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

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

satisfies the Pauli principle

Let us try a simpler ansatz

$$\psi = \begin{vmatrix} \varphi_1(\vec{r}_1) & \ldots & \varphi_N(\vec{r}_1) \\ \varphi_1(\vec{r}_2) & & \vdots \\ \vdots & & \\ \varphi_1(\vec{r}_N) & \ldots & \varphi_N(\vec{r}_N) \end{vmatrix},$$

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

We only fix the general structure of ψ.

The variational condition of the energy minimum is

$$\frac{\delta E(\varphi_1(\vec{r}), \ldots, \varphi_N(\vec{r}))}{\delta \varphi_i} = 0 \qquad (*)$$

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

$$-\frac{\hbar^2}{2m} \Delta \varphi_i(\vec{r}) + \varphi_i(\vec{r})\, V[\vec{r}, \{\varphi_k(\vec{\rho})\}, k \neq i] = \ldots$$

where V is a complicated function.

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

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

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

Hund'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

Hund'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 than $J = |L - S|$
If it is more than half-filled than $J = L + S$.

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

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

The total wave function is antisymmetric
The spin wave function is symmetric

$$\chi(\sigma_1^z, \sigma_2^z) = \delta_{\sigma_1^z, 1/2}\,\delta_{\sigma_2^z, 1/2}.$$

The orbital wave function must be antisymmetric. Hence, $l_1^z \neq l_2^z$.
The same follows from the Pauli principle. Thus, $\max L_z = 1+0=1$
($l=1, |l_z| \leq 1$ for all p-electrons)
Thus, $L = \max L_z = 1.$ Hence,
$J = |S-L| = 0$

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

$L_z = l_z^1 + l_z^2 + l_z^3$. All three l_z's must be different. Hence, $l_z^1 + l_z^2 + l_z^3 = 1+0+(-1) = 0.$

Thus, $L_z = 0$, ~~max~~ $\max L_z = 0 \Rightarrow L = 0.$

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

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!

$S = 1/2 + 1/2 = 1$ $\quad L = 1 + 0 = 1$

↑ ↑

the same as for $2p^2$.

A different rule for J:

$$J = L + S = 2$$

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

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

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.

$$V_{SL} = A \vec{S} \vec{L}$$

↑ no $\hbar$ in S 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, $\frac{A}{Ry} \sim \frac{A}{e^2/a_0} \sim \frac{\hbar^2}{m a_0^2} / mc^2 \sim \frac{10\,eV}{0.5\,MeV} = 2 \cdot 10^{-5}$.

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

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

↑ 1st order perturbation theory.

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

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

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 $\vec{B} \Rightarrow \vec{A} = \frac{1}{2}\vec{B}\times\vec{r}$

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

$$= V + \sum \frac{\vec{p}_i^{\,2}}{2m} + \sum \frac{e^2\vec{A}^2}{2mc^2} - \frac{e}{2mc}\sum\left[\vec{p}_i\vec{A}(\vec{r}_i) + \vec{A}(\vec{r}_i)\vec{p}_i\right].$$

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

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

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

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

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

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

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 $\vec{B}=0$.

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

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

We forgot about the spin!

$$H = \hat{H}_0 - \frac{eB\hat{L}}{2mc} - \frac{ehB\hat{S}}{mc} =$$

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

↖ let z be the direction of the field.

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

Wigner–Eckart theorem:

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

↖ constant

In particular,

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

We need to find g.

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

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

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

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

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

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

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

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

Thus, $g\,J(J+1) = \frac{3}{2}J(J+1) - \frac{L(L+1)}{2} + \frac{S(S+1)}{2}$

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

↑ Landé factor

$$\boxed{\delta E = -\frac{e B g_t}{2mc} J_z}$$