Lecture 13.

II. Variational principle:

II.1 Prelude: Helium atom (perturbation theory)

By now we have got to know the atomic structure of the hydrogen atom pretty well.

(or hydrogen-like ions)

The next simplest atom is Helium:

(or Helium-like ions)

\[ \text{Nucleus: } 2 \text{ proton} + 2 \text{ neutron} \]

with \[ +2e \]

Two electrons orbit around the nucleus.
Ignoring the fine structure and smaller corrections, we can write the Hamiltonian for the system of 2 electrons as:

\[ H = -\frac{\hbar^2}{2m} \left( \nabla_1^2 + \nabla_2^2 \right) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|r_1 - r_2|} \]

\[ \uparrow \quad \text{Attractive Coulomb force due to nucleus} \]

\[ \uparrow \quad \text{repulsive Coulomb force between 2 electrons} \]

Note the sign before each term.
Want to find the ground state energy and eigenvalues.

\[ H \psi_{gs} = E_{gs} \psi_{gs} \]

It is not known how to solve this equation exactly.

Need to do approximations.

First attempt: (perturbation theory)

Write \[ H = H_0 + H' \]

with

\[ H_0 = -\frac{\hbar^2}{2m} \nabla^2 - \frac{2e^2}{r_1} - \frac{\hbar^2}{2m} \nabla^2 - \frac{2e^2}{r_2} \]

\[ H' = \frac{e^2}{|r_1 - r_2|} \]

\( H_0 \): exactly solvable, treat \( H' \) as perturbation.
Ho: two electrons decouple, the Hamiltonian for each of them is that of the Hydrogen atom except that the nucleus has now charge $2e$.

The eigen vectors and eigenvalues of $H_0$ are exactly known.

\[ H_{\text{hyd}} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{2e^2}{r} \]

\[ E_n = \frac{-Z^2 \hbar^2}{2m} \frac{1}{n^2} c^2 \quad (d = \frac{e^2}{\hbar c}) \]

\[ \psi_{100} = \frac{\sqrt{2^2}}{\pi^{1/2} \alpha_B^3} e^{-\frac{Z r}{\alpha_B}} \quad (\alpha_B = \frac{\hbar^2}{2mc e^2} = \frac{\hbar}{mc} \frac{1}{a_B}) \]

$Z = 1$ - hydrogen.

\[ r \to \Theta \]

\[ +2e \]

\[ \text{Bohr radius} \]
0-th order: (ignore $H'$, treating two electrons)

\[
H_0 = \psi^{(0)}_{gs} = E^{(0)}_{gs} \psi^{(0)}_{gs}
\]

\[
\psi^{(0)}_{gs} = \psi_{100} \left( Z=2, r_1 \right) \psi_{100} \left( Z=2, r_2 \right)
\]

\[
= \frac{8}{\pi a_b^2} e^{-\frac{2(r_1+r_2)}{a_b}}
\]

\[
E^{(0)}_{gs} = E_0 \left( Z=2, r_1 \right) + E_0 \left( Z=2, r_2 \right)
\]

\[
= -\frac{2\hbar^2}{2m} + \frac{Z^2}{2}\left( \frac{1}{r_1} + \frac{1}{r_2} \right)
\]

\[
= -8 \cdot 13.6 \text{ (eV)}
\]

\[
= -109 \text{ eV}
\]
How good is the approximation of completely ignoring the Coulomb force between 2 electrons?

Exp value: \( E_{gs} = -78.975 \text{ eV} \)

\( E_{gs}^{(0)} \) is off by 38%.

\( \geq 1 \) Coulomb interaction between electrons is important.

Note: Coulomb energy between electrons is positive.
1st order:

\[
E_{2s}^{\text{2s}} = \langle \psi_{2s}^{\text{2s}} | H' | \psi_{2s}^{\text{2s}} \rangle > 0
\]

\[
= \frac{e^2}{4\pi\alpha^2} \int d^3r \int d^3r' \frac{2}{r - r'} - \frac{4}{a} (n + r_2)
\]

\[
= e^2 \int d^3r_1 \int d^3r_2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} |\psi_{100}(z=2, r_1)|^2 |\psi_{100}(z=2, r_2)|^2
\]

\[
= \epsilon^{xy} I(z=2)
\]

\[
I(z) = \frac{e^2}{4\pi\alpha^2} \int d^3r \int d^3r' \frac{e^{-\frac{2z}{a\beta}(r + r')}}{|\mathbf{r} - \mathbf{r}'|}
\]

\[
= \frac{5z e^2}{8a\beta} \quad \text{(doable, but tedious see Griffiths)}
\]

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plugging numbers:  \( \left( \frac{e^2}{2a_B} = 13.6 \text{ eV} \right) \)

\[ E_{gs''} = 34 \text{ eV} \]

\[ E_{gs} \approx E_{gs''} + E_{gs'''} \]

\[ = -75 \text{ eV} \]

New Nano only off 5%.

\[ \psi_{gs''} = \sum_{m+gs} \frac{\langle \psi_{m'} | H | \psi_{gs} \rangle}{E_{gs''} - E_{m'}} \left| \psi_{m'} \right> \]

\[ \left| \psi_{m'} \right> \text{: wave functions of higher levels for } H_0 \]

\[ E_{m'} \text{: eigenvalues } \ldots \ldots \text{ for } H_0. \]

Infinite sum, very complicated.
Variational principle

The variational principle is based on the following simple observation:

**Theorem.** The ground state energy $E_g$ for a system described by the Hamiltonian $H$ satisfies

$$E_g \leq \langle \psi | H | \psi \rangle = E I \psi J$$

for any normalized function $\psi$.

**Note:**

1) obviously true if $\chi$ is an energy eigenstate.

2) More generally, it says that the energy expectation value in any state $\psi$ is no smaller than the ground state energy. (Intuitively reasonable)
Proof: Expand $\Psi$ in terms of energy eigenstates of $H$.

$$\Psi = \sum_n C_n \phi_n, \quad H \Psi_n = E_n \Psi_n$$

Since $\langle \Psi \rangle$ is normalized,

$$\langle \Psi | \Psi \rangle = \langle \sum_n C_n \phi_n | \sum_n C_n \phi_n \rangle = \sum_n |C_n|^2 = 1$$

$$\langle \Psi | H | \Psi \rangle = \sum_{m,n} C_m^* C_n \langle \phi_m | H | \phi_n \rangle = \sum_{m,n} C_m^* C_n E_n \delta_{mn}$$

$$= \sum_m |C_m|^2 E_m \quad \text{(since } E_n \geq E_m \text{)}$$

$$\geq \sum_n |C_n|^2 E_n \geq \sum_n E_n \geq E_{\Psi} \quad QED$$
How do we use this observation?

Strategy: make an educated guess $|\psi\rangle$ (trial wave function).

Then $E[|\psi\rangle] = \langle \psi | H | \psi \rangle$ provides an upper bound $E_{\text{gs}}$.

Perturbation theory: mechanical.

Variational method: art (requires physical insights to choose a good trial wave function).
In practice:

Choose a family of wave functions

\[ \psi(x; \lambda_1, \ldots, \lambda_k) \]

which can depend on a number of parameters:

\[ \lambda_1, \ldots, \lambda_k. \]

Evaluate

\[ \mathcal{E}(\lambda_1, \ldots, \lambda_k) = \langle \psi | H | \psi \rangle \]

Minimize:

\[ \mathcal{E}(\lambda_1, \ldots, \lambda_k) \] with respect to \( \lambda_1, \ldots, \lambda_k. \)

i.e.

\[ \frac{\partial \mathcal{E}}{\partial \lambda_1} = \frac{\partial \mathcal{E}}{\partial \lambda_2} = \ldots = \frac{\partial \mathcal{E}}{\partial \lambda_k} = 0 \]

\[ \mathcal{E}(\lambda^*_1, \ldots, \lambda^*_k) \]

\[ \Rightarrow \] best wave function within the family.
Remark: new light on perturbation theory.

\[ E gs = E gs^{(0)} + \langle \Psi gs^{(0)} | H' | \Psi gs^{(0)} \rangle + \cdots \]

\[ = \langle \Psi gs^{(0)} | H_0 + H' | \Psi gs^{(0)} \rangle + \cdots \]

\[ = \langle \Psi gs^{(0)} | H | \Psi gs^{(0)} \rangle + \cdots \]

\[ \Rightarrow \]

(a): 1st order perturbation theory for \( E gs^{(0)} \)

\( E gs^{(0)} \) is in fact also a variational approximation with a trial wave function \( \Psi gs^{(0)} \).

(b): Since \( \langle \Psi gs^{(0)} | H | \Psi gs^{(0)} \rangle \geq E gs \), all higher order corrections must be non-positive.
14.3 Helium atom: Variational Method

Earlier: \[ E_g = E_{g''} + E_{g''} \]

using 1st order perturbation theory.

New understanding: Equivalent to variational approximation

using trial function

\[ \psi = \psi_{100}(Z=2, r_1) \psi_{100}(Z=2, r_2) \]

Can we find a better trial function?
An idea:

From the point of view of one electron, the presence of the cloud of the other electron partially screens the nucleus. This suggests the following strategy:

1) Take: trial wave function

\[ \psi(r_1, r_2) = \psi_{100}(z_1, r_1) \psi_{100}(z_2, r_2) \]

with \( z \) a free parameter.
Compute $E(2)$:

A trick:

We write:

$$H = -\frac{\hbar^2}{2m} (\frac{1}{r_1} + \frac{1}{r_2}) - e^2 \left( \frac{2}{r_1} + \frac{2}{r_2} \right)$$

$$+ e^2 \left( \frac{2-2}{r_1} + \frac{2-2}{r_2} + \frac{1}{|r_1 - r_2|} \right)$$

$$\left. - E(2) = \right| \langle \psi | H | \psi \rangle = -2z^2 (13.6 \text{ eV}) + 2(2-2) \left< \frac{e^2}{r} \right>_2$$

$$+ \theta e^2 \left< \frac{1}{|r_1 - r_2|} \right>_2$$

Note:

$$\left< \frac{1}{r} \right>_{z=1} = \frac{1}{a}$$

$$\left< \frac{1}{r} \right>_2 = \frac{2}{a}$$

$$e^2 \left< \frac{1}{|r_1 - r_2|} \right>_2 = \Theta I(2) = \frac{52 e^2}{8a} = \frac{5}{2} \cdot 2 \cdot (13.6 \text{ eV})$$

(from eq. (1))
\[ E(x) = -2z^2 \left( 13.6 \right) + \frac{2z}{z-2} \frac{e^2}{a} \]

\[ + \frac{5}{4} z \left( 13.6 \right) \]

**Note:** \( \frac{e^2}{2a} = 0 \text{.3} \text{.6 eV} \)

\[ \Rightarrow \]

\[ \frac{E(x)}{13.6} = -2z^2 + 4 \frac{e^2}{a} (z-2) + \frac{5}{4} z \]

\[ = 2z^2 - \frac{27}{4} z \]

\[ \Rightarrow \text{4z} - \frac{27}{4} = 0 \]

\[ \Rightarrow z = \frac{27}{16} \]
\[ \frac{dE}{d^2} = 0 \]

\[ Z_\infty = \frac{2}{3} - \frac{5}{16} = 1.69 \]

\[ \text{Difference from Exp value: } 1.89\% \]

In 1959, pekeris constructed a 1075 parameter trial wave function, and got E\(_\infty\) agreed with exp to one part in 20 million!

See Bethe + Jackiw.
2.4 Excited states:

Can we use variational method to find the energy of excited states?

Corollary: If \( \langle \psi | \psi_{gs} \rangle = 0 \)

Then \( \langle \psi | H | \psi \rangle \geq E_{fe} \)

\( E_{fe} \) is the energy of first excited state.

Of course, we often do not know \( (\psi_{gs}) \) exactly.

1. Find best trial \( (\psi_{gs}) \), take

\( \text{let } \langle \psi | \psi_{gs} \rangle = 0 \)
2. When there is some symmetry,

\[ \text{e.g. if } \Psi(\mathbf{x}) \text{ is even in } \mathbf{x} \]

then choose \( \psi \) \( \text{odd} \).

\[ \Rightarrow \quad \langle \psi | \Psi \rangle = 0 \]