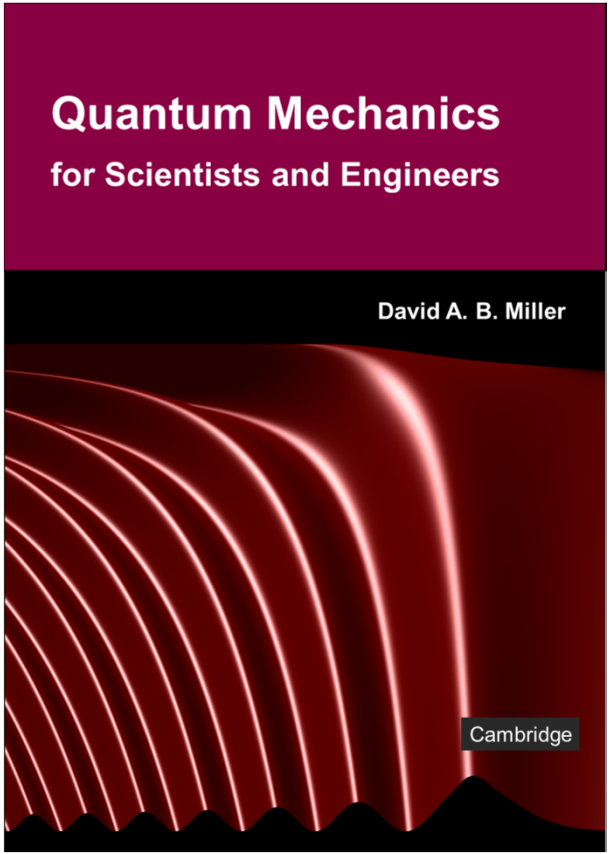
# 7.3 The hydrogen atom

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

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

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 $V\left(\left|\mathbf{r}_e-\mathbf{r}_p\right|\right)=-\dfrac{e^2}{4\pi\varepsilon_o\left|\mathbf{r}_e-\mathbf{r}_p\right|}$

depends on the distance $\left|\mathbf{r}_e-\mathbf{r}_p\right|$ between the electron and proton coordinates

which is important in simplifying the solution

The Schrödinger equation can now be written explicitly

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

$$=E\psi\left(x_e,y_e,z_e,x_p,y_p,z_p\right)$$

# Center of mass coordinates

The potential here is only a function of $\left|\mathbf{r}_e - \mathbf{r}_p\right|$

the separation of the electron and proton

We could choose a new set of six coordinates

in which three are the relative positions

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

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

from which we obtain

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

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

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

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

$$\left.\frac{\partial^2}{\partial x_e^2}\right|_{x_p} = \left.\frac{\partial}{\partial x_e}\right|_{x_p}\left(\left.\frac{\partial}{\partial x_e}\right|_{x_p}\right) = \frac{m_e}{M}\left.\frac{\partial}{\partial x_e}\right|_{x_p}\left.\frac{\partial}{\partial X}\right|_{x} + \left.\frac{\partial}{\partial x_e}\right|_{x_p}\left.\frac{\partial}{\partial x}\right|_{X}$$

$$= \left(\frac{m_e}{M}\right)^2\left.\frac{\partial^2}{\partial X^2}\right|_{x} + \left.\frac{\partial^2}{\partial x^2}\right|_{X} + \frac{m_e}{M}\left(\left.\frac{\partial}{\partial x}\right|_{X}\left.\frac{\partial}{\partial X}\right|_{x} + \left.\frac{\partial}{\partial X}\right|_{x}\left.\frac{\partial}{\partial x}\right|_{X}\right)$$

and similarly

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

# Center of mass coordinates

So

dropping the explicit statement of variables held constant

$$\frac{1}{m_e}\frac{\partial^2}{\partial x_e^2}+\frac{1}{m_p}\frac{\partial^2}{\partial x_p^2}=\frac{m_e+m_p}{M^2}\frac{\partial^2}{\partial X^2}+\left(\frac{1}{m_e}+\frac{1}{m_p}\right)\frac{\partial^2}{\partial x^2}$$

$$=\frac{1}{M}\frac{\partial^2}{\partial X^2}+\frac{1}{\mu}\frac{\partial^2}{\partial x^2}$$

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

# 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

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

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