

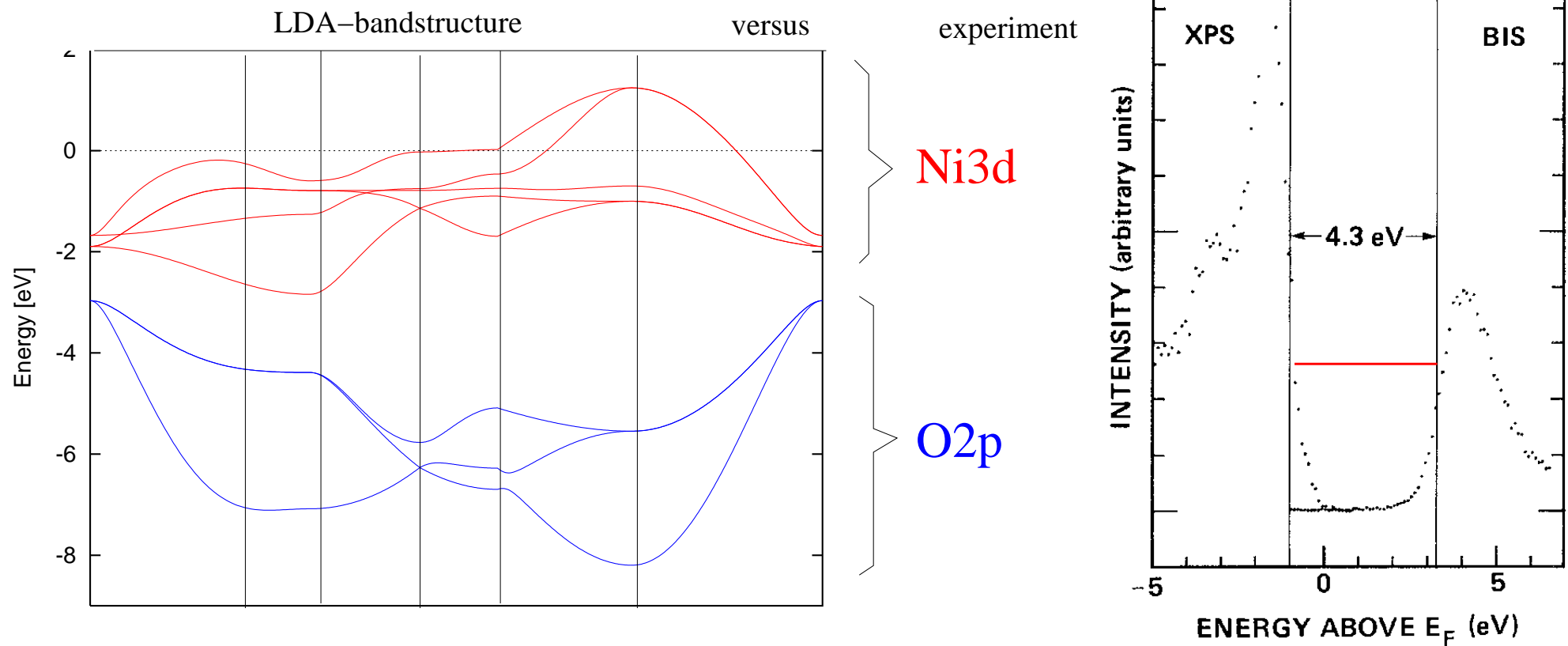
Multiplets in transition metal ions

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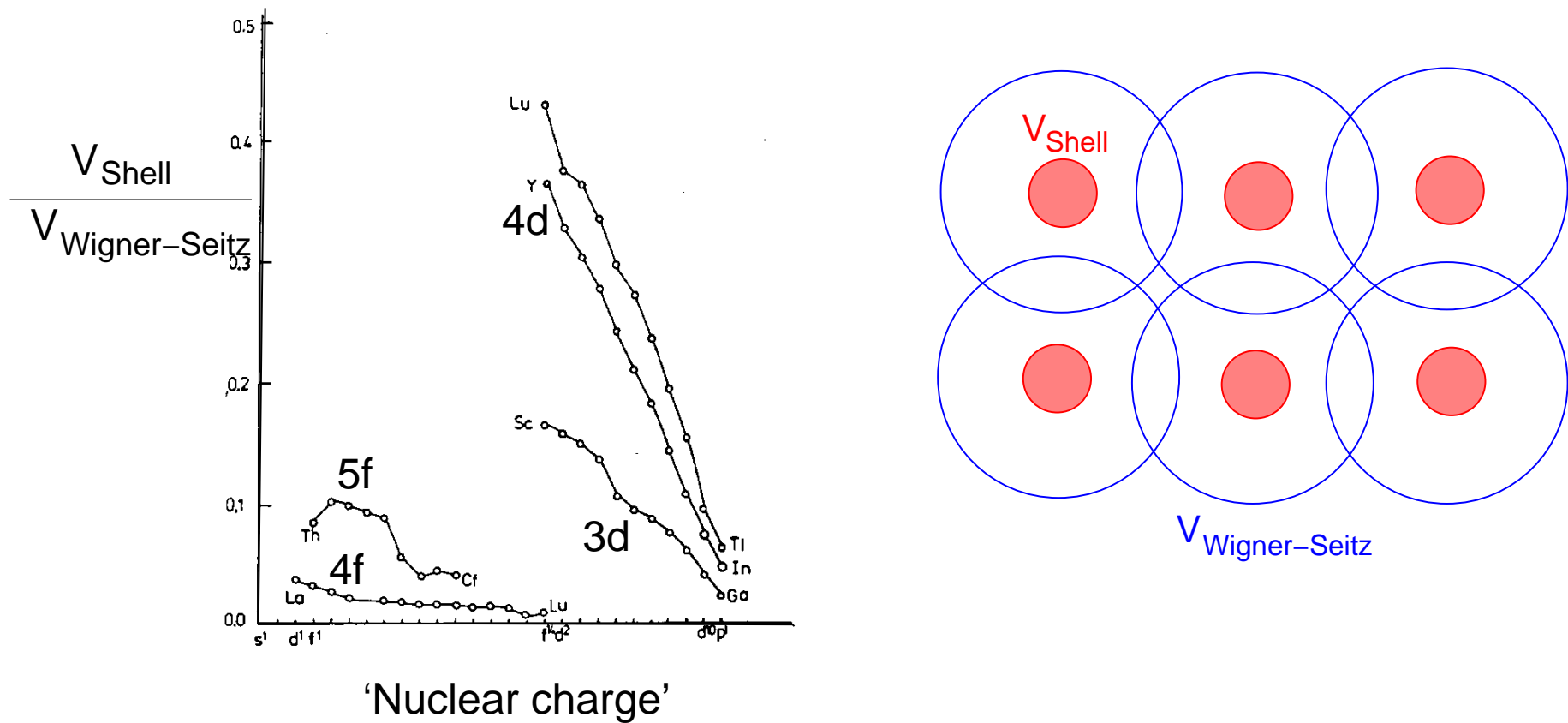
3d Transition Metals - a problem for single-electron theory

- NiO has rocksalt structure \rightarrow unit cell contains one Ni-atom ($[Ar] 3d^8 4s^2$) and one O-atom ($1s^2 2s^2 2p^4$)
- Assuming strong ionicity we have O^{2-} and Ni^{2+} \rightarrow Ni is $[Ar] 3d^8$



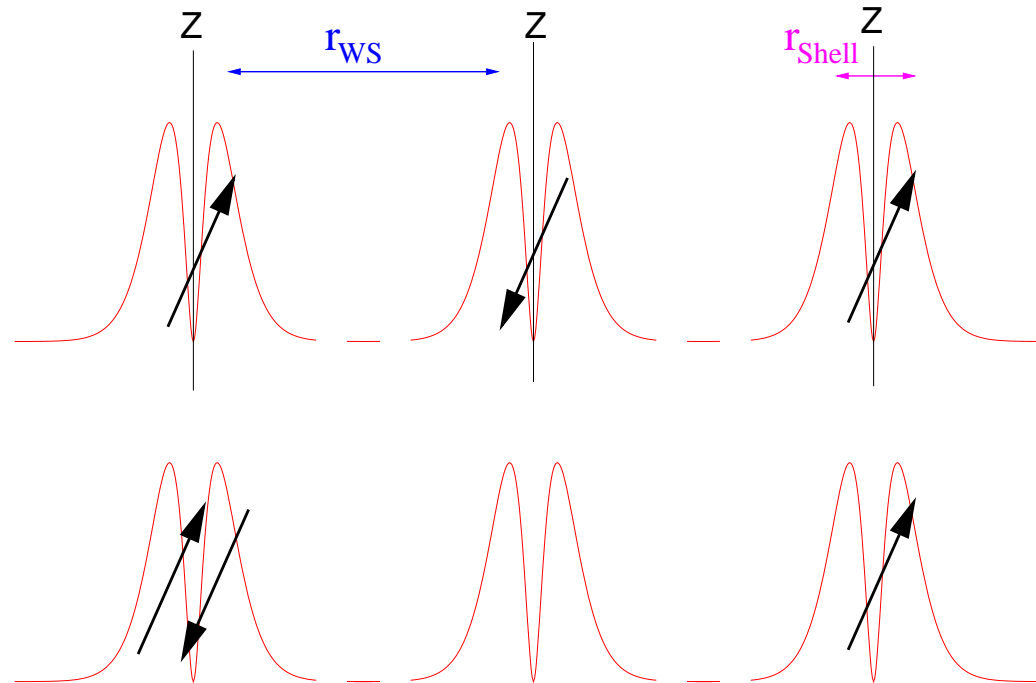
Experiment: G. A. Sawatzky and J. W. Allen, Phys. Rev. Lett. 53, 2239 (1984).

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



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

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

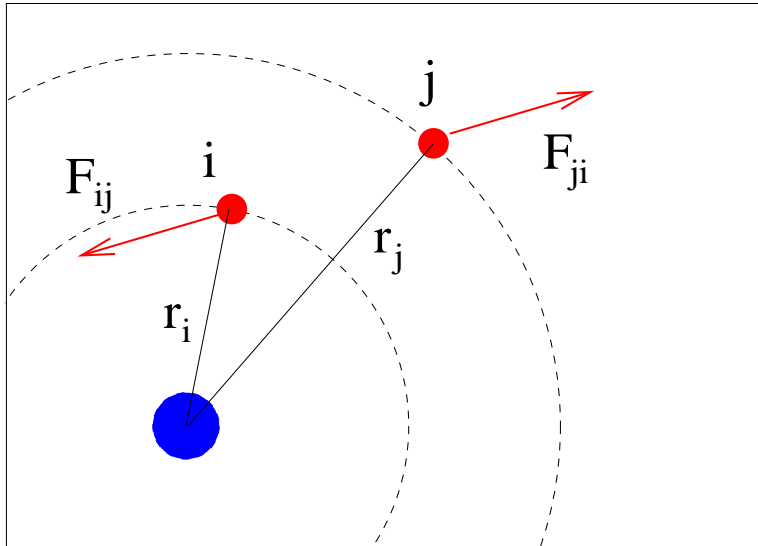
For a nondegenerate orbital we have

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

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

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

Coulomb repulsion between electrons - Classical picture



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

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

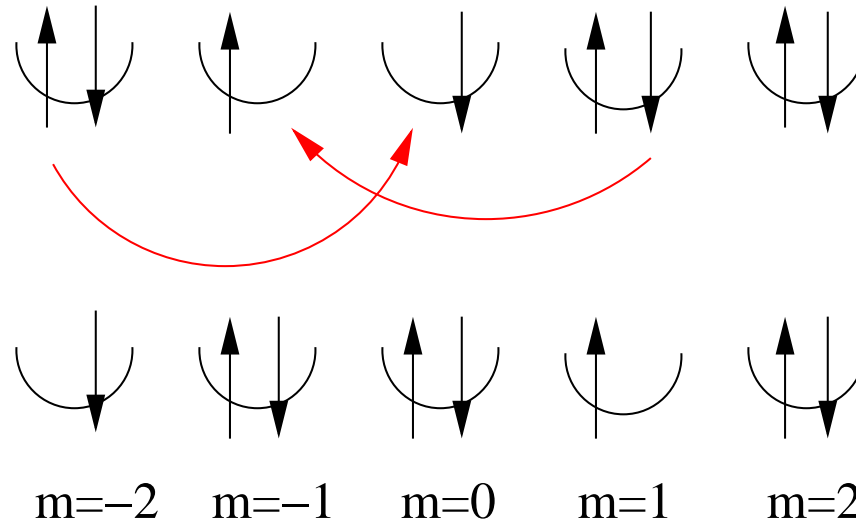
$$\mathbf{F}_{ji} = \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|^3} (\mathbf{r}_j - \mathbf{r}_i)$$

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

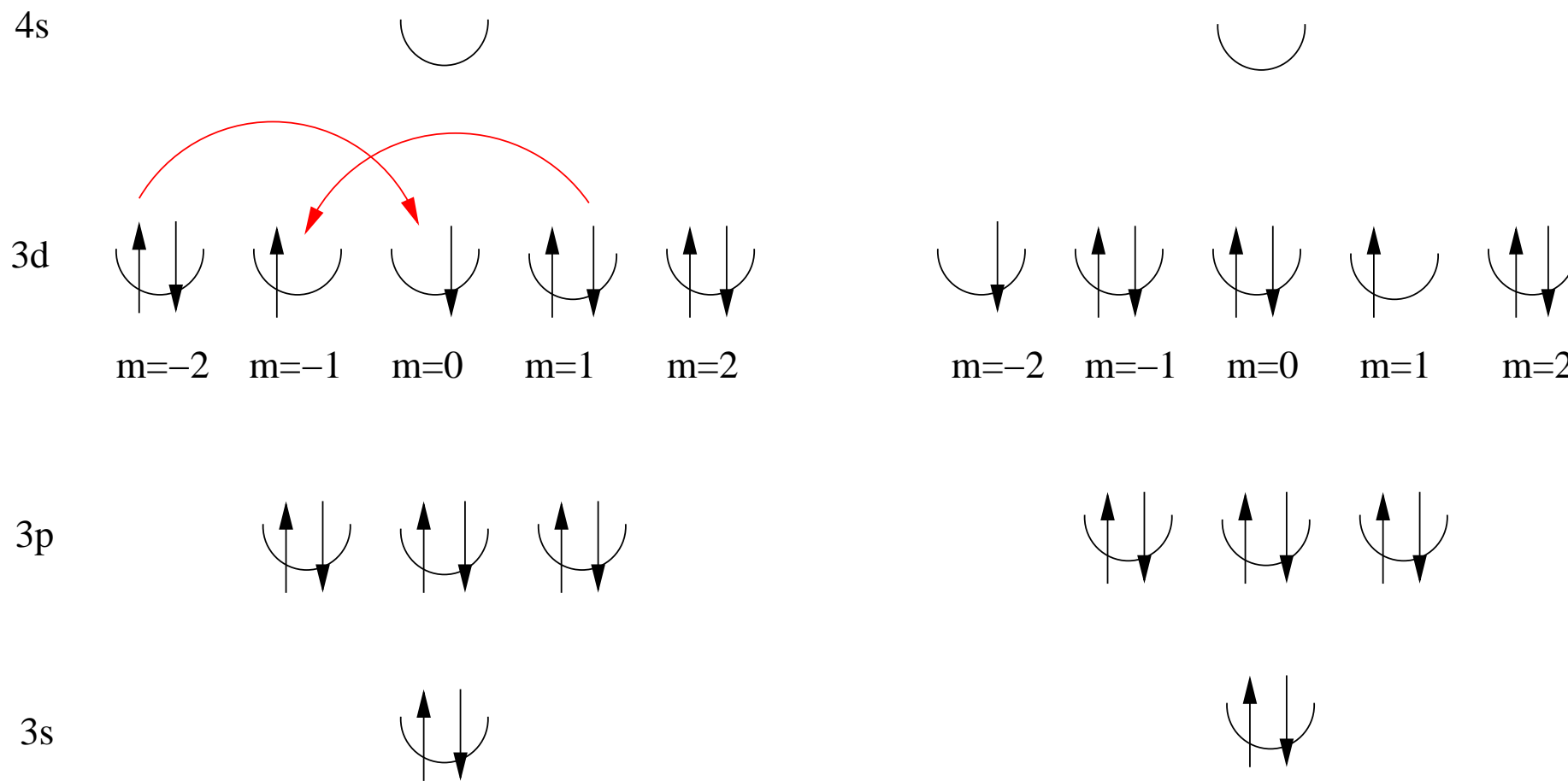
→ Exchange of angular momentum

Exchange of angular momentum - Quantum mechanical version

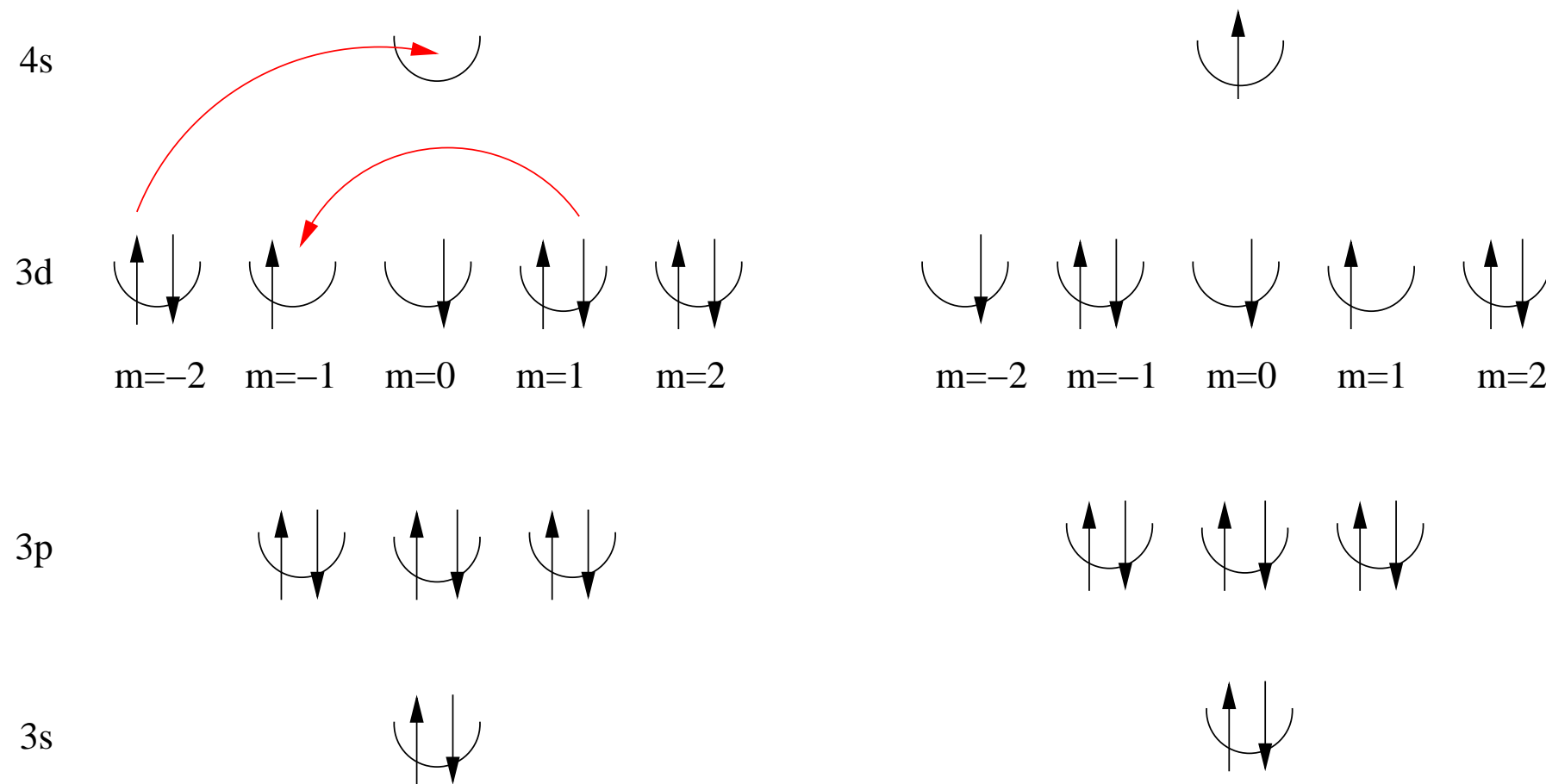


- Electrons in a partially filled shell **scatter from each other** due to their Coulomb interaction
- This amounts to a redistribution of the electrons within the partially filled shell
- For L^z to be conserved the scattering electrons must 'move along the m-ladder' in exactly opposite ways

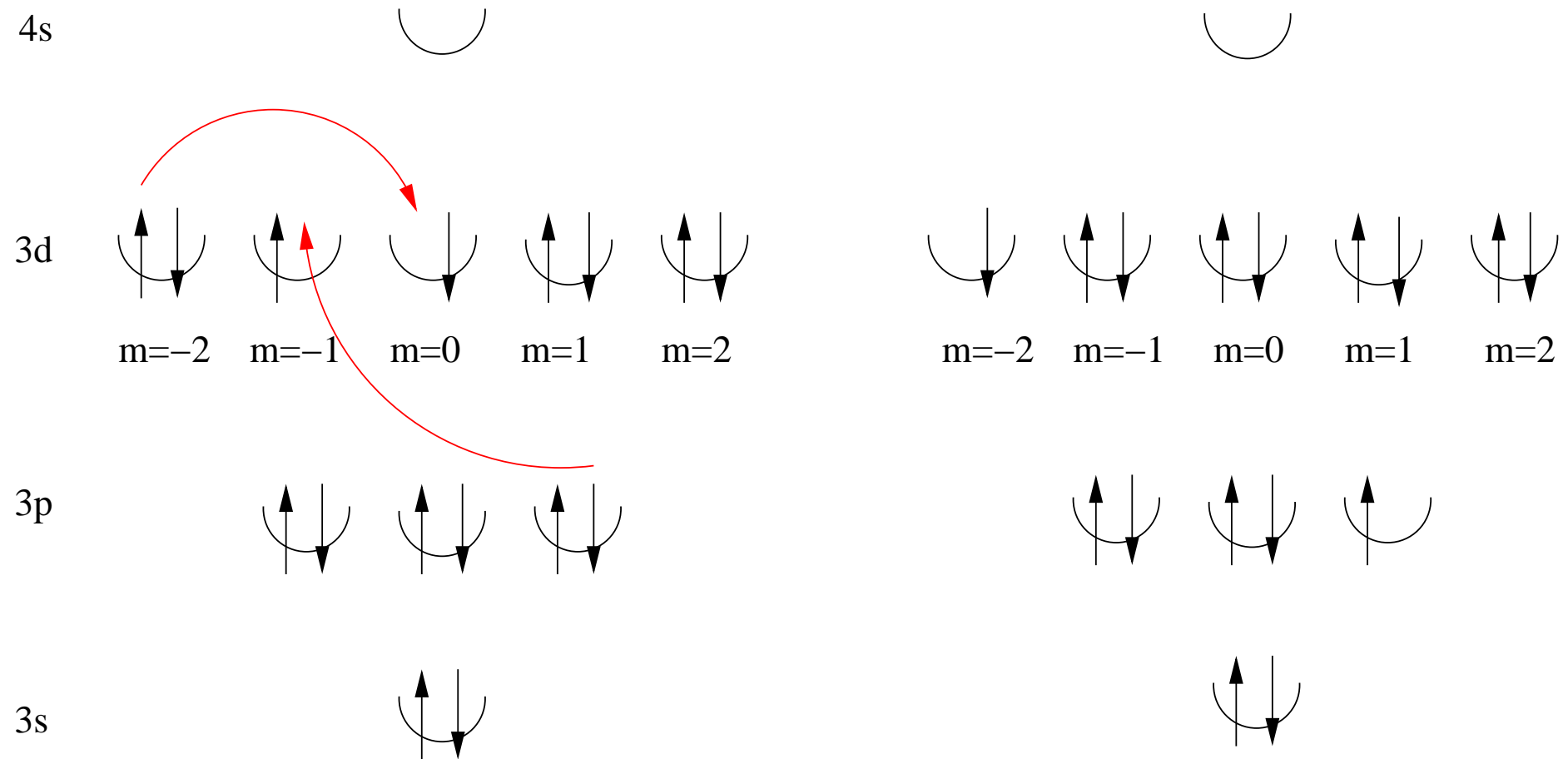
We take processes like this one



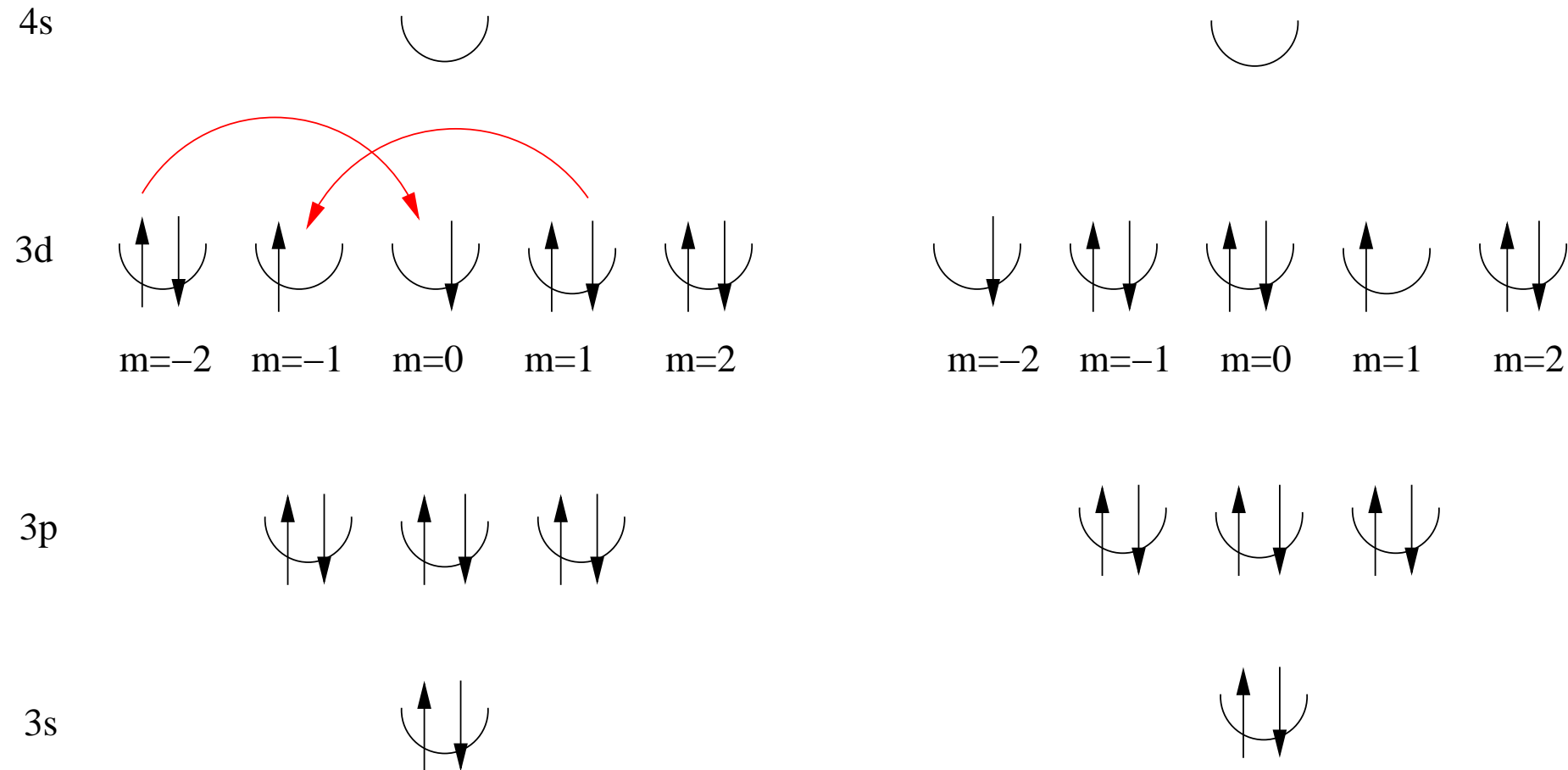
But not this one....



... or this one



We take processes like this one



- The states which are mixed by the Coulomb scattering are **degenerate with respect to orbital energy** $n \in_{3d}$
- 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 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 functions

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

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

- 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**: $c_{\nu_i}^\dagger = c_{n_i, l_i, m_i, \sigma_i}^\dagger$

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

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

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

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

$$\int dx \dots = \sum_{\sigma} \int d\mathbf{r} \dots$$

We need to calculate

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

Now insert

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

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

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

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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

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

Now insert

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

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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

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

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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

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

Now insert

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

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(Θ, ϕ) -Integration

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

(Θ', ϕ') -Integration

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

We need to calculate

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

Now insert

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

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

(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

→ **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

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

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

$$\begin{aligned} &\sqrt{\frac{4\pi}{2k+1}} \int d\Omega' Y_{l_2, m_2}^*(\Theta', \phi') Y_{k, m}^*(\Theta', \phi') Y_{l_3, m_3}(\Theta', \phi') \\ &= \sqrt{\frac{4\pi}{2k+1}} \int d\Omega' Y_{l_3, m_3}^*(\Theta', \phi') Y_{k, m}(\Theta', \phi') Y_{l_2, m_2}(\Theta', \phi') \\ &= \delta_{m, m_3 - m_2} c^k(l_3, m_3; l_2, m_2) \end{aligned}$$

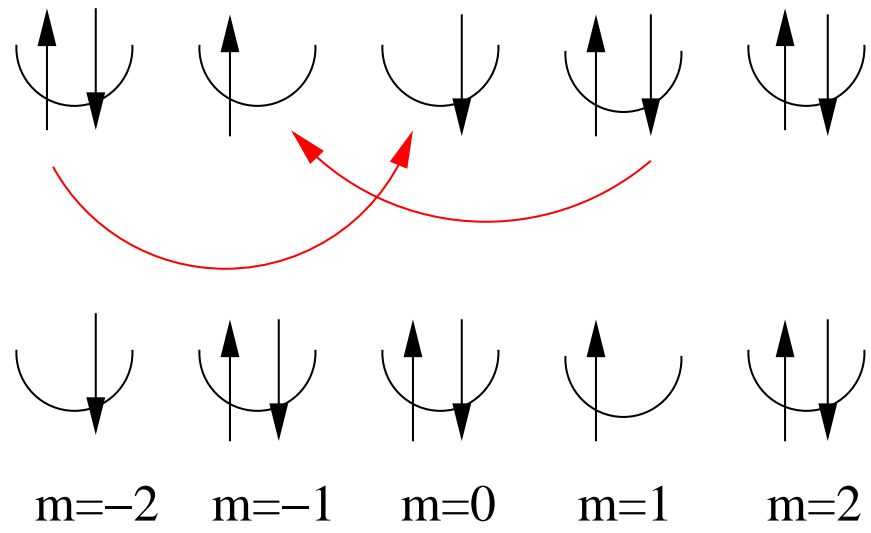
Collecting everything:

$$\begin{aligned}
V(\nu_1, \nu_2, \nu_3, \nu_4) &= \int dx \int dx' \psi_{\nu_1}^*(x) \psi_{\nu_2}^*(x') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_{\nu_4}(x) \psi_{\nu_3}(x') \\
&= \delta_{\sigma_1, \sigma_4} \delta_{\sigma_2, \sigma_3} \sum_{k=0}^{\infty} \sum_{m=-k}^k \delta_{m, m_1 - m_4} c^k(l_1, m_1; l_4, m_4) \delta_{m, m_3 - m_2} c^k(l_3, m_3; l_2, m_2) \\
&\hspace{25em} R^k(n_1 l_1, n_2 l_2, n_3 l_3, n_4 l_4) \\
&= \delta_{\sigma_1, \sigma_4} \delta_{\sigma_2, \sigma_3} \sum_{k=0}^{\infty} \delta_{m_1 + m_2, m_3 + m_4} c^k(l_1, m_1; l_4, m_4) c^k(l_3, m_3; l_2, m_2) R^k(n_1 l_1, n_2 l_2, n_3 l_3, n_4 l_4)
\end{aligned}$$

with

$$\begin{aligned}
c^k(l_1, m_1; l_4, m_4) &= \sqrt{\frac{4\pi}{2k+1}} \int d\Omega Y_{l_1, m_1}^*(\Theta, \phi) Y_{k, m_1 - m_4}(\Theta, \phi) Y_{l_4, m_4}(\Theta, \phi) \\
R^k(n_1 l_1, n_2 l_2, n_3 l_3, n_4 l_4) &= e^2 \int_0^{\infty} dr r^2 \int_0^{\infty} dr' r'^2 R_{n_1, l_1}(r) R_{n_2, l_2}(r') \frac{r^k}{r^{k+1}} R_{n_4, l_4}(r) R_{n_3, l_3}(r')
\end{aligned}$$

Reminder:



Collecting everything:

$$\begin{aligned}
V(\nu_1, \nu_2, \nu_3, \nu_4) &= \int dx \int dx' \psi_{\nu_1}^*(x) \psi_{\nu_2}^*(x') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_{\nu_4}(x) \psi_{\nu_3}(x') \\
&= \delta_{\sigma_1, \sigma_4} \delta_{\sigma_2, \sigma_3} \sum_{k=0}^{\infty} \sum_{m=-k}^k \delta_{m, m_1 - m_4} c^k(l_1, m_1; l_4, m_4) \delta_{m, m_3 - m_2} c^k(l_3, m_3; l_2, m_2) \\
&\hspace{25em} R^k(n_1 l_1, n_2 l_2, n_3 l_3, n_4 l_4) \\
&= \delta_{\sigma_1, \sigma_4} \delta_{\sigma_2, \sigma_3} \sum_{k=0}^{\infty} \delta_{m_1 + m_2, m_3 + m_4} c^k(l_1, m_1; l_4, m_4) c^k(l_3, m_3; l_2, m_2) R^k(n_1 l_1, n_2 l_2, n_3 l_3, n_4 l_4)
\end{aligned}$$

with

$$\begin{aligned}
c^k(l_1, m_1; l_4, m_4) &= \sqrt{\frac{4\pi}{2k+1}} \int d\Omega Y_{l_1, m_1}^*(\Theta, \phi) Y_{k, m_1 - m_4}(\Theta, \phi) Y_{l_4, m_4}(\Theta, \phi) \\
R^k(n_1 l_1, n_2 l_2, n_3 l_3, n_4 l_4) &= e^2 \int_0^\infty dr r^2 \int_0^\infty dr' r'^2 R_{n_1, l_1}(r) R_{n_2, l_2}(r') \frac{r^k}{r^{k+1}} R_{n_4, l_4}(r) R_{n_3, l_3}(r')
\end{aligned}$$

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. $c^k(l_i, m_{li}; l_j, m_{lj})$ for s, p, d Electrons

	m_{li}	m_{lj}	k				
			0	1	2	3	4
<i>ss</i>	0	0	1	0	0	0	0
<i>sp</i>	0	± 1	0	$-\sqrt{1/3}$	0	0	0
	0	0	0	$\sqrt{1/3}$	0	0	0
<i>pp</i>	± 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
<i>sd</i>	0	0	1	0	$\sqrt{4/25}$	0	0
	0	± 2	0	0	$\sqrt{1/5}$	0	0
	0	± 1	0	0	$-\sqrt{1/5}$	0	0
<i>pd</i>	0	0	0	0	$\sqrt{1/5}$	0	0
	± 1	± 2	0	$\sqrt{9/15}$	0	$\sqrt{35/245}$	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	$-\sqrt{80/245}$	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
<i>dd</i>	0	0	0	$\sqrt{4/15}$	0	$\sqrt{27/245}$	0
	± 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:

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

$l_1 + l_2 + k$ even (Parity)

For Coulomb scattering in a d-shell our final result thus reads

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

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

$$|\nu_1, \nu_2 \dots \nu_n\rangle = c_{\nu_1}^\dagger c_{\nu_2}^\dagger \dots c_{\nu_n}^\dagger |0\rangle.$$

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

Ordering convention (absolutely necessary!)

$$m_1 \leq m_2 \leq m_3 \leq \dots \leq m_n$$

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

Then we order them as

$$\dots c_{3,2,m_\downarrow}^\dagger c_{3,2,m_\uparrow}^\dagger \dots |0\rangle$$

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

We consider the matrix element

$$\begin{aligned} \langle \mu_1, \mu_2 \dots \mu_n | V(\lambda_1, \lambda_2, \lambda_3, \lambda_4) c_{\lambda_1}^\dagger c_{\lambda_2}^\dagger c_{\lambda_3} c_{\lambda_4} | \nu_1, \nu_2 \dots \nu_n \rangle \\ = \langle 0 | c_{\mu_n} \dots c_{\mu_1} V(\lambda_1, \lambda_2, \lambda_3, \lambda_4) c_{\lambda_1}^\dagger c_{\lambda_2}^\dagger c_{\lambda_3} c_{\lambda_4} c_{\nu_1}^\dagger c_{\nu_2}^\dagger \dots c_{\mu_n}^\dagger | 0 \rangle \end{aligned}$$

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

$$c_{\lambda_3} c_{\lambda_4} c_{\nu_1}^\dagger c_{\nu_2}^\dagger \dots c_{\lambda_3}^\dagger \dots c_{\lambda_4}^\dagger \dots c_{\mu_n}^\dagger | 0 \rangle = \underline{(-1)^{n_3+n_4}} c_{\nu_1}^\dagger c_{\nu_2}^\dagger \dots c_{\lambda_3} c_{\lambda_3}^\dagger \dots c_{\lambda_4} c_{\lambda_4}^\dagger \dots c_{\mu_n}^\dagger | 0 \rangle$$

Next we use Fermion commutation relations to write $c_{\lambda_3} c_{\lambda_3}^\dagger = 1 - c_{\lambda_3}^\dagger c_{\lambda_3}$ - the second term vanishes

Doing the same with $c_{\lambda_1}^\dagger c_{\lambda_2}^\dagger$ 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!

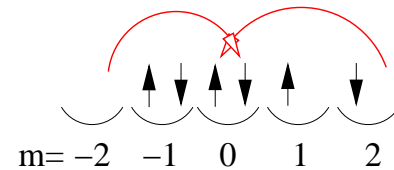
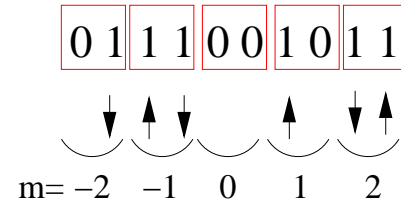
Solution of the Coulomb problem by exact diagonalization

Number of basis states with n electrons

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

These can be coded as integers

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



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

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

Resulting eigenenergies for d^8 and d^7

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

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 $\langle \mathbf{S}^2 \rangle = S(S + 1)$ and $\langle \mathbf{L}^2 \rangle = L(L + 1)$
- 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 Ni²⁺

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	³ F	0.0000
1.8420	0	2	5	¹ D	1.7396
1.9200	1	1	9	³ P	2.0829
2.7380	0	4	9	¹ G	2.8649
13.2440	0	0	1	¹ S	6.5129

→ Relative error ≤ 10% (except for ¹S)

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

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

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

Diagonal matrix elements of the Coulomb interaction

We want to calculate the diagonal matrix element $\langle 0 | c_{\nu_2} c_{\nu_1} H_1 c_{\nu_1}^\dagger c_{\nu_2}^\dagger | 0 \rangle$ with the two-electron state $c_{\nu_1}^\dagger c_{\nu_2}^\dagger | 0 \rangle$

We rewrite the Coulomb interaction

$$\begin{aligned}
 H_1 &= \frac{1}{2} \sum_{i,j,k,l} V(\nu_i, \nu_j, \nu_k, \nu_l) c_{\nu_i}^\dagger c_{\nu_j}^\dagger c_{\nu_k} c_{\nu_l} \\
 &= \frac{1}{2} \left(V(\nu_1, \nu_2, \nu_1, \nu_2) c_{\nu_1}^\dagger c_{\nu_2}^\dagger c_{\nu_1} c_{\nu_2} + V(\nu_1, \nu_2, \nu_2, \nu_1) c_{\nu_1}^\dagger c_{\nu_2}^\dagger c_{\nu_2} c_{\nu_1} \right. \\
 &\quad \left. + V(\nu_2, \nu_1, \nu_1, \nu_2) c_{\nu_2}^\dagger c_{\nu_1}^\dagger c_{\nu_1} c_{\nu_2} + V(\nu_2, \nu_1, \nu_2, \nu_1) c_{\nu_2}^\dagger c_{\nu_1}^\dagger c_{\nu_2} c_{\nu_1} \right) + \dots \\
 &= \left(V(\nu_1, \nu_2, \nu_2, \nu_1) - V(\nu_1, \nu_2, \nu_1, \nu_2) \right) c_{\nu_1}^\dagger c_{\nu_2}^\dagger c_{\nu_2} c_{\nu_1} + \dots
 \end{aligned}$$

Here we have used $V(\nu_1, \nu_2, \nu_3, \nu_4) = V(\nu_2, \nu_1, \nu_4, \nu_3)$ which follows from the definition

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

by exchanging $x \leftrightarrow x'$

It follows that $\langle 0 | c_{\nu_2} c_{\nu_1} H_1 c_{\nu_1}^\dagger c_{\nu_2}^\dagger | 0 \rangle = V(\nu_1, \nu_2, \nu_2, \nu_1) - V(\nu_1, \nu_2, \nu_1, \nu_2)$.

We had $\langle 0 | c_{\nu_2} c_{\nu_1} H_1 c_{\nu_1}^\dagger c_{\nu_2}^\dagger | 0 \rangle = V(\nu_1, \nu_2, \nu_2, \nu_1) - V(\nu_1, \nu_2, \nu_1, \nu_2)$ with

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

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 introduce some abbreviations

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

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

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

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

Then we obtain the diagonal matrix element

$$\langle 0 | c_{\nu_2} c_{\nu_1} H_1 c_{\nu_1}^\dagger c_{\nu_2}^\dagger | 0 \rangle = \sum_k (a^k(l_1 m_1, l_2, m_2) F^k - \delta_{\sigma_1 \sigma_2} b^k(l_1 m_1, l_2, m_2) G^k)$$

We had $\langle 0|c_{\nu_2}c_{\nu_1} H_1 c_{\nu_1}^\dagger c_{\nu_2}^\dagger|0\rangle = V(\nu_1, \nu_2, \nu_2, \nu_1) - V(\nu_1, \nu_2, \nu_1, \nu_2)$ with

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

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 introduce some abbreviations

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

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

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

Then we obtain the diagonal matrix element

$$\langle 0|c_{\nu_2}c_{\nu_1} H_1 c_{\nu_1}^\dagger c_{\nu_2}^\dagger|0\rangle = \sum_k (a^k(l_1 m_1, l_2, m_2) F^k - \delta_{\sigma_1 \sigma_2} b^k(l_1 m_1, l_2, m_2) G^k)$$

We had $\langle 0 | c_{\nu_2} c_{\nu_1} H_1 c_{\nu_1}^\dagger c_{\nu_2}^\dagger | 0 \rangle = V(\nu_1, \nu_2, \nu_2, \nu_1) - V(\nu_1, \nu_2, \nu_1, \nu_2)$ with

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

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 introduce some abbreviations

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

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

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

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

Then we obtain the diagonal matrix element

$$\langle 0 | c_{\nu_2} c_{\nu_1} H_1 c_{\nu_1}^\dagger c_{\nu_2}^\dagger | 0 \rangle = \sum_k (a^k(l_1 m_1, l_2, m_2) F^k - \delta_{\sigma_1 \sigma_2} b^k(l_1 m_1, l_2, m_2) G^k)$$

For a state with more than 2 electrons we obtain

$$\langle 0 | c_{\nu_n} \dots c_{\nu_2} c_{\nu_1} H_1 c_{\nu_1}^\dagger c_{\nu_2}^\dagger \dots c_{\nu_n}^\dagger | 0 \rangle = \sum_{i < j} \sum_k (a^k(l_i m_i, l_j, m_j) F^k - \delta_{\sigma_i \sigma_j} b^k(l_i m_i, l_j, m_j) G^k)$$

i.e. a sum over pairs of electrons

The a^k and b^k are tabulated for example in Slater's textbook

For scattering within a single shell (where all n_i and all l_i are equal) we moreover have $G^k = F^k$

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

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

We write operators as $c_{l, m, \sigma}^\dagger$ - 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: $c_{1, 0, \uparrow}^\dagger c_{1, 1, \uparrow}^\dagger |0\rangle$ - this state belongs to 3P

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

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

We write operators as $c_{l,m,\sigma}^\dagger$ - 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: $c_{1,0,\uparrow}^\dagger c_{1,1,\uparrow}^\dagger |0\rangle$ - this state belongs to 3P

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

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

$$\begin{aligned} 1 F^0 - \frac{2}{25} F^2 - \frac{3}{25} F^2 &= F^0 - \frac{5}{25} F^2 \\ \rightarrow E[{}^3P] &= F^0 - \frac{5}{25} F^2 \end{aligned}$$

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

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

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

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

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

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

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

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

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

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

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

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

→ only one state is missing which must form a multiplet of its own and can only be 1S

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

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

There are three states in this sector:

$$|1\rangle = c_{1,0,\downarrow}^\dagger c_{1,0,\uparrow}^\dagger |0\rangle,$$

$$|2\rangle = c_{1,-1,\uparrow}^\dagger c_{1,1,\downarrow}^\dagger |0\rangle,$$

$$|3\rangle = c_{1,-1,\downarrow}^\dagger c_{1,1,\uparrow}^\dagger |0\rangle$$

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

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

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

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

The diagonal sum-rule then tells us

$$\begin{aligned}
 E(^3P) + E(^1D) + E(^1S) &= \sum_{i=1}^3 \langle i | H_1 | i \rangle \\
 F^0 - \frac{5}{25} F^2 + F^0 + \frac{1}{25} F^2 + E(^1S) &= \sum_{k \in \{0,2\}} (a^k(1, 0; 1, 0) + 2 a^k(1, -1; 1, 1)) F^k \\
 E(^1S) + 2 F^0 - \frac{4}{25} F^2 &= 3 F^0 + \left(\frac{4}{25} + 2\frac{1}{25}\right) F^2 \\
 \rightarrow E(^1S) &= F^0 + \frac{10}{25} F^2
 \end{aligned}$$

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

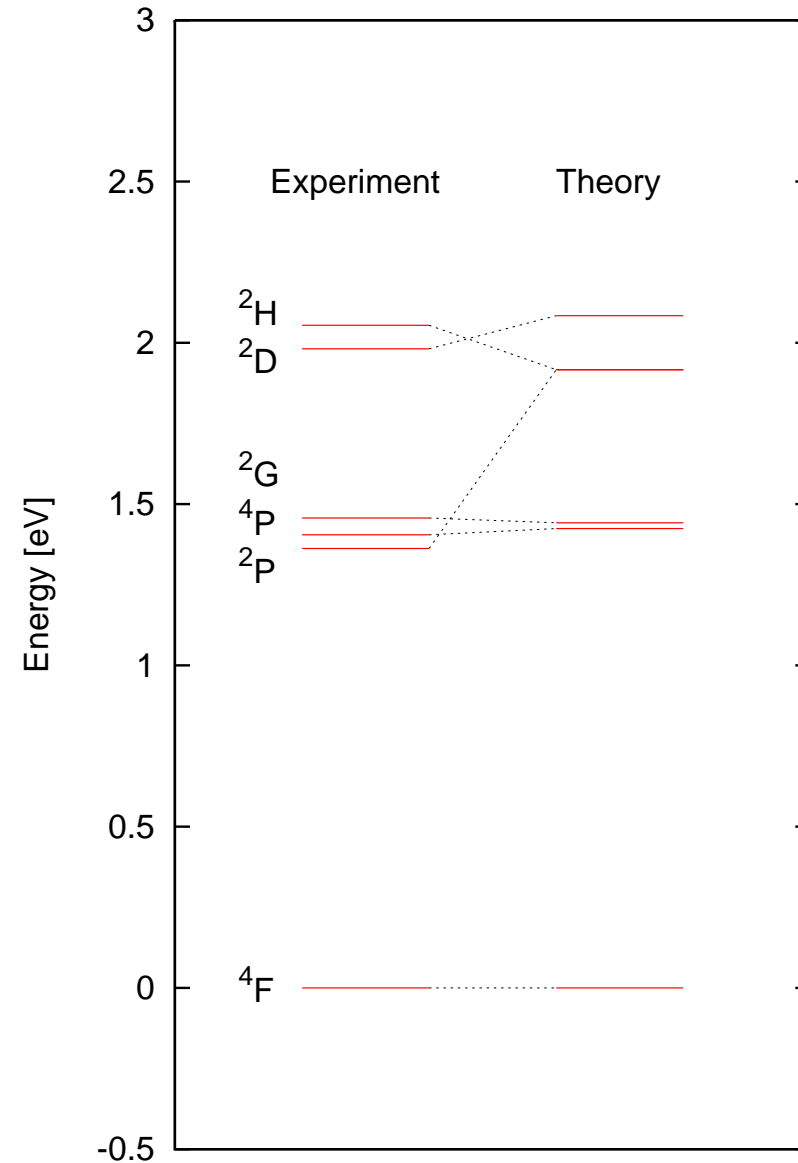
$$r = \frac{E(^1S) - E(^1D)}{E(^1D) - E(^3P)} = \frac{3}{2}$$

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		

Example for a d-shell: V^{2+} corresponding to d^3

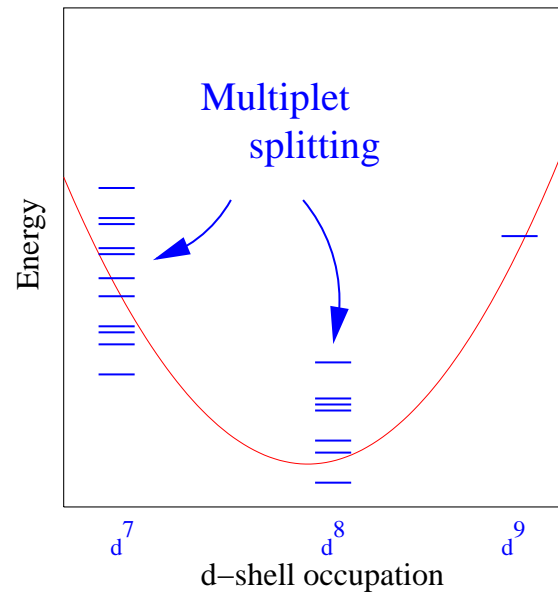
The diagonal sum-rule gives

$$\begin{array}{l|l}
 {}^4F & 3F^0 - \frac{135}{441} F^2 - \frac{72}{441} F^4 \\
 {}^4P & 3F^0 \qquad \qquad \qquad - \frac{147}{441} F^4 \\
 {}^2G & 3F^0 - \frac{99}{441} F^2 - \frac{13}{441} F^4 \\
 {}^2H & 3F^0 - \frac{54}{441} F^2 - \frac{12}{441} F^4 \\
 {}^2P & 3F^0 - \frac{54}{441} F^2 - \frac{12}{441} F^4 \\
 {}^2F & 3F^0 + \frac{81}{441} F^2 - \frac{97}{441} F^4
 \end{array}$$



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 coefficients (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



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

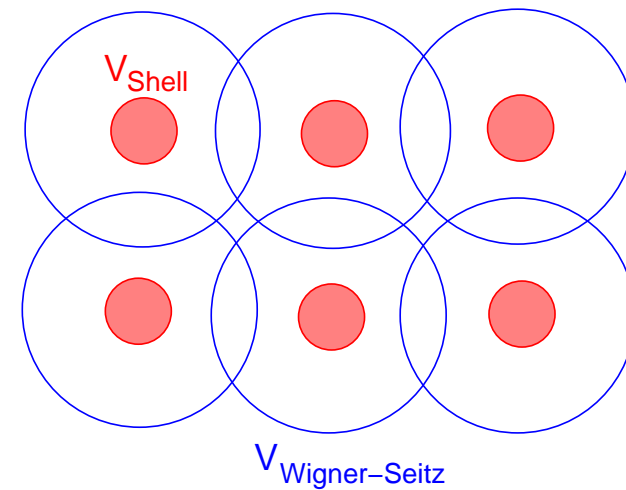
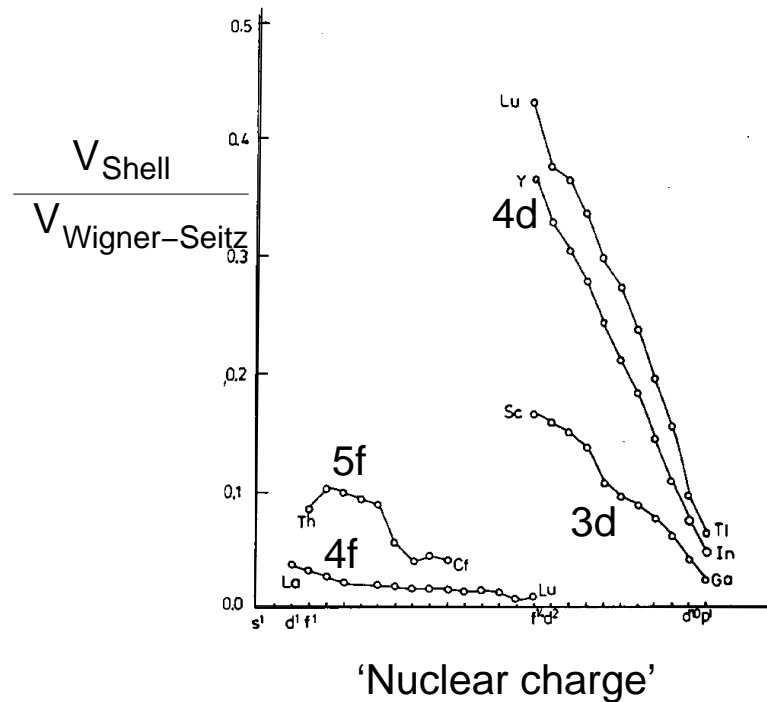
III: The transition metal ion in a solid

So far we considered an atom/ion in vacuum

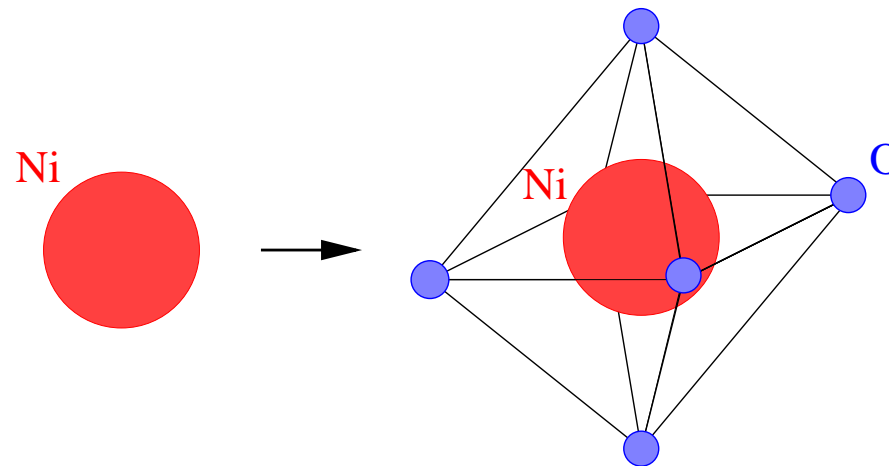
In solid state physics we are interested in an atom/ion in a solid

Will the results for the free atom retain any significance in this case?

Probably yes....



Effect of the immediate environment in the solid: adding ligands



- To study the effect of embedding a TM ion in a solid we study a **cluster** comprising a single TM ion and its nearest neighbors in the solid, the so-called **ligands**. Adding ligands has a twofold effect:
- Since the ligands usually are charged (e.g. O^{2-}) they produce a static electric field - the **crystalline electric field (CEF)**
- This lowers the symmetry \rightarrow **lifting of degeneracies**
- In addition there may be **charge transfer** e.g. in NiO: $Ni\ 3d^8\ O\ 2p^6 \rightarrow Ni\ 3d^9\ O\ 2p^5$
- This is strongly opposed by the Coulomb interaction in the 3d-shell!

The Crystalline Electric Field

- We represent the ligands as n point charges of strength $Z_i e$ at the positions \mathbf{R}_i
- We denote the electrostatic field caused by these charges by $V_{CEF}(\mathbf{r})$
- The corresponding Hamiltonian in second quantization is

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

$$V_{CEF}(\nu_1, \nu_2) = \int dx \psi_{\nu_1}^*(x) V_{CEF}(\mathbf{r}) \psi_{\nu_2}(x)$$

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

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

The Crystalline Electric Field

- We represent the ligands as n point charges of strength $Z_i e$ at the positions \mathbf{R}_i
- We denote the electrostatic field caused by these charges by $V_{CEF}(\mathbf{r})$
- Using again the multipole expansion of electrostatics we find

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

With R_{av} and Z_{av} : average distance and charge of the ligands

$\gamma_{k,m}$ depends on the position and strength of the point charges

We now calculate the matrix element

$$V_{CEF}(\nu_1, \nu_2) = \int dx \psi_{\nu_1}^*(x) V_{CEF}(\mathbf{r}) \psi_{\nu_2}(x)$$

$$\psi_{\nu_1}^*(x) = R_{n_1, l_1}(r) Y_{l_1, m_1}^*(\Theta, \phi) \delta_{\sigma, \sigma_1}$$

$$V_{CEF}(\mathbf{r}) = -\frac{Z_{av} e^2}{R_{av}} \sum_{k=0}^{\infty} \sum_{m=-k}^k \gamma_{k, m} \left(\frac{r}{R_{av}} \right)^k \sqrt{\frac{4\pi}{2k+1}} Y_{k, m}(\Theta, \phi)$$

$$\psi_{\nu_2}(x) = R_{n_2, l_2}(r) Y_{l_2, m_2}(\Theta, \phi) \delta_{\sigma, \sigma_2}$$

We now calculate the matrix element

$$V_{CEF}(\nu_1, \nu_2) = \int dx \psi_{\nu_1}^*(x) V_{CEF}(\mathbf{r}) \psi_{\nu_2}(x)$$

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$$\psi_{\nu_2}(x) = R_{n_2, l_2}(r) Y_{l_2, m_2}(\Theta, \phi) \delta_{\sigma, \sigma_2}$$

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

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

For a d-shell we thus find

$$V_{CEF}(\nu_1, \nu_2) = \delta_{\sigma_1, \sigma_2} \sum_{k \in \{0, 2, 4\}} \gamma_{k, m_1 - m_2} I_k c^k(l_1, m_1; l_2, m_2)$$

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

Reminder:

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

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

$$\begin{aligned} \gamma_{4, 4} &= \sqrt{\frac{35}{8}} \\ \gamma_{4, -4} &= \sqrt{\frac{35}{8}} \\ \gamma_{4, 0} &= \sqrt{\frac{49}{4}} \end{aligned}$$

Using the tabulated values of the $c^4(l, m; l' m')$ we thus find

$$V_{CEF}(\nu_1, \nu_2) = \frac{I_4}{6} \begin{pmatrix} 1 & 0 & 0 & 0 & 5 \\ 0 & -4 & 0 & 0 & 0 \\ 0 & 0 & 6 & 0 & 0 \\ 0 & 0 & 0 & -4 & 0 \\ 5 & 0 & 0 & 0 & 1 \end{pmatrix} .$$

Using the tabulated values of the $c^4(l, m; l' m')$ we thus find

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Eigenvalues:

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

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Eigenvalues:

$$I_4, -\frac{2}{3}I_4, -\frac{2}{3}I_4, (1 \pm 5)\frac{I_4}{6}$$

Using the tabulated values of the $c^4(l, m; l' m')$ we thus find

$$V_{CEF}(\nu_1, \nu_2) = \frac{I_4}{6} \begin{pmatrix} 1 & 0 & 0 & 0 & 5 \\ 0 & -4 & 0 & 0 & 0 \\ 0 & 0 & 6 & 0 & 0 \\ 0 & 0 & 0 & -4 & 0 \\ 5 & 0 & 0 & 0 & 1 \end{pmatrix}.$$

Eigenvalues:

$$I_4, -\frac{2}{3}I_4, -\frac{2}{3}I_4, (1 \pm 5)\frac{I_4}{6}$$

$$I_4 \text{ (2 times)}, -\frac{2}{3}I_4 \text{ (3 times)}$$

For negatively charged ligands (e.g. O^{2-}) we have $I_4 > 0$

The difference between the eigenvalues is $\frac{5}{3}I_4$ - this is often called $10Dq \rightarrow$ for the octahedron $Dq = \frac{I_4}{6}$

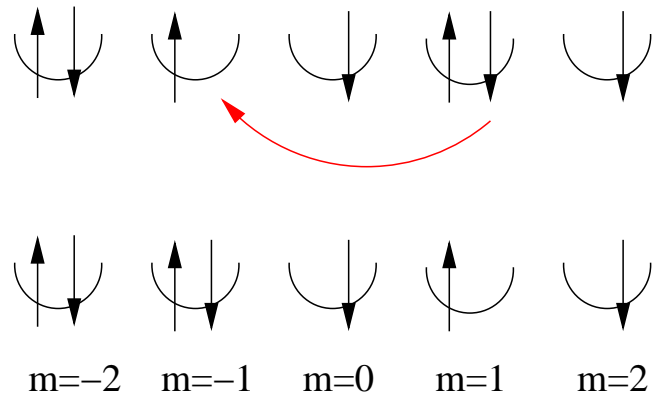
The eigenfunctions for eigenvalue $I_4 = 6Dq$ are the real-valued spherical harmonics $d_{x^2-y^2}$ and $d_{3z^2-r^2}$

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

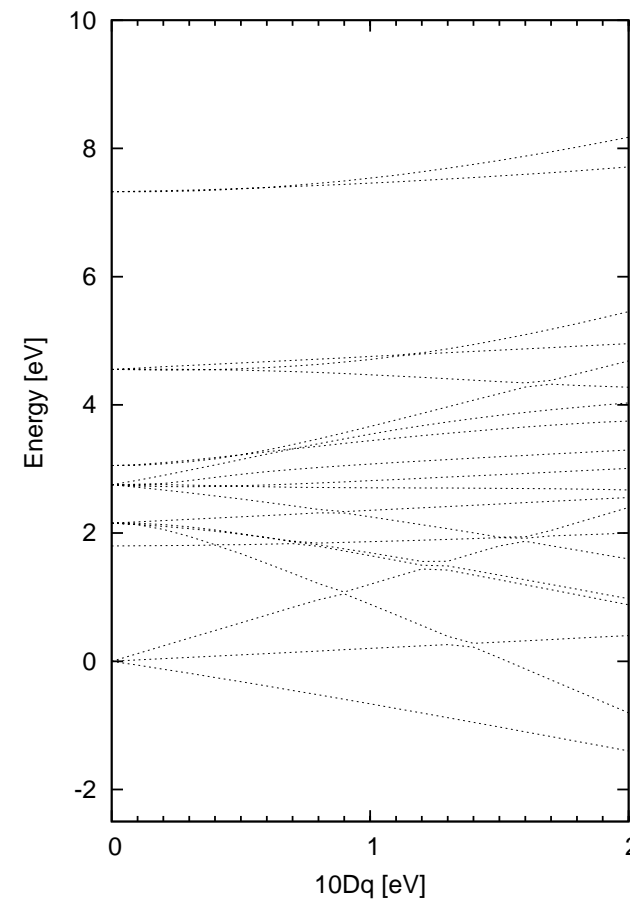
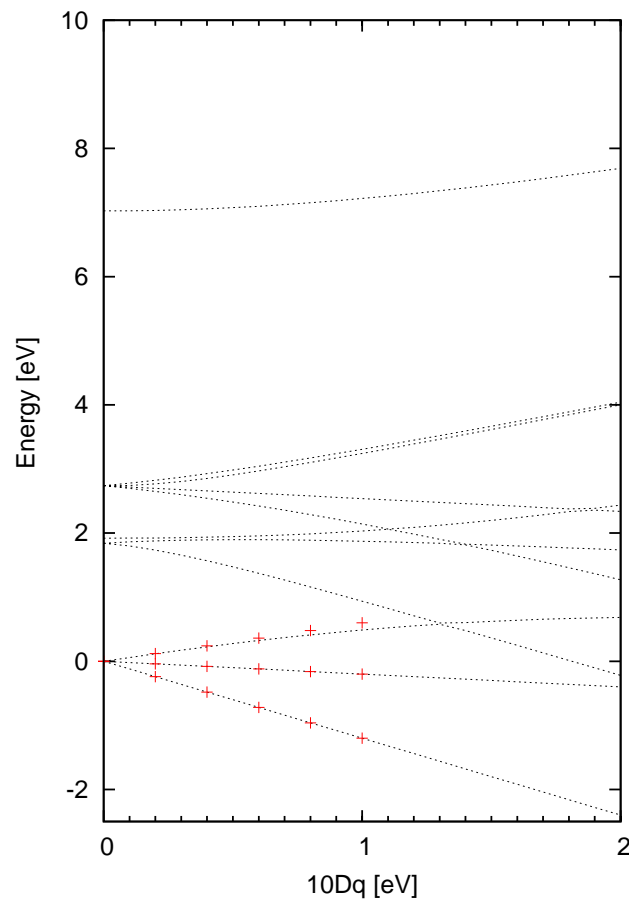
The Hamiltonian

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

can now easily be included into the exact diagonalization program (mind the Fermi sign!)

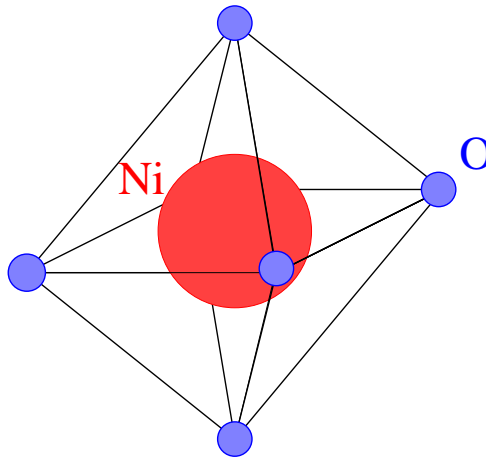


As an example we show the development of the eigenvalue spectrum as the strength of the CEF increases for d^8 and d^7 - a so-called **Tanabe-Sugano-diagram**



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



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

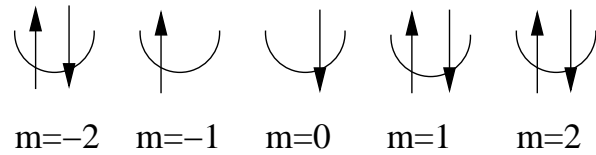
$$H = \sum_{i,j} \left(t_{\nu_i, \mu_j} c_{\nu_i}^{\dagger} l_{\mu_j} + H.c. \right) + \sum_j \epsilon_{\mu_j} l_{\mu_j}^{\dagger} l_{\mu_j} + \sum_i \epsilon_{\nu_i} c_{\nu_i}^{\dagger} c_{\nu_i}.$$

- 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, see lectures in this school)

Reminder:

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

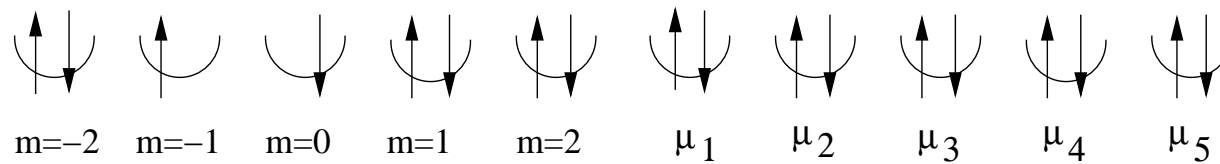
In principle this is easily implemented in the exact diagonalization program (mind the Fermi sign!)



Reminder:

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

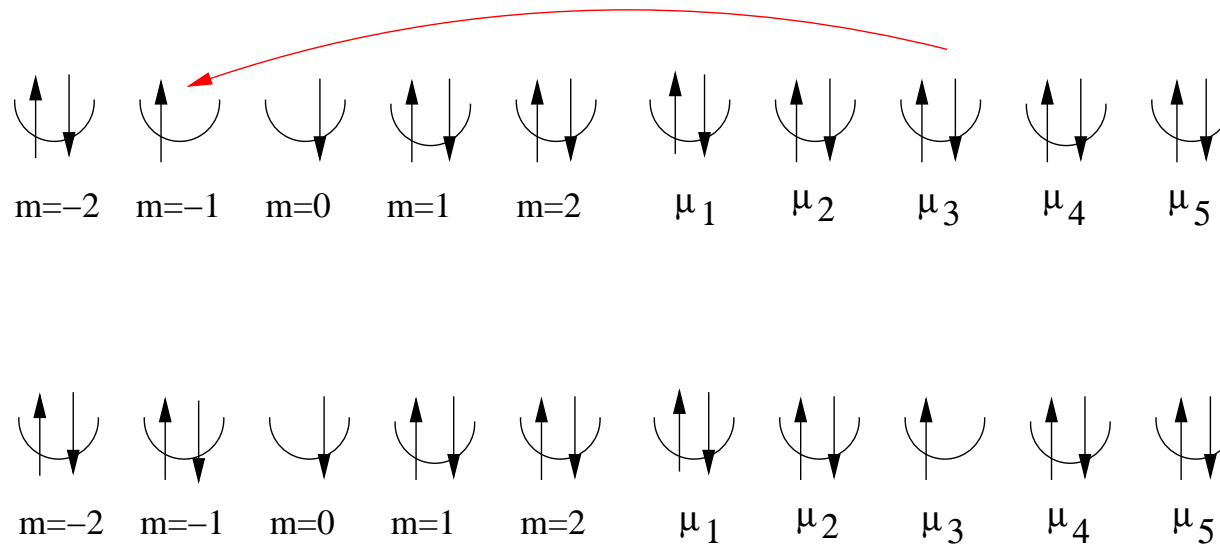
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Reminder:

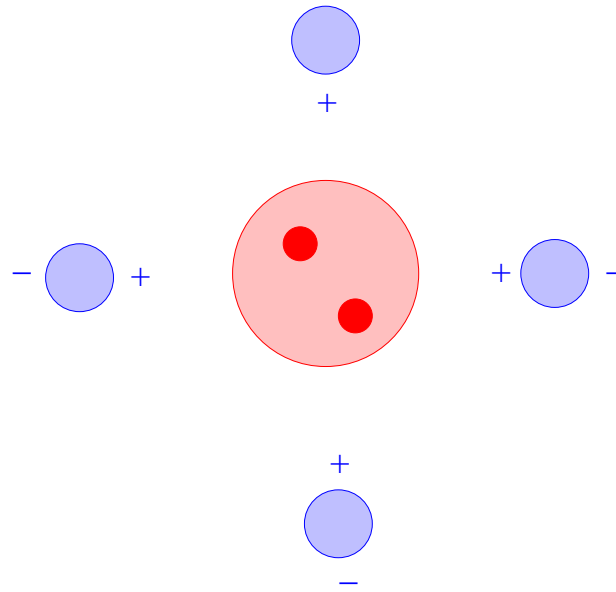
$$H = \sum_{i,j} \left(t_{\nu_i, \mu_j} c_{\nu_i}^\dagger l_{\mu_j} + H.c. \right) + \sum_j \epsilon_{\mu_j} l_{\mu_j}^\dagger l_{\mu_j} + \sum_i \epsilon_{\nu_i} c_{\nu_i}^\dagger c_{\nu_i}.$$

In principle this is easily implemented in the exact diagonalization program (mind the Fermi sign!)



For exact diagonalization addition of ligands brings about a problem: they increase the number of basis states
 The problem stays manageable for the case of an ideal octahedron because symmetry allows to reduce the number of relevant ligand orbitals

Another solid state effect: Screening of Coulomb parameters



- Electrons in the TM 3d-shell can induce polarization charges on the surrounding ions
- This will lead to a modification of their Coulomb interaction
- Empirically, for F^2 and F^4 (quadrupole and hexadecupole interaction) this can be taken into account by a reduction by a factor 0.8 as compared to the Hartree-Fock value for free ions
- For F^0 (monopole interaction or Hubbard U) this is much more complicated - see other lectures in this school

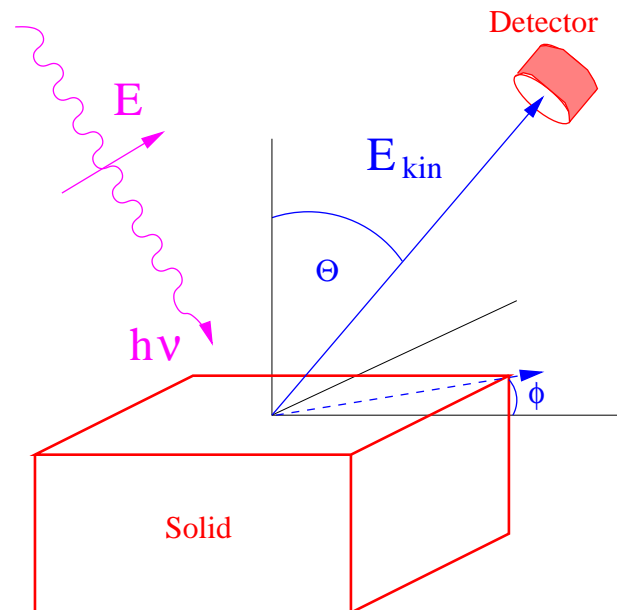
Summary so far

- 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

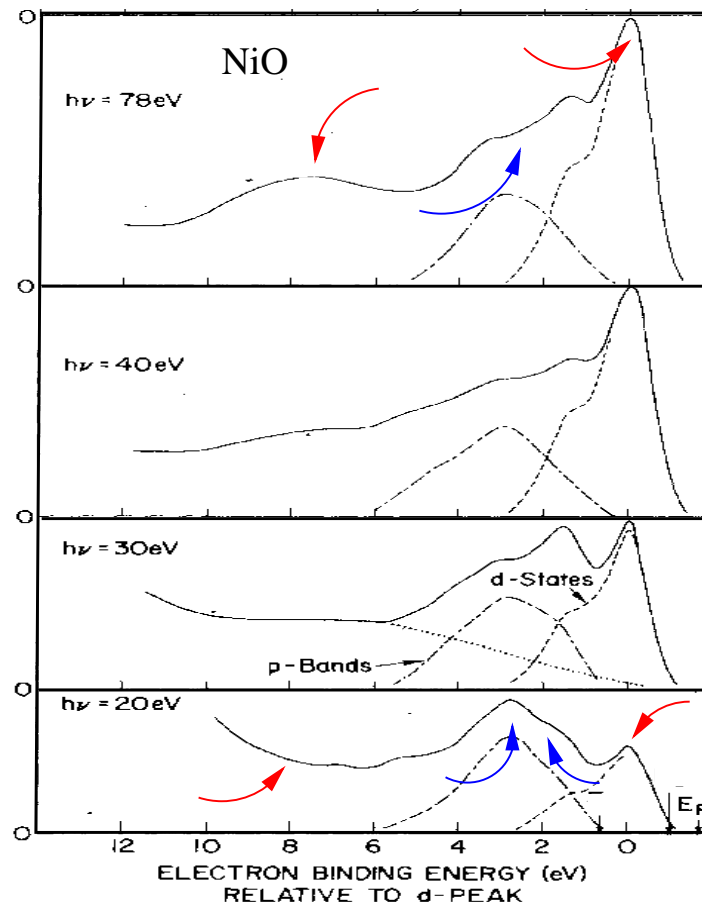
IV: Applications of multiplet theory in spectroscopy

Valence band photoemission

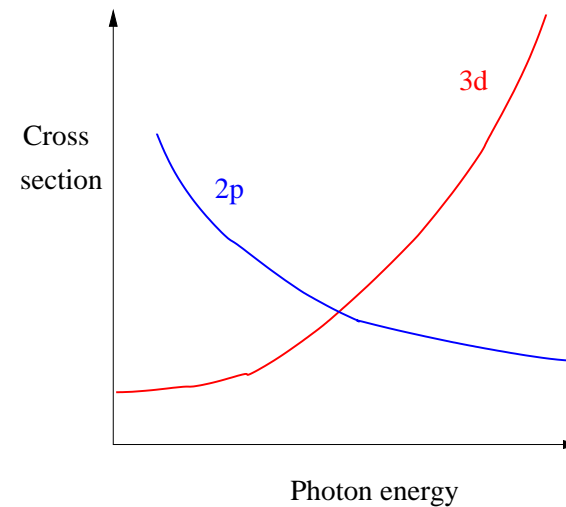
- In this experiment photons impinge onto the sample which then emits photoelectrons - i.e. the familiar **photoelectric effect**
- 'Valence band photoemission' means that the photoelectron is emitted from a state 'near' the Fermi energy
- What is measured is the photoelectron current I as a function 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 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



The mechanism of the smoother variation is the photon energy dependence of the photoionization cross section



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**

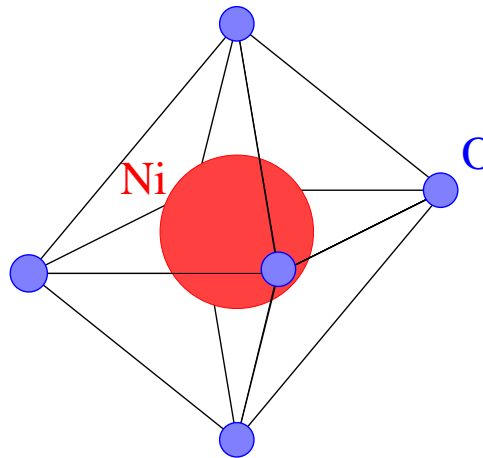
$$\begin{aligned} A(\omega) &= -\frac{1}{\pi Z} \Im \sum_{m=-2}^2 \sum_{\mu} e^{-\beta E_{\mu}} \langle \Psi_{\mu} | c_{3,2,m,\sigma}^{\dagger} \frac{1}{\omega + (H - E_{\mu}) + i0^+} c_{3,2,m,\sigma} | \Psi_{\mu} \rangle \\ &= \frac{1}{Z} \sum_{m=-2}^2 \sum_{\mu,\nu} e^{-\beta E_{\mu}} |\langle \Psi_{\nu}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

- 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 probability 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

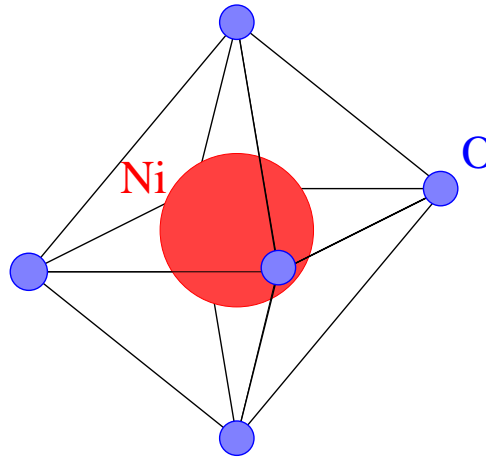
Reminder:

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

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:

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

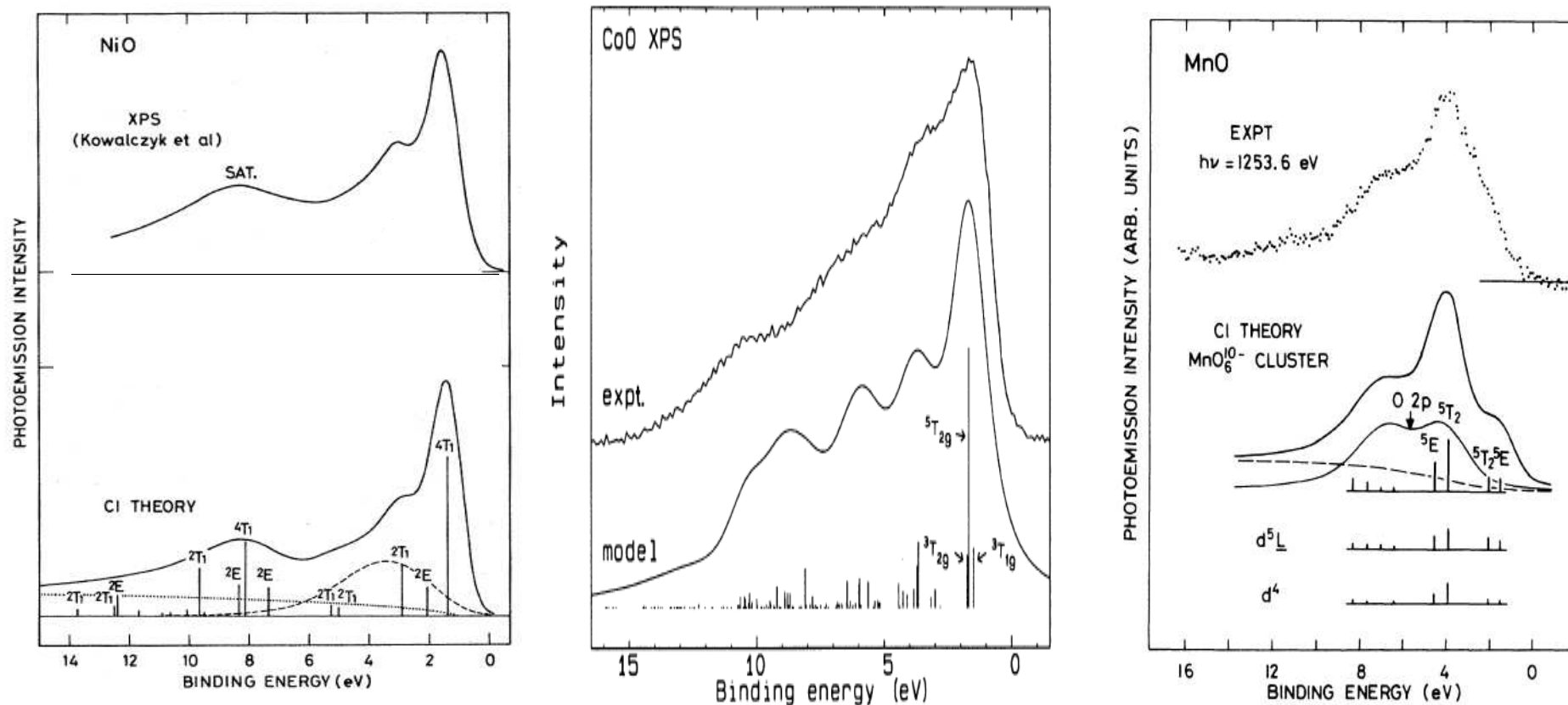
This comprises the Coulomb interaction in the TM 3d-shell, the Crystalline electric field, the charge transfer between TM 3d-shell and ligands, and the orbital energies of transition metal d-orbitals and ligands

Reminder:

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

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

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

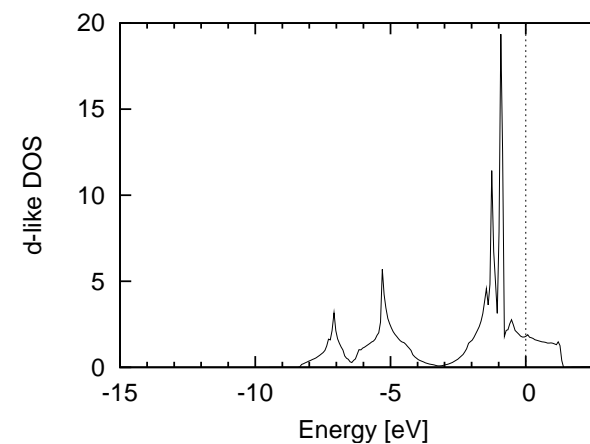
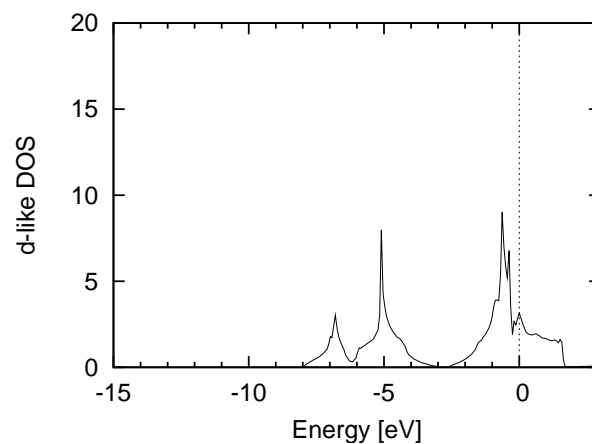
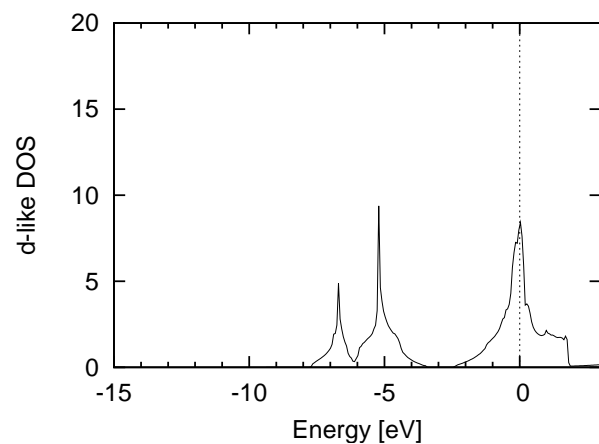
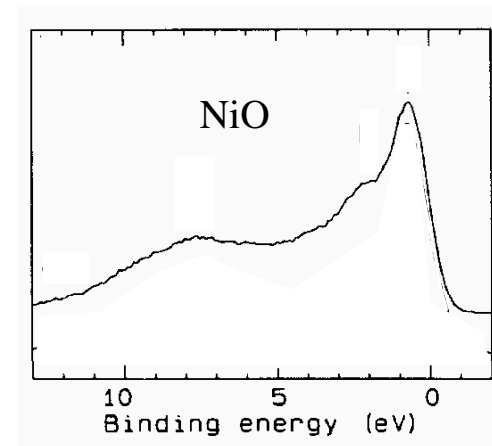
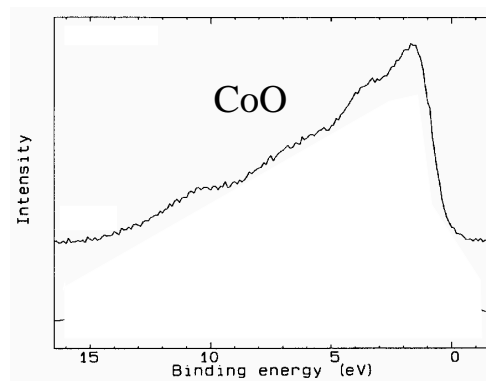
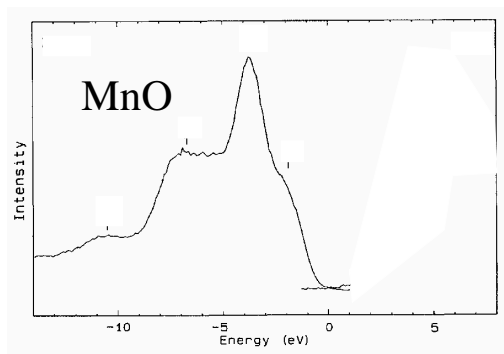


NiO: A. Fujimori and F. Minami, Phys. Rev. B **30**, 957 (1984)

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

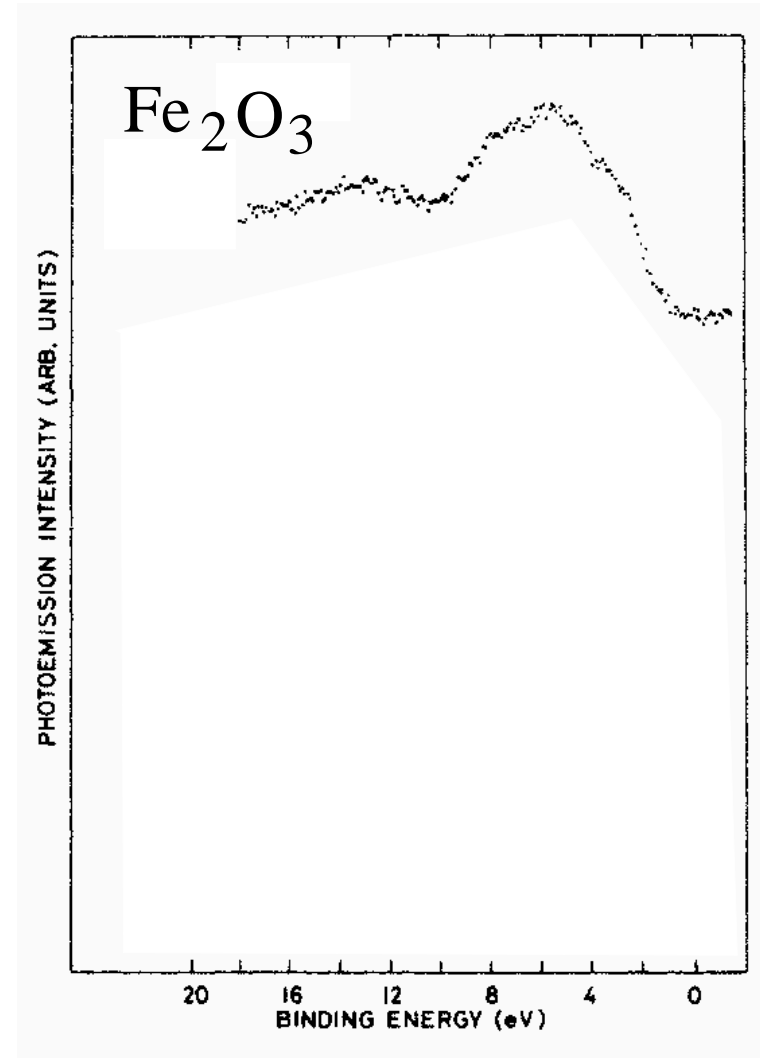
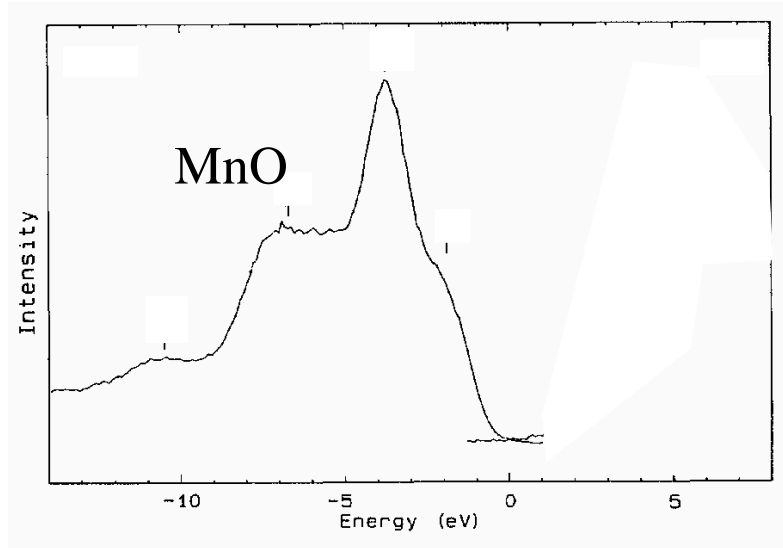
MnO: A. Fujimori *et al.*, Phys. Rev. B **42**, 7580 (1990)

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!

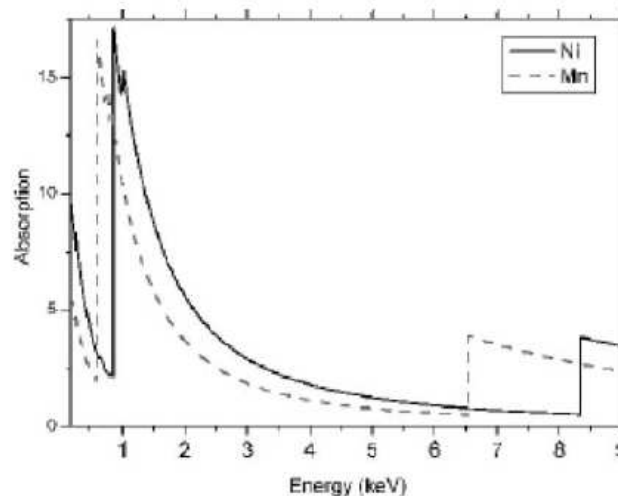
Now the other way round: MnO versus Fe₂O₃ - Mn²⁺ versus Fe³⁺ - d⁵ versus d⁵



Fe₂O₃ 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 **absorption coefficient** is measured versus photon-energy: $\kappa(h\nu)$
- The X-rays are absorbed 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

$$\begin{aligned}\kappa(\omega) &= -\frac{1}{\pi Z} \Im \sum_{\mu} e^{-\beta E_{\mu}} \langle \Psi_{\mu} | D(\mathbf{n}) \frac{1}{\omega - (H - E_{\mu}) + i0^+} D(\mathbf{n}) | \Psi_{\mu} \rangle \\ &= \frac{1}{Z} \sum_{\mu, \nu} e^{-\beta E_{\mu}} |\langle \Psi_{\nu} | D(\mathbf{n}) | \Psi_{\mu} \rangle|^2 \delta(\omega - (E_{\nu} - E_{\mu})).\end{aligned}$$

- 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 probability of $|\Psi_{\mu}\rangle$
- The operator $D(\mathbf{n})$ is the dipole-operator (with \mathbf{n} the photon polarization) - it may be written as

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

- 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

XAS at the transition metal 2p-edge: spin orbit coupling in the 2p-shell

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

$$H_{SOC} = \lambda_{SOC} \mathbf{L} \cdot \mathbf{S}$$

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

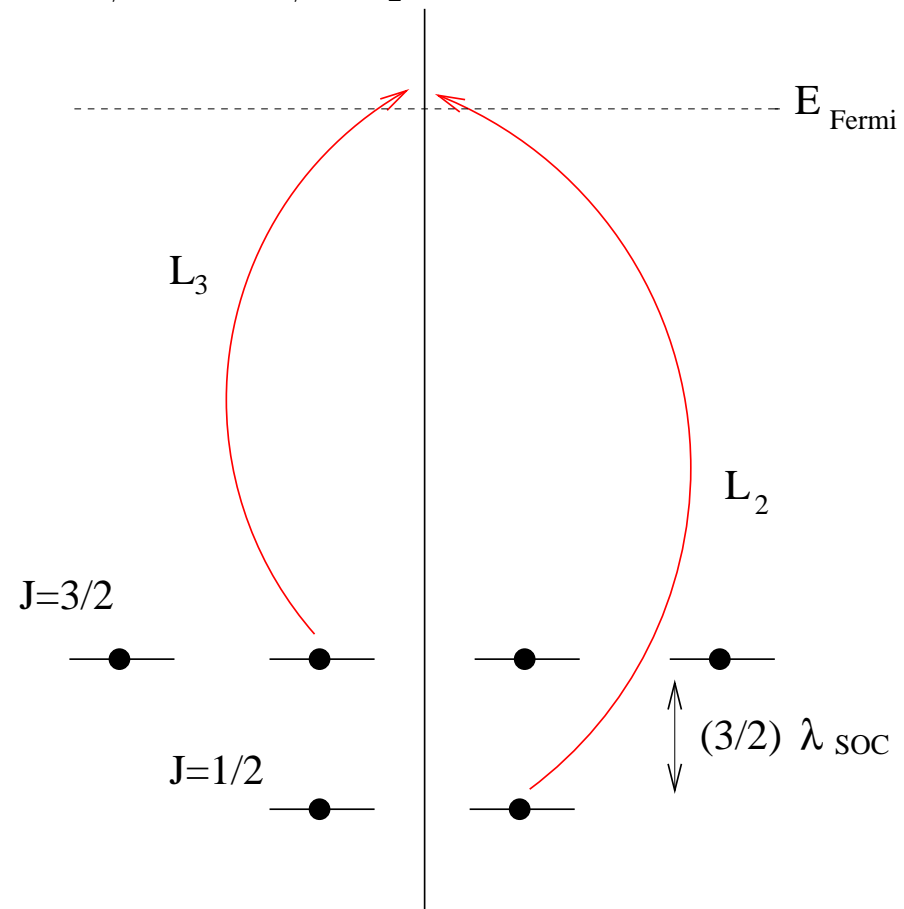
We use $\mathbf{J} = \mathbf{L} + \mathbf{S}$ - square this - and form the expectation value with a state with sharp J , $|J\rangle$:

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

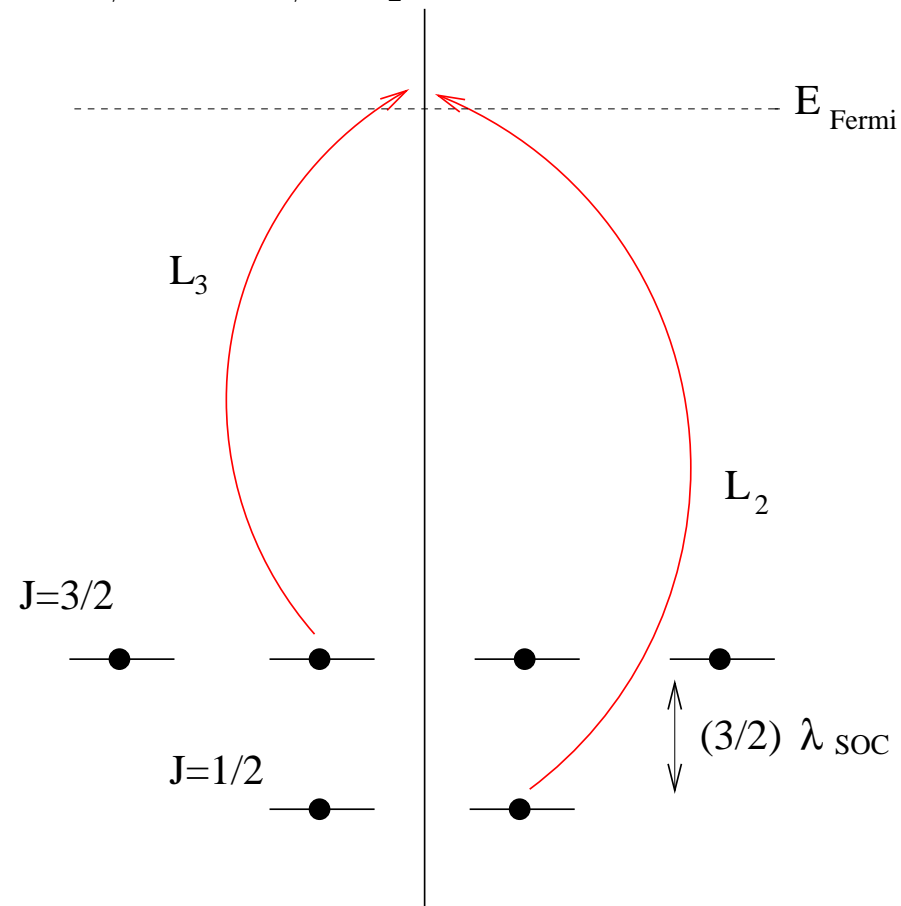
We thus find for the difference in energy between the two SOC-levels

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

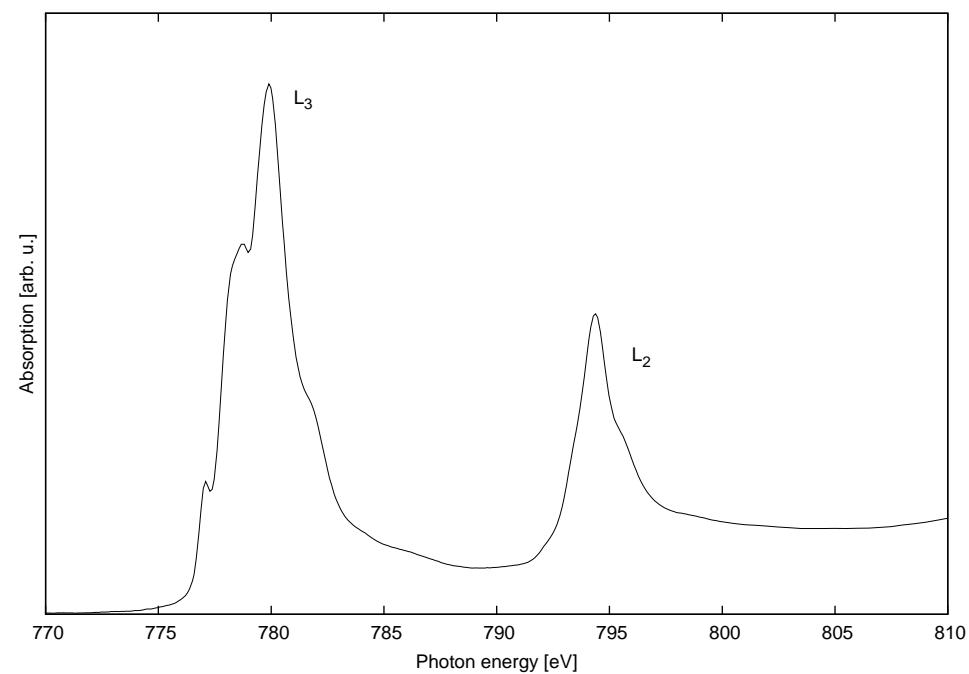
$$E_{J=3/2} - E_{J=1/2} = \frac{3}{2} \lambda_{SOC}$$



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



In experiment: Co-L-edge in $\text{La}_{1.5}\text{Ca}_{0.5}\text{CoO}_4$
 (M. Merz, private communication)



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

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

Then, in 2^{nd} quantization we have

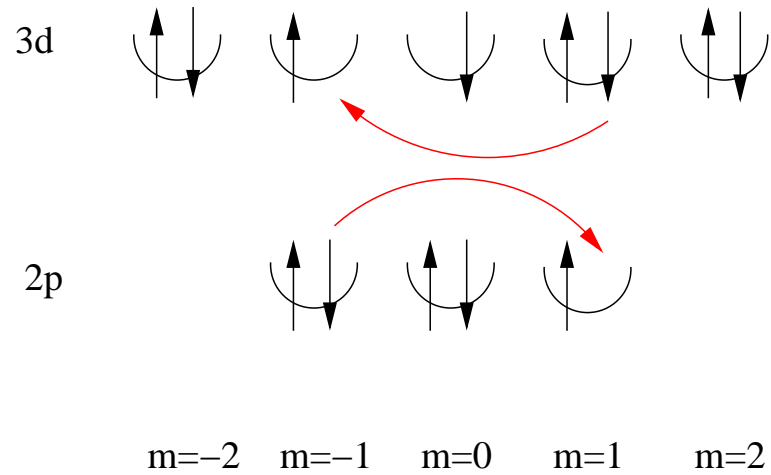
$$H_{SOC}^{\parallel} = \lambda_{SOC} \sum_{m=-l}^l \frac{m}{2} (c_{l,m,\uparrow}^\dagger c_{l,m,\uparrow} - c_{l,m,\downarrow}^\dagger c_{l,m,\downarrow}).$$

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

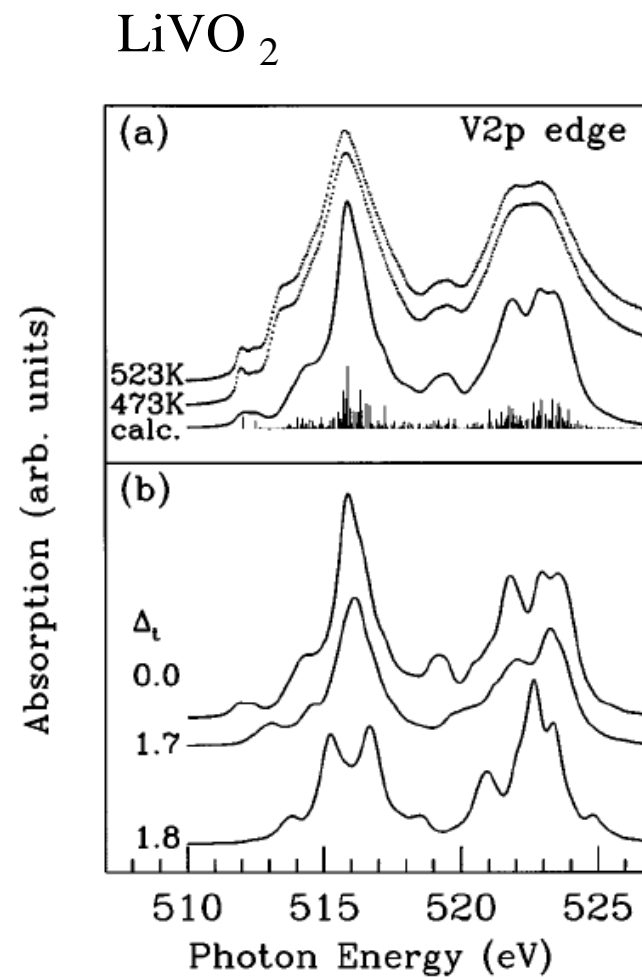
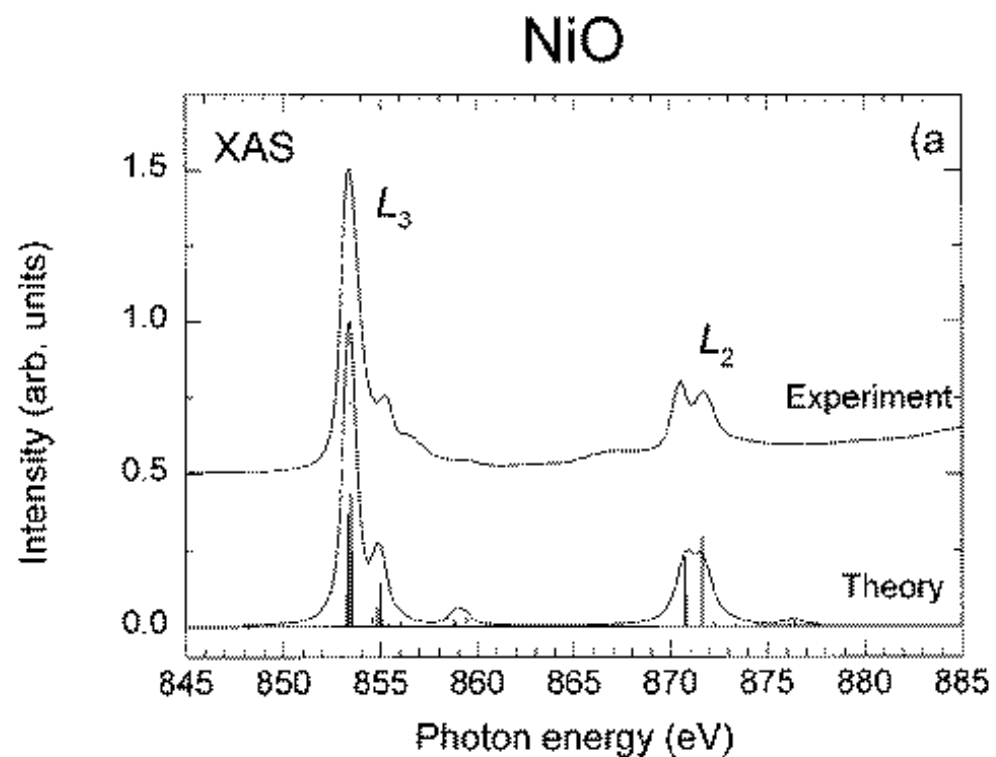
New feature in XAS: Coulomb scattering between 3d-electrons and 2p electrons



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

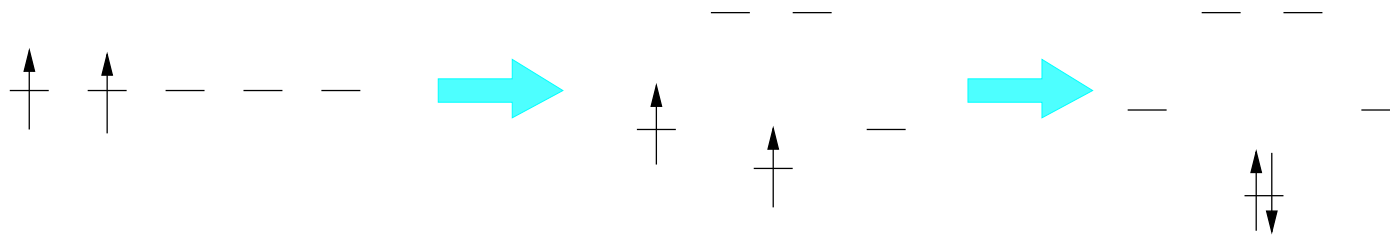


NiO: M. Finazzi *et al.*, Phys. Rev. B **59**, 9933 (1999)

LiVO₂: H. F. Pen *et al.*, Phys. Rev. B **55**, 15500 (1997)

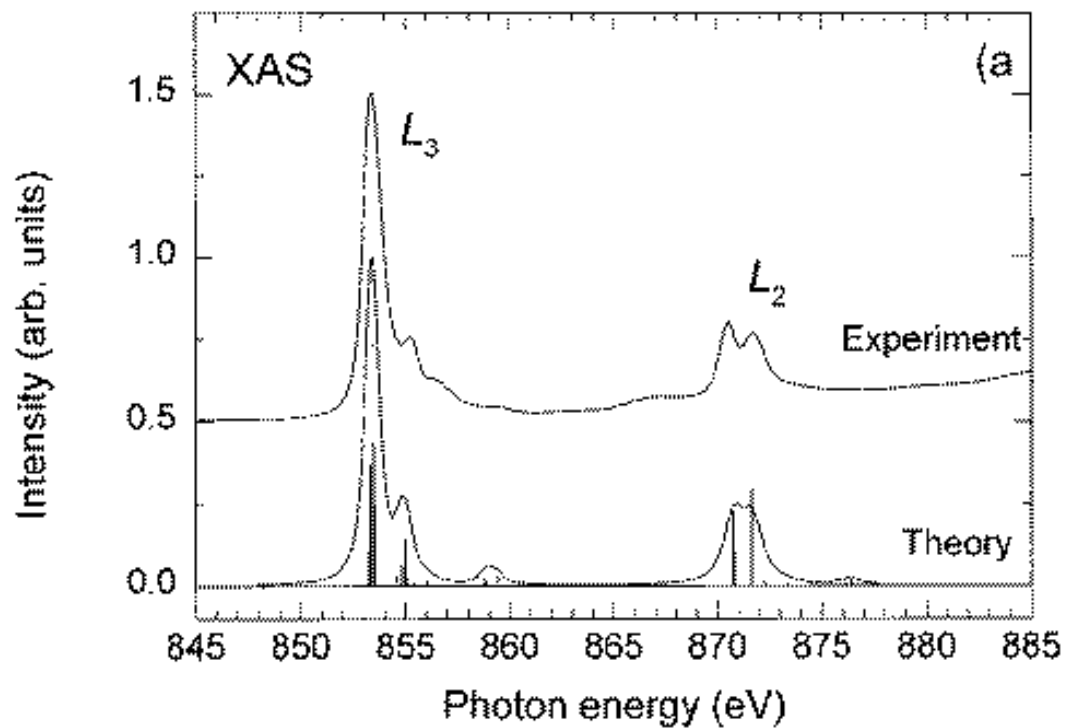
More on LiVO_2

- At 500 K LiVO_2 undergoes a first order phase transition - this is accompanied by trigonal distortion in the low temperature phase
- Above the transition, the magnetic susceptibility has **Curie-Weiss behaviour**, indicating antiferromagnetic coupling between Vanadium 3d-spins
- Below the transition the magnetic susceptibility is practically zero
- A possible mechanism would be a **high spin - low spin transition**
- Vanadium is $\text{V}^{3+} \rightarrow d^2$ in LiVO_2

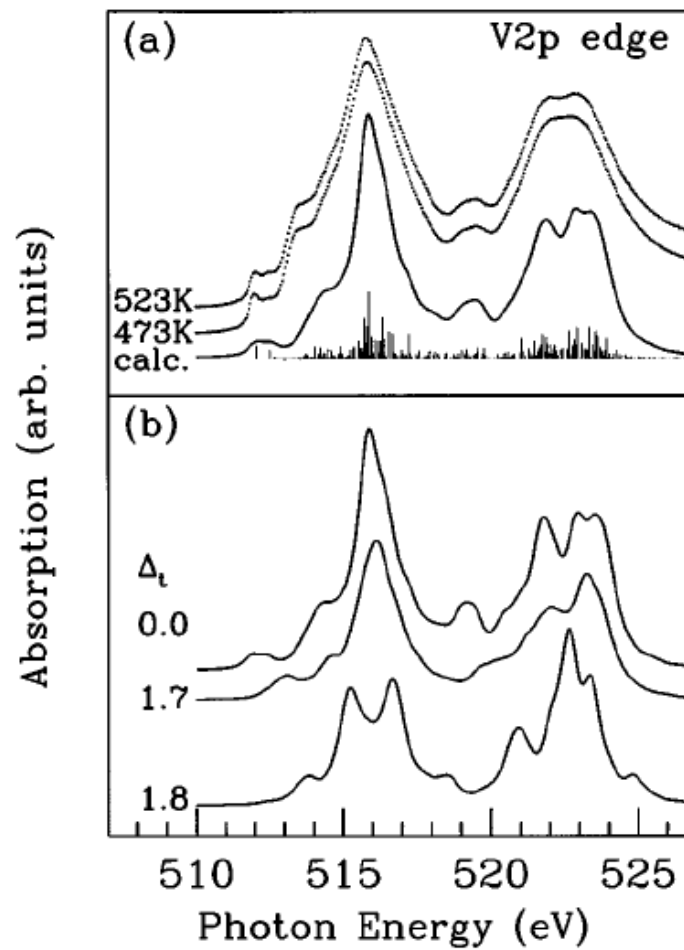


However, the XAS spectra clearly rule this out

NiO



LiVO₂



- 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)

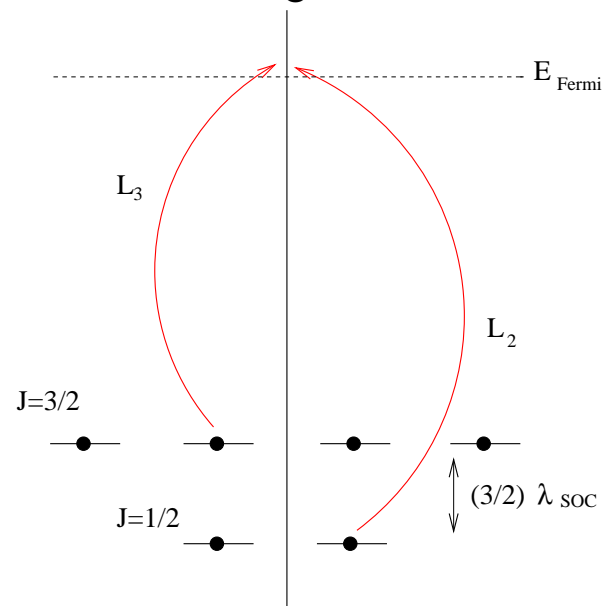
Core-level photoemission

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

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



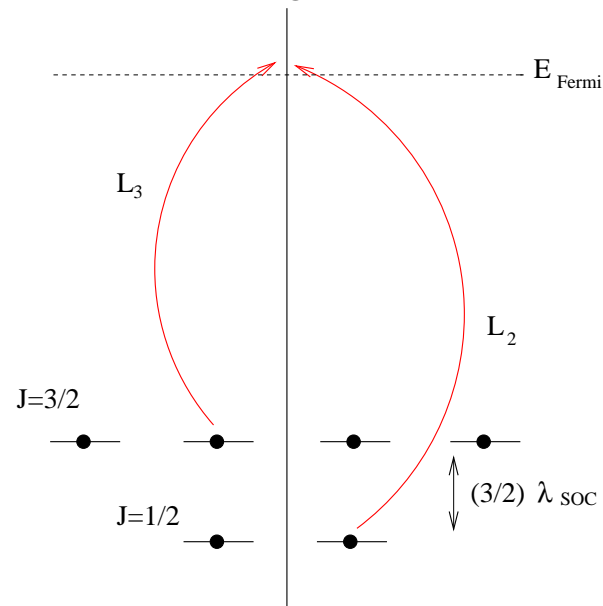
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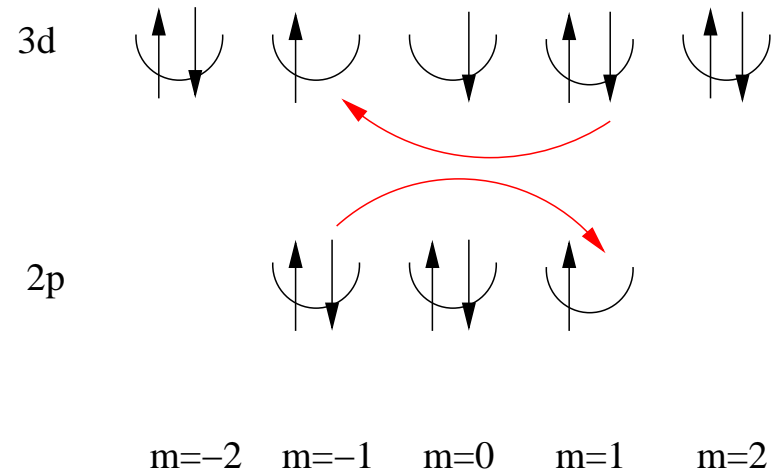
In valence band photoemission the photoelectrons come from states near the Fermi energy

In core level photoemission the photoelectrons come from an inner shell

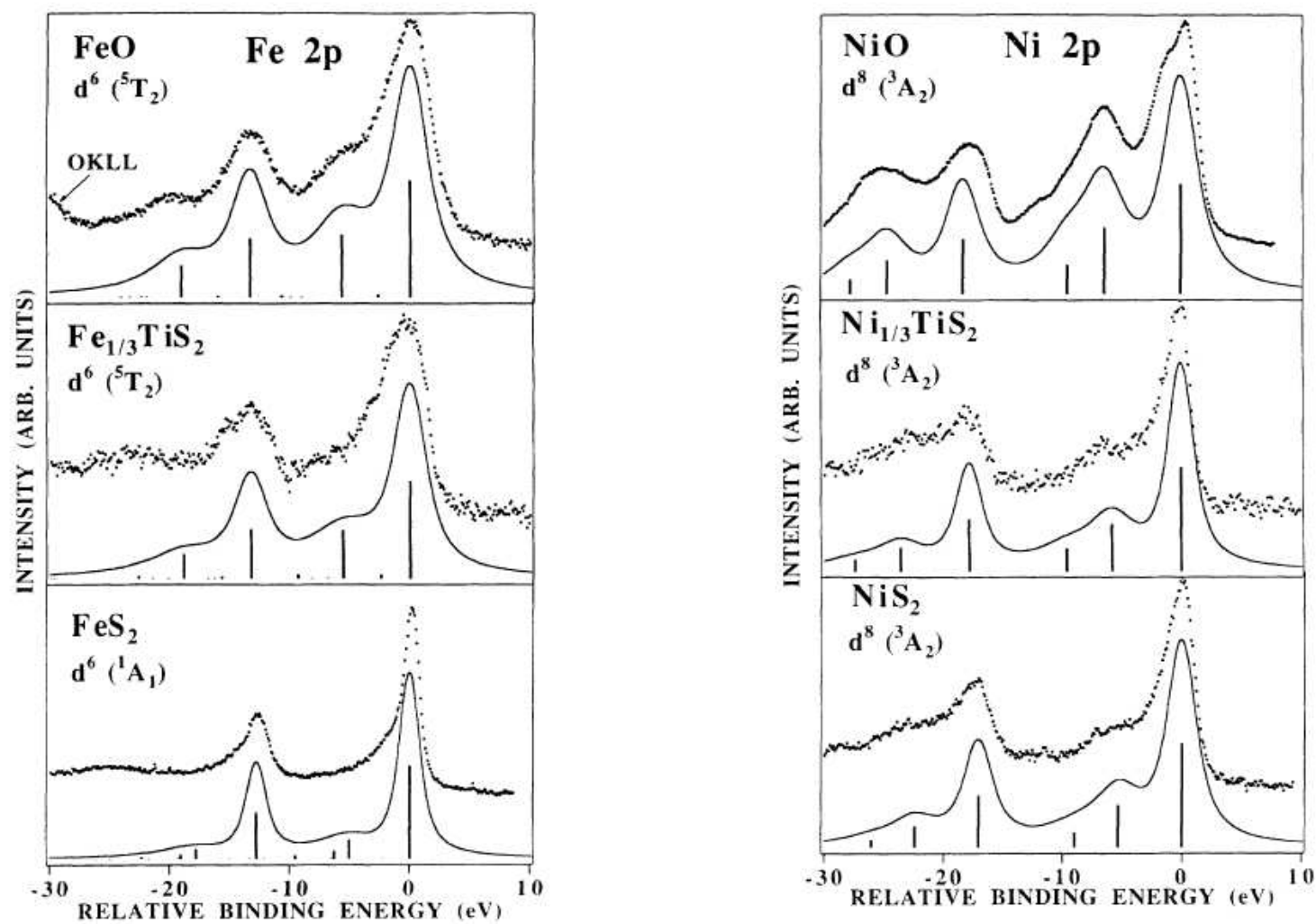
If we remember the discussion on spin-orbit coupling we might expect a core-level photoemission spectrum to be rather boring:



However:



Core-level photoemission: Experiment vs Cluster spectra



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

Summary

- The 3d-shell in iron group elements 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

Simplified Coulomb Hamiltonian

Often one can see in the literature simplified Coulomb Hamiltonians like

$$H_1 = U_0 \left(\sum_{m,m'} \sum_{\sigma,\sigma'} n_{m\sigma} n_{m'\sigma'} - \sum_{m,\sigma} n_{m\sigma} \right) - J_H \sum_{m \neq m'} n_{m,\uparrow} n_{m',\downarrow}$$

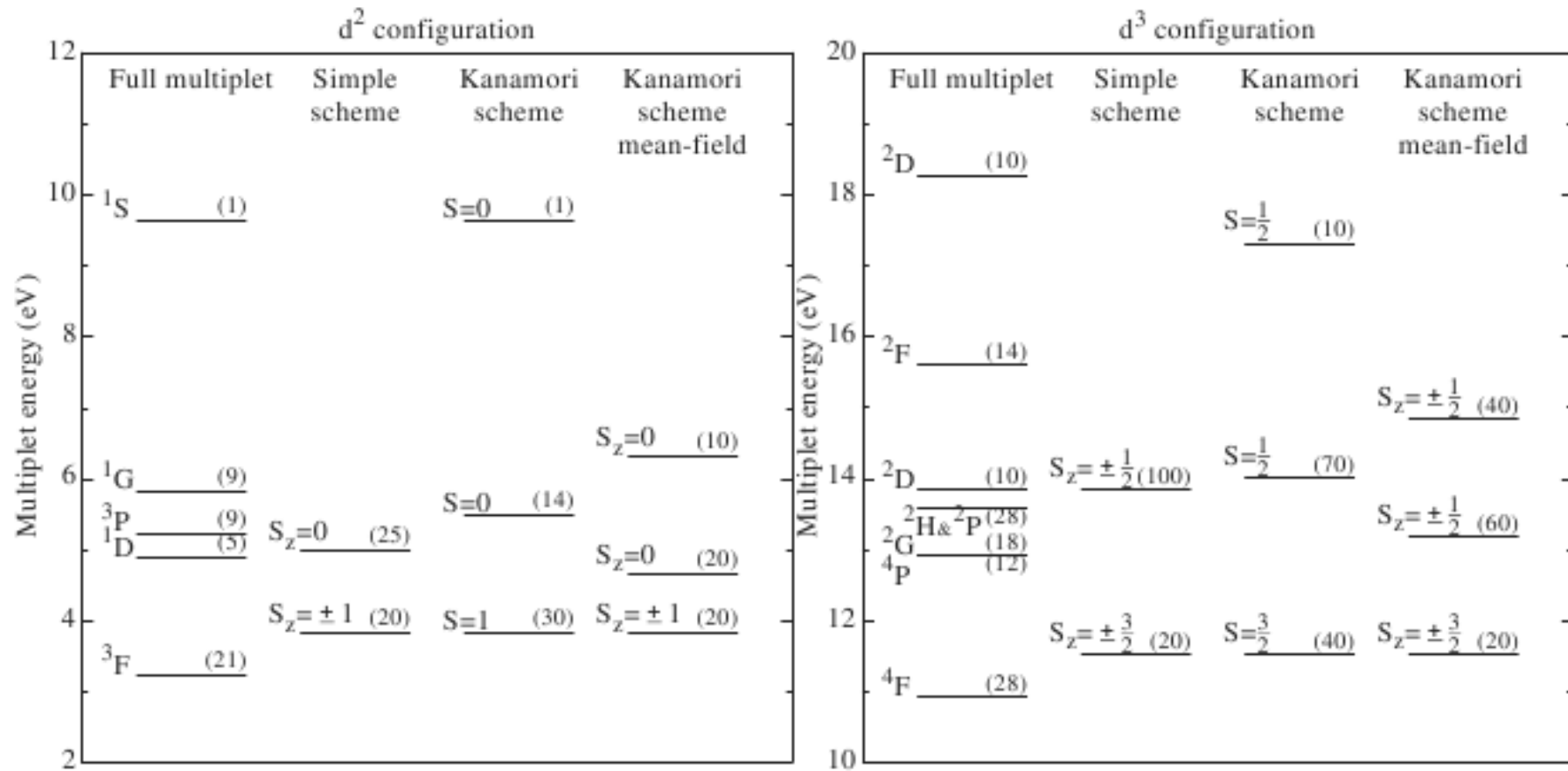
This represents a pure truncation of the true Coulomb interaction for which there is **no justification whatsoever**
More precisely: the discarded terms of the Coulomb Hamiltonian are of comparable magnitude to those which are kept

$$H_1 = U_0 \left(\sum_{m,m'} \sum_{\sigma,\sigma'} n_{m\sigma} n_{m'\sigma'} - \sum_{m,\sigma} n_{m\sigma} \right) - J_H \sum_{m \neq m'} n_{m,\uparrow} n_{m',\downarrow}$$

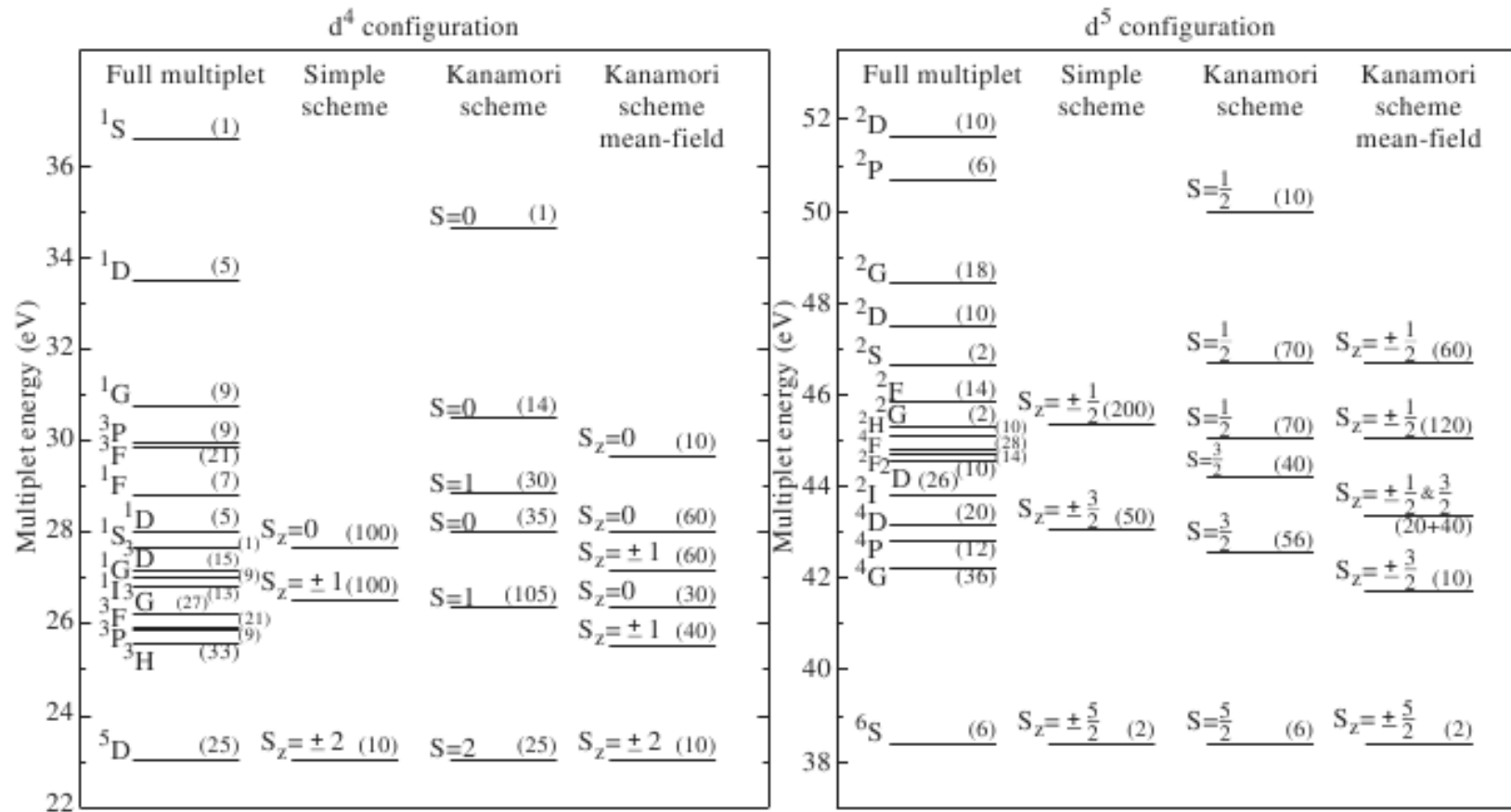
Still, by adjusting the parameters $U_0 = F^0$ and $J_H = (F^2 + F^4)/14$ and introduce $C = (\frac{9}{7}F^2 - \frac{5}{7}F^4) \leq 1 \text{ eV}$ one can obtain nearly correct values for the ground state energies of d^n (M. Haverkort, Ph. D. thesis)

	Coulomb energy of Hund's rule ground-state				
	Full Hamiltonian	Simple	Kanamori	Kanamori mean field	
d^0	0	0	0	0	
d^1	0	0	0	0	
d^2	$F^0 - \frac{8}{49}F^2 - \frac{9}{441}F^4$	$U_0 - J_H - C$	$U_0 - J_H$	$U' - J$	$U' - J$
d^3	$3F^0 - \frac{15}{49}F^2 - \frac{441}{72}F^4$	$3U_0 - 3J_H - C$	$3U_0 - 3J_H$	$3U' - 3J$	$3U' - 3J$
d^4	$6F^0 - \frac{21}{49}F^2 - \frac{441}{189}F^4$	$6U_0 - 6J_H$	$6U_0 - 6J_H$	$6U' - 6J$	$6U' - 6J$
d^5	$10F^0 - \frac{35}{49}F^2 - \frac{315}{441}F^4$	$10U_0 - 10J_H$	$10U_0 - 10J_H$	$10U' - 10J$	$10U' - 10J$
d^6	$15F^0 - \frac{49}{35}F^2 - \frac{441}{315}F^4$	$15U_0 - 10J_H$	$15U_0 - 10J_H$	$14U' + U - 10J$	$14U' + U - 10J$
d^7	$21F^0 - \frac{49}{43}F^2 - \frac{441}{324}F^4$	$21U_0 - 11J_H - C$	$21U_0 - 11J_H$	$19U' + 2U - 11J$	$19U' + 2U - 11J$
d^8	$28F^0 - \frac{49}{50}F^2 - \frac{441}{387}F^4$	$28U_0 - 13J_H - C$	$28U_0 - 13J_H$	$25U' + 3U - 13J$	$25U' + 3U - 13J$
d^9	$36F^0 - \frac{49}{56}F^2 - \frac{441}{504}F^4$	$36U_0 - 16J_H$	$36U_0 - 16J_H$	$32U' + 4U - 16J$	$32U' + 4U - 16J$
d^{10}	$45F^0 - \frac{49}{70}F^2 - \frac{441}{441}F^4$	$45U_0 - 20J_H$	$45U_0 - 20J_H$	$40U' + 5U - 20J$	$40U' + 5U - 20J$

However, as regards agreement with the true Hamiltonian that's about it.....



However, as regards agreement with the true Hamiltonian that's about it.....



In summary a Hamiltonian like this one

$$H_1 = U_0 \left(\sum_{m,m'} \sum_{\sigma,\sigma'} n_{m\sigma} n_{m'\sigma'} - \sum_{m,\sigma} n_{m\sigma} \right) - J_H \sum_{m \neq m'} n_{m,\uparrow} n_{m',\downarrow}$$

cannot be expected to produce - say - photoemission spectra which have much similarity with experiment.

This can be seen in many recent works in the literature....