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 \(j = l + s\).

\[
\langle H_{so} \rangle = \frac{1}{2}hcA \langle j(j+1) - l(l+1) - s(s+1) \rangle
\]

where \(\langle A \rangle\) 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

\[
\langle \frac{1}{r^3} \rangle = \int \Psi^*\frac{\hat{L}\cdot\hat{S}}{r^3}\Psi\,d\tau
\]

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

\[
\langle \frac{1}{r^3} \rangle = \frac{Z}{2(137)^2}\langle \frac{1}{r^3} \rangle
\]

For example for Y210 we have

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

so that the integral is

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

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

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

Therefore in atomic units we have

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

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

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

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.

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