Term Symbols for Diatomic Molecules

Term Symbols Defined

Term Symbols for molecules are of the form: ${}^{2S+1}\Lambda^{+}_{g}$

2S+1 is the spin multiplicity (i.e. S= the net spin of the electrons in the molecule) just like in atomic term symbols.

Λ is the angular momentum of the molecule and corresponds to the L term in atomic term symbols. The possible values of L are Σ (Λ=0), Π (Λ=1), Δ (Λ=2), Φ (Λ=3), Γ (Λ=4). etc.

The + term can be + or – and refers to σ_v symmetry (reflection across a plane which is parallel to the internuclear axis (z). This term is only relevant for Σ states.

The g term can be g or u and refers to inversion symmetry, if a molecule has an inversion center (this is only true for homonuclear diatomics).

Finding the Term Symbols

The following is a procedure for verifying the existence of a given term symbol for an electron configuration.

1. Finding g/u: this is the easiest part to find. We get the g/u term by multiplying the g terms from all of the electrons together (based on which MOs they are in) using the rules u^2=g, g^2=g. This is equivalent to counting the # of u electrons and if it is odd, then we get u, and if it is even, we get g.

2. Now choose a Λ value that we can construct out of the λ values of the individual electrons.

3. Write out the spatial wave function for this term.

4. Check for symmetry (symmetric or antisymmetric) under transposition of electrons.

5. If symmetry requirement is not satisfied in 4, take a linear combination of the original wavefunction and the transposition to satisfy symmetry requirement.

6. Choose a possible spin state. (either singlet or triplet for 2 electron systems)

7. Apply Pauli principle so that one and only one of the spin/space functions is antisymmetric.

8. If Λ=Σ, proceed to step 9 find the +/- symmetry, if not then you are finished.

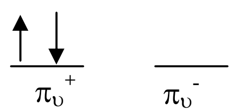
9. Carry out a reflection on your spatial wavefunction (send π^+ to π^- and π^- to π^+), and check to see if it is symmetric ,antisymmetric or neither.

10. If symmetric then term is +, if anitsymmetric then term is -, if neither then take a linear combination (+ or -) and then reflect new function to get + or -.

Example 1: π_u^2 (2 electrons in the same π_u system), find microstates corresponding to the $^1\Delta_g$, $^1\Sigma^+_g$ and $^3\Sigma^+_g$ states.

The orbitals look like this:

So we put 2 electrons in to get Λ=2 like this because π_υ^+ has λ=1 and π_υ^- has λ=-1:



Now following the steps above we get:

1. u^2=g, so we have a g state.

2. Λ=2.

3. $\pi_u^+(1)\ \pi_u^+(2)$.

4. Transposition gives: $\pi_u^+(2)\ \pi_u^+(1)$, therefore already symmetric so proceed to 6.

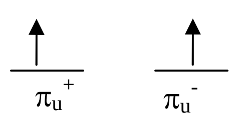
5. skip

6. must be singlet state as evident from diagram above so $(\alpha\beta - \beta\alpha)$

7. Pauli principle is already satisfied b/c spin function is antisymmetric and spatial function is symmetric.

8. If Λ not= Σ, so we are finished.

Now to find $^3\Sigma^-_g$ state we put 2 electrons in to get Λ=0 (Σ state) like:



Now following the steps above we get:

1. u^2=g, so we have a g state.

2. Λ=0.

3. $\pi_u^-(1)\ \pi_u^+(2)$.

4. Transposition gives: $\pi_\upsilon^-(2)\ \pi_\upsilon^+(1)$, therefore no symmetry so must use linear combination.

5. linear combination could be $\{\pi_u^-(1)\ \pi_u^+(2) + \pi_u^-(2)\ \pi_u^+(1)\}$
   or $\{\pi_u^-(1)\ \pi_u^+(2) - \Pi_\upsilon^-(2)\ \pi_u^+(1)\}$

6. we're looking for a triplet state so we use ($\alpha\alpha$)

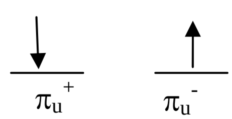
7. Pauli principle is satisfied by taking the minus combination of the spatial function to make it antisymmetric since the spin function is symmetric.

8. $\Lambda=\Sigma$, so proceed to step 9 to find the +/- symmetry.

9. reflection gives: $\{\pi_u^+(1)\ \pi_u^-(2) - \pi_u^+(2)\ \pi_u^-(1)\}$

10. This is antisymmetric so we have a - state.

Finally to find $^1\Sigma^+_g$ state we put 2 electrons in to get Λ=0 (Σ state) like this:



Now following the steps above we get:

1. u^2=g, so we have a g state.

2. Λ=0.

3. $\pi_u^-(1)\ \pi_u^+(2)$.

4. Transposition gives: $\pi_u^-(2)\ \pi_u^+(1)$, therefore no symmetry so must use linear combination.

5. linear combination could be $\{\pi_u^-(1)\ \pi_u^+(2) + \pi_u^-(2)\ \pi_u^+(1)\}$
   or $\{\pi_u^-(1)\ \pi_u^+(2) - \pi_u^-(2)\ \pi_u^+(1)\}$

6. we're looking for a singlet state so we use ($\alpha\beta-\beta\alpha$)

7. Pauli principle is satisfied by taking the plus combination of the spatial function to make it symmetric since the spin function is antisymmetric.

8. $\Lambda = \Sigma$, so proceed to step 9 to find the +/- symmetry.

9. reflection gives: $\{\pi_u^+(1)\ \pi_u^-(2) + \pi_u^+(2)\ \pi_u^-(1)\}$

10. This is symmetric so we have a + state.