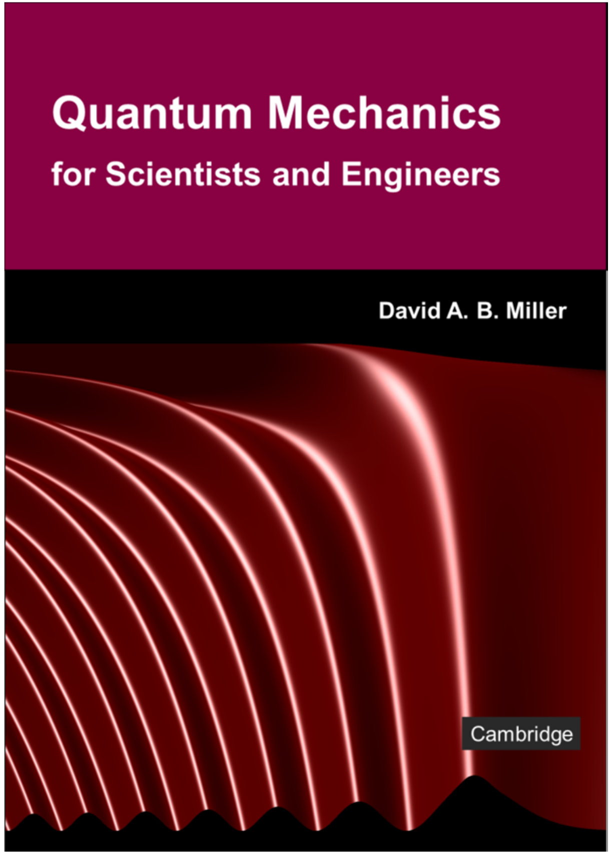
8.1 The hydrogen atom solutions

Slides: Video 8.1.1 Separating for the radial equation

Text reference: Quantum Mechanics for Scientists and Engineers

Section 10.4 (up to “Solution of the hydrogen radial wavefunction”).



The hydrogen atom solutions

Separating for the radial equation

Quantum mechanics for scientists and engineers

David Miller

Internal states of the hydrogen atom

We start with the equation for

the relative motion of electron and proton

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

We use the spherical symmetry of this equation

and change to spherical polar coordinates

From now on, we drop the subscript $\mathbf{r}$ in the operator ∇^2

Internal states of the hydrogen atom

In spherical polar coordinates, we have

$$\nabla^2 \equiv \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

where the term in square brackets

is the operator $\nabla^2_{\theta,\phi} \equiv -\hat{L}^2/\hbar^2$ we introduced

in discussing angular momentum

Knowing the solutions to the angular momentum problem

we propose the separation

$$U(\mathbf{r}) = R(r)Y(\theta,\phi)$$

Internal states of the hydrogen atom

The mathematics is simpler using the form

$$U(\mathbf{r}) = \frac{1}{r}\chi(r)Y(\theta,\phi)$$

where, obviously

$$\chi(r) = rR(r)$$

This choice gives a convenient simplification of the radial derivatives

$$\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\frac{\chi(r)}{r} = \frac{1}{r}\frac{\partial^2\chi(r)}{\partial r^2}$$

Internal states of the hydrogen atom

Hence the Schrödinger equation becomes

$$-\frac{\hbar^2}{2\mu}Y(\theta,\phi)\frac{1}{r}\frac{\partial^2\chi(r)}{\partial r^2}+\frac{\chi(r)}{r^3}\frac{1}{2\mu}\hat{L}^2Y(\theta,\phi)+Y(\theta,\phi)V(r)\frac{\chi(r)}{r}$$

$$=E_H\frac{1}{r}\chi(r)Y(\theta,\phi)$$

Dividing by $-\hbar^2\chi(r)Y(\theta,\phi)/2\mu r^3$

and rearranging, we have

$$\frac{r^2}{\chi(r)}\frac{\partial^2\chi(r)}{\partial r^2}+r^2\frac{2\mu}{\hbar^2}\left(E_H-V(r)\right)=\frac{1}{\hbar^2}\frac{1}{Y(\theta,\phi)}\hat{L}^2Y(\theta,\phi)$$

Internal states of the hydrogen atom

In

$$\frac{r^2}{\chi(r)}\frac{\partial^2\chi(r)}{\partial r^2}+r^2\frac{2\mu}{\hbar^2}\left(E_H-V(r)\right)=\frac{1}{\hbar^2}\frac{1}{Y(\theta,\phi)}\hat{L}^2Y(\theta,\phi)=l(l+1)$$

in the usual manner for a separation argument

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

and the right hand side depends only on θ and ϕ

so both sides must be equal to a constant

We already know what that constant is explicitly

i.e., we already know that $\hat{L}^2Y_{lm}(\theta,\phi)=\hbar^2 l(l+1)Y_{lm}(\theta,\phi)$

so that the constant is $l(l+1)$

Internal states of the hydrogen atom

Hence, in addition to the $\hat{L}^2$ eigenequation

which we had already solved

from our separation above, we also have

$$\frac{r^2}{\chi(r)}\frac{\partial^2 \chi(r)}{\partial r^2} + r^2 \frac{2\mu}{\hbar^2}\left(E_H - V(r)\right) = l(l+1)$$

or, rearranging

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(r)}{dr^2} + \left(V(r) + \frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right)\chi(r) = E_H\chi(r)$$

which we can write as an ordinary differential equation

All the functions and derivatives are in one variable, r

Internal states of the hydrogen atom

Hence we have mathematical equation

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(r)}{dr^2}+\left(V(r)+\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right)\chi(r)=E_H\chi(r)$$

for this radial part of the wavefunction

which looks like a Schrödinger wave equation

with an additional effective potential energy term of the form

$$\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}$$

Central potentials

Note incidentally that

though here we have a specific form for $V(r)$

in our assumed Coulomb potential

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

the above separation works for any potential

that is only a function of r

sometimes known as a central potential

Central potentials

The precise form of the equation

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(r)}{dr^2}+\left(V(r)+\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right)\chi(r)=E_H\chi(r)$$

will be different for different central potentials

but the separation remains

We can still separate out the $\hat{L}^2$ angular momentum eigenequation

with the spherical harmonic solutions

Central potentials

Since a reasonable first approximation for more complicated atoms

- is to say that the potential is still approximately "central"
  - approximately independent of angle
- we can continue to use the spherical harmonics
  - as the first approximation to the angular form of the orbitals
    - and use the "hydrogen atom" labels for them
      - e.g., s, p, d, f, etc.