Nine Question on Energy Decomposition Analysis

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Abstract

The paper collects the answers of the authors to the following questions:

1. Is the lack of precision in the definition of many chemical concepts one of the reasons for the coexistence of many partition schemes?
2. Does the adoption of a given partition scheme imply a set of more precise definitions of the underlying chemical concepts?

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3. How can one use the results of a partition scheme to improve the clarity of definitions of concepts?
4. Are partition schemes subject to scientific Darwinism? If so, what is the influence of a community's sociological pressure in the ”natural selection” process?
5. To what extent does/can/should investigated systems influence the choice of a particular partition scheme?
6. Do we need more focused chemical validation of EDA methodology and descriptors/terms in general?
7. Is there any interest in developing common benchmarks and test sets for cross-validation of methods?
8. Is it possible to contemplate a unified partition scheme (let's call it the “standard model” of partitioning, that is proper for all applications in chemistry, in the foreseeable future or even in principle?
9. In the end, science is about experiments and the real world. Can one therefore use any experiment or experimental data be used to favor one partition scheme over another?

Keywords: Energy decomposition analysis, Interaction energy, Partitioning, Chemical bonding, Status of the methods. ■

Bernard Silvi: During the preparation of the second European Symposium on Chemical Bonding held last summer in Oviedo I have been asked by the organizers to propose a reflection topic for the Bond Slam session. I chose the Energy Decomposition Analyses (EDAs) because these methods are among the most useful as well as controversial tools helping to get insights on the electronic structure of molecules. I further thought that it should be helpful to collect opinions on the epistemological issues of these methods. I had the experience of a collective paper in which a panel of scientists were invited to give their opinions on the topological approaches in Theoretical Chemistry [1] and I proposed to renew this exciting approach. Nine questions have been selected and proposed to the contributors.

Bernard Silvi, Eduard Matito and Martin Rahm: We begin with a brief overview of EDA methodology and development. This introduction is not meant to be a comprehensive review and the interested reader is encouraged to consult the literature for more details. One comprehensive description of several different EDA schemes can be found in the article of Phipps et al [2]. In their from 2015 review Phipps et al. describe two groups of EDAs, classified depending on the nature of their underlying theories. Perturbation-based methods express the interaction energy in terms of corrections to a non-interacting description. Variational-based methods explicitly require the use of intermediate fragment wave functions corresponding to idealized non-physical situations.

Perturbation based methods stem from the theory of intermolecular forces pioneered by Eisenschitz and London in 1930 [3,4]. The method has been consistently improved over decades [5–14] yielding the Symmetry-Adapted Perturbation Theory (SAPT) which appears to be the latest link in of the evolution process [15–18]. For each order of perturbation, the energy contributions are derived directly from the expressions of perturbation operators. In this way, perturbation-based energy terms can be related to physical effects. Put differently, these methods explain interactions in terms of physical arguments based on properties of monomers. For this reason, and by construction, perturbation-based methods only apply to weak interactions, where they are typically quite successful [19,20].

Variational-based EDAs require quantum chemical descriptions of the entire system as well as the considered fragments. This approach is able to treat weak intermolecular interactions as well as multiple kinds of bonds [21,22]. A decomposition of the interaction energy of the water dimer was published in 1957 by C. A. Coulson [23]. However, the first acknowledged variational EDA method is due to Morokuma and coworkers [24–27]. This first EDA method is limited to the Hartree-Fock level of theory and it suffers from the presence of non-physical contribution to the interaction energy. The latter problem is significantly reduced in the reduced variational space (RVS) EDA [28]. A few years after Morokuma's seminal article, Ziegler and Rauk proposed an energy decomposition of the energy calculated in the framework of the Hartree-Fock-Slater method known as Transition State (ETS)-EDA. [29,30]. This method enables the analysis of both weaker and stronger bonds. There are several approaches in which localized orbitals are used to define EDAs. For example, Natural Energy Decomposition Analysis (NEDA) [31,32], Block Localized Wave functions (BLW-EDA) [33,34], and Fragment Molecular Orbitals (FMO) in the Pair Interaction Energy Decomposition Analysis (PIEDA) [35], Absolutely Localized Molecular Orbitals in ALMO-EDA [36–39], and Natural Orbitals for Chemical Valence [40] (NOCV-EDA) [41]. The use of the variational based EDA is mostly limited to HF and DFT calculations although post Hartree-Fock correlation methods do exist. For example, for partitioning energies within the Local Pair Natural Orbital Coupled Cluster Framework [42], for MP2 wave functions [43] and for evaluating dispersion corrections [44].

A third family of EDA only requires electronic data (wave function or electron densities) of the entire system. The "Chemical Hamiltonian" approach [45], makes use of atomic projection operators to express the total Hamiltonian as a sum of one-centre and two-centre terms. The resulting energy decomposition yields true intra-atomic and true inter-atomic energy components and basis extension terms. As the projection operators are defined in the LCAO-MO formalism, the method is restricted to this kind of calculations. In position space partitioning, the interaction energy is defined in terms of contributions of the one-electron and of the two-electron density distribution functions. The considered domains may have either sharp or fuzzy boundaries. The quantum theory of atoms in molecules (QTAIM) considers domains bounded by zero-flux surfaces of the density as defined by Bader, which are open systems that, among other properties, have associated energies [46]. In this sense, the QTAIM provides an atomic partition. An extension of this partition, considering atomic and diatomic terms, as well as individual energy components, is known as the Interacting Quantum Atoms scheme [47–50] considers domains bounded by zero-flux surfaces of the density as defined by Bader[46]. However, other non-overlapping partition schemes, such as ELF basins[51], can be considered at the expense of the determination of the fragment kinetic energies. Methods for fuzzy atom partitioning have been developed by Salvador and Mayer[52,53].

Finally, Experimental Quantum Chemistry (EQC) is an energy-based partitioning unique in that it can interchangeably rely on quantum chemical calculation, at any level of theory, as well as on experimental thermochemical data, vibrational and photoelectron and X-ray diffraction and absorbtion measurements[54,55]. Developed by Rahm and Hoffmann, EQC makes use of observable "reference frames". For example, when studying chemical bonding, the EQC partitioning refers to the bond dissociation process. EQC is, in principle, applicable to any chemical or physical transformations yet consists of relatively few energetic terms. One of these terms is defined as the electronegativity of the system[56].

EDA methods are multipurpose methods used to quantify, characterize and explain interactions between fragments of quantum systems. Whereas we have not mentioned all varieties here, most EDAs can provide important pieces of information on chemical interactions. This class of methods can also have other practical uses, maybe most notably for the design of molecular mechanics force fields[14,57,58]. The explanations offered by EDAs are seldom "chemical explanations" in the sense that interactions are not directly described in terms of "atom in molecules" chemical properties, such as electronegativity, valence, ionic and covalent radii. The latter properties being determined by the location of the constituent atoms in the periodic table. Most EDA methods instead rely on either physical or quantum chemical concepts. In EDAs, interaction energies are described as the sum of contributions arising from a sequence of equations that typically are specific to each method. The physical (or quantum chemical) interpretations of these of these equations, and the balance of the resulting energy contributions, yields a deterministic explanation focused on the dominant terms. Challenges for EDA methodology and future development of the field is what we will discuss in this article.

Alston Misquitta and Krzysztof Szalewicz: We will address the 9 Questions from the perspective of symmetry-adapted perturbation theory (SAPT), sometimes also called exchange perturbation theory. SAPT has been presented in detail in many original papers[15,59–68], reviews[16,18], and textbooks[20,69,70]. Thus, there is no need for its extensive description here. But we will briefly lay out the main features of SAPT, particularly those that do not seem to have been understood in the non-SAPT literature. We will also dispel some myths about SAPT as these can cloud our understanding of this method in the context of the questions posed in this paper.

SAPT is a perturbation theory that calculates interaction energy directly, starting from isolated monomers. Thus, in contrast to the supermolecular approach, no subtractions are involved and, in consequence, SAPT is free of basis-set superposition error. The interaction operator V is the sum of all Coulomb interactions between particles of different monomers. The simplest approach is to use Rayleigh-Schrödinger (RS) perturbation theory, but such approach is unphysical at short separations since it does not predict the existence of the repulsive wall. To include repulsion, one has to properly antisymmetrize the cluster wave function, i.e., enforce Pauli's exclusion principle, resulting in a symmetry-adapted perturbation theory. There are several ways to perform such adaptation, the simplest one is to symmetrize the wave functions of the RS method, leading to symmetrized RS (SRS)[59].

SAPT is *the* theory of intermolecular forces and most textbooks discussing intermolecular interactions use SAPT concepts even if the SAPT acronym is not mentioned. SAPT is also known under several other names, e.g., the effective fragment potential (EFP) method[71]. SAPT provides what can be called the standard model of energy decomposition analysis (EDA) for intermolecular interactions (also called noncovalent interactions). This is because SAPT by design defines the interaction energies in terms of electrostatic, induction (polarization and charge-transfer, or charge-delocalisation), dispersion, and exchange terms. These terms are defined in a unique way and can be calculated with potentially arbitrary accuracy and at complete basis set (CBS) limits.

Since exact wave functions are unknown for larger monomers, SAPT approximates these functions at several available levels of electronic structure theory. In fact, SAPT is a double perturbation theory with the other perturbation due to the intramonomer correlation operator $W = W_A + W_B$, where W_X is the Møller-Plesset (MP) fluctuation potential of monomer X. If W is neglected, monomers are described at the Hartree-Fock (HF) level. Higher levels include consecutive powers of W, possibly with selective summations to infinite order applying the coupled-clusters (CC) method. A version of SAPT, denoted as SAPT(DFT), uses monomers described at the Kohn-Sham (KS) density-functional (DFT) level (however, interaction energies are computed using wave-function theory).

While SAPT has become a mainstream electronic structure method, various myths about SAPT are in circulation and these are far from truth. In particular, it is sometimes stated that SAPT is "just" one more EDA method, useful only for interpreting interaction energies. This is not strictly correct. An EDA takes a total interaction energy and, by various manipulations of the density matrices or basis sets, seeks to decompose this energy into terms that reflect something physical. What is done in SAPT, is conceptually quite different: one starts from physical components, term-by-term, and sums them up to get the total interaction energy. This process does not involve any arbitrary choices. Thus, instead of decomposing a quantity, SAPT assembles it from well-defined components. What is important, if this assembly is performed up to sufficiently high order (second order in V and fourth order in W are adequate for most purposes), SAPT gives interaction energies similarly accurate to those given by the supermolecular approach in the fourth order (MP4) or the CC method with single, double, and nonpertubative triple excitations [CCSD(T)].

SAPT, in fact, is an exact method in the sense that it reproduces the exact interaction energy as the order in V goes to infinity provided that appropriate symmetry-enforcing techniques and exact monomer wave functions are used (or the number of excitations in the CC method used to describe monomers approaches the number of electrons in each monomer). These statements are based on high-order calculations for small systems, see Ref.[65] for a review of this work.

Since SAPT is a perturbation expansion in powers of V, one may expect that SAPT will start to diverge as R becomes small and consequently V is no longer a small perturbation. Apparently, with proper symmetry enforcing this divergence is not observed even for interactions as strong as those characteristic of chemical bonds[65]. Also, low-order SAPT calculations for larger systems show only a minimal worsening of convergence when one goes to small R's, see Ref.[72] for an analysis of the Ar_2 SAPT results at $R = 1.5$ Å, where the interaction energy is more than three orders of magnitude larger than the absolute value of this quantity at the van der Waals minimum, $R = 3.76$ Å.

Another myth is that the programmed general version of SAPT[73–75] is at the best equivalent to MP2. In fact, the version of SAPT that is applicable to interactions of arbitrary closed-shell molecules and some open-shell ones includes terms up to third-order in V and a high-order treatment of electron correlation in monomers. By analyzing individual terms, one can show that this version of SAPT is approximately equivalent to the CCSD(T). This is confirmed by the agreement between these two methods to within a few percent found in most calculations. In particular, for the helium dimer the calculations of Refs.[76,77] performed at CBS limits and including also a benchmark all-order calculation estimated to be accurate to about 0.01% show that the potential from SAPT at the level available in the SAPT codes[73] and the CCSD(T) potential are similarly accurate, although SAPT is slightly more accurate at the van der Waals minimum.

A broader comparison of SAPT with CCSD(T) was performed in Ref.[78]. In this work, CCSD(T)/CBS benchmarks were computed for ten dimers, containing up to 28 atoms, varying R from asymptotic to repulsive configurations. The median unsigned percentage error of SAPT(DFT) is only about 1% larger than that of CCSD(T), both methods computed in the same basis set [the CCSD(T) error here is, of course, entirely due to basis set incompleteness]. SAPT(DFT) performs significantly better than all other DFT-based methods investigated in Ref.[78].

The next myth is that SAPT(DFT) is an approximation to the KS DFT supermolecular approach. While it should be already clear from the discussion above that this is not the case, a dramatic illustration is presented in Refs.[72,79]. Figure 1 in Ref.[72] shows that CCSD(T) and SAPT [SAPT(DFT) is almost indistinguishable from SAPT] potential energy curves for Ar_2 are very close to each other. In stark contrast, supermolecular DFT calculations produce curves spread all over the place.

Question 1: Is the lack of precision in the definition of many chemical concepts one of the reasons for the coexistence of many partition schemes?

Ramon Carbó-Dorca: Lack of precision is a mild description term. Chemistry has a heavy historical influence of intuitive concepts, which possess no well-defined physical basis. If such a physical basis must rely on quantum mechanics, then there might be one can chemically consider well defined just isolated atoms, molecules and molecular swarms (a molecule surrounded by other molecules, for instance) only. These systems cannot be separated into parts or fragments from the quantum mechanical point of view. Atomic and bond contributions to the electronic energy of molecular systems are to be considered approximate and mainly related to the LCAO MO theoretical structure under Born-Oppenheimer approach. A simple situation might illustrate the difficulties of energy (or other molecular characteristics) partition. Whenever in LCAO MO theory one allows using AO or basis set functions in a general manner, allowing them being not centered in an atom, but a point within the three-dimensional space of the molecular neighborhood. For example, one can choose the molecular center of charge, or even better: the center of charge of every atomic pair, as a locus where to center one electron basis functions. In this case, there might be defined a one center contribution, which cannot be associated with any physical atomic electron source. At the same time, there could be bicentric partition contributions, made by a hybrid basis set center and the physical atom centers. This might illustrate the arbitrariness of any partition scheme.

Shant Shahbazian: It is usually perceived that evolution of a “qualitative” chemical concept to a “quantitative” one is the hallmark of precision; this is the business of the indices in computational chemistry, e.g. indices probing the presence and/or strength of bonding/aromaticity. However, lack of precision may have another face: “over-quantification”, which is many mathematically rigorous but “non-equivalent” definitions of a chemical concept; the mentioned bonding and aromaticity indices belong to this category (although sometimes it is tried to sell this non-equivalence as revelation of the “complementary” nature of definitions, it seems hard to conceive how “contradictory” results must be avoided in case studies). There is no bound on the number of proposed indices so the over-quantification grows with time and ruins the whole initial program of reaching precision by the qualitative to quantitative transition. This is the same situation for the large number of proposed energy partitioning schemes in the last decades. So, the reverse question is more legitimate to me: “Is the coexistence of many partitioning schemes the reason for lack of precision in the definition of many chemical concepts?”. As I stressed elsewhere[80], as far as one does not have a comprehensive theory for the concept of interest and just tries to make the qualitative to quantitative transition intuitively, the problem of over-quantification will be prevailed.

István Mayer: Physicists consider the molecule as a set of electrons and nuclei, chemist treats it as a set of chemically bonded atoms. These conceptually different approaches can be connected by performing partition of different physically (chemically) relevant quantities in terms of atoms or pairs of atoms. However, while the electrons and nuclei used in the calculations are quite well defined entities (at least at the energies relevant to chemistry), the individual atoms within a molecule are in some sense only constructions of the human mind. They represent very good generalizations of the enormous chemical experience but, if looking closely, are somewhat fuzzy concepts: one cannot tell apart exactly where one atom is ended and the other is started—if that question has a meaning at all. The absence of a unique definition of the atom within the molecule makes inevitable “the coexistence of many partition schemes”. (Note that the bond order index also emerges from a partitioning: it is the integral of the diatomic component of the exchange density[81].)

Martin Rahm: I think so, yes. However, I do not see an inherent problem with trying to quantify the same “fuzzy” concepts in several different ways. Future cross-comparison efforts, discussed in questions six and seven, will hopefully indicate which precise EDA definitions are more predictive and chemically useful.

Frank Weinhold: On the contrary, we contend that the dubious physical assumptions underlying EDA partitions (i.e., existence of mutually exclusive and simply additive “components” whose labels correspond to chemical concepts as broadly understood) are the issue. This is particularly so when the partition is formulated in terms of non-orthogonal "reference fragment" orbitals and their attendant conceptual ambiguities. Dubious premises lead inevitably to a multiplicity of (equally dubious) EDA partitions.

Ángel Martín Pendás: In a sense, the lack of precision in defining concepts will inevitably lead to different partition schemes. However, there are several levels at which differences will arise, and much as in other fields of Chemistry, a set of minimal rules for an EDA to be acceptable for the community should be given. Are there references? If so, are they well defined, or may they be chosen at will by the user? Similarly, are there intermediate states from which particular energy components are defined? If so, are they well behaved, i.e. are they compliant with the quantum mechanical framework? It is my opinion that, in many cases, it is not the fuzziness of chemical concepts that multiplies the number of available EDAs, but on the contrary, the somewhat forced construction of partitioning schemes fitting available computational or methodological levels.

Julien Pilmé: Yes, it can be argued that the lack of precision or the lack of physical basis of some simple chemical concepts such as the "lone pair" concept, promotes the coexistence of numerous partition schemes. However, even if these concepts were better defined, one might think that the abundance of partition schemes will be sustained due to the difficulty to build a rigorous bridge between an unique definition of an atom and the quantum mechanics. So, the lack of clear relationship between the chemical concepts and the quantum mechanics leads to an arbitrary character in the definition of partitions dictated by a compelling need to rationalize the diversity of interactions observed in the matter at the microscopic level.

Carlo Gatti: In my view, rather than the lack of precision in the definition of many chemical concepts, it is the quite different perspective of the various partitioning schemes that lead to and motivate, to some extent, their coexistence. Indeed, broadly speaking, energy decomposition analyses (EDAs) may be grouped in two main categories, according to whether the decomposition is performed in Fock (orbital) space or in the position space R3, using some convenient partitioning of R3 in subdomains (e.g. QTAIM). Advantages and shortcomings of the two approaches have been masterfully analysed and discussed by Martín Pendás et al.[82]. In the former, attention is directed to the composing energies of the (often fictitious) intermediate steps through which the analysed system is formed from some initial moieties, whereas in the second kind of approaches attention is focussed on dissecting intra- and inter-subdomains energy contributions for the very final step of such system (and with a similar analysis performed on a given initial step of the system, if the approach is applied to the interaction energy also). The proposers of the real space EDAs are like a film director or a mystery writer which focus and analyse the last scene of the movie or of the murder based only on what they see, using unbiased scissors and zooming lenses. Instead, those of the orbital space EDAs are eager to reconstruct a sequence of gedanken facts which have led the actors to the final outcome. Actors keep changing (and often loosing) their identity through this process and in most cases represent purely imaginary characters. Clearly, in the case of "orbital space" EDAs, the film directors or mystery writers enjoy more freedom in their work and their products may more largely differ among each other and raise more vibrant, yet often nonsense, debates.

Paul Popelier: Yes, is the short answer. I can think of one important example of a chemical concept that causes a proliferation of EDAs. The concept is that of the molecule itself and, in particular, the identity of a molecule when in close contact with other molecules. More precisely, non-topological EDAs suffer from an unclear definition of a molecule at short range. At close intermolecular distances the separation of charge transfer and polarization then becomes increasingly ill-defined. Of course, at long range the identity of a molecule is not problematic. Rayleigh-Schrödinger perturbation theory is based on this clear idea of a molecule at long range but this theory's vulnerability is that it breaks down at short range. In that regime, molecules stop "owning" their electrons and strong delocalisation (i.e. exchange) starts spoiling the classical picture of what a given molecule is within a molecular assembly. In other words, if one is uncomfortable with finite (bounded) subsystems (i.e. the "real space" approach) then the challenge is to determine where a given molecule stops and starts. On the other hand, if one is inclined towards infinite and overlapping subsystems (i.e. the "fuzzy" or "orbital" or "Hilbert space" approach) then the challenge is to determine which orbital or basis function still belong to the molecule in question. In any event, without a clear decision on the matter of how to carve out a molecule from a molecular assembly, one will face ambiguities down the line, such as the one mentioned above. It is important to make the right decision upfront in other to avoid issue that need fixing later. I still like to think that the topological partitioning offers a clear definition of a molecule at short range and is thus a good starting point for an EDA. Indeed, IQA defines charge transfer and polarization in a well-defined way.

Finally, I'd to comment on Carlo's nice metaphor. Of course, at first sight it is true that IQA does not invoke any intermediate steps unlike non-topological EDAs. However, strictly speaking this is not really true, depending on one's starting point. Granted, IQA does not introduce a state that violates the Pauli principle but it could do this, and still apply its topological partitioning to it. To me, how one partitions and which reference states one brings in are two independent things. In fact, one can argue that IQA also refers to an artificial reference state, by the fine structure of the second order reduced density matrix. This object contains an electrostatic part, an exchange part and an electron correlation part. The latter is a by-product of the fictitious Hartree-Fock state, while the exchange part can be seen as a by-product of the fictitious Hartree state. So maybe the last scene of the IQA movie had some predecessor scenes after all. . .

Pedro Salvador: To some extent, yes. But, I think it is worth to start by pointing out that we are referring here to two main families of energy decomposition schemes, as the reason for not having a unique, unambiguously defined, scheme is different in each case. I do not consider either of these two approaches superior from a conceptual point of view, they merely provide different insight.

On one hand there are the approaches that decompose the total energy into a number of global contributions that bear some physical/chemical significance. In this case, the main issue appears to be that some of these global energy contributions are defined with respect to a reference. Another family of methods decompose the total energy into domain contributions, the latter often identified with the atoms within the molecule. In this case we essentially have different realizations of the same scheme, using one or another atom-in-molecule (AIM) definition. Indeed, by introducing real-space atomic weight functions one can accommodate both disjoint and overlapping AIM approaches. Furthermore, there is no need to further distinguish between "Hilbert-space" and real-space methods in this context. Some years ago[83,84] it was shown that on the (numerical) one-electron basis set formed by the so-called effective atomic orbitals (obtained for a given real-space AIM definition), the classical "Hilbert-space" and the real-space formulae yield exactly the same results (even beyond the LCAO-MO framework, e.g. for plane-wave calculations[85]). Hence, the arbitrariness in this scheme comes solely from the definition of AIM, as is the case of many other descriptors such as partial atomic charges or, to some extent, bond orders.

However, it is also worth to point out that, contrary to e.g. electron population analyses, energy decomposition schemes may differ from one particular electronic structure method to another, just because the way the total energy is determined can also be different. This adds an additional source of ambiguity even if we merely consider the case of formally exact theories such as density functional theory of full-CI methods.

Jerzy Cioslowski: The coexistence of many schemes is a direct consequence of the concept of energy partitioning being replete with ambiguities. To begin with, it encompasses two very different approaches, namely: 1) partitioning into contributions due to physical phenomena and 2) partitioning into contributions due to subsystems and clusters comprising them. This observation, already made by Pedro Salvador in his answer above, deserves further elaboration.

In the first case, the interaction between two subsystems is analyzed by application of a sequence of contrived processes such as geometry relaxation, charge transfer, polarization, etc. . . , each giving rise to a particular energy component. It is important to understand the distinction between the terms "sequence" and "superposition" in this context as the contributions of these processes to the total energy are not commutative. To further complicate matters, not all permutations among the members of the sequence in question are allowed. Thus, e.g. one can relax the nuclear and electronic degrees of freedom in arbitrary order (by unfreezing the geometries of subsystems while keeping their electron densities frozen, or vice versa), each time obtaining different values of the respective energy components. On the other hand, if one defines polarization as complete relaxation of the electron density and charge transfer as relaxation of the total charges of the subsystems, then obviously that the latter has to precede the former. To summarize, the plethora of the possible energy partitioning schemes of the first kind arises not only from certain degree of arbitrariness in the definitions of the individual physical processes (polarization, charge transfer, etc...) but also from the (limited) arbitrariness of the order in which they are applied. Another layer of ambiguity is added by the necessity of specifying the definition of the partitioning of the electronic properties into subsystem contributions that underlies the entire energy partitioning scheme.

In the second case, one attempts to write the total energy as a sum of contributions due to individual subsystems, pairs of subsystems, clusters of three subsystems, and so on. Usually, these subsystems are atoms or functional groups. Again, all of such schemes derive from particular definitions of properties of atoms in molecules. However, there is another conceptual difficulty that has to be considered. The electronic Hamiltonian is composed of one- and two-particle terms that give rise to the respective one- and two-electron energy densities. Integration of these densities over the entire Cartesian space produces the corresponding energy components (i.e. kinetic, electron-nuclear attraction, and electron-electron repulsion) whose atomic and diatomic contributions are obtained by analogy upon multiplication of the integrands by atomic projection functions (whose sum over all atoms equals one; the functions themselves can be smooth or not). Consequently, the atomic contributions can be defined for all the three energy components, whereas the diatomic contributions arise strictly from the electron-electron repulsion energy (though one may further partition the electron-nuclear attraction energy by separating it into terms due to individual nuclei). Thus, the "many-body" energy contributions due to clusters of more than two atoms cannot be defined in a meaningful way, which runs contrary to expectations from chemists (who would often prefer to deal with atomic and diatomic energies transferable from one system to another, the residual energy being accounted for by interactions involving more than two atoms) and physicists (who are inspired by the cluster expansions of energies of systems composed of noble gas atoms, etc...). Even worse, this observation appears to contradict at the first glance the results of perturbative treatments of the dispersion interactions that produce closed-form expressions for e.g. three-body interactions (the AxilrodTeller potential).

Gernot Frenking: The coexistence of many partition schemes is due to the fact that different concepts and bonding models exist, which come from different viewpoints and which address different questions. Chemical bonding is a very complex phenomenon, which can be interpreted in various ways. There will always be several chemical concepts in chemical research, which consider diverse aspects of chemical phenomena. Chemical concepts and bonding models are not right or wrong, but they are more or less useful and the usefulness depends on the question that is asked. Partition schemes are tools in the arsenal of bonding models, which serve as a bridge between the numerical results of quantum chemical calculations and the human desire to understand them in terms of classical concepts. Chemistry has rather a problem with the coexistence of (a) historically developed and poorly defined heuristic concepts and (b) more recently suggested quantum chemical partitioning schemes. The conclusions of the two models may contradict each other. In such cases it is important to examine the origin of both approaches.

Julia Contreras: Indeed there is an inherent lack of precision in chemistry, but I would not call them "physical", but rather "mathematical". It is mathematically impossible to univocally define an atom in a molecule, or the point-wise energy in a molecule. However, I completely disagree there are no physics behind. There are physics behind from the moment people have been able to find patterns and make predictions in chemistry in terms of atoms and functional groups way before Quantum Chemistry entered the scene. This makes some partitions more physically sound than others, and the use of some bases more physically sound than others. Atomic basis sets are used in molecules because atoms are still a good physical entity/model. Although mathematically we could choose any function, atomic basis sets (located at the atomic nuclei) are a good option to describe the molecule in the sense that it accelerates convergence and reduces the number of functions to use. This basically means there is a physical truth behind the choice, even though other functions would also be mathematically good options to expand a function. Of course, this is not elegantly mathematically defined, but one should not forget the physics behind it, and deny the predictive power of chemistry because it is not mathematically nor elegantly univocally defined. So just like in any other theory, we should look for partitions that contain the physics we need to reveal following a very simple principle: "as simple as it can be, but not simpler". Just like many models coexist for describing other problems in physics, I also agree that what we probably need is not less models, but a good hierarchy of them, so that we know when a given model is valid or we should go for a higher rung and more complex- description of chemical reality. I agree with C. Gatti that equivalencies among partitions as the one carried out in Ref [82], and the limits of each method, are absolutely needed in this respect.

Henry Chermette: The ambiguity of the bond concept relies on the fact that only nuclei and electrons are well-defined objects whereas the atoms in molecules are not, since the electrons in molecules are not stuck to nuclei. Therefore, although some definitions look more reasonable than others, the coexistence of several definitions is unavoidable. The lack of precision in the definitions are therefore a by-product.

Émilie-Laure Zins: In contrast with most of the previous answers, I think that the lack of precision of many key chemical concepts is not the main reason for the existence of many partition schemes. The phenomena that theoretical chemists seek to describe nowadays are highly complex, which fully justifies the development of suitable and tunable tools adapted to each type of problem. It seems to me that this phase of coexistence of many partition schemes could be temporary: a convergence towards a single or a small number of partition schemes could take place in the coming years via fundamental theorems such as Hellman-Feynmann's, Bethe-Salpeter's equation or quantum field theory. This "unification" could be an objective in itself for the community, leading to a simplification of concepts and descriptions. Shant Shahbazian proposed another question: "Is the coexistence of many partitioning schemes the reason for lack of precision in the definition of many chemical concepts?" I think that the development of a "universal" partition scheme could lead to a simplification of chemical concepts and an easier dialogue between theoretical and experimental chemists.

Laurent Joubert and Vincent Tognetti: We think that the reciprocal question is also interesting: do we need an energy decomposition to define chemical concepts? For instance, conceptual DFT has often provided firm physical ground to empirical concepts using very simple equations: Pearson's molecular hardness and Parr's electrophilicity index can be derived in two lines, in contrast with many EDAs that require much more maths...

Paul W. Ayers: Yes and no. Insofar as people can't agree on the precise definition of induction, or dispersion, or electron transfer, or polarization, there can never be a unique EDA. (As a pernicious example, electron transfer energy can always be viewed as an extreme form of polarization, where the electron density of a fragment becomes extremely delocalized. Similarly, the mere idea of a local or regional kinetic energy is mathematically ill-defined.) So yes. However, the existence of many partitioning methods leads to ambiguity in chemical concepts, since different EDA methods give qualitatively different explanations of chemical phenomena in many cases. So no–it isn't fair to "blame" the coexistence of many partition systems on the ambiguity in chemical concepts any more than it is fair to blame the ambiguity of chemical concepts on the existence of myriad partitioning schemes.

Farnaz Heidar-Zadeh: Given that chemical concepts are nonempirical, any attempt towards quantifying them is doomed to be non-unique. Partitioning schemes are no exception! Considering the fact that partitioning schemes cannot be defined accurately, putting too much effort into the precision of various definitions is futile. Each scheme starts from a different set of assumptions (some of which may be unknown or not carefully laid out at the beginning) and consequently gives a different set of results. The best one can hope for is having a rigorous mathematical definition of partitioning schemes (and other concepts) which confirms chemical trends and aids us in rationalizing the behavior of molecules and materials. So, even though it is interesting to quantitatively compare various schemes (i.e. the so-called precision of various schemes), only their qualitative comparison can truly testify to their value (i.e. assessing how various schemes comply with or improve chemical reasoning is the closest thing to an accuracy check we can dream of). As G. Frenking clearly explained, these schemes are tools for making sense of numerical results of quantum chemistry calculations in terms of familiar classical chemical concepts and depending on the problem at hand, some of these tools will be more/less useful than the others.

Juan Andrés: Many chemical concepts (aromaticity, chemical bonds, oxidation states, and atomic charges) employed in chemistry today can be traced to the early stages of the field, notwithstanding the significant developments, refinements, and extensions made during the last years. Chemical nature aside, the terminology is introduced by these chemical concepts is now ubiquitous and has had a pronounced effect on the way that chemistry is practiced and taught. These concepts remain invaluable in providing frameworks that allow us to rationalize trends in chemical structure and reactivity, as well to realm current knowledge, consideration of new observations, and finally as pedagogic instruments.

These concepts described above were established without fully understanding the physical principles underlying the interactions between electrons and atomic nuclei. As Robert Heinlein wrote "The difference between science and the fuzzy subjects is that science requires reasoning while those other subjects merely require scholarship". The work of Jansen and Wedig[86] serves as an example for how chemical concepts (in this case, atomic charge and oxidation state) can achieve progressively improved operational definition. Unfortunately, there concepts are not observables, i.e. there is no quantum mechanical operator that would work on the wave function to give the corresponding value as an observable. They can be criticized for being unphysical and non-observable; although are highly useful but often not backed by solid theory, in particular, not by quantum mechanics. This a very common situation approach in chemistry and it is an inherent part of various quantum tools utilizing chemical concepts in molecules and crystals. One way of overcoming this conundrum was proposed recently by Ayers et al.[87] in which an axiomatic approach to chemical concepts is introduced. Therefore, it is lack of precision in the definition of many chemical concepts one of the reasons for the coexistence and proliferation of many partition schemes. Moreover, our future findings have immediate implications for the development of the next generation of physically motivated procedures to be able to capture the physics of the chemical concepts properly, a new strategy is needed to take the benefits of fully into account.

Yirong Mo: The literal definitions and conceptual understanding of various concepts are often consistent and shared by all chemists. But in the process of realizing these concepts, one need use approximations and set up rules within one's field (for example, either molecular orbital theory or valence bond theory, or different MO methods). This can be understood as getting more precise definitions. As a consequence, different approximations lead to different partition schemes with different (sometime conflicting) outcomes. For instance, we often regard charge transfer as a process occurring from one monomer to another monomer, or from one fragment to another fragment of one molecule, or approximately from one fragmental HOMO to another fragmental LUMO. But in computations we need define the fragmental orbitals. Here the disparity comes up, because we usually get only canonical MOs which are extended over the whole system. Approximations are introduced to get fragmental orbitals and different approaches lead to different solutions, and eventually different energy terms.

Eduard Matito: Yes, but in my opinion, it is actually one particular chemical concept that is most responsible for the proliferation of energy partitions. Since an atom in a molecule (AIM) is a fuzzy chemical concept, it is only natural that many partition schemes coexist. This most evident in the case of real-space energy partitions: we can have as many such energy partitions as definitions of AIMs. In this sense, one way to reduce the number of energy partitions would be to focus on the reliability of the AIM definition. For instance, we have found that some AIMs do not provide correct predictions when they are used to analyze certain properties (see my answer to Question 4).

Eloy Ramos-Cordoba: Since traditional chemical concepts are not observables, they are not well defined in the context of quantum mechanics. As a consequence, a given chemical concept can, in principle, be described by many different mathematically rigorous partition schemes. The number of reasonable schemes can be reduced by imposing a series of physical constraints on the partition formalism. For instance, in variational EDA, one can impose that all the intermediate wavefunctions must be antisymmetrized.

W. H. Eugen Schwarz: Many chemical concepts should not only comply with the general laws of basic physics, but at best also match the set of specific chemical materials of interest, the properties and reactions of main interest, and the ways different chemists are trained to understand and intuitively guess and predict them. The chemical concepts should be designed in a clear, unique, rational, consistent, purposive manner. Accordingly, there will and shall emerge related, slightly different concepts, without lack of conceptual quality. A simple example is the partitioning of interatomic distances, modeled by sums of various types of "atomic radii" (van der Waals radii opposite and orthogonal to a bond, ionic radii for different formal charges and coordination numbers, covalent radii for different formal bond orders, hydrogen bond radii, etc.). The richness of chemistry requires a richness of concepts and schemes.

Namely: *Physics* is the science of matter in simple, prototypical, ideal sectors of reality, to be described in the most general and most accurate way. *Chemistry* is the science of matter in complex, special, realistic and "human" cases, to be described in a useful, simple and appropriately and reasonably reliable way. ("Human" conditions here typically mean matter around temperatures of 300K $\times 10^{\pm 2}$ and pressures of 1at$\times 10^{\pm 4}$ during timespans of 1h $\times 10^{\pm 6}$.) Physics and chemistry are two hard sciences of different kind.

In principle, physics is more distinct and chemistry is more fuzzy. That is, "lack of precision" may exists in cases where one is still in the phase of development of the chemical concepts, but it is misleading and biased discrediting the principle of *fuzziness* as a lack of some improper requirement in *mature scientific cases*. Also note that the clear physical concept of, e.g., an electronic particle (in a molecule) in the low-energy approximation fades away in the high energy regime (near heavy nuclei), where it must be replaced by the electron-positron matter field of non-coinciding charge, mass and spin distributions. Or the clear physical concept of a sharp spatial boundary (sometimes postulated between "atoms" in a molecule) in the low-velocity approximation fades away in the realistic relativistic regime.

Therefore, many chemical concepts cannot be that general and unique as most of the basic physical concepts. They have to be appropriately adjusted to the ranges of materials, to the typical conditions and to the useful purposes, which the researchers want them to apply to. Experienced researchers with some special interest in some field of chosen materials will search for useful parameters as a quantification of their *experience-guided fuzzy ideas*. Related concepts of different scholars may be analyzed with the help of statistical techniques, see below.

Finally, we must distinguish between *descriptive*, *analytic* and *explanative* concepts. Description is the qualitative or quantitative specification of the interactions of some specimen with its surrounding, as given by nature and its laws. (The specimen may be a molecule or nanoparticle or droplet or crystallite or surface layer etc. of some material or compound. The interaction properties may be described by mass, charge, polarizability, color, chirality, various specific reactivity parameters, etc.) Respective probability distributions and source functions of these interaction properties can be analyzed in spatial detail, as for instance in the QTAIM. As long as no restraints of the description are imposed, such as monopole approximations, or same average values for whole sets of specimens or homologous series, the descriptive parameters should be comparatively unique.

There are then two further steps toward a deeper *understanding* of WHY is WHAT is. First there is the question of the internal structure of the data, and relations between them. That is so to say an 'automomous' intra-chemical approach. One approach is by additive increment systems, approximating the property parameters of compounds by sums over atomic, di-atomic, and possibly multi-atomic (3-center or ring) contributions. Examples are effective atomic radii, effective atomic charges, ionic conductivities, diamagnetic (Pascal) increments, diatomic bond energy increments, spectroscopic ligand field parameters, stereospecific ligand parameters and so on. Depending on the chosen set of compounds, the chosen types of properties, and the perspectives of the researchers, related alternative partition schemes may emerge, where the increments may have different meanings. As long as observable properties P_j of specimens j can reasonably well be approximated by different sets of increments b_k and d_l as in equation (1), it is fine.

$$P_j \approx \sum_{k \mathrm{for} j} b_k \approx \sum_{l \mathrm{for} j} d_l \tag{1}$$

We remember the interchange theorem of double-perturbation theory, where a response property for two perturbations can be represented by two different types of expressions, giving different perspectives of insight. The success in the development of research and teaching of chemistry should decide which schemes survive. Suggestions as by the Bader school that chemists should give up those useful analysis tools that do not fit into their special frame of the QTAIM approach do not appear fruitful.

Second, one shall search for connections between specific sectors of chemical experiences and the general framework of physical theories. That is the *reductive* inter-physico-chemical approach. In order to construct intuitively convincing and theoretically sound arguments, one usually needs a two-step analysis. To understand, *why* a chemical compound system forms and behaves in this manner, one also needs to understand why the chosen fragments or reference states relax or response in the manner they do. To this end, measuring or calculating the stationary molecule of interest or the overall changes upon a chemical reaction is not enough. One must choose both appropriate references and *appropriate intermediates*, which both are not uniquely determined by nature, for instance when analyzing covalent or dative or ionic or various secondary interactions. The real world is a quantum world (with emergence of classical features due to quantum decoherence), yet it is admissible to apply classical physical concepts in real chemistry, as more or less excellent approximations. Similarly one may, at least for 'separated' fragments and even for overlapping intermediates, discuss what would happen in a classical world with states that are "nonexistent" in reality, since they violate the Pauli principle, and talk about Pauli forces.

In summary, the main reason for the *coexistence of related chemical concepts* is that chemists may take different viewpoints and ask *non-identical questions*, looking into real space and/or onto the quantum field in space. The development of computational methods may open the birth and survival of more options, while unreliable approaches of extreme computational simplicity (the arbitrary AO basis in the Mulliken population analyses) may disappear. Modern scientific chemistry was given birth in the 1780s (by Lavoisier, his wife Marie-Anne Pierrette Paulze, and their Parisian colleagues) with the invention of the chemical elements as the conserved entities in chemical reactions, and the representation of macroscopic materials by atoms in molecules (by Dalton in the 1800s). The very basis of *scientific chemistry is the fuzzy concept* of microscopic elemental atoms in macroscopic stuffs; therefore the typically chemical concepts are fuzzy. Introducing physical theory to *explain chemistry in an intuitive manner* thereby supporting intuitive predictions, which are the basis of fruitful chemical science and technology for the benefit of society, requires the smart choice of physical reference states and more or less physical intermediate states for discussion of the specific physical situation in the case at hand.

Alston Misquitta and Krzysztof Szalewicz: On the basis of the description of SAPT presented above, we will now address question number 1. As we have shown above, the physical components of SAPT are uniquely defined and can be computed to potentially arbitrary accuracy. These terms have a precise physical interpretation. The electrostatic energy is the Coulomb interaction of unperturbed charge distributions. The induction energy of second order in V results from response of monomer A (B) to the field of unperturbed charge distribution of monomer B (A). The dispersion energy results from correlations of electron positions between monomer A and B. All these components are precisely defined at all R's, not only in the asymptotic region. Finally, the exchange-repulsion component results from exchange tunneling of electrons between interacting systems. Thus, in the case of SAPT there is no lack of precision in defining these chemical concepts. Consequently, SAPT can be used as the standard model for EDAs in the intermolecular interaction sector and EDAs inconsistent with SAPT should be discarded.

For induction interactions, one should always consider the sum of induction and exchange-induction corrections, sometimes denoted as E_{indx}. The reason is that at R near the van der Waals minimum and smaller, the overlap contributions in induction energies become large, leading to large discrepancies between the asymptotic expansion of induction energy and SAPT values [88], larger in magnitude than typical damping effects and of opposite sign. This is due to the fact that for systems with one of the monomers having more than two electrons, the interacting system is submerged in the continuum of Pauli-forbidden states unless such states are projected out by enforcing antisymmetry [64], which is not done in RS. If the exchange-induction term is added, the contributions coming from the violation of symmetry are canceled out to a large extent. When higher-order induction effects are important, as they are in strongly bound systems with a large polarization and charge-delocalisation, one should include E_{indx} computed to third order in V, as well as the $\delta^{\text{HF}}_{\text{int}}$ term. This term is defined as the difference between the supermolecular interaction energy $E^{\text{HF}}_{\text{int}}$ and the sum of the first-order, induction, and exchange-induction components.

Question 2: Does the adoption of a given partition scheme imply a set of more precise definitions of the underlying chemical concepts?

Ramon Carbó-Dorca: Looks like it doesn't. The impression is that the great number of partition schemes worsen the definitions of underlying chemical concepts, adding a bit of more fuzziness to their already fuzzy character.

Shant Shahbazian: In my opinion there is no such thing as "more" or "less" precise quantitative definition of a chemical concept and all mathematically rigorous definitions of a concept are equally precise and definitions lacking mathematical rigor do not deserve to be categorized as quantitative. Assuming that the intended partitioning schemes are rigorously constructed, the concept of interest is also precisely defined within the "context" of each given partitioning scheme. The problematic situation appears when one tries to compare the non-equivalent definitions not within, but between various partitioning schemes. As I stressed also in answering to question 1, this is the result of "over-quantification". At a personal level, one may simply dismiss all available partitioning schemes but a single one and adopt the preferred scheme trying to avoid the dilemma though, at the level of community the problem retains (the relevant literature however hardly supports that even at personal level this is the preferred strategy). Since part of what we mean by precise definition is the "consensus" of a scientific "community", not a single person, to use the "preferred" partitioning scheme, without a consensus the above mentioned formal mathematical viewpoint on the precise definition is at best handicap. These are the motivations to address questions 8 and 9.

István Mayer: Any partition scheme is based on a selected well-defined definition of the atoms within the molecule.

Martin Rahm: In one way of looking at it, yes. Chemical concepts are what we make of them. Different chemists can and will have different opinions on the best definition of what is covalence, electronegativity, etc. Differences in such definitions is also a consequence of the development of the concepts over time. Different partition schemes will naturally be a reflection of this. As such, different EDA schemes can provide precise definitions within their respective frameworks. If a particular incarnation is chemically useful is another question.

Frank Weinhold: Not in any rational process of advancing science. Any EDA component "label" is a language construct, not a "concept" per se. The correlations (if any) between EDA component labels and more broadly understood chemical concepts should be demonstrated, not assumed.

Ángel Martín Pendás: If an EDA is seen as a way to compress (or to compact) the complex energy information content of a wavefunction (or set of wavefunctions if references are needed), different EDAs should provide different readings of the same physical (or mathematical) objects. In this sense, all EDAs should be compatible among themselves (and that is why I advocate partitions which can be applied to any or at least to a large class of wavefunctions). By understanding how different methods read the same function providing different answers, the limits and windows of applicability of the underlying chemical concepts might probably be sharpened.

David L. Cooper: There are indeed senses in which the adoption of a particular partitioning scheme leads to more precise definitions of particular EDA "labels" within that scheme, but such "labels" are likely to have somewhat different meanings in equally-valid alternative approaches. I agree with Frank Weinhold that supposed correlations with underlying chemical concepts need to be demonstrated, without any such links simply being assumed. I am also struck by a point that is reiterated in a recent perspective article:[89] the use of models (including EDA schemes) can risk blurring the distinction between what is really mathematical modelling and what is, at least in some sense, an underlying chemical/physical "reality" or a "meaningful set of concepts". [That particular article classifies exchange, Pauli repulsion and orbital interactions as being part of the mathematical model, and it also addresses the extent to which there is really any proper distinction between charge transfer and polarization. Then again, picking (say) exchange, it can be important to remember that not everyone agrees as to what such entities really signify even in a *qualitative* sense.[90]]

Carlo Gatti: Not necessarily and surely not in the present state of affairs. Chemical concepts are in general very much intertwined in the energetic terms of the various EDAs based on orbital space decompositions and they may be so to a different extent, depending on the given scheme adopted. A clear and enlightening analysis of this rather convoluted problem is presented in 82. I'm personally in favour of retaining only those energy partitioning schemes where each energy component has a clearly defined physical basis and then of possibly observing whether and which of these components may be roughly related to chemical concepts, if any. This is the typical situation one is facing with position space EDAs, like IQA. To make an example, charge transfer, which is a typical chemical concept, may be clearly defined and easily evaluated with all these approaches. However, it is not possible to isolate its energetic impact in standard real space EDA schemes. One should make recourse to the theory of resonance structures in real space to estimate such energy component[91].

Paul Popelier: According to the way I answered Question 1 the current question sounds almost like the opposite of Question 1, and thus I am inclined to answer yes. As a fan of IQA (a sentiment to be updated when something better comes along) I am happy (hopefully not naively) with the way this EDA defines the following chemical concepts: covalency (via exchange), ionicity and polarity (via electrostatics), dispersion (via electron correlation) and steric effects[92] (via the intra-atomic or self-energy). Because IQA is able to also provide intra-atomic "dispersion" it has the potential to perhaps define a new chemical concept, which focuses on stability of weakly bound van der Waals complexes but then from an (intra)atomic point of view.

Pedro Salvador: If we assume an atom-in-molecule definition being a partition scheme, I think the answer is yes. Not only the numerical results differ from one AIM to another (sometimes quite dramatically), but some particular chemical concepts may only be achieved by making use of a given AIM. This is for instance the case of the so-called "overlap population", which can only be accounted for with "fuzzy" atomic domains. This, however, compromises this particular concept, which probably should be considered deprecated. In a way, one should stick to chemical concepts that can be achieved, at least quantitatively, with any reasonable (see Question 7) partition scheme.

Jerzy Cioslowski: As put succinctly by István Mayer in his answer above, "any partition scheme is based on a selected well-defined definition of the atoms within the molecule." However, in the case of energy partitioning schemes formulated in terms of (imaginary) physical processes, specification of the order of their application is equally important (see my response to question 1). Thus, the implication is always one way, namely definitions of chemical/physical concepts) energy partitioning

Gernot Frenking: I agree with Martin Rahm that "Chemical concepts are what we make of them." A useful partitioning scheme should indeed lead to a more precise definition of the underlying chemical concept. Five conditions are to be fulfilled by a reasonable partitioning scheme: (a) it should be based on accurate quantum chemical calculations; (b) it should be mathematically unambiguously defined; (c) the results should be largely independent of the level of theory used; (d) the different terms should lead to a plausible interpretation;(e) it should be useful for chemical problems. The adoption of a particular partition scheme comes from its usefulness. The agreement with chemical concepts is a fuzzy condition, because chemical concepts are fuzzy. I think that this comes out of the necessity to bring the pandemonium of chemical facts into an ordering scheme in terms of rules and models, which are accessible to the human mind. I was puzzled by the statement in ref. 82, that the use of bonding models "sometimes leads to a blurring of the distinction between mathematical modelling and physical reality." In the quantum world, physical reality of an electron is not entirely assigned to its electronic charge distribution , which represents only a projection onto a space of lower information content; its completeness is only provided by its wave function Ψ. The wave function Ψ contains more information about the behavior of the electron than ρ. In chemistry, this comes to the fore for example in the outcome of pericyclic reactions, or in any spectroscopic investigation, which can only be explained when the symmetry and sign pattern of are Ψ considered.

Émilie-Laure Zins: Most of the current chemical concepts are based on the observations, interpretations and intuitions of experimental chemists. One of the roles of theoretical chemistry is to explain and develop chemical concepts based on the fundamental equations of quantum physics, and to link these concepts to those of the experimental chemists. Thus, the use of any partition scheme to explain any empirical chemical concept should lead to more precise definitions of the underlying chemical concepts from the perspective of our community, provided that the energy partition is based on variables that have physical significance.

However, experimental chemists will not necessarily be immediately convinced by the increase in precision that we can bring to empirical concepts they work with on a daily.

Miquel Solà: It is an advantage, not a problem, to have different partitions schemes as far as they prove to be useful, to be rooted in quantum mechanics, to be mathematically unambiguous, to provide physically meaningful energy terms, to give insight, and to possess predictive power. Let me quote Dewar who said: "the only criterion of a model is usefulness, not its *truth*"[93].

Paul W. Ayers: In a narrow sense, once one chooses a partitioning method (either for the atom-in-molecule or the energy-into-fragments) then those choices can be profitably used as a "model chemistry" to elucidate chemical phenomena, to observe trends, and to draw inferences. In this sense all computed quantities within the selected partitioning are "precise" (in the sense of being exactly defined) within the context. But a different partitioning method might reveal different trends and different insights that are not less precise, but merely more or less useful (as a matter of preference and opinion).

Farnaz Heidar-Zadeh: A well-defined scheme is based on a rigorous set of physical assumptions, consequently, it consistently prescribes the definition of underlying chemical concepts. So, I would use the term "consistent" instead of "precise". This gives an elegant and unambiguous framework for further developing concepts. Even if a concept was proposed on heuristic grounds, but proved to be useful, establishing a framework within which it is mathematically justified is essential.

Juan Andrés: As Solà remarked recently[94]: "My usual answer is that the most fruitful concepts in chemistry share the same lack of strict definitioni[95]". In addition, there is not a unique way to compute quantities related with such intuitive chemical concepts and therefore, partition schemes. As Martín Pendás et al. write[96] "A chemical bond has an energetic strength (its bond energy) that is somehow connected to a particular electron count (its bond order). Interestingly, neither bond energies nor bond orders are (Dirac) observables. The former vanish into thin air once we pass from diatomics to polyatomics, whereas the latter too often rely on the orbital approximation. Notwithstanding, chemists feel comfortable with such an edifice otherwise built on shifting sands". Therefore, the different partition schemes need to be rooted in quantum mechanics, to be mathematically unambiguous, in order to provide physical basis of the underlying chemical concepts.

Yirong Mo: Due to the lack of direct experimental data to endorse any partition scheme as individual energy terms are not observables, it is hard to reach any consensus in adopting any particular partition scheme. Users adopt certain partition schemes often based on the accessibility and their own familiarity. Nevertheless, there are indirect experimental data to justify partition schemes, though it is everyone's taste whether to believe or not.

Eduard Matito: As it has been repeatedly said, a model should be judged by its usefulness. In the context of this question, the usefulness refers to the faithfulness with which it represents the underlying chemical concept. Since I understand the question as "can the energy partition go beyond the definition of some concepts", I am inclined to say that it pretty much depends on the fuzziness of the concept. Fuzzy concepts can be surpassed (and replaced!) by the model, the temperature is a nice example of this kind, as Shant indicated earlier. Aromaticity could be a more current example of a fuzzy concept that has been influenced by computational models and tools. However, it is difficult to imagine that energy partitions can go beyond long-standing and more consistent concepts. In particular, concepts that transgress computational chemistry (and even chemistry) are difficult to change.

Eloy Ramos-Cordoba: By selecting a particular partition scheme, the ambiguities on the underlying chemical concepts disappear within the framework of that particular decomposition. As Prof. Mayer stated above, energy partitioning schemes are mathematically well-defined, and so are the energetic components that one can extract from them.

W. H. Eugen Schwarz: No: In principle, experimental and theoretical inquiries are autonomous, with theoretically defined and empirically originated concepts to be connected as well as possible. Empirically motivated concepts need improvement if theoretically shown to be internally inconsistent, while theoretical constructs are senseless if unrelated to empirical concepts. The correspondence of a particular theoretical partitioning scheme to some particular chemical observation-coupled concepts attaches quantum chemical meaning to the latter ones. This may in some cases help more precisely specifying the empirical concepts. Since most chemical concepts *are* fuzzy to become broadly applicable, this correspondence will remain somewhat fuzzy.

Alston Misquitta and Krzysztof Szalewicz: As stated in the answer to Q1, SAPT partition scheme does provide a precise definition of the chemical concepts such as electrostatic, induction, dispersion, and exchange energies. While EDAs that are in a significant disagreement with SAPT should not be used, the question arises what is the threshold for such cutoff. While it is difficult to set any strict limits, perhaps a few percent agreement should be the goal. The agreement is best for Morokuma-type methods which are based on iterations of Hartree-Fock equations starting from monomer orbitals. See Ref.[97] for recent comparisons. On the other hand, methods decomposing supermolecular interaction energies using localized molecular orbitals (LMO) can only agree with SAPT in an approximate way.

Another criterion is the asymptotic behaviour. The exchange components should decay purely exponentially, i.e., should not involve any $1/R^n$ terms. The electrostatic, induction, and dispersion components should decay as appropriate powers of $1/R$. In methods based on LMOs these criteria are difficult to satisfy at very large intermolecular separations since, by the very nature of LMOs, the dispersion terms always have a small component originating from the intramonomer correlation contribution to electrostatic energies, so that for polar systems at a large R, the $1/R^3$ decay of the latter energies will dominate.

The electronic structure theories that are most advanced are also most complex and therefore most difficult to interpret physically. Therefore, one sometimes chooses to use manifestly inaccurate theories like Hückel theory because of the understanding it yields. Here is where SAPT shines as it constructs the interaction energy from the sum of physical components. Importantly, there is nothing ambiguous about these definitions, although there are some issues we need to be aware of, as described in the next paragraph.

There is no ambiguity in the asymptotic region where orbital overlap effects can be neglected, and, what is very important for physical interpretation, in this region the multipole expansion can be used to cast the interaction energy components (electrostatic, induction, and dispersion) in terms of the molecular properties like the electrostatic multipoles, and static and frequency-dependent polarizabilities. SAPT interaction energies agree with those from the multipole expansion to arbitrary accuracy provided that R is large enough. Thus, SAPT is seamlessly connected to the multipole expansion. Since the multipole expansion of interaction energy is expressed in terms of multipole moments and static and frequency-dependent polarizabilities of monomers, this adds another level of physical insight into SAPT interaction energies. Furthermore, there is a smooth transition between the overlap region and the asymptotic region. The monomer densities used to calculate the electrostatic energies can be replaced by a set multipole moments at large R. Similarly the density-density response functions can be replaced by polarizabilities. The multipole moments as well as static and frequency-dependent polarizabilities are measurable, thus providing a strong link of SAPT components to experiment. This is, at least in the region of small density-overlap, an unambiguous link. This feature alone separates SAPT from all EDA methods since, to our knowledge, no relation to experiment is possible in these methods.

While all acceptable variants of SAPT must have the same asymptotic behaviour as SRS, and therefore the components are asymptotically unique, one may question the uniqueness in the overlap region. Fortunately, all acceptable SAPT variants give identical first-order energies and second-order induction and dispersion energies. The non-uniqueness appears only in the second-order exchange corrections. Of those, the exchange-dispersion energies are relatively small so the potential differences can usually be safely ignored. The differences in exchange-induction corrections are eliminated by the $\delta_{\mathrm{int}}^{\mathrm{HF}}$ term. Also, some variants that perform best in all orders are equivalent or very close to SRS in low order. In conclusion, whereas there is a small non-uniqueness in definitions of physical contributions resulting from the flavours of SAPT, differences between best theories can be ignored.

Question 3: How can one use the results of a partition scheme to improve the clarity of definitions of concepts?

Ramon Carbó-Dorca: In case one can observe such a publication phenomenon, time which provides with various research fashions and hypes the research panorama, will act as the way partition schemes appear from previous techniques and evolve into new schemes, according to the increasing number of researchers in quantum chemistry and their publication needs. Perhaps leaving apart the real research task of understanding molecular behavior within a general framework valid in any circumstance.

Shant Shahbazian: In my opinion there is no direct relationship between the results of a partitioning scheme and the clarity of chemical concepts. As I stressed in answer to question 1, to have a well-defined concept, a comprehensive theory for the concept of interest must be developed. Let me give an example. While humans had always an intuitive qualitative understanding of temperature, since the time of Galileo people tried to quantify this intuition through constructing various thermometers. In one sense, in this period temperature was an index of hotness/coldness but temperature only conceived as a physical "observable" when thermodynamics was formulated and the absolute temperature was introduced independent from thermometers, based on its relationship with internal energy and entropy. In other words, thermodynamics is an organized web of connections between various thermal concepts and the position of each concept, e.g. temperature, in the web makes it a well-defined and clarified concept[98]. What currently lacks in theoretical chemistry is a similar comprehensive theory (or theories) that not only introduce each chemical concept quantitatively but also makes a web of relationships between various concepts. Index-based view in computational chemistry that focuses only on quantitative definition of a single concept lacks such capability and, in my opinion, current partitioning schemes are also no exceptions.

Martin Rahm: It would depend on the concept in question. For example, I have, together with Roald Hoffmann, redefined the chemical concept of electronegativity within the framework of the "Experimental Quantum Chemistry"-partitioning[54]. Together with Tao Zeng, this precise definition allowed us to revise the scale of atomic electronegativity in a way that compares well with previous scales, such as Pauling, Mulliken and Allen[56]. Other chemical concepts such as "covalence" and "ionicity" are less straightforward. One way towards clarifying such concepts is to use EDA-descriptors and creates maps of chemical interactions. In well-known materials under ambient conditions we mostly know what to expect: NaCl should come out as ionic, a C-C bond better have some covalency, and the helium dimer should be different from the previous two[55]. A partitioning scheme that agrees with conventional wisdom, while providing new insight, has a better chance of improving the clarity of definitions of chemical concepts.

Frank Weinhold: Reference [99] serves as an example for how a concept (in this case, "hydrogen bond") can achieve progressively improved operational definition. Can any component of any current EDA partitioning scheme meet the operational criteria of mutually consistent correlations with experimental properties, as illustrated in this work?

Roberto A. Boto: On the one hand a partition scheme is built from some theoretical framework, which at the same time, is built from a set of, in principle, well-defined concepts. Therefore, the quality of the results should be determined by the theory behind. It is hard to imagine a feedback process.

On the other hand, energy partitions could be constrained to follow some conditions, such as produce energy contributions within the chemical scale, or equalize energy terms obtained by different partition schemes. These would not improve or worsen the definition of concepts but would add some uniformity into the different definitions of the same chemical concepts.

Ángel Martín Pendás: Uhm, well, some of the most cherished chemical concepts do implicitly rely on some kind of partitioning. Covalency, for instance, is one of them. Whatever source is used to find an operational definition (including IUPAC's gold book) of what we mean by a covalent bond will include the word "sharing". And sharing implies at least two objects which share, so a partition. Typically those objects are understood as atoms, so in some sense, partitioning schemes may help develop a concept in a bootstrapping process, as in the temperature example commented by Dr. Shahbazian.

Julien Pilmé: In my opinion, results obtained from only one partition scheme are probably not sufficient to really clarify the definition or the meaning of simple concepts commonly used in chemistry because most of these concepts go beyond any partition scheme. Maybe, if the targeted concept has a typical "signature" which can be identified through several partition schemes, the confrontation of results arising from numerous partition schemes would be useful to improve the definition of the concept. I think for example that the case of the covalent bond, already reported by Ángel, falls into this category.

Carlo Gatti: I see a risk in this process as chemical concepts evolve and generally become wider and more general with time. One good example is aromaticity. Though hardly definable, the concept of aromaticity has now largely expanded and it is no longer limited to pi-orbital organic chemistry but proved useful in describing bonding and energy stabilization in many inorganic molecular compounds and also in the solid state. Not to talk about recently discussed organic molecules where pi- and sigma-aromatic chains seem to coexist. Therefore, in my view, a physically grounded partition scheme should not be aimed at improving the clarity of definition of a concept, which may possibly evolve, but be able to include and to some extent predict the future evolution of that concept. It is only through this process that the partition scheme will help to improve the clarity of a concept. Non-nuclear attractors and their properties were defined while studying Li clusters as a straightforward extension of Bader's space and virial partitioning. But have then recovered in many other chemical situations, both at ambient or at high pressure, and featuring the broad concept of interstitial or "isolated" electrons.

Paul Popelier: An example of how to use the results of a partition scheme is that of the EDA called IQA being combined with the newly proposed Relative Energy Gradient (REG) method[100]. The REG method is able to handle, automatically and exhaustively, the typically hundreds of individual energy contributions that IQA generates. REG ranks atoms to the degree that they act like the total system they are part of, in terms of energy changes. This minimal method can handle competing energy contributions, which may appear contradictory and thereby fuelled ongoing debates. For example, in our very recent biphenyl case study[101] we use REG-IQA to explain its planar rotation barrier. The central torsion angle in biphenyl prefers to be 45 degrees and, when at 0 deg, biphenyl's total energy profile reaches a local maximum. REG shows that IQA's intra-atomic energies of the ortho-hydrogens dominate the barrier, which is compatible with the textbook explanation of a steric clash. However, at the same time the exchange energy between these two ortho-hydrogens becomes most stabilising at 0 deg, indicative of the formation of a covalent bond. REG is not confused by these two opposing effects and concludes that, while they largely cancel out, it is the energy behaviour of the ortho-carbons that causes the rotation barrier. This is an example of the Dutch expression "als twee honden vechten om een been loopt de derde er mee heen." (Note: just in case you GoogleTranslate this then know that "been" actually means "bot")

Pedro Salvador: As Martin stated, that would depend on the particular concept. For instance, the concept of Oxidation State has lacked a clear definition for years, but the problem was not related to any partitioning, but to the rather vague terminology used. After IUPAC has recently revised the concept (albeit not in a fully satisfactory way in my view), new first-principles schemes[102] (which at the end of the day also make use of a partitioning scheme) can be devised to match with the so-called chemical intuition. Another illustrative example is that of the "local spin". In this case, it is the nature of the mathematical object that needs to be partitioned (which particular formulation of the expectation value of the spin-squared operator), rather than the actual partition used that brings about meaningful numbers for this concept[103].

As I stated in the previous question, concepts that can be achieved only by using specific partition schemes are undesirable. At the same time, a given partition scheme is put into jeopardy when it cannot reproduce even qualitatively the expected results/trends of a well-established concept. So, instead, concepts could be (wisely) used to improve the definition of partition schemes.

Gernot Frenking: Chemical concepts are fuzzy objects, which may be defined in different ways. Carlo Gatti mentioned already aromaticity, which can be defined by energetic, geometric, magnetic or other criteria such as chemical reactivity. I refer to the five conditions given in my answer to question 2, which should be fulfilled by a partitioning scheme. Other than this, I see no further clarification of the definition of a concept.

Julia Contreras: For a partition scheme to improve clarity, it should be able to do just what any other theory is expected to do: describe what we know and predict what we dont. Both Hilbert and real space energetic decompositions have been focused in describing what we know, plaguing the literature with different views of things for what we have an intuition. However, in my viewpoint, more efforts should be paid in describing things for which we do not have an intuition (e.g. high pressure) and predict what will happen in those cases. After all, that is what most chemical concepts were born for. I have the impression we have been focused on giving mathematical definitions to concepts that were born without the need of a mathematical framework, and we have barely gone beyond that.

Émilie-Laure Zins: I am not convinced that there can be a single way to use the results of a partition scheme to improve the clarity of all chemical concepts as suggested by the question. In the case of definitions of weak intermolecular and intramolecular interactions, it seems to me that a quantitative approach based on energy decomposition analysis followed by a principal component analysis may be a promising way to clarify the definitions and to properly classify the interactions.

Laurent Joubert and Vincent Tognetti: It is not obvious from our point of view that the exactness of an energy partition (or even its usefulness) is correlated to its use for deciphering chemistry. To expand this point, it is important to recall that (as already stated by Jerzy Cioslowski in discussion for question 1) EDAs can be divided into two main categories: those obtained during the generation of wavefunction or molecular energy, and those coming from a subsequent post-treatment. Let us for instance consider a MPn calculation: it will naturally provide a decomposition into various additive contributions, from the zeroth to the n-th perturbation orders. Alternatively, KS energy is by definition split into the KS kinetic energy, the interaction energy between electrons and nuclei, the Hartree and exchange-correlation contributions. One can then wonder whether such decompositions may convey chemical information. For instance, the second-order correction in MP treatments is often linked to dispersion (London) effects. Conversely, the chemical meaning of KS kinetic energy (related to the fictitious non-interacting system, and not to the real one) is far from being obvious, as well as exchange-correlation since it involves corrections to kinetic energy and electron repulsion. KS thus provides direct energy decomposition without meaningful chemical information. Note that a second exact additive KS decomposition could be straightforwardly obtained from first principles with the orbital energies and exchange-correlation potential. However, it is not deprived from drawbacks: 1) what is the meaning of KS orbital energies? 2) how to interpret the other terms? For the first point, the only exact result is that the HOMO energy is opposite to the vertical ionization potential if the exact exchange-correlation functional is used. The second problem can be cured using Mel Levy's recent potential shift[104] that allows for expressing the total energy as the only sum of orbital energies. Such a scheme would certainly simplify energy decompositions, but it is still in the youth age.

Paul W. Ayers: If the "clarity of definition" of a concept was dependent on the "results of a [one specific] partitioning scheme" then I am reluctant to embrace that definition. On the other hand, if the "clarity of definition" of a concept is supported by the "results of a [many nonspecific] partitioning schemes", then that concept is well-founded and defined qualitatively (even if the partitionings might give different quantitative results).

Farnaz Heidar-Zadeh: The results of the partitioning schemes (and other concepts) can clarify their usefulness in capturing chemical and physical phenomena. That is, numerical results can demonstrate the domain of applicability of a scheme and lead us to improve our definitions. So, I believe the results can act as a feedback loop: guiding us to a better formulation of the problem and strengthen our intuition.

Juan Andrés: An underlying theme of the above questions has been the gap that exists, in general, between quantitative quantum theory and chemical concepts. In this context, we agree with the comment by Grunenberg[95] "I am not writing against the use of qualitative chemical concepts per se, but against their quantification. In many cases, qualitative concepts even in combination with non perfect experiments led to real progress in chemistry. However, one striking attribute of the aforementioned disputes in the literature is the fact, that many of these quantifications are triggered by a conceptual farrago and by this, most of these scientific quarrels are inherently insoluble Some even resemble mock discussions. (Interestingly, in the course of such discussions, usually one side is referring to a medieval scholastic "questio." Therefore, we need partition schemes precisely defined mathematically from the underlying physics to reach clarity on the definitions of concepts.

Yirong Mo: The conflicting results from different partition schemes certainly will certainly attract attentions and stimulate discussion and further research work. In this way, the definitions of concepts can be progressively clarified and eventually quantified.

Eduard Matito: I refer to my answer to Question 2: I believe this can only be achieved in the case of concepts that lack consistency. In these cases, there must be a consensus among different partitions (and within the community) before walking the dangerous path of changing (clarifying, if you prefer) the definition of concepts. Again, I believe the concept of aromaticity serves as a nice example. In the 90s, the definition of aromaticity given by the IUPAC applied only to ground-state pi-aromatic compounds and, although the current definition of aromaticity is not less blurry than it used to be, now recognizes different aspects of aromaticity such as electron delocalization, particular reactivity, thermodynamic stability, and certain structural features. Many of the latter features have been repeatedly confirmed by the corresponding computational measures/models of aromaticity. In fact, the work still continues. The "Aromaticity" conference organized in Riviera Maya in 2018 by Gabriel Merino, Miquel Solà, and Henrik Ottosson included a round-table session to find a consensus among the members of this community (experimental and theoretical) about an updated definition of the concept.

W. H. Eugen Schwarz: Yes, for instance: statistical correlations and factor and cluster analyses can work out whether one or more conceptual main-components are behind a group of related empirical or theoretical concepts, and how narrow the relations between them are. Theoretical schemes may need revision in the case of poor relation to well-proven empirical concepts.

Alston Misquitta and Krzysztof Szalewicz: The SAPT partition scheme gives indeed a clear definition of concepts. Consider two polar systems. One of the main concepts appearing in many undergraduate courses is that at large separations this interaction is determined by the simple interaction of the permanent dipole moments with its $1/R^3$ decay. As R decreases, contributions from higher multipole moments become important. The sum of all these contributions agrees to a high accuracy with the SAPT electrostatic energy. Once R is so small that the $1/R^6$ terms matter, contributions from induction and dispersion energies are becoming important. At these R, such contributions can be expressed in terms of dipole moments and of the static and dynamics polarizabilities. Again, both components are very accurately reproduced by SAPT. As R decreases further, overlap and exchange effects come into play. This does not mean any loss of physical insight despite things getting a bit more complicated. For example, the electrostatic energy is still just the Coulomb interaction of two charge distributions. For the induction and dispersion energies, we have to use the concept of density-density response function which also has a clear physics meaning. As the distance between monomers is now of the order of a few angstroms, electrons can tunnel through the potential barrier. Tunneling is one of the main concepts of quantum mechanics, with a clear interpretation. Such clarity of definitions of concepts as outlined above cannot be achieved if a decomposition starts from the dimer wave function.

Question 4: Are partition schemes subject to scientific Darwinism? If so, what is the influence of a community's sociological pressure in the "natural selection" process?

Ramon Carbó-Dorca: A chemically and physically bound piece of research cannot be influenced by anything but the theoretical scheme itself. A partition scheme, if it really conforms according to quantum mechanics, shall be appropriate to any electronic system. If a system influences the construction of a partition scheme, then there cannot be any hope to obtain a general procedure.

Shant Shahbazian: If at the level of a community there is a consensus on the "intrinsic" preference of a method or tool then such question would be irrelevant. So, asking such question means that currently there is no consensus on the intrinsic preference of the available partitioning schemes. As I stressed elsewhere[80], at the extreme level this means the lack of the scientific "objectivity" and "realism" that scientists are proud of and is usually used to distinguish science from other human endeavors like philosophy, politics and religion where the intrinsic preference is always disputable. Accordingly, sometimes it seems to me that the implementation of an index or a partitioning scheme in a well-known or a user-friendly software had been the prime factor in its dominance in competition with similar indices or schemes. In short term such factors are tolerable and probably even inevitable since in the end science is also a human activity, but when such factors are dominant after decades, to me, it is a sign of a crisis…

István Mayer: Yes, I think so. One needs results that help interpret the calculated and/or experimental quantities. The observation that Mulliken's gross populations often fail to provide chemically reasonable results, motivated the quest for alternative schemes of population analysis. (This was the case although Mulliken's gross population is that definition which is consistent with the internal mathematical structure of the LCAO formalism[105].) When EDA methods are concerned, I have experienced a pressure from chemists to produce a scheme in which the diatomic bonding energies are on the "chemical scale", i.e., not equal but comparable with the accepted bonding energies. (Also see my answer to Question 6.)

Martin Rahm: I hope we all can agree that EDAs should be subject to scientific Darwinism. Cross-comparison and "benchmarking" of EDA methods, even if it difficult to do, is one way forward that should allow for more "evolutionary pressure". I stress this point further in my answers to questions six and seven. However, rather than risking extinction, I suspect that EDA methods subjected to comparative studies will thrive. Comparisons will bring out complementarities in different approaches and ultimately allow us to get a better overall grasp of electronic structure and chemical bonding. A nice example highlighting the benefits of comparative studies of EDA methodology is that of Fugel et al.[106]

Frank Weinhold: Yes, of course. By the evidence of their usage, adoption, and cited-applications (or not) in the broader chemical community, EDA approaches should be subject to "selection" according to their impact on how chemistry is actually practiced and taught.

Roberto A. Boto: In my opinion, a partition scheme should not be influenced by anything but its theoretical framework. However, in theoretical chemistry, there has always been a balance between quality and computational resources. It is often found that the more elaborate is the theory, more demanding is the computation of terms derived from it, and approximative routes should be taken. Energy partitions are not an exception, and the pressure of the community towards more complex, often larger, chemical systems could bias the selection of EDAs.

Ángel Martín Pendás: Like anything in Science, partition schemes are subjected to Darwinism. Whether Darwinism in Science chooses the best solution or only the fanciest one is another problem, since, as a human activity, Science does not escape fashion. Since, unfortunately, many EDAs are intimately associated with particular electronic structure paradigms (e.g. molecular orbital or valence bond descriptions), the waves in the former are clearly conditioned by those in the latter.

David L. Cooper: Experience suggests that the partitioning schemes that are likely to be the most widely used in the scientific literature will not necessarily be the "best" ones, as determined by cross-comparison and "benchmarking", nor indeed those that are best suited to impacting the practice and teaching of Chemistry by non-theoreticians. Although "fashion" can indeed be an important factor, ultimately it is the availability of particular methods in certain "standard packages" that could end up being the deciding factor. This could of course be ameliorated to some extent by the availability of free and easy-to-use facilities that implement other schemes.

Carlo Gatti: Yes, they probably do, but are we sure that the more fitted to survive are those schemes with largest scientific rigour? The sociological pressure of the community may largely bias the selection process. Factors like ease of use, simplicity of analysis (few composing energetic terms rather than a potential plethora of progressively finer dissections like in the real space EDAs), adoption by large and numerically dominant communities, may clearly bias the game, offsetting the purely scientific selection process. Other counterweighting and disturbing factors might be the implementation of given schemes rather than others in popular quantum-mechanical codes.

Julien Pilmé: Yes I agree with that. In my opinion, the "natural" selection process, which should be conducted according to scientific requirements, is hardly efficient owing to the lack of the straight forward link with the experimental data. Maybe, this process becomes more "fashion-driven" and more sensitive to a sociological pressure. Yes, it seems also that the selection process is flawed by the ready availability (or not) of EDA methods in the quantum chemistry softwares.

Paul Popelier: The metaphor of natural selection is useful to think about where the zoo of EDAs is at, and where it should to head for. The answer to Question 4 is yes because natural selection is already happening. For example, the recent review by Skylaris et al.[2] compares and discusses six test sets. The authors conclude that "Overall the ALMO EDA scheme is shown to provide the most chemically sensible EDA results for our systems relevant to drug optimization." Unfortunately, this comparative study was confined to non-topological EDAs. Building on the Darwinistic metaphor, this means that topological EDAs happily live on some island or disconnected continent that has had no contact yet with non-topological EDAs (although Ángel and co-workers have published such a comparative study[107].

We should keep in mind how natural selection actually works. Ultimately, it is the interaction between the creature (i.e. a given EDA) and its environment (the other EDAs and the community of users) that determines if the creature survives or not. I think that as a community we should be a more demanding environment, even if that means that an EDA becomes extinct. Experimentalists can only take the work of theoreticians seriously if it provides future-proof insight, or correct predictions. There is no harm in two different EDAs coming to the same conclusion; what is a problem is if they contradict each other. Although I don't have precise references in mind my feeling is that the community allows contradiction to exist, and even worse, allow them to thrive under the false banner of diversity and richness. This is dangerous for Science. I am still dreaming of a consistent world of interpretations and predictions, one where $\mathbf{F} = ma$ is the only equation that puts a person on the moon rather than $\mathbf{F} = m/a$ or $\mathbf{F} = ma^2$. However, equivalent theories (e.g. Matrix Mechanics and Wave Mechanics ,or Valence Bond and Molecular Orbital, or String Theory and Quantum Gravity) can coexist as long as they make the same predictions.

Jerzy Cioslowski: Like almost everything in science, the energy partitioning schemes are subject to surges and ebbs in popularity, and even extinction. However, I am reluctant to use the term "Darwinism" in this context as the concept of the "survival of the fittest" (if one defines the fittest as the most rigorous and scientifically justified) obviously does not apply here. I am afraid that the popularity of various definitions of chemical concepts is mostly driven by the prejudices (politely called "chemical intuition") of those regarded as contemporary authorities in (not necessarily theoretical) chemistry. This situation would correspond to the evolution of species being due to supernatural powers (gods, aliens, or whomever) eliminating living organisms according to their preferences, which is not exactly what Darwin had on his mind.

A simple prescription to avoid this undesirable status quo would be axiomatization of chemical concepts. Spelling out a set of axioms that all the concepts have to satisfy would greatly reduce the room for personal preferences and thus diminish the importance of the "human factor in interpretation of electronic wavefunctions.

Gernot Frenking: Darwinism means the survival of the fittest. In that sense I do think that those concepts will eventually be adopted by the community, which are considered as the most useful ones. However, I see an ongoing preference for simple models that are intuitively easy to accept even when the underlying assumptions are incorrect, instead of a more complicated model, which agrees with a thorough quantum chemical analysis. There seems to be a human tendency even in science to prefer a known disease to unknown health, because one is afraid of the work that comes along with the cure. The great acceptance of the NBO method is at least partly due to the smoothing tranquilizer effect for addicts of the Lewis model who do not want to be bothered by the complexity of the electronic structure. The sociological pressure could lead to a situation where the well-known illness is preferred over the unknown health. With other words, the frequent use of NBO results may lead to the acceptance of the method even when the shortcoming are well known.

Julia Contreras: Absolutely. I see that there are two main trends: mathematical and physical Darwinism and I totally advocate for physical Darwinism. Theories can be very elegant, but what I really expect from an energetic partition (or as well any other theory), is to describe the physics of the system. To provide a descriptive and predictive framework. What should not be interpreted as social pressure (and we have seen much of these lobbies in this community): MY method is BETTER than the others (and I reject papers otherwise).

Henry Chermette: Darwinism. . . , yes or no: selection of the survival scheme(s) can be biased by factors like ease of use, availability in (the widely used) softwares, and simplicity of analysis. And a scheme can be "rediscovered" 20 or 30 later after its (first) description in a (specialized, not popular) journal.

Émilie-Laure Zins: This question suggests a comparison between the theory of evolution and the description of the chemical bond. This comparison seems to me to be particularly relevant and desserves a short comment. Experimental chemists, during their observations or interpretations, have proposed and developed many concepts, which can be compared (metaphorically) to different living species: they can appear, persist, evolve or disappear. It can be hypothesized that some chemical concepts could be merged, in particular through the use and development of adapted partition schemes. It seems to me that a "massive extinction" in the zoo of chemical concepts, caused by a "universal" partition scheme, or by a limited number of partition schemes based on the fundamental theorems of quantum physics, would be beneficial to chemistry.

Laurent Joubert and Vincent Tognetti: We think that different communities may have preferences guided by some historical reasons or, let us say, some traditions in interpreting the same results. Assume that we are interested in the energy difference between two conformations (that can be measured experimentally in some cases). The virial theorem actually brings us two explanations: 1) it is due to the electron kinetic energy, 2) it is due to the potential energy. No one is preferable, being both correct, since, quoting Godard, "The essential difference between classical mechanics and quantum mechanics is that in classical mechanics the kinetic energy and the potential energy are independent (one is determined by momentum, the other by position), whereas in quantum mechanics T and V are simultaneously determined by the wavefunction." However, an experimental chemist is much more accustomed to think of potential energy (linked to interactions between atoms) than of kinetic energy, and we are thus facing different habits in various chemical communities. T features the advantage of being derived from a one-body operator, while V involves a two-body operator. When decomposed into N atoms, it thus generates about N2 values, a number that may make the analysis inextricable. Noteworthy, Popelier recently proposed a powerful relative energy gradient approach to select the most relevant contributions[100]. Certainly, such analyses will clearly benefit from the big data and artificial intelligence fields. Maybe, they will thus lead to favour some partitions to the detriment of others. However, from our point of view, there is nowadays rather coexistence of various theories, within different frameworks (real-space analysis, wavefunction analysis). The fact that there is such a debate indicates that there is currently no natural selection process at work... One can also say that natural selection actually requires a very long evolution time, much more than the age of quantum chemistry. . .

Paul W. Ayers: Yes, but in a strange way. Science is both "red in tooth and claw" in the sense that the most vociferous, forceful, ruthless, and prominent researchers (and referees) have an advantage. It's also true that people who write/convey their ideas most clearly (and forcefully) have an advantage. Yet (fortunately) vehemence and salesmanship is not everything (though I do feel we often underestimate its importance). Most scientists possess an idealism and thus the drive towards utility and simplicity is strong. I think many of us seek decompositions/partitionings that "can fit on a T-shirt" (Occam's razor). And all of us seek definitions that are helpful to experimentalists. I.e., while I often call my work on concepts "chemical philosophy," just like traditional epistemology, the goal is to find precepts/concepts that have broad and practical utility for everyone.

Farnaz Heidar-Zadeh: There is no doubt that partitioning schemes (and other concepts) evolve over time and the fittest survive, i.e., the ones which are well-defined and make better predictions. However, this natural selection is commonly disturbed by our biases and prejudices as humans, which makes the scientific discourse not very scientific. (This was a very disappointing realization for me as a young scientist!)

Juan Andrés: As Ayala wrote[108] "There is a contradiction between Darwin's methodology and how he described it for public consumption. Darwin claimed that he proceeded "on true Baconian [inductive] principles and without any theory collected facts on a wholesale scale." He also wrote, "How odd it is that anyone should not see that all observation must be for or against some view if it is to be of any service!" The scientific method includes 2 episodes. The first consists of formulating hypotheses; the second consists of experimentally testing them. What differentiates science from other knowledge is the second episode: subjecting hypotheses to empirical testing by observing whether or not predictions derived from a hypothesis are the case in relevant observations and experiments. A hypothesis is scientific only if it is consistent with some but not other possible states of affairs not yet observed, so that it is subject to the possibility of falsification by reference to experience" But, the more important yet is that Darwin discovered natural selection, the process that accounts for the adaptations of organisms and their complexity and diversification, in a wide range of research fields, including biology, geology and also chemistry and physics. In our case, it is necessary to remember that theories such Lewis, Valence Shell Electron Pair Repulsion (VSEPR), molecular orbital (MO), its extension to natural bond orbital (NBO), frontier molecular orbital (FMO) of Fukui, valence bond (VB), or even conceptual density functional (CDF). These theories have their advantages and shortcomings, work in some cases but not in another, and are still used in the current bibliography. Therefore, it is expected that in the partition schemes occurs the same, and that many of these are still used. The important and desirable thing is to know if they are used correctly and as far as you can get with the results obtained. A large dose of self-criticism is necessary to overcome the sociological pressure.

Yirong Mo: This may be true. Most computational chemistry practitioners are users of software and tend to follow the majority and use whatever put into the software designed by others, as in this way, works can be relatively easy to be accepted by the community. In this process, prominent figures may lead the majority to particular partition schemes.

Eduard Matito: Yes, energy partitions and, in general, chemical bonding tools are subject to extinction and, inevitably (and regrettably), they depend on its "popularity". As it has been pointed out, the popularity depends on its availability, its usefulness, if they are easy to compute, the cost of its calculation, scientific "marketing" and, to some extent, scientific rigor. As developers and experts of chemical bonding tools, we should be well aware of this and act accordingly. In the field of aromaticity, NICS became the most popular measure because it is available on a large package (Gaussian) and it could be easily computed with a single keyword. NBO is known to computational and experimental chemists alike because there has been a large effort to advertise it (books and online tutorials, reviews, workshops, and hands-on sessions). I believe is our responsibility to work to facilitate the use of the most useful and rigorous partitions, making them available and as user-friendly as possible. Otherwise, they became complicated and obscure objects that only a handful of people (the so-called experts) can use and understand. Last but not least, we should encourage benchmarks and comparisons that put forward the boundaries and limitations of the energy partitions. For instance, we identified that some atomic partitions could not be employed to compute aromaticity indices [109] and and Ponec, Cooper, and others found that only with some atomic partitions the bond index attained a maximum value close to the avoided crossing of the two lowest-lying states of LiH [110–112].

W. H. Eugen Schwarz: Yes. *First, some sociological pressure* may be induced by charismatic colleagues and their followers influencing the fashions of a time. We all know it, concerning 'overlapping VB concepts' *vs.* 'orthogonal MO concepts', concerning aromaticity as a single-dimensional concept best represented by the NICS parameter, concerning QTAIM based molecular partition schemes, or that molecules only consist of atomic one-center parts and diatomic two-center bonding parts, and so on. *Second, the viewpoints in common teaching* are partly determined by historical traditions and ideologies and by well-written and well-priced textbooks, influencing the convictions of the majority in the scientific community. *Third, the availability of technical options:* an analysis scheme will best survive if it can be applied with little investment of money or knowledge and with user-friendly tools; or if it can be easily applied to available data sets. For instance, one can better derive density distributions than wave-functions from x-ray diffraction patterns, so x-ray diffraction research supports analyses of densities in 3-dimensional space.

Alston Misquitta and Krzysztof Szalewicz: A necessary condition for a partition scheme to be of value is that the sum of components should give an accurate interaction energy at all physically important dimer configurations, so that a potential energy surface (PES) based on this scheme can be used to predict observables in agreement with experiment. Thus, partitions based on CCSD(T) satisfy this condition, but based on DFT will not unless particular care is taken to partly control the self-interaction error (by using a hybrid or range-separated hybrid functional) and an adequate dispersion correction is included. As discussed above, SAPT satisfies this condition very well. The second conditions is that components are not excessively large in magnitude so that there are no large cancellations in adding them to form the total interaction energy. The third condition is that if components are meant to represent electrostatic, induction, dispersion, and exchange energies, they should agree to within a few percent with SAPT. All methods satisfying these conditions are basically equivalent from the point of view of getting insights into physical mechanisms of intermolecular interactions.

This set of conditions can be used to evaluate various EDAs for the component called charge-transfer energy. While SAPT includes all charge-transfer effects, it does not compute a separate charge-transfer energy, but rather this component is included in the induction energy. As the other part of this energy is the polarization energy, which is negative at the two-body level, the charge-transfer energy cannot be smaller, i.e., more negative, than the induction energy. For example, for the water dimer at the minimum configuration, the sum of the second-order induction, exchange-induction, and $\delta^{\mathrm{HF}}_{\mathrm{int}}$ terms is -2.24 kcal/mol [113,114]. This can be compared to the total SAPT interaction energy of -4.65 kcal/mol and to the CCSD(T) interaction energy of -4.95 kcal/mol. Thus, SAPT gives a lower bound for the charge-transfer term of -2.24 kcal/mol. Taking into account differences between SAPT and CCSD(T), one may assign an uncertainty of ± 0.3 kcal/mol to this value. However, the non-charge-transfer part of induction energy, i.e., the polarization energy, is not negligible and it is by definition negative. This energy can be estimated from the classical polarization model and if the procedure developed in Ref. [115] is applied to the water dimer, one gets -0.8 kcal/mol in the first iteration, corresponding to the second-order in V, and an additional -0.2 kcal/mol from the further iterations. Thus, the total polarization energy amounts to -1.0 kcal/mol, giving an estimate for the infinite-order charge-transfer energy of -1.2 ± 0.3 kcal/mol. Values much larger in magnitude, often found in literature (see a discussion in Refs. [116,117]), cannot be considered to represent true charge-transfer energies. Some EDA schemes are consistent with our estimate, for example, the absolutely-localized molecular orbitals (ALMO) method based on CCSD [118] gives -0.8 kcal/mol. The method of estimating charge-transfer terms based on the regularized-SAPT(DFT) approach, developed by one of us [119], gives a smaller in magnitude value of -0.4 kcal/mol (however, this estimate includes only the second-order terms and would increase in magnitude if higher-order corrections were accounted for).

Question 5: To what extent does/can/should investigated systems influence the choice of a particular partition scheme?

Ramon Carbó-Dorca: It seems difficult to foresee how partition schemes clarify anything, being somehow (or quite) arbitrary. Perhaps they could add more obscurity to the certainly not very clear usual chemical concepts.

Shant Shahbazian: In principle, a mathematically rigorous partitioning scheme must be applicable to any molecular system regardless of the size, type of atoms or complexity of its electronic structure. However, in practice the "interpretational" problems emerging from applying a scheme to certain systems may have a strong influence on favoring or dismissing the scheme. As an example, the popular "misinterpretation" of the (3, -1) critical points (CPs) emerging from the topological analysis of the molecular electron densities as indicator of bonds has been a source of confusion[120,121]. There are certain systems that if one insists that (3, -1) CPs are "bond" CPs, i.e. BCPs, then inevitably there would be a clash between the QTAIM (quantum theory of atoms in molecules) analysis and most of other partitioning schemes on the presence/absence of bonds between certain atoms. In such problematic cases people usually try to avoid the use of the QTAIM analysis, though a proper reinterpretation may fix the problem[96]. However, such problems are not confined to just misinterpretations and there are cases where a partitioning scheme does not support (or is at odds with) an established viewpoint regarding a system and people try to avoid the scheme. Such "expectational bias" regarding what "must" emerge for a system may unconsciously (or even consciously) affect the preference/dismissal of a partitioning scheme. For me, this is an unpleasant element of "subjectively"....

Martin Rahm: I suspect it often does not. This in large part because most EDA methods requires quite some expertise to execute and interpret. There are also a lot of methods out there, and it is not always easy to evaluate pros and cons in an objective manner. Publishing work addressing chemical validation and cross-validation of EDA methods, discussed in questions six and seven, should help in this respect.

Frank Weinhold: In principle, the EDA method of choice should be independent of the problem. To the extent that such influence exists (i.e., for possible subjective choice of EDA method or "reference fragments"), it seems to represent a particularly dangerous aspect of the partitioning approach.

Roberto A. Boto: A well-defined partition scheme should be valid for any chemical system. Energy partitions are based on chemical concepts such as covalency, ionicity, and polarizability. These concepts should be well-defined regardless of the nature of the system. Otherwise, we may create a chaotic scenario with a panoply of partitions, one for each chemical system.

Ángel Martín Pendás: Ideally, it should not. However, it is usually the case that, as it happens with density functionals, basis sets, or many other of our computational knobs, ideas propagate that advice the use of this or that method to deal with these or those problems. In many cases, the partition scheme is chosen a posteriori, a practice that should not be allowed.

Carlo Gatti: Generally speaking, if someone believes that his or her favourite partitioning scheme is suited for some classes of compounds and (much) less for others, he/she should probably make a step back and ask himself or herself what prevent his or her favourite method to be general enough to be applied equally well to any chemical system. This is an important exercise that may lead to an improvement of the scheme or to abandon it in favour of a more general one. I also believe that more than the investigated system, it is the chemical question to be addressed that may influence the choice of a particular partition scheme.

Paul Popelier: I agree with the general consensus building up here, which is that the nature of a system should not influence the choice of the partition scheme used, in the end. Unfortunately, this is not the case at the moment. For example, anionic systems or systems with large rings need diffuse Gaussian primitives in order for their wave functions to be properly described. Partitioning schemes that depend on the location of the center of these primitives suffer from the use of diffuse functions (because the mapping between center and ownership starts breaking down). Hence such partitioning schemes cannot be used in that case or they have to be modified. Anthony Stone did the latter by injecting some real-space partitioning character into his original DMA scheme[122].

Pedro Salvador: Of course, I also agree that in principle any reasonable partitioning scheme should be applicable to any chemical system at hand. However, I also have the impression that EDAs and topological EDAs (borrowing Paul's terminology) are somehow designed to answer different type of questions, so the nature of the system under scrutiny could drive one to use one or another scheme. Unfortunately, there are not too many works where both topological and non-topological EDAs are applied to the same problem aiming at answering the same questions (I do remember a nice poster at the ESB2 Oviedo this year showing striking similarities of both approaches).

Jerzy Cioslowski: As illustrated by the recent proliferation of density functionals, there is great temptation (especially among those not well-versed in quantum chemistry) to select the theoretical approach on the basis of the expected answer. It is quite disconcerting to observe the ongoing harkening back to the times of semiempirical approaches when there was at least one method for each set of electronic properties (CNDO/S for excitation energies, ZINDO for molecules with transition elements, MNDO and its endless modifications for geometries and heats of formation, etc. . .). Back then, this plethora of approaches was justified by the very limited power of computational hardware that dictated the use of various approximations. Since this is not an excuse nowadays, whenever carrying out computations of electronic wavefunctions or their interpretations, one should strive to limit the variety of the methods employed. Otherwise, there will always be pressure to legitimize one's interpretative prejudices and/or experimental results with a suitably chosen "theoretical justification".

Gernot Frenking: The investigated systems and associated questions rightfully influence the choice of a partitioning scheme. Different systems and questions may request different methods. For example, the chemical bond in LiF may be analysed in terms of interactions between the ions Li^+ and F^- or the neutral atoms Li and F. The former choice of the fragments is better suited to investigate the final bond, while the choice of Li and F as fragments encompasses all changes in the electronic structure along the bond formation/dissociation. It is strength and not a weakness of partitioning schemes to be able to choose different fragments as interacting moieties. But it is often only the combination of several methods (chargeand energy decomposition schemes) that provide a faithful account of the electronic structure in terms of a model.

Laurent Joubert and Vincent Tognetti: An important related question is: can we compare EDA results for systems that stringly differ? In question 3, we stated that there are two categories of EDA and we discussed there the first one. The second EDA category gathers those carried out after the initial quantum chemistry calculation. They aim at dividing energies into physico-chemical components (charge transfer, polarization, induction) whose definitions are in general not unique, and/or into subsystems (atoms, substituents. . .) for which various partitions also exist. All these energy decomposition can be based either on the wavefunction and/or the electron density, but they are performed independently of how these functions were obtained. For such reasons, they can reproduce or not the molecular energy obtained at the previous step. In such case, two corrections are often implemented: 1/ defining an ad-hoc new contribution to fill the gap, 2/ scaling the energy sum to the targeted energy. This strategy is very often used with the virial theorem. Indeed, for the exact wavefunction, the molecular energy is equal to minus the electron kinetic energy, or, equivalently, to half the potential energy. Unfortunately, the scaling parameter that is used in practice can be significantly different from one system to another. It can lead to questionable conclusions when comparing molecules of too much different type [4]. Coming back to question 5, it thus appears that some EDAs should not be used to investigate a molecular dataset composed of several different classes. From this point of view, the investigate systems will influence the EDA choice by precluding the use of some of them[123].

Miquel Solà : I agree that ideally the choice of the EDA method employed should not be dependent on the system studied. What is critical, however, is the definition of the fragments to analyze a given bonding situation. For instance, the answer to the question of how much covalent is the LiF bond may change from 14% to 91% depending whether the fragments considered in the EDA are Li^+ and F- ions or Lir$\cdot$ and F$\cdot$ radicals, respectively[124]. Moreover, in a series of similar bimolecular chemical reactions, the use of the activation strain model[125,126] provides deep insight into the origin of the energy barriers associated to these chemical reactions by taking the reactants as the fragments of choice. However, if one wants to analyze the whole reaction profile from reactants to products, then after the transition state, in the product region, the use of reactants as fragments is generally not a good choice. The whole reaction profile is probably better analyzed considering the different atoms as fragments. Moreover, if reactions are unimolecular, in most cases it could be hard to define two fragments to perform an EDA and probably considering atoms as fragments may be the smartest choice. Finally, the analysis of isomerization energies can be performed using different fragments. In many cases one can use the same fragments to build the two isomers just placing them with different orientation (we called this procedure the turn-upside-down approach)[127,128]. With this procedure, one usually gets a deep understanding on the physical origin of the isomerization energy.

Paul W. Ayers: I wish there were a universally applicable and useful partitioning scheme, but I'm not convinced any such scheme exists at present. For example, some methods are strongly dependent on a specific electronic structure ansatz, and would not be applicable, for example, to a diffusion quantum Monte Carlo calculation, or to a calculations that uses non-atom-centered basis sets (e.g., plane waves). Others could not be applied to a lattice (e.g. a Hubbard or Pariser-Parr-Pople model for an aromatic system), or to a periodic solid. Even among the few methods that are universal in scope (and there are very few such methods), their utility is unlikely to be universal.

Farnaz Heidar-Zadeh: In theory, a partitioning scheme should be applicable to any system, because the same physical laws apply to them all. Any deviation from universal applicability is a warning sign that should give one second thoughts about using the scheme. If a scheme is suitable for only a specific class of systems, it is very unlikely to be physically sound.

Juan Andrés: It is not appropriate or desirable to investigate a i system in order to choose a particular partition scheme. We must remember that history tells us that opening this path can cause great confusion with the proliferation of different methods. One has to remember the extensive number of semiempirical methods, basis sets, functional hybrids, and so on, as also have pointed by Profs. Martin-Pendás, Cioslowski, and Ayers.

Yirong Mo: May be not much. See Q3.

Eduard Matito: I believe it depends on the motivation. Making a choice of the partition based on the premise that it provides the answer you are looking for is obviously scientific misconduct. As Jerzy points out, a scenario in which a large collection of energy partitions is available, each being adequate for a particular problem is highly undesirable. Ideally, any method should be universally valid and provide a correct and complete description of the system. However, in practice, they are not. If validation tests (see Questions 6 and 7) offer us some hints of flaws and boundaries of current energy partitions, I find adequate to use these results to select (or discard) an energy partition scheme. For instance, a method having a slow convergence with the basis set size should probably be discarded in situations where we cannot afford a sufficiently large basis set.

Eloy Ramos-Cordoba: Ideally, the molecular system under study or the electronic structure method employed should not influence the choice of a particular EDA scheme. In practice, the system dependency seems to be unavoidable since there are EDAs which are only defined for some electronic structure methods, and some of them are restricted to be used in conjunction with atomic-centered basis sets. In this sense, topological energy decompositions seem to be more general since they can always be employed provided the 1- and 2-particle density matrices are available.

W. H. Eugen Schwarz: They must. The field of chemical substances with static and reactive properties is unboundedly rich. Useful and fruitful partition schemes should be intuitively understandable, i.e. simpler than reality. A scheme that is applicable to everything will be too complicated. It is better to have different schemes say, for primarily and for weakly bonded systems, or for weakly and for heavily electron-correlated systems.

Alston Misquitta and Krzysztof Szalewicz: SAPT partition works for all closed-shell dimers and so should all other schemes.

Question 6: Do we need more focused chemical validation of EDA methodology and descriptors/terms in general?

Ramon Carbó-Dorca: Might be what it is needed is a reflection on the chemical practical use of EDA. Perhaps the problem lies on the fact that there appears to be a large variety of procedures, [see the recent review by M. J. S. Phipps, T. Fox, C. S. Tautermann and C.-K. Skylaris[2]] Along the past three years since this publication, possibly, even more techniques have been defined.

Martin Rahm : Yes, we do! And this one I feel quite strongly for. EDA methods are most often used as descriptive tools, i.e. they analyze a given electronic structure and provide a picture of the bonding situation. There are many elegant EDA definitions that can provide detailed information of electronic structure in this manner. Whereas this can be useful, the ultimate goal of any electronics structure analysis should be predictive utility. "Chemical validation" can, of course, come in many forms, but it offers the safest route to demonstrating predictive utility. One approach towards "chemical validation" is to attempt thorough answers to the following three questions:

1. What chemically relevant experimental observable does the EDA-term [X] correlate with?
2. When does the correlation break down?
3. Why does the correlation exist [here] and not [there]?

Shant Shahbazian: I find the question to some extent vague. For validation process we must have a reference set of data that the EDA method under study may reproduce them properly. In the case of validation of ab initio methods, these are thermodynamics or spectroscopic experimental data that no one disputes their authenticity as an objective reference set. What is the reference set of data in the case of an EDA? Can we come to a "consensus" what is the "standard" reference set for such chemical validation? I am currently pessimistic about the whole idea (please also check my answer to question 9).

István Mayer: Ideally, the energy decomposition produces diatomic energy components representing the interatomic bonding (or repulsion) at the actual configuration of the molecule, and one center ones describing the promotion of the atoms when the molecule is formed. However, in several EDA schemes (including semiempirical e.g. MNDO ones) one encounters the difficulty, that delocalizations responsible for bond formation also give rise to ionic wave function components (in VB terminology) that increase the intraatomic electron repulsion energies, thus also the apparent atomic promotion energies. As a compensation, one obtains very negative diatomic energy components, that are not on the "chemical scale". No doubt, such a straightforward energy decomposition may be quite useful for comparing different bonds, etc., or even making some predictions. But chemists are inclined "not to buy" these large (in absolute values) numbers. This reservation of colleagues chemists served for me as a strong stimulus to introduce a corrected scheme[129]. The ionic terms are due to the bond formation, so their interelectronic energy was distributed between the different bonds in accord with partial bond orders formed by different "effective atomic orbitals".

Frank Weinhold: Yes (see Q3).

Ángel Martín Pendás: I tend to agree with the need of validation to properly screen the different methods available, but I also acknowledge the difficulty in finding a suitable set of quantities that might be taken as a reference validation set. To focus just a bit, let us simply take the Pauling repulsion term of many EDAs. What chemical relevant observable (In Martin's words) does it correlate with? In the absence of a consensus on what types of energetic terms should be allowed/not-allowed in a partitioning scheme, validation is desirable but difficult.

Paul Popelier: Yes, I believe so. I come back to this question in Question 7 because the latter question overlaps with Question 6, in which the word "focused" pops out. I'd like to interpret this word in a sociological sense. the community of interpretative theoretical chemistry, especially that of Quantum Chemical Topology (which is younger and somewhat lags behind), should scour more for "hot case studies" and work on them. These regularly appear in the popular scientific magazines (e.g. Chemistry World of the Royal Society of Chemistry). We can then to test (and showcase) partitioning methods. In the medium and longer term we can find out what we can do for experimentalists (e.g. material scientists and synthetic chemists). After all, there is a reason why the largest scientific funding body in Britain, called EPSRC, launched as one of its main research themes the Grand Challenge of "Directed Assembly" (short title). The associated vision for the next 50 years is, in EPSRC's own words, to be able to control the assembly of matter with sufficient certainty and precision to allow preparation of materials and molecular assemblies with far more sophisticated and tuneable properties and functions. To me, our goal should be to produce a minimal, trustworthy and well-thought-through partitioning scheme that delivers trustworthy and consistent insight. Partitioning schemes should not be "afterthoughts" to what experimentalists already know, nor should they confuse experimentalists with contradictions. Instead, they should guide and boldly but robustly confirm or correct the intuition of the experimentalist.

Jerzy Cioslowski: In my opinion, "chemical validation" should be limited to checking whether energy components (and other descriptors) computed for similar systems are themselves similar. This may also include the "chemical scale" argument of István Mayer, i.e. that diatomic (bond) contributions should have values similar in order to those encountered experimentally (bond dissociation energies, etc...). Anything more than that amounts to falling back into the trap of "chemical intuition", which is what one presumably hoped to avoid from the start.

Gernot Frenking: "Chemical validation" is an ill-defined fuzzy expression. I agree with Jerzy Cioslowski that chemical validation leads to the danger of using "chemical intuition" as measure for the validity of the EDA results, which is one step towards alchemy. A useful partitioning scheme should provide a self-consistent ordering scheme for the pandemonium of chemical facts. The physical interpretation of the energy terms will always be debatable.

Julia Contreras: YES! In this direction, chemical interpretation has always been too much influenced by pre-QM concepts, trying to reproduce what was already there. However, these concepts were introduced to predict composition, reactivity. I think we should go back to these roots. Just like in many other fields where theoretical/computational answers are difficult and the field is still at a strong development stage (e.g. solvation energies, molecular solid structure), we could propose "games" to predict the outcome of a given molecular change (not easy to calculate). Extremely naive, but double blind tests are a wonderful way of testing methods! Of course, this means being able to predict the behavior or energy terms upon perturbations, a point that has not been paid much attention..., and which chemists overcame long ago. But it would provide a clearcut (and fun) way of taken the next step in energy decomposition.

Paul W. Ayers: Hell yes. We should be careful about what we mean by "validation." There are a few molecules that might be proposed as such canonical examples of a concept that any EDA/partitioning that disagrees with them should at least be heavily scrutinized, and probably discarded outright. (E.g., a method that did not predict that benzene has an "aromatic stabilization energy" (however one might define that) has questionable utility.) There are more sequences of molecules for which a clear chemical trend may be asserted, and EDA can be validated against that.

Farnaz Heidar-Zadeh: Definitely, and this is long overdue! The systematic study of partitioning schemes in order to put them on equal footing is necessary and gives us a better understanding of their strengths and shortcomings. However, we first need to agree on this "validation protocol". As elaborated by many contributors, as a community, we need to make a comprehensive list of desirable axioms/features (distancing ourselves from intuitive measures) to assess and scrutinize various schemes and concepts. The five conditions suggested by G. Frenking are a great starting point.

Juan Andrés: Yes, chemical validation of EDA methodology is mandatory. But this opens the door to start a path with many slopes to be able to solve and know to what extent a method and/or model can be used and gives good results in particular situations, which in some cases coincide with the experimental results. With this, the fundamental problem that must be managed is transformed and masked, that is to achieve a methodology based on quantum mechanics, which manages observables, and which is based on an adequate mathematical apparatus.

One can remember, for example, how the semi-empirical method MINDO/3 failed in the study of systems involving hydrogen bonds, or how, depending on the type of function used, one can calculate band gaps values in solids that agree with experimental values. This is a computational task.

On the other hand, we also need descriptors/terms in general, but many of these descriptors/terms derived from chemical concepts that can be considered fuzzy concepts, compared to unicorns or even noumenons. This is because here exists no physical observable associated with them. Therefore, is very challenging task to reach this aim, we need, first clarify EDA methodology and descriptors/terms in order to obtain a chemical validation of both subjects.

Yirong Mo: Absolutely.

Eduard Matito: Indeed! This is probably a quite arduous task but is certainly needed in the field. Given the proliferation of energy partitions, "outsiders" from the chemical bonding community need guidance and, therefore, benchmarks (see Question 7) and "chemical validation tests" are essential. However, as many people pointed out before, it is not straightforward to design a chemical validation test. In this sense, it is important putting the focus on the reliability of the tests (for which we need consensus within the community) rather than on having extensive tests that cover the many facets of energy partitions. Indeed, some aspects of energy partitions cannot be easily tested (for instance, the Pauli repulsion term mentioned by Ángel) and, hence, the validation test is deemed to be incomplete. However, this should not preclude the search for such validation tests because they do not only help in classifying and assessing energy partitions, they also provide important hints to modify and improve current energy partition schemes. Maybe a challenge for our community in the next editions of ECCB conferences (and bond slams) could be suggesting chemical validation tests that would be subsequently debated openly in a forum like this until a consensus test set is obtained.

W. H. Eugen Schwarz: Yes. Statistical data analyses (cluster analyses, factor analyses) can clarify what is behind a group of related concepts, and quantify the correspondence of different partition schemes.

Alston Misquitta and Krzysztof Szalewicz: No, this is soft science with a weak connection to experiments. EDAs as such have no predictive power (the methods that are decomposed may have such power, but it is independent of an EDA applied). Such research should be reduced to a minimum.

Question 7: Is there any interest in developing common benchmarks and test sets for cross-validation of methods?

Ramon Carbó-Dorca: The fact is that every EDA technique must be described, and probably it has been with a benchmark set of his own. However, the question is: to prove what? If the answer is: that it works! Then one needs to continue asking what is the sense of working: it means a given EDA technique explains better a molecular situation (perhaps some kind of interaction) than others? If so, why there are different abilities (as it seems there are) to describe some particular EDA nuances?

Martin Rahm: I very much hope so. Reasons for validation against experiment is outlined in the answer to the previous question. Benchmarks can help in this by including experimental data but could additionally serve another important service to the community: facilitating for more straightforward comparison of EDA methods. This is beneficial for several reasons. Benchmarks will allow newcomers to the field to more easily get acquainted with advantages and drawbacks with the different methods, which is of relevance to question four. Benchmarks will also help the community to come to better terms with issues raised in all previous questions, 1-6, and question nine. For example, by revealing which EDA-terms and descriptors that do or might relate to the same chemical concepts. In other words, which terms that show the same trends in relation to relevant chemistry. Ultimately, the ability to cross-correlate different approaches should help highlight complementarities between EDA methods and aid future development of them. One successful example of EDA-term comparison is work of Racioppi et al.[130]

Shant Shahbazian: As I stressed in my answer to question 6, I find it extremely unlikely that a standard set of data (I mean a set of numbers) may be proposed that all scientists find them equally objective and reliable. Think about the concept of bond energy (or something similar to this concept) that probably most people would agree that a good EDA method must deliver as its output. How we may find the proper set of bond energies to start the cross-validation? If there is no such standard set then any cross-validation study will simply reveal the similarities and differences between the applied EDA methods, not the "objectivity" of any EDA method (please also check my answer to question 9).

István Mayer: Yes, it could be of interest to have a selection of different molecules with fixed geometries and a few different basis sets, for which the results of each method are tabulated. Results obtained with different wave functions (HF, DFT, CAS-SCF. CCA etc.) could be included as well. For the Hilbert space analysis basis sets of sufficiently atomic character (as e.g., STO-NG, 6-31G** or cc-pVTZ) should be considered and no diffuse functions (augmented basis sets) should be admitted.

Frank Weinhold: Self-correlation among closely related EDA variants is of little value. Tests with experimental data (such as those suggested in the reply to Q3) could give a more effective reality check to cull the ranks of proposed partitions. The development of the field would benefit from some common benchmarks that are well chosen to represent a diversity of phenomena and species (cf. Q9). Only then can meaningful differences in methods be illuminated and discussed.

Ángel Martín Pendás: An interesting initiative might be choosing a selection of molecules, basis sets and methods to construct an EDA benchmarking data set. Although, in agreement with Shant, it would be difficult to find a proper set of values for the chemical concepts that would then be cross-validated, a simple cross-correlation among the different EDA energetic terms would provide relevant data about their similarities and differences.

Carlo Gatti: Since aims might be quite diverse from method to method (see my answer to Q1), I envisage complementary insights, more than cross-validation from the suggested procedure. However, common benchmarks and test sets could be useful to observe which concepts and conclusions survive the various methods. If concepts and conclusions were found to vary significantly within a class of related EDAs schemes, then this would be a serious indication that these schemes might be deceptive and seemingly unphysical.

Paul Popelier: Yes, having common benchmarks and test sets would be nice. Developers of force fields, density functionals and machine learning methods already work with quite a few test sets that offer their development communities clarity on progress made. Designing and using those sets is easy because there is always a crisp and clear measure of success, i.e. "golden reference" such as CCSD(T)/CBS wave functions or experimental properties. The problem with test sets for energy partitioning schemes is the usual difficulty that ab initio calculations and experiment typically deliver whole-system information. Nevertheless, it appears that some kind of test set has already naturally emerged in the case of the bond critical point problem. In an attempt to settle the controversial relation of this critical point to chemical bonding papers often report on the same molecular systems. Closer to the subject of EDA comparison, the recent review by Skylaris et al.[2] compares and discusses six test sets containing ions, water and biomolecules (with hydrogen bonding and $\pi\pi$ stacking interactions).

Pedro Salvador: Coming back to my answer to Q1, topological EDAs only differ on the underlying atomin-molecule definition used. Thus, rather than merely energy-based tests sets, which in agreement with Ángel and Shant are rather difficult to build, one could make up a multidimensional test set aiming at finding the best AIM definition, analogous to the aromaticity test set put forward by Feixas et. al.[131] in order to grade the different aromaticity indicators. Some work along this line has already been attempted. For instance, the harpoon effect expected in the dissociation of LiH cannot be recovered with Becke's or Hirshfeld's AIM partitioning[111]. Iterative Hirshfeld was also unable to reproduce the higher carbon-carbon electron delocalization in para *vs* meta position in benzene[109]. Semiqualitative energy-based tests could be added to the mix. For instance, when using Hirshfeld-type approaches in X−H bonds, the value of the atomic weight function of H at the nucleus significantly differs from 1, and consequently that of the X atom is non-zero. Is the diatomic electron-nuclear attraction contribution of X−H bonds reasonable?

Jerzy Cioslowski: The only reason for embarking upon cross-validation of different definitions of a given chemical concept (including energy components/contributions) should be the detection of the cases where the concept in question is (using physicist's language) not a scalar. For example, as it is well known, all the known definitions of ionicity are highly correlated, which means that essentially ionicity is specified by just one set of values. A counterexample is provided by aromaticity that is (at least) a two-component vector, i.e. it encompasses two sets of values that are linearly independent. Thus, if one insists upon cross-validation of energy partitioning schemes, it should be carried out with a set comprising a large number of "unusual" molecules, the results being subject to the principal component analysis.

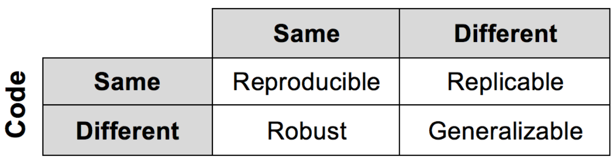
Gernot Frenking: It is a good idea to have a test set of species, which are then used to explore the performance of a method for different types of electronic structures. For molecules, this should include e.g. compounds with polar and non-polar as well as localized and delocalized bonds and it should encompass transition metal complexes as well as main group compounds with "normal" valency and "hypervalent" compounds.

Miquel Solà: Benchmarks to prove the reliability of the different energy decomposition analysis (EDA) approaches are highly desirable. While the dissociation energy is an observable, the components of the dissociation energy obtained from an EDA are not observables. To validate concepts or quantities that cannot be precisely defined mathematically from the underlying physics, such as the components of the EDA, Ayers et al[87] proposed to take an axiomatic approach, which consist on listing the chemical, mathematical, and computational properties that one desires for a concept to possess. In our group, we followed this approach to prove the reliability of a series of descriptors used to quantify aromaticity, a quantity that is not observable, either. To this end, we designed benchmarks containing a series of tests[131–133]. The chosen tests fulfilled two requirements: first and most important, they were based on the accumulated chemical experience in such a way that one expects most chemists agree about the expected aromaticity trend and, second, the size of the systems involved were relatively small to facilitate a fast application. As an example, we considered different deformations of benzene, such as the bond length alternation (BLA). Any good indicator of aromaticity should detect a reduction of aromaticity of the benzene ring when BLA increases. Or, for instance, when going from benzene to pyridine (one heteroatom in the ring), pyrazine (two heteroatoms in the ring) and triazine (three heteroatoms in the ring), aromaticity should decrease. In the case of EDA, one may proceed similarly. Is is probably not a good idea to consider results for a particular molecule instead of analyzing particular trends in a series of molecules. Let's consider for instance LiF. According to IQA calculations[96], covalency, defined as the percentage between orbital interaction and the sum of electrostatic plus orbital interactions, is 14the other hand, for the same molecule, a Morokuma-like EDA considering Li^+ and F^- as fragments indicates that covalency represents an 8% of the total stabilizing interactions[124]. It is not possible to know which of these two results is the correct one. To make things more complicated, if fragments considered in the Morokuma-like EDA are F· and Li· radicals, covalency of LiF increases to 91%. The reader could ask whether the ionic or the radical fragments is the best option to discuss bonding in LiF. One may argue that radical fragments should be preferred because, for the gas-phase LiF molecule, the homolytic dissociation costs less energy than the heterolytic one, the latter being favored only if one includes at least five water molecules, i.e., for the $LiF(H_2O)_5$ species[134]. However, in the equilibrium geometry the electronic distribution is closer to Li^+ and F^- ions than to F· and Li· radicals, so maybe results employing ionic fragments are more realistic. Anyway, using one or the other fragmentation scheme is a matter of choice and, in principle, both are acceptable and none of them is unphysical, although the results differ enormously. In this case, the IQA analysis in terms of atoms has the advantage of not requiring a fragmentation scheme for its application. Because of the difficulty to discuss EDA results for a single molecule, except in some particular cases (like LiH, vide infra), I consider that an EDA benchmark should discuss trends and not particular molecules. For instance, for alkalimetal chloride salts, the covalency should increase in the order LiCl > NaCl > KCl > RbCl > CsCl, in the same order of increasing the ionization potential. Or for lithium halogen salts, considering the trend of electron affinities of the halogen atoms, one could reach the conclusion that the covalency should increase in the order LiCl > LiBr > LiI > LiAt. Another interesting example corresponds to the dissociation of LiH for which a maximum of covalency should be found around the avoided crossing at about 3.5 - 4 Å[112]. Pauli repulsion energy, on the other hand, should increase in the order H_2 < LiH < BeH < BH < CH < NH < OH < HF, at least if all of these diatomic species are considered at the same bond length. Or whereas orbital interaction should dominate the formation of H_2 from two H atoms, Pauli repulsion should be the main component of the interaction between two RH molecules to form the RH···HR complex. These are possible tests to prove the reliability of EDA methods but I am sure the reader can think of many others.

Paul W. Ayers: Yes. And the benchmarks should be very broad. It is not necessary to have consensus on all the systems (even things as simple as the interaction energy in the water dimer or the energetic barrier to rotation in ethane are interpreted differently by different partitioning methods). But a panoply of results helps establish the similarities/differences between models and, perhaps, also the cases where their nuances are most helpful. I do not want benchmark sets to become the battleground upon which religious wars about chemical concepts are fought, but rather a proving ground upon which they are understood. It is also important, even critical, that the benchmarks be provided together with data and software tools that allow them to be easily used, so that few (if any) new EDA methods are proposed without first being scrutinized against said benchmark(s).

Farnaz Heidar-Zadeh: Benchmarking various schemes extensively is the way to go forward! These give us a better understanding of current partitioning schemes and sets that stage evaluating the future schemes. As elaborated by many contributors, it is crucial to have benchmarks that are diverse and comprehensive, both in terms of systems studies and levels of theories considered. It is also very important, even though less discussed, results generated for a specific schemes' implementation (code) and molecule (system) need to be reproducible, robust, replicable, and generalizable as depicted in the image below.

Reliability of a Given Scheme's Results.



		System	
		Same	Different
Code	Same	Reproducible	Replicable
	Different	Robust	Generalizable

Juan Andrés: It is desirable to develop common benchmarks and test sets for cross-validation of methods. Ayers et al.[87] propose an axiomatic approach, as it was previously noted by us (see Q1) and by Prof. Solá (see Q7)

Yirong Mo: Not sure about this. Experimental evidences are always the gold standards.

Eduard Matito: The short answer is yes, there is a large interest in designing validation tests. There is some overlap between questions Q6 and Q7. I decided to comment on "chemical validation tests" on Q6 and here, I will comment on another kind of validation tests. Benchmarking should also consider other essential features of energy partitions such as basis set dependency (and convergence towards complete basis set), size extensivity, and method dependency. Some of these features might be easy to anticipate from the construction of some energy partition schemes (e.g. size extensivity) but other require the design of tests that are appropriate to this purpose.

W. H. Eugen Schwarz: Yes, it would be very deserving. However, at first a set of useful decomposition methods and a set of empirical, valid, reliable data must be agreed upon

Alston Misquitta and Krzysztof Szalewicz: The only test that can be conducted are those outlined in the answer to Q4, so each method can be tested individually since this is a pass/fail test.

Question 8: Is it possible to contemplate a unified partition scheme (let's call it the "standard model" of partitioning, that is proper for all applications in chemistry, in the foreseeable future or even in principle?

Ramon Carbó-Dorca: The previous question leads to the present one. One can answer it like: if EDA techniques are somehow arbitrary, then it seems difficult to obtain a unified universal partitioning scheme. However, perhaps research on this topic is missing something, which could transform the EDA problem into a precise description. I must confess that I cannot imagine what might be the nature of this missing link.

Shant Shahbazian: This question is tightly connected to questions 1-3. If the answer to this question is "no" in principle, then I find it really hard to believe that currently used chemical concepts may have any universally precise definition. This means that there will be always an inherent fuzziness in chemical concepts that personally, I find it quite an unpleasant situation. I am interested to see if anyone have a clue or a proposal for a "yes" answer, at least in principle.

István Mayer: I do not think it possible to get a single "standard partitioning model" right because it does not seem possible to get an ultimate unique definition of an individual atom within the molecule. But introduction of two or three standardized procedures—one for Hilbert space analysis and one or two for the 3D one—seems to be quite possible. (In the latter case separate standard schemes for exclusive and fuzzy atoms can be contemplated.)

Martin Rahm: Unification seems unlikely at present, but that is not necessarily a bad thing. There is strength in diversity. I suspect most in the community strive towards development of as generally applicable methods as possible. In the long term, methods with higher degrees of chemically relevant predictive utility are likely to see more common use.

Frank Weinhold: Probably not. The idea of universally partitioning chemical phenomena into mutually exclusive and additive components is inherently superficial, except as a tautological accounting device. The fact that such "components" commonly exhibit greater variations than the energy difference they purport to analyze is itself a telling indicator that their usefulness to the broader chemical community will be marginal. The NAO-based NEDA variant, which alone avoids the conceptual ambiguities of fragment overlap, seems to be the only plausible candidate for such generality.

Roberto A. Boto: In my opinion, a unified partition scheme would require a unified theory of chemical bonding, something that as far as I know, is far from being achieved. From a more pragmatical point of view, the only way of accomplishing this uniformity in partition schemes is not by means of theory, but by consensus.

Ángel Martín Pendás: Unification is probably not possible for the time being, but thinking about the characteristics that would allow the different available methods to ”converge” might be a worthwhile enterprise. In my probably biased opinion, if a standard model can be envisaged it should rely on orbital invariant quantities, so that one is not limited by any underlying computational methodology. In the end, this ultimately leads, in agreement with István Mayer, to the atom-in-the-molecule conundrum.

David L. Cooper: I remain very deeply sceptical that a utopian model of partitioning could ever emerge that not only is applicable to, but also (almost) universally agreed to be the "best" choice for, all applications in Chemistry. There is even a sense in which it would be more than a little disappointing if no new Chemistry could ever be discovered for which such a "standard" model might not be the most appropriate.

Carlo Gatti: Perhaps yes, but I doubt it would be the most appealing one for most of the chemists. In principle I would be highly in favour of a unified approach and I fully agree with Ángel Martín Pendás that it should rely on orbital invariant quantities. However, as I discussed in my answer to Q1, the aims behind the present partitioning methods are different. Therefore, adoption of a standard model, while favouring scientific rigor, could also result in a significant loss of richness of interpretation.

Paul Popelier: I want to be optimistic about a "standard model of partitioning" and indeed strive for it although it could be a long process. As explained in Question 4, schemes that make the same predictions can co-exist, but if they produce contradictory outcomes then they cannot. Allow me to comment on the related and perhaps less sensitive topic of population analyses. In the plethora of population analyses the (original) Hirshfeld method and the QTAIM typically produced answers at the two opposite extremes: Hirshfeld was judged to give too small an answer and QTAIM too large. The community often regarded both as suspicious. However, over time Hirshfeld was modified (in response to a theoretical deficiency related to the reference state it invokes) and then gave less extreme values. This is an example of convergence, which is a weaker form of unification. A further step towards convergence would be to finally ditch the Mulliken population analysis, which has been heavily criticised for decades but still regularly pops up. In my PhD thesis, Mulliken charges served the purpose creating a sufficiently reliable crystal field in which solid state molecular geometries could be obtained. However, when I saw a few years later that the Mulliken population analysis assigned a non-negligible negative net charge (-0.26ie) to a boron atom[135] then I am happy to ditch Mulliken because its answer violates any of the dozen electronegativity scales. In terms of Darwinian selection, a harsher environment consisting of the now more demanding user results in Mulliken not surviving ultimately. To make the main point again: diversity is good provided it leads to a stronger end product. However, diversity for its own sake, in terms of wallowing in contradictory interpretations and lauding this situation as the richness of Chemistry is wrong. Yes, chemistry is a complex science, which is we should do an utmost effort to keep it clean and logical. When I look at typical undergraduate textbooks then I think there is still much work to do. However, I think we will get there. The traditional Sciences of Chemistry and Biology continue to undergo a physicalisation process: they become better and better connected with an underlying physical and indeed quantum mechanical reality. Whereas a typical biochemistry textbook of today is still nave in its typically introductory chapters on physical chemistry, the enzymology it reports later is full of protein crystal structures that take away the yesteryear mysteries of the atomistic working of an enzyme. Optimistically I believe in an irreversible gradient of knowledge. Yes, there are temporary regressions but I would be horrified if Science mere oscillated between stagnating alternative theories.

Pedro Salvador: I agree with general view here that a unified partition scheme is unlikely to be set in the near future. Yet, by gathering a sufficient number of "stress tests" for the existing partition schemes as I suggest in Q7, one can probably narrow the search to a handful of them, which hopefully will produce similar outputs for most purposes. On the other hand, in the present context of energy decomposition schemes, unification in the formulation applied to different levels of theory is also desirable. In particular, a rigurous topological EDA for Kohn-Sham DFT that is able to provide energy contributions comparable to those obtained for correlated wavefunction methods is still lacking, in my opinion.

Jerzy Cioslowski: I very much doubt that it is possible to design "the one and only" energy partitioning scheme within each of the two classes I discussed in my answer to question 1. However, would be very desirable to agree on a set of rules (or axioms) that have to be satisfied by any admissible scheme. At present, some of such axioms (like that the partitioned properties should approach those of isolated systems as the intersystem separation goes to infinity) are both obvious and widely accepted, whereas others (like that the partitioned properties should be retrievable with equal ease from wavefunctions given on a grid or in terms of atom-centered basis functions, single-centered basis functions, or plane waves), while being equally obvious, are ignored by a surprisingly large segment of practitioners of quantum chemistry.

Gernot Frenking: No! The complexity and diversity of electronic structures in molecules and solids requests partitioning schemes that are appropriate for the given situation. The species may be grouped into classes that have similar properties, for which a particular model may be used, while it is less suitable for others. It holds in general to use more than one partitioning scheme and to compare the results before a statement about the best description of the bonding situation is made.

Paul W. Ayers: It's useful to contemplate, but it is a bit like contemplating nirvana. Useful, but it is best to live in the real (imperfect) world most of the time. I tend to feel that while unified partitioning schemes may exist (in the sense that there may be atom-in-molecule partitioning schemes and energy decomposition analysis methods with broad utility and applicability and, indeed, some of our current tools approach this lofty standard) there will always be room for improvement. At some point, though, the "improvements" one might make will be achieved only by adding complexity ("engineering" the model in a way that risks overfitting), and some convergence may occur. However, as every person has a different tolerance for model complexity (in a different context, some prefer PBE, some BLYP, and some M06L), the idea that our community could ever agree upon a "standard model" seems... unfathomable. Indeed, it seems we cannot even agree whether such a standard model should be pursued!

Farnaz Heidar-Zadeh: Having a unified partitioning scheme is the holy grail. As such, it is not possible to find a universal definition or even get close to one. However, this shouldn't lead one to underestimate the usefulness and value of partitioning schemes (and other concepts), and the need for improving/validating the existing approaches.

Juan Andrés: It is possible to contemplate a unified partition scheme, but it must be recognized that this is still a pretension. In the current state, I do not see a possible way to reach it.

Yirong Mo: I am not optimistic about this. Researchers always intend to be unique and propose something different from others. So there will be a constant endeavor to propose "novel" and "for the first time" kind of partition schemes.

Eduard Matito: I highly doubt that an energy partition "to unite them all" will ever be found. In the best case scenario, I would expect that we find a partition (or a set of them) that gives reasonable predictions for "chemical validation tests".

Eloy Ramos-Cordoba: I also agree that it is unlikely that a unique "standard model" can be defined. However, as Prof. Cioslowski stated above, I also think it would be convenient to establish a set of axiom or requirements (e.g. well-defined basis set limit), based on mathematical or quantum mechanical arguments, that every EDA has to fulfill.

W. H. Eugen Schwarz: No: The various partition schemes yielding a few small numbers to explain a given class of molecules w.r.t. a given type of questions (e.g. concerning stability or reactivities) are quite diverse. The universal cover approach consists of general quantum mechanics combined with a comprehensive set of questions, which is too demanding to be useful.

Alston Misquitta and Krzysztof Szalewicz: Not only contemplate, SAPT already provides the standard model and we believe this has been generally recognized in recent years.

Question 9: In the end, science is about experiments and the real world. Can one therefore use any experiment or experimental data be used to favor one partition scheme over another?

Ramon Carbó-Dorca: If experimental data could relate to EDA, then possibly the precise description of the theoretical scheme might be solved. The adequate (ultimate) EDA will be the one adapting better to this kind of experiment. Can one imagine any experiment of this kind to be performed soon? However, if there is an experiment which can be (completely) adapted to some EDA, this will mean that the EDA terms will become observables. Therefore, a quantum mechanical operator (or operators) might be constructed to describe the experiment. Can one foresee this observable nature of the EDA partition terms?

Martin Rahm: Aside from valiant efforts towards X-ray constrained wavefunctions[136], which might move all EDA's closer to experiment, most of what we do in the field requires a quantum mechanical calculation to approximate a wave function or density. My personal preference is towards concepts and quantities that are, at least in principle, experimentally measurable. For this reason, I am exploring the possibilities of an EDA that can interchangeably rely on both measurements and quantum chemical calculations[54]. Of course, plenty of non-observable quantities are conceptually valuable. Time will tell when and where an "Experimental Quantum Chemistry" EDA approach is more advantageous in some respects. Experimental comparison and cross-validation, discussed in questions six and seven, should help to highlight complementarities between EDA methods and be a good basis for making more informed choices for particular sets of systems and questions.

Shant Shahbazian: This question is tightly connected to questions 6 and 7. Without any reference to experimental data, which are free from subjective judgments and chemical prejudice, it is hard to see how a positive operational answer may be given to questions 6 and 7. I am interested to see if someone have any clue or proposal how a partitioning scheme may, in a non-trivial way, to be connected to quantitative experimental data. However, if there is no link, I see no way of real progress.

István Mayer: Probably not directly. However, the different partition schemes should be globally consistent with the chemical experience in order to be practically useful.

Frank Weinhold: For H-bonding phenomena, the mentioned reference in Q3 suggests the correlative test that can be applied to the "electrostatics" component common to most EDA partitions. A recent critique of the SAPT partition[137][1] also shows how "steric" or "induction" components can be tested for consistency with measurable properties of prototype chemical species.

Ángel Martín Pendás: Besides X-constrained wavefunction approaches, some EDAs like IQA rely only on an atomic partition of space, that can be retrieved from experimental charge densities, and first and second order densities, which despite being observables, are very difficult to access experimentally. Even though a whole experimental energetic decomposition might still not be possible, some of its components, like the electrostatic energies, indeed are. Electrostatic potentials, which can be envisaged as a by-product

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[1] **Bernard Silvi:** the reply of A. Stone and K. Szalewicz has been published in the same issue of J. Phys. Chem. A[117]

of EDAs, are routinely obtained from experiment and partitioned into atomic contributions. So, although the global answer to the question may be not, I expect some advances in the near future.

David L Cooper: Much as it could be very interesting to live in a Universe in which most of the components returned by a well-constructed energy partitioning scheme could be directly related to expectation values of operators or even to experimental data, I strongly suspect that we do not. Even if we did, it would also be important that we could associate the relevant experimental data with a realistic level of chemical interpretation. Otherwise we could just have decomposed one number into a sum of others that might not really have brought with them any additional useful chemical/physical insights. In this sense, I agree wholeheartedly with István Mayer that useful partitioning schemes need to be consistent with chemical experience.

Paul Popelier: I wrote about the need[138] for falsification in the research of interpretational theoretical chemistry, which is in the spirit of this question. There I proposed the potentially falsifiable example of B_2H_6 where IQA states that the interatomic exchange energy between the bridging hydrogen atoms is about 3 times larger than that between the two borons. When presented with this information, Roald Hoffmann responded that the HH interaction is something new to him and that there is some BB bonding is easier to understand, based on a molecular orbital argument. Since writing about falsification I have received very little response, probably because it is very difficult to set up experiments that can falsify a partitioning scheme. If one looks at the review of Phipps et al.[2], then it appears that the comparison between EDAs is not against some experiment but by comparison of disadvantages and problems of the various EDAs. Examples of observations or judgements (see Table 2) sound like: "Observed overestimation of polarization and underestimation of charge transfer." or "Presence of the DEMIX energy unascribable to any particular component. Problems of numerically unstable charge transfer and polarization energies with large basis sets and at short intermolecular distance". It appears that we are still a long way off of making contact with experiment.

Pedro Salvador: My answer to Q7 and Q8 can also fit in here. In agreement with István and David, agreement with chemical intuition is essential. We should be able to "quantify" such agreement with the chemical experience, at least in a semiquantitative way (e.g. this value should be larger than that other value, or this value must be non-negative, etc…) to build up a survival-of-the-fittest strategy.

Julien Pilmé: Yes, this is a fundamental question, in principle any theory needs to be supported (or refuted) by a "face-to-face" meeting with experiment data. Currently, results obtained from EDA methods globally skip this process, these results nevertheless need to be in agreement with the chemical experience based on numerous "fuzzy" concepts, so we go back to question 1. Of course, this latter confrontation is very useful for our daily work but it can be also a little "dangerous" when results contradict the chemical experience, it can become a deadlock situation.

Jerzy Cioslowski: The only quantities that are presently amenable to experimental measurement are those given by matrix elements (including expectation values) of global operators. In practice, this means energies (and their differences), and the electric/magnetic response properties such as multipole moments, polarizabilities, etc… The one-electron densities have never been measured experimentally as: 1) the number of experimental points is always finite whereas the density is a function of a continuous argument and 2) since the amplitudes (but not phases) are measured in scattering experiments, the "measured" densities are really model densities that fit best the amplitudes with the phases approximately inferred from (admittedly clever) inaccurate methods. These model densities are very useful as a tool for location of nuclei and may even yield reasonable multipole moments but nevertheless they have nothing to do with the expectation values of the sum of one-electron Dirac deltas. Keeping this in mind, one has to be very skeptical about the possibility of (to use Martin Rahm's words) "moving EDA's closer to experiment" as many of the partitioning schemes rely explicitly on both local and global properties of one-electron densities.

Gernot Frenking: The preference of a particular partitioning scheme is not decided by an experiment, but by the interpretation of the experimental results. This is done by the human mind of the observer. "Real world" implies a definition of physical reality in a region where quantum theory is valid but not classical physics. The outcome of a Diels-Alder reaction can only be explained when the symmetry (sign) of the wave functions of the interactions species is considered. This gives the wave function the status of physical reality. Three statements at the end: a) Physical reality becomes a fuzzy concept when quantum effects are considered. b) When chemical facts are reduced to physical laws alone, they become mere stamp collection. Fuzzy concepts are an integral part of chemistry. c) Historically developed concepts must be examined with quantum chemical calculations, because they may be based on assumptions that are not correct.

Julia Contreras: My answer to this is pretty similar to Question 6.

Émilie-Laure Zins: I agree with the general opinion of the previous contributors: a comparison and a dialogue between theoretical and experiental chemists is essential. But what experimental tools could be used in comparison with theoretical studies on energy partition schemes? Do the existing partition schemes allow a comparison with observable or deductible quantities from experiments? Would it be possible to develop new partition schemes allowing an easier comparison with experimental data? I think the answer to the latter question is "yes", and that it would be interesting to move in this direction, probably by using a combination of complementary experimental approaches, or even by developing new experimental approaches. Of course, experimental techniques do not allow an energetic decomposition, but in-depth investigations involving complementary experimental techniques allows to deduce information on polarization and polarizability, the contribution of the spin... Among the most versatile tools, we can mention the technique of isolation of the investigated species in a matrix (rare gas, para-hydrogen,... at cryogenic temperatures (typically below 20°K). This technique allows to characterize weak interactions, such as hydrogen bonds or agostic interactions. This technique is also useful to probe the spin state of a metal atom in an organometallic complex, or even to induce changes in spin states by photo-excitation. Isomerizations between different interor intramolecular complexes can also be detected by annealing. This isolation technique is often coupled with vibrational spectroscopy. One could imagine the development of such an experimental set-up allowing to apply a magnetic field. The use of such advanced experimental approaches to deduce somes of the physical components of an energy partition scheme would need to be discussed with the experimental chemists and/or physicists.

Laurent Joubert and Vincent Tognetti: Another important point to emphasize, from our point of view, is that experimental energies are often Gibbs energies. Most energy decompositions discussed here only deal with electronic ones, and thus do no include entropy. However, it is known that entropy is a quantity of fundamental importance to account for experimental results (see ref. [139] for a recent example in organic i chemistry where the experimental selectivity in dipolar cycloadditions is governed by such factors). As well known, entropy can be decomposed into electronic, translational, rotational, and vibrational ones. The last term is the sum of contributions from each normal mode. Unfortunately, the most important ones correspond to the lowest frequency values, characteristic of vibrations of small amplitudes delocalized over the whole molecule. They are thus difficult to analyze from a chemical (regional) point of view. This is an important limit to rationalizing experimental chemical results, in particular for complex systems. In such cases, even if very accurate and meaningful EDAs are obtained for the electronic part, the thermodynamic contributions remained an issue, notably for condensed phases. From this point of view, EDAs cannot guide us for selecting the most relevant physicochemical propertiesi [139].

Paul W. Ayers: I often use the following quote from Willard van Orman Quine [140], 1953], "Our acceptance of an ontology is, I think, similar in principle to our acceptance of a scientific theory, say a system of physics; we adopt, at least insofar as we are reasonable, the simplest conceptual scheme into which the disordered fragments of raw experience can be fitted and arranged."

The real world provides the "disordered fragments of raw experience" which we try to "fit and arrange" into our theories. All of our arguments (at least the ones I judge to have some value) are about which theoretical scheme is the simplest (an aesthetic judgment) and how well experimental data fit and arrange into various schemes (which standardized benchmark datasets help us to quantify).

Farnaz Heidar-Zadeh: It can, but indirectly! The partitioning schemes can be used in interpreting the outcome of experiments (i.e., justification) or designing a specific experimental outcome (i.e., prediction). These indirect experimental tests can ultimately leave us with a smaller set of favorable schemes which perform better in justifying/predicting the experimental results. Ultimately these schemes will help us design molecules and materials with desired properties.

Juan Andrés: In this context it should be noted that in principle a partition scheme is more desirable if it is based on electron density, since it is an observable and also can be derived from charge density that are obtained experimentally.

Yirong Mo: It is the only way. Even there is little direct experimental data for partition schemes, there are many indirect evidences to examine individual energy terms. Structural and spectral parameters are good indicators for partition schemes. In the study of intermolecular interaction, distance-dependent energy profiles are often instructive for the verification of partition schemes. For instance, in the void of orbital (electron transfer) interactions, the optimal intermolecular distances should be comparable to regular van der Waals distances (unless strong electrostatic interactions exist). Unfortunately, so far, very few partition schemes can perform geometry optimization. But at least numerical test calculations with small systems can be done for all partition schemes.

Eduard Matito: Maybe, but I doubt we will generate numbers that can be directly compared to the experimental ones and, at the same time, provide undeniable chemical insight. For instance, in the future, perhaps we can obtain reliable electron density data that leads to accurate prediction of, let us say, QTAIM atomic energies. However, the fact that we can measure these energies does not make them any more useful to provide chemical insight. On the other hand, I believe experimental evidence can provide qualitative information that is useful in assessing energy partitions.

Eloy Ramos-Cordoba: In principle since energy components are not observables, it seems not possible to quantify them by direct observation. However, some energetic information can be extracted from experiments. For instance, molecular-beam scattering experiments have been used to indirectly quantify the charge-transfer stabilization energy.

W. H. Eugen Schwarz: Yes. Ultimately, the purposes of theory and partition schemes are creating models that help to intuitively understand and extrapolate (predict) the experimental facts. The answer to this last question 9 therefore depends on three points: *First,* the partition scheme should appropriately *explain the experimental trends* as seen by the chemists If a theoretical model cannot reproduce differences chemists are commonly talking about (such as non-bonded repulsion *vs.* chemical bonding attraction, or strong *vs.* very strong ionic or covalent interactions) then probably the theoretical scheme should be modified. *Second,* the observation of a positive value may be theoretically represented by the sum of one or two positive terms and several small corrections, or as a sum of several large numbers of different signs. The latter model is not satisfactory. It may then help combining some numbers to get only medium-sized contributions of same sign, for instance summing large positive Pauli repulsion and large negative quasi-classical electric attraction to construct the 'steric interaction' (or some other combination, *depending on the case*). Namely, not only the values of a specific partitioning characterize the real system, but also which type of partitioning is simple in the given case. *Third,* whether a partitioning is useful and efficient also depends on the cognitive *competences and preferences of the users.* Some experimentalists and theoreticians focus on the observable numbers only; some other ones also consider the process of relaxation that results in the observed outcome. Different partition schemes may be required for different addressees.

Alston Misquitta and Krzysztof Szalewicz: Indirectly, due to SAPT-based PESs providing close interplay with experiments and due to the fact that SAPT interaction energy is built up from components (rather than decomposed), comparisons with experiments provide a real world connection for these components. SAPT has been used to develop pPESs for a large number of dimers. SAPT PESs are among the most accurate ones published and if used in nuclear dynamics calculations predict observables in excellent agreement with experiment, e.g., for the water dimer spectra[141,142]. Also, SAPT PESs allow precise predictions of crystal structures[143]. Thus, there is a strong connection between SAPT and experiment. Although these comparisons involve the total PESs, there is a weaker connection to SAPT components as well. For example, to predict correctly crystal densities, on has to have the repulsive walls at the right places, which tests the exchange-repulsion energy. Crystals of monomers dominated by dispersion interactions, like for example the argon crystal[144], indirectly test this component of SAPT. There is a further broad connection to the real world: construction of force fields based on SAPT components and using forms of the fitting functions that reflect the behaviour of SAPT components[88,145]. One can fit intermolecular interaction energies by several types of analytic functions or even use methods such as neural networks, but fitting with physically relevant forms enables such PES to be transferable. Use of SAPT to develop biomolecular force fields has become increasingly popular[146]. A particular example are water clusters. There is experimental data available for such clusters, for example, the authors of Ref.[147] performed measurements on hexamer, heptamer, and nonamer. A very accurate force field developed in Ref.[148] was fitted to CCSD(T) calculations for the water dimer and trimer. Predictions of properties of clusters from this force field agree very well with accurate *ab initio* data available for some clusters. Thus, component-based force fields enable calculations for water clusters of essentially arbitrary size, whereas reasonably accurate *ab initio* calculations are limited to about 20 water molecules. In Ref.[148], not only the form of the fitting function was designed based on the behaviour of SAPT components, also the long-range asymptotics was computed *ab intio* using SAPT codes. In contrast, while damping and exchange-repulsion parameters are also consistent with SAPT, the parameters in these terms are just free parameters of the fit. This can be improved by performing SAPT calculations for close-range separations and fitting component-by-component (as done for water in Ref.[141]). While such direct fits can currently be done for dimers and for small trimers, there remains an issue with higher than three-body contributions. Reference[148] approximated such contributions by a damped classical polarization model iterated to convergence over the whole cluster. While the polarization model alone is a poor approximation to three-body interaction energies, it was shown in Ref.[148] that this model recovers the four- to six-body interaction energies surprisingly well. Since the many-many body polarization model is so critical for clusters and condensed phases, work on improved forms of this model is essential. Here the work of Refs.[115,119] is important since it both extends the model beyond the isotropic dipole-dipole polarizability case and designs better damping functions which are essential at shorter separations. Furthermore, the decomposition of induction energy into polarization (including a part of the exchange components) and charge-transfer terms may lead to improved models of damping.

Concluding remark

Bernard Silvi: For this article I tried to collect a large panel of opinions on the use of EDA methods in Quantum Chemistry. I had no preconceived ideas about the outcome and therefore, I have been surprised by the diversity of points of view often apparently contradictory. Whereas some contributors reject EDA methods, many others consider them as a fundamental contribution of Quantum Chemistry. The origin of this dispersion of opinions is not a crisis of our discipline announcing the advent of a new paradigm but rather a consequence of its good health. As we wrote in the introduction, EDAs are tools (not theories) providing pieces of information enabling to set up explanations. They belong to normal science processes and as tools they have not to strictly satisfy demarcation criteria. They are mostly used to understand geometries and stabilities of molecules and molecular complexes on the basis of quantum chemical and physical arguments. Here *quantum chemical* is related to systems of explanations based on quantum chemical concepts such as those of orbital, valence-bond structure, etc... whereas *physical* concerns arguments rooted on the theory of intermolecular forces. These systems of explanation may be interdependent and complementary, never contradictory: they address different meanings of a given question and are intended for different scientific (sub)communities. Each system corresponds to its own representation of the microscopic matter, adopts its own point of view and uses its own vocabulary.

Moreover, there is an inherent source of difficulty in our attempt to explain the microscopic matter because we try to understand the behaviour of quantum objects which is not deterministic in a deterministic fashion. Most explanations in science belong to the deductive-nomological account[149] which provides a scheme for any deterministic explanation of a particular event and consists in a deductive derivation of the occurrence of the event from a set of true propositions involving at least a scientific law or principle. The choice of rules and principles leavesi additional degrees of freedom.

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