QUANTUM MECHANICS: LECTURE 12

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Abstract

An extended review for the Hydrogen atom in the light of quantum theory

CONTENTS

THE CLASSICAL TWO-BODY PROBLEM: A REVIEW

In classical mechanics, the Hamiltonian H for two bodies interacting via a -time independent- potential is given by :

$$(H = \sum_{i=1}^{2} \frac{(p_i)^2}{2\mu} + V(r) \tag{1}$$

Where, $\mu = \frac{M+m}{Mm}$ is the reduced mass, and r is the radial separation between the bodies. p_i is the canonical momentum, that we may decompose into two parts :

$$p_r = \text{linear momentum} \qquad p_t = \frac{L}{r} \quad \text{angular momentum} \tag{2}$$

Hence, we may write (1) as :

$$H = \frac{p^2}{2\mu} + \frac{L^2}{2\mu r^2} + V(r) \tag{3}$$

since we know that the moment of inertia $I = \mu r^2$ we can therefore write: *recall that $L = I\omega$*

$$H = \frac{p^2}{2\mu} + \frac{L^2}{2I} + V(r) \tag{4}$$

The potential for the Hydrogen atom is the Coulomb potential, given by the formula:

$$V(r) = -\frac{ke^2}{r} \tag{5}$$

Hence we write the Hamiltonian function as :

$$H(p,r) = \frac{p^2}{2\mu} + \frac{L^2}{2\mu r^2} - \frac{ke^2}{r} \tag{6}$$

CANONICAL QUANTISATION OF THE H-ATOM HAMILTONIAN

We have the state $|\Psi\rangle$ of the H-atom. We the define the Hamiltonian operator $\hat{H}$ from quantising the Hamiltonian function in (6) that is :

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \frac{\hat{L}^2}{2\mu\hat{r}^2} - \frac{ke^2}{\hat{r}} \tag{7}$$

Due to the spherical symmetry, it is logical to project the state $|\Psi\rangle$ into the configuration space in spherical polar coordinates, hereby the the Hilbert space is :

$$\mathcal{H} : (\mathcal{L}, d\mu)$$

where $d\mu = dr \; d^2 d\phi \; \sin\phi^2 d\theta$, the volume element in the spherical polar coordinates and the wavefunction:

$$\psi(r, \phi, \theta) = \langle r, \phi, \theta | \psi \rangle$$

The H-atom is surely a stationary state $\Psi(r, \phi, \theta; t) = \psi(r, \phi, \theta) e^{-i\omega t}$. Hence the time-independent Schrödinger's equation is written as :

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(r, \phi, \theta) - \frac{ke^2}{r}\psi(r, \phi, \theta) = E\psi(r, \phi, \theta) \tag{8}$$

It was found -mathematically- that the wavefunction can be separated into three parts:

$$\psi(r, \phi, \theta) = R(r)P(\phi)F(\theta) \tag{9}$$

Where $R(r)$ is the radial function, and $P(\phi)F(\theta)$ make up the spherical Harmonics $Y(\phi, \theta)$.

QUANTUM NUMBERS

Each of the functions above is an eigenfunction for some observable about the hydrogen atom with an associated quantum number:

$R(r) \longrightarrow n = 1, 2, 3 \dots \qquad$ Principle quantum number

$F(\theta) \longrightarrow \ell = 0, 1, 2 \dots, n-1 \qquad$ orbital quantum number

$P(\phi) \longrightarrow m_\ell = -\ell, -\ell+1, \dots, +\ell \qquad$ megnatic quantum number

SOLUTION OF THE TISE FOR THE HYDROGEN

In fact, the H-atom is the only physical problem in quantum mechanics that can be solved exactly without using perturbation theory or other approximation methods. The TISE (8) can written as three differential equations:

$$\frac{1}{R(r)}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) + \frac{2\mu}{\hbar^2}\left(Er^2 + ke^2\right) = \ell(\ell+1) \tag{10a}$$

$$\frac{\sin\theta}{F(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{dF(\theta)}{d\theta}\right) + C_r\sin^2\theta = -C_\phi \tag{10b}$$

$$\frac{1}{P(\phi)}\frac{d^2P(\phi)}{d\phi^2} = C_\phi \tag{10c}$$

Solving the above equations to obtain the full expression for the wavefunction:

$$\boxed{\psi_{n,\ell,m_ell}(r, \phi, \theta) = A_{r\ell}\, e^{-r/a_0 r}\, r^\ell L_{n\ell}(\frac{r}{a_0}) \cdot Y_m^\ell(\phi, \theta)} \tag{11}$$

Where:

- $A_{r\ell}$, a normalisation constant.

- a_0, Bohr radius and it is equal to $\approx 0.53 \mathring{A}$.

- $L_{n\ell}(\frac{r}{a_0})$, the associated Laguerre polynomial.

- $Y_m^\ell(\phi, \theta)$, the associated spherical harmonics, the eigenfunction for the operators $\hat{L}$ and $\hat{L}_z$.

We can find the energy spectrum for the Hydrogen atom from 11 :

$$E_n = -\left(\frac{\mu e^2}{8\epsilon_0^2 \hbar^2}\right)\frac{1}{n^2} = -\frac{13.6 \ eV}{n^2} \tag{12}$$

With ϵ_o the vacuum permittivity.

As expected, the spectrum is discrete, but the spacing between the energy levels gets smaller and smaller as the principle quantum umber increases, figure 4

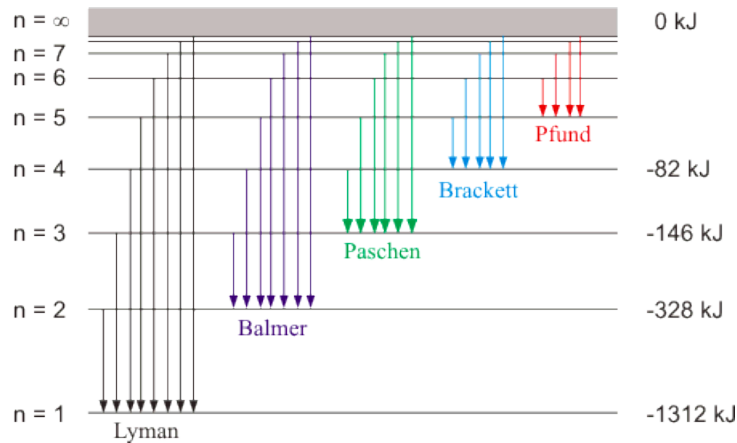If we wish to find the *ionisation energy* for hydrogen atom (i.e. the energy

Figure 1: Energy levels of the idealised H-atom and the well-known spectral series associated with electron transitions

required to free the electron from the atom) we let $n \rightarrow \infty$ we obtain:

$$E_\infty = 13.606 \ eV = Ry$$

it is equal to the Rydberg energy . For generality we can approximate the energy spectrum for any atom having Z electrons and μ reduced mass by:

$$E \sim -Z^2 \frac{\mu}{m_e} Ry \tag{13}$$

We ought to emphasise this is merely a hand-waving approximation ! The true energy spectrum for atoms (even the H-atom) is far more complicated, as we shall see later when we study the Real Hydrogen atom.

DEGENERACIES IN THE IDEAL H-ATOM

Since (11) depends on three quantum numbers , ℓ and m_ℓ, but the energy spectrum only depends on n, we have *degenerate states* in the idealised H-atom. Where we can have multiple wavefunctions having the same energy. For example, in the first excited state $n = 2$ we have the following wavefunctions:

$$\psi_{2,0,0} \quad \psi_{2,1,0} \quad \psi_{2,1,-1} \quad \psi_{2,1,1},$$

and so on . However, the number of electrons that can occupy each energy level is determined by **Pauli exclusion principle:** stating that no two electrons in the atom can wave an overlapping wavefunctions. In other words each wavefunction can describe one electron only. Meaning no electrons in the atom can have all of their quantum numbers identical.

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In addition to the quantum numbers (n, ℓ, m_ℓ) there is a forth quantum number of the electron, corresponding to its **spin**, which is an internal degree of freedom electrons are found to possess. The spin quantum number m_s can take one of two values $\pm\frac{1}{2}$ of multiples of $\hbar$. So far, this new quantum number does not seem to affect the energy spectrum. However, we shall see later that it player a röle in an interaction inside the H-atom affecting the energy spectrum.