Exam: Mean = 27
15 or lower = not so good

Lecture 21

Last time, introduced variational principle
= way to estimate ground state of a system

- Make up ψ that seems reasonable
  depends on parameter(s) b
- Calculate $\langle\psi|H|\psi\rangle$ as fcn of b
- Choose b to minimize: $\frac{d}{db}\langle H\rangle = 0$

Today apply to "real" problem: He atom

We've discussed He before, Ch 5

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, $\boxed{E_{gs} = -78.975\,eV}$

Would like to calculate, but can't solve exactly.
Consider various approximation methods:

Simplest: Neglect $\frac{1}{|\vec{r}_1 - \vec{r}_2|}$ term

Then He looks like two hydrogenic atoms with $Z = 2$

Ground state $\psi_0(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2)\,|s=0, m=0\rangle$

Energy $E = \underbrace{2}_{\text{two electrons}} \times \underbrace{(4E_1)}_{\text{energy} \propto Z^2} = -109\,eV$

Perturbation theory: Treat $\frac{1}{|\vec{r}_1-\vec{r}_2|}$ as perturbation

First order, evaluate

$$\Delta E = \frac{e^2}{4\pi\varepsilon_0}\left\langle \Psi_0(\vec{r}_1,\vec{r}_2) \middle| \frac{1}{|\vec{r}_1-\vec{r}_2|} \middle| \Psi_0(\vec{r}_1,\vec{r}_2) \right\rangle$$

You did this in HW 5.11

Get $\Delta E = \frac{e^2}{4\pi\varepsilon_0} \cdot \frac{5}{4a} = 34\,eV$ (not really small)

Total energy $= -109+34 = \underline{-75\,eV}$ ... closer

Variational method

Note 1st order PT is same thing as variational method using trial wave func $= \Psi_0$, with no parameters

Know that $\langle \Psi_0 | H | \Psi_0 \rangle \geq E_{gs}$, which we got

Do better by including a parameter to vary

What to use? See that Ψ_0 does reasonably well
Start with that

Note electrons repel each other
Partially counteracts attraction between electron & nucleus

Simple way to model: try reducing nuclear charge Z
$\Rightarrow$ make Z a variational parameter

Recall for arb Z, hydrogenic wave func is

$$\frac{Z^{3/2}}{\sqrt{\pi a^3}} e^{-Zr_1/a} \qquad \left(\text{remember as } a \to \frac{a}{Z}\right)$$

So try $\psi(r_1, r_2) = \frac{Z^3}{\pi a^2} e^{-Z(r_1+r_2)/a}$

Steps:

1) Check ψ is normalized ✓

2) Evaluate $\langle\psi|H|\psi\rangle$

Write $H = H_1 + H_2$

$$H_1 = \frac{p_1^2 + p_2^2}{2m} - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right) \quad \text{hydrogenic}$$

$$\langle\psi_0|H_1|\psi_0\rangle = 2Z^2E_1$$

$$H_2 = \frac{e^2}{4\pi\varepsilon_0}\left[\frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{|r_1 - r_2|}\right] \quad \text{what's left}$$

Need $\langle H_2 \rangle$

Know $\left\langle \frac{1}{r_1} \right\rangle = \left\langle \frac{1}{r_2} \right\rangle$ by symmetry

For hydrogen $\left\langle \frac{1}{r} \right\rangle = \frac{1}{a} \to \frac{Z}{a}$

and in $\left\langle \frac{1}{|r_1 - r_2|} \right\rangle$, have $\frac{5}{4a}$ for $Z = 2$

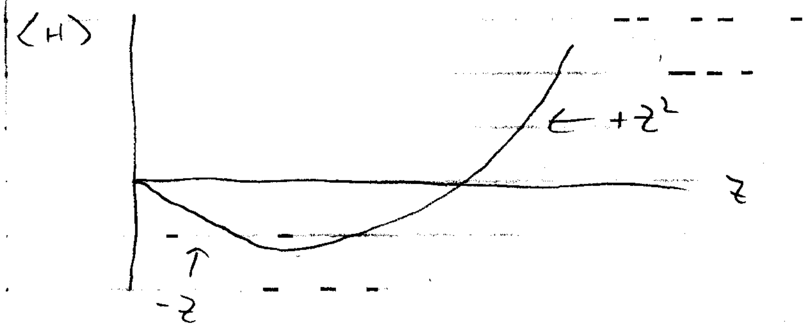
$$\to \frac{5}{4a} \times \frac{Z}{2} \quad \text{for arb } Z$$

So total $\langle H \rangle = 2Z^2E_1 + 2(Z-2)\frac{e^2}{4\pi\varepsilon_0}\frac{Z}{a} + \frac{e^2}{4\pi\varepsilon_0}\frac{5Z}{8a}$

$\frac{e^2}{4\pi\varepsilon_0} = -2E_1 a \quad \Rightarrow \quad \langle H \rangle = E_1\left[2Z^2 - 4(Z-2) - \frac{5}{4}Z\right]$

$$\langle H \rangle = E_1 \left(-2Z^2 + \frac{27}{4} Z\right)$$

Sketch $(E_1 < 0)$



Step 3: $$\frac{d\langle H \rangle}{dZ} = 0 = E_1 \left(-4Z + \frac{27}{4}\right)$$

$$Z = \frac{27}{16} = 1.69$$

< 2 as expected

Plug back in, get $\langle H \rangle = E_1 \frac{3^6}{2^7} = -77.5\,eV$

So we have

Experiment:	-79 eV	
Hydrogenic approx:	-109 eV	30% error
Perturbation theory:	-75 eV	5% error
Variational theory:	-77.5 eV	2% error

If we want to do even better, use more parameters, Sketch out problem 7.18

Idea: don't put electrons in same state
Imagine one electron close to nucleus, see effective charge Z_1
Other further away, sees charge Z_2

Still need to satisfy exchange:

$$\psi(r_1, r_2) = A\left[\psi_1(r_1)\psi_2(r_2) + \psi_2(r_1)\psi_1(r_2)\right] |S=0, m=0\rangle$$

$$\psi_1 = \frac{Z_1^{3/2}}{\sqrt{\pi a^3}} e^{-Z_1 r/a}$$

$$\psi_2 = \frac{Z_2^{3/2}}{\sqrt{\pi a^3}} e^{-Z_2 r/a}$$

vary Z_1 & Z_2

Much harder to work out

1) Normalization hard since $\langle \psi_1 | \psi_2 \rangle \neq 0$

Need to evaluate integral directly

2) To evaluate $\langle H \rangle$, use similar tricks to avoid evaluating ∇^2's but still have to do several spatial integrals

3) Get answer that is very complicated func of Z_1 & Z_2

Can't solve $\frac{\partial \langle H \rangle}{\partial Z_1} = 0$ and $\frac{\partial \langle H \rangle}{\partial Z_2} = 0$ equations analytically, need computer

Find $Z_1 = 2.18$ $Z_2 = 1.18$, makes some sense

Gives $\langle H \rangle = -78.2\,eV$, 1% error

Results improve slowly with complexity of calculation

- One-parameter calc is also useful for other system

Cyrus will present prob 7.7