Lecture 24.10.2022

TM.

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{ee} + \mathcal{H}_{cf} + \mathcal{H}_{SO} + \mathcal{H}_z$$

App.

$$\mathcal{H}_{SI} = -\hat{S} \begin{pmatrix} D_{xx} & & \\ & D_{yy} & \\ & & D_{zz} \end{pmatrix} \hat{S}$$

$$\underbrace{\phantom{D_{xx} \quad D_{yy} \quad D_{zz}}}_{\underline{\underline{D}}}$$

OUR

GOAL

(Part 1)

effective
single ion
spin Hamm.

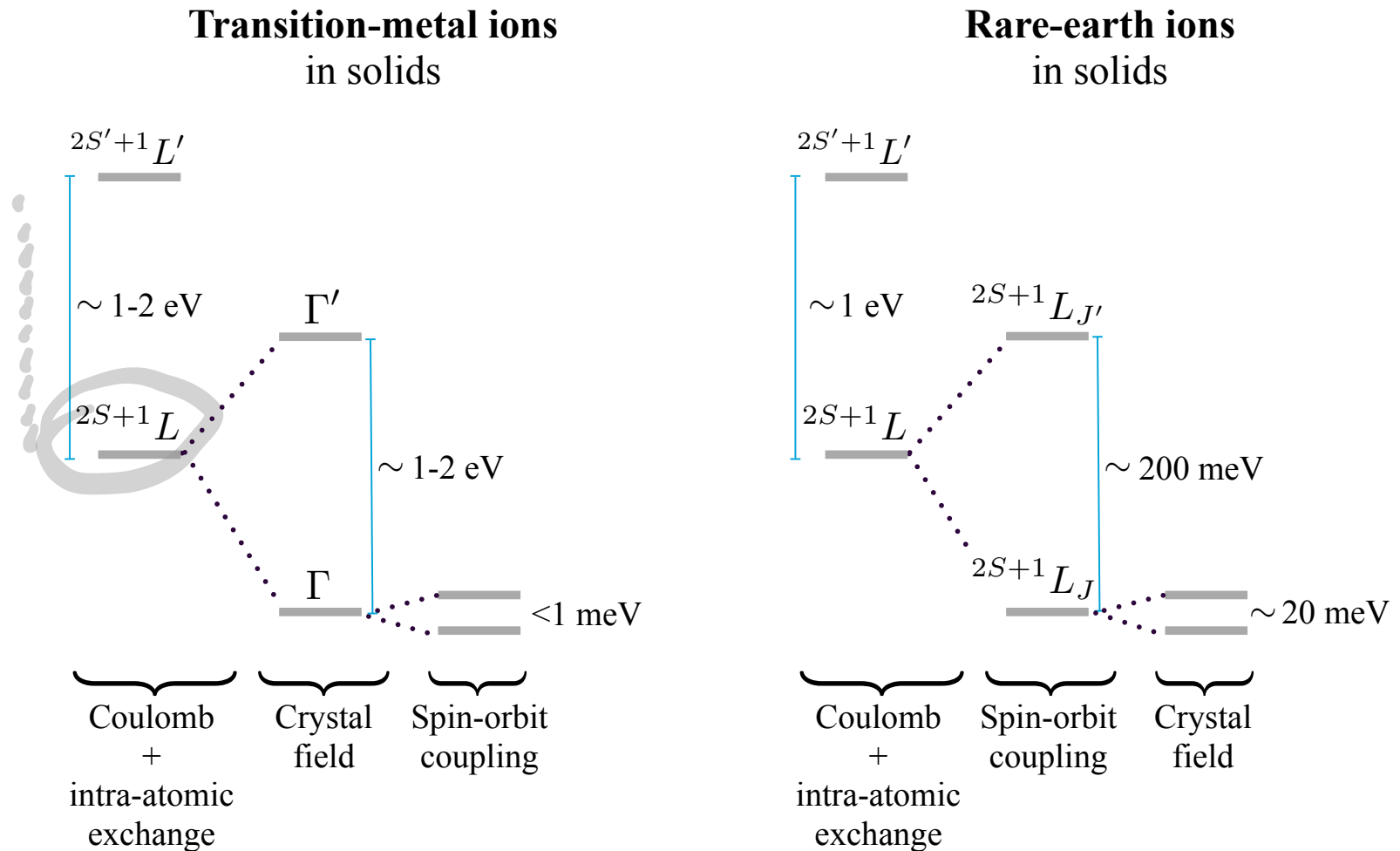$$-\mu_B \hat{S} \begin{pmatrix} g_{xx} & & \\ & g_{yy} & \\ & & g_{zz} \end{pmatrix} \vec{B}$$

$$\underbrace{\phantom{g_{xx} \quad g_{yy} \quad g_{zz}}}_{}$$

$$\underline{\underline{g}} \text{ tensor}$$

OUR GOAL   Effective Spin Hamiltonian
(part 2)

$$\mathcal{H} = \underbrace{\sum_i \mathcal{H}_{SI}^i}_{\text{single ion}} \underbrace{- 2 J_{inter} \sum_{i \neq j} \hat{S}_i \cdot \hat{S}_j}_{\text{Exchange coupling}}$$

i, j indicate $\neq$ Atoms

Spin-orbit splitting

Transition-metal ions
in solids

Rare-earth ions
in solids

$^{2S'+1}L'$

$\sim 1\text{-}2$ eV

Γ'

^{2S+1}L

$\sim 1\text{-}2$ eV

Γ

<1 meV

$\underbrace{\qquad}$ Coulomb + intra-atomic exchange

$\underbrace{\qquad}$ Crystal field

$\underbrace{\qquad}$ Spin-orbit coupling

$^{2S'+1}L'$

~ 1 eV

$^{2S+1}L_{J'}$

^{2S+1}L

~ 200 meV

$^{2S+1}L_J$

~ 20 meV

$\underbrace{\qquad}$ Coulomb + intra-atomic exchange

$\underbrace{\qquad}$ Spin-orbit coupling

$\underbrace{\qquad}$ Crystal field

Why is the strength of SO coupling indicated as < 1 meV for TM if $\zeta_{nl} = 10 - 100$ meV?

Crystal-field levels for many electrons
Spin-orbit interaction for many electrons
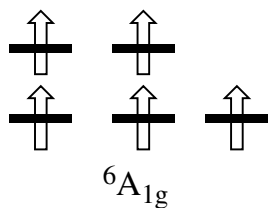Single-ion spin Hamiltonian

Classroom activity

17.10.2016

Knowing that in Fe^{3+} O_h complexes

High Spin

CF frustrated

$^6A_{1g}$

Low Spin

Hund frustrated

$^2T_{2g}$

$3d^n$ ions in solids

$3d^{n-1}$

$3d^{n+1}$

$3d^n$

$^{2S'+1}L'$

Γ'

~ 1- 2 eV

~ 5 eV

^{2S+1}L

~ 1- 2 eV

< 1 meV

Γ

Coulomb and exchange | Bonding | Spin-orbit

Excited configurations, ionic | Single configuration, charge neutral

What happens here?

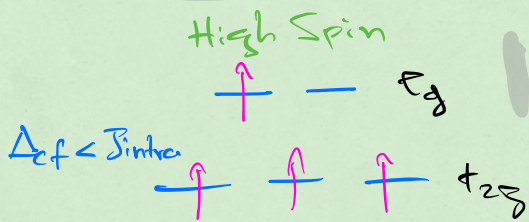χT, emu·K/mol vs Temperature, K
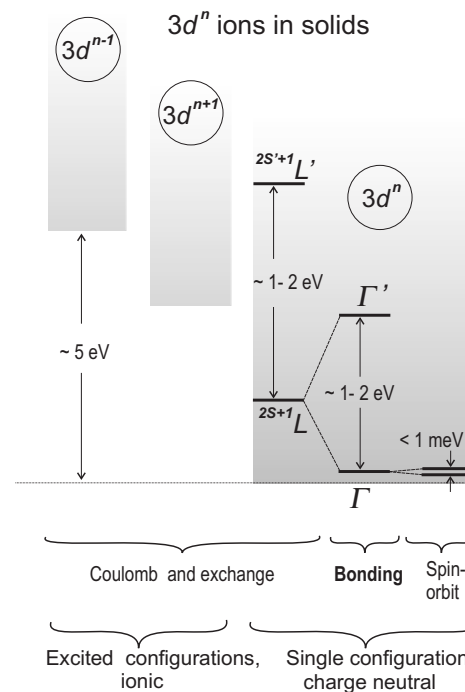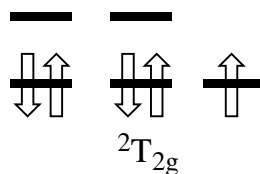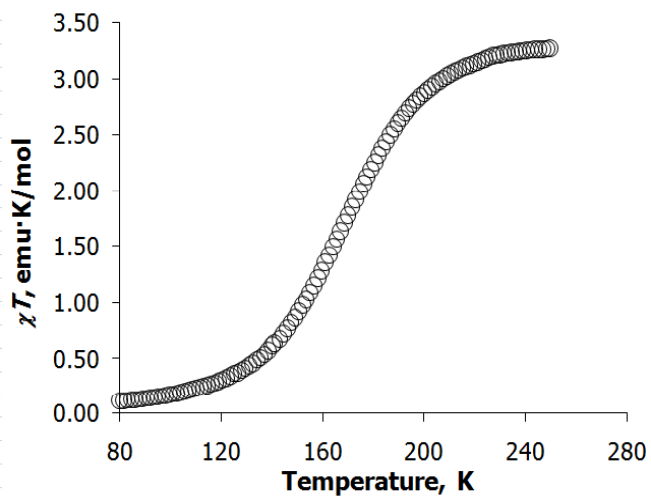
Based on this susceptibility plot, try to give a rough estimate of the energy difference between the two multi-electron configurations sketched above on the left

$\underline{\underline{g}}$ and $\underline{\underline{D}}$ tensors

Mn^{3+} $(3d)^4$

1. free ion   ↑ ↑ ↑ ↑ — $S=2$
                              $L=2$

2. $\mathcal{H}_{cf}$

High Spin

↑ — e_g

$\Delta_{cf} < J_{intra}$ ↑ ↑ ↑ t_{2g}

$S = 2$ ${}^5E_g$

Low Spin

— —

$\Delta_{cf} > J_{intra}$

↑↓ ↑ ↑

$S = 1$ STOP

3. $\mathcal{H}_{so} = \lambda \hat{L} \cdot \hat{S}$
   not effective 1st order
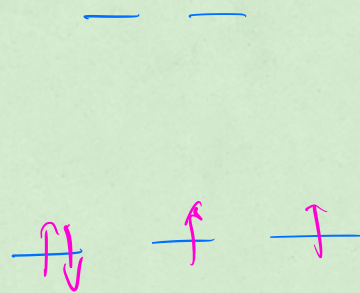
4. Jahn-Teller distortion

$\overline{\mp}\ \begin{array}{l}x^2-y^2\\z^2\end{array}$

↑ xy

xz ↑ ↑ yz
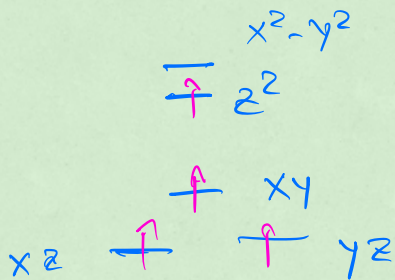
Unique g.s. after points

1. + 2. + 3. + 4.

$\Rightarrow |\Gamma, \gamma\rangle$

$\mathcal{H}_0 + \mathcal{H}_{ee} + \mathcal{H}_{cf} + \mathcal{H}_{so} + \mathcal{H}_z$

$\underbrace{\phantom{\mathcal{H}_0 + \mathcal{H}_{ee} + \mathcal{H}_{cf}}}$

$|\Gamma, \gamma\rangle$

Perturbation
$\mathcal{H}_{pert.}$

working w.f.

$|\Gamma, r\rangle \otimes |S, M_S\rangle$

$\overline{\text{spatial}}$
d.o.f

spin
d.o.f.

$|\Gamma', \gamma'\rangle \sim |\psi_{n'}\rangle$

$e\gamma$

$|\Gamma, r\rangle \sim |\psi_n\rangle$

$\mathcal{H}_{SO}$

$\overbrace{\hspace{5cm}}^{\mathcal{H}_Z}$
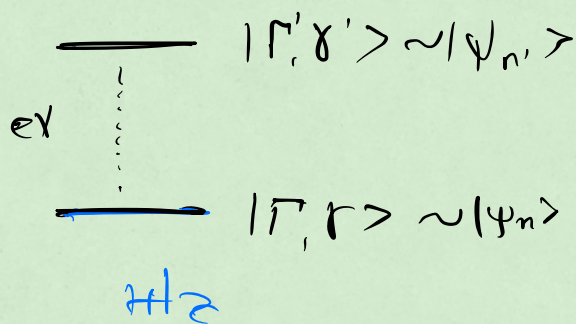
$$\mathcal{H}_{pert} = \lambda \, \hat{L} \cdot \hat{S} + \mu_B \, \vec{B} \cdot \hat{L} + \mu_B g_I \, \vec{B} \cdot \hat{S}$$

only
spin d.o.f

Perturbation theory (Nutshell!)

$$\mathcal{H} = \mathcal{H}_0 + \underline{\epsilon V} \quad \text{perturb.}$$

0th order $\quad H_0 |\psi_n\rangle = E_0^n |\psi_n\rangle$

1st order $\quad E^n = E_o^n + \epsilon \langle \psi_n | V | \psi_n \rangle$

2nd order $\quad E^n = E_o^n + \epsilon \langle \dots \rangle$

$$- \epsilon^2 \sum_{n' \neq n} \frac{|\langle \psi_{n'} | V | \psi_n \rangle|^2}{E_{n'} - E_n}$$

for our case $\quad \epsilon V = \lambda \, \hat{L} \cdot \hat{S} + \mu_B \, \vec{B} \cdot \hat{L}$

contributions to its Hamiltonian:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{ee}} + \mathcal{H}_{\text{cf}} + \mathcal{H}_{\text{so}} + \mathcal{H}_{\text{Z}}. \tag{2.19}$$

We express the orbital part of the wave function on the symmetry-adapted basis $|\Gamma, \gamma\rangle$, on which the leading free-ion contribution $\mathcal{H}_0$ and the crystal-field Hamiltonian $\mathcal{H}_{\text{cf}}$ are simultaneously diagonal. Concretely, the notation $|\Gamma, \gamma\rangle$ represents multi-electron configurations like those sketched in Fig. (2.4), including excited states. We would like to treat the spin-orbit and the Zeeman interactions,

$$\begin{aligned} \mathcal{H}_{\text{so}} &= \lambda \hat{\mathbf{S}} \cdot \hat{\mathbf{L}} \\ \mathcal{H}_{\text{Z}} &= \mu_B \left(\hat{\mathbf{L}} + g_s \hat{\mathbf{S}} \right) \cdot \vec{B}, \end{aligned} \tag{2.20}$$

as perturbations and project out the dependence on the orbital coordinates. The final goal is to obtain an effective Hamiltoninan that retains only the dependence on spin coordinates. For simplicity, we focus ourselves on an orbitally non-degenerate ground state defined by the multiplet $|\Gamma, \gamma, S, M_s\rangle = |\Gamma, \gamma\rangle \otimes |S, M_s\rangle$. The spin part of the Zeeman interaction acts only on spin coordinates and is not affected by the integration over orbital coordinates; therefore, we shall write it as it appears in the second line $(\mathcal{H}_{\text{Z}})$ of Eq. (2.20). The remaining parts of the Hamiltonians (2.20) depend on $\hat{\mathbf{L}}$ and do not give any correction to the energy of the ground-state to the first order of perturbation theory in the absence of orbital degeneracy (as assumed). To the second order of perturbation theory, instead, one has

$$\mathcal{H}_{\text{eff}} = g_s \mu_B \hat{\mathbf{S}} \cdot \vec{B} - \sum_{\Gamma', \gamma'} \frac{|\langle \Gamma', \gamma' | \mu_B \hat{\mathbf{L}} \cdot \vec{B} + \lambda \hat{\mathbf{S}} \cdot \hat{\mathbf{L}} | \Gamma, \gamma \rangle|^2}{E_{\Gamma', \gamma'} - E_{\Gamma, \gamma}}, \tag{2.21}$$

where the sum runs – in principle – over all the excited states $|\Gamma', \gamma'\rangle$ with energy $E_{\Gamma', \gamma'} > E_{\Gamma, \gamma}$. The square in Eq. (2.21) can be expanded to yield

$$\begin{aligned} \mathcal{H}_{\text{eff}} = g_s \mu_B \hat{\mathbf{S}} \cdot \vec{B} - 2\mu_B \lambda \sum_{\alpha, \nu} \Lambda_{\alpha\nu} B^\alpha \hat{S}^\nu \\ - \lambda^2 \sum_{\alpha, \nu} \Lambda_{\alpha\nu} \hat{S}^\alpha \hat{S}^\nu - \mu_B^2 \sum_{\alpha, \nu} \Lambda_{\alpha\nu} B^\alpha B^\nu \end{aligned} \tag{2.22}$$

with

$$\Lambda_{\alpha\nu} = \sum_{\Gamma', \gamma'} \frac{\langle \Gamma, \gamma | \hat{L}^\alpha | \Gamma', \gamma' \rangle \langle \Gamma', \gamma' | \hat{L}^\nu | \Gamma, \gamma \rangle}{E_{\Gamma', \gamma'} - E_{\Gamma, \gamma}}. \tag{2.23}$$

5. Treating the spin-orbit interaction at the second order of perturbation theory, the following *effective* spin Hamiltonian can be defined

$$\mathcal{H}_{\text{eff}} = \mu_B \sum_{\alpha,\nu} g_{\alpha\nu} B^\alpha \hat{S}^\nu - \sum_{\alpha,\nu} D_{\alpha\nu} \hat{S}^\alpha \hat{S}^\nu \qquad (1)$$

where

$$g_{\alpha\nu} = g_s \delta_{\alpha\nu} - 2\lambda \Lambda_{\alpha\nu} \qquad \text{and} \qquad D_{\alpha\nu} = \lambda^2 \Lambda_{\alpha\nu} \qquad (2)$$
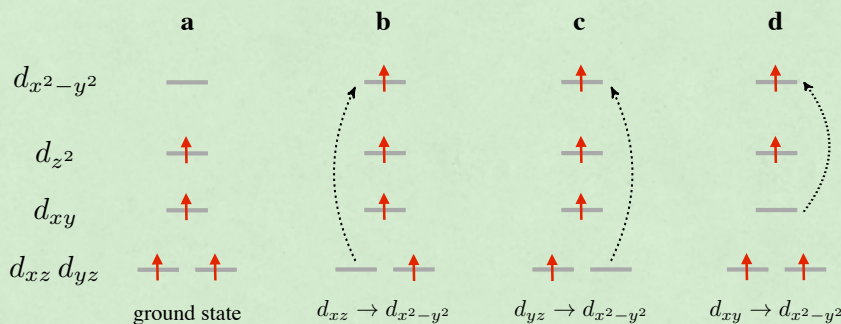
are the g-tensor (or Landé tensor) and the magnetic-anisotropy tensor. Within the subspace $S = 2$ the only non-zero matrix elements are

$$\Lambda_{xx} = \frac{|\langle d_{yz}|\hat{L}^x|d_{x^2-y^2}\rangle|^2}{\Delta E(d_{yz} \to d_{x^2-y^2})}$$

$$\Lambda_{yy} = \frac{|\langle d_{xz}|\hat{L}^y|d_{x^2-y^2}\rangle|^2}{\Delta E(d_{xz} \to d_{x^2-y^2})} \qquad (3)$$

$$\Lambda_{zz} = \frac{|\langle d_{xy}|\hat{L}^z|d_{x^2-y^2}\rangle|^2}{\Delta E(d_{xy} \to d_{x^2-y^2})},$$

with

$$|\langle d_{yz}|\hat{L}^x|d_{x^2-y^2}\rangle|^2 = 1$$
$$|\langle d_{xz}|\hat{L}^y|d_{x^2-y^2}\rangle|^2 = 1 \qquad (4)$$
$$|\langle d_{xy}|\hat{L}^z|d_{x^2-y^2}\rangle|^2 = 4$$
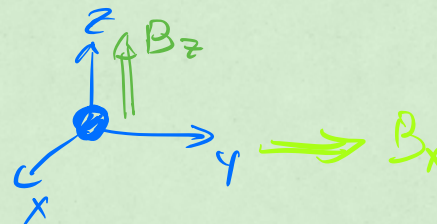
associated with the transitions sketched in the Figure. Assuming the values $\Delta E(d_{xy} \to d_{x^2-y^2}) = 18000$ cm^{-1}, $\Delta E(d_{xz} \to d_{x^2-y^2}) = \Delta E(d_{yz} \to d_{x^2-y^2}) = 21000$ cm^{-1} and the spin-orbit coupling constant is $\lambda = 90$ cm^{-1}, determine the components of the g-tensor $g_{xx} = g_{yy}$ and g_{zz}; compute the value of the uniaxial anisotropy parameter $D = D_{zz} - D_{xx}$.

	a	b	c	d
$d_{x^2-y^2}$				
d_{z^2}				
d_{xy}				
$d_{xz}\, d_{yz}$				
	ground state	$d_{xz} \to d_{x^2-y^2}$	$d_{yz} \to d_{x^2-y^2}$	$d_{xy} \to d_{x^2-y^2}$

$g_{xx} = g_{yy} = 1.99$

$g_{zz} = 1.96$

2

$H_{\text{An.}} = -\hat{S}\begin{pmatrix} D_{xx} & & \\ & D_{yy} & \\ & & D_{zz} \end{pmatrix}\hat{S}$

Mag. Anisotropy Energy

$$\mathcal{H} = -\hat{S} \underline{\underline{D}} \, \hat{S} = -D(\hat{S}^z)^2 + \text{const.}$$

<u>Single ion Hamiltonian for TMs</u>

⊛ $\mathcal{H} = -D(\hat{S}^z)^2 - \mu_B B \, \underline{\underline{g}} \, \hat{S}$

$$\begin{pmatrix} D & & \\ & D & \\ & & D \end{pmatrix} = \begin{pmatrix} D_k & & \\ & D_\perp & \\ & & D_{zz} \end{pmatrix} - \mathbb{1} D_\perp$$

Effective ⊛
Hamiltonian

$$\mathcal{H} = -2 \, \boxed{J} \, \hat{S}_i \cdot \hat{S}_j$$

J_{inter} = interatomic
exchange
interaction

Heitler-London (HL) model 1

The Hamiltonian: $\mathcal{H}_{\mathrm{H}_2} = \mathcal{H}_a + \mathcal{H}_b + \mathcal{H}_{\mathrm{ee}} + \mathcal{H}_{\mathrm{NN}} + \mathcal{H}_{1b} + \mathcal{H}_{2a}$

The HL trial wave functions are

$$\Psi^{\mathrm{T}}(\underline{r}_1, \underline{r}_2) = \frac{1}{\sqrt{2(1-S^2)}} \left[\psi_{1s}(\underline{r}_{1a})\psi_{1s}(\underline{r}_{2b}) - \psi_{1s}(\underline{r}_{1b})\psi_{1s}(\underline{r}_{2a}) \right]$$

$$\Psi^{\mathrm{S}}(\underline{r}_1, \underline{r}_2) = \frac{1}{\sqrt{2(1+S^2)}} \left[\psi_{1s}(\underline{r}_{1a})\psi_{1s}(\underline{r}_{2b}) + \psi_{1s}(\underline{r}_{1b})\psi_{1s}(\underline{r}_{2a}) \right]$$

where S is the *overlap integral*

$$S = \langle \psi_{1s}(\underline{r}_{1a}) | \psi_{1s}(\underline{r}_{1b}) \rangle = \langle \psi_{1s}(\underline{r}_{2b}) | \psi_{1s}(\underline{r}_{2a}) \rangle = \int \psi_{1s}(\underline{r}_{1a}) \psi_{1s}(\underline{r}_{1b}) \, d^3 r_1$$

The expectation value of the Hamiltonian $\mathcal{H}_{\mathrm{H}_2}$ evaluated on the trial wave functions is

$$E^{\mathrm{T}} = \langle \Psi^{\mathrm{T}} | \mathcal{H}_{\mathrm{H}_2} | \Psi^{\mathrm{T}} \rangle = 2E_{1s} + \frac{Q - X}{1 - S^2}$$

$$E^{\mathrm{S}} = \langle \Psi^{\mathrm{S}} | \mathcal{H}_{\mathrm{H}_2} | \Psi^{\mathrm{S}} \rangle = 2E_{1s} + \frac{Q + X}{1 + S^2} \, .$$

Heitler-London (HL) model 2

The *Coulomb* integral reads

$$
\begin{aligned}
Q &= \langle \psi_{1s}(\underline{r}_{1a})\psi_{1s}(\underline{r}_{2b})| \left[\mathcal{H}_{\mathrm{NN}} + \mathcal{H}_{\mathrm{ee}} + \mathcal{H}_{1b} + \mathcal{H}_{2a} \right] |\psi_{1s}(\underline{r}_{1a})\psi_{1s}(\underline{r}_{2b})\rangle \\
&= \frac{e^2}{4\pi\epsilon_0} \left\{ \frac{1}{R} + \langle \psi_{1s}(\underline{r}_{1a})\psi_{1s}(\underline{r}_{2b})| \frac{1}{r_{12}} |\psi_{1s}(\underline{r}_{1a})\psi_{1s}(\underline{r}_{2b})\rangle \right. \\
&\quad \left. - \langle \psi_{1s}(\underline{r}_{1a})| \frac{1}{r_{1b}} |\psi_{1s}(\underline{r}_{1a})\rangle - \langle \psi_{1s}(\underline{r}_{2b})| \frac{1}{r_{2a}} |\psi_{1s}(\underline{r}_{2b})\rangle \right\} .
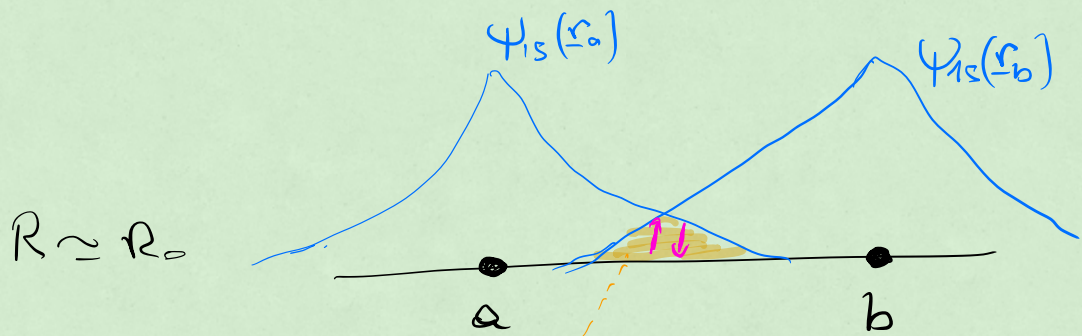\end{aligned} \tag{1}
$$

The *exchange* integral reads

$$
\begin{aligned}
X &= \langle \psi_{1s}(\underline{r}_{1a})\psi_{1s}(\underline{r}_{2b})| \left[\mathcal{H}_{\mathrm{NN}} + \mathcal{H}_{\mathrm{ee}} + \mathcal{H}_{1b} + \mathcal{H}_{2a} \right] |\psi_{1s}(\underline{r}_{1b})\psi_{1s}(\underline{r}_{2a})\rangle \\
&= \frac{e^2}{4\pi\epsilon_0} \left\{ \frac{S^2}{R} + \langle \psi_{1s}(\underline{r}_{1a})\psi_{1s}(\underline{r}_{2b})| \frac{1}{r_{12}} |\psi_{1s}(\underline{r}_{1b})\psi_{1s}(\underline{r}_{2a})\rangle \right. \\
&\quad \left. - S \langle \psi_{1s}(\underline{r}_{1a})| \frac{1}{r_{1b}} |\psi_{1s}(\underline{r}_{1b})\rangle - S \langle \psi_{1s}(\underline{r}_{2b})| \frac{1}{r_{2a}} |\psi_{1s}(\underline{r}_{2a})\rangle \right\} .
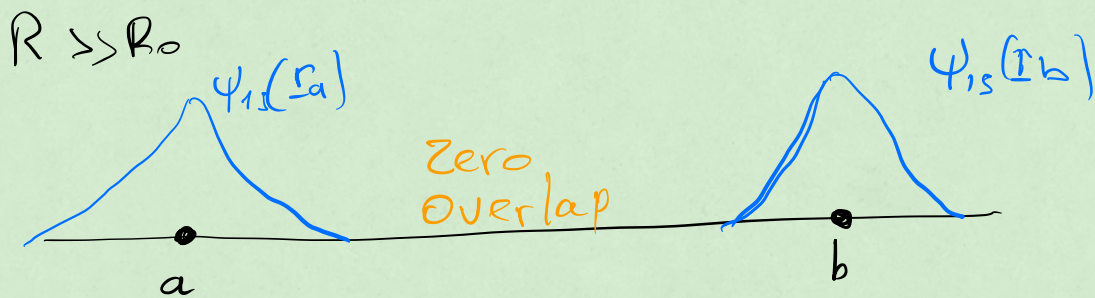\end{aligned} \tag{2}
$$

Heitler-London (HL) singlet-triplet splitting
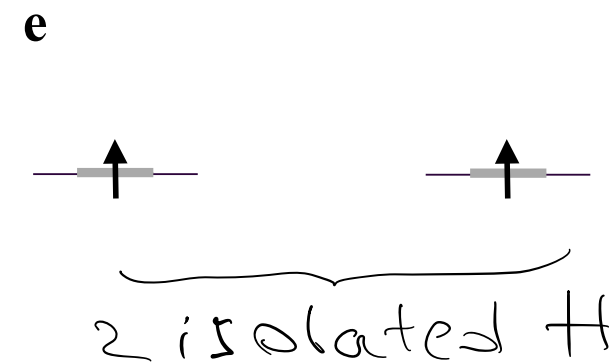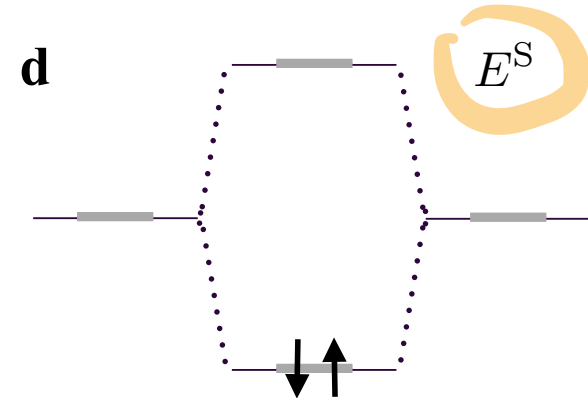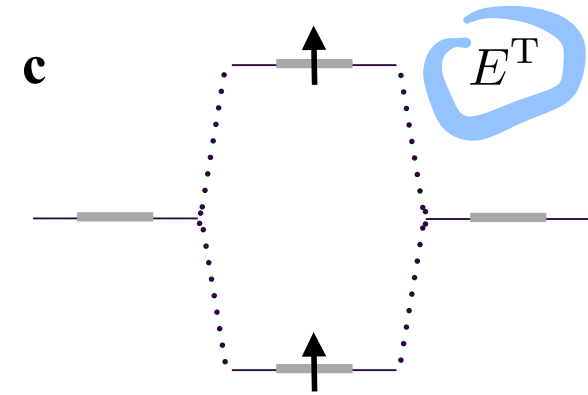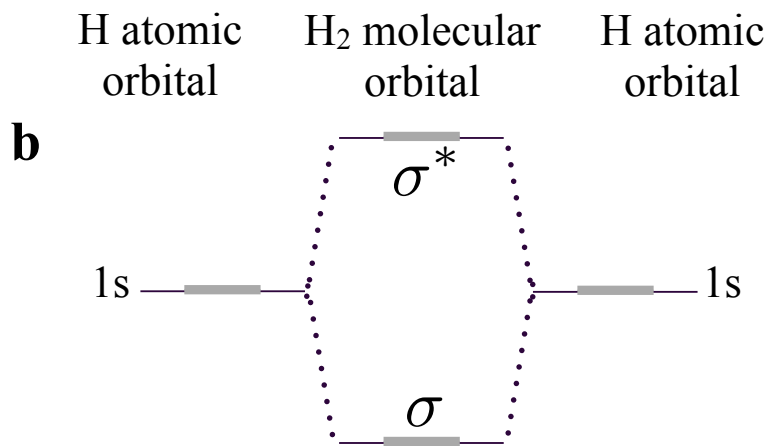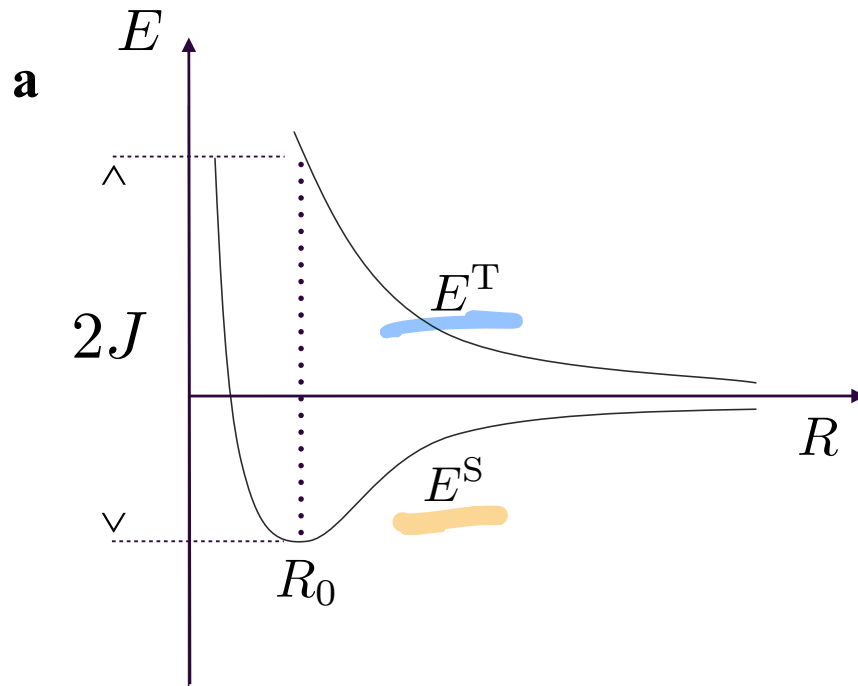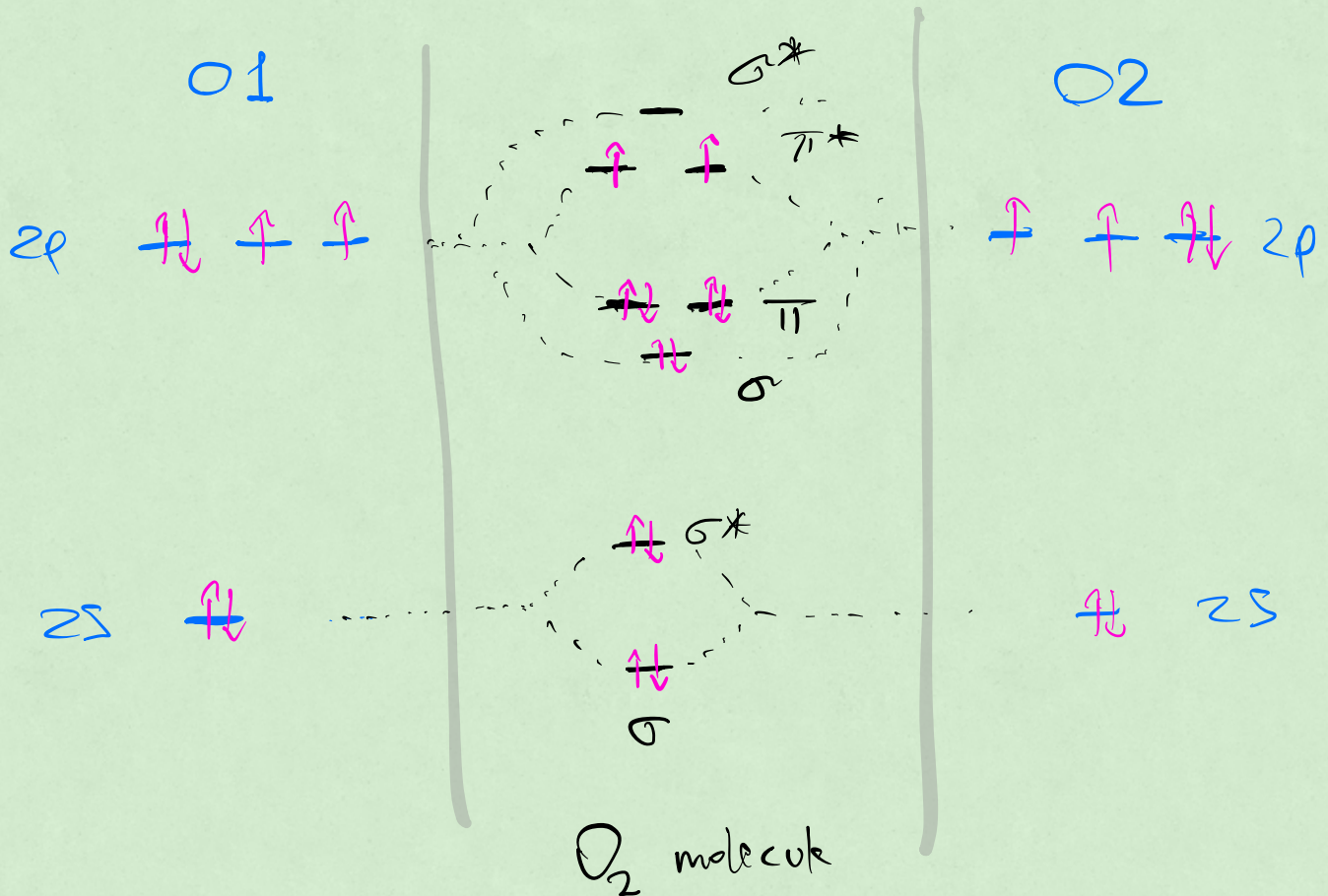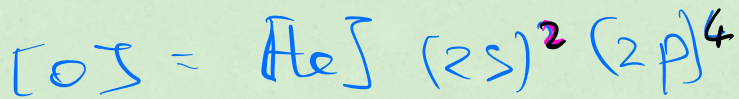
Intuitive view Overlap Integral

$\psi_{1s}(r_a)$

$\psi_{1s}(r_b)$

$R \simeq R_0$

a

b

Overlap region "in which, roughly
speaking, we may expect a "weak Pauli
Principle" to occur.

$R \gg R_0$

$\psi_{1s}(r_a)$

Zero
Overlap

$\psi_{1s}(r_b)$

a

b

$LCMO$

Linear Combination of Molecular Orbitals

O_2

$$[O] = [He] (2s)^2 (2p)^4$$

O1

O2

O_2 molecule

$S = 1$

Chemical bond does not always act against Magnetism!