Spin-orbit coupling refers to the interaction of a particle's "spin" motion with its "orbital" motion.

The Spin-orbit coupling Hamiltonian

The magnitude of spin-orbit coupling splitting is measured spectroscopically as
\[
H_{so} = \frac{1}{2} \hbar c A \left( (l+s)(l+s+1)-l(l+1)-s(s+1) \right)
\]
\[
= \frac{1}{2} \hbar c A \left(l^2 + s^2 + 2ls + l + s - l^2 - l - s^2 - s \right)
\]
where \(A\) is the magnitude of the spin-orbit coupling in wave numbers. The magnitude of the spin orbit coupling can be calculated in terms of molecule parameters by the substitution
\[
H_{so} = \frac{1}{2} \hbar c A \left(j(j+1) - l(l+1) - s(s+1) \right)
\]
where \(j = l + s\).

\[
\langle \frac{1}{2} \hbar c A \hat{L} \cdot \hat{S} \rangle = \frac{Z}{2(137)^2} \langle \frac{1}{r^3} \rangle
\]
where \(a\) is the fine structure constant \((a = 1/137.037)\) and the carrots indicate that \(\hat{L}\) and \(\hat{S}\) are operators. The fine structure constant is a dimensionless constant, \(a = \frac{e^2}{\alpha c}\). \(Z\) is an effective atomic number. The spin orbit coupling splitting can be calculated from
\[
E_{so} = \int \Psi^* H_{SO} \Psi \, d\tau = \frac{Z}{2(137)^2} \int \Psi^* \frac{\hat{L} \cdot \hat{S}}{r^3} \Psi \, d\tau
\]
This expression can be recast to give an spin-orbit coupling energy in terms of molecular parameters
\[
E_{so} = \frac{1}{2} \left( j(j+1) - l(l+1) - s(s+1) \right) = \frac{Z}{2(137)^2} \langle \frac{1}{r^3} \rangle
\]
where
\[
\langle \frac{1}{r^3} \rangle = \int \Psi^* \frac{1}{r^3} \Psi \, d\tau
\]

We can evaluate this integral explicitly for a given atomic orbital.

For example for Y210 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
\[
\langle \frac{1}{r^3} \rangle = \frac{1}{32\pi} \left( \frac{Z}{a_0} \right)^5 \int_0^{2\pi} d\phi \int_0^\pi \cos^2\theta \sin\theta \, d\theta \int_0^\infty r^2 e^{Zr/a_0} \frac{1}{r^3} \, dr
\]
which integrates to
\[\langle \frac{1}{r^3} \rangle = \frac{1}{32\pi} \left( \frac{Z}{a_0} \right)^5 2\pi \left( \frac{2}{3} \right) \left( \frac{a_0^2}{Z^2} \right) = \frac{1}{24} \left( \frac{Z}{a_0} \right)^3\]

Or \(\frac{Z^3}{24}\) in atomic units.

Therefore in atomic units we have

\[\langle \frac{1}{r^3} \rangle = \frac{Z^3}{n^3 l(l+1/2)(l+1)}\]

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

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

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.

**Contributors**

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