ARE AB INITIO QUANTUM CHEMISTRY METHODS ABLE TO PREDICT VIBRATIONAL STATES UP TO THE DISSOCIATION LIMIT FOR MULTI-ELECTRON MOLECULES CLOSE TO SPECTROSCOPIC ACCURACY?

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The aim of the study was to explore the limits of initio methods towards the description of excited vibrational levels up to the dissociation limit for molecules having more than two electrons. To this end a high level *ab initio* potential energy function was constructed for the four-electron LiH molecule in order to accurately predict a complete set of bound vibrational levels corresponding to the electronic ground state. It was composed from: a) an *ab initio* non-relativistic potential obtained at the MR-CISD level including size-extensivity corrections and quintuple-sextuple $\zeta$ extrapolation of the basis, b) MVD (Mass-velocity-Darwin) relativistic corrections obtained at icMR-CISD/cc-pwCV5Z level, and c) DBOC (Diagonal Born-Oppenheimer correction) obtained at the MR-CISD/cc-pwCVTZ level. Finally, the importance of non-adiabatic effects was also tested by using atomic masses in the vibrational kinetic energy operator and by calculation of non-adiabatic coupling by *ab initio* methods.

The calculated vibrational levels were compared with those obtained from experimental data [J.A. Coxon and C.S. Dickinson, *J. Chem. Phys.*, 2004, **121**, 9378]. Our best estimate of the potential curve results in vibrational energies with a RMS deviation of only $\sim$1 $\mathrm{cm}^{-1}$ for the entire set of all empirically determined vibrational levels known so far. These results represent a drastic improvement over previous theoretical predictions of vibrational levels of $^7$LiH up to dissociation, $D_0$, which was predicted to be 19594 cm$^{-1}$.

In addition, rotational levels have also been calculated. The RMS deviation between our ab initio calculations and empirical results by Coxon and Dickinson for rotational spacings $\Delta E = E(v, J = 1) - E(v, J = 0)$ over all available vibrational states of $^7$LiH from $v = 0$ to $v = 20$ is 0.010 $\mathrm{cm}^{-1}$ (with nuclear masses) and 0.006 $\mathrm{cm}^{-1}$ (with atomic masses). Note that for high vibrational states with $v > 6$ this falls within the uncertainty of the measurements.