

Structure of Matter II.

Valence Bond Theory

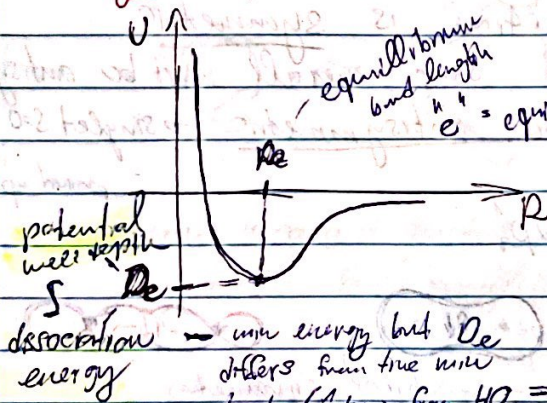
- old, before QM but useful for approx. w/o solving Schrödinger eq.
- bonds form if 2 e⁻ of different atoms share orbitals and their spins pair up

! exam

Born - Oppenheimer approximation

- nuclei are significantly more massive than rest
 ⇒ treat nuclei as stationary
- solve Schröd. eq. for same distance between nuclei
 ⇒ repeat for different arrangements → choose lowest E state

Typical plots



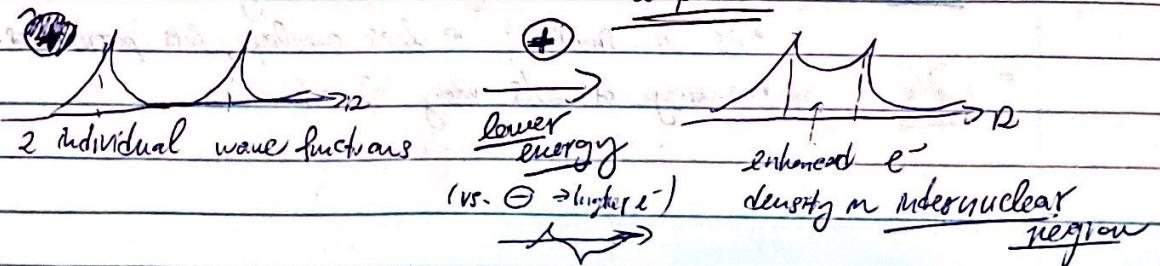
Mates is sometimes too difficult → use intuition of numerical sol.

* (H_2) - assume two separate atoms

$$\Psi(1,2) = \Psi_{H1A}(r_1) \Psi_{H1B}(r_2) \quad \text{or} \quad \Psi_{H1A}(r_2) \Psi_{H1B}(r_1)$$

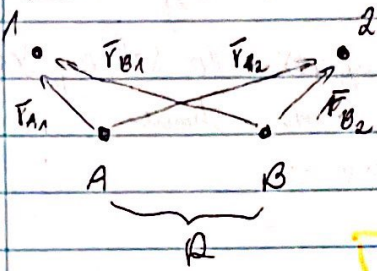
Better: $\Psi(1,2) = X_{H1A}(1) X_{H1B}(2) (\pm) X_{H1A}(2) X_{H1B}(1)$
 ⇒ wave function of pair

2 options



⇒ lowers energy compared to isolated atoms → bond forms
 If high energy → cannot form stable bonds

H₂: orbital \equiv state / wavefunction

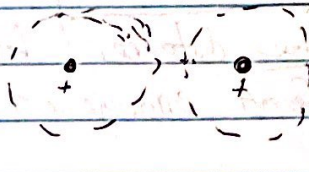


$$\Psi_+(1,2) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r_{A1}}{a_0}} \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r_{B2}}{a_0}} + \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r_{A2}}{a_0}} \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r_{B1}}{a_0}}$$

$$\Rightarrow \Psi_+(1,2) = \frac{1}{\pi a_0^3} \left[e^{-\frac{(r_{A1} + r_{B2})}{a_0}} + e^{-\frac{(r_{A2} + r_{B1})}{a_0}} \right]$$

σ -band

Symmetric about internuclear axis



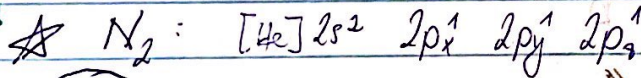
s orbitals

\rightarrow s symmetry \rightarrow σ band
greek $\sigma \rightarrow \sigma$

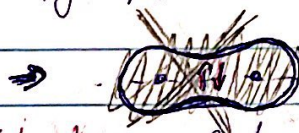
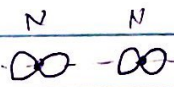
spatial wavefunction is symmetric

but Pauli says overall must be antisymmetric
 \Rightarrow spin must be antisymmetric \rightarrow singlet $S=0$
paired up spins

know of usual orbitals



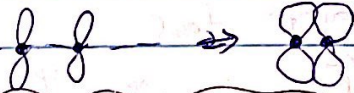
$2p_z$



$z =$ internuclear axis

σ -band - cylindrical symmetry

$2p_x, 2p_y \rightarrow \pi$ -bands from p-symmetry



$$\Rightarrow N_2: 1 \sigma\text{-band} \\ 2 \pi\text{-bands}$$

watch symmetry about internuclear axis

Note: $1s^2$ is not involved in bonding:

- $1s$ is "smaller" \Rightarrow less overlap, less possibilities for bond to occur
- energy of $1s$ may lower

Resonance

★ HCl : e^- mostly on Cl \rightarrow partial charges

• usually: $H^{\delta+} Cl^{\delta-}$

• rarely: $H^{\delta-} Cl^{\delta+}$ but has contributor to Ψ

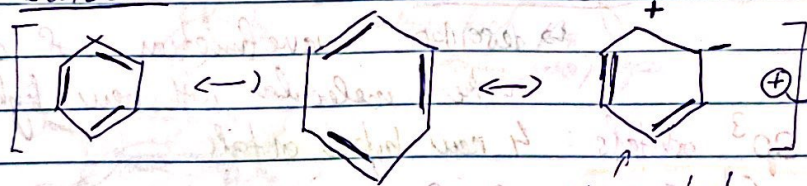
• sometimes $H \cdots Cl$ etc. other arrangements can be included for other molecules

$$\Psi_{HCl}^{\text{real}} = \underbrace{\Psi_{HCl}^{\text{covalent}}}_{\text{lowest energy}} + \lambda_1 \Psi_{H^+Cl^-} + \lambda_2 \Psi_{H^-Cl^+} + \dots$$

ionic contributions

\leftarrow can be further improved by adding terms

★ benzene



more states to increase accuracy but we need to stop somewhere

less important contribution

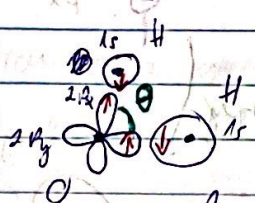
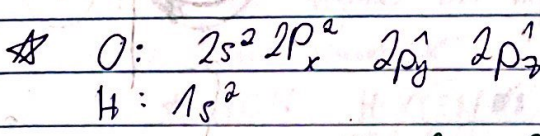
\rightarrow more resonant structures
 \Rightarrow more stable molecule

$$\Psi_1 \rightarrow E_1 \quad (\text{approximate with 1 state} \Rightarrow 1 \text{ energy})$$

$$\Psi_{1+2} \rightarrow E_{1+2} < E_1$$

adding more states to the wavefunction such that energy is lowered = resonance

$$\sum_{\text{states}} \text{weight} \cdot \Psi_{\text{state}}$$



prediction: $\theta = 90^\circ$ but experimentally: 104.5°
 Why? Hybridization

★ C: $2s^2 2p_x^1 2p_y^1$ → 2 bonds but we know that C has 4 bonds

⇒ promotion: C^* : $2s^1 2p_x^1 2p_y^1 2p_z^1$

↳ promotion costs energy but this price is easily compensated for by ~~formation~~ formation of more bonds (bonding lowers energy)

↳ CH₄ - all 4 C-H bonds are the same

↳ contradiction ~~with~~ with the fact that different orbitals are used

(carbon has ~~valence~~ valence e^- in $2s$ and $2p$ orbitals)

⇒ hybridization

↳ describe wavefunction of carbon

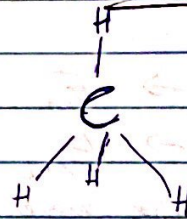
in the molecule with new hybrid orbitals

★ ⇒ sp^3 orbitals: 4 new hybrid orbitals

$$\begin{cases} h_1 = s + p_x + p_y + p_z \\ h_2 = s - p_x + p_y - p_z \\ h_3 = s - p_x - p_y + p_z \\ h_4 = s + p_x - p_y - p_z \end{cases}$$

⇒ angle between h 's = 109.5°

⇒ tetrahedron

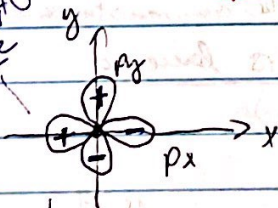


↳ orthogonal

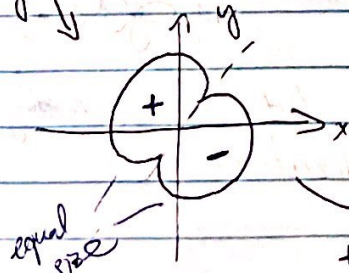
$$\langle h_i | h_j \rangle = \delta_{ij}$$

h_1 :

same orbitals but must be opposite

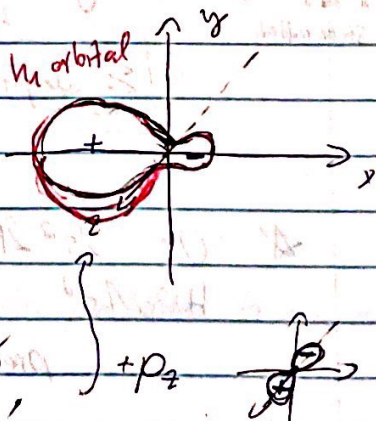
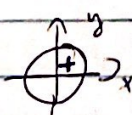


$p_x + p_y$



equal size

+s

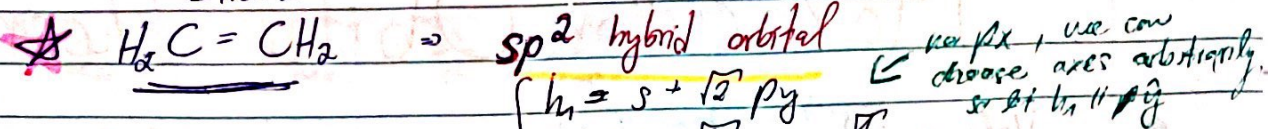


h_1 orbital

+p_z



Ethene

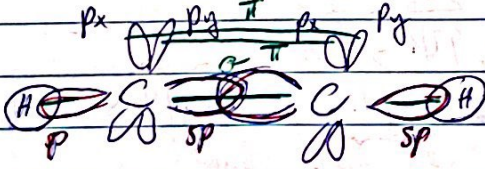
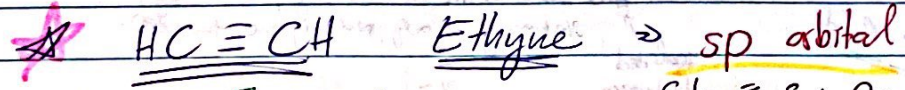
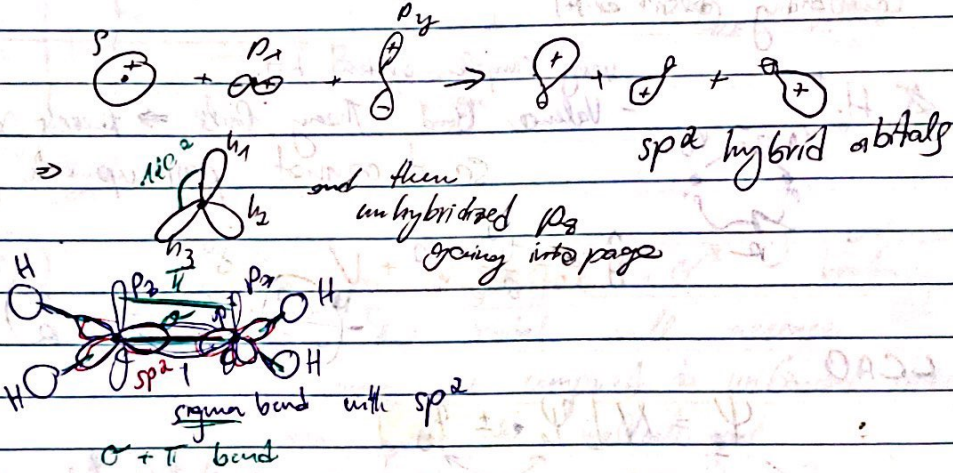


using p_x, p_y
not p_z because we try to keep

$$\begin{cases} h_1 = s + \sqrt{2} p_y \\ h_2 = s + \sqrt{\frac{3}{2}} p_x - \sqrt{\frac{1}{2}} p_y \\ h_3 = s - \sqrt{\frac{3}{2}} p_x - \sqrt{\frac{1}{2}} p_y \end{cases}$$

p_x, p_y to have same symmetry, while p_z is the one with different symmetry as needed

$\hookrightarrow 120^\circ$ angle between h 's



$$\begin{cases} h_1 = s + p_z \\ h_2 = s - p_z \end{cases}$$

(?) How to figure out hybridization of a given molecule?

\hookrightarrow steric number = # regions in space of e^- density

\star HCN: $H-C \equiv N$

2 regions of electron density of C $\Rightarrow sp$

\Rightarrow N also has 2 regions of electron density $\Rightarrow sp$

per atom in molecule \downarrow incl. lone pairs

\star H_2O { Oxygen has steric number 4

- 2 $\rightarrow sp$
- 3 $\rightarrow sp^2$
- 4 $\rightarrow sp^3$

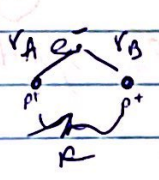
Molecular Orbital Theory

exam!

Valence Bond Theory (VB) vs. Molecular Orbital Theory (MO)

- shared e^- pairs with paired up spins $\uparrow\downarrow$
 - σ, π bonds - created by combination of atomic orbitals
 - promotion, hybridization, resonance structures [$\dots \leftrightarrow \dots \leftrightarrow \dots$] (antibonding doesn't exist)
- Ψ extends over entire molecule (conceptually at least) **LCAO**
 \hookrightarrow using ^{lin. comb.} ~~superposition~~ of atomic orbitals
 \sim approx. of molecular Ψ
 \Rightarrow each molecular orbital (MO) can accommodate/house $2e^-$

$\star H_2^+$ very simple system but
 - Valence Bond Theory fails \Rightarrow there's only $1e^-$, so it cannot pair up with anything



$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 + V \equiv \hat{h}^0$$

$$V = -\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_A} + \frac{1}{r_B} - \frac{1}{R} \right)$$

LCAO:

$$\Psi_{\pm} = N [\Psi_A \pm \Psi_B]$$

describes σ -Bond
 Ψ_A, Ψ_B wavefunctions (normalised), stationary \rightarrow only real, ignore time-dep.
 isolated hydrogen

Ψ_+

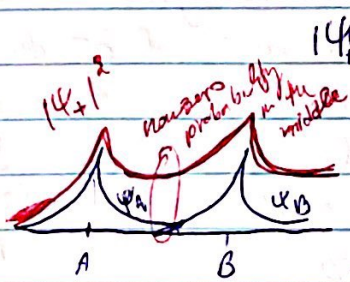
from normalisation: $\langle \Psi_+ | \Psi_+ \rangle \equiv 1$

$$= N^2 [2 \langle \Psi_A | \Psi_B \rangle + \langle \Psi_A | \Psi_A \rangle + \langle \Psi_B | \Psi_B \rangle]$$

not eigenfunctions of same \hat{H}
 \Rightarrow not necessarily orthogonal
 $\Rightarrow S \neq 0$

$$= 2(1+S) N^2 \equiv 1$$

$$\Rightarrow N = \frac{1}{\sqrt{2(1+S)}}$$



$|\Psi_+|^2 \propto$ probability of finding e^- at some position

$\langle \Psi_A | \Psi_B \rangle \propto$ probability of finding e^- in the internuclear region

\Rightarrow Bonding σ -orbital $1\sigma^1$
 lowest sigma orbital $1e^-$ in there

$$E_0(R) = E_{H1s} + \frac{j_0}{R} - \frac{j+k}{1-S}$$

$$S = \langle \psi_A | \psi_B \rangle = \left[1 + \frac{R}{a_0} + \frac{1}{3} \left(\frac{R}{a_0} \right)^2 \right] e^{-R/a_0}$$

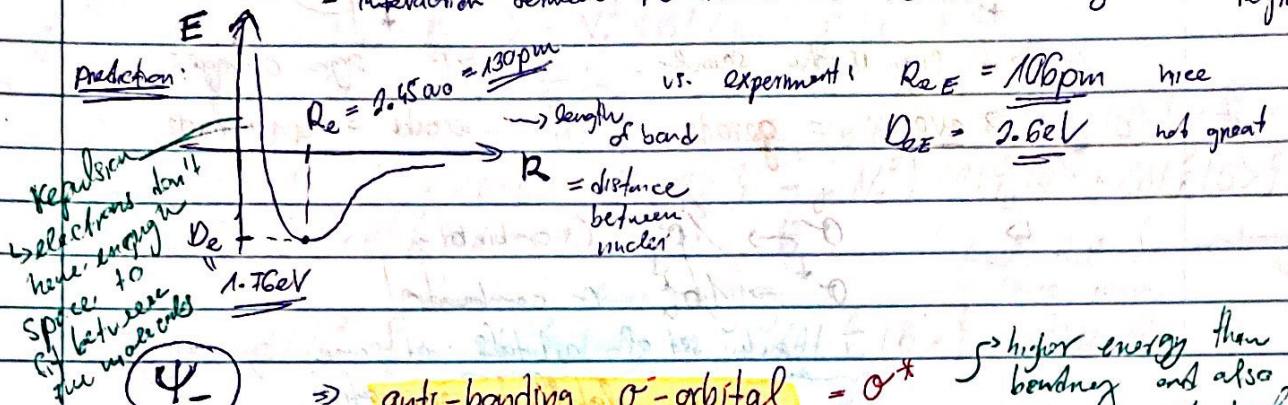
overlap integral

$$j = j_0 \langle \psi_A | \frac{1}{R} | \psi_A \rangle = \frac{j_0}{R} \left[1 - \left(1 + \frac{R}{a_0} \right) e^{-2R/a_0} \right]$$

↪ $\psi_A = \psi_B$ so doesn't matter which nucleus (this says $1/10$)

$$k = j_0 \langle \psi_A | \frac{1}{R} | \psi_B \rangle = \frac{j_0}{R} \left(1 + \frac{R}{a_0} \right) e^{-R/a_0}$$

interaction between the nuclei and the excess e^- density in the intermolecular region



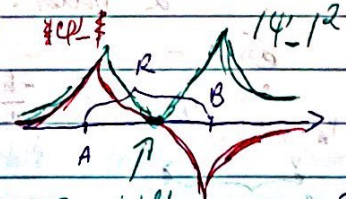
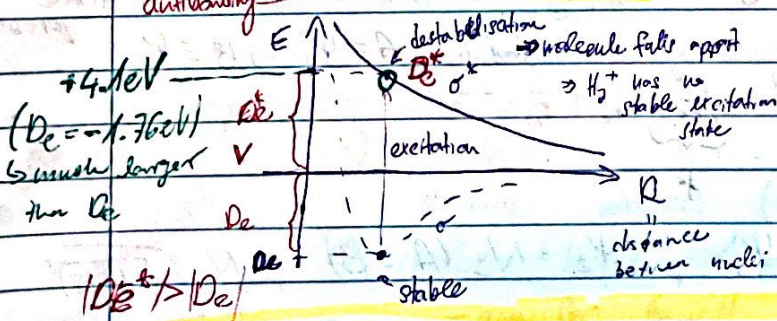
\Rightarrow anti-bonding σ^* -orbital = σ^* \rightarrow higher energy than bonding and also \rightarrow electron in this orbital will increase the energy as compared to unbound state and splits the molecule apart

$$\langle \psi_- | \psi_- \rangle = N^2 \left[\langle \psi_A | \psi_A \rangle + \langle \psi_B | \psi_B \rangle - 2 \langle \psi_A | \psi_B \rangle \right]$$

destructive interference \uparrow overlap integral S

$$E_{0^*}(R) = E_{H1s} + \frac{j_0}{R} - \frac{j-k}{1-S}$$

antibonding



dissociation energy = energy needed to place electron into that molec. orbital

anti-bonding orbital is more anti-bonding (destabilising) than the bonding orbital is bonding

\Rightarrow if $1e^-$ in bonding and $1e^-$ in antibonding \Rightarrow not stable

\rightarrow reason why He doesn't form molecule ($2e^-$ bonding and $2e^-$ antibonding bigger $\rightarrow E_{H1s}$)

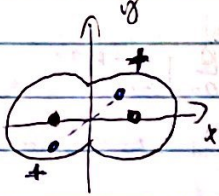
$$|E_{0^*} - E_{H1s}| > |E_0 - E_{H1s}|$$

\rightarrow energy of isolated H atom

Inversion Symmetry

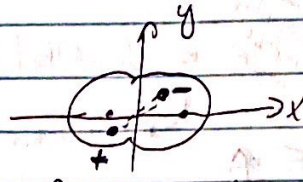
• only for homonuclear diatomic molecules (e.g. N_2)

① Does the sign of the wavefunction change when we invert it through the center of the molecule?



↳ if sign is the same

⇒ even = gerade



↳ if sign changes

⇒ odd = ungerade

↳ $\sigma \rightarrow 1\sigma_g$ (+ combination)
 $\sigma^* \rightarrow 1\sigma_u^*$ (- combination)
 each set of orbitals of same symmetry are labelled separately

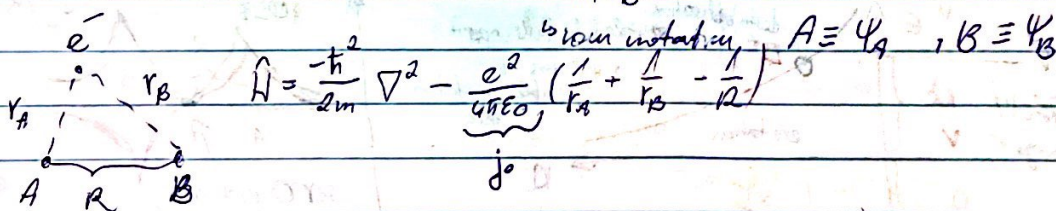
• for heteronuclear \rightarrow no label (because it's not symmetric)

↳ if we have molecule made of various atoms \rightarrow don't use labels

Derivation

② Energy of σ and σ^* of H_2^+ ?

• 2 nuclei: A & B : ψ_A, ψ_B = solution of isolated H-atom problem



$$\langle H \rangle = \langle \Psi | H | \Psi \rangle, \quad \Psi_{\pm} = N_{\pm} (A \pm B), \quad N_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}}$$

$$\langle \Psi_{\pm} | -\frac{\hbar^2}{2m} \nabla^2 - j_0 \left(\frac{1}{r_A} + \frac{1}{r_B} - \frac{1}{R} \right) | \Psi_{\pm} \rangle =$$

does not operate on ψ_{\pm} - acts only on molecular but not on atomic orbitals ψ_A, ψ_B

$$= \langle \psi_{\pm} | -\frac{\hbar^2}{2m} \nabla^2 - j_0 \left(\frac{1}{r_A} + \frac{1}{r_B} \right) | \psi_{\pm} \rangle + \frac{j_0}{R} \langle \psi_{\pm} | \psi_{\pm} \rangle =$$

$$= \frac{1}{2} (N_{\pm})^2 \langle A \pm B | -\frac{\hbar^2}{2m} \nabla^2 - j_0 \left(\frac{1}{r_A} + \frac{1}{r_B} \right) | A \pm B \rangle + \frac{j_0}{R} =$$

A, B are solutions of H-Atom Schröd. Eq. $\hat{H}_H A = \left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{j_0}{r_A} \right) A = E_{Hj} A$
 $\hat{H}_H B = \dots \Rightarrow E_{Hj} B$

$$\langle \psi \rangle = N_{\pm}^2 \langle A | \hat{H}_H - \frac{j_0}{r_B} | A \rangle \pm N_{\pm}^2 \langle A | \hat{H}_H - \frac{j_0}{r_A} | B \rangle$$

$$\pm N_{\pm}^2 \langle B | \hat{H}_H - \frac{j_0}{r_B} | A \rangle + N_{\pm}^2 \langle B | \hat{H}_H - \frac{j_0}{r_A} | B \rangle + \frac{j_0}{R} =$$

$$\langle A | -\frac{\hbar^2}{2m} \nabla^2 - \frac{j_0}{r_B} | B \rangle = \langle A | \hat{H}_H - \frac{j_0}{r_A} | B \rangle$$

$$= N_{\pm}^2 \langle A | E_{Hj} - \frac{j_0}{r_B} | A \rangle \pm N_{\pm}^2 \langle A | E_{Hj} - \frac{j_0}{r_A} | B \rangle$$

$$\pm N_{\pm}^2 \langle B | E_{Hj} - \frac{j_0}{r_B} | A \rangle + N_{\pm}^2 \langle B | E_{Hj} - \frac{j_0}{r_A} | B \rangle + \frac{j_0}{R} =$$

$$= N_{\pm}^2 \left[E_{Hj} \langle A | A \rangle - \langle A | \frac{j_0}{r_B} | A \rangle \pm E_{Hj} \langle A | B \rangle - \langle A | \frac{j_0}{r_A} | B \rangle \right]$$

$$\pm E_{Hj} \langle B | A \rangle - \langle B | \frac{j_0}{r_B} | A \rangle + E_{Hj} \langle B | B \rangle - \langle B | \frac{j_0}{r_A} | B \rangle + \frac{j_0}{R} =$$

$$= N_{\pm}^2 E_{Hj} \{ \langle A | A \rangle + \langle B | B \rangle \pm \langle A | B \rangle \} - j_0 N_{\pm}^2 \{ \langle A | \frac{1}{r_B} | A \rangle + \langle B | \frac{1}{r_A} | B \rangle \}$$

$\langle A | B \rangle = \frac{1}{2(1+s)}$

$$= E_{Hj} - 2 N_{\pm}^2 \left[j_0 \langle A | \frac{1}{r_B} | A \rangle \pm j_0 \langle A | \frac{1}{r_A} | B \rangle \right] + \frac{j_0}{R}$$

$$= E_{Hj} - 2 N_{\pm}^2 (j \neq k) + \frac{j_0}{R} = E_{Hj} - \frac{j \neq k}{1 \pm s} + \frac{j_0}{R}$$

$$\Rightarrow E_{0/0^*} = E_{Hj} + \frac{j_0}{R} - \frac{j \neq k}{1 \pm s}$$

Labels A, B are arbitrary \Rightarrow same thing

Homonuclear diatomic molecules

- each orbital can be occupied by up to 2e⁻
- procedure for populating orbitals
 - ① Construct Molecular Orbitals from the available atomic orbitals (LCAO)
 - ② Aufbau / build up principle - for ground state
 - aim for lowest ~~total~~ overall energy while respecting Pauli's exclusion principle
 - if several degenerate orbitals exist \rightarrow first is single occupancy (min. e⁻e⁻ repulsion)
 - Hund's rule of maximum multiplicity: if 2e⁻ in different degenerate orbitals \Rightarrow spins parallel ($\uparrow \uparrow$)
 - is why? see next page

Why ground state? spacing between states: order of eV \leftarrow at room temp $k_B T = 25 \text{ meV}$
 even use thermal prob. $\propto e^{-E/(k_B T)}$ (Boltzmann) $\sim 10^3$ small \Rightarrow (nearly) all molecules will be in the ground state at room temp.

Hund's rule:

- two degenerate orbitals, two e^- singlet
↳ to me place them $\uparrow\uparrow$ or $\uparrow\downarrow$ (?)
which provides lower energy?

• by Pauli's: $\Psi_+(1,2) = -\Psi_+(2,1)$ incl. spin

↳ Ψ_+ spatial part of Ψ is symmetric,

⇒ spin must be asymmetric ⇒ singlet state $\uparrow\downarrow$

↳ Ψ_- spatial part of Ψ is asymmetric,

⇒ spin must be symmetric ⇒ triplet state $\uparrow\uparrow$

if $\Psi_-(r_1=r_2) = 0$ ⇒ e^- never meet

⇒ less e^-e^- repulsion ⇒ lower energy

⇒ it is more favourable to be in the $\uparrow\uparrow$ triplet state because it implies asymmetric spatial Ψ which minimizes ~~rep~~ energy from repulsion

Trivia Time

1. Are there anti-bonding orbitals in VB? No
2. Differences between VB and MO theories?

- MO orbitals extend over entire molecule

- VB: bonding always for even number of e^- with paired spins $\uparrow\downarrow$
- ⇒ VB cannot explain H_2^+ bonding with only $1e^-$

- MO: molecular orbitals are built up as LCAO = linear combination of atomic orbitals

- MO: mol. orb. can be bonding, antibonding, non-bonding

- VB: defines hybridization of atom orbit. to explain shape of molecules such as CH_4 (MO doesn't need this)

- VB: resonance is important, in MO it isn't

3.

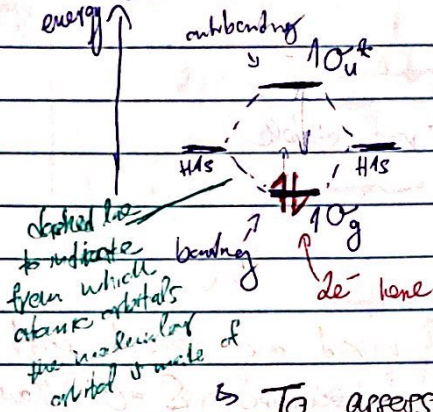
3. Inversion symmetry

- inversion through the center of symmetry leaves the molecule unchanged - passing each part through center of inversion and out to the same distance on other side

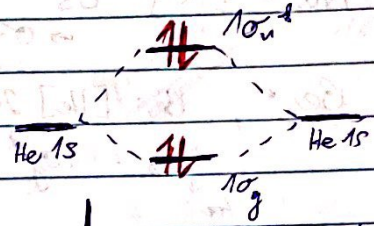
- g = gerade, u = ungerade

- ↳ only applies to molecules w/ inversion symmetry ~ homonuclear
- ↳ doesn't make sense for e.g. HCl ⇒ g/u labels don't apply

★ H_2 : $1\sigma_g$ $1\sigma_u^*$
molecular orbital diagram:



★ He_2 : $1\sigma_g$ $1\sigma_u^*$



unstable because $|E_{\sigma_u^*} - E_{\sigma_g}| > |E_{\sigma_g} - E_{1s}|$

↳ To assess stability we compare to E of separate individual atoms

General principle

• all orbitals of appropriate symmetry contribute to molecular orbital

e.g. σ -bond: $2s, 2p_z$ contribute (same cylindrical symmetry)

* also each add $1s, 3s, \dots$

$$\psi = C_{A2s} \chi_{A2s} + C_{B2s} \chi_{B2s} + C_{A2p_z} \chi_{A2p_z} + C_{B2p_z} \chi_{B2p_z}$$

but ↳ How much each contributes depends but all can

↳ amount of contribution depends on difference in energy & overlap integral S

ΔE { small \rightarrow big contribution
large \rightarrow negligible contribution

$(E_{2s} - E_{2p_z})$ or $(E_{2p} - E_{3s})$ is large \rightarrow $3s$ doesn't contribute almost anything

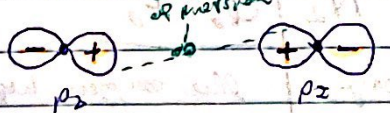
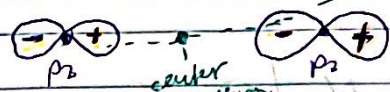
FOR NOW

$$\psi_1 = \sum X_{1,2s} = C_{A2s} \chi_{A2s} + C_{B2s} \chi_{B2s}$$

$$\psi_2 = \sum X_{1,2p_z} = C_{A2p_z} \chi_{A2p_z} + C_{B2p_z} \chi_{B2p_z}$$

$2s$ and $2p_z$ form different orbitals

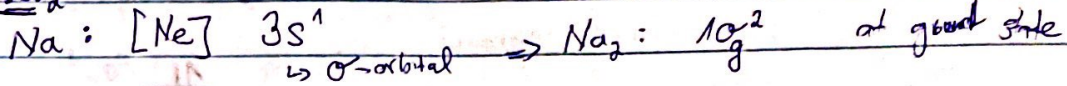
$2p_z$ forming σ -orbitals symmetric but gets inverted \rightarrow ungerade $2\sigma_u^*$



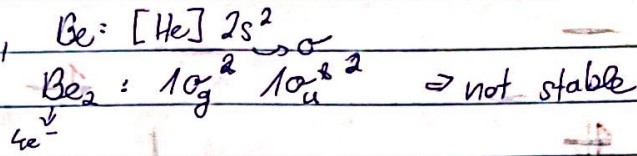
sign remains \Rightarrow gerade $2\sigma_g$

$1\sigma_u^*$
 $1\sigma_g$ } from $2s$

★ Na_2

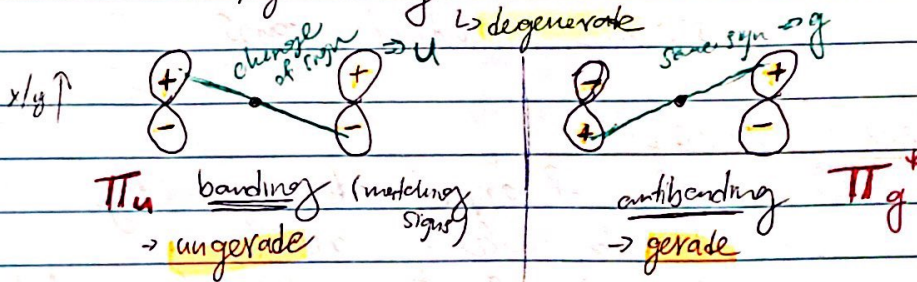


★ Be_2^+

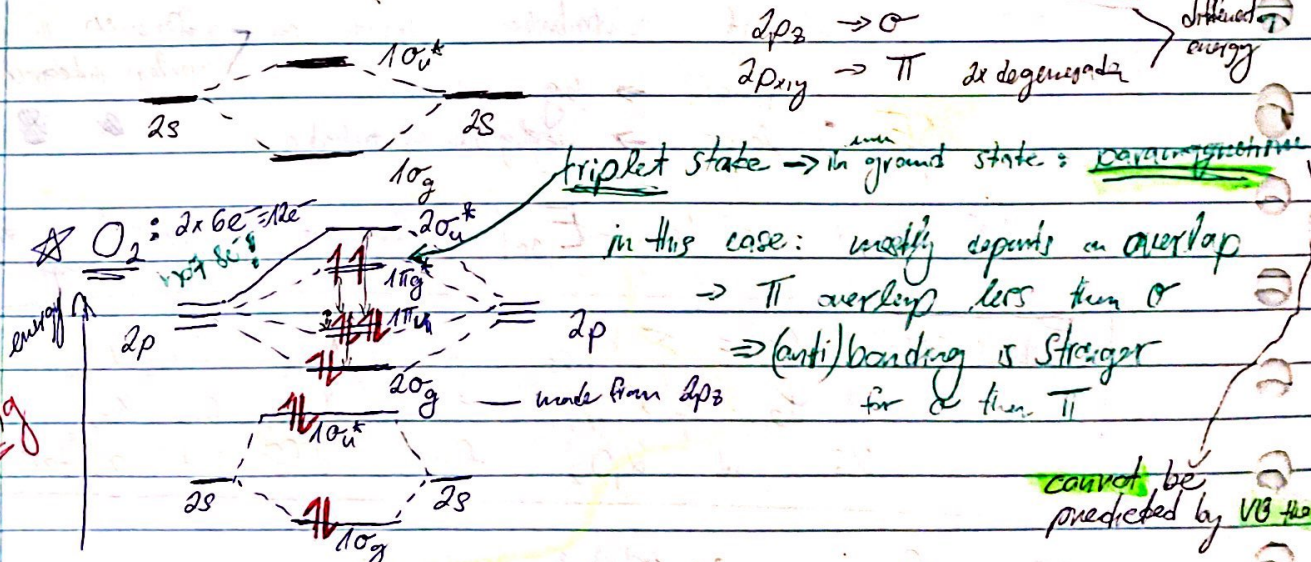
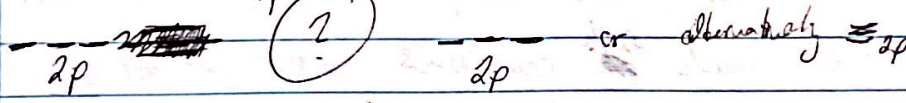


$2p_{x,y} \rightarrow$ form π orbitals

$2p_x \rightarrow \pi_x$
 $2p_y \rightarrow \pi_y$ } mixed one doesn't exist because $S=0$ (overlap) ^{no}

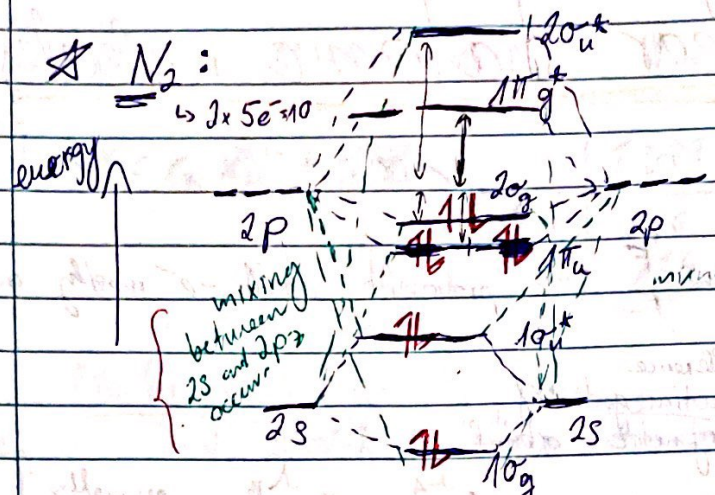


depends per molecule whether 2σ or π is higher



O_2, F_2

$\text{Li}_2, \text{Be}_2, \text{B}_2, \text{C}_2, \text{N}_2 \mid \text{O}_2, \text{F}_2$
 diatomic like N_2 on next page | like oxygen here above

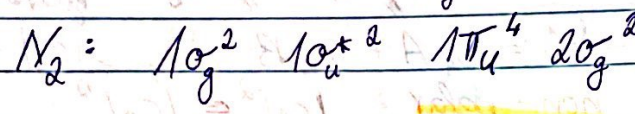


$\leftarrow Li_2, \dots, N_2$

$10e^-: 2s-2p_2$
 $11e^-: 2p_2-2s$

SP-mixing

mixing for N_2 - not necessary to draw in the exam
 \rightarrow but the blue ones are very important



Band order: $b = \frac{1}{2}(N - N^*)$

number of bonds between two atoms: N
 #e⁻ in bonding: N^*
 #e⁻ in antibonding: N^*

$b_{N_2} = \frac{1}{2}(8 - 2) = 3$
 triple bond between N_2

$b_{H_2^+} = \frac{1}{2}(1 - 2) = -0.5$
 \leftarrow less stable than N_2

self-test 10C.3

	b
O_2	2
O_2^-	$1\frac{1}{2}$
O_2^+	$2\frac{1}{2}$
O_2^{2-}	1

Photoelectron Spectroscopy \rightarrow frequency ν

UVS/XPS - high energy photons (UV, X-ray) knock out electrons from molecules

$h\nu = \frac{1}{2} m_e v^2 + I_i$

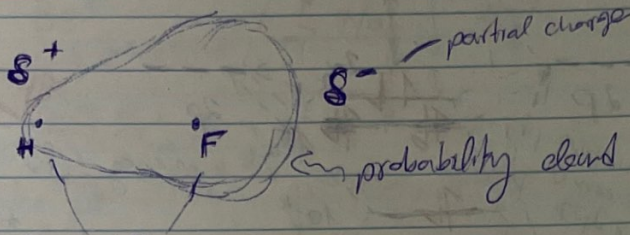
$h\nu$ (known) = measured \sim ionisation energy of orbital i

\Rightarrow ~~complex~~ ^{few} of peaks

\rightarrow energy levels of orbitals separated by 10^2-10^4 eV's but each energy level is split into few peaks from thermal oscillations

Heteronuclear diatomic molecules

* HF



large difference in electronegativity \Rightarrow asymmetric orbital

Molecular orbital: $\Psi = c_A A + c_B B$, generally $|c_A| \neq |c_B|$

non-polar: $|c_A|^2 \approx |c_B|^2$

pure ionic: $|c_A|/|c_B| \approx 0$

Bonding MO: consists mostly of atomic orbitals of the more electronegative atom

Anti-bonding MO: consists mostly of atomic orbitals of the less electronegative atom

Ionization energy (I) > 0

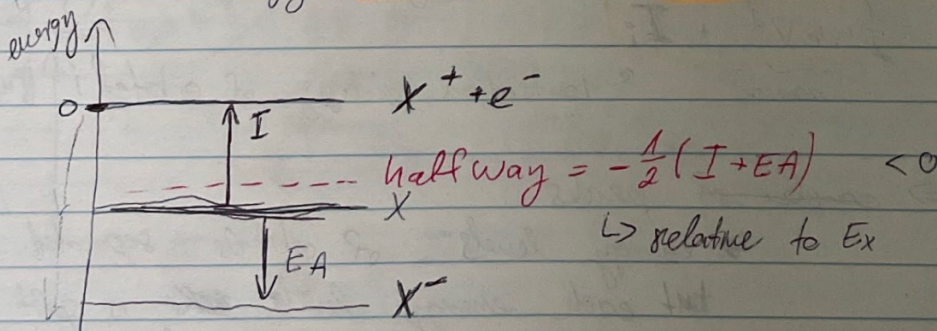
= minimum energy required to remove e^- from the molecule

Electron affinity (EA) > 0

= energy released when e^- attaches

$\uparrow(I, EA)$ means the atom likes e^-

similar order of magnitude but not the same process/value



Mulliken electronegativity: $\chi = \frac{1}{2}(I + EA) > 0$

HF

$\Psi = c_H \Psi_H + c_F \Psi_F$

e^- mostly on F \leftarrow

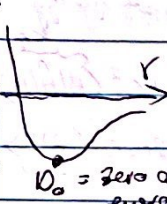
	I [eV]	EA [eV]	χ [eV]
H	13.6	0.75	7.2
F	17.4	3.34	10.4

\rightarrow for bonding: $|c_F| > |c_H|$
for antibonding: $|c_F| < |c_H|$

Pauling electronegativity

one absolute - relative scale - based on differences between atoms

E_a



D_0 = zero oscillation energy

D_e = dissociation energy

$|X_A - X_B| = \sqrt{D_0(AB) - \frac{1}{2}[D_0(AA) + D_0(BB)]}$

\uparrow in eV
 \uparrow dissociation energy

then try to find out difference values which approx. work

which would fit for all pairs of elements

Periodic table

H: 2.2

C: 2.6

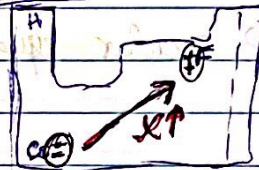
N: 3.0

O: 3.4

F: 4.0

Cl: 3.2

very electronegative



$X_{Pauling} \approx X_{Mull} - 1.37$

Variation principle

If an arbitrary wavefunction is used to calculate the energy, then the calculated energy is no less than real energy

$E_{calc} \geq E_{real}$

normalised

$\Psi_{\pm} = \Psi_{trial} = \sum_n c_n \Psi_n$
 Ψ_n eigenfunctions of \hat{H}

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

E_0 = eigenvalue of Ψ_0 ground state \Rightarrow to prove: $E_{\pm} - E_0 \geq 0$
 Ψ_0 real wavefunction

$$\begin{aligned}
 E_+ - E_0 &= \langle \Psi_+ | \hat{H} - E_0 | \Psi_+ \rangle = \langle \Psi_+ | \hat{H} | \Psi_+ \rangle - E_0 \langle \Psi_+ | \Psi_+ \rangle = \\
 &= \langle \sum c_n \Psi_n | \hat{H} | \sum c_{n'} \Psi_{n'} \rangle - E_0 = \\
 &= \sum_{n,n'} c_n^* c_{n'} \langle \Psi_n | \hat{H} | \Psi_{n'} \rangle - E_0 = \sum_{n,n'} c_n^* c_{n'} (E_{n'} - E_0) \langle \Psi_n | \Psi_{n'} \rangle = \\
 &= \sum_n |c_n|^2 (E_n - E_0) \geq 0
 \end{aligned}$$

normalised > 0 because E_0 is the ground state \Rightarrow lowest energy $B =$ resonance integral

$$\begin{aligned}
 \Psi &= c_A A + c_B B \\
 E &= \langle \hat{H} \rangle = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{c_A^2 \langle A | \hat{H} | A \rangle + c_B^2 \langle B | \hat{H} | B \rangle + 2c_A c_B \langle A | \hat{H} | B \rangle}{c_A^2 \langle A | A \rangle + 2c_A c_B \langle A | B \rangle + c_B^2 \langle B | B \rangle} \\
 \Rightarrow E &= \frac{c_A^2 \alpha_A + c_B^2 \alpha_B + 2c_A c_B \beta}{c_A^2 + c_B^2 + 2c_A c_B S}
 \end{aligned}$$

\Rightarrow find minimum: $\frac{\partial E}{\partial c_{A,B}} = 0$

\Rightarrow secular equations

$$\begin{aligned}
 (\alpha_A - E) c_A + (\beta - SE) c_B &= 0 \\
 (\alpha_B - E) c_B + (\beta - SE) c_A &= 0
 \end{aligned}$$

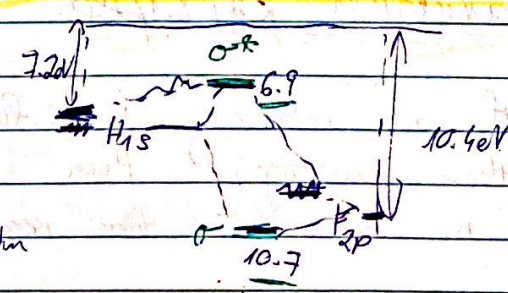
$\langle A | \hat{H} | A \rangle$ $\langle B | \hat{H} | B \rangle$ resonance integral $\langle A | \hat{H} | B \rangle$ overlap integral

For homonuclear: $E_{\pm} = \frac{\alpha \pm \beta}{1 \pm S}$, $c_A = c_B$

$S \rightarrow 0$ for clear expression:

$$E_{\pm} = \frac{1}{2}(\alpha_A + \alpha_B) \pm \frac{1}{2}(\alpha_A - \alpha_B) \sqrt{1 + \left(\frac{2\beta}{\alpha_A - \alpha_B}\right)^2}$$

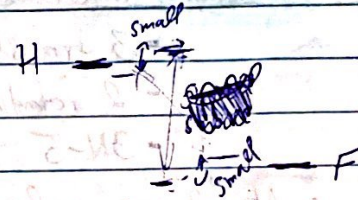
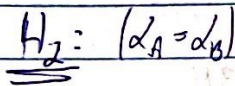
* HF: $\frac{1}{2}(I + EA)$
 $\alpha_H = -13.2 \text{ eV}$
 $\alpha_F = -10.4 \text{ eV}$
 $\beta = -1 \text{ eV}$



$\Psi_+ = 0.28 \chi_{H1s} + 0.96 \chi_{F2p}$ more electronegative \rightarrow higher c in bonding
 $\Psi_- = 0.96 \chi_{H1s} - 0.28 \chi_{F2p}$ less electronegative \rightarrow higher c in antibonding

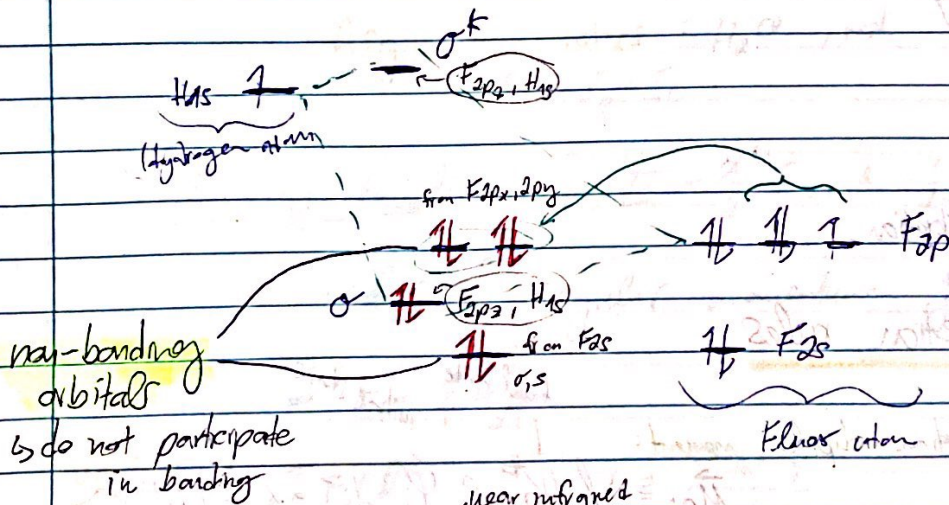
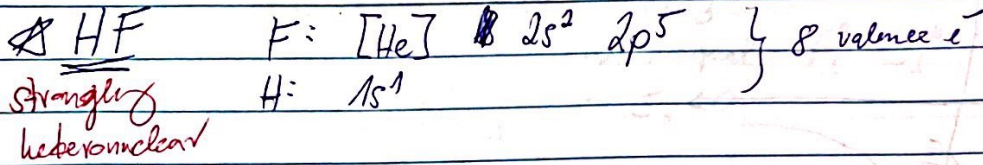
From E_{\pm} :

if $|d_A - d_B|$ is small, then the bonding and antibonding effects are strong.



When do atomic orbitals contribute strongly?

- symmetry
- overlap (S)
- ΔE



UV - Visible - NIR

• electronic \rightarrow \sim eV
 • transition between shells (n)

infrared

• vibrational
 \sim tens of meV

microwave

• rotational
 \sim meV

$$E = \frac{1238}{\lambda [nm]}$$

all in ground state

at room temp because

$$\Delta E \sim \text{eV or } 10^4 \text{ meV} > k_B T \sim 25 \text{ meV}$$

most in excited state

$$k_B T \sim 25 \text{ meV} > \text{meV}$$

Degrees of Freedom

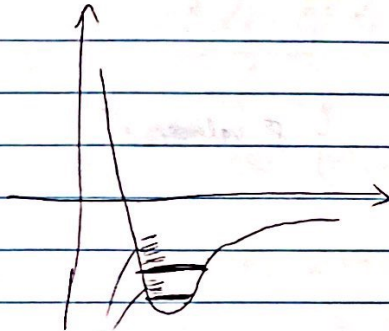
• N atoms \rightarrow $3N$ degrees of freedom
 incl. translation, rotation, vibration

Linear molecule

- 3 translational
 - 2 rotational
 - $3N - 5$ vibrational
- } $3N$

Non-linear molecule

- 3 translational
 - 3 rotational
 - $3N - 6$ vibrational
- } $3N$



extra energy levels from vibration

For rotational transitions

Selection rules

transition dipole moment: $\mu_{fi} = \int \psi_f^* \hat{\mu} \psi_i d\tau = \langle \psi_f | \hat{\mu} | \psi_i \rangle$

final state
initial state

from initial to final

$\Delta J = \pm 1$

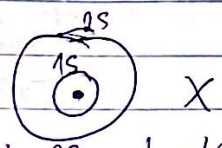
electric dipole operator

$$\hat{\mu} = \sum_i q_i \vec{r}_i = - \sum_i e \vec{r}_i$$

for electrons

✗ $1s \rightarrow 2s$

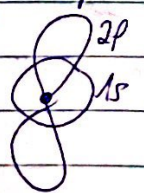
✗ $1s \rightarrow 2p$



not allowed - dipole forbidden

$\mu_{fi} = 0$

because photons can't subtract with it



dipole allowed ✓

18

Rotations

Molecular Rotors

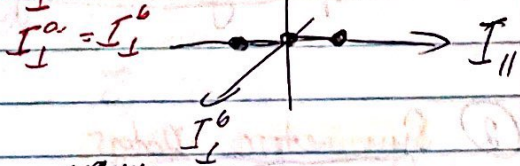
moment of inertia $I = \sum m_i x_i^2$

Rigid rotors - 4 types, don't vibrate, no changes in bond length/angle

• Linear rotors : $\text{CO}_2, \text{HCl}, \dots$

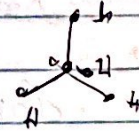
$I_{\parallel} = 0, I_{\perp} \neq 0$

→ unique principal figure axis



• Spherical rotors : CH_4, \dots

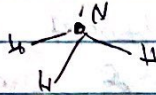
$I_x = I_y = I_z$



• Symmetric rotors : NH_3, \dots

• 2 I's equal: $I_x^a = I_x^b$

• $I_{\parallel} = 0$



• Asymmetric rotors : $\text{H}_2\text{O}, \text{rest}$

$I_a < I_b < I_c$

Energy levels

$E = \frac{1}{2} I \omega^2 = \frac{1}{2} I_a \omega_a^2 + \frac{1}{2} I_b \omega_b^2 + \frac{1}{2} I_c \omega_c^2$

• classical angular momentum $J = I\omega$

$E = \sum \frac{J_i^2}{2I_i}$

diatomic

$I = \mu r^2, \mu = \frac{m_1 m_2}{m_1 + m_2}$

① Spherical rotors :

• I's are equal

$E = \frac{J^2}{2I}$

$I = \frac{8}{3} m_a R^2$

$E_J = J(J+1) \frac{\hbar^2}{2I}$

$|J^2|_{max} = J(J+1) \hbar^2$

include

$J = 0, 1, 2, \dots \Rightarrow E_J = h^2 B J(J+1)$

frequency $[s^{-1}]$

speed of light

$B = c\tilde{B}$

rotational constant \tilde{B} of the molecule

$hc\tilde{B} = \frac{\hbar^2}{2I}$

$\tilde{B} = \frac{h}{8\pi^2 c I}$

wavenumbers $[cm^{-1}]$

general

$$E_J = hB J(J+1)$$

• rotational terms:

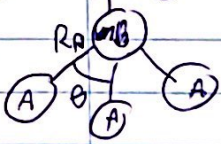
$$\tilde{F}_J = \frac{E_J}{hc} = \tilde{B} J(J+1)$$

• in spectroscopy we observe transitions: spacings of adjacent levels

$$\tilde{F}_{J+1} - \tilde{F}_J = 2\tilde{B}(J+1)$$

② Symmetric Rotors

① 2 equal I 's, 3rd $I \neq 0 \rightarrow I_{||}$ unique/principal/figure



classically: $E = \frac{J_a^2 + J_c^2}{2I_a} + \frac{J_a^2}{2I_{||}}$

$I_{||} = 2m_A(1 - \cos\theta)R_A^2$ \rightarrow total $J^2 \rightarrow J(J+1)\hbar^2$ from QM only for total J , doesn't work for individual components

$$I_{\perp} = m_A(1 - \cos\theta)R_A^2$$

+ $\frac{m_B}{m}(m_B + m_A)(1 + 2\cos\theta)R_A^2$ \rightarrow QM: component of angular momentum

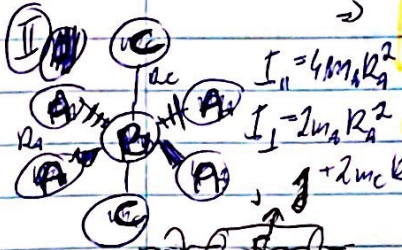
+ $\frac{m_C}{m}(3m_A + m_B)R_C$ around unique axis \rightarrow quantized $K\hbar$; $K=0, \pm 1, \dots, \pm J$

+ $6m_A R_A \sqrt{\frac{1}{3}(1 - 2\cos\theta)}$ \rightarrow $J_a^2 \rightarrow K^2\hbar^2$ with internal axes

$$m = \sum m_i = 3m_A + m_B + m_C$$

$$\tilde{F}_{J,K} = \tilde{B} J(J+1) + (\tilde{A} - \tilde{B})K^2 \quad J=0, 1, 2, \dots$$

$$K=0, \pm 1, \dots, \pm J$$



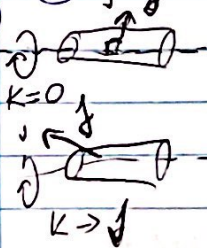
$$I_{||} = 4m_A R_A^2$$

$$I_{\perp} = 2m_A R_A^2$$

$$I_C = 2m_C R_C^2$$

$$\tilde{A} = \frac{\hbar}{4\pi c I_{||}}$$

$$\tilde{B} = \frac{\hbar}{4\pi c I_{\perp}}$$



M_J : allowed values $M_J \hbar$, $M_J = 0, \pm 1, \pm 2, \dots, \pm J$

\rightarrow component of angular momentum along an externally chosen axis

- $2J+1$ orientations (M_J values) \rightarrow degenerates (E indep.)
- for $K \neq 0$: \pm value of K doesn't influence energy \rightarrow 2 deg
- for $K=0$: 1 deg

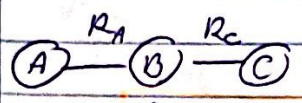
$$\rightarrow \begin{cases} K \neq 0 & 2(2J+1) \\ K = 0 & 2J+1 \end{cases} \text{ degenerate energies}$$

usually

$$\tilde{B} = \frac{h}{4\pi c I} \approx 0.1 - 10 \text{ cm}^{-1}$$

$$E_J = h c \tilde{B} J(J+1)$$

③ Linear Rotors



rot. const.

$$\tilde{F}_J = \tilde{B} J(J+1)$$

for $J=0, 1, 2, \dots$

$$I = m_A R_A^2 + m_C R_C^2 + \frac{(m_A R_A - m_C R_C)^2}{m}$$

$m = m_A + m_B + m_C$

• If not rigid e.g. (spinning very fast)
 → e.g. centrifugal distortion

$$F_J = \tilde{B} J(J+1) - \tilde{D} J^2(J+1)^2$$

② Can we go from one rotational state to the next by absorption/emission of a photon?

* Polar has permanent el. dipole
 ↳ based on el. neg.

→ Yes, if the molecule has a permanent electric dipole = polar
 ↳ not for spherical symmetry ($C_{\infty v}$)
 (if spins very quickly $J \gg 1 \Rightarrow$ not rigid \Rightarrow gets μ)
 = rotationally active

$$\Delta J = \pm 1 \quad \Rightarrow \quad \Delta M_J = 0, \pm 1$$

Total wavefunction: $\Psi_{tot} = \Psi_{cm} \Psi_{int}$

center of mass internal motion

• using Born-Oppenheimer approx: $\Psi_{tot} = \Psi_e \Psi_v \Psi_r$
 electric vibrational rotational

Transition dipole moment f_{ei}

$$\mu_{ei} = \langle \Psi_{ef} \Psi_{vf} \Psi_{rf} | \hat{\mu} | \Psi_{ei} \Psi_{vi} \Psi_{ri} \rangle = \kappa$$

for purely rot. change of state: not affected by $f = i$ for e, v

$$\Rightarrow \langle \Psi_{ef} \Psi_{vf} | \hat{\mu} | \Psi_{ei} \Psi_{vi} \rangle = \langle \Psi_{ei} \Psi_{vi} | \hat{\mu} | \Psi_{ei} \Psi_{vi} \rangle = \frac{\mu}{\sqrt{2}} = \mu_i$$

permanent electric dipole moment

$$\mu_{ef} = \kappa = \langle \Psi_{rf} | \mu_i | \Psi_{ri} \rangle$$

non-zero only if $\mu_i \neq 0$
 ↳ only if initial state has a permanent dipole moment

$$|\mu_{J+1} - \mu_J|^2 = \left(\frac{J+1}{2J+1} \right)^2 \mu_i^2 \rightarrow \text{dipole moment}$$

↳ for symmetric rotors

$$\Delta K = 0$$

K: quantum number of component along

the figure axis

↳ no "related dipole" associated with rotation around this axis

↳ upon rotation, nothing changes

→ cannot be changed by absorption/emission of γ

For linear

$$\tilde{\nu}_{(J+1 \leftarrow J)} = \tilde{F}_{J+1} - \tilde{F}_J = 2\tilde{B}(J+1)$$

Wavenumber

$$\star \text{ } ^{14}\text{NH}_3, \tilde{B} = 9.977 \text{ cm}^{-1}$$

• $\chi_N > \chi_H \Rightarrow$ polar \Rightarrow has permanent dipole moment

• symmetric rotor $\Rightarrow \Delta K = 0$

• absorption: $\Delta J = +1$

transitions: $J \leftarrow J+1$	J	0	1	2	3
$\tilde{\nu}(\text{cm}^{-1})$		19.95	39.91	59.86	...
frequency $\nu(\text{GHz})$		598.1	1197

↳ Line spacing - between lines - each line = transition

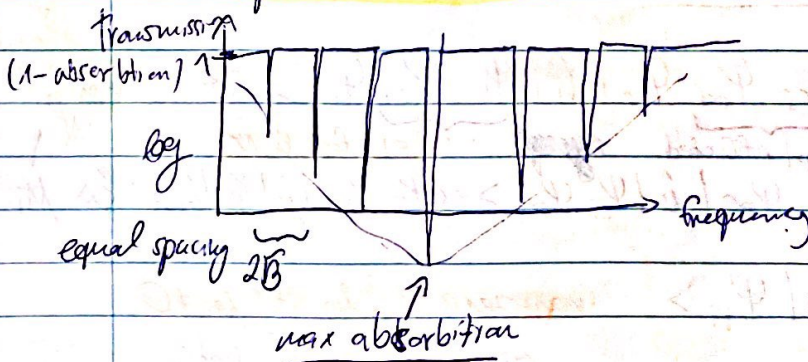
$$= 19.95 \text{ cm}^{-1} = 2\tilde{B}$$

→ between two transitions

↳ transitions in table above

→ take diffraction

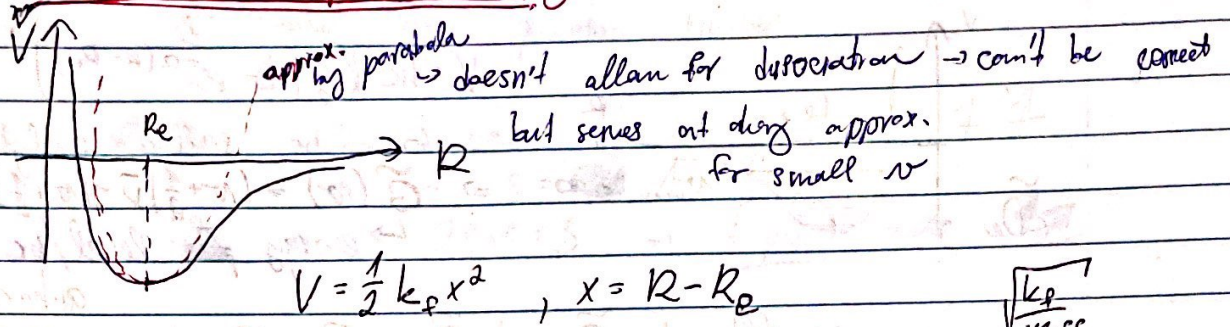
Spectral lines



Boltzmann \rightarrow higher $f (=E) \Rightarrow$ population of state \downarrow

22 but also degeneracy \uparrow \rightarrow opposing factors \rightarrow maximum

Vibrational Spectroscopy - IR = very analytical tool



$$V = \frac{1}{2} k_f x^2, \quad x = R - R_e$$

\Rightarrow QM: Harmonic oscillator: $E_v = (v + \frac{1}{2}) h\nu$

$$E_v = hc \tilde{G}(v) = hc \left(v + \frac{1}{2}\right) \tilde{\nu}$$

vibrational terms (function of v)

$$\mu_{eff} = \frac{m_1 m_2}{m_1 + m_2}$$

= effective mass

Wavenumber [cm^{-1}]

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k_f}{\mu_{eff}}}$$

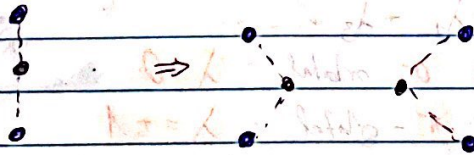
frequency $\nu = c\tilde{\nu}$

energy $E = h\nu = hc\tilde{\nu}$

For vibrational transitions

Selection rules

- electric dipole moment must change if atoms are displaced
- \Rightarrow no permanent dipole moment is required



diatomic $\left\{ \begin{array}{l} \text{homonuclear} - \text{inactive} \\ \text{heteronuclear} - \text{active} \end{array} \right.$

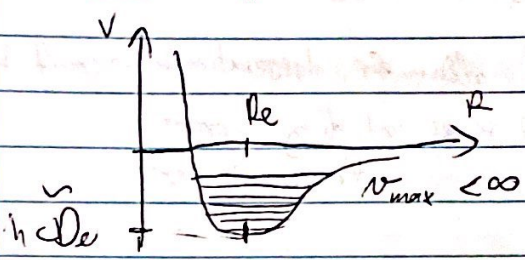
• $\Delta v = \pm 1$

• $\Delta \tilde{G}_{v+1/2} = \tilde{G}_{v+1} - \tilde{G}_v = \tilde{\nu}$ indep. of $v \Rightarrow$ 1 absorption line
as long as HO approx. holds mostly $> 200 cm^{-1} \sim \frac{k_B T}{hc}$ at room temp.

molecules mostly in vib. ground state

dissociation energy: $\tilde{D}_0 = \frac{hc \tilde{D}_e}{hc} - G(0)$

Morse potential



$V = hc \tilde{D}_e (1 - e^{-a(R - R_e)})^2$

↳ can be solved analytically
 $\tilde{G}(v) = (v + \frac{1}{2}) \tilde{\nu} - (v + \frac{1}{2})^2 x_e \tilde{\nu}$
 ↳ energy level / hc / anharmonicity constant

OR empirically: $\tilde{G}_{v+1/2} - \tilde{G}_{v-1/2} = \tilde{\nu} - 2(v+1)x_e \tilde{\nu}$

~~$\Delta v = \pm 1$~~ doesn't hold for anharmonicity

$\Delta v = \pm 1, \pm 2, \dots$ overtones

$\lambda = \frac{1238}{\tilde{\nu}}$
 nm / eV

Term symbols

$^3\Sigma_g^-, ^3\Delta_u$

- Greek upper case letter = total orbital angular momentum about internuclear axis - diatomic molecules
- Λ = total orbital angular number $\Rightarrow \Lambda = 0, \pm 1, \pm 2, \dots$

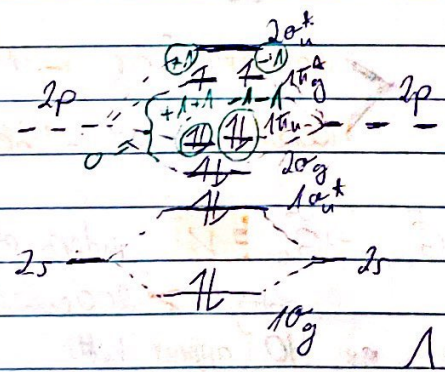
$\Sigma, \Pi, \Delta, (\dots) \phi$

$\Lambda = \lambda_1 + \lambda_2 + \lambda_3 + \dots$

↳ e⁻ in σ -orbital: $\lambda = 0$

↳ e⁻ in π -orbital: $\lambda = \pm 1$

O_2



σ -orbitals give: $\Lambda = 0$
 $1\pi_u$ gives: $\lambda = 1 - 1 + 1 = 1$
 $1\pi_g$ gives: $\lambda = 1 - 1 = 0$
 ↳ both e⁻ have same spin
 ⇒ they must have opposite ang. momentum

$\Lambda = 0$
 Σ

• multiplicity of the term \rightarrow left superscript
 S = total spin quantum number
 $\rightarrow 2S+1$

* O_2 : only unpaired are two $\pi g^* e^-$: $\uparrow \uparrow$
 $\rightarrow S = \frac{1}{2} + \frac{1}{2} = 1$
 $2S+1 = 3 \rightarrow$ triplet $\Rightarrow 3\Sigma$

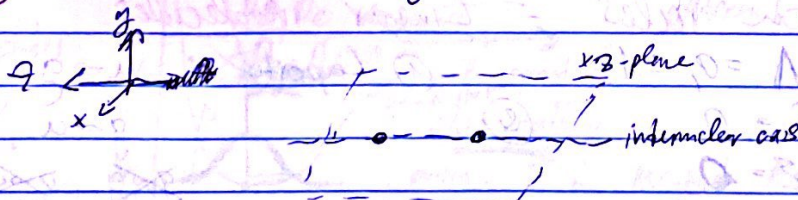
• parity \rightarrow right subscript
 = inversion symmetry
 - if several e^- :

$g \cdot g = g$ $g \sim +1$, even fun
 $u \cdot g = u$ $u \sim -1$, odd fun
 $u \cdot u = g$

* O_2 : $\dots \uparrow \pi g^* \Rightarrow g \cdot g = g \Rightarrow 3\Sigma g$
 (paired up \rightarrow no contribution)

ground state - closed shell
 \rightarrow for diatomic molecule $^1\Sigma_g$
 \rightarrow heteronuclear diatomic \rightarrow no u/g label

Only For Σ -terms: right superscript[†]



• if upon reflection in xz-plane, ~~the sign~~
 - the sign[†] changes \ominus
 - the sign[†] doesn't change \oplus

* of the orbital wavefunction

$3\Sigma_g^-$

Reflection

$\hat{\sigma}_{xz} : \phi \mapsto -\phi \Rightarrow \hat{\sigma}_{xz} \Psi_{-}(1,2) = \pi_{-1}(1) \pi_{-1}(2) - \pi_{-1}(2) \pi_{-1}(1) = -\Psi_{-}(1,2) \Rightarrow \oplus$

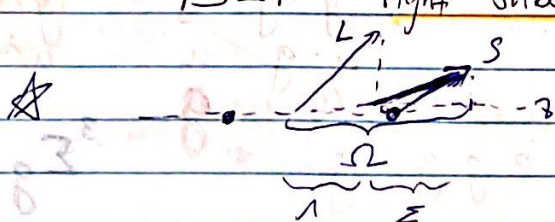
$\Psi_{m_l} \propto \exp(\pm i\phi)$ ~~no ϕ -dep. for $m_l = 0$~~

$\Rightarrow \pi_{+1} \rightarrow -\pi_{-1}$
 $\pi_{-1} \rightarrow -\pi_{+1}$
 * Triplet: $\uparrow \uparrow$ spatial part = antisymmetric triplet
 $\Psi_{-}(1,2) = \frac{1}{\sqrt{2}} (\pi_{+1}(1) \pi_{-1}(2) - \pi_{-1}(2) \pi_{+1}(1)) = \Psi_{-}(1,2)$

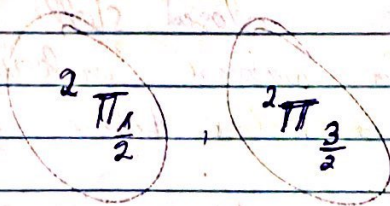
\star excited O_2 : $\uparrow\uparrow$ = singlet: spatially symmetric
 $\psi_+(1,2) = \pi_{1+}(1)\pi_{-1+}(2) + \pi_{1+}(2)\pi_{-1+}(1) = \psi_+(2,1)$
 $\Rightarrow \boxed{^1\Sigma_g^+}$

Total electronic angular momentum around internuclear axis
 $= \Omega \hbar$
 $\Omega = \Lambda + \Sigma$ component of spin (S) on internuclear axis
 $\Sigma = S_1, S-1, \dots, -S$

$\Rightarrow |\Omega|$ - right subscript
 italic / sloping sigma



\star NO ... π^1 $S = \frac{1}{2} \Rightarrow \Sigma = -\frac{1}{2}, \frac{1}{2}$
 $\Lambda = -1, -1 \Rightarrow \Omega = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$
 $|\Omega| = \frac{1}{2}, \frac{3}{2}$



For electronic transitions

Selection rules - Linear molecules

- $\Delta \Lambda = 0, \pm 1$
 - $\Delta S = 0$
 - $\Delta \Sigma = 0$
 - $\Delta \Omega = 0, \pm 1$
- ① Laporte: $u \rightarrow g$
 $g \rightarrow u$
 ~~$g \rightarrow g$, $u \rightarrow u$~~
- ② in case of Σ :
 $\Sigma^+ \leftrightarrow \Sigma^+$
 $\Sigma^- \leftrightarrow \Sigma^-$

Transition dipole moment

$\Sigma_1^+ \leftrightarrow \Sigma_1^+$

$\mu_{fi} = \langle \psi_f | \hat{\mu} | \psi_i \rangle$, $\hat{\mu} = \sum_i q_i \vec{r}_i$
 \hat{z} - internuclear axis

x, y - components cancelled because $\Lambda = 0$

$\Rightarrow \hat{\mu} = \hat{\mu}_z \oplus$

\star $\Sigma_1^+ \leftrightarrow \Sigma_1^+$

doesn't change direction upon reflection
 \oplus parity

$\langle \psi_f | \hat{\mu}_z | \psi_i \rangle = \langle \oplus | \oplus | \ominus \rangle = \langle \ominus \rangle = 0 \Rightarrow$ forbidden transition

$g \rightarrow u$: components of \hat{m} odd: $x \rightarrow -x$
 \rightarrow so if $g \rightarrow g$: $\int g \cdot u \cdot g = \int u = 0$
 \rightarrow $g \leftrightarrow g$ } forbidden
 $u \leftrightarrow u$ }

★ O_2 : ${}^3\Sigma_g^-$ allowed?

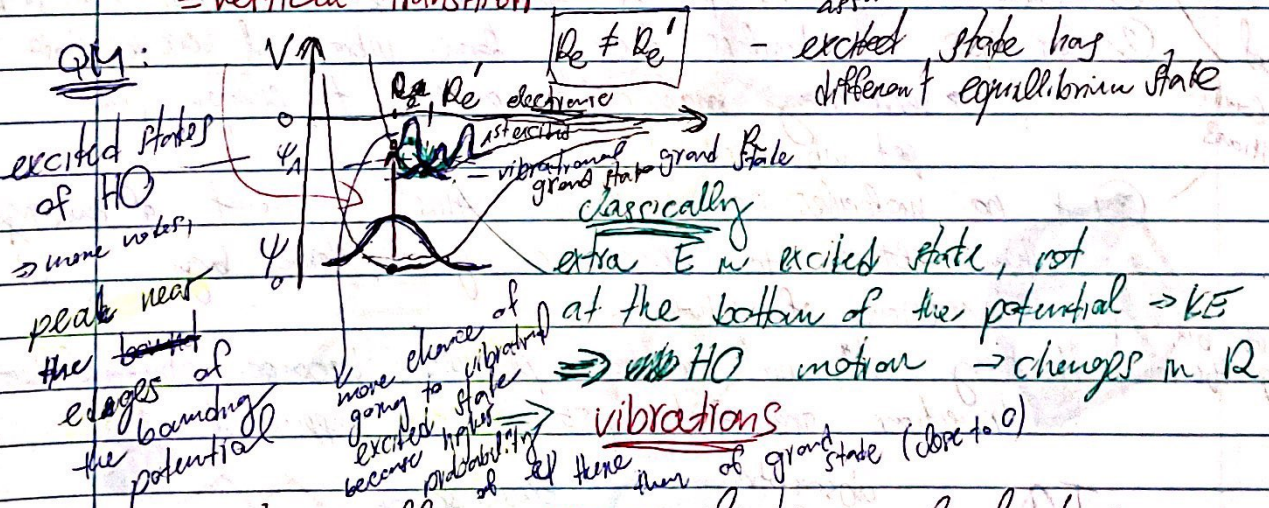
	${}^3\Sigma_g^- \leftarrow {}^3\Sigma_u^-$	${}^3\Sigma_g^- \leftarrow {}^1\Delta_g$	ΔS	Δl	$\Sigma^+ \leftrightarrow \Sigma^-$	g/u	overall
			0 ✓	0 ✓	- - ✓	✓	allowed
			$\neq 0$ ✗	$\neq 0$ ✗	N/A ✗	✗	forbidden

in case of multiphotons: $g \leftrightarrow g$: weakly allowed
 $u \leftrightarrow u$

Frank-Condon principle

- nuclei are heavy ions \rightarrow can be treated as stationary during transitions
- nuclei are much heavier than e^-
 \Rightarrow electronic transition is much faster from the response of the nuclei (movement) \rightarrow nuclei remain stationary

= vertical transition



each el. state

has own series of vibrational states

Transition dipole moment : μ_{ij}

↳ Franck-Condon factor: $|S(v_f, v_i)|^2 = \left| \int \psi_{v_f}^* \psi_{v_i} d\tau \right|^2$

overlap between initial and final vibrational mode

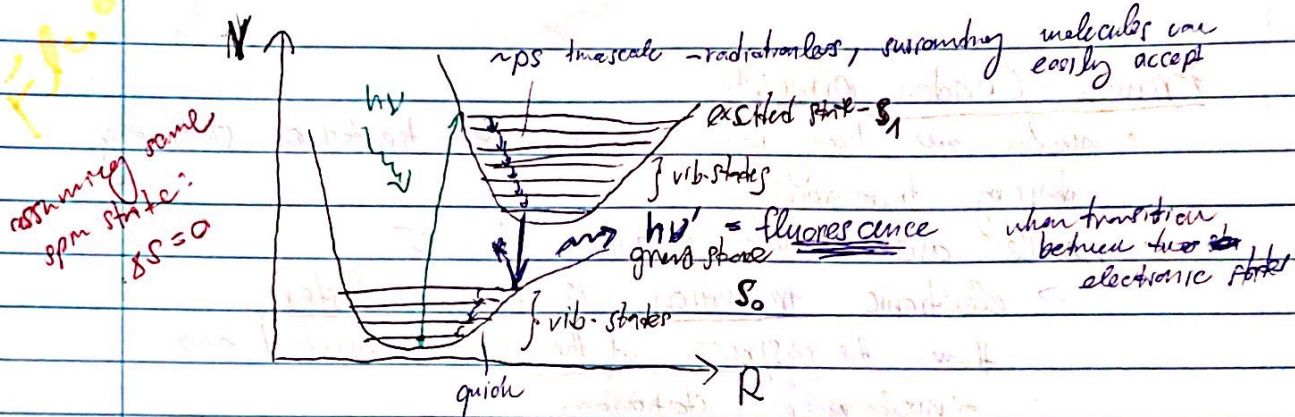


Fluorescence vs. Phosphorescence

↳ ns - ms

↳ s - h

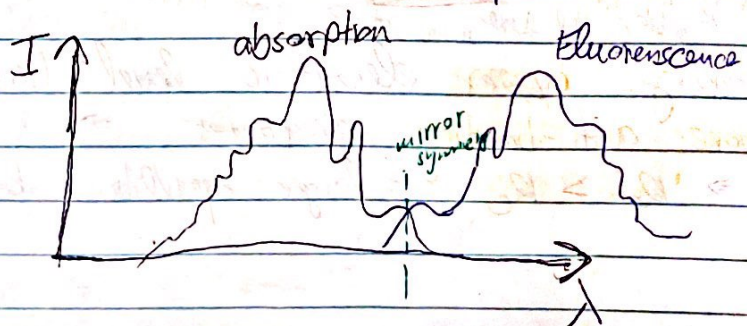
excited state decay :
 → radiation (γ) → Fl. & Ph.
 → heat (radiationless)



assuming same spin state: $\Delta S = 0$

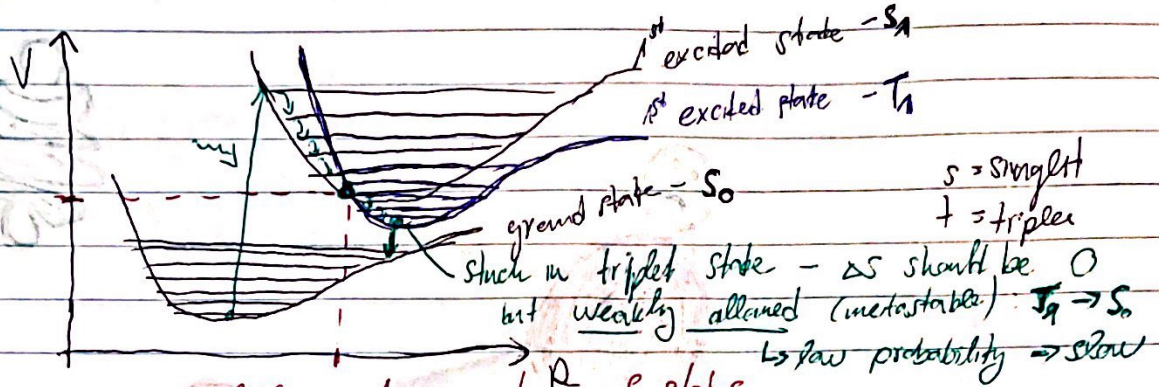
- Vertical (Franck-Condon) transitions
- ① molecule absorbs photon → higher electronic & vibrational state
 - ② after ps → radiationless decay from vibrational excited state → surrounding molecules accept the energy (vib get vib. excited)
 - ③ if no molecules cannot accept this amount of energy, then return to electronic ground state by emission of photon.
- if they can't, no radiation produced because vibrational/heat transitions are faster, so it would happen first

hard but e.g. H2O can



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Phosphorescence



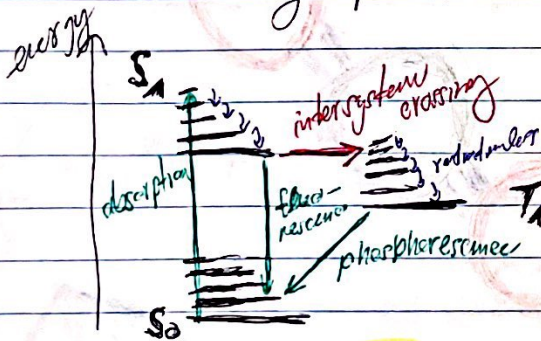
same energy and geometry of states
 \rightarrow for molecule can transition $S_1 \rightarrow T_1 : \sqrt{M} \rightarrow 11$
if there is enough S-O coupling (heavy atoms)

★ smartphones - phosphorescence because

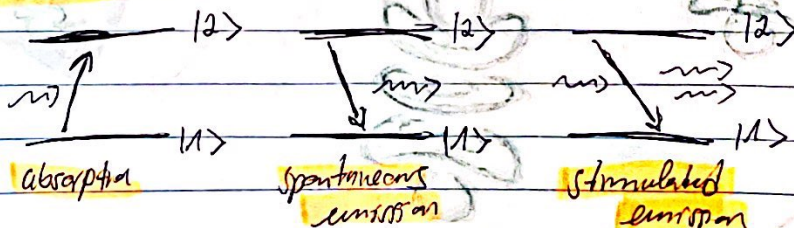
$11 \sim 3$ multiplicity \Rightarrow more likely
 $1 \sim 1$ but in fluorescence doesn't occur
 \downarrow
 loss of energy

Jablonski diagram

- electronic levels
- vibrational levels
- every spm has own separate column



LASERS



Einstein coefficients:

B_{12}

A_{21}

B_{21}

\Rightarrow

$B_{21} = B_{12} = B$
 $\frac{A_{21}}{B} = 8\pi h \left(\frac{\nu}{c}\right)^3$

$\frac{1}{\tau}$
 lifetime of the state

Light, energy, density → frequency

$$\rho(\nu) d\nu = \frac{n h \nu}{V}$$

ν volume

stimulated emission $\propto \rho$

$$B_{21} \rho(\nu) = \frac{c^3}{8\pi h \nu^3} \frac{h \nu}{d\nu V} n = \Gamma n$$

B_{12} B_{21} $\equiv \Gamma$

change in # ν (?) # molecules in lower state

$$\frac{\partial n}{\partial t} =$$

- absorption: $-\Gamma n N_1$
- spontaneous emission: $+A N_2$ # molecules in upper state
- stimulated emission: $+\Gamma n N_2$
- loss: $-\Gamma_0 n$ = what you see coming out of lasers

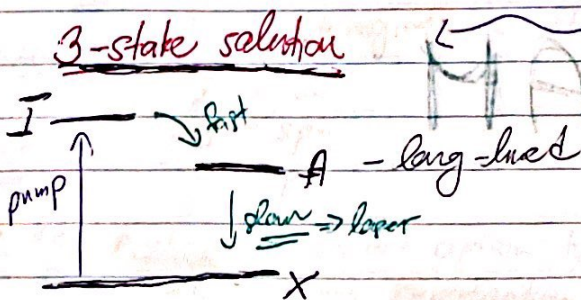
↳ when $\frac{\partial n}{\partial t} \geq 0 \Rightarrow$ no decrease in # ν

$$\frac{\partial n}{\partial t} = \Gamma(N_2 - N_1)n + A N_2 - \Gamma_0 n \geq 0$$

small - if A is big (Γ is small) - we cannot construct a laser

$$N_2 - N_1 \geq \frac{\Gamma_0}{\Gamma} \geq 0$$

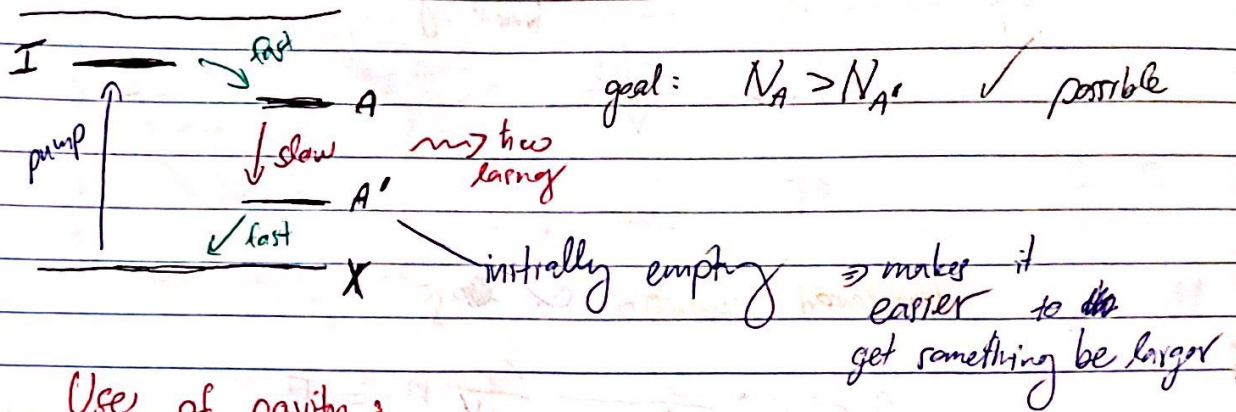
\Rightarrow we need $N_2 \geq N_1 \Rightarrow$ population inversion



two level system doesn't allow

possible to achieve $N_2 > N_1$ but still very difficult

4-state selection



Use of cavity:

\rightarrow length of cavity $L = n \cdot \frac{\lambda}{2}$

n integer

only standing wavelength of light after bouncing back and forth

- monochromatic light
- coherent (in phase)

\hookrightarrow coherence length: how long does it take to be out of coherence

- 2 beams: $\lambda, \lambda + \delta\lambda$

- every cycle, the phase difference grows by $\frac{\delta\lambda}{\lambda}$

\Rightarrow out-of-phase after N -cycles

$$N \frac{\delta\lambda}{\lambda} = \frac{1}{2}$$

$$\Rightarrow N = \frac{\lambda}{2\delta\lambda}$$

\Rightarrow define coherence length

$$l_c = N\lambda = \frac{\lambda^2}{2\delta\lambda}$$

* He-Ne laser: $\lambda = 633\text{nm}$, $\delta\lambda = 2\text{pm}$ $\Rightarrow l_c = 10\text{cm}$

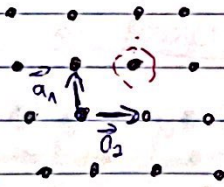
EXAM

Solid state Physics

- Crystals → perfect
 - ↳ if less than perfect, usually also work

Lattice

→ environment looks the same from every point
 → points form **Bravais lattice**



→ specify all points by:

$$\vec{r} = l_1 \vec{a}_1 + l_2 \vec{a}_2 + l_3 \vec{a}_3$$

↳ integers

lattice vectors primitive (basis) vectors

→ # nearest neighbours = **coordination number CN**

in 2D: • if $|\vec{a}_1| = |\vec{a}_2| \rightarrow \underline{CN=4}$

• if not and $\vec{a}_1 \perp \vec{a}_2 \rightarrow \underline{CN=2}$

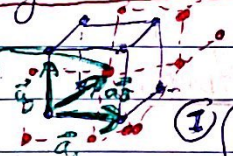
in 3D:

① simple cubic → all angles: 90°

SC → length a_i 's same: CN=6

② body centered cubic BCC, CN=8

↳ looks like 2 interpenetrating S.C. lattices



②

$$\vec{a}'_1 = \frac{a}{2}(\hat{j} + \hat{k} - \hat{i})$$

$$\vec{a}'_2 = \frac{a}{2}(\hat{k} + \hat{i} - \hat{j})$$

$$\vec{a}'_3 = \frac{a}{2}(\hat{i} + \hat{j} - \hat{k})$$

not unique

$$\vec{a}_1 = a\hat{i} = \vec{a}'_2 + \vec{a}'_3$$

$$\vec{a}_2 = a\hat{j} = \vec{a}'_1 + \vec{a}'_3$$

$$\vec{a}_3 = \frac{a}{2}(\hat{i} + \hat{j} + \hat{k}) = \vec{a}'_1 + \vec{a}'_2 + \vec{a}'_3$$

symmetric

③ SC lattice with a basis of 2 atoms

$$\vec{a}_1 = \hat{i}$$

$$\vec{a}_2 = \hat{j}$$

$$\vec{a}_3 = \hat{k}$$

$(0, \frac{a}{2}(\hat{i} + \hat{j} + \hat{k}))$

Crystal = lattice + basis

has it repeats in space

↳ "vectors" used to repeat the basis

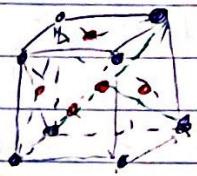
the thing that repeats

↳ points which we will be repeating

③. face centered cubic FCC, CN=12

ABC cube stacking gives FCC lattice

- ↳ A layer
- ↳ B in between
- ↳ C not above A



$$\begin{cases} \vec{a}_1 = \frac{a}{2}(\hat{j} + \hat{k}) \\ \vec{a}_2 = \frac{a}{2}(\hat{k} + \hat{i}) \\ \vec{a}_3 = \frac{a}{2}(\hat{i} + \hat{j}) \end{cases}$$

A
B
C
A
B
C

2 more Bravais lattices

Unit cells

• a "unit cell fills all of space if translated over lattice vectors"

• Primitive unit cells

- ① parallelepiped & a_i 's
- ② Wigner - Seitz → unique



2D: (i) lines to neighbors

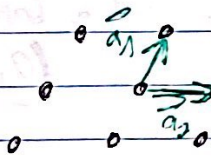


(ii) perpendicular bisectors
(iii) unit cell enclosed

3D: In 3D: same but perpendicular bisectors are planes → unit cell is volume enclosed

Other crystal structures

• diamond lattice = 2 interpenetrating FCC lattices
 *C, Si, Ge, ZnS | - basis $(0, \frac{a}{4}(\hat{i} + \hat{j} + \hat{k}))$
 + FCC vectors as above



$\vec{r} = l_1 \vec{a}_1 + l_2 \vec{a}_2$ = direct lattice

→ 1D freely moving electron in a periodic potential

$\psi(x) = e^{ikx}$, momentum: $p = \hbar k$

$|\psi(x)|^2$ must have periodicity of lattice

↳ also requires $\psi(x)$ periodic in lattice (two different reasons)

→ when is $\psi(x)$ periodic in the lattice? $k = ?$

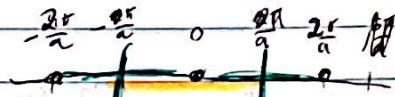
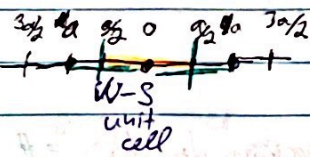
$$\psi(a) = \psi(0) \Rightarrow ka = \frac{2\pi n}{a}, n \in \mathbb{Z}$$

$$\Rightarrow k = \frac{2\pi}{a} n$$

belong to a set of vectors which span a 1D lattice

Direct vs. Reciprocal lattice

(1D)



unit cell of reciprocal lattice

= Brillouin zone

$$\vec{L} = m\vec{a}$$

$$\vec{g} = \frac{2\pi}{a} n = \frac{2\pi}{a} n \vec{a}$$

$$e^{i\vec{g} \cdot \vec{L}} = 1$$

$$\vec{L} = \sum_i n_i \vec{a}_i$$

$$\vec{g} = \sum_j m_j \vec{b}_j$$

(3D)

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = \frac{2\pi}{V} (\vec{a}_2 \times \vec{a}_3)$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = \frac{2\pi}{V} (\vec{a}_3 \times \vec{a}_1)$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = \frac{2\pi}{V} (\vec{a}_1 \times \vec{a}_2)$$

\vec{a} and \vec{b} are orthogonal: $\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$

reciprocal lattice vectors
Volume of parallelepiped = primitive cell

(?) How to represent functions that have periodicity of lattice?

→ Fourier series

$$(1D) \quad f(x) = \sum_n F_n \exp(i \frac{2\pi n x}{a}) = \sum_g F_g e^{i\vec{g} \cdot \vec{r}} \quad | \quad F_g = \frac{1}{a} \int_{\text{unit cell}} f(x) e^{-i\vec{g} \cdot \vec{r}} dx$$

(3D)

$$f(\vec{r}) = \sum_g F_g e^{i\vec{g} \cdot \vec{r}} \quad | \quad F_g = \frac{1}{V_{\text{cell}}} \int_{\text{unit cell}} f(\vec{r}) e^{-i\vec{g} \cdot \vec{r}} dV$$

Prove: $e^{i\vec{g}\cdot\vec{l}} = 1$

$$\vec{g} = n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3$$

$$\vec{l} = l_1 \vec{a}_1 + l_2 \vec{a}_2 + l_3 \vec{a}_3$$

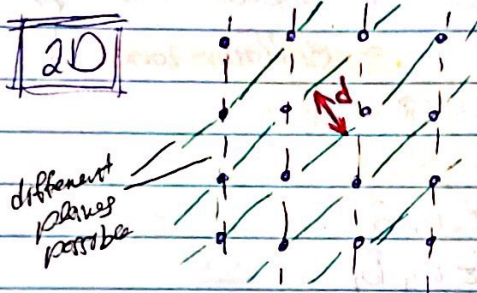
$$\vec{g}\cdot\vec{l} = (n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3) \cdot (l_1 \vec{a}_1 + l_2 \vec{a}_2 + l_3 \vec{a}_3) =$$

$$= 2\pi [n_1 l_1 + n_2 l_2 + n_3 l_3] \Rightarrow e^{i\vec{g}\cdot\vec{l}} = e^{i2\pi N} = 1$$

by $\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$ n, l are integers \Rightarrow integer N

Lattice Planes

packing fraction = amount of volume of "oranges" per total volume (incl. air)



$d \rightarrow$ packing density = # points in plane
distance between plane

if closely spaced planes = $\downarrow d$
 \Rightarrow fewer atoms per area
 \Rightarrow lower packing density

each atom on 1 plane (of a given family)
 \hookrightarrow number of atoms and their spacing are constant but we can draw different lines (with bigger/smaller d)
 \Rightarrow each will then hit different number of atoms.

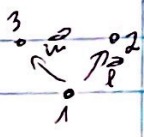
If $\downarrow d \rightarrow$ more lines/planes per unit area
 \rightarrow less atoms on each line/plane
 \Rightarrow low packing density

Features

1. a vector between 2 lattice points is itself a lattice vector $\vec{l} \rightarrow \sum n_i \vec{a}_i$

proof: $\vec{l} = l_1 \vec{a}_1 + l_2 \vec{a}_2 + l_3 \vec{a}_3$
 $\vec{m} = m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3$
 $\vec{m} - \vec{l} = (m_1 - l_1) \vec{a}_1 + (m_2 - l_2) \vec{a}_2 + (m_3 - l_3) \vec{a}_3$
 $\Rightarrow \vec{m} - \vec{l}$ also a lattice vector

2. any ~~direct~~ plane in the direct lattice is normal to some vector of the reciprocal lattice



proof: $\vec{l}: 1 \rightarrow 2$ } s.t. 1, 2, 3 are not on a line: $\vec{l} \parallel \vec{m} \Rightarrow \vec{l} \& \vec{m}$ define a plane
 $\vec{m}: 1 \rightarrow 3$ } $\vec{n} = \vec{l} \times \vec{m} \Rightarrow \vec{n} \perp$ plane (\vec{l}, \vec{m})

$$\vec{l} \times \vec{m} = l_1 m_2 (\vec{a}_1 \times \vec{a}_2) + l_1 m_3 (\vec{a}_1 \times \vec{a}_3) + l_2 m_3 (\vec{a}_2 \times \vec{a}_3) + l_2 m_1 (\vec{a}_2 \times \vec{a}_1) + l_3 m_1 (\vec{a}_3 \times \vec{a}_1) + l_3 m_2 (\vec{a}_3 \times \vec{a}_2)$$

$$= (\vec{a}_1 \times \vec{a}_2) (l_1 m_2) + (\vec{a}_3 \times \vec{a}_1) (l_3 m_1) + (\vec{a}_2 \times \vec{a}_3) (l_2 m_3) + \dots \Rightarrow \vec{l} \cdot \vec{n} \parallel \vec{g}$$

3. Each vector of the reciprocal lattice is normal to a set of lattice planes of the direct lattice.

proof:

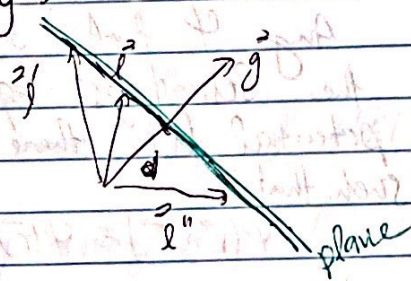
$$\vec{g} = n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3$$

$$\vec{l} = l_1 \vec{a}_1 + l_2 \vec{a}_2 + l_3 \vec{a}_3 \quad \rightarrow N \vec{b}_i$$

$$\vec{g} \cdot \vec{l} = 2\pi (n_1 l_1 + n_2 l_2 + n_3 l_3) = 2\pi N$$

* projector of \vec{l} on \vec{g} : $d = \frac{\vec{l} \cdot \vec{g}}{|\vec{g}|} = \frac{2\pi N}{|\vec{g}|}$

any other vector \vec{l}' that also satisfies $\vec{g} \cdot \vec{l}' = 2\pi X$ will have the same projection \rightarrow we can create a plane



4. consider \vec{g} . if n_1, n_2, n_3 have no common factors, then \vec{g} is the shortest vector pointing in \vec{g} . The family of planes normal to \vec{g} are separated by a distance $d = \frac{2\pi}{|\vec{g}|}$

Miller indices: if $\vec{g} = (n_1, n_2, n_3)$, then plane is written as: $(n_1 \ n_2 \ n_3)$

* $\vec{g} = 4\vec{b}_1 - 2\vec{b}_2 + \vec{b}_3 \Rightarrow$ plane: $(4 \ \bar{2} \ 1)$

ONLY CUBIC LATTICES: $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

distance between planes $\{h, k, l\}$: $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

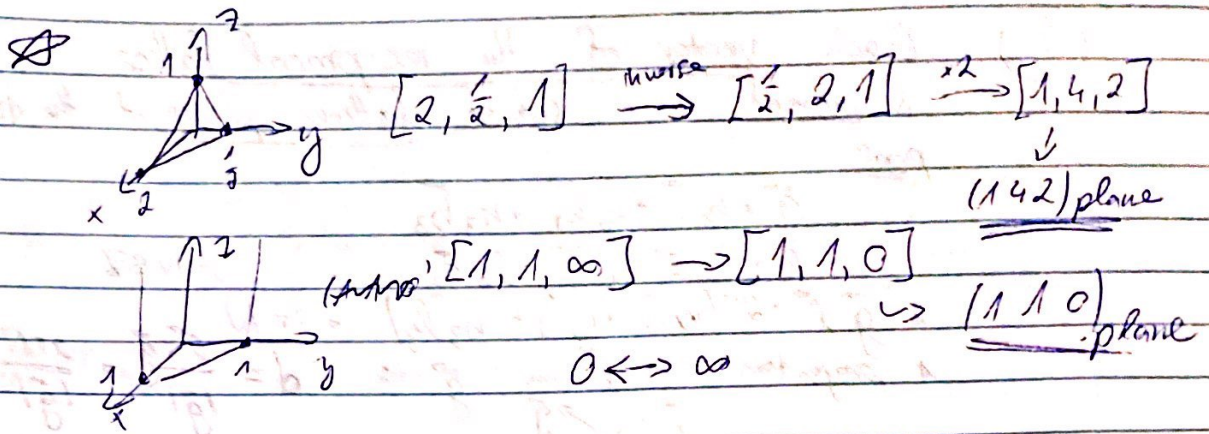
and direction $[h \ k \ l] \perp (h \ k \ l)$ plane

direction (vector)

specific plane

family of planes

$\langle \rangle$ - family of vectors



Bloch functions

Bloch's Thm: Any ψ that satisfies the Schrödinger eq. w/ a periodic potential $V(\vec{r})$, there is a wave vector \vec{k} such that:

$$\psi(\vec{r} + \vec{l}) = \psi(\vec{r}) e^{i\vec{k} \cdot \vec{l}}$$

Alternatively:

define $u_{\vec{k}}(\vec{r}) = e^{-i\vec{k} \cdot \vec{r}} \psi_{\vec{k}}(\vec{r})$

$$u_{\vec{k}}(\vec{r} + \vec{l}) = e^{-i\vec{k} \cdot (\vec{r} + \vec{l})} \psi_{\vec{k}}(\vec{r} + \vec{l}) = e^{-i\vec{k} \cdot \vec{r}} e^{-i\vec{k} \cdot \vec{l}} \psi_{\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{l}} = e^{-i\vec{k} \cdot \vec{r}} \psi_{\vec{k}}(\vec{r})$$

$$\Rightarrow u_{\vec{k}}(\vec{r} + \vec{l}) = \psi_{\vec{k}}(\vec{r}) e^{-i\vec{k} \cdot \vec{l}}$$

$$\Rightarrow \text{if } u_{\vec{k}} \text{ is periodic: } \psi_{\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{\vec{k}}(\vec{r})$$

same lattice-periodic function

wavefunction in periodic potential

plane wave

function with periodicity of the lattice

$$\psi \text{ periodic in lattice} \rightarrow \vec{g}$$

$$\|\psi\|^2 \text{ periodic in lattice} \rightarrow \vec{k}$$

Bloch's Thm: $e^{-i\vec{k} \cdot \vec{r}}$ in Bravais lattice \Rightarrow periodic potential. the solutions to Schröd. eq. = ψ are a plane wave \cdot a periodic function

For free e^- : $\psi(r) = Ae^{i\vec{k}\cdot\vec{r}}$

In crystal: $A \rightarrow u_{\vec{k}}(\vec{r}) = \text{periodic function}$

What is \vec{k} ?

• periodic boundary conditions: Born-van Karman boundary condition
 $\psi(x + Na) = \psi(x)$

atoms in lattice: large
 in overall

\Rightarrow we want: $\psi_k(x + Na) = e^{i\vec{k}\cdot Na} \psi_k(x)$
 $= 1$

$\Rightarrow \vec{k}\cdot Na = 2\pi n$

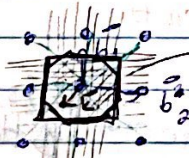
$\Rightarrow \vec{k} = \frac{2\pi}{Na} \vec{n}, n \in \mathbb{Z}$

$\psi_k(x) = A_k \exp(ikx)$

\leadsto normalised: $\int_0^L |\psi|^2 dx = 1 \rightarrow \psi_k = \frac{1}{\sqrt{L}} e^{ikx}$
 with $L = Na$

\leadsto by orthogonality: $\int_0^L \psi_k^* \psi_{k'} dV = \delta_{k,k'}$

2D: $\vec{k} = \frac{n_1}{N_1} \vec{b}_1 + \frac{n_2}{N_2} \vec{b}_2, n_i \in \mathbb{Z}$



Brillouin zone

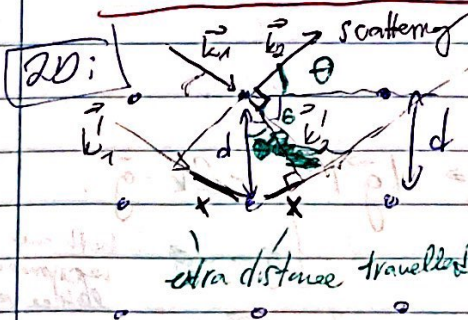
= Wigner-Seitz

unit cell of

reciprocal lattice

(intersection of fine ~~marks~~ lines give possible values for \vec{k})

Electron Diffraction



constructive interference: $2x = n\lambda$

Bragg's law: $2d \sin \theta = n\lambda$

~~$\sin \theta = \frac{x}{d}$~~
 ~~$\sin(\theta - \theta) = \frac{x}{d}$~~
 $\Rightarrow \sin \theta = \frac{x}{d} \Rightarrow x = d \sin \theta$

Scattering $\vec{k} \rightarrow \vec{k}'$

Probability $\propto |I_{\vec{k}, \vec{k}'}|^2$

$$\rightarrow I_{\vec{k}, \vec{k}'} = \int \Psi_{\vec{k}'}^*(\vec{r}) V(\vec{r}) \Psi_{\vec{k}}(\vec{r}) d^3r$$

transition
integral

Coulomb potential: $V(\vec{r}) = \sum_{\vec{g}} V_{\vec{g}} e^{i\vec{g} \cdot \vec{r}} = \text{FS}$

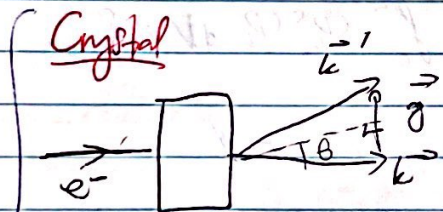
$$\Psi_{\vec{k}} = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}} \rightarrow I_{\vec{k}, \vec{k}'} = \sum_{\vec{g}} V_{\vec{g}} \int \frac{1}{V} e^{i(\vec{k}' + \vec{g} - \vec{k}) \cdot \vec{r}} d^3r$$

$$= \sum_{\vec{g}} V_{\vec{g}} \int \Psi_{\vec{k}'}^* \Psi_{\vec{k} + \vec{g}} d^3r$$

applying orthogonality

$$\Rightarrow I_{\vec{k}, \vec{k}'} = \begin{cases} V_{\vec{g}} & \vec{k}' = \vec{k} + \vec{g} \\ 0 & \text{otherwise} \end{cases}$$

Equivalence
between
Bragg's law
and
PM description
above



for elastic scattering

$$|\vec{k}| = |\vec{k}'|$$

$$|\vec{g}| = 2|\vec{k}| \sin \theta$$

$$= \frac{2\pi}{\lambda}$$

reciprocal
lattice
vector

$$d = \frac{2\pi}{|\vec{g}|} N$$

distance between
2 consecutive planes
between plane 1 and N

$$|\vec{g}| = \frac{2\pi}{d} N = 2|\vec{k}| \sin \theta = \frac{2\pi}{\lambda} \sin \theta$$

$$N\lambda = 2d \sin \theta$$

$$\vec{k}' = \vec{k} + \vec{g}$$

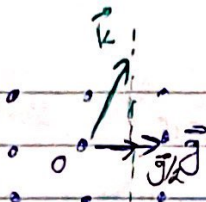
$$|\vec{k}'|^2 = |\vec{k} + \vec{g}|^2 = |\vec{k}|^2 + 2\vec{k} \cdot \vec{g} + |\vec{g}|^2 \Rightarrow |\vec{g}|^2 = -2\vec{k} \cdot \vec{g}$$

$\vec{g} \rightarrow -\vec{g}$ = both are
reciprocal
lattice vectors

$$\Rightarrow |\vec{g}|^2 = 2\vec{k} \cdot \vec{g}$$

$$\left(\frac{|\vec{g}|}{2}\right)^2 = \vec{k} \cdot \frac{\vec{g}}{2}$$

Bragg's law in 3D



projection of \vec{k} onto \vec{g} : $\frac{\vec{k} \cdot \vec{g}}{|\vec{g}|}$

⇒ scattering $\vec{k} \rightarrow \vec{k}'$ if \vec{k} sits on a plane $\perp \frac{\vec{g}}{2}$ = on boundary of the Brillouin zone

$\psi = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}}$

• free e^- : $E = \frac{\hbar^2 k^2}{2m}$

→ $|\vec{k}| <$ Brillouin zone

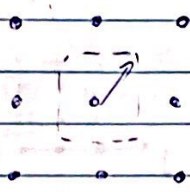
• nearly free e^- model: for small $|\vec{k}|$

→ $m \rightarrow m^*$ effective mass:

$E = \frac{\hbar^2 k^2}{2m^*}$

$\frac{m^*}{m} = 0.1 - 10$
 $m = 9.1 \cdot 10^{-31} \text{ kg}$

change in curvature of parabola

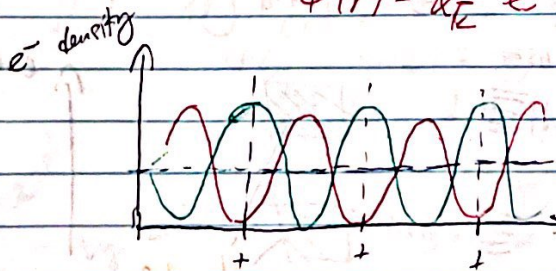


• doesn't hold for $k \rightarrow$ BZ edge

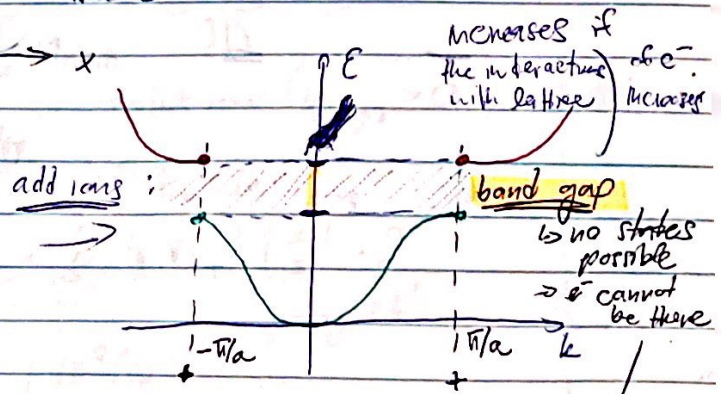
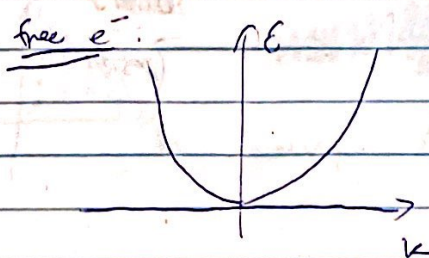
because scattering occurs: $\vec{k}' \rightarrow \vec{k} + \vec{g}$

↳ close to the edge of BZ:

→ standing wave $\psi(\vec{r}) = \int_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} + \int_{\vec{k} + \vec{g}} e^{i(\vec{k} + \vec{g}) \cdot \vec{r}}$



- two solutions: max on ions ($\downarrow E$)
 for e^- min on ions ($\uparrow E$)



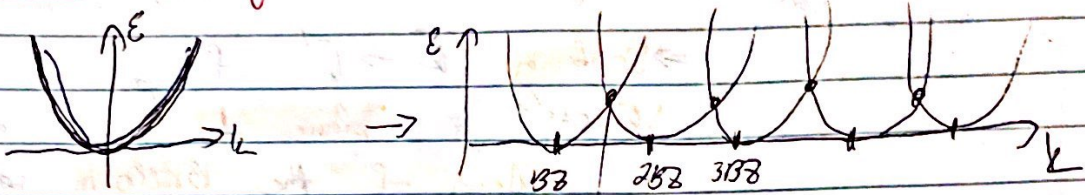
increases if the interaction with lattice increases

↳ no states possible
 → e^- cannot be there

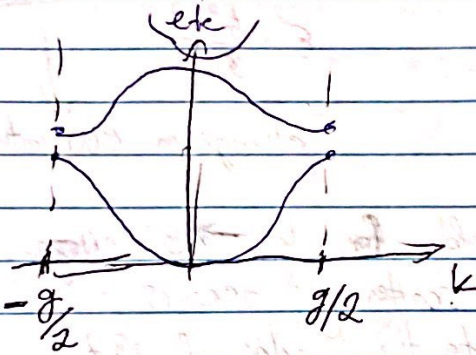
weaker → disappearance for imperfect crystals (periodicity)

just because of periodicity of lattice, there are band gaps for allowed energies for e^-

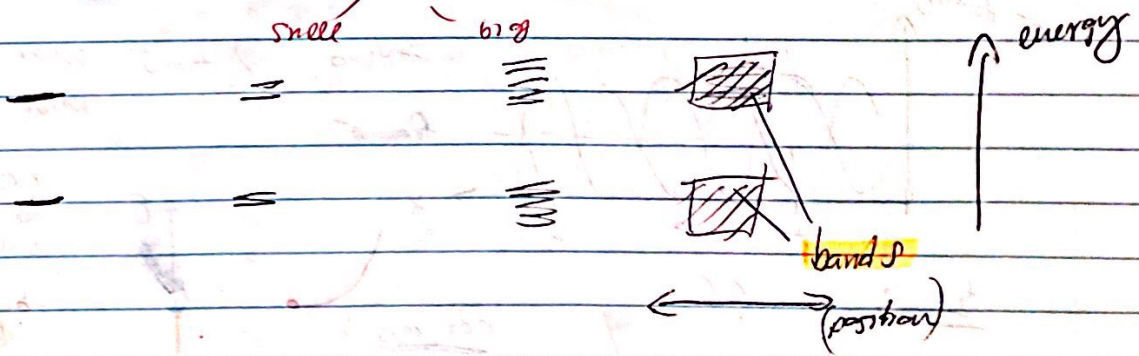
* Zone Folding - multiple Brillouin zone



incl. interaction → lifts degeneracy



Atoms → Molecules → Solid



Free electrons in metal model

method (I) • if free $E = \frac{\hbar^2 k^2}{2m}$

• density of e^- $n = \frac{N_e}{V}$ ^{#e} _{- volume}

• periodicity - simple cube: $\psi(0) = \psi(La) \Rightarrow k_x = \frac{2\pi}{Na}$

(1D) \Rightarrow only 1 unique k-value per: $\frac{2\pi}{Na} = \frac{2\pi}{L}$

(3D) $k^2 = k_x^2 + k_y^2 + k_z^2 \Rightarrow 1k$ per $\left(\frac{2\pi}{L}\right)^3$

temp.

$T=0$ in grand state: max $k = k_F$ - Fermi

$$N_e = \frac{4}{3} \pi k_F^3 \left(\frac{L}{2\pi}\right)^3 \cdot 2$$

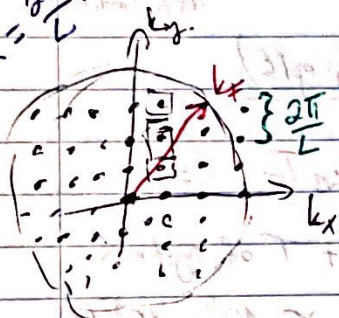
value of sphere $\left(\frac{L}{2\pi}\right)^3$ $\cdot 2$ - spin
divisor by space occupied by each k

$$\Rightarrow N_e = 2 \cdot \frac{4}{3} \pi k_F^3 \left(\frac{L}{2\pi}\right)^3$$

$$N_e = \frac{2^3}{3} \frac{k_F^3 L^3}{2^3 \pi^3}$$

$$\Rightarrow k_F = \left(\frac{3\pi^2 N_e}{V}\right)^{1/3}$$

$$k = \frac{2\pi}{L} n, m, p$$



method (II)

1D crystal of length L

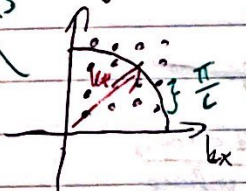
$$\psi(0) = \psi(L) = 0$$

$$\psi(x) = A \sin(k_x x) \sin(k_y y) \sin(k_z z)$$

closer spaced dots

by allowed k: $k_{x,y,z} = \frac{\pi}{L} n_{x,y,z}$ 3D

but now $(n_{x,y,z} > 0)$ in 1/8



~~scribble~~

only 1/8 of the cube

$$\text{now, } N_e = \left(\frac{1}{8}\right) \frac{4}{3} \pi k_F^3 \left(\frac{L}{\pi}\right)^3 \cdot 2$$

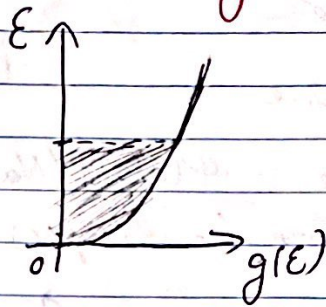
1/8 of k^3 $\cdot 2$ spin

$$\Rightarrow k_F = \left(\frac{3\pi^2 N_e}{V}\right)^{1/3}$$

- Fermi energy: $E_F(k=k_F) = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N_e}{V}\right)^{2/3}$ at 0 temperature

density of states: $g(\epsilon), D(\epsilon) = \frac{\partial N}{\partial \epsilon}$

$\Rightarrow g(\epsilon) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\epsilon}$ for 3D
 $g(\epsilon) \propto \sqrt{\epsilon}$



for $T \neq 0$: $n(\epsilon)d\epsilon = g(\epsilon) f(\epsilon, E_F)$

#e⁻ in $[\epsilon, \epsilon+d\epsilon]$ | density of states | Fermi-Dirac distribution

$\Rightarrow E_F$ follows from #e⁻, T, $g(\epsilon)$

\Rightarrow we can find Fermi temperature $k_B T_F = E_F$

Kenn. Fermi temp.

hot T of system

FD \approx Boltzmann for high T $T_F \sim 10^4 - 10^5$ K

FD \approx step-like: $T \lesssim 0.1 T_F$

work function $\approx |E_F|$ \downarrow ϕ work function
 \hookrightarrow measurable with Kelvin probe E_F

\otimes Na: monovalent $\Rightarrow 1e^-/atom$

$\rho = 0.971 \text{ g/cm}^3$

$M = \text{atomic weight} = 23 \text{ amu}$

$n = \frac{N}{V} = ? = n_c (= \text{valency}) \cdot \frac{\# \text{ atoms}}{\text{volume}}$

$= n_c \frac{\rho}{\text{molar weight}} N_A$

$= n_c \frac{\rho}{M} N_A$

$E_F = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V}\right)^{2/3} = 2.54 \cdot 10^{22} \text{ eV/cm}^3$

$= 3.2 \text{ eV} \rightarrow$ theoreticaly 2.3 eV

$\Rightarrow T_F = 37 \text{ K}$

Electric Field → current

force acting on e^- : $F = -qE = m \frac{dv}{dt} = \frac{dp}{dt} = \hbar \frac{dk}{dt}$

charge, el. field \uparrow $\frac{p}{\hbar} = k$ (wave vector)

avg time τ between scatterings (collisions) = scattering time

$\Rightarrow \Delta k = -\frac{qE}{\hbar} \tau \Rightarrow \Delta p = -qE\tau$

current density: $J = nqv = n \frac{qE\tau}{m\tau}$

conductivity σ : $J = \sigma E \Rightarrow \sigma = \frac{nq^2\tau}{m}$ [σ] = S/m

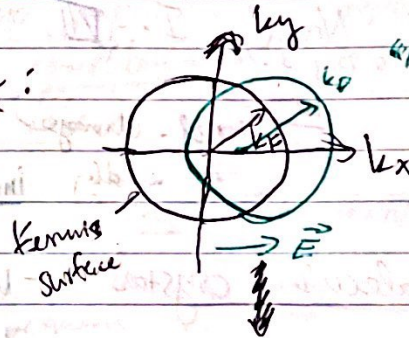
resistivity $\rho = \sigma^{-1}$

Siemens = $\frac{1}{\Omega} = \text{mho}$

mobility $\mu = \frac{q\tau}{m}$ [m^2/Vs]

effective mass

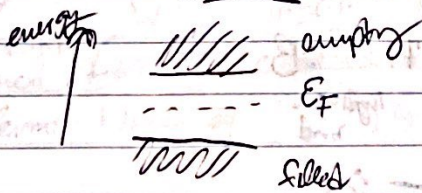
Fermi Sphere:



upon applying field \rightarrow same radius but shifted origin of Fermi surface

given that there exist such states \uparrow there don't for insulators (or semicond.)

for insulator:



e^- cannot move here because there are no states around E_f

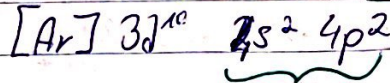
Types of Bonds

- 5 types: covalent, ionic, molecular, hydrogen, metallic

covalent

* Ge : semiconductor
diamond lattice

↳ bonds with 4 neighbours - IV type semiconductor



sp³ hybridization

x = 1.8, 2.2

increase in
el. neg.
difference ↓

* GaAs : semiconductor III - V.

* ZnS II - VI.

* NaCl I - VII.

x = 0.93 | 3.16

ionic

↳ el. charge on one of the atoms (localised)

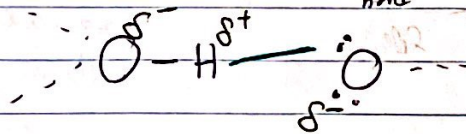
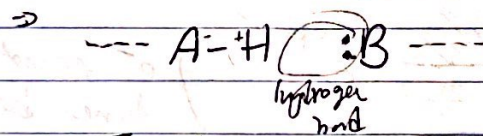
⇒ mostly insulators (solid)

molecular crystals - Van der Waals interaction

* CO₂ crystals

hydrogen bonding

• A, B atoms ∈ {N, O, F} - high el. neg.



metallic

• valence e⁻ nearly free gas

→ charge is very delocalised

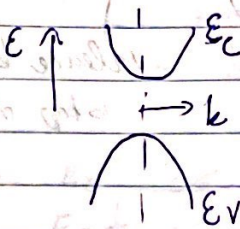
→ conductors

Semiconductors

band gaps \rightarrow inner e^- - weakly perturbed \rightarrow core states
 states that are significantly perturbed yet remain localized = valence states
 states that are completely delocalised = conducting state

$\approx 0.5 - 3 \text{ eV}$
 $\rightarrow 25 \mu\text{m}$ (microwaves) $\rightarrow 400 \text{ nm}$ (visible)

$k_B T \sim 25 \text{ meV}$ at room temp \Rightarrow very few excited (1)



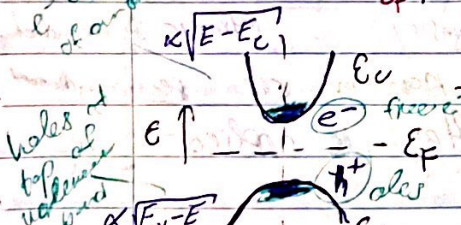
① Intrinsic semiconductors * Si - quite cheap

no defects, no impurities, no doping

$n = p$ in equilibrium

e^- / Volume = # holes = n^+ / Volume

E_F Fermi level is near the middle of the gap



states between E_1 and E_2 :

$$g(E) dE = \frac{4\pi V}{h^3} (2m_c)^{3/2} \sqrt{E - E_c} dE$$

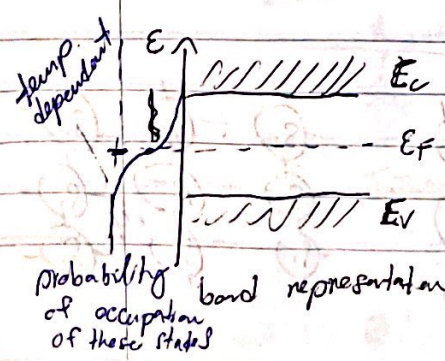
energy density of allowed states for electrons in conduction band

eff. mass associated with the conduction band

Fermi-Dirac eq. : $f(E, E_F) = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1}$

density of e^- : $n(E) dE = \frac{f(E, E_F) g(E) dE}{V}$ per volume

$$\Rightarrow n(E) dE = \frac{4\pi}{h^3} (2m_c)^{3/2} \frac{\sqrt{E - E_c}}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1} dE$$



$E_F : f(E, E_F) = \frac{1}{2}$ but not in the middle between E_c & E_v (see next page)

$$n = N_c \exp\left[-\frac{E_c - E_F}{k_B T}\right]$$

per volume and energy
 $g(E) [J^{-1} m^{-3}]$
 $\propto \frac{46}{eV, cm^{-3}}$

effective density of states $[m^{-3}]$ - per volume

effective density of states

$$N_c = 2 \left(\frac{2\pi m_e k_B T}{h^2} \right)^{3/2}$$

If $m_c = m_e$, then $N_c = 2.5 \cdot 10^{25} \text{ m}^{-3}$ at room temp.

for holes: $1 - f(E, E_F) = 1 - \frac{1}{\exp(\frac{E - E_F}{k_B T}) + 1}$

density of states: $g(E) dE = \frac{4\pi V}{h^3} (2m_v)^{3/2} \sqrt{E_v - E} dE$

$$p = \frac{N_v}{V} \exp\left[-\frac{E_F - E_v}{k_B T}\right]$$

effective density of states

$$N_v = 2 \left(\frac{2\pi m_v k_B T}{h^2} \right)^{3/2}$$

N_v
more common
book uses

eff. mass
valence band max
↳ top of parabola

band gap energy

$$n \cdot p = N_c N_v \exp\left[-\frac{E_c - E_v}{k_B T}\right] = N_c N_v \exp\left(-\frac{E_g}{k_B T}\right) = n_i^2 = p_i^2$$

- ↳ Law of mass action: $np = n_i^2$
- ↳ holds in equilibrium (also non-intrinsic) generally but $n \neq p$ for non-intrinsic semiconductors
- ↳ does not hold when e.g. voltage is applied
→ no longer equilibrium
- ↳ however still holds when doped

② Extrinsic semiconductors

$\cdot 10^{-10}$ electrons in conducting band

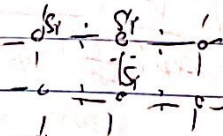
→ not very conducting

Band model for Si: bands with 4 neighbours

extra valence e^-

Doping

replace Si with P or B



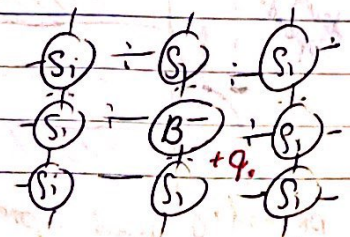
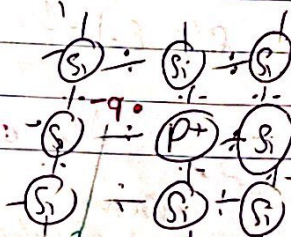
because has 4e⁻ in outer shell

intrinsic

more e⁻ & h⁺

→ increases conductivity

n-type:



extra valence e⁻

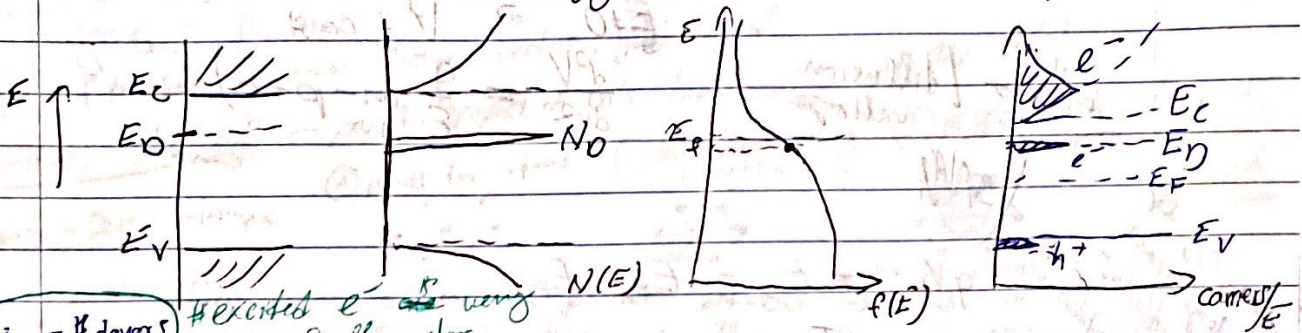
Ionisation potential of P: 10.5eV but P embedded in semiconductor \rightarrow binding energy dramatically lowered

- P in Si \rightarrow n-doping \rightarrow donor, extra valence e
- B in Si \rightarrow p-doping \rightarrow acceptor, creates hole in valence band

misspelling diagrams!

Ionisation E of H: $E = \frac{mg^4}{8\epsilon_0 h^2} = 13.6eV$

but in Si: $E = M \cdot E_0$, $\frac{m^*}{m} = 0.2$
 \Rightarrow ionisation energy of donor: $E_D \approx E \frac{m^*}{m} \approx 0.02eV$



#e- here = #donors

#excited e- using small number

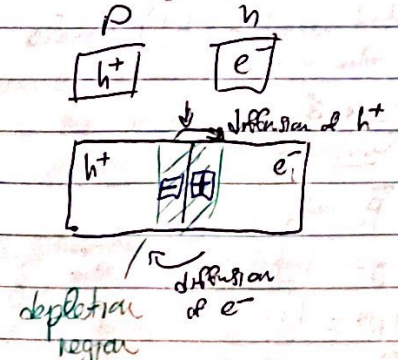
100% efficiency at doping

n-type Si
 $n \gg p$: $np = n_i^2$
 $n \approx N_D$ (300K)
 "# donors"
 $n = 1 \times 10^{20} \text{ cm}^{-3}$
 $p = \frac{n_i^2}{n} = 2.25 \times 10^4 \text{ cm}^{-3}$
 $E_C - E_F = 0.04eV$

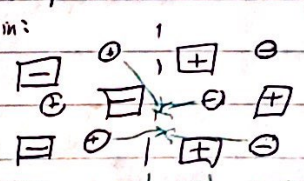
p-type Si
 $n \ll p$, $np = n_i^2$
 $p \approx N_A$ (300K)
 "# acceptor"
 $p = 1 \times 10^{17} \text{ cm}^{-3}$
 $n = \frac{n_i^2}{p} = 2.25 \times 10^4 \text{ cm}^{-3}$
 $E_F - E_V = 0.14eV$

$p = N_A \exp\left(\frac{E_V - E_F}{k_B T}\right)$

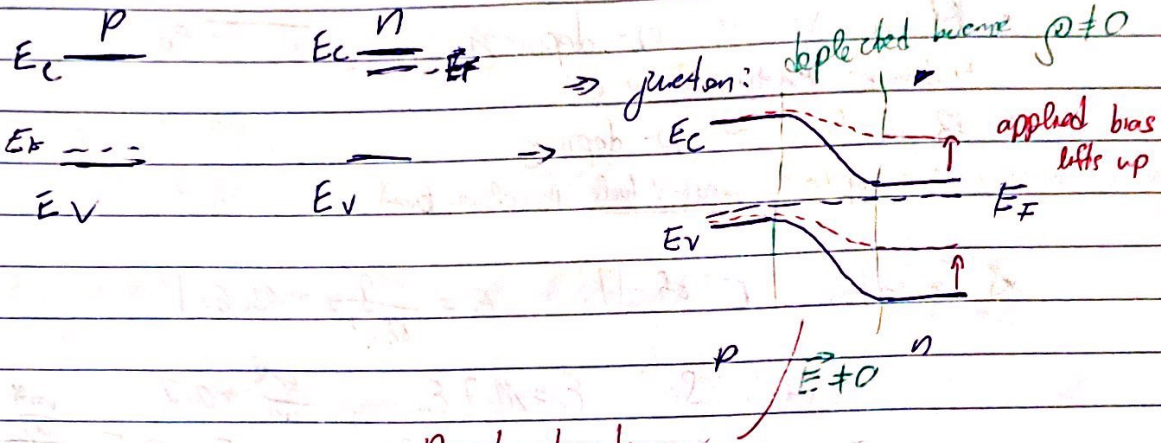
PN-junction - rectifiers, LEDs, transistors, etc.



- N_D, N_A also there but cannot move
 so an in:



is no free h+ and e- but N_A, N_D are present \rightarrow voltage difference \rightarrow drift \rightarrow equal diffusion
 meet and recombine \Rightarrow no free e- and h+ anymore



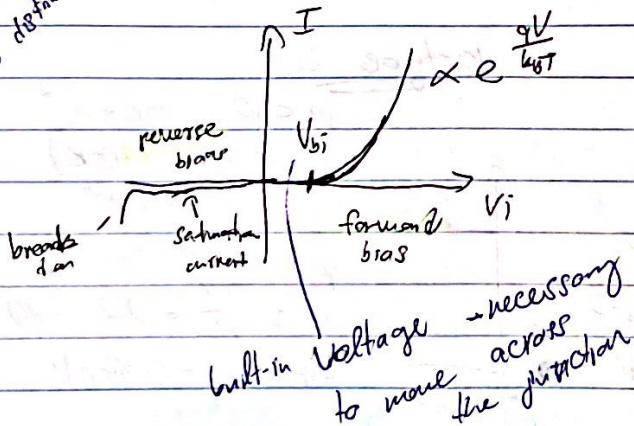
Band-bending

$E \neq 0 \Rightarrow V \neq \text{const.}$
 $\frac{d^2V}{dx^2} = \frac{q}{\epsilon} (n - p + c)$ missing carrier

built-in voltage / diffusion voltage
 qV_{bi}

all energy for non-degenerate semiconductor
 $\rightarrow F0 \sim MB$ distribution

$qV_{bi} = E_g - E_{Fn} - E_{Fp}$



$qV_{bi} = k_B T \ln\left(\frac{N_A N_D}{n_i^2}\right)$