Periodic table and Hund's rule Masatsugu Sei Suzuki Department of Physics State University of New York at Binghamton (Date: March 27, 2014)

1. Pauli exclusion principle

The **Pauli exclusion principle** is the quantum mechanical principle that no two identical fermions (particles with half-integer spin) may occupy the same quantum state simultaneously. A more rigorous statement is that the total wave function for two identical fermions is anti-symmetric with respect to exchange of the particles. The principle was formulated by Austrian physicist Wolfgang Pauli in 1925.

(http://en.wikipedia.org/wiki/Pauli_exclusion_principle)

For example, no two electrons in a single atom can have the same four quantum numbers; if n, l, and m_l are the same, m_s must be different such that the electrons have opposite spins, and so on. Integer spin particles, bosons, are not subject to the Pauli exclusion principle: any number of identical bosons can occupy the same quantum state, as with, for instance, photons produced by a laser and Bose–Einstein condensate.

2. Periodic table

The Pauli principle produces any two electrons being in the same state (i.e., having the set of (n, l, m_l, m_s) .

For fixed *n*,

$$l = n-1, n-2, ..., 2, 1$$

 $m_1 = l, l-1, ..., -l (2l + 1).$

Therefore there are n^2 states for a given *n*.

$$\sum_{l=0}^{n-1} (2l+1) = n^2$$

There are two values for m_s (= ±1/2). Thus, corresponding to any value of *n*, there are $2n^2$ states.

K shell	1					
	п	l	m	S	m_s	
	1	0	0	1/2	$\pm 1/2$	$(1s)^{2}$
L shell						
	п	l	m	S	m_s	
	2	0	0	1/2	$\pm 1/2$	$(2s)^{2}$
	2	1	1,0,-1	1/2	$\pm 1/2$	$(2p)^{6}$

l	т	S	m_s	
0	0	1/2	$\pm 1/2$	$(3s)^2$
1	1,0,-1	1/2	$\pm 1/2$	$(3p)^{6}$
2	2,1,0,-1,-2	1/2	$\pm 1/2$	$(3d)^{10}$
l	т	S	m_s	
0	0	1/2	$\pm 1/2$	$(4s)^2$
1	1,0,-1	1/2	$\pm 1/2$	$(4p)^{6}$
2	2,1,0,-1,-2	1/2	$\pm 1/2$	$(4d)^{10}$
3	3,2,1,0,-1,-2,-3	1/2	$\pm 1/2$	$(4f)^{14}$
	l 0 1 2 l 0 1 2 3	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

 $(1s)^2 |(2s)^2 (2p)^6 |(3s)^2 (3p)^6 (3d)^{10} |(4s)^2 (4p)^6 (4d)^{10} (4f)^{14} |(5s)^2 (5p)^6 \ ((5d)^{10} \dots$

Atoms with filled n shells have a total angular momentum and a total spin of zero. Electrons exterior these closed shells are called valence electrons.

(1s)
$(1s)^2$
$(1s)^2 (2s)^1 $
$(1s)^2 (2s)^2 $
$(1s)^2 (2s)^2 (2p)^1$
$(1s)^2 (2s)^2 (2p)^2$
$(1s)^2 (2s)^2 (2p)^3$
$(1s)^2 (2s)^2 (2p)^4$
$(1s)^2 (2s)^2 (2p)^5$
$(1s)^2 (2s)^2 (2p)^6 $
$(1s)^{2} (2s)^{2}(2p)^{6} (3s)^{1}$
$(1s)^2 (2s)^2 (2p)^6 (3s)^2$
$(1s)^{2} (2s)^{2}(2p)^{6} (3s)^{2}(3p)^{1}$
$(1s)^{2} (2s)^{2}(2p)^{6} (3s)^{2}(3p)^{2}$
$(1s)^{2} (2s)^{2}(2p)^{6} (3s)^{2}(3p)^{3}$
$(1s)^{2} (2s)^{2}(2p)^{6} (3s)^{2}(3p)^{4}$
$(1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^5$
$(1s)^{2} (2s)^{2}(2p)^{6} (3s)^{2}(3p)^{6}$
$(1s)^{2} (2s)^{2}(2p)^{6} (3s)^{2}(3p)^{6}(3d)^{1}$
$(1s)^{2} (2s)^{2}(2p)^{6} (3s)^{2}(3p)^{6}(3d)^{2}$
$(1s)^{2} (2s)^{2}(2p)^{6} (3s)^{2}(3p)^{6}(3d)^{3}$
$(1s)^{2} (2s)^{2}(2p)^{6} (3s)^{2}(3p)^{6}(3d)^{4}$
$(1s)^{2} (2s)^{2}(2p)^{6} (3s)^{2}(3p)^{6}(3d)^{5}$
$(1s)^{2} (2s)^{2}(2p)^{6} (3s)^{2}(3p)^{6}(3d)^{6}$
$(1s)^{2} (2s)^{2}(2p)^{6} (3s)^{2}(3p)^{6}(3d)^{7}$
$(1s)^{2} (2s)^{2}(2p)^{6} (3s)^{2}(3p)^{6}(3d)^{8}$
$(1s)^{2} (2s)^{2}(2p)^{6} (3s)^{2}(3p)^{6}(3d)^{9}$
$(1s)^{2} (2s)^{2}(2p)^{6} (3s)^{2}(3p)^{6}(3d)^{10} $

Cu
$$(1s)^2 |(2s)^2 (2p)^6 |(3s)^2 (3p)^6 (3d)^{10} |(4s)^1$$

3. Commutation relations for total orbital and spin angular momenta We consider the Hamiltonian

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_3$$

where

$$\hat{H}_1 = \frac{1}{2m_e} \hat{p}_1^2 - \frac{Ze^2}{|\hat{r}_1|}, \qquad \hat{H}_2 = \frac{1}{2m_e} \hat{p}_2^2 - \frac{Ze^2}{|\hat{r}_2|}, \qquad \hat{H}_3 = \frac{e^2}{|\hat{r}_1 - \hat{r}_2|}.$$

where there are Coulomb interactions among the nucleus with the charge Ze, and two electrons with a charge -e outside the nucleus. Note that \hat{H}_1 , \hat{H}_2 , and \hat{H}_3 are central fields, where the interactions depends only on the distances between the particles. The angular momentum $\hat{L}_1 = \hat{r}_1 \times \hat{p}_1$ commutes with \hat{H}_1 .

$$[\hat{H}_1, \hat{L}_1] = 0.$$

We note that all observables relating to one of the particles (particle 1, in our case) commute with all those corresponding to the other one (particle 2, in our case).

$$[\hat{H}_2, \hat{L}_1] = 0.$$

which means that

$$[\hat{H}_1 + \hat{H}_2, \hat{L}_1] = 0$$

Similarly, we have

$$[\hat{H}_1 + \hat{H}_2, \hat{L}_2] = 0$$

Then we get

$$[\hat{H}_1 + \hat{H}_2, \hat{L}] = 0$$

where

$$\hat{\boldsymbol{L}} = \hat{\boldsymbol{L}}_1 + \hat{\boldsymbol{L}}_2$$

How about the commutation relation on $[\hat{H}, \hat{L}] = 0$? We note that

$$[\hat{H}, \hat{L}] = [\hat{H}_1 + \hat{H}_2 + \hat{H}_3, \hat{L}] = [\hat{H}_3, \hat{L}]$$

Using the Mathematica, we show that

$$[\hat{H}_3, \hat{L}] = 0.$$

or

$$\langle \mathbf{r}_{1}, \mathbf{r}_{2} | [\hat{H}_{3}, \hat{L}_{z}] | \psi \rangle = H_{3}(|\mathbf{r}_{1} - \mathbf{r}_{2}|) L_{z} \psi(\mathbf{r}_{1}, \mathbf{r}_{2}) - L_{z} H_{3}(|\mathbf{r}_{1} - \mathbf{r}_{2}|) \psi(\mathbf{r}_{1}, \mathbf{r}_{2})$$

where

$$H_{3}(|\mathbf{r}_{1}-\mathbf{r}_{2}|) = \frac{e^{2}}{|\mathbf{r}_{1}-\mathbf{r}_{2}|}, \qquad L_{z} = L_{1z} + L_{2z}$$

$$L_{1z} = \frac{\hbar}{i}(x_{1}\frac{\partial}{\partial y_{1}} - y_{1}\frac{\partial}{\partial x_{1}}), \qquad L_{2z} = \frac{\hbar}{i}(x_{2}\frac{\partial}{\partial y_{2}} - y_{2}\frac{\partial}{\partial x_{2}})$$

$$r_{1} = (x_{1}, y_{1}, z_{1}), \qquad r_{2} = (x_{2}, y_{2}, z_{2}).$$
((Mathematica))
Clear ["Global" *"];
R12 = $\sqrt{(\mathbf{x}1 - \mathbf{x}2)^{2} + (\mathbf{y}1 - \mathbf{y}2)^{2} + (\mathbf{z}1 - \mathbf{z}2)^{2}}; H3 = \frac{\mathbf{e}1^{2}}{\mathbf{R}12};$
L1z := $\frac{\hbar}{\mathbf{n}}(\mathbf{x}1 D[\#, \mathbf{y}1] - \mathbf{y}1 D[\#, \mathbf{x}1]) \&;$
L2z := $\frac{\hbar}{\mathbf{n}}(\mathbf{x}2 D[\#, \mathbf{y}2] - \mathbf{y}2 D[\#, \mathbf{x}2]) \&;$
Lz := (L1z[#] + L2z[#]) $\&;$
 $\psi_{1} = \psi[\mathbf{x}1, \mathbf{y}1, \mathbf{z}1, \mathbf{x}2, \mathbf{y}2, \mathbf{z}2];$
H3 Lz [ψ_{1}] - Lz [H3 ψ_{1}] // Simplify
0

Then we have the commutation relations

$$[\hat{H}, \hat{L}] = 0,$$

Similarly for the total spin angular momentum, we have

$$[\hat{H},\hat{S}]=0$$

Note that

$$[\hat{L}_{i},\hat{S}_{j}]=0$$

In other words, there is a simultaneous eigenket of the operators \hat{L}^2 , \hat{S}^2 , \hat{L}_z , and \hat{S}_z . So the total orbital angular momentum and the total spin angular momentum are good quantum numbers which denote the resulting states.

4. Commutation relations for total angular momentum,

The total angular momentum is defined by

 $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S} \; .$

We note that

$$[\hat{H}, \hat{L}] = 0, \quad [\hat{H}, \hat{S}] = 0, \quad [\hat{H}, \hat{L}^2] = 0, \quad [\hat{H}, \hat{S}^2] = 0$$

From this relation we find that

 $[\hat{H}, \hat{J}] = [\hat{H}, \hat{L}] + [\hat{H}, \hat{S}] = 0$

So the total angular momentum is also a good quantum number.

5. Wave function for two particle system ((Cohen-Tannoudji))

We now consider the wave function of the two electron system.

Because of the fermion, the wave function should be anti-symmetric under the exchange operator

$$\left|\psi\right\rangle = c(\hat{1} - \hat{P}_{12})\left|L, M_L; 1:n,l;2;n',l'\right\rangle \otimes \left|S, M_S\right\rangle$$

using the exchange operator

$$\hat{P}_{12} = \hat{P}_{12}^{(space)} \hat{P}_{12}^{(spin)}$$

where c is a normalization constant, and $|L, M_L; 1: n, l; 2; n', l'\rangle$ are formed of the superpositions of $|n, l\rangle_1$ and $|n', l'\rangle_2$ through the the Clebsch-Gordan co-efficients. We note that

$$\hat{P}_{12}^{(spin)} | S, M_s \rangle = (-1)^{S+1} | S, M_s \rangle$$

where S = 1 (triplet, $M_s = 1, 0, -1$) for the symmetric case and S = 0 (singlet, $M_s = 0$) for the anti-symmetric case.

(i)
$$|n,l\rangle \neq |n',l'\rangle$$

 $|\psi\rangle = c[\hat{1} - (-1)^{S+1}\hat{P}_{12}^{(space)})|L,M_L;1:n,l;2;n',l'\rangle \otimes |S,M_S\rangle$

When S = 1 (symmetric)

$$\begin{split} \left|\psi\right\rangle &= c(\hat{1} - \hat{P}_{12}^{(space)}) \left|L, M_L; 1:n,l;2;n',l'\right\rangle \otimes \left|S, M_S\right\rangle \\ &= c\sqrt{2}\hat{A}^{(space)} \left|L, M_L; 1:n,l;2;n',l'\right\rangle \otimes \left|S, M_S\right\rangle \end{split}$$

When S = 0 (anti-symmetric),

$$\begin{aligned} \left|\psi\right\rangle &= c(\hat{1} + \hat{P}_{12}^{(space)}) \left|L, M_L; 1:n,l;2;n',l'\right\rangle \otimes \left|S, M_S\right\rangle \\ &= c\sqrt{2}\hat{S}^{(space)} \left|L, M_L; 1:n,l;2;n',l'\right\rangle \otimes \left|S, M_S\right\rangle \end{aligned}$$

(ii) $|n,l\rangle = |n',l'\rangle$

$$|\psi\rangle = c[\hat{1} - (-1)^{S+1}\hat{P}_{12}^{(space)})|L, M_L; 1:n,l; 2;n,l\rangle \otimes |S, M_S\rangle$$

We use the fomula,

$$\hat{P}_{12}^{(space)} | L, M_L; 1: n, l; 2; n, l \rangle = (-1)^L | L, M_L; 1: n, l; 2; n, l \rangle,$$

Then we have

$$|\psi\rangle = c[\hat{1} - (-1)^{L+S+1}]|L, M_L; 1:n, l; 2; n, l\rangle \otimes |S, M_S\rangle$$

When L + S = even,

$$|\psi\rangle = 2c|L, M_L; 1:n,l; 2;n,l\rangle \otimes |S, M_S\rangle$$

When L + S = odd,

 $|\psi\rangle = 0$

6. Clebsch-Gordan co-efficient for the case of He

Here we show the Clebsh-Gordan coefficients for the two particles in the same or the different orbital states. The ground state of the He atom is denoted by $(1s)^2$, where two electrons

are in the $|1s\rangle$ state. We consider the excited states such as (1s)(2s), where one electron is in the $|1s\rangle$ state and the other electron is in the $|2s\rangle$ state.

(1s)(2s), (1s)(3s)

$$l = 0, l = 0$$

 $D_0 \times D_0 = D_0$ $L = 0$

L = 0 (symmetric)

$$|L = 0, M_L = 0\rangle = |l_1 = 0, m_1 = 0\rangle |l_2 = 0, m_2 = 0\rangle$$

= $|0,0\rangle_1 |0,0\rangle_2$

(1s)(2p), (1s)(3p)

$$l = 0, l = 1$$

 $D_0 \times D_1 = D_1$ $L = 1$

L = 1

$$|L = 1, M_{L} = 1\rangle = |1,1\rangle_{1}|0,0\rangle_{2},$$
$$|L = 1, M_{L} = 0\rangle = |1,0\rangle_{1}|0,0\rangle_{2},$$
$$|L = 1, M_{L} = -1\rangle = |1,-1\rangle_{1}|0,0\rangle_{2}$$

<u>(2p)(3p)</u>

$$l = 1, l = 1$$

$$D_1 \times D_1 = D_2 + D_1 + D_0 \qquad L = 2, 1, 0$$

L = 2 (symmetric)

$$\begin{split} |L &= 2, M_L = 2 \rangle = |1,1\rangle_1 |1,1\rangle_2 \\ |L &= 2, M_L = 1 \rangle = \frac{1}{\sqrt{2}} (|1,1\rangle_1 |1,0\rangle_2 + |1,0\rangle_1 |1,1\rangle_2) \\ |L &= 2, M_L = 0 \rangle = \frac{1}{\sqrt{6}} (|1,1\rangle_1 |1,-1\rangle_2 + |1,-1\rangle_1 |1,1\rangle_2 + 2|1,0\rangle_1 |1,0\rangle_2) \\ |L &= 2, M_L = -1\rangle = \frac{1}{\sqrt{2}} (|1,-1\rangle_1 |1,0\rangle_2 + |1,0\rangle_1 |1,-1\rangle_2) \end{split}$$

$$|L=2, M_{L}=-2\rangle = |1,-1\rangle_{1}|1,-1\rangle_{2}$$

L = 1 (anti-symmetric)

$$|L = 1, M_{L} = 1\rangle = \frac{1}{\sqrt{2}}(|1,1\rangle_{1}|1,0\rangle_{2} - |1,0\rangle_{1}|1,1\rangle_{2})$$

$$|L = 1, M_{L} = 0\rangle = \frac{1}{\sqrt{2}}(|1,1\rangle_{1}|1,-1\rangle_{2} - |1,-1\rangle_{1}|1,1\rangle_{2})$$

$$|L = 1, M_{L} = -1\rangle = \frac{1}{\sqrt{2}}(|1,0\rangle_{1}|1,-1\rangle_{2} - |1,-1\rangle_{1}|1,0\rangle_{2})$$

L = 0 (symmetric)

$$|L=0, M_{L}=0\rangle = \frac{1}{\sqrt{3}}(|1,1\rangle_{1}|1,-1\rangle_{2}+|1,-1\rangle_{1}|1,1\rangle_{2}-|1,0\rangle_{1}|1,0\rangle_{2})$$

<u>(2p)(3d)</u>

$$l = 1, l = 2$$

 $D_1 \times D_2 = D_3 + D_2 + D_1$ $L = 3, 2, 1$

L = 3

$$\begin{split} |L &= 3, M_L = 3 \rangle = |1,1\rangle_1 |2,2\rangle_2 \\ |L &= 3, M_L = 2 \rangle = \sqrt{\frac{2}{3}} |1,1\rangle_1 |2,1\rangle_2 + \frac{1}{\sqrt{3}} |1,0\rangle_1 |2,2\rangle_2 \\ |L &= 3, M_L = 1 \rangle = \sqrt{\frac{2}{5}} |1,1\rangle_1 |2,0\rangle_2 + 2\sqrt{\frac{2}{15}} |1,0\rangle_1 |2,1\rangle_2 + \frac{1}{\sqrt{15}} |1,-1\rangle_1 |2,2\rangle_2 \\ |L &= 3, M_L = 0 \rangle = \frac{1}{\sqrt{5}} |1,1\rangle_1 |2,-1\rangle_2 + \sqrt{\frac{3}{5}} |1,0\rangle_1 |2,0\rangle_2 + \frac{1}{\sqrt{5}} |1,-1\rangle_1 |2,1\rangle_2 \\ |L &= 3, M_L = -1\rangle = \sqrt{\frac{2}{5}} |1,-1\rangle_1 |2,0\rangle_2 + 2\sqrt{\frac{2}{15}} |1,0\rangle_1 |2,-1\rangle_2 + \frac{1}{\sqrt{15}} |1,1\rangle_1 |2,-2\rangle_2 \\ |L &= 3, M_L = 2\rangle = \sqrt{\frac{2}{3}} |1,-1\rangle_1 |2,-1\rangle_2 + \frac{1}{\sqrt{3}} |1,0\rangle_1 |2,-2\rangle_2 \\ |L &= 3, M_L = 3\rangle = |1,-1\rangle_1 |2,-2\rangle_2 \end{split}$$

L = 2

$$\begin{split} |L &= 2, M_L = 2 \rangle = -\sqrt{\frac{2}{3}} |1,0\rangle_1 |2,2\rangle_2 + \frac{1}{\sqrt{3}} |1,1\rangle_1 |2,1\rangle_2 \\ |L &= 2, M_L = 1 \rangle = \frac{1}{\sqrt{2}} |1,1\rangle_1 |2,0\rangle_2 - \frac{1}{\sqrt{6}} |1,0\rangle_1 |2,1\rangle_2 - \frac{1}{\sqrt{3}} |1,-1\rangle_1 |2,2\rangle_2 \\ |L &= 2, M_L = 0 \rangle = \frac{1}{\sqrt{2}} |1,1\rangle_1 |2,-1\rangle_2 - \frac{1}{\sqrt{2}} |1,-1\rangle_1 |2,1\rangle_2 \\ |L &= 2, M_L = -1\rangle = \frac{1}{\sqrt{3}} |1,1\rangle_1 |2,-2\rangle_2 + \frac{1}{\sqrt{6}} |1,0\rangle_1 |2,-1\rangle_2 - \frac{1}{\sqrt{2}} |1,-1\rangle_1 |2,0\rangle_2 \\ |L &= 2, M_L = -2\rangle = \sqrt{\frac{2}{3}} |1,0\rangle_1 |2,-2\rangle_2 - \frac{1}{\sqrt{3}} |1,1\rangle_1 |2,1\rangle_2 \end{split}$$

L = 1

$$|L = 1, M_{L} = 1\rangle = \frac{1}{\sqrt{10}} |1,1\rangle_{1} |2,0\rangle_{2} - \sqrt{\frac{3}{10}} |1,0\rangle_{1} |2,1\rangle_{2} - \sqrt{\frac{3}{5}} |1,-1\rangle_{1} |2,2\rangle_{2}$$
$$|L = 1, M_{L} = 0\rangle = \sqrt{\frac{3}{10}} |1,1\rangle_{1} |2,-1\rangle_{2} - \sqrt{\frac{2}{5}} |1,0\rangle_{1} |2,0\rangle_{2} + \sqrt{\frac{3}{10}} |1,-1\rangle_{1} |2,1\rangle_{2}$$
$$|L = 1, M_{L} = -1\rangle = \frac{1}{\sqrt{10}} |1,-1\rangle_{1} |2,0\rangle_{2} - \sqrt{\frac{3}{10}} |1,0\rangle_{1} |2,-1\rangle_{2} + \sqrt{\frac{3}{5}} |1,1\rangle_{1} |2,-2\rangle_{2}$$

7. Hund's rule for the ground state; how to find the ground state Electron states in the atom

(n, l, m), s = 1/2

For a given *l*, the number *m* takes 2l + 1 values. The number *s* is restricted to only two values $\pm 1/2$. Hence there are altogether 2(2l+1) different states with the same *n* and *l*.

These states are said to be equivalent.

According to Pauli's principle, there can be only one electron in each such state. Thus at most 2(2l+1) electrons in an atom can simultaneously have the same *n* and *l*.

Hund's rule is known concerning the relative position of levels with the same configuration but different *L* and *S*.

- (i) The maximum values of the total spin *S* allowed by the exclusion principle.
- (ii) The maximum values of the total orbital angular momentum L consistent with this value of S.
- (iii) J = |L S| for less than half full.
- (iv) J = L + S for more than half full.

The electron configuration $(3d)^n$ (l = 2, n = 1 - 10)

A *d* shell corresponds to l = 2, with five values of ml. Multiplying this by 2 for the spin states gives a total of 10. Then the configuration $(3d)^{10}$ represents a full shell. It is non-degenerate, and the state is ${}^{1}S_{0}$. This is a general rule for a full shell. It follows because each of electrons must have a different pair of m_{l} and m_{s} values.





$$L = 3, S = 3/2, J = 3/2,$$

(iv)
$$(3d)^4$$
: Cr²⁺, Mn³⁺

$${}^{5}D_{0}$$



$$L = 0, S = 5/2, J = 5/2$$

(vi) $(3d)^6$: Fe²⁺

$$^{5}D_{4}$$





$$L = 3, S = 3/2, J = 9/2$$

(viii) $(3d)^8: Ni^{2+}$

(vii)

$$^{3}F_{4}$$



$$L = 3, S = 1, J = 4$$

(ix) $(3d)^9$: Cu²⁺



$$L = 2, S = 1/2, J = 5/2$$

 $(3d)^{9}$

This configuration represents a set of electrons one short of a full shell. Since a full shell has zero angular momentum (both orbital and spin), it follows that if one electron is removed from a full shell, the spin angular momentum of the remainder are minus those of the one that was removed. So the L, S, and J values of remainder are the same as if there were only one electron in the shell.

(x) $(3d)^{10}$

A d shell corresponds to l = 2, with five values of m_l . Multiplying this by two for the spin states gives 10. Thus the configuration (3d)¹⁰ represents a full shell. L = 0. S = 0. J = 0.



8. Observed spectral lines

All observed spectral lines can be explained correctly by assuming that the only wave functions actually appearing are those which are antisymmetric with respect to simultaneous exchange of both space and spin-co-ordinates of any two electrons. This rule leads to the Pauli exclusion principle. It has been found that the rule of antisymmetry is obeyed, not only by electrons, but also by many other elementary particles including neutrons, protons, and neutrino (fermions)

In order to satisfy the requirement of complete anti-symmetry, it is necessary to choose either symmetric spin wave functions and anti-symmetric space wave functions, or anti-symmetric spin and symmetric space wave functions.

9. Two electrons in Helium atom

Here we try to determine the nature of the symmetry for the orbital wave function for electrons in He using the nature of the parity for the orbital state and spin state for the relative motion of two identical particles. (see the Clebsch-Gordan co-efficient for He).

9.1 $(1s)^2$

From the Hund's law (in the same shell), we conclude that the ground state is $\frac{1}{S_0}$



$$D_0 \times D_0 = D_0 \tag{L=0}$$

$$D_{1/2} \times D_{1/2} = D_1 + D_0$$
 (S=1, S=0)

L = 0 (symmetric)

$$|L = 0, M_L = 0\rangle = |l_1 = 0, m_1 = 0\rangle |l_2 = 0, m_2 = 0\rangle$$
$$= |n = 1; 0, 0\rangle_1 |n = 1; 0, 0\rangle_2$$
$$= |1s\rangle_1 |1s\rangle_2$$

However, we cannot construct the anti-symmetric orbital state since

$$|\psi_{a}\rangle = \frac{1}{\sqrt{2}}(|1s\rangle_{1}|1s\rangle_{2} - |0,0\rangle_{2}|0,0\rangle_{1}) = 0$$

For L = 0 (symmetric) and S = 0 (antisymmetric), J = 0

 $^{1}S_{0}$ (allowed): Ground state (Hund's law)

Note that L + S = 0 (even).

9.2 (1s)(2s)

$$D_0 \times D_0 = D_0$$
 (L=0)
 $D_{1/2} \times D_{1/2} = D_1 + D_0$ (S=1, S = 0)

L = 0 (symmetric)

$$|L = 0, M_{L} = 0\rangle = |l_{1} = 0, m_{1} = 0\rangle|l_{2} = 0, m_{2} = 0\rangle$$
$$= |n = 1; 0, 0\rangle_{1}|n = 2, 0, 0\rangle_{2}$$
$$= |1s\rangle_{1}|2s\rangle_{2}$$

For $|\psi_1\rangle = |1s\rangle$ and $|\psi_2\rangle = |2s\rangle$, we can construct the symmetric and anti-symmetric orbital states such that

$$|\psi_s\rangle = \frac{1}{\sqrt{2}}(|1s\rangle_1|2s\rangle_2 + |2s\rangle_1|1s\rangle_2), \quad |\psi_a\rangle = \frac{1}{\sqrt{2}}(|1s\rangle_1|2s\rangle_2 - |2s\rangle_1|1s\rangle_2)$$

where L = 0 (symmetric, and anti-symmetric).

(i) L = 0 (anti-symmetric), S = 1 (symmetric), leading to J = 1

 $^{3}S_{1}$ (allowed)

(ii) L = 0 (symmetric), S = 0 (anti-symmetric), leading to J = 0

¹S₀ (allowed),

9.3 (1s)(2p)

$$\mathbf{D}_0 \ge \mathbf{D}_1 = \mathbf{D}_1 \tag{L=1}$$

$$D_{1/2} \ge D_{1/2} = D_1 + D_0 \qquad (S=1, 0)$$

L = 1

$$|L = 1, M_{L} = 1\rangle = |0,0\rangle_{1}|1,1\rangle_{2},$$
$$|L = 1, M_{L} = 0\rangle = |0,0\rangle_{1}|1,0\rangle_{2},$$
$$|L = 1, M_{L} = -1\rangle = |0,0\rangle_{1}|1,-1\rangle_{2}$$

For $|\psi_1\rangle = |0,0\rangle_1 = |1s\rangle_1$ and $|\psi_2\rangle = |2p\rangle_2 = |1,m\rangle_2$ (*m* = 1, 0, -1), we can construct the symmetric orbital state and anti-symmetric state such that

$$|\psi_{s}\rangle = \frac{1}{\sqrt{2}} (|1s\rangle_{1}|2p\rangle_{2} + |2p\rangle_{1}|1s\rangle_{2}), \qquad L = 1 \text{ (symmetric)}$$
$$|\psi_{a}\rangle = \frac{1}{\sqrt{2}} (|1s\rangle_{1}|2p\rangle_{2} - |2p\rangle_{1}|1s\rangle_{2}), \qquad L = 1 \text{ (anti-symmetric)}.$$

(i) L = 1 (anti-symmetric) and S = 1 (symmetric), leading to J = 2, 1, 0

 $^{3}P_{2}$, $^{3}P_{1}$ $^{3}P_{0}$ (allowed)

(ii)
$$L = 1$$
 (symmetric) and $S = 0$ (anti-symmetric), leading to $J = 1$

¹ P_1 (allowed).

9.4 (1s)(3s)

$$D_0 \times D_0 = D_0 \tag{L=0}$$

$$D_{1/2} \times D_{1/2} = D_1 + D_0 \qquad (S=1, S=0)$$
$$|L=0, M_L=0\rangle = |l_1=0, m_1=0\rangle |l_2=0, m_2=0\rangle$$
$$= |n=1;0,0\rangle_1 |n=3;0,0\rangle_2$$
$$= |1s\rangle_1 |3s\rangle_2$$

For $|\psi_1\rangle = |1s\rangle$ and $|\psi_2\rangle = |3s\rangle$, we can construct the symmetric and antisymmetric orbital states such that

$$|\psi_{s}\rangle = \frac{1}{\sqrt{2}} (|1s\rangle_{1}|3s\rangle_{2} + |3s\rangle_{1}|1s\rangle_{2}), \qquad L = 0 \text{ (symmetric)}$$
$$|\psi_{a}\rangle = \frac{1}{\sqrt{2}} (|1s\rangle_{1}|3s\rangle_{2} - |3s\rangle_{1}|1s\rangle_{2}) \qquad L = 0 \text{ (anti-symmetric)}$$

(i) L = 0 (anti-symmetric) and S = 1 (symmetric), leading to J = 1³S₁ (allowed).

(ii)
$$L = 0$$
 (symmetric) and $S = 0$ (antisymmetric), leading to $J = 0$
¹S₀ (allowed)

9.5 (1s)(3p)

$$D_1 \times D_0 = D_1 \tag{L=1}$$

$$D_{1/2} \times D_{1/2} = D_1 + D_0$$
 (S=1, S = 0)

L = 1

$$|L = 1, M_{L} = 1\rangle = |0,0\rangle_{1}|1,1\rangle_{2},$$
$$|L = 1, M_{L} = 0\rangle = |0,0\rangle_{1}|1,0\rangle_{2},$$
$$|L = 1, M_{L} = -1\rangle = |0,0\rangle_{1}|1,-1\rangle_{2}$$

For $|\psi_1\rangle = |0,0\rangle_1 = |1s\rangle_1$ and $|\psi_2\rangle = |3p\rangle_2 = |1,m\rangle_2$ (*m* = 1, 0, -1), we can construct the symmetric orbital state and anti-symmetric state such that

$$|\psi_{s}\rangle = \frac{1}{\sqrt{2}} (|1s\rangle_{1}|3p\rangle_{2} + |3p\rangle_{2}|1s\rangle_{1}), \qquad L = 1 \text{ (symmetric)}$$
$$|\psi_{a}\rangle = \frac{1}{\sqrt{2}} (|1s\rangle_{1}|3p\rangle_{2} - |3p\rangle_{2}|1s\rangle_{1}), \qquad L = 1 \text{ (anti-symmetric)}$$

(i)
$$L = 1$$
 (antisymmetric) and $S = 1$ (symmetric), $J = 2, 1, 0$
³P₀, ³P₁, ³P₂, (allowed)
(ii) $L = 1$ (symmetric) and $S = 0$ (antisymmetric), $J = 1$
¹P₁ (allowed)



Fig. An energy-level diagram of the excited states of He. ${}^{3}S_{1}$ and ${}^{1}S_{0}$ from (1s)(3s). ${}^{3}P_{0}$, ${}^{3}P_{1}$, ${}^{3}P_{2}$, ${}^{3}P_{3}$, and ${}^{1}P_{1}$ from (1s)(2p). From the textbook of Gasiorowicz.



Fig. Energy level diagram of He atom. ${}^{1}S_{0}$ from $(1s)^{2}$. ${}^{1}S_{0}$ and ${}^{3}S_{1}$ from (1s)(2s). ${}^{1}P_{1}$, ${}^{3}P_{0}$, ${}^{3}P_{1}$, ${}^{3}P_{2}$ from (1s)(2p). ${}^{1}S_{0}$ and ${}^{3}S_{1}$ from (1s)(3s).). ${}^{1}P_{1}$, ${}^{3}P_{0}$, ${}^{3}P_{1}$, ${}^{3}P_{2}$ from (1s)(3p).

10. Two electrons in carbon

We consider the energy-level diagram for the states of carbon.

Carbon: $2s^22p^2$

10.1 The configuration of $(2p)^2$

We consider the two electrons in

$(2p)^2$

The ground state can be determined from the Hund's rule. <u>According to the Hund's rule</u>: the ground state is given by.

$2^{3}P_{0}$

since



L = 1, and S = 1. J = |L - S| = 0 because of the less than half.

The addition of the orbital angular momentum:

 $l = 1, l = 1 \qquad \rightarrow \qquad L = 2, 1, 0.$

The addition of the spin angular momentum:

$$s = 1/2, s = 1/2, \rightarrow S = 1, 0$$

<u>(2p)</u>²

L = 2 (symmetric)

$$\begin{split} |L &= 2, M_L = 2 \rangle = |1,1\rangle_1 |1,1\rangle_2 \\ |L &= 2, M_L = 1 \rangle = \frac{1}{\sqrt{2}} (|1,1\rangle_1 |1,0\rangle_2 + |1,0\rangle_1 |1,1\rangle_2) \\ |L &= 2, M_L = 0 \rangle = \frac{1}{\sqrt{6}} (|1,1\rangle_1 |1,-1\rangle_2 + |1,-1\rangle_1 |1,1\rangle_2 + 2|1,0\rangle_1 |1,0\rangle_2) \\ |L &= 2, M_L = -1\rangle = \frac{1}{\sqrt{2}} (|1,-1\rangle_1 |1,0\rangle_2 + |1,0\rangle_1 |1,-1\rangle_2) \\ |L &= 2, M_L = -2\rangle = |1,-1\rangle_1 |1,-1\rangle_2 \end{split}$$

L = 1 (anti-symmetric)

$$|L = 1, M_{L} = 1\rangle = \frac{1}{\sqrt{2}}(|1,1\rangle_{1}|1,0\rangle_{2} - |1,0\rangle_{1}|1,1\rangle_{2})$$
$$|L = 1, M_{L} = 0\rangle = \frac{1}{\sqrt{2}}(|1,1\rangle_{1}|1,-1\rangle_{2} - |1,-1\rangle_{1}|1,1\rangle_{2})$$
$$|L = 1, M_{L} = -1\rangle = \frac{1}{\sqrt{2}}(|1,0\rangle_{1}|1,-1\rangle_{2} - |1,-1\rangle_{1}|1,0\rangle_{2})$$

L = 0 (symmetric)

	$\left L=0,M_{L}=0\right\rangle = \frac{1}{\sqrt{3}}($	 1,1 > ₁ 1,	$-1\rangle_{2}+ 1,-1\rangle_{1} 1,$	$ 1\rangle_{2} - 1,0\rangle_{1} 1,0\rangle_{2}$	
(1) L =	= 1 and S = 1	J = 0	${}^{3}P_{0}$ (at	nti-symmetric)	
	(ground state from the	Hund'	s law)		
	L = 1 (antisymmetric).		S = 1 (symmetry	etric).	
(2) <i>L</i> =	= 1 and S = 1	<i>J</i> = 1	${}^{3}P_{1}$ (at	nti-symmetric)	
	L = 1 (antisymmetric).		S = 1 (symmetry)	etric).	
(3) <i>L</i> =	= 1 and S = 1	J = 2	${}^{3}P_{2}$ (at	nti-symmetric)	
	L = 1 (antisymmetric).		S = 1 (symmetry)	tyric)	
(4) L =	= 2 and S = 0	<i>J</i> = 2	$^{1}D_{2}$ (at	nti-symmetric)	_
	L = 2 (symmetric).		S = 0 (anti-system)	mmetric).	
(5) <i>L</i> =	= 0 and S = 0	J = 0	${}^{1}S_{0}$ (at	nti-symmetric)	
	L = 0 (symmetric).		S = 0 (anti-system)	mmetric).	
(6) L =	= 2 and S = 1	<i>J</i> = 3	${}^{3}D_{3}$ (s)	ymmetric, not allowed)	
	L = 2 (symmetric).		S = 1 (symmetry)	etric).	
(7) <i>L</i> =	= 2 and S = 1	<i>J</i> = 2	$^{3}D_{2}$	Symmetric (not allowed)	
	L = 2 (symmetric).		S = 1 (symmetry)	etric).	
(8) L =	= 2 and S = 1	<i>J</i> = 1	${}^{3}D_{1}$	Symmetric (not allowed)	
	L = 2 (symmetric).		S = 1 (symme	etric).	
<mark>(9)</mark>	L = 1 and $S = 0$,	<i>J</i> = 1	${}^{1}\mathbf{P}_{1}$	Symmetric (not allowed)	
	L = 1 (anti-symmetric)).	S = 0 (anti-sys	mmetric).	

<mark>(10)</mark>	L = 0 and S	'=1		J = 1	${}^{3}S_{1}$ (symmetric, not allowed)
	L = 0 (sym	metric).		S = 1 (sy	vmmetric).
Table					
	S	L	J		
	õ	0	0	${}^{1}\mathbf{S}_{0}$	(antisymmetric)
	0	1	1	${}^{1}P_{1}$	(symmetric)
	0	2	2	$^{1}\text{D}_{2}$	(antisymmetric)
	1	0	1	$^{3}S_{1}$	(symmetric)
				-	
	1	1	2	$^{3}P_{2}$	(antisymmetric)
	1	1	1	${}^{3}P_{1}$	(antisymmetric)
	1	1	0	$^{3}P_{0}$	(ground state; antisymmetric)
	1	2	3	$^{3}D_{3}$	(symmetric)
	1	2	2	$^{3}D_{2}$	(symmetric)
	1	2	1	³ D,	(symmetric)

By the selection rules, $\Delta L = \pm 1$, $\Delta S = 0$, $\Delta J = 0$, ± 1 , no transitions are allowed between the levels shown in Fig. the selection rule $\Delta S = 0$ prohibits singlet to triplet transitions.

$$\frac{1}{P_{0}} (L = 0, S = 0, J = 0)$$

$$\frac{1}{P_{2}} (L = 3, S = 0, J = 2)$$

$$\frac{3}{P_{2}} (L = 2, S = 1, J = 2)$$

$$\frac{3}{P_{1}} (L = 2, S = 1, J = 1)$$

$$\frac{3}{P_{0}} (L = 2, S = 1, J = 0)$$

The ${}^{3}P_{0}$ state has the lowest energy, because the antisymmetry of the spatial part of the wave function for the two 2p electrons lowers their Coulomb repulsion energy (Hund's law). Just above ${}^{3}P_{0}$ are the ${}^{3}P_{1}$ and ${}^{3}P_{1}$ states at 2 meV and 5 meV above the ground state, their energies being increased by the spin-orbit interaction. The ${}^{1}D_{2}$ states are 1.26 eV above the ground state, the ${}^{1}S_{0}$ another 1.42 eV higher.

	$l = 1, l = 0 \longrightarrow$ s = 1/2, s = 1/2,	\rightarrow	L = 1 S = 1, 0	
(1) (2)	L = 1 and $S = 1L = 1$ and $S = 0$		J = 2, 1, 0 J = 1	${}^{3}P_{2}, {}^{3}P_{1}, {}^{3}P_{0}, {}^{1}P_{1}$

(2p)(3s)

L = 1

 $|L = 1, M_{L} = 1\rangle = |1,1\rangle_{1}|0,0\rangle_{2},$ $|L = 1, M_{L} = 0\rangle = |1,0\rangle_{1}|0,0\rangle_{2},$ $|L = 1, M_{L} = -1\rangle = |1,-1\rangle_{1}|0,0\rangle_{2}$

Using the operator $\hat{P}_{12}^{(space)}$, we can construct both

the symmetric L = 1 state (with S = 0 anti-symmetric state) the anti-symmetric L = 1 state (with S = 1 symmetric state).

For carbon the excitation of a 2p electron to a 3s orbit gives rise to a ${}^{3}P_{2}$, ${}^{3}P_{1}$, ${}^{3}P_{0}$, and ${}^{1}P_{1}$.

 $^{3}P_{0}$ (anti-symmetric) (1) L = 1 and S = 1J = 0(ground state from the Hund's law) S = 1 (symmetric). L = 1 (antisymmetric). $^{3}P_{1}$ (anti-symmetric) (2) L = 1 and S = 1J = 1L = 1 (antisymmetric). S = 1 (symmetric). $^{3}P_{2}$ (anti-symmetric) (3) L = 1 and S = 1J = 2L = 1 (antisymmetric). S = 1 (symmetric) (4) L = 1 and S = 0J = 1 ${}^{1}P_{1}$ L = 1 (symmetric). S = 0 (antisymmetric).



Fig. Energy level diagram of carbon H. White, Introduction to atomic spectra

11. Nitrogen

Electron configuration: $(2p)^3$

 $D_1 \times D_1 \times D_1 = (D_2 + D_1 + D_0) \times D_1 = D_3 + 2D_2 + 3D_1 + D_0$

The ground state: Hund's rule

S = 3/2 and L = 0. j = 3/2: ${}^{4}S_{3/2}$

((Total orbital angular momentum L))

L = 3 (symmetric), L = 0 (anti-symmetric)

L=3 (7 states)	once (totally symmetric)
L = 2 (5 states))	twice (both mixed symmetry)
L = 1 (3 states)	three times (one totally symmetric, two mixed symmetry)
L=0 (1 state)	once (totally antisymmetric).

(see Young's tableau)



((Total spin angular momentum Spin))

$$S = \frac{3}{2}$$
 (symmetric)

	1	1	1		1	1	2		1	2	2		2	2	2
1	m=3	8/2		,	, m=1/2		, m=-1/2			,	m	=-3/	2		

where

$$\left| S = \frac{3}{2}, M_s = \frac{3}{2} \right\rangle = \left| + + + \right\rangle$$

$$\left|\frac{3}{2},\frac{1}{2}\right\rangle = \frac{1}{\sqrt{3}}[|++-\rangle+|+-+\rangle+|-++\rangle]$$
$$\left|\frac{3}{2},-\frac{1}{2}\right\rangle = \frac{1}{\sqrt{3}}[|+--\rangle+|-+-\rangle+|--+\rangle]$$
$$\left|\frac{3}{2},-\frac{3}{2}\right\rangle = |---\rangle$$

Then we have the following cases for the total angular momentum

S = 3/2 (symmetric), L=0 (antisymmetric), leading to j = 3/2



which is the same one predicted from the Hund's law.



Fig. Energy level diagram of nitrogen

12. Oxygen Electron configuration: (2p)⁴

The ground state: Hund's rule

S = 1 and L = 1. J=2: ³P₂



Energy level diagram of oxygen. H. White, Introduction to atomic spectra Fig.

$13.$ Detection rates for electric apple ir ansitions in the L - β coupling set	nng seneme
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1.	$\Delta j = 0, \pm 1$	(the transition between $j=0$ and $j'=0$ is not allowed)
2	$\Delta m_{\rm j}=0,\pm 1$	(the transition between $m_j = 0$ and $m_j = 0$ is not allowed if $j = j'$).

3.	$\Delta L = \pm 1$	Term
4	$\Delta S = 0$	Term

REFERENCES

H. White, Introduction to Atomic Spectra.S. Gasiorowicz, *Quantum Mechanics*, third edition (John Wiley & Sons, Inc., New York, 2003).