Indian Institute of Technology, Guwahati

Guwahati, INDIA 781 039

Department of Chemistry Date: September - October 2017

CH101

Classes 6; Physical Chemistry

Hydrogenic Atoms

Hydrogenic atoms: Atoms (ions) with nuclear charge Ze, atomic number Z and single electron.

Examples: H, He^{+}, Li^{2+}, Be^{3+}, etc.

Both the nucleus and the electron are moving and the interaction between the nucleus and the electron is Coulombic interaction.

Potential energy, $V = -\dfrac{Ze^2}{4\pi\varepsilon_0 r}$

The Hamiltonian for the electron with mass m_e and nucleus with mass m_N is

$$H = \hat{E}_{k,electron} + \hat{E}_{k,nucleus} + \hat{V} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

r is the distance of the electron from the nucleus and ε_0 is the vacuum permittivity.

The first two terms (the kinetic energy operator) in the Hamiltonian corresponds to the coordinates of the electron and nucleus respectively, while the last term is the distance of the electron with from the nucleus.

Overall, there are two kinds of motions- the motion of the atom as a whole (nucleus and the electron) and the motion of the electron with respect to the nucleus. We need to convert the above Hamiltonian into coordinates involving these motions and then separate them.

That is we need to first convert the Hamiltonian into motions involving centre of mass and the motion of the electron with respect to that of the nucleus.

We have in essence

$$E = \frac{p_e^2}{2m_e} + \frac{p_N^2}{2m_N} + V$$

Where, $p_e = m_e \dot{x}_e$ and $p_N = m_N \dot{x}_N$

The centre of mass is located at $X = \frac{m_e}{m} x_e + \frac{m_N}{m} x_N$; where, $m = m_e + m_N$ and the separation of the particles is $x = x_e - x_N$

One can work out a little algebra and show that

$E = \frac{p_{c.m.}^2}{2m} + \frac{p^2}{2\mu} + V$; where $p_{c.m.}$ signifies the momentum of the whole atom and p signifies the momentum of the electron with respect to nucleus and the reduced mass, $\mu = \frac{m_e m_N}{m_e + m_N}$.

Thus one can rewrite the Hamiltonian as

$H = -\frac{\hbar^2}{2m}\nabla_{c.m.}^2 - \frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$; One can see that the first term of the Hamiltonian is independent of the relative position of the electron and nucleus and defines the motion of the atom as a whole; while the second and third terms are dependent on the relative positions of electron and nucleus.

Workout for the transformation of Cartesian coordinate of individual nucleus and electron (Hamiltonian) to Centre of Mass coordinates.

$$E = \frac{p_e^2}{2m_e} + \frac{p_N^2}{2m_N} + V$$

Where, $p_e = m_e \dot{x}_e$ and $p_N = m_N \dot{x}_N$

The centre of mass is located at $X = \frac{m_e}{m} x_e + \frac{m_N}{m} x_N$; where, $m = m_e + m_N$ and the separation of the particles is $x = x_e - x_N$

One can work out further

$$x_e = X + \frac{m_N}{m} x \text{ and } x_N = X - \frac{m_e}{m} x$$

$$p_e = m_e \dot{x}_e = m_e \dot{X} + \frac{m_e m_N}{m} \dot{x} \text{ and } p_N = m_N \dot{x}_N = m_N \dot{X} - \frac{m_e m_N}{m} \dot{x}$$

It follows that $\frac{p_e^2}{2m_e} + \frac{p_N^2}{2m_N} = \frac{1}{2} m\dot{X}^2 + \frac{1}{2}\mu\dot{x}^2 = \frac{p_{c.m.}^2}{2m} + \frac{p^2}{2\mu}$

$E = \frac{p_{c.m.}^2}{2m} + \frac{p^2}{2\mu} + V$; where $p_{c.m.}$ signifies the momentum of the whole atom and p signifies the momentum of the electron with respect to nucleus and the reduced mass, $\mu = \frac{m_e m_N}{m_e + m_N}$.

Thus one can rewrite the Hamiltonian as

$$H = -\frac{\hbar^2}{2m}\nabla_{c.m.}^2 - \frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r};$$

One can then use the principle of separation of variables and write

$\Psi_{total} = \Psi_{c.m.}\Psi$ and $E_{total} = E_{c.m.} + E$; where the first terms in the two equations relate to the total motion of the atom (wavefunction and energy) while the second terms relate to the relative motion.

One can finally write

$-\frac{\hbar^2}{2m}\nabla_{c.m.}^2\Psi_{c.m.} = E\Psi_{c.m.}$. This is the Schrödinger wave equation corresponding to the total motion of the atom and does not concern us at this moment (we want to find out the energy states of electron) and

$-\frac{\hbar^2}{2\mu}\nabla^2\Psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\Psi = E\Psi$. This is the Schrödinger wave equation corresponding to the motion of electron relative to nucleus and interaction between them and concerns us at the moment. The above equation will help us find the energy states of the electron in hydrogenic atoms.

If one looks carefully at the potential energy expression in the above wave equation, one sees that the interaction between the electron and nucleus depends on the distance of separation between the two and is centrosymmetric (independent of angle). Hence, it is easier to solve the equation if one converts the equation from Cartesian coordinate system to spherical polar coordinate system.

One can write the laplacian in spherical polar coordinate as

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2;$$

Where the legendrian, Λ^2, is

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$

One can write $\Psi(r,\theta,\phi) = R(r)\mathrm{Y}(\theta,\phi)$

The Schrödinger wave equation can then be written as,

$$-\frac{\hbar^2}{2\mu}\left\langle\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2\right\rangle R\mathrm{Y} + VR\mathrm{Y} = ER\mathrm{Y}$$

or

$$-\frac{\hbar^2}{2\mu}\left\langle\mathrm{Y}\frac{d^2R}{dr^2} + \frac{2\mathrm{Y}}{r}\frac{dR}{dr} + \frac{R}{r^2}\Lambda^2\mathrm{Y}\right\rangle + VR\mathrm{Y} = ER\mathrm{Y}$$

We multiply both sides by $\frac{r^2}{R\mathrm{Y}}$, then we get

$$-\frac{\hbar^2}{2\mu R}\left\langle r^2\frac{d^2R}{dr^2} + 2r\frac{dR}{dr}\right\rangle + Vr^2 - \frac{\hbar^2}{2\mu\mathrm{Y}}\Lambda^2\mathrm{Y} = Er^2$$

The third term in the above equation is independent of r and depends on the angular coordinates only.

One can write $\frac{\hbar^2}{2\mu Y}\Lambda^2 Y = \frac{\hbar^2 l(l+1)}{2\mu}$; (In order to get this one needs to solve the angle dependent wavefunctions called spherical harmonics and beyond the scope of the present class).

Then Schrödinger wave equation can then be written as,

$$-\frac{\hbar^2}{2\mu R}\left\langle r^2\frac{d^2R}{dr^2}+2r\frac{dR}{dr}\right\rangle+Vr^2-\frac{\hbar^2 l(l+1)}{2\mu}=Er^2$$

or

$$-\frac{\hbar^2}{2\mu}\left\langle\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}\right\rangle+V_{eff}R=ER$$

where

$$V_{eff}=-\frac{Ze^2}{4\pi\varepsilon_0 r}-\frac{\hbar^2 l(l+1)}{2\mu r^2}$$

The general solution for the radial wavefunctions for an electron with quantum numbers n and l are the real functions and written as

$$R_{n.l}(r) = N_{n.l}\left(\frac{\rho}{n}\right)^{l} L_{n,l}(\rho)e^{-\rho/2n}$$

Here L is a polynomial in ρ called an associated Laguerre polynomial.

Hydrogenic Radial Wavefunctions; Some examples; Here $\rho = \frac{2Zr}{a_0}$			
Orbital	n	l	**$R_{n.l}$**
1s	1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho/2}$
2s	2	0	$\frac{1}{2(2)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\frac{1}{2}\rho)e^{-\rho/4}$
2p	2	1	$\frac{1}{4(6)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}\rho e^{-\rho/4}$
3s	3	0	$\frac{1}{9(3)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}(6-2\rho+\frac{1}{9}\rho^2)e^{-\rho/6}$
3p	3	1	$\frac{1}{27(6)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}(4-\frac{1}{3}\rho)\rho e^{-\rho/6}$
3d	3	2	$\frac{1}{81(30)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}\rho^2 e^{-\rho/6}$

The Spherical Harmonics, $Y_{l,m_l}(\theta,\phi)$		
l	m	$Y_{l,m_l}(\theta,\phi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{\pm i\phi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
2	±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta e^{\pm i\phi}$
2	±2	$\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta e^{\pm 2i\phi}$
3	0	$\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta-3\cos\theta)$
3	±1	$\mp\left(\frac{21}{64\pi}\right)^{1/2}(5\cos^2\theta-1)\sin\theta e^{\pm i\phi}$
3	±2	$\left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta e^{\pm 2i\phi}$
3	±3	$\mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta e^{\pm 3i\phi}$

The energy of the hydrogenic orbit is given by

$$E_n = -\frac{Z^2\mu e^4}{32\pi^2\varepsilon_0^2\hbar^2 n^2} \text{ with n = 1, 2, 3….}$$