Chemistry 431

Lecture 9
Spin-orbit coupling

NC State University

Spin-orbit Hamiltonian

The magnitude of spin-orbit coupling is measured spectroscopically as a splitting of spectral lines. The Hamiltonian is:

$$H_{so} = \frac{1}{2}hcA\left(j(j + 1) - l(l + 1) - s(s + 1)\right)$$

Where l is the orbital angular momentum quantum number and s is the spin quantum number. The total angular moment is $j = l + s$ and A is the magnitude of the spin-orbit coupling in wavenumbers.

$$H_{so} = \frac{1}{2}hcA\left((l+s)(l + s + 1) - l(l + 1) - s(s + 1)\right)$$

$$= \frac{1}{2}hcA\left(l^2 + s^2 + ls + sl + l + s - l^2 - l - s^2 - s)\right) = hcA\ \boldsymbol{l \cdot s}$$

Spin-orbit Hamiltonian

The magnitude of the spin orbit coupling can be calculated in terms of molecular parameters by the substitution

$$hcA \, L{\cdot}S = \frac{Z\alpha^2}{2} <\frac{1}{r^3}> L{\cdot}S$$

where α is the fine structure constant $\alpha = e^2/\hbar c 4\pi\varepsilon_0$, which is a dimensionless constant ($\alpha = 1/137.037$). L and S are operators.

Z is an effective atomic number.

The spin orbit coupling splitting can be calculated from

$$E_{so} = \int \Psi^* H_{so} \Psi \, d\tau = \frac{Z}{2(137)^2} \int \Psi^* \frac{\hat{L}{\cdot}\hat{S}}{r^3} \Psi \, d\tau$$

Spin-orbit Hamiltonian

This can be evaluated using the above identity that can be recast

$$L \cdot S = \frac{1}{2}\left(J^2 - L^2 - S^2\right)$$

to give an spin-orbit coupling energy in terms of molecular parameters

$$E_{SO} = \frac{1}{2}\left(j(j+1) - l(l+1) - s(s+1)\right)\frac{Z}{2(137)^2}\frac{1}{r^3}$$

where

$$\left\langle \frac{1}{r^3} \right\rangle = \int \Psi^*\left(\frac{1}{r^3}\right)\Psi d\tau$$

Spin-orbit Hamiltonian

We can evaluate this integral explicity for a given atomic orbital. For example for Ψ_{210} we have

$$\Psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0}e^{-Zr/2a_0}\cos\theta$$

so that the integral is

$$\left\langle\frac{1}{r^3}\right\rangle = \frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^5\int_0^{2\pi}d\phi\int_0^{\pi}\cos^2\theta\sin\theta d\theta\int_0^{\infty}r^2e^{Zr/a_0}\left(\frac{1}{r^3}\right)r^2dr$$

which integrates to

$$<\frac{1}{r^3}> = \frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^5 2\pi\left(\frac{2}{3}\right)\left(\frac{a_0^2}{Z^2}\right) = \frac{1}{24}\left(\frac{Z}{a_0}\right)^3$$

or $Z^3/24$ in atomic units.

Spin-orbit Hamiltonian

Therefore, we have

$$< \frac{1}{r^3} > = \frac{Z^3}{n^3 a_o^3 l(l + 1/2)(l + 1)}$$

Therefore, in general the spin-orbit splitting is given by

$$E_{SO} = \frac{Z^4}{2(137)^2 a_o^3 n^3}\left(\frac{j(j + 1) - l(l + 1) - s(s + 1)}{2l(l + 1/2)(l + 1)} \right)$$

Note that the spin-orbit coupling increases as the fourth power of the effective nuclear charge Z, but only as the third power of the principal quantum number n. This indicates that spin orbit-coupling interactions are significantly larger for atoms that are further down a particular column of the periodic table.

The Sodium D Line

One notable atomic spectral line of sodium vapor is the so-called D-line, which may be observed directly as the sodium flame-test line and also the major light output of low-pressure sodium lamps (these produce an unnatural yellow. The D-line is one of the classified Fraunhofer lines. Sodium vapor in the upper layers of the sun creates a dark line in the emitted spectrum of electromagnetic radiation by absorbing visible light in a band of wavelengths around 589.5 nm. This wavelength corresponds to transitions in atomic sodium in which the valence-electron transitions from a 3s to 3p electronic state.

The Splitting of the D Line

Closer examination of the visible spectrum of atomic sodium reveals that the D-line actually consists of two lines called the D_1 and D_2 lines at 589.6 nm and 589.0 nm, respectively. The splitting between These lines arises because of spin-orbit coupling. The constant A is usually given in cm^{-1}. For Na, it is 11.5 cm^{-1}. Na has one unpaired electron (s = ½). If we consider the s -> p transition, then for the excited state, p, we have l = 1. Thus, j = 3/2 or ½.

Practical calculations using the Spin-orbit Hamiltonian

The two energy levels can be calculated in terms of the constant A.

$$E_{3/2} = \frac{1}{2}A\left(3/2(3/2 + 1) - 1(1 + 1) - 1/2(1/2 + 1)\right) = \frac{1}{2}A$$

$$E_{1/2} = \frac{1}{2}A\left(1/2(1/2 + 1) - 1(1 + 1) - 1/2(1/2 + 1)\right) = -A$$

The energy difference between the lines is 3/2A. Thus, the energy splitting for Na is 17.3 cm^{-1}.