PostDoc Journal: Reviews
Vol.2, No.2, February 2014

Journal of Postdoctoral Research
www.postdocjournal.com

Atomic Charges in Molecules: A Classical Concept in Modern Computational Chemistry

James X. Mao

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260.
E-mail: xim17@pitt.edu

Atomic charge is one of the most important concepts in chemistry. It provides a simple picture of electron density distribution within a molecule. Atomic charges are central roles in many theories which aim to understand structure-property relation of molecules. There exist various ways to calculate atomic charges and they serve different purposes. The correct applications of atomic charges rely on fully understanding the way they are defined.

1 Introduction

In chemistry, atomic charge is a classical and fundamental concept. Many observables of molecules, such as dipole moments, electric potentials, NMR chemical shifts, reactivities, and electromagnetic spectra can be correlated to atomic charges in the molecule, and many structure-property theories of molecules are based on the idea of atomic charges. Today, obtaining the atomic charges for interested molecules to interpret experimental data with the help of computational chemistry seems routine. Actually, it is by far a trivial task. The concept of atomic charges in molecules is so successful that sometimes it is forgotten that atomic charge is indeed a man-made concept: atomic charges in molecules are not experimentally observable. The only charge can be observed is the net charge of the whole molecule. Assigning charges to individual atoms in a molecule is essentially arbitrary and can never be verified as "correct" or "wrong" from experimental data. Various methods of assigning charges have been proposed. These methods stem from different roots, fit for specific uses, and can be "correct" or "wrong" when applying them to interpret different types of experimental data. It is extremely important to fully understand the definition of atomic charges before demanding their applications. It is the purpose of this review to briefly go through the most popular definitions of atomic charges in molecules and to help researchers outside of computational chemistry to choose the "correct" method while it is in need.

2 Orbital-Based Charges

According to quantum mechanics, a system is completely described by its wave function, which can be obtained by solving its Schrödinger equation. However, Schrödinger equation with multiple electrons is non-solvable. As a result, there is no way to obtain the exact form of a molecule's wave function. In computational chemistry, wave functions are approximated by a linear combination of orbitals' product. Orbital is another widely used man-made concept in chemistry, referring to a one-electron wave function. Since the wave function contains all information of the system, it is not surprising that there exist efforts in which atomic charges are derived from the wave function and its orbitals.

2.1 Mulliken Charge

Mulliken atomic charge[1–3] is defined based on orbitals. For each atom, all electronic charge contributions from orbitals centered at that atom are summed up, and electronic overlap clouds between two atoms are divided equally to the two atoms.

Mathematically, Mulliken charges can be obtained easily as a byproduct of a quantum mechanic calculation. The calculation of wave function requires density matrix and overlap matrix of the system. As a result, at the end of a quantum mechanic calculation, the density matrix and overlap matrix are always handy. With density matrix and overlap matrix at hand, the Mulliken charges can be obtained by a simple multiplication:

$$P_{ij} = D_{ij} S_{ij}$$

where P is the Mulliken population matrix, D is the density matrix, and S is the overlap matrix.

Since Mulliken charges are easy to calculate, they have been widely used since being proposed. However, it is well known today that Mulliken charge comes with several serious weaknesses, both mathematically and physically. Mathematically, Mulliken charges are only meaningful if the basis functions used to build orbitals can be associated with an atomic site. They are extremely basis-function dependent: changing basis functions could result in a big difference for the charge on the same atom[4,5]. Moreover, basis functions are normally not a complete orthogonal set, and using a nonorthogonal basis always results in overlap terms. As mentioned above, Mulliken charges partition the overlap term equally between two atoms, regardless of the difference between the two atoms. Physically, this is only true in case the two atoms are the same. Different atoms possess different properties such as electronegativities, and the overlap cloud should not be divided equally. The way Mulliken scheme treats overlap leads to exaggerated charge separations. With these shortcomings, Mulliken charges should only be used as a quick and qualitative guild for the atomic charges in molecules.

2.2 Löwdin Charge

Löwdin charge[5,6] is an effort of improvement from Mulliken charge. It applies a symmetric transformation for all the orbitals (Löwdin orthogonalization) to form an orthogonal basis:

$$\chi_{i'} = \sum_i S_{i'i}^{-1/2} \chi_i, \quad \chi : \text{orbital}, \quad S : \text{overlap matrix}$$

As a result of orthogonal basis, all overlap terms are eliminated so the problem of overlap partition in Mulliken charges is avoided.

There exist various way to generate orthogonal basis functions from original basis functions. Among all the possible orthogonal basis, the one given by Löwdin symmetric orthogonalization is the closest in the least-squares sense to the original nonorthogonal basis.

Compared to Mulliken charges, Löwdin charges are much less sensitive to basis functions. However, the Löwdin orthogonalization is purely a mathematical consideration. The overlap partition problem is hidden by requiring a mixing of orbitals centered on different atoms. There is no reason to believe Löwdin charges is more physically “correct” than Mulliken charges.

2.3 NBO Charge

NBO (natural bond orbitals) charge[7] is another orbital-based atomic charge. In NBO analysis, orbitals are orthogonalized and localized to form one or two center orbitals (natural bond orbitals). These orbitals are classified as core orbitals, valence orbitals, and Rydberg orbitals to provide the most accurate possible Lewis structure of wave function. In this respect NBO charge is more chemically meaningful than Mulliken charge.

NBO charge is less basis-set dependent than Mulliken charge, and converge as the basis set size increases. It is computationally more expensive than Mulliken charge, but usually this is not a problem with today’s computers. Along with natural energy decomposition analysis[8–10], NBO charge is the best candidate if researches are interested in correlating interaction properties such as charge transfer to atomic charges.

3 Potential Derived Charges

For a molecule which is composed of n atoms with their positions r_j, the molecular electrostatic potential (MEP) at position r_i can be calculated using a simple point-charge model by assuming each atom possesses an effective atomic charge q_j:

$$E(r_i) = \sum_{j=1}^{n} \frac{q_j}{|r_i - r_j|}$$

In another side, molecular electrostatic potential $V(r)$ is experimentally observable, and can also be calculated from quantum mechanics. By choosing a set of sample points r_i in space around a molecule, and using least-squares method to fit the electrostatic potential $V(r_i)$ evaluated at these points to the point-charge model, a set of effective atomic charges for the molecule can be obtained. Mathematically this is achieved by varying values of q_j to minimize the quantity

$$\sum_i (V(r_i) - E(r_i))^2$$

The fitting is usually carried out under the constraint that the total charge of the molecule should be correct. The requirement of reproducing the overall molecular dipole moment sometimes serves as another constraint.

There exist several versions of MEP derived charges and they differ from each other mainly on the way of choosing sampling points. It was shown that these schemes could produce different results for the same molecule[16]: MEP derived charges strongly depend on how and where the sampling points are selected.

3.1 Merz-Kollman Charge

For Merz-Kollman charge[12,13], sampling points locate in a number of shells at a specified distance (namely, 1.4, 1.6, 1.8, and 2.0 times the van der Waals radii of the atoms) from the molecule. In each shell the density of sampling points is 1 point/Å^2.

3.2 CHELP Charge

For CHELP (charges from electrostatic potentials) charge[14], sampling points locate in spherical shells around each atom. Shells are 2.5, 3.5, 4.5, 5.5, and 6.5Å from the atoms. In each shell, fourteen points were symmetrically placed.

3.3 CHELPG Charge

CHELPG (charges from electrostatic potentials using a grid based method) charge[15] uses an equally-spaced array of points: the dimensions of the sampling cube are chosen such that the molecule is located at the center of the cube, with

2.8Å of headspace on all sides. Sampling points are spaced 0.3Å apart within the cube.

3.4 RESP Charge

MEP fitting charges can reproduce the electrostatic interactions between molecules quite well and they are widely used to build force fields. However, MEP is a surface characteristic and during the fitting all sampling points falling inside the Van der Waals radius of the molecule are discarded. As a result optimized charges do not work well for large systems in which there exist atoms buried deeply inside the molecule. RESP (restrained electrostatic potential fit) charge[11] was proposed to improve this weakness. In RESP scheme, an extra constraint of restraining each atom's charge to an "optimal" value is applied. RESP charge does produce more stable results for buried-in atoms; however, the extra constraint has no physical meaning. The constraint is introduced by a pure mathematical consideration.

4 Density Related Charges

Another observable property which is closely related to atomic charges of a molecular system is the electron density of the system. Atomic charges in molecules serve to provide a simple picture of the electron density distribution of the molecule. It is also well known that the ground state properties of a many-electron system are uniquely determined by its electron density[17]. Defining atomic charges from the system's electron density seems natural.

4.1 AIM Charge

AIM (Atoms in Molecules)[18] theory defines the spatial volume of an atom in a molecule by electron density topology analysis. An atom's spatial volume is defined as volume enclosed by zero-flux surfaces of the electron density. The zero-flux surfaces are the union of all points where $\nabla\rho \cdot \mathbf{n} = 0$ (ρ is the electron density and $\mathbf{n}$ is the unit vector normal to the surface). These volumes are nonspherical and do not overlap to each other. Once the atom's spatial volume is determined, its atomic charge (AIM charge) is obtained by integrating electron density over the volume.

The electron density includes the information of each atoms' electronegativities, therefore AIM charge does take the atom's electronegativity into account. Since electron density is the only quantity used to define the charges, AIM charge is stable with basis functions change. However, both density topology analysis and numerical integration of the atomic volume are computationally expensive.

4.2 Hirshfeld Charge

Hirshfeld[19] charge is another atomic charge based on electron density: each atom's charge is also obtained by integrating the electron density over its volume. Different from AIM charge, the atomic volumes in Hirshfeld analysis overlap with each other. There are no boundary surfaces between Hirshfeld atomic volumes of a molecule.

To define the volumes, a promolecule is first constructed by the superposition of spherically averaged electron densities of isolated atoms:

$$\rho^{\text{pro}}(r) = \sum_i \rho_i^{\text{at}}(r)$$

The atomic volumes are then defined through sharing function for each atom:

$$\omega_i(r) = \rho_i^{\text{at}}(r)/\rho^{\text{pro}}(r)$$

The electron density of a real molecule at any position among the several atoms is shared in proportion to their isolated atom densities at the corresponding distances from the atom.

The same as AIM charge, Hirshfeld charge is alone defined by electron density of the molecule and of its component atoms. A reference to basis functions is not required. Hirshfeld charge reflects the density change between promolecule and real molecule, and is useful to interpret molecular properties that arise from the redistribution of density on bonding.

5 APT Charge

APT (atomic polar tensor) charge[20,21] is different from any charge mentioned above. It is defined using atomic polar tensor:

$$q_i = \frac{1}{3}\left(\frac{\partial \mu_x}{\partial x_i} + \frac{\partial \mu_y}{\partial y_i} + \frac{\partial \mu_z}{\partial z_i}\right)$$

Here μ is the dipole moment of a molecule, and x_i, y_i, z_i is the position of atom i. Although the components of dipole moment change with the choice of coordinate system, the defined APT charge for each atom is invariant under rotation and translation of the molecule, and they sum up to the total charge of molecule correctly.

Atomic polar tensor may be derived experimentally from the intensities of infrared bands, but in reality APT charge is derived using quantum mechanically calculated dipole moment. Since the dipole moment is sensitive to the level of calculation, APT charge is sensitive to the level of calculation as well.

Among all popular atomic charges, APT charge is the most expensive one: its calculation requires the calculation of second order derivatives of wave function, which normally means a high computational cost. While a lot of spectra properties of a molecule, such as IR spectrum intensity or NMR chemical shift, are actually second order properties, APT charge should be considered as the first candidate to correlate these experimental data, providing the molecule is not too big and the calculation is feasible.

6 Conclusions

Although atomic charges in a molecule are not experimentally observable quantities, they are fundamental and useful tools to understand and relate properties of molecules to their structures. There exist many different ways to partition the total charge of a molecule to its component atoms, and no one such partition procedure can be claimed as superior for all purposes to its various alternatives. To illustrate relations between structure and various properties of molecules, the choice of "best" atomic charges is by far a solved problem. Nonetheless, fully understanding the purpose of applications and the definition of atomic charges is essential to choosing a proper atomic charge scheme.

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