SEPARABILITY OF SPIN-ORBIT AND CORRELATION ENERGIES FOR THE SIXTH-ROW MAIN GROUP HYDRIDE GROUND STATES

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The spin-orbit energy contributions to the ground state potential energy curves for the main group hydrides, TlH through AtH, are estimated by differencing multireference, single promotion, configuration interaction (MRS-CI) energies with and without the spin-orbit operator. The spin-orbit contributions are then summed into the energies determined at the λ-s MRSD-CI level (both single and double promotions). The agreement between the resultant curves and those obtained using intermediate coupling MRSD-CI is within 1.2 kcal/mole over a range of internuclear separations. This suggests that, contrary to previous arguments, spin-orbit coupling and correlation energies are very nearly separable for the main group hydride ground states. Furthermore, the computational effort expended by this separate evaluation is up to 12 times less than that for a comparable intermediate coupling CI. The analysis of some properties of these hydrides indicates that bond length shifts due to spin-orbit coupling are small (0.03 Å) while harmonic vibrational frequencies decrease by up to 9%. Dissociation energies are predicted to change considerably in the pressence of the operator, in agreement with previous findings.