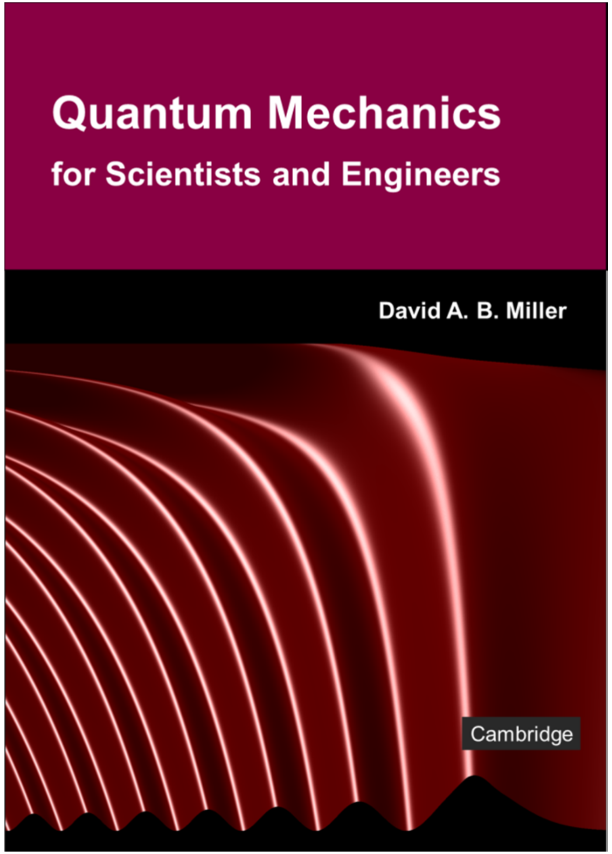
7.3 The hydrogen atom

Slides: Video 7.3.5 Informal solutions for the relative motion

Text reference: Quantum Mechanics for Scientists and Engineers

Section 10.3 (“Bohr radius and Rydberg energy”)



The hydrogen atom

Informal solution for the relative motion

Quantum mechanics for scientists and engineers

David Miller

Bohr radius and Rydberg energy

We presume that the hydrogen atom will have some characteristic size

which is called the Bohr radius a_o

We expect that the "average" potential energy

strictly, its expectation value

will therefore be

$$\langle E_{potential} \rangle \approx -\frac{e^2}{4\pi\varepsilon_o a_o}$$

Bohr radius and Rydberg energy

For a reasonable smooth wavefunction $\psi(\mathbf{r})$ of size $\sim a_o$

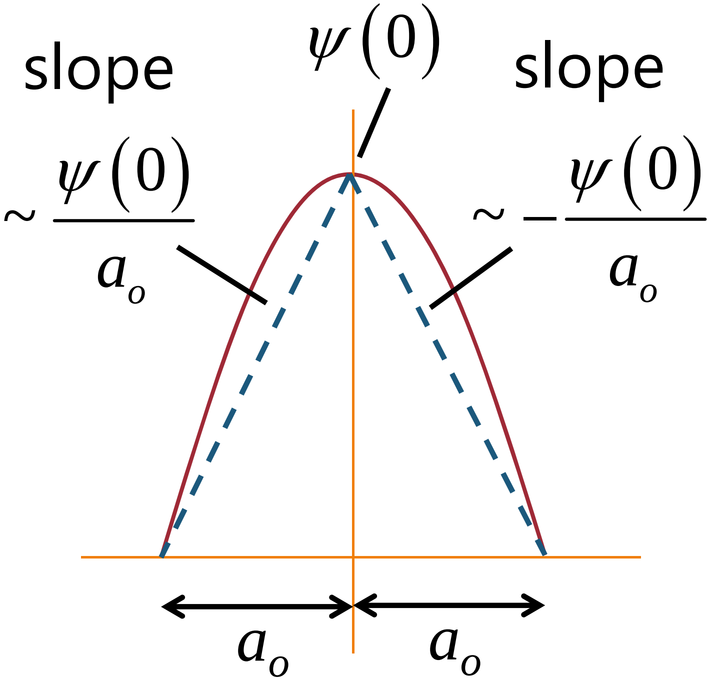
the second spatial derivative will be

$$\sim \frac{\left[-\psi(0)/a_o\right]-\left[\psi(0)/a_o\right]}{2a_o}$$

$$\sim -\psi(0)/a_o^2$$

Note this is only meant to a rough estimate

only within some moderate factor



Bohr radius and Rydberg energy

Remembering that for a mass μ

the kinetic energy operator is $-\left(\hbar^2 / 2\mu\right)\nabla^2$

The "average" kinetic energy will therefore be

$$\left\langle E_{kinetic} \right\rangle \approx \frac{\hbar^2}{2\mu a_o^2}$$

Now, in the spirit of a "variational" calculation

we adjust the parameter a_o to get the lowest value of the total energy

Such variational approaches can be justified rigorously as approximations for the lowest energy

Bohr radius and Rydberg energy

With our very simple model, the total energy is

$$\left\langle E_{total} \right\rangle = \left\langle E_{kinetic} \right\rangle + \left\langle E_{potential} \right\rangle \approx \frac{\hbar^2}{2\mu a_o^2} - \frac{e^2}{4\pi\varepsilon_o a_o}$$

The total energy is a balance between

- the potential energy
  - which is made lower (more negative) by choosing a_o smaller
- and the kinetic energy
  - which is made lower (less positive) by making a_o larger

Bohr radius and Rydberg energy

For this simple model

$$\langle E_{total} \rangle = \langle E_{kinetic} \rangle + \langle E_{potential} \rangle \approx \frac{\hbar^2}{2\mu a_o^2} - \frac{e^2}{4\pi\varepsilon_o a_o}$$

differentiation shows that the choice of a_o that minimizes the energy overall is

$$\boxed{a_o = \frac{4\pi\varepsilon_o \hbar^2}{e^2 \mu} \simeq 0.529\ \text{Å} = 5.29\ x\ 10^{-11}\text{m}}$$

which is the standard definition of the Bohr radius

We therefore see that the hydrogen atom is approximately 1 Å in diameter

Bohr radius and Rydberg energy

With this choice of a_o

the corresponding total energy of the state is

$$\langle E_{total} \rangle = -\frac{\hbar^2}{2\mu a_o^2} = -\frac{\mu}{2}\left(\frac{e^2}{4\pi\varepsilon_o \hbar}\right)^2$$

We can usefully define the "Rydberg" energy unit

$$\boxed{Ry = \frac{\hbar^2}{2\mu a_o^2} = \frac{\mu}{2}\left(\frac{e^2}{4\pi\varepsilon_o \hbar}\right)^2 \simeq 13.6 \text{ eV}}$$

in which case $\langle E_{total} \rangle = -Ry$

Bohr radius and Rydberg energy

Though we have produced

the Bohr radius

$$a_o = \frac{4\pi\varepsilon_o \hbar^2}{e^2 \mu} \simeq 0.529 \ \mathring{A} = 5.29 \ x \ 10^{-11} \text{m}$$

and the Rydberg

$$Ry = \frac{\hbar^2}{2\mu a_o^2} = \frac{\mu}{2}\left(\frac{e^2}{4\pi\varepsilon_o \hbar}\right)^2 \simeq 13.6 \text{ eV}$$

by informal arguments

they will turn out to be rigorously meaningful

The energy of the lowest hydrogen atom state is -*Ry*