Theoret. Chim. Acta (Berl.) 38, 159—163 (1975)

Relationes

A Misconception Concerning the Electronic Density Distribution of an Atom

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Received July 31, 1974/October 29, 1974

It is shown that the electronic charge density of a ground-state atom decreases monotonically as a function of radial distance from the nucleus, contrary to the widespread belief that the shell structure is reflected by relative maxima in the density. Any proposed relationship between chemical bonding and the maxima in the radial density functions of atoms should therefore be regarded with caution. It is proven that the electrostatic potential of an atom must be monotonically decreasing. The changes in charge distribution upon molecule formation are also discussed.

Key words: Electron density distribution in atoms

There appears to be a fairly widespread belief [1] that the electronic density of a ground-state atom, when plotted against the radial distance from the nucleus, will show one or more relative maxima for $r > 0$. For example, the Thomas-Fermi theory has recently been criticized on the grounds that it leads to a monotonically-decreasing electronic density function for an atom in its ground state [2]. It is the purpose of this paper to point out that the electronic density of a ground-state atom does in fact decrease monotonically for all values of r.

Figures 1 and 2 show the behavior of the electronic densities of six different atoms, ranging in size from $Z = 4$ to $Z = 36$. All of the atoms are in their ground states, which include ^1S, ^3P, and ^5D states. The electronic densities were computed from extended-basis-set self-consistent-field (near-Hartree-Fock) wave functions [3], so that they should be of first-order accuracy [4].

The figures show clearly the monotonically-decreasing nature of the electronic density[1]. While it has some interesting bumps and wiggles, which are being further investigated, at no point away from the nucleus is there a relative maximum.

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[1] This feature can also be seen in earlier atomic density plots; see, for example, [5]. However, it seems to have been largely overlooked, and its significance not appreciated.

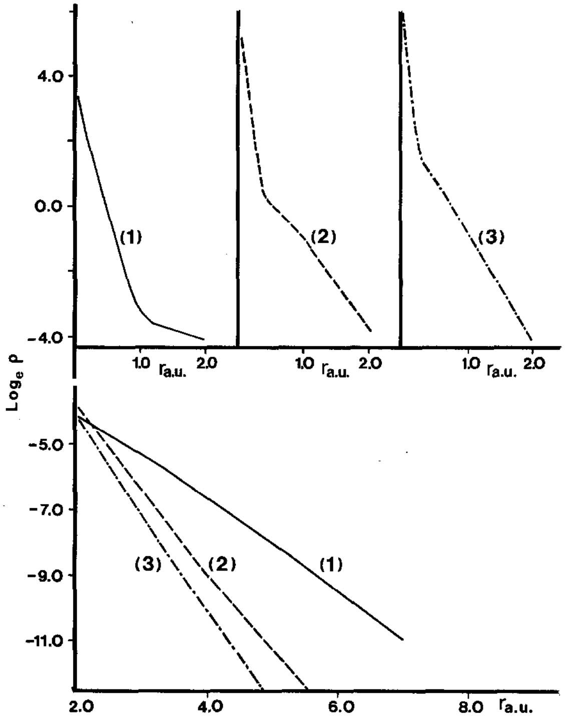

Fig. 1. Spherically-averaged electronic density plotted as a function of radial distance from the nucleus for: (1) beryllium; (2) oxygen; (3) neon. Each atom is presented separately out to a distance of 2.0 atomic units (top portion of figure). Logarithmic plots are given in order to permit the complete range of density values to be included

We are not aware of any general proof that the electronic density of a ground-state atom decreases monotonically, but our investigations definitely indicate this to be the case. It is not necessarily true for excited states, however, as can be seen from the simple example of a hydrogen atom with its electron in the 2*s* orbital (which has a node at $r = 2.0$ a.u.).

The steadily-decreasing nature of $\varrho(r)$ makes it reasonable to anticipate that the electrostatic potential due to the nucleus and electrons,

$$V(r) = Z/r - \int [\varrho(r')dr'/|r'-r|],$$

may behave in some similar fashion. Indeed, it can easily be demonstrated that $V(r)$ is monotonic. Since $V(r)$ approaches its maximum value as $r \to 0$ and diminishes to zero as $r \to \infty$, then if it were not monotonically decreasing, there would have to be at least one relative maximum and one relative minimum. At a relative maximum, $dV/dr = 0$ and $d^2V/dr^2 < 0$; at a relative minimum, $dV/dr = 0$ and $d^2V/dr^2 > 0$. But by Poisson's equation for a spherically-symmetric system,

$$d^2V/dr^2 + (2/r)dV/dr = 4\pi\varrho,$$

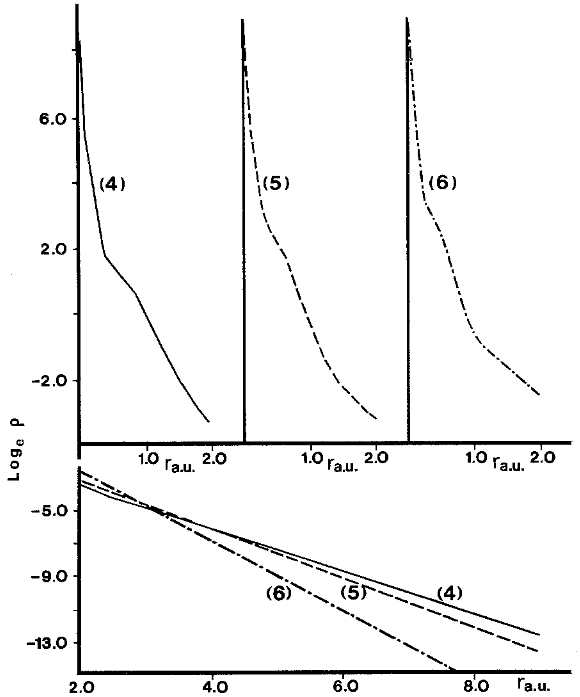

Fig. 2. Spherically-averaged electronic density plotted as a function of radial distance from the nucleus for: (4) iron; (5) germanium; (6) krypton (See caption for Fig. 1)

the first set of conditions is incompatible with the fact that ϱ must always be positive. Therefore, $V(r)$ must be monotonically decreasing[2]. This is confirmed by Fig. 3. This further justifies the various pseudo-potential and related approaches which approximate the effects of inner electrons by means of some effective potential, which is generally of a decreasing character [6].

The density diagrams often seen in textbooks which show one or more maxima are representations of the *radial* electronic density, $4\pi r^2\varrho(r)$, rather than the electronic density, $\varrho(r)$. $4\pi r^2\varrho(r)dr$ is equal to the average quantity of electronic charge in a spherical *shell* of thickness dr, at a distance r from the nucleus, whereas $\varrho(r)dr$ is the average electronic charge in a volume element $d\tau$ at the distance r[3].

The monotonic decrease of $\varrho(r)$ clearly shows that the maxima observed for the function $4\pi r^2\varrho(r)$ are, from a mathematical standpoint, the consequence of the increasing size of the spherical shells. They do *not* reflect regions of charge buildup. It follows that any attempt to establish a direct relationship between these maxima (specifically the outermost one) and chemical bonding [7, 8] must be regarded with caution. For example, contrary to a previous suggestion [7], there is no general relationship between the internuclear distance corresponding

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[2] This proof assumes that $\varrho \neq 0$ for $0 \leqq r < \infty$.

[3] It is a deficiency of the Thomas-Fermi theory that it does not predict maxima, for $r > 0$, in the function $4\pi r^2\varrho(r)$.

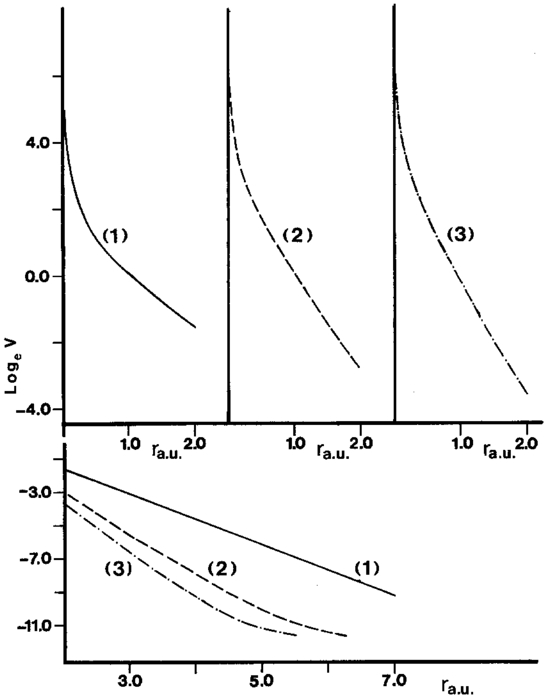

Fig. 3. Logarithmic plot of total potential as a function of radial distance from the nucleus for: (1) beryllium; (2) oxygen; (3) neon

to the maximum overlap between two atomic orbitals and the sum of the distances to the maxima of the radial electronic density functions of these orbitals. This can be seen, for example, from the plots showing overlap as a function of internuclear distance which were computed by Mulliken for various combinations of Slater-type orbitals [9]. $2s_A - 2s_B$ and $2p\pi_A - 2p\pi_B$ overlaps (as well as $1s_A - 1s_B$) do not show a maximum for *any* internuclear distance except zero. The $2p\sigma_A - 2p\sigma_B$ overlap does have a maximum; for equal orbital exponents, $\zeta_A = \zeta_B = \zeta$, it comes at a distance of about $4.55/\zeta$ atomic units. The sum of the distances to the maxima of the radial electronic density functions, on the other hand, is $4.0/\zeta$, a difference of 12%.

Finally, it is interesting to note the monotonic aspects of the electronic density distributions of molecules. Considering first diatomic molecules, many studies have shown that there is invariably a monotonic decrease in density in the region about each nucleus, culminating in a saddle-point somewhere along the internuclear axis [10]. Relative maxima are rarely found elsewhere than at the positions of the nuclei[4], not even in the regions occupied by "lone pairs". For polyatomic molecules, the situation is basically the same [12]. All this reflects the fact that the change in electronic density distribution which accompanies the formation of a covalent molecule from its constituent atoms is rather small. Density difference

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[4] The intriguing case of Li_2, which has a small relative maximum at the midpoint of the bond, has been discussed in detail in [11].

diagrams show that the change in density at any given point in space is typically 10% or less of the original value.

Acknowledgements. We are grateful to Professor Robert G. Parr for his encouragement and support of this work. It was aided by a research grant to The Johns Hopkins University from the National Institutes of Health.

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