

LECTURE 6

Electronic Configurations of the Elements and the Periodic Table

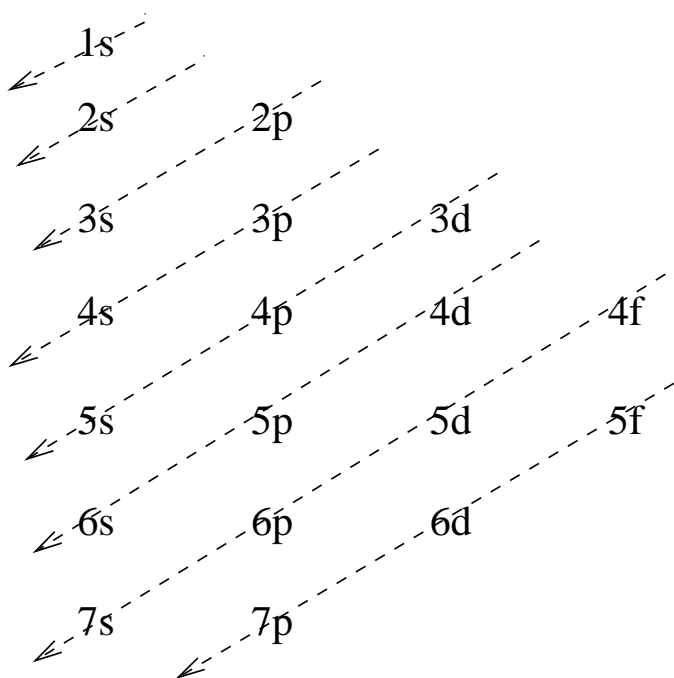
(Reference: Charles E. Mortimer, *Chemistry: A Conceptual Approach*, 3rd ed. (1975))

A pretty good way to determine the electronic configurations of the elements is to imagine adding one electron at a time to the energy levels of an atom. Each electron is added in accordance with the Pauli exclusion principle and Hund's rule. Several factors determine the energy of an electron in an orbital. These include the number of protons in the nucleus (Z), the average distance of the orbital from the nucleus (larger n means larger distance), the screening of the nuclear charge by the inner electrons, and the degree to which the orbital penetrates the charge cloud of the other electrons and approaches the nucleus (given by ℓ).

A word about screening. In a multielectron atom, the positive charge of the nucleus is partially screened from an outer electron by the negative cloud of intervening electrons; the electron does not "feel" the full nuclear charge. The screening, however, is not uniform for all the orbitals of a given level. The orbitals of an atom overlap the region surrounding the nucleus, and there is a slight probability that an electron of any type orbital will be found close to the nucleus where the electron is more fully subject to the nuclear charge. The more an orbital penetrates the negative cloud of the screening electrons, the more strongly the electron is attracted to the nucleus and the lower is its energy. For orbitals of the same level (same value of n), the smaller the value of ℓ , the higher the probability of finding the electron near the nucleus. Thus, in a given atom a $2s$ electron ($\ell = 0$) is more penetrating and has a lower energy than a $2p$ electron ($\ell = 1$). For a given level the order by energy is: $s < p < d < f$.

There is no standard order of sublevels, based on energy, that pertains to all atoms. In the potassium atom ($Z = 19$), the $4s$ orbital has a lower energy than a $3d$ because the $4s$ penetrates the screening electrons more than the $3d$. In atoms of higher Z (at approximately $Z = 29$, Cu), this situation reverses and a $3d$ orbital has a lower energy than the $4s$ presumably because the higher nuclear charge makes the penetration effect (related to ℓ) less important than the distance of maximum electron probability (given by n).

Aufbau ordering is one good rule of thumb for deducing the electronic configurations.



One can correlate the aufbau ordering with the periodic table.

1s		1s
2s - ➤		2p - - - - - ➤
3s - ➤	Transition elements	3p - - - - - ➤
4s - ➤	3d - - - - - ➤	4p - - - - - ➤
5s - ➤	4d - - - - - ➤	5p - - - - - ➤
6s - ➤	5d - - - - - ➤	6p - - - - - ➤
7s - ➤	6d	

4f - - - - - ➤
5f - - - - - ➤

The transition elements are the ones where the last electron added is a *d* electron. For example the first transition element is scandium ($Z = 21$) which has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$. The rare earth or actinide elements are the ones where the last electron added is an *f* electron. The alkali metals, which are in

the first column have one s electron. Lithium, sodium, potassium are some of the alkali metals. The noble gases (like helium, neon, and argon) are the ones in the last column and have a filled shell. They are very stable chemically because they have a filled shell. Atoms like filled shells, and their chemical reactivity with other atoms is determined by how easy it is for them to have a filled shell. For example, fluorine and chlorine are very reactive (electronegative) because they are just one electron short of a filled shell. This next-to-last column has elements called halogens.

Zeeman Effect

(Reference: Robert B. Leighton, *Principles of Modern Physics*, McGraw–Hill (1959).) In lecture 2 we said that the orbital and spin angular momenta are associated with magnetic moments:

$$\vec{M}_{orb} = -\frac{e\hbar}{2mc}\vec{L} \quad (1)$$

and

$$\vec{M}_{spin} = -g\frac{e\hbar}{2mc}\vec{S} \quad (2)$$

where the Landé g factor $g = 2$ for an electron. Here \vec{L} is the orbital angular momentum for all the electrons. \vec{S} is the spin angular momentum for all the electrons in the atom. Here we are assuming that LS coupling applies. The total magnetic moment is

$$\vec{M}_{tot} = \vec{M}_{orb} + \vec{M}_{spin} = -\frac{e\hbar}{2mc}(\vec{L} + 2\vec{S}) = -\frac{e\hbar}{2mc}(\vec{J} + \vec{S}) \quad (3)$$

Notice that \vec{M}_{tot} is not parallel to the net angular momentum \vec{J} because the orbital and spin g factors are different. When an atom is placed in an external magnetic field \vec{B} , the orientational energy shift ΔE is

$$\Delta E = -\vec{M}_{tot} \cdot \vec{B} \quad (4)$$

Let's suppose that $\vec{B} = B\hat{z}$. Then

$$\Delta E = -M_{z,tot}B = \frac{eB\hbar}{2mc}(L_z + 2S_z) = \frac{eB\hbar}{2mc}(m_L + 2m_S) \quad (5)$$

Notice that different values of m_L and m_S will have different energies. This is loosely called the Zeeman effect. It's official name is the Paschen–Bach effect. It's true in strong external magnetic fields (somewhat greater than 1 Tesla) where the external magnetic field is so much larger than the atomic magnetic field that it overwhelms the coupling between L and S .

For external magnetic fields which are weaker than the atomic magnetic field, one cannot ignore the spin–orbit coupling $\vec{L} \cdot \vec{S}$. In this case, with $\vec{B} = B\hat{z}$, m_J is a good quantum number and the level splitting is given by

$$\Delta E = \mu_B g m_J B \quad (6)$$

where the Bohr magneton $\mu_B = e\hbar/2mc$ and the Landé g factor is given by

$$g = 1 + \frac{j(j+1) + s(s+1) - \ell(\ell+1)}{2j(j+1)} \quad (7)$$

Notice that the magnetic field splits each energy level into $2j + 1$ components, one for each value of m_J . This splitting is called the *Zeeman effect*. To get some idea of why $\vec{L} \cdot \vec{S}$ coupling leads to the Landé g factor, note that since $\vec{J} = \vec{L} + \vec{S}$,

$$\vec{J}^2 = (\vec{L} + \vec{S})^2 = \vec{L}^2 + \vec{S}^2 + 2\vec{L} \cdot \vec{S} \quad (8)$$

So

$$\vec{L} \cdot \vec{S} = \frac{1}{2}(\vec{J}^2 - \vec{L}^2 - \vec{S}^2) \quad (9)$$

Or

$$\langle nJLS | \vec{L} \cdot \vec{S} | nJLS \rangle = \frac{1}{2}C\hbar^2(J(J+1) - L(L+1) - S(S+1)) \quad (10)$$

where C is a constant. Here we are using *bra* and *ket* notation to denote the expectation value of $\vec{L} \cdot \vec{S}$ with respect to a state with quantum numbers n , J , L , and S .

In case you're not familiar with bracket notation, let me go over it briefly. Recall Schrodinger's equation:

$$H\psi_n = E_n\psi_n \quad (11)$$

The energy expectation value E_n can be written as

$$E_n = \int \psi_n^* H \psi_n \quad (12)$$

where the integral is over the relevant coordinates—space, spin, etc. This can also be written as

$$E_n = \langle n | H | n \rangle \quad (13)$$

The bra vector $\langle n |$ corresponds to ψ_n^* and the ket vector $|n\rangle$ corresponds to ψ_n . We can also regard this as a diagonal matrix element $H_{n,n}$. Suppose we have a basis set of wavefunctions $\psi_1, \psi_2, \dots, \psi_N$. The diagonal matrix elements of some operator \hat{A} are the expectation values a of \hat{A} :

$$a_n = \int \psi_n^* \hat{A} \psi_n \quad (14)$$

where $n = 1, 2, \dots, N$. If the basis set of wavefunctions are the eigenfunctions of the Hamiltonian H , then the diagonal matrix elements are the energy eigenvalues and the off-diagonal matrix elements are all zero. But if the basis set of wavefunctions are not eigenfunctions of H , then the off-diagonal matrix elements will not be zero, in general. In this case the off-diagonal matrix elements are the transition amplitudes from one state n to another n' . The transitions are induced by the Hamiltonian H .

$$\int \psi_{n'}^* \hat{H} \psi_n = \langle n' | H | n \rangle \quad (15)$$

The probability that there will be a transition from n to n' induced by the coupling H is the square of the amplitude:

$$|\int \psi_{n'}^* \hat{H} \psi_n|^2 = |\langle n' | H | n \rangle|^2 \quad (16)$$

(For a Hermitian operator \hat{A} , $\langle \alpha | \hat{A} | \beta \rangle^* = \langle \beta | \hat{A}^\dagger | \alpha \rangle$, where $*$ means complex conjugate and \hat{A}^\dagger is the hermitian adjoint of \hat{A} .)

Transition Rates Between Atomic Energy Levels

Discussing transition probabilities brings up the topic of electron transitions between states. An electron which occupies an excited state n' in an atom can jump to a lower energy state n by emitting a photon whose energy $\hbar\omega = E_{n'} - E_n$. The photon is needed for energy conservation. Similarly an electron can jump from a lower energy state to a higher energy state by absorbing a photon whose energy equals the energy difference. Classically electromagnetic radiation is produced by accelerated charges. The most efficient way to do this is with an electric dipole antenna. The electric dipole term is the first term in a multipole expansion. When one treats the atom quantum mechanically, there is an electric dipole term H_{ED} in the Hamiltonian which is responsible for virtually all of the observed electronic transitions. In other words the transition rate due to H_{ED} is much higher than that due to other terms (like the magnetic dipole and electric quadrupole terms). The transition rate $R_{f \leftarrow i}$ from an initial state i to a final state f is given by Fermi's Golden Rule:

$$R_{f \leftarrow i} = \frac{2\pi}{\hbar} |\langle f | H_{ED} | i \rangle|^2 \delta(E_f - E_i \pm \hbar\omega) \quad (17)$$

where $+\hbar\omega$ corresponds to photon emission and $-\hbar\omega$ corresponds to photon absorption. Notice that the transition rate is proportional to the transition probability. The δ function ensures energy conservation. The units work out to give the right units for a rate (inverse time). Fermi's Golden Rule is one of the most useful formulas in quantum mechanics. Often there is a group of final states that are nearly equal in energy and for which $\langle f | H | i \rangle$ is roughly independent of f . Then we can sum over final states which have energy very close to E and write the transition rate as

$$R_{f \leftarrow i} = \frac{2\pi}{\hbar} |\langle f | H | i \rangle|^2 N(E) \quad (18)$$

where $N(E)$ is the density of final states with energy E . This is a more useful form of Fermi's Golden Rule.

Not every possible transition occurs. There are other constraints imposed by other conservation rules. This results in selection rules which tell us which transitions are allowed. The selection rules for electric dipole transitions are (assuming LS coupling):

1. Only one electron jumps at a time.

2. The ℓ -value of the jumping electron must change by one unit

$$\Delta\ell = \pm 1 \quad (19)$$

This is because the parity of the wavefunction must change in an electric dipole transition. To determine the parity of a wavefunction $\psi(\vec{r})$, let $\vec{r} \rightarrow -\vec{r}$ and see if the wavefunction changes sign:

$$\begin{aligned} \psi(\vec{r}) &= \psi(-\vec{r}) && \text{even parity} \\ \psi(\vec{r}) &= -\psi(-\vec{r}) && \text{odd parity} \end{aligned}$$

A parity operation changes spherical coordinates in the following way:

$$r \rightarrow r, \quad \theta \rightarrow \pi - \theta, \quad \phi \rightarrow \pi + \phi \quad (20)$$

If the orbital angular momentum ℓ is a good quantum number, the parity of the wavefunction is given by $(-1)^\ell$. So if ℓ is an even integer, the wavefunction has even parity, and if ℓ is an odd integer, the wavefunction has odd parity. Since the electric dipole moment $\vec{p} = e\vec{r}$, $H_{ED} \sim \vec{r}$, and H_{ED} is odd under parity because \vec{r} changes sign when $\vec{r} \rightarrow -\vec{r}$. Remember that $\langle f|H_{ED}|i \rangle$ represents an integral and integrating an odd integrand over all space gives zero. In order for the matrix element to be nonzero, $\langle f|H_{ED}|i \rangle$ must have even parity, so the initial and final states must have opposite parity.

3. For the atom as a whole, the quantum numbers L , S , J , and M_J must change as follows:

$$\begin{aligned} \Delta S &= 0 && \text{electron spin doesn't change} \\ \Delta L &= 0, \pm 1 \\ \Delta J &= 0, \pm 1 && \text{but } J = 0 \rightarrow J = 0 \text{ forbidden} \\ \Delta M_J &= 0, \pm 1 && \text{but } M_J = 0 \rightarrow M_J = 0 \text{ forbidden if } \Delta J = 0 \end{aligned}$$

Since a photon has angular momentum 1, the total angular momentum J_f of the final state must equal the vector sum of the angular momentum of the photon and of the total angular momentum J_i of the initial state. Recall from lecture 2 that when we add angular momentum j_1 and j_2 , the total j obeys

$$|j_1 - j_2| \leq j \leq j_1 + j_2 \quad (21)$$

So $J_f = J_i$, $J_i \pm 1$ unless $J_i = 0$. If $J_i = 0$, $J_f = 1$. The fact that the sum of the angular momenta of $|i \rangle$ and H_{ED} equals the angular momentum of the final state

$|f\rangle$ in $\langle f|H_{ED}|i\rangle$ is an example of the Wigner–Eckart theorem. It’s also just conservation of angular momentum.

Note on $\Delta L = 0, \pm 1$. Usually $\Delta L = \pm 1$, and occasionally $\Delta L = 0$, even though for the electron making the transition $\Delta\ell = \pm 1$. This is due to the way that angular momenta are added in quantum mechanics as one can see from (21).

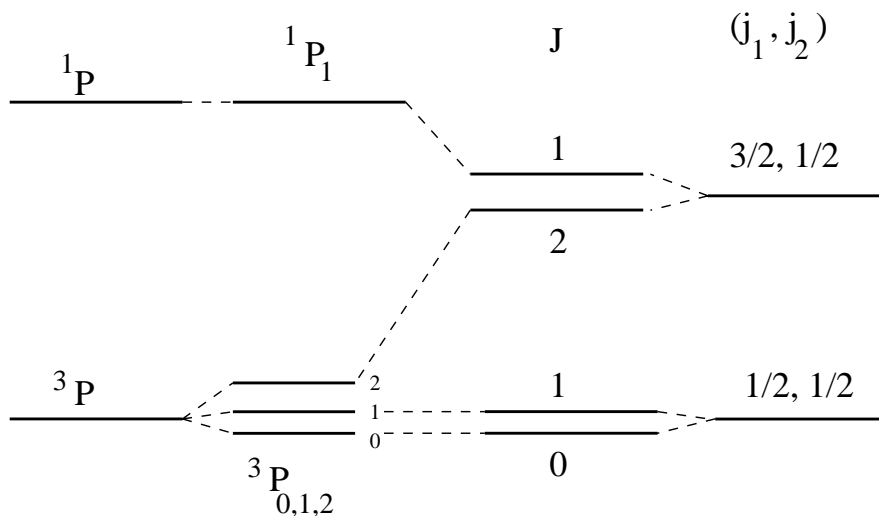
$j - j$ Coupling

When we assume the opposite case to Russell–Saunders coupling—namely, *not* that there is a strong interaction of the ℓ_i with one another and the s_i with one another, but rather that there is considerable interaction between each ℓ_i and the s_i belonging to it—we obtain the so-called $j - j$ coupling: Each ℓ_i combines with the corresponding s_i to give a j_i , the total angular momentum of the individual electron. The individual j_i are less strongly coupled with one another and form the total angular momentum J of the atom. Such coupling can be written symbolically:

$$(\ell_1 s_1)(\ell_2 s_2)(\ell_3 s_3)\dots = (j_1 j_2 j_3 \dots) = J \tag{22}$$

There is no definite L and S for this coupling. However J remains well defined. The same holds for M .

Let us consider, as an example, the configuration ps , which gives ${}^3P_{0,1,2}$ and a 1P_1 state on the basis of Russell–Saunders coupling. Assuming $j - j$ coupling, however, the p orbital has $\ell_1 = 1$ and $s_1 = 1/2$ which gives $j_1 = 1/2, 3/2$. From the assumption of strong coupling between ℓ and s , these two states can have very different energies. The s orbital has $\ell_2 = 0$ and $s_2 = 1/2$ which gives $j_2 = 1/2$. The two states may be characterized as $(j_1, j_2) = (3/2, 1/2)$ and $(1/2, 1/2)$. To the same approximation, the analogous Russell–Saunders states are 1P and 3P . When the small $j - j$ coupling is taken into account, a slight splitting of each of the two (j_1, j_2) states occurs. For $(3/2, 1/2)$, J is 2 or 1; for $(1/2, 1/2)$, J is 0 or 1. For Russell–Saunders coupling, the small spin–orbit coupling splits 3P into 3 components, $J = 0, 1, 2$.



j-j coupling

LS Coupling

The selection rules for $j - j$ coupling are

1. Only one electron jumps at a time.
2. The ℓ -value of the jumping electron must change by one unit or, more generally, the parity must change.
3. $\Delta j = 0, \pm 1$ for the jumping electron, and $\Delta j = 0$ for all the other electrons.
4. For the atom as a whole

$$\begin{aligned} \Delta J &= 0, \pm 1 && \text{but } J = 0 \rightarrow J = 0 \text{ forbidden} \\ \Delta M_J &= 0, \pm 1 && \text{but } M_J = 0 \rightarrow M_J = 0 \text{ forbidden if } \Delta J = 0 \end{aligned}$$

Most atoms follow LS coupling rather than $j - j$ coupling, so we won't discuss $j - j$ coupling further.