

Commentationes

Valence Bond Functions for the Hydrogen Molecule*

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Valence bond wavefunctions were constructed for H_2 . Use of Slater exponents resulted in very slow convergence to the ground state energy. Convergence was improved by optimizing exponents which were found to increase as the principal quantum number n . However, this gave problems of linear dependence since optimum orbitals were strikingly similar for all n . The best function without angular correlation contained 27 terms constructed from $1s$, $3s$, $2p_0$, $3d_0$, $4f_0$, and $5g_0$ orbitals and gave an energy of -1.1594 a.u. The best function with angular correlation gave $E = -1.1656$ a.u.

Für das H_2 -Molekül werden Wellenfunktionen nach der Valenzstrukturmethode konstruiert. Die Benutzung von Exponenten nach Slater führt zu einer sehr langsamen Konvergenz zur Grundzustandsenergie. Die Konvergenz wurde durch Optimierung der Exponenten verbessert, wobei diese mit der Hauptquantenzahl ansteigen. Dabei ergab sich jedoch das Problem linearer Abhängigkeit der Funktionen, da die optimalen Orbitale sehr ähnlich für alle n waren. Die beste Funktion ohne Winkelkorrelation enthielt 27 Terme, die aus den Orbitalen $1s$, $3s$, $2p_0$, $3d_0$, $4f_0$ und $5g_0$ konstruiert waren, und ergab eine Energie von $-1,1594$ A.E. Die beste Funktion mit Winkelkorrelation ergab $E = -1,1656$ A.E.

Des fonctions d'onde de liaison de valence sont construites pour H_2 . L'emploi d'exposants de Slater entraîne une très faible convergence vers l'énergie de l'état fondamental. La convergence a été améliorée par optimisation des exposants qui croissent comme le nombre quantique principal n . Cependant, ceci crée des problèmes de dépendance linéaire car les orbitales optimales sont étonnement similaires pour tous les n . La meilleure fonction sans corrélation angulaire contient 27 termes construits à partir d'orbitales $1s$, $3s$, $2p_0$, $3d_0$, $4f_0$ et $5g_0$ et donne une énergie de $-1,1594$ u.a. La meilleure fonction avec corrélation angulaire donne $E = -1,1656$ u.a.

1. Introduction

In the course of some other work we wanted a fairly complete valence bond (VB) wavefunction for H_2 and were surprised to find none among the many published H_2 calculations. We present here the results of such a calculation using type orbitals (STO's) through principal quantum number 6.

When this work was begun, the only published VB calculations on H_2 were the original Heitler and London calculation [1] which gave binding energy of

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3.14 eV (= a total energy of 1.115 a.u.¹) and early modifications of this by Wang [5] (scaling), Rosen [6] (polarization) and Weinbaum [7] (ionic terms). It is interesting to note that the Heitler-London calculation was not done variationally, and in fact preceded Eckart's statement of the variational principle [8] by several years. After our calculations were underway, Bowen [9], in a short note, reported a 12-term VB calculation using $1s$, $2p\sigma$ and $3d\sigma$ orbitals with a common orbital exponent. His best total energy was -1.1540 a.u.

The LCAO MO CI calculations of McLean, Weiss and Yoshimine [10] should also be mentioned. Their MO's were of particularly simple form and hence, some of their wavefunctions are equivalent to VB functions. In particular their function X (see Table 1 of Ref. [10]) which gives a total energy of -1.1672 a.u. can be rewritten as a VB function involving $1s$, $1s'$, $2s$, $2s'$, $2p\sigma$ and $2p\pi$ orbitals. However, McLean, Weiss and Yoshimine do not give details of their function X. They list instead coefficients and exponents for their slightly poorer function IX with which most of their calculations were made. Function IX is not equivalent to a VB function.

These calculations and ours to be mentioned below may be compared to the very accurate 100-term expansion of Kołos and Wolniewicz [11] who compute the H_2 potential curve and find it to have a minimum of -1.17447983 a.u. at $R_e = 1.4010784$ a.u. Their curve gives a computed dissociation energy which agrees with the experimental to within a fraction of a wave number. The 3.8 cm^{-1} discrepancy reported by Kołos and Wolniewicz has since been removed by a reexamination of the experimental data [12].

2. Computational Details

Since we shall consider only the singlet ground state of the 2-electron hydrogen molecule, the antisymmetric spin part of the wavefunction may be factored out and discarded. Henceforth, the symmetric space part of the wavefunction will be referred to simply as "the wavefunction".

It will be convenient to introduce some notation before proceeding. Given the pair of atomic orbitals (AO's) χ_i and χ_j , let a second subscript be used to indicate the H atom on which the AO is centered, and define the covalent function constructed from this pair by

$$(\chi_i\chi_j)_C = \frac{1}{4}[\chi_{iA}(1)\chi_{jB}(2) + \chi_{iA}(2)\chi_{jB}(1) + \chi_{jA}(1)\chi_{iB}(2) + \chi_{jA}(2)\chi_{iB}(1)] \quad (1)$$

with the special case

$$(\chi_i\chi_i)_C = \frac{1}{2}[\chi_{iA}(1)\chi_{iB}(2) + \chi_{iA}(2)\chi_{iB}(1)] \quad (2)$$

¹ This is not actually the energy reported by Heitler and London. They used an upper bound approximation to the exchange integral, and from their Fig. 1, their best binding energy appears to be about 2.3 eV. Sugiura [2] evaluated the integral exactly to obtain a binding energy of 3.2 eV. Coulson [3] found numerical errors in Sugiura's work and reported a corrected binding energy of 3.14 eV. Many of the early papers do not state the conversion factors used. Here we shall use 1 a.u. of length = 0.52917 \AA and 1 a.u. of energy = $27.211 \text{ eV} = 627.5 \text{ kcal/mole}$ [4]. The total energy of 1.115 a.u. mentioned above was obtained using this energy conversion factor and Coulson's binding energy.

and the ionic function by

$$(\chi_i \chi_j)_I = \frac{1}{4} [\chi_{iA}(1) \chi_{jA}(2) + \chi_{iA}(2) \chi_{jA}(1) + \chi_{iB}(1) \chi_{jB}(2) + \chi_{iB}(2) \chi_{jB}(1)] \quad (3)$$

with the special case

$$(\chi_i \chi_i)_I = \frac{1}{2} [\chi_{iA}(1) \chi_{iA}(2) + \chi_{iB}(1) \chi_{iB}(2)]. \quad (4)$$

The AO's used were complex Slater type orbitals

$$\chi = \chi_{nlm} = (2\zeta)^{(n+\frac{1}{2})} [(2n)!]^{-\frac{1}{2}} r^{n-1} e^{-\zeta r} Y_{lm}(\vartheta, \phi), \quad (5)$$

with the spherical harmonics defined by

$$Y_{lm}(\vartheta, \phi) = \bar{P}_{lm}(\cos \vartheta) \Phi_m(\phi) = \bar{P}_{lm}(\cos \vartheta) (2\pi)^{-\frac{1}{2}} e^{im\phi} \quad (6)$$

and the normalized associated Legendre polynomials by

$$\bar{P}_{lm}(\cos \vartheta) = \frac{1}{2^l l!} \left[\frac{2l+1}{2} \times \frac{(l-m)!}{(l+m)!} \right]^{\frac{1}{2}} \times (-\sin \vartheta)^m \left(\frac{d}{d \cos \vartheta} \right)^{l+m} (\cos^2 \vartheta - 1)^l. \quad (7)$$

These complex STO's transform easily to prolate spheroidal coordinates and somewhat simplify evaluation of the necessary 2-center integrals. Such an STO on center A becomes

$$\begin{aligned} \chi_A(\mu, \nu, \phi) &= (2\zeta)^{n+\frac{1}{2}} [(2n)!]^{-\frac{1}{2}} (R/2)^{n-1} (\mu + \nu)^{n-1} e^{-\zeta R(\mu+\nu)/2} \\ &\times \bar{P}_{lm}[(1 + \mu\nu)/(\mu + \nu)] \Phi_m(\phi) \end{aligned} \quad (8)$$

which is related to a similar STO on B by

$$\chi_B(\mu, \nu, \phi) = \chi_A(\mu, -\nu, \phi). \quad (9)$$

Our total wave function was of the form

$$\psi(1, 2) = \sum_{i,j} [a_{ij}(\chi_i \chi_j)_C + b_{ij}(\chi_i \chi_j)_I] \quad (10)$$

where the coefficients a_{ij} and b_{ij} were determined variationally (or set equal to zero for those terms to be omitted). The calculations were carried out in standard fashion. Required integrals over AO's were first computed and then compiled to give elements of the Hamiltonian matrix which was diagonalized to give the total molecular energy and the corresponding best coefficients in Eq. (10). The total energy was then minimized with respect to orbital exponents (ζ in Eq. (5) and Eq. (8)) by a steepest descents procedure coupled to a search by "golden section" (see Appendix) along the gradient. We shall only outline these steps to indicate the methods used. Details, including listings of all programs, are given in the Ph. D. Thesis of Thomas [13].

One-electron integrals were expressed in terms of overlap integrals which were evaluated in double-precision using Kontani's auxiliary functions $A_n(x)$ and $B_n(x)$ [14]. Our computed A_n 's and B_n 's were checked against the 14-place tables of Miller, Gerhauser and Matsen [15]. The first 7 figures of the overlap integrals themselves were compared, up to principal quantum number 2, to Sahni and Cooley's table [16]. For higher principal quantum numbers, our formulas were compared to those of Lofthus [17]. An alternative method of evaluating overlap

integrals described by Wahl, Cade and Roothaan [18] was not used because we lacked the necessary amount of core storage.

One-center electron repulsion integrals were evaluated in closed form making use of the usual expansion of $1/r_{12}$ in spherical harmonics and a program for the evaluation of Clebsch-Gordan coefficients. Two-center Coulomb and hybrid integrals were computed by the method of Wahl, Cade and Roothaan [18] which consists of an analytical integration over the coordinates of electron 1 followed by a Gauss-Legendre numerical integration over electron 2. For the difficult exchange integrals we again followed Wahl, Cade and Roothaan [18] who transform to prolate spheroidal coordinates and use the Neumann expansion for $1/r_{12}$. Integration over the coordinate ϕ is then straightforward, that over ν is more difficult, but can be accomplished by recurrence relations, leaving integration over μ which was done numerically by Simpson's rule. One-center electron repulsion integrals and 2-center Coulomb and hybrid integrals were checked against Sahni and Cooley's tables [16] for principal quantum number less than or equal to 2. Those with higher principal quantum number and exchange integrals were checked against hand calculations.

Matrix diagonalizations were carried out by the Givens method [19] using a modified version of a program written by Prosser [20]. To test the stability of the entire calculation, the last three digits of all integrals were replaced by random numbers. The energy was unchanged up to the fifth digit. As a further check, Weinbaum's VB calculation [7] was repeated with our program. Total energy and ionic-covalent mixing coefficient agreed with his to as many figures as listed. As a result of these checks, we feel that the energies quoted below are accurate to at least 5 figures.

3. Results

A. Two-STO Functions without Angular Correlation

Some preliminary calculations were made using wavefunctions constructed from only 2 STO's. This was done to estimate the importance of various terms to be included in more complete wavefunctions below, and also in part to test various optimization schemes. In each case the total wavefunctions (10) included all 4 possible covalent terms (1) and (2) plus the two ionic functions (4). Ionic functions of the form (3) were not used.

Results with exponents fixed by Slater's rules [21] for $1s-nl$ functions are shown in Table 1. The energies are very poor and in fact, caused us to abandon our original plan of using only orbitals of this type.

Optimization of orbital exponents improves the energy considerably as shown in Tables 2 and 3. All optimizations were carried out from at least 3 different sets of starting parameters. Wavefunctions and energies always converged to the same values with no indication of multiple minima. Perhaps the most notable feature of these results is that all energies are almost the same. The best differs from the worst by only 0.6 kcal/mole. This implies that in going from $n=2$ to $n=6$ for the second STO there is very little change in the wavefunction. Apparently optimization forces all the second STO's to become very nearly equal. This is

Table 1. *Energies of 1s-*nl* functions with Slater exponents^a*

<i>n</i>	<i>l</i>	ζ	Energy
2	0	0.5000	-1.1200727
3	0	0.3333	-1.1074739
4	0	0.2500	-1.1067287
2	1	0.5000	-1.1067332
3	1	0.3333	-1.1067712
4	1	0.2500	-1.1066601

^a The exponent of the 1s orbital is 1.0000, and the internuclear distance is held fixed at 1.4008 a.u.; *m* = 0 for all orbitals.

Table 2. *Optimum orbital exponents, internuclear distances and energies of 1s-*ns* functions*

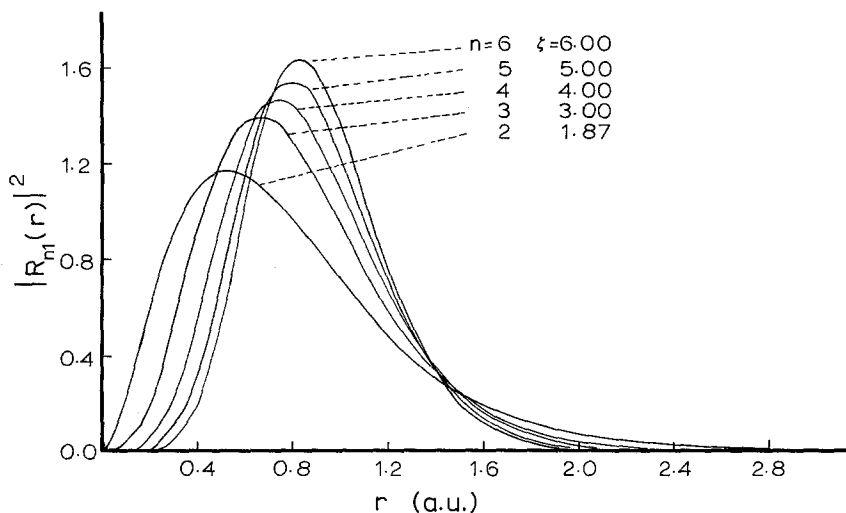
	<i>n</i>				
	2	3	4	5	6
ζ_{1s}	0.9648	1.0770	1.1105	1.1389	1.1498
ζ_{ns}	1.1216	1.6005	2.0211	2.4665	2.9989
<i>R</i> (a.u.)	1.4201	1.3995	1.4172	1.4120	1.4023
<i>E</i> (a.u.)	-1.1524792	-1.1529231	-1.1527434	-1.1524906	-1.1521590

Table 3. *Optimum exponents, internuclear distances and energies of 1s-*np* functions^a*

	<i>n</i>				
	2	3	4	5	6
ζ_{1s}	1.1876	1.1888	1.1957	1.1780	1.1840
ζ_{np}	1.9102	3.0000	3.9993	5.0005	6.0034
<i>R</i> (a.u.)	1.4150	1.4289	1.4156	1.4366	1.4320
<i>E</i> (a.u.)	-1.1529030	-1.1529804	-1.1526246	-1.1523442	-1.1519400

^a Only the *pσ* (*m* = 0) functions were used.

confirmed by a plot of the square of the *p* radial wavefunction in Fig. 1. The wavefunctions here are not quite those of Table 3, but are from very similar results in which the internuclear distance and the 1s exponent were fixed at 1.4100 a.u. and 1.19 while the second orbital exponent was optimized. (This gave a best $\zeta_{2p} = 1.87$ in agreement with McLean, Weiss and Yoshimine [10]). The similarity of these functions with varying *n* is the more striking if one realizes that the radial functions with Slater exponents and with *n* > 2 are too small to be visible on Fig. 1. A plot of the optimized *ns* orbitals also shows them all to be nearly the same. It is of course well known that functions with Slater or hydrogenic exponents, the magnitudes of which decrease as (1/*n*), rapidly become too diffuse. In fact, as Shull and Löwdin [22] have pointed out, hydrogenic orbitals do not form a complete set without the continuum. They recommend instead a set with constant exponent. From our results it appears that even that set is too

Fig. 1. Square of optimized radial wavefunctions for np orbitals

diffuse for the best representation of a single shell, and that the magnitude of the exponent should increase with n .

Fixing one electron on one nucleus and plotting the density of the other along the internuclear axis [13] shows that p functions contribute somewhat more than s functions to left-right correlation. On the other hand, s functions are better than p 's for in-out correlation as seen from similar plots with one electron fixed at the center of the bond and the density graphed along a line from the center and perpendicular to the bond. Thus, one would expect a mixture of s and p functions to be more efficient than the same number of either alone. Other than this rather trivial result, the preliminary calculations with $1s - ns$ and $1s - np$ functions were not as helpful as anticipated. Since optimization made all the functions much the same, all lowered the energy by roughly the same amount, and we could not tell which would contribute most to more elaborate wavefunctions.

Several $1s - nl$ functions with $l > 2$ were also tried (Table 4). The exponents were not as carefully optimized as above, but a comparison of Table 4 with the completely optimized Weinbaum energy of -1.1479 a.u. shows that these functions do not help much. Coefficients of the nl terms in the complete wavefunction are found to be small.

Table 4. Results with $1s - nl$ functions^a

	n, l			
	3,2	4,3	5,4	6,5
ζ_{nl}	3.0000	4.0000	5.0000	6.0000
$E(\text{a.u.})$	-1.1482173	-1.1478240	-1.1477488	-1.1477211

^a The exponent of the $1s$ orbital is 1.1800, and the internuclear distance is 1.4250; $m = 0$ for all orbitals.

B. Many-STO Functions without Angular Correlation

From Tables 2 and 3 it would appear that the best 3-STO function should be constructed from a 1s orbital and two of the three 3s, 2p, 3p. The 1s, 2p, 3p function was tried first resulting in a computer overflow during matrix diagonalization. Difficulty was not experienced at the start of the calculation with equal 2p and 3p orbital exponents, but arose as the orbital optimization proceeded. A 1s, 2s, 3s function also gave trouble, but 1s, 2p, 3s did not. Tracing down the overflow showed these results to be a further and more compelling demonstration of the point made in Fig. 1. The optimized orbitals 2p and 3p are so similar, as are 2s and 3s, that their integrals are identical to the accuracy of the computer. In view of this, no further wavefunctions were constructed using two orbitals of the same symmetry, save the 1s - ns combinations which gave no trouble.

Table 5 summarizes results with various optimized 3-STO functions. The 2- and 3-STO wavefunctions are listed in Thomas' thesis and will not be given here. Examination of these functions shows that the coefficient of a given term is nearly the same in the 3- as in the 2-STO calculation. This means that the contribution of a given term is almost independent of the other terms in the wavefunction. This will also be seen to hold for most coefficients in Table 7 below.

The best 3-STO function, that constructed from 1s, 2p, and 3s orbitals, was then improved by the addition of 3d; 3d and 4f; 3d, 4f and 5g orbitals. The last two of these were not optimized completely with respect to orbital exponents and internuclear distance. Results are in Tables 6 and 7. Although the contribution of each term is usually fairly constant from function to function, it would have been difficult to predict the relative importance of the terms. For example, the coefficient of $(2p2p)_C$ is less than 1/100 times that of $(2p3s)_C$, and $(3s3d)_C$ is as important as $(1s2p)_C$.

Table 5. Orbital exponents, internuclear distances and energies of 3-STO functions with $m=0$

	n, \bar{n}					
	2,2	3,3	3,2	4,2	5,2	6,2
ζ_{1s}	1.0257	1.0771	1.0735	1.1378	1.1540	1.1600
ζ_{ns}	1.2062	1.6121	1.6349	2.0180	2.5013	3.0000
ζ_{np}	1.8847	3.0226	1.9179	1.9046	1.9013	1.9000
R(a.u.)	1.4172	1.4168	1.4133	1.4211	1.4216	1.4219
E(a.u.)	-1.1588018	-1.1587281	-1.1588177	-1.1583010	-1.1580559	-1.1577347

Table 6. Orbital exponents, internuclear distances and energies of 4-, 5- and 6-STO functions with $m=0$

ζ_{1s}	ζ_{2p}	ζ_{3s}	ζ_{3d}	ζ_{4f}	ζ_{5g}	R(a.u.)	E(a.u.)
1.0900	1.9000	1.6300	3.0000	—	—	1.4100	-1.1592942
1.0800	1.9000	1.6400	3.0000	4.0000	—	1.4100	-1.1593746
1.0800	1.9000	1.6400	3.0000	4.0000	5.0000	1.4100	-1.1594022

Table 7. Coefficients of the 4-, 5- and 6-STO functions with $m=0$

Number of STO's			
Term	4	5	6
(1s1s) _c	1.045	1.067	1.067
(1s2p) _c	0.02544	0.02422	0.02453
(1s3s) _c	-0.06164	-0.09264	-0.09228
(1s3d) _c	-0.01516	-0.01566	-0.01574
(1s4f) _c	—	-0.001916	-0.001994
(1s5g) _c	—	—	0.001531
(2p2p) _c	0.0003636	0.0008942	0.0007832
(2p3s) _c	0.08904	0.08992	0.08976
(2p3d) _c	0.0009548	0.001276	0.001126
(2p4f) _c	—	0.0003048	0.0001748
(2p5g) _c	—	—	-0.0001186
(3s3s) _c	0.03204	0.03368	0.03314
(3s3d) _c	0.02664	0.02632	0.02640
(3s4f) _c	—	0.004144	0.004136
(3s5g) _c	—	—	-0.0003009
(3d3d) _c	0.00002680	0.00004872	-0.00001110
(3d4f) _c	—	0.00001954	-0.00009060
(3d5g) _c	—	—	0.00002137
(4f4f) _c	—	0.0003046	0.0002588
(4f5g) _c	—	—	0.0005228
(5g5g) _c	—	—	0.0002084
(1s1s) _i	0.2718	0.2796	0.2788
(2p2p) _i	-0.02468	-0.02506	-0.02498
(3s3s) _i	-0.1912	-0.1957	-0.1950
(3d3d) _i	-0.004482	-0.004380	-0.004320
(4f4f) _i	—	-0.002462	-0.002452
(5g5g) _i	—	—	-0.001279

The computation time became excessive for these larger functions. Each energy evaluation required about 1 hour for 4-STO, 2 hours for 5-STO, and 5 hours for 6-STO functions on an IBM 7072.

The 6-STO σ function with energy -1.1594022 a.u. is below the σ result of -1.15881 a.u. obtained by Schwartz and Schaad [23] from a 7-term Gaussian function, and also below the -1.15919 a.u. of Fraga and Ransil's 12-term LCSTO SCF MO + CI calculation with $1s$, $2s$ and $2p\sigma$ basis functions [24]. It is within 0.015 a.u. = 0.9 kcal/mole of Hagstrom and Shull's near σ limit from a 21-term elliptical coordinate expansion [25].

C. Functions with Angular Correlation

Tables 8 and 9 show the effect of including np_+ and np_- to account for angular correlation. The first two wavefunctions contain 3 STO's and the third and fourth contain 5 and 6. Because of symmetry (i.e. angular momentum around the internuclear axis equals zero) the orbitals np_+ and np_- must appear together and terms such as $(1snp_+)$ do not contribute to the ground state.

The effect of angular correlation can be seen in Fig. 2. One electron is held fixed at a distance 0.4 a.u. along a perpendicular constructed at the midpoint of

Table 8. *Optimized orbital exponents, internuclear distances and energies for functions with angular correlation*

	<i>n</i>			
	2	3	2	2
ζ_{1s}	1.1983	1.1994	1.0800	1.1000
ζ_{2p}	—	—	1.9016	1.9000
ζ_{3s}	—	—	1.6396	1.6400
$\zeta_{np^{\pm a}}$	1.9971	3.0021	1.8847	1.9000
ζ_{3d}	—	—	—	3.0000
<i>R</i> (a.u.)	1.4128	1.4148	1.3930	1.3935
<i>E</i> (a.u.)	-1.1535740	-1.1530245	-1.1651503	-1.1655531

^a The same exponent was used for np_+ as for np_- .

Table 9. *Optimized wavefunctions with angular correlation*

Term	Number of STO's, <i>n</i>			
	3,2	3,3	5,2	6,2
(1s1s) _c	0.9356	0.9364	1.079	1.022
(1s2p ₀) _c	—	—	0.03390	0.02854
(1s3s) _c	—	—	-0.08868	-0.04144
(1s3d ₀) _c	—	—	—	-0.01620
(2p ₀ 2p ₀) _c	—	—	-0.0003374	0.001463
(2p ₀ 3s) _c	—	—	0.08300	0.08924
(2p ₀ 3d ₀) _c	—	—	—	0.0005660
(3s3s) _c	—	—	0.02986	0.03162
(3s3d) _c	—	—	—	0.02650
($np_+ np_-$) _c	0.07884	0.07312	0.08648	0.08544
(3d ₀ 3d ₀) _c	—	—	—	-0.00008978
(1s1s) _h	0.2524	0.2526	0.2674	0.2712
(2p ₀ 2p ₀) _h	—	—	-0.02406	-0.02450
(3s3s) _h	—	—	-0.2014	-0.1882
(3d ₀ 3d ₀) _h	—	—	—	-0.04246

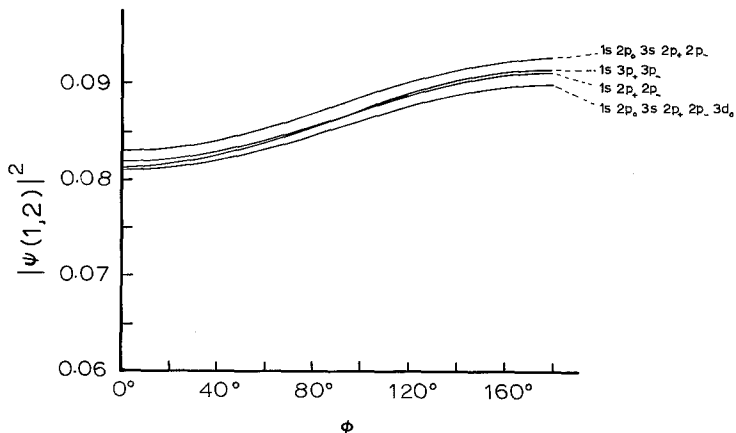


Fig. 2. Probability densities of wavefunctions with angular correlation (see text for description)

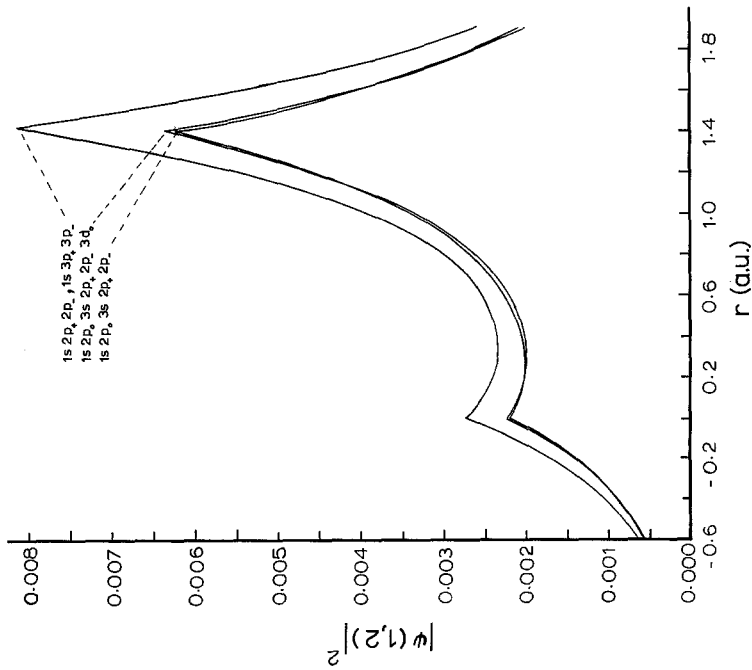
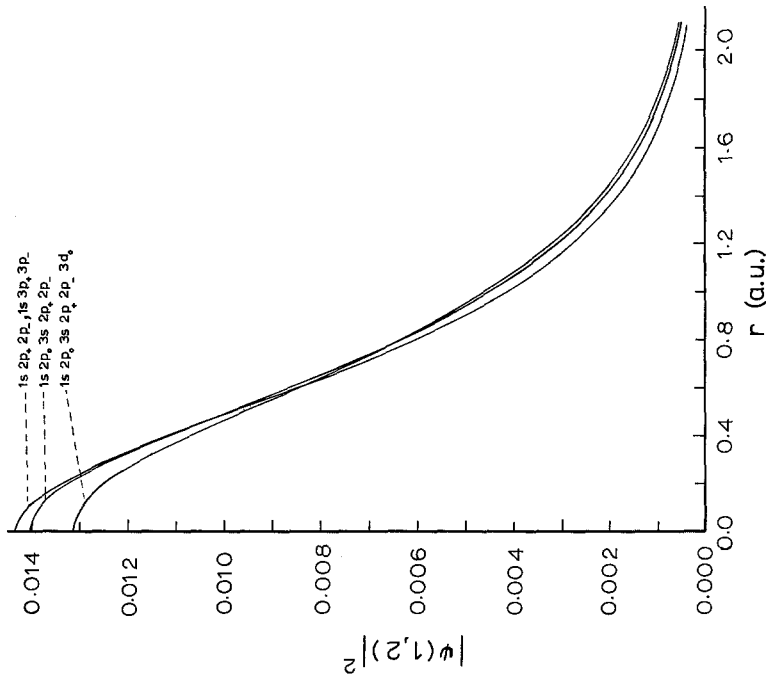


Fig. 4. In-out correlation of wavefunctions with angular correlation (see text)

Fig. 3. Left-right correlation of wavefunctions with angular correlation (see text)

the internuclear axis; the other electron starts at the same point and is allowed to move around the internuclear axis along a circle of radius 0.4 a.u. It can be seen that $|\psi|^2$ is largest when the two electrons are on opposite sides of the internuclear axis. Note that the wavefunction with $3p_+$ and $3p_-$ shows more angular correlation than the one with $2p_+$ and $2p_-$ in spite of the fact that the latter gives a lower energy. One might expect that the $2p_{\pm}$ function would show more right-left or in-out correlation to account for this, but this is not the case. In Fig. 3, one electron is fixed at one nucleus and the other is moved along the internuclear axis. The $2p_{\pm}$ and $3p_{\pm}$ functions show identical left-right correlation. Similarly, the two functions have identical in-out correlation in Fig. 4 where one electron is fixed at the midpoint of the internuclear axis and the other is moved perpendicularly outward from that point.

The energy of the 5-STO function with angular correlation is better by 0.0058 a.u. than the 6-STO function without. Further, because of symmetry there are only 10 terms in the former but 27 terms in the latter function. The 6-STO function listed in the last column of Table 9 was the best obtained in our work and gave an energy of -1.16555 a.u. The addition of further terms was attempted, but even the wavefunction constructed from $1s, 3s, 2p_+, 2p_-, 3d_+$ and $3d_-$ STO's which gave $E = -1.159438$ a.u. saturated the storage of the IBM 7072 computer used in this work.

Appendix

Optimization of orbital exponents was done by the method of steepest descents which involves computation of the gradient in the space of $E(\zeta_1, \zeta_2, \dots)$ followed by a search for minimum E along the direction of the gradient. The process is then repeated starting at this point. The method has the advantage that the multiparameter search is replaced by repeated application of a 1 parameter search; the 1 parameter being distance along the gradient. Such searches, at least under the assumption of a single minimum, are particularly susceptible to analysis so that one knows the interval of uncertainty after a given number of sample points. These matters are all clearly discussed by Wilde [26], but we shall sketch the method used since we are aware of no reference to it in quantum chemical applications.

Search by "golden section" was used to locate the minimum along the gradient. This is one of the class of minimax methods which seek to minimize the maximum interval in which the extremum being sought could lie. As a class these methods are conservative (i.e. non-gambling) in that they take account of the worst possible outcome in the drawing of sample points.

Consider $f(x)$ with a single minimum in the interval $0 \leq x \leq L$. If one wants to locate the minimum of $f(x)$ as closely as possible by only two evaluation of f , then the two should be as near as possible the midpoint of the interval, say at $\frac{1}{2}L \pm \delta$. If $f(\frac{1}{2}L + \delta) < f(\frac{1}{2}L - \delta)$, then the minimum lies in the interval of length $\frac{1}{2}L + \delta$ between $x = \frac{1}{2}L - \delta$ and $x = L$. Note that this length is smallest if the points are near the midpoint. The function could then be examined at two points near the center of the remaining interval and the process continued. This is called the method of "dichotomous search" and is the most efficient only if the total number of points is to be limited to 2.

In the method of golden section the two points are placed symmetrically in the interval so that $x_1 + x_2 = L$ and in the ratio $L/x_2 = x_2/x_1 = \tau$, called the "golden section". These conditions give $\tau^2 - \tau - 1 = 0$, hence $\tau = 1.6180$. If $f(x_1) > f(x_2)$, then the minimum must be in the interval $0 \leq x \leq x_2$. Only about 0.38 of the interval has been eliminated as compared to 0.5 in the dichotomous search. However, note that x_1 already provides one of the required points for searching the remaining interval. In the next cycle the function need be evaluated only at one further point placed so that it and x_1 are symmetric about the center of the interval $(0, x_2)$. In the long run then, search by golden section becomes about 0.38/0.25 as efficient as dichotomous search.

A somewhat more efficient method still, the "Fibonacci Search Technique", requires that the number of sample points be fixed ahead of time [26], a condition one does not usually want to apply in energy minimizations.

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References

1. Heitler, W., London, F.: Z. Physik **44**, 455 (1927).
2. Sugiura, Y.: Z. Physik **45**, 484 (1927).
3. Coulson, C. A.: Trans. Faraday Soc. **33**, 1479 (1937).
4. Cohen, E. R., DuMond, J. W.: Rev. mod. Physics **37**, 537 (1965).
5. Wang, S. C.: Physic. Rev. **31**, 579 (1928).
6. Rosen, N.: Physic. Rev. **38**, 2099 (1931).
7. Weinbaum, S.: J. chem. Physics **1**, 593 (1933).
8. Eckart, C.: Physic. Rev. **36**, 878 (1930).
9. Bowen, H. C.: Molecular Physics **10**, 299 (1966).
10. McLean, A. D., Weiss, A., Yoshimine, M.: Rev. mod. Physics **32**, 211 (1960).
11. Kołos, W., Wolniewicz, L.: J. chem. Physics **49**, 404 (1968).
12. Herzberg, G.: J. Mol. Spect. **33**, 147 (1970).
13. Thomas, I. L.: Ph. D. Thesis in chemistry, Vanderbilt University, January, 1968.
14. Kotani, M., Amemiya, A., Ishiguro, E., Kimura, T.: Tables of molecular integrals. Tokyo: Maruzen Co., Ltd. 1963.
15. Miller, J., Gerhauser, J. M., Matsen, F. A.: Quantum chemistry integrals and tables. Austin: University of Texas Press 1959.
16. Sahni, R. C., Cooley, J. W.: Derivation and tabulation of molecular integrals, supplement I, II. Washington: National Aeronautics and Space Administration Technical Note D-146 1959.
17. Lofthus, A.: Molecular Physics **5**, 105 (1962).
18. Wahl, A. C., Cade, P. E., Roothaan, C. C. J.: J. chem. Physics **41**, 2578 (1964).
19. Givens, W.: Numerical computation of the characteristic values of a real symmetric matrix. Oak Ridge National Laboratory Report ORNL-1574 1954.
20. Prosser, F.: GIVENS, program 62, Quantum Chemistry Program Exchange, Indiana University.
21. Slater, J. C.: Physic. Rev. **36**, 57 (1930).
22. Shull, H., Löwdin, P. O.: J. chem. Physics **23**, 1362 (1955).
23. Schwartz, M. E., Schaad, L. J.: J. chem. Physics **46**, 4112 (1967).
24. Fraga, S., Ransil, B. J.: J. chem. Physics **35**, 1967 (1961).
25. Hagstrom, S., Shull, H.: Rev. mod. Physics **35**, 624 (1963).
26. Wilde, D. J.: Optimum seeking methods. Englewood Cliffs, N. J.: Prentice-Hall, Inc. 1964.

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