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Hydrogen molecule in a magnetic field: The lowest states of the Π manifold and the global ground state of the parallel configuration

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The electronic structure of the hydrogen molecule in a magnetic field is investigated for parallel internuclear and magnetic field axes. The lowest states of the Π manifold are studied for spin singlet and triplet ($M_s = -1$) as well as gerade and ungerade parity for a broad range of field strengths $0 \leqslant B \leqslant 100$ a.u. For both states with gerade parity we observe a monotonic decrease in the dissociation energy with increasing field strength up to $B = 0.1$ a.u. and metastable states with respect to the dissociation into two H atoms occur for a certain range of field strengths. For both states with ungerade parity we observe a strong increase in the dissociation energy with increasing field strength above some critical field strength B_c. As a major result we determine the transition field strengths for the crossings among the lowest $^1\Sigma_g$, $^3\Sigma_u$, and $^3\Pi_u$ states. The global ground state for $B \lesssim 0.18$ a.u. is the strongly bound $^1\Sigma_g$ state. The crossings of the $^1\Sigma_g$ with the $^3\Sigma_u$ and $^3\Pi_u$ state occur at $B \approx 0.18$ and $B \approx 0.39$ a.u., respectively. The transition between the $^3\Sigma_u$ and the $^3\Pi_u$ state occurs at $B \approx 12.3$ a.u. Therefore, the *global ground state* of the hydrogen molecule for the parallel configuration is the *unbound* $^3\Sigma_u$ state for $0.18 \lesssim B \lesssim 12.3$ a.u. The ground state for $B \gtrsim 12.3$ a.u. is the strongly bound $^3\Pi_u$ state. This result is of great relevance to the chemistry in the atmospheres of magnetic white dwarfs and neutron stars. [S1050-2947(98)08003-2]

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I. INTRODUCTION

The behavior and structure of matter in the presence of strong external magnetic fields is a research area of increasing interest. This increasing interest is motivated by the occurrence of strong fields and strong field effects in different branches of physics such as astrophysics [1–3], atomic and molecular physics of Rydberg states [4], and certain areas of solid state physics such as excitons and/or quantum nanostructures [5].

A number of theoretical investigations were performed concerning the properties of atomic and molecular systems in strong magnetic fields. Most of them, however, deal with the hydrogen atom. For molecular systems only the electronic structure of the H_2^+ ion was investigated in some detail (see Refs. [6–10] and references therein). Very interesting phenomena can be observed already for this simple diatomic system. For the ground state of the H_2^+ molecule the dissociation energy increases and the equilibrium internuclear distance simultaneously decreases with increasing field strength. Furthermore it was shown [11,12] that a certain class of excited electronic states, which possess a purely repulsive potential energy surface in the absence of a magnetic field, acquire a well-pronounced potential well in a sufficiently strong magnetic field. Moreover the electronic potential energies depend not only on the internuclear distance but also on the angle between the magnetic field and molecular axes, which leads to a very complex topological behavior of the corresponding potential energy surfaces [7–9].

In contrast to the H_2^+ ion there exist only a few investigations dealing with the electronic structure of the hydrogen molecule in the presence of a strong magnetic field. Highly excited states of H_2 were studied for a field strength of 4.7 T in Ref. [13]. For intermediate field strengths two studies of almost qualitative character investigate the potential energy curve (PEC) of the lowest $^1\Sigma_g$ state [14,15]. A few investigations were performed in the high field limit [16–19], where the magnetic forces dominate over the Coulomb forces and therefore several approximations can be performed. Very recently a first step has been done in order to elucidate the electronic structure of the H_2 molecule for the parallel configuration, i.e., for parallel internuclear and magnetic field axes [20]. In that investigation the ground states of the Σ manifold were studied for gerade and ungerade parity as well as singlet and triplet states. Hereby accurate adiabatic electronic energies were obtained for a broad range of field strengths from field free space up to strong magnetic fields of 100 a.u. A variety of interesting effects were revealed. As in the case of the H_2^+ ion, the lowest strongly bound states, i.e., the lowest $^1\Sigma_g$, $^3\Sigma_g$, and $^1\Sigma_u$ states, show a decrease of the bond length and an increase in the dissociation energy for sufficiently strong fields. Furthermore a change in the dissociation channel occurs for the lowest $^1\Sigma_u$ state between $B = 10.0$ and 20.0 a.u. due to the existence of strongly bound H^- states in the presence of a magnetic field. The $^3\Sigma_g$ state was shown to exhibit an additional outer minimum for intermediate field strengths, which could provide vibrationally bound states.

An important result of Ref. [20] is the change of the ground state from the lowest $^1\Sigma_g$ state to the lowest $^3\Sigma_u$ state between $B = 0.1$ and 0.2 a.u. This crossing is of particular relevance for the existence of molecular hydrogen in the vicinity of white dwarfs. The $^3\Sigma_u$ state is an unbound state and possesses only a very shallow van der Waals minimum, which does not provide any vibrational level. Therefore, the ground state of the hydrogen molecule for the parallel configuration is an unbound state for $B \gtrsim 0.2$ a.u. up to some much higher critical field strength B_c, which is not known exactly. In Ref. [18] it has been shown that for very strong fields ($B \gtrsim 3\times10^3$ a.u.) the strongly bound $^3\Pi_u$ state is the global ground state of the hydrogen molecule oriented parallel to the magnetic field. Therefore a second transition that involves the unbound $^3\Sigma_u$ and the strongly bound $^3\Pi_u$ state has to occur at some field strength between 0.2 and 3×10^3 a.u.

The above considerations show that detailed studies of the electronic properties of the hydrogen molecule in a magnetic field are very desirable. The present investigation deals with the electronic structure of the lowest states of the important Π subspace, i.e., the lowest singlet and triplet ($M_s=-1$) states with gerade and ungerade parity. This subspace contains, as mentioned above, the global ground state of the H_2 molecule for sufficiently strong magnetic fields. We hereby consider the case of parallel internuclear and magnetic field axes. The parallel configuration is distinct by its high symmetry compared to the case of an arbitrary angle between the internuclear and magnetic field axes and is expected to play an important role in the electronic structure of the hydrogen molecule [21]. In the present investigation we focus on the hydrogen molecule with negligible value of the pseudomomentum, i.e., negligible motional Stark term and collective motion perpendicular to the magnetic field. For instance, in the atmosphere of white dwarfs this corresponds to the situation of not too high temperatures. The results of our calculations include accurate adiabatic PECs for the complete range of field strengths $0\leqslant B\leqslant100$ a.u. We present detailed data for the total and dissociation energies, equilibrium internuclear distances, and positions of maxima for the corresponding electronic states. Moreover we provide a discussion of the global ground state of the parallel configuration and give the transition field strengths for the crossings between the $^1\Sigma_g$, $^3\Sigma_u$, and $^3\Pi_u$ states.

The paper is organized as follows. In Sec. II we describe the theoretical aspects of the present investigation, including a discussion of the Hamiltonian and a description of the basis set of our CI calculations. In Sec. III we discuss the general aspects of the potential energy curves (PECs) in field free space for the lowest states of the Π subspace. Section IV contains a detailed investigation of the electronic structure of the lowest Π states in the presence of a magnetic field for the range $0.001\leqslant B\leqslant100$ a.u. Finally the global ground state of the hydrogen molecule oriented parallel to the magnetic field is studied in Sec. V. The summary and conclusions are given in Sec. VI.

II. THEORETICAL ASPECTS

Our starting point is the total nonrelativistic molecular Hamiltonian in Cartesian coordinates. The total pseudomomentum is a constant of motion and therefore commutes with the Hamiltonian [22,23]. For that reason the Hamiltonian can be simplified by performing a so-called pseudoseparation of the center-of-mass motion [24,25,22], which introduces the center-of-mass coordinate and the conserved pseudomomentum as a pair of canonical conjugated variables. Further simplifications can be achieved by a consecutive series of unitary transformations [24,25].

In order to separate the electronic and nuclear motion we perform the Born-Oppenheimer approximation in the presence of a magnetic field [26,24,25]. As a first-order approximation we assume infinitely heavy masses for the nuclei. The origin of our coordinate system coincides with the midpoint of the internuclear axis of the hydrogen molecule and the protons are located on the z axis. The magnetic field is chosen parallel to the z axis of our coordinate system and the symmetric gauge is adopted for the vector potential. The gyromagnetic factor of the electron is chosen to be equal to two. The Hamiltonian, therefore, takes on the following appearance:

$$H=\sum_{i=1}^{2}\left\{\frac{1}{2}\boldsymbol{p}_i^2+\frac{1}{8}(\boldsymbol{B}\times\boldsymbol{r}_i)^2+\frac{1}{2}\boldsymbol{L}_i\cdot\boldsymbol{B}-\frac{1}{|\boldsymbol{r}_i-\boldsymbol{R}/2|}-\frac{1}{|\boldsymbol{r}_i+\boldsymbol{R}/2|}\right\}+\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}+\frac{1}{R}+\boldsymbol{S}\cdot\boldsymbol{B}. \qquad (1)$$

The symbols $\boldsymbol{r}_i$, $\boldsymbol{p}_i$, and $\boldsymbol{L}_i$ denote the position vectors, the canonical conjugated momenta, and the angular momenta of the two electrons, respectively. $\boldsymbol{B}$ and $\boldsymbol{R}$ are the vectors of the magnetic field and internuclear distance, respectively, and R denotes the magnitude of $\boldsymbol{R}$. With $\boldsymbol{S}$ we denote the vector of the total electronic spin. Throughout the paper we will use atomic units.

The Hamiltonian (1) commutes with the following operators: the parity operator P, the projection L_z of the electronic angular momentum on the internuclear axis, the square S^2 of the total electronic spin, and the projection S_z of the total electronic spin on the internuclear axis. In the case of field-free space we encounter an additional independent symmetry, namely, the reflections of the electronic coordinates at the xz (σ_v) plane. The eigenfunctions possess the corresponding eigenvalues ±1. This symmetry does not hold in the presence of a magnetic field! Therefore, the resulting symmetry groups for the hydrogen molecule are $D_{\infty h}$ in the case of field-free space and $C_{\infty h}$ in the presence of a magnetic field [21].

In order to solve the fixed-nuclei electronic Schrödinger equation belonging to the Hamiltonian (1) we expand the electronic eigenfunction in terms of molecular configurations. In a first step the total electronic eigenfunction Ψ_{tot} of the Hamiltonian (1) is written as a product of its spatial part Ψ and its spin part χ; i.e., we have $\Psi_{\text{tot}}=\Psi\chi$. For the spatial part Ψ of the wave function we use the linear combination of atomic orbitals—molecular orbitals (LCAO-MO) ansatz, i.e., we decompose Ψ with respect to molecular orbital configurations ψ of H_2, which respect the corresponding symmetries (see above) and the Pauli principle:

$$\Psi=\sum_{i,j}c_{ij}[\psi_{ij}(\boldsymbol{r}_1,\boldsymbol{r}_2)\pm\psi_{ij}(\boldsymbol{r}_2,\boldsymbol{r}_1)]=\sum_{i,j}c_{ij}[\Phi_i(\boldsymbol{r}_1)\Phi_j(\boldsymbol{r}_2)\pm\Phi_i(\boldsymbol{r}_2)\Phi_j(\boldsymbol{r}_1)].$$

The molecular orbital configurations ψ_{ij} of H_2 are products of the corresponding one-electron $H_2{}^+$ molecular orbitals Φ_i and Φ_j. The $H_2{}^+$ molecular orbitals are built from atomic orbitals centered at each nucleus. A key ingredient of this procedure is a basis set of nonorthogonal optimized nonspherical Gaussian atomic orbitals, which has been established previously [27,28]. For the case of a H_2 molecule parallel to the magnetic field these basis functions read as follows:

$$\phi_{kl}^{m}(\rho,z,\alpha,\beta,\pm R/2)=\rho^{|m|+2k}(z\mp R/2)^{l}\exp\{-\alpha\rho^{2} \\ -\beta(z\mp R/2)^{2}\}\exp\{im\phi\}. \qquad (2)$$

The symbols $\rho=+\sqrt{x^2+y^2}$ and z denote the electronic coordinates. m, k, and l are parameters depending on the subspace of the H atom for which the basis functions have been optimized and α and β are variational parameters. For a more detailed description of the construction of the molecular electronic wave function we refer the reader to Ref. [20].

In order to determine the molecular electronic wave function of H_2 we use the variational principle, which means that we minimize the variational integral $\int\Psi^{*}H\Psi/\int\Psi^{*}\Psi$ by varying the coefficients c_i. The resulting generalized eigenvalue problem reads as follows:

$$(\underline{H}-\epsilon\underline{S})\boldsymbol{c}=\boldsymbol{0}, \qquad (3)$$

where the Hamiltonian matrix $\underline{H}$ is real and symmetric and the overlap matrix is real, symmetric, and positive definite. The vector $\boldsymbol{c}$ contains the expansion coefficients. The matrix elements of the Hamiltonian matrix and the overlap matrix are certain combinations of matrix elements with respect to the optimized nonspherical Gaussian atomic orbitals. A description of the technique of the evaluation of these matrix elements is given in Ref. [20].

For the numerical solution of the eigenvalue problem (3) we used the standard NAG library. The typical dimension of the Hamiltonian matrix for each Π subspace varies between approximately 1700 and 3300 depending on the magnetic field strength. Depending on the dimension of the Hamiltonian matrix, it takes between 70 and 250 min for simultaneously calculating one point of a PEC of each Π subspace on a IBM RS6000 computer. The overall accuracy of our results with respect to the total energy is estimated to be typically of the order of magnitude of 10^{-4} and for some cases of the order of magnitude of 10^{-3}. It should be noted that this estimate is rather conservative; in some ranges of the magnetic field strength and internuclear distance, e.g., close to the separated atom limit, the accuracy is 10^{-5} or even better. The positions, i.e., internuclear distances, of the maxima and the minima in the PECs were determined with an accuracy of 10^{-2} a.u. Therefore about 350 points were calculated on an average for each PEC. It was not necessary to further improve this accuracy since a change in the internuclear distance about 1×10^{-2} a.u. results in a change in the energy that is typically of the order of magnitude of 10^{-4} or smaller.

III. THE GROUND STATES OF THE Π MANIFOLD IN FIELD-FREE SPACE

Let us start with the discussion of the general properties of the low-lying Π states in field-free space whose PECs are given in Fig. 1. A detailed description of these states can be found in Ref. [29]. At large internuclear distances both the lowest $^1\Pi_g$ as well as the $^3\Pi_g$ state can be approximately described by a Heitler-London–type wave function consisting of the orbital configuration $(1s2p\pi)_g$. An avoided crossing with the attractive $(1\sigma_g 3d\pi)$ type state leads to the occurrence of a minimum in both of the Π_g PECs (see Fig. 1). For the singlet $^1\Pi_g$ state we encounter a second minimum of van der Waals type at large internuclear distances, which has been shown to accommodate several vibrational levels within the Born-Oppenheimer approximation [30]. The united atom limit for the $^1\Pi_g$ and $^3\Pi_g$ state is the ^1D $1s3d$ and ^3D $1s3d$ helium state, respectively. A remarkable feature of the $^1\Pi_g$ and $^3\Pi_g$ states is the fact that their wave functions are almost indistinguishable for small internuclear distances, i.e., $R\lesssim2.5$ a.u. (see also their PECs in Fig. 1). For $R\lesssim2.3$ a.u. the triplet state has a slightly lower energy than the singlet. The energy difference between the singlet and triplet state at the equilibrium internuclear distance amounts to 4.92×10^{-5} a.u. and reaches a maximum of 6.38×10^{-5} a.u. at $R\approx1.6$ a.u. With further decreasing internuclear distance the energy difference decreases finally, reaching a value of 1.55×10^{-5} a.u. in the united atom limit [30].

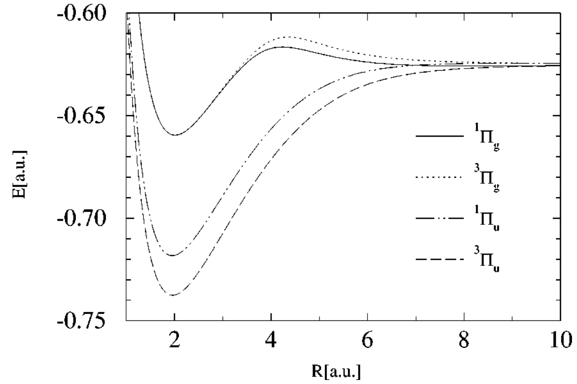

FIG. 1. PECs (total energy) for the lowest $^1\Pi_g$, $^3\Pi_g$, $^1\Pi_u$, and $^3\Pi_u$ states in field-free space.

The Π_u states whose PECs are also illustrated in Fig. 1 can be represented by a Heitler-London type wave function $(1s2p\pi)_u$ for large internuclear distances. Near the equilibrium internuclear distance the wave function can approximately be described by a $(1\sigma_g 2p\pi)$ type configuration. The PEC of the $^1\Pi_u$ state exhibits a hump at $R\approx9$ a.u. due to a first order London dispersion force. For the $^1\Pi_u$ and $^3\Pi_u$ state the united atom limit is given by the ^1P $1s2p$ and ^3P $1s2p$ helium state, respectively. An overall feature of the lowest Π states with ungerade parity is the fact that the PEC of the $^3\Pi_u$ triplet state is lower in energy than the corresponding PEC of the $^1\Pi_u$ singlet state. Extensive studies have been performed in order to explain the difference in the energy of the $^1\Pi_u$ and $^3\Pi_u$ states, i.e., the singlet-triplet energy splitting. Intuitively one would expect the interelectronic repulsion to be smaller for the triplet state than for the singlet due to the zero of the wave function if the coordinates of both electrons are equal. However, it has been shown that, similar to the case of the ^1P and ^3P states of helium, the interelectronic repulsion is larger in the triplet state. The greater stability, i.e., lower energy, of the triplet state occurs due to a larger electron-nucleus attraction energy [31]. With increasing internuclear distances both the PECs of the $^1\Pi_g$ and $^3\Pi_u$ state as well as those of the $^1\Pi_u$ and $^3\Pi_g$ state

TABLE I. Data for the lowest $^1\Pi_g$ state: Total energies E_{t1},E_{t2} and dissociation energies E_{d1},E_{d2} at the equilibrium internuclear distance, the equilibrium internuclear distances $R_{\mathrm{eq1}},R_{\mathrm{eq2}}$, the positions R_{max}, and total energies E_{max} of the maxima and the total energies in the dissociation limit $\lim_{R\to\infty}E_t$ as a function of the field strength $0\leqslant B\leqslant 100$ (all quantities are given in atomic units).

B	R_{eq1}	E_{d1}	E_{t1}	R_{eq2}	E_{d2}	E_{t2}	R_{max}	E_{max}	$\lim_{R\to\infty}E_{\mathrm{tot}}$
0.0	2.01	0.034502	−0.659501	8.14	8.038×10^{-4}	−0.625803	4.24	−0.616547	−0.624999
0.001	2.01	0.034501	−0.659997	8.14	8.039×10^{-4}	−0.626230	4.24	−0.617068	−0.625496
0.005	2.01	0.034268	−0.661686	8.14	8.045×10^{-4}	−0.628222	4.24	−0.618976	−0.627418
0.01	2.01	0.033959	−0.663634	8.14	8.087×10^{-4}	−0.630484	4.23	−0.621186	−0.629675
0.05	2.02	0.026191	−0.668625	7.95	9.100×10^{-4}	−0.643344	4.06	−0.632934	−0.642434
0.1	2.04	0.014450	−0.662821	7.60	1.132×10^{-3}	−0.649503	3.77	−0.636987	−0.648371
0.2	2.09	0.011130[a]	−0.636414	7.00	1.586×10^{-3}	−0.642506	3.28	−0.625284	−0.640920
0.5				5.99	2.437×10^{-3}	−0.549125			−0.546687
1.0				5.25	2.853×10^{-3}	−0.290617			−0.287765
2.0				4.66	2.702×10^{-3}	0.375473			0.378174
5.0				4.18	1.707×10^{-3}	2.758062			2.759769
10.0				4.05	8.791×10^{-4}	7.125902			7.126781
20.0				4.11	3.751×10^{-4}	16.318719			16.319094
50.0				4.32	1.137×10^{-4}	44.925181			44.925295
100.0				4.55	4.57×10^{-5}	93.575395			93.575441

[a] This electronic state is metastable with respect to the dissociation into two H atoms.

approach each other and finally end up in the same separated atom limit, which is H(1*s*)+H(2*p*).

After describing the general aspects of the PECs for the lowest states of the four Π subspaces let us compare our numerical results for these states with the existing data in the literature. For the $^1\Pi_g$ state very accurate energies within the Born-Oppenheimer approximation were obtained by Wolniewicz [32] and Kolos and Rychlewski [30]. For the equilibrium internuclear distance $R=2.01$ a.u. we obtained a total energy of -0.69501 a.u., which yields a dissociation energy of 0.034 502 a.u. (cf. Table I). This corresponds to a relative accuracy in the total energy of 3.2×10^{-5} compared to the result in [32]. The relative accuracy of our data further improves with increasing internuclear distance. As an example we mention $R=12$ a.u., where the relative accuracy is 2.4×10^{-6}. For the second minimum we obtained an equilibrium internuclear distance of 8.14 a.u. with a total energy of $-0.625\,803$ a.u. The dissociation energy for this minimum therefore amounts to 8.038×10^{-4} a.u. The maximum in the PEC with a total energy of $-0.616\,547$ a.u. occurs at an internuclear distance of 4.24 a.u.

As a reference for the Born-Oppenheimer energies of the $^1\Pi_u$ state we use the data given in Ref. [33]. Results of our calculations concerning the PEC of the $^1\Pi_u$ state are pre-

TABLE II. Data for the lowest $^3\Pi_g$ state: Total energy E_t and dissociation energy E_d at the equilibrium internuclear distance, the equilibrium internuclear distances R_{eq}, the positions R_{max} and total energies E_{max} of the maximum and the total energies in the dissociation limit $\lim_{R\to\infty}E_t$ as a function of the field strength $0\leqslant B\leqslant 100$ (all quantities are given in atomic units).

B	R_{eq}	E_d	E_t	R_{max}	E_{max}	$\lim_{R\to\infty}E_{\mathrm{tot}}$
0.0	2.01	0.034554	−0.659553	4.35	−0.611691	−0.624999
0.001	2.01	0.034551	−0.661047	4.35	−0.613211	−0.626496
0.005	2.01	0.034320	−0.666738	4.35	−0.619112	−0.632418
0.01	2.01	0.034012	−0.673687	4.34	−0.626296	−0.639675
0.05	2.02	0.026271	−0.718705	4.18	−0.677419	−0.692434
0.1	2.03	0.014550	−0.762921	3.93	−0.730337	−0.748371
0.2	2.06	0.019590[a]	−0.836343	3.53	−0.816753	−0.840920
0.5	2.15	0.002483[a]	−1.009346	2.76	−1.006863	−1.046687
1.0						−1.287765
2.0						−1.621825
5.0						−2.240231
10.0						−2.873218
20.0						−3.680905
50.0						−5.074705
100.0						−6.424559

[a] These electronic states are metastable with respect to the dissociation into two H atoms. The difference between the minimum and the maximum of the PEC is given instead of the dissociation energy.

TABLE III. Data for the lowest $^1\Pi_u$ state: Total energy E_t and dissociation energy E_d at the equilibrium internuclear distance, the equilibrium internuclear distances R_{eq}, the positions $R_{\max}$ and total energies $E_{\max}$ of the maxima and the total energies in the dissociation limit $\lim_{R\to\infty}E_t$ as a function of the field strength $0 \leqslant B \leqslant 100$ (all quantities are given in atomic units).

B	R_{eq}	E_d	E_t	$R_{\max}$	$E_{\max}$	$\lim_{R\to\infty}E_{\mathrm{tot}}$
0.0	1.95	0.093220	−0.718219	9.03	−0.624528	−0.624999
0.001	1.95	0.093215	−0.718711	9.02	−0.625025	−0.625496
0.005	1.95	0.093178	−0.720596	9.02	−0.626945	−0.627418
0.01	1.95	0.093163	−0.722838	9.01	−0.629200	−0.629675
0.05	1.94	0.092348	−0.734782	8.73	−0.641874	−0.642434
0.1	1.93	0.090740	−0.739111	8.29	−0.647645	−0.648371
0.2	1.90	0.087969	−0.728889	7.56	−0.639842	−0.640920
0.5	1.80	0.087080	−0.633767	6.47	−0.544981	−0.546687
1.0	1.65	0.097448	−0.385213	5.72	−0.285750	−0.287765
2.0	1.41	0.126544	0.251630	5.05	0.380278	0.378174
5.0	1.11	0.207874	2.551895	4.26	2.761807	2.759769
10.0	0.89	0.315707	6.811074	3.73	7.128738	7.126781
20.0	0.70	0.481139	15.837955	3.27	16.320973	16.319094
50.0	0.51	0.822810	44.102485	2.75	44.927090	44.925295
100.0	0.40	1.208626	92.366815	2.43	93.577178	93.575441

sented in Table III. At the equilibrium internuclear distance $R_{\mathrm{eq}}=1.95$ a.u. our calculations yield a total energy of $-0.718\,219$ a.u. corresponding to a dissociation energy of $0.093\,220$ a.u. The relative accuracy compared to the data given in Ref. [33] is 2.4×10^{-4} at R_{eq} and 2.7×10^{-6} at $R=12$ a.u. As in the case of the $^1\Pi_g$ state the acccuracy of our calculations increases with increasing internuclear distances. The position of the maximum has been determined to be $R_{\max}=9.03$ a.u. and the total energy at $R_{\max}$ evaluates to $-0.624\,528$ a.u.

Accurate Born-Oppenheimer energies for the lowest triplet states can be found in Ref. [30]. Data of the present investigation for the total energies and positions of maxima and minima are given in Table II for the $^3\Pi_g$ and Table IV for the $^3\Pi_u$ state, respectively. Within our calculations the total energy of the $^3\Pi_g$ state at the equilibrium internuclear distance $R=2.01$ a.u. amounts to $-0.659\,553$ a.u. Therefore, the relative accuracy of the total energy compared to the data given in Ref. [30] is 2.2×10^{-5}. For the $^3\Pi_u$ state an equilibrium internuclear distance of $R=1.96$ a.u. with a total energy of $-0.737\,521$ a.u. has been obtained corresponding to a relative error of 6.3×10^{-5}. For both states the accuracy for larger internuclear distances is of the order of magnitude of 10^{-6}.

IV. THE LOWEST Π STATES IN THE PRESENCE OF A MAGNETIC FIELD

A. The $^1\Pi_g$ state

First we consider the dissociation channel of the $^1\Pi_g$ state in the presence of a magnetic field. In our notation atomic hydrogen states are labeled by $\mathrm{H}(m_a^{\pi_a})$, where m_a is the atomic magnetic quantum number and π_a the atomic z parity. For the entire range of field strengths $0<B\leqslant100$ a.u. the dissociation channel of the $^1\Pi_g$ state is given by $\mathrm{H}_2\to\mathrm{H}(0^+)+\mathrm{H}(1^+)$. This means that the energy in the dissociation limit corresponds to the total energy of two hydrogen atoms in the lowest electronic state within the (0^+) and (1^+) subspace, respectively. This dissociation channel holds also for all the other electronic Π states considered in the present work.

Let us now investigate the PEC of the $^1\Pi_g$ state with varying field strength, which is illustrated in Fig. 2(a). For the first minimum and/or well we observe that the corresponding depth decreases strongly with increasing magnetic field strength. The dissociation energy, which amounts to $E_{d1}=0.034\,502$ a.u. in field-free space, monotonously de-

TABLE IV. Data for the lowest $^3\Pi_u$ state: Total energy E_t and dissociation energy E_d at the equilibrium internuclear distance, the equilibrium internuclear distances R_{eq}, and the total energies in the dissociation limit $\lim_{R\to\infty}E_t$ as a function of the field strength $0 \leqslant B \leqslant 100$ (all quantities are given in atomic units).

B	R_{eq}	E_d	E_t	$\lim_{R\to\infty}E_{\mathrm{tot}}$
0.0	1.96	0.112522	−0.737521	−0.624999
0.001	1.96	0.112533	−0.739029	−0.626496
0.005	1.96	0.112544	−0.744962	−0.632418
0.01	1.96	0.112559	−0.752234	−0.639675
0.05	1.95	0.113862	−0.806296	−0.692434
0.1	1.95	0.116912	−0.865283	−0.748371
0.2	1.91	0.125028	−0.965948	−0.840920
0.5	1.79	0.153029	−1.199716	−1.046687
1.0	1.59	0.196553	−1.484318	−1.287765
2.0	1.35	0.267435	−1.889260	−1.621285
5.0	1.03	0.418679	−2.658910	−2.240231
10.0	0.82	0.593026	−3.466244	−2.873218
20.0	0.65	0.838135	−4.519040	−3.680905
50.0	0.48	1.308786	−6.383491	−5.074705
100.0[a]	0.38	1.811759	−8.236318	−6.424559

[a] This electronic state exhibits a second minimum and an additional maximum. $R_{\mathrm{eq}2}=4.51$ a.u.; $E_{d2}=4.604\times10^{-5}$; $E_{t2}=-6.424\,605$. $R_{\max}=3.11$; $E_{\max}=-6.424\,531$.

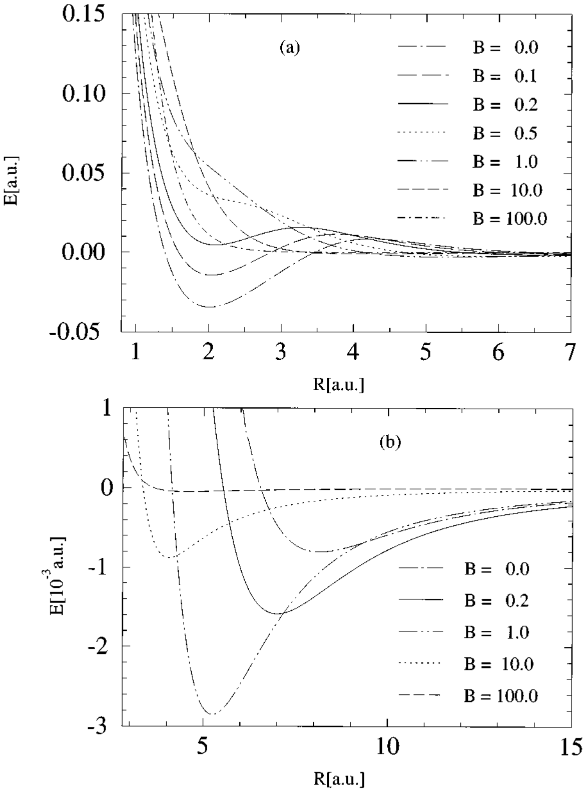

FIG. 2. (a) PECs for $B=0.0$, 0.1, 0.2, 0.5, 1.0, 10.0, and 100.0 a.u. of the lowest $^1\Pi_g$ state illustrating the first minimum and the maximum. The energy is given with respect to the dissociation limit, i.e., $E(R)=E_t(R)-\lim_{R\rightarrow\infty}E_t(R)$. (b) PECs for $B=0.0$, 0.2, 1.0, 10.0, and 100.0 a.u. for the lowest $^1\Pi_g$ state illustrating the second minimum. The energy is shown with respect to the dissociation limit, i.e., $E(R)=E_t(R)-\lim_{R\rightarrow\infty}E_t(R)$.

creases to $E_{d1}=0.014\,460$ a.u. for $B=0.1$ a.u. The corresponding equilibrium internuclear distance R_{eq1} hereby remains approximately constant up to a field strength of $B \approx 0.01$ a.u. With further increasing field strength we observe a minor increase to $R_{\mathrm{eq1}}=2.04$ a.u. for $B=0.1$ a.u. Between $B=0.1$ and 0.5 a.u. we observe a drastic change in the shape of the PEC. For a field strength of 0.2 a.u. we encounter a metastable state with respect to the dissociation into two hydrogen atoms. The minimum in the corresponding PEC occurs at an internuclear distance $R_{\mathrm{eq1}}=2.09$ a.u. and the difference between the total energies at R_{eq1} and R_{max} evaluates to $E_{t1}-E_{\mathrm{max}}=0.011\,130$ a.u. For even larger field strengths, i.e., $B \gtrsim 0.5$ a.u., the first minimum disappears. Simultaneously we observe a moderate change in the position of the maximum R_{max} in the regime $0 \leqslant B \lesssim 0.2$ a.u. With increasing magnetic field strength R_{max} is shifted to decreasingly smaller internuclear distances, i.e., from $R_{\mathrm{max}}=4.24$ a.u. in field-free space to $R_{\mathrm{max}}=3.28$ a.u. for a field strength of 0.2 a.u. Figure 2(a) shows the PECs of the $^1\Pi_g$ state for different field strengths, illustrating the shape of the PEC near the first equilibrium internuclear distance. The corresponding data concerning the positions of the maxima and minima, total and dissociation energies, and total energies in the separated atom limit are presented in Table I.

Despite the fact that the first minimum and the maximum of the PEC disappear for field strengths $B \gtrsim 0.5$ a.u. the PECs possess some interesting features for larger field strengths. In the following discussion we focus on the rough shape of the PECs shown in Fig. 2(a) for $B \gtrsim 0.5$ a.u. From Fig. 2(a) we observe that the PEC of the $^1\Pi_g$ state exhibits two turning points at $R \approx 2.3$ a.u. and $R \approx 3.2$ a.u. for the field strength $B=0.5$ a.u. For $B=1$ a.u. these two turning points are shifted to smaller internuclear distances, e.g., $R \approx 2.2$ a.u. and $R \approx 2.4$ a.u. From Fig. 2(a) we see that these turning points are much less pronounced for a field strength of $B=1$ than for 0.5 a.u., which is also confirmed by an investigation of the corresponding first derivatives of the above PECs. With further increasing field strength, i.e., in the range $2 \lesssim B \lesssim 20$ a.u., no turning points can be found in the PEC of the $^1\Pi_g$ state. Only for field strengths $B \gtrsim 50$ a.u. two turning points again exist, which, however, cannot be seen in the PEC for $B=100$ a.u. in Fig. 2(a) since they occur for very small values of the internuclear distance. This behavior is of importance for the singlet-triplet energy splitting between the PECs of the $^1\Pi_g$ and $^3\Pi_g$ $(M_s=0)$ state, which will be discussed in the following subsection.

In addition to the deep minimum at $R_{\mathrm{eq1}}=2.01$ a.u. in the PEC of the $^1\Pi_g$ state, a second minimum exists that in field-free space is very shallow and located at $R_{\mathrm{eq2}}=8.14$ a.u. The corresponding region of the PECs is illustrated in Fig. 2(b). In the presence of a magnetic field this minimum becomes more and more pronounced with increasing field strength. The depth of the well monotonously increases up to a field strength of $B=1$ a.u. (cf. Table I). The dissociation energy E_{d2} for $B=1$ a.u. amounts to 2.853×10^{-3}, which is more than three times as much as the corresponding dissociation energy in field-free space. For field strengths $B \gtrsim 2$ a.u. the dissociation energy decreases monotonously. The corresponding equilibrium internuclear distance R_{eq2} for this second minimum first decreases with increasing field strength from 8.14 a.u. in field-free space to 4.05 a.u. at $B=10$ a.u. but exhibits a minor increase for $B \gtrsim 20$ a.u. with further increasing magnetic field strength. From Fig. 2(b) we can also observe the monotonous decrease in R_{eq2} up to a field strength of 10 a.u.

Next let us discuss the existence of bound states. We have to investigate whether vibrational levels exist in the PECs discussed above. The determination of vibrational levels in the presence of a magnetic field is a complicated task since the Born-Oppenheimer approximation known from field-free space breaks down in the presence of a magnetic field: The nuclear charges are treated as ''naked'' charges, which is an incomplete description since they are at least partially screened by the electrons against the magnetic field. In order to describe this screening correctly, the diagonal terms of the nonadiabatic coupling elements have to be included in the nuclear equation of motion [34,25,24]. The screening of the nuclear charges depends not only on the internuclear distance but also on the angle between the internuclear axis and the magnetic field. As a consequence the nuclear equation of motion is much more complex in the presence of a magnetic field compared to the field free space. In the present investigation we are dealing with the case of parallel internuclear and magnetic field axes and therefore cannot determine the exact vibrational levels. However, we are able to provide estimations for the positions of the vibrational levels and on the basis of these estimates we can decide whether bound states exist with respect to the vibrational mode R.

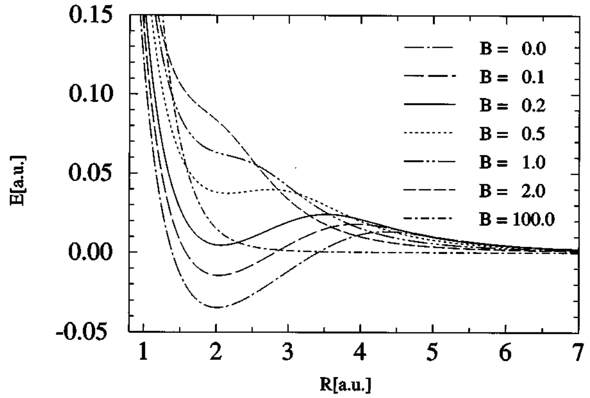

FIG. 3. PECs for $B=0.0$, 0.1, 0.2, 0.5, 1.0, 2.0, and 100.0 a.u. for the lowest $^3\Pi_g$ state. The energy is shown with respect to the dissociation limit, i.e., $E(R)=E_t(R)-\lim_{R\to\infty}E_t(R)$.

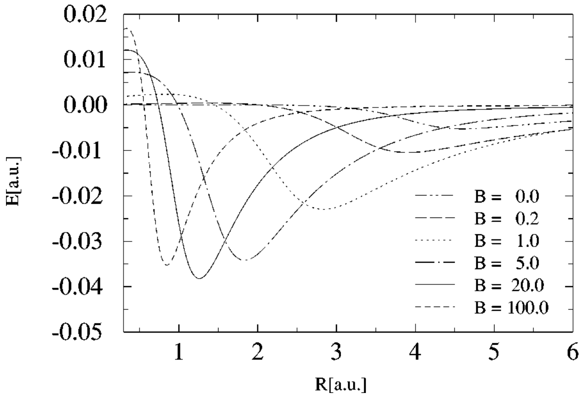

FIG. 4. Singlet-triplet splitting between the $^1\Pi_g$ and $^3\Pi_g(M_s=0)$ state for $B=0.0$, 0.2, 1.0, 5.0, 20.0, and 100.0 a.u.

A lower estimate of the vibrational energy can be obtained by solving the nuclear equation of motion known from field-free space $P^2/2\mu+V$, where the potential V is given by the corresponding PEC in the magnetic field. The corresponding Schrödinger equation is then solved by using a discrete variable method [35]. An upper estimate for the energy of a vibrational state is obtained by simply adding the Landau energy of the nuclear equation of motion to the lower estimate of the energy level. Estimations concerning the existence of vibrational levels were performed for each PEC shown in all figures. The number of vibrational levels with quantum number $J=\Lambda=0$ in the first well of the PEC of the $^1\Pi_g$ state [see Fig. 2(a)] decreases monotonously with increasing field strength up to $B=0.1$ a.u. Bound states exist in the entire range of field strengths $0.0\leqslant B\lesssim 0.1$ a.u. For the second, i.e., outer, well bound states exist up to a field strength of 2 a.u. In the range $5\lesssim B\lesssim 50$ a.u. the lower estimate of the vibrational energy was found below the energy in the separated atom limit where the upper bound is above. Therefore, the existence of bound states depends on the detailed nuclear motion and cannot be decided within the present approach. For even larger magnetic fields ($B\gtrsim 100$ a.u.) no vibrational states exist in the PEC of the $^1\Pi_g$ state.

B. The $^3\Pi_g$ state

The shape of the PEC of the $^3\Pi_g$ state depending on the magnetic field strength is shown in Fig. 3 and the corresponding data are given in Table II. With increasing field strength the absolute value of the total energy in the dissociation limit monotonously increases due to the spin Zeeman shift in the magnetic field. As in the case of the $^1\Pi_g$ state we observe a decrease in the dissociation energy with increasing field strength from $E_d=0.034\,554$ a.u. in field-free space to $E_d=0.014\,550$ a.u. for a field strength of 0.1 a.u. For $B=0.2$ and 0.5 a.u. we encounter metastable states with respect to the dissociation into two hydrogen atoms. For these states, the difference of the total energy of the maximum and the minimum of the corrresponding PEC instead of the dissociation energy is given in Table II. The position of the equilibrium internuclear distance is shifted to slightly larger values with increasing field strength, i.e., from $R_{\mathrm{eq}}=2.01$ a.u. in field-free space to 2.15 a.u. for $B=0.5$ a.u. Simultaneously the position of the maximum $R_{\max}$ decreases from 4.35 a.u. in field-free space to 2.76 a.u. for $B=0.5$ a.u. For field strengths $B\gtrsim 1$ a.u. no maxima or minima occur in the PEC of the $^3\Pi_g$ state. However, the PEC possesses two turning points for $B\geqslant 1$ a.u. that can be clearly seen in Fig. 3 for $B=1$ and 2 a.u. The positions of these two turning points are shifted from 2.16 and 2.98 a.u. for $B=1$ a.u. to 0.54 and 0.8 a.u. for $B=100$ a.u. In contrast to the PECs of the $^1\Pi_g$ state, well pronounced turning points exist for arbitrary field strengths in the range $1\lesssim B\lesssim 100$ a.u.

The above considerations indicate that the singlet-triplet energy splitting between the $^1\Pi_g$ state and the $^3\Pi_g$ state for $M_s=0$ depends on the magnetic field strength. To investigate this let us first consider small internuclear distances, i.e., the regime for which the triplet state is lower in energy than the singlet. From Tables I and II we can see that the singlet-triplet energy splitting does not vary strongly for $0\leqslant B\leqslant 0.05$ a.u., which is also confirmed by the equality of the equilibrium internuclear distances $R_{\mathrm{eq1}}(^1\Pi_g)=R_{\mathrm{eq}}(^3\Pi_g)$ for that range of field strengths. The equilibrium internuclear distances R_{eq1} and R_{eq} differ for $B\gtrsim 0.1$ a.u. where R_{eq} is located at smaller internuclear distances. Figures 2(a) and 3 reveal an obvious difference for $B=0.5$ a.u. where a metastable state occurs in the PEC of the $^3\Pi_g$ state which has no counterpart in the corresponding PEC of the $^1\Pi_g$ state. A careful look at Fig. 4 reveals that for $B\lesssim 0.2$ a.u. the singlet-triplet splitting differs not too much from the splitting in field-free space and both PECs are therefore similar. With further increasing field strength the maximum of the energy splitting is shifted to smaller internuclear distances and becomes more and more pronounced. For a broad range of internuclear distances $R_c<R<\infty$ the singlet state is lower in energy than the triplet state and the position of the minimum and turnover in the singlet-triplet splitting decreases monotonously with increasing field strength. The maximum absolute value of the splitting shown in Fig. 4 occurs at a field strength of 20 a.u.

Vibrational bound states for the PECs of the $^3\Pi_g$ state were found to exist for $0\leqslant B\leqslant 0.1$ a.u. As for the PEC of the $^1\Pi_g$ state the number of levels decreases with increasing field strength.

C. The $^1\Pi_u$ state

The PEC of the $^1\Pi_u$ state exhibits a strongly pronounced potential well in field-free space whose minimum is located

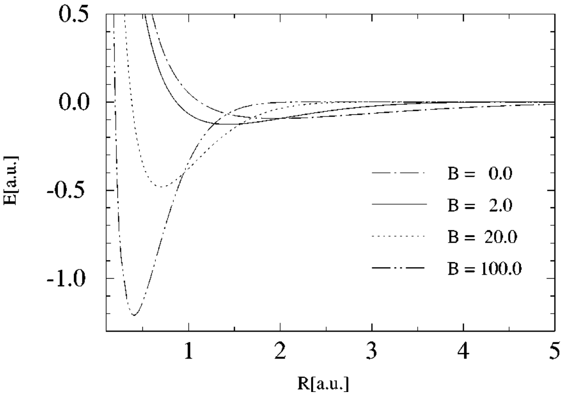

FIG. 5. PECs for $B=0.0$, 2.0, 20.0, and 100.0 a.u. for the lowest $^1\Pi_u$ state. The energy is shown with respect to the dissociation limit, i.e., $E(R)=E_t(R)-\lim_{R\to\infty}E_t(R)$.

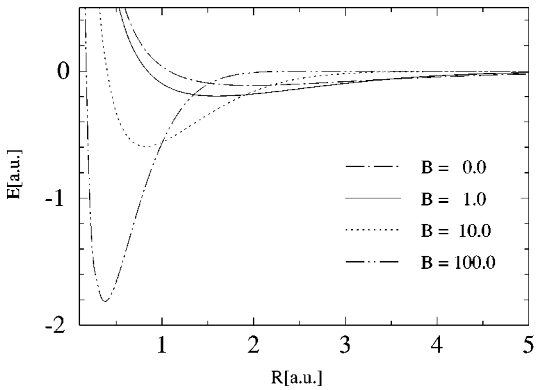

FIG. 6. PECs for $B=0.0$, 1.0, 10.0, and 100.0 a.u. for the lowest $^3\Pi_u$ state. The energy is shown with respect to the dissociation limit, i.e., $E(R)=E_t(R)-\lim_{R\to\infty}E_t(R)$.

at 1.95 a.u., and a maximum for large internuclear distances, i.e. at $R=9.03$ a.u. For the entire range of field strengths $0 \leqslant B \leqslant 100$ a.u. the minimum and maximum persist in the PEC of the $^1\Pi_u$ state. The corresponding data, i.e., total and dissociation energies and equilibrium internuclear distances, are given in Table III and the PEC is illustrated for different field strengths in Fig. 5. With increasing field strength the dissociation energy E_d first decreases slightly for small values of B, i.e., from $E_d=0.093\,220$ a.u. in field-free space to 0.087 080 a.u. for $B=0.5$ a.u. Simultaneously the position of the equilibrium internuclear distance R_{eq} is shifted from 1.95 to 1.80 a.u. However, the dissociation energy increases strongly with further increasing field strength. At the same time the position of R_{eq} is shifted to monotonously decreasing internuclear distances. As an example we mention the PEC of the $^1\Pi_u$ state for $B=100$ a.u. where the dissociation energy amounts to 1.208 626 a.u. and the equilibrium internuclear distance is 0.40 a.u. The PEC of the $^1\Pi_u$ state for $B=100$ a.u. is also shown in Fig. 5. In this figure we particularly observe the strongly increasing dissociation energy for large values of B. For the position of the maximum $R_{\max}$ in the PEC we obtain a monotonous behavior in the range $0 \leqslant B \leqslant 100$ a.u. First, $R_{\max}$ exhibits only a minor decrease from 9.03 to 8.29 a.u. for $B=0$ and 0.1 a.u., respectively. Subsequently the position of $R_{\max}$ decreases more rapidly with further increasing field strength, i.e, in the range $0.1 \leqslant B \leqslant 100$ a.u. where $R_{\max}$ is shifted from 8.29 to 2.43 a.u. Since the height of the maximum is very small, it cannot be observed in Fig. 5.

Many vibrational states exist in the entire range of field strengths $0 \leqslant B \leqslant 100$ a.u. Compared to the number of levels in field free space the number of levels slightly increases with increasing magnetic field strength.

D. The $^3\Pi_u$ state

The PEC of the $^3\Pi_u$ state exhibits a deep potential well in field-free space that is located at an internuclear distance of 1.96 a.u. In the presence of a magnetic field the equilibrium internuclear distance R_{eq} remains approximately constant for $0 \leqslant B \leqslant 0.01$ a.u. At the same time the dissociation energy E_d varies only slightly, i.e., increases from 0.115 522 to 0.112 559 a.u. for $B=0$ and $B=0.01$ a.u., respectively. For larger field strengths we observe a strong increase in the dissociation energy and a simultaneous decrease in the corresponding equilibrium internuclear distance. The corresponding data for the $^3\Pi_u$ state are presented in Table IV and the PEC is shown for different field strengths in Fig. 6. The dissociation energy for $B=100$ a.u. amounts to 1.811 759 a.u. (cf. Table IV) which documents the enormous increase in E_d to be clearly seen also in Fig. 6. An interesting phenomenon can be observed around a field strength of $B=100$ a.u. For that field strength regime the PEC of the $^3\Pi_u$ state exibits a shallow hump with a maximum located at $R_{\max}=3.11$ a.u. and a second minimum at $R_{\mathrm{eq2}}=4.51$ a.u. (see Table IV). However, this additional minimum is very shallow and the dissociation energy amounts to only 4.604×10^{-5} a.u. Therefore, both the second minimum and the maximum cannot be seen in Fig. 6.

In the high field regime, i.e., for field strengths larger than 1×10^{7} T, the $^3\Pi_u$ state has been investigated by Ortiz and co-workers [18] and Lai [17]. The equilibrium internuclear distance R_{eq} for the $^3\Pi_u$ state at a field strength of 1×10^{7} T was determined to be 0.51 a.u. with a total ground-state energy of 163.03 eV at the equilibrium internuclear distance R_{eq} [18]. In the present investigation we performed a calculation for the same field strength 1×10^{7} T (42.544 14 a.u.) and obtained a slightly different equilibrium internuclear distance of 0.50 a.u. with a somewhat lower total energy of 163.54 409 eV. The difference in the total energy at $R=0.50$ and 0.51 a.u. within our calculations amounts to only 3.57×10^{-4} eV. The total energy in the separated atom limit within our calculations was determined to be $-4.798\,851$ a.u. Compared with the best available data in the literature (see Ref. [18]) our result shows an improvement of approximately 0.31% in the total energy and of 1.19% in the corresponding dissociation energy.

The number of vibrational levels for the first well, which is about 20 in field-free space, remains of the same order of magnitude for arbitrary field strengths $0 \leqslant B \leqslant 100$ a.u. For the second minimum occurring at a field strength of 100 a.u., the lower estimate of the vibrational energy is located inside the well while the upper estimate lies above and we therefore cannot decide whether it accommodates a vibrational bound state.

V. THE GROUND STATE OF THE HYDROGEN MOLECULE IN A MAGNETIC FIELD

The ground state of the hydrogen molecule in field-free space is the $^1\Sigma_g^+$ singlet state. In the presence of a magnetic field, the diamagnetic term in the Hamiltonian (1) causes an increase in the total energy with increasing field strength. At the same time, due to the interaction of the total electronic spin with the magnetic field, the spin Zeeman shift occurring for triplet states with $(M_s=-1)$ lowers the total energy. As a result the $^1\Sigma_g$ singlet state is not expected to remain the global ground state of the parallel configuration for sufficiently strong fields. In Ref. [20] the crossing between the PECs of the singlet $^1\Sigma_g$ and triplet $^3\Sigma_u$ state was determined to occur between $B=0.1$ and 0.2 a.u. For $B \gtrsim 0.2$ a.u. the PEC of the $^3\Sigma_u$ state is lower in energy than that of the $^1\Sigma_g$ state and therefore represents the global ground state of the H_2 molecule for a certain range of field strengths (see below). Since the PEC of the $^3\Sigma_u$ state is, apart from a very shallow van der Waals minimum, a purely repulsive curve the hydrogen molecule is unstable (unbound) in the corresponding regime of field strengths. For much higher field strengths $(B \gtrsim 3\times 10^3$ a.u.) it has been shown [18] that the ground state of the parallel configuration is the $^3\Pi_u$ state. The field strength belonging to the $^3\Sigma_u/^3\Pi_u$ crossing is, however, not yet known.

In the following we determine and discuss the crossings among the above-mentioned three states as a function of the field strength. In Figs. 7(a) and 7(b) we show the total energies at the corresponding equilibrium internuclear distances of the $^1\Sigma_g$ and $^3\Pi_u$ states as well as the total energy in the dissociation limit of the $^3\Sigma_u$ state as a function of the field strength. First we focus on the crossings of the $^1\Sigma_g$ with the $^3\Sigma_u$ and $^3\Pi_u$ states, which is illustrated in Fig. 7(a). The transition between the $^1\Sigma_g$ and $^3\Sigma_u$ state occurs at a field strength of approximately 0.18 a.u. and the crossing field strength between the $^3\Sigma_u$ and $^3\Pi_u$ state is determined to be at $B\approx 0.39$ a.u. With further increasing magnetic field strength the total energy of the $^1\Sigma_g$ state increases strongly and in particular the total energy of the $^3\Pi_u$ state decreases more rapidly than that of the $^3\Sigma_u$ state. Therefore, a transition occurs between the two latter states, which is illustrated in Fig. 7(b). As can be seen from Fig. 7(b), the transition field strength occurs at $B\approx 12.3$ a.u.

In conclusion we encounter the following situation for the H_2 molecule oriented parallel to a magnetic field: For $B \lesssim 0.18$ a.u. the ground state is the strongly bound $^1\Sigma_g$ state. For an intermediate range of field strengths, i.e., for $0.18 \lesssim B \lesssim 12.3$ a.u., the ground state is the unbound $^3\Sigma_u$ state. This state exhibits only a very shallow minimum, which does not provide any vibrational level [20]. Therefore the ground state of the parallel configuration is not bound in the regime $0.18 \lesssim B \lesssim 12.3$ a.u. This result is of great importance for astrophysics in order to decide whether hydrogen molecules exist in the vicinity of white dwarfs. For magnetic fields $B \gtrsim 12.3$ a.u. the ground state is again strongly bound, namely, the $^3\Pi_u$ state and molecular hydrogen may exist in the vicinity of astrophysical objects, which exhibit such huge magnetic field strengths.

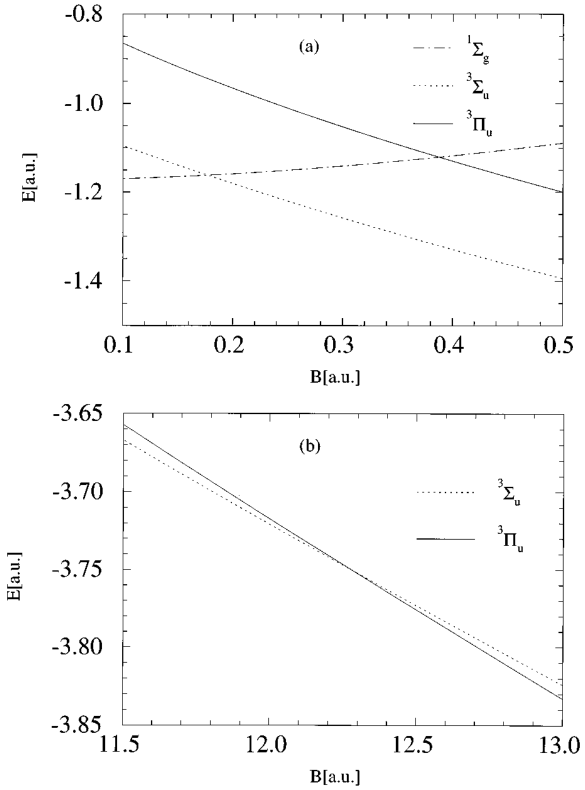

FIG. 7. (a) Transitions between the lowest $^1\Sigma_g$ and the $^3\Sigma_u$ and $^3\Pi_u$ states showing the total energy of the $^1\Sigma_g$ and $^3\Pi_u$ states (bound) at the corresponding equilibrium internuclear distance and the total energy in the dissociation limit of the $^3\Sigma_u$ state (unbound). (b) Transition between the lowest $^3\Sigma_u$ and $^3\Pi_u$ state showing the total energy in the dissociation limit of the $^3\Sigma_u$ state (unbound) and the total energy at the corresponding equilibrium internuclear distance of the $^3\Pi_u$ state (bound).

VI. SUMMARY AND CONCLUSIONS

In the present investigation we studied the electronic structure of the hydrogen molecule subjected to an external magnetic field, which is oriented parallel to the internuclear axis. We hereby focused on the lowest electronic states of the Π subspace, i.e., the lowest states with molecular magnetic quantum number equal to one. We discussed our basis set of nonorthogonal nonspherical Gaussian orbitals and briefly described the theoretical aspects of our CI calculations.

First of all we discussed the general properties of the lowest Π states in field-free space and compared our results with the existing data in the literature. Our results show an overall relative accuracy better than $\lesssim 10^{-4}$ at the equilibrium internuclear distances of the PECs and even further improves with increasing internuclear distance. Compared to the results obtained for the lowest Σ states in field-free space [20], we approximately improved the accuracy in the energy by one order of magnitude. This is most probably due to the smaller portion of correlation energy for the Π states.

Next we considered the lowest Π states in the presence of a magnetic field. For the $^1\Pi_g$ state we observed a monotonous decrease in the dissociation energy with increasing field strength up to 0.1 a.u. and a simultaneous minor increase in the equilibrium internuclear distance. At the same time the position of the occurring maximum was shifted to smaller values of the internuclear distance. For a field strength of 0.2 a.u. a metastable state with respect to the dissociation into two hydrogen atoms exists in the PEC and for $B \gtrsim 0.5$ a.u. both the minimum and the maximum disappear. For the second, i.e., outer, minimum the dissociation energy first increases up to $B \lesssim 1$ a.u. and then decreases with further increasing field strength. In order to decide whether vibrationally bound states exist in the discussed PECs we determined upper and lower estimates for the vibrational energies. Up to a field strength of 0.1 a.u. the $^1\Pi_g$ state was shown to accommodate a few vibrational levels. For the second well vibrationally bound states exist in the range $0 \leqslant B \lesssim 2$ a.u. For $5 \lesssim B \lesssim 50$ a.u. the existence of bound states depends on the detailed nuclear dynamics of the molecule. For even larger field strengths no vibrational levels were found.

For the PEC of the $^3\Pi_g$ state we observe a decrease in the dissociation energy and a simultaneous increase in the equilibrium internuclear distance with increasing field strength in the regime $0 \leqslant B \lesssim 0.1$ a.u. Metastable states with respect to the dissociation into two H atoms were shown to exist for the range $0.2 \lesssim B \lesssim 0.5$ a.u. For the position of the maximum in the PEC we observed a monotonous decrease with increasing field strength. For $B \gtrsim 1$ a.u. the maximum and the minimum disappear. We also studied the singlet-triplet energy splitting between the $^1\Pi_g$ and $^3\Pi_g$ $(M_s=0)$ state as a function of the magnetic field strength. This is motivated by the fact that the corresponding PECs in field-free space are almost indistinguishable for sufficiently small internuclear distances. We hereby focused on the rough shape of the PECs and neglected the properties due to the very shallow second minimum occurring in the PEC of the $^1\Pi_g$ state. In the presence of a magnetic field and with increasing field strength we found an increase of the splitting between these two states for small internuclear distances, i.e., for the region where the corresponding PECs are almost identical in field-free space. For larger internuclear distances we found a significant difference between the PECs of the $^1\Pi_g$ and $^3\Pi_g$ $(M_s=0)$ state for $1 \lesssim B \lesssim 20$ a.u. For this regime of field strengths the PEC of the $^3\Pi_g$ state exhibits no extrema but two turning points that do not exist in the corresponding PEC of the $^1\Pi_g$ state. The maximum of the absolute value of the splitting was found to occur at a field strength of approximately 20 a.u. Vibrationally bound states were shown to exist up to $B = 0.1$ a.u.

For the PEC of the $^1\Pi_u$ state we first observe a decrease in the dissociation energy up to a field strength of $B \approx 0.5$ a.u. with increasing field strength and subsequently a strong increase in the dissociation energy with further increasing field strength. At the same time the equilibrium internuclear distance decreases monotonously. For the number of vibrational levels we found a minor increase by a few levels compared to the number of levels in field-free space.

Next we studied the PEC of the $^3\Pi_u$ state in the presence of a magnetic field. The dissociation energy and the equilibrium internuclear distance remain nearly constant for small values of B, i.e., for $0 \leqslant B \lesssim 0.1$ a.u. With further increasing field strength we observe a strong increase in the dissociation energy. An interesting phenomenon is the existence of an additional minimum and a maximum for a field strength regime around 100 a.u. Despite the shallowness of the corresponding well it may accommodate a vibrationally bound state. For the first, i.e., well-pronounced, well vibrational states exist for all field strengths $0 \leqslant B \leqslant 100$ a.u.

Finally we investigated the important transitions occurring among the $^1\Sigma_g$, $^3\Sigma_u$, and $^3\Pi_u$ states. It was shown recently [20] that the strongly bound $^1\Sigma_g$ state is the global ground state of the hydrogen molecule for $B \lesssim 0.18$ a.u. and that the global ground state beyond 0.18 a.u. is the unbound $^3\Sigma_u$ state up to some unknown critical field strength B_c. The $^3\Sigma_u$ state exhibits a purely repulsive PEC apart from a shallow van der Waal minimum, which does not provide any vibrational level. An important result of the present investigation is that at approximately 12.3 a.u. the ground state changes from the $^3\Sigma_u$ state to the strongly bound $^3\Pi_u$ state. This is of great importance for the chemistry in the atmosphere of certain degenerate astrophysical objects: it may help to decide whether molecular hydrogen can exist in the vicinity of white dwarfs. We emphasize that the present investigation was performed for the case of parallel internuclear and magnetic field axes. Due to the θ independence of the spin Zeeman shift, which is relevant in this context, and relying on our experience with $H_2{}^+$ we assume that the ordering of the lowest states is retained also for $\theta \neq 0$. However, in order to draw a definite conclusion concerning the ground state of the H_2 molecule the electronic structure has to be investigated for arbitrary angles between the molecule and the magnetic field.

The above results may also give rise to an experimental scenario. Let us consider configurations with an angle in the range $0 < \theta < 90°$, i.e., the internuclear axis is inclined with respect to the magnetic field. Since the electronic potential energy depends on both the internuclear distance R as well as the angle θ we are dealing with two-dimensional potential energy surfaces. The only remaining symmetry for such configurations for a homonuclear diatomic molecule is the parity, i.e., the corresponding molecular symmetry group is C_i. We now briefly address the question of whether different electronic states may interact strongly through the nuclear motion. This problem was investigated in some detail in Ref. [21]. It was shown that for a homonuclear diatomic molecule a two-dimensional avoided crossing occurs for electronic states with the same spatial symmetry and in particular that *conical intersections* can occur at $\theta=0$ or 90° for crossings of states with the same parity.

For $\theta \neq 0°$ we expect a crossing without interaction between the lowest state with gerade and the lowest state with ungerade parity. More interestingly we expect a conical intersection to occur at $\theta=0°$ for the PECs of the two lowest states ($^3\Pi_u - {}^3\Sigma_u$) with ungerade parity. The hydrogen molecule in the presence of a magnetic field therefore is an ex ample of a simple system for which the *ground state* in strong fields exhibits a *conical intersection*.

Note added in proof: For completeness of references we point out that recently a communication has been published which reports on HF calculations of the hydrogen molecule in strong magnetic fields [Y. Kravchenko and M. Libermann, Phys. Rev. A **56**, R2510 (1997)].

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