Intermediate Quantum Mechanics
Lecture 18 Notes (4/1/15)

The Hydrogen Atom I

Historical importance of the hydrogen atom

- The hydrogen atom was the principle tool that allowed the physicists developing quantum mechanics in the 1920's to test their calculations. They were able to precisely calculate the discreet energy levels in the hydrogen atom. These were then compared with the values measured from atomic spectroscopy. The hydrogen atom provided a perfect test system. If for no other reason, we should spend time examining the solutions to the hydrogen atom.

The hydrogen atom Hamiltonian

- The hydrogen atom consists of an electron bound by the Coulomb field due of the nuclear proton.

$$\hat{H} = \frac{p^2}{2m} + V(\hat{x}, \hat{y}, \hat{z}) = \frac{\hat{P}^2{}_x + \hat{P}^2{}_y + \hat{P}^2{}_z}{2m} - \frac{e^2}{4\pi\epsilon_0\sqrt{\hat{x^2} + \hat{y^2} + \hat{z^2}}}$$

- In terms of the energy eigenstates and energy eigenvalues:

$$\langle x, y, z \,|\, \psi_E \rangle = \psi_E(x, y, z)$$

$$\langle x, y, z|\hat{H}\,|\psi_E\rangle = \left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{e^2}{4\pi\epsilon_0\sqrt{x^2 + y^2 + z^2}}\right]\psi_E(x, y, z)$$

The differential equation to be solved is:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0\sqrt{x^2 + y^2 + z^2}}\right)\psi_E(x, y, z) = E\,\psi_E(x, y, z)$$

- This equation does not have an analytical solution because the square root dependence makes it a non linear differential equation.

Differential equation in spherical coordinates

- In spherical coordinates, the differential equation becomes:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}\right)\psi_E(r, \theta, \phi) = E\,\psi_E(r, \theta, \phi)$$

that can now be solved analytically.

- One difficulty is that the expression for the Laplacian, ∇^2, in spherical coordinates is somewhat complicated.

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

$$\left(-\frac{\hbar^2}{2mr^2}\left[\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] - \frac{e^2}{4\pi\epsilon_0 r}\right)\psi_E(r, \theta, \phi) = E\,\psi_E(r, \theta, \phi)$$

- Since the hydrogen atom has spherical symmetry, the angular dependence of its wave function is given by the spherical harmonics. Also, because of the spherical symmetry, the Hamiltonian commutes with the $\hat{L^2}$ and $\hat{L}_z$ operators::

$$[\hat{H}, \hat{L^2}] \;=\; 0 \qquad\qquad [\hat{H}, \hat{L}_z] \;=\; 0$$

That means that energy eigenstates are also eigenstates of $\hat{L^2}$ and $\hat{L}_z$. We then have:

$$\psi_{Elm}(r,\theta,\phi) \;=\; R_{El}(r) Y_l^m(\theta,\phi)$$

and we only need to solve for $R_{EL}(r)$.

- It can be shown (you can do it yourself if you are so inclined) that in the position representation with spherical coordinates, the expression for the$\hat{L^2}$ operator is:

$$\langle\theta,\phi|\hat{L^2}\,|\psi_{lm}\rangle \;=\; -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} \;+\; \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) Y_l^m(\theta,\phi) \;=\; \hbar^2 l(l{+}1) Y_l^m(\theta,\phi)$$

We then have:

$$\left[-\frac{\hbar^2}{2mr^2}\left(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right) \;+\; \frac{\hat{L^2}}{mr^2} \;-\; \frac{e^2}{4\pi\epsilon_0 r}\right] R_{El}(r)Y_l^m(\theta,\phi) \;=\; E\,R_{El}(r)Y_l^m(\theta,\phi)$$

$$\Rightarrow \qquad \left[-\frac{\hbar^2}{2mr^2}\left(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right) \;+\; \frac{l(l+1)\hbar^2}{mr^2} \;-\; \frac{e^2}{4\pi\epsilon_0 r}\right] R_{El}(r) \;=\; E\,R_{El}(r)$$

- This can be simplified by making the substitution $\chi_{El}(r) \;=\; rR_{El}(r)$. Then:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} \;+\; \frac{l(l+1)\hbar^2}{mr^2} \;-\; \frac{e^2}{4\pi\epsilon_0 r}\right] \chi_{El}(r) \;=\; E\,\chi_{El}(r)$$

Correspondence with classical physics

- The above equation for the energy eigenstates has a term involving the square of the angular momentum that is familiar from the classical physics of an orbiting planet. The energy of a planet in terms of the radial distance from the star is given by:

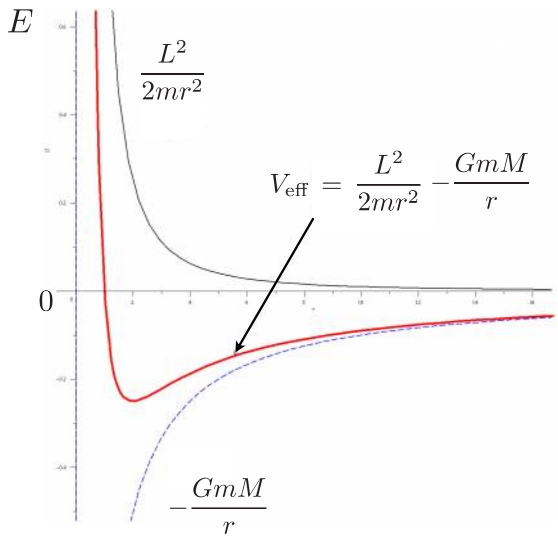
$$E \;=\; \frac{p_r^2 \,+\, p_\theta^2}{2m} \;-\; G\frac{mM}{r^2}$$

where p_r and p_θ are the components of the momentum parallel and perpendicular to the radial vector.

- For an orbiting planet in a central force field, the angular momentum, $\vec{L} \;=\; \vec{r}\times\vec{p}$ is conserved. The magnitude of the angular momentum $L \;=\; p_\theta r$. Then

$$E \;=\; \frac{p_r^2}{2m} \;+\; \frac{L^2}{2mr^2} \;-\; G\frac{mM}{r^2} \;=\; \frac{p_r^2}{2m} \;+\; V_{\text{eff}}(r)$$

$$\text{where} \qquad\qquad V_{\text{eff}}(r) \;=\; \frac{L^2}{2mr^2} \;-\; G\frac{mM}{r^2}$$



- The differences with the quantum mechanical hydrogen atom are that L^2 is replaced by $l(l+1)\hbar^2$ and the gravitation factor, GmM, is replaced by the Coulomb factor, $e^2/4\pi\epsilon_0$.

The radial solutions

- In order to solve the differential equation for $\chi_{El}(r)$, try a power series solution of the form:

$$\chi_{El}(r) = \sum_{i=0}^{\infty} c_i r^i e^{-r/a_0}$$

In order that the solution correspond to a physically state, we must have:

$$\lim_{r\to\infty} \chi_{El}(r) = 0$$

This requires that the power series must terminate at some finite power n. This leads to a set of eigenstates with discreet eigenvalues E_n. This is what we expect because the electron is bound. If the total energy of the electron is positive, then it is not bound and there is a continuous set of eigenstates.

Fundamental constants

- We'll now determine the numerical values of the energy eigenvalues and the value of the characteristic length of the radial wave functions. These can only depend on the fundamental constants in the problem. There are four of these:

$$\hbar, \qquad c, \qquad m_e, \qquad \frac{e^2}{4\pi\epsilon_0}$$

where $e^2/4\pi\epsilon_0$ is the fundamental strength of electricity.

- There is actually another constant, the mass of the proton, m_p. Since this is about 2000 times larger than the mass of the electron we will ignore it for now and approximate it to be infinity.

- As written $e^2/4\pi\epsilon_0$ has units of [Joules · meters]. Its numerical value depends then upon the arbitrary SI system of units. It is useful to express it instead as a unit-less quantity independent of the system of units chosen. The product of the two most fundamental constant in physics $\hbar c$ also has units of [energy · length]. If we divide by, $\hbar c$, we get a number that reflects the fundamental strength of electricity.

$$\alpha \;=\; \frac{e^2}{4\pi\epsilon_0 \hbar c} \;=\; \frac{1}{137}$$

- The four constants we will use are: $\hbar$, c, m_e and α

The Bohr radius

- For the ground state $l = 0$ and there is no angular momentum barrier term. We then have:

$$E \;=\; \overline{T} + \overline{V} \;=\; \frac{\langle p^2 \rangle}{2m} - \frac{e^2}{4\pi\epsilon_0 \langle r \rangle} \;=\; \frac{\langle p^2 \rangle}{2m} - \frac{\alpha \hbar c}{\langle r \rangle}$$

- By the Heisenberg Uncertainty Principle: $\langle p \rangle \approx \hbar/\langle r \rangle$. This gives:

$$E \;=\; \frac{\hbar^2}{2m\langle r^2 \rangle} - \frac{\alpha \hbar c}{\langle r \rangle}$$

- Note that for a classical planetary system, the ground state must have $L > 0$ since if $L = 0$, the planet would fall in to the Sun. The electron even with $l = 0$ is kept from collapsing onto the the proton by the Heisenberg uncertainty relation between momentum and position that introduces a $1/r^2$ dependence similar to the angular momentum barrier term.

- We can find an approximate value of $\langle r \rangle$ by minimizing the energy:

$$\frac{dE}{dr} \;=\; -\frac{\hbar^2}{mr^3} + \frac{\alpha \hbar c}{r^2} \;=\; 0 \qquad \Rightarrow \qquad r \;=\; \frac{\hbar}{mc\alpha}$$

  This is called the **Bohr radius** and has the value:

$$a_0 \;=\; \frac{\hbar}{mc\alpha} \;=\; 0.059 \text{ nm} \;=\; 0.59 \times 10^{-10} \text{ m}$$

The Virial Theorem

- In classical mechanics, the Virial Theorem relates the average values of the kinetic and potential energies for a particle in a potential that varies as r^n:

$$\overline{T} \;=\; \frac{n}{2}\overline{V}$$

  This applies in quantum mechanics as well.

- For the Coulomb potential with $n = -1$, we have:

$$\overline{T} \;=\; -\frac{1}{2}\overline{V} \qquad E \;=\; \overline{T} + \overline{V} \;=\; \frac{1}{2}\overline{V} \;=\; -\overline{T}$$

Ground state energy

$$E_1 \;=\; \frac{1}{2}\,\overline{V} \;=\; -\,\frac{\alpha\hbar c}{a_0} \;=\; -\,\frac{1}{2}\,m(\alpha c)^2 \;=\; -\,13.6\text{ eV}$$

Non relativistic velocity

- $$\overline{T} \;=\; \frac{1}{2}\,m\langle v^2\rangle \;=\; -\,E \;=\; \frac{1}{2}\,m(\alpha c)^2$$
  $$\Rightarrow \quad \langle v^2\rangle \;=\; (\alpha c)^2$$

- This tells us that the typical velocity of the electron in the hydrogen ground state is about $0.01c$. Since relativistic effects generally depend on $(v/c)^2$, relativistic corrections to the hydrogen atom are of the order of 10^{-4}.

Higher energy states and dependence on n

- If we were to solve for the energy eigenstates and eigenvalues, we would find that the energy levels of the hydrogen atom are quantized. The energy eigenvalue are given by:
  $$E_n \;=\; \frac{E_1}{n^2} \;=\; -\,\frac{13.6\text{ eV}}{n^2}$$

- Since the energy depends on the square of the velocity and inversely with the typical radial distance, we have:

$$v_n \;\propto\; \sqrt{E_n} \;\propto\; n \qquad\qquad r_n \;\propto\; \frac{1}{E_n} \;\propto\; n^2$$