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Contribution to general Discussion

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General Discussion

Professor Bader opened the discussion of Professor De Proft's paper: Your method of calculating the hardness using HOMO and LUMO energies necessarily refers to the entire molecule. How does one relate this to the hardness of the individual atoms which is what one desires in using the hardness concept in the discussion of chemical reactivity?

Professor De Proft replied: This is an important remark. In order to use this quantity in studies of chemical reactivity and site selectivity, one needs to have a local counterpart of the hardness. Providing a satisfying theoretical definition of the local hardness has proven to be particularly troublesome, so, in order to probe the local hardness, one often uses the electrostatic potential of the system to study charge-controlled interactions.

Professor Savin asked: Can you be more explicit about the problems in the definition of the local hardness?

Professor De Proft answered: In density functional reactivity theory or conceptual DFT, the local softness $s(\mathbf{r})$ has been introduced as the derivative of the electron density $\rho(\mathbf{r})$ with respect to the chemical potential μ at a constant external potential $\nu(\mathbf{r})$:

$$s(\mathbf{r}) \equiv \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu} \right)_{\nu}$$

The local hardness can then be defined as:

$$\eta(\mathbf{r}) \equiv \left(\frac{\delta \mu}{\delta \rho(\mathbf{r})} \right)_{\nu}$$

It has been pointed out¹ that this functional derivative is ambiguous for a ground state, because for a ground state, $\rho(\mathbf{r})$ and $\nu(\mathbf{r})$ are dependent. By the Hohenberg–Kohn theorem, $\rho(\mathbf{r})$ completely determines $\nu(\mathbf{r})$. Other definitions of the local hardness have proceeded *via* the so-called hardness kernel.

- 1 (a) M. Berkowitz, S. K. Ghosh and R. G. Parr, *J. Am. Chem. Soc.*, 1985, **107**, 6811; (b) M. K. Harbola, P. K. Chattaraj and R. G. Parr, *Isr. J. Chem.*, 1991, **31**, 395.

Professor Bultinck asked: With a local xc functional, there is no integer discontinuity. Then it seems that $\chi = -\zeta + I$. Does this mean anything physical?

Professor De Proft answered: Within a finite difference approximation to the chemical hardness η and the electronegativity χ , this equation is exact. This implies that the hardness of the system, within this approximation, is equal to the negative of the electronegativity plus a system dependent constant (the ionization energy). For functionals averaging over the discontinuity, the discontinuity contributions approximately cancel for the electronegativity so it can be approximated as minus the average of the HOMO and LUMO eigenvalues, equivalent to the addition of an approximate I to the electron affinity calculated using eqn (11). For the chemical hardness however, half of the HOMO–LUMO gap underestimates the exact Parr and Pearson hardness by approximately half of the discontinuity.

Professor Mayer remarked: I would like to comment on your remark in a previous reply, according to which 'density determines potential'. I am not a specialist in DFT, but I think that physically it is the potential which determines

the density and the usual statement in DFT that ‘density determines potential’ only means that if given the density corresponding to the solution of the Schrödinger equation, then one can reconstruct from it the potential. Therefore, I do not see any problems with calculating partial derivatives $\delta/\delta\rho$ under constant potential.

Professor De Proft answered: I think that it is indeed the density that determines the full (non-relativistic, Born–Oppenheimer) Hamiltonian of the system. If one has the external potential $\nu(\mathbf{r})$, one can determine the ground state electron density of the system. By the Hohenberg–Kohn theorem, the ground state density determines the external potential. Thus, for a ground state, the density and the external potential are related so the derivative $\eta(\mathbf{r}) \equiv \left(\frac{\delta\mu}{\delta\rho(\mathbf{r})}\right)_\nu$ will indeed be ambiguous.

Dr Gatti said:

(1) This paper shows that the unconventional electron affinity approximation, as defined by eqn (11) in your paper

$$A = -(\epsilon_{\text{LUMO}} + \epsilon_{\text{HOMO}}) - I$$

affords reasonable values for this quantity and that the correlation of these computed values with the experimental affinities from electron transmission spectroscopy is much better than that obtained with other theoretical approaches.

Inspection of Fig. 1, which displays such a correlation, seems to suggest that at very low A values ($A < -3.0$) a different intercept (close to zero, as it should be in the absence of a shift between experimental and theoretical data) would probably be operative. Since there are only two data below -3.0 this could be just fortuitous. However, a check with more data in this region, could provide some interesting insight on the origin of the intercept shift (0.5), which seems to be mostly determined by the A values in the range between -1 and -2 .

Professor De Proft replied: This is an interesting remark. However, there are, as you state, only two data points with very low A values in our set of molecules so conclusions based on these values have to be taken with care. It is indeed true that the intercept of approximately 0.5 eV is determined predominantly by the systems with electron affinities above 3 eV. In a previous contribution, we have investigated the performance of eqn (11) on a limited set of molecules possessing negative electron affinities, including systems with very negative electron affinities such as CH_4 ($A_{\text{exp}} = -7.8$ eV), NH_3 ($A_{\text{exp}} = -5.6$ eV), H_2O ($A_{\text{exp}} = -6.4$ eV) and HF ($A_{\text{exp}} = -6.0$ eV). For these cases, eqn (11) was found to perform not as well in the estimation of the electron affinities; the intercept of the correlation line between the computed and experimental electron affinity values was comparable, however, with the intercept found in the present study, but the slope was considerably higher than 1.

Dr Havenith remarked: Do you get, like as usual in Hartree–Fock theory, positive LUMO energies? If so, I would guess that the electron affinities as defined by equation (11) are still very dependent on the basis set.

Professor De Proft replied: The LUMO energies obtained for a gradient corrected pure functional such as PBE used in this work are negative. Adding exact exchange increases the energy of the LUMO. However, whether it is positive or not will depend on the fraction of exchange that has been added.

Dr Karadakov asked: Can you provide a rigorous derivation of eqn (11)? The reason for asking this is that there is no formal extension of Koopman’s theorem to

virtual Kohn–Sham orbitals. If eqn (11) cannot be derived rigorously, then perhaps it should be flagged as an approximation, similarly to eqn (7)–(10)?

Professor De Proft replied: You are indeed right. If we had a functional that exactly averages over the discontinuity in the region where the LUMO is located, eqn (11) would be exact. As such, this equation should indeed be flagged as an approximation. It has to be added also that everything in this paper is in principle valid only for ground states.

Dr Torrent Sucarrat asked: The vertical electron affinity of eqn (11), $A = -\epsilon_{\text{lumo}} - (\epsilon_{\text{homo}} + I)$ can be considered as a correction of the ϵ_{lumo} , where this correction is the difference between the Koopman's approximation and the first vertical ionization potential and it can be used to correct the ϵ_{lumo} . Perhaps, an interesting application of this equation can be the extrapolation to the Janak theorem, *e.g.* $I_2 = -\epsilon_{\text{homo}-1} - (\epsilon_{\text{homo}} + I)$ or $A_2 = -\epsilon_{\text{lumo}+1} - (\epsilon_{\text{homo}} + I)$.

The N -differentiability of the hardness and chemical potential is usually solved using the finite difference, *i.e.* increment of one electron, and their applicability is checked with experimental values of the vertical ionization potentials and electron affinities. However, the chemical potential and hardness are defined as the first and second derivatives, respectively, of the energy with respect to the number of electrons and not necessarily the finite difference step of 1 electron can produce a stable numerical derivative. This fact perhaps can explain the failures of the experimental and theoretical methodologies to evaluate the chemical potential and hardness for some systems, *e.g.* the anions in gas phase.

Professor De Proft responded: As to the first part of the question, what you suggest would indeed provide an interesting extension. However, the approximation for the integer discontinuity is only valid for functionals that approximately average over the discontinuity. As such, the orbital considered (*e.g.* the HOMO–1 or the LUMO+1) has to lie in a region where the exchange–correlation potential approximately averages over the discontinuity. In practice, the exact Koopman's relationships are only exact for the HOMO and LUMO, not for the others.

In this contribution, we have indeed been working within the finite difference approximations to the definition of the chemical potential and the chemical hardness. I do agree that the finite difference step of 1 electron is indeed a large one, but, within the zero temperature limit, the energy is linear in the number of electrons on the left and right hand side of the N -electron system, the slope being different at the electron-deficient and electron abundant side. As such, the left hand and right hand side derivative $\partial E/\partial N$ of the energy with respect to the number of electrons would be exactly equal to the finite difference results. In such an approach however, the hardness $\partial^2 E/\partial N^2$ (left hand and right hand side) would equal zero.

Professor Bader opened the discussion of Professor Ayers' paper: The chemical potential μ that you equate to the negative of the electronegativity χ is given locally by the functional derivative of the energy expressed as a functional of the g.s. density $\rho(\mathbf{r})$. Thus every point in a molecule has the same chemical potential and electronegativity. I have trouble extending this idea to the Sanderson's electronegativity equalization principle, that I understand to mean that electronic charge is transferred from say group A to group B to an extent required to equalize their electronegativities in the final equilibrium adduct. But once A and B are considered to approach one another, they are part of a common system and possess the same electronegativity and this is true for all separations, not just the final equilibrium separation.

Professor Ayers responded: This observation is related to what Max Berkowitz calls “the EPR paradox of conceptual DFT.” Suppose I have a lithium atom and a fluorine atom that are very far away from each other; according to the electronegativity equalization principle, these two atoms should have the same electronegativity. That is, if you measure the electronegativity of the fluorine atom you would somehow be able to sense that there is a lithium atom very far away.

There are two responses to this dilemma. First of all, one notes that there is no formal mathematical difficulty. When a system consists of two fragments that are infinitely far apart, $\frac{\delta E_v[\rho]}{\delta \rho(r)}$ is not uniquely defined. In fact, $\frac{\delta E_v[\rho]}{\delta \rho(r)}$ has two values in that case, corresponding to the values for the two subsystems. (This happens because this is one of the rare cases where density-functional theory is exact not only for the ground states of the molecule and its ions ($\text{Li}\cdots\text{F}$, $\text{Li}^+\cdots\text{F}$, $\text{Li}\cdots\text{F}^-$, *etc.*), but also for some of the electronic excited states ($\text{Li}^+\cdots\text{F}^-$, $\text{Li}\cdots\text{F}^+$, $\text{Li}^-\cdots\text{F}^{2+}$, $\text{Li}^-\cdots\text{F}$, *etc.*).

The second thing to note is that the electron-transfer properties of the fluorine atom *are* dependent on the fact that there is a lithium atom far away. When one has LiF with a huge bond length, it is still true that the ionization potential of the whole system is the ionization potential of the lithium atom. If you remove an electron from fluorine, the energy of the system goes up by $\text{IP}(\text{F}) = 17.4$ eV. In time, however, an electron from Li will tunnel to F^+ , and the system will give off energy equivalent to the ionization potential difference ($\text{IP}(\text{F}) - \text{IP}(\text{Li}) = 12.0$ eV). If the atoms are well-separated, this time-dependent relaxation might be too slow to observe, but it is still there. Time-independent quantum mechanics (which is what the electronegativity equalization principle is based on) only sees the final stationary state. The electronegativity equalization principle, then, does not address the time-dependent nature of the electron-transfer phenomenon. This is conceptually intriguing, but it is not-so-important; one is usually interested in electron transfer between atoms that are bonded together.

Professor Bader said: Your paper contains the sentence “This constant [the one appearing in eqn (7) for the variation of $E_v(\rho, \text{g.s.})$ with respect to ρ] is identified with the Lagrange multiplier, μ , that forces the electron density to remain normalized to the number of electrons in the molecule.” A paper appeared in 1982¹ demonstrating that the value of μ_0 , the value of μ obtained at the point of variation, is independent of the normalization imposed on ρ . This result is obtained using Levys constrained variational procedure that extends the domain of variation to a domain that requires only that ρ be N representable, that is, that ρ must only integrate to some finite number, not necessarily N . The constraining parameters ϵ and μ in the variation of the energy functional expressed as a functional of ψ , $G[\psi, \epsilon]$, and the density functional $G[\rho, \mu]$ respectively, play corresponding roles. At the point of variation they have the values $\epsilon_0 = E_0$ and $\mu_0 = E_0/N$. However, ϵ_0 and μ_0 have meaning only at the point of variation and these values must be sharply distinguished from the arbitrary values assigned to the undetermined multipliers employed as normalization constraints on ψ and of ρ , respectively, during the variational procedure.

1 T. T. Nguyen-Dang, R. F. W. Bader and H. Essén, *Int. J. Quantum Chem.*, 1982, **XXII**, 1049–1058.

Professor Ayers answered: The evaluation of the chemical potential, $\mu = \left(\frac{\partial E}{\partial N}\right)_{v(r)}$, is very subtle. It cannot be done using the ordinary constrained search procedure (or any method based on the ordinary N -electron Schrödinger equation) because it requires calculating how the energy responds to changes in the number of electrons. As you vary the number of electrons, the normalization of the electron density changes (from N to $N + dN$) but the wave function must remain normalized to unity; there are many results in the literature that do not respect the normalization of the wave function and effectively define the density of an $N + dN$ electron system by

assuming that the wave function is normalized to $1 + dN/N$. I believe that Professor Bader was the first person to discover this difficulty.

If one attempts to compute the chemical potential using only information about the N -electron system (using, *e.g.*, the Levy constrained search¹), then one finds that the chemical potential is E_0/N , where E_0 is the ground state energy and N is the number of electrons. This result arises because all the electrons in the system are equivalent; the energy per electron is thus E_0/N . If one adds (or removes) a bit of an electron from the system, then the energy would decrease (or increase) by E_0/N . This is the wrong result because it neglects the subsequent relaxation of the other electrons; after one reduces the number of electrons by dN , then the remaining $N - dN$ electrons relax to “fill the gaps” left by the “partial electron” that was removed. This relaxation lowers the energy and means that E_0/N is a lower bound to the true chemical potential.

$$\mu = \lim_{dN \rightarrow 0^+} \left(\frac{E_0(N) - E_0(N - dN)}{dN} \right)$$

$$= \lim_{dN \rightarrow 0^+} \frac{1}{dN} \left[\underbrace{dN \left(\frac{E_0(N)}{N} \right)}_{\substack{\text{energy change for removing} \\ dN \text{ electrons}}} + \underbrace{\left(E_0(N - dN) - \left(E_0(N) - \left(\frac{dN}{N} \right) E_0(N) \right) \right)}_{\substack{\text{relaxation energy; the remaining electrons} \\ \text{contract toward the nucleus to fill the vacancy} \\ \text{left after the electron density was removed.}}} \right]$$

The relaxation term is not small: because all the electrons are equivalent, the electron density that is removed comes equally from the core regions (1s orbitals) and the valence regions; the relaxation of the remaining electrons into the “holes” in the core orbitals lowers the energy significantly. Thus, while E_0/N is a lower bound to the true chemical potential, it is not a tight lower bound except for systems with less than one electron; in such cases the “relaxation” term is zero and the lower bound is exact.

One reason that this is confusing is that in classical thermodynamics, the energy is an extensive property: for large numbers of classical particles, the energy increases linearly with the number of particles and thus $\mu = \left(\frac{\partial E}{\partial N} \right)_{V,S} = \frac{E_0}{N}$. Even for systems with very many electrons, the energy is not a linear function of the number of electrons because the Pauli exclusion principle dictates that additional electrons must occupy states with higher energy; which implies that $\mu > \frac{E_0}{N}$.

It is clear that correctly evaluating the chemical potential requires a model for the response in energy when the number of electrons (and thus the molecular Hamiltonian) changes; this simply cannot be done in the context of the N -electron Schrödinger equation. It can be done using the grand-canonical ensemble,² using Fock space Hamiltonians and wave functions,³ using size-consistency arguments and composite systems,⁴ or using electron propagator theory.⁵

1 M. Levy, *Proc. Natl. Acad. Sci. USA*, 1979, **76**, 6062.

2 J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Jr, *Phys. Rev. Lett.*, 1982, **49**, 1691.

3 P. W. Ayers, dissertation, University of North Carolina at Chapel Hill, 2001.

4 W. Yang, Y. Zhang, and P. W. Ayers, *Phys. Rev. Lett.*, 2000, **84**, 5172.

5 J. Melin, P. W. Ayers, and J. V. Ortiz, *J. Chem. Sci.*, 2005, **117**, 387.

Professor Frenking remarked: You are saying that the hardness increases with increasing charge. I can understand this for acids but not for bases. If you add an electron to a molecule the basicity increases and so does the polarizability which means that the hardness *decreases* with increasing charge.

Professor Ayers answered: This is a subtle point and I apologize for not being clearer. I agree for that for an atom or a molecule, adding electrons makes the molecule more negative and less hard.

By this comment, however, I mean to compare different molecules, and not different oxidation states of the same molecule. In most hard bases, the reactive site is an electronegative element from the upper-right-hand corner of the periodic table (e.g., nitrogen and oxygen). Owing to the high electronegativity of these atoms, the hard-base reactive sites tend to be more negatively charged than the soft-base reactive sites, which are typically located on larger (and less electronegative) atoms.

Professor Mayer asked: In your preprint you have provoked me by writing that in DFT “it is easy to . . . obtain the $N + \varepsilon$ electron density . . . Try doing this within the orbital model. How does one write a Slater determinant with $N + \varepsilon$ orbitals?”

In my opinion DFT does not invalidate the Schrödinger equation—it is a special mathematical technique for solving the Schrödinger equation in an implicit manner. Nothing can legitimately be done in the DFT framework, behind which there is—at least in principle—no wave function counterpart.

Therefore, it is legitimate to use fractional electron numbers in DFT *if and only if* one can define them in the wave function theory, too: one must not claim that DFT permits something which is not possible in the orbital model.

I have tried to solve the problem of writing down Slater determinants which behave as those with $N \pm \varepsilon$ electrons:

Slater determinant with $N - \varepsilon$ electrons: ($\varepsilon > 0$):

$$\Psi |_{N-\varepsilon} = \lim_{R \rightarrow \infty} \hat{\mathcal{A}}\{\varphi(1) \dots \varphi_i^{-\varepsilon}(i) \dots \varphi(N)\}$$

Where

$$\varphi_i^{-\varepsilon}(i) = p\varphi_i(\vec{r}_i, \sigma_i) + q\chi(\vec{R} - \vec{r}_i, \sigma_i)$$

$$p = \sqrt{1 - \varepsilon}; \quad q = \sqrt{\varepsilon}$$

At *finite distances* behaves as a determinant for $N - \varepsilon$ electrons.

Slater determinant with $N + \varepsilon$ electrons: ($\varepsilon > 0$):

$$\Psi |_{N+\varepsilon} = \lim_{R \rightarrow \infty} \hat{\mathcal{A}}\{\varphi(1) \dots \varphi(N)\varphi_{N+1}^{+\varepsilon}(N+1)\}$$

Where

$$\varphi_{N+1}^{+\varepsilon}(N+1) = q\varphi_i(\vec{r}_{N+1}, \sigma_{N+1}) + p\chi(\vec{R} - \vec{r}_{N+1}, \sigma_{N+1})$$

$$p = \sqrt{1 - \varepsilon}; \quad q = \sqrt{\varepsilon}$$

At *finite distances* behaves as determinant for $N + \varepsilon$ electrons.

As these two procedures are conceptually different, the functional derivatives $\frac{\delta E}{\delta \rho}$ of DFT may also be different depending on whether $\int \delta \rho(\vec{r}) d\nu < 0$ or $\int \delta \rho(\vec{r}) d\nu > 0$.

Professor Ayers answered: The question of how to define a Slater determinant (or, in general, any wave function) with a fractional number of electrons is quite old; it is a problem that my thesis advisor (Bob Parr) has been interested in for at least 25 years.

Much is known at this stage. The construction that Professor Mayer proposes resembles one that I proposed, along with Weitao Yang and Yingkai Zhang.¹ In this approach, the number of electrons in the whole system is an integer, but the “population” of the subsystems is a fractional number of electrons because the excess electrons are located elsewhere. The idea is very simple: a system with $N + p/q$

electrons can be constructed by taking q copies of the system and placing them infinitely far apart. Add p extra electrons and choose the totally symmetric choice for the ground state wave function. One ends up with q identical systems, and so each system must have $N + p/q$ electrons. Moreover, all of the systems must have the same energy, and so their energy is $(1 - p/q)E^{(N)} + p/qE^{(N+1)}$. ($E^{(N)}$ and $E^{(N+1)}$ denote the energies of the N -electron and $N + 1$ -electron systems.) This approach gives the same results that one would obtain using the zero-temperature grand canonical ensemble² or using a Fock-space approach to electrons with a non-integer electron number.³ As Professor Mayer notes, this sort of construction implies that number-increasing processes ($\langle\delta r(\mathbf{r})\rangle > 0$ and number-decreasing processes ($\langle\delta r(\mathbf{r})\rangle < 0$ are fundamentally different. (This well-known feature is responsible for the “band gap problem” in approximate density functionals.)

While I agree with Professor Mayer that everything in density-functional theory must, as an exact theory, be formally reducible to wavefunction theory, I still do not believe that wavefunction theory treats fractional electron numbers as naturally as DFT does. The most primitive models in wavefunction theory (single Slater determinants without any “delocalized” extra electrons) build in the fact that the number of electrons in a closed system is always an integer. The most primitive models for density functional theory (Thomas–Fermi-type models) automatically include fractional electron number. Indeed, such models include fractional electron number *too well*, and thus fail to predict that heteronuclear diatomic molecules dissociate into neutral atoms.

- 1 W. Yang, Y. Zhang, and P. W. Ayers, *Phys. Rev. Lett.*, 2000, **84**, 5172.
- 2 J. P. Perdew, R. G. Parr, M. Levy and J. L. Balduz, Jr, *Phys. Rev. Lett.*, 1982, **49**, 1691.
- 3 P. W. Ayers, *PhD Thesis*, University of North Carolina at Chapel Hill, 2001.

Professor Ayers opened the discussion of Professor Nguyen’s paper: There have been some preliminary indications (based largely on the work of Chamorro, with help from Geerlings, De Proft, and others) that spin-dependent reactivity indicators are especially useful for describing radical reactions. I wonder if the author has investigated spin-dependent indices, to see if they might help in the problematic cases cited in his paper.

Professor Nguyen responded: We have carried out some work on the spin-philicity and spin-donicity, as introduced by Perez *et al.*,¹ for simple high spin species such as nitrenes and phosphinidenes.² There is a correlation between their spin-donicity, spin release indices and singlet–triplet energy gaps, but we have not yet considered these parameters in radical reactions. This is certainly a way of approaching the radical reactivities.

- 1 P. Perez, J. Andres, V. S. Safont, O. Topia and R. Contreras, *J. Phys. Chem. A*, 2002, **106**, 5353.
- 2 J. Olah, T. Veszpremi and M. T. Nguyen, *Chem. Phys. Lett.*, 2005, **401**, 337.

Professor Geerlings asked: You write the Fukui function for radical attack as a weighted average of f^+ and f^- . How would you estimate the corresponding weight factors?

Professor Nguyen replied: We have indeed proposed to use a weighted Fukui function for radical attack:

$$f(0) = a f(+) + b f(-)$$

with coefficients a and b being smaller or larger than 0.5, but we did not yet carry out a systematic test to determine them for a large series of radicals. Our approach is

electrons can be constructed by taking q copies of the system and placing them infinitely far apart. Add p extra electrons and choose the totally symmetric choice for the ground state wave function. One ends up with q identical systems, and so each system must have $N + p/q$ electrons. Moreover, all of the systems must have the same energy, and so their energy is $(1 - p/q)E^{(N)} + p/qE^{(N+1)}$. ($E^{(N)}$ and $E^{(N+1)}$ denote the energies of the N -electron and $N + 1$ -electron systems.) This approach gives the same results that one would obtain using the zero-temperature grand canonical ensemble² or using a Fock-space approach to electrons with a non-integer electron number.³ As Professor Mayer notes, this sort of construction implies that number-increasing processes ($\langle\delta r(\mathbf{r})\rangle > 0$ and number-decreasing processes ($\langle\delta r(\mathbf{r})\rangle < 0$ are fundamentally different. (This well-known feature is responsible for the “band gap problem” in approximate density functionals.)

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with coefficients a and b being smaller or larger than 0.5, but we did not yet carry out a systematic test to determine them for a large series of radicals. Our approach is

based on the differences between the vertical ionization energies and electron affinities of the radicals considered with respect to those of a 'reference' system. The choice of such a reference is not obvious. In addition, determination of a consistent set of electron affinities remains a problem. We hope to be able to address this issue in the near future.

Dr Torrent Sucarrat asked: The Fukui function has been an useful tool to describe reactions in terms of the properties of isolated systems, however the reactions are the result of different kinds of interactions (electrostatic, orbital interaction, steric repulsions, *etc.*), where the only correction description is the kinetic and the thermodynamic study of the system. The radical additions are very complex reactions and perhaps it is demanding too much for the Fukui functions to predict their reactivity.

Professor Nguyen answered: That is exactly the purpose of the reactivity indices, based either on MO or DF theories, to use the properties of the unperturbed reactants to understand the outcome of their reactions. It does not make much sense to consider reactivity parameters on the basis of perturbed supersystems along the reaction pathways. Don't forget that chemists have at hand a powerful tool, also provided by quantum mechanics, which is the orbital concept. The frontier orbital theory is successful in interpreting the selectivities in different classes of organic reactions. In view of the fact that, in the actual definition, the local softness $s(r)$, which is related to the Fukui function $f(r)$ by the global softness S :

$$s(r) = f(r) \cdot S$$

includes not only the frontier orbital term in S but also the difference in atomic charges in $f(r)$, the inherent advantages and limitations of both MO and DFT-based approaches are expected to be similar.

I fully agree that we cannot expect too much from any qualitative approach. For a process in which the electronic and geometric changes are large (such as protonation), reactivity indices simply fail to predict its regioselectivity. Concerning the DFT-based indices, an additional difficulty is that they are defined with respect to a constant external potential, a condition which can hardly be satisfied during the course of a chemical reaction.

It has been shown¹ that the "principle of maximum hardness", which states that under constant chemical potential and external potential, the hardness should be a maximum when the energy has a minimum value, is correct only under severe conditions. In fact, this has been proved to be correct only when both HOMO and LUMO energies have extrema at the transition structure, with respect to the reaction coordinate.

Although some similar requirements might be expected for the use of local softness, the current difficulties arise rather from their quantitative evaluation, in particular the determination of vertical electron affinities of neutral systems and atomic net charges.

1 A. Chandra and T. Uchimaru, *J. Phys. Chem. A*, 2001, **105**, 3578.

Professor Bultinck opened a general discussion of the papers by Professor De Proft, Professor Ayers and Professor Nguyen: The world of conceptual Density Functional Theory makes regular use of the properties of Atoms-In-the-Molecule (AIM). As is commonly known, there exists an entire plethora of methods to distinguish the AIM, ranging from Mulliken's method to 3D-space methods such as the one by Bader. Other examples include the Hirshfeld method, Fuzzy atoms, *etc.*

Several of these methods seem questionable to me in some respect. Taking as an example the Hirshfeld procedure,¹ one distinguishes an AIM density for atom A as:

$$\rho_A(\mathbf{r}) = w_A(\mathbf{r})\rho(\mathbf{r}) \quad (1)$$

with

$$w_A(\mathbf{r}) = \frac{\rho_A^0(\mathbf{r})}{\rho_{\text{Mol}}^0(\mathbf{r})} = \frac{\rho_A^0(\mathbf{r})}{\sum_A \rho_A^0(\mathbf{r})} \quad (2)$$

$\rho_A^0(\mathbf{r})$ is the electron density computed for the isolated atom A, and the promolecular density $\rho_{\text{Mol}}^0(\mathbf{r})$ is the density of the superposition of all $\rho_A^0(\mathbf{r})$ with all atoms A positioned as in the real molecule with density function $\rho_{\text{Mol}}(\mathbf{r})$.

The Hirshfeld AIM is often used to obtain atomic populations by straightforward integration. Problems, however, do arise since:

1. The charges are often virtually zero, in clear contrast to other schemes
2. The charges depend quite heavily on the promolecule chosen. As an example take LiF. With the promolecule: $\text{Li}^0 + \text{F}^0$ one gets $q = 0.57$ $\text{Li}^+ + \text{F}^-$ one gets $q = 0.98$ $\text{Li}^- + \text{F}^+$ one gets $q = 0.30$ (always Li positive)
3. Charged molecules are problematic
4. Current computational schemes are not in line with the information entropy background of the Hirshfeld scheme.

An information entropy background for the Hirshfeld AIM2-4 is based on the entropy:

$$I = \int \rho_A(\mathbf{r}) \ln \left(\frac{\rho_A(\mathbf{r})}{\rho_A^0(\mathbf{r})} \right) d\mathbf{r} + \int \rho_B(\mathbf{r}) \ln \left(\frac{\rho_B(\mathbf{r})}{\rho_B^0(\mathbf{r})} \right) d\mathbf{r} \quad (3)$$

but this implicitly implies that:

$$N_A = \int \rho_A(\mathbf{r}) d\mathbf{r} = \int \rho_A^0(\mathbf{r}) d\mathbf{r} = N_A^0 \quad (4)$$

That is: the AIM needs to have the same occupation number as the promolecular atom. Failure to meet this condition hampers the connection between the Hirshfeld approach and information theory. It would therefore seem advisable to explicitly consider requirement (4) in the Hirshfeld AIM population calculations so that what one computes is effectively the AIM population in the molecule when all net charge transfer has stopped. This can be done in an iterative fashion,⁵ which makes that:

1. Charges from the iterative scheme are a factor of 3 bigger.
2. The dependence on the promolecule chosen is removed.
3. Charged molecules are perfectly well possible.
4. The information entropy background is fulfilled.

This means that the Hirshfeld scheme should not be used as it is currently, but an iterative scheme is required. Only then one can make rigorously sure that the AIM charges do reflect the AIM properties in the molecule when no net charge transfer is taking place any more. This also means that rather than relying on a user based decision of what the promolecule should be for a given molecule, the molecular density function determines its own promolecule. This is similar to having Bader's theory determine the atomic basins in a given molecular density function without external intervention.

I do not see how this is straightforwardly possible in fuzzy atoms or Voronoi deformation densities. The presently described new Hirshfeld approach gives results that differ significantly from the original scheme and therefore raises some questions on the effect of using only *e.g.*, geometrical information to identify AIM or to rely on parameters that are independent on the molecular density function. At least in the Hirshfeld scheme several reactivity descriptors also tend to change quite drastically when applying the iterative scheme. These changes are found to be reminiscent to the findings on Fukui functions by Ciosloski *et al.* when using Bader's method.⁶

- 1 F. L. Hirshfeld, *Theor. Chim. Acta*, 1977, **44**, 129.
- 2 R. F. Nalewajski, R. G. Parr, *Proc. Natl. Acad. Sci. USA*, 2000, **97**, 8879.
- 3 R. G. Parr, P. W. Ayers and R. F. Nalewajski, *J. Phys. Chem. A*, 2005, **109**, 3957.
- 4 P. W. Ayers, *Theor. Chem. Acc.*, 2006, **115**, 370.
- 5 P. Bultinck, C. Van Alsenoy, P. W. Ayers, R. J. Carbó-Dorca, *J. Chem. Phys.*, 2006, in press.
- 6 J. Cioslowski, M. Martinov and S. T. Mixon, *J. Am. Chem. Soc.*, 1993, **97**, 10948.

Professor Nguyen responded: Before the arrival of the “zoo of density functionals”, a “zoo of atomic charges” already existed! As we long know, there is no unified definition for this important concept. Any partition of the electron density is inherently arbitrary, and there is no general way of evaluating them accurately.

Concerning the evaluation of condensed Fukui functions $f(\mathbf{r})$ from stockholder charges, Van Alsenoy and coworkers (another Belgian group)¹ pointed out that these types of charges are neither better nor worse than other partitions.

I don't know if there is any difference between your actual calculations of the stockholder charges and that of our colleagues from Antwerpen.

Another interesting point I wish to mention is that you showed some negative Fukui function values. We also obtained some negative values for this index (*cf.* our paper²). There has been some discussion about the nonnegativity of $f(\mathbf{r})$,³ but I don't see a reason for the argument that $f(\mathbf{r})$ cannot have a negative value. It could be as it corresponds to a large change of the electron density in going from a neutral to a charged state, or even from an anionic to a cationic state.

- 1 J. Olah, C. Van Alsenoy and A. B. Sannigrahi, *J. Phys. Chem. A*, 2002, **106**, 3885.
- 2 A. K. Chandra and M. T. Nguyen, *Faraday Discuss.*, 2007, **135**, DOI: 10.1039/b605667a
- 3 R. K. Roy, K. Hirao and S. Pal, *J. Chem. Phys.*, 2000, **113**, 1372.

Dr Salvador answered: Unfortunately, in the report of Professor Bultinck there are not many details of such an iterative procedure which could, indeed, be very promising. The only condition that the promolecule densities must fulfil (apparently) is that they integrate to the same population as the actual atomic density.

While the apparent lack of a reference state does itself represent a major improvement in the Hirshfeld fuzzy atom framework, I don't see why the fulfilment of some particular condition from information entropy itself makes a Hirshfeld fuzzy atom *necessarily superior*. (For instance, one could also argue that *any* disjoint partitioning in non-overlapping domains is superior to *any* fuzzy atom treatment just because only the latter are considered within Loge Theory¹).

One also wonders to what extent the promolecule density after the iterative procedure depends on its initial choice. It is hard to believe that the solution is unique provided that the condition

$$N_A = \int \rho_A(\mathbf{r}) d\mathbf{r} = \int \rho_A^0(\mathbf{r}) = N_A^0$$

can be held by an infinite set of properly normalized one-electron functions.

Minor comments to points raised by Professor Bultinck are:

Concerning the Hirshfeld fuzzy atom approach using neutral promolecule densities, it is claimed that “the charges are often virtually zero, in clear contrast to other schemes”. In my opinion, the reported value of 0.57e for the partial charge in the case of LiF looks pretty reasonable.

There is an explicit distinction between Hirshfeld and fuzzy atoms. One might (wrongly) infer that Hirshfeld atoms are not *fuzzy* as well.

1. R. Daudel, G. Leroy, D. Peeters and M. Sana, *Quantum Chemistry*, John Wiley and Sons Ltd., Chichester, W. Sussex, UK, 1983.

Dr Bickelhaupt† replied: I consider Professor Bultinck's idea of a "self-consistent Hirshfeld charge" highly interesting and worth exploring. At the same time, I would like to stress that this new definition does not make the concept of an atomic charge more absolute. It is evident that the iterative scheme tends to amplify any polarization that occurs. I think one should be aware that atomic charges are very useful but not absolute polarity indicators. Different atomic charge methods have different scales and yield evidently different values for the same situation: Only trends of atomic charges computed with one and the same method can be physically meaningful.

Professor Geerlings said: The field of conceptual DFT is now about 25 years old. Can we consider that the field is now 'mature', for example is it stable towards further expansion of the number of descriptors (danger of proliferation); should we not think of some guidelines for 'good practice' and did the field yield the level of 'predictability', important when it is used by *e.g.* experimentalists?

Professor Nguyen responded: That is a long period as compared with the life of the frontier orbital theory (first proposed by Fukui in 1952) or the Woodward–Hofmann rules (put forward around 1965). These theories were rapidly adopted by chemists not only by their success but also by their simplicity. That was greatly helped by the fact that in the 1960s, there was a severe lack of a qualitative theory which could help organic chemists to interpret the mechanisms of their reactions, and up to the 1970s, quantitative MO calculations were not available (or not accurate with wavefunctions hardly going beyond the HF level with a minimal basis set).

Nowadays, accurate quantum chemical calculations, using either MO or DF theories, performed on a PC, become a multi-purpose spectrometer (having the same status as a mass, IR or NMR spectrometer), which allows experimental chemists to characterize their compounds with confidence (or to obtain additional information) and to understand the relevant reactive processes. On the other hand, the concept of orbital remains powerful in the chemists thinking. Therefore, the future of DFT-based indices as an alternative to the existing qualitative indices, lies in their inherent abilities, as to whether they are equally powerful to explain, but also simple to use and easy to understand.

I do not think that any 'standard' or 'good practice' could be imposed or put forward in a qualitative approach, and nothing could stop theoretical chemists from proposing new and new methods, functionals or indices. That is actually their role! A minimum point one could agree upon is about the way of evaluating the atomic charges!

Much work remains to be done for the applications of DFT-indices in different novel fields, beyond the classical domains of organic and organometallic chemistry. In a time of globalization of every thing, a global index is perhaps not avoidable.

Professor Ayers answered: I think that conceptual DFT is nearing maturity, but not quite there yet. Perhaps the field is in a state of adolescence: the main ideas and methodology were learned long ago (mostly in the 80s) and—with a few exceptions—have been mastered in the intervening years. Like an adolescent, the field is

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more fundamental indicators. This is not to say that the more specific “derived” indicators are not useful, but they tend to be specialized indicators that are designed to describe specific chemical processes, in contrast to the fundamental “perturbation-based” indicators, which are universally valid (but often less directly applicable).

Professor Bultinck remarked: Good computational practice! As in QSAR, one should do proper cross correlation analysis. There is no need to use conceptual DFT descriptors for all studies. Sometimes one could simply do with the numbers of atoms.

Professor Lecomte opened the discussion of Dr Glukhov’s paper: Just a quick question about the hydrogens’ refinement: did you try to have neutron data (even if boron is present), what about the H’s anisotropic displacement parameters?

Dr Glukhov responded: No, we did not. But before the multipole refinement all C–H and B–H bonds were “normalized” to the values, obtained from the quantum–chemical calculations. For B–H bonds the value was 1.20 Å.

Professor Bader stated: QTAIM defines an atom as an open quantum system and it is natural for one to enquire as to the possibility of using QTAIM to recover the ideas put forth by Parr regarding the chemical potential μ : could such an atomic definition recover the constancy of μ throughout the charge distribution and hence its equalization among all of the atoms. In analogy with the thermodynamic definition of μ , one could consider a molecule as a system containing a single component—the electrons—distributed over a number of phases—the atoms. The number of electrons in a given atom A , $N(A)$, is an average number with a non-vanishing fluctuation, as required by the thermodynamic analogy with an open system. The chemical potential of atom A is then given by the derivative of the total energy E with respect to $N(A)$: $\mu(A) = \partial E / \partial N(A)$. [Note that one is not interested in $\partial E(A) / \partial N(A)$ if one wishes to retain the thermodynamic analogy]. I think that such a definition of $\mu(A)$ has meaning within chemistry only if one specifies what causes the change in $N(A)$. To my mind, for any adiabatic change, one is restricted to a change in an external parameter X that appears in the molecular Hamiltonian, which for chemical purposes would mean changes in nuclear coordinates or the application of an external electric field. (Interestingly, the first-order correction to the wave function is imaginary and the density is correspondingly unperturbed by the application of a uniform magnetic field). If one takes X to be a nuclear coordinate, then one could use the open system derivation of the Feynman force theorem as given by the atomic average of the commutator of H and X . This approach generates a complicated surface term involving gradients of the derivative of the wave function with respect to the nuclear displacement. One could instead simply consider the quantity $\mu(A)$ to be defined as $\mu(A) = [\partial E / \partial X] [\partial X / \partial N(A)]$ where the inverse of the final derivative, $\partial N(A) / \partial X$, determines the dependence of $N(A)$ on X . The term $\partial E / \partial X$ could be evaluated numerically while the dependence of $N(A)$ on X would involve two contributions; a basin term involving $\partial \rho / \partial X$ and a surface term determined by the averaging of ρ over the shift in the atomic surface. Todd Keith [private communication] has derived an analytical expression for the basin contribution in terms of the nuclear induced changes in the basis functions and in their coefficients. The surface term may be evaluated numerically. The sum of the $\partial N(A) / \partial X$ terms over the molecule will vanish because of charge conservation and the inverse of each such term determines the atomic contribution to the change in E caused by a nuclear displacement. Consequently, such a definition of $\mu(A)$ does not recover the equality of chemical potentials, since in a diatomic molecule for example, $\mu(A)$ necessarily equals the negative of $\mu(B)$.

Professor Ayers replied: Professor Bader raises a good point: understanding molecular electronic structure based on the electron density (AIM theory) and understanding molecular reactivity theory based on the electron density (density functional reactivity theory) are sister disciplines, but this has not been exploited. Finding links between the disciplines is a priority for future research. Many of Professor Bader's detailed comments pertain to the change in atomic population with respect to a displacement of the atomic nuclei; such reactivity indicators are ordinarily called "nuclear" reactivity indicators. They date back to the work of Morrell Cohen and his coworkers¹

I find it interesting to speculate about how one might compute the electronegativity directly using perturbations. First of all, I would confirm what Professor Bader suggests: one is certainly interested in the change in the *total* energy with respect to a change in the number of electrons in a fragment. That is the content of the electronegativity equalization principle; the derivative of the atom-in-a-molecule's energy with respect to the population of the AIM does not need to be the same for all the AIM. (In fact, I doubt that it is.)

I think, however, that computing $\left(\frac{\partial E}{\partial N_A}\right)_{v(r); N_{B \neq A}}$ directly will be difficult. One approach would be to measure the molecular response to an electric field, which will polarize the molecule and shift electrons from one fragment to another. Using the relationship between polarizability and softness would give information about the second derivative (the local softness). One might be able to extract information about the first derivative also, but matters are complicated because imposing the field changed the electronic population of all of the atoms, and not just one or two. (This is a general feature: changing the Hamiltonian usually changes the electronic population of all the atoms at once.) One speculative possibility would be to perturb the molecule with an electric field, and then remove the field. The molecule is now in a non-stationary state, and by studying how the electron density redistributes one might learn something about $\left(\frac{\partial E}{\partial N_A}\right)_{v(r); N_{B \neq A}}$. In general, this would require a time-dependent treatment of electron dynamics.

Another way to address this problem is to consider the AIM as a grand canonical ensemble of electrons. The density matrix of the AIM can then be written as: $D = p_0|0\rangle\langle 0| + p_1 D_1(r_1, r_1') + p_2 D_2(r_1, r_2; r_1', r_2') + \dots$ p_k is the probability of observing exactly k electrons on the AIM of interest while the remaining $N - k$ electrons are in other atoms and D_k is the density matrix for this k -electron atom. This mathematical formulation allows one to compute any property of an AIM, and so it provides a (theoretical) link between AIM theory and conceptual DFT (which are based on response properties of the molecule as a whole). The challenge is how one can use this mathematically unwieldy density matrix to compute the response properties of the AIM. Even more, perhaps, the challenge is how to approximate this density matrix in a way that is more mathematically facile than "brute strength" regional integration methods.

1 M. H. Cohen, M. V. Ganduglia-Pirovano, and J. Kudrnovsky, *J. Chem. Phys.*, 1994, **101**, 8988.

Professor Ponec commented: The design and the use of reactivity indices based on conceptual DFT theory is certainly one of the active fields of contemporary chemical research. Although it is true that the design and the calculation of these indices can certainly be valuable from the computational point of view of DFT theory, I am much less optimistic about their application as reactivity indices. Chemical reactions very often proceed by reaction mechanisms involving several steps and the hope that the reactivity could be understood only on the basis of indices derived from initial starting reactants without taking into account also the attacking reactant and without being sure what step of the actual reaction mechanism is rate determining seems a bit naïve to me. In this respect these indices resemble the static reactivity

indices such as electron densities, free valences, super delocalisabilities, *etc.* which were studied many years ago using Hückel theory and which were abandoned mostly because people became aware of their limitations. Nowadays such reactivity indices seem to be reintroduced at a much more sophisticated level of the theory but one should keep in mind that the sophistication of the modern computational tools cannot remove the conceptual limitations of such an approach.

Professor Mayer responded: Although it is true that “chemical reactions very often proceed by reaction mechanisms involving several steps”, making it impossible the “reactivity...[to] be understood only on the basis of indices derived from initial starting reactants”, the properties of the reactants often are of decisive importance. This is indicated by the successes of the empirical reactivity parameters like Hammett constants and different QSAR methods, and is also confirmed by our experience concerning the prediction of the simple mass-spectrometric cleavages on the basis of considering merely the vertical ionization of the starting molecule and even that in a “quasi-Koopman’s” approximation, either at semiempirical or at *ab initio* levels.¹

Therefore, I think studying reactant indices of monomers is not a futile task.

1 I. Mayer and Á. Gömör, *THEOCHEM*, 1994, **311**, 331; *Chem. Phys. Lett.* 2001, **344**, 553.

Professor Ayers replied: I agree with the gist of this comment. I would go further and say that density-functional reactivity theory is only rigorously valid when the transition state lies early on the reaction path, so that the perturbation expansion about the separated reagent limit (which is what DFT reactivity theory is based on) contains information that is relevant to the structure of the transition state. (The fact that DFT reactivity theory works well even when the transition state does not lie especially early on the reaction path may be related to the empirical success of hill climbing methods and attributed to the smoothness of the potential energy surface away from conical intersections and nuclear–nuclear coalescence points.)

That said, I am more optimistic than Professor Ponec for multi-step reactions. First of all, in many cases the location where the reagent attacks controls the subsequent steps. (In many multi-step reactions, the reaction proceeds inexorably to a given product molecule after the initial attack. This is certainly the case in many organic substitution reactions.) But DFT reactivity indices can be used even in less favorable cases. As Professor Ponec notes, the reactivity indices usually predict the first step of the reaction. This is enough information to predict the first reactive intermediate. The reactivity indices of the first reactive intermediate can then be computed; this will provide information about the second step of the reaction. Likewise, computing the reactivity indices of the second reactive intermediate gives a prediction for the structure of the third reactive intermediate. And so on. (If one does not wish to use this stepwise procedure, there are formal mathematical arguments that DFT reactivity would still work, provided one went to high enough orders in the perturbation series. I believe that approach is computationally daunting and has limited conceptual utility. But at a purely formal level, it works.)

I also agree with Professor Ponec that the main ideas in DFT reactivity theory are not new. One of the innovative features of DFT reactivity theory is that the dependence of the system on the number of electrons appears in a very natural way, but many of the most important implications (*e.g.*, the electronegativity equalization principle and the Hard/Soft Acid/Base principle) had been discovered prior to the advent of DFT reactivity theory.

As Professor Ponec notes, computing DFT reactivity indicators at the level of Hückel theory often recovers familiar reactivity ideas and concepts. I believe that this mimicking of the classic reactivity indicators is powerful and useful. DFT reactivity theory extends the classical concepts because it includes the effects of orbital relaxation and electron correlation. (While these effects are not important in most cases, sometimes they are decisive.) DFT reactivity theory also supersedes

orbital models because every fundamental reactivity indicator is an experimentally observable response of the system to a perturbation. This stands in stark contrast to orbital-based methods, which are based on unobservable (albeit very useful) quantities. I find it remarkable and reassuring, then, that DFT recovers these classic reactivity indicators. DFT reactivity theory is based on exact quantum mechanics (and not a nonquantitative MO-based or VB-based model) and DFT reactivity indicators are observables. This leads me to make the provocative statement: orbital-based qualitative tools work *because* the orbital-based tools are often good approximations to the more rigorous and more fundamental DFT-based quantities.

Professor Lecomte addressed Dr Glukhov: When I look to intermolecular interactions, one can guess at B–H···H–C interactions to stabilize the structure. Did you calculate the AIM charges of the H atom and if yes, what is their contribution to the crystal energy? It should be important because H may be as large as $-0.7 e$ (as we obtained in a molecule containing B–N, B–H bonds). How do you explain B–H···H–B interactions? Dynamic polarization of the hydrogen density?

Dr Glukhov responded: For the compounds, described in this paper we have not performed such a calculation. We have done this for a different compound—8,9,10,12-tetrafluoro-*o*-carborane, where we have shown that hydrogens bonded to borons have significant negative charge (*ca.* $-0.55 e$), while for C–H group it is equal to $+0.15 e$.¹ So for the B–H···H–C interactions one can clearly expect an electrostatic contribution to the bonding. But we were really amazed, that for the B–H···H–B interactions with equal charges on the hydrogen atoms we see no difference neither in geometry nor in energy in comparison to the former ones. We are not quite sure how one should explain these interactions but it is clear that due to their big number they should govern the formation of crystal packages in the absence of stronger interactions.

1 Glukhov *et al.*, *Struct. Chem.*, 2007, in press.

Professor Bader commented: Your finding of intermolecular H–H bonding in the carborane systems provides a pathway into a discussion of the role of charge transfer in bonding. A number of papers presented at this meeting distinguish between electrostatic as opposed to orbital or covalent interactions as the source of chemical bonding. This can lead to the misconception that bonding either requires an interatomic transfer of charge or that in its absence, the mechanics of bonding is somehow different. One finds bond paths denoting H–H bonding in cases extending over the complete spectrum of possible interatomic charge transfer. At one extreme, one H atom is negatively charged and acts as the base atom in forming a hydrogen bond with another H atom bearing a positive charge. This is the case in your finding a bond path between a H bonded to a boron and another H bonded to a carbon. However, H–H bond paths and their associated interactions are found to occur over the complete spectrum of charge transfer, down to the case where both H atoms bear quite small, equal charges as found in planar biphenyl or the nonlinear polybenzenoids such as phenanthrene.¹ To argue, as some do, that the presence of a bond path in the case of H–H hydrogen bonding correctly indicates the presence of a bonded interaction, while denoting a repulsive interaction in the limit of vanishing charge transfer makes no physical sense. The bonding in both cases is determined by the dominant attractive electrostatic interaction between the nuclei and the electron density whose distribution in the former case is more localized in the binding region of one atom more than the other and equally shared by both atoms in the latter. To argue otherwise would require that one impose an arbitrary cut-off on the value of the charge transfer, stating that a value above this denotes bonding while a value below this denotes repulsion.

1 R. F. W. Bader and J. I. Generosa, *Chem.–Eur. J.*, 2003, **9**, 1940–1951.

Dr Gatti said:

(1) I was pleasingly surprised by the excellent agreement you found between DFT and “topological” estimates of lattice energies of carboranes.

However, I wonder whether such an agreement might just result because of error compensations. Indeed, these points seem to require consideration:

(a) The energy formula adopted in the “topological” estimate, $E = 1/2 V(r_{cp})$ was originally calibrated on a set of gas-phase X–H···O (X = C, N, O) hydrogen bonded systems while you adopted it, without any change, for H···H and C–H··· π interactions.

(b) All other energy terms (electrostatic, as due to the existing CT within the monomers, dispersion, *etc.*) are neglected in the experimental estimate.

(c) The standard DFT functionals are known to describe rather poorly energy dispersion effects, although the use of fixed experimental cell parameters should in part reduce such a problem.

(2) The detailed topological analysis of C–C bond in *o*-carborane presented in this paper suggests that this bond may be regarded as the probable prototype of a “single π -bond”. Does the value of $\delta(C-C')$ corresponds to one shared pair of electrons, or is this value lower than expected for a single bond?

1 E. Espinosa, E. Molins and C. Lecomte, *Chem. Phys. Lett.*, 1998, **285**, 170.

Dr Glukhov replied:

(1) We are quite aware of all the drawbacks of DFT theory in the description of weak interactions and that the empirical formula we use was initially created for a certain class of hydrogen bonds, but we have a big number of papers where it is shown that such an approach gives very good results and that they are in a good agreement with different available data *e.g.* for the sublimation enthalpy. Unfortunately MP_n calculations for the crystal structures are too time-demanding.

(2) We did not examine the value of $\delta(C-C')$.

Professor Bader opened the discussion of Professor Lecomte’s paper: Your paper describes a state of the art study in the use of experimentally and theoretically determined electron densities in obtaining an understanding of crystal properties, in this case of the intermolecular interactions and their role in a study of the charge transfer observed in neutral–ionic transitions in a donor–acceptor crystal. This is a challenging problem but one which should not be clouded by indecision as to how one describes the intermolecular charge transfer. Your paper contains the statement: “In fact, it is impossible to determine unambiguously the atomic boundary inside which an atomic charge is located”, a statement I take exception with. An atomic population, and hence its charge, is the expectation value of a quantum observable, that in the case of an atom in a crystal, is an experimentally determinable quantity. I find it difficult to understand how one can publish a quantum theory of an atom in a molecule, QTAIM, in reputable journals, such as *Phys. Rev.*, and have the statements contained therein simply ignored. Equally difficult to understand, is the ignoring of the recovery of all measurable properties by QTAIM, including those determined by atomic charge: all multipole moments and both static and induced and in particular, for the present discussion, the contribution of atomic charges to infrared vibrational intensities as recently demonstrated by the recovery of measured atomic polar tensors. The alternative partitionings referred to in your paper, since they are not based on physics, predict no experimentally determined properties.

Your discussion concerning the possibility of ‘repulsive’ intermolecular interactions between Cl atoms linked by a bond path is at odds with the statement that a bond path links atoms in an equilibrium geometry—as found in your experimental density distribution. Hence there are no repulsive forces acting on the nuclei of the Cl

atoms, the Feynman force being the only possible source of repulsion. Intermolecular Cl–Cl bond paths are not only necessarily present in a crystal of solid molecular chlorine, their presence accounts beautifully for the unique layered structure of these crystals, the intermolecular alignment being determined by the ‘lump-hole’ property of the Laplacian of the density. Have you determined the Laplacian distribution for your crystal?

Professor Lecomte answered: In our paper we described how experimental charges were described in the literature. I think that all our work for over 10 years proves that we agree that the physical way to derive an atomic charge is the AIM method.

Cl···Cl interactions, or more generally X···X interactions, are very subtle and chemists classify them as attractive/repulsive. We do not claim that the Cl···Cl interactions are repulsive but we address the question of intermolecular halogen–halogen interactions, the analysis of which should certainly include the closest neighbours within 5 Å.

Professor Frenking addressed Professor Lecomte and Professor Bader: I want to comment on the nature of interatomic interactions and the definition of a chemical bond. Two He-atoms confined in a fullerene have a short equilibrium distance and a He–He bond path. According to the AIM theory they are bonded, but for a chemist it would not be a chemical bond.

Professor Bader responded: Holding two He atoms at some finite separation within a molecule in an equilibrium geometry wherein no forces act on any of the nuclei fits any chemists definition of bonding. What else is meant by bonding other than two atoms ‘stationary’ at some finite separation with the forces of repulsion exerted on their nuclei balanced by the forces of attraction? Even an isolated He dimer exists and has been detected experimentally. A bond path with the characteristics of a closed-shell interaction linking the He nuclei satisfies all of the requirements for bonding set by the Ehrenfest, Feynman and virial theorems. After all, the noble gases used to be referred to as ‘inert’. One should simply accept what nature gives and give up the model—not nature.

Professor Savin asked: Could you comment on the role of temperature on the measurement of densities, both in general, and in the particular case of your measurements (which were at different temperatures)?

Professor Lecomte answered: The accuracy of modeled density depends on the way $\rho(\mathbf{r})$ is deconvoluted for the thermal motion: our rigid bond tests for TTF-CA at both temperatures confirm that the deconvolution is adequate for both temperatures. Then, the obtained charge transfer is accurate I would say within 0.05 e.

Professor Geerlings commented: At the end of your paper you report results on the measurement of the (Molecular) Electrostatic Potential. Could you comment on the methodology and reliability of the results?

Professor Lecomte responded: Electrostatic properties are analytically derived in direct space from the model electron density for molecules withdrawn from the crystal. We then obtained accurate electrostatics given this hypothesis. Another possibility is to calculate $V(\mathbf{r})$ in reciprocal space and lead to the crystal potential by inverse Fourier transform of $F(\mathbf{H})/H^2$.

Dr Wedig stated: When comparing experimental and computed electron densities, not only the parameters used in the quantum mechanical calculations like basis sets and functionals should be considered, but also the procedure of how the experimental density was determined. Nobody ever measured an electron density directly. What is observed are the directions and intensities of an X-ray beam diffracted in a crystal. To get the electron density, a lot of concepts and a choice of computational parameters have to be involved. Depending on the procedure and the parameters, the density and thus the results of a topological analysis may vary, *e.g.* the bond paths in elemental Zn change significantly when the radial decay of the multipoles used in the refinement procedure is modified (A. Kirfel). I remember a recent talk of T. Koritsansky at a colloquium within the DFG priority program on experimental electron densities, where he pointed out this basis set dependence of the electron density obtained from diffraction experiments.

Professor Lecomte answered: Molecular crystal electron densities are obtained from a set of limited resolution structure factors and the deconvolution between thermal and density parameters may be a problem. But in this TTF-CA complex, success of rigid bond tests certify adequate deconvolution. I agree that in simple materials, the multipole modelling may be a problem (few LO data, high symmetry) but it is less the case for molecular compounds where the multipole model is adequate. Basis sets or multipole order dependence has been tested and does not seem to be a problem compared to the DFT discrepancies.

Dr Glukhov said: Of course, multipole refinement is not a straightforward thing, but the same is true of the AIM study of theoretical EDDF. There are systems which are basis set dependant, method dependant. So one should always treat these results with a certain degree of caution. Both in the case of theoretical and experimental EDDF.

Professor Lecomte answered: I agree but we have to find the best tool to compare and then improve our experimental and theoretical methods: Experiment and theory are able to use AIM; if both experimental and theory lead to the same AIM results within experimental error, then we can be confident with the theory and go on to calculate properties not attainable from experimental density.

Professor Savin addressed Professor Lecomte and Dr Wedig: I believe that there is a viewpoint unifying your position and that of Dr Wedig. One can ask that the quantum chemistry program provides the quantities which are experimentally measured. This is a philosophy defended by Professor Dovesi in the CRYSTAL program. In a following step, one can ask about the quantities derived from them, like electron densities, *etc.*, and argue about the trust we can have in the theoretical model we used for obtaining them.

Professor Lecomte answered: Confrontation between experimental and theoretical crystal properties are the only way to improve both methods.

Dr Wedig responded: The philosophy mentioned by Professor Savin makes sense, as in this way the responsibility of the experimentalist to determine the data to be measured and of the theoretician to predict this data *ab-initio* is clearly separated. However, to calculate *e.g.* diffraction angles and intensities *ab-initio*, in order to compare them with experiment, besides experience in quantum chemistry,

knowledge about the influence of thermal motion, absorption, extinction, experimental setup *etc.*, on the results is necessary. Concerning these influences a lot of expertise exists in crystallography. As a quantum chemist I am less familiar with these topics. That's why it is more efficient to use this expertise and try to meet the 'experimentalist' somewhere on the route of theory, *e.g.* at the stage where the electron density is determined. However we should be aware at this stage, that we don't compare theoretical with experimental results, but values being computed starting from different origins and using different approximations.

Dr Gatti communicated to Professor Lecomte:

(1) This paper shows that estimates of charge transfer (CT) occurring during the Neutral–Ionic phase Transition (NIT) from Kappa, Multipole and AIM topological methods lead to statistically similar results (0.53, 0.59 and 0.53 e). These results are obtained despite the definitions of the Kappa, multipolar and AIM charges being clearly different. In your paper, you propose that such an unexpected agreement of results is because the CT is the result of a difference between molecular rather than individual atomic charges, the former being much less affected by spatial partitioning.

I wish to point out that the agreement mentioned above is already present among the net charges of the **chemical groups** of the individual molecules (when these groups may be easily recognized). For instance:

The q differences among the various partitioning methods for a chemical group (C–O or C–Cl) are of the same order of magnitude of the deviations from the electroneutrality constraint for the unit cell.

(2) I'm surprised to see, in Fig. 2 of your paper, (3, –1) bond critical points (BCPs), like for instance S4··C17;C15 from which two different steepest ascent ρ paths originate and thus ending up at two different (3, –3) attractors. This is not *topologically* possible. Either there are two BCPs, very close to each other, but belonging to two different bond paths (BPs), one connecting S4 to C15, the other connecting S4 to C17, or there is a single BP connecting S4 to either C15 or C17, or, finally, there is a single BP connecting S4 to the BCP of the C15–C17 BP.

I understand that this might be the result of the use of a too large sampling grid in the case of the Integrity program, or of a not precise enough evaluation of critical points and BPs in the NEWPROP program—that works on densities expressed in analytical form.

The question is: have you tried to locally reduce the grid size in Integrity to solve the problem? Or to increase the precision of the BP tracing procedure in NEWPROP? Even if the density is rather flat, the problems should not be insurmountable in obtaining the correct BP, provided the electron density is given in analytical form.

(3) The fact that the Cl··Cl interactions lengths do not appreciably change with NIT does not necessarily mean that they are “repulsive”, admitted that this “pair-wise” bond energy classification might retain a physical meaning when applied to a potential energy hypersurface (and for a “nearly” equilibrium energy configuration where forces on the nuclei should “nearly” vanish). The Cl··Cl distances are at their “optimal” values, given the energetic constraints due to the presence of the other atoms in the crystal and to the ensuing necessity to adopt in both phases a “head-on” rather than a “side-on” and “attractive” C1–C11··C12–C2 conformation.

Professor Lecomte communicated in reply:

(1) I totally agree with your comment.

(2) Yes, our results are not topologically possible but are within experimental accuracy: I do not think that our precision is able to distinguish between two very close bond paths.

(3) We do not claim that Cl··Cl interactions are repulsive, but we address the question about the strength of intermolecular halogen–halogen interactions.

Professor Sutcliffe asked: What has happened to the N -representability problem? Has it been solved?

Professor Ayers answered: It depends on what is meant by “solved.” In many cases of interest (*e.g.*, the electron density; reduced density matrices) formal solutions to the N -representability problem are known. In most cases, the solution is not practical. For the electron density, however, the solution is very practical: every nonnegative electron density that is normalized to the number of electrons is N -representable. That is, for every electron density, there exists an antisymmetric wavefunction with that density. An exceptionally simple proof of this fact was given by Gilbert,¹ who (i) divided the system into N non-overlapping regions, each of which contains one electron; (ii) took the square root of the electron density for each of these regions, $\psi_i = \sqrt{\rho_{\text{region } i}}$; (iii) demonstrated that the Slater determinant of these orthonormal “orbitals”, ψ_i , gave the original density. This is not a very “useful” wave function, but it suffices to prove the existence of a wave function; this is all that is required for the rigor of the variational principle in DFT. If one wishes to construct a “useful” wave function—*i.e.*, a wave function that is the ground state eigenfunction for some electronic system—then one must wrestle with the thornier ν -representability problem. The ν -representability problem is exceedingly subtle, but the related “ensemble- ν -representability” problem is basically solved. (In the ensemble- ν -representability problem, one relaxes the requirements and accepts not only ground-state wave functions of an electronic Hamiltonian, but also fermionic density matrices that correspond to the ground state.) Every electron density is either ensemble- ν -representable or can be approximated infinitely accurately by an ensemble- ν -representable density.^{2–5} This is not to say that determining the density-matrix precursor to a given electron density is computationally easy; the procedure is many times more difficult than solving the electronic Schrödinger equation (although it can be done, approximately⁶).

For density matrices, the N -representability was essentially solved by the landmark paper of Garrod and Percus.⁷ For the one-electron reduced density matrix, one need merely satisfy the Pauli principle [the occupation numbers of the natural orbitals must be not be negative and cannot be greater than one]. For multi-electron reduced density matrices, the solution is only a “formal” solution, however, because it requires predetermining the ground state energy of every N -fermion Hamiltonian. Approximate implementations (based on special classes of N -fermion Hamiltonians for which either the ground state energy or bounds to the ground-state energy are known) of the Garrod–Percus result are of great interest nowadays,⁸ and it seems reasonable to surmise that this field is being held back mostly by the lack of competitive algorithms,^{9–12} and not an insufficient theoretical understanding of N -representability.

The N -representability problems for other functions (*e.g.*, the Wigner distribution^{13,14} and diagonal elements of many-electron density matrices^{15–18}) are also “solved.” The results range from semi-practical to computationally daunting.

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3 H. Englisch and R. Englisch, *Phys. Status Solidi B*, 1984, **123**, 711.

4 H. Englisch and R. Englisch, *Phys. Status Solidi B*, 1984, **124**, 373.

5 P. W. Ayers, *Phys. Rev. A*, 2006, **73**, 012513.

6 F. Colonna and A. Savin, *J. Chem. Phys.*, 1999, **110**, 2828.

7 C. Garrod and J. K. Percus, *J. Math. Phys.*, 1964, **5**, 1756.

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- 9 M. Nakata, H. Nakatsuji, M. Ehara, M. Fukuda, K. Nakata, and K. Fujisawa, *J. Chem. Phys.*, 2001, **114**, 8282.
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- 15 E. R. Davidson, *Int. J. Quantum Chem.*, 2003, **91**, 1.
- 16 W. B. McRae and E. R. Davidson, *J. Math. Phys.*, 1972, **13**, 1527–1538.
- 17 E. R. Davidson, *J. Math. Phys.*, 1969, **10**, 725.
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Professor Lecomte responded: No, despite many trials to combine charge and momentum densities results.

Professor Geerlings commented: *Continuing* on from the two sections of this morning (Conceptual DFT and Experimental Electron Densities and their analysis), *realizing* moreover that the more important DFT descriptors are those which can be considered as response functions of the system towards perturbations in the number of electrons and/or external potential, *can* one foresee that ED measurements can be made on perturbed systems so that the above mentioned descriptors would be experimentally accessible?

Professor Lecomte replied: Charge density on systems which are perturbed by external conditions is the goal of many groups. First Coppens *et al.*¹ proposed new experiments to derive crystal structures of photoexcited metastable systems ($\tau \leq 10^{-6}$ s) but describing the resulting charge density is not for the near future. The work of Hansen and Pietsch² on piezoelectric systems under electric fields are close to describing the resulting electron density modifications. Legrand, Pillet and myself³ have described for the first time the electron density of an iron coordination in its high spin low temperature metastable state, but the metastable system is stable over hours.

- 1 P. Coppens, I. I. voronostov, T. Graber, M. Gembickyand, A. Y. Kovalevsky, *Acta Crystallogr., Sect. A*, **A61**, 2005, 162–171.
- 2 R. Guillot, P. Fertey, H. K. Hansen, P. All, E. Elkaim and C. Lecomte, *Eur. Phys. J. B: Condens. Matter*, 2004, **42**(3), 373–380.
- 3 Vincent Legrand, Sébastien Pillet, Mohamed Souhassou, Noël Lugan, and Claude Lecomte, *J. Am. Chem. Soc.*, 2006, **128**(42), 13921–13931.

Professor Bultinck commented: On the question of the use of experimental density and density changes *versus* conceptual DFT. Is an experimental density not perturbed from the start?

Professor Lecomte replied: No as soon as the experiment is made with a wavelength (or energy) far from the absorption edge which is always the case because we want to minimize absorption effects; furthermore this method now allows insights on the electronic structure of crystals excited by external constraints such as electric fields¹ and photoexcitation.²

- 1 R. Guillot, P. Fertey, H. K. Hansen, P. All, E. Elkaim and C. Lecomte, *Eur. Phys. J. B: Condens. Matter*, 2004, **42**(3), 373–380.
- 2 Vincent Legrand, Sébastien Pillet, Mohamed Souhassou, Noël Lugan, and Claude Lecomte, *J. Am. Chem. Soc.*, 2006, **128**(42), 13921–13931 and references therein.

Professor Sutcliffe said: If you could use electron and X-ray diffraction on the same molecule, would you get the same electron density?

Professor Lecomte responded: These two techniques are complementary for small unit cells: X-Rays will give accurate position and thermal parameters which can be used by electron diffraction. High energy synchrotron data are also able to provide accurate charge density on simple materials suffering the problem of no information at very low diffraction angles.

But as soon as we deal with molecular materials or proteins, the only way to get experimental electron density is by X-ray diffraction on conventional sources or synchrotrons.