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

\[
H_{so} = \dfrac{1}{2} \hbar c A \left( (l+s)(l+s+1)-l(l+1)-s(s+1) \right)
\]

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

\[
|H_{so}| = \dfrac{1}{2} \hbar c A (j(j+1)-l(l+1)-s(s+1)) = \dfrac{1}{2} \hbar c A \mathbf{l} \cdot \mathbf{s}
\]

where \( j = l + s \).

The expression can be modified by realizing that \( |A| \) 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

\[
|H_{so}| = \dfrac{1}{2} \hbar c A \mathbf{l} \cdot \mathbf{s} = \dfrac{Z \alpha^2}{2} \dfrac{1}{r^3} \mathbf{l} \cdot \mathbf{s}
\]

where \( \alpha \) is the fine structure constant \((\alpha = 1/137.037)\) and the carrots indicate that \( \mathbf{l} \) and \( \mathbf{s} \) are operators. The fine structure constant is a dimensionless constant, \( \alpha = \dfrac{e^2}{\hbar c \alpha} \). \( Z \) is an effective atomic number. The spin orbit coupling splitting can be calculated from

\[
E_{so} = \int \Psi^* H_{SO} \Psi \, d\tau = \dfrac{Z}{2(137)^2} \int \Psi^* \dfrac{\mathbf{l} \cdot \mathbf{s}}{r^3} \Psi \, d\tau
\]

This expression can be recast to give an spin-orbit coupling energy in terms of molecular parameters

\[
E_{so} = \dfrac{1}{2} (j(j+1)-l(l+1)-s(s+1)) = \dfrac{Z}{2(137)^2} \langle \dfrac{1}{r^3} \rangle
\]

where

\[
\langle \dfrac{1}{r^3} \rangle = \int \Psi^* \dfrac{1}{r^3} \Psi \, d\tau
\]

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

For example for Y210 we have

\[
|\Psi_{210} = \dfrac{1}{4\sqrt{2\pi}} (\dfrac{Z}{a_0})^{3/2} \dfrac{Zr}{a_0} e^{-Zr/2a_0} \cos \theta
\]

so that the integral is

\[
\langle \dfrac{1}{r^3} \rangle = \int \Psi^* \dfrac{1}{r^3} \Psi \, d\tau
\]

which integrates to
\[
\langle \frac{1}{r^3} \rangle = \frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^52\pi\left(\frac{2}{3}\right)\left(\frac{a_0}{Z^2}\right) = \frac{1}{24}\left(\frac{Z}{a_0}\right)^3
\]

Or \(\langle Z^3/24 \rangle\) in atomic units.

Therefore in atomic units we have

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

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

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

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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