(IS THERE) CHEMISTRY IN MOMENTUM SPACE

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Quantum chemistry can be described in what is most familiar to chemists: position space. Moreover, most chemists also prefer to think within the so-called Born-Oppenheimer approximation because in this way classical chemical ideas such as conformations, molecular structures in general, absolute configuration etc. all can be transferred to the quantum world. In position space we eventually derive a wave function where electrons *live* in orbitals and their kinetic energy is obtained via the Laplacian because of the quantum translation of the linear momentum.

On the other hand, one can perfectly equivalently decide to do not express the kinetic energy in terms of this position space kinetic energy term but simply use directly the momentum because

$$\frac{\hat{p}^2}{2} = \hat{T} \qquad\qquad\qquad (1)$$

One can then transform also the potential energy part of the Hamiltonian operator from position space by a Fourier transform and express it entirely in terms of momenta. This is a much less often taken route principally because of the complicated expression of the potential energy term and related problems to solve Schrödinger's equation.

Nevertheless, thanks to electron momentum spectroscopy, a small community has continued to work on chemistry in momentum space albeit seldomly through solving (approximately) the Schrödinger equation in momentum space but by first solving it in position space and then transforming the wave function obtained using the Fourier transform. The formulae needed, although involved for higher angular momentum basis functions, are basically easy to implement and one can run analysis on the wave function in a similar way as in position space. Moreover, the analysis is even easier if one restricts oneself to the density matrices. This way one can transform the one density matrix by simply transforming the basis functions as the matrix in basis function space in position space remains the same for the expansion in terms of the Fourier transforms of the basis functions. Completely equivalently to position space, the momentum density can be obtained as the diagonal element of the one density matrix. Note that a direct transformation from position space to momentum space of the electron density is not possible!

Momentum space density has been used previously by several attendants of the Girona 2010 workshop with the major contributors D.L. Cooper and N.L. Allan[1-4]. Recently we have also started to show an interest in this same field[5], namely the use of momentum density to express molecular quantum similarity[6]. But during our first steps in momentum space we have come across many features of this space that inspire us to the challenging title of this talk.

The first quite unexpected venture was based on a previous Hirshfeld partitioning of electron momentum densities by Balanarayan et al.[7]. These authors came up with an atom in the molecule

(AIM) in momentum space via of the molecular momentum density in atomic parts. This struck our interest as our research has handled extensively the extension of the Hirshfeld AIM[8] by introducing self consistency[9-10]. The reason for our amazement is that electron density in momentum space should have lost the relation with atomic positions through the Fourier transform. Moreover, a Fourier transform introduces a symmetry center that makes clear that holding on to Born-Oppenheimer position space views of molecules is questionable at best.

In short, Balanarayan et al. suggested to split the molecular momentum space density in the following way:

$$\rho_A(\mathbf{p}) = w_A(\mathbf{p})\rho_{Mol}(\mathbf{p}) \tag{2}$$

with the weight functions given as:

$$w_A(\mathbf{p}) = \frac{\rho_A^0(\mathbf{p}, N_A)}{\sum_B \rho_B^0(\mathbf{p}, N_B)} \tag{3}$$

Under the conditions:

$$\sum_A w_A(\mathbf{r}) = 1 \tag{4}$$

And for every atom:

$$0 \le w_A(\mathbf{r}) \le 1 \tag{5}$$

An obvious problem is then that when starting from a set of atoms where the electronic occupation equals the atomic number, every atom of the same element will have the same weight function value and this in every point in $\mathbf{p}$ space. This means that no distinction can be made between different atoms of the same element whereas it is this difference that plays the key role in much of chemistry. This is of course due to the centerpoint focused nature of $\mathbf{p}$ space. Balanarayan et al. avoided this problem in a pragmatic way by introducing in $\mathbf{p}$ space the difference between the atoms through a counterpoise like approach. The isolated atoms have their $\rho_A^0(\mathbf{p}, N_A)$ then computed in the molecular basis set. This means that the atom A is distinguished from the non-symmetry equivalent ones through the use of the difference in basis function surrounding of the atom. Reliance on a basis set, however, is undesirable especially since in this case if a complete atom centered basis set for every atom would be used, the distinction would again disappear. The problem of this approach is thus two-fold. First, neutral atoms are used in (3) possibly leading to arbitrary results and second incompleteness of the basis set is relied on.

Both problems were addressed by us in the following way. First the Hirshfeld or self-consistent Hirshfeld-I method is carried out in $\mathbf{r}$-space, leading to atomic populations N_A that will in general differ for non-symmetry equivalent atoms. Once these populations have been found, a density function must be constructed for the isolated atom in $\mathbf{p}$ space but for (usually) fractional numbers of electrons. This is done in a similar way as in Hirshfeld-I[9-10]. Atomic densities are computed for the isolated atom with $\text{int}(N_A)$ and $\text{int}(N_A) + 1$ electrons. As in $\mathbf{r}$ space, for an exact method there is a

linear relationship between the density function of an atom and the electronic occupancy so that the density function can be computed from:

$$\rho_A^0\left(\mathbf{p}, N_A\right) = \rho_A^0\left(\mathbf{p}, \mathrm{int}\left(N_A\right)\right)\left[\mathrm{int}\left(N_A\right) + 1 - N_A\right] + \rho_A^0\left(\mathbf{p}, \mathrm{int}\left(N_A\right) + 1\right)\left[N_A - \mathrm{int}\left(N_A\right)\right] \quad (6)$$

For each integer electronic occupancy the momentum space density is computed through a Hartree-Fock calculation of the one particle density matrix which is then Fourier transformed to $\mathbf{p}$ space and from which spherically averaged momentum space electron densities are computed using the formulae presented by Kaijser and Smith[11].

Once these data are available, the classical Hirshfeld analysis can be carried out in the usual way. However, an extra step can be again included by allowing for self consistency. In this scenario we proceed by application of the iterative scheme of known as Hirshfeld-I but now in $\mathbf{p}$ space.

As could be expected; the results show a dramatic failure. We used the same set of molecules as Balanarayan et al. and find the following results for the following types of calculations:

1. A Classical (non-iterative) Hirshfeld analysis in $\mathbf{r}$-space and subsequent use of the AIM electronic populations obtained for a classical Hirshfeld analysis in $\mathbf{p}$-space.
2. A Classical (non-iterative) Hirshfeld analysis in $\mathbf{r}$-space and subsequent use of the AIM electronic populations obtained for Hirshfeld-I analysis in $\mathbf{p}$-space.
3. Hirshfeld-I analysis in $\mathbf{r}$-space and subsequent use of the AIM electronic populations obtained for a classical Hirshfeld analysis in $\mathbf{p}$-space.
4. Hirshfeld-I analysis in $\mathbf{r}$-space and subsequent use of the AIM electronic populations obtained for Hirshfeld-I analysis in $\mathbf{p}$-space.

		H_2O	H_2S	NH_3	H_2CO
r space					
Hirshfeld	H	0.16 (*0.15*)	0.05	0.09	0.05
	X	-0.32(*0.31*)	-0.11	-0.27	-0.27
	C				0.17
Hirshfeld-I	H	0.47	0.12	0.34	0.02
	X	-0.93	-0.25	-0.27	-0.49
	C				0.46
p space					
Type 1	H	0.29 (*0.13*)	0.10	0.20	0.18
	X	-0.58 (*0.26*)	-0.20	-0.60	-0.68
	C				0.31
Type 2	H	1.00	0.983	>0.67	>0.62
	X	-2.00	-1.966	<-2.00	<-2.00
	C				>0.76
Type 3	H	0.55	0.17	0.42	0.16
	X	-1.10	-0.34	-1.26	-0.88
	C				0.57
Type 4	H	1.00	0.983	>0.67	>0.62
	X	-2.00	-1.966	<-2.00	<-2.00
	C				>0.76

Table 1: Atomic charges for $\mathbf{r}$ space Hirshfeld and Hirshfeld-I analyses and the 4 different types of momentum space Hirshfeld and Hirshfeld-I calculations in $\mathbf{p}$ space for all molecules. X denotes the heteroatom different from C. Where applicable, results by Balanarayan et al. are given in italics, based on their method to distinguish symmetry non-equivalent atoms.

Results for type 1 calculations
This type of calculations is the most similar to that presented by Balanarayan et al. except that we use a different strategy to initiate the Hirshfeld analysis in **p** space with different isolated atoms for non-symmetry equivalent atoms. In case of Balanarayan et al., this is done using the fact that in an incomplete atomic basis, atoms with a different surrounding have a different set of density matrices and thus also a different momentum density distribution. In our case, we use as distinguishing feature the different atomic electronic populations obtained from the Hirshfeld analysis in **r** space. According to Balanarayan et al., one of the gratifying features of their technique was the fact that the atomic charges resulting from the Hirshfeld analysis in **p** space seem chemically acceptable, meaning that they are in line with electronegativity considerations. Table 1 shows that similar results are obtained using our present algorithm. Within each molecule the trends are very similar to those in **r** space Hirshfeld. They are somewhat more outspoken than the results of Balanarayan et al., which is a consequence of the fact that the first (and here also the only) Hirshfeld step in momentum space is similar to a second iteration in Hirshfeld-I. Although the results within one molecule are in line with chemical intuition, comparison among molecules tells a different story. Both calculations in **r** space for instance give a more negative charge to the oxygen atom in H_2O compared to that in formaldehyde. The opposite is found in the type 1 calculations in **p** space. Based on the difference in electronegativity, the **r** space results do seem more intuitive. For the molecule H_2O, an interesting difference is found between the results of Balanarayan et al. and those in table 1. The **r**-space Hirshfeld charges on the atoms are quite similar but when going to **p**-space their charges grow smaller instead of the usual increase observed by them. We also find an increase in the charge. This points out that even the trends when comparing between **r**-space and **p**-space can be reversed depending on the method used to perform the Hirshfeld type analyses in **p**-space.

Results for type 2 calculations
The type 2 calculations start from a regular Hirshfeld procedure in **r** space starting from neutral atoms followed by the Hirshfeld-I procedure in **p** space. The interest in these calculations stems from the possibility to investigate whether the Hirshfeld-I procedure will also lead to a unique solution in **p** space, as in **r** space, but also from the fact that it allows to carry out a completely self consistent scheme in **p** space. As table 1 shows, the results are quite dramatic. Introduction of the self consistency step reveals that the atomic charges become very large resulting in hydrogen atoms losing virtually all electrons in H_2O and H_2S. The larger atoms very clearly have a dominant weight in virtually every point in **p** space. As a self consistent scheme is much better than the arbitrary Hirshfeld scheme where the results of the analysis depend on the starting points, this infers that AIM models in **p** space may have to be treated with care. This is further supported by the finding that for NH_3 and H_2CO the charges go over the bounds of the set of populations for which isolated atomic calculations were carried out. The latter calculations were limited to atomic electronic populations in the interval Z-2 to Z+2. Atomic calculations beyond these limits tend to suffer large consequences from inadequacies of the theoretical methods used here. Moreover; especially for the molecules considered here, atomic charges above 2 in absolute value are quite debatable.

Results for type 3 calculations
In these calculations, first a Hirshfeld-I type calculation is carried out in **r**-space and the electronic occupancies of the AIM used as a starting point for Hirshfeld analysis in **p** space. The results of these types of calculations reveal, in line with what was found for **r** space, that the choice of the set of starting points in a single step classical Hirshfeld calculation has a major effect. The charges obtained in **p** space are now much more outspoken than in the type 1 calculations. This clearly shows that, as in **r** space, the Hirshfeld analysis is inappropriate as it relies on a set of arbitrarily chosen starting electronic populations.

Results for type 4 calculations
The results from these calculations clearly show that, as in **r** space, building in the self consistency

requirement in Hirshfeld type of analyses results in a unique solution for the atomic charges although as in the type 2 calculations the results may lie out of bounds of what is available as starting atomic data. An interesting finding is that the population on the oxygen and sulfur atoms in H_2O and H_2S respectively lead to very similar results. This could be related to the fact that in momentum space the focus lies on valence electron density and since this is expected to be fairly similar in these two molecules similar populations should result. However, such a conclusion cannot be drawn based on these limited data and even if there is a relationship, the results are far from chemically intuitive nor acceptable within the limits one considers for atomic charges in these types of molecules.

The results above clearly show that the apparently interesting results for the Hirshfeld method in **p** space are mainly a consequence of the fact that the classical Hirshfeld method tends to lead to very small changes in population compared to the starting set of populations. So when a chemically somewhat acceptable set of atomic populations is used, the Hirshfeld procedure is likely to lead to a result that remains acceptable. This is what happens for types 1 and 3 in the calculations. However, the results are very dependent on the starting point.

The least one can say is that the results are debatable and that the results obtained in ref. 7 are, at best, the result of sticking to only the simplest approach and disregarding the need for self-consistency.

A second problem that was soon encountered in our first momentum space endeavours was that of alignment between molecules in momentum space. If one wants to compute quantum similarity, one needs to search for some maximum in some chosen similarity measure such as the Carbo index[12] or the (squared) Euclidean distance. Through the Fourier transformation, alignment is simpler in momentum space as we avoid the translation problem. We have implemented analytical formulae for the optimization of rotation angles for the maximization of the molecular quantum similarity measure and applied it to different molecules. When considering cases such as propane, dimethylether and its thio-analogue, the outcome looked quite promising because the (too) large influence of the core electron densities is absent in momentum space as the latter focuses more on the slow moving "valence" electrons. However, what do we measure in the quantum similarity measures mentioned when used in momentum space ? It is relatively straightforward to show that momentum space densities do not contain the nuclear coordinates anymore but rather differences in the coordinates. As such, we have lost the explicit nuclear framework which, in one respect is what we want to loose in the similarity measure but on the other hand, what effect does it have ? The effect, for a chemist, is quite amazing: there is no such thing as absolute configuration anymore in momentum space. Given the point of symmetry arising from the Fourier transformation, one cannot tell from the optimization of the rotation angles between molecules how the backtransform of the aligned geometry looks in position space. Was it the molecule in some absolute configuration or its inverse that was aligned with the other molecule, or was it also its inverse ? And the problem quickly appears that momentum space is insensitive to absolute configuration. There is no difference between a molecule and its mirror image. If the essential feature of life on earth is lost, what is to be thought in chemical terms of momentum space density ? On the other hand, one could argue that maybe the density matrix, which still holds information on the nuclear coordinates, would help. Unfortunately, it appears not. As the Fourier transformation obeys Parseval's theorem, it conserves orthonormality and as the basis representation of the density does not change, the so-called NOEL index[13] is the same in position and momentum space.

Hence the two open questions for discussion:

1. What to think about AIM in momentum space ? Can something be said on this issue or is this just a lost cause.

2. What to think of a space where absolute configuration has disappeared ? Where there is no distinction between two enantiomers ?

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