Supplementary Material (ESI) for Dalton Transactions

Kinetic Energy Density and Covalent Bonding – A Complementary Analysis at the Border of Bond and No Bond

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Supporting Information

Kinetic energy densities and the localized orbital locator LOL – a brief background

Early work by Ruedenberg [S1] and Kutzelnigg [S2] provides the foundation of the kinetic-energy perspective on chemical bonding. The central property on which LOL [S3] is built is the kinetic-energy density τ:

$$\tau = \frac{1}{2}\sum_i (\nabla\psi_i \cdot \nabla\psi_i^*) \qquad (1)$$

The kinetic energy density is not unique. As it is the case for the local kinetic energy,[S4] an infinite number of valid kinetic energy densities can easily be defined.[S5] Two important forms of the kinetic energy density either depend on the Laplacian of the Kohn-Sham orbitals or are defined as being positive definite, and the latter definition of kinetic-energy density is followed within the framework of LOL.

The kinetic-energy density τ presents a few drawbacks that limit its use a descriptor for chemical bonds. Kinetic-energy densities τ are usually monotonic for atoms, and the structural features of τ are less pronounced than one would wish. Regions with high charge density tend to dominate so strongly that salient features of bonding become invisible. To circumvent this problem, the kinetic-energy density τ is compared to some suitable reference value τ_0. LOL take as a reference the homogeneous spin-neutral electron gas with electron density ρ and $\tau_0 = (3/10)\cdot(3\pi^2)^{2/3}\rho^{5/3}$. LOL analysis then defines the dimensionless variable t:

$$t = \frac{\tau_0}{\tau} \qquad (2)$$

The ratio t is bounded by zero from below, but it is not bounded from above. To lower the semi-infinite range of the variable t, the Localized-Orbital Locator LOL, which is referred to as ν , is a measure of t in a mapping onto the finite range [0,1]:

$$\nu = \frac{t}{1+t} = \frac{\tau_0/\tau}{1+\tau_0/\tau} = \frac{1}{1+\tau/\tau_0} \qquad (3)$$

A value of $\nu = 1/2$ indicates that the kinetic-energy content of the corresponding region is what would be expected from a spin-neutral electron gas of that density. Values of $\nu < 1/2$ mean that the electrons have higher kinetic energy than expected from their local density. Regions with

a LOL value $\nu > 1/2$ are characterized by relatively slow electrons and might be identified as bonding regions.[S3]

Ideas borrowed from the topological analysis of electron charge density,[S6] are used to locate critical points and in particular (3,-3) attractors Γ in the gradient vector field of LOL.[S7] Each nucleus position is associated with one attractor Γ, with ν-values of 0.985 and larger. The LOL characteristics of the core region of atoms are sensitive to basis set extension, and ghost maxima might appear that do not carry meaningful chemical information. An analysis of the gradients associated with ghost maxima reveals that these points might represent erroneous inflection points within the topology of LOL. LOL also features attractors Γ between bonded atoms and in molecular regions associated with lone pairs. It is the set of these attractors that reveal information about chemical bonding.

For both definitions of the kinetic energy density, it can be shown that the kinetic energy density of a quantum system can be correctly expressed in terms of the first-order density matrix $\rho(r,r')$ and its trace, the charge density $\rho(r)$,[S8,S6] which in turn is accessible in the X-ray diffraction experiment. Since it is possible that the approximate kinetic energy density can be derived from accurate electron density X-ray diffraction data,[S9] the approximate kinetic energy density has been determined from parameters of the multipole model fitted to experimental structure factors,[S10] and LOL profiles have been obtained from experimentally determined electron densities.[S11] Thus, the localized orbital locator LOL is a member of the group of functions and quantities, for which approximate values can be derived from the experimental electron density. [S12]

Computational Details

Density functional calculations utilizing the PBE functional [S13] have been carried out with the Gaussian03 system of programs.[S14] The corresponding basis set for all atoms is of triple-ζ quality augmented by two diffuse and two polarization functions. The molecular densities used in topology analyses were obtained from single point calculations on optimized geometries with the explicit exclusion of molecular symmetry. Topological analyses of molecular electron densities employed a modified version of the program MORPHY.[S15] Spatial grids of LOL values have

been created with the program CheckDen.[S16] 3D pictures were generated using the graphical package Jmol.[S17]

Additional References

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[S15] Popelier, P. L. A. Comput Phys Commun 1996, 93, 212.
[S16] Pacios, L.F.; Fernandez, A. J. Mol. Graph. Mod 2009, 28, 102.
[S17] Jmol: an open-source Java viewer for chemical structures in 3D. http://www.jmol.org/

Phenanthrene

Route: #P PBEPBE/6-311++G(2d,2p) GFInput Freq

Atom Coordinates (x,y,z) in Angstrom

C	0.000000	2.883989	-1.531836
C	0.000000	-2.883989	-1.531836
C	0.000000	3.564558	-0.298523
C	0.000000	-3.564558	-0.298523
H	0.000000	4.654551	-0.275246
H	0.000000	-4.654551	-0.275246
C	0.000000	2.840488	0.880212
C	0.000000	-2.840488	0.880212
C	0.000000	1.424369	0.869043
C	0.000000	-1.424369	0.869043
C	0.000000	0.728294	-0.380559
C	0.000000	-0.728294	-0.380559
C	0.000000	1.498521	-1.568046
C	0.000000	-1.498521	-1.568046
H	0.000000	1.001096	-2.536939
H	0.000000	-1.001096	-2.536939
C	0.000000	-0.682169	2.095905
C	0.000000	0.682169	2.095905
H	0.000000	1.236488	3.036178
H	0.000000	-1.236488	3.036178
H	0.000000	-3.448941	-2.464483
H	0.000000	3.448941	-2.464483
H	0.000000	-3.354302	1.843312
H	0.000000	3.354302	1.843312

Energy E(RPBE-PBE) -538.98402651 a.u.

SCF Convergence: 0.2153D-08
<S**2>: 0.0000
Charge: 0.0000
Maximum Force: 0.000257

ZPE-correction : 0.188645 a.u.
Energy (298K) : -538.785569 a.u.
Enthalpy (298K) : -538.784625 a.u.
Free Energy (298K): -538.829865 a.u.

Lowest Frequency 92.7967 cm-1

He@adamantane

Route: #P PBEPBE/6-311++G(2d,2p) GFInput Freq

Atom Coordinates (x,y,z) in Angstrom

C	0.000000	1.844330	0.000000
C	0.936443	0.936443	0.936443
C	0.000000	0.000000	1.844330
C	-0.936443	-0.936443	0.936443
C	-1.844330	0.000000	0.000000
C	-0.936443	0.936443	-0.936443
C	0.000000	0.000000	-1.844330
C	0.936443	-0.936443	-0.936443
C	0.000000	-1.844330	0.000000
C	1.844330	0.000000	0.000000
H	-1.572836	1.572836	-1.572836
H	0.626244	-2.499144	0.626244
H	-0.626244	-2.499144	-0.626244
H	1.572836	-1.572836	-1.572836
H	2.499144	-0.626244	0.626244
H	2.499144	0.626244	-0.626244
H	-0.626244	-0.626244	-2.499144
H	0.626244	0.626244	-2.499144
H	-2.499144	0.626244	0.626244
H	-2.499144	-0.626244	-0.626244
H	-1.572836	-1.572836	1.572836
H	-0.626244	0.626244	2.499144
H	0.626244	-0.626244	2.499144
H	1.572836	1.572836	1.572836
H	-0.626244	2.499144	0.626244
H	0.626244	2.499144	-0.626244
He	0.000000	0.000000	0.000000

Energy E(RPBE-PBE) -392.94681590 a.u.

SCF Convergence: 0.5227D-08
<S**2>: 0.0000
Charge: 0.0000
Maximum Force: 0.000261

ZPE-correction : 0.240663 a.u.
Energy (298K) : -392.698549 a.u.
Enthalpy (298K) : -392.697604 a.u.
Free Energy (298K): -392.734925 a.u.

Lowest Frequency 326.5927 cm-1

LOL profile of phenanthrene

X,Y,Z coordinates of(3,-3) attractors Γ and corresponding ν-values. Nuclear attractors with ν > 0.985 have been omitted.

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0.000000	1.097510	-2.346640	0.923860
0.000000	-1.097510	-2.346640	0.923860
0.000000	1.127900	2.849930	0.924210
0.000000	-1.127900	2.849930	0.924210
0.000000	-3.252710	1.654090	0.924290
0.000000	3.252710	1.654090	0.924290
0.000000	4.395310	-0.281210	0.925360
0.000000	-4.395310	-0.281210	0.925360
0.000000	-3.315210	-2.243000	0.925130
0.000000	3.315210	-2.243000	0.925130
0.000000	2.191040	-1.548350	0.796340
0.000000	3.230330	-0.918660	0.803660
0.000000	-2.191040	-1.548350	0.796340
0.000000	-3.230330	-0.918660	0.803660
0.000000	3.205240	0.293180	0.796460
0.000000	-3.205240	0.293180	0.796460
0.000000	2.131040	0.875360	0.805650
0.000000	-2.131040	0.875360	0.805650
0.000000	1.072100	0.246980	0.806080
0.000000	1.055750	1.482440	0.811850
0.000000	-1.072100	0.246980	0.806080
0.000000	-1.055750	1.482440	0.811850
0.000000	1.106150	-0.977580	0.803940
0.000000	0.000000	-0.386850	0.814120
0.000000	-1.106150	-0.977580	0.803940
0.000000	0.000000	2.096340	0.791490

LOL profile of He@adamantane

X,Y,Z coordinates of(3,-3) attractors Γ and corresponding ν-values. Nuclear attractors with ν > 0.985 have been omitted.