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Analysis of the r-Dependence of *Ab Initio* Parameters α_i of the Xα Method for Different Molecular Orbitals in the Molecule H₂O

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Ab initio exchange parameters α_i of the Xα method have been determined for molecular orbitals of the H₂O molecule. It is pointed out that these exchange parameters α_i are not constants but functions of the position vector $\vec{r}$. The $\vec{r}$-dependence of α_i for the molecular orbitals is presented.

I. INTRODUCTION

The Xα method[1] has proved to be one of the most efficient methods in the quantum chemistry. Several values of α are applied in molecular Xα calculations. The atomic values of α are often used even for molecules. Parameters α_{HF} have been calculated by Schwarz[2] so that the total Xα energy of the atom is equal to the total Hartree-Fock energy. It would be very time-consuming to determine parameters α_{HF} for molecules from molecular calculations. That is why a kind of averages of atomic values of α_{HF} are generally used. In the MSXα method the atomic α_{HF} is applied in the atomic spheres and weighted averages of the atomic values are used in the interatomic and outer regions. On the other hand, the value of 0.7 proposed by Baerends and Ros[3] or 2/3 are usually applied in the LCAO and DV Xα calculations.

Seldom has a parameter α varying with the position vector $\vec{r}$ been used, Wood[4] Trickey, Green and Averill[5] and Sabin, Worth and Trickey[6] have proposed that the atomic value of $\alpha = 0.7772$ if $r < r_c$ and $\alpha = 2/3$ if $r > r_c$. Wood has suggested a simple Z-dependent formula for r_c. Sabin et al. have calculated r_c by matching the total Xα energy obtained by their method to the total Xα energy with the constant value of α_{HF}. Gáspár[7] suggested an *ab initio* way of calculating the parameters of the Xα method. This method provides different values of α for different spin orbitals. Moreover, these parameters α are not constants but functions of the position vector $\vec{r}$. Earlier, Lindgren and Schwarz[8] defined values of α for different shells. However, these values are constants. Recently, the r-dependence of the parameters α of different shells in Ne, Ar and Kr have been studied[9].

Here, the functions $\alpha(\vec{r})$ of the molecular orbitals in the H_2O molecule are analyzed.

II THE Xα METHOD WITH SELF-CONSISTENT PARAMETER α

The Xα method with self-consistent parameter α has been discussed in detail in earlier papers[7]. Here, only a summary is presented.

In the free-electron gas model[10] the exchange potential of an electron with spin up is given by

$$V_{X\uparrow}(\vec{r}) = -8 \, F(\eta) \left(\frac{3}{4\pi} \, \varrho_\uparrow(\vec{r}) \right)^{1/3} \tag{1}$$

where

$$F(\eta) = \frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln \left| \frac{1+\eta}{1-\eta} \right| \tag{2}$$

and $\eta = p/p_F$ is the reduced momentum of the electron in question. p_F and $\rho_\uparrow$ are the fermi momentum and the total electron density for electron density for electrons with spin up, respectively. A similar formula can be given for electrons with spin down. (The energy is in Rydberg units and other quantities are in atomic units.) To get rid of the momentum dependence, it is customary to average expression (1) in the Fermi sphere.

$$\overline{V_{X\uparrow}}(1) = -6\alpha \left[\frac{3}{4\pi} \, \varrho_\uparrow(1) \right]^{1/3}, \tag{3}$$

where

$$\alpha = \left[\frac{1}{2}(\eta^3 + \eta) - \frac{1}{4}(\eta^2-1)^2 \ln \left| \frac{1+\eta}{1-\eta} \right| \right]_{\eta_1}^{\eta_2} \left[(\eta^3)_{\eta_1}^{\eta_2} \right]^{-1} \tag{4}$$

The exchange parameter suggested by Slater[1] — $\alpha = 1$ — can be obtained by averaging the exchange potential (1) over the whole Fermi sphere ($\eta_1 = 0$, $\eta_2 = 1$). If we average over a layer with thickness of ε near the Fermi surface and $\varepsilon \to 0$, the value of 2/3 is given. This is the value of α proposed by Gáspár[11] and later Kohn and Sham[12]. Gáspár[7] suggested another way of averaging between these extreme ones. Averaging is performed over a layer having $\nu_i = u_i^* \, u_i$ electrons in the unit volume near the Fermi surface, where u_i is the i-th spin orbital. So, exchange potentials

$$V_{X\uparrow}^i(\vec{r}) = -6\alpha_i(\vec{r}) \left(\frac{3}{4\pi} \, \varrho_\uparrow(\vec{\varrho}) \right)^{1/3} \tag{5}$$

are obtained, where

$$\alpha_i = \frac{\varrho_\uparrow}{\nu_\uparrow} \left(1 - \frac{1}{2} \eta_i^3 - \frac{1}{2} \eta_i + \frac{1}{4}(\eta_i^2-1)^2 \ln \left| \frac{1+\eta_i}{1-\eta_i} \right| \right) \tag{6}$$

and

$$\eta_i = \left(1 - \frac{\nu_i}{\varrho_\uparrow} \right)^{1/3} \tag{7}$$

α_i are not constant parameters but functions of the position vector $\vec{r}$. Func-

tions α_i are different for different spin orbitals. Exchange potentials (5) and functions $\alpha_i(\vec{r})$ can be calculated self-considerably. From an initial potential the Kohn-Sham equations are solved. Then, the one-electron and the total electron densities are calculated and the exchange potentials of the next interaction are obtained from Eqs. (5)—(7). This procedure goes on until self-consistently is reached.

III. FUNCTIONS $\alpha(\vec{r})$ FOR MOLECULAR ORBITALS

Functions $\alpha(\vec{r})$ have been calculated for the molecular orbitals of the H₂O molecule. The geometry of the molecule was taken from Basch and Snyder[13]. Results are shown in Figures 1—7. Functions α_i have different shapes for different molecular orbitals. Figure 1. presents function $\alpha(\vec{r})$ for the molecular orbital 1a₁ in the plane of the molecule (y-z plane). Functions $\alpha(\vec{r})$ in the x-z and y-z planes are almost the same as the molecular orbital 1a₁ is nearly spherically symmetric. As it can be easily seen from Eqs. (6) and (7), $\alpha = 1$ when $\nu/\rho = 1$ and $\alpha = 2/3$ when $\nu/\rho = 0$. That is why $\alpha(\vec{r})$ is near to 1 (0.92) in the vicinity of the nucleus 0. Then ν_{1a_1} rapidly falls off to 0, and α drops to 2/3. Figure 2. shows function $\alpha(\vec{r})$ for the molecular orbital 2a₁ in the plane of the molecule. Functions α in the planes perpendicular to the plane of the molecule are very similar to Figure 2. At nucleus 0, the value of α is 0.77, then α increases up to 0.92—0.98 where ν_{2a_1} reaches its maximum value and finally α drops to 2/3. Function $\alpha(\vec{r})$ cannot be considered spherically symmetric for the 2a₁ orbital. Ho-
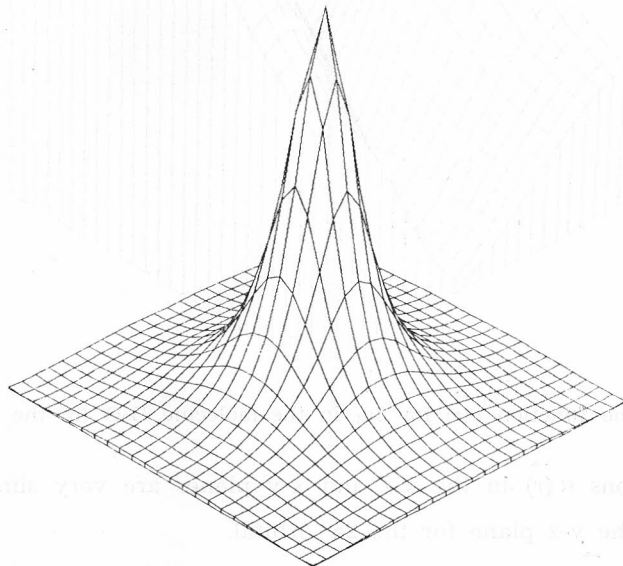

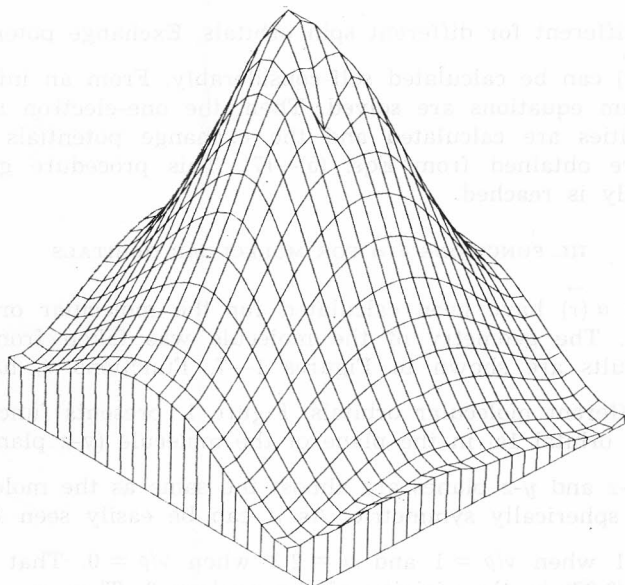Figure 1. The function $\alpha(\vec{r})$ for 1a₁ in the molecule H₂O (in the y—z plane)

Figure 2. The function $\overrightarrow{\alpha(r)}$ for $2a_1$ in the molecule H_2O (in the y—z plane)
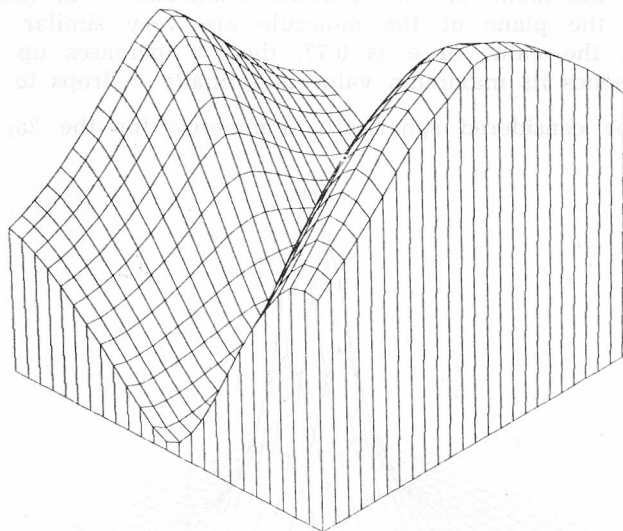

Figure 3. The function $\overrightarrow{\alpha(r)}$ for $3a_1$ in the molecule H_2O (in the y—z plane)

wever, functions $\alpha\overrightarrow{(r)}$ in the x-z and x-y planes are very similar to func-
tion $\alpha\overrightarrow{(r)}$ in the y-z plane for the $2a_1$ orbital.

Function $\alpha\overrightarrow{(r)}$ for the molecular orbital $3a_1$ in the y-z plane can be seen
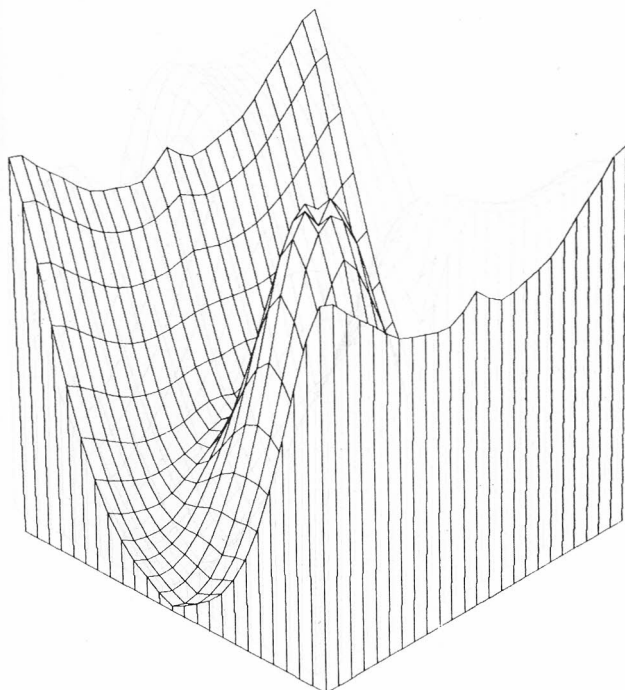in Figure 3. The value of α is very close to 2/3 along the y axis. If we go

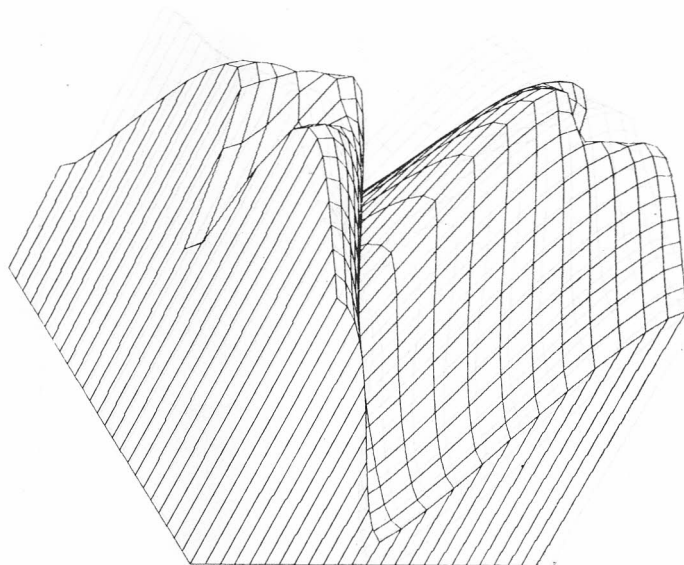Figure 4. The function $\alpha(\vec{r})$ for 3a$_1$ in the molecule H$_2$O (in the x—y plane)

Figure 5. The function $\alpha(\vec{r})$ for 1b$_2$ in the molecule H$_2$O (in the x—z plane)
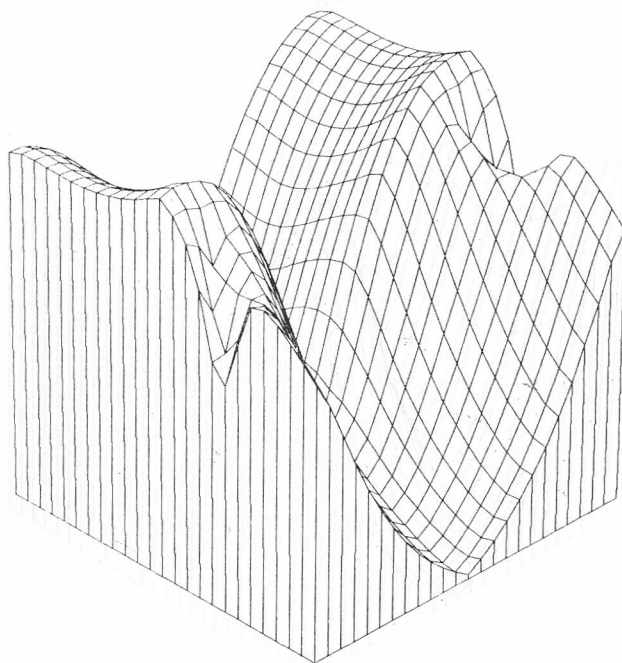
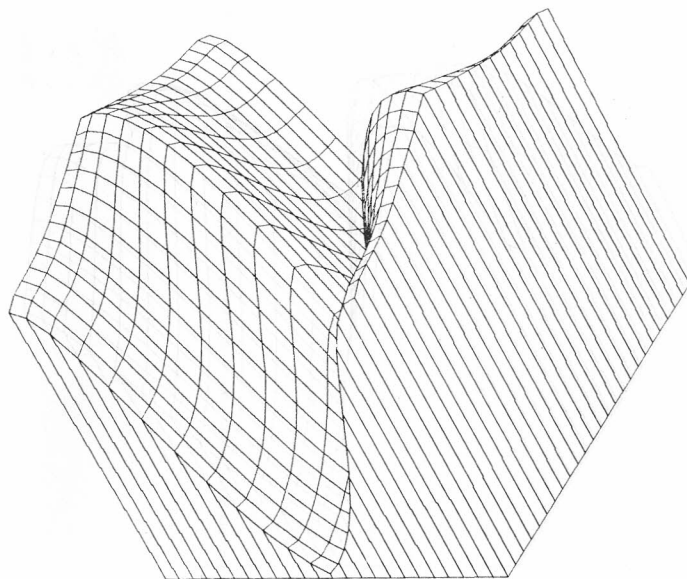Figure 6. The function $\vec{a(r)}$ for $1b_1$ in the molecule H_2O (in the y—z plane)

Figure 7. The function $\vec{a(r)}$ for $1b_1$ in the molecule H_2O (in the x—z plane)

along the z axis the value of α gradually increases from the value of 2/3 up to 0.95. Function α for orbital $3a_1$ has a slightly different shape in the x-y plane. As it is seen in Figure 4., there is a small peak (0.72) at nucleus O. Moving away from the origin along the x axis the value of α drops to 2/3. However, moving off from the origin along the y axis α has minima (2/3) and then increases up to 0.7. Function $\alpha(\vec{r})$ for orbital $3a_1$ in the x-z plane is quite similar to the one in y-z plane.

Figure 5. presents function $\alpha(\vec{r})$ for orbital $1b_2$ in the x-y plane. (α is 2/3 in the y-z plane as function $\nu(\vec{r})$ for $1b_2$ is zero in this plane.) The value of α is about 2/3 along the z axis. However, α increases up to 0.96—0.99 going along the x axis. The plot of $\alpha(\vec{r})$ in the x-y plane is very similar to that of α in the x-z plane.

Figure 6. shows function $\alpha(\vec{r})$ for orbital $1b_1$ in the y-z plane. The function takes the value of 2/3 along the y axis. It is not symmetrical to the y axis. The value of α is 2/3 in the x-y plane as the one-electron density function is 0 in this plane. Figure 7. presents function $\alpha(\vec{r})$ for $1b_1$ in the x-y plane. It resembles Figure 3.

It can be seen from Figures 3—7. that the value of α does not always drop to 2/3 when moving away from the molecule. This is due to the electron densities of the other molecular orbitals being relatively small as compared to the electron density of the orbital in question. Thus, the ν/ρ ratio is relatively large and α is relatively far from 2/3.

IV. CONCLUSION

The method studied in this paper is a generalization of the original Xα method. It is an *ab initio* method, there is no fitting or adjustment in it. The exchange potentials and functions $\alpha_i(\vec{r})$, which are a generalization of parameter α of the original Xα method, can be determined self-consistently.

Thus is actually a special kind of local density functional theory in which different exchange potentials and functions $\alpha_i(\vec{r})$ are obtained for different orbitals.

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SAŽETAK

Analiza r-ovisnosti *ab initio* α_i **parametara molekulskih orbitala u molekuli H_2O za X_α metodu**

Agnes Nagy

Određeni su *ab initio* α_i parametri u X_α metodi za molekulske orbitale u molekuli H_2O. Pokazano je da su oni ovisni o vektoru položaja r.