

FY2045 Quantum Mechanics I

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Week 12

Variational method

Motivation and basic formulation

It is not always possible to separate a Hamiltonian H into a solvable part H_0 and a small perturbation, **making perturbation theory unsuitable**. In such cases the **variational method** can be very useful.

It is based on the following fact:

For **any** state $|\psi\rangle$, the ground state energy satisfies

$$E_0 \leq \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}.$$

The variational method can therefore be seen as an **optimization problem**.

Example — Harmonic Oscillator

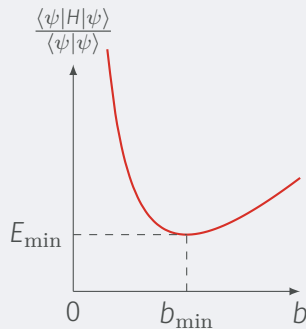
We want to find the ground state energy of the harmonic oscillator,

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

Choose a trial wavefunction with one or more free parameters, e.g. the Gaussian

$$\psi(x) = Ae^{-bx^2},$$

with $b > 0$, and minimize $\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$.



Excited states

In principle one can use the variational method also for excited states. If we have a set of energies

$$\{E_n\} = \{E_0, E_1, \dots\} \text{ with } E_{n+1} > E_n \forall n = 0, 1, \dots,$$

with corresponding ψ_n , then a test function ψ for ψ_N must fulfill

$$\langle \psi | \psi_n \rangle = 0 \forall n < N.$$

However, we often don't know the ψ_n 's exactly, leading to intrinsic errors.

Symmetry can help us choose orthogonal trial functions: If there exists a Hermitian operator A such that $[A, H] = 0$, two eigenstates of A are orthogonal if they have different eigenvalues.

Example — Helium atom

For a neutral atom of atomic number Z , with a nucleus with charge Ze and Z electrons with mass m_e and charge $-e$, we have the Hamiltonian

$$H = \sum_{j=1}^Z \left\{ -\frac{\hbar^2}{2m_e} \nabla_j^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_j} \right. \quad (\text{kinetic + el-nucl interaction}) \\ \left. + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{k \neq j} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_k|} \right\} \quad (\text{el-el interaction}).$$

We need to solve $H\psi = E\psi$ for wavefunction $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z)$, but can **only be solved exactly for hydrogen**, $Z = 1$. In practice one must use approximation methods. We will look at $Z = 2$, the helium atom

For $Z = 2$, we get

$$H = \left\{ -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_1} \right\} + \left\{ -\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_2} \right\} + \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$
$$\equiv H_1 + H_2 + H_{\text{el-el}},$$

with hydrogenic Hamiltonians H_i , $i = 1, 2$ with nuclear charge $2e$, and electron-electron repulsion term $H_{\text{el-el}}$.

If we ignore $H_{\text{el-el}}$:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{nlm}(\mathbf{r}_1) \psi_{n'l'm'}(\mathbf{r}_2),$$
$$E = 4(E_n + E_{n'}),$$

with hydrogen wavefunctions ψ_{nlm} with half the Bohr radius, and $E_n = -13.6/n^2$ eV.

Ground state

Using this approximation, we get

$$E_0 = -109 \text{ eV},$$

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2),$$

with electrons in the singlet state. This is lower than the experimental value

$$E_0^{\text{exp}} = -78.975 \text{ eV},$$

since we neglected the **positive** $H_{\text{el-el}}$.

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Using the variational method:

$$\begin{aligned} E_0 &\leq \langle \psi_0 | H | \psi_0 \rangle = 8E_1^{\text{hydr}} + \langle \psi_0 | H_{\text{el-el}} | \psi_0 \rangle \\ &\leq \left(8 - \frac{5}{2}\right) E_1^{\text{hydr}} = -74.8 \text{ eV}, \end{aligned}$$

which is much better!

Ground state

We can do even better by using the trial wavefunction

$$\phi(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z^3}{\pi a_0^3} e^{-Z(r_1+r_2)/a_0}.$$

and rewriting the Hamiltonian

$$H = -\frac{\hbar^2}{2m}[\nabla_1^2 + \nabla_2^2] - \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z}{r_1} + \frac{Z}{r_2} \right] + \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right],$$

resulting in

$$E_0 \leq \langle H \rangle(Z) = \left[-2Z^2 + \frac{27}{4}Z \right] E_1^{\text{hydr}}.$$

The minima is at $Z_{\min} = 1.69$: $\langle H \rangle_{\min} = -77.5 \text{ eV}$, only 2% off E_0^{exp} !

Excited states

For excited states, one electron is in $n = 1$, one is in $n > 1$,

$$\psi_{nlm}\psi_{100}.$$

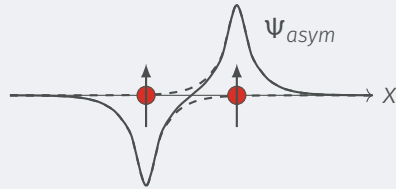
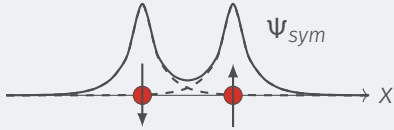
Total state must be antisymmetric:

Parahelium

$$\underbrace{[\psi_{nlm}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) + \psi_{nlm}(\mathbf{r}_2)\psi_{100}(\mathbf{r}_1)]}_{\text{symmetric}} \underbrace{[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle]}_{\text{singlet}}$$

Orthohelium

$$\underbrace{[\psi_{nlm}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) - \psi_{nlm}(\mathbf{r}_2)\psi_{100}(\mathbf{r}_1)]}_{\text{antisymmetric}} \underbrace{\left\{ \begin{array}{l} |\uparrow\uparrow\rangle \\ |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \\ |\downarrow\downarrow\rangle \end{array} \right\}}_{\text{triplet}}$$



The expectation value for the separation is smaller for the symmetric wavefunction.

Helium — Excited states

For excited states, one electron is in $n = 1$, one is in $n > 1$,

$$\psi_{nlm}\psi_{100}.$$

Total state must be antisymmetric:

Parahelium

$$\underbrace{[\psi_{nlm}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) + \psi_{nlm}(\mathbf{r}_2)\psi_{100}(\mathbf{r}_1)]}_{\text{symmetric}} \underbrace{[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle]}_{\text{singlet}}$$

Orthohelium

$$\underbrace{[\psi_{nlm}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) - \psi_{nlm}(\mathbf{r}_2)\psi_{100}(\mathbf{r}_1)]}_{\text{antisymmetric}} \left\{ \begin{array}{l} |\uparrow\uparrow\rangle \\ |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \\ |\downarrow\downarrow\rangle \end{array} \right\}$$

triplet

Interaction energy due to $H_{\text{el-el}}$ higher for parahelium, giving parahelium states slightly higher energies than orthohelium states with the same (nlm) .