Atomic

Atoms: Nucleus Ze surrounded by $-Z$ electrons (Z = atomic #)

Hamiltonian: $H = \sum_{j=1}^{Z} \left\{ \frac{-\hbar^2}{2m}\nabla_j^2 - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_j} \right\}_{j^{th}\text{ electron}} + \underbrace{\frac{1}{2}\frac{1}{4\pi\varepsilon_0}\sum_{j\neq k}^{Z}\frac{e^2}{|\vec{r}_j - \vec{r}_k|}}_{\text{mutual repulsion}}$

(Z: # electrons, # proton; m: e mass)

electron state $\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_Z)\,\chi(\vec{s}_1, \dots, \vec{s}_Z)$ antisym

---

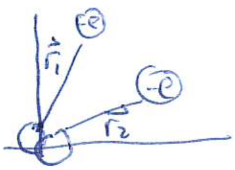
Hydrogenic atom: Consists of one electron orbiting nucleus w/ Z proton

$e,\ {}_1H^{0}\ e,\ {}_2He^{+}\ e,\ {}_3Li^{2+}\ e,\ {}_4Be^{3+}\ e$

---

ex Helium $Z=2$ nuclear charge $2e$

Hamiltonian: $H = \underbrace{\left\{\frac{-\hbar^2}{2m}\nabla_1^2 - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r_1}\right\}}_{\text{to electron 1}} + \underbrace{\left\{\frac{-\hbar^2}{2m}\nabla_2^2 - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r_2}\right\}}_{\text{to electron 2}} + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$



$E = 4[E_n + E_{n'}]$ $\quad E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2} \Rightarrow E_0 = 8(-13.6\,eV)$

Ignore repulsion:

$\psi(\vec{r}_1, \vec{r}_2) = \psi_{n\ell m}(\vec{r}_1)\,\psi_{n'\ell' m'}(\vec{r}_2)$

Ground state

$\psi_0(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a} \Rightarrow$ sym ∴

- χ singlet (parahelium) sym spatial high energy interac.
- χ triplet (orthohelium) excited state both likely occur

Recall E_n $n=1$ ground, $n=2,3\dots$ excited <-> corresponds to shell

Periodic table

Bohr Model n shell n^2 degeneracy $\quad \ell = 0,1,2\dots$ $\quad m = -\ell, -\ell+1, \dots, \ell$ $\quad (n = j_{max} + \ell + 1)$

Orbitals (n, ℓ, m)

Pauli exclusion

n	ℓ	m	Shell n	label	Orbital angular Mom. $\ell^{(n-1)}$	magnetic quantum # m	# electron state at each ℓ: $2(2\ell+1)$
1	0	0	1	1S (n, $\ell=0$, $m=0$)	0	0	2
2	0	0	2	2S (n, $\ell=0$, $m=0$)	0 <-> $m=0$	0	2
	1	1, 0, -1		2p ($\ell=1$, $m = -1\ 0\ 1$)	1 <-> $m=-1,0,1$	$\pm1, 0$	6
3	0	0	3	3s	0	0	2
	1	1, 0, -1		3p	1	$\pm1, 0$	6
	2	2, 1, 0, -1, -2		3d	2 <-> $m=-2,-1,0,1,2$	$\pm2, \pm1, 0$	10

Pattern of staggering electron on shells

1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s

the jump/skipping is due to screening effect

ex. w/ notation $\quad C\ Z=6\ \ (1s)^2(2s)^2(2p)^2$ ground state

* screening effect: inner electrons see full nuclear charge, outmost hardly feel charge, greater than Ze.

Common atomic #

Na $Z=11$ $\quad$ O $Z=8$ $\quad$ He $Z=2$ $\quad$ Ne $Z=10$ $\quad$ Ar $Z=18$ $\quad$ Cl $Z=17$

Spectroscopic notation. $\quad {}^{2S+1}L_J$

Can replace 2nd rule by way of electron locates in m slots.

Hund's 1st rule: outmost shell w/ highest total electron spin

2nd rule: given spin w/ highest total orbital momentum consistent w/ overall antisymmetry.

3rd rule: If outmost shell less than half fill $J = |L-S|$
more than half fill $J = L+S$

ex $C\ Z=6\ \ (1s)^2(2s)^2(2p)^2$ outmost shell

$S = 2(\frac{1}{2})$, Total angular momentum $p=1 \Rightarrow 2p = 2$

Top ladder $|2\ 2\rangle = |1\ 1\rangle_1 |1\ 1\rangle_2$ sym, lower one level of $L=1$ antisym $\Big\}$ ⇒ ${}^3P_0$

$|s\ m\rangle = |\frac{1}{2}\ \frac{1}{2}\rangle_1 |\frac{1}{2}\ \frac{1}{2}\rangle_2$ sym $\Big\}$ & $J = |1-1|$ ∴ half filled

↑ ↑ on $1\ 0\ -1$: $(0+1)=1$

Solid

Particle in the box $V(x,y,z) = \begin{cases} 0 & 0<x<l_x,\ 0<y<l_y,\ 0<z<l_z \\ \infty & \text{else} \end{cases}$

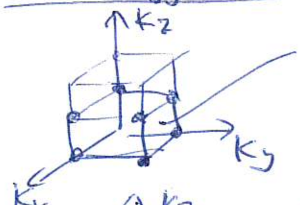
Solve Schrödinger by sep. var $\psi(x,y,z) = X(x)Y(y)Z(z)$

$\boxed{k_i = \frac{\sqrt{2mE_i}}{\hbar}}$ $E = E_x + E_y + E_z$ $\boxed{E_{n_xn_yn_z} = \frac{\hbar^2 k^2}{2m} \quad \vec{k} = (k_x,k_y,k_z) \quad k_i = \frac{\pi n_i}{l_i}}$

$$\boxed{\psi_{n_xn_yn_z} = \sqrt{\frac{8}{V}} \sin\left(\frac{n_x\pi x}{l_x}\right)\sin\left(\frac{n_y\pi y}{l_y}\right)\sin\left(\frac{n_z\pi z}{l_z}\right) \quad V = l_xl_yl_z}$$

b/c 3 sin ~~its one~~ $\sqrt{\frac{2}{l}}$

Fermi energy & surface



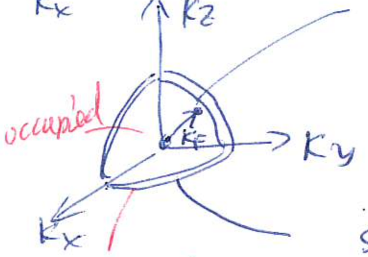
vol occupied by each state $k_xk_yk_z = \frac{\pi^3}{V}$ per electron pair

N atoms each w/ q free electron occupied vol:

$$\frac{1}{8}\left(\frac{4}{3}\pi k_F^3\right) = \frac{Nq}{2}\left(\frac{\pi^3}{V}\right) \Rightarrow k_F = (3\rho\pi^2)^{\frac{1}{3}} \text{ Fermi surface radius}$$

$\rho = \frac{Nq}{V}$

$$E_F = \frac{\hbar^2 k_F^2}{2m} \text{ Fermi energy.}$$



Fermi surface: separate occupied & unoccupied state. (outside)

Total energy.

shell vol: $\frac{1}{8}4\pi k^2 dk$ # electron state in shell: $\frac{2\left(\frac{1}{2}\pi k^2 dk\right)}{\pi^3/V} = \frac{V}{\pi^2}k^2dk$

Integrate: $E_{tot} = \frac{\hbar^2 k_F^5 V}{10\pi^2 m}$

note $\frac{dE}{dV}$ & $dW = PdV$, $dE = -dW \Rightarrow P = -\frac{dE}{dV}$ (ex. Bulk Modulus $B = -V\frac{dP}{dV} = \frac{5}{3}P$)

$$P = -\frac{dE_{tot}}{dV} = \boxed{\frac{2}{3}\frac{E_{tot}}{V}}$$

degeneracy pressure prevent cold object from collapsing.

Time independent perturbation

for nondegenerate unperturbed energy

1st order $\Delta E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle$ $\psi_n^1 = \sum_{m\neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0}\psi_m^0$

2nd order $\Delta E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}$

Time dependent perturbation

H' small, transition rate from initial (i) to final (n) state due to H'

$R_{i\to n} = \frac{2\pi}{\hbar}\rho_n |\langle n|H'|i\rangle|^2$ ρ_n density of state.

Classical E&M result

Larmor formula: $\boxed{P = \frac{q^2a^2}{6\pi\varepsilon_0 c^2}}$ Power radiating by accelerating charge q.

Variation principle: Approx system ground state energy by picking trial wave func w/ adjustable parameter. Compute $\langle E \rangle$ & minimize parameter. ie $\psi(x) = Ae^{-bx^2}$ Gaussian

Adiabatic thm: Particle in n^{th} eig state of H.
adiabatic: slowly change H to H', particle end up in corresponding H' eig. state.

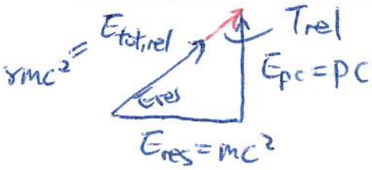
Hierarchy of Bohr energies corrections to hydrogen atom

	Order	
Bohr	$\alpha^2 mc^2$	
Fine structure	$\alpha^4 mc^2$	$\leftrightarrow$ interaction btw electron dipole moment and its B field from self motion.
Lamb shift	$\alpha^5 mc^2$	$\leftrightarrow$ quantization of E field
Hyperfine splitting	$\left(\frac{m}{m_p}\right)\alpha^4 mc^2$	$\leftrightarrow$ interaction btw dipole moment of electron & proton.

note: $\frac{\text{hyperfine}}{\text{fine}} \sim \frac{1}{100}$ $\quad \alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} \sim \frac{1}{137}$ (fine structure constant)

Fine Structure due to mechanisms: • relativistic correction
is a perturbation. • spin-orbit coupling
• perturbed by α.

relativistic correction

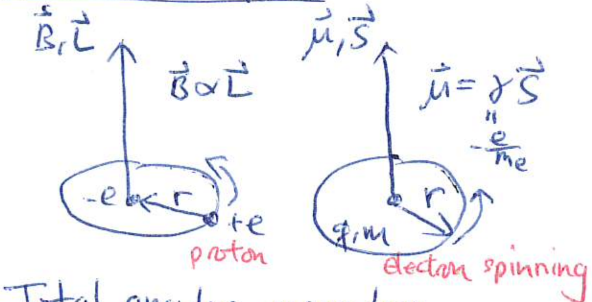


Taylor expand T in non-rel limit $p \ll mc$

$$T = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \cdots \Rightarrow H_r' = -\frac{p^4}{8m^3c^2}$$

• lowest order rel. correction
• good quantum # n, l, m
i.e. nondeg. perturb. theory legit to degenerate hydrogen atom

• Spin-orbit coupling



Hamiltonian

• $H = \vec{\mu} \cdot \vec{B}$ under Thomas procession $H_{so}' = \left(\frac{1}{2}\right) H$

$\Rightarrow \underline{H_{so}' \propto \vec{S} \cdot \vec{L}}$ so as E_{fs}'

Total angular momentum

• $\vec{J} = \vec{L} + \vec{S}$ $\quad \vec{J}^2 = (\vec{L}+\vec{S}) \cdot (\vec{L}+\vec{S})$ • $\vec{L} \cdot \vec{S} = \frac{1}{2}(J^2 - L^2 - S^2)$

eig. val : $\frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]$ (*)

• • H_{so}' commute w/ L^2, S^2 not $\vec{L}$ or $\vec{S}$

• • spin & orbital angular momentum not seperately conserved.

Stark effect ; Shift atomic energy level due to E_{ext} : $H' = e\vec{E} \cdot \vec{r}$

Zeeman effect : Shift atomic " " due to B_{ext} :

• $H_Z' = -(\vec{\mu}_l + \vec{\mu}_s) \cdot \vec{B}_{ext}$ • $\underbrace{\vec{\mu}_l = -\frac{e}{2m}\vec{L}}_{\text{orbital motion}}$ $\quad \underbrace{\vec{\mu}_s = -\frac{e}{m}\vec{S}}_{\text{electron spin}}$

Bohr magneton $\mu_B = \frac{e\hbar}{2m}$

weak-field effect

$B_{ext} \ll B_{int} \longrightarrow$ fine structure : good quantum # n, l, j, m_j : m_l, m_s not conserved

- : (*)

strong-field effect

$B_{ext} \gg B_{int} \longrightarrow$ Zeeman effect dominated : good quantum # ~~n, l, j, m_j~~ n, l, m_l, m_s

$\vec{B}_{ext}$ in $\hat{z}$ $\quad H_Z' = \frac{e}{2m} B_{ext}(L_z + 2S_z)$ external torque $\vec{J}$ not conserved. $\vec{J} = \vec{L} + \vec{S}$

Hyperfine splitting

Same classical result

Proton : $\boxed{\vec{\mu}_p = \frac{g_p e}{2m_p}\vec{S}_p \qquad \vec{\mu}_e = -\frac{e}{m_e}\vec{S}_e}$

∘ $\vec{B} = \frac{\mu_0}{4\pi r^3}\left[3(\vec{\mu}\cdot\hat{r})\hat{r} - \vec{\mu}\right] + \frac{2\mu_0}{3}\vec{\mu}\,\delta(\vec{r})$

∘ $H = \vec{\mu}\cdot\vec{B} \Rightarrow E'_{hf} \propto \langle \vec{S}_p \cdot \vec{S}_e \rangle$ Spin-Spin coupling $\quad \vec{S} \equiv \vec{S}_e + \vec{S}_p$

∘ unperturbed — Triplet / Singlet $\quad \Delta E \sim 5.88 \times 10^{-6}\,eV$

wavelength $\Delta E = h\nu \qquad \lambda = \frac{c}{\nu} \sim 21\,cm!$

Selection rule :

Photon emission in hydrogen atom

Spherically symmetric Hamiltonian

orbital coupling dominate :

$$\left.\begin{aligned}\Delta l &= \pm 1\\ \Delta m &= \pm 1, 0\end{aligned}\right\}$$ else no transition, photon spin 1; E_{inc} in $\hat{z}$ no transition unless $\Delta m = 0$.

Base on electric dipole approx : $\lambda \gg$ atom size, uniform EM field oscillate sinusoidally

Classical Scattering

Scattering
- Classical · $\frac{d\sigma}{d\Omega} = \frac{b}{\sin\theta}\frac{db}{d\theta}$
- L : $\frac{d\sigma}{d\Omega} = \frac{1}{L}\frac{dN}{d\Omega}$
- Quantum · $\frac{d\sigma}{d\Omega} = |f(\theta)|^2$
- Rutherford $T = \frac{q_1 q_2}{8\pi\varepsilon_0 b}\cot\left(\frac{\theta}{2}\right)$
- Xray

Luminosity $L \equiv$ # incident particle/area/time

$dN = L\,d\sigma$

hard sphere

$$\frac{d\sigma}{d\Omega} = \frac{1}{L}\frac{dN}{d\Omega} \qquad \frac{d\sigma}{d\Omega} = \frac{b}{\sin\theta}\left|\frac{db}{d\theta}\right|$$

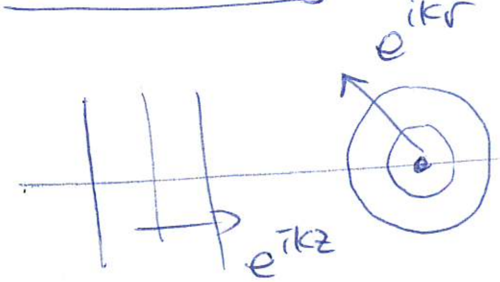
Rutherford Scattering : scattering by charge particle due to coulomb interaction.

$b = \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 m v_0^2}\cot\left(\frac{\theta}{2}\right)$ Impact parameter : $\cancel{b = \frac{E}{2}\left(\frac{q_1 q_2}{4\pi\varepsilon_0}\right)\cot\left(\frac{\theta}{2}\right)} \quad \cancel{b = \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 M v_0^2}\cot\left(\frac{\theta}{2}\right)}$

differential x-section:

$$D(\theta) = \left[\frac{Z_1 Z_2 e^2}{8\pi\varepsilon_0 m V_0^2}\csc^2\left(\frac{\theta}{2}\right)\right]^2 \quad \cancel{D(\theta) = \left[\frac{q_1 q_2}{4\pi\varepsilon_0}\frac{1}{4E\sin^2\left(\frac{\theta}{2}\right)}\right]^2} \quad \cancel{D(\theta) = \left[\frac{Z_1 Z_2 e^2}{8\pi\varepsilon_0 V_0^2}\csc^2\left(\frac{\theta}{2}\right)\right]^2}$$

Quantum Scattering



Soln of Schrödinger eqn

assume azimuthal

$$\psi(r,\theta) \simeq A\left\{e^{ikz} + f(\theta)\frac{e^{ikr}}{r}\right\}$$

scattering amplitude
probability of scattering in $\hat{\theta}$

$k = \frac{\sqrt{2mE}}{\hbar}$ (from sep. var.)

$$\boxed{\frac{d\sigma}{d\Omega} = |f(\theta)|^2}$$