

Gerade-ungerade mixing in the hydrogen molecule

Krzysztof Pachucki^{1,*} and Jacek Komasa^{2,†}

¹*Faculty of Physics, University of Warsaw, Hoża 69, PL-00-681 Warsaw, Poland*

²*Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, PL-60-780 Poznań, Poland*

(Received 1 February 2011; revised manuscript received 17 March 2011; published 19 April 2011)

In homonuclear molecules, such as H₂, the rovibrational levels close to the dissociation threshold do not have definite symmetry with respect to the inversion of electronic variables. This effect—the *gerade-ungerade* mixing—results from interactions between magnetic moments of electrons and protons. We calculate this mixing on the level of adiabatic approximation and numerically solve the system of nuclear differential equations. It turns out that the corrections to the dissociation energy of rovibrational levels resulting from the mixing are negligible in comparison with the present accuracy of experiments. As a coproduct, an accurate clamped nuclei potential for the $b^3\Sigma_u^+$ state has been obtained.

DOI: [10.1103/PhysRevA.83.042510](https://doi.org/10.1103/PhysRevA.83.042510)

PACS number(s): 31.30.Gs, 31.15.aj, 31.15.vn, 31.50.Df

I. INTRODUCTION

The hydrogen molecule, due to its simplicity, can be accurately calculated from first principles using the quantum electrodynamic (QED) theory. At the current accuracy of about 0.001 cm⁻¹, apart from nonadiabatic and relativistic effects, the $O(\alpha^3)$ and the dominating part of $O(\alpha^4)$ QED corrections have to be included. The excellent agreement with recent experimental results for H₂ [1,2], D₂ [1,3], and HD [4,5] indicates a good understanding of all physically significant effects and is a basis for a further improvement in theoretical description of the hydrogen molecule. At present, the main uncertainty comes from the higher order nonadiabatic $O(\mu_n^{-3})$, relativistic recoil $O(\alpha^2/\mu_n)$, and QED $O(\alpha^4)$ corrections. Once these three terms are known, the accuracy of rovibrational levels could be increased up to about 10⁻⁶ cm⁻¹ (~30 kHz), provided that all other small effects are determined, in particular those due to the finite proton charge radius r_p and the *gerade-ungerade* mixing.

The correction due to r_p can easily be calculated, but the accurate value of r_p is presently an issue. The result of the recent determination of r_p from the muonic hydrogen Lamb shift [6] is 5% smaller than previous determinations from the hydrogen spectrum and from the electron-proton scattering. This 5% gives uncertainty in H₂ dissociation energy of about 5×10^{-6} cm⁻¹, thus the proton charge radius discrepancy has to be resolved to be able to reach 10⁻⁶ cm⁻¹ accuracy.

The correction resulting from *gerade-ungerade* mixing appears due to the interactions between the electron and the proton magnetic moments. An experimental evidence of this phenomenon has been reported for iodine [7] and cesium [8] dimers and a detailed theoretical account of hyperfine interactions in diatomic homonuclear molecules has been given in [9]. The energy shift caused by such interactions in H₂ can, in principle, be as large as the hyperfine splitting in the hydrogen atom, which amounts to 1420 MHz \approx 0.05 cm⁻¹. Until now however, the magnitude of this effect for the hydrogen molecule has been unknown and its determination is the purpose of this work.

At the accuracy level of 10⁻⁶ cm⁻¹ the predicted H₂ spectrum is sensitive to uncertainties in fundamental constants. In particular, the present uncertainty in the proton-to-electron mass ratio, equal to 0.4 ppb, yields about 14 kHz uncertainty for the ground state dissociation energy. This means, that the proton-to-electron mass ratio can be determined from the H₂ spectrum more accurately than it is known presently, if both theory and experiment pass the threshold of 14 kHz uncertainty. Experimentalists [10] have already considered such level of precision, while from a theoretical point of view we have not yet investigated in detail the feasibility of such an uncertainty in H₂. Certainly the most challenging is the accurate calculation of $O(\alpha^4)$ and estimation of $O(\alpha^5)$ corrections.

II. WAVE FUNCTIONS AND HAMILTONIAN

In the adiabatic approximation, the total spatial wave function ϕ is approximated by a product of electronic and nuclear functions

$$\phi(\vec{r}, \vec{R}) = \phi_{\text{el}}(\vec{r}) \chi(R) Y_{LM}(\vec{n}) \quad (1)$$

with ϕ_{el} being the solution to the clamped nuclei Schrödinger equation

$$H_{\text{el}} \phi_{\text{el}} = \mathcal{E}(\vec{R}) \phi_{\text{el}}, \quad (2)$$

$Y_{LM}(\vec{n})$ is a spherical harmonic with $\vec{n} = \vec{R}/R$. The nuclear function χ fulfills the Born-Oppenheimer radial Schrödinger equation

$$\left[-\frac{1}{2\mu_n} \frac{1}{R} \frac{\partial^2}{\partial R^2} R + \frac{L(L+1)}{2\mu_n R^2} + \mathcal{E}(R) \right] \chi_{vL}(R) = E_{vL} \chi_{vL}(R), \quad (3)$$

where μ_n is the ratio of the nuclear reduced mass to the electron mass, and atomic units are used throughout the paper.

In the nonrelativistic approximation the symmetry of the inversion of electronic coordinates (\vec{r}_1, \vec{r}_2) with respect to the geometrical center of the H₂ molecule is conserved, and the splitting $\delta\mathcal{E}$ of the clamped nuclei energies between the

*krp@fuw.edu.pl

†komasa@man.poznan.pl

lowest *gerade* and *ungerade* states vanishes exponentially for large internuclear distances R [11,12] (in atomic units),

$$\delta\mathcal{E}(R) = \mathcal{E}_u(R) - \mathcal{E}_g(R) = R^{5/2} e^{-2R} [1 + O(1/\sqrt{R})]. \quad (4)$$

Since these states become asymptotically degenerate, a small perturbation may significantly mix them, and *gerade* and *ungerade* symmetry will not be preserved. To describe this mixing, let us define the following two electronic spatial functions:

$$\phi_g(\vec{r}_1, \vec{r}_2; \vec{R}) = \phi_g(-\vec{r}_1, -\vec{r}_2, \vec{R}) = \phi_g(\vec{r}_2, \vec{r}_1, \vec{R}) \quad (5)$$

for the *gerade* ($X^1\Sigma_g^+$) state and

$$\phi_u(\vec{r}_1, \vec{r}_2; \vec{R}) = -\phi_u(-\vec{r}_1, -\vec{r}_2, \vec{R}) = -\phi_u(\vec{r}_2, \vec{r}_1, \vec{R}) \quad (6)$$

for *ungerade* ($b^3\Sigma_u^+$) state. Both functions are assumed to be solutions to the clamped nuclei Schrödinger equation (2) with corresponding energies \mathcal{E}_g and \mathcal{E}_u . In the asymptotic region they take the Heitler-London form [13]

$$\phi_g(\vec{r}_1, \vec{r}_2, \vec{R}) = \frac{[\phi_H(r_{1A})\phi_H(r_{2B}) + \phi_H(r_{1B})\phi_H(r_{2A})]}{\sqrt{2}}, \quad (7)$$

$$\phi_u(\vec{r}_1, \vec{r}_2, \vec{R}) = \frac{[\phi_H(r_{1A})\phi_H(r_{2B}) - \phi_H(r_{1B})\phi_H(r_{2A})]}{\sqrt{2}}, \quad (8)$$

where ϕ_H is the ground state atomic hydrogen function.

The leading relativistic corrections, as given by the Breit-Pauli Hamiltonian, violate the inversion symmetry of electron coordinates with respect to the geometrical center. As a result, electronic states do not have a definite symmetry and rovibrational energies are slightly shifted. One expects this shift to be the most significant for states laying close to the dissociation threshold, where nuclei are far apart from each other. Among all the relativistic corrections, the dominating one at large internuclear distances results from the magnetic interactions between all the four particles, electrons, and protons, represented by a and b , ($e^2 = 4\pi\alpha$)

$$\delta H = m^2\alpha \sum_{a>b} \frac{e_a e_b}{4\pi} \left[-\frac{2\pi}{3} \frac{g_a g_b}{m_a m_b} \vec{s}_a \cdot \vec{s}_b \delta^{(3)}(r_{ab}) + \frac{g_a g_b}{4m_a m_b} \frac{s_a^i s_b^j}{r_{ab}^3} \left(\delta^{ij} - 3 \frac{r_{ab}^i r_{ab}^j}{r_{ab}^3} \right) \right]. \quad (9)$$

δH causes the *gerade-ungerade* mixing and also contributes to the *gerade-ungerade* splitting of the clamped nuclei energies. In fact, the relativistic correction to this splitting goes like R^{-3} (for $J \neq 0$) and, at large R , dominates over the nonrelativistic splitting [Eq. (4)]. To account for the splitting and the mixing, we will include in the nuclear equation both the diagonal and off-diagonal matrix elements between *gerade* and *ungerade* states.

III. MATRIX ELEMENTS FOR THE GERADE-UNGERADE MIXING AND SPLITTING

Among all the spin interactions in Eq. (9), the proton-proton and the local (Dirac δ) electron-electron interactions can be neglected. The first one is very small and the second one vanishes exponentially for large distances. We neglect also the tensor electron-nucleus interaction because it is much smaller than the scalar interaction, which is proportional to the Dirac

δ . As a result of these approximations, δH is a sum of the tensor electron-electron spin and the local electron-nucleus interactions. In atomic units they take the form

$$\begin{aligned} \delta H &= \alpha^2 \frac{s_1^i s_2^j}{r_{12}^3} \left(\delta^{ij} - 3 \frac{r_{12}^i r_{12}^j}{r_{12}^2} \right) \\ &+ \sum_{a,X} \frac{4\pi\alpha^2}{3} \frac{g_p m}{m_p} \vec{s}_a \cdot \vec{I}_X \delta^{(3)}(r_{aX}) \\ &= \delta H_1 + \delta H_2, \end{aligned} \quad (10)$$

where $a = 1, 2$ labels electrons and $X = A, B$ (nuclei). Let us introduce the notation \vec{L} for rotational angular momentum, $\vec{S} = \vec{s}_1 + \vec{s}_2$ for the total electron spin, $\vec{I} = \vec{s}_A + \vec{s}_B$ for the total nuclear spin, $\vec{J} = \vec{L} + \vec{S}$, and $\vec{F} = \vec{J} + \vec{I}$. We will use the basis $|L, S, J, I, F, m_F\rangle$ in the evaluation of matrix elements. Not all the values of angular momenta are allowed, due to the Pauli exclusion principle. For the *gerade* state of the H_2 molecule ($S = 0$), $I = 0$ for even L and $I = 1$ for odd L , for the *ungerade* state ($S = 1$), $I = 1$ for even and $I = 0$ for odd L . Let us consider now the first component δH_1 in Eq. (10) and rewrite it in terms of the total electron spin

$$\delta H_1 = \frac{\alpha^2}{2} \frac{S^i S^j}{r_{12}^3} \left(\delta^{ij} - 3 \frac{r_{12}^i r_{12}^j}{r_{12}^2} \right). \quad (12)$$

Its expectation value in the *ungerade* state is

$$\delta H_{1uu} \equiv \langle \phi_u | \delta H_1 | \phi_u \rangle = \beta(R) S^i S^j (\delta^{ij} - 3n^i n^j), \quad (13)$$

where $n^i = R^i/R$ and

$$\beta(R) = \frac{\alpha^2}{4} b(R), \quad (14)$$

$$b(R) = \left\langle \phi_u \left| \frac{3(\vec{r}_{12} \cdot \vec{n})^2 - r_{12}^2}{r_{12}^5} \right| \phi_u \right\rangle. \quad (15)$$

For asymptotic internuclear distances the electron-electron distance r_{12} can be replaced by R , thus $b(R) \approx 2/R^3$, and δH_{1uu} becomes much larger than the nonrelativistic splitting $\delta\mathcal{E}$.

Matrix elements of δH_{1uu} in the basis $|L, S, J, m_J\rangle$ are diagonal in S and J , and do not vanish only for $S = 1$ and $\Delta L = 0, \pm 2$. Hence we are left with only four types of matrix elements:

$$\langle\langle L, 1, L+1 | \delta H_{1uu} | L, 1, L+1 \rangle\rangle = \beta \frac{2L(L-2)}{(2L+3)(2L-1)}, \quad (16)$$

$$\langle\langle L, 1, L | \delta H_{1uu} | L, 1, L \rangle\rangle = -\beta \frac{2[2L(L+1)-3]}{(2L+3)(2L-1)}, \quad (17)$$

$$\langle\langle L, 1, L-1 | \delta H_{1uu} | L, 1, L-1 \rangle\rangle = \beta \frac{2(L+1)(L+3)}{(2L+3)(2L-1)}, \quad (18)$$

$$\langle\langle L-1, 1, L | \delta H_{1uu} | L+1, 1, L \rangle\rangle = -3\beta \frac{\sqrt{L(L+1)}}{2L+1}, \quad (19)$$

where we have introduced the double-bracket notation

$$\langle\langle J, M | Q | J, M' \rangle\rangle = \delta_{M'M} \langle\langle J | Q | J \rangle\rangle \quad (20)$$

for a scalar operator Q .

The second term in Eq. (10) (δH_2) is at first rewritten as

$$\begin{aligned} \delta H_2 = & \frac{\pi \alpha^2}{3} \frac{g_p m}{m_p} \{ \vec{S} \cdot \vec{I} [\delta^{(3)}(r_{1A}) + \delta^{(3)}(r_{1B}) \\ & + \delta^{(3)}(r_{2A}) + \delta^{(3)}(r_{2B})] + (\vec{s}_1 - \vec{s}_2) \cdot (\vec{I}_A - \vec{I}_B) \\ & \times [\delta^{(3)}(r_{1A}) - \delta^{(3)}(r_{1B}) - \delta^{(3)}(r_{2A}) + \delta^{(3)}(r_{2B})] \}, \end{aligned} \quad (21)$$

where A and B refer to the two nuclei. Although other terms containing $(\vec{s}_1 \pm \vec{s}_2) \cdot (\vec{I}_A \mp \vec{I}_B)$ might also be present in the above, they were omitted because their matrix elements between ϕ_g and ϕ_u states vanish. The diagonal matrix element of δH_2 is

$$\delta H_{2uu} \equiv \langle \phi_u | \delta H_2 | \phi_u \rangle = \gamma(R) \vec{S} \cdot \vec{I}, \quad (22)$$

$$\gamma(R) = \frac{\pi \alpha^2}{3} \frac{g_p m}{m_p} c(R), \quad (23)$$

$$c(R) = \langle \phi_u | \delta^{(3)}(r_{1A}) + \delta^{(3)}(r_{1B}) + \delta^{(3)}(r_{2A}) + \delta^{(3)}(r_{2B}) | \phi_u \rangle \quad (24)$$

and the off-diagonal is

$$\delta H_{2gu} \equiv \langle \phi_g | \delta H_2 | \phi_u \rangle = \gamma'(R) (\vec{s}_1 - \vec{s}_2) \cdot (\vec{I}_A - \vec{I}_B), \quad (25)$$

$$\gamma'(R) = \frac{\pi \alpha^2}{3} \frac{g_p m}{m_p} c'(R), \quad (26)$$

$$c'(R) = \langle \phi_g | \delta^{(3)}(r_{1A}) - \delta^{(3)}(r_{1B}) - \delta^{(3)}(r_{2A}) + \delta^{(3)}(r_{2B}) | \phi_u \rangle. \quad (27)$$

In the asymptotic region the matrix elements of the electron-nucleus Dirac δ function approach the atomic hydrogen value, thus

$$c(\infty) = c'(\infty) = \frac{2}{\pi}. \quad (28)$$

Nonvanishing matrix elements in the angular momentum basis $|L, S, J, I, F, M_F\rangle$ are

$$\langle L, 1, L+1, 1, L | \delta H_{2uu} | L, 1, L+1, 1, L \rangle = -\gamma \frac{L+2}{L+1}, \quad (29)$$

$$\langle L, 1, L, 1, L | \delta H_{2uu} | L, 1, L, 1, L \rangle = -\gamma \frac{1}{L(L+1)}, \quad (30)$$

$$\langle L, 1, L-1, 1, L | \delta H_{2uu} | L, 1, L-1, 1, L \rangle = -\gamma \frac{L-1}{L}, \quad (31)$$

$$\langle L, 1, L+1, 1, L | \delta H_{2uu} | L, 1, L, 1, L \rangle = -\gamma \frac{L}{L+1} \sqrt{\frac{2L+3}{2L+1}}, \quad (32)$$

$$\langle L, 1, L, 1, L | \delta H_{2uu} | L, 1, L-1, 1, L \rangle = -\gamma \frac{L+1}{L} \sqrt{\frac{2L-1}{2L+1}}, \quad (33)$$

$$\langle L, 1, J, 1, L | \delta H_{2gu} | L, 0, L, 0, L \rangle = -\gamma' \sqrt{\frac{2J+1}{2L+1}}, \quad (34)$$

$$\langle L, 1, J, 0, J | \delta H_{2gu} | L, 0, L, 1, J \rangle = \gamma'. \quad (35)$$

All these matrix elements depend implicitly on R and are included in the clamped nuclei potential in the nuclear Schrödinger equation.

IV. NUCLEAR EQUATIONS FOR THE GERADE-UNGERADE MIXING

To take into account the states mixing, we employ the matrix form of Eq. (3),

$$\left[-\frac{1}{2\mu_n} \frac{1}{R} \frac{\partial^2}{\partial R^2} R + \frac{L(L+1)}{2\mu_n R^2} + \mathcal{E}_g(R) + \delta \mathcal{E}_{\text{spin}}(R) - \tilde{E}_{vL} \right] \tilde{\chi}_{vL}(R) = 0, \quad (36)$$

where $\delta \mathcal{E}_{\text{spin}}(R)$ is a matrix formed from matrix elements of δH [Eq. (10)] in a pertinent basis. The dimension of the matrix $\delta \mathcal{E}_{\text{spin}}(R)$ is determined by the number of close lying levels and it depends on the rotational quantum number L . The principal question we ask is what is the value of the difference

$$\delta E_{gu} = E_{vL} - \tilde{E}_{vL}, \quad (37)$$

which we shall call the *gerade-ungerade* mixing correction to the dissociation energy of a rovibrational level (v, L) .

In what follows we consider three separate cases depending on the quantum number L . We note in passing that the L mixing in Eq. (19) can potentially play a role only for $L = 0$ because in this case the diagonal spin-spin interaction represented by β is absent in $\delta \mathcal{E}_{\text{spin}}(R)$.

A. Case: L even and $\neq 0$

We span the nuclear wave function in the following basis:

$$\begin{aligned} & |L, 0, L, 0, L, M\rangle \\ & |L, 1, L+1, 1, L, M\rangle \\ & |L, 1, L, 1, L, M\rangle \\ & |L, 1, L-1, 1, L, M\rangle. \end{aligned} \quad (38)$$

The $\delta \mathcal{E}_{\text{spin}}(R)$ matrix is now obtained using Eqs. (16)–(18) and (29)–(35) and assumes the form

$$\delta \mathcal{E}_{\text{spin}} = \begin{pmatrix} 0 & -\gamma' \sqrt{\frac{2L+3}{2L+1}} & -\gamma' & -\gamma' \sqrt{\frac{2L-1}{2L+1}} \\ -\gamma' \sqrt{\frac{2L+3}{2L+1}} & \delta \mathcal{E} + \beta \frac{2L(L-2)}{(2L+3)(2L-1)} - \gamma \frac{L+2}{L+1} & -\gamma \frac{L}{L+1} \sqrt{\frac{2L+3}{2L+1}} & 0 \\ -\gamma' & -\gamma \frac{L}{L+1} \sqrt{\frac{2L+3}{2L+1}} & \delta \mathcal{E} - \beta \frac{2[2L(L+1)-3]}{(2L+3)(2L-1)} - \gamma \frac{1}{L(L+1)} & -\gamma \frac{L+1}{L} \sqrt{\frac{2L-1}{2L+1}} \\ -\gamma' \sqrt{\frac{2L-1}{2L+1}} & 0 & -\gamma \frac{L+1}{L} \sqrt{\frac{2L-1}{2L+1}} & \delta \mathcal{E} + \beta \frac{2(L+1)(L+3)}{(2L+3)(2L-1)} - \gamma \frac{L-1}{L} \end{pmatrix}. \quad (39)$$

B. Case: L odd

The basis is

$$\begin{aligned} &|L, 0, L, 1, J, M\rangle \\ &|L, 1, J, 0, J, M\rangle. \end{aligned} \quad (40)$$

$\delta\mathcal{E}_{\text{spin}}(R)$ matrices for three different values of $J = L + 1, L, L - 1$ read

$$\delta\mathcal{E}_{\text{spin}}^{L+1} = \begin{pmatrix} 0 & \gamma' \\ \gamma' & \delta\mathcal{E} + \beta \frac{2L(L-2)}{(2L+3)(2L-1)} \end{pmatrix}, \quad (41)$$

$$\delta\mathcal{E}_{\text{spin}}^L = \begin{pmatrix} 0 & \gamma' \\ \gamma' & \delta\mathcal{E} - \beta \frac{2[2L(L+1)-3]}{(2L+3)(2L-1)} \end{pmatrix}, \quad (42)$$

$$\delta\mathcal{E}_{\text{spin}}^{L-1} = \begin{pmatrix} 0 & \gamma' \\ \gamma' & \delta\mathcal{E} + \beta \frac{2(L+1)(L+3)}{(2L+3)(2L-1)} \end{pmatrix}. \quad (43)$$

C. Case: $L = 0$

This is the only case where we include the L mixing and thus the basis is

$$\begin{aligned} &|0, 0, 0, 0, 0, 0\rangle \\ &|0, 1, 1, 1, 0, 0\rangle \\ &|2, 1, 1, 1, 0, 0\rangle \end{aligned} \quad (44)$$

and the $\delta\mathcal{E}_{\text{spin}}(R)$ becomes

$$\delta\mathcal{E}_{\text{spin}} = \begin{pmatrix} 0 & -\sqrt{3}\gamma' & 0 \\ -\sqrt{3}\gamma' & \delta\mathcal{E} - 2\gamma & -\sqrt{2}\beta \\ 0 & -\sqrt{2}\beta & \delta\mathcal{E} + 3/(\mu_n R^2) \end{pmatrix}. \quad (45)$$

The nuclear equation (36) with the matrices $\delta\mathcal{E}_{\text{spin}}(R)$ presented above has been solved numerically as described in the following section.

TABLE I. The clamped nuclei energy $\mathcal{E}_u(R)$ of the $b^3\Sigma_u^+$ state of H_2 in atomic units.

$R(\text{a.u.})$	$\mathcal{E}_u(\mathcal{R})$	$R(\text{a.u.})$	$\mathcal{E}_u(\mathcal{R})$
0.1	7.888 200 480 23(54)	3.6	-0.988 000 298 079 213(12)
0.2	2.936 760 506 575(82)	3.7	-0.989 633 582 435 914(12)
0.3	1.330 347 123 362(18)	3.8	-0.991 058 561 176 051 6(9)
0.4	0.560 681 722 812 9(49)	3.9	-0.992 300 031 116 625(14)
0.5	0.123 480 488 020 3(22)	4.0	-0.993 380 066 851 054 1(6)
0.6	-0.150 099 824 524 6(19)	4.2	-0.995 132 117 890 052(4)
0.7	-0.332 558 167 254 7(26)	4.4	-0.996 446 550 339 835(4)
0.8	-0.460 092 123 159 5(33)	4.6	-0.997 426 637 512 202(3)
0.9	-0.552 703 600 189 6(36)	4.8	-0.998 152 794 502 693(1)
1.0	-0.622 264 427 116 5(35)	5.0	-0.998 687 257 154 895 1(7)
1.1	-0.676 183 005 341 9(32)	5.2	-0.999 077 894 411 954 0(7)
1.2	-0.719 236 477 996 0(12)	5.4	-0.999 361 294 472 878 9(2)
1.3	-0.754 563 452 043 48(33)	5.6	-0.999 565 246 549 560 0(3)
1.4	-0.784 244 677 619 29(72)	5.8	-0.999 710 722 820 312 1(2)
1.5	-0.809 666 653 435 89(18)	6.0	-0.999 813 449 850 999(3)
1.6	-0.831 760 208 300 362(68)	6.5	-0.999 952 835 631 005 7(3)
1.7	-0.851 159 923 317 480(27)	7.0	-1.000 004 005 774 949(3)
1.8	-0.868 310 062 295 094 4(85)	7.5	-1.000 018 923 410 887(1)
1.9	-0.883 533 627 911 107 1(53)	8.0	-1.000 020 221 124 853(3)
2.0	-0.897 076 330 763 106 1(23)	8.5	-1.000 017 233 424 615(2)
2.1	-0.909 133 962 635 680 2(92)	9.0	-1.000 013 517 806 560
2.2	-0.919 869 128 398 169 5(17)	9.5	-1.000 010 246 361 593(1)
2.3	-0.929 421 350 735 748(16)	10.0	-1.000 007 673 917 731(3)
2.4	-0.937 913 152 520 715 1(30)	10.5	-1.000 005 743 973 625(3)
2.5	-0.945 453 752 062 622 5(47)	11.0	-1.000 004 322 969 006(11)
2.6	-0.952 141 369 351 322 0(25)	11.5	-1.000 003 281 400 72(49)
2.7	-0.958 064 737 708 345 3(7)	12.0	-1.000 002 515 543 228(2)
2.8	-0.963 304 166 798 342 2(98)	13.0	-1.000 001 524 303 681(3)
2.9	-0.967 932 353 700 267 9(23)	14.0	-1.000 000 959 875 243(1)
3.0	-0.972 015 051 026 530 3(30)	15.0	-1.000 000 625 324 878
3.1	-0.975 611 650 653 440 7(28)	16.0	-1.000 000 419 565 938
3.2	-0.978 775 713 339 384 8(4)	17.0	-1.000 000 288 823 044
3.3	-0.981 555 459 117 719 8(4)	18.0	-1.000 000 203 340 009
3.4	-0.983 994 225 321 188 2(20)	19.0	-1.000 000 146 028 160
3.5	-0.986 130 895 163 431 6(23)	20.0	-1.000 000 106 740 117

V. NUMERICAL PROCEDURES AND RESULTS

Very accurate clamped nuclei potential for the $X^1\Sigma_g^+$ state has been reported recently in [12]. For the whole energy curve, an accuracy of the order of 10^{-15} has been reached. It is the most accurate result to date for H_2 itself but also for any molecular system with two or more electrons. Increasing the accuracy to this level has been possible thanks to the discovery of analytic formulas for two-center two-electron integrals with exponential functions [14]. In this work we report on an analogous calculation for the $b^3\Sigma_u^+$ state. In order to achieve the highest numerical accuracy, different basis sets are used, depending on the internuclear distance R . For $R < 12$ bohrs, the James-Coolidge basis functions [15,16] of the form

$$\begin{aligned} \psi_{(n)}(\vec{r}_1, \vec{r}_2) = & (1 \pm \hat{P}_{12})(1 \pm \hat{i}) e^{-\alpha(r_{1A}+r_{1B})-\beta(r_{2A}+r_{2B})} \\ & \times r_{12}^{n_1} (r_{1A} - r_{1B})^{n_2} (r_{2A} - r_{2B})^{n_3} \\ & \times (r_{1A} + r_{1B})^{n_4} (r_{2A} + r_{2B})^{n_5} \end{aligned} \quad (46)$$

have been employed. The antisymmetry projector $(1 \pm \hat{P}_{12})$ ensures singlet (+) or triplet (−) state, while the spatial projector $(1 \pm \hat{i})$ —the *gerade* (+) or *ungerade* (−) symmetry. Since in the actual numerical calculations one can use only a finite number of basis functions, one has to somehow select the most appropriate finite subset of functions in Eq. (46). We assume therefore, that the finite basis consists of all functions with nonnegative integers n_i such that

$$\sum_{i=1}^5 n_i \leq \Omega \quad (47)$$

with $\Omega = 3, \dots, 18$, and the final result is obtained by a numerical extrapolation to $\Omega \rightarrow \infty$. For $R < 1.2$ bohrs we used the James-Coolidge basis with two different nonlinear parameters $\alpha \neq \beta$, whereas for $1.2 \leq R \leq 12$ bohrs—with $\alpha = \beta$. The nonlinear parameters were optimized separately for each internuclear distance R , and then the exponential convergence to a complete basis set as $\Omega \rightarrow \infty$ has been observed.

To describe the molecule at $12 \leq R \leq 20$ bohrs, the generalized Heitler-London functions [13]

$$\begin{aligned} \psi_k(\vec{r}_1, \vec{r}_2) = & (1 \pm \hat{P}_{12})(1 \pm \hat{i}) \\ & \times e^{-(r_{1A}+r_{2B})} r_{12}^{n_{1k}} r_{1A}^{n_{2k}} r_{1B}^{n_{3k}} r_{2A}^{n_{4k}} r_{2B}^{n_{5k}} \end{aligned} \quad (48)$$

with Ω up to 16 have been applied. These functions are the most appropriate for large internuclear distances, and we have checked that at $R = 12$ bohrs the accuracy achieved with generalized Heitler-London functions is close to that with the symmetric James-Coolidge basis.

The region of $R > 20$ bohrs is found to be numerically insignificant, as $\delta\mathcal{E}$ vanishes exponentially at large R [see Eq. (4)]. All the numerical results for $R \leq 20$ bohrs, after extrapolation to a complete basis set, are listed along with the estimated error in Table I. This is the most accurate clamped nuclei energy curve for the $b^3\Sigma_u^+$ state among all obtained so far. Numerical calculations were performed in the quadrupole precision, which nevertheless was not always sufficient. For some values of R we observed numerical instabilities for highest values of Ω , these results had to be dropped, and thus numerical extrapolation includes much larger uncertainties.

For small values of R we observed much slower numerical convergence. It is related to the fact that r_{iA} is then close to r_{iB} and the one parameter selection of the finite basis set Eq. (47) is not the most effective.

To evaluate the matrix elements in the functions β , γ , and γ' [see Eqs. (14), (24), and (27)] we employed exponentially correlated Gaussian (ECG) functions [17,18] of the form

$$\begin{aligned} \psi_k(\vec{r}_1, \vec{r}_2) = & (1 \pm \hat{P}_{12})(1 \pm \hat{i}) \\ & \times \exp \left[- \sum_{i,j=1}^2 A_{k,ij} (\vec{r}_i - \vec{s}_{k,i})(\vec{r}_j - \vec{s}_{k,j}) \right], \end{aligned} \quad (49)$$

where the matrices \mathbf{A}_k and vectors \vec{s}_k contain nonlinear parameters, five per basis function, to be variationally optimized. For both $X^1\Sigma_g^+$ and $b^3\Sigma_u^+$ states 600-term bases were optimized with respect to \mathcal{E}_g or \mathcal{E}_u for R spread over the range 0–12 bohrs. For each R , the *gerade* $\{\psi_{g,k}\}_{k=1}^{600}$ and *ungerade* $\{\psi_{u,k}\}_{k=1}^{600}$ basis sets were merged together to form 1200-term expansions $\sum_{k=1}^{600} (c_k \psi_{g,k} + c_{k+600} \psi_{u,k})$ for ϕ_g (ϕ_u) yielding the \mathcal{E}_g (\mathcal{E}_u) accurate to a fraction of microhartree. Next, using these ϕ_g and ϕ_u we evaluated the electronic matrix elements of δH [Eqs. (15), (24), and (27)]. Their numerical values are presented in Table II.

TABLE II. The matrix elements for $\delta\mathcal{E}_{\text{spin}}$ in atomic units. For c and c' the relative uncertainty is better than 10^{-3} , whereas for b all displayed digits are significant.

R (a.u.)	$b(R)$	$c(R)$	$c'(R)$
0.00	0.036 04	5.035	0.0
0.01	0.036 04	4.929	0.004 396
0.10	0.036 32	4.000	0.040 20
0.50	0.042 75	1.708	0.1626
1.00	0.062 32	0.8818	0.3242
1.30	0.073 67	0.7345	0.4188
1.40	0.075 88	0.7128	0.4450
1.50	0.077 11	0.6989	0.4675
1.60	0.077 39	0.6910	0.4867
1.70	0.076 84	0.6866	0.5027
1.80	0.075 57	0.6846	0.5157
2.00	0.071 50	0.6833	0.5352
2.30	0.063 36	0.6818	0.5539
2.50	0.057 56	0.6795	0.5631
3.00	0.044 12	0.6696	0.5824
3.50	0.033 35	0.6585	0.6004
4.00	0.025 21	0.6500	0.6156
4.50	0.019 16	0.6439	0.6253
5.00	0.014 70	0.6404	0.6309
5.50	0.011 41	0.6383	0.6336
6.00	0.008 969	0.6373	0.6351
7.00	0.005 760	0.6365	0.6360
8.00	0.003 887	0.6364	0.6363
9.00	0.002 737	0.6363	0.6363
10.00	0.001 998	0.6364	0.6364
11.00	0.001 502	0.6364	0.6364
12.00	0.001 157	0.6364	0.6364
∞	0.0	$2/\pi$	$2/\pi$

TABLE III. The *gerade-ungerade* mixing corrections δE_{gu} to the dissociation energy of all the bound rovibrational levels of H_2 . The entries are given in units of 10^{-8} cm^{-1} .

$v \setminus L$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	1	2	1	2	1	2	1	2	1	2	1	3	1	3	1	3	1
1	1	0	1	0	1	0	1	0	1	0	2	1	2	1	2	1	2	1	2	1	2	1	3	1	3	1	3	1	4	1	5	
2	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	3	1	3	1	3	1	4	1	4	2	5			
3	2	1	2	1	2	1	2	1	2	1	2	1	2	1	3	1	3	1	3	1	4	1	4	2	5	2	6	2				
4	2	1	2	1	2	1	2	1	2	1	3	1	3	1	3	1	4	1	4	1	5	2	6	2	7	3						
5	3	1	3	1	3	1	3	1	3	1	3	1	4	1	4	1	5	2	5	2	6	2	8	3								
6	3	1	3	1	3	1	4	1	4	1	4	1	5	2	5	2	6	2	7	3	10	4	14									
7	4	1	4	1	4	1	5	2	5	2	5	2	6	2	7	3	9	3	12	5	17											
8	5	2	5	2	6	2	6	2	7	2	7	3	9	3	11	4	14	6	21													
9	7	2	7	2	8	3	8	3	9	3	11	4	14	5	18	7	28															
10	10	3	11	4	11	4	13	4	15	5	18	7	25	10	40																	
11	16	5	17	6	18	6	21	8	26	10	37	16	65																			
12	30	10	31	11	36	13	45	18	66	30	138																					
13	74	25	81	30	104	42	170	90																								
14	438	159	583	280																												

The regular radial Schrödinger equation (3) as well as the coupled set of radial differential equations (36) have been solved using the discrete variable representation (DVR) method [19]. The discrete spectrum consists of 301 eigenvalues, each corresponding to a bound rovibrational level (v, L) accommodated by the \mathcal{E}_g potential of H_2 . The *gerade-ungerade* mixing corrections δE_{gu} to the dissociation energy of all the levels are listed in Table III. For a vast part of the levels the corrections are of the order of 10^{-8} cm^{-1} or even smaller. Only for the highest vibrational quantum numbers $v \geq 12$, values two orders of magnitude larger can be found. The largest correction of approximately $6 \times 10^{-6} \text{ cm}^{-1}$ appears for the $v = 14, L = 2$ level. In all cases the corrections increase the dissociation energy, that is, lower the energy level.

Among the components of the Breit-Pauli Hamiltonian, which are due to the magnetic interaction between all the particles [Eq. (9)] the proton-proton interaction and the electron-electron contact interaction have been *a priori* discarded, as expected to be very small. It turns out that the relativistic corrections to *gerade-ungerade* splitting do not play any role either. The main contribution to the overall mixing effect comes from the off-diagonal matrix elements δH_{2gu} expressed through the $\gamma'(R)$ [Eq. (27)].

VI. CONCLUSION

We have shown that *gerade-ungerade* mixing gives corrections to most of the rovibrational levels of hydrogen molecules smaller than 10^{-6} cm^{-1} . Since the present accuracy of theoretical predictions for the dissociation energy in the ground electronic state of the hydrogen molecule is 10^{-3} – 10^{-4} cm^{-1} [1,4], these corrections appear to be negligible. The mixing corrections become more significant only for highly excited rovibrational states, where they approach 10^{-5} cm^{-1} . It means that further improvement in the precision of the dissociation energies can be obtained by the calculation of the higher order nonadiabatic and QED effects, assuming that the *gerade-ungerade* symmetry is conserved.

ACKNOWLEDGMENTS

K.P. and J.K. acknowledge the support of the Polish Ministry of Science and Higher Education via Grants No. N N204 182840 and No. N N204 015338, correspondingly. Part of the computations has been performed within a computing grant from Poznań Supercomputing and Networking Center.

- [1] K. Piszczatowski, G. Lach, M. Przybytek, J. Komasa, K. Pachucki, and B. Jeziorski, *J. Chem. Theory Comput.* **5**, 3039 (2009).
- [2] J. Liu, E. J. Salumbides, U. Hollenstein, J. C. J. Koelemeij, K. S. E. Eikema, W. Ubachs, and F. Merkt, *J. Chem. Phys.* **130**, 174306 (2009).
- [3] J. Liu, D. Sprecher, C. Jungen, W. Ubachs, and F. Merkt, *J. Chem. Phys.* **132**, 154301 (2010).
- [4] K. Pachucki and J. Komasa, *Phys. Chem. Chem. Phys.* **12**, 9188 (2010).
- [5] D. Sprecher, J. Liu, C. Jungen, W. Ubachs, and F. Merkt, *J. Chem. Phys.* **133**, 111102 (2010).
- [6] R. Pohl *et al.*, *Nature (London)* **466**, 213 (2010).
- [7] J. P. Pique, F. Hartmann, R. Bacis, S. Churassy, and J. B. Koffend, *Phys. Rev. Lett.* **52**, 267 (1984).
- [8] H. Weickenmeier, U. Diemer, W. Demtröder, and M. Broyer, *Chem. Phys. Lett.* **124**, 470 (1986).
- [9] M. Broyer, J. Vigué, and J. Lehmann, *J. Phys. France* **39**, 591 (1978).
- [10] D. Sprecher, C. Jungen, W. Ubachs, and F. Merkt, *Faraday Discuss.* **150** (2011), in press.
- [11] C. Herring and M. Flicker, *Phys. Rev.* **134**, A362 (1964).
- [12] K. Pachucki, *Phys. Rev. A* **82**, 032509 (2010).
- [13] W. Heitler and F. London, *Z. Phys. C* **44**, 455 (1927).

- [14] K. Pachucki, *Phys. Rev. A* **80**, 032520 (2009).
- [15] H. M. James and A. S. Coolidge, *J. Chem. Phys.* **1**, 825 (1933).
- [16] J. S. Sims and S. A. Hagstrom, *J. Chem. Phys.* **124**, 094101 (2006).
- [17] K. Singer, *Proc. R. Soc. London Ser. A* **258**, 412 (1960).
- [18] J. Rychlewski and J. Komasa, in *Explicitly Correlated Wave Functions in Chemistry and Physics. Theory and Applications*, edited by J. Rychlewski (Kluwer, Dordrecht, The Netherlands, 2003), p. 91.
- [19] G. C. Groenenboom and D. T. Colbert, *J. Chem. Phys.* **99**, 9681 (1993).