

Calculations with some basic Floating Spherical Gaussian Orbital (FSGO) sets for the H₂ molecule

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Summary: The floating spherical gaussian orbital (FSGO) model has been used to compute energy and orbital parameters for the H₂ molecule using concentric, non-concentric and cusp functions. The results are discussed in terms of well known localized and non-localized molecular orbital theories.

Introduction

The floating spherical Gaussian orbital (FSGO) model of molecular structure using single Gaussians has yielded good quantitative features of the electronic and geometric structures of a number of molecules.¹

Double gaussians have been used to improve molecular energies and geometries.² In certain case, analysis of energy terms affecting the geometry of various molecules, has been affected.³ All this has been achieved using the concept of localized orbitals through which the molecular orbital method of Hund⁴, Mulliken⁵ and Lennard Jones⁶ is related to the original valence bond method due to Heitler and London⁷ and Slater⁸ and Pauling⁹. Mathematically speaking, the molecular orbital wavefunction is represented by a single determinantal wavefunction while a singlet state valence bond wavefunction is represented by a linear combination of Slater's determinants. In case the electron pairs forming a bond for a valence bond wavefunction occupy the same orbital, the linear combination of determinants is then represented by a single determinant.

The purpose of this paper is to show as to how a simple FSGO model using multiple gaussians for H₂ molecule throws light on the energy, bond distance and other relevant parameters. The results obtained from single, double (cusp concentric), triple (two cusp and one concentric), four and five gaussians in various ways have been tabulated and compared with the experimental values for energy and bond distance for the H₂ molecule. Cusps are gaussians centered on the nuclei.

Orthogonal and nonorthogonal orbitals: Energy of a closed-shell system.

Each localized spherical gaussians orbital function has the form:

$$\varphi_i(r) = \left(\frac{2}{\pi \rho_i^2}\right)^{3/4} \exp [-(r/\rho_i)^2] \quad (1)$$

with variable 'orbital radius' ρ_i and variable position. These orbitals are nonorthogonal and require a rather complex energy expression involving three and four orbital interaction.

The electronic energy formula for a Slater determinantal wavefunction for closed shells of orthogonal orbitals, χ_i is well known:

$$E_{el} = 2 \sum_i [i/i] + \sum_{i,j} 2[ii/jj] - [ii/ij] \quad (2)$$

summations are from 1 to n unless otherwise indicated;

$$[i/i] = \int \chi_i^* h \chi \, dv \quad (3)$$

are one electron integrals involving the one electron Hamiltonian operator

$$h = \frac{1}{2} \nabla^2 - \sum_{\nu} \frac{Z_{\nu}}{r_{\nu}} \quad (4)$$

Z_ν being the atomic number of nucleus ν and r_ν the distance of the electron from that nucleus. N is the number of nuclei;

$$[ij/kl] = \chi f \chi_i^* (1) f \chi_i (1) \chi_k^* (2) \chi_l (2) (1/r_{12}) dv_1 dv_2 \quad (5)$$

are the two-electron repulsion integrals. Equation (2) is obtained from

$$E_{el} = \chi f \psi^* H \psi d T_1 \dots \dots \dots d T_{2n}$$

with the total Hamiltonian

$$H = \sum_{i=1}^{2n} h_i + \sum_{i<j} r_{ij}^{-1} \quad (6)$$

and

$$\psi = (1/\sqrt{2n!}) \det (x_1 x_1 x_2 x_2 \dots x_n)$$

The original non-orthogonal orbitals ϕ_i may be transformed to an orthogonal set χ_i . This may be achieved by a nonunitary transformation converting the overlap matrix to the unit matrix. Lowdin¹⁰ has shown such transformations for a determinantal wavefunction of $2n$ orbital all with parallel spin. For a closed-shell case the transformation from the original non-orthogonal orbitals ϕ_i to an orthogonal set χ_i may be carried out by the following formula given in matrix notation

$$X = \varphi T^{1/2} \quad (7)$$

where $T = S^{-1}$ is the inverse overlap matrix and χ and φ are row vectors of the corresponding orbitals, S and T are assumed to be real. The integrals of Equation (3) may then be transformed to give

$$\sum_i [i/i] = \sum_i \sum_j \sum_k (j/k) (T^{1/2})_{ij} (T)_{ik}^{1/2} = \sum_{j,k} (j/k) T_{jk} \quad (8)$$

where

$$(j/k) = \int \varphi_j^* h \varphi_k dv$$

similarly

$$\sum_{i,j} [ii/jj] = \sum_{k,l,p,q} (kl/pq) T_{kl} T_{pq} \quad (9)$$

and

$$\sum_{i,j} [ij/ji] = \sum_{k,l,p,q} (kl/pq) T_{kq} T_{lp} \quad (10)$$

where

$$(kl/pq) = \int \varphi_k^* (1) \varphi_l (1) \varphi_p^* (2) \varphi_q (2) r_{12}^{-1} dv_1 dv_2 \quad (11)$$

(Here the parentheses refer to integrals over nonorthogonal orbitals while the brackets involve orthogonal orbitals). The electronic energy then becomes

$$E_{el} = 2 \sum (j/k) T_{jk} + \sum_{k,l,p,q} (kl/pq) [2T_{kl} T_{pq} - T_{kq} T_{lp}] \quad (12)$$

and the total energy is then

$$E = E_{el} + \sum_{\mu < \nu}^N \frac{Z_\mu Z_\nu}{r_{\mu\nu}} \quad (13)$$

after adding the internuclear repulsion energy.

The FSGO model and the H_2 molecule

The initial parameters and coordinates are fixed at random; the molecule is then allowed to relax to achieve its most stable nuclear configuration. The values of coordinates and normalized coefficients after equilibrium for the H_2 molecule using various basic orbitals have been listed in table I.

With only two nuclei with +1 charges and a pair of electrons with paired spins form a singlet electronic state. The localized orbitals ϕ_i are not required to be orthogonal. The $2n$ - electron wavefunction may be written as a single Slater determinat

$$\psi = N |\varphi_1 (1) \varphi_1 (2) \varphi_2 (3) \varphi_2 (4) \dots$$

$$\varphi_n (2n-1) \varphi_n (2n) | \quad (14)$$

with the normalizing factor

$$N = 1 / [(2n)!]^{1/2} \det S \quad (15)$$

The bars over orbitals indicate β spin as opposed to α for others. Det S is the determinant of the orbital overlap matrix S with element

$$S_{ij} = \int \varphi_i^* \varphi_j \, dv \quad (16)$$

The energy is varied to determine the best localized orbitals followed by the calculation of such observable properties as bond angles, bond distances, kinetic and total energies.

The main aim her has been to obtain a relatively simple model of calculation to reproduce major trends in electronic geometric structure of H₂ molecule and not to seek a solution of the Schrodinger wave equation which has so abundantly been done. The calculation are here strictly ab initio with no semiempirical parameters involved.

Results and Discussion

In table I are listed the basic orbital sets used which vary from single to five gaussian containing cusp, concentric and nonconcentric orbitals along with their orbital radii. First two columns show energy values -E and kinetic energy T.

The simplest calculation is in the case of one spherical gaussian surrounding two hydrogen nuclei for which the results have been reported in reference 1 at number 2. The bond length here is accurate within 5% of the experimental value, while the energy is off by about 20%. Our calculation agrees completely with the calculation of reference 1.

The inaccuracy in the energy calculation has been attributed to lack of cusps in the wavefunction and hence the lack of electron density at the nuclei (ref 1 number 1). Our second calculation in table I has been done by using two cusp orbitals which somewhat improves the energy value (from 0.9559 hartrees to 0.9808 hartress) but enlarges the bond distance from 1.4742 to 1.5551. The lengthening of the bond distances with double cusp orbitals is understandable in terms of decrease of charge density between the nuclei which significantly

increases the nuclear-nuclear repulsion term and hence increases the bond distance. Double nonconcentric orbitals behave in a similar fashion as the double cusps. The double nonconcentric have the tendency to become double cusps when allowed to float. This is clear from their orbital radii given in table I (1.644 bohrs for double cusps) and (1.654 bohrs for non-concentric) and their nuclear coordinates (1.555 bohrs for double cusps) and 1.555 bohrs for nonconcentric).

It is known that the electron density is given by the following equation

$$\begin{aligned} \gamma &= 2n \int \psi^* \psi \, dT_2 \dots dT_{2n} \, d\eta_1 \\ &= 2 \sum_i^n \chi_i^* \chi_i ; \end{aligned} \quad (17)$$

$dT_i = dv_i \, d\eta_i$; where dv_i is the volume element of the electron i and $d\eta_i$ is the spin coordinate. For non orthogonal orbitals ϕ_i the corresponding result can be obtained by applying the transformation of equation (7) to give

$$\gamma = 2 \sum_{j-k} \phi_j \phi_k \, T_{jk} \quad (18)$$

If ϕ_i be normalized floating Gaussian functions

$$\phi_i = (2 a_i/\pi)^{3/4} \exp [-a_i (r - R_i)^2] \quad (19)$$

where the orbital exponent a_i and the components of the orbital vector R_i are variation parameters. In the present model, the electron density and 'orbital radius' may be related in the following way.

The paramter a_i in ϕ_i is replaced by

$$a_i = \frac{1}{\rho_i^2} \quad (20)$$

$$\text{so that } \varphi_i = (2/\pi\rho_i^2)^{3/4} \exp [-(r-R_i)^2/\rho_i^2] \dots \quad (21)$$

The new parameter ρ_i is termed an "orbital radius" and has the dimensions of length.

Integrating

$$4 \pi \int_0^{\rho_i} \varphi_i^2 \, r_i^2 \, dr_i \simeq 0.74 \quad (22)$$

Table I. Calculated results for H₂ molecule with full minimization. All quantities in atomic units. Distance in bohrs. Energies in Hartrees.

No	Orbitals	-Energy	Kinetic energy	Orbital Radii	Bond length	Normalized coefficient	Orbital positions
1.	Single	0.95594	0.95576	1.7717	1.4742	-	-
2	Double cusps	0.98080	0.98071	1.6442	1.5551	0.55227	-
				1.6442		0.55227	
3	Double non concentric	0.98155	0.98216	1.6536	1.5546	0.54592	+0.72932
				1.6536		0.54592	-0.72932
4	Double concentric	1.03815	1.03804	2.3061	1.2634	0.66669	-
				1.0958		0.41819	
5	Triple two cusps one concentric	1.09826	1.09792	2.0921		0.7776	
				0.8099	1.3935	0.1941	-
				0.8099		0.1941	
6	Four orbitals two cusps two non concen.	1.10414	1.10412	1.96686	1.4143	0.1702	+0.63697
				1.96686		0.1702	
				0.7566		0.4314	-0.63597
				0.7566		0.4314	
7	Four orbitals two cusps two concentric	1.11254	1.11242	2.6421	1.3589	0.4818	
				1.4527		0.4668	-
				0.6369		0.1117	
				0.6369		0.1117	
8	Five orbitals four cusps one concentric	1.11520	1.11518	2.3111	1.3705	0.3054	
				2.3111		0.3054	
				0.6193		0.1036	-
				0.6193		0.1036	
				1.3282		0.3658	

Expt. values : Bond distance = 1.4006
-Energy = 1.1745

The orbital radius is therefore interpreted by saying that it is the radius of the sphere containing about 74% of the orbital density. Table I lists orbital radii for cusp, concentric and nonconcentric orbitals which contain about three fourths of the electron density.

The values of bond distance, energy E and kinetic energy T are also listed in table I. For H₂, the experimental value of energy E (-1.1745 hartrees) and bond distance (1.4006 Bohr) compared well within 20% of all values obtained for eight calculations.

The values obtained for triple gaussian calculation (two cusps and a concentric) gives the best overall fit reproducing bond distance with almost complete accuracy and the energy value of 1.09826 hartrees which is within 6% of the experimental value. Addition of more

orbitals of various kind, as is expected, improves the energy value but spoils the bond distance. Using five gaussian orbitals, one obtains energy value which is off by less than 5.

The virial theorem expressed as $-E = T$ is satisfied by all calculations except perhaps for the calculation with two non concentric orbitals where the kinetic energy increase is larger than $-E$. The difference, however, is less than 1%. the virial theorem is obeyed as expected since in all our calculations a scale factor is a variation parameter¹².

It is, therefore, apparant that the FSGO model gives fairly encouraging results with various multiple gaussians. The best results for the bond distance and energy are those where the cusp as well as concentric orbitals

have been used. This points to the fact that the best electron density distribution is the one where the electron density between the nuclei as well as on the nuclei is fairly represented.

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