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

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

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

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

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

\[
hcA, \widehat{L} \cdot \widehat{S} = \frac{Z\alpha^2}{2(137)^2} \langle \frac{1}{r^3} \rangle
\]

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

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

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

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

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

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

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

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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