Direct Comparison of EH and CNDO Charge Distributions for Adenine

Donald B. Boyd

The Lilly Research Laboratories, Indianapolis

Isodensity contour diagrams of adenine computed from extended Hückel and complete-neglect-of-differential-overlap molecular orbital theories reveal the effects of iterating to a self-consistent field and of including off-diagonal density matrix elements.

Two semi-empirical molecular orbital theories popular for the study of very large molecules are the extended Hückel (EH) and complete-neglect-of-differential-overlap (CNDO/2) methods [1, 2]. Because of their extensive application to many molecular systems, it is important to understand their similarities and differences. We wish to carry out for the first time a direct comparison of how they distribute charge in space using electron density maps. Adenine is treated because it has been used as a model for comparison of the methods via other criteria [3, 4].

Ordinarily, for an N-electron, single determinantal wave function, the electron density at each point in space r is given [5] by $D(r) = \sum_{p,q} D_{pq}\chi_p(r)\chi_q(r)$, where $D_{pq} = \sum_{i=1}^{N} C_{pi}C_{qi}$ are the density matrix elements computed from the LCAO–MO coefficients and the $\chi_p(r)$ are the Slater-type basis functions. However, the use of this expression fails with the CNDO/2 wave function because the normalization of the coefficients is based on the neglect of overlap, $\int \chi_p\chi_q \, d\tau = \delta_{pq}$, which follows from the neglect of differential overlap, $\chi_p\chi_q = \delta_{pq}$. Accepting the statement [6] that the CNDO/2 method employs Slater-type basis functions (and not some unspecified orthogonalized atomic orbitals), then this drastic approximation of neglecting the differential overlap leads to a CNDO/2 total density of $D(r) = \sum_{p} D_{pp}^{CNDO/2} \chi_p(r)\chi_p(r)$. The difference in EH and CNDO/2 densities is given by $\Delta D(r) = \sum_{p,q} D_{pq}^{EH} \chi_p(r)\chi_q(r) - \sum_{p} D_{pp}^{CNDO/2} \chi_p(r)\chi_p(r)$. We are interested in this difference function because it allows a more detailed comparison than the visual inspection of two total density maps and because neither total density function would show the contribution of the core electrons.

Fig. 1 shows that the EH method puts more density in the lone pair regions (lobes directed out from N_1, N_3, and N_7) and in the σ bonding regions (along the internuclear axes as drawn). The CNDO/2 method puts more charge near the nuclei as indicated by the frequent occurrence of negative contours around the nuclei. Note that each hydrogen atom is surrounded by a negative contour
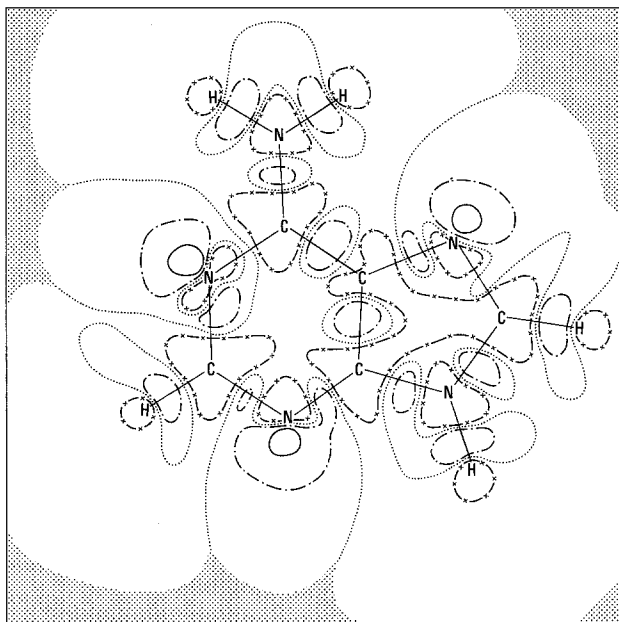
Fig. 1. Plot of the difference in EH and CNDO/2 molecular densities. Contours depict $\Delta D(r)$ computed in the plane of the molecule with positive regions corresponding to where the EH density is greater and negative regions to where the CNDO/2 density is greater. Contours are at $+0.126$ e/bohr^3 (———), $+0.016$ (— · —), and -0.016 (— × —). Nodes and areas where $\Delta D(r)$ is less than 10^{-6} e/bohr^3 are dotted. The map covers an area of 9×9 Å

corresponding to CNDO/2 theory making hydrogens less positive than EH theory [3].

The π electron distribution (Fig. 2) from the EH method has electrons concentrated in the $2p_\pi$ orbitals of the imine nitrogens and in the π bonding regions (between the atoms but out of the molecular plane). Such a region is seen in the perpendicular plane passing close to the C–NH$_2$ axis. EH theory also puts more charge within the pyrimidine and imidazole rings.

The characteristic of EH theory to exaggerate charge separation is well recognized [3]. Regions around each atom where the iterative process of the CNDO/2 theory smooths out the charge distribution can be associated with the peaks and valleys in the figures. The large negative net atomic charges on the imine nitrogens are due to both σ (in-plane) and π (out-of-plane) electrons. Thus, the two types of electron clouds do not appear to offset each other to minimize charge separation.

The nitrogens of adenine have been classified into "pyrrole or amino" and "pyridine" types based on electron density distributions computed from *ab initio* wave functions [7]. Distinctions between the protonated and imine nitrogens can also be seen in the differences in the two valence-electron distributions. For example, in Fig. 1, the two protonated nitrogens are surrounded by triangular contours of density loss, whereas the imine nitrogens have a lone pair region
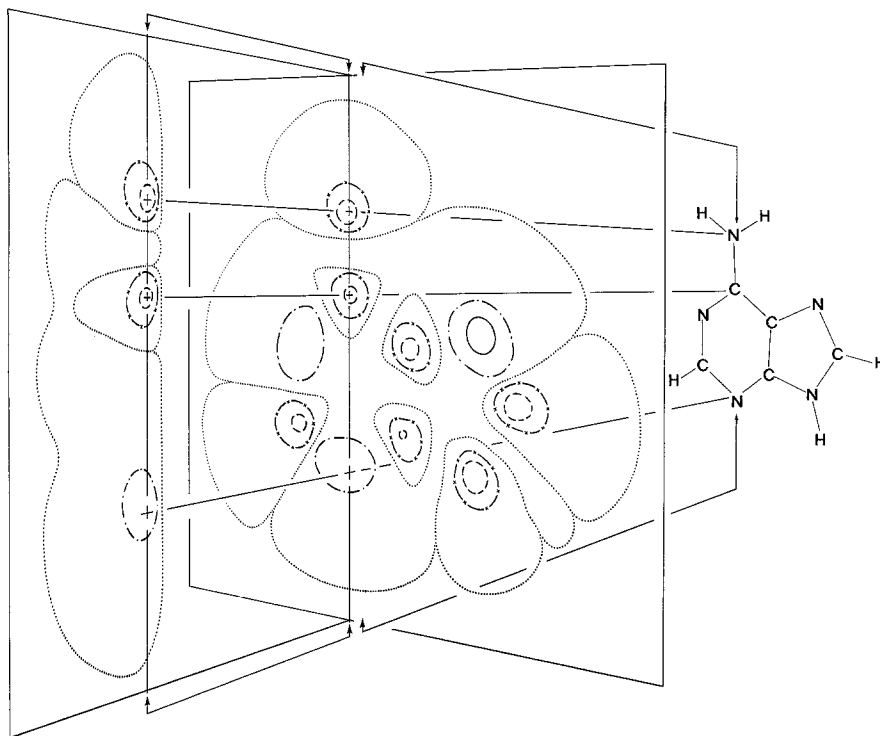
Fig. 2. Plot of the difference in EH and CNDO/2 π-electron densities alone. $\Delta D(r)$ is computed using the π MO's as expanded on the $2p_\pi$ basis functions with the EH and CNDO/2 coefficients. The difference function is computed in a plane $0.4\,\text{Å}$ above the molecular plane and in an intersecting, perpendicular plane passing through atoms N_3 and C_6. The two planes have been separated in this perspective to avoid overlapping of the contours. The line of intersection of the two planes and the spatial relation to the nuclear framework are also indicated. Contours are at $+0.032\,\text{e/bohr}^3$ (———), -0.032 (— — —), $+0.008$ (— · —), and -0.008 (— × —). Beyond the outermost dotted contour, $\Delta D(r)$ is less than $10^{-6}\,\text{e/bohr}^3$

separated from the nucleus by a node tangential to the ring. In Fig. 2, the protonated nitrogens have less density around them in the EH wave function, whereas the imine nitrogens have less density in the CNDO wave function.

We have seen that the EH method puts more charge in those parts of the molecule associated with the effects [5] of molecular formation. This feature means that the EH density distribution is more reasonable, or at least corresponds more closely to the concepts of valence than does the CNDO/2 density. A similar conclusion is expected on other molecules amenable to treatment by EH and CNDO/2 theories. On the other hand, this feature is partly due to the required neglect of the off-diagonal density matrix elements in the CNDO/2 formulation. It is therefore expected that the deorthogonalization [8] of the CNDO/2 LCAO–MO coefficients, thereby allowing the inclusion of all orbital products, but at the same time utilizing self-consistent molecular orbitals, may give the most reasonable charge distribution of adenine.

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Dr. D. B. Boyd
The Lilly Research Laboratories
Eli Lilly and Company
Indianapolis, Indiana 46206, USA