Parity

- We should also take account of the fact that the Hamiltonian for an atom is symmetric with respect to coordinate inversion. That is, the point group should be $O(3)$ rather than $SO(3)$.

- For one-electron functions the parity with respect to inversion is $(-1)^l$ (so $s, d\ldots$ are even parity and $p, f\ldots$ are odd).

- For many-electron configurations, each electron $i$ contributes a factor $(-1)^{l_i}$ to the overall parity.

- Thus $p^3$ configurations all have odd parity, for example: $^4S^o$, $^2D^o$, $^2P^o$ (or sometimes $^4S_u$ etc.).
Coupling of Spin and Orbital Angular Momenta

- In reality, our spin-independent Hamiltonian is an approximation. If we take account of relativity, spin-dependent terms appear in the Hamiltonian.

- This becomes quite complicated and is mostly outside the scope of the course.

- We will, however, look qualitatively at some of the consequences.

- If the Hamiltonian is spin-dependent, we can no longer treat the spin angular momentum separately.
Coupling of Spin and Orbital Angular Momenta

- An important question is how strong is the interaction between electron spin and spatial motion?
- If it is rather weak, we can use our decoupled space/spin picture and add the *spin-orbit coupling* as a perturbation.
- If it is very strong, we should probably change our picture to deal with this first.
- We will look at both of these limiting cases.
Weak Spin-Orbit Coupling

- Here we construct electronic states in the usual way (e.g., $^3P$, $^2\Pi$, $^4A_2$, etc.). This is $LS$-coupling.

- Spin-orbit coupling is then assumed to affect only the various $J$ values that arise for this state.

- For instance, for $^3P$ we have $^3P_0$, $^3P_1$, $^3P_2$, and these $J$ states will no longer be degenerate. However, there is no interaction between these states and, e.g., the $^1D_2$ level.

- This is Russell-Saunders coupling.
Hund’s Rules

- In two states arising from the same electron configuration:
  - The higher spin multiplicity is preferred.
  - After that the higher orbital angular momentum is preferred.
  - After that the lowest $J$ value is preferred for a shell less than half-full; the highest $J$ value for a shell more than half-full.
- Requires a spatially degenerate state and a spin state higher than singlet.
- Thus in $LS$-coupling we will have $^3P < ^1D < ^1S$, and in Russell-Saunders $^3P_0 < ^3P_1 < ^3P_2$ for a shell less than half-full, otherwise the reverse.
Russell-Saunders Coupling

- The assumption that only levels from a given state interact leads to the Landé interval rule:

\[ E(2S+1L_J) - E(2S+1L_{J-1}) = J\zeta_{LS}, \]

where \( \zeta \) is the spin-orbit coupling constant.

- The extent to which levels deviate from this rule indicates breakdown of the Russell-Saunders scheme.

- Deviations of up to 10% or so are typical, even for light elements like C.
$jj$-Coupling

- As nuclei get heavier, electrons will move faster, and thus we expect relativistic effects to get larger.

- Eventually, we should couple the orbital and spin angular momentum of the individual electrons to produce a combined individual angular momentum $j$ for each electron.

- Then couple the individual $j$ values to get the overall $J$: $jj$-coupling.
\textbf{$jj$-Coupling}

- For a $p$ electron we can have $m_l m_s$ components $p_1 \alpha$, $p_0 \alpha$, $p_{-1} \alpha$, $p_1 \beta$, $p_0 \beta$, $p_{-1} \beta$, or a total of six components.

- These give respectively $m_j = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$, which arise from $j = \frac{3}{2}, \frac{1}{2}$.

- For $p^2$, then, we can have $(\frac{3}{2})^2$, $(\frac{1}{2})^2$, or $(\frac{1}{2})^{1,3}$.

- We can reduce this, or look it up in a book. Note that in general we need the “half-integer” irreps of $SO(3)$!

- We get $J = 0, 0, 1, 2, 2$. Number of components 15.

- Even Pb is not at this limit.
Double Groups

- The presence of the double-valued representations causes problems, as we recall: for example, rotation through $2\pi$ is not the same as the identity.

- One way to deal with this is to redefine rotation through $2\pi$ as a new operation (conventionally denoted $R$), with rotation through $4\pi$ as the identity.

- The resulting set of operations is referred to as a “double group” or sometimes as an “extended point group”, denoted by a superscript + as in $O^+ (3)$ or $C_{2v}^+$.

- Note that this does not necessarily result in a group of twice the original order, but it does add new degenerate (sometimes separable) irreps.
Crystal-field Splitting

- Consider an atom or ion in a degenerate state (in $O(3)$).

- If this atom is placed in an external potential that is not spherically symmetric, the symmetry will be lowered and the degeneracy of the state (may be) lifted.

- The most important example is transition-metal atoms or ions in fields generated by ions or ligands.

- As with spin-orbit coupling, the results depend on the relative strength of the external field and the “internal” field (electron-electron interaction).
Crystal-field Splitting

- If the external field is weak, the final many-electron state is determined by the many-electron state of the atom.

- Consider a Ti(2+) ion with electron configuration $d^2$. From Hund’s rules we expect the lowest state of this configuration to be $^3F$.

- If this ion is placed in an external potential of tetrahedral symmetry, the $^3F$ (even parity!) state will split into $^3A_2$, $^3T_1$, and $^3T_2$ states.

- The relative energy of these states cannot be determined by purely group-theoretical arguments.
Ligand-Field Theory

- Argue first how the energy of the $d$ orbitals is affected by the ligands (hand-waving).

- For a tetrahedral field they split into $e$ and $t_2$. The expected ordering is that $e$ lies below $t_2$.

- Allocate electrons to orbitals. For our $d^2$ example we expect $e^2 \left( ^3A_2 \right)$.

- What happens with more than two electrons?

- This depends on the “strength” of the field.
Ligand-Field Theory

- If the effect of the field is relatively weak, the normal atomic Hund’s rule arguments will apply, and the highest spin multiplicity will be preferred. For, say $d^3$ in a tetrahedral field, this will be $e^2 t^1_2$ coupled as $^4T_1$.

- However, if the external field is stronger than the interaction between the electrons, we would expect $e^3$ ($^2E$).

- Both situations are encountered in practice, and there will be a critical “ligand-field strength” at which the ground state changes from $^4T_1$ to $^2E$. 