SOME PROPERTIES AND USES OF TORSIONAL OVERLAP INTEGRALS

MIRZA A. MEKHTIEV and JON T. HOUGEN, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*.

The first diagonalization step in a rho-axis-method treatment of methyl-top internal rotation problems involves finding eigenvalues and eigenvectors of a torsional Hamiltonian which depends on the rotational projection quantum number K as a parameter. Traditionally the torsional quantum number v_t = 0,1,2 ... is assigned to eigenfunctions of given K in order of increasing energy. In this talk we propose an alternative labeling scheme, using the torsional quantum number v_T, which is based on properties of the K-dependent torsional overlap integrals $< v_t, K|v_t', K' >$. In particular, the quantum number v_T is assigned in such a way that torsional wavefunctions $|v_T, K >$ vary as slowly as possible when K changes by unity. Roughly speaking, $v_T = v_t$ for torsional levels below the barrier, whereas v_T is more closely related to the free-rotor quantum number for levels above the barrier. Because of the latter fact, we believe v_T will in general be a physically more meaningful torsional quantum number for levels above the barrier. The usefulness of $< v_t, K|v_t', K' >$ overlap integrals for qualitative prediction of torsion- rotation band intensities and for rationalizing the magnitudes of perturbations involving some excitation of the small-amplitude vibrations in an internal rotor problem is also discussed.