

9.4: Hund's coupling cases (a) and (b)

There are clearly sources of angular momentum in a molecule due to orbital and spin considerations. But unlike atoms, molecules can also have angular momentum contributions from molecular rotation. There are many ways to describe the coupling of these different types of angular momentum. This text will focus on two specific cases, Hund's coupling cases a and b.

Hund's case (a)

In **Hund's case (a)** coupling, the orbital and spin angular momenta are strongly coupled to the internuclear axis of the molecule. This defines the quantum number Λ and Σ , which are the internuclear axis projections of L and S . The sum of Λ and Σ give the total electronic angular momentum along the internuclear axis, Ω .

$$\Lambda + \Sigma = \Omega$$

Ω is then coupled to the end-over-end rotational angular momentum of the molecule (R) to give J , the total angular momentum.

$$J = \Omega + R$$

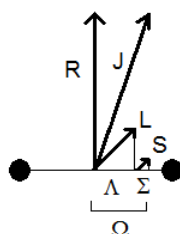


Figure 9.4.1

For a molecule that is well described by Hund's case (a) coupling, that is in a $^1\Pi$ electronic state, the lowest value of J possible is $J = 1$. The one unit of angular momentum comes from the orbital part of the wave function, so $J = 1$ actually describes a non-rotating molecule ($R = 0$)!

Hund's case (a) does a good job of describing molecules which exhibit moderate spin-orbit coupling. If the coupling is extremely strong, another case (case (c), for example) is needed to describe the molecule's properties.

Hund's case (b)

Hund's case (b) is slightly different from case (a) in that the spin angular momentum is uncoupled from the internuclear axis. As such, in Hund's case (b) coupling, the quantum numbers Σ and Ω are undefined. In this case, the end-over-end rotation (R) of the molecule couples with Λ to produce N , which describes the sum of rotation plus orbital angular momentum.

$$N = \Lambda + R$$

N can then couple with S to give J , the total angular momentum.

$$J = N + S$$

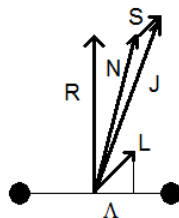


Figure 9.4.2

Singlet states, with $S = 0$, are always well described by Hund's case (b) coupling. Hund's case (b) is a good description for molecules where spin-orbit coupling is weak (or immeasurably small.)

In the section describing the rotation of molecules as rigid rotators, the quantum number J was used to describe the total angular momentum due to rotation. This is consistent with both Hund's cases (a) and (b) for molecules in $^1\Sigma$ states, where $\Lambda = 0$ and $S = 0$ (implying where appropriate that $\Sigma = 0$ as well.)

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