

Lecture 22

(Last time ...)

Today apply variational principle to a typical "real" problem: estimate ground state energy of He

Talked about He before, recall problem 5.11

Hamiltonian

$$H = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right)$$

Experimentally, $E_{gs} = -78.975 \text{ eV}$

Neglecting $\frac{1}{|\vec{r}_1 - \vec{r}_2|}$ term, we can solve just like hydrogen:

$$\psi(r_1, r_2) = \psi_{100}(\vec{r}_1) \psi_{100}(\vec{r}_2) \times \text{spin singlet}$$

with $E = 8E_1 = -109 \text{ eV}$

If we treat interaction term with first order PT, we found -75 eV

- Already did in problem, I won't go through it again

Note, variational theorem applies here too:

$\psi_{100}(r_1) \psi_{100}(r_2)$ is our trial wave function,

First order PT gives $\langle \psi | H | \psi \rangle > E_{gs}$, as theorem demands

But here no variational parameters, not really the variational technique.

What's a better trial wavefunction?

Electrons repel each other
Partially counteracts attraction between
electron & nucleus

But electrons are in s state -
- costs a lot of energy to, say, localize electrons
on opposite sides of nucleus
- more or less keep spherical symmetry

Then one electron "sees" net charge of nucleus
& other electron ~ centered at origin
Acts like nuclear charge is reduced
effect called "screening" ... very important
in many systems

Account for this by allowing effective nuclear
charge Z to vary.

For arbitrary Z , hydrogenic wavefunction is

$$\frac{Z^{3/2}}{\sqrt{\pi a^3}} e^{-Zr/a}$$

Note
a) $9/12$

So try $\psi(r_1, r_2) = \frac{Z^3}{\pi a^3} e^{-Z(r_1 + r_2)/a}$

To evaluate $\langle H \rangle$, write

$$H = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right) \quad \left. \vphantom{H} \right\} \text{Hydrogenic atoms with charge } Z$$
$$+ \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{|r_1 - r_2|} \right] \quad \left. \vphantom{H} \right\} \text{the rest}$$

Our ψ is eigenstate of the hydrogenic part,
with energy $2Z^2 E_1$

↑
two
atoms

So we get

$$\langle H \rangle = 2Z^2 E_1 + \underbrace{2(Z-2) \left(\frac{e^2}{4\pi\epsilon_0} \right)}_{\substack{\text{Note symmetry} \\ \text{between } r_1 \text{ and } r_2}} \left\langle \frac{1}{r} \right\rangle + \frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{|r_1 - r_2|} \right\rangle$$

We got a formula for $\left\langle \frac{1}{r} \right\rangle$ in last chapter,
for fine structure calc.

$$\text{Here } n=1 \text{ and } \left\langle \frac{1}{r} \right\rangle = \frac{Z}{a} = \left(\frac{Z}{n^2 a} \text{ generally} \right)$$

Before, we worked out $\left\langle \frac{1}{|r_1 - r_2|} \right\rangle$ for hydrogenic
states,

$$\text{got } \frac{5}{4a}, \text{ for } Z=2$$

Note that when Z changes, you effectively
just change $a \rightarrow a/Z$

$$\text{So for arb } Z, \text{ we get } \frac{5}{4a} \times \frac{Z}{2}$$

Then

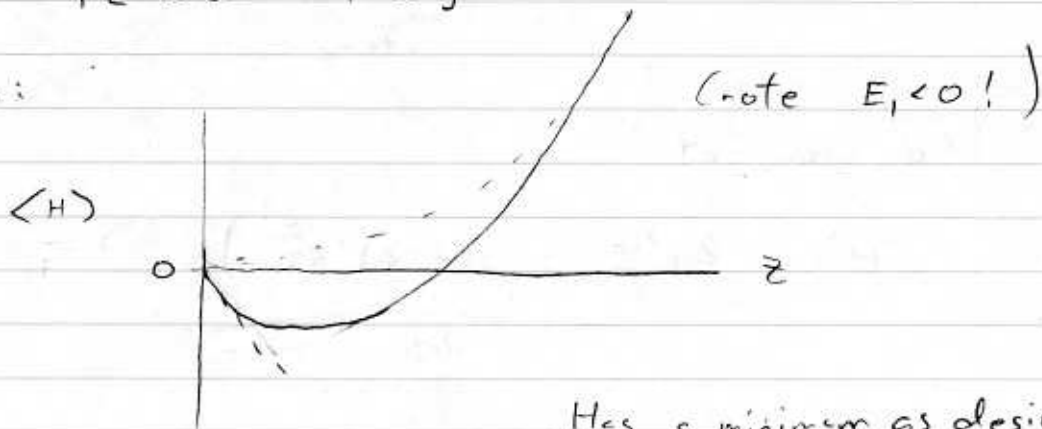
$$\langle H \rangle = 2Z^2 E_1 + 2(Z-2) \frac{e^2}{4\pi\epsilon_0} \frac{Z}{a} + \frac{e^2}{4\pi\epsilon_0} \frac{5Z}{8a}$$

$$\text{But recall } E_1 = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{2a}$$

$$\langle H \rangle = E_1 \left[2z^3 - 4z(z-2) - \frac{5}{4}z \right]$$

$$= E_1 \left[-2z^2 + \frac{27}{4}z \right]$$

Sketch:



$$\frac{\partial \langle H \rangle}{\partial z} = E_1 \left(-4z + \frac{27}{4} \right) = 0$$

$$z = \frac{27}{16} = 1.69 < 2, \text{ as we expected}$$

Plug back in, get

$$\langle H \rangle = E_1 \frac{3^6}{2^7} = -77.5 \text{ eV}$$

Recall experiment:	-79 eV	
PT result:	-75 eV	15% error
Variational:	-77.5 eV	12% error

Problem 7.18 gives a trial wavefunction with two parameters. Quite a bit more tedious:
3 pages in Griffiths solutions.