1 D

$$i\hbar \frac{\partial \Psi}{\partial t}(x,t) = \hat{H}(x)\,\Psi(x,t)$$

$$\int_{-\infty}^{\infty} |\Psi|^2 \, dx = 1$$

$$\hat{H}\Psi_n = E_n \Psi_n$$

$$\exists\ \Psi_n(x,t) = \Psi_n(x)\, e^{\frac{-iE_n t}{\hbar}}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

$$[\hat{X}, \hat{P}] = i\hbar$$

$$\hat{P} \equiv -i\hbar \frac{d}{dx}$$

3 D

$$i\hbar \frac{\partial \Psi(\bar{r},t)}{\partial t} = \hat{H}(\bar{r})\,\Psi(\bar{r},t)$$

$$\int_{-\infty}^{\infty} |\Psi|^2 \, d^3\bar{r} = 1$$

$$d^3\bar{r} = dx\,dy\,dz$$
$$= r^2\, d\theta\, d\phi \sin\theta\, dr$$

$$\hat{H}\,\Psi_n(\bar{r}) = E_n \Psi_n(\bar{r})$$

$$\exists\ \Psi_n(\bar{r},t) = \Psi_n(\bar{r})\, e^{\frac{-iE_n t}{\hbar}}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\bar{\nabla}^2 + V(\bar{r})$$

$$[\hat{R}_i, \hat{P}_j] = i\hbar\,\delta_{ij}$$

$$\hat{R}_i \equiv x, y, z$$

$$\hat{P}_j \equiv -i\hbar\frac{d}{dx},\ -i\hbar\frac{d}{dy},\ -i\hbar\frac{d}{dz}$$

$$\hat{\bar{P}} \equiv -i\hbar\bar{\nabla} = -i\hbar\left(\frac{d}{dx}, \frac{d}{dy}, \frac{d}{dz}\right)$$

Spherical coordinates

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

$$f(\bar{r}) = f(x, y, z) = f(r, \theta, \phi)$$

$$\Psi(\bar{r}) = R(r)\, Y(\theta, \phi)$$

$$\hat{H}\Psi = E\Psi$$

$$\hat{H} R Y = E R Y$$

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]$$

$$+ VRY = ERY$$

$$\Rightarrow \quad \frac{1}{R}\frac{d}{dr} r^2\frac{dR}{dr} - \frac{2mr^2}{\hbar^2}\left[V(r) - E\right]$$

$$+ \frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\} = 0$$

$$= l(l+1)$$

$$Y_l^m(\theta, \phi) = \epsilon\left\{\frac{(2l+1)}{4\pi}\left[\frac{(l-|m|)!}{(l+|m|)!}\right]\right\}^{1/2} e^{im\phi} P_l^m(\cos\theta)$$

$$\epsilon = (-1)^m, \ \forall m \geq 0$$
$$= 1, \ \forall m \leq 0$$

$$P_l^m(x) \equiv (1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|} P_l(x)$$

$$P_l(x) \equiv \frac{1}{2^l l!}\frac{d^l}{dx^l}(x^2-1)^l$$

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \left[Y_\ell^m(\theta,\phi)\right]^* Y_{\ell'}^{m'}(\theta,\phi) = \delta_{\ell,\ell'}\delta_{m,m'}$$

$$u = r R(r)$$

$$\Rightarrow \frac{d^2 u}{dr^2} - \frac{2m}{\hbar^2}\left[V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u(r) = E\,u(r)$$

$$\int_0^\infty |u|^2 dr = 1$$

For H atom $V(r) = \dfrac{-e^2}{4\pi\epsilon_0 r}$

Now use $K = \sqrt{\dfrac{-2mE}{\hbar^2}}$, $\rho = Kr$

$$\rho_0 = \frac{me^2}{2\pi\epsilon_0\hbar^2 K}$$

$$\Rightarrow \frac{d^2u(\rho)}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right]u(\rho)$$

For $\rho \to \infty$ we get $u''(\rho) \approx u(\rho)$

$$\Rightarrow u(\rho) \sim e^{-\rho}$$

For $\rho \to 0$ we get

$$u''(\rho) \approx \frac{\ell(\ell+1)u}{\rho^2}$$

$$\Rightarrow \quad u(\rho) \approx C\rho^{1+l} + D\rho^{-l}$$

$$D = 0 \quad \Rightarrow u(\rho) \sim \rho^{1+l}$$

Now substitute $u(\rho) = \rho^{1+l} e^{-\rho} v(\rho)$

$$\Rightarrow \rho \frac{d^2 v}{d\rho^2} + 2(l+1-\rho)\frac{dv}{d\rho} + [\rho_0 - 2(l+1)]v = 0$$

Now try $v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$

$$\Rightarrow \sum_{j=0}^{\infty} j(j+1)\rho^j c_{j+1} + 2(l+1)\sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j$$

$$-2\sum_{j=0}^{\infty} j c_j \rho^j + [\rho_0 - 2(l+1)]\sum_{j=0}^{\infty} c_j \rho^j = 0$$

Equating co-efficients at each j gives

$$c_{j+1} = \left[\frac{2(j+1+l) - \rho_0}{(j+1)(j+2l+2)}\right] c_j$$

For large j we get $c_{j+1} = \dfrac{2c_j}{j+1}$

$$\Rightarrow c_j = \frac{2^j}{j!} c_0 \quad \Rightarrow v(\rho) = c_0 e^{2\rho}$$

$$\Rightarrow u(\rho) \to \infty \text{ as } \rho \to \infty$$

Not physical.

$$\Rightarrow C_{1+j_{max}} = 0 \quad \Rightarrow 2(j_{max} + l + 1) - \rho_0 = 0$$

$$\Rightarrow n \equiv j_{max} + l + 1$$

= principal quantum number

$$\rho_0 = 2n$$

$$E = \frac{-\hbar^2 k^2}{2m} = \frac{-me^4}{8\pi^2 \epsilon_0^2 \hbar^2 \rho_0^2}$$

$$E_n = \left[\frac{-m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3 \ldots$$

$$E_1 = -13.6 \, eV$$

$$K = \frac{1}{an}, \quad a = \frac{4\pi\epsilon_0 \hbar^2}{me^2} = 0.529 \times 10^{-10} \, m$$

a = Bohr radius, $\rho = \frac{r}{an}$

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi)$$

$$R_{nl}(r) = \frac{\rho^{l+1} e^{-\rho}}{r} v(\rho)$$

$v(\rho)$ is a polynomial of degree $n-l-1$.

$$\psi_{100}(\bar{r}) = \frac{e^{-r/a}}{\sqrt{\pi a^3}}$$

$$l = 0, 1, 2, \ldots n-1$$

$$d(n) = \sum_{l=0}^{n-1} (2l+1) = n^2$$

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho)$$

where $L_{q-p}^{p}(x) \equiv (-1)^p \frac{d^p}{dx^p} L_q(x)$

where $L_q(x) = e^x \frac{d^q}{dx^q}\left(e^{-x} x^q\right)$.

$$\psi_{nlm}(\bar{r}) = \left[\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{1/2} e^{-\frac{r}{na}} \left[L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)\right] Y_l^m(\theta,\phi)$$

$$\int \psi_{nlm}^* \psi_{n'l'm'} r^2 \sin\theta \, d\theta \, d\phi \, dr = \delta_{n,n'} \delta_{l,l'} \delta_{m,m'}$$

Note $l \geq 0$, $l < n$, $n > 0$

$|m| \leq l$.

Hydrogen spectrum

$$E_\gamma = E_i - E_f = -13{\cdot}6\,\text{eV}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$E_\gamma = h\nu, \quad \lambda = c/\nu$$

$$\Rightarrow \lambda^{-1} = R\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$$

$$R = \frac{m}{4\pi c\hbar^3}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 = 1{\cdot}097 \times 10^7 \, m^{-1}$$ = Rydberg constant