ALKALI DIATOMICS: ASYMPTOTIC LONG RANGE BEHAVIOR OF ELECTRONIC MATRIX ELEMENTS BASED ON AB INITIO CALCULATIONS

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Ultracold molecules have been widely utilized in various fields of study from the search for new physics in the ultracold regime to ultracold chemistry. Systems at such ($< 1\mu$K) temperatures are usually made with laser cooling techniques, i.e. photoassociation and stimulated Raman adiabatic passage, which utilize closed optical schemes with rovibronic levels of electron-excited states serving as intermediate steps to create ultracold molecules from pre-cooled atoms. This process requires full and detailed data for the ground and excited states in a wide range of internuclear distances, R. Sufficiently accurate data requires going beyond the adiabatic approximation, calculating non-adiabatic interaction matrix elements (IME), i.e. the spin-orbit (SO) and L-coupling (LC) IMEs, with special attention paid to correct long-range behavior.

Here, the asymptotic behavior near the dissociation limit (DL) of IMEs is studied focusing on the transition-dipole moment (TDM), SO and LC IMEs [a]. These were calculated for LiNa, LiK, LiRb, LiCs using spin-averaged wavefunctions corresponding to Hund's case (a) and effective core pseudopotentials. The electronic correlation is accounted for using a 2 valence electron multi-reference configuration interaction calculation. Core-polarization potentials take the core–valence effect into account. Where possible, theoretical curves were compared to ones derived from experiment. The leading asymptotic trends for the TDMs, and SO and LC IMEs, have been determined for three groups of state pairs: (a) dipole allowed transitions between an excited state and one converging to the first DL; (b) forbidden transitions between two states converging to the same DL$>$1; (b) forbidden transitions between two states converging to different DL$>$1. Thus, for the TDMs type (a) pairs converge as R^{-3} to the atomic dipole moment, while type (b,c) pairs converge to zero as R^{-4}. The SO IMEs converge: as R^{-7} to zero for (a); as R^{-6} to the atomic SO splitting for (b); as R^{-3} to zero for (c). Finally, the LC functions: approach infinity linearly for (a); converge as R^{-6} to a constant for (b); converge as R^{-3} to zero for (c).

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