\langle H\rangle \geq E_g \sum\limits_{k} |C_k|^2 = E_g$ ∎

very general, powerful method! If we define a trial ket $|\psi\rangle$ with some parameter, we can evaluate $\langle H\rangle$ w.r.t. that parameter and take derivative to minimize energy, setting tighter upper bound on energy. Can define multiple parameters $\lambda_1, \lambda_2, ... \rightarrow \dfrac{\partial\langle H\rangle}{\partial\lambda_1} = 0, \quad \dfrac{\partial\langle H\rangle}{\partial\lambda_2} = 0, ...$

Example 1:

Estimate ground state energy of 1-d Harmonic oscillator

$H = -\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2} + \dfrac{1}{2}m\omega^2 x^2$

Suppose we are clever enough to choose a Gaussian form $\psi(x) = A e^{-bx^2}$ where A is a normalization constant and b is "$\frac{1}{2\sigma^2}$" for width of the distribution.

First, normalize $1 = \int |\psi(x)|^2 dx = |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} dx$

$$= |A|^2 \sqrt{\frac{\pi}{2b}}$$

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

Now

$$\langle H \rangle = -\frac{\hbar^2}{2m} |A|^2 \int_{-\infty}^{\infty} e^{-bx^2} \frac{\partial^2}{\partial x^2} e^{-bx^2} + \frac{1}{2} m\omega^2 |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} x^2 dx$$

$$= \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b}$$

$$\frac{\partial \langle H \rangle}{\partial b} = 0 = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} \Rightarrow b = \frac{m\omega}{2\hbar}$$

Plug back into $\langle H \rangle \rightarrow \langle H \rangle_{min} = \frac{1}{2}\hbar\omega$
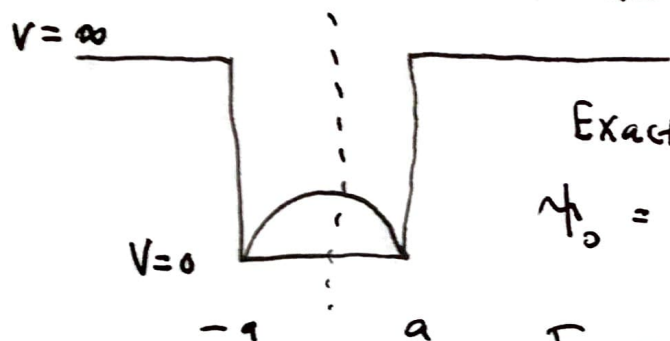
we happened to get exact G.S. wavefunction, so makes sense.

oscillator length $X_o = \sqrt{\frac{\hbar}{m\omega}}$

$$b = \frac{1}{2\sigma^2} \qquad \boxed{\sigma = X_o}$$

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Ex. 2 : Consider a Hydrogen atom, choose a

wavefunction $\psi = A e^{-r/a}$ with "a" as a variational

parameter, you'd find value $\dfrac{-e^2}{2 a_0}$ for g.s. energy

and $a = a_0$, the Bohr radius.

Ex. 3 : Consider the infinite square well potential

$V = \infty$

$V = 0$

$-a \qquad a$

Exact solution

$$\psi_0 = \frac{1}{\sqrt{a}} \cos\left(\frac{\pi x}{2a}\right)$$

$$E_0 = \frac{\hbar^2}{2m}\left(\frac{\pi^2}{4a^2}\right)$$

Consider a trial function $\psi(x) = a^2 - x^2$

$$\langle H \rangle = \frac{\dfrac{-\hbar^2}{2m}\displaystyle\int_{-a}^{a} (a^2 - x^2)\frac{\partial^2}{\partial x^2}(a^2 - x^2)\,dx}{\displaystyle\int_{-a}^{a}(a^2 - x^2)^2\,dx}$$

$$= \frac{10}{\pi^2}\frac{\pi^2 \hbar^2}{8 a^2 m} \approx 1.01\, E_0 \quad (\text{about } 1\% \text{ error}).$$

no "variational" parameter here. But if we choose

$\psi(x) = |a|^\lambda - |x|^\lambda$. $\Rightarrow$ $\overset{\text{find}}{\text{with}}$ $\lambda = 1.72$, get $1.003\, E_0$.

Less trivial example : He ground state

Helium, can't find exact solution analytically for Schrödinger equation.

The Hamiltonian

$$H = \frac{\hat{p_1}^2}{2m} + \frac{\hat{p_2}^2}{2m} + \frac{e^2}{4\pi\epsilon_0}\left(\frac{-Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right)$$

Here nucleus has charge Ze ($Z=2$ for He)

$r_{12} = |\vec{r_1} - \vec{r_2}|$ is separation between electrons.

we could treat $\frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}}$ as a perturbation.

Consider 2 "bare" Hamiltonians

$$H_1 = \frac{-\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} \qquad H_2 = \frac{-\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_2}$$

we could write wave function of electrons as a product

$$\psi = \psi(1)\psi(2)$$ with two single-electron

Schrödinger equations:

$H_1\psi(1) = E_1\psi(1)$

$H_2\psi(2) = E_2\psi(2)$

$E_1 = E_2 = -54.4\text{eV}$

$= -4(13.6\text{eV})$

since $Z = 2$

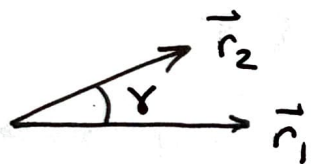Neglecting electron repulsion $E = -108.8 \, eV$

$$= -8 \left(\frac{e^2}{2a_0} \right) \frac{1}{4\pi\epsilon_0}$$

use 1st-order perturbation theory

$$\Delta_{1s^2} = \left\langle \frac{e^2}{4\pi\epsilon_0 \, r_{12}} \right\rangle_{1s^2}$$

$$= \iint \frac{Z^6}{\pi^2 a_0^6} \, e^{-2z(r_1+r_2)/a_0} \, \frac{e^2}{4\pi\epsilon_0 \, r_{12}} \, d^3\vec{r_1} \, d^3\vec{r_2}$$

$$\frac{1}{r_{12}} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\gamma}} = \sum_{\ell=0}^{\infty} \frac{r_<^\ell}{r_>^{\ell+1}} P_\ell(\cos\gamma)$$

$r_<$ ($r_>$) is the smaller (larger) of $r_1 + r_2$

$$P_\ell(\cos\gamma) = \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} Y_\ell^{m\,*}(\theta_1, \phi_1) \, Y_\ell^m(\theta_2, \phi_2)$$

Now you can perform angular integrals separately

$$\int Y_\ell^m(\theta_i, \phi_i) \, d\Omega_i = \frac{1}{\sqrt{4\pi}} (4\pi) \, \delta_{\ell 0} \, \delta_{m 0}$$

we have radial integral

$$\int_0^\infty \left[\int_0^{r_1} \frac{1}{r_1} e^{-2Z/a_0(r_1+r_2)} r_2^2 \, dr_2 + \int_{r_1}^\infty \frac{1}{r_2} e^{-2\left(\frac{Z}{a_0}\right)(r_1+r_2)} r_2^2 \, dr_2 \right] r_1^2 \, dr_1$$

$$= \frac{5}{128} \frac{a_0^5}{Z^5}$$

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Finally,

$$\Delta_{1s^2} = \frac{1}{4\pi\epsilon_0}\left(\frac{e^2}{2a_0}\right)\frac{5}{2}$$

Corrected energy is

$$E = \left(-8 + \frac{5}{2}\right)\frac{e^2}{4\pi\epsilon_0}\frac{1}{2a_0} = -74.8\,eV$$

experimental value is $-78.8\,eV$

using variational method, can treat $Z \to Z_{eff}$ as a variational parameter.

(since one electron can "screen" the nuclear charge for other)

Choose trial wavefunction

$$\langle \vec{r}_1, \vec{r}_2 | \psi \rangle = \frac{Z_{eff}^3}{\pi a_0^3}\left(e^{-Z_{eff}(r_1+r_2)/a_0}\right)$$

Can minimize $\langle H \rangle$ w.r.t. Z_{eff}.

$$\Rightarrow \quad E = -77.5\,eV \quad \underline{\text{much closer!}}$$

Also need to consider spin-statistics.

spin

the state must also respect fermi statistics and

Pauli exclusion principle.

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the helium ground state (unperturbed) would be

$$\psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2)\,\chi_{singlet}$$

$$\chi_{singlet} = \tfrac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$

total state must be anti-symmetric w.r.t. particle exchange.

Spatial w.f. is symmetric, spin is anti-symmetric ∎

Corollary to variational principle

If we have a trial ket $|\psi\rangle$ which is orthogonal to the true ground state $|\psi_0\rangle$, i.e. $\langle\psi|\psi_0\rangle = 0$ then we can put a bound $\langle H\rangle_\psi \geq E_1$ where E_1 is energy of 1st excited state.

Proof : Consider expectation value

$$\langle H\rangle = \langle\psi|H|\psi\rangle = \left(\sum_k c_k^* \langle k|\right)\left(\sum_\ell E_\ell c_\ell |\ell\rangle\right)$$

$$\text{If} \quad c_0 = \langle 0|\psi\rangle\Big|_{=0}$$

$$= \sum_{k\neq 0} E_k |c_k|^2$$

But $E_1 \leq E_k \;\forall\, k\neq 0$ since it's the 1st excited state.

$$\Rightarrow \quad \langle H\rangle_\psi \geq E_1.$$

Remark: useful for estimating energy of 1st excited state. Even if you don't know exact ground state wave function $\langle x | 0 \rangle$, you can often use symmetry arguments e.g. if you know ground state is symmetric and 1st excited is anti-symmetric you can choose any anti-symmetric w.f. with a trial parameter λ as long as it stays anti-symmetric.

    Ex: (HW exercises)

Remark 2:

Note the variational principle can be used to prove that e.s. first order non-degenerate perturbation theory (including wave function correction & normalization) always will over-estimate or get exact the true ground state energy of perturbed Hamiltonian (never under-estimates it).

other useful systems for variational method

    Molecular Hydrogen Ion H_2^+
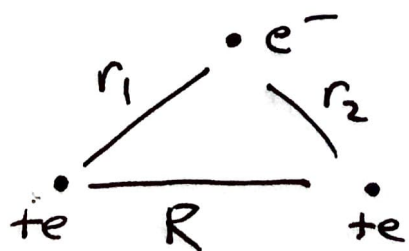
$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{R}$$

For electron, consider trial function
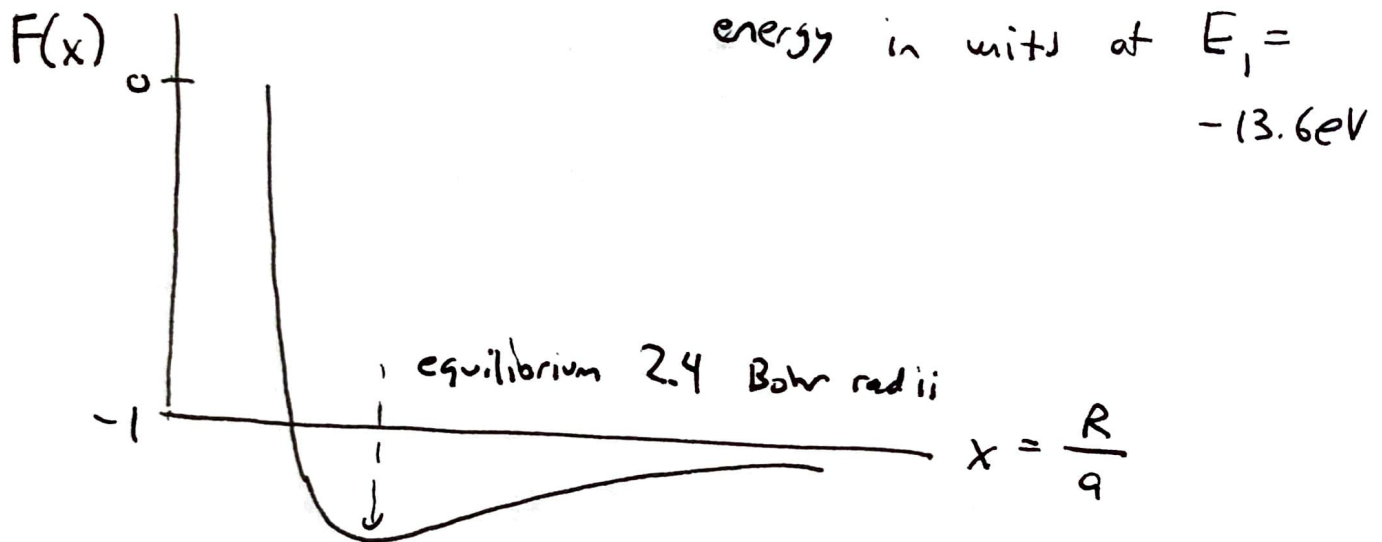$$\psi_g = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$
$$g.$$

Consider a trial wave-function

$$\psi = A \left[\psi_g(r_1) + \psi_g(r_2) \right]$$

Linear combination of atomic orbitals technique

Evaluate $\langle H \rangle$, find that bonding exists.

$F(x)$ energy in units of $E_1 =$

$-13.6 eV$

equilibrium 2.4 Bohr radii

$x = \dfrac{R}{a}$

Note if you choose a minus sign

$$\psi = A \left[\psi_g(r_1) - \psi_g(r_2) \right]$$

$\rightarrow$ no evidence of bonding!

doesn't prove since its only an upper bound, but suggestive.