

# A Boundary Condition Determined Wave Function for the H<sub>2</sub> (<sup>1</sup>Σ) molecule

U. Kleinekathöfer<sup>1,2</sup>, S.H. Patil<sup>1,3</sup>, K.T. Tang<sup>1,4</sup>, and J.P. Toennies<sup>1</sup>

<sup>1</sup>*Max-Planck-Institut für Strömungsforschung, Bunsenstr.10, D-37073 Göttingen, Germany*

<sup>2</sup>*Department of Chemical Physics, Weizmann Institute of Science, Rehovot 76100, Israel*

<sup>3</sup>*Department of Physics, Indian Institute of Technology, Bombay 400076, India*

<sup>4</sup>*Institute of Atomic and Molecular Sciences, Academia Sinica, P.O.Box 23-166, Taipei, Taiwan 106, Republic of China*

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Two relatively simple non-variational wave functions for two electron diatomic molecules are proposed. The electron-electron cusp condition is satisfied rigorously by a correlation function which has the correct behavior for  $r_{12} \rightarrow 0$  and  $r_{12} \rightarrow \infty$ . The electron-nucleus cusp conditions are also rigorously satisfied by the proposed functional forms of the wave functions. The parameters are chosen to match the asymptotic conditions in two different approximations. Both wave functions yield very good energies for the chemical bond. This demonstrates that these local conditions have a big effect on the wave function.

## I. INTRODUCTION

One of the milestones in our understanding of the chemical bond was the variational calculation of hydrogen molecules by Kołos and coworkers [1,2]. It was a great achievement of quantum mechanics in which detailed calculations including adiabatic, non-adiabatic, relativistic, and radiative corrections brought theory into complete agreement with experiments [3]. It also provided an unequivocal standard for testing our conceptual understanding of molecular interactions.

The exact eigenstates of the Hamiltonian have several well known properties. For example, the expectation value of the Hamiltonian has a minimum at the exact eigenfunction. This global property is the basis of variational calculations. In addition, there are local properties such as the spatial behavior of the wave functions in specific regions of the configuration space. Usually these local properties are not explicitly incorporated in the trial wave functions. Only by including a large number of terms are these local conditions satisfied collectively in an accurate variational calculation.

The importance of the local properties in two-electron-atoms and ions has been shown by us in a previous paper [4]. In this paper we wish to examine the importance of these local properties in the calculation of a chemical bond. We will show, that a relatively simple hydrogen molecular wave function with these properties can be constructed to yield fairly accurate results. Throughout the paper atomic units are used.

## II. LOCAL PROPERTIES OF THE WAVE FUNCTION

### A. Cusp conditions

For a system of charged particles, the wave function must satisfy certain cusp conditions when any interparticle distance goes to zero. Fundamentally the cusp conditions arise from the following two facts. First the eigenfunctions  $\Psi$  satisfying the Schrödinger equation,

$$(H - E)\Psi = 0, \tag{1}$$

are everywhere bounded. This was first proved by Kato [5]. Secondly the Coulomb interaction between two charged particles produces a diverging potential as they approach each other. Therefore the kinetic energy must provide a compensating divergence so that the sum of the kinetic and potential energies remains finite. This divergence is manifested as a cusp in the electronic wave function at zero interparticle separation.

Let us consider two charged particles (with masses  $m_i, m_j$  and charges  $q_i, q_j$ ) approaching each other while all other interparticle distances remain larger than zero. Under this situation,  $r_{ij} \rightarrow 0$ , the Coulomb interaction between these two particles dominates, and a compensating divergence must come from the kinetic energies of these two particles. Transforming the kinetic energy operators into the center of mass system of these two particles, we have

$$-\frac{1}{2m_i}\nabla_i^2 - \frac{1}{2m_j}\nabla_j^2 = -\frac{1}{2M}\nabla_S^2 - \frac{1}{2\mu}\nabla_{r_{ij}}^2, \quad (2)$$

where

$$M = m_i + m_j, \quad (3)$$

$$\mu = \frac{m_i m_j}{m_i + m_j}, \quad (4)$$

$$\vec{S} = \frac{m_i \vec{r}_i + m_j \vec{r}_j}{m_i + m_j}, \quad (5)$$

$$\vec{r}_{ij} = \vec{r}_i - \vec{r}_j. \quad (6)$$

Thus the main terms involving  $r_{ij}$  are

$$-\frac{1}{2\mu}\nabla_{r_{ij}}^2 + \frac{q_i q_j}{r_{ij}}. \quad (7)$$

Around the regular singular point  $r_{ij} = 0$ , the wave function can be expanded into a power series

$$\Psi = C_0 + C_1 r_{ij} + \mathcal{O}(r_{ij}^2). \quad (8)$$

With this wave function it is easy to show

$$\left(-\frac{1}{2\mu}\nabla_{r_{ij}}^2 + \frac{q_i q_j}{r_{ij}}\right)\Psi = \left(-\frac{1}{\mu}C_1 + q_1 q_2 C_0\right)\frac{1}{r_{ij}} + \mathcal{O}(1). \quad (9)$$

Therefore one gets

$$C_1 = \mu q_i q_j C_0. \quad (10)$$

This relation is usually expressed as the Kato condition

$$\lim_{r_{ij} \rightarrow 0} \left(\frac{\partial \Psi}{\partial r_{ij}}\right)_{av} = \mu q_i q_j \Psi(r_{ij} = 0), \quad (11)$$

where “ $av$ ” stands for spherical averaging. If we are dealing only with  $s$ -states, the average is not necessary [6].

For the two electron molecule shown in Fig. 1, the electronic wave function must have the behavior

$$\Psi \xrightarrow{r_{12} \rightarrow 0} \Phi_0(\vec{r}_1, \vec{r}_2) \cdot \left(1 + \frac{1}{2}r_{12} + \dots\right) \quad (12)$$

to take into account the electron-electron coalescence, since in this case  $m_1 = m_2 = 1$  and  $q_1 = q_2 = -1$ , therefore  $\mu q_1 q_2 = \frac{1}{2}$ . The function  $\Phi_0(\vec{r}_1, \vec{r}_2)$  in Eq. (12) is independent of  $r_{12}$ .

When  $r_{1a}$  in Fig. 1 goes to zero, the wave function must exhibit the coalescence behavior of electron 1 with nucleus  $a$ . In this case, assuming the nucleus is infinitely heavy compared with the electron, one has  $\mu = 1$  and  $\mu q_1 q_2 = -Z$ . Therefore the wave function must have the local property

$$\Psi \xrightarrow{r_{1a} \rightarrow 0} G_1(1 - Zr_{1a}), \quad (13)$$

where  $G_1$  is a function independent of  $r_{1a}$ . Similarly

$$\Psi \xrightarrow{r_{1b} \rightarrow 0} G_2(1 - Zr_{1b}), \quad (14)$$

$$\Psi \xrightarrow{r_{2a} \rightarrow 0} G_3(1 - Zr_{2a}), \quad (15)$$

$$\Psi \xrightarrow{r_{2b} \rightarrow 0} G_4(1 - Zr_{2b}). \quad (16)$$

These cusp conditions have been given for the hydrogen molecule by Kołos and Roothaan [7].

## B. Asymptotic behavior

The Hamiltonian of the two electron molecule shown in Fig. 1 can be written as

$$H = H^{(1)} + H^{(2)} \quad (17)$$

$$H^{(1)} = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_{1a}} - \frac{Z}{r_{1b}} + \frac{1}{r_{12}} \quad (18)$$

$$H^{(2)} = -\frac{1}{2}\nabla_2^2 - \frac{Z}{r_{2a}} - \frac{Z}{r_{2b}} + \frac{Z^2}{R}. \quad (19)$$

The ground state eigenfunction  $\Psi$  of the Hamiltonian  $H$  with eigenvalue  $E$  can be expanded in terms of the eigenfunctions of  $H^{(2)}$  as follows, with  $\vec{r}_1$  and  $\vec{r}_2$  also defined in Fig. 1:

$$\Psi = \sum_{n=0} u_n(\vec{r}_1) \phi_n(\vec{r}_2), \quad (20)$$

where  $\phi_n$  are eigenfunction of

$$H^{(2)} \phi_n(\vec{r}_2) = E_n^{(2)} \phi_n(\vec{r}_2). \quad (21)$$

For  $Z = 1$ ,  $E_n^{(2)}$  are clearly eigenvalues of the  $\text{H}_2^+$  system. Substituting Eq. (20) into Eq. (1) and projecting out  $\phi_n(\vec{r}_2)$ , we are left with

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_{1a}} - \frac{Z}{r_{1b}}\right) u_n(\vec{r}_1) + \sum_{n'} \langle \phi_n | \frac{1}{r_{12}} | \phi_{n'} \rangle u_{n'}(\vec{r}_1) = \epsilon_n u_n(\vec{r}_1) \quad (22)$$

where

$$\epsilon_n = E - E_n^{(2)}. \quad (23)$$

If  $r_1 \rightarrow \infty$  and  $r_1 \gg r_2$ , then the approximations  $r_{1a} \simeq r_{1b} \simeq r_1$  are all valid. Under these conditions, Eq. (22) becomes

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{2Z-1}{r_1}\right) u_n(\vec{r}_1) = \epsilon_n u_n(\vec{r}_1). \quad (24)$$

It is well known [8] that the solution of Eq. (24) has the asymptotic form

$$u_n(r_1) \xrightarrow{r_1 \rightarrow \infty} r_1^{(2Z-1)/\sqrt{2|\epsilon_n|}-1} e^{-\sqrt{2|\epsilon_n|}r_1}. \quad (25)$$

Asymptotically the leading term in the wave function of Eq. (20) is the one with the smallest exponent. Since we are dealing with negative energy bound states  $E < E_n^{(2)}$ , the smallest  $|\epsilon_n|$  of Eq. (23) is for  $n = 0$ . Therefore asymptotically

$$\Psi \xrightarrow{r_1 \rightarrow \infty} r_1^{(2Z-1)/\beta_1-1} e^{-\beta_1 r_1} \quad (26)$$

where, for the sake of clarity in later discussions  $\sqrt{2|\epsilon_0|}$  is designated as  $\beta_1$ ,

$$\beta_1 = \sqrt{2|\epsilon_0|}. \quad (27)$$

It is seen from Eq. (23) that  $|\epsilon_0|$  is the separation (ionization) energy of one electron from the molecule.

In the case where  $r_2$  is also large, that is  $r_2 \gg 1$  but still smaller than  $r_1$ , we can make similar approximations in Eq. (21). For  $r_{2a} \simeq r_{2b} \simeq r_2$ , Eq. (21) becomes

$$\left(-\frac{1}{2}\nabla_2^2 - \frac{2Z}{r_2}\right) \phi_0(\vec{r}_2) = \epsilon_1 \phi_0(\vec{r}_2) \quad (28)$$

where

$$\epsilon_1 = E_0^{(2)} - \frac{Z^2}{R}. \quad (29)$$

Since  $E_0^{(2)}$  is the ground state energy of the molecular ion, the value of  $\epsilon_1$  is the electronic energy (or separation energy) of the molecular ion. Again the asymptotic behavior of  $\phi_0(r_2)$  is

$$\phi_0(r_2) \longrightarrow r_2^{2Z/\beta_2-1} e^{-\beta_2 r_2} \quad (30)$$

where

$$\beta_2 = \sqrt{2|\epsilon_1|}. \quad (31)$$

Thus if both  $r_1$  and  $r_2$  are large, the wave function must have the following exponential behavior

$$\Psi \xrightarrow{r_1 > r_2 \gg 1} e^{-\beta_2 r_2} e^{-\beta_1 r_1}. \quad (32)$$

Using the relations of Eq. (27) and Eq. (31), we have

$$\beta_1^2 + \beta_2^2 = 2(|\epsilon_0| + |\epsilon_1|) = 2|\epsilon_t|, \quad (33)$$

where  $\epsilon_t$  is the total electronic energy.

### III. MODEL WAVE FUNCTIONS

In our approach the wave function is separated into two parts

$$\Psi(r_1, r_2, r_{12}) = \Phi(r_1, r_2) \cdot f(r_{12}), \quad (34)$$

where the second factor, which depends only on  $r_{12}$ , is called the correlation function  $f(r_{12})$ . This approximation was already introduced by Hylleraas in 1929 [9] and used often afterwards. In this paper we will use a new correlation function [4] which was used recently in treating two electron atoms and ions. We will then propose two different functional forms for  $\Phi$ , both of which rigorously satisfy all the electron-nucleus local boundary conditions. They also approximately satisfy the asymptotic conditions. These functional forms are therefore expected to provide realistic descriptions of the true wave function in the entire configuration space.

#### A. Electron-electron correlation function $\mathbf{f}(\mathbf{r}_{12})$

A wave function that does not satisfy the cusp condition of Eq. (12) will suffer a diverging local energy. Although the failure may not be too serious since the region of the configuration space where the cusp dominates is very small, it is still desirable to have the correct representation of the cusps since they provide the boundary conditions for the true wave function. This is demonstrated by the so called R12CI quantum chemistry calculations [10,11]. Essentially with an explicit correlation function

$$f(r_{12}) = 1 + \frac{1}{2}r_{12} \quad (35)$$

included in the trial wave function, the rate of convergence is drastically increased. However since this function increases linearly without bounds, it can give good results only in cases where the wave function is compact, that is the rest of the function is already very small in places where  $r_{12}$  becomes large. To remove this limitation, Le Sech [12] used a correlation function proposed by Hirschfelder [13]

$$f(r_{12}) = 1 + \frac{r_{12}}{2} e^{-r_{12}/d} \quad (36)$$

in his  $\text{H}_2$  calculation. This correlation function increases with  $r_{12}$  up to  $r_{12} = d$ , and then decreases to one as  $r_{12}$  goes to infinity. Since there is no *a priori* reason why the correlation function should have a local maximum the behavior of Eq. (36) is not entirely realistic.

Roothaan and Weiss [14] made a very accurate numerical investigation of the correlation function for the ground state of the He atom. They found that in the vicinity of  $r_{12} = 0$ , the correlation function is linear and satisfies the cusp condition of Eq. (12). It monotonically increases and approaches a constant as  $r_{12}$  becomes very large.

Recently we have proposed the following simple correlation function [4] which has the desired properties at  $r_{12} = 0$  and  $r_{12} \rightarrow \infty$ :

$$f(r_{12}) = 1 - \frac{1}{1 + 2\lambda} e^{-\lambda r_{12}}, \quad (37)$$

where  $\lambda$  is a parameter which can be determined variationally or by some other means (see below). The small  $r_{12}$  expansion of Eq. (37) is

$$f(r_{12}) = \frac{2\lambda}{1 + 2\lambda} \left( 1 + \frac{1}{2} r_{12} - \frac{\lambda}{4} r_{12}^2 + \dots \right). \quad (38)$$

Clearly it satisfies the cusp condition of Eq. (12) as  $r_{12} \rightarrow 0$ . Also  $f(r_{12})$  of Eq. (37) increases monotonically to unity as  $r_{12}$  goes to infinity. In this paper, we will use Eq. (37) as our correlation function.

### B. Space functions that satisfy the electron-nucleus cusp conditions

The electron-nucleus cusp conditions of Eq. (13) to Eq. (16) do not uniquely define the space wave function. In this paper we propose two different functional forms for  $\Phi(\vec{r}_1, \vec{r}_2)$  which satisfy these conditions. First let us consider

$$\Phi_1(\vec{r}_1, \vec{r}_2) = e^{-Z(r_{1a} + r_{1b} + r_{2a} + r_{2b})} [\cosh(Z' r_{1a}) \cosh(Z' r_{2b}) + \cosh(Z' r_{2a}) \cosh(Z' r_{1b})]. \quad (39)$$

Since

$$e^{-Z r_{1a}} \xrightarrow{r_{1a} \rightarrow 0} 1 - Z r_{1a} + \mathcal{O}(r_{1a}^2), \quad (40)$$

it is clear that the exponential function alone satisfies the four cusp conditions Eq. (13) to Eq. (16). The hyperbolic cosine function

$$\cosh(Z' r_{1a}) \xrightarrow{r_{1a} \rightarrow 0} 1 + \mathcal{O}(r_{1a}^2) \quad (41)$$

has no linear term as  $r_{1a}$  goes to zero. Therefore it does not alter the cusp condition of the exponential function. Thus Eq. (39) satisfies all the electron-nucleus coalescence conditions and at the same time has a free parameter  $Z'$ . Again this parameter can be determined variationally or by the asymptotic conditions as discussed in the next section.

If one wishes to maintain the electronic configuration idea with an independent particle picture, one can adopt the following form of the space wave function:

$$\Phi_2(\vec{r}_1, \vec{r}_2) = \phi(r_1)\phi(r_2) \quad (42)$$

with

$$\phi(r_1) = e^{-Z_1 r_{1a} - Z_2 r_{1b}} + e^{-Z_1 r_{1b} - Z_2 r_{1a}} \quad (43)$$

and an identical function for  $r_2$ . As  $r_{1a}$  approaches zero

$$\phi(r_1) \xrightarrow{r_{1a} \rightarrow 0} (1 - Z_1 r_{1a}) e^{-Z_2 R} + (1 - Z_2 r_{1a}) e^{-Z_1 R}. \quad (44)$$

Imposing the condition in Eq. (40) we get

$$(Z_1 e^{-Z_2 R} + Z_2 e^{-Z_1 R}) / (e^{-Z_2 R} + e^{-Z_1 R}) = Z \quad (45)$$

which leads to

$$Z_1 = Z + (Z - Z_2) e^{-(Z_1 - Z_2) R}. \quad (46)$$

Thus if  $Z_1$  and  $Z_2$  are related as in Eq. (45), then the electron-nucleus cusp conditions of Eq. (13) to Eq. (16) are automatically satisfied. Again one parameter  $Z_1$  (or  $Z_2$ ) can be determined either variationally or by the asymptotic condition as discussed in the next section.

## IV. DETERMINATION OF PARAMETERS IN THE WAVE FUNCTION

### A. Approximation for $\lambda$ in $f(\mathbf{r}_{12})$

With  $f(r_{12})$  written in the form of Eq. (37), the electron-electron cusp condition is automatically satisfied regardless of the value of the parameter  $\lambda$ . Therefore the energy is not expected to be very sensitive to  $\lambda$ . Indeed in our previous study [4] of the two electron atomic systems from He to Ne<sup>8+</sup>,  $\lambda$  can be changed by as much as 6 %, the energy remains the same for the first six significant digits. It was found that the energies computed with the variationally determined  $\lambda$  are essentially the same as given by the analytical expression,

$$\lambda = \frac{5}{12}Z - \frac{1}{3}, \quad (47)$$

derived from a theory in which  $1/r_{12}$  is treated as a perturbation.

In the molecular system, as long as the internucleus distance  $R$  is small, we assume  $\lambda$  can be determined in a similar way except with  $Z$  replaced by an effective charge  $Z_e$ . We estimate  $Z_e$  in the following way. First let us recall that in the original derivation [4] of Eq. (47), the zeroth order wave function is simply the product of two atomic orbitals

$$\phi_0 = e^{-Zr_1}e^{-Zr_2} \quad (48)$$

where  $Z$  is the nuclear charge which also enters into Eq. (47). Now in the molecular case, with  $1/r_{12}$  treated as a perturbation the zeroth order wave function is the product of a pair of molecular orbitals (index  $m$  for molecular)

$$\phi_0 = \psi_m(\vec{r}_1)\psi_m(\vec{r}_2) \quad (49)$$

where  $\psi_m(\vec{r}_1)$  satisfies

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_{1a}} - \frac{Z}{r_{1b}}\right)\psi_m(\vec{r}_1) = E\psi_m(\vec{r}_1). \quad (50)$$

Now we seek to approximate  $\psi_m(\vec{r}_1)$  with an atomic orbital  $e^{-Z_e r_1}$  where the effective charge  $Z_e$  is at the center of  $a$  and  $b$ . We determine  $Z_e$  by requiring the atomic energy  $-Z_e^2/2$  to be equal to the energy  $E$  of Eq. (50). Furthermore, we solve Eq. (50) perturbatively. Writing Eq. (50) as

$$(H_0 + H')\psi_m = E\psi_m \quad (51)$$

$$H_0 = -\frac{1}{2}\nabla_1^2 - \frac{2Z}{r_1} \quad (52)$$

$$H' = \frac{2Z}{r_1} - \frac{Z}{r_{1a}} - \frac{Z}{r_{1b}}, \quad (53)$$

we have a zeroth order wave function

$$\psi_0 = Ne^{-2Zr_1} \quad (54)$$

with zeroth order energy

$$\epsilon_0 = -\frac{4Z^2}{2}. \quad (55)$$

For evaluating the first order change in the energy we use the expansion

$$\frac{1}{r_{ij}} = \sum_l \frac{r_{\leq}^l}{r_{>}^{l+1}} P_l(\cos \Theta_{ij}) \quad (56)$$

which leads to

$$\langle \psi_0 | H' | \psi_0 \rangle = 64Z^4 \int_0^{R/2} \left(\frac{1}{r_1} - \frac{2}{R}\right) e^{-4Zr_1} r_1^2 dr_1 \xrightarrow{R \rightarrow 0} \frac{8}{3} Z^4 R^2. \quad (57)$$

Thus the energy of Eq. (50) to first order is

$$E \simeq -\frac{4Z^2}{2} + \frac{8}{3}Z^4R^2. \quad (58)$$

We require

$$-\frac{Z_e^2}{2} = -\frac{4Z^2}{2} + \frac{8}{3}Z^4R^2, \quad (59)$$

therefore

$$Z_e \simeq 2Z - \frac{4}{3}Z^3R^2. \quad (60)$$

By replacing  $Z$  in Eq. (47) by this  $Z_e$  and setting  $Z = 1$  we have for small  $R$

$$\lambda = \frac{5}{12}\left(2 - \frac{4}{3}R^2\right) - \frac{1}{3} = \frac{1}{2}\left(1 - \frac{10}{9}R^2\right), \quad R \rightarrow 0. \quad (61)$$

As  $R$  increases, we expect  $\lambda$  to decrease monotonically and become vanishing small for  $R \rightarrow \infty$ . It can be easily verified that the simplest Padé approximation to Eq. (61)

$$\lambda = \frac{1}{2} \frac{1}{1 + \frac{10}{9}R^2} \quad (62)$$

will give the small  $R$  behavior of Eq. (61) and also satisfy the large  $R$  requirement. Therefore we will use  $\lambda$  of Eq. (62) in the correlation function  $f(r_{12})$  of Eq. (37).

### B. Approximation for $Z'$ in $\Phi_1(\vec{r}_1, \vec{r}_2)$

In this subsection we will determine the parameter  $Z'$  in  $\Phi_1$  of Eq. (39) in such a way that the asymptotic conditions of the wave function are at least approximately satisfied. In the asymptotic region where  $r_1 \rightarrow \infty$  and  $r_1 \gg r_2$ ,  $r_{1a} \simeq r_{1b} \simeq r_1$ . The wave function of Eq. (39) will then have the behavior

$$\Phi(\vec{r}_1, \vec{r}_2) \xrightarrow{r_1 \rightarrow \infty} e^{-2Zr_1} e^{Z'r_1} g(r_2). \quad (63)$$

Since this does not exactly coincide with the asymptotic condition of Eq. (26), an additional approximation is necessary. First we write the asymptotic wave function of Eq. (26) in the following form:

$$\Psi_{asym}(r_1) = e^{-\beta_1 r_1 + ((2Z-1)/\beta_1 - 1) \ln r_1}. \quad (64)$$

Then we approximate  $\ln r_1$  by its linear behavior around the maximum point of the asymptotic density. That is

$$\ln r_1 = \ln r_0 + (r_1 - r_0) \frac{1}{r_0} + \dots \quad (65)$$

where  $r_0$  is the root of

$$\frac{d}{dr_1}(r_1^2 \Psi_{asym}^2) = 0. \quad (66)$$

With  $\Psi_{asym}$  given by Eq. (64), it is easy to show

$$r_0 = \frac{2Z-1}{\beta_1^2}. \quad (67)$$

Thus the  $r_1$  dependence of the asymptotic wave function of Eq. (64) is approximately

$$\Psi \xrightarrow{r_1 \rightarrow \infty} e^{-\beta_1^2/(2Z-1)r_1}. \quad (68)$$

Matching the  $r_1$  dependence of Eq. (63) with Eq. (68) we have

$$2Z - Z' = \frac{\beta_1^2}{2Z - 1}. \quad (69)$$

From Eq. (27) we recall that  $\beta_1^2$  is twice the ionization energy of the molecule which depends on the distance  $R$ ,

$$\beta_1^2 = 2E_i(R). \quad (70)$$

Specifically for the hydrogen molecule,  $Z = 1$ . When  $R$  goes to zero, the hydrogen molecule becomes a helium atom. The ionization energy of helium is 0.9037. When  $R \rightarrow \infty$ , it reduces to two hydrogen atoms. The ionization energy of a hydrogen atom is 0.5. Based on these limits, we estimate the ionization energy of the hydrogen molecule with the simple Padé approximation

$$E_i(R) = \frac{0.9037 + R}{1 + 2R}. \quad (71)$$

Thus for the hydrogen molecule,  $Z'$  from Eq. (69) is given by

$$Z' = 2 - 2\frac{0.9037 + R}{1 + 2R}. \quad (72)$$

This value of  $Z'$  was used in Eq. (39) for the energy computation.

### C. Determination of $Z_1$ and $Z_2$ in $\Phi_2(\vec{r}_1, \vec{r}_2)$

The alternative choice for the wave function  $\Phi_2$  is based on the independent particle picture of Eq. (42). Since  $r_1$  and  $r_2$  are treated on an equal footing, it is not possible to satisfy the asymptotic conditions of Eq. (26) and Eq. (30). Therefore we will use only the combined asymptotic condition of Eq. (33) which can be satisfied with  $\beta_1 = \beta_2$ .

For  $r_1 \rightarrow \infty$ ,  $r_{1a} \simeq r_{1b} \simeq r_1$ , Eq. (43) takes the form

$$\phi(r_1) \xrightarrow{r_1 \rightarrow \infty} e^{-(Z_1 + Z_2)r_1}. \quad (73)$$

Since  $\phi(r_2)$  must also have the same asymptotic behavior, therefore

$$\beta_1 = \beta_2 = Z_1 + Z_2. \quad (74)$$

It follows from Eq. (33) that

$$(Z_1 + Z_2)^2 = -\epsilon_t \quad (75)$$

where  $\epsilon_t$  is the total electronic energy of the molecule. On the other hand,  $Z_1$  and  $Z_2$  are related by Eq. (46) in order to satisfy the electron-nucleus cusp condition. Thus we can determine  $Z_1$  and  $Z_2$  iteratively in a self-consistent way. For example, we can first set  $Z_1 = 1$  and solve for  $Z_2$  from Eq. (46). With  $Z_1$  and  $Z_2$ , we calculate the energy. Then  $Z_1$  is calculated from Eq. (75) and the process is repeated. In our calculation for the hydrogen molecule, it took at most five iterations for the energy to converge within  $5 \cdot 10^{-4} E_h$ . The values of  $Z_1$  and  $Z_2$  obtained in this way are listed in Table I.

## V. ENERGY COMPUTATION

In this section we summarize the formulas used for the energy calculation. They are given as a function of the nuclear charge  $Z$ . For the hydrogen molecule,  $Z$  is of course equal to one.

The energy as the expectation value of the Hamiltonian is given by

$$E = \frac{-\langle \Psi | \nabla_1^2 | \Psi \rangle + \langle \Psi | V | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (76)$$

where



$$V = -Z \left( \frac{1}{r_{1a}} + \frac{1}{r_{1b}} + \frac{1}{r_{2a}} + \frac{1}{r_{2b}} \right) + \frac{1}{r_{12}} + \frac{Z^2}{R}. \quad (77)$$

With  $\Psi = \Phi \cdot f$ , it can be shown [12] that

$$-\langle \Psi | \nabla_1^2 | \Psi \rangle = \int \left( -\Phi f^2 \nabla_1^2 \Phi + \Phi^2 \vec{\nabla}_1 f \cdot \vec{\nabla}_1 f \right) d^3 r_1 d^3 r_2. \quad (78)$$

With  $f$  given by Eq. (37),  $\vec{\nabla}_1 f$  becomes

$$\vec{\nabla}_1 f = \frac{\lambda}{1 + 2\lambda} \cdot \frac{\vec{r}_{12}}{r_{12}} e^{-\lambda r_{12}}. \quad (79)$$

For  $\Phi = \Phi_1$  of Eq. (39),

$$\begin{aligned} \nabla_1^2 \Phi = & \left( 2Z^2 + Z'^2 + 2Z^2 \frac{\vec{r}_{1a} \cdot \vec{r}_{1b}}{r_{1a} r_{1b}} - \frac{2Z}{r_{1a}} - \frac{2Z}{r_{1b}} \right) \Phi_1 \\ & + 2 \left[ \left( -ZZ' \frac{\vec{r}_{1a} \cdot \vec{r}_{1b}}{r_{1a} r_{1b}} - ZZ' + \frac{Z'}{r_{1b}} \right) \sinh(Z' r_{1b}) \cosh(Z' r_{2a}) \right. \\ & \left. + \left( -ZZ' \frac{\vec{r}_{1a} \cdot \vec{r}_{1b}}{r_{1a} r_{1b}} - ZZ' + \frac{Z'}{r_{1a}} \right) \sinh(Z' r_{1a}) \cosh(Z' r_{2b}) \right] e^{-Z(r_{1a} + r_{1b} + r_{2a} + r_{2b})}. \end{aligned} \quad (80)$$

For  $\Phi = \Phi_2$  of Eq. (42),

$$\begin{aligned} \nabla_1^2 \Phi = & \left( Z_1^2 + Z_2^2 + 2Z_1 Z_2 \frac{\vec{r}_{1a} \cdot \vec{r}_{1b}}{r_{1a} r_{1b}} \right) \phi(r_1) \phi(r_2) \\ & - \left[ \left( \frac{2Z_1}{r_{1a}} + \frac{2Z_2}{r_{1b}} \right) e^{-Z_1 r_{1a} - Z_2 r_{1b}} + \left( \frac{2Z_1}{r_{1b}} + \frac{2Z_2}{r_{1a}} \right) e^{-Z_1 r_{1b} - Z_2 r_{1a}} \right] \phi(r_2), \end{aligned} \quad (81)$$

where  $\phi(r_1)$  is given by Eq. (43) and  $\phi(r_2)$  is given by an identical formula with  $r_1$  replaced  $r_2$ .

The five dimensional integrals were carried out with the Monte Carlo method using the program VEGAS [21]. Sufficient points are chosen such that the maximum estimated error in energy is nowhere greater than  $8 \times 10^{-4} E_h$ . For the most part, the accuracy is considerably better.

## VI. RESULTS AND DISCUSSION

The energies of the hydrogen molecule computed from  $\Psi_1 = \Phi_1 \cdot f$  (with  $\Phi_1$  given by Eq. (39) and  $f$  by Eq. (37)) and from  $\Psi_2 = \Phi_2 \cdot f$  (with  $\Phi_2$  given by Eq. (42)) are shown in Table II and Fig. 2. The exact energies of Kołos et al. [1,2] are also shown for comparison as diamonds. Since the wave function  $\Psi_1$  is an analytical continuous function of  $R$ , the corresponding energies are shown in Fig. 2 as the solid curve, whereas the energies from  $\Psi_2$ , which are obtained from the self-consistent calculation, are shown in Fig. 2 as crosses. For  $R \geq 3.6a_0$  they lie above the asymptotic limit  $-1$ . This is not unexpected. Since  $\Psi_2$  has the character of an independent particle wave function, it will dissociate to the wrong energy limit as is well known in single configuration molecular orbital calculations. It is however very gratifying to see in the region of chemical bond, that the present results from either  $\Psi_1$  and  $\Psi_2$  closely follow the exact values. To put these results in proper perspective, we list the energies at the potential minimum obtained from various calculations in Table III. There it can be seen that the present results are even better than the energies computed from double configuration SCF and from molecular orbital calculations with 28 configurations.

Both  $\Psi_1$  and  $\Psi_2$  used in our calculations are non-variational wave functions. All parameters are determined by the cusp and asymptotic conditions. If the two parameters (one in  $\Phi$  and one in  $f$ ) are determined variationally, the results will be either as good as or better than the present ones, because the energies are bounded from below by the minimum principle.

Despite these very good results, we wish to emphasize that neither the form of the wave function nor the procedure in matching the asymptotic conditions used here are unique. The purpose of the present study was to demonstrate that the local properties such as the cusp and asymptotic conditions can be exploited to place rather stringent bounds on the wave function, without using the variational principle. As far as we are aware, no previous attempt has been made to explicitly incorporate all these conditions into the wave function. It is indeed quite surprising that even a relatively simple wave function as derived here is able to yield such accurate results.

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$R$	$Z_1$	$Z_2$
0.5	1.4487	0.1345
1.0	1.2744	0.1818
1.2	1.2320	0.1801
1.4	1.1977	0.1755
1.6	1.1681	0.1696
2.0	1.1221	0.1553
3.0	1.0534	0.1190
4.0	1.0220	0.0865

TABLE I. Parameters  $Z_1$  and  $Z_2$  in  $\Phi_2$  of Eq. (43) obtained iteratively from Eq. (46) and Eq. (75) for the hydrogen molecule as function of internuclear distance  $R$ .

$R$	exact [1]	$\Psi_1$	$\Psi_2$
0.5	-0.5266	-0.51190	-0.5066
1.0	-1.1245	-1.1166	-1.1206
1.2	-1.1649	-1.1575	-1.1610
1.4	-1.1745	-1.1677	-1.1713
1.6	-1.1686	-1.1623	-1.1645
2.0	-1.1381	-1.1304	-1.1318
3.0	-1.0573	-1.0460	-1.0410
4.0	-1.0164	-1.0099	-0.9782

TABLE II. Total energies of  $\text{H}_2$ . Present results are calculated from  $\Psi_1 = \Phi_1 \cdot f$  and from  $\Psi_2 = \Phi_2 \cdot f$ ;  $f$  is given by Eq. (37),  $\Phi_1$  by Eq. (39) and  $\Phi_2$  by Eq. (42). The exact energies are from Ref. [1].

Method	Diss. energy	bond length
Heitler-London [15]	0.1160	1.64
Heitler-London with effective nuclear charge ( $Z = 1.166$ ) [16]	0.1389	1.39
Simple molecular orbital [17]	0.0990	1.61
Simple molecular orbital with effective nuclear charge ( $Z = 1.197$ ) [17]	0.1282	1.38
Hartree-Fock [18]	0.1336	1.40
Double configuration SCF [19]	0.1521	1.40
Molecular orbital with 28 configurations [20]	0.1672	1.40
Present ( $\Psi_1 = \Phi_1 f$ )	0.1677	1.40
Present ( $\Psi_2 = \Phi_2 f$ )	0.1713	1.40
Exact [1]	0.1744	1.40

TABLE III. Comparison of the dissociation energies and bond lengths of the hydrogen molecule (atomic units). The present results at  $R = 1.4a_0$  have a statistical error of  $5 \cdot 10^{-4} E_h$  due to the Monte Carlo integration.

FIG. 1. Definition of distances in the Hamiltonian of a two-electron homo-nuclear molecule. For  $\text{H}_2$ ,  $Z = 1$ .  $r_1$  and  $r_2$  are defined with respect to the mid-point of  $a$  and  $b$ .

FIG. 2. Comparison of the exact [1] potential energy curve (diamonds) with the present results with  $\Psi_1$  (solid line) and with the present results with  $\Psi_2$  (crosses).