4. The Hydrogen Atom

spectrum of atomic hydrogen

electric discharge through hydrogen gas; molecules are dissociated and excited atoms emit light

spectrum has discrete lines

[Figure: spectrum of atomic hydrogen, Fig. 10.1]

lines in the visible region: *Balmer series*

$$\tilde{\nu} = \frac{1}{\lambda} = R_{\mathrm{H}}\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \quad n = 3, 4, \ldots$$

$R_{\mathrm{H}} = 109677\,\mathrm{cm}^{-1}$ Rydberg constant for hydrogen

further series of lines discovered later:
Lyman series: ultraviolet
Paschen series: infrared

general fit for spectral lines

$$\tilde{\nu} = \frac{1}{\lambda} = R_{\mathrm{H}}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right), \quad n_2 = n_1 + 1, n_1 + 2, \ldots$$

$n_1 = 1$: Lyman
$n_1 = 2$: Balmer
$n_1 = 3$: Paschen

goal: understand the line spectrum

hydrogen atom = proton + electron

six degrees of freedom

wavefunction has six arguments, three spatial coordinates for the nucleus, $\vec{x}_N = (x_N, y_N, z_N)$, and three spatial coordinates for the electron, $\vec{x}_e = (x_e, y_e, z_e)$

consider the more general case of hydrogen-like or hydrogenic atoms: nucleus with atomic number Z and *one* electron

single hydrogen-like atom in empty space

$$\hat{H}_{\text{tot}}\psi(\vec{x}_N, \vec{x}_e) = E_{\text{tot}}\psi(\vec{x}_N, \vec{x}_e)$$

$$\hat{H}_{\text{tot}} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 + V(r)$$

$$\nabla_N^2 = \frac{\partial^2}{\partial x_N^2} + \frac{\partial^2}{\partial y_N^2} + \frac{\partial^2}{\partial z_N^2}$$

$$\nabla_e^2 = \frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2}$$

$$V(r) = -\frac{Ze \cdot e}{4\pi\epsilon_0}\frac{1}{r}$$

r distance of electron from nucleus

$$\epsilon_0 = 8.854 \times 10^{-12}\,\mathrm{J}^{-1}\mathrm{C}^2\mathrm{m}^{-1}$$

central theorem of mechanics: motion of a complex system = motion (translation) of the center of mass plus motion around the center of mass

$$\hat{H}_{\text{tot}} = -\frac{\hbar^2}{2m}\nabla^2_{\text{c.m.}} - \frac{\hbar^2}{2\mu}\nabla^2 + V(r)$$

$m = m_N + m_e$ total mass

$$\frac{1}{\mu} = \frac{1}{m_N} + \frac{1}{m_e}, \qquad \mu \text{ reduced mass}$$

$m_N \gg m_e \Longrightarrow \mu \approxeq m_e$, $\vec{x}_{\text{c.m.}} \approxeq \vec{x}_N$ and $\vec{x} \approxeq \vec{x}_e$

$$\psi(\vec{x}_N, \vec{x}_e) = \psi(\vec{x}_{\text{c.m.}}, \vec{x})$$

$$\hat{H}_{\text{tot}} = \hat{H}_{\text{c.m.}} + \hat{H}$$

$$E_{\text{tot}} = E_{\text{c.m.}} + E$$

separation of variables

$$\psi(\vec{x}_{\text{c.m.}}, \vec{x}) = \psi_{\text{c.m.}}(\vec{x}_{\text{c.m.}})\psi(\vec{x})$$

$$\hat{H}_{\text{c.m.}}\psi_{\text{c.m.}} = E_{\text{c.m.}}\psi_{\text{c.m.}}$$

Schrödinger equation for a free particle

$$\psi_{\text{c.m.}}(\vec{x}_{\text{c.m.}}) \sim \exp(i\vec{k} \cdot \vec{x}_{\text{c.m.}})$$

$$\hat{H}\psi(\vec{x}) = E\psi(\vec{x})$$

Schrödinger equation for internal degrees of freedom

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r}\psi = E\psi$$

$$\nabla^2\psi + \frac{Ze^2\mu}{2\pi\epsilon_0\hbar^2}\frac{1}{r}\psi = -\frac{2\mu E}{\hbar^2}\psi$$

$$\nabla^2\psi + \frac{\gamma}{r}\psi = \epsilon\psi$$

$$\gamma \equiv \frac{Ze^2\mu}{2\pi\epsilon_0\hbar^2}, \quad \epsilon \equiv -\frac{2\mu E}{\hbar^2}$$

$$[\epsilon] = (\mathrm{kg\,J})/(\mathrm{J^2\,s^2}) = \mathrm{kg}/(\mathrm{kg\,m^2 s^{-2} s^2}) = 1/\mathrm{m^2}$$

Coulomb potential: spherical symmetry $\Longrightarrow$ spherical coordinates

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

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

$$\frac{1}{r}\frac{\partial^2}{\partial r^2} r\psi + \frac{1}{r^2}\Lambda^2\psi + \frac{\gamma}{r}\psi = \epsilon\psi$$

Coulomb potential has no angular dependence $\Longrightarrow$ separation of variables

$$\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)$$

$$\left(\frac{1}{r}\frac{\partial^2}{\partial r^2} rR\right) Y + \frac{1}{r^2} R\Lambda^2 Y + \frac{\gamma}{r} RY = \epsilon RY$$

multiply on both sides by $r^2/(RY)$

$$r^2 \frac{1}{rR}\frac{d^2}{dr^2} rR + \frac{1}{Y}\Lambda^2 Y + \gamma r = \epsilon r^2$$

$$\Longrightarrow$$

$$\frac{1}{Y}\Lambda^2 Y = \text{const}$$

$$r^2 \frac{1}{rR}\frac{d^2}{dr^2} rR + \gamma r - \epsilon r^2 = -\text{const}$$

$$\Lambda^2 Y = \text{const}\, Y, \qquad \text{3-D rigid rotor}$$

$$-l(l+1) \equiv \text{const}$$

$$\Lambda^2 Y = -l(l+1)\, Y$$

$$Y_{l,m_l}(\theta,\phi) = \Theta_{l,m_l}(\theta)\Phi_{m_l}(\phi)$$

$$r^2 \frac{1}{rR}\frac{d^2}{dr^2} rR + \gamma r - \epsilon r^2 = l(l+1)$$

$$\frac{d^2}{dr^2} rR + \left(\frac{\gamma}{r} - \frac{l(l+1)}{r^2}\right) rR = \epsilon r R \qquad \text{radial wave equation}$$

↑ Coulomb potential

↑ effective potential, centripetal force

solve the radial wave equation

large r:

$$\frac{d^2}{dr^2} rR = \epsilon r R$$

$$(rR' + R)' = rR'' + 2R' = \epsilon r R$$

$rR'' = \epsilon r R$ for large r

$$R'' = \epsilon R$$

$$R(r) \sim \exp(-\sqrt{\epsilon} r)$$

$$R(r) = f(r) \exp(-\sqrt{\epsilon} r)$$

nondimensionalize:

$$r = \frac{\varrho}{2\sqrt{\epsilon}}, \qquad n \equiv \frac{\gamma}{2\sqrt{\epsilon}}$$

$$f(\varrho) \equiv \varrho^l L(\varrho)$$

insert into radial wave equation

$$L''(\varrho) + \left[2(l+1) - \varrho\right] L'(\varrho) + [n - (l+1)]\, L(\varrho) = 0$$

associated Laguerre equation

acceptable solutions if

$\boldsymbol{n = 1, 2, \ldots}$ **and** $\boldsymbol{0 \le l \le n-1}$

$$n = \frac{\gamma}{2\sqrt{\epsilon}} \Longrightarrow$$

$$\boldsymbol{E_n = -\frac{Z^2 e^4 \mu}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2}}$$

$E < 0$: bound states

$E = 0$: electron at ∞ and at rest: $V(\infty) = 0$

$$R_{n,l}(\varrho) = \varrho^l L_{n,l}(\varrho)\,\exp(-\varrho/2)$$

$L_{n,l}$ associated Laguerre polynomials

$$\varrho = 2\sqrt{\epsilon}\, r = 2\sqrt{-\frac{2\mu E}{\hbar^2}}\, r$$

$$= 2\frac{\mu Z e^2}{4\pi\epsilon_0 \hbar^2}\frac{r}{n}$$

$$= 2Z\frac{\mu}{m_e}\frac{m_e e^2}{4\pi\epsilon_0 \hbar^2}\frac{r}{n}$$

$$r = n\frac{m_e}{\mu}\frac{a_0}{2Z}\varrho$$

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 52.9177\,\text{pm} \qquad \text{Bohr radius}$$

$$\mu \approxeq m_e \Rightarrow r = n\frac{a_0}{2Z}\rho$$

$$\rho \equiv \frac{2Z}{a_0}r$$

besides the discrete spectrum, the Schrödinger equation for hydrogenic atoms also has a continuous part:

$E \geq 0$: nucleus plus free electron; atom has been completely ionized

three quantum numbers for bound states:

principal quantum number: $\boldsymbol{n = 1, 2, \ldots}$
energy level, radial wavefunction

azimuthal quantum number:
$\boldsymbol{l = 0, 1, 2, \ldots, n-1}$

magnetic quantum number:
$\boldsymbol{m_l = -l, -l+1, \ldots, l-1, l}$

} angular wavefunction (azimuthal and magnetic quantum numbers)

energy: E_n*, no dependence on* l *and* m_l
energy levels are degenerate, except $n = 1$, ground state

$$\boldsymbol{\psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)\Theta_{l,m_l}(\theta)\Phi_{m_l}(\phi)}$$ **atomic orbital**

by definition, an orbital depends on the *spatial* coordinates of *one* and *only one* electron

hydrogen atom

$$E_n = -\frac{e^4\mu}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2}$$

$$E_n = -\frac{hcR_H}{n^2}, \quad hcR_H \equiv \frac{e^4\mu}{32\pi^2\epsilon_0^2\hbar^2}$$

[Figure: energy levels of hydrogen atom, Fig. 10.5]

spectrum of atomic hydrogen

$$E_{n_2} - E_{n_1} = -\frac{hcR_H}{n_2^2} - \left(-\frac{hcR_H}{n_1^2}\right), \quad h\nu = \left|E_{n_2} - E_{n_1}\right|$$

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \left|\frac{R_H}{n_1^2} - \frac{R_H}{n_2^2}\right|$$

agrees with experiments $\Longrightarrow$ **we have calculated** $\boldsymbol{R_H}$

$$R_H = \frac{e^4 \mu}{32\pi^2 \epsilon_0^2 \hbar^2 hc}$$

$$\frac{1}{\mu} = \frac{1}{m_p} + \frac{1}{m_e} = \frac{1}{1.67262 \times 10^{-27}\,\mathrm{kg}} + \frac{1}{9.10938 \times 10^{-31}\,\mathrm{kg}}$$

$$\mu = 9.10444 \times 10^{-31}\,\mathrm{kg}$$

$$4\pi\epsilon_0 = 1.11265 \times 10^{-10}\,\mathrm{J^{-1}C^2m^{-1}}$$

$$R_H = \frac{(1.602176 \times 10^{-19}\,\mathrm{C})^4 \cdot 9.10444 \times 10^{-31}\,\mathrm{kg}}{2\,(1.11265 \times 10^{-10}\,\mathrm{J^{-1}C^2m^{-1}})^2\,(1.05457 \times 10^{-34}\,\mathrm{J\,s})^2} \times \frac{1}{6.62608 \times 10^{-34}\,\mathrm{J\,s} \cdot 2.997925 \times 10^8\,\mathrm{m\,s^{-1}}}$$

$$R_H = 1.09678 \times 10^7\,\mathrm{m^{-1}} = 1.09678 \times 10^5\,\mathrm{cm^{-1}}$$

experimental value: $R_H = 109677\,\mathrm{cm^{-1}}$

ionization energy: electron goes from ground state, $E_1 = -hcR_H$ to the lowest unbound state, $E_\infty = 0$:

$$I = hcR_H = 2.17869 \times 10^{-18}\,\mathrm{J} = 13.598\,\mathrm{eV}$$

shell: orbitals with the same value of n

n	=	1	2	3	4	...
		K	L	M	N	...

subshell: orbitals with the same value of n and value of l

l	=	0	1	2	3	4	5	6	...
		s	p	d	f	g	h	i	...

[Figure: energy levels, shells and subshells, Fig. 10.7 and 10.8]

$\mu = 0.999456 m_e$ for H-atom

use $\mu = m_e$ (exact for hydrogenic atom with infinitely massive or fixed nucleus)

ground state orbital : $n = 1, l = 0, m_l = 0$

$$\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \exp(-Zr/a_0)$$

$1s$-orbital spherically symmetric; all s-orbitals are spherically symmetric

$$\mathrm{Prob}\{\vec{x}_e \in d\tau(\vec{x})\} = \left|\psi_{n,l,m_l}(\vec{x})\right|^2 d\tau(\vec{x})$$

generally contains radial and angular information; no angular dependence for s-orbitals

[Figure: probability density, Fig. 10.13]

often only interested how far the electron is from the nucleus: volume element $d\tau$ = thin spherical shell of radius r and thickness dr

for s-orbitals

$$\mathrm{Prob}\{\vec{x}_e \in \text{shell at } r\} = \left|\psi_s\right|^2 4\pi r^2 dr$$

$P(r) = 4\pi r^2 \left|\psi_s\right|^2$ radial distribution function

if the wavefunction is not spherically symmetrical, integrate over the angles

$$P(r) = \int_0^{\pi} \int_0^{2\pi} \left|\psi_{n,l,m_l}(r,\theta,\phi)\right|^2 r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$P(r) = r^2 [R_{n,l}(r)]^2 \int_0^{\pi} \left|\Theta_{l,m_l}(\theta)\right|^2 \sin\theta \, d\theta \int_0^{2\pi} \left|\Phi_{m_l}(\phi)\right|^2 d\phi$$

$$P(r) = r^2 [R_{n,l}(r)]^2$$

H-atom: ground state radial distribution function

$$P(r) = 4\pi r^2 \frac{1}{\pi a_0^3} \exp(-2r/a_0)$$

[Figure: radial distribution function, Fig. 10.14]

$P(r) \to 0$ as $r \to \infty$: $\psi_{100} \to 0$ exponentially

$P(r) \to 0$ as $r \to 0$: $\psi_{100} \not\to 0$, $V_{\text{shell}} \to 0$

most probable radius r_0: $P(r_0) =$max

$$\left.\frac{dP(r)}{dr}\right|_{r=r_0} = 0$$

$$\frac{8r_0}{a_0^3} e^{-2r_0/a_0} + \frac{4r_0^2}{a_0^3}\left(-\frac{2}{a_0}\right) e^{-2r_0/a_0} = 0$$

$$1 - \frac{r_0}{a_0} = 0 \implies r_0 = a_0$$

$n = 2$: four orbitals

$l = 0$: $2s$-orbital ($\rho = 2Zr/a_0$)

$$\psi_{200}(r,\theta,\phi) = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{1}{2}\rho\right)\exp(-\rho/4) \times \sqrt{\frac{1}{4\pi}}$$

$\psi_{100}(0,0,0) \neq 0$, $\psi_{200}(0,0,0) \neq 0$

s-orbitals: electron has a *non*zero probability of being at the nucleus

$l = 1$: $2p$-orbitals

$$\psi_{210}(r,\theta,\phi) = \frac{1}{4\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \rho \exp(-\rho/4) \times \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$\psi_{21-1}(r,\theta,\phi) = \frac{1}{4\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \rho \exp(-\rho/4) \times$$
$$(+1)\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta \exp(-i\phi)$$

$$\psi_{21+1}(r,\theta,\phi) = \frac{1}{4\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \rho \exp(-\rho/4) \times$$
$$(-1)\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta \exp(+i\phi)$$

p-orbitals: radial node at $r = 0$: $\psi_p(0,0,0) = 0$

$\mathrm{Prob}\{\mathrm{e}^-$ at nucleus$\} = 0$: centripetal effect

$m_l = 0$: $\psi_{210} \sim \cos\theta \Rightarrow \theta = \pi/2 =$ x-y-plane = nodal plane: angular node

ψ_{210}^2 lies along the z-axis: $2p_z$ orbital

$\psi_{21-1} \sim \sin\theta$ and $\psi_{21+1} \sim \sin\theta$: vanish on the z-axis; ψ_{21-1} and ψ_{21+1} are complex and have no further angular nodes

construct real wavefunctions with proper nodal planes by linear superposition:

$$2p_x = -\frac{1}{\sqrt{2}}\left(2p_+ - 2p_-\right) \sim \cos\phi$$

$$2p_y = \frac{i}{\sqrt{2}}\left(2p_+ + 2p_-\right) \sim \sin\phi$$

$$\hat{l}_z 2p_z = 0\hbar \cdot 2p_z$$

$$\hat{l}_z 2p_- = (-1)\hbar \cdot 2p_-$$

$$\hat{l}_z 2p_+ = (+1)\hbar \cdot 2p_+$$

$$\hat{l}^2 2p_z = 1 \cdot 2 \cdot \hbar^2 \cdot 2p_z$$

$$\hat{l}^2 2p_- = 1 \cdot 2 \cdot \hbar^2 \cdot 2p_-$$

$$\hat{l}^2 2p_+ = 1 \cdot 2 \cdot \hbar^2 \cdot 2p_+$$

$$\hat{l}_z 2p_x \neq c \cdot 2p_x, \quad \hat{l}_z 2p_y \neq c \cdot 2p_y$$

spectroscopic transitions and selection rules

$$(n_2, l_2, m_{l2}) \longrightarrow (n_1, l_1, m_{l1}): \quad \Delta E$$

Bohr frequency condition: $|\Delta E| = h\nu$: conservation of energy

conservation of angular momentum: photon spin $s = 1 \implies$

$$\Delta l = \pm 1, \qquad \Delta m_l = 0, \pm 1$$

[Figure: Grotrian diagram, Fig. 10.17]

$\hat{H}_{\text{tr}}$ energy operator for the transition; e.g., for electric dipole transition, $\hat{H}_{\text{tr}} = -\vec{\mu} \cdot \vec{E}(t)$, where $\vec{\mu} = q\vec{r}$ = electric dipole moment and $\vec{E}$ = electric field

transition is *forbidden* if

$$\int \psi^*_{n_f, l_f, m_{lf}} \hat{H}_{\text{tr}} \psi_{n_i, l_i, m_{li}} d\tau = 0$$

magnetic dipole transition, $\hat{H}_{\text{tr}} \sim \nabla \vec{E}$: 10^5 times weaker than electric dipole transition

electric quadrupole transition: 10^8 times weaker than electric dipole transition ($\Delta l = 0, \pm 2$)