5 Multiplets and Spin-Orbit Coupling

Erik Koch
Jülich Supercomputer Centre
Forschungszentrum Jülich

Contents

E. Pavarini and E. Koch (eds.)
Topology, Entanglement, and Strong Correlations
Modeling and Simulation Vol. 10
Forschungszentrum Jülich, 2020, ISBN 978-3-95806-466-9
http://www.cond-mat.de/events/correl20

1 Atomic configurations

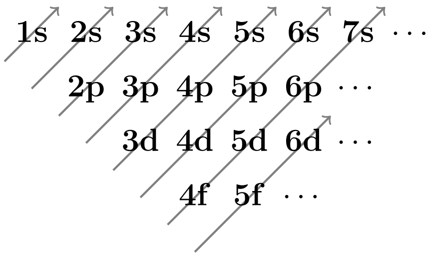
Given their modest size and symmetry, atoms are among the simplest many-electron problems. On the other hand, they are of outstanding importance as the building blocks of all matter, with their level structure determining the to a large extent the electronic structure in the condensed state. Their symmetry, combined with the early availability of high-accuracy spectral data, made it possible to analyze the electronic structure of atoms and ions already before the Schrödinger equation was known [1]. Knowing the (non-relativistic) Hamiltonian for an N-electron ion of charge $Z-N$ (in atomic units, see App. A)

$$H=\sum_{i=1}^{N}\left(-\frac{1}{2}\Delta_i-\frac{Z}{|\vec{r}_i|}\right)+\sum_{i<j}\frac{1}{|\vec{r}_i-\vec{r}_j|} \tag{1}$$

does, however, not mean that we can determine its ground state exactly. To get an impression of the complexity of the problem presented by a system of many interacting electrons, we may consider a simple iron atom, Fe, with $N=Z=26$ electrons. Its wave-function is a function of 3×26 coordinates. Writing a numerical approximation to it, even on a coarse discretization grid of 10 grid-points per coordinate would require us to store 10^{76} amplitudes, for which we would need a classical memory device containing more atoms than exist in the visible universe—a practical impossibility. We thus need “approximate practical methods” [2] to deal with the problem.

The approximate practical approach for dealing with the atomic many-body problem consists of treating the electron-electron repulsion in two steps. First, equation (1) is solved in the central-field approximation. This provides us with orbitals $\varphi_{n,l,m,\sigma}(\vec{r})=u_{n,l}(r)/r\,Y_{l,m}(\vartheta,\varphi)\,\chi_\sigma$. If we were to stop at the mean-field level, we might look for unrestricted mean-field solutions that break the spherical and spin symmetry to lower the mean-field energy. When we continue the calculation by reintroducing the electron-electron interaction, we stay with the symmetry-restricted mean-field solutions, as the many-body treatment otherwise would have to restore the broken symmetries.

Filling the central-field orbitals by the Aufbauprinzip already gives the structure or the periodic table: orbitals are filled—roughly—with increasing quantum numbers $n+l$ and for given $n+l$ with increasing principle quantum number n:



The reordering of the atomic shells relative to the hydrogen levels is a result of the mean-field: inner electrons screen the nuclear charge, so that electrons further away from the nucleus see only a small effective charge. Since $u_{n,l}(r\to 0)\sim r^{l+1}$ orbitals with higher angular momentum l have a lower probability of coming close to the nucleus, so their energy tends to go up.

In the central-field approximation the orbital energy only depends on the quantum numbers n and l, but not on m and σ. Thus, when a shell (n,l) is filled with less than $2(2l{+}1)$ electrons, there will be many different ways of distributing the electrons over spin-orbitals, all of the same energy. Thus open shells are highly degenerate.

This degeneracy is lifted when we re-introduce the electron-electron interaction in degenerate perturbation theory, or, when including more than the degenerate orbitals, in a variational way. The actual perturbation is the two-body interaction minus the mean-field (double-counting correction)

$$\sum_i V_{MF}(\vec{r}_i) := \left\langle \frac{1}{2}\sum_{j\neq i}\frac{1}{|\vec{r}_i-\vec{r}_j|}\right\rangle. \tag{2}$$

When the mean-field density is close to the true density as, e.g., in a density-functional calculation, the long-range Hartree potential is already properly included V_{MF}, so that the perturbation becomes short-ranged—of the order of the exchange-correlation hole. This perturbation arising from the electron-electron repulsion splits a configuration l^N of N electrons in an (n,l)-shell into multiplet terms. They are characterized by their total orbital momentum L and spin S quantum numbers and are in general still highly degenerate. The total spin is usually given by its multiplicity $2S{+}1$ so that the multiplet term is written as ${}^{2S+1}L$. When the relativistic spin-orbit coupling is included in a second step of degenerate perturbation theory, these terms split into multiplet levels, which are characterized by the additional total angular momentum as ${}^{2S+1}L_J$. This two-step degenerate perturbation approach is called LS or Russell-Saunders coupling and works well when the splitting due to spin-orbit coupling is much smaller than that due to the electron-electron repulsion.

Doing perturbation theory in the opposite order, i.e., calculating the splitting of the open shell l^N under spin-orbit interaction and then doing perturbation theory for the electron-electron repulsion on the degenerate spin-orbit levels is called jj coupling. It is appropriate in extremely heavy atoms, where the spin-orbit splitting dominates the multiplet splitting. In practice this is not realized for stable atoms. In heavy atoms the spin-orbit interaction can, however, become sufficiently strong that LS coupling breaks down and one has to treat electron-electron repulsion and spin-orbit coupling on the same footing, i.e., in a single step of degenerate perturbation theory. This is called intermediate coupling.

In the following we will start by analyzing the two-body electron-electron repulsion that makes the N-electron atom a many-body problem. We will see that the multiplet terms are almost completely determined by symmetry—which was instrumental in making the analysis of spectra before the introduction of the Schrödinger equation possible. We will then turn to the construction of the electron-electron Hamiltonian bring it into matrix form and investigate its properties, in particular under an electron-hole transformation. This will involve a number of technical concepts, in particular the addition theorem for spherical harmonics and its implications as well as Gaunt coefficients, which are explained in separate appendices. Finally, we will briefly discuss the much simpler one-body spin-orbit interaction and its interplay with the electron-electron repulsion. For an introduction to multiplets with a focus of different aspects of the theory, see also the excellent lecture of Robert Eder on multiplets in transition metal ions in [3].

2 Multiplets

We start by considering the splitting of an open shell of N electrons in orbitals $\varphi_{n,l,m,\sigma}$ of angular momentum l. There are $2(2l{+}1)$ such spin-orbitals and, by the antisymmetry of the N-electron wave function, $\binom{2(2l+1)}{N}$ degenerate states in the shell l^N. The computational approach of dealing with the electron-electron repulsion is to write $H_{ee}\sum_{i<j} 1/|\vec{r}_i{-}\vec{r}_j|$ in second quantization in the N-electron space spanned by the spin-orbitals and diagonalize the resulting $\binom{4l+2}{N}$-dimensional matrix numerically. The techniques for this exact diagonalization are explained in [4]. As a result we will find a highly degenerate spectrum.

The degeneracies are the consequence of the symmetries of the perturbation: H_{ee} is invariant under inversions and simultaneous rotations of all electrons, as well as independent of spin. This means, in particular, that it commutes with the total spin $\vec{S} = \sum_i \vec{S}_i$ operator and total orbital momentum $\vec{L} = \sum_i \vec{L}_i$, where $\vec{L}_i = \vec{r}_i \times \vec{p}_i$. Thus, there will be simultaneous eigenstates of H_{ee}, $\vec{L}$, and $\vec{S}$. The symmetry-based approach to calculating multiplet terms and their energies is thus based on constructing the eigenstates $|L, M;\, S, \Sigma\rangle$ of the total angular momenta, spanning the multiplet term ${}^{2S+1}L$. When the terms are unique, the $|L, M;\, S, \Sigma\rangle$ are automatically eigenstates of H_{ee}. When there is more than one term with quantum numbers L and S, H_{ee} needs only be diagonalized on this small space. Written in multiplet states, H_{ee} is thus block diagonal, with most blocks being one-dimensional.

Constructing eigenstates of L and S can, however, be quite tedious: the resulting states when adding more that two angular momenta depend on the order in which the momenta are added, and the resulting states need to be antisymmetrized. The traditional approach [5–10] proceeds by constructing the multiplet states for the l^N shell from the states for the simpler l^{N-1}-shell by adding the angular momentum of the additional electron and antisymmetrizing the resulting function. To ease this task, there are tables of coefficients of fractional parentage [10]:

> Fractional parentage coefficients were introduced by Racah [7] to facilitate computation of matrix elements for complicated configurations. They are important because all antisymmetric states of N electrons can be expressed as linear combinations of the states obtained by angular-momentum coupling one additional electron to the antisymmetric states of $N{-}1$ electrons. The coefficients of these linear combinations are the fractional parentage coefficients.

The problem simplifies drastically when we work in a formalism that only allows us to express physical quantities, i.e., when working in second quantization [11]: all states must be antisymmetric and all operators must be symmetric: total orbital momentum can be represented, while unphysical operators acting on only a single electron cannot (if such an operator would be physical, we could use it to distinguish the electron it acts on from the others...). The procedure starts by identifying the state with maximum M and Σ (i.e., that vanishes under L_+ and S_+ so that it is a states with $L = M$ and $S = \Sigma$). Using ladder operators L_- and S_- then produces the other states of multiplet ${}^{2S+1}L$, after which the procedure is repeated with the remaining states.

2.1 Constructing multiplet states

The key tools for constructing multiplet state are the ladder operators of total orbital momentum

$$\hat{L}_\pm = \sum_{l,m,\sigma} \sqrt{(l\pm m+1)(l\mp m)}\, c^\dagger_{l,m\pm1,\sigma}\, c_{l,m,\sigma}$$

and total spin

$$\hat{S}_+ = \sum_{l,m} c^\dagger_{l,m,\uparrow}\, c_{l,m,\downarrow} \quad \text{and} \quad \hat{S}_- = \sum_{l,m} c^\dagger_{l,m,\downarrow}\, c_{l,m,\uparrow}.$$

In addition we have to fix some order of the orbitals in our basis determinants, which we choose to be sorted according to their eigenvalues m, σ: operators with spin $\uparrow$ to the left of $\downarrow$ and, for given spin, m to the left of m' when $m > m'$.

2.1.1 Multiplet terms of p^2

To see how multiplets are identified and their states are constructed in practice, we look at the simple case of two electrons in a p shell. To start, we arrange the $\binom{6}{2} = 15$ basis determinants according to their eigenvalues of L_z and S_z:

			$\varSigma$	
		1	0	-1
	2		$p^\dagger_{1\uparrow}p^\dagger_{1\downarrow}\lvert 0\rangle$	
	1	$p^\dagger_{1\uparrow}p^\dagger_{0\uparrow}\lvert 0\rangle$	$p^\dagger_{1\uparrow}p^\dagger_{0\downarrow}\lvert 0\rangle$ $p^\dagger_{0\uparrow}p^\dagger_{1\downarrow}\lvert 0\rangle$	$p^\dagger_{1\downarrow}p^\dagger_{0\downarrow}\lvert 0\rangle$
M	0	$p^\dagger_{1\uparrow}p^\dagger_{-1\uparrow}\lvert 0\rangle$	$p^\dagger_{1\uparrow}p^\dagger_{-1\downarrow}\lvert 0\rangle$ $p^\dagger_{0\uparrow}p^\dagger_{0\downarrow}\lvert 0\rangle$ $p^\dagger_{-1\uparrow}p^\dagger_{1\downarrow}\lvert 0\rangle$	$p^\dagger_{1\downarrow}p^\dagger_{-1\downarrow}\lvert 0\rangle$
	-1	$p^\dagger_{0\uparrow}p^\dagger_{-1\uparrow}\lvert 0\rangle$	$p^\dagger_{0\uparrow}p^\dagger_{-1\downarrow}\lvert 0\rangle$ $p^\dagger_{-1\uparrow}p^\dagger_{0\downarrow}\lvert 0\rangle$	$p^\dagger_{0\downarrow}p^\dagger_{-1\downarrow}\lvert 0\rangle$
	-2		$p^\dagger_{-1\uparrow}p^\dagger_{-1\downarrow}\lvert 0\rangle$	

For the states with $\varSigma = 1$ both electron spins are up, so that applying S_+ produces zero. From the relation $\vec{J}^2 = J_z^2 + J_z + J_- J_+$ for general angular momenta $\vec{J}$, it then follows that these states are eigenstates of $\vec{S}^2$ with $S = 1$. Similarly, when a state vanishes under L_+ it is an eigenstate of $\vec{L}^2$. We can thus identify a state $|L, M;\, S, \varSigma\rangle$

$$|1,1;\,1,1\rangle = p^\dagger_{1\uparrow}p^\dagger_{0\uparrow}|0\rangle \tag{3}$$

from which we can construct more eigenstates $|1,1;\,1,\varSigma\rangle$ by applying $S_- = \sum_m p^\dagger_{m\downarrow}p_{m\uparrow}$, using $[S_-,\, p^\dagger_{m\sigma}] = \delta_{\sigma,\uparrow}\, p^\dagger_{m\downarrow}$. For example

$$\sqrt{2}\,|1,1;\,1,0\rangle = S_-\,|1,1;\,1,1\rangle = \big(-p^\dagger_{0\uparrow}p^\dagger_{1\downarrow} + p^\dagger_{1\uparrow}p^\dagger_{0\downarrow}\big)|0\rangle,$$

where in the last term we have brought the operators in the order required by our choice of basis. Note how the factor on the left just ensures normalization of the state on the right.

Also using L_-, we can construct all nine states $|1,M;\,1,\Sigma\rangle$ of the ^3P multiplet term

$\boxed{^3P}$			Σ	
		1	0	-1
	1	$p^\dagger_{1\uparrow}p^\dagger_{\ 0\uparrow}\lvert 0\rangle$	$\frac{1}{\sqrt{2}}\big(p^\dagger_{\ 1\uparrow}p^\dagger_{\ 0\downarrow}-p^\dagger_{\ 0\uparrow}p^\dagger_{\ 1\downarrow}\big)\lvert 0\rangle$	$p^\dagger_{1\downarrow}p^\dagger_{\ 0\downarrow}\lvert 0\rangle$
M	0	$p^\dagger_{1\uparrow}p^\dagger_{-1\uparrow}\lvert 0\rangle$	$\frac{1}{\sqrt{2}}\big(p^\dagger_{\ 1\uparrow}p^\dagger_{-1\downarrow}-p^\dagger_{-1\uparrow}p^\dagger_{\ 1\downarrow}\big)\lvert 0\rangle$	$p^\dagger_{1\downarrow}p^\dagger_{-1\downarrow}\lvert 0\rangle$
	-1	$p^\dagger_{0\uparrow}p^\dagger_{-1\uparrow}\lvert 0\rangle$	$\frac{1}{\sqrt{2}}\big(p^\dagger_{\ 0\uparrow}p^\dagger_{-1\downarrow}-p^\dagger_{-1\uparrow}p^\dagger_{\ 0\downarrow}\big)\lvert 0\rangle$	$p^\dagger_{0\downarrow}p^\dagger_{-1\downarrow}\lvert 0\rangle$

Similarly, we see that

$$|2,2;\,0,0\rangle = p^\dagger_{1\uparrow}p^\dagger_{1\downarrow}|0\rangle \tag{4}$$

from which by repeated application of $L_- = \sqrt{2}\sum_\sigma\big(p^\dagger_{0\sigma}p_{1\sigma}+p^\dagger_{-1\sigma}p_{0\sigma}\big)$ we can construct all five states of the ^1D term

$\boxed{^1D}$		$\Sigma=0$
	2	$p^\dagger_{1\uparrow}p^\dagger_{1\downarrow}\ \lvert 0\rangle$
	1	$\frac{1}{\sqrt{2}}\big(p^\dagger_{1\uparrow}p^\dagger_{0\downarrow}+p^\dagger_{0\uparrow}p^\dagger_{1\downarrow}\big)\lvert 0\rangle$
M	0	$\frac{1}{\sqrt{6}}\big(p^\dagger_{1\uparrow}p^\dagger_{-1\downarrow}+2p^\dagger_{0\uparrow}p^\dagger_{0\downarrow}+p^\dagger_{-1\uparrow}p^\dagger_{1\downarrow}\big)\lvert 0\rangle$
	-1	$\frac{1}{\sqrt{2}}\big(p^\dagger_{0\uparrow}p^\dagger_{-1\downarrow}+p^\dagger_{-1\uparrow}p^\dagger_{0\downarrow}\big)\lvert 0\rangle$
	-2	$p^\dagger_{-1\uparrow}p^\dagger_{-1\downarrow}\ \lvert 0\rangle$

The remaining state in the 3-dimensional eigenspace $M{=}0$, $\Sigma{=}0$ must be a singlet state ^1S. We can construct it by finding the state orthogonal to $|1,0;\,1,0\rangle$ and $|2,0;\,0,0\rangle$:

$$\boxed{^1S}\qquad |0,0;\,0,0\rangle = \frac{1}{\sqrt{3}}\big(-p^\dagger_{1\uparrow}p^\dagger_{-1\downarrow}+p^\dagger_{0\uparrow}p^\dagger_{0\downarrow}-p^\dagger_{-1\uparrow}p^\dagger_{1\downarrow}\big)|0\rangle\,. \tag{5}$$

The procedure is quite remarkable. Simply counting the number of basis determinants with given M and Σ we could identify states of maximum L_z and S_z eigenvalues and see that p^2 splits into ^3P, ^1D, and ^1S. Constructing the multiplet states explicitly then involved merely ladder-operator algebra. For the ^3P and ^1D multiplets the starting state $|L,L;\,S,S\rangle$ turned out to be just a Slater determinant. Only the singlet state had to be constructed by orthogonalizing to the already constructed states.

The p^2-shell is, of course, quite a simple case. Adding two angular momenta is a unique procedure. Already for three angular momenta this is no longer true: Adding two spins gives a triplet $S{=}1$ and one singlet $S{=}0$ state. Adding another spin to the triplet gives a quadruplet $S{=}\frac{3}{2}$ and a doublet $S{=}\frac{1}{2}$, adding the third spin to the singlet gives another doublet. While the triplet is unique, the choice of the basis in the two-doublet space is arbitrary. It is usually resolved by specifying in which order the spins are added: $(\vec{S}_1{+}\vec{S}_2){+}\vec{S}_3$ results in doublet states different from those obtained by adding, e.g., $\vec{S}_1{+}(\vec{S}_2{+}\vec{S}_3)$. For shells of more than two electrons we might therefore expect that there will be multiplets that appear several times. Because of the antisymmetry constraint this does, however, not happen in any of the p-shells. The first time we see multiple multiplets is for d^3, which we study next.

2.1.2 Multiplet states of d^3

The d^3-shell has considerably more states than p^2. We can reduce the discussion from $\binom{10}{3} = 120$ down to the 35 basis states with $M \geq 0$ and $\Sigma \geq 0$, since the space spanned by these contains all states that vanish under L_+ and S_+.

		Σ		
		$\frac{3}{2}$	$\frac{1}{2}$	
	5		$d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{2\downarrow}\vert 0\rangle$	
	4		$d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{1\downarrow}\vert 0\rangle$	$d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{2\downarrow}\vert 0\rangle$
	3	$d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{0\uparrow}\vert 0\rangle$	$d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{0\downarrow}\vert 0\rangle$ $d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{1\downarrow}\vert 0\rangle$	$d^\dagger_{2\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{2\downarrow}\vert 0\rangle$ $d^\dagger_{1\uparrow}d^\dagger_{0\uparrow}d^\dagger_{2\downarrow}\vert 0\rangle$
M	2	$d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{-1\uparrow}\vert 0\rangle$	$d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{-1\downarrow}\vert 0\rangle$ $d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{0\downarrow}\vert 0\rangle$ $d^\dagger_{2\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{1\downarrow}\vert 0\rangle$	$d^\dagger_{1\uparrow}d^\dagger_{0\uparrow}d^\dagger_{1\downarrow}\vert 0\rangle$ $d^\dagger_{2\uparrow}d^\dagger_{-2\uparrow}d^\dagger_{2\downarrow}\vert 0\rangle$ $d^\dagger_{1\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{2\downarrow}\vert 0\rangle$
	1	$d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{-2\uparrow}\vert 0\rangle$ $d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{-1\uparrow}\vert 0\rangle$	$d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{-2\downarrow}\vert 0\rangle$ $d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{-1\downarrow}\vert 0\rangle$ $d^\dagger_{2\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{0\downarrow}\vert 0\rangle$ $d^\dagger_{1\uparrow}d^\dagger_{0\uparrow}d^\dagger_{0\downarrow}\vert 0\rangle$	$d^\dagger_{2\uparrow}d^\dagger_{-2\uparrow}d^\dagger_{1\downarrow}\vert 0\rangle$ $d^\dagger_{1\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{1\downarrow}\vert 0\rangle$ $d^\dagger_{1\uparrow}d^\dagger_{-2\uparrow}d^\dagger_{2\downarrow}\vert 0\rangle$ $d^\dagger_{0\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{2\downarrow}\vert 0\rangle$
	0	$d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{-2\uparrow}\vert 0\rangle$ $d^\dagger_{1\uparrow}d^\dagger_{0\uparrow}d^\dagger_{-1\uparrow}\vert 0\rangle$	$d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{-2\downarrow}\vert 0\rangle$ $d^\dagger_{2\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{-1\downarrow}\vert 0\rangle$ $d^\dagger_{1\uparrow}d^\dagger_{0\uparrow}d^\dagger_{-1\downarrow}\vert 0\rangle$ $d^\dagger_{2\uparrow}d^\dagger_{-2\uparrow}d^\dagger_{0\downarrow}\vert 0\rangle$	$d^\dagger_{1\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{0\downarrow}\vert 0\rangle$ $d^\dagger_{1\uparrow}d^\dagger_{-2\uparrow}d^\dagger_{1\downarrow}\vert 0\rangle$ $d^\dagger_{0\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{1\downarrow}\vert 0\rangle$ $d^\dagger_{0\uparrow}d^\dagger_{-2\uparrow}d^\dagger_{2\downarrow}\vert 0\rangle$

From $|3,3;\,\frac{3}{2},\frac{3}{2}\rangle = d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{0\uparrow}|0\rangle$ we can construct the twenty states in ${}^4F$.
Using $L_- = \sum_\sigma \big(2d^\dagger_{-2\sigma}d_{-1\sigma} + \sqrt{6}\,d^\dagger_{-1\sigma}d_{0\sigma} + \sqrt{6}\,d^\dagger_{0\sigma}d_{1\sigma} + 2d^\dagger_{1\sigma}d_{2\sigma}\big)$ and remembering that L_- on the left-hand side ensures normalization we obtain

$$\begin{aligned}
|3,3;\,\tfrac{3}{2},\tfrac{3}{2}\rangle &= d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{0\uparrow}\,|0\rangle\\
|3,2;\,\tfrac{3}{2},\tfrac{3}{2}\rangle &= d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{-1\uparrow}\,|0\rangle\\
|3,1;\,\tfrac{3}{2},\tfrac{3}{2}\rangle &= \tfrac{1}{\sqrt{5}}\big(\sqrt{3}\,d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{-1\uparrow} + \sqrt{2}\,d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{-2\uparrow}\big)|0\rangle\\
|3,0;\,\tfrac{3}{2},\tfrac{3}{2}\rangle &= \tfrac{1}{\sqrt{5}}\big(d^\dagger_{1\uparrow}d^\dagger_{0\uparrow}d^\dagger_{-1\uparrow} + 2\,d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{-2\uparrow}\big)|0\rangle
\end{aligned}$$

The state $|\Psi_\perp\rangle$ orthogonal to $|3,1\;\frac{3}{2},\frac{3}{2}\rangle$ in the two-dimensional eigenspace must vanish under L_+, since it is orthogonal also to $L_-L_+|3,1;\,\frac{3}{2},\frac{3}{2}\rangle$ so that $0 = \langle L_+\Psi_\perp|3,2;\,\frac{3}{2},\frac{3}{2}\rangle$. It is thus

$$|1,1;\,\tfrac{3}{2},\tfrac{3}{2}\rangle = \frac{1}{\sqrt{5}}\big(\sqrt{2}\,d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{-1\uparrow} - \sqrt{3}\,d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{-2\uparrow}\big)|0\rangle$$

from which we can construct the twelve states of ${}^4P$.

Starting from $|5,5;\,\frac{1}{2},\frac{1}{2}\rangle = d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{2\downarrow}|0\rangle$ we obtain the twenty-two ${}^2H$ states, e.g.,

$$\begin{aligned}
|5,5;\tfrac{1}{2},\tfrac{1}{2}\rangle &= & d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{2\downarrow}\;|0\rangle \\
|5,4;\tfrac{1}{2},\tfrac{1}{2}\rangle &= & \tfrac{1}{\sqrt{5}}\big(\sqrt{3}\,d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{2\downarrow}+\sqrt{2}\,d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{1\downarrow}\big)|0\rangle \\
|5,3;\tfrac{1}{2},\tfrac{1}{2}\rangle &= & \tfrac{1}{\sqrt{15}}\big(\sqrt{2}\,d^\dagger_{1\uparrow}d^\dagger_{0\uparrow}d^\dagger_{2\downarrow}+\sqrt{3}\,d^\dagger_{2\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{2\downarrow}+\sqrt{8}\,d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{1\downarrow}+\sqrt{2}\,d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{0\downarrow}\big)|0\rangle \\
&\vdots &
\end{aligned}$$

There remains one state orthogonal to $|5,4;\,\frac{1}{2},\frac{1}{2}\rangle$ in the eigenspace for $M{=}4$, $\Sigma{=}\frac{1}{2}$

$$|4,4;\,\tfrac{1}{2},\tfrac{1}{2}\rangle = \frac{1}{\sqrt{5}}\big(\sqrt{2}\,d^\dagger_{2\uparrow}d^\dagger_{d\uparrow}d^\dagger_{0\downarrow}2-\sqrt{3}\,d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{1\downarrow}\big)|0\rangle$$

from which we can construct the eighteen states in ${}^2G$. Similarly, in the four-dimensional eigenspace of $M{=}3$, $\Sigma{=}\frac{1}{2}$ there remains one state orthogonal to the already constructed states $|5,3;\,\frac{1}{2},\frac{1}{2}\rangle$, $|4,3;\,\frac{1}{2},\frac{1}{2}\rangle$, and $|3,3;\,\frac{3}{2},\frac{1}{2}\rangle \propto S_-|3,3;\frac{3}{2},\frac{3}{2}\rangle$

$$|3,3;\,\tfrac{1}{2},\tfrac{1}{2}\rangle = \frac{1}{\sqrt{12}}\big(2\,d^\dagger_{1\uparrow}d^\dagger_{0\uparrow}d^\dagger_{2\downarrow}-\sqrt{6}\,d^\dagger_{2\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{2\downarrow}+d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{1\downarrow}-d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{0\downarrow}\big)|0\rangle$$

from which we obtain the fourteen ${}^2F$ states.

In the next step we encounter a new situation: the eigenspace of $M{=}2$, $\Sigma{=}\frac{1}{2}$ is six-dimensional, but so far we could only construct four states out of it: $|5,2;\,\frac{1}{2},\frac{1}{2}\rangle$, $|4,2;\,\frac{1}{2},\frac{1}{2}\rangle$, $|3,2;\,\frac{1}{2},\frac{1}{2}\rangle$, and $|3,2;\,\frac{3}{2},\frac{1}{2}\rangle$. Any state out of the remaining two-dimensional orthogonal space will vanish under L_+ and S_+, i.e., it will be an eigenfunction of the type $|2,2;\,\frac{1}{2},\frac{1}{2}\rangle$, so that there will be two ${}^2D$ multiplets. This ambiguity is, of course, lifted in a natural way by diagonalizing the Hamiltonian on the two dimensional space and using the resulting energy eigenstates to construct the two multiplets. If we insist on defining states independently of the Hamiltonian, we need to define a recipe for lifting the ambiguity. This route has been taken by Racah by introducing the concept of seniority [8]. Before discussing this, we finish the determination of the multiplets of a d^3-shell by noting that after constructing the two ${}^2D$ multiplet states, there is still one undetermined state in the $M{=}1$, $\Sigma{=}\frac{1}{2}$ eigenstate, which gives rise to a ${}^2P$ multiplet.

Thus the 120-fold degenerate d^3-shell splits into ${}^4F$, ${}^4P$, ${}^2H$, ${}^2G$, ${}^2F$, $2{\times}{}^2D$, and ${}^2P$.

2.1.3 Seniority and Kramers pairs

The key to understanding seniority are the Kramers pair creators

$$K_l^\dagger := \frac{1}{\sqrt{2l{+}1}}\sum_{m=-l}^{l}(-1)^m\, l^\dagger_{m\uparrow}l^\dagger_{-m\downarrow} \tag{6}$$

which create electron-pairs in a singlet state (note the analogy to Cooper pairs), i.e., $[\vec{L},\,K_l^\dagger] = 0 = [\vec{S},\,K_l^\dagger]$. For the z-components this is straightforward

$$\begin{aligned}
\big[L_z,\,l^\dagger_{m\uparrow}l^\dagger_{-m\downarrow}\big] &= \big[L_z,\,l^\dagger_{m\uparrow}\big]l^\dagger_{-m\downarrow}+l^\dagger_{m\uparrow}\big[L_z,\,l^\dagger_{-m\downarrow}\big] = (m{-}m)\,l^\dagger_{m\uparrow}l^\dagger_{-m\downarrow} = 0 \\
\big[S_z,\,l^\dagger_{m\uparrow}l^\dagger_{-m\downarrow}\big] &= \big[S_z,\,l^\dagger_{m\uparrow}\big]\,l^\dagger_{-m\downarrow}+l^\dagger_{m\uparrow}\big[S_z,\,l^\dagger_{-m\downarrow}\big] = \big(\tfrac{1}{2}{-}\tfrac{1}{2}\big)\;l^\dagger_{m\uparrow}l^\dagger_{-m\downarrow} = 0
\end{aligned}$$

For the other components, we use the ladder operators. The principle is most easily seen for the simple case of $l = 1$:

$$\begin{aligned}\big[L_+,\, -p^\dagger_{1\uparrow}p^\dagger_{-1\downarrow} + p^\dagger_{0\uparrow}p^\dagger_{0\downarrow} - p^\dagger_{-1\uparrow}p^\dagger_{1\downarrow}\big] &= -\sqrt{2}p^\dagger_{1\uparrow}p^\dagger_{0\downarrow} + \sqrt{2}p^\dagger_{1\uparrow}p^\dagger_{0\downarrow} + \sqrt{2}p^\dagger_{0\uparrow}p^\dagger_{1\downarrow} - \sqrt{2}p^\dagger_{0\uparrow}p^\dagger_{1\downarrow} = 0\\ \big[S_+,\, -p^\dagger_{1\uparrow}p^\dagger_{-1\downarrow} + p^\dagger_{0\uparrow}p^\dagger_{0\downarrow} - p^\dagger_{-1\uparrow}p^\dagger_{1\downarrow}\big] &= -p^\dagger_{1\uparrow}p^\dagger_{-1\downarrow} + 0 - p^\dagger_{-1\uparrow}p^\dagger_{1\downarrow} = 0\end{aligned}$$

This means that $K^\dagger$ adds two electrons to a state without changing its angular momentum. The simplest example is the singlet state of p^2 in equation (5): $K^\dagger_1|0\rangle \propto |0,0;\,0,0\rangle$. For d^3 we can obtain a ${}^2D$ state by adding a Kramers pair to a ${}^2D$ state in d^1, e.g.,

$$|2,2;\,\tfrac{1}{2},\tfrac{1}{2}\rangle_{d^1} = d^\dagger_{2\uparrow}|0\rangle, \tag{7}$$

which after normalization gives the state

$$|2,2;\,\tfrac{1}{2},\tfrac{1}{2}\rangle_1 = \frac{1}{2}\big(-d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{-1\downarrow} + d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{0\downarrow} - d^\dagger_{2\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{1\downarrow} + d^\dagger_{2\uparrow}d^\dagger_{-2\uparrow}d^\dagger_{2\downarrow}\big)|0\rangle. \tag{8}$$

The corresponding ${}^2D$ multiplet in d^3 is assigned seniority 1 as it originates from the multiplet in the d^1 shell. The second ${}^2D$ multiplet in d^3, which can now be uniquely constructed from the remaining (orthogonal) state in the eigenspace of $M{=}2$, $\Sigma{=}\frac{1}{2}$, is assigned the seniority 3

$$\begin{aligned}&|2,2;\,\tfrac{1}{2},\tfrac{1}{2}\rangle_3 = \\ &\frac{1}{\sqrt{84}}\big(3d^\dagger_{2\uparrow}d^\dagger_{1\uparrow}d^\dagger_{-1\downarrow} - 3d^\dagger_{2\uparrow}d^\dagger_{0\uparrow}d^\dagger_{0\downarrow} - d^\dagger_{2\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{1\downarrow} + 5d^\dagger_{2\uparrow}d^\dagger_{-2\uparrow}d^\dagger_{2\downarrow} + \sqrt{24}d^\dagger_{1\uparrow}d^\dagger_{0\uparrow}d^\dagger_{-1\downarrow} - 4d^\dagger_{1\uparrow}d^\dagger_{-1\uparrow}d^\dagger_{2\downarrow}\big)|0\rangle.\end{aligned} \tag{9}$$

This approach works for all d shells and the grand-parentage relations can be read off table 1. It also shows that there are far to few grandparents to define unique multiplets in f systems. The situation becomes quite involved, quoting [10], page v:

> Because more than one multiplet of a given L, S may occur, some further differentiation of the multiplets is required. For this purpose we have followed consistently the classification scheme of Racah [8] wherein additional quantum numbers, usually not of physical significance, are introduced by reference to the properties of certain mathematical groups. Specifically, the groups used are those denoted by R_5 in the case of the configuration d^n and by R_7 and G_2 for the configurations f^n. The so-called seniority quantum number is consistent with this scheme. Even with these additional quantum numbers, some duplications occur for f^n configurations, which were resolved arbitrarily by Racah in his work on the electrostatic energy of f^n configurations [8].

In practice it is more economical to directly work with energy eigenstates. For this we need, of course, the representation of the electron-electron interaction in our basis of spherically symmetric orbitals. Before turning our attention to the Hamiltonian, however, let us briefly discuss the particle-hole transformation between configurations l^N and $l^{2(2l+1)-N}$ which is apparent from the table of multiplets.

s^0, s^2	^1S							
s^1		^2S						
p^0, p^6	^1S							
p^1, p^5		^2P						
p^2, p^4	$^1S\,^1D$		^3P					
p^3		$^2P\,^2D$		^4S				
d^0, d^6	^1S							
d^1, d^9		^2D						
d^2, d^8	$^1S\,^1D\,^1G$		$^3P\,^3F$					
d^3, d^7		$^2P\,\overset{2\times}{{}^2D}\,^2F\,^2G\,^2H$		$^4P\,^4F$				
d^4, d^6	$\overset{2\times}{{}^1S}\,\overset{2\times}{{}^1D}\,^1F\,\overset{2\times}{{}^1G}\,^1I$		$\overset{2\times}{{}^3P}\,^3D\,\overset{2\times}{{}^3F}\,^3G\,^3H$		^5D			
d^5		$^2S\,^2P\,\overset{3\times}{{}^2D}\,\overset{2\times}{{}^2F}\,\overset{2\times}{{}^2G}\,^2H\,^2I$		$^4P\,^4D\,^4F\,^4G$		^6S		
f^0, f^{14}	^1S							
f^1, f^{13}		^2F						
f^2, f^{12}	$^1S\,^1D\,^1G\,^1I$		$^3P\,^3F\,^3H$					
f^3, f^{11}		$^2P\,\overset{2\times}{{}^2D}\,\overset{2\times}{{}^2F}\,\overset{2\times}{{}^2G}\,\overset{2\times}{{}^2H}\,^2I\,^2K\,^2L$		$^4S\,^4D\,^4F\,^4G\,^4I$				
f^4, f^{10}	$\overset{2\times}{{}^1S}\,\overset{4\times}{{}^1D}\,^1F\,\overset{4\times}{{}^1G}\,\overset{2\times}{{}^1H}\,\overset{3\times}{{}^1I}\,^1K\,\overset{2\times}{{}^1L}\,^1N$		$\overset{3\times}{{}^3P}\,\overset{2\times}{{}^3D}\,\overset{4\times}{{}^3F}\,\overset{3\times}{{}^3G}\,\overset{4\times}{{}^3H}\,\overset{2\times}{{}^3I}\,\overset{2\times}{{}^3K}\,^3L\,^3M$		$^5S\,^5D\,^5F\,^5G\,^5I$			
f^5, f^9		$\overset{4\times}{{}^2P}\,\overset{5\times}{{}^2D}\,\overset{7\times}{{}^2F}\,\overset{6\times}{{}^2G}\,\overset{7\times}{{}^2H}\,\overset{5\times}{{}^2I}\,\overset{5\times}{{}^2K}\,\overset{3\times}{{}^2L}\,\overset{2\times}{{}^2M}\,^2N\,^2O$		$^4S\,\overset{2\times}{{}^4P}\,\overset{3\times}{{}^4D}\,\overset{4\times}{{}^4F}\,\overset{4\times}{{}^4G}\,\overset{3\times}{{}^4H}\,\overset{3\times}{{}^4I}\,\overset{2\times}{{}^4K}\,^4L\,^4M$		$^6P\,^6F\,^6H$		
f^6, f^8	$\overset{4\times}{{}^1S}\,^1P\,\overset{6\times}{{}^1D}\,\overset{4\times}{{}^1F}\,\overset{8\times}{{}^1G}\,\overset{4\times}{{}^1H}\,\overset{7\times}{{}^1I}\,\overset{3\times}{{}^1K}\,\overset{4\times}{{}^1L}\,\overset{2\times}{{}^1M}\,\overset{2\times}{{}^1N}\,^1Q$		$\overset{6\times}{{}^3P}\,\overset{5\times}{{}^3D}\,\overset{9\times}{{}^3F}\,\overset{7\times}{{}^3G}\,\overset{9\times}{{}^3H}\,\overset{6\times}{{}^3I}\,\overset{6\times}{{}^3K}\,\overset{3\times}{{}^3L}\,\overset{3\times}{{}^3M}\,^3N\,^3O$		$^5S\,^5P\,\overset{3\times}{{}^5D}\,\overset{2\times}{{}^5F}\,\overset{3\times}{{}^5G}\,\overset{2\times}{{}^5H}\,\overset{2\times}{{}^5I}\,^5K\,^5L$		^7F	
f^5		$\overset{2\times}{{}^2S}\,\overset{5\times}{{}^2P}\,\overset{7\times}{{}^2D}\,\overset{10\times}{{}^2F}\,\overset{10\times}{{}^2G}\,\overset{9\times}{{}^2H}\,\overset{9\times}{{}^2I}\,\overset{7\times}{{}^2K}\,\overset{5\times}{{}^2L}\,\overset{4\times}{{}^2M}\,\overset{2\times}{{}^2N}\,^2O\,^2Q$		$\overset{2\times}{{}^4S}\,\overset{2\times}{{}^4P}\,\overset{6\times}{{}^4D}\,\overset{5\times}{{}^4F}\,\overset{7\times}{{}^4G}\,\overset{5\times}{{}^4H}\,\overset{5\times}{{}^4I}\,\overset{3\times}{{}^4K}\,\overset{3\times}{{}^4L}\,^4M\,^4N$		$^6P\,^6D\,^6F\,^6G\,^6H\,^6I$		^8S

Table 1: *Multiplet terms of l^N shells. The last entry in each row is the Hund's rule ground state.*

2.1.4 Electron-hole symmetry

Because of the Pauli principle, $\left(c^\dagger\right)^2 = 0$, the state of a filled shell

$$|n,l\rangle := \prod_{m=l}^{-l} c^\dagger_{n,l,m,\uparrow} \prod_{m=l}^{-l} c^\dagger_{n,l,m,\downarrow}|0\rangle =: \prod_{m,\sigma} c^\dagger_{n,l,m,\sigma}|0\rangle \tag{10}$$

behaves as vacuum state for the creators $c^\dagger_{n,m,l,\sigma}$, while the annihilators create holes in the shell, e.g., $s_{0\uparrow}|n,0\rangle = s_{0\uparrow}\, s^\dagger_{0\uparrow} s^\dagger_{0\downarrow}|0\rangle = s^\dagger_{0,\downarrow}|0\rangle$ or $p_{1\downarrow}|n,1\rangle = -p^\dagger_{1\uparrow}p^\dagger_{0,\uparrow}p^\dagger_{-1\uparrow}p^\dagger_{0,\downarrow}p^\dagger_{-1\downarrow}|0\rangle$, or in general

$$c_{n,l,m,\sigma}|n,l\rangle = (-1)^{l-m+1/2-\sigma} \prod_{m',\sigma'} \left(c^\dagger_{n,l,m',\sigma'}\right)^{1-\delta_{m,m'}\delta_{\sigma,\sigma'}}|0\rangle. \tag{11}$$

Applying a lexicographically ordered product of operators $\tilde{h}^\dagger_{n,l,m,\sigma} := (-1)^{l-m+1/2-\sigma} c_{n,l,m,\sigma}$ specified by occupation numbers $n_{n,l,m,\sigma} \in \{0,1\}$ on $|n,l\rangle$ thus simply creates the corresponding holes in the shell

$$\prod_{m,\sigma} \left(\tilde{h}^\dagger_{n,l,m,\sigma}\right)^{n_{m\sigma}}|n,l\rangle = \prod_{m,\sigma} \left(c^\dagger_{n,l,m,\sigma}\right)^{1-n_{m\sigma}}|0\rangle. \tag{12}$$

For more than half-filling, this is an economical way of representing the $2(2l{+}1){-}N$-electron states as N-hole states. To work in this hole-representation, we also have to express the observables in the new operators, e.g.,

$$L_z = \sum m\, c^\dagger_{n,l,m,\sigma} c_{n,l,m,\sigma} = -\sum m\, \tilde{h}^\dagger_{n,l,m,\sigma} \tilde{h}_{n,l,m,\sigma} \tag{13}$$

and likewise for S_z. We can make the operators have the same form in electron- and hole-representation by defining

$$h^\dagger_{n,l,-m,-\sigma} := \tilde{h}^\dagger_{n,l,m,\sigma} = (-1)^{l-m+1/2-\sigma} c_{n,l,m,\sigma} \tag{14}$$

so that

$$L_z = \sum m\, c^\dagger_{n,l,m,\sigma} c_{n,l,m,\sigma} = \sum m\, h^\dagger_{n,l,m,\sigma} h_{n,l,m,\sigma} \tag{15}$$

$$S_z = \sum \sigma\, c^\dagger_{n,l,m,\sigma} c_{n,l,m,\sigma} = \sum \sigma\, h^\dagger_{n,l,m,\sigma} h_{n,l,m,\sigma} \tag{16}$$

while

$$\begin{aligned} L_\pm &= \sum_{n,l,m,\sigma} \sqrt{(l{\pm}m{+}1)(l{\mp}m)}\, c^\dagger_{n,l,m\pm1,\sigma}\, c_{n,l,m,\sigma} \\ &= \sum_{n,l,m,\sigma} \sqrt{(l{\pm}m{+}1)(l{\mp}m)}\, h^\dagger_{n,l,-m,-\sigma}\, h_{n,l,-m\mp1,-\sigma} \\ &= \sum_{n,l,m',\sigma'} \sqrt{(l{\mp}m')(l{\pm}m'{+}1)}\, h^\dagger_{n,l,m'\pm1,\sigma'}\, h_{n,l,m',\sigma'} \end{aligned} \tag{17}$$

and similarly for $S_\pm$. Thus $\vec{L}$ and $\vec{S}$ operate in the same way on N-electron basis states $\prod \left(c^\dagger_{n,l,m,\sigma}\right)^{n_{m\sigma}}|0\rangle$ as they do on the corresponding N-hole basis $\prod \left(h^\dagger_{n,l,-m,-\sigma}\right)^{n_{m\sigma}}|n,l\rangle$. We

can thus translate any N-electron state constructed in the previous sections into an N-hole state with the same quantum numbers by simply replacing the basis states. The corresponding $2(2l{+}1){-}N$-electron state is then obtained from the relation (12), where we have to remember to invert the ordering of the N-hole operators, which just gives an overall sign of $(-1)^{N-1}$.
As an example we consider the p^2 singlet (5)

$$|0,0;\,0,0\rangle_2 = \frac{1}{\sqrt{3}}\big(-p^\dagger_{1\uparrow}p^\dagger_{-1\downarrow} + p^\dagger_{0\uparrow}p^\dagger_{0\downarrow} - p^\dagger_{-1\uparrow}p^\dagger_{1\downarrow}\big)|0\rangle\,.$$

Replacing $p^\dagger_{m\sigma} \to h^\dagger_{-m,-\sigma}$ and $|0\rangle \to |n,2\rangle$, the corresponding 2-hole/4-electron state is

$$\begin{aligned}|0,0;\,0,0\rangle_4 &= \frac{1}{\sqrt{3}}\big(-h^\dagger_{-1\downarrow}h^\dagger_{1\uparrow} + h^\dagger_{0\downarrow}h^\dagger_{0\uparrow} - h^\dagger_{1\downarrow}h^\dagger_{-1\uparrow}\big)|n,2\rangle\\ &= -\frac{1}{\sqrt{3}}\big(-p^\dagger_{0\uparrow}p^\dagger_{-1\uparrow}p^\dagger_{1\downarrow}p^\dagger_{0\downarrow} + p^\dagger_{1\uparrow}p^\dagger_{-1\uparrow}p^\dagger_{1\downarrow}p^\dagger_{-1\downarrow} - p^\dagger_{1\uparrow}p^\dagger_{0\uparrow}p^\dagger_{0\downarrow}p^\dagger_{-1\downarrow}\big)|0\rangle,\end{aligned}$$

Using the Kramers pair (6) it is easily verified that this is indeed the p^4 singlet $\propto \big(K_1^\dagger\big)^2|0\rangle$.

2.2 Hamiltonian matrix elements

So far we have merely used the symmetries of the Hamiltonian to construct its eigenstates. For d- and f-shells we saw, however, that certain multiplet terms can appear several times. In these cases we might use, e.g., seniority to get a unique prescription for constructing the states in those terms. The seniority states are, however, in general no longer eigenstates of the Hamiltonian. To proceed further we need to look at the Hamiltonian in more detail.
As we are working in the spherical mean-field basis, the spin-orbitals

$$\varphi_{n,l,m,\sigma}(\vec{r}) = \frac{u_{n,l}(r)}{r}\,Y_{l,m}(\vartheta,\varphi)\,\chi_\sigma \tag{18}$$

diagonalize $H_{\mathit{eff}} = -\nabla^2/2 - Z/|\vec{r}| + V_{MF}(r)$ and we consider the operator

$$\varDelta H = \sum_{i<j}\frac{1}{|\vec{r}_i{-}\vec{r}_j|} - \sum_i V_{MF}(|\vec{r}_i|) \tag{19}$$

In second quantization the spherical mean-field has matrix elements

$$\langle n,l,m,\sigma|V_{MF}|n',l',m',\sigma'\rangle = \delta_{l,l'}\,\delta_{m,m'}\,\delta_{\sigma,\sigma'}\int dr\,\overline{u_{n,l}(r)}\,V_{MF}(r)\,u_{n',l}(r)\,. \tag{20}$$

For an l^N-shell spanned by N spin-orbitals with the same quantum numbers n and l the spherical mean-field is thus proportional to the identity, giving a mere shift of the entire shell. We can therefore neglect it when we are only interested in the splitting of the shell. The matrix elements of the electron-electron repulsion are, obviously, more interesting. Abbreviating the quantum numbers of a spin-orbital as $\alpha := n_\alpha, l_\alpha, m_\alpha, \sigma_\alpha$ and using the expansion of the Coulomb repulsion in products of spherical harmonics (85) we get

$$\Big\langle \alpha,\beta \Big| \frac{1}{|\vec{r}-\vec{r}\,'|} \Big| \gamma,\delta \Big\rangle = \int d^3r\, d^3r'\, \overline{\varphi_\alpha(\vec{r})}\,\overline{\varphi_\beta(\vec{r}\,')}\, \frac{1}{|\vec{r}-\vec{r}\,'|}\, \varphi_\gamma(\vec{r}\,')\varphi_\delta(\vec{r})\; \delta_{\sigma_\alpha,\sigma_\delta}\, \delta_{\sigma_\beta,\sigma_\gamma}$$

$$= \sum_k F^{(k)}_{\alpha,\beta,\gamma,\delta}\, \frac{4\pi}{2k+1} \sum_{\mu=-k}^{k} \langle Y_\alpha | Y_{k,\mu}\, Y_\delta\rangle\, \langle Y_\beta Y_{k,\mu} | Y_\gamma\rangle\; \delta_{\sigma_\alpha,\sigma_\delta}\, \delta_{\sigma_\beta,\sigma_\gamma} \tag{21}$$

with the Slater integrals

$$F^{(k)}_{\alpha,\beta,\gamma,\delta} := \int_0^\infty dr\, \overline{u_\alpha(r)}\, u_\delta(r) \int_0^\infty dr'\, \overline{u_\beta(r')}\, u_\gamma(r')\; \frac{\min(r,r')^k}{\max(r,r')^{k+1}}. \tag{22}$$

For a shell with fixed n and l they simplify to

$$F^{(k)}_{n,l} := \int_0^\infty dr\, \big|u_{n,l}(r)\big|^2 \left(\frac{1}{r^{k+1}} \int_0^r dr'\, r'^k\, \big|u_{n,l}(r')\big|^2 + r^k \int_r^\infty dr'\, \frac{\big|u_{n,l}(r')\big|^2}{r'^{k+1}} \right) \tag{23}$$

with $F^{(0)}_{n,l} > F^{(2)}_{n,l} > \cdots > 0$. In practice the ratios of the Slater integrals turn out to be quite close to those obtained for hydrogen orbitals, e.g., $F^{(4)}_{3,2}/F^{(2)}_{3,2} \approx 15/23$. The μ sum-rule for the Gaunt coefficients (App. D) implies $m_\delta - m_\alpha = \mu = m_\beta - m_\gamma$, so that also using the l sum-rule and the notation (94) we can write the electron-electron repulsion in an l^N shell as

$$H_{ee} = \frac{1}{2} \sum_{m\sigma,m'\sigma'} \sum_{k=0,2,\ldots,2l} F^{(k)}_{n,l} \sum_{\Delta m=-k}^{k} (-1)^{\Delta m} c^{(k,l,l)}_{m+\Delta m,m}\, c^{(k,l,l)}_{m'-\Delta m,m'}\; l^\dagger_{m+\Delta m,\sigma}\, l^\dagger_{m'-\Delta m,\sigma'}\, l_{m',\sigma'}\, l_{m,\sigma} \tag{24}$$

The direct terms, $\Delta m = 0$, have a simple classical interpretation: expanding the charge density of orbital $\varphi_{n,l,m}(\vec{r})$ using (90) into multipole components, we see that the diagonal matrix elements of the Hamiltonian $U^{(k)}_{m.m'} := F^{(k)}_{n,l}\, c^{(k,l,l)}_{m,m}\, c^{(k,l,l)}_{m',m'}$ are nothing but electrostatic interaction energies: k=0 the monopole-monopole interaction, k=2 dipole-dipole, etc. For $\sigma = \sigma'$ there are additional density-density terms when $\Delta m = m'-m$, with, using (95), matrix elements $J^{(k)}_{m,m'} := F^{(k)}_{n,l}\big(c^{(k,l,l)}_{m,m'}\big)^2$. The diagonal part of (24) can then be written as

$$H_{diag} = \frac{1}{2} \sum_{m,\sigma,m',\sigma'} \sum_k \big(U^{(k)}_{m,m'} - \delta_{\sigma,\sigma'} J^{(k)}_{m,m'}\big)\big(n_{m'\sigma'} - \delta_{m,m'}\delta_{\sigma,\sigma'}\big) n_{m\sigma}. \tag{25}$$

Exchange terms appear only for equal spins, and the subtraction of the self interaction is already ensured by the matrix elements, since $U^{(k)}_{m,m} = J^{(k)}_{m,m}$.

The $k=0$ contribution to H_{ee} is easily evaluated using $c^{(0,l,l)}_{m,m'} = \delta_{m,m'}$

$$H^{(k=0)}_{ee} = \frac{F^{(0)}_{n,l}}{2} \sum_{m,\sigma,m'\sigma'} \big(1 - \delta_{\sigma,\sigma'}\delta_{m,m'}\big) n_{m'\sigma'} n_{m\sigma}. \tag{26}$$

We see that any state with N electrons $H^{(0)}_{ee}$ contributes $F^{(0)}_{n,l}\, N(N-1)/2$ to the energy; i.e., the monopole-monopole interaction gives the charging energy of the shell but does not contribute to the splitting.

Because of the spin-independence of the electron-electron repulsion, H_{ee} is block-diagonal in the spin-indices. In the $\uparrow\downarrow$-sector we have, e.g., for a p-shell, using $c^{(2,1,1)}_{m,m'}$ from App. D

$$H^{(k=2)}_{S_z=0} = \begin{pmatrix} p_{-1\uparrow}p_{-1\downarrow} \\ p_{-1\uparrow}p_{\ 0\downarrow} \\ p_{-1\uparrow}p_{\ 1\downarrow} \\ p_{\ 0\uparrow}p_{-1\downarrow} \\ p_{\ 0\uparrow}p_{\ 0\downarrow} \\ p_{\ 0\uparrow}p_{\ 1\downarrow} \\ p_{\ 1\uparrow}p_{-1\downarrow} \\ p_{\ 1\uparrow}p_{\ 0\downarrow} \\ p_{\ 1\uparrow}p_{\ 1\downarrow} \end{pmatrix}^{\dagger} \frac{F^{(2)}_{n,1}}{5^2} \begin{pmatrix} 1 &&&&&&&& \\ & -2 && 3 &&&&& \\ && 1 && -3 && 6 && \\ & 3 && -2 &&&&& \\ && -3 && 4 && -3 && \\ &&&&& -2 && 3 & \\ && 6 && -3 && 1 && \\ &&&&& 3 && -2 & \\ &&&&&&&& 1 \end{pmatrix} \begin{pmatrix} p_{-1\uparrow}p_{-1\downarrow} \\ p_{-1\uparrow}p_{\ 0\downarrow} \\ p_{-1\uparrow}p_{\ 1\downarrow} \\ p_{\ 0\uparrow}p_{-1\downarrow} \\ p_{\ 0\uparrow}p_{\ 0\downarrow} \\ p_{\ 0\uparrow}p_{\ 1\downarrow} \\ p_{\ 1\uparrow}p_{-1\downarrow} \\ p_{\ 1\uparrow}p_{\ 0\downarrow} \\ p_{\ 1\uparrow}p_{\ 1\downarrow} \end{pmatrix} \tag{27}$$

where we have ordered the operators in the same way as in the basis states. In the particular ordering we chose, terms with Δm appear on the $2l\ \Delta m$-th side diagonal. Note how fixing the order of the operators ($\sigma=\downarrow$ and $\sigma'=\uparrow$) not only removes the prefactor $1/2$ but also makes the matrix of coefficients a two-electron *matrix* $\boldsymbol{H}^{(k)}_{\uparrow\downarrow}$ rather than a tensor in orbital space (App. B). The average direct interaction is defined via the trace of this $(2l{+}1)^2$-dimensional sector of the two-body matrix, which is invariant under basis changes that respect the spin symmetry,

$$U^{(k)}_{avg} := \sum_k \frac{\mathrm{Tr}\,\boldsymbol{H}^{(k)}_{\uparrow\downarrow}}{(2l{+}1)^2} = \frac{1}{(2l{+}1)^2}\sum_{m,m'} U^{(k)}_{m,m'} = \sum_k F^{(k)}_{n,l}\left(\frac{\mathrm{Tr}\,\boldsymbol{c}^{(k,l,l)}}{2l{+}1}\right)^2 = F^{(0)}_{n,l}\,\delta_{k,0} \tag{28}$$

where we used (84) in evaluating $\mathrm{Tr}\,\boldsymbol{c}^{(k,l,l)} = \delta_{k,0}$. We define the sum $U_{avg} := \sum_k U^{(k)}_{avg} = F^{(0)}_{n,l}$. The $\uparrow\uparrow$- and $\downarrow\downarrow$-sectors have identical matrices $\boldsymbol{H}^{(k)}_{\uparrow\uparrow} = \boldsymbol{H}^{(k)}_{\downarrow\downarrow}$ of dimension $(2l{+}1)2l/2$, e.g.,

$$H^{(k=2)}_{S_z=+1} = \begin{pmatrix} p_{0\uparrow}p_{-1\uparrow} \\ p_{1\uparrow}p_{-1\uparrow} \\ p_{1\uparrow}p_{\ 0\uparrow} \end{pmatrix}^{\dagger} \frac{F^{(2)}_{n,1}}{5^2} \begin{pmatrix} -5 && \\ & -5 & \\ && -5 \end{pmatrix} \begin{pmatrix} p_{0\uparrow}p_{-1\uparrow} \\ p_{1\uparrow}p_{-1\uparrow} \\ p_{1\uparrow}p_{\ 0\uparrow} \end{pmatrix}. \tag{29}$$

Since the matrix elements are spin-independent, these matrices are closely related to $\boldsymbol{H}^{(k)}_{\uparrow\downarrow}$: Defining the rectangular matrix $M_{(\tilde{m}'>\tilde{m}),\,(m',m)} = \big(\delta_{\tilde{m}',m'}\delta_{\tilde{m},m} - \delta_{\tilde{m}',m}\delta_{\tilde{m},m'}\big)/\sqrt{2}$, e.g., for $l{=}1$

$$\boldsymbol{M} := \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & -1 & 0 \end{pmatrix} \tag{30}$$

which maps $\uparrow\downarrow$-states into the corresponding ordered $\uparrow\uparrow$ basis states, we get

$$\boldsymbol{H}^{(k)}_{\uparrow\uparrow} = \boldsymbol{M}\boldsymbol{H}^{(k)}_{\uparrow\downarrow}\boldsymbol{M}^{\dagger} = \boldsymbol{H}^{(k)}_{\downarrow\downarrow}. \tag{31}$$

The average exchange interaction is defined similar to (28) in a basis-independent way via

$$U^{(k)}_{avg} - J^{(k)}_{avg} := \sum_k \frac{\mathrm{Tr}\,\boldsymbol{H}^{(k)}_{\uparrow\uparrow} + \mathrm{Tr}\,\boldsymbol{H}^{(k)}_{\downarrow\downarrow}}{(2l{+}1)2l} = \frac{1}{2l(2l{+}1)}\sum_{m,m'}\big(U^{(k)}_{m,m'} - J^{(k)}_{m,m'}\big) \tag{32}$$

so that

$$J^{(k)}_{avg} = \frac{1}{2l(2l{+}1)}\sum_{m,m'} J^{(k)}_{m,m'} - \frac{1}{2l}U^{(k)}_{avg} = \frac{1}{2l}\sum_{k=2}^{2l} F^{(k)}_{n,l}\, c^{(k,l,l)}_{0,0} \tag{33}$$

by using addition theorem (83) and multipole expansion (85) to rewrite the angular integrals

$$\sum_k \sum_{m,m'} J^{(k)}_{m,m'} = \int d^3r\, d^3r' \frac{\big|u_{n,l}(r)\big|^2}{r^2}\frac{\big|u_{n,l}(r')\big|^2}{r'^2}\Big|\underbrace{\sum_m \overline{Y_{l,m}(\vartheta,\varphi)}Y_{l,m}(\vartheta',\varphi')}_{\sqrt{(2l+1)/4\pi}Y_{l,0}(\arccos(\hat{r}\cdot\hat{r}'),0)}\Big|^2\ \underbrace{\frac{1}{|\vec{r}-\vec{r}'|}}_{\sum_k \frac{r_<^k}{r_>^{k+1}}P_k(\hat{r}\cdot\hat{r}')}\,.$$

The average exchange for the different shells is thus, using the (99) from App. D, given by

$$J_{avg} = \sum_k J^{(k)}_{avg} = \begin{cases} \frac{1}{5}\,F^{(2)}_{n,1} & p\text{-shell} \\ \frac{1}{14}\,F^{(2)}_{n,2} + \frac{1}{14}\,F^{(4)}_{n,2} & d\text{-shell} \\ \frac{2}{45}\,F^{(2)}_{n,3} + \frac{1}{33}\,F^{(4)}_{n,3} + \frac{50}{3^2{\cdot}11{\cdot}13}\,F^{(6)}_{n,3} & f\text{-shell} \end{cases} \tag{34}$$

2.2.1 Electron-hole symmetry

We have already seen that the eigenstates of the total angular momenta for a shell with N electrons and N holes are related by the simple transformation (14). Replacing the electron operators in (24) by the corresponding hole operators, renaming indices $\tilde{m} = -m{-}\Delta m$ and $\tilde{m}' = -m'{+}\Delta m$, and using the symmetries (95) and (96) of the Gaunt coefficients, we obtain

$$\begin{aligned} H_{ee} &= \frac{1}{2}\sum_{\tilde{m}\tilde{\sigma},\tilde{m}'\tilde{\sigma}'}\sum_k F^{(k)}_{n,l}\sum_{\Delta m=-k}^{k}(-1)^{\Delta m} c^{(k,l,l)}_{-\tilde{m},-\tilde{m}-\Delta m} c^{(k,l,l)}_{-\tilde{m}',-\tilde{m}'+\Delta m} h_{\tilde{m},\tilde{\sigma}}\, h_{\tilde{m}',\tilde{\sigma}'}\, h^\dagger_{\tilde{m}'-\Delta m,\tilde{\sigma}'}\, h^\dagger_{\tilde{m}+\Delta m,\tilde{\sigma}} \\ &= \frac{1}{2}\sum_{\tilde{m}\tilde{\sigma},\tilde{m}'\tilde{\sigma}'}\sum_k F^{(k)}_{n,l}\sum_{\Delta m=-k}^{k}(-1)^{\Delta m} c^{(k,l,l)}_{\tilde{m}+\Delta m,\tilde{m}} c^{(k,l,l)}_{\tilde{m}'-\Delta m,\tilde{m}'} \Big(h^\dagger_{\tilde{m}+\Delta m,\tilde{\sigma}}\, h^\dagger_{\tilde{m}'-\Delta m,\tilde{\sigma}'}\, h_{\tilde{m}',\tilde{\sigma}'}\, h_{\tilde{m},\tilde{\sigma}} \\ &\qquad\qquad + \big(\delta_{\Delta m,0} - \delta_{\tilde{m},\tilde{m}-\Delta m}\,\delta_{\tilde{\sigma},\tilde{\sigma}'}\big)\big(1 - n^h_{\tilde{m},\tilde{\sigma}} - n^h_{\tilde{m}',\tilde{\sigma}'}\big)\Big). \end{aligned} \tag{35}$$

The two-body part has the same form as when written in electron operators. The additional terms arising from normal-ordering the hole operators give the difference between the N-electron and the N-hole states, the superscript on the density operators is a reminder that they give the hole occupations. These terms involve only diagonal matrix elements such that we can write them in a concise form using the basis-independent averages (28) and (34), giving the relation between the energy of a state with N electrons and the conjugate $K{-}N$-electron state, where $K = 2(2l{+}1)$ is the number of spin-orbitals in the shell:

$$E(K{-}N) = E(N) + \left(\frac{K{-}1}{2}U_{avg} - \frac{K{-}2}{4}J_{avg}\right)\big((K{-}N) - N\big). \tag{36}$$

2.2.2 Racah parameters

For expressing energies in a compact way several conventions have been introduced. Condon and Shortley (table 1^6 of [12]) introduced parameters that include the least common prefactors of the Gaunt matrices (p. 30 in App. D) in the Slater integrals

$$\begin{aligned}
p\text{-shell:}\quad & F_0 := F^{(0)}_{n,1} \\
& F_2 := F^{(2)}_{n,1}/5^2 \\
d\text{-shell:}\quad & F_0 := F^{(0)}_{n,2} \\
& F_2 := F^{(2)}_{n,2}/7^2 \\
& F_4 := F^{(4)}_{n,2}/(3{\cdot}7)^2 \\
f\text{-shell:}\quad & F_0 := F^{(0)}_{n,3} \\
& F_2 := F^{(2)}_{n,3}/(3{\cdot}5)^2 \\
& F_4 := F^{(4)}_{n,3}/(3{\cdot}11)^2 \\
& F_6 := F^{(6)}_{n,3}\big(5/(3{\cdot}11{\cdot}13)\big)^2
\end{aligned}$$

so that, e.g., the diagonal terms in (25)

$$U^{(k)}_{m,m'}/F_k = c^{(k,l,l)}_{m,m}\,c^{(k,l,l)}_{m',m'} \qquad \text{and} \qquad J^{(k)}_{m,m'}/F_k = \big(c^{(k,l,l)}_{m,m'}\big)^2 \tag{37}$$

in the basis of spherical harmonics become integer matrices (App. D):

p-shell:

$$\boldsymbol{U}^{(2)} = F_2\begin{pmatrix} 1 & -2 & 1 \\ -2 & 4 & -2 \\ 1 & -2 & 1 \end{pmatrix} \qquad \boldsymbol{J}^{(2)} = F_2\begin{pmatrix} 1 & 3 & 6 \\ 3 & 4 & 3 \\ 6 & 3 & 1 \end{pmatrix} \tag{38}$$

d-shell:

$$\begin{aligned}
&\boldsymbol{U}^{(2)} = F_2\begin{pmatrix} 4 & -2 & -4 & -2 & 4 \\ -2 & 1 & 2 & 1 & -2 \\ -4 & 2 & 4 & 2 & -4 \\ -2 & 1 & 2 & 1 & -2 \\ 4 & -2 & -4 & -2 & 4 \end{pmatrix} \qquad \boldsymbol{J}^{(2)} = F_2\begin{pmatrix} 4 & 6 & 4 & 0 & 0 \\ 6 & 1 & 1 & 6 & 0 \\ 4 & 1 & 4 & 1 & 4 \\ 0 & 6 & 1 & 1 & 6 \\ 0 & 0 & 4 & 6 & 4 \end{pmatrix} \\
&\boldsymbol{U}^{(4)} = F_4\begin{pmatrix} 1 & -4 & 6 & -4 & 1 \\ -4 & 16 & -24 & 16 & -4 \\ 6 & -24 & 36 & -24 & 6 \\ -4 & 16 & -24 & 16 & -4 \\ 1 & -4 & 6 & -4 & 1 \end{pmatrix} \qquad \boldsymbol{J}^{(4)} = F_4\begin{pmatrix} 1 & 5 & 15 & 35 & 70 \\ 5 & 16 & 30 & 40 & 35 \\ 15 & 30 & 36 & 30 & 15 \\ 35 & 40 & 30 & 16 & 5 \\ 70 & 35 & 15 & 5 & 1 \end{pmatrix}
\end{aligned} \tag{39}$$

f-shell:

$$
\begin{aligned}
\frac{\boldsymbol{U}^{(2)}}{F_2} &= \begin{pmatrix} 25 & 0 & -15 & -20 & -15 & 0 & 25 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -15 & 0 & 9 & 12 & 9 & 0 & -15 \\ -20 & 0 & 12 & 16 & 12 & 0 & -20 \\ -15 & 0 & 9 & 12 & 9 & 0 & -15 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 25 & 0 & -15 & -20 & -15 & 0 & 25 \end{pmatrix}
&
\frac{\boldsymbol{J}^{(2)}}{F_2} &= \begin{pmatrix} 25 & 25 & 10 & 0 & 0 & 0 & 0 \\ 25 & 0 & 15 & 20 & 0 & 0 & 0 \\ 10 & 15 & 9 & 2 & 24 & 0 & 0 \\ 0 & 20 & 2 & 16 & 2 & 20 & 0 \\ 0 & 0 & 24 & 2 & 9 & 15 & 10 \\ 0 & 0 & 0 & 20 & 15 & 0 & 25 \\ 0 & 0 & 0 & 0 & 10 & 25 & 25 \end{pmatrix} \\
\frac{\boldsymbol{U}^{(4)}}{F_4} &= \begin{pmatrix} 9 & -21 & 3 & 18 & 3 & -21 & 9 \\ -21 & 49 & -7 & -42 & -7 & 49 & -21 \\ 3 & -7 & 1 & 6 & 1 & -7 & 3 \\ 18 & -42 & 6 & 36 & 6 & -42 & 18 \\ 3 & -7 & 1 & 6 & 1 & -7 & 3 \\ -21 & 49 & -7 & -42 & -7 & 49 & -21 \\ 9 & -21 & 3 & 18 & 3 & -21 & 9 \end{pmatrix}
&
\frac{\boldsymbol{J}^{(4)}}{F_4} &= \begin{pmatrix} 9 & 30 & 54 & 63 & 42 & 0 & 0 \\ 30 & 49 & 32 & 3 & 14 & 70 & 0 \\ 54 & 32 & 1 & 15 & 40 & 14 & 42 \\ 63 & 3 & 15 & 36 & 15 & 3 & 63 \\ 42 & 14 & 40 & 15 & 1 & 32 & 54 \\ 0 & 70 & 14 & 3 & 32 & 49 & 30 \\ 0 & 0 & 42 & 63 & 54 & 30 & 9 \end{pmatrix} \\
\frac{\boldsymbol{U}^{(6)}}{F_6} &= \begin{pmatrix} 1 & -6 & 15 & -20 & 15 & -6 & 1 \\ -6 & 36 & -90 & 120 & -90 & 36 & -6 \\ 15 & -90 & 225 & -300 & 225 & -90 & 15 \\ -20 & 120 & -300 & 400 & -300 & 120 & -20 \\ 15 & -90 & 225 & -300 & 225 & -90 & 15 \\ -6 & 36 & -90 & 120 & -90 & 36 & -6 \\ 1 & -6 & 15 & -20 & 15 & -6 & 1 \end{pmatrix}
&
\frac{\boldsymbol{J}^{(6)}}{F_6} &= \begin{pmatrix} 1 & 7 & 28 & 84 & 210 & 462 & 924 \\ 7 & 36 & 105 & 224 & 378 & 504 & 462 \\ 28 & 105 & 225 & 350 & 420 & 378 & 210 \\ 84 & 224 & 350 & 400 & 350 & 224 & 84 \\ 210 & 378 & 420 & 350 & 225 & 105 & 28 \\ 462 & 504 & 378 & 224 & 105 & 36 & 7 \\ 924 & 462 & 210 & 84 & 28 & 7 & 1 \end{pmatrix}
\end{aligned}
\tag{40}
$$

In addition, Racah introduced sets of parameters

d-shell: [6], Eq. (77)

$$
\begin{aligned}
A &:= F_0 - 7^2 F_4 \\
B &:= F_2 - 5\, F_4 \\
C &:= 5{\cdot}7\, F_4
\end{aligned}
\tag{41}
$$

f-shell [8], Eq. (66)

$$
\begin{aligned}
E^0 &:= F_0 - 2{\cdot}5 F_2 - 3{\cdot}11 F_4 - 2{\cdot}11{\cdot}13 F_6 \\
9E^1 &:= 2{\cdot}5{\cdot}7\, F_2 + 3{\cdot}7{\cdot}11 F_4 + 2{\cdot}7{\cdot}11{\cdot}13 F_6 \\
9E^2 &:= F_2 - 3\, F_4 + 7\, F_6 \\
3E^3 &:= 5\, F_2 + 2{\cdot}3\, F_4 - 7{\cdot}13 F_6
\end{aligned}
\tag{42}
$$

which are “different from those adopted empirically” in [6], Eq. (96)

$$
\begin{aligned}
A &:= F_0 - 3{\cdot}7\, F_4 - 2^2{\cdot}3^2{\cdot}13\, F_6 \\
5\, B &:= 5\, F_2 + 2{\cdot}3\, F_4 - 7{\cdot}13\, F_6 \\
5\, C &:= 7\, F_4 + 2{\cdot}3{\cdot}7\, F_6 \\
D &:= 2{\cdot}3{\cdot}7{\cdot}11\, F_6
\end{aligned}
\tag{43}
$$

2.2.3 Hund's rules

Quite remarkably, Friedrich Hund was able formulate rules for determining the multiplet term of lowest energy even before the many-body Schrödinger equation was known. Using addition of angular momenta and Pauli principle to analyze spectral data, he found that [1]

1. The lowest term has maximum multiplicity, i.e., maximum total spin S
2. For given multiplicity, the lowest term has largest total orbital momentum L

We can understand these two rules heuristically: 1. Because of the Pauli principle electrons of the same spin have a lower probability of close encounters, reducing their repulsion due to the exchange hole. 2. An electron configuration of larger total orbital momentum must have the electrons contribute in a more coordinated way to the angular momentum, helping them avoid each other.
Because the Hund's rule states are defined by maximum S and, given S, maximum L, they must vanish under application of the ladder operators S_+ and L_+. Hence at least some states of the Hund's rule term must be Slater determinants. They are easily constructed. Using the occupation number representation in our chosen sorting of the basis

$$|n_{l\uparrow}, n_{l-1\uparrow}, \cdots, n_{-l\uparrow}, n_{l\downarrow}, \dots, n_{-l\downarrow}\rangle := \big(l^\dagger_{l,\uparrow}\big)^{n_{l\uparrow}} \cdots \big(l^\dagger_{-l,\uparrow}\big)^{n_{-l\uparrow}} \big(l^\dagger_{l,\downarrow}\big)^{n_{l\downarrow}} \cdots \big(l^\dagger_{-l,\downarrow}\big)^{n_{-l\downarrow}} |0\rangle \tag{44}$$

the Hund's rule determinant with maximum Σ and M for N electrons are given by filling the orbitals from left to right, i.e., setting the first N occupations to one. For the p-shell this gives $\Phi_{p^1}{=}|100000\rangle$, $\Phi_{p^2}{=}|110000\rangle$, $\Phi_{p^3}{=}|111000\rangle$, $\Phi_{p^4}{=}|111100\rangle$, and $\Phi_{p^5}{=}|111110\rangle$. The total spin and angular momentum of the Hund's term are

$$S_{Hund}(l^N) = \tilde{N}/2\,,\; L_{Hund}(l^N) = \big((2l{+}1){-}\tilde{N}\big)\tilde{N}/2 \quad \text{with } \tilde{N} = (2l{+}1){-}\big|(2l{+}1){-}N\big|. \tag{45}$$

To find the energy of Hund's determinants we only need the diagonal elements of the Hamiltonian (25) that are collected in the $\boldsymbol{U}$ and $\boldsymbol{J}$ matrices

$$E_{Hund} = \langle \Phi_{Hund}|H_{ee}|\Phi_{Hund}\rangle = \sum_{m\sigma<m'\sigma':occ} \big(U_{m,m'} - \delta_{\sigma,\sigma'} J_{m,m'}\big), \tag{46}$$

where the sum is over the ordered pairs of occupied orbitals. For shells with less than two electrons there are obviously no pairs of occupied orbitals, so that the energy vanishes. For higher fillings we get, using the matrix elements given in Sec. 2.2.2, e.g.,

$$E_{Hund}(p^2) = F_0 - 5F_2 \quad E_{Hund}(p^3) = 3F_0 - 15F_2$$

$$E_{Hund}(d^2) = F_0 - 8F_2 - 9F_4 \quad E_{Hund}(d^3) = 3F_0 - 15F_2 - 72F_4$$

$$E_{Hund}(d^4) = 6F_0 - 21F_2 - 189F_4 \quad E_{Hund}(d^5) = 10F_0 - 35F_2 - 315F_4$$

For $N > 2l{+}1$ there are also pairs of opposite spin, for which the exchange term does not contribute. They are most easily calculated using the electron-hole relation (36).

2.2.4 Moments and spectral variance

The Slater-Condon integrals give no direct measure of the size of the multiplet splitting: with identical parameters the splitting changes, e.g., substantially with the number of electrons N in the shell. A measure of the width of the spectrum is its variance $\langle E^2\rangle - \langle E\rangle^2$, with the average defined by

$$\big\langle f(E)\big\rangle := \frac{1}{\dim_H}\sum_n f(E_n)\,, \tag{47}$$

where $\dim_H = \binom{K}{N}$ is the dimension of the Hilbert space. Quite remarkably, we can determine these moments from the representation of the Hamiltonian in terms of a two-body matrix $\boldsymbol{H}$ with blocks given by, e.g., (27) and (29), obtaining information about the N-electron spectrum without having to do any many-body calculations.

By the invariance of the trace, the average energy $\langle E\rangle$ involves only the diagonal terms in the N-electron Hamiltonian. For a density-density term $n_{m\sigma}n_{m'\sigma'}$ to contribute, the two orbitals must be occupied. In the Slater determinant basis for N electrons in $K=2(2l{+}1)$ spin-orbitals this fixes two electrons in two orbitals, so that for any $m,\sigma > m',\sigma'$ there are $\binom{K-2}{N-2}$ such configurations, hence

$$\binom{K}{N}\langle E\rangle := \sum_n E_n = \mathrm{Tr}_N\, H_{ee} = \binom{K{-}2}{N{-}2}\,\mathrm{Tr}\,\boldsymbol{H} \tag{48}$$

which simplifies with $\binom{n}{k} = \frac{n}{k}\binom{n-1}{k-1}$ to

$$\langle E\rangle = \frac{N(N{-}1)}{K(K{-}1)}\,\mathrm{Tr}\,\boldsymbol{H}. \tag{49}$$

Since U_{avg} and J_{avg} are defined via the traces of the blocks $\boldsymbol{H}_{\uparrow\downarrow}$ and $\boldsymbol{H}_{\uparrow\uparrow} = \boldsymbol{H}_{\downarrow\downarrow}$, we can write

$$\mathrm{Tr}\,\boldsymbol{H} = (2l{+}1)^2 U_{avg} + 2\cdot(2l{+}1)2l/2\big(U_{avg} - J_{avg}\big) = (2l{+}1)\big((4l{+}1)U_{avg} - 2lJ_{avg}\big), \tag{50}$$

so that the center of gravity of the multiplet terms of l^N is

$$\big\langle E(l^N)\big\rangle = \frac{N(N{-}1)}{2}\left(U_{avg} - \frac{2l}{4l{+}1}J_{avg}\right). \tag{51}$$

To calculate the second moment, we split the N-electron Hamiltonian into its diagonal, and the parts that create single and double excitations: $H_{ee} = H_{diag}{+}H_{single}{+}H_{double}$. To contribute to the trace of H_{ee}^2 calculated in the Slater determinant basis, every excitation must be undone, i.e.,

$$\binom{K}{N}\langle E^2\rangle = \mathrm{Tr}_N\, H_{diag}^2 + \mathrm{Tr}_N\, H_{single}^2 + \mathrm{Tr}_N\, H_{double}^2. \tag{52}$$

The traces over the N-electron space can, again, be reduced to traces over two-electron matrices $\boldsymbol{H} = \boldsymbol{H}_{diag} + \boldsymbol{H}_{single} + \boldsymbol{H}_{double}$. A double excitation involves two electrons moving from occupied to unoccupied orbitals, so that the reduction to $\mathrm{Tr}\,\boldsymbol{H}_{double}^2$ involves a combinatorial factor $\binom{K-4}{N-2}$

$$\mathrm{Tr}_N\, H_{double}^2 = \binom{K{-}4}{N{-}2}\sum_{\substack{\alpha<\beta,\,\gamma>\delta\\ \{\alpha,\beta\}\cap\{\gamma,\delta\}=\emptyset}}\big|H_{(\alpha\beta)(\gamma\delta)}\big|^2 = \binom{K{-}4}{N{-}2}\,\mathrm{Tr}\,\boldsymbol{H}_{double}^2. \tag{53}$$

Single excitations are one-body-like, so it is convenient to define the single-electron part of $\boldsymbol{H}$ by collecting all the matrix elements contributing to the same excitation $\alpha \leftarrow \beta$, e.g., $c^\dagger_\alpha n_\gamma c_\beta$

$$\big(\boldsymbol{H}_1\big)_{\alpha,\beta} := \sum_{\alpha,\beta<\gamma} H_{(\alpha\gamma)(\gamma\beta)} - \sum_{\alpha<\gamma<\beta} H_{(\alpha\gamma)(\beta\gamma)} - \sum_{\beta<\gamma<\alpha} H_{(\gamma\alpha)(\gamma\beta)} + \sum_{\gamma<\alpha,\beta} H_{(\gamma\alpha)(\beta\gamma)} = \sum_{\gamma} H_{(\alpha\gamma)(\gamma\beta)}, \tag{54}$$

where the last sum has no ordering but we know that sorting the indices $(\alpha\gamma)$ and $(\gamma\beta)$ gives the appropriate signs. For $\alpha \neq \beta$, $\boldsymbol{H}_1$ contains all single excitations, so

$$\begin{aligned}\mathrm{Tr}_N\, H^2_{single} &= \binom{K{-}3}{N{-}2} \sum_{\alpha\neq\beta,\gamma} \big|H_{(\alpha\gamma)(\gamma\beta)}\big|^2 + \binom{K{-}4}{N{-}3} \sum_{\alpha\neq\beta,\gamma\neq\tilde\gamma} H_{(\alpha\gamma)(\gamma\beta)} H_{(\beta\tilde\gamma)(\tilde\gamma\alpha)} \\ &= \binom{K{-}4}{N{-}2}\, \mathrm{Tr}\, \boldsymbol{H}^2_{single} + \binom{K{-}4}{N{-}3} \sum_{\alpha\neq\beta,\gamma,\tilde\gamma} H_{(\alpha\gamma)(\gamma\beta)} H_{(\beta\tilde\gamma)(\tilde\gamma\alpha)}\end{aligned} \tag{55}$$

where we used $\binom{n}{k} = \binom{n-1}{k} + \binom{n-1}{k-1}$ to split the first term and add part of it to the second to eliminate the constraint $\gamma \neq \tilde\gamma$. For the diagonal contribution we get three terms, depending on how many orbitals are involved in the density-density operators

$$\begin{aligned}&\mathrm{Tr}_N H^2_{diag} = \\ &= \binom{K{-}2}{N{-}2} \sum_{\alpha<\beta} H^2_{(\alpha\beta)(\beta\alpha)} + \binom{K{-}3}{N{-}3} \sum_{\substack{\alpha<\beta;,\tilde\alpha<\tilde\beta \\ |\{\alpha,\beta\}\cap\{\tilde\alpha,\tilde\beta\}|=1}} H_{(\alpha\beta)(\beta\alpha)} H_{(\tilde\alpha\tilde\beta)(\tilde\beta\tilde\alpha)} + \binom{K{-}4}{N{-}4} \sum_{\substack{\alpha<\beta;,\tilde\alpha<\tilde\beta \\ |\{\alpha,\beta\}\cap\{\tilde\alpha,\tilde\beta\}|=0}} H_{(\alpha\beta)(\beta\alpha)} H_{(\tilde\alpha\tilde\beta)(\tilde\beta\tilde\alpha)} \\ &= \binom{K{-}4}{N{-}2}\, \mathrm{Tr}\, \boldsymbol{H}^2_{diag} + \binom{K{-}4}{N{-}3} \Bigg(2 \sum_{\alpha<\beta} H^2_{(\alpha\beta)(\beta\alpha)} + \sum_{\substack{\alpha<\beta;,\tilde\alpha<\tilde\beta \\ |\{\alpha,\beta\}\cap\{\tilde\alpha,\tilde\beta\}|=1}} H_{(\alpha\beta)(\beta\alpha)} H_{(\tilde\alpha\tilde\beta)(\tilde\beta\tilde\alpha)}\Bigg) + \binom{K{-}4}{N{-}4} \big(\mathrm{Tr}\, \boldsymbol{H}_{diag}\big)^2\end{aligned} \tag{56}$$

where the first and second term were split as above. Writing the middle terms as unsorted sums over orbitals and combining them with the corresponding single-excitation term, we get

$$\mathrm{Tr}_N\, H^2 = \binom{K{-}4}{N{-}2}\, \mathrm{Tr}\, \boldsymbol{H}^2 + \binom{K{-}4}{N{-}3}\, \mathrm{Tr}\, \boldsymbol{H}_1^2 + \binom{K{-}4}{N{-}4} \big(\mathrm{Tr}\, \boldsymbol{H}\big)^2, \tag{57}$$

This expression holds for a general two-body operator [13]. For the electron-electron interaction H_{ee} it simplifies further, since there are no single excitations (they would change the L_z eigenvalue), so that we obtain for the N-dependence of the splitting

$$\mathrm{var}_l(N) := \frac{\langle E^2\rangle - \langle E\rangle^2}{N(N{-}1)(4l{+}2-N)(4l{+}1-N)} \tag{58}$$

$$\mathrm{var}_p(N) = \frac{9}{20} {F_2}^2 \tag{59}$$

$$\mathrm{var}_d(N) = \frac{5{\cdot}13}{2} \left(\frac{F_2}{9}\right)^2 + \frac{5}{8} \left(\frac{F_2}{9} - 5F_4\right)^2 \tag{60}$$

$$\mathrm{var}_f(N) = 3{\cdot}5{\cdot}7 \left(\frac{{F_2}^2}{11{\cdot}13} + \frac{5{F_4}^2}{2^2{\cdot}13} + \big(7F_6\big)^2\right) + \frac{5}{2} \left(11\frac{F_2}{13} + 9\frac{F_4}{13} - 7F_6\right)^2. \tag{61}$$

3 Spin-orbit coupling

We started our discussion with the non-relativistic N-electron Hamiltonian (1). It only operates on the electron coordinates. In the non-relativistic theory, spin is added to the wave function in an ad-hoc way. An electron spin is, in fact, required by relativity, and has, through the Pauli principle, a major effect on the "non-relativistic" electronic structure. Relativistic corrections to the Hamiltonian, on the other hand, tend to be quite weak, as they scale with powers of the inverse speed of light, $1/c \approx 1/137$ in atomic units. The most prominent relativistic effect splitting the levels in an open shell is the coupling of the orbital- with its spin-moment, the spin-orbit coupling

$$H_{SO} = \sum_i \xi(r_i)\, \vec{L}_i \cdot \vec{S}_i \quad \text{with} \quad \xi(r) = \frac{1}{2c^2\, r} \frac{dV_{MF}(r)}{dr}\,. \tag{62}$$

It is a one-body interaction, that is easily diagonalized by a Clebsch-Gordan transformation from our spin-orbitals $\varphi_{n,l,m,\sigma}$ to orbitals of given total angular momentum $\vec{J}_i = \vec{L}_i + \vec{S}_i$, giving two sets of orbitals with total angular momentum quantum numbers $j{=}l{\pm}1/2$ and $\mu{=}-j\dots j$:

$$j^\dagger_{n,l\pm\frac{1}{2},\mu;l;\frac{1}{2}} := \sqrt{\frac{l{\mp}\mu{+}\frac{1}{2}}{2l{+}1}}\, c^\dagger_{n,l,\mu+\frac{1}{2},\downarrow} \pm \sqrt{\frac{l{\pm}\mu{+}\frac{1}{2}}{2l{+}1}}\, c^\dagger_{l,\mu-\frac{1}{2},\uparrow}\,. \tag{63}$$

In this basis we can easily calculate the variance of the spin-orbit-split spectrum:

$$\frac{\mathrm{var}_l^{SO}(N)}{N((4l{+}2){-}N)} = \frac{l(l{+}1)}{4(4l{+}1)} \int_0^\infty dr\, |u_{n,l}(r)|^2\, \xi(r). \tag{64}$$

The variance does, however, not show a simple quadratic dependence on N since, unlike the Slater integrals, the spin-orbit matrix elements increase strongly within a period. In fact, assuming a hydrogen-like system, they scale, for given quantum numbers n and l, as Z^4.

For light atoms the splitting is much smaller than the multiplet splitting, so that it can be treated by perturbation theory, splitting the multiplet terms ${}^{2S+1}L$ into multiplet levels ${}^{2S+1}L_J$ characterized by their total angular momentum J. By the third of Hund's rules, the lowest level is the one with $J = |L{-}S|$ when the shell is less than half-filled, while it has $J = L{+}S$ for $N > 2l{+}1$ (H_{SO} changes sign under the electron-hole transformation (14)). This two-step perturbation approach is called LS or Russell-Saunders coupling. The opposite approach, called jj coupling, of first doing perturbation theory in H_{SO} and then in H_{ee} is only of theoretical interest, since the spin-orbit coupling only becomes dominant for atoms that are so heavy that they are unstable.

Still, as H_{SO} does not commute with $\vec{L}$ and $\vec{S}$ individually, it couples different multiplet terms. For heavy atoms, where the spin-orbit splitting can become appreciable compared to the multiplet splitting, we have to treat H_{ee} and H_{SO} on the same footing, i.e., to diagonalize their sum on the states of an open shell. This approach is called intermediate coupling. Since the Hamiltonian in intermediate coupling has a significantly lower symmetry, the levels can no longer be (almost) uniquely characterized by angular momentum quantum numbers, so that the approach is more numerical in nature. Nevertheless, often the Russell-Saunders levels can give a good indication of the character of the intermediate-coupling levels.

4 Conclusions

We have seen that the description of even a single atom or ion poses a complex many-body problem. Atoms are round [14], so the algebra of angular momenta is key to understanding the structure of their electronic states: Arguments based on angular momenta together with the Pauli exclusion principle allowed Friedrich Hund to formulate rules for the ground-state multiplets even before the Schrödinger equation was known.

Starting from the N-electron Schrödinger equation, we saw that switching from a wave function picture to the representation of many-body states in second quantization provided a crucial simplification by allowing us to represent only physical states and observables, making the construction of the multiplet states of the electron-electron interaction a problem of simple operator algebra. Writing the two-body interaction not as a tensor but as a matrix in 2-electron space makes it easy to perform basis transformations, define basis independent quantities like U_{avg} and J_{avg} from its trace, and even calculate the moments of the N-electron Hamiltonian entirely in terms of a small 2-body matrix. Finally we saw how simple it is in second quantization to relate states with the same number of electrons and holes.

A relativistic effect modifying the multiplet terms originates from the coupling of the orbital momentum with the electron spin. It is a single-body effect that is usually weak, so that it can be well described in degenerate perturbation theory on the multiplet terms. This is the LS- or Russell-Saunders coupling. The opposite procedure of first diagonalizing the spin-orbit Hamiltonian and then introducing the electron-electron repulsion on the degenerate spin-orbit terms, called jj coupling, is only of theoretical interest. For heavy atoms the spin-orbit splitting can, however, become large enough that H_{SO} has to be treated on the same footing as H_{ee}, which is the intermediate coupling scheme.

A systematic study of the interaction parameters including practical parametrizations can be found in [13]. Of particular practical relevance is the analysis of the relative importance of the electron-electron interaction versus the spin-orbit coupling across the periodic table, based on the ratio of the variance of the splitting induced by the respective interaction.

Our main interest in atoms is, of course, as the building block of matter. It is quite remarkable that a large part of their electronic structure survives in the solid, where atomic levels broaden into bands so that an understanding of the constituent atoms allows us to gain deep insights into the electronic structure of the resulting material [14].

Putting an atom in a crystal environment, of course does change its level structure. Particularly interesting is the effect of the potential created by the neighboring ions, which lifts the degeneracy of the levels in an atomic shell already on the single-electron level. Filling those crystal-field levels, following the Aufbauprinzip, results in low-spin states, competing with Hund's first rule, which favors high spin. A nice discussion of this can be found in [3].

To try out the methods explained in this chapter, you may perform practical calculations at

`https://www.cond-mat.de/sims/multiplet/`

A Atomic units

Practical electronic structure calculations are usually done in atomic units, a.u. for short. While the idea behind the atomic units is remarkably simple, in practice there is often some confusion when trying to convert to SI units. We therefore give a brief explanation.

The motivation for introducing atomic units is to simplify the equations. For example, in SI units the Hamiltonian of a hydrogen atom is

$$H = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0\, r}\,. \tag{65}$$

When we implement such an equation in a computer program, we need to enter the numerical values of all the fundamental constants. We can avoid this by inventing a system of units in which the *numerical values* of the electron mass m_e, the elementary charge e, the Planck-constant $\hbar$, and the dielectric constant $4\pi\epsilon_0$ are all equal to one. In these units the above equation can be programmed as

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r}\,. \tag{66}$$

This immediately tells us: 1 a.u. mass $= m_e$ and 1 a.u. charge $= e$. To complete the set of basis units we still need the atomic unit of length, which we call a_0, and of time, t_0. To find the values of a_0 and t_0 we write $\hbar$ and $4\pi\epsilon_0$ (using simple dimensional analysis) in atomic units: $\hbar = 1\, m_e a_0^2/t_0$ and $4\pi\epsilon_0 = 1\, t_0^2 e^2/(m_e a_0^3)$. Solving this system of equations, we find

$$\begin{array}{llllll}
\text{1 a.u. length} & = a_0 & = & 4\pi\epsilon_0\hbar^2/m_e e^2 & \approx 5.2918\cdot 10^{-11} & \text{m}\\
\text{1 a.u. mass} & = m_e & = & & \approx 9.1095\cdot 10^{-31} & \text{kg}\\
\text{1 a.u. time} & = t_0 & = & (4\pi\epsilon_0)^2\hbar^3/m_e e^4 & \approx 2.4189\cdot 10^{-17} & \text{s}\\
\text{1 a.u. charge} & = e & = & & \approx 1.6022\cdot 10^{-19} & \text{C}
\end{array}$$

The atomic unit of length, a_0, is the Bohr radius. As the dimension of energy is mass times length squared divided by time squared, its atomic unit is $m_e a_0^2/t_0^2 = m_e e^4/(4\pi\epsilon_0)^2\hbar^2$. Because of its importance the atomic unit of energy has a name, the Hartree. One Hartree is minus twice the ground-state energy of the hydrogen atom, about 27.211 eV.

It would be tempting to try to set the numerical value of all fundamental constants to unity. But this must obviously fail, as the system of equations to solve becomes overdetermined when we try to prescribe the numerical values of constants that are not linearly independent in the space of basis units. Thus, we cannot, e.g., choose also the speed of light to have value one, as would be practical for relativistic calculations. Instead, in atomic units it is given by $c\, t_0/a_0 = 4\pi\varepsilon_0\hbar c/e^2 = 1/\alpha$, where α is the fine structure constant. Thus $c = \alpha^{-1}$ a.u. $\approx$ 137 a.u. The Bohr magneton is $\mu_B = 1/2$ a.u. The Boltzmann constant k_B, on the other hand, is independent of the previous constants. Setting its value to one fixes the unit of temperature to 1 a.u. temperature $= m_e e^4/(4\pi\epsilon_0)^2\hbar^2 k_B = Ha/k_B \approx 3.158\cdot 10^5$ K.

B Second quantization

The formalism of second quantization for electrons is the generalization of the Dirac formalism of single-electron quantum mechanics to many-electron system. The key idea is to eliminate the coordinates of the wave function and absorb them in the representation of the operators instead. Wave functions are then written in terms of Dirac states using the Dirac delta function: $\varphi_n(x) = \langle x|n\rangle$. In second quantization, field operators $\hat{\Psi}(x)$ take the role of $\langle x|$, so that $\varphi_n(x) = \langle 0|\hat{\Psi}(x)\, c_n^\dagger|0\rangle$, where the orbital is represented by

$$c_n^\dagger := \int dx\, \varphi_n(x)\, \hat{\Psi}^\dagger(x)\,, \tag{67}$$

$|0\rangle$ is the zero-electron (vacuum) state defined by

$$\hat{\Psi}(x)|0\rangle = 0 \quad \text{and} \quad \langle 0|0\rangle = 1\,, \tag{68}$$

and the field operators are defined to fulfill the anticommutation relations $\big(\{a,\, b\} := ab + ba\big)$

$$\big\{\hat{\Psi}(x),\, \hat{\Psi}(x')\big\} = 0 \quad \text{and} \quad \big\{\hat{\Psi}(x),\, \hat{\Psi}^\dagger(x')\big\} = \delta(x{-}x')\,. \tag{69}$$

From the adjoint of the first anticommutator follows, in particular, that $\big(\hat{\Psi}(x)^\dagger\big)^2 = 0$, which is the Pauli exclusion principle in second quantization. These relations define the formalism completely.

The representation of single-electron functions generalizes to N-electron Slater determinants

$$\Phi_{\alpha_1\ldots\alpha_N}(x_1\ldots x_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \varphi_{\alpha_1}(x_1)\cdots & \varphi_{\alpha_N}(x_1) \\ \vdots & \vdots \\ \varphi_{\alpha_1}(x_N)\cdots & \varphi_{\alpha_N}(x_N)\end{vmatrix} = \frac{1}{\sqrt{N!}}\langle 0|\hat{\Psi}(x_1)\cdots\hat{\Psi}(x_N)\; c_{\alpha_N}^\dagger\cdots c_{\alpha_1}^\dagger|0\rangle. \tag{70}$$

Their overlap is

$$\begin{aligned}\int dx_1\cdots dx_N\, &\overline{\Phi_{\alpha_1\ldots\alpha_N}(x_1\ldots x_N)}\, \Phi_{\beta_1\ldots\beta_N}(x_1\ldots x_N) \\ &= \langle 0|c_{\alpha_1}\cdots c_{\alpha_N}\, c_{\beta_N}^\dagger\cdots c_{\beta_1}^\dagger|0\rangle = \begin{vmatrix}\langle\alpha_1|\beta_1\rangle\cdots & \langle\alpha_1|\beta_N\rangle \\ \vdots & \vdots \\ \langle\alpha_N|\beta_1\rangle\cdots & \langle\alpha_N|\beta_N\rangle\end{vmatrix}\end{aligned} \tag{71}$$

so that N-electron Slater determinants constructed from a complete orthonormal set of single-electron orbitals form an orthonormal basis of the N-electron Hilbert space, when only Slater determinants with some given ordering of the orbitals, e.g., $\alpha_1 < \alpha_2 < \ldots < \alpha_N$, are chosen.

The key point of (70) is that the second quantized form allows us to split the coordinates form the orbital content. The latter is the generalization of the Dirac state. Introducing the occupation number representation with $n_i \in \{0,1\}$ to make the chosen sorting of the orbitals and the corresponding operators manifest, a Slater state is written as

$$|n_1, n_2, \ldots\rangle := \prod_i \big(c_{n_i}^\dagger\big)^{n_i}|0\rangle. \tag{72}$$

The coordinates are then included in with the operators, giving the operators in second quantization. For a one-electron observable $\sum_{i=1}^{N} M_1(x_i)$ we find (see [4] for the derivations)

$$\hat{M}_1 = \int dx\, \hat{\Psi}^\dagger(x)\, M(x)\, \hat{\Psi}(x)\,, \tag{73}$$

for a two-electron operator $\sum_{i<j} M_2(x_i, x_j)$ we get

$$\hat{M}_2 = \frac{1}{2}\int dx \int dx'\, \hat{\Psi}^\dagger(x)\hat{\Psi}^\dagger(x')\, M(x,x')\, \hat{\Psi}(x')\hat{\Psi}(x)\,. \tag{74}$$

Quite remarkably, while the operators in first quantization contain an explicit N-dependence, the form of the same operator in second quantization is independent of the particle number. This makes second quantization so suitable for working in Fock space, as, e.g., in BCS theory. Another crucial advantage of working in the second-quantization formalism is that it only allows us to express physical, i.e., antisymmetric, wave functions and physical operators, i.e., those that act on all electrons in the same way (e.g., total angular momenta, but not angular momenta acting on an individual electron, which would violate the indistinguishability of electrons [4]). Given a complete orthonormal orbital basis $\{\varphi_n\}$, we can invert (67) to write the field-operators $\hat{\Psi}^\dagger$ as a linear combination of the orbital operators $c_n^\dagger$. Inserting this into (73), we get

$$\hat{M}_1 = \sum_{\alpha\beta} \langle\alpha|M_1|\beta\rangle\, c_\alpha^\dagger c_\beta \tag{75}$$

where the $\langle\alpha|M|\beta\rangle$ are the matrix elements of the one-body operator in the orbital basis. Similarly, we obtain

$$\hat{M}_2 = \frac{1}{2}\sum_{\alpha\beta\gamma\delta} \langle\alpha\beta|M_2|\gamma\delta\rangle\, c_\alpha^\dagger c_\beta^\dagger c_\gamma c_\delta \tag{76}$$

with the four-index tensor

$$\langle\alpha\beta|M_2|\gamma\delta\rangle \ := \int dx \int dx'\, \overline{\varphi_\alpha(x)\varphi_\beta(x')}\, M(x,x')\, \varphi_\gamma(x')\varphi_\delta(x). \tag{77}$$

Realizing that exchanging the two creation or annihilation operators in (76) connects the same many-body states, we can collect all four such terms by imposing an ordering on the operators:

$$\hat{M}_2 = \sum_{\alpha<\beta;\gamma>\delta} \big(\underbrace{\langle\alpha\beta|M_2|\gamma\delta\rangle - \langle\alpha\beta|M_2|\delta\gamma\rangle}_{=:M_{(\alpha\beta)(\gamma\delta)}}\big) c_\alpha^\dagger c_\beta^\dagger c_\gamma c_\delta\,. \tag{78}$$

Instead of a tensor, the $M_{(\alpha\beta)(\gamma\delta)}$ form a matrix in the two-electron-like space spanned by sorted pairs of operators. This makes them quite convenient to handle. Changes in the orbital basis like $c_\alpha^\dagger = \sum_n c_n^\dagger U_{n,\alpha}$ described by a unitary single-electron matrix $\boldsymbol{U}$ are then easily written as unitary transformation in two-electron space

$$c_\alpha^\dagger c_\beta^\dagger = \sum_{n,m} c_n^\dagger c_m^\dagger U_{n,\alpha} U_{m,\beta} = \sum_{n<m} c_n^\dagger c_m^\dagger \big(U_{n,\alpha}U_{m,\beta} - U_{m,\alpha}U_{n,\beta}\big) \tag{79}$$

which effects the basis change in the two-electron matrix $M_{(\alpha\beta)(\gamma\delta)}$.

C Addition theorem for spherical harmonics

Using the completeness of the spherical harmonics, we can expand any function of a single coordinate $f(\vec{r})=\sum_{m,l} a_{l,m}(r)\, Y_{l,m}(\vartheta,\varphi)$. Similarly, we can expand functions of two coordinates

$$f(\vec{r},\vec{r}\,') = \sum_{l,m} a_{l,m}(r,\, r',\vartheta',\varphi')\, Y_{l,m}(\vartheta,\varphi) = \sum_{l,m}\Big(\sum_{l',m'} a_{\substack{l,m,\\ l',m'}}(r,r')\, Y_{l',m'}(\vartheta',\varphi')\Big) Y_{l,m}(\vartheta,\varphi).$$

The expansion simplifies considerably when the function is invariant under simultaneous rotations of $\vec{r}$ and $\vec{r}\,'$, i.e., when $\big(\vec{L}+\vec{L}'\big)s(\vec{r},\vec{r}\,')=0$. This is, e.g., the case for any function that depends only on the scalar products of $\vec{r}$ and $\vec{r}\,'$, e.g.,

$$iL_x\, s(\vec{r}\cdot\vec{r}\,') = \left(r_y\frac{\partial}{\partial r_z} - r_z\frac{\partial}{\partial r_y}\right) s(r_x r_{x'} + r_y r_{y'} + r_z r_{z'}) = s'(\vec{r}\cdot\vec{r}\,')\big(r_y r_{z'} - r_z r_{y'}\big) = -iL'_x s(\vec{r}\cdot\vec{r}\,').$$

Then $s(\vec{r},\vec{r}\,')$ must be an eigenfunction of $\big(\vec{L}+\vec{L}'\big)^2$ with eigenvalue 0. From adding angular momenta we know that the products may only contain an $l_{tot}=0$ contribution when $l=l'$. In addition, $\big(L_z+L'_z\big)s(\vec{r},\vec{r}\,')=0$, i.e., $m'=-m$, so that

$$s(\vec{r},\vec{r}\,') = \sum_{l,m} a_{l,m}(r,r')\, Y_{l,-m}(\vartheta',\varphi')\, Y_{l,m}(\vartheta,\varphi)\,.$$

Using $\big(\vec{L}+\vec{L}'\big)^2 = \vec{L}^2 + \vec{L}'^2 + 2L_zL'_z + L_+L'_- + L_-L'_+$ with $L_\pm Y_{l,m} = \sqrt{(l\pm m+1)(l\mp m)}\, Y_{l,m\pm 1}$ we obtain a homogeneous linear system of equations

$$\begin{aligned} 0 &= \big(\vec{L}+\vec{L}'\big)^2\, s(\vec{r},\vec{r}\,') \\ &= \sum_{l,m}\Big(a_{l,m}\big(2l(l+1)-2m^2\big) + a_{l,m-1}(l+m)(l-m+1) + a_{l,m+1}(l-m)(l+m+1)\Big) Y'_{l,-m} Y_{l,m} \end{aligned}$$

with the non-trivial solution $a_{l,m}(r,r') = (-1)^m a_l(r,r')$. Hence

$$\begin{aligned} s(\vec{r},\vec{r}\,') &= \sum_{l=0}^{\infty} a_l(r,r') \sum_{m=-l}^{l} (-1)^m Y_{l,-m}(\vartheta',\varphi')\, Y_{l,m}(\vartheta,\varphi) &\quad (80)\\ &= \sum_{l=0}^{\infty} a_l(r,r') \sum_{m=-l}^{l} \overline{Y_{l,m}(\vartheta',\varphi')}\, Y_{l,m}(\vartheta,\varphi) &\quad (81) \end{aligned}$$

where (80) is reminiscent of a Kramers pair singlet (6). The expansion coefficients are easily calculated when choosing coordinates such that $\vec{r}\,' = r'\hat{z}$, i.e., $\vartheta'=0$

$$a_l(r,r') = \int_0^{2\pi} d\varphi \int_{-1}^{1} d\cos\vartheta\, \overline{Y_{l,0}(\vartheta,\varphi)} \sqrt{\frac{4\pi}{2l+1}}\, s(\vec{r},r'\hat{z}) \qquad (82)$$

For $s(\vec{r},\vec{r}\,') = P_l(\hat{r}\cdot\hat{r}')$ we find the addition theorem for spherical harmonics

$$P_l(\hat{r}\cdot\hat{r}') = \sqrt{\frac{4\pi}{2l+1}}\, Y_{l,0}(\arccos(\hat{r}\cdot\hat{r}'),0) = \frac{4\pi}{2l+1}\sum_{m=-l}^{l} \overline{Y_{l,m}(\vartheta',\varphi')}\, Y_{l,m}(\vartheta,\varphi)\,. \qquad (83)$$

Setting $\hat{r}' = \hat{r}$, it follows as a corollary that the charge density of closed shells is spherical

$$\sum_{m=-l}^{l} \big|Y_{l,m}(\vartheta,\varphi)\big|^2 = \frac{2l+1}{4\pi}\,. \tag{84}$$

For the electron-electron repulsion we obtain the multipole expansion

$$\frac{1}{|\vec{r}-\vec{r}'|} = \frac{1}{\sqrt{r^2-2\vec{r}\cdot\vec{r}'+r'^2}} = \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}}\, P_l(\hat{r}\cdot\hat{r}') = \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \overline{Y_{l,m}(\vartheta',\varphi')}\, Y_{l,m}(\vartheta,\varphi), \tag{85}$$

where the choice $r_< := \min(r,r')$ and $r_> := \max(r,r')$ makes the power series converge. The series is obtained from the generating function of the Legendre polynomials

$$\frac{1}{\sqrt{1-2xt+t^2}} = \sum_{n=0}^{\infty} P_n(x)\, t^n\,. \tag{86}$$

To convince ourselves that the $P_n(x)$ are indeed the Legendre polynomials, we expand the left-hand side in powers of t and find $P_0(x) = 1$ and $P_1(x) = x$. Taking the derivative of (86) with respect to t gives

$$\frac{x-t}{\big(1-2xt+t^2\big)^{3/2}} = \sum_{n=1}^{\infty} n\, P_n(x)\, t^{n-1}.$$

multiplying by $1-2xt+t^2$, inserting (86) on the left-hand side, and comparing coefficients for $n{>}0$, gives the recursion relation for the Legendre polynomials

$$(n{+}1)P_{n+1}(x) = (2n{+}1)x\, P_n(x) - n\, P_{n-1}(x)\,. \tag{87}$$

Likewise, a plane wave can be expanded into spherical plane waves

$$e^{i\vec{k}\cdot\vec{r}} = 4\pi \sum_{l=0}^{\infty} i^l\, j_l(kr) \sum_{m=-l}^{l} \overline{Y_{l,m}(\vartheta',\varphi')}\, Y_{l,m}(\vartheta,\varphi), \tag{88}$$

using the integral representation of the spherical Bessel functions

$$a_l(r,k) = 2\pi \int_{-1}^{1} dx\, P_l(x)\, e^{ikr\,x} = 4\pi\, i^l\, j_l(kr). \tag{89}$$

D Gaunt coefficients

Gaunt coefficients appear when expanding products of spherical harmonics

$$Y_{l,m}(\vartheta,\varphi)\,Y_{l',m'}(\vartheta,\varphi) = \sum_{k=0}^{\infty}\sum_{\mu=-k}^{k} \big\langle Y_{k,\mu}\big|Y_{l,m}Y_{l',m'}\big\rangle\, Y_{k,\mu}(\vartheta,\varphi)\,. \tag{90}$$

Because of the product rule, the angular momentum operators act on the product of the spherical harmonics the same way as they act on independent angular momenta, e.g.,

$$L_+\,Y_{l,m}\,Y_{l',m'} = \big(L_+\,Y_{l,m}\big)Y_{l',m'} + Y_{l,m}\,\big(L_+\,Y_{l',m'}\big)\,. \tag{91}$$

Thus, for fixed l, l', and k, the integrals of three spherical harmonics $\big\langle Y_{k,\mu}\big|Y_{l,m}Y_{l',m'}\big\rangle$ fulfill the same recursion relation as the Clebsch-Gordan coefficients $\langle k,\mu;\ l;\ l'|l,m;\ l',m'\rangle$ (Wigner-Eckart theorem). In particular, evaluating $\big\langle Y_{k,\mu}\big|L_z\big|Y_{l,m}Y_{l',m'}\big\rangle$ shows that the integrals vanish for $\mu \neq m{+}m'$ and consequently are real. More generally, the products $Y_{l,m}\,Y_{l',m'}$ behaves as if we were adding two angular momenta l and l', so that the $\big\langle Y_{k,m+m'}\big|Y_{l,m}Y_{l',m'}\big\rangle$ vanish for $k < |l{-}l'|$ and $k > l{+}l'$. The difference to adding angular momenta is that the products of spherical harmonics are not orthonormal (e.g., $\langle Y_{0,0}Y_{0,0}|Y_{l,m}Y_{l,-m}\rangle = (-1)^m/4\pi$), so that the space spanned by the $Y_{l,m}Y_{l',m'}$ for fixed l and l' may be smaller than $(2l{+}1){\times}(2l'{+}1)$. In fact, from the inversion symmetry $Y_{l,m}(\pi{-}\vartheta,\varphi{+}\pi) = (-1)^l\,Y_{l,m}(\vartheta,\varphi)$ of the spherical harmonics we see by changing the variables of integration that

$$\big\langle Y_{k,\mu}\big|Y_{l,m}Y_{l',m'}\big\rangle = (-1)^{k+l+l'}\big\langle Y_{k,\mu}\big|Y_{l,m}Y_{l',m'}\big\rangle \tag{92}$$

so that the coefficients also vanish when $k{+}l{+}l'$ is odd, and (90) consequently simplifies to

$$Y_{l,m}(\vartheta,\varphi)\,Y_{l',m'}(\vartheta,\varphi) = \sum_{k=|l-l'|,\,|l-l'|+2,\dots,\,l+l'} \big\langle Y_{k,m+m'}\big|Y_{l,m}Y_{l',m'}\big\rangle\, Y_{k,m+m'}(\vartheta,\varphi)\,. \tag{93}$$

Using $\overline{Y_{l,m}} = (-1)^m\,Y_{l,-m}$ we can write the Gaunt coefficients in a form more convenient for the use in the electron-electron repulsion part of the Hamiltonian

$$c^{(k,l,l')}_{m,m'} := \sqrt{\frac{4\pi}{2k{+}1}}\,\big\langle Y_{l,m}\big|Y_{k,m-m'}Y_{l',m'}\big\rangle = (-1)^{m'}\sqrt{\frac{4\pi}{2k{+}1}}\,\big\langle Y_{k,m'-m}\big|Y_{l,-m}Y_{l',m'}\big\rangle\,. \tag{94}$$

They can be readily written as matrices $\boldsymbol{c}^{(k,l,l')}$ with indices m and m', where matrix elements with $|m{-}m'| = |\mu| > k$ (on the μth side-diagonal) vanish so that $\boldsymbol{c}^{(k,l,l')}$ is a $2k{+}1$-diagonal $(2l{+}1)\times(2l'{+}1)$ matrix, in particular $c^{(k=0,l,l')}_{m,m'} = \delta_{l,l'}\,\delta_{m,m'}$. Matrices with exchanged $l{\leftrightarrow}l'$ are related by

$$c^{(k,l,l')}_{m,m'} = (-1)^{m+m'}\,c^{(k,l',l)}_{-m',-m} \quad\text{and}\quad c^{(k,l,l')}_{m,m'} = (-1)^{m-m'}\,c^{(k,l',l)}_{m',m} \tag{95}$$

where in the last relation we used that the Gaunt coefficients are real. Combining the two transformations gives the inversion symmetry of each $\boldsymbol{c}^{k,l,l'}$ matrix

$$c^{(k,l,l')}_{m,m'} = c^{(k,l,l')}_{-m,-m'}\,. \tag{96}$$

For the special case $l'{=}l$ eq. (95) give the symmetries of $\boldsymbol{c}^{(k,l,l)}$ under reflection along the anti-diagonal and the diagonal, respectively.
Using

$$L_\pm Y_{l,m} = \sqrt{(l{\pm}m{+}1)(l{\mp}m)}\, Y_{l,m\pm1}\,,$$

the elements of the matrix $\boldsymbol{c}^{(k,l,l')}$ are related via $\big\langle Y_{l,m}|L_\pm\, Y_{k,m-m'\mp1}Y_{l',m'}\big\rangle$ by

$$\sqrt{(l{\mp}m{+}1)(l{\pm}m)}\,c^{(k,l,l')}_{m\mp1,m'} = \sqrt{(k{\pm}(m{-}m')(k{\mp}(m{-}m'){+}1)}\,c^{(k,l,l')}_{m,m'} + \sqrt{(l'{\pm}m'{+}1)(l'{\mp}m')}\,c^{(k,l,l')}_{m,m'\pm1} \tag{97}$$

which relates matrix elements according to the patterns └ for L_+ and ┐ for L_-. With one of the prefactors vanishing, these relations become simple two-point recursions along the border of the matrix ($m' = \pm l'$ for the L_+ or $m = \pm l$ for the L_- formula), as well as along the outermost side-diagonals ($m{-}m' = k{+}1$ for L_+ or $m{-}m' = -k{-}1$ for L_-).
Filling the matrix $\boldsymbol{c}^{(k,l,l')}$ according to (97) starting, e.g., from $c^{(k,l,l')}_{-l,-l'} = 1$, using the L_+ recursion to fill the top row and then the L_- recursion to fill the subsequent rows from right to left, we get the matrix of Clebsch-Gordan coefficients

$$\langle k, m{+}m';\, l; l'|l, m;\, l', m'\rangle = (-1)^{m'}\,\bar{c}^{(k,l,l')}_{-m,m'}$$

by normalizing any of the (side)diagonals of $\boldsymbol{c}$ to get $\bar{\boldsymbol{c}}$ (since the μ-th side diagonal holds the expansion coefficients of $|k, \mu;\, l;\, l'\rangle$).
To obtain the Gaunt matrices, we still need the reduced matrix element. A simple approach for small values of l and l' is to use

$$Y_{l,0}(\vartheta,\varphi) = \sqrt{\frac{2l{+}1}{4\pi}}\,P_l(\cos\vartheta)$$

and calculate $c^{(k,l,l')}_{0,0}$ by explicit integration over the corresponding Legendre polynomials, e.g.,

$$c^{(k,l,l)}_{0,0} = \sqrt{\frac{4\pi}{2k{+}1}}\big\langle Y_{l,0}|Y_{k,0}\,Y_{l,0}\big\rangle = \frac{2l{+}1}{2}\int_{-1}^{1} dx\, P_l(x)^2\, P_k(x) \tag{98}$$

Using the recursion relation for the Legendre polynomials (87) with starting points $P_0(x) = 1$ and $P_1(x) = x$, we get by explicit integration over the product of polynomials

l	1	2		3		
k	2	2	4	2	4	6
$c^{(k,l,l)}_{0,0}$	$\frac{2}{5}$	$\frac{2}{7}$	$\frac{2}{7}$	$\frac{2^2}{3\cdot5}$	$\frac{2}{11}$	$\frac{2^2\cdot5^2}{3\cdot11\cdot13}$

(99)

from which we obtain the Gaunt matrices for p-, d-, and f-shells listed below. There are, of course, more refined methods that remain fast and accurate also for large angular momenta [13].

p-shell:

$$c^{(2,1,1)}_{m,m'} = \frac{1}{5}\begin{pmatrix} -1 & \sqrt{3} & -\sqrt{6} \\ -\sqrt{3} & 2 & -\sqrt{3} \\ -\sqrt{6} & \sqrt{3} & -1 \end{pmatrix}$$

d-shell:

$$c^{(2,2,2)}_{m,m'} = \frac{1}{7}\begin{pmatrix} -2 & \sqrt{6} & -2 & 0 & 0 \\ -\sqrt{6} & 1 & 1 & -\sqrt{6} & 0 \\ -2 & -1 & 2 & -1 & -2 \\ 0 & -\sqrt{6} & 1 & 1 & -\sqrt{6} \\ 0 & 0 & -2 & \sqrt{6} & -2 \end{pmatrix}$$

$$c^{(4,2,2)}_{m,m'} = \frac{1}{3\cdot 7}\begin{pmatrix} 1 & -\sqrt{5} & \sqrt{15} & -\sqrt{35} & \sqrt{70} \\ \sqrt{5} & -4 & \sqrt{30} & -\sqrt{40} & \sqrt{35} \\ \sqrt{15} & -\sqrt{30} & 6 & -\sqrt{30} & \sqrt{15} \\ \sqrt{35} & -\sqrt{40} & \sqrt{30} & -4 & \sqrt{5} \\ \sqrt{70} & -\sqrt{35} & \sqrt{15} & -\sqrt{5} & 1 \end{pmatrix}$$

f-shell:

$$c^{(2,3,3)}_{m,m'} = \frac{1}{3\cdot 5}\begin{pmatrix} -5 & 5 & -\sqrt{10} & 0 & 0 & 0 & 0 \\ -5 & 0 & \sqrt{15} & -\sqrt{20} & 0 & 0 & 0 \\ -\sqrt{10} & -\sqrt{15} & 3 & \sqrt{2} & -\sqrt{24} & 0 & 0 \\ 0 & -\sqrt{20} & -\sqrt{2} & 4 & -\sqrt{2} & -\sqrt{20} & 0 \\ 0 & 0 & -\sqrt{24} & \sqrt{2} & 3 & -\sqrt{15} & -\sqrt{10} \\ 0 & 0 & 0 & -\sqrt{20} & \sqrt{15} & 0 & -5 \\ 0 & 0 & 0 & 0 & -\sqrt{10} & 5 & -5 \end{pmatrix}$$

$$c^{(4,3,3)}_{m,m'} = \frac{1}{3\cdot 11}\begin{pmatrix} 3 & -\sqrt{30} & \sqrt{54} & -\sqrt{63} & \sqrt{42} & 0 & 0 \\ \sqrt{30} & -7 & \sqrt{32} & -\sqrt{3} & -\sqrt{14} & \sqrt{70} & 0 \\ \sqrt{54} & -\sqrt{32} & 1 & \sqrt{15} & -\sqrt{40} & \sqrt{14} & \sqrt{42} \\ \sqrt{63} & -\sqrt{3} & -\sqrt{15} & 6 & -\sqrt{15} & -\sqrt{3} & \sqrt{63} \\ \sqrt{42} & \sqrt{14} & -\sqrt{40} & \sqrt{15} & 1 & -\sqrt{32} & \sqrt{54} \\ 0 & \sqrt{70} & -\sqrt{14} & -\sqrt{3} & \sqrt{32} & -7 & \sqrt{30} \\ 0 & 0 & \sqrt{42} & -\sqrt{63} & \sqrt{54} & -\sqrt{30} & 3 \end{pmatrix}$$

$$c^{(6,3,3)}_{m,m'} = \frac{5}{3\cdot 11\cdot 13}\begin{pmatrix} -1 & \sqrt{7} & -\sqrt{28} & \sqrt{84} & -\sqrt{210} & \sqrt{462} & -\sqrt{924} \\ -\sqrt{7} & 6 & -\sqrt{105} & \sqrt{224} & -\sqrt{378} & \sqrt{504} & -\sqrt{462} \\ -\sqrt{28} & \sqrt{105} & -15 & \sqrt{350} & -\sqrt{420} & \sqrt{378} & -\sqrt{210} \\ -\sqrt{84} & \sqrt{224} & -\sqrt{350} & 20 & -\sqrt{350} & \sqrt{224} & -\sqrt{84} \\ -\sqrt{210} & \sqrt{378} & -\sqrt{420} & \sqrt{350} & -15 & \sqrt{105} & -\sqrt{28} \\ -\sqrt{462} & \sqrt{504} & -\sqrt{378} & \sqrt{224} & -\sqrt{105} & 6 & -\sqrt{7} \\ -\sqrt{924} & \sqrt{462} & -\sqrt{210} & \sqrt{84} & -\sqrt{28} & \sqrt{7} & -1 \end{pmatrix}$$

References

[1] F. Hund, Z. Phys. **33**, 345 (1925)

[2] P.M.A. Dirac, Proc. Roy. Soc. **123**, 714 (1929)

[3] R. Eder: *Multiplets in Transition Metal Ions*, in
E. Pavarini, E. Koch, F. Anders, and M. Jarrell (eds):
Correlated Electrons: From Models to Materials
Modeling and Simulation Vol. 2 (Forschungszentrum Jülich, 2012)

[4] E. Koch: *Exact Diagonalization and Lanczos Method*, in
E. Pavarini, E. Koch, and S. Zhang (eds.): *Many-Body Methods for Real Materials*
Modeling and Simulation Vol. 9 (Forschungszentrum Jülich, 2019)

[5] G.Racah, Phys. Rev. **61**, 186 (1942)

[6] G. Racah, Phys. Rev. **62**, 438 (1942)

[7] G. Racah, Phys. Rev. **63**, 367 (1943)

[8] G. Racah, Phys. Rev. **76**, 1352 (1949)

[9] B.R. Judd: *Operator Techniques in Atomic Spectroscopy*
(Princeton University Press, 1998)

[10] C.W. Nielson and G.F. Koster: *Spectroscopic Coefficients for the* p^n, d^n, *and* f^n *Configurations* (MIT Press, 1963)

[11] J. Avery: *Creation and Annihilation Operators* (McGraw-Hill, 1976)

[12] E.U. Condon and G.H. Shortley: *The Theory of Atomic Spectra*
(Cambridge University Press, 1935)

[13] Q. Zhang: *Building Effective Models for Correlated Electron Systems*
(PhD Thesis, RWTH Aachen University, 2020)

[14] O.K. Andersen: *From Materials to Models: Deriving Insight from Bands*, in
E. Pavarini, E. Koch, A. Lichtenstein, and D. Vollhardt (eds.):
DMFT: From Infinite Dimensions to Real Materials
Modeling and Simulation, Vol. 8 (Forschungszentrum Jülich, 2018)