1)

86(6): Rotational Motion in the H Atom

As described in Atkins the Schrödinger equation can be written as:

$$\frac{d^2 P}{dr^2} + \frac{2m}{\hbar^2} V_{eff} P = -\frac{2mE}{\hbar^2} P \quad -(1)$$

i.e.:

$$-\frac{\hbar^2}{2m}\frac{d^2 P}{dr^2} - V_{eff} P = EP \quad -(2)$$

where

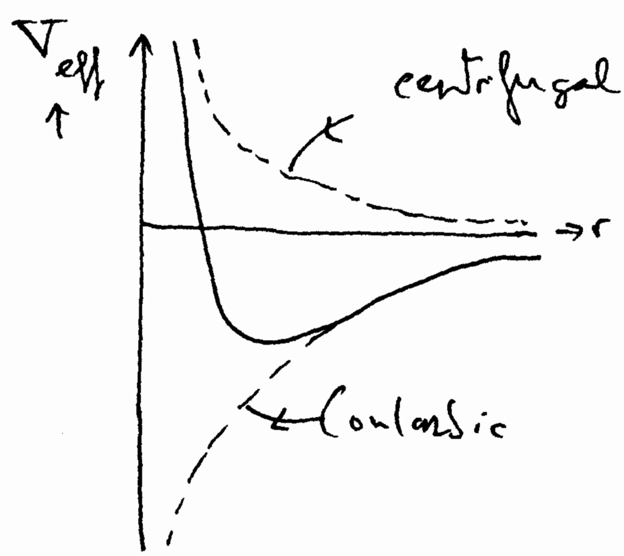
$$V_{eff} = \frac{e^2}{4\pi\epsilon_0 r} - \frac{l(l+1)\hbar^2}{2mr^2} \quad -(3)$$

Here:

$$P(r) = rR(r) \quad -(4)$$

where $R(r)$ is the radial wavefunction.

Here l is the rotational quantum number.



Therefore the next step is to incorporate the second term in eq (3) into previous calculations. This is the repulsive centrifugal term. The factor $l(l+1)$ comes from the equation of the spherical harmonics:

$$\Lambda^2 Y(\theta, \phi) = -l(l+1)\, Y(\theta, \phi) \quad -(5)$$

2) expressed in spherical polar coordinates:

$$\left.\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta \end{aligned}\right\} \quad -(6)$$,

Thus:

$$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}$$

$$:= \frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi) + \frac{1}{r^2}\Lambda^2. \quad -(7)$$

For constant r:

$$H = -\frac{\hbar^2}{2mr^2}\Lambda^2 \quad -(8)$$

where

$$I = mr^2 \quad -(9)$$

is the moment of inertia. Thus:

$$\Lambda^2\psi = -\frac{2IE}{\hbar^2}\psi \quad -(10)$$

which has the same form as eq. (5). Here:

$$l = 0, 1, 2, \ldots, \quad m_l = l, l-1, \ldots, -l. \quad -(11)$$

$$E = \frac{\hbar^2}{2I}l(l+1) \quad -(12)$$

by using:

$$J = I\omega, \quad E = \frac{J^2}{2I} \quad -(13)$$

3) and:

$$|\underline{J}| = \hbar \left(l(l+1)\right)^{1/2} \quad — (14)$$

Here l is the angular momentum quantum number. The m_l integer is the space quantum number. Angular momentum theory is central to quantum mechanics and is built up from these basic principles and operator theory. If for example we consider the component of $\underline{J}$ in Z, the m_l specifies its value. This must be integral, so the Z component of angular momentum is quantized. This is called space quantization.

The spherical harmonics are:

$$Y = \Theta \, \Phi \quad — (15)$$

where:

$$\Phi(\phi) = \left(\frac{1}{2\pi}\right)^{1/2} \exp\left(i m_l \phi\right) \quad — (16)$$

and

$$\Theta(\theta) = \left(\frac{(2l+1)(l-|m_l|))!}{2(l+|m_l|)!}\right) P_l^{|m_l|}(\cos\theta) \quad — (17)$$

where P are the associated Legendre functions.

Angular momentum is therefore specified by l and m_l (Z axis).

Radiative corrections are now incorporated into eq. (2) as follows:

$$-\frac{\hbar^2}{2m}\left(1+\frac{\alpha}{4\pi}\right)^2\frac{d^2P}{dr^2} - V_{eff}^{(0)}P = EP \quad -(18)$$

and this is equivalent by hypothesis to:

$$-\frac{\hbar^2}{2m}\frac{d^2P}{dr^2} - V_{eff}P = EP \quad -(19)$$

where:

$$V_{eff} = \frac{e^2}{4\pi\epsilon_0(r+r_{vac})} - \frac{l(l+1)\hbar^2}{2m(r+r_{vac})^2} \quad -(20)$$

and

$$V_{eff}^{(0)} = \frac{e^2}{4\pi\epsilon_0 r} - \frac{l(l+1)\hbar^2}{2mr^2} \quad -(21)$$

So to first order in α:

$$\boxed{-\frac{\hbar^2\alpha}{4\pi m}\frac{d^2P_0}{dr^2} = \left(V_{eff}^{(0)} - V_{eff}\right)P_0} \quad -(22)$$

and we assume:

$$P = P_0 \quad -(23)$$

where

$$P_0 = rR(r), \quad -(24)$$

$R(r)$ being the H radial wave functions. The computer algebra task is to solve eq. (22) for $r_{vac}(2s)$ and $r_{vac}(2p)$ and r.