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S. H. Patil

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Hydrogen molecular ion and molecule in two dimensions

S. H. Patil
Department of Physics, Indian Institute of Technology, Bombay 400 076, India

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We discuss some general properties of the wave functions of H$_2^+$ in two dimensions, when the electron is close to the nucleus, and when it is far away from the nucleus. Based on these properties, some simple, parameter-free wave functions are developed for some of the states. They lead to quite accurate energies and give an insight into the structure of H$_2^+$ in two dimensions. These wave functions and appropriate correlation functions, are then used to develop reliable wave functions for H$_2$ in two dimensions. They provide a clear and interesting comparison with the corresponding results in three dimensions. © 2003 American Institute of Physics. [DOI: 10.1063/1.1531103]

I. INTRODUCTION

The energies and wave functions of H$_2^+$ and H$_2$ are illustrative examples of molecular properties. As such they have received a great deal of attention. Analysis of these systems is generally based on the Born–Oppenheimer approximation in which the electronic wave functions are developed with localized nuclei. Many different types of model wave functions have been developed, numerical, perturbative, and variational, which have produced results of varying accuracy, simplicity, and insight. An important result is that the interaction produces an attractive potential in the ground state, for both H$_2^+$ and H$_2$.

Recently, two dimensional problems have received considerable attention. They can be used to simulate particles in a thin layer, for example in semiconductor layers. Theoretically, Bastard has analyzed the hydrogen impurity states in a quantum well. As the width of the well tends to zero, the problem reduces to that of an atom in two dimensions. The hydrogen atom in two dimensions has analytical solutions. The hydrogen molecular ion H$_2^+$ in two dimensions has been analyzed numerically using the method of continued fractions to solve the Schrödinger equation, and energy plots are available for the ground state and the first excited state. For the ground state of H$_2$ in two dimensions, Heitler-London type of wave function has been considered, which provides a broad understanding of the properties of the molecule. However, the H$_2^+$ and H$_2$ in two dimensions are of considerable importance and deserve a more comprehensive structural analysis, and an extension to excited states. It may be noted that one has interdimensional degeneracy which relates energy eigenstates in different dimensions for one electron systems. In particular, the D-dimensional eigenstates of H$_2^+$ are related to the suitably scaled three-dimensional eigenstates of H$_2^+$ with modified quantum numbers. This has been analyzed in detail by Frantz and Herschbach, especially their behavior in larger dimensions.

Here, we consider the energy eigenfunctions of H$_2^+$ in two dimensions in terms of confocal elliptic coordinates which are related to the three dimensional elliptic cylinder coordinates. Some general properties of these wave functions are analyzed and a designation for the states in terms of the symmetry properties and the properties of the united atom, is suggested. Numerical solutions are obtained for some of the low-lying states. We also analyze some general properties of the wave functions in the domains when an electron is close to the nucleus, when the two electrons are close to each other, and when an electron is far away from other particles. We then develop simple but accurate model wave functions for some states of H$_2^+$ in two dimensions, which provide an insight into the physical structure of the states. We use these wave functions and an appropriate electron correlation function to develop wave functions for the ground state of H$_2$ in two dimensions. These parameter-free wave functions provide fairly accurate values for the energies of the molecule, and an interesting comparison with the corresponding results in three dimensions.

We use atomic units throughout, e = m$_e$ = ℏ = 1.

II. SOME GENERAL PROPERTIES

Here we discuss the two-dimensional elliptic coordinates and some general properties of the energy eigenfunctions of H$_2^+$ and H$_2$ in two dimensions. We take the nuclei A and B to be on the y axis, at (0, –R/2) and (0,R/2) with R being the internuclear separation.

A. Equations for H$_2^+$ in elliptic coordinates

The electronic Hamiltonian for H$_2^+$ is given by

$$H = -\frac{1}{2} \nabla^2 - \left( \frac{1}{r_a} + \frac{1}{r_b} \right),$$

(2.1)

where$r_a$ and$r_b$ are the distances of the electron form the nuclei A and B. In terms of confocal elliptic coordinates,

$$u = \frac{r_a + r_b}{R}, \quad v = \frac{r_a - r_b}{R},$$

(2.2)

one has
\[ \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{4}{R^2(u^2-v^2)} \left[ (u^2-1) \frac{\partial^2}{\partial u^2} + u \frac{\partial}{\partial u} + (1-v^2) \frac{\partial^2}{\partial v^2} - v \frac{\partial}{\partial v} \right], \quad (2.3) \]

and for the area element,

\[ dA = \left( \frac{R}{2} \right)^2 \frac{u^2-v^2}{[(u^2-1)(1-v^2)]^{1/2}} du \, dv. \tag{2.4} \]

These expressions can be obtained by taking appropriate derivatives and differential elements, or as part of three-dimensional elliptic cylinder coordinates.\(^{11}\) We also have for the electron position in terms of Cartesian coordinates with the origin at the center,

\[ x = \frac{1}{2} R [(u^2-1)(1-v^2)]^{1/2}, \quad y = \frac{1}{2} R u v. \tag{2.5} \]

It is pertinent to observe that for a given pair of values for \((u,v)\), \(x\) can take positive and negative values but with the same magnitude. Therefore, the ranges of \(u\) and \(v\) are

\[ u: \quad 1 \to \infty \]
\[ v: \quad -1 \to 1 \tag{2.6} \]

for positive values of \(x\), and for negative values of \(x\).

The Schrödinger equation for \(H_2^+\) in two dimensions is

\[ -\frac{1}{2} \left( \frac{2}{R} \right)^2 \frac{1}{u^2-v^2} \left[ (u^2-1) \frac{\partial^2}{\partial u^2} + u \frac{\partial}{\partial u} + (1-v^2) \frac{\partial^2}{\partial v^2} - v \frac{\partial}{\partial v} \right] \psi = \frac{4u}{R} \frac{1}{u^2-v^2} \psi = E \psi. \tag{2.7} \]

Taking a separable form

\[ \psi(u,v) = F(u)G(v), \tag{2.8} \]

we obtain from Eq. (2.7),

\[ (u^2-1) \frac{d^2F}{du^2} + u \frac{dF}{du} + 2RuF + \frac{1}{2} R^2E(u^2-1)F = SF, \tag{2.9} \]
\[ (v^2-1) \frac{d^2G}{dv^2} - v \frac{dG}{dv} + \frac{1}{2} R^2E(1-v^2)G = -SG, \]

with \(S\) being the separation constant. To separate out the singularity at \(u^2=1\) and \(v^2=1\), we take

\[ F(u) = (u^2-1)^{k/2} f(u), \]
\[ G(v) = (1-v^2)^{k/2} g(v), \tag{2.10} \]

which leads to

\[ (u^2-1) \frac{d^2f}{du^2} + (2k+1)u \frac{df}{du} + \left[ k + (k-1) \frac{u^2}{u^2-1} \right] f + \frac{2Ru + \frac{1}{2} R^2E(u^2-1) - S}{2} f = 0, \tag{2.11} \]
\[ (v^2-1) \frac{d^2g}{dv^2} - (2k+1)v \frac{dg}{dv} - \left[ k - (k-1) \frac{v^2}{1-v^2} \right] g + \frac{1}{2} R^2E(1-v^2) + S g = 0. \]

For \(f(u)\) and \(g(v)\) to be nonsingular at \(u^2=1\) and \(v^2=1\), we take

\[ k = 0,1. \tag{2.12} \]

The two possibilities correspond to solutions which are even or odd under \(x \to -x\). With this choice of \(k\), the equations reduce to

\[ (u^2-1) \frac{d^2f}{du^2} + (2k+1)u \frac{df}{du} + \left[ k + 2Ru + \frac{1}{2} R^2E(u^2-1) - S \right] f = 0, \tag{2.13} \]
\[ (v^2-1) \frac{d^2g}{dv^2} + (2k+1)v \frac{dg}{dv} + \left[ k + \frac{1}{2} R^2E(1-v^2) - S \right] g = 0. \]

These equations are to be solved under the conditions that \(f(u)\) and \(g(v)\) are nonsingular and bounded in the physical domain. It is interesting to observe that these equations could be obtained\(^{10}\) from the corresponding equations in three dimensions, with an appropriate choice of half-integer values for the angular momentum quantum number.

### B. Symmetry properties for \(H_2^+\)

Since the Hamiltonian for \(H_2^+\) is invariant under \(v \to -v\) and/or \(x \to -x\), the energy eigenfunctions will have well defined parity, i.e., they will be even or odd under \(v \to -v\) and/or \(x \to -x\). We will designate our states as

\[ g/u \quad \text{for even/odd states under } (v \to -v, x \to -x) \tag{2.14} \]

and

\[ +l- \quad \text{for even/odd under } (x \to -x) \tag{2.15} \]

which correspond to \(k=0,1\). It may also be noted that one has

\[ u \to \frac{2r}{R}, \quad v \to \hat{r} \cdot \hat{R} \quad \text{for } R \to 0, \tag{2.16} \]

where \(\hat{r}, \hat{R}\) are unit vectors, and the wave function tends to a factorized form in which one part depends only on \(r\) and the other factor only on the angle. Therefore, for \(R \to 0\), our solutions tend to the united atom energy eigenstates with well defined values for \(|m|\) where \(m^2\) are the eigenvalues of the operator.
\[ L_\phi^2 = (xp_y - yp_x)^2 = -\frac{\partial^2}{\partial \phi^2}, \]  
\[ n = n + |m| + 1, \]  
where \( n = 1.2 \ldots \) is the principal quantum number, and \( n_p \) is the radial quantum number. Altogether, the H\(_2^+\) states in two dimensions will be specified by the combined atom designation with the principal quantum number \( n \), the value of \( |m| \) in terms of \( s,p,d, \ldots \) and symmetry properties under \( x \rightarrow -x \) and total inversion. To be specific, the ground state will be represented by

\[ \text{ground state: } 1s_g^+, \]  
where \( + \) indicates that the wave function is even under \( x \rightarrow -x \) and \( g \) denotes that it is even under total inversion \( x \rightarrow -x, v \rightarrow -v \). The first excited states will be

\[ 2p_{u}^+, 2p_{g}^+, 2s_g^+, \]  
where \( + \) and \( - \) denote reflection parity in \( x \), i.e., \( k=0,1 \) in Eq. (2.10), \( g \) and \( u \) are the gerade and ungerade states, and \( p \) and \( s \) correspond to \( |m| = 1,0 \), respectively.

### C. Coalescence and cusp conditions

The singular nature of the Coulomb potential reflects itself in terms of the behavior of the wave function when two particles approach each other. When the separation \( \vec{r} \) between the two particles tends to zero, the main terms in the Hamiltonian are

\[ \left( -\frac{1}{2\mu} \nabla^2 + \frac{q_1 q_2}{r} \right) \psi, \]  
where \( \mu \) is the reduced mass of the two particles with charges \( q_1, q_2 \). Taking only the angle-independent part of the wave function and using the expansion

\[ \psi_0 = C_0 + C_1 r, \]  
one gets for the two-dimensional case

\[ \left( -\frac{1}{2\mu} \nabla^2 + \frac{q_1 q_2}{r} \right) \psi = \left[ -\frac{1}{2\mu} \left( \frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} \right) + \frac{q_1 q_2}{r} \right] \psi = \left( -\frac{1}{2\mu} C_1 + q_1 q_2 C_0 \right) \frac{1}{r} + O(1). \]  
Therefore one gets the coalescence relation

\[ C_1 = 2\mu q_1 q_2 C_0, \]  
which refers to the angle-independent part of the expansion in Eq. (2.22). For example, when two electrons approach each other, the angle-independent part has the cusp behavior

\[ \psi_0 \rightarrow C_0(1 + r_{12}), \]  
where \( r_{12} \) is the separation between the electrons. It may be noted that coefficient of \( r_{12} \) is larger by a factor of 2 in the two-dimensional case than the corresponding coefficient in the three-dimensional case.

One can get a compact expression for the coalescence relation in terms of elliptic coordinates when the electron approaches one of the nuclei. Taking \( u \rightarrow 1, v \rightarrow \pm 1 \) in Eq. (2.13), one obtains

\[ \frac{1}{f} \frac{df}{du} \bigg|_{u=1} - \frac{1}{g} \frac{dg}{dv} \bigg|_{v=1} = -\frac{2R}{2k+1}, \]  
\[ \frac{1}{f} \frac{df}{du} \bigg|_{u=1} + \frac{1}{g} \frac{dg}{dv} \bigg|_{v=-1} = -\frac{2R}{2k+1}, \]  
where the second relation follows from the first relation with the observation that the function \( g(v) \) is odd or even under \( v \rightarrow -v \). These relations are similar to the corresponding relations in three dimensions, the main difference being that the term on the right-hand side is now larger by a factor of 2.

### D. Asymptotic behavior

The asymptotic region in \( u \) is important in determining the structure of the wave function for H\(_2^+\). For the \( u \)-part of Eq. (2.9), one considers

\[ F(u) = e^{-au} \sum_{i=0}^{\infty} C_i u^{B-i} \]  
for \( u \rightarrow \infty \).

Substituting this expression in Eq. (2.9) and equating the coefficients of the two leading terms in \( 1/u \), one obtains

\[ \alpha = R(-E/2)^{1/2}, \]  
\[ \beta = \frac{R}{\alpha - \frac{1}{2}}. \]  
The exponential part is particularly important in developing model wave functions.

### III. NUMERICAL SOLUTIONS FOR H\(_2^+\)

Numerical solutions are obtained for the first four states. This is done by solving Eq. (2.13) with two parameters, separation constant \( S \) and energy \( E \), with the requirement that the solutions are nonsingular and bounded in the physical domain, \( u: (1,\infty), v: (-1,1) \). It is convenient to use the variables

\[ u_1 = u - 1, \quad v_1 = v - 1, \]  
in terms of which Eq. (2.13) reduces to
$u_1(u_1 + 2) \frac{d^2 f}{du_1^2} + (2k + 1)(u_1 + 1) \frac{df}{du_1}$

$+ \left[ k + 2R(u_1 + 1) + \frac{1}{2} R^2 E u_1(u_1 + 2) - S \right] f = 0,$

$= 0.$

With the series expansions

$$f = \sum_{i=0} C_i u_i^I,$$

$$g = \sum_{i=0} D_i v_i^I,$$

we get recursion relations

$$C_{i+1} = \frac{\left[ i(i+2k) + k + 2R - S \right] C_i + \left( 2R + R^2 E \right) C_{i-1} + \frac{1}{2} R^2 E C_{i-2}}{2(i+1)(i+k+1/2)},$$

$$D_{i+1} = \frac{\left[ i(i+2k) - k - S \right] D_i + R^2 E D_{i-1} + \frac{1}{2} R^2 E D_{i-2}}{2(i+1)(i+k+1/2)}.$$ (3.4)

which can be used for obtaining the series solution. It may be noted that

$$C_{i+1} \to - \frac{1}{2} C_i \quad \text{for} \quad i \to \infty,$$

$$D_{i+1} \to - \frac{1}{2} D_i \quad \text{for} \quad i \to \infty,$$ (3.5)

which imply that the series converge for $|u_1| < 2$ and $|v_1| < 2.$

For obtaining nonsingular and bounded solutions in the domains $u_1: (0, \infty), \quad v_1: (-2, 0),$ one deduces from Eq. (3.2),

$$- (2k + 1) \frac{dg}{dv_1} \bigg|_{v_1 = -2} + (k - S) g \bigg|_{v_1 = -2} = 0.$$ (3.6)

We use the series solution in Eq. (3.3) and require that Eq. (3.6) is satisfied, which implies

$$\sum_{i=0} \left[ (k+1/2)i + k - S \right] (-2)^i D_i = 0.$$ (3.7)

This imposes one condition on $S$ and $E$ and ensures that we have a nonsingular solution for $g(v)$ in the domain $v: (-1, 1).$ For obtaining a bounded solution for $f(u),$ we first use the series in Eq. (3.3) to obtain the solutions at $u_1 = 1/2 - \Delta$ and $u_1 = 1/2$ for small $\Delta.$ Then we continue to higher values of $u_1$ by converting Eq. (3.2) into a different equation which leads to

$$f(u_1 + \Delta) = \frac{f(u_1)(2h_2 - h_2 \Delta^2) + f(u_1 - \Delta)(-h_2 + h_1 \Delta/2)}{h_2 + h_1 \Delta/2},$$

$$h_2 = k + 2R(u_1 + 1) + \frac{1}{2} R^2 E u_1(u_1 + 2) - S,$$ (3.8)

$$h_1 = (2k + 1)(u_1 + 1),$$

$$h_2 = u_1(u_1 + 2).$$

We now develop model wave functions for the lowest energy states with $k = 0.1,$ i.e., states which are even and odd under $x \to -x.$ We consider two types of wave functions which are similar to the James wave function\textsuperscript{13} and Guillemin–Zener wave function\textsuperscript{14} in three dimensions.
A. James type of wave function

We consider a wave function of the form

$$\psi = N (u^2 - 1)^{k/2} (1 - u^2)^{k/2} e^{-ax} (1 + au^2)^{1/2},$$

(4.1)

where $N$ is the normalization constant. Here, $k = 0$ corresponds to the $1s^2$ state and $k = 1$ to the $2p^2$ state. Requiring that the exponential asymptotic condition in Eqs. (2.27) and (2.28) is satisfied, one gets

$$\alpha = R (-E/2)^{1/2}.$$  

(4.2)

Furthermore, the coalescence condition in Eq. (2.26) implies that

$$-\alpha = \frac{2a}{1 + a} = -\frac{2R}{2k + 1},$$

(4.3)

which leads to

$$a = \frac{(2k + 1)\alpha - 2R}{2R - (2k + 1)(\alpha + 2)}.$$  

(4.4)

Thus, the parameters $\alpha$ and $a$ are related to the energy $E$ which is determined iteratively by requiring that the input energy and the output energy

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FIG. 1. Plot of the potential energy \( V(R) = E_{\text{tot}}(R) - E_{\text{int}}(\infty) \) as a function of the internuclear separation \( R \), for \( \text{H}_2^+ \) in two dimensions and three dimensions.

\[
E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \tag{4.5}
\]

are equal. Only about two or three iterations are required to ensure the equality to four decimal places.

The evaluation of the integrations is quite straightforward. In particular we note that for the integrations we may use the area element in Eq. (2.4) with limits of \((-1,1)\) for \( v \) and \((1,\infty)\) for \( u \), but also multiply it by a factor of 2 since the integration is to be carried out for both positive and negative values of \( x \). To be specific, we have

\[
\langle \psi_l | H | \psi_l \rangle = \frac{1}{2} R^2 N^2 \int dv \, du \, (u^2 - v^2)(u^2 - 1)^{k-1/2} \\
\times (1-v^2)^{k-1/2} e^{-2au} (1 + av^2)^{x}, \tag{4.6}
\]

where the \( v \)-integrations all reduce to terms of the type

\[
I_n = \int_{-1}^{1} \frac{dv}{(1-v^2)^{1/2}} u^n e^{-2au} \tag{4.8}
\]

The \( u \)-integrations are of the type

\[
J_n = \int_{1}^{\infty} \frac{du}{(u^2 - 1)^{1/2}} u^n e^{-2au} \tag{4.9}
\]

which are evaluated numerically. The predicted values of the total energy \( E_{\text{tot}} = E + 1/R \), normalization constant \( N \), and the parameter \( a \) are given in Tables III and IV, for the \( 1s^2 \) state with \( k = 1 \) and for the \( 2p^6 \) state with \( k = 0 \).

The predicted energies are generally close to the numerically deduced values over the range of interest. In particular, the predicted values of the position and depth of the potential well in the ground state are 0.515 and 0.8081 a.u. to be compared with the numerically derived values of 0.51 and 0.8221 a.u., respectively. The shallow well of the \( 2p^6 \) state is well described, the predicted values of the position and depth being 4.5 and 0.0238 a.u. to be compared with the

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numerically derived values of 4.5 and 0.0271 a.u., respectively. However, the description of the $1s_{g}^{+}$ state at larger values of $R$ is not adequate.

### B. Guillemin–Zener type of wave function

We now consider a Guillemin–Zener type\(^14\) of wave function

$$
\psi_{II} = N(u^{2} - 1)^{k/2}(1 - u^{2})^{k/2}e^{-\alpha u} \cosh(bv),
$$

(4.10)

where $N$ is the normalization constant. Here, $k = 0$ corresponds to the $1s_{g}^{+}$ state and $k = 1$ to the $2p_{u}^{+}$ state. The asymptotic condition in Eqs. (2.27) and (2.28) implies

$$
\alpha = R(-E/2)^{1/2}
$$

(4.11)

and the cusp condition in Eq. (2.26) leads to

$$
b \tanh(b) = \frac{2R}{2k+1} + \alpha = 0.
$$

(4.12)

Thus, for a given energy $E$, parameters $\alpha$ and $b$ are determined by using the relations in Eqs. (4.11) and (4.12). The energy $E$ is determined iteratively by requiring that the input energy and the output energy in Eq. (4.5) are equal. Again, only two or three iterations are required to ensure equality to four decimal places. The main quantities to be evaluated are,

\[
\langle \psi_{II}|\psi_{II} \rangle = \frac{1}{2}R^{2}N^{2} \int du dv (u^{2} - v^{2})(u^{2} - 1)^{k-1/2} \times (1 - u^{2})^{k-1/2}e^{-2a\alpha u} \cosh(bv)^2,
\]

(4.13)

\[
\langle \psi_{II}|H|\psi_{II} \rangle = -N^{2} \int du dv (u^{2} - 1)^{k-1/2} \times (1 - u^{2})^{k-1/2}e^{-2a\alpha u} \cosh(bv) \times [\alpha^{2}u^{2}a^{2} - \alpha^{2}u^{2} - \alpha^{2}u^{2} - 2k\alpha u + 2k\alpha u - \alpha^{2}] \cosh(bv)

+ (1 - u^{2})b^{2}\cosh(bv) - (2k + 1)bv \sinh(bv) + 2Ru \cosh(bv)].
\]

(4.14)

The $v$-integrations are of the type

$$
I_{v}^{n} = \int_{-1}^{1} \frac{dv}{(1 - v^{2})^{1/2}} u^{2n}[\cosh(bv)]^{2}
$$

$$
= \frac{\pi}{2^{2n+1}} \frac{(2n)!}{n!} \sum_{i=0}^{\infty} \frac{(2n + 2i)!b^{2i}}{(n + i)!(n + i + 1)! (2i)!}.
$$

(4.15)

\[
I_{u}^{n} = \int_{-1}^{1} \frac{dv}{(1 - u^{2})^{1/2}} u^{2n+1} \cosh(bv) \sinh(bv)
\]

$$
= \frac{\pi}{2^{2n+2}} \sum_{i=0}^{\infty} \frac{(2n + 2i + 1)!b^{2i+1}}{(n + i + 1)!(n + i + 2)!(2i + 1)!}.
$$

V. MODEL WAVE FUNCTION FOR $\text{H}_2$

Here, wave functions for the ground state of $\text{H}_2$ in two dimensions are developed using the James and Guillemin–Zener type of wave functions. They are taken to be a product of one-electron wave functions with an additional correlation function introduced to take into account the interaction between the electrons.

We first consider a wave function

$$
\psi = N \psi_{j}(\mathbf{r}_{1}) \psi_{k}(\mathbf{r}_{2}) f(r_{12}),
$$

(5.1)

where $\psi_{i}$ is the James type of wave function in Eq. (4.1),
with

\[ f(r_{12}) = 1 + r_{12}. \]  

(5.3)

This correlation function ensures the correct cusp behavior in Eq. (2.25) when the two electrons are close to each other. For the evaluation of energy \( E \),

\[ E_\text{tot} = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} + \frac{1}{R}, \]  

(5.4)

with

\[ H = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) - \frac{1}{r_{1a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} + \frac{1}{r_{12}}, \]  

(5.5)

it is very convenient to use the relation\(^{15}\)

\[ \int (\phi f) \nabla_1^2 (\phi f) d\tau = \int [f^2 \phi \nabla_1^2 \phi - \phi^2 (\nabla_1^2 f)^2] d\tau. \]  

(5.6)

The relevant quantities are

\[ \nabla_1^2 \psi_f(\vec{r}_1) = \left[ \frac{2 \alpha^2}{R^2} \left( \frac{1}{r_{1a}} + \frac{1}{r_{1b}} \right) \frac{1}{R} \left( \frac{1}{r_{1a}} + \frac{1}{r_{1b}} \right) \right] \psi_f(\vec{r}_1) \]

\[ + \frac{2a}{R^2} \left[ \frac{4 - 2 \frac{\vec{r}_{1a} \cdot \vec{r}_{1b}}{r_{1a} r_{1b}} \frac{r_{1a}}{r_{1a} r_{1b}} \frac{r_{1b}}{r_{1a} r_{1b}}}{r_{1a} r_{1b}} \right] e^{-a(r_{1a} + r_{1b})/R} \]  

(5.7)

and

\[ \nabla_1 f = \frac{\vec{r}_{12}}{r_{12}}. \]  

(5.8)

The integrations are carried out numerically using polar coordinates with origin at the center. The calculated values of the normalization constant \( N \), total energy \( E_\text{tot} \), and the potential energy \( V(R) \),

\[ V(R) = E_\text{tot}(R) - E_\text{tot}(\infty) \]  

(5.9)

are given in Table V. It is interesting to observe that the potential energy of H\(_2\) in two dimensions has a deep well of depth 1.286 a.u. at \( R = 0.4 \) a.u. which may be compared with the corresponding well\(^{1} \) of depth 0.1745 a.u. at \( R = 2.0 \) a.u. for H\(_2\) in three dimensions.

We also consider a wave function of the type

\[ \psi = N \psi_f(\vec{r}_1) \psi_f(\vec{r}_2) f(r_{12}), \]  

(5.10)

where \( \psi_f \) is the Guillemin–Zener type of wave function in Eq. (4.10),

\[ \psi_f(\vec{r}_1) = e^{-a r_{1a}} \cosh(b v) \]

\[ = \frac{1}{2} (e^{z_1 r_{1a} - z_2 r_{1b}} + e^{-z_1 r_{1a} - z_2 r_{1b}}), \]  

(5.11)

and \( f \) is the correlation function in Eq. (5.3). For the evaluation of the energy in Eq. (5.4), we again use the identity in Eq. (5.6) with

\[ \nabla_1^2 \psi_f(\vec{r}_1) = \left[ z_1^2 + z_2^2 + 2 z_1 z_2 \frac{r_{1a}}{r_{1a} r_{1b}} \right] \psi_f(\vec{r}_1) \]

\[ - \left( z_1 \frac{r_{1a}}{r_{1a} r_{1b}} + z_2 \frac{r_{1b}}{r_{1a} r_{1b}} \right) e^{-z_1 r_{1a} - z_2 r_{1b}} \]  

(5.12)

The calculated values of the normalization constant \( N \), total energy \( E_\text{tot} \) and the potential energy \( V(R) \) in Eq. (5.9) are given in Table V. The values of the potential energy \( V(R) \) are very close to the ones obtained from the James-type of wave function.

The potential energy \( V(R) \) for H\(_2\) in two dimensions, as a function of the internuclear separation \( R \) is plotted in Fig. 2. Since the values from James and Guillemin–Zener type of wave functions are very close to each other, we have plotted the average of the two values. This curve may be compared with the corresponding one for H\(_2\) in three dimensions. Clearly the potential well for H\(_2\) in two dimensions is much deeper and sharper than the one in three dimensions.
the united atom designation, numerically. The states are conveniently denoted in terms of ternuclear separations, by solving the separable equations.

energy eigenvalues are obtained for some states, for some in-

5 a.u. at R

and H 2 molecule in two dimensions.

The Schro¨ dinger equation for H 2 is separable in terms of two-dimensional elliptic coordinates which are related to the three-dimensional elliptic cylinder coordinates.11 The energy eigenvalues are obtained for some states, for some internuclear separations, by solving the separable equations numerically. The states are conveniently denoted in terms of the united atom designation, \( (n, |m|) \), where \( n \) is the principal quantum number and \( |m| \) is related to the eigenvalues \( m^2 \) of the square of the angular momentum in two dimensions. We use the notation \( s, p, \ldots \) for \( |m| = 0, 1, \ldots \). The states are also characterized by the reflection symmetry \( \pm \) under \( x \rightarrow -x \), and inversion symmetry \( g, u \) (gerade and ungerade states).

The ground state \( 1s^+_g \) has a deep well of depth 0.8221 a.u. at \( R = 0.515 \) a.u. which may be compared with the three-dimensional well\(^1\) of depth 0.1026 a.u. at \( R = 2.0 \) a.u. for the \( 1s \sigma_g \) state. The \( 2p^+_u \) state has a shallow well of depth 0.0271 a.u. at \( R = 4.5 \) a.u. which may be compared with the three-dimensional well\(^1\) of depth 0.0095 a.u. at \( R = 8.0 \) a.u. for the \( 2p \pi_u \) state. The position of the well seems to be inversely proportional to the united atom electron energy \( E_o \),

\[
R \approx \frac{4}{|E_o|},
\]

which gives positions of 2.0 a.u., 8.0 a.u. for the \( 1s \sigma_g \), and \( 2p \pi_u \) states, respectively, in three dimensions, and 0.5 a.u. and 4.5 a.u. for the \( 1s^+_g \) and \( 2p^+_u \) states, respectively, in two dimensions, which are quite close to the numerically calculated values.

The energy eigenfunctions have some simple properties in some specific domains. These are cusp, or coalescence conditions when two charged particles are close to each other, and asymptotic behavior when an electron is far away from other particles. We have developed two types of simple, model, parameter-free wave functions for the \( 1s^+_g \) and \( 2p^+_u \) states of \( H_2 \), incorporating these properties. They give quite accurate values for the energies in the domains of interest.

We have then used products of these one-electron wave functions and a correlation function for the two electrons to obtain model wave functions for \( H_2 \) in two dimensions. These wave functions imply the presence of a deep potential well of depth 1.286 a.u. at an internuclear separation of 0.4 a.u.

These model wave functions provide an insight into the physical structure of the energy eigenfunctions.

Apart from the theoretical interest, the \( H_2^+ \) and \( H_2 \) in two dimensions would be relevant for the description of \( H_2^+ \) and \( H_2 \) located in the junction of two parallel plates.

VI. SUMMARY

We have analyzed some properties of \( H_2^+ \) molecules ion and \( H_2 \) molecule in two dimensions.

The Schrödinger equation for \( H_2^+ \) is separable in terms of two-dimensional elliptic coordinates which are related to the three-dimensional elliptic cylinder coordinates.11 The energy eigenvalues are obtained for some states, for some internuclear separations, by solving the separable equations numerically.

The ground state \( 1s^+_g \) has a deep well of depth 0.8221 a.u. at \( R = 0.515 \) a.u. which may be compared with the three-dimensional well\(^1\) of depth 0.1026 a.u. at \( R = 2.0 \) a.u. for the \( 1s \sigma_g \) state. The \( 2p^+_u \) state has a shallow well of depth 0.0271 a.u. at \( R = 4.5 \) a.u. which may be compared with the three-dimensional well\(^1\) of depth 0.0095 a.u. at \( R = 8.0 \) a.u. for the \( 2p \pi_u \) state. The position of the well seems to be inversely proportional to the united atom electron energy \( E_o \),

\[
R \approx \frac{4}{|E_o|},
\]

which gives positions of 2.0 a.u., 8.0 a.u. for the \( 1s \sigma_g \), and \( 2p \pi_u \) states, respectively, in three dimensions, and 0.5 a.u. and 4.5 a.u. for the \( 1s^+_g \) and \( 2p^+_u \) states, respectively, in two dimensions, which are quite close to the numerically calculated values.

The energy eigenfunctions have some simple properties in some specific domains. These are cusp, or coalescence conditions when two charged particles are close to each other, and asymptotic behavior when an electron is far away from other particles. We have developed two types of simple, model, parameter-free wave functions for the \( 1s^+_g \) and \( 2p^+_u \) states of \( H_2 \), incorporating these properties. They give quite accurate values for the energies in the domains of interest.

We have then used products of these one-electron wave functions and a correlation function for the two electrons to obtain model wave functions for \( H_2 \) in two dimensions. These wave functions imply the presence of a deep potential well of depth 1.286 a.u. at an internuclear separation of 0.4 a.u. These model wave functions provide an insight into the physical structure of the energy eigenfunctions.

Apart from the theoretical interest, the \( H_2^+ \) and \( H_2 \) in two dimensions would be relevant for the description of \( H_2^+ \) and \( H_2 \) located in the junction of two parallel plates.


