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

\[
\begin{align*}
H_{so} &= \frac{1}{2} \hbar c A \left( (l+s)(l+s+1)-l(l+1)-s(s+1) \right) \\
&= \frac{1}{2} \hbar c A \left(l^2 +s^2 +ls +sl + l +s -l^2 -l -s^2 -s \right) \\
&= \hbar c A \mathbf{l} \cdot \mathbf{s}
\end{align*}
\]

The expression can be modified by realizing that \( j = l + s \).

\[
[H_{so}] = \hbar c A (j(j+1)-(l+1)s(s+1)) \]

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

\[
hcA, \widehat{L} \cdot \widehat{S} = \frac{Z \alpha^2}{2} \frac{1}{r^3} \widehat{L} \cdot \widehat{S}
\]

where \(|\alpha|\) is the fine structure constant ((|\alpha| = 1/137.037)) and the carrots indicate that \(|L|\) and \(|S|\) are operators. The fine structure constant is a dimensionless constant, \(|\alpha| = \frac{\hbar c \epsilon}{\alpha c} \). \(|Z|\) is an effective atomic number. The spin orbit coupling splitting can be calculated from

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

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

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

where

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

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

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

which integrates to
\[ \langle \frac{1}{r^3} \rangle = \frac{1}{32\pi} \left( \frac{Z}{a_0} \right)^5 2\pi \left( \frac{2}{3} \right) \left( \frac{a_0}{Z^2} \right) = \frac{1}{24} \left( \frac{Z}{a_0} \right)^3 \]

Or \( \langle \frac{Z^3}{24} \rangle \) 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 and Attributions

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