



Representing Born–Oppenheimer breakdown radial correction functions for diatomic molecules

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Abstract

The empirical determination of Born–Oppenheimer breakdown (BOB) correction functions from the analysis of high resolution diatomic molecule spectra is becoming increasingly common. However, in virtually all applications to date, the analytic expressions used to represent those functions have unphysical limiting behaviour which makes the resulting overall potential energy functions unusable at long-range. This paper delineates the limiting physical constraints, which should be imposed on the form of such BOB correction functions, and presents flexible new expressions incorporating those constraints. The utility of these new forms is illustrated by a re-analysis of recent high resolution IR data for the ground electronic state of AgH, which yields an updated potential energy function and more meaningful adiabatic (potential) and non-adiabatic (centrifugal) BOB correction functions for this system. Further examination of this AgH system also illustrates the problem of model dependence associated with efforts to determine physically unique potential energy and centrifugal BOB correction functions. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years it has become increasingly common to analyse diatomic molecule spectroscopic data by comparing observed transition energies with eigenvalue differences calculated numerically from an effective radial Schrödinger equation for some parameterized potential energy function, and using a least-squares fit to optimize the values of those potential function parameters [1–15]. For systems with small reduced mass, analyses of this type usually have to allow for Born–Oppenheimer breakdown (BOB) effects, particularly if

data for more than one isotopomer are being considered simultaneously [4–6,8–10,12,14]. For a wide variety of cases this approach has been shown to represent the experimental data with equivalent accuracy, and much more compactly than do conventional analyses based on fits to empirical level energy expressions. Unfortunately, the significance and practical utility of the BOB correction functions determined in this way, and hence also of the overall effective potential energy functions, have been undermined by shortcomings of the analytic functional forms used for those correction functions. The present paper illustrates those limitations, discusses appropriate limiting behaviour which may be expected for such functions, and introduces suitable new analytic forms which resolve these problems.

Almost all work of this type reported to date has

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been based on the use of an effective radial Schrödinger equation derived by Watson [16], in which BOB effects are accounted for by incorporation of atomic-mass-dependent correction functions in the electronic and the centrifugal parts of the effective potential energy function. For isotopomer- α of the species A–B, this equation can be written as [14–17]:

$$\left\{ -\frac{\hbar^2}{2\mu_\alpha} \frac{d^2}{dr^2} + \left[V_{\text{ad}}^{(1)}(r) + \Delta V_{\text{ad}}^{(\alpha)}(r) \right] + \frac{\hbar^2 J(J+1)}{2\mu_\alpha r^2} \left[1 + q^{(\alpha)}(r) \right] - E_{v,J} \right\} \psi_{v,J}(r) = 0 \quad (1)$$

where μ_α is the reduced mass of atoms A and B with atomic masses $M_A^{(\alpha)}$ and $M_B^{(\alpha)}$, $V_{\text{ad}}^{(1)}(r)$ is the total effective internuclear potential for the isotopomer selected as the reference species (labelled $\alpha = 1$), $\Delta V_{\text{ad}}^{(\alpha)}(r)$ the ‘adiabatic’ BOB radial potential correction for isotopomer α , the *difference* between the effective adiabatic potentials for isotopomer- α and for the reference species ($\alpha = 1$), and $q^{(\alpha)}(r)$ is the non-adiabatic centrifugal potential correction function for isotopomer- α . In addition, both $\Delta V_{\text{ad}}^{(\alpha)}(r)$ and $q^{(\alpha)}(r)$ may be written as a sum of two terms, one for each component atom, whose magnitudes are inversely proportional to the mass of the particular atomic isotope:

$$\Delta V_{\text{ad}}^{(\alpha)}(r) = \frac{\Delta M_A^{(\alpha)}}{M_A^{(\alpha)}} \Delta V_{\text{ad}}^A(r) + \frac{\Delta M_B^{(\alpha)}}{M_B^{(\alpha)}} \Delta V_{\text{ad}}^B(r) \quad (2)$$

$$q^{(\alpha)}(r) = \frac{M_A^{(1)}}{M_A^{(\alpha)}} q_A(r) + \frac{M_B^{(1)}}{M_B^{(\alpha)}} q_B(r) \quad (3)$$

where $\Delta M_A^{(\alpha)} = M_A^{(\alpha)} - M_A^{(1)}$ and $\Delta M_B^{(\alpha)} = M_B^{(\alpha)} - M_B^{(1)}$ are the differences between the atomic masses in the isotopomer of interest and in the chosen reference isotopomer [17].

Note that the reference to $\Delta V_{\text{ad}}^{(\alpha)}(r)$ as an ‘adiabatic’ correction function is not strictly correct, as a more general treatment shows [14,16] that in addition to the conventional adiabatic diagonal correction for nuclear motion [18,19], this function contains contributions

associated with non-adiabatic corrections to the radial kinetic energy operator. Moreover, the shape of these functions near the equilibrium internuclear distance depends on assumptions regarding the leading contribution to $q_A(r)$ (see Section 4.2). However, for present purposes the origin of this correction function is not particularly relevant, and the conventional identification of it as an ‘adiabatic’ potential correction function will be used.

Also note that a formally equivalent older representation of the adiabatic correction writes the total electronic potential energy for isotopomer- α , $V_{\text{ad}}^{(\alpha)}(r) = [V_{\text{ad}}^{(1)}(r) + \Delta V_{\text{ad}}^{(\alpha)}(r)]$, as the sum [16,20,21]:

$$V_{\text{ad}}^{(\alpha)}(r) = V_{\text{cn}}(r) + \frac{m_e}{M_A^{(\alpha)}} \Delta V_A(r) + \frac{m_e}{M_B^{(\alpha)}} \Delta V_B(r) \quad (4)$$

In this case, the analytic radial potential function determined by the analysis is not the effective electronic potential for a real molecular species, $V_{\text{ad}}^{(1)}(r)$, but rather is the potential associated with the ‘clamped nuclei’ version of the Born–Oppenheimer approximation, $V_{\text{cn}}(r)$ [16,21]. However, the associated adiabatic correction functions are related to those of Eq. (2) by the simple mass scaling factor [$M_A^{(1)}/m_e$] [17].

In much of the work published to date, the atom-specific Born–Oppenheimer breakdown correction functions $\Delta V_{\text{ad}}^A(r)$ (or $\Delta V_A(r)$) and $q_A(r)$ were represented by power series in a linear vibrational stretching coordinate such as $(r - r_e)/r_e$, where r_e is the equilibrium internuclear distance. However, such functions always become singular as $r \rightarrow \infty$, which is physically absurd. Thus, although the resulting fitted potential energy and BOB correction functions provide an extremely accurate and compact representation of the spectroscopic data used in the analysis, the resulting potentials cannot be used for predicting the properties of very high vibrational levels, or for calculating scattering cross-sections or other collisional properties of the system.

Somewhat better behaviour is achieved if the BOB correction functions are expanded in terms of a radial variable which remains finite at all distances, and to this end a number of applications have used power series expansions in the variable [11,12] $y = (r - r_e)/(r + r_e)$ whose domain is $[-1, +1]$, or in the

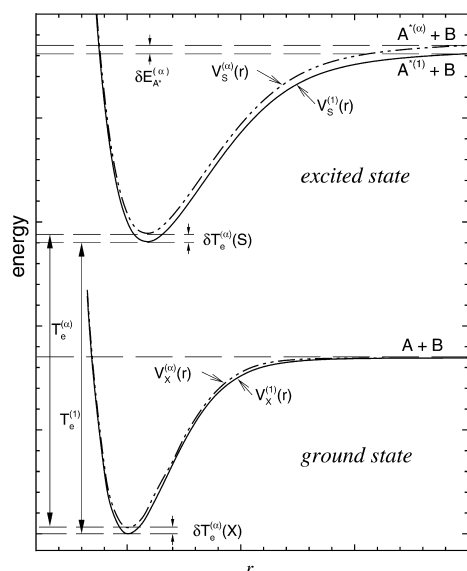


Fig. 1. Schematic potential energy curves for isotopomer- α (dot-dot-dash curves) and reference species isotopomer-1 (solid curves) of chemical species A–B in its ground state (labelled X) and in excited electronic state S.

equivalent variable [9,13,14] $z_{\text{OT}} = 2y$ with domain $[-2, +2]$. However, the fact that such functions are everywhere finite does not guarantee that they will behave well outside the region spanned by the data used to determine them (e.g. see Section 4 below). An ad hoc means of addressing the latter problem involves the use of switching functions to force power series expansions in $y(r)$ to approach a specified limit as $r \rightarrow \infty$ [9,13,14]. However, such switching functions add clutter and are inconvenient to work with, and no guidance was offered regarding what the limiting values being switched to should be. Another common shortcoming of previous work has been a tendency to treat the isotope shift in an electronic molecular transition as an independent correction, rather than recognizing it to be simply the value of the adiabatic potential correction function at the distance r_e .

The next two sections discuss appropriate limiting behaviour which may be expected for potential energy and centrifugal BOB correction functions, and introduce flexible new analytic forms which resolve the above problems. The utility of the new forms is then illustrated by a reanalysis of data for the $X^1\Sigma^+$ state of AgH.

2. The adiabatic potential correction functions $\Delta V_{\text{ad}}^A(\mathbf{r})$

2.1. Limiting behaviour

The presence of the adiabatic potential correction functions $\Delta V_{\text{ad}}^A(\mathbf{r})$ in Eq. (1) (or $\Delta V_A(\mathbf{r})$ in Eq. (4)) reflects the fact that the potential energy functions for different isotopomers of a given chemical species differ slightly from one another [19,22]. Fig. 1 schematically illustrates such differences for two electronic states of isotopomers 1 and α of species A–B, where isotopomer- α is formed from the same isotope of atom B and a second isotope of atom A. In this example, the lower electronic state dissociates to ground-state atoms A and B, while the excited electronic state dissociates to an electronically excited atom A^* plus a ground-state atom B. The large energy spacing between the lower and the two upper asymptotes is simply the energy for the excitation $A^* \leftarrow A$ of an isolated atom of species-A. Similarly, the difference between the two upper asymptotes is the atomic isotope shift, $\delta E_{A^*}^{(\alpha)} = E_{A^*}^{(\alpha)} - E_{A^*}^{(1)}$ the difference between the level spacings for those two isotopes of atom A, which is in general a known small quantity.

Derivations of the Born–Oppenheimer separation of electronic and nuclear motion show that the dominant contribution to the correction function $\Delta V_{\text{ad}}^{(\alpha)}(r)$ is the ‘diagonal correction for nuclear motion’, which can in principle be calculated ab initio from the electronic wavefunction of the state in question [18,19,22,23]. While such ab initio correction functions approach finite values as $r \rightarrow \infty$, their absolute energy there is not relevant to the calculation of any dynamical properties. The most logical convention is therefore to define the zero of their energy scale so that for any molecular state which dissociates to yield a ground-state atom of species A,

$$\lim_{r \rightarrow \infty} \Delta V_{\text{ad}}^A(r) = 0 \quad (5)$$

This implies that for all molecular states correlating with ground-state atoms, the molecular correction function $\Delta V_{\text{ad}}^{(\alpha)}(r \rightarrow \infty) = 0$. This constraint is schematically illustrated in Fig. 1 by the fact that the ground-state potentials for the two isotopomers go to exactly the same asymptote.

For light atoms, for which they have significant magnitude, the dominant contribution to atomic isotope shifts is a hydrogenic-atom reduced mass effect which scales as the difference in the inverse of the atomic masses, $\delta E_{A^*}^{(\alpha)} \propto \Delta M_{A^*}^\alpha / M_A^\alpha$ [24]. Thus, these shifts merge naturally with the conventional atomic mass dependence of the molecular correction function $\Delta V_{\text{ad}}^{(\alpha)}(r)$, seen in Eq. (2). For the general case of an electronic state which dissociates to yield both atoms in excited states, atom A in state s_a and atom B in state s_b , as $r \rightarrow \infty$ the molecular adiabatic potential correction must approach the sum of the associated atomic isotope shifts:

$$\lim_{r \rightarrow \infty} \Delta V_{\text{ad}}^{(\alpha)}(r) = \delta E_{A^*}^{(\alpha)}(s_a) + \delta E_{B^*}^{(\alpha)}(s_b) \quad (6)$$

or more particularly, the individual atomic adiabatic correction functions must approach limiting values defined by the associated atomic isotope shift:

$$\lim_{r \rightarrow \infty} \Delta V_{\text{ad}}^{A^*}(r) = \left(M_A^{(\alpha)} / \Delta M_A^{(\alpha)} \right) \delta E_{A^*}^{(\alpha)}(s_a) \quad (7)$$

This provides a natural asymptotic constraint on the values of adiabatic potential correction functions, and suggests that the limiting asymptotic value of an atomic adiabatic correction function $\Delta V_{\text{ad}}^A(r)$ should be an explicit (known) parameter in the functional form used to represent it.

For heavy atoms, a competing contribution to isotope shifts arises from differences in the size of the excluded volume associated with the finite size of the nucleus. Such effects scale linearly with the nuclear size, both for the molecule and for the separated atoms they dissociate to [24–27], so this has no effect on the validity of Eq. (6). Taking account of such effects would merely require the inclusion of additional r -dependent contributions to $\Delta V_{\text{ad}}^{(\alpha)}(r)$ which scale as the differences in nuclear size, rather than as the atomic mass differences $\Delta M_A^{(\alpha)}$ [17]. However, for the heavy-atom systems for which these become the dominant contribution to adiabatic-type corrections to the potential, the overall magnitudes of BOB-corrections tend to become so small that they become difficult to resolve, except in high resolution microwave spectra. Thus, the present discussion explicitly considers only the atomic-mass-dependent corrections of Eq. (2).

A second natural parameter for characterizing a molecular adiabatic BOB correction function is the isotopic correction to the potential at its equilibrium

distance,

$$\delta T_e^{(\alpha)} = \Delta V_{\text{ad}}^{(\alpha)}(r_e) \quad (8)$$

This quantity is directly related to the differences between the dissociation energies $\mathfrak{D}_e^{(\alpha)}$ for different isotopomers. In general

$$\delta \mathfrak{D}_e^{(\alpha)} \equiv \mathfrak{D}_e^{(\alpha)} - \mathfrak{D}_e^{(1)} = \Delta V_{\text{ad}}^{(\alpha)}(r = \infty) - \Delta V_{\text{ad}}^{(\alpha)}(r = r_e) \quad (9)$$

while for any state dissociating to yield ground-state atoms, the constraint of Eq. (5) implies that $\delta \mathfrak{D}_e^{(\alpha)} = -\delta T_e^{(\alpha)} = -\Delta V_{\text{ad}}^{(\alpha)}(r_e)$. Unlike the isotope shift at the asymptote, one has no a priori way of knowing what this shift should be. However, it would clearly be desirable for this physically interesting quantity to be (or be closely related to) one of the free parameters used to characterize the atomic $\Delta V_{\text{ad}}^A(r)$ functions.

From consideration of Fig. 1, it also is clear that the molecular isotope shift for transitions into upper electronic state S is

$$\begin{aligned} \Delta T_e^{(\alpha)}(S) &\equiv T_e^{(\alpha)}(S) - T_e^{(1)}(S) = \delta T_e^{(\alpha)}(S) - \delta T_e^{(\alpha)}(X) \\ &= \Delta V_{\text{ad},S}^{(\alpha)}(r_e^S) - \Delta V_{\text{ad},X}^{(\alpha)}(r_e^X) \end{aligned} \quad (10)$$

We note that while the experimental determination of this difference $\Delta T_e^{(\alpha)}(S)$ is often fairly straightforward, one cannot determine the individual-state isotope shifts $\delta T_e^{(\alpha)}(S)$ unless the difference between the potential well depths $[\mathfrak{D}_e^{(\alpha)} - \mathfrak{D}_e^{(1)}]$ for different isotopomers can be determined accurately for at least one of the electronic states under consideration [12].

One final constraint on the form of the adiabatic potential correction functions arises from the fact that in the limiting long-range region, all molecular potential energy functions take on the simple inverse-power form

$$V(r) \simeq \mathfrak{D} - C_n / r^n \quad (11)$$

where n is a positive integer determined by the nature at the atomic species yielded on dissociation [19,28,29]. This behaviour must be the same for all isotopomers of a given species in a given electronic state. This in turn means that the functions $\Delta V_{\text{ad}}^A(r)$ defining the differences between the overall effective adiabatic potentials for different isotopomers must

have that same inverse-power long-range behaviour. Some of the functional forms used for the reference-isotopomer potential $V_{\text{ad}}^{(1)}(r)$ of Eq. (1) (or clamped-nuclei potential $V_{\text{cn}}(r)$ of Eq. (4) explicitly incorporate both this limiting inverse-power behaviour and a theoretically predicted value of the long-range coefficient C_n [10,30]. When such forms are used, the associated BOB potential correction functions should also have this same limiting behaviour, as otherwise the long-range behaviour of the total effective potentials $V_{\text{ad}}^{(\alpha)}(r)$ would differ from one isotopomer to another. Thus, the ability to incorporate the correct inverse-power long-range behaviour is another important requirement of an optimum functional form for an adiabatic potential correction function.

2.2. Proposed form for the $\Delta V_{\text{ad}}^{(\alpha)}(r)$ correction functions

In view of the above, it is clear that it would be highly desirable to represent the atomic adiabatic correction functions $\Delta V_{\text{ad}}^{\text{A}}(r)$ by expressions in which their values both at the equilibrium distance of the reference isotopomer and at the molecular asymptote are explicit parameters. That functional form should also be able to incorporate a selected inverse-power long-range behaviour. Moreover, it would be highly desirable to have a form in which it is not necessary to introduce ad hoc switching functions to ensure reasonable behaviour in the region between the interval spanned by the experimental data and the asymptotic limit.

All of the earlier objectives are satisfied by the functional form:

$$\begin{aligned} \Delta V_{\text{ad}}^{\text{A}}(r) &= u_{\infty}^{\text{A}} \left(\frac{r^m - r_e^m}{r^m + r_e^m} \right) \\ &+ \left(\frac{2r_e^m}{r^m + r_e^m} \right) \sum_{i=0} u_i^{\text{A}} \left(\frac{r^p - r_e^p}{r^p + r_e^p} \right)^i \\ &= u_{\infty}^{\text{A}} y_m(r) + [1 - y_m(r)] \sum_{i=0} u_i^{\text{A}} [y_p(r)]^i \end{aligned} \quad (12)$$

where $y_p(r) = (r^p - r_e^p)/(r^p + r_e^p)$ and m and p are fixed positive integers specified as outlined later. This expression has a number of key features. The first is that, independent of the number of terms included in

the power series expansion, the function values at $r = r_e$ and $r \rightarrow \infty$ are defined by individual linear parameters,

$$\Delta V_{\text{ad}}^{\text{A}}(r = r_e) = u_0^{\text{A}} \quad \text{and} \quad \Delta V_{\text{ad}}^{\text{A}}(r = \infty) = u_{\infty}^{\text{A}} \quad (13)$$

A knowledge of atomic isotope shifts can be used to specify a fixed value for the coefficient u_{∞}^{A} , which is zero (by definition) for a ground-state atom, while $u_{\infty}^{\text{A}} = (M_{\text{A}}^{(2)}/\Delta M_{\text{A}}^{(2)})\delta E_{\text{A}^*}^{(2)}$ for an excited state atom. Since such shifts scale with the atomic mass differences [24], only one experimental isotope shift (here, that for isotope $\alpha = 2$) is required to define the coefficient u_{∞}^{A} . Similarly, at the equilibrium distance r_e , this expression collapses to the single coefficient u_0^{A} . Hence, the overall molecular adiabatic potential correction function has the limiting values

$$\Delta V_{\text{ad}}^{(\alpha)}(r = r_e) = \frac{\Delta M_{\text{A}}^{(\alpha)}}{M_{\text{A}}^{(\alpha)}} u_0^{\text{A}} + \frac{\Delta M_{\text{B}}^{(\alpha)}}{M_{\text{B}}^{(\alpha)}} u_0^{\text{B}} = \delta T_e^{(\alpha)} \quad (14)$$

$$\Delta V_{\text{ad}}^{(\alpha)}(r = \infty) = \frac{\Delta M_{\text{A}}^{(\alpha)}}{M_{\text{A}}^{(\alpha)}} u_{\infty}^{\text{A}} + \frac{\Delta M_{\text{B}}^{(\alpha)}}{M_{\text{B}}^{(\alpha)}} u_{\infty}^{\text{B}} \quad (15)$$

Since the physically significant limiting values at r_e and $r = \infty$ are defined by the leading coefficients in Eq. (12), this form is well suited for imposing limiting constraints due to the known atomic isotope shifts, and for fitting to determine molecular isotope shifts. Note, however, that as discussed before and in Ref. [12], unless isotopic differences in molecular well depths can be accurately determined, only the coefficient differences $\tilde{u}_0^{\text{A}}(S) \equiv u_0^{\text{A}}(S) - u_0^{\text{A}}(X)$ may be determined from $S - X$ electronic spectra.

Another important feature of Eq. (12) is the use of the quantities $y_p(r)$ and $y_m(r)$ with positive integer values of p and $m > 1$, a special case of a generalized radial variable introduced by Šurkus et al. [31] as the radial expansion variable. On the molecular interval $r \in [0, \infty)$ the domain of $y_p(r)$ is $[-1, 1]$ for all values of p , and for r close to r_e , $y_p(r)$ is approximately linear in $(r - r_e)$, which makes it a suitable expansion variable for the region where most experimental data are available. However, the key property of this variable is the fact that as $|r - r_e|$ increases, $y_p(r)$ approaches its limiting values (of ± 1) much more rapidly for larger values of p [32]. For example, on the

interval spanned by the data for ground state AgH considered in Section 4, $0.826 \leq r/r_e \leq 1.330$, the domain of the variable $y_p(r)$ increases from $[-0.095, +0.14]$ to $[-0.19, +0.28]$ to $[-0.28, +0.40]$ to $[-0.36, +0.52]$ to $[-0.45, +0.61]$ to $[-0.52, +0.69]$ as p is increased from 1 to 6. Moreover, ‘all else being equal’, coefficients of equivalent expansions in powers of $y_p(r)$ become smaller for larger values of p . Thus, use of $y_p(r)$ with $p > 1$ as the expansion variable has the effect of dramatically reducing the possible range of values attainable by functions of this variable in the extrapolation region beyond the range of the experimental data. This effectively removes the need for the ad hoc switching functions used in some previous work [9,13,14] to prevent spurious behaviour of BOB correction functions in the extrapolation region. Note, however, that if p is too large, the interval close to r_e in which $|y_p(r)|$ is significantly different from unity becomes too narrow to allow an adequate description of the experimental data [32]. In practical applications considered to date, fixing $p = 3$ has often proved most effective [32] (Section 4), but other values may be appropriate in particular cases.

The other special power appearing in Eq. (12), m , is introduced as a means of requiring the adiabatic correction functions $\Delta V_{\text{ad}}^A(r)$ to have the same limiting inverse-power behaviour as the potential energy function itself. In particular, if the potential function $V_{\text{ad}}^{(1)}(r)$ is constrained to have the limiting behaviour of Eq. (11), one should fix $m = n$, the (inverse) power associated with the long-range potential itself. On the other hand, if the potential itself is not constrained to have any specific inverse-power long-range behaviour, there is little point in requiring such behaviour for the adiabatic correction functions, and it is probably most appropriate to fix m at the same value selected to define the power series expansion variable, $m = p$.

3. The ‘non-adiabatic’ centrifugal-potential correction functions $q_A(r)$

3.1. Limiting constraints

The centrifugal potential energy term in the radial

Schrödinger equation of Eq. (1) may be written as

$$\frac{\hbar^2 J(J+1)}{2\mu_\alpha r^2} [1 + q^{(\alpha)}(r)] = \frac{\hbar^2 J(J+1)}{2\mu_\alpha^{\text{rot}} r^2} \quad (16)$$

where $\mu_\alpha^{\text{rot}}(r) \equiv \mu_\alpha/[1 + q^{(\alpha)}(r)]$ may be thought of as an effective reduced mass associated with rotation. It is intuitively reasonable that at ‘molecular distances’ (near r_e) the electrons might not instantaneously follow the motion of the nuclei, and hence that μ_α^{rot} might differ from μ_α . However, as $r \rightarrow \infty$ all of the electrons become uniquely associated with one nucleus or the other, and the effective mass associated with rotation must approach the pure atomic reduced mass, μ_α . This physical argument suggests that necessarily

$$\lim_{r \rightarrow \infty} q^{(\alpha)}(r) = 0 \quad (17)$$

and hence that for the individual atomic correction functions of Eq. (3),

$$\lim_{r \rightarrow \infty} q_A(r) = \lim_{r \rightarrow \infty} q_B(r) = 0 \quad (18)$$

An alternate justification for this constraint is based on the fact that the $q^{(\alpha)}(r)$ functions are due to non-adiabatic coupling between different electronic states [16,21]. From this viewpoint, Eqs. (17) and (18) merely reflect the fact that all intermolecular interactions go to zero as $r \rightarrow \infty$.

An exception to the earlier behaviour is required for the case of molecular ions or ion-pair states. Some years ago Watson [16] argued that in describing the dynamics of a molecular ion, the ‘charge-modified reduced mass’

$$\mu_\alpha^C = M_A^{(\alpha)} M_B^{(\alpha)} / [M_A^{(\alpha)} + M_B^{(\alpha)} - Qm_e] \quad (19)$$

where $M_A^{(\alpha)}$ and $M_B^{(\alpha)}$ are the usual masses of the neutral atoms A and B, m_e is the mass of the electron, and Q is the (\pm integer) charge on the ion, should be used in the radial Schrödinger equation Eq. (1) in place of the conventional neutral-atom or atom plus ion reduced mass. Recent work by Coxon and Hajigeorgiou [13] showed that use of μ_α^C in place of the reduced mass of the two nuclei μ_{nuc} yielded an order of magnitude improvement in the quality of a combined fit to extensive data sets for the three hydrogenic isotopomers of HeH^+ , which provides strong empirical support for Watson’s proposal.

However, as the molecular ion dissociates, it is clear that the correct reduced mass for relative motion of the product species is the atom-plus-ion reduced mass, which is relatively close to μ_{nuc} for this system.

As far as angular motion is concerned, the earlier problem can be readily accommodated by using μ_{α}^C in Eq. (1), but requiring that (for example) for the case of a molecular ion AB^{+Q} which dissociates to yield $A^{+Q} + B$,

$$\lim_{r \rightarrow \infty} q_A(r) \equiv q_{\infty}^A = \frac{\mu_1^C}{\mu_1(A^{+Q}, B)} - 1 \quad (20)$$

where $\mu_{\alpha}(A^{+Q}, B)$ is the usual two-particle reduced mass of the atomic ion A^{+Q} with the neutral atom B . Ignoring relativistic mass corrections (whose relative magnitude is only ca. 1.2×10^{-8} for an H atom, and distinctly smaller for any other singly-charged ion), the difference between the masses of an atomic ion and the associated neutral atom is given by $M_{A^{+Q}} = M_A - Qm_e$, in which case Eq. (20) may be rewritten as

$$q_{\infty}^A = \frac{Qm_e}{M_A^{(1)}} + \left(\frac{Qm_e}{M_A^{(1)}}\right)^2 + \left(\frac{Qm_e}{M_A^{(1)}}\right)^3 \dots \quad (21)$$

It may readily be shown that for a general isotopomer, α , this yields

$$\mu_{\alpha}^{\text{rot}}(r \rightarrow \infty) = \mu_{\alpha}(A^{+Q}, B) \left/ \left(1 + \frac{\Delta M_A^{(\alpha)}}{M_A^{(1)}} \left(\frac{Qm_e}{M_A^{(1)}} \right)^2 \right. \right. \\ \left. \left. \times \left[1 + \frac{Qm_e}{M_A^{(1)}} + \left(\frac{Qm_e}{M_A^{(1)}} \right)^2 + \dots \right] \right) \right. \quad (22)$$

where as above, $\Delta M_A^{(\alpha)} = M_A^{(\alpha)} - M_A^{(1)}$. For the reference isotopomer $\alpha = 1$, $\mu_{\alpha}^{\text{rot}}(r \rightarrow \infty) \equiv \mu_{\alpha}(A^{+Q}, B)$, while for other isotopomers deviations from this near identity will be negligible, since the dimensionless factor $(Qm_e/M_A^{(1)})^2 \approx 7.4 \times 10^{-8}$ for a D (^2H) atom, and will be much smaller for other atomic isotopes.

In their HeH^+ analysis [13], Coxon and Hajigeorgiou also found that use of the effective reduced mass $\mu_{\text{eff}} \equiv \mu(\text{He}^{+1/2}, \text{H}^{+1/2})$, in which $(1/2)m_e$ is subtracted from each of the neutral-atom masses, gave a slightly better quality of fit and required fewer fitting parameters than did a fit using Watson's μ_{α}^C .

However, these μ_{eff} values are intermediate between μ_{α}^C and the reduced mass of the ion-plus-neutral fragments $\mu_{\alpha}(A^{+Q}, B)$, so it seems likely that the proposed constraint of Eq. (21), which interpolates between these values, will effectively supersede that somewhat ad hoc treatment.

The behaviour which may be expected of, or imposed on $q^{(\alpha)}(r)$ at $r = r_e$ is currently still a matter of discussion [14,33]. Some years ago Watson pointed out that the treatment of non-adiabatic coupling in the derivation which gave rise to the effective radial Schrödinger equation of Eq. (1) involved the introduction of an arbitrary integration constant, and he pointed out that in the absence of other information it would be most convenient to choose it so that $q^{(\alpha)}(r = r_e) = 0$ [14,16]. On the other hand, Ogilvie and others [33–35] have pointed out that the value of $q^{(\alpha)}(r)$ at r_e is related to certain electronic properties of the molecule. When the values of such properties are known, one may wish to require that $q^{(\alpha)}(r)$ have some specific non-zero value at r_e , while if that is not the case, it would seem appropriate to follow the Watson convention [16] of requiring that $q^{(\alpha)}(r_e) = 0$. However, both approaches involve imposing a specific value on this function at $r = r_e$.

It has been argued that physically significant values of $q^{(\alpha)}(r_e)$ may be determined from fits to transition frequency data alone [36,37]. However, when this has been done, it was done using a more general effective radial Schrödinger equation than Eq. (1), one in which non-adiabatic BOB contributions to the kinetic energy operator were explicitly considered [14,36,37]. In the context of fits to data using Eq. (1), the essential effect of both $q^{(\alpha)}(r_e)$ and the linear coefficients u_1^A and u_1^B in the BOB potential correction functions is to introduce atomic-mass-dependent isotopomer shifts of the minimum of the overall effective potential energy function. As a result, if one is using Eq. (1), the effect of these two types of parameters should be essentially 100% correlated, so $q^{(\alpha)}(r_e)$ may not be treated as an independent fitting parameter in an analysis which considers only transition energy data. A numerical illustration of this assertion is presented in Section 4.2.

3.2. Proposed form for the $q_A(r)$ correction functions

The limiting constraints discussed before are

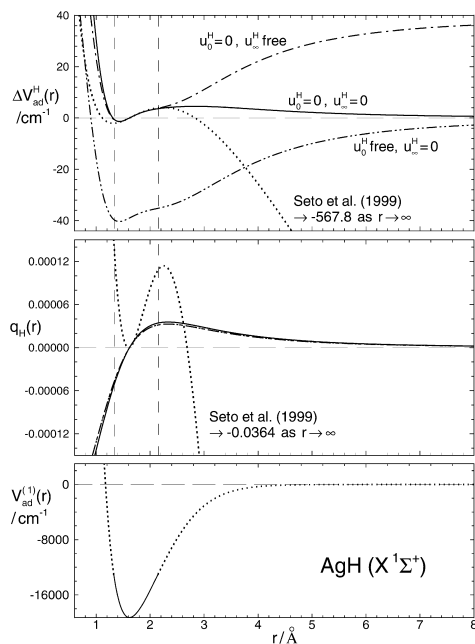


Fig. 2. Potential energy function (bottom segment), and potential energy (top segment) and centrifugal potential (middle segment) BOB correction functions for the ground $^1\Sigma^+$ state of AgH. The vertical dashed lines in the two upper segments bracket the interval spanned by the experimental data.

readily incorporated into the same type of functional form introduced in Section 2.2 for describing the adiabatic potential correction functions. In this case, however, we have no a priori knowledge of the functional behaviour to be expected of $q_A(r)$ in the long-range region, so there is no need to invoke a separate power ‘ m ’ to impose any particular long-range behaviour. The general form recommended here is therefore:

$$\begin{aligned}
 q_A(r) &= q_\infty^A \left(\frac{r^p - r_e^p}{r^p + r_e^p} \right) + \left(\frac{2r_e^p}{r^p + r_e^p} \right) \sum_{i=0} q_i^A \left(\frac{r^p - r_e^p}{r^p + r_e^p} \right)^i \\
 &= q_\infty^A y_p(r) + [1 - y_p(r)] \sum_{i=0} q_i^A [y_p(r)]^i
 \end{aligned}
 \tag{23}$$

where $y_p(r)$ is defined above and p is again a positive integer chosen to be >1 , and $q_\infty^A = 0$ except for a molecular ion, in which case Eq. (21) should be used, or an ion-pair state, for which case $Q = Q_A + Q_B$ in the Eq. (19) definition of μ_α^C and the constraint of Eq. (21) must be applied to both atomic partners. Since

$q_A(r = r_e) = q_0^A$, the proposed form allows one to readily impose any chosen value (zero or otherwise) at $r = r_e$, simply by fixing the value of q_0^A . In addition, use of a power $p > 1$ again ensures that the resulting functions will rapidly approach their limiting values (usually zero) in the extrapolation region beyond the interval associated with the experimental data, without first undergoing spurious excursions [32].

4. Illustrative application to the ground state of AgH

4.1. Analysis using the new BOB correction function forms

Ref. [12] reported accurate new IR data for the ground $X^1\Sigma^+$ electronic state of the four silver hydride isotopomers ^{107}AgH , ^{109}AgH , ^{107}AgD and ^{109}AgD , and analysed them by using direct fits to level energy differences calculated from Eq. (1) to determine an effective radial potential and (adiabatic) potential energy and (non-adiabatic) centrifugal BOB correction functions. In spite of the high accuracy of the data (uncertainties ca. $\pm 0.001 \text{ cm}^{-1}$), BOB corrections associated with the Ag atoms were too small to be resolved, and only the H-atom correction functions $\Delta V_{\text{ad}}^{\text{H}}(r)$ and $q_{\text{H}}(r)$ could be determined. In that work, however, both of those functions were represented by simple power series expansions in the variable $y = y_1(r) = (r - r_e)/(r + r_e)$ with the constant terms set to zero ($q_0^{\text{H}} = u_0^{\text{H}} = 0$). Because the domain of $y_1(r)$ is $[-1, +1]$, the resulting functions remain finite as $r \rightarrow \infty$. However, their behaviour outside the interval spanned by the experimental data turns out to be quite unrealistic.

The lowest segment of Fig. 2 shows the overall potential energy function determined for this system [12], drawn as a solid curve in the region spanned by the experimental data and as dotted curve segments in the extrapolation regions. In the two upper sections of this figure the BOB correction functions determined in Ref. [12] are shown as dotted curves, and the experimental data region (the region spanned by the turning points of the data used in the analysis) is delineated by vertical dashed lines. The very large negative limiting values of those two functions are clearly quite unreasonable. In particular, the

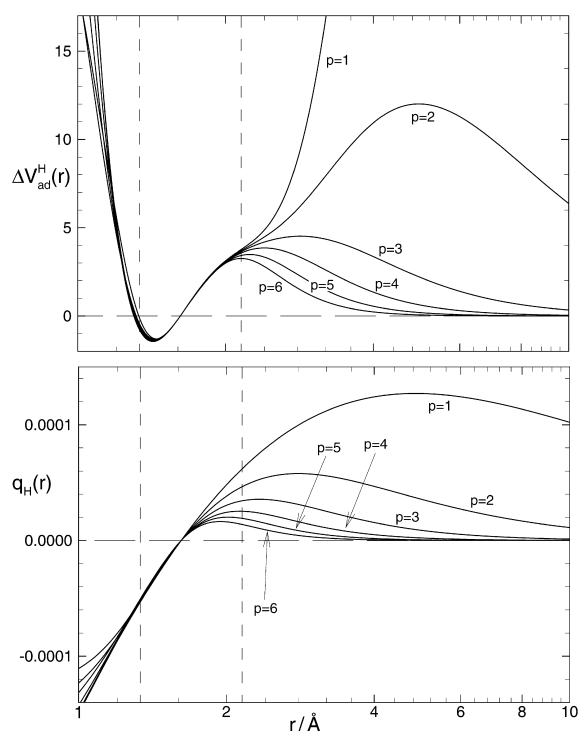


Fig. 3. Fitted BOB correction functions for AgH determined using different choices for the radial expansion variable $y_p(r)$, with $u_1^H - u_4^H$ and q_1^H being fitted and $u_0^H = u_\infty^H = q_0^H = q_\infty^H = 0$.

extrapolated limiting value of $\Delta V_{\text{ad}}^H(r \rightarrow \infty) = -568.75 \text{ cm}^{-1}$ would imply (see Eq. (9)) that the AgD well depth is smaller than that of AgH by some 284.16 cm^{-1} , a difference which is orders of magnitude larger than would be physically plausible. Similarly, the extrapolated value of $q_H(r \rightarrow \infty) = -0.0364$ would imply that as $r \rightarrow \infty$ the rotational reduced mass of AgH approaches a limiting value almost 4% larger than actual reduced mass of the two atoms. These values show that the unconstrained extrapolation implicitly associated with the types of BOB correction functions used in earlier work should henceforth be avoided.

The present work repeated the analysis of Ref. [12], but with the BOB correction functions represented by the new functional forms of Eqs. (12) and (23). The effective radial potential was again represented by the ‘extended Morse oscillator’ (EMO) function

$$V_{\text{ad}}^{(1)}(r) = \mathcal{D}_e \left(1 - e^{-\beta(y_p)(r-r_e)} \right)^2 \quad (24)$$

where $\beta(y_p) = \sum_{i=0} \beta_i y_p^i$ is a power series expansion in the radial variable $y_p(r)$, except that while Ref. [12] used $p \equiv 1$, the present work considers $p > 1$ cases too. Because this potential form does not incorporate the theoretical long-range behaviour of Eq. (11), the second integer power (m) in Eq. (12) was fixed as $m = p$. Since the $X^1\Sigma^+$ state correlates with ground-state atoms, one should set $u_\infty^H = 0$, and since the available data span barely one third of the well depth the analysis cannot be expected to determine a meaningful estimate of the isotopomer-dependence of \mathcal{D}_e , so one should also fix $u_0^H = 0$. However, in order to explore the model-dependence of this type of analysis, the present work also considered fits in which one of u_∞^H or u_0^H was allowed to vary. Similarly, except for analogous illustrative examples, all of the present fits fixed $q_0^H = q_\infty^H = 0$. As in Ref. [12], ^{107}AgH was chosen to be the reference isotopomer $\alpha = 1$, and its well depth was fixed at the literature value of Ref. [38] $\mathcal{D}_e = 19300 \text{ cm}^{-1}$.

Fits were performed for a number of different values of p and for a range of choices for the numbers of free BOB correction function parameters. For all values of p considered, an excellent quality of fit was achieved on allowing the analysis to determine five BOB parameters (one fewer than in Ref. [12]): one non-adiabatic (centrifugal) correction function parameter q_1^H , and four u_i^H adiabatic (potential) correction function parameters. Of course, these fits also determined values of r_e and of the exponent parameters $\{\beta_i\}$ of the EMO potential. Fig. 3 shows the BOB correction functions yielded by these $u_0^H = u_\infty^H = q_0^H = q_\infty^H = 0$ fits in which the radial expansion variable was defined by values of p ranging from 1 to 6.

One of the noteworthy features of the upper segment of Fig. 3 is that in the data region (bounded by vertical dashed lines), the potential correction functions $\Delta V_{\text{ad}}^H(r)$ determined in all six cases are essentially equivalent. Another is that at larger distances the $p = 1$ and 2 functions undergo (almost certainly spurious) excursions to relatively large function values, before dropping off to zero as $r \rightarrow \infty$ (note that the $p = 1$ function, which abruptly shoots off scale in the upper segment of Fig. 3, does return and go to zero as $r \rightarrow \infty$). Thus, it is clear that simply incorporating the correct limiting asymptotic value into the form of the function used to represent $\Delta V_{\text{ad}}^H(r)$

Table 1

Parameters defining the potential energy and BOB correction functions for the ground $X^1\Sigma^+$ state of AgH, where $m = p = 3$ and the reference isotopomer is ^{107}AgH ; 95% confidence limit uncertainties in the last digits shown are given in parentheses

Potential parameters		BOB correction parameters	
$\mathcal{D}_e(\text{cm}^{-1})$	19300.0	$u_0^{\text{H}}(\text{cm}^{-1})$	0.0
$R_e(\text{\AA})$	1.6179135(20)	$u_1^{\text{H}}(\text{cm}^{-1})$	11.48(44)
$\beta_0(\text{\AA}^{-1})$	1.54156827(380)	$u_2^{\text{H}}(\text{cm}^{-1})$	18.042(520)
$\beta_1(\text{\AA}^{-1})$	0.0360158(500)	$u_3^{\text{H}}(\text{cm}^{-1})$	-45.6(30)
$\beta_2(\text{\AA}^{-1})$	0.1651647(1200)	$u_4^{\text{H}}(\text{cm}^{-1})$	57.6(53)
$\beta_3(\text{\AA}^{-1})$	0.095767(1500)	$u_{\infty}^{\text{H}}(\text{cm}^{-1})$	0.0
$\beta_4(\text{\AA}^{-1})$	0.14689(190)		
$\beta_5(\text{\AA}^{-1})$	0.084(11)	q_0^{H}	0.0
$\beta_6(\text{\AA}^{-1})$	0.2594(200)	q_1^{H}	0.000143(50)
#data	369		
$\bar{\sigma}_f$	1.04		

does not suffice to prevent implausible behaviour in the extrapolation region. On the other hand, combining that constraint with use of $p \geq 3$ in the definition of the expansion variable did successfully ensure reasonable extrapolation behaviour.

The same qualitative conclusions apply to the $q_{\text{H}}(r)$ plots in the lower half of Fig. 3. In this case, however, the degree of agreement among the various functions in the data region is not nearly so good, while for small values of p the amplitude of the (spurious) excursions of the extrapolating functions at larger r is not nearly so bad. The former reflects the fact that this property is not nearly so well determined by the data as is $\Delta V_{\text{ad}}^{\text{H}}(r)$, a point demonstrated by the fact that the fitted values of q_1^{H} have (95% confidence limit) uncertainties of ca. 35%. The latter reflects the fact that with only a single (linear) term in the expansion, the extrapolation cannot readily behave very badly, even if it wants to.

While the comparisons shown in Fig. 3 places a lower bound of $p \geq 3$ on the range of acceptable values for p , the selection of an upper bound or an optimum value requires consideration of other factors. In the present case, high quality fits with $y_p(r)$ defined by $p = 1 - 3$ were all obtained with the exponent of the EMO potential energy function of Eq. (24) defined by seven expansion parameters, $\beta_0 - \beta_6$. However, for larger values of p higher-order $\beta(y_p)$ expansions were required to give the same quality of fit: eight β'_i s were required for $p = 4$, nine for $p = 5$ and ten for $p = 6$. This trend

reflects the fact that the increasingly abrupt flattening off of $y_p(r)$ at larger values of r/r_e for the larger values of p makes it increasingly difficult to represent the requisite functional behaviour of $\beta(y_p)$, and hence of the potential energy function, within the data region. Indeed, for other systems, for the larger values of p , no increase in the number of exponent expansion parameters successfully compensates for this loss of flexibility in $y_p(r)$ at large r/r_e , and the quality of fit rapidly degrades for the larger p values [32]. It would be possible, of course, to use a different value of p to define the expansion parameter used in the potential function exponent and those used to define the BOB correction functions. However, this seems an unnecessary additional complication, so in the present case we select $p = 3$ as the optimum choice for all three functions.

In conclusion, our new recommended potential energy and BOB correction functions for the ground state of AgH correspond to the fit in which $p = 3$ and $u_0^{\text{H}} = u_{\infty}^{\text{H}} = q_0^{\text{H}} = q_{\infty}^{\text{H}} = 0$; the resulting parameters are listed in Table 1, and the associated BOB correction functions are shown as solid curves in the upper segments of Fig. 2. As seen in Fig. 2, the new $\Delta V_{\text{ad}}^{\text{H}}(r)$ correction function is very similar to that of Ref. [12] (dotted curves) in the data region, and both new functions behave much more sensibly in the extrapolation regions. The increasing disagreement between the old and new $q_{\text{H}}(r)$ functions at distances away from r_e merely reflects the fact that this property is actually much less accurately determined than was

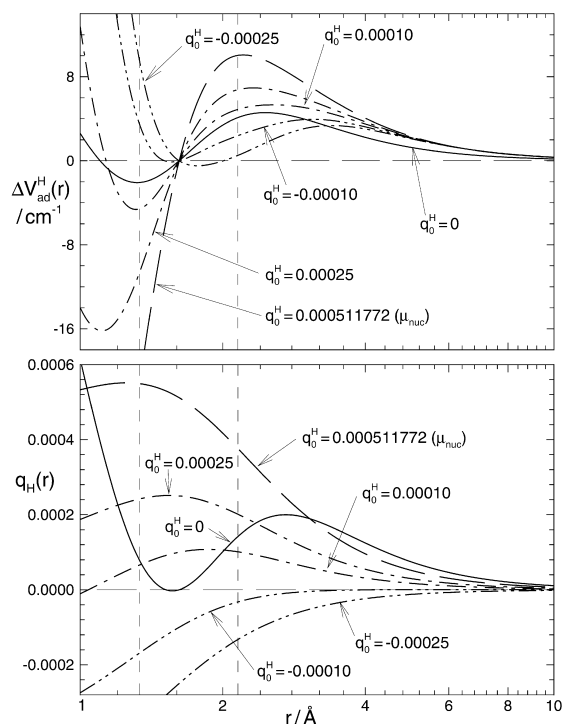


Fig. 4. Fitted BOB correction functions determined for ground-state AgH using different choices for the value of parameter q_0^H .

believed earlier [15]. In conclusion, therefore, these new isotope-dependent potential energy functions can be used for realistic calculations of collisional and other properties of this system, while the old ones could not.

4.2. Illustrative tests of BOB function constraints

As discussed earlier, the limiting constraints $u_0^H = u_\infty^H = q_0^H = q_\infty^H = 0$ are the most appropriate for obtaining the best possible physical description of the AgH system from the data considered. However, a number of other cases were also considered, in order to explore their effect on the resulting BOB correction functions. In particular, with $p = m = 3$, $q_0^H = q_\infty^H = 0$, and q_1^H free, fits were performed using three different four-free-parameter versions of the $\Delta V_{\text{ad}}^H(r)$ function: (i) fix $u_0^H = u_\infty^H = 0$ and fit to determine $u_1^H - u_4^H$ (solid curves in the two upper segments of Fig. 2), (ii) fix $u_0^H = 0$ and fit to determine $u_1^H - u_3^H$ and the asymptotic value u_∞^H (dot–dash curves), and (iii) fix the asymptotic value $u_\infty^H = 0$ and fit to

determine $u_1^H - u_3^H$ and $u_0^H = \Delta V_{\text{ad}}^H(r = r_e)$ (dot–dot–dash curves).

The quality of the case (i) fit (which yielded the recommended parameters of Table 1) was equivalent to that for the previously published analysis of Ref. [12], while those for the two other cases were slightly (ca. 4%) worse, since freeing u_0^H or u_∞^H does not provide as much additional flexibility to the $\Delta V_{\text{ad}}^H(r)$ function as does freeing u_4^H . However, the quality of fit and the resulting fitted parameters for cases (ii) and (iii) are essentially identical, except that the fitted value of $u_0^H(\text{ii}) = -39.9(\pm 3.9) \text{ cm}^{-1} = -u_\infty^H(\text{iii})$. This is to be expected, since the only difference between those two models lies in the definition of the energy zero for the adiabatic potential correction function. For a system in which multi-isotopomer data spanned a large fraction of the well depth, it would be reasonable to use a fit with u_0^H free to determine the isotopomer dependence of the well depth. However, this is not possible with the present data for AgH, and while the stable extrapolation properties of the $y_3(r)$ radial variable mean that the apparent well-depth isotope shift implied by this fit is not as unrealistic as that associated with the results of Ref. [12], the resulting value would imply an AgD isotope shift of $\delta D_e^{(\alpha=2)} \approx 20 \text{ cm}^{-1}$, which is an order of magnitude larger than is physically reasonable. This further affirms the value of introducing the limits on this correction function incorporated into Eq. (12).

The superposition of the dot–dash and dot–dot–dash curves in the middle segment of Fig. 2 show that the simple (one-free-parameter) $q_H(r)$ functions associated with the case (ii) and (iii) fits described earlier are indeed equivalent to one another, while the (solid curve) function yielded by the recommended case (i) fit clearly differs very little from them. This agreement reflects the fact that the shapes of the three $\Delta V_{\text{ad}}^H(r)$ functions are very similar to one another, and shows that a simple energy shift does not affect the otherwise strongly correlated (see below) $q_H(r)$ function. This gives us some confidence regarding the physical significance of the resulting $q_H(r)$ function, at least in the region close to r_e , since it is not affected by different assumptions about the limiting behaviour of the adiabatic potential correction function.

As a further examination of model-dependence in this type of analysis, for a number of fixed values of

q_0^H , fits were performed with $p = m = 3$ and $u_0^H = u_\infty^H = q_\infty^H = 0$, while q_1^H and $u_1^H - u_4^H$ were determined by the fit. The solid curves in Fig. 4 show the (present recommended) BOB correction functions obtained with $q_1^H = 0$, while the long-dash curves show the result obtained with $q_H(r_e) = q_0^H$ fixed at a value for which $\mu_H^{\text{rot}}(r = r_e) = \mu_\alpha^{\text{nuc}}$ (the reduced mass of the two nuclei), and the four other curves show results obtained using the indicated intermediate values of q_0^H . While all of these fits are of essentially equivalent quality, the sharp differences in the slope at r_e of the various $\Delta V_{\text{ad}}^H(r)$ functions confirms the very high correlation between this property and q_0^H , as predicted in Section 3.1. While below the resolution discernable on Fig. 4, where they are the locations of the zeros of the $\Delta V_{\text{ad}}^H(r)$ functions, the fitted reference-isotopomer equilibrium bond lengths for these four cases systematically increase from $r_e = 1.617711(2)$ to $1.618327(2)$ Å as q_1^H is increased from -0.00025 to $+0.000511772$.

5. Conclusions

The present work introduces new functional forms for the atomic-mass-dependent Born–Oppenheimer breakdown (adiabatic) potential energy and (non-adiabatic) centrifugal potential correction functions which can readily incorporate theoretical constraints on the function values at $r = r_e$ and/or $r = \infty$. Appropriate limiting constraints on the asymptotic values expected for such functions are introduced and justified. In particular, the potential correction function should asymptotically approach a value defined by the magnitude of the isotope shift for the atomic species formed at dissociation, which we define to be zero for ground state atoms in order to provide a common reference energy for different isotopomers. Similarly, the value of $\Delta V_{\text{ad}}^{(\alpha)}(r_e)$ is directly related to isotopic differences in the molecular dissociation energy, and to the isotopic shifts of the electronic energy $T_e^{(\alpha)}$. Moreover, since the effective adiabatic potentials for all isotopomers of a given species should have the same inverse-power long-range behaviour, the associated BOB potential correction function must also have this same long-range form. It is also argued that the

atomic non-adiabatic centrifugal BOB correction function should always approach zero as $r \rightarrow \infty$ for neutral dissociation products, and approach the value $q_\infty^A = Qm_e/M_A^{(1)} + (Qm_e/M_A^{(1)})^2 + \dots$ which gives the correct ion-plus-neutral or ion-plus-ion atomic masses, for other cases, and a flexible analytic form incorporating this behaviour is introduced.

These forms have been incorporated into our general least-squares computer program for performing direct fits of multi-isotopomer spectroscopic data to analytic potential energy functions [39], and applied to high resolution data for four isotopomers of the ground $X^1\Sigma^+$ state of AgH. The results of this analysis demonstrate that the proposed BOB correction function are robust and flexible, and in particular, that for $p \geq 3$ they smoothly approach their asymptotic limits without showing the types of spurious behaviour in the extrapolation region associated with much previous work. Moreover, our new description of the ground state of AgH obtains the same quality of fit while requiring the same number of potential function parameters and one fewer fitted BOB correction parameter than did the analysis of Ref. [12].

While a main focus of the present discussion has been on the long-range behaviour of the BOB functions, the same rapid flattening-off of $|y_p(r)|$ at large $|r - r_e|$ for larger p values which suppressed spurious long-range behaviour helps ensure that the small- r extrapolation behaviour of the proposed functional forms remains ‘reasonable’. Moreover, the overall potential energy function grows exponentially at small r , while the proposed $\Delta V_{\text{ad}}^A(r)$ and $q_A(r)$ functions involve (generally) low order polynomials in a variable with domain $[-1, +1]$. As a result, the latter simply cannot cause unphysical behaviour in the extrapolated inner wall of the overall potential energy function at small- r .

Finally, we note that the examination of model-dependence in Section 4.2 confirms the suggestion implicit in the results of Ref. [14], that while a given combination of $\Delta V_{\text{ad}}^A(r)$ and $q_A(r)$ functions empirically determined from fits based on Eq. (1) may give a unique and physically significant description of BOB behaviour, the absolute physical significance of the individual functions will often require further analysis.

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