Theor Chem Acc (2010) 127:149–155
DOI 10.1007/s00214-009-0710-1

REGULAR ARTICLE

An empirical formula to estimate off-diagonal adiabatic corrections to rotation–vibrational energy levels

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Received: 28 August 2009 / Accepted: 26 November 2009 / Published online: 20 December 2009

Abstract The empirical one-parameter formula proposed by Alijah and Hinze (Philos Trans R Soc Lond A 364:2877, 2006) to estimate the off-diagonal adiabatic energy corrections has been tested systematically on the diatomic molecules for which exact data are known. It was found that the simple formula reproduces at least 90% of the energy shift. The parameter of the model, called c, is dimensionless and approximately independent of the molecule. Thus, the method can be applied to arbitrary molecules, diatomic or polyatomic, using the recommended value $c = 0.11$ of the parameter.

Keywords Adiabatic correction · Non-Born-Oppenheimer approach · Rotation–vibrational states

1 Introduction

Molecular dynamics is very often treated within the Born-Oppenheimer [1, 2] approximation which leads to the picture of nuclei moving on a potential energy surface provided by the electrons. In the absence of close-by electronic states this is a very good approximation for most molecules, an exception being light ones such as H_2, H_2^+, H_3^+ etc. and their isotopologs. Here, the ratio between the electron mass and a typical nuclear mass, m_e/M, is so big that adiabatic corrections, both diagonal and off-diagonal, the latter involving excited electronic states, become important as they scale with this mass ratio. The non-adiabatic theory for diatomic molecules has been formulated by Kołos and Wolniewicz [3]. These authors have then computed the first accurate vibronic energies for H_2, D_2 and T_2 using a variational four-particle wavefunction depending explicitly on all nuclear and electronic coordinates [4]. They also obtained relativistic corrections. This classic work has been extended to higher rotational, vibrational and electronic states of H_2 and isotopologs [5] and some other one- [6] and two-electron diatomics [7]. Bishop and Wetmore [8] performed adiabatic calculations on H_2 and H_2^+ and applied perturbation theory to get the non-adiabatic corrections. Herman and Asgharian [9] and Bunker and Moss [10] followed a different strategy and transformed the Hamiltonian to incorporate non-adiabatic effects in a single-surface operator. Their transformations introduce coordinate-dependent effective nuclear masses. Based on this approach, Schwenke [11, 12] computed the non-adiabatic corrections for H_2^+, H_2 and water. For a summary of work performed on H_2^+ up to the year 1995 see Leach and Moss [13]. In the last few years these small diatomics have received new attention, with focus on the non-adiabatic effects. We mention here the work on H_2^+ and isotopologs [14, 15], H_2 [16, 17], HD [18, 19] and HeH^+ [20]. The application of those methods to polyatomics is possible but appears cumbersome. Recently, Alijah and Hinze [21] proposed an empirical method to estimate

J. Hinze: deceased.

Dedicated to the memory of Professor Jürgen Hinze and published as part of the Hinze Memorial Issue.

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non-adiabatic effects. It does not claim having the same accuracy as the ab initio methods, but can simulate a large part of this usually small correction, more than 90% in the case of H_2. It may permit a much easier access to diatomics and polyatomics.

Here, the most obvious application would be H_3^+, which plays the same role among the polyatomics that H_2 and H_2^+ play among the diatomics: It is a test system for the development of adequate, non-standard theoretical and numerical methods. It is also fascinating in its own right, owing to its importance in astrophysical processes [22]. The need to go beyond the adiabatic approximation for accurate calculations of its rotation–vibrational states has become apparent in 1994 when a highly accurate potential energy surface, obtained as a local fit to 69 points calculated with an r_{12} method, and first vibrational energies were published by Röhse et al. [23]. The authors concluded that above all the diagonal adiabatic correction would still be needed if the quality of the vibrational energies was to be improved. Four years later, Cencek et al. [24] published a surface of unprecedented, sub-microhartree, accuracy based on Gaussian geminals calculations of the electronic energies and addition of diagonal adiabatic and relativistic corrections. At the same time, highly sophisticated methods employing Jacobi or Radau coordinates [25, 26], or hyperspherical ones [27, 28] had become available to treat the nuclear dynamics of this light and floppy molecule. Comparison of newly calculated rotation–vibrational energy levels [29–31] with experimental data [32] obtained in the energy region $E \leq 10{,}000\ \mathrm{cm}^{-1}$ revealed remaining discrepancies of up to $0.8\ \mathrm{cm}^{-1}$, not reflecting the accuracy of the theoretical methods. Though different analytical representations [29, 30, 33] of the 69 points had been used, the origin of the discrepancies was thought to be most likely due to the neglect of non-adiabatic coupling to higher electronic states. Coupled surface calculations have not been performed so far, but two methods have been developed to treat the non-adiabatic effects in a single-surface calculation: Polyansky and Tennyson [30] and Jaquet [34] adjusted the vibrational reduced mass, while the present authors applied energy-dependent shifts to the band origins [21, 35]. Since then, extended non-adiabatic calculations have been published, sampling different regions of the potential energy surface [36, 37] or high-energy rotation–vibrational states [38] or tritiated isotopologs [39].

Our method of energy-dependent shifts has been used successfully for extrapolation purposes [40] at energies above the barrier to linearity at $E \approx 10{,}000\ \mathrm{cm}^{-1}$. Morong et al. [41] related the shift coefficients to the moment of inertia and rotational magnetic moments, following an approach by Oka and Morino [42]. The extrapolated rovibronic energy values turned out helpful in the analysis of new experimental data [41, 43, 44]. However, the energy shifts were found to be slightly too big, leading to over-correction. Alijah and Hinze [21] analyzed the energy dependence of non-adiabatic corrections and devised a simple one-parameter formula which they tested on H_2. The purpose of the present paper is to study further diatomic molecules for which the effects of non-adiabatic coupling are exactly known and thereby demonstrate the general applicability of the proposed formula. As we have mentioned above, the formula would lend itself also to an application in polyatomics due to its simplicity.

2 The adiabatic approximation

For the practical solution of the molecular Schrödinger equation one usually performs two steps: First, the translational motion is separated yielding a Schrödinger equation in molecule-fixed coordinates which is then subjected to the adiabatic coordinate separation [1, 2]

$$\Psi_\alpha(\mathbf{R},\mathbf{r}) = \sum_n \Phi_n(\mathbf{R};\mathbf{r})\Theta_{n\alpha}(\mathbf{R}), \tag{1}$$

where the electronic state functions $\Phi_n(\mathbf{R};\mathbf{r})$ are solutions of the electronic Schrödinger equation

$$\left(\hat{T}_e(\mathbf{r}) + V(\mathbf{R},\mathbf{r})\right)\Phi_n(\mathbf{R};\mathbf{r}) = U_n(\mathbf{R})\Phi_n(\mathbf{R};\mathbf{r}). \tag{2}$$

The expansion of the total wave function, Eq. 1, yields a set of coupled equations to be solved for the nuclear motion,

$$\sum_{n'}\left\{\left[\hat{T}_N(\mathbf{R}) + U_{n'}(\mathbf{R}) - E_\alpha\right]\delta_{nn'} + C_{nn'} + D_{nn'}\right\}\Theta_{n'\alpha}(\mathbf{R}) = 0. \tag{3}$$

The operators $C_{nn'}$ and $D_{nn'}$ in the above equation are defined as

$$C_{nn'}(\mathbf{R}) = \left\langle \Phi_n(\mathbf{R};\mathbf{r}) \mid \left[\left(\hat{T}_N(\mathbf{R}) + \hat{T}_{mp}(\mathbf{r})\right)\Phi_{n'}(\mathbf{R};\mathbf{r})\right]\right\rangle_{\mathbf{r}} \tag{4}$$

$$D_{nn'}(\mathbf{R}) = \frac{\hbar^2}{M_N}\sum_{I=2}^{N}\sum_{J=2}^{N}\mathbf{W}_{nn',I}(\mathbf{R})\cdot\nabla_J - \sum_{I=2}^{N}\frac{\hbar^2}{M_I}\mathbf{W}_{nn',I}(\mathbf{R})\cdot\nabla_I, \tag{5}$$

where $\mathbf{W}$ denotes the first derivative coupling matrix with elements

$$\mathbf{W}_{nn',I}(\mathbf{R}) = \langle\Phi_n(\mathbf{R};\mathbf{r}) \mid [\nabla_I\Phi_{n'}(\mathbf{R};\mathbf{r})]\rangle_{\mathbf{r}}. \tag{6}$$

The summation index of the nuclei starts at $I = 2$ since three degrees of freedom have been removed when separating the centre-of-mass motion. The particular form of the operators depends on the details of this separation and on the choice of the internal coordinates. A systematic discussion has been given by Zülicke [45].

Both operators, $C_{nn'}$ and $D_{nn'}$ are in general non-diagonal in the basis of electronic wave functions. Their diagonal matrix elements, which give rise to the diagonal adiabatic correction, can be evaluated easily. For the determination of C_{nn}, the Born-Handy formula [46], in which the second derivative operator is written in laboratory coordinates, may be applied since Kutzelnigg [47] has proved its general validity. The diagonal element D_{nn} is zero for real and normalizable electronic wavefunctions. In the one-state (simple adiabatic) approximation and for real electronic wave functions, we thus obtain

$$\left[\hat{T}_N(\mathbf{R}) + U_n(\mathbf{R}) + C_{nn}(\mathbf{R}) - E_\alpha\right]\Theta_{n\alpha}(\mathbf{R}) = 0. \quad (7)$$

In general, a one-state approximation is good as long as the potential energy surface of the electronic state n never gets close to that of another electronic state. But even if this condition is satisfied, the rotation–vibrational eigenvalues E_α may be affected by coupling to a remote electronic state. For such a coupling to a remote electronic state, i.e. far away from an avoided crossing, the resulting off-diagonal adiabatic energy corrections are small, and thus negligible, in most common molecules due to the large difference between the nuclear and electronic masses. For the light systems H_2^+, H_2, H_3^+ and their isotopologs they become important. Since non-adiabatic coupling is a dynamical effect, one may wonder whether it is possible to describe it by a simple coordinate-dependent additional term to the potential energy surface.

The problem was first studied by Herman and Asgharian [9] by means of perturbation theory and later by Bunker and Moss [10] who applied a contact transformation to the molecular Hamiltonian. Both treatments yielded one-state Hamiltonians in which the effects of the excited electronic states are folded in. The results, which are quite complicated, show that the effect of these electronic states can be simulated if different reduced masses be used in the vibrational and rotational parts of the Hamiltonian. Furthermore, such effective reduced masses would have to depend on the nuclear coordinates $\mathbf{R}$. The issue has recently been studied by Rey and Tyuterev [48] and by Kutzelnigg [49]. We will discuss mass-scaling approaches further down, presenting and analysing in the next section a simple but accurate empirical approach.

3 A simple empirical approach

For an understanding of the empirical formula, it is useful to call to mind the physical origin of the non-adiabatic correction. In the adiabatic separation of nuclear and electronic motions, the electrons are assumed to follow instantaneously any change of the nuclear configuration. Such a change can be due to vibrations or, to a lesser extent, to rotation. As opposed to the idealization made in the adiabatic separation, the electrons are not clamped to the nuclei in the real molecule where they lag behind as the nuclei vibrate and thereby reverse directions. To a first approximation, this deviation from idealized adiabatic behaviour should lead to energy shifts which scale as a linear function of the vibrational kinetic energy of the nuclei. Rotational effects, which are due to Coriolis coupling of nuclear and electronic motions, are expected to be much less pronounced.

Linear behaviour of the non-adiabatic energy shifts with the vibrational energy has indeed been found in the analysis of the rotation–vibrational states of H_3^+ up to $E = 10{,}000\ \mathrm{cm}^{-1}$. Above this energy, the shifts are smaller than predicted by linear scaling. The empirical correction formula by Alijah and Hinze [21] takes this into account. Consider the force acting on the nuclei due to a vibration,

$$F = Ma = -\frac{\mathrm{d}U(R)}{\mathrm{d}R}. \quad (8)$$

Here, M is the effective nuclear mass associated to this vibration and R is the vibrational coordinate. If the force is multiplied by the deviation from equilibrium, $R - R_e$ and the expectation value of the resulting expression taken over the nuclear wavefunction, one obtains upon division by M

$$\Delta E \sim \frac{1}{M}\left\langle \frac{\mathrm{d}U(R)}{\mathrm{d}R}(R - R_e)\right\rangle. \quad (9)$$

The proportionality factor must have the dimension of a mass and is written as $c\ n\ m_e$ to yield

$$\Delta E = c\frac{n m_e}{M}\left\langle \frac{\mathrm{d}U(R)}{\mathrm{d}R}(R - R_e)\right\rangle. \quad (10)$$

In the above equation, n denotes the total number of electrons, m_e is the electron rest mass and c a dimensionless parameter. With such a definition, the energy correction becomes zero in the limits of zero electron mass or infinite nuclear masses. It also goes to zero at the dissociation energy, as it should, since there is no vibration anymore above dissociation.

The empirical formula, Eq. 10, derived in Ref. [21] and applied there to H_2, is now tested on those molecules for which the potentials, rotation–vibrational states and non-adiabatic shifts are known exactly. These are H_2, H_2^+ and their isotopologs. For diatomic molecules, the relevant effective nuclear mass M entering into Eq. 10 is the reduced mass of the nuclei ($M \equiv \mu$) and the coordinate R is the internuclear distance.

For H_2 and isotopologs, the ground state potential energy curve as well as the diagonal and off-diagonal adiabatic corrections have been obtained by Wolniewicz

[5, 50]. His high-precision data will serve as a reference for the present study. Using the renormalized Numerov method [51, 52], we have obtained numerically the wavefunctions and calculated the expectation values needed in Eq. 10. The potential energy curve has been interpolated by cubic splines [53] from the tabulated exact values given by Wolniewicz. The first derivative of the potential was obtained using the spline coefficients. With the expectation values $\langle \frac{dU(R)}{dR}(R-R_e)\rangle$ at hand, we have determined the best value of the parameter c by least squares fits to the off-diagonal energy corrections by Wolniewicz [5]. For each isotopolog, two calculations were performed, without and with inclusion of the diagonal adiabatic correction term C_{00}. The latter was given by Wolniewicz [50]. The results of these fits are shown in Table 1. First of all, we note that there is no significant difference in the two sets of calculations performed for each molecule, demonstrating the robustness of the method. Second, we find that the numerical value of the parameter c is of the order of $c = 0.11$ for the homonuclear molecules and for DT, but is somewhat larger for HD and HT. The reason for the slightly increased value of c for the two latter molecules is not clear yet, but we attribute it to the significant differences of the two nuclear masses involved. Representative plots for the cases of H_2, T_2 and HT showing our empirical shifts together with Wolniewicz's exact ones are displayed in Figs. 1, 2 and 3. At low energies, linear behaviour is found. The absolute value of the correction (it is negative) then passes through a maximum and reaches zero at dissociation. Our formula does not only yield a qualitatively but also a quantitatively correct behaviour, being accurate to better than 90%. For H_2 the corrections amount to up to 5 cm^{-1} but are less for the heavier isotopologs. The corresponding figures for the remaining molecules show the same behaviour and are not presented here.

We have also considered the rotational dependence of the off-diagonal corrections. Here, the expectation values needed in Eq. 10 have been taken over rotation–vibrational wavefunctions. The numerical values of the parameter c are presented in Table 2 for J = 0–4. A representative plot

Table 1 Results of fits

Molecule	μ/m_e	c	c_{dac}
H_2	918.0763	0.1134 ± 2.7%	0.1133 ± 2.7%
D_2	1,835.2415	0.1126 ± 2.2%	0.1120 ± 2.2%
T_2	2,748.4608	0.1119 ± 2.1%	0.1119 ± 2.1%
HD	1,223.8992	0.1277 ± 2.2%	0.1275 ± 2.1%
DT	2,200.8800	0.1175 ± 2.1%	0.1174 ± 2.0%
HT	1,376.3923	0.1458 ± 2.0%	0.1456 ± 2.0%

c and c_{dac} denote the parameters obtained without and with inclusion of the diagonal adiabatic correction

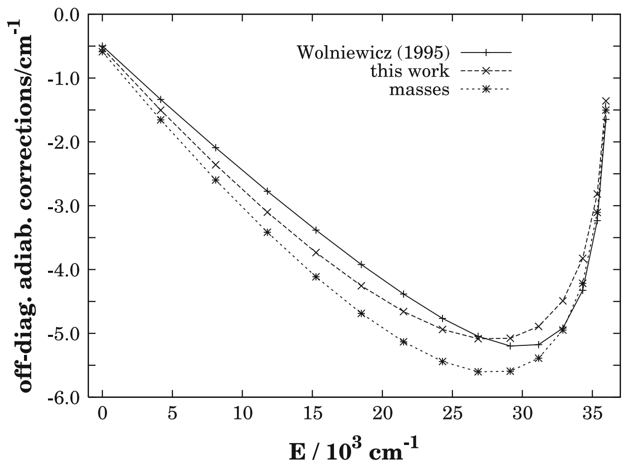

Fig. 1 Off-diagonal adiabatic corrections for pure vibrational states ($J = 0$) in H_2 as obtained by exact calculation by Wolniewicz [5], the present method and through mass-scaling using atomic masses, see Sect. 4

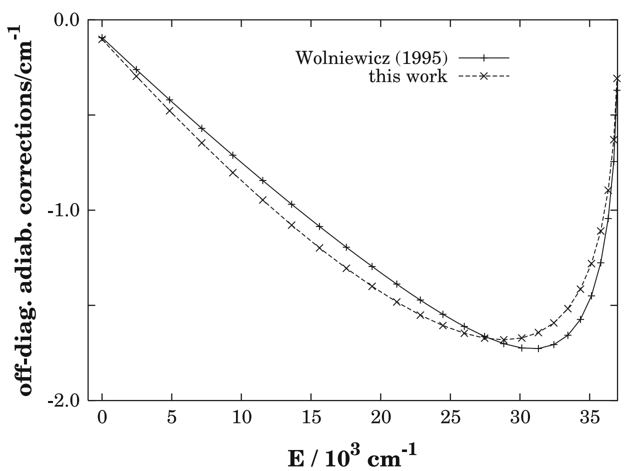

Fig. 2 Off-diagonal adiabatic corrections for pure vibrational states ($J = 0$) in T_2

is shown in Fig. 4. As expected from our preceding analysis, there is a slight increase of c with the rotational quantum number J. Indeed, the rotational contribution to the energy shift is weaker than the vibrational one by two orders of magnitude.

The scaling of the energy shifts with the number of electrons can be explored by consideration of the one-electron molecules H_2^+ and HD^+. For those, off-diagonal corrections have been reported by Wolniewicz and Poll [6]. The potential energy curve used in our calculations was taken from Bishop and Wetmore [8]. Results are presented in Table 3 and Figs. 5 and 6. The numerical values of c are similar to those obtained for H_2 and HD and confirm the linear scaling of the energy correction with the number of electrons n according to our formula, Eq. 10.

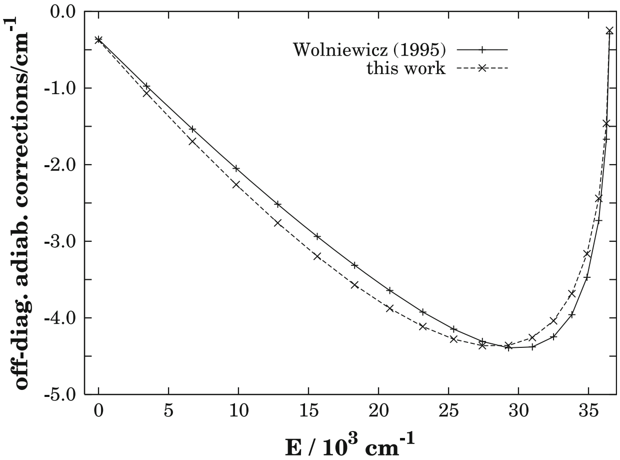

Fig. 3 Off-diagonal adiabatic corrections for pure vibrational states ($J = 0$) in HT

Table 2 Results of fits for H_2 with rotation included

J	c
0	0.1134 ± 2.7%
1	0.1139 ± 2.7%
2	0.1147 ± 2.7%
3	0.1161 ± 2.7%
4	0.1181 ± 2.7%

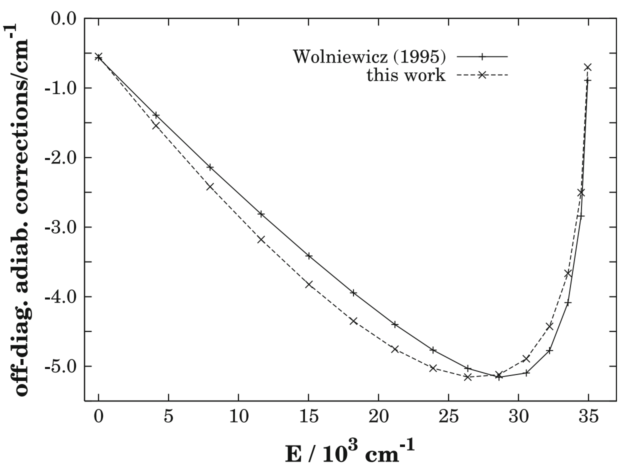

Fig. 4 Off-diagonal adiabatic corrections in H_2, $J = 4$

Our examples demonstrate that the simple formula, Eq. 10, reproduces well over 90% of the energy shifts due to non-adiabatic coupling. Effects of isotopic substitution enter through the different effective masses and the particular wavefunctions used to calculate the expectation values $\langle \frac{\mathrm{dU(R)}}{\mathrm{d}R}(R - R_e) \rangle$. Thus, effects of symmetry breaking which are responsible, for example, for the two dissociation limits of HD^+, are not included. An empirical method

Table 3 Results of fits for H_2^+ and HD^+

Molecule	μ/m_e	c
H_2^+	918.0763	0.1059 ± 2.5%
HD^+	1,223.8992	0.1085 ± 2.2%

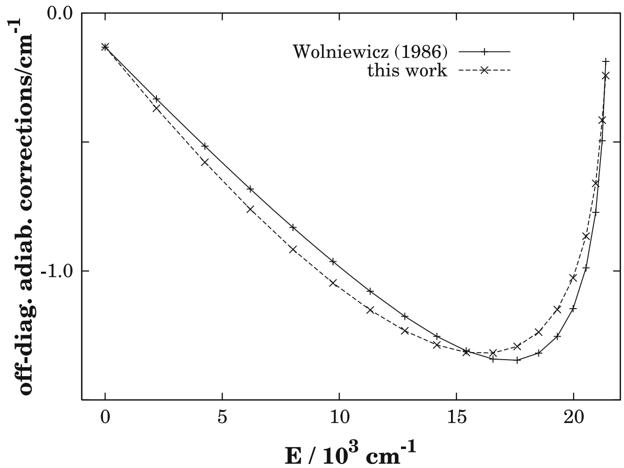

Fig. 5 Off-diagonal adiabatic corrections for pure vibrational states ($J = 0$) in H_2^+

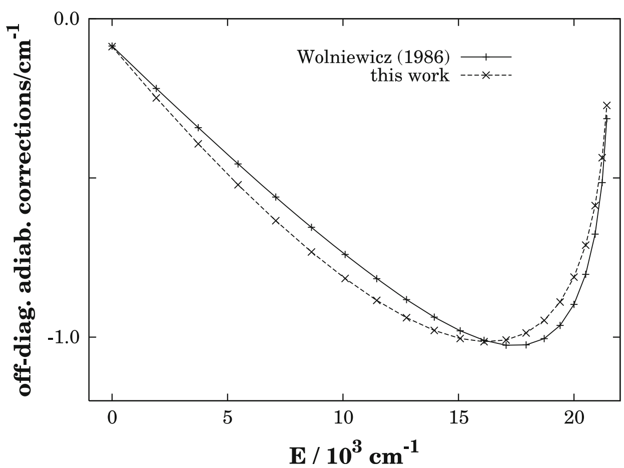

Fig. 6 Off-diagonal adiabatic corrections for pure vibrational states ($J = 0$) in HD^+

capable of describing symmetry breaking effects has been proposed by Gonçalves and Mohallem [54–56].

4 The mass-scaling approach

The mass-scaling approach is a simple method frequently used in rotation–vibrational calculations to approximately include the non-adiabatic effects of other electronic states in a one-state approach. Its origin can be traced back to the derivation of an effective Schrödinger equation for nuclear motion in ${}^1\Sigma$ states of diatomics by Herman and Asgharian [9] and to the derivation of an effective vibration-rotation Hamiltonian for a diatomic molecule via contact transformation by Bunker and Moss [10]. They showed that the radial function $P_{nvJ}(R)$ of a ro-vibrational state function $\Theta_{nvJ}(\mathbf{R}) = R^{-1}P_{nvJ}(R)Y_{JM}(\mathbf{R}/R)$ has to satisfy an effective radial Schrödinger equation that can be written as

$$\left\{-\frac{\hbar^2}{2\mu_{\mathrm{vib}}(R)}\frac{\mathrm{d}^2}{\mathrm{d}R^2} + \frac{\hbar^2}{2\mu_{\mathrm{rot}}(R)}\frac{J(J+1)}{R^2} + U_n(R) + C_{nn}(R) - E_{nvJ}\right\}P_{nvJ}(R) = 0 \tag{11}$$

with an effective potential energy function $U_n(R) + C_{nn}(R)$, that includes the mass-dependent diagonal adiabatic correction as well as possibly relativistic and radiative corrections, and effective reduced masses $\mu_{\mathrm{vib}}(R)$ and $\mu_{\mathrm{rot}}(R)$ that depend on internuclear distance R and account for non-adiabatic effects. Attempts to fully solve Eq. 11 have been made only in the recent past [14, 16, 48, 49]. However, the more pragmatic way has been, and still is, to ignore the R-dependence of the effective masses, i. e., to solve

$$\left\{-\frac{\hbar^2}{2\mu_{\mathrm{vib}}}\frac{\mathrm{d}^2}{\mathrm{d}R^2} + \frac{\hbar^2}{2\mu_{\mathrm{rot}}}\frac{J(J+1)}{R^2} + U_n(R) + C_{nn}(R) - E_{nvJ}\right\} \times P_{nvJ}(R) = 0 \tag{12}$$

ideally without modification of $U_n(R)$. The effective masses are now being considered as adjustable parameters used to improve the agreement between theoretically and experimentally determined ro-vibrational energy levels. Non-adiabatic corrections may then be defined from this two-parameter approach as the differences between energy eigenvalues calculated with atomic and nuclear masses. However, the widely observed outcome of this mass-scaling approach is that the optimum value of the effective *vibrational* reduced mass is close to a reduced mass derived from *atomic* masses, $\mu_{\mathrm{vib,opt}} \approx ((M_A + Z_A m_e)^{-1} + (M_B + Z_B m_e)^{-1})^{-1}$, whereas the optimum for the effective *rotational* reduced mass lies close to a reduced mass derived from *nuclear* masses, $\mu_{\mathrm{rot,opt}} \approx (1/M_A + 1/M_B)^{-1}$. This behaviour, already encountered in the early work by Bunker et al. [57] for H_2 and D_2, has also been found for the cations H_2^+, D_2^+ [58] and HD^+ [59]. Modelling non-adiabatic corrections in this way, by the use of different reduced masses for vibration and rotation, respectively, allows to reduce the absolute errors in ro-vibrational eigenvalues by an order of magnitude, to about a few 0.01 cm^{-1} in favourable cases. A problematic issue, however, with this approach to the non-adiabatic corrections is that it is an a posteriori approach because highly accurate and properly assigned experimental energy levels are required as reference data. In order to avoid the requirement of re-adjustment of masses for every new system, various simpler recipes have been proposed, e.g., using nuclear masses for rotation, but atomic masses for vibration. For ionic systems, atomic masses must be calculated with a suitably assigned fractional electron number. Along these lines a generalization of the mass-scaling approach from diatomics to polyatomics is possible and has been attempted with success for H_3^+ [23, 30, 33, 34] and water [60]. Since we focus on diatomics in this work, a detailed discussion of the mass-scaling approach in H_3^+ and its isotopologs is postponed to a later publication.

It is interesting here to compare the performance of the simple mass scaling approach with that of our empirical formula. To this end, we have recalculated the vibrational levels of H_2 using atomic masses. The off-diagonal adiabatic correction is then obtained for each vibrational state as the difference between the energy values calculated with atomic masses and with nuclear masses, respectively. These data are also shown in Fig. 1 and demonstrate the reliability of the two methods. Better accuracy, however, is obtained with our simple one-parameter formula.

5 Conclusions

The empirical method proposed by Alijah and Hinze [21] to estimate the effect of non-adiabatic coupling to rotation–vibrational states has been tested extensively on those diatomic molecules for which exact results are available for comparison. The method, containing only one empirical parameter, performs well and the parameter seems to be nearly universal. H_2 has the largest corrections, of up to 5 cm^{-1}, and these are reproduced to within 90%. If the method is applied to other molecules, which have larger reduced masses, the absolute error is of the order of 0.1 cm^{-1} or less. The method is robust, i.e., the corrections are not very sensitive to small changes of the potential.

Nevertheless, some deviations from the recommended value of the parameter, $c = 0.11$, are observed when this parameter is optimized for particular systems, most noticeably in the case of the heteronuclear diatomics HD and HT, see Table 1. This may be easily remedied by making c dependent on κ^2, where κ depends on the nuclear masses via $\kappa = (M_A - M_B)/(M_A + M_B)$. In addition, there is the expected drift with J, see Table 2, such that a dependence on $J(J + 1)$ is conjectured. Inclusion of all these dependencies is possible, but requires additional parameters and easily leads to awkward expressions without much improvement in the physical content. Thus, we recommend the use of the simple one-parameter formula with the numerical value of $c = 0.11$ which should account for at least 90% of the energy correction due to non-adiabatic effects.

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