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Molecular Fragments in Density Functional Theory

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The second-order density functional approach to the partitioning of the molecular density of Cedillo, Chattaraj, and Parr (*Int. J. Quantum Chem.* **2000**, *77*, 403−407) is used, together with a local assumption for the function that projects the total density into its components, to show that the distribution function adopts a stockholders form, in terms of the local softness of the isolated fragments, and that the molecular Fukui function is distributed in the molecular fragments in the same proportion as the electronic density.

Introduction

The description of atoms or functional groups in molecules has always been a desirable goal in chemistry. Knowledge of how the atoms or the functional groups change, with respect to their structure when they are isolated, due to the polarization and charge transfer that occurs on bond formation, allows one to understand different aspects of the chemical behavior of a molecule or a family of molecules and how will they interact with different reactants.

In this context, Bader and co-workers[1] developed a theory in which the molecular density is divided into nonoverlapping regions separated by surfaces on which the flux of the density gradient is zero. The atoms thus obtained have several important properties. However, the absence of overlap between the atoms could not be as adequate to describe the chemical bonds.

Parr and co-workers[2−6] established a definition of atoms in molecules by introducing the concept of promotion energy, which is the change in the energy of each atom from its isolated ground state to its state in the molecule. This way, by making use of the chemical potential equalization principle and through the minimization of the total promotion energy, one finds a unique set of densities for the atoms in the molecule, whose sum is equal to the molecular density, and that are not disjoint. That is, this approach leads to fuzzy overlapping atoms.

Later, by taking into account that a fragment in a molecule is an open system that can exchange energy and electrons with the rest of the molecule, Cedillo, Chattaraj, and Parr[7] defined a partitioning of the molecular density, through the minimization of the molecular grand potential with respect to the densities of the fragments, subject to the constraint that they add up to the molecular density.

Another definition of molecular fragments, proposed by Hirshfeld,[8] is based on the assumption that the molecular density at each point may be divided among the fragments, in proportion to their respective contributions to the promolecular density at that point. The promolecular density is the sum of the isolated fragment densities at the actual positions of the nuclei. Thus

$$\rho_i^{\mathrm{H}}(\mathbf{r}) = \frac{\rho_i^0(\mathbf{r})}{\rho_{\mathrm{pm}}^0(\mathbf{r})}\,\rho_{\mathrm{m}}(\mathbf{r}) = w_i^{\mathrm{H}}(\mathbf{r})\,\rho_{\mathrm{m}}(\mathbf{r}) \qquad (1)$$

where $\rho_i^{\mathrm{H}}(\mathbf{r})$ is the density of the ith fragment in the molecule, the superscript H indicates a Hirshfeld fragment, $\rho_i^0(\mathbf{r})$ is the density of the ith isolated fragment, $\rho_{\mathrm{m}}(\mathbf{r})$ is the molecular ground-state density

$$\rho_{\mathrm{pm}}^0(\mathbf{r}) = \sum\nolimits_i \rho_i^0(\mathbf{r}) \qquad (2)$$

is the promolecular density, and $w_i^{\mathrm{H}}(\mathbf{r}) = \{\rho_i^0(\mathbf{r})/\rho_{\mathrm{pm}}^0(\mathbf{r})\}$ is the Hirshfeld stockholders distribution function. The sum of all the fragment densities, $\rho_i^{\mathrm{H}}(\mathbf{r})$, is equal to the molecular ground-state density, $\rho_{\mathrm{m}}(\mathbf{r})$.

Recently, there has been a renewed interest in the Hirshfeld stockholder partitioning, motivated by the important demonstrations of the information−theoretic basis of this division scheme[9−15] and the thermodynamic-like properties of the Hirshfeld subsystems.[16] In addition, the Hirshfeld partitioning has also been applied to calculate condensed Fukui functions, leading to very reasonable values of these reactivity criteria that have been used to explain several aspects about the chemical behavior of a wide variety of chemical systems.[17−22] However, the calculation of the condensed Fukui functions, with the Hirshfeld distribution function, implies the assumption of using the distribution function that is employed in the neutral system for the cases in which the molecule has a net positive or negative charge. A situation that also implies that the molecular Fukui function is distributed in the molecular fragments in the same proportion as the electronic density. That is, through this approximation one has that $w_i^{\mathrm{H}}(\mathbf{r}) = \{\rho_i^0(\mathbf{r})/\rho_{\mathrm{pm}}^0(\mathbf{r})\} = \{\rho_i^{\mathrm{H}}(\mathbf{r})/\rho_{\mathrm{m}}(\mathbf{r})\} = \{f_i^{\mathrm{H}}(\mathbf{r})/f_{\mathrm{m}}(\mathbf{r})\}$, where $f_{\mathrm{m}}(\mathbf{r}) = (\{\partial\rho_{\mathrm{m}}(\mathbf{r})/\partial N\})_v$ is the ground-state molecular Fukui function, and $f_i^{\mathrm{H}}(\mathbf{r}) = w_i^{\mathrm{H}}(\mathbf{r}) f_{\mathrm{m}}(\mathbf{r})$ such that $\sum_i f_i^{\mathrm{H}}(\mathbf{r}) = f_{\mathrm{m}}(\mathbf{r})$.

It is important to note that Ayers, Morrison, and Roy[23] have established a formal mathematical and physical basis for the condensed Fukui functions, originally introduced by Yang and

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Mortier.[24] In their derivations, it is implicitly assumed that the existence of a single distribution function can be applied to different local properties, such as the energy density, the electronic density, or the Fukui function.

The purpose of the present work is to show that the molecular partitioning of density functional theory based on the grand potential leads to a distribution function of the stockholders type, in terms of the local softness of the isolated fragments, from which one can derive the relationship between the fragment densities and the fragment Fukui functions.

Density Functional Theory Partitioning

The starting point of Cedillo, Chattaraj, and Parr[7] is to consider an isolated N-electron molecule with density $\rho_m(\mathbf{r})$, external potential $v(\mathbf{r})$, and chemical potential μ, formed by fragments with the corresponding quantities N_i, $\rho_i(\mathbf{r})$, $v_i(\mathbf{r})$, and μ_i, in such a way that

$$\sum_i \rho_i(\mathbf{r}) = \rho_m(\mathbf{r}) \tag{3}$$

with $\sum_i N_i = N$. In the equilibrium ground state, the chemical potential of each fragment, μ_i, is equal to the molecular chemical potential, μ. The isolated fragments, in some reference state that could be the ground state or a promoted state, are characterized by the parameters N_i^0, $\rho_i^0(\mathbf{r})$, $v_i^0(\mathbf{r})$, and μ_i^0.

Thus, they have shown that, if one performs the appropriate Taylor series expansions and keeps only the terms up to second-order derivatives of the energy, the change in grand potential of each fragment may be expressed in the form

$$\Delta\Omega_i = N_i^0(\mu_i - \mu_i^0) - \int \rho_i^0(\mathbf{r})\eta_i^0(\mathbf{r}, \mathbf{r}')\Delta\rho_i(\mathbf{r}')\, d\mathbf{r}'\, d\mathbf{r} - (1/2) \int \Delta\rho_i(\mathbf{r})\eta_i^0(\mathbf{r}, \mathbf{r}')\Delta\rho_i(\mathbf{r}')\, d\mathbf{r}'\, d\mathbf{r} \tag{4}$$

and the molecular grand potential is given by

$$\Delta\Omega_{\text{tot}} = \sum_i \Delta\Omega_i = \sum_i (\Omega_i - \Omega_i^0) = \sum_i (\Delta E_i - \mu_i \Delta N_i) \tag{5}$$

In eq 4, $\eta_i^0(\mathbf{r}, \mathbf{r}')$ is the hardness kernel[25] for the isolated fragment.

Cedillo, Chattaraj, and Parr have shown that the fragment densities may be obtained through the minimization of eq 5 with respect to each $\rho_i(\mathbf{r})$, subject to the restriction given by eq 3. This procedure leads to[7]

$$\rho_i(\mathbf{r}) = \int w_i(\mathbf{r}, \mathbf{r}')\rho_m(\mathbf{r}')\, d\mathbf{r}' \tag{6}$$

where the function $w_i(\mathbf{r}, \mathbf{r}')$ projects the total density into the corresponding fragment component, and it is given by

$$w_i(\mathbf{r}, \mathbf{r}') = \int s_i^0(\mathbf{r}, \mathbf{r}'')h(\mathbf{r}'', \mathbf{r}')\, d\mathbf{r}'' \tag{7}$$

where $h(\mathbf{r}'', \mathbf{r}')$ is the inverse kernel of $\sum_i s_i^0(\mathbf{r}'', \mathbf{r}')$, and $s_i^0(\mathbf{r}'', \mathbf{r}')$ is the softness kernel[25] of the isolated fragment. The summation over all fragments in eq 7 leads to $\sum_i w_i(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$, and therefore using this result in eq 6, one can see that the sum of the fragment densities is equal to the molecular density.

If we approximate the function $w_i(\mathbf{r}, \mathbf{r}')$ by a local one, $w_i(\mathbf{r}, \mathbf{r}') = w_i(\mathbf{r}')\delta(\mathbf{r} - \mathbf{r}')$, then, substituting this expression in eq 7, one finds, after some algebraic manipulations, that

$$w_i(\mathbf{r}) = \frac{s_i^0(\mathbf{r})}{s_{\text{pm}}^0(\mathbf{r})} \tag{8}$$

where $s_i^0(\mathbf{r})$ is the local softness of the isolated fragment, and

$$s_{\text{pm}}^0 = \sum_i s_i^0(\mathbf{r}) \tag{9}$$

is the promolecular local softness. In the derivation of eq 8, one makes use of the fact that the integral of the softness kernel over one of the variables leads to the local softness.

Equation 8 establishes that the molecular density at each point may be divided among the fragments, in proportion to their respective contributions to the promolecular local softness at that point. Thus, the comparison of eq 8 with eq 1 shows that the density functional expression is similar to the Hirshfeld expression, in the sense that it is of the stockholders type, but in this case, the distribution is made through the local softness of the isolated fragments instead of the density. It is important to note that, in the present approach, eq 8 has been derived without using stockholders arguments.

Now, one may assume that the molecular local softness $s_m(\mathbf{r}) = (\{\partial\rho_m(\mathbf{r})/\partial\mu\})_v$ and the molecular Fukui function $f_m(\mathbf{r}) = (\{\partial\rho_m(\mathbf{r})/\partial N\})_v$ may also be distributed in the fragments, that is, $s_m(\mathbf{r}) = \sum_i s_i(\mathbf{r})$, where $s_i(\mathbf{r})$ is the local softness of the ith fragment in the molecule and $f_m(\mathbf{r}) = \sum_i f_i(\mathbf{r})$. Thus, by recalling that the density functional approach of Cedillo, Chattaraj, and Parr was established through a truncated Taylor series expansion that only kept terms up to second-order derivatives of the energy, under the same assumption, one has $s_i(\mathbf{r}) \approx s_i^0(\mathbf{r})$ and $s_m(\mathbf{r}) = \sum_i s_i(\mathbf{r}) \approx s_{\text{pm}}^0(\mathbf{r})$. Therefore,

$$w_i(\mathbf{r}) = \frac{s_i^0(\mathbf{r})}{s_{\text{pm}}^0(\mathbf{r})} \approx \frac{s_i(\mathbf{r})}{s_m(\mathbf{r})} \tag{10}$$

and the local softnesses may be expressed as

$$s_m(\mathbf{r}) = S_m f_m(\mathbf{r}) \quad \text{and} \quad s_i(\mathbf{r}) = S_m f_i(\mathbf{r}) \tag{11}$$

where S_m is the ground-state molecular global softness.

It is important to note that the integral of $f_m(\mathbf{r})$ over the whole space is equal to 1, while the integral of $f_i(\mathbf{r})$ is $F_i \equiv \int f_i(\mathbf{r})\, d\mathbf{r}$, so that $\sum_i F_i = 1$. The quantities F_i can define the condensed Fukui functions of the fragments in the molecule. Thus, since the integral of the molecular local softness is equal to the molecular global softness, the integral of the ith fragment local softness corresponds to the condensed local softness, $S_i \equiv \int s_i(\mathbf{r})\, d\mathbf{r}$, and $S_i = S_m F_i$, where $\sum_i S_i = S_m$. With eq 11, the approximate last equality of eq 10 becomes

$$w_i(\mathbf{r}) = \frac{s_i^0(\mathbf{r})}{s_{\text{pm}}^0(\mathbf{r})} \approx \frac{s_i(\mathbf{r})}{s_m(\mathbf{r})} = \frac{f_i(\mathbf{r})}{f_m(\mathbf{r})} \tag{12}$$

The comparison of eq 6, with the local assumption $w_i(\mathbf{r}, \mathbf{r}') = w_i(\mathbf{r}')\delta(\mathbf{r} - \mathbf{r}')$, and eq 12 implies that

$$w_i(\mathbf{r}) = \frac{s_i^0(\mathbf{r})}{s_{\text{pm}}^0(\mathbf{r})} = \frac{\rho_i(\mathbf{r})}{\rho_m(\mathbf{r})} \approx \frac{s_i(\mathbf{r})}{s_m(\mathbf{r})} = \frac{f_i(\mathbf{r})}{f_m(\mathbf{r})} \tag{13}$$

This relationship establishes that the molecular Fukui function is distributed in the fragments in the same proportion as the molecular electronic density. However, note that in the present derivation one does not invoke the assumption of using the distribution function that is employed in the neutral system for the cases in which the molecule has net positive or negative charge. Thus, the present demonstration provides support to the use of a density-based partitioning scheme to determine other fragment properties such as the softness or the Fukui function.[26] The present procedure does not involve additional assumptions to the ones already established for the density functional approach, namely, the second-order truncation and the locality of $w_i(\mathbf{r}, \mathbf{r}')$. The relation given by eq 13 is a consequence of these two assumptions, and it requires knowledge of one of the ratios to calculate the other ratios. Thus, the results for the condensed Fukui functions reported in the literature for a wide variety of molecules[19−22] using $w_i^{\mathrm{H}}(\mathbf{r}) = \{\rho_i^0(\mathbf{r})/\rho_{\mathrm{pm}}^0(\mathbf{r})\}$, as a distribution function, can be supported by the present density functional theory approach to molecular fragments.

Conclusions

Recently, Parr, Ayers, and Nalewajski[15] have argued that, although the concept of atoms in molecules is central to chemistry, it is ambiguous, in the sense that there are multiple ways to partition molecules into atoms which are consistent with observed chemical trends and experimental data. However, while some definitions may be useful in certain cases, there is no unique partitioning that could be experimentally verified or defined. Thus, they have concluded that the concept of atoms in molecules, while highly useful, constitutes a noumenon in the sense of Kant ("an object of purely rational apprehension; specifically, with Kant, a nonempirical concept, or an object knowable by the mind or intellect, not by the senses; specifically, in Kantian philosophy, an object of purely intellectual intuition").

In this context, the result established for the distribution of other properties, like the Fukui function or the local softness, with the density-based distribution function provides support for the calculation of these fragment properties in other density-based partitioning schemes, particularly, to the Hirshfeld stockholders partitioning, which leads to very reliable values of the condensed Fukui function. In addition, this result is in agreement with the work of Ayers, Morrison, and Roy,[23] in the sense that the same distribution function may be used for several local properties.

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