

LCAO Approach to SCF-X α Method

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An LCAO approach to the Slater SCF-X α method is described. The equilibrium distances and Hellman-Feynman forces are determined.

The merit of the Slater version¹ (SCF-X α) of the Hartree-Fock theory is well known. Especially a great attention has been payed to the muffin-tin approximation combined with the scattered-wave² technique. Ros et al.³ have shown that the main reason for the bad description of the molecular conformation is in the muffin-tin approximation and not in the Slater approach to the exchange potential in the Hartree-Fock theory. The approach of Ros et al.³ meets some problems with the accuracy of calculating the total energy and therefore also the geometry of a molecule. The approach we followed is the LCAO approach a normally used approximation in molecular calculations. When the present attempt was elaborated a similar approach was proposed by Sambe and Felton⁴. The basic idea of using the LCAO approximation is the same, but the whole computational procedure differs from ours quite a lot.

The X α method is based on the equation

$$H \psi_k = \epsilon_k \psi_k$$

with

$$H = -\frac{1}{2} \nabla^2(1) + \sum_n -\frac{Z_n}{r_{1n}} + \int \frac{\varrho(2)}{r_{12}} dV_1 + V_{X\alpha}$$

where

$$V_{X\alpha} = -3 \alpha \left[\frac{3}{8\pi} \varrho(1) \right]^{1/3} \quad \text{and} \quad \varrho = \sum_k \psi_k^* \psi_k.$$

Each ψ_k is expanded into a linear combination of atomic orbitals Φ_i .

$$\psi_k = \sum_i C_{ki} \Phi_i.$$

The direct minimization of the energy with respect to the C_{ki} does not lead to an equation that can be written in a closed form. To overcome this problem we have used the following procedure: Equation (1) was solved, but in each iteration the exchange part of the potential was expanded into

$$\varrho^{1/3} = \sum_i a_i \Phi_i^{*1/3} \Phi_i^{1/3}. \quad (2)$$

Slater atomic orbitals Φ_i 's and p types were used. A further approximation was made to simplify the computational work. Each Slater orbital (Φ_i or

$\Phi_i^{1/3}$) was expanded into three Gaussian orbitals in a way suggested by Pople et al.⁵. With such an expansion the integrals of the type

$$\int \Phi_i(1) \Phi_j^{1/3}(1) \Phi_k^{1/3}(1) \Phi_l(1) dv$$

appearing in Eq. (1), can be evaluated analytically. The procedure we followed has some advantages over the one proposed by Sambe and Felton. The expansion of $\varrho^{1/3}$ maintains the directional character and we do not expand the Coulomb potential. In each iteration step $\varrho^{1/3}$ was fitted [Eq. (2)] using 132 points sampled over the molecules. The density of points was fixed during the energy optimization. We have varied the α parameter in a range 0.7–1 but the only changes are the shifting of energy values without changing the position of the energy minimum. The energy has been calculated either by the statistical expression¹ or by using ψ_k in the energy expression of the Hartree-Fock theory. The numerical values differ but the positions of the energy minima remain at the same distances.

Table 1. Bond lengths (Å) and Hellman-Feynman forces (a.u.) on H and F,

	X α	STO-3G ^a	Expt. ^b	Forces (X α)	Forces (STO-3G)
F ₂	1.51	1.315	1.435	1.044	2.529
FH	0.99	0.956	0.917	-0.011(H) 1.377(F)	-0.055(H) 3.033(F)
CO	1.33	1.145		1.128	
N ₂	1.21	1.134		1.094	

^a Reference 7. ^b Reference 8.

The results are given in Table 1. The bond lengths are in good agreement with the experimental ones and with values determined by the standard ab initio SCF procedure. Our results thus confirm the observation of Ros et al.³ and Sambe and Felton⁴ that the muffin-tin approximation can not be used for geometry determinations at least for systems with atoms from the first and second period.

Some time ago Slater⁶ pointed out that the X α method obeys the Hellman-Feynman theorem. It is well known that wavefunctions from Hartree-Fock-Roothaan ab initio calculations give at the equilibrium distances erratic values for the Hellman-Feynman forces. Only with wave functions at the Hartree-Fock level these forces vanish. One cannot predict whether a wavefunction computed from X α theory satisfies the Hellman-Feynman theorem better than one obtained from an ab initio SCF calculation with a limited basis set. The results (Table 1) show that the Hellman-Feynman forces are closer to zero than the forces of ab initio SCF calculations with STO-3G basis sets⁵, but the improvement is not large.

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