SOME PROPERTIES AND USES OF TORSIONAL OVERLAP INTEGRALS

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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 $v_{\rm t}$ = 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 $v_{\rm T}$, which is based on properties of the K-dependent torsional overlap integrals $< v_{\rm t}, K|v'_{\rm t}, K' >$. In particular, the quantum number $v_{\rm T}$ is assigned in such a way that torsional wavefunctions $|v_{\rm T}, K >$ vary as slowly as possible when K changes by unity. Roughly speaking, $v_{\rm T} = v_{\rm t}$ for torsional levels below the barrier, whereas $v_{\rm T}$ is more closely related to the free-rotor quantum number for levels above the barrier. Because of the latter fact, we believe $v_{\rm T}$ will in general be a physically more meaningful torsional quantum number for levels above the barrier. The usefulness of $< v_{\rm t}, K|v'_{\rm t}, K' >$ 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.