PUC

BR7501651

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A LCAO-MO APPROACH

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A LCAO-MO APPROACH[*]

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1. INTRODUCTION

The behaviour of molecules in very strong magnetic fields (10^8G < B < 10^{13}G) has been described in a number of recent papers [1-4]. For fields higher than 10^9G a simple perturbation treatment is inadequate since the energy associated with the magnetic field ($\mu_B \cdot B$) becomes larger than the Coulomb terms [5].

In a recent variational treatment of the hydrogen molecule ion [4] a wave function of the type $\Phi_{n,\nu}(\rho,\varphi) \cdot f(z)$ has been proposed, where $\Phi_{n,\nu}(\rho,\varphi)$ is a Landau orbital and $f(z)$ was chosen as a Gaussian along z, 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}G ≤ B ≤ 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 [6,7,8] that bellow 10^{10}G the Landau orbital character is questionable for the hydrogen atom itself, and a LCAO-MO treatment of the H_2^+ based on hydrogen-like atomic orbitals could possibly be more adequate. Such a treatment is described in the present paper.

2. METHODS

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

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$$\hat{\mathcal{H}} = \frac{p^2}{2m} + \omega_L L_z + \frac{1}{2} m\omega_L^2 r^2 sen^2\theta - \frac{e^2}{r_a} - \frac{e^2}{r_b} + \frac{e^2}{R_{ab}} \qquad (1)$$

where $\omega_L = \frac{eB}{2mc}$ is the cyclotron frequency of the electron and θ is the angle between the position vector of the electron, r, and the magnetic field axis B. Our first wave function is simply

$$\psi = c_a \psi_a + c_b \psi_b \qquad (2)$$

where ψ_a and ψ_b are Slater type 1s orbitals centered in nuclei $\underline{a}$ and $\underline{b}$, respectively, and used by Rajagopal et al. [7] in their treatment of the hydrogen atom:

$$\psi = \beta_1^{3/2} R_{10}(\beta_1, r) Y_{00}(\theta, \phi) \qquad (3)$$

β_1 is a variational parameter chosen as to minimise $<E_H>$ with respect to B. From a physical point of view the exponential parameter β_1 describes the contraction of orbitals ψ_a and ψ_b in the magnetic field, and it remains very close to unity up to B = 10^5G.

The second wave function used in the present work is a linear combination of 1s and 2s STO's centered in nuclei $\underline{a}$ and $\underline{b}$:

$$\psi = c_1 \psi_a^{1s} + c_2 \psi_a^{2s} + c_3 \psi_b^{1s} + c_4 \psi_b^{2s} \qquad (4)$$

where

$$\psi^{1s} = \beta_1^{3/2} R_{10}(\beta_1, r) Y_{00}(\theta, \phi) \qquad (5)$$

$$\varphi^{2s} = \beta_2^{3/2} \, R_{20}(\beta_2,r) Y_{00}(\vartheta,\varphi) \tag{6}$$

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 STO's. These are clearly non-orthogonal, since β_1 and β_2 are variational parameters. We have repeated their calculation for the atomic case and have reproduced their results with wave function (3), as well as those calculated from a linear combination of (5) and (6) 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 Figure 1, where we have also included Brandi's results [8] for comparison [9].

3. RESULTS AND DISCUSSION

Figure 2 shows the potential curves of H_2^+ in the presence of magnetic fields in the range $10^8 G \le B \le 10^{10} G$, 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 Figure 3.

As shown, ω_0 remains approximately constant up to $B = 10^9G$ and then increases sharply to 5,200 cm^{-1} at $10^{10}G$.

The second trial wave function (eq. 4) produced a slight improvement in the binding energies. In terms of the dissociation energies, E_D, this is shown in Figure 4 (for $B = 10^9G$). We also tried a third wave function for the H_2^+ molecule, adding a Slater type 3d orbital (2p orbitals being forbidden by parity), but the improvement was negligible.

For magnetic fields higher than $10^{10}G$ the present approach breaks down and techniques similar to those of reference [4] must be used. As shown in the case of atoms [10], a smooth connection between high field and low field regions cannot be obtained if fundamentally different trial wave functions are used to describe each of the regions.

REFERENCES AND NOTES

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[9]   We tried to reproduce the results described in
      reference [7] in the following way: we varied the total
      energy with respect to the linear parameters, obtaining
      secular equations, the roots being functions of β_1
      and β_2. The lowest eigenvalue is then minimized simul-
      taneously with respect to β_1 and β_2. We cannot explain
      why our results differ from those of reference [7].

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FIGURE CAPTIONS

Fig. 1 - Electronic binding energy of H_2^+ as a function of the magnetic field. (———) present work; (————) Rajagopal et al. (Ref. 7); (.....) Brandi (Ref. 8).

Fig. 2 - Dissociation energy of H_2^+ as a function of the internuclear distance for differing magnetic fields.

Fig. 3 - Fundamental vibrational frequency of H_2^+ as a function of the magnetic field.

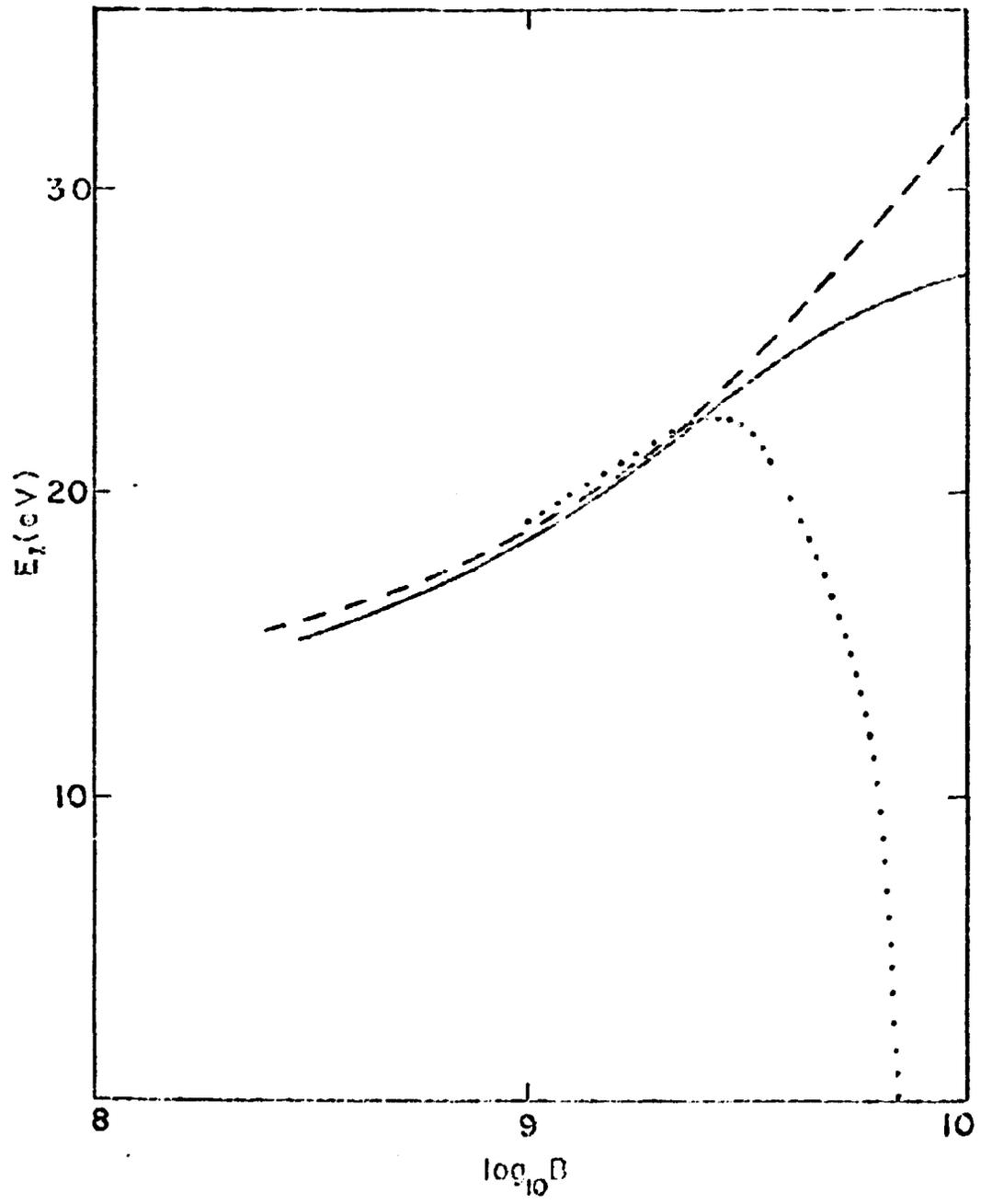Fig. 4 - Potential curves of H_2^+ showing the effect of the inclusion of 2s orbitals for $B = 10^9 G$.
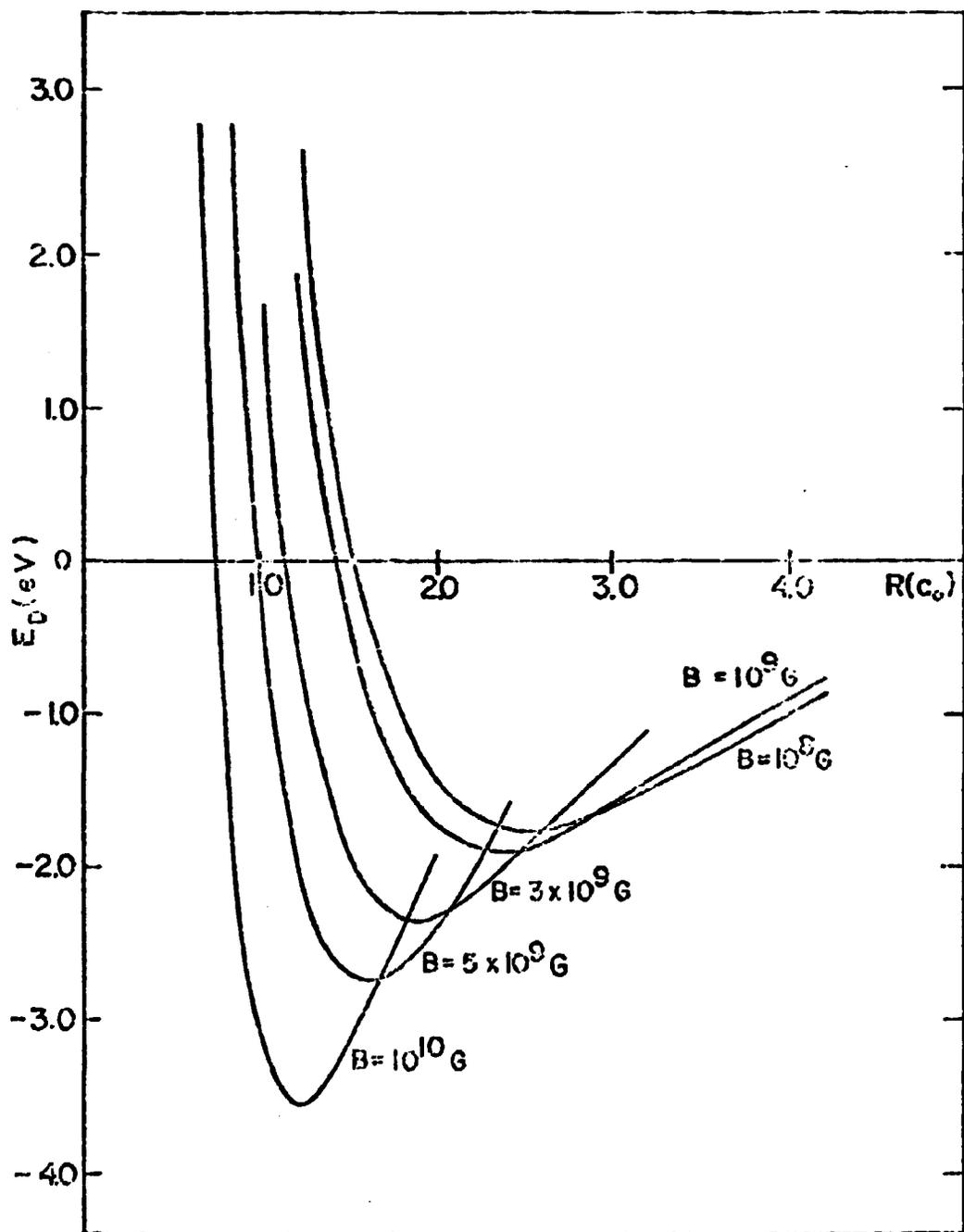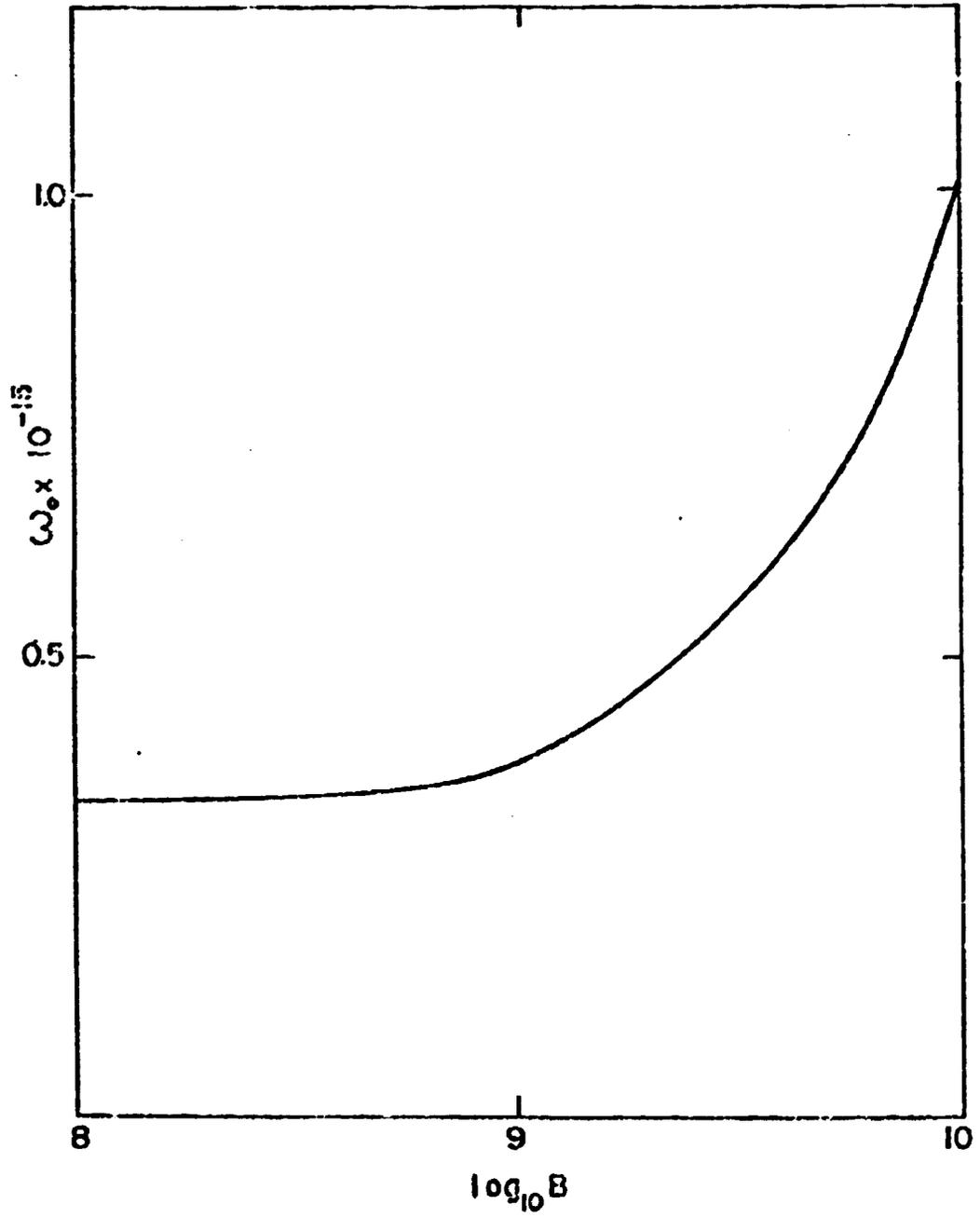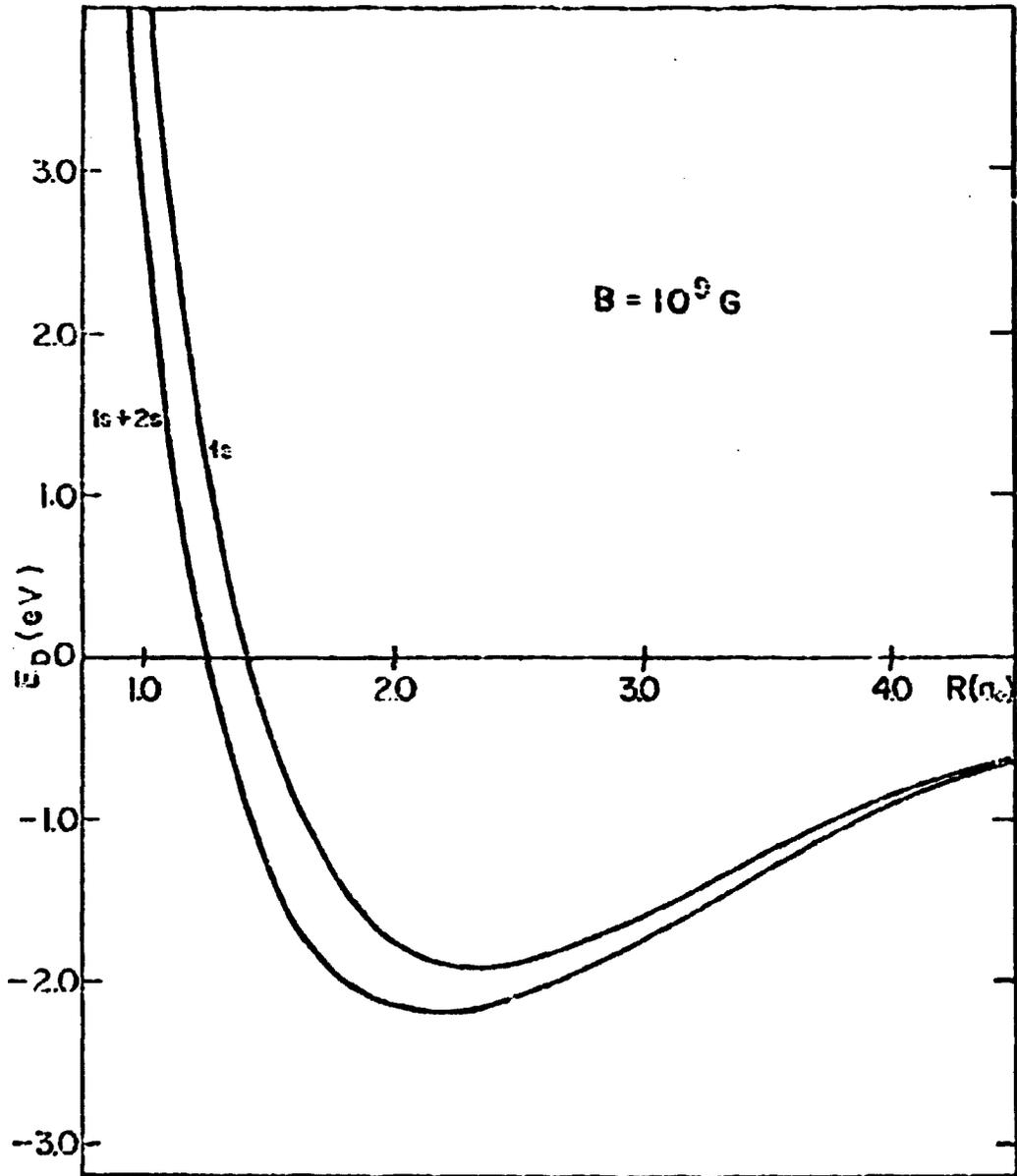
FIG.1

FIG. 2

FIG. 3

FIG. 4