Hydrogen-molecule : 1-electron theory

Direct Exchange   [see also Ashcroft & Mermin ch.32]

* 2 sites : a and b
* basis functions : s-like orbitals $|a\rangle$, $|b\rangle$
* $\langle a|a\rangle = 1$, $\langle b|b\rangle = 1$, $\langle a|b\rangle = 0$, $\langle b|a\rangle = 0$
* $\langle a|H|a\rangle = E_0$, $\langle b|H|b\rangle = E_0$: on-site energy.
* $\langle a|H|b\rangle = t$, $\langle b|H|a\rangle = t$: hopping integral ($t<0$)

$$H\varphi = E\varphi \quad : \quad H = \begin{bmatrix} E_0 & t \\ t & E_0 \end{bmatrix}, \quad \varphi = \alpha a + \beta b, \quad \alpha^2 + \beta^2 = 1$$

$$\varphi_+ = \frac{a+b}{\sqrt{2}} \qquad E_+ = -|t| \quad (t<0) \quad : \text{ lowest state}$$

$$\varphi_- = \frac{a-b}{\sqrt{2}} \qquad E_- = +|t|$$

Remark: $a, b, \varphi_+, \varphi_-$ are all 1-electron orbitals.

The hydrogen molecule contains 2 electrons.
In the 1-electron theory, one takes the calculated
1-electron orbitals and fill these with 2 electrons.
The ground state will then be 2 electrons residing
both in the φ_+ orbitals, one with spin up ($\uparrow$) and
one with spin-down ($\downarrow$). The ground state will be
a singlet :

$$\psi_s = \varphi_+\uparrow\, \varphi_+\downarrow = \frac{1}{\sqrt{2}} \begin{vmatrix} \frac{a(1)+b(1)}{\sqrt{2}}\,\uparrow(1) & \frac{a(2)+b(2)}{\sqrt{2}}\,\uparrow(2) \\[2mm] \frac{a(1)+b(1)}{\sqrt{2}}\,\downarrow(1) & \frac{a(2)+b(2)}{\sqrt{2}}\,\downarrow(2) \end{vmatrix}$$

$$= \frac{a(1)+b(1)}{\sqrt{2}} \cdot \frac{a(2)+b(2)}{\sqrt{2}} \cdot \frac{\uparrow(1)\downarrow(2)-\downarrow(1)\uparrow(2)}{\sqrt{2}}$$

$$= \left\{ \frac{a(1)\,a(2)}{2} + \frac{a(1)\,b(2)}{2} + \frac{b(1)\,a(2)}{2} + \frac{b(1)\,b(2)}{2} \right\} \cdot \frac{\uparrow(1)\downarrow(2)-\downarrow(1)\uparrow(2)}{\sqrt{2}}$$

The probability to find 2 electrons on site a is:

$$|\langle a(1) a(2) | \psi_s \rangle|^2 = |\tfrac{1}{2}|^2 = \tfrac{1}{4}$$

The probability to find 2 electrons on site b is:

$$|\langle b(1) b(2) | \psi_s \rangle|^2 = |\tfrac{1}{2}|^2 = \tfrac{1}{4}$$

The probability to find 1 electron on a and 1 on b is:

$$|\langle a(1) b(2) | \psi_s \rangle|^2 + |\langle b(1) a(2) | \psi_s \rangle|^2 = |\tfrac{1}{2}|^2 + |\tfrac{1}{2}|^2 = \tfrac{1}{2}.$$

The first excited state will have one electron in the ψ_+ orbital and one in the ψ_- orbital. This can be a triplet or a singlet. Let us consider the triplet: $\uparrow\uparrow$ (or $\downarrow\downarrow$).

$$\psi_t = \psi_+\uparrow \, \psi_-\uparrow = \frac{1}{\sqrt{2}} \begin{vmatrix} \frac{a(1)+b(1)}{\sqrt{2}}\uparrow(1) & \frac{a(2)+b(2)}{\sqrt{2}}\uparrow(2) \\[2mm] \frac{a(1)-b(1)}{\sqrt{2}}\uparrow(1) & \frac{a(2)-b(2)}{\sqrt{2}}\uparrow(2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} \left\{ \frac{a(1)+b(1)}{\sqrt{2}} \cdot \frac{a(2)-b(2)}{\sqrt{2}} - \frac{a(1)-b(1)}{\sqrt{2}} \cdot \frac{a(2)+b(2)}{\sqrt{2}} \right\} \uparrow(1)\uparrow(2)$$

$$= \frac{1}{\sqrt{2}} \left\{ \frac{-a(1)b(2)+b(1)a(2) - a(1)b(2)+b(1)a(2)}{\sqrt{2}\cdot\sqrt{2}} \right\} \uparrow(1)\uparrow(2)$$

$$= \frac{b(1)a(2)-a(1)b(2)}{\sqrt{2}} \cdot \uparrow(1)\uparrow(2) \quad \text{(and } \downarrow\downarrow \text{ equivalently)}$$

The probability to find 2 electrons on site a is zero
The probability to find 2 electrons on site b is zero
The probability to find 1 electron on a and 1 on b is 100%.

Remark: the state $\psi_+\uparrow \psi_-\downarrow$ or $\psi_+\downarrow \psi_-\uparrow$ is
partly a singlet and partly a triplet.
Within the 1-electron Theory these two
are indistinguishable! $m_s=0$ belongs to $S=0$ and $S=1$

The highest excited state will have the 2 electrons residing in the φ_- orbital: one with spin↑ and one with spin↓. Let us label this singlet state as ψ_s^*.

$$\psi_s^* = \varphi_-\uparrow \, \varphi_-\downarrow = \frac{1}{\sqrt{2}} \begin{vmatrix} \frac{a(1)-b(1)}{\sqrt{2}}\uparrow(1) & \frac{a(2)-b(2)}{\sqrt{2}}\uparrow(2) \\[2mm] \frac{a(1)-b(1)}{\sqrt{2}}\downarrow(1) & \frac{a(2)-b(2)}{\sqrt{2}}\downarrow(2) \end{vmatrix}$$

$$= \left\{ \frac{a(1)a(2)}{2} - \frac{a(1)b(2)}{2} - \frac{b(1)a(2)}{2} + \frac{b(1)b(2)}{2} \right\} \cdot \frac{\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)}{\sqrt{2}}$$

The probability to find 2 electrons on site a = ¼
The probability to find 2 electrons on site b = ¼
The probability to find 1 electron on a and 1 on b = ½.

Remark: $\psi_s = \varphi_+\uparrow \, \varphi_+\downarrow$, $\psi_t = \varphi_+\uparrow \, \varphi_-\uparrow$ or $\varphi_+\downarrow \, \varphi_-\downarrow$
and $\psi_s^* = \varphi_-\uparrow \, \varphi_-\uparrow$ are all single slater-determinant wavefunctions!
in other words: they are all one-electron theory wavefunctions! (we have constructed them as such).

How about the energies ?

→ We have to evaluate $\langle \psi_s | H | \psi_s \rangle$, $\langle \psi_t | H | \psi_t \rangle$ and $\langle \psi_s^* | H | \psi_s^* \rangle$.

→ from the one-electron wavefunctions φ_+ and φ_- with eigen energies $E_+ = E_0 - |t|$ and $E_- = E_0 + |t|$, respectively, we get: $E(\psi_s) = E(\varphi_+ \varphi_+) = 2E_+ = 2E_0 - 2|t| \quad (t<0)$

$\qquad E(\psi_t) = E(\varphi_+ \varphi_-) = E_+ + E_- = 2E_0$

$\qquad E(\psi_s^*) = E(\varphi_- \varphi_-) = 2E_- = 2E_0 + 2|t| \quad (t<0)$

Within this 1-electron theory, the hydrogen molecule will have 3 possible energies :

$\quad 2E_0 - 2|t| \quad$ (1 state, the lowest singlet, $t<0$)

$\quad 2E_0 \qquad$ (4 states, the triplet plus one singlet)

$\quad 2E_0 + 2|t| \quad$ (1 state, the highest singlet, $t<0$)

The singlet-triplet splitting is: $E(\psi_t) - E(\psi_s) = +2|t|$
This is a usefull quantity to describe the low energy excitations of the system :

$$H^{spin} = -J \cdot S_1 \cdot S_2 \quad \text{with} \quad J = -2|t| \quad (t<0 \implies -J>0)$$

$\quad \rightarrow$ "anti-parallel" spin alignment (singlet)
$\qquad$ is favoured.

Remark: alternatively, one may wish to evaluate
$\langle \psi_s | H | \psi_s \rangle$, $\langle \psi_t | H | \psi_t \rangle$ or $\langle \psi_s^* | H | \psi_s^* \rangle$ using
$\psi_s = \frac{1}{2} \{ a(1)a(2) + a(1)b(2) + b(1)a(2) + b(1)b(2) \} \frac{\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)}{\sqrt{2}}$
and $\psi_t = \cdots$, $\psi_s^* = \cdots$

This means that we have to evaluate terms like
$\langle a(1)a(2) | H | a(1)a(2) \rangle$, $\langle a(1)a(2) | H | a(1)b(2) \rangle$,
$\langle a(1)a(2) | H | b(1)a(2) \rangle$, $\langle a(1)a(2) | H | b(1)b(2) \rangle$,
and 12 more other terms (16 terms in total).

Here we have to be accurate in how to "label" H.
$H = H(1) + H(2)$ with: $H(1)$ working only on electron 1
and $H(2)$ working only on electron 2

$H(1)$: $\langle a(1) | H(1) | a(1) \rangle = E_0$ $\quad$ $\langle b(1) | H(1) | b(1) \rangle = E_0$
$\quad\quad$ $\langle a(1) | H(1) | b(1) \rangle = t$ $\quad$ $\langle b(1) | H(1) | a(1) \rangle = t$

$H(2)$: $\langle a(2) | H(2) | a(2) \rangle = E_0$ $\quad$ $\langle b(2) | H | b(2) \rangle = E_0$
$\quad\quad$ $\langle a(2) | H(2) | b(2) \rangle = t$ $\quad$ $\langle b(2) | H | a(2) \rangle = t$

Thus: $\langle a(1)a(2) | H | a(1)a(2) \rangle = \langle a(1)a(2) | H(1) + H(2) | a(1)a(2) \rangle =$
$\langle a(1)a(2) | H(1) | a(1)a(2) \rangle + \langle a(1)a(2) | H(2) | a(1)a(2) \rangle =$
$\langle a(1) | H(1) | a(1) \rangle \langle a(2) | a(2) \rangle + \langle a(1) | a(1) \rangle \langle a(2) | H(2) | a(2) \rangle =$
$E_0 \cdot 1 + 1 \cdot E_0 = 2E_0$

$\langle a(1)a(2) | H | a(1)b(2) \rangle = \langle a(1)a(2) | H(1) + H(2) | a(1)b(2) \rangle =$
$\langle a(1)a(2) | H(1) | a(1)b(2) \rangle + \langle a(1)a(2) | H(2) | a(1)b(2) \rangle =$
$\langle a(1) | H | a(1) \rangle \langle a(2) | b(2) \rangle + \langle a(1) | a(1) \rangle \langle a(2) | H(2) | b(2) \rangle =$
$E_0 \cdot 0 + 1 \cdot t = t$

$\langle a(1)a(2) | H | b(1)a(2) \rangle = \cdots = t$

$$\langle a(1)a(2)|H|b(1)b(2)\rangle = \langle a(1)a(2)|H(1)+H(2)|b(1)b(2)\rangle =$$

$$\langle a(1)a(2)|H(1)|b(1)b(2)\rangle + \langle a(1)a(2)|H(2)|b(1)b(2)\rangle =$$

$$\langle a(1)|H(1)|b(1)\rangle \langle a(2)|b(2)\rangle + \langle a(1)|b(1)\rangle \langle a(2)|H|b(2)\rangle =$$

$$t \cdot 0 + 0 \cdot t = 0$$

$$\langle a(1)b(2)|H|b(1)a(2)\rangle = \langle a(1)b(2)|H(1)+H(2)|b(1)a(2)\rangle =$$

$$\langle a(1)b(2)|H(1)|b(1)a(2)\rangle + \langle a(1)b(2)|H(2)|b(1)a(2)\rangle =$$

$$\langle a(1)|H(1)|b(1)\rangle \langle b(2)|a(2)\rangle + \langle a(1)|b(1)\rangle \langle b(2)|H(2)|a(2)\rangle =$$

$$t \cdot 0 + 0 \cdot t = 0.$$

etc

So one must realize here that $H = H(1) + H(2)$ can only couple states which have the same orbitals or differ only in 1 orbital. In other words, this Hamiltonian can only transfer at most <u>one</u> electron at a time (and not two).

Show that
$$\langle \psi_s|H|\psi_s\rangle = 2E_0 - 2|t| \quad (t<0) \quad (16 \text{ terms})$$
$$\langle \psi_t|H|\psi_t\rangle = 2E_0 \quad\quad\quad\quad (4 \text{ terms})$$
$$\langle \psi_s^*|H|\psi_s^*\rangle = 2E_0 + 2|t| \quad (t<0) \quad (16 \text{ terms})$$

Hydrogen-molecule: Hubbard Model 1

Direct Exchange [see also Ashcroft & Mermin, ch. 32, 33]

* 2 sites; s-like orbitals a, b ; spin $\uparrow, \downarrow$; 2 electrons.
* hopping integral $t \equiv \langle a|H|b \rangle$ $\langle a|b \rangle = \langle b|a \rangle = 0$
* on-site energy $E_0 \equiv \langle a|H|a \rangle = \langle b|H|b \rangle$ $\langle a|a \rangle = \langle b|b \rangle = 1$
* Coulomb energy U for doubly occupied sites:

$$U = \langle a\uparrow a\downarrow |H| a\uparrow a\downarrow \rangle = \langle b\uparrow b\downarrow |H| b\uparrow b\downarrow \rangle \text{ ; 2 electron operator}$$

Basis set:

$\uparrow \quad \uparrow$: $a\uparrow b\uparrow = \frac{1}{\sqrt{2}} \begin{vmatrix} a(1)\uparrow(1) & a(2)\uparrow(2) \\ b(1)\uparrow(1) & b(2)\uparrow(2) \end{vmatrix} = \left\{ \dfrac{a(1)b(2) - a(2)b(1)}{\sqrt{2}} \right\} \uparrow(1)\uparrow(2)$

$\downarrow \quad \downarrow$: $a\downarrow b\downarrow = \qquad\qquad\qquad\qquad = \left\{ \dfrac{a(1)b(2) - a(2)b(1)}{\sqrt{2}} \right\} \uparrow(1)\uparrow(2)$

$\uparrow \quad \downarrow$: $a\uparrow b\downarrow = \frac{1}{\sqrt{2}} \begin{vmatrix} a(1)\uparrow(1) & a(2)\uparrow(2) \\ b(1)\downarrow(1) & b(2)\downarrow(2) \end{vmatrix} = \dfrac{a(1)b(2)\uparrow(1)\downarrow(2) - a(2)b(1)\downarrow(1)\uparrow(2)}{\sqrt{2}}$

$\downarrow \quad \uparrow$: $a\downarrow b\uparrow = \qquad\qquad\qquad = \dfrac{a(1)b(2)\downarrow(1)\uparrow(2) - a(2)b(1)\uparrow(1)\downarrow(2)}{\sqrt{2}}$

$\uparrow\downarrow \quad -$: $a\uparrow a\downarrow = \frac{1}{\sqrt{2}} \begin{vmatrix} a(1)\uparrow(1) & a(2)\uparrow(2) \\ a(1)\downarrow(1) & a(2)\downarrow(2) \end{vmatrix} = a(1)a(2)\left\{ \dfrac{\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)}{\sqrt{2}} \right\}$

$- \quad \uparrow\downarrow$: $b\uparrow b\downarrow = \qquad\qquad\qquad = b(1)b(2)\left\{ \dfrac{\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)}{\sqrt{2}} \right\}$

Hamiltonian:

	$a\uparrow b\uparrow$	$a\downarrow b\downarrow$	$a\uparrow b\downarrow$	$a\downarrow b\uparrow$	$a\uparrow a\downarrow$	$b\uparrow b\downarrow$
$a\uparrow b\uparrow$	$2E_0$					
$a\downarrow b\downarrow$	$\bullet$	$2E_0$				
$a\uparrow b\downarrow$	$\bullet$	$\bullet$	$2E_0$			
$a\downarrow b\uparrow$	$\bullet$	$\bullet$	$\bullet$	$2E_0$		
$a\uparrow a\downarrow$	$\bullet$	$\bullet$	t	t	$2E_0 + U$	
$b\uparrow b\downarrow$	$\bullet$	$\bullet$	t	t	$-$	$2E_0 + U$

$\bullet = 0$ (no spin-flip in Hamiltonian)

$- = 0$ (no hopping for 2 electrons at the same time)

$a\uparrow b\uparrow$, $a\downarrow b\downarrow$: triplet : antisymmetric in orbital and symmetric in spin upon interchange of particle coordinates

$a\uparrow a\downarrow$, $b\uparrow b\downarrow$: singlet : symmetric in orbital and antisymmetric in spin.

How about $a\uparrow b\downarrow$ and $a\downarrow b\uparrow$?

Let us make the following linear combinations:

$$\frac{a\uparrow b\downarrow + a\downarrow b\uparrow}{\sqrt{2}} = \frac{a(1)b(2)\uparrow(1)\downarrow(2) - a(2)b(1)\downarrow(1)\uparrow(2) + a(1)b(2)\downarrow(1)\uparrow(2) - a(2)b(1)\uparrow(1)\downarrow(2)}{\sqrt{2}\cdot\sqrt{2}}$$

$$= \frac{\{a(1)b(2) - a(2)b(1)\}\uparrow(1)\downarrow(2) + \{a(1)b(2) - a(2)b(1)\}\downarrow(1)\uparrow(2)}{\sqrt{2}\cdot\sqrt{2}}$$

$$= \left\{\frac{a(1)b(2) - a(2)b(1)}{\sqrt{2}}\right\}\left\{\frac{\uparrow(1)\downarrow(2) + \downarrow(1)\uparrow(2)}{\sqrt{2}}\right\}$$

$$= \text{"ab-triplet"} \qquad \Rightarrow \text{question : is this a single Slater-determinant ?}$$

$$\frac{a\uparrow b\downarrow - a\downarrow b\uparrow}{\sqrt{2}} = \left\{\frac{a(1)b(2) + a(2)b(1)}{\sqrt{2}}\right\}\left\{\frac{\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)}{\sqrt{2}}\right\}$$

$$= \text{"ab-singlet"} \qquad \Rightarrow \text{question : is this a single Slater-determinant ?}$$

The Hamiltonian is then:

	$a\uparrow b\uparrow$	$a\downarrow b\uparrow$	ab-triplet	ab-singlet	$a\uparrow a\downarrow$	$b\uparrow b\downarrow$
$a\uparrow b\uparrow$	$2E_0$					
$a\downarrow b\uparrow$	·	$2E_0$				
ab-triplet	∘	·	$2E_0$			
ab-singlet	∘	·	∘	$2E_0$		
$a\uparrow a\downarrow$	·	·	0	$\sqrt{2}t$	$2E_0+U$	
$b\uparrow b\downarrow$	∘	·	0	$\sqrt{2}t$	—	$2E_0+U$

The 6×6 Hamiltonian falls apart into three 1×1 Hamiltonians
and one 3×3 Hamiltonians.
The three 1×1 Hamiltonians are all triplet in character
and have the same energy E_0. This 3-fold degeneracy
is after all the reason to call these states triplets
The 3×3 Hamiltonian belongs to the singlet Hilbert space.

Remark: The factor $\sqrt{2}$ in the hopping matrix element basically
indicates that there are two ways to let an electron
hop from a doubly occupied site to a neighbor
while being in the singlet state : namely with spin ↑ or ↓

For the 3×3 Hamiltonian can be simplified further by taking the following linear combination of the singlet states $a\uparrow a\downarrow$ and $b\uparrow b\downarrow$, namely

$$\frac{a\uparrow a\downarrow + b\uparrow b\downarrow}{\sqrt{2}} \quad \text{and} \quad \frac{a\uparrow a\downarrow - b\uparrow b\downarrow}{\sqrt{2}} \quad \text{(these are still singlets):}$$

$$
\begin{array}{l}
\text{ab-singlet} \\
\frac{a\uparrow a\downarrow + b\uparrow b\downarrow}{\sqrt{2}} \\
\frac{a\uparrow a\downarrow - b\uparrow b\downarrow}{\sqrt{2}}
\end{array}
\begin{bmatrix}
2E_0 & & \\
2t & 2E_0 + U & \\
0 & 0 & 2E_0 + U
\end{bmatrix}
$$

The 2×2 submatrix will have $2E_0 - \frac{(2t)^2}{U}$ as the lowest energy (for $t \ll U$), and $2E_0 + \frac{(2t)^2}{U}$ as the highest. The 1×1 submatrix keeps $2E_0 + U$ as energy eigenvalue.

Conclusion:

The spins on the two sites will form a singlet state, since the lowest singlet state has an energy which is lower by $\underline{4t^2/U}$ as compared to the triplets.

$$\rightarrow \quad H^{spin} = -J \cdot S_1 \cdot S_2 ,$$

$$J = E_{singlet} - E_{triplet} = -4t^2/U$$

$$\rightarrow \text{anti parallel spins are favored}$$

Remarks: in the Hubbard model, the H_2 molecule will have 4 energies: $2E_0 - \frac{4t^2}{U}, \quad 2E_0, \quad 2E_0 + U, \quad 2E_0 + \frac{4t^2}{U}$

: for $U = 0 \rightarrow$ singlet state $=$ a single slater determinant
for $U \neq 0 \rightarrow$ singlet state $=$ combination of 3 slater. Det.

Hydrogen molecule: anti-ferromagnetic vs. singlet   1

Antiferromagnetic state:

- we have to choose between $\uparrow\downarrow = a\uparrow b\downarrow$ or $\downarrow\uparrow = a\downarrow b\uparrow$.
- this means that we can no longer make the Linear combination "ab-singlet" $= \frac{1}{\sqrt{2}}(a\uparrow b\downarrow - a\downarrow b\uparrow)$ or "ab-triplet" $= \frac{1}{\sqrt{2}}(a\uparrow b\downarrow + a\downarrow b\uparrow)$.

- remark: $a\uparrow b\downarrow$ is thus nor a singlet nor a triplet. $a\downarrow b\uparrow$ is thus nor a singlet nor a triplet.

- Let us make the choise $a\uparrow b\downarrow$ for our antiferromagnetic state. The states which couple to this is $a\uparrow a\downarrow$ and $b\uparrow b\downarrow$.

$$
\begin{array}{l}
a\uparrow b\downarrow \\
a\uparrow a\downarrow \\
b\uparrow b\downarrow
\end{array}
\begin{bmatrix}
2E_0 & & \\
t & 2E_0 + U & \\
t & - & 2E_0 + U
\end{bmatrix}
$$

This can be rewritten to:

$$
\begin{array}{l}
a\uparrow b\downarrow \\
\frac{1}{\sqrt{2}}(a\uparrow a\downarrow + b\uparrow b\downarrow) \\
\frac{1}{\sqrt{2}}(a\uparrow a\downarrow - b\uparrow b\downarrow)
\end{array}
\begin{bmatrix}
2E_0 & & \\
\sqrt{2}\,t & 2E_0 + U & \\
0 & - & 2E_0 + U
\end{bmatrix}
$$

The energy of the antiferromagnetic is then $(t \ll U)$:

$$
E_{AF} = 2E_0 - \left(\frac{\sqrt{2}\,t}{U}\right)^2 = 2E_0 - \frac{t^2}{U}.
$$

Compare this to $E_{singlet} = 2E_0 - \frac{2t^2}{U}$

There is a factor of two difference: this has to do
with the fact that there are <u>two</u> ways to hop away
from a singlet, while there is only <u>one</u> way to
hop from an AF state to a singlet.
An example for hopping from or to site a:

$$a\uparrow a\downarrow \longrightarrow a\uparrow b\downarrow \qquad\qquad \text{hopping away from a singlet,}$$
$$\longrightarrow b\uparrow a\downarrow = -a\downarrow b\uparrow$$

$$a\uparrow b\downarrow \longrightarrow a\uparrow a\downarrow \qquad\qquad \text{hopping from a AF to a singlet,}$$

PES/IPES — Bandgaps — energy reference - chemical potential μ

system with N-electrons:

PES: $N \rightarrow N-1$ initial: E_N^{Gs}
                          final : $E_{N-1}^{i} + E_{ref}$ $\Big\}$ $E_{PES}^{i} = E_{N-1}^{i} - E_N^{Gs} + E_{ref}$
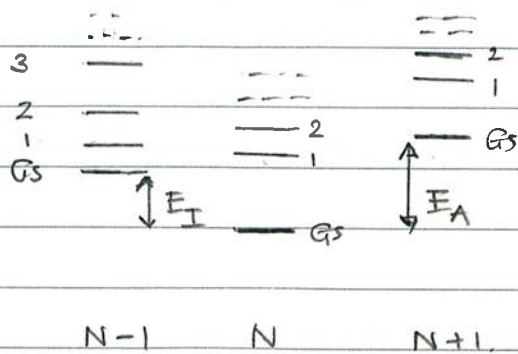
IPES: $N \rightarrow N+1$ initial : E_N^{Gs}
                           final : $E_{N+1}^{i} - E_{ref}$ $\Big\}$ $E_{IPES}^{i} = E_{N+1}^{i} - E_N^{Gs} - E_{ref}$

$[Gs = \text{Ground state}, \quad i = Gs, 1, 2, 3, \cdots \text{(excited states)}]$

Bandgap :
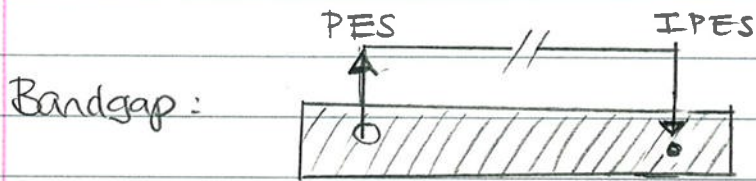
$$E_{gap} = E_{PES}^{Gs} + E_{IPES}^{Gs} = E_{N-1}^{Gs} - E_N^{Gs} + E_{N+1}^{Gs} - E_N^{Gs}$$
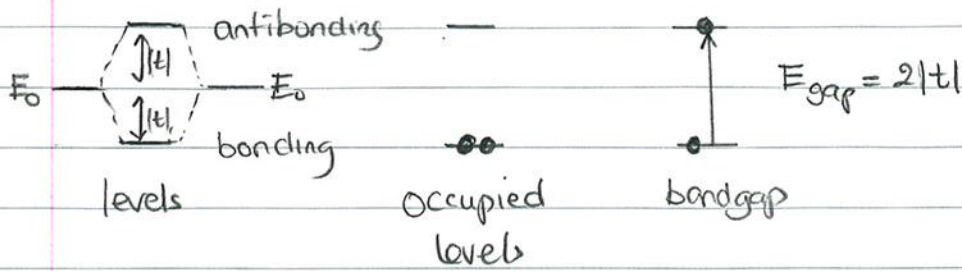$$= E_{N-1}^{Gs} + E_{N+1}^{Gs} - 2 E_N^{Gs}$$

$E_{gap} = E_I + E_A$
$(E_I \equiv E_{PES}^{Gs}, \quad E_A \equiv E_{IPES}^{Gs})$
$E_I = $ Ionization energy
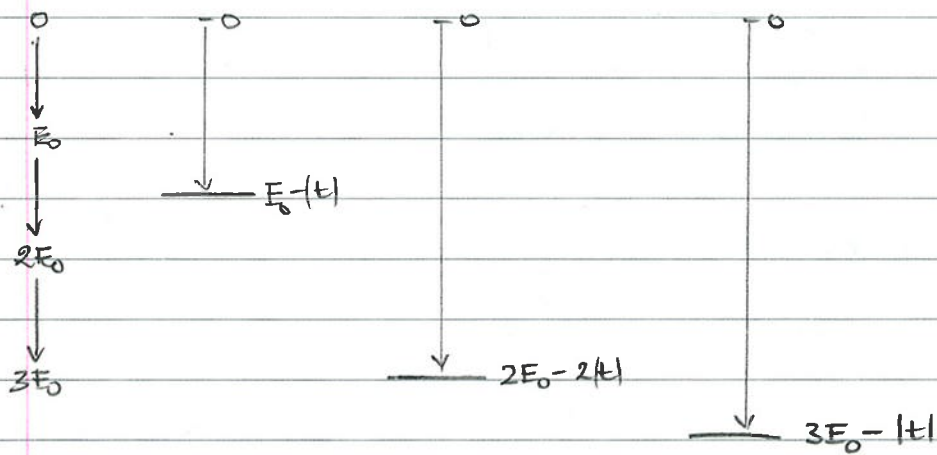$E_A = $ affinity energy

example 1 : H_2-molecule , 1 electron theory.

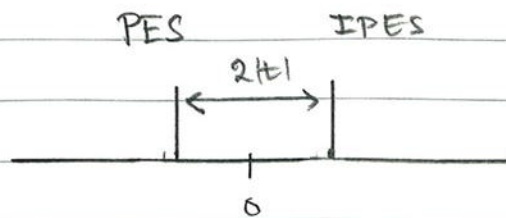* description in terms of 1-electron energy diagram :

levels   occupied   bandgap
                 levels

$E_{gap} = 2|t|$

* description in terms of total energy diagram :

$$E_{N-1}^{G} = E_0 - |t|$$ $$E_N^{G} = 2(E_0 - |t|)$$ $$E_{N+1}^{G} = 2(E_0 - |t|) + (E_0 + |t|)$$

1 electron in   2 electron in   3 electrons : 2 in the bonding
the bonding state   the bonding state   and 1 in the antibonding state

$E_0 - |t|$

$2E_0 - 2|t|$

$3E_0 - |t|$

Bandgap : $E_{gap} = E_0 - |t| + 3E_0 - |t| - 2\{2E_0 - 2|t|\} = 2|t|$
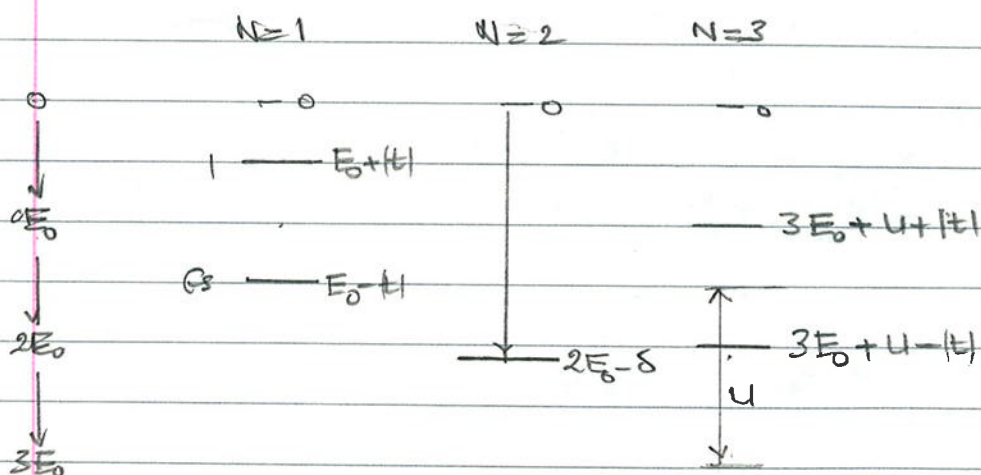
PES   IPES

$2|t|$

0

example 2 : H_2-molecule, Hubbard model with $U \gg t$
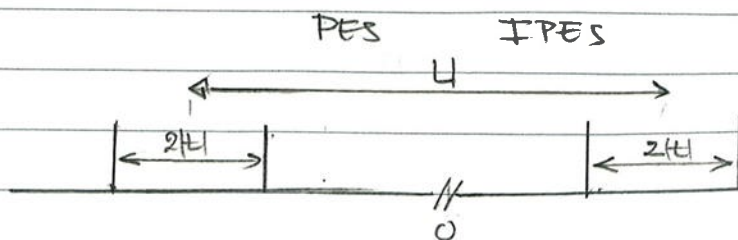
* description in terms of total energy diagram:

$N=2$: for $U \gg t \rightarrow E_N^{Gs} \approx 2E_0 - \delta$ $\qquad \delta \approx 4t^2/U$

$N=1$: PES has 2 states : $E_{N-1}^{Gs} = E_0 - |t|$, $\quad E_{N-1}^1 = E_0 + |t|$

$N=3$: IPES has 2 states : $E_{N+1}^{Gs} = 3E_0 + U - |t|$, $\quad E_{N+1}^1 = 3E_0 + U + |t|$.

Bandgap : $E_{gap} = E_0 - |t| + 3E_0 + U - |t| - 2\{2E_0 - \delta\} = U - 2|t| + 2\delta$
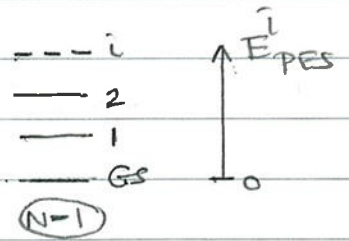
Thermodynamics : Internal Energy

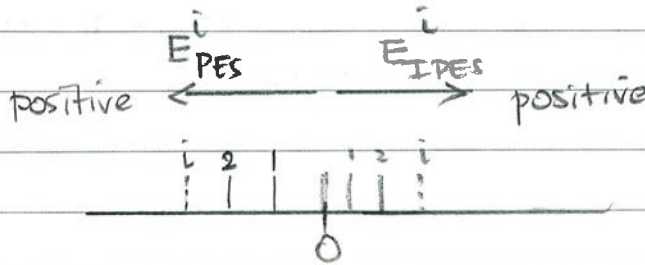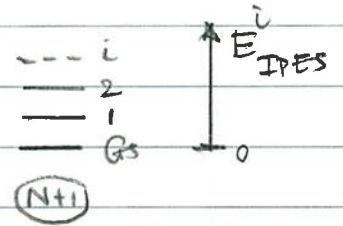$$dU = TdS - pdV + \mu dN \rightarrow \mu = \frac{dU}{dN}$$

$$\mu = \frac{dE}{dN} \; ; \; dN = 1 \rightarrow \mu = E_{N+1}^{GS} - E_N^{GS} = E_N^{GS} - E_{N-1}^{GS} \quad \text{(for metals)}$$

PES/IPES experiments : choose $E_{ref} = \mu$ $\qquad$ (also possible : $E_{ref} = E_{vac}$).

PES: $E_{PES}^{i} = E_{N-1}^{i} - E_N^{GS} + E_{ref}$

$\qquad = E_{N-1}^{i} - E_N^{GS} + E_N^{GS} - E_{N-1}^{GS}$

$\qquad = E_{N-1}^{i} - E_{N-1}^{GS}$

$$\begin{array}{ll} \text{- - - } i & \uparrow E_{PES}^{i} \\ \text{———} 2 & \\ \text{———} 1 & \\ \text{———} GS & \downarrow_0 \end{array}$$

$(N-1)$

IPES. $E_{IPES}^{i} = E_{N+1}^{i} - E_N^{GS} - E_{ref}$

$\qquad = E_{N+1}^{i} - E_N^{GS} - (E_{N+1}^{GS} - E_N^{GS})$

$\qquad = E_{N+1}^{i} - E_{N+1}^{GS}$

$$\begin{array}{ll} \text{- - - } i & \uparrow E_{IPES}^{i} \\ \text{———} 2 & \\ \text{———} 1 & \\ \text{———} GS & \downarrow_0 \end{array}$$

$(N+1)$

$$\underset{\text{positive}}{\xleftarrow{\quad E_{PES}^{i} \quad}} \quad \underset{\text{positive}}{\xrightarrow{\quad E_{IPES}^{i} \quad}}$$
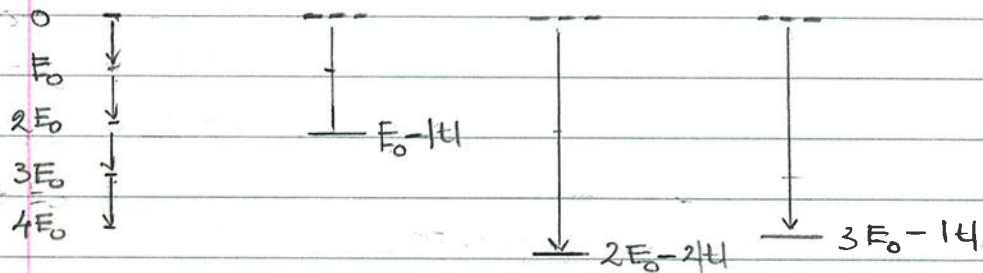
Energy referencing in total energy diagrams.

If the system has N electrons in its most stable state, then adjust the 1-electron potential "E_0" such that the groundstate of the N electron system has a lower energy than the groundstate of the N-1 and N+1 system:

$$E_N^{GS} < E_{N-1}^{GS}, \qquad E_N^{GS} < E_{N+1}^{GS}$$

example 1' (see example 1: E_0 is reduced by a factor $2\frac{1}{2}$)

E_0 is a 1-electron potential by the charge of the atom core and by the crystal (e.g. Madelung potential).

- Example: Mn can be 2+, 3+, 4+ depending on the compound →
  $d^5, d^4, d^3 \rightarrow$ N=5, N=4, N=3.
  E_0 is different for each compound → Madelung potential.

- example: $E(n) = n \cdot E_0 + \frac{1}{2} n \cdot (n-1) \cdot U$.
  If n_0 is to be the most stable situation then:
  $$\frac{\partial E}{\partial n} = 0 \text{ for } n=n_0 \iff E_0 = -(n_0 - \frac{1}{2}) U_0$$

- Remark: $\dfrac{\partial^2 E(n)}{\partial n^2} = U$ ‼ → (constraint LDA+U calculations)

To determine U one must do an experiment involving a change of 2 particles, e.g. Bandgap $= \left(E_{N+1}^{GS} - E_N^{GS} \right) - \left(E_N^{G} - E_{N-1}^{GS} \right)$.

H_2 molecule, Hubbard model, PES/IPES weights.

$N=2$ $\frac{1}{\sqrt{2}}(a\uparrow b\downarrow - a\downarrow b\uparrow)$ $\begin{bmatrix} 2E_0 & 2t \\ 2t & 2E_0+U \end{bmatrix}$ $\begin{bmatrix} \Delta & t \\ t & \Delta \end{bmatrix} \rightarrow E_{\mp} = \frac{\Delta \pm \sqrt{\Delta^2+4t^2}}{2}$
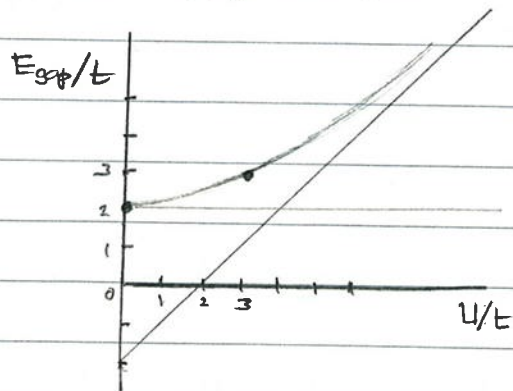
$\qquad \frac{1}{\sqrt{2}}(a\uparrow a\downarrow + b\uparrow b\downarrow)$

$$E_{N=2}^{GS} = 2E_0 + \frac{U - \sqrt{U^2+16t^2}}{2}$$

$N=1$ $\begin{matrix} a\uparrow \\ b\uparrow \end{matrix}$ $\begin{bmatrix} E_0 & t \\ t & E_0 \end{bmatrix}$ $E_{N=1}^{GS} = E_0 - |t|$, $E_{N-1}' = E_0 + |t|$.

$N=3$ $\begin{matrix} \underline{a\uparrow} \\ \underline{b\uparrow} \end{matrix}$ $\begin{bmatrix} 3E_0+U & t \\ t & 3E_0+U \end{bmatrix}$ $E_{N+1}^{GS} = 3E_0+U-|t|$, $E_{N+1}' = 3E_0+U+|t|$

$$E_{gap} = E_0-|t| + 3E_0+U-|t| - 2\left\{2E_0 + \frac{U-\sqrt{U^2+16t^2}}{2}\right\} = \sqrt{U^2+16t^2} - 2|t|$$

$U=0 \rightarrow E_{gap} = 2|t|$, $U=3t \rightarrow E_{gap} = 3t$, $U \gg t \rightarrow E_{gap} \simeq U - 2|t|$

$$\psi_{N=2}^{Gs} = \alpha \left| \tfrac{1}{\sqrt{2}} (a\uparrow b\downarrow - a\downarrow b\uparrow) \right\rangle + \beta \left| \tfrac{1}{\sqrt{2}} (a\uparrow a\downarrow + b\uparrow b\downarrow) \right\rangle.$$

$$\psi_{N-1}^{Gs} = \tfrac{1}{\sqrt{2}} |a\uparrow\rangle + \tfrac{1}{\sqrt{2}} |b\uparrow\rangle \qquad \text{(bonding)} \qquad \text{(also for } \downarrow)$$

$$\psi'_{N-1} = \tfrac{1}{\sqrt{2}} |a\uparrow\rangle - \tfrac{1}{\sqrt{2}} |b\uparrow\rangle, \qquad \text{(anti-bonding)} \qquad \text{(also for } \downarrow)$$

Spectral weight → PES at site ⓐ, e.g. remove a↓ electron.

$$I_{PES}^{Gs} = \left| \langle \tfrac{1}{\sqrt{2}} \langle a\uparrow | + \tfrac{1}{\sqrt{2}} \langle b\uparrow | \right| a\downarrow \left| \alpha \left| \tfrac{a\uparrow b\downarrow - a\downarrow b\uparrow}{\sqrt{2}} \right\rangle + \beta \left| \tfrac{a\uparrow a\downarrow + b\uparrow b\downarrow}{\sqrt{2}} \right\rangle \right\rangle \right|^2$$

$$= \tfrac{1}{4} \left| \langle a\uparrow | a\downarrow | \beta | a\uparrow a\downarrow \rangle + \langle b\uparrow | a\downarrow | -\alpha \, a\downarrow b\uparrow \rangle \right|^2$$

$$= \tfrac{1}{4} \left| \beta + \alpha \right|^2$$

$$I_{PES}^1 = \left| \langle \tfrac{1}{\sqrt{2}} \langle a\uparrow | - \tfrac{1}{\sqrt{2}} \langle b\uparrow | \right| \cdots \left| \cdots \cdots \cdots \right\rangle \right|^2$$

$$= \tfrac{1}{4} \left| \beta - \alpha \right|^2$$

$* \; U=0 \rightarrow \alpha = \beta = \tfrac{1}{\sqrt{2}} \rightarrow I_{PES}^{Gs} = \tfrac{1}{4} \left| \tfrac{1}{\sqrt{2}} + \tfrac{1}{\sqrt{2}} \right|^2 = \tfrac{1}{2}, \quad I_{PES}^1 = 0.$

$* \; U \rightarrow \infty \rightarrow \alpha = 1, \beta = 0 \rightarrow I_{PES}^{Gs} = \tfrac{1}{4} |0+1|^2 = \tfrac{1}{4}, \quad I_{PES}^1 = \tfrac{1}{4} |0-1|^2 = \tfrac{1}{4}.$

The total PES intensity is $\tfrac{1}{4}|\beta+\alpha|^2 + \tfrac{1}{4}|\beta-\alpha|^2 =$
$\tfrac{1}{4}\{\beta^2 + \alpha^2 + 2\alpha\beta + \beta^2 + \alpha^2 - 2\alpha\beta\} = \tfrac{1}{2}(\beta^2 + \alpha^2) = \tfrac{1}{2}$

Considering also the PES in which a spin up is annihilated, (ending up with a spin down final state), one also has a total PES intensity of ½.

So in total we can remove ½ + ½ = 1 electron.

2x2 Hamiltonian: addendum.

$$H = \begin{bmatrix} 0 & t \\ t & \Delta \end{bmatrix} \quad \psi = \begin{bmatrix} \alpha \\ \beta \end{bmatrix} \quad \varphi_1 = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad \varphi_2 = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

$$H\psi = E\psi, \quad \psi = \alpha\varphi_1 + \beta\varphi_2, \quad \alpha^2 + \beta^2 = 1, \quad E_\pm = \frac{\Delta \pm \sqrt{\Delta^2 + 4t^2}}{2}$$

$$\Rightarrow \alpha \equiv \cos\theta, \quad \beta \equiv \sin\theta, \quad 0 \leq \theta \leq \frac{\pi}{2}$$

$$\tan 2\theta = \frac{\sin 2\theta}{\cos 2\theta} = \frac{2\sin\theta\cos\theta}{\cos^2\theta - \sin^2\theta} = \frac{2\alpha\beta}{\alpha^2 - \beta^2}$$

$$\begin{bmatrix} -E & t \\ t & \Delta-E \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = 0 \longrightarrow -E\alpha + t\beta = 0 \longrightarrow \beta = \frac{E}{t}\alpha$$

$$\tan 2\theta = \frac{2 \cdot \frac{E}{t} \cdot \alpha^2}{\alpha^2 - \left(\frac{E}{t}\right)^2 \alpha^2} = \frac{2 E/t}{1 - (E/t)^2} = \frac{2tE}{t^2 - E^2} = \frac{t(\Delta \pm \sqrt{\Delta^2 + 4t^2})}{t^2 - \frac{1}{4}\Delta^2 - \frac{1}{4}(\Delta^2 + 4t^2) \pm \frac{1}{2}\Delta\sqrt{\Delta^2 + 4t^2}}$$

$$= t(\Delta \pm \sqrt{\Delta^2 + 4t^2}) \Big/ \left(-\frac{1}{2}\Delta^2 \pm \frac{1}{2}\Delta\sqrt{\Delta^2 + 4t^2}\right) = \pm\frac{2t}{\Delta}$$

If $t < 0$ then ground state is $\psi = \cos\theta \cdot \varphi_1 + \sin\theta \, \varphi_2$
with $0 \leq \theta \leq \frac{\pi}{2}$

Bonding state.

$$\Rightarrow \tan 2\theta = \frac{2|t|}{\Delta}$$

Spectral weights

$$\psi_G = \alpha |d^9 p^6\rangle + \beta |d^{10} p^5\rangle \qquad \alpha = \cos\theta, \ \beta = \sin\theta$$

$$\psi_{\underline{c},1} = \alpha' |\underline{c} d^9 p^6\rangle + \beta' |\underline{c} d^{10} p^5\rangle \qquad \alpha' = \cos\theta', \ \beta' = \sin\theta'$$
$$\psi_{\underline{c},2} = \beta' |\underline{c} d^9 p^6\rangle - \alpha' |\underline{c} d^{10} p^5\rangle$$

$$I_{\underline{c},1} = |\langle \psi_{\underline{c},1}| \underline{c} |\psi_G\rangle| = |\alpha'\alpha + \beta'\beta|^2$$
$$I_{\underline{c},2} = |\langle \psi_{\underline{c},2}| \underline{c} |\psi_G\rangle| = |\beta'\alpha - \alpha'\beta|^2$$

$$\frac{I_{c,2}}{I_{c,1}} = \left| \frac{\sin\theta'\cos\theta - \cos\theta'\sin\theta}{\cos\theta'\cos\theta + \sin\theta'\sin\theta} \right|^2 = \left| \frac{\sin(\theta'-\theta)}{\cos(\theta'-\theta)} \right|^2 = \tan^2(\theta'-\theta)$$

$\rightarrow$ If $\theta' = \theta$ Then $I_{c,2}/I_{c,1} = 0$

$\rightarrow$ If $Q \gg \Delta$, $(Q-\Delta) \gg t$ Then $(\alpha' \doteq 0, \beta' = 1) \doteq (\theta' = 90°) \rightarrow \frac{I_{c2}}{I_{c1}} = \tan^2(90°-\theta)$

$$\tan^2(90°-\theta) = \frac{\sin^2(90°-\theta)}{\cos^2(90°-\theta)} = \frac{\cos^2\theta}{\sin^2\theta} = \frac{\alpha^2}{\beta^2} = \frac{1}{\tan^2\theta}$$

$$\sin 2\theta = 2\sin\theta\cos\theta \qquad\qquad\qquad \sin^2\theta + \cos^2\theta = 1$$
$$\cos 2\theta = \cos^2\theta - \sin^2\theta$$
$$\sin(\alpha\pm\beta) = \sin\alpha\cos\beta \pm \cos\alpha\sin\beta$$
$$\cos(\alpha\pm\beta) = \cos\alpha\cos\beta \mp \sin\alpha\sin\beta$$
$$\sin\alpha \pm \sin\beta = 2\sin\tfrac{1}{2}(\alpha\pm\beta)\cos\tfrac{1}{2}(\alpha\mp\beta)$$
$$\cos\alpha + \cos\beta = 2\cos\tfrac{1}{2}(\alpha+\beta)\cos\tfrac{1}{2}(\alpha-\beta)$$
$$\cos\alpha - \cos\beta = -2\sin\tfrac{1}{2}(\alpha+\beta)\sin\tfrac{1}{2}(\alpha-\beta)$$

Electronic Structure of Cu_2O and CuO

Cu_2O : Cu^+, O^{2-} $\rightarrow$ Cu : $3d^{10}4s^0$, O : $2p^6$.
CuO : Cu^{2+}, O^{2-} $\rightarrow$ Cu : $3d^9 4s^0$, O : $2p^6$.

Remark: The Cu $4s$ plays an important role for the bonding, in fact, it gives the main contribution for the formation of Cu_2O. Nevertheless, we will ignore its role for the excitation spectra of Cu_2O and CuO, thereby assuming that most of its effect can be taken into account in a "mean field manner", as a "background". So for the next sections we will continue with :
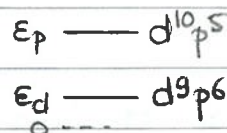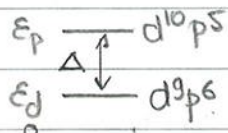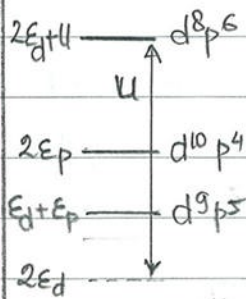
Cu_2O: Cu^+, O^{2-} $\rightarrow$ Cu $3d^{10}$, O $2p^6$
CuO : Cu^{2+}, O^{2-} $\rightarrow$ Cu $3d^9$, $O 2p^6$

We now will look into the valence band spectra and the Cu $2p$ core level spectra. The Cu $2p$ is split by the large spin-orbit interaction into $2p_{3/2}$ and $2p_{1/2}$, and in the following we will denote each of them as $\underline{c}$ (core hole). We will neglect the multiplet splitting for simplicity.

See J. Ghijsen et al., Phys. Rev B $\underline{38}$, 11322 (1988)
     G. van der Laan et al., Phys. Rev, B $\underline{23}$, 4369 (1981)

CuO

$\varepsilon_c + \varepsilon_d + Q$ —— $\underline{c}d^9p^6$

Q

$\varepsilon_c + \varepsilon_p$ —— $\underline{c}d^{10}p^5$

Δ

$2\varepsilon_d + U$ —— d^8p^6

U

$2\varepsilon_p$ —— $d^{10}p^4$

$\varepsilon_d + \varepsilon_p$ —— d^9p^5

$2\varepsilon_d$ ----

0

ε_p —— $d^{10}p^5$

Δ

ε_d —— d^9p^6

0

N-1 · N

PES · GS, XAS

OPTICS

Cu₂O

ε_c —— $\underline{c}d^{10}p^6$

ε_p —— $d^{10}p^5$

ε_d —— d^9p^6

0 —— $d^{10}p^6$

N-1 · N

PES · GS, XAS

OPTICS

CuO: $\Delta \approx 3$ eV , $\Delta = \varepsilon_p - \varepsilon_d$
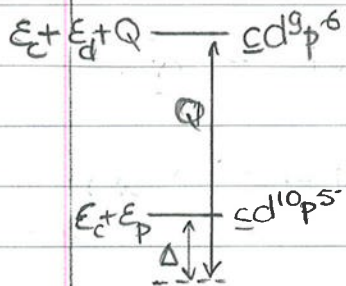
$U \approx 8$ eV

$Q \approx 9$ eV

remark: no correlations on
the oxygen in this
simplified model

Cu₂O: $\varepsilon_d \approx 3$ eV

$\varepsilon_p \approx 6$ eV

$\varepsilon_c \approx 930$ eV ($2p_{3/2}$)

≈ 950 eV ($2p_{1/2}$)

Cu_2O:

The electronic structure of Cu_2O is rather simple (in this model): the ground state is made out of 1 configuration, namely the full-shell state $d^{10}p^6$. The valence band photoemission spectrum will show 2 peaks, reflecting the d^9p^5 and $d^{10}p^6$ final states. In terms of 1 electron theories (band theory) these 2 states represent the Cu-3d and O-2p partial density of states, respectively. The Cu 2p core level photoemission spectrum consists of only 1 peak for each of the spin-orbit split levels: 1 peak for the Cu $2p_{3/2}$ and 1 peak for the Cu $2p_{1/2}$, each denoted as $\underline{c}d^{10}p^6$ in this model.

CuO:

The electronic structure of CuO is "richer" in comparison with Cu_2O. The ground state of CuO is formed out of 2 configurations:

$$\Psi_{GS} = \alpha|d^9p^6\rangle + \beta|d^{10}p^5\rangle \qquad H = \begin{bmatrix} \varepsilon_d & t \\ t & \varepsilon_p \end{bmatrix} = \begin{bmatrix} \varepsilon_d & 0 \\ 0 & \varepsilon_d \end{bmatrix} + \begin{bmatrix} 0 & t \\ t & \Delta \end{bmatrix}$$

$$E_{GS} = \varepsilon_d + \frac{\Delta - \sqrt{\Delta^2 + 4t^2}}{2}$$

The valence band photoemission spectrum consist of 3 peaks and the calculation of their relative weights will be discussed later.

The Cu 2p core level spectrum consists of 2 peaks:

$$\Psi_{\underline{c},1} = \alpha'|\underline{c}d^9p^6\rangle + \beta'|\underline{c}d^{10}p^5\rangle$$
$$\Psi_{\underline{c},2} = \beta'|\underline{c}d^9p^6\rangle - \alpha'|\underline{c}d^{10}p^5\rangle$$

$$H = \begin{bmatrix} \varepsilon_c + \varepsilon_d + Q & t \\ t & \varepsilon_c + \varepsilon_p \end{bmatrix} =$$

$$E_{\underline{c},1,2} = \varepsilon_c + \varepsilon_d + Q + \frac{(\Delta - Q) \pm \sqrt{(\Delta - Q)^2 + 4t^2}}{2}$$

$$\begin{bmatrix} \varepsilon_c + \varepsilon_d + Q & 0 \\ 0 & \varepsilon_c + \varepsilon_d + Q \end{bmatrix} + \begin{bmatrix} 0 & t \\ t & \Delta - Q \end{bmatrix}$$

approximations for CuO

$$t \ll \Delta \rightarrow E_{GS} \approx \varepsilon_d - t^2/\Delta$$

$$\left.\begin{array}{l} t \ll |\Delta - Q| \\ \Delta < Q \end{array}\right\} \rightarrow E_{\underline{c},1} \approx \varepsilon_c + \varepsilon_d + Q - \frac{t^2}{\Delta - Q} \qquad = \varepsilon_c + \varepsilon_d + Q + \frac{t^2}{|\Delta - Q|}$$

$$E_{\underline{c},2} \approx \varepsilon_c + \varepsilon_d + Q + (\Delta - Q) + \frac{t^2}{\Delta - Q} = \varepsilon_c + \varepsilon_d + \Delta - \frac{t^2}{|\Delta - Q|}$$

$$E_{\underline{c},2} \text{ will be lower than } E_{\underline{c},1} \qquad (\Delta < Q)$$

Cu 2p spectral weights for CuO

$$I_{c,1} = |\langle \psi_{\underline{c},1}|\underline{c}|\psi_{GS}\rangle|^2 = |\alpha'\alpha + \beta'\beta|^2$$

$$I_{c,2} = |\langle \psi_{c,2}|\underline{c}|\psi_{GS}\rangle|^2 = |\beta'\alpha - \alpha'\beta|^2$$

example 1
$$Q = 0 \rightarrow \alpha' = \alpha, \beta' = \beta \rightarrow I_{c,1} = 1, I_{c,2} = 0.$$
$$\text{remark: independent of } \alpha, \beta \text{ values !}$$

example 2
$$Q \gg \Delta, (Q - \Delta) \gg t \rightarrow \alpha' \approx 0, \beta' = 1 \rightarrow I_{c,1} \approx \beta^2, I_{c,2} \approx \alpha^2$$

$$\downarrow \qquad\qquad\qquad \downarrow$$

$$\psi_{\underline{c},1} \approx |\underline{c} d^{10} p^5\rangle \qquad \psi_{\underline{c},2} \approx |\underline{c} d^9 p^6\rangle$$

$$E_{\underline{c},1} \approx \varepsilon_c + \varepsilon_p \qquad E_{\underline{c},2} \approx \varepsilon_c + \varepsilon_d + Q$$

$$E_{\underline{c},1} - E_{GS} \approx \varepsilon_c + \Delta \qquad E_{\underline{c},2} - E_{GS} \approx \varepsilon_c + Q$$
$$\text{(lower in energy)}$$

Remark:
$$\alpha^2 = \text{component of } Cu^{2+} (d^9 p^6) \text{ in ground state}$$
$$\beta^2 = \text{component of } Cu^+ (d^{10} p^5) \text{ in ground state.}$$

N-1 : PES   N-1 : PES   N-1 : PES

example 1: $Q=0$ example 3: $Q=\Delta$ example 2: $Q \gg \Delta$

N: GS problem
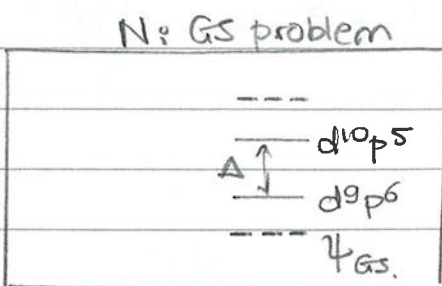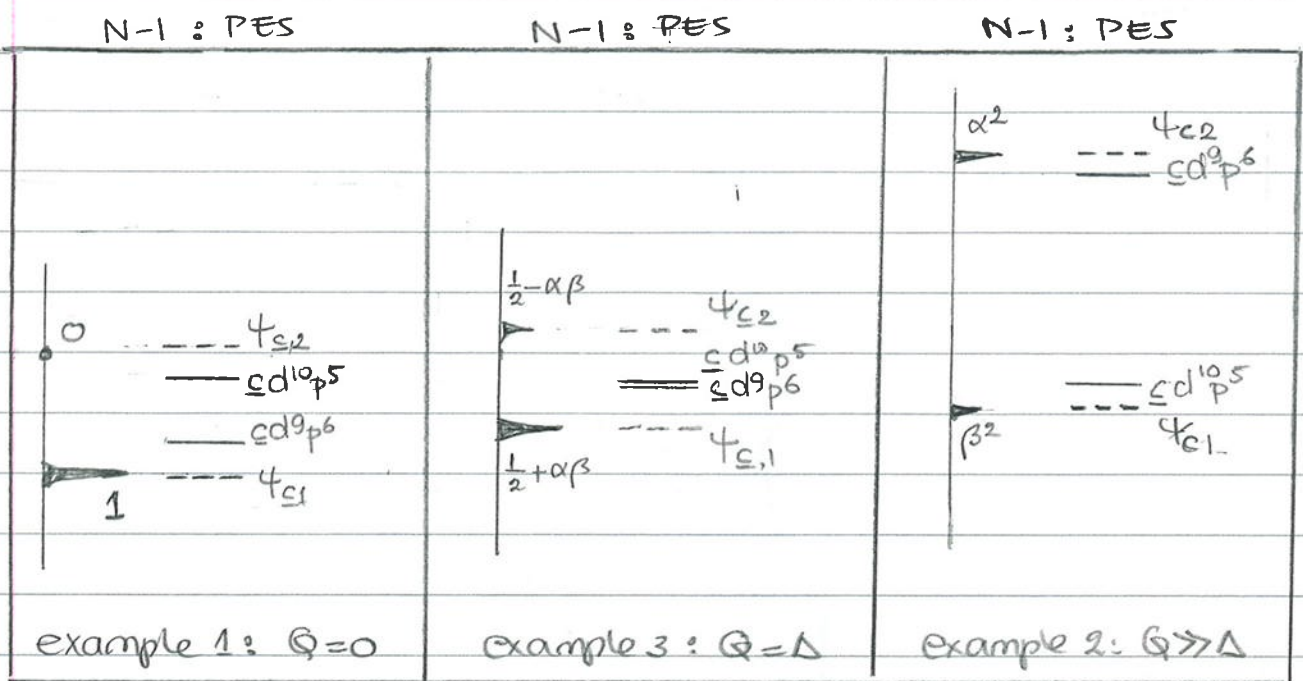
example 3

$$Q=\Delta \longrightarrow \alpha' = \beta' = \frac{1}{\sqrt{2}} \longrightarrow I_{c_1} = \frac{1}{2}|\alpha+\beta|^2 = \frac{1}{2}|\alpha^2+\beta^2+2\alpha\beta| = \frac{1}{2}|1+2\alpha\beta|$$

$$I_{c_2} = \frac{1}{2}|\alpha-\beta|^2 = \frac{1}{2}|\alpha^2+\beta^2-2\alpha\beta| = \frac{1}{2}|1-2\alpha\beta|$$

$$\Delta > 0, t < 0, \alpha > \beta > 0 \Longrightarrow I_{c_1} = \frac{1}{2}+\alpha\beta, \quad I_{c_2} = \frac{1}{2}-\alpha\beta$$