



A Reference-Free Stockholder Partitioning Method Based on the Force on Electrons

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We argue that when one divides a molecular property into atom-in-a-molecule contributions, one should perform the division based on the property density of the quantity being partitioned. This is opposition to the normal approach, where the electron density is given a privileged role in defining the properties of atoms-in-a-molecule. Because partitioning each molecular property based on its own property density is inconvenient, we design a reference-free approach that does not (directly) refer atomic property densities. Specifically, we propose a stockholder partitioning method based on relative influence of a molecule's atomic nuclei on the electrons at a given point in space. The

resulting method does not depend on an "arbitrary" choice of reference atoms and it has some favorable properties, including the fact that all of the electron density at an atomic nucleus is assigned to that nucleus and the fact all the atoms in a molecule decay at a uniform asymptotic rate. Unfortunately, the resulting model is not easily applied to spatially degenerate ground states. Furthermore, the practical realizations of this strategy that we tried here gave disappointing numerical results. © 2017 Wiley Periodicals, Inc.

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Motivation

Inspired by Nalewajski and Parr's realization that Hirshfeld's stockholder partitioning can be derived from the principles of information theory,^[1–5] the last decade has seen a proliferation of population analysis approaches.^[6–17] These methods are mostly based on partitioning the electron density, though other quantities (e.g., the local hardness and the one-electron reduced density matrix) have also been considered.^[18–20]

Putting aside the mathematical rationale for the stockholder partitioning,^[3,5,17,21–25] the stockholder partitioning is intuitively reasonable. Slightly generalizing the original argument of Hirshfeld,^[4] let $p_{\text{mol}}(\mathbf{r}) \geq 0$ be a local property density for the molecule, and $p_A^0(|\mathbf{r}-\mathbf{R}_A|)$ be the corresponding spherically-averaged reference property densities for the atoms composing the molecule, with atomic charges $\{Z_A\}$ at the positions $\{\mathbf{R}_A\}$. Typically one chooses the electron density,^[4] but any other property with nonnegative (or nonpositive) values could also be considered. (For example, one could consider any positive-semidefinite definition of the local kinetic energy.^[26–30]) The property-specific atomic weight is based on the idea that the local property value at the point \mathbf{r} is constructed as a sum of the contributions from all of the atoms, and the relative contribution of any specified atom can be defined based on the relative contributions of the reference atoms,

$$w_A(\mathbf{r}) = \frac{p_A^0(\mathbf{r})}{\sum_{B=1}^{N_{\text{atoms}}} p_B^0(\mathbf{r})}. \quad (1)$$

The property densities of the atoms-in-a-molecule are then obtained as partitions of the molecular properties,

$$p_A(\mathbf{r}) = w_A(\mathbf{r}) p_{\text{mol}}(\mathbf{r}) \quad (2)$$

Clearly the same weight function could be used to partition other properties, though it is appealing philosophically (but inconvenient computationally) for each property to be partitioned according to its own specific weight function.

Intuitively, Eq. (1) measures the relative "investment" of atom A to the property of interest at the point \mathbf{r} , in the absence of interaction between the atoms. After the atoms interact, the molecular property value at \mathbf{r} is partitioned to the atoms in the molecule according to their initial investment, Eq. (2). Equivalently, each atom shares in the profit/loss (increase/decrease) in molecular property value relative to the sum of the reference atomic contributions) according to its initial investment.^[4]

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$$p_A(\mathbf{r}) = p_A^0(\mathbf{r}) + w_A(\mathbf{r}) \left(p_{\text{mol}}(\mathbf{r}) - \sum_{B=1}^{N_{\text{atoms}}} p_B^0(\mathbf{r}) \right). \quad (3)$$

One disadvantage of the stockholder partitioning strategy is the need for reference atomic distributions. We have already indicated that, for philosophical consistency, it is desirable to partition each property separately. Similarly, the choice of reference atom states—does one use the property densities of the isolated neutral atoms, or of ions, or of promoted atomic states?—is ambiguous. This motivates the pursuit of reference-free stockholder methods.

Our strategy for developing a reference-free stockholder method is to recognize that the only property of a molecule that can be unequivocally assigned to an individual atom is the atom's own nucleus. This suggests a naïve partitioning based on the external potential (or some power thereof), giving weight functions like

$$w_A(\mathbf{r}) = \frac{(v_A^0(\mathbf{r}))^n}{(v_{\text{mol}}^0(\mathbf{r}))^n} \quad (4)$$

where

$$v_A^0(\mathbf{r}) = -\frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} \quad (5)$$

$$v_{\text{mol}}^0(\mathbf{r}) = \sum_{A=1}^{N_{\text{atoms}}} v_A^0(\mathbf{r}) \quad (6)$$

This approach is not recommended, however, because the atomic weight functions decay slowly, as $1/|\mathbf{r} - \mathbf{R}_A|^n$. Atomic partitioning methods that are this highly nonlocal have been observed to give poor transferability between functional groups. One also expects that the strong dependence of this type of approach on the atomic number means that the electropositive atom in size-mismatched molecules like Cesium Fluoride or Potassium Hydride will have unchemical negative charges.

Instead of this approach, we wish to quantify the influence, or force, that each atomic nucleus asserts at a location, $\iota_A(\mathbf{r})$, and define the atomic weight functions,

$$w_A(\mathbf{r}) = \frac{\iota_A(\mathbf{r})}{\sum_{B=1}^{N_{\text{atoms}}} \iota_B(\mathbf{r})} \quad (7)$$

accordingly. In the remainder of this paper we will describe several approaches of this type, along with a discussion of their favorable and unfavorable features. This approach is inspired in part by Ehrenfest force partitioning methods, which are also reference free and which also have no direct dependence on the electron density.^[31–34]

Strategy

Atomic force partitioning

The average force that the electrons in a system at the point \mathbf{r} feel due to the atomic nuclei and the other electrons is given by the expression

$$\begin{aligned} \mathbf{F}_{\text{mol}}(\mathbf{r}) &= -\rho_{\text{mol}}(\mathbf{r}) \nabla_{\mathbf{r}} v_{\text{mol}}^0(\mathbf{r}) - \int \rho_{2;\text{mol}}(\mathbf{r}, \mathbf{r}') (\nabla_{\mathbf{r}} |\mathbf{r} - \mathbf{r}'|^{-1}) d\mathbf{r}' \\ &= -\int \rho_{2;\text{mol}}(\mathbf{r}, \mathbf{r}') \nabla_{\mathbf{r}} \left(\frac{v_{\text{mol}}^0(\mathbf{r})}{N-1} + \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) d\mathbf{r}' \end{aligned} \quad (8)$$

In this expression for the Ehrenfest force,^[35] $\rho_{\text{mol}}(\mathbf{r})$ denotes the ground-state electron density and $\rho_{2;\text{mol}}(\mathbf{r}, \mathbf{r}')$ is the ground state pair density.^[36,37] The Ehrenfest force per electron per unit volume is therefore

$$\phi_{\text{mol}}(\mathbf{r}) = \frac{\mathbf{F}_{\text{mol}}(\mathbf{r})}{\rho_{\text{mol}}(\mathbf{r})}. \quad (9)$$

These expressions do not distinguish between the force on the electrons from different nuclei. To determine the force on the electrons from nucleus A , we might imagine removing nucleus A from the molecule, and then define the force due to the nucleus A as $\mathbf{F}_A(\mathbf{r}) = \mathbf{F}_{\text{mol}}(\mathbf{r}) - \mathbf{F}_{\text{mol without } A}(\mathbf{r})$. In general, however, if one removes a nucleus from the molecule then some of the electrons are unbound. Instead of using this ill-defined procedure, we can estimate the same effect using the linear response approximation. This corresponds to the following definition for the atomic Ehrenfest force,

$$\begin{aligned} \mathbf{F}_A(\mathbf{r}) &= Z_A \frac{\partial \mathbf{F}_{\text{mol}}(\mathbf{r})}{\partial Z_A} \\ &= -\rho_{\text{mol}}(\mathbf{r}) \nabla_{\mathbf{r}} \frac{-Z_A}{|\mathbf{r} - \mathbf{R}_A|} - Z_A \left(\frac{\partial \rho_{\text{mol}}(\mathbf{r})}{\partial Z_A} \right)_N \nabla_{\mathbf{r}} v_{\text{mol}}^0(\mathbf{r}) \\ &\quad - Z_A \int \left(\frac{\partial \rho_{2;\text{mol}}(\mathbf{r}, \mathbf{r}')}{\partial Z_A} \right)_N (\nabla_{\mathbf{r}} |\mathbf{r} - \mathbf{r}'|^{-1}) d\mathbf{r}' \end{aligned} \quad (10)$$

We could then define the influence of nucleus A on the point \mathbf{r} as being proportional to the magnitude of the force,

$$\iota_A^F(\mathbf{r}) = |\mathbf{F}_A(\mathbf{r})| \quad (11)$$

This definition has the conceptually appealing feature that because Eq. (10) diverges at the location of nucleus A , the point \mathbf{R}_A is wholly assigned to nucleus A . That is, $w_A(\mathbf{R}_B) = \delta_{AB}$. However, this definition is difficult to compute (primarily because the response of the pair density to a change in external potential is difficult to compute) and does not completely remedy the issue we encountered in Eq. (4). In particular, the last two terms in Eq. (10) are more nearsighted than the first term. This means that the atomic weight functions constructed from $\iota_A^F(\mathbf{r})$ have a long-range component that is not completely screened. Since the problematic term is the first term, this problem can be avoided by using one (or both) of the next two terms as a proxy for the influence of the atomic nucleus. This is the strategy we explore in the next subsection. Alternatively, one could replace the long-ranged Coulomb potential with a screened Coulomb potential like the Yukawa potential, the error function potential, or the erf-gau interaction.^[38–42]

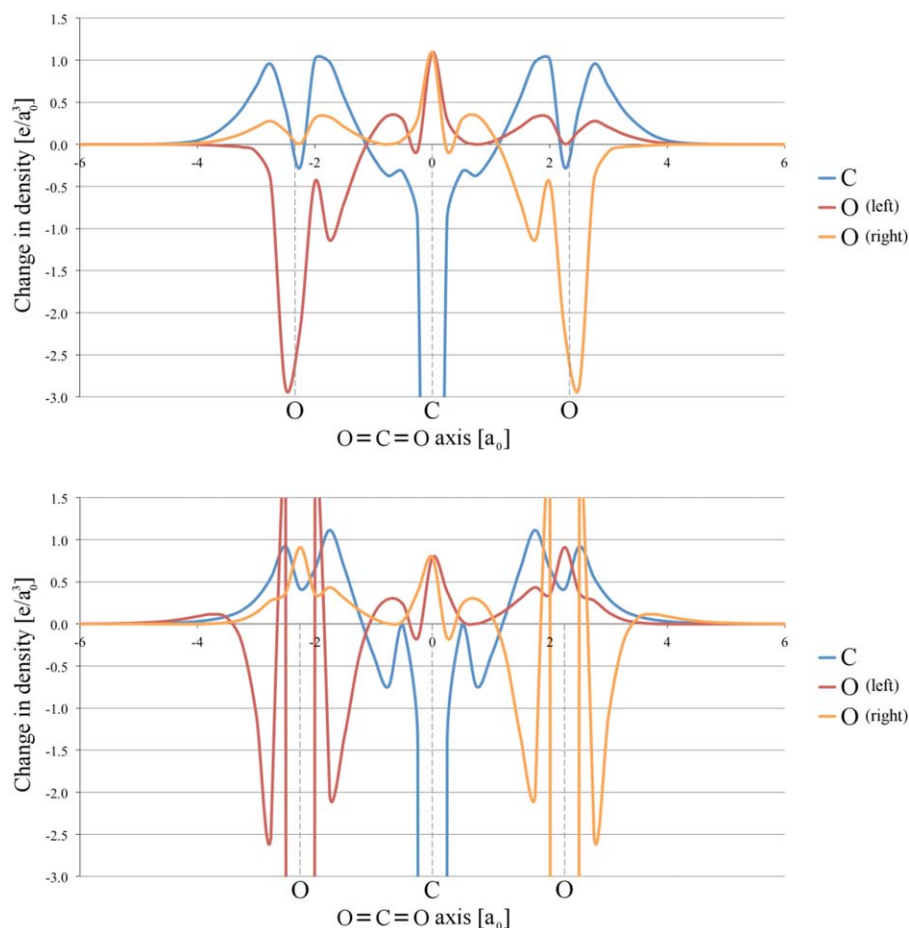


Figure 1. The change in electron density under constant chemical potential conditions (Eq. 16) for CO₂ along the O = C = O axis at the PBE/PBE/sto-3g (top) and PBE/PBE/6-311++G** (bottom). [Color figure can be viewed at wileyonlinelibrary.com]

Density response partitioning

Instead of measuring the influence of an atomic nucleus on the electrons directly (as through the atomic Ehrenfest force), we could measure it indirectly by measuring the change in electron density due to scaling the atom's nuclear charge. This is an alchemical derivative,^[43] and it can be computed directly with a finite difference approximation or modelled exactly using the linear response function,^[44–47]

$$\begin{aligned} \iota_A^{(N)}(\mathbf{r}) &= -Z_A \left(\frac{\partial \rho(\mathbf{r})}{\partial Z_A} \right)_N \\ &= \int \left(\frac{\delta \rho(\mathbf{r})}{\delta V(\mathbf{r}')} \right)_N \left(\frac{Z_A}{|\mathbf{r}' - \mathbf{R}_A|} \right) d\mathbf{r}' = \int \chi(\mathbf{r}, \mathbf{r}') \left(\frac{Z_A}{|\mathbf{r}' - \mathbf{R}_A|} \right) d\mathbf{r}' \quad (12) \end{aligned}$$

To first order, $\iota_A^{(N)}(\mathbf{r})$ is the change in electron density that would result from removing nucleus A from the molecule. The problem is that the linear response function is normalized to zero, and so

$$\int \iota_A^{(N)}(\mathbf{r}) d\mathbf{r} = 0 \quad (13)$$

Reducing the charge of nucleus A therefore causes (a) a local decrease in the electron density near the nucleus and (b) a

compensating increase in the electron density away from the atom, so that the total number of electrons in the molecule remains unchanged.^[48] The fact that $\iota_A^{(N)}(\mathbf{r})$ has both positive and negative values makes it inappropriate for stockholder partitioning via Eq. (7). Furthermore, $\iota_A^{(N)}(\mathbf{r})$ has long-range non-nearsighted terms, which means that the atomic weight functions will not be localized, leading to a loss of chemical transferability.^[49] The first problem can be fixed by defining a revised, nonnegative influence functional like

$$\tilde{\iota}_A^{(N, \max)}(\mathbf{r}) = \max(0, -\iota_A^{(N)}(\mathbf{r})) \quad (14)$$

(which is nondifferentiable) or

$$\tilde{\iota}_A^{(N, \exp-\alpha)}(\mathbf{r}) = \exp(-\alpha \iota_A^{(N)}(\mathbf{r})) \quad (15)$$

(which introduces an arbitrary parameter, $\alpha > 0$). Unfortunately, these revised influence functions do not fix the problem of nonlocal atomic weight functions and the associated loss of chemical transferability.

Chemical transferability can be regained by computing the change in electron density under constant chemical potential conditions, i.e.,

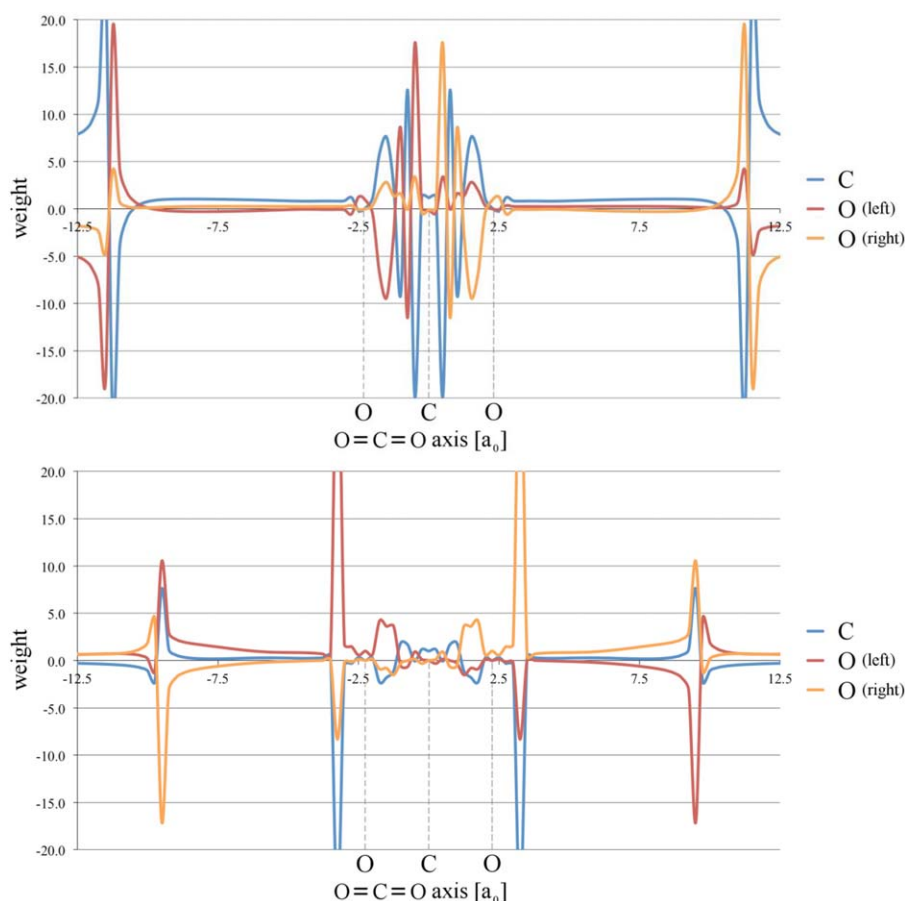


Figure 2. The atomic weight functions (Eq. 7) for CO₂ along the O = C = O axis at the PBE/PBE/sto-3g (top) and PBE/PBE/6-311++G** (bottom). [Color figure can be viewed at wileyonlinelibrary.com]

$$\begin{aligned} \iota_A^{(\mu)}(\mathbf{r}) &= -Z_A \left(\frac{\partial \rho(\mathbf{r})}{\partial Z_A} \right)_\mu \\ &= \int \left(\frac{\delta \rho(\mathbf{r})}{\delta v(\mathbf{r}')} \right)_\mu \left(\frac{Z_A}{|\mathbf{r}' - \mathbf{R}_A|} \right) d\mathbf{r}' = - \int s(\mathbf{r}, \mathbf{r}') \left(\frac{Z_A}{|\mathbf{r}' - \mathbf{R}_A|} \right) d\mathbf{r}' \end{aligned} \quad (16)$$

where $s(\mathbf{r}, \mathbf{r}')$ is the softness kernel.^[44,48–51] In this case, removing charge from at atomic nucleus still causes the electron density to decrease locally, but because the system is in equilibrium with an electron bath with constant chemical potential, the whole molecule donates electrons to the bath. As a result,

$$\int \iota_A^{(\mu)}(\mathbf{r}) d\mathbf{r} < 0 \quad (17)$$

However, it is not necessarily true that $\iota_A^{(\mu)}(\mathbf{r})$ is nonpositive everywhere. In particular, one expects that $\iota_A^{(\mu)}(\mathbf{r})$ may become slightly positive in regions that are far from A where the molecular Fukui function is negative.^[52–59] Since $\iota_A^{(\mu)}(\mathbf{r})$ decays rapidly with increasing distance from \mathbf{R}_A , however, the transformations in Eqs. (14) and (15) should suffice. (If the denominator in Eq. (7) were strictly negative, even using $\iota_A^{(\mu)}(\mathbf{r})$ directly should suffice, albeit with the caveat that atomic densities, $\rho_A(\mathbf{r}) = w_A(\mathbf{r})\rho_{\text{mol}}(\mathbf{r})$, might not be strictly nonnegative.)

Atomic-influence-based partitioning based on $\iota_A^{(\mu)}(\mathbf{r})$ potentially has desirable properties, including the locality/transferability of

atomic densities. One of the desirable features of the force-based partitioning, namely that the location of each atomic nucleus is assigned wholly to that atom, $w_A(\mathbf{R}_B) = \delta_{AB}$, is lost however.^[60] While that feature is conceptually appealing, it is not present in most molecule partitioning methods, so clearly this condition is not required for the utility of a partitioning method.^[17]

All of the methods considered here are potentially catastrophic for degenerate ground states. In degenerate states, a infinitesimal change in the external potential can break the degeneracy, causing a finite and global rearrangement of the ground-state electron density and the ground-state electron pair density;^[61–64] this causes the influence functions $\iota_A^{(F)}(\mathbf{r})$, $\iota_A^{(N)}(\mathbf{r})$, and $\iota_A^{(\mu)}(\mathbf{r})$ to diverge. The solution to this conundrum is via degenerate perturbation theory: one must first identify the appropriate ground state through first-order perturbation theory; then one can compute response of that electron (pair) density. Although this is a formal solution, a desirable symmetry from nondegenerate ground states—the magnitude of $\iota_A(\mathbf{r})$ was invariant to whether one considered an infinitesimal increase or a small decrease in Z_A —is now lost.

Numerical Assessment

We implemented the partitioning based on Eq. (16) using a recently developed approach to evaluating the softness kernel,^[49]

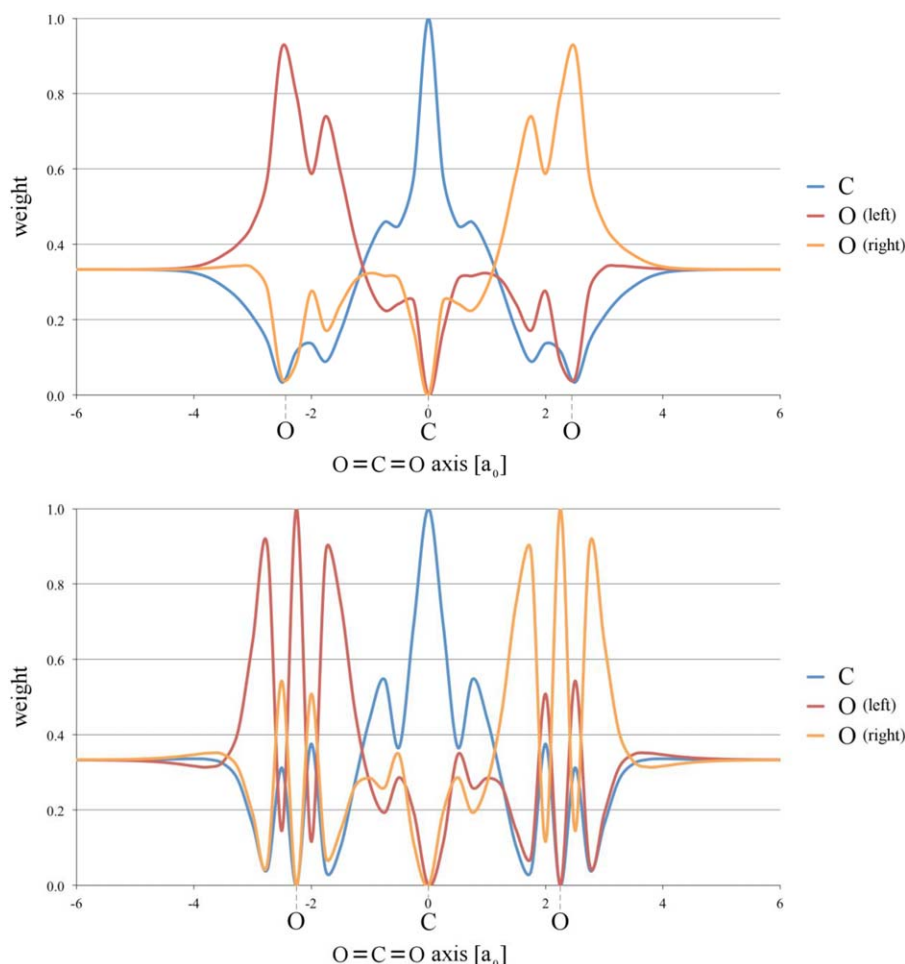


Figure 3. The atomic weight functions using the exponential transformation with $\alpha=0$ (Eqs. 15 and 19) for CO₂ along the O = C = O axis at the PBE/PBE/sto-3g (top) and PBE/PBE/6-311++G** (bottom). [Color figure can be viewed at wileyonlinelibrary.com]

which builds on earlier work for analytically evaluating the linear response kernel.^[45,46,65] It should be noted that the softness kernel is only a first order approximation to the change in the electron density. In theory higher order terms could be included as well, but the calculation of those terms would become computationally very demanding and our recent work shows they are usually unimportant.^[49] We started by studying the carbon dioxide molecule, using the PBE exchange-correlation functional with the STO-3G and 6-311++G(d,p) basis sets, at the optimized geometry obtained using *Gaussian*.^[66,67] The density response for each atom, Eq. (16), is shown in Figure 1. The response is large, nonlocal and very sensitive to the choice of basis set. At the 6-311++G(d,p) basis, the density response has a particularly large oscillatory behavior close to the nucleus, which is undesirable for partitioning the density. The non-locality and oscillatory behavior of the response causes the denominator in

$$w_A(\mathbf{r}) = \frac{\iota_A^{(\mu)}(\mathbf{r})}{\sum_{B=1}^{N_{\text{atoms}}} \iota_B^{(\mu)}(\mathbf{r})} \quad (18)$$

to sometimes become zero by cancelation of regions with positive and negative changes in the electron density, causing

divergences in the atomic weights, as shown in Figure 2. To avoid this, we used the exponential transformation (cf. Eq. (15)),

$$w_A(\mathbf{r}) = \frac{\exp\left(\iota_A^{(\mu)}(\mathbf{r})\right)}{\sum_{B=1}^{N_{\text{atoms}}} \exp\left(\iota_B^{(\mu)}(\mathbf{r})\right)} \quad (19)$$

but as we see in Figure 3, the atomic weights are still quite delocalized: the softness kernel does not seem to be “nearsighted enough” for this strategy to work. Moreover, this behavior is more pronounced for the larger 6-311++G(d,p) basis, compared to STO-3G, leading to very different distribution for the atomic weights. It is particularly problematic that due to the shell structure in the induced atomic density changes, there are regions in the vicinity of each oxygen nucleus where the dominant atomic weight is from the *other* oxygen atom. Including higher order terms might improve the results, but the calculation of those terms would make the method computationally impractical. We also tested to see if including Hartree-Fock exchange would improve the results. Results from the PBE0 functional^[68] were quantitatively similar and qualitatively indistinguishable from the PBE results.

Qualitatively similar results were obtained for the formaldehyde molecule, indicating that this approach, despite its appealing philosophical and mathematical properties, is inadequate, simply because of the strong nonlocality in the induced density change (Figure 1).

Summary

Hirshfeld's stockholder partitioning strategy is conceptually appealing and mathematically elegant, but it requires one to choose reference "pro-densities" for molecular pieces. These pro-densities are typically chosen to be the reference densities of neutral (or charged) atoms, though in the literature one also sees atomic shells, radial shells, and other more *ad hoc* choices.^[16,69,70] Not only is it unclear which of these reference pro-densities should be chosen, it seems questionable to partition properties other than the molecular density using pro-densities. For example, if one wishes to partition the molecular kinetic energy, one can argue that the appropriate analogue of the traditional stockholder partitioning would use the local kinetic energy pro-densities of isolated molecular pieces as the reference.

To avoid the vagaries of choosing an appropriate reference state and an appropriate reference property, we decided to exploit the fact that the atomic nuclei within a molecule can be unambiguously assigned to an atom. This suggests that we should use the relative *influence* of each atomic nuclei, suitably defined, to partition the molecule into atomic fragments. We considered several methods to achieve this. The most appealing, to us, measures the influence of each atomic nucleus, *A*, at the point *r* by imagining how the electron density of the molecule would change at *r* if the nucleus of atom *A* was suddenly removed, at constant chemical potential. While this is impractical to compute, estimating this quantity in the linear response approximation, Eq. (16), is practical. This definition is reference-free and gives (due to its dependence on the softness kernel) manifestly nearsighted atoms-in-molecules, which is philosophically appealing. However, the induced density change is not nearsighted enough, and the resulting atomic weights do not have the locality one needs for practically successful and chemically intuitive partitioning.

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explicitly dedicate this paper to their scientific and personal friendship.

Keywords: hirshfeld partitioning · ehrenfest force · atoms in molecules · stockholder population analysis · softness kernel · linear response function · conceptual density functional theory

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