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A simple measure of electron localization in atomic and molecular systems

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We introduce in this work a new approach to the identification of localized electronic groups in atomic and molecular systems. Our approach is based on local behavior of the Hartree-Fock parallel-spin pair probability and is completely independent of unitary orbital transformations. We derive a simple "electron localization function" (ELF) which easily reveals atomic shell structure and core, binding, and lone electron pairs in simple molecular systems as well.

I. INTRODUCTION

Of major importance in descriptive chemistry is the concept of localized groups of electrons, encompassing such notions as atomic shells, binding and lone electron pairs, pi-electron subsystems, etc. However, despite its undeniable utility, the concept of spatially localized electrons is theoretically and mathematically elusive. The canonical orbitals of Hartree-Fock theory are *delocalized* throughout the space of a molecule or crystal, and do not suggest localized electronic groups. On the other hand, it is well known that equivalent *localized* orbitals can be generated by unitary transformations of canonical orbitals, leaving Hartree-Fock total energy unchanged, according to various prescriptions. Unfortunately, such transformations are not unique and may even result in qualitatively different views of certain bonding situations. The dichotomy between " σ - π " and "bent" multiple bonds is a classic example. Ultimately, neither of such equivalent views can be given preference at the Hartree-Fock theoretical level. Hartree-Fock theory is defined entirely by its one-body *density matrix* (see Sec. II), which is completely invariant with respect to unitary orbital transformations. Theoretically meaningful definitions of electron localization must therefore be sought in the density matrix itself (or related functions) and not in the orbitals.

Alternative, orbital-independent descriptions of electron localization have received some attention in recent literature. Bader and co-workers¹ have noted that the total electronic density alone reveals atomic shell structure, electron pairs, etc., through the topography of its Laplacian $\nabla^2\rho$. This approach fully invokes the spirit of the so-called "density-functional" theory of multielectron systems, which rigorously asserts that the total electronic density is the fundamental independent variable of many-electron theory.² The Laplacian of the density does not, however, completely reveal the expected shell structure of heavy atomic systems.³ Also, its wide variability, ranging from negatively infinite value at atomic nuclei to unbounded positive value elsewhere, is somewhat inconvenient for purposes of graphical representation.

Moreover, Bader and co-workers⁴ have emphasized that electron localization is fundamentally related to parallel-spin pair probability and its associated *Fermi hole* function, through which the effects of Pauli exchange repulsion are directly reflected. In the present work, a new orbital-independent measure of electron localization based on consi-

deration of the Hartree-Fock pair probability is developed. This work is a natural extension of previous investigations by one of the authors (A.D.B.) of the short-range behavior of the Fermi hole function in inhomogeneous systems⁵ and is similar in some respects to the work of Luken⁶ on localized orbitals and Fermi hole mobility.

In Sec. II of this paper, we introduce a new "electron localization function" (ELF) which depends on total electronic density, its gradient, and also the *kinetic energy* density. Application of this ELF to the noble gas atoms Ne through Rn in Sec. III easily and completely reveals their expected shell structure. In Sec. IV, ELF is applied to some classic freshman chemistry problems to illustrate its usefulness in identifying core, binding, and lone-pair regions in molecular systems, and, finally, concluding remarks are offered in Sec. V.

II. BASIC THEORY

We assume in this section that the reader is familiar with the *density matrix* formulation of Hartree-Fock theory. An excellent account is provided in Ref. 7, though numerous other sources may also be consulted.

The Hartree-Fock probability of finding two particles of the same spin σ simultaneously at positions 1 and 2 in a multielectron system is given by the following expression:

$$P_2^{\sigma\sigma}(1,2) = \rho_\sigma(1)\rho_\sigma(2) - |\rho_1^\sigma(1,2)|^2, \quad (1)$$

where $P_2^{\sigma\sigma}(1,2)$ is the same-spin pair probability and $\rho_1^\sigma(1,2)$ is the σ -spin one-body *density matrix* of the Hartree-Fock determinant:

$$\rho_1^\sigma(1,2) = \sum_i^\sigma \psi_i^*(1)\psi_i(2) \quad (2)$$

with summation restricted to orbitals of σ spin only. If a σ -spin electron is located *with certainty* at position 1, hereafter called the "reference" point, then the *conditional* probability of finding a second σ -spin electron at position 2 is obtained by dividing the above pair probability by the total σ -spin density at 1:

$$\begin{aligned} P_{\text{cond}}^{\sigma\sigma}(1,2) &= P_2^{\sigma\sigma}(1,2)/\rho_\sigma(1) \\ &= \rho_\sigma(2) - \frac{|\rho_1^\sigma(1,2)|^2}{\rho_\sigma(1)}. \end{aligned} \quad (3)$$

Both the total Hartree-Fock density and the Hartree-Fock

density matrix are invariant with respect to unitary transformations of the occupied orbitals, and thus the pair probabilities of Eqs. (1) and (3) are invariant as well.

Well-known properties of the one-body density matrix regarding its value when coordinate 2 equals the reference point:

$$\rho_1^\sigma(1,1) = \rho_\sigma(1) \quad (4)$$

and the integrated value of its squared magnitude:

$$\int |\rho_1^\sigma(1,2)|^2 d2 = \rho_\sigma(1) \quad (5)$$

ensure, respectively, that the conditional probability of finding a second σ -spin electron at the reference point vanishes,

$$P_{\text{cond}}^{\sigma\sigma}(1,1) = 0 \quad (6)$$

and that the total conditional probability is given by

$$\int P_{\text{cond}}^{\sigma\sigma}(1,2) d2 = N_\sigma - 1, \quad (7)$$

where N_σ is the total number of σ -spin electrons in the system. Equation (6) is, of course, a reflection of the Pauli exclusion principle and Eq. (7) is a logical consequence of the statistical interpretation of the conditional pair probability (i.e., if a σ -spin electron is definitely at point 1, then the total probability of finding *another* σ -spin electron elsewhere in the system is $N_\sigma - 1$).

Though Hartree-Fock exchange correlation is described fully by Eqs. (1) and (3), useful information is also contained in its *local* or *short-range* behavior for position 2 approaching the reference point. Indeed, local information has been utilized by one of the present authors (A.D.B.) to generate models of exchange-correlation hole functions in inhomogeneous electronic systems.^{5,8} It can be shown^{5,9} that the leading term of the *Taylor expansion* of the *spherically averaged* conditional pair probability is given by

$$P_{\text{cond}}^{\sigma\sigma}(\mathbf{r}, s) = \frac{1}{3} \left[\tau_\sigma - \frac{1}{4} \frac{(\nabla \rho_\sigma)^2}{\rho_\sigma} \right] s^2 + \dots, \quad (8)$$

where the arguments (\mathbf{r}, s) denote the spherical average on a shell of radius s about the reference point \mathbf{r} , and τ_σ is the positive-definite *kinetic energy density* defined by

$$\tau_\sigma = \sum_i |\nabla \psi_i|^2 \quad (9)$$

and where the contents of the squared brackets in Eq. (8) are evaluated at the reference point. Higher-order terms can be generated also, but are rather complicated and will not be considered here.

The Taylor expansion [Eq. (8)] of the spherically averaged pair probability succinctly conveys electron localization information. The smaller the probability of finding a second like-spin electron near the reference point, the more highly localized is the reference electron. Hence, electron localization is related to the smallness of the expression

$$D_\sigma = \tau_\sigma - \frac{1}{4} \frac{(\nabla \rho_\sigma)^2}{\rho_\sigma}, \quad (10)$$

which, by virtue of the fact that Eq. (8) is a probability

density, is necessarily nonnegative (see Ref. 10 for proof). Moreover, it is easily verified that D_σ vanishes in the special case of one-electron systems and hence also vanishes in *multielectron* systems in regions dominated by a single, localized, σ -spin orbital. This latter observation reinforces our interpretation of D_σ as a measure of electron localization.

Unfortunately, the relationship between electron localization and Eq. (10) is an "inverse" relationship in the sense that high localizability is implied by *small* D_σ . Also, D_σ is not bounded from above. Therefore, we propose the following alternative "electron localization function" (ELF) having somewhat more desirable features:

$$\text{ELF} = (1 + \chi_\sigma^2)^{-1} \quad (11)$$

where

$$\chi_\sigma = D_\sigma / D_\sigma^0 \quad (12)$$

and

$$D_\sigma^0 = \frac{2}{3} (6\pi^2)^{2/3} \rho_\sigma^{5/3}, \quad (13)$$

where D_σ^0 corresponds to a *uniform electron gas* with spin-density equal to the local value of $\rho_\sigma(\mathbf{r})$. The ratio χ_σ is thus a *dimensionless* localization index calibrated with respect to the uniform-density electron gas as reference. The more-or-less arbitrary transformation of Eq. (11) is designed to restrict ELF's possible values to the range

$$0 \leq \text{ELF} \leq 1 \quad (14)$$

with the upper limit $\text{ELF} = 1$ corresponding to perfect localization and the value $\text{ELF} = 1/2$ corresponding to electron-gas-like pair probability. We shall demonstrate in Secs. III and IV that this convenient orbital-independent (i.e., with respect to unitary transformations) localization function nicely reveals the location of atomic shells, and core, binding, and lone electron pairs in atomic and molecular systems.

III. ATOMIC SHELL STRUCTURE

As a first application of our proposed ELF, we analyze the shell structure of the noble gas atoms Ne through Rn employing the Hartree-Fock orbitals of Clementi and Roetti,¹¹ and McLean and McLean.¹² The problem of discerning shell structure in atomic systems has been discussed by many authors (see, e.g., Refs. 3 and 13–15 for recent work) and, at least for heavy atoms, is hardly straightforward. Analysis of the radial density distribution $4\pi r^2 \rho(r)$, a well-known indicator of shell structure in light atoms, is unreliable for the valence shells of heavier atoms, failing to show more than five shells in even the heaviest elements.¹⁴ The Laplacian of the density $\nabla^2 \rho$ has also been proposed as an indicator of shell structure,¹ but similarly fails to reveal more than five atomic shells.³ Work by Sagar *et al.*¹⁵ on the one-electron potential of Hunter¹⁶ successfully extracts up to seven shells in heavy atoms, but still fails to reveal expected shell structure in many cases (e.g., the N shell, corresponding to principal quantum number $n = 4$, is not firmly established until atomic number $Z = 32$).

The present ELF reveals atomic shell structure in a remarkably clear and simple manner, as depicted in Figs. 1–5

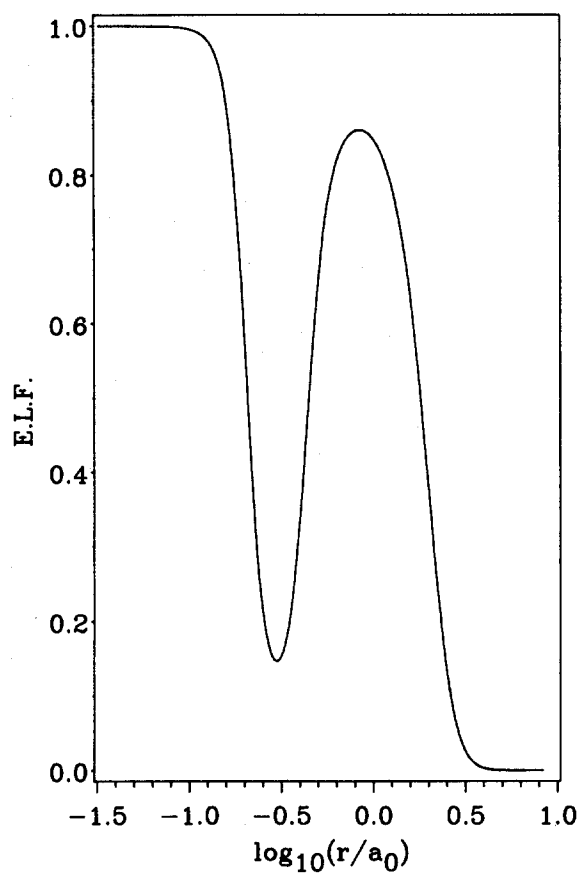


FIG. 1. Shell structure of Ne.

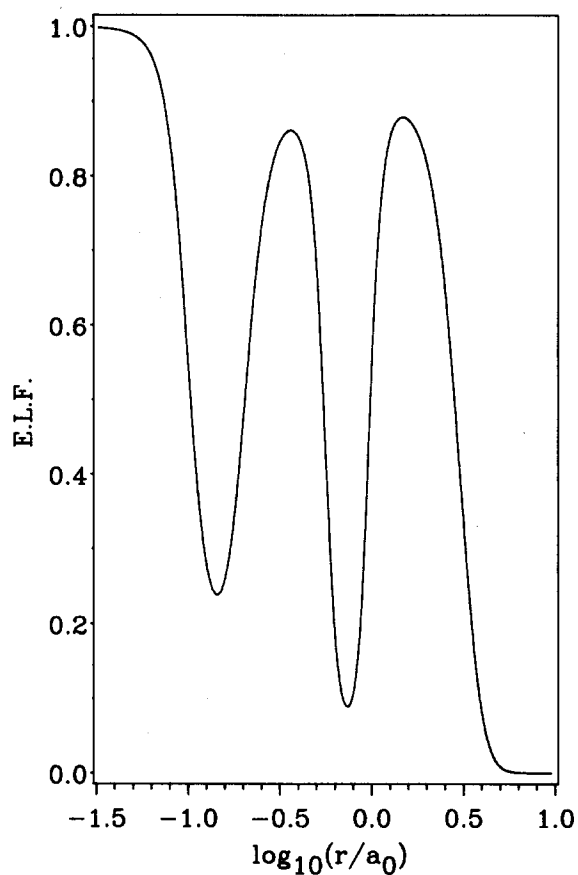


FIG. 2. Shell structure of Ar.

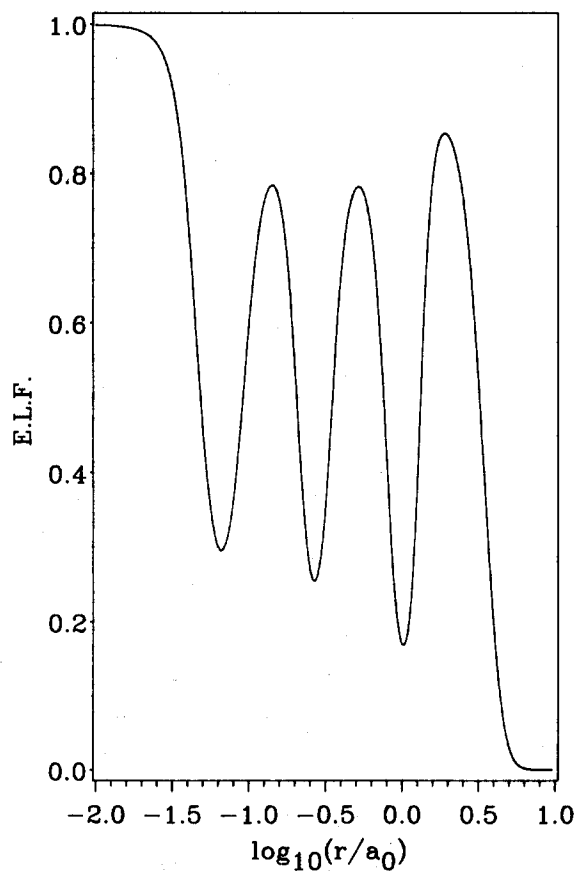


FIG. 3. Shell structure of Kr.

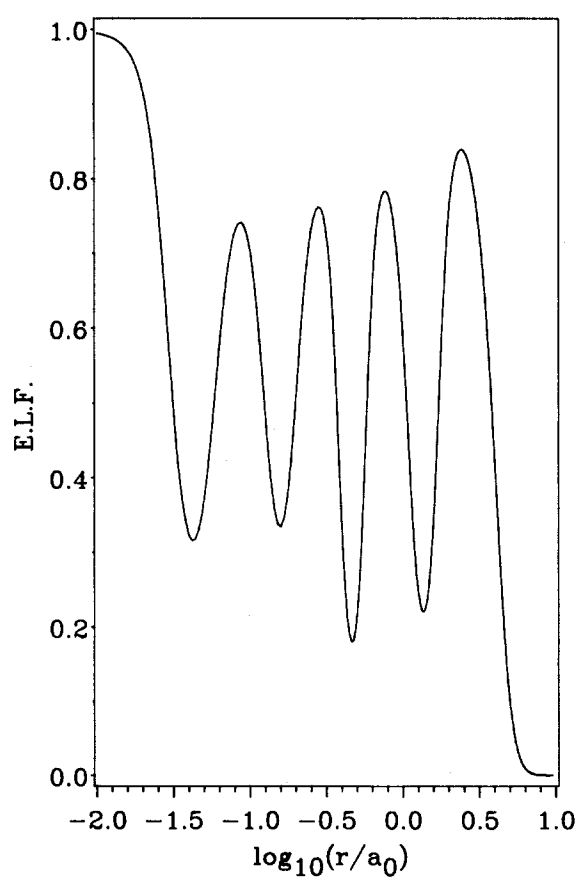


FIG. 4. Shell structure of Xe.

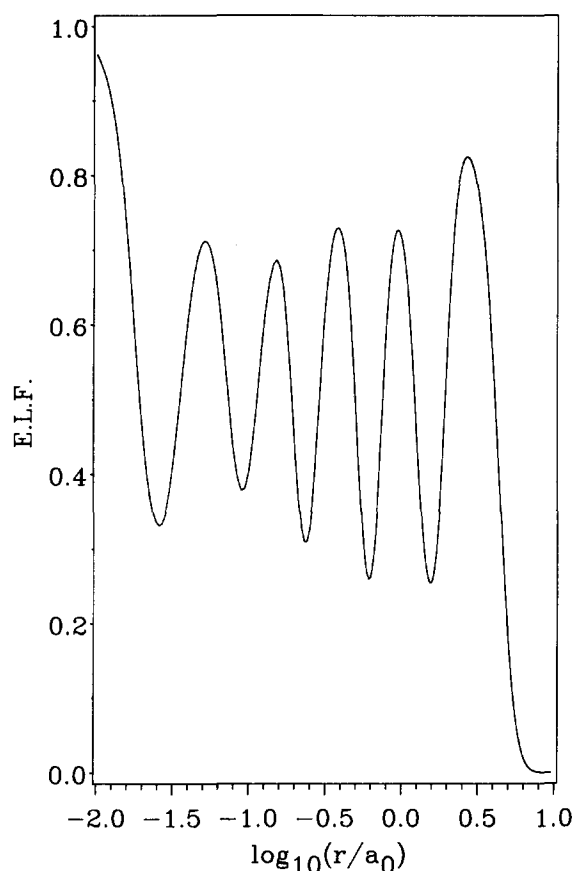


FIG. 5. Shell structure of Rn.

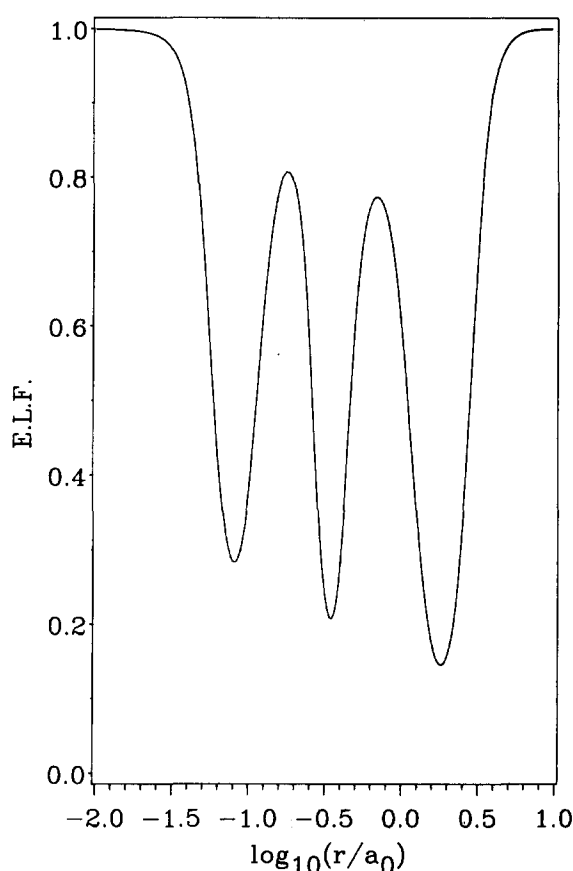


FIG. 6. Shell structure of Zn.

for the noble gas atoms Ne through Rn. Our plots are conveniently contained between the limits 0 and 1, and display distinct maxima and minima corresponding to regions within shells and between shells, respectively. For example, Fig. 5 clearly exhibits five intershell minima for radon, leaving no doubt that Rn has six electronic shells as expected on the basis of its highest occupied principal quantum number. Also, as noted above, the $n = 4$ shell is difficult to distinguish in first-series transition-metal systems on the basis of previous methods. The present ELF, on the other hand, clearly reveals the $4s$ shell of Zn, e.g., in Fig. 6. Furthermore, cursory inspection of the positions of the intershell minima in Figs. 1–6 indicates good agreement with intershell minima of Ref. 13.

Also, it is important to remark on an interesting feature of Figs. 1–6 regarding asymptotic (i.e., $r \rightarrow \infty$) behavior. Function D_σ of Eq. (10) *vanishes asymptotically* in finite systems,¹⁰ as it does in the case of perfect localizability, and hence ELF should presumably assume unit value asymptotically. On the contrary, all plots in the present paper (except Fig. 6) display vanishing ELF in asymptotic regions. This is a consequence of the $\rho_\sigma^{5/3}$ electron gas reference D_σ^0 in the denominator of Eq. (12) vanishing much more strongly at infinite distance than the actual *atomic* or *molecular* D_σ , which vanishes exponentially (except for $l = 0$ outer shells, in which case D_σ vanishes *identically*, and hence ELF approaches unity, as happens with Zn in Fig. 6). We consider

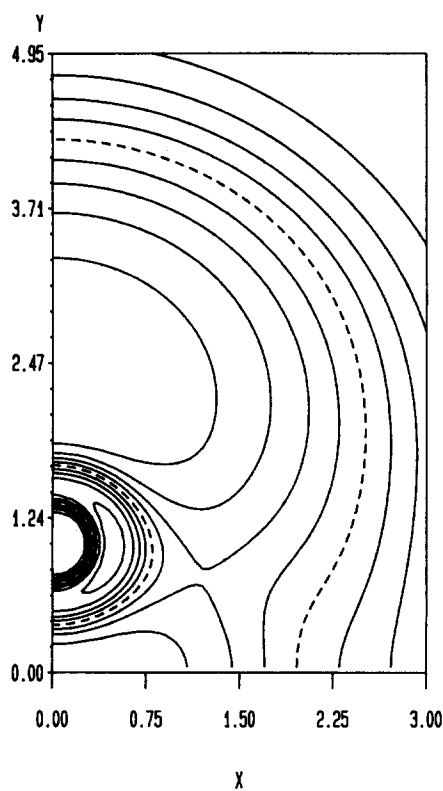
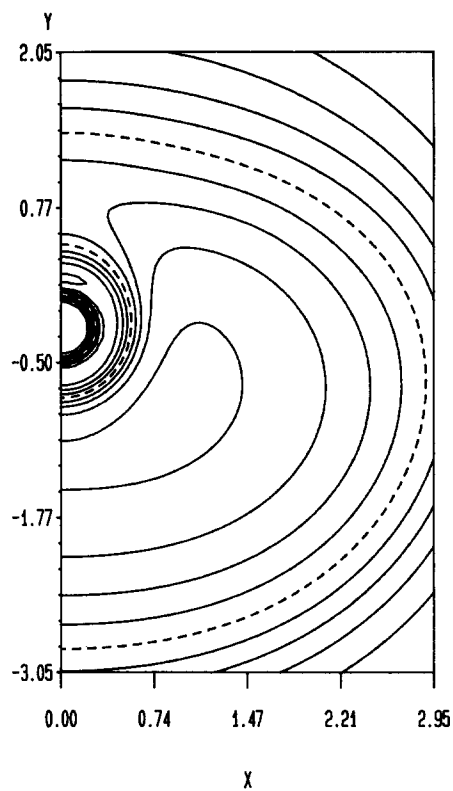
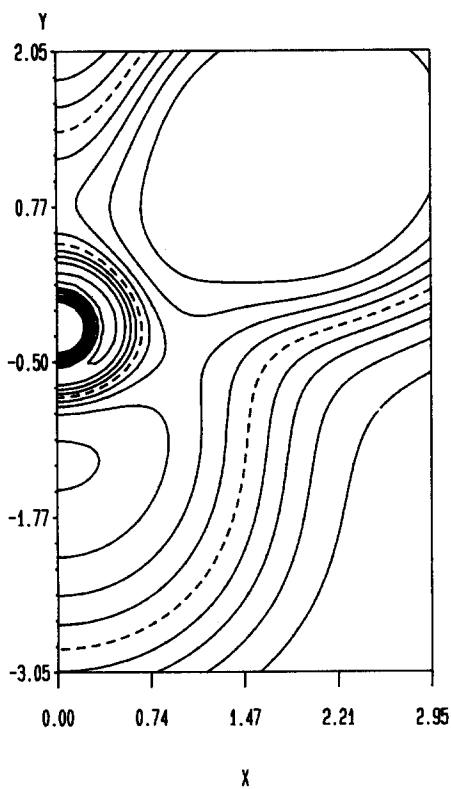
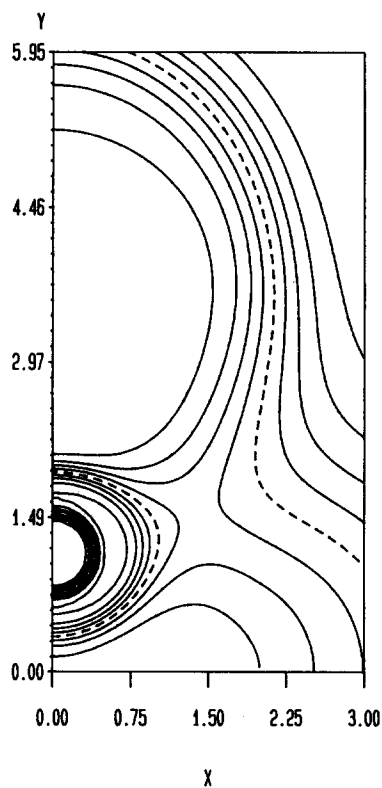
this a fortunate artifact of our definition, since an asymptotic ELF of unity is perhaps disconcerting when the total electronic density itself approaches zero.

Having thus demonstrated the ability of the present localization function to define atomic shells, we proceed with some simple applications to molecules in the following section.

IV. ELECTRON LOCALIZATION IN MOLECULES

We examine the relatively simple molecules N_2 , H_2O , $HCCH$, H_2CCH_2 , and H_3CCH_3 , for which wave functions were generated at experimental geometries¹⁷ using the GAUSSIAN 86 program system¹⁸ at the 6-311G** Hartree-Fock level.¹⁹ Values of ELF were obtained using routine PSI and a specially adapted version of routine POINT from the AIMPAC series of programs.²⁰ ELF contours for each of these species are plotted in Figs. 7–12.

The origin (0,0) of Fig. 7 for N_2 is located at the bond midpoint and the Y axis of the figure is the principal axis of the molecule. Dashed contours correspond to $ELF = 0.5$ (electron-gas-like pair probability) with each solid contour corresponding to an increment of ± 0.1 . Thus, proceeding from the bond midpoint at (0,0) toward the nitrogen nucleus, ELF initially declines in value until the core-valence intershell minimum is encountered and then increases dramatically on approach to the nucleus. Thereafter, ELF

FIG. 7. ELF contours for the quarter-plane of N_2 .FIG. 8. ELF contours for the half-plane of H_2O bisecting HOH bond angle.FIG. 9. ELF contours for the half-plane of H_2O containing HOH bond angle.FIG. 10. ELF contours for the quarter-plane of $HCCH$.

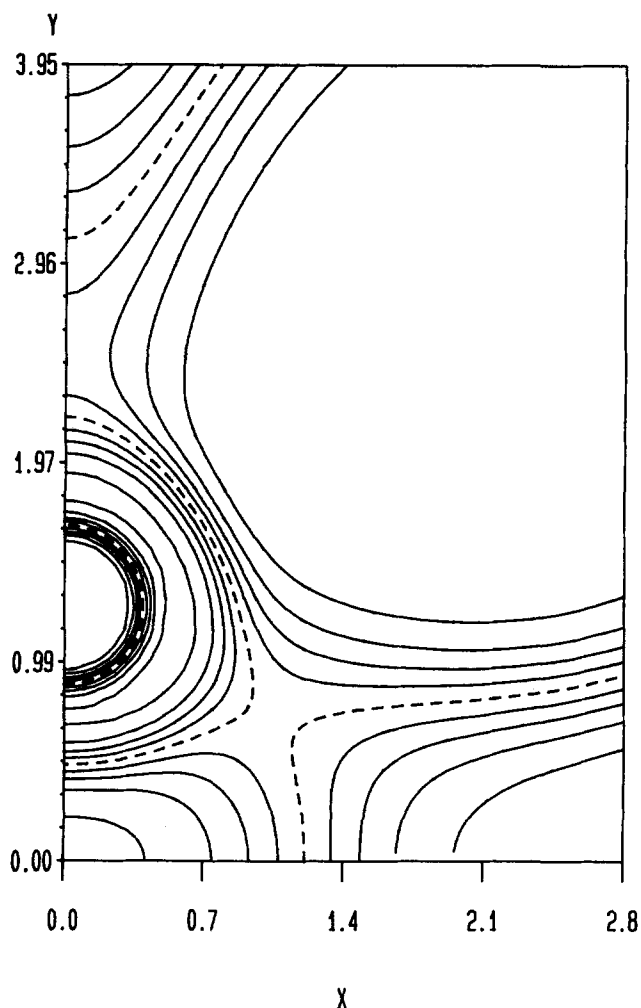


FIG. 11. ELF contours for the quarter-plane of H_2CCH_2 containing CH bond.

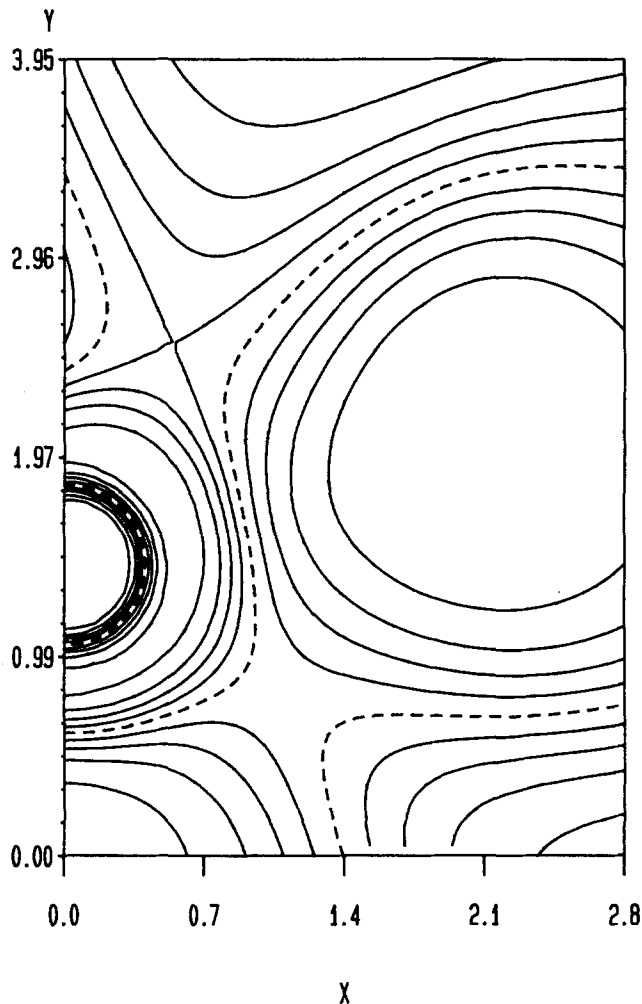


FIG. 12. ELF contours for a quarter-plane of H_3CCH_3 containing CH bond.

drops again into the core–valence intershell minimum and then quite distinctly increases its value in the area normally associated with a lone electron pair. All the expected features of the electronic structure of N_2 are readily apparent in our figure: the obvious “valley” separating core and valence regions, the easily distinguished triple bond region, and the notably large lone pair region.

Contours of ELF for the molecule H_2O are depicted in Figs. 8 and 9. Consider, first of all, Fig. 8, representing the perpendicular half-plane bisecting the HOH bond angle with the Y axis corresponding to the C_2 axis of the molecule. We observe again an obvious core–valence intershell valley, but of greater interest is the broad lone pair maximum in the lower part of the figure. This lone electron pair and its partner in the opposite half-plane are not dramatically distinct, but are nevertheless clearly represented. Figure 9, for the half-plane containing the HOH bond angle, displays a remnant of the lone pair region just below the oxygen nucleus, but now clearly reveals one of the binding O–H electron pairs as well.

Contour plots for the series HCCH , H_2CCH_2 , and H_3CCH_3 are presented in Figs. 10–12, with origin (0,0) in

each case at the C–C bond midpoint, and with each figure containing an H atom (note the difference in scale between Fig. 10, 11 and 12). The core–valence minimum is, as usual, clearly depicted in all figures, as are the expected C–H bonding pairs and the C–C bonding regions, with the triply bonded C–C region in HCCH notably large. Further such molecular applications of ELF will be reported in subsequent communications.

V. CONCLUSIONS

Essentially, we have here introduced a novel and simple method for the mapping of electron pair probability (Hartree–Fock parallel spin) in multielectron systems. Pair probability is properly, of course, a six-dimensional function, so we focus on its spherically averaged local behavior as a function of reference point. Nevertheless, we find that local pair probability, as conveyed by our proposed electron localization function (ELF), generates interesting pictures of atomic shell, core, binding, and lone-pair regions in atomic and molecular systems. Such information is not contained in the

total electronic density itself, though its Laplacian $\nabla^2\rho$ is very useful in this regard. Our ELF does not require the calculation of localized molecular orbitals and, indeed, is invariant with respect to unitary orbital transformations.

ELF provides a faithful visualization of valence shell electron pair repulsion theory (VSEPR)²¹ in action. After all, the source of "electron pair repulsion" in VSEPR theory is predominantly *exchange* (i.e., not dynamical) correlation, which through its origins in the Hartree-Fock parallel-spin pair probability, is precisely what ELF represents. We feel that the present electron localization function is therefore a valuable addition to the quantum chemical arsenal of descriptive and interpretative theoretical tools.

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