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Through nonlocal density functional calculations (B/LYP/6 -31G**), we show that the minimum of the molecular electrostatic potential along an internuclear axis provides a more realistic boundary point between two bonded atoms than does the electronic density minimum. We also suggest that the two bonded atoms contribute approximately equally to the magnitude of the minimum potential along the axis.

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Molecular Electrostatic Potentials as Indictors of Covalent Radii

by

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The electrostatic potential $V^{at}(\mathbf{r})$ in the space around an atom with nuclear charge Z and electronic density $\rho^{at}(\mathbf{r})$ is given by eq. (1), which invokes the spherical symmetry of the charge distribution.[1]

$$V^{at}(\mathbf{r}) = V^{at}(r) = \frac{Z}{r} - \int \frac{\rho^{at}(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \qquad (1)$$

For neutral atoms, $V^{at}(r)$ decreases monotonically with radial distance from the nucleus.[2] Figure 1 shows that $\ln V^{at}(r)$ varies nearly linearly with radial distance in the valence region, indicating that the relationship is essentially exponential, $V^{at}(r) = A\exp(-Br)$. In Figure 1 are given $\ln V^{at}(r)$ equations for nine atoms, obtained by fitting the electrostatic potentials computed from Hartree-Fock atomic wave functions.[3] These equations, all of which have correlation coefficients better than 0.997, cover the ranges $r_o \leq r \leq 3$ bohr, where r_o was taken to be the radius of the inner boundary of the valence shell, defined as the radial distance to the outermost inflection point of the average local ionization energy of the atom.[4] (Other criteria could also be used for defining this boundary,[5-7] without significantly affecting our conclusions.)

The electrostatic potential of a molecule with electronic density $\rho^{mol}(\mathbf{r})$ is given by eq. (2):

$$V^{mol}(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho^{mol}(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \qquad (2)$$

Z_A is the charge on nucleus A, located at $\mathbf{R}_A$. Pathak and Gadre have shown that a molecular electrostatic potential has no local maxima.[8] (At nuclear sites, it is of course undefined.) Along the axis between two bonded atoms, therefore, $V^{mol}(\mathbf{r})$ must decrease monotonically with distance from each nucleus and reach an axial minimum at some point $\mathbf{r}_m$.[9] Since $(\partial V^{mol}/\partial r_{axial})_{\mathbf{r}_m} = 0$, an infinitesimal charge δq placed at $\mathbf{r}_m$ will feel no electrostatic force from either direction along the internuclear axis. We have accordingly explored the possibility that $\mathbf{r}_m$ may be a meaningful axial boundary point between the two bonded atoms.

We have computed optimized geometries, electronic densities and electrostatic potentials for the 19 molecules listed in Table I. The calculations were carried out using a non-local density functional procedure (Gaussian 94,[10] Becke exchange[11] and Lee, Yang and Parr correlation functionals,[12] 6-31G** basis set). For the bonds indicated, we found the distances from each nucleus to the minima of both $V_{mol}(\mathbf{r})$ and (following Bader *et al*[13]) $\rho^{mol}(\mathbf{r})$ along the internuclear axis. As a test to determine whether either of these points is an effective boundary indicator, we compare these distances to literature values of the covalent radii of the respective atoms.

Overall, the distances to the minima of $V_{mol}(\mathbf{r})$ are in reasonable agreement with the covalent radii, especially in view of the fact that the latter do not refer to any specific molecule but

rather were obtained from experimental structural studies of a number of compounds.[14] The greatest deviations occur for some of the hydrogens. On the other hand, the distances to the minima of $\rho^{mol}(\mathbf{r})$ usually differ significantly more from the covalent radii and show some major discrepancies, more than 0.30 Å in ten instances. The relative radii given by the density minima are often not what would be anticipated; particularly striking examples are PH_3 and SiH_4, in which the hydrogens are larger than the central atoms. The electron density wells also tend to be wider and flatter than those of the electrostatic potential. Table II summarizes the data in Table I, giving for each atom the averages of the covalent radii obtained from the potential minima and the density minima. The former are closer to the literature values, often considerably so, for every atom.

These results indicate that the location of the minimum electrostatic potential along the internuclear axis does define a meaningful boundary between two bonded atoms. The less realistic covalent radii obtained from the minimum electronic density are consistent with the unexpectedly large magnitudes of the atomic charges found by using this point on the internuclear axis as the basis for partitioning the electronic charge.[13,15] (For a relevant critical analysis, see Perrin.[16])

If $V^{mol}(\mathbf{r})$ at its minimum on the internuclear axis, i.e. $V^{mol}(\mathbf{r}_m)$, can be regarded as reflecting largely the electrostatic potentials of the two bonded atoms A and B, then within this approximation, the point $\mathbf{r}_m$ corresponds to the intersection of $V^A(\mathbf{r})$ and $V^B(\mathbf{r})$, and their contributions to $V^{mol}(\mathbf{r}_m)$ should be equal. (This does not preclude other contributions to $V^{mol}(\mathbf{r}_m)$.) One can arrive at the same conclusion by noting that several proposed definitions of electronegativity express it as an electrostatic potential or force created by an atom at a distance equal to its covalent radius.[17-19] It then follows from the principle of electronegativity equalization[20-22] that these potentials or forces should be the same for two bonded atoms at their internuclear axial boundary point.

To test the proposed condition $V^A(\mathbf{r}_m) \approx V^B(\mathbf{r}_m)$, we have found the points of intersection of all of the various pairwise combinations of the $\ln V(\mathbf{r})$ equations in Figure 1, when the respective nuclei are separated by the sum of the literature covalent radii of the atoms. The objective was to determine how well the radial distances to the points of intersection reproduce the literature covalent radii.

For those combinations in which both atoms are in the first row of the periodic table (C – F) or both are in the second row (Si - Cl), the differences between the calculated and the literature covalent radii are very small, the average being 0.013 Å. Excellent agreement is also obtained for the second row/third row pairs (Si–Br, P–Br, S–Br and Cl–Br); the average discrepancy is 0.015 Å. The deviations are larger for combinations of a first-row atom with one in the second row or with bromine; the average difference is 0.066 Å. Among these, the covalent radius of the first-row atom is invariably overestimated and that of the second-row atom or bromine is underestimated.

This may reflect the well-known discontinuities in many properties between atoms of the first and subsequent rows.[23-27] Overall, these results do provide significant support for the idea that bonded atoms contribute approximately equally to $V^{mol}(\mathbf{r}_m)$.

The main point that we have tried to make in this paper is that the electrostatic potential minimum along the internuclear axis provides a realistic boundary point between two bonded atoms, more so than does the electronic density minimum. (In this context it is relevant to recall earlier work indicating that the locations of the electrostatic potential minima of monoatomic negative ions can be identified with their ionic radii.[28]) We have also suggested that the two bonded atoms contribute approximately equally to the minimum potential along the axis. It is reasonable to suppose that these conclusions are related to the observation that the covalent radius of an atom is quite close to the radial distance at which its electrostatic potential equals its chemical potential.[29] The relationship is being investigated.

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Figure Caption:

Figure 1. Natural logarithm of calculated electrostatic potential, in kcal/mole, plotted against radial distance, in bohr, for the atoms indicated. The equations describing these plots in the valence regions of the atoms are also given. (See text for definition of valence region.)

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TABLE I. Literature values of covalent radii compared to results obtained in terms of axial minima of (a) electrostatic potential and (b) electronic density.

Molecule	Bond, A–B	Bond Length, Å			Covalent radii, Å		
		Calc.	Exp.[a]		Literature[b]	Min., V^{mol}	Min., ρ^{mol}
CH_4	C–H	1.099	1.094	C: H:	0.772 0.30	0.699 0.400	0.686 0.413
HCN	C–H	1.076	1.065	C: H:	0.772 0.30	0.683 0.393	0.703 0.373
NH_3	N–H	1.028	1.024	N: H:	0.70 0.30	0.656 0.372	0.754 0.274
H_2O	O–H	0.976	0.972	O: H:	0.66 0.30	0.623 0.353	0.774 0.202
SiH_4	Si–H	1.494	1.481	Si: H:	1.17 0.30	1.01 0.487	0.724 0.769
PH_3	P–H	1.436	1.427	P: H:	1.10 0.30	0.971 0.465	0.699 0.737
H_2S	S–H	1.359	1.336	S: H:	1.04 0.30	0.921 0.438	0.837 0.521
CH_3NH_2	C–N	1.480	1.471	C: N:	0.772 0.70	0.748 0.732	0.620 0.860
CH_3NO_2	C–N	1.520	1.489	C: N:	0.772 0.70	0.768 0.752	0.617 0.903
$(H_3C)_2O$	C–O	1.427	1.410	C: O:	0.772 0.66	0.729 0.698	0.512 0.914
C_2H_5OH	C–O	1.441	1.431	C: O:	0.772 0.66	0.738 0.703	0.523 0.918
H_3C–OCl	C–O	1.439	1.418	C: O:	0.772 0.66	0.735 0.703	0.513 0.925
CH_3F	C–F	1.398	1.383	C: F:	0.772 0.64	0.724 0.674	0.482 0.916
CH_3PH_2	C–P	1.896	1.863	C: P:	0.772 1.10	0.846 1.05	1.14 0.754
CH_3SH	C–S	1.857	1.819	C: S:	0.772 1.04	0.836 1.02	0.875 0.983
CH_2Cl_2	C–Cl	1.814	1.772	C: Cl:	0.772 0.99	0.829 0.985	0.793 1.02

(Continued)

TABLE I. Literature values of covalent radii compared to results obtained in terms of axial minima of (a) electrostatic potential and (b) electronic density (continued).

Molecule	Bond, A–B	Bond Length, Å			Covalent radii, Å		
		Calc.	Exp.[a]		Literature[b]	Min., V^{mol}	Min., ρ^{mol}
FNNF	F–N	1.428	1.385	F:	0.64	0.691	0.778
				N:	0.70	0.737	0.648
FSSF	F–S	1.698	1.635	F:	0.64	0.722	0.988
				S:	1.04	0.976	0.710
SiH_3Cl	Si–Cl	2.098	2.049	Si:	1.17	1.08	0.759
				Cl:	0.99	1.02	1.34

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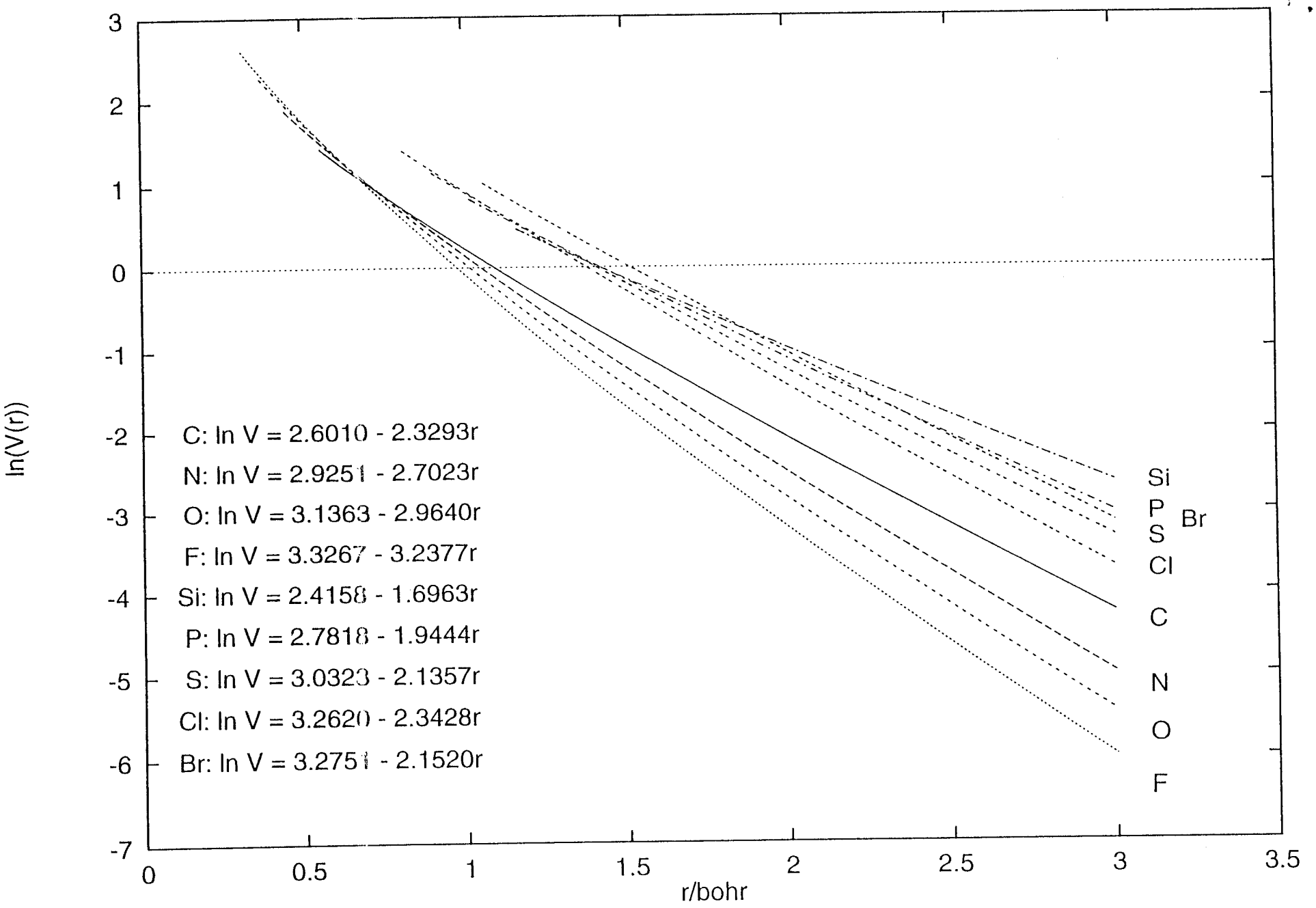
TABLE II. Literature covalent radii compared to averages of values given in Table I, correspondingly to axial minima of (a) electrostatic potential and (b) electronic density.

Atom	Number of values	Covalent radii, Å		
		Literature	Average, min., V^{mol}	Average, min., ρ^{mol}
H	7	0.30	0.415	0.470
C	11	0.772	0.758	0.679
N	4	0.70	0.719	0.791
O	4	0.66	0.682	0.883
F	3	0.64	0.696	0.894
Si	2	1.17	1.05	0.742
P	2	1.10	1.01	0.727
S	3	1.04	0.97	0.843
Cl	2	0.99	1.00	1.18


ln(V(r))
r/bohr
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
0
0.5
1
1.5
2
2.5
3
3.5
C: ln V = 2.6010 - 2.3293r
N: ln V = 2.9251 - 2.7023r
O: ln V = 3.1363 - 2.9640r
F: ln V = 3.3267 - 3.2377r
Si: ln V = 2.4158 - 1.6963r
P: ln V = 2.7818 - 1.9444r
S: ln V = 3.0323 - 2.1357r
Cl: ln V = 3.2620 - 2.3428r
Br: ln V = 3.2751 - 2.1520r
Si
P
S
Cl
Br
C
N
O
F