Nonadiabatic corrections to the wave function and energy

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Nonadiabatic corrections in molecules composed of a few atoms are considered. It is demonstrated that a systematic perturbative expansion around the adiabatic solution is possible, with the expansion parameter being the electron-nucleus mass ratio to the power 3/4. Closed form formulae for the leading corrections to the wave function and to the energy are derived. Their applicability is demonstrated by a comparison of numerical results for the hydrogen molecule with the former nonadiabatic calculations and the experimental values. Good agreement with the recent experiment is achieved for the ground state dissociation energy of both H_2 and D_2 .

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I. INTRODUCTION

One of the most fundamental approximations of the theory of molecular structure, the so called clamped nuclei approximation, assumes separation of the electronic and nuclear motion and computing the electronic wave function and energy for a fixed position of nuclei [1–4]. In the more accurate adiabatic approximation, one includes the diagonal matrix element of the nuclear kinetic energy, see Eq. (8). The reminder beyond this term is described as the nonadiabatic correction. In their calculations Kołos and Wolniewicz [5] pointed out significance of nonadiabatic corrections in obtaining accurate results for H_2. They claimed that within the Born-Oppenheimer (BO) approximation or adiabatic variants thereof, it is not possible to estimate quantitatively the accuracy of the method, and suggested that one should drop from the very beginning the idea of separation of the electronic and nuclear motions, and start instead with the exact Schrödinger equation for all the particles involved. Since that work, calculations including the nonadiabatic as well as the relativistic effects in the hydrogen molecule have been significantly improved, among others, by Wolniewicz and Kołos [6–10], Adamowicz [11–14], Bishop [15], Anderson [16] and their coworkers. However, no systematic theory of nonadiabatic corrections to dissociation energies or rovibrational splittings has been pursued. For simple molecules such as H_2, direct nonadiabatic calculations with explicitly correlated Gaussians are at present possible [11–14], but no reliably estimate of their numerical uncertainties has been made. In fact, results from Refs. [12] and [14] are not in good agreement with each other, if all presented digits are significant. However, the recent results of the variational calculation in Ref. [14] are in remarkable agreement with the original work of Wolniewicz [7], but our results obtained here for total nonrelativistic energies lie slightly below their predictions, outside the estimated uncertainties.

At present, the lack of nonadiabatic corrections in simple molecules limits the knowledge of physical properties, such as the dissociation energy, vibrational, and rotational energy spacings. In certain instances the nonadiabatic effects can not be considered small at all. For example, a recent study of the spontaneous ortho-para transition in H_2 [17] reveals that the contribution of the nonadiabatic effects to the transition probability reaches as much as 40%. Another example concerns the helium dimer. The nonadiabatic corrections are expected [18] to significantly contribute to the dissociation energy of the highest vibrational level D_{14} of the spin polarized helium molecule in $^5\Sigma$ electronic state, for which precise measurement has recently been performed [19]. Indeed, authors of [20] observed that using the atomic mass instead of the nuclear mass in Eq. (8) [4] changes the dissociation energy of the D_{14} level by as much as 5%. This mass change is in accordance with the result obtained here, Eq. (33), and indicates an importance of the nonadiabatic effects.

In this work, we construct a systematic perturbative expansion for nonadiabatic corrections to the wave function and energy in molecules composed of a few atoms, with the expansion parameter being the electron-nucleus mass ratio to the power 3/4 $[(m_{\rm e}/M)^{3/4}]$. We derive closed form formulae for the leading nonadiabatic corrections and present accurate numerical results for the H_2 and D_2 molecules. This method, we suppose, can be applied to more complex molecules, where fully nonadiabatic calculations are infeasible, which is the main advantage of the presented here perturbative approach.

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II. METHODOLOGY

A. Theoretical framework

Let us first consider a diatomic molecule, and assume the reference frame be related to the mass center of the two nuclei. The total wave function ϕ is the solution of the stationary Schrödinger equation

$$H\,\phi = E\,\phi\,, \tag{1}$$

with the Hamiltonian

$$H = H_{\rm el} + H_{\rm n}\,, \tag{2}$$

split into the electronic and nuclear parts. In the electronic Hamiltonian $H_{\rm el}$

$$H_{\rm el} = -\sum_i \frac{\nabla_i^2}{2\,m_{\rm e}} + V \tag{3}$$

the nuclei have fixed positions $\vec{R}_A$ and $\vec{R}_B$, while the nuclear Hamiltonian is

$$\begin{aligned} H_{\rm n} &= -\frac{\nabla_{R_A}^2}{2\,M_A} - \frac{\nabla_{R_B}^2}{2\,M_B} & (4)\\ &= -\frac{\nabla_R^2}{2\,\mu_{\rm n}} - \frac{(\sum_i \vec{\nabla}_i)^2}{2\,(M_A+M_B)}, & (5)\end{aligned}$$

where $\vec{R} = \vec{R}_A - \vec{R}_B$ and $\mu_{\rm n}$ is the nuclear reduced mass.

In the adiabatic approximation the total wave function of the molecule

$$\phi_{\rm a}(\vec{r},\vec{R}) = \phi_{\rm el}(\vec{r})_{\vec{R}}\;\chi(\vec{R}) \tag{6}$$

is represented as a product of the electronic wave function $\phi_{\rm el}$ and the nuclear wave function χ. The electronic wave function obeys the clamped nuclei electronic Schrödinger equation

$$\big[H_{\rm el} - E_{\rm el}(R)\big]\,|\phi_{\rm el}\rangle = 0, \tag{7}$$

while the nuclear wave function obeys the Schrödinger equation in the effective potential generated by electrons

$$\big[H_{\rm n} + \big\langle H_{\rm n}\big\rangle_{\rm el} + E_{\rm el} - E_{\rm a}\big]\,|\chi\rangle = 0\,. \tag{8}$$

To account for corrections to the adiabatic wave function $\phi_{\rm a}$ and the energy $E_{\rm a}$ resulting from the coupling between the motion of nuclei and electrons, we formulate a systematic perturbative expansion around the adiabatic solution, and derive explicit expression for the leading nonadiabatic corrections to the wave function $\delta\phi_{\rm na}$ and to the energy $\delta E_{\rm na}$.

B. Derivation of the nonadiabatic corrections

The total wave function

$$\phi = \phi_{\rm a} + \delta\phi_{\rm na} = \phi_{\rm el}\,\chi + \delta\phi_{\rm na} \tag{9}$$

is the sum of the adiabatic solution and a nonadiabatic correction. Due to the normalization of ϕ and $\phi_{\rm a}$, the nonadiabatic correction is orthogonal to $\phi_{\rm a}$ in the leading order of the electron-nucleus mass ratio

$$\langle\delta\phi_{\rm na}|\phi_{\rm a}\rangle = 0\,. \tag{10}$$

Let us consider the electronic matrix element

$$\langle\delta\phi_{\rm na}|\phi_{\rm el}\rangle_{\rm el} \equiv \delta\chi, \tag{11}$$

which is a function of the internuclear distance R. The nonadiabatic correction $\delta\phi_{\rm na}$ will be decomposed into two parts

$$\delta\phi_{\rm na} = \phi_{\rm el}\,\delta\chi + \delta'\phi_{\rm na}. \tag{12}$$

It follows from Eqs. (10) and (11) that these two parts obey the following orthogonality conditions

$$\begin{aligned} \langle\delta'\phi_{\rm na}|\phi_{\rm el}\rangle_{\rm el} &= 0\,, & (13)\\ \langle\delta\chi|\chi\rangle &= 0\,. & (14)\end{aligned}$$

Let us now revert to the stationary Schrödinger equation in (1)

$$\big[H_{\rm el} + H_{\rm n} - E_{\rm a} - \delta E_{\rm na}\big]\,\big|\phi_{\rm el}\,\chi + \delta\phi_{\rm na}\big\rangle = 0\,, \tag{15}$$

and rewrite it to the following form

$$\begin{aligned} &\big[E_{\rm el}(R) - H_{\rm el}\big]\,|\delta\phi_{\rm na}\rangle & (16)\\ &\quad = \big[E_{\rm el}(R) + H_{\rm n} - E_{\rm a} - \delta E_{\rm na}\big]\,\big|\phi_{\rm el}\,\chi + \delta\phi_{\rm na}\big\rangle. \end{aligned}$$

The solution can be formally written as

$$\begin{aligned} |\delta\phi_{\rm na}\rangle &= |\phi_{\rm el}\,\delta\chi\rangle + \frac{1}{(E_{\rm el}-H_{\rm el})'} & (17)\\ &\quad\times\big[E_{\rm el} + H_{\rm n} - E_{\rm a} - \delta E_{\rm na}\big]\,\big|\phi_{\rm el}\,\chi + \delta\phi_{\rm na}\big\rangle, \end{aligned}$$

where the symbol prime in the denominator denotes exclusion of the reference state $\phi_{\rm el}$ from the Hamiltonian inversion. Since $\delta\phi_{\rm na}$ is expected to be a small correction to $\phi_{\rm a}$, it can be neglected on the right hand side in the leading order. Then $E_{\rm el} - E_{\rm a} - \delta E_{\rm na}$ does not contribute in the above matrix element and this equation takes the form

$$|\delta\phi_{\rm na}\rangle = |\phi_{\rm el}\,\delta\chi\rangle + \frac{1}{(E_{\rm el}-H_{\rm el})'}\,H_{\rm n}\,|\phi_{\rm el}\,\chi\rangle. \tag{18}$$

Let us point out, that the difference $E_{\rm el} - E_{\rm a}$ in Eq. (17) is not necessarily small for higher rovibrational levels, so the neglect of $\delta\phi_{\rm na}$ on the right hand side might be questionable. However, we will show later, that this neglect of $\delta\phi_{\rm na}$ is in fact justified by considering the next order nonadiabatic correction. The presence of $E_{\rm el}$ instead of $E_{\rm a}$ in the denominator in Eq. (18) is an important difference with the former calculations of nonadiabatic corrections by Wolniewicz [7].

The perturbed function, $\delta\chi$, is as yet unknown—we obtain it from Eq. (15) by taking a matrix element with $\phi_{\rm el}$, namely

$$\big\langle\phi_{\rm el}\big|E_{\rm el}+H_{\rm n}-E_{\rm a}-\delta E_{\rm na}\big|\,\phi_{\rm el}\,(\chi+\delta\chi)+\delta'\phi_{\rm na}\big\rangle_{\rm el}=0 \quad (19)$$

The nuclear function χ obeys Eq. (8), which can be rewritten in the form

$$\big\langle\phi_{\rm el}\big|E_{\rm el}+H_{\rm n}-E_{\rm a}\big|\,\phi_{\rm el}\,\chi\big\rangle_{\rm el}=0\,. \quad (20)$$

The difference of Eqs. (19) and (20), neglecting the small higher order term $\delta E_{\rm na}\,\delta\chi$ is

$$\begin{aligned}&\big[H_{\rm n}+\big\langle H_{\rm n}\big\rangle_{\rm el}+E_{\rm el}-E_{\rm a}\big]\,|\delta\chi\rangle \qquad (21)\\ &\qquad=\delta E_{\rm na}\,\chi-\big\langle\phi_{\rm el}\big|H_{\rm n}\big|\delta'\phi_{\rm na}\big\rangle_{\rm el}.\end{aligned}$$

If one multiplies the above equation from the left by χ and integrates over R, then obtains

$$\begin{aligned}\delta E_{\rm na} &= \big\langle\phi_{\rm el}\,\chi\big|H_{\rm n}\big|\delta'\phi_{\rm na}\big\rangle\\ &= \bigg\langle\phi_{\rm el}\,\chi\bigg|H_{\rm n}\,\frac{1}{(E_{\rm el}-H_{\rm el})'}\,H_{\rm n}\bigg|\phi_{\rm el}\,\chi\bigg\rangle. \quad (22)\end{aligned}$$

This is the final formula for the leading nonadiabatic correction to energy. At first sight, it resembles the Van Vleck sum-over-states formula [3, 21], but the essential difference is in that, no summation over the nuclear states is present here, which makes Eq. (22) of practical use. The perturbed function $\delta\chi$ can now be inferred from Eq. (21). The solution to this differential equation can be formally written as

$$|\delta\chi\rangle = \frac{1}{\big[E_{\rm a}-E_{\rm el}-H_{\rm n}-\big\langle H_{\rm n}\big\rangle_{\rm el}\big]'}\big\langle\phi_{\rm el}\big|H_{\rm n}\big|\delta'\phi_{\rm na}\big\rangle_{\rm el}. \quad (23)$$

This completes the treatment of leading nonadiabatic corrections in diatomic molecules. The extension of the perturbative nonadiabatic expansion to polyatomic molecules is straightforward. Let the total Hamiltonian be decomposed into the electronic and nuclear parts as in Eq. (2), with the condition that $H_{\rm el}$ does not contain derivatives with respect to nuclear coordinates. Then the nonadiabatic correction to energy again takes the form of Eq. (22). This general formula is also valid in the case when the R-independent term in $H_{\rm n}$ in Eq. (5) is shifted to $H_{\rm el}$, which can simplify the numerical calculation of nonadiabatic energies.

C. Higher order corrections

The perturbative theory presented here can be extended also to higher orders in the electron-nucleus mass ratio in a manner similar to the standard time independent Rayleigh-Schrödinger perturbative expansion. Indeed, the next order nonadiabatic correction to the energy is

$$\begin{aligned}\delta^{(3)}E_{\rm na} &= \bigg\langle\phi_{\rm el}\,\chi\bigg|H_{\rm n}\,\frac{1}{(E_{\rm el}-H_{\rm el})'}\,(H_{\rm n}+E_{\rm el}-E_{\rm a})\\ &\quad\times\frac{1}{(E_{\rm el}-H_{\rm el})'}\,H_{\rm n}\bigg|\phi_{\rm el}\,\chi\bigg\rangle\\ &\quad+\bigg\langle\phi_{\rm el}\,\chi\bigg|H_{\rm n}\,\frac{1}{(E_{\rm el}-H_{\rm el})'}\,H_{\rm n}\bigg|\phi_{\rm el}\,\delta\chi\bigg\rangle, \quad (24)\end{aligned}$$

where $\delta\chi$ is given in Eq. (23), and its detailed derivation is postponed to the next paper. Let us note, that $H_{\rm n}+E_{\rm el}-E_{\rm a}$ in the first term of the right hand side of Eq. (24) is indeed small, because χ satisfies differential equation (8). Therefore, the neglect of $\delta\phi_{\rm na}$ on the right hand side of Eq. (17) in the derivation of the leading nonadiabatic correction is fully justified.

The order of magnitude of the higher order corrections can be estimated by noting that in atomic units the kinetic energy of the nuclei is of order of the square of the nuclear displacement δR from the equilibrium value. It follows that $\delta R\sim(m_{\rm e}/\mu_{\rm n})^{1/4}$, and the nuclear kinetic energy is nominally of order $\sqrt{m_{\rm e}/\mu_{\rm n}}$. However, it can be shown that each $H_{\rm n}$ in Eqs. (22) and (24) contributes $(m_{\rm e}/\mu_{\rm n})^{3/4}$, therefore the nonadiabatic correction to the energy is of order $O\big[(m_{\rm e}/\mu_{\rm n})^{3/2}\big]$, and the total energy can be written as

$$E=E_{\rm a}+\delta E_{\rm na}\left[1+O\bigg(\frac{m_{\rm e}}{\mu_{\rm n}}\bigg)^{3/4}\right]. \quad (25)$$

This estimate may break down however, when Born-Oppenheimer potential curves for different electronic states approach each other at certain distance, then the denominator in Eq. (22) can be arbitrarily small. For this situation a kind of multireference perturbation theory should be developed and this is not a subject of the present work.

D. Working equations

The general formula (22) can be readily rearranged to a more practical form. For this purpose, we separate out electronic matrix elements from the nuclear ones in $\delta E_{\rm na}$ and assume that the states χ are purely vibrational

$$\begin{aligned}\delta E_{\rm na} &= \int_0^\infty R^2\,dR\,\bigg[\chi^2\bigg\langle H_{\rm n}\,\phi_{\rm el}\bigg|\frac{1}{(E_{\rm el}-H_{\rm el})'}\bigg|H_{\rm n}\,\phi_{\rm el}\bigg\rangle_{\rm el}\\ &\quad-2\,\frac{\chi\,\nabla_R^i\chi}{\mu_{\rm n}}\,\bigg\langle H_{\rm n}\,\phi_{\rm el}\bigg|\frac{1}{(E_{\rm el}-H_{\rm el})'}\bigg|\nabla_R^i\phi_{\rm el}\bigg\rangle_{\rm el} \quad (26)\\ &\quad+\frac{\nabla_R^i\chi\,\nabla_R^j\chi}{\mu_{\rm n}^2}\,\bigg\langle\nabla_R^i\phi_{\rm el}\bigg|\frac{1}{(E_{\rm el}-H_{\rm el})'}\bigg|\nabla_R^j\phi_{\rm el}\bigg\rangle_{\rm el}\bigg]\\ &\equiv \int_0^\infty R^2\,dR\,\big[\chi^2(R)\,\mathcal{U}(R)-2\,\chi(R)\,\chi'(R)\,\mathcal{V}(R)\\ &\quad+[\chi'(R)]^2\,\mathcal{W}(R)\big]\,. \quad (27)\end{aligned}$$

Eq. (27) can be rewritten as an integral of the sum of two terms which have simple physical interpretation

$$\delta E_{\rm na} = \int_0^\infty R^2\,dR\,\Big\{\chi^2(R)\,\Big[\mathcal{U}(R)+\frac{2}{R}\,\mathcal{V}(R)+\mathcal{V}'(R)\Big] +[\chi'(R)]^2\,\mathcal{W}(R)\Big\}. \tag{28}$$

The first term, the coefficient of χ^2, is a nonadiabatic correction to the adiabatic energy curve, while the second term, the coefficient of χ'^2, is an R-dependent correction to the nuclear reduced mass $\mu_{\rm n}$, namely

$$\frac{1}{2\,\mu_{\rm n}(R)} \equiv \frac{1}{2\,\mu_{\rm n}} + \mathcal{W}(R). \tag{29}$$

An obvious advantage of the representations (27) and (28) is that the electronic matrix elements comprising the pseudopotentials $\mathcal{U}$, $\mathcal{V}$, and $\mathcal{W}$ need to be evaluated for each R only once for all rovibrational levels.

The electronic matrix elements in Eq. (26) involve multiple differentiation of the electronic wave function with respect to the internuclear distance R, which is difficult to calculate directly. Therefore, we rewrite these terms to a more convenient form, where differentiation is taken of the Hamiltonian, namely

$$\vec\nabla_R\phi_{\rm el} = \frac{1}{(E_{\rm el}-H_{\rm el})'}\,\vec\nabla_R(H_{\rm el})\,\phi_{\rm el}\,, \tag{30}$$

$$\nabla^2_R\phi_{\rm el} \approx \frac{1}{(E_{\rm el}-H_{\rm el})'}\Big\{\nabla^2_R(H_{\rm el})\,\phi_{\rm el} + 2\,\vec\nabla_R(H_{\rm el}-E_{\rm el}) \times\frac{1}{(E_{\rm el}-H_{\rm el})'}\,\vec\nabla_R(H_{\rm el})\,\phi_{\rm el}\Big\}, \tag{31}$$

where, in the last equation, a term proportional to $\phi_{\rm el}$ has been omitted as it does not contribute to the matrix element in Eq. (26).

E. Asymptotics

The adiabatic energy $E_{\rm a}$ in Eq. (8) and the nonadiabatic correction $\delta E_{\rm na}$ in Eq. (22) do not vanish at large internuclear distances. It is because they partially include the atomic reduced mass and the so called mass polarization term. For example, for the large atomic separation in the hydrogen molecule, $\langle H_{\rm n}\rangle_{\rm el}$ in Eq. (8) and $\mathcal{U}(R)$ in Eq. (26) are equal to $m_{\rm e}/m_{\rm p}$ and $-(m_{\rm e}/m_{\rm p})^2$, accordingly, which corresponds to first terms in the expansion of the reduced mass in the electron-nucleus mass ratio

$$1-\frac{\mu}{m_{\rm e}} = \frac{m_{\rm e}/m_{\rm p}}{1+m_{\rm e}/m_{\rm p}} = \frac{m_{\rm e}}{m_{\rm p}} - \left(\frac{m_{\rm e}}{m_{\rm p}}\right)^2 + \left(\frac{m_{\rm e}}{m_{\rm p}}\right)^3 - \ldots \tag{32}$$

The asymptotics of $\mathcal{W}(R)$ equal to $-m_{\rm e}/m_{\rm p}^2$ corresponds to the change in Eq. (29) of the reduced nuclear mass $\mu_{\rm n}$ to the reduced atomic mass $\mu_{\rm A}$, namely

$$\frac{1}{2\,\mu_{\rm A}} = \frac{1}{2\,\mu_{\rm n}(\infty)} = \frac{1}{m_{\rm p}+m_{\rm e}} = \frac{1}{m_{\rm p}}\left(1-\frac{m_{\rm e}}{m_{\rm p}}+\cdots\right). \tag{33}$$

Therefore, if one uses, instead of the nuclear reduced mass $\mu_{\rm n}$, the atomic reduced mass $\mu_{\rm A}$ in the radial equation for χ, then the large R asymptotics should be subtracted from $\mathcal{W}(R)$.

III. CALCULATIONS

In order to test validity of the presented perturbation theory, we consider in more detail the hydrogen and deuterium molecules, for which the nonadiabatic corrections were calculated perturbatively by Wolniewicz [7], and nonperturbatively by Adamowicz and coworkers [11–14]. The nuclear masses used in our calculations were $m_{\rm p} = 1836.15267247\,m_{\rm e}$ for the proton and $m_{\rm d} = 3670.4829654\,m_{\rm e}$ for the deuteron, and the conversion factor was 1 hartree = 219474.6313705 cm^{-1} [22].

The electronic potential for the nuclear Schrödinger equation (8) consists of two contributions: the BO energy curve $E_{\rm el}$ and the adiabatic correction curve $\langle H_{\rm n}\rangle_{\rm el}$. In our calculations we used the most accurate currently available BO potential of H_2 computed with subnanohartree accuracy by Cencek [23] using 1200-term exponentially correlated Gaussian (ECG) wave functions [24].

The adiabatic corrections for H_2 and D_2 were computed as expectation values of the Hamiltonian $H_{\rm n}$, Eq. (5),

$$\langle\phi_{\rm el}|H_{\rm n}|\phi_{\rm el}\rangle_{\rm el} = -\frac{1}{M}\langle\phi_{\rm el}|\nabla^2_R|\phi_{\rm el}\rangle_{\rm el} -\frac{1}{4M}\langle\phi_{\rm el}|\big(\vec\nabla_1+\vec\nabla_2\big)^2|\phi_{\rm el}\rangle_{\rm el}\,. \tag{34}$$

While the evaluation of the last term is straightforward, the first term on the right hand side is cumbersome since it involves differentiation of the electronic wave function with respect to the internuclear distance. Several methods of evaluation, either analytically [6, 25, 26] or numerically [27–29] of the adiabatic correction $\langle H_{\rm n}\rangle_{\rm el}$ have been reported in literature. In this work, we note that the expectation value $\langle\phi_{\rm el}|\nabla^2_R|\phi_{\rm el}\rangle_{\rm el}$, by virtue of $\vec\nabla_R\langle\phi_{\rm el}|\phi_{\rm el}\rangle_{\rm el}=0$, is equivalent to $-\langle\vec\nabla_R\phi_{\rm el}|\vec\nabla_R\phi_{\rm el}\rangle_{\rm el}$, and with the help of Eq. (30) is expressed as

$$\langle\phi_{\rm el}|\nabla^2_R|\phi_{\rm el}\rangle_{\rm el} = -\langle\phi_{\rm el}|\vec\nabla_R(H_{\rm el})\,\frac{1}{\big[(E_{\rm el}-H_{\rm el})'\big]^2} \times\vec\nabla_R(H_{\rm el})\,|\phi_{\rm el}\rangle, \tag{35}$$

which can be conveniently calculated in a similar way as the nonadiabatic correction.

The numerical calculations were performed at a few tens of internuclear distances, R. For each R, three different electronic functions expanded in an ECG basis set were involved in the evaluation of the components of the vector $\vec{\nabla}_R\phi_{\rm el}$ of Eq. (30). The two-electron ECG basis functions were of the following form

$$\psi_k(\vec{r}_1,\vec{r}_2) = (1+\hat{P}_{12})(1+\hat{\imath})\,\Xi_k \times \exp\left[-\sum_{i,j=1}^{2} A_{ij,k}(\vec{r}_i-\vec{s}_{i,k})(\vec{r}_j-\vec{s}_{j,k})\right], \quad (36)$$

where the matrices $\mathbf{A}_k$ and vectors $\vec{s}_k$ contain nonlinear parameters, 5 per basis function, to be optimized. The antisymmetry projector $(1+\hat{P}_{12})$ ensures singlet symmetry, the spatial projector $(1+\hat{\imath})$—the gerade symmetry, and Ξ_k prefactor enforces Σ state when equal to 1, and Π state when equal to y_i—the perpendicular Cartesian component of the electron coordinate.

The first basis, composed of 600 ECG functions (36), was employed to expand the $\mathrm{X}^1\Sigma_g^+$ electronic ground state wave function $\phi_{\rm el}$. The nonlinear parameters were optimized variationally with respect to the BO energy with the target accuracy of the order of nanohartree. Two other basis sets were employed to represent the two components of $\vec{\nabla}_R\phi_{\rm el}$: a 1200-term basis set of ${}^1\Sigma_g^+$ symmetry for the component parallel to the molecular axis and a 1200-term basis set of ${}^1\Pi_g$ symmetry for the perpendicular component. The nonlinear parameters of these two basis sets were also optimized. This optimization was carried out with respect to the following functional

$$\mathcal{J} = \langle\phi_{\rm el}|\vec{\nabla}_R(H_{\rm el})\,\frac{1}{(H_{\rm el}-E_{\rm el})'}\,\vec{\nabla}_R(H_{\rm el})\,|\phi_{\rm el}\rangle \quad (37)$$

with the fixed external wave function $\phi_{\rm el}$ and in the case of the Σ basis set, with the subtraction of the internal wave function $\phi_{\rm el}$ from the Hamiltonian inversion. This is achieved as follows. The first 600 terms of this basis were taken from $\phi_{\rm el}$ wave function and their nonlinear parameters were kept fixed during the optimization, only the remaining 600 terms of Σ symmetry were optimized. This ensures that the internal wave function $\phi_{\rm el}$ is well represented at every step of optimization. Then the subtraction is achieved by orthogonalization of $\vec{\nabla}_R(H_{\rm el})\,|\phi_{\rm el}\rangle$ with respect to the internal $|\phi_{\rm el}\rangle$. In the final calculations the 1200-term Σ basis obtained according to the above description was used also for the expansion of the external ground state function $\phi_{\rm el}$.

The optimized functions were employed to evaluate the adiabatic correction (34) yielding an excellent agreement with the most accurate results obtained by Cencek and Kutzelnigg [29] by using the numerical Born-Handy method—all six digits reported in [29] were confirmed by our analytic calculations. The diagonal correction function obtained this way was combined with the BO energy curve to form the electronic potential for the movement of the nuclei. The nuclear Schrödinger equation was solved numerically for the adiabatic energies $E_{\rm a}$ and the nuclear wave functions $\chi(R)$.

The electronic matrix elements $\mathcal{U}$, $\mathcal{V}$, $\mathcal{W}$ entering Eq. (27) were evaluated within the same two 1200-term ECG basis sets described above yielding smooth functions of R. Because for the highest vibrational levels the nuclear wave functions are spread out and contributions from larger internuclear distances are non-negligible, the functions $\mathcal{U}(R)$, $\mathcal{V}(R)$, and $\mathcal{W}(R)$ were represented by their asymptotic forms: $\mathcal{U}(R) = u_0 + u_6/R^6 + u_8/R^8$, $\mathcal{V}(R) = v_6/R^6 + v_8/R^8$, and $\mathcal{W}(R) = w_0 + w_6/R^6 + w_8/R^8$, subject to $u_0 = w_0 = -(m_{\rm e}/M)^2$ restriction (in atomic units). The remaining, free parameters u_i, v_i, and w_i were determined by fitting the above functions to calculated points in the range of $(5.5 : 10)$ bohrs.

IV. RESULTS AND DISCUSSION

Results of the computations are collected in Tables I and II, where the nonadiabatic corrections $\delta E_{\rm na}$ obtained for all purely vibrational levels of H_2 and D_2 are listed and compared with the existing data. We observe small deviation from results of Wolniewicz [7] for both H_2 and D_2. Apart from the highest vibrational levels, the deviation is about -0.013 cm^{-1} for H_2 and -0.003 cm^{-1} for D_2. It can be attributed to the slightly different perturbation approach of Wolniewicz in Ref. [7]. Since, the fully nonadiabatic calculation by Stanke *et al.* in Ref. [14] is in remarkable agreement with results of Ref. [7] for H_2, the most probable explanation of this deviation is the neglect of the probably significant second term in the higher correction of Eq. (24). We note, that with the variational approach the obtained results are upper bounds to the nonadiabatic energies and the estimate of uncertainty is not necessarily simple, as shows the comparison with the former calculations by Bubin and Adamowicz in [12]. While we cannot judge here which result is more accurate, we observe, after inclusion of relativistic and QED corrections [30], a very good agreement of our final values with the precise experimental result for the ground state dissociation energy in both, H_2, see Table III, and D_2 molecule in Table IV.

A. Simplified approach

In the case of the lowest rovibrational states, the nonadiabatic correction of Eq. (26) can be significantly simplified. Since the derivatives of $\phi_{\rm el}$ are here much smaller than that of χ, the contribution from terms proportional to $\chi\,\chi'$ and χ^2 can be neglected. Moreover, the nuclear wave function χ is strongly localized around R_0, the av-

TABLE I: Comparison of the nonadiabatic corrections to the adiabatic energy levels of H_2, computed using Eq. (22), with results of Wolniewicz [7] as well as of Stanke *et al.* [14] (in cm^{-1}). Relative uncertainty of our results due to the neglect of higher order corrections is 0.36%. In the second column, our reference adiabatic energy E_a is given for all the vibrational levels.

			H_2			
v	E_a[au]	δE_{na}	[7]	Diff.	[14]	Diff.
0	−1.164 022 757	−0.511	−0.4988	−0.012	−0.499	−0.012
1	−1.145 059 286	−1.347	−1.3350	−0.012	−1.336	−0.012
2	−1.127 168 403	−2.104	−2.0913	−0.013	−2.092	−0.012
3	−1.110 327 841	−2.785	−2.7728	−0.013	−2.773	−0.012
4	−1.094 523 757	−3.395	−3.3824	−0.013	−3.383	−0.012
5	−1.079 751 576	−3.934	−3.9208	−0.013	−3.921	−0.013
6	−1.066 017 251	−4.398	−4.3847	−0.013	−4.385	−0.013
7	−1.053 339 044	−4.779	−4.7654	−0.013	−4.765	−0.013
8	−1.041 750 041	−5.059	−5.0459	−0.013	−5.046	−0.013
9	−1.031 301 694	−5.210	−5.1980	−0.012	−5.197	−0.013
10	−1.022 068 803	−5.187	−5.1772	−0.010	−5.175	−0.012
11	−1.014 156 653	−4.926	−4.9176	−0.008	−4.915	−0.010
12	−1.007 711 399	−4.333	−4.3270	−0.006	−4.324	−0.009
13	−1.002 935 436	−3.287	−3.2844	−0.002	−3.281	−0.006
14	−1.000 108 439	−1.646	−1.6482	0.002	−1.645	−0.001

TABLE II: Comparison of the nonadiabatic corrections to the adiabatic energy levels of D_2, computed using Eq. (22), with results of Wolniewicz [7] (in cm^{-1}). Relative uncertainty of our results due to the neglect of higher order corrections is 0.21%. In the second column, our reference adiabatic energy E_a is given for all the vibrational levels.

		D_2		
v	E_a[au]	δE_{na}	[7]	Diff.
0	−1.1671680230	−0.176	−0.1725	−0.003
1	−1.1535267225	−0.480	−0.4769	−0.003
2	−1.1404282296	−0.764	−0.7605	−0.003
3	−1.1278630079	−1.028	−1.0246	−0.003
4	−1.1158235203	−1.273	−1.2698	−0.003
5	−1.1043043280	−1.500	−1.4970	−0.003
6	−1.0933022295	−1.710	−1.7062	−0.004
7	−1.0828164445	−1.901	−1.8977	−0.004
8	−1.0728488533	−2.075	−2.0709	−0.004
9	−1.0634043039	−2.228	−2.2246	−0.004
10	−1.0544910050	−2.361	−2.3568	−0.004
11	−1.0461210239	−2.468	−2.4646	−0.004
12	−1.0383109190	−2.547	−2.5434	−0.004
13	−1.0310825465	−2.590	−2.5869	−0.004
14	−1.0244640945	−2.590	−2.5868	−0.003
15	−1.0184914179	−2.534	−2.5316	−0.003
16	−1.0132097815	−2.410	−2.4071	−0.002
17	−1.0086761569	−2.197	−2.1951	−0.002
18	−1.0049622689	−1.875	−1.8742	−0.001
19	−1.0021585658	−1.420	−1.4196	0.000
20	−1.0003781627	−0.805	−0.8055	0.000
21	−0.9997348811	−0.079	−0.0860	0.007

erage distance between nuclei, so the electronic matrix element can be taken just at R_0. The resulting simplified form of nonadiabatic correction to energy for low lying vibrational states is

$$\delta E_{\rm na} \approx \frac{1}{\mu_{\rm n}^2}\,\langle\chi'|\chi'\rangle\Big\langle\phi_{\rm el}\Big|\vec n\cdot\vec\nabla_R(H_{\rm el}) \frac{1}{\big[(E_{\rm el}-H_{\rm el})'\big]^3}\,\vec n\cdot\vec\nabla_R(H_{\rm el})\Big|\phi_{\rm el}\Big\rangle_{R_0}, \tag{38}$$

where

$$\vec n\cdot\vec\nabla_R(H_{\rm el}) = \frac{\vec n}{2}\cdot\left(-\frac{\vec r_{1A}}{r_{1A}^3}+\frac{\vec r_{1B}}{r_{1B}^3}-\frac{\vec r_{2A}}{r_{2A}^3}+\frac{\vec r_{2B}}{r_{2B}^3}\right)-\frac{1}{R^2}\,, \tag{39}$$

and $\vec n = \vec R/R$. The corresponding result, obtained for the ground vibrational state of H_2, -0.453 cm^{-1} differs from the accurate one (with the asymptotics subtracted out) -0.4458 cm^{-1} only by 1.5%. Moreover, this approximation can be applied also to heavier molecules, where its accuracy should be even higher. Indeed, the simplified calculations for the ground state of D_2 yield -0.161 cm^{-1} which differs from the accurate result -0.1594 cm^{-1} by as few as 1.0%.

V. SUMMARY

We have formulated the perturbative approach to the calculation of nonadiabatic effects. The leading order nonadiabatic correction to the energy, given by Eq. (22), is conveniently rewritten in terms of three state independent pseudopotentials introduced in Eq. (27), and calculated in Sec. III for all vibrational levels of H_2 and D_2. Our numerical results are slightly below, and thus in small disagreement with calculations by Wolniewicz [7] and by Stanke *et al.* [14].

Several important advantages of the approach presented here are worth emphasizing. The first one is the possibility to systematically derive higher order nonadiabatic corrections and to control its accuracy. Secondly, the result for the leading correction of Eq. (22) can conveniently be applied to more complex molecules. Thirdly, for the lowest vibrational states one can apply the approximate Eq. (38), which is accurate to about 99%, even for very light molecules such as H_2 and D_2. Finally, the nonadiabatic corrections to the wave function Eq. (18) significantly contribute to radiative transition rates, such as ortho-para transition in H_2 [17], or make the transition possible, as in the case of rovibrational electric dipole transitions in HD.

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TABLE III: Dissociation energy of H_2 $v=0$ state (in cm^{-1}). Total uncertainty is due to higher order nonadiabatic corrections (0.0019 cm^{-1}) and approximate α^4 QED correction (0.0008 cm^{-1}).

	Correction	Subtotal
BO		36112.593
+ ad. corr. + asymp. (II E)		36118.364
+ nonad. corr., Eq. (22)	0.5109	36118.875
+ asymp. (II E)	−0.0651	36118.810[a]
+ α^2 relat. corr. [30]	−0.5178	36118.292
+ α^3 QED corr. [30]	−0.2359	36118.056[b]
+ α^4 QED corr. [30]	−0.0017	36118.054
uncertainty	±0.0027	36118.054(3)
Experiment [31]		36118.062(10)
difference		0.008(13)

[a] Bubin and Adamowicz [12]: 36118.798
[b] Wolniewicz [7] (includes approximate QED corr.): 36118.069

TABLE IV: Dissociation energy of D_2 $v=0$ state (in cm^{-1}). Total uncertainty is due to higher order nonadiabatic corrections (0.0004 cm^{-1}) and approximate α^4 QED correction (0.0008 cm^{-1}).

	Correction	Subtotal
BO		36746.162
+ adiab. corr. + asymp. (II E)		36748.935
+ nonad. corr., Eq. (22)	0.1757	36749.111
+ asymp. (II E)	−0.0163	36749.094[a]
+ α^2 relat. corr. [30]	−0.5178	36748.577
+ α^3 QED corr. [30]	−0.2359	36748.341[b]
+ α^4 QED corr. [30]	−0.0017	36748.339
uncertainty	±0.0012	36748.339(1)
Experiment [31]		36748.343(10)
difference		0.004(11)

[a] Bubin and Adamowicz [12]: 36749.085
[b] Wolniewicz [7] (includes approximate QED corr.): 36748.364

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