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Hydrogen molecular ion in a high magnetic field

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The ground and several excited states of the hydrogen molecular ion in a homogeneous magnetic field aligned along the molecular axis are studied. A pair of self-consistent equations is derived in prolate spheroidal coordinates and solved numerically. The results are exact at the limit of vanishing magnetic field and more accurate than previous results up to about 10^9 G. The equilibrium internuclear separation and binding energy for a number of electronic states are reported as functions of the magnetic field strength. The dissociation energy is deduced from the study of the hydrogen atom in the same coordinate system.

I. INTRODUCTION

The possible existence of extremely high magnetic fields in white dwarf and neutron stars has motivated the investigation of their effects on the electronic structure and spectrum of atoms.[1] Several attempts at studying the effects of such fields on simple diatomic molecules have also been undertaken.[2-7] In all the reported studies of molecules use is made of relatively simple variational wave functions, which yield results of limited accuracy.

The available variational treatments of H_2^+ can be grouped into approaches emphasizing the molecular point of view, which are expected to be adequate as long as the electrostatic interactions are dominant, and oscillator(Landau)-like wave functions, which better describe the regime of extremely high magnetic fields.[2,3,5] The latter approaches provide exact solutions of the corresponding Schrödinger equation at the limit of an infinite magnetic field, though their neglect of quantum electrodynamic corrections makes them unrealistic above $\sim 10^{13}$ G. The former have only been implemented with respect to linear-combination-of-atomic-orbitals (LCAO)-type wave functions,[4,6,7] which remain approximate even at a vanishing magnetic field. An interesting variational wave function, which conceptually belongs in the high-field approach, but in fact yields useful results even for low magnetic fields, is studied in Ref. 3. For its limiting behavior at a vanishing magnetic field see Ref. 8.

In view of the special position of the hydrogen molecular ion (H_2^+) in molecular quantum theory, it is both desirable and possible to consider this system within an approach which at the low-field limit reduces to the exact solution of the free molecule. The construction of a variational approximation satisfying this requirement is presented. Computations using this approach were carried out for the ground state as well as for the $2p\sigma_u$, $3d\sigma_g$, $2p\pi_u$, and $4f\sigma_u$ excited states. In all the cases considered, the magnetic field, aligned along the molecular axis, enhances the binding by reducing the bond length and increasing the dissociation energy. The results reported here are more accurate than previously reported computations up to about 10^9 G, covering not only the whole range of laboratory-accessible fields but also an important part of the range of fields of astrophysical interest.

II. FORMALISM

The Hamiltonian for the one-electron diatomic molecule in a homogeneous magnetic field directed along the molecular axis is

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Z_a e^2}{r_a} - \frac{Z_b e^2}{r_b} + \frac{Z_a Z_b e^2}{R} + \frac{eB}{2mc}L_z + \frac{e^2 B^2}{8mc^2}(x^2+y^2) . \tag{1}$$

As is well known, for a vanishing magnetic field this Hamiltonian is separable in prolate spheroidal coordinates[9]

$$\lambda = (r_a + r_b)/R , \quad 1 \leq \lambda < \infty ,$$

$$\mu = (r_a - r_b)/R , \quad -1 \leq \mu \leq 1 ,$$

$$0 \leq \phi \leq 2\pi .$$

The linear term in the magnetic field can be dealt with trivially, but the operator in the quadratic term obtains in these coordinates the nonseparable form $x^2 + y^2 = (\frac{1}{2}R)^2(\lambda^2 - 1)(1 - \mu^2)$. We shall attempt to construct the best wave function, in a variational sense, which can be written in the product form $\psi = L(\lambda)M(\mu)\Phi(\phi)$. After integrating over ϕ, we obtain the following variational expression for the energy (in atomic units $\hbar = e = m = 1$):

$$-\epsilon\tfrac{1}{2}R^2\left(\int \lambda^2 L^2 d\lambda \int M^2 d\mu - \int L^2 d\lambda \int \mu^2 M^2 d\mu\right)$$

$$= \int d\lambda\, d\mu\, LM[\hat{\mathfrak{L}} + \hat{\mathfrak{M}} + \beta(\mu^4\lambda^2 - \mu^2\lambda^4)]LM\ , \qquad (2)$$

where

$$\hat{\mathfrak{L}} = \frac{d}{d\lambda}(\lambda^2 - 1)\frac{d}{d\lambda} - \frac{m_z^2}{\lambda^2 - 1} + R\lambda(Z_A + Z_B) + \beta(\lambda^4 - \lambda^2)\ ,$$

$$\hat{\mathfrak{M}} = \frac{d}{d\mu}(1 - \mu^2)\frac{d}{d\mu} - \frac{m_z^2}{1 - \mu^2} + R\mu(Z_B - Z_A) + \beta(\mu^2 - \mu^4)$$

$$\epsilon = E - Z_A Z_B/R - Bm_z/2c\ , \quad \beta = -R^4B^2/64c^2\ .$$

We shall use the abbreviated notation

$$\langle\mu^n\rangle \equiv \int_{-1}^{1} \mu^n M^2 d\mu\ , \quad \langle\lambda^n\rangle \equiv \int_{1}^{\infty} \lambda^n L^2 d\lambda\ ,$$

$$\langle\hat{\mathfrak{M}}\rangle \equiv \int_{-1}^{1} M\hat{\mathfrak{M}}M\, d\mu\ , \quad \langle\hat{\mathfrak{L}}\rangle \equiv \int_{1}^{\infty} L\hat{\mathfrak{L}}L\, d\lambda\ .$$

Variation of Eq. (2) with respect to L results in

$$[\hat{\mathfrak{L}} - p^2(\lambda^2 - 1) + c + \beta(\langle\mu^4\rangle\lambda^2 - \langle\mu^2\rangle\lambda^4)]L = 0\ , \qquad (3)$$

where $c = \langle\mathfrak{M}\rangle + p^2(\langle\mu^2\rangle - 1)$ and $p^2 = -\frac{1}{2}\epsilon R^2$. Similarly, variation with respect to M results in

$$[\hat{\mathfrak{M}} - p^2(1 - \mu^2) - c' + \beta(\langle\lambda^2\rangle\mu^4 - \langle\lambda^4\rangle\mu^2)]M = 0\ , \qquad (4)$$

where $c' = -\langle\hat{\mathfrak{L}}\rangle - p^2(1 - \langle\lambda^2\rangle)$. Multiplying Eq. (3) by L and integrating, we obtain the connection between c and c',

$$c' = c + \beta(\langle\mu^4\rangle\langle\lambda^2\rangle - \langle\mu^2\rangle\langle\lambda^4\rangle)\ .$$

The same connection can be derived from Eq. (4). For $\beta = 0$ (a vanishing magnetic field), the L and M equations reduce to the exactly separated equations of the free hydrogen molecular ion.

III. METHOD OF SOLUTION

The pair of eigenparameters (p, c), or (p, c'), is determined in the process of finding normalizable solutions L and M to Eqs. (3) and (4). This is very much like the H_2^+ eigenvalue problem without a magnetic field and the commonly used method of series representations in terms of convenient functions[10] is applicable. Very accurate results can be obtained rapidly by this technique[11] if one is careful to choose efficient representations. The introduction of a magnetic field means that the efficiency of a representation must be studied as the field strength varies. Another technical difficulty is the introduction of more complex recurrence relationships for the expansion coefficients of most representations. These reasons, plus the fact that for nonvanishing magnetic fields Eqs. (3) and (4) are approximate and extreme precision is therefore not warranted, indicate that alternate methods should be given consideration.

A numerical method that meets the restrictions just stated has recently been reported[12] and applied to the one-electron–diatomic-molecule problem.[13] This technique generates the eigenfunctions and eigenvalues to problems such as that defined by Eqs. (3) and (4) by numerical integration techniques. (See Refs. 12 and 13 for a more detailed discussion.) The adaptation of the computer code described in Ref. 12 to the problem defined in Sec. II is now described.

Values for the expectation values $\langle\mu^2\rangle$, $\langle\mu^4\rangle$, $\langle\lambda^2\rangle$, and $\langle\lambda^4\rangle$ are required to define the eigenvalue problem. The L and M eigenfunctions are not initially available, so an iteration technique is used. The initial guesses for the expectation values are generated by extrapolating in β from $\beta = 0$ for a fixed R and/or extrapolating in R for fixed β. Once guesses for the expectation values are available, a set of eigenvalues is found by use of the code described in Ref. 12 and new expectation values are generated from the resulting eigenfunctions. Seven or fewer of these iterations were used in obtaining the data presented here. The differences between the last two iterations were used as the accuracy guide. On this basis, the last figure presented here may be uncertain.

This iteration technique appears to become unstable for large β as well as for poor guesses of the initial expectation values. It was observed computationally that once β becomes large enough to make convergence difficult, any improvement in the expectation-value guess can only slightly extend the useful range of β. Since the physical model is observed to become inaccurate before the iteration technique breaks down, these convergence properties were not studied in detail.

Two special features of this problem have an influence on the adaptation of the two-parameter eigenvalue computer code described in Ref. 12. The gerade-ungerade symmetry makes it possible to replace one of the boundary conditions on M by a condition at the regular point $\mu = 0$ that reflects the desired symmetry. Half of the integration range for μ can then be ignored, and precise conformity to the symmetry conditions is ensured. The second feature concerns the nature of the singularities at $\mu = \pm 1$ and $\lambda = 1$. The behavior of M and L is known to be as $(1 - \mu)^{\pm m/2}$ for $\mu \sim 1$, $(\mu + 1)^{\pm m/2}$ for $\mu \sim -1$, and $(\lambda - 1)^{\pm m/2}$ for $\lambda \sim 1$. Obviously either of the two independent solutions is integrable in the neighborhoods of these singularities if $|m| < 2$. This type of singular behavior can seriously limit the accuracy available from the numerical techniques being used.[12] The obvious device of replacing these singular problems with conditions derived from the appropriate series representations and applied at points slightly removed from the singular points was used. This makes the adaptation of the program described in Ref. 12 a little more awkward but its performance is considerably improved, allowing an increase of the range of parameters for which a given accuracy can be obtained.

IV. HYDROGEN ATOM

Setting $Z_a = 1$ and $Z_b = 0$, we see that the Hamiltonian reduces to that of the hydrogen atom in a magnetic field. The Hamiltonian still contains a dependence on R through the definition of the prolate spheroidal coordinates, but the exact eigenvalues and eigenfunctions are, of course, R independent. In view of the fact that the separable variational wave function is not an exact eigenfunction of this Hamiltonian, the corresponding energy still depends on R. However, this energy is an upper bound to the exact (R-independent) energy for the lowest electronic states with a given symmetry. R can therefore be treated as an additional variational parameter. Solutions to Eqs. (3) and (4) cannot be generated for $R = 0$. However, the optimum hydrogen-atom energies for the $1s$, $2p_0$, and $2p_{+1}$ states were found for the smallest R values for which the numerical techniques were stable. For the $2s$ state the $R \rightarrow \infty$ energy is the optimal result. The hydrogen-atom energies for large R define the $R \rightarrow \infty$ results for H_2^+ and are, therefore, used in computing the H_2^+ dissociation energies. Energies for the best R as well as for $R \rightarrow \infty$ are presented in Table I. The results indicate that the dependence of the energy on R is rather weak for fields below ~10^9 G, suggesting that the form of the wave function is adequate, up to that magnetic field strength.

TABLE I. Hydrogen atom in a magnetic field.

State	B(G)	$E_{R_{\mathrm{opt}}}$ (a.u.)		$E_{R=\infty}$ (a.u.)
$1s$	1×10^8	−0.499 548		−0.499 548
	5×10^8	−0.489 06		−0.488 96
	1×10^9	−0.459 68		−0.458 37
	5×10^9	0.053 34		0.104 8
	1×10^{10}	0.925 1		1.077
	3×10^{10}	5.010		
	5×10^{10}	9.414		
	1×10^{11}	20.88		
$2s$	1×10^8		−0.120 7	
	5×10^8		−0.055 08	
	1×10^9		0.060 80	
$2p_0$	1×10^8	−0.122 37		−0.120 5
	5×10^8	−0.077 58		−0.051 4
	1×10^9	0.010 18		0.071 9
$2p_{+1}$	1×10^8	−0.098 59		−0.098 52
	5×10^8	0.064 73		0.069 33
	1×10^9	0.315 2		0.330 6

This conclusion agrees well with other computations, which indicate that the present results are fairly accurate up to fields of ~10^9 G. At 4.7×10^9 G the ground-state binding energy is 27.03 eV, compared to 27.8 eV obtained by Surmelian and O'Connell[14] using a linear combination of Slater-type orbitals and 26.9 eV obtained by Rau and Spruch[15] using a product of a hydrogenic and a Landau wave function. For fields higher than ~10^{10} G the quality of the present results deteriorates very rapidly. These are clear indications that this approach is valid for intermediate fields such as those typical of white dwarfs, but not for the much higher fields of pulsars.

V. RESULTS AND DISCUSSION

The procedure described in Secs. II and III is applicable to all the discrete states of the hydrogen molecular ion. For obvious reasons we have con-

TABLE II. Equilibrium bond length, energy, ionization and dissociation energies for the ground state of H_2^+.

B (G)	R_e (a.u.)[a]	E_e (a.u.)	E_I (eV)[a]	E (a.u.)
0	1.997 (2.0)	−0.602 63	16.398 (16.09)	0.102 63
1×10^8	1.996 (2.0)	−0.602 35	16.969 (16.64)	0.102 80
5×10^8	1.976 (1.95)	−0.595 48	19.097 (18.77)	0.106 52
1×10^9	1.921 (1.90)	−0.575 06	21.436 (21.12)	0.116 69
5×10^9	1.448 (1.40)	−0.152 25	33.084 (33.05)	0.257 0
1×10^{10}	1.159 (1.10)	0.625 87	40.851 (41.36)	0.451
3×10^{10}	0.768 (0.70)	4.425 7	53.220 (56.25)	
5×10^{10}	0.630 (0.60)	8.595 1	55.534 (45.98)	
1×10^{11}	0.487	19.560	46.58	

[a] Values in parentheses from Lai and Suen, Ref. 4. The ionization energy is defined relative to a free electron in the same magnetic field.

TABLE III. Equilibrium bond length, energy, and dissociation energy for low-lying excited states of H_2^+.

State	B(G)	R_e (a.u.)	E_e (a.u.)	E(a.u.)
$2p\sigma_\mu$	0	12.55	−0.500 061	0.000 061
	1×10^8	12.55	−0.499 610	0.000 062
	5×10^8	11.90	−0.489 050	0.000 09
	1×10^9	10.55	−0.458 567	0.000 20
	5×10^9	5.73	0.100 97	0.003 8
	1×10^{10}	4.18	1.064 7	0.012
$3d\sigma_g$	0	8.834	−0.175 049	0.050 05
	1×10^8	8.780	−0.172 703	0.052 2
	5×10^8	8.217	−0.129 393	0.078 0
	1×10^9	7.792	−0.040 912	0.112 9
	5×10^9	7.258	0.895 65	
	8×10^9	7.375	1.661 6	
$2p\pi_u$	0	7.931	−0.134 514	0.009 51
	1×10^8	7.700	−0.109 157	0.010 64
	5×10^8	5.920	0.044 811	0.024 52
	1×10^9	4.725	0.284 957	0.045 6
	5×10^9	2.482	2.559 31	
$4f\sigma_u$	0	20.93	−0.130 655	0.005 655
	1×10^8	20.62	−0.126 819	0.006 1
	5×10^8	18.21	−0.067 250	0.012 2
	1×10^9	16.78	0.039 150	0.021 6

centrated on the ground state. Results are also presented for several excited states. These states are defined as the self-consistent solutions to Eqs. (3) and (4) that have a nodal structure identical to the $\beta=0$ limit. Such solutions are exact in the $\beta=0$ limit.

The results for the ground-state equilibrium energy and bond length are presented in Table II. It follows from the structure of the computational method that the results for the lower magnetic fields ought to be very accurate. The comparison with the variational results of Lai and Suen[4] indicates that at least up to 5×10^9 G our results are superior. The situation at higher magnetic fields is somewhat confusing, as the energy values at 1×10^{10} and 3×10^{10} G are lower in the Lai and Suen approach, but our method takes over again at higher fields, before breaking down at ~10^{11} G.

The excited states that have been considered are $2p\sigma_u$, $3d\sigma_g$, $2p\pi_u$, and $4f\sigma_u$ (Table III). These four states represent different physical situations, namely, repulsive states, a state on nonzero angular momentum, and states which are not the lowest of their symmetry species.

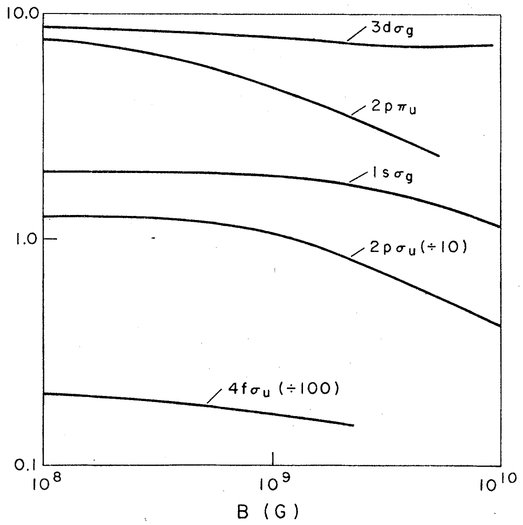

FIG. 1. Equilibrium bond length of H_2^+ in a magnetic field.

The essentially repulsive $2p\sigma_u$ state does possess a shallow polarization minimum at $R\sim12.5$ a.u. The effect of the magnetic field on the location of this minimum is very similar to that observed for the ground state (see Fig. 1). This is remarkable in view of the fact that the origin of the minimum in the $2p\sigma_u$ state is very different from that in the ground state. The same decrease in equilibrium bond length is observed for the $2p\pi_u$, $3d\sigma_g$, and $4f\sigma_u$ states. However, the $3d\sigma_g$ results indicate a remarkable feature above ~5×10^9 G, namely, the equilibrium bond length goes through a minimum and seems to start increasing with increasing magnetic field. This is the first observation of this type of behavior, but since it occurs for magnetic fields higher than those for which our method is quantitatively reliable, it may not be indicative of the actual situation. However, the possibility of an increase in the equilibrium internuclear distance at very high magnetic fields, probably only for states with a sufficiently complex nodal structure, must be kept in mind until further examination.

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[1] For a recent comprehensive review see R. H. Garstang, Rep. Prog. Phys. 40, 105 (1977).

[2] C. P. de Melo, R. Ferriera, H. S. Brandi, and L. C. M. Miranda, Phys. Rev. Lett. 37, 676 (1976).

[3] R. K. Bhaduri, Y. Nogami, and C. S. Warke, Astrophys. J. 217, 324 (1977).

[4] C. S. Lai and B. Suen, Can. J. Phys. 55, 609 (1977).

[5] C. S. Lai, Can. J. Phys. 55, 1013 (1977).

[6] L. C. de Melo, T. K. Das, R. C. Ferreira, L. C. M. Miranda, and H. S. Brandi, Phys. Rev. A 18, 12 (1978).

[7] M. Zaucer and A. Azman, Phys. Rev. A 18, 1320 (1978).

[8] J. Katriel and G. Adam, Chem. Phys. Lett. 10, 533 (1971).

[9] H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (Wiley, New York, 1967).

[10] D. R. Bates and R. H. G. Reid, *Advances in Atomic and Molecular Physics*, edited by D. R. Bates and I. Estermann (Academic, New York, 1968), Vol. 4, p. 13.

[11] J. M. Peek, J. Chem. Phys. 43, 3004 (1965).

[12] P. B. Bailey, Appl. Math. Comput. (to be published).

[13] P. B. Bailey, J. Chem. Phys. 69, 1676 (1978).

[14] G. L. Surmelian and R. F. O'Connell, Astrophys. J. 190, 741 (1974); 204, 311(E) (1976).

[15] A. R. P. Rau and L. Spruch, Astrophys. J. 207, 671 (1976).