The H_2^+ molecule in strong magnetic fields, studied by the method of linear combinations of orbitals

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We have studied the ground state of the H_2^+ molecular ion in the presence of a homogeneous magnetic field, basing this study on a linear combination of atomic orbitals obtained from the hydrogen atom in a magnetic field. The calculations have shown that this scheme is adequate to describe the binding energy of the molecule at field strengths up to approximately 10^{10} G.

I. INTRODUCTION

The behavior of molecules in very strong magnetic fields ($10^8 < B < 10^{13}$ G) has been described in a number of recent papers.[1-4] For fields higher than 10^9 G a simple perturbation treatment is inadequate since the energy associated with the magnetic field ($\mu_B B$) becomes larger than the Coulomb term.[1-4]

In a recent variational treatment of the hydrogen-molecule ion[4] a wave function of the type $\Phi_{n,\nu}(\rho, \phi)f(z)$ has been proposed, where $\Phi_{n,\nu}(\rho, \phi)$ is an unperturbed electronic orbital in a magnetic field parallel to the z axis[5] and $f(z)$ was chosen as a Gaussian along the magnetic field axis. This trial function leads to pronounced minima in the potential curves of the H_2^+ molecule in the region $10^{10} \leq B \leq 10^{13}$ G, but for $B < 10^{10}$ G, the curves based on this wave function do not indicate any stability of the H_2^+ ion. It is known[6,8] that below 10^{10} G the $\Phi_{n,\nu}(\rho, \phi)$ orbital character is questionable for the hydrogen atom itself, and a linear-combination-of-atomic-orbitals–molecular-orbitals treatment of the H_2^+ based on hydrogenlike atomic orbitals is possibly more adequate. Such a treatment is described in the present paper.

II. METHODS

Within the Born-Oppenheimer approximation and neglecting spin and relativistic effects the molecular Hamiltonian is

$$\mathcal{H} = \frac{p^2}{2m} + \omega_L L_z + \tfrac{1}{2} m \omega_L^2 r^2 \sin^2\theta - \frac{e^2}{r_a} - \frac{e^2}{r_b} + \frac{e^2}{R_{ab}}, \quad (1)$$

where $\omega_L = eB/2mc$ is the cyclotron frequency of the electron and θ is the angle between the position vector of the electron $\vec{r}$ and the magnetic field axis z. The Zeeman term was neglected because all the spins are lined up in the magnetic field. Our first wave function is simply

$$\Psi = C_a \phi_a + C_b \phi_b, \quad (2)$$

where ϕ_a and ϕ_b are hydrogenlike $1s$ orbitals centered in nuclei a and b, respectively, and used by Rajagopal et al.[7] in their treatment of the hydrogen atom:

$$\phi(\vec{r}) = \beta_1^{3/2} R_{10}(\beta_1, r) Y_{00}(\theta, \Phi) = N_1(\beta_1)e^{-\beta_1 r/a_0}, \quad (3)$$

where β_1 is a variational parameter chosen as to minimize $\langle \psi|\mathcal{H}|\psi\rangle/\langle\psi|\psi\rangle$ for the H atom with respect to B, and $N_1(\beta_1)$ is a normalization factor. From a physical point of view the exponential parameter β_1 describes the contraction of the radial part of orbitals ϕ_a and ϕ_b in the magnetic field, and it remains very close to unity up to $B \simeq 10^8$ G. The angular function remains constant, which means that the electronic eigenvalues are independent of the orientation of the molecule with respect to the field.

The second wave function used in the present work is a linear combination of $1s$- and $2s$-type orbitals centered in nuclei a and b:

$$\Psi = c_1 \phi_a^{1s} + c_2 \phi_a^{2s} + c_3 \phi_b^{1s} + c_4 \phi_b^{2s}, \quad (4)$$

where ϕ^{1s} is given in (3) and

$$\phi^{2s} = \beta_2^{3/2} R_{20}(\beta_2, r) Y_{00}(\theta, \Phi) = N_2(\beta_2)e^{-\beta_2 r/2a_0}. \quad (5)$$

Before going into a discussion of our results it should be pointed out that for the hydrogen atom Rajagopal et al.[7] also used a linear combination of $1s$- and $2s$-type orbitals. These are clearly nonorthogonal, since β_1 and β_2 are variational parameters. We have repeated their calculation
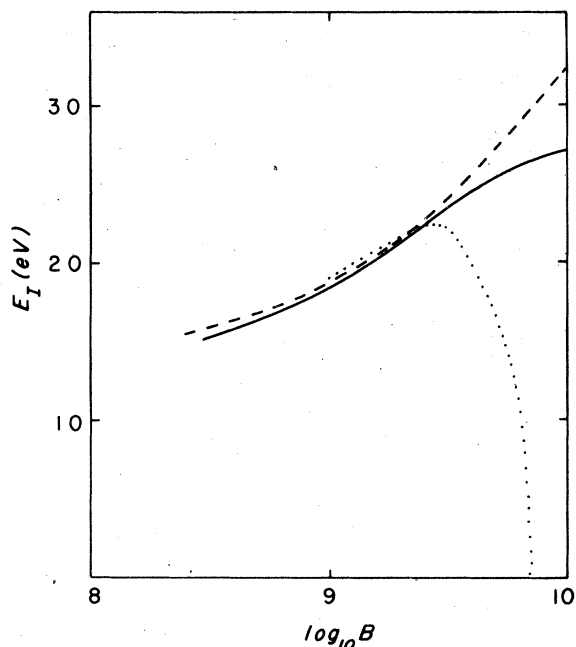
FIG. 1. Comparison of the electronic binding energies of the H atom as a function of the magnetic field.
(———) present work; (-----) Rajagopal *et al.* (Ref. 7); (.....) Brandi (Ref. 8).

for the atomic case and have reproduced their results with the wave function (3), as well as those calculated from a linear combination of (3) and (5) up to $B = 3 \times 10^9$ G. However, for higher
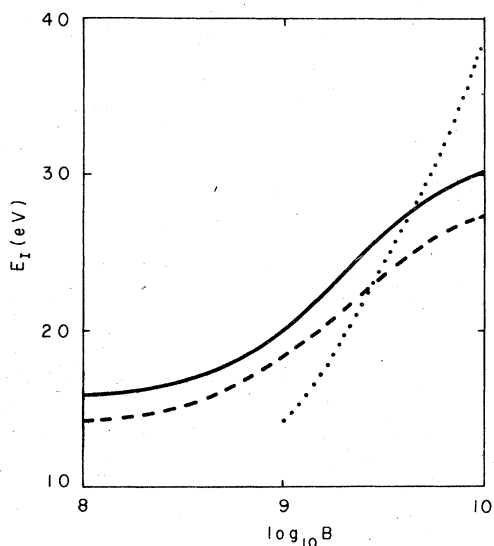
fields our binding energy is systematically higher than their values. This is shown in Fig. 1, where we have also included Brandi's results[8] for comparison.[9] Figure 2 compares the ionization energy for the H$_2^+$ molecule and the hydrogen atom.

III. RESULTS AND DISCUSSION

Figure 3 shows the potential curves of H$_2^+$ in the presence of a magnetic field in the range $10^8 \leq B \leq 10^{10}$ G, according to our first trial function [Eq. (3)].

We define the dissociation energy as the difference $E_D = E_{H_2^+} - E_H$, where $E_{H_2^+}$ is the energy of the $1\sigma_g$ orbital in H$_2^+$ and E_H is the energy of the hydrogen atom,[7] both for a given value of the magnetic field. The curves indicate a decreasing internuclear distance with increasing B values. The vibration frequencies were calculated by assuming the harmonic approximation for the bottom of the curves; their values as a function of the magnetic field are plotted in Fig. 4.

As shown, ω_0 remains approximately constant up to $B = 10^9$ G and then increases sharply to 5300 cm^{-1} at 10^{10} G.

The second wave function [Eq. (4)] produced a slight improvement in the binding energies. This is shown in Fig. 5 in terms of the dissociation energies E_D (for $B = 10^9$ G). We also tried a third wave function for the H$_2^+$ molecule, adding a $3d$-type orbital ($2p$ orbitals being forbidden by parity), but the improvement was negligible. This indicates that enlarging the basis set would not change our
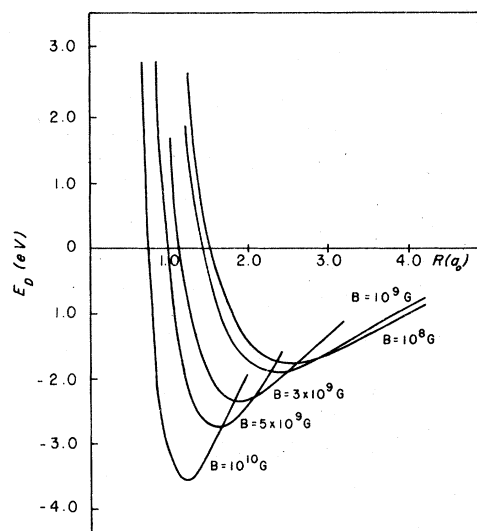

FIG. 2. Comparison of the ionization energies of the H atom and H$_2^+$ molecule as a function of the magnetic field. (———) H$_2^+$ molecule; (-----) hydrogen atom; (.....) H$_2^+$ molecule (Ref. 4).

FIG. 3. Dissociation energy of H$_2^+$ as a function of the internuclear distance for different values of the magnetic field.

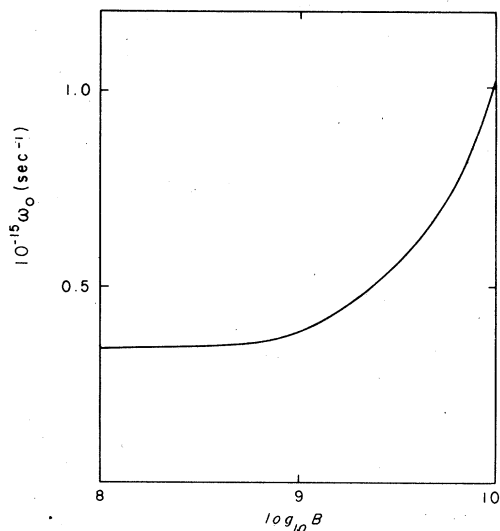FIG. 4. Fundamental vibrational frequency of H_2^+ as a function of the magnetic field.

FIG. 5. Potential curves of H_2^+ showing the effect of the inclusion of $2s$ orbitals for $B = 10^9$ G.

result significantly.

For magnetic fields higher than 10^{10} G the present approach breaks down and techniques similar to those of Ref. 4 must be used. As shown in the case of atoms,[10] a smooth connection between high- and low-field regions cannot be obtained if fundamentally different trial wave functions are used to describe each of the regions. More recently, Bhaduri et al.[11] proposed a variational method valid for arbitrary field intensities for the treatment of H_2^+ which gives better results for the binding energy than Ref. 4 for $B < 10^{12}$ G, but does not yield the correct dissociation energy and internuclear separation in the absence of the field. The present scheme gives values for the ground-state energy lower than those in Ref. 11 for fields up to $1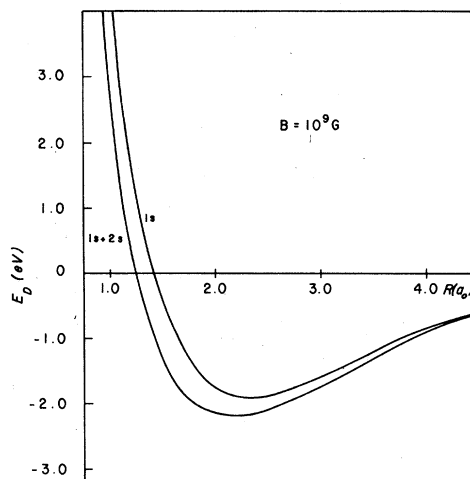0^9$ G. In particular, for $B = 0$, the experimental ground-state energy is -16.39 eV, while the present method gives -15.85 eV, to be compared with -15.11 eV obtained in Ref. 11.

ACKNOWLEDGMENTS

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