Classical hamiltonian of two charged particles ($\bar{e}$ & p^+)

$$H = \frac{p^2}{2\mu} - \frac{e^2}{r}$$ Hydrogen atom at rest (no CM motion)

$$\mu = \frac{m_e m_p}{m_e + m_p} \approx m_e\left(1 - \frac{m_e}{m_p}\right)$$ reduced mass

One of the first "solved" quantum problems

Bohr's quantization rules

$$E = \frac{1}{2}\mu v^2 - \frac{e^2}{r} \qquad \frac{\mu v^2}{r} = \frac{e^2}{r^2}$$

$$\mu v r = n \cdot \hbar$$ Quantization of Ang. Mom

$$\boxed{\begin{array}{l} E_R \simeq 13.6\,\text{eV} \\ a_0 \simeq 0.52\,\text{Å} \end{array}}$$
$\alpha = 1/137$

$$E_n = -\left(\frac{\mu e^4}{2\hbar^2}\right)\frac{1}{n^2} = -\frac{E_R}{n^2}$$

$$r_n = n^2 a_0 = n^2 \frac{\hbar^2}{\mu e^2}$$

$$E_R = \frac{\mu e^4}{2\hbar^2} = \frac{\alpha^2}{2}\mu c^2 = \frac{e^2}{2a_0} \qquad \alpha = \frac{e^2}{\hbar c}$$ fine structure constant

More "realistic" atom

$$H = \frac{p^2}{2\mu} - \frac{e^2}{r} = \frac{1}{2}\mu\left(v_r^2 + v_\perp^2\right) - \frac{e^2}{r}$$

$$\vec{v}_\perp = \frac{\vec{r} \times \vec{v}}{r} = \frac{1}{\mu r}|\vec{L}|$$

$$H = \frac{1}{2}\mu \dot{r}^2 + \frac{1}{2\mu r^2}L^2 - \frac{e^2}{r}$$

Quantum Hamiltonian [r-representation, central symmetry)

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{r} \qquad \hat{H}\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi)$$

3 ind. variables → 3 quantum numbers

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \underbrace{\frac{1}{2\mu r^2}\frac{\hat{L}^2}{\hbar^2}}_{}\right] - \frac{e^2}{r}$$

acts only on angular part of the wave function

As expected for the spherically symmetric potential

$$[\hat{H}, \hat{L}^2] = 0$$

if $\hat{H}|\psi\rangle = E|\psi\rangle$ then $L^2|\psi\rangle = \hbar^2 \ell(\ell+1)|\psi\rangle$

and $\psi(r,\theta,\varphi) = R(r)\, Y_{\ell m}(\theta,\varphi)$

$Y_{\ell m}(\theta,\varphi)$ – spherical harmonics

$$\hat{L}^2\, Y_{\ell m} = \ell(\ell+1)\, Y_{\ell m}$$

$$L_z\, Y_{\ell m} = m\, Y_{\ell m}$$

$$Y_{\ell m}(\theta,\varphi) = (-1)^m \sqrt{\frac{2\ell+1}{4\pi}\,\frac{(\ell-m)!}{(\ell+m)!}}\; P_\ell^m(\cos\theta)\, e^{im\varphi}$$

$$\int Y_{\ell m}^*(\theta,\varphi)\, Y_{\ell' m'}(\theta,\varphi)\, d\Omega = \delta_{\ell\ell'}\,\delta_{mm'}$$

$$\hat{L}^\pm = \hat{L}_x \pm i\hat{L}_y$$

$$\hat{L}^+\, Y_{\ell m} = \sqrt{(\ell-m)(\ell+m+1)}\; Y_{\ell,m+1}$$

$$\hat{L}^-\, Y_{\ell m} = \sqrt{(\ell+m)(\ell-m+1)}\; Y_{\ell,m-1}$$

Remaining radial part

$$\left[-\frac{\hbar^2}{2\mu}\,\frac{1}{r}\,\frac{\partial^2}{\partial r^2} r + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} - \frac{e^2}{r}\right] R_{n\ell}(r) = E_n R_{n\ell}(r)$$

No explicite m dependence

$$R_{n\ell} = -\sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}}\; e^{-\varrho/2}\, \varrho^\ell\, L_{n+\ell}^{2\ell+1}(\varrho)$$

here $\varrho = \frac{2r}{na_0}\; Z$

No E-dependence on ℓ either!

$$E_n = -\frac{e^2}{2n^2 a_0} = -\frac{E_R}{n^2}$$

n state is $2n^2$ degenerate

for H-like ions Z^2

$\ell = 0 \longrightarrow S$ — sharp

$\ell = 1 \longrightarrow P$ — principle

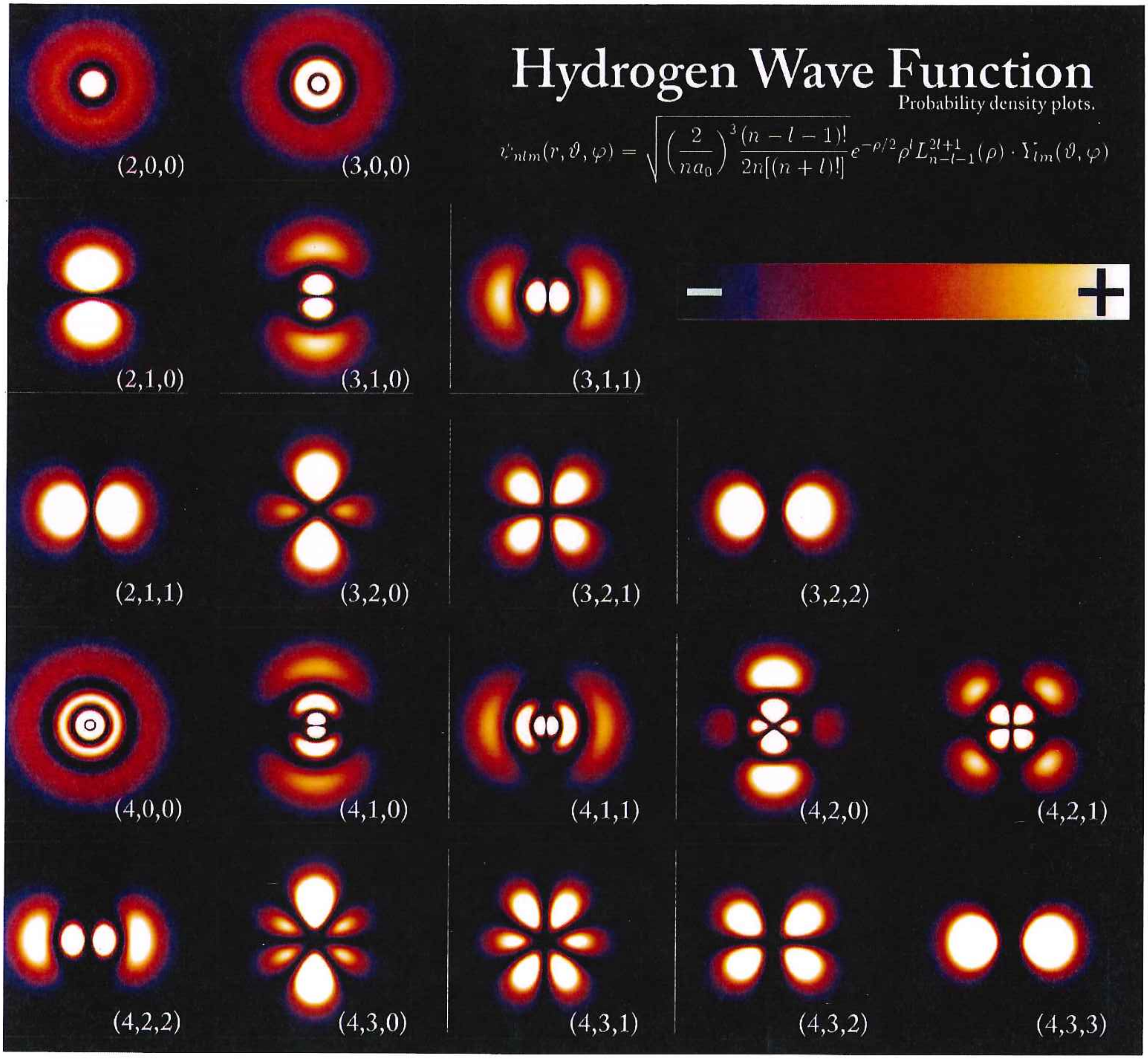
$\ell = 2 \longrightarrow D$ — diffuse

$\ell = 3 \longrightarrow F$ — fundamental

$\ell = 4 \longrightarrow G$

$\ell = 5 \longrightarrow H$

$n = 3 \quad \ell = 2 \longrightarrow 3D$ state



Hydrogen Wave Function
Probability density plots.
$\psi_{nlm}(r,\vartheta,\varphi)=\sqrt{\left(\frac{2}{na_0}\right)^3\frac{(n-l-1)!}{2n[(n+l)!]}}e^{-\rho/2}\rho^l L_{n-l-1}^{2l+1}(\rho)\cdot Y_{lm}(\vartheta,\varphi)$
−
+
(2,0,0)
(3,0,0)
(2,1,0)
(3,1,0)
(3,1,1)
(2,1,1)
(3,2,0)
(3,2,1)
(3,2,2)
(4,0,0)
(4,1,0)
(4,1,1)
(4,2,0)
(4,2,1)
(4,2,2)
(4,3,0)
(4,3,1)
(4,3,2)
(4,3,3)

Electro-magnetic field → approximate with a plane wave

$$\vec{A}(\vec{r},t) = A(t)\, e^{i\vec{k}\vec{r}}$$

$$\vec{r} = \vec{r}_0 + \delta\vec{r}$$

$$\vec{A}(\vec{r},t) = \vec{A}(\vec{r}_0 + \delta\vec{r}, t) \simeq \vec{A}(t)\, e^{i\vec{k}\vec{r}_0} \cdot e^{i\vec{k}\delta\vec{r}} =$$

$$= \vec{A}(t)\, e^{i\vec{k}\vec{r}_0} \, (1 + \underbrace{\vec{k}\,\delta\vec{r}}_{\text{dipole approximation}} + \dots$$

$$\vec{k}\,\delta\vec{r} = \frac{2\pi\,\delta r}{\lambda} \ll 1$$

Hamiltonian

$$\hat{H} = \frac{1}{2\mu}\left(\hat{\vec{p}} + \frac{e}{c}\hat{\vec{A}}\right)^2 + V(r) = -\frac{\hbar^2}{2\mu}\Big(\nabla - \underbrace{\frac{ie}{\hbar c}\vec{A}(\vec{r}_0,t)}_{\text{does not depend on } \vec{r}}\Big)^2 + V(\vec{r})$$

$$\psi(\vec{r},t) \longrightarrow e^{\frac{ie}{\hbar c}\vec{A}(\vec{r}_0,t)\cdot\vec{r}}\, \tilde{\psi}(\vec{r},t)$$

$$\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t}$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2\tilde{\psi} + V(\vec{r})\tilde{\psi}\right)\cancel{e^{\frac{ie}{c\hbar}\vec{A}(\vec{r}_0,t)\cdot\vec{r}}} = i\hbar\, \cancel{e^{\frac{ie}{c\hbar}A(\vec{r}_0,t)\vec{r}}}\left[\frac{\partial\tilde{\psi}}{\partial t} + \underbrace{\frac{ie}{c\hbar}\dot{\vec{A}}\vec{r}\tilde{\psi}}_{\text{extra term}}\right]$$

$$-\frac{\hbar^2}{2\mu}\nabla^2\tilde{\psi} + \frac{e}{c}\underbrace{\dot{\vec{A}}}_{= -\vec{E}}\cdot\vec{r}\,\tilde{\psi} + V(r)\tilde{\psi} = i\hbar\frac{\partial\tilde{\psi}}{\partial t}$$

reminder $\vec{E} = -\frac{1}{c}\frac{\partial\vec{A}}{\partial t}$

$$\hat{H} = \underbrace{\frac{\hat{p}^2}{2\mu} + V(r)}_{H_0} - \underbrace{e\vec{r}\cdot\vec{E}}_{\text{interaction Hamiltonian}}$$

Notice that we would get the same result by using $V_{int} = -\vec{d}\cdot\vec{E}$ ↑ dipole moment

H- atom in external e-m fields

Proper description $\vec{A}$ - vector potential

$$\vec{B} = \nabla \times \vec{A}(r)$$

$$\vec{E} = -\nabla \varphi - \frac{1}{c}\frac{\partial \vec{A}}{\partial t}$$

We'll usually work at radiation gauge

$\varphi = 0 \quad \nabla \vec{A} = 0$

Then proper modification of the Hamiltonian

$$\hat{H} = \frac{1}{2\mu}\left[\hat{\vec{p}} - \underbrace{\frac{e}{c}\hat{A}}_{\text{external field}}\right]^2 + V(\vec{r})$$

Uniform magnetic field (it is easy to be uniform on atomic scale)

$$\hat{\vec{A}} = -\frac{1}{2}\hat{\vec{r}} \times \vec{B}$$

$$\left[\hat{\vec{p}} - e\hat{\vec{A}}\right]^2 = \hat{p}^2 + \frac{e}{2c}\left[\hat{\vec{p}}(\hat{\vec{r}} \times \vec{B}) + (\hat{\vec{r}} \times \vec{B})\hat{\vec{p}}\right] + \frac{e^2}{4c^2}(\hat{\vec{r}} \times \vec{B})^2$$

$$= \hat{p}^2 + \frac{e}{2c}\left[\vec{B}\underbrace{(\hat{\vec{p}} \times \hat{\vec{r}})}_{-\vec{L}} - \underbrace{(\hat{\vec{r}} \times \hat{\vec{p}})}_{\vec{L}}\vec{B}\right] + \frac{e^2}{4c^2}r_\perp^2 B^2$$

$$\hat{H} = \underbrace{\frac{\hat{p}^2}{2\mu} + V(\vec{r})}_{\hat{H}_0 \text{ internal hamiltonian}} - \frac{e}{2\mu c}\vec{L}\cdot\vec{B} + \frac{e^2}{8\mu c^2}r_\perp^2 B^2$$

Linear term

$$\hat{H}_1 = -\frac{e}{2\mu c}\hat{\vec{L}}\cdot\vec{B} = \underbrace{\frac{|e|\hbar}{2\mu c}}_{\mu_B \text{ Bohr magneton}} \cdot \frac{1}{\hbar}\hat{\vec{L}}\cdot\vec{B} = \underbrace{\mu_B \frac{\hat{\vec{L}}}{\hbar}}_{-\vec{\mu}_e} \cdot \vec{B} = -\vec{\mu}_e \cdot \vec{B}$$

equivalent to the potential energy of a magnetic dipole $\vec{\mu}$ in the external magnetic field $-\vec{\mu}\cdot\vec{B}$

$$\hat{H}_2 = \frac{e^2}{8\mu c^2}r_\perp^2 B^2 = \frac{e^2}{8\mu c^2}(x^2+y^2)\cdot B^2 \quad \text{for } \vec{B} = B e_z$$