ON THE PROJECTION APPROACH TO INTERPRETATION OF CHEMICAL VALENCE CONCEPTS

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It is shown that Roby's general approach to the analysis of molecular wave functions from the standpoint of basic chemical valence concepts is equivalent to the method based on the construction of "localized natural" orbitals, if the approximation of a single-determinant wave function is adopted.

Recently, Roby[1,2] has outlined a method for analysing molecular wave functions from the point of view of certain chemical concepts, such as localized chemical bond, lone electron pair, hybridization and charge on an atom in a molecule. The unified approach is derived in terms of projection and density operators. Specifically, the formulation relies on the definition of projectors representig suitable molecular subspaces associated with a particular orbital χ_μ^A centered on atom A, or with a set of atomic orbitals χ_O related to an atom or a bond. For the matrix representation of such a kind of operator we can write

$$P_O = \chi_O\, S_O^{-1} \chi_O^+ , \qquad (1)$$

where use is made of the notation of Montet, Keller and Mayer[3] and S_O^{-1} denotes the inverse of the metric matrix related to the set χ_O. The performance of Roby's method is not restricted to single-determinant wave functions and can be applied to any kind of wave functions.

However, within single-determinant approximation, this method becomes identical to that which is based on the construction of "localized natural" orbitals[4–6] as will be shown in this note. Because of the limited quantitative meaning of the discussed chemical concepts, the restriction of the form of the wave function is by far mor relevant to the applicability of the approach than to the recovered quantities themselves. It is safe to say that these quantities are within the single-determinant approximation of sufficient accuracy to give reliable quantitative information on molecular electronic structure.

Localized and hybrid orbitals

In our former papers[4−6] we have suggested a procedure for constructing localized and hybrid orbitals from wave functions calculated within the Hartree–Fock LCAO-MO framework. This procedure relies upon the projection property[7] of the Fock–Dirac density matrix ϱ_{FD} and consists particularly in solving the variational equation

$$\delta[\eta^+ \varrho_{FD}\eta] = 0 , \tag{2}$$

where the trial one-electron function η satisfies certain constraints reflecting its behaviour of being localized in a given region of the molecule, *i.e.* only those linear coefficients D_i are considered as variational parameters which multiply the selected set of atomic orbitals χ_O, that presumably plays a rôle in forming the localized function $\eta = \chi_O \, D$. In order to achieve the maximum coincidence of the localized function η with the "exact" solution represented by the density matrix, that particular η_m is considered as the desired solution among all stationary functions which corresponds to the maximum value of ε_m

$$\varepsilon_m = \eta_m^+ \varrho_{FD}\eta_m , \tag{3}$$

where ε_m is interpreted as the occupation number of the given orbital.

Alternatively, on grounds of the "outer projection theorem" of Löwdin[8], Roby[2] derived that that eigenvector φ_m of the operator $P_O \varrho \, P_O$ satisfies the projection criterion for optimum hybridization or localization in the given molecular region which belongs to the maximum eigenvalue (ϱ stands for the molecular first-order density operator). Since according to the verbal definition of η given above it holds

$$\eta = P_O\varphi , \tag{4}$$

both formulations lead within the same level of approximation (*i.e.* for $\varrho = \varrho_{FD}$) to identical results. However, it should be stressed once more that Roby's formulation is quite general and permits to treat wave functions of any kind of approximation.

Charges on Atoms in a Molecule

Reducing η to a single atomic orbital, χ_μ say, the expression (3) becomes

$$\varepsilon_\mu = \chi_\mu^+ \varrho_{FD}\chi_\mu = (SRS)_{\mu\mu} , \tag{5}$$

where S and R are the overlap and charge-and-bond-order matrices, respectively, related to the atomic orbital basis set. Because of the physical interpretation of the quantity ε_μ it is evident that relation (5) furnishes a measure of the atomic charge in a molecule by summing up contributions belonging to a given atom.

Generally, according to Gleason's theorem[9], the probability of occupancy of the subspace represented by the projector P_O is $Tr\varrho P_O$. This relation has been used by Roby[1] to define charge and shared electron densities in molecules which in the Hartree–Fock approximation take the same form as indicated by Eq. (5). It is note-worthy that also Davidson[10] on grounds of a different argumentation arrived at the same definition of the atomic charge in a molecule.

DISCUSSION

The theoretical aspects of the above given definitions of chemical valence concepts have been presented in earlier papers[1,2,4–6,10,11]. A further our paper will be devoted to the problem of defining the charge on an atom in a molecule. Therefore, we merely mention here the considerably wide range of applicability of the method in connection
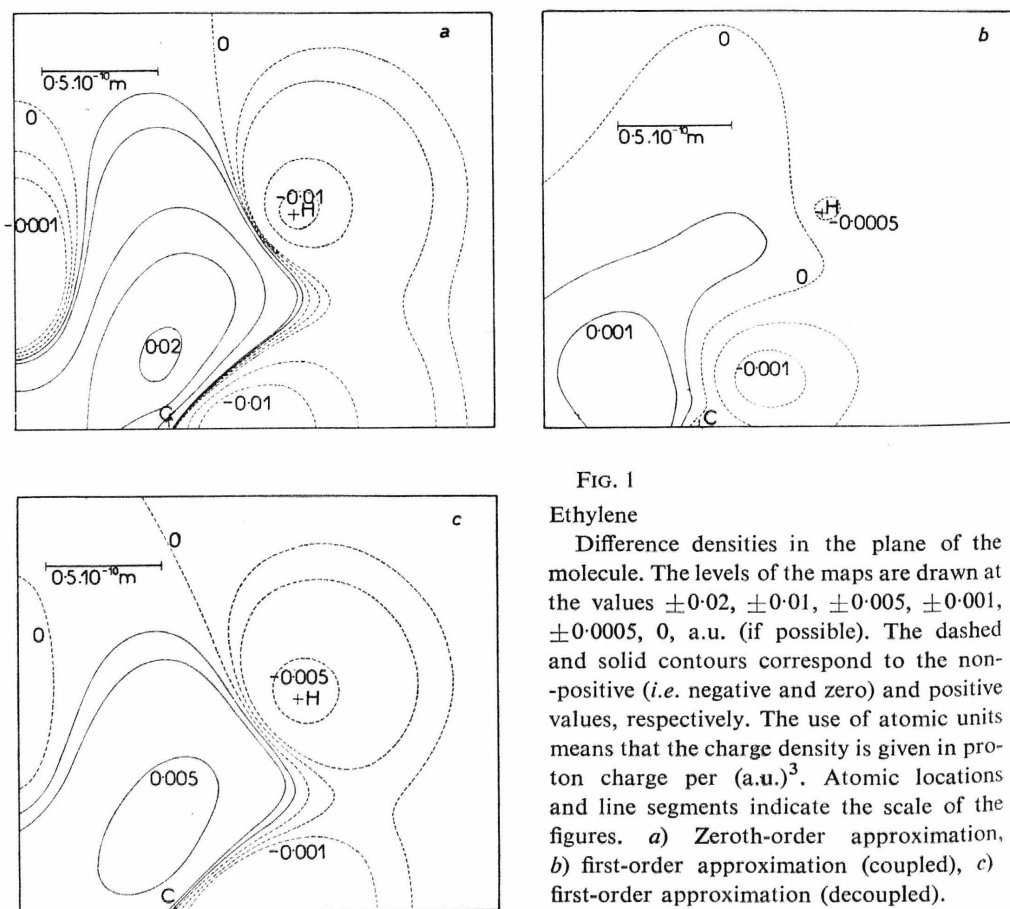

FIG. 1

Ethylene

Difference densities in the plane of the molecule. The levels of the maps are drawn at the values ± 0.02, ± 0.01, ± 0.005, ± 0.001, ± 0.0005, 0, a.u. (if possible). The dashed and solid contours correspond to the non-positive (i.e. negative and zero) and positive values, respectively. The use of atomic units means that the charge density is given in proton charge per (a.u.)^3. Atomic locations and line segments indicate the scale of the figures. a) Zeroth-order approximation, b) first-order approximation (coupled), c) first-order approximation (decoupled).

with electron localization and hybridization. In our previous papers[12] we paid particular attention to examining the kind of hybridization and the extents of localizability and transferability of bond and lone pair orbitals, and the construction of minimum contracted basis sets by means of localized orbitals.

The procedure based on the projection approach yields orbitals expanded over a given number of centers. Consequently, the single-determinant wave function expressed in terms of such localized orbitals is generally inferior in accuracy to the SCF description of the electronic system. This shortcoming, however, is compensated by the property of being in some cases for certain molecular conformations transferable from one molecule to another, since no difficulties with delocalized "tails" are here encountered. The transferability offers the possibilities of providing good initial guesses for molecular calculations. The benefit of this behaviour has ben utilized within the many-[13] and single-determinant[14] wave function approximations. For instance, on grounds of analysing optimized strictly localized orbitals for various C—H and C—C bonds, obtained within the INDO scheme[15], it was possible to set up a prescription for constructing one- and two-centre orbitals depending on the hybridization type of the carbon atom. The results concerning the use of these orbitals in the SC-perturbation treatment[14] were quite encouraging and will be demonstrated here in terms of electron density maps for a typical example, the ethylene molecule. The contour diagrams drawn for a deorthogonalized AO basis set[16] are given in terms of differences in electron density distributions between the perturbation and SCF solutions. Fig. 1a is related to the zeroth-order approximation corresponding to the transferable strictly localized orbitals. As expected, an increase of charge has occured in the internuclear regions, accompanied by a decrease in charge density to the outsides of the bonding regions. The first-order correction to the density matrix brings about a substantial improvement in the difference densities (Fig. 1b). The first-order decoupled solution (Fig. 1c) lies between the displayed two cases. It is seen that the calculated perturbation electron densities are of satisfactory accuracy when compared with reference SCF values. This property and the good convergence of the perturbation expectation values[14] indicate that the SC-perturbation procedure can substitute the regular SCF solution of the problem in cases when the latter is accompanied by numerical difficulties.

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