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Short Communication

Chemical Bonding from Superposition of One-Center Charge Densities*

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The trial wave function

$$\varphi = (2)^{-1/2}(a^2 + b^2)^{1/2}$$

gives the classical electron density, ρ. Contrary to the common belief, this electron density gives a very substantial covalent bonding for H_2^+ and H_2. The stabilization energy comes from a favorable kinetic energy. This in turn arises because $(\partial\rho/\partial z)$ has opposite signs for electron densities centered on each atom in the critical bonding region between the nuclei.

Key words: Classical charge density – One-center charge densities – Covalent bonding

A molecular orbital between two identical atoms, A and B, may be written as

$$\varphi = (2 + 2S)^{-1/2}(a + b), \tag{1}$$

with a and b normalized atomic orbitals. The charge density per electron is then

$$\rho = (2 + 2S)^{-1}(a^2 + 2ab + b^2), \tag{2}$$

where $\frac{1}{2}(a^2 + b^2)$ is called the quasiclassical charge density. The remaining charge density is called the overlap, or exchange, or interference density. It is commonly believed that the latter density leads to covalent bonding. It is thought that a classical superposition of atomic charge densities can give, at most, only a very minor stabilization [1].

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* Dedicated to Prof. Hermann Hartmann on the occasion of his 65th birthday.

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Surprisingly, this turns out not to be the case. Consider the trial wave function

$$\varphi = (2)^{-1/2}(a^2 + b^2)^{1/2}, \tag{3}$$

which gives the quasi-classical electron density. Our examples will be H_2^+ and H_2, where $a = (\alpha^3/\pi)^{1/2} e^{-\alpha r_A}$ and $b = (\alpha^3/\pi)^{1/2} e^{-\alpha r_B}$, α being the effective nuclear charge.

The energies of both H_2^+ and H_2 are readily calculated. The potential energy is particularly easy because of the one-center nature of ρ. The kinetic energy is put in the form [2]

$$\langle T \rangle = \frac{1}{8} \int \frac{\nabla\rho \cdot \nabla\rho}{\rho}\, d\tau. \tag{4}$$

In confocal elliptic coordinates, ρ is given by

$$\rho = \frac{w^3}{2R^3\pi} \left(e^{-w(\lambda+\mu)} + e^{-w(\lambda-\mu)}\right), \tag{5}$$

where $w = \alpha R$. The kinetic energy is

$$\langle T \rangle = \frac{\alpha^2}{2} - \frac{\alpha^2 w\, e^{-w}}{2} \tan^{-1}(\sinh w) + \frac{\alpha^2 w^2\, e^{-w}}{8} \int_{-1}^{1} \operatorname{sech}(\mu w)\mu^2\, d\mu. \tag{6}$$

The last term can be evaluated by expanding sech (μw), for $w > 1$ or $w < 1$. For the former case

$$\langle T \rangle = \frac{\alpha^2}{2} - \frac{\alpha^2 e^{-w}}{2w} \left[\frac{w^2}{2} \tan^{-1}(\sinh w) - \frac{2\pi^3}{32} + e^{-w}(w^2 + 2w + 2) + e^{-3w}\left(\frac{w^2}{3} + \frac{2w}{9} + \frac{2}{27}\right) \cdots \right]. \tag{7}$$

There is a reduction in the kinetic energy due to an interaction of the two charge densities. If they did not interact, the kinetic energy would be simply $\alpha^2/2$. The reduction, $-\Delta T$, is zero at $R = 0$ and $R = \infty$, and has a maximum value of $0.0710\alpha^2$ at $w = 1.7$ (atomic units). Figure 1 shows $-\Delta T/\alpha^2$ plotted against w.

For both H_2^+ and H_2 the total energy is given by $E = \alpha^2 A_1 + \alpha A_2$, where A_1 and A_2 are functions of w (the internuclear repulsion is expressed as α/w). For each value of w, $(\partial E/\partial \alpha) = 0$ gives the best value of α, and also ensures that the virial theorem is satisfied.

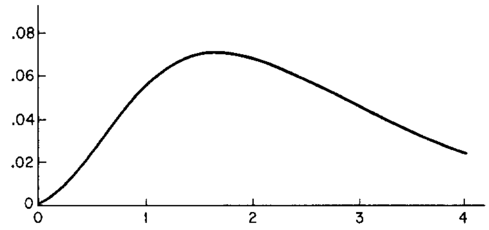

Fig. 1. Plot of kinetic energy lowering, $-\Delta T/\alpha^2$, versus $w = \alpha R$

The minimum energy for H_2^+ comes at $w = 2.35$, $\alpha = 1.126$, and $R_0 = 2.09$ a.u. The energy is -0.556 a.u., which gives a binding energy of 1.51 eV. This may be compared to 2.79 eV, experimental, and to 2.35 eV, the value for the best MO function of the form given by (1).

For H_2 the best energy for (3) comes at $w = 1.6$, $\alpha = 1.130$, $R_0 = 1.42$ a.u. The energy is -1.097 a.u., with a binding energy of 2.64 eV. The experimental value is 4.75 eV and the best MO of form (1) gives 3.47 eV.

The origin of the bonding energy for (3) lies in the lowering of the kinetic energy factor A_1. This permits a higher value of α so that $\langle T \rangle$ is actually increased relative to the separated atoms, but $\langle V \rangle$ is decreased. The favorable kinetic energy factor results from the small values of the gradient, $(\partial \rho / \partial z)$, in the region between the nuclei.

These results provide strong support for Ruedenberg's views concerning the nature of the chemical bond. He has consistently stressed the overriding importance of the lowering of the kinetic energy factor in molecule formation [1, 3]. He has also pointed out that the accumulation of charge in the overlap region is actually antibonding as far as potential energy is concerned. The results also agree with Ruedenberg in assigning the bonding to the bond parallel component of the kinetic energy Goddard and Wilson have shown that it is the contragradience (opposite signs for $(\partial \varphi / \partial z)$ or orbitals on different atoms) which is responsible [4]. The same contragradience exists in the bonding region for electron densities centered on different atoms.

We can improve the energy by modifying (3) so that more electron density is placed in the region between the nuclei. One way to do this is to float the two charge densities, a^2 and b^2, towards each other [5]. If this is done for H_2^+, the energy is lowered about 0.37 eV by floating each orbital by 0.11 a.u. towards the bond center. For H_2, the energy can be lowered by 0.88 eV by floating 0.13 a.u.

The floating orbital method operates almost entirely by lowering the potential energy. It would be more efficient to polarize the atomic orbitals so that it is the kinetic energy that changes. This can be done by using a Guillemin–Zener type of function [6].

$$\rho = N(e^{-2\alpha r_{\mathrm{A}} - 2\alpha' r_{\mathrm{B}}} + e^{-2\alpha r_{\mathrm{B}} - 2\alpha' r_{\mathrm{B}}}) \equiv N e^{-w\lambda} \cosh(w'\mu). \tag{8}$$

This function can readily be used for the energy of H_2^+. The minimum comes at $w = 2.7$ and $w' = w/2$. These numbers correspond to $\alpha = 1.017$ and $\alpha' = 0.339$. The equilibrium distance, R_0, is 1.99 and the bonding energy is 2.78 eV. Thus like the Guillemin–Zener function (where (8) is φ and not ρ), essentially exact answers are found.

It is interesting that $w = w'$ corresponds to ρ of Eq. (3), and $w' = 0$ corresponds to the density function

$$\rho = \frac{\alpha^3}{\pi S} ab \tag{9}$$

which is the overlap charge density of the usual MO function (1). If α is held fixed, this function gives the lowest kinetic energy for any value of w. However, the potential energy is also the highest. The best value for (9) corresponds to $w = 2.4$, $\alpha = 1.348$, $R_0 = 1.78$ a.u., and bonding energy = 2.20 eV. The value of $w' = w/2$ represents a density function intermediate between (3) and (9) and similar to the usual MO density (2). It is not advantageous to use the function (8) for H_2, since the electron density is no longer a sum of one-center densities, and the potential energy calculation becomes difficult.

Of course (3) cannot be seriously considered as a good wavefunction, since it is poorer than the usual molecular orbital. Also the quasi-classical charge density is far from satisfying the Hellmann–Feynman theorem. Finally, it is not clear what the anti-bonding orbital corresponding to (3) would be.

However, it appears that all of these objections could be overcome by adding additional one-center charge densities to the bonding region. For example, an atomic density centered at the mid-point of the bond could give a better energy and also help to balance the electrostatic forces. Such a function makes the kinetic energy difficult to evaluate in closed form, but numerical integration should be relatively easy.

It seems clear that a sum of one-center charge densities can be constructed which matches as closely as desired any given MO charge density. By a suitable subtraction of one-center charge densities, anti-bonding MO's could also be matched. Kinetic energies would require numerical integration, but potential energies, including interelectronic repulsions, would be rather easy to calculate.

Finally, it may be mentioned that there is considerable interest in finding new ways to evaluate many-electron kinetic energies from one-electron density functions [7]. A successful solution to this problem would greatly enhance the attractiveness of one-center charge densities as basis sets for ρ.

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