

Relativistic correction from the four-body nonadiabatic exponential wave function

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Abstract

We present a method for calculating the relativistic correction in hydrogen molecules that significantly exceeds the accuracy of all the previous literature results. This method utilizes the explicitly correlated nonadiabatic exponential wave function, and thus treats electrons and nuclei equivalently. The proposed method can be applied to any rovibrational state, including highly excited ones. The numerical precision of the relativistic correction reaches several kHz ($\sim 10^{-7} \text{ cm}^{-1}$), which is below the best experimental accuracy.

1 Introduction

Since the dawn of quantum mechanics, the measurements of the hydrogen molecule spectra have been used to verify the computational methods. Modern spectroscopic experiments determine the dissociation energy of the H_2 molecule with an accuracy of $10^{-5} - 10^{-4} \text{ cm}^{-1}$.¹⁻³ Measurements of transitions between rovibrational levels reach even higher accuracy, of the

order of $10^{-7} - 10^{-6} \text{ cm}^{-1}$.⁴⁻¹⁰ Achieving similar accuracy in theoretical calculations is a severe challenge. Currently, it is possible to construct a non-relativistic wave function that fully accounts for electronic correlation and the coupling of the motion of nuclei and electrons,¹¹ allowing for an accuracy better than 10^{-7} cm^{-1} for non-relativistic energy.¹²⁻¹⁵ This study aims to devise a method for achieving similar accuracy for the relativistic correction.

The significance of relativistic effects in the dissociation energy $D_{0,0}$ of the hydrogen molecule has been recognized long ago. In 1959, Ladik¹⁶ approached, although not very successfully, this issue and estimated the relativistic correction as $\approx -30 \text{ cm}^{-1}$. Fröman,¹⁷ using a simplistic model binding the relativistic correction with the non-relativistic energy, arrived at $+7 \text{ cm}^{-1}$ as an estimated relativistic correction. An upper bound to this correction $< -1.4 \text{ cm}^{-1}$, was obtained by Kołos and Wolniewicz.^{18,19} The dispersion of these results, found without the use of any computer, reveals the theoretical challenges faced by the pioneering researchers in this field. Only in 1964, Kołos and Wolniewicz conducted computer-assisted calculations of the relativistic correction to $D_{0,0}$ in H_2 . They obtained the first reliable estimate of this value as -0.5 cm^{-1} ,^{20,21} in disagreement with their previous upper bound. After a 30-year hiatus, Wolniewicz revisited this topic and, using more accurate wave functions and new algorithms for calculating integrals, he obtained a value of -0.5330 cm^{-1} , which confirmed the previous estimate.²² Advances in computing power, wave function optimization, and techniques for accelerating the convergence of relativistic expectation values²³ have enabled systematic improvements in the accuracy of relativistic corrections. Over time, the contribution of the finite mass of the nuclei has also been taken into account, either perturbatively²⁴ or variationally.²⁵⁻²⁷

2 Relativistic correction

Let us now introduce a formal theory of molecular levels. The total energy of a rovibrational level of a light molecule with vibrational (v) and rotational (J) quantum numbers can be

expressed as a series in powers of the fine structure constant α :

$$E^{(v,J)} = \alpha^2 E_{\text{nr}}^{(v,J)} + \alpha^4 E_{\text{rel}}^{(v,J)} + \alpha^5 E_{\text{qed}}^{(v,J)} + \dots, \quad (1)$$

where expansion coefficients may involve powers of $\ln \alpha$. The coefficients are commonly interpreted as, respectively, the nonrelativistic, relativistic, quantum electrodynamic, etc., components of the energy and can be determined in the framework of the quantum electrodynamic (QED) theory.

The primary objective of this work is to accurately calculate $E_{\text{rel}}^{(v,J)}$ – the relativistic correction for rovibrational states of H_2 and its isotopologues. This correction is given by

the expectation value of the mass-dependent Breit-Pauli Hamiltonian

$$E_{\text{rel}}^{(v,J)} = \langle \Psi | H_{\text{BP}} | \Psi \rangle$$

$$\equiv MV + D_{\text{ee}} + D_{\text{en}} + B_{\text{ee}} + B_{\text{en}} + B_{\text{nn}} \quad (2)$$

$$MV = \left\langle \Psi \left| -\frac{p_1^4}{8m^3} - \frac{p_2^4}{8m^3} - \frac{p_A^4}{8m_A^3} - \frac{p_B^4}{8m_B^3} \right| \Psi \right\rangle \quad (3)$$

$$D_{\text{ee}} = \left\langle \Psi \left| \frac{\pi}{m^2} \delta^{(3)}(r_{12}) \right| \Psi \right\rangle \quad (4)$$

$$D_{\text{en}} = \left\langle \Psi \left| \frac{\pi}{2} \left(\frac{1}{m^2} + \frac{\delta_{IA}}{m_A^2} \right) (\delta^{(3)}(r_{1A}) + \delta^{(3)}(r_{2A})) \right. \right. \\ \left. \left. + \frac{\pi}{2} \left(\frac{1}{m^2} + \frac{\delta_{IB}}{m_B^2} \right) (\delta^{(3)}(r_{1B}) + \delta^{(3)}(r_{2B})) \right| \Psi \right\rangle \quad (5)$$

$$B_{\text{ee}} = \left\langle \Psi \left| -\frac{1}{2m^2} p_1^i \left(\frac{\delta^{ij}}{r_{12}} + \frac{r_{12}^i r_{12}^j}{r_{12}^3} \right) p_2^j \right| \Psi \right\rangle \quad (6)$$

$$B_{\text{nn}} = \left\langle \Psi \left| -\frac{1}{2m_A m_B} p_A^i \left(\frac{\delta^{ij}}{r_{AB}} + \frac{r_{AB}^i r_{AB}^j}{r_{AB}^3} \right) p_B^j \right| \Psi \right\rangle \quad (7)$$

$$B_{\text{en}} = \left\langle \Psi \left| \frac{1}{2m m_A} p_1^i \left(\frac{\delta^{ij}}{r_{1A}} + \frac{r_{1A}^i r_{1A}^j}{r_{1A}^3} \right) p_A^j \right. \right. \\ + \frac{1}{2m m_B} p_1^i \left(\frac{\delta^{ij}}{r_{1B}} + \frac{r_{1B}^i r_{1B}^j}{r_{1B}^3} \right) p_B^j \\ + \frac{1}{2m m_A} p_2^i \left(\frac{\delta^{ij}}{r_{2A}} + \frac{r_{2A}^i r_{2A}^j}{r_{2A}^3} \right) p_A^j \\ \left. \left. + \frac{1}{2m m_B} p_2^i \left(\frac{\delta^{ij}}{r_{2B}} + \frac{r_{2B}^i r_{2B}^j}{r_{2B}^3} \right) p_B^j \right| \Psi \right\rangle \quad (8)$$

with the nonrelativistic wave function Ψ . This wave function is obtained by solving the Schrödinger equation with the nonrelativistic Hamiltonian H

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{p_A^2}{2m_A} + \frac{p_B^2}{2m_B} + \frac{1}{r_{12}} + \frac{1}{r_{AB}} \\ - \frac{1}{r_{1A}} - \frac{1}{r_{2A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2B}}. \quad (9)$$

In the above equations, the subscripts A and B that appear alongside the symbols of mass (m), momentum (p), and coordinate (r) are associated with the nuclei, while the subscripts

1 and 2 are associated with the electrons. The nuclear-spin factor δ_I , present in D_{en} , depends on the nucleus' spin I : δ_I equals 1 when $I = 1/2$, and 0 otherwise. It comes from the so-called Darwin term for the spin 1/2 particles. In $\langle \Psi | H_{\text{BP}} | \Psi \rangle$ we have omitted all the electron spin-dependent terms because they vanish for the ground electronic state of ${}^1\Sigma_g^+$ symmetry. We have also omitted the nuclear-spin-dependent terms because we do not consider the fine and hyperfine structure in the present paper. Lastly, the term proportional to the nucleus-nucleus Dirac delta, involving strong interactions, is left out due to its negligible value.

3 Wave function

We utilize the direct nonadiabatic (DNA) approach,¹¹ with the wave function Ψ expanded in the basis of the nonadiabatic James-Coolidge (naJC) functions that are introduced in this section. Formally, the nonadiabatic wave function Ψ^J of a rotational level J contains terms depending also on the quantum number M , which represents the projection of the total angular momentum \vec{J} on the axis Z of the laboratory frame. We shall use expectation values averaged over M

$$\langle \Psi^J | \hat{O} | \Psi^J \rangle = \frac{1}{2J+1} \sum_{M=-J}^J \langle \Psi^{J,M} | \hat{O} | \Psi^{J,M} \rangle, \quad (10)$$

which is equivalent to neglecting the fine and hyperfine structure. When the rotational angular momentum of nuclei couples to the electronic angular momentum \vec{L} , it forms the total angular momentum \vec{J} of the molecule. Therefore, the wave function should reflect this coupling by involving components relevant to appropriate electronic states. To distinguish between such states, we use the quantum number Λ , which is the eigenvalue of $\vec{n} \cdot \vec{L}$ (\vec{n} is defined below Eq. (15)), and the inversion symmetry symbol g or u (for gerade or ungerade). These states include $\Sigma_{g,u}$, $\Pi_{g,u}$, $\Delta_{g,u}$, etc., and they correspond to $|\Lambda| = 0, 1, 2, \dots$, respectively. The general wave function is thus represented as a sum of components with

increasing Λ

$$\Psi^{J,M} = \Psi_{\Sigma_g}^{J,M} + \Psi_{\Sigma_u}^{J,M} + \Psi_{\Pi_g}^{J,M} + \Psi_{\Pi_u}^{J,M} + \Psi_{\Delta_g}^{J,M} + \Psi_{\Delta_u}^{J,M} + \dots \quad (11)$$

In the evaluation of expectation values of H_{BP} , we limit the expansion (11) to Σ and Π terms. It is fully justified because each Λ -component of the wave function enters with a power of electron-to-reduced-nuclear-mass ratio, $(m/\mu_{AB})^{|\Lambda|}$, thus we neglect terms with factors of $(m/\mu_{AB})^4 \approx 10^{-12}$, which are much smaller than our target numerical uncertainty for the relativistic correction.

The functions $\Psi_{\Lambda}^{J,M}$ are represented as linear expansions

$$\Psi_{\Lambda}^{J,M} = \sum_{\{k\}} c_{\{k\}} \mathcal{A}_{12} \psi_{\{k\},\Lambda}^{J,M} \quad (12)$$

in the following four-particle nonadiabatic James-Coolidge (naJC) basis functions

$$\psi_{\{k\},\Lambda}^{J,M} = \mathcal{Q}_{\Lambda} e^{-\alpha R - \beta(\zeta_1 + \zeta_2)} R^{k_0} r_{12}^{k_1} \eta_1^{k_2} \eta_2^{k_3} \zeta_1^{k_4} \zeta_2^{k_5} \quad (13)$$

with $\zeta_1 = r_{1A} + r_{1B}$, $\eta_1 = r_{1A} - r_{1B}$, $\zeta_2 = r_{2A} + r_{2B}$, $\eta_2 = r_{2A} - r_{2B}$, and $\vec{R} = \vec{r}_{AB}$. α and β denote nonlinear variational parameters, and k_i are non-negative integers collectively denoted as $\{k\}$. The inversion symmetry of the state is encoded in the sum of the two exponents $k_2 + k_3$. The basis function is symmetric with respect to the inversion when this sum is even and antisymmetric when it is odd. The preexponential factor \mathcal{Q}_{Λ} depends explicitly on the quantum numbers J and M , and determines the electronic angular momentum to which the basis function pertains

$$\mathcal{Q}_{\Sigma} = \mathcal{Y}_J^M(\vec{n}) \quad \text{for } J \geq 0, \quad (14)$$

$$\mathcal{Q}_{\Pi} = \sqrt{\frac{2}{J(J+1)}} R \rho^i \nabla_R^i \mathcal{Y}_J^M(\vec{n}) \quad \text{for } J \geq 1, \quad (15)$$

where $\vec{\rho} \equiv \vec{\rho}_1$ or $\vec{\rho}_2$, $\rho_a^i = (\delta^{ij} - n^i n^j) r_{aA}^j$, and $n^i \equiv R^i/R$, and where the Einstein summation convention was assumed. The solid harmonic \mathcal{Y}_J^M , which carries the angular part of the nuclear variables, is related to the spherical harmonic by $\mathcal{Y}_J^M(\vec{n}) = R^J Y_J^M(\vec{n})$. The remaining, ‘electronic’ part of the basis function will be denoted $\phi_{\{k\}}$, so that in short

$$\psi_{\{k\},\Lambda}^{J,M} = \mathcal{Q}_\Lambda \phi_{\{k\}}. \quad (16)$$

In Eq. (12), the antisymmetry projector $\mathcal{A}_{12} = \frac{1}{2}(1 \pm P_{12})$, where the symbol P_{12} denotes the electron permutation operator and the internal sign is adapted to the electronic spin of the state. Finally, the linear coefficients $c_{\{k\}}$ are determined variationally by solving the eigenvalue problem in the matrix form.

Details on the wave function properties, on evaluation of the nonrelativistic matrix elements, and on solving the general symmetric eigenvalue problem, were described in¹¹⁻¹⁴ and will not be repeated here.

4 Matrix elements

In the following sections, we are going to discuss evaluation of the matrix elements

$$\frac{4\pi}{2J+1} \sum_{M=-J}^J \langle \psi_{\{k\},\Lambda}^{J,M} | \hat{\mathcal{O}} | \psi_{\{l\},\Lambda'}^{J,M} \rangle \quad (17)$$

of subsequent operators $\hat{\mathcal{O}}$ that compose the Breit-Pauli Hamiltonian. To reduce the computational cost, we consider such an operator $\hat{\mathcal{O}}$, which commutes with \mathcal{A}_{12} . The factor 4π in Eq. (17) comes from an implicit integration over angles of \vec{R} , which from now on is pulled out in front of all matrix elements.

4.1 Reduction of the angular dependence

Summation over M makes use of an addition theorem for spherical harmonics, which in our notation reads

$$\begin{aligned} \frac{4\pi}{2J+1} \sum_{M=-J}^J [\mathcal{Y}_J^M(\vec{n}')]^* \mathcal{Y}_J^M(\vec{n}) &= R'^J R^J P_J(\vec{n}' \cdot \vec{n}) \\ &\equiv \mathcal{P}_J(\vec{R}', \vec{R}), \end{aligned} \quad (18)$$

where P_J is the Legendre polynomial expressible in terms of the hypergeometric function ${}_2F_1$

$$\begin{aligned} \mathcal{P}_J(\vec{R}', \vec{R}) &= R'^J R^J P_J(\vec{n}' \cdot \vec{n}) \\ &= R'^J R^J {}_2F_1\left(-J, J+1, 1, \frac{1}{2}(\vec{n}' \cdot \vec{n} - 1)\right) \end{aligned} \quad (19)$$

suitable for symbolic differentiation at $\vec{R}' = \vec{R}$. Such a differentiation, $\nabla_{R'}^i \nabla_R^j \dots \mathcal{P}_J(\vec{R}', \vec{R})|_{\vec{R}'=\vec{R}}$, yields factors that explicitly depend on J . A list of such factors is placed in Appendix A.

For example, for an operator $\hat{\mathcal{O}}_{\text{el}}$, which contains no nuclear derivative, the reduction is as follows

$$\begin{aligned} &\frac{4\pi}{2J+1} \sum_{M=-J}^J \left\langle \psi_{k,\Sigma}^{JM}(R) \left| \hat{\mathcal{O}}_{\text{el}} \right| \psi_{l,\Sigma}^{JM}(R) \right\rangle \\ &= \frac{4\pi}{2J+1} \sum_{M=-J}^J \left\langle \mathcal{Y}_J^M(\vec{n}') \phi_k(R') \left| \hat{\mathcal{O}}_{\text{el}} \right| \mathcal{Y}_J^M(\vec{n}) \phi_l(R) \right\rangle_{\vec{R}'=\vec{R}} \\ &\stackrel{(18)}{=} \left\langle \phi_k(R) \left| \mathcal{P}_J(\vec{R}', \vec{R}) \right|_{\vec{R}'=\vec{R}} \hat{\mathcal{O}}_{\text{el}} \left| \phi_l(R) \right\rangle \\ &\stackrel{(36)}{=} \left\langle \phi_k(R) \left| R^{2J} \hat{\mathcal{O}}_{\text{el}} \right| \phi_l(R) \right\rangle. \end{aligned} \quad (20)$$

For $-\nabla_R^2$ we get

$$\begin{aligned}
& \frac{4\pi}{2J+1} \sum_{M=-J}^J \left\langle \nabla_R^i \psi_{k,\Sigma}^{JM}(R) \left| \nabla_R^i \psi_{l,\Sigma}^{JM}(R) \right. \right\rangle \\
&= \frac{4\pi}{2J+1} \sum_{M=-J}^J \left\langle \nabla_{R'}^i \mathcal{Y}_J^M(\vec{n}') \phi_k(R') \left| \nabla_R^i \mathcal{Y}_J^M(\vec{n}) \phi_l(R) \right. \right\rangle_{\vec{R}'=\vec{R}} \\
&\stackrel{(18)}{=} \left\langle \nabla_{R'}^i \nabla_R^i \left[\phi_k(R') \left| \mathcal{P}_J(\vec{R}', \vec{R}) \right| \phi_l(R) \right] \right\rangle_{\vec{R}'=\vec{R}} \\
&= \left\langle \nabla_R^i \phi_k(R) \left| \nabla_R^i \mathcal{P}_J(\vec{R}', \vec{R}) \right|_{\vec{R}'=\vec{R}} \phi_l(R) \right\rangle \\
&\quad + \left\langle \nabla_R^i \phi_k(R) \left| \mathcal{P}_J(\vec{R}', \vec{R}) \right|_{\vec{R}'=\vec{R}} \nabla_R^i \phi_l(R) \right\rangle \\
&\quad + \left\langle \phi_k(R) \left| \nabla_{R'}^i \nabla_R^i \mathcal{P}_J(\vec{R}', \vec{R}) \right|_{\vec{R}'=\vec{R}} \phi_l(R) \right\rangle \\
&\quad + \left\langle \phi_k(R) \left| \nabla_{R'}^i \mathcal{P}_J(\vec{R}', \vec{R}) \right|_{\vec{R}'=\vec{R}} \nabla_R^i \phi_l(R) \right\rangle \\
&\stackrel{A}{=} \left\langle \nabla_R^i \phi_k(R) \left| R^{2J} \right| \nabla_R^i \phi_l(R) \right\rangle, \tag{21}
\end{aligned}$$

and similarly for a Π state

$$\begin{aligned}
& \frac{4\pi}{2J+1} \sum_{M=-J}^J \left\langle \nabla_R^i \psi_{k,\Pi}^{JM}(R) \left| \nabla_R^i \psi_{l,\Pi}^{JM}(R) \right. \right\rangle \\
&= \left\langle \nabla_R^i \phi_k \left| \rho'^j R^{2J} \rho^j \right| \nabla_R^i \phi_l \right\rangle. \tag{22}
\end{aligned}$$

The elementary matrix elements $\left\langle \phi_k \left| \hat{O} \phi_l \right. \right\rangle$ were evaluated using symbolic algebra software Wolfram Mathematica²⁸ and coded in Fortran 95. In general, such matrix elements may contain thousands of terms, which prevents its explicit presentation. The simplest example

of such a matrix element is the overlap integral

$$\begin{aligned}
& \langle \phi_k | \phi_l \rangle \\
&= \frac{1}{16} \left(G(t, u; \{n_0 + 1, n_1 + 1, n_2, n_3, n_4 + 2, n_5 + 2\}) \right. \\
&\quad - G(t, u; \{n_0 + 1, n_1 + 1, n_2, n_3 + 2, n_4 + 2, n_5\}) \\
&\quad - G(t, u; \{n_0 + 1, n_1 + 1, n_2 + 2, n_3, n_4, n_5 + 2\}) \\
&\quad \left. + G(t, u; \{n_0 + 1, n_1 + 1, n_2 + 2, n_3 + 2, n_4, n_5\}) \right)
\end{aligned} \tag{23}$$

expressed by the basic integrals G defined below.

4.2 Integrals in the nonadiabatic James-Coolidge basis

Matrix elements of the nonrelativistic Hamiltonian in the naJC basis are expressible by integrals of the form

$$\begin{aligned}
G(t, u; \{n_i\}) &= \int dV \frac{e^{-tR} e^{-u(\zeta_1 + \zeta_2)}}{R r_{12} r_{1A} r_{1B} r_{2A} r_{2B}} \\
&\quad \times R^{n_0} r_{12}^{n_1} \eta_1^{n_2} \eta_2^{n_3} \zeta_1^{n_4} \zeta_2^{n_5}.
\end{aligned} \tag{24}$$

Techniques developed by one of the authors to find such integrals were described in Refs. [29,30](#). However, calculating the matrix elements of the Breit-Pauli Hamiltonian requires a

more extensive set of integrals, including those with a square of a variable in the denominator

$$G_{AB}(t, u; \{n_i\}) = \int dV \frac{e^{-tR} e^{-u(\zeta_1+\zeta_2)}}{R^2 r_{12} r_{1A} r_{1B} r_{2A} r_{2B}} \times R^{n_0} r_{12}^{n_1} \eta_1^{n_2} \eta_2^{n_3} \zeta_1^{n_4} \zeta_2^{n_5}, \quad (25)$$

$$G_{12}(t, u; \{n_i\}) = \int dV \frac{e^{-tR} e^{-u(\zeta_1+\zeta_2)}}{R r_{12}^2 r_{1A} r_{1B} r_{2A} r_{2B}} \times R^{n_0} r_{12}^{n_1} \eta_1^{n_2} \eta_2^{n_3} \zeta_1^{n_4} \zeta_2^{n_5}, \quad (26)$$

$$G_{1B}(t, u; \{n_i\}) = \int dV \frac{e^{-tR} e^{-u(\zeta_1+\zeta_2)}}{R r_{12} r_{1A} r_{1B}^2 r_{2A} r_{2B}} \times R^{n_0} r_{12}^{n_1} \eta_1^{n_2} \eta_2^{n_3} \zeta_1^{n_4} \zeta_2^{n_5}. \quad (27)$$

The remaining integrals (G_{1A} , G_{2A} , and G_{2B}) can be obtained by permuting variables. A method for determining all such extended integrals has recently been invented,³¹ enabling the evaluation of the relativistic correction within the framework of the DNA approach using the naJC wave function.

In the following sections we shall describe methods of regularization of the relativistic operators contained in H_{BP} : the mass velocity, the Dirac delta, and the orbit-orbit (Breit) interaction.

5 Mass velocity MV

The first expectation value we are going to consider consists of four p^4 operators, each pertinent to one particle, see Eq. (3). First, we will subject it to a transformation that aims to avoid intractable integrals and speed up its numerical convergence with the increasing basis set size. For this purpose, we will add to the formula (3) a null term of the form

$$\langle \Psi | \hat{Q}(E - \hat{H}) + (E - \hat{H})\hat{Q} | \Psi \rangle = 0. \quad (28)$$

In the above equation, \hat{H} is the nonrelativistic Hamiltonian (9) with the eigenvalue E and the eigenfunction Ψ , while \hat{Q} is an arbitrary operator. Assuming

$$\begin{aligned}\hat{Q} = & -\frac{1}{8m^2}p_1^2 - \frac{1}{8m^2}p_2^2 - \frac{1}{8m_A^2}p_A^2 - \frac{1}{8m_B^2}p_B^2 \\ & + \frac{1}{4m}(E - \hat{V}),\end{aligned}\tag{29}$$

we eliminate all p^4 terms and the slowly convergent $p_a^2(E - \hat{V})$ terms. As a result, the expectation value (3) can be expressed as a sum of five terms

$$\begin{aligned}MV = & \frac{1}{4m^3} \langle p_1^2 \Psi | p_2^2 \Psi \rangle + \frac{1}{8m} \left\langle (p_1^2 + p_2^2) \Psi \left| \left(\frac{p_A^2}{\mu_A m_A} + \frac{p_B^2}{\mu_B m_B} \right) \Psi \right. \right\rangle + \frac{1}{8\mu_{AB} m_A m_B} \langle p_A^2 \Psi | p_B^2 \Psi \rangle \\ & - \frac{1}{8} \left(\left\langle [\lambda_A p_A^2 + \lambda_B p_B^2] \Psi \left| (E - \hat{V}) \Psi \right. \right\rangle + \left\langle (E - \hat{V}) \Psi \left| [\lambda_A p_A^2 + \lambda_B p_B^2] \Psi \right. \right\rangle \right) \\ & - \frac{1}{2m} \left\langle (E - \hat{V}) \Psi \left| (E - \hat{V}) \Psi \right. \right\rangle \equiv \sum_{i=1}^5 MV_i,\end{aligned}\tag{30}$$

where the following mass factors were used: $\mu_{AB} = \frac{m_A m_B}{m_A + m_B}$, $\mu_X = \frac{m_X m}{m_X + m}$, and $\lambda_X = \frac{1}{m_X} \left(\frac{1}{m_X} - \frac{1}{m} \right)$. All these expectation values can be calculated using the extended set of integrals mentioned in Sec. 4.2. Because their matrix elements are calculated with basis functions $\psi_{k,\Lambda}^{J,M}$ of both $\Lambda = \Sigma$ and $\Lambda = \Pi$, three kinds of such matrix elements have to be considered: $\Sigma - \Sigma$, $\Pi - \Pi$, and $\Pi - \Sigma$. For each kind, the reduction of the angular variables yields a different combination of elementary matrix elements in the ϕ_k basis. Examples of such matrix elements are presented in Appendix B.

The numerical convergence of the five terms composing the regularized formula (30) is presented in Table 1. As can be inferred from this table, at least eight significant figures can be achieved for these components, and the extrapolated total MV is converged up to nine significant figures. The absolute accuracy of this expectation value is limited by the uncertainty of the $\langle p_1^2 \Psi | p_2^2 \Psi \rangle$ term.

Table 1: Convergence of the five terms of Eq. (30) composing the expectation value MV , Eq. (3). Calculations performed (in a.u.) using the nonadiabatic James-Coolidge (naJC) wave function for the ground rovibrational level of H_2 with the nuclear mass $M/m = 1836.15267343(11)$.³² K is the size of the naJC basis set employed, governed by Ω – the largest shell enabled.

Ω	K	MV_1	$MV_2 \cdot 10^3$	$MV_3 \cdot 10^8$	$MV_4 \cdot 10^3$	MV_5	MV
11	61 152	0.324991 868 26	3.843 967 596	1.082 552 031 65	3.880 833 262	-1.958 628 773 53	-1.625 912 093 58
12	85 904	0.324991 895 48	3.843 967 558	1.082 552 031 21	3.880 833 241	-1.958 628 767 62	-1.625 912 060 51
13	117 936	0.324991 905 85	3.843 967 592	1.082 552 031 06	3.880 833 259	-1.958 628 767 61	-1.625 912 050 09
14	159 120	0.324991 910 53	3.843 967 568	1.082 552 031 89	3.880 833 246	-1.958 628 766 49	-1.625 912 044 33
	∞	0.324991 916 (5)	3.843 967 6(1)	1.082 552 032 (1)	3.880 833 25(3)	-1.958 628 767 (1)	-1.625 912 039 (5)
Rel. uncert.		$2 \cdot 10^{-8}$	$3 \cdot 10^{-8}$	$9 \cdot 10^{-10}$	$8 \cdot 10^{-9}$	$5 \cdot 10^{-10}$	$3 \cdot 10^{-9}$

6 Dirac delta, $D_{\alpha\beta}$

The expectation value of the Dirac delta operator for two particles α and β , see Eqs. (4) and (5), can be evaluated directly as a numerical value of the probability density $|\Psi|^2$ at $r_{\alpha\beta} = 0$. However, experience shows that such calculations have relatively poor convergence.

A significantly higher rate of convergence can be achieved when the expectation value is evaluated using its regularized form^{23,33} which, for particles of the reduced mass $\mu_{\alpha\beta} = \frac{m_\alpha m_\beta}{m_\alpha + m_\beta}$, reads

$$\langle \Psi | \delta^{(3)}(r_{\alpha\beta}) | \Psi \rangle = \frac{\mu_{\alpha\beta}}{\pi} \left(E \left\langle \Psi \left| \frac{1}{r_{\alpha\beta}} \right| \Psi \right\rangle - \left\langle \Psi \left| \frac{1}{r_{\alpha\beta}} \hat{V} \right| \Psi \right\rangle - \frac{1}{2} \sum_a \frac{1}{m_a} \left\langle \vec{\nabla}_a \Psi \left| \frac{1}{r_{\alpha\beta}} \right| \vec{\nabla}_a \Psi \right\rangle \right). \quad (31)$$

The right-hand-side integrals have to be evaluated in a similar manner as in the previous sections. For each, out of three kinds of matrix elements, the angular variables must be integrated out using the formulas given in Appendix A, and then matrix elements in the elementary basis ϕ_k can be derived using symbolic algebra software.²⁸ At the expense of the evaluation of three new expectation values on the right hand side of Eq. (31), we can obtain results orders of magnitude more accurate than in direct calculation of $\langle \Psi | \delta^{(3)}(r_{\alpha\beta}) | \Psi \rangle$. This is exemplified in Table 2, in which the convergence of both the direct and the regularized methods, applied to the interelectron Dirac delta expectation value, D_{ee} , is compared. It

can be concluded in this case that the regularization enables three orders of magnitude higher accuracy to be achieved. The convergence of the regularized expectation value of the nuclear-mass-dependent electron-nucleus Dirac delta D_{en} enables 10 significant figures in the extrapolated value, as shown in Table 3.

Table 2: Comparison of the convergence of D_{ee} calculated (in a.u.) using the direct and regularized [Eq. (31)] methods. The naJC wave function Ψ of the ground rovibrational level of H_2 was used. K is the size of the naJC basis set employed, and Ω is the largest shell enabled.

Ω	K	Direct	Regularized
10	42 588	0.050 707 696 496	0.050 707 579 154
11	61 152	0.050 707 626 769	0.050 707 579 440
12	85 904	0.050 707 599 520	0.050 707 579 525
13	117 936	0.050 707 589 148	0.050 707 579 548
14	159 120	0.050 707 584 473	0.050 707 579 551
	∞	0.050 707 579(5)	0.050 707 579 554(3)
Rel. uncert.		$1. \cdot 10^{-7}$	$6. \cdot 10^{-11}$

7 Breit interaction, $B_{\alpha\beta}$

The expectation value of the Breit interaction between two particles, α and β , cannot be directly evaluated from the formulas (6)-(8), as they require access to integrals beyond those discussed in Sec. 4.2. To address this issue, we have rearranged the original formulas to equivalent forms

$$\begin{aligned}
 B_{\alpha\beta} = & -2 \left\langle \nabla_{\alpha}^i \Psi \left| \frac{1}{r_{\alpha\beta}} \right| \nabla_{\beta}^i \Psi \right\rangle \\
 & - \left\langle \nabla_{\alpha}^i \nabla_{\alpha}^i \Psi \left| \frac{r_{\alpha\beta}^j}{r_{\alpha\beta}} \right| \nabla_{\beta}^j \Psi \right\rangle - \left\langle \nabla_{\alpha}^i \Psi \left| \frac{r_{\alpha\beta}^j}{r_{\alpha\beta}} \right| \nabla_{\alpha}^i \nabla_{\beta}^j \Psi \right\rangle
 \end{aligned} \tag{32}$$

that are suitable for the available set of integrals. The expression (32) was applied to the electron-electron, B_{ee} , electron-nucleus, B_{en} , and the nucleus-nucleus B_{nn} interactions. After

necessary reduction of the angular variables it was represented in the form of elementary expectation values in the ϕ_k basis. The obtained numerical convergence with the increasing size of the basis set is shown in Table 3, from which it is evident that nine significant figures can be achieved.

Table 3: Convergence of the operators composing the expectation value of the Breit-Pauli Hamiltonian calculated (in a.u.) using the nonadiabatic James-Coolidge (naJC) wave function for the ground rovibrational level of H₂. K is the size of the naJC basis set employed, governed by Ω – the largest shell enabled. Calculations were performed using the nuclear mass $M/m = 1836.152\,673\,43(11)$.³²

Ω	K	D_{en}	B_{ee}	B_{en}	$B_{\text{nn}} \cdot 10^6$	E_{rel}
11	61 152	1.418 309 983 439	-0.046 296 300 064 6	-0.001 358 468 834 24	1.832 600 007 36	-0.204 547 467 00
12	85 904	1.418 309 982 287	-0.046 296 299 353 9	-0.001 358 468 828 22	1.832 600 007 27	-0.204 547 434 28
13	117 936	1.418 309 982 844	-0.046 296 299 124 3	-0.001 358 468 828 36	1.832 600 007 25	-0.204 547 423 05
14	159 120	1.418 309 982 463	-0.046 296 299 047 1	-0.001 358 468 827 19	1.832 600 007 29	-0.204 547 417 59
	∞	1.418 309 982 5(5)	-0.046 296 298 98(7)	-0.001 358 468 828(2)	1.832 600 007 3(1)	-0.204 547 412(5)
Rel. uncert.		$4 \cdot 10^{-10}$	$2 \cdot 10^{-9}$	$2 \cdot 10^{-9}$	$6 \cdot 10^{-11}$	$2 \cdot 10^{-8}$

8 Numerical results

The convergence of the final relativistic correction for the ground energy level of H₂ is shown in the last column of Table 3. It is apparent that it is only the ninth significant digit in the extrapolated value that is burdened with an uncertainty. We have performed analogous convergence analysis for HD and D₂ isotopologues, obtaining (in a.u.)

$$E_{\text{rel}} = \begin{cases} -0.204\,547\,412(5) & \text{for H}_2 \\ -0.204\,660\,995(5) & \text{for HD} \\ -0.204\,805\,040(5) & \text{for D}_2 \end{cases} . \quad (33)$$

The relativistic contribution to the dissociation energy can be obtained by subtracting the relativistic correction of a given rovibrational level $E_{\text{rel}}^{v,J}$ from the sum of the atomic

relativistic corrections³⁴ given by

$$E_{\text{rel}}(X) = -\frac{m_X(m_X^2 + 3m_X + 5 - 4\delta_X)}{8(m_X + 1)^3} \quad (34)$$

with $\delta_{H/T} = 1$ and $\delta_D = 0$. In terms of the dissociation energy of the rovibrational levels $D_{v,J}^{\text{rel}}$, the achieved accuracy is of the order of $10^{-7} - 10^{-6} \text{ cm}^{-1} \approx 0.003 - 0.03 \text{ MHz}$, which makes the contribution from the relativistic correction $\alpha^4 E_{\text{rel}}^{v,J}$ to the overall error budget of Eq. (1) negligible. This result follows a similar achievement reported for the nonrelativistic component $\alpha^2 E_{\text{nr}}^{v,J}$,¹²⁻¹⁵ so that from now on the quantum electrodynamic terms $\mathcal{O}(\alpha^5)$ limit the overall accuracy of the theoretical predictions. For low-lying rotational levels of H_2 such a contribution to the total uncertainty is of the order of $2 \cdot 10^{-4} \text{ cm}^{-1} \approx 7 \text{ MHz}$. The only exception is the ground rovibrational level, where the leading QED correction was calculated using the DNA method^{35,36} with the accuracy of $10^{-7} \text{ cm}^{-1} \approx 0.003 \text{ MHz}$. The α^6 and α^7 terms of the α -expansion (1) contribute the uncertainty of about $7 \cdot 10^{-6} \text{ cm}^{-1} \approx 0.2 \text{ MHz}$ and $3 \cdot 10^{-5} \text{ cm}^{-1} \approx 0.8 \text{ MHz}$, respectively. Figure 1 provides a comprehensive view of the error budget's components, enabling assessment of their importance.

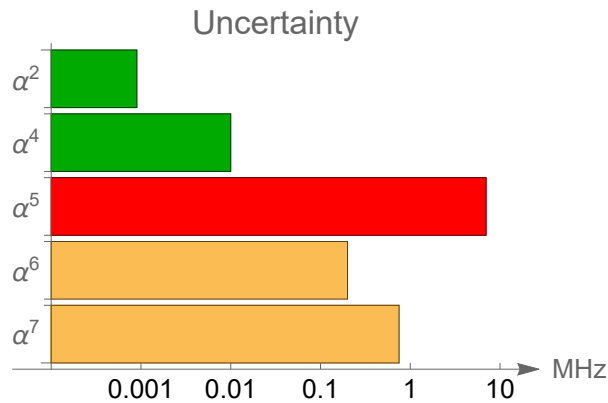


Figure 1: The error budget of the dissociation energy for the low-lying rotational levels of H_2 . The α^2 and α^4 contributions come from DNA calculation, while the remaining ones are from NAPT. Note the logarithmic scale.

8.1 Comparison with NAPT

Previous estimates of the relativistic correction for all the isotopologues of H_2 were obtained in the nonadiabatic perturbation theory (NAPT) framework,^{37–39} which relies on the Born-Oppenheimer (BO) approximation. Within that approach, E_{rel} was represented as an expansion in powers of the m/μ_{AB} mass ratio around the BO value $E_{\text{rel}}^{(0)}$

$$E_{\text{rel}} = E_{\text{rel}}^{(0)} + \frac{m}{\mu_{AB}} E_{\text{rel}}^{(1)} + \mathcal{O} \left[\left(\frac{m}{\mu_{AB}} \right)^2 \right]. \quad (35)$$

Till now, the higher-order terms remain unknown and are the source of the uncertainty of this correction. The missing contribution was estimated using simple scaling of the first-order term by the mass factor m/μ_{AB} ,⁴⁰ i.e. $\mathcal{O} \left[(m/\mu_{AB})^2 \right] \approx (m/\mu_{AB})^2 E_{\text{rel}}^{(1)}$. So far, there have been no means to check the reliability of such an assessment. The DNA results reported in this work correspond to the expansion (35) summed up to infinity and provide a reliable tool to verify previous estimations of both the correction itself and its uncertainty. The numerical values of E_{rel} obtained from DNA and NAPT methods for several of the lowest rotational levels of H_2 are compared in Table 4. In the fourth column of the table and in Fig. 2, these differences are confronted with the uncertainties assigned within NAPT, while the last column of the table reveals the factor by which the uncertainty was underestimated. On the basis of these results, we can conclude that for the individual energy levels the simple scaling of the leading known term by the mass ratio does not account for the J -dependence of the missing terms and provides only a crude estimation. A very similar picture was found for HD and D_2 .

9 Conclusions

Recently developed integral formulas³¹ have been used to calculate expectation values of the relativistic operators included in the Breit-Pauli Hamiltonian. Both the Hamiltonian

Table 4: Comparison of the relativistic correction to dissociation energy $D_{0,J}^{\text{rel}}$ (in MHz) obtained from direct nonadiabatic (DNA) and nonadiabatic perturbation theory (NAPT) methods for the lowest rotational levels of H_2 .

J	DNA	NAPT	Difference	Diff./ σ_{NAPT}
0	-15925.493(2)	-15925.34(7)	0.16(7)	2.3
1	-16002.87(1)	-16002.79(7)	0.08(7)	1.2
2	-16155.90(1)	-16155.96(7)	-0.06(7)	-0.9
3	-16381.19(1)	-16381.48(7)	-0.29(7)	-4.2
4	-16673.89(1)	-16674.49(7)	-0.60(7)	-8.6

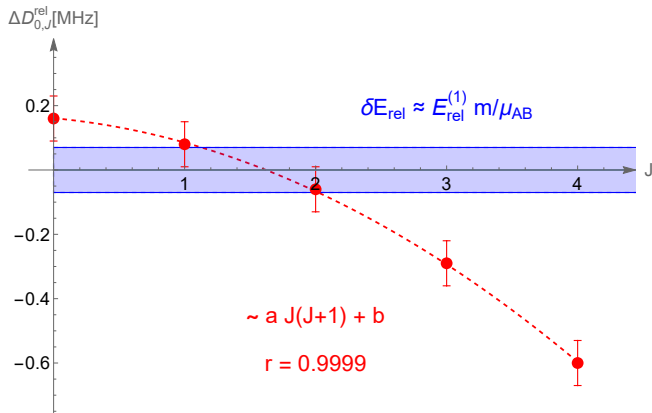


Figure 2: Plot of the difference between the dissociation energy of a level $(0, J)$ obtained from DNA and NAPT calculations, $\Delta D_{0,J}^{\text{rel}}$ (red dots), against the NAPT uncertainty (blue band) for several of the lowest rotational levels of H_2 . The $\Delta D_{0,J}^{\text{rel}}$ values fit to the $aJ(J+1) + b$ model with the correlation coefficient $r = 0.9999$.

and the wave function account fully for the finite nuclear masses, significantly reducing the uncertainty of the relativistic correction. The achieved numerical convergence of the individual operators enabled stabilization of at least nine significant digits, resulting in the final accuracy of the relativistic correction of the order of 10^{-9} a.u. or 10^{-8} relative. The DNA/naJC method, applied to rovibrational levels of molecular hydrogen isotopologues, yields the relativistic correction to dissociation energy with the absolute accuracy of the order of $10^{-7} - 10^{-6} \text{ cm}^{-1} \approx 0.003 - 0.03 \text{ MHz}$. Most importantly, the uncertainty of the relativistic and nonrelativistic contributions has been practically eliminated from the error budget of total energy. Therefore, future efforts to improve the accuracy of theoretical

predictions will focus on the QED and higher-order corrections.

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A Reduction of the rotational factors

$$\mathcal{P}_J(\vec{n}' \cdot \vec{n}) \Big|_{R'=R} = R^{2J} \quad (36)$$

$$\nabla_{R'}^i \mathcal{P}_J(\vec{n}' \cdot \vec{n}) \Big|_{R'=R} = JR^{2J-2} R^m \quad (37)$$

$$\nabla_{R'}^i \nabla_R^n \mathcal{P}_J(\vec{n}' \cdot \vec{n}) \Big|_{R'=R} = \frac{1}{2}J(J+1)R^{2J-2} \delta^{mn} + \frac{1}{2}J(J-1)R^{2J-4} R^m R^n \quad (38)$$

$$\nabla_R^i \nabla_R^n \mathcal{P}_J(\vec{n}' \cdot \vec{n}) \Big|_{R'=R} = -\frac{1}{2}J(J-1)R^{2J-2} \delta^{mn} + \frac{3}{2}J(J-1)R^{2J-4} R^m R^n \quad (39)$$

$$\nabla_{R'}^i \nabla_R^i \mathcal{P}_J(\vec{n}' \cdot \vec{n}) \Big|_{R'=R} = J(2J+1)R^{2J-2} \quad (40)$$

$$\nabla_R^i \nabla_R^i \mathcal{P}_J(\vec{n}' \cdot \vec{n}) \Big|_{R'=R} = 0 \quad (41)$$

$$\nabla_{R'}^i \nabla_R^n \nabla_R^n \mathcal{P}_J(\vec{n}' \cdot \vec{n}) \Big|_{R'=R} = 0 \quad (42)$$

$$\nabla_{R'}^i \nabla_R^n \nabla_R^i \mathcal{P}_J(\vec{R}', \vec{R}) \Big|_{R'=R} = (J-1)J(2J+1)R^{2J-4} R^n \quad (43)$$

$$\nabla_{R'}^i \nabla_R^n \nabla_R^i \nabla_R^i \mathcal{P}_J(\vec{n}' \cdot \vec{n}) \Big|_{R'=R} = 0 \quad (44)$$

$$\nabla_{R'}^n \nabla_{R'}^n \nabla_R^i \nabla_R^i \mathcal{P}_J(\vec{R}', \vec{R}) \Big|_{R'=R} = 0 \quad (45)$$

$$\nabla_{R'}^n \nabla_{R'}^i \nabla_R^n \nabla_R^i \mathcal{P}_J(\vec{R}', \vec{R}) \Big|_{R'=R} = (J-1)J(2J-1)(2J+1)R^{2J-4} \quad (46)$$

B Examples of $\Sigma - \Sigma$, $\Pi - \Pi$, and $\Pi - \Sigma$ matrix elements

$$\begin{aligned}
& \frac{4\pi}{2J+1} \sum_{M=-J}^J \left\langle p_A^2 \psi_{k,\Sigma}^{J,M} \left| p_B^2 \psi_{l,\Sigma}^{J,M} \right. \right\rangle \tag{47} \\
&= \langle \nabla_A^i \nabla_A^i \phi_k \left| R^{2J} \right| \nabla_B^j \nabla_B^j \phi_l \rangle \\
&+ 2J \left[\langle \nabla_A^i \phi_k \left| R^{2J-2} R^i \right| \nabla_B^j \nabla_B^j \phi_l \rangle - \langle \nabla_A^i \nabla_A^i \phi_k \left| R^{2J-2} R^j \right| \nabla_B^j \phi_l \rangle \right. \\
&\quad \left. - (J+1) \langle \nabla_A^i \phi_k \left| R^{2J-2} \right| \nabla_B^i \phi_l \rangle - (J-1) \langle \nabla_A^i \phi_k \left| R^{2J-4} R^i R^j \right| \nabla_B^j \phi_l \rangle \right]
\end{aligned}$$

$$\begin{aligned}
& \frac{4\pi}{2J+1} \sum_{M=-J}^J \left\langle p_A^2 \psi_{k,\Pi_a}^{J,M} \left| p_B^2 \psi_{l,\Pi_b}^{J,M} \right. \right\rangle \tag{48} \\
&= \langle \nabla_A^i \nabla_A^i \phi_k \left| R^{2J} r_a^k r_b^k \right| \nabla_B^j \nabla_B^j \phi_l \rangle \\
&- (J^2 - 3J - 2) \langle \nabla_A^i \phi_k \left| R^{2J-2} r_a^k r_b^k \delta^{ij} \right| \nabla_B^j \phi_l \rangle \\
&+ (5J^2 - 7J - 2) \langle \nabla_A^i \phi_k \left| R^{2J-4} r_a^k r_b^k R^i R^j \right| \nabla_B^j \phi_l \rangle \\
&- (J^2 + J + 2) \langle \nabla_A^i \phi_k \left| R^{2J-2} (r_a^j r_b^i + r_a^i r_b^j) \right| \nabla_B^j \phi_l \rangle \\
&+ (J-1) \langle \nabla_A^i \phi_k \left| R^{2J-4} [(r_{bA}^2 - r_{bB}^2)(R^j r_a^i + R^i r_a^j) + (r_{aA}^2 - r_{aB}^2)(R^j r_b^i + R^i r_b^j)] \right| \nabla_B^j \phi_l \rangle \\
&+ (J+1)(2J-1) [\langle \nabla_A^i \phi_k \left| R^{2J-2} r_a^k r_b^k \right| \nabla_A^i \phi_l \rangle + \langle \nabla_B^j \phi_k \left| R^{2J-2} r_a^k r_b^k \right| \nabla_B^j \phi_l \rangle] \\
&+ \frac{1}{2} [\langle \nabla_A^i \phi_k \left| R^{2J-4} (r_{aA}^2 - r_{aB}^2)(r_{bA}^2 - r_{bB}^2) \right| \nabla_A^i \phi_l \rangle + \langle \nabla_B^j \phi_k \left| R^{2J-4} (r_{aA}^2 - r_{aB}^2)(r_{bA}^2 - r_{bB}^2) \right| \nabla_B^j \phi_l \rangle] \\
&+ 4J(J+1) \langle \phi_k \left| R^{2J-4} r_a^k r_b^k \right| \phi_l \rangle
\end{aligned}$$

$$\begin{aligned}
& \frac{4\pi}{2J+1} \sum_{M=-J}^J \left\langle p_A^2 \psi_{k,\Pi}^{J,M} \left| p_B^2 \psi_{l,\Sigma}^{J,M} \right. \right\rangle \tag{49} \\
&= \sqrt{2J(J+1)} \left\{ 2(J-1) \left[\langle \rho^i \nabla_A^i \phi_k \left| R^{2J-3} \right| R^j \nabla_B^j \phi_\Sigma \rangle + \langle \rho^j \nabla_B^j \phi_k \left| R^{2J-3} \right| R^i \nabla_A^i \phi_\Sigma \rangle \right. \right. \\
&\quad \left. \left. + \langle \phi_k \left| R^{2J-3} \right| \rho^i (\nabla_B^i - \nabla_A^i) \phi_\Sigma \rangle + \langle \phi_k \left| R^{2J-3} \nabla_R^i \rho^i \right| R^i (\nabla_B^i - \nabla_A^i) \phi_\Sigma \rangle \right] \right. \\
&\quad \left. + \langle \rho^j \nabla_B^j \phi_k \left| R^{2J-1} \right| \nabla_A^i \nabla_A^i \phi_\Sigma \rangle - \langle \rho^i \nabla_A^i \phi_k \left| R^{2J-1} \right| \nabla_B^j \nabla_B^j \phi_\Sigma \rangle \right. \\
&\quad \left. - \langle \phi_k \left| R^{2J-1} \nabla_R^i \rho^i \right| (\nabla_B^j \nabla_B^j + \nabla_A^i \nabla_A^i) \phi_\Sigma \rangle \right\}
\end{aligned}$$