

Influence of a strong magnetic field on the chemical bond of the excited H_2^+ ion

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The excited electronic states with the magnetic quantum numbers $4 \leq |m| \leq 10$ of the hydrogen molecular ion are investigated. In the field-free case the lowest electronic states with $|m| \geq 5$ possess purely repulsive potential-energy curves and are, therefore, unbound. In the presence of a strong magnetic field the shape of these electronic states changes drastically. For parallel internuclear and magnetic-field axes we observe well-pronounced potential wells that contain many vibrational states; the corresponding electronic states are, therefore, strongly bound. The coupling of the electronic degrees of freedom to the ionic center-of-mass motion is estimated.

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I. INTRODUCTION

One of the initial motivations for studying atomic and molecular systems in strong magnetic fields was the discovery of the huge magnetic-field strengths in the vicinity of degenerate astrophysical objects, e.g., field strengths of the order of magnitude of 10^2 – 10^4 T for white dwarfs, and 10^7 – 10^9 T for pulsars [1]. Most of the investigations have been made on the behavior of the hydrogen atom in a strong homogeneous magnetic field. Its spectrum and eigenfunctions have been calculated with different methods over the whole range of magnetic-field strengths. Nowadays the ground state as well as a large number of excited states of the hydrogen atom in such strong fields are known to a high accuracy (see Refs. [2] and [3] and references therein).

In contrast to the numerous investigations on the hydrogen atom, there exists much less information on the behavior and properties of many-electron atoms and molecules in strong magnetic fields. In particular, our knowledge about molecules is, in general, restricted to the simplest of all molecular systems, the H_2^+ ion (see Ref. [4] and references therein). The few works dealing with many-electron molecules are of qualitative character (see Refs. [5–10] for an almost complete list of references). Nevertheless, the existing literature on molecules in strong magnetic fields indicates a variety of phenomena. Examples are the contraction of the bond length and the increase of the dissociation energy with increasing magnetic-field strength as well as the new topology of the electronic potential-energy surface and the rich complexity of the corresponding nuclear dynamics. With increasing excitation of the molecular electronic states and/or increasing field strength the effects of the influence of the external field on the chemical bond, e.g., the bond length and dissociation energy, could become very drastic. As an example, let us compare the $3d\delta_g$ state of the H_2^+ ion in the absence of a magnetic field with the corresponding $1\delta_g$ state of the H_2^+ ion for a field strength of $B = 1.0$

a.u.; (which corresponds to 2.35×10^5 T). For the $3d\delta_g$ state a bond length of 18 a.u. and a dissociation energy of 1.6×10^{-3} a.u. was found [11]. In the presence of a field with the above-mentioned strength, we obtain for the corresponding $1\delta_g$ state a bond length of 4.87 a.u. and a dissociation energy of roughly 3.6×10^{-2} a.u. [4,13]. This example and the existing results on the electronic potential-energy surfaces for low-lying states of the H_2^+ ion in a strong magnetic field [4] indicate that there may exist excited states which are unbound in the absence of a magnetic field and which become strongly bound in the presence of a magnetic field. To give an answer to this, up to now, open question is exactly the subject of the present paper.

Our investigation deals with the H_2^+ ion for parallel orientation of the internuclear axis with respect to the magnetic-field axis. We consider the lowest electronic states of the H_2^+ ion with the magnetic quantum numbers $-4 \leq m \leq -10$. As a main result of our investigation we have found strongly bound states of the H_2^+ ion in the presence of a magnetic field whose corresponding counterparts in the absence of a magnetic field show a purely repulsive behavior of the potential-energy curves, i.e., they are unbound.

The paper is organized as follows. In Sec. II we describe the method for the calculation of the molecular wave functions and electronic potential-energy surfaces. In particular, we give a brief introduction to our atomic orbital basis set which has recently been introduced [12] and optimized [13]. In Sec. III we present and discuss the results of our investigation. The influence of the strong external magnetic field on the properties of the chemical bond is discussed in detail.

II. *Ab Initio* METHOD FOR THE CALCULATION OF THE POTENTIAL-ENERGY SURFACES

The existing numerical investigations on molecules in strong magnetic fields (see Refs. [4–10] and references

therein) are based on special choices of variational electronic wave functions which take into account the strong anisotropy due to the presence of an external magnetic field. The underlying methods are, in particular, restricted to the one-electron problem, i.e., the H_2^+ ion. In addition, they are valid only within a certain range of magnetic-field strengths, i.e., they are restricted either to the low, to the intermediate, or to the high-field region. In view of the lack of a general method for calculation of molecular properties in a magnetic field, a basis set of atomic orbitals has been established in Ref. [12]. These atomic orbitals are well suited to describe molecular electronic wave functions and spectra at arbitrary magnetic-field strengths, and for an arbitrary orientation of the molecule with respect to the magnetic field. In order to use this basis set for *ab initio* calculations of molecular electronic wave functions and potential energy surfaces the nonlinear variational parameters of these atomic orbitals have to be optimized. This has been done recently for the case of the hydrogen atom [13]. Since we take advantage of the optimized basis set for our investigation of the binding properties of the H_2^+ ion in a strong homogeneous magnetic field, we give in the first part of this section a brief introduction to these atomic orbital basis functions. Finally, in the remaining part we describe the method used for calculating the molecular electronic energy curves of the H_2^+ ion.

Our basis set of atomic orbitals [12] takes on the following appearance:

$$\Psi_n(\mathbf{r}, \underline{\alpha}, \mathbf{R}) = \exp\{-i \mathbf{A}(\mathbf{R}) \cdot \mathbf{r}\} (\mathbf{x} - \mathbf{R}_x)^{n_x} (\mathbf{y} - \mathbf{R}_y)^{n_y} \times (\mathbf{z} - \mathbf{R}_z)^{n_z} \exp\{-(\mathbf{r} - \mathbf{R})^T \cdot \underline{\alpha} \cdot (\mathbf{r} - \mathbf{R})\}, \quad (1)$$

where $\mathbf{R}^T = (R_x, R_y, R_z)$ is the nuclear position vector and the triad $\mathbf{n} = (n_x, n_y, n_z)$ characterizes the type of atomic orbital. The basis set of atomic orbitals (1) contains two exponentials: the first one represents a magnetic field-dependent phase $\exp\{-i \mathbf{A}(\mathbf{R}) \cdot \mathbf{r}\}$ and the second one represents a Gaussian-like function with a real symmetric matrix $\underline{\alpha}$ of nonlinear variational parameters.

The phase $\exp\{-i \mathbf{A}(\mathbf{R}) \cdot \mathbf{r}\}$ ensures that the energy eigenvalues calculated with the basis functions (1) are approximately gauge invariant. It shifts the origin of the gauge of the vector potential \mathbf{A} , which we choose to be in the symmetric gauge $\mathbf{A}(\mathbf{R}) = \frac{1}{2}[\mathbf{B} \times \mathbf{R}]$, to the position of the individual nucleus. We note that this is of particular importance for the dissociation limit of the molecular system into separated atoms (see Refs. [12] and [14] and references therein).

In the present investigation, we consider the H_2^+ ion for the special case of parallel internuclear and magnetic-field axes $\mathbf{B} \parallel \mathbf{R}$. In this case, the vector potential dependent phase becomes one, and our atomic orbital basis set (1) differs from the spherical Gaussian one by the general quadratic form in the exponent. For the spherical Gaussian basis set we have $\underline{\alpha} = \alpha \mathbf{1}$ and, therefore, only one variational parameter α corresponding to the spherical symmetry. In the presence of a magnetic field the exponent of the spherical Gaussian basis set pro-

vides an insufficient description of the electronic wave function. This fact can be easily illustrated for the example of the hydrogen atom in a homogeneous magnetic field. The magnetic-field axis is assumed to point along the z axis. In the limit $|\mathbf{B}| \rightarrow \infty$, we obtain in the plane perpendicular to the field axis a pure two-dimensional harmonic-oscillator wave function. The motion parallel to the field axis is described by a one-dimensional Coulomb wave function. These properties cannot approximately be reproduced by a basis function with only one variational parameter in the exponent. In contrast to the spherical Gaussian basis functions the exponent of our basis set (1) contains a real symmetric matrix $\underline{\alpha}$ of six independent variational parameters, i.e., the exponent of the atomic orbitals (1) is able to describe any anisotropy and, in particular, the anisotropy due to the presence of a magnetic field. However, if we want to obtain accurate electronic wave functions for molecules in a strong magnetic field with a few of the above basis functions (1) we have to optimize the nonlinear variational parameters $\{\alpha_{ij}\}$ of the matrix $\underline{\alpha}$. This can be performed by minimizing the total calculated energy of the individual atomic states with respect to these parameters. For the hydrogen atom the results of this optimization have been presented in Ref. [13] for the ground state as well as for many excited states, and for a range of magnetic field strengths from 10^{-3} a.u. up to 10^2 a.u.

Since we want to study the electronic structure of the H_2^+ ion, we separate the electronic and nuclear motion by an adiabatic approximation, i.e., we perform the Born-Oppenheimer approximation in the presence of a magnetic field. The performance of an adiabatic approximation in the presence of a magnetic field has been investigated in detail in Refs. [14] including all corrections due to the finite nuclear mass. For the present investigation, we choose as a zeroth-order approach for the electronic Hamiltonian the fixed nuclei electronic Hamiltonian, i.e., we assume infinitely heavy nuclei. This choice will be justified in Sec. III (see also Ref. [17]).

In order to specify the fixed-nuclei electronic Hamiltonian let us locate the two protons on the z axis and choose the midpoint of the internuclear axis as the coordinate origin. Since we consider the case of parallel magnetic field and internuclear axes the magnetic-field vector also points along the z axis. The electronic Hamiltonian, therefore, takes on the following appearance

$$H = -\frac{1}{2}\nabla^2 + \frac{1}{2}BL_z + \frac{1}{8}B^2(x^2 + y^2) - \frac{1}{|\mathbf{r} - \mathbf{R}/2|} - \frac{1}{|\mathbf{r} + \mathbf{R}/2|}, \quad (2)$$

where $\mathbf{r} = (x, y, z)^T$ and \mathbf{R} is the internuclear vector.

The Hamiltonian (2) possesses the following symmetries due to the charge symmetry (both nuclei have the same charge number $Z_1 = Z_2 = 1$) the parity operator P commutes with the Hamiltonian (2). This symmetry is conserved even for an arbitrary orientation of the internuclear axis with respect to the magnetic-field axis. Also, the angular-momentum component L_z provides a good quantum number m in the case of parallel orientation. Therefore both quantum numbers, P and m , will be used

to characterize the eigenfunctions and the corresponding eigenvalues $\varepsilon(R)$ of the Hamiltonian (2). The eigenfunctions will be labeled 1γ (γ for $m=-4$), 1η (η for $m=-5$), 1ι (ι for $m=-6$), etc. with an additional subscript g or u (corresponding to "gerade" and "ungerade") to indicate the parity of the orbitals. In the absence of a magnetic field we will use the usual united-atom notation $5g\gamma_g, 6h\gamma_u, 6h\eta_u, 7h\eta_g, \dots$, to label the field-free orbitals [11,15].

In order to solve the electronic Schrödinger equation with the Hamiltonian (2), we expand the wave functions in terms of nonorthogonal molecular orbitals. These molecular orbitals are built up by the corresponding optimized atomic orbitals (1). The resulting Hamiltonian and overlap matrix elements have been evaluated in Ref. [12]. For the numerical solution of the resulting general eigenvalue, we used standard methods. The construction of the molecular orbital basis set as well as the method for building the Hamiltonian and overlap matrix will be described in detail elsewhere [17].

III. RESULTS AND DISCUSSION

In order to investigate the influence of a strong magnetic field on the properties of the chemical bond of the H_2^+ ion we compare the electronic potential-energy curves of the magnetically dressed states with their corresponding counterparts in the field-free case. We, thereby, have to ensure that the magnetically dressed molecular states can be related to the corresponding field-free molecular states in a unique way. For the case of the H_2^+ ion in a homogeneous magnetic field with parallel internuclear and magnetic field axes, only the lowest state of a given manifold m^P can be associated with the likewise lowest state with the same magnetic quantum number m and parity P in the field-free case. For example, the magnetically dressed states of the H_2^+ ion $1\sigma_g, 1\pi_u, 1\delta_g, \dots$, evolve from the $1s\sigma_g, 2p\pi_u, 3d\delta_g, \dots$, field-free states in a definite way [13]. For excited states of a given subspace m^P such a one to one correlation between the magnetically dressed molecular states and the states in the field-free case does not exist. The reason for this fact is the breakdown of the noncrossing rule for the case of the H_2^+ ion in the absence of a magnetic field (see Ref. [16] for a detailed discussion of this subject). If we switch on a magnetic field the noncrossing rule is valid and we are, therefore, not able to relate an excited magnetically dressed molecular state of a given subspace m^P to only one molecular state in the field-free case.

The magnetically dressed lowest states of the manifolds m^P are also interesting from another point of view. With increasing magnetic quantum number m , i.e., increasing size of the "electronic cloud" perpendicular to the magnetic field, the influence of the diamagnetic energy term becomes stronger and the diamagnetism is, therefore, expected to play an increasingly important role for the formation of a chemical bond.

After having briefly discussed the relation between the magnetically dressed states of the H_2^+ ion and their corresponding counterparts in the field-free case we begin

now our study of the lowest states of the manifolds m^P both in the absence and presence of a magnetic field. Let us first consider the properties of the lowest so-called "bonding" states with the quantum numbers $m=0$ to -10 in the absence of a magnetic field, i.e., $1s\sigma_g, 2p\pi_u, \dots, 5g\gamma_g, 5h\eta_u, \dots, 11m\mu_g$. All electronic potential-energy curves of the above-mentioned states with the magnetic quantum numbers $|m| \leq 4$ exhibit a potential well. In addition, these states, with the exception of the $1s\sigma_g$ state, possess also a hump, i.e., a local potential-energy maximum, whose value lies above the energy in the dissociation limit. The dissociation energy ε_D , given by the difference between the local maximum and the equilibrium energy, decreases rapidly with increasing absolute value of the magnetic quantum number whereas the equilibrium distance increases, e.g., for the $2p\pi_u$ state ($|m|=1$) a equilibrium distance of $R_{eq}=8$ a.u. and a dissociation energy of $\varepsilon_D \approx 9 \times 10^{-3}$ a.u. was found, whereas the equilibrium distance R_{eq} and the dissociation energy ε_D of the $5g\gamma_g$ state ($|m|=4$) are roughly 53 a.u. and 2.28×10^{-5} a.u., respectively. The lowest electronic eigenstates and eigenenergies with the magnetic quantum numbers $0 \leq |m| \leq 4$ have been calculated in Ref. [11]. Representatively for these states we have plotted the potential-energy curve of the $5g\gamma_g$ state in Fig. 1(a) (straight line). In contrast to the states with $0 \leq |m| \leq 4$ which exhibit potential wells in their potential-energy curves our calculation shows that the potential-energy curves of the $6h\eta_u, \dots, 11m\mu_g$ states with $5 \leq |m| \leq 10$ exhibit a purely repulsive behavior. As a typical example for these states we have plotted in Fig. 1(a) the potential-energy curve of the $6h\eta_u$ state (dashed line). The absence of an attractive part in the potential-energy curve of the states with magnetic quantum numbers $5 \leq |m| \leq 10$ simply means that they are unstable with respect to the dissociation $H_2^+ \rightarrow H + p$.

Let us now consider how the shapes of the potential-energy curves of the above-mentioned states change if we switch on a strong homogeneous magnetic field. As a typical value of the field strength we choose $B=1.0$ a.u. which corresponds to the intermediate or high-field regime, depending on the degree of excitation. Without loss of generality we restrict our discussion in the case of the presence of a magnetic field to the $1\gamma_g$ state and $1\eta_u$ state which are the corresponding counterparts of the above-discussed $5g\gamma_g$ and $6h\eta_u$ state in the absence of a magnetic field. In Fig. 1(b) we have plotted the potential-energy curves of the $1\gamma_g$ state (straight line) and of the $1\eta_u$ state (dashed line). First of all, we observe that the energy curves of both states, the $1\gamma_g$ state as well as the $1\eta_u$ state, exhibit an attractive behavior with a well-pronounced potential well. Also the hump, which is still present in the energy curve of the $5g\gamma_g$ state in the absence of a magnetic field, vanished in the potential-energy curve of the corresponding $1\gamma_g$ state in the presence of a magnetic field. The bond length of the $1\gamma_g$ state ($R_{eq}=6.55$) is in comparison with that of the $5g\gamma_g$ state ($R_{eq}=53$) strongly contracted. We also obtain an increase of the dissociation energy from $\varepsilon_D=2.28 \times 10^{-5}$ a.u. for the $5g\gamma_g$ state in the field-free case to 2.38×10^{-2}

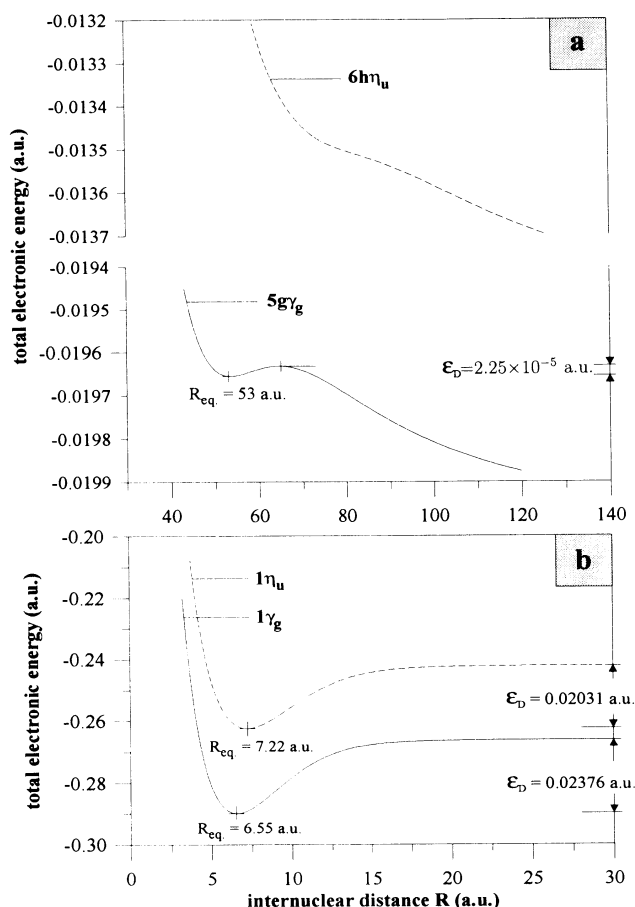


FIG. 1. (a) The total electronic energy curves of the lowest states with the magnetic quantum numbers $|m|=4$ ($5g\gamma_g$) and $|m|=5$ ($6h\eta_u$) in the absence of a magnetic field. (b) The total electronic energy curves of the corresponding magnetically dressed states ($1\gamma_g$ and $1\eta_u$) for a magnetic-field strength of $B = 1.0$ a.u.

a.u. for the $1\gamma_g$ state in the presence of the magnetic field. It is a remarkable fact that the potential-energy curve of the $1\eta_u$ -state exhibits a well-pronounced potential well. Remember, the corresponding counterpart of the $1\eta_u$ state in the field-free case, the $6h\eta_u$ state, has a purely repulsive potential-energy curve. In the presence of a magnetic field ($B = 1.0$ a.u.) the potential well of the $1\eta_u$ state has a depth of 2.03×10^{-2} a.u. at the equilibrium distance $R_{eq} = 7.22$ a.u. Hence, the binding energy and the equilibrium distance of the $1\eta_u$ state are of the same order of magnitude as the corresponding quantities of the $1\gamma_g$ state.

In order to understand the drastic change of the shape of the potential-energy curve for the η_u state from the field-free case to the case of the presence of a magnetic field let us consider the electronic probability density of this state in both cases. In Fig. 2(a) and 2(b) we have plotted the probability density $|\Psi(x, y=0, z)|^2$ in the x - z plane for the $6h\eta_u$ state in the absence a magnetic field, and for the $1\eta_u$ state in the presence of the magnetic

field, respectively. Due to the polynomial structure $(x - iy)^m$ of the orbitals (1) used to build up the molecular electronic wave function of the lowest η_u state, the probability density distributions in Figs. 2(a) and 2(b) possess a node line along the z axis. For the considered states the probability distribution $|\Psi(x, y, z)|^2$ have a rotational symmetry around the z axis.

Let us again first consider the situation in the field-free case. In Fig. 2(a) the electronic probability density distribution of the $6h\eta_u$ state is presented for an internuclear distance of $R = 80.0$ a.u. This distance corresponds roughly to the midpoint of the "shoulder" of the potential energy curve of the $6h\eta_u$ state. The maxima values of the electronic probability density occur roughly for the z values $\pm R/2$, which correspond to the z components of the positions of the nuclei. The absolute values of the maxima are about 3×10^{-6} and are located at a distance of roughly 30 a.u. from the z axis. The saddle point of the density, which has a value of approximately 7×10^{-7} , occurs at $z = 0$ a.u. and has a distance of roughly 40 a.u. from the molecular axis. In comparison with the probability density of, for example, the strongly bound $2p\pi_u$ state at its equilibrium distance, the obtained values of the probability density distribution of the $6h\eta_u$ state are very low: the values of the maxima of the probability density of the $2p\pi_u$ state are about 1.4×10^{-3} and their distance to the molecular axis is roughly 2 a.u. The value of the density distribution of the $2p\pi_u$ state at the saddle point, which is about 2.7 a.u. from the internuclear axis, is of the order of magnitude of 10^{-3} . The purely repulsive behavior of the electronic potential curves for the lowest state with $|m|=5$ in the field-free case has its origin in the low and widely distributed electronic probability density which is particularly small close to the internuclear axis between the two nuclei and, therefore, does not enable the formation of a chemical bond.

In the presence of a magnetic field the structure of the probability distribution of the $1\eta_u$ state, illustrated in Fig. 2(b) for the equilibrium internuclear distance $R_{eq} = 7.22$ a.u., is completely different from that of the $6h\eta_u$ state in the field-free case. The maximal values of the electronic probability density distribution occur close to the internuclear axis at approximately $x = \pm 3$ a.u. and within the accuracy of our numerical calculations for the whole range $-1.0 \leq z \leq 1.0$ a.u. of the z coordinate which lies in between the positions $z = \pm R_{eq}/2$ of the two nuclei. Apart from the decrease of the overall size of the molecule and the increase of the absolute values of the probability density we also observe that the density is in the direction perpendicular to the magnetic field very much peaked around its maxima values. The enhanced probability of finding the electron in the region close to the internuclear axis and for z values between both nuclei leads to a more complete screening of the nuclear charges and consequently to an overcompensation of the nucleus-nucleus Coulomb repulsion by the electronic cloud. As a consequence, the potential energy curve of the $1\eta_u$ state exhibits a potential-energy well.

So far we have discussed the influence of a strong magnetic field on the ground states of (m^P) manifolds only

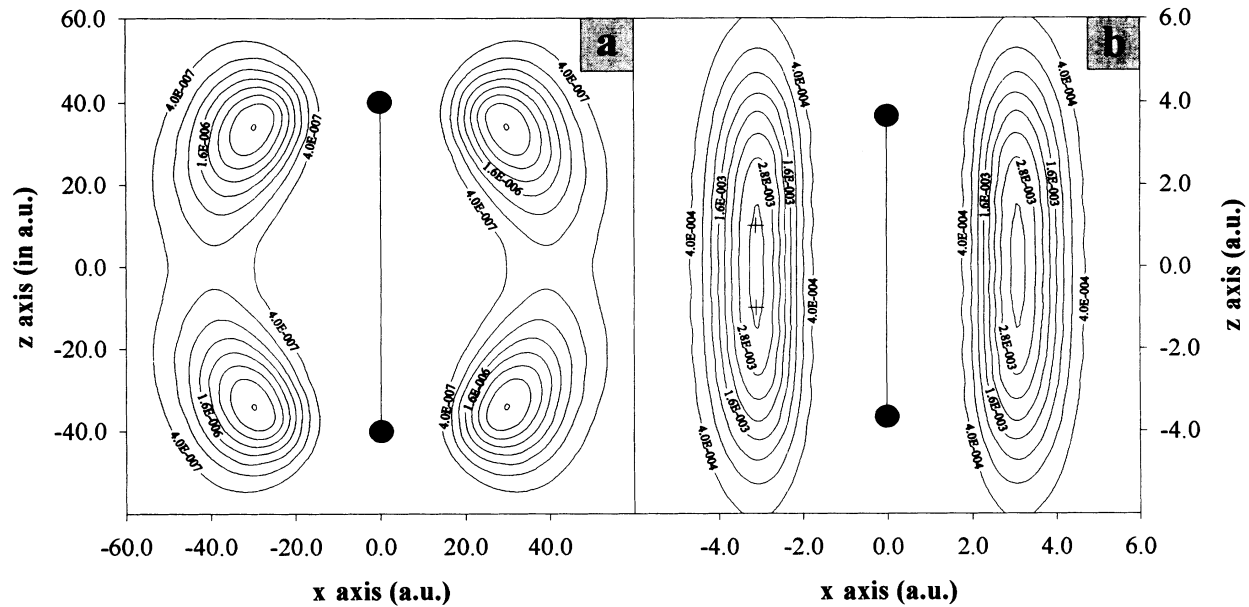


FIG. 2. (a) The electronic probability density distribution of the $6h\eta_u$ state in the absence of a magnetic field and for an internuclear distance of 80 a.u. The difference in density between neighboring contour lines is 4×10^{-7} . (b) The electronic probability density distribution of the corresponding magnetically dressed $1\eta_0$ state for the equilibrium internuclear distance $R_{eq} = 7.22$ a.u. In the left half-plane the positions of the maxima of the density distribution are marked with crosses. The difference in density between neighboring contour lines is 4×10^{-4} . The notation 4.0E-007 denotes 4.0×10^{-7} , etc.

for the special example of the lowest η_u state ($m = -5$). However, the properties of the potential-energy curves and the electronic probability density distributions for the $1\epsilon_g(m = -6)$, \dots , $1\mu_g(m = -10)$ states in the presence of a magnetic field are analogous to that of the discussed $1\eta_u$ state. The above results of the properties of the $1\eta_u$ state are, therefore, representative for all magnetically dressed ground states (for a complete list of the equilibrium distances and dissociation energies see Table I).

The existence of a potential well in the adiabatic electronic potential-energy curve is a necessary but not sufficient condition for the formation of a stable molecular state. In addition, we have to show that vibrational states do exist in the potential wells of the considered magnetically dressed $1\gamma_g, \dots, 1\mu_g$ states. We approxi-

mate the electronic potential well by a harmonic potential and estimate the ground-state energy of the nuclear motion in this harmonic potential well under the influence of the external magnetic field. In a rough approximation the energy of the vibrational ground state for the H_2^+ ion is then given by the sum of the ground-state energy in the harmonic potential and the corresponding zero-point cyclotron energy. The zero-point cyclotron energy is for $B = 1.0$ a.u. approximately 3×10^{-4} a.u. For the considered electronic states $1\gamma_g, \dots, 1\mu_g$ we obtain harmonic vibrational ground-state energies of the order of magnitude of 10^{-3} a.u. The estimated vibrational ground-state energies for the nuclear motion in each of the electronic potential curves of the $1\gamma_g, \dots, 1\mu_g$ states is, therefore, much smaller than the depth of the corresponding potential wells. Therefore,

TABLE I. The equilibrium internuclear distances R_{eq} and the dissociation energies ϵ_D of the bonding γ, η, \dots, μ states ($m = -4, \dots, -10$) of the hydrogen molecular ion in the absence of a magnetic field as well as in the presence of a magnetic field with $B = 1.0$ a.u. and $\theta = 0^\circ$. Energies as well as internuclear distances are given in atomic units. In the field-free case ($B = 0$) the electronic states with $|m| \geq 5$ are unbound.

Magnetic-field strength B (a.u.)	State	Magnetic quantum number m	R_{eq} (a.u.)	ϵ_D (a.u.)
0.0	$5g\gamma_g$	-4	53.0	2.278×10^{-5}
1.0	$1\gamma_g$	-4	6.55	2.376×10^{-2}
	$1\eta_u$	-5	7.22	2.031×10^{-2}
	$1\epsilon_g$	-6	7.82	1.800×10^{-2}
	$1\varphi_u$	-7	8.35	1.611×10^{-2}
	$1\kappa_g$	-8	8.86	1.480×10^{-2}
	$1\lambda_u$	-9	9.35	1.362×10^{-2}
	$1\mu_g$	-10	9.80	1.266×10^{-2}

many vibrational states can exist in the wells of the potential-energy curves for the $1\gamma_g, \dots, 1\mu_g$ states, i.e., these states are stable.

In the above investigation of the excited electronic states of the H_2^+ ion in a strong magnetic field we have restricted ourselves to the configuration of parallel internuclear and magnetic field axis. The electronic potential energy, however, is a two-dimensional surface which depends on both the internuclear distance as well as the angle Θ between the internuclear and magnetic field axis. It has been shown in Ref. [18] that the potential-energy curves exhibit extrema at the two positions which are distinct by their higher symmetry, i.e., the parallel ($\Theta=0$) and orthogonal ($\Theta=\pi/2$) configuration. For the case that vibronic interaction between different electronic energy levels is negligible it can be shown [18] by considering the second derivative of the diabatic/adiabatic energy surfaces with respect to the angle Θ that for negative magnetic quantum numbers and a "not too large" extension of the electronic probability density perpendicular to the magnetic field, the parallel configuration ($\Theta=0$) represents a minimum of the electronic energy. By estimating the second derivative ($\partial^2 E / \partial \Theta^2$) we could show that our considered lowest electronic states of the (m^P) manifolds exhibit a minimum of the electronic energy at $\Theta=0$. Apart from effects due to the vibronic coupling of adjacent energy levels, we, therefore, have investigated the equilibrium configuration of the orientation of the ion with respect to the field.

Let us now briefly consider the influence of the magnetic field on the so-called "antibonding" states, i.e., $6h\gamma_u, 7i\eta_g, \dots, 12n\mu_u$ in the absence of a magnetic field and their corresponding counterparts $1\gamma_u, 1\eta_g, \dots, 1\mu_u$ in the presence of a magnetic field. The potential-energy curves of the antibonding $6h\gamma_u, 7i\eta_g, \dots, 12n\mu_u$ states in the field-free case exhibit a purely repulsive behavior. In a previous investigation (see in particular Ref. [13] and for the $1\gamma_u$ and $1\eta_g$ state also Ref. [19]) it was shown that the potential-energy curves of the corresponding magnetically dressed counterparts, the $1\gamma_u, 1\eta_g, \dots, 1\mu_u$ states, exhibit above some critical field strength shallow minima. The depth of these shallow potential wells is, for a field strength of $B=1.0$ a.u., of the order of magnitude of 10^{-5} a.u. An exception is the $1\gamma_u$ state, which has a dissociation energy of 1.1×10^{-4} a.u. All these energies are smaller than the cyclotron energy of the nuclear motion and, consequently, these antibonding states are supposed to be unbound.

The above discussed effects of the magnetic field on the electronic structure of the H_2^+ ion are based on the assumption of infinitely heavy nuclei, i.e., the validity of the fixed nuclei electronic Hamiltonian (2). However, the H_2^+ ion is a charged three-body system for which, in particular, the center-of-mass motion couples to the electronic degrees of freedom if a magnetic field is present. A more elaborate electronic Hamiltonian, therefore, contains apart from additional mass correction terms which are due to the finite nuclear mass also the coupling of the zeroth-order Landau motion of the center of mass of the ion to the electronic degrees of freedom [14,20]. In order

to ensure that our fixed-nuclei approach is valid for the above-discussed magnetically dressed electronic states we have to estimate the coupling of the center-of-mass motion of the ion to the corresponding electronic states. To this end we expand the total electronic wave function in a series of products of the so-called Landau orbitals for the center-of-mass motion and the electronic eigenfunctions belonging to the Hamiltonian (2). Each off-diagonal element of the resulting Hamiltonian matrix couples different total electronic states consisting of certain Landau orbitals and electronic fixed-nuclei eigenstates. These coupling elements contain a product of two dipole matrix elements between different Landau orbitals and electronic molecular eigenfunctions, respectively. With the aid of the selection rules for both types of dipole matrix elements (the selection rules for the matrix elements between the Landau orbitals are given in Ref. [20]) we could restrict our investigation to a coupled two state problem. The relevant quantity κ , which tells us whether the strength of the coupling is of relevance or not, is then the square of the ratio of the absolute value of the coupling matrix elements and the energy gap between the considered electronic states. If κ is much smaller than one, the coupling between the collective and the electronic motion can be neglected. We have calculated the values of κ for the $1\gamma_g, \dots, 1\mu_g$ states at the equilibrium distances and for the lowest Landau states. In all considered cases κ is of the order of magnitude of 10^{-4} . We, therefore, conclude that the influence of the coupling between the collective and electronic motion on the properties of the chemical bond of the $1\gamma_g, \dots, 1\mu_g$ states in a magnetic field of $B=1.0$ a.u. is negligible (for a detailed discussion of this subject we refer the reader to Ref. [17]).

Finally, we remark that the mass correction terms can to lowest order of the ratio of the electron and nuclear mass be taken into account by simply replacing the mass of the electron by its reduced mass. Apart from the constant Zeeman shift the inclusion of the lowest-order mass correction terms, therefore, corresponds to a rescaling of the energy.

IV. BRIEF SUMMARY

In the present paper, we have investigated the influence of a strong homogeneous magnetic field on the chemical bond of the excited H_2^+ ion for parallel internuclear and magnetic-field axes. We used a recently optimized atomic orbital basis set in order to calculate the molecular electronic potential-energy curves in the fixed-nuclei approximation. Since the most significant effects of the external magnetic field on the chemical bond were expected for those states with large quantum numbers m we restricted our investigation to the lowest states of the H_2^+ ion with magnetic quantum numbers $4 \leq |m| \leq 10$. First, we considered the so-called bonding states. In the absence of a magnetic field the electronic potential-energy curves of the lowest bonding states with the magnetic quantum numbers $5 \leq |m| \leq 10$ exhibit purely repulsive behavior, i.e., these states are unbound. The potential-energy curve of the lowest electronic state with $|m|=4$ still exhibits a small and shallow potential well. In the presence of a

strong magnetic field with a typical field strength of $B = 1.0$ a.u. all the potential-energy curves of the corresponding magnetically dressed states exhibit well-pronounced potential wells. By a harmonic approximation of the wells we have shown that in all considered cases the vibrational ground-state energy is much smaller than the depth of the potential well and, therefore, many vibrational states do exist in the wells. That is, all considered magnetically dressed states, in particular, also those whose corresponding counterparts show in the absence of a magnetic field purely repulsive potential-energy curves, are stable.

In contrast to the potential energy curves of the bonding states in the presence of a magnetic field the potential energy curves of the lowest antibonding states with the above-mentioned magnetic quantum numbers exhibit only shallow minima. The depth of these potential wells is in each of the considered cases smaller than the corresponding zero-point cyclotron energy of the nuclear

motion. Hence, the considered magnetically dressed antibonding states are physically unbound.

Since all of the above-discussed effects of the magnetic field on the electronic structure of the H_2^+ ion are based on the fixed-nuclei approximation we had to estimate whether the corrections beyond this approximation, i.e., the coupling between the collective and electronic motion of the H_2^+ ion and the mass corrections, are small. We showed that the relevant quantity which is a measure for the strength of the coupling of the collective and electronic motion is much smaller than unity and thus the coupling can be neglected for the considered states and field strength.

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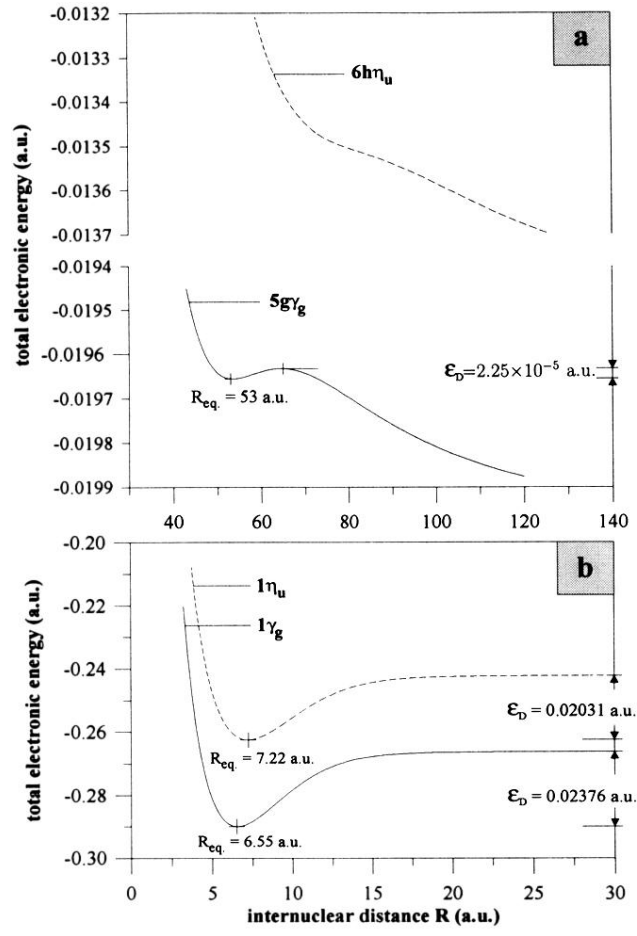


FIG. 1. (a) The total electronic energy curves of the lowest states with the magnetic quantum numbers $|m|=4$ ($5g\gamma_g$) and $|m|=5$ ($6h\eta_u$) in the absence of a magnetic field. (b) The total electronic energy curves of the corresponding magnetically dressed states ($1\gamma_g$ and $1\eta_u$) for a magnetic-field strength of $B = 1.0$ a.u.

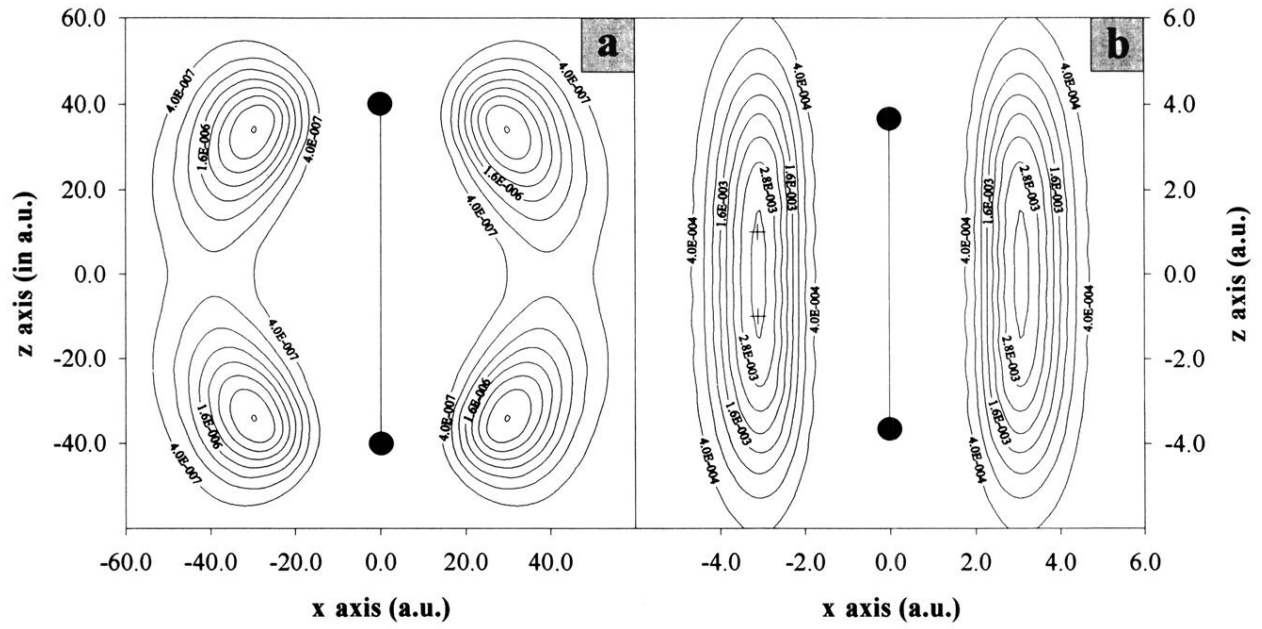


FIG. 2. (a) The electronic probability density distribution of the $6h\eta_u$ state in the absence of a magnetic field and for an internuclear distance of 80 a.u. The difference in density between neighboring contour lines is 4×10^{-7} . (b) The electronic probability density distribution of the corresponding magnetically dressed $1\eta_0$ state for the equilibrium internuclear distance $R_{\text{eq}} = 7.22$ a.u. In the left half-plane the positions of the maxima of the density distribution are marked with crosses. The difference in density between neighboring contour lines is 4×10^{-4} . The notation 4.0E-007 denotes 4.0×10^{-7} , etc.