Multiplets in transition metal ions

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

- Metallic Ferromagnets like Fe, Co, Ni

- Mott insulators like NiO

- High temperature superconductors such as copper oxide superconductors or iron pnictide superconductors

- Colossal magnetoresistance in Mn-based perovskites

- and many more......

The reason for the unexpected behaviour: Small radius of the transition metal $3d$ shell

$$\frac{V_{Shell}}{V_{Wigner-Seitz}}$$

'Nuclear charge'
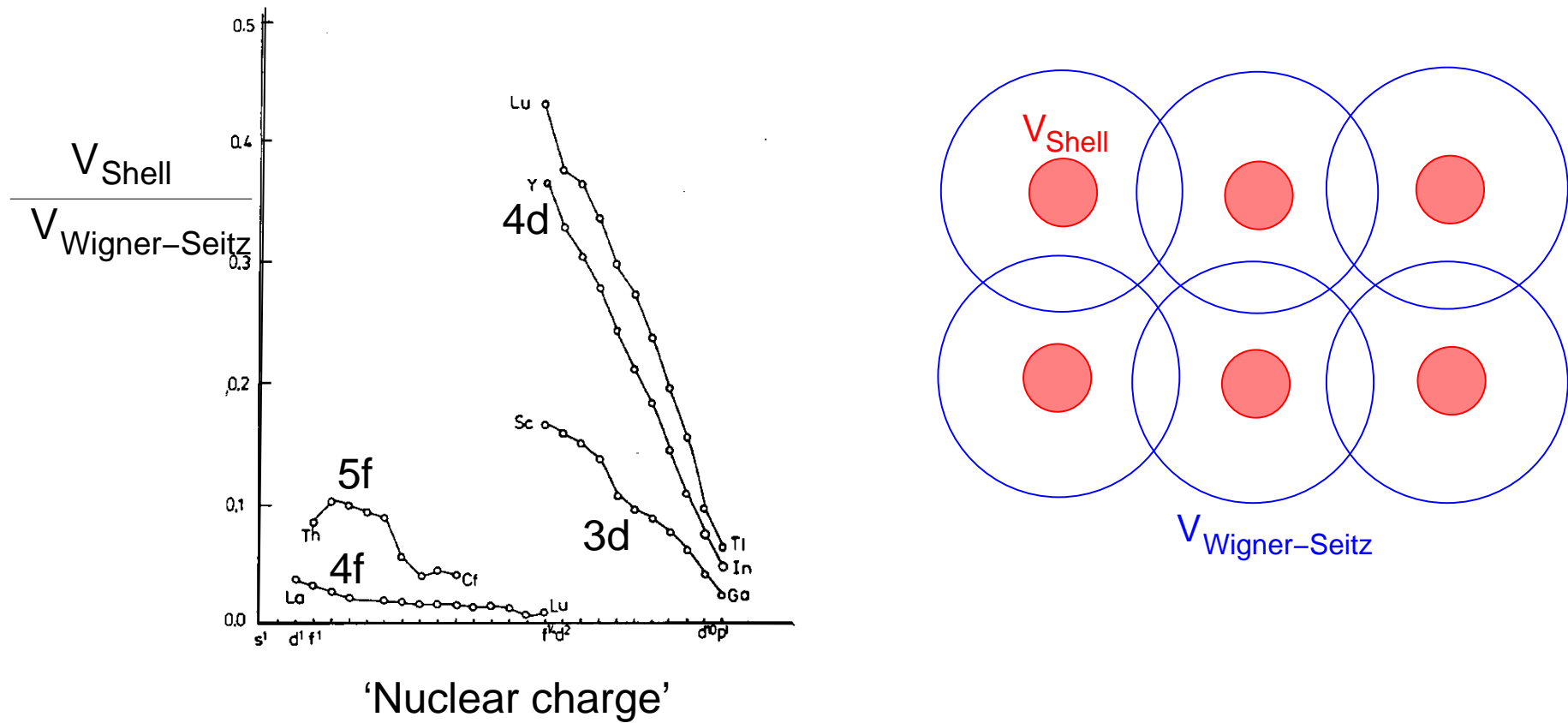
Taken from: D. van der Marel and G. A. Sawatzky, Phys. Rev. B **37**, 10674 (1988).

The small spatial extent of the $3d$ shell makes the Coulomb repulsion between electrons very strong
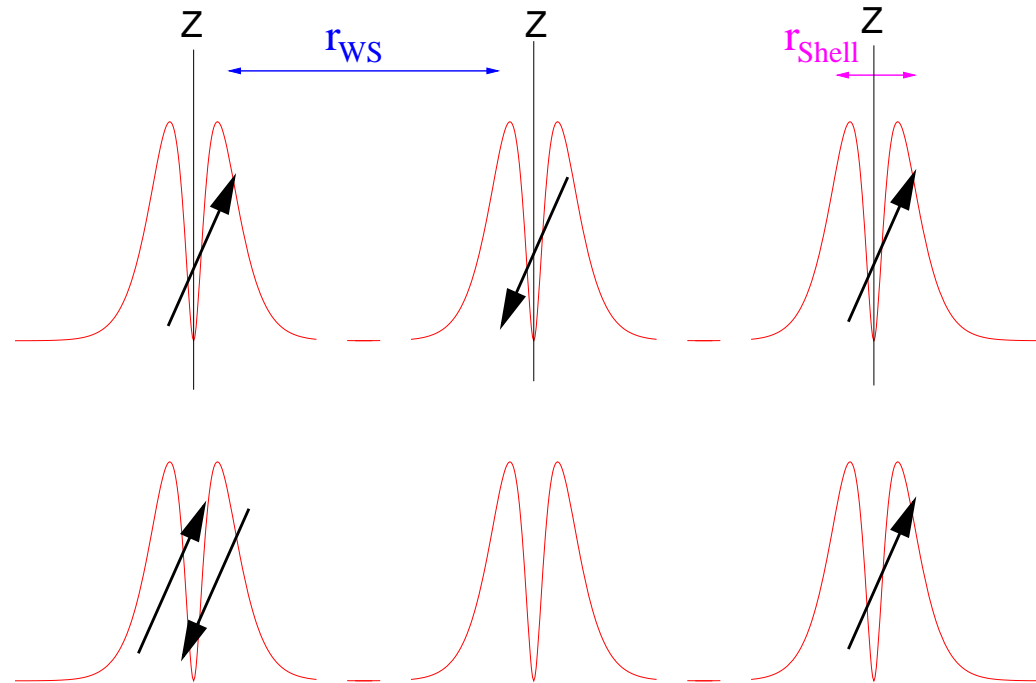
Up to 10eV increase in energy!

We thus need a detailed understanding of the Coulomb interaction in a partly filled atomic shell

II: Coulomb interaction between electrons in a free atom/ion

- 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})
$3p^6 3d^8$	^{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
$3p^6 3d^8$	^{1}S	0	52 532.0

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

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
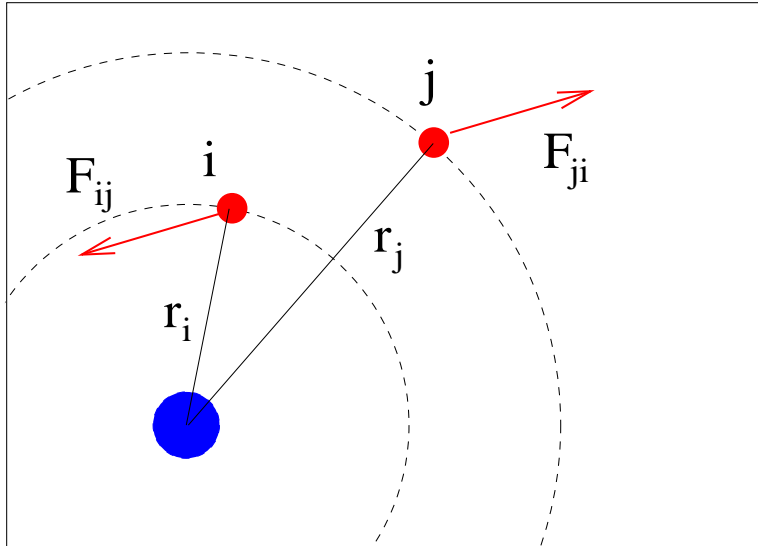
U: Average Coulomb energy for a pair of electrons

For a nondegenerate orbital we have

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

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

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

Coulomb repulsion between electrons - Classical picture

$$\boldsymbol{F}_{ij} = \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|^3} \left(\boldsymbol{r}_i - \boldsymbol{r}_j\right)$$

$$\boldsymbol{\tau}_{ij} = \boldsymbol{r}_i \times \boldsymbol{F}_{ij} = -\frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|^3} \ \boldsymbol{r}_i \times \boldsymbol{r}_j$$

$$\boldsymbol{\tau}_{ji} = \boldsymbol{r}_j \times \boldsymbol{F}_{ji} = -\frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|^3} \ \boldsymbol{r}_j \times \boldsymbol{r}_i$$

$$\boldsymbol{\tau}_{ji} = -\boldsymbol{\tau}_{ij}$$

$\rightarrow$ Exchange of angular momentum

Exchange of angular momentum - Quantum mechanical version
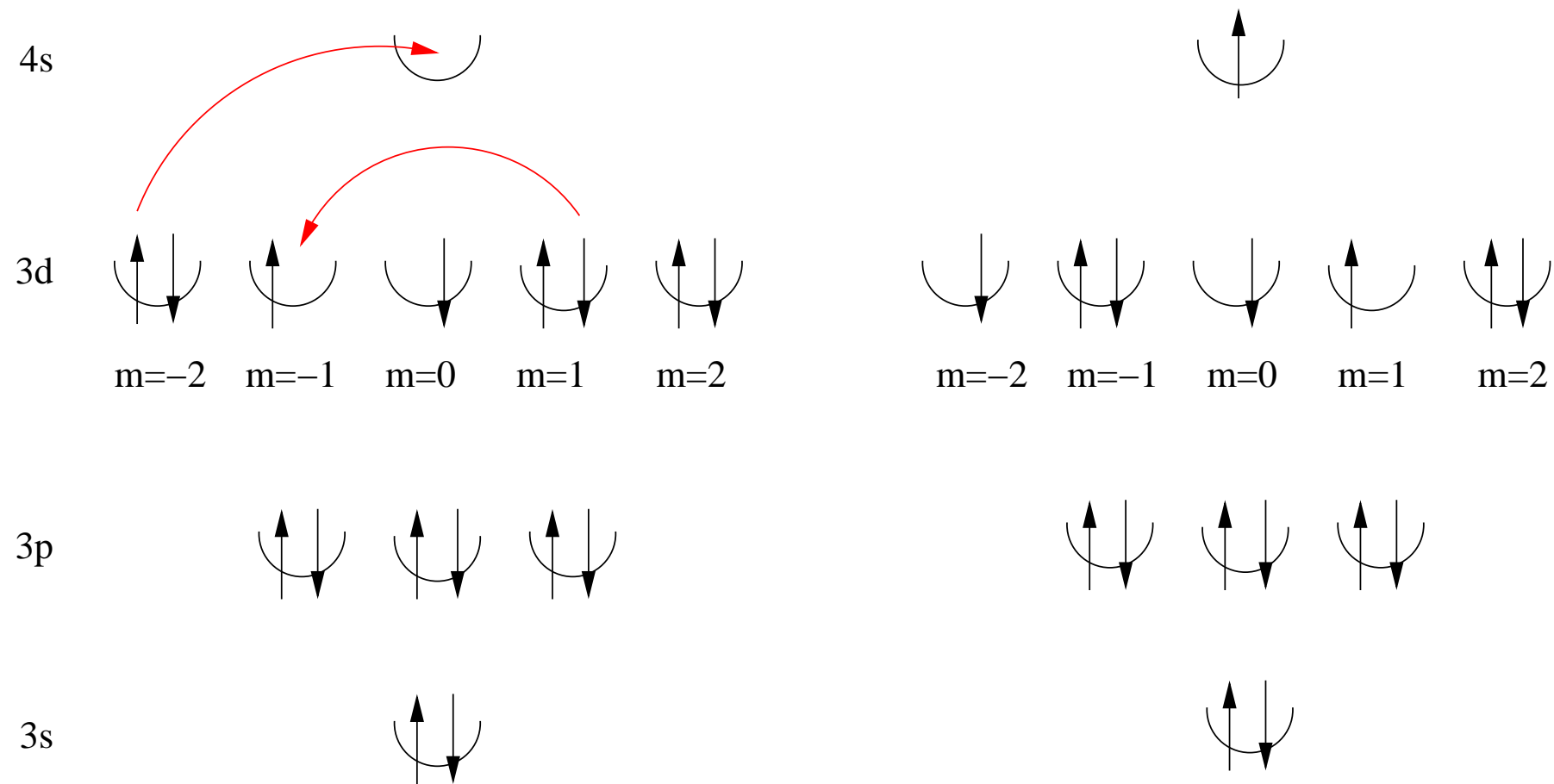

m=−2   m=−1   m=0   m=1   m=2
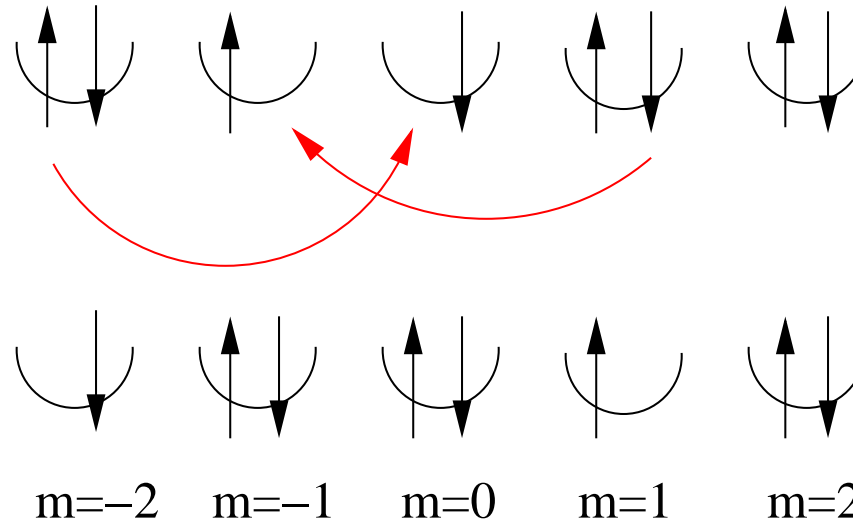
- Electrons in a partially filled shell scatter from each other due to their Coulomb interaction

- This amounts to a redistribution of the electrons within the partially filled shell

- For L^z to be conserved the scattering electrons must 'move along the m-ladder' in exactly opposite ways

- To study these scattering processes we assume that the separation in energy between the different atomic atomic orbitals - such as $3d$, $4s$, $3p$ - is much larger than the matrix element for the above scattering process

- in other words: we take the orbital energies as H_0, the Coulomb interaction as perturbation H_1

In other words: we take into processes like this one...

4s

3d

m=−2   m=−1   m=0   m=1   m=2   m=−2   m=−1   m=0   m=1   m=2

3p

3s

...but not this one....
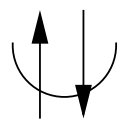
4s

3d

m=−2   m=−1   m=0   m=1   m=2   m=−2   m=−1   m=0   m=1   m=2

3p

3s
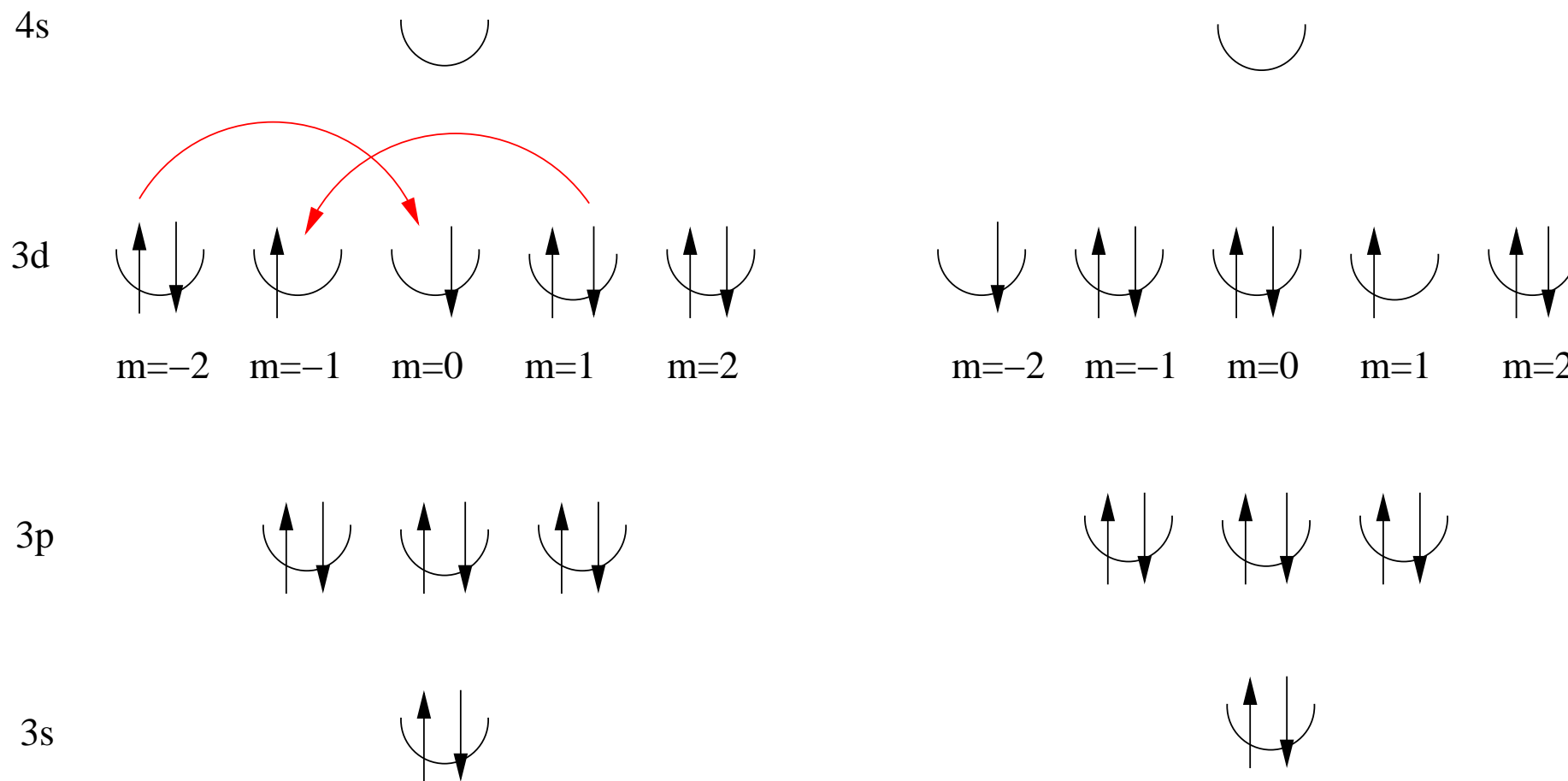
... or this one

4s

3d
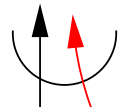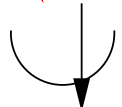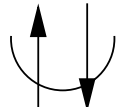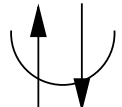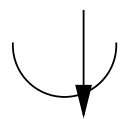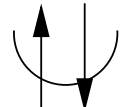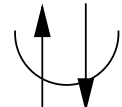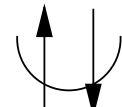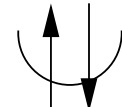
m=−2 m=−1 m=0 m=1 m=2   m=−2 m=−1 m=0 m=1 m=2

3p
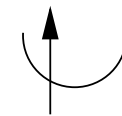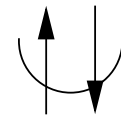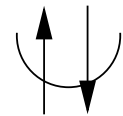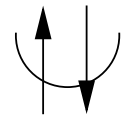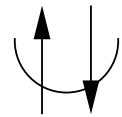
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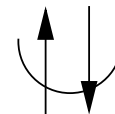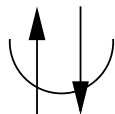
We take processes like this one
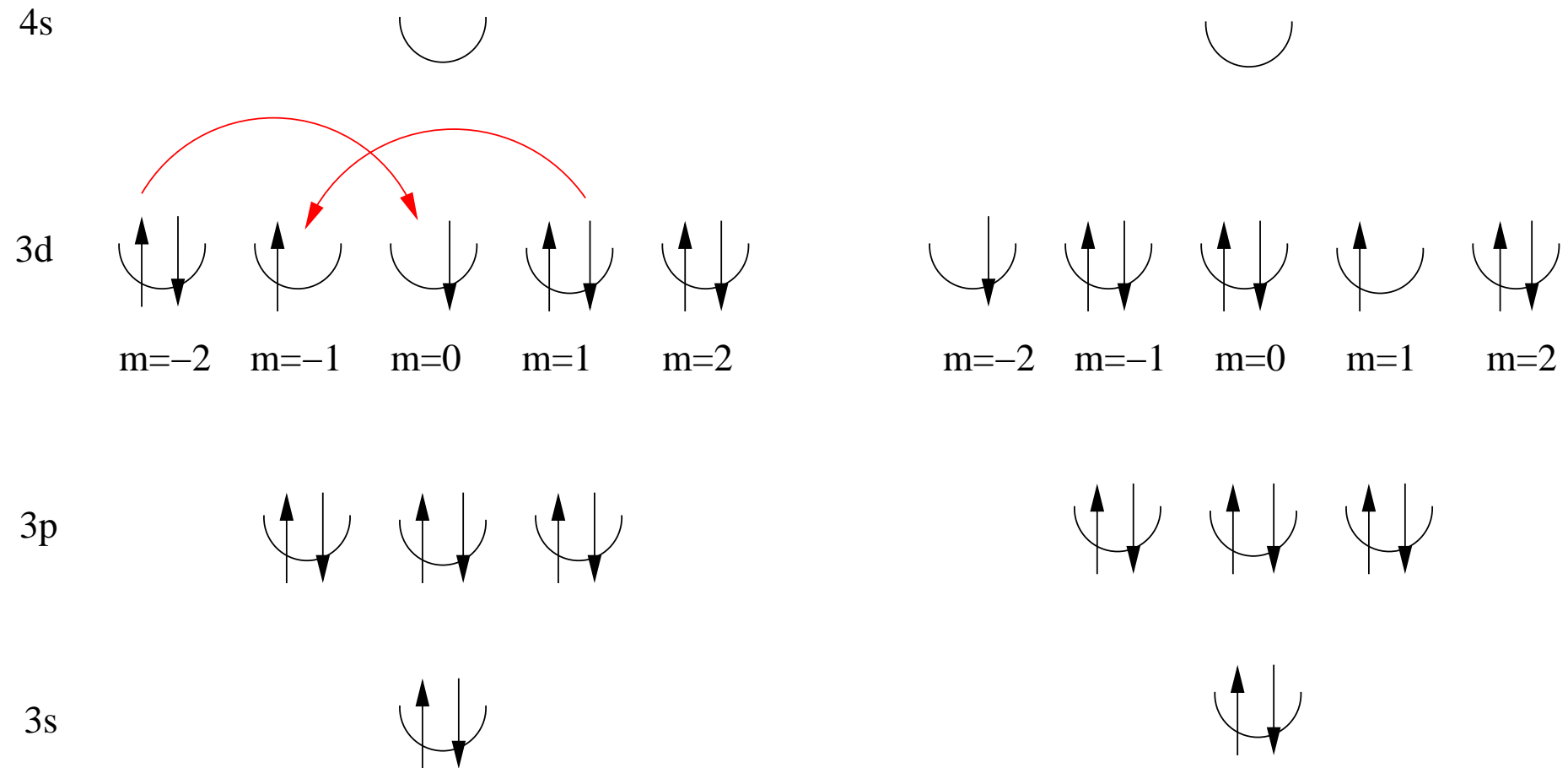
- The states which are mixed by the Coulomb scattering all have the same to orbital energy $n\,\epsilon_{3d}$

- If we consider the orbital energy as H_0, the Coulomb interaction as perturbation H_1, we have the textbook situation of degenerate 1st 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 $(x = (\boldsymbol{r}, \sigma),\ \boldsymbol{r} \to (r, \Theta, \phi))$

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

- 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

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

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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)

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

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

$$V_c(x, x') = \frac{e^2}{|\boldsymbol{r} - \boldsymbol{r}'|}$$

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

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

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

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

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

We need to calculate

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

Now insert

$$\psi_{\nu_1}^*(x) \, \psi_{\nu_2}^*(x') = R_{n_1,l_1}(r) \, Y_{l_1,m_1}^*(\Theta, \phi) \, \underline{\delta_{\sigma,\sigma_1}} \, R_{n_2,l_2}(r') \, Y_{l_2,m_2}^*(\Theta', \phi') \, \delta_{\sigma',\sigma_2}$$

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

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

Spin-sum over σ

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

We need to calculate

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

Now insert

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

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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

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

Now insert

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

(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

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

Now insert

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(Θ, ϕ)-Integration

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

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

(r, r')-Integration

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

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

For scattering within a d-shell all (n_i, l_i) are equal

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)

This gives

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

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

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

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

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

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

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

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

Collecting everything:

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

$$= \delta_{\sigma_1,\sigma_4} \, \delta_{\sigma_2,\sigma_3} \sum_{k=0}^{\infty} \sum_{m=-k}^{k} \delta_{m,m_1-m_4} \, c^k(l_1, m_1; l_4, m_4) \, \delta_{m,m_3-m_2} \, c^k(l_3, m_3; l_2, m_2)$$

$$R^k(n_1 l_1, n_2 l_2, n_3 l_3, n_4 l_4)$$

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

with

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

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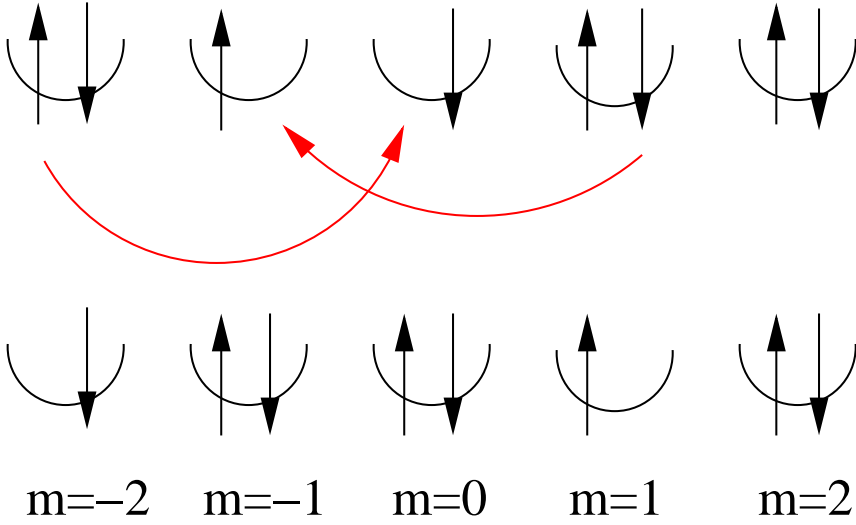
Reminder:

m=−2   m=−1   m=0   m=1   m=2

Collecting everything:

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

$$= \delta_{\sigma_1,\sigma_4} \, \delta_{\sigma_2,\sigma_3} \sum_{k=0}^{\infty} \sum_{m=-k}^{k} \delta_{m,m_1-m_4} \, c^k(l_1, m_1; l_4, m_4) \, \delta_{m,m_3-m_2} \, c^k(l_3, m_3; l_2, m_2)$$

$$R^k(n_1l_1, n_2l_2, n_3l_3, n_4l_4)$$

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

with

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

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

Conditions on nonvanishing Gaunt coefficients I: Triangular condition

It can be shown 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: $l_1 \leq l_2 + l_3$

- otherwise the coefficient is zero

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 $k \leq 4$, for Coulomb scattering in a p-shell this means $k \leq 2$ etc.

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 in a d-shell we have $l_1 = l_4 = 2 \rightarrow k$ must be even

Table A20a-1. $c^k(l_i m_{l_i}; l_j, m_{l_j})$ for s, p, d Electrons

	m_{l_i}	m_{l_j}	k				
			0	1	2	3	4
ss	0	0	1	0	0	0	0
sp	0	±1	0	$-\sqrt{1/3}$	0	0	0
	0	0	0	$\sqrt{1/3}$	0	0	0
pp	±1	±1	1	0	$-\sqrt{1/25}$	0	0
	±1	0	0	0	$\sqrt{3/25}$	0	0
	±1	∓1	0	0	$-\sqrt{6/25}$	0	0
	0	0	1	,0	$\sqrt{4/25}$	0	0
sd	0	±2	0	0	$\sqrt{1/5}$	0	0
	0	±1	0	0	$-\sqrt{1/5}$	0	0
	0	0	0	0	$\sqrt{1/5}$	0	0
pd	±1	±2	0	$\sqrt{6/15}$	0	$\sqrt{3/245}$	0
	±1	±1	0	$\sqrt{3/15}$	0	$-\sqrt{9/245}$	0
	±1	0	0	$-\sqrt{1/15}$	0	$\sqrt{18/245}$	0
	±1	∓1	0	0	0	$-\sqrt{30/245}$	0
	±1	∓2	0	0	0	$\sqrt{45/245}$	0
	0	±2	0	0	0	$\sqrt{15/245}$	0
	0	±1	0	$-\sqrt{3/15}$	0	$-\sqrt{24/245}$	0
	0	0	0	$\sqrt{4/15}$	0	$\sqrt{27/245}$	0
dd	±2	±2	1	0	$-\sqrt{4/49}$	0	$\sqrt{1/441}$
	±2	±1	0	0	$\sqrt{6/49}$	0	$-\sqrt{5/441}$
	±2	0	0	0	$-\sqrt{4/49}$	0	$\sqrt{15/441}$
	±2	∓1	0	0	0	0	$-\sqrt{35/441}$
	±2	∓2	0	0	0	0	$\sqrt{70/441}$
	±1	±1	1	0	$\sqrt{1/49}$	0	$-\sqrt{16/441}$
	±1	0	0	0	$\sqrt{1/49}$	0	$\sqrt{30/441}$
	±1	∓1	0	0	$-\sqrt{6/49}$	0	$-\sqrt{40/441}$
	0	0	1	0	$\sqrt{4/49}$	0	$\sqrt{36/441}$

Taken from: J. C. Slater,

Quantum Theory of Atomic Structure

(McGraw-Hill, New York, 1960)

Reminder:

$k \le l_1 + l_2$ (Triangular condition)

$l_1 + l_2 + k$ even (Parity)

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

$$V(\nu_1, \nu_2, \nu_3, \nu_4) = \delta_{\sigma_1,\sigma_4} \, \delta_{\sigma_2,\sigma_3} \sum_{k \in \{0,2,4\}} \delta_{m_1+m_2,m_3+m_4} \, c^k(l_1, m_1; l_4, m_4) \, c^k(l_3, m_3; l_2, m_2) \, R^k(n_1 l_1, n_2 l_2, n_3 l_3, n_4 l_4)$$

- 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

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

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

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

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

It is absolutely necessary to obtain correct results!

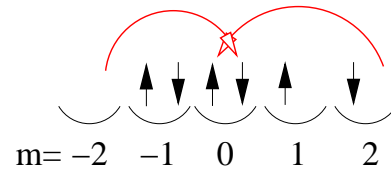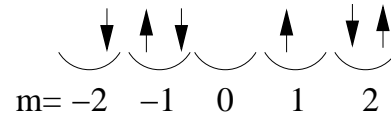## Solution of the Coulomb problem by exact diagonalization

Number of basis states with n electrons

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

These can be coded as integers

$$459 = 0\;1\;1\;1\;0\;0\;1\;0\;1\;1$$

$$\boxed{0\;1}\;\boxed{1\;1}\;\boxed{0\;0}\;\boxed{1\;0}\;\boxed{1\;1}$$

$$\text{m=} \quad -2 \quad\; -1 \quad\;\; 0 \quad\;\; 1 \quad\;\; 2$$

$$\text{m=} \quad -2 \quad\; -1 \quad\;\; 0 \quad\;\; 1 \quad\;\; 2$$

$$0\;0\;1\;1\;1\;1\;1\;0\;1\;0 \;=\; 250$$

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

Resulting eigenenergies for d^8 and d^7

$\left(R^2 = 10.479 \ eV,\ R^4 = 7.5726 \ eV \text{ for d}^8 \text{ and } R^2 = 9.7860 \ eV,\ R^4 = 7.0308 \ eV \text{ for d}^7\right)$

E	S	L	n	Term	E	S	L	n	Term
0.0000	1	3	21	^3F	0.0000	3/2	3	28	^4F
1.8420	0	2	5	^1D	1.8000	3/2	1	12	^4P
1.9200	1	1	9	^3P	2.1540	1/2	4	18	^2G
2.7380	0	4	9	^1G	2.7540	1/2	5	22	^2H
13.2440	0	0	1	^1S	2.7540	1/2	1	8	^2P
					3.0545	1/2	2	10	^2D
					4.5540	1/2	3	14	^2F
					9.9774	1/2	2	10	^2D

- High degeneracy of eigenvalues - all degenerate eigenstates must have the same $\langle \boldsymbol{S}^2 \rangle = S(S+1)$ and $\langle \boldsymbol{L}^2 \rangle = L(L+1)$

- Ground states are consistent with the first two Hund's rules

- Multiplet spectrum has a width of several eV - comparable to bandwidth in solids
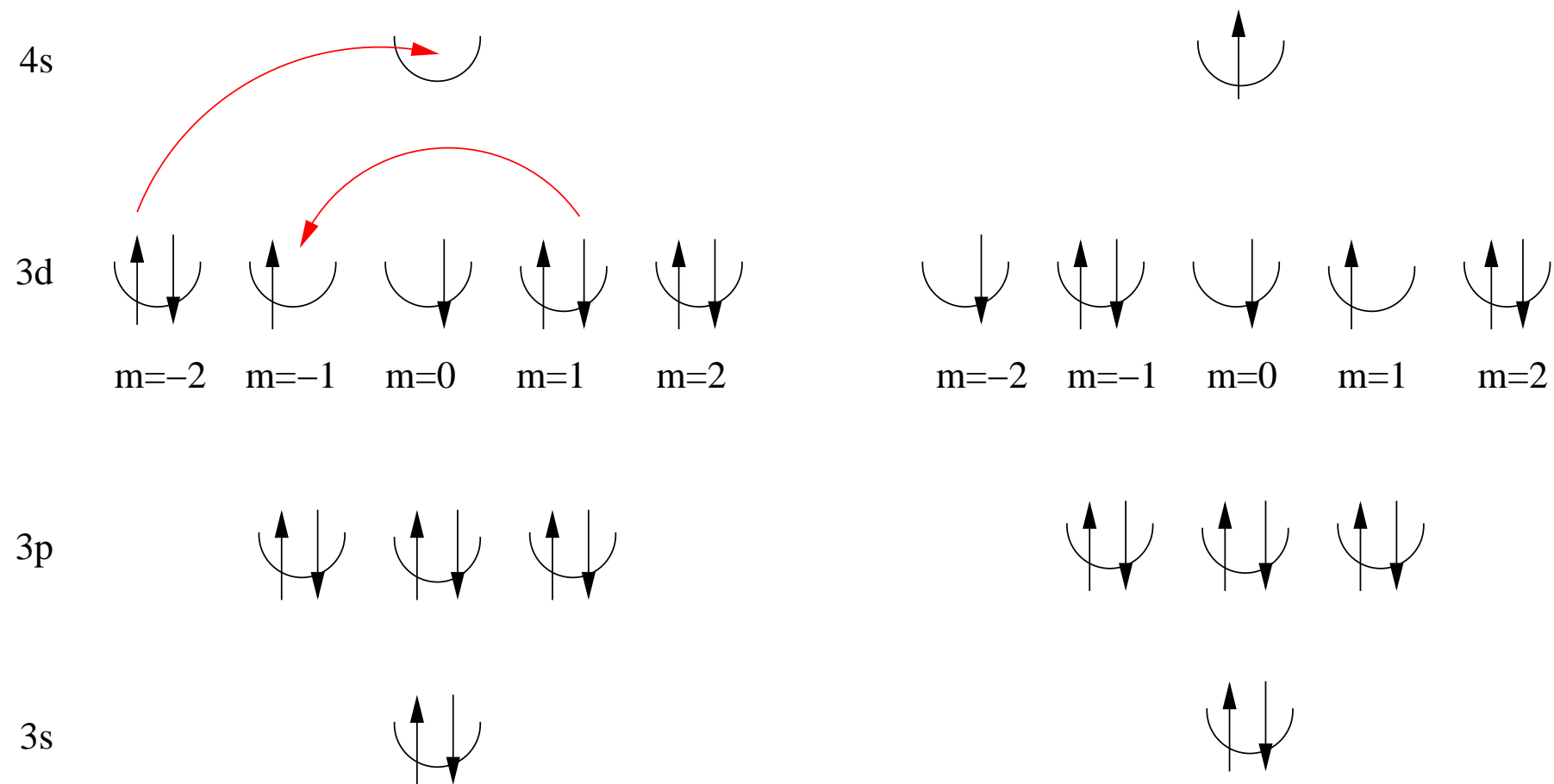
Comparison to experiment for Ni^{2+}

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
$3p^6 3d^8$	^{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

$\rightarrow$ 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})
$3p^6 3d^8$	^3F	4	0.0
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An Identity

We had

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

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

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

$$= V(\nu_2, \nu_1, \nu_4, \nu_3)$$

Diagonal matrix elments of the Coulomb interaction

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

We rewrite the Coulomb interaction

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

$$= \frac{1}{2} \sum_{\nu_1 < \nu_2} \left(\; V(\nu_1, \nu_2, \nu_1, \nu_2) \; c_{\nu_1}^\dagger c_{\nu_2}^\dagger c_{\nu_1} c_{\nu_2} + V(\nu_1, \nu_2, \nu_2, \nu_1) \;\; c_{\nu_1}^\dagger c_{\nu_2}^\dagger c_{\nu_2} c_{\nu_1} \right.$$

$$\left. + \; V(\nu_2, \nu_1, \nu_1, \nu_2) \; c_{\nu_2}^\dagger c_{\nu_1}^\dagger c_{\nu_1} c_{\nu_2} + V(\nu_2, \nu_1, \nu_2, \nu_1) \; c_{\nu_2}^\dagger c_{\nu_1}^\dagger c_{\nu_2} c_{\nu_1} \right) \;\; + \ldots$$

$$= \sum_{\nu_1 < \nu_2} \left(V(\nu_1, \nu_2, \nu_2, \nu_1) - V(\nu_1, \nu_2, \nu_1, \nu_2) \right) \;\; n_{\nu_1} \, n_{\nu_2} + \ldots$$

Here $\sum_{\nu_1 < \nu_2}$ means that each pair (ν_1, ν_2) is counted only once

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

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

This gives

$$V(\nu_1, \nu_2, \nu_2, \nu_1) \;=\; \sum_{k=0}^{\infty} c^k(l_1 m_1; l_1, m_1)\, c^k(l_2 m_2; l_2, m_2)\, R^k(n_1 l_1, n_2 l_2, n_2 l_2, n_1 l_1),$$

$$V(\nu_1, \nu_2, \nu_1, \nu_2) \;=\; \delta_{\sigma_1, \sigma_2} \sum_{k=0}^{\infty} c^k(l_1 m_1; l_2, m_2)\, c^k(l_1 m_1; l_2, m_2)\, R^k(n_1 l_1, n_2 l_2, n_1 l_1, n_2 l_2).$$

We had

$$V(\nu_1, \nu_2, \nu_2, \nu_1) \;=\; \sum_{k=0}^{\infty} c^k(l_1 m_1; l_1, m_1)\, c^k(l_2 m_2; l_2, m_2)\, R^k(n_1 l_1, n_2 l_2, n_2 l_2, n_1 l_1),$$

$$V(\nu_1, \nu_2, \nu_1, \nu_2) \;=\; \delta_{\sigma_1, \sigma_2} \sum_{k=0}^{\infty} c^k(l_1 m_1; l_2, m_2)\, c^k(l_1 m_1; l_2, m_2)\, R^k(n_1 l_1, n_2 l_2, n_1 l_1, n_2 l_2).$$

We introduce some abbreviations...

$$a^k(lm; l'm') \;=\; c^k(lm; lm)\;\; c^k(l'm'; l'm')$$

$$b^k(lm; l'm') \;=\; c^k(lm; l'm')\, c^k(lm; l'm')$$

$$F^k(nl; n'l') \;=\; R^k(nl, n'l', n'l', nl)$$

$$G^k(nl; n'l') \;=\; R^k(nl, n'l', nl, n'l')$$

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

$$F^k(n_1 l_1, n_2 l_2) = R^k(n_1 l_1, n_2 l_2, n_2 l_2, n_1 l_1) = e^2 \int_0^\infty dr\, r^2 \int_0^\infty dr'\, r'^2\, R^2_{n_1,l_1}(r)\, \frac{r_<^k}{r_>^{k+1}}\, R^2_{n_2,l_2}(r')$$

$$G^k(n_1 l_1, n_2 l_2) = R^k(n_1 l_1, n_2 l_2, n_1 l_1, n_2 l_2) = e^2 \int_0^\infty dr\, r^2 \int_0^\infty dr'\, r'^2\, \rho_{ex}(r)\, \frac{r_<^k}{r_>^{k+1}}\, \rho_{ex}(r')$$

$$\rho_{ex}(r) = R_{n_1,l_1}(r)\, R_{n_2,l_2}(r)$$

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 $F^k = G^k$

We had

$$V(\nu_1, \nu_2, \nu_2, \nu_1) = \sum_{k=0}^{\infty} c^k(l_1 m_1; l_1, m_1) \, c^k(l_2 m_2; l_2, m_2) \, R^k(n_1 l_1, n_2 l_2, n_2 l_2, n_1 l_1),$$

$$V(\nu_1, \nu_2, \nu_1, \nu_2) = \delta_{\sigma_1, \sigma_2} \sum_{k=0}^{\infty} c^k(l_1 m_1; l_2, m_2) \, c^k(l_1 m_1; l_2, m_2) \, R^k(n_1 l_1, n_2 l_2, n_1 l_1, n_2 l_2).$$

We introduce some abbreviations...

$$a^k(lm; l'm') = c^k(lm; lm) \quad c^k(l'm'; l'm')$$

$$b^k(lm; l'm') = c^k(lm; l'm') \, c^k(lm; l'm')$$

$$F^k(nl; n'l') = R^k(nl, n'l', n'l', nl)$$

$$G^k(nl; n'l') = R^k(nl, n'l', nl, n'l')$$

... and obtain

$$V(\nu_1, \nu_2, \nu_2, \nu_1) - V(\nu_1, \nu_2, \nu_1, \nu_2) = \sum_k (\, a^k(l_1 m_1, l_2, m_2) \, F^k(n_1, l_1, n_2, l_2)$$

$$-\delta_{\sigma_1, \sigma_2} \, b^k(l_1 m_1, l_2, m_2) \, G^k(n_1, l_1, n_2, l_2) \,)$$

We had

$$V(\nu_1, \nu_2, \nu_2, \nu_1) \;=\; \sum_{k=0}^{\infty} c^k(l_1 m_1; l_1, m_1)\, c^k(l_2 m_2; l_2, m_2)\, R^k(n_1 l_1, n_2 l_2, n_2 l_2, n_1 l_1),$$

$$V(\nu_1, \nu_2, \nu_1, \nu_2) \;=\; \delta_{\sigma_1, \sigma_2} \sum_{k=0}^{\infty} c^k(l_1 m_1; l_2, m_2)\, c^k(l_1 m_1; l_2, m_2)\, R^k(n_1 l_1, n_2 l_2, n_1 l_1, n_2 l_2).$$

We introduce some abbreviations...

$$a^k(lm; l'm') \;=\; c^k(lm; lm)\;\; c^k(l'm'; l'm')$$

$$b^k(lm; l'm') \;=\; c^k(lm; l'm')\, c^k(lm; l'm')$$

$$F^k(nl; n'l') \;=\; R^k(nl, n'l', n'l', nl)$$

$$G^k(nl; n'l') \;=\; R^k(nl, n'l', nl, n'l')$$

... and obtain

$$V(\nu_1, \nu_2, \nu_2, \nu_1) - V(\nu_1, \nu_2, \nu_1, \nu_2) \;=\; \sum_k \big(\; a^k(l_1 m_1, l_2, m_2)\, F^k(n_1, l_1, n_2, l_2)$$

$$-\delta_{\sigma_1, \sigma_2}\, b^k(l_1 m_1, l_2, m_2)\, G^k(n_1, l_1, n_2, l_2)\;\big)$$

The diagonal part of the Hamiltonian therefore is

$$H_{diag} = \sum_{\nu_1 < \nu_2} \left(V(\nu_1, \nu_2, \nu_2, \nu_1) - V(\nu_1, \nu_2, \nu_1, \nu_2) \right) \ n_{\nu_1} \ n_{\nu_2}$$

$$= \sum_{\nu_1 < \nu_2} \left(\sum_k a^k(l_1 m_1, l_2, m_2) \ F^k - \delta_{\sigma_1, \sigma_2} \sum_k b^k(l_1 m_1, l_2, m_2) \ G^k \right) \ n_{\nu_1} \ n_{\nu_2}$$

To calculate the diagonal matrix element of this for a state like $|\Psi\rangle = c_{\nu_1}^\dagger c_{\nu_2}^\dagger \ldots c_{\nu_n}^\dagger |0\rangle$ 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 $3d$-shell: $n_i = 3$ and $l_i = 2$, for each k there is only one F^k and one G^k and $F^k = G^k \rightarrow$ we only sum over m_1, m_2, σ_1 and σ_2

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

- We must have $(m_1, \sigma_1) \neq (m_2, \sigma_2)$ (in the original H_1 we had $c_{\nu_1}^\dagger c_{\nu_2}^\dagger$)
- 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 $m_1 \neq m_2$

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

We consider again a partially filled $3d$-shell: $n_i = 3$ and $l_i = 2$, for each k there is only one F^k and one G^k and $F^k = G^k \rightarrow$ we only sum over m_1, m_2, σ_1 and σ_2

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

- We must have $(m_1, \sigma_1) \neq (m_2, \sigma_2)$ (in the original H_1 we had $c_{\nu_1}^\dagger c_{\nu_2}^\dagger$)

- 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 $m_1 \neq m_2$

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

We consider again a partially filled $3d$-shell: $n_i = 3$ and $l_i = 2$, for each k there is only one F^k and one G^k and $F^k = G^k \rightarrow$ we only sum over m_1, m_2, σ_1 and σ_2

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

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

- We must have $(m_1, \sigma_1) \neq (m_2, \sigma_2)$ (in the original H_1 we had $c^\dagger_{\nu_1} c^\dagger_{\nu_2}$)

- 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 $m_1 \neq m_2$

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

We had

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

Now we use $n_m = n_{m,\uparrow} + n_{m,\downarrow}$ and $2\, S_m^z = n_{m,\uparrow} - n_{m,\downarrow}$ to find

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

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

We had

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

Now we use $n_m = n_{m,\uparrow} + n_{m,\downarrow}$ and $2\,S_m^z = n_{m,\uparrow} - n_{m,\downarrow}$ to find

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

$$\sum_{\sigma} n_{m_1,\sigma}\, n_{m_2,\sigma} = 2S_{m_1}^z\, S_{m_2}^z + \frac{n_{m_1}n_{m_2}}{2}$$

We had

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

Now we use $n_m = n_{m,\uparrow} + n_{m,\downarrow}$ and $2\, S_m^z = n_{m,\uparrow} - n_{m,\downarrow}$ to find

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

$$
\textcolor{red}{\sum_{\sigma} n_{m_1,\sigma}\, n_{m_2,\sigma}} = 2S_{m_1}^z\, S_{m_2}^z + \frac{n_{m_1} n_{m_2}}{2}
$$

We had

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

Now we use $n_m = n_{m,\uparrow} + n_{m,\downarrow}$ and $2\,S_m^z = n_{m,\uparrow} - n_{m,\downarrow}$ to find

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

$$\sum_{\sigma} n_{m_1,\sigma}\, n_{m_2,\sigma} = 2 S_{m_1}^z\, S_{m_2}^z + \frac{n_{m_1} n_{m_2}}{2}$$

so that

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

All in all

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

$$U_{m_1,m_2} = \sum_{k \in \{0,2,4\}} a^k(m_1, m_2)\, F^k = \sum_{k \in \{0,2,4\}} c^k(l_1, m_1; l_1, m_1)\, c^k(l_2, m_2; l_2, m_2)\, F^k$$

$$J_{m_1,m_2} = \sum_{k \in \{0,2,4\}} b^k(m_1, m_2)\, F^k = \sum_{k \in \{0,2,4\}} c^k(l_1, m_1; l_2, m_2)^2\, F^k$$

- This is the sum of a Hubbard-like term for each m, and both, a 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 correct Coulomb Hamiltonian but only the sum of diagonal elements

We had

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

- By adding a selected class of off-diagonal elements (see notes) one can 'complete the Hund's rule exchange' to obtain the fully spin-rotation invariant Hamiltonian

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

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

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

  with experiment

The diagonal sum-rule

Let H be a Hermitean matrix. Then the sum of the eigenvalues E_i of H is equal to its trace

$$
\begin{aligned}
trace(H) &= \sum_{i=1}^{n} H_{i,i} \\
&= \sum_{i,j=1}^{n} H_{i,j}\ \delta_{j,i} \\
&= \sum_{i,j,l=1}^{n} H_{i,j}\ (U_{j,l}^{-1} U_{l,i}) \\
&= \sum_{l=1}^{n} \sum_{i,j=1}^{n} U_{l,i}\ H_{i,j}\ U_{j,l}^{-1} \\
&= \sum_{l=1}^{n} (UHU^{-1})_{l,l} \\
&= \sum_{l=1}^{n} E_l
\end{aligned}
$$

Here U is the unitary matrix which transforms to the basis of eigenstates of H

Multiplets of p² - calculation by the diagonal sum-rule

m	m'	a^0	$25a^2$	b^0	$25b^2$
± 1	± 1	1	1	1	1
± 1	0	1	-2	0	3
0	0	1	4	1	4
± 1	∓ 1	1	1	0	6

The diagonal elements were

$$\langle \nu | H_1 | \nu \rangle = \sum_{i<j} \sum_{k \in \{0,2\}} \left(a^k(l_i m_i, l_j, m_j)\, F^k - \delta_{\sigma_i \sigma_j}\, b^k(l_i m_i, l_j, m_j)\, F^k \right)$$

We write operators as $c^\dagger_{l,m,\sigma}$ - the principal quantum number n is omitted

We consider states with $S^z = 1 \rightarrow$ the highest possible L^z is $L^z = 1$

This is realized for a single state: $c^\dagger_{1,0,\uparrow}\, c^\dagger_{1,1,\uparrow}|0\rangle$ - this state belongs to ^{3}P

In the sector $S^z = 1$, $L^z = 1$ the Hamiltonian is 1×1 so that the energy of ^{3}P is just the single diagonal element

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

m	m'	a^0	$25a^2$	b^0	$25b^2$
± 1	± 1	1	1	1	1
± 1	0	1	-2	0	3
0	0	1	4	1	4
± 1	∓ 1	1	1	0	6

The diagonal elements were

$$\langle \nu | H_1 | \nu \rangle = \sum_{i<j} \sum_{k \in \{0,2\}} \left(a^k(l_i m_i, l_j, m_j) \, F^k - \delta_{\sigma_i \sigma_j} \, b^k(l_i m_i, l_j, m_j) \, F^k \right)$$

We write operators as $c^\dagger_{l,m,\sigma}$ - the principal quantum number n is omitted

We consider states with $S^z = 1 \rightarrow$ the highest possible L^z is $L^z = 1$

This is realized for a single state: $c^\dagger_{1,0,\uparrow} \, c^\dagger_{1,1,\uparrow} |0\rangle$ - this state belongs to ^{3}P

In the sector $S^z = 1$, $L^z = 1$ the Hamiltonian is 1×1 so that the energy of ^{3}P is just the diagonal element

The diagonal element of $c^\dagger_{1,0,\uparrow} \, c^\dagger_{1,1,\uparrow} |0\rangle$ is

$$1 \, F^0 - \frac{2}{25} F^2 - \frac{3}{25} F^2 = F^0 - \frac{5}{25} F^2$$

$$\rightarrow E[^3P] = F^0 - \frac{5}{25} F^2$$

Multiplets of p² - calculation by the diagonal sum-rule

m	m'	a^0	$25a^2$	b^0	$25b^2$
± 1	± 1	1	1	1	1
± 1	0	1	-2	0	3
0	0	1	4	1	4
± 1	∓ 1	1	1	0	6

The diagonal elements were

$$\langle \nu | H_1 | \nu \rangle = \sum_{i<j} \sum_{k \in \{0,2\}} \left(a^k(l_i m_i, l_j, m_j)\, F^k - \delta_{\sigma_i \sigma_j}\, b^k(l_i m_i, l_j, m_j)\, F^k \right)$$

We write operators as $c^\dagger_{l,m,\sigma}$ - the principal quantum number n is omitted

We consider states with $S^z = 0 \to$ the highest possible L^z is $L^z = 2$

This is realized for a single state: $c^\dagger_{1,1,\downarrow}\, c^\dagger_{1,1,\uparrow} |0\rangle$ - this state belongs to ^{1}D

In the sector $S^z = 0$, $L^z = 2$ the Hamiltonian is 1×1 so that the energy of ^{1}D is just the diagonal element

The diagonal element of $c^\dagger_{1,1,\downarrow}\, c^\dagger_{1,1,\uparrow} |0\rangle$ is

$$\to E[^1D] = F^0 + \frac{1}{25} F^2$$

$$E[^3P] = F^0 - \frac{5}{25} F^2$$

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

m	m'	a^0	$25a^2$	b^0	$25b^2$
± 1	± 1	1	1	1	1
± 1	0	1	-2	0	3
0	0	1	4	1	4
± 1	∓ 1	1	1	0	6

The diagonal elements were

$$\langle \nu | H_1 | \nu \rangle = \sum_{i<j} \sum_{k \in \{0,2\}} \left(a^k(l_i m_i, l_j, m_j)\, F^k - \delta_{\sigma_i \sigma_j}\, b^k(l_i m_i, l_j, m_j)\, F^k \right)$$

The total number of states of p^2 is $\frac{6 \cdot 5}{2} = 15$

So far we found the multiplets ^{3}P and ^{1}D which together have $3 \cdot 3 + 1 \cdot 5 = 14$ states

$\rightarrow$ only one state is missing which must form a multiplet of its own and can only be ^{1}S

To find the energy of ^{1}S we need to consider the sector $S^z = 0$ and $L^z = 0$

Note: ^{3}P and ^{1}D each also have one member in this sector!

There are three states in this sector:

$$|1\rangle = c^\dagger_{1,0,\downarrow}\; c^\dagger_{1,0,\uparrow} |0\rangle,$$
$$|2\rangle = c^\dagger_{1,-1,\uparrow}\; c^\dagger_{1,1,\downarrow} |0\rangle,$$
$$|3\rangle = c^\dagger_{1,-1,\downarrow}\; c^\dagger_{1,1,\uparrow} ||0\rangle$$

Multiplets of p² - calculation by the diagonal sum-rule

m	m'	a^0	$25a^2$	b^0	$25b^2$
± 1	± 1	1	1	1	1
± 1	0	1	-2	0	3
0	0	1	4	1	4
± 1	∓ 1	1	1	0	6

The diagonal elements were

$$\langle \nu | H_1 | \nu \rangle = \sum_{i<j} \sum_{k \in \{0,2\}} \left(a^k(l_i m_i, l_j, m_j)\, F^k - \delta_{\sigma_i \sigma_j}\, b^k(l_i m_i, l_j, m_j)\, F^k \right)$$

We considered the sector $S^z = 0$ and $L^z = 0$ - ^{3}P and ^{1}D each also have one member in this sector!

There are three states in this sector $|1\rangle = c^\dagger_{1,0,\downarrow}\, c^\dagger_{1,0,\uparrow}|0\rangle$, $|2\rangle = c^\dagger_{1,-1,\uparrow}\, c^\dagger_{1,1,\downarrow}|0\rangle$ and $|3\rangle = c^\dagger_{1,-1,\downarrow}\, c^\dagger_{1,1,\uparrow}|0\rangle$

The diagonal sum-rule then tells us

$$E(^3P) + E(^1D) + E(^1S) = \sum_{i=1}^{3} \langle i | H_1 | i \rangle$$

$$F^0 - \frac{5}{25} F^2 + F^0 + \frac{1}{25} F^2 + E(^1S) = \sum_{k \in \{0,2\}} \left(a^k(1,0;1,0) + 2\, a^k(1,-1;1,1) \right) F^k$$

$$E(^1S) + 2\, F^0 - \frac{4}{25} F^2 = 3\, F^0 + \left(\frac{4}{25} + 2\frac{1}{25} \right) F^2$$

$$\rightarrow E(^1S) = F^0 + \frac{10}{25} F^2$$

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

All in all we found the multiplets and their energies

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

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 O^{2+}

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

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

p^2	C	N$^+$	O^{2+}	Si	P$^+$	S^{2+}
	1.124	1.134	1.130	1.444	1.430	1.399

p^4	O	F$^+$	S	Cl$^+$
	1.130	1.152	1.401	1.392

Summary so far

- The Coulomb interaction in a partially filled 3d-shell 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 (angular integrals over three spherical harmonics) and Slater-Condon parameters (double radial integrals of the radial wave functions)

- Reasonable agreement with experiment can be obtained

- The energy of d^n versus n looks approximately like this

Multiplet splitting

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

Energy

d^7 d^8 d^9

d—shell occupation
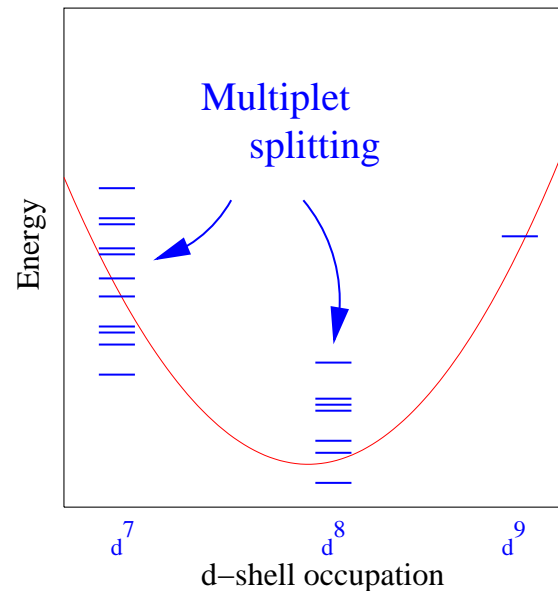
III: The transition metal ion in a solid

So far we considered an atom/ion in vacuum

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....

$$\frac{V_{Shell}}{V_{Wigner-Seitz}}$$

'Nuclear charge'
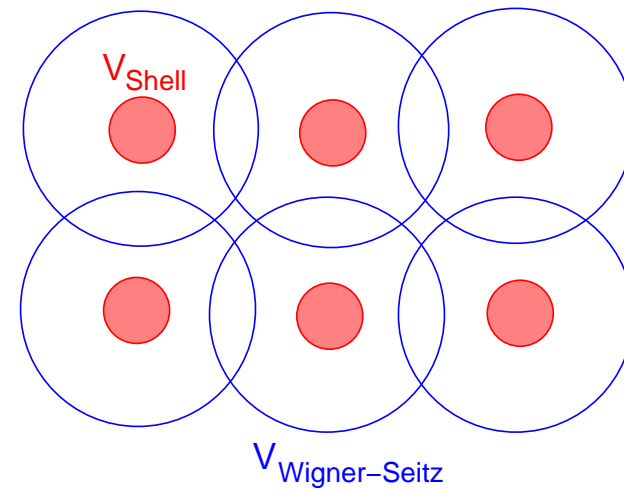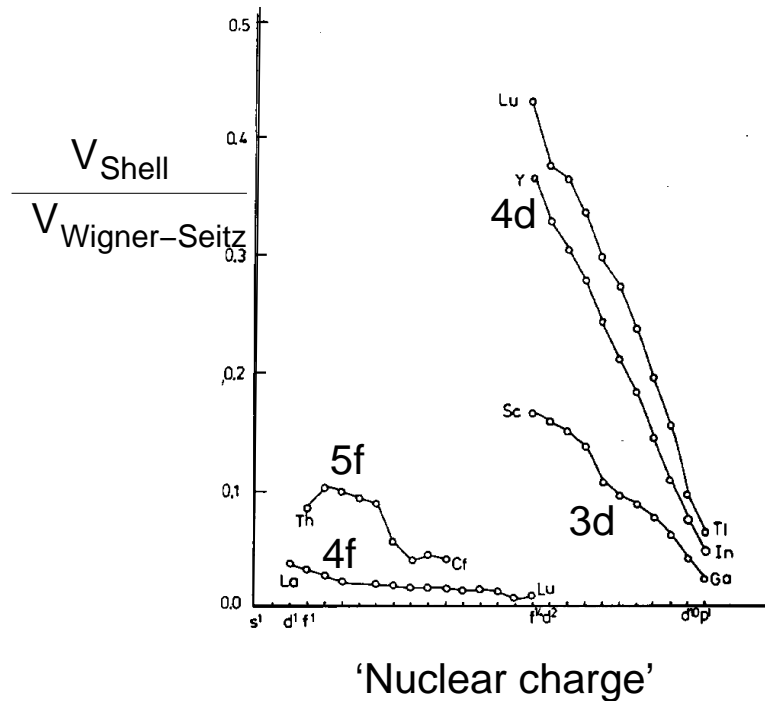
Effect of the environment - Symmetry considerations

- We consider a transition metal ion in a crystal - what is the effect of the electrostatic potential V_{CEF} of the other ions? (CEF=Crystalline Electric Field)
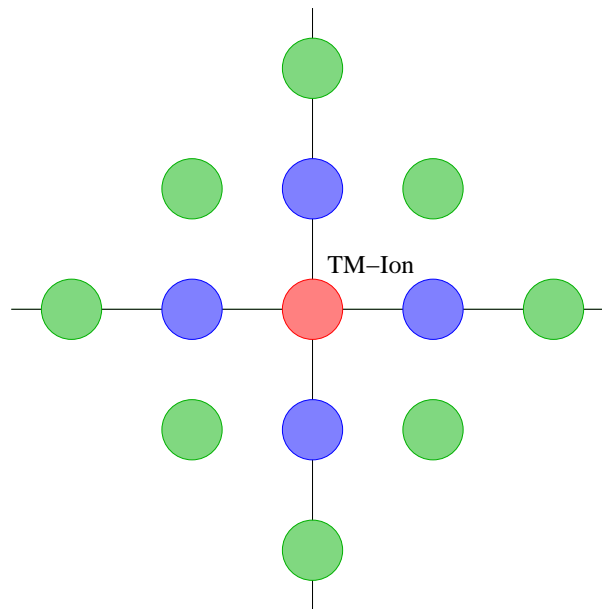
- We assume that there are a number of symmetry operations α - defined by unitary 3×3 matrices m_α - which leave the ion in question unchanged and map the remainder of the crystal invariant

- We define the operator $T_\alpha f(\boldsymbol{r}) = f(m_\alpha^{-1}\boldsymbol{r})$ - the result corresponds to the 'rotated function'

- If the symmetry operation α maps the crystal onto itself we have $T_\alpha \, V_{CEF}(\boldsymbol{r}) = V_{CEF}(\boldsymbol{r})$

- Defining $\tilde{H} = H_{ion} + V_{CEF} = H_0 + H_1 + V_{CEF}$ it follows that $[T_\alpha, \tilde{H}] = 0$

Reminder: $[T_\alpha, \tilde{H}] = 0$ - now let ψ be an eigenstate of $\tilde{H}$: $\tilde{H}\psi = E\psi$

It follows that

$$\tilde{H}\, T_\alpha\, \psi = T_\alpha\, \tilde{H}\, \psi = E\, T_\alpha\, \psi$$

$\rightarrow T_\alpha\, \psi$ is an eigenstate with energy E as well

- We can find out what degeneracies remain under the crystalline electric field by investigating which eigenstates are mixed into each other by the symmetry transformations of the crystal
- For the general case this can be done using group theory
- For the special case of cubic symmetry - and a d-shell - we can take a shortcut

Consider e.g.

$$Y_{2,2}(\Theta, \phi) = \frac{1}{\sqrt{4\pi}}\sqrt{\frac{15}{8}}\,\sin^2\Theta\, e^{\,2i\phi} = \frac{1}{\sqrt{4\pi}}\sqrt{\frac{15}{8}}\,\sin^2\Theta\,\left(\cos^2(\phi) - \sin^2(\phi) + 2i\sin(\phi)\cos(\phi)\right)$$

$$= \frac{1}{\sqrt{4\pi}}\sqrt{\frac{15}{8}}\left(\frac{x^2 - y^2}{r^2} + 2i\,\frac{xy}{r^2}\right).$$

The d-like sperical harmonics are 2nd order polynomials in the three components of the unit vector $\frac{x}{r}$, $\frac{y}{r}$ and $\frac{z}{r}$

- All 48 cubic symmetry operations are the product of one of $3! = 6$ permutations of the three coordinate axes and one of the $2^3 = 8$ sign changes

- The three mixed products $\frac{xy}{r^2}$, $\frac{xz}{r^2}$ and $\frac{yz}{r^2}$ are transformed into each other

- The three squares $\frac{x^2}{r^2}$, $\frac{y^2}{r^2}$ and $\frac{z^2}{r^2}$ are transformed into each other

- One special combination of the squares is $1 = \frac{x^2}{r^2} + \frac{y^2}{r^2} + \frac{z^2}{r^2}$ so that only 2 combinations of squares remain

- It follows purely by symmetry considerations that in <u>any</u> environment with a cubic symmetry a d-level splits into a 3-fold degenerate (t_{2g}) level and a two-fold degenerate (e_g) level

$$
d_{xy} = \frac{i}{\sqrt{2}} (Y_{2,-2} - Y_{2,2}) = \sqrt{\frac{15}{4\pi}} \frac{xy}{r^2},
$$

$$
d_{yz} = \frac{i}{\sqrt{2}} (Y_{2,-1} + Y_{2,1}) = \sqrt{\frac{15}{4\pi}} \frac{yz}{r^2},
$$

$$
d_{xz} = \frac{1}{\sqrt{2}} (Y_{2,-1} - Y_{2,1}) = \sqrt{\frac{15}{4\pi}} \frac{xz}{r^2},
$$

$$
d_{x^2-y^2} = \frac{1}{\sqrt{2}} (Y_{2,-2} + Y_{2,2}) = \sqrt{\frac{15}{16\pi}} \frac{x^2 - y^2}{r^2},
$$

$$
d_{3z^2-r^2} = Y_{2,0} = \sqrt{\frac{5}{16\pi}} \frac{3z^2 - r^2}{r^2}.
$$

We consider the difference $E(e_g) - E(t_{2g}) = 10Dq$ as an additional parameter - we can then summarize the effect of any enviroment with cubical symmetry by the following Hamiltonian

$$
H_{CEF} = C - 4Dq \sum_{\alpha \,\in\, t_{2g}} d^\dagger_{\alpha,\sigma} d_{\alpha,\sigma} + 6Dq \sum_{\alpha \,\in\, e_g} d^\dagger_{\alpha,\sigma} d_{\alpha,\sigma}
$$

$$H_{CEF} = C - 4Dq \sum_{\alpha \in t_{2g}} d^{\dagger}_{\alpha,\sigma} d_{\alpha,\sigma} + 6Dq \sum_{\alpha \in e_g} d^{\dagger}_{\alpha,\sigma} d_{\alpha,\sigma}$$

- The center of gravity C is largely irrelevant

- $10Dq$ is a phenomenological parameter - similarly to the Slater integrals or the Slater-Coster parameters

- It may be estimated by fits to experiment or to a band structure calculation

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However: the above considerations all apply to a single d-electron

What about the multiplets of d^n?

$$H_{CEF} = C - 4Dq \sum_{\alpha \in t_{2g}} d^\dagger_{\alpha,\sigma} d_{\alpha,\sigma} + 6Dq \sum_{\alpha \in e_g} d^\dagger_{\alpha,\sigma} d_{\alpha,\sigma}$$

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What about the multiplets of d^n?

By reverting the unitary transformation...

$$d_{xy} = \frac{i}{\sqrt{2}} (Y_{2,-2} - Y_{2,2}) = \sqrt{\frac{15}{4\pi}} \frac{xy}{r^2},$$

$$d_{yz} = \frac{i}{\sqrt{2}} (Y_{2,-1} + Y_{2,1}) = \sqrt{\frac{15}{4\pi}} \frac{yz}{r^2},$$

$$d_{xz} = \frac{1}{\sqrt{2}} (Y_{2,-1} - Y_{2,1}) = \sqrt{\frac{15}{4\pi}} \frac{xz}{r^2},$$

$$d_{x^2-y^2} = \frac{1}{\sqrt{2}} (Y_{2,-2} + Y_{2,2}) = \sqrt{\frac{15}{16\pi}} \frac{x^2 - y^2}{r^2},$$

$$d_{3z^2-r^2} = Y_{2,0} = \sqrt{\frac{5}{16\pi}} \frac{3z^2 - r^2}{r^2}.$$

...we may bring the CEF Hamiltonian to the form $H_{CEF} = \sum_{i,j} V_{CEF}(\nu_i, \nu_j) c^\dagger_{\nu_i} c_{\nu_j}$ (with $\nu = (n, l, m, \sigma)$)

We had

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

This can now easily be included into the exact diagonalization program for the Coulomb problem

m=−2   m=−1   m=0   m=1   m=2
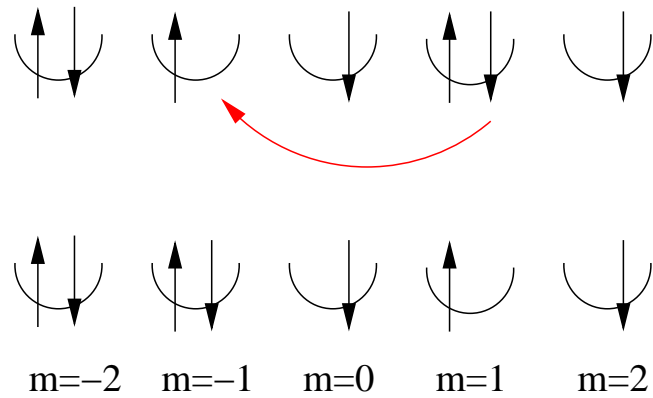
As an example we show the development of the eigenvalue spectrum as the strength of the CEF increases for d^8 and d^7 - the so-called Tanabe-Sugano-diagrams
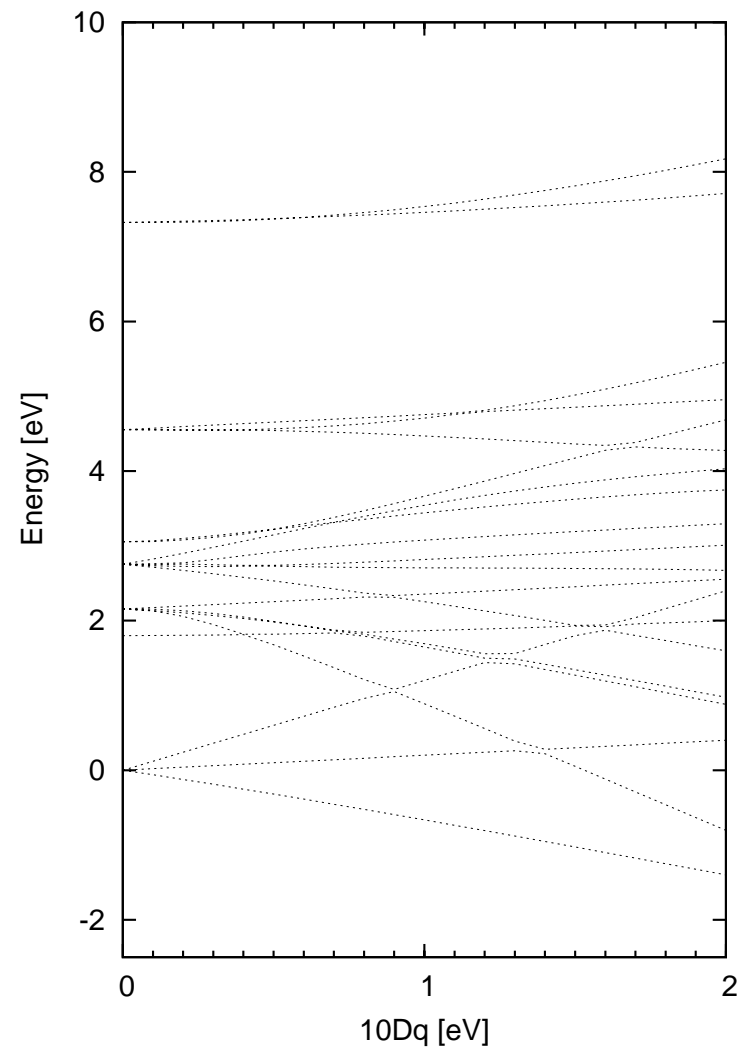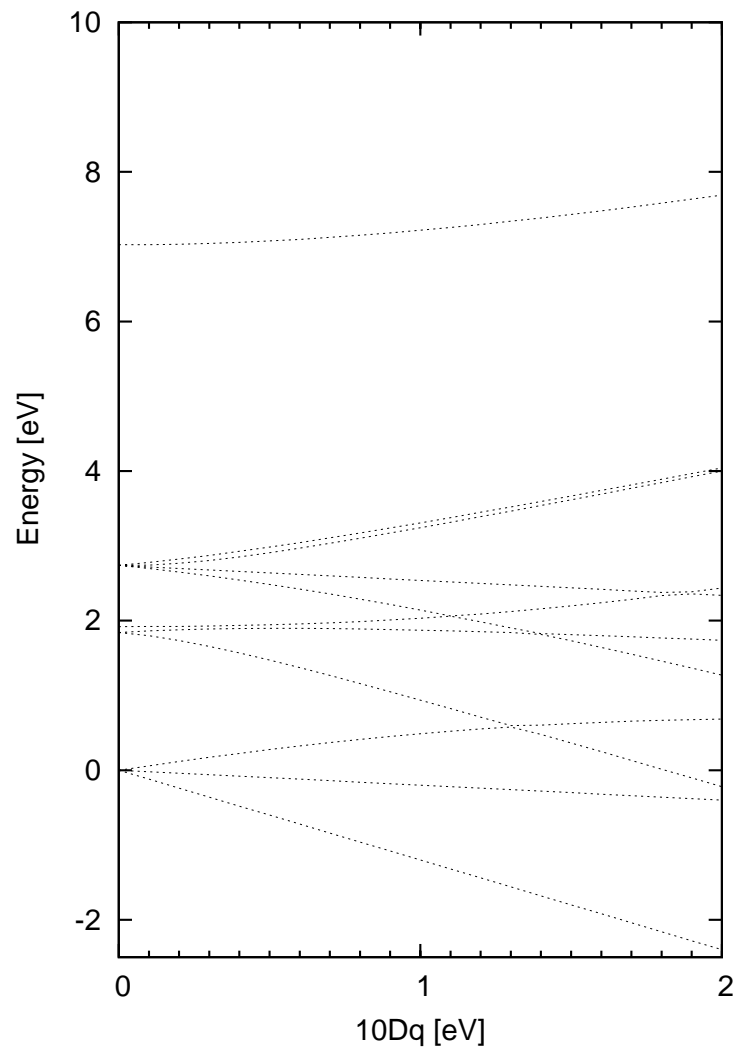
Charge transfer

- 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

- We introduce creation/annihilation operators for electrons in the ligand orbitals: $l_\mu^\dagger / l_\mu$, with $\mu = (i, n, l, m, \sigma)$

- The 'compound index' μ for the ligands has an additional entry: i, the number/position of the ligand
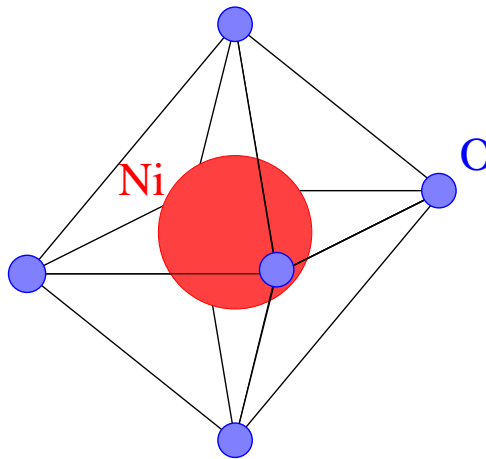
Charge transfer

To describe the charge transfer we therefore add the following terms to the Hamiltonian

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

- The hybridization integrals t_{ν_i,μ_j} may be expressed in terms of relatively few parameters by using the Slater-Koster tables

- In the presence of hybridization the site-energies ϵ_{μ_j} and ϵ_{ν_i} become important as well

- Estimates for these parameters can be obtained from LCAO-fits to LDA band structures (recently much effort has been devoted to obtaining such parameters ab initio)

Charge transfer

The Hamiltonian describing hybridization:

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

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

m=−2   m=−1   m=0   m=1   m=2

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m=−2   m=−1   m=0   m=1   m=2 μ_1 μ_2 μ_3 μ_4 μ_5

Charge transfer

The Hamiltonian describing hybridization:

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

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

Only problem: addition of ligands increases the number of basis states $\rightarrow$ need to use Lanczos

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 momenets point away from the ion

- 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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Co   Cr   Ni   Cu   Mn

CEF-splitting observed with the bare eye!

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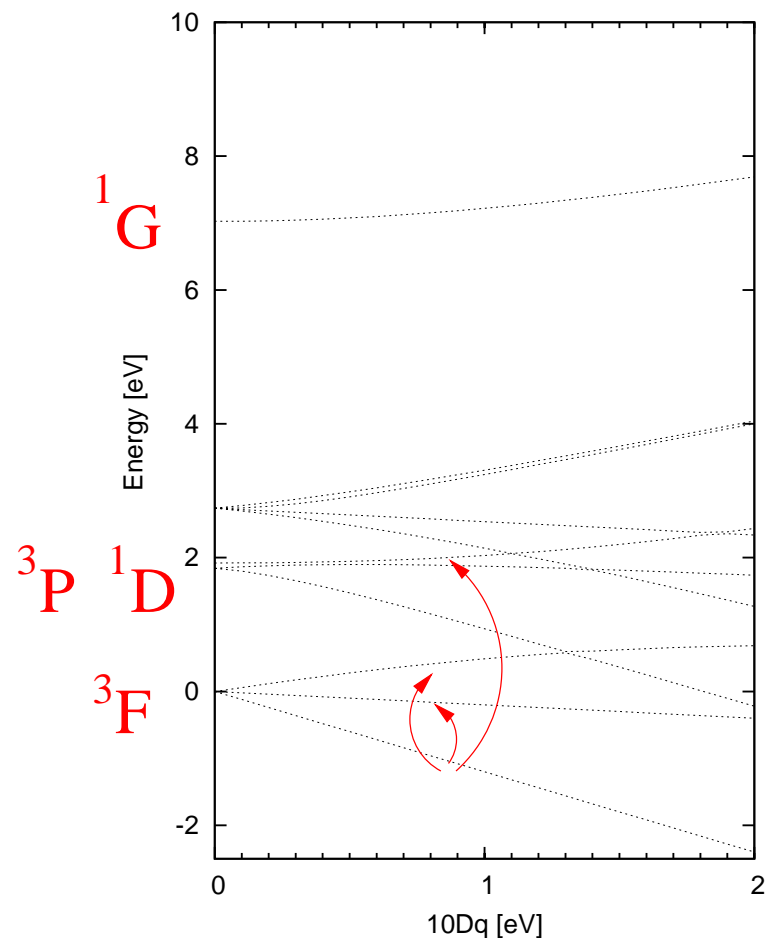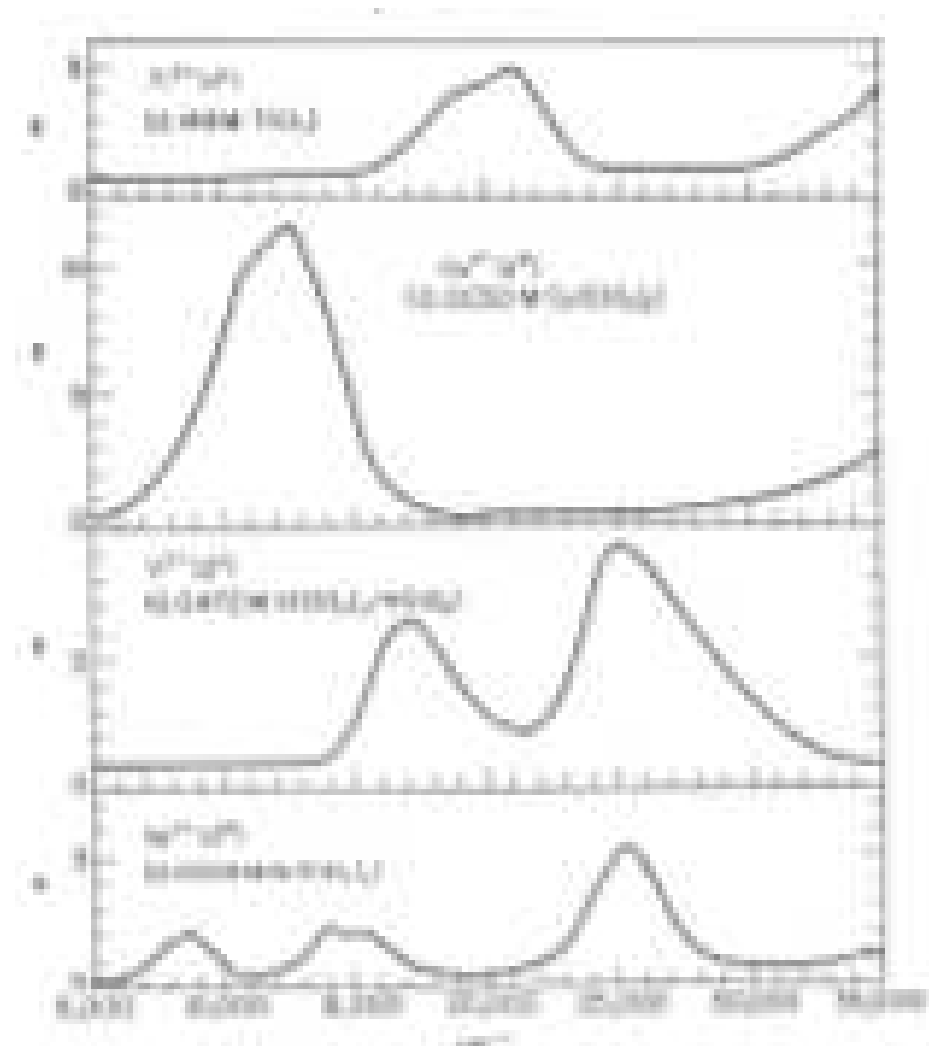
Model Hamiltonians

- In constructing 'model' Hamiltonians - few-band Hubbard models - one often takes the limit $10Dq \to \infty$

- Depending on the filling of the d-shell only the e_g or the t_{2g} orbitals are kept

- The Coulomb matrix elements can be transformed without problems from the 'm-representation' to the 'e_g/t_{2g}-representation'

Summary so far

- Embedding a transition metal ion into a solid gives rise to new effects:

  Crystalline electric field and charge transfer

- These can be included easily into the exact diagonalization formalism - the main problem is the increase

  of the dimension of the Hilbert space due to ligand orbitals

IV: Applications of multiplet theory in spectroscopy

Valence band photoemission

- In this experiment photons impinge onto the sample which then emits photoelectrons - i.e. the familiar photoelectric effect

- 'Valence band photoemission' means that the photoelectron is emitted from a state 'near' the Fermi energy

- What is measured is the photoelectron current I as a function of the kinetic energy of the photoelectrons E_{kin}, the direction relative to crystallographic axis of the sample (Θ, ϕ), and the incoming photon energy $h\nu$ and polarization $\boldsymbol{E}$
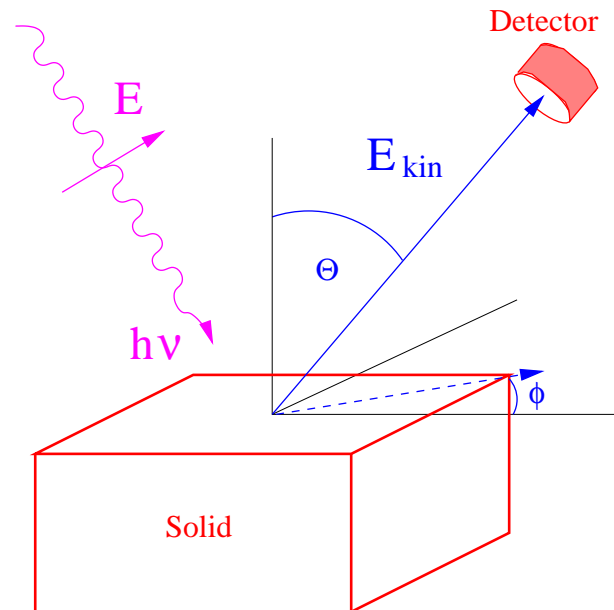
- Often one considers angle-integrated spectra, which are obtained by averaging over (Θ, ϕ) - or measuring on a polycrystalline sample in the first place...

- A certain simplification occurs when the photons have X-ray energies

NiO

$h\nu = 78\,eV$

$h\nu = 40\,eV$

$h\nu = 30\,eV$

d-States

p-Bands

$h\nu = 20\,eV$

E_F

12   10   8   6   4   2   0

ELECTRON BINDING ENERGY (eV)
RELATIVE TO d-PEAK
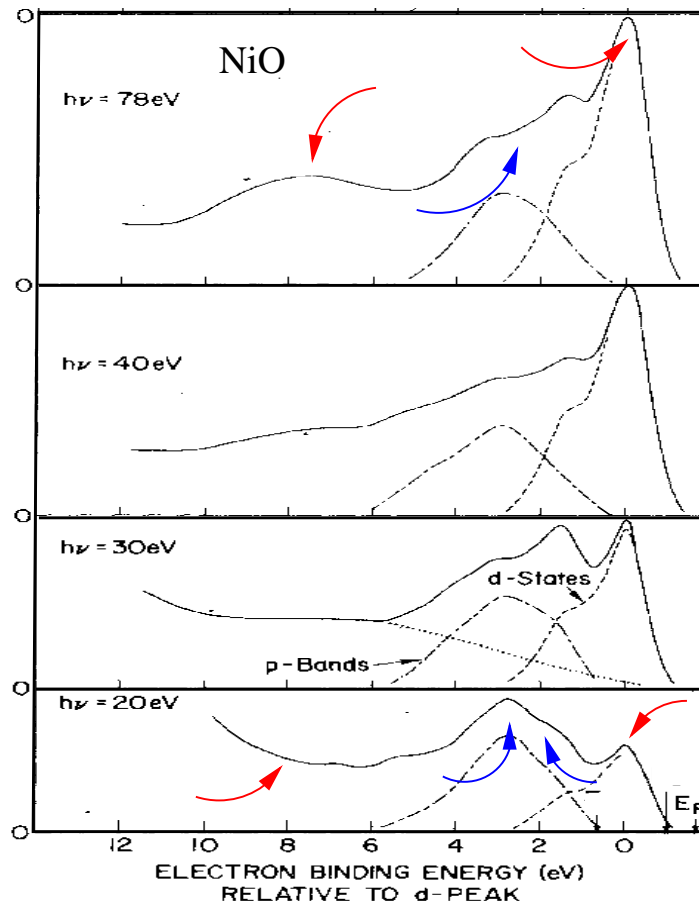
The mechanism of the smoother variation is the photon energy dependence of the photoionization cross section

Cross section

3d

2p

Photon energy

Data from Eastman & Freeouf, PRL 34, 395 (1975)
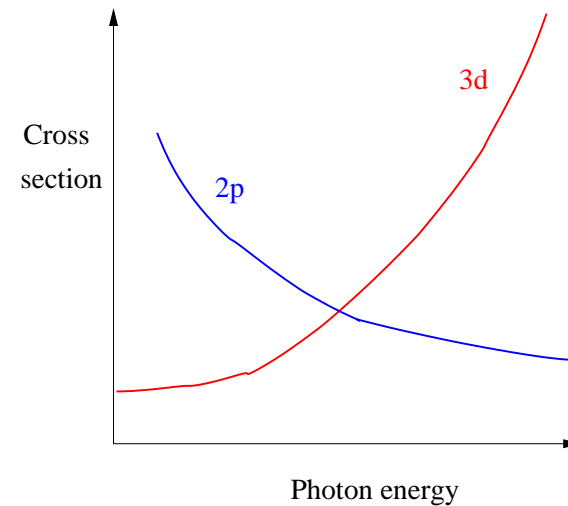
Cluster calculation of XPS spectra

- For photon energies in the X-ray region only the transition metal 3d electron contribute to the spectrum

- This is called an XPS spectrum - X-ray Photoemission Spectrum

- While the theory of photoemission is complicated it can be shown that the angle-integrated XPS-spectrum is given approximately by the so-called single-particle spectral function

$$
A(\omega) = -\frac{1}{\pi Z} \Im \sum_{m=-2}^{2} \sum_{\mu} e^{-\beta E_\mu} \langle \Psi_\mu | c^\dagger_{3,2,m,\sigma} \frac{1}{\omega + (H - E_\mu) + i0^+} c_{3,2,m,\sigma} | \Psi_\mu \rangle
$$

$$
= \frac{1}{Z} \sum_{m=-2}^{2} \sum_{\mu,\nu} e^{-\beta E_\mu} |\langle \Psi_\nu | c_{3,2,m,\sigma} | \Psi_\mu \rangle|^2 \delta(\omega + (E_\nu - E_\mu)).
$$

- Here $|\Psi_\mu\rangle$ and E_μ are eigenstates and corresponding energy of the solid

- $\frac{1}{Z} e^{-\beta E_\mu}$ with $\beta = (k_B T)^{-1}$ is the thermal occupation probablity of $|\Psi_\mu\rangle$

- The operator $c_{3,2,m,\sigma}$ annihilates an electron with $L^z = m$ and $S^z = \sigma$ from the TM 3d-shell of some atom in the solid

Reminder:

$$A(\omega) = -\frac{1}{\pi Z}\Im \sum_{m=-2}^{2} \sum_{\mu} e^{-\beta E_\mu} \langle \Psi_\mu | c_{3,2,m,\sigma}^{\dagger} \frac{1}{\omega + (H - E_\mu) + i0^+} c_{2,m,\sigma} | \Psi_\mu \rangle$$

$$= \frac{1}{Z} \sum_{m=-2}^{2} \sum_{\mu,\nu} e^{-\beta E_\mu} |\langle \Psi_\nu | c_{3,2,m,\sigma} | \Psi_\mu \rangle|^2 \delta(\omega + (E_\nu - E_\mu)).$$

Now we use the approximation by Fujimori and Minami and evaluate this expression using the wave functions $|\Psi_\mu\rangle$ and energies E_μ of a cluster comprising a single TM 3d-shell and its nearest neighbors, e.g.
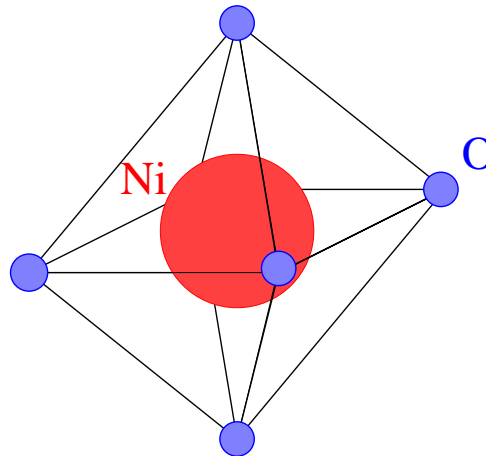
The cluster:
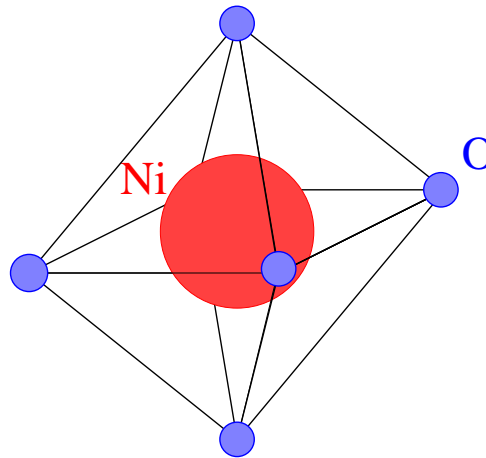
The Hamiltonian:

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

This comprises the Coulomb interaction in the TM 3d-shell, the Crystalline electric field, the charge transfer between TM 3d-shell and ligands, and the orbital energies of transition metal d-orbitals and ligands

Reminder:

$$A(\omega) = -\frac{1}{\pi Z}\Im \sum_{m=-2}^{2} \sum_{\mu} e^{-\beta E_\mu} \langle \Psi_\mu | c^\dagger_{3,2,m,\sigma} \frac{1}{\omega + (H - E_\mu) + i0^+} c_{2,m,\sigma} | \Psi_\mu \rangle$$

$$= \frac{1}{Z} \sum_{m=-2}^{2} \sum_{\mu,\nu} e^{-\beta E_\mu} |\langle \Psi_\nu | c_{3,2,m,\sigma} | \Psi_\mu \rangle|^2 \delta(\omega + (E_\nu - E_\mu)).$$

To simulate lifetime-effects and broadening of the ionization states of the cluster into 'bands' the δ-Functions are usually replaced by Loretzians (or $i0^+ \rightarrow i\eta$ with $\eta > 0$)

Cluster calculation of XPS spectra - results for 3d transition metal compounds with rocksalt structure
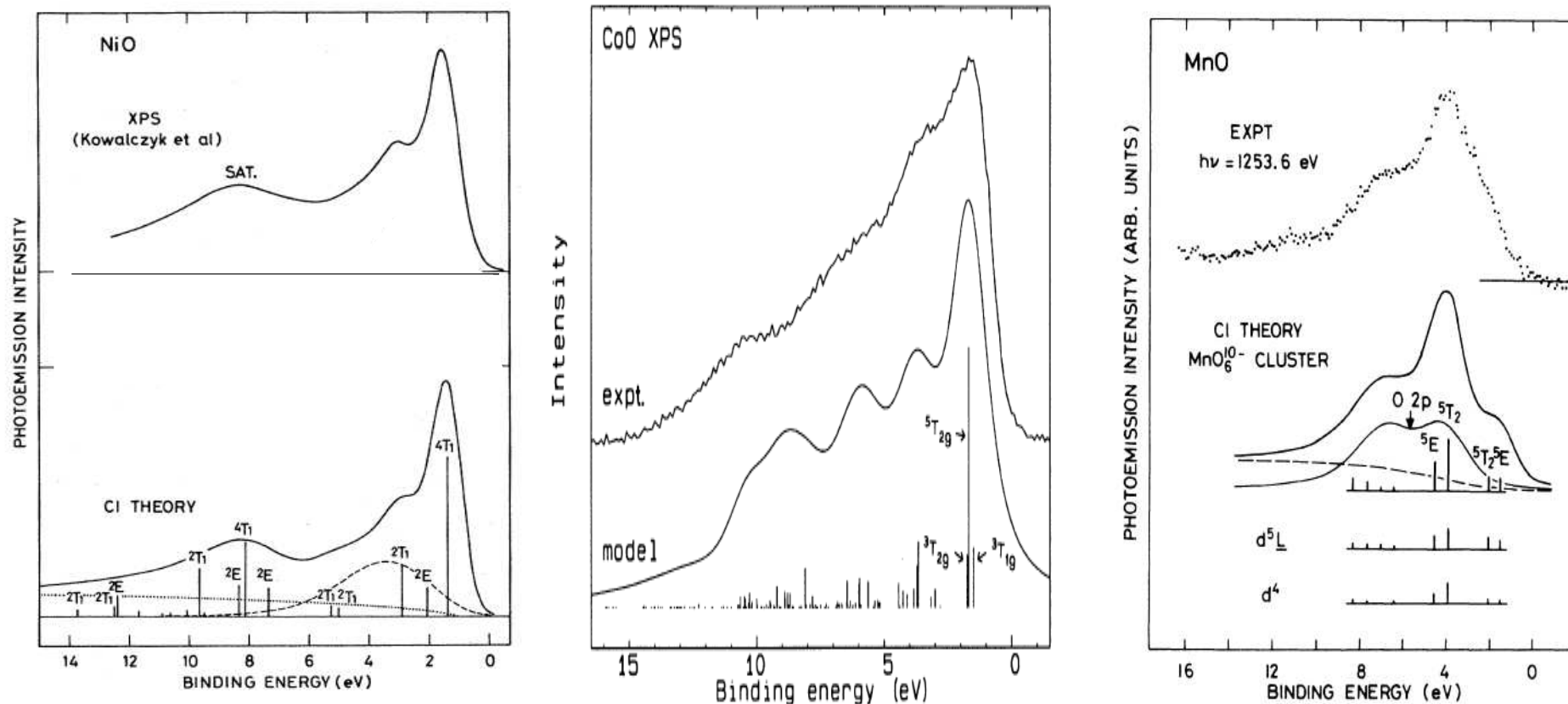
NiO: A. Fujimori and F. Minami, Phys. Rev. B **30**, 957 (1984)

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
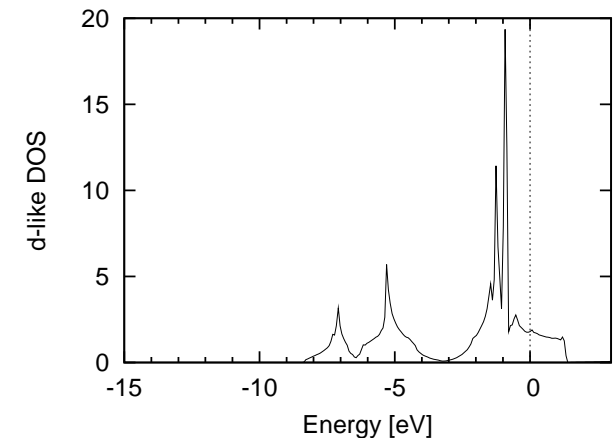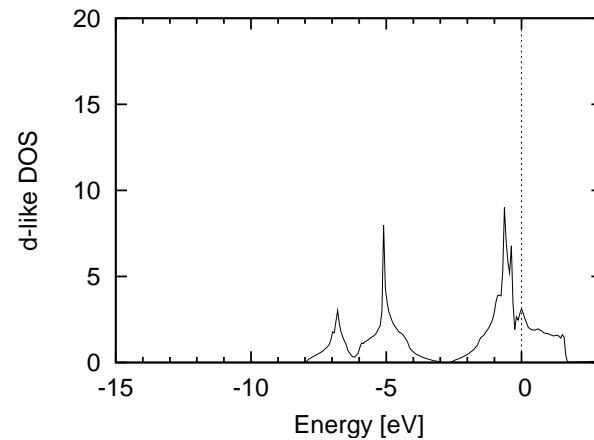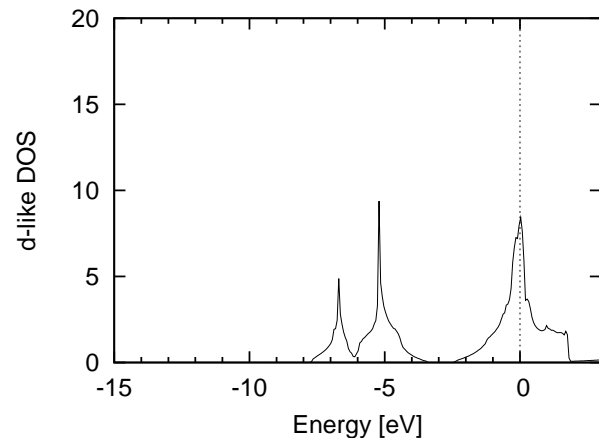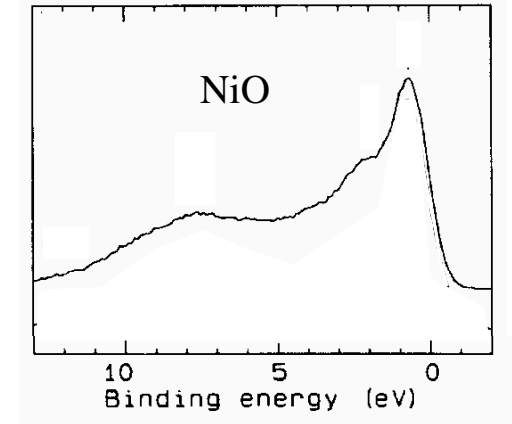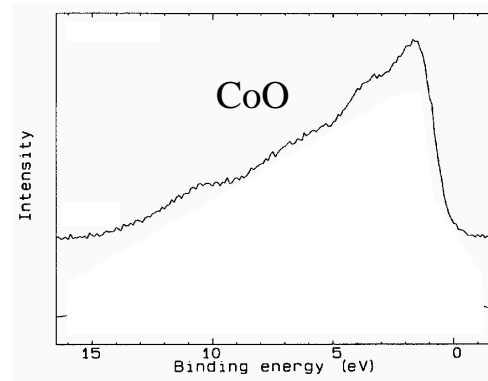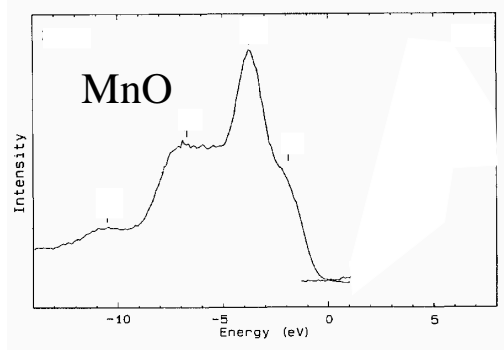
What determines the shape of the spectrum is not so much the single-particle band structure but the charge and spin state of the TM ion!

Now the other way round: MnO versus Fe_2O_3 - Mn^{2+} versus Fe^{3+} - d^5 versus d^5
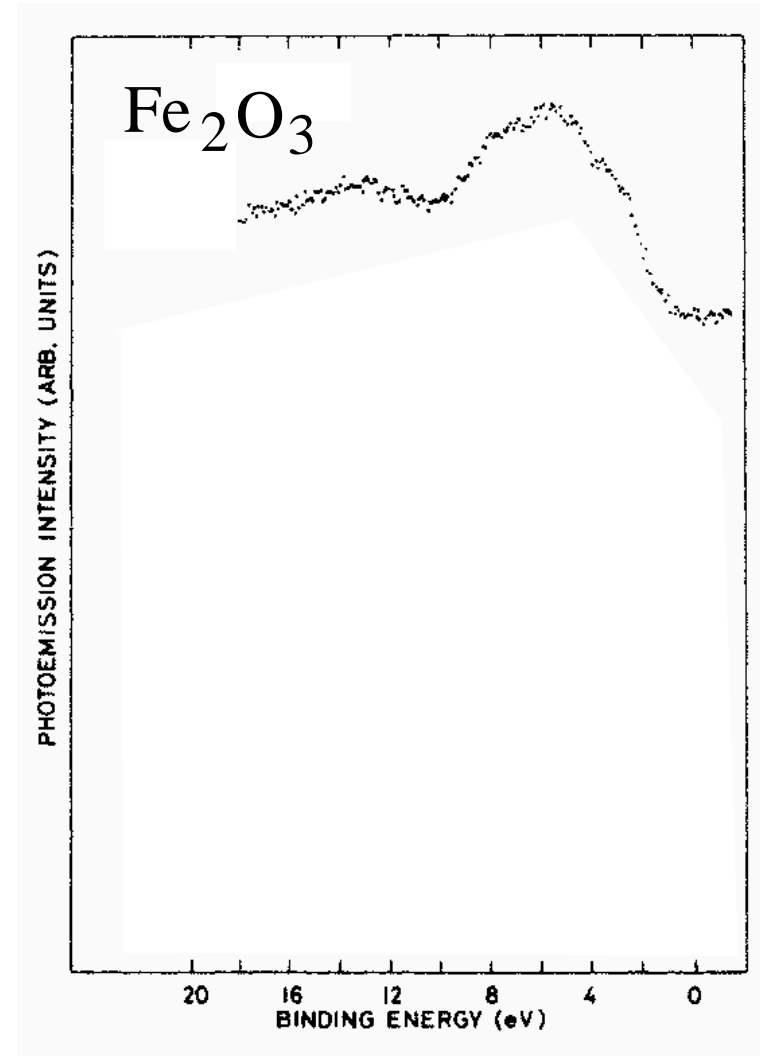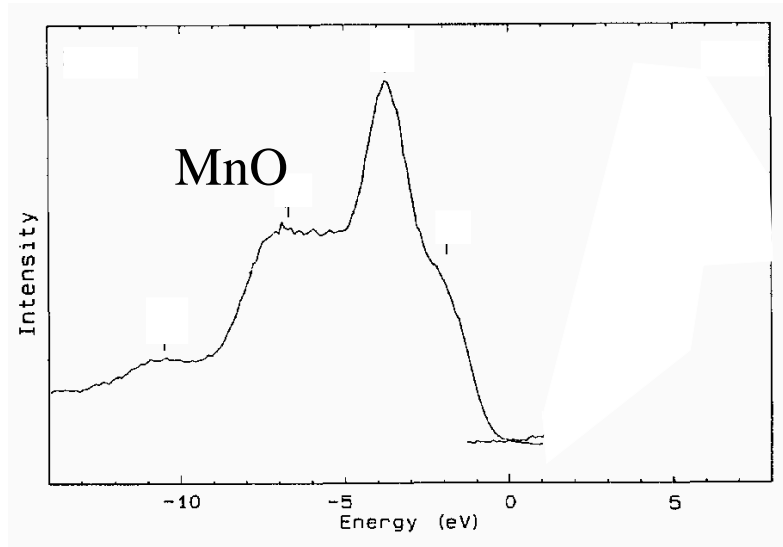
Fe_2O_3 data from A. Fujimori *et al.*, Phys. Rev. B **34**, 7318 (1986)

X-ray absorption spectra (XAS)

- X-rays impinge onto the sample and the absoption coefficient is measured versus photon-energy: $\kappa(h\nu)$

- The X-rays are aborbed due to (mainly) dipole-transitions of an electron from a core level (1s, 2s, 2p....) to an unoccupied level

- Let $E_0 < 0$ be the energy of the core level relative to the Fermi energy

- For $E_0 + h\nu < 0$ no dipole transition is possible because no unoccupied final state exists

- As soon as $E_0 + h\nu \geq 0$ the absorption will rise sharply - this is called an absorption edge

- In combination with multiplet theory the variation of $\kappa(h\nu)$ for energies within $10 - 20\ eV$ above the absorption edge can give information about the state of the transition metal ion
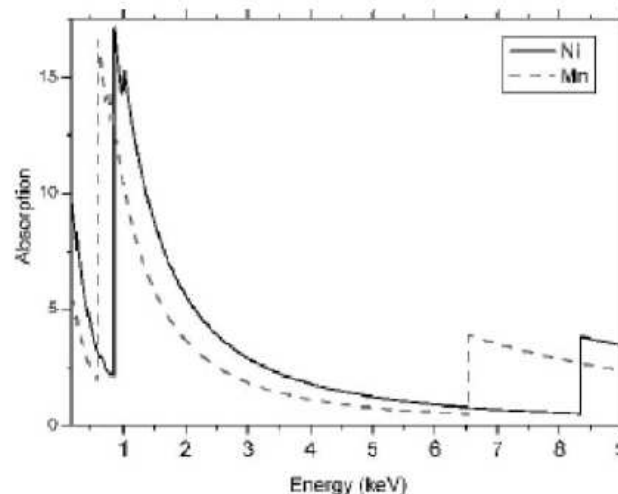
XAS by cluster calculation

The absorption coefficient is proportional to

$$\kappa(\omega) = -\frac{1}{\pi Z}\Im \sum_{\mu} e^{-\beta E_\mu} \langle \Psi_\mu | D(\boldsymbol{n}) \frac{1}{\omega - (H - E_\mu) + i0^+} D(\boldsymbol{n}) | \Psi_\mu \rangle$$

$$= \frac{1}{Z}\sum_{\mu,\nu} e^{-\beta E_\mu} |\langle \Psi_\nu | D(\boldsymbol{n}) | \Psi_\mu \rangle|^2 \delta(\omega - (E_\nu - E_\mu)).$$

- Here $|\Psi_\mu\rangle$ and E_μ again are eigenstates and corresponding energy of the solid
- $\frac{1}{Z}e^{-\beta E_\mu}$ with $\beta = (k_B T)^{-1}$ is the thermal occupation probablity of $|\Psi_\mu\rangle$
- The operator $D(\boldsymbol{n})$ is the dipole-operator (with $\boldsymbol{n}$ the photon polarization) - it may be written as

$$\sum_{m,m'} \sum_{\sigma} \left(D_{m,m'}(\boldsymbol{n})\ c^{\dagger}_{3,2,m,\sigma}\ c_{2,1,m',\sigma} + H.c. \right)$$

- The dipole operator promotes an electron from the 2p-shell to the 3d-shell - and vice versa
- The final states $|\Psi_\nu\rangle$ therefore have a new new feature: a hole in the 2p-shell
- We therefore need to include two new terms into the Hamiltonian: spin-orbit-coupling in the 2p-shell and Coulomb interaction between the hole in the 2p-shell and the electrons in the 3d-shell

The Hamiltonian for a single 2p electron reads (with $\lambda_{SOC} \approx 10 \; eV$ for 3d transition metals)

$$H_{SOC} = \lambda_{SOC} \; \boldsymbol{L} \cdot \boldsymbol{S}$$

The eigenfunctions have $J = \frac{3}{2}$ (4-fold degenerate) and $J = \frac{1}{2}$ (2-fold degenerate)

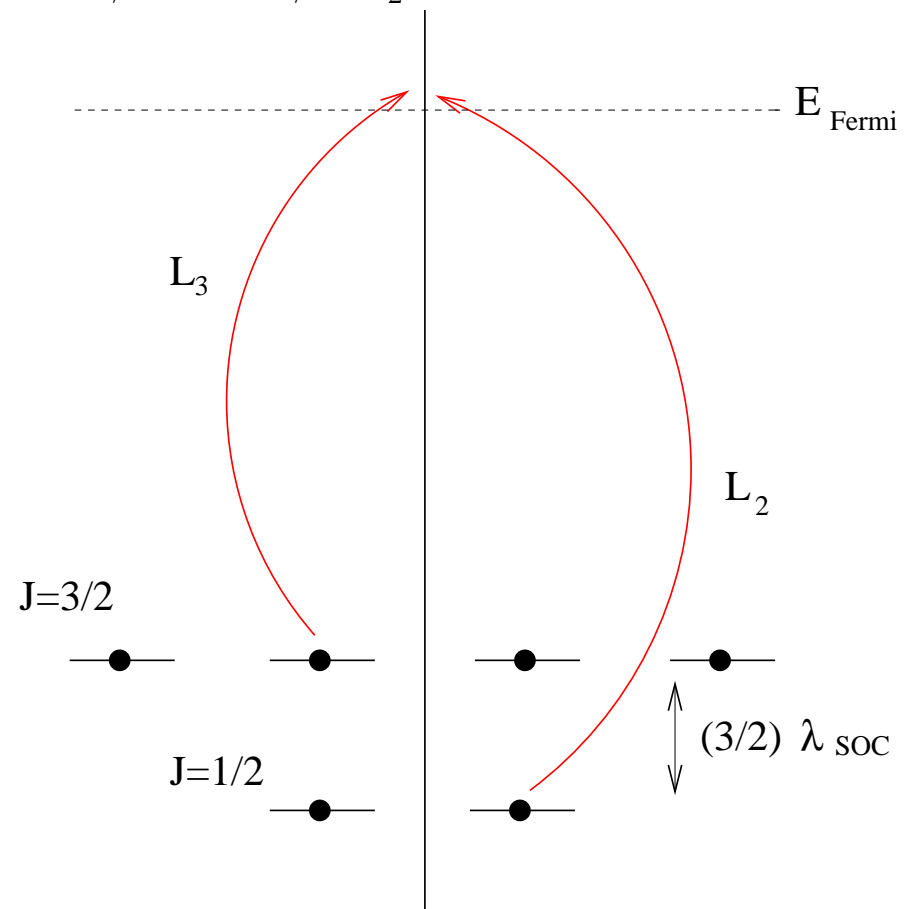We squre $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$ and form the expectation value with a state with sharp J^2, S^2 and L^2: $|J\rangle$:

$$
\begin{aligned}
J(J+1) \; &= \; L(L+1) + 2 \; \langle J|\boldsymbol{L} \cdot \boldsymbol{S}|J\rangle + S(S+1) \\
&= \; 2 \; \langle J|\boldsymbol{L} \cdot \boldsymbol{S}|J\rangle + \frac{11}{4} \\
\langle J|\boldsymbol{L} \cdot \boldsymbol{S}|J\rangle \; &= \; \frac{J(J+1)}{2} - \frac{11}{8}
\end{aligned}
$$

We thus find for the difference in energy between the two SOC-levels

$$
\begin{aligned}
E_{J=3/2} - E_{J=1/2} \; &= \; \lambda_{SOC} \left(\; \langle \frac{3}{2} |\boldsymbol{L} \cdot \boldsymbol{S}| \frac{3}{2} \rangle - \langle \frac{1}{2} |\boldsymbol{L} \cdot \boldsymbol{S}| \frac{1}{2} \rangle \; \right) \\
&= \; \lambda_{SOC} \; \frac{1}{2} \left(\frac{3}{2} \cdot \frac{5}{2} - \frac{1}{2} \cdot \frac{3}{2} \right) \\
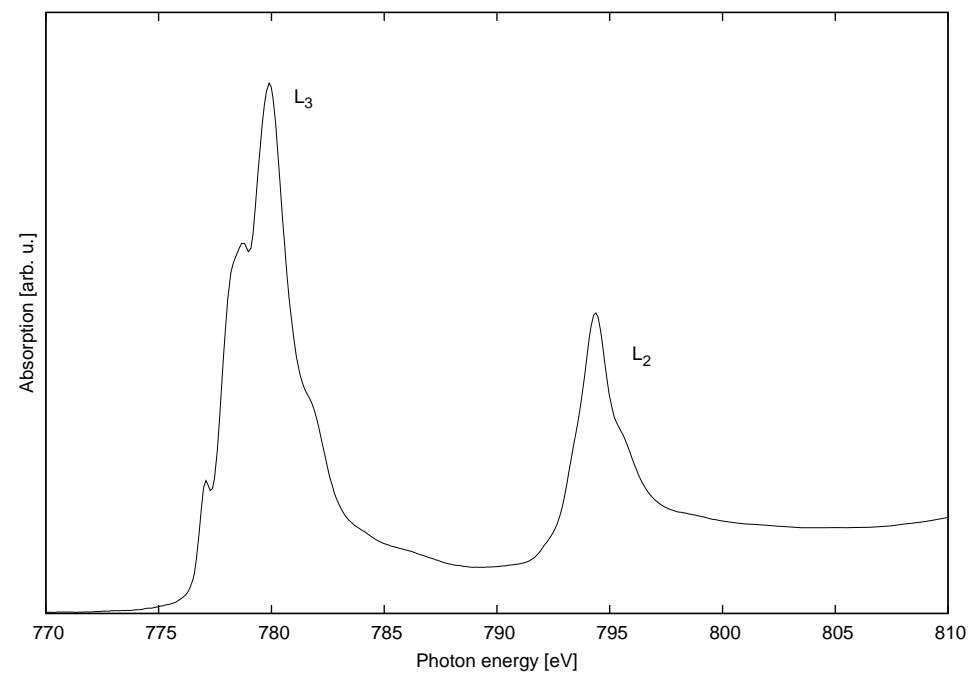&= \; \frac{3}{2} \; \lambda_{SOC}
\end{aligned}
$$

$$E_{J=3/2} - E_{J=1/2} = \frac{3}{2}\,\lambda_{SOC}$$

E_{Fermi}

L_3

L_2

J=3/2

J=1/2

$(3/2)\ \lambda_{SOC}$

$$E_{J=3/2} - E_{J=1/2} = \tfrac{3}{2}\,\lambda_{SOC}$$
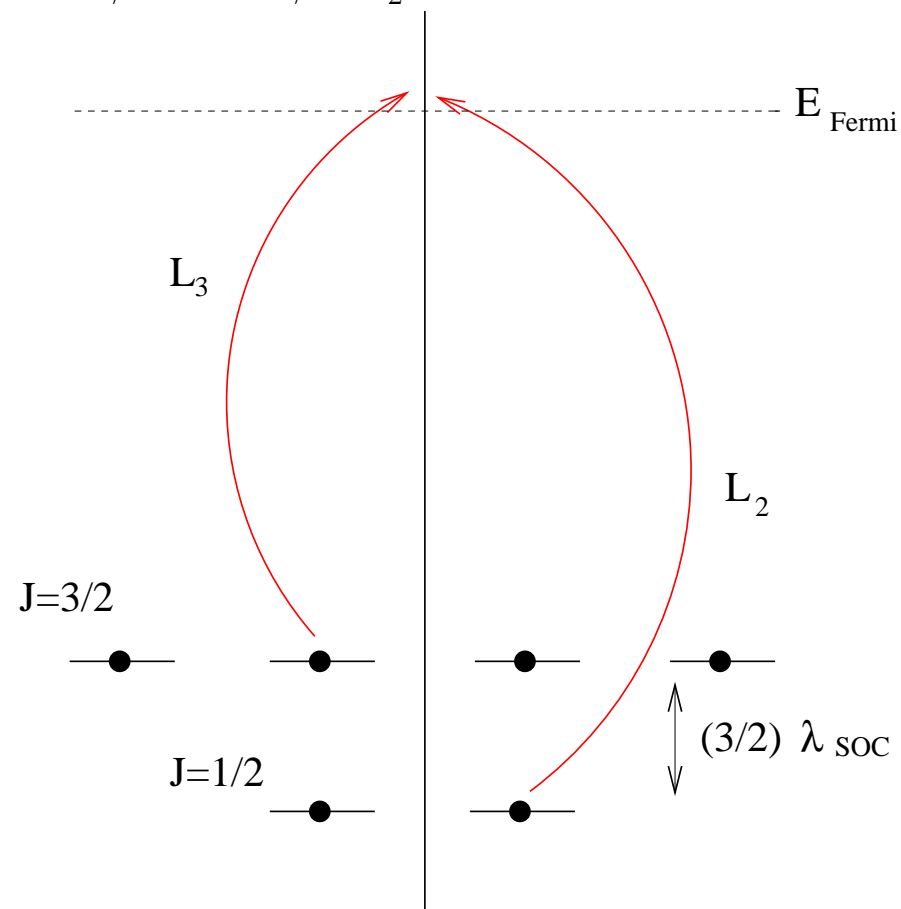
In experiment: Co-L-edge in $La_{1.5}Ca_{0.5}CoO_4$

(M. Merz, private communication)

To implement spin-orbit-coupling we must convert H_{SOC} to 2nd quantized form - we write

$$H_{SOC} = \lambda_{SOC} \sum_{i=1}^{n} \boldsymbol{l}_i \cdot \boldsymbol{S}_i = \lambda_{SOC} \sum_{i=1}^{n} \left(l_i^z S_i^z + \frac{1}{2}(l_i^+ S_i^- + l_i^- S_i^+) \right).$$

Then, in 2nd quantization we have

$$H_{SOC}^{\parallel} = \lambda_{SOC} \sum_{m=-l}^{l} \frac{m}{2} (c_{l,m,\uparrow}^{\dagger} c_{l,m,\uparrow} - c_{l,m,\downarrow}^{\dagger} c_{l,m,\downarrow}).$$

For the transverse part we use $\langle l, m \pm 1 | l^{\pm} | l, m \rangle = \sqrt{(l \mp m)(l \pm m + 1)}$ (Landau-Lifshitz) and find

$$H_{SOC}^{\perp} = \frac{\lambda_{SOC}}{2} \sum_{m=-l}^{l-1} \sqrt{(l-m)(l+m+1)} \, (c_{l,m+1,\downarrow}^{\dagger} c_{l,m,\uparrow} + c_{l,m,\uparrow}^{\dagger} c_{l,m+1,\downarrow}).$$

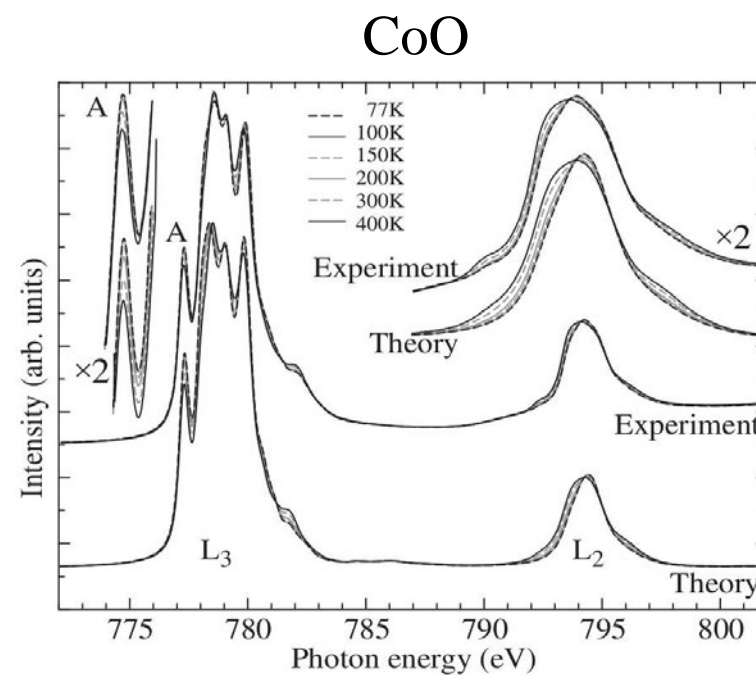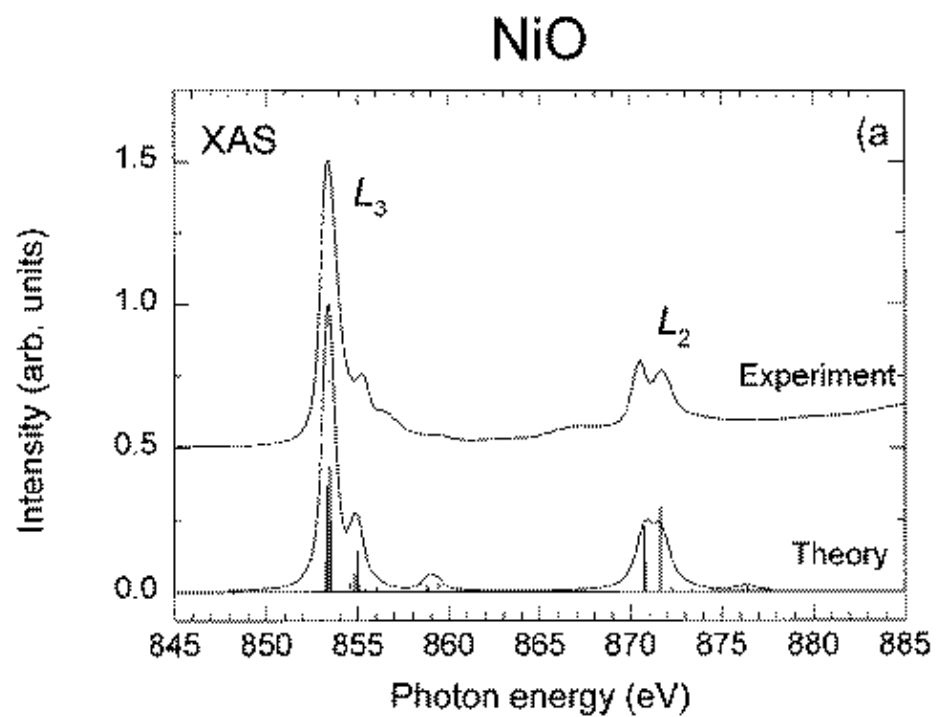This is easily implemented in exact diagonalization

New feature in XAS: Coulomb scattering between 3d-electrons and 2p electrons
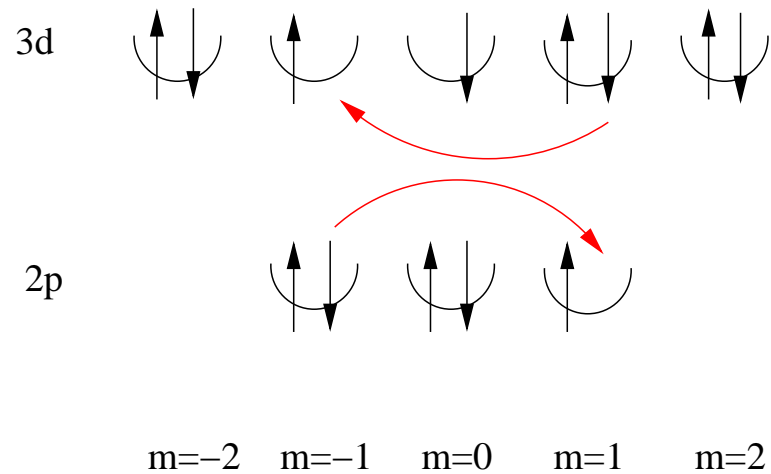
The Coulomb matrix elements are given by the general formula derived above

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

Cluster calculation of XAS: Results

NiO

CoO

NiO: M. Finazzi *et al.*, Phys. Rev. B **59**, 9933 (1999)

CoO: M. Haverkort, Ph. D, thesis (2002)

- When combined with multiplet-calculations, XAS-experiments can give detailed information about the charge and spin state of transition metal ions in solids and molecules

- This is a powerful technique which is nowadays used routinely in research on TM-compounds in physics and chemistry

- For reviews see

F. M. F. de Groot, Journal of Electron Spectroscopy and Related Phenomena, **67** 525 (1994)

F. M. F. de Groot, Coordination Chemistry Reviews, **249** 31 (2005)

F. M. F. de Groot and A. Kotani: *Core Level Spectroscopy of Solids* (Taylor And Francis, 2008)
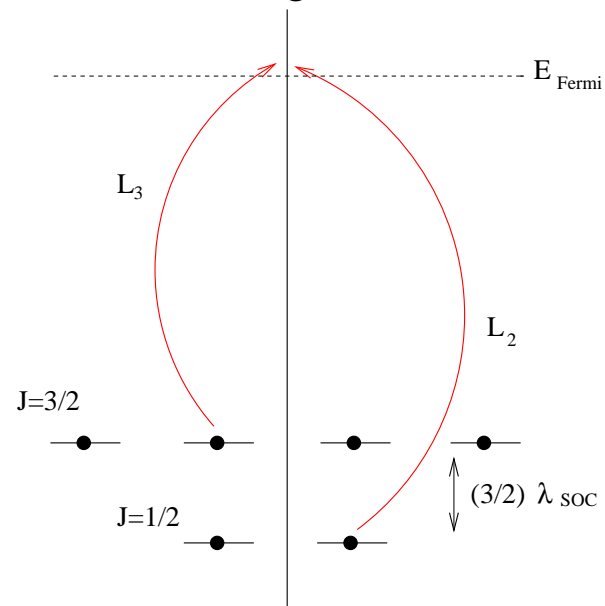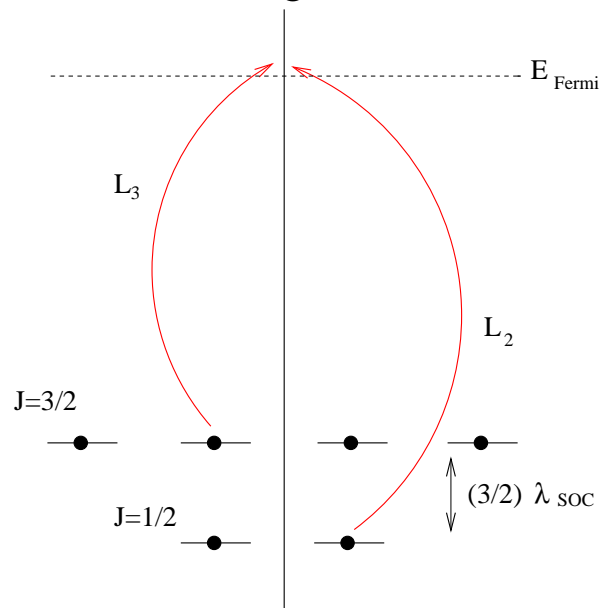
Core-level photoemission

We had already discussed valence-band photoemission: electrons are ejected after the solid is hit by light

In valence band photoemission the photoelectrons come from states near the Fermi energy

In core level photoemission the photoelectrons come from an inner shell

It we remember the discussion on spin-orbit coupling we might expect a core-level photoemission spectrum to be rather boring:

Core-level photoemission

We had already discussed valence-band photoemission: electrons are ejected after the solid is hit by light
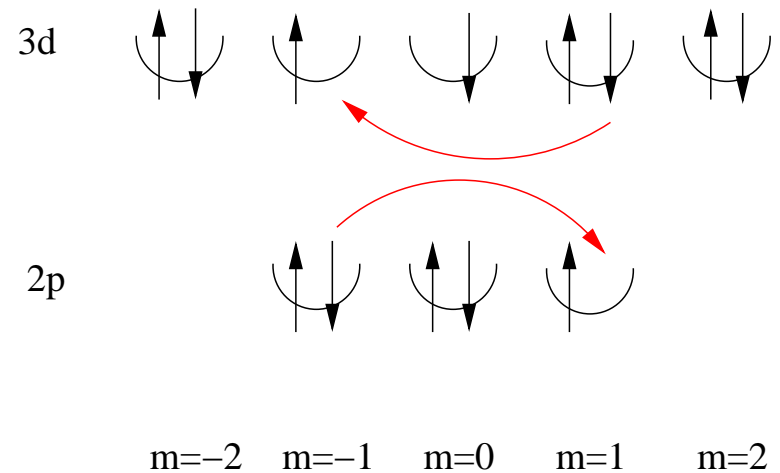
In valence band photoemission the photoelectrons come from states near the Fermi energy

In core level photoemission the photoelectrons come from an inner shell
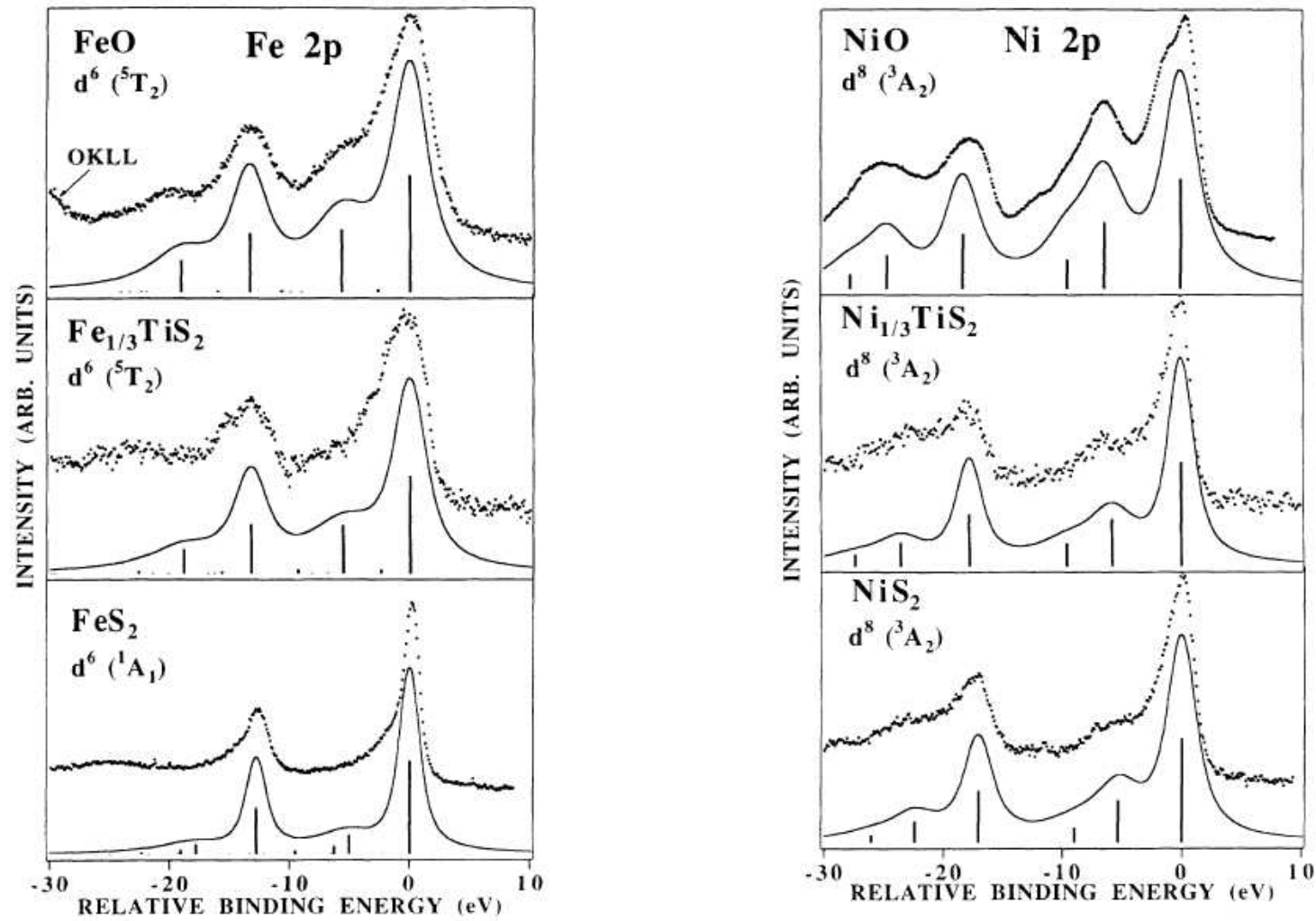
It we remember the discussion on spin-orbit coupling we might expect a core-level photoemission spectrum to

be rather boring:

However:

Core-level photoemission: Experiment vs Cluster spectra

Summary

- The 3d-shell in transition metals has a small spatial extent - the small average distance between electrons in this shell thus results in particularly large matrix elements of the Coulomb interaction (more precisely: particularly large Slater-Condon parameters F^0, F^2 and F^4)

- The Coulomb interaction in a partially filled atomic shell generates multiplet splitting

- In a solid the multiplet structure of a transition metal ion is modified by the crystalline electric field and charge transfer to ligands - both effects can be modelled well theoretically

- A wide variety of spectroscopies can be described by multiplet theory, whereby usually quantitative agreement with experiment can be obtained

- Examples are valence band photoemission, XAS, core-level photoemission but also optical absorption, electron-spin resonance, inelastic neutron scattering....

- The agreement is in fact so good that the combination of - say - X-ray absorption spectroscopy and multiplet theory/exact diagonalization allows to pin down the valence and spin state of TM ions in solids

- This all is unambiguous evidence that the multiplet structure of the free ion - modified by CEF and charge transfer - persists in the solid and is crucial for understanding 3d TM oxides