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Theory and applications of an atoms in molecules approach to the $X\alpha$ -SCF method*

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We have studied the $X\alpha$ -SCF problem with an *atoms in molecules* approach. LCAO-molecular orbitals are used and the molecular charge and exchange densities are built up from atomic contributions. We have applied our method to CH_3F with subsequent comparison to *ab initio* calculations. The $X\alpha$ -SCF dipole moment of CH_3F is 1.76 D compared with an experimental value of 1.79 D. We also give calculations of TCNQ and TTF with comparisons to recent $X\alpha$ calculations using the overlapping sphere modification of a muffin-tin potential. Quadrupole moments for TCNQ and TTF have also been determined.

I. INTRODUCTION

The correct treatment of exchange in *ab initio* calculations of electronic structure presents difficulties which become exceedingly severe in large systems. These difficulties stem in large part from the inherently nonlocal character of the exchange operator. The electron gas exchange approximation or $X\alpha$ method¹ has been proposed to provide an approximate, more easily handled operator of local character for the exchange effect.

Johnson and co-workers² have combined the $X\alpha$ method with the KKR³ multiple scattered wave procedure to do electronic structure calculations. Ellis and co-workers⁴ have devised a numerical procedure involving Diophantine integration, and more recently Sambe and Felton⁵ have investigated the structures of some small molecules using LCAO-MO- $X\alpha$ -SCF procedure.

The present article describes an LCAO-MO- $X\alpha$ -SCF technique which is designed with two specific goals in mind:

- The efficient handling of large systems;
- The duplication, insofar as possible, of the *ab initio* values of occupied orbital energies.

In order to implement the first of these we use an atoms in molecules approximation to the electronic charge and exchange densities, by building up the molecular quantities as sums of atomic contributions.

The second goal is accomplished by starting with the *ab initio* Hartree-Fock equations and applying the various approximations at this stage.

In the next section we describe our procedure. This is followed by sections giving some approximations for atomic charge and exchange densities and applications of our method to CH_3F , TCNQ (tetracyano-*p*-quinodimethane) and TTF (bis-tetrathiofulvalene).

II. MATHEMATICAL DETAILS

We use as a starting point the Hartree-Fock Equations for the system,

$$Hu_k = -\frac{1}{2}\nabla^2 u_k(1) - \sum \frac{Z_r}{r_r} u_k(1) + 2 \int \sum_i |u_i(2)|^2 \frac{d\tau_2}{r_{12}} u_k(1) - \sum_i u_i(1) \int u_i^*(2) u_k(2) \frac{d\tau_2}{r_{12}}$$

$$= \epsilon_k u_k. \quad (1)$$

The bulk of the labor of *ab initio* calculations lies with the Coulomb and exchange terms of the Fock operator, and it is clear that the development of effective approximations for these terms would bring the calculation of large systems into an easily accessible region. We emphasize that approximations are needed for both the Coulomb and exchange terms to produce the desired decrease in labor of the calculations.

Our atoms in molecules approach consists of writing the charge density, ρ , as a sum of atomic contributions

$$2 \sum |u_k|^2 = \rho \approx \sum \delta_\gamma \rho_\gamma, \quad (2)$$

where the ρ_γ are charge densities of individual atoms and the δ_γ are constants which measure the effective charge on the atom. The ρ_γ are spherically symmetric approximations to the charge densities of individual atoms. We discuss these functions in the next section.

We use the standard $X\alpha$ approximation for the exchange term,

$$V_{X\alpha} = -6\alpha \left[\left(\frac{3}{8}\pi \right) \rho \right]^{1/3} = -6\alpha \left(\frac{3}{8}\pi \right)^{1/3} \sum \delta_\gamma^{1/3} \rho_\gamma^{1/3} + R, \quad (3)$$

where we have replaced ρ with the approximation given by (2). The remainder R , is added since the cube root of a sum is not equal to the sum of cube roots. The nature of R is easy to deduce. It is small in any region of space where only one of the terms $\delta_\gamma \rho_\gamma$ is significantly different from zero, or where ρ is very small. The regions of largest R occur where there is significant overlap of two or more of the ρ_γ . An approximation with some analogies to semiempirical CNDO methods would result if we take R to be zero everywhere. A less drastic alternative involves modifying $\rho_\gamma^{1/3}$ with an auxiliary function so as to minimize the serious effects of dropping R without compensations, and we have

$$V_{X\alpha} \approx -6\alpha \left(\frac{3}{8}\pi \right)^{1/3} \sum \delta_\gamma^{1/3} \rho_\gamma^{1/3} \zeta_\gamma. \quad (4)$$

A number of function types for ζ_γ would undoubtedly work, but a convenient and satisfactory choice consists of a Gaussian function, $\zeta_\gamma = \exp(-\epsilon r_\gamma^2)$ with ϵ the same for all atoms. The calculations described in this article use $\epsilon = 0.12$, a value giving $X\alpha$ bound state orbital energies close to those from *ab initio* calculations. The

TABLE I. Coefficients and exponential scale factors for least square approximations to charge and exchange densities of hydrogen, carbon, nitrogen, oxygen, fluorine, neon, and sulfur. [See Eqs. (5) and (6).]

$k =$		1	2	3	4	5
H	s_k	119.9984	19.84331	5.06226	1.64182	0.59198
	a_k	0.13632	0.22387	0.26210	0.17486	0.03226
	t_k	40.00	6.614	1.678	0.5472	0.1973
	b_k	0.09102	0.14018	0.23560	0.18134	0.27704
C	s_k	119.09696	27.28693	6.06064	1.60340	0.46932
	a_k	26.95817	30.97315	1.79244	0.05466	0.22263
	t_k	39.67	9.075	2.0202	0.5345	0.15644
	b_k	1.16214	1.90694	0.09989	0.04348	0.59146
N	s_k	125.81507	26.97817	6.08744	1.13328	0.44937
	a_k	94.71361	33.78108	0.46759	0.61020	0.12411
	t_k	42.605	8.993	2.029	0.3777	0.1498
	b_k	2.59468	1.38888	0.02586	0.50809	0.33958
O	s_k	131.98357	28.04665	6.46593	2.37572	0.66052
	a_k	145.90291	36.91763	-1.40304	1.72551	0.37901
	t_k	43.994	9.346	2.155	0.7919	0.2203
	b_k	3.48510	0.85545	0.09331	0.38982	0.64669
F	s_k	135.34790	27.99038	7.10991	3.75935	0.86597
	a_k	203.73935	37.80394	-5.64042	4.91189	0.69148
	t_k	45.118	9.330	2.370	1.253	0.2887
	b_k	4.34673	0.156629	0.49047	0.16314	0.86562
Ne	s_k	155.55228	27.18310	8.19035	5.63028	1.18456
	a_k	290.72259	41.41658	-18.21111	14.63973	1.33422
	t_k	51.851	9.061	2.730	1.877	0.3948
	b_k	5.08178	-0.44724	1.58680	-0.69876	1.14821
S	s_k	411.4861	13.83517	3.733565	3.370554	0.4471470
	a_k	2031.984	39.68394	26.52671	-19.36931	0.3922622
	t_k	140.0096	11.55385	7.579065	0.1758505	0.07150376
	b_k	4.147832	-1.401360	9.031689	0.5754152	0.1430481

real convenience of a Gaussian function for ξ_γ is, of course, a result of our use of this same function type to represent ρ and $\rho^{1/3}$. This correction produces a value for the exchange energy which is very close to the *ab initio*. In CH_3F the $X\alpha$ gives 16.04 a. u. compared with 16.46 a. u. for *ab initio*. These results on CH_3F are discussed more fully below.

Once the types of atoms and their positions in the system are fixed, the only variables in ρ and $\rho^{1/3}$ are the δ_γ . If the molecular orbitals for the system are known, the values of δ_γ may be determined by a standard Mulliken population analysis. This connection between δ_γ and MO's provides an iterative procedure for the $X\alpha$ -SCF. An initial set of δ_γ may be guessed, from which a Fock-matrix is determined, which provides a set of orbitals from which a set of δ_γ may be calculated; the process is then carried to self-consistence. An initial guess of $\delta_\gamma = 1$ has been satisfactory in all cases tried.

Because of our approximations, the procedural step in which the Fock matrix is evaluated may be executed without the extensive tensorial contraction operations characteristic of *ab initio* LCAO-MO methods. The number of integrals for the atoms in molecules $X\alpha$ -SCF is much smaller than that for *ab initio* methods. Thus, we must evaluate integrals for the overlap kinetic energy, Coulomb interaction, charge density and the ex-

change potential. A system comprising N_A atoms to be studied with a basis of N_0 AO's requires the evaluation and storage of $(2N_A + 3)N_0(N_0 + 1)/2$ integrals. These need be calculated only once, since the SCF steps involve the manipulation of the δ_γ and the MO's only. The small number of integrals and the simplicity of the SCF step are the reasons for the rapidity of our atoms in molecules $X\alpha$ -SCF method. (AIM- $X\alpha$ -SCF).

III. GAUSSIAN APPROXIMATION TO ρ_γ AND $\rho_\gamma^{1/3}$

The $X\alpha$ -SCF calculation procedure outlined in the previous section depends crucially upon having adequate approximations for atomic charge and exchange densities. In all cases ρ_γ and $\rho_\gamma^{1/3}$ are represented as sums of spherical Gaussians:

$$\rho_\gamma = \sum_k a_k \exp(-s_k r_\gamma^2); \quad (5)$$

$$\rho_\gamma^{1/3} = \sum_k b_k \exp(-t_k r_\gamma^2). \quad (6)$$

The constants a_k , s_k , b_k , and t_k in (5) and (6) may be determined by a least squares fit of ρ_γ to spherically averaged *ab initio* atomic charge density functions, followed by another least squares fit of $(\rho_\gamma^{1/3})^3$ to ρ_γ . This has been done for H, the second row atoms, C, N, O, and F, and the third row atom, S. Five term approximations for ρ_γ and $\rho_\gamma^{1/3}$ are given in Table I for each of

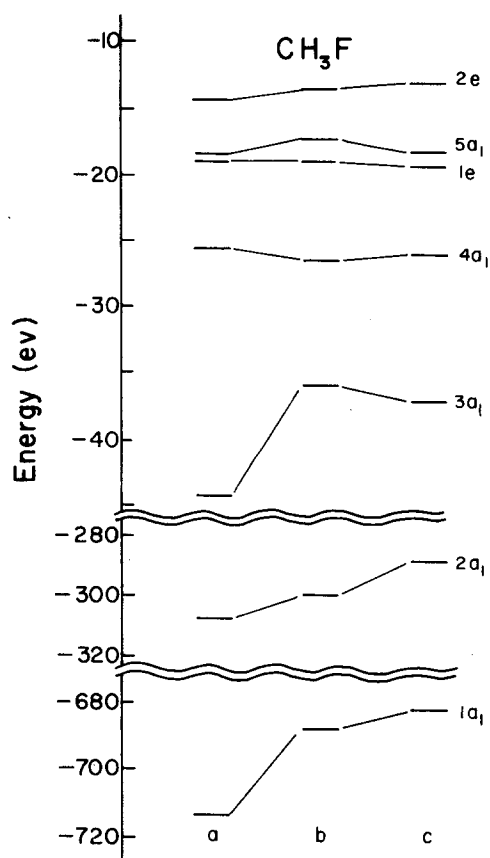


FIG. 1. Comparison of orbital energies for various calculations of the CH_3F molecule: (a) *Ab initio* results, (b) $X\alpha$ -SCF with Whitten basis, and (c) $X\alpha$ -SCF with 3G-STO basis.

these atoms. These are in atomic units so that the integral of ρ_r is just the atomic number.

Approximations equivalent to those in Table I are in principle obtainable for every element and studies are underway to obtain approximations to ρ and $\rho^{1/3}$ for

many other atoms.

IV. SPECIFIC CALCULATIONS USING THE ATOMS IN MOLECULES $X\alpha$ -SCF METHOD

A. Methyl fluoride

The orbital energies and electric dipole moment of CH_3F have been determined using two different AO bases:

(a) The Gaussian lobe basis given by Whitten;⁶

(b) The 3G-STO basis and scale factors given by Pople and co-workers.⁷

The atomic charge and exchange densities from Table I were used. Figure 1 shows a comparison of the orbital energies of our two CH_3F calculations with *ab initio* results obtained with the (b) basis above. The AIM- $X\alpha$ -SCF reproduces the *ab initio* energies well and the relatively small differences resulting from the basis change also show our method to have satisfactory stability. This is also shown by the values of the dipole moment: Gaussian lobe, 1.76 D; 3G-STO, 1.79 D. There is very satisfactory agreement of both of these with the experimental value of 1.79 D.⁸ The *ab initio* dipole moment of 1.48 D for basis (b) is rather poor. The exact agreement of the 3G-STO calculations cannot be considered more than fortuitous.

B. Tetracyanoquinodimethane

TCNQ is the acceptor molecule in several organic electron-donor-acceptor crystals which show electrical conductivity and its properties are of considerable interest. In addition, the electronic structure of TCNQ has been obtained recently with the overlapping sphere modification of the $X\alpha$ -scattered wave method.⁹ We have calculated TCNQ to provide a comparison of our results with those from the modified muffin-tin potential.

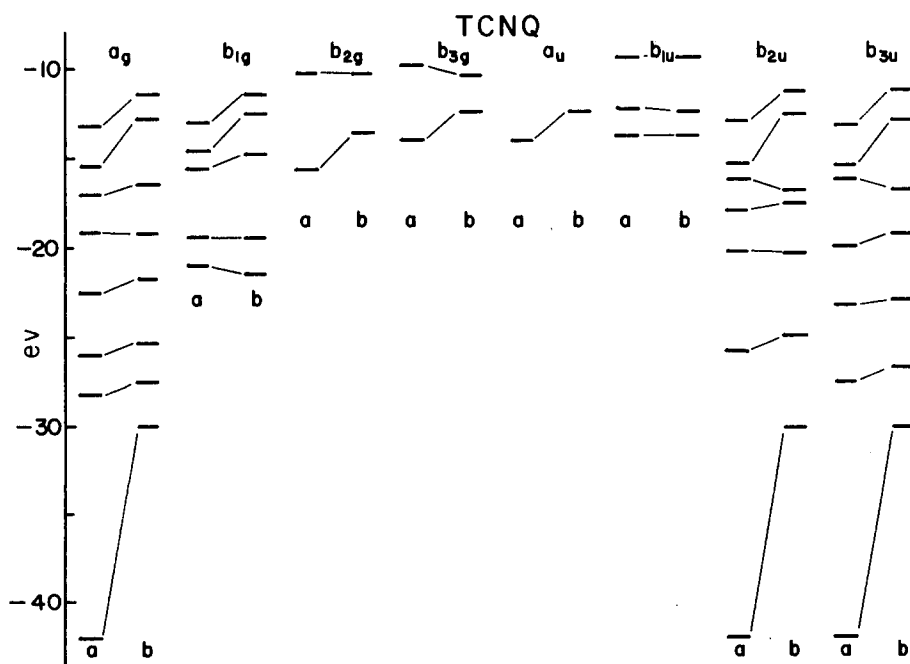


FIG. 2. Comparison of orbital energies of TCNQ for AIM- $X\alpha$ -SCF approach and modified muffin-tin potential; (a) Ref. 9 and (b) this work.

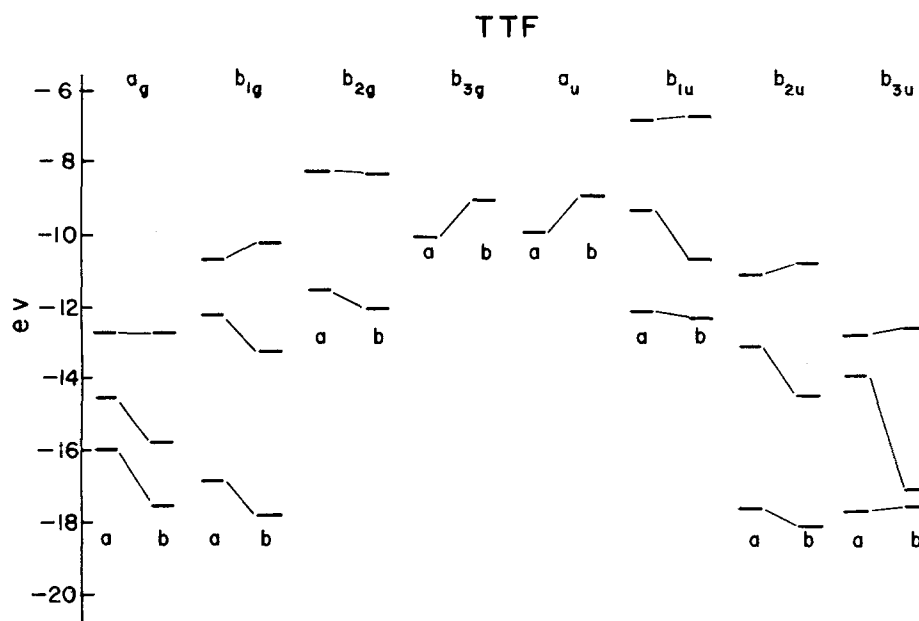


FIG. 3. Comparison of orbital energies of TTF for AIM- $X\alpha$ -SCF approach and modified muffin-tin potential: (a) Ref. 10 and (b) this work.

The functions given in Table I provide the necessary atomic densities to do the calculations and the 3G-STO's are used for the AO basis. We show our valence orbital energies and those of Herman, Williams, and Johnson⁹ (Model IV), in Fig. 2. We see that the orbital energies from the two calculations are qualitatively very similar although there are quantitative differences. These differences are reflected most strongly in the region of CN group orbitals at the bottom of the diagram. The positions of these were reported to be very sensitive to the differing overlapping sphere models.⁹

C. Tetrathiofulvalene

TTF is the second component of the most familiar TCNQ charge transfer crystal. We have calculated the electronic structure of TTF and our valence orbital energies are compared with those of Bennett and Herman¹⁰ in Fig. 3. The latter workers also used the overlapping sphere approximation in this determination. Our calculation was again done with a 3G-STO basis. The sulfur orbital exponential scale factors were obtained from the single- ζ SCF results of Clementi and Roetti.¹¹

We see that the two computation methods again predict a similar qualitative structure for the valence orbital energies but with some quantitative differences. The differences are similar to those in the upper part of Fig. 2. Although TTF and TCNQ have the same total

number of electrons, TTF has significantly fewer valence electrons because of the sulfur.

D. Quadrupole moments

Recent results on the *ab initio* calculation of interaction potential of two hydrogen molecules indicates that the influence of these small molecular electric quadrupoles can be as important as dispersion interactions.¹² Thus, the ability to easily calculate quadrupole moments for systems such as TTF and TCNQ from reasonable wavefunctions may be a useful feature of any theoretical method. The quadrupole moments of both TCNQ and TTF are given in Table II. The values here are quite sizeable and indicate that consideration of quadrupole interactions may be necessary to the understanding of electronic interactions and structures of complexes of these molecules.

V. CONCLUSIONS

The AIM- $X\alpha$ -SCF method promises to be a useful calculative procedure for determining the electronic properties of large molecules. A particular benefit of this approach is that the method uses analytical functions in all steps of the procedure. Finally, MO's which are linear combinations of Gaussians or STO's are obtained. This greatly facilitates efficient calculations for large systems and alleviates the sensitivity of numerical $X\alpha$ calculations to the choice of the overlapping sphere. The results of calculations on the large systems, TTF and TCNQ, are in agreement with reported overlapping sphere $X\alpha$ -scattering calculations.

TABLE II. Quadrupole moments (esu cm²) of TCNQ and TTF.

	TCNQ	TTF
Q_{xx}	4.80×10^{-25}	0.93×10^{-25}
Q_{yy}	-0.74×10^{-25}	-4.58×10^{-25}
Q_{zz}	-4.06×10^{-25}	3.65×10^{-25}

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