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

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

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

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

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

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

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

For example for Y210 we have

\[
\langle \frac{1}{r^3} \rangle = \int \Psi_{210}^* \frac{1}{r^3} \Psi_{210} \, d\tau
\]

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

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

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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