# General and Unique Partitioning of Molecular Electronic Properties into Atomic Contributions

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We demonstrate that any first-order property can be uniquely partitioned into atomic contributions. The atomic contribution is given as a trace of the respective generalized atomic polar tensor and can be evaluated without invoking numerical integration. Partitionings of the potential energy in a model one-electron problem and of the electric charge in some molecules containing lithium atoms are used to illustrate the new formalism.

The partitioning of molecular properties into atomic contributions is an old art. For example, the first system of atomic contributions to the molecular polarizabilities was developed as early as 1911,[1] a long time before quantum-mechanical calculations of the molecular properties were envisioned. In the course of his research the physical chemist encounters partitioning schemes quite frequently. The magnetic susceptibilities[2] and the dipole moments[3] serve as examples of the properties that can be calculated from the atomic and bond contributions. The so-called population analysis,[4] widely used by both quantum and organic chemists, constitutes in fact a partitioning of the molecular electric charges into the atomic contributions.

Despite their extensive usage, the partitioning schemes have not been shown to have very solid theoretical foundations. Until only very recently, theoretically consistent partitioning techniques were unknown. In 1981 Bader and co-workers[5] put forward a topological definition of atoms in molecules which made it possible to assign various portions of space to particular atoms. This, in turn, allows one to calculate the atomic contributions to arbitrary properties by means of a numerical integration.

Bader's definition is certainly very elegant, but it suffers from some problems. The numerical integration is slow and troublesome for computer programming. There is a possibility of "empty loges," e.g., portions of space that do not belong to any particular atom. Topological properties of some molecular systems can intrinsically preclude the partitioning. In this paper I propose a new general and unique partitioning scheme that does not require any numerical integration and is general enough to be valid for any molecule.

Let us consider a molecule $M$ with $N$ electrons. The validity of the Born-Oppenheimer approximation is assumed and the atomic units are used throughout the text. We denote the coordinates of nuclei by $\mathbf{r}_A \equiv (x_A, y_A, z_A)$ and the coordinates of electrons by $\mathbf{r}_i \equiv (x_i, y_i, z_i)$. The positions of nuclei do not have to correspond to the stationary points on the hypersurface of the molecular total energy. We are interested in the partitioning of a first-order property associated with the operator $\hat{V}$,

$$\langle \hat{V} \rangle = \langle 0 | \left[ \sum_i^N \hat{V}_i^{(1)} + \sum_{i>j}^N \hat{V}_{ij}^{(2)} + \cdots \right] | 0 \rangle. \tag{1}$$

$|0\rangle$ is the electronic wave function of the molecule under consideration. We assume that $\hat{V}$ is invariant with respect to changes of the origin of the coordinate system, $\mathbf{r}_0 \equiv (x_0, y_0, z_0)$. We use the following abbreviation:

$$\langle \hat{x}\hat{V} \rangle = \langle 0 | \left[ \sum_i^N \hat{x}_i \hat{V}_i^{(1)} + \tfrac{1}{2} \sum_{i>j}^N (\hat{x}_i + \hat{x}_j) \hat{V}_{ij}^{(2)} + \cdots \right] | 0 \rangle,$$

$$\text{etc.} \tag{2}$$

Let $\langle \hat{V} \rangle_A$ be the atomic contribution of atom $A$ to $\langle \hat{V} \rangle$. A proper partitioning scheme should yield $\langle \hat{V} \rangle_A$ having the following properties: (1) proper additivity,

$$\sum_{A \in M} \langle \hat{V}_A \rangle = \langle \hat{V} \rangle, \tag{3}$$

$$\langle \hat{V} + \hat{W} \rangle_A = \langle \hat{V} \rangle_A + \langle \hat{W} \rangle_A. \tag{4}$$

(2) Invariance with respect to $\mathbf{r}_0$,

$$\frac{\partial \langle \hat{V} \rangle_A}{\partial x_0} = \frac{\partial \langle \hat{V} \rangle_A}{\partial y_0} = \frac{\partial \langle \hat{V} \rangle_A}{\partial z_0} = 0. \tag{5}$$

(3) If $\langle \hat{V} \rangle$ transforms like a scalar, vector, etc., $\langle \hat{V} \rangle_A$ should transform in the same way.

The simplest possible definition of $\langle \hat{V} \rangle_A$ that has all the above properties reads

$$\langle \hat{V} \rangle_A = \langle \hat{V} \rangle_A^{xx} + \langle \hat{V} \rangle_A^{yy} + \langle \hat{V} \rangle_A^{zz}, \tag{6}$$

where the generalized atomic polar tensor (GAPT) is given by

$$\langle \hat{V} \rangle_A^{pq} = \frac{1}{3} \left[ \frac{\partial \langle \hat{p}\hat{V} \rangle}{\partial q_A} - N^{-1} \langle \hat{p} \rangle \frac{\partial \langle \hat{V} \rangle}{\partial q_A} \right], \tag{7}$$

$$p, q = x, y, z.$$

The partitioned properties are unique in the following sense: First, the definition [Eqs. (6) and (7)] is the same

for all electronic properties. Second, it can be applied to both exact and approximate wave functions. In the case of one-electron theories, such as the self-consistent field (SCF), the partitioned properties are invariant to localization and delocalization of orbitals or any other transformation that leaves the $N$-electron wave function unchanged. Third, in the case of separated subsystems, the partitioned properties are the same as for the isolated subsystems alone.

As an example of the proposed partitioning let us consider the charge distribution in molecules

$$\hat{V} \equiv \hat{1} .  \tag{8}$$

In this case, the GAPT's reduce to the atomic polar tensors (APT's) widely used in ir spectroscopy.[6]

Free atoms have a vanishing electric charge. However, in the molecular environment the charge is induced. According to Eqs. (6) and (7), for the charge of the atom $A$ we obtain

$$Q_A = -\langle \hat{1} \rangle_A + Z_A$$

$$= -\frac{1}{3} \left[ \frac{\partial}{\partial x_A} \langle \hat{x} \rangle + \frac{\partial}{\partial y_A} \langle \hat{y} \rangle + \frac{\partial}{\partial z_A} \langle \hat{z} \rangle \right] + Z_A , \tag{9}$$

where $Z_A$ is the atomic number of $A$.

Table I presents the calculated atomic charges in some lithium molecules. (A compilation of the atomic charges in various molecules will be published elsewhere.[7]) An extended Gaussian basis set (6-31++G**, Ref. 8) has been used for computing the electronic wave functions at the SCF level. The magnitudes of the atomic charges are close to the ones obtained from the numerical integration of the electron density.[9] On the other hand, the Mulliken analysis substantially underestimates the

bond ionicities.[9] Even more dramatic proof of the advantage of the present approach is demonstrated by comparing the charges calculated within different basis sets. For example, the charges on the Li atom in LiH equal 0.2642, 0.1935, 0.5358 (Mulliken) and 0.6513, 0.6470, 0.6819 (APT) for the 4-31G, 6-31G**, 6-31++G** basis sets, respectively. The APT charges are virtually insensitive to the choice of basis set.

As pointed out above, our definition is valid for both the SCF and correlated wave functions. The charges do not change significantly upon inclusion of electron correlation, provided it does not change the electron distribution substantially. The following figures can serve as a pertinent example: $Q_{Li}$ in LiF, 0.8379 (SCF, 6-31G**) and 0.7727 (MP2, 6-31G**); $Q_C$ in CO, 0.3712 (SCF, 6-31G**) and 0.1211 (MP2, 6-31G**) (MP2 denotes Møller-Plesset second-order perturbation theory).

Another example concerns a one-electron problem with two positive charges $Z_A$ and $Z_B$ separated by a distance $R_{AB}$. This system can serve as the simplest model of a chemical bond. The electronic wave function depends on two parameters

$$r = (Z_A + Z_B) R_{AB} \text{ and } \beta = (Z_A - Z_B)/(Z_A + Z_B) . \tag{10}$$

We can mimic different ionicities of the one-electron bond by varying the magnitude of $\beta$. Figure 1 shows the partitioning of the electronic potential energy obtained within both Bader's scheme (TOPOL) and the present scheme (APT). The Bader partitioning is possible only for $\beta < 0.30$. For larger values of $\beta$ the topological boundary between centers (atoms) disappears and there is no way of assigning the portions of space to a particular center. The present scheme does not face these

TABLE I. Atomic charges in some lithium molecules. The optimized geometries at the relativistic Hartree-Fock (RHF), 6-31++G** level have been used (the Mulliken charges are given in parentheses).

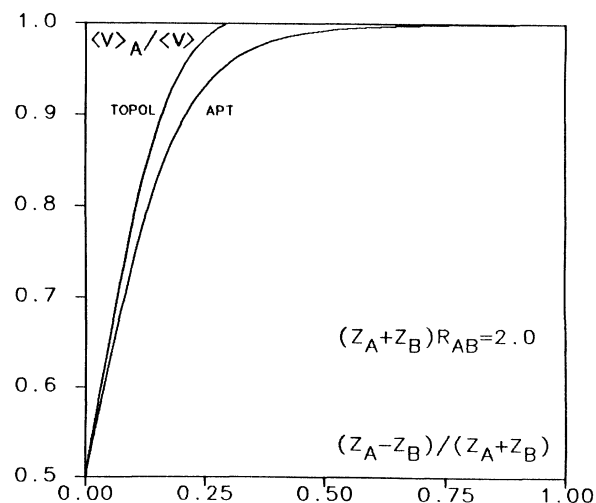| | | | |
|---|---|---|---|
| LiH | $Q_{Li}=0.6819$ | $Q_H=-0.6819$ | |
| | (0.5358) | (−0.5358) | |
| LiCN | $Q_{Li}=0.8682$ | $Q_C=-0.4930$ | $Q_N=-0.3752$ |
| | (0.1475) | (−0.3623) | (−0.5099) |
| LiNC | $Q_{Li}=0.9231$ | $Q_N=-0.9815$ | $Q_C=-0.0584$ |
| | (0.5230) | (−0.4233) | (−0.0996) |
| LiNO | $Q_{Li}=0.8025$ | $Q_N=-0.0178$ | $Q_O=-0.7846$ |
| | (0.3564) | (−0.2244) | (−0.1320) |
| LiOH | $Q_{Li}=0.8758$ | $Q_O=-1.1582$ | $Q_H=0.2825$ |
| | (0.6034) | (−0.9541) | (0.3507) |
| Li$_2$O | $Q_{Li}=0.7880$ | $Q_O=-1.5760$ | |
| | (0.4452) | (−0.8905) | |
| LiOF | $Q_{Li}=0.9089$ | $Q_O=-0.4849$ | $Q_F=-0.4240$ |
| | (0.5931) | (−0.4568) | (−0.1362) |
| LiF | $Q_{Li}=0.9039$ | $Q_F=-0.9039$ | |
| | (0.7401) | (−0.7401) | |



FIG. 1. Partitioning of the electronic potential energy for the one-electron problem.

difficulties.

Generalization of this partitioning technique to the second-order properties is quite straightforward. I believe that the present scheme will bring more insight into the electronic properties of molecules, enabling one to study the atomic contributions and their variations due to the molecular environment.

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