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Hydrogen molecular ion in a magnetic field

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The energy of the ground electronic state of H_2^+ is studied as a function of the internuclear separation R_{12}, the angle, θ, between the molecular axis and the magnetic field, and the field strength B. For small B the molecular diamagnetism reaches its maximum value when $\theta=\pi/2$ and $R_{12}\cong5$ Bohr radii. This maximum value is about 50% greater than the diamagnetism of an isolated H atom. At large B the molecule shrinks due to magnetic compression of the electron wave function, and the molecular vibration frequencies increase substantially. A strong diamagnetic torque appears which tends to align the molecular axis along the field. This gives rise to a zero-point rotational oscillation about $\theta=0$ whose energy can substantially exceed that of the zero-point vibrational oscillation. The calculations presented indicate that even if the protons had infinite mass, the molecule would become unstable to dissociation at $\theta=\pi/2$ in fields $\gtrsim 1.6\times10^{11}$ G.

I. INTRODUCTION

Since the pioneering work of Schiff and Snyder,[1] numerous papers have appeared on the problem of the H atom in a magnetic field. At present the energies and wave functions of the low-lying states are accurately known for arbitrary field strength, and progress is being made in understanding the more highly excited bound states.

By contrast, relatively little attention has been paid to the corresponding problem of the hydrogen molecular ion, H_2^+, in a magnetic field. This problem has fundamental interest since H_2^+ is the simplest of all the molecules; an understanding of its behavior in magnetic fields should offer insights into the effect of strong magnetic fields on covalent bonds in general and, in particular, on covalently bonded diatomic molecules. Systems more or less analogous to H_2^+ have been observed in the spectroscopy of impurities in semiconductors. For example, photoluminescence experiments in a number of semiconductors give evidence for bound states consisting of a relatively massive hole, a light electron, and a donor ion. The magnetic properties of such a system may be quite similar in important respects to that of the H_2^+. In addition, recent experiments on the diamagnetism of donors in Ge show anomalies at the higher concentrations which may be attributable to the sharing of an electron by two donor ions.[2] In fact, the present study of H_2^+ was motivated by these latter experimental results.

Not a great deal is known about the behavior of H_2^+ in magnetic fields. Variational calculations of the electronic ground state of H_2^+ have been carried out in the low-field[3,4] and high-field[5] regions but only for the magnetic field parallel to the molecular axis. Moreover, none of these calculations appear to be highly accurate over any range of fields, as we shall see.

Previous authors have implicitly presumed that the axis of the H_2^+ molecule will tend to align along the direction of an applied magnetic field. However, this presumption cannot be checked unless one considers the situation in which field makes nonzero angles, θ, with the molecular axis. We shall describe calculations which yield, at each magnetic field strength, the energy as a function of θ, $V(\theta)$. With $V(\theta)$ in hand, the low-lying rotational levels can be calculated, and, because $V(\theta)$ is found to have its minimum at $\theta=0$, the molecule in its ground rotational state can indeed be expected to align along the field. At sufficiently large magnetic fields we find that $V(\theta)$ becomes so steep that the zero-point rotational oscillations around $\theta=0$ have higher energy than the zero-point vibrational energy evaluated at the same field; the rotational energy under these circumstances can represent a significant fraction of the dissociation energy of the molecule. Further, for θ approaching $\pi/2$ our calculations indicate that the bond becomes unstable at high fields.

In the first part of this paper we shall describe calculations of the electronic energy of H_2^+ in the limit of weak magnetic field for arbitrary field direction and arbitrary internuclear separation. Next we shall present results for the energy and equilibrium separation of the protons for arbitrary field strength but with the field aligned along the molecular axis. The energies obtained will be compared to the best previously published results. In the third section we discuss the electronic energy as a function of θ, deriving $V(\theta)$. Finally, we shall calculate the lowest-lying rotation-vibration levels of H_2^+ in a magnetic field.

The nonrelativistic spinless Hamiltonian for the H_2^+ ion in a uniform static magnetic field is H_1+H_2 given by

$$H_1=\frac{1}{2M_p}\left[\left[\vec{p}_1-\frac{e}{c}\vec{A}_1\right]^2+\left[\vec{p}_2-\frac{e}{c}\vec{A}_2\right]^2\right], \tag{1}$$

$$H_2=\frac{[\vec{p}+(e/c)\vec{A}]^2}{2m}-\frac{e^2}{|\vec{r}-\vec{R}_1|}-\frac{e^2}{|\vec{r}-\vec{R}_2|}+\frac{e^2}{|\vec{R}_1-\vec{R}_2|}, \tag{2}$$

where the subscripts 1 and 2 attached to quantities on the right-hand side of Eqs. (1) and (2) refer to the protons; $\vec{p}$, m, $\vec{A}$, and $\vec{r}$ are the momentum operator, mass, vector potential, and position of the electron, respectively; M_p is the proton mass, and $\vec{A}_{1,2}=\frac{1}{2}\vec{B}\times\vec{R}_{1,2}$, where $\vec{B}$ is the magnetic field. We may rewrite H_1 by going to the center-of-mass system of the protons

$$H_{1A}=\frac{1}{4M}\left[\vec{P}-\frac{e}{c}(\vec{B}\times\vec{R})\right]^2,$$

$$H_{1B}=\frac{1}{2\mu m}\left[\vec{P}_{12}-\frac{e}{4c}(\vec{B}\times\vec{R}_{12})\right]^2,$$

$$H_1=H_{1A}+H_{1B},$$

where $\vec{P}=\vec{p}_1+\vec{p}_2$, $\vec{R}=\frac{1}{2}(\vec{R}_1+\vec{R}_2)$, $\vec{P}_{12}=\frac{1}{2}(\vec{p}_1-\vec{p}_2)$, $\vec{R}_{12}=\vec{R}_1-\vec{R}_2$, $\mu=M_p/2m=918$, and $M=2M_p$.

Although the kinetic energy of the center-of-mass motion of the H_2^+ ion cannot be zero in the presence of a magnetic field, we shall neglect it compared to vibrational or rotational energies by setting H_{1A} equal to zero. In addition, we neglect field-dependent terms in H_{1B}, leaving

$$H_1\cong H_{1B}\cong P_{12}^2/2\mu m\ . \tag{3}$$

In making these approximations we are neglecting the cyclotron energy of the ion as well as effects of motional electric fields.[6] Clearly for ions with large center-of-mass kinetic energy, these approximations will be poor.

We seek first variational estimates of the ground state of H_2 with $\vec{R}_1$ and $\vec{R}_2$ regarded as fixed parameters. The ground-state eigenvalue will turn out to be a function of $|\vec{R}_{12}|$ and θ, the angle between $\vec{B}$ and $\vec{R}_{12}$. Invoking the Born-Oppenheimer approximation, we then use this function as an effective potential for the rotational-vibrational motion. Wave functions and energy levels associated with this motion are, in turn, calculated by the variational method.

We begin by considering the ground-state diamagnetism of the H_2^+ ion for arbitrary R_{12} and magnetic field direction in the limit $B\rightarrow0$. There are, to my knowledge, no accurate calculations available even in this relatively simple limit. Moreover, the results will illuminate the behavior of the ion at higher fields.

II. WEAK-FIELD DIAMAGNETISM

We address here the problem of finding the lowest-order correction to the zero-field ground-state eigenvalues of H_2 in the presence of an arbitrarily weak magnetic field. In our earlier discussions we employed the symmetric gauge $\vec{A}=\frac{1}{2}\vec{B}\times\vec{r}$. However, it is advantageous at this point to introduce a more general gauge. Let us assume in all our calculations of electronic energy that the molecule axis lies along the z direction and that the magnetic field has only components $B_z=B\cos\theta$ and $B_y=B\sin\theta$ along z and y axes, respectively. We introduce the gauge

$$\vec{A}=[\xi_yB_yz-\xi_zB_zy,(1-\xi_z)B_zx\ ,\ -(1-\xi_y)B_yx]\ , \tag{4}$$

where ξ_y and ξ_z are constants which are to be determined variationally. It is easy to verify that, independent of the choice of ξ_y and ξ_z, $\vec{\nabla}\times\vec{A}=(0,B_y,B_z)$ hence that $\vec{A}$ properly describes the magnetic field. Taking henceforth energy and length in units of the hydrogen Rydberg, $\mathscr{R}$, and Bohr radius, a_0, respectively, Eq. (2) becomes

$$H_2=\left[\frac{1}{i}\frac{\partial}{\partial x}+\xi_y\gamma_yz-\xi_z\gamma_zy\right]^2+\left[\frac{1}{i}\frac{\partial}{\partial y}+(1-\xi_z)\gamma_zx\right]^2+\left[\frac{1}{i}\frac{\partial}{\partial z}-(1-\xi_y)\gamma_yx\right]^2-2/R_A-2/R_B+1/z_0\ , \tag{5}$$

where $\gamma_y = \gamma \sin\theta$, $\gamma_z = \gamma \cos\theta$, and $\gamma = (\hbar e B / mc)/2\mathscr{R}$; $R_A = [x^2 + y^2 + (z - z_0)^2]^{1/2}$ and $R_B = [x^2 + y^2 + (z + z_0)^2]^{1/2}$ corresponding to protons fixed on the z axis at $+z_0$ and $-z_0$ ($z_0 = \frac{1}{2} R_{12}$). The dimensionless parameter γ measures the strength of the magnetic field. In vacuum $\gamma = 1$ when $B = 2.35 \times 10^9$ G. (Notice, however, in many semiconductors $\gamma = 1$ for $B \lesssim 10^5$ G because the effective Rydberg and effective electron mass are much smaller than in vacuum.)

We shall attempt to find the energy to order γ^2 by a variational approach. To motivate a choice of trial wave function we consider the problem of a single hydrogen atom centered at $x = y = z = 0$ in a weak magnetic field along the y direction. The appropriate Hamiltonian is

$$\left[\frac{1}{i}\frac{\partial}{\partial x} + \xi_y \gamma_y z\right]^2 - \frac{\partial^2}{\partial y^2} + \left[\frac{1}{i}\frac{\partial}{\partial z} - (1 - \xi_y)\gamma_y x\right]^2 - \frac{2}{r} . \tag{6}$$

Taking the trial function e^{-r} we find that the energy is

$$-1 + [\xi_y^2 + (1 - \xi_y)^2]\gamma_y^2 .$$

Minimizing this energy with respect to ξ_y gives $\xi_y = 0.5$, leading to the well-known diamagnetic energy of $0.5\gamma_y^2$. Suppose now that the atom is centered at $x = y = 0$, $z = z_0$. Then $-2/r$ in (6) changes to $-2/R_A$. If we employ simply the trial function e^{-R_A} and repeat the variational calculation, we obtain an energy

$$-1 + [(1 + z_0^2)\xi_y^2 + (1 - \xi_y)^2]\gamma_y^2 ,$$

which yields an optimum ξ_y of $1/(2 + z_0^2)$ and a diamagnetic energy, $(1 + z_0^2)\gamma_y^2/(2 + z_0^2)$, which is clearly higher than the correct value, $0.5\gamma_y^2$. To cure this problem we can apply a gauge tranformation, $e^{-i\xi_y \gamma_y z_0 x}$, to e^{-R_A} which will "center" the gauge at $z = z_0$ instead of at $z = 0$. Thus the trial function $e^{-iqx} e^{-R_A}$, where $q = \xi_y \gamma_y z_0$, will again give the correct diamagnetic energy.

For large R_{12} the H_2^+ wave function approaches $e^{-R_A} + e^{-R_B}$. To obtain the correct diamagnetism in this limit, it is clear that we should use the trial function[7]

$$e^{-iqx} e^{-R_A} + e^{iqx} e^{-R_B} .$$

For general R_{12} an excellent zero-field trial function is the Guillemin-Zener (GZ) function[8]

$$\psi_{GZ} = e^{-\alpha R_A - \beta R_B} + e^{-\alpha R_B - \beta R_A} , \tag{7}$$

where α and β are determined variationally as a function of R_{12}. Comparison of energies at various values of z_0 obtained from the GZ function, E_{GZ}, and the more nearly exact energies of Ref. 9 is given in Table I.

To calculate the diamagnetism of H_2^+ we have employed the trial function

$$e^{-iq\zeta x} e^{-\alpha R_A - \beta R_B} + e^{iq\zeta x} e^{-\alpha R_B - \beta R_A} , \tag{8}$$

where ζ is an additional variational parameter which permits the gauge to be centered at an arbitrary point on the z axis. For $\zeta = 1$ the gauge is centered on the protons; for $\zeta = 0$, midway between them. The calculation is carried out in two steps. First, the field is set equal to zero and α and β are varied for lowest energy at the value of z_0 of in-

TABLE I. Zero-field energies, E_{GZ} and E, and diamagnetic coefficients, D_z and D_y, for computing the ground-state energy of H_2^+ in a weak magnetic field from Eq. (9). z_0 is half of the interproton separation in units of a_0. E_{GZ}, calculated using the trial function of Eq. (7), is a variational estimate of the "exact" H_2^+ energy, E, taken from Ref. 9.

z_0	E_{GZ}	E	D_z	D_y
0.2	−3.6011	−3.6016	0.152	0.155
0.4	−3.1083	−3.1090	0.194	0.207
1.0	−2.2049	−2.2053	0.326	0.405
1.6	−1.7662	−1.7665	0.436	0.609
2.0	−1.5918	−1.5922	0.482	0.706
2.5	−1.4483	−1.4488	0.512	0.756
3.0	−1.3567	−1.3573	0.517	0.727
4.0	−1.2549	−1.2551	0.508	0.604
6.0	−1.1670		0.500	0.509

terest. Then ξ_y and ζ are varied to produce the smallest coefficient of γ_y^2 possible in the diamagnetic energy. (ξ_z is always best chosen to be 0.5 because the zero-field wave function is cylindrically symmetric.)

The energy of $H_2{}^+$ in the limit $\gamma \to 0$ can be written

$$\begin{aligned} E(\gamma,\theta) &= E(0)+\gamma^2[D_z(z_0)\cos^2\theta + D_y(z_0)\sin^2\theta] \\ &= E(0)+\gamma^2 D_z(z_0) \\ &\quad + \gamma^2[D_y(z_0)-D_z(z_0)]\sin^2\theta \, . \end{aligned} \tag{9}$$

Our variational estimates of D_z and D_y are tabulated in Table I and plotted in Fig. 1. Over most of the z_0 range $0.45<\xi_y<0.52$ and $0.8<\zeta\leq 1$.

From Fig. 1. and Eq. (9) we observe that weak magnetic fields contribute an effective potential which, at least for $z_0<2.5$, tends to push the two protons together. This effect becomes more pronounced as the axis of the $H_2{}^+$ is rotated out of alignment with the magnetic field. As we shall see the behavior just described persists, qualitatively, even at high magnetic field.

III. FIELD ALONG MOLECULAR AXIS

Calculations of the ground-state energy of $H_2{}^+$ in magnetic fields of arbitrary strength directed along the line connecting the two protons have been carried out previously. Here we introduce a new ansatz which yields energies, $E_{p\parallel}$, apparently superior to previous energies at all fields.[3-5] The trial function chosen is

$$\psi = \exp(-Dz^2 - \gamma' \rho^2/4)\psi_{\rm GZ} \, , \tag{10}$$

where D and γ' as well as α and β in $\psi_{\rm GZ}$ are variational parameters. In Table II we compare the electronic binding energies (including interproton repulsion) obtained from H_2 and Eq. (10) at equilibrium separation to those of other authors. It is implicitly assumed in these calculations that the protons are infinitely massive. The energies quoted for each ansatz are obtained at the optimimum proton separation for that ansatz. By "binding energy" we mean the least energy required to produce, in the presence of the field, a free electron

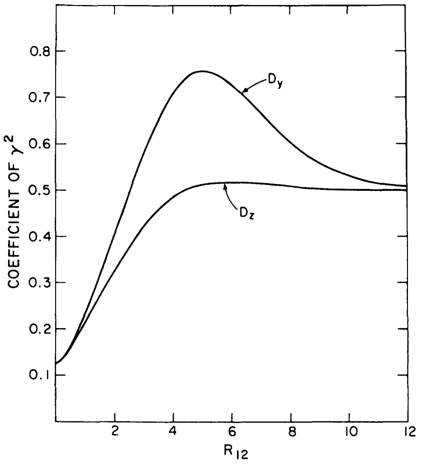

FIG. 1. Variation with internuclear separation, R_{12}, of coefficients D_y and D_z determining the energy shift of the ground state of $H_2{}^+$ due to application of a sufficiently weak magnetic field [see Eq. (9)]. R_{12} is in units of a_0.

TABLE II. Comparison of various variational lower bounds to the binding energy of $H_2{}^+$ at equilibrium interproton separation for magnetic field parallel to the line connecting the two protons. $E_{p\parallel}$, $E_{\rm BNW}$, and $E_{\rm MFBM}$ are from the present calculation [trial function of Eq. (10)] and from Refs. 4 and 5, respectively. $E_{\rm MDFBM}$ is calculated from the trial function $e^{-\alpha r_A}+e^{-\alpha r_B}$ taken from Ref. 3 (a slightly better trial function is also discussed in this reference). $z_0^{(e)}$ is half of the equilibrium interproton separation in units of a_0 determined from the present calculation and has a numerical uncertainty of about ±0.002. All energies are evaluated at the equilibrium z_0 for their respective trial functions and are in units of $\mathscr{R}$.

γ	$z_0^{(e)}$	$E_{p\parallel}$	$E_{\rm MDFMB}$	$E_{\rm BNW}$	$E_{\rm MFBM}$
0	1.000	1.2049	1.1730	1.1109	
1	0.876	1.9498	1.8817	1.8612	
3	0.688	2.7903	2.5137	2.7064	
10	0.479	4.3500		4.2592	4.0777
100	0.224	10.270			10.033
1000	0.111	22.67			22.22

and two protons, all infinitely far from each other. This energy is always greater than the "dissociation energy," which is the least energy required to remove one of the protons to infinity, leaving an H atom in its ground state in the magnetic field.

Parameters maximizing the $H_2{}^+$ binding at $\gamma = 100$ are $\gamma' = 92.7$, $D = 1.33$, $\alpha = 1.58$, and $\beta = -0.078$. As is true for any wave function which is cylindrically symmetric about the z axis, $\xi_z = 0.5$ in Eq. (5).

We believe that $E_{p\parallel}$ becomes progressively less accurate as γ increases. Improvement in $E_{p\parallel}$ by 0.01 and 0.04 at $\gamma = 100$ and $\gamma = 1000$, respectively, has been obtained by multiplying ψ in (10) by $\exp[-S\rho^2(R_A + R_B)]$, where S is an additional variational parameter, and reminimizing with respect to all parameters. Undoubtedly further energy improvements of similar or even greater magnitude remain possible.

At extremely high fields the wave function

$$\psi_P = e^{-\gamma'\rho^2/4} f(z) ,$$

with $f(z)$ a one-dimensional analog of the GZ wave function defined by

$$f(z) = \exp\{-\alpha[(z-z_0)^2 + A^2]^{1/2} - \beta[(z+z_0)^2 + B^2]^{1/2}\} + \exp\{-\alpha[(z+z_0)^2 + A^2]^{1/2} - \beta[(z-z_0)^2 + B^2]^{1/2}\},$$

is superior to ψ given by Eq. (10). For $\gamma = 1000$ an energy improvement of 0.055 is obtained. However, at $\gamma = 100$, ψ gives the lower energy.

We have examined the $H_2{}^+$ vibrational potential at $\gamma = 1$ and $\gamma = 100$ by minimizing the energy $\langle\psi | H_2 | \psi\rangle / \langle\psi | \psi\rangle$ at various fixed values of z_0 near the respective equilibrium values, $z_0^{(e)}$, listed in Table II. Potential curves are obtained by least-squares fitting the function

$$\begin{aligned} &x^2(A_v + B_v x + C_v x^2)/(1 - D_v x^4) , \\ &x \equiv z_0 - z_0^{(e)} , \end{aligned} \tag{11}$$

to the change in minimized energies from the energy at $z_0 = z_0^{(e)}$. For $\gamma = 1$ and $0.6 \le z_0 \le z_0^{(e)}$ the fitted parameters are $A_v = 0.719$, $B_v = -1.20$, $C_v = 2.63$, and $D_v = -3.81$; for $z_0^{(e)} \le z \le 1.4$ we find $A_v = 0.719$, $B_v = -1.27$, $C_v = 1.25$, and $D_v = 3.20$. At $\gamma = 100$ and $0.09 \le z_0 \le z_0^{(e)}$, $A_v = 73.5$, $B_v = -122$, $C_v = 4{,}930$, $D_v = -397$, whereas in the range $z_0^{(e)} \le z_0 \le 0.6$, $A_v = 73.5$, $B_v = -529$, $C_v = 1{,}869$, and $D_v = 512$. The fitted curves deviate by $0.01\mathscr{R}$ or less from the calculated energies in the stated ranges of z_0 for $\gamma = 100$ and are very much more accurate than that for $\gamma = 1$.

IV. FIELD PERPENDICULAR TO MOLECULAR AXIS

For this configuration $\gamma_z = 0$ in Eq. (5). An appropriate trial function for z_0 not too large is thought to be

$$\exp(-Dz^2 - A\rho^2 - Tx^2)\psi_{\text{GZ}} , \tag{12}$$

where D, A, T, α, and β are variational parameters [see Eq. (7)].[10] Energies and equilibrium values of z_0 are given in Table III. Parameters found for $\gamma = 100$ are $\xi_y = 0.265$, $D = 11.4$, $A = 0.944$, $T = 32.9$, $\alpha = 1.90$, and $\beta = 0.102$. Notice that the relatively large value of T indicates that the wave function of (12) is strongly compressed along x, the direction perpendicular to the plane determined by the molecular axis and the magnetic field. The charge density along the z axis is strongly peaked between the protons.

TABLE III. Variational lower bounds, $E_{p\perp}$, to the binding energy of $H_2{}^+$ for fields perpendicular to the line connecting the protons as calculated from trial function (12). $\tilde{z}_0^{(e)}$ is half of the equilibrium interproton separation in units of a_0, and E_{donor} is the donor binding energy, believed accurate to the number of figures quoted. All energies are in units of $\mathscr{R}$. Note that $\tilde{z}_0^{(e)}$ is always smaller than the corresponding value of $z_0^{(e)}$ in Table II.

γ	$\tilde{z}_0^{(e)}$	$E_{p\perp}$	E_{donor}
1	0.817	1.8988	1.6623
10	0.386	3.7620	3.4956
100	0.160	7.229	7.579
1000	0.0789	11.58	> 15.325

Notice also that the ionization energies and equilibrium separations in Table III are uniformly lower than the corresponding quantities in Table II. Of special interest is the fact that at $\gamma = 100$ and $\gamma = 1000$ the ionization energy of the $H_2{}^+$ at its "equilibrium" separation is lower than that of the donor, implying that the $H_2{}^+$ becomes unstable to dissociation at these high fields when $\vec{B}$ is perpendicular to the molecular axis.

V. FIELD AT ARBITRARY ANGLE TO MOLECULAR AXIS

When θ is between 0 and $\pi/2$ a more general wave function than either (10) or (12) is required. In this case cross terms in H_2 proportional to $\gamma_y \gamma_z zy$ may not be negligible (especially at high fields), and, it is thought, a trial function of the form

$$\exp(-Dz^2 - A\rho^2 - Tx^2 + Bzy)\psi_{GZ} \tag{13}$$

might be appropriate. However, this function, although giving satisfactory results at $z_0 = 0$ (the He^+ limit) seemed rather difficult to work with when $z_0 > 0$, and two simple variants defined by Eqs. (14) and (15) were employed instead:

$$\psi_1 = (1 + Ty^2)\exp(-A'\rho^2 - Dz^2 + Bzy)\psi_{GZ} \tag{14}$$

(relatively accurate for smaller θ values) and

$$\psi_2 = \left[1 + \sum_{i=1}^{3} C_i (zy)^i\right] \times \exp(-A\rho^2 - Dz^2 - Tx^2)\psi_{GZ} \tag{15}$$

(relatively accurate for θ near $\pi/2$).

The expectation that T in (13) would remain small at small θ motivates the replacement

$$\begin{aligned} &\exp(-A\rho^2 - Tx^2) \\ &\quad \equiv \exp[-(A + T)\rho^2 + Ty^2] \\ &\quad\quad \to (1 + Ty^2)\exp(-A'\rho^2) \end{aligned}$$

made in obtaining (14). In choosing (15) we have in effect approximated $\exp(Bzy)$ in (13) by the series $(1 + \sum_{i=1}^{3} C_i (zy)^i)$, where the C_i are variational parameters.

Over the range $0 < \theta < \pi/2$ two sets of energies were calculated, one set from ψ_1, the other from ψ_2, by varying all parameters in (14) and (15) as well as z_0. At $\gamma = 100$, ψ_1 gave lower energies for $0 < \theta \leq 0.6$ and ψ_2 for $0.75 \leq \theta \leq \pi/2$. At $\gamma = 1$, ψ_2 proved superior for $\theta \geq 0.5$ and ψ_1 for $0 < \theta \leq 0.25$.

In general we find that the change in energy with θ can be well fit by an expression of the form

$$(A_R + B_R \sin^2\theta)\sin^2\theta \ . \tag{16}$$

For $\gamma = 100$, $A_R = 5.85$ and $B_R = -2.85$. At small values of γ we expect from (9) that

$$A_R \cong \gamma^2 [D_y(z_0^{(e)}) - D_z(z_0^{(e)})]$$

and $B_R \cong 0$.

In the presence of the potential (16) the $H_2{}^+$ molecule will not in general rotate freely in its lowest-lying rotational states but rather oscillate like a pendulum pivoted at the molecular center of mass. Simultaneously, the molecule will vibrate in the potential (11). We discuss the ensuing low-lying rotational and vibrational levels in Sec. VI.

VI. ROTATION AND VIBRATION OF $H_2{}^+$ IN MAGNETIC FIELDS

In Secs. III and V we discussed how vibrational and rotational potentials, approximated by Eqs. (11) and (16), respectively, can be calculated for $H_2{}^+$ from various trial functions for the electronic motion. For low-lying vibrational states the wave functions describing the proton motion are large only for small displacement of z_0 from $z_0^{(e)}$ ($|x|$ small). Likewise, for low-lying rotational levels and $\gamma \gtrsim 1$, the molecular axis makes only small angles with the B field with significant probability so that $|\theta|$ is also small. In this region it turns out to be a fairly good approximation to write the total potential for the proton motion in the form

$$v(x) + V(\theta) \ , \tag{17}$$

where $v(x)$ is evaluated at $\theta = 0$ and is approximated by (11) as discussed earlier; $V(\theta)$ is evaluated at $x = 0$ for a number of discrete θ values and is least-squares fitted by (16). For $\gamma = 100$ we find $A_R = 6.13$ and $B_R = -2.49$, for $\gamma = 1$, 0.0583, and -0.00439, respectively.

In the approximation leading to (3) we have the Schrödinger equation

$$\left[-\frac{1}{\mu}\nabla_{R_{12}}^2 + v(x) + V(\theta)\right]\Psi = E\Psi \quad [R_{12} = 2x + 2z_0^{(e)}] \ , \tag{18}$$

for which we seek eigenvalues by the variational method. Although (18) is not separable in R_{12} and θ, we shall adopt, as a first attempt, a trial function of the form

$$S_v(R_{12})e^{iM_L\phi}R_{n,M_L}(\theta)\ . \tag{19}$$

To obtain a semiquantitative overview of the low-lying energy levels of (18) we can neglect the rotation-vibration interaction and also the anharmonicity of $v(x)$ [replacing, for the moment, $v(x)$ by $A_v x^2$]. In that case, S_v becomes the harmonic oscillator (HO) wave function associated with the energy level

$$(v+\tfrac{1}{2})\hbar\omega_{\rm HO}\ , \qquad \omega_{\rm HO}=(A_v/\mu)^{1/2}\ . \tag{20}$$

The ground-state oscillator wave function (unnormalized) is

$$\exp[-(\mu A_v)^{1/2}(R_{12}-r_e)^2/4]\ ,$$

where $r_e=2z_0^{(e)}$, and is therefore the internuclear separation at $x=0$, the minimum of $v(x)$.

The equation satisfied by $R_{n,M_L}(\theta)$ is approximately

$$\frac{1}{\mu\bar{r}^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\right]-\frac{M_L^2}{\sin^2\theta}\right]R + V(\theta)R=E_R R\ , \tag{21}$$

where we have omitted subscripts n and M_L. We will approximate

$$\frac{1}{\bar{r}^2}\equiv\frac{\langle S_v(R_{12})\,|\,1/R_{12}^2\,|\,S_v(R_{12})\rangle}{\langle S_v(R_{12})\,|\,S_v(R_{12})\rangle}$$

by $1/r_e^2$.

For γ sufficiently small that $V(\theta)$ can be neglected ($\gamma<<1$) the solutions of (21) are the familiar rotational eigenfunctions

$$P_L^{M_L}(\cos\theta)\ , \tag{22}$$

with eigenvalues $L(L+1)/\mu\bar{r}^2$. In the small-γ limit $V(\theta)$ produces energy shifts which are easily calculated in perturbation theory. For γ large, on the other hand, $V(\theta)$ can be approximated by $A_R\theta^2$, where A_R is evaluated at $R_{12}=r_e$. In this limit approximate eigenvalues of (21) may be found by making the small-amplitude approximation ($\sin\theta\rightarrow\theta$) in (21), leading to the equation

$$\left[-\frac{1}{\mu r_e^2}\left[\frac{d^2}{d\theta^2}+\frac{1}{\theta}\frac{d}{d\theta}-\frac{M_L^2}{\theta^2}\right]+A_R\theta^2\right]R=E_R R\ . \tag{23}$$

Equation (23) describes the quantum-mechanical pendulum in the harmonic approximation; the quantum pendulum is closely related to the usual one-dimensional harmonic oscillator and can be solved in a similar way, leading to the energy spectrum

$$\begin{aligned} &E_R(n,M_L)=2\alpha[2n+\delta(M_L)]/\mu\bar{r}^2\ ,\\ &\alpha=(A_R\mu\bar{r}^2)^{1/2}\ ,\\ &n=n_0,n_0+1,n_0+2,\ldots,\\ &n_0=\begin{cases}|M_L|/2 & \text{for } M_L \text{ even}\ ,\\ (|M_L|-1)/2 & \text{for } M_L \text{ odd}\ ,\end{cases}\\ &\delta(M_L)=\begin{cases}1 & \text{for } M_L \text{ even}\ ,\\ 2 & \text{for } M_L \text{ odd}\ .\end{cases}\end{aligned} \tag{24}$$

For all n $R_{n,M_L}(\theta)$ is even in θ if M_L is even and odd otherwise. The general form of R is

$$R_{n,M_L}(\theta)=\theta^{|M_L|}P_{n,M_L}(\theta^2)e^{-\alpha\theta^2/2}\ , \tag{25}$$

where P_{n,M_L} is a polynomial of degree $n-|M_L|/2$ for M_L even, $n-(|M_L|-1)/2$ for M_L odd, and $P_{n,M_L}(0)\neq 0$. The ground-state eigenfunction, therefore, has the form $R_{0,0}(\theta)=e^{-\alpha\theta^2/2}$.

In Table IV we list pertinent parameters for the

TABLE IV. Quantities related to the vibration-rotation ground state of H_2^+ in a magnetic field. $\hbar\omega_{\rm HO}$ is calculated from Eq. (20) with A_v determined by fitting (11) to $v(x)$. A_R is obtained by fitting (16) to $V(\theta)$ evaluated at the $z_0^{(e)}$ value of Table II. $E_R(0,0)$ and α are defined in (24) with $\bar{r}=r_e$; α is used in wave function (25). Energies are in units of $\mathscr{R}$.

γ	$\frac{1}{2}\hbar\omega_{\rm HO}$	A_R	α	$E_R(0,0)$
0	0.0105	0	0	0
1	0.0140	0.0583	12.8	0.0091
10	0.0397	0.925	14.0	0.133
100	0.141	6.12	33.6	0.365
1000	0.38	35.6	40.1	1.77

vibrational and rotational states over a wide range of γ values.

The total energy of the proton motion is the sum of vibrational and rotational contributions,

$$(v+\tfrac{1}{2})\hbar\omega_{\mathrm{HO}}+E_R(n,M_L)\ .$$

From Table IV it is apparent that for the larger values of γ rotational oscillation rather than vibration along the molecular axis makes the predominant contribution to the ground-state energy, $\frac{1}{2}\hbar\omega_{\mathrm{HO}}+E_R(0,0)$.

For more accurate calculations of the low-lying eigenvalues of (18) we introduce variational trial functions for R and S in (19). To construct trial functions for R, which interpolate between (22) and (25) and which obey the symmetry condition

$$R(\theta)=\pm R(\theta+\pi)$$

[not satisfied by (25)], we simply replace θ by $\sin\theta$ in (25) and treat α and the constants appearing in P_{n,M_L} as variational parameters. Trial functions so constructed are symmetric in the sense $R(\theta) = +R(\theta+\pi)$. Antisymmetric trial functions can be formed from these functions by multiplying by $\cos\theta$.[11] Thus for the lowest-lying rotational states we use $\exp(-\alpha\sin^2\theta/2)$ (symmetric) and $\cos\theta\exp(-\tilde{\alpha}\sin^2\theta/2)$ (antisymmetric). Due to the high rotational potential barrier these states are practically degenerate when γ is not small, but in the limit $\gamma\to 0$ $[V(\theta)\to 0]$ the symmetric state approaches the rotational ground state ($L=0$) of (21), whereas the antisymmetric state approaches the first excited rotational level $P_1^0(\cos\theta)$ ($\propto \cos\theta$).

Physically we expect states of high $|M_L|$ to have high energies when γ is large because the large centrifugal force in such states tends to align the molecular axis perpendicular to the magnetic field direction, where $V(\theta)$ is large. At $\gamma=0$, states of different M_L but with the same L are, of course, degenerate.

As an example, the states $e^{-i\phi}\sin\theta$ and $\cos\theta$ are degenerate at $\gamma=0$ since they have the same L values ($L=1$). However, the former state, which has $|M_L|=1$, transforms into $e^{-i\phi}\sin\theta e^{-\alpha\sin^2\theta}$ at high γ and therefore is higher than the latter by an energy of $2\alpha/(\mu\bar{r}^2)$, according to Eqs. (24).

To take into account the rotation-vibration interaction and the anharmonicity of $v(x)$, we have used Morse-type trial functions for S_v adopting

$$\begin{aligned}&S_0=y^{b_0}\exp(-c_0y)/x\ ,\\&S_1=(1+dy)y^{b_1}\exp(-c_1y)/x\ ,\\&y=\exp[-a(R_{12}-r_E)]\ ,\end{aligned}\tag{26}$$

where for given R_{n,M_L} parameters a, r_E, b_0, and c_0 are found by minimizing the ground vibrational state energy, d is chosen to orthogonalize S_1 to S_0, and b_1 and c_1 are varied to minimize the $v=1$ energy.

Energies resulting from employing the wave functions of (19) and the Hamiltonian (18) in the variational calculations are denoted $E_{v,n,|M_L|}$, where $E_{0,0,0}$ is the ground-state energy. For $\gamma=100$ we have obtained the results:

$$\begin{aligned}&E_{0,0,0}=0.476,\quad E_{1,0,0}=0.716\ ,\\&E_{0,0,1}=0.780,\quad E_{0,1,0}=1.087\ .\end{aligned}\tag{27}$$

Comparison of these results with the parameters in Table IV and the energy spectra of (20) and (24) gives an idea of the accuracy of the simple harmonic oscillator approximations at high γ.

In adopting a trial function in the form (19) one is implicitly assuming that the rotational motion associated with each vibrational state is associated with a molecule of fixed moment of inertia. To investigate the error introduced by such an approximation we have replaced $R_{n,M_L}(\theta)$ given by (25) with

$$R_{n,M_L}(\theta)=(\sin\theta)^{|M_L|}P_{n,M_L}(\sin^2\theta)e^{-kR_{12}\sin^2\theta}\ ,$$

where k is a variational parameter. This nonrigid pendulum ansatz at $\gamma=100$ gives only a 0.4% improvement in the ground-state energy relative to that obtained with (25) with θ there replaced by $\sin\theta$.

Finally, we have investigated the adequacy of the approximation (17) for the rotation-vibration potential. At $\gamma=100$ we find that for small $|x|$ and θ^2 a potential much more accurate that (17) is

$$v(x)+V(\theta)+37.5x\sin^2\theta\ .\tag{28}$$

The new term, $37.5x\sin^2\theta$, produces a significant increase in the energies of Eq. (27). This is because both the centrifugal force associated with the rotational motion and the asymmetry of $v(x)$ about $x=0$ have the effect of displacing the center of oscillation from $x=0$ to some positive value of x which, for large γ, can be quite sizeable. Thus the expectation value of $x\sin^2\theta$ in the wave functions of (19) is positive, producing an increase in the energy. Using (28) and trial functions (19) we find, for example, that $E_{0,0,0}$ is increased to 0.495 and $E_{0,0,1}$ to 0.829 as compared to the values given in (27).

VII. SUMMARY AND CONCLUSIONS

We have examined the hydrogen molecular ion in its electronic ground state in magnetic fields of arbitrary strength and direction.

The electronic energy is calculated assuming that the protons are fixed in position. The proton motion is calculated in the Born-Oppenheimer approximation.

In the weak-field limit the electronic diamagnetism of the $H_2{}^+$ is found to reach a maximum value when the separation of the protons, R_{12}, is near five Bohr radii; the diamagnetism at this separation is strongly dependent on θ, the angle between the interproton axis and the magnetic field, reaching a maximum at $\theta=\pi/2$. Roughly speaking, the diamagnetism depends on the degree of spread of the electronic wave function in planes perpendicular to the magnetic field. When R_{12} is zero the electron is strongly localized in a He^+ atom. As R_{12} increases the electron wave function spreads out, at first filling the space between the protons, and the diamagnetism increases; but finally, at large R_{12}, the electron becomes localized around each of the two protons. In the limit $R_{12}\rightarrow\infty$, the diamagnetism has decreased back to that of a single hydrogen atom.

For magnetic fields of intermediate or large strength ($\gamma \gtrsim 1$) the electronic wave function is altered by the presence of the field in a way which depends upon field strength and orientation. When the field lies along the molecular axis ($\theta=0$), the electronic wave function is compressed, primarily in planes perpendicular to the axis, producing increased charge between the protons and drawing them together. When the field is perpendicular to the axis ($\theta=\pi/2$), the diamagnetism is much higher than for $\theta=0$, and the electronic wave function suffers moderate compression along the molecule axis (resulting in a strong tendency for the protons to draw closer together) and very strong compression (at high γ) along axes perpendicular to the plane of $\vec{B}$ and the molecular axis.

At some critical value of γ, γ_c, which the present calculations place at $\gamma_c < 70$, the molecule, assumed to be held perpendicular to the field, becomes unstable to dissociation into a proton and a hydrogen atom. For $0<\theta<\pi/2$ the diamagnetic energy increases monotonically with θ and the wave function of the electron is skewed by the field in a complicated way.

As a first approximation at high field the electronic energy as a function of proton position can be written $v(z_0-z_0^{(e)})+V(\theta)$, where v is calculated at $\theta=0$, the angle minimizing $V(\theta)$, and V is calculated at $z_0^{(e)}$, the displacement minimizing v. This electronic energy acts as a potential for the proton motion, which becomes a superposition of a vibration along the molecular axis and a pendulum oscillation about the magnetic field. At large fields the energy of the pendulum motion is considerably greater than that of the vibration in the ground rotation-vibration state.

The vibration of $H_2{}^+$ in high magnetic fields in the absence of rotation has been investigated previously by Melo and co-workers.[5] We would have expected that their results and our estimates (indicated by $\frac{1}{2}\hbar\omega_{HO}$ in Table IV) would agree well at large γ since the potential curves, $v(x)$, are not very different. However, we find their values of $\hbar\omega_{HO}$ larger than ours by more than a factor of 2. We are unable to explain this discrepancy.

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$$\{e^{-iq\zeta x}\exp[-D(z-\zeta z_0)^2]e^{-\alpha r_A-\beta r_B}$$

$$+e^{iq\zeta x}\exp[-D(z+\zeta z_0)^2]e^{-\alpha r_B-\beta r_A}\}e^{-A\rho^2-Tx^2}$$

would seem more appropriate. However, computer experiments indicate that for z_0 near $z_0^{(e)}$ the trial function (12) turns out to be almost as good as the above function.

[11] Consideration of trial functions formed in this way leads to a general connection rule between $\gamma=0$ and $\gamma\rightarrow\infty$ rotational states. The suggested rule is

$$P_L^{M_L}(\cos\theta)\leftrightarrow\begin{cases} R_{L/2,M_L}(\theta) & \text{for } L \text{ even, } M_L \text{ even ,}\\ \cos\theta R_{(L-1)/2,M_L}(\theta) & \text{for } L \text{ odd, } M_L \text{ even ,}\\ \cos\theta R_{(L-2)/2,M_L}(\theta) & \text{for } L \text{ even, } M_L \text{ odd ,}\\ R_{(L-1)/2,M_L}(\theta) & \text{for } L \text{ odd, } M_L \text{ odd .}\end{cases}$$