

EXPONENTIALLY CORRELATED GAUSSIAN FUNCTIONS IN VARIATIONAL CALCULATIONS. THE $EF\ ^1\Sigma_g^+$ STATE OF HYDROGEN MOLECULE*

JACEK KOMASA¹ AND WOJCIECH CENCEK²

¹*Quantum Chemistry Group, Department of Chemistry, A. Mickiewicz University
Grunwaldzka 6, 60-780 Poznań, Poland*

²*Department of Physics and Astronomy, University of Delaware, Newark, DE 19716, USA*

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Abstract: The Born-Oppenheimer (BO) potential energy curve, the adiabatic and the relativistic corrections for the EF state of the hydrogen molecule are calculated for the internuclear distances ranging from 0.01 to 20 bohr. 600-term variational expansions of exponentially correlated Gaussian (ECG) functions are used. The BO energies and the adiabatic corrections are more accurate than previously reported and the relativistic calculations confirm existing literature values.

1. INTRODUCTION

The $EF\ ^1\Sigma_g^+$ state of the hydrogen molecule is the lowest excited state having the same symmetry as the ground state. Its most striking feature is the potential energy curve with two deep and well separated minima, resulting from the avoided crossing of two diabatic states, E and F [1]. The united atom configuration is $^1S(1s2s)$. The dominant configuration for the inner part of the potential is $(1s\sigma_g2s\sigma_g)$, whereas in the outer part of the energy curve the $(2p\sigma_u)^2$ configuration is contributing the most to the wave function, although the $(1s\sigma_g2s\sigma_g)$ and $(1s\sigma_g)^2$ configurations are also present. Finally, the EF state dissociates onto $H(1s) + H(2s)$. As a result of the two-minimum potential, two separate band systems can be observed in certain energy regions. The EF state has drawn significant interest and a number of variational calculations of increasing accuracy has been reported over the last 40 years [2-8]. The current most accurate electronic energy was obtained in 1999 by Orlikowski *et al.* [8], who used a 443-term expansion of the Kołos-Wolniewicz-type (KW) wave function [3] and evaluated also the adiabatic corrections. At $R = 1.5$ bohr, the Born-Oppenheimer (BO) energy of Ref. [8] is, however, over 0.3 μ hartree higher than the older result [9] obtained by the present authors as a test of our exponentially correlated Gaussian (ECG) package. In the present paper we extend our ECG calculation to the complete BO energy curve of the EF state and calculate the adiabatic and relativistic corrections. The aim of this work is twofold. Firstly, to generate new and more accurate benchmark results. Secondly, to test the performance of our correction

* Dedicated to the memory of Professor Jacek Rychlewski

packages. We use the direct perturbation theory (DPT) of Kutzelnigg [10] and Rutkowski [11] in relativistic calculations and the Born-Handy approach [12-14] to adiabatic corrections, both methods never used before in studies of excited states of the hydrogen molecule.

2. METHOD OF CALCULATION

2.1. Born-Oppenheimer energy

The electronic wave function used in this work is expressed in the form of the linear combination of properly symmetrized two-electron basis functions, ψ_k

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = (1 + \hat{P}_{12})(1 + \hat{i}_e) \sum_{k=1}^K c_k \psi_k(\mathbf{r}_1, \mathbf{r}_2), \quad (1)$$

where \hat{P}_{12} and \hat{i}_e are the electron exchange and the inversion operators, respectively. The expansion terms were assumed in the form of the ECG functions [15, 16], which in the two-electron case are equivalent to Gaussian type geminals (GTG) [17-19]

$$\psi_k(\mathbf{r}_1, \mathbf{r}_2) = \exp\left[-\alpha_k r_{1a}^2 - \beta_k r_{1b}^2 - \zeta_k r_{2a}^2 - \eta_k r_{2b}^2 - \gamma_k r_{12}^2\right], \quad (2)$$

where 1 and 2 denote electrons and a and b – nuclei. The linear, c_k , and the nonlinear parameters α_k , β_k , ζ_k , η_k and γ_k were determined variationally. The wave function was optimized with respect to the second eigenvalue of the Hamiltonian using Powell's conjugate directions method [20]. More details on the optimization of this type of the wave function can be found in Refs. [9, 21].

Historically, the most successful ansatz used in the studies of the hydrogen molecule was the KW function, which contains terms linear in electron-nucleus and electron-electron distances and, in contrast to the ECGs, fulfills the necessary cusp conditions. All existing complete high-accuracy potentials of the EF state were obtained in this way [5, 6, 8]. Only in the last 10 years it was discovered that the ECG functions, which can easily be integrated analytically and therefore allow one to use larger and carefully optimized expansions without stability problems or prohibitive cost, can surpass the accuracy provided by the KW functions [9, 22, 23].

2.2. Adiabatic corrections

Traditionally, the adiabatic corrections to the BO energies of molecules are obtained as expectation values of a perturbation operator \hat{H}' defined by first separating off the center-of-mass (COM) motion and then collecting all the terms depending on nuclear masses. Such approach has been many times successfully used in studies of various states of the hydrogen molecule, including the EF state [5, 8], but becomes prohibitively complicated for larger molecules, because the operator \hat{H}' contains in such cases extremely cumbersome terms

coupling electronic and nuclear coordinates [24]. As shown in 1997 by Kutzelnigg [14], the complications occurring after the separation of the COM motion can be entirely avoided if one chooses to work in the laboratory (instead of relative) coordinates. The use of the operator

$$\hat{H}' = - \sum_I \frac{\nabla_I^2}{2M_I} \quad (3)$$

leads to the correct value of the adiabatic correction, because the COM degrees of freedom are zeroed out when the expectation value of (3) is calculated with electronic wave functions, which are translation- and rotation-invariant. The sum in Eq. (3) is over all the nuclei (with masses M_I). To calculate the adiabatic correction

$$\Delta E_{\text{ad}} = \int \Psi \hat{H}' \Psi d\tau, \quad (4)$$

one has to evaluate the derivatives of the electronic wave function with respect to the Cartesian nuclear coordinates, $Q_I (= X_I, Y_I, Z_I)$. These derivatives can be approximated numerically by a three-point differentiation quotient

$$\frac{\partial \Psi}{\partial Q_I} \approx \frac{\Psi(Q_I + \Delta Q_I/2) - \Psi(Q_I - \Delta Q_I/2)}{\Delta Q_I}, \quad (5)$$

leading to the following compact expression for ΔE_{ad} :

$$\Delta E_{\text{ad}} \approx \sum_I \frac{3 - S_I^X - S_I^Y - S_I^Z}{M_I (\Delta Q_I)^2}, \quad (6)$$

where S_I^O represent the overlap integrals of two distorted wave functions

$$S_I^O = \int \Psi(Q_I + \Delta Q_I/2) \Psi(Q_I - \Delta Q_I/2) d\tau. \quad (7)$$

In the case of the hydrogen molecule placed on the x axis, the evaluation of the adiabatic correction at a given internuclear distance requires two different expectation values,

$$\Delta E_{\text{ad}} = -\frac{1}{2} \left(\frac{1}{M_a} + \frac{1}{M_b} \right) \left(\left\langle \frac{\partial^2}{\partial X_I^2} \right\rangle + 2 \left\langle \frac{\partial^2}{\partial Y_I^2} \right\rangle \right), \quad (8)$$

which can be calculated as

$$\left\langle \frac{\partial^2}{\partial Q_I^2} \right\rangle \approx \frac{2(S_I^O - 1)}{(\Delta Q_I)^2}. \quad (9)$$

Formally speaking, the distorted functions in Eq. (7) should be solutions of the Schrödinger equation corresponding to the nuclear configurations $Q_I + \Delta Q_I/2$ and $Q_I - \Delta Q_I/2$. In practice, it is sufficient to construct them from the original function $\Psi(Q_I)$ by recalculating the linear

coefficients only. If the expansion (1) is long enough, the changes of c_k can compensate for the slightly non-optimal values of nonlinear parameters. Evidently, the accuracy of the numerical evaluation of (4) depends critically on the chosen value of ΔQ_I in Eq. (5). As follows from tests on the ground state of H_2 [25], the choice of $\Delta Q_I = 5 \times 10^{-4}$ bohr gives an accuracy of 6-7 significant digits and we used this value in the present work. An additional check of the calculated adiabatic corrections exploits the identity

$$\int \Psi \left(\sum_I \nabla_I \right)^2 \Psi d\tau = \int \Psi \left(\sum_i \nabla_i \right)^2 \Psi d\tau, \quad (10)$$

resulting from the total momentum conservation condition. The right-hand side of Eq. (10) represents an ordinary expectation value (the operator depends only on the electronic coordinates) and can be evaluated analytically. This value can then be confronted with the left-hand-side value obtained numerically, if one uses Eq. (5) to calculate also the off diagonal nuclear expectation values $\langle \partial^2 / (\partial X_a \partial X_b) \rangle$ and $\langle \partial^2 / (\partial Y_a \partial Y_b) \rangle$.

2.3. Relativistic corrections

According to the DPT, the lowest-order relativistic correction can be calculated from the expression [10, 23, 26]

$$E_2 = \langle \hat{H}_{\text{BP}} \rangle + \Delta_{\text{DPT}}, \quad (11)$$

where

$$\Delta_{\text{DPT}} = \frac{1}{2} c^{-2} \langle \hat{T} (\hat{H}_0 - E_0) \rangle \quad (12)$$

and $\langle \hat{H}_{\text{BP}} \rangle$ is the expectation value of the Breit-Pauli (BP) Hamiltonian [27], which for singlet states of two-electron systems can be expressed as

$$\hat{H}_{\text{BP}} = c^{-2} (\hat{H}_1 + \hat{H}_2 + \hat{H}_4 + \hat{H}_5), \quad (13)$$

with

$$\hat{H}_1 = -\frac{1}{2} (\hat{T}_1^2 + \hat{T}_2^2), \quad (14)$$

$$\hat{H}_2 = -\frac{1}{2} \frac{1}{r_{12}} \left(\mathbf{p}_1 \mathbf{p}_2 + \frac{\mathbf{r}_{12} (\mathbf{r}_{12} \mathbf{p}_1) \mathbf{p}_2}{r_{12}^2} \right) \quad (15)$$

$$\hat{H}_4 = \frac{\pi}{2} \left\{ \sum_I Z_I [\delta(\mathbf{r}_{1I}) + \delta(\mathbf{r}_{2I})] - 2\delta(\mathbf{r}_{12}) \right\}, \quad (16)$$

$$\hat{H}_5 = 2\pi\delta(\mathbf{r}_{12}). \quad (17)$$

In the Eqs. (12)-(17), $c = 137.03600$ a.u. is the speed of light, \hat{T} is the kinetic energy operator, \hat{H}_0 and E_0 are the nonrelativistic Hamiltonian and energy, \mathbf{p} is the momentum operator, and δ the Dirac delta function. In all previous relativistic calculations on excited states of H_2 , including the work on the EF state by Wolniewicz [7], the conventional BP theory was used instead of the DPT, that is, the corrections were calculated as the expectation values of the operator (13). Both theories become equivalent (to the lowest order) in the limit of the exact nonrelativistic wave function, because (12) vanishes in such a case. In practical calculations, the DPT is preferable and leads to faster convergence towards the basis set limit [28]. It can be explained by the fact that the operators present in the BP Hamiltonian, especially \hat{H}_1 and \hat{H}_4 , are highly singular, whereas the whole sum in Eq. (11) can be alternatively written using only global operators with fast convergent expectation values [26].

3. RESULTS AND DISCUSSION

The 600-term wave functions of the form of Eq. (1) and (2) were generated for internuclear distances ranging from $R = 0.01$ to $R = 20.0$ bohr. The extensive nonlinear optimization process was led separately at each distance. Table 1 lists the energies and the derivatives at a large selection of distances. The derivatives of the energy were inferred from the virial theorem. Our ECG curve lies everywhere below the best previous Born-Oppenheimer curve calculated by Orlikowski *et al.* [8], the improvement ΔE_{BO} ranging from 0.007 cm^{-1} at $R = 3.0$ bohr to as much as 0.5 cm^{-1} at $R = 0.5$ bohr, see the last column of Table 1 and Fig. 1. Note that the full list of energy values and adiabatic corrections obtained by Orlikowski *et al.* is available on their web page [29]. Since the integrals containing the KW wave function are too time consuming for a full optimization of nonlinear parameters, the usual procedure is to optimize them in the most relevant regions and interpolate between them. This probably explains a relative drop of accuracy of results from Ref. [8] around 10 bohr and at very short distances. In Ref. [9] we analyzed the convergence of our ECG expansions for various two-electron systems, including the EF state of H_2 at $R = 1.5$ bohr. We concluded that it was difficult to estimate the error of the 600-term expansion for the EF state because of a somewhat irregular convergence pattern. However, the 600-term expansions for other excited states of H_2 yielded accuracy of the order of 0.001 cm^{-1} , and even in the least favorable (because of the lack of the inversion symmetry) case of HeH^+ it was better than 0.01 cm^{-1} . We can, therefore, conservatively estimate the error of the present BO energies as about 0.01 cm^{-1} (0.05 \mu hartree) in the vicinity of $R = 1.5$ bohr, which corresponds to the accuracy better by almost one order of magnitude than the best previous results. Since our wave functions were fully optimized at each value of R , the error should not change dramatically along the potential energy curve, although we expect some gradual lowering of accuracy when moving from larger towards smaller internuclear distances.

Table 1. Born-Oppenheimer energy curve for the $EF \ ^1\Sigma_g^+$ state of H_2 . The last column denotes the improvement with respect to Ref. [8]

R bohr	E hartree	dE/dR hartree/bohr	ΔE_{BO} μ hartree	R bohr	E hartree	dE/dR hartree/bohr	ΔE_{BO} μ hartree
0.010	97.854294759	-9999.9467812	-	3.150	-0.689736266	-0.0053293	-0.067
0.125	5.887275372	-63.5347143	-	3.200	-0.690223204	-0.0140858	-0.091
0.250	1.958420900	-15.3590224	-	3.300	-0.692387386	-0.0280531	-0.118
0.500	0.127042176	-3.3305808	-2.354	3.350	-0.693901153	-0.0321672	-0.133
0.750	-0.381959097	-1.1911454	-	3.500	-0.699079636	-0.0349556	-0.121
1.000	-0.580085574	-0.5035865	-0.473	3.750	-0.706850445	-0.0259588	-0.186
1.250	-0.666021558	-0.2215005	-	4.000	-0.711884469	-0.0144330	-0.208
1.500	-0.703000229	-0.0899254	-0.321	4.200	-0.713939091	-0.0063453	-0.226
1.600	-0.710336960	-0.0582442	-0.244	4.300	-0.714395534	-0.0028456	-0.231
1.700	-0.714897926	-0.0340535	-0.279	4.350	-0.714497162	-0.0012348	-
1.750	-0.716348139	-0.0241746	-	4.400	-0.714520534	0.0002849	-0.237
1.800	-0.717335853	-0.0155265	-0.187	4.450	-0.714470159	0.0017154	-
1.900	-0.718147401	-0.0013378	-0.169	4.500	-0.714350439	0.0030592	-0.242
1.910	-0.718154650	-0.0001176	-	4.600	-0.713919902	0.0054975	-0.245
1.920	-0.718149864	0.0010700	-	4.750	-0.712855991	0.0085783	-
1.950	-0.718066446	0.0044449	-	5.000	-0.710203357	0.0123922	-0.261
2.000	-0.717715240	0.0094868	-0.143	5.250	-0.706769219	0.0148918	-
2.100	-0.716337865	0.0176695	-0.153	5.500	-0.702838682	0.0164139	-0.290
2.200	-0.714251301	0.0237474	-0.144	5.750	-0.698621148	0.0172270	-
2.300	-0.711645171	0.0281165	-0.119	6.000	-0.694267005	0.0175361	-0.334
2.400	-0.708675417	0.0310580	-0.103	6.500	-0.685540178	0.0172103	-0.380
2.500	-0.705475032	0.0327503	-0.088	7.000	-0.677165620	0.0162183	-0.444
2.625	-0.701333700	0.0331978	-	8.000	-0.662220979	0.0136172	-0.573
2.750	-0.697261256	0.0315667	-0.060	9.000	-0.649936051	0.0109705	-0.766
2.900	-0.692910016	0.0254689	-0.052	10.000	-0.640254736	0.0083915	-0.920
3.000	-0.690747014	0.0170127	-0.033	12.000	-0.628742051	0.0032091	-0.825
3.050	-0.690044969	0.0108307	-0.050	15.000	-0.625202952	0.0002006	-0.097
3.100	-0.689687326	0.0032597	-0.050	20.000	-0.625005625	0.0000026	-0.008

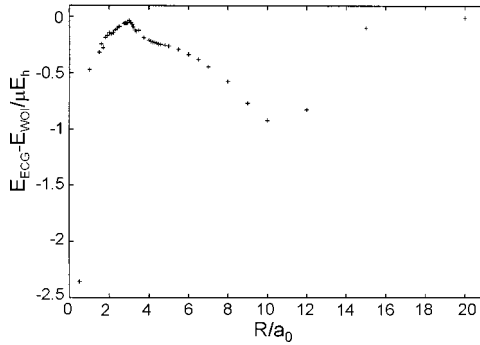
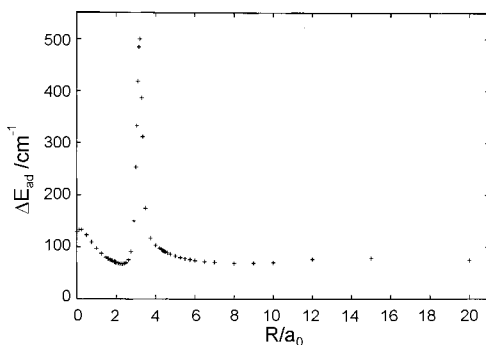
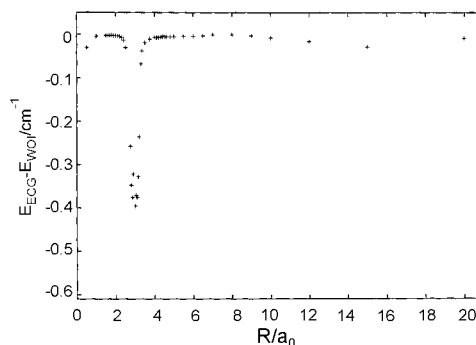
Fig. 1. Born-Oppenheimer energy improvement over the best previous calculations of Orlikowski *et al.* [8] as a function of R

Table 2: The expectation values of the nuclear coordinate derivative operators (in atomic units). X is the direction parallel and Y – perpendicular to the internuclear axis. In Eq. (5) $\Delta Q_I = 0.0005$ bohr. $\eta = 1 - \langle (\sum_I \nabla_I)^2 \rangle \langle (\sum_i \nabla_i)^2 \rangle^{-1}$ and $a(b)$ stands for $a \times 10^b$

R/bohr	$\left\langle \frac{\partial^2}{\partial X_I^2} \right\rangle$	$\left\langle \frac{\partial^2}{\partial X_1 \partial X_2} \right\rangle$	$\left\langle \frac{\partial^2}{\partial Y_I^2} \right\rangle$	$\left\langle \frac{\partial^2}{\partial Y_1 \partial Y_2} \right\rangle$	η
0.010	-0.3600307	-0.3581237	-0.3591528	-0.3591082	8.8(-7)
0.125	-0.4164156	-0.2643921	-0.3479757	-0.3436510	-8.7(-6)
0.250	-0.4649744	-0.1453421	-0.3264068	-0.3138338	3.4(-6)
0.500	-0.4639602	-0.0103415	-0.2828173	-0.2538456	-3.8(-6)
0.750	-0.4163910	0.0424656	-0.2485876	-0.2067459	9.1(-7)
1.000	-0.3660064	0.0624198	-0.2232351	-0.1714003	-1.5(-6)
1.250	-0.3228201	0.0687900	-0.2045268	-0.1444724	2.6(-6)
1.500	-0.2879138	0.0691512	-0.1907203	-0.1234153	7.0(-6)
1.600	-0.2761016	0.0684294	-0.1862934	-0.1162245	6.8(-6)
1.700	-0.2654376	0.0674294	-0.1824064	-0.1096031	2.8(-6)
1.750	-0.2605258	0.0668609	-0.1806519	-0.1064812	-1.2(-6)
1.800	-0.2558934	0.0662727	-0.1790177	-0.1034751	-2.7(-6)
1.900	-0.2474827	0.0650953	-0.1760952	-0.0977718	3.4(-6)
1.910	-0.2467073	0.0649834	-0.1758277	-0.0972235	-2.6(-7)
1.920	-0.2459479	0.0648777	-0.1755649	-0.0966784	-1.8(-6)
1.950	-0.2437351	0.0645616	-0.1748016	-0.0950612	6.8(-6)
2.000	-0.2403099	0.0640913	-0.1736186	-0.0924355	-3.2(-6)
2.100	-0.2345823	0.0635351	-0.1715768	-0.0874048	-1.2(-6)
2.200	-0.2307858	0.0639486	-0.1699783	-0.0826189	3.3(-6)
2.300	-0.2298658	0.0662756	-0.1688530	-0.0780077	5.9(-6)
2.400	-0.2337740	0.0724234	-0.1682688	-0.0734847	-3.3(-6)
2.500	-0.2466014	0.0863705	-0.1683480	-0.0689257	-5.1(-6)
2.625	-0.2900189	0.1292561	-0.1697603	-0.0628660	-3.7(-6)
2.750	-0.4111460	0.2468319	-0.1735777	-0.0556895	1.3(-6)
2.900	-0.8885486	0.7131977	-0.1846863	-0.0431693	7.4(-6)
3.000	-1.7230149	1.5332348	-0.2001394	-0.0295062	3.2(-6)
3.050	-2.3612874	2.1613619	-0.2116850	-0.0200779	-2.1(-6)
3.100	-3.0499390	2.8379566	-0.2260603	-0.0087302	-5.6(-6)
3.150	-3.5648001	3.3395418	-0.2426247	0.0040418	-1.2(-6)
3.200	-3.6607205	3.4222607	-0.2597756	0.0170402	7.9(-6)
3.300	-2.6610613	2.4017673	-0.2879108	0.0379024	-7.3(-6)
3.350	-2.0145710	1.7488409	-0.2966649	0.0442161	1.7(-6)
3.500	-0.8513577	0.5787460	-0.3049550	0.0497455	-5.7(-6)
3.750	-0.3979030	0.1323681	-0.2927160	0.0407324	-5.2(-8)
4.000	-0.3182442	0.0658013	-0.2744055	0.0286684	-1.8(-6)
4.200	-0.2948685	0.0533061	-0.2606282	0.0203057	7.9(-6)
4.300	-0.2867201	0.0503626	-0.2543534	0.0166954	-4.3(-6)

Table 2 – continued

4.350	-0.2830812	0.0492416	-0.2513825	0.0150325	-6.0(-7)
4.400	-0.2796533	0.0482667	-0.2485248	0.0134622	4.2(-6)
4.450	-0.2764002	0.0473962	-0.2457775	0.0119777	-1.6(-6)
4.500	-0.2732889	0.0465986	-0.2431417	0.0105798	-2.3(-6)
4.600	-0.2674348	0.0451521	-0.2381913	0.0080265	3.9(-6)
4.750	-0.2594209	0.0431903	-0.2315358	0.0047496	-6.8(-7)
5.000	-0.2477945	0.0402020	-0.2222808	0.0005396	2.4(-6)
5.250	-0.2380820	0.0374813	-0.2149687	-0.0024383	-2.8(-6)
5.500	-0.2300557	0.0350483	-0.2092101	-0.0044987	-2.1(-6)
5.750	-0.2234685	0.0329114	-0.2046771	-0.0058856	-2.4(-6)
6.000	-0.2180621	0.0310407	-0.2010997	-0.0067832	-2.8(-6)
6.500	-0.2100193	0.0280768	-0.1960138	-0.0076176	-7.7(-7)
7.000	-0.2046584	0.0260305	-0.1927722	-0.0077040	-3.2(-6)
8.000	-0.1993553	0.0245875	-0.1893611	-0.0069124	5.4(-6)
9.000	-0.2004066	0.0277029	-0.1882512	-0.0056460	-3.9(-7)
10.000	-0.2104451	0.0386223	-0.1888564	-0.0041058	-2.7(-6)
12.000	-0.2474153	0.0707733	-0.1956154	-0.0003236	2.2(-6)
15.000	-0.2516821	0.0517939	-0.2058240	0.0003343	5.6(-6)
20.000	-0.2084313	0.0003027	-0.2083102	-0.0000701	1.5(-6)

Fig. 2. Adiabatic correction of $^1\text{H}_2$ Fig. 3. Differences in the adiabatic correction of $^1\text{H}_2$ obtained from ECG and KW wave functions

The optimized electronic wave functions were used to calculate the expectation values of the second derivatives over the nuclear coordinates according to (9). The results are listed in Table 2, along with the off-diagonal expectation values obtained from an analogous equation. The coefficients η in the last column are measures of the inaccuracies introduced by the numerical differentiation (see Eq. (10)) and $-\log_{10} |\eta|$ roughly corresponds to the number of exact significant digits in the results calculated at a given value of R . The adiabatic corrections calculated from Eq. (8) are listed in Table 3 for all six isotopomers of the hydrogen molecule and presented graphically (for H_2) in Fig. 2. Judging from the very high quality of

Table 3. The adiabatic correction curves (in cm^{-1}) for 6 isotopic species. The following nuclear masses were used (in units of electron mass): $M(H) = 1836.153$, $M(D) = 3670.483$, $M(T) = 5496.921$. The conversion factor $1 E_H = 219474.631 \text{ cm}^{-1}$ has been used throughout the table

R/bohr	H_2	HD	HT	D_2	DT	T_2
0.010	128.893	96.686	85.974	64.4 9	53.767	43.055
0.125	132.961	99.737	88.687	66.513	55.463	44.413
0.250	133.609	100.223	89.119	66.838	55.734	44.630
0.500	123.067	92.316	82.088	61.564	51.336	41.108
0.750	109.198	81.912	72.837	54.626	45.551	36.476
1.000	97.115	72.848	64.777	48.582	40.511	32.440
1.250	87.481	65.621	58.351	43.762	36.492	29.221
1.500	80.008	60.016	53.366	40.024	33.374	26.725
1.600	77.537	58.163	51.719	38.788	32.344	25.900
1.700	75.334	56.510	50.249	37.685	31.425	25.164
1.750	74.327	55.755	49.577	37.182	31.005	24.828
1.800	73.383	55.046	48.947	36.710	30.611	24.512
1.900	71.679	53.768	47.811	35.857	29.900	23.943
1.910	71.522	53.650	47.706	35.779	29.835	23.891
1.920	71.368	53.535	47.604	35.702	29.771	23.839
1.950	70.921	53.200	47.306	35.478	29.584	23.690
2.000	70.229	52.681	46.844	35.132	29.295	23.459
2.100	69.057	51.801	46.062	34.545	28.806	23.067
2.200	68.221	51.174	45.504	34.127	28.458	22.788
2.300	67.842	50.890	45.251	33.938	28.300	22.661
2.400	68.169	51.135	45.470	34.101	28.436	22.771
2.500	69.721	52.300	46.505	34.878	29.084	23.289
2.625	75.249	56.446	50.192	37.643	31.389	25.136
2.750	90.639	67.991	60.458	45.342	37.809	30.277
2.900	150.359	112.788	100.292	75.217	62.721	50.225
3.000	253.796	190.379	169.286	126.961	105.869	84.776
3.050	332.849	249.678	222.016	166.507	138.845	111.183
3.100	418.600	314.002	279.213	209.404	174.615	139.826
3.150	484.101	363.136	322.903	242.171	201.938	161.706
3.200	499.666	374.812	333.286	249.957	208.431	166.905
3.300	386.903	290.226	258.071	193.548	161.393	129.238
3.350	311.721	233.830	207.923	155.938	130.032	104.125
3.500	174.665	131.020	116.504	87.376	72.860	58.344
3.750	117.538	88.168	78.400	58.798	49.030	39.261
4.000	103.639	77.742	69.129	51.845	43.232	34.619
4.200	97.551	73.175	65.068	48.800	40.693	32.585
4.300	95.077	71.320	63.418	47.562	39.661	31.759
4.350	93.932	70.461	62.654	46.989	39.183	31.376
4.400	92.839	69.641	61.925	46.443	38.727	31.011

Table 3. – continued

4.450	91.793	68.856	61.228	45.919	38.291	30.662
4.500	90.791	68.105	60.559	45.418	37.873	30.327
4.600	88.908	66.692	59.303	44.476	37.087	29.698
4.750	86.359	64.780	57.603	43.201	36.024	28.847
5.000	82.757	62.078	55.200	41.399	34.521	27.644
5.250	79.848	59.896	53.260	39.944	33.308	26.672
5.500	77.512	58.144	51.702	38.775	32.333	25.892
5.750	75.641	56.740	50.454	37.839	31.553	25.267
6.000	74.140	55.614	49.452	37.088	30.927	24.765
6.500	71.962	53.981	48.000	35.999	30.018	24.038
7.000	70.547	52.919	47.056	35.291	29.428	23.565
8.000	69.097	51.832	46.089	34.566	28.823	23.081
9.000	68.958	51.727	45.996	34.496	28.765	23.034
10.000	70.302	52.735	46.893	35.169	29.326	23.483
12.000	76.337	57.262	50.918	38.188	31.843	25.499
15.000	79.288	59.476	52.886	39.663	33.074	26.485
20.000	74.712	56.043	49.834	37.375	31.165	24.956

the electronic wave functions and from the fact that the numerical differentiation affected the expectation values at most at the sixth significant digit, we believe that all the numbers in Table 3 are exact, possibly with the exception of the last digit in the cases where the corrections have exceptionally large values. In the ground state of H_2 , where a careful error analysis has been performed [25], a 600-term ECG wave function yields a relative accuracy of 10^{-6} . The behavior of the adiabatic correction mirrors that of the electronic wave function, which is most clearly pronounced in the region between 3.0 and 3.5 bohr. Because of the avoided crossing between the diabatic E and F states, the BO function rapidly changes its character, which causes large values of the derivatives over the nuclear coordinates.

The difference between the present adiabatic corrections for the H_2 isotopomer and the results of Orlikowski *et al.* [8, 29] is presented in Fig. 3. It reaches its absolute maximum value of 0.4 cm^{-1} where the correction itself reaches the maximum. Since we estimate the error of our results as much less than 0.4 cm^{-1} , these discrepancies are probably due to the fact that the wave functions used in Ref. [8] were less accurate.

Table 4 contains the expectation values of the relativistic operators (14)-(17) and the relativistic corrections calculated both from the DPT expression (11) and from the BP theory, the latter choice corresponding to the neglect of Δ_{DPT} in Eq. (11). The quantities depending on the electron-nucleus coalescence, described by operators (14) and (16), are known to converge very poorly in Gaussian basis sets. Indeed, a comparison with previous results obtained with the KW wave functions [7, 30] reveals an agreement in only 3 to 4 significant digits, and there is no doubt that the expectation values calculated by Wolniewicz

Table 4: The relativistic corrections and their components

R bohr	$\langle \hat{H}_1 \rangle$ a.u.	$\langle \hat{H}_2 \rangle$ a.u.	$\langle \hat{H}_4 \rangle$ a.u.	$\langle \hat{H}_5 \rangle$ a.u.	E_2 (BP) cm^{-1}	E_2 (DPT) cm^{-1}
0.000	-10.275860	-0.009255	8.196487	0.054871	-23.7692	-23.7694
0.010	-10.100664	-0.009251	8.026765	0.054404	-23.7106	-23.7110
0.125	-7.902042	-0.009015	6.144947	0.051470	-20.0395	-20.0396
0.250	-5.951883	-0.008511	4.602686	0.045635	-15.3346	-15.3347
0.500	-3.607864	-0.007346	2.805998	0.033842	-9.0620	-9.0620
0.750	-2.423061	-0.006301	1.905735	0.024923	-5.8285	-5.8285
1.000	-1.769578	-0.005446	1.406808	0.018600	-4.0861	-4.0861
1.250	-1.379315	-0.004763	1.106149	0.014071	-3.0838	-3.0838
1.500	-1.131757	-0.004227	0.913375	0.010734	-2.4762	-2.4763
1.600	-1.058365	-0.004049	0.855742	0.009637	-2.3028	-2.3028
1.700	-0.995795	-0.003892	0.806357	0.008646	-2.1585	-2.1585
1.750	-0.968003	-0.003821	0.784332	0.008184	-2.0956	-2.0956
1.800	-0.942254	-0.003755	0.763868	0.007743	-2.0382	-2.0382
1.900	-0.896367	-0.003638	0.727240	0.006915	-1.9383	-1.9383
1.910	-0.892154	-0.003627	0.723865	0.006835	-1.9293	-1.9293
1.920	-0.888005	-0.003617	0.720540	0.006757	-1.9205	-1.9205
1.950	-0.875931	-0.003587	0.710847	0.006524	-1.8951	-1.8951
2.000	-0.856999	-0.003542	0.695604	0.006148	-1.8558	-1.8558
2.100	-0.823290	-0.003468	0.668305	0.005432	-1.7884	-1.7884
2.200	-0.794566	-0.003419	0.644818	0.004755	-1.7345	-1.7345
2.300	-0.770360	-0.003397	0.624777	0.004108	-1.6932	-1.6931
2.400	-0.750352	-0.003404	0.607914	0.003482	-1.6638	-1.6638
2.500	-0.734452	-0.003446	0.594120	0.002868	-1.6469	-1.6469
2.625	-0.720680	-0.003546	0.581343	0.002114	-1.6452	-1.6452
2.750	-0.715187	-0.003684	0.574459	0.001396	-1.6715	-1.6715
2.900	-0.725319	-0.003759	0.577713	0.000781	-1.7599	-1.7599
3.000	-0.749016	-0.003454	0.591321	0.000939	-1.8724	-1.8724
3.050	-0.768078	-0.003034	0.602991	0.001428	-1.9482	-1.9482
3.100	-0.792070	-0.002341	0.618018	0.002346	-2.0341	-2.0342
3.150	-0.819595	-0.001352	0.635547	0.003779	-2.1227	-2.1227
3.200	-0.847693	-0.000135	0.653690	0.005698	-2.2024	-2.2024
3.300	-0.892246	0.002290	0.683129	0.010232	-2.2977	-2.2978
3.350	-0.905309	0.003183	0.692119	0.012400	-2.3095	-2.3095
3.500	-0.914323	0.004218	0.699942	0.017353	-2.2534	-2.2534
3.750	-0.884261	0.002962	0.683238	0.021458	-2.0640	-2.0640
4.000	-0.841711	0.000840	0.657172	0.023016	-1.8780	-1.8780

Table 4 – continued

4.200	-0.808528	-0.000762	0.636130	0.023397	-1.7503	-1.7503
4.300	-0.793045	-0.001481	0.626148	0.023414	-1.6942	-1.6942
4.350	-0.785636	-0.001817	0.621338	0.023390	-1.6681	-1.6680
4.400	-0.778464	-0.002137	0.616664	0.023349	-1.6431	-1.6431
4.450	-0.771541	-0.002442	0.612136	0.023291	-1.6194	-1.6194
4.500	-0.764855	-0.002731	0.607744	0.023218	-1.5968	-1.5968
4.600	-0.752203	-0.003265	0.599386	0.023039	-1.5549	-1.5549
4.750	-0.735018	-0.003960	0.587936	0.022702	-1.4999	-1.5000
5.000	-0.710848	-0.004864	0.571636	0.022023	-1.4265	-1.4265
5.250	-0.691608	-0.005507	0.558472	0.021273	-1.3718	-1.3718
5.500	-0.676470	-0.005945	0.547969	0.020506	-1.3317	-1.3316
5.750	-0.664631	-0.006225	0.539633	0.019744	-1.3029	-1.3029
6.000	-0.655429	-0.006384	0.533047	0.019015	-1.2827	-1.2827
6.500	-0.642814	-0.006448	0.523749	0.017656	-1.2606	-1.2606
7.000	-0.635398	-0.006290	0.517929	0.016439	-1.2543	-1.2543
8.000	-0.629080	-0.005596	0.511851	0.014272	-1.2687	-1.2685
9.000	-0.629647	-0.004537	0.510187	0.012053	-1.3083	-1.3083
10.000	-0.635176	-0.003064	0.511067	0.009521	-1.3750	-1.3750
12.000	-0.662412	0.000724	0.521311	0.003353	-1.6014	-1.6014
15.000	-0.710661	0.000726	0.550702	0.000159	-1.8591	-1.8592
20.000	-0.725792	0.000008	0.561763	0.000001	-1.9170	-1.9170

are more accurate than ours, because the KW wave functions describe properly the electron-nucleus and electron-electron cusps. However, the big advantage provided by the DPT is the fact that the total correction, E_2 (DPT), has usually much smaller error than its components, because it is an expectation value of a global operator. Indeed, the values of E_2 (DPT) are very close to that reported by Wolniewicz [7, 30], the difference being in most cases smaller than 0.001 cm^{-1} and reaching the maximum value of 0.0033 cm^{-1} at $R = 1.0$ bohr, where the result that can be extracted from the data given in Ref. [30] amounts to -4.0828 cm^{-1} . It is rather hard to find out which results are more accurate without performing a detailed convergence analysis, but it is worth noting that the expectation value of (15), fast convergent in the ECG functions, is actually the least accurate of the four relativistic expectation values in some reported calculations involving the KW functions [23], apparently because of the numerical problems caused by the necessity to use series expansions [7]. In some cases, the agreement between the expectation values of (15) from Table 4 and those in Ref. [30] hardly reaches one significant digit, for example our value of 0.000726 versus Wolniewicz's 0.000660 at $R = 15.0$ bohr. In the ground state of H_2 [23], a 600-term ECG wave function yields more than 5 significant digits of accuracy and it is rather unlikely that

the values in the third column of Table 4 are much less accurate. This discrepancy between the present results and those in Ref. [30] does not cause significant differences in the total relativistic corrections, because the expectation values of (15) are fairly small in the *EF* state.

The fact that the last two columns of Table 4 are almost indistinguishable seems to contradict the superiority of the DPT and question the purpose of calculating the DPT term (12). However, this near-equality of DPT and BP results is not a general behavior, but rather a manifestation of an interesting phenomenon first observed and explained in Ref. [23]. In the special case of Gaussian functions with all linear and nonlinear parameters completely optimized, the errors of expectation values of (14) and (16) cancel to a large extent and the term (12) vanishes even for a finite basis set expansion. The value of (12) is in such cases determined more by the quality of the nonlinear optimization than by the overall accuracy of the wave function.

4. CONCLUSIONS

The results presented in this work represent the current most accurate adiabatic curve of the *EF* state of the hydrogen molecule. The obtained relativistic corrections have, for all practical purposes, the same accuracy as those obtained from the Kołos-Wolniewicz expansions, despite the well-known deficiencies of the Gaussian functions in describing the electron density in the close vicinity of the nuclei. The Born-Handy approach to adiabatic corrections with numerical computation of derivatives over nuclear coordinates, as introduced in Ref. [25], proved very efficient and sufficiently accurate even in the cases where the adiabatic corrections reach several hundreds of cm^{-1} .

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