

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, \dots are even parity and p, f, \dots 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: $^4S^\circ$, $^2D^\circ$, $^2P^\circ$ (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*:

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

where ζ 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.



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 $(\frac{1}{2}^1 \frac{3}{2})^1$.
- 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 2π is not the same as the identity.
- One way to deal with this is to redefine rotation through 2π as a new operation (conventionally denoted R), with rotation through 4π 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 (3A_2).
- 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 $e^2t_2^1$ 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 .

