A problematic issue for atoms in molecules: Impact of (quasi-)degenerate states on Quantum Theory Atoms in Molecules and Hirshfeld-I properties

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A B S T R A C T

We examine the dependence of atomic properties derived from the Quantum Theory of Atoms in Molecules and the Hirshfeld-I method on the existence of (quasi-)degenerate states. As atomic charges are mostly used to quickly assess chemical reactivity using the molecular electrostatic potential, we computed the correct zeroth order density matrices using degenerate perturbation theory for a perturbing point charge of given magnitude, sign and position. This density matrix is then used as input for Atoms in Molecules (AIM) analysis and the dependence of atomic charges on the nature of the perturbation examined for two molecules. It is shown that in simple cases, the atomic charges are deceptively robust due to symmetry reasons whereas in a less symmetrical case the atomic charges vary significantly. This establishes that for the prediction of reactivity, for every kind of perturbation, a specific perturbation matrix needs to be diagonalised and the resulting density matrix used for AIM analysis.

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1. Introduction

Much of chemistry is based on the idea that molecules can be considered systems composed of atoms or functional groups where these atoms or groups retain much of their properties irrespective of the precise environment they are found in. The remarkable success of such transferability models for the classification of molecules and the subsequent success of interpretation of chemical reactions based on such classification has made that atoms in molecules have retained a much higher status than one would think based on its rather weak quantum mechanical foundations. Even today, with the most modern electronic structure methods allowing the calculation of ever more accurate molecular data, models for atoms in molecules remain a chief area of interest although already roughly 50 years ago, Mulliken realised that with the advent of sufficiently powerful calculations, more and more chemical concepts seem to go up in thin air [1]. That these models are still of interest is to large extent due to the continuing desire of chemists to classify and rationalise observations such that

predictions can be made based on insight rather than mere computation. *To calculate a molecule is not to understand it* [2].

Assuming the concept of an Atom in the Molecule (AIM) is indeed a worthwhile endeavour, its lack of a clear and unique definition from the founding principles of quantum mechanics has given rise to a wealth of different models [3–5]. Restricting ourselves to models that effectively lead to an AIM that has a density function attached to it, two main groups of models can be distinguished [6]. First there are those based on the attachment of basis functions to atomic centres, thereby relying on Hilbert spaces as in e.g., the Mulliken method [7] and – in a more advanced fashion – Natural Population Analysis [8]. The main focus of the present paper lies on the second group where the AIM is derived from a 3D partitioning of space. This group can then be further subdivided in the binary or non-fuzzy subgroup, where the AIM do not overlap and thus where there are strict boundaries between atoms (note that they can still extend to infinity in some directions) and the non-binary or "fuzzy" subgroup where all atoms extend to infinity in all directions albeit that at every point a proportion of the density at that point is divided over all atoms with (usually) the largest weights for the atoms (identified by their nucleus) nearest by. Both types of methods rely on a common expression for the density of the AIM through:

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$$\rho_A^N(\mathbf{r}) = w_A^N(\mathbf{r})\rho_{Mol}^N(\mathbf{r}) \tag{1}$$

Here $\rho_{Mol}^N(\mathbf{r})$ is the electron density of the molecule with N electrons at point $\mathbf{r}$ as experimentally or theoretically obtained, $\rho_A^N(\mathbf{r})$ is likewise the density of the AIM A obtained by multiplication of the molecular density with the weight function $w_A^N(\mathbf{r})$. It is in the last function that the different methods belonging to the second group differ. In the binary subgroup, $w_A^N(\mathbf{r})$ can only have a value of zero or one whereas in the second subgroup any value $0 \leqslant w_A^N(\mathbf{r}) \leq 1$ is allowed. Note that explicit reference is made to N in $w_A^N(\mathbf{r})$. In both subgroups, methods do exist that are independent of N, e.g., in the Voronoi binary method [9] and the Hirshfeld method [10] but we focus on methods that use different weights for the same molecule and molecular geometry but different number of electrons. These include the binary QTAIM method (also known as Quantum Chemical Topology or Bader's AIM) [11,12] and recent developments of Hirshfeld methods like Hirshfeld-I [13,14] or ISA [15,16] or by treating the N-entropy and shape entropy separately [17]. Properly accounting for the N-dependence is important for the calculation of Fukui functions [18–20] and in general to stick better to the information theory foundations of Hirshfeld methods [13,21,22].

The main purpose of AIM methods is to classify and interpret (experimental) observations to eventually predict outcomes of new experiments. In most modelling work atomic charges are used to represent the molecular electrostatic potential (MEP) surrounding a molecule in as concise a way as possible without loosing too much accuracy. Although this infers that electrostatic potential derived charges would be the optimal choice, this method suffers from major drawbacks of statistical nature [23,24] and does not lead to a density function attached to an AIM so that not only charges but also other density function based expectation values can be computed [4]. Methods like QTAIM are therefore to be preferred although in order to reproduce the MEP on a molecular surface, one needs to go rather far beyond atomic monopoles [25,26]. This is much less the case for Hirshfeld-I atomic charges where a monopole approximation is already quite good [27,28]. In the same realm, electronegativity equalisation methods also work significantly better when using Hirshfeld-I charges [29,30] than when using QTAIM charges [31]. Still, as neither QTAIM or Hirshfeld-I can be rightfully considered uniquely linked to quantum mechanics, no definite method is known and either method has its advantages and disadvantages [32].

Eq. (1) clearly shows that, besides a model for $w_A^N(\mathbf{r})$, no other information beyond the molecular electron density is needed to generate AIM density functions. Any quantum chemical method yields this quantity such that it is essentially trivial to obtain the AIM density function and properties that can be derived from it. Furthermore, in the next stage, it is possible to derive atomic density matrices from both QTAIM [33–35] and Hirshfeld-I [36]. However, this simplicity is somewhat deceptive. AIM charges are mainly used to predict molecular reactivity through the MEP. The MEP is the first order change in energy due to an infinitesimally small perturbation such as a classical point charge of some charge at some location. Assuming no degenerate states exist, the electronic contribution to the MEP can be computed easily via first order variation from (note: the nuclear contribution is independent of the electronic state):

$$\phi(\mathbf{r}_0) = \frac{\delta E}{dq} = \frac{\int \rho_{Mol}^N(\mathbf{r})\delta v(\mathbf{r};\mathbf{r}_0)d\mathbf{r}}{dq} \tag{2}$$

$$\delta v(\mathbf{r};\mathbf{r}_0) = \lim_{q \to 0} \frac{q}{|\mathbf{r}_0 - \mathbf{r}|} \tag{3}$$

where $\delta v(\mathbf{r};\mathbf{r}_0)$ is an infinitesimally small change in the external perturbation in the Hamiltonian. This establishes a unique chain of information: the MEP connects to the electron density which in itself gives rise to the AIM density function through Eq. (1) and this

independent of $\delta v(\mathbf{r};\mathbf{r}_0)$, i.e. the sign and magnitude of the point charge q and its precise location $\mathbf{r}_0$. The same expression is obtained from perturbation theory which will play a key role in the following where we go from non-degenerate to degenerate perturbation theory. If the quantum chemical system has (quasi-)degenerate states, it has indeed been shown that one must switch to degenerate perturbation theory [37,38]. If a g-fold degeneracy does exist, one needs to consider the perturbation matrix:

$$\begin{bmatrix} \langle \Psi_1|\delta\hat{v}|\Psi_1\rangle & \langle \Psi_1|\delta\hat{v}|\Psi_2\rangle & \cdots & \langle \Psi_1|\delta\hat{v}|\Psi_g\rangle \\ \langle \Psi_2|\delta\hat{v}|\Psi_1\rangle & \langle \Psi_2|\delta\hat{v}|\Psi_2\rangle & \cdots & \langle \Psi_2|\delta\hat{v}|\Psi_g\rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle \Psi_g|\delta\hat{v}|\Psi_1\rangle & \langle \Psi_g|\delta\hat{v}|\Psi_2\rangle & \cdots & \langle \Psi_g|\delta\hat{v}|\Psi_g\rangle \end{bmatrix} \tag{4}$$

where $\delta\hat{v}$ stands for a perturbation in the external potential and the $\{\Psi_i\}$ are the degenerate states. The eigenvectors of the above matrix correspond to the correct zeroth-order wave functions accompanying each eigenvalue. So there no longer is a one-to-one correspondence between the electron density obtained from that eigenvector and that from a single state. Alternatively, one can consider that $\rho_{Mol}^N(\mathbf{r})$ should be replaced by $\rho_{Mol}^N(\mathbf{r};q,\mathbf{r}_0)$ in Eq. (1) to make it explicit that the results depend on the sign and magnitude of the point charge and its location. Assuming for simplicity two degenerate states ($g = 2$), given a specific q and $\mathbf{r}_0$, the perturbation matrix (4) leads to two eigenvectors that correspond to a linear combination of the two degenerate wave functions. A new density matrix $\rho_{ii}(\mathbf{r},\mathbf{r}') = \int \Phi_i^*(\mathbf{x}_1 \ldots \mathbf{x}_N)\Phi_i(\mathbf{x}_1' \ldots \mathbf{x}_N)d\sigma_1 d\mathbf{x}_2 \ldots d\mathbf{x}_N$ can be constructed for each of the new states Φ_i obtained from (4). As the Φ_i are a linear combination of the original set $\{\Psi_i\}$, this density matrix consists of the original density matrices of the two states *and* the transition density matrix. This in turn gives rise to a new density that can then be used in Eq. (1). From the nature of the perturbation matrix, it is clear that the eigenvector for the lowest energy response for a point charge q of positive sign at $\mathbf{r}_0$ is the same as the one for the highest energy response for the same point charge at the same location but opposite sign [37,38]. This is the key feature of the problem: the derivative needed to compute the electrostatic potential as the derivative of the energy from (4) with respect to the magnitude of the point charge does not exist which gives rise to a different derivative to the left and to the right [37,38]. As a consequence, even for the same magnitude of point charge at the same location, different signs of the point charge give different new density matrices. Therefore, it can be expected that the AIM densities and thus charges also depend on the same parameters. Such an effect has been observed previously for Mulliken charges and electrostatic potential derived charges [38] but has not yet been investigated for methods belonging to the generic group represented by Eq. (1). This is the question considered in the present paper: how large is the effect of a point charge of different signs and at different positions on the AIM in case of degenerate states. Can one rationalise e.g., the MEP based on a set of AIM data for one state only or should one consider e.g., the average of the AIM data over both states or is the only proper way to consider explicitly the perturbation matrix ? This is important because the AIM is often used to concisely predict reactivity. If, on the other hand, the ESP needs to be computed for every charge and every location through degenerate perturbation theory, the AIM looses much of its importance for such predictions.

To stress the importance of the subject we consider the calculation of atomic charges in a practical computational setup. Different users using different programs for the same type of calculation may easily find a different state among the degenerate set as any linear combination will result in the same energy. Despite finding the same energy, the analysis of e.g., atomic charges may result in quite different conclusions. This explains the need for using a

correct zeroth order wave function and this depends on the nature of the perturbation considered. Near degeneracy also needs to be considered and is likely to play a major role as systems grow larger. AIM charges are just one example of the drastic effect of degeneracy and e.g., polarisability calculations can be expected to be influenced quite heavily by (near) degeneracy.

2. Computational details

The precise procedures used for the calculation of the perturbation matrices have been described before in detail and the reader is referred to the relevant sections elsewhere [38,39].

The molecular radical NO is chosen as an example as it has a degenerate neutral state and occurs in biomodelling (see for example recent work by Lee and Meuwly [40]) where the MEP plays an important role. Hence, considering that AIM charges are mostly used to serve as a condensed representation of the MEP, it serves as a good example to check the dependence on the nature of the perturbation. Moreover, it belongs to a very high symmetry point group which may largely affect this dependence, including hiding it. The second molecule considered, the trans butadiene radical, was chosen because of the low-lying electronic states [41] that should be handled as quasi-degenerate states. It also serves to show that the impact of degeneracy is not limited to highly symmetric molecules, but goes far beyond this. As level of theory for both geometry optimisation and the calculation of properties, we opted for CAS (11,8)/cc-pvtz in case of NO and CAS with an active space of 3 electrons in 4 orbitals (π and π^*) with the cc-pvdz basis set. In all cases an equal weight state averaging over the (quasi-)degenerate states was used. The perturbation matrix (4) was computed as described above and all required calculations were performed using our own software except for the CAS calculations, where Gamess (US) [42] was used.

As perturbing operators, we opt for a unit magnitude point charge $\pm q_0$ at $\mathbf{r}_0$. A unit point charge is quite a strong perturbation but in the scheme we work in, reducing the magnitude of the point charge will merely affect the eigenvalues. The eigenvectors remain the same and it are these that determine the density matrix that in the end determines the AIM properties. The eigenvalues and eigenvectors of the perturbation matrix 4 have the same magnitude spectrum for q_0 of the same magnitude but in order to reach the lowest energy, the most opposite eigenvector is followed upon a change of sign of the point charge. In the simplest case of twofold degeneracy, this means that the eigenvector for the eigensystem that gives the lowest energy for a positive point charge, gives the largest energy for a negative point charge and vice versa. As a physically significant grid of $\mathbf{r}_0$ values, we have chosen a set of points on the surface of the molecule as obtained from the geodesic algorithm by Spackman [43]. The points are located on a series of surfaces obtained from the van der Waals radii multiplied by 1.4, 1.6, 1.8 and 2.0 and a point density of 1 point per square Å, producing a grid of 1036 points for $C_4H_6^+$. Using the resulting density (matrices), we then compute the QTAIM and Hirshfeld-I atomic charges and compare the values obtained from the different eigenvectors with the values based on the individual states. All calculations of QTAIM charges were done using the AimAll program [44]. The Hirshfeld-I atomic densities required for the Hirshfeld-I calculations were obtained using the same basis sets as for the molecules, albeit always using full valence CAS atomic calculations.

3. Results and discussion

The first molecule considered is NO, a radical with a doubly degenerate ground state. Its symmetry is $C_{\infty v}$. Such high symmetry may have important consequences as it may give a false impression of stability of the AIM properties under the effect of the perturbation. Using a set of points located on the van der Waals surface, we computed the eigenvector eigenvalue pairs of the perturbation matrix for every point for both a positive and a negative unit point charge. As described previously, the effect can be rationalised easily [39]. When a negative point charge is put in the nodal plane of one of the π orbitals, this one orbital will remain empty and the electron will be found in the other π orbital to minimise the repulsive Coulomb interaction. Conversely, if a positive unit point charge is placed at this same location, the electron will be found in the π orbital with a lobe pointing towards the point charge. For other positions of the point charge, the two orbitals are expected to mix in such a way that again one orbital points exactly at the point charge whereas the other is orthogonal to this first orbital. As a consequence, the density matrix obtained from the lowest energy eigenvector for a positive point charge equals the density matrix for the highest energy eigenvector in case of a negative point charge. From these density matrices, one can then generate the density as the diagonal and proceed with the topological analysis of this density, i.e. finding the zero flux surfaces. As argued previously [39] in the context of Fukui matrices [45,46] for systems with degenerate states [39], the density matrices obtained for a unit point charge of both different signs, differ significantly. The densities will also differ spatially but it is important to note that due to the nature of the system, the zero flux surfaces also evolve along with the location of the point charge. In other words, although a new density matrix is obtained, all aspects of the topology are equivalent and are mere symmetry transformations. The differences in the density matrices may therefore go unnoticed if concentrating solely on atomic populations (and charges if taking into account the nuclear charge) obtained from integration of $\rho_A^N(\mathbf{r})$ in Eq. (1) or if considering other quantities strongly influenced by the high symmetry as present here. Indeed, the QTAIM atomic charges do not change with the nature of the perturbation although the underlying density matrices do [39]. The same conclusions are obviously also valid for the Hirshfeld-I data.

A more interesting case is the trans butadiene cation radical. This system has the significantly lower C_{2h} symmetry and has been reported to exhibit low-lying excited states [41]. Although exact degeneracy does not occur in this case, depending on the sort of interaction and especially its strength, one needs to consider low-lying excited states as part of a quasi-degenerate system and thus include them in the perturbation theory. We use the present molecule as an illustration of the consequences of near degeneracy although the limit of state separation below which one considers the states important to be dealt with in the degenerate perturbation theory is a matter of choice. We have previously suggested to use as a guideline the Fermi level and to reflect on the need to consider all states obtained from excitations involving orbitals with energies within 0.25 au of this level [38]. It is up to the user to decide on the need of including some of these states. This requires assessing how large the perturbation is compared to the gap between the different states. Also note in this context that the effect of the perturbation scales linearly with the magnitude of the perturbing charge. However, the key physical effect of the splitting remains and in a practical application of predicting e.g., reactivity one would rather use as a perturbation e.g., a set of point charges on the atomic positions of an approaching molecule. These charges could be chosen from e.g. a population analysis technique and are therefore rather fixed. On the other hand, the effect of the perturbation and the need to consider including more states drops if one considers the MEP computed at farther distances from the molecule with the (quasi-)degenerate states. So whereas for truly degenerate states there is no discussion that one needs to use degenerate perturbation theory, for quasi-degenerate states, it is up to the user to make a judicious choice of whether higher states

should be included or not. In order to show the significant effect of inclusion of higher states, here we consider three pure doublet states in the quasi degenerate system, and thus obtain three different density matrices from the eigenvectors of the perturbation matrix. All three were submitted to QTAIM and Hirshfeld-I analysis. Looking at QTAIM atomic charges, we computed the atomic charge on the first carbon atom (C1, a peripheral carbon atom) for a negative point charge located on a set of 1036 points on the van der Waals molecular surface. It was found that upon changing the location of the perturbing point charge, differences in QTAIM atomic charge on this atom occur of up to roughly 0.74 units. Within QTAIM this is a very significant difference (we consider charge differences below 0.10 as rather insignificant). More interesting, however, is the effect of changing the sign of the point charge but keeping it fixed at the same point in space. This entails that for the lowest energy response for a positive unit point charge, the molecular density used in Eq. (1) corresponds to the one obtained from the highest eigenvector of the negative point charge based perturbation matrix. The effect is quite dramatic and the QTAIM atomic charge on C1 changes maximally by 0.72 upon a change in sign of the point charge located at the same point on the van der Waals surface. One can therefore, unlike in the non-quasidegenerate case, definitely not use the results of one sign of the point charge for the other. Fig. 1 shows how the QTAIM atomic charge on C1 for a negative point charge at every location on the van der Waals surface atom varies. The indices on the abscissa correspond to points on the van der Waals surface and are arranged to order the atomic charges on C1 in the ordinate from highest to lowest for a perturbing negative point charge. Also indicated on this same plot are the charges for the same atom but for the second and third density matrices arising from the degenerate perturbation theory treatment. Fig. 1 also includes data on the QTAIM atomic charge for the same atom in the three individual quasi-degenerate states. These correspond to horizontal lines as they are obtained from a non-degenerate treatment. There is clearly significant variation. Fig. 1 also illustrates the dramatic effect of changing the sign of the charge on the different locations. As shown previously, the data for the third, and thus highest energy, eigenvector for a negative point charge correspond to the lowest energy solution for a positive point charge located at the same point. For each point on the abscissa, the distance between the curves for the first and third response thus reflects the effect of the sign of the perturbing charge at that location on the C1 QTAIM atomic charge. The second response is the same for both a negative

and a positive point charge as is to be expected but also computationally confirmed. Such figures can be drawn for all atoms revealing in all cases a very similar effect, i.e. significant variation of the atomic charges for a given perturbing charge at different locations and a more dramatic effect for a change in sign of the perturbing charge at the same location.

Turning to Hirshfeld-I AIM charges, the symmetry relationships described above for NO also apply to the case of Hirshfeld-I and thus require no further discussion. For $C_4H_6^+$, however, similar splitting of the C1 atomic charge is observed when using the Hirshfeld-I method. Fig. 2 shows the analogous graph as Fig. 1 but for the Hirshfeld-I charge on C1. Note that the sorting of the points on the abscissa is the same as in Fig. 1 to maximise comparability. There are significant differences in values of the atomic charges although we stress that we do not compare values of the C1 charges between QTAIM and Hirshfeld-I as any quantitative discussion is bound to suffer from the lack of a definite definition of atomic charge. What is, however, relevant is the observation that the QTAIM versus Hirshfeld-I charge variation upon changing the sign and location of the perturbing charge is very similar. The atomic charge ordering between the three individual states is the same and from the very few spikes in the "response 1" curve for the C1 Hirshfeld-I charges we indeed conclude that both techniques give very coherent results.

For the inner carbon atoms, the agreement in trends is somewhat less which is probably due to the more catastrophic nature of QTAIM but still quite good. This catastrophic nature refers to the fact that any change in the weight function is immediately the maximum change whereas this is not the case in Hirshfeld-I. For the hydrogen atoms, the agreement in trends is rather poorer but this is due to the fact that their charges also change very little, often down to thousandths such that differences become chemically insignificant. This is coherent with the nature of the active space which consists of π and π^* orbitals.

Also of interest is the analysis of the composition of the eigenvectors in terms of the coefficients of the three states. Analysis of the eigenvectors of the perturbation matrix reveals that the different states get mixed quite strongly, a degree of mixing that also differs greatly depending on the sign and location of the point charge. Looking at Figs. 1 and 2, it is clear that the transition densities play an important role in the density matrices as otherwise the atomic charges would not result outside the extremes of states 2 and 3. This thereby also establishes that no simple average density matrix over the degenerate states is sufficiently accurate.
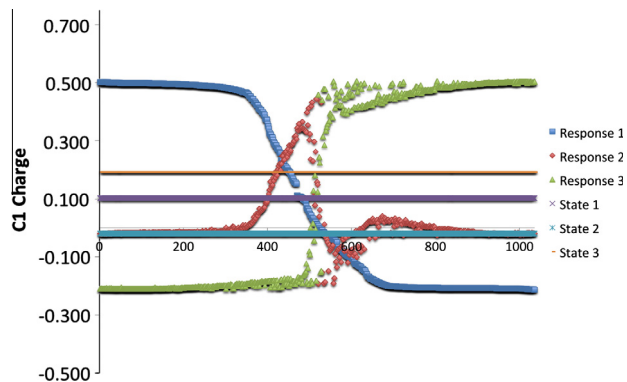

Fig. 1. QTAIM atomic charge on carbon atom C1 for a negative unit point charge perturbation on different points on the van der Waals surface. The indices on the abscissa are arranged to order the atomic charge from high to low for the lowest energy response (response 1). The two other sets of points show the atomic charges for the second and third responses (response 2 and response 3). The horizontal lines indicate the atomic charges using the three individual states (state 1, state 2 and state 3), thus ignoring the (quasi)-degeneracy.
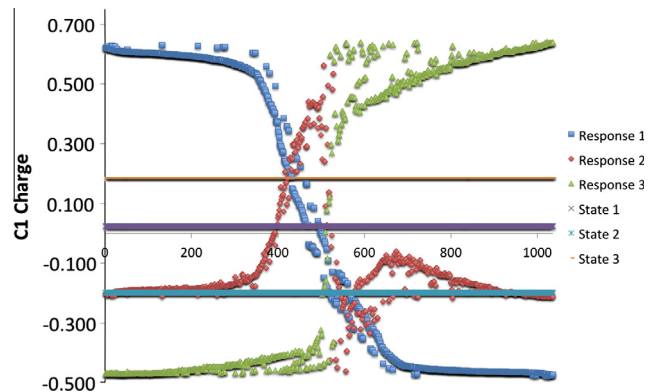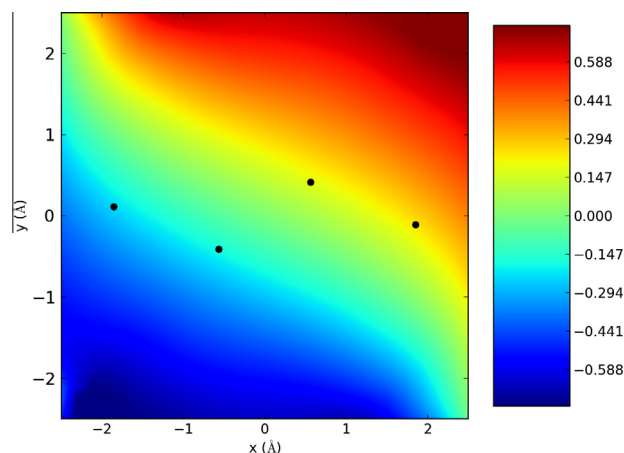
Fig. 2. Hirshfeld-I atomic charge on carbon atom C1 for a negative unit point charge perturbation on different points on the van der Waals surface. The indices on the abscissa are arranged to order the atomic charge from high to low for the lowest energy response (response 1). The two other sets of points show the atomic charges for the second and third responses (response 2 and response 3). The horizontal lines indicate the atomic charges using the three individual states (state 1, state 2 and state 3), thus ignoring the (quasi)-degeneracy.

Fig. 3. Coefficient of the first quasi degenerate state in $C_4H_6^+$ in the eigenvector associated with the lowest energy response for a negative point charge located at each point with coordinates X, Y (the black dots indicate the location of the carbon nuclei).

This is in line with the previous finding that for the Fukui matrix, one can also not rely on averages of frontier molecular orbitals to compute the Fukui function [39]. This finding was previously established for NO which also supports the present finding that one must be careful not to conclude from some integrated properties any invariance of underlying density matrices. For a more complex molecule, Figs. 1 and 2 clearly illustrate that from an atomic charge view no simple average over two or three states can be universally used. A more explicit illustration is shown in Fig. 3. There we considered a set of 116 points in the molecular plane where a unit negative point charge is placed. The colour plot shows the resulting coefficient of the first quasi-degenerate state in $C_4H_6^+$ in the eigenvector associated with the lowest energy eigenvalue of the perturbation matrix for such a point charge placed in the point with coordinates X, Y. There is, indeed, a clear variation in the coefficient such that a unique value for this coefficient (as would be done using a simple density matrix average) is inappropriate.

4. Conclusion

When a molecule has degenerate states or states that are close enough in energy to the ground state to be taken into account in a degenerate perturbation theory treatment of the impact of some perturbation, the results of a QTAIM analysis may depend significantly on the nature of the perturbation. This is illustrated explicitly for a point charge located on a van der Waals surface of the radicals NO and $C_4H_6^+$ where indeed the AIM atomic charges depend strongly on the location of the point charge but also on the sign of the charge. The response density matrix that leads to the lowest energy for a positive unit point charge, leads to the highest energy for a negative unit point charge. In cases where the degeneracy is exact, however, this effect may not be noticeable in all integrated AIM properties due to symmetry reasons. Comparison of QTAIM and Hirshfeld-I atomic charges reveals that QTAIM and Hirshfeld-I give very mutually coherent results despite differences on an absolute scale. Given the simplicity of using a degenerate perturbation theory setup, it is strongly suggested to do not use any average over individual states but to always use the degenerate perturbation theory method. This is strongly supported by the observation that atomic charges from the proper degenerate treatment can never be reached with a simple average. The main conclusion is therefore that, although from a physical point of view the perturbation theory treatment is straightforward and coherent, this paper stresses that one should be very aware to check whether the most and routinely used single state approach is accounted for. If it is

not properly accounted for, the results of a single state treatment may become very unreliable. In case of truly degenerate states only the full perturbation treatment is appropriate. In the case of low lying excited states, a very judicious choice needs to made based on the magnitude of the gap versus the effect of the perturbation.

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