

Hund's rules

Lecture notes. Physics 206.

An atom includes N electrons. Let $\psi_{k_i}(x)$ be a complete set of single-electron wave functions.

A general antisymmetric N -particle wave-function

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum a_{k_1 \dots k_N} \begin{vmatrix} \psi_{k_1}(\vec{r}_1) & \dots & \psi_{k_N}(\vec{r}_1) \\ \psi_{k_1}(\vec{r}_2) & & \psi_{k_N}(\vec{r}_2) \\ \vdots & & \vdots \\ \psi_{k_1}(\vec{r}_N) & \dots & \psi_{k_N}(\vec{r}_N) \end{vmatrix}$$

satisfies the Pauli principle

Let us try a simpler ansatz

$$\psi = \begin{vmatrix} \psi_1(\vec{r}_1) & \dots & \psi_N(\vec{r}_1) \\ \psi_1(\vec{r}_2) & & \vdots \\ \vdots & & \vdots \\ \psi_1(\vec{r}_N) & \dots & \psi_N(\vec{r}_N) \end{vmatrix},$$

where $\psi_k(\vec{r})$ are arbitrary.

We only fix the general structure of ψ .
The variational condition of the energy minimum is

$$\frac{\delta E(\psi_1(\vec{r}), \dots, \psi_N(\vec{r}))}{\delta \psi_i} = 0. \quad (*)$$

This is known as the Hartree-Fock approximation. Equation (*) reduces to

$$-\frac{\hbar^2}{2m} \Delta \psi_i(\vec{r}) + \psi_i(\vec{r}) V[\vec{r}, \{\psi_k(\vec{r})\}, k \neq i]$$

where V is a complicated function.

Eq. (*) can be solved numerically $\Rightarrow$ 5% accuracy
The solution is simplified by the fact that

$\bar{V}(\vec{r}) = \int V(\vec{r}, \theta, \varphi) d\Omega$ is very close to $V(\vec{r})$,
i.e., the potential V turns out to be almost
spherically symmetric. Hence, $\psi_i(\vec{r}) \approx Y_{\ell}^m(\theta, \varphi) \Phi_i(r)$

Thus, L^2 and L_z are good quantum numbers for
every electron. However, their conservation is only
approximate since the spherical symmetry of ψ_i is
only approximate. On the other hand, the total
 $\vec{L}$ and $\vec{S}$ conserve.

Mund's rules tell us the
total $\vec{L}$ and $\vec{S}$, if we know the
electronic configuration such as $1s^2 2s^2 2p^2$ etc

~~The quantum~~ Mund's rules are derived from
the experiment:

Rule 0. Each filled shell (like $2s^2$ or $3p^6$)
has $S=0$ and $L=0$.

Rule 1. In each incomplete shell S takes
the maximal value compatible with the
Pauli principle.

Rule 2. L is maximal possible for given S in
each shell.

Rule 3. If the shell is not more than half-
filled then $J = |L - S|$
If it is more than half-filled
then $J = L + S$.

Examples.

1) $1s^2 \Rightarrow L=0, S=0, J=0.$

2) $1s^1 \Rightarrow L=0$ (S-state!) $S=1/2, J=1/2.$

3) $1s^2 2s^1$ - the same as $1s^1.$

4) $1s^2 2s^2$ - the same as $1s^2.$

5) $1s^2 2s^2 2p^1: S=1/2, l=1, J=1$ $|L-S|=1/2.$

6) $\dots 2p^2: S=1/2+1/2=1.$

The total wave function is antisymmetric.

The spin wave function is symmetric.

$$\chi(l_1^z, l_2^z) = \delta_{l_1^z, 1/2} \delta_{l_2^z, 1/2}.$$

The orbital wave function must be antisymmetric. Hence, $l_1^z \neq l_2^z.$

The same follows from the Pauli principle. Thus, $\max L_z = 1+0=1$

$$(l=1, |l_z| \leq 1 \text{ for all } p\text{-electrons})$$

Thus, $L = \max L_z = 1.$ Hence,

$$J = |S-L| = 0$$

7) $2p^3: S=3/2.$

$$L_z = l_z^1 + l_z^2 + l_z^3. \text{ All three } l_z\text{'s must be different. Hence, } l_z^1 + l_z^2 + l_z^3 = 1+0+0$$

$$\text{Thus, } L_z = 0, \max L_z = 0 \Rightarrow L = 0.$$

$$J = |S-L| = 3/2.$$

8) $2p^4$. Holes! Imagine 6 electrons + 2 holes whose mass and charge are opposite to the electron mass and charge. 6 electrons form a filled shell. We are interested only in the holes!

$$S = \frac{1}{2} + \frac{1}{2} = 1$$

$$L = 1 + 0 = 1$$

the same as for $2p^2$.

A different rule for J :

$$J = L + S = 2$$

9) $2p^5$ 1 hole. $S = 1/2, L = 1, J = 3/2$.

10) $2p^6$ $S = L = J = 0$.

Spin-orbit interaction.

$\vec{S}$ and $\vec{L}$ interact. This is a relativistic effect. Its origin cannot be understood without QED. The interaction is weak in most atoms.

$$\vec{V}_{SL} = A \vec{S} \cdot \vec{L} \quad \text{no } \hbar \text{ in } S \text{ and } L$$

$A = \frac{e^2 \hbar^2}{m^2 c^2 a_0^3} f(Z)$, where a_0 is the Bohr radius, $f(Z) \sim 1$ for light atoms.

Hence, $\frac{A}{\text{Ry}} \sim \frac{A}{e^2/a_0} \sim \frac{\hbar^2}{m a_0^2} / mc^2 \sim \frac{10 \text{ eV}}{0.5 \text{ MeV}} = 2 \cdot 10^{-5}$.

On the other hand, A can be large at large Z !

$$E_{SL} = A \langle \vec{S} \cdot \vec{L} \rangle$$

1st order perturbation theory.

$$E_{SL} = A \langle \vec{S} \cdot \vec{L} \rangle = \frac{A}{2} \langle (\vec{S} + \vec{L})^2 - \vec{S}^2 - \vec{L}^2 \rangle =$$

$$= \frac{A}{2} [-S(S+1) - L(L+1)] + \frac{A}{2} J(J+1)$$

Thus, $E = E(S+L) + \frac{A}{2} J(J+1)$

One can derive the 3d Hund's rule from this!

Zeeman effect.

Magnetic field $\vec{B} \Rightarrow \vec{A} = \frac{1}{2} \vec{B} \times \vec{z}$

$$\hat{H} = \sum_i \frac{1}{2m} \left(\vec{p}_i - \frac{e \vec{A}(\vec{r}_i)}{c} \right)^2 + V(\vec{r}_1, \dots, \vec{r}_N) =$$

$$= V + \sum_i \frac{\vec{p}_i^2}{2m} + \sum_i \frac{e^2 \vec{A}^2}{2mc^2} - \frac{e}{2mc} \sum_i [\vec{p}_i \cdot \vec{A}(\vec{r}_i) +$$

$$+ \vec{A}(\vec{r}_i) \cdot \vec{p}_i].$$

$$\vec{p}_i \cdot \vec{A}(\vec{r}_i) |\psi\rangle = -i\hbar \frac{\partial}{\partial \vec{r}_i} (\vec{A}(\vec{r}_i) |\psi\rangle) =$$

$$= -i\hbar \vec{A}(\vec{r}_i) \frac{\partial |\psi\rangle}{\partial \vec{r}_i} - i\hbar \frac{\partial \vec{A}}{\partial \vec{r}_i} |\psi\rangle = -i\hbar (\vec{\nabla} \cdot \vec{A}) |\psi\rangle$$

$$- \vec{A}(\vec{r}_i) \vec{p}_i |\psi\rangle.$$

$$\vec{\nabla} \cdot \vec{A} = \frac{\partial}{\partial x_i} \frac{1}{2} e^{ijk} B_j x_k = \delta_{ik} \frac{1}{2} e^{ijk} B_j =$$

$$= \frac{1}{2} e^{iji} B_j = 0.$$

We consider weak $\vec{B}$ and neglect $\frac{e^2 \vec{A}^2}{2mc^2}$.

Then

$$\hat{H} = \hat{H}_0 - \frac{e}{mc} \sum [\vec{A}(\vec{r}_i) \cdot \vec{p}_i], \text{ where}$$

$\hat{H}_0$ is the Hamiltonian at $\vec{B}=0$.

$$- \frac{e}{mc} \sum \vec{A} \cdot \vec{p} = - \frac{e}{2mc} \sum [\vec{B} \times \vec{r}_i] \cdot \vec{p}_i = - \frac{e}{2mc} \sum \vec{B} \cdot [\vec{r}_i \times \vec{p}_i] =$$

$$= - \frac{e \vec{B}}{2mc} \sum [\vec{r}_i \times \vec{p}_i] = - \frac{e \vec{B} \vec{L}}{2mc}.$$

We forgot about the spin!

$$H = \hat{H}_0 - \frac{eB\hat{L}_z}{2mc} - \frac{e\hbar B\hat{S}_z}{mc} =$$

$$= \hat{H}_0 - \frac{eB\hbar}{2mc} (\hat{L}_z + 2\hat{S}_z)$$

let z be the direction of the field.

$$\delta E = - \frac{eB\hbar}{2mc} \langle \hat{L}_z + 2\hat{S}_z \rangle.$$

Wigner - Eckart theorem:

$$\langle J_{z_1} | \hat{L} + 2\hat{S} | J_{z_2} \rangle = g \langle J_{z_1} | \hat{J} | J_{z_2} \rangle$$

In particular,

$$\langle J_z | \hat{L}_z + 2\hat{S}_z | J_z \rangle = g J_z$$

We need to find g .

$$\langle J_{z_1} | \hat{J} (\hat{L} + 2\hat{S}) | J_{z_2} \rangle = \sum_{J_{z_3}} \langle J_{z_1} | \hat{J} | J_{z_3} \rangle \cdot$$

$$\langle J_{z_3} | \hat{L} + 2\hat{S} | J_{z_2} \rangle = \sum_{J_{z_3}} \langle J_{z_1} | \hat{J} | J_{z_3} \rangle g \langle J_{z_3} | \hat{J} | J_{z_2} \rangle$$

$$= g \sum_{J_{z_3}} \langle J_{z_1} | \hat{J} | J_{z_3} \rangle \langle J_{z_3} | \hat{J} | J_{z_2} \rangle = g \langle J_{z_1} | \hat{J}^2 | J_{z_2} \rangle$$

$$= g J(J+1) \delta_{J_{z_1}, J_{z_2}}. \quad \text{On the other hand,}$$

$$\langle J_{z_1} | \hat{J} (\hat{L} + 2\hat{S}) | J_{z_2} \rangle =$$

$$= \langle J_{z_1} | \hat{J} (\hat{J} + \hat{S}) | J_{z_2} \rangle =$$

$$= \langle J_{z_1} | \hat{J}^2 + \frac{1}{2}(\hat{J} - \hat{S})^2 + \frac{\hat{J}^2}{2} + \frac{\hat{S}^2}{2} | J_{z_2} \rangle =$$

$$= \langle J_{z_1} | \frac{3}{2}\hat{J}^2 - \frac{\hat{L}^2}{2} + \frac{\hat{S}^2}{2} | J_{z_2} \rangle = \delta_{J_{z_1}, J_{z_2}} \left[\frac{3}{2}J(J+1) - \frac{L(L+1)}{2} + \frac{S(S+1)}{2} \right]$$

⑥

$$\text{Thus, } g(j+1) = \frac{3}{2} j(j+1) - \frac{4(4+1)}{2} + \frac{5(5+1)}{2}$$

$$g = 1 + \frac{j(j+1) - 4(4+1) + 5(5+1)}{2j(j+1)}$$

↑
Landé factor

$$\boxed{\delta E = - \frac{e B g \hbar}{2 m c} j_z}$$

APPENDIX CALCULATION OF SINGLES CUMULANTS

Derivative derivatives in λ of the logarithm of the generating function, see Eq. (11), yield the cumulants. Using the expression (8) each cumulant is expressed in terms of derivatives of the matrix A , introduced in section IV. Derivatives of A of k -th order can be written in terms of a matrix $K = \partial A / \partial \lambda$ and the matrix n , defined in section IV. n is a projection matrix with only non-vanishing elements, $n_{22} = 1$. Note that K has non-vanishing elements only in the upper diagonal 2×2 block. Because projecting is excluded in the MZL, the product nK vanishes and we obtain the simple form

$$(A.1) \quad \frac{\partial^k A}{\partial \lambda^k} = n^k n (K + (-1)^k n^k) \quad (A.1)$$

The matrix K is separated into constant matrices A_0 and λ -dependent scalar functions as follows: $K = A_0 + \lambda K_1 + \lambda^2 K_2 + \dots$. Here n is the characteristic parameter $n = e^{i\omega t}$, introduced in section V. The average is calculated by replacing the generating function in Eq. (6) by the phase factor; at this point we explicitly assume a Gaussian fluctuating potential $\tilde{V}(t)$ and use $\omega \tau \ll \tau$.

The average of the matrix K is denoted by $\langle K \rangle$, it is determined only by the parameters K_0 , Φ , and α . The averaging of the constants only affects the time-dependent functions $(e^{i\omega t})^n = \langle e^{i\omega t} \rangle^n$. Depending on the order k of the cumulants one obtains products of the functions $(e^{i\omega t})^n$ at k different times. The averaging then defines correlation functions of different order.

In the case we get two correlation functions, depending on one time variable and determined by the parameter α .

$$(A.2) \quad \langle K \rangle = \frac{1}{2} \left(\langle e^{i\omega t} \rangle + \langle e^{-i\omega t} \rangle \right) = \frac{1}{2} \left(\langle e^{i\omega t} \rangle + \langle e^{-i\omega t} \rangle \right) \quad (A.2)$$

The procedure of the average is similar to the calculation of the parameter α .