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AN EXAMPLE OF GAUSSIAN MOLECULAR ORBITAL AB-INITIO CALCULATIONS INCLUDING CONFIGURATION INTERACTION. THE H_2 MOLECULE

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ABSTRACT

Ab-Initio 1GTO calculations are presented for the H_2 molecule. The object of these calculations is to show a very detailed treatment for integral evaluation and SCF procedure for ab-initio computations.

RESUMEN

Se presentan cálculos ab-initio 1GTO para la molécula de H_2. El objetivo de estos cálculos es mostrar, de una manera muy detallada, la evaluación de las integrales y el método SCF para cálculos ab-initio.

INTRODUCTION

Since the formulation of the late Professor Boys$^{(1)}$ on the evaluation of two electron integrals involving gaussian type orbitals (GTO's), a number of programs have been developed to evaluate integrals used in molecular orbital (MO) calculations. Some of them are:

POLYATOM, IBMOL, ATMOL, MOLECULE, HONDO, etc.; all of them make use of the extremely important property, that a product of two gaussians centered in different atoms can be represented by one gaussian whose center lies somewhere in the line joining them.

Most of theoretical chemistry students have access to, at least, one of the above mentioned programs to perform quantum chemistry calculations; however, very few of the students have a detailed knowledge of the programs they use.

The purpose of the present paper is to show, in a very systematic way, a calculation of the H_2 molecule (for several bond lengths) using one GTO to represent each atomic orbital. These calculations have been performed in the Hartree-Fock scheme$^{(2)}$, and also configuration interaction (CI) (see ref. (3)), has been included. Dewer and Kelemen$^{(4)}$, have performed a systematic calculation on H_2 using one Slater type orbital (STO) in each atom; however, as most programs make use of GTO's rather than STO's, we feel that it will be very useful to have a very detailed computation using GTO's.

METHOD OF CALCULATIONS

I. Self-Consistent Field Equations

In Hartree units for H_2 ground state having only one double occupied molecular orbital ($1\sigma_g$) defined as $1\sigma_g = N_g\ (1S_A + 1S_B)$ where $1S_A$ and $1S_B$ represent GTO's ($e^{-\alpha r^2}$) centered on atoms A and B respectively, N_g being a normalization constant to be defined below. Then the total energy (E_t) of the molecule can be written as $E_t = E_e + \frac{1}{R_{AB}}$ where E_e is the electronic energy and R_{AB} is the internuclear separation.

The electronic energy can be written as

$$E_e = 2N_g^2 \left[T_{11} + T_{12} + V_{11} + 2V_{12} \right] + J_{11} \qquad (1)$$

with the following definitions:

Normalization constant:

$$N_g = \left[2(S_{12} + 1) \right]^{-1/2} . \tag{2}$$

Overlap integral:

$$S_{12} = \langle 1S_A | 1S_B \rangle \tag{3}$$

where

$$\langle 1S_A | 1S_B \rangle \equiv \int 1S_A(1)^* \; 1S_B(1) \; d\tau_1 \tag{4}$$

Kinetic energy integrals:

$$T_{11} = \langle 1S_A | -\frac{1}{2} \nabla^2 | 1S_A \rangle = \langle 1S_B | -\frac{1}{2} \nabla^2 | 1S_B \rangle \tag{5}$$

$$T_{12} = \langle 1S_A | -\frac{1}{2} \nabla^2 | 1S_B \rangle = \langle 1S_B | -\frac{1}{2} \nabla^2 | 1S_A \rangle \tag{6}$$

Potential energy integrals:

$$V_{11} = V_{11}^A + V_{11}^B \tag{7}$$

where

$$V_{11}^A = \langle 1S_A | -\frac{1}{r_A} | 1S_A \rangle = \langle 1S_B | -\frac{1}{r_B} | 1S_B \rangle \tag{8}$$

and

$$V_{11}^B = \langle 1S_A | -\frac{1}{r_B} | 1S_A \rangle = \langle 1S_B | -\frac{1}{r_A} | 1S_B \rangle \tag{9}$$

$$V_{12} = \langle 1S_A | -\frac{1}{r_A} | 1S_B \rangle = \langle 1S_B | -\frac{1}{r_B} | 1S_A \rangle =$$

$$= \langle 1S_A | -\frac{1}{r_B} | 1S_B \rangle = \langle 1S_B | -\frac{1}{r_A} | 1S_A \rangle ,$$

and so-called Coulomb integral:

$$J_{11} = N_g^4 <1\sigma_g(1) \mid \frac{1}{r_{12}} \mid 1\sigma_g(2)> \ , \tag{10}$$

which after some very simple algebraic manipulations reduces to:

$$J_{11} = 4N_g^4 \left[\frac{1}{2} <1S_A\ 1S_A \mid 1S_A\ 1S_A> + \frac{1}{2} <1S_A\ 1S_A \mid 1S_B\ 1S_B> + \right.$$
$$\left. <1S_A\ 1S_B \mid 1S_B\ 1S_A> + 2 <1S_A\ 1S_A \mid 1S_A\ 1S_B> \right] \tag{11}$$

where

$$<1S_A\ 1S_B \mid 1S_B\ 1S_A> = \iint 1S_A^*(1)\ 1S_B(1)\ 1S_B^*(2)\ 1S_A(2)\ \frac{1}{r_{12}}\ d\tau_1 d\tau_2 . \tag{12}$$

These (two-electron) integrals are the most difficult to evaluate, and their computation is the most time-consuming of all the above-mentioned quantities.

II. Configuration-Interaction Scheme

In the Hartree-Fock scheme, where the ground state spatial wavefunction is represented by

$$\psi = \sigma_g(1)\sigma_g(2) = 1S_A(1)1S_A(2) + 1S_B(1)1S_B(2) + 1S_A(2)1S_B(1) + 1S_A(1)1S_B(2) . \tag{13}$$

The first two terms are the so-called ionic terms, the last two are called covalent.

The ionic terms appear with the same weight as the covalent, causing the unphysical situation that the H_2 molecule can be equally predicted to dissociate either into two hydrogen atoms or into a hydrogen anion and a proton. This situation can be corrected by the introduction of Configuration Interaction (CI). In this formalism the wave function is represented by a linear combination of Slater determinants$^{(3)}$.

For this H_2 1 GTO example, the only available molecular orbitals are the previously defined σ_g, and $\sigma_u = N_u\ (1S_A - 1S_B)$. Therefore the wave function can be written as a linear combination of the six Slater determinants which can be constructed for two electrons, starting with these two molecular orbitals, namely

$$\psi = C_1|\sigma_g(1)\ \alpha\ \sigma_g(2)\beta| + C_2|\sigma_g(1)\ \alpha\ \sigma_u(2)\alpha| + C_3|\sigma_g(1)\ \alpha\ \sigma_u(2)\beta| + C_4|\sigma_g(1)\ \beta\ \sigma_u(2)\alpha| + C_5|\sigma_g(1)\ \beta\ \sigma_u(2)\beta| + C_6|\sigma_u(1)\ \alpha\ \sigma_u(2)\beta| \ . \tag{14}$$

With this wave function, the total energy is given by $E = \langle\psi|\hat{H}|\psi\rangle$ where $\hat{H}$ is the Hamiltonian which, for the present case, is given by

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} \ . \tag{15}$$

Here, subindices 1 and 2 refer to electrons and A and B denote the two nuclei; r_{12} is the distance between the two electrons.

The coefficients C_i can be calculated by solving the so-called secular determinant

$$\begin{vmatrix} H_{11} & H_{12} & \dots & H_{16} \\ \cdot & & & \\ \cdot & & & \\ \cdot & & & \\ H_{61} & H_{62} & \dots & H_{66} \end{vmatrix} \begin{vmatrix} C_1 \\ \\ C_2 \\ \vdots \\ C_6 \end{vmatrix} = E \begin{vmatrix} C_1 \\ \\ C_2 \\ \vdots \\ C_6 \end{vmatrix} \tag{16}$$

where

$$H_{ij} = \langle \mathrm{Det}(i)|\hat{H}|\mathrm{Det}(j)\rangle \ .$$

However, the Brillouin$^{(5)}$ theorem, which states that all matrix elements between the ground state and singly excited configurations vanish, allows us to write this wave function as a linear combination of only two Slater determinants, namely:

$$\psi = C_1 |\sigma_g(1)\, \alpha\, \sigma_g(2) \beta| + C_6 |\sigma_u(1)\, \alpha\, \sigma_u(2) \beta| \ . \tag{17}$$

There are several proofs of the Brillouin theorem$^{(5,6,7)}$, however, for this simple case the proof follows immediately for two simple reasons, a) Spin Orthogonality, b) Symmetry Orthogonality; let us consider them separately:

a) Spin Orthogonality

An example of this situation could be the matrix element $H_{12} = \langle \sigma_g(1)\alpha(1)\sigma_g(2)\beta(2)|\hat{H}|\sigma_g(1)\alpha(1)\sigma_u(2)\alpha(2)\rangle$, which, as the Hamiltonian does not involve spin terms, it can be written as

$$H_{12} = \langle \sigma_g(1)\sigma_g(2)|\hat{H}|\sigma_g(2)\sigma_u(2)\rangle \quad \langle \alpha(1)\beta(2)|\alpha(1)\alpha(2)\rangle \tag{18}$$

and the second factor on the right-hand side is immediately seen to vanish.

b) Symmetry Orthogonality

Let us consider the matrix element

$$H_{13} = \langle \sigma_g(1)\alpha(1)\sigma_g(2)\beta(2)|\hat{H}|\sigma_g(1)\alpha(1)\sigma_u(2)\beta(2)\rangle \tag{19}$$

the integration over spin can be performed upon inspection, remaining only the spatial part:

$$H_{13} = \langle \sigma_g(1)\sigma_g(2)|\hat{H}|\sigma_g(1)\sigma_u(2)\rangle \ . \tag{20}$$

Explicitly, omitting normalization constants,

$$\begin{aligned} H_{13} = \langle (1S_A + 1S_B)(1)(1S_A + 1S_B)(2) \ \Big| & -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{A1}} \\ & - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} - \frac{1}{r_{B2}} + \frac{1}{r_{12}} \ \Big| \ (1S_A + 1S_B)(1)(1S_A - 1S_B)(2)\rangle \ . \end{aligned} \tag{21}$$

Now if A is exchanged with B, the physical situation should not change, as there should be no difference between both "ends" of the molecule; it is easily seen that with this exchange, H_{13} becomes $- H_{13}$, and the only way to preserve the equality $H_{13} = - H_{13}$ is $H_{13} = 0$.

Then the only two non-vanishing terms are

$$H_{16} = \langle \sigma_g(1)\alpha(1)\sigma_g(2)\beta(2)|\hat{H}|\sigma_u(1)\alpha(1)\alpha_u(2)\beta(2)\rangle \tag{22}$$

which after some very straight forward manipulation is seen to be

$$H_{16} = \left[2(1 - S_{AB}^2)\right] \left[\langle 1S_A\ 1S_A \,\middle|\, 1S_A\ 1S_A\rangle - \langle 1S_A\ 1S_A \,\middle|\, 1S_B\ 1S_B\rangle\right] \tag{23}$$

and

$$H_{66} = \langle \sigma_u(1)\alpha(1)\sigma_u(2)\beta(2)|\hat{H}|\sigma_u(1)\alpha(1)\sigma_u(2)\beta(2)\rangle \tag{24}$$

which is easily shown to become

$$H_{66} = 2N_u^2 \left[T_{11} - T_{12} + V_{11} - 2V_{12}\right] + J_{22} \tag{25}$$

where

$$J_{22} = \langle 1\sigma_u(1)1\sigma_u(2) \left| \frac{1}{r_{12}} \right| 1\sigma_u(1)1\sigma_u(2)\rangle \tag{26}$$

$$= 4N_u^4 \left[\frac{1}{2}\ \langle 1S_A\ 1S_A \,\middle|\, 1S_A\ 1S_A\rangle + \frac{1}{2}\ \langle 1S_A\ 1S_A \,\middle|\, 1S_B\ 1S_B\rangle + \right.$$

$$\left. \langle 1S_A\ 1S_B \,\middle|\, 1S_A\ 1S_B\rangle - 2\ \langle 1S_A\ 1S_A \,\middle|\, 1S_A\ 1S_B\rangle\right]$$

and

$$N_u = \frac{1}{\left(2\left[1 - S_{12}\right]\right)^{1/2}} \tag{27}$$

which is the normalization constant for the $1\sigma_u$ orbital.

With these definitions, the CI equations can be written as

$$\begin{pmatrix} H_{11} & H_{16} \\ H_{16} & H_{66} \end{pmatrix} \begin{pmatrix} C_1 \\ C_6 \end{pmatrix} = E \begin{pmatrix} C_1 \\ C_6 \end{pmatrix} \tag{28}$$

and the two eigenvalues of these equations are

$$E_{0,1} = \frac{1}{2} \left\{ H_{11} + H_{66} \mp \left[(H_{11} + H_{66})^2 - 4(H_{11}H_{66} - H_{16}^2) \right] \right\}^{1/2} \tag{29}$$

where E_0 is the lowest energy root.

III. Evaluation of the Integrals Involved

For the sake of brevity, here we will present only the final formulae to evaluate the integrals involved; however, for the interested reader, there is an excellent account of the mathematical details of the derivations due to Boys(1).

All the formulae presented in this work are for non-normalized gaussians. The normalization constant for "s" type gaussian with exponent a is

$$N = \left(\frac{2a}{\pi} \right)^{3/4} \tag{30}$$

a) Overlap Integral Between the Two Atoms (S_{AB})

$$S_{AB} = \left(\frac{\pi}{a + b} \right)^{3/2} e^{-\frac{ab}{(a+b)} \overline{AB}^2} , \tag{31}$$

$\overline{AB}$ denotes the distance between atoms A and B.

b) Kinetic Energy Integrals (T_{11} , T_{12})

$$T_{11} = \left(\frac{\pi}{a + b} \right)^{3/2} 3\, ab/(a + b) \tag{32}$$

$$T_{12} = \left[\frac{3ab}{a + b} - \frac{2\overline{AB}^2\, a^2b^2}{(a + b)^2} \right] S_{AB} . \tag{33}$$

c) Potential Energy Integrals (V_{11} , V_{12})

To express these integrals in a convenient way, it is useful to define a point $P = (P_x, P_y, P_z)$ in terms of the coordinates of centers A and B. $\underline{A} = (A_x, A_y, A_z)$, $\underline{B} = (B_x, B_y, B_z)$, and the gaussian exponents, a and b respectively; then

$$P_i = \frac{aA_i + bB_i}{a + b} \quad , \quad i = x,y,z \ . \tag{34}$$

Furthermore, it is useful to define a function F(z)

$$F(z) = \frac{1}{\sqrt{z}} \int_0^{\sqrt{z}} e^{-u^2} \, du = \left(\frac{\pi}{2} \right)^{1/2} \operatorname{erf}(\sqrt{z}) \tag{35}$$

then

$$\langle aA|V_c|bB\rangle = \left(\frac{2\pi}{a + b} \right) e^{-\overline{AB}^2 \frac{ab}{a + b}} \, F\left[\overline{CP}^2 \, (a + b) \right] \tag{36}$$

where the subindex C denotes the coordinates of any of the centers A or B. $\langle aA|V_c|bB\rangle$ written in a more compact way by making use of the overlap integral S_{AB}; then

$$\langle aA|V_c|bB\rangle = \left(\frac{2\pi}{a + b} \right) \left[\frac{\pi}{\overline{CP}^2 \, (a + b)} \right]^{1/2} \operatorname{erf}\left(\left[\overline{CP}^2 \, (a + b) \right]^{1/2} \right) S_{AB} \ . \tag{37}$$

With a change of independent variable such as $u = \sqrt{z} \ t$ it is easily shown that F(z) becomes

$$F(z) = \int_0^1 e^{-zt^2} dt \ . \tag{38}$$

Hence, it is clear that $F(o) = 1$.

Finally, the two electron integrals can be evaluated in the following way:

$$\left< aAbB \left| \frac{1}{r_{12}} \right| cCdD \right> = \tag{39}$$

$$\frac{2\pi^{5/2}}{(a+b)(c+d)\left[a+b+c+d\right]^{1/2}} \; \frac{S_{AB}\,S_{CD}\,\sqrt{\pi}}{\left[\dfrac{\overline{PQ}^2\,(a+b)\,(c+d)}{a+b+c+d}\right]^{1/2}}$$

$$\mathrm{erf}\left(\left[\frac{\overline{PQ}^2\,(a+b)(c+d)}{a+b+c+d}\right]^{1/2}\right)$$

which making use of the function F(z) previously defined, becomes:

$$\left< aAbB \left| \frac{1}{r_{12}} \right| cCdD \right> =$$

$$\frac{2\pi^{5/2}\,S_{AB}\,S_{CD}}{(a+b)(c+d)\left[a+b+c+d\right]^{1/2}} \; F\left(\frac{\overline{PQ}^2\,(a+b)(c+d)}{a+b+c+d}\right) \tag{40}$$

where cC and dD may take the values aA or bB and the point Q is defined in analogous way to P, namely

$$Q_i = \frac{cC_i + dD_i}{c+d} \; . \tag{41}$$

With these formulae it is straightforward to compute the total energy in the Hartree-Fock scheme including Configuration Interaction.

RESULTS AND DISCUSSION

Table 1 shows the basic integrals, computed with an optimized exponent for each bond length together with their value using an STO with an exponent of 1.0 for all cases (see ref. (4)). There are some points worthy of notice; the optimized exponent decreases as the bond lenght increases, and reaches the optimized value of the infinitely separated atoms (the interested reader may like to verify that the optimized exponent of a gaussian for the hydrogen atom is $8/9\pi$). The overlap integrals are larger for STO's than for GTO's decay more rapidly than STO's for large r. For all the other integrals it is observed that for some bond lengths gaussian integrals are larger, whereas for other bond lengths the situation reverses. However this odd fact may be the result of not optimizing the STO exponent.

TABLE 1

BASIC INTEGRALS FOR SEVERAL BOND LENGTHS. SEE TEXT FOR ONE GTO (G) AND STO*(S) CALCULATIONS

r_{AB}(au)	α**		S_{12}	T_{11}	T_{12}	$-V_{11}$	$-V_{12}$	$\langle 11\|11\rangle$	$\langle 11\|12\rangle$	$\langle 12\|12\rangle$	$\langle 11\|22\rangle$
1.0	0.49	S	0.85839	0.50000	0.30658	1.72933	1.47152	0.62500	0.50705	0.43665	0.55452
		G	0.78270	0.73500	0.48132	1.95553	1.61573	0.78987	0.59389	0.48389	0.67780
1.5	0.38	S	0.72517	0.50000	0.19524	1.58369	1.11565	0.62500	0.40537	0.29684	0.49033
		G	0.64848	0.58500	0.26689	1.62256	1.11964	0.70467	0.42325	0.29302	0.54317
2.0	0.33	S	0.58465	0.50000	0.11278	1.47253	0.81201	0.62500	0.30804	0.18416	0.42597
		G	0.51685	0.49500	0.14327	1.40591	0.77466	0.64820	0.30155	0.17316	0.44790
3.0	0.28	S	0.34851	0.50000	0.02489	1.33003	0.39830	0.62500	0.16074	0.05851	0.31980
		G	0.28365	0.42000	0.01906	1.17724	0.33569	0.59708	0.13962	0.04804	0.32508
5.0	0.28	S	0.09658	0.50000	-0.00780	1.19995	0.08086	0.62500	0.03495	0.00372	0.19957
		G	0.03019	0.42000	-0.01691	1.04440	0.02395	0.59708	0.01134	0.00054	0.19996
7.0	0.28	S	0.02219	0.50000	-0.00381	1.14286	0.01456	0.62500	0.00654	0.00017	0.14264
		G	0.00105	0.42000	-0.00157	0.98726	0.00060	0.59708	0.00030	0.00000	0.14286

* Exponent of 1.0

**With optimized exponent.

Table 2 provides a comparison between the total energy using GTO's and STO's as well as showing the effect of CI on the total energy for several bond lengths. It is observed that the STO calculations give lower energies than the GTO ones (as it was expected); however, the optimum bond length is roughly the same for both STO and GTO, a very fortunate situation. It is also observed (see Fig. 1 for the GTO results) that the inclusion of CI has no appreciable effect on the optimum bond length, but as discussed earlier, CI provides the correct dissociation into two H atoms. The dissociation energy is calculated to be -4.043 eV which can be compared with the experimental and one-STO values of -4.746 and -2.644 eV (ref. (4)) respectively. It is to be noted that the GTO gives better dissociation energy (DE) than the STO, which may be due to the fact that upon computing DE with STO's one has to substract the energy of H_2 from the exact energy of 2H, while when computing DE with GTO's one substracts from the energy of 2H as computed with the optimized exponent.

TABLE 2

TOTAL ENERGY FOR SEVERAL BOND LENGTHS, FOR ONE STO (S) AND ONE (GTO) CALCULATIONS

r_{AB}(au)	- Energy (au)		
	G(CI)*	S	C
1.0	0.8956	0.9859	0.8850
1.5	0.9962	1.0972	0.9800
2.0	0.9805	1.0808	0.9580
3.0	0.9089	0.9828	0.8613
5.0	0.8525	0.8343	0.6942
7.0	0.8488	0.7708	0.6250
∞	0.8488	1.0	0.5737

$E_H = -0.4244$

$E_{H^-} = -0.2487$

* Energy calculated Including Configuration Interaction.

Figure 2 shows a plot of the square of the CI wavefunction coefficients (C_1, C_6) against the H-H bond length. The resulting graph has a curious shape and shows that about 3.5 on the value of C_6^2 starts to be of importance.

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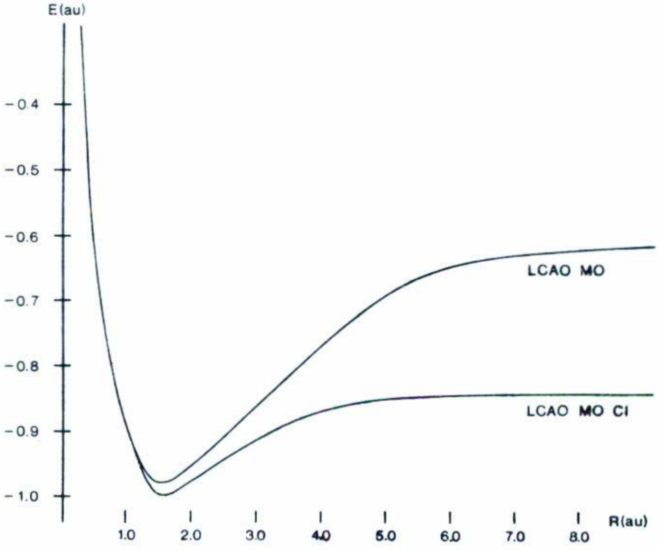

Fig. 1. Total energies as a function of bond length.

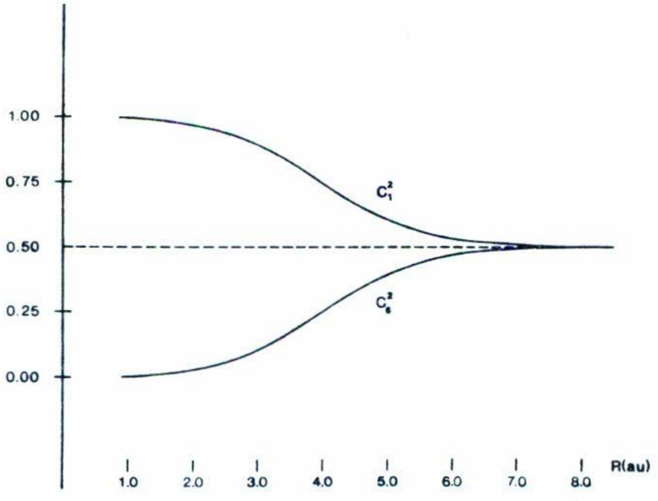

Fig. 2. Square of the coefficients of the CI wave function as a function of the bond length.

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