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On the Molecular Electrostatic Potentials Obtained with CNDO and INDO Wave Functions

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Molecular electrostatic potentials computed with CNDO/2 and INDO wave functions are shown to present systematic differences with respect to *ab initio* potentials in the case of out-of-plane π potentials and in-plane vicinal hetero atoms in planar hetero molecules.

Key words: Molecular electrostatic potentials – CNDO and INDO versus *ab initio* – Basicity of hetero molecules

It has been shown recently that non-empirical isoenergy maps of the molecular electrostatic potential felt by an approaching proton give very reliable indications [1–10] on the most probable protonation site of a heteromolecule. Since *ab initio* calculations are necessarily limited to compounds of medium size, it is important to determine what are the possibilities of utilizing semi-empirical wave functions for computing such potentials. We have previously [11, 12] investigated the performances of CNDO wave functions in this respect and concluded that [12] in order to obtain quantitatively good isopotential maps from such functions one must transform the eigenvectors from the admittedly orthogonal basis set into a regular Slater basis ("deorthogonalization" [13]) and introduce all the nuclear attraction integrals as well as all the density matrix elements $P_{\mu\nu}$ in the expression [1] of the molecular potential at a point P:

$$V = \sum_A \frac{Z_A}{R_{PA}} - \sum_{\mu\nu} P_{\mu\nu} \int \frac{\chi_\mu \chi_\nu}{r_P} d\tau .$$

This was approximation IV of Ref. [12]. On the other hand, for large molecules, where this elaborate procedure becomes costly, we suggested the exploratory use of a simpler, very rapid, approach (approximation II of Ref. [12]) utilizing only the diagonal elements of the original density matrix and the nuclear attraction integrals V_{ss} over s orbitals (2s or 1s depending on the principal quantum number of the valence shell of the atom carrying the $\chi_\mu \chi_\nu$ distribution).

In the light of recent computations we would like to draw attention in this note to particular limitations of CNDO (and also INDO) wave functions in two types of cases frequently encountered planar conjugated heteromolecules and concerned, one with the basicity of amino groups, the other with the discrimination between vicinal positions corresponding to σ lone-pairs on different atoms.

1. π-Potentials

Figure 1 reports the isopotential curves computed in approximations II (V_{ss}) and IV (deorthogonalized) for formamide, cytosine and adenine in a plane perpendicular to the molecular plane and containing the C–N bond to the amino group. It appears that on the basis of the simple V_{ss} approach one would not predict a potential well above (or below) the NH_2 group, whereas such a well definitely exists in the *ab initio* results [5, 6]. If deorthogonalization is performed and all integrals introduced the absent minima appear. For formamide and adenine, they have a depths of the same magnitude as in the *ab initio* computation of Ref. [5], and the ratio of these depths to those of the in-plane minima is also reproduced. However the width of the attractive out-of-plane region is much smaller here than in the non-empirical curves.

For cytosine, although a minimum appears above the NH_2 group, the difference with respect to the *ab initio* map is more pronounced, a feature already contained in the V_{ss} approximation where the whole area above the molecular plane is repulsive.

These examples show that for π-potentials, the V_{ss}-exploration may be deceiving in the sense that in does not necessarily lead to suspect the existence of a minimum. It is only upon the introduction of the two-center distributions that the strong repulsions are decreased. (We have verified that the averaging of the one-center terms is not responsible for the effect observed.)

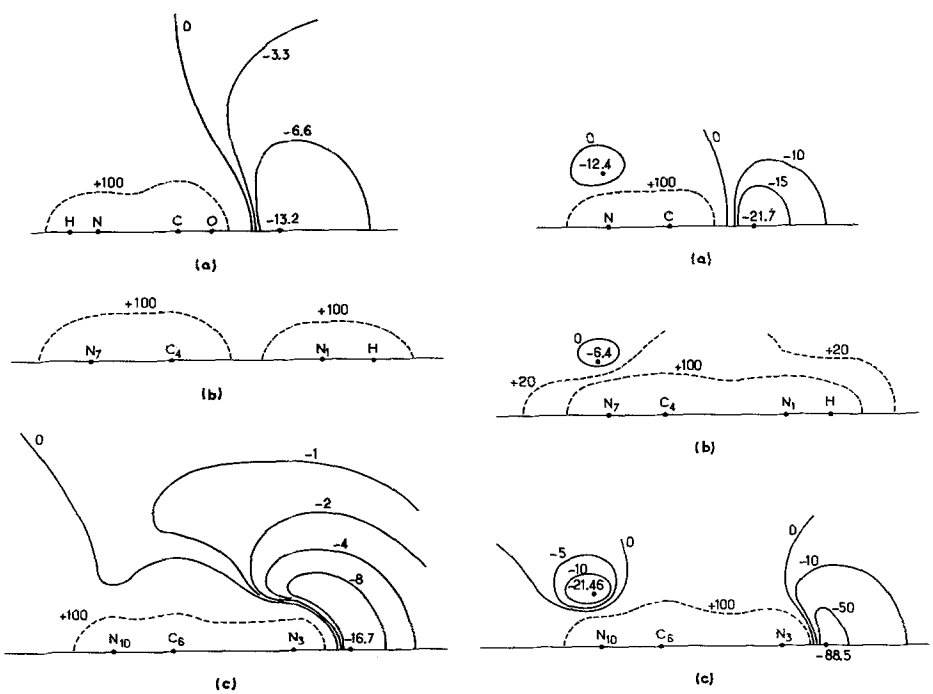

Fig. 1. Isopotential maps for: a) formamide, b) cytosine, c) adenine; left: in the V_{ss} approximation in a plane perpendicular to the molecule and containing the CN bond to the amino group; right: after deorthogonalization

2. In-Plane Vicinal Heteroatoms

The second case of interest may again be illustrated on cytosine. Figure 2a reports the isopotential curves for the part of the molecular plane located near the carbonyl oxygen and the pyridine-like nitrogen. Although these two atoms are in the same region of the molecule, the *ab initio* results [5] indicate that they have distinct potential wells. This distinction is not shown at all in the V_{ss} approximation which indicates only a single large area of negative potential encompassing the nitrogen region, but with its minimum near the extremity of the CO bond. (A similar large region was found to include the CO and N_7 neighbourhood of guanine [11].) Figure 2b shows that the elaborate computation reestablishes correctly a distinct potential well near the nitrogen atom. One notes, however, a reversal in the ordering of the depth of the two wells with respect to that of the *ab initio* map. A similar exaggeration of the oxygen potentials with respect to that of the nitrogen has also been found recently in oxaziridine [14]. This result tends to indicate a subtle inappropriate balance between the two atoms in the CNDO wave function which is not easily detected in the gross charge distribution.

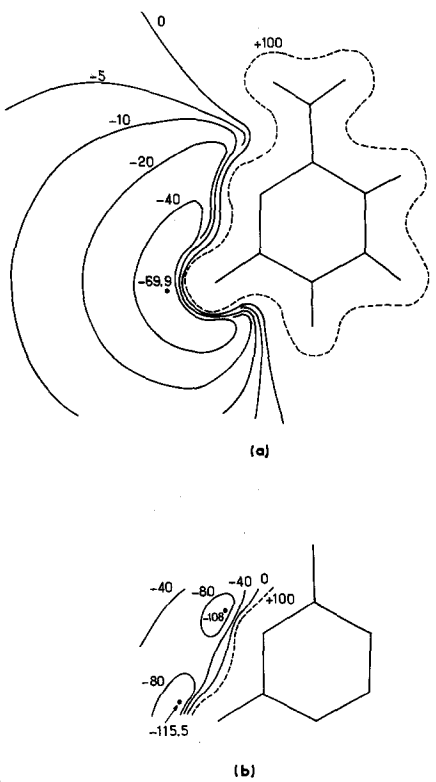

Fig. 2. In-plane isopotential curves for cytosine a) V_{ss} approximation, b) after deorthogonalization

3. INDO Wave Functions

We have extended our evaluation of semiempirical approximations to the INDO wave functions, in view of their recent use for the computation of molecular potentials [15]. Since the INDO ground state electron distribution differs little in general from the CNDO distribution [16] we did not expect much difference in the corresponding molecular potential maps. Indeed the results show exactly the same behavior: for the INDO potential of formamide in a plane perpendicular to the molecule and containing the NC bond, the V_{ss} approximation shows no minimum above the amino group as in the corresponding CNDO approximation, and the deorthogonalized INDO function with all the integrals included reestablishes the minimum. (Approximation III of Ref. [12] gives also results practically identical to the CNDO-ones.)

The situation for the in-plane potential of cytosine is identical to that described in the CNDO case. The maps are completely identical to those of Fig. 1 and the nitrogen minimum remains smaller than the oxygen one after deorthogonalization (104 and 113 kcal/mole instead of 108 and 115 in CNDO). (The INDO maps, not reproduced for economy reasons, are available upon request.)

4. Conclusion

These examples show that although gross features of the potential maps are generally obtainable with CNDO or INDO functions, some care and considerable experience is required for fine distinctions, even after deorthogonalization.

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