T59(4): Theory of Absorption in Atomic H.

Consider one electron interacting with one proton. The classical hamiltonian is of the system is:

$$H = \frac{1}{2}\mu v^2 - \frac{e^2}{4\pi\epsilon_0 r} \quad -(1)$$

$$= \frac{p^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 r}$$

where p is the momentum associated with the reduced mass:

$$\mu = \frac{mM}{m+M}. \quad -(2)$$

Here $m << M$ is the mass of the electron and M is the mass of the proton. So:

$$\mu \sim m. \quad -(3)$$

In eq. (1):

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

is the Coulomb potential for interaction of $-e$ and e separated by r. The minus sign denotes attraction, and ϵ_0 is the vacuum permittivity in S.I. units.

Now use the operator equivalence of quantum mechanics:

$$\underline{p} = -i\hbar\,\underline{\nabla} \quad -(5)$$

to obtain the hamiltonian operator:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}. \quad -(6)$$

The $\hat{H}$ operator acts on the wave function ψ of the

2) Schroedinger equation:

$$\hat{H}\psi = E\psi. \quad -(7)$$

The solutions of eq. (7) are:

$$E_n = -\frac{\mu e^4}{32\pi^2\epsilon_0^2\hbar^2}\cdot\frac{1}{n^2}, \quad -(8)$$

$n = 1, 2, 3, \ldots$ Usually E_n are written:

$$E_n = -\frac{hcR_H}{n^2} \quad -(9)$$

where R_H is the Rydberg constant:

$$R_H = \frac{\mu e^4}{8\epsilon_0^2 h^2 c} = 2.179908\times10^{-18}\,J \quad -(10)$$

$= 1.097373\times10^5\ cm^{-1}$
$= 1319\ kJ\ mole^{-1}$
$= 13.67\ eV$

This is the minimum energy required to ionize the H atom from its ground state. The change in energy from state 1 to state 2 is:

$$\Delta E = hcR_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad -(11)$$

In the usual theory of absorption:

$$\Delta E = \hbar\omega \quad -(12)$$

and the mass of the photon is not considered.

3) Consider now the classical basis of the H atom, which is eq. (1). This equation is the non-relativistic limit of

$$H = \left(\mu^2 c^4 + p^2 c^2\right)^{1/2} - \mu c^2 + V \quad -(13)$$

which is the total relativistic energy of one electron attracted by one proton. The centre of mass of the system is moving with momentum $\underline{p}$. In eq. (13) the hamiltonian H has been written as the sum of the relativistic kinetic energy T and the potential energy V. If a photon is scattered by the H atom of reduced mass μ, the conservation of energy equation is:

$$\gamma m c^2 + \mu c^2 = \gamma' m c^2 + \left(\mu^2 c^4 + p^2 c^2\right)^{1/2} \quad -(14)$$

i.e.

$$T = (\gamma - \gamma') m c^2$$

$$= \left(\mu^2 c^4 + p^2 c^2\right)^{1/2} - \mu c^2 \quad - (15)$$

In this effect, the photon collides with the reduced mass μ of the electron / proton system, and the latter is set in motion with its <u>centre of mass</u> moving at momentum $\underline{p}$. In this collision, the Coulomb potential is not changed. The photon is <u>scattered off the atom</u>. <u>This is the Compton effect of one photon and one H atom.</u>

4) By comparison of eqns. (13) and (15), it is seen that the photon transfers the kinetic energy:

$$\boxed{T = (\gamma - \gamma')mc^2} \quad -(16)$$

to the atom.

If for some reason the potential energy changes from V_1 to V_2 in this process, then:

$$\gamma mc^2 + \mu c^2 + V_1 = \gamma' mc^2 + (\mu^2 c^4 + p^2 c^2)^{1/2} + V_2 \quad -(17)$$

where

$$V_1 = -\frac{e^2}{4\pi\epsilon_0 r_1}, \quad -(18)$$

$$V_2 = -\frac{e^2}{4\pi\epsilon_0 r_2}. \quad -(19)$$

So:

$$(\gamma - \gamma')mc^2 = (\mu^2 c^4 + p^2 c^2)^{1/2} - \mu c^2 + V_2 - V_1 \quad -(20)$$

If the photon ejects the electron from the atom, then:

$$r_2 \rightarrow \infty, \quad -(21)$$

so

$$(\gamma - \gamma')mc^2 = (\mu^2 c^4 + p^2 c^2)^{1/2} - \mu c^2 - V_1 \quad -(22)$$

and this is the photoelectric effect. The electron is ejected and the photon is scattered.

3)

From conservation of energy in the process of atomic absorption, the following equation is obtained:

$$E_1 + \gamma mc^2 = E_2 + \gamma' mc^2 \quad -(23)$$

where $$\gamma = \left(1 - \frac{v^2}{c^2}\right)^{-1/2}, \quad \gamma' = \left(1 - \frac{v'^2}{c^2}\right)^{-1/2} \quad -(24)$$

so: $$E_2 - E_1 = (\gamma - \gamma')mc^2 = \Delta T \quad -(25)$$

If the photon is stopped by the atom and not scattered:

$$\gamma' mc^2 = mc^2 \quad -(26)$$

so $$\boxed{\Delta E = (\gamma - 1)mc^2} \quad -(27)$$

Here E_2 is the final energy of the electron in the H atom from the Schroedinger equation, E_1 is the initial energy.

In the Einstein theory:

$$\Delta E = \hbar\omega, \quad -(28)$$

which is incorrect, because:

$$\hbar\omega = \gamma mc^2. \quad -(29)$$

Therefore Einstein was right to think of his theory of atomic absorption as heuristic. Momentum transfer is not even considered in that theory, but momentum transfer is observable in the Compton effect and Rayleigh scattering