PHYSICAL REVIEW A **76**, 042502 (2007)

Ground state of the H_2^+ molecule in oblique magnetic fields

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(Received 7 March 2007; published 4 October 2007)

Calculations in the Born-Oppenheimer approximation of curves for the ground-state energy of the H_2^+ ion vs the separation, R, of its protons in magnetic fields making oblique angles θ with the line connecting the protons have recently been published. It is shown here that these curves are qualitatively incorrect. The variational trial function employed fails to approximate well the wave function of the H_2^+ ground state for oblique fields, even though this function gives very accurate results for $\theta=0$. A trial function is proposed which gives much more accurate potential curves in oblique fields. It is used to plot and tabulate ground-state binding energies for various values of θ, R, and magnetic field strength.

DOI: 10.1103/PhysRevA.76.042502 PACS number(s): 31.15.Pf

I. INTRODUCTION

The discovery of extremely strong magnetic fields associated with white dwarf and neutron stars has fostered interest in the structure of molecules in such fields. A comprehensive review of theoretical studies of a number of simple molecules has been given by Turbiner and Vieyra [1]. Copious references can be found there to the considerable work devoted to the simplest of all molecules, H_2^+, at high magnetic fields, B. High magnetic fields, for the purposes of the present paper, are fields for which $\gamma \geq 1$, where $\gamma = B/B_0$ and $B_0 = 2.35 \times 10^5$ T. (Physically, γ is the ground-state energy of a free electron in the magnetic field B in units of the hydrogen Rydberg.) Much attention has been focussed on finding the equilibrium separation of the protons, R_{eq}, and the corresponding molecular binding energy when the field lies along the molecular axis. Quite recently, extremely accurate values of these quantities as a function of magnetic field have been calculated, in the Born-Oppenheimer approximation [2].

Less well explored is the situation in which the magnetic field makes some arbitrary nonzero angle, θ, with the molecular axis. This situation is important because even though high magnetic fields tend to produce strong alignment of the molecular axis along the magnetic field, the molecule cannot be completely aligned; it must execute zero-point oscillations around $\theta=0$ [3].

"Weak-field" binding energies as a function of R, the proton separation, and θ have been given in [3]. Energies at $\theta=90°$ and $\gamma=1$ have been tabulated as a function of R by Wille [4]. Wille, in that same paper, has presented molecular energies for all values of θ at $R=2$ and $\gamma=1$ graphically (Fig. 17), showing that to a good approximation the increase of energy with θ from its value at $\theta=0$ is proportional to $\sin^2\theta$, as it is in the weak-field limit.

In contrast to the work of Vincke and Baye and of Wille, who employ expansions in large sets of basic functions to describe the ground state (and excited states) of H_2^+, Turbiner and Vieyra (TV) have attempted a variational description of the ground state (and excited states) using a superposition of a small number (three) functions in which the energy is minimized with respect to variational parameters [5]. A similar, though less elaborate, study along the same lines was carried out by Brigham and Wadehra [6]. This kind of approach, where only one or a linear combination of a few physically motivated trial functions are employed, is adopted here also; it can offer, in principle, a relatively transparent physical understanding of the wave function, as well as provide accurate energies.

At $\theta=0$ values of R_{eq} and the corresponding energies found by TV are very close to the results of Ref. [2], which are effectively exact. For $\theta=90°$, there exists at present no published calculation comparable in accuracy to those at $\theta=0$, nonetheless the results obtained by TV were consistently better than those in Ref. [3] and quite comparable to those of Wille for $R=R_{eq}$ for $\gamma \leq 10$, where Wille's calculations are most accurate. The only tabulated results for energies of H_2^+ at $0 < \theta < 90°$ available in the literature are those of TV. Given the high degree of accuracy displayed at these end-point values of θ one might well have expected that the ansatz of TV should give comparably accurate values at intermediate values. As is shown in the present paper, that does not turn out to be the case. Furthermore, each curve of energy vs R for fixed values of θ intermediate between 0 and 90° displayed in Ref. [5] has an unphysical discontinuity in the first derivative at one value of R, R_{cr}, where it also shows an unphysical maximum.

In the first part of this paper a brief discussion is given of a simple variational approximation to the ground-state wave function of a hydrogen atom in a high magnetic field, assuming that the proton has infinite mass. With this wave function in hand, trial functions for the ground state of the H_2^+ molecule are constructed, again assuming infinite proton mass. Results are presented in the second section and compared to previous calculations along with discussion of the origin of inaccuracies of the TV trial function.

II. CONSTRUCTING THE H_2^+ GROUND-STATE TRIAL FUNCTION

The Hamiltonian for the hydrogen atom in a uniform magnetic field along the z direction, γ, is conventionally written:

$$H_{at}(0,0) = -\nabla^2 - 2/r + (\gamma/i)\,\partial/\partial\phi + \gamma^2\rho^2/4, \qquad (1)$$

where atomic units are employed, except that the unit of energy is the Rydberg. Spin is neglected throughout this pa-

TABLE I. Comparison of hydrogen atom binding energies in the ground state from the present paper, $E_{at}^{(p)}$, and values which are exact to the number of places quoted, $E_{at}^{(K)}$, vs dimensionless magnetic field, γ.

γ	$E_{at}^{(p)}$	$E_{at}^{(K)}$
1	1.66232	1.66234
10	3.4944	3.4956
100	7.5637	7.5796

per. In writing Eq. (1) it is assumed that the proton is at the origin and that the vector potential, $\vec{A}$, which describes the uniform magnetic field is in the symmetric gauge and centered at the origin (by "centered at the origin" is meant that $\vec{A}$ vanishes there):

$$\vec{A}=0.5\gamma(-y,x,0). \tag{2}$$

In Eq. (2) $\rho^2=(x^2+y^2)$ and $r=(\rho^2+z^2)^{1/2}$, where x, y, and z are the Cartesian coordinates of the electron position.

There is substantial literature devoted to finding eigenvalues and eigenfunctions of Eq. (1). In this paper, only the ground state is of interest, and it will be approximated by the five-parameter variational trial function

$$\psi_{at}(\vec{r})=\phi(\vec{r})\exp(-\kappa\tilde{r}), \tag{3}$$

where

$$\phi(\vec{r})=\exp(-g\rho^2-s\rho^2\tilde{r}-\delta z^2), \tag{4}$$

and $\tilde{r}=(\rho^2+\alpha z^2)^{1/2}$. Binding energies (the least energies required to tear apart the atom so that the electron has infinite separation from the proton but still remains in the magnetic field) are given in Table I in the column $E_{at}^{(p)}$. There they are compared to the effectively exact results of Kravchenko *et al.*, $E_{at}^{(K)}$, which are truncated to facilitate comparison [7]. Since variational energies are always greater than the corresponding exact energies, variational binding energies are always too low; they are lower bounds to the exact binding energy. The errors apparent in the variational binding energies in Table I increase with increasing γ, but they seem to be reasonably small considering that only five parameters are employed [8].

In the absence of magnetic field the hydrogen-atom Hamiltonian (unlike that of H_2^+) is isotropic, thus the energy cannot depend at all on the direction of an applied magnetic field, but only on its magnitude. Suppose now that the magnetic field is rotated counterclockwise in the y-z plane about an arbitrarily chosen x axis so that it makes an angle θ with the z axis. Then

$$\vec{B}=B(0,-\sin\theta,\cos\theta). \tag{5}$$

It is desirable, at this point, to introduce rotated coordinate systems for which the z axis lies along the magnetic field direction and the origin of coordinates lies at an arbitrary general point on the z axis $(0,0,Z)$,

$$x'=x, \tag{6}$$

$$y'=y\cos\theta+(z-Z)\sin\theta, \tag{7}$$

$$(z-Z)'=-y\sin\theta+(z-Z)\cos\theta. \tag{8}$$

The appropriate wave function for the hydrogen atom thus becomes $\psi_{at}(\vec{r}\,')=\phi(\vec{r}\,')\exp(-\kappa\tilde{r}')$ with the primed variables defined by the equations above with $Z=0$.

A vector potential centered at the origin which is appropriate in this case can be written [3]

$$\vec{A}(\theta)=[-\xi_y\gamma_y z-\xi_z\gamma_z y,(1-\xi_z)\gamma_z x,(1-\xi_y)\gamma_y x], \tag{9}$$

where $\gamma_y=B_y/B_0$, $\gamma_z=B_z/B_0$ and ξ_y and ξ_z are variational parameters. The vector potential given by Eq. (2) is the special case for which $\gamma_y=0$ and $\xi_z=0.5$.

Now suppose that the proton is not at the origin, but is located at point z_0 on the z axis. Then one has two choices. One can redefine the vector potential of Eq. (9) by replacing z by $(z-z_0)$ (so that it is once again centered on the proton) and retain the atomic wave function $\psi_{at}(\vec{r}\,')$ but simply replace the coordinate z' by $(z-z_0)'$ in that wave function. This shifted wave function is denoted by $\psi_{at}(\vec{r}\,',z_0)$, and the corresponding shifted factor ϕ in Eq. (4) by $\phi(\vec{r}\,',z_0)$. Here the relations between the rotated variables (primed system) and the unrotated variables are given by Eq. (7) and Eq. (8) with $Z=z_0$. Alternatively, one could retain the original vector potential of Eq. (9) but multiply the shifted atomic wave function by

$$U(z_0)=\exp(-i\xi_y\gamma_y z_0 x). \tag{10}$$

One can think of $U(z_0)$ as a unitary operator which shifts the gauge center from the origin to the point $(0,0,z_0)$. To see this, note that the Hamiltonian for the H atom with nucleus at z_0 in a magnetic field at angle θ to the z axis can be written [3]

$$H_{at}(\theta,z_0)=\left(\frac{1}{i}\frac{\partial}{\partial x}-\xi_y\gamma_y z-\xi_z\gamma_z y\right)^2+\left[\frac{1}{i}\frac{\partial}{\partial y}+(1-\xi_z)\gamma_z x\right]^2+\left[\frac{1}{i}\frac{\partial}{\partial z}+(1-\xi_y)\gamma_y x\right]^2-2/r_B, \tag{11}$$

where $r_B=[x^2+y^2+(z-z_0)^2]^{1/2}$. It is simple to verify that $U(z_0)^{-1}H_{at}(\theta,z_0)U(z_0)$ is just the expression on the right-hand side of the above equation with z inside the leftmost parenthetical expression replaced by $z-z_0$. Thus the gauge center has been shifted from the origin to the point $(0,0,z_0)$.

Having completed discussion of how one can write a hydrogen atom wave function in a magnetic field with the gauge center at the origin, the proton displaced from the origin and the magnetic field in an arbitrary direction, we can now proceed to construct an elementary trial function for the H_2^+ molecule in oblique fields, using the linear combination of atomic orbitals (LCAO) method. [9] The Hamiltonian for H_2^+ is

$$H_{mol}=H_{at}(\theta,z_0)-2/r_A+2/R, \tag{12}$$

where the distance of the electron from proton A is given by $r_A=[x^2+y^2+(z+z_0)^2]^{1/2}$, $2/R$ represents the proton-proton repulsive energy and $z_0=R/2$. The proposed LCAO wave function, which is the superposition of atomic orbitals centered on protons located at $(0,0,-z_0)$ (proton A) and $(0,0,z_0)$ (proton B), has the form

$$\psi_{mol}^{(0)} = U(z_0)\psi_{at}(\vec{r}',z_0) + U(-z_0)\psi_{at}(\vec{r}',-z_0). \tag{13}$$

It is important to note that the Hamiltonian of Eq. (12) is invariant under reflection in the x-y plane [10], and that $\psi_{mol}^{(0)}$ is likewise invariant. This follows from the fact that the component of magnetic field perpendicular to the molecular axis (in this case, the y component of the field) changes sign upon this reflection, so that under reflection $U(z_0)\to U(-z_0)$.

In the absence of a magnetic field, the exact eigenfunctions of H_{mol} can be classified as either even (gerade) or odd (ungerade) under reflection through the plane (the x-y plane) which perpendicularly bisects the line connecting the protons. This classification is not possible in general when a magnetic field is present because the gauge chosen need not preserve this reflection symmetry. (For example, if the magnetic field has a component perpendicular to the line connecting the protons, and the gauge chosen is centered on one of the protons, the Hamiltonian will clearly have lost its reflection symmetry; its exact eigenfunctions will be neither gerade nor ungerade.) However, for any choice of gauge corresponding to a uniform magnetic field there will always exist a unitary transformation which carries the eigenfunctions of such an unsymmetrical Hamiltonian into a set of eigenfunctions, each of which is either gerade or ungerade. (This is merely a transformation which moves the gauge center to the center of the line connecting the protons.) To avoid this complication, it is desirable to choose the gauge center initially at the midpoint of the line connecting the protons (the origin in the coordinate system employed here), as has been done above, so that the resulting Hamiltonian in the presence of a uniform magnetic field in an arbitrary direction achieves the highest possible degree of symmetry.

Although suitable in the limit $R\to\infty$, $\psi_{mol}^{(0)}$ is not sufficiently accurate for values of R at which the overlap of $\psi_{at}(\vec{r}',z_0)$ and $\psi_{at}(\vec{r}',-z_0)$ is not negligible. To improve upon it, one must realize that the x' and y' directions are not physically equivalent unless $\theta=0$ so that the factor $\exp(-g\rho'^2)$ should be replaced by $\exp(-\tau x'^2 - Ay'^2)$.

A further improvement is made if one employs a Guillemin-Zener type wave function [9], which, introducing the variational parameter β, has the form

$$\psi_{mol}^{(1)} = U(z_0)\phi_{at}(\vec{r}',z_0)\exp(-\beta\tilde{r}_A' - \kappa\tilde{r}_B') + \mathcal{R} \tag{14}$$

where

$$\begin{aligned}\tilde{r}_A' &= [x'^2 + y'^2 + \alpha(z+z_0)'^2]^{1/2}\\ &= \{r_A^2 + (\alpha-1)[y\sin\theta - (z+z_0)\cos\theta]^2\}^{1/2},\end{aligned} \tag{15}$$

$$\begin{aligned}\tilde{r}_B' &= [x'^2 + y'^2 + \alpha(z-z_0)'^2]^{1/2}\\ &= \{r_B^2 + (\alpha-1)[y\sin\theta - (z-z_0)\cos\theta]^2\}^{1/2},\end{aligned} \tag{16}$$

and

$$\phi_{at}(\vec{r}',z_0) = \exp[-\tau x'^2 - \mathrm{A}y'^2 - s\rho'^2\tilde{r}_B' - \delta(z-z_0)'^2]. \tag{17}$$

In Eq. (14) and elsewhere, $\mathcal{R}$ denotes the reflected function formed by replacing z by $-z$ everywhere in the function multiplied by U and replacing $U(z_0)$ by $U(-z_0)$.

To produce a more accurate trial function, a very important additional ingredient must be added. There is no reason that the gauge transformations U must be chosen to center the gauges on the proton positions as has been assumed above. It is preferable to allow the gauge centers associated with the U factors to be determined variationally. This can be accomplished by the replacement $U(z_0)\to U(\zeta z_0)$, which centers the gauge for proton B at ζz_0 rather than at the proton position, z_0, where ζ is a variational parameter [3]. At $\gamma=0$ $\psi_{mol}^{(1)}$ becomes equal to the Guillemin-Zener wave function and $\phi_{at}(\vec{r}',z_0)=1$. Since the nontrivial functional dependence of $\phi_{at}(\vec{r}',z_0)$ on the electron coordinates is "created" by the magnetic field it would seem reasonable to center this function at the center of the gauge (ζz_0). This leads finally to the ansatz

$$\psi_{mol}^{(2)} = \psi_B + \mathcal{R}, \tag{18}$$

where

$$\begin{aligned}\psi_B = {}&\exp(-i\xi_y\gamma_y\zeta z_0 x)\exp[-\tau x'^2 - \mathrm{A}y''^2 - s\rho''^2\tilde{r}_B''(\zeta z_0)\\ &- \delta(z-\zeta z_0)''^2]\exp(-\beta\tilde{r}_A' - \kappa\tilde{r}_B'),\end{aligned} \tag{19}$$

and where $\tilde{r}_B''(\zeta z_0)=[\rho''^2+\alpha(z-\zeta z_0)''^2]^{1/2}$, $\rho''^2=x^2+y''^2$ and the connection of y'' and $(z-\zeta z_0)''$ to the unprimed variables is given by Eq. (7) and Eq. (8) with $Z=\zeta z_0$. This is a ten-parameter wave function [in addition to the four parameters which arise from the hydrogen atom wave function (κ, α, δ, and s) there are τ, A, β, ξ_z,ξ_y, and ζ]. These are all varied independently to minimize the energy at fixed values of R and θ. The binding energies $E_B^{(2)}$ reported here are defined by

$$E_B^{(2)}(\theta,R) = \gamma - \langle\psi_{mol}^{(2)}|H_{mol}|\psi_{mol}^{(2)}\rangle/\langle\psi_{mol}^{(2)}|\psi_{mol}^{(2)}\rangle. \tag{20}$$

They represent lower bounds to the exact minimum energies required to produce infinite separation of all three constituent particles with the free electron remaining in the magnetic field. The integrals are carried out in prolate spheroidal coordinates in single precision.

At the cost of adding two more variational parameters, w and c, it is possible to produce a wave function which is slightly more accurate than $\psi_{mol}^{(2)}$ for $0<\theta<90°$, giving most improvement for θ near 45°, especially at large γ. This final ansatz is given by

$$\psi_{mol}^{(3)} = \{1 + c[y(z-\zeta z_0)]^2\}\exp[-wy''(z-\zeta z_0)'']\psi_B + \mathcal{R} \tag{21}$$

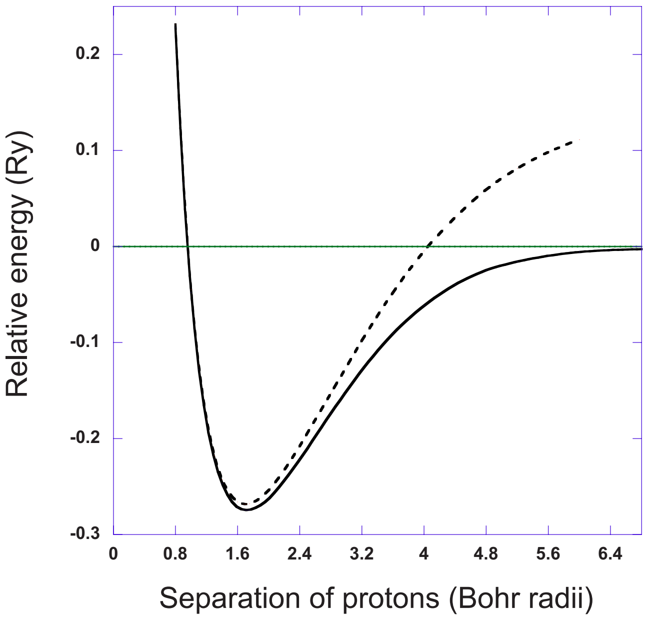

FIG. 1. (Color online) Difference between the energy of the H_2^+ ion and that of the H atom at $\gamma=1$ and $\theta=30°$ vs the separation of the protons. The dashed line arises from an approximation of the TV energies using Ψ_2. The solid curve is calculated from $\psi^{(3)}$ of the present paper.

and the corresponding binding energies, $E_B^{(3)}(\theta,R)$, by Eq. (20) with $\psi_{mol}^{(2)}$ replaced by $\psi_{mol}^{(3)}$. At the end points $\theta=0$ and $\theta=90°$, the optimum values of the two new parameters in $\psi_{mol}^{(3)}$ are zero, so that at the end points $\psi_{mol}^{(3)}=\psi_{mol}^{(2)}$.

III. RESULTS

It is of interest to compare the results of the present calculations to those of TV. The TV wave function was not easy for the author to reproduce, being the linear combination of three variational functions, each with its own set of parameters [5]. Its behavior can be usefully approximated by choosing just one of the three. For the following special parameter values in $\psi_{mol}^{(2)}$ of Eq. (18): $\zeta=s=\delta=0$, $\alpha=1$, and $\xi_y=\xi_z\equiv 1-\xi$, one obtains the wave function Ψ_2 in TV. This is the second of the three wave functions in the linear superposition employed in Ref. [5] when the parameter d in that paper is zero (which is its optimum value for $R<R_{cr}$). Using that wave function one can reproduce fairly closely the behavior of the binding energy for $R<R_{cr}$ reported in TV. As an example, for $\gamma=1$ and $\theta=30°$, the energies obtained from Ψ_2, plotted as the dashed curve in Fig. 1, are qualitatively very similar to the corresponding plot in Ref. [5]. The curve has been terminated at $R=6$, just slightly above the value of R_{cr} found in that reference. This curve shows the difference between the binding energy of the H atom and that of H_2^+ as a function of R. Since both the present calculation and that of TV are variational, the lower values plotted at each value of R are the more accurate ones.

It would seem intuitively that the large errors in the TV curve, which develop as R gets larger, reflect the increasing difficulty of the TV wave function to expand along the molecular axis in the presence of a component of magnetic field perpendicular to that axis. The wave function seeks to do this by decreasing the value of $1-\xi$ as R increases. This has the effect of reducing the compressive term $[(1-\xi)\gamma y']^2$ (which compresses the wave function along the y' direction) but at the cost of increasing the term $(\xi\gamma x)^2$ in the H_2^+ Hamiltonian in Ref. [5]. As a consequence, the wave function is compressed excessively along the x direction and too little along y, resulting in a spurious increase in energy. An extreme example of this occurs at the end point $R=6$ in Fig. 1 $(\gamma=1,\theta=30°)$ where the expectation values of x^2 and y^2 are 0.41 and 0.81, respectively, in Ψ_2 as compared to 0.52 and 0.60 in $\psi_{mol}^{(2)}$.

TABLE II. Coefficient, $A_{R_{eq}}$, of $\sin^2\theta$ in expansion of the ground state energy of H_2^+ when R assumes its equilibrium value, R_{eq}, vs dimensionless magnetic field, γ. $E_B^{(2)}(0,R_{eq})$ and $E_B^{(V)}$ are, respectively, ground state binding energies at $\theta=0$ from Eq. (20) and from Ref. [2].

γ	$A_{R_{eq}}$	R_{eq}	$E_B^{(2)}(0,R_{eq})$	$E_B^{(V)}$
1	0.057	1.752	1.94994	1.949976
10	0.818	0.958	4.34970	4.34977
100	5.92	0.448	10.2873	10.2922

The wave functions proposed here can adapt more freely to spreading of the wave function in the z direction by means of the parameter ζ, which is found to increase smoothly with R, approaching the value 1 at very large R values. Values of ξ_y and ξ_z remain not far from 0.5 over the whole range of R.

Cusps in curves of variational energy as a function of R were found by TV for $\theta\neq 0$. As a consequence of the Feynman-Hellman theorem and the fact that the ground state is nondegenerate at finite R, this cannot be a property of the exact ground-state energies of H_2^+. No such cusps (or discontinuities in the wave function) are found in the present calculation.

To focus attention on the θ dependence of the binding energy, it is useful to introduce E_θ defined by

$$E_\theta(\theta,R)=E_B(0,R)-E_B(\theta,R). \tag{22}$$

It seems likely that the calculation of TV, which gives excellent ground-state energies for $\theta=0$, significantly overestimates the rate of increase of E_θ with increasing θ, even when $\sin^2\theta\ll 1$. At small angles E_θ can be written $A_R\sin^2\theta$. The low-lying rotational energy levels of the H_2^+ molecule are sensitive to the value of $A_{R_{eq}}$. To estimate that value we

TABLE III. Comparison of binding energies at $\theta=45°$ from the present paper, $E_B^{(3)}(45,R)$, and from Ref. [5], $E_B^{(TV)}(45,R)$.

γ	R	$E_B^{(3)}(45,R)$	$E_B^{(TV)}(45,R)$
1	1.667	1.92438	1.918494
10	0.812	4.01919	3.97670
100	0.337	8.39046	8.29520

TABLE IV. Comparison of binding energies at θ=90° from the present paper, $E_B^{(2)}(90,R)$, and from Ref. [5], $E_B^{(TV)}(90,R)$.

γ	R	$E_B^{(2)}(90,R)$	$E_B^{(TV)}(90,R)$
1	1.635	1.9012	1.89911
10	0.772	3.7759	3.76830
100	0.320	7.3026	7.26543

TABLE VI. Binding energies calculated from $\psi_{mol}^{(3)}$ at various values of R at θ=30° for γ=100.

R	0.3	0.374	0.6	0.8	1.0	2.0
$E_B^{(3)}(30,R)$	8.9359	9.1612	7.657	7.605	7.583	7.565

have made polynomial fits to our calculations of E_θ as a function of $\sin^2\theta$ at γ=1, 10, and 100. Although the polynomial coefficients found depend on the order of the fitting polynomial, the coefficients of the linear term ($\sin^2\theta$) were quite stable to a change in order. For γ=1, the calculated E_θ curve is nearly linear in $\sin^2\theta$ (as mentioned earlier) but as γ increases those curves become more and more strongly concave downward. Results for $A_{R_{eq}}$ are given in Table II along with values of R_{eq}. Binding energies at θ=0 from the present calculation, $E_B^{(2)}(0,R_{eq})$, and effectively exact values [2], $E_B^{(V)}$, are also listed.

At γ=100, $A_{R_{eq}}$ calculated from Ψ_2 is more than 20% greater than the value listed in Table II at R_{eq}=0.448. That result supports the supposition that TV significantly overestimates $A_{R_{eq}}$. The values of $A_{R_{eq}}$ previously quoted by the present author [3] are only slightly higher than corresponding values in Table II for γ=1 and γ=100. A rather large discrepancy (13%) of unknown origin occurs at γ=10 [11].

At present the only published numerical values for energies of the ground state of H_2^+ with θ lying between 0 and 90° are those of TV, at θ=45°. Table III gives a comparison of $E_B^{(3)}$ and $E_B^{(TV)}$, binding energies reported by TV [5]. The improvement afforded by the present calculation is quite large, especially at γ=100 where the difference in binding energies is almost 0.1.

The values of R listed in Table III are those for which TV found minima in curves of energy vs R at θ=45°. The present calculations suggest that the exact positions of these minima lie at somewhat higher values of R. (Since the rotational equilibrium point of the molecule is at θ=0, the location of these minima do not appear to have any special physical significance.) For γ=100, the improvement in binding energy afforded by using $\psi_{mol}^{(3)}$ as in Table III as compared to $\psi_{mol}^{(2)}$ amounts to 0.0058. On the other hand, no improvement was detected at γ=1.

For θ=90° Wille gives the best existing tabulated energies available at the lower fields [4] and TV at the higher fields [5]. The present calculations are close to those of Wille at low fields and superior to those of TV (and Wille) at the high fields. Comparing $E_B^{(2)}(90,R)$ with Wille's results at γ=1 one finds that $E_B^{(2)}(90,R)$ is systematically lower than Wille's for $R \leq 5.0$ and higher for larger values of R. The largest difference found between Wille's values at γ=1 and $E_B^{(2)}(90,R)$ occurs at R=3.5 where the Wille's value is higher by 0.0005.

In Table IV comparison for θ=90° is made between binding energies from the present calculation, $E_B^{(2)}(90,R)$ [or equivalently $E_B^{(3)}(90,R)$] and the results of TV [5] quoted at R values at curve minima (as determined by TV). For all fields the present calculations give more accurate energies. Wille has quoted a binding energy at γ=4.255 ($B=10^6$ T) of 2.8992 and R=1.067 which is higher than $E_B^{(2)}(90,1.067)$ by 0.0006; however, with increasing field Wille's calculation rapidly loses accuracy. At γ=42.55 ($B=10^7$ T) and R =0.428, Wille's binding is much lower than $E_B^{(2)}(90,0.428)$ evaluated at that field.

It would seem useful to present some benchmark energies with which future calculations could be compared as they become available. This is done in Tables V and VI. Table V lists binding energies at various fields and angles at values of R_{eq} corresponding to the equilibrium separation at θ=0 for each field (these values of R_{eq} are listed in Table II). Table VI gives binding energies at θ=30° and γ=100 for various values of R including the maximum binding, which occurs at R=0.374.

Note added. I was originally unable to come up with a definitive estimate of the errors of the binding energies reported here. In all cases where comparisons had been possible, the results found here are close to or better than the most accurate binding energies tabulated in the current literature. However, recently, I became aware of preliminary nonvariational results by Baye [12] which indicate that at γ=1 the error of the present calculations increases monotonically from 4×10^{-5} at θ=0 to 16×10^{-5} at θ=90° in Table IV. There can be little doubt that $E_B^{(3)}(\theta,R)$ calculated here becomes less accurate with increasing γ; however, even at γ =100 the error at θ=0 is only 0.005. There is no obvious reason why the error of the present calculation should be expected to rise rapidly with increasing θ, at least for those small values of θ important for low-lying rotational states of the molecule. That supposition is confirmed for γ=1 by the results of Baye quoted above.

TABLE V. Binding energies calculated from $\psi_{mol}^{(3)}$ at various values of θ and at R_{eq} for θ=0 at each value of dimensionless magnetic field, γ.

γ	$E_B^{(3)}(15,R_{eq})$	$E_B^{(3)}(30,R_{eq})$	$E_B^{(3)}(45,R_{eq})$	$E_B^{(3)}(60,R_{eq})$	$E_B^{(3)}(75,R_{eq})$
1	1.94634	1.93669	1.92372	1.91102	1.90187
10	4.29597	4.15800	3.98952	3.84211	3.74628
100	9.9069	9.0385	8.1815	7.6079	7.3200

ACKNOWLEDGMENTS

I wish to express my gratitude to Professor Alexander Turbiner for bringing his very useful and comprehensive review article to my attention, for a number of stimulating discussions, and especially for his encouragement. I am also grateful to Professor Daniel Baye for communicating to me some of his preliminary results. I am grateful to the Department of Mathematics at Tufts University for their generous hospitality during the time this work was performed.

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[11] It should be noted that there is a contribution to the rotational motion of the H_2^+ molecule resulting from the diamagnetism of the protons themselves. Imagine a rigid molecule consisting only of two protons with fixed separation R in a uniform magnetic field making angle θ with the molecular axis. The molecule will seek to align itself along the field via a diamagnetic interaction term given by $(\gamma R \sin \theta)^2/8M_p$, where M_p is the ratio of the proton mass to the electron mass. (See the equation for H_{1B} in Ref. [3].) This term is a correction to E_θ and, for $R=R_{eq}$, is not negligible at very high fields.

[12] D. Baye (private communication).