Phys 231 2021

Lecture 33

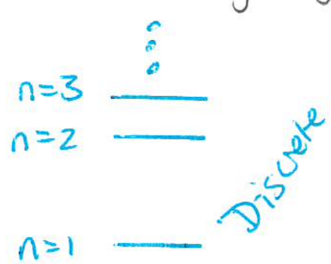
Mon: Read 7.4, 7.5

Tues: HW 12

Quantum theory and the hydrogen atom

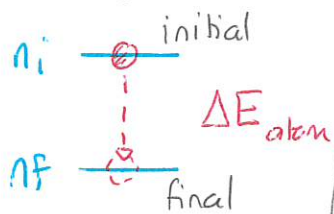
Experiments show that the emission spectrum of hydrogen is discrete. Early quantum theory described this via the Bohr model.

Model predicts energy levels for hydrogen



$E_n = -13.6\,\text{eV}\,\frac{1}{n^2}$

→ Atom emits light when energy level changes



Only discrete ΔE_{atom} possible

→ Photon emitted has wavelength λ given via

$$E_{ph} = \frac{hc}{\lambda}$$

and $E_{ph} = -\Delta E_{atom}$

$$\Rightarrow \frac{hc}{\lambda} = |\Delta E_{atom}|$$

Demo: PhET Hydrogen Atom Models

→ predictions

→ Schrödinger

→ show spectrometer

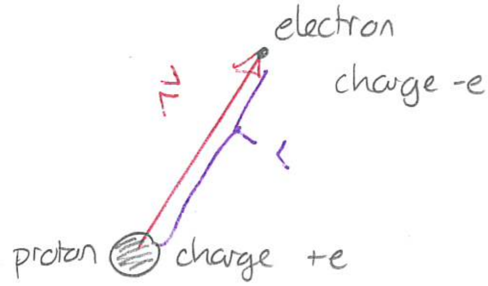
– show energy level diagram.

The Bohr model was assembled in an ad-hoc fashion. Can its predictions be reproduced via the Schrödinger equation.

Schrödinger equation for a hydrogen atom

The hydrogen atom consists of a negatively charged electron in the presence of an approximately stationary positive proton. The location of the electron will be described as a point in three dimensional space,

$$\vec{r} = (x, y, z)$$



Thus we will need the three-dimensional Schrödinger equation. The crucial ingredient will be the potential. In electrostatics the potential energy of two point charges is

$$U = \frac{1}{4\pi\epsilon_0}\frac{q_1 q_2}{r}$$

where q_i are the charges and r is the distance between them. In this case $q_1 = e$, $q_2 = -e$ and thus

$$U(r) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}$$

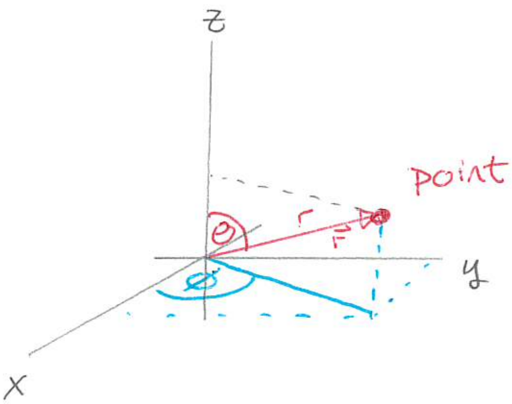
where $r = \sqrt{x^2+y^2+z^2}$. Then the time-independent Schrödinger equation is:

$$-\frac{\hbar^2}{2M}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) - \frac{1}{4\pi\epsilon_0}\frac{e^2}{\sqrt{x^2+y^2+z^2}}\psi(x,y,z) = E\psi(x,y,z)$$

The presence of the square root means that Cartesian co-ordinates will not be as practical as alternative co-ordinates.

Spherical co-ordinates

Spherical co-ordinates are defined in terms of a single distance from the origin and two angles. These are as illustrated



$r =$ distance from the origin

$\theta =$ angle from z-axis to $\vec{r}$

$\phi =$ angle in xy plane from +x axis to projection line

They are related to Cartesian co-ordinates by:

$$\left.\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta \end{aligned}\right\} \Longleftrightarrow \left\{\begin{aligned} r &= \sqrt{x^2+y^2+z^2} \\ \phi &= \tan^{-1}(y/x) \\ \theta &= \tan^{-1}\left(z/\sqrt{x^2+y^2}\right) \end{aligned}\right.$$

Quiz 1 60% → 100%

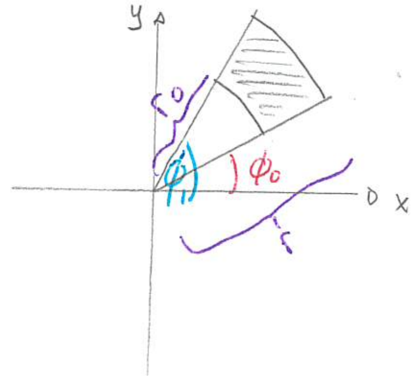
Quiz 2 70% →

Quiz 3 100%

We need to express the wavefunction, probabilities, Schrödinger equation and all the mathematics in terms of these variables. So the wavefunction will be

$$\psi \to \psi(r,\theta,\phi)$$

Probabilities will refer to measurement outcomes in terms of spherical co-ordinates. So we get

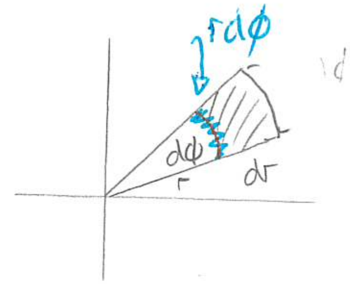


$$\text{Prob}\left[r_0 \le r \le r_1 \text{ AND } \theta_0 \le \theta \le \theta_1 \text{ AND } \phi_0 \le \phi \le \phi_1 \right]$$

$$= \int_{r_0}^{r_1} \int_{\theta_0}^{\theta_1} \int_{\phi_0}^{\phi_1} |\psi(r,\theta,\phi)|^2 \, dV$$

A projection of dV is illustrated in the shaded segment. Even this two dimensional projection has curved edges. So will a three dimensional region. So $dV \neq dr\,d\theta\,d\phi$.

Using a diagram such as Fig 7.8 or some general rules from calculus for transformation of variables we find



$$dV = r^2 \sin\theta \, dr\, d\theta\, d\phi.$$

Thus

$$\boxed{\begin{aligned} &\text{Prob}\left[r_0 \le r \le r_1 \text{ AND } \theta_0 \le \theta \le \theta_1 \text{ AND } \phi_2 \le \phi \le \phi_1 \right] \\ &= \int_{r_0}^{r_1} \int_{\theta_0}^{\theta_1} \int_{\phi_0}^{\phi_1} |\psi(r,\theta,\phi)|^2 \, r^2 \sin\theta \, dr\, d\theta\, d\phi \end{aligned}}$$

More generally

$$\boxed{\text{Prob}\,(\text{ position in region }) = \underset{\text{region limits}}{\iiint} |\psi(r,\theta,\phi)|^2 r^2 \sin\theta \, dr\, d\theta\, d\phi}$$

Infinitesimally

$$\text{Prob}\left[r \to r+dr,\ \theta \to \theta+d\theta,\ \phi \to \phi+d\phi\right] = |\Psi(r,\theta,\phi)|^2\, r^2 \sin\theta\, dr\, d\theta\, d\phi$$

Example: Suppose that the wavefunction for a particle is

$$\Psi(r,\theta,\phi) = A\, e^{-r/a}\, e^{2i\phi}$$

where A and a are constants.

a) Determine A s.t. the wavefunction is normalized.

b) Determine the probability that a position measurement outcome gives $r > a$, regardless of θ, ϕ.

c) Determine the probability density for outcomes of r regardless of θ, ϕ.

Answer: a)

$$P(r,\theta,\phi) = |\Psi(r,\theta,\phi)|^2$$

$$= |Ae^{-r/a}\, e^{2i\phi}|^2$$

$$= |A|^2\, |e^{-r/a}|^2\, \underbrace{|e^{2i\phi}|^2}_{1}$$

$$= A^2 e^{-2r/a}$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} P(r,\theta,\phi)\, r^2 \sin\theta\, dr\, d\theta\, d\phi = 1$$

This implies:

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} A^2 e^{-r2/a} \; r^2 \sin\theta \, dr \, d\theta \, d\phi = 1$$

$$\Rightarrow \quad A^2 \int_0^\infty r^2 e^{-r2/a} dr \underbrace{\int_0^\pi \sin\theta \, d\theta}_{} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} = 1$$

$$-\cos\theta \Big|_0^\pi = -\cos\pi + \cos 0 = 2.$$

$$\Rightarrow \quad 4\pi A^2 \underbrace{\int_0^\infty r^2 e^{-2r/a} dr}_{} = 1$$

look up: $\dfrac{2}{(2/a)^3} = \dfrac{2a^3}{8} = \dfrac{a^3}{4}.$

$$\Rightarrow \quad \cancel{4}\pi A^2 \frac{a^3}{\cancel{4}} = 1 \quad \Rightarrow \quad A = \frac{1}{\sqrt{\pi a^3}} \quad \Rightarrow \quad \Psi(r,\theta,\phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} e^{2i\phi}$$

b) $$\text{Prob}[\ldots] = \int_a^\infty \int_0^\pi \int_0^{2\pi} \frac{1}{\pi a^3} e^{-2r/a} \; r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= \frac{1}{\pi a^3} \int_a^\infty e^{-2r/a} r^2 dr \underbrace{\int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi}_{4\pi}$$

$$= \frac{4}{a^3} \int_a^\infty e^{-2r/a} r^2 dr.$$

$$\text{Prob } (r > r_0) = \frac{4}{a^3}\left[\frac{5a^3 e^{-2}}{4}\right]$$

$$= 5e^{-2} = 0.68 \quad \boxtimes$$

c) This is

$$\int_0^{\pi}\int_0^{2\pi} P(r,\theta,\phi)\; r^2 \sin\theta \, dr\, d\theta\, d\phi$$

$$= \frac{1}{\pi a^3} e^{-2r/a}\, r^2 dr \underbrace{\int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi}_{4\pi}$$

$$= \underbrace{\frac{4}{a^3} e^{-2r/a}\, r^2}dr$$

Prob density $\frac{4}{a^3} r^2 e^{-2r/a}$