Gerade-ungerade mixing in the hydrogen molecule

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In homonuclear molecules, such as H_2, 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 co-product, the most accurate to date clamped nuclei potential for the b $^3\Sigma_\mathrm{u}^+$ state has been obtained.

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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 $\mathcal{O}(\alpha^3)$ and the dominating part of $\mathcal{O}(\alpha^4)$ QED corrections have to be included. The excellent agreement with recent experimental results for H_2 [1, 2], D_2 [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 $\mathcal{O}(\mu_\mathrm{n}^{-3})$, relativistic recoil $\mathcal{O}(\alpha^2/\mu_\mathrm{n})$, and QED $\mathcal{O}(\alpha^4)$ corrections. Once these three terms are known, the accuracy of rovibrational levels could be increased up to about 10^{-6} cm^{-1} ($\sim$ 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 H_2 dissociation energy of about 5×10^{-6} cm^{-1}, thusxs 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 H_2 can, in principle, be as large as the hyperfine splitting in the hydrogen atom, which amounts to 1420 MHz ≈ 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 H_2 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 H_2 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 theoretical point of view, we have not yet investigated in detail the feasibility of such an uncertainty in H_2. Certainly the most challenging is the accurate calculation of $\mathcal{O}(\alpha^4)$ and estimation of $\mathcal{O}(\alpha^5)$ 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

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

with ϕ_el being the solution to the clamped nuclei Schrödinger equation

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

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

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

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

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geometrical center of the H_2 molecule is conserved, and the splitting $\delta\mathcal{E}$ of the clamped nuclei energies between the lowest *gerade* and *ungerade* states vanishes exponentially for large internuclear distances R [11, 12] (in atomic units)

$$\delta\mathcal{E}(R) = \mathcal{E}_{\rm u}(R) - \mathcal{E}_{\rm g}(R) = R^{5/2}\, e^{-2\,R}\, [1+\mathcal{O}(1/\sqrt{R})]\,. \quad (4)$$

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

$$\phi_{\rm g}(\vec r_1, \vec r_2; \vec R) = \phi_{\rm g}(-\vec r_1, -\vec r_2, \vec R) = \phi_{\rm g}(\vec r_2, \vec r_1, \vec R) \quad (5)$$

for the *gerade* ($\mathrm{X}\,^1\Sigma_{\rm g}^+$) state, and

$$\phi_{\rm u}(\vec r_1, \vec r_2; \vec R) = -\phi_{\rm u}(-\vec r_1, -\vec r_2, \vec R) = -\phi_{\rm u}(\vec r_2, \vec r_1, \vec R) \quad (6)$$

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

$$\phi_{\rm g}(\vec r_1, \vec r_2, \vec R) = \frac{[\phi_H(r_{1A})\,\phi_H(r_{2B}) + \phi_H(r_{1B})\,\phi_H(r_{2A})]}{\sqrt{2}} \quad (7)$$

$$\phi_{\rm u}(\vec r_1, \vec r_2, \vec R) = \frac{[\phi_H(r_{1A})\,\phi_H(r_{2B}) - \phi_H(r_{1B})\,\phi_H(r_{2A})]}{\sqrt{2}} \quad (8)$$

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, ($e^2 = 4\,\pi\,\alpha$)

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

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

$$\begin{aligned}\delta H &= \alpha^2\,\frac{s_1^i\,s_2^j}{r_{12}^3}\left(\delta^{ij} - 3\,\frac{r_{12}^i\,r_{12}^j}{r_{12}^2}\right)\\ &\quad+\sum_{a,X}\frac{4\,\pi\,\alpha^2}{3}\,\frac{g_p\,m}{m_p}\,\vec s_a\cdot\vec I_X\,\delta^{(3)}(r_{aX}) \quad (10)\\ &= \delta H_1 + \delta H_2\,, \quad (11)\end{aligned}$$

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 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

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

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

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

$$b(R) = \Big\langle\phi_{\rm u}\Big|\frac{3(\vec r_{12}\cdot\vec n)^2 - r_{12}^2}{r_{12}^5}\Big|\phi_{\rm u}\Big\rangle\,. \quad (15)$$

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

Matrix elements of $\delta H_{1\rm uu}$ 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:

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

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

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

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

where we have introduced the double-braket notation

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

for a scalar operator Q.

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

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

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

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

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

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

and the off-diagonal is

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

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

$$c'(R) = \langle\phi_{\rm g}|\delta^{(3)}(r_{1A})-\delta^{(3)}(r_{1B}) - \delta^{(3)}(r_{2A})+\delta^{(3)}(r_{2B})|\phi_{\rm u}\rangle\,. \quad (27)$$

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

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

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

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

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

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

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

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

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 the equation 3

$$\biggl[-\frac{1}{2\,\mu_{\rm n}}\,\frac{1}{R}\,\frac{\partial^2}{\partial R^2}\,R+\frac{L\,(L+1)}{2\,\mu_{\rm n}\,R^2} +\mathcal{E}_{\rm g}(R)+\delta\mathcal{E}_{\rm spin}(R)-\tilde{E}_{vL}\biggr]\tilde{\chi}_{vL}(R) = 0\,, \quad (36)$$

where $\delta\mathcal{E}_{\rm spin}(R)$ is a matrix formed from matrix elements of δH, Eq. (10), in a pertinent basis. The dimension of the matrix $\delta\mathcal{E}_{\rm spin}(R)$ 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

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

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 $\delta\mathcal{E}_{\rm spin}(R)$.

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

We span the nuclear wave function in the following basis

$$\begin{array}{l} |L,0,L,0,L,M\rangle \\ |L,1,L+1,1,L,M\rangle \\ |L,1,L,1,L,M\rangle \\ |L,1,L-1,1,L,M\rangle\,. \end{array} \tag{38}$$

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

$$\delta\mathcal{E}_{\rm spin} = \begin{pmatrix} 0 & -\gamma'\sqrt{\frac{2L+3}{2L+1}} & -\gamma' & -\gamma'\sqrt{\frac{2L-1}{2L+1}} \\ -\gamma'\sqrt{\frac{2L+3}{2L+1}} & \delta\mathcal{E}+\beta\,\frac{2\,L\,(L-2)}{(2L+3)(2L-1)}-\gamma\,\frac{L+2}{L+1} & -\gamma\,\frac{L}{L+1}\,\sqrt{\frac{2L+3}{2L+1}} & 0 \\ -\gamma' & -\gamma\,\frac{L}{L+1}\,\sqrt{\frac{2L+3}{2L+1}} & \delta\mathcal{E}-\beta\,\frac{2(2L(L+1)-3)}{(2L+3)(2L-1)}-\gamma\,\frac{1}{L(L+1)} & -\gamma\,\frac{L+1}{L}\,\sqrt{\frac{2L-1}{2L+1}} \\ -\gamma'\sqrt{\frac{2L-1}{2L+1}} & 0 & -\gamma\,\frac{L+1}{L}\,\sqrt{\frac{2L-1}{2L+1}} & \delta\mathcal{E}+\beta\,\frac{2\,(L+1)(L+3)}{(2L+3)(2L-1)}-\gamma\,\frac{L-1}{L} \end{pmatrix} \tag{39}$$

B. Case: L odd

The basis is

$$\begin{array}{l} |L,0,L,1,J,M\rangle \\ |L,1,J,0,J,M\rangle\,. \end{array} \tag{40}$$

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

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

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

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

C. Case: $L = 0$

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

$$\begin{array}{l} |0,0,0,0,0,0\rangle \\ |0,1,1,1,0,0\rangle \\ |2,1,1,1,0,0\rangle \end{array} \tag{44}$$

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

$$\delta\mathcal{E}_{\rm spin} = \begin{pmatrix} 0 & -\sqrt{3}\gamma' & 0 \\ -\sqrt{3}\gamma' & \delta\mathcal{E}-2\,\gamma & -\sqrt{2}\,\beta \\ 0 & -\sqrt{2}\,\beta & \delta\mathcal{E}+3/(\mu_{\rm n}\,R^2) \end{pmatrix}. \tag{45}$$

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

V. NUMERICAL PROCEDURES AND RESULTS

Very accurate clamped nuclei potential for the $\mathrm{X}\,^1\Sigma_{\rm g}^+$ 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 $\mathrm{b}\,^3\Sigma_{\rm u}^+$ state. In order to achieve the highest numerical accuracy, different basis sets are used, depending on the internuclear distance R. For $R < 12$ bohr, the James-Coolidge basis functions [15, 16] of the form

$$\begin{aligned} \psi_{\{n\}}(\vec r_1,\vec r_2) &= (1\pm\hat P_{12})(1\pm\hat\imath)\,e^{-\alpha\,(r_{1A}+r_{1B})-\beta\,(r_{2A}+r_{2B})} \\ &\quad\times r_{12}^{n_1}\,(r_{1A}-r_{1B})^{n_2}\,(r_{2A}-r_{2B})^{n_3} \\ &\quad\times(r_{1A}+r_{1B})^{n_4}\,(r_{2A}+r_{2B})^{n_5} \end{aligned} \tag{46}$$

have been employed. The antisymmetry projector $(1\pm\hat P_{12})$ ensures singlet $(+)$ or triplet $(-)$ state, while the spatial projector $(1\pm\hat\imath)$—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

$$\sum_{i=1}^{5} n_i \leq \Omega \tag{47}$$

with $\Omega = 3,\ldots 18$, and the final result is obtained by a numerical extrapolation to $\Omega\to\infty$. For $R < 1.2$ bohr we used the James-Coolidge basis with two different nonlinear parameters $\alpha \neq \beta$, whereas for $1.2 \leq R \leq 12$ bohr—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 $\Omega\to\infty$ has been observed.

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

$$\psi_k(\vec r_1,\vec r_2) = (1\pm\hat P_{12})(1\pm\imath) \quad (48)$$
$$e^{-(r_{1A}+r_{2B})}\, r_{12}^{n_{1k}}\, r_{1A}^{n_{2k}}\, r_{1B}^{n_{3k}}\, r_{2A}^{n_{4k}}\, r_{2B}^{n_{5k}}$$

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

The region of $R > 20$ bohr is found to be numerically insignificant, as $\delta\mathcal{E}$ vanishes exponentially at large R, see Eq. (4). All the numerical results for $R < 20$ bohr, 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

$$\psi_k(\vec r_1,\vec r_2) = (1\pm\hat P_{12})(1\pm\imath) \quad (49)$$
$$\times\ \exp\left[-\sum_{i,j=1}^{2} A_{k,ij}(\vec r_i-\vec s_{k,i})(\vec r_j-\vec s_{k,j})\right],$$

where the matrices $\mathbf{A}_k$ and vectors $\vec s_k$ contain nonlinear parameters, 5 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 $(0, 12)$ bohr. 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 $\phi_{g/u}$ yielding the $\mathcal{E}_{g/u}$ accurate to a fraction of microhartree. Next, using these $\phi_{g/u}$, we evaluated the electronic matrix elements of δH, Eqs. (15), (24), and (27). Their numerical values are presented in Table II.

The regular radial Schrödinger equation (3) as well as the coupled set of radial differential equations (36) have been solved using 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 ca. $6\cdot10^{-6}$ cm^{-1} appears for the $v = 14$, $L = 2$ level. In all cases, the corrections increase the dissociation energy, i.e. 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 the most of rovibrational levels of hydrogen molecule 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.

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TABLE I: The clamped nuclei energy $\mathcal{E}_\mathrm{u}(R)$ of the $\mathrm{b}\,^3\Sigma_\mathrm{u}^+$ state of H_2 in atomic units.

R/au	$\mathcal{E}_\mathrm{u}(R)$	R/au	$\mathcal{E}_\mathrm{u}(R)$
0.1	7.88820048023(54)	3.6	−0.988000298079213(12)
0.2	2.936760506575(82)	3.7	−0.989633582435914(12)
0.3	1.330347123362(18)	3.8	−0.9910585611760516(9)
0.4	0.5606817228129(49)	3.9	−0.992300031116625(14)
0.5	0.1234804880203(22)	4.0	−0.9933800668510541(6)
0.6	−0.1500998245246(19)	4.2	−0.995132117890052(4)
0.7	−0.3325581672547(26)	4.4	−0.996446550339835(4)
0.8	−0.4600921231595(33)	4.6	−0.997426637512202(3)
0.9	−0.5527036001896(36)	4.8	−0.998152794502693(1)
1.0	−0.6222644271165(35)	5.0	−0.9986872571548951(7)
1.1	−0.6761830053419(32)	5.2	−0.9990778944119540(7)
1.2	−0.7192364779960(12)	5.4	−0.9993612944728789(2)
1.3	−0.75456345204348(33)	5.6	−0.9995652465495600(3)
1.4	−0.78424467761929(72)	5.8	−0.9997107228203121(2)
1.5	−0.80966665343589(18)	6.0	−0.999813449850999(3)
1.6	−0.831760208300362(68)	6.5	−0.9999528356310057(3)
1.7	−0.851159923317480(27)	7.0	−1.000004005774949(3)
1.8	−0.8683100622950944(85)	7.5	−1.000018923410887(1)
1.9	−0.8835336279111071(53)	8.0	−1.000020221124853(3)
2.0	−0.8970763307631061(23)	8.5	−1.000017233424615(2)
2.1	−0.9091339626356802(92)	9.0	−1.000013517806560
2.2	−0.9198691283981695(17)	9.5	−1.000010246361593(1)
2.3	−0.929421350735748(16)	10.0	−1.000007673917731(3)
2.4	−0.9379131525207151(30)	10.5	−1.000005743973625(3)
2.5	−0.9454537520626225(47)	11.0	−1.000004322969006(11)
2.6	−0.9521413693513220(25)	11.5	−1.00000328140072(49)
2.7	−0.9580647377083453(7)	12.0	−1.000002515543228(2)
2.8	−0.9633041667983422(98)	13.0	−1.000001524303681(3)
2.9	−0.9679323537002679(23)	14.0	−1.000000959875243(1)
3.0	−0.9720150510265303(30)	15.0	−1.000000625324878
3.1	−0.9756116506534407(28)	16.0	−1.000000419565938
3.2	−0.9787757133393848(4)	17.0	−1.000000288823044
3.3	−0.9815554591177198(4)	18.0	−1.000000203340009
3.4	−0.9839942253211882(20)	19.0	−1.000000146028160
3.5	−0.9861308951634316(23)	20.0	−1.000000106740117

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

R/au	$b(R)$	$c(R)$	$c'(R)$
0.00	0.03604	5.035	0.0
0.01	0.03604	4.929	0.004396
0.10	0.03632	4.000	0.04020
0.50	0.04275	1.708	0.1626
1.00	0.06232	0.8818	0.3242
1.30	0.07367	0.7345	0.4188
1.40	0.07588	0.7128	0.4450
1.50	0.07711	0.6989	0.4675
1.60	0.07739	0.6910	0.4867
1.70	0.07684	0.6866	0.5027
1.80	0.07557	0.6846	0.5157
2.00	0.07150	0.6833	0.5352
2.30	0.06336	0.6818	0.5539
2.50	0.05756	0.6795	0.5631
3.00	0.04412	0.6696	0.5824
3.50	0.03335	0.6585	0.6004
4.00	0.02521	0.6500	0.6156
4.50	0.01916	0.6439	0.6253
5.00	0.01470	0.6404	0.6309
5.50	0.01141	0.6383	0.6336
6.00	0.008969	0.6373	0.6351
7.00	0.005760	0.6365	0.6360
8.00	0.003887	0.6364	0.6363
9.00	0.002737	0.6363	0.6363
10.00	0.001998	0.6364	0.6364
11.00	0.001502	0.6364	0.6364
12.00	0.001157	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}.

$v\backslash L$	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																												