Multiplets in transition metal ions and introduction to multiband Hubbard models

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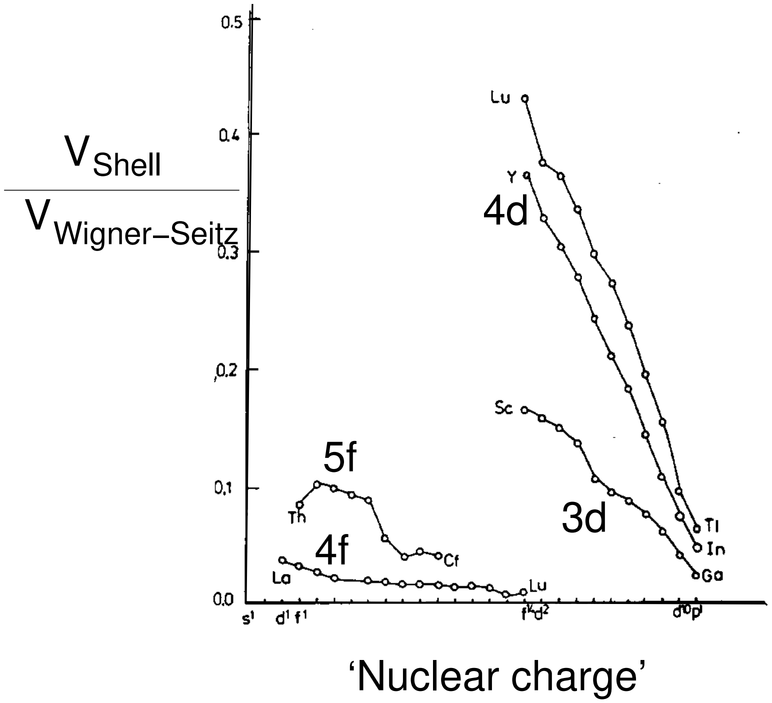
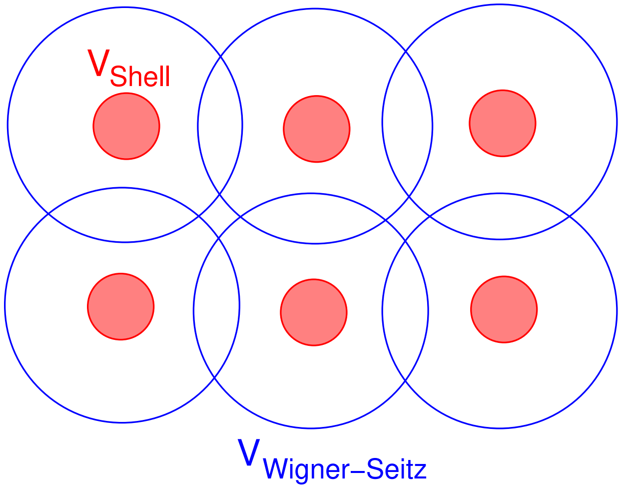
3d and 4f transition metals and their compounds - a sure bet for spectacular physics...

- Metallic Ferromagnets like Fe, Co, Ni
- Mott insulators like NiO
- Heavy Fermion compounds such as CeCoIn_5
- High temperature superconductors such as copper oxide superconductors or iron pnictide superconductors
- and many more......

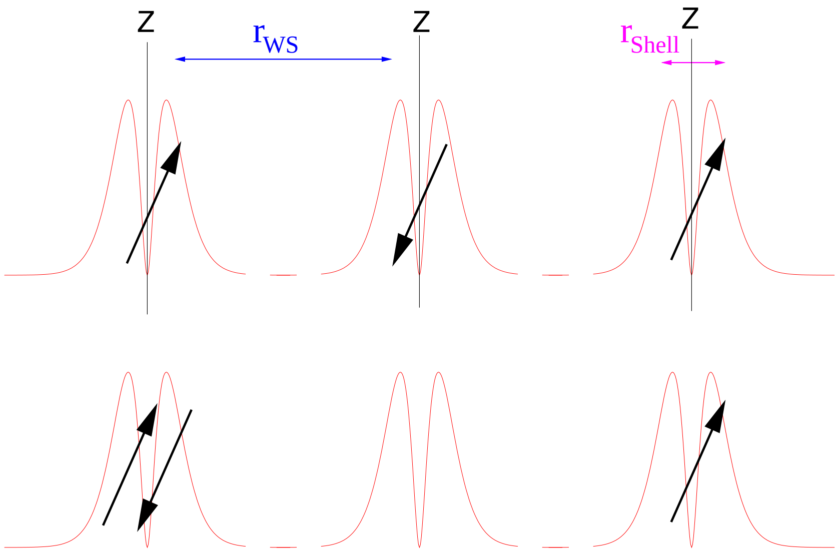
The reason for these phenomena: Small radius of the $3d$ or $4f$ shell





Taken from: D. van der Marel and G. A. Sawatzky, Physical Review B **37**, 10674 (1988)

The small radius of these shells enhances the Coulomb repulsion between electrons in these shells



Up to 10eV increase in energy!

The reason for exotic physics: strong Coulomb interaction in partly filled atomic shells
- let us discuss this

Coulomb interaction between electrons - Simplest guess

The simplest guess for the energy of d^n would be

$$E[d^n] \approx n \cdot \epsilon_d + U \cdot \frac{n(n-1)}{2}.$$

ϵ_d: Energy of the d-orbital

U: Average Coulomb energy for a pair of electrons

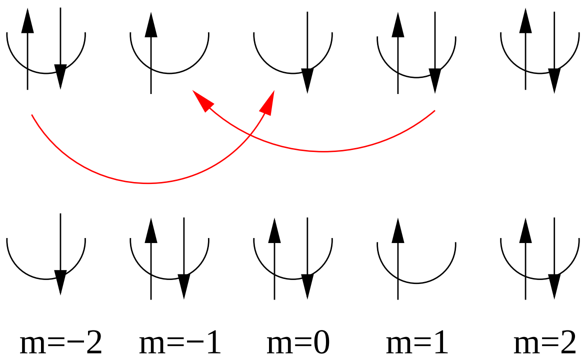
For a nondegenerate orbital we have

	$\vert 0\rangle$	$\vert\uparrow\rangle$	$\vert\downarrow\rangle$	$\vert\uparrow\downarrow\rangle$
n	0	1	1	2
E_C	0	0	0	U

This is equivalent to $H = Un_\uparrow\, n_\downarrow$ - see Hubbard model or Anderson model

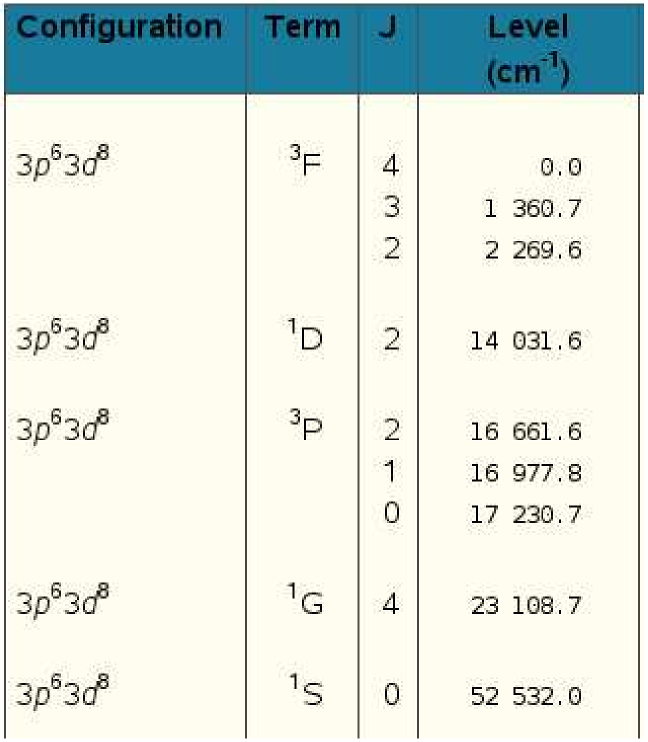
However, for a degenerate orbital there are additional aspects.....

Coulomb scattering within an atomic shell



- Electrons in a partially filled shell scatter from each other due to their Coulomb interaction
- For L^z to be conserved the scattering electrons must 'move along the m-ladder' in exactly opposite ways
- The Coulomb interaction between electrons in partially filled atomic shells gives rise to multiplet splitting

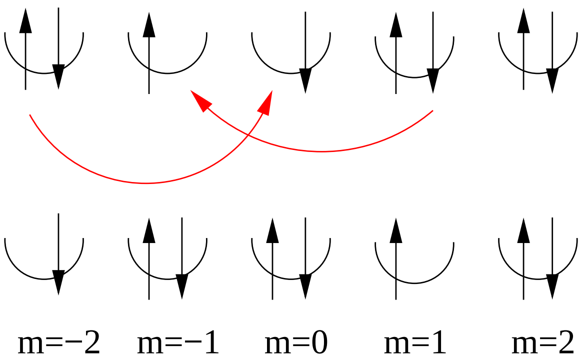
- We consider an Ni^{2+}-ion in vacuum - it has electron configuration $[Ar]\ 3d^8$
- From textbooks of atomic physics we know that d^8 has the multiplets (or terms) ^{3}F, ^{3}P, ^{1}G, ^{1}D and ^1S
- This is what they look like in experiment (taken from NIST database):



Configuration	Term	J	Level (cm^{-1})
$3p^63d^8$	^{3}F	4	0.0
		3	1 360.7
		2	2 269.6
$3p^63d^8$	^{1}D	2	14 031.6
$3p^63d^8$	^{3}P	2	16 661.6
		1	16 977.8
		0	17 230.7
$3p^63d^8$	^{1}G	4	23 108.7
$3p^63d^8$	^{1}S	0	52 532.0

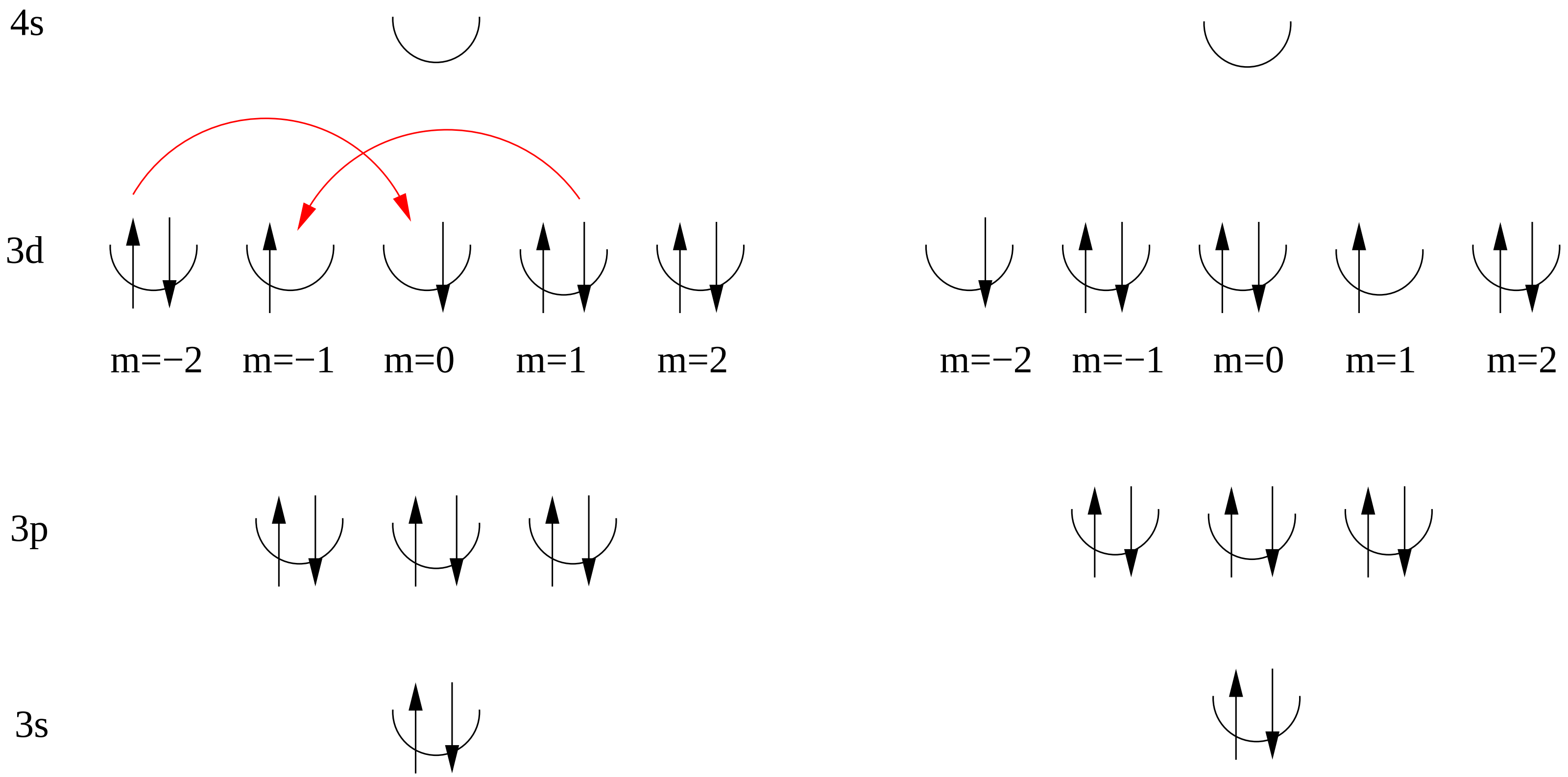
The splitting of the multiplets is caused by the Coulomb interaction between electrons

Coulomb scattering within an atomic shell

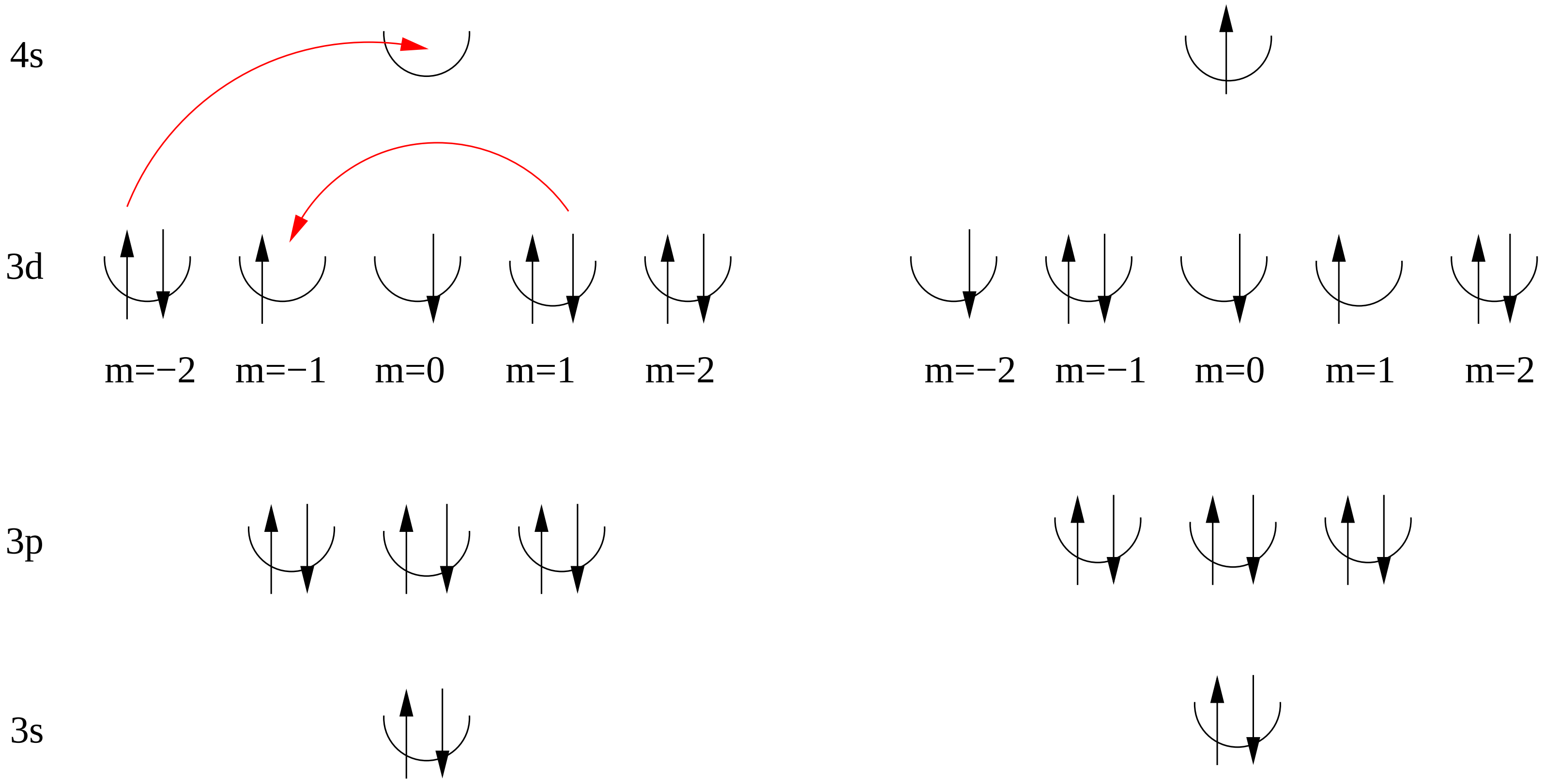


- Electrons in a partially filled shell scatter from each other due to their Coulomb interaction
- For L^z to be conserved the scattering electrons must ‘move along the m-ladder’ in exactly opposite ways

We take into account processes like this one...



We do not take into account processes like this one...



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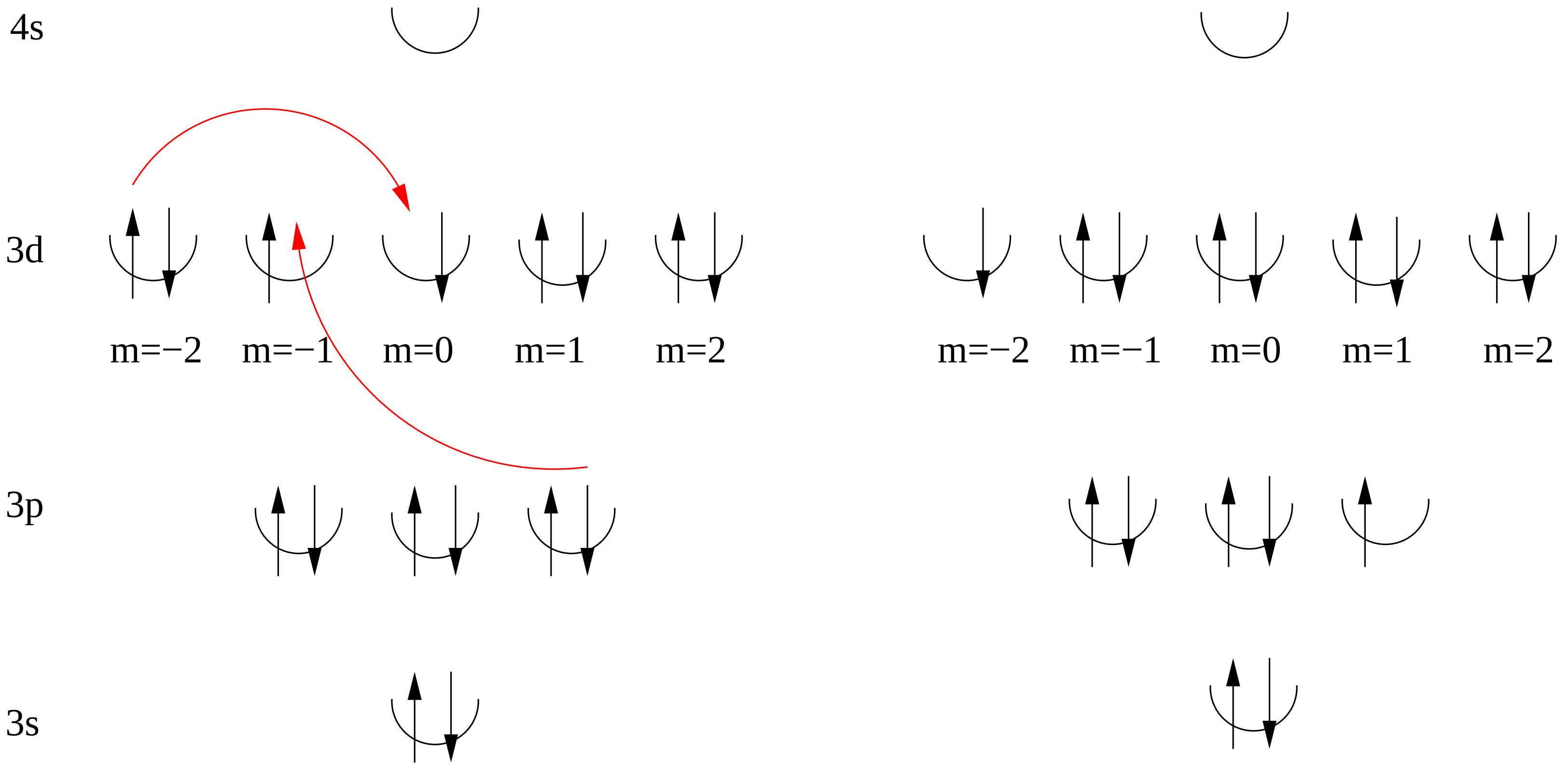

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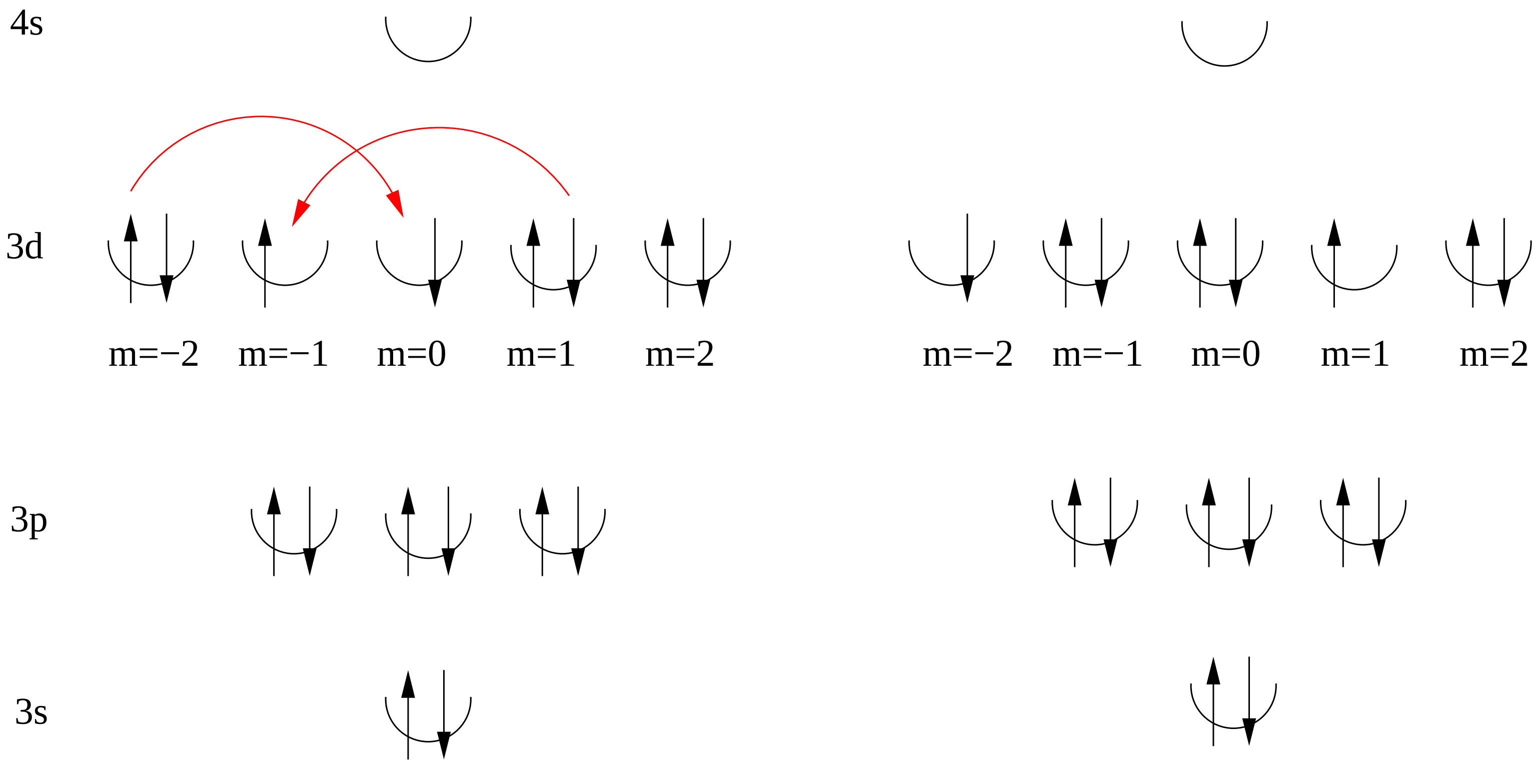

- The states which are mixed by the Coulomb scattering all have the same orbital energy $n\ \epsilon_{3d}$
- If we consider the orbital energy as H_0, the Coulomb interaction as perturbation H_1, we have the textbook situation of degenerate 1^{st} order perturbation theory

The textbook procedure to deal with this is as follows:

- Find all degenerate states $|\nu\rangle$ of d^{n}
- Set up the secular matrix $\langle\mu|H_1|\nu\rangle$ - H_1 is the Coulomb interaction
- Diagonalize it to obtain the 1st order energies and wave functions
- These are the energies and wave functions of the multiplets

Basis functions

As basis funtions we use atomic orbitals ($x = (\boldsymbol{r}, \sigma)$, $\boldsymbol{r} \rightarrow (r, \Theta, \phi)$)

$$\psi_{n_i,l_i,m_i,\sigma_i}(x) \;=\; R_{n_i,l_i}(r)\; Y_{l_i,m_i}(\Theta,\phi)\; \delta_{\sigma,\sigma_i}$$

- n_i - Principal quantum number ($n_i = 3$ for 3d-shell)
- l_i - Total orbital angular momentum quantum number ($l_i = 2$ for 3d-shell)
- m_i - z-component of orbital angular momentum ($-l_i \leq m_i \leq l_i$)
- σ_i - z-component of spin $\sigma_i = \pm\frac{1}{2}$

We will often use the 'compound index' ν_i

$$(n_i, l_i, m_i, \sigma_i) = \nu_i$$

so that we write for example

$$\psi_{n_i,l_i,m_i,\sigma_i}(x) \rightarrow \psi_{\nu_i}(x)$$

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Coulomb interaction in second quantization

We pass to second quantization and introduce Fermionic creation/annihilation operators: $c^\dagger_{\nu_i} = c^\dagger_{n_i,l_i,m_i,\sigma_i}$

The Coulomb Hamiltonian becomes (see e.g. Fetter-Walecka or Negele-Orland)

$$H_1 \;=\; \frac{1}{2} \sum_{i,j,k,l} V(\nu_i, \nu_j, \nu_k, \nu_l) \;\; c^\dagger_{\nu_i} \, c^\dagger_{\nu_j} \, c_{\nu_k} \, c_{\nu_l}$$

$$V(\nu_1, \nu_2, \nu_3, \nu_4) \;=\; \int dx \int dx' \; \psi^*_{\nu_1}(x) \; \psi^*_{\nu_2}(x') \, \frac{e^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \;\; \psi_{\nu_4}(x) \; \psi_{\nu_3}(x')$$

$$\int dx \ldots \;=\; \sum_{\sigma} \int d\boldsymbol{r} \ldots$$

We need to calculate

$$V(\nu_1,\nu_2,\nu_3,\nu_4) \;=\; \int dx \int dx' \;\psi^*_{\nu_1}(x)\;\psi^*_{\nu_2}(x')\;\;\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}\;\;\psi_{\nu_4}(x)\;\psi_{\nu_3}(x')$$

Now insert

$$\psi^*_{\nu_1}(x)\;\psi^*_{\nu_2}(x') \;=\; R_{n_1,l_1}(r)\;Y^*_{l_1,m_1}(\Theta,\phi)\;\delta_{\sigma,\sigma_1}\quad R_{n_2,l_2}(r')\;Y^*_{l_2,m_2}(\Theta',\phi')\;\delta_{\sigma',\sigma_2}$$

$$\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|} \;=\; \sum_{k=0}^{\infty}\sum_{m=-k}^{k} Y_{k,m}\,(\Theta,\phi)\;\;\frac{4\pi e^2}{2k+1}\,\frac{r_<^k}{r_>^{k+1}}\quad Y^*_{k,m}\,(\Theta',\phi')$$

$$\psi_{\nu_4}(x)\;\psi_{\nu_3}(x') \;=\; R_{n_4,l_4}(r)\;Y_{l_4,m_4}(\Theta,\phi)\;\delta_{\sigma,\sigma_4}\quad R_{n_3,l_3}(r')\;Y_{l_3,m_3}(\Theta',\phi')\;\delta_{\sigma',\sigma_3}$$

We need to calculate

$$V(\nu_1,\nu_2,\nu_3,\nu_4) \;=\; \int dx \int dx' \;\psi^*_{\nu_1}(x)\;\psi^*_{\nu_2}(x')\;\; \frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}\;\; \psi_{\nu_4}(x)\;\psi_{\nu_3}(x')$$

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Spin-sum over σ

$$\sum_{\sigma} \delta_{\sigma\;,\sigma_1}\delta_{\sigma\;,\sigma_4} = \delta_{\sigma_1,\sigma_4}$$

We need to calculate

$$V(\nu_1,\nu_2,\nu_3,\nu_4) \;=\; \int dx \int dx'\; \psi^*_{\nu_1}(x)\; \psi^*_{\nu_2}(x')\;\; \frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}\;\; \psi_{\nu_4}(x)\; \psi_{\nu_3}(x')$$

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Spin-sum over σ'

$$\sum_{\sigma'} \delta_{\sigma',\sigma_2}\delta_{\sigma',\sigma_3} = \delta_{\sigma_2,\sigma_3}$$

We need to calculate

$$V(\nu_1,\nu_2,\nu_3,\nu_4) \;=\; \int dx \int dx'\; \psi^*_{\nu_1}(x)\;\psi^*_{\nu_2}(x')\;\; \frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}\;\; \psi_{\nu_4}(x)\;\psi_{\nu_3}(x')$$

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(Θ,ϕ)-Integration

$$\sqrt{\frac{4\pi}{2k+1}}\int d\Omega\;\; Y^*_{l_1,m_1}(\Theta,\phi)\;\; Y_{k,m}(\Theta,\phi)\;\; Y_{l_4,m_4}(\Theta,\phi)$$

We need to calculate

$$V(\nu_1,\nu_2,\nu_3,\nu_4) \;=\; \int dx \int dx' \; \psi^*_{\nu_1}(x)\; \psi^*_{\nu_2}(x') \;\; \frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|} \;\; \psi_{\nu_4}(x)\; \psi_{\nu_3}(x')$$

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(Θ',ϕ')-Integration

$$\sqrt{\frac{4\pi}{2k+1}} \int d\Omega' \;\; Y^*_{l_2,m_2}(\Theta',\phi') \;\; Y^*_{k,m}(\Theta',\phi') \;\; Y_{l_3,m_3}(\Theta',\phi')$$

We need to calculate

$$V(\nu_1,\nu_2,\nu_3,\nu_4) \;=\; \int dx \int dx' \; \psi^*_{\nu_1}(x)\;\psi^*_{\nu_2}(x')\;\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}\;\psi_{\nu_4}(x)\;\psi_{\nu_3}(x')$$

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(r,r')-Integration

$$R^k(n_1l_1,n_2l_2,n_3l_3,n_4l_4) = e^2\int_0^\infty dr\;r^2\int_0^\infty dr'\;r'^2\;R_{n_1,l_1}(r)\;R_{n_2,l_2}(r')\;\frac{r_<^k}{r_>^{k+1}}\;R_{n_4,l_4}(r)\;R_{n_3,l_3}(r')$$

Note: R^k does not involve any m and has the dimension of energy

For scattering within - say - the 3d-shell all (n_i,l_i) are equal: $n_i=3,\; l_i=2$

Gaunt coefficients

In calculating the Coulomb matrix elements we had obtained integrals over three spherical harmonics

$$\sqrt{\frac{4\pi}{2k+1}}\int d\Omega\;\; Y^*_{l_1,m_1}(\Theta,\phi)\;\; Y_{k,m}(\Theta,\phi)\;\; Y_{l_4,m_4}(\Theta,\phi)$$

These are called Gaunt coefficients

We now use the fact that $Y_{l,m}(\Theta,\phi) = P_{l,m}(\Theta)\; e^{im\phi}$ with $P_{l,m}(\Theta)$ real (e.g.: Landau-Lifshitz):

$$\int d\Omega\;\; Y^*_{l_1,m_1}(\Theta,\phi)\;\; Y_{k,m}(\Theta,\phi)\;\; Y_{l_4,m_4}(\Theta,\phi) \;\;\propto\;\; \int_0^{2\pi} e^{i(m_4+m-m_1)\;\phi}\;\; d\phi = 2\pi\;\; \delta_{m,m_1-m_4}$$

This is real and the remaining factor of $\int d\Theta\; P_{l_1,m_1}(\Theta)\;\; P_{k,m}(\Theta)\;\; P_{l_4,m_4}(\Theta)$ is real as well

$\rightarrow$ all Gaunt coefficients are real

Reminder:

$$\int d\Omega \;\; Y^*_{l_1,m_1}(\Theta,\phi) \;\; Y_{k,m}(\Theta,\phi) \;\; Y_{l_4,m_4}(\Theta,\phi) \;\; \propto \;\; \int_0^{2\pi} e^{i(m_4+m-m_1)\,\phi} d\phi = 2\pi \;\; \delta_{m,m_1-m_4}$$

We introduce a shorthand notation for Gaunt coefficients

$$\sqrt{\frac{4\pi}{2k+1}} \int d\Omega \;\; Y^*_{l_1,m_1}(\Theta,\phi) \;\; Y_{k,m_1-m_4}(\Theta,\phi) \;\; Y_{l_4,m_4}(\Theta,\phi) \;\; = \;\; c^k(l_1,m_1;l_4,m_4)$$

$$\rightarrow \sqrt{\frac{4\pi}{2k+1}} \int d\Omega \;\; Y^*_{l_1,m_1}(\Theta,\phi) \qquad Y_{k,m}(\Theta,\phi) \qquad Y_{l_4,m_4}(\Theta,\phi) \;\; = \;\; \delta_{m,m_1-m_4} \;\; c^k(l_1,m_1;l_4,m_4)$$

The factor from the (Θ',ϕ') integration was

$$\sqrt{\frac{4\pi}{2k+1}} \int d\Omega' \;\; Y^*_{l_2,m_2}(\Theta',\phi') \;\; Y^*_{k,m}(\Theta',\phi') \;\; Y_{l_3,m_3}(\Theta',\phi')$$

$$= \;\; \sqrt{\frac{4\pi}{2k+1}} \int d\Omega' \;\; Y^*_{l_3,m_3}(\Theta',\phi') \;\; Y_{k,m}(\Theta',\phi') \;\; Y_{l_2,m_2}(\Theta',\phi')$$

$$= \quad \delta_{m,m_3-m_2} \;\; c^k(l_3,m_3;l_2,m_2)$$

Collecting everything:

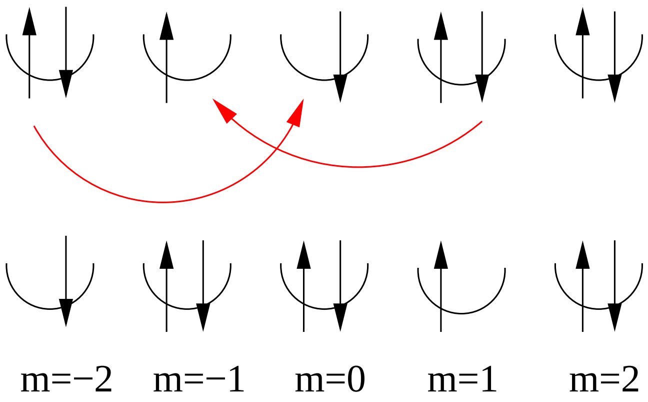
$$
\begin{aligned}
V(\nu_1,\nu_2,\nu_3,\nu_4) &= \int dx \int dx' \, \psi^*_{\nu_1}(x)\, \psi^*_{\nu_2}(x') \, \frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|} \, \psi_{\nu_4}(x)\, \psi_{\nu_3}(x') \\
&= \delta_{\sigma_1,\sigma_4}\, \delta_{\sigma_2,\sigma_3} \sum_{k=0}^{\infty} \sum_{m=-k}^{k} \delta_{m,m_1-m_4} \;\; c^k(l_1,m_1;l_4,m_4) \;\; \delta_{m,m_3-m_2} \;\; c^k(l_3,m_3;l_2,m_2) \\
&\qquad\qquad R^k(n_1l_1,n_2l_2,n_3l_3,n_4l_4) \\
&= \delta_{\sigma_1,\sigma_4}\, \delta_{\sigma_2,\sigma_3} \sum_{k=0}^{\infty} \delta_{m_1+m_2,m_3+m_4} \;\; c^k(l_1,m_1;l_4,m_4) \;\; c^k(l_3,m_3;l_2,m_2) \\
&\qquad\qquad R^k(n_1l_1,n_2l_2,n_3l_3,n_4l_4)
\end{aligned}
$$

with

$$
c^k(l_1,m_1;l_4,m_4) = \sqrt{\frac{4\pi}{2k+1}} \int d\Omega \;\; Y^*_{l_1,m_1}(\Theta,\phi) \;\; Y_{k,m_1-m_4}(\Theta,\phi) \;\; Y_{l_4,m_4}(\Theta,\phi)
$$

$$
R^k(n_1l_1,n_2l_2,n_3l_3,n_4l_4) = e^2 \int_0^{\infty} dr\; r^2 \int_0^{\infty} dr'\; r'^2 \, R_{n_1,l_1}(r)\, R_{n_2,l_2}(r') \, \frac{r_<^k}{r_>^{k+1}} \, R_{n_4,l_4}(r)\, R_{n_3,l_3}(r')
$$

Reminder:



Collecting everything:

$$
\begin{aligned}
V(\nu_1,\nu_2,\nu_3,\nu_4) &= \int dx \int dx' \; \psi^*_{\nu_1}(x)\; \psi^*_{\nu_2}(x') \; \frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|} \; \psi_{\nu_4}(x)\; \psi_{\nu_3}(x') \\
&= \delta_{\sigma_1,\sigma_4}\, \delta_{\sigma_2,\sigma_3} \sum_{k=0}^{\infty} \sum_{m=-k}^{k} \delta_{m,m_1-m_4}\;\; c^k(l_1,m_1;l_4,m_4)\;\; \delta_{m,m_3-m_2}\;\; c^k(l_3,m_3;l_2,m_2) \\
&\qquad R^k(n_1 l_1, n_2 l_2, n_3 l_3, n_4 l_4) \\
&= \delta_{\sigma_1,\sigma_4}\, \delta_{\sigma_2,\sigma_3} \sum_{k=0}^{\infty} \delta_{m_1+m_2,m_3+m_4}\;\; c^k(l_1,m_1;l_4,m_4)\;\; c^k(l_3,m_3;l_2,m_2)\;\; R^k(n_1 l_1, n_2 l_2, n_3 l_3, n_4
\end{aligned}
$$

with

$$
c^k(l_1,m_1;l_4,m_4) = \sqrt{\frac{4\pi}{2k+1}} \int d\Omega \;\; Y^*_{l_1,m_1}(\Theta,\phi)\;\; Y_{k,m_1-m_4}(\Theta,\phi)\;\; Y_{l_4,m_4}(\Theta,\phi)
$$

$$
R^k(n_1 l_1, n_2 l_2, n_3 l_3, n_4 l_4) = e^2 \int_0^\infty dr\; r^2 \int_0^\infty dr'\; r'^2\; R_{n_1,l_1}(r)\; R_{n_2,l_2}(r')\; \frac{r_<^k}{r_>^{k+1}}\; R_{n_4,l_4}(r)\; R_{n_3,l_3}(r')
$$

Conditions on nonvanishing Gaunt coefficients I: Triangular condition

The Wigner-Eckart theorem tells us that Gaunt coefficients are proportional to Clebsch-Gordan coefficients:

$$\sqrt{\frac{4\pi}{2k+1}} \int d\Omega \;\; Y^*_{l_1,m_1}(\Theta,\phi) \;\; Y_{k,m}(\Theta,\phi) \;\; Y_{l_4,m_4}(\Theta,\phi) \propto \langle l_1, m_1 | k, m, l_4, m_4 \rangle$$

The three angular momenta in a Clebsch-Gordan coefficient have to obey the triangular condition: $l_1 \leq l_2 + l_3$

It follows that ...

$$I = \sqrt{\frac{4\pi}{2k+1}} \int d\Omega \;\; Y^*_{l_1,m_1}(\Theta,\phi) \;\; Y_{k,m}(\Theta,\phi) \;\; Y_{l_4,m_4}(\Theta,\phi)$$

... is different from zero only if $k \leq l_1 + l_4$

For Coulomb scattering in a d-shell this means $k \leq 4$, in a p-shell $k \leq 2$

Conditions on nonvanishing Gaunt coefficients II: Parity

$$I = \sqrt{\frac{4\pi}{2k+1}} \int d\Omega \;\; Y^*_{l_1,m_1}(\Theta,\phi) \;\; Y_{k,m}(\Theta,\phi) \;\; Y_{l_4,m_4}(\Theta,\phi)$$

- The parity of $Y_{l,m}$ is $(-1)^l$ (e.g.: Landau-Lifshitz)
- For $I \neq 0$ the integrand must have even parity
- It follows that $l_1 + k + l_4$ must be even
- For Coulomb scattering within an atomic shell we have $l_1 = l_4 \rightarrow k$ must be even

For Coulomb scattering in a d-shell our final result is:

$$V(\nu_1,\nu_2,\nu_3,\nu_4) \;=\; \delta_{\sigma_1,\sigma_4}\,\delta_{\sigma_2,\sigma_3} \sum_{k\in\{0,2,4\}} \delta_{m_1+m_2,m_3+m_4}\, c^k(l_1,m_1;l_4,m_4)\, c^k(l_3,m_3;l_2,m_2)\; R^k(n_1l_1,n_2l_2,n_3l_3,n_4l_4)$$

- The radial wave function $R_{3,2}(r)$ enters only via the three integrals R^0, R^2 and R^4
- These may be viewed as ‘Hubbard-U for k-pole interaction’
- In many applications they are computed from Hartree-Fock wave functions for free atoms/ions
- The nonvanishing $c^k(l_1,m_1;l_4,m_4)$ are few in number and tabulated in textbooks

The textbook procedure to deal with this is as follows:

- Find all degenerate states $|\nu\rangle$ of d^n
- Set up the secular determinant $\langle\mu|H_1|\nu\rangle$ - H_1 is the Coulomb interaction
- Diagonalize it to obtain the 1st order energies and wave functions
- These are the energies and wave functions of the multiplets

Basis states and Fermi statistics

We define the basis states for d^n (Reminder: $\nu_i = (n_i, l_i, m_i, \sigma_i)$)

$$|\nu_1, \nu_2 \ldots \nu_n\rangle = c^\dagger_{\nu_1} c^\dagger_{\nu_2} \ldots c^\dagger_{\nu_n} |0\rangle$$

For a 3d-shell: all $n_i = 3$, all $l_i = 2$, only m_i and σ_i vary

Ordering convention (absolutely necessary!)

$$m_1 \leq m_2 \leq m_3 \leq \cdots \leq m_n$$

If two m are equal the corresponding σ must be $\uparrow$ and $\downarrow$

Then we order them as

$$\ldots c^\dagger_{3,2,m\downarrow} \, c^\dagger_{3,2,m\uparrow} \ldots |0\rangle$$

Every state with n electrons in the d-shell is included exactly once in this basis

We consider the matrix element

$$\langle \mu_1, \mu_2 \ldots \mu_n |\; V(\lambda_1, \lambda_2, \lambda_3, \lambda_4)\; c^\dagger_{\lambda_1} c^\dagger_{\lambda_2} c_{\lambda_3} c_{\lambda_4}\; | \nu_1, \nu_2 \ldots \nu_n \rangle$$

$$= \;\; \langle 0 | c_{\mu_n} \ldots c_{\mu_1}\; V(\lambda_1, \lambda_2, \lambda_3, \lambda_4)\; c^\dagger_{\lambda_1} c^\dagger_{\lambda_2} c_{\lambda_3} c_{\lambda_4}\; c^\dagger_{\nu_1} c^\dagger_{\nu_2} \ldots c^\dagger_{\mu_n} | 0 \rangle$$

For this to be nonzero, λ_3 and λ_4 must appear amongst the ν_i - then we have a product like

$$c_{\lambda_3} c_{\lambda_4}\; c^\dagger_{\nu_1} c^\dagger_{\nu_2} \ldots c^\dagger_{\lambda_3} \ldots c^\dagger_{\lambda_4} \ldots c^\dagger_{\mu_n} | 0 \rangle \;=\; (-1)^{n_3+n_4}\;\; c^\dagger_{\nu_1} c^\dagger_{\nu_2} \ldots c_{\lambda_3} c^\dagger_{\lambda_3} \ldots c_{\lambda_4} c^\dagger_{\lambda_4} \ldots c^\dagger_{\mu_n} | 0 \rangle$$

Doing the same with $c^\dagger_{\lambda_1} c^\dagger_{\lambda_2}$ we obtain the total matrix element

$$(-1)^{n_1+n_2+n_3+n_4}\;\; V(\lambda_1, \lambda_2, \lambda_3, \lambda_4)$$

The Fermi sign $(-1)^{n_1+n_2+n_3+n_4}$ must be computed by keeping track of all interchanges of Fermion operators

This is absolutely necessary to obtain correct results!

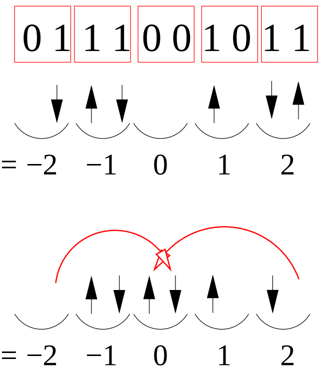
Solution of the Coulomb problem by exact diagonalization

Number of basis states with n electrons

$$n_c = \frac{10!}{(10-n)!\;n!} \approx 100...500$$

These can be coded as integers

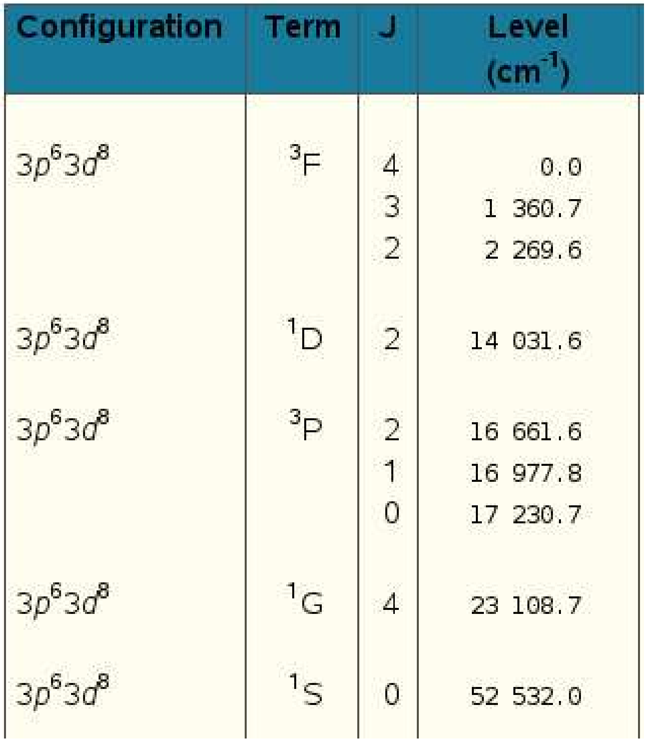
459 = 0 1 1 1 0 0 1 0 1 1



0 0 1 1 1 1 1 0 1 0 = 250

$$\langle 250|H_1|459\rangle = (-1)^{n_1+n_2+n_3+n_4}\;\delta_{\sigma_1,\sigma_4}\;\delta_{\sigma_2,\sigma_3}\sum_{k\in\{0,2,4\}}\delta_{m_1+m_2,m_3+m_4}\;c^k(l_1,m_1;l_4,m_4)\;\;c^k(l_3,m_3;l_2,m_2)\;\;R^k$$

Comparison to experiment for Ni^{2+}

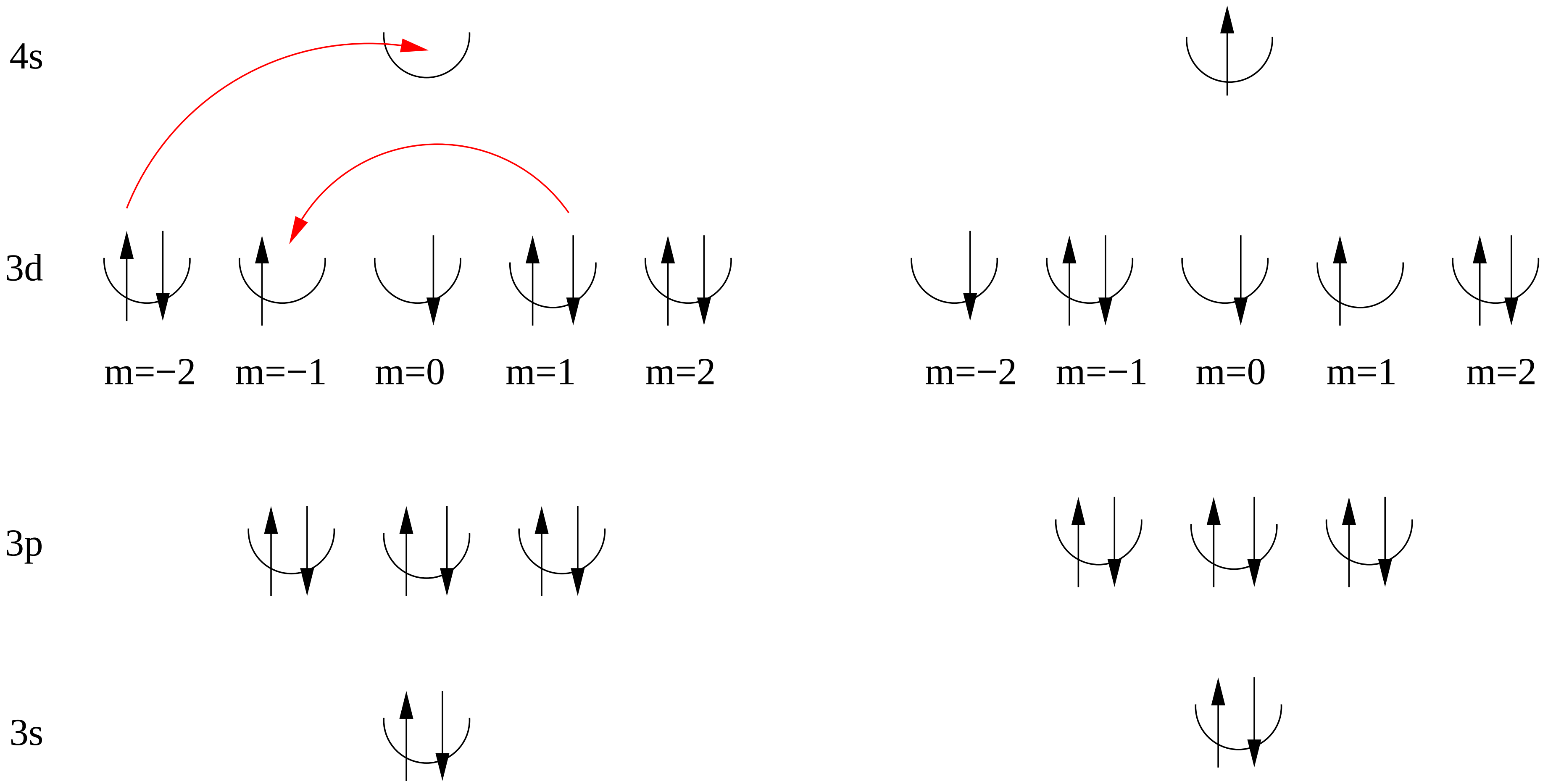


Configuration	Term	J	Level (cm^{-1})
$3p^6 3d^8$	^{3}F	4 3 2	0.0 1 360.7 2 269.6
$3p^6 3d^8$	^{1}D	2	14 031.6
$3p^6 3d^8$	^{3}P	2 1 0	16 661.6 16 977.8 17 230.7
$3p^6 3d^8$	^{1}G	4	23 108.7
$3p^6 3d^8$	^{1}S	0	52 532.0

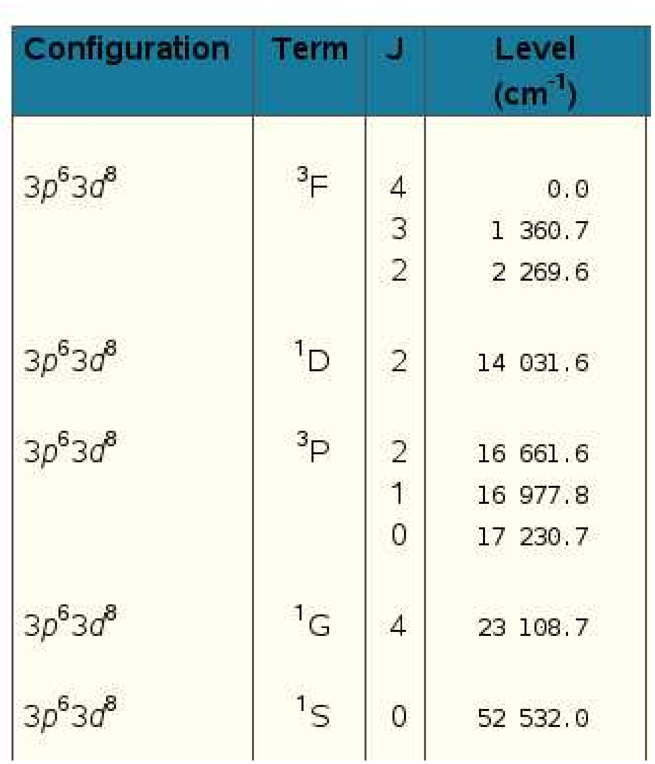
E	S	L	n	Term	E$_{exp}$
0.0000	1	3	21	^3F	0.0000
1.8420	0	2	5	^1D	1.7396
1.9200	1	1	9	^3P	2.0829
2.7380	0	4	9	^1G	2.8649
13.2440	0	0	1	^1S	6.5129

→ Relative error $\leq 10\%$ (except for ^{1}S)

Remember that we neglected processes like these:



Comparison to experiment for Ni^{2+}



Configuration	Term	J	Level (cm^{-1})
$3p^6 3d^8$	^{3}F	4	0.0
		3	1 360.7
		2	2 269.6
$3p^6 3d^8$	^{1}D	2	14 031.6
$3p^6 3d^8$	^{3}P	2	16 661.6
		1	16 977.8
		0	17 230.7
$3p^6 3d^8$	^{1}G	4	23 108.7
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2.7380	0	4	9	^1G	2.8649
13.2440	0	0	1	^1S	6.5129

→ Relative error $\leq 10\%$ (except for ^{1}S)

An Identity

We had

$$\begin{aligned}
V(\nu_1,\nu_2,\nu_3,\nu_4) &= \int dx \int dx'\; \psi^*_{\nu_1}(x)\; \psi^*_{\nu_2}(x')\; V_c(x,x')\; \psi_{\nu_4}(x)\; \psi_{\nu_3}(x') \\
&= \int dx \int dx'\; \psi^*_{\nu_1}(x')\; \psi^*_{\nu_2}(x)\; V_c(x,x')\; \psi_{\nu_4}(x')\; \psi_{\nu_3}(x) \\
&= \int dx \int dx'\; \psi^*_{\nu_2}(x)\; \psi^*_{\nu_1}(x')\; V_c(x,x')\; \psi_{\nu_3}(x)\; \psi_{\nu_4}(x') \\
&= V(\nu_2,\nu_1,\nu_4,\nu_3)
\end{aligned}$$

Diagonal matrix elments of the Coulomb interaction

We want to calculate the diagonal matrix elements of the Coulomb Hamiltonian

$$H_1 \;=\; \frac{1}{2}\sum_{i,j,k,l} V(\nu_i,\nu_j,\nu_k,\nu_l)\;\; c^\dagger_{\nu_i}\; c^\dagger_{\nu_j}\; c_{\nu_k}\; c_{\nu_l}$$

In diagonal terms the product $c^\dagger_{\nu_i}\; c^\dagger_{\nu_j}\; c_{\nu_k}\; c_{\nu_l}$ must not change the occupation numbers - therefore:

$$\begin{aligned} H_{1,diag} \;&=\; \frac{1}{2}\sum_{\nu_1<\nu_2} \Big(\; V(\nu_1,\nu_2,\nu_1,\nu_2)\;\; c^\dagger_{\nu_1}c^\dagger_{\nu_2}c_{\nu_1}c_{\nu_2} + V(\nu_1,\nu_2,\nu_2,\nu_1)\Big)\;\; c^\dagger_{\nu_1}c^\dagger_{\nu_2}c_{\nu_2}c_{\nu_1} \\ &\qquad\qquad + \; V(\nu_2,\nu_1,\nu_1,\nu_2)\;\; c^\dagger_{\nu_2}c^\dagger_{\nu_1}c_{\nu_1}c_{\nu_2} + V(\nu_2,\nu_1,\nu_2,\nu_1)\;\; c^\dagger_{\nu_2}c^\dagger_{\nu_1}c_{\nu_2}c_{\nu_1} \;\;\Big) \;\; + \ldots \\ &= \sum_{\nu_1<\nu_2} \big(\; V(\nu_1,\nu_2,\nu_2,\nu_1) - V(\nu_1,\nu_2,\nu_1,\nu_2)\;\big)\;\; n_{\nu_1}\; n_{\nu_2} + \ldots \end{aligned}$$

- $\sum_{\nu_1<\nu_2}$ means that each pair (ν_1,ν_2) is counted only once
- We must have $\nu_1 \neq \nu_2$ - otherwise $c^\dagger_{\nu_1}c^\dagger_{\nu_2} = 0$!

We consider $V(\nu_1,\nu_2,\nu_2,\nu_1) - V(\nu_1,\nu_2,\nu_1,\nu_2)$ whereby $\nu = (n,l,m,\sigma)$ and recall

$$V(\nu_1,\nu_2,\nu_3,\nu_4) = \delta_{\sigma_1,\sigma_4}\ \delta_{\sigma_2,\sigma_3} \sum_{k=0}^{\infty}\ \delta_{m_1+m_2,m_3+m_4}\ c^k(l_1,m_1;l_4,m_4)\ c^k(l_3,m_3;l_2,m_2)\ R^k(n_1l_1,n_2l_2,n_3l_3,n_4l_4)$$

This gives

$$\begin{aligned} V(\nu_1,\nu_2,\nu_2,\nu_1) &= \qquad\quad \sum_{k=0}^{\infty} c^k(l_1m_1;l_1,m_1)\ c^k(l_2m_2;l_2,m_2)\ R^k(n_1l_1,n_2l_2,n_2l_2,n_1l_1) \\ V(\nu_1,\nu_2,\nu_1,\nu_2) &= \delta_{\sigma_1,\sigma_2} \sum_{k=0}^{\infty} c^k(l_1m_1;l_2,m_2)\ c^k(l_1m_1;l_2,m_2)\ R^k(n_1l_1,n_2l_2,n_1l_1,n_2l_2) \end{aligned}$$

We consider $V(\nu_1, \nu_2, \nu_2, \nu_1) - V(\nu_1, \nu_2, \nu_1, \nu_2)$ whereby $\nu = (n, l, m, \sigma)$ and recall

$$V(\nu_1, \nu_2, \nu_3, \nu_4) = \delta_{\sigma_1, \sigma_4}\ \delta_{\sigma_2, \sigma_3} \sum_{k=0}^{\infty}\ \delta_{m_1+m_2, m_3+m_4}\ c^k(l_1, m_1; l_4, m_4)\ c^k(l_3, m_3; l_2, m_2)\ R^k(n_1 l_1, n_2 l_2, n_3 l_3, n_4 l_4)$$

This gives

$$\begin{aligned} V(\nu_1, \nu_2, \nu_2, \nu_1) &= \sum_{k=0}^{\infty} \qquad a^k(l_1 m_1; l_2, m_2) \qquad R^k(n_1 l_1, n_2 l_2, n_2 l_2, n_1 l_1) \\ V(\nu_1, \nu_2, \nu_1, \nu_2) &= \delta_{\sigma_1, \sigma_2} \sum_{k=0}^{\infty} \qquad b^k(l_1 m_1; l_2, m_2) \qquad R^k(n_1 l_1, n_2 l_2, n_1 l_1, n_2 l_2) \end{aligned}$$

We consider $V(\nu_1, \nu_2, \nu_2, \nu_1) - V(\nu_1, \nu_2, \nu_1, \nu_2)$ whereby $\nu = (n, l, m, \sigma)$ and recall

$$V(\nu_1, \nu_2, \nu_3, \nu_4) = \delta_{\sigma_1,\sigma_4}\, \delta_{\sigma_2,\sigma_3} \sum_{k=0}^{\infty}\, \delta_{m_1+m_2,m_3+m_4}\, c^k(l_1, m_1; l_4, m_4)\, c^k(l_3, m_3; l_2, m_2)\, R^k(n_1 l_1, n_2 l_2, n_3 l_3, n_4 l_4)$$

This gives

$$\begin{aligned} V(\nu_1, \nu_2, \nu_2, \nu_1) &= \sum_{k=0}^{\infty} a^k(l_1 m_1; l_2, m_2)\, F^k(n_1 l_1, n_2 l_2) \\ V(\nu_1, \nu_2, \nu_1, \nu_2) &= \delta_{\sigma_1,\sigma_2} \sum_{k=0}^{\infty} b^k(l_1 m_1; l_2, m_2)\, G^k(n_1 l_1, n_2 l_2) \end{aligned}$$

We consider $V(\nu_1, \nu_2, \nu_2, \nu_1) - V(\nu_1, \nu_2, \nu_1, \nu_2)$ whereby $\nu = (n, l, m, \sigma)$ and recall

$$V(\nu_1, \nu_2, \nu_3, \nu_4) = \delta_{\sigma_1,\sigma_4}\, \delta_{\sigma_2,\sigma_3} \sum_{k=0}^{\infty} \delta_{m_1+m_2,m_3+m_4}\, c^k(l_1, m_1; l_4, m_4)\, c^k(l_3, m_3; l_2, m_2)\, R^k(n_1l_1, n_2l_2, n_3l_3, n_4l_4)$$

This gives

$$V(\nu_1, \nu_2, \nu_2, \nu_1) = \sum_{k=0}^{\infty} a^k(l_1m_1; l_2, m_2) \quad F^k(n_1l_1, n_2l_2)$$

$$V(\nu_1, \nu_2, \nu_1, \nu_2) = \delta_{\sigma_1,\sigma_2} \sum_{k=0}^{\infty} b^k(l_1m_1; l_2, m_2) \quad G^k(n_1l_1, n_2l_2)$$

... and obtain

$$V(\nu_1, \nu_2, \nu_2, \nu_1) - V(\nu_1, \nu_2, \nu_1, \nu_2) = \sum_k \Big(a^k(l_1m_1; l_2, m_2)\, F^k(n_1l_1, n_2l_2) \\ -\delta_{\sigma_1,\sigma_2}\, b^k(l_1m_1; l_2, m_2)\, G^k(n_1l_1, n_2l_2) \Big)$$

F^k and G^k are called Slater-Condon parameters

$$
\begin{aligned}
F^k(n_1l_1, n_2l_2) &= R^k(n_1l_1, n_2l_2, n_2l_2, n_1l_1) = e^2 \int_0^\infty dr\ r^2 \int_0^\infty dr'\ r'^2\ R^2_{n_1,l_1}(r)\ \frac{r_<^k}{r_>^{k+1}}\ \ R^2_{n_2,l_2}(r') \\
G^k(n_1l_1, n_2l_2) &= R^k(n_1l_1, n_2l_2, n_1l_1, n_2l_2) = e^2 \int_0^\infty dr\ r^2 \int_0^\infty dr'\ r'^2\ \rho_{ex}(r)\ \frac{r_<^k}{r_>^{k+1}}\ \ \rho_{ex}(r') \\
\rho_{ex}(r) &= R_{n_1,l_1}(r)\ R_{n_2,l_2}(r)
\end{aligned}
$$

F^k is a Coulomb-like integral, G^k and exchange-like integral

For $(n_1, l_1) = (n_2, l_2)$ (scattering within a shell) we have $F^k = G^k$

The diagonal part of the Hamiltonian therefore is

$$\begin{aligned} H_{diag} &= \sum_{\nu_1<\nu_2} \left(V(\nu_1,\nu_2,\nu_2,\nu_1) - V(\nu_1,\nu_2,\nu_1,\nu_2) \right) \; n_{\nu_1}\, n_{\nu_2} \\ &= \sum_{\nu_1<\nu_2} \left(\sum_k a^k(l_1 m_1, l_2, m_2)\, F^k - \delta_{\sigma_1,\sigma_2} \sum_k b^k(l_1 m_1, l_2, m_2)\, G^k \right) \; n_{\nu_1}\, n_{\nu_2} \end{aligned}$$

To calculate the diagonal matrix element of this for a state like $|\Psi\rangle = c^\dagger_{\nu_1} c^\dagger_{\nu_2} \dots c^\dagger_{\nu_n} |0\rangle$ we have to sum this over all occupied pairs

$$\langle\Psi|H_1|\Psi\rangle = \sum_{i<j} \left(\sum_k a^k(l_i m_i, l_j, m_j)\, F^k - \delta_{\sigma_1,\sigma_2} \sum_k b^k(l_i m_i, l_j, m_j)\, G^k \right) \; n_{\nu_i}\, n_{\nu_j}$$

This will be used later on....

We consider again a partially filled shell: all $n_i = n$ and all $l_i = l$, for each k only one $F^k = G^k$

→ we only sum over m_1, m_2, σ_1 and σ_2

$$H_{diag} = \frac{1}{2} \sum_{(m_1,\sigma_1)\neq(m_2,\sigma_2)} \left(\sum_{k\in\{0,2,4\}} a^k(m_1,m_2)\ F^k - \delta_{\sigma_1,\sigma_2} \sum_{k\in\{0,2,4\}} b^k(m_1,m_2)\ F^k \right) n_{m_1,\sigma_1}\ n_{m_2,\sigma_2}$$

We consider again a partially filled shell: all $n_i = n$ and all $l_i = l$, for each k only one $F^k = G^k$

$\rightarrow$ we only sum over m_1, m_2, σ_1 and σ_2

$$H_{diag} = \frac{1}{2} \sum_{(m_1,\sigma_1)\neq(m_2,\sigma_2)} \left(\underbrace{\sum_{k\in\{0,2,4\}} a^k(m_1, m_2)\ F^k}_{} - \delta_{\sigma_1,\sigma_2} \underbrace{\sum_{k\in\{0,2,4\}} b^k(m_1, m_2)\ F^k}_{} \right) n_{m_1,\sigma_1}\ n_{m_2,\sigma_2}$$

$$= \frac{1}{2} \sum_{(m_1,\sigma_1)\neq(m_2,\sigma_2)} \left(U_{m_1,m_2} - \delta_{\sigma_1,\sigma_2} J_{m_1,m_2} \right) n_{m_1,\sigma_1}\ n_{m_2,\sigma_2}$$

- Recall that $(m_1, \sigma_1) \neq (m_2, \sigma_2)$ (otherwise $c^\dagger_{\nu_1} c^\dagger_{\nu_2} = 0$)
- In the first term we may have $m_1 = m_2$ but then $\sigma_2 = -\sigma_1$
- In the second term $\sigma_1 = \sigma_2$ therefore $m_1 \neq m_2$

$$H_{diag} = \sum_m U_{m,m}\ n_{m,\uparrow}\ n_{m,\downarrow} + \frac{1}{2} \sum_{m_1\neq m_2} \left(U_{m_1,m_2} \sum_{\sigma,\sigma'} n_{m_1,\sigma} n_{m_2,\sigma'} - J_{m_1,m_2} \sum_{\sigma} n_{m_1,\sigma} n_{m_2,\sigma} \right),$$

Recall:

$$H_{1,diag} \;=\; \sum_{m} U_{m,m}\; n_{m,\uparrow} n_{m,\downarrow} + \frac{1}{2} \sum_{m_1 \neq m_2} \left(U_{m_1,m_2} \sum_{\sigma,\sigma'} n_{m_1,\sigma} n_{m_2,\sigma'} - J_{m_1,m_2} \sum_{\sigma} n_{m_1,\sigma} n_{m_2,\sigma} \right),$$

Introduce $n_m = n_{m,\uparrow} + n_{m,\downarrow}$ and $2\; S^z_m = n_{m,\uparrow} - n_{m,\downarrow}$, then

$$\sum_{\sigma,\sigma'} n_{m_1,\sigma}\; n_{m_2,\sigma'} \;=\; n_{m_1}\; n_{m_2}$$

$$\sum_{\sigma} n_{m_1,\sigma}\; n_{m_2,\sigma} \;=\; 2 S^z_{m_1}\; S^z_{m_2} + \frac{n_{m_1} n_{m_2}}{2}$$

Recall:

$$H_{1,diag} \;=\; \sum_m U_{m,m}\; n_{m,\uparrow} n_{m,\downarrow} + \frac{1}{2} \sum_{m_1 \neq m_2} \left(U_{m_1,m_2} \sum_{\sigma,\sigma'} n_{m_1,\sigma} n_{m_2,\sigma'} - J_{m_1,m_2} \sum_{\sigma} n_{m_1,\sigma} n_{m_2,\sigma} \right),$$

Introduce $n_m = n_{m,\uparrow} + n_{m,\downarrow}$ and $2\ S^z_m = n_{m,\uparrow} - n_{m,\downarrow}$, then

$$\sum_{\sigma,\sigma'} n_{m_1,\sigma}\; n_{m_2,\sigma'} \;=\; n_{m_1}\; n_{m_2}$$

$$\sum_{\sigma} n_{m_1,\sigma}\; n_{m_2,\sigma} \;=\; 2 S^z_{m_1}\; S^z_{m_2} + \frac{n_{m_1} n_{m_2}}{2}$$

Recall

$$H_{1,diag} = \sum_{m} U_{m,m}\, n_{m,\uparrow} n_{m,\downarrow} + \frac{1}{2} \sum_{m_1 \neq m_2} \left(U_{m_1,m_2} \sum_{\sigma,\sigma'} n_{m_1,\sigma} n_{m_2,\sigma'} - J_{m_1,m_2} \sum_{\sigma} n_{m_1,\sigma} n_{m_2,\sigma} \right),$$

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Recall

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Introduce $n_m = n_{m,\uparrow} + n_{m,\downarrow}$ and $2\; S^z_m = n_{m,\uparrow} - n_{m,\downarrow}$, then

$$\begin{aligned} \sum_{\sigma,\sigma'} n_{m_1,\sigma}\; n_{m_2,\sigma'} &= n_{m_1}\; n_{m_2} \\ \sum_{\sigma} n_{m_1,\sigma}\; n_{m_2,\sigma} &= 2 S^z_{m_1}\; S^z_{m_2} + \frac{n_{m_1} n_{m_2}}{2} \end{aligned}$$

so that

$$H_{diag} \;=\; \sum_{m} U_{m,m}\; n_{m,\uparrow}\; n_{m,\downarrow} + \frac{1}{2} \sum_{m_1 \neq m_2} \left((U_{m_1,m_2} - \frac{1}{2}\; J_{m_1,m_2})\; n_{m_1} n_{m_2} - 2 J_{m_1,m_2}\; S^z_{m_1} S^z_{m_2} \right).$$

All in all

$$\begin{aligned} H_{diag} &= \sum_m U_{m,m}\, n_{m,\uparrow}\, n_{m,\downarrow} + \frac{1}{2} \sum_{m_1 \neq m_2} \left(\left(U_{m_1,m_2} - \frac{1}{2}\, J_{m_1,m_2}\right) n_{m_1} n_{m_2} - 2J_{m_1,m_2}\, S^z_{m_1} S^z_{m_2} \right) \\ U_{m_1,m_2} &= \sum_{k\, \in\{0,2,4\}} a^k(m_1,m_2)\, F^k = \sum_{k\, \in\{0,2,4\}} c^k(l_1,m_1;l_1,m_1)\, c^k(l_2,m_2;l_2,m_2)\, F^k \\ J_{m_1,m_2} &= \sum_{k\, \in\{0,2,4\}} b^k(m_1,m_2)\, F^k = \sum_{k\, \in\{0,2,4\}} c^k(l_1,m_1;l_2,m_2)^2\, F^k \end{aligned}$$

- This is the sum of a Hubbard-like term for each m, and both, a density-density interaction and a ferromagnetic Ising-like 'Hunds rule exchange', between electrons in different orbitals
- An additional approximation is to replace U_{m_1,m_2} and J_{m_1,m_2} by their average values
- A 'Coulomb Hamiltonian' of this type can often be found in the literature
- It has to be kept in mind that this is not the full Coulomb Hamiltonian but the sum of diagonal elements

All in all

$$H_{diag} \;=\; \sum_{m} U_{m,m}\; n_{m,\uparrow}\; n_{m,\downarrow} + \frac{1}{2} \sum_{m_1 \neq m_2} \left(\left(U_{m_1,m_2} - \frac{1}{2}\; J_{m_1,m_2}\right)\; n_{m_1} n_{m_2} - 2J_{m_1,m_2}\; S^z_{m_1} S^z_{m_2} \right)$$

- By adding a selected class of off-diagonal elements one can ‘complete the Hund’s rule exchange’ to obtain the fully spin-rotation invariant Hamiltonian

$$\tilde{H}_1 \;=\; \sum_{m} U_{m,m}\; n_{m,\uparrow}\; n_{m,\downarrow} + \frac{1}{2} \sum_{m_1 \neq m_2} \left(\left(U_{m_1,m_2} - \frac{1}{2}\; J_{m_1,m_2}\right)\; n_{m_1} n_{m_2} - 2J_{m_1,m_2}\; \boldsymbol{S}_{m_1} \cdot \boldsymbol{S}_{m_2} \right)$$

- However this still contains only a subset of all Coulomb matrix elements

  Only the full Coulomb Hamiltonian derived above is really the correct one which gives agreement with experiment

Multiplets of p^2 - calculated by the diagonal sum-rule

- One can derive analytical expressions for the energies of all multiplets using the so-called diagonal sum-rule
- This is explained in my notes - for example the multiplets of p^2 are

$$\begin{aligned} E[^3P] &= F^0 - \frac{5}{25}\,F^2 \\ E[^1D] &= F^0 + \frac{1}{25}\,F^2 \\ E[^1S] &= F^0 + \frac{10}{25}\,F^2 \end{aligned}$$

This allows for a simple cross-check:

$$r = \frac{E(^1S) - E(^1D)}{E(^1D) - E(^3P)} = \frac{3}{2}$$

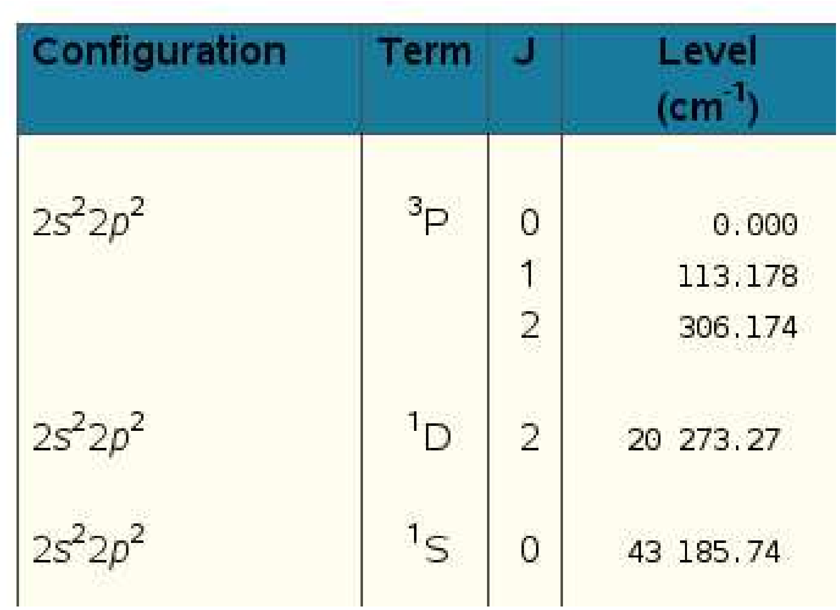
The values of F^0 and F^2 have dropped out in r!

This should be obeyed by all atoms/ions with p^2 or - by particle-hole symmetry - with p^4 configuration!

Multiplet energies can be obtained from databases e.g. at NIST

Example: Multiplets of S^{2+}

$$r = \frac{E(^1S) - E(^1D)}{E(^1D) - E(^3P)} = \frac{3}{2}$$

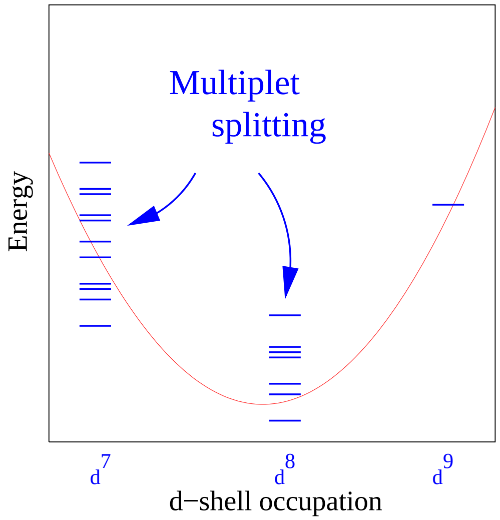


Configuration	Term	J	Level (cm^{-1})
$2s^2 2p^2$	^{3}P	0	0.000
		1	113.178
		2	306.174
$2s^2 2p^2$	^{1}D	2	20 273.27
$2s^2 2p^2$	^{1}S	0	43 185.74

	Si	P^+	S^{2+}
^{3}P	0.0000	0.0000	0.0000
^{1}D	0.7809	1.1013	1.4038
^{1}S	1.9087	2.6750	3.3675
r	1.4442	1.4289	1.3988

Summary so far

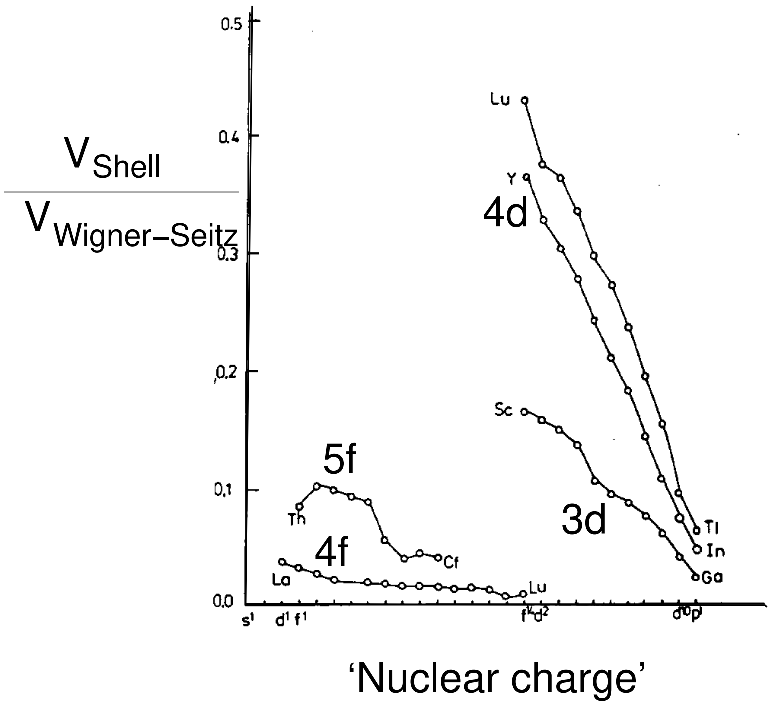
- The Coulomb interaction in a partially filled 3d/4f-shells is particularly strong
- The Coulomb interaction in a free atom/ion leads to the formation of multiplets
- The matrix elements of the Coulomb interaction can be expressed in terms of Gaunt oefficients and Slater-Condon parameters
- Reasonable agreement with experiment can be obtained

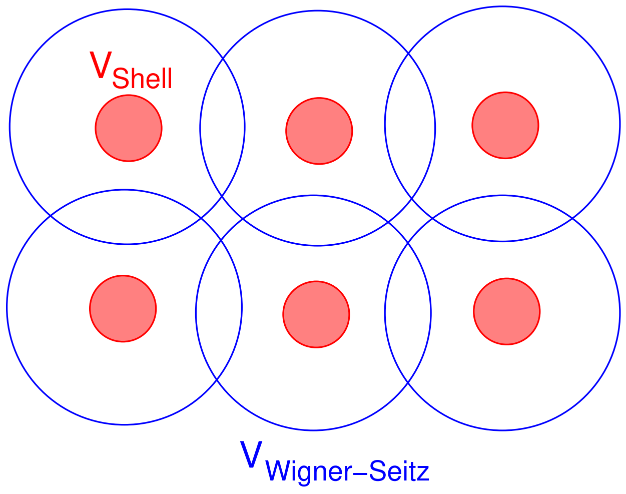


$$E(n) = n\ \varepsilon_d + A\ \frac{n\,(n-1)}{2}$$

We considered an atom/ion in vacuum but in solid state physics we are interested in an atom/ion in a solid

Will the results for the free atom retain any significance in this case? - Probably yes:



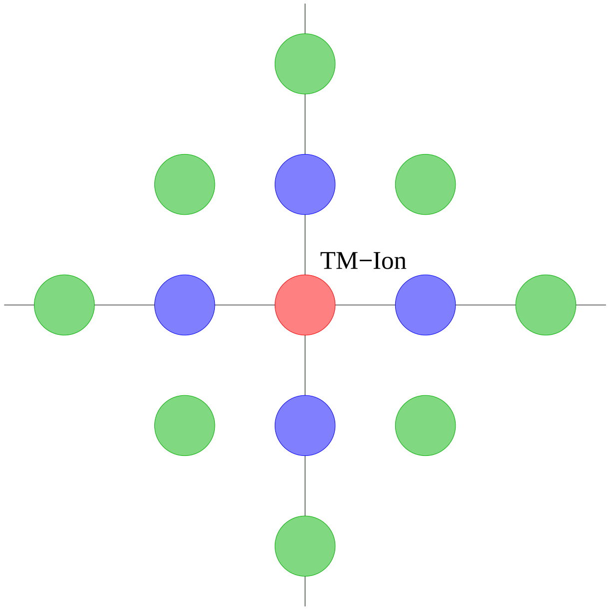


There are two mechanisms by which the environment can affect the electron states of the embedded ion:

Crystalline Electric field and Charge Transfer

Crystalline Electric Field

- A transition metal ion in a crystal is subject to the electrostatic potential V_{CEF} of the surrounding ions
- This is called the Crystalline Electric Field (CEF)



- V_{CEF} is not spherically symmetric $\Rightarrow$ the symmetry is lowered $\Rightarrow$ degeneracies are lifted
- We represent the ions surrounding the TM ion - called ligands - as point charges

The Crystalline Electric Field

- We represent the ligands as n point charges of strength $Z_i e$ at the positions $\boldsymbol{R}_i$
- Using again the multipole expansion of the Coulomb potential we find the electrostatic potential

$$V_{CEF}(\boldsymbol{r}) \; = \; -\sum_{i=1}^{n} \frac{1}{|\boldsymbol{r} - \boldsymbol{R}_i|} \, Z_i \, e^2$$

The Crystalline Electric Field

- We represent the ligands as n point charges of strength $Z_i e$ at the positions $\boldsymbol{R}_i$
- Using again the multipole expansion of the Coulomb potential we find the electrostatic potential

$$
\begin{aligned}
V_{CEF}(\boldsymbol{r}) &= -\sum_{i=1}^{n} \overbrace{\frac{1}{|\boldsymbol{r}-\boldsymbol{R}_i|}}^{} Z_i\, e^2 \\
&= -\sum_{i=1}^{n} \underbrace{\sum_{k=0}^{\infty} \sum_{m=-k}^{k} Y^*_{k,m}(\Theta_i,\phi_i) \frac{4\pi}{2k+1} \frac{r^k}{R_i^{k+1}} Y_{k,m}(\Theta,\phi)}_{} Z_i\, e^2 \\
&= -\frac{Z_{av}e^2}{R_{av}} \sum_{k=0}^{\infty} \sum_{m=-k}^{k} \gamma_{k,m} \left(\frac{r}{R_{av}}\right)^k \sqrt{\frac{4\pi}{2k+1}}\, Y_{k,m}(\Theta,\phi), \\
\gamma_{k,m} &= \sqrt{\frac{4\pi}{2k+1}} \sum_{i=1}^{n} \frac{Z_i}{Z_{av}} \left(\frac{R_{av}}{R_i}\right)^{k+1} Y^*_{k,m}(\Theta_i,\phi_i).
\end{aligned}
$$

- R_{av} and Z_{av}: average distance and charge of the ligands
- The geometry of the ligands is encoded in the dimensionless parameters $\gamma_{k,m}$

The Crystalline Electric Field

- The corresponding Hamiltonian in second quantization then is

$$
\begin{aligned}
H_{CEF} &= \sum_{i,j} V_{CEF}(\nu_i,\nu_j)\; c^\dagger_{\nu_i} c_{\nu_j}, \\
V_{CEF}(\nu_1,\nu_2) &= \int dx\; \psi^*_{\nu_1}(x)\; V_{CEF}(\boldsymbol{r})\; \psi_{\nu_2}(x) \\
\nu_i &= (n_i, l_i, m_i, \sigma_i) \\
\psi_{n_i,l_i,m_i,\sigma_i}(x) &= R_{n_i,l_i}(r)\; Y_{l_i,m_i}(\Theta,\phi)\; \delta_{\sigma,\sigma_i}
\end{aligned}
$$

We need the matrix element

$$
\begin{aligned}
V_{CEF}(\nu_1,\nu_2) &= \int dx\ \psi^*_{\nu_1}(x)\ V_{CEF}(\boldsymbol{r})\ \psi_{\nu_2}(x) \\
\psi^*_{\nu_1}(x) &= R_{n_1,l_1}(r)\ \ Y^*_{l_1,m_1}(\Theta,\phi)\quad \delta_{\sigma,\sigma_1} \\
V_{CEF}(\boldsymbol{r}) &= -\frac{Z_{av}e^2}{R_{av}}\ \sum_{k=0}^{\infty}\ \sum_{m=-k}^{k}\gamma_{k,m}\ \left(\frac{r}{R_{av}}\right)^k\ \sqrt{\frac{4\pi}{2k+1}}\ \ Y_{k,m}\ \ (\Theta,\phi) \\
\psi_{\nu_2}(x) &= R_{n_2,l_2}(r)\ \ Y_{l_2,m_2}(\Theta,\phi)\quad \delta_{\sigma,\sigma_2}
\end{aligned}
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V_{CEF}(\nu_1, \nu_2) &= \int dx\ \psi^*_{\nu_1}(x)\ V_{CEF}(\boldsymbol{r})\ \psi_{\nu_2}(x) \\
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\psi_{\nu_2}(x) &= R_{n_2,l_2}(r) \qquad Y_{l_2,m_2}(\Theta, \phi) \qquad \delta_{\sigma,\sigma_2} \\
V_{CEF}(\nu_1, \nu_2) &= \sum_{k=0}^{\infty} \sum_{m=-k}^{k} \gamma_{k,m} \quad I_k \quad \delta_{m,m_1-m_2}\; c^k(l_1, m_1; l_2, m_2) \quad \delta_{\sigma_1,\sigma_2}
\end{aligned}$$

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$$
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V_{CEF}(\nu_1,\nu_2) &= \int dx\ \psi^*_{\nu_1}(x)\ V_{CEF}(\boldsymbol{r})\ \psi_{\nu_2}(x) \\
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\psi_{\nu_2}(x) &= \qquad R_{n_2,l_2}(r) \qquad Y_{l_2,m_2}(\Theta,\phi) \qquad \delta_{\sigma,\sigma_2}
\end{aligned}
$$

$$
V_{CEF}(\nu_1,\nu_2) = \sum_{k=0}^{\infty} \sum_{m=-k}^{k} \gamma_{k,m} \quad I_k \quad \delta_{m,m_1-m_2}\ c^k(l_1,m_1;l_2,m_2)\ \ \delta_{\sigma_1,\sigma_2}
$$

Doing the m-sum we find

$$
V_{CEF}(\nu_1,\nu_2) = \delta_{\sigma_1,\sigma_2} \sum_{k=0}^{\infty} \gamma_{k,m_1-m_2}\ I_k\ \ c^k(l_1,m_1;l_2,m_2)
$$

We specialize to a d-shell:

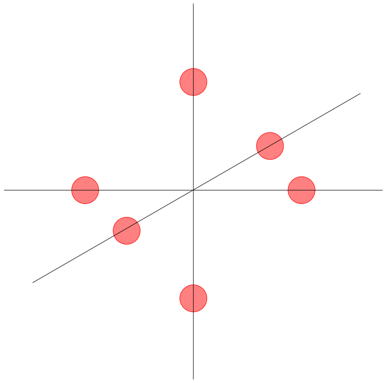
$$V_{CEF}(\nu_1,\nu_2) \;=\; \delta_{\sigma_1,\sigma_2} \sum_{k\in\{0,2,4\}} \gamma_{k,m_1-m_2}\; I_k\;\; c^k(2,m_1;2,m_2)$$

Recall that $I_k \propto \left(\frac{r_{3d}}{R_{av}}\right)^k$ - since $\frac{r_{3d}}{R_{av}} \ll 1$ we can terminate this for the lowest $k>0$ where $\gamma_{k,m} \neq 0$

Now consider

$$\gamma_{k,m} = \sqrt{\frac{4\pi}{2k+1}}\sum_{i=1}^{n} \frac{Z_i}{Z_{av}} \left(\frac{R_{av}}{R_i}\right)^{k+1}\; Y^*_{k,m}(\Theta_i,\phi_i)$$

For an ideal octahedron of identical charges $(R_i = R$ and $Z_i = Z)$ one finds $\gamma_{k,m} = 0$ for $0 < k < 4$ and



$$\gamma_{4,\;\;4} \;=\; \sqrt{\frac{35}{8}}$$
$$\gamma_{4,\;\;0} \;=\; \sqrt{\frac{49}{4}}$$
$$\gamma_{4,-4} \;=\; \sqrt{\frac{35}{8}}$$

(see my notes)

Using the tabulated values of the $c^4(2, m_1; 2, m_2)$ (see notes) we thus find

$$V_{CEF}(m_1, m_2) \;=\; \frac{I_4}{6} \begin{pmatrix} 1 & 0 & 0 & 0 & 5 \\ 0 & -4 & 0 & 0 & 0 \\ 0 & 0 & 6 & 0 & 0 \\ 0 & 0 & 0 & -4 & 0 \\ 5 & 0 & 0 & 0 & 1 \end{pmatrix}.$$

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Eigenvalues: I_4, $-\frac{2}{3}\,I_4$, $-\frac{2}{3}\,I_4$

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Eigenvalues: I_4, $-\frac{2}{3}\,I_4$, $-\frac{2}{3}\,I_4$, $\frac{1\pm 5}{6}\,I_4$

All in all: I_4 (2 times), $-\frac{2}{3}\,I_4$ (3 times)

Recall:

$$I_k = -\frac{Z_{av}e^2}{R_{av}} \int_0^\infty dr\; r^2 R_{3,2}(r) \left(\frac{r}{R_{av}}\right)^k R_{3,2}(r)$$

- All information about the radial wave functions is condensed in a single parameter
- For negatively charged ligands (e.g. O^{2-}) $I_4 > 0$
- The difference between the eigenvalues is $\frac{5}{3}\,I_4$ - this is often called $10Dq$ → for the octahedron $Dq = \frac{I_4}{6}$

Eigenfunctions

- The eigenfunctions for eigenvalue $-\frac{2I_4}{3} = -4Dq$ are the real-valued spherical harmonics d_{xy}, d_{xz} and d_{yz}

$$\begin{aligned} d_{xy} &= \frac{i}{\sqrt{2}}\,(Y_{2,-2} - Y_{2,2}) = \sqrt{\frac{15}{4\pi}}\,\frac{xy}{r^2}, \\ d_{yz} &= \frac{i}{\sqrt{2}}\,(Y_{2,-1} + Y_{2,1}) = \sqrt{\frac{15}{4\pi}}\,\frac{yz}{r^2}, \\ d_{xz} &= \frac{1}{\sqrt{2}}\,(Y_{2,-1} - Y_{2,1}) = \sqrt{\frac{15}{4\pi}}\,\frac{xz}{r^2}, \end{aligned}$$

- The eigenfunctions for eigenvalue $I_4 = 6Dq$ are the real-valued spherical harmonics $d_{x^2-y^2}$ and $d_{3z^2-r^2}$

$$\begin{aligned} d_{x^2-y^2} &= \frac{1}{\sqrt{2}}\,(Y_{2,-2} + Y_{2,2}) = \sqrt{\frac{15}{16\pi}}\,\frac{x^2-y^2}{r^2}, \\ d_{3z^2-r^2} &= Y_{2,0} = \sqrt{\frac{5}{16\pi}}\,\frac{3z^2-r^2}{r^2}. \end{aligned}$$

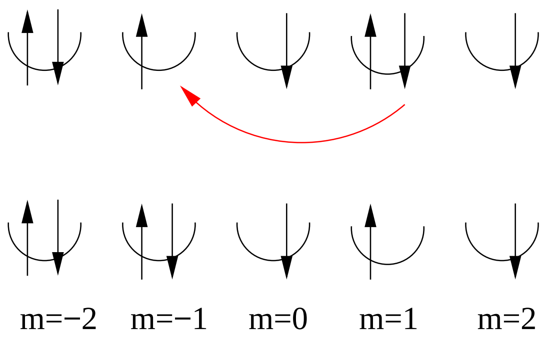
- d_{xy}, d_{xz} and d_{yz} are called the t_{2g} orbitals, $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ are the e_g orbitals

Effect of the CEF on Multiplets

- We have now calculated the matrix elements $V_{CEF}(\nu_i, \nu_j)$ of the Crystalline Electric Field

$$H_{CEF} = \sum_{i,j} V_{CEF}(\nu_i, \nu_j)\; c_{\nu_i}^{\dagger}\; c_{\nu_j}$$

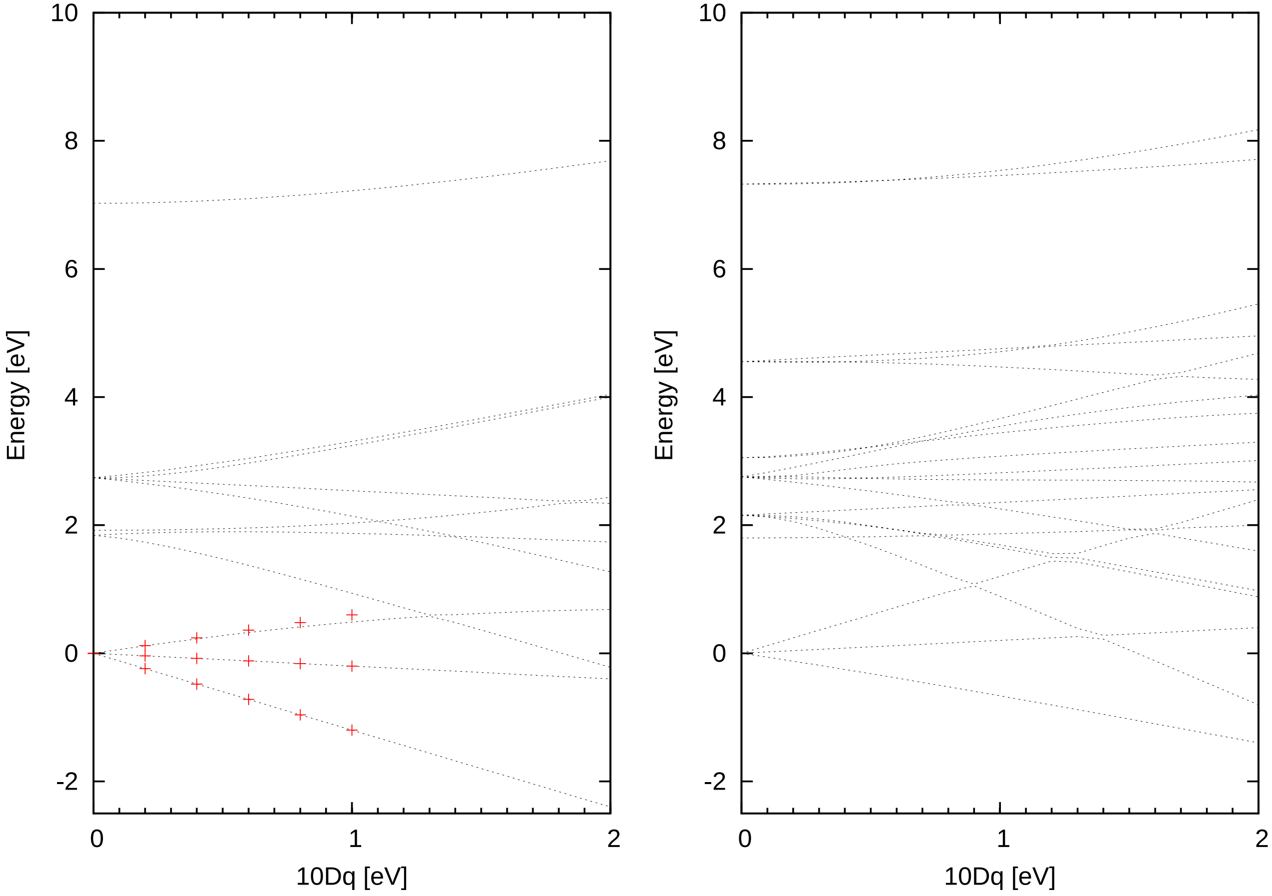
- For octahedral coordination this involves a single parameter $10Dq = E(e_g) - E(t_{2g})$ which depends on the radial wave function - this can again be determined by fit to experiment
- To find how the multiplets of the TM-ion are affected by the CEF we can simply include it into the exact diagonalization program (mind the Fermi sign!)



- The splitting of multiplets can also be calculated analytically using the Wigner-Eckart theorem

Effect of the CEF on Multiplets

Eigenvalue spectrum for Ni^{2+} and Co^{2+} as $10Dq$ increases - such plots are called Tanabe-Sugano-diagrams



A colorful application: Transition metal ions in aqueous solution

- TM ions immersed in water surround themselves by an octahedron of water molecules whereby all 6 dipole moments point away from the ion
- Such an object - TM $(H_2O)_6$ - is called a complex
- This also creates an electric field with cubic symmetry which splits e_g and t_{2g} levels
- The multiplets are split according to the Tanabe-Sugano diagrams
- Phonon assisted optical transitions between the CEF-split multiplets involve energy differences corresponding to photons with wavelengths in the visible range give such solutions intense colors

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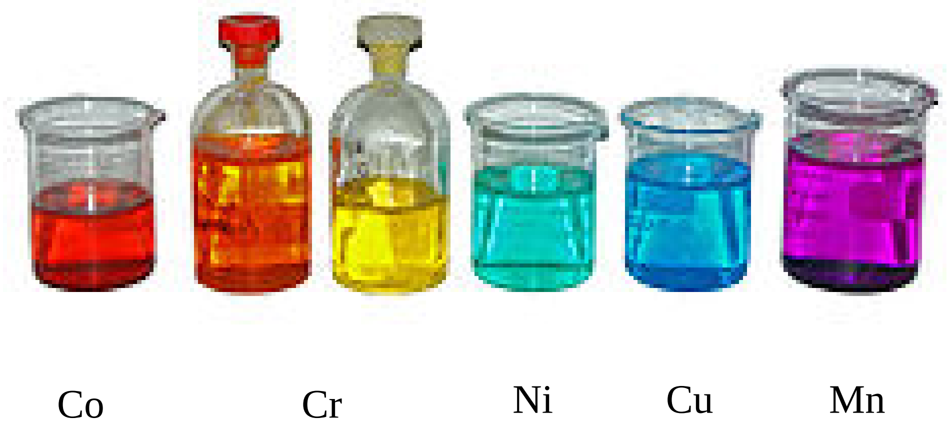
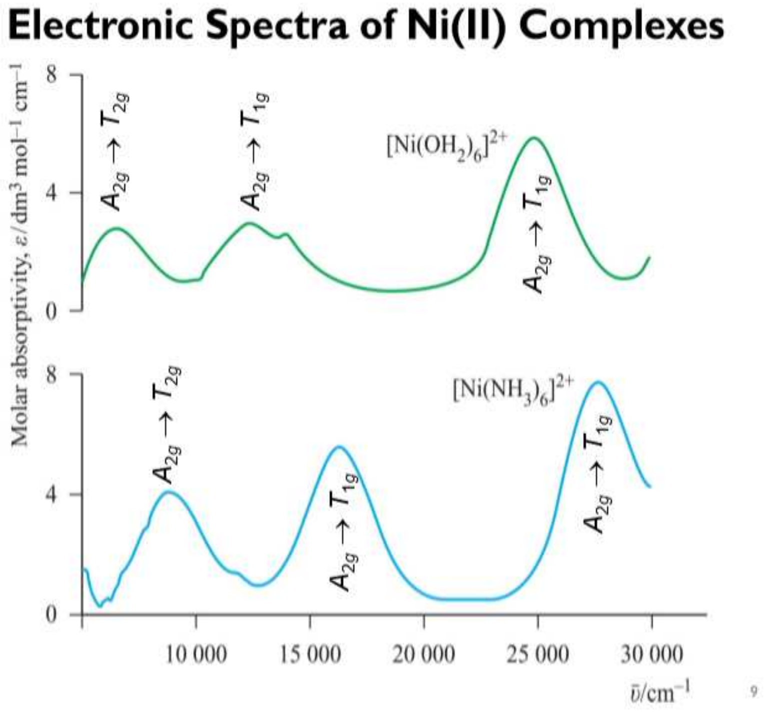
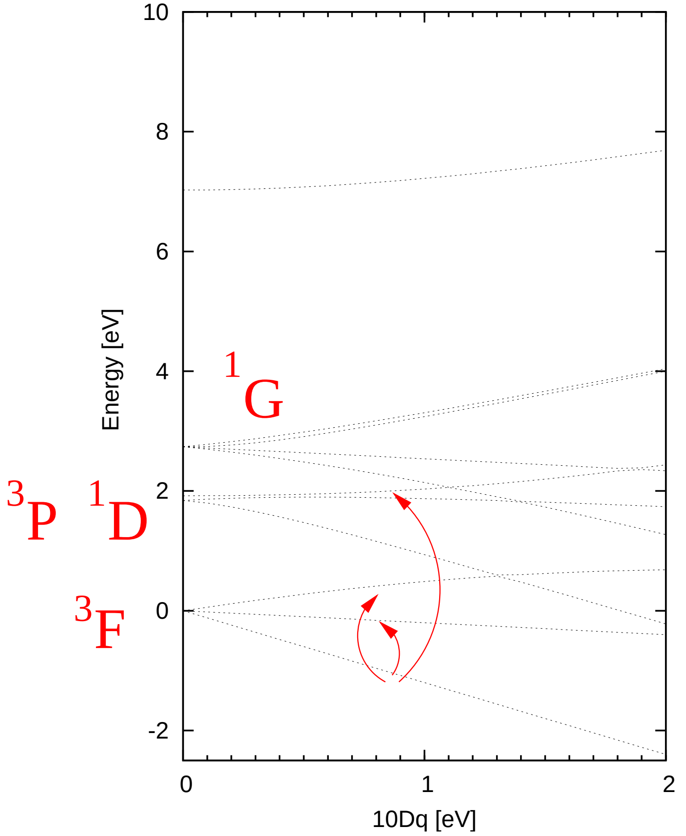


CEF-splitting observed with the bare eye!

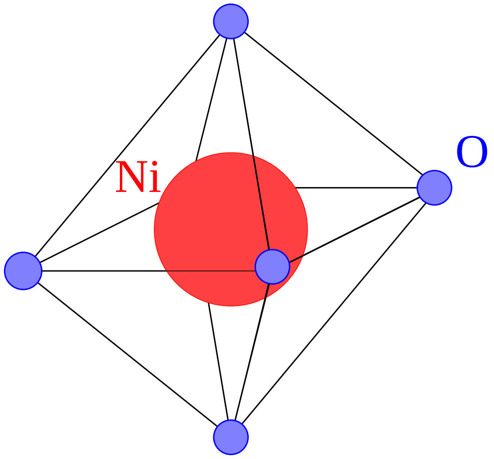
The absorption spectra can be analyzed quantitatively using the Tanabe-Sugano diagrams e.g. Ni^{2+} or d^8

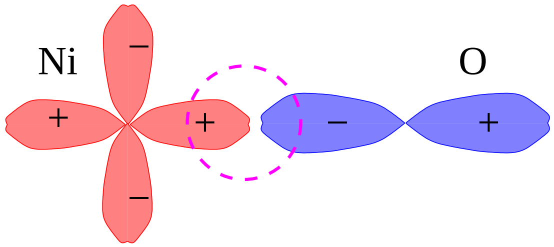

Electronic Spectra of Ni(II) Complexes



Charge transfer

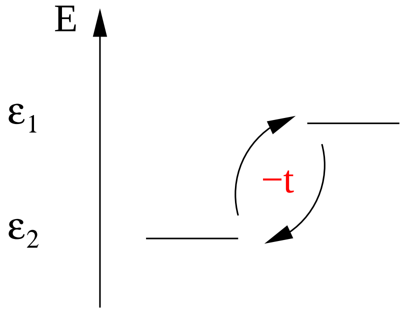
- Due to the overlap of the TM 3d wave functions and the atomic orbitals on the ligands there may be charge transfer, i.e. electrons may tunnel from a ligand orbital into a TM 3d orbital





- This modifies the multiplets of the TM-ion by a mechanism called level repulsion

A toy model



- Consider a single 'ligand-orbital' $|\psi_1\rangle$ (energy ϵ_1) coupled to a single 'd orbital' $|\psi_2\rangle$ (energy ϵ_2):

$$H \;=\; \epsilon_1\, c_1^\dagger\, c_1 + \epsilon_2\, c_2^\dagger\, c_2 - t \left(\, c_1^\dagger\, c_2 + c_2^\dagger\, c_1 \,\right)$$

- The hybridization matrix element is $-t = \langle\psi_1|H|\psi_2\rangle$
- We make the ansatz $|\psi\rangle = u|\psi_1\rangle + v|\psi_2\rangle$ - this leads to

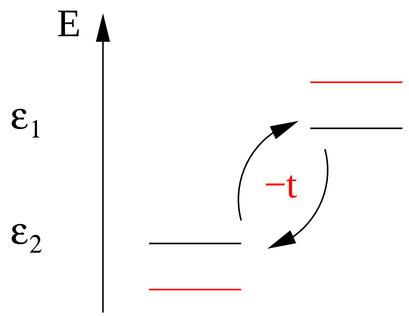
$$h = \begin{pmatrix} \epsilon_1 & -t \\ -t & \epsilon_2 \end{pmatrix} \;\Rightarrow\; E_\pm = \frac{\epsilon_1+\epsilon_2}{2} \pm \sqrt{\left(\frac{\epsilon_1-\epsilon_2}{2}\right)^2 + t^2}$$

- Let $\epsilon_1 > \epsilon_2$ - then ...

$$\sqrt{\left(\frac{\epsilon_1-\epsilon_2}{2}\right)^2 + t^2} = \frac{\epsilon_1-\epsilon_2}{2} + \Delta$$

... with some $\Delta > 0$ $\quad\Rightarrow\quad$ $E_+ = \epsilon_1 + \Delta$ $\qquad$ $E_- = \epsilon_2 - \Delta$

A toy model



- Consider a single ‘ligand-orbital’ $|\psi_1\rangle$ (energy ϵ_1) coupled to a single ‘d orbital’ $|\psi_2\rangle$ (energy ϵ_2):

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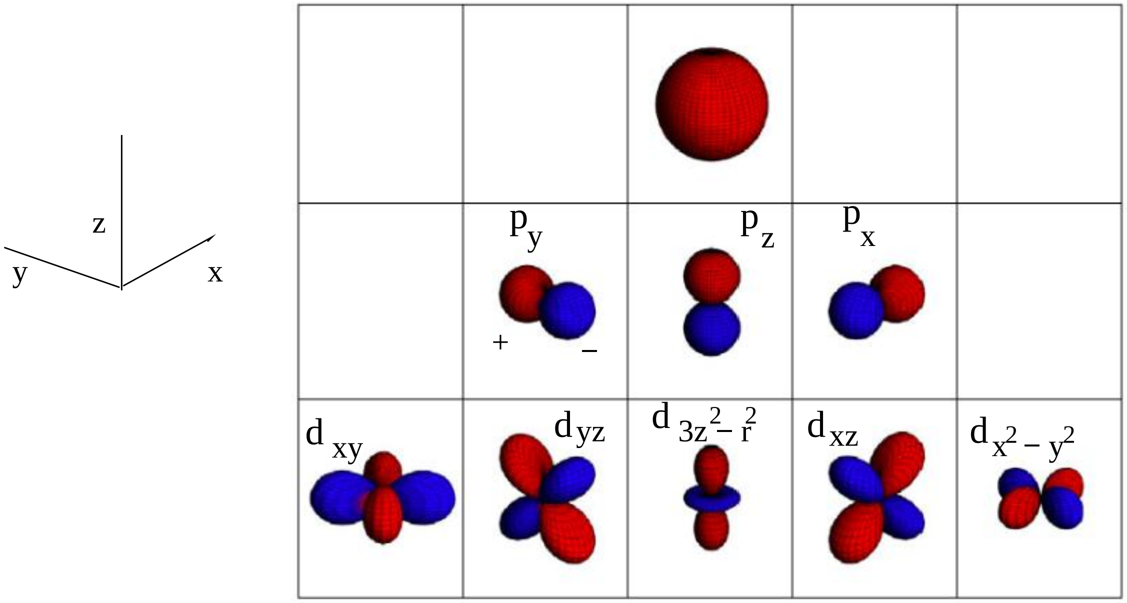
- Let $\epsilon_1 > \epsilon_2$ - then ...

$$\sqrt{\left(\frac{\epsilon_1-\epsilon_2}{2}\right)^2 + t^2} = \frac{\epsilon_1-\epsilon_2}{2} + \Delta$$

... with some $\Delta > 0$ $\Rightarrow$ $E_+ = \epsilon_1 + \Delta$ $E_- = \epsilon_2 - \Delta$

d-level splitting by level repulsion



- All orbitals other than s-like have ‘lobes’ which point in different directions
- The matrix element $-t = \langle\psi_1|H|\psi_2\rangle$ will be larger/smaller if the lobe points towards the ligand
- Different d-orbitals get ‘repelled’ differently depending on the position of ligands

Toy model 2 real material

We recall the toy model

$$H = \epsilon_1 \, c_1^\dagger \, c_1 + \epsilon_2 \, c_2^\dagger \, c_2 - \left(t \, c_1^\dagger \, c_2 + H.c. \right).$$

More realistic version

$$H = \sum_i \; \epsilon_{\nu_i} \; c_{\nu_i}^\dagger c_{\nu_i} + \sum_j \; \epsilon_{\mu_j} \; l_{\mu_j}^\dagger l_{\mu_j} - \sum_{i,j} \left(t_{\nu_i,\mu_j} \; c_{\nu_i}^\dagger \; l_{\mu_j} + H.c. \right)$$

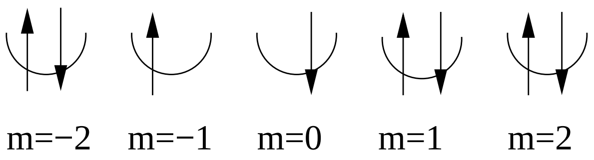
- $c_{\nu_i}^\dagger$ with $\nu_i = (m_i, \sigma_i)$, $m_i \in \{-2, \ldots, 2\}$, are creation operators for d-electrons
- $l_{\mu_j}^\dagger$ with $\mu_j = (\mathbf{R}_j, \beta_j, \sigma_j)$, $\beta_j \in \{s, p_x, p_y, p_z\}$ are creation operators for electrons in ligand orbitals
- The orbital energies of d-orbitals/ligand orbitals are ϵ_{μ_j} and ϵ_{ν_i}
- The hybridization integrals t_{ν_i,μ_j} may be expressed in terms of relatively few parameters by using the Slater-Koster tables (see notes for an example)

Charge transfer

The Hamiltonian including hybridization:

$$H = H_{Cou} + H_{CEF} + \sum_i \epsilon_{\nu_i} \; c^\dagger_{\nu_i} c_{\nu_i} + \sum_j \epsilon_{\mu_j} \; l^\dagger_{\mu_j} l_{\mu_j} - \sum_{i,j} \left(t_{\nu_i,\mu_j} \; c^\dagger_{\nu_i} \; l_{\mu_j} + H.c. \right)$$

This is easily implemented in the exact diagonalization program (mind the Fermi sign!)



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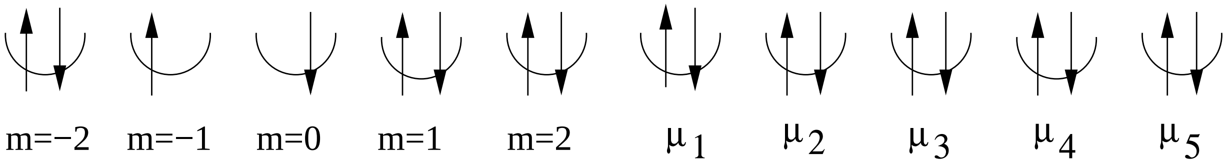

Charge transfer

The Hamiltonian including hybridization:

$$H = H_{Cou} + H_{CEF} + \sum_i \epsilon_{\nu_i} \; c^\dagger_{\nu_i} c_{\nu_i} + \sum_j \epsilon_{\mu_j} \; l^\dagger_{\mu_j} l_{\mu_j} - \sum_{i,j} \left(t_{\nu_i,\mu_j} \; c^\dagger_{\nu_i} \; l_{\mu_j} + H.c. \right)$$

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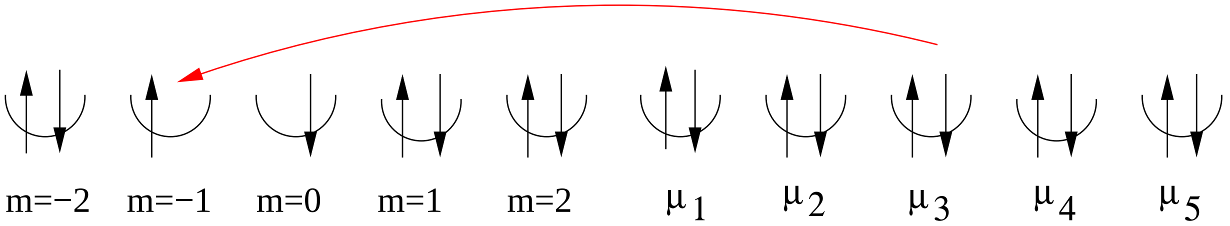
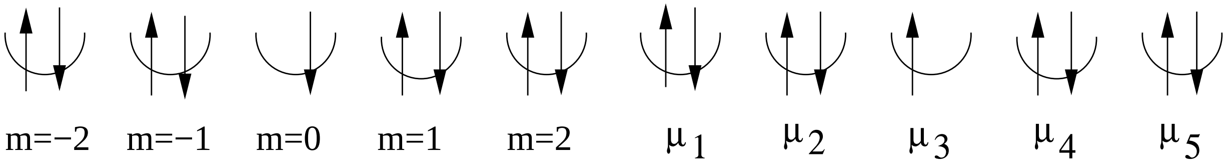
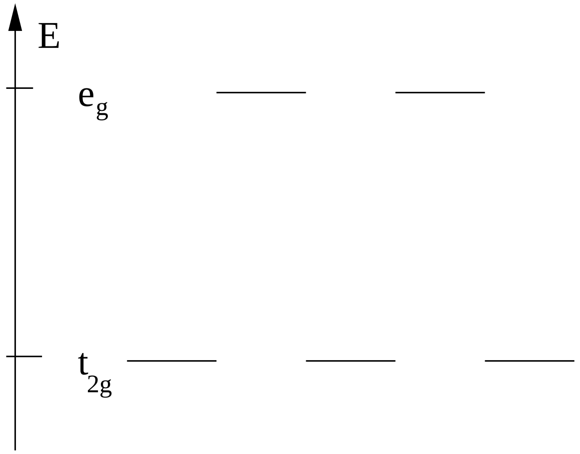




Charge transfer

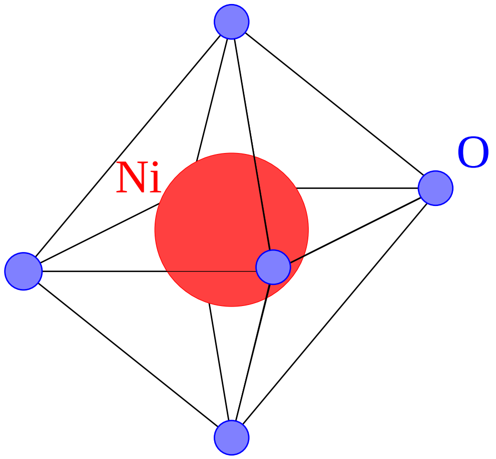
- For an ideal octahedron of ligands with s- or p-orbitals this procedure gives the same splitting as the CEF
- The 5-fold degenerate d-level is again split into the three t$_{2g}$ levels and the two e$_g$-levels



- See my notes for details
- This is no coincidence but can be understood in terms of irreducible representations of the cubic group - see the book by Griffiths cited in my notes
- In general the effects of CEF and charge transfer have to be added

An important application of multiplet theory: cluster simulation of experimental spectra

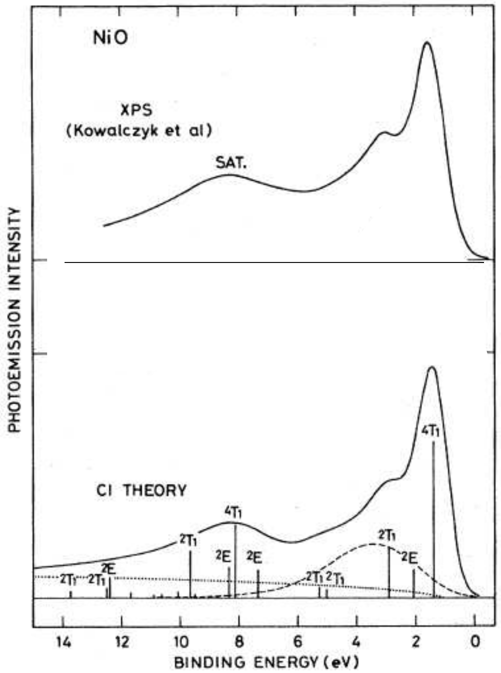
- Various spectroscopies on transition metal compounds can be simulated by calculating these spectra for a cluster which consists of a TM ion and its nearest neighbors:

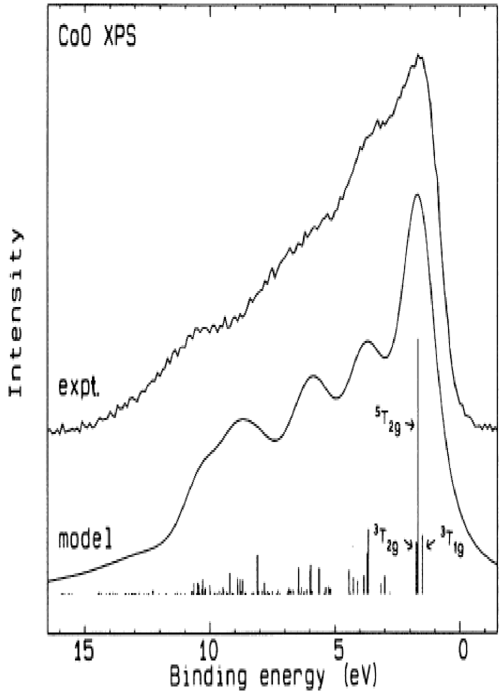


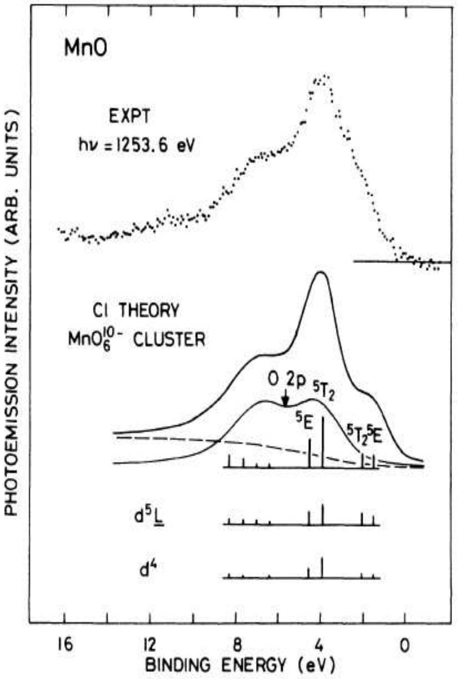
Examples are

- X-ray photoemission spectra (XPS)
- X-ray absorption spectra (XAS)
- Core-level photoemission spectra (XPS)
- Resonant inelastic X-ray scattering (RIXS)

Cluster calculation of XPS spectra - results for 3d transition metal compounds with rocksalt structure





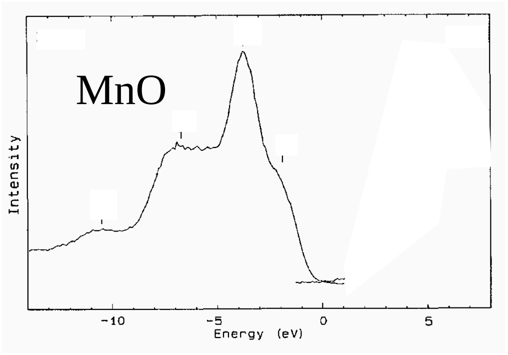


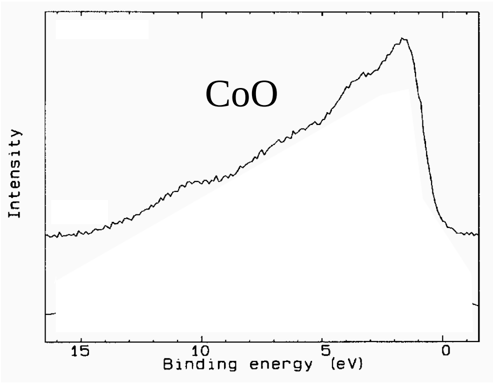
NiO: A. Fujimori and F. Minami, Phys. Rev. B **30**, 957 (1984)

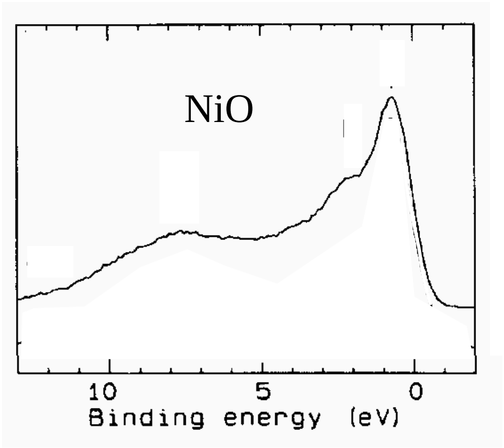
CoO: J. van Elp *et al.*, Phys. Rev. B **44**, 6090 (1991)

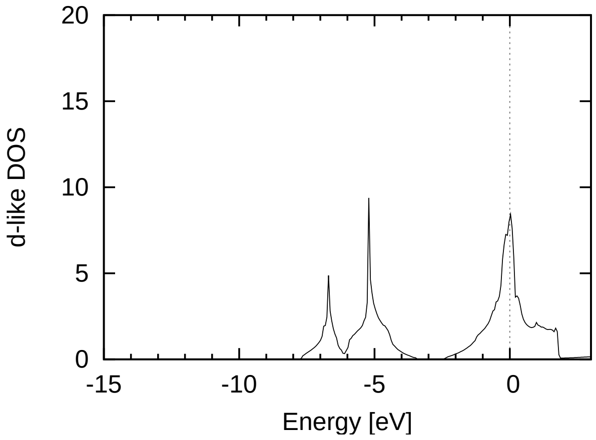
MnO: A. Fujimori *et al.*, Phys. Rev. B **42**, 7580 (1990)

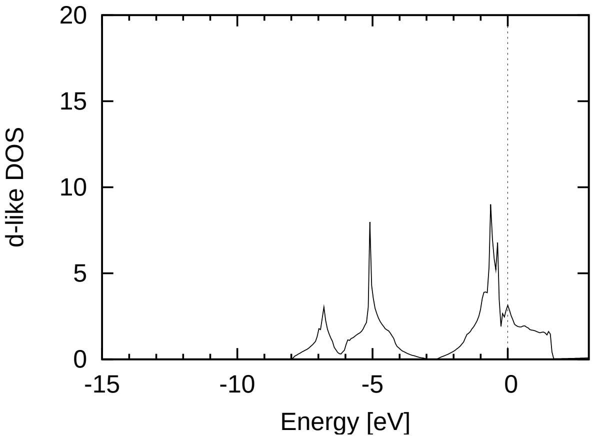
Experimental XPS spectra versus TM 3d-like DOS from LDA calculations

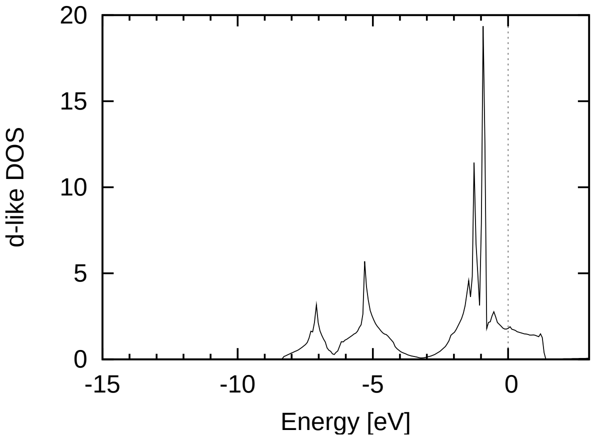








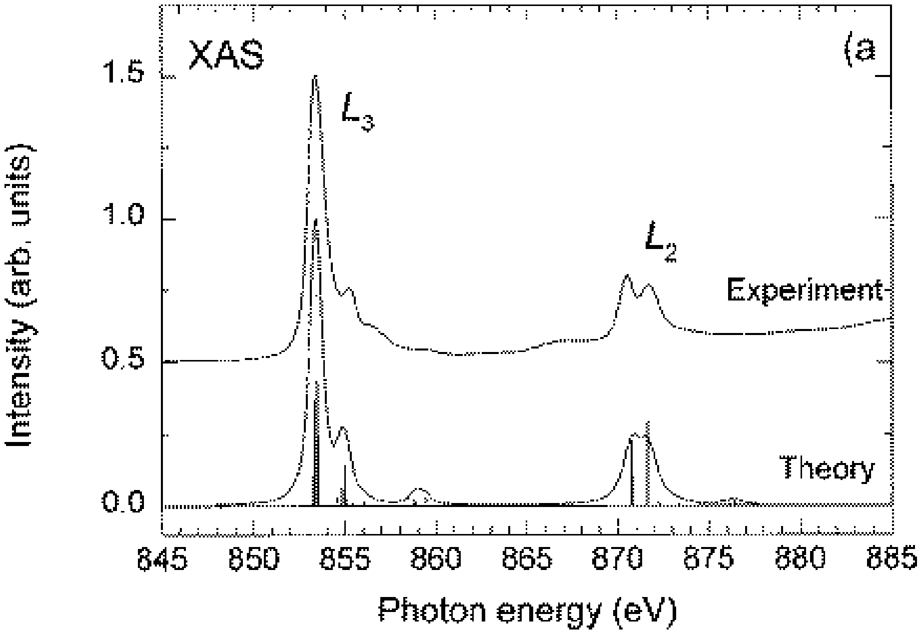




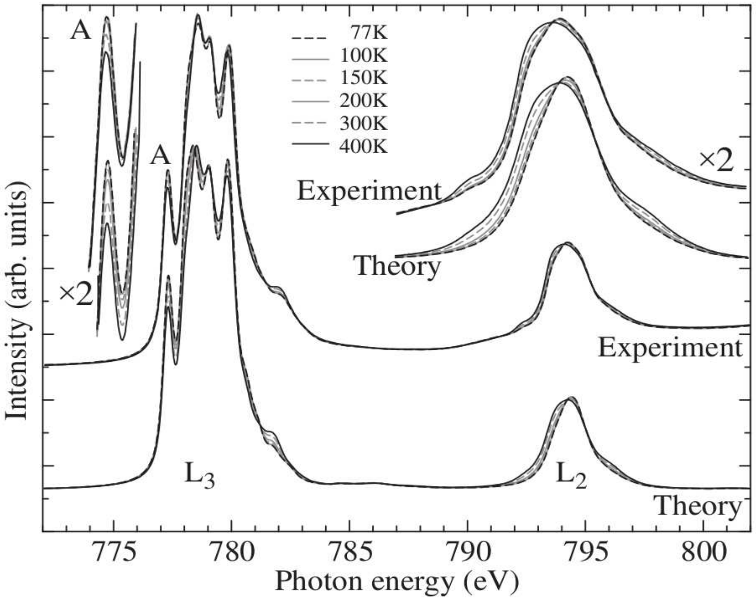
What determines the spectrum is not the single-particle band structure but the multiplets of the TM ion!

Cluster calculation of XAS

NiO

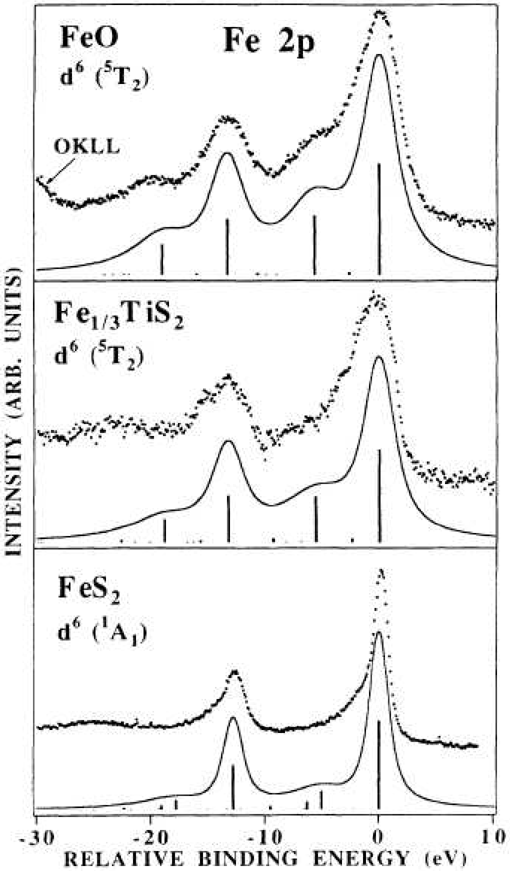


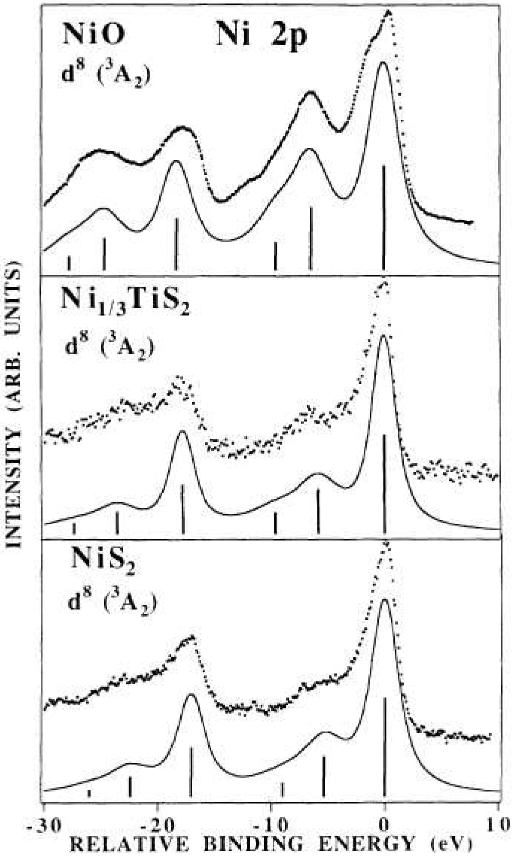
CoO



NiO: M. Finazzi *et al.*, Phys. Rev. B **59**, 9933 (1999)
CoO: M. Haverkort, Ph. D, thesis (2002)

Core-level photoemission: Experiment vs Cluster spectra





Taken from A. E. Bocquet *et al.*, Phys. Rev. B **46**, 3771 (1992)

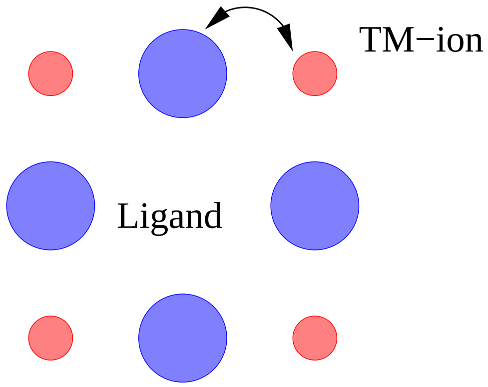
Multiband Hubbard models

- All in all, the most complete Hamiltonian to describe transition metal compounds would be like this

$$
\begin{aligned}
H \;=\; & \frac{1}{2}\sum_{i,j,k,l} V(\nu_i,\nu_j,\nu_k,\nu_l)\; c^\dagger_{\nu_i}\, c^\dagger_{\nu_j}\, c_{\nu_k}\, c_{\nu_l} + \sum_{i,j} V_{CEF}(\nu_i,\nu_j)\; c^\dagger_{\nu_i} c_{\nu_j} + \sum_{i,j} V_{SOC}(\nu_i,\nu_j)\; c^\dagger_{\nu_i} c_{\nu_j} \\
& - \sum_{i,j} \left(t_{\nu_i,\mu_j}\;\; c^\dagger_{\nu_i}\;\; l_{\mu_j} + H.c. \right) + \sum_{j}\; \epsilon_{\mu_j}\;\; l^\dagger_{\mu_j} l_{\mu_j} + \sum_{i}\; \epsilon_{\nu_i}\;\; c^\dagger_{\nu_i} c_{\nu_i}
\end{aligned}
$$

This comprises

- The Coulomb interaction in the TM d/f-shell
- The Crystalline electric field in the TM d/4-shell
- The spin-orbit coupling in the TM d/f-shell
- The charge transfer between TM d/f-shell and ligands
- The orbital energies



This is probably an accurate description but the number of orbitals/unit cell often is prohibitively large....

Multiband Hubbard models

- The large number of orbitals/unit cell is a major problem - we need simplifications!

$$H = \frac{1}{2}\sum_{i,j,k,l} V(\nu_i,\nu_j,\nu_k,\nu_l)\ c^\dagger_{\nu_i}\, c^\dagger_{\nu_j}\, c_{\nu_k}\, c_{\nu_l} + \sum_{i,j} V_{CEF}(\nu_i,\nu_j)\ c^\dagger_{\nu_i} c_{\nu_j} + \sum_{i,j} V_{SOC}(\nu_i,\nu_j)\ c^\dagger_{\nu_i} c_{\nu_j}$$
$$- \sum_{i,j} \left(t_{\nu_i,\mu_j}\ c^\dagger_{\nu_i}\ l_{\mu_j} + H.c. \right) + \sum_{j} \epsilon_{\mu_j}\ l^\dagger_{\mu_j} l_{\mu_j} + \sum_{i} \epsilon_{\nu_i}\ c^\dagger_{\nu_i} c_{\nu_i}$$

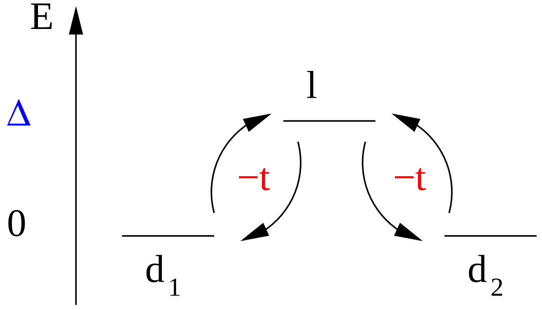
Frequently used simplifications are

- We can ‘project out’ ligands and derive a Hamiltonian with only d/f-orbitals
- We can use the limit of large CEF-splitting and omit high-energy d-levels
- We can use the simplified form of the Coulomb interaction

Projecting out the ligands

- Consider a toy model with to 'd-levels' and one 'bridging orbital'

$$H = \Delta\, l^\dagger l - t\left(\, d_1^\dagger l + l^\dagger d_1 + d_2^\dagger l + l^\dagger d_2 \right),$$



- H is invariant under the exchange $1 \leftrightarrow 2$
- Introduce symmetric and antisymmetric combinations

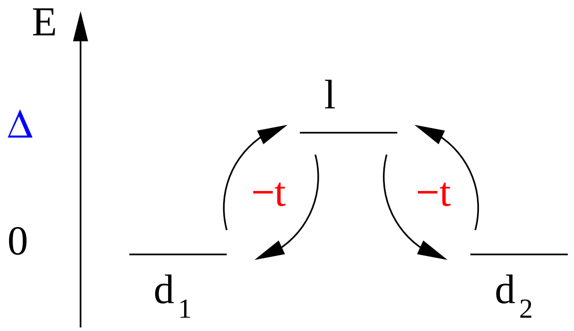
$$d_\pm^\dagger = \frac{1}{\sqrt{2}}\left(d_1^\dagger \pm d_2^\dagger\right)$$

$$\Rightarrow H = \Delta\, l^\dagger l - \sqrt{2}t\left(\, d_+^\dagger l + l^\dagger d_+ \right)$$

$\Rightarrow$ One solution is $d_-^\dagger|0\rangle$ with energy $E = 0$ - for the remainder make the *ansatz* $|\psi\rangle = (A_+ d_+^\dagger + A_l l^\dagger)|0\rangle$:

$$h = \begin{pmatrix} 0 & -\sqrt{2}t \\ -\sqrt{2}t & \Delta \end{pmatrix} \Rightarrow E = \begin{cases} \frac{1}{2}(\Delta + \sqrt{\Delta^2 + 8t^2}) \\ \frac{1}{2}(\Delta - \sqrt{\Delta^2 + 8t^2}) \end{cases}$$

Now let $\Delta \gg t$ or $\frac{t}{\Delta} \ll 1$



$$h = \begin{pmatrix} 0 & -\sqrt{2}t \\ -\sqrt{2}t & \Delta \end{pmatrix} \Rightarrow E = \begin{cases} \frac{1}{2}(\Delta + \sqrt{\Delta^2 + 8t^2}) & \xrightarrow{\Delta \gg t} \quad \Delta + \frac{2t^2}{\Delta} \\ \frac{1}{2}(\Delta - \sqrt{\Delta^2 + 8t^2}) & \xrightarrow{\Delta \gg t} \quad -\frac{2t^2}{\Delta} \end{cases}$$

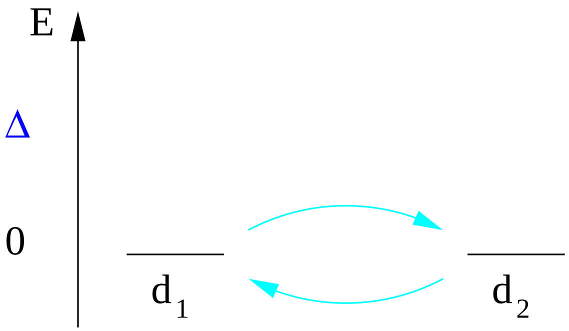
Eigenfunctions:

$$\Delta + \frac{2t^2}{\Delta} \qquad \left[\, l^\dagger + \frac{\sqrt{2}t}{\Delta}\, d_+^\dagger \right] |0\rangle$$

$$0 \qquad d_-^\dagger \; |0\rangle$$

$$-\frac{2t^2}{\Delta} \qquad \left[\, d_+^\dagger - \frac{\sqrt{2}t}{\Delta}\, l^\dagger \right] |0\rangle$$

Now let $\Delta \gg t$



$$h = \begin{pmatrix} 0 & -\sqrt{2}t \\ -\sqrt{2}t & \Delta \end{pmatrix} \;\Rightarrow\; E = \begin{cases} \frac{1}{2}(\Delta + \sqrt{\Delta^2 + 8t^2}) & \xrightarrow{\Delta \gg t} \quad \Delta + \frac{2t^2}{\Delta} \\ \frac{1}{2}(\Delta - \sqrt{\Delta^2 + 8t^2}) & \xrightarrow{\Delta \gg t} \quad -\frac{2t^2}{\Delta} \end{cases}$$

Eigenfunctions:

$$\Delta + \frac{2t^2}{\Delta} \qquad \left[\, l^\dagger + \frac{\sqrt{2}t}{\Delta}\, d_+^\dagger \right] |0\rangle$$

$$0 \qquad d_-^\dagger \;\; |0\rangle$$

$$-\frac{2t^2}{\Delta} \qquad \left[\, d_+^\dagger - \frac{\sqrt{2}t}{\Delta}\, l^\dagger \right] |0\rangle$$

$\Rightarrow$ Effektive Hamiltonian for ‘low energy sector’

$$H_{eff} \;=\; -\frac{t^2}{\Delta} \sum_{i=1,2} d_i^\dagger d_i - \frac{t^2}{\Delta}(d_1^\dagger d_2 + d_2^\dagger d_1)$$

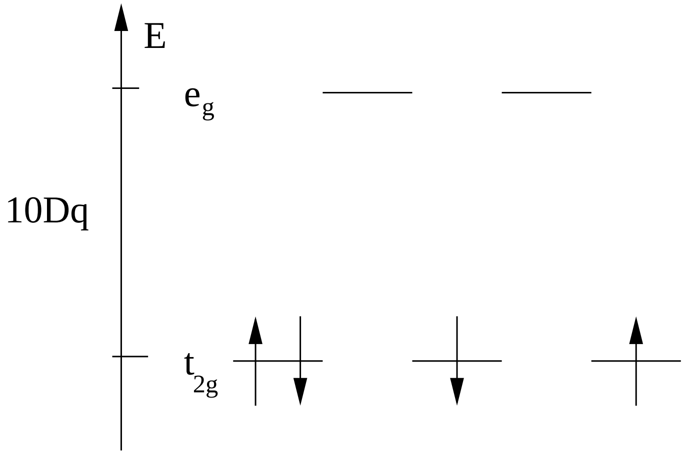
$$= \left(-\frac{t^2}{\Delta} + \frac{t^2}{\Delta}\right) d_-^\dagger d_- + \left(-\frac{t^2}{\Delta} - \frac{t^2}{\Delta}\right) d_+^\dagger d_+ = -\frac{2t^2}{\Delta}\, d_+^\dagger d_+$$

Projecting out the ligands

- When ligand orbitals are high in energy one may omit the ligands and instead introduce 'effective d-d-hopping integrals' which describe 'excursions' into the high-energy ligand orbitals
- This reduces the number of orbitals significantly
- The effective hopping integrals may be deduced by a fit to the band structure - but using only bands with d-character!

Limit of strong CEF

- Let us consider Cr^{2+} - this has d^4 - in octahedral coordination
- Considering only the CEF and assume large $10Dq$:



- For large $10Dq$ we may consider only the t_{2g} orbitals → reduction in ther number of orbitals
- To deal with the Coulomb scattering within the d-shell it is advantageous to compute the Coulomb matrix elements with $d_{xy}(\Theta,\phi),\ldots$ instead of the $Y_{2,m}(\Theta,\phi)$ - see the textbook by Griffiths (referenced in notes)

$$V(\nu_1,\nu_2,\nu_3,\nu_4) \;=\; \int dx \int dx'\; \psi^*_{\nu_1}(x)\; \psi^*_{\nu_2}(x')\; V_c(x,x')\; \psi_{\nu_4}(x)\; \psi_{\nu_3}(x')$$

Simplified Coulomb interaction

- Lastly one can use the simplified Coulomb interaction ...

$$\tilde{H}_1 \ = \ \sum_m U \ n_{m,\uparrow} \, n_{m,\downarrow} + \frac{1}{2} \sum_{m_1 \neq m_2} \left(\ (U' - \frac{1}{2} \, J) \, n_{m_1} n_{m_2} - 2J \ \boldsymbol{S}_{m_1} \cdot \boldsymbol{S}_{m_2} \ \right)$$

Summary

- The Coulomb interaction in partly filled shells of transition metals is particularly strong - this leads to numerous interesting phenomena
- The Coulomb interaction can be described by multiplet theory - this is an extremely successful theory which describes many experimental results quantitatively
- The Coulomb Hamiltonian derived in multiplet theory therefore is a natural starting point for building models for transition metal compounds - i.e. multiband Hubbard models
- Unfortunately the resulting Hamiltonian is quite complex, but simplifications are possible