Nonadiabatic corrections to rovibrational levels of H_2

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The leading nonadiabatic corrections to rovibrational levels of a diatomic molecule are expressed in terms of three functions of internuclear distance: corrections to the adiabatic potential, the effective nuclear mass, and the effective moment of inertia. The resulting radial Schrödinger equation for nuclear motion is solved numerically yielding accurate nonadiabatic energies for all rovibrational levels of H_2 molecule. Results for states with $J \leq 10$ are in excellent agreement with previous calculations by Wolniewicz, and for states with $J > 10$ are new.

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I. INTRODUCTION

In the fully nonadiabatic approach the total nonrelativistic energy of a molecular state is obtained by solving the Schrödinger equation with kinetic energy of electrons and of nuclei on the same footing. This approach has been applied to vibrational states of several small diatomic molecules [1–5]. Much more commonly though, the total energy of a molecular state is obtained in a two-step procedure based on the Born-Oppenheimer (BO) approximation [6, 7] in which a separation of electronic and nuclear motion is assumed. Namely, in the first step, the electronic Schrödinger equation with the clamped nuclei Hamiltonian is solved for different nuclear configurations yielding the electronic energy as a function of the nuclear coordinates. This function, called the potential energy surface (PES), serves as a potential for the motion of nuclei in the nuclear Schrödinger equation. Solving this equation in the second step yields the total rovibronic energy of the system.

The accuracy of theoretical predictions for molecular states, limited due to the BO approximation, can be increased by including the adiabatic, relativistic, and radiative corrections without renouncing the notion of PES. Further increase in the accuracy requires the nonadiabatic effects to be taken into account. A desirable way of inclusion of these effects is in terms of a geometry dependent function, which can be added to PES in the same manner as all the other corrections. On one hand, the nuclear Schrödinger equation, when solved with such a potential, gives the molecular energy levels with spectroscopic precision. On the other, the notion of the PES is preserved with all its advantages.

Several, more or less successful attempts to construct such a nonadiabatic correction function for a diatomic molecule can be found in literature [8–12]. Bunker and Moss have derived [9], in the second order of the perturbative expansion, an effective nuclear Hamiltonian for the ground electronic state of diatomic molecules, in terms of the nonadiabatic potential, vibrational and rotational masses. Assuming constant vibrational and rotational masses and neglecting the nonadiabatic potential, they obtained values of these effective masses for H_2 and D_2 by fitting to the experimental data. Later Schwenke in [13] used the Bunker and Moss [9, 14] effective Hamiltonian to perform ab initio calculations of nonadiabatic corrections for H_2 and H_2O. His results for purely vibrational spectrum of H_2 differ from that of Wolniewicz [15] by about 20% due to the inaccurate numerical representation of the wave function and, what we demonstrate in this work, due to the approximate second order nonadiabatic potential of Bunker and Moss [9]. The accuracy of Schwenke calculations [13] for H_2O is probably not higher, but clearly demonstrates wide applicability of the perturbative approach. Very recently Kutzelnigg *et al.* [11, 12] performed simplified calculations of the nonadiabatic correction and both effective masses as functions of the internuclear distance in H_2^+ and H_2. In our recent work [16] we have introduced nonadiabatic perturbative theory and derived formulae for the leading nonadiabatic corrections to energies and wave functions. The formula for the nonadiabatic energy from that work, although apparently different, is in fact equivalent to that of Bunker and Moss [9]. Our results for rotationless vibrational states have been obtained as the expectation value of nonadiabatic corrections with the adiabatic wave function. Although numerically accurate, due to the neglected third order nonadiabatic corrections [see Eq. (47)], our results differed by about 2% from the previous calculations by Wolniewicz [15] and by Stanke *et al.* [17].

In this paper, the nonadiabatic perturbation theory has been extended in two directions. Firstly, we generalize the previous derivation to rotational states. Secondly, we include the previously missing third order correction, which has proved significant. Moreover, we present a rigorous formulation of the nonadiabatic perturbative

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theory and include the numerical example of the H_2 molecule. This can be extended to any diatomic molecule and potentially to an arbitrarily large molecule. We derive formulae valid to all orders, present the leading corrections of order $\mathcal{O}(\mu_n^{-2})$, and express them in terms of the nonadiabatic correction to the potential and the effective R-dependent nuclear mass and the moment of inertia. These three functions enter the nuclear Schrödinger equation, which can be solved numerically for an arbitrary energy level. As a test of the presented perturbative theory, we perform calculations of all 301 rovibrational levels of H_2 molecule. We find an excellent 0.1% agreement with the accurate nonadiabatic corrections for states with the angular momentum $J \leq 10$, which were obtained by Wolniewicz in [15], and present for the first time results for states with $J > 10$.

II. THE ADIABATIC APPROXIMATION

The total wave function ϕ is the solution of the stationary Schrödinger equation

$$[H - E]\,|\phi\rangle = 0\,, \tag{1}$$

with the Hamiltonian

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

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

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

nuclear masses are, by definition, set to infinity, and the potential V includes all the Coulomb interactions with fixed positions $\vec{R}_A$ of nuclei. The nuclear Hamiltonian involves kinetic energies of all nuclei

$$H_{\rm n} = -\sum_A \frac{\nabla_{R_A}^2}{2\,M_A}\,. \tag{4}$$

The separation of center of mass motion and the choice of the reference frame depends on the particular molecule. For example, for a diatomic molecule in the space fixed reference frame attached to the geometrical center of two nuclei $H_{\rm n}$ takes the form

$$H_{\rm n} = -\frac{\nabla_R^2}{2\,\mu_{\rm n}} - \frac{\nabla_{\rm el}^2}{2\,\mu_{\rm n}} - \left(\frac{1}{M_B} - \frac{1}{M_A}\right)\vec{\nabla}_R\cdot\vec{\nabla}_{\rm el}\,, \tag{5}$$

where

$$\vec{\nabla}_{\rm el} \equiv \frac{1}{2}\sum_a \vec{\nabla}_a\,, \tag{6}$$

$\vec{R} = \vec{R}_{AB} = \vec{R}_A - \vec{R}_B$, and $1/\mu_{\rm n} = 1/M_A + 1/M_B$ is the nuclear reduced mass. The last term in Eq. (5) vanishes for homonuclear diatomic molecules.

In the adiabatic approximation the total wave function of an arbitrary molecule

$$\phi_{\rm a}(\vec{r},\vec{R}) = \phi_{\rm el}(\vec{r})\;\chi(\vec{R}) \tag{7}$$

is represented as a product of the electronic wave function $\phi_{\rm el}$ and the nuclear wave function χ. We note, that $\phi_{\rm el}$ depends implicitly on the nuclear coordinates $\vec{R}$. The electronic wave function obeys the clamped nuclei electronic Schrödinger equation

$$\left[H_{\rm el} - \mathcal{E}_{\rm el}(\vec{R})\right]|\phi_{\rm el}\rangle = 0, \tag{8}$$

while the nuclear wave function is a solution to the Schrödinger equation in the effective potential generated by electrons

$$\left[H_{\rm n} + \mathcal{E}_{\rm a}(\vec{R}) + \mathcal{E}_{\rm el}(\vec{R}) - E_{\rm a}\right]|\chi\rangle = 0\,, \tag{9}$$

where

$$\mathcal{E}_{\rm a}(\vec{R}) = \left\langle\phi_{\rm el}|H_{\rm n}|\phi_{\rm el}\right\rangle_{\rm el}\,. \tag{10}$$

For the diatomic molecule the nuclear radial equation reads

$$\begin{aligned}\Bigg[-\frac{1}{2\,R^2}\frac{\partial}{\partial R}\frac{R^2}{\mu_{\rm n}}\frac{\partial}{\partial R} + \frac{J\,(J+1)}{2\,\mu_{\rm n}\,R^2}\\ +\mathcal{E}_{\rm a}(R) + \mathcal{E}_{\rm el}(R) - E_{\rm a}\Bigg]\chi_J(R) \;=\; 0\,,\end{aligned} \tag{11}$$

where J is the rotational quantum number.

III. PERTURBATIVE FORMALISM

The total wave function

$$\phi = \phi_{\rm a} + \delta\phi_{\rm na} = \phi_{\rm el}\,\chi + \delta\phi_{\rm na} \tag{12}$$

is the sum of the adiabatic solution and a nonadiabatic correction. The nonadiabatic correction $\delta\phi_{\rm na}$ is decomposed into two parts

$$\delta\phi_{\rm na} = \phi_{\rm el}\,\delta\chi + \delta'\phi_{\rm na}\,, \tag{13}$$

which obey the following orthogonality conditions

$$\langle\delta'\phi_{\rm na}|\phi_{\rm el}\rangle_{\rm el} \;=\; 0\,, \tag{14}$$

$$\langle\delta\chi|\chi\rangle \;=\; 0\,. \tag{15}$$

The last equation means that normalization of ϕ is of the form

$$\langle\phi_{\rm el}\,\chi|\phi\rangle = 1\,. \tag{16}$$

The total energy

$$E = E_{\rm a} + \delta E_{\rm na} \tag{17}$$

is the sum of the adiabatic energy $E_{\rm a}$ and the nonadiabatic correction $\delta E_{\rm na}$. Using above definitions we proceed with the derivation of perturbative formulae.

The starting point is the Schrödinger equation (1) with the Hamiltonian H, the wave function ϕ, and the energy E decomposed into adiabatic and nonadiabatic parts

$$\big[(H_{\rm el}-\mathcal{E}_{\rm el})+(\mathcal{E}_{\rm el}+H_{\rm n}-E_{\rm a}-\delta E_{\rm na})\big]|\phi_{\rm el}\,(\chi+\delta\chi)+\delta'\phi_{\rm na}\rangle = 0. \tag{18}$$

One rewrites this equation to the form

$$\begin{aligned}(\mathcal{E}_{\rm el}-H_{\rm el})|\delta'\phi_{\rm na}\rangle &= (\mathcal{E}_{\rm el}+H_{\rm n}-E_{\rm a}-\delta E_{\rm na})\\ &\quad |\phi_{\rm el}\,(\chi+\delta\chi)+\delta'\phi_{\rm na}\rangle\end{aligned} \tag{19}$$

and, since $\delta'\phi_{\rm na}$ is orthogonal to $\phi_{\rm el}$, Eq. (14), the formal solution

$$\begin{aligned}|\delta'\phi_{\rm na}\rangle &= \frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\big[H_{\rm n}|\phi_{\rm el}\,(\chi+\delta\chi)\rangle\\ &\quad +(\mathcal{E}_{\rm el}+H_{\rm n}-E_{\rm a}-\delta E_{\rm na})|\delta'\phi_{\rm na}\rangle\big],\end{aligned} \tag{20}$$

is obtained, where the prime in the denominator denotes subtraction of the reference state from the Hamiltonian inversion. When $\delta\chi$ and $\delta'\phi_{\rm na}$ on the right hand side are neglected, Eq. (20) becomes the leading nonadiabatic correction to the wave function. In the next step one takes Eq. (18) and multiplies it from the left by $\langle\phi_{\rm el}|$

$$\langle\phi_{\rm el}|\mathcal{E}_{\rm el}+H_{\rm n}-E_{\rm a}-\delta E_{\rm na}|\phi_{\rm el}\,(\chi+\delta\chi)+\delta'\phi_{\rm na}\rangle_{\rm el} = 0. \tag{21}$$

Since χ satisfies Eq. (9) the above can be simplified to

$$\begin{aligned}&(\mathcal{E}_{\rm el}+\mathcal{E}_{\rm a}+H_{\rm n}-E_{\rm a})|\delta\chi\rangle\\ &= \delta E_{\rm na}|\chi+\delta\chi\rangle - \langle\phi_{\rm el}|H_{\rm n}|\delta'\phi_{\rm na}\rangle_{\rm el}\end{aligned} \tag{22}$$

and due to Eq. (15) the solution is

$$\begin{aligned}|\delta\chi\rangle &= \frac{1}{(E_{\rm a}-\mathcal{E}_{\rm el}-\mathcal{E}_{\rm a}-H_{\rm n})'}\\ &\quad \big(\langle\phi_{\rm el}|H_{\rm n}|\delta'\phi_{\rm na}\rangle_{\rm el}-\delta E_{\rm na}|\chi+\delta\chi\rangle\big).\end{aligned} \tag{23}$$

In the last step, one takes Eq. (22), multiplies it from the left by $\langle\chi|$, and obtains

$$\delta E_{\rm na} = \langle\phi_{\rm el}\,\chi|H_{\rm n}|\delta'\phi_{\rm na}\rangle. \tag{24}$$

The set of recursive equations (20), (23), and (24) forms the perturbative expansion of the wave functions $\delta'\phi_{\rm na}$, $\delta\chi$ and energy $\delta E_{\rm na}$. For example, starting from (24) one gets

$$\begin{aligned}\delta E_{\rm na} &= \langle\phi_{\rm el}\,\chi|H_{\rm n}\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\Big[H_{\rm n}|\phi_{\rm el}\,(\chi+\delta\chi)\rangle\\ &\quad +(\mathcal{E}_{\rm el}+H_{\rm n}-E_{\rm a}-\delta E_{\rm na})|\delta'\phi_{\rm na}\rangle\Big],\end{aligned} \tag{25}$$

which is the sum of the leading, Eq. (28), and the higher order nonadiabatic correction, Eq. (44). This perturbative expansion in general assumes that $\mathcal{E}_{\rm el}+H_{\rm n}-E_{\rm a}$ is small with respect to the electronic excitation energy. It is not always true, especially for rovibrational levels close to the dissociation threshold. In spite of this fact, we claim that each power of $\mathcal{E}_{\rm el}+H_{\rm n}-E_{\rm a}$ in these particular matrix elements is at least of the order $\mathcal{O}(\sqrt{m_{\rm e}/\mu_{\rm n}})$, which we demonstrate in next sections for the leading terms $\delta^{(2)}E_{\rm na}$ and $\delta^{(3)}E_{\rm na}$ of the nonadiabatic perturbative expansion.

A. Second-order nonadiabatic corrections

In the leading order of perturbative treatment of nonadiabatic effects one has

$$|\delta'\phi_{\rm na}\rangle = \frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,H_{\rm n}\,|\phi_{\rm el}\,\chi\rangle, \tag{26}$$

$$|\delta\chi\rangle = \frac{1}{(E_{\rm a}-\mathcal{E}_{\rm el}-\mathcal{E}_{\rm a}-H_{\rm n})'}\big\langle\phi_{\rm el}\big|H_{\rm n}\big|\delta'\phi_{\rm na}\big\rangle_{\rm el}, \tag{27}$$

$$\delta^{(2)}E_{\rm na} = \Big\langle\phi_{\rm el}\,\chi\Big|H_{\rm n}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,H_{\rm n}\Big|\phi_{\rm el}\,\chi\Big\rangle. \tag{28}$$

The general formula (28), following [16], can be readily rearranged to a more practical form. From now on we consider the homonuclear diatomic two-electron molecule and separate out electronic matrix elements from the nuclear ones

$$\begin{aligned}\delta^{(2)}E_{\rm na} &= \int d^3R\,\Big[\chi^\star\,\chi\Big\langle H_{\rm n}\,\phi_{\rm el}\Big|\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\Big|H_{\rm n}\,\phi_{\rm el}\Big\rangle_{\rm el}\\ &\quad -\frac{\chi^\star\,\nabla^i_R\chi}{\mu_{\rm n}}\Big\langle H_{\rm n}\,\phi_{\rm el}\Big|\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\Big|\nabla^i_R\phi_{\rm el}\Big\rangle_{\rm el}\\ &\quad -\frac{\nabla^i_R\chi^\star\,\chi}{\mu_{\rm n}}\Big\langle \nabla^i_R\,\phi_{\rm el}\Big|\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\Big|H_{\rm n}\,\phi_{\rm el}\Big\rangle_{\rm el}\\ &\quad +\frac{\nabla^i_R\chi^\star\,\nabla^j_R\chi}{\mu_{\rm n}^2}\Big\langle \nabla^i_R\phi_{\rm el}\Big|\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\Big|\nabla^j_R\phi_{\rm el}\Big\rangle_{\rm el}\Big]\end{aligned} \tag{29}$$

$$\begin{aligned}&\equiv \int d^3R\,\Big[\chi^\star\,\chi\,\mathcal{U}(R)-\nabla^i_R\left[\chi^\star\,\chi\right]\mathcal{V}^i(R)\\ &\qquad +\nabla^i_R\,\chi^\star\,\nabla^j_R\,\chi\,\mathcal{W}^{ij}(R)\Big],\end{aligned} \tag{30}$$

where the last equation is the definition of potentials $\mathcal{U},\mathcal{V}^i$ and $\mathcal{W}^{ij}$. For the Σ electronic state $\phi_{\rm el}$

$$\mathcal{V}^i = n^i\,\mathcal{V}, \tag{31}$$

$$\mathcal{W}^{ij} = n^i\,n^j\,\mathcal{W}_\parallel+(\delta^{ij}-n^i\,n^j)\,\mathcal{W}_\perp, \tag{32}$$

where $\vec{n}=\vec{R}/R$, hence

$$\begin{aligned}\delta^{(2)}E_{\rm na} &= \int d^3R\,\Big\{\chi^\star\chi\,\delta\mathcal{E}_{\rm na}(R)\\ &\quad +n^i\,n^j\,\nabla^i_R\,\chi^\star\,\nabla^j_R\,\chi\,\mathcal{W}_\parallel(R)\\ &\quad +(\delta^{ij}-n^i\,n^j)\,\nabla^i_R\,\chi^\star\,\nabla^j_R\,\chi\,\mathcal{W}_\perp(R)\Big\}.\end{aligned} \tag{33}$$

The function

$$\delta\mathcal{E}_{\rm na}(R) = \mathcal{U}(R) + \left(\frac{2}{R} + \frac{\partial}{\partial R}\right)\mathcal{V}(R) \tag{34}$$

is the nonadiabatic correction to the adiabatic energy curve $\mathcal{E}_{\rm el}(R) + \mathcal{E}_{\rm a}(R)$ and pseudopotentials $\mathcal{U}, \mathcal{V}, \mathcal{W}$ are:

$$\mathcal{U}(R) = \left\langle H_{\rm n}\,\phi_{\rm el}\middle|\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\middle|H_{\rm n}\,\phi_{\rm el}\right\rangle_{\rm el}, \tag{35}$$

$$\mathcal{V}(R) = \frac{1}{\mu_{\rm n}}\left\langle H_{\rm n}\,\phi_{\rm el}\middle|\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\middle|\vec{n}\cdot\vec{\nabla}_R\phi_{\rm el}\right\rangle_{\rm el}, \tag{36}$$

$$\mathcal{W}_{\parallel}(R) = \frac{1}{\mu_{\rm n}^2}\left\langle \vec{n}\cdot\vec{\nabla}_R\phi_{\rm el}\middle|\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\middle|\vec{n}\cdot\vec{\nabla}_R\phi_{\rm el}\right\rangle_{\rm el}, \tag{37}$$

$$\mathcal{W}_{\perp}(R) = \frac{1}{\mu_{\rm n}^2}\,\frac{(\delta^{ij} - n^i\,n^j)}{2} \times\left\langle \nabla^i_R\phi_{\rm el}\middle|\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\middle|\nabla^j_R\phi_{\rm el}\right\rangle_{\rm el}. \tag{38}$$

In order to simplify the nonadiabatic correction of Eq. (33), one notes that the nuclear wave function χ has a definite angular momentum

$$\chi = \chi_{Jm}(\vec{R}) = \chi_J(R)\,Y_{Jm}(\vec{n}), \tag{39}$$

where Y_{Jm} are spherical harmonics, thus the nonadiabatic correction can be transformed to the form

$$\delta^{(2)}E_{\rm na} = \int R^2\,dR\left\{{\chi'_J}^2\,\mathcal{W}_{\parallel}(R) + \chi_J^2\left[\delta\mathcal{E}_{\rm na}(R) + \frac{J\,(J+1)}{R^2}\,\mathcal{W}_{\perp}(R)\right]\right\}. \tag{40}$$

Let us note, that Eq. (40) can also be expressed in terms of an expectation value of an effective nonadiabatic Hamiltonian $\delta H_{\rm na}$

$$\delta^{(2)}E_{\rm na} = \langle\chi_J|\delta H_{\rm na}|\chi_J\rangle\,, \tag{41}$$

where

$$\delta H_{\rm na} = -\frac{1}{R^2}\,\frac{\partial}{\partial R}\,R^2\,\mathcal{W}_{\parallel}(R)\,\frac{\partial}{\partial R} + \frac{J\,(J+1)}{R^2}\,\mathcal{W}_{\perp}(R) + \delta\mathcal{E}_{\rm na}(R). \tag{42}$$

Now, the nonadiabatic correction $\delta\chi$ of Eq. (27) can be conveniently rewritten in terms of $\delta H_{\rm na}$

$$|\delta\chi_J\rangle = \frac{1}{\big(E_{\rm a} - \mathcal{E}_{\rm el} - \mathcal{E}_{\rm a} - H_{\rm n}\big)'}\,\delta H_{\rm na}|\chi_J\rangle\,, \tag{43}$$

where it is understood, that the derivatives with respect to electronic variables of the function χ do vanish.

B. Third-order nonadiabatic correction

The third order nonadiabatic correction of Eq. (25) is

$$\delta^{(3)}E_{\rm na} = \left\langle\phi_{\rm el}\,\chi\middle|H_{\rm n}\,\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\,(H_{\rm n} + \mathcal{E}_{\rm el} - E_{\rm a}) \times\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\,H_{\rm n}\middle|\phi_{\rm el}\,\chi\right\rangle + \left\langle\phi_{\rm el}\,\chi\middle|H_{\rm n}\,\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\,H_{\rm n}\middle|\phi_{\rm el}\,\delta\chi\right\rangle, \tag{44}$$

where $\delta\chi$ is given in Eq. (27). Let us split this sum into two parts accordingly

$$\delta^{(3)}E_{\rm na} = \delta^{(3)}E'_{\rm na} + \delta^{(3)}E''_{\rm na}\,. \tag{45}$$

While the first part $\delta^{(3)}E'_{\rm na}$ involves many terms which are negligible, since they include the third power of μ_n in the denominator, the dominating $\mathcal{O}(\mu_n^{-2})$ term is

$$\delta^{(3)}E'_{\rm na} = \frac{1}{\mu_{\rm n}^2}\left\langle\nabla^i_R\phi_{\rm el}\,\nabla^i_R\chi\middle|\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}(H_{\rm n} + \mathcal{E}_{\rm el} - E_{\rm a}) \times\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\middle|\nabla^j_R\phi_{\rm el}\,\nabla^j_R\chi\right\rangle + \mathcal{O}(\mu_n^{-3}) \tag{46}$$

$$\approx -\int d^3R\,\vec{n}\cdot\vec{\nabla}_R(\chi^*\,\chi)\,\delta\mathcal{V}(R) + \mathcal{O}(\mu_n^{-3})\,, \tag{47}$$

where

$$\delta\mathcal{V}(R) = \frac{1}{2\,\mu_{\rm n}^2}\,\frac{\partial\mathcal{E}_{\rm el}}{\partial R} \times\left\langle\vec{n}\cdot\vec{\nabla}_R\phi_{\rm el}\middle|\frac{1}{[(\mathcal{E}_{\rm el} - H_{\rm el})']^2}\middle|\vec{n}\cdot\vec{\nabla}_R\phi_{\rm el}\right\rangle_{\rm el}, \tag{48}$$

and this correction is included into $\delta\mathcal{E}_{\rm na}$ of Eq. (34), which becomes now

$$\delta\mathcal{E}_{\rm na}(R) = \mathcal{U}(R) + \left(\frac{2}{R} + \frac{\partial}{\partial R}\right)[\mathcal{V}(R) + \delta\mathcal{V}(R)]\,. \tag{49}$$

The second term $\delta^{(3)}E''_{\rm na}$ can be obtained from the nonperturbative solution of the nuclear equation with the nonadiabatic Hamiltonian $\delta H_{\rm na}$ from Eq. (42). Namely, for the states with the rotational quantum number J, $\delta^{(3)}E''_{\rm na}$ takes the form

$$\delta^{(3)}E''_{\rm na} = \langle\chi_J|\delta H_{\rm na}|\delta\chi_J\rangle = \left\langle\chi_J\middle|\delta H_{\rm na}\,\frac{1}{\big(E_{\rm a} - \mathcal{E}_{\rm el} - \mathcal{E}_{\rm a} - H_{\rm n}\big)'}\,\delta H_{\rm na}\middle|\chi_J\right\rangle, \tag{50}$$

which is interpreted as a second order correction due to $\delta H_{\rm na}$.

C. Nuclear equation with effective potentials

Instead of calculating the second order correction Eq. (41) and the third order correction of Eq. (50), it is more appropriate to solve nonperturbatively the corresponding equation

$$\left[H_{\rm n} + \mathcal{E}_{\rm el}(R) + \mathcal{E}_{\rm a}(R) + \delta H_{\rm na}\right] \chi_J = E\, \chi_J\,, \tag{51}$$

where the total energy E is

$$E = E_{\rm a} + \delta^{(2)} E_{\rm na} + \delta^{(3)} E_{\rm na} + \ldots \tag{52}$$

and this is done in this work. Moreover, from comparison of subsequent terms of Eq. (42) with those of Eq. (11), one concludes that the first term can be interpreted as an R-dependent correction to the nuclear reduced mass $\mu_{\rm n}$,

$$\frac{1}{2\,\mu_{\|}(R)} \equiv \frac{1}{2\,\mu_{\rm n}} + \mathcal{W}_{\|}(R), \tag{53}$$

whereas the second term—as an R-dependent correction to the inverse of the moment of inertia $\mu_\perp(R)\,R^2$

$$\frac{1}{2\,\mu_\perp(R)} \equiv \frac{1}{2\,\mu_{\rm n}} + \mathcal{W}_\perp(R). \tag{54}$$

With these newly defined functions one can write the radial equation as

$$\left[-\frac{1}{2\,R^2}\frac{\partial}{\partial R}\frac{R^2}{\mu_{\|}(R)}\frac{\partial}{\partial R} + \frac{J\,(J+1)}{2\,\mu_\perp(R)R^2} + \mathcal{Y}(R)\right]\chi_J(R) = E\,\chi_J(R)\,, \tag{55}$$

where

$$\mathcal{Y}(R) = \mathcal{E}_{\rm el}(R) + \mathcal{E}_{\rm a}(R) + \delta\mathcal{E}_{\rm na}(R) \tag{56}$$

forms the effective nonadiabatic potential.

D. Asymptotics of the effective masses

The adiabatic correction $\mathcal{E}_{\rm a}(R)$, Eq. (10), and the nonadiabatic correction $\delta\mathcal{E}_{\rm na}(R)$, Eq. (34), do not vanish at large internuclear distances. For example, for the large atomic separation in the hydrogen molecule, $\mathcal{E}_{\rm a}(R)$ and $\delta\mathcal{E}_{\rm na}(R)$ are equal to $m_{\rm e}/m_{\rm p}$ and $-(m_{\rm e}/m_{\rm p})^2$, respectively, which corresponds to the first terms in the expansion of the atomic reduced mass $\mu = (1/m_{\rm p} + 1/m_{\rm e})^{-1}$ in the electron-nucleus mass ratio

$$1 - \frac{\mu}{m_{\rm e}} = \frac{m_{\rm e}/m_{\rm p}}{1 + m_{\rm e}/m_{\rm p}} = \frac{m_{\rm e}}{m_{\rm p}} - \left(\frac{m_{\rm e}}{m_{\rm p}}\right)^2 + \left(\frac{m_{\rm e}}{m_{\rm p}}\right)^3 - \ldots \tag{57}$$

Large R asymptotics of the pseudopotentials $\mathcal{W}_{\|}(R)$ and $\mathcal{W}_\perp(R)$ are equal to $-m_{\rm e}/m_{\rm p}^2$, which is related to the change in Eqs. (53) and (54) of the reduced nuclear mass $\mu_{\rm n}$ to the reduced mass $\mu_{\rm A} = (m_{\rm p} + m_{\rm e})/2$ of two hydrogen atoms :

$$\begin{aligned}\frac{1}{2\,\mu_{\|}(\infty)} &= \frac{1}{2\,\mu_\perp(\infty)} = \frac{1}{2\,\mu_{\rm A}} \\ &= \frac{1}{m_{\rm p} + m_{\rm e}} = \frac{1}{m_{\rm p}}\left(1 - \frac{m_{\rm e}}{m_{\rm p}} + \cdots\right).\end{aligned} \tag{58}$$

E. Evaluation of the wave function derivatives

The electronic matrix elements in Eq. (29) involve multiple differentiation of the electronic wave function with respect to the internuclear distance R, which is difficult to calculate directly. Therefore, following Ref. [16], we rewrite these terms to a more convenient form, where differentiation is taken of the Coulomb potential, namely

$$\vec\nabla_R\phi_{\rm el} = \frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\,\vec\nabla_R(V)\,\phi_{\rm el}\,, \tag{59}$$

$$\nabla_R^2\phi_{\rm el} = \frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\left\{\nabla_R^2(V)\,\phi_{\rm el} + 2\,\vec\nabla_R(V - \mathcal{E}_{\rm el})\,\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\,\vec\nabla_R(V)\,\phi_{\rm el}\right\} + \phi_{\rm el}\,\langle\phi_{\rm el}|\nabla_R^2|\phi_{\rm el}\rangle_{\rm el}, \tag{60}$$

The derivatives of the potential V

$$V = -\frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}}\,, \tag{61}$$

are the following

$$\vec\nabla_R(V) = \frac{1}{2}\left(-\frac{\vec r_{1A}}{r_{1A}^3} + \frac{\vec r_{1B}}{r_{1B}^3} - \frac{\vec r_{2A}}{r_{2A}^3} + \frac{\vec r_{2B}}{r_{2B}^3}\right) - \frac{\vec R}{R^3}\,, \tag{62}$$

$$\nabla_R^2(V) = \pi\left[\delta(\vec r_{1A}) + \delta(\vec r_{1B}) + \delta(\vec r_{2A}) + \delta(\vec r_{2B})\right] - 4\,\pi\,\delta(\vec R)\,, \tag{63}$$

and the matrix elements with these operators are readily evaluated. The presence of the Dirac delta operators in Eq. (60) may potentially decrease the accuracy of the evaluation of those quantities which contain $\nabla_R^2\phi_{\rm el}$. If we note that

$$\nabla_{\rm el}^2(V) = \pi\left[\delta(\vec r_{1A}) + \delta(\vec r_{1B}) + \delta(\vec r_{2A}) + \delta(\vec r_{2B})\right], \tag{64}$$

we can get rid of Dirac deltas by a simple rearrangement of the nuclear part of the Hamiltonian $H_{\rm n}$ to the form

$$H_{\rm n} = -\frac{1}{2\mu_n}\left(\nabla_R^2 - \nabla_{\rm el}^2\right) - \frac{1}{\mu_n}\,\nabla_{\rm el}^2\,. \tag{65}$$

The difference in parenthesis collects the terms of Eq. (63) and (64) which cancel out, up to the negligible $-4\,\pi\,\delta(\vec R)$ term, so that we can write it down as

$$\begin{aligned}&\left(\nabla_R^2 - \nabla_{\rm el}^2\right)\phi_{\rm el} = \\ &\frac{2}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\vec\nabla_R(V - \mathcal{E}_{\rm el})\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\vec\nabla_R(V)\,\phi_{\rm el} \\ &-\frac{2}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\,\vec\nabla_{\rm el}(V)\frac{1}{\mathcal{E}_{\rm el} - H_{\rm el}}\vec\nabla_{\rm el}(V)\,\phi_{\rm el} + \lambda\phi_{\rm el}\end{aligned} \tag{66}$$

with some constant λ. In this way the Dirac delta terms are eliminated at the expense of employing additional basis sets for evaluation of the last resolvent in Eq. (66).

IV. NUMERICAL CALCULATIONS

In order to form the radial nonadiabatic equation (55), apart from the clamped nuclei energy $\mathcal{E}_{\rm el}(R)$ and the adiabatic correction $\mathcal{E}_{\rm a}(R)$, it is necessary to know the pseudopotentials $\mathcal{U}(R), \mathcal{V}(R) + \delta\mathcal{V}(R), \mathcal{W}_{\parallel}(R)$, and $\mathcal{W}_{\perp}(R)$. The evaluation of these functions is the main numerical task described here. Calculations were performed at 80 points including long and very short internuclear distances R. At each point several electronic wave functions of different symmetry were generated. All these functions were represented as linear expansions of properly symmetrized two-electron basis functions. The basis functions were taken in the form of exponentially correlated Gaussians (ECG)

$$\psi_k(\vec{r}_1, \vec{r}_2) = (1 + \hat{P}_{12})(1 \pm \imath)\, \Xi_k \times \exp\left[-\sum_{i,j=1}^{2} A_{ij,k}(\vec{r}_i - \vec{s}_{i,k})(\vec{r}_j - \vec{s}_{j,k})\right], \tag{67}$$

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

Six different basis sets have been prepared to represent the variety of the electronic wave functions. To ensure high accuracy of the potentials, the basis sets have been variationally optimized with respect to pertinent goal functions according to the specification in Table I.

TABLE I: Goal functions used in optimization of the basis sets.

Label	Size	Symmetry	Goal function
A	600	Σ_g	$\mathcal{E}_{\rm el}$
B	600†	Σ_g	$\left\langle \nabla_R^{\parallel}(V) \frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'} \nabla_R^{\parallel}(V) \right\rangle$
C	1200	Π_g	$\left\langle \nabla_R^{\perp}(V) \frac{1}{\mathcal{E}_{\rm el} - H_{\rm el}} \nabla_R^{\perp}(V) \right\rangle$
D	600†	Σ_g	$\left\langle \nabla_{\rm el}^2 \frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'} \nabla_{\rm el}^2 \right\rangle$
E	600	Σ_u	$\left\langle \nabla_{\rm el}^{\parallel}(V) \frac{1}{\mathcal{E}_{\rm el} - H_{\rm el}} \nabla_{\rm el}^{\parallel}(V) \right\rangle$
F	600	Π_u	$\left\langle \nabla_{\rm el}^{\perp}(V) \frac{1}{\mathcal{E}_{\rm el} - H_{\rm el}} \nabla_{\rm el}^{\perp}(V) \right\rangle$

† Optimized along with the fixed basis A.

Particular goal functions have been chosen to reflect the contents of the expression the basis set is to be used for. The first basis (labeled A), composed of 600 ECG functions (67), was employed to expand the $X^1\Sigma_g^+$ electronic ground state wave function $\phi_{\rm el}$. Their nonlinear parameters were optimized variationally with respect to the clamped nuclei energy with the target accuracy of the order of a fraction of microhartree. The bases B, C, and D were intended for evaluation of the resolvents present in Eqs. (59) and (66). The two Σ_g^+ bases (B and D) were optimized in the presence of the basis A: the first 600 terms were taken from $\phi_{\rm el}$ wave function and their nonlinear parameters were kept fixed during the optimization, only the remaining 600 terms were actually optimized. This ensures that the internal wave function $\phi_{\rm el}$ is well represented at every step of optimization. Then, the subtraction of the reference state, denoted by the $'$ symbol within the resolvent, was achieved by orthogonalization of $\vec{\nabla}_R(V)\,|\phi_{\rm el}\rangle$ to the internal $|\phi_{\rm el}\rangle$. In the final calculations the three bases A, B, and D were assembled together to form a 1800-term Σ_g^+ basis applied not only to evaluate the pertinent resolvents but also to expand the external ground state function $\phi_{\rm el}$. The two ungerade bases (E and F) were employed to evaluate the resolvent and to form the components of the scalar product in the second term of the right hand side of Eq. (66).

The adiabatic potential of the nuclear Schrödinger equation (12) was composed of the clamped nuclei energy, $\mathcal{E}_{\rm el}(R)$, and the adiabatic correction $\mathcal{E}_{\rm a}(R)$. For $\mathcal{E}_{\rm el}(R)$ we used the analytic potential constructed by Łach [18] on the basis of the energy points computed by Cencek from 1200-term ECG wave functions [19] and Sims and Hagstrom from Hylleraas wave functions [20]. Their energy points where converged up to 13 significant digits. The adiabatic correction $\mathcal{E}_{\rm a}(R)$ was evaluated as an expectation value of the Hamiltonian $H_{\rm n}$, Eq. (10),

$$\mathcal{E}_{\rm a}(R) = -\frac{1}{2\mu_{\rm n}}\langle\phi_{\rm el}|\nabla_R^2 + \nabla_{\rm el}^2|\phi_{\rm el}\rangle_{\rm el}\,. \tag{68}$$

To avoid the cumbersome differentiation of the electronic wave function with respect to the internuclear distance we replaced the expectation value in the first term on the right hand side of Eq. (68) by an equivalent expression

$$\langle\phi_{\rm el}|\nabla_R^2|\phi_{\rm el}\rangle_{\rm el} = -\langle\vec{\nabla}_R\phi_{\rm el}|\vec{\nabla}_R\phi_{\rm el}\rangle_{\rm el}\,, \tag{69}$$

which, with the help of Eq. (59), can be further transformed to

$$\langle\phi_{\rm el}|\nabla_R^2|\phi_{\rm el}\rangle_{\rm el} = -\left\langle \vec{\nabla}_R(V)\frac{1}{\left[(\mathcal{E}_{\rm el} - H_{\rm el})'\right]^2}\vec{\nabla}_R(V)\right\rangle_{\rm el}. \tag{70}$$

The formula (70), when evaluated with the optimized bases A, B, and C, yields the adiabatic correction with an accuracy of at least 1 ppm. The adiabatic potential curve was then obtained by means of 10-point piecewise polynomial interpolation.

The electronic matrix elements $\mathcal{U}$, $\mathcal{V}+\delta\mathcal{V}$, $\mathcal{W}_{\parallel}$, $\mathcal{W}_{\perp}$ entering Eq. (33) were evaluated with the ECG basis sets described above, yielding smooth functions of R. Because for the highest vibrational levels the nuclear wave functions are spread out and the 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:

$$\begin{aligned}
\mathcal{U}(R) &\approx u_0 + u_6/R^6 + u_8/R^8, \\
\mathcal{V}(R) &\approx v_9/R^9 + v_{11}/R^{11}, \\
\delta\mathcal{V}(R) &\approx v_7/R^7 + v_0/R^9, \\
\mathcal{W}_{\|}(R) &\approx w_{\|0} + w_{\|12}/R^{12} + w_{\|14}/R^{14}, \\
\mathcal{W}_{\perp}(R) &\approx w_{\perp 0} + w_{\perp 12}/R^{12} + w_{\perp 14}/R^{14}, \quad (71)
\end{aligned}$$

subject to $u_0 = w_{\|0} = w_{\perp 0} = -(m_e/m_p)^2$ restriction (in atomic units). The remaining, free parameters u_i, v_i, and w_i were determined by fitting the above functions to the calculated points in the range of $\langle 6.0, 10.0\rangle$ bohrs. Because at distances $R > 6$, the numerical precision of the potentials $\mathcal{U}$ and $\mathcal{V}$ was not high enough, we used lower R-values for the extrapolation. At the origin $R = 0$ all the potentials are finite with $\mathcal{V} \sim R$, $\mathcal{W}_{\|} \sim R^2$, and $\mathcal{W}_{\perp} \sim R^2$. Numerical results for $\delta\mathcal{E}_{\rm na}$, $\mathcal{W}_{\|}$, and $\mathcal{W}_{\perp}$ are shown graphically in Fig. 1.

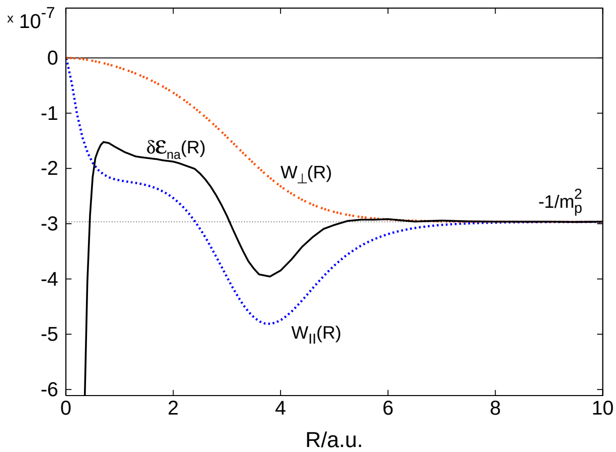

FIG. 1: (Color online) The nonadiabatic potentials (in a.u.): $\delta\mathcal{E}_{\rm na}(R)$ (bolded, black), $\mathcal{W}_{\|}(R)$ (lower dotted, blue), and $\mathcal{W}_{\perp}(R)$ (upper dotted, red). The potentials asymptote goes at $-1/m_p^2 = -2.966077 \times 10^{-7}$.

The nonadiabatic correction to energy levels can be computed perturbatively from Eq. (40) as has been done in our previous paper [16], or, in a more accurate way, the radial equation (51) can be solved for the total nonadiabatic energy. This second method is described shortly below. The first term including the second order derivative is rewritten to the more convenient form

$$\begin{aligned}
&-\frac{1}{R^2}\frac{\partial}{\partial R}R^2\left(\frac{1}{2\,\mu_{\rm n}} + \mathcal{W}_{\|}(R)\right)\frac{\partial}{\partial R} \\
&= -\frac{1}{R}\frac{\partial}{\partial R}\left(\frac{1}{2\,\mu_{\rm n}} + \mathcal{W}_{\|}(R)\right)\frac{\partial}{\partial R}R + \frac{\mathcal{W}_{\|}'(R)}{R}\,. \quad (72)
\end{aligned}$$

The resulting radial equation

$$\begin{aligned}
&\frac{\partial}{\partial R}\frac{1}{\mu_{\|}(R)}\frac{\partial}{\partial R}\eta_J(R) \\
&= -2\left[E - \mathcal{Y}(R) - \frac{\mathcal{W}_{\|}'(R)}{R} - \frac{J\,(J+1)}{2\,\mu_{\perp}(R)\,R^2}\right]\eta_J(R), \quad (73)
\end{aligned}$$

is solved numerically for the function $\eta_J(R) = R\,\chi_J(R)$. We used the code developed by W. Johnson, described recently in his book [21], and modified it to account for the dependence of the mass on the internuclear distance. In the calculations we used the following constants [22]: the proton mass $m_p = 1836.15267247\ m_e$ and the energy units conversion factor 1 hartree = 219474.6313705 cm^{-1}.

V. RESULTS AND DISCUSSION

In a molecule, the moving nuclei are 'coated' with electrons and the amount of additional mass carried by the nuclei changes with R. For a homonuclear molecule in a purely vibrational state, the effective mass of the nucleus at given R, $m_{\|}(R)$, is just twice the reduced mass $\mu_{\|}(R)$ defined in Eq. (53). Analogously, for a rigid rotating molecule, the effective nuclear mass $m_{\perp}(R)$ is related to $\mu_{\perp}(R)$ of Eq. (54). Thus, their R-dependence can be determined explicitly from the potentials $\mathcal{W}_{\|}(R)$ and $\mathcal{W}_{\perp}(R)$, respectively. Fig. 2 illustrates the changes in the two effective nuclear masses with the internuclear distance in H_2. The functions $m_{\|}(R)$ and $m_{\perp}(R)$ join smoothly the proton mass at the united atom limit with the hydrogen atomic mass $(m_p + m_e)$ at the separated atoms limit. Interestingly, for $R \geq 2.41$ a.u., the effective mass $m_{\|}(R)$ is greater than the sum of proton and electron masses, reaching $m_p + 1.6\,m_e$ at the maximum located near $R = 3.8$ a.u.

The radial equation (73) has been solved for all bound states with three versions of the potential $\mathcal{Y}(R)$:

$$\begin{array}{ll}
\mathcal{Y}(R) = \mathcal{E}_{\rm el}(R), & \text{BO} \\
\mathcal{Y}(R) = \mathcal{E}_{\rm el}(R) + \mathcal{E}_{\rm a}(R), & \text{adiabatic} \\
\mathcal{Y}(R) = \mathcal{E}_{\rm el}(R) + \mathcal{E}_{\rm a}(R) + \delta\mathcal{E}_{\rm na}(R), & \text{nonadiabatic}
\end{array}$$

yielding three sets of dissociation energies. The corresponding dissociation thresholds were -1 hartree in the BO approximation, $-1 + m_e/m_p$ hartree in adiabatic approximation, and $-1 + m_e/m_p - (m_e/m_p)^2$ hartree in the nonadiabatic level of theory. The results are listed in Table II, where for each pair of quantum numbers v and J three entries are given (in cm^{-1}): the BO dissociation energy, the adiabatic correction, and the nonadiabatic correction to the dissociation energy. Thus, the total nonrelativistic dissociation energy can be obtained by summing up all three entries. The only exception is the state with $v = 14$ and $J = 4$, for which a nonadiabatic level lying just beneath the dissociation threshold has been predicted although neither BO nor adiabatic bound states exist. The entry given for this state is the energy separation from the nonadiabatic dissociation threshold.

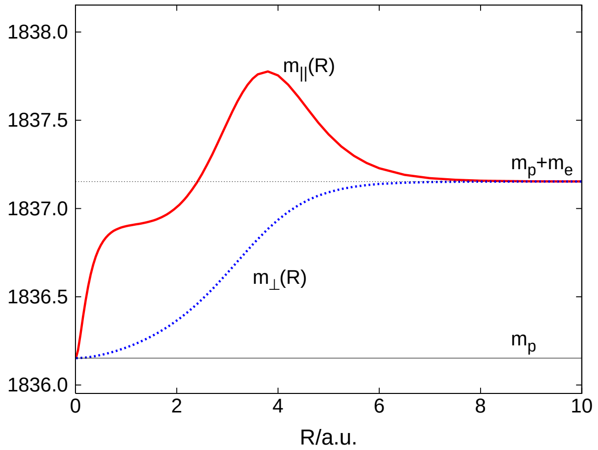

FIG. 2: (Color online) The R-dependence of the effective nuclear masses $m_\parallel(R)$ and $m_\perp(R)$ (in a.u.).

Our nonadiabatic corrections agree very well with those computed by Wolniewicz [15] for rovibrational states of $J \leq 10$. For all rotational states of the lowest vibrational level the difference is merely 0.0002 cm^{-1} or less. In all the cases the difference is smaller than 0.1%, which corresponds to the magnitude of the neglected higher order terms of relative order $\mathcal{O}(1/\mu_\mathrm{n})$. This is the first confirmation of the Wolniewicz's results [15] for $J > 0$ rovibrational states and, simultaneously, a numerical validation of the nonadiabatic perturbation theory presented in this work. Let us note, that the nonadiabatic corrections to the dissociation energy from Table II differ in sign from the corrections to the adiabatic energy of [15] and their absolute values differ by the constant $1/m_\mathrm{p}^2 = 0.06509787$ cm^{-1} corresponding to the asymptotic value of the nonadiabatic potential $\delta\mathcal{E}_\mathrm{na}(R)$, discussed in Subsec. III D.

VI. SUMMARY

We have presented the nonadiabatic perturbation theory applicable to any molecule in an arbitrary rovibrational state. The leading nonadiabatic corrections for the diatomic molecule are expressed in terms of three R-dependent functions depicted in Fig. 1: the nuclear reduced mass in Eq. (53), the moment of inertia in Eq. (54), and the correction Eq. (49) to the adiabatic potential, which enter the radial Schrödinger equation for nuclei Eq. (51). This equation can be solved for an arbitrary molecular states by standard numerical methods [21]. Although representation of the nonadiabatic correction by pseudopotentials has been studied previously (see [9, 11, 12] and references therein), we have rigorously derived new expressions for $\mathcal{W}_\parallel$, $\mathcal{W}_\perp$, and $\delta\mathcal{E}_\mathrm{na}$ functions of the internuclear distance, which give nonadiabatic corrections with $O(m_\mathrm{e}/\mu_\mathrm{n})$ accuracy. Moreover, we have performed explicit numerical calculations for the simplest example of H_2 molecule in order to verify the obtained perturbative formulae. All the electronic matrix elements with differentiation of the wave function over the internuclear distance were rewritten in a convenient form involving differentiation of the Coulomb potential. Such an approach enables achieving much higher numerical precision even for the well known adiabatic correction. The final accuracy of all three nonadiabatic functions is limited only by the neglected higher order terms, namely $\mathcal{O}(m_\mathrm{e}/\mu_\mathrm{n})$ relative to the leading order, and results for rovibrational levels agree within this uncertainty with former results of Wolniewicz [15]. Having accurate nonrelativistic energies one can include relativistic and QED corrections, which become significant for the states close to the dissociation threshold. Relativistic corrections for the electronic ground state of H_2 are known accurately for a wide range of internuclear distances [23]. Their large R asymptotics, including QED corrections, is presently investigated by the Jeziorski group [24]. Combining all the knowledge together would enable achieving at least an order of magnitude increase in the precision of theoretical prediction for all molecular states of H_2.

Analogous calculations can be performed for D_2 and HD molecules. It is worth noting, that in the former case there is no need to recompute the pseudopotentials and only a proper rescaling due to different reduced masses is required. The calculations on the latter system, due to difference in mass of the proton and deuteron, would involve additional correction to $\delta\mathcal{E}_\mathrm{na}$ coming from the last term of Eq. (5). While this perturbative approach can be further extended to larger diatomic molecules, it would be more challenging to investigate three-atomic molecules such as H_3^+—a system of great astrophysical interest. We expect no principal difficulties in such calculations except for much more increased demands in computer resources needed to perform optimization of pertinent wave functions.

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TABLE II: The dissociation energy of the rovibrational states of H_2 (in cm^{-1}). For each pair of vibrational (v) and rotational (J) quantum numbers, three entries are given: the BO dissociation energy, the adiabatic correction, and the nonadiabatic correction. The sum of the three numbers gives the total nonrelativistic dissociation energy of the (v, J) state.

$v\backslash J$	0	1	2	3	4	5	6	7
0	36112.5927	35994.0372	35758.0143	35406.6660	34943.1216	34371.4040	33696.3152	32923.3094
0	5.7711	5.8348	5.9611	6.1481	6.3931	6.6924	7.0418	7.4367
0	0.4339	0.4406	0.4539	0.4739	0.5005	0.5338	0.5736	0.6200
1	31949.1892	31836.5534	31612.3337	31278.6001	30838.3755	30295.5437	29654.7385	28921.2187
1	7.1740	7.2311	7.3443	7.5119	7.7310	7.9983	8.3096	8.6605
1	1.2704	1.2761	1.2874	1.3044	1.3271	1.3555	1.3896	1.4294
2	28021.4345	27914.5889	27701.9154	27385.4159	26968.0130	26453.4605	25846.2343	25151.4125
2	8.3336	8.3840	8.4839	8.6314	8.8240	9.0583	9.3304	9.6358
2	2.0271	2.0318	2.0414	2.0557	2.0749	2.0989	2.1279	2.1618
3	24324.4498	24223.3066	24022.0055	23722.4851	23327.5744	22840.9061	22266.8106	21610.1998
3	9.2420	9.2855	9.3714	9.4982	9.6632	9.8633	10.0945	10.3525
3	2.7088	2.7127	2.7206	2.7326	2.7485	2.7686	2.7929	2.8214
4	20855.2072	20759.7245	20569.7150	20287.0583	19914.4976	19455.5548	18914.4286	18295.8815
4	9.8890	9.9251	9.9966	10.1017	10.2378	10.4019	10.5902	10.7985
4	3.3187	3.3219	3.3283	3.3379	3.3508	3.3670	3.3868	3.4100
5	17612.7145	17522.9036	17344.2107	17078.4626	16728.3253	16297.2225	15789.2368	15209.0018
5	10.2629	10.2915	10.3476	10.4298	10.5356	10.6618	10.8049	10.9606
5	3.8576	3.8599	3.8647	3.8719	3.8816	3.8938	3.9087	3.9262
6	14598.2891	14514.2237	14346.9982	14098.3935	13771.0098	13368.1874	12893.9129	12352.7160
6	10.3525	10.3729	10.4130	10.4712	10.5449	10.6313	10.7268	10.8271
6	4.3218	4.3232	4.3262	4.3306	4.3365	4.3440	4.3531	4.3639
7	11815.9479	11737.7779	11582.3242	11351.3310	11047.3466	10673.6480	10234.1517	9733.3170
7	10.1486	10.1606	10.1839	10.2169	10.2573	10.3020	10.3476	10.3901
7	4.7029	4.7031	4.7037	4.7044	4.7055	4.7067	4.7081	4.7095
8	9272.9561	9200.9278	9057.7445	8845.1263	8565.5890	8222.3732	7819.3619	7360.9906
8	9.6483	9.6517	9.6577	9.6648	9.6707	9.6726	9.6670	9.6500
8	4.9838	4.9824	4.9796	4.9752	4.9692	4.9614	4.9516	4.9393
9	6980.5984	6915.0837	6784.9238	6591.8323	6338.3203	6027.6323	5663.6708	5250.9187
9	8.8590	8.8537	8.8422	8.8232	8.7945	8.7533	8.6963	8.6196
9	5.1364	5.1325	5.1246	5.1124	5.0958	5.0743	5.0472	5.0138
10	4955.2699	4896.8118	4780.7739	4608.8912	4383.7137	4108.5514	3787.4126	3424.9438
10	7.8021	7.7882	7.7597	7.7151	7.6525	7.5691	7.4616	7.3260
10	5.1160	5.1082	5.0925	5.0684	5.0354	4.9926	4.9386	4.8720
11	3220.0418	3169.4253	3069.1017	2920.8723	2727.3991	2492.1652	2219.4373	1914.2414
11	6.5140	6.4918	6.4469	6.3777	6.2821	6.1573	5.9996	5.8045
11	4.8566	4.8429	4.8151	4.7725	4.7140	4.6379	4.5418	4.4224
12	1806.9489	1765.3260	1683.0605	1562.1049	1405.3733	1216.7368	1001.0464	764.2101
12	5.0372	5.0068	4.9451	4.8505	4.7203	4.5506	4.3360	4.0685
12	4.2657	4.2429	4.1965	4.1254	4.0271	3.8984	3.7345	3.5281
13	760.3903	729.5279	668.9437	580.9383	469.0254	338.0600	194.5461	47.4825
13	3.3933	3.3526	3.2697	3.1417	2.9631	2.7253	2.4123	1.9886
13	3.2221	3.1850	3.1095	2.9927	2.8294	2.6113	2.3232	1.9317
14	141.7951	124.7523	92.3077	48.0033				
14	1.5343	1.4739	1.3479	1.1416				
14	1.5847	1.5226	1.3933	1.1825	0.0887†			

† This state appears as a resonance in BO and adiabatic approximations. The entry is a dissociation energy of this nonadiabatic level.

TABLE II: continued

$v\backslash J$	8	9	10	11	12	13	14	15
0	32058.3583	31107.8190	30078.3065	28976.5781	27809.4302	26583.6105	25305.7462	23982.2860
0	7.8718	8.3418	8.8411	9.3642	9.9055	10.4596	11.0212	11.5852
0	0.6728	0.7322	0.7981	0.8704	0.9491	1.0343	1.1260	1.2240
1	28100.7394	27199.4234	26223.6397	25179.8929	24074.7260	22914.6378	21706.0160	20455.0847
1	9.0458	9.4605	9.8991	10.3562	10.8264	11.3045	11.7850	12.2629
1	1.4749	1.5263	1.5834	1.6464	1.7154	1.7903	1.8713	1.9584
2	24374.5496	23521.5539	22598.5709	21611.8782	20567.7938	19472.5994	18332.4783	17153.4682
2	9.9697	10.3271	10.7026	11.0910	11.4869	11.8851	12.2802	12.6671
2	2.2008	2.2449	2.2942	2.3488	2.4089	2.4744	2.5456	2.6225
3	20876.4463	20071.2651	19200.6029	18270.5391	17287.1990	16256.6838	15185.0135	14078.0862
3	10.6327	10.9300	11.2393	11.5554	11.8729	12.1865	12.4908	12.7804
3	2.8543	2.8917	2.9337	2.9804	3.0320	3.0885	3.1500	3.2167
4	17605.1247	16847.7045	16029.3982	15156.1198	14233.8415	13268.5282	12266.0890	11232.3425
4	11.0221	11.2561	11.4954	11.7348	11.9690	12.1923	12.3995	12.5849
4	3.4370	3.4677	3.5023	3.5409	3.5836	3.6304	3.6814	3.7365
5	14561.5917	13852.4141	13087.1119	12271.4764	11411.3755	10512.6972	9581.3093	8623.0355
5	11.1244	11.2915	11.4566	11.6146	11.7601	11.8873	11.9906	12.0642
5	3.9466	3.9699	3.9962	4.0254	4.0576	4.0926	4.1304	4.1704
6	11749.5653	11089.7678	10378.8781	9622.6208	8826.8275	7997.3920	7140.2429	6261.3368
6	10.9279	11.0242	11.1110	11.1829	11.2344	11.2597	11.2528	11.2071
6	4.3763	4.3903	4.4058	4.4226	4.4406	4.4592	4.4779	4.4957
7	9176.0486	8567.6048	7913.5170	7219.5226	6491.5173	5735.5270	4957.7045	4164.3543
7	10.4250	10.4474	10.4524	10.4343	10.3876	10.3060	10.1831	10.0114
7	4.7108	4.7118	4.7119	4.7108	4.7076	4.7012	4.6902	4.6724
8	6852.1602	6298.1569	5704.5851	5077.3199	4422.4828	3746.4465	3055.8806	2357.8507
8	9.6172	9.5638	9.4847	9.3741	9.2260	9.0337	8.7892	8.4833
8	4.9241	4.9053	4.8820	4.8528	4.8160	4.7692	4.7092	4.6313
9	4794.3657	4299.4465	3771.9991	3218.2507	2644.8437	2058.9184	1468.2878	881.7751
9	8.5188	8.3891	8.2250	8.0203	7.7678	7.4587	7.0814	6.6193
9	4.9730	4.9232	4.8624	4.7880	4.6962	4.5819	4.4375	4.2515
10	3026.3806	2597.5217	2144.7391	1675.0460	1196.2612	717.3517	249.1650	
10	7.1577	6.9514	6.7003	6.3963	6.0280	5.5786	5.0193	
10	4.7905	4.6909	4.5694	4.4200	4.2343	3.9995	3.6930	
11	1582.3694	1230.4417	866.0734	498.2452	138.1669			
11	5.5658	5.2756	4.9227	4.4892	3.9416			
11	4.2752	4.0939	3.8689	3.5852	3.2148			
12	513.3908	257.4738	8.3253					
12	3.7358	3.3166	2.7633					
12	3.2682	2.9354	2.4878					

TABLE II: continued

$v\backslash J$	16	17	18	19	20	21	22	23
0	22619.4577	21223.2371	19799.3296	18353.1603	16889.8728	15414.3355	13931.1527	12444.6818
0	12.1465	12.7005	13.2425	13.7681	14.2729	14.7525	15.2029	15.6196
0	1.3286	1.4396	1.5572	1.6814	1.8122	1.9497	2.0939	2.2451
1	19167.8656	17850.1517	16507.4922	15145.1868	13768.2885	12381.6135	10989.7585	9597.1235
1	12.7332	13.1911	13.6317	14.0502	14.4420	14.8023	15.1262	15.4086
1	2.0516	2.1512	2.2570	2.3693	2.4881	2.6134	2.7453	2.8838
2	15941.4274	14702.0131	13440.6714	12162.6372	10872.9422	9576.4337	8277.7999	6981.6067
2	13.0406	13.3957	13.7272	14.0300	14.2988	14.5281	14.7122	14.8446
2	2.7052	2.7938	2.8884	2.9890	3.0955	3.2080	3.3263	3.4502
3	12941.6497	11781.2863	10602.4104	9410.2757	8209.9952	7006.5729	5804.9493	4610.0657
3	13.0501	13.2944	13.5077	13.6843	13.8181	13.9026	13.9307	13.8939
3	3.2886	3.3657	3.4479	3.5352	3.6272	3.7237	3.8240	3.9274
4	10172.9970	9093.6453	7999.7724	6896.7794	5790.0229	4684.8764	3586.8202	2501.5762
4	12.7427	12.8672	12.9520	12.9905	12.9756	12.8991	12.7513	12.5207
4	3.7957	3.8587	3.9253	3.9948	4.0665	4.1392	4.2113	4.2803
5	7643.6478	6648.8775	5644.4446	4636.1112	3629.7676	2631.5640	1648.1214	686.8842
5	12.1016	12.0965	12.0417	11.9291	11.7496	11.4918	11.1414	10.6779
5	4.2124	4.2556	4.2990	4.3412	4.3801	4.4126	4.4344	4.4383
6	5366.6735	4462.3376	3554.5745	2649.9163	1755.3887	878.8631	29.7112	
6	11.1158	10.9712	10.7645	10.4851	10.1192	9.6476	9.0402	
6	4.5115	4.5235	4.5291	4.5249	4.5055	4.4629	4.3836	
7	3361.9951	2557.4749	1758.1694	972.3301	209.7400			
7	9.7827	9.4869	9.1113	8.6376	8.0373			
7	4.6449	4.6038	4.5430	4.4532	4.3193			
8	1660.0067	970.9237	300.7647					
8	8.1037	7.6332	7.0443					
8	4.5286	4.3911	4.2015					
9	309.8952							
9	6.0447							
9	4.0047							

TABLE II: continued

$v\backslash J$	24	25	26	27	28	29	30	31
0	10959.0542	9478.2014	8005.8846	6545.7303	5101.2727	3676.0048	2273.4444	897.2218
0	15.9981	16.3340	16.6221	16.8572	17.0329	17.1423	17.1769	17.1261
0	2.4031	2.5682	2.7404	2.9199	3.1066	3.3006	3.5019	3.7105
1	8207.9415	6826.3161	5456.2676	4101.7929	2766.9437	1455.9363	173.3131	
1	15.6440	15.8264	15.9492	16.0045	15.9831	15.8734	15.6600	
1	3.0290	3.1807	3.3389	3.5032	3.6734	3.8488	4.0283	
2	5692.3452	4414.4956	3152.6140	1911.4560	696.1630			
2	14.9184	14.9254	14.8559	14.6980	14.4356			
2	3.5795	3.7135	3.8516	3.9923	4.1340			
3	3426.9550	2260.8735	1117.5022					
3	13.7827	13.5850	13.2850					
3	4.0327	4.1379	4.2403					
4	1435.3165	395.0112						
4	12.1920	11.7435						
4	4.3427	4.3926						