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Nonadiabatic relativistic correction in H_2, D_2, and HD

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We calculate the nonadiabatic relativistic correction to rovibrational energy levels of H_2, D_2, and HD molecules using the nonadiabatic perturbation theory. This approach allows one to obtain nonadiabatic corrections to all the molecular levels with the help of a single effective potential. The obtained results are in very good agreement with the previous direct calculation of nonadiabatic relativistic effects for dissociation energies and resolve the reported discrepancies of theoretical predictions with recent experimental results.

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I. INTRODUCTION

The hydrogen molecule has not yet been used for determination of fundamental physical constants, unlike atomic hydrogen. This is due to difficulties in accurate solution of the molecular Schrödinger equation and an inherence of an electron correlation, combined with relativistic, quantum electrodynamic, and nonadiabatic effects. At the precision level of 10^{-7} cm^{-1}, vibrational excitations are sensitive to uncertainties in the electron-proton mass ratio, in the nuclear charge radii, and in the Rydberg constant. Therefore, from sufficiently accurate theoretical predictions and corresponding measurements, one can obtain those fundamental physical constants.

To deal with the problem of accurate calculation of molecular levels in a systematic manner, one employs the nonrelativistic quantum electrodynamic (NRQED) approach [1], which is a perturbation theory that can be made to agree with the full quantum electrodynamics (QED) up to an arbitrary order in the fine structure constant α. It assumes an expansion of the binding energy in α

$$E(\alpha) = \alpha^2 E^{(2)} + \alpha^4 E^{(4)} + \alpha^5 E^{(5)} + \alpha^6 E^{(6)} + \alpha^7 E^{(7)} + O(\alpha^8), \tag{1}$$

where $E^{(n)}$ is a contribution of order $\alpha^n m$ and may include powers of $\ln\alpha$. Each $E^{(n)}$ can be expressed as an expectation value of some effective Hamiltonian with the nonrelativistic wave function. These expansion terms can, in turn, be expanded further—in another series of the electron-nuclear mass ratio—to obtain the contributions of the Born-Oppenheimer, adiabatic, and nonadiabatic effects. These contributions can be calculated within the so-called nonadiabatic perturbation theory (NAPT) [2].

Significant progress has been achieved in recent years by the accurate ($\sim 10^{-7}$ cm^{-1}) direct solution of the four-body Schrödinger equation [3], while the calculations of relativistic ($\alpha^4 m$), quantum electrodynamic ($\alpha^5 m$), and higher order quantum electrodynamic ($\alpha^6 m$) corrections were performed within the Born-Oppenheimer (BO) approximation. The resulting theoretical predictions happened to be in about $3\,\sigma$ disagreement with recent experimental results. It was suggested, for the resolution of these discrepancies, that an estimate of relativistic nonadiabatic corrections by the factor of the electron-nucleus mass ratio might not be correct. Indeed, very recent fully nonadiabatic calculations for the ground molecular state [4–6] have demonstrated that these corrections are about 10 times larger than expected and explain the apparent discrepancy with measured dissociation energies for H_2 and D_2. For HD, however, a $2\,\sigma$ discrepancy remains and this requires further investigations.

In this paper, we provide the results for the relativistic nonadiabatic correction obtained with a perturbative approach based on NAPT. More important, this method retains the key benefit of the adiabatic approximation—the existence of the potential energy curve, which, calculated once for a given electronic state, can be utilized to easily obtain all rovibrational energies. The obtained results are in a very good agreement with the direct calculation of nonadiabatic relativistic correction for the ground molecular state and explain almost all previously reported discrepancies for various transition energies.

II. DERIVATION OF FORMULAS

We pass now to the derivation of formulas for the nonadiabatic relativistic correction. The Schrödinger equation for a bielectronic, binuclear molecule, written in a center-of-mass frame, with the origin in the geometric center of the nuclei, is

$$(H + H_{\rm n} - E^{(2)})\,|\Psi(\vec r_1, \vec r_2, \vec R)\rangle = 0, \tag{2}$$

where

$$H = -\frac{1}{2}\big(\vec\nabla_1^2 + \vec\nabla_2^2\big) + V, \tag{3}$$

$$V = -\frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R}, \tag{4}$$

$$H_{\rm n} = -\frac{1}{2\mu_{\rm n}}\big(\vec\nabla_R^2 + \vec\nabla_{\rm el}^2\big) + \left(\frac{1}{M_A} - \frac{1}{M_{\rm B}}\right)\vec\nabla_R\vec\nabla_{\rm el}, \tag{5}$$

and where 1, 2 indices denote electrons, A, B indicate nuclei, the nuclear reduced mass $\mu_{\rm n} = M_A M_{\rm B}/(M_A + M_{\rm B})$, $\vec R = \vec R_A - \vec R_B$, and $\vec\nabla_{\rm el} = (\vec\nabla_1 + \vec\nabla_2)/2$. In homonuclear

2469-9926/2018/98(5)/052506(8)

molecules, such as H_2 or D_2, the last term in H_n vanishes, whereas in HD it is present. However, it is neglected anyway because it contributes in the second order of the electron-nuclear mass ratio, while our calculations of relativistic nonadiabatic corrections are performed only to the first order. The magnitude of these neglected terms is estimated in Sec. VII and verified against nonperturbative calculations for the ground molecular state [4–6].

The function $\Psi(\vec r_1, \vec r_2, \vec R)$ in Eq. (2) is the solution of the full Schrödinger equation for H_2, describing both the electrons and the nuclei. Here, however, we employ the NAPT formalism and represent the wave function as

$$\Psi(\vec r_1, \vec r_2, \vec R) = \psi(\vec r_1, \vec r_2)\chi(\vec R) + \delta\Psi_{na}(\vec r_1, \vec r_2, \vec R), \tag{6}$$

where the matrix element in the electron space vanishes $\langle\delta\Psi_{na}|\psi\rangle = 0$, and $\psi(\vec r_1, \vec r_2)$ is an eigenfunction of the electronic Schrödinger equation

$$H\,|\psi\rangle = \mathcal{E}^{(2,0)}(R)\,|\psi\rangle\,, \tag{7}$$

with the eigenvalue dependent on the internuclear distance R. The function χ satisfies the following nuclear equation:

$$\left[-\frac{\nabla_R^2}{2\,\mu_\mathrm{n}} + \mathcal{E}^{(2,0)}(R) - E^{(2,0)}\right]\chi(\vec R) = 0. \tag{8}$$

For convenience, from now on we will denote $\mathcal{E}(R) \equiv \mathcal{E}^{(2,0)}(R)$. The leading finite nuclear correction is given by

$$E^{(2,1)} = \langle\chi|\mathcal{E}^{(2,1)}(R)|\chi\rangle, \tag{9}$$

where $\mathcal{E}^{(2,1)}$ is the expectation value of H_n, known as the adiabatic correction,

$$\begin{aligned}\mathcal{E}^{(2,1)}(R) &= \langle\psi|H_\mathrm{n}|\psi\rangle\\ &= \frac{1}{2\mu_\mathrm{n}}\,\langle\vec\nabla_R\psi|\vec\nabla_R\psi\rangle + \frac{1}{2\mu_\mathrm{n}}\,\langle\vec\nabla_\mathrm{el}\psi|\vec\nabla_\mathrm{el}\psi\rangle\,.\end{aligned} \tag{10}$$

This correction is known with a high accuracy from Ref. [7]. The remainder $\delta\Psi_\mathrm{na}$ will not be needed because we calculate here only the leading corrections in the electron nuclear mass ratio.

In analogy to the nonrelativistic energies, the relativistic BO correction is an expectation value of the Breit-Pauli Hamiltonian with the electronic wave function

$$\mathcal{E}^{(4,0)}(R) = \langle\psi|H^{(4,0)}|\psi\rangle\,, \tag{11}$$

where

$$\begin{aligned}H^{(4,0)} = &-\frac{p_1^4 + p_2^4}{8} - \frac{1}{2}\,p_1^i\left(\frac{\delta^{ij}}{r_{12}} + \frac{r_{12}^i r_{12}^j}{r_{12}^3}\right)p_2^j + \pi\,\delta^3(r_{12})\\ &+ \frac{\pi}{2}\big[\delta^3(r_{1A}) + \delta^3(r_{2A}) + \delta^3(r_{1B}) + \delta^3(r_{2B})\big].\end{aligned} \tag{12}$$

It has recently been recalculated with a high accuracy in Ref. [8]. The topic of this work is a combined, nonadiabatic-relativistic correction $\mathcal{E}^{(4,1)}(R)$, which is represented as a sum of three terms,

$$\mathcal{E}^{(4,1)}(R) = \frac{1}{\mu_\mathrm{n}}\big[\mathcal{E}_1^{(4,1)}(R) + \mathcal{E}_2^{(4,1)}(R) + \mathcal{E}_3^{(4,1)}(R)\big], \tag{13}$$

where

$$\mathcal{E}_1^{(4,1)}(R) = \langle\vec\nabla_R\psi_\mathrm{rel}|\vec\nabla_R\psi\rangle\,, \tag{14}$$

$$\mathcal{E}_2^{(4,1)}(R) = -\,\langle\psi_\mathrm{rel}|\vec\nabla_\mathrm{el}^2|\psi\rangle\,, \tag{15}$$

$$\mathcal{E}_3^{(4,1)}(R) = \mu_\mathrm{n}\,\langle\psi|H_M^{(4,1)}|\psi\rangle\,, \tag{16}$$

and where

$$|\psi_\mathrm{rel}\rangle = \frac{1}{(\mathcal{E} - H)'}H^{(4,0)}\,|\psi\rangle\,, \tag{17}$$

$$H_M^{(4,1)} = -\sum_{a=1,2}\sum_{N=A,B}\frac{1}{2\,M_N}\nabla_a^i\left(\frac{\delta^{ij}}{r_{aN}} + \frac{r_{aN}^i r_{aN}^j}{r_{aN}^3}\right)\nabla_N^j. \tag{18}$$

In our coordinate system, with the center-of-mass at rest and the origin in the geometric center of the nuclei, $H_M^{(4,1)}$ takes the form

$$\begin{aligned}H_M^{(4,1)} = &-\frac{1}{4\mu_\mathrm{n}}\sum_{a=1,2}\nabla_a^i\left(\frac{\delta^{ij}}{r_{aA}} + \frac{r_{aA}^i r_{aA}^j}{r_{aA}^3} - \frac{\delta^{ij}}{r_{aB}} - \frac{r_{aB}^i r_{aB}^j}{r_{aB}^3}\right)\nabla_R^j\\ &+ \frac{1}{4\mu_\mathrm{n}}\sum_{a=1,2}\nabla_a^i\left(\frac{\delta^{ij}}{r_{aA}} + \frac{r_{aA}^i r_{aA}^j}{r_{aA}^3} + \frac{\delta^{ij}}{r_{aB}} + \frac{r_{aB}^i r_{aB}^j}{r_{aB}^3}\right)\nabla_\mathrm{el}^j.\end{aligned} \tag{19}$$

Potentials $\mathcal{E}_1^{(4,1)}$ and $\mathcal{E}_3^{(4,1)}$ involve $\vec\nabla_R$—a gradient with respect to the internuclear vector $\vec R$. It should be handled properly, which is described in the next section.

III. NUCLEAR GRADIENTS

We consider at first $\vec\nabla_R$ acting on the nonrelativistic wave function. It can be obtained by differentiation of the Shrödinger equation

$$\vec\nabla_R\,|\psi\rangle = \frac{1}{(\mathcal{E} - H)'}\vec\nabla_R(V)\,|\psi\rangle = \vec n\;|\psi_\mathrm{a}\rangle - \vec n \times |\vec\psi_\mathrm{a}\rangle\,, \tag{20}$$

where $\vec n = \vec R/R$ and

$$|\psi_\mathrm{a}\rangle = \vec n\cdot\vec\nabla_R\,|\psi\rangle = \frac{\vec n}{(\mathcal{E} - H)'}\vec\nabla_R(V)\,|\psi\rangle\,, \tag{21}$$

$$|\vec\psi_\mathrm{a}\rangle = \vec n \times \vec\nabla_R\,|\psi\rangle = \frac{1}{(\mathcal{E} - H)'}\vec n \times \vec\nabla_R(V)\,|\psi\rangle\,, \tag{22}$$

and where

$$\vec\nabla_R(V) = \frac{1}{2}\left(-\frac{\vec r_{1A}}{r_{1A}^3} + \frac{\vec r_{1B}}{r_{1B}^3} - \frac{\vec r_{2A}}{r_{2A}^3} + \frac{\vec r_{2B}}{r_{2B}^3}\right) - \frac{\vec R}{R^3}\,. \tag{23}$$

The analogous derivative of ψ_rel would be quite complicated, and therefore we recast the expression for $\mathcal{E}_1^{(4,1)}$ into a more tractable form as follows:

$$\mathcal{E}_1^{(4,1)}(R) = \vec\nabla_R\,\langle\psi_\mathrm{rel}|\vec\nabla_R\psi\rangle - \langle\psi_\mathrm{rel}|\vec\nabla_R^2|\psi\rangle\,. \tag{24}$$

The first term above can be evaluated by numerical differentiation:

$$\vec\nabla_R\,\langle\psi_\mathrm{rel}|\vec\nabla_R|\psi\rangle = \frac{1}{R^2}\frac{\partial}{\partial R}\big(R^2\,\langle\psi_\mathrm{rel}|\psi_\mathrm{a}\rangle\big)\,. \tag{25}$$

In practical application, it is done by polynomial interpolation of $\langle\psi_{\rm rel}|\psi_{\rm a}\rangle$ and a subsequent derivative.

The second term in Eq. (24) is obtained as follows,

$$\vec{\nabla}_R^{\,2}\,|\psi\rangle = |\psi_{\rm na}\rangle + c\,|\psi\rangle\,, \tag{26}$$

where

$$|\psi_{\rm na}\rangle = \frac{1}{(\mathcal{E}-H)'} \times\left[\vec{\nabla}^2_R(V)\,|\psi\rangle + 2\,\vec{\nabla}_R(V-\mathcal{E})\frac{1}{(\mathcal{E}-H)'}\vec{\nabla}_R(V)\,|\psi\rangle\right] \tag{27}$$

is orthogonal to $|\psi\rangle$, and

$$\vec{\nabla}^2_R(V) = \pi[\delta^3(r_{1A})+\delta^3(r_{2A})+\delta^3(r_{1B})+\delta^3(r_{2B})], \tag{28}$$

$$\vec{\nabla}_R(\mathcal{E}) = \langle\psi|\vec{\nabla}_R(V)|\psi\rangle\,. \tag{29}$$

The term $c\,|\psi\rangle$ in Eq. (26) would appear next to a reduced resolvent from $|\psi_{\rm rel}\rangle$ in Eq. (24), so it does not contribute. Next, we decompose the second resolvent into Σ and Π parts. Such partition enables one to represent the resolvent in states of specific symmetry, which simplifies the numerical implementation. Gathering it all together, we obtain the following transformed form of Eq. (24),

$$\mathcal{E}_1^{(4,1)}(R) = \frac{1}{R^2}\frac{\partial}{\partial R}(R^2\,\langle\psi_{\rm rel}|\psi_{\rm a}\rangle) - \langle\psi_{\rm rel}|\psi_{\rm na}\rangle\,, \tag{30}$$

where

$$\begin{aligned}|\psi_{\rm na}\rangle =& \frac{1_{\Sigma^+}}{(\mathcal{E}-H)'}\,\vec{\nabla}^2_R(V)\,|\psi\rangle\\ &+2\,\frac{1_{\Sigma^+}}{(\mathcal{E}-H)'}\vec{n}\cdot\vec{\nabla}_R(V-\mathcal{E})\,|\psi_{\rm a}\rangle\\ &+2\,\frac{1_{\Sigma^+}}{(\mathcal{E}-H)'}\vec{n}\times\vec{\nabla}_R(V)\,|\vec{\psi}_{\rm a}\rangle\,.\end{aligned} \tag{31}$$

The analogous separation of intermediate states of definite symmetry is performed for Eq. (19):

$$\begin{aligned}\mathcal{E}_3^{(4,1)}(R) =& \frac{1}{4}\sum_{a=1,2}\Bigg[\langle\psi|\nabla_a^i\left(\frac{\delta^{ij}}{r_{aA}}+\frac{r_{aA}^i r_{aA}^j}{r_{aA}^3}+\frac{\delta^{ij}}{r_{aB}}+\frac{r_{aB}^i r_{aB}^j}{r_{aB}^3}\right)\nabla_{\rm el}^j|\psi\rangle - \langle\psi|n^j\nabla_a^i\left(\frac{\delta^{ij}}{r_{aA}}+\frac{r_{aA}^i r_{aA}^j}{r_{aA}^3}-\frac{\delta^{ij}}{r_{aB}}-\frac{r_{aB}^i r_{aB}^j}{r_{aB}^3}\right)|\psi_{\rm a}\rangle\\ &-\langle\psi|\epsilon^{mkj}n^k\nabla_a^i\left(\frac{\delta^{ij}}{r_{aA}}+\frac{r_{aA}^i r_{aA}^j}{r_{aA}^3}-\frac{\delta^{ij}}{r_{aB}}-\frac{r_{aB}^i r_{aB}^j}{r_{aB}^3}\right)|\psi_{\rm a}^m\rangle\Bigg],\end{aligned} \tag{32}$$

while $\mathcal{E}_2^{(4,1)}$ does not need any further transformations.

IV. REGULARIZATION

The Breit-Pauli Hamiltonian contains singular type operators, like Dirac δ and p^4, whose matrix elements have slow numerical convergence. For this reason, we perform a regularization that is based on various expectation value identities [9] (see also Ref. [10]). In the case of Gaussian basis, due to a poor representation of the wave function at coalescence points, the regularization improves the convergence dramatically [8]. These identities are the following:

$$\begin{aligned}4\pi\delta^3(r_{1A}) =& \frac{4}{r_{1A}}(\mathcal{E}-V) - \vec{p}_1\frac{2}{r_{1A}}\vec{p}_1 - \vec{p}_2\frac{2}{r_{1A}}\vec{p}_2\\ &+\left\{\frac{2}{r_{1A}}, H-\mathcal{E}\right\},\end{aligned} \tag{33}$$

$$\begin{aligned}p_1^4+p_2^4 =& 4(\mathcal{E}-V)^2 - 2p_1^2p_2^2 + 4(H-\mathcal{E})^2\\ &+4\{\mathcal{E}-V, H-\mathcal{E}\}.\end{aligned} \tag{34}$$

Furthermore, should the $p_1^2p_2^2$ in the above expression act on a wave function that satisfies the Kato's cusp condition, the arising $\delta^3(r_{12})$ function cancels out exactly with that from the Breit-Pauli Hamiltonian and the remainder will be denoted by $\tilde{p}_1^2\,\tilde{p}_2^2$. This regularization has been already employed in calculations of the BO relativistic corrections [8]. The only, but important, difference is that now the Breit-Pauli Hamiltonian acts on a wave function other than the reference state's, and subsequently the terms in the anticommutators cannot be neglected.

After making use of the above formulas, we obtain

$$H^{(4,0)} = [H^{(4,0)}]_r + \{Q, H-\mathcal{E}\} - \frac{1}{2}(H-\mathcal{E})^2, \tag{35}$$

$$\begin{aligned}[H^{(4,0)}]_r =& -\frac{1}{2}(\mathcal{E}-V)\left(\mathcal{E}-\frac{1}{R}-\frac{1}{r_{12}}\right)\\ &+\frac{1}{4}\left(\tilde{p}_1^2\tilde{p}_2^2 + p_1\tilde{V}p_1 + p_2\tilde{V}p_2\right)\\ &-\frac{1}{2}p_1^i\left(\frac{\delta^{ij}}{r_{12}}+\frac{r_{12}^i r_{12}^j}{r_{12}^3}\right)p_2^j,\end{aligned} \tag{36}$$

and

$$\vec{\nabla}^2_R(V) = \left[\vec{\nabla}^2_R(V)\right]_r - \tfrac{1}{2}\{\tilde{V}, H-\mathcal{E}\}, \tag{37}$$

$$\left[\vec{\nabla}^2_R(V)\right]_r = -(\mathcal{E}-V)\tilde{V} + \tfrac{1}{2}\,p_1\tilde{V}p_1 + \tfrac{1}{2}\,p_2\tilde{V}p_2, \tag{38}$$

where

$$Q = -\frac{1}{2}(\mathcal{E}-V) - \frac{1}{4}\tilde{V}, \tag{39}$$

$$\tilde{V} = -\frac{1}{r_{1A}} - \frac{1}{r_{2A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2B}}. \tag{40}$$

V. NUMERICAL CALCULATIONS

The calculations were performed with a variational wave function represented as a linear combination

$$|\psi\rangle = \sum_i c_i \psi_i(\vec{r}_1, \vec{r}_2), \tag{41}$$

$$\psi_i = (1 + \hat{\imath})(1 + P_{1\leftrightarrow 2})\phi_i(\vec{r}_1, \vec{r}_2), \tag{42}$$

where $\hat{\imath}$ is an inversion operator and $P_{1\leftrightarrow 2}$ exchanges the electrons. The basis functions $\phi_i(\vec{r}_1, \vec{r}_2)$ are of the explicitly correlated Gaussian (ECG) type

$$\phi_{\Sigma^+} = e^{-a_{1A} r_{1A}^2 - a_{1B} r_{1B}^2 - a_{2A} r_{2A}^2 - a_{2B} r_{2B}^2 - a_{12} r_{12}^2}, \tag{43}$$

$$\vec{\phi}_\Pi = \vec{n} \times \vec{r}_{1A}\, \phi_{\Sigma^+}, \tag{44}$$

where the parameters a_{1A}, a_{2A}, a_{1B}, a_{2B}, and a_{12} were optimized individually for each basis function. In addition, for the ground-state wave function we employed the so-called rECG basis

$$\phi'_{\Sigma^+} = (1 + r_{12}/2)\, e^{-a_{1A} r_{1A}^2 - a_{1B} r_{1B}^2 - a_{2A} r_{2A}^2 - a_{2B} r_{2B}^2 - a_{12} r_{12}^2}, \tag{45}$$

which satisfies exactly the interelectronic cusp condition. It significantly improves the numerical convergence and allows for algebraic cancellation of the $\delta^3(r_{12})$ term from the Breit-Pauli Hamiltonian. Both kinds of Gaussian bases have been used before in Refs. [5,8]. All the integrals can be performed either analytically or, in the worst case, numerically with fast extended Gaussian quadrature [11]. As a consequence, we can achieve high accuracy with a reasonable low computational cost.

The method for performing integrals has been already described extensively in Refs. [8,12], but—for the sake of completeness—we repeat the main formulas. All the matrix elements needed can be written down as linear combinations of f's:

$$\begin{aligned} f(n_1, n_2, n_3, n_4, n_5) &= \frac{1}{\pi^3} \int d^3 r_1 \int d^3 r_2\, r_{1A}^{n_1} r_{1B}^{n_2} r_{2A}^{n_3} r_{2B}^{n_4} r_{12}^{n_5} \\ &\quad \times e^{-c_{1A} r_{1A}^2 - c_{1B} r_{1B}^2 - c_{2A} r_{2A}^2 - c_{2B} r_{2B}^2 - c_{12} r_{12}^2}. \end{aligned} \tag{46}$$

The integrals with even powers of the interparticle distance can be obtained by differentiation over the variational parameters of the "master" integral

$$f(0, 0, 0, 0, 0) = A^{-3/2} e^{-R^2 \frac{B}{A}}, \tag{47}$$

where

$$A = (c_{1A} + c_{1B} + c_{12})(c_{2A} + c_{2B} + c_{12}) - c_{12}^2, \tag{48}$$

$$\begin{aligned} B &= (c_{1B} + c_{1A}) c_{2A} c_{2B} + c_{1A} c_{1B} (c_{2A} + c_{2B}) \\ &\quad + c_{12}(c_{1A} + c_{2A})(c_{1B} + c_{2B}). \end{aligned} \tag{49}$$

If one of the n_k indices is odd, the ECG integrals can also be obtained analytically by differentiation of other master integrals. As an example, the master integral for $n_1 = -1$ is

$$f(-1, 0, 0, 0, 0) = \frac{1}{A\sqrt{A_1}}\, e^{-R^2 \frac{B}{A}} F\left[R^2\left(\frac{B_1}{A_1} - \frac{B}{A}\right)\right], \tag{50}$$

where $A_1 = \partial_{c_{1A}} A$, $B_1 = \partial_{c_{1A}} B$, and $F(x) = \mathrm{erf}(x)/x$. Molecular ECG integrals, as opposed to the atomic case, have no known analytic form when two or more n_k indices are odd. In this case, we use the quadrature adapted to the end-point logarithmic singularity [11], which has fast numerical convergence.

Eventually, for a given basis size N, we had to optimize eight different sets. The first two, with and without the cusp, are for the ground electronic state and correspond to optimization of the ground state energy $\mathcal{E}(R) = \langle\psi|H|\psi\rangle$. The next four basis sets are for intermediate states with the following matrix elements:

$$\langle\psi|\, [H^{(4,0)}]_r \frac{1}{(\mathcal{E} - H)'} [H^{(4,0)}]_r \,|\psi\rangle\,, \tag{51}$$

$$\langle\psi|\, \vec{n} \cdot \vec{\nabla}_R (V - \mathcal{E}) \frac{1}{(\mathcal{E} - H)'} \vec{n} \cdot \vec{\nabla}_R (V - \mathcal{E}) \,|\psi\rangle\,, \tag{52}$$

$$\langle\psi|\, \vec{n} \times \vec{\nabla}_R (V) \frac{1}{(\mathcal{E} - H)} \vec{n} \times \vec{\nabla}_R (V) \,|\psi\rangle\,, \tag{53}$$

$$\langle\psi|\, [\vec{\nabla}_R^2 (V)]_r \frac{1}{(\mathcal{E} - H)'} [\vec{\nabla}_R^2 (V)]_r \,|\psi\rangle\,, \tag{54}$$

which can be directly optimized. The last two basis sets are for intermediate states with

$$\langle\psi_{\rm a}|\, \vec{n} \cdot \vec{\nabla}_R (V - \mathcal{E}) \frac{1}{(\mathcal{E} - H)'} \vec{n} \cdot \vec{\nabla}_R (V - \mathcal{E}) \,|\psi_{\rm a}\rangle\,, \tag{55}$$

$$\langle\vec{\psi}_{\rm a}|\, \vec{n} \times \vec{\nabla}_R (V) \frac{1}{(\mathcal{E} - H)'} \vec{n} \times \vec{\nabla}_R (V) \,|\vec{\psi}_{\rm a}\rangle\,. \tag{56}$$

To ensure proper subtraction of the ground state from the reduced resolvents, we extended each Σ_+ basis with a fixed sector consisting of $N/2$ basis functions optimized for the ground state without a cusp. Its nonlinear variational parameters were kept constant and were not further optimized.

The calculations were performed for three different basis sizes, $N = 128$, 256, 512, to observe numerical convergence and estimate the corresponding uncertainty. The electronic $\mathcal{E}^{(4,1)}(R)$ potential was calculated for 59 points in the range of 0–8 a.u. Results are presented in Table I and plotted in Fig. 1. The exact value at $R = 0$, $\mathcal{E}^{(4,1)}(0) = -1.079\,69$ a.u., is deduced from the relativistic recoil for helium atom, while at $R \to \infty$ it behaves like $\sim 1/R^4$.

VI. NUCLEAR SCHRÖDINGER EQUATION

To obtain the total energy levels, one represents $\chi(\vec{R})$ as

$$\chi(\vec{R}) = \frac{\chi(R)}{R}\, Y_{lm}(\vec{n}) \tag{57}$$

and solves the radial nuclear Schrödinger equation for $\chi(R)$ in the following form,

$$H_{\rm N}\, \chi(R) = E^{(2,0)} \chi(R), \tag{58}$$

$$H_{\rm N} = -\frac{1}{2\mu_{\rm n}} \frac{d^2}{dR^2} + \mathcal{E}(R) + \frac{J(J+1)}{2\mu_{\rm n} R^2}, \tag{59}$$

TABLE I. The mass-independent nonadiabatic relativistic correction $2\mu_{\rm n}\mathcal{E}^{(4,1)}$ (in a.u.) for different values of the internuclear distance R (in a.u., for 512 basis size). For most of the points, the last digit is uncertain.

R	$2\mu_{\rm n}\mathcal{E}^{(4,1)}$	R	$2\mu_{\rm n}\mathcal{E}^{(4,1)}$
0.0	−1.079 69	2.1	−0.122 89
0.05	−0.761	2.15	−0.107 12
0.1	−0.5116	2.2	−0.091 78
0.15	−0.3847	2.3	−0.062 21
0.2	−0.383 85	2.4	−0.034 67
0.25	−0.433 56	2.5	−0.008 80
0.3	−0.505 79	2.6	0.014 69
0.4	−0.630 36	2.7	0.035 88
0.5	−0.702 97	2.8	0.054 42
0.6	−0.725 41	2.9	0.069 94
0.7	−0.713 63	3.0	0.082 16
0.8	−0.681 06	3.2	0.097 14
0.9	−0.637 11	3.4	0.099 47
1.0	−0.587 82	3.6	0.091 98
1.1	−0.537 03	3.8	0.078 60
1.2	−0.486 52	4.0	0.063 08
1.3	−0.437 70	4.2	0.048 65
1.4	−0.390 85	4.4	0.036 55
1.45	−0.368 28	4.6	0.027 37
1.5	−0.346 24	4.8	0.020 32
1.6	−0.304 09	5.0	0.015 45
1.65	−0.283 70	5.2	0.011 82
1.7	−0.263 96	5.4	0.009 19
1.75	−0.244 62	5.6	0.007 30
1.8	−0.225 83	5.8	0.005 90
1.85	−0.207 76	6.0	0.004 91
1.9	−0.189 95	6.5	0.003 13
1.95	−0.172 52	7.0	0.002 05
2.0	−0.155 56	7.5	0.001 43
2.05	−0.139 04	8.0	0.001 11

where J is the rotational quantum number. We solve it numerically with a discrete variable representation (DVR) method [13] and obtain a numerical representation of $\chi(R)$ for a specific molecular state. Note that in some of our previous works we used an adiabatically corrected nuclear function, which may lead to slight differences between the values presented in this work and the previous ones. The results of this work clearly demonstrate that, as a result of cancellation between different nuclear mass corrections in Eq. (62), the proper choice for χ is the BO potential without the adiabatic correction—Eq. (59).

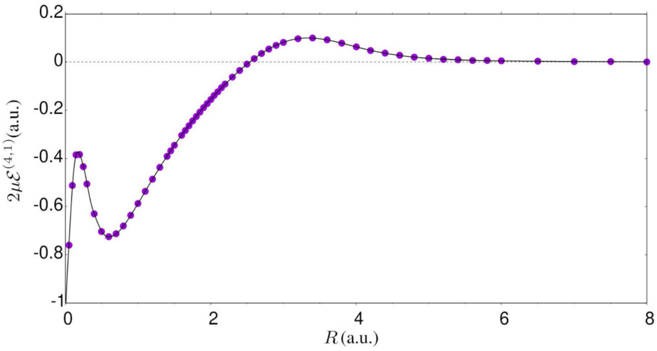

FIG. 1. Mass-independent nonadiabatic relativistic correction $2\mu\mathcal{E}^{(4,1)}$ for the ground electronic state as a function of the internuclear distance R.

The nuclear wave function $\chi(R)$ is subsequently used to calculate the $\alpha^4 m$ relativistic correction, according to the following formulas:

$$E^{(4)} = E^{(4,0)} + E^{(4,1)}, \tag{60}$$

$$E^{(4,0)} = \langle\chi|\mathcal{E}^{(4,0)}(R)|\chi\rangle\,, \tag{61}$$

$$E^{(4,1)} = \langle\chi|\mathcal{E}^{(4,1)}(R)|\chi\rangle + 2\,\langle\chi|\delta\chi\rangle\,, \tag{62}$$

where

$$|\delta\chi\rangle = \mathcal{E}^{(4,0)}(R)\frac{1}{(E^{(2,0)} - H_{\rm n})'}\mathcal{E}^{(2,1)}(R)\,|\chi\rangle\,. \tag{63}$$

The electronic potentials $\mathcal{E}^{(2,1)}(R)$ from Ref. [7], $\mathcal{E}^{(4,0)}(R)$ from Ref. [8], and $\mathcal{E}^{(4,1)}(R)$ from this work were evaluated on evenly spaced (0.05 a.u.) grid of 200 points and subsequently used in DVR calculation of matrix elements. After testing different interpolation schemes, we settled on using the ninth-order piecewise Hermite interpolation. We observed that the interpolation introduces a relatively significant error to our results, which could be removed in future via proper analytic fits to $\mathcal{E}^{(4,0)}(R)$ and $\mathcal{E}^{(4,1)}(R)$.

We extrapolate $E^{(4,0)}$, $2\,\langle\chi|\delta\chi\rangle$, and $\langle\chi|\mathcal{E}^{(4,1)}(R)|\chi\rangle$ separately, from the results with progressing basis size, and utilize the following model,

$$E(N) = \frac{A}{N^k} + E(\infty), \tag{64}$$

where N is the basis set size and A and $E(\infty)$ are fitted parameters. We used $k = 2$ for $\langle\chi|\mathcal{E}^{(4,1)}(R)|\chi\rangle$ and $k = 3$ in the two other cases. The choice of k is based on the observation of convergence of individual terms. The extrapolation error is estimated conservatively to be 50% of the difference between the results with the two largest basis sets.

VII. RESULTS AND DISCUSSION

The total relativistic contribution $E^{(4)}$ to the dissociation energy of H_2, HD, and D_2 in comparison to fully

TABLE II. Convergence of $\langle\chi|\mathcal{E}^{(4,1)}(R)|\chi\rangle$ contribution to the dissociation energy (in cm^{-1}). The remaining components of $E^{(4)}$, Eq. (60), are also shown for completeness. The uncertainties of the final $E^{(4)}$ values contain an estimate of the higher order nonadiabatic effects of the order $E^{(4,1)}/\mu_{\rm n}$.

Basis	H_2	HD	D_2
128	0.002 376 07	0.001 794 00	0.001 205 590
256	0.002 370 19	0.001 789 61	0.001 202 694
512	0.002 368 67	0.001 788 48	0.001 201 951
∞	0.002 368(1)	0.001 788(1)	0.001 201 7(4)
$2\,\langle\chi|\delta\chi\rangle$	−0.000 451 1	−0.000 342 0	−0.000 230 9
$E^{(4,1)}$	0.001 917(1)	0.001 446(1)	0.000 970 8(4)
$E^{(4,0)}$	−0.533 130(1)	−0.531 334(1)	−0.529 179(1)
$E^{(4)}$	−0.531 213(2)	−0.529 888(2)	−0.528 208(1)
naECG [5]	−0.531 215 6(5)	−0.529 887 5(2)	−0.528 206 1(1)
Difference	0.000 003(2)	−0.000 001(2)	−0.000 002(1)

TABLE III. Contributions to the dissociation energy of the first rotationally excited level $(v, J) = (0, 1)$ and to two selected transitions in H_2 (in cm^{-1}), in comparison to experimental values. $E^{(2)}_{\rm rel} \sim \alpha^6 m$ is a second-order correction to relativistic BO potential, which in former works was automatically included in $\alpha^4 m$; $E_{\rm FS}$ is the finite nuclear size correction with $r_p = 0.84087(39)$ fm [16].

Contribution/(v, J)	(0,1)	$(3, 5) \to (0, 3)$	$(1, 0) \to (0, 0)$	References
$\alpha^2 m$	36 000.312 485 66(6)	12 559.749 918 95(8)	4 161.163 977 09(6)	[3], [8], [8]
$\alpha^4 m$	−0.533 796(2)	0.065 878(8)	0.023 554(2)	[7] + [8] + this work
$\alpha^5 m$	−0.194 00(21)	−0.065 81(7)	−0.021 32(2)	[8] + [17]
$\alpha^6 m$	−0.002 058(6)	−0.000 599(1)	−0.000 192	[12]
$E^{(2)}_{\rm rel}$	0.000 009	0.000 004	0.000 001	[8]
$\alpha^7 m$	0.000 117(59)	0.000 037(19)	0.000 012(6)	[8]
$E_{\rm FS}$	−0.000 031	−0.000 010	−0.000 003	[8]
Total	35 999.582 73(22)	12 559.749 42(7)	4 161.166 03(2)	
Experiment	35 999.582 894(25)	12 559.749 52(5)	4 161.166 36(15)	[18], [19], [20]
Difference	−0.000 16(22)	−0.000 10(9)	−0.000 33(15)	

nonadiabatic naECG calculations from Ref. [5] is shown in Table II. The $E^{(4,0)}$ values were obtained as expectation values of the potential from Ref. [8] with a BO nuclear function χ. We used the recommended CODATA values [14] for the mass ratios $m_{\rm p}/m_{\rm e} = 1836.152\,673\,89(17)$ and $m_{\rm d}/m_{\rm e} = 3670.482\,967\,85(13)$, as well as for the fine structure $\alpha = 7.297\,352\,566\,4(17) \times 10^{-3}$ and Rydberg $R_\infty = 10\,973\,731.568\,508(65)$ m^{-1} constants. The uncertainty of theoretical results contains the interpolation and extrapolation errors, as well as the neglected higher order nonadiabatic corrections estimated by $E^{(4,1)}/\mu_{\rm n}$.

A good agreement between results of the naECG from Ref. [5] and of NAPT obtained here for the ground molecular state (see Table II) justifies the perturbative approach, the main advantage of which is the common potential $\mathcal{E}^{(4,1)}(R)$ for all the rovibrational states of all isotopes of molecular hydrogen in the ground electronic state.

The $\alpha^n m$ contributions with $n = 5, 6, 7$ in the following tables are expectation values of the potentials from the references given in the last column, with the BO nuclear wave function χ. While all the $\alpha^n m$ contributions are calculated according to known formulas, the formula for $\alpha^7 m$ correction is yet unknown. Their values presented in Tables III–V are only estimates, hence the 50% error, based on the leading term analogous as in atomic hydrogen, namely [15]

$$H^{(7)} \approx -[\delta^3(r_{1A}) + \delta^3(r_{2A}) + \delta^3(r_{1B}) + \delta^3(r_{2B})]\ln^2(\alpha^{-2}). \tag{65}$$

TABLE IV. Contributions to selected transitions in HD (in cm^{-1}). $E^{(2)}_{\rm rel} \sim \alpha^6 m$ is a second-order correction due to relativistic BO potential, which in former works was automatically included in $\alpha^4 m$. $E_{\rm FS}$ is the finite nuclear size correction with $r_p = 0.84087(39)$ fm [16] and $r_d = 2.12771(22)$ fm [21]. There are two additional measurements of $(2, 2) \to (0, 1)$ transition, namely 7 241.849 386(3) cm^{-1} [22] and 7 241.849 345 6(32) [23], which are in disagreement with that in the table.

Contribution/(v, J)	$(1, 0) \to (0, 0)$	$(0, 1) \to (0, 0)$	$(1, 1) \to (0, 1)$	References
$\alpha^2 m$	3 632.158 204 27(1)	89.226 757 95(1)	3 628.302 279 75(1)	[24]
$\alpha^4 m$	0.020 999(1)	0.001 950 56(1)	0.020 856(1)	[7] + [8] + this work
$\alpha^5 m$	− 0.018 64(2)	− 0.000 770 9(6)	− 0.018 60(2)	[8] + [17]
$\alpha^6 m$	− 0.000 168	− 0.000 006 74(1)	− 0.000 168	[12]
$E^{(2)}_{\rm rel}$	0.000 001	0.000 000 06	0.000 001	[8]
$\alpha^7 m$	0.000 010(5)	0.000 000 43(22)	0.000 010(5)	[8]
$E_{\rm FS}$	− 0.000 010	− 0.000 000 43	− 0.000 010	[8]
Total	3 632.160 40(2)	89.227 930 9(6)	3 628.304 37(2)	
Experiment	3 632.160 52(22)	89.227 931 6(8)	3 628.304 50(22)	[20], [25], [20]
Difference	− 0.000 12(22)	− 0.000 000 7(10)	− 0.000 13(22)	
Contribution/(v, J)	$(2, 2) \to (0, 1)$	$(2, 3) \to (0, 2)$	$(2, 4) \to (0, 3)$	References
$\alpha^2 m$	7 241.846 168 22(2)	7 306.479 554 52(2)	7 361.899 285 85(1)	[24]
$\alpha^4 m$	0.040 927(4)	0.041 927(3)	0.042 559(3)	[7] + [8] + this work
$\alpha^5 m$	− 0.037 46(3)	− 0.037 97(3)	− 0.038 38(3)	[8] + [17]
$\alpha^6 m$	− 0.000 339	− 0.000 343	− 0.000 347	[12]
$E^{(2)}_{\rm rel}$	0.000 002	0.000 002	0.000 002	[8]
$\alpha^7 m$	0.000 021(11)	0.000 021(11)	0.000 022(11)	[8]
$E_{\rm FS}$	− 0.000 021	− 0.000 021	− 0.000 021	[8]
Total	7 241.849 30(3)	7 306.483 17(3)	7 361.903 12(3)	
Experiment	7 241.849 356 16(67)	7 306.483 227 84(93)	7 361.903 178 73(93)	[26]
Difference	− 0.000 06(3)	− 0.000 06(3)	− 0.000 06(3)	

TABLE V. Contributions to selected transitions in D_2 (in cm^{-1}). $E_{\mathrm{rel}}^{(2)} \sim \alpha^6 m$ is a second-order correction due to relativistic BO potential, which in former works was automatically included in $\alpha^4 m$. E_{FS} is the finite nuclear size correction with $r_d = 2.12771(22)$ fm [21].

Contribution/(v, J)	$(2, 4) \to (0, 2)$	$(1, 0) \to (0, 0)$	$(1, 2) \to (0, 2)$	References
$\alpha^2 m$	6 241.120 920(1)	2 993.614 856 52(4)	2 987.291 387 6(2)	[27], this work, this work
$\alpha^4 m$	0.040 173 9(15)	0.017 732 2(2)	0.017 498	[7] + [8] + this work
$\alpha^5 m$	– 0.033 167(18)	– 0.015 397(8)	– 0.015 33(1)	[8] + [17]
$\alpha^6 m$	– 0.000 298 9(2)	– 0.000 138 7(1)	– 0.000 138	[12]
$E_{\mathrm{rel}}^{(2)}$	0.000 001 9	0.000 000 9	0.000 001	[8]
$\alpha^7 m$	0.000 019(10)	0.000 008 6(43)	0.000 009(4)	[8]
E_{FS}	– 0.000 031 5	– 0.000 014 6	– 0.000 015	[8]
Total	6 241.127 617(21)	2 993.617 048(9)	2 987.293 41(1)	
Experiment	6 241.127 647(11)	2 993.617 06(15)	2 987.293 52(15)	[27], [20], [20]
Difference	– 0.000 030(24)	– 0.000 01(15)	– 0.000 11(15)	

The expectation values of the Dirac δ were taken from Ref. [8]. They were used also in the evaluation of the correction due to the finite nuclear size [15]:

$$E_{\mathrm{FS}} = \alpha^4 \frac{2\pi}{3}[\delta^3(r_{1A}) + \delta^3(r_{2A}) + \delta^3(r_{1B}) + \delta^3(r_{2B})] \times \frac{(r_A^2 + r_B^2)}{2}, \tag{66}$$

where $r_{A/B}$ is the root-mean-square charge radius of the A/B nucleus. The higher order effects due to the nuclear size or nuclear polarizability are negligible at the current precision level, which we know from the atomic hydrogen and deuterium [15].

In Table III, we present the theoretical predictions for the dissociation energy of $v = 0$, $J = 1$ state of H_2, and two selected transitions in comparison to the most accurate experimental data. We find an agreement for the dissociation energy of the former level and for the $(3, 5) \to (0, 3)$ transition energy, whereas for the $(1, 0) \to (0, 0)$ transition a 2σ disagreement persists. For this reason, the experimental value for this transition should be verified.

Because all the relativistic and QED corrections are calculated through effective potentials, they can be employed to obtain all the rovibrational energies of all isotopes of the hydrogen molecule for the ground electronic state. In Tables IV and V, we present results for a selection of transitions in HD and D_2 which have been measured with a high accuracy. In general, we observe very good agreement between theoretical and experimental data, except for the series of $R_2(J)$ transitions in HD, presented in the lower panel of Table IV, which requires further investigations.

VIII. CONCLUSIONS

The main achievement of this work is a significant reduction of the contribution to the total error budget coming from the nonadiabatic relativistic (recoil) effects. As a result, the current main source of theoretical uncertainty is the unknown combined QED and nonadiabatic correction, which is estimated by the ratio of the electron to the reduced nuclear masses $1/\mu_{\mathrm{n}}$. We have already undertaken calculation of this missing term. Once this contribution is known, the main uncertainty will come from the approximate value of the $\alpha^7 m$ term, accurate calculation of which is very challenging. If these calculations are accomplished, together with the leading nonadiabatic $\alpha^6 m$ correction, one can use precisely measured transitions in the molecular hydrogen to determine fundamental physical constants, such as the proton-electron mass ratio or the nuclear charge radii, for which discrepant values have been obtained in the literature.

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