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Resolution of a convergence problem in direct-potential-fit data analyses: Applications to GaH($X^1\Sigma^+$) and ArH $^+$ ($X^1\Sigma^+$)

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Abstract

An internal convergence problem encountered when utilizing wavefunction propagator methods for direct-potential-fit diatomic data analyses using the Herman–Asgharian Hamiltonian [R.M. Herman, A. Asgharian, *J. Mol. Spectrosc.* 19 (1966) 305] is described and corrected. Improved Hamiltonian parameters for the ground states of GaH and ArH $^+$ are reported.

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1. Introduction

In recent years it has become increasingly common for diatomic molecule spectroscopic data analyses to use direct fits of eigenvalue differences calculated from a model Hamiltonian to determine parameters defining analytic potential energy and Born–Oppenheimer breakdown (BOB) radial functions. It has been shown that this “direct-potential-fit” (DPF) approach can represent large, multi-state, multi-isotopologue data sets to within the full accuracy of the data, while requiring much smaller sets of empirical parameters than do traditional fits to analytic expressions for the level energies. Apparent differences between results of this type obtained using algebraic rather than direct numerical methods to solve the relevant radial Schrödinger equation [1–6] have been shown to be due to an internal convergence problem in some implementations of the algebraic method [7], and possible questions about the reliability of the DPF approach to diatomic data analysis had apparently been resolved.

In recent work, however, Rey and Tyuterev [8,9] were testing a new variational method of determining the eigenvalues and eigenfunctions of the Herman–Asgharian (HA) Hamiltonian [10,11] for a diatomic molecule, and they discovered a problem. This Hamiltonian includes terms $\beta(r)$ and $\alpha(r)$ which take account of non-adiabatic corrections to the radial and angular kinetic energy operators, respectively, as well as the adiabatic correction $\Delta V_{\text{ad}}(r)$ to the “clamped nuclei” potential energy function $V_{\text{CN}}(r)$:

$$\begin{aligned} & -\frac{\hbar^2}{2\mu}[1 + \beta(r)]\frac{d^2\psi_{v,J}(r)}{dr^2} + \left\{ [V_{\text{CN}}(r) + \Delta V_{\text{ad}}(r)] \right. \\ & \left. + \frac{\hbar^2}{2\mu r^2}[J(J+1)][1 + \alpha(r)] \right\} \psi_{v,J}(r) \\ & = E_{v,J}\psi_{v,J}(r) \end{aligned} \quad (1)$$

Rey et al. [8,9] tested their variational approach by comparing its predictions with results for a number of systems which had been studied previously using numerical propagator (Numerov–Cooley–Zare [12–14]) techniques for solving Eq. (1). In cases for which the $\beta(r)$ term was not included or was relatively weak, the agreement was essentially exact. However, when that was not the case,

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the results obtained by numerical propagator methods differed significantly from those obtained with their new variational method. As an independent check on those problems, and as a test of the consistency of algebraic and numerical methods in this domain, the high-order contact transformations developed by Tyuterev et al. [15] were also applied to these cases [8]. Results obtained using that independent algebraic method [16] were in perfect agreement with the new variational results of Rey et al. [8,16], and both disagreed with the numerical propagator method results for cases in which the $\beta(r)$ function was present and was relatively strong.

We show here that these discrepancies were the result of a non-essential approximation which was utilized in previous implementations of numerical propagator methods for this Hamiltonian. With this approximation removed, corrected HA Hamiltonian parameters are presented for two of the systems to which the inappropriately simplified version of Eq. (1) had been applied.

2. Theory

Eq. (1) cannot be solved directly by conventional Numerov–Cooley wavefunction propagation methods [17,18] because of the presence of the non-adiabatic correction function $\beta(r)$ pre-multiplying the radial kinetic energy term. However, this term can be removed by multiplying this equation from the left by the factor $[1 + \beta(r)]^{-1}$. Since $|\beta(r)| \ll 1$, when applying this factor to all but the first term in Eq. (1) we may use the binomial expansion

$$\begin{aligned} [1 + \beta(r)]^{-1} &= 1 - \beta(r) + \beta(r)^2 - \beta(r)^3 + \dots \\ &\approx 1 - \beta(r)(1 - \beta(r) + \dots) \end{aligned} \quad (2)$$

This converts Eq. (1) to the form

$$\begin{aligned} &-\frac{\hbar^2}{2\mu} \frac{d^2\psi_{v,J}(r)}{dr^2} \\ &+ \left\{ [V_{\text{CN}}(r) + \Delta V_{\text{ad}}(r)] + \frac{\hbar^2}{2\mu r^2} [J(J+1)][1 + \alpha(r)] \right\} \psi_{v,J}(r) \\ &+ [\beta(r)(1 - \beta(r) + \dots)] \left\{ E_{v,J} - [V_{\text{CN}}(r) + \Delta V_{\text{ad}}(r)] \right. \\ &\left. - \frac{\hbar^2}{2\mu r^2} [J(J+1)][1 + \alpha(r)] \right\} \psi_{v,J}(r) = E_{v,J} \psi_{v,J}(r) \end{aligned} \quad (3)$$

As was shown by Watson [19] and formally presented by Herman and Ogilvie [11], the function $\beta(r)$ is isotopologue-dependent, and may be written as a sum of contributions from the two atoms A and B which form the molecule,

$$\beta(r) = \beta^{(\kappa)}(r) = \frac{m_e}{M_A^{(\kappa)}} S_A(r) + \frac{m_e}{M_B^{(\kappa)}} S_B(r) \quad (4)$$

in which m_e is the electron mass, $M_A^{(\kappa)}$ and $M_B^{(\kappa)}$ are the masses of atoms A and B in isotopologue κ , and $S_A(r)$ and $S_B(r)$ are mass-independent functions associated with

atoms A and B , respectively. In general, these functions are found to have magnitudes of order unity, so $|\beta(r)| \ll 1$. As a result, practical solution of Eq. (3) using conventional wavefunction numerical propagation techniques may proceed by first omitting the term pre-multiplied by $\beta(r)$ and solving to obtain a preliminary estimate of the eigenvalue $E_{v,J}$. When that value is substituted into the left-hand side of Eq. (3), the term pre-multiplied by $\beta(r)$ may be treated simply as an additional contribution to the effective radial potential function for that particular vibration–rotation level, and the resulting linear homogeneous equation may be readily solved by standard techniques [12–14,18] to obtain an improved estimate of $E_{v,J}$. This procedure is then repeated until $E_{v,J}$ is fully converged to the desired precision, which requires very few iterations.

The above approach will yield solutions of Eq. (1) of essentially any desired precision. However, a number of practical applications of this approach to the analysis of experimental data had made the additional approximation that all terms of order two or higher in the Born–Oppenheimer breakdown (BOB) correction functions $\beta(r)$, $\alpha(r)$, and $\Delta V_{\text{ad}}(r)$ may be neglected. If this is done, Eq. (3) collapses to the simplified form

$$\begin{aligned} &-\frac{\hbar^2}{2\mu} \frac{d^2\psi_{v,J}(r)}{dr^2} \\ &+ \left\{ [V_{\text{CN}}(r) + \Delta \tilde{V}_{\text{ad}}(r)] + \frac{\hbar^2}{2\mu r^2} [J(J+1)][1 + \tilde{\alpha}(r)] \right\} \psi_{v,J}(r) \\ &+ \tilde{\beta}(r) \left\{ E_{v,J} - V_{\text{CN}}(r) - \frac{\hbar^2}{2\mu r^2} [J(J+1)] \right\} \psi_{v,J}(r) \\ &= E_{v,J} \psi_{v,J}(r) \end{aligned} \quad (5)$$

in which a ‘tilde’ (\sim) label is introduced to indicate that effective Born–Oppenheimer breakdown (BOB) radial functions $\tilde{\beta}(r)$ (or $\tilde{S}_A(r)$ and $\tilde{S}_B(r)$), $\tilde{\alpha}(r)$ and $\Delta \tilde{V}_{\text{ad}}(r)$ determined from fits to experimental data based on Eq. (5) will in general differ from the analogous functions associated with Eqs. (1) and (3). Eq. (5) may of course be solved in the same iterative manner described above. However, for cases in which the kinetic energy BOB function $\beta(r)$ is not sufficiently weak, the neglect of terms in Eq. (3) which are quadratic or higher-order in the BOB correction functions means that although the resulting (iteratively converged) level energies are accurate eigenvalues of Eq. (5), they may not be accurate eigenvalues of the original HA Hamiltonian of Eqs. (1) and (3). On the other hand, it is easy to correct for this by simply choosing to work with Eq. (3) rather than with (5), and the computational effort is essentially the same.

3. Applications to GaH and ArH⁺

Coxon and co-workers had used the approximate HA differential equation of Eq. (5) in direct-potential-fit analyses of experimental data for five systems [20,6]. For all of

those cases, the empirically determined mass-independent functions $\tilde{S}_{A,B}(r)$ had magnitudes of order unity. Thus, the effective strength of the associated BOB functions $\tilde{\beta}^{(k)}(r)$ were determined by the isotope-dependent factors $m_e/M_A^{(k)}$ (see Eq. (4)).

From the form of Eqs. (3) or (5), it is clear that the effect of the $\beta(r)$ term on a calculated level energy is approximately equal to the product of the factor $\tilde{\beta}(r) = \beta(r)[1 - \beta(r) + \dots]$ times the expectation value of the radial kinetic energy for that vibration–rotation level. For virtually all atoms *other* than $A = \text{H}$ or D , the factors $m_e/M_A^{(k)}$, and hence also the strength of the $\beta(r)$ function, will have magnitudes of order 10^{-5} , in which case the neglect of quadratic and higher-power terms in the expansion of Eq. (2) is justified, and the use of Eq. (5) to approximate Eqs. (1) or (3) will have introduced negligible error. This is the case for the analyses of data for GeS and BrCl reported in Ref. [6]. However, when the $\tilde{S}_A(r)$ correction function is associated with a hydrogen atom, the associated $\tilde{\beta}^{(k)}(r)$ functions have magnitudes of order 10^{-3} , and the quadratic terms may not be negligible relative to the accuracy of high quality experimental data. This is the case for published analyses of GaH , ArH^+ and HCl [6,20].

Corrected HA Hamiltonian parameters for the GaH and ArH^+ systems obtained from direct potential fits using Eq. (3) are presented in Table 1. In both cases, the radial

functions are expressed as power series in the Ogilvie–Tipping variable [21]

$$\xi = \zeta(r) = 2 \left(\frac{r - r_e}{r + r_e} \right) \quad (6)$$

and the radial functions themselves are represented by the expansions

$$V_{\text{CN}}(r) = c_0 \xi^2 \left(1 + \sum_{j=1} c_j \xi^j \right) \quad (7)$$

$$\Delta V_{\text{ad}}(r) = \sum_{k=\{A,B\}} \frac{m_e}{M_k} \sum_{j=1} u_j^k \xi^j \quad (8)$$

$$\beta(r) = \sum_{k=\{A,B\}} \frac{m_e}{M_k} \sum_{j=0} s_j^k \xi^j \quad (9)$$

$$\alpha(r) = \sum_{k=\{A,B\}} \frac{m_e}{M_k} \sum_{j=0} t_j^k \xi^j \quad (10)$$

with the same numbers and types of parameters being used as in the original data analyses of Ref. [6].

Coxon and Molski had used the approximate HA differential equation of Eq. (5) in a direct-potential-fit analysis of infrared data for the four GaH isotopologues ^{69}GaH , ^{71}GaH , ^{69}GaD , and ^{71}GaD [6]. The one non-zero $\tilde{\beta}(r)$ parameter determined from that analysis was $\tilde{s}_0^{\text{H}} = -0.8449(\pm 0.11)$, and their fit to the experimental

Table 1
Updated parameters $\{p_j\}$ for the ground electronic states of GaH and ArH^+ as determined from fits of experimental data to converged eigenvalues of the corrected HA Hamiltonian of Eq. (3)

	GaH (X = Ga)		ArH ⁺ (X = Ar ⁺)	
	Ref. [6] $\{\tilde{p}_j\}$ from Eq. (5)	Present $\{p_j\}$ from Eq. (3)		Present $\{p_j\}$ from Eq. (3)
		Unrounded	Recommended	
$r_e/10^{-10}$ m	1.6601497	1.660 1502	1.660 150 (1)	1.280 373 (1)
c_0/cm^{-1}	104630.43	104630.44	104630.42 (28)	175700.34 (58)
c_1	-1.347490	-1.347491	-1.3474896 (42)	-1.5637139 (210)
c_2	1.038627	1.038629	1.038626 (22)	1.193488 (72)
c_3	-0.524955	-0.524960	-0.524999 (110)	-0.5852 (4)
c_4	0.054478	0.054486	0.05471 (68)	0.226 (3)
c_5	-0.076238	-0.076250	-0.076 (4)	-0.116 (6)
c_6	-0.025834	-0.025832	-0.03 (1)	-0.19 (3)
c_7	0.247837	0.247881	0.2574 (440)	0.377 (82)
c_8	-0.193675	-0.193731	-0.2 (1)	-0.2 (1)
s_0^{H}	-0.844923	-0.844477	-0.8 (0.1)	0.45 (4)
s_1^{H}	—	—	—	0.37(10)
t_0^{H}	-3.210387	-3.208222	-3.1854 (580)	0.4624 (120)
t_1^{H}	6.497848	6.493497	6.514 (53)	0.05 (4)
t_2^{H}	-11.949040	-11.940735	-11.92 (7)	—
t_3^{H}	12.027954	12.016790	11.99 (14)	—
t_4^{H}	-11.614769	-11.604543	-11.7 (4)	—
t_0^{X}	-3.811110	-3.811563	-3.83 (35)	-0.1 (1)
t_1^{X}	4.953108	4.996714	5.0 (8)	—
$u_1^{\text{H}}/10^4$ cm ⁻¹	-10.453802	-10.445902	-10.6866 (6100)	-5.49 (21)
$u_2^{\text{H}}/10^4$ cm ⁻¹	7.713817	7.707786	7.97 (66)	—
$u_1^{\text{X}}/10^4$ cm ⁻¹	1.603372	1.600809	1.6 (2)	2.4 (9)
No. of data		1086		445
No. parameters		21		17
$\bar{\sigma}_f$		0.877		0.915

The numbers in parentheses are one standard error uncertainties in the last digits shown.

data using Eq. (5) had a dimensionless standard error of $\bar{\sigma}_f = 0.877$. However, if the resulting potential energy and BOB parameters are utilized directly in the full HA Hamiltonian of Eq. (1), the resulting dimensionless root mean square discrepancy was $\bar{d}d = 1.984$. This factor of two discrepancy was discovered by Rey et al. [8,9] when testing their new variational method for solving Eq. (1).

When Eq. (3) (rather than Eq. (5)) is used in a repeat of the original analysis, the resulting fit (Table 1) again has $\bar{\sigma}_f = 0.877$, and the parameters defining the clamped nuclei potential function $V_{CN}(r)$ were essentially unchanged. However, as is suggested by comparison of Eqs. (1) and (5), most of the new BOB function parameters (“unrounded” parameters in column 2 of Table 1) were slightly smaller than those of Ref. [6] (column 1 of Table 1). Direct solution of Eq. (1) with the radial functions defined by our new fitted (rounded or unrounded) parameters using either the new variational procedure of Rey et al. [8,9] or the contact transformation algebraic method of Tyuterev et al. [15,8,16] yielded exactly this same ($\bar{\sigma}_f = 0.877$) agreement with the experimental data. This confirms the fact that for cases in which $|\beta(r)| \lesssim 10^{-3}$, inclusion of quadratic terms in $\beta(r)$ makes Eq. (3) fully equivalent to the original HA Hamiltonian of Eq. (1).

Coxon and Molski also used the approximate HA differential equation of Eq. (5) in a direct-potential-fit analysis of 445 pure rotational and vibration–rotational line positions for ArH^+ and ArD^+ . Their analysis determined the linear function $\tilde{S}_H(r) = 0.452 + 0.37\xi$ to represent the BOB correction to the kinetic energy term in Eq. (5), and the associated fit had a standard error of $\bar{\sigma}_f = 0.915$. However, when the variational method of Rey et al. [8,9] was used to solve the original HA Hamiltonian of Eq. (1) using those parameters, the resulting average discrepancy with experiment was found to be $\bar{d}d = 1.148$. The fact that this 25% discrepancy is not as large as was the case for GaH is to be expected, because the $\tilde{S}_H(r)$ function for this case is only about half as strong.

Refitting those ArH^+ data using using Eq. (3) instead of Eq. (5) yielded the parameters in the last column of Table 1, and the fit had exactly same standard error as before, $\bar{\sigma}_f = 0.915$. As was the case for GaH, solution of Eq. (1) with these parameters using the variational method of Rey et al. [8,9] yields exactly the same quality of agreement. This provides further confirmation of the fact that iterative solution of Eq. (3) using numerical wavefunction propagation methods is fully equivalent to solving Eq. (1) directly.

4. Discussion and conclusions

The variational method for direct solution of Eq. (1) developed by Rey et al. [9,8] and the high-order contact transformation method of Tyuterev et al. [15,16,8] are quite different techniques for solving Eq. (1) than is the

numerical propagator method discussed above. These two techniques provided critical tests which discovered deficiencies in previous work using wavefunction propagator methods based on the approximate Eq. (5). However, the present work shows that use of Eq. (3) in diatomic molecule DPF data analyses using numerical wavefunction propagation techniques yields results in full agreement with these two independent procedures for directly solving Eq. (1). This agreement further confirms the validity of DPF methods, by confirming that all methods so far considered for implementing it can yield exactly the same results if proper convergence techniques are applied [7].

Improved radial Hamiltonian parameters for the $X^1\Sigma^+$ states of GaH and ArH^+ have been obtained from analysis based on Eq. (3).

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