

AN EXTENSION OF THE ‘MLR’ POTENTIAL FUNCTION FORM WHICH ALLOWS FOR AN ACCURATE DPF TREATMENT OF $\text{Li}_2(1^3\Sigma_g^+)$, WHICH COUPLES TO TWO OTHER STATES NEAR THEIR ASYMPTOTES

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The only potential energy functions for the $1^3\Sigma_g^+$ state of Li_2 published to date were conventional RKR curves based on experimental data for the vibrational levels $v = 1 - 7$,^a and they do not yield realistic predictions for the very weakly bound levels $v = 62 - 89$ for $^7,7\text{Li}_2$ and $v = 59-79$ for $^6,6\text{Li}_2$, which were subsequently observed using photoassociation spectroscopy (PAS).^b A recent analysis of data for the $1^3\Sigma_g^+ - a^3\Sigma_u^+$ and $2^3\Pi_g - a^3\Sigma_u^+$ systems of Li_2 was unable to incorporate these PAS data, and this was due to the lack of a potential function form with the ability to accurately describe the behaviour of the potential for a molecule which becomes coupled to two other distinct states near the dissociation asymptote.^c The current work presents and tests an extension of the ‘Morse/Long-Range’ (MLR) potential function form^d which *does* provide an accurate description of the $1^3\Sigma_g^+$ -state potential at *all* internuclear distances, including the long-range region where the three-state coupling occurs. The extension is based on expressions reported by Aubert-Frécon and co-workers,^e which show that the long-range tail of this potential is one of the eigenvalues of a 3x3 Hamiltonian matrix. Accordingly, this extension requires the diagonalization of this matrix at each internuclear distance r . Although this can be done analytically, we show that the diagonalization is in fact computed more efficiently numerically, and leads to a more accurate potential energy function.

^a F. Martin *et al.*, *Spectrochimica Acta* **44A**, 1369 (1988); C. Linton *et al.*, *J. Chem. Phys.* **91**, 6036 (1989).

^b W.I. McAlexander *et al.*, *Phys. Rev. A* **51**, R871 (1995); E.R.I. Abraham *et al.* *J. Chem. Phys.* **103**, 7773 (1995).

^c N.S. Dattani, *et al.*, 63rd Ohio State University Int. Symp. on Molec. Spec. (2008), paper RC11.

^d R.J. Le Roy and R.D.E. Henderson, *Mol. Phys.* **105**, 663 (2007); R.J. Le Roy *et al.*, *J. Chem. Phys.* (2009, submitted).

^e Martin *et al.*, *Phys. Rev. A* **55**, 3458 (1997); M. Aubert-Frécon *et al.*, *J. Mol. Spectrosc.* **192**, 239 (1998).