INDETERMINACIES IN DIATOMIC BORN-OPPENHEIMER CORRECTIONS, WITH AN APPLICATION TO THE FITTING OF LiH DATA

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The principal corrections to the Born-Oppenheimer Hamiltonian for a $^1\Sigma$ diatomic molecule can be written[a] $\Delta H = \sum_i (m_\mathrm{e}/M_i)[p_r Q_i(r) p_r/2\mu_C + \hbar^2 R_i(r) J(J+1)/2\mu_C r^2 + S_i(r)]$, where i refers to the two atoms, $\mu_C = M_\mathrm{A} M_\mathrm{B}/(M_\mathrm{A}+M_\mathrm{B}-Cm_\mathrm{e})$ is a charge-modified reduced mass of the atoms for molecular electric charge C, and $Q_i(r)$, $R_i(r)$, and $S_i(r)$ are isotope-independent functions that allow for non-adiabatic and adiabatic electronic effects. By a transformation of the Hamiltonian[a] the $Q_i(r)$ term can be eliminated, and $R_i(r)$ and $S_i(r)$ are replaced by

$$\tilde{R}_i(r) = R_i(r) - \frac{1}{r} A^i(r), \qquad \tilde{S}_i(r) = S_i(r) + \frac{1}{2}\frac{dV_\mathrm{BO}(r)}{dr} A^i(r), \qquad A^i(r) = A_0^i + \int_{r_\mathrm{e}}^{r} Q_i(r')dr'. \tag{1}$$

There remains the indeterminacy due to the arbitrary constant A_0^i. The present study of the fitting of the BO corrections for the isotopomers of the LiH molecule shows the way that this indeterminacy appears in numerical fits. The net effect is that the parameter $R_i(r_\mathrm{e})$, which is a function of the equilibrium dipole moment and rotational g-factor of the molecule, cannot be determined from field-free frequency fits. Only the combination

$$\left[R_i + \frac{r_\mathrm{e}}{a_0}\frac{dS_i}{dr}\right]_{r_\mathrm{e}}, \tag{2}$$

which involves the adiabatic correction to the potential $S_i(r)$, can be determined.[b] Here $a_0 = \omega_\mathrm{e}^2/4B_\mathrm{e}$.

[a] J. K. G. Watson, *J. Mol. Spectrosc.* **80**, 411-21 (1980).
[b] J. K. G. Watson, *J. Mol. Spectrosc.*, in press