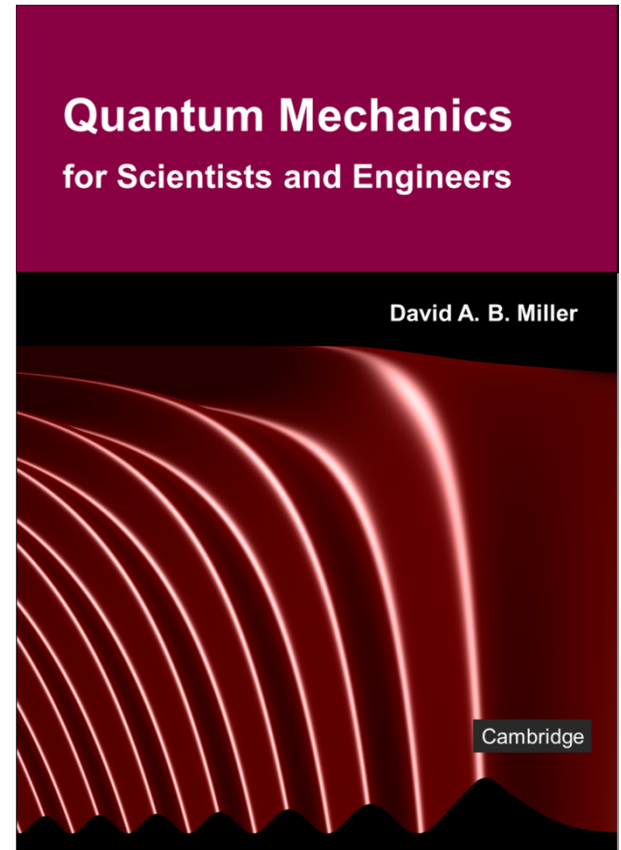


## 7.3 The hydrogen atom

Slides: Video 7.3.1 Multiple particle wavefunctions

Text reference: Quantum Mechanics  
for Scientists and Engineers

Chapter 10 introduction and  
Section 10.1





# The hydrogen atom



Multiple particle wavefunctions

Quantum mechanics for scientists and engineers

David Miller

# Multiple particle systems

How should we tackle this problem of two particles, electron and proton?

We start by generalizing the Schrödinger equation  
writing generally for time-independent problems

$$\hat{H}\psi = E\psi$$

where now we mean that

the Hamiltonian  $\hat{H}$  is the operator  
representing the energy of the entire system  
and  $\psi$  is the wavefunction representing the  
state of the entire system

# Multiple particle wavefunctions

For the hydrogen atom

there are two particles

the electron and the proton

Each of these has a set of coordinates associated with it

$x_e, y_e$  and  $z_e$  for the electron and

$x_p, y_p$  and  $z_p$  for the proton

The wavefunction will therefore in general be  
a function of all six of these coordinates



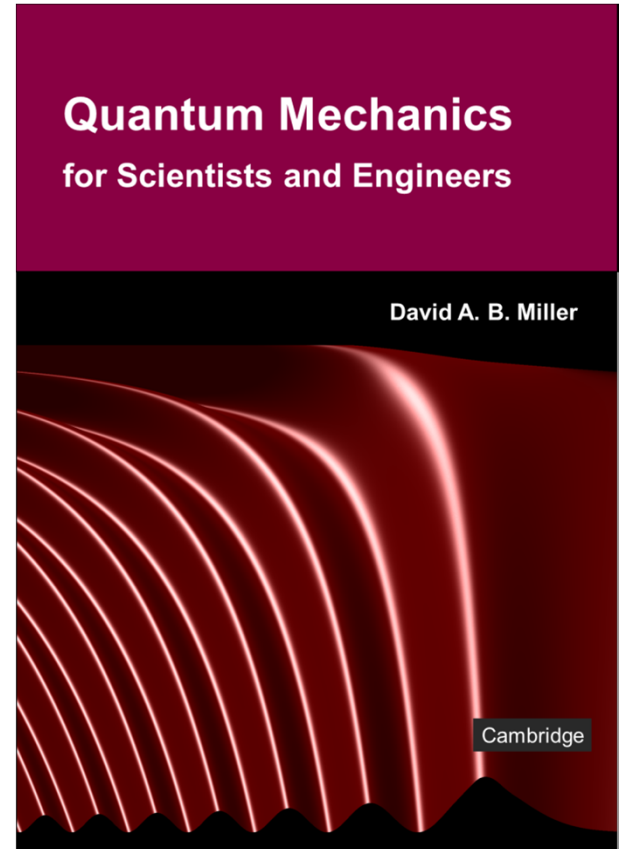


## 7.3 The hydrogen atom

Slides: Video 7.3.3 Solving the hydrogen atom problem

Text reference: Quantum Mechanics for Scientists and Engineers

Sections 10.2 – 10.3 (up to “Bohr radius and Rydberg energy”)







# The hydrogen atom



Solving the hydrogen atom problem

Quantum mechanics for scientists and engineers

David Miller

# Hamiltonian for the hydrogen atom

The electron and proton each have a mass

$m_e$  and  $m_p$  respectively

We expect

kinetic energy operators

associated with each of these masses

potential energy

from the electrostatic attraction of  
electron and proton



# Hamiltonian for the hydrogen atom

Hence, the Hamiltonian becomes

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_p} \nabla_p^2 + V(|\mathbf{r}_e - \mathbf{r}_p|)$$

where we mean  $\nabla_e^2 \equiv \frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2}$

and similarly for  $\nabla_p^2$

and  $\mathbf{r}_e = x_e \mathbf{i} + y_e \mathbf{j} + z_e \mathbf{k}$

is the position vector of the electron coordinates

and similarly for  $\mathbf{r}_p$

# Hamiltonian for the hydrogen atom

The Coulomb potential energy  $V(|\mathbf{r}_e - \mathbf{r}_p|) = -\frac{e^2}{4\pi\epsilon_o |\mathbf{r}_e - \mathbf{r}_p|}$   
depends on the distance  
 $|\mathbf{r}_e - \mathbf{r}_h|$  between the electron and proton coordinates  
which is important in simplifying the solution

The Schrödinger equation can now be written explicitly

$$\left[ -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_p} \nabla_p^2 + V(|\mathbf{r}_e - \mathbf{r}_p|) \right] \psi(x_e, y_e, z_e, x_p, y_p, z_p) \\ = E\psi(x_e, y_e, z_e, x_p, y_p, z_p)$$

# Center of mass coordinates

The potential here is only a function of  $|\mathbf{r}_e - \mathbf{r}_p|$   
the separation of the electron and proton

We could choose a new set of six coordinates  
in which three are the relative positions

$$x = x_e - x_p \quad y = y_e - y_p \quad z = z_e - z_p$$

i.e., a relative position vector  $\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$

from which we obtain

$$r = \sqrt{x^2 + y^2 + z^2} = |\mathbf{r}_e - \mathbf{r}_p|$$

What should we choose for the other three coordinates?



# Center of mass coordinates

The position  $\mathbf{R}$  of the center of mass of two masses is the same as

the balance point of a light-weight beam  
with the two masses at opposite ends

and so is

the weighted average of the positions  
of the two individual masses

$$\mathbf{R} = \frac{m_e \mathbf{r}_e + m_p \mathbf{r}_p}{M}$$

where  $M$  is the total mass  $M = m_e + m_p$

# Center of mass coordinates

Now we construct the differential operators we need

in terms of these coordinates

With

$$\mathbf{R} = X\mathbf{i} + Y\mathbf{j} + Z\mathbf{k}$$

then for the new coordinates in the  $x$  direction  
we have

$$X = \frac{m_e x_e + m_p x_p}{M} \quad x = x_e - x_p$$

and similarly for the  $y$  and  $z$  directions

# Center of mass coordinates

Using the standard method of changing partial derivatives to new coordinates

and fully notating the variables held constant  
the first derivatives in the  $x$  direction become

$$\left. \frac{\partial}{\partial x_e} \right|_{x_p} = \left. \frac{\partial X}{\partial x_e} \right|_{x_p} \left. \frac{\partial}{\partial X} \right|_x + \left. \frac{\partial x}{\partial x_e} \right|_{x_p} \left. \frac{\partial}{\partial x} \right|_X = \frac{m_e}{M} \left. \frac{\partial}{\partial X} \right|_x + \left. \frac{\partial}{\partial x} \right|_X$$

and similarly

$$\left. \frac{\partial}{\partial x_p} \right|_{x_e} = \left. \frac{\partial X}{\partial x_p} \right|_{x_e} \left. \frac{\partial}{\partial X} \right|_x + \left. \frac{\partial x}{\partial x_p} \right|_{x_e} \left. \frac{\partial}{\partial x} \right|_X = \frac{m_p}{M} \left. \frac{\partial}{\partial X} \right|_x - \left. \frac{\partial}{\partial x} \right|_X$$



# Center of mass coordinates

The second derivatives become

$$\begin{aligned}\frac{\partial^2}{\partial x_e^2} \Big|_{x_p} &= \frac{\partial}{\partial x_e} \Big|_{x_p} \left( \frac{\partial}{\partial x_e} \Big|_{x_p} \right) = \frac{m_e}{M} \frac{\partial}{\partial x_e} \Big|_{x_p} \frac{\partial}{\partial X} \Big|_x + \frac{\partial}{\partial x_e} \Big|_{x_p} \frac{\partial}{\partial x} \Big|_X \\ &= \left( \frac{m_e}{M} \right)^2 \frac{\partial^2}{\partial X^2} \Big|_x + \frac{\partial^2}{\partial x^2} \Big|_X + \frac{m_e}{M} \left( \frac{\partial}{\partial x} \Big|_X \frac{\partial}{\partial X} \Big|_x + \frac{\partial}{\partial X} \Big|_x \frac{\partial}{\partial x} \Big|_X \right)\end{aligned}$$

and similarly

$$\frac{\partial^2}{\partial x_p^2} \Big|_{x_e} = \left( \frac{m_p}{M} \right)^2 \frac{\partial^2}{\partial X^2} \Big|_x + \frac{\partial^2}{\partial x^2} \Big|_X - \frac{m_p}{M} \left( \frac{\partial}{\partial x} \Big|_X \frac{\partial}{\partial X} \Big|_x + \frac{\partial}{\partial X} \Big|_x \frac{\partial}{\partial x} \Big|_X \right)$$

# Center of mass coordinates

So

dropping the explicit statement of variables held constant

$$\begin{aligned}\frac{1}{m_e} \frac{\partial^2}{\partial x_e^2} + \frac{1}{m_p} \frac{\partial^2}{\partial x_p^2} &= \frac{m_e + m_h}{M^2} \frac{\partial^2}{\partial X^2} + \left( \frac{1}{m_e} + \frac{1}{m_p} \right) \frac{\partial^2}{\partial x^2} \\ &= \frac{1}{M} \frac{\partial^2}{\partial X^2} + \frac{1}{\mu} \frac{\partial^2}{\partial x^2}\end{aligned}$$

where  $\mu$  is the so-called reduced mass  $\mu = \frac{m_e m_p}{m_e + m_p}$

# Center of mass coordinates

The same kinds of relations can be written for each of the other Cartesian directions

so if we define

$$\nabla_{\mathbf{R}}^2 \equiv \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \quad \text{and} \quad \nabla_{\mathbf{r}}^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

we can write the Hamiltonian in a new form  
with center of mass coordinates

$$\hat{H} = -\frac{\hbar^2}{2M} \nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2\mu} \nabla_{\mathbf{r}}^2 + V(\mathbf{r})$$

which now allows us to separate the problem



# Center of mass coordinates

To separate the six-dimensional differential equation  
using these coordinates

next, presume the wavefunction can be written

$$\psi(\mathbf{R}, \mathbf{r}) = S(\mathbf{R})U(\mathbf{r})$$

Substituting this form in the Schrödinger equation with

the Hamiltonian  $\hat{H} = -\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + V(\mathbf{r})$   
we obtain

$$-U(\mathbf{r})\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 S(\mathbf{R}) + S(\mathbf{R})\left[-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + V(\mathbf{r})\right]U(\mathbf{r}) = ES(\mathbf{R})U(\mathbf{r})$$

# Center of mass coordinates

With

$$-U(\mathbf{r})\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 S(\mathbf{R}) + S(\mathbf{R})\left[-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + V(\mathbf{r})\right]U(\mathbf{r}) = ES(\mathbf{R})U(\mathbf{r})$$

then dividing by  $S(\mathbf{R})U(\mathbf{r})$  and moving some terms

$$-\frac{1}{S(\mathbf{R})}\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 S(\mathbf{R}) = E - \frac{1}{U(\mathbf{r})}\left[-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + V(\mathbf{r})\right]U(\mathbf{r}) = E_{CoM}$$

The left hand side depends only on  $\mathbf{R}$

and the right hand side depends only on  $\mathbf{r}$

so both must equal a “separation” constant

which we call  $E_{CoM}$

# Center of mass coordinates

Hence we have two separated equations

$$-\frac{\hbar^2}{2M} \nabla_{\mathbf{R}}^2 S(\mathbf{R}) = E_{CoM} S(\mathbf{R}) \quad \text{Center of mass motion}$$

$$\left[ -\frac{\hbar^2}{2\mu} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}) \right] U(\mathbf{r}) = E_H U(\mathbf{r}) \quad \text{Relative motion}$$

where  $E_H = E - E_{CoM}$

We can now solve these separately



# Center of mass motion

$$-\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 S(\mathbf{R}) = E_{CoM} S(\mathbf{R})$$

is the Schrödinger equation for a free particle of mass  $M$   
with wavefunction solutions

$$S(\mathbf{R}) = \exp(i\mathbf{K} \cdot \mathbf{R})$$

and eigenenergies

$$E_{CoM} = \frac{\hbar^2 K^2}{2M}$$

This is the motion of the entire hydrogen atom  
as a particle of mass  $M$

# Relative motion equation

The other equation

$$\left[ -\frac{\hbar^2}{2\mu} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}) \right] U(\mathbf{r}) = E_H U(\mathbf{r})$$

corresponds to the “internal” relative  
motion of the electron and proton  
and will give us the internal states  
i.e., the orbitals and energies  
of the hydrogen atom

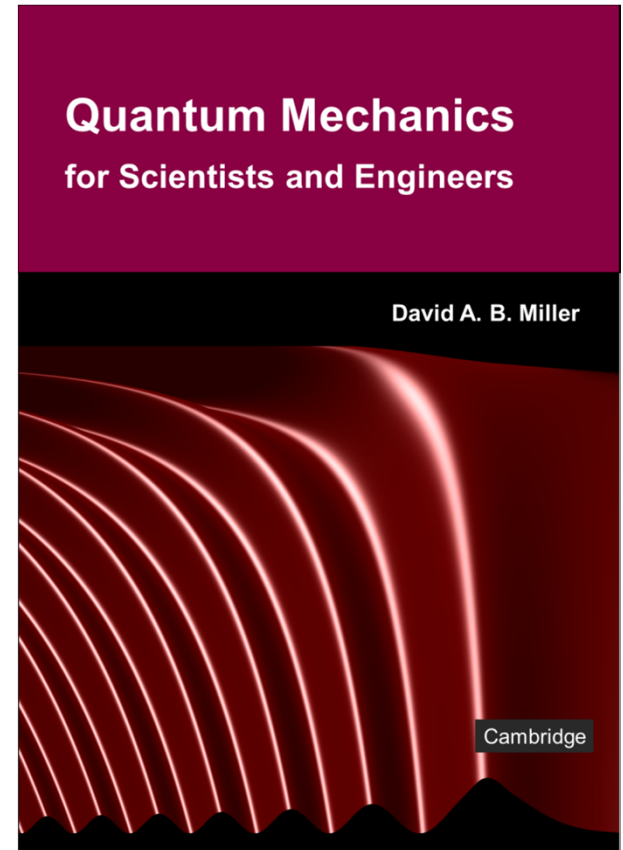


## 7.3 The hydrogen atom

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

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

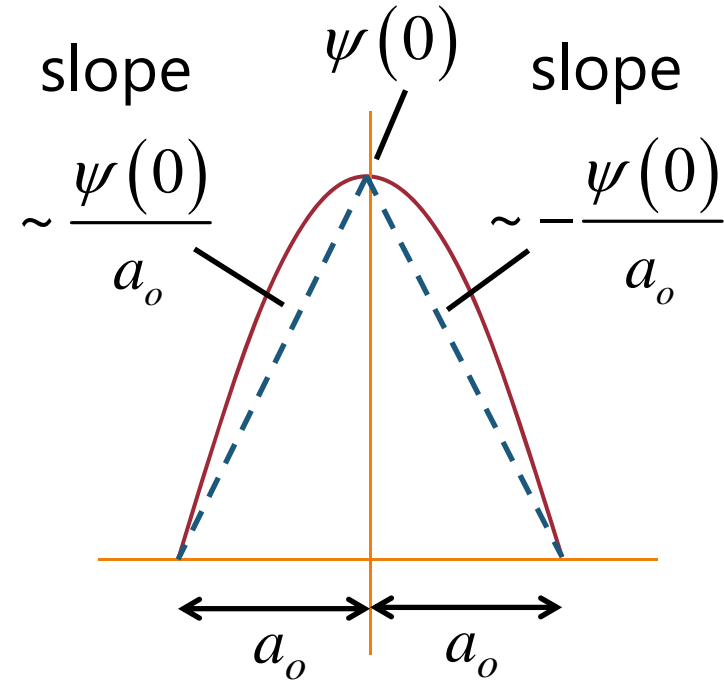
# Bohr radius and Rydberg energy

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  $\mu$

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

The “average” kinetic energy will therefore be

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

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

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

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

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

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

$$a_o = \frac{4\pi\epsilon_o \hbar^2}{e^2 \mu} \cong 0.529 \text{ \AA} = 5.29 \times 10^{-11} \text{ m}$$

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

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

We can usefully define the “Rydberg” energy unit

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

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

# Bohr radius and Rydberg energy

Though we have produced

the Bohr radius

$$a_o = \frac{4\pi\epsilon_o\hbar^2}{e^2\mu} \cong 0.529 \text{ \AA} = 5.29 \times 10^{-11} \text{ m}$$

and the Rydberg

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

by informal arguments

they will turn out to be rigorously meaningful

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

