Dirac-Fock calculation for H, H\textsuperscript{2+} and H\textsubscript{2} in a strong magnetic field by the Hermitian basis of B-splines

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(February 8, 2022)

Abstract

A two-dimensional, fully numerical approach to the solution of four-component Dirac-Fock equation using the moderately long Hermitian basis of B-splines is applied to H, H\textsuperscript{2+} and H\textsubscript{2} in a strong magnetic field. The geometric parameters, including different behavior of wave-functions relativistic components are analyzed. The accuracy of the solutions as a function of the basis length is estimated. The relativistic corrections are calculated by transformation of the matrix equations to the equations for large relativistic components. Application of the finite-element method to solution of the Dirac-Fock equation without supplementary assumption about exchange in case of the H\textsubscript{2} excited states is discussed.

The maximum localization of the basis functions provides applicability of the quadrature formulae for five-dimensional two-electron integral calculations within reasonable period.

PACS number(s): 32.60.+i, 33.15, 03.65.Pm
I. INTRODUCTION

The problem of the hydrogen atom and hydrogen molecular ion in the strong magnetic field has wide application in the investigations of "white dwarfs" spectral properties in astrophysics. Many numerical and analytical calculations have been reported in literature \[1–4, 6–8, 12\]. The moderately low temperature (5000K - 25000K) of the "white dwarfs" \[13\] make reasonable the consideration not only of the one-electron system (H, \(H^+\)), but also of the hydrogen molecule \[8–10\]. Most of the previous works treat the effect of strong \((\approx 10^9 \text{ G})\) magnetic fields on the electron structure in the framework of non-relativistic theory, but in case of the magnetic field magnitude is comparable with that of the light velocity \((137 \text{ in a.u.})\), the relativistic approach is then more consistent. First and foremost because the relativistic one describes the features of the particle with spin in electromagnetic field more correctly. In present paper we neglect the proton motion in magnetic field. Movement of this type may have an expressed effect on energetic structure in case of superstrong \((\approx 10^{12} \text{ G})\) magnetic field \((\text{it was estimated i.c. in \[5\]})\). We aware of the fact that the relativistic correction in our case may be comparable to effect of the nuclear motion and this problem calls for further investigation.

The one-electron system of H was studied in framework of relativistic theory in detail with high accuracy (see Ref. \[4\]). The molecular systems \(H^+_2\) and \(H_2\) in the strong magnetic field were studied, as a rule, as a non-relativistic problem (see recent papers ref. \[6\] for \(H^+_2\) and \[9–11\] for \(H_2\)). In the field-free relativistic case the maximum accuracy (better then \(10^{-10} \text{ au}\)) was obtained with use of the finite element method \[18, 23\]. The authors used the Lagrangian-type finite elements defined as two-dimensional fifth(and more)-order polynomials within triangular regions \[17\]. But for the molecular system with the exchange the cited authors would have to use supplementary Dirac-Fock-Slater approximation \[18\]. From our viewpoint the reason is that the Lagrangian-type finite elements are not enough localized for calculations of electron interaction matrix elements in a reasonable time (e.g. the fifth-order polynomial occupies 21 nodal points). As it was shown in \[11\] the state \(^3\Sigma_u^+\)
with parallel spin becomes the ground state of the hydrogen molecule in magnetic field of strengths $B/B_0 > 0.2(B_0 = 2.35 \times 10^9 G)$. I.e. the exchange interaction must be taken into account.

The main difficulty in relativistic calculations consists in a generalized matrix problem enlarged by four times. Furthermore the energy matrix with an exchange loses the band structure and the time of calculation mainly depends on the exchange matrix construction. For the solution of exchange problem in a reasonable time we have used the B-splines basis set with minimum overlap. Taking into account the high accuracy of up-to-date relativistic solutions for H in the magnetic field and for $H_2^+$ in free-field case, we can estimate the capabilities of the finite function basis with maximum localization. The results of this work have shown that even with the moderate length it is possible to use this basis for the successful calculations of the energy relativistic corrections and geometric parameters of H, $H_2^+$ and $H_2$ in strong magnetic field. Following Z.Chen and S.P.Goldman we have noted that variation method in relativistic case "may have difficulties of variational collapse, spurious roots, continuum dissolution in case of system with more then one electron" (in the one-electron system the wave functions with poor quality may have the lower-lying state energy, than that from the exact solution of the problem). To avoid spurious roots in case of $H_2$ we used the direct QL-algorithm for finding all of the generalized eigenvalue problem eigenvectors. Since we investigated the different behavior of one-electron wave-function relativistic components in the magnetic field, the calculation of $H_2$ was performed only in the framework of the one-determinant approximation.

By these means in this work we realize a two-dimensional, fully numerical approach to the solution of the four-component Dirac-Fock equation using the Hermitian-type basis of B-splines. We use the Hermitian basis set with maximum localization of each finite element (i.e. the overlap exists only between the nearest neighbors). In addition, the Hermitian basis sets provide the fast expansion and re-expansion of wave function only with use of function values and their derivatives in every nodal point. These features of the basis set allow to calculate the Dirac-Fock equation without supplementary assumption of exchange in
the case of the H₂ states in the magnetic field.

In this paper we have compared the energy levels of the hydrogen atom and the hydrogen molecular ion with the corresponding values in relativistic and non-relativistic calculations, have demonstrated the difference in behavior between the large and small relativistic components under action of magnetic field and have estimated the magnitude of magnetic field for transitions in the hydrogen molecule in the framework of one-determinant approach.

II. DIRAC-FOCK FINITE-ELEMENT CALCULATION

The finite-element method (FEM) is a well established technique for solution of several quantum mechanical problems. Recently, it has been demonstrated [17,18] that this method can also be used for solving the many-electron Dirac problem. The finite basis functions presented in these publications have the following features. First, each finite function (FF) occupies more space than a region between the main function nodal point and the nearest nodal points. Second, the increasing of accuracy is provided, as a rule, by increasing the nodal points number for every finite function. The insufficient localization of FF impedes the calculation of two-electron matrix elements, therefore usually [17,18] a Slater’s local approximation for exchange potential in diatomic molecules calculations is used. In this work we present a FF basis set with maximum localization for the two-center many-electron Dirac problem. This set we have constructed from Hermitian basis of B-splines (HBS) at every nodal point. The HBS analytical properties and their application to the solution of the one-center Fock-Dirac equations we have discussed in the above Ref. [14]. The relativistic Hamiltonian operator for a diatomic molecule electron subsystem is defined as

\[ H = \sum_j \left( c \alpha_j (p_j - i \frac{A}{c}) + c^2 \beta_j - \frac{Z_1}{r_{1j}} - \frac{Z_2}{r_{2j}} \right) + \sum_{i,j} \frac{1}{r_{ij}}, \]  

(1)

where \( \alpha \) and \( \beta \) are usual Dirac matrices, \( Z_1 \) and \( Z_2 \) are the nuclear charges, \( r_1 \) and \( r_2 \) are the distances to the nuclei, \( A = (-By, Bx, 0) \) is the vector-potential of the electromagnetic field, \( B \) is the magnetic field magnitude in z-direction. Because of axial symmetry of diatomic
molecules, we describe the four-component spinor of a single electron wave function $\Phi$ in elliptic coordinates $(\rho, \tau, \varphi)$:

\[
\rho = \frac{r_1 + r_2}{D}, \\
\tau = \frac{r_1 - r_2}{D},
\]

where $D$ - is the distance between nuclei. After separation of the angular coordinate $\varphi$ and modification of $(\rho, \tau)$ coordinates by the introduction of the parameters for the coordinates "stretching" ($d_\rho$ and $d_\tau$)

\[
s(\rho) = \frac{\rho^2}{\rho - (1 - d_\rho)}; \\
t(\tau) = \frac{\tau}{(1 + d_\tau)^2 - \tau^2}
\]

we obtain for single electron wave function within z-projection of total momentum $\mu$ the following expression:

\[
\Phi = \begin{pmatrix}
\phi_0(s, t) e^{i(\mu - 1/2)\varphi} \\
\phi_1(s, t) e^{i(\mu + 1/2)\varphi} \\
\phi_2(s, t) e^{i(\mu - 1/2)\varphi} \\
\phi_3(s, t) e^{i(\mu + 1/2)\varphi}
\end{pmatrix}.
\]

The relativistic components $\phi_k$ are expanded in terms of the FF:

\[
\phi_k(s, t) = [(\rho^2 - 1)(1 - \tau^2)]^{(\mu - 1/2 + \lambda)/2} \sum_{i_s, i_t, h_s, h_t} C(i_s, i_t, h_s, h_t, k) F(i_s, i_t, h_s, h_t; s, t),
\]

where $(i_s = 1..N_s, i_t = 1..N_t)$ are the nodal indices for $(s, t)$ coordinates, $(h_s, h_t)$ are the Hermit component indices and $\lambda=(0,1,0,1)$ for $k=(0,1,2,3)$. In our work the two-dimensional FF is constructed as a product of the one-dimensional elements from the HBS $f(i, h; x)$:

\[
F(i_s, i_t, h_s, h_t; s, t) = f(i_s, h_s; s) f(i_t, h_t; t)
\]

The analytical properties of two first Hermit components of the B-splines $f(i, h; x)$ are the following:
\[ f(i, 0; x) = \begin{cases} 
0, |a| \geq 1 \\
(1 - a)^2 (1 + 2a), a \geq 0, \\
(1 + a)^2 (1 - 2a), a < 0, 
\end{cases} \] 

\[ f(i, 1; x) = \begin{cases} 
0, |a| \geq 1 \\
(1 - a)^2 a, a \geq 0, \\
(1 + a)^2 a, a < 0, 
\end{cases} \] 

(6)

where \( a = (x - id)/d \), \( d \) is the distances between the nearest nodal points.

Therefore, each FF occupies the region between the main function nodal point \((i_s, i_t)\) and the nearest nodal points \((i_s \pm 1, i_t \pm 1)\) only. We shall call this region the FF local space. We have calculated the \( H \) matrix elements in the crossing of the FF local spaces numerically, using the seven-point quadrature formula (these formulae are exact for the polynomials with the degree 6 and under). We have used the equi-distant net with 24 points of integration between the nodal points. The expansion (4) leads to a \((16N_s N_t) \times (16N_s N_t)\) symmetric eigenvalue self-consistent-field equation for the one-electron vector \( C \)

\[(H_m + J - K)C = ESC,\] 

(7)

where \( H_m, J, K \) and \( S \) are the one-electron, Colombs’, exchange and overlap matrix operator, respectively. The number \( m = \mu - 1/2 \) defines the symmetry properties of the wave function \( \Phi \). The choice of the two-dimension FF as a product of one-dimensional ones allows to reduce most of one-electron matrix elements to the one-dimension integrals. In case of the two-electron elements we used the interpolation properties of the Hermitian-type FF

\[ Z(x, y) \approx \sum_{i_x, i_y, h_x, h_y} C(i_x, i_y, h_x, h_y) f(i_x, h_x; x) f(i_y, h_y; y), \] 

(8)

with the nodal values

\[ C(i_x, i_y, h_x, h_y) = \left( \frac{\partial}{\partial x} \right)^{h_x} \left( \frac{\partial}{\partial y} \right)^{h_y} Z(x, y) \big|_{i_x, i_y}, \] 

(9)
by the approximation of an arbitrary differentiable function the nodal values $C$ are defined by the function and derivative values in the nodal points.

Let us consider, for example, the exchange matrix element for the single-determinant case (in Matsuoka’s [20] notations):

$$K_{\alpha,\alpha_1}^{k,k_1} = <\alpha|\phi_{k_1}|g(s,t,s_1,t_1)|\alpha_1> = <\alpha|G_{\alpha_1,k_1}(s,t)|\phi_k>, \quad (10)$$

where $\alpha = (i_s,i_t,h_s,h_t,k)$ is the generalized FF index. Function $G_{\alpha_1,k_1}(s,t)$ is the result of the integration over a relatively small-sized region of the FF $F(\alpha; s,t)$ non-zero values. Moreover; in view of Eq.(8) and (9), the function $G_{\alpha_1,k_1}(s,t)$ and its derivation can be calculated for the nodal points $(i_s,i_t)$ only. In the end of this section we present our results for $H_2^+$ ground state in the field-free case (third-order piecewise polynomials (6)) in comparison with relativistic calculation on the base of fifth-order polynomials (Table I). The "exact" values in Table I for the relativistic orbital energies are obtained in the calculation of L.Yang et al. [23] by adding the relativistic energy correction to the nonrelativistic energy of Madsen and Peek [24]. In Table II are presented the values of the ground state energy for $H$ and $H_2$ with the same parameters of FF (except internuclear distance) as for $H_2^+$ in Table I. The energy values for $H$ are compared with analytical Dirac equation solution for Coulomb field. The calculation accuracy of $H$ and $H_2^+$ are closely allied, the accuracy for $H_2$ is one order of magnitude less then for one-electron case. The relativistic corrections are defined by nonrelativistic limit of (7) (a matrix equation for large relativistic components). The accuracy of relativistic corrections for $H$, $H_2^+$ and $H_2$ in the field-free case are in good agreement with the results of special-purpose relativistic FF calculations. The values of the relativistic corrections is calculated as a difference (result of substraction) between relativistic value and value in non-relativistic limit (for matrix one-electron Fock-Dirac equation (7)) in the same finite functions basis. The aproach of this kind allows to compensate (in great part) in the relativistic corrections uniform errors, associated with the basis lenght, and to obtain the reasonable values with using the moderately long B-splines basis. This correction (as it is shown in Tables I,II for field-free case and III for H in magnetic field) good fit to
the results, obtained with the energy high-precision calculation.

III. RESULTS

In the one-electron case, the equation (7) was solved for the ground states of the hydrogen atom and hydrogen molecular ion. The nuclei were placed into the coordinate system focal points. In the coordinates (2), the $N_s \times N_t$ equi-distant nodal net was built for the finite functions $F$ from the expansion (4). The parameters $d\rho$ and $d\tau$ were chosen with use of the optimization for field-free case. The $13 \times 9$ for $H$ and $10 \times 11$ for $H^+_2$ nodal net with two Hermitian components of B-splines (6) and four relativistic components of wave functions leads correspondingly to the $1872 \times 1872$ and $1760 \times 1760$ generalized matrix problem and to the $468$ and $440$ basis function per one relativistic component (See $N_b$ in Table I and Table II for the accuracy estimation). This problem was solved for all of the eigenvalues by the method from Wilkinson and Reinsch handbook [22]. It takes about 150 min for $H$ or, if we take into account the system symmetry, 45 min for $H^+_2$ of CPU time on a P-II-233 IBM compatible computer. The equilibrium internuclear distance was calculated with use of the quadratic approximation or with use of relativistic virial theorem for diatomic molecule in magnetic field (the specific cases of relativistic virial theorem for atoms was considered in [4,25]). Both of these methods lead to the near results. The results are listed in Tables III and IV. For comparison with other results, we have used as the convention the parameter $B/B_0$, with $B_0 = 2.35 \times 10^9 G$ (137 a.u.).

Our results for $H$ presented in Table III are compared with detailed data from the non-relativistic B-splines calculations made by Jinhua Xi et al. [12] and with relativistic finite basis set calculations by Z.Chen and S.P.Goldman [1]. For the field values ($B/B_0$ from 0 to 10) Jinhua Xi et al. have used $35 \times 16 = 560$ nodal net, that is by 1.2 times more than for the separated relativistic component in our calculations (468). Although in our calculations the accuracy of energy is less then in [1], the magnitudes of relative relativistic corrections are in good agreement with the results of Z.Chen and S.P.Goldman. Table III shows the
magnetic field compression effect on the relativistic wave function too. The average radius in x-y-direction \( R_{xy} \) (i.e. average radius in cylindrical coordinat system) decreases monotonical both for the total density and for the small component \((k=2,3\) in \( \mathbb{B} \)). But for the small component, one decreases to a greater extent for \( B/B_0 \) values from 0 to 20.0. The average length in z-direction \( R_z \) (root-mean-square deviation of z-projection vector from nucleus) for the total density decreases to a greater degree then the small component.

In the Table \[\text{IV}\] our results for the ground state of \( \text{H}_2^+ \) are presented. The symmetrical state \( 1(-1/2_g)^1 \) in Herzberg’s notation for double group symmetry (See \[\text{[18,21]}\]) is considered.

In case of antiparallel orientation of the field and z-projection of total moment (positive \( B/B_0 \)) the relativistic correction, transversal size of the ion electronic density and size of small component decrease under effect of the magnetic field in the same manner as for \( H \).

The reverse statement is true for parallel orientation (negative \( B/B_0 \)). The relativistic correction quadratically increases by increasing of magnetic field intensity. The similar behaviour can be recognized for \( H \) in Table \[\text{II}\] (marked with \([\epsilon]\)). The transversal size \( R_{xy} \) of small component increases by changing \( B/B_0 \) from 0 to about -0.2, restores its original dimension at \( B/B_0 \approx -1.0 \) and decreases at \( B/B_0 < -1.0 \).

In the Table \[\text{V}\] we present the ”unrestricted” Dirac-Fock (different orbitals for different z-projection of total momentum) results for the singlet state of \( \text{H}_2 \) with the relativistic configuration \( 1(1/2_g)^2 \). The state energy has the local minimum as the function of the internuclear distance for all of the considered field magnitudes. The equilibrium internuclear distance was calculated by the quadratic approximation in the vicinity of the minimum. The total longitudinal and transversal sizes of the hydrogen molecule decreases, as well as for the hydrogen ion, but the field dependence of the small components is different for electrons with \( \mu = -1/2 \) and \( \mu = +1/2 \) (\( \mu \) is z-projection of total one-electron momentum). Average radius of the small component in x-y-direction for the electron with \( \mu = -1/2 \) decreases under the field compression effect monotonously. By contrast, for the electron with \( \mu = +1/2 \) one increases up to the field magnitude \( B/B_0 = 0.4 \) and remains greater than the radius in the field-free case up to \( B/B_0 = 1.0 \). The same behavior of the small component
is to be observed for the $1(-1/2_g)$ and $1(+1/2_g)$ configurations of $H_2^+$ ($\pm B/B_0$ in Table IV).

The relativistic correction of total energy increases quadratically in the same manner as for $H_2^+$ in the case of parallel orientation.

Comparison between total energies for $H_2$ and the sum of two energies for hydrogen atoms (see Table II) shows that at $B/B_0 > 0.2$ the state with two insulated atoms has the total energy less than that of the molecule. For better visualization of dissociation channel of $H_2$ into the single atoms, we have considered the energies of the nearest configuration ($1(-1/2_g)1(-1/2_u)$) with no change of the equilibrium internuclear distance. The energy of this configuration lie in the field-free case well above the ground state. With increasing of the field magnitude, this energy decreases and become equal to the $1(1/2)_2$ configuration energy in the vicinities $B/B_0 \approx 0.35...0.4$. It is nessesary to stress that we have used the one-determinant approximation. In the non-relativistic configuration-interaction calculation by T.Detmer at al. \cite{11} the $^1 \Sigma_g$ and $^3 \Sigma_u$ states cross over at $B/B_0 \approx > 0.2$. When taken into account Detmer’s total energy of the $^1 \Sigma_g$ state at $B/B_0 = 0.2 (-1.158766\text{a.u.})$ and total energy of two unsulated $H$ atoms by Jinhua Xi et al. \cite{12} (-1.18076313 a.u.) the cross point is found to be at $B/B_0 < 0.2$.

The energy of the $1(-1/2_g)1(-1/2_u)$ state is free of minimum \cite{11} as being an internuclear distance function. And so, in the case of transition into $1(-1/2_g)1(-1/2_u)$ configuration, the hydrogen molecule dissociates into single atoms.

As it is shown in Table VI the z-direction compression coefficient for $H$ has given better fit to the relative reduction of internuclear distance in $H_2^+$ and $H_2$ than x-y compression one.

ACKNOWLEDGEMENTS

This work has been implemented under financial support of the Russian Foundation of Fundamental Investigations (Grant No. 96-03-33903a). The author would like to thank Professor I.V. Abarenkov and Dr. I.I. Tupitsin for their helpful comments and encouragement.
The author is grateful to Professor Elizabeth Davis for reading the manuscript.
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**TABLE I.** Hydrogen ion ground state energies (Es), accuracy of Es, relativistic energy corrections (Rc) with increasing number of basic function per one relativistic component (Nb in our calculation) or number of grid points (Np by L.Yang et al.). The values are given in au. Internuclear distance for $H_2^+$ is 2.0 a.u.

| Nb  | Es        | Accur.Es | Rc   | Np  | Es        | Accur.Es | Rc   |
|-----|-----------|----------|------|-----|-----------|----------|------|
|     | $\times 10^{-6}$ |          |      | $\times 10^{-6}$ |          |      |
|     | Present work | L.Yang et al. |      | exact $^a$ |          |      |
| 120 | -1.1027204866 | 7.9$\times 10^{-5}$ | -7.3689 | 121 | -1.10408781 | 1.3$\times 10^{-3}$ | -7.22 |
| 168 | -1.1026813906 | 4.0$\times 10^{-5}$ | -7.3667 | 224 | -1.1026596742 | 1.8$\times 10^{-5}$ | -7.3667 |
| 288 | -1.1026512414 | 9.6$\times 10^{-6}$ | -7.3666 | 256 | -1.102694840 | 5.3$\times 10^{-5}$ | -7.358 |
| 360 | -1.1026473438 | 5.7$\times 10^{-6}$ | -7.3666 | 441 | -1.1026462146 | 4.6$\times 10^{-6}$ | -7.3660 |
| 440 | -1.1026452809 | 3.7$\times 10^{-6}$ | -7.3666 | 624 | -1.1026433680 | 1.8$\times 10^{-6}$ | -7.3665 |
| 528 | -1.1026440929 | 2.5$\times 10^{-6}$ | -7.3665 | 676 | -1.10264199741 | 4.0$\times 10^{-7}$ | -7.36651 |
| 961 | -1.10264160652 | 2.6$\times 10^{-8}$ | -7.366544 | 2601 | -1.1026415813086 | 1.0$\times 10^{-10}$ | -7.36653872 |
| exact $^a$ | -1.1026415810336 |          | -7.3665387 |          |          |          |      |

$^a$ See text
TABLE II. $H$ and $H_2$ ground state energies (Es), accuracy of Es, relativistic corrections (Rc) with increasing number of basic function per one relativistic component (Nb). Internuclear distance for $H_2$ is 1.4 a.u. The values are given in a.u.

| Nb  | Es            | Accur. Es | Rc       | Nb  | Es            | Accur. Es | Rc       |
|-----|---------------|-----------|----------|-----|---------------|-----------|----------|
|     | ×10^{-6}      | ×10^{-6}  |          |     | ×10^{-6}      | ×10^{-6}  |          |
| $H$ |               |           |          | $H_2$ |               |           |          |
| 120 | -0.500098633  | 9.2×10^{-5} | -6.664   | 288 | -0.5000247572 | 1.8×10^{-5} | -6.6575  |
| 168 | -0.500079978  | 7.3×10^{-5} | -6.660   | 288 | -0.5000247572 | 1.8×10^{-5} | -6.6575  |
| 224 | -0.500044313  | 3.8×10^{-5} | -6.658   | 288 | -0.5000247572 | 1.8×10^{-5} | -6.6575  |
| 288 | -0.5000167610 | 1.0×10^{-5} | -6.6572  | 360 | -0.5000167610 | 1.0×10^{-5} | -6.6572  |
| 440 | -0.5000128771 | 6.2×10^{-6} | -6.6570  | 360 | -0.5000167610 | 1.0×10^{-5} | -6.6572  |
| 528 | -0.5000106448 | 3.3×10^{-6} | 6.6569   | 360 | -0.5000167610 | 1.0×10^{-5} | -6.6572  |

2116 $^a$  $^-$1.133643970950 $<10^{-10}$  -14.399093

24897 $^b$  -1.133643970  -14.397

analyt.  -0.50000665659718  -6.656597

$^a$ See [18]

$^b$ See [19]
TABLE III. Hydrogen atom ground state energies (Es), relativistic correction (Rc), relative correction ($R_c/E_{nrl}$), compression magnitude (K) for: - average radius in x-y-direction for the total (Rxy) density and small (Qxy) relativistic component; - dimension in z-direction for the total (Rz) density and small (Qz) relativistic component. In the calculations we have used 468 of basis function per one relativistic component. The values are given in a.u.; nr - nonrelativistic calculations, nrl - present work nonrelativistic limit.

| $B/B_0$ | Es     | $R_c/E_{nrl}$ | $R_c$ | K(Rxy)        | K(Qxy)        | K(Rz)        | K(Qz)        |
|---------|---------|--------------|-------|---------------|---------------|---------------|---------------|
| 0.0     | -0.5000066415 | 13.31        | -6.657| 1.0(1.17777)  | 1.0(1.17811)  | 1.0(0.99959)  | 1.0(1.81014)  |
| 0.0     | -0.4999999843 | nr           |       |               |               |               |               |
| 0.1     | -0.5475340019 | 10.82        | -5.928| 0.9914        | 0.9484        | 0.9955        | 0.9987        |
| 0.1     | -0.5475280736 | nr           |       |               |               |               |               |
| 0.1$^a$ | -0.5475324083429 | 10.8       |       |               |               |               |               |
| 0.2     | -0.5903904145 | 9.222        | -5.445| 0.9694        | 0.8985        | 0.9839        | 0.9958        |
| 0.2     | -0.5903849695 | nr           |       |               |               |               |               |
| 0.2$^b$ | -0.5903815   | nr           |       |               |               |               |               |
| -1.0$^c$| 0.16878489816 | -40.112      | 0.7552| 1.0057        | 0.8632        | 0.8856        |               |
| 1.0     | -0.8311793578 | 5.208        | -4.329| 0.7552        | 0.6601        | 0.8632        | 0.9587        |
| 1.0     | -0.8311750285 | nr           |       |               |               |               |               |
| 1.0$^b$ | -0.831169    | nr           |       |               |               |               |               |
| 1.0$^a$ | -0.831173226 | 5.21         |       |               |               |               |               |
| 2.0     | -1.0222267871 | 4.031        | -4.121| 0.6072        | 0.5336        | 0.7716        | 0.9114        |
| 2.0     | -1.0222226658 | nr           |       |               |               |               |               |
| 2.0$^b$ | -1.0222214   | nr           |       |               |               |               |               |
| 2.0$^a$ | -0.022218029 | 4.03         |       |               |               |               |               |
| 3.0     | -1.1645485075 | 3.476        | -4.048| 0.5222        | 0.4634        | 0.7150        | 0.8738        |
| 3.0     | -1.1645444592 | nr           |       |               |               |               |               |
| 3.0$^b$ | -1.164533    | nr           |       |               |               |               |               |
| Value | Value2 | Value3 | Value4 | Value5 | Value6 | Value7 |
|-------|-------|-------|-------|-------|-------|-------|
| 3.0\(^a\) | -1.164537038 | 3.48 | 4.0 | -1.2808163924 | 3.117 | -3.992 | 0.4656 | 0.4166 | 0.6752 | 0.8440 | 4.0\(^b\) | -1.280798 | nr | 8.0 | -1.6194194786 | 2.289 | -3.707 | 0.3463 | 0.3167 | 0.5845 | 0.7680 | 8.0\(^b\) | -1.619384 | nr | 10.0 | -1.7478463122 | 2.015 | -3.523 | 0.3134 | 0.2886 | 0.5574 | 0.7437 | 10.0\(^b\) | -1.7477965 | nr | 20.0 | -2.2157351467 | 1.077 | -2.388 | 0.2278 | 0.2140 | 0.4798 | 0.6714 | 20.0\(^a\) | -2.215400913 | 1.09 |

\(^a\) Z.Chen and S.P.Goldman \[4\]

\(^b\) Jinhua Xi et al. \[12\]

\(^c\) See comment to Table \[IV\]
TABLE IV. $H_2^+$ ground state electronic energies (Es), relativistic correction (Rc), total energies(Et), equilibrium internuclear distance(Re), compression magnitude (K) of average radius in x-y-direction for the total (Rxy) density and small (Qxy) relativistic component. In the calculations we have used 440 of basis function per one relativistic component. All values are given in au; nr - non-relativistic calculations, nrl - present work non-relativistic limit.

| $B/B_0^a$ | Es (×10^{-6}) | Rc (×10^{-6}) | Et (×10^{-6}) | Re | K(Rxy) | K(Qxy) |
|-----------|----------------|----------------|----------------|---|--------|--------|
| 0.00b     | nr -0.60263462 | 1.99719        |                |   |        |        |
| 0.00      | nrl -0.60263788| 1.997194       | (0.957659)     |   |        |        |
| 0.00      | -7.3772        | -0.60264525    | 1.997194       | 1.0(0.95764) | 1.0(1.08362) |
| 0.02b     | nr -0.61257052 | 1.99699        |                |   |        |        |
| 0.02      | nrl -0.61257377| 1.99697        |                |   |        |        |
| 0.02      | -7.1850        | -0.61258096    | 1.99697        | 0.99985 | 0.99449 |
| 0.10b     | nr -0.65103820 | 1.99221        |                |   |        |        |
| 0.10      | nrl -0.65104149| 1.99221        | 0.99647        | 0.97084 |
| -0.10     | -6.5229        | -0.65104801    | 1.99221        | 0.99646 | 0.97084 |
| -0.20     | -8.5243        | -0.55105001    | 0.99647        | 1.02410 |
| 0.20      | -5.8942        | -0.69633157    | 1.97806        | 0.98651 | 0.93907 |
| -0.20     | -10.027        | -0.49633570    | 0.98652        | 1.04133 |
| 1.00c     | nr -0.97321    | 1.76           |                |   |        |        |
| 1.00      | nrl -0.97499184| 1.752008       | 0.83666        |   |        |        |
| 1.00      | -4.1401        | -0.97499598    | 1.752008       | 0.83666 | 0.72811 |
| -1.00     | -38.663        | 0.02500815     | 0.83666        | 0.99836 |
| 2.00      | -3.6984        | -1.2129584     | 1.524824       | 0.69635 | 0.59015 |
| -2.00     | -120.62        | 0.7869246      | 0.69635        | 0.86803 |
| 3.00      | -3.4913        | -1.3955526     | 1.375369       | 0.60793 | 0.51121 |
| 4.00      | -3.3227        | -1.5472894     | 1.269011       | 0.54672 | 0.45855 |
| B/B₀ (T) | Rxy | Qxy | \( Rxy \) | \( Qxy \) |
|------|-----|-----|-----------|-----------|
| -4.00 | 1.66425498 | -443.67 | 2.4522702 | 0.54674 | 0.69928 |
| 8.00  | -2.97278069 | -2.5994 | -1.9998079 | 1.027778 | 0.41299 | 0.34670 |
| 10.00 | -3.21982390 | -2.1806 | -2.17498954 | 0.957089 | 0.37519 | 0.31551 |
| -10.0 | 6.77747928 | -2698.9 | 7.82231364 | 0.37522 | 0.48819 |

\(^a\) sign \( B/B₀ \) corresponds to the field orientation

\(^b\) See Ref. [6]

\(^c\) See Ref. [7]

\(^d\) In the parentheses brackets the magnitudes \( Rxy \) and \( Qxy \) at \( B/B₀ = 0.0 \) are shown
TABLE V. \( H_2 \) total energies (\( E_t \)), electronic energies (\( E_s \)), relativistic correction (\( R_c \)), equilibrium internuclear distance (\( R_e \)) for \( 1(1/2_g)^2 \) configuration of \( H_2 \), compression magnitude (\( K \)) of average radius in x-y-direction for the total (\( R_{xy} \)) density and small (\( Q_{xy} \)) relativistic component.

In the calculations we have used 432 of basis function per one relativistic component. All values are given in a.u.

| Config. \( ^a \) | \( E_t \) | \( R_c \) | \( R_e \) | Shell | \( E_s \) | \( K(R_{xy}) \) | \( K(Q_{xy}) \) |
|-----------------|-------|-------|-------|-------|-------|-------------|-------------|
| \( B/B_0 = 0.0 \) | \( \times 10^{-6} \) |       |       |       |       |             |             |
| \( 1(1/2_g)^2 \) | -1.1336822 | -14.57 | 1.3866 \( ^b \) | \( 1(\pm 1/2_g) \) | -0.5967979 | 1.0(1.0336) | 1.0(1.0906) |
| \( 1(-1/2_g)1(-1/2_u) \) | -0.7707848 | -17.17 | \( 1(-1/2_g) \) | -0.9121185 | 1.0(0.9030) | 1.0(0.9969) |
| | | | \( 1(-1/2_u) \) | -0.2091545 | 1.0(1.5096) | 1.0(1.3773) |             |
| \( B/B_0 = 0.1 \) |       |       |       |       |       |             |             |
| \( 1(1/2_g)^2 \) | -1.1298513 | -14.89 | 1.3825 | \( 1(-1/2_g) \) | -0.6446553 | 0.99461 | 0.96101 |
| | | | \( 1(+1/2_g) \) | -0.5446584 | 0.99461 | 1.03376 |           |
| \( B/B_0 = 0.2 \) |       |       |       |       |       |             |             |
| \( 1(1/2_g)^2 \) | -1.1186323 | -15.82 | 1.3719 | \( 1(-1/2_g) \) | -0.6882655 | 0.98020 | 0.92150 |
| | | | \( 1(+1/2_g) \) | -0.4882717 | 0.98019 | 1.05855 |           |
| \( B/B_0 = 0.35 \) |       |       |       |       |       |             |             |
| \( 1(1/2_g)^2 \) | -1.0894853 | -18.35 | 1.3459 | \( 1(-1/2_g) \) | -0.74725115 | 0.98020 | 0.94478 |
| | | | \( 1(+1/2_g) \) | -0.39726222 | 0.98019 | 1.17371 |           |
| \( 1(-1/2_g)1(-1/2_u) \) | -1.0493226 | -13.89 | \( 1(-1/2_g) \) | -1.06381193 | 0.96928 | 0.94771 |
| | | | \( 1(-1/2_u) \) | -0.33520119 | 0.86675 | 0.78693 |           |
| \( B/B_0 = 0.4 \) |       |       |       |       |       |             |             |
| \( 1(1/2_g)^2 \) | -1.0768969 | -19.47 | 1.3373 | \( 1(-1/2_g) \) | -0.7651523 | 0.93671 | 0.84965 |
| | | | \( 1(+1/2_g) \) | -0.3651650 | 0.93670 | 1.07798 |           |
| \( 1(-1/2_g)1(-1/2_u) \) | -1.0806772 | -13.76 | \( 1(-1/2_g) \) | -1.0827429 | 0.96148 | 0.88676 |
| | | | \( 1(-1/2_u) \) | -0.3476192 | 0.84301 | 0.76626 |           |
\[
B / B_0 = 0.8 \\
1(1/2_g)^2 & -0.9370938 & -33.45 & 1.2554 & 1(-1/2_g) & -0.8901447 & 0.84388 & 0.74181 \\
& 1(+1/2_g) & -0.0901747 & 0.84387 & 1.04590 \\
\]

\[
B / B_0 = 1.0 \\
1(1/2_g)^2 & -0.8476702 & -43.69 & 1.21696 & 1(-1/2_g) & -0.9430515 & 0.80358 & 0.70150 \\
& 1(+1/2_g) & 0.0569073 & 0.80357 & 1.01730 \\
\]

\[
B / B_0 = 2.0 \\
1(1/2_g)^2 & -0.2894183 & -126.9 & 1.06766 & 1(-1/2_g) & -1.1539132 & 0.66011 & 0.57082 \\
& 1(+1/2_g) & 0.8459591 & 0.66010 & 0.87837 \\
\]

\[
B / B_0 = 4.0 \\
1(1/2_g)^2 & 1.0954315 & -454.2 & 0.898 & 1(-1/2_g) & -1.4463909 & 0.51404 & 0.44690 \\
& 1(+1/2_g) & 2.5531496 & 0.51404 & 0.70365 \\
\]

\[
B / B_0 = 10.0 \\
1(1/2_g)^2 & 5.9491461 & -2726.6 & 0.68682 & 1(-1/2_g) & -1.9869365 & 0.35056 & 0.31030 \\
& 1(+1/2_g) & 8.0103148 & 0.35059 & 0.48887 \\
\]

\[a\] In the nonrelativistic case, the configuration symbols \(1(1/2_g)^2\) and \(1(-1/2_g)1(-1/2_u)\) correspond to \(1\sigma_g^2\) and \(1\sigma_g1\sigma_u\) molecular configurations.

\[b\] See Hartree-Fock calculation by Kolos W. and Roothaan C.C.J. \[26\]
TABLE VI. The comparison of Hydrogen atom compression magnitudes $K$ for $R_{xy}$ and $R_z$ with relative contraction of internuclear distance $D/D_0$ under effect of magnetic field

| $B/B_0$ | $K(R_z)$ | $K(R_{xy})$ | $D/D_0$ | $D/D_0$ |
|---------|----------|-------------|--------|--------|
| H       | H        | $H_2^+$     | $H_2$  |
| 0.00    | 1.0      | 1.0         | 1.0    | 1.0    |
| 0.10    | 0.9955   | 0.9914      | 0.9975 | 0.9970 |
| 0.20    | 0.9839   | 0.9694      | 0.9904 | 0.9894 |
| 1.00    | 0.8632   | 0.7552      | 0.8772 | 0.9137 |
| 2.00    | 0.7716   | 0.6070      | 0.7634 | 0.7699 |
| 3.00    | 0.7156   | 0.5222      | 0.6886 |
| 4.00    | 0.6752   | 0.4656      | 0.6354 | 0.6476 |
| 8.00    | 0.5845   | 0.3463      | 0.5146 |
| 10.00   | 0.5574   | 0.3134      | 0.4791 | 0.4953 |