

Leading order nonadiabatic corrections to rovibrational levels of H₂, D₂, and T₂

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An efficient computational approach to nonadiabatic effects in the hydrogen molecule (H₂, D₂, T₂) is presented. The electronic wave function is expanded in the James-Coolidge basis set, which enables obtaining a very high accuracy of nonadiabatic potentials. A single point convergence of the potentials with growing size of the basis set reveals a relative accuracy ranging from 10⁻⁸ to 10⁻¹³. An estimated accuracy of the leading nonadiabatic correction to the rovibrational energy levels is of the order of 10⁻⁷ cm⁻¹. After a significant increase in the accuracy of the Born-Oppenheimer and adiabatic calculations, the nonadiabatic results presented in this report constitute another step towards highly accurate theoretical description of the hydrogen molecule.

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I. INTRODUCTION

Molecular hydrogen is the simplest neutral molecule, and it has been a benchmark system for calculations and spectroscopy since the explanation of its stability by quantum mechanics¹ in 1927. Determination of the dissociation energy of H₂ has led to a fruitful interplay between theory and experiment, continued over several decades and resulting in ever increasing accuracies of both.^{2–24} The progress made by 2001 is the subject of a detailed review by Stoicheff.²⁵

In recent years, the accuracy of experimental determination of the dissociation and ionization energies of H₂ and its isotopomers has reached the level of 10 ppb.^{26–30} Simultaneously, significant progress in theory^{31–35} has enabled *ab initio* calculations with precision rivaling or even surpassing that of the best measurements. To keep up with the increasing experimental accuracy, theory needs to take into account tiny nonadiabatic, relativistic and even quantum electrodynamic effects. The latter effects contribute about 5 ppm to the total dissociation energy and their rigorous treatment is crucial in state-of-the-art calculations. Excellent compliance between contemporary experimental and theoretical data on rovibrational levels of the ground electronic state of H₂ has allowed the first observation of the QED effects in the rotational progressions of the H₂ spectrum.^{35,36} To push the accuracy of the theoretical predictions to a level limited by uncertainties in the proton-to-electron mass ratio³⁷ or in the proton-charge radius,³⁸ it is necessary both to include higher order effects and to level up the accuracy of the already known contributions.

The theoretically determined energy of a rovibrational level contains several contributions: nonrelativistic, relativistic, radiative, and others. A convenient interpretation of these contributions is obtained by expanding the energy as a power series in α —the fine structure constant.^{39–41} The finite nuclear mass effects can be treated using the nonadiabatic perturbation theory (NAPT),^{31,32} which relies on the expansion of the energy in m_e/M —the electron-nucleus mass ratio. Such a double power expansion provides a firm framework for theoretical description of molecular systems.

In our multistage program of improving the overall accuracy of theoretical outcome, two steps have already been successfully accomplished. They concern the two largest terms of the energy expansion—the Born-Oppenheimer (BO) and the adiabatic contributions. Thanks to a new technique⁴² for the evaluation of molecular integrals in the James-Coolidge basis,

an improvement of several orders of magnitude in accuracy of these contributions has been possible.^{43,44} Here we report on the next step concerning the leading nonadiabatic correction evaluated using the improved approach and the James-Coolidge functions. The following section sets theoretical background for the perturbative treatment of the nonadiabatic effects, and subsequent sections go deeper into technical details of the project.

II. PERTURBATIVE FORMALISM

The formalism presented in the following sections is a modification of that introduced several years ago.^{31,32} A more efficient treatment of wave-function derivatives is shown, as well as explicit expressions for the higher order effective Hamiltonians in the NAPT approach are derived.

Let the total wave function ϕ be a solution of the stationary Schrödinger equation $[H - E]|\phi\rangle = 0$, with the Hamiltonian $H = H_{\text{el}} + H_{\text{n}}$, partitioned into the electronic and nuclear parts. The clamped nuclei electronic Hamiltonian (with fixed positions of nuclei)

$$H_{\text{el}} = - \sum_a \frac{\nabla_a^2}{2m_e} + V \quad (1)$$

consists of the electronic kinetic energy term and the potential V , which includes all the Coulomb interactions. The nuclear Hamiltonian of a homonuclear diatomic molecule, after the center of mass motion separation and with the space-fixed reference frame attached to the geometrical center of two nuclei, has the form

$$H_{\text{n}} = -\frac{1}{2\mu_{\text{n}}} (\nabla_R^2 + \nabla_{\text{el}}^2), \quad (2)$$

where

$$\vec{\nabla}_{\text{el}} \equiv \frac{1}{2} \sum_a \vec{\nabla}_a, \quad (3)$$

R means the internuclear distance, and μ_{n} is the nuclear reduced mass.

Now, let the unperturbed (zeroth-order) wave function be taken as the adiabatic wave function

$$\phi_{\text{a}}(\vec{r}, \vec{R}) = \phi_{\text{el}}(\vec{r}) \chi(\vec{R}) \quad (4)$$

i.e. as a product of the nuclear wave function χ and the electronic wave function ϕ_{el} depending implicitly on the nuclear coordinates \vec{R} . The electronic wave function obeys the

electronic Schrödinger equation with the clamped nuclei Hamiltonian

$$\left[H_{\text{el}} - \mathcal{E}_{\text{el}}(\vec{R}) \right] |\phi_{\text{el}}\rangle = 0. \quad (5)$$

The total wave function can be expressed as a sum of terms parallel to and orthogonal to ϕ_{el}

$$\phi = \phi_{\text{el}} \chi + \delta\phi_{\text{na}}. \quad (6)$$

The latter condition means that

$$\langle \delta\phi_{\text{na}} | \phi_{\text{el}} \rangle_{\text{el}} = 0, \quad (7)$$

where $\langle \dots \rangle_{\text{el}}$ represents integration over electronic coordinates only. As a consequence, the Schrödinger equation with the Hamiltonian H and the energy E can be decomposed into parallel and orthogonal parts

$$[(H_{\text{el}} - \mathcal{E}_{\text{el}}) + (\mathcal{E}_{\text{el}} + H_{\text{n}} - E)] |\phi_{\text{el}} \chi + \delta\phi_{\text{na}}\rangle = 0 \quad (8)$$

and further transformed to

$$(\mathcal{E}_{\text{el}} - H_{\text{el}}) |\delta\phi_{\text{na}}\rangle = (\mathcal{E}_{\text{el}} + H_{\text{n}} - E) |\phi_{\text{el}} \chi + \delta\phi_{\text{na}}\rangle. \quad (9)$$

Since $\delta\phi_{\text{na}}$ is orthogonal to ϕ_{el} , see Eq. (7), the formal recursive solution to the above equation can be written as

$$|\delta\phi_{\text{na}}\rangle = \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} [H_{\text{n}} |\phi_{\text{el}} \chi\rangle + (\mathcal{E}_{\text{el}} + H_{\text{n}} - E) |\delta\phi_{\text{na}}\rangle], \quad (10)$$

where the prime in the denominator denotes subtraction of the reference state ϕ_{el} from the Hamiltonian inversion.⁴⁵ In the next step, Eq. (8) is left-multiplied by $\langle \phi_{\text{el}} |$ to yield

$$\langle \phi_{\text{el}} | \mathcal{E}_{\text{el}} + H_{\text{n}} - E | \phi_{\text{el}} \chi + \delta\phi_{\text{na}} \rangle_{\text{el}} = 0, \quad (11)$$

which can be rewritten to the form

$$(\mathcal{E}_{\text{el}} + \mathcal{E}_{\text{a}} + H_{\text{n}} - E) |\chi\rangle = -\langle \phi_{\text{el}} | H_{\text{n}} | \delta\phi_{\text{na}} \rangle_{\text{el}} \quad (12)$$

with $\mathcal{E}_{\text{a}} \equiv \langle \phi_{\text{el}} | H_{\text{n}} | \phi_{\text{el}} \rangle_{\text{el}}$. Recursive substitution of Eq. (10) into (12) forms a perturbative expansion for the effective nuclear Hamiltonian

$$(\mathcal{E}_{\text{el}} + \mathcal{E}_{\text{a}} + H_{\text{n}} - E) |\chi\rangle = -(H_{\text{n}}^{(2)} + H_{\text{n}}^{(3)} + H_{\text{n}}^{(4)} + \dots) |\chi\rangle \quad (13)$$

the leading terms of which have the following explicit form

$$H_n^{(2)} = \left\langle \phi_{\text{el}} \left| H_n \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} H_n \right| \phi_{\text{el}} \right\rangle_{\text{el}}, \quad (14)$$

$$H_n^{(3)} = \left\langle \phi_{\text{el}} \left| H_n \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} (H_n + \mathcal{E}_{\text{el}} - E) \right. \right. \\ \left. \left. \times \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} H_n \right| \phi_{\text{el}} \right\rangle_{\text{el}}, \quad (15)$$

and

$$H_n^{(4)} = \left\langle \phi_{\text{el}} \left| H_n \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} (H_n + \mathcal{E}_{\text{el}} - E) \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} \right. \right. \\ \left. \left. \times (H_n + \mathcal{E}_{\text{el}} - E) \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} H_n \right| \phi_{\text{el}} \right\rangle_{\text{el}}. \quad (16)$$

Taking into account the actual form (2) of the nuclear Hamiltonian we can transform further the above formulas, e.g.

$$H_n^{(2)} = \left\langle H_n \phi_{\text{el}} \left| \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} \right| H_n \phi_{\text{el}} \right\rangle_{\text{el}} \quad (17) \\ + \frac{1}{\mu_n} \vec{\nabla}_R \left\langle \vec{\nabla}_R \phi_{\text{el}} \left| \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} \right| H_n \phi_{\text{el}} \right\rangle_{\text{el}} \\ - \frac{1}{\mu_n} \left\langle H_n \phi_{\text{el}} \left| \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} \right| \vec{\nabla}_R \phi_{\text{el}} \right\rangle_{\text{el}} \vec{\nabla}_R \\ - \frac{1}{\mu_n^2} \vec{\nabla}_R \left\langle \vec{\nabla}_R \phi_{\text{el}} \left| \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} \right| \vec{\nabla}_R \phi_{\text{el}} \right\rangle_{\text{el}} \vec{\nabla}_R.$$

In order to make the following expressions more compact, we shall introduce two abbreviations

$$|\phi_{\text{el}}\rangle = \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} \left| H_n \phi_{\text{el}} \right\rangle, \quad (18)$$

$$|\vec{\phi}_{\text{el}}\rangle = \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} \left| \vec{\nabla}_R \phi_{\text{el}} \right\rangle, \quad (19)$$

and then

$$H_n^{(3)} = \left(\langle \phi_{\text{el}} | + \frac{1}{\mu_n} \vec{\nabla}_R \langle \vec{\phi}_{\text{el}} | \right) (H_n + \mathcal{E}_{\text{el}} - E) \left(|\phi_{\text{el}}\rangle - \frac{1}{\mu_n} |\vec{\phi}_{\text{el}}\rangle \vec{\nabla}_R \right) \quad (20)$$

and

$$H_n^{(4)} = \left(\langle \phi_{\text{el}} | + \frac{1}{\mu_n} \vec{\nabla}_R \langle \vec{\phi}_{\text{el}} | \right) (H_n + \mathcal{E}_{\text{el}} - E) \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} (H_n + \mathcal{E}_{\text{el}} - E) \left(|\phi_{\text{el}}\rangle - \frac{1}{\mu_n} |\vec{\phi}_{\text{el}}\rangle \vec{\nabla}_R \right) \quad (21)$$

The Hamiltonian $H_n^{(2)}$ contains only the terms proportional to $(m_e/\mu_n)^2$, but $H_n^{(3)}$ may have the terms with the second and higher powers of the electron-to-nucleus mass ratio. We are interested in the leading nonadiabatic correction, which means in the terms proportional to $(m_e/\mu_n)^2$.

III. IMPLEMENTATION OF DERIVATIVES

Let ψ_k be the basis functions of electronic coordinates, then the electronic ground state wave function can be expressed as

$$\phi_{\text{el}}(\vec{r}_1, \vec{r}_2) = \sum_{k=1}^N v_k(R) \psi_k(\vec{r}_1, \vec{r}_2), \quad (22)$$

where \vec{v} is a vector consisting of real coefficients of this expansion. From now on we shall drop the 'el' subscript in the bracket symbol as all the following integrations will be performed in the electronic domain. The matrix elements of the nuclear Hamiltonian (2) in the ψ_i basis are

$$\begin{aligned} \langle \psi_i | H_{\text{n}} | \psi_j \rangle &= -\frac{1}{2\mu_{\text{n}}} \vec{\nabla}_R \langle \psi_i | \psi_j \rangle \vec{\nabla}_R \\ &- \frac{1}{4\mu_{\text{n}}} \langle \psi_i | (\nabla_R^2 + \nabla_{\text{el}}^2) \psi_j \rangle - \frac{1}{4\mu_{\text{n}}} \langle (\nabla_R^2 + \nabla_{\text{el}}^2) \psi_i | \psi_j \rangle \\ &+ \frac{1}{4\mu_{\text{n}}} \left\{ \langle \vec{\nabla}_R \psi_i | \psi_j \rangle - \langle \psi_i | \vec{\nabla}_R \psi_j \rangle, \vec{\nabla}_R \right\}, \end{aligned} \quad (23)$$

where the braces are used to denote the anticommutator.

Let us introduce the following symbols for the new matrix elements

$$\begin{aligned} \mathcal{H}_{kl} &= \langle \psi_k | H_{\text{el}} \psi_l \rangle, \\ \mathcal{N}_{kl} &= \langle \psi_k | \psi_l \rangle, \\ \mathcal{A}_{kl} &= \langle \psi_k | \partial_R \psi_l \rangle, \\ \mathcal{B}_{kl} &= \langle \vec{\nabla}_R \psi_k | \vec{\nabla}_R \psi_l \rangle + \langle \vec{\nabla}_{\text{el}} \psi_k | \vec{\nabla}_{\text{el}} \psi_l \rangle, \\ \mathcal{C}_{kl} &= \langle \psi_k | \nabla_{\text{el}}^2 + \nabla_R^2 | \psi_l \rangle, \\ \mathcal{R}_{kl} &= \left\langle \psi_k \left| \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} \right| \psi_l \right\rangle. \end{aligned} \quad (24)$$

With this notation the electronic Schrödinger equation (5) reads

$$(\mathcal{H} - \mathcal{E}_{\text{el}} \mathcal{N}) \vec{v} = 0, \quad (25)$$

the normalization condition

$$\vec{v}^T \mathcal{N} \vec{v} = 1, \quad (26)$$

and the reduced resolvent⁴⁵

$$\mathcal{R} = \frac{1}{(\mathcal{E}_{\text{el}} \mathcal{N} - \mathcal{H})'}. \quad (27)$$

Let us consider now the first order R -derivative of ϕ_{el}

$$\partial_R \phi_{\text{el}} = \sum_k (\partial_R v_k \psi_k + v_k \partial_R \psi_k). \quad (28)$$

The term $\partial_R \psi_k$ is assumed to be known, as it is a derivative of the basis function. The $\partial_R v_k$ is obtained by differentiation of Eq. (25)

$$(\mathcal{H} - \mathcal{E}_{\text{el}} \mathcal{N}) \partial_R \vec{v} + (\partial_R \mathcal{H} - \partial_R \mathcal{E}_{\text{el}} \mathcal{N} - \mathcal{E}_{\text{el}} \partial_R \mathcal{N}) \vec{v} = 0 \quad (29)$$

and of the normalization condition, Eq. (26),

$$2 (\partial_R \vec{v})^T \mathcal{N} \vec{v} + \vec{v}^T \partial_R \mathcal{N} \vec{v} = 0, \quad (30)$$

which combined together give

$$\partial_R \vec{v} = \mathcal{R} (\partial_R \mathcal{H} - \mathcal{E}_{\text{el}} \partial_R \mathcal{N}) \vec{v} - \frac{1}{2} (\vec{v}^T \partial_R \mathcal{N} \vec{v}) \vec{v}. \quad (31)$$

The first derivative of ϕ_{el} projected onto the basis function ψ_k gives

$$u_k \equiv \langle \psi_k | \partial_R \phi_{\text{el}} \rangle = \sum_l (\mathcal{A}_{kl} v_l + \mathcal{N}_{kl} \partial_R v_l). \quad (32)$$

Let us turn now to the second order R -derivative of ϕ_{el}

$$\begin{aligned} \nabla_R^2 \phi_{\text{el}} = \sum_k \left(\partial_R^2 v_k \psi_k + \frac{2}{R} \partial_R v_k \psi_k + 2 \partial_R v_k \partial_R \psi_k \right. \\ \left. + v_k \nabla_R^2 \psi_k \right). \end{aligned} \quad (33)$$

Its projection onto the basis function ψ_l is

$$\begin{aligned} w_l \equiv \langle \psi_l | \nabla_{\text{el}}^2 + \nabla_R^2 | \phi_{\text{el}} \rangle \\ = \sum_k \left(\mathcal{N}_{lk} \partial_R^2 v_k + \frac{2}{R} \mathcal{N}_{lk} \partial_R v_k + 2 \mathcal{A}_{lk} \partial_R v_k + \mathcal{C}_{lk} v_k \right). \end{aligned} \quad (34)$$

The second order derivative of \vec{v} is obtained by double differentiation of Eqs. (25) and (26)

$$\begin{aligned} \partial_R^2 [(\mathcal{H} - \mathcal{E}_{\text{el}} \mathcal{N}) \vec{v}] &= 0 \\ (\mathcal{H} - \mathcal{E}_{\text{el}} \mathcal{N}) \partial_R^2 \vec{v} + 2 (\partial_R \mathcal{H} - \partial_R \mathcal{E}_{\text{el}} \mathcal{N} - \mathcal{E}_{\text{el}} \partial_R \mathcal{N}) \partial_R \vec{v} \\ + (\partial_R^2 \mathcal{H} - \partial_R^2 \mathcal{E}_{\text{el}} \mathcal{N} - \mathcal{E}_{\text{el}} \partial_R^2 \mathcal{N} - 2 \partial_R \mathcal{E}_{\text{el}} \partial_R \mathcal{N}) \vec{v} &= 0 \end{aligned} \quad (35)$$

$$\begin{aligned}
& 2 \partial_R^2 \vec{v}^T \mathcal{N} \vec{v} + 2 \partial_R \vec{v}^T \mathcal{N} \partial_R \vec{v} \\
& + 4 \partial_R \vec{v}^T \partial_R \mathcal{N} \vec{v} + \vec{v}^T \partial_R^2 \mathcal{N} \vec{v} = 0
\end{aligned} \tag{36}$$

which leads to

$$\begin{aligned}
\partial_R^2 \vec{v} = \mathcal{R} & \left[2 (\partial_R \mathcal{H} - \partial_R \mathcal{E}_{\text{el}} \mathcal{N} - \mathcal{E}_{\text{el}} \partial_R \mathcal{N}) \partial_R \vec{v} \right. \\
& \left. + (\partial_R^2 \mathcal{H} - \mathcal{E}_{\text{el}} \partial_R^2 \mathcal{N} - 2 \partial_R \mathcal{E}_{\text{el}} \partial_R \mathcal{N}) \vec{v} \right] \\
& - \left(\partial_R \vec{v}^T \mathcal{N} \partial_R \vec{v} + 2 \partial_R \vec{v}^T \partial_R \mathcal{N} \vec{v} + \frac{1}{2} \vec{v}^T \partial_R^2 \mathcal{N} \vec{v} \right) \vec{v},
\end{aligned} \tag{37}$$

where the first order derivative of \mathcal{E}_{el} is

$$\partial_R \mathcal{E}_{\text{el}} = \vec{v}^T (\partial_R \mathcal{H} - \mathcal{E}_{\text{el}} \partial_R \mathcal{N}) \vec{v}. \tag{38}$$

The matrices and vectors derived in this Section set the grounds for the expressions of the nonadiabatic potentials comprising the effective Hamiltonians presented in the next Section.

IV. CONSTRUCTION OF THE EFFECTIVE NUCLEAR HAMILTONIANS AND THE RADIAL SCHRÖDINGER EQUATION

The adiabatic correction \mathcal{E}_a , appearing in Eq (12), has been derived in Ref. 44 using the notation introduced in the previous section

$$\mathcal{E}_a = \frac{1}{2 \mu_n} (\vec{v}^T \mathcal{B} \vec{v} + \partial_R \vec{v}^T \mathcal{N} \partial_R \vec{v} + 2 \partial_R \vec{v}^T \mathcal{A} \vec{v}). \tag{39}$$

In the following sections we shall present expressions for the second- and third-order effective nuclear Hamiltonians, appearing in Eq. (13), using quantities introduced in the preceding sections.

A. Second-order Hamiltonian

The second-order nonadiabatic effective Hamiltonian of Eq. (17) is transformed to the form^{31,32}

$$\begin{aligned}
H_n^{(2)} = \mathcal{U}(R) & + \left(\frac{2}{R} + \frac{\partial}{\partial R} \right) \mathcal{V}(R) \\
& - \frac{1}{R^2} \frac{\partial}{\partial R} R^2 \mathcal{W}_{\parallel}(R) \frac{\partial}{\partial R} + \frac{J(J+1)}{R^2} \mathcal{W}_{\perp}(R)
\end{aligned} \tag{40}$$

where

$$\begin{aligned} \mathcal{U}(R) &= \left\langle H_n \phi_{\text{el}} \left| \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} \right| H_n \phi_{\text{el}} \right\rangle \\ &= \frac{1}{4\mu_n^2} w^T \mathcal{R} w, \end{aligned} \quad (41)$$

$$\begin{aligned} \mathcal{V}(R) &= \frac{1}{\mu_n} \left\langle \partial_R \phi_{\text{el}} \left| \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} \right| H_n \phi_{\text{el}} \right\rangle \\ &= -\frac{1}{2\mu_n^2} u^T \mathcal{R} w, \end{aligned} \quad (42)$$

$$\begin{aligned} \mathcal{W}_{\parallel}(R) &= \frac{1}{\mu_n^2} \left\langle \partial_R \phi_{\text{el}} \left| \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} \right| \partial_R \phi_{\text{el}} \right\rangle \\ &= \frac{1}{\mu_n^2} u^T \mathcal{R} u, \end{aligned} \quad (43)$$

$$\begin{aligned} \mathcal{W}_{\perp}(R) &= \frac{1}{\mu_n^2} \frac{(\delta^{ij} - n^i n^j)}{2} \left\langle \nabla_R^i \phi_{\text{el}} \left| \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} \right| \nabla_R^j \phi_{\text{el}} \right\rangle \\ &= \frac{1}{2\mu_n^2 R^2} \left\langle \phi_{\text{el}} \left| \vec{L}_{\text{el}} \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} \vec{L}_{\text{el}} \right| \phi_{\text{el}} \right\rangle \end{aligned} \quad (44)$$

In the last equation, it is assumed that the molecule has a null total angular momentum (Σ state), which implies $\vec{L}_n = -\vec{L}_{\text{el}}$ with $\vec{L}_n = -iR \times \vec{\nabla}_R$ and $\vec{L}_{\text{el}} = -i \sum_a \vec{r}_a \times \vec{\nabla}_a$.

B. Third-order Hamiltonian

The third-order Hamiltonian (20) can be expressed as a sum of three distinct terms

$$H_n^{(3)} = A + B + C, \quad (45)$$

where

$$\begin{aligned} A &= \langle \phi_{\text{el}} | (H_n + \mathcal{E}_{\text{el}} - E) | \phi_{\text{el}} \rangle, \\ B &= \frac{1}{\mu_n} \vec{\nabla}_R \langle \vec{\phi}_{\text{el}} | (H_n + \mathcal{E}_{\text{el}} - E) | \phi_{\text{el}} \rangle \\ &\quad - \frac{1}{\mu_n} \langle \phi_{\text{el}} | (H_n + \mathcal{E}_{\text{el}} - E) | \vec{\phi}_{\text{el}} \rangle \vec{\nabla}_R, \\ C &= -\frac{1}{\mu_n^2} \vec{\nabla}_R \langle \vec{\phi}_{\text{el}} | (H_n + \mathcal{E}_{\text{el}} - E) | \vec{\phi}_{\text{el}} \rangle \vec{\nabla}_R. \end{aligned} \quad (46)$$

All these three expressions are transformed by commuting the term $H_n + \mathcal{E}_{\text{el}} - E$ to the right and left

$$\begin{aligned} A &= \frac{1}{2\mu_n} \langle \nabla_R \phi_{\text{el}} | \nabla_R \phi_{\text{el}} \rangle + \frac{1}{2} (H_n + \mathcal{E}_{\text{el}} - E) \langle \phi_{\text{el}} | \phi_{\text{el}} \rangle \\ &\quad + \frac{1}{2} \langle \phi_{\text{el}} | \phi_{\text{el}} \rangle (H_n + \mathcal{E}_{\text{el}} - E). \end{aligned} \quad (47)$$

Since χ satisfies Eq. (13), A can be approximated, neglecting the terms of the order higher than fourth in m_e/μ_n , by

$$A = \frac{1}{2\mu_n} \langle \nabla_R \phi_{\text{ell}} | \nabla_R \phi_{\text{ell}} \rangle - \mathcal{E}_a \langle \phi_{\text{ell}} | \phi_{\text{ell}} \rangle. \quad (48)$$

Similarly the term B is transformed to

$$B = \frac{1}{\mu_n} [\vec{\nabla}_R, \langle \vec{\phi}_{\text{ell}} | H_n \phi_{\text{ell}} \rangle - \mathcal{E}_a \langle \vec{\phi}_{\text{ell}} | \phi_{\text{ell}} \rangle] - \frac{2}{\mu_n^2} \vec{\nabla}_R \cdot \langle \vec{\phi}_{\text{ell}} | \vec{\nabla}_R \phi_{\text{ell}} \rangle \cdot \vec{\nabla}_R \quad (49)$$

and the term C becomes

$$C = -\frac{1}{2\mu_n^3} \nabla_R^i [\langle \nabla_R^k \phi_{\text{ell}}^i | \nabla_R^k \phi_{\text{ell}}^j \rangle - \mathcal{E}_a] \nabla_R^j + \frac{1}{2\mu_n^2} [\nabla_R^i, \langle \phi_{\text{ell}}^i | \phi_{\text{ell}}^j \rangle \nabla_R^j (\mathcal{E}_{\text{el}} + \mathcal{E}_a)]. \quad (50)$$

All the components of $H_n^{(3)}$ are $\mathcal{O}(\mu_n^{-3})$ except the last one in C , which is proportional to μ_n^{-2} . In the present calculations, only this term was accounted for. Its explicit form reads

$$\begin{aligned} \delta\mathcal{V}(R) &= -\frac{1}{2\mu_n^2} \partial_R \mathcal{E}_{\text{el}} \left\langle \partial_R \phi_{\text{el}} \left| \left[\frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} \right]^2 \right| \partial_R \phi_{\text{el}} \right\rangle \\ &= -\frac{1}{2\mu_n^2} \partial_R \mathcal{E}_{\text{el}} u^T \mathcal{R}^T \mathcal{N} \mathcal{R} u \end{aligned} \quad (51)$$

and it was added to $\mathcal{V}(R)$ in Eq (40). The omitted components of $H_n^{(3)}$ and of the higher order Hamiltonians remain the main source of the uncertainty of the nonrelativistic results.

C. Radial Schrödinger equation

Now, our goal is to solve Eq. (13) to the second order in the m_e/μ_n , which means that the right hand side series of Hamiltonians is limited to the terms proportional to $(m_e/\mu_n)^2$. The explicit form of the radial Schrödinger equation reads (see Ref. 32 for detailed derivation)

$$\begin{aligned} &\left[-\frac{1}{R^2} \frac{\partial}{\partial R} \frac{R^2}{2\mu_{\parallel}(R)} \frac{\partial}{\partial R} + \frac{J(J+1)}{2\mu_{\perp}(R)R^2} + \mathcal{Y}(R) \right] \chi_J(R) \\ &= E \chi_J(R), \end{aligned} \quad (52)$$

where the functions

$$\frac{1}{2\mu_{\parallel}(R)} \equiv \frac{1}{2\mu_n} + \mathcal{W}_{\parallel}(R), \quad (53)$$

and

$$\frac{1}{2\mu_{\perp}(R)} \equiv \frac{1}{2\mu_n} + \mathcal{W}_{\perp}(R). \quad (54)$$

are interpreted as R -dependent vibrational and rotational masses, and where the potential $\mathcal{Y}(R)$ for the movement of the nuclei consists of the BO curve $\mathcal{E}_{\text{el}}(R)$, the adiabatic correction curve $\mathcal{E}_a(R)$, and the nonadiabatic correction curve $\delta\mathcal{E}_{\text{na}}(R)$

$$\mathcal{Y}(R) = \mathcal{E}_{\text{el}}(R) + \mathcal{E}_a(R) + \delta\mathcal{E}_{\text{na}}(R). \quad (55)$$

The latter correction is expressed in terms of the functions defined in previous sections as

$$\delta\mathcal{E}_{\text{na}}(R) = \mathcal{U}(R) + \left(\frac{2}{R} + \frac{\partial}{\partial R} \right) [\mathcal{V}(R) + \delta\mathcal{V}(R)]. \quad (56)$$

As we are interested in dissociation energy D_0 of rovibrational levels we fix the origin of the energy scale to the separated atoms limit, and correspondingly, we convert all the potentials to the following form

$$\mathcal{Y}^{\text{int}}(R) = \mathcal{Y}(R) - \mathcal{Y}(\infty), \quad (57)$$

$$\mathcal{W}^{\text{int}}(R) = \mathcal{W}(R) - \mathcal{W}(\infty). \quad (58)$$

In the separated atoms limit, \mathcal{V} and $\delta\mathcal{V}$ vanish, whereas $\mu_n^2 \mathcal{W}$ and $\mu_n^2 \mathcal{U}$ are equal to $-\frac{1}{4}$ a.u. In this convention, the eigenvalue E of the Hamiltonian in Eq. (52) corresponds to the negative of D_0 .

For convenience, the radial equation (52) was further transformed, using $\eta_J(R) = R\chi_J(R)$, to the following working form

$$\begin{aligned} & \frac{\partial}{\partial R} \frac{1}{\mu_{\parallel}(R)} \frac{\partial}{\partial R} \eta_J(R) \\ & = -2 \left[E - \frac{\mathcal{Z}(R)}{R} - \frac{J(J+1)}{2\mu_{\perp}(R)R^2} \right] \eta_J(R), \end{aligned} \quad (59)$$

with

$$\mathcal{Z}(R) = R\mathcal{Y}^{\text{int}}(R) + \frac{\partial}{\partial R} \mathcal{W}_{\parallel}^{\text{int}}(R). \quad (60)$$

Eq. (59) was solved numerically using the procedure described in Ref. 46 modified by us to account for the variable masses. A significant advantage of the above approach is the possibility of obtaining all the nonadiabatic levels from a single set of the potentials.

V. NUMERICAL RESULTS

Our goal is to obtain as high numerical accuracy of the nonadiabatic corrections as possible. For this reason, we implemented the working formulas of Sec. III and IV in FORTRAN 90 using the 212-bit (~ 64 digits) precision with a support from the quad-double arithmetic QD library.⁴⁷

A. Basis set and matrix elements

To evaluate all the required matrix elements (24) we have employed the James-Coolidge (JC)⁴ basis functions. In recent studies on the ground state BO potential energy of H_2 ⁴³ and on the adiabatic correction⁴⁴, the JC basis has been found very effective in analytic evaluation of all the needed integrals, and has proven to yield highly accurate results. The symmetric JC basis function is of the form

$$\begin{aligned} \psi &= (1 + P_{12})(1 + \hat{i}) \\ & (r_{1A} - r_{1B})^{n_2} (r_{2A} - r_{2B})^{n_3} (r_{1A} + r_{1B})^{n_4} (r_{2A} + r_{2B})^{n_5} \\ & e^{-\beta(r_{1A}+r_{1B}+r_{2A}+r_{2B})} r_{12}^{n_1} R^{-n_1-n_2-n_3-n_4-n_5-3}. \end{aligned} \quad (61)$$

The basis function depends parametrically on the internuclear distance R in two ways: through the explicit power of the internuclear distance R , introduced to ensure that the overlap integrals are dimensionless, and implicitly through the electron-nucleus distances $r_{1A}, r_{1B}, r_{2A}, r_{2B}$. The numerical value of the nonlinear parameter β was optimized with respect to the electronic energy $\mathcal{E}_{\text{el}}(R)$ for each R separately. Proper spin and inversion symmetry (singlet *gerade* for the ground electronic state) of the wave function was imposed using two projectors containing the electron exchange P_{12} and the electron-coordinate inversion \hat{i} operators. In the JC basis, the matrix elements (24) are expressible by combinations of the closed-form functions f derived in Ref. 42

$$\begin{aligned} f(n_1, n_2, n_3, n_4, n_5; R, \beta) &= R^{-n_1-n_2-n_3-n_4-n_5-1} \\ & \int \frac{d^3 r_1}{4\pi} \int \frac{d^3 r_2}{4\pi} \frac{e^{-\beta r_{1A}}}{r_{1A}} \frac{e^{-\beta r_{1B}}}{r_{1B}} \frac{e^{-\beta r_{2A}}}{r_{2A}} \frac{e^{-\beta r_{2B}}}{r_{2B}} \frac{1}{r_{12}^{1-n_1}} \\ & (r_{1A} - r_{1B})^{n_2} (r_{2A} - r_{2B})^{n_3} (r_{1A} + r_{1B})^{n_4} (r_{2A} + r_{2B})^{n_5}, \end{aligned} \quad (62)$$

therefore, their evaluation requires no numerical integration to be involved.

For ψ_k , the k -th element of the basis set, the subscript k can be treated as a multi-index composed of integer exponents $\{n_1, n_2, n_3, n_4, n_5\}$. To simplify the description of the arrangement of the basis set we introduce here an integer parameter Ω related to the exponents n_i by

$$\sum_i n_i \leq \Omega. \quad (63)$$

The parameter Ω is pivotal in the basis set convergence study discussed below. For the evaluation of \mathcal{W}_{\parallel} potential, we split the expansion (22) into two sectors, one limited by Ω and the other by $\Omega - 2$, each with his own nonlinear parameter β and $\{n_i\}$.

B. Convergence of the nonadiabatic potentials

There are five nonadiabatic potentials involved in the radial Schrödinger equation (52): $\mathcal{U}(R)$, $\mathcal{V}(R)$, $\delta\mathcal{V}(R)$, $\mathcal{W}_{\parallel}(R)$, and $\mathcal{W}_{\perp}(R)$. At first, we shall analyze the accuracy of a single-point evaluation of all these potentials. An estimate of the accuracy can be obtained by watching the convergence of given potential with increasing size of the basis set. Table I contains a selection of representative data illustrating the convergence of the nonadiabatic potentials with increasing size of the basis set governed by the shell parameter Ω of Ineq. (63). A general conclusion which can be drawn from these data is that the relative accuracy obtained from the largest expansions is better than 10^{-9} for the whole range of internuclear distances R . Exceptions appear only in the vicinity of those R at which a potential changes its sign. In such a region, the accuracy is lower than that mentioned above but simultaneously the absolute value of the potential itself is close to zero. Both, the reduced resolvent and the matrix elements of the four potentials of Table I were evaluated with the same basis functions used to represent the electronic wave function ϕ_{el} , i.e. the functions of ${}^1\Sigma_g^+$ symmetry. In contrast, the \mathcal{W}_{\perp} potential requires a basis function of Π_g symmetry to represent the resolvent, because of the presence of the \vec{L}_{el} operator raising the angular momentum. In this case we have employed the JC function (61) multiplied by $x_1 + iy_1$. For this reason the convergence of the \mathcal{W}_{\perp} potential depends on two separate expansions. Examples of the convergence are presented in Table II, where the left panel shows the convergence with increasing expansion size of the unperturbed ${}^1\Sigma_g^+$ wave function and the fixed size of the first order correction function, whereas the right panel with the opposite combination of functions. The convergence with the size of the Π_g basis set is apparently slower and determines

the final relative accuracy reached for the $\mathcal{W}_\perp(R)$ but again the accuracy is definitely better than 10^{-9} for all R 's.

TABLE I. A sample of the convergence of the mass-independent nonadiabatic functions (in a.u.) with growing size of JC basis at selected internuclear distances R . Ω is the shell parameter of Eq. (63) and N is the number of basis functions.

Ω	N	$\mu_n^2 \mathcal{U}(0.8)$	$\mu_n^2 \mathcal{U}(1.4)$	$\mu_n^2 \mathcal{U}(6.0)$	$\mu_n^2 \mathcal{U}(12.0)$
16	5301	-0.698 940 569 0	-0.310 003 263 43	-0.257 867 067 598 06	-0.250 010 225 524 99
17	6831	-0.698 940 600 8	-0.310 003 273 13	-0.257 867 067 602 95	-0.250 010 225 530 25
18	8701	-0.698 940 608 0	-0.310 003 275 26	-0.257 867 067 603 87	-0.250 010 225 529 88
19	10956	-0.698 940 609 6	-0.310 003 275 74	-0.257 867 067 604 15	-0.250 010 225 529 75
estim. relative accuracy		$3 \cdot 10^{-9}$	$2 \cdot 10^{-9}$	$2 \cdot 10^{-12}$	$3 \cdot 10^{-13}$
Ω	N	$\mu_n^2 \mathcal{V}(0.8)$	$\mu_n^2 \mathcal{V}(1.4)$	$\mu_n^2 \mathcal{V}(6.0)$	$\mu_n^2 \mathcal{V}(12.0)$
16	5301	+0.325 244 212 96	+0.185 995 802 15	-0.012 637 379 028	-0.000 011 494 697 30
17	6831	+0.325 244 226 98	+0.185 995 808 73	-0.012 637 379 017	-0.000 011 494 711 74
18	8701	+0.325 244 229 93	+0.185 995 810 10	-0.012 637 379 017	-0.000 011 494 713 30
19	10956	+0.325 244 230 62	+0.185 995 810 41	-0.012 637 379 017	-0.000 011 494 713 59
estim. relative accuracy		$3 \cdot 10^{-9}$	$2 \cdot 10^{-9}$	$4 \cdot 10^{-11}$	$3 \cdot 10^{-8}$
Ω	N	$\mu_n^2 \delta\mathcal{V}(0.8)$	$\mu_n^2 \delta\mathcal{V}(1.4)$	$\mu_n^2 \delta\mathcal{V}(6.0)$	$\mu_n^2 \delta\mathcal{V}(12.0)$
16	5301	-0.078 959 645 30	-0.000 049 612 744	+0.000 355 367 878 713	+0.000 000 340 744 777 4
17	6831	-0.078 959 659 00	-0.000 049 612 742	+0.000 355 367 879 519	+0.000 000 340 744 743 6
18	8701	-0.078 959 661 88	-0.000 049 612 742	+0.000 355 367 879 635	+0.000 000 340 744 742 0
19	10956	-0.078 959 662 56	-0.000 049 612 743	+0.000 355 367 879 662	+0.000 000 340 744 741 9
estim. relative accuracy		$9 \cdot 10^{-9}$	$2 \cdot 10^{-8}$	$9 \cdot 10^{-11}$	$3 \cdot 10^{-10}$
$\Omega/\Omega - 2$	N	$\mu_n^2 \mathcal{W}_\parallel(0.8)$	$\mu_n^2 \mathcal{W}_\parallel(1.4)$	$\mu_n^2 \mathcal{W}_\parallel(6.0)$	$\mu_n^2 \mathcal{W}_\parallel(12.0)$
15/13	6324	-0.181 944 170 901 16	-0.192 143 401 019 4	-0.268 758 564 643 1	-0.250 010 683 358 996
16/14	8361	-0.181 944 170 898 96	-0.192 143 401 019 4	-0.268 758 564 649 7	-0.250 010 683 362 978
17/15	10887	-0.181 944 170 898 64	-0.192 143 401 019 4	-0.268 758 564 651 9	-0.250 010 683 362 914
18/16	14002	-0.181 944 170 898 31	-0.192 143 401 019 4	-0.268 758 564 652 7	-0.250 010 683 362 904
estim. relative accuracy		$2 \cdot 10^{-12}$	$3 \cdot 10^{-13}$	$3 \cdot 10^{-12}$	$4 \cdot 10^{-14}$

C. Analytic fits of the nonadiabatic potentials

In the next stage, the numerical values of the nonadiabatic potentials were used to determine the least-square fits of the following functional forms

$$e^{-aR} \sum_{i=0}^{i_{\max}} P_i R^i + e^{-bR-cR^2} \sum_{j=1}^{j_{\max}} Q_j R^j \quad (64)$$

TABLE II. Typical examples of convergence of the mass-independent $\mu_n^2 \mathcal{W}_\perp(R)$ potential (in a.u.) with growing basis set size of both the unperturbed and perturbed wave function at selected internuclear distances R . Ω_0 and Ω_1 are the shell parameters of Eq. (63), whereas N_0 and N_1 symbolize the corresponding number of basis functions. The subscripts '0' or '1' correspond to the unperturbed and the first order correction function, respectively.

$\Omega_1 = 15$ and $N_1 = 11832$				$\Omega_0 = 19$ and $N_0 = 17787$			
Ω_0	N_0	$\mu_n^2 \mathcal{W}_\perp(1.4)$	$\mu_n^2 \mathcal{W}_\perp(12.0)$	Ω_1	N_1	$\mu_n^2 \mathcal{W}_\perp(1.4)$	$\mu_n^2 \mathcal{W}_\perp(12.0)$
16	8361	-0.027 202 029 805 512 0	-0.249 998 747 996 01	12	4480	-0.027 202 029 805 127	-0.249 998 737 19
17	10887	-0.027 202 029 805 513 5	-0.249 998 747 997 80	13	6328	-0.027 202 029 805 466	-0.249 998 747 25
18	14002	-0.027 202 029 805 514 0	-0.249 998 747 997 86	14	8736	-0.027 202 029 805 507	-0.249 998 747 95
19	17787	-0.027 202 029 805 514 1	-0.249 998 747 997 92	15	11832	-0.027 202 029 805 514	-0.249 998 748 00
estim. relative accuracy						$6 \cdot 10^{-13}$	$2 \cdot 10^{-10}$

for short and medium distances $R < R_c$, and

$$\sum_{k=k_{\min}}^{k_{\max}} A_k R^{-k} \quad \text{for } R > R_c. \quad (65)$$

The nonlinear parameters a , b , and c , the linear parameters P_i , Q_j , and A_k , as well as the sum limits and the threshold R_c were selected individually for each nonadiabatic potential. The optimum values of the parameters of potential (64) were determined by the fits to 88 points covering the range $0.1 \leq R/\text{bohr} \leq 12.0$. Table III contains a selection of numerical values of the five potentials in their mass-independent form, whereas the full list of 88 points is deposited in the Supplemental Material.⁴⁸ The parameters pertinent to the long-range formula (65) were fitted to the points from the range $8 \leq R/\text{bohr} \leq 12$. The discrete values of the potentials were shifted beforehand by pertinent atomic values, so that the interaction potentials vanishing in the $R \rightarrow \infty$ limit were obtained (see Eqs (57) and (58)).

The two parts of the potentials were joined together at the internuclear distance R_c , at which we imposed a requirement that both parts as well as their first and second derivatives were the same. The A_k parameters of the long-distance potential were fitted with these constraints, whereas the parameters present in formula (64) were determined freely. We do not present tables with the best fit parameters, instead we supply in the Supplemental Material⁴⁸ several Fortran'90 code routines which evaluate the potentials at an arbitrary internuclear distance.

The fitting procedure is another source of error in the final results and our priority

TABLE III. An excerpt of the full-length table of the nonadiabatic potentials. The numerical values of the potentials correspond to the mass-independent form. All figures displayed are supposed to be exact. Full-length table is available in the Supplemental Material.⁴⁸

R/bohr	$\mu_n^2 \mathcal{W}_{\parallel}(R)$	$\mu_n^2 \mathcal{W}_{\perp}(R)$	$\mu_n^2 \mathcal{U}(R)$	$\mu_n^2 \mathcal{V}(R)$	$\mu_n^2 \delta\mathcal{V}(R)$
0.4	-0.143 550 860 20	-0.002 957 170 260	-2.000 079 5	+0.519 763 56	$-3.683 742 0 \cdot 10^{-1}$
0.8	-0.181 944 170 8983	-0.010 137 821 1172	-0.698 940 61	+0.325 244 231	$-7.895 966 3 \cdot 10^{-2}$
1.4	-0.192 143 401 0194	-0.027 202 029 8055	-0.310 003 276	+0.185 995 810	$-4.961 274 3 \cdot 10^{-5}$
2.0	-0.213 757 395 328	-0.053 144 277 8343	-0.211 804 814	+0.117 115 821	$+1.368 916 3 \cdot 10^{-2}$
2.7	-0.288 087 420 668	-0.097 457 080 0382	-0.187 498 745	+0.063 409 104	$+1.943 650 9 \cdot 10^{-2}$
3.2	-0.363 338 633 46	-0.136 807 508 995	-0.200 371 498	+0.019 329 540	$+2.079 514 38 \cdot 10^{-2}$
3.8	-0.405 638 269 03	-0.182 849 879 952	-0.237 779 769 9	-0.036 627 715 4	$+1.463 931 83 \cdot 10^{-2}$
4.4	-0.369 830 983 118	-0.216 276 864 418	-0.266 019 254 0	-0.053 351 141 8	$+6.321 608 76 \cdot 10^{-3}$
4.8	-0.332 980 176 923	-0.230 071 222 613	-0.269 639 888 81	-0.044 299 463 7	$+3.108 514 65 \cdot 10^{-3}$
6.0	-0.268 758 564 653	-0.246 504 028 951	-0.257 867 067 604	-0.012 637 379 017	$+3.553 678 797 \cdot 10^{-4}$
12.0	-0.250 010 683 3629	-0.249 998 748 0	-0.250 010 225 530	-0.000 011 494 714	$+3.407 447 42 \cdot 10^{-7}$

was to minimize the error even at the expense of the length of analytic expressions (64) and (65). The quality of the obtained fits was characterized by means of the square root of the estimated variance ($10^{-12} < \sigma < 10^{-8}$) and the maximum distortion ($3 \cdot 10^{-12} < \varepsilon < 10^{-8}$).

In order to estimate the error in the rovibrational energy due to the uncertainties in the individual points, for each potential we constructed a fit to the residuals. Such a fit was then added to or subtracted from the main potential and its effect on the rovibrational energy was obtained. On the basis of the above procedure, we estimate that the fitting procedure described above introduces approximately a hundred times greater error than the individual points of the potential, that means the error is about 10^{-7} cm^{-1} .

D. Numerical solution of the radial Schrödinger equation

The analytic nonadiabatic correction potentials, together with the previously reported BO⁴³ and adiabatic correction⁴⁴ potentials, were employed to construct the total nonadi-

abatic potential $\mathcal{Z}(R)$ of Eq. (60). Eq. (59) was integrated numerically on a nonuniform grid⁴⁶

$$r_i = r_0 (e^{t_i} - 1) \quad (66)$$

where

$$t_i = (i - 1)h, \quad i = 1, 2, \dots, N. \quad (67)$$

The grid parameters $r_0 = 0.0001$ bohr, $N = 2400$, $r_N = 40$ bohr, and $h \approx 0.000537$ bohr were adjusted experimentally to permit at least 10^{-7} cm⁻¹ accuracy of the eigenvalues.

To confirm these results we employed additionally the discrete variable representation (DVR) method.⁴⁹ Prior to the construction of the DVR Hamiltonian on $(0, \infty)$ interval, we first transform Eq. (52), using notation of Sec. IV C, to a more convenient form

$$\left[-\frac{\partial}{\partial R} \left(\frac{1}{2\mu_a} + \mathcal{W}_{\parallel}^{\text{int}}(R) \right) \frac{\partial}{\partial R} + \frac{J(J+1)}{R^2} \left(\frac{1}{2\mu_a} + \mathcal{W}_{\perp}^{\text{int}}(R) \right) + \frac{\mathcal{W}_{\parallel}^{\text{int}'}(R)}{R} + \mathcal{Y}(R) \right] \eta_J(R) = E \eta_J(R), \quad (68)$$

where μ_a is a reduced mass of separated atoms. Next, for the grid of radial points $x_i = a + i\frac{b-a}{N}$, $i = 1, \dots, N-1$, we introduce the following associated functions $\tau_n(x_i) = \sqrt{\frac{2}{b-a}} \sin\left(\frac{n\pi i}{N}\right)$. Then, the diagonal and non-diagonal DVR Hamiltonian operators are, respectively,

$$\begin{aligned} H_{jj} &= \frac{1}{2\Delta x} \mathcal{W}_{\parallel}^{\text{int}'}(x_j) \frac{1}{j} \\ &+ \frac{1}{(\Delta x)^2} \left(\frac{1}{2\mu_a} + \mathcal{W}_{\parallel}^{\text{int}}(x_j) \right) \left[\frac{\pi^2}{3} - \frac{1}{2j^2} \right] \\ &+ \frac{J(J+1)}{x_j^2} \left(\frac{1}{2\mu_a} + \mathcal{W}_{\perp}^{\text{int}}(x_j) \right) + \mathcal{Y}(x_j), \end{aligned} \quad (69)$$

$$\begin{aligned} H_{ij} &= (-1)^{i-j} \left\{ \frac{1}{\Delta x} \mathcal{W}_{\parallel}^{\text{int}'}(x_j) \left[\frac{1}{i-j} + \frac{1}{i+j} \right] \right. \\ &\left. + \frac{2}{(\Delta x)^2} \left(\frac{1}{2\mu_a} + \mathcal{W}_{\parallel}^{\text{int}}(x_j) \right) \left[\frac{1}{(i-j)^2} - \frac{1}{(i+j)^2} \right] \right\} \end{aligned} \quad (70)$$

with $\Delta x = \frac{b-a}{N}$.

Another potential source of error affecting the final results comes from the uncertainty in the nuclear mass. The currently most accurate value of the proton mass³⁷ $m_p/m_e = 1836.15267377(17)$ carries the uncertainty at eleventh significant figure. The nuclear masses

for D₂ and T₂ are less accurate and amount to $m_d/m_e = 3\,670.482\,9652(15)$ and $m_t/m_e = 5\,496.921\,5267(50)$, respectively. To establish the influence of this uncertainty on the leading nonadiabatic correction to D_0 of rovibrational levels, the mass parameter was changed by $\pm 1\sigma$, while solving Eq. (59). The observed changes in energy levels were lower than 10^{-8} cm^{-1} for H₂ and $< 3 \cdot 10^{-8}\text{ cm}^{-1}$ for D₂ and T₂.

The main conclusion drawn from this analysis is that the final accuracy of the leading order nonadiabatic corrections is limited by the efficiency of the fitting procedure and equals to 10^{-7} cm^{-1} . Certain room for further improvement still exists and would require using finer grid for single point calculations and refinement of the fitting functions.

In the best available in literature total energy of H₂, the overall error introduced by higher order nonadiabatic corrections, estimated in Ref. 32, and by relativistic and QED corrections (see Ref. 33) is of the order of 10^{-3} cm^{-1} . The results reported in this work, accurate to 10^{-7} cm^{-1} , enable removal of the uncertainties of the leading order nonadiabatic corrections along with the BO and adiabatic correction errors^{43,44} from the overall error budget.

E. Nonadiabatic corrections to rovibrational levels

Our final values of the leading order nonadiabatic corrections to the dissociation energy of the ground level of the symmetric isotopologues of hydrogen molecule are collected in Table IV. For H₂ and D₂ these values agree perfectly with previous estimations (0.4339(2) and 0.1563(2) of Ref. 33) but are three orders of magnitude more accurate. The third value, for T₂, also agrees with 0.0859 obtained by Wolniewicz²⁴ albeit his value has no uncertainty assigned. Extensive tables with the leading order nonadiabatic correction to all rovibrational

TABLE IV. The leading order nonadiabatic corrections to the dissociation energy of the ground level of the symmetric isotopologues of hydrogen molecule. The Rydberg constant $2\text{Ry} = 219\,474.631\,370\,78(110)\text{ cm}^{-1}$ was used to convert D_0 from atomic units to cm^{-1} .

Molecule	$\Delta D_0/\text{cm}^{-1}$
H ₂	0.433 961 8(1)
D ₂	0.156 316 0(3)
T ₂	0.085 966 4(6)

levels of H₂, D₂, and T₂ are available in the Supplemental Material repository.⁴⁸

In the perturbative approach to the nonrelativistic energy employed here, what remains to be established and possibly eliminated is the error originating from the neglect of the higher order terms in the electron-to-nucleus mass ratio. One could expect that in the sequence of H₂, D₂, and T₂, such terms would scale proportionally to the m_e/μ_n factor. In a very simplistic approach to this problem one could estimate these corrections for D_0 of the ground level by multiplying the leading order value by this factor to obtain $5 \cdot 10^{-4} \text{ cm}^{-1}$, $8 \cdot 10^{-5} \text{ cm}^{-1}$, and $3 \cdot 10^{-5} \text{ cm}^{-1}$. Another manner of such estimation relies on subtraction of the total nonadiabatic energy obtained directly in variational calculations⁵⁰⁻⁵² (displayed in Table V) from our perturbative nonadiabatic energy. Such an estimation leads to $6 \cdot 10^{-5} \text{ cm}^{-1}$, $-3 \cdot 10^{-6} \text{ cm}^{-1}$, and $1 \cdot 10^{-6} \text{ cm}^{-1}$. Apparently this series lacks the proper dependence on nuclear mass as is not even monotonic. Perhaps the accuracy of the variational calculations is near the value of the evaluated effect, which prevents a reliable estimation.

VI. CONCLUSIONS

The theoretical total dissociation energy of a molecule can be considered using nonrelativistic QED (NRQED) in which D_0 is composed of several contributions resulting from the expansion in powers of the fine-structure constant. NRQED enables approaching the total D_0 by successively collecting smaller and smaller terms of its expansion. The ultimate error of the theoretical D_0 has then two main sources: one is the cutoff of the perturbational series, and the other is the limited accuracy of determination of the leading terms. This observation sets the strategic directions for improvement in theoretical predictions. The present publication, along with the two preceding articles,^{43,44} aims at increasing the accuracy of the nonrelativistic contribution to D_0 , which appears to be the largest of all the components. This goal has been reached thanks to the improved methodology connected with explicitly correlated exponential wave function. Further development of this method in relation to the relativistic effects is underway in our group. One should realize though that it is insufficient just to increase the accuracy of a particular term of the NRQED expansion. The main factor limiting the accuracy of the predictions are the missing small terms of higher order in α or m_e/M as well as the relativistic recoil terms. Determination of these contributions requires significant theoretical efforts, but once it is successfully performed, the negligible effects, like

TABLE V. Comparison of the leading order nonadiabatic dissociation energy obtained in the present calculations with literature results.

Reference	D_0/cm^{-1}
H_2	
This work, 2015	36 118.797 675
Bubin <i>et al.</i> , 2009 ⁵⁰	36 118.797 74
Bubin, Adamowicz, 2003 ⁵³	36 118.797 552
ECG, 2009 ³²	36 118.797 8
Wolniewicz, 1995 ²⁴	36 118.795
Bishop, Cheung, 1978 ¹⁸	36 118.60
D_2	
This work, 2015	36 749.090 978
Bubin <i>et al.</i> , 2011 ⁵¹	36 749.090 975
ECG, 2009 ³³	36 749.091 0
T_2	
This work, 2015	37 029.224 863
Stanke, Adamowicz, 2014 ⁵²	37 029.224 863
ECG, 2009	37 029.224 9

finite size of the nuclei³⁸ or gerade-ungerade mixing,⁵⁴ will enter then into play.

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