A NEW UNDERSTANDING OF LAMBDA DOUBLING

ROBERT J GORDON, *Department of Chemistry, University of Illinois at Chicago, Chicago, IL, USA*; ROBERT W FIELD, *Department of Chemistry, MIT, Cambridge, MA, USA*.

Lambda-doubling is the splitting of rotational levels that have the same quantum numbers and differ only in their parity. This phenomenon has been understood for nearly a century to be caused by an asymmetric perturbation by an energetically remote electronic state acting on otherwise degenerate rovibronic states. The terms in the Hamiltonian responsible for this perturbation are $\hat{\mathcal{H}}^c = -B(\hat{J}^+\hat{L}^- + \hat{J}^-\hat{L}^+) + (B + \frac{1}{2}A)(\hat{L}^+\hat{S}^- + \hat{L}^-\hat{S}^+)$, where $\hat{J}^\pm$, $\hat{L}^\pm$ and $\hat{S}^\pm$ are ladder operators for total, orbital, and spin angular momenta, and B and A are the rotational and spin-orbit coupling constants. The time-honored method for calculating the level-splitting is to calculate off-diagonal matrix elements of this operator that connect macroscopic terms of the form $|^{2S+1}\Lambda_\Omega\rangle_{e,f}$, using second-order perturbation theory (the Van Vleck transformation) to determine the energy difference between states of e- and f-symmetry. We have discovered that neglect of the microscopic electronic structure of the molecule may lead to incorrect values of the level-splitting and erroneous assignment of the parity of some of the levels. The breakdown of the macroscopic method lies in its failure to recognize that the rotational component of $\hat{\mathcal{H}}^c$ contains two-electron operators, whereas the spin-orbit component is a one-electron operator. In addition, the macroscopic formulation fails to account for exchange symmetry of electrons in partially-filled spin-orbitals. We have shown that the macroscopic formulation gives correct results for inhomogeneous (Ω-changing) perturbations and fails for homogeneous (Ω-preserving) perturbations produced by the rotational part of the Hamiltonian. The breakdown is especially marked for the splitting of $^2\Pi_{\frac{1}{2}}$ by $^2\Sigma^\pm_{\frac{1}{2}}$ states, for which both homogeneous and inhomogeneous perturbations are involved.