

# ON THE REPRESENTATION OF THE DISTORTIONS IN $1s$ ORBITALS IN THE BONDING MOLECULAR ORBITAL OF A HOMONUCLEAR DIATOMIC MOLECULE

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**ABSTRACT.** The energy of the lowest state ( ${}^2\Sigma_g^+$ ) of  $H_2^+$  has been calculated by using Inui-Nordsieck type orbitals. The results show that this type of orbitals are flexible enough to give a very satisfactory representation of the distortions in  $1s$  orbitals in the bonding orbital of a homonuclear diatomic molecule.

## INTRODUCTION

The success of the *ab initio* calculation of the molecular energies depends largely on the choice of molecular wave functions. Till now, mostly linear combinations of Slater type orbitals (S.T.O.'s) have been used for constructing molecular orbitals. However, a serious drawback of these orbitals is the inability to represent adequately and economically the distortion in the atomic charge cloud when it becomes a part of the molecular system. This aspect of the problem has recently been discussed in some detail by Geller, Frost and Lykos (1962) and Miller and Lykos (1962). They have shown that the main effect in the electron cloud of an atom when it forms a part of a molecule is the 'charge shift' which means the movement of the centre of electron density from around the attractive nucleus in an atom to a region between the nuclei in a diatomic system. A second order effect is the deformation of the charge cloud associated with a particular nucleus as it is stretched along the internuclear axis.

It has been pointed out by Harris (1960) and Barua and Chatterjee (1964) that attempts to represent the deformations in molecular orbitals by using S.T.O.'s of added complexities may not be worth while. For diatomic molecules, wave functions in the ellipsoidal coordinates with the nuclei at the foci, though quite simple in form, are expected to represent the distortion of the atomic orbitals to a large degree. The success of this approach has been proved by the recent calculation of the repulsive energy of the H-He system by using Inui-Nordsieck type orbitals (Barua and Chatterjee, 1964).

The Inui-Nordsieck type orbitals have been used by Sakamoto and Ishiguro (1956) for the calculation of the repulsive energy of the He-He system which was

not quite successful. The reason for this has been shown by Huzinaga (1957) to be the failure of the same set of parameter for both the bonding and anti-bonding orbitals to represent properly the distortions of the atomic orbitals. For a hetero-nuclear system like H-He, the sets of parameters for the atomic orbitals of the two atoms are independently variable and the limitation found in the case of He-He is not present.

For the calculation of the lowest  ${}^2\Sigma_g^+$  state of  $\text{H}_2^+$  molecule only the bonding orbital is to be used. It is interesting to see how far the Inui-Nordsieck type orbitals can represent the distortions in the  $1s$  orbitals of the bonding molecular orbital. With this end in view, in this paper we have made sample calculations of the energy of the  ${}^2\Sigma_g^+$  state of  $\text{H}_2^+$ . It is also expected that the use of different sets of parameters for the  $1s$  orbitals will make it possible to represent the distortions in the antibonding state properly.

#### CALCULATION OF ENERGY INTEGRALS

For the  ${}^2\Sigma_g^+$  state of  $\text{H}_2^+$  molecule, the molecular orbital may be represented as,

$$\psi = \chi_a + \chi_b \quad \dots (1)$$

$\chi_a$  and  $\chi_b$  being the atomic orbitals of the two nuclei of  $\text{H}_2^+$  and are given as

$$\left. \begin{aligned} \chi_a &= e^{-\alpha\xi - \beta\eta} \\ \chi_b &= e^{-\alpha\xi + \beta\eta} \end{aligned} \right\} \quad \dots (2)$$

$\alpha$  and  $\beta$  being the parameters of the atomic orbitals and

$$\left. \begin{aligned} \xi &= (r_a + r_b)/R \\ \eta &= (r_a - r_b)/R \end{aligned} \right\} \quad \dots (3)$$

where  $R$  is the distance between two nuclei,  $r_a$  and  $r_b$  are the distances of the electron from the nuclei  $a$  and  $b$  respectively.

The Hamiltonian of the system, in atomic units is given by

$$H = -\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R} \quad \dots (4)$$

The energy of the system may be written as

$$E = \frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau} \quad \dots (5)$$

We define the following integrals

$$\left. \begin{aligned} \int \chi_a^2 d\tau &= \frac{\pi R^3}{4} E \\ \int \chi_a \chi_b d\tau &= \frac{\pi R^3}{4} F \end{aligned} \right\} \quad \dots (6)$$

$$\left. \begin{aligned}
 \int \chi_a(-\nabla^2)\chi_a d\tau &= \int \chi_b(-\nabla^2)\chi_b d\tau = \pi R G \\
 \int \chi_a(-\nabla^2)\chi_b d\tau &= \int \chi_b(-\nabla^2)\chi_a d\tau = \pi R I \\
 \int \chi_a^2 \frac{1}{r_a} d\tau &= \frac{\pi R^2}{2} K \\
 \int \chi_a^2 \frac{1}{r_b} d\tau &= \frac{\pi R^2}{2} L \\
 \int \chi_a \chi_b \frac{1}{r_a} d\tau &= \frac{\pi R^2}{2} M \\
 \int \chi_a \chi_b \frac{1}{r_b} d\tau &= \frac{\pi R^2}{2} N
 \end{aligned} \right\} \dots (7)$$

The expressions for the integrals in Eq. (6) have been given in the Appendix.

In terms of (7) the energy may be written as,

$$E(\alpha, \beta; R) = \frac{X}{R} + \frac{Y}{R^2} \dots (8)$$

with

$$X = 2[-(K+L+M+N)/(E+F)] + 1 \dots (9a)$$

$$Y = 2(G+I)/(E+F) \dots (9b)$$

For a particular value of  $R$ , the values of  $\alpha, \beta$  are to be varied till the minimum value of the energy is obtained. First, the parameters were varied at an interval of 0.125 by using the tables of Miller *et al.* (1958). The exact values of  $\alpha, \beta$  which gave the minimum value of  $E$  were obtained by the method of Sakamoto and Ishiguro (1956).

TABLE I  
 Energy of the  $^2\Sigma_g^+$  state of  $H_2^+$  for  $R = 2au$

Wave function	Values of the parameters	Energy $-E au$
One parameter <sup>a</sup>	$\zeta = 1$	0.55377
One parameter <sup>a</sup>	$\zeta = 1.293$	0.58651
Two parameter <sup>a</sup>		0.59980
Three parameter <sup>a</sup>		0.60183
Present	$\alpha = 1.3625$ $\beta = .9100$	0.60228
Bates <i>et. al.</i> (1953) (actual)		0.60262

<sup>a</sup> Miller and Lykos (1962)

## RESULTS AND DISCUSSION

The results of our calculation at  $R = 2 au$  are shown in Table I together with the result of a few other accurate calculations including the exact values obtained by Bates *et al.* (1954). It may be seen that our values obtained with only a two-parameter wavefunction is in better agreement with the exact values of Bates *et al.* (1954) than even the values obtained with three parameter hybrid orbitals used by Miller and Lykos (1962). The present sample calculations show that the Inui-Nordsieck orbitals are flexible enough to represent adequately the distortions in the  $1s$  orbitals in the bonding orbital of a homonuclear diatomic molecule. In fact, they represent the atomic charge clouds in a molecule better than the complicated combinations of different S.T.O.'s. Further studies of the representation of the distortion of atomic orbitals in molecular orbitals on the basis of Inui-Nordsieck type orbitals are in progress.

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## REFERENCES

- Bates, D. R., Ledsham, K., and Stewart, A. L., 1953, *Phil. Trans. Roy. Soc. (London)*, **A 246**, 215.  
Barua, A. K., and Chatterjee, S., 1964, *Mol. Phys.*, **7**, 443.  
Geller, M., Frost, A. A., and Lykos, P. G., 1962, *J. Chem. Phys.*, **36**, 2693.  
Harris, F. E., 1960, *J. Chem. Phys.*, **32**, 3.  
Huzinaga, S., 1957, *Prog. Theor. Phys.*, **17**, 169.  
Miller, R. V., and Lykos, P. G., 1962, *J. Chem. Phys.*, **37**, 993.  
Miller, J., Gerhauer, J. M., and Matsen, F. A., 1958, *Quantum Chemistry Integrals and Tables* (Austin: University of Texas Press).  
Sakamoto, M., and Ishiguro, E., 1956, *Prog. Theor. Phys.*, **15**, 37.