

What Is an Atom in a Molecule?

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The derivation of the Hirshfeld atoms in molecules from information theory is clarified. The importance for chemistry of the concept of atoms in molecules (AIM) is stressed, and it is argued that this concept, while highly useful, constitutes a noumenon in the sense of Kant.

Much interest attaches to the question of how atoms are modified when they are built into molecules or crystals. For example, this is a significant matter for crystallography or for molecular dynamic modeling. How should atoms be described in molecules?

Suppose one is given a molecular electron density, $\rho(\mathbf{r}) = N\sigma(\mathbf{r})$, where N is the number of electrons and $\sigma(\mathbf{r})$ is the shape function.^{1,2} (Note that the shape function is normalized to unity.) It is a consequence of the density functional theory of electronic structure that the density determines all properties, and thus, one can address the determination of atoms in molecules (AIM) by employing the density alone. For simplicity, consider a diatomic molecule, AB. What would be the best way to divide its electron density, $\rho_{\text{mol}}(\mathbf{r})$, into “atomic” components,

$$\rho_{\text{mol}}(\mathbf{r}) = \rho_{\text{A}}(\mathbf{r}) + \rho_{\text{B}}(\mathbf{r})? \quad (1)$$

$\rho_{\text{A}}(\mathbf{r})$ and $\rho_{\text{B}}(\mathbf{r})$ might or might not be close to some “reference” densities, $\rho_{\text{A}}^{\circ}(\mathbf{r})$ and $\rho_{\text{B}}^{\circ}(\mathbf{r})$. It would be good if they were. It also would be good if the resultant atomic densities transferred well between molecules.³

An elegant and much employed solution to this problem was suggested and developed by Richard Bader and others.⁴ Examine maps of $\rho_{\text{mol}}(\mathbf{r})$, and divide all space into nonoverlapping regions separated by surfaces on which $\nabla\rho_{\text{mol}}(\mathbf{r}) \cdot \mathbf{n}$ is zero, where \mathbf{n} is a vector normal to the surfaces. The resultant atomic regions are cut off at mutual boundaries, but the resultant “atoms” have favorable properties, including a high degree of transferability and certain variational stabilities.

Another AIM definition has been proposed by F. L. Hirshfeld, called the “stockholder partitioning”.⁵ This is

$$\begin{aligned} \rho_{\text{A}}(\mathbf{r}) &= \frac{\rho_{\text{A}}^{\circ}(\mathbf{r})}{\rho_{\text{A}}^{\circ}(\mathbf{r}) + \rho_{\text{B}}^{\circ}(\mathbf{r})} \rho_{\text{mol}}(\mathbf{r}) \\ \rho_{\text{B}}(\mathbf{r}) &= \frac{\rho_{\text{B}}^{\circ}(\mathbf{r})}{\rho_{\text{A}}^{\circ}(\mathbf{r}) + \rho_{\text{B}}^{\circ}(\mathbf{r})} \rho_{\text{mol}}(\mathbf{r}) \end{aligned} \quad (2)$$

with obvious extension to polyatomics. This has been widely used and is an alternative to the Bader definition. Each Hirshfeld

atom extends over all space, and Hirshfeld atoms are highly transferable.³

Recently, Nalewajski and Parr demonstrated⁶ that Hirshfeld atoms are “best” in the Kullback–Liebler information-theoretical sense.⁷ One obtains Hirshfeld AIM by minimizing with respect to $\rho_{\text{A}}(\mathbf{r})$ and $\rho_{\text{B}}(\mathbf{r})$ the functional

$$I = \int \rho_{\text{A}}(\mathbf{r}) \ln \left(\frac{\rho_{\text{A}}(\mathbf{r})}{\rho_{\text{A}}^{\circ}(\mathbf{r})} \right) d\mathbf{r} + \int \rho_{\text{B}}(\mathbf{r}) \ln \left(\frac{\rho_{\text{B}}(\mathbf{r})}{\rho_{\text{B}}^{\circ}(\mathbf{r})} \right) d\mathbf{r} \quad (3)$$

subject to the condition that $\rho_{\text{mol}}(\mathbf{r})$ of eq 1 is fixed. The quantity I , which necessarily always is positive, is a measure of the information loss by the two reference-atom densities, $\rho_{\text{A}}^{\circ}(\mathbf{r}) = N_{\text{A}}^{\circ}\sigma_{\text{A}}^{\circ}(\mathbf{r})$ and $\rho_{\text{B}}^{\circ}(\mathbf{r}) = N_{\text{B}}^{\circ}\sigma_{\text{B}}^{\circ}(\mathbf{r})$, as they change to the AIM with densities $\rho_{\text{A}}(\mathbf{r}) = N_{\text{A}}\sigma_{\text{A}}(\mathbf{r})$ and $\rho_{\text{B}}(\mathbf{r}) = N_{\text{B}}\sigma_{\text{B}}(\mathbf{r})$. For each atom, the shape can change and the number of electrons can change, with the changes driven by the fact that the true molecular density contains effects of promotion, hybridization, charge transfer, and so forth. It is assumed that $N_{\text{A}} + N_{\text{B}} = N_{\text{A}}^{\circ} + N_{\text{B}}^{\circ} = N$. When ground-state atoms are chosen as references, the Hirshfeld AIM resemble ground-state atoms as much as possible in information content.

There is an apparent weakness in this argument, however, having to do with normalization. Should there be electron transfer between A and B (change in electron numbers), then eq 3 appears to be unsatisfactory as an information measure. The conventional Kullback–Liebler formula for the information loss in going from a distribution of $p^{\circ}(\mathbf{r})$ to a distribution of $p(\mathbf{r})$, namely, $\langle p(\mathbf{r}) \ln(p(\mathbf{r})/p^{\circ}(\mathbf{r})) \rangle$, holds only when both distributions have the same normalization.⁷ With the same normalizations ($\langle \rho_{\text{A}}(\mathbf{r}) \rangle = \langle \rho_{\text{A}}^{\circ}(\mathbf{r}) \rangle$, $\langle \rho_{\text{B}}(\mathbf{r}) \rangle = \langle \rho_{\text{B}}^{\circ}(\mathbf{r}) \rangle$), eq 3 is a clean conventional measure of information loss. The Hirshfeld result, eq 2, makes the sum of the information losses of A and B as small as possible. This then constitutes an appropriate way to design a set of AIM. However, what if electron transfer occurs? Then, while the sum of the two terms in eq 3 still is positive, one of the terms can be negative, which calls into question interpretation of it as an information loss.

First Resolution of the Difficulty

To do away with the normalization problem associated with eq 3, we rewrite eq 3 in terms of numbers of electrons and shape functions for the reference atoms and for the AIM:

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$$I = N_A \left\langle \sigma_A(\mathbf{r}) \ln \left(\frac{\sigma_A(\mathbf{r})}{\sigma_A^\circ(\mathbf{r})} \right) \right\rangle + N_B \left\langle \sigma_B(\mathbf{r}) \ln \left(\frac{\sigma_B(\mathbf{r})}{\sigma_B^\circ(\mathbf{r})} \right) \right\rangle + N_A \ln \left(\frac{N_A}{N_A^\circ} \right) + N_B \ln \left(\frac{N_B}{N_B^\circ} \right) \quad (4)$$

Then, one can show that minimization of I with respect to N_A , N_B , $\sigma_A(\mathbf{r})$, and $\sigma_B(\mathbf{r})$, subject to the normalization condition for the shape functions and eq 1, gives the Hirshfeld atoms of eq 2.

In eq 4, the first line is the sum of two positive terms, each an information per electron times a number of electrons. The second line is the positive sum of two terms, constituting the information lost (or entropy gained—the entropy of mixing) as electrons are redistributed (mixed) between A and B upon charge transfer. Minimizing eq 3 constitutes an acceptable process for determining AIM, with eq 4 available for meaningfully decomposing information loss (entropy gain) into component pieces. A and B are distinct, separate entities, each prepared for the rigors of binding.

This manner of thinking constitutes a Pauling-like way to envision AIM. An atom in a molecule is not a spherically symmetric ground-state atom. Rather, there are changes of atomic shape prerequisite for binding, and also, for heteropolar cases, changes of atomic electron number. These are the ideas of hybridization, promotion, and charge transfer, as well described in the book by McWeeny and Coulson.⁸ The resultant AIM are hypothetical states of atoms; one might compare Pauling's discussion on the unreality of the contributing structures in a resonating system.⁹

Second Resolution of the Difficulty

Following is a more direct way to validate eq 3 as a correct information-loss measure for the transformation $(A^\circ)(B^\circ) \rightarrow (A)(B)$. This invokes recognizing that we are not dealing, in either $\rho_A^\circ(\mathbf{r}) + \rho_B^\circ(\mathbf{r})$ or $\rho_A(\mathbf{r}) + \rho_B(\mathbf{r})$, with separate systems but with subsystems of a bigger single system, the molecule as a whole. In the molecule, the N_A electrons in A, still corresponding with eq 1, form a fragment of a larger system containing N_B electrons in B, with every bit of space inhabited by both A and B electrons. In the molecule, the correct probability distribution function for A is not the normalized $\rho_A(\mathbf{r})/N_A$, as employed in eq 4 above. Instead, the normalizations that should be used are

$$p_A(\mathbf{r}) + p_B(\mathbf{r}) = \frac{\rho_{\text{mol}}(\mathbf{r})}{N} \quad (5)$$

with

$$p_A(\mathbf{r}) = \frac{\rho_A(\mathbf{r})}{N} \quad (6)$$

$$p_B(\mathbf{r}) = \frac{\rho_B(\mathbf{r})}{N}$$

and corresponding definitions for the reference atoms. We then have the identity

$$I = N \left[\int p_A(\mathbf{r}) \ln \left(\frac{p_A(\mathbf{r})}{p_A^\circ(\mathbf{r})} \right) d\mathbf{r} + \int p_B(\mathbf{r}) \ln \left(\frac{p_B(\mathbf{r})}{p_B^\circ(\mathbf{r})} \right) d\mathbf{r} \right] \quad (7)$$

Minimization subject to the constraint of eq 5 then gives

$$\frac{p_A(\mathbf{r})}{p_A^\circ(\mathbf{r})} = \frac{p_B(\mathbf{r})}{p_B^\circ(\mathbf{r})} \quad (8)$$

This is equivalent to eq 2, again Hirshfeld.

Discussion

We conclude that a normalization problem does not exist with the Nalewajski–Parr prescription for determining AIM: Minimize the information loss as defined by eq 3 subject to eq 1. There follow the Hirshfeld AIM. This result depends on the use of the Kullback–Liebler information measure. Other information measures give the same answer, but not all. As well illustrated in a recent monograph on information theory,¹⁰ some information measures are good for one purpose, some for another. However, a firm information-theory basis exists for the Hirshfeld AIM.

Note that the minimization of eq 3 provides a universal definition of AIM free of all atomic and molecular parameters other than densities once a reference state has been chosen. Incorporation of additional properties is possible. Thus, Pauling models charge transfer effects with electronegativity differences, while the Hirshfeld picture of eq 4 includes only a universal entropy term. Note, however, that Pauling models are aimed at reproducing bond energies, while the Hirshfeld model is designed to reproduce the true total molecular electron density.

Epilogue

Despite its utility, the atom in a molecule cannot be directly observed by experiment, nor can one measure enough properties of an atom in a molecule to define it unambiguously. While different definitions may be more useful in specific contexts, we cannot conceive of any experimental measurement which would confirm one definition as uniquely correct, while refuting all other possibilities. Furthermore, it follows rigorously from density functional theory that it is impossible for the electron density of a molecular subsystem to be exactly transferable from one molecule to another.¹¹ There are multiple ways to partition molecules into atoms that are consistent with various observed chemical trends and experimental data.

Consequently, what AIM are remains ambiguous, subject to arbitrary (but disciplined) personal choice when specificity is desired. This type of concept is what may be called a *noumenon*. From one dictionary, we read, as the complete definition of this term, “An object of purely rational apprehension; specifically, with Kant, a nonempirical concept”. From another, the Oxford English, “An object knowable by the mind or intellect, not by the senses; specifically (in Kantian philosophy) an object of purely intellectual intuition”.

We believe that the term “noumenon” is deadily correct for describing AIM, as a conceptual construct ultimately unknowable by observation or unique definition but conceivable by reason. The idea of atoms in molecules is compulsively needed in chemistry, for the facilitation of the modeling of molecules and the prediction of experiments. Chemical science is built upon the atom, and the atom in molecule is a vital, central chemical concept, yet forever elusive.

Elsewhere, R.F.N. and collaborators have been broadly developing and applying information theory to many aspects of electronic structure phenomena.¹² Some of the thoughts in the present contribution may be found in those works. Also pertinent for continuing AIM discussion is a detailed analysis by P.W.A.¹³

References and Notes

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