Correlated Gaussian Wavefunctions for the Hydrogen Molecule

R A THURAISINGHAM* & S H M NILAR

Department of Chemistry, University of Colombo, Sri Lanka

Configuration interaction (CI) wavefunctions using correlated gaussians are presented for the H_2 molecule, and properties such as equilibrium bond distance, ionisation potentials and dissociation energy have been evaluated. These wavefunctions are compared with the conventional CI wavefunctions. The results illustrate the possibility of constructing rapidly converging CI wavefunctions and also the choice of configurations in the CI expansion.

The determination of wavefunctions for small molecules, which are more accurate than Hartree-Fock, remains a difficult problem. Configuration interaction (CI) techniques and explicit introduction of interelectronic coordinates are the approaches commonly employed. The disadvantage of the CI method is the large number of configurations required. An alternative method is to use a function of the form,

$$\Psi = \sum_{i,j} f(r_i, r_j) \Phi$$

where Φ is a determinant and $f(r_i, r_j)$ is some suitable function which would include the interelectronic distance r_{ij}. This approach was first adopted by Hylleraas[1] for helium and by James and Coolidge[2], and Kolos and Wolniewicz[3] for the hydrogen molecule. In this method integral evaluation proves to be a formidable task and extension of this method is, therefore, limited. The work reported here attempts to combine the two methods described above. The interelectronic distances, r_{ij}, are introduced to facilitate convergence of the CI expansion and gaussian basis orbitals, and correlation functions are used to simplify integral evaluation. Previously[4] a CI wavefunction for the helium atom using correlated gaussians was reported. This paper extends this method to the hydrogen molecule.

Theoretical

The trial wavefunction Ψ for the molecule is written in the usual CI form, $\Psi = \sum_i c_i \Phi_i$, the first configuration Φ_0 being chosen as the self consistent field (SCF) wavefunction, while the succeeding configurations are constructed using the molecular orbitals (MOs) of the SCF calculation and correlating factors, correlating pairs of electrons, which are of the gaussian type.

In the studies presented here a minimal basis gaussian type orbital (GTO) was used. The wavefunction Φ_0 is then given by, Φ_0 $= A(\varphi_1(1)\alpha(1)\varphi_1(2)\beta(2))$, where A is the anti-symmetriser and φ_1, the occupied MO, is of the form $\varphi_1 = C_1(\eta_P + \eta_Q)$, η_P being a GTO of the form $\exp(-ar_P^2)$ centred on atom P, with a being a positive constant and $r_P = [(X - P_x)^2 + (Y - P_y)^2 + (Z - P_z)^2]^{1/2}$. The other configurations, Φ_i, are of the form $\Phi_i = \exp(-\alpha r_{12}^2)\chi_i$, where χ_i is a linear combination of determinants of the form $A(\varphi_k(1)\alpha(1)\varphi_l(2)\beta(2))$, the combinations being such that they are eigenfunctions of S^2 and S_z. The evaluation of the matrix elements over these configurations results in integrals, and formulae for closed form evaluation of these have been given by Boys[5,6]. For example the two electron repulsion integral is given by,

$$I = \iint \exp(-Ur_{1P}^2 - Vr_{2Q}^2 - Wr_{12}^2)\frac{1}{r_{12}}d\tau_1 d\tau_2$$

$$= [\Pi^3 \exp(-UVW\overline{PQ}^2/E)\,\mathrm{erf}(UV\overline{PQ}/(U+V)^{1/2}E^{1/2})]/[UV\overline{PQ}E^{1/2}]$$

where $E = UV + W(U + V)$, $PQ = |P - Q|$

$$\mathrm{erf}(x) = 2\Pi^{-1/2}\int_0^x \exp(-t^2)dt$$

The error function $\mathrm{erf}(x)$ is a tabulated function which can easily be evaluated using standard library subroutines. Hence the evaluation of I is direct. Similar type of formulae exist for the nuclear attraction, kinetic energy and overlap integral, all of which can be evaluated analytically. The analytical evaluation of the integrals is a distinct advantage in the use of gaussians and correlated gaussians in molecular and atomic calculations. The calculations described below were done using atomic units unless otherwise stated.

Calculations and Discussion

An SCF calculation using a minimal GTO basis was done at the internuclear distance of $R = 1.4$ a.u. with the gaussian exponent a chosen as 0.4 (approximately the best one gaussian expansion). An SCF energy of -0.9762 a.u. was obtained which is in agreement with an earlier reported calculation[7]. The energies of the following CI wavefunctions, Ψ_a, Ψ_b and Ψ_c, were then

determined for different values of the correlation parameter α.

$$\Psi_a = C_0\Phi_0 + C_1\exp(-\alpha r_{12}^2)\Phi_0$$

$$\Psi_b = C_0'\Phi_0 + C_1'\exp(-\alpha r_{12}^2)\Phi_1$$

$$\Psi_c = C_0''\Phi_0 + C_1''\exp(-\alpha r_{12}^2)\Phi_2$$

$$\Phi_1 = A(\varphi_1(1)\alpha(1)\varphi_2(2)\beta(2)) + A(\varphi_2(1)\alpha(1)\varphi_1(2)\beta(2))$$

$$\Phi_2 = A(\varphi_2(1)\alpha(1)\varphi_2(2)\beta(2))$$

Φ_1 and Φ_2 correspond to single and double excitation configurations. The results of these calculations are shown in Table 1.

A CI calculation was then performed using a three term CI expansion given by the equation,

$$\Psi_d = b_1\Phi_0 + b_2e^{-0.4r_{12}^2}\Phi_0 + b_3e^{-0.2r_{12}^2}\Phi_2$$

This gave an energy of -0.9980 and a correlation energy of 0.0218.

The results of Table 1 indicate that the optimum correlation parameter α for Ψ_a is in the interval 0.2-0.6 while for Ψ_c it is 0.2. In the case of Ψ_b no lowering in energy is observed for α in the range 0.0-1.0. The correlation energy[7] obtained using these wavefunctions is about 36%, 0%, and 53% of the total correlation energy. This must be compared with that of helium, for which using a two gaussian basis we obtained 46%, 11% and 24% of the total correlation energy using a two term wavefunction of the types Ψ_a, Ψ_b and Ψ_c respectively[4]. Clearly for $\alpha = 0$, the Brillouin theorem holds for Ψ_b. But, for α not equal to zero it is not immediately obvious why there is no improvement in Φ_0. This, however, is not a general result, since for helium there was a reduction in energy, though much smaller when compared to Ψ_a and Ψ_c. This means that $\langle\Phi_0|H|\Phi_1\rangle = 0$ is sufficiently strong so as to cause least mixing of Φ_0 even with $e^{-\alpha r_{12}^2}\Phi_1$.

Although singly excited configurations have a vanishing matrix element for the Hamiltonian with the ground state SCF wavefunction, there is a non-vanishing matrix element with the doubly excited configurations. However, this effect is small since the coefficients of the singly excited configuration are very small in the CI expansion. Sinanoglu's theory also predicts a lesser importance for the singly excited configuration[8-10]. This along with the results of

Table 1 made us to choose Ψ_d as a suitable three term CI wavefunction instead of

$$\Psi_e = C_0\Phi_0 + C_1e^{-\alpha r_{12}^2}\Phi_1 + C_2e^{-\alpha r_{12}^2}\Phi_2, \quad \alpha \neq 0$$

In the conventional CI method, it is the doubly excited configuration which contributes most to the correlation energy. This is clearly seen from Table 1 for $\alpha = 0$. However, multiplication by $\exp(-\alpha r_{12}^2)$ of Φ_2 has recovered a further 0.006 a.u. about 15% of the correlation energy. In the helium atom the main contribution to the correlation from a two gaussian basis arises from Ψ_a, while in the case of hydrogen it is from Ψ_c.

The calculations were extended to a series of bond distances, R. A minimal GTO basis SCF calculation was carried out at each R for various values of the exponent a in order to obtain the best SCF energy with the type of basis we have used. The optimum gaussian exponent a and SCF energy at each R are given in Table 2.

The energies of the CI wavefunctions, Ψ_a, Ψ_b and Ψ_c, were then determined for each R for different values of the correlation parameter α. The optimum value of α did not vary with R and was found to be 0.2, except at $R = 1.4$ a.u. where the α value was 0.4. However, even at this distance the difference in energies between the values of $\alpha = 0.2$ and 0.4 was only 0.0001 a.u. For Ψ_b, α was always 0.0 and for Ψ_c it varied from 0.2, at distances close to the equilibrium distance, to zero at large internuclear distances. The energies and the optimum α values at each internuclear distance for Ψ_a, Ψ_b and Ψ_c are shown in Table 3. Also given in Table 3 are the energies of the usual CI wavefunction $\Psi_c^{\alpha=0}$ for various internuclear distances R.

Table 2—Optimum Values of the Exponent a and SCF Energy for Various R of the H_2 Molecule

R	Optimum exponent, a	SCF Energies
1.00	0.48	−0.8849
1.15	0.45	−0.9388
1.20	0.44	−0.9505
1.25	0.43	−0.9597
1.30	0.42	−0.9668
1.40	0.40	−0.9762
1.45	0.38	−0.9786
1.50	0.38	−0.9803
1.55	0.37	−0.9808
1.60	0.36	−0.9805
1.65	0.36	−0.9794
1.70	0.35	−0.9778
2.00	0.32	−0.9587
6.00	0.22	−0.6799
10.00	0.21	−0.6241
25.00	0.19	−0.5952
35.00	0.19	−0.5895
50.00	0.19	−0.5851

Table 1—The Energies $E(\Psi_a)$, $E(\Psi_b)$, $E(\Psi_c)$ for Different α values

α	$E(\Psi_a)$	α	$E(\Psi_b)$	α	$E(\Psi_c)$
0.2	−0.9906	0.0	−0.9762	0.0	−0.9912
0.4	−0.9907	0.2	−0.9762	0.2	−0.9975
0.6	−0.9907	0.4	−0.9762	0.4	−0.9945
0.8	−0.9904	0.6	−0.9762	0.6	−0.9913
1.0	−0.9899	0.8	−0.9762	0.8	−0.9888
		1.0	−0.9762	1.0	−0.9873

Table 3—Energies $E(\Psi_a)$, $E(\Psi_b)$, $E(\Psi_c)$, $E(\Psi_c^{\alpha=0})$ at Each R Value and the Optimum Exponent α.

R	$E(\Psi_a)$	α
1.00	−0.8961	0.2
1.15	−0.9516	0.2
1.20	−0.9636	0.2
1.25	−0.9692	0.2
1.30	−0.9850	0.2
1.40	−0.9907	0.4
1.45	−0.9918	0.2
1.50	−0.9950	0.2
1.55	−0.9955	0.2
1.60	−0.9951	0.2
1.70	−0.9938	0.2
1.85	−0.9868	0.2
2.00	−0.9777	0.2
6.00	−0.7266	0.2
10.00	−0.6816	0.2
25.00	−0.6553	0.2
50.00	−0.6482	0.2

R	$E(\Psi_b)$	α
1.4	−0.9762	0.0
25.00	−0.5952	0.0
50.00	−0.5851	0.0

R	$E(\Psi_c)$	α	$E(\Psi_c^{\alpha=0})$
1.00	−0.9056	0.4	−0.8968
1.20	−0.9712	0.2	−0.9639
1.35	−0.9963	0.2	—
1.40	−0.9975	0.2	−0.9912
1.45	−0.9999	0.2	−0.9937
1.50	−1.0017	0.2	−0.9961
1.55	−1.0032	0.2	−0.9972
1.60	−1.0020	0.2	−0.9970
1.65	−0.9999	0.2	−0.9968
1.70	—	—	−0.9956
2.00	−0.9807	0.2	−0.9805
6.00	−0.8382	0.2	−0.8382
10.00	−0.8325	0.0	−0.8325
25.00	−0.8211	0.0	−0.8211
50.00	−0.8211	0.0	−0.8211

Table 4—Properties of the H_2 Molecule for Different Wavefunctions

Wave function	Bond distance	Force constant (m dynes/A)	Ionisation potential (eV)	Dissociation energy (eV)
Φ_0	1.55	2.49	12.184	—
Ψ_a	1.55	2.04	12.645	—
Ψ_c	1.55	6.48	12.862	4.95
$\Psi_c^{\alpha=0}$	1.55	4.05	12.631	4.79
experimental[11,12]	1.40	5.7	15.426	4.75

The properties evaluated with Φ_0, Ψ_a, Ψ_c and $\Psi_c^{\alpha=0}$ are shown in Table 4. To determine the vertical ionisation potential of H_2, the energy of H_2^+ was evaluated at the calculated bond distance of 1.55 a.u. using the same basis as for H_2, the exponent a being chosen so as to obtain the minimum energy.

The energies of the wavefunctions Ψ_c, $\Psi_c^{\alpha=0}$, Ψ_a and Φ_0 are in the order: $E(\Psi_c) \leqslant E(\Psi_c^{\alpha=0}) < E(\Psi_a) < E(\Phi_0)$ for internuclear distance $1.00 \leqslant R \leqslant 50.00$. According to the variation theorem, Ψ_c is, therefore, the most accurate amongst them. Just beyond $R = 2.00$ a.u. both Ψ_c and $\Psi_c^{\alpha=0}$ become identical, the optimum value for α in Ψ_c being 0.0. Inclusion of the correlation parameter is, therefore, important near the equilibrium distance and it is here that one needs to include such functions. The force constant which depends on the curvature of the E versus R curve near the equilibrium is, therefore, best obtained from Ψ_c. This is verified from Table 4. The poor bond distance obtained with all wavefunctions is due to the small basis set employed[13]. The wavefunctions Φ_0 and Ψ_a show incorrect dissociation as can be seen from Tables 2 and 3.

The results indicate the possibility of constructing rapidly converging CI wavefunctions including interelectronic coordinates at least for small molecular systems. The use of correlated gaussians has simplified the evaluation of integrals and one could expect that once the integral evaluation algorithm is made more efficient it could compete with the available CI programmes, reducing at the same time the number of configurations chosen. However, this should be tested with bigger basis set before the viability of the method is fully assessed.

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