

VSCF in Internal Coordinates and the Calculation of Anharmonic Torsional Mode Transitions

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Abstract

The Vibrational Self-Consistent Field (VSCF) method employing normal modes is often used to calculate the anharmonic vibrational spectra of polyatomic molecules. However, the method fails in certain cases, such as the calculation of soft torsional mode transitions. In this work, the VSCF equations and algorithm are developed in internal coordinates, which can adequately describe torsional modes.

The VSCF method with internal coordinates is applied to several test systems: *trans*-HONO, *cis*-HONO, H₂S₂, and H₂O₂. Our code uses directly points from *ab initio* calculations, and the method proves to be accurate in all types of transitions. In typical torsional modes, the improvement in the frequency is of factor three compared to the VSCF in normal coordinates. In the other types of modes, some results are better than those of the VSCF in normal coordinates and some are worse; the geometry of the described motion determines the efficiency of using internal coordinates in the non-torsional modes in comparison to the normal ones. The single wave function for the ground and for the first excited state of the torsional mode is compared with the corresponding harmonic wave functions. The differences are large, showing the failure of the harmonic and the anharmonic normal mode approximations for this mode.