AN EXTENSION OF THE 'MLR' POTENTIAL FUNCTION FORM WHICH ALLOWS FOR AN ACCURATE DPF TREATMENT OF $Li_2(1^3\Sigma_g^+)$, 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 $^{7,7}Li_2$ and $v = 59{-}79$ for $^{6,6}Li_2$, 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.

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[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).
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