

Overview of Atomic Wavefunctions Notation & Spectra

- We ~~solve~~ can solve exactly for

Hydrogen atom

→ symmetrical spherically

→ special $\frac{1}{r}$ potential

→ chem notation $1s\ 2s\ 2p.$

→ filled shell + 1 extra e^-

→ Group I elements

• inner shells filled

→ spherically symmetric charge distribution

→ We can modify Coulomb potential of nucleus

[Central potential approximation]

• partially filled shells

→ using the same orbital notation

↳ filling determined by the Coulomb interaction between e^-s

→ exchange interaction

→ Hund's Rule

→ introducing additional notation

→ effective potential is

no longer spherically symmetric

→ orbital angular momentum of

each e^- is no longer

a good quantum number

→ Total quantum number

→ Terms symbols, $2S^2 L_J$

Spin Orbit - Coupling

→ relativistic

→ splits spectral lines

↳ small Z : start w/
above construction

→ include the coupling
as a correction

⇒ Large Z :

dominate over some of
the $e^- e^-$ interaction
effects

Hyperfine Coupling

→ between nuclear spins

& se^-s

→ lower energy

→ weaker splitting

$$\left[\sum_i \left(\frac{1}{2m_e} \sigma_{x_i}^2 - \frac{Ze^2}{4\pi\epsilon_0 r_{ni}} + \sum_{j \neq i} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \right) \right] \psi(n_1, n_2, \dots, n_n) \\ = E \psi(n_1, n_2, \dots, n_n)$$

Principle Quantum Number

2.1 Hamiltonian:

S.E.

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

$$\hat{H} = -\frac{\hbar^2}{m} \nabla^2 - \frac{Z_{\text{core}} e^2}{4\pi\epsilon_0 r}$$

→ assumes a super heavy nucleus
which does not move

2.2 Energy levels:

$$E_n = -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{Z_{\text{core}}^2}{n^2}$$

n : principle quantum number

impartful

but

$$E_{n=1} = -2.17987 \times 10^{-18} \text{ J}$$

$$= -109737.36 \text{ cm}^{-1}$$

high precision
expts

2.2.1 Emission & absorption

$$\Delta E = -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} Z_{\text{core}} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$\frac{\Delta E}{h c} = R \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$= \frac{m_e}{4\pi\epsilon_0} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \left[\frac{1}{n_i^2} - \frac{1}{n_f^2} \right]$$

R

$$R_{\text{oo}} = 109737.31 \text{ cm}^{-1}$$

infinite mass
for nucleus

2.2.2 Accounting for finite mass of core

$$m_e \rightarrow m_m = \frac{m_e m_{\text{core}}}{m_e + m_{\text{core}}}$$

→ reduced mass

Derivation

$$F_{p,e} = m_p \frac{d^2 R_p}{dt^2}$$

$$F_{e,p} = m_e \frac{d^2 R_p}{dt^2}$$

$$\frac{F_{p,e}}{m_p} = \ddot{R}_p$$

$$\frac{F_{e,p}}{m_e} = \ddot{r}_e$$

$$\frac{F_{e,p}}{m_e} - \frac{F_{p,e}}{m_p} = \ddot{r}_e - \ddot{R}_p = \ddot{r}$$

$$\not\! F_{p,e} = -F_{e,p}$$

$$\Rightarrow F_{e,p} \left(\frac{1}{m_e} + \frac{1}{m_p} \right) = \ddot{r}$$

$\frac{1}{\mu_m}$

eq^{nr} of motion of the 2-body system

$$\Rightarrow F_{e,p} = \mu_m \ddot{r}$$

$$m_m = \frac{m_e m_p}{m_e + m_p}$$

Spectrum of Hydrogen:

$n \rightarrow 1$: Lyman series

$n \rightarrow 2$: Balmer series

$$E_n = E_{ion} \left(-\frac{hc R_m}{n^2} \right)$$

const

for H^+ ; define = 0

$$R_m = R_\infty Z^2 \text{core } \mu_m / M_e$$

$$\mu_m = \frac{m_e m_{core}}{m_e + m_{core}}$$

2.2.3 Spectroscopic units

$$\frac{1}{\lambda} \sim \text{cm}^{-1}$$

Atomic units:

$$\text{mass } m_e \text{, } m_{core} \text{, } e$$

$$\text{charge } e \text{, } \text{length } a_0 = \frac{4\pi \epsilon_0 h^2}{e^2 m_e}$$

$$\text{energy } 2hcR$$

$$\hbar = 4\pi \epsilon_0 = a_0 = e = m_e = 1$$

$$V(r) = -\frac{e^2}{4\pi \epsilon_0 r} \rightarrow -\frac{1}{r}$$

$$\text{a.u. } \times a_0 = \frac{4\pi \epsilon_0 h^2}{e^2 S I}$$

Wavefunctions of H

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

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

2.3.1 Angular momentum:

$$\vec{L} = (L_x, L_y, L_z) = \vec{r} \times \vec{p}$$

$$\vec{S} = (S_x, S_y, S_z)$$

$\cancel{\text{X}}$ corresponding principle

$$f \Rightarrow \hat{f} = -i\hbar \nabla \quad \text{commutation relationships:}$$

$$S \Rightarrow \hat{S} = S$$

$$L \Rightarrow \hat{L} = -i\hbar (\vec{r} \times \vec{p})$$

$$[\hat{L}_i, \hat{L}_j] = i\hbar \sum_k \epsilon_{ijk} \hat{L}_k$$

einstein summation
we do not write the summation over k explicitly

Eisen: Levi-Civita Tensor using 2

$$[\hat{L}_i, \hat{L}_j] = 0 \quad \hat{L}_i \& \hat{L}_j \quad \text{by convention}$$

\Rightarrow are eigenvalues simultaneously to characterize our state
 \Rightarrow good quantum numbers

$\cancel{\text{X}}$ we cannot know n by ℓ at the same time

$$\hat{L}^2 Y_{lm}(\theta, \phi) = \ell(\ell+1) \hbar^2 Y_{lm}(\theta, \phi)$$

$$\hat{L}_z Y_{lm}(\theta, \phi) = m \hbar Y_{lm}(\theta, \phi)$$

ℓ commutes \Rightarrow simultaneously observable
 \rightarrow measurement of one observable has no effect on the result of measuring another

Orbital angular momentum Q_N

$$\ell = 0, 1, 2, 3, \dots n-1$$

Azimuthal angular Q_m

$$m = 0, \pm 1, \pm 2, \pm 3, \dots \pm \ell$$

2.3.3 Parity

$$\hat{P} \Rightarrow \text{swaps } S \Rightarrow -S$$

$$\hat{P} f(r) = f(-r) = \begin{cases} f(r) & \text{even parity} \\ -f(r) & \text{odd} \end{cases}$$

for $Y_{lm} \rightarrow$ parity: $(-)^l$

VIP V. important point:

$\cancel{\text{X}}$ spherical symmetry of the coulomb potential allows us to solve exactly in terms of spherical harmonics

2.3.5 Radial Wavefunctions:

$$\Psi_{nlm}(\theta, \phi) = R_{nl}(r) \cdot Y_{lm}(\theta, \phi)$$

$$R_{nl}(r) = N_{nl} \left(\frac{2}{n\alpha_s} r \right)^l e^{-\frac{2}{n\alpha_s} r} \underbrace{L_{n-l-1}^{2l+1} \left(\frac{2}{n\alpha_s} r \right)}_{\text{Associated Legendre Polynomials}}$$

{ magic of the $\frac{1}{r}$ potential

parity of $e^{i\phi}$: $(-1)^{m\ell}$

parity of $P_l^m(\cos\theta) = (-1)^{l-m}$

$$\Rightarrow \hat{P} Y_{lm}(\theta, \phi) = (-1)^{m\ell} Y_{lm}(\theta, \phi)$$

Normalised Ψ : $J = \int d^3r |\Psi|^2$

$$= \int r^2 dr d\theta \sin\theta d\phi |R(r)|^2 |Y(l,m_l)|^2$$

$\rightarrow 0 \text{ as } r \rightarrow 0$
 $r^2 |R|^2$
finite as $r \rightarrow 0$

See graphs in notes.

2.3.8 Degeneracy:

m_l degenerate \because of spherical symmetry

l degenerate \because of $\frac{1}{r}$

for one-e ℓ atom $\Rightarrow E$ depends only on n .

\Rightarrow for given n : $l = 0, 1, 2, \dots, n-1$
given l : $m_l = -l, \dots, 0, \dots, l$

$$\sum_{j=0}^{m_l} (2l+1) = n^2$$

of m_l values
for each l

different allowed values of l
for given n

3.1 Hamiltonian:

$$H = \sum_{i=1}^N \left(\underbrace{\frac{-\hbar^2}{2me} \nabla_i^2}_{\text{KE}} - \underbrace{\frac{Ze^2}{4\pi\epsilon_0 r_i}}_{e\ell \text{ nuclear interaction}} \right)$$

$$+ \sum_{i < j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \text{Weaker terms}$$

separation of e ℓ s; δ_{ij}
avoid double counting.

3.2 First Approximations

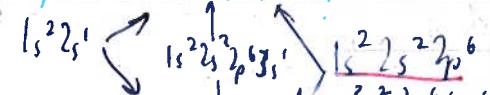
1. Independent e ℓ model

- ignoring e ℓ -e ℓ interaction
- not terribly good

3.2.2. Central Field Approximation I

Filled shell + 1 e ℓ

Group I: Li, Na, K, Rb, Cs

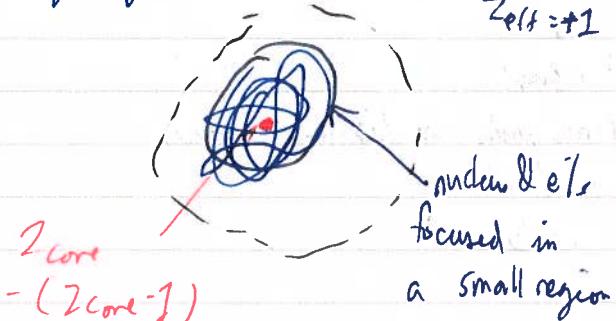


Group II: Be $^+$, Mg $^+$, Ca $^+$

Filled shells are spherically symmetric
high n state

Rydberg Atoms

$Z_{eff} = +1$



Filled shell avg charge density is spherically symmetric

Rydberg atom: treat the e⁻s & nuclear charge as spherically symmetric

$$\Rightarrow \sum_{ij}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}} \rightarrow V(r_i) = \sum_{j \neq i} \left(\frac{e^2}{4\pi\epsilon_0 r_{ij}} \right)$$

add to the potential due to the nuclear core

spherically symmetric function of r_i

[we only take account of effect of inner e⁻s on avg]

See NPD [normalized prob density]

$$r^2 |R_{nl}(r)|^2 \text{ vs } r$$

in notes

As angular momentum \uparrow , $l \uparrow$ as well

\Rightarrow less penetration into the core
 \rightarrow different orbital states w/ same n ,

have different radial profile
 of their charge density
 can explain more! \hookrightarrow penetrate to a different amount
 into the electronic core

centrifugal \hookrightarrow feel a different V_{eff}

barrier maxes to different energies

e⁻ from the nucleus

* No $\frac{1}{r}$ potential

\therefore no degeneracy of different l w/ same n

* Effective potential

\rightarrow depends upon both m & l

$$V_{eff}(r_i) = \sum_{j \neq i} \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{ij}} \right)$$

for X⁺ atom: (see notes)

$l \geq 5$ levels similar to that of H⁺

\hookrightarrow centrifugal force
 \rightarrow little penetration to the core

$\hookrightarrow Z_{eff} \rightarrow 1$ for $l \geq 5$

3.2.3 Quantum Defects

- account for $E \rightarrow E(n, l)$

$$E_{n,l} = -\frac{R_M}{hc} \frac{1}{(n - D_{n,l})^2}$$

effective principle quantum number need to solve S.E. to get an equation

quantum defect fudge factor

* as $l \geq 5, D \rightarrow 0$

$\lambda \uparrow$, weaker dependence

$\ell \uparrow$, stronger dependence

- superconducting computers

- Trapped ion computers

weak ergodicity breaking

from many-body scars

2.3.2 Spin

Electron spin & indistinguishable electrons

2.3.8 Spin (Fermion / Boson & passive)

↑
intrinsic spin angular momentum
↓
some commutation relations
as the orbital angular momentum

$$[\hat{S}_i, \hat{S}_j] = i\hbar \epsilon_{ijk} \hat{S}_k$$

$$[\hat{S}_1^2, \hat{S}_2^2] = 0 \Rightarrow$$

label spin state w/ total spin

S^z azimuthal component of angular momentum M_S

$$\hat{S}^2 \chi_{s,m_s} = s(s+1) \hbar^2 \chi_{s,m_s}$$

e's have to rotate twice to get back to its original wave function.

$$\hat{S}_z \chi_{s,m_s} = m_s \hbar \chi_{s,m_s}$$

$$\hat{S}^2 \chi_{s,m_s} = s(s+1) \hbar^2 \chi_{s,m_s} = \frac{3}{4} \hbar^2 \chi_{s,m_s}$$

$$\hat{S}_z \chi_{s,m_s} = m_s \hbar \chi_{s,m_s} = \pm \frac{\hbar}{2} \chi_{s,m_s}$$

Notation:

$$\chi_{s,m_s} = |\frac{1}{2}, \frac{1}{2}\rangle = \alpha = \uparrow$$

$$\chi_{\frac{1}{2}, -\frac{1}{2}} = |\frac{1}{2}, -\frac{1}{2}\rangle = \beta = \downarrow$$

3.3 Indistinguishable Particles

$$\langle \hat{O} \rangle = \int d^3r \psi^*(r) \hat{O} \psi(r)$$

↑
 $\hat{r} = -i\hbar \nabla$
Some tel behavior independent of sign

$$\hat{p} = -i\hbar \nabla$$

$$\hat{p} = -\frac{i\hbar^2}{2m} \nabla^2$$

if indistinguishable:

$$|\psi(1, 2)|^2 = |\psi(2, 1)|^2$$

→ probability is same if swapping 2 particles

↳ Any observable is same if we swap two particles

$$\Rightarrow \psi(1, 2) = \pm \psi(2, 1)$$

↑ for fermions (e.g. e⁻) take -ve sign

3.3.1

Pauli Principle

Total wavefunction of e⁻s must be antisymmetric under the interchange of any pair of e⁻s

- spatial, spin \Rightarrow if spatial symm.
 \hookrightarrow spin antisymm
 \Rightarrow if spatial antisymm
 \hookrightarrow spin symm
- 2 e⁻s cannot occupy the same state

e.g. 2 e⁻s:

$$\Psi(1,2) = \frac{[\Psi_A(1)\Psi_B(2) - \Psi_A(2)\Psi_B(1)]}{\sqrt{2}}$$

↑ Both spin & spatial ↑ to satisfy antisymm
 ↓ to normalize

\rightarrow when $A=B \rightarrow 0$

∴ cannot have e⁻s in the same state

More generally:

$$\Psi = \underbrace{\phi}_{\text{total}} \underbrace{\chi}_{\text{wavefunction}} \left\{ \begin{array}{l} \phi_{+} \text{ symm} \\ \chi_{S} \text{ antisymm (S)} \\ \text{on} \\ \phi_{-} \text{ antisymm} \\ \chi_{T} \text{ symm (T)} \end{array} \right.$$

3.4 Effect of Pauli on Atomic System

Helium:

$$\Psi(1,2) = \phi(r_1, r_2) \chi(\sigma_1, \sigma_2)$$

$$= -\phi(r_1, r_2) \chi(\sigma_2, \sigma_1)$$

\hookrightarrow for antisymm

3.4.1 Spin part

$\chi(\sigma_1, \sigma_2)$ - eigenfunction of total spin

$$\Rightarrow \vec{S} = \vec{s}_1 + \vec{s}_2$$

S : quantum number of \vec{S}^2

\rightarrow takes values for
 $|S_1 - S_2|, \dots, |S_1 + S_2|$

in integer steps

$2S+1$: Spin

\rightarrow for 2 spins $\frac{1}{2}$
 $0, 1 \leftarrow (\frac{1}{2}, \frac{1}{2})$

triplet

$$S=1 \quad 2S+1 = 2 \cdot 1 + 1 = 3$$

$$m_s = -1, 0, +1$$

$$\alpha(1)\alpha(2) = \uparrow\uparrow \Rightarrow \chi_{m=1}^T$$

$\beta(1)\beta(2) = \downarrow\downarrow = \chi_{m=-1}^T$ symmetric

$$(\alpha(1)\beta(2) + \beta(1)\alpha(2)) \frac{1}{\sqrt{2}} = (\uparrow\downarrow + \downarrow\uparrow) \frac{1}{\sqrt{2}} = \chi_{m=0}^T$$

Chose $m_s=0$

That is symmetric

Singlet

$$S=0 \Rightarrow m_s=0$$

$$\begin{pmatrix} \alpha(1) \beta(2) \\ - \\ \alpha(2) \beta(1) \end{pmatrix}_{\frac{1}{\sqrt{2}}} =$$

$$= (\uparrow\downarrow - \downarrow\uparrow)_{\frac{1}{\sqrt{2}}} = X^S$$

Helium:

2 e/s

Spatial part:

$$\Psi_{\pm}(r_1, r_2) \stackrel{\frac{1}{\sqrt{2}}}{=} (\phi_{n'2m_2}(r_1) \phi_{n'2'm_2}(r_2) \pm \phi_{n'm_2}(r_2) \phi_{n'2m_2}(r_1))$$

using Pauli's principle:

$$\begin{array}{ccc} \text{symmetric spatial} & \longleftrightarrow & \text{antisymmetric spin part} \\ \phi^+ & & X^S \end{array}$$

$$\begin{array}{ccc} \text{antisymmetric spatial} & \longleftrightarrow & \text{symmetric spin part} \\ \phi^- & & X^T \end{array}$$

Ground state:

$$\text{He } 1s^2$$

$$\Rightarrow \Psi_{\pm}(1,2) = \frac{1}{\sqrt{2}} [\phi_{1s}(1) \phi_{1s}(2) \pm \phi_{1s}(2) \phi_{1s}(1)]$$

if taking -ve: $\rightarrow 0$

\hookrightarrow we must have a

↓
symmetric spatial part
anti-symmetric spin part

$$\Rightarrow \text{He } 1s^2: \Psi(1,2) = \phi_+(r_1, r_2) X^S$$

Excited states:

$$\text{He } 1s^1 2s^1$$

Spatial part:

$$\Phi_{\pm}(1,2) = \frac{1}{\sqrt{2}} [\phi_{1s}(1) \phi_{2s}(2) \pm \phi_{2s}(1) \phi_{1s}(2)]$$

\hookrightarrow both \pm are possible

$$\Psi(1,2) = \Psi_+ \underbrace{X^S}_{\text{or}} - \underbrace{1 \otimes (\uparrow\downarrow - \downarrow\uparrow)_{\frac{1}{\sqrt{2}}}}$$

$$\Psi_- \underbrace{X^T}_{\text{or}} = \underbrace{1 \otimes (\uparrow\uparrow + \downarrow\downarrow)_{\frac{1}{\sqrt{2}}}}$$

Φ_{\pm} have different spatial distribution of charge (think of $\Psi(r_1, r_2, r)$)

$\neq \rightarrow$ symmetric state $\Psi(c, c) \neq 0$ @ same pt

$\neq \rightarrow$ antisymmetric state $\Psi(c, c) = 0$

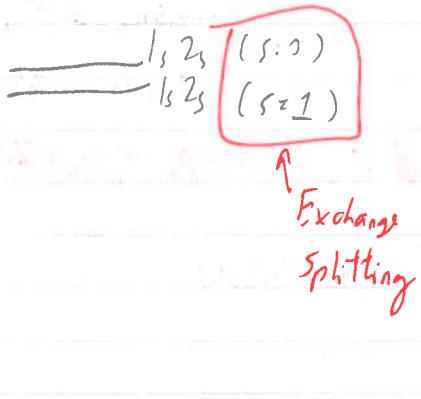
\Rightarrow different coulomb interaction energy of the two states

\Rightarrow exchange energy

$\psi(r, r) = \text{spatially sym } \neq 0$

specifically antisym = 0

$S=1$ ↗
Electrons avoid one another
to reduce Coulomb repulsion



$1s^2 (S=0)$

Fermi Analysis of Exchange I

Change in energy stems from the e^-/e^- - Coulomb repulsion

$$\hat{H}_{ee} = \frac{e^2}{4\pi\epsilon_0 \hat{r}_{12}}$$

Expectation of energy

$$\Rightarrow \langle \hat{H}_{ee} \rangle = \frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{\hat{r}_{12}} \right\rangle$$

writing an explicit form for the expectation

• exchanging particle labels

writing an explicit form for the expectation

$$= \frac{e^2}{4\pi\epsilon_0} \iiint \psi^*(\vec{r}_1) \frac{1}{\hat{r}_{12}} \psi(\vec{r}_2) dV d\sigma$$

\downarrow
 d^3r, d^3r_2

for singlet configuration: $\psi(12) = \phi_S \chi^S$

↪ substituting ψ into the integral

$$= \frac{e^2}{4\pi\epsilon_0} \iint \frac{1}{\sqrt{2}} (\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1))^* \times \frac{1}{\hat{r}_{12}} \times \frac{1}{\sqrt{2}} (\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)) \chi^S$$

\Rightarrow Separating spin & spatial parts

$$\Rightarrow \frac{e^2}{4\pi\epsilon_0} \iint \frac{1}{\sqrt{2}} (\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1))^* \times \frac{1}{\hat{r}_{12}} (\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)) dV \times \underbrace{\int \chi^S^* \chi^S d\sigma}_{=1} \quad \begin{matrix} \text{spin part of} \\ \psi \text{ is normalized} \end{matrix}$$

⇒ multiplying out stuff

$$\Rightarrow \frac{e^2}{4\pi\epsilon_0} \frac{1}{2} \left[\int \phi_a(1)^* \phi_a(1) \frac{1}{\hat{r}_{12}} \phi_b^*(2) \phi_b(2) dV + \int \phi_b(1)^* \phi_b(1) \frac{1}{\hat{r}_{12}} \phi_a^*(2) \phi_a(2) dV \right]$$

direct term

$$+ \int \phi_a^*(1) \phi_b(1) \frac{1}{\hat{r}_{12}} \phi_b^*(2) \phi_a(2) dV$$

exchange term

$$+ \int \phi_b^*(1) \phi_a(1) \frac{1}{\hat{r}_{12}} \phi_a^*(2) \phi_b(2) dV$$

$$dV = d'_{\Sigma} d'_{\Sigma}$$

* r_1, r_2 are dummy integration variables

$$\Rightarrow r_1 \rightarrow r'_1$$

$$r_2 \rightarrow r'_2$$

$$\Rightarrow \frac{e^2}{4\pi\epsilon_0} \left(\int |\phi_a(1)|^2 \frac{1}{r_{12}} |\phi_b(2)|^2 dV + \right.$$

$$\left. \int \phi_a^*(1) \phi_b(1) \frac{1}{r_{12}} \phi_b^*(2) \phi_a(2) dV \right)$$

$$= J+K$$

\uparrow indirect term
 \downarrow direct term or exchange integral

Coloumb Term

for triplet configuration: $\Psi(12) = \Phi_- \chi^T$

$$\Rightarrow + \rightarrow - \quad w/ \text{ same steps}$$

$$S \rightarrow T$$

$$\Rightarrow \frac{e^2}{4\pi\epsilon_0} \left(\int |\phi_a(1)|^2 \frac{1}{r_{12}} |\phi_b(2)|^2 dV - \int \phi_a^*(1) \phi_b(1) \frac{1}{r_{12}} \phi_b^*(2) \phi_a(2) dV \right)$$

$$= J-K$$

* exchange splitting = $2K$

$$E = J \pm K$$

$\xleftarrow{\text{singlet (antisym)}} \chi^S$
 $\xleftarrow{\text{triplet (sym)}} \chi^T$

integrand are ≥ 0

\hookrightarrow semi definite integrals

\Rightarrow triplet configurations has lower energies

When we go from 2 e/s to many exchange ranks, rules give rise to Hund's rule

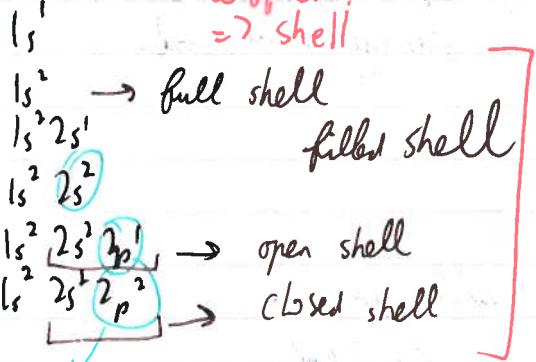
Results agree w/ Hund's Rule.

Electronic configurations & nomenclature

→ using hydrogen-like orbitals & fill w/ e⁻s

→ configuration refers to how the orbitals are filled

Set of orbitals w/ same n :
⇒ shell



- valence e⁻s
- outer shell
- optically active occupied shell

these names are for all of the orbitals in a given shell

Multiplicity of orbitals:

$$l \Rightarrow m_l \in -l, -(l-1) \dots l \\ \Rightarrow 2l+1 \text{ values}$$

nl orbitals
 $\Rightarrow 2(2l+1)$

s	$l=0$	$2(2l+1)$ from spin = 4
p	1	= 6
d	2	= 10
f	3	
g	4	

Shell w/ principle quantum number n

→ l takes values up to $n-1$

→ for each l : $m_l \in -l \dots l$

→ 2 spin states for each m_l

$$2n^2 \text{ states in shell} = 2 \sum_{l=0}^{n-1} (2l+1) = 2n^2$$

↑
Spin ↑
all values
of l ↑
 m_l values

Periodic table

- chem from Schrödinger eq^{nr}

- p. table: - electrons align w/ S.F.
- constructed before QM was discovered

for new nomenclature:

→ partially filled shell
↳ potential seen by any particular e⁻

is not spherically symmetric
e.g. He: $1s^1 2s^1$ do not give a full account of the quantum states

Angular momentum of an individual e⁻ is no longer a conserved quantity

$[A, \hat{l}_i] \neq 0 \Rightarrow \hat{l}_i$ is not a good quantum number

∴ need to consider the total angular momentum of all the e⁻s

$$\underline{L} = \sum_i \underline{l}_i \rightarrow L$$

Orbital angular momentum

$$\sum_i \underline{s}_i \rightarrow S$$

Spin angular momentum

$$\Rightarrow [\underline{L}, \underline{A}] = 0 \rightarrow \text{good quantum number}$$

$$[\underline{S}, \underline{A}] = 0$$

Term symbols:

$$\begin{matrix} 2s+1 \\ L \\ \downarrow s, p, d, f \end{matrix}$$

but how

- filled shells don't contribute to term symbols

$$\sum_i \underline{l}_i = 0 ; \sum_i \underline{s}_i = 0$$

only partially filled shells contribute to term symbols

Term symbols for two- e^- atoms
for non-equivalent e^- s

$$[e_g \ n'l \ \& \ n'l', n'f'n']$$

n & n' are different

↳ can always satisfy the Pauli exclusion principle

[if $\chi^s \Rightarrow$ sym spatial part]

[if $\chi^a \Rightarrow$ antisym spatial part]
we are free to use either sym or antisym spatial part once $n \neq n'$

$$L = l_1 + l_2$$

$$L = |l_1 - l_2| \dots \text{steps of } 1 \dots |l_1 + l_2|$$

$$= 0, 1, 2 \dots 2L = S, P, D \dots$$

$$S = (s_1 - s_2) \dots \text{steps of } 1 \dots |s_1 + s_2|$$

$$= 0, 1$$

↑↑↑, all contributions allowed.

e.g. $2p \ 3p \ l:1$

$$L = 0, 1, 2 \rightarrow S, P, D$$

$$S = 0, 1 \rightarrow 2s+1 = 0, 2, 3$$

$$\begin{matrix} 's & 'p & 'd \\ :s & :p & :d \end{matrix} \quad \begin{matrix} 1 \\ 3 \\ 5 \end{matrix} \quad \text{multiplicity of terms}$$

\Rightarrow # of quantum states corresponding to each term

$$\equiv \# \text{ values of } M_S, M_L$$

$$\equiv (2s+1)(2L+1)$$

Term symbols for equivalent e[±]'s

$n, l \Rightarrow$ Pauli exclusion

↳ different m_s, m_l

e.g. He ns^2

$n, l = 0$ & is same

⇒ both e[±]'s have $m_l = 0$

⇒ spatial part of
 Ψ is symmetrical

⇒ must have different m_s

⇒ spin wave functions
antisymmetric

↳ $S=0 \Rightarrow$ singlet

Term Symbol: 1S

e.g. He np^2

$l=1$ for both e[±]'s

$L = 0, 1, 2$

S P D

$S=0, 1$

triplet symmetric

singlet

antisymmetric

allowed terms given by those whose
total wavefunction is antisymmetric
under interchange of particles
spatial part: parity / symmetry
given by $(-)^L$

$L=0 \Rightarrow (-)^0 = 1 \Rightarrow$ spatially symm
⇒ Spin antisymm χ^S

$S=0, 2S+1=1$

1S

$L=1 \Rightarrow (-1)^1 = -1$

⇒ spatially antisymmetric

⇒ Spin symmetrical χ^T
 $S=1, 2S+1=3$

$L=2 \Rightarrow (-1)^2 = +1$

⇒ spatially symm

⇒ spin antisymmetric
 χ^S

$S=2, 2S+1=1$

Allowed term symbols are

$^1S, ^3P, ^1D$

Hund's Rule:

Obtained empirically → matches calculations
of the effects of the exchange
on the ordering of levels

⇒ 1. Term w/ the highest spin S
has lowest E

All spins // ⇒ spatially separated
↳ lowers the repulsive
Coulomb energy

⇒ 2. Given S - Term w/ highest L
has lowest E

$L = \sum l_i \Rightarrow$ all e[±]'s orbiting in
the same direction

→ keep them as far apart

for exchange
symmetry

as possible

e.g.

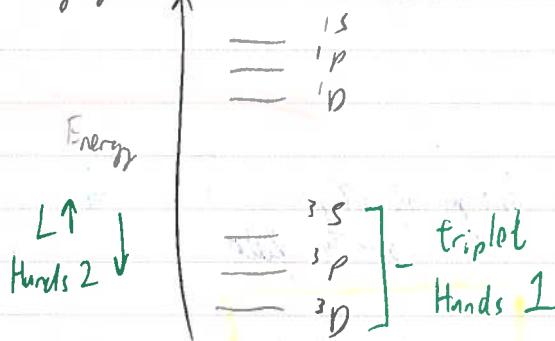
$$1s^2 \ 2s^2 \ 2p^1 \ 3p^1$$

$$\begin{matrix} S=1, 1 \\ L=0, 1, 2 \end{matrix} \Rightarrow \begin{matrix} ^1S^1P^1D \\ ^3S^3P^3D \end{matrix}$$

\therefore hfn' can have all

possible terms

ordering by Hund's rule



~~R577~~ effect requires spin ↑, $E \downarrow \frac{1}{2}$
- Normal case $L = \sum l_i \uparrow, E \downarrow \frac{1}{2}$

spin-orbit coupling:

interaction of the magnetic dipole moment
associated w/ the $e\ell$ spin in an atom

w/ the magnetic dipole moment
associated w/ the $e\ell$
orbital angular momentum

Spin-orbit & Hyperfine Coupling

- further fine structure for energy levels

due to relativistic effect

see HW3

\Rightarrow spin-orbit coupling Q6.4

$$\Delta^{2s+1} L_J \quad J = L + S = |L - S|, \dots, |L + S|, m_J = -J, \dots, J$$

$$\hat{H}_{SO} = A(L, S) \hat{L} \cdot \hat{S}$$

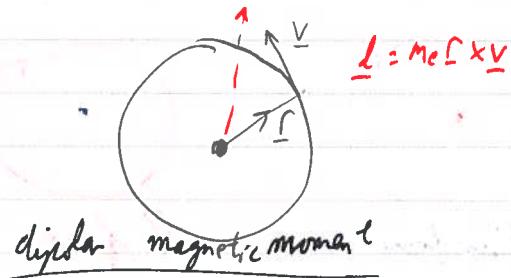
new notation

(derived @ the back)

- neither L or S will have a conservative z-component

$J \Rightarrow$ total angular QN.

deriving the spin-orbit coupling:
orbital Magnetic moment:



dipole magnetic moment

$$\mu_e^2 = I A = -\frac{e v r^2}{2 m_e} \frac{l_2}{l_2}$$

\downarrow due to L \downarrow $\frac{e}{l_2} = \frac{ev}{2\pi r}$

$$\mu_e^2 = -\frac{e}{2m_e} l_2 = \gamma e l$$

$\gamma_e \Rightarrow$ def. gyromagnetic ratio

$$\mu_e^2 = -\frac{e}{2m_e} l_2 = -\frac{e \hbar}{2m_e} m_e = -\mu_B m_e$$

\downarrow time $\downarrow \mu_B = \frac{e\hbar}{2m_e}$

$9.274079994 \times 10^{-24}$

$T T^{-1} \Leftarrow$ Bohr magneton

Magnetic moment due to the Spin-angular momentum

$$\mu_s^{\text{classical}} = -\frac{e}{2me} \vec{s}$$

assuming a classical non-relativistic distribution of charge

$$\mu_s^{\text{Dirac}} = -2 \frac{e}{2me} \vec{s}$$

\vec{e}/spin g-factor [QED corrections
2.002319304362]

- magnetic field induced by orbital motion couples to the intrinsic spin magnetic moment
- consider the atom in the \vec{e}/frame



Atom frame



\vec{e}/frame

effective magnetic field induced by nuclear motion

- couple of ways to derive this

a) Field due to a current loop I

$$B = \frac{\mu_0 I}{2r} = \frac{\mu_0 e \sqrt{r/m_e}}{4\pi r^2 (m_e)}$$

$$B = \frac{e \mu_0 I}{4\pi r^3 m_e} = \frac{e \mu_0 I}{4\pi r^3 m_e}$$

b) Special relativity

$$B = \frac{\vec{E} \times \vec{v}}{c^2}$$

$$= \frac{1}{rc^2} \frac{d\phi}{dr} \frac{d}{m_e} \frac{(\vec{x} \cdot \vec{v}) (m_e)}{m_e}$$

$$B = -\frac{1}{mc^2} \frac{d\phi}{dr} \frac{\vec{l}}{l}$$

$$B = -\frac{1}{mc^2} \frac{d\phi}{dr} \frac{\vec{l}}{l} = \frac{e \mu_0 I}{4\pi r^3 m_e}$$

using $c = \frac{1}{\sqrt{\mu_0 \epsilon_0}}$

Energy of e/spin in orbital field

$$V_{\text{mag}} = -\mu \cdot \vec{B}$$

$$= -\left(\frac{e}{m_e} \vec{s}\right) \cdot \left(\frac{1}{mc^2} \frac{d\phi}{dr} \frac{\vec{l}}{l}\right)$$

$$= -\frac{e}{m_e^2 c^2 r} \frac{d\phi}{dr} \vec{s} \cdot \vec{l}$$

$$= -\frac{e}{2 m_e^2 c^2 r} \frac{d\phi}{dr} \vec{l} \cdot \vec{s}$$

additional factor of 2

⇒ Circular motion

is not inertial

(?)

[Larmor + Thomas precession]

⇒ Answer turns out to be the same as from a purely classical calculation

Plugging in ϕ & allowing for Z

$$V_{mag} = H_{so} = -\frac{e}{2m_e c^2 r} \frac{Ze}{4\pi \epsilon_0 r^3} L \cdot S \propto \frac{Z}{r^3}$$

b.g. for small
orbitals @ large Z
large for
heavy atoms

$$\left(\frac{1}{r^3}\right) = \int \psi_{nlm_l}^* \frac{1}{r^3} 4\pi m_e dV$$

$$= \frac{Z^3}{n^3 a_0^3 l(l+\frac{1}{2})(l+1)}$$

↑
Bohr radius

$$\hookrightarrow H_{so} \propto \frac{Z^4}{n^3}$$

Spin-orbit operator

$$\text{For single } e/\!/: H_{so} = \frac{-e}{2m_e c^2 r} \frac{d\phi}{dr} \hat{L} \cdot \hat{S}$$

$A(L, S)$

$$\text{For many } e/\!/: H_{so} = \frac{-e}{2m_e c^2 r} \frac{d\phi}{dr} \hat{L} \cdot \hat{S}$$

\uparrow total \hat{L} \uparrow total \hat{S}

$$= \sum_i \hat{L}_i \cdot \hat{S}_i$$

$L \otimes S$ no longer have a fixed z-component

$S M_L$ & M_S no longer good quantum numbers

\Rightarrow but total angular momentum $J = L + S$
does have a fixed z-component

$\hookrightarrow \hat{J}_z \rightarrow M_J$ is a good quantum number

\therefore splitting terms:

$2s+1$
terms

L
 \Rightarrow split into levels

determined by:
 \hat{J}^2 \hat{J}_z \hat{L}_z \hat{S}_z
 \downarrow \downarrow \downarrow \downarrow
 J M_J L S

Notation:

$$J = L + S \Rightarrow J = |L - S| \dots \text{steps of 1} \dots |L + S|$$

$$M_J = -J \dots \text{steps of 1} \dots J$$

$$\Delta E \propto 2J+1 \quad \text{if } M_J$$

Hamiltonian:

$$\frac{H_{so}}{\hbar c} = A(L, S) L \cdot S$$

$$= \frac{A}{2} [J^2 - L^2 - S^2]$$

$$\hookrightarrow J = L + S \quad \text{why minus}$$

$$= J^2 = L^2 + S^2 + 2L \cdot S$$

$$\Rightarrow L \cdot S = \frac{J^2 - L^2 - S^2}{2}$$

Shift in energy levels:

- small relativistic correction ($\frac{1}{c}$ term)

↳ calculate its effect using
1st order perturbation theory

↳ we don't need to allow for change in Ψ
to leading order to get change in energy

$$A = -\frac{1}{\hbar c} \frac{e}{2m_e c^2 \hbar^2 r} \frac{Ze}{4\pi \epsilon_0 r^2}$$

$$\Delta E_{so} = \langle \hat{A}_{so} \rangle$$

derivation
in notes

$$= \frac{\hbar c A}{2} [\langle \hat{J}^2 - \hat{L}^2 - \hat{S}^2 \rangle]$$

$$= \frac{\hbar c A}{2} [J(J+1) - L(L+1) - S(S+1)]$$

Examples of level notation & so splitting

$2p$ for hydrogen

$$L=l=1 \quad J: (-\frac{1}{2}) \dots (1+\frac{1}{2})$$

$$S=s=\frac{1}{2} \quad = \frac{1}{2} \text{ or } \frac{3}{2}$$

$\Rightarrow {}^3P_{\frac{1}{2}}$ and ${}^3P_{\frac{3}{2}}$

$$A_{2p}(L, S) = 0.243 \text{ cm}^{-1}$$

$$\Rightarrow \frac{\Delta E_{so}}{\hbar c} (J=\frac{1}{2}) = \frac{A}{2} \left(\frac{1}{2} \left(\frac{3}{2} \right) - 1 \cdot 2 - \frac{1}{2} \cdot \frac{3}{2} \right)$$

$$= -A_{2p}(L, S)$$

$$\Rightarrow \frac{\Delta E_{so}}{\hbar c} (J=\frac{3}{2}) = \frac{A}{2} \left(\frac{3}{2} \cdot \frac{5}{2} - 1 \cdot 2 - \frac{1}{2} \cdot \frac{3}{2} \right)$$

$$= +\frac{A_{2p}}{2} (L, S)$$

Difference: Splitting of level due to SO
spin-orbit coupling

$$\Rightarrow \frac{3}{2} A_{2p}(L, S) = 0.364 \text{ cm}^{-1}$$

Lande interval rule:

$$\Delta E_{so}(J) - \Delta E_{so}(J-1) = \hbar c A(L, S) J$$

Strong & Weak spin-orbit coupling limits

low Z

Weak SO

high Z

$$A(L, S) \propto Z^4$$

(Russell-Saunders coupling) L.S coupling

JJ coupling

Russel-Saunders coupling:

$$\text{consider: } \underline{S} = \sum_i S_i, \underline{L} = \sum_i L_i$$

combine to give $\underline{J} = \underline{L} + \underline{S}$

Hund's 3rd Rule

Allows us to order S.O. split levels
on top of the 1st two rules

a) Normal

- less than $\frac{1}{2}$ full shell

$\hookrightarrow J \uparrow \Rightarrow E \uparrow \Rightarrow$

\hookrightarrow lowest J has lowest E

b) Inverted

- more than $\frac{1}{2}$ full

$\hookrightarrow J \uparrow \Rightarrow E \downarrow \Rightarrow$ highest J taken

c) Full shell

\Rightarrow no splitting

$\because L.S = 0$

$\therefore L, S = 0$

• Cast treat as perturbation
- Take account of all charge

JJ coupling (Strong) in H.F.

[for heavy atoms]

individual e⁻s are strongly

spin-orbit coupled

$$\Rightarrow \text{use } \vec{j}_i = \vec{l}_i + \vec{s}_i$$

↳ combine to get $\underline{J} = \sum \vec{j}_i$:

\Rightarrow for 2 e⁻s

$$|\vec{j}_1 - \vec{j}_2| \dots \text{steps of } 1 \dots |\vec{j}_1 + \vec{j}_2|$$

Parity of terms: exchange symmetry

spatial inversion

one e⁻ $\Rightarrow Y_{lm_2} \rightarrow \text{parity } (-)^l$

Many e⁻s $\Rightarrow (-)^{\sum l_i}$
not same as $(-)^L$
eg. as $L = |l_1 - l_2| \dots |L + l_2|$

Notation:

$2p^0$ odd parity

$2p$ even parity

$$A_{HFS} = 2.9 \times 10^{-13} \text{ s}^{-1}$$

↑ Hyperfine splitting

$$T = \frac{1}{A_{HFS}} = 11 \times 10^6 \text{ years}$$

- v. long lifetime

Hyperspace coupling

Coupling of electron μ_e to nuclear μ_n

Nuclear magnetic moment

$$M_I = g_N \mu_N \frac{I}{\hbar}$$

total nuclear spin
gyromagnetic ratio
nuclear g-factor
 $\frac{M_e}{M_N} \mu_B$
Nuclear magneton

For nuclear spin \Rightarrow even more complicated than the atomic structure

Hyperspace energy

$$\Delta E \propto I \cdot J$$

$$I \cdot S$$

further splitting of J

total electronic angular momentum
nuclear angular momentum

$$\Rightarrow \text{look at } F = J + I$$

$$F = |J - I| \dots \text{steps of } 1 \\ (J + I)$$

M_F

e.g. H: 1s $^2S_{\frac{1}{2}}$ ground state

$S = \frac{1}{2}$ transitions between hyperspace levels

$J = \frac{1}{2}$ @ $\lambda = 21 \text{ cm}$ [radio, VTPR in radio astronomy]

$I = \frac{1}{2}$ single proton $I = \frac{1}{2}$

$$F = |J - I| \dots |J + I| \\ = 0 \text{ or } 1$$

More on the shift in energy levels using
1st order Perturbation theory?

$$\Delta E_{ss}^{(1)} = \langle \hat{H}_{ss} \rangle = \int \Psi_{JLSM_J}^* \hat{V}_{\text{perturb}} \Psi_{JLSM_J} dt$$

Weak

in general: $\Delta E^{(1)} = \langle V_{\text{perturb}} \rangle = \int \Psi_0^* V_{\text{perturb}} \Psi_0 dt$

$$\therefore \hat{H}_{ss} = \frac{\hbar c A(L,s)}{2} [\hat{J}^2 - \hat{L}^2 - \hat{S}^2]$$

$$= \frac{A(L,s)}{2} \left[\int \Psi^* \hat{J}^2 \Psi dt - \int \Psi^* \hat{L}^2 \Psi dt - \int \Psi^* \hat{S}^2 \Psi dt \right]$$

$$= \frac{A(L,s)}{2} [\langle \Psi | \hat{J}^2 | \Psi \rangle - \langle \Psi | \hat{L}^2 | \Psi \rangle - \langle \Psi | \hat{S}^2 | \Psi \rangle]$$

* $\hat{J}^2 \Psi = J(J+1) \Psi$ (?)
from eigenvalue of \hat{J}^2

$$\hat{H}_{ss} = \frac{A(L,s)}{2} \left[J(J+1) \cancel{\langle \Psi | \Psi \rangle} - L(L-1) \underbrace{\langle \Psi | \Psi \rangle}_{=1} - S(S+1) \langle \Psi | \Psi \rangle \right]_{s=1}$$

$$\frac{\Delta E_s}{\hbar c} = \frac{A(L,s)}{2} [J(J+1) - L(L+1) - S(S+1)]$$

$$\hat{L}^2 |L, m_L\rangle = \hbar^2 \langle (L+1) | L, m_L \rangle$$

$$\hat{L}^2 |L, m_L\rangle$$

$$\langle \tilde{L}, m_L | L, m_L \rangle$$

$$\hat{S}^2 |S, m_S\rangle$$

$$\langle \tilde{S}, m_S | S, m_S \rangle$$

$$\hat{J}^2 |J, m_J\rangle \langle \tilde{J}^2 | J, m_J \rangle$$

Forni's Golden Rule:

Never let a customer leave

without a smile.

Always be friendly,

never say no,

and always be helpful.

Always be friendly,
never say no,
and always be helpful.

Always be friendly,

never say no,

and always be helpful.

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Selection Rules for Dipole Transitions:

Basic Idea: probability of a transition w/t ↑ per unit time ???

- Fermi's Golden Rule:

$$\Gamma = \frac{2\pi}{\hbar} |\langle f | \hat{H}_{int} | i \rangle|^2 \delta(E_f - E_i - h\nu)$$

- Selection Rules are determined by

2 things

$$\hat{H}_{int} = \hat{H}_{dipole}$$

⇒ dipole electromagnetic transition

↳ integrals in $|\langle i | \hat{H}_{int} | f \rangle|^2$

↳ integral zero by symmetry
[forbidden transitions]

[integral is zero or not]

Single e/ atoms

$$E = E_0 e^{i\omega t} \quad \omega = 2\pi\nu$$

$$\hat{H}_{dipole} = -e \vec{r} \cdot \vec{E}$$

↖ dipole moment of
the electric field

operator whose expectation
gives us the dipole moment

assuming E-field in the z-direction

in writing in polar coordinates:

$$A_{dipole} = e r \cos\theta E_0^z e^{i\omega t}$$

using Fermi's Golden Rule:

$$\Psi_i = R_{ne}(r) Y_{l,m_l}(0, \phi)$$

$$\Psi_f = R_{n'e'}(r') Y_{l',m'_l}(0, \phi)$$

$n_l m_l \rightarrow n' l' m'$
are allowed

$$P_{if} = \frac{2\pi}{\hbar} \left| \int \Psi_f^* \hat{H}_{int} \Psi_i dV \right|^2$$

$$= \frac{2\pi}{\hbar} \int \int \int R_{n'e'}^*(r') R_{ne}(r) r^2 dr$$

from \hat{H}_{dipole}

$$\int \int \int Y_{l',m'_l}(0, \phi) \cos\theta Y_{l,m_l}(0, \phi) \sin\theta d\phi d\theta d\psi$$

Radial part gives a finite number

⇒ doesn't determine selection rule

The other does determine selection rule

• Selection rules determined by whether angular integral is zero

$$\int Y_{l',m'_l}^* Y_{l,m_l} Y_{l,m_l} d\phi \sin\theta d\phi$$

$$= \sqrt{\frac{4\pi}{3}} \cos\theta \Rightarrow \cos\theta = \sqrt{\frac{4\pi}{3}} Y_{l,0}(0, \phi)$$

$$Y_{l,m_l}^*(0, \phi) = (-1)^{m_l} Y_{l,-m_l}(0, \phi)$$

giving us the integral:

$$\Rightarrow (-1)^{m_l} \sqrt{\frac{4\pi}{3}} \int_0^{2\pi} \int_0^\pi Y_{l,m_l}(0, \phi) Y_{l,0}(0, \phi) Y_{l,m_l}(0, \phi) \sin\theta d\theta d\phi$$

The integral is non-zero only when:

$$l' = l \pm 1 \Rightarrow \Delta l = \pm 1$$

$$m'_l = m_l \Rightarrow \Delta m_l = 0$$

[Same calculations for

$$x, y \text{ corrections} \Rightarrow m'_l = m_l \pm 1]$$

$H_{\text{dipole}} \Rightarrow \text{odd parity} \because e\vec{r} \cdot \vec{E}$
 $\int \psi_f^* V_{\text{dipole}} \psi_i \text{ must be even for } T_{1/2} \neq 0$
 $\Rightarrow \psi_f^* \psi_i - \text{odd parity}$

* origin of \Rightarrow parity must change
the selection rule \rightarrow for initial & final state

Selection Rules

for single - $e\bar{e}$ atoms

$$\Delta l = \pm 1$$

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

$\Delta s = 0 \Rightarrow H_{\text{dipole}}$ doesn't depend
on spin

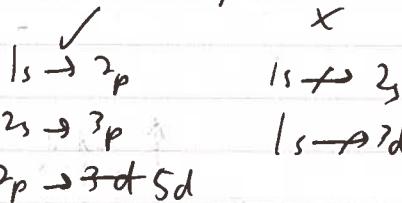
The selection rules above are only
valid for weak SO coupling
for strong SO:

$$\Delta j = 0, \pm 1$$

but

$$j=0 \rightarrow j'=0$$

eg. H: allowed dipole trans:



Selection Rules for many- $e\bar{e}$ atoms

Rigorous: Fermi's Golden rule
is strictly zero

$$\Delta J = 0, \pm 1$$

$$\Delta M_J = 0, \pm 1$$

* parity must change

BUT $J=0 \rightarrow J'=0$

* just like singlet rules
in terms of total J

Weak unless:

$$\Delta S = 0$$

$$\Delta L = 0, \pm 1, \text{ but } L=0 \rightarrow L'=0$$

eg. C excited state: $1s^2 2s^2 2p^1 4d^1 3F_2^0$

$$\Rightarrow S=1$$

$$L=3$$

$$J=2$$

0 - odd parity

Transitions:

$$^3F_2 \rightarrow ^3P_1 \text{ weak } \Delta L \neq \pm 1$$

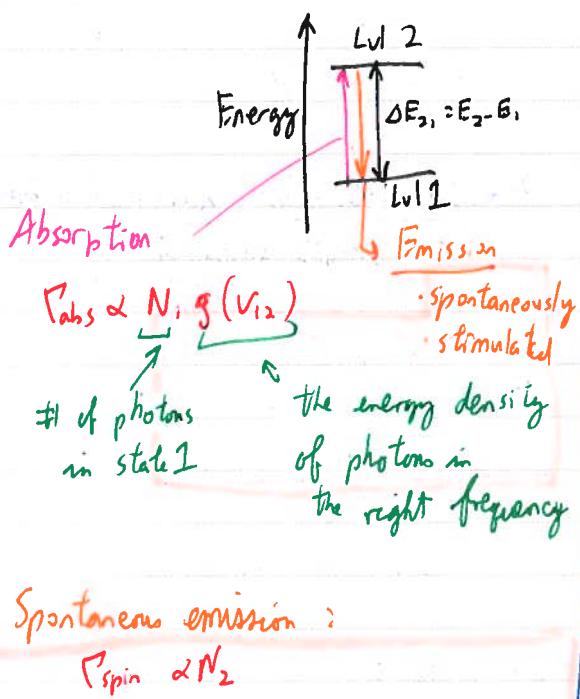
$$^3F_2 \rightarrow ^3P_1 \text{ forbidden parity doesn't change}$$

$$^3F_2 \rightarrow ^1D_2 \text{ weak as } \Delta S \neq 0$$

\Rightarrow stronger than first transition above

$$^3F_2^0 \rightarrow ^3D_2 \text{ strong allowed}$$

Rates of Emission + Absorption



Stimulated emission:

$$R_{stim} \propto N_2 g(v_{21})$$

- emitted photon is coherent w/ photon which stimulate it
 - ↳ same phase
 - ↳ same direction
 - ↳ LASER

Two-Level rate equations

Thermal radiation

- random directions
- random polarization
- satisfy black body distribution

$$\frac{dN_1}{dt} = -[Cg(v_{12})N_1 + AN_2] + [BS(v_{12})N_2]$$

Abs Spontaneous Stimulated

$$\frac{dN_2}{dt} = [Cg(v_{12})N_1 - AN_2] - [BS(v_{12})N_2]$$

A, B, C are called Einstein coefficients

At Equilibrium $N_1 = N_2 > 0$

$$CgN_1 - AN_2 - BN_2S = 0$$

$$\Rightarrow \frac{N_1}{N_2} = \frac{A + BS}{CS} = e^{\frac{-\beta E_1}{h\nu_{12}\beta}}$$

thermal distribution

$$\Rightarrow g(v_{12}) = \frac{A/B}{C/B e^{h\nu_{12}\beta} - 1}$$

Excited state lifetimes

Compare to black body radiation to deduce A, B & C

$$g(v_{12}) = \frac{8\pi v_{12}^2}{c^3} \frac{h v_{12}}{e^{hv_{12}/kT} - 1}$$

$$= \frac{8\pi h v_{12}^3}{c^3} \frac{1}{e^{hv_{12}/kT} - 1}$$

$$\Rightarrow C = B$$

$$\Rightarrow A = \frac{8\pi h v_{12}^3}{c^3} B$$

can calculate the overall amplitude from Fermi's Golden rule

$$B = \frac{2\pi}{3h^2} \left(\frac{1}{4\pi\epsilon_0} \right) \left| \int \psi_2^* \hat{\mu} \psi_1 d\tau \right|^2$$

$$= \frac{2\pi}{3h^2} \left(\frac{1}{4\pi\epsilon_0} \right) \left| \int \psi_2^* e \vec{\mu} \psi_1 d\tau \right|^2$$

↳ derivation ??

Two lvl systems

- No EM field rotation in its excited state

$$N_2 = -AN_1$$

$$P_{\text{spin}} = A = \frac{8\pi^2 V_{12}}{3\epsilon_0 \hbar c^3} \left| \int \psi_f^* e \vec{\mu} \psi_i d^3 r \right|^2$$

$$T_{\text{spin}} = \frac{1}{A}$$

Mult. lvl system

→ adding rates of all decay channels

$$P_i = \sum_f A_{if}$$

$$T_i = \frac{1}{P_i} = \left(\sum_f A_{if} \right)^{-1}$$

Eg Hydrogen atom: $2p \rightarrow 2s$

$$\begin{array}{ccc} nlm & & nl'm' \\ 210 & & 110 \end{array}$$

⇒ there's only one emitted decay
↳ effective 2 level system

$$A = 6.25 \times 10^8 s^{-1} \Rightarrow \tau = \frac{1}{A} = 1.6 \times 10^{-9} s$$

$$4s \xrightarrow[2p]{3p} T_{4s} = \frac{1}{A_{4s3p} + A_{4s2p}} = 227 ns$$

Lifetime vs Linewidth

$$\Delta E \delta t \geq \frac{\hbar}{2}$$

* \rightarrow long lifetime \rightarrow narrow width

* \rightarrow short lifetime \rightarrow broad width

Metastable states

\hookrightarrow spontaneous decay forbidden by the selection rules for electric dipole transitions [$A_{f\ell} = 0$] for all final states

eg. $2s$ state of Hydrogen is meta stable

- \therefore forbidden to decay to the $1s$ ground state by selection rules [$\Delta L = \pm 1$]

eg. $1s2s$ excited state for He

\Rightarrow Metastable in both singlet & triplet configurations

$$1s2s \quad 1^1S_0 \rightarrow 1s^2 \quad 1^1S_0$$

i parity same

$$ii \quad J=0 \rightarrow J=0$$

$$iii \quad L=2 \rightarrow L=0$$

$$1s2s \quad 3^3S_1 \rightarrow 1s^2 \quad 1^1S_0$$

i parity same

$$ii \quad \Delta S \neq 0$$

$$iii \quad L=0 \rightarrow L=0$$

longest lived excited state of an atom
7870 s

Las for cooling of atoms

crucial enabling technique for fundamental physics &

new quantum technologies

Hot gas of atoms:

e.g. ^{133}Cs @ $T = 300\text{ K}$

using equipartition:

$$\frac{1}{2} M_{^{133}\text{Cs}} V^2 r_{\text{rms}} = \frac{1}{2} kT$$

$$V_{\text{rms}} = 37 \text{ m s}^{-1}$$

$$Pr_{\text{rms}} = M V_{\text{rms}}$$

$$= 3 \times 10^{-23} \text{ kg ms}^{-1}$$

Laser cooling of Cs

Alkali metals (Li Na K Rb Cs)

have one outer shell/optically active e^-

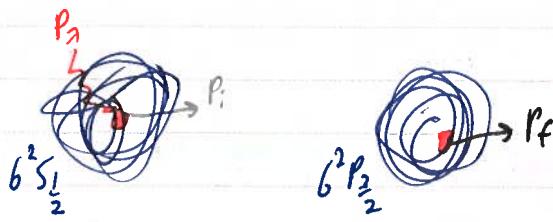
$^2S_{\frac{1}{2}} \rightarrow ^2P_{\frac{1}{2}}$ \Rightarrow forms an effective 2-level system

\Rightarrow use these for laser cooling

$$\lambda = 852 \text{ nm}$$

$$P_h = \frac{\hbar}{\tau} = 1.8 \times 10^{-28} \text{ kg ms}^{-1}$$

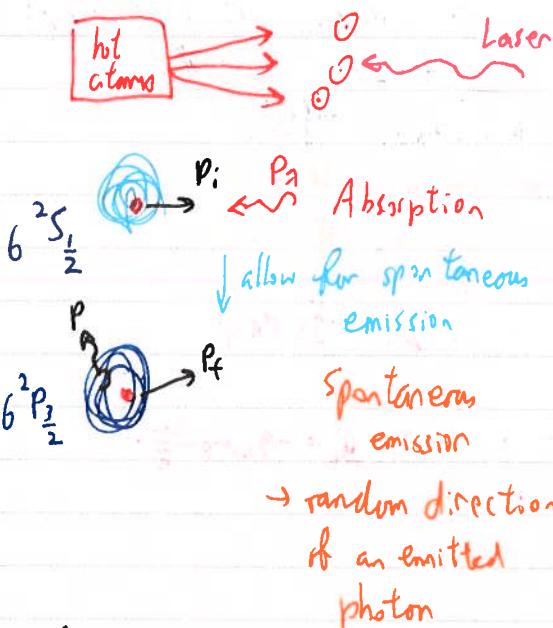
Absorption & Emission of photons
conserves momentum & energy



$$p_i + p_{\gamma} = p_f$$

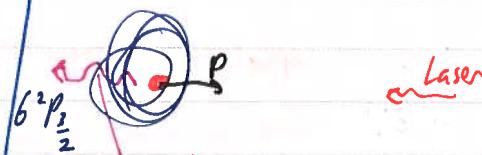
* $P_{Cs} \gg P_{\gamma}$] → about 40K
32461 : 1 scattering events
for it to be brought to rest
which leads to

Laser deceleration



- ⇒ Absorption processes $\Rightarrow \Delta p$ accumulate
- ⇒ Emission processes $\Rightarrow \Delta p$ average $\rightarrow 0$

Need to avoid stimulated emission
why?



is coherent w/
the photon which
stimulates the emission

⇒ reverses the initial absorption process
it takes us back to where we started

$$\Rightarrow 2T_{Cs} = \Delta t_{abs}$$

↑ decay time of Cs ↓ time between absorption events, tuned by adjusting laser intensity

time to decelerate

$$t = \frac{P_{Cs}}{P_{\gamma}} 2T_{Cs} = 2.3\text{ms}$$

[acceleration is 600G

Minimum temp ⇒

photon $P_{\gamma} \Rightarrow$ minimum avg momentum for Cs atoms
 \Rightarrow minimum KE \Rightarrow minimum temperature

$$V_{Cs} = \frac{P_{\gamma}}{m} = \frac{\hbar}{2M} \approx 0.003\text{ms}^{-1}$$

$$T_{min} = \frac{1}{k_B} M V_{Cs min}^2 = \frac{1}{k_B} \frac{\hbar^2}{2M} = 2 \times 10^{-7}\text{K}$$

Poppler shift

$$v' = \frac{v_L}{(1 + \frac{v_{\text{rel}}}{c})} \quad (\text{effective frequency of laser in atomic frame})$$

↳ need this to be resonant w/ the transition

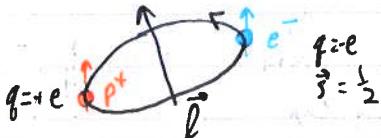
⇒ condition for resonance changes through the deceleration process

do all of this in 2.3 ms

Molecular Schrödinger Eq.

Zeeman & Stark effect

Spin-orbit interactions!



→ spin-orbit interaction give rise to fine-structure in atoms

⇒ interactions of internal magnetic moments associated w/ S & \underline{l}

$$\frac{E_{LS}}{hc} = \frac{A(L, S)}{2} [J(J+1) - L(L+1) - S(S+1)]$$

Zeeman effect

1896 reported by Zeeman

↳ interpreted by Lorentz

TWO regimes

Weak Field: **Zeeman effect**

ΔE shift is small compared to S-O E-splitting
normal anomalous

Strong Fields: **Foster-Rowland effect**

Normal: agrees w/ classical theory of Lorentz

Anomalous: depend on e/spin

↳ purely quantum mechanical

↳ measure splitting of spectral lines
⇒ can measure B-field strength
→ intrinsic magnetic moment: $\vec{\mu}_{\text{mag}}$

Interaction potential:

$$V_B = \pm \mu_{\text{mag}} \cdot \underline{B}$$

$$\text{from spin: } \Delta E_s = -g_e \mu_B \frac{\underline{s}}{\hbar} \quad g_e \approx 2 \\ \text{e/ spin-factor}$$

$$\text{from orbital spin: } \Delta E_L = -g_L \mu_B \frac{\underline{l}}{\hbar} \quad g_L = 1 \\ \text{orbital g-factor}$$

Normal Zeeman effect ($S=0$)

$$\text{total spin: } \hat{S} = \sum_{i=1}^N \hat{s}_i$$

- filled shells have no net spin

↳ considering only valence e[−]s

- $\therefore S=0$ for e[−]s

↳ X obtain $S=0$ from atoms

w/ odd number of valence e[−]s

($S=0$) state \Rightarrow produced by

even n. of e[−]s

[for two valence e[−]s, $S=0$ or $S=1$]

all ground states of C_{sp} II (divalent atoms) have ns^2 configurations

↳ always have $S=0$

\because 2 e[−]s align w/ their spins
anti-parallel

$$\therefore S=0 \Rightarrow \mu_S - \mu_S = 0$$

\therefore magnetic moment will be entirely due to orbital motion

$$\mu = -\frac{\mu_B}{\hbar} \hat{L} \quad \begin{matrix} \text{interaction energy} \\ \text{by 1st order} \end{matrix}$$

$$V_B = \frac{\mu_B}{\hbar} \hat{L} \cdot \hat{B} \quad \begin{matrix} \text{perturbation theory} \\ \Delta E = -\mu \cdot \hat{B} \end{matrix}$$

$$\text{assuming } \hat{B} = (0, 0, B_2)^T \text{ (unif. horiz.)}$$

$$V_B = \frac{\mu_B}{\hbar} \hat{L} \cdot \hat{B}$$

$$= \frac{\mu_B}{\hbar} L_2 B_2$$

$$\Delta E = \langle \Psi_0 | V_B | \Psi_0 \rangle$$

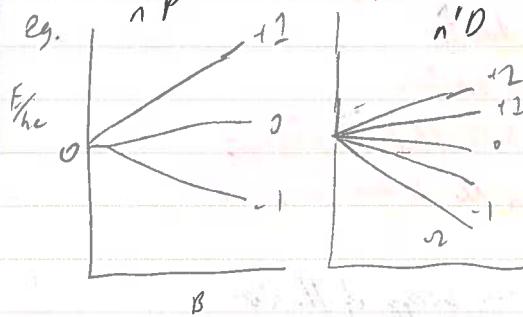
$$= \frac{\mu_B}{\hbar} B_2 \underbrace{\langle \Psi_0 | \hat{L}_2 | \Psi_0 \rangle}_{m_L \hbar}$$

$$\Delta E = \mu_B B_2 m_L = -\mu_B B_2$$

\Rightarrow B splits the degeneracy of the m_L states evenly ($m_L = -1, 0, 1$)

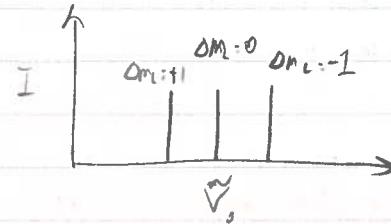
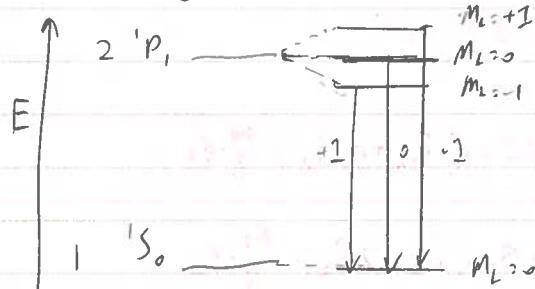
\Rightarrow for a total orbital angular momentum Q.N.

$$L \Rightarrow \text{split into } 2L+1$$



electronic transitions $\Delta m_L = 0, \pm 1$

$S=0 \quad \text{He}$



Anomalous Zeeman effect (SF 0)

- atoms w/ odd number of e⁻s

- still weak field

- In $\leftarrow S$ LS-coupling:

$$\vec{J} = \vec{L} + \vec{S}$$

In B -field: J precesses about
 B @ Larmor frequency

L+S precesses more rapidly
about J due to
spin-orbit interaction

↳ i. S.O. effect is stronger
than the interaction w/ R

=) interaction energy of the atom

= sum of spin & orbital μ_2 w/ B -field

$$\Delta E = -\mu_2 B_2$$

$$= -(\mu_2^{orbital} + \mu_2^{spin}) B_2$$

$$\Delta E = \langle \hat{L}_z + g_s \hat{S}_z \rangle \frac{\mu_B}{\hbar} B_2$$

: 2

$$\Delta E = \langle \hat{L}_z + 2\hat{S}_z \rangle \frac{\mu_B}{\hbar} B_2$$

external B -field is too weak

to uncouple L & S

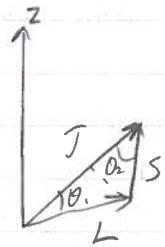
↳ m_L & M_S are not good
quantum numbers

→ precessing atomic magnetiz moment,
neither S_2 nor L_2 are constant

↳ only $\hat{J}_z = m_J$ is well defined

projecting L+S onto J

↳ project to z-axis:



$$\hat{J} = \sqrt{J(J+1)} \cos \theta \hat{J}_z$$

$$\hat{J} = -\left(\langle \hat{L}_z \cos \theta, \frac{\hat{J}}{|\hat{J}|} \rangle + 2 \langle \hat{S}_z \cos \theta, \frac{\hat{J}}{|\hat{J}|} \rangle \right) \frac{\mu_B}{\hbar}$$

from scalar products:

$$\hat{L} \cdot \hat{J} = |\hat{L}| |\hat{J}| \cos \theta_1$$

$$\hat{J} \cdot \hat{L} = |\hat{J}| |\hat{L}| \cos \theta_2$$

getting θ_1, θ_2

$$\Rightarrow \hat{A} = -\left(\frac{\hat{L} \cdot \hat{J}}{|\hat{J}|^2} + 2 \frac{\hat{S} \cdot \hat{J}}{|\hat{J}|^2} \right) \frac{\mu_B}{\hbar} \hat{J}$$

$$\hat{S} = \hat{J} - \hat{L}$$

$$\Rightarrow \hat{S}^2 = (\hat{J} - \hat{L}) \cdot (\hat{J} - \hat{L})$$

$$\hat{S} \cdot \hat{S} = \hat{J} \cdot \hat{J} + \hat{L} \cdot \hat{L} - 2 \hat{L} \cdot \hat{J}$$

$$\hat{L} \cdot \hat{J} = \underbrace{\hat{J} \cdot \hat{J} + \hat{L} \cdot \hat{L} - \hat{S} \cdot \hat{S}}_{\sum}$$

with from quantum numbers

$$\Rightarrow \left\langle \frac{\hat{L} \cdot \hat{J}}{|\hat{J}|^2} \right\rangle = \frac{[j(j+1) + 2m+2] - s(s+1)] \hbar^2}{j(j+1) \hbar^2}$$

$$= \frac{[j(j+1) + j(j+1) - s(s+1)]}{2j(j+1)}$$

Similarly

$$\hat{S} \cdot \hat{J} = (\hat{J} \cdot \hat{J} + \hat{S} \cdot \hat{S} - \hat{L} \cdot \hat{L}) / 2$$

$$\left\langle \frac{\hat{S} \cdot \hat{J}}{|\hat{J}|^2} \right\rangle = \frac{[j(j+1) + s(s+1) - 2(j+1)]}{2j(j+1)}$$

Subbing in back $\hat{\mu}$

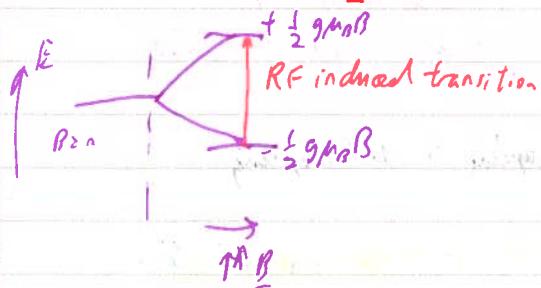
$$\hat{\mu} = - \left(\frac{[j(j+1) + 2(J+1) - S(S+1)]}{2j(j+2)} - 2 \frac{[j(j+1) + S(S+1) - J(J+1)]}{2j(j+2)} \right) \frac{\mu_0 \hat{J}}{\hbar}$$

$$\hat{\mu} = -g_J \frac{\mu_0}{\hbar} \hat{J}$$

Electron paramagnetic resonance

magnetic pot. energy of
 S in a B -field

$$U = \mu \cdot B \pm \frac{1}{2} g \mu_B B$$



* Landé g -factor:

$$g_J = 1 + \frac{j(j+1) + S(S+1) - J(J+1)}{2j(j+1)}$$

Z-component: $\mu_z = -g_J \mu_B m_j$

Interaction energy w/ B -field

$$\Delta E = -\mu_z B_z = g_J \mu_B B_z m_j$$

[classical theory predicts $g_J = 1$
departure from this is due to
spin in quantum picture]

See
D. line & D. line by Na $3p \rightarrow 3s$
transition

* shifts of all of the m_j sublevels
are smaller than the
split-orbit energy splitting E_{so}

$$E_{shift} < E_{so}$$

Packen-Back (SFO strong field)

$$V_B \gg H_{SO}$$

$$\hookrightarrow \Delta E_B \gg \Delta E_S$$

\hookrightarrow external magnetic field can be considered larger than the internal B -fields of the atom

J - B coupling $>$ L - S coupling

L - S decouple from each other

\hookrightarrow precess independently about B -field

J is no longer a good quantum number

$$\begin{aligned} V_B &= -\vec{\mu}_S \cdot \vec{B} - \vec{\mu}_L \cdot \vec{B} \\ &= \frac{\mu_B}{\hbar} g_e \vec{S} \cdot \vec{B} + \frac{\mu_B}{\hbar} g_L \vec{L} \cdot \vec{B} \\ &= \frac{\mu_B}{\hbar} \vec{B} \cdot (\vec{L} + 2\vec{S}) \end{aligned}$$

$$\vec{B} = (0, 0, B_z)^T$$

$$V_B = \frac{\mu_B}{\hbar} B_z (\hat{L}_z + 2\hat{S}_z)$$

$$\Delta E_B = \langle \psi_0 | \frac{\mu_B}{\hbar} B_z (\hat{L}_z + 2\hat{S}_z) | \psi_0 \rangle$$

$$\Delta E_B = \mu_B B_z (m_L + 2m_S)$$

electric dipole selection rule:

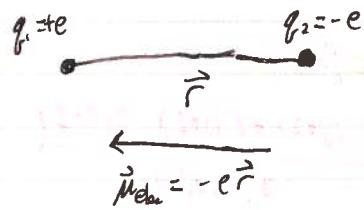
$$\Delta m_L = 0, \pm 1$$

$$\Delta S = 0$$

Atom in E-fields

Weak: Quadratic Stark shift
(non-degenerate levels)

Strong: Linear Stark energy shift
(degenerate levels)



electric dipole moment: $\vec{\mu}_{elec} = -e \vec{r}$

In E-field: potential energy: $V_{\text{F}} =$

$$-V_F = -\vec{\mu}_{elec} \cdot \vec{F}$$

assuming $\vec{F} = (0, 0, F_z)$

$$\Rightarrow V_F = -e z F_z$$

Consider 2 regions:

$$\textcircled{1} \text{ Weak field} \Rightarrow V_F \ll \frac{e^2}{4\pi\epsilon_0 r}$$

stark energy shift smaller than energy interval between unperturbed atomic energy levels

$$\textcircled{2} \text{ Strong field} \Rightarrow V_F \gg \frac{e^2}{4\pi\epsilon_0 r}$$

E-field strongly modifies Coulomb potential
→ ionisation

Quadratic Stark Effect

→ for states w/ no intrinsic electric dipole moment
↳ non-degenerate state

e.g. [H atom $1s \rightarrow n^2$ degeneracy]

For H atom $1s$ orbital $\Rightarrow 2^1S_{\frac{1}{2}}$ ground state

$$\Psi_{n0m} = \Psi_{100}$$

$$\Delta E_F = \int \Psi_{100}^* V_F \Psi_{100} dz$$

\downarrow odd \downarrow even $y=2$

$$= \langle \Psi | V_F | \Psi \rangle = e F_z \int \underbrace{\Psi_{100}^*}_{\text{even}} \underbrace{\Psi_{100}}_{\text{even}} dz$$

$$\Delta E_F = 0$$

→ the part of the operator associated with the electric dipole moment, $\hat{\mu}_{elec} = e\vec{r}$
 $= 0$

↳ atom has no intrinsic electric dipole moment
↳ no first order Stark shift

BUT E-field can polarize atom

→ redistribute e/ charge

→ induced electric dipole moment $\mu_{ind} \propto \vec{F}$

→ Using 2nd order perturbation theory to determine the resulting energy level shifts

$$\Delta E = \underbrace{\int \Psi_0^* V \Psi_0 dz}_{{\text{1st order}} \atop {\text{perturbation}}} + \sum \underbrace{\frac{|\int \Psi_0^* V \Psi_0 dz|^2}{E' - E}}_{{\text{2nd order}} \atop {\text{perturbation}}}$$

using 2nd order pert. theory

$$\Rightarrow \Delta E_F = e^2 F_z^2 \sum_{n'} \sum_{l'=l+1}^{l-1} \frac{|\int \Psi_{n'l'}^* \hat{z} \Psi_{100} dz|^2}{E_{n'l'} - E_{100}}$$

$$\hat{z} = \cos \theta$$

$$= r \sqrt{\frac{4\pi}{3}} Y_{10}(\theta, \phi)$$

For the ground state

$$\hookrightarrow \Delta E_F = e^2 F_z^2 \sum_{n'} \frac{|\int \Psi_{n'0}^* \hat{z} \Psi_{100} dz|^2}{E_{100} - E_{n'0}}$$

$$= -\frac{1}{2} \alpha F_z^2$$

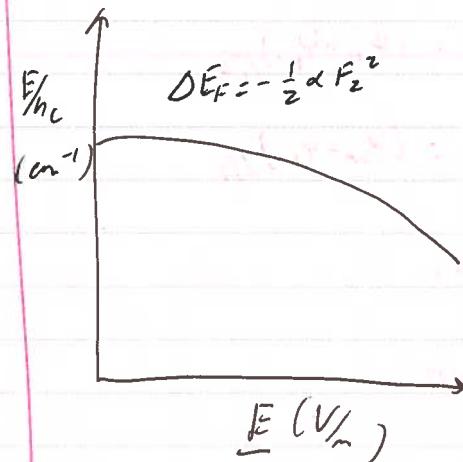
$$\alpha = -2e^2 \sum_{n'} \frac{|\int \Psi_{n'0}^* \hat{z} \Psi_{100} dz|^2}{E_{100} - E_{n'0}}$$

For the induced electric dipole moment

$$-\frac{dE}{dF_z} = \alpha F_z$$

$$\alpha = 747 \times 10^{-41} \text{ C m}^2 \text{ V}^{-1}$$

for H atom $1s$ orbital



Linear Stark Effect

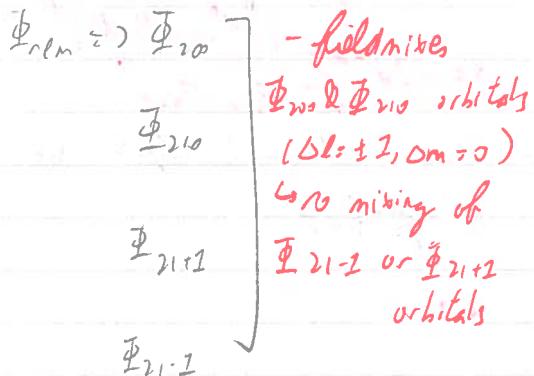
for atoms possessing intrinsic electric dipole moment

i.e. \rightarrow is in an electronic state with d degeneracy

for Atom: $n > 1$

- = linear Stark energy shift
[non-zero first order perturbation]
- \therefore above field mixes orbitals for which $\Delta l = \pm 1, \Delta m = 0$

e.g. Atom: $n = 2$



Now New eigenstates of $\hat{H} = \hat{H}_0 + V_F$:

$$\Psi_1 = \Psi_+ = (\Psi_{210} + \Psi_{210})/\sqrt{2} \quad (\text{sym})$$

$$\Psi_2 = \Psi_- = (\Psi_{210} - \Psi_{210})/\sqrt{2} \quad (\text{anti-sym})$$

$$\Psi_3 = \Psi_{21-1}$$

$$\Psi_4 = \Psi_{21+1}$$

determining the energy shifts of 4_{\pm} states in E-field using first order pert. theory
 $E \ll V_F$

ΔE_F :

$$\Delta E_F = \int \Psi_{21\pm 1}^* V_F \Psi_{21\pm 1} d\tau$$

\Rightarrow [non-degenerate case]

$$\Delta E_F = \int \Psi_{\pm}^* V_F \Psi_{\pm} d\tau$$

$$= \frac{1}{2} \int (\Psi_{200} + \Psi_{200})^* eF_2 (\Psi_{200} + \Psi_{200}) d\tau$$

$$= \frac{1}{2} eF_2 \left[\int \Psi_{210}^* \hat{z} \Psi_{210} d\tau + \int \Psi_{211}^* \hat{z} \Psi_{211} d\tau + \int \Psi_{21-1}^* \hat{z} \Psi_{21-1} d\tau + \int \Psi_{200}^* \hat{z} \Psi_{200} d\tau \right]$$

$$\Rightarrow \Psi_{200} = R_{20}(r) Y_0(0, \phi)$$

$$\Rightarrow \Psi_{210} = R_{21}(r) Y_1(0, \phi)$$

$$z = r \cos \theta$$

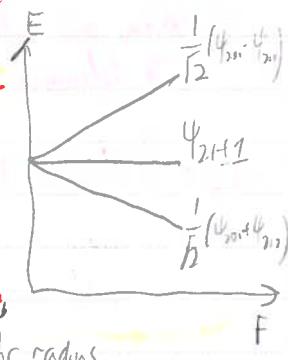
$$= r \sqrt{\frac{4\pi}{3}} Y_{10}(0, \phi)$$

↓ plugging in

$$\Rightarrow \Delta E_F^{\pm} = \mp 3e a_H F_2$$

$$\therefore \Delta E_F = -\mu_{\text{elec}} \cdot \vec{E}$$

$$\Rightarrow \mu_{\text{elec}}^{\pm} = \mp 3ea_H$$



Ψ_1 are also eigenstates of \hat{H}_0
 \hat{H}_0 (field-free Hamiltonian)

\Rightarrow no energy required
 to mix these states

\Rightarrow no need to induce dipole moment
 $\Delta E_F \propto F_z$

Electron charge distributions:

$$\Psi_{\pm} = \frac{1}{\sqrt{2}} [R_{00}(r) Y_0(0, \phi) \pm R_{11}(r) Y_1(0, \phi)]$$

$$= \frac{1}{\sqrt{2}} [R_{00}(r) \pm R_{11}(r) \sqrt{3} \cos \theta]$$

Electron probability distribution
 $\Rightarrow |4\Psi_{\pm}|^2 r^2$

$\Psi_+ \Rightarrow$ el charge localised along E
 behind proton (-ve Z)
 \hookrightarrow molec oriented // to E

$$\boxed{\Delta E_p^+ < 0}$$

$\Psi_- \Rightarrow$ el charge localised along E
 beyond proton (+ve Z)
 \hookrightarrow molec oriented // to E

$$\boxed{\Delta E_p^- > 0}$$

See graph in note

Ionisation in strong electric fields

considering the potential energy part of Hamiltonian
 in presence of E-field ($V(z)$)

$$V(z) = \underbrace{V_c(z)}_{\text{Coulomb interaction}} + \underbrace{V_F}_{\text{E-field}}$$

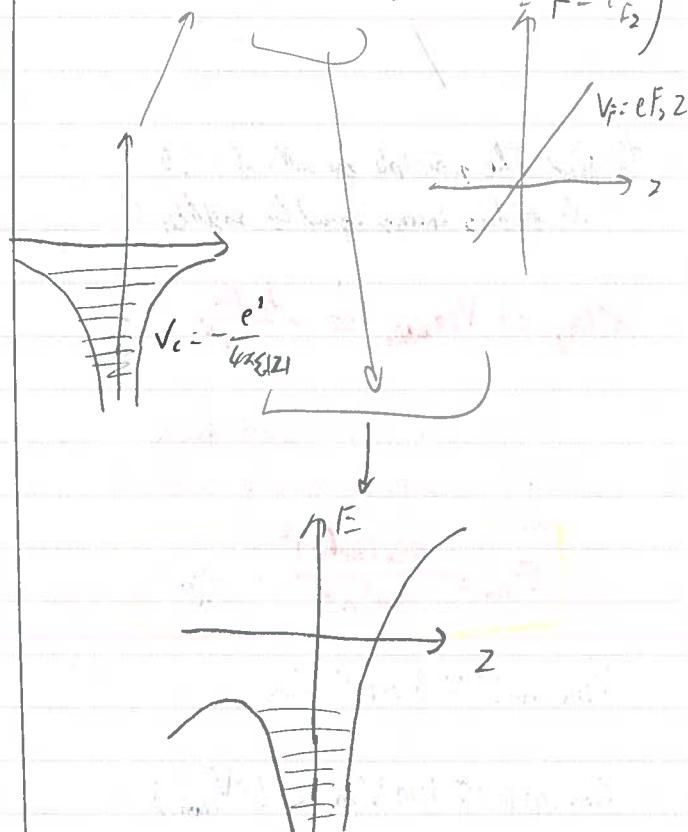
Coulomb
 interaction

$$e^{-pr}$$

$$= -\frac{e^2}{4\pi\epsilon_0|z|} + eF_z z$$

$$E = \begin{pmatrix} 0 \\ 0 \\ F_z \end{pmatrix}$$

$$V_F = eF_z z$$



\Rightarrow @ which n does not take
 to ionize in an electric field

$$\star V(z) = -\frac{e^2}{4\pi\epsilon_0|z|} + eF_z z$$

determining the saddle point

$$\frac{dV(z)}{dz} = \frac{e^2}{4\pi\epsilon_0 z^2} + eF_z = 0$$

$$z_{\text{saddle}} = -\sqrt{\frac{e}{4\pi\epsilon_0 F_z}}$$

$$\Rightarrow V(z_{\text{saddle}}) = -\frac{e^2}{4\pi\epsilon_0} \sqrt{\frac{e}{4\pi\epsilon_0 F_z}} - eF_z \sqrt{\frac{e}{4\pi\epsilon_0 F_z}}$$

$$= -2 \sqrt{\frac{e^3 F_z}{4\pi\epsilon_0}}$$

To find the principle quantum number of state w/ binding energy equal to saddle pt

$$\text{letting } \Rightarrow V(z_{\text{saddle}}) \approx -\frac{hcR_H}{n^2}$$

i. The ionisation electric field for a state w/ principle quantum number n will be:

$$\Rightarrow F_{\text{ion}} = \frac{\pi\epsilon_0 (hcR_H)^2}{e^3 n^4} \propto \frac{1}{n^4}$$

$$F_{\text{ion}}(n=1) \approx 3 \times 10^{13} \text{ V/m}$$

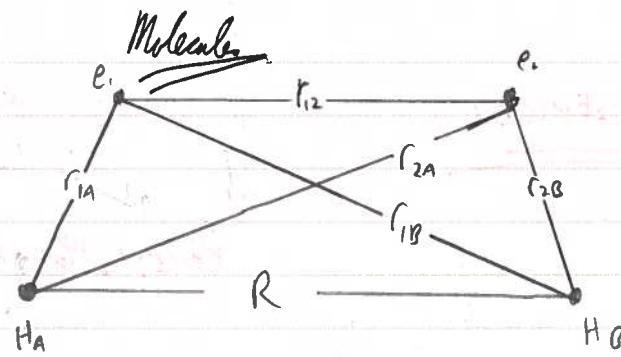
$$F_{\text{ion}}(n=30) \approx 300 \text{ V/m} \quad (3 \text{ V/cm})$$

Diatomic molecule

$A-B$

Now e.g. H_2

(just 2 e⁻/s)



Constructing the Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2M}(\nabla_1^2 + \nabla_2^2) - \frac{Z_A e^2}{4\pi\epsilon_0 r_{1A}} - \frac{Z_B e^2}{4\pi\epsilon_0 r_{1B}} - \frac{Z_A e^2}{4\pi\epsilon_0 r_{2A}} - \frac{Z_B e^2}{4\pi\epsilon_0 r_{2B}}$$

$\hat{T}_n(R)$

$\hat{T}_E(r)$

$\hat{V}_{EN}(r, R)$

$$+ \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}}$$

$\hat{V}_{EE}(r)$

$\hat{V}_{NN}(R)$

⇒ using atomic units

$$\hat{H} = \left[\frac{1}{2M} (\nabla_A^2 + \nabla_B^2) \right] + \left[\frac{1}{2} (\nabla_1^2 + \nabla_2^2) \right] + \left[-\frac{Z_A}{r_{1A}} - \frac{Z_B}{r_{1B}} - \frac{Z_A}{r_{2A}} - \frac{Z_B}{r_{2B}} \right] + \frac{1}{r_{12}} + \frac{1}{R_{AB}}$$

$\hat{H}_n(R)$

$\hat{H}_{el}(r, R)$

$$\Rightarrow \hat{H}(r, R) \psi(r, R) = E \psi(r, R)$$

In a general case:

$$\hat{H} = \hat{H}(R_1, R_2, \dots, R_N, \Sigma_1, \Sigma_2, \dots, \Sigma_N)$$

$$= \sum_N \left[-\frac{\hbar^2}{2m_N} \nabla_N^2 \right] + \sum_i \left[-\frac{\hbar^2}{2m_i} \nabla_i^2 \right] + \frac{e^2}{4\pi\epsilon_0} \left[\sum_{i>j} \frac{1}{(r_{ij} - \Sigma_i)} + \sum_{N>M} \frac{Z_N Z_M}{|R_N - R_M|} \right] - \sum_{N>i} \frac{Z_N}{|R_N - \Sigma_i|}$$

$V(R_N, \Sigma_i)$

e⁻/e⁻ repulsion

N-N repulsion

e⁻/-N attraction

$$H(r, R) \psi(r, R) = E \psi(r, R)$$

* $V = V(R_n; \xi_i)$

↳ interaction between

$e^- & N$ depends on BOTH

positions of $e^- (\xi_i)$ & $N (R_n)$

$$V(r, R) \Rightarrow e^- - N \text{ interaction}$$

couple the coordinates

∴ not possible to separate

the nuclear $v(R_n)$

& e^- nic part $\psi(\xi_i)$ of the total wavefunction (Ψ)

↳ $\Psi(R_n; \xi_i) \neq v(R_n) \psi(\xi_i)$

Applying Born-Oppenheimer [adiabatic] approximation

Notion:

* nuclei is much more massive than e^- s \Rightarrow nuclei are much slower

$$\left[\frac{m_e}{M} \ll 1 \right]$$

adiabatic: for small displacements of nuclei, e^- s will be able to adiabatically adjust its position

We can solve for SE. for fixed no. (R)

$$\psi_r(R_1)$$

↳ instantaneous position of nuclei (x motion)

$$H_{el}(r; R_2) \psi_{el}(r; R_2) = E_{el}(R_1) \psi_{el}(r; R_1)$$

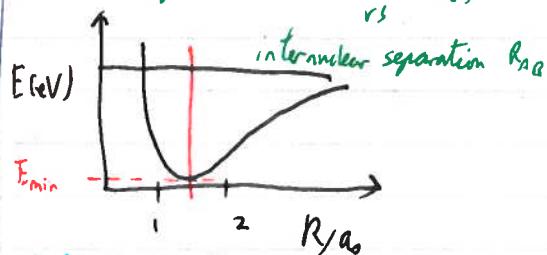
(i) ∴ solving for fixed Nuclear position R_1

- assume no KE in ψ_{el}

- including nuclear repulsion & e^- -nuclear attraction w/ fixed nuclei

↳ gives electronic orbitals & energies for the selected nuclear geometry (representing measurements of multiple nuclear positions)

↳ Plotting energies $E_{el}(R) = E_{el}(R_{AB})$



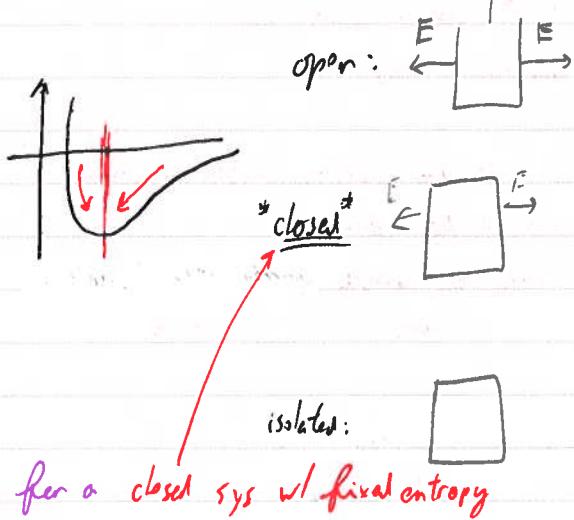
Solving of S.E. for each value of R_{AB} yields a set of eigenvalues $E_{el,n}(R_{AB})$ & eigenfunctions $\psi_{el,n}(r, R_{AB})$ [molecular orbitals]

* $E_{min} \Rightarrow$ most stable nuclear geometry

*) $R_{AB} \rightarrow \infty$: separated atoms, not separated particles

*) $E_{el}(R_{AB} \rightarrow \infty)$: include atomic orbital energies

The minimum energy principle matter



for a closed sys w/ fixed entropy

∴ energy is minimized @ eq^{rr}

closed systems cannot exchange particles
but can exchange energy w/ another system

when the molecule will 'relax' into its
min energy position

↳ it will exchange energy w/
other systems (molecules, surrounding
(l), (s), wall, etc)

in some cases: min energy corresponds to
non-interacting atoms
[far apart [expansion,
dissociation]]

Derivation for BO approach:

write complete wavefunction as a product

$$\Psi(r, R) = \psi_{el}(r, R) \psi_n(R)$$

↳ we can solve for $\psi_{el}(r, R)$ @ const (R)

to determine $\psi_{el}(r, R) = \hat{H}_{el}(R) \psi_{el}(r, R)$

solving complete S.E.:

$$\hat{H}(r, R) \Psi(r, R) = E \Psi(r, R) \Rightarrow \text{expand}$$

$$\Rightarrow [\hat{H}_{el}(r, R) + \hat{H}_n(r, R)] \psi_{el}(r, R) \psi_n(R)$$

$$= E \psi_{el}(r, R) \psi_n(R)$$

$$\hat{H}_{el}(r, R) \psi_{el}(r, R) \psi_n(R) + \hat{H}_n(r, R) \psi_{el}(r, R) \psi_n(R) = E \psi_{el}(r, R) \psi_n(R)$$

↳ $\hat{H}_{el}(r, R) \psi_{el}(r, R) \psi_n(R) = \psi_n(R) \hat{H}_{el}(r, R) \psi_{el}(r, R)$
which includes:

$$\psi_n(R) \hat{H}_{el}(r, R) \psi_{el}(r, R)$$

$$= \psi_n(R) \left[-\frac{1}{2} (\nabla_1^2 + \nabla_2^2) \psi_{el}(r, R) \right]$$

$$\text{for } (2): \hat{H}_n = -\frac{1}{2} \frac{m_e}{N} (\nabla_1^2 + \nabla_2^2)$$

operates on both ψ_{el} & ψ_n , but $\frac{m_e}{M} \ll 1$

$$\Rightarrow \hat{H}_n(R) \psi_{el}(r, R) \ll \hat{H}_{el}(r, R) \psi_{el}(r, R)$$

$$\Rightarrow \hat{H}_n(R) \psi_{el}(r, R) \psi_n(R) \approx \psi_{el}(r, R) \hat{H}_n(R) \psi_n(R)$$

almost a
constant

using the previous stated approach

$$\hat{H}_{el}(C, R) \Psi_{el}(C, R) \Psi_n(R) + \hat{h}_n(R) \Psi_{el}(C, R) \Psi_n(R)$$

$$\approx \Psi_n(R) \hat{H}_{el}(C, R) \Psi_{el}(C, R) + \Psi_{el}(C, R) \hat{h}_n(R) \Psi_n(R)$$

$$\approx \Psi_n(R) E_{el}(R) \Psi_{el}(C, R) + (\hat{h}_n(R)) \hat{\Psi}_n(R) \Psi_n(R) \\ = E \Psi_{el}(C, R) \Psi_n(R)$$

∴ decoupled

↳ no more electronic coordinates

$$\Psi_n(R) E_{el}(R) + \hat{\Psi}_n(R) \Psi_n(R) = E \Psi_n(R)$$

Now we have 2 coupled eq's

$$①: \hat{H}_{el}(C, R) \Psi_{el}(C, R) = E_{el}(R) \Psi_{el}(C, R)$$

$$②: [\hat{h}_n(R) + E_{el}(R)] \Psi_n(R) \\ = [\hat{T}_n(R) + V(R)] \Psi_n(R) = E \Psi_n(R)$$

$V(R)$ is determined through
electronic wavefunctions & energies

$E_{el}(R)$ - determined from eigenvalues of
electronic S.E.

$$E_{el}(R) = V(R)$$

Total molecular energy

↳ includes electronic contribution

↳ the part due to nuclear motion

⇒ can use to solve for
potential energy curve

→ solve for electronic energies & orbitals
w/ nuclei fixed

↳ electronic energies ground the potential
in which the nuclei move

⇒ it's don't lag behind
vibrating/rotating/translating nuclei.
↳ each nuclear geometry has just
one electronic energy

↳ $E_{el}(R)$ vs (R) is single-valued

Overview for BO approx

→ terms involving gradient wrt nuclear coordinates,
 $\nabla_R \Psi_{el}(C, R)$ & $\nabla^2_R \Psi_{el}(C, R)$

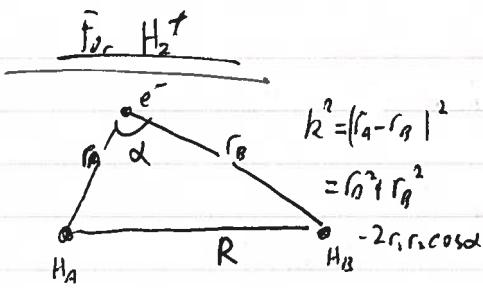
are neglected

⇒ can expect BO approx to break
anytime the nuclear derivative of
the Ψ_{el} changes rapidly

⇒ classical approach for nuclei:

$$\Rightarrow \frac{m_e}{m} \ll 1$$

These approx do not always work



3 body problems: $H_e \& H_2^+$

S.I.E. in only relative variables:

$$\begin{aligned} & -\frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2) \Psi_{e1}(r_1, r_2) \\ & - \frac{2e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \Psi_{e1}(r_1, r_2) \\ & + \frac{e^2}{4\pi\epsilon_0 r_1 r_2} \Psi_{e1}(r_1, r_2) = E \Psi_{e1}(r_1, r_2) \end{aligned}$$

$$A_{e1}(r; R) \Psi_{e1}(r; R) = E_{e1}(R) \Psi_{e1}(r; R)$$

$$A_{e1} = -\frac{\nabla^2}{2} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R}$$

* R is fixed, hence the semicolon (;

↳ determine $E_{e1}(R)$ by fixing R

@ many different values

→ A_{e1} is a function of just one e1's coordinates

→ forming MO as a linear comb of AO

$$\Psi_{e1} = C_1 |1s_A\rangle + C_2 |1s_B\rangle$$

[LCAO]

[are e1 func (Mo)]



↳ functions of the same electron's coordinates



but centred on diff atoms]

C_1, C_2 are mixing coeffs

* we can also say that the MO

has been expanded in terms of

a minimal basis set of

one $1s$ orbital on each atom

$$P(r) = |\Psi_{e1}|^2 = C_1^2 (1s_A)^2 + C_2^2 (1s_B)^2$$

$$+ 2C_1 C_2 \int |1s_A| |1s_B| dr$$

→ which is the e1 prob density

* must have inversion symm : mol. is symm

$$\Rightarrow C_1^2 = C_2^2 \quad || \text{ squared coeff}$$

↳ prob to find

$$C_1 = \pm C_2 \text{ an e1}$$

@ each nucleus

cannot separate the variables

& solve exactly : of electronic repulsion term

need to use Approx Methods

- Perturbation Theory

- Variational Method \Rightarrow applying to H_2^+ mol
in following:

Variational Method

for ground state

Energy E_0 & eigenfunction ψ_0 exist
but not known

↳ calling $\psi = \tilde{\chi}$

$$\hat{H}\psi = E_0\psi \quad (\text{if normalized})$$

$$\langle \psi | \hat{H} | \psi \rangle = \langle \psi | E_0 | \psi \rangle = E_0$$

$$\langle \hat{A} \rangle = E_{\text{var}}$$

$$E_{\text{var}} = \frac{\langle \tilde{\chi} | \hat{A} | \tilde{\chi} \rangle}{\langle \tilde{\chi} | \tilde{\chi} \rangle} = \langle \tilde{\chi} | \hat{A} | \tilde{\chi} \rangle$$

18 Variational Theorem

$E_{\text{var}} \geq E_0$ for any choice
of wavefunction $\tilde{\chi}$

⇒ Proof:

expand $\tilde{\chi}$ as lin comb of ψ_n
Normalized ↓
 Orthonormal

$$\tilde{\chi} = \sum_n a_n \psi_n$$

$$\langle \tilde{\chi} | \tilde{\chi} \rangle = \sum_n |a_n|^2 \cdot 1$$

$$E_{\text{var}} = \langle \tilde{\chi} | \hat{A} | \tilde{\chi} \rangle = \int \sum_n a_n^2 \psi_n^2 \hat{A} \sum_n a_n \psi_n d\tau$$

$$= \sum_n |a_n|^2 E_n \underbrace{\langle \psi_n | \hat{A} | \psi_n \rangle}_{= 1}$$

$$E_{\text{var}} = \sum_n |a_n|^2 E_n$$

Similarly

$$E_0 = |E_0| \sum_n |a_n|^2 E_0$$

Subject to from Var

$$\begin{aligned} E_{\text{var}} - E_0 &= \sum_n |a_n|^2 E_n \\ &\quad - \sum_n |a_n|^2 E_0 \\ &= \sum_n |a_n|^2 (E_n - E_0) \geq 0 \\ \therefore E_n &\geq E_0 \end{aligned}$$

Variational method is powerful

↳ can try lots of $\tilde{\chi}$,
calc E_{var} for each

⇒ lowest value is closest to E_0

For a closed sys w/ fixed entropy
→ E_{var} is minimized @ eqⁿ

Total potential energy of a system
w/ dissipation will be @ minimum
@ eqⁿ

⇒ minimizing

$$\tilde{E} = \int d\tau \tilde{\psi}_n \tilde{V} \tilde{\psi}_n$$

w.r.t $\tilde{\psi}(x)$

Var. principle ensures we never go
below the right energy

⇒ $\tilde{E} \geq E$

Applying this principle

$$\Psi_{el}(1) = c_1|s_A(1) + c_2|s_B(1) \Rightarrow LCAO$$

[one e/ MO's extend over entire molecule]

[last values of c_1 & c_2 give min(E_{el})]

$$\Psi_{el} = \Psi_{el}(r; R)$$

Ψ_{el} not yet normalized

$$\rightarrow E_{el} \neq \langle \Psi_{el} | \hat{H} | \Psi_{el} \rangle$$

$$E_{el} = \frac{\langle \Psi_{el} | \hat{H} | \Psi_{el} \rangle}{\langle \Psi_{el} | \Psi_{el} \rangle}$$

$$= \frac{\langle (c_1|s_A + c_2|s_B) | \hat{H} | (c_1|s_A + c_2|s_B) \rangle}{\langle (c_1|s_A + c_2|s_B) | (c_1|s_A + c_2|s_B) \rangle}$$

$$= c_1^2 \langle 1s_A | \hat{H}_{el} | 1s_A \rangle + c_1 c_2 \langle 1s_A | \hat{H}_{el} | 1s_B \rangle$$

$$+ c_1 c_2 \langle 1s_B | \hat{H}_{el} | 1s_A \rangle + c_2^2 \langle 1s_B | \hat{H} | 1s_B \rangle$$

$$c_1^2 \langle 1s_A | 1s_A \rangle + c_1 c_2 \langle 1s_A | 1s_B \rangle$$

$$+ c_1 c_2 \langle 1s_B | 1s_A \rangle + c_2^2 \langle 1s_B | 1s_B \rangle$$

we have two centres, there is a new quantity - overlap integral (S_{AB}) between the orbitals on two centres

$$S_{AB} = \langle 1s_A | 1s_B \rangle = S_{BA} = \langle 1s_B | 1s_A \rangle = S$$

Within all valid functions of Ψ for the ground state
 \Rightarrow looking for the func.
w/ the lowest exp value for E_{var}
 $E_{var} \rightarrow \text{Minimum}$

Practical procedure

choose some form of trial Ψ w/ free variational parameters $\alpha_i: \Psi(\alpha_1, \alpha_2, \dots, \alpha_n)$

\hookrightarrow determine parameters using var principle
 \hookrightarrow this gives the best possible solⁿ
for this particular form of the trial wavefunction

$$\delta F_{\Psi}(\alpha_1, \alpha_2, \dots) = \frac{\partial E_{\Psi}}{\partial \alpha_1},$$

$$+ \frac{\partial E_{\Psi}}{\partial \alpha_2} \frac{d\alpha_2}{d\alpha_1} + \dots = 0$$

Variations $d\alpha_i$ are arbitrary

$$\hookrightarrow \frac{\partial E_{\Psi}}{\partial \alpha_i} = 0 \text{ for all } i$$

\rightarrow change the form of the trial func.
& the number of free parameters

& try again until the lowest energy is reached

Abbreviate Integrals

$$E_{el} = \frac{c_1^2 H_{AA} + c_1 c_2 H_{AB} + c_2 c_1 H_{BA} + c_2^2 H_{BB}}{c_1^2 S_{AA} + c_1 c_2 S_{AB} + c_2 c_1 S_{BA} + c_2^2 S_{BB}}$$

\Rightarrow

$$(c_1^2 S_{AA} + c_1 c_2 S_{AB} + c_2 c_1 S_{BA} + c_2^2 S_{BB}) E_{el}$$

$$= c_1^2 H_{AA} + c_1 c_2 H_{AB} + c_2 c_1 H_{BA} + c_2^2 H_{BB}$$

differentiate w/ parameter c_1, c_2

$$\frac{\partial E_{el}}{\partial c_1} = 0 ; \frac{\partial E_{el}}{\partial c_2} = 0$$

\hookrightarrow obtain two eq's for $c_1, 0, c_2$
+

a normalization condition

\Rightarrow ultimately determine $c_1, 0, c_2$ uniquely

\hookrightarrow using **secular determinant**

$$\begin{vmatrix} 2(H_{AA} - S_{AA}E) & [H_{AB}H_{BA} - (S_{AB} + S_{BA})E] \\ [H_{AB}H_{BA} - (S_{AB} + S_{BA})E] & 2(H_{BB} - S_{BB}E) \end{vmatrix} = 0$$

$$\begin{aligned} \frac{\partial E_{el}}{\partial c_1} &= c_1^2 S_{AA} + c_1 c_2 S_{AB} + c_2 c_1 S_{BA} + c_2^2 S_{BB} \\ &+ E_{el} (2c_1 S_{AA} + c_2 S_{AB} + c_2 S_{BA}) \\ &= 2c_1 H_{AA} + c_1 H_{AB} + c_1 H_{BA} \\ \frac{\partial E_{el}}{\partial c_2} &= (c_1^2 S_{AA} + c_1 c_2 S_{AB} + c_2 c_1 S_{BA} + c_2^2 S_{BB}) \\ &+ E_{el} (2c_2 S_{AB} + c_1 S_{AB} + c_1 S_{BA}) \\ &= 2c_2 H_{BB} + c_1 H_{AB} + c_1 H_{BA} \end{aligned}$$

Giving two lin eq's w.r.t $c_1, 0, c_2$

$$2c_1(H_{AA} - S_{AA}E) + c_2(H_{AB} + H_{BA} - S_{AB} - S_{BA}) = 0$$

$$c_1(H_{AB} + H_{BA} - S_{AB} - S_{BA}) + 2c_2(H_{BB} - S_{BB}E) = 0$$

\hookrightarrow solving by Matrix

have the secular det

- simplifying the determinant

$$\leftrightarrow S_{AA} = S_{BA} \quad (H \text{ is Hermitian})$$

$$\leftrightarrow H_{AB} = H_{BA}$$

$$\begin{vmatrix} H_{AA} - S_{AA}E & H_{AB} - S_{BA}E \\ H_{AB} - S_{BA}E & H_{BB} - S_{BB}E \end{vmatrix} = 0$$

More generally

writing wavefunctions as a
lin comb of N functions

$$\psi = c_1 \phi_1 + c_2 \phi_2 + \dots + c_N \phi_N$$

If analogously yielding
 N energies through
secular det

$$\begin{vmatrix} H_{AA} - S_{AA}E & H_{AB} - S_{BA}E & \dots & H_{AN} - S_{BN}E \\ H_{AB} - S_{BA}E & H_{BB} - S_{BB}E & \dots & H_{NB} - S_{NB}E \\ \vdots & \vdots & \ddots & \vdots \\ H_{AN} - S_{BN}E & H_{NB} - S_{NB}E & \dots & H_{NN} - S_{NN}E \end{vmatrix} = 0$$

Calculating matrix elements:

For the case of H_2^+ :

$$\langle 1s_A | 1s_B \rangle = \langle 1s_B | 1s_A \rangle$$

$$S_{AA} = S_{BB} = 1$$

$$\langle 1s_A | 1s_B \rangle = \langle 1s_B | 1s_A \rangle$$

$$S_{AB} = S_{BA} = S$$

\therefore both AO's are the same

\Rightarrow

$$H_{AA} = \langle 1s_A | \hat{H}_{el} | 1s_A \rangle$$

$$= \langle 1s_B | \hat{H}_{el} | 1s_B \rangle = H_{BB}$$

$$\hookrightarrow \begin{bmatrix} H_{AA} - E & H_{AB} - SE \\ H_{AB} - SE & H_{BB} - E \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$\hookrightarrow \begin{vmatrix} H_{AA} - E & H_{AB} - SE \\ H_{AB} - SE & H_{BB} - E \end{vmatrix} = 0$$

$$\hookrightarrow (H_{AA} - E)^2 - (H_{AB} - SE)^2 = 0$$

$$\begin{aligned} E^2(1-S^2) - 2E(H_{AA} - H_{AB}S) \\ + (H_{AA}^2 - H_{AB}^2) = 0 \end{aligned}$$

$$[(E(1-S) - (H_{AA} - H_{AB})) [E(1+S) - (H_{AA} + H_{AB})]] = 0$$

$$E_{el}^I(R) = \frac{H_{AA} \pm H_{AB}}{1 \mp S}$$

$$\hat{H}_{el} = \left(-\frac{\nabla^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right)$$

$$H_{AA} = \langle 1s_A | \hat{H}_{el} | 1s_A \rangle$$

$$= \int d\tau 1s_A^* \left(-\frac{\nabla^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_A$$

$$H_{AB} = \int d\tau 1s_A^* \hat{H}_{el} 1s_B = \int d\tau 1s_A^* \left(-\frac{\nabla^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_B$$

Energy of 1H atom AB in a.u.

$$\Rightarrow \left(-\frac{\nabla^2}{2} - \frac{1}{r_A} \right) 1s_A = -\frac{1}{2} s_A$$

$$\Rightarrow \left(-\frac{\nabla^2}{2} - \frac{1}{r_B} \right) 1s_B = -\frac{1}{2} s_B$$

$$\Rightarrow H_{AA} = -\frac{1}{2} + \int d\tau 1s_A^* \left(-\frac{1}{r_A} + \frac{1}{R} \right) 1s_A = -\frac{1}{2} + J'$$

$$\Rightarrow H_{AB} = -\frac{1}{2} + \int d\tau 1s_A^* \left(-\frac{1}{r_A} + \frac{1}{R} \right) 1s_B = -\frac{1}{2} + K'$$

J' : Coulomb integral

$(1s_A^* 1s_A)$ is the charge density of e^- around proton A

r represents the coordinate of the e^- relative to proton A

$\therefore r_A$ = distance of this e^- to proton B,

$\hookrightarrow J'$ gives the avg pot. energy of the charge density

around e^- p⁻A interacting w/ p⁺B

K' : exchange integral

\hookrightarrow pot. energy due to the interaction of the overlap charge densities w/ one of the protons

$(1s_A^* 1s_B)$ = overlap charge density

\therefore overlap charge density is significant in the region of space between nuclei

\hookrightarrow important contribution to bond.

$$E_{el}^{\pm}(R) = \frac{H_{1s} \pm H_{1s}}{1+s}$$

$$= \frac{(-\frac{1}{2} + J') \pm (-\frac{1}{2} + K')}{1+s}$$

$$E_{el}^{\pm}(R) = -\frac{1}{2} + \frac{J' \pm K'}{1+s}$$

Energy of H_2^+ molecule - ion

↳ total electronic energy for 2 protons & an e^- brought from ∞ distance

H atom energy $= -\frac{1}{2}$ in an or rest energy to form the MO

$$\Delta E_{el}^{\pm}(R) = \frac{J' \pm K'}{1+s}$$

energy of H_2^+ molecule - ion relative to separated H atom & proton

for H^+ :

↳ balance between the repulsion of the two protons $\frac{1}{R}$, J' , K' , which are both negative

→ minimum energy produced @ 134 pm

* Minimum represents the formation of a chemical bond

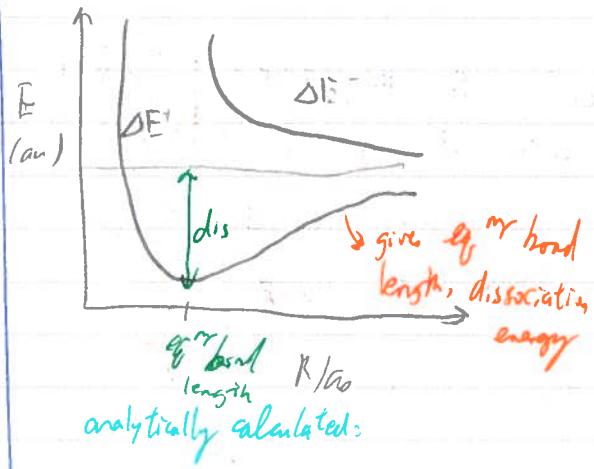
for H^- : (glue does not stick)
 K' is a positive quantity

⇒ cancels J'

↳ insufficient compensation

↳ Coulomb repulsion of the protons

* no overlap charge density between proton to compensate their repulsion



analytically calculated:

$$S = e^{-R} \left(1 + R + \frac{R^2}{3} \right)$$

$$J' = e^{-2R} \left(1 + \frac{1}{R} \right)$$

$$K' = \frac{S}{R} + e^{-R} (1 + R)$$

BUT bad approx in term of real numericals

→ could vary functional form of AO's to do better

* See graphs in slides

Now to determine the MOs

→ values of coeff c_1, c_2

using:

$$E_{el}^{\pm}(R) = \frac{H_{aa} \pm H_{bb}}{1+s}$$

- all parameters are known;
- either $\neq 0$ for c_1 or c_2
can be used

$$c_1(H_{aa} - E) + c_2(H_{bb} - S\bar{E}) = 0$$

taking E^+

$$c_1\left(H_{aa} - \frac{H_{aa} + H_{bb}}{1+s}\right) + c_2\left(H_{bb} - S \frac{H_{aa} + H_{bb}}{1+s}\right) = 0$$

$$\Rightarrow c_1\left(\frac{SH_{aa} - H_{bb}}{1+s}\right)$$

$$+ c_2\left(\frac{H_{bb} - SH_{aa}}{1+s}\right) = 0$$

$$\Rightarrow \underline{\underline{c_1 = c_2}} \quad \begin{bmatrix} \text{Can also be} \\ \text{known by} \\ \text{Symmetry} \end{bmatrix}$$

$$\Psi_{el} = c_1(1s_A + 1s_B)$$

↓ Normalization

$$\langle \Psi_{el} | \Psi_{el} \rangle = c_1^2 \int d\zeta (1s_A^2 + 2 \cdot 1s_A 1s_B + 2s_B^2)$$

$$= c_1^2 (1 + 2S + 1) = 1$$

Boundary:

$$\Psi_{el}^+ = \frac{1}{\sqrt{2(1+s)}} (1s_A + 1s_B)$$

[normalized ground state
(bonding) molecular orbital]

In Interpretation:

looks like a Schrödinger cat type of state

- e^- is in $1s$ $1s$ orbital of nucleus A

$1s$ orbital of nucleus B

UNLESS being measured

Expt^{tr} \Rightarrow when $R \rightarrow \infty$

↳ molecule dissociates

↳ e^- will end up on one of the nuclei \Rightarrow can measure as H atom

BUT do not know which one

- $1s$ orbitals have the same energies

if we try to prepare another trial wave function

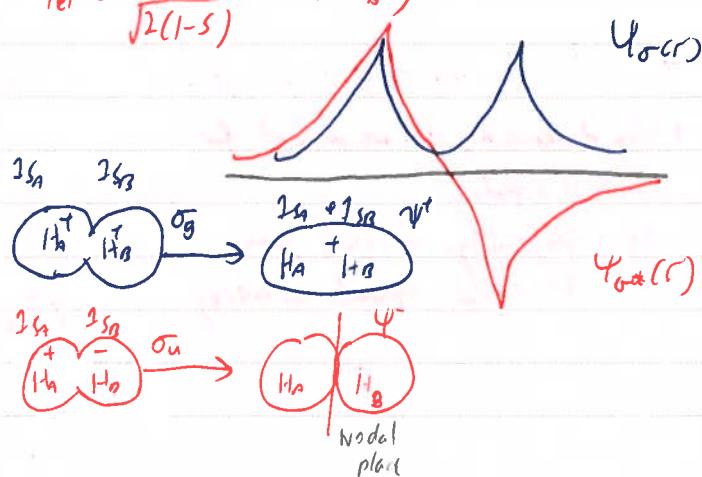
$$\Psi_{el} = c_1 2s_A + c_2 2s_B$$

[intuitively, energies of $1s$ & $2s$ states
are v. different \Rightarrow expect $c_1 \gg c_2$]

Antibonding: $1s^-$ symmetric

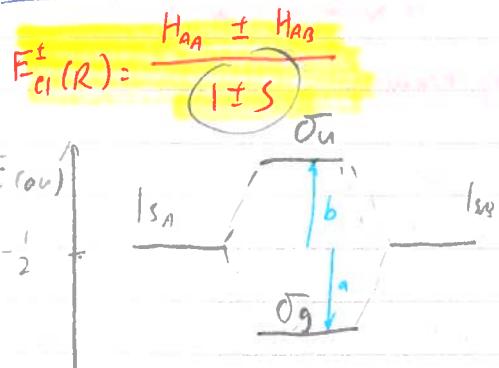
$$c_1 = -c_2$$

$$\Psi_{el}^- = \frac{1}{\sqrt{2(1-s)}} (2s_A - 2s_B)$$



if sym about the molecular axis: σ_{sym}

- if sym w.r.t. inversion through centre: g (gerade)
- antisym $\rightarrow u$ (ungerade)



- antibonding orbital is shifted sym more than the binding orbital is shifted down $\rightarrow (b > a)$
[Overlap repulsion] $\cos S$ is a fraction

[might not be true for all diatomic molecules, but is a good rule of thumb]

When S_{12} is non zero, there are 2 effects that shift the energies

- \rightarrow physical interaction between atoms,
- \rightarrow $1s_A \& 1s_B$ orbitals are not orthogonal
- \rightarrow When diagonalizing H , we account for R_s / H effects
 \hookrightarrow orthogonality constraint pushes the orbitals upwards in energy

Moving on to the H_2 atom
[many- e^- atoms]
(previous page)

$$H = -\frac{r_1}{2} - \frac{r_2}{2} - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{R}$$

$\rightarrow \text{H}_2$ contains:

- $2e^-/\text{s}$
- $\frac{1}{r_n} e^-/\text{repulsion term}$
- $\hookrightarrow V_{\text{tot}} = V_{\text{el}}(r_1, r_2; R)$
- Variables are non-separable
- Cannot solve SE separately

- Can consider:

$$\text{A: } \text{Bohr approximation}$$

$$R$$

neglecting $e^- - e^-$ interaction

$$\hookrightarrow V(r_{12}, \dots, r_N) = V(r_1) \cdot V(r_2) \times \dots \times V(r_N)$$

(v. crude approx for the)

(1927) Heitler-London / Valence Bond method
is held by bonds

1. construct a probe Ψ : $\Psi(r_1, r_2) = 1s_A(1)1s_B(2)$

$$\hookrightarrow R_e \text{ (eq dist)} \approx 1.7 \text{ au}$$

i.e. [cm from molecule]

$$\hookrightarrow E_b \text{ (binding energy)} \approx 0.25 \text{ eV}$$

\hookrightarrow too small to

account for strongly-bound H_2 molecule

$$\hat{E}(R) = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

2. idea: e⁻s in Hydrogen
are indistinguishable
∴ using a symmetrised

wavefunction:

$$\Psi(r_1, r_2) = 1s_1(1) 1s_0(2) \\ + 1s_0(2) 1s_1(1)$$

w/ more realistic results:

$$R_e \approx 80 \text{ pm}$$

$$E_e \approx 3.2 \text{ eV}$$

But can do better

(1927) Hartree self-consistent field method:

→ assuming electrons interact
BUT use trial N -e⁻ wavefunction
in a form of a product of one-e⁻ fun.

$$\Psi(r_1, r_2, r_3, \dots, r_n) = \psi_1(r_1) \psi_2(r_2) \dots \psi_n(r_n)$$

→ no restrictions to any form of wavefunc.
→ use variational method to find sol. Ψ
e⁻s assumed to interact BUT
move independently: screening the
nuclei & repelling each other

↳ no correlation between e⁻s

use this approach to improve the
quality of an initial guess function (H-like)
UNTIL E_{tot} is minimised
&
does not change

Pauli Exclusion principle (again)
no more than 2 e⁻s per orbital

↳ or
no e⁻s w/ all the same quantum numbers

∴ e⁻s will have to "pile up" on top
of each other "within an atom"

↳ i.e. atoms occupy a volume

↳ cannot be squeezed too close \exists t_{rep}
[Pauli repulsion]

- 1967: Freeman Dyson & Andrew Lenard

↳ considered the balance of

forces [• attractive [e⁻-nuclear]
• repulsive [e⁻-e⁻ & nuclear - nuclear]]

↳ ordinary matter would collapse

↳ occupy a much smaller volume
w/o the Pauli principle

⇒ consequence:

e⁻s of the same spin are kept
apart by a repulsive exchange force
or exchange interaction

↳ e⁻s are indistinguishable (as before)

→ identifying e⁻s is not possible
in QM, ∵ each particle does not
follow a trajectory described classically

↳ we only have probabilities,
from Ψ^2 for finding
the particles @ each pt in space

↳ no way of determining which e⁻ it
is theoretically / except

~~Welford's method~~

Two particle system
expressed mathematically

→ Label particles as
 ψ_1 & ψ_2

Here $\hat{H}_{\text{elec}} = \hat{H}(1,2)$
 $= \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} + V(q_1, q_2)$

if: $i \in \{1, 2\}$

↳ 3-D continuous spatial coord r_i
&

The discrete spin coordinate σ_i
of particle i

* for the 2 identical particles to be
indistinguishable

↳ \hat{H} must be symm w.r.t. particle interchange

↳ under the interchange of coord (spatial + spin)

$H(1,2)$ must remain invariant

$$H(1,2) = H(2,1)$$

→ TISE for the two-particle sys

$$\hat{H}(1,2)\Psi_r(1,2) = E_r\Psi_r(1,2)$$

$$\Rightarrow \hat{H}(2,1)\Psi_r(1,2) = \hat{H}(1,2)\Psi_r(1,2) = E_r\Psi_r(2,1)$$

↳ also an eigenfunction of $\hat{H}(1,2)$
belonging to the same eigenvalue E_r

∴ any lin. comb. of $\Psi_r(1,2)$ & $\Psi_r(2,1)$

is also an eigenfunction of $\hat{H}(1,2)$

w/ eigenvalue E_r .

→ introducing linear hamiltonian
Exchange operator \hat{P}

$$\Rightarrow \hat{P}\Psi(1,2) = \Psi(2,1)$$

check whether it commutes w/
the \hat{H}

$$\begin{aligned} \hat{P}[\hat{H}(1,2)\Psi(1,2)] &= \hat{H}(2,1)\hat{P}\Psi(1,2) \\ &= \hat{H}(2,1)\Psi(2,1) \\ &= \hat{H}(2,1)\hat{P}\Psi(1,2) \end{aligned}$$

\hat{P} & $\hat{H}(1,2)$ commute

$$\Rightarrow [\hat{P}, \hat{H}(1,2)] = 0$$

∴ operator \hat{P} & $\hat{H}(1,2)$ have
simultaneous eigenfunctions

$$\hat{P}\Psi(1,2) = \lambda\Psi(1,2)$$

$$\hookrightarrow \hat{P}^2\Psi(1,2) = \hat{P}\lambda\Psi(2,1) = \lambda\Psi(1,2)$$

$$\Rightarrow \hat{P}^2 = 1, \lambda = \pm 1$$

They are only two functions which are
simultaneous eigenfunctions of
 $\hat{H}(1,2)$ & \hat{P} with respective eigenvalues
 ± 1

such functions are the combinations

$$\Psi_S = [\Psi(1,2) + \Psi(2,1)]/\sqrt{2} \quad \left. \right\} \text{orthogonal}$$

$$\Psi_A = [\Psi(1,2) - \Psi(2,1)]/\sqrt{2}$$

Ψ_S & Ψ_A satisfy the following relations:

$$\hat{P}\Psi_S = \Psi_S$$

$$\hat{P}\Psi_A = -\Psi_A$$

* Ψ_A is antisymm. w.r.t particle interchange

∴ it changes sign,
∴ LSE: unchanged when particles are exchanged.

Detailed descrip^t of H₂ molecule

[see also p. 119-130 in notes]

⇒ To construct all lowest energy states of H₂:

↳ using 1s orbitals of H atom as a basis

$$\Psi^T = \frac{1}{\sqrt{2}} [\phi_{1s}(c_{A1})\phi_{1s}(c_{B2}) - \phi_{1s}(c_{A2})\phi_{1s}(c_{B1})] X^T$$

$$\Psi^S = \frac{1}{\sqrt{2}} [\phi_{1s}(c_{A1})\phi_{1s}(c_{B1}) + \phi_{1s}(c_{A2})\phi_{1s}(c_{B2})] X^S$$

$$E_T(R) = \frac{\langle \Psi^{S,T} | H | \Psi^{S,T} \rangle}{\langle \Psi^{S,T} | \Psi^{S,T} \rangle}$$

⇒ Hund-Mulliken method: (poor result)

→ use trial wavefunction as an antisymmetrised product of two one-e[−] functions

$$\Rightarrow \Psi = A \phi(1)\phi(2)\phi(2)\beta(2)$$

$$= \phi(1)\phi(2) \cdot \frac{1}{\sqrt{2}} [\alpha(1)p(1) - \beta(1)\alpha(2)]$$

→ represent each one-e[−] function

as a sum of 1s orbitals
centred on each proton: Mo LCAO

$$\phi(1)\phi(2) = \frac{1}{2(HS)} [1s_a(1) + 1s_b(1)][1s_a(2) + 1s_b(2)]$$

$$= \frac{1}{2(HS)} [1s_a 1s_a + 1s_a 1s_b + 1s_b 1s_a + 1s_b 1s_b]$$

H_a⁻ + H_a⁺
(Ionic dissociation limit)

↓ ↓ ↓
overlap charge density

H_a⁺ + H_a⁻

apart from covalent term) also have ionic term

BUT now result

- neglected $e^- - e^-$ correlation
- ↳ 2nd e^- "knows" only the avg distribution of the 1st e^-
- w/ equal probability on each nucleus [not its actual location]
 - ↳ chooses th nuclei w/ equal probability
- ∴ has 50% chance of ending up on the same nucleus as the 1st e^-

→ a general phenomenon

↳ not suitable for describing the whole mol. surface

→ region around the eq^{rry} pos.
is usually described
w/ reasonable accuracy

ANOTHER method:

using the lowest energy one- e^- /MO,
for H_2^+ as a basis:

$$\psi_{M_0}^{ots} = \frac{1}{\sqrt{2(1+s)}} (2s_A + 2s_B)$$

$2e^-$ s w/ opposite spin in this MO
[just like He atom 1s orbital]

$$\begin{aligned}\psi_{el}^{ots}(1,2) &= \psi_{el}^{ots}(1)\psi_{el}^{ots}(2) \\ &= \frac{1}{2(1+s)} [2s_A(1) + 1s_B(2)][1s_A(2) + 1s_B(1)]\end{aligned}$$

symm. func.

→ complete Ψ including antisymm. spin part

$$\begin{aligned}\psi_{el}^{ots}(1,2) &= \frac{1}{2(1+s)} [2s_A(1) + 1s_B(2)][1s_A(2) + 1s_B(1)] \\ &\times \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \\ &= \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{\alpha(1)} & \psi_{\beta(1)} \\ \psi_{\alpha(2)} & \psi_{\beta(2)} \end{vmatrix} \quad \text{Is slater det.}\end{aligned}$$

Remember as by:

$$\hat{H}_{el} = \underbrace{\left(-\frac{\nabla_1^2}{2} - \frac{1}{r_{1A}}\right)}_{h_{1A}} + \underbrace{\left(-\frac{\nabla_2^2}{2} - \frac{1}{r_{2A}}\right)}_{h_{2A}} + \underbrace{\left(-\frac{1}{r_{1A}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R}\right)}_{Coulomb}$$

$$= \underbrace{\left(-\frac{\nabla_1^2}{2} - \frac{1}{r_{1B}}\right)}_{h_{1B}} + \underbrace{\left(-\frac{\nabla_2^2}{2} - \frac{1}{r_{2B}}\right)}_{h_{2B}} + \underbrace{\left(-\frac{1}{r_{1A}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R}\right)}_{Coulomb}$$

Molecular electronic energy:

$$E_{el} = \langle \psi_{el}^{1s} | \hat{H} | \psi_{el}^{1s} \rangle$$

$$= \iint d\sigma_1 d\sigma_2 \iint dr_1 dr_2 \psi_{el}^{1s*} \hat{H}_{el} \psi_{el}^{1s}$$

↓

$$E_{el}(R) = 2E_{1s} - \frac{1}{R} - \frac{2J(R) + 2K'(R)}{1 + S(R)}$$

$$+ \frac{J''(R) + 2K''(R) + m(R) + 4L(R)}{2(1 + S(R))^2}$$

diagonal $\ell = 0$ integral $\therefore e^- / A$ w/ nuclei B

$$J' = \left\langle 1s_A \left| -\frac{1}{r_A} + \frac{1}{R} \right| 1s_A \right\rangle$$

Coulomb

} single e^- integrals

$$K' = \left\langle 1s_A \left| -\frac{1}{r_A} + \frac{1}{R} \right| 1s_B \right\rangle$$

exchange

Coulomb int: represents the repulsion between the $2e^-$ clouds

Exchange int: E-shift arising from the restrictions imposed on the wavefunction by the Pauli principle

$$J'(R) = \left\langle 1s_A^2(1) \left| \frac{1}{r_{12}} \right| 1s_A^2(2) \right\rangle$$

Coulomb type

$\hookrightarrow e^-$ densities of $e^- 1 \otimes 2$

overlap density, overlap density

$$K'(R) = \left\langle 1s_A(1) 1s_B(1) \left| \frac{1}{r_{12}} \right| 1s_A(2) 1s_B(2) \right\rangle$$

repelling each other \hookrightarrow exchange type

→ result of Pauli Exclusion Principle

\therefore apply antisymmetrisation to wavefunctions

$$M(R) = \left\langle 2s_A^2(1) \left| \frac{1}{r_{12}} \right| 2s_A^2(2) \right\rangle$$

Coulomb type

$$L(R) = \left\langle 2s_A^2(1) \left| \frac{1}{r_{12}} \right| 1s_A(2) 1s_B(2) \right\rangle$$

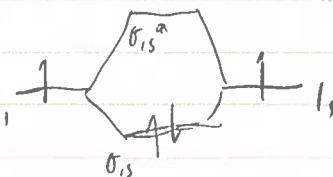
Coulomb exchange type

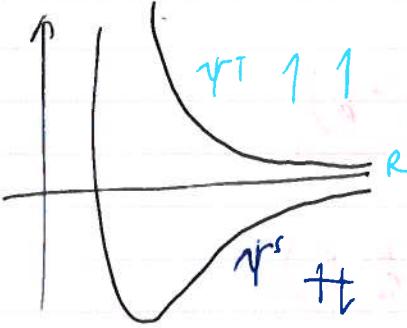
$2e^-$ integrals

both repulsive \therefore both true for $J \otimes K$

\hookrightarrow repulsive interactions for the singlet states

$\&$ increase their energies



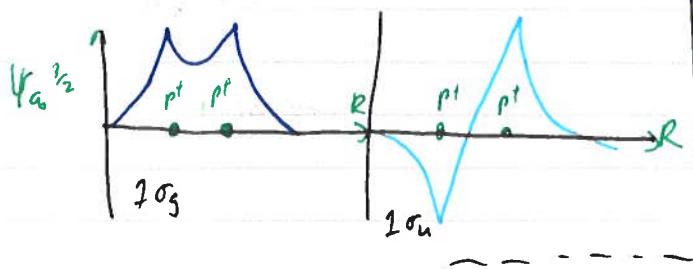


r^p spin $\uparrow\downarrow$, cannot be on the same orbital

∴ Energy is much higher

$\min E \text{ as } R \rightarrow \infty$

for $2r^s$,



Using variational principle
to improve results

1) Choose an Atomic Orbital Basis

- big basis; fine
- can vary exponents as well
- bigger basis = lower energy

[longer AO expansion always gets us closer to the ground state energy]

(see James D. Carlidge in 1933 in notes)

Towards bigger,
more complex molecules

extending the idea of LCAO:

→ MO can be represented by

a column vector:

$$\vec{\Psi} = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{pmatrix}$$

* for accuracy

↳ better to include
more basis set of AO,

$$\Psi = \sum_{i=1}^N c_i \phi_i^{AO} \quad \text{with } \star$$

↳ accurate if AO's form
a complete set

[real calc: use incomplete basis sets
due to computational difficulties]

dimension of matrices which
need to be calculated ↑↑

↳ N = sum # of basis func
e.g. plane wave

c_i :

$|c_i|^2$ = weight of the contributions
of the i^{th} atomic orbital
to the molecular orbital
OR

P(finding an e^- on that orbital
in the molecule)

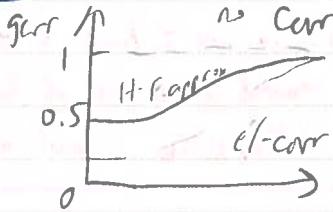
* total MO normalized → $\text{prob total} = 1$

Correlation between e/s

→ consideration for more acc. results

using Hartree-Fock Model

- ↳ repulsion energy between 2e/s is calculated between
 - ↳ one e/s & avg e/s density of the other e/s
- does NOT take into account the fact that the e/s will push away the other e/s w/ opposite spin as it moves around
- each e/s std be surrounded by an "empty volume" excluding the presence of another e/s



tendency for e/s to stay apart due to correlation

↳ diminishes the e/s repulsion energy

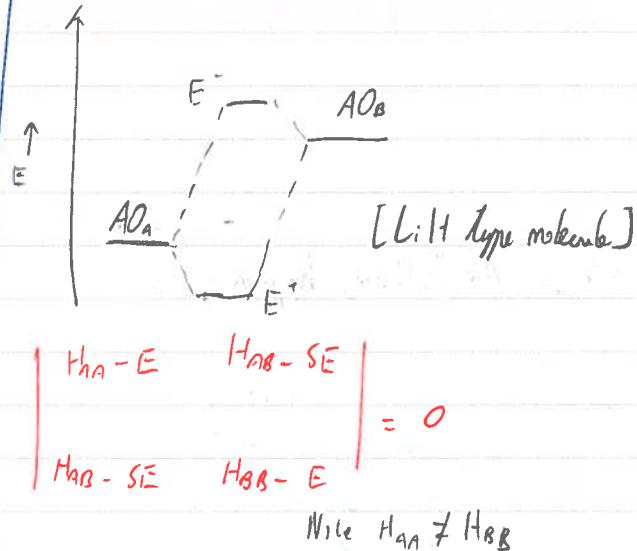
↳ total energy goes down when the correlation is included

Hetero-nuclear diatomic molecule

- if atoms are similar (e.g. NO & CO) considerations are similar
- ⇒ same MOs & energy ordering can be used

Generally:

MOs for heteronuclear diatomics must be formed from AOs of unequal energies



to the first approx [neglecting overlap (S_{AO})]

$$E = \frac{H_{aa} + H_{ab} \pm (H_{aa} - H_{ab})^2 [(0.4H_{ab})(H_{aa} - H_{ab})]^{\frac{1}{2}}}{2}$$

* H_{ab} measures interactions between AOs centred on diff. atoms

↳ small when energies are v. different.

For H_2^+ & H_2 type molecule

$$H_{AA} = \langle 1s_A | \hat{H} | 1s_A \rangle = \langle 1s_A | -\frac{\nabla^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} | 1s_A \rangle$$

$$\left(-\frac{\nabla^2}{2} - \frac{1}{r_A} \right) 1s_A = -\frac{1}{2} 1s_A$$

$$H_{AA} = -\frac{1}{2} + \langle 1s_A | -\frac{1}{r_B} + \frac{1}{R} | 1s_A \rangle = -\frac{1}{2} + J'$$

↑
ionization potential
of hydrogen

Related to the ionization potential
of atom A]

Stating the following hypothesis:

1. IF their atomic energy levels
are close to one another

⇒ two AOs contribute significantly
to bond formation.

2. 2 AOs contribute to bond formation
IF they overlap significantly

Meaning: they must combine
in such a way as to
have substantial overlap

In the region between
the 2 nuclei

for heteronuclear molecule

- ⇒ CAN NOT use "s" & "p"
- ∴ Orbitals have no particular sym whr $r \rightarrow r$
- ⇒ can still use $\sigma, \sigma^*, \pi, \pi^*$ notation

⇒ derived from 6.4:

$$|H_{AA}| \gg |H_{AB}| \text{ or } |H_{AA}| \ll |H_{AB}|$$

↳ coeffs will be v. diff.

e.g. $C_A \gg C_B$ or $C_A \ll C_B$

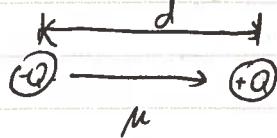
In this case

- ⇒ resulting MO is not really an MO at all,
but more like the AO w/ the larger coeff.
- ⇒ if we are to have a reasonable amount of mixing of the two AOs,
 $|H_{AA}| \& |H_{AB}|$ cannot be v. diff.

↳ supports the idea that only orbitals w/ similar energies can be combined in the LCAO scheme

Dipole moments

→ in Debye:



classical dipole moment

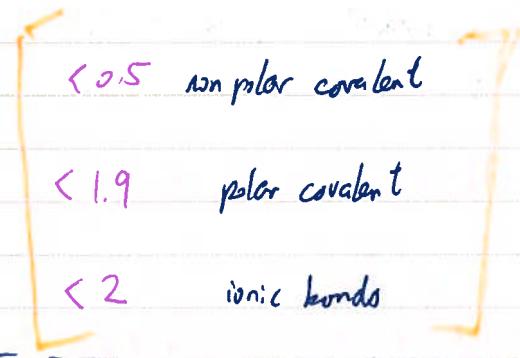
$$\mu = Q \times d$$

electronegativity

↳ ability of an atom to attract e⁻s

more electronegativity,

↳ e⁻s spend more time near that atom



Extreme case: Li:F

meeting in gas phase:

Harpooning mechanism:



$$\text{ionization} : -\Delta E_{\text{H}_2} = -5.4 \text{ eV} \\ (\text{Li})$$



$$\text{Affinity} = \Delta E_{\text{Ca}} = 3.4 \text{ eV} \\ \approx 0.125 \text{ au} (\text{F})$$

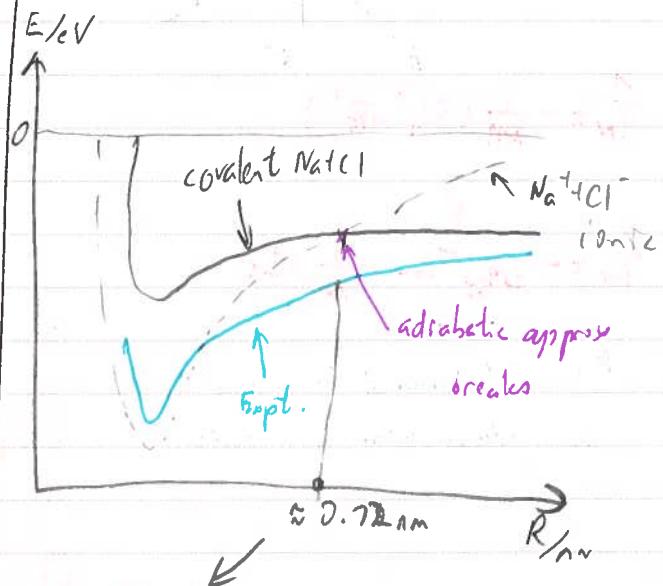
r.t.

$$r_{\text{transition}} = \frac{1}{0.011} \text{ au} \approx 91.7 \text{ au}$$

⇒ e⁺ tunnelling requires energy conservation

$$\Delta E = \frac{e^2}{r_{\text{transfer}}} = |1/t_{\text{Z}}| - |1/t_{\text{Ca}}|$$

Energy from
Coulomb interaction



Sudden change

from Na to Na⁺ → Cl to Cl⁻
OR

e⁺ tunnelling suddenly from 1 atom to another

at a distance between them (e.g. 0.72 nm)

→ wavefunction changes

→ gradient of Ψ^2 changes significantly wrt R

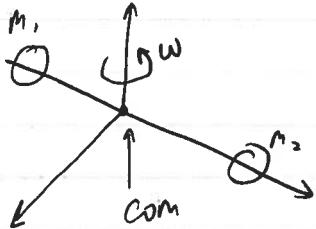
from atomic type to ionic type

Li adiabatic approx breaks

Solving for nuclear part
of a diatomic molecule

$$[\hat{T}_N(R) + V(R)] \Psi_N(R) = E \Psi_N(R)$$

↓ go to COM coor
w/ internal spherical
polar coor.



$$\hat{T}_N = -\frac{1}{2m} (\nabla_1^2 - \nabla_2^2)$$

$$\hat{T}_N = -\frac{1}{2M_{\text{tot}}} \nabla_{\text{COM}}^2 - \frac{1}{2\mu} \nabla_{\text{int}}^2$$

M_{tot} = total mass of the molecule

μ : reduced mass of the molecule

$$\begin{aligned} \nabla_{\text{int}}^2 &= \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) \\ &+ \frac{1}{R^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{R^2 \sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \\ &= \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) - \frac{L^2(\theta, \phi)}{R^2} \end{aligned}$$

Nuc. S.E. now:

$$\left[-\frac{\nabla_{\text{COM}}^2}{2M_{\text{tot}}} + \frac{-\nabla_{\text{int}}^2}{2\mu} + V(R) \right] \Psi_N(R) = E \Psi_N(R)$$

⇒ separable into COM & INT coor

COM: translational

INT: vib & rot

$$\Psi_N(R) = \Psi_{\text{trans}}(R_{\text{COM}}) \Psi_{\text{int}}(R_{\text{int}})$$

$$= \Psi_{\text{trans}}(R_{\text{COM}}) \Psi_{\text{int}}(R, \theta, \phi)$$

$$E = E_{\text{trans}} + E_{\text{int}}$$

↓ separate SEs for INT & COM

$$i) \frac{-\nabla_{\text{COM}}^2}{2M_{\text{tot}}} \Psi_{\text{trans}}(R_{\text{COM}}) = E_{\text{trans}} \Psi_{\text{trans}}(R_{\text{COM}})$$

$$ii) \left[\frac{-\nabla_{\text{int}}^2}{2\mu} + V(R) \right] \Psi_{\text{int}}(R, \theta, \phi) = E_{\text{int}} \Psi_{\text{int}}(R, \theta, \phi)$$

i) ⇒ free particle

on

Particle in a Box

↳ F.S. Ls tell us little about molecule itself

für ii): separable in $R \& (\theta, \phi)$ corr

$$-\frac{1}{2\mu R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \Psi_{int}(R, \theta, \phi) \right) + \frac{L^2(\theta, \phi)}{2\mu R^2} \Psi_{int}(R, \theta, \phi) + V(R) \Psi_{int}(R, \theta, \phi), E_{int} \Psi_{int}(R, \theta, \phi)$$

$$\Psi_{int}(R, \theta, \phi) = X(R) Y_{l,m}(\theta, \phi) = X(R) Y_l^m(\theta, \phi)$$

$$E_{int} = E_{el-vib} + E_{rot}$$

$$\frac{L^2(\theta, \phi)}{2\mu R^2} \Psi_{int}(R, \theta, \phi) = X(R) \frac{L^2(\theta, \phi)}{2\mu R^2} Y_l^m(\theta, \phi) \\ = X(R) \frac{J(J+1)}{2\mu R^2} Y_l^m(\theta, \phi)$$

$$\left[-\frac{1}{2\mu R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{J(J+1)}{2\mu R^2} + V(R) \right] X(R) = E_{int} X(R)$$

↪ similar to H atom

für eq' in vib corr R

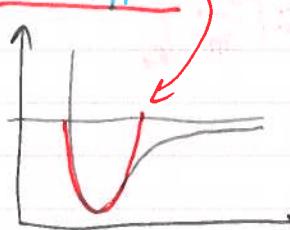
→ expand $V(R)$ around eq^{mr} bond length R_e

$$V(R) = V(R_e) + (R - R_e) \left(\frac{dV}{dR} \right)_{R_e} + \frac{1}{2} (R - R_e)^2 \left(\frac{d^2V}{dR^2} \right)_{R_e} + \dots$$

$$V(R) \approx V(R_e) + \frac{1}{2} k (R - R_e)^2 = V(R_e) + \frac{1}{2} k n^2$$

$$n = R - R_e$$

harmonic approx



define:

$$X(R - R_e) = \Psi_{vib}(R - R_e) / R$$

$$\Rightarrow -\frac{1}{2\mu R} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) \left[\frac{\Psi_{vib}(R - R_e)}{R} \right] \\ = -\frac{1}{2\mu R} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \left(\frac{\Psi_{vib}(R - R_e)}{R} \right) \right. \\ \left. - \frac{\partial R}{\partial R} (\Psi_{vib}(R - R_e)) \right) \\ = -\frac{1}{2\mu R} \frac{\partial^2}{\partial R^2} (\Psi_{vib}(R - R_e))$$

approximating:

$$\frac{J(J+1)}{2\mu R^2} \approx \frac{J(J+1)}{2\mu R_e^2}$$

rigid rotor

model

$$\left[-\frac{1}{2\mu^2} \frac{\partial^2}{\partial R^2} + \frac{1}{2} k n^2 \right] \Psi_{vib}(n)$$

$$= \left[E_{int} - \frac{J(J+1)}{2\mu R_e^2} - V(R_e) \right] \Psi_{vib}(n)$$

$$= E_{vib} \Psi_{vib}(n)$$

Basis of molecular spectroscopy:

1) $V(R_e) \rightarrow E_{elec}$

\Rightarrow electronic energy @

potential energy minimum

2) $\frac{J(J+1)}{2\mu R^2} = E_{rot}$

\Rightarrow rotational energy

(rigid rotor model)

3) $\sqrt{\frac{k}{\mu}} (n + \frac{1}{2}) = E_{vib}$

\Rightarrow vibrational energy

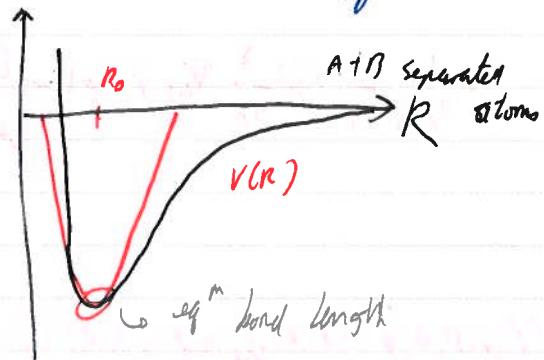
(HO model)

~~4) $E_{int} = E_{elec} + E_{vib} + E_{rot}$~~

$$E_{elec} > E_{vib} > E_{trans} > E_{rot}$$

Visible / UV IR Microwave

Vibrational spectroscopy



\Rightarrow nuclei move on a pot. energy surface determined by sol'n of electron eq's

@ low T: molecule will sit

near the bottom of this PES

\Rightarrow nuclei will feel a nearly harmonic potential

\Rightarrow H.D. is gd model for nuclear motion

H-D H.D.:

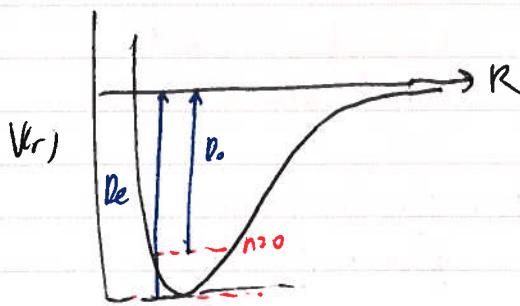
$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} k_0 \hat{R}^2 = \frac{\hat{p}^2}{2\mu} + \frac{1}{2} m\omega_0^2 \hat{R}^2$$

force constant

\hookrightarrow measures how stiff the bond is & can be approximately related to the 1st derivative to the true anharmonic PES near R_e

$$\hookrightarrow k_0 \approx \left| \frac{\partial^2 V}{\partial R^2} \right|_{R_e}$$

Some definitions



D_0 : depth of potential well

dissociation energy of molecule
in the ground vib state:

$$D_0 = D_e - \frac{1}{2} \hbar \omega_0$$

$$\omega_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (\text{Hz})$$

$$\bar{\omega}_0 = \frac{1}{2\pi c} \sqrt{\frac{k}{m}} \quad (\text{cm}^{-1})$$

$$E_{\text{vib}} = (v + \frac{1}{2}) \hbar \omega_0 \quad (\text{J})$$

$$E_{\text{vib}} = (v + \frac{1}{2}) \bar{\omega}_0 \quad (\text{cm}^{-1})$$

↑ often used.

$$\bar{\omega} = \frac{1}{2\pi} \text{cm}^{-1}$$

$$\cancel{V_{15}} \quad v_0 \propto \frac{1}{\sqrt{m}}$$

$$\omega = C \bar{\omega}$$

$$\bar{v} = C v$$

Vibrational spectra

(probing dist w_0 from diff molecule)

See detailed derivation in HW 8 & notes

⇒ HO will only absorb/emit photons
of freq ω_0
= freq of oscillator

∴ absorption spectrum should show
line @ only ONE freq

$$W_{\text{if}} \propto |E_a|^2 \{ (i+1) \delta_{f,i+1,i} + (i,-1) \} \delta(\hbar\omega - \hbar\omega)$$



strength of transition between
2 vib states: $v' | v''$

$$\hookrightarrow R_v = \langle v' | \mu | v'' \rangle$$

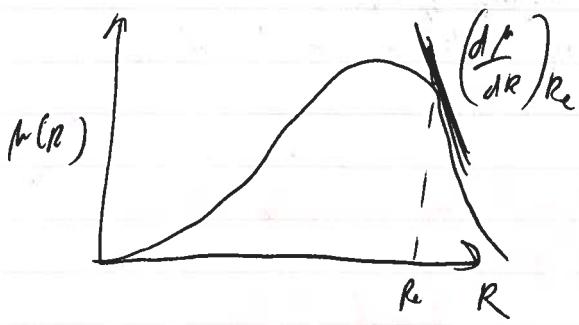
↓ dipole moment
Taylor expand
& use the fact that

$$\langle v' | v'' \rangle = \delta_{v',v''} = 0$$

$$R_v = \left(\frac{d\mu}{dR} \right)_{R_0} \langle v' | R - R_0 | v'' \rangle$$

⇒ strength of a vibrational band
depends on the
magnitude of the derivative of the dipole moment

w/ internuclear distance

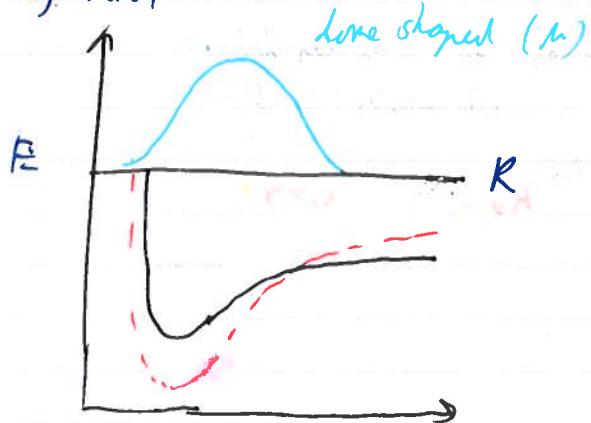


molecule w/ relatively small μ

may still have a large $(\frac{d\mu}{dR})_{R_e}$

\Downarrow
molecule w/ relatively large μ
may still have a small $(\frac{d\mu}{dR})_{R_e}$

e.g. NaCl



① Homonuclear molecule ($\mu=0$)

for all R

$$\Rightarrow \frac{d\mu}{dR} = 0$$

↳ no electric dipole
vib absorption at all

↳ have neither vib/vib
electric dipole allowed
transitions

[Raman spectra only]

is used instead to probe these

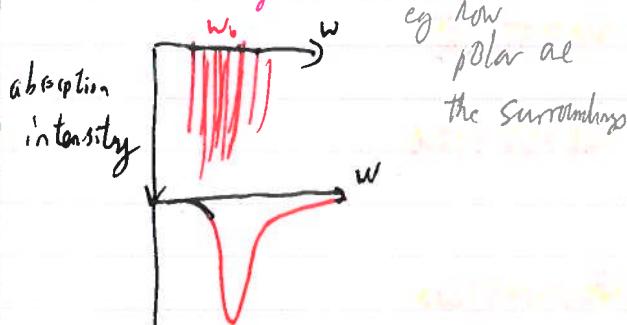
② Smart time (K, T, P)
molecules will start
in its ground state

range major contribution
from $0 \rightarrow 1$ transition

If other transitions occur @
Same freq
↳ also contribute to
absorption]

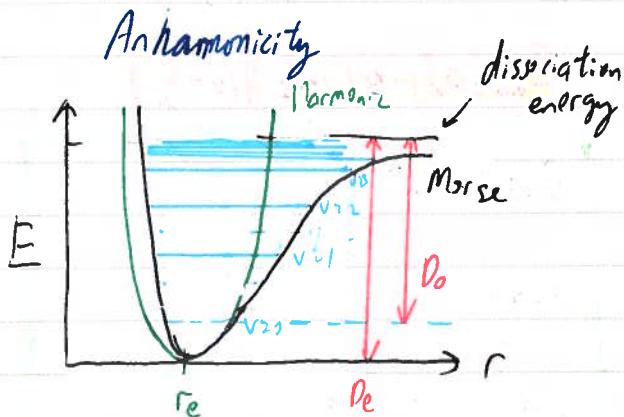
Lineshape:

→ reflects the diff environments
surrounding the oscillators



③ vib spectra in the gas phase
have v. narrow linewidths

Accounting for



i. solving S.E. for this potential gives:

$$E_{vib} = \hbar\omega_0(v + \frac{1}{2}) - \hbar\omega_0\chi_e(v + \frac{1}{2})^2$$

anharmonicity constant

$$\chi_e \approx 0.01 \text{ to } 0.02$$

2nd term: anharmonicity correction

↳ shows us that energy levels get closer together as v.b. quant # ↑↑
(often in cm^{-1})

$$\therefore \text{in cm}^{-1}$$

$$\tilde{E}_{vib} = \tilde{\omega}_0(v + \frac{1}{2}) - \hbar\omega_0\chi_e(v + \frac{1}{2})^2$$

$$\tilde{E}_{vib} = \tilde{\omega}_0 \left(1 - \hbar\omega_0\chi_e(v + \frac{1}{2}) \right) (v + \frac{1}{2})$$

$$\tilde{\omega}_{osc} = \tilde{\omega}_0 \left(1 - \hbar\omega_0\chi_e(v + \frac{1}{2}) \right)$$

$$\text{when } v = -\frac{1}{2} \quad \tilde{\omega}_{osc} = \tilde{\omega}_0$$

$\tilde{\omega}_{osc}$: formally defined as
eq^m oscillation freq

if the anharmonic system
for v. small vibs @ $\tilde{\omega}_0^m \text{ pl}$

↳ anharmonic Hamiltonian are not equally spaced

↳ ΔE no longer constant

→ higher transitions have lower (red shifted) energies due to the shape of the PES

→ tends to zero approaching the dissociation limit

∴ using Morse potential for V(r)

$$V(r) = D_e(1 - e^{-\alpha(r-r_e)})^2 \quad | q = r - r_e$$

$$V(r) = D_e [e^{-2\alpha q} - 2e^{-\alpha q}] \quad |$$

$$= D_e [-1 + \alpha^2 q^2 + \dots] ; \quad D_e \alpha^2 = \frac{1}{2} k$$

Overtones: $\Delta v = \pm 2$

→ anharmonicity

↳ relaxed $\Delta v = \pm 1$ selection rule

[true only for H.O. states]

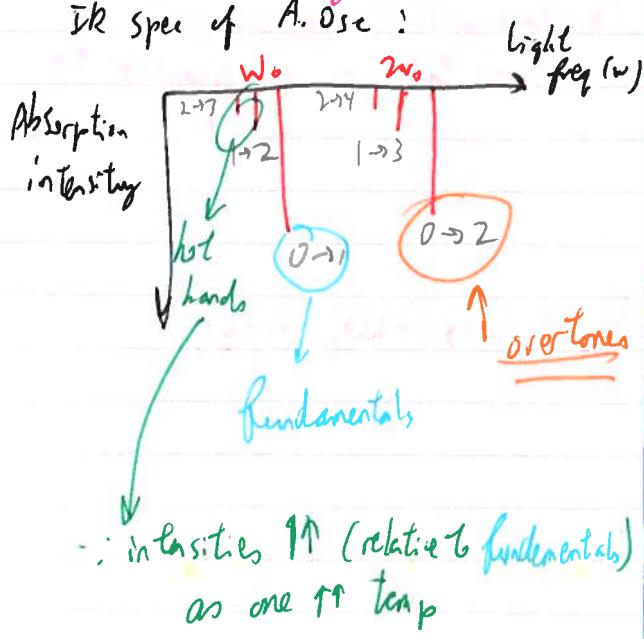
↳ $\Delta v = \pm 2, \pm 3\dots$

↳ no longer be forbidden

for A.Osc

BUT weakly allowed

IR Spec of A.Osc:



populations:

$$\frac{N_{v+1}}{N_{v=0}} = e^{-\left(\frac{\Delta E}{kT}\right)}$$

* $N_{v=1}$ is only 1-2% of the ground state population

∴ @ 300K in first approximations

↳ can ignore transitions

originating from $v=1$ state

Dependence on temp

@ $T=300K \rightarrow 3$ transitions

$$E_{vib} = \bar{w}_0 [1 - \alpha_e (v + \frac{1}{2})] (v + \frac{1}{2})$$

$0 \rightarrow 1$ large intensity

$$\Delta E = \bar{w}_0 (1 - 2\alpha_e)$$

$0 \rightarrow 2$ small intensity

$$\Delta E = 2\bar{w}_0 (1 - 3\alpha_e)$$

$0 \rightarrow 3$ negligibly small intensity

$$\Delta E = 3\bar{w}_0 (1 - 4\alpha_e)$$

$1 \rightarrow 2$ first overtone

for $T > 500K$

can find \bar{w}_0 & α_e from expt

Polyatomic Molecules

↳ think of potential as many dimensional H.O.

$$V = V(R_1, R_2, R_3)$$

$$= \frac{1}{2} k_1 R_1^2 + \frac{1}{2} k_2 R_2^2 + \frac{1}{2} k_3 R_3^2 + \dots$$

only thing we can solve

realistically, have cross terms $R_i R_j$

↳ coupling of diff vibrations

Harmonic potential of this form:

→ eigenstates are products of 1D eigenstates

→ energies are the sum of the 1D eigenenergies

complicated eqⁿ → easier eqⁿ
quadratic sys w/ off-diagonal cross terms
change var → no cross terms

Change coordinates
to get:

$$V = \frac{1}{2} \sum_{n=1}^N k_{nn} R_n^2$$

→ half of this term can
be separated

Such new coordinates are called
normal modes

↳ allow reduction of a polyatomic molecule
to a collection of 1D oscillators

Normal modes:

1. all atoms oscillate in phase & have same freq.

2. Orthogonal

3. C.I.M does not move

4. motions can be described as
superposition of normal vib mode

5. process of determining what normal modes
of a molecule look like → normal mode analysis

linear molecule: #1. normal modes
 $= 3n - 5$

non-linear molecule: #1. normal modes
 $= 3n - 6$

Spectra:

can be interpreted as a
Sum of many independent oscillators

general picture we see in IR spec
includes anharmonicity effects

AND ALSO

combination of diff modes

$w_1 + w_2$ & $w_3 - w_1$, etc

→ combination bands

↳ can predict the existence of
various hotbands & overtones for
each of the normal mode oscillators
in the molecule

↳ in solid: heterogeneity leads to
→ smearing out of peaks
→ broadening of peaks

Hence the complex IR figures

To extract info:

→ assign the spectrum

[distinguish hot bands from overtones
&

associate various normal modes
w/ physical motions
of the molecule]

→ extremely challenging

↳ need computers

IR Active normal modes

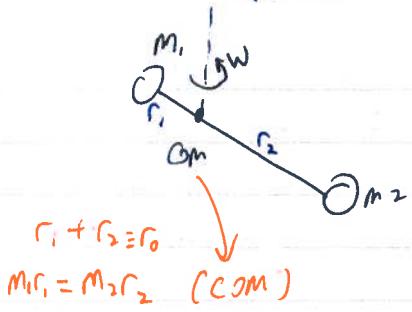
- in terms of dipole moments
1. $\mu \neq 0$
 2. if $\mu = 0$ $\frac{d\mu}{dQ} \neq 0$

Rotational Spectroscopy (Microwave)

using E_{rot} as b/c

$$E_{rot} = \frac{\hbar^2 J(J+1)}{2\mu R^2}$$

Rigid Rotor approx:



KE:

$$K = \frac{1}{2} m_1 r_1^2 \omega^2 + \frac{1}{2} m_2 r_2^2 \omega^2$$

$$= \frac{1}{2} (m_1 r_1^2 + m_2 r_2^2) \omega^2$$

$I \equiv$ moment of inertia

$$K = \frac{1}{2} I \omega^2$$

$$B_e = \frac{\hbar \omega}{2\pi \mu R_e^2 \hbar} = \frac{\hbar \omega}{4\pi \mu R_e^2}$$

$$\tilde{\nu} = \hbar \tilde{\omega}$$

$$\tilde{\nu} = \frac{\hbar}{\mu c}$$

$$B_e = \frac{\hbar}{4\pi \mu R_e^2} \frac{K}{c}$$

Energies:

$$\hat{H} Y_J^m = E_{Jm} Y_J^m$$

switch $J \rightarrow \tilde{J}$

conventional form

molecular rotational quant #

$$E_J = \frac{\hbar^2}{2I} J(J+1)$$

$J=2$

$$J=1 \quad E_J = \frac{\hbar^2}{I} Y_1^1, Y_1^{-1} \quad (3 \text{ degenerate})$$

$$J=0 \quad E_J = 0 \quad Y_0^0 \quad (\text{nondegenerate})$$

* degeneracy of each state

$$g_J = (2J+1)$$

$$m \in \{0, \pm 1, \pm 2, \dots, \pm J\}$$

spacing between states Δ as ΔJ

$$\Delta E_{J+1} - \Delta E_J = \Delta E = \frac{\hbar^2}{2I} [(J+2)(J+1) - J(J+1)]$$

$$= \frac{\hbar^2}{I} (J+1)$$

$$E_{J+1, J, m} = \frac{\hbar^2}{2\mu} \left(\frac{1}{R_e^2} \right) J(J+1)$$

$$\text{in 1st approx } \left(\frac{1}{R_e^2} \right) = \frac{1}{R_e^2} \quad (\text{eq dist})$$

from the minimum in the potential energy curve

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

\Rightarrow eqⁿ moment of inertia

$$I = \mu R_e^2$$

$$\leftarrow \Rightarrow \text{eqⁿ rotational constant: } R_e = \frac{\hbar}{4\pi I c} = \frac{\hbar}{4\pi \mu R_e^2 c}$$

$$\Rightarrow E_{rot, J, m} = R_e J(J+1) \quad (\text{cm}^{-1})$$

Rotational term:

$$F(J) = \frac{E(J)}{\hbar c} \quad \text{often used instead of energies}$$

$$F_{\text{rot}}(J) = \frac{J(J+1)\hbar^2}{2\hbar c \mu R_e^2} = B_e J(J+1)$$

$$B_e = \frac{\hbar}{4\pi c \mu R_e^2}$$

∇ $V_{\text{rot}}(J) = (E(J+1) - E(J)) / \hbar$

$$\bar{V}_{\text{rot}}(J) = 2 B_e (J+1) \quad [\text{cm}^{-1}]$$

Rotational selection rule

\Rightarrow transition probabilities for electric dipole radiation
 \propto square of trans. moment between lower (l) & upper state (u)

$$R = \langle \Psi_u^{\text{tot}} | \vec{d} | \Psi_l^{\text{tot}} \rangle$$

dipole moment operator:

$$\vec{d} = \vec{d}^{\text{el}} + \vec{d}^{\text{nuc}} = -\sum_i \vec{r}_i + \sum_\alpha Z_\alpha \vec{R}_\alpha$$

Using Born Oppenheimer approx

$$R = \langle \Psi_u^{\text{el}} | \Psi_u^{\text{vib}} | \Psi_u^{\text{rot}} | \vec{d}^{\text{el}} + \vec{d}^{\text{nuc}} | \Psi_l^{\text{el}} | \Psi_l^{\text{vib}} | \Psi_l^{\text{rot}} \rangle$$

using e, v, J quantum numbers

$$\equiv \langle e' v' J' | \vec{d}^{\text{el}} + \vec{d}^{\text{nuc}} | e'' v'' J'' \rangle$$

for pure rotational transitions

$$e' = e'' \quad \& \quad v' = v''$$

$\hookrightarrow R = \langle v'' J' | \vec{d}^{\text{el}} + \vec{d}^{\text{nuc}} | e'' \rangle v'' J'' \rangle$
 permanent dipole moment
 of the electronic state

\hookrightarrow : selection rules for pure rotational transitions are:

1. molecule must have a permanent dipole moment
2. $\Delta J = J' - J'' = \pm 1$

using the J^{st} rule:

as pure rotational transitions in

1. homonuclear diatomic molecules (H_2, O_2, N_2)

OR

2. linear polyatomics ($O_3, H-CC-H$)

\hookrightarrow electric dipole forbidden

allowed for

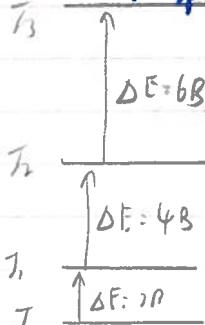
1. heteronuclear diatomics

(CO, NO, OH, SiO)

2. other linear polyatomics

(HCl & H_2N)

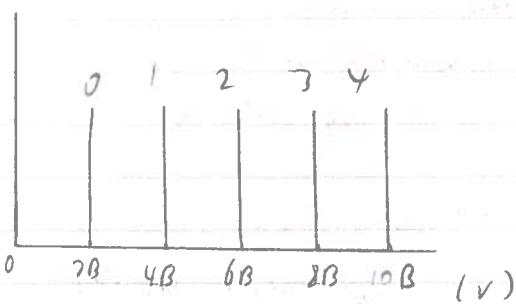
Rotation spectra (in microwave spectrum)



* transitions can only occur between adjacent rotational levels in all cases

↳ drift transition energies are superimposed in a spectrum hence a regularly spaced spectra.

$$\nu_{rot}(J) = 2B_0(J+1)$$

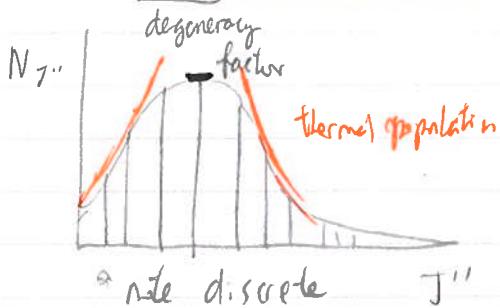


Intensities of rotation lines:

↳ relative intensities \propto populations in the various levels

↳ by Boltzmann distribution

$$N_J \sim (2J+1) \exp\left[\frac{-BJ(J+1)}{kT}\right]$$



J_{max} : rotational quantum number corresponding to the most intense line

$$\Rightarrow \text{integer nearest to } 0.59 \left[\frac{T(K)}{B(\text{cm}^{-1})} \right]^{\frac{1}{2}}$$

Vib-Rot Spectroscopy: (IR spec)

(IR spec concern change of vib & rot state w/o change of electronic state)

Selection rules:

1. $\Delta v = \pm 1$

↳ transitions of higher order

↳ over long bonds

↳ occur @ higher freq.

2. $\Delta v = 0 \rightarrow$ pure rotational transitions

3. $\Delta J = \pm 1 \rightarrow$ for heteronuclear diatomics

4. $\Delta J = 0$ IMPOSSIBLE for diatomics

↳ vib transitions are always accompanied by rot transitions

5. Molecule must have:

a) permanent dipole

b) $\frac{d\mu}{dR} \neq 0$

→ typically @ R.T. temp

↳ only ground vib state is populated BUT

several rotational levels may be populated

B dependence on vibrational state

→ Considering a REAL diatomic molecule

avg over the vib state

means that B_e is not exactly B_e

↳ depends on vib state

: need to include correction terms

B_n & B_v

↳ explicit dependence on the vib state (n or v) indicated by subscript

→ rotational energy of a diatomic molecule in a state w/ quantum #s n, J, m :

$$E_{nJm} = B_n J(J+1)$$

↳ Using perturbation theory in first approx:

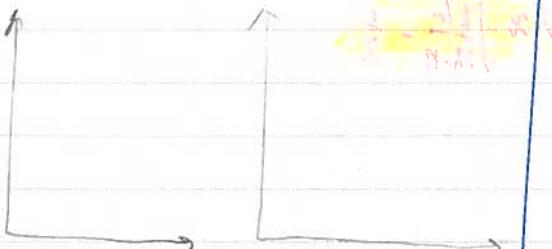
$$B_n = B_e - \alpha_e(n + \frac{1}{2})$$

Vib-rot constant

(a parameter to be determined experimentally)

↳ describes how th

vib state affects rot energy



Centrifugal distortion of non-rigid rotor

↳ purely rotational perturbation

changing the E of a state

↳ centrifugal force acts on the atoms

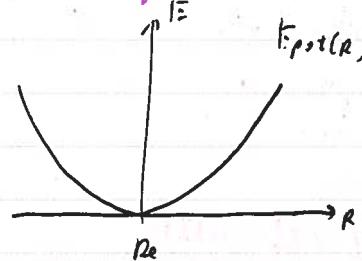
& the inter-nuclear distance $\uparrow\uparrow$ to a value R

$$\Rightarrow \text{Centrifugal force: } F_c = -M\omega^2 R$$

compensated by

$$\text{restoring force: } F_r = -\frac{dE_{\text{rot}}(R)}{dR}$$

holding the 2 atoms tog



for non-rigid rotor:

$$E_{\text{rot}} = \frac{J(J+1)\hbar^2}{2\mu R^2} + \frac{1}{2}k(R-R_e)^2$$

⇒ for a given J

↳ centrifugal widening makes $I = \mu R^2$ large

↳ ↓ F_c

which overcompensate for ↑ T↑ in P.E.

↳ taken into account by an additional correction term in the energy

Centrifugal distortion coefficient D_c

$$D_c = \frac{\hbar^3}{4\pi ck\mu^2 R_e^6}$$

↳ from eqⁿⁿ of forces

~~box~~

total internal energy of a diatomic molecule:

$$\frac{E_{\text{rot}} J_m}{\hbar c} = D_e + \left(n + \frac{1}{2}\right) \omega_e - \left(n + \frac{1}{2}\right)^2 \alpha_e \omega_e$$

$$+ B_n J(J+1) - D_c J^2 (J+1)^2$$

$$B_e = \frac{\hbar}{4\pi c k_e \mu^2 R_e^2} \quad D_e = \frac{\hbar^3}{4\pi c k_e \mu^2 R_e^6} \quad || \quad D = \frac{4B^3}{V^2}$$

w/ initial rot state = J
final $n = n' \approx J'$ vibrational frequency

\Rightarrow considering only transitions
that involve the
ground vib state

$$\Delta E = \omega_e - 2n_e \omega_e + B_e [J'(J'+1) - J(J+1)]$$

$$- \frac{\alpha_e}{2} [3J(J'+1) - J(J+1)]$$

$$- D_c [J^2 (J+1)^2 - J'^2 (J'+1)^2]$$

P & R branches of rovibronic spectra

R : $J' = J+1 \rightarrow$ net absorption
of rot Energy

$$\Delta E = \omega_e (1 - 2n_e) + 2(B_e - \alpha_e)(J+1) - \alpha_e (J+1)^2$$

P : $J' = J-1 \rightarrow$ net emission of
rotational energy

$$\Delta E = \omega_e (1 - 2n_e) - 2(B_e + \alpha_e)J - \alpha_e J^2$$

$\Delta J = 0$ rotational transition is prohibited
for most diatomic molecules

See diagrams in slides

intensity of an absorption line:

proportional to:

1. no. of molecules in the particular initial state

2. transition moment (strength)

of the particular transition
 \Rightarrow assumed equal for all trans. transitions

\rightarrow IR spectrum consists of a series of transitions due to diff rot. states involved

\hookrightarrow intensity distribution gives relative probabilities of occupation of the initial rot states

\hookrightarrow can define a rotational temp. T_r for this distribution (assuming Boltzmann form)

accounting for degeneracy:

$$\frac{I_J}{I_0} = \frac{N_J}{N_0} = \frac{g_J}{g_0} e^{-\frac{E_J}{kT_r}}$$

$$= (2J+1) \exp[-B_n \hbar c J(J+1) / kT_r]$$

population maximum: \Rightarrow use this one!

$$J \approx \sqrt{\frac{kT_r}{m_e B_n}} - \frac{1}{2}$$

* if α_e is small

$$B_e = B_n = \frac{\hbar}{T_r k_e}$$

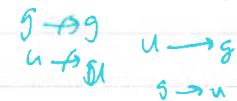
* can calc K_e from IR spectra

Selection rules in molecules

[as b^4]

$$\Delta S = 0$$

- initial & final wavefunctions must change in parity



- vibrational transitions occur if:

- electronic transition dipole moment $\neq 0$
- &

Franch-Condon factors $\neq 0$

for anharmonic molecules

↳ Δv can be whatever

↳ overtones are allowed,

altho even though

w/ rapidly \downarrow intensity

⇒ for vib trans between electronic levels,

↳ no restrictions for Δv

↳ every $v' \leftarrow v''$ has same probability thus giving rise to many spectral lines

* double peak → due to isotopes

Electronic Spectra:

- @ E^{min} , molecule is in the ground state
↳ lowest energy electric state
(typically in $V=0$)

- transitions to higher lying electronic states are accompanied by
↳ changes in V, J .

→ excitations are accompanied by vibrational excitation
↳ feels restoring force in excited state

Excited state surfaces:

1) Unbound / repulsive state [antibonding]
⇒ dissociates into atoms on excitation

2) Bound state [bonding]
→ has stable minimum
→ excitation to bound state usually leads to [large] nuclear displacement

Strength of an electronic transition

Strength \propto square of the matrix element between upper & lower state

$$R = \langle V' | d | V'' \rangle = \int \Psi' d | \Psi'' d | C(R) \rangle$$

$$d = d^{el} + d^{nuc} = -\sum_i e \bar{r}_i + \sum_a e Z_a R_a$$

$$\text{in g.u.} = -\sum_i e \bar{r}_i + \sum_a Z_a R_a$$

↳ Using B.O. approach [neglecting rotation
e. electron-vibrational for simplicity]

$$\langle e' | d | e'' \rangle = \langle v' | e' | d^{el} + d^{nuc} | e'' \rangle_v$$

$$\text{open} = \langle v' | e' | d^{el} | e'' \rangle_v$$

$$+ \langle e' | e'' \rangle \langle v' | d^{nuc} | v'' \rangle$$

$$= 1$$

\therefore orthonormal

only acting
on nuclear
coordinate

$$D^{el}(R) = \langle e' | d^{el} | e'' \rangle$$

$$R = \langle v' | D^{el}(R) | v'' \rangle$$

$$= \int \Psi'^* (R) D^{el} \Psi'' (R) dR$$

only nuclear corr

Approx.: if D^{el} varies little w/R
in the vicinity of the eq^{eq}/inter-nuclear coordinate,
 $\Rightarrow D^{el}(R) \approx D^{el}(R_0)$

$\Rightarrow D^{el}$ can be taken out of the integral:

$$\vec{R} = D^{el}(R_0) \langle v' | v'' \rangle$$

Relative intensity of a transition between any two vibrational states depends on the square of the "vibrational overlap integral"
 $q_{vv''} = |\langle v' | v'' \rangle|^2$

* Franck-Condon factor

Sum rule holds for the such factors

$$\sum_v q_{vv''} = \sum_{v''} \langle v' | v'' \rangle \langle v'' | v' \rangle$$

$$= \langle v' | v'' \rangle = 1$$

Franck-Condon Principle:

nuclei are moving much more slowly than the e⁻s, in the 'time' required for an electronic transition to occur [order of $\sim 10^{-14}$ s]

∴ band w/ the highest transition probability is the one for which the transition is "vertical"

↳ molecule finds itself in the excited electronic state w/ the same internuclear seg.

as it had in the ground electronic state

Intensities are determined by
Franck-Condon factor

→ most probable excitation is
to classical turning point

→ intensities tell us about $R''e - R_e'$
[the displacement of nuclei]

1. $R' \approx R_e'$

→ best overlap $(v'=0) - (v''=0)$
[short progression]

→ most probable transition: $(0,0)$

+ non-zero probability of $(1,0), (2,0) \dots$

↳ successive lines have
rapidly diminishing intensities

2. $R'' > R_e'$ [excited electronic state has
a slightly larger nuclear
separation than the ground state]

[long progression]

→ most probable: $(2,0)$

↳ intensities in neighbouring
transitions are lower

3. $R'' \gg R_e'$ [excited electronic state has a
considerably larger nuclear separation
than the ground state]

[long progression]

↳ vibration state to which
the transition takes place
has a high v' value

* transition can occur to levels
where the molecule has energy
in excess of its dissociation energy

⇒ molecule will dissociate w/o any vibrations
from such states

⇒ fragments which are formed
may take any value of KE
⇒ transitions are not quantized
↳ continuum results

Relaxation of Electronic States
[what goes up must come down]

→ typically, when a molecule is electronically excited
↳ there follows a displacement of charge

& a new eq^{rr} nuclear separation

⇒ leads to vib excitation also

↳ system vibrationally relaxes
non-radiatively

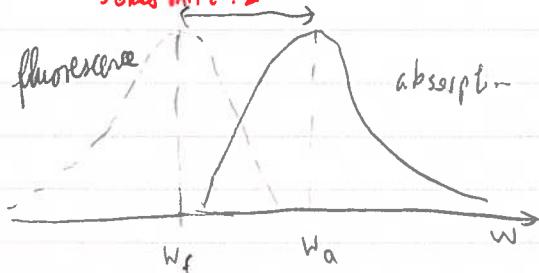
→ energy dissipated is ΔE
[reorganization energy]

↳ huge amount of energy to
release out of the ground state

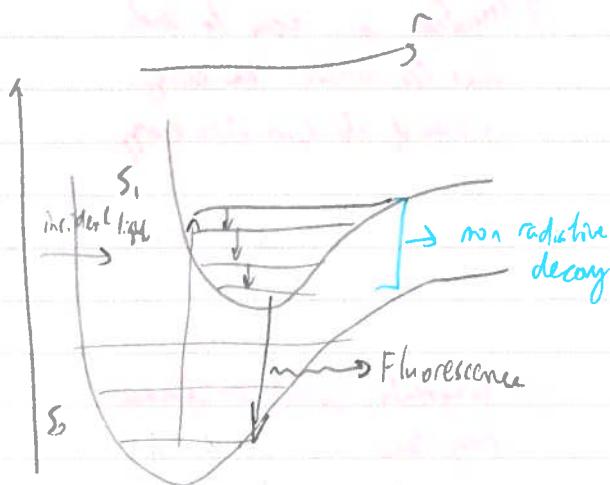
⇒ most probable way is fluorescence

↳ always redshifted relative to absorption

[characteristic time: 1-10 ns]
Stokes shift: ΔE



Fluorescence:



ground singlet state molecule: S_0

↳ goes to

first excited singlet state, S_1

Non-radiative decay:

collision w/ surrounding media

partition the excess energy

to other possible modes of

vibration & rotation

Fluorescence

↳ may appear as an apparent
minic of the absorption

at a lower energy

↳ i. lower freq than absorption

⇒ difference in cm^{-1} between
the two corresponding bands

⇒ Stoke shift

emission may show vibrational structure

↳ can provide info about
force constants of the molecule
in its ground state

↳ electronic structure provides info
about force constants in
the excited state

* Time of radiation = time of fluorescence

Phosphorescence:

:= emission occurring due to the
radiative transition between
2 states of diff multiplicity

[e.g. $T_1 \rightarrow S_0$]

⇒ generally delayed relative to
the exciting radiation

↳ may persist for several seconds
after the exciting source is removed

initial stage: excited singlet state,

$S_1 \rightarrow$ Radiatless decay occurs

molecule may convert, under the influence
of SO coupling, to triplet state

⇒ following intersys crossing,

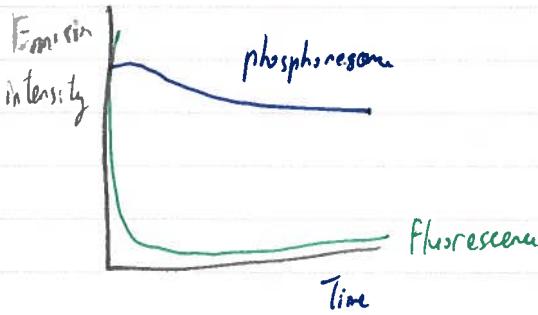
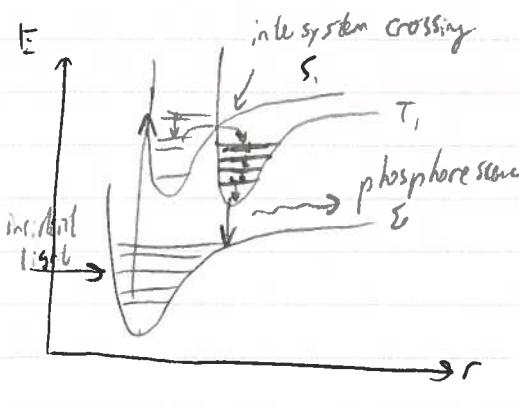
↳ radiatless decay continues

at lowest excited triplet state (T_1)

↳ molecule becomes trapped

* SO coupling is sufficient to partially break down
the Singlet-Triplet selection rules

↳ making the transition weakly allowed

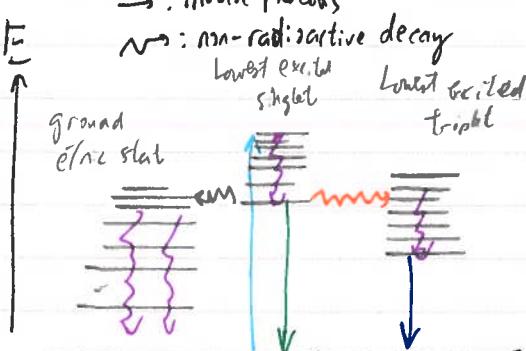


Possible physical processes following absorption of a photon by a molecule

A V.Tough diagram

\rightarrow : involve photons

\rightsquigarrow : non-radiative decay



1. Absorption
2. Fluorescence
3. Phosphorescence
4. Vibrational relaxation
5. intersystem crossing
6. internal conversion

