Quantum Physics Lecture 6

Bohr model of hydrogen atom \((cont.)\)

- Line spectra formula
- Correspondence principle

Quantum Mechanics – \textit{formalism}

- General properties of waves
- Expectation values
- Free particle wavefunction
- 1-D Schroedinger Equation
Experimental Evidence for Bohr model

From optical emission spectrum of hydrogen:
Consists of line spectra (*in contrast to blackbody continuum*)

Balmer series; fitted to formula

\[ \frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad \text{for } n = 3, 4, 5, \ldots \]

Experimental value of \( R = 1.097 \times 10^7 \text{ m}^{-1} \)

In general, use two integers \( n_i \) (initial) and \( n_f \) (final)

\[ \frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \quad \text{for } n_i > n_f \]

Where \( n_f = 1 \) (Lyman), \( = 2 \) (Balmer), \( = 3 \) (Paschen) etc
Connect expt. with Bohr model

\[ \frac{1}{\lambda} = R \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \]
\[ E_n = -\frac{me^4}{8\varepsilon_0^2\hbar^2} \left( \frac{1}{n^2} \right) \]

Optical emission: result of a “down transition” of electron from a higher energy orbit \((n_i)\) to a lower energy orbit \((n_f)\). Energy difference is emitted as a photon:

\[ \hbar \omega = E_{n_i} - E_{n_f} = -\frac{me^4}{8\varepsilon_0^2\hbar^2} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = \frac{hc}{\lambda} \]

\[ \frac{1}{\lambda} = \frac{me^4}{8\varepsilon_0^2\hbar^3 c} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \Rightarrow R = \frac{me^4}{8\varepsilon_0^2\hbar^3 c} \]
Centre-of-mass correction

\[ R = \frac{me^4}{8\varepsilon_o^2\hbar^3 c} = 1.097 \times 10^7 \text{ m}^{-1} \]

This value of \( R \) agreed with expt. of the time!
However, later (more accurate) experiments gave \( R_{\text{expt}} = 1.0967785 \)
whereas model gave \( R = 1.0973731 \)

Replace \( m \) with \( m^* = mM/(m + M) = 0.99945(m) \)
In centre-of-mass description of electron (\( m \)) and proton (\( M \))

Correspondence Principle

“The greater the quantum number…….
the closer Quantum Physics approaches Classical Physics!”
Correspondence Principle

Compare orbit frequency \((f)\) and emitted photon frequency \((\omega/2\pi)\)

\[
f = \frac{v}{2\pi r} = \frac{e}{2\pi \sqrt{4\pi \varepsilon_o mr^3}} = \frac{me^4}{8\varepsilon_o^2 h^3} \left(\frac{2}{n^3}\right)
\]

\[
\omega/2\pi = E/h = \frac{me^4}{8\varepsilon_o^2 h^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)
\]

Note same pre-factor! Write \(n_i = n\) and \(n_f = n - p\)

\[
\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = \left(\frac{1}{(n - p)^2} - \frac{1}{n^2}\right) = \left(\frac{2np - p^2}{n^2(n - p)^2}\right) \approx \left(\frac{2p}{n^3}\right)
\]

When \(n \gg p\), \((2np - p^2) \sim 2np\) and \((n - p)^2 \sim n^2\)

then \(\omega/2\pi \sim pf\) and letting \(p=1\), a transition: \(n\) to \((n-1)\) gives \(\omega/2\pi \sim f\)
Bohr criterion for allowed orbits

The Bohr requirement for orbits can also be stated as:

“angular momentum is quantised in units of $\hbar$”

\[ mvr = n\left(\frac{h}{2\pi}\right) = n\hbar \]

\[ \Rightarrow 2\pi r = n\left(\frac{h}{mv}\right) = n\lambda \]

i.e. Equivalent to “fitting de Broglie wavelengths”

In fact, the concept of quantised angular momentum $n\hbar$ is the fuller and broader criterion, with further consequences to be seen; the other is merely illustrative, not factual!

Complete description of atom requires at least three different quantum numbers (see later lectures)
General properties of waves

Recall 1-D wave: \[ y = A\cos(\omega t - kx) \]
This is just one possible solution of the 1-D wave equation:
\[ \frac{\delta^2 y}{\delta x^2} = \frac{1}{v^2} \frac{\delta^2 y}{\delta t^2} \]

In general \[ y = A\exp[-i(\omega t - kx)] \quad \text{where} \quad i = \sqrt{-1} \]
\[ = A[\cos(\omega t - kx) - i\sin(\omega t - kx)] \quad \text{— the general (complex) solution}. \]

For ‘waves’ (of existence) in QM use wavefunction \( \psi \)

Recall UP and probability:
\[ |y|^2 \text{ is a measure of probability of finding a particle at location } x \]

In QM, \( \psi \) is in general complex, and not usually a “measureable” parameter (such a momentum etc.)
However, \[ |\psi|^2 \text{ is! So must retain full complex solution, not just real part.} \]
General properties of waves cont.

Three other required properties of wavefunction $\psi$

1. single-valued and continuous
2. derivative ($d\psi/dx$) single-valued and continuous
3. normalisable: $\int |\psi|^2 dx = 1$
   - i.e. integrated probability density over all space is unity
   i.e. for 1-D case require
   \[
   \int_{-\infty}^{+\infty} |\psi|^2 \, dx = 1
   \]

If $\psi$ is complex, what about $|\psi|^2$?

$|\psi|^2 = \psi^* \psi$ where $\psi^*$ is complex conjugate of $\psi$

$\psi = A + iB$ and $\psi^* = A - iB$

$\psi^* \psi = (A - iB)(A + iB) = A^2 - (iB)^2 = A^2 + B^2$ (i.e. real)
Expectation values

Expectation value: “the most probable value of a variable”

Multiply variable by probability density ($|\psi|^2$) and integrate!

eg. expectation value of 1-D position:

$$\langle x \rangle = \frac{\int_{-\infty}^{+\infty} x|\psi|^2 \, dx}{\int_{-\infty}^{+\infty} |\psi|^2 \, dx}$$

If $\psi$ is normalised then denominator = 1, in which case

$$\langle x \rangle = \int_{-\infty}^{+\infty} x|\psi|^2 \, dx$$

and for a general variable $G(x)$ the expectation value is

$$\langle G(x) \rangle = \int_{-\infty}^{+\infty} G(x)|\psi|^2 \, dx$$
Free particle wavefunction

….think simple wave, rather than wavegroup……

$$\psi = A \exp[-i(\omega t - kx)]$$

$$\omega = \frac{E}{\hbar}$$

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{\hbar} = \frac{p}{\hbar}$$

$$\psi = A \exp[-i\left(\frac{E}{\hbar}t - \frac{p}{\hbar}x\right)]$$

Replacing “wave-notation” ($\omega, k$) with “particle notation” ($E, p$)

What is the “equation of motion”, just as in Newton’s Laws, but for quantum particle……?
Free particle functions

\[ \psi = A \exp \left( -\frac{iEt}{\hbar} + \frac{ipx}{\hbar} \right) = Ae^{-iEt/\hbar} e^{ipx/\hbar} \]

Now consider partial differential with \(x\)

\[ \frac{\partial \psi}{\partial x} = Ae^{-iEt/\hbar} \cdot \frac{ip}{\hbar} e^{ipx/\hbar} = \frac{ip}{\hbar} \psi \]

Re-arranged:

\[ \frac{\hbar}{i} \frac{\partial}{\partial x} \psi = p \psi \]

Or:

\[ -i\hbar \frac{\partial}{\partial x} \psi = p \psi \]

i.e. if we “operate” on \(\psi\) with \(-i\hbar \delta/\delta x\)

- we get the value of momentum \(p\) multiplied by \(\psi\)

\(-i\hbar \delta/\delta x\ is the momentum ‘operator’ \(\hat{p}\)

Expect Kinetic Energy operator

\[ \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \]

General Equation: Operator on \(\psi\) = value \(\times\) \(\psi\)
1-D Schroedinger Equation

Is the equation for energy.

Consider:

\[ \psi = A \exp \left[ -i \left( \frac{E}{\hbar} t - \frac{p}{\hbar} x \right) \right] \]

\[ \frac{\partial \psi}{\partial x} = + \frac{ip}{\hbar} \psi \]

\[ \frac{\partial^2 \psi}{\partial x^2} = - \frac{p^2}{\hbar^2} \psi \quad \Rightarrow \quad p^2 \psi = -\hbar^2 \frac{\partial^2 \psi}{\partial x^2} \]

\[ \frac{\partial \psi}{\partial t} = -i \frac{E}{\hbar} \psi \quad \Rightarrow \quad E \psi = +i\hbar \frac{\partial \psi}{\partial t} \]

Compare with ordinary (non-relativistic) mechanics……
1-D Schroedinger Equation developed

\[ E = KE + PE = \frac{p^2}{2m} + U(x,t) \]

multiply across by \( \psi \)

\[ E\psi = \left(\frac{p^2}{2m}\right)\psi + U\psi \]

and substitute for \( E\psi \) and \( p^2\psi \)

\[
i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U\psi \quad \text{1-D Schroedinger Equation}
\]

\[
i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + U\psi \quad \text{3-D Schroedinger Equation}
\]

Patently true for free particle \((U=0)\),
also found to be true for constrained particle……a basic principle
Steady State Simplification

When $U$ is not a function of $t$, get considerable simplification:

- The time-independent, or steady state Schrödinger Equation.

Recall free particle wavefunction:

$$\psi = A \exp \left[ -i \left( \frac{E}{\hbar} t - \frac{p}{\hbar} x \right) \right]$$

$$\psi = A \exp \left( -i \frac{E}{\hbar} t \right) \exp \left( i \frac{p}{\hbar} x \right)$$

$$\psi = \psi' \exp \left( -i \frac{E}{\hbar} t \right) \quad \text{where} \quad \psi' = A \exp \left( i \frac{p}{\hbar} x \right)$$

Fortunately, this separation of time and position dependences is also possible for all wavefunctions when $U$ is indep. of $t$!

…substitute this form of $\psi$ into 1D Schrödinger Equation…..
Steady State Schroedinger Equation

\[ i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U\psi \]

LHS = \[ i\hbar \frac{\partial}{\partial t} (\psi' \exp(-i E/\hbar t)) = E\psi' \exp(-i E/\hbar t) \]

RHS = \[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} (\psi' \exp(-i E/\hbar t)) + U(\psi' \exp(-i E/\hbar t)) \]

\[ = -\frac{\hbar^2}{2m} \exp(-i E/\hbar t) \frac{\partial^2 \psi'}{\partial x^2} + U\psi' \exp(-i E/\hbar t) \]

\[ \Rightarrow E\psi' = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi'}{\partial x^2} + U\psi' \]

“drop the dash & re-write as”:

\[ \frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - U) \psi = 0 \]