

# Molecular Calculations with Two-Center Correlated Orbitals

Marlan O. Scully,<sup>1,2</sup> Roland E. Allen,<sup>2</sup> Yusheng Dou,<sup>1,2</sup> Kishore T. Kapale,<sup>1,2</sup> Moochan Kim,<sup>1,2</sup> Goong Chen,<sup>3</sup> and Anatoly Svidzinsky<sup>2</sup>

<sup>1</sup>*Department of Chemistry and Center for Ultrafast Laser Applications, Princeton University, Princeton, NJ 08544*

<sup>2</sup>*Department of Physics and Institute for Quantum Studies, Texas A&M University, TX 77843*

<sup>3</sup>*Department of Mathematics and Institute for Quantum Studies, Texas A&M University, TX 77843*

The usual building blocks of molecular orbital theory are one-center atomic orbitals. If we instead use two-center orbitals derived from the exact solution for  $H_2^+$ , a simple calculation of the  $H_2$  binding energy yields 4.5 eV, with a Hylleraas correlation factor having no adjustable parameters. Variational minimization with respect to a couple of parameters in our trial function then shifts the binding energy to 4.7 eV, very near the experimental value. The approach is also applicable to heteronuclear molecules; e.g.  $HeH^+$ , whose ground state energy we calculate to be -2.96 hartree with no adjustable parameters. This is to be compared with -2.98 hartree previously calculated using a wavefunction with 83 terms.

## INTRODUCTION

The description of the covalent bond is one of the crowning achievements of quantum mechanics, and undergirds all of quantum chemistry [1]. In the words of a recent insightful article [2]

“It can be said without fear of contradiction that the two-electron bond is the single most important stereoelectronic feature of chemistry.”

The venerable molecular orbital (MO) theory of Hund and Mulliken [3] provides a particularly useful tool and is the basis for much of molecular science. The physics underlying the two-electron covalent bond of diatomic molecules is most easily understood by building the two-electron two-center wavefunctions, e.g. for  $H_2$  and  $LiH$ , from the associated one-electron two-center MO's of, e.g.,  $H_2^+$  and  $LiH^+$ .

The two-center one-electron molecular ion problem is, of course, exactly solvable [4–7], and is a logical starting point for the calculation of diatomic wavefunctions. However, to quote a good standard text on quantum chemistry [8]:

“The difficulty with this calculation lies in the fact that the exact (two center) MO's of  $H_2^+$  which we should use ... are rather an intractable mathematical form. As a crude approximation we shall replace these exact  $H_2^+$  MO's with their zeroth-order (one center) approximations. The approximate zeroth-order functions for the hydrogen molecule now become”

$$\begin{aligned} \Psi_{H_2^+, 1\sigma}(i) &= [(2\pi/\alpha_S^3)(1+S)]^{-\frac{1}{2}} (e^{-\alpha_S r_{ai}} + e^{-\alpha_S r_{bi}}) \\ &= 2 [(2\pi/\alpha_S^3)(1+S)]^{-\frac{1}{2}} \\ &\quad \times \exp(-\alpha_S R \lambda_i/2) \cosh(\alpha_S R \mu_i/2), \end{aligned} \quad (1)$$

where  $r_{ai}$  and  $r_{bi}$  are the distances of the  $i^{th}$  electron from nuclei a and b, as shown in Fig. 1,  $\lambda_i$  and  $\mu_i$  are the ellipsoidal coordinates of the  $i^{th}$  electron ( $i = 1, 2$ ), as described in Fig. 2,  $\alpha_S$  is the scaling (screening) parameter, and  $S$  is the overlap integral. The expectation value of the binding energy, obtained using the wavefunction represented by Eq. (1), is in good qualitative, but not quantitative agreement with the experimental value [9].

The zeroth-order MO function (1) is nothing more than the sum of 1s ground state hydrogenic wavefunctions in which the  $\alpha_S$  variational parameter accounts for screening effects due to the other bonding electrons. In order to obtain better MO's, higher lying atomic configurations, e.g. 2s and 2p states, are added. Motivated by such considerations, James and Coolidge [10] were led to a trial wavefunction for  $H_2$  of the form

$$\begin{aligned} \Psi^{(J.C.)} &= \frac{1}{2\pi} \sum C_{mnmkl} e^{-\alpha(\lambda_1 + \lambda_2)} \\ &\quad \times (\lambda_1^m \lambda_2^n \mu_1^j \mu_2^k r_{12}^l + \lambda_1^n \lambda_2^m \mu_1^k \mu_2^j r_{12}^l) \end{aligned} \quad (2)$$

where the notation is explained in Figs. 1 and 2, and the coefficients  $C_{mnmkl}$  are variational parameters. Following such an approach, they and others who improved on this approach, for example, Kolos, Szalewicz and Monkhorst [11], got a binding energy 4.74 eV for  $H_2$  by taking 10 to 249 terms in the series. This is an important result because it shows that quantum mechanics can describe the chemical bond quantitatively. However the physically appealing picture of the bond has been lost. To quote Mulliken [12]:

“[T]he more accurate the calculations become the more the concepts tend to vanish into thin air”.

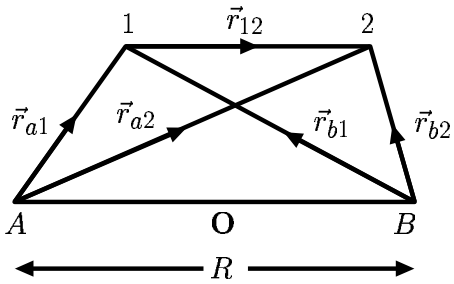


FIG. 1: Electronic distances in diatomic molecule.  $A$  and  $B$  are the positions of the nuclei with nuclear charges  $Z_a$  and  $Z_b$  respectively. The nuclei are fixed and the distance between them is taken to be the equilibrium bond length for the given molecule,  $R = R_0$ . The positions of the electrons are denoted by 1 and 2.

We are thus motivated to search for a middle ground between wavefunctions of the types represented by Eqs. (1) and (2). In particular we note that  $H_2$  in the united atom limit, i.e. He, is modeled quite well by the Hylleraas wavefunction

$$\Psi_{He}(1, 2) = \Psi_{H,1s}(1)\Psi_{H,1s}(2)\chi_{00}(1 + \kappa r_{12}), \quad (3)$$

where  $\Psi_{H,1s}(1)$  is the H atom  $1s$  orbital, and the effective nuclear charge and  $\kappa$  are variational parameters. The singlet spin function  $\chi_{00}$  is given by  $\chi_{00} = [|\uparrow_1\downarrow_2\rangle - |\downarrow_1\uparrow_2\rangle]/\sqrt{2}$  and the Hylleraas correlation factor,  $(1 + \kappa r_{12})$ , accounts for the electron-electron repulsion. This yields a ground state energy which is accurate to better than 1% [14].

We are therefore motivated to consider a separated atom wavefunction for  $H_2$  of the form

$$\Psi_{H_2}(1, 2) = \Psi_{H_2^+,1\sigma}(1)\Psi_{H_2^+,1\sigma}(2)\chi_{00}(1 + \kappa r_{12}), \quad (4)$$

as indicated in Fig. 3, where now  $\Psi_{H_2^+,1\sigma}$  is the exact two-center orbital obtained from solving the Schrödinger equation for the ground state of  $H_2^+$  in prolate-spheroidal (ellipsoidal) coordinates. As is explained in the discussion,  $\kappa = \frac{1}{2}$  in the Hylleraas correlation factor is obtained by solving for the wavefunction of the two electron problem and going to the small  $r_{12}$  limit. (Another choice for the correlation factor is a Jastrow factor like that employed by Chin [13].) With this choice ( $\kappa = \frac{1}{2}$ ) and no variational or adjustable parameters whatsoever (e.g., effective charge of nucleus = 1), the molecular binding energy is already remarkably close to the experimental value, as shown in Table I. The calculated results can be improved significantly by allowing one parameter (the  $\alpha$  parameter in Eq. (10)) to be adjusted to minimize the energy, as also shown in Table I.

To summarize: In the present paper we use only one ground state molecular orbital, modified by a simple electronic correlation factor and without any free (variational) fitting and find a binding energy of 4.5 eV. With

Orbital	Binding Energy (eV)	
	no free parameter	1 free (screening) parameter
Bates: Eq. (13)	4.50	4.60
Laguerre: Eq. (15)	4.51	4.62

TABLE I: The binding energy of the  $H_2$  molecule for the Bates and Laguerre forms of the  $H_2^+$  orbitals given by Eqs. (13) and (15) representively. When we allow the  $\alpha$  and A parameters of Eq. (15) to vary, we obtain a binding energy of 4.7 eV. The binding energy is comparable to the experimental value of 4.74 eV.

the same form (the exact solution for  $H_2^+$ ), but with a couple of the constants interpreted as variational parameters, the binding energy is found to be 4.7 eV. The present results are obtained (and strengthened) by independent numerical and analytical calculations, with different choices for the representation of the exact  $H_2^+$  solutions.

## METHODOLOGY AND RESULTS

In this section, we review the HM theory of  $H_2$  in a way which makes natural contact with and assists in the implementation and interpretation of the present calculations. We then proceed to sketch the analysis using the  $H_2^+$  orbitals. In the concluding paragraphs we summarize the results and mention straightforward extensions.

Consider a molecule with two nuclei and two valence electrons, having the Hamiltonian

$$H = H_0(1) + H_0(2) + \frac{e^2}{r_{12}} - \frac{Z_a Z_b e^2}{R}, \quad (5)$$

in the Born-Oppenheimer approximation, where

$$H_0(i) = -\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Z_a e^2}{r_{ai}} - \frac{Z_b e^2}{r_{bi}} + \frac{Z_a Z_b e^2}{R}, \quad i = 1, 2 \quad (6)$$

is the one-electron Hamiltonian. The notation is illustrated in Fig. 1.

The one-electron Hamiltonian operating on the two electron wavefunction without correlation factor yields  $2E_{H_2^+}$ , the exact electronic energy in the absence of electron-electron repulsion. That is,

$$[H_0(1) + H_0(2)]\Psi(\vec{r}_1, \vec{r}_2) = 2E_{H_2^+}\Psi(\vec{r}_1, \vec{r}_2). \quad (7)$$

The binding energy  $\Delta E_{H_2}$  is then found to be

$$\Delta E_{H_2} = 2E_{H_2^+} - \frac{Z_a Z_b e^2}{R} + \left\langle \frac{e^2}{r_{12}} \right\rangle_{H_2^+} + 2|E_H|. \quad (8)$$

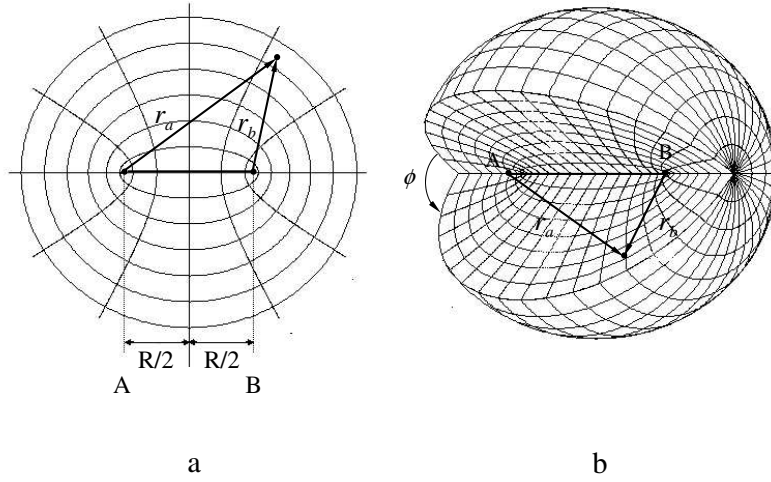


FIG. 2: (a) Elliptical coordinates  $(\lambda, \mu)$ . (b) Prolate Spheroidal coordinates  $(\lambda, \mu, \phi)$  with  $\lambda = (r_a + r_b)/R$  and  $\mu = (r_a - r_b)/R$ . The range of coordinates is  $1 \leq \lambda \leq \infty$ ,  $-1 \leq \mu \leq 1$  and  $0 \leq \phi \leq 2\pi$ .

The final term,  $2|E_H|$ , accounts for the fact that the electrons are bound to their individual atomic sites when the molecule dissociates.

The wavefunction for the  $H_2^+$  molecule, in ellipsoidal coordinates, is given by [4–6]

$$\varphi(\lambda, \mu, \phi) = \Lambda(\lambda)M(\mu)e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \dots, \quad (9)$$

where

$$\Lambda(\lambda) = e^{-\alpha\lambda}\mathcal{L}(\lambda), \quad (10)$$

$$\mathcal{L}(\lambda) = (\lambda^2 - 1)^{|m|/2}(\lambda + 1)^\sigma \sum_n a_n \left(\frac{\lambda - 1}{\lambda + 1}\right)^n, \quad (11)$$

$$M(\mu) = \sum_{s=0}^{\infty} b_{2s} P_{m+2s}^m(\mu), \quad (12)$$

$\alpha$  is a function of  $R$ , and  $\sigma$  is related to the effective charge  $Z^*$  by  $\sigma = \frac{RZ^*}{\alpha}$ . ( $Z^*$  is a variational parameter in the trial wavefunction for  $H_2$ , whereas  $Z^* = 1$  in the exact wavefunction for  $H_2^+$ .) For the case  $m = 0$ , we have the ground state solution [4–6]:

$$\begin{aligned} \varphi^I(\lambda, \mu) &= \mathcal{N}e^{-\alpha\lambda}(\lambda + 1)^\sigma \\ &\times \left[ 1 + a_1 \left(\frac{\lambda - 1}{\lambda + 1}\right) + a_2 \left(\frac{\lambda - 1}{\lambda + 1}\right)^2 + \dots \right] \\ &\times [1 + b_2 P_2(\mu) + b_4 P_4(\mu) + \dots], \quad (13) \end{aligned}$$

where  $P_l(\mu)$  is a Legendre polynomial and the coefficients  $a_1, a_2, b_2, b_4, \dots$  are determined by simple recursion relations.

We then proceed to solve for  $\langle H \rangle$  and thus determine the binding energy in several ways. First we evaluate the energy integrals numerically in ellipsoidal coordinates.

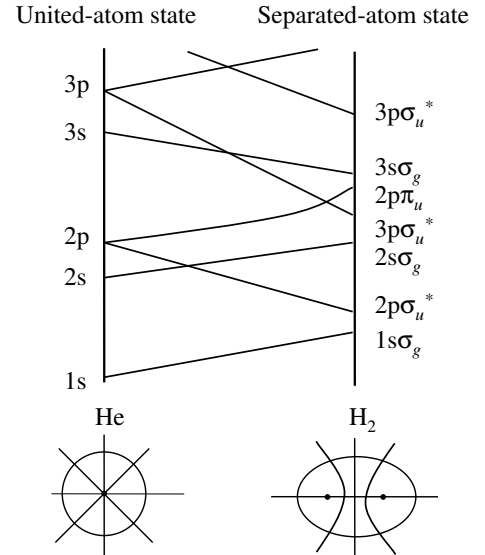


FIG. 3: Schematic correlation diagram for He, the united-atom limit, and  $H_2$ , the separated-atom case.

The ground state wavefunction (13) was truncated after the first few terms. The various convergence checks and other details will be presented elsewhere. To incorporate the electron-electron correlation we introduce a simple correlation factor  $f(r_{12}) = 1 + \frac{1}{2}r_{12}$  into the wavefunction. The binding energy with this correlation factor is found to be  $\Delta E_{H_2}^{\text{numerical}} = -4.50$  eV. All the parameters ( $\alpha, a_1, a_2, b_2, b_4$ , etc.) are determined by solving the Schrödinger equation for the one-electron two-center problem of  $H_2^+$ . There are no free (“fitting”) parameters; e.g. the nuclear charge is not screened.

Parameter	$\Psi^I(1, 2)$	$\Psi^I(1, 2) f(r_{12})$	Parameter	$\Psi^{II}(1, 2)$	$\Psi^{II}(1, 2) f(r_{12})$
$Z^*$	0.7786	0.9370	$Z^*$	0.7806	0.9407
$\mathcal{N}$	0.8606	0.8088	$\mathcal{N}$	1.0305	1.0148
$\alpha$	0.9152	1.0647	$\alpha$	0.9171	1.0680
$a_1$	0.0072	0.0096	$A_1$	-0.0376	-0.0412
$a_2$	0.0004	0.0004	$A_2$	-0.0045	-0.0043
$b_2$	0.0955	0.1303	$B_2$	0.0959	0.1312
$b_4$	0.0014	0.0026	$B_4$	0.0014	0.0026
$2\langle H(1) \rangle$	-2.5126	-2.4757	$2\langle H(1) \rangle$	-2.5125	-2.4757
$\langle 1/r_{12} \rangle$	0.6718	0.5923	$\langle 1/r_{12} \rangle$	0.6710	0.5917
$\langle H \rangle$	-1.1265	-1.1691	$\langle H \rangle$	-1.1272	-1.1697
BE (eV)	3.44	4.60	BE (eV)	3.46	4.62

TABLE II: Numerical and analytical results for  $\text{H}_2$  wavefunctions constructed out of the exact solution for the  $\text{H}_2^+$  problem. The only variational parameter here is the nuclear charge  $Z^*$ , and all other parameters are calculated by solving the  $\text{H}_2^+$  eigenvalue problem for a variationally best effective charge. Here  $\Psi^I(1, 2) = \varphi^I(\lambda_1, \mu_1)\varphi^I(\lambda_2, \mu_2)$ ,  $\Psi^{II}(1, 2) = \varphi^{II}(\lambda_1, \mu_1)\varphi^{II}(\lambda_2, \mu_2)$ , and  $f(r_{12}) = 1 + \frac{1}{2}r_{12}$ . The energy unit is the Hartree unless indicated.

We next perform a variational calculation by minimizing with respect to the effective nuclear charge for both the uncorrelated and correlated wavefunctions. We find  $\Delta E_{\text{H}_2}^{\text{Numerical}} = -3.44$  eV for the uncorrelated case and -4.60 eV for the correlated wavefunction (i.e. without and with the Hylleraas factor). When a couple of variational parameters are included, the calculated binding energy is still closer to the experimental value. Some of the numerical results and corresponding parameter values are summarized in  $\Psi^I(1, 2)$  and  $\Psi^I(1, 2) f(r_{12})$  columns of Tables II.

We next outline an alternative approach, in which the integrals (e.g. the two-center Coulomb integrals) are evaluated analytically. To facilitate this analytical formulation, it is helpful to replace (11) by an alternative representation involving Laguerre functions. We recall that the single-electron two-center wavefunction is given by Eq. (9), but the factor  $\Lambda(\lambda)$  is now expanded as a series in Laguerre polynomials, following Hylleraas [14] and Baber and Hasse [7]. For the ground state ( $m = 0$ ), it takes the form

$$\Lambda(\lambda) = e^{-\alpha\lambda} \sum_{n=0}^{\infty} \frac{A_n}{n!} L_n(x) \quad (14)$$

where  $x = 2\alpha(\lambda - 1)$ . The  $M(\mu)$  part is again given by an even series of Legendre polynomials as in Eq. (12). The details of the analytical calculations will also be given elsewhere. We truncate the series for both  $\Lambda(\lambda)$  and  $M(\mu)$  after the leading terms, and write the single-electron two-center wavefunction as

$$\varphi^{II}(\lambda, \mu) = \mathcal{N}e^{-\alpha\lambda} \left[ 1 + A_1 L_1(x) + \frac{A_2}{2} L_2(x) \right] \times [1 + B_2 P_2(\mu)] \quad (15)$$

where the parameters  $A_1, A_2, B_2$  and  $\alpha$  are again determined by solving the Schrödinger equation for  $\text{H}_2^+$ .

To incorporate electron-electron correlations into the wavefunction we again introduce the correlation factor  $f(r_{12}) (1 + \frac{1}{2}r_{12})$  and repeat the calculation. The results are summarized in the  $\Psi^{II}(1, 2)$ , and  $\Psi^{II}(1, 2) f(r_{12})$  columns of Tables II.

## DISCUSSION

1. The choice of the correlation factor  $f$  is best understood as follows. Write the trial ground state wavefunction as  $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_1)\Psi(\mathbf{r}_2)f(\mathbf{r}_1, \mathbf{r}_2)$ , where  $\Psi(\mathbf{r}_1)$  and  $\Psi(\mathbf{r}_2)$  are exact one electron solutions in the absence of interaction between electrons. For  $\Psi(\mathbf{r}_1, \mathbf{r}_2)$  the Schrödinger equation is (in atomic units)

$$\begin{aligned} & \Psi(\mathbf{r}_2)f \left( -\frac{\nabla_1^2}{2} - \frac{Z_a}{r_{a1}} - \frac{Z_b}{r_{b1}} \right) \Psi(\mathbf{r}_1) \\ & + \Psi(\mathbf{r}_1)f \left( -\frac{\nabla_2^2}{2} - \frac{Z_a}{r_{a2}} - \frac{Z_b}{r_{b2}} \right) \Psi(\mathbf{r}_2) \\ & + \Psi(\mathbf{r}_1)\Psi(\mathbf{r}_2) \left( -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + \frac{1}{r_{12}} \right) f \\ & - [\Psi(\mathbf{r}_2)\nabla_1\Psi(\mathbf{r}_1)\nabla_1 f + \Psi(\mathbf{r}_1)\nabla_2\Psi(\mathbf{r}_2)\nabla_2 f] \\ & = \left( E - \frac{Z_a Z_b}{R} \right) \Psi(\mathbf{r}_1)\Psi(\mathbf{r}_2)f. \end{aligned} \quad (16)$$

The solution with only the first two terms is just that for  $\text{H}_2^+$  as given by Eqs. (13) or (15). The functions  $\Psi(\mathbf{r}_1)$  and  $\Psi(\mathbf{r}_2)$  exponentially decay at large distances from the nuclei. The third term corresponds to essentially the Schrödinger equation for two electrons. The solution is well known [15] and is given in term of confluent hypergeometric function.

Due to the fact  $\Psi(\mathbf{r}_1)$  and  $\Psi(\mathbf{r}_2)$  sharply confine the electrons, only the behavior of  $f$  at small distances is important in determining the molecular energy as an inte-

gral involving the trial function. We thus take the asymptotic expression for  $f$ , and choose the correlation factor  $f$  by using the condition that the trial function  $\Psi(\mathbf{r}_1, \mathbf{r}_2)$  reproduces the correct asymptotic behavior of the exact two particle wave function at small distances. We then obtain  $f = 1 + r_{12}/2$ . This gives a “natural” factor in the  $H_2$  trial wave function that takes into account correlation between electrons in the ground state. The term  $r_{12}/2$  appears in order to compensate for the divergent potential energy of the two electron interaction  $1/r_{12}$  in the Schrödinger equation. Thus the usual Hylleraas form  $(1 + \kappa r_{12})$  is motivated by solving the two (free) electron problem. However, the idea of matching asymptotic expansion allows us to construct trial wave functions with no variational parameters and still obtain the energy with good accuracy.

The helium atom is the simplest system with which we can make this point. According to our construction scheme, the trial wave function for the helium ground state should be

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = C e^{-2(r_1+r_2)} \left(1 + \frac{r_{12}}{2}\right), \quad (17)$$

where  $C$  is the normalization constant. This wave function has no variational parameters and reproduces the correct asymptotic form of the exact two electron wave function at small  $r_1, r_2, r_{12}$ :  $\Psi \propto 1 - 2r_1 - 2r_2 + r_{12}/2$ . With the trial function (17), we obtain a ground state energy of helium  $E_{\text{He}} = -78.28$  eV, which agrees with the exact value  $-79.01$  eV with an accuracy of better than 1%. It is worthwhile to note that the Hylleraas trial wavefunction for helium

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = C e^{-\alpha(r_1+r_2)} (1 + \kappa r_{12}), \quad (18)$$

which contains two variational parameters  $\alpha$  and  $\kappa$ , only cuts the error in half, yielding  $E_{\text{He}} = -78.67$  eV (obtained for  $\alpha = 1.85$  and  $\kappa = 0.366$ ). I.e., one already gets close to chemical accuracy with (17), and it is not a trivial matter to obtain a solution which is substantially more accurate.

**2.** The atomic orbital of Eq. (1) inserted into Eq. (4) with  $R = 1.4 a_0$  and  $\alpha_S = 1$ , yields a binding energy  $\Delta E_{\text{LCAO}} \approx -2.47$  eV. However, when we include the correlation factor  $(1 + \frac{1}{2}r_{12})$  the molecule is no longer bound. When we treat  $\alpha_S$  as a variational parameter, we find  $\Delta E_{\text{LCAO}} = -3.4$  eV when  $\alpha_S = 1.25$  without the  $f(r_{12})$  factor. Upon adding the correlation factor  $(1 + \frac{1}{2}r_{12})$ , we find  $\Delta E_{\text{LCAO}} = -4.2$  eV in this case [16].

It is interesting to note that the LCAO binding energy without the correlation factor is in quite reasonable agreement with that obtained using the exact  $H_2^+$  two center orbitals of Eqs. (13) and (15). But when the correlation factor is included, one finds  $\Delta E_{\text{LCAO}} = -4.2$  eV compared to the 4.6 eV binding energy obtained using the two-center orbitals.

When performing variational minimization with respect to two or three parameters, we find the binding energy to be 4.7 eV, very near the experimental value. This will be presented in detail elsewhere.

The reason that the correlation energy calculated using the LCAO trial wave function (1) differs from that given by the exact two-center  $H_2^+$  orbitals of Eqs. (13) and (15) is clear from Eq. (16). The extra terms of the form  $\nabla\Psi_i \cdot \nabla f(r_{12})$  have a stronger dependence on the precise form of  $\Psi$  than does the binding energy in the absence of configuration mixing or correlation effects. That is, the latter depends on integrals over  $\Psi$ , whereas the effect of electron correlation is governed by derivatives of  $f(r_{12})$ , see Eq. (16).

**3.** The numerical calculations of the electron integrals use the Neumann expansion of the interelectronic distance  $r_{ij}^{-1}$ . The detailed description of the numerical method will be published in a future paper and here we only give a brief introduction to the algorithm.

Let  $\Psi_{\sigma i} = \Psi_{H_2^+, 1\sigma}(i)$ . Then the two-center two-electron integrals with the correlation factor incorporated can be written as:

$$K_2^i = \langle \Psi_{\sigma 1} \Psi_{\sigma 2} | r_{12}^l h(i) r_{12}^{l'} | \Psi_{\sigma' 1} \Psi_{\sigma' 2} \rangle, i = 1, 2, \quad (19)$$

where  $h(i)$  is

$$h(i) = -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Z_a e^2}{r_{ai}} - \frac{Z_b e^2}{r_{bi}} = -\frac{\hbar^2}{2m} \nabla_i^2 - d(r_i). \quad (20)$$

Using the relation

$$r_{12}^l (\nabla_i^2 r_{12}^{l'} \Psi_{\sigma' i}) = \frac{l'}{l+l'} \nabla_i^2 r_{12}^{l+l'} \Psi_{\sigma' i} - l l' r_{12}^{l+l'-2} \Psi_{\sigma' i} + \frac{l}{l+l'} r_{12}^{l+l'} \nabla_i^2 \Psi_{\sigma' i}, \quad (21)$$

it is easy to obtain [17]

$$K_2^i = \langle \Psi_{\sigma 1} \Psi_{\sigma 2} | r_{12}^{l+l'} d(r_i) | \Psi_{\sigma' 1} \Psi_{\sigma' 2} \rangle - \frac{1}{2} \frac{l'}{l+l'} \langle \nabla_i^2 \Psi_{\sigma 1} \Psi_{\sigma 2} | r_{12}^{l+l'} | \Psi_{\sigma' 1} \Psi_{\sigma' 2} \rangle + \frac{1}{2} l l' \langle \Psi_{\sigma 1} \Psi_{\sigma 2} | r_{12}^{l+l'-2} | \Psi_{\sigma' 1} \Psi_{\sigma' 2} \rangle - \frac{1}{2} \frac{l}{l+l'} \langle \Psi_{\sigma 1} \Psi_{\sigma 2} | r_{12}^{l+l'} | \nabla_i^2 \Psi_{\sigma' 1} \Psi_{\sigma' 2} \rangle. \quad (22)$$

The resulting integrals are a linear combination of the products of one-dimensional integrals for  $\mu$  and two-dimensional integrals for  $\lambda$ . The one-dimensional integration is performed using the TD01AHF routine of the NAG library, and the two-dimensional integration is performed with the TD01DAF routine of the same library. The numerical results for the wavefunction given by Eq. (15) is confirmed to be accurate to at least 10 significant digits when compared with the analytical calculation is described in the next section.

4. For the trial function using the Laguerre expansion for  $\Lambda(\lambda)$ , there is an analytical technique to integrate each component of the Hamiltonian, because we know the functional form of the trial wavefunction. After writing the expressions for the expectation value of the Hamiltonian in spheroidal coordinates (including  $1/r_{12}$  using the Neumann expansion), each integration can be done by several methods. In 1931, Rosen [18] derived all the necessary integration formulas with recurrence relations that are very useful for two-center molecular calculations.

For example, including the Jacobian which is proportional to  $(\lambda^2 - \mu^2)$ , we can decompose the whole integration over  $\lambda$  and  $\mu$ . In particular, one of the  $\lambda$ -integrations for the repulsive Coulomb interaction between two electrons is

$$S(m, n; \alpha) \equiv \int_1^\infty d\lambda_1 \int_1^{\lambda_1} d\lambda_2 e^{-\alpha(\lambda_1 + \lambda_2)} \lambda_1^m \lambda_2^n. \quad (23)$$

The recurrence relation to get arbitrary  $S(m, n)$  is

$$S(m, n; \alpha) = \frac{1}{\alpha} [mS(m-1, n; \alpha) + A(m+n; \alpha)] \quad (24)$$

$$S(0, n; \alpha) = \frac{1}{\alpha} A(n; 2\alpha) \quad (25)$$

where

$$\begin{aligned} A(m; \alpha) &= \int_1^\infty e^{-\alpha\lambda} \lambda^m d\lambda \\ &= \frac{1}{\alpha} [e^{-\alpha} + mA(m-1; \alpha)], \end{aligned} \quad (26)$$

$$A(0; \alpha) = \frac{e^{-\alpha}}{\alpha}. \quad (27)$$

Using the proper recurrence relations, we can calculate the expectation value of the Hamiltonian using an analytic method.

5. The trial wavefunction given by Eq. (16), in terms of Laguerre functions, sheds some light on the James-Coolidge wave function. To show this, consider our trial wavefunction

$$\Psi(1, 2) = \Psi(1)\Psi(2) \left(1 + \frac{1}{2}r_{12}\right), \quad (28)$$

where

$$\begin{aligned} \Psi(1) &= \tilde{N} e^{-\alpha\lambda_1} \left( \sum_p \frac{A_p}{p!} L_p(2\alpha(\lambda_1 - 1)) \right) \\ &\quad \times \left( \sum_q B_{2q} P_{2q}(\mu_1) \right). \end{aligned} \quad (29)$$

We may compare this to the James-Coolidge trial wavefunction (2) by writing  $L_p$  and  $P_{2q}$  explicitly. For example, if we truncate the sum on  $p$  and  $q$  to get  $\Psi^{II}(1, 2)$  as given in Table II, we find a wavefunction of the form (2), a typical term of which is

$$\frac{1}{2\pi} C_{21200} (\lambda_1^2 \lambda_2 \mu_1^2 + \lambda_1 \lambda_2^2 \mu_2^2), \quad (30)$$

where

$$C_{21200} = -6\pi \tilde{N}^2 \alpha^3 A_2 (A_1 + A_2 + \alpha A_2) B_2 \left(1 - \frac{B_2}{2}\right). \quad (31)$$

The other coefficients are easily calculated.

Thus we see that the various terms in the series of Eq. (2) are closely related to the two-center orbital result (18).

6. After completing this research we became aware of an important paper by Stern and Lefebvre (SL) [19]. They used exact two-center  $H_2^+$  orbitals with an approach that is complementary to that of the present paper. In particular, they obtained a binding energy of 4.74 eV for  $H_2$  using 10 diatomic orbitals, with the effective nuclear charge as a variable parameter. This is to be compared with the earlier work of Kolos and Wolniewicz [20], who get the same result using 80 single-center atomic orbitals, and the pioneering calculation of James and Coolidge [21] who obtained 4.7 eV using a 13 term wavefunction which includes the interelectronic distance explicitly. Thus the SL results demonstrate nicely the advantage of using two-center, diatomic orbitals. Other workers have used diatomic orbitals but with less success. For example, Condon [22] used the  $H_2^+$  wavefunction to calculate the binding energy of  $H_2$ , but completely neglected the key electron-electron interaction term, so the results are not very meaningful. Wallis and Hulbert [23] used  $H_2^+$  diatomic orbitals with effective nuclear charges, and by careful calculation found a binding energy of 3.41 eV.

We have very recently become aware of two additional papers which treat the  $H_2$  molecule in a kindred spirit [24, 25], making use of the exact  $H_2^+$  solution and a quite similar correlation factor. These papers deal, in part, with a controversy concerning numerical results. We will publish our calculations relevant to this issue elsewhere.

7. Accurate wavefunctions for the excited states of  $H_2$  have been given by e.g. Kolos and Roothan [26] and Kolos and Rychlewsk [27] by extensions of wavefunctions of the kind given by Eq. (3). However, the ground state (4) suggests an immediate form for the excited states. For example, the attractive  $^1\Sigma_u^+$  state is given by

$$\begin{aligned} \Psi_{H_2, ^1\Sigma_u^+}(1, 2) &= [\Psi_{H_2^+, 1\sigma}(1)\Psi_{H_2^+, 1u}(2) \\ &\quad + \Psi_{H_2^+, 1\sigma}(2)\Psi_{H_2^+, 1u}(1)] \\ &\quad \times \chi_{00} \left(1 + \frac{1}{2}r_{12}\right), \end{aligned} \quad (32)$$

where  $\Psi_{H_2^+, 1u}$  is the first excited (ungerade) state of  $H_2$ . Clearly similar expressions can be written down for other excited states such as the  $^3\Sigma_u^+$  state etc.

8. The same ideas can be carried over to other diatomics, since an exact solution also exists for the heteronuclear case [28], with different effective nuclear charges in (13) and (15). A detailed treatment of this problem will be given elsewhere [29], and here we

TABLE III: Ground state energy of  $HeH^+$  molecular ion obtained with different forms for the wavefunction and different approximations.

Wave function	Energy (hartree)	
	no variational parameters	2 adjustable parameters
$\Psi_{HeH^+}^I$	-2.9531	-2.9664
$\Psi_{HeH^+}^{II}$	-2.9596	-2.9738

present only some central results: Let  $\Psi_{HeH^{++},1s\sigma}$  be the ground state wavefunction for the  $HeH^{++}$  molecular ion, obtained by solving the Schrödinger equation for this heteronuclear problem in prolate-spheroidal coordinates. We then adopt the same approach that was used above for  $H_2^+$ , employing a simple form for the two-electron ground-state wavefunction of  $HeH^+$ :

$$\Psi_{HeH^+}^I(1,2) = \Psi_{HeH^{++},1s\sigma}(1)\Psi_{HeH^{++},1s\sigma}(2) \times \chi_{00} \left(1 + \frac{1}{2}r_{12}\right). \quad (33)$$

The electronic energy of the ground state is found to be -2.9531 hartree without any variational parameters. On the other hand, if the effective charges are treated as variational parameters, we find that the energy is lowered to -2.9596 hartree. We then repeat the above calculations using a state with two configurations, having the form

$$\Psi_{HeH^+}^{II}(1,2) = [c_1\Psi_{(HeH^{++},1s\sigma)^2} + c_2\Psi_{(HeH^{++},2p\sigma)^2}] \times \chi_{00} \left(1 + \frac{1}{2}r_{12}\right), \quad (34)$$

where

$$\Psi_{(HeH^{++},1s\sigma)^2} = \Psi_{HeH^{++},1s\sigma}(1)\Psi_{HeH^{++},1s\sigma}(2) \quad (35)$$

$$\Psi_{(HeH^{++},2p\sigma)^2} = \Psi_{HeH^{++},2p\sigma}(1)\Psi_{HeH^{++},2p\sigma}(2) \quad (36)$$

In Eq. (36),  $\Psi_{HeH^{++},2p\sigma}$  is the wavefunction for the first electronically excited state of  $HeH^{++}$ . The electronic energy of the ground state is then further lowered to -2.9664 hartree when there are no variational parameters, and -2.9738 hartree when the effective charges are used as parameters in a variational calculation. The results of all four calculations are given in Table III.

The electronic energy calculated above with a simple two-center wavefunction is to be compared with the -2.9787 hartree obtained using a Hylleraas type wavefunction with 83 terms [30], or -2.9736 hartree obtained in an ab initio calculation at the MP4/6-311++G(3df, 3dp) level [31].

## CONCLUSION

In traditional quantum chemistry calculations, the pursuit of accuracy has typically led to more and more complicated representations, which obscure the fundamental chemistry and physics. (See the quotations from Mulliken given above.) The present approach, on the other hand, focuses on a two-center picture that directly incorporates the chemical bond from the outset. In addition, it incorporates the effects of electron correlation in a physically appealing way, through a correlation factor that expresses the tendency of two electrons to avoid each other because of their Coulomb repulsion. Configuration interaction is viewed as a separate effect, which has a direct physical and chemical interpretation of its own, and which can be included after the basic effect of electron correlation has already been accounted for in each configuration.

In conclusion, the two-center correlated basis functions of the present paper are a promising route to more efficient and more physically meaningful calculations in quantum chemistry.

## Acknowledgements

MOS wishes to thank L. Allen, M. Barnett, S. Chin, L. Cohen, A. Cotton, M. Hall, K. Lehmann, R. Lucchese, L. Massa, H. Rabitz, P. Reynolds, G. Süssmann, and W. Warren for helpful and stimulating discussions. This work was supported by DARPA, ONR, and the Robert A. Welch Foundation.

- 
- [1] W. Heitler and F. London, *Z. Physik* 44 (1927) 455.
  - [2] F. A. Cotton and D.G. Nocera, *Acc. Chem. Res.* 33 (2000) 483.
  - [3] R. S. Mulliken, *Phys. Rev.* 32 (1928) 186.
  - [4] V. Johnson, *Phys. Rev.* 60 (1941) 373.
  - [5] D. Bates, K. Ledsham, and A. S. Stewart, *Phil Trans. Roy. Soc. London* 246 (1953) 215.
  - [6] G. Jaffé, *Zeit. für Physik* 87 (1934) 535.
  - [7] W. Baber and H. Hasse, *Proc. Cambridge Phil. Soc.* 31 (1935) 564.
  - [8] F. Pilar, *Elementary Quantum Chemistry*, McGraw-Hill, 1990.
  - [9] J. Slater, *Quantum Theory of Molecules and Solids*, McGraw-Hill, 1963.
  - [10] H. James and A. Coolidge, *J. Chem. Phys.* 1 (1933) 825.
  - [11] W. Kolos, K. Szalewicz and H.J. Monkhorst, *J. Chem. Phys.* 84 (1986) 3278.
  - [12] R. S. Mulliken, *J. Chem. Phys.* 43 (1965) S2.
  - [13] S. A. Chin, *Phys. Rev. A* 42 (1990) 6991.
  - [14] E. Hylleraas, *Zeit. für Physik* 71 (1931) 739.
  - [15] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory*, Volume 3, Fourth Edition, Moscow, Nauka, 1986.

- [16] We thank S. Chin for pointing out that another argument for taking  $\alpha$  to be different than unity derives from reconsidering the  $H_2^+$  ion and seeking a better solution at that level. We intend to discuss this elsewhere.
- [17] J. Budzinski, M. Firszt and W. Woznicki, *Int. J. Quant. Chem.*, 41 (1992) 359.
- [18] N. Rosen, *Phys. Rev.* 38 (1931) 2099.
- [19] B. Stern and R. Lefebvre, *J. Mol. Struct. (Theochem)* 434 (1998) 169. MOS wishes to thank M. Barnett for bringing this paper to his attention.
- [20] W. Kolos, and L. Wolniewicz, *J. Chem. Phys.* 41 (1964) 3663.
- [21] H. James and A. Coolidge, *Phys. Rev.* 43 (1933) 588.
- [22] E. Condon, *Proc. Nat. Acad. Sci.* 13 (1927) 466.
- [23] R. Wallis and H. Hulburt, *J. Chem. Phys.* 22, (1954) 774.
- [24] L.D.A. Siebbeles and C. Le Sech, *J. Phys. B* 27 (1994) 4443.
- [25] L. Wolniewicz, *Phys. Rev. A*, 53 (1996) 4609.
- [26] W. Kolos and C. C. J. Roothaan, *Rev. Mod. Phys.* 32, (1960) 219.
- [27] W. Kolos and J. Rychlewski, *J. Mol. Spectrosc.* 177 (1996) 146.
- [28] D. Bates, and T. R. Carson, *Proc. Royal Soc. London, Ser. A* 234 (1956) 207.
- [29] Y. Dou et al., to be published.
- [30] W. Kolos and J. M. Peek, *Chem. Phys.* 12 (1976) 381.
- [31] C. J. H. Schutte, *Chem. Phys. Lett.* 353 (2002) 389.