THE USE OF ONE-CENTER ATOMIC ORBITALS FOR THE BUILDING UP OF HYDROGEN ORBITALS IN A TETRAHEDRAL SYMMETRIC HYDRID MOLECULE

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Slater orbitals have been applied to the building up of a trial wave function of the $1s$ ground state of a H atom being at a distance of 2 a.u. from the midpoint. If the angular part is a combination of the orbitals s, p corresponding to a sp^3 hybrid enlarging the radial part $re^{-\gamma r}$ by further terms $r^{n_i-1} e^{-\gamma_i r}$ only an irrelevant improvement appears in the energy (about 0,01 a.u.) Combining the simple radial part $re^{-\gamma r}$ with angular parts p, d, f an improvement of about 0,14 a.u. may be attained in the energy.

1. Introduction

The application of the one-center wave function approach to tetrahedral symmetric hydrid molecules (particularly to methane) has been investigated by several authors [1, 2, 3, 4, 5, 6, 7]. According to the MO method the valence shell may be simply described by the electron configuration $(ns)^2\,(np)^6\,{}^1S_0$ (spherically symmetric approximation) and the radial part of the atomic orbitals the center of which is in the midpoint of the molecule may be determined by the variational method. (The orbitals may be Slater or hydrogen-like, etc. atomic orbitals, the radial part of which contains variational parameters.) The binding of the molecule cannot be interpreted by this model and the electronic density is too diffuse in the external regions (this manifests itself in the computed value of the diamagnetic susceptibility, which is — even after taking into account the high-frequency paramagnetism — higher than the empirical value). These insufficiencies can be eliminated within the framework of the MO method taking into account the configurational interaction [4] (for instance adding to the molecular orbitals apart from the atomic orbitals s, p also the atomic orbitals d, f etc.).* The one-center wave functions can be built up also according to the VB method, by expanding the orbitals of the four H atoms in a suitable set of functions (for instance the Slater atomic orbitals with center in the midpoint of the molecule) [6]. If in the expansion only terms provided with angular parts s and p are taken into account and moreover in such a proportion which corresponds to the orthogonal hybrid

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* Such a computation for methane has been promised in [8].

orbitals sp^3, the diagonal part of the first order density matrix will be spherically symmetric (this means a considerable simplification in the computation). Applying to the 4 hydrogen orbitals a simple radial part $re^{-\gamma r}$ the energy improves to a slight extent only (about 1,6 eV, but the bond cannot be interpreted by the model), whereas the electronic density is flattened [7]. A value of correct sign is obtained for the binding energy

$$E^{\mathrm{B}}_{\mathrm{CH}_4} = E_{\mathrm{CH}_4} - E_{\mathrm{C}} - 4\,E_{\mathrm{H}},$$

which in order of magnitude equals the experimental one if the energy values E_{C} and E_{H} are computed by a similar method as the E_{CH_4}. This means that the energy of the H atom has to be computed with the orbital $Nre^{-\gamma r}(1 + 3\cos\vartheta)$. Thus $E_H = 0{,}26603$ a.u. is obtained, whereas the empirical value is $-0{,}50000$ a.u. For the four H atoms the sum of the difference is about 0,93 a.u., whereas the difference between the computed and empirical value of E_{CH_4} is about 1,1 a.u. (Thus in the approximation applied above the main insufficiency of the one-center wave function is that the orbitals of the 4 H atoms are approximated badly. It should be emphasized, however, that it is not the good approximation of the unperturbed atomic orbitals of the H atoms which is important but rather the chosen trial function has to be flexible enough for the description of the atomic orbitals of H contributing to the bond.

The orbital 1*s* of the unperturbed H atom is spherically symmetric, it has a peak at the H nucleus and falls down exponentially further away from it [6]. The orbitals of the H atoms in a tetrahedral symmetric molecule are subjected to the following variations :

a) One of the atomic orbitals of H is overlapped by one of the hybrid orbitals sp^3 of the central atom directed to it, on the other hand orbitals of the H atoms are polarized by the electrostatic field of the central atom. These together are causing a deformation directed towards the bonds, owing to which the electronic density increases in the region between the central atom and the H nucleus, whereas it decreases in the region outside the H nucleus (if it is allowed by the Pauli principle). The binding is actually brought about by this. By these effects only a cylindrically symmetric deformation is caused.

b) Due to the polarization effect of the other three bonds and protons the cylindrical symmetry ceases : each bond has a symmetry axis C_3.

c) Owing to the electron correlation the electrons are not moving independently from each other : the probability of finding an electron in a given point depends on the position of the other electrons.

From the energetical point of view in general the effect *a)* is the most important one.

Let us examine now the case of the trial atomic orbital of H : $Nre^{-\gamma r}(1 + 3\cos\vartheta)$. The electron density corresponding to it has a higher flat maximum in the region between the center and the H nucleus (closer to the H nucleus) and a smaller maximum at the other side of the center. Therefore the electron distribution is not concentrated near the H nucleus and thus the value of the kinetic as well as of the potential energy is smaller than the exact value (in absolute value). However, the advantage of that trial orbital is that the displacement of the electron density into the direction of the central nucleus can be carried out easily with the decreasing of the parameter γ.

The aim of this paper is to investigate in case of a H atom being at a distance $R = 2{,}00$ a.u. from the center:

a) the effect produced by the radial part on the energy obtained variationally with an angular part $(1 + 3\cos\vartheta)$;

b) the effect of the angular part with a given radial part $re^{-\gamma r}$.

2. Analytical computation

Let the nucleus of the H atom be at a distance R a.u. from the origin of the coordinate system on the Z axis. Thus with the usual denotations the Hamilton operator of the H atom in atomic units is

$$-\frac{1}{2}\Delta - \frac{1}{\sqrt{r^2 + R^2 - 2Rr\cos\vartheta}}\,.$$

The trial wave function of the H atom is built up from the following normalized Slater atomic orbitals:

$$\varphi_i = R_i\, Y_{l_i 0} = \sqrt{\frac{(2\gamma_i)^{2n_i+1}}{(2n_i)\,!}}\, r^{n_i-1}\, e^{-\gamma_i r} \sqrt{\frac{2l_i+1}{4\pi}}\, P_{l_i}(\cos\vartheta)\,.$$

The parameters γ_i are varied, whereas for the n_i the integers 2, 3, 4 are taken.

With these denotations

$$S_{ij} = \int \varphi_i\, \varphi_j\, d\tau = \delta_{l_i l_j} \sqrt{\frac{(2\gamma_i)^{2n_i+1}\,(2\gamma_j)^{2n_j+1}}{(2n_i)!\,(2n_j)!}}\, \frac{(n_i+n_j)!}{(\gamma_i+\gamma_j)^{n_i+n_j+1}}\,.$$

The expression of the kinetic energy will be

$$K_{ij} = -\frac{1}{2}\int \varphi_i\, \Delta\varphi_j\, d\tau = S_{ij}\, \frac{1}{8\,(n_i+n_j)^2 - 4\,(n_i+n_j)} \Big[2\gamma_i\gamma_j n_i n_j - \gamma_i^2 n_j (n_j-1) - \gamma_j^2 n_i (n_i-1) + l_i (l_i+1)(\gamma_i+\gamma_j)^2 \Big]\,.$$

For the computation of the potential energy $\dfrac{1}{\sqrt{r^2 + R^2 - 2Rr\cos\vartheta}}$ is expanded [9]:

$$\frac{1}{\sqrt{r^2+R^2-2Rr\cos\vartheta}}=\begin{cases}\sum\limits_{k=0}^{\infty}\frac{r^k}{R^{k+1}}P_k(\cos\vartheta)P_k(1), & \text{if } R>r,\\ \sum\limits_{k=0}^{\infty}\frac{R_k}{r^{k+1}}P_k(\cos\vartheta)P_k(1), & \text{if } R<r,\end{cases}$$

hence

$$V_{lj}=-\int\frac{\varphi_l\varphi_j}{\sqrt{r^2+R^2-2Rr\cos\vartheta}}d\tau=-\sum_{k=0}^{\infty}C^k(l_l,\ 0;\ l_j,\ 0)P_k(1)I_{lj}^k.$$

The coefficients C^k have been defined and tabulated by **Condon** and **Shortley** (from $l=0$ to $l=3$) [10], whereas the integrals I_{lj}^k are the following:

$$I_{lj}^k=\sqrt{\frac{(2\gamma_l)^{2n_l+1}(2\gamma_j)^{2n_j+1}}{(2n_l)!\ (2n_j)!}}\begin{cases}\Bigg\{-\frac{1}{R^{k+1}}\left[\sum\limits_{\nu=1}^{n_l+n_j+k}\frac{(n_l+n_j+k)!}{(n_l+n_j+k-\nu)!}\frac{R^{n_l+n_j+k-\nu}e^{-(\gamma_l+\gamma_j)R}}{(\gamma_l+\gamma_j)^{\nu+1}}-\frac{(n_l+n_j+k)!}{(\gamma_l+\gamma_j)^{n_l+n_j+k+1}}\right]+\\ +R^k\left[\sum\limits_{\nu=1}^{n_l+n_j-k-1}\frac{(n_l+n_j-k-1)!}{(n_l+n_j-k-1-\nu)!}\frac{R^{n_l+n_j-k-1-\nu}e^{-(\gamma_l+\gamma_j)R}}{(\gamma_l+\gamma_j)^{\nu+1}}\right]\Bigg\},\ \text{if } n_l+n_j-k>0,\\ \Bigg\{-\frac{1}{R^{k+1}}\left[\sum\limits_{\nu=0}^{n_l+n_j+k}\frac{(n_l+n_j+k)!}{n_l+n_j+k-\nu)!}\frac{R^{n_l+n_j+k-\nu}e^{-(\gamma_l+\gamma_j)R}}{(\gamma_l+\gamma_j)^{\nu+1}}-\frac{(n_l+n_j+k)!}{(\gamma_l+\gamma_j)^{n_l+n_j+k+1}}\right]+\\ +R^k\left[\sum\limits_{\nu=0}^{k-n_l-n_j-1}\frac{(k-n_l-n_j-1-\nu)!}{(k-n_l-u_j)!}(-1)^\nu\frac{(\gamma_l+\gamma_j)^\nu e^{-(\gamma_l+\gamma_j)R}}{R^{k-n_l-n_j-\nu}}-\right.\\ \left.-(-1)^{k-n_l-n_j}\frac{(\gamma_l+\gamma_j)^{k-n_l-n_j}}{(k-n_l-n_j)!}Ei(-(\gamma_l+\gamma_j)R)\right]\Bigg\},\\ \text{if } n_l+n_j-k\leq 0.\end{cases}$$

The trial ψ function is taken in the following form:

$$\psi = \sum_i c_i \varphi_i .$$

The variation of the energy expression

$$E = \frac{\int \psi H \psi \, d\tau}{\int \psi\psi \, d\tau}$$

with respect to the c_i leads to the system of equations

$$\sum_i c_i (H_{ij} - ES_{ij}) = 0, \quad H_{ij} = K_{ij} + V_{ij} ,$$

the corresponding values of E and parameters c_i can be determined from the secular equation [9]:

$$\det \left[(H_{ij} - ES_{ij}) \right] = 0 .$$

The energy is depending not only on the c_i but also on the parameters γ_i, therefore secular equation has to be solved separately in case of several different values of γ_i in order to obtain the energy minimum.

3. Results

a) As demonstrated in [7] with the use of the trial function

$$\psi_1^R = R_1 (Y_{00} + \sqrt{3}\, Y_{10})$$

in case of $n_1 = 2$ and $R = 2{,}000$ a.u. $E_1^R = -0{,}26603$ a.u. is obtained for the energy. At the energy minimum $\gamma_1 = 0{,}72$. The trial function

$$\psi_2^R = (c_1 R_1 + c_2 R_2)(Y_{00} + \sqrt{3}\, Y_{10})$$

gives $E_2^R = -0{,}272$ a.u. if $n_1 = 2, n_2 = 3$. At the energy minimum: $\gamma_1 = 0{,}72$, $\gamma_2 = 1{,}4$, $c_1 = 0{,}731$, $c_2 = 0{,}294$. Completing the radial part of ψ_2^R by a term $c_3 R_3 \, (n_3 = 4)$ the lowering of the energy with respect to E_2^R can be estimated to be maximally 0,003 a.u.

b) For the examination of the effect of the angular part the following trial functions have been applied:

$$\psi_1^A = R_1 \, Y_{00} ,$$

$$\psi_2^A = R_1 (c_1 \, Y_{00} + c_2 \, Y_{10}) ,$$

$$\psi_3^A = R_1 (c_1 \, Y_{00} + c_2 \, Y_{10} + c_3 \, Y_{20}) ,$$

$$\psi_4^A = R_1 (c_1 \, Y_{00} + c_2 \, Y_{10} + c_3 \, Y_{20} + c_4 \, Y_{30}) .$$

The γ_1 and the coefficients c_i have been varied. Energy minima and the corresponding values of γ_1 and c_i for the case $R = 2{,}00$ are shown in the following Table.

	ψ_1^A	ψ_2^A	ψ_3^A	ψ_4^A
c_1	1,000	0,862	0,803	0,787
c_2	—	0,508	0,552	0,564
c_3	—	—	0,225	0,240
c_4	—	—	—	0,076
E_i	—0,245	—0,334	0,373	—0,387
γ_1	0,85	0,86	0,86	0,86

4. Conclusions

a) No considerable improvement is obtained by the trial function ψ_1^R provided with the angular part $(Y_{00} + \sqrt{3}\, Y_{10})$ in an increase of the number of the R_i. The expression of the form $r^{n_i-1} e^{-\gamma_i r}$ is not flexible enough to concentrate the electrons near the H nucleus. Some improvement may be expected as is shown by the computation carried out by JOY and PARR for the H_2 molecule when varying also the exponents n_i [8]. It should perhaps be examined whether by special expressions more suitable to the nature of the problem greater lowering of the energy is obtained than by Slater and hydrogen-like atomic orbitals.

b) Increasing of the number of terms with different angular parts seems to be effective. It is worth while to note that for ψ_2^A $c_2/c_1 = 0{,}589$ and $\gamma_1 = 0{,}85$, which differ considerably from the values $c_2/c_1 = \sqrt{3}$ and $\gamma_1 = 0{,}72$ taken up in the case of ψ_1^R. The improvement of about 0,06 a.u. is due to the fact that the ratio c_2/c_1 has been varied and has not been equated to $\sqrt{3}$. A considerable improvement is attained by the angular parts of character *d, f,* also increasing the electronic density near the H nucleus. This is in accordance with GÁSPÁR's calculations carried out for H_2^+ [11] who found that also the contribution of the term provided with angular part *g* is considerable.

In case calculations are to be carried out for CH_4 (or NH_4^+) it is advisable to use ψ_4^A possibly completed with an angular part of character *g*, because probably a considerable contribution is given also by this). A further improvement may be attained by providing each term of ψ_4^A with a different radial part and separately varying their parameters γ_i and possibly also the exponents n_i. The deviation from the cylindrical symmetry of the bonds may be taken into consideration by building into the ψ_4^A and hybrid orbitals sp^3 of the central atom terms provided with suitable P_{lm}. Building up the wave function of the molecule according to the VB method (considering possibly also the so-called ionic homopolar resonance) also part of the correlation energy of the valence electrons is obtained.

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ПРИМЕНЕНИЕ ОДНОЦЕНТРОВЫХ АТОМНЫХ ОРБИТ ДЛЯ ПОСТРОЕНИЯ ВОДОРОДНЫХ ОРБИТ В МОЛЕКУЛАХ ГИДРИДОВ С ТЕТРАЭДРИЧЕСКОЙ СИММЕТРИЕЙ

Э. КАПУИ

Резюме

Для построения аппроксимирующей волновой функции основного состояния $1s$ атома H, находящегося на расстоянии в 2 a.e. от центра, были применены орбиты Слэтера. Если зависящая от угла часть является комбинацией s, p, соответствующей гибридной орбите sp^3, то в случае дополнения исходной радиальной части $re^{-\gamma_1 r}$ последующими членами $r^{n_i-1}e^{-\gamma_i r}$ в энергии обнаруживаются лишь незначительные улучшения (прибл. 0,01 a.e). При комбинации простой радиальной части $re^{-\gamma_1 r}$ с зависящими от угла частями характера p, d, f в энергии можно добиться улучшения в 0,14 a. e.