10 The Hydrogen Atom

Bring solutions along to the class at 10am on 7/12/20.

Questions marked # are beyond the syllabus. We may discuss them in the class if there is time. Attempt all questions. Feel free to discuss with friends. Don't worry if you cannot answer a question fully as you will discuss the solutions in the class.

10.1 Spherically symmetric potentials

The TISE in spherical polar co-ordinates reads

$$\hat{H}\psi(\boldsymbol{r},t) = E\psi(\boldsymbol{r},t) \tag{225}$$

where

$$\hat{H} = -\frac{\hbar^2}{2\mu r^2}\partial_r\left(r^2\partial_r\right) + \frac{1}{2\mu r^2}\hat{L}^2 + V(\boldsymbol{r}) \tag{226}$$

and

$$\hat{L}^2 = -\hbar^2\left(\frac{1}{\sin(\theta)}\partial_\theta\left(\sin(\theta)\,\partial_\theta\right) + \frac{1}{\sin^2(\theta)}\partial_\phi^2\right). \tag{227}$$

The symbol μ here is used in place of m for the mass of the particle. In the hydrogen atom μ will be the reduced mass.

Explain why, if the potential is symmetric such that $V(\boldsymbol{r}) = V(r)$ where $\boldsymbol{r} = (r, \theta, \phi)$, the TISE is separable using the ansatz

$$\psi(\boldsymbol{r},t) = T(t)\,R(r)\,Y(\theta,\phi). \tag{228}$$

Carry out the separation, and, defining the separation constant $\hbar^2 k^2$, write down the radial and angular equations.

10.2 Angular equation

Explain why the angular equation is itself separable. Using the ansatz

$$Y(\theta,\phi) = P(\cos(\theta))\,F(\phi) \tag{229}$$

and separation constant m^2 write down the azimuthal equation for θ and the polar equation for ϕ. Show that both are now ordinary differential equations (ODEs).

10.2.1 Polar equation

Show that the solutions to the polar equation take the form

$$F(\phi) = A\exp(\pm im\phi) \tag{230}$$

with A a complex constant. Thinking about the meaning of ϕ in the spherical polar co-ordinate system, explain why you might expect m to be restricted to integers. Show that $F_m(\phi)$ are eigenstates of $\hat{L}_z$. What physical observable does the operator $\hat{L}_z$ correspond to? Therefore explain the physical meaning of m being integer.

10.2.2 Azimuthal equation

By making the change of variables

$$x = \cos(\theta) \tag{231}$$

show that the azimuthal equation can be rewritten as the *associated Legendre equation*:

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(\left(1-x^2\right)\frac{\mathrm{d}}{\mathrm{d}x}\right)P(x) + \left(l(l+1) - \frac{m^2}{1-x^2}\right)P(x) = 0 \tag{232}$$

giving an equation for l. The solutions $P_l^m(x)$ are called the associated Legendre polynomials, and are valid for $l \geq 0$ integer and $|m| \leq l$ integer. Find the un-normalised solutions $P_0^0(x)$ and $P_1^0(x)$.

10.3 Radial equation

Explain why the results found for the angular equation tell us that the radial equation now takes the form

$$\hbar^2\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right)R_l(r) + 2mr^2(E-V)R_l(r) = \hbar^2 l(l+1)R_l(r). \tag{233}$$

10.4 The hydrogen atom

10.4.1

Explain why the TISE of the electron in the hydrogen atom takes the form

$$\left(-\frac{\hbar^2}{2\mu r^2}\partial_r\left(r^2\partial_r\right) + \frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{e^2}{4\pi\epsilon_0 r}\right)\varphi_{n,l,m}(\boldsymbol{r}) = E_n\varphi_{n,l,m}(\boldsymbol{r}). \tag{234}$$

10.4.2

Using the ansatz

$$\varphi_{n,l,m}(\boldsymbol{r}) = \frac{\chi_{n,l}(r)}{r}Y_l^m(\theta,\phi) \tag{235}$$

show that the radial equation can be rewritten

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2\chi_{n,l}(r)}{\mathrm{d}r^2} - \frac{e^2}{4\pi\epsilon_0 r}\chi_{n,l}(r) + \frac{\hbar^2 l(l+1)}{2mr^2}\chi_{n,l}(r) = E_n\chi_{n,l}(r). \tag{236}$$

10.4.3

Defining the Bohr radius

$$a_0 \triangleq \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} \tag{237}$$

the dimensionless radial co-ordinate

$$\rho \triangleq \frac{r}{a_0} \tag{238}$$

the dimensionless energy variable

$$\lambda^2 \triangleq -\frac{2\mu E a_0^2}{\hbar^2} \tag{239}$$

and the rescaled function

$$\Xi\left(\rho\right) \triangleq \chi\left(r\right) \tag{240}$$

show that the radial equation can be rewritten

$$\Xi''\left(\rho\right) - \frac{l\left(l+1\right)}{\rho^2}\Xi\left(\rho\right) + \frac{2}{\rho}\Xi\left(\rho\right) = \lambda^2\Xi\left(\rho\right) \tag{241}$$

where the primes now indicate derivatives with respect to ρ rather than r.

10.4.4

Show that in the limit $\rho \gg 1$ the solution takes the form

$$\Xi\left(\rho\right) = A\exp\left(-\lambda\rho\right) \tag{242}$$

and in the limit $\rho \ll 1$ it takes the form

$$\Xi\left(\rho\right) = B\rho^{l+1}. \tag{243}$$

10.4.5 #

These limiting forms suggest the following ansatz:

$$\Xi\left(\rho\right) = \rho^{l+1}\exp\left(-\lambda\rho\right)\alpha\left(2\lambda\rho\right). \tag{244}$$

Defining

$$y = 2\lambda\rho \tag{245}$$

Show that this leads to Laguerre's equation:

$$y\alpha''(y) + \alpha'(y)(2(l+1) - y) - \left(l + 1 - \frac{1}{y}\right)\alpha(y) = 0 \tag{246}$$

where primes now indicate derivatives with respect to y. The solutions are the Laguerre polynomials $L_{n-l-1}^{2l+1}(y)$ with $n > 0$ an integer, where the eigenvalues are

$$E_n = \frac{-\hbar^2}{2\mu a_0^2 n^2}. \tag{247}$$

10.4.6

Put everything together to find the (un-normalised) energy eigenfunctions of the hydrogen atom $\psi_{n,l,m}(\boldsymbol{r}, t)$.

10.5 The Bohr model

10.5.1

Write down the assumptions going into Bohr's (incorrect) model of the electronic states in the atom. Write a mathematical expression encoding Bohr's statement regarding the quantization of angular momentum.

10.5.2

Assuming (incorrectly) that the electron orbits the nucleus classically, equate the centripetal force to the electrostatic force to obtain an expression for the velocity in terms of the radius (and other quantities). Hence derive Bohr's formula for the radius of possible orbits:

$$r_n = \frac{4\pi\epsilon_0 n^2 \hbar^2}{e^2 m_e} \tag{248}$$

and find the Bohr radius r_1 (conventionally denoted a_0).

10.5.3

Using the same model, show that the energy levels of the atom are:

$$E_n = \frac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2 n^2}. \tag{249}$$

Use this formula to calculate the ionization energy of hydrogen.

10.5.4

What would be the equivalent formulae for positronium (an electron-positron bound state)?

10.5.5

A 656.3 nm photon is detected from a hydrogen atom. What is the principal quantum number of the electron in the atom immediately after this detection?