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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 us 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? © 2019 Wiley Periodicals, Inc.

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Introduction

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 was 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 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 noninteracting description. Variational-based methods explicitly require the use of intermediate fragment wave functions corresponding to idealized nonphysical 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 co-workers.^[24–27] This first EDA method is limited to the Hartree–Fock level of theory and it suffers from the presence of nonphysical 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-center and two-center terms. The resulting energy decomposition yields true intra-atomic and true interatomic 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

1 molecules (QTAIM) considers domains bounded by zero-flux
2 surfaces of the density as defined by Bader, which are open sys-
3 tems that, among other properties, have associated energies.^[46]
4 In this sense, the QTAIM provides an atomic partition. An exten-
5 sion of this partition, considering atomic and diatomic terms, as
6 well as individual energy components, is known as the Inter-
7 acting Quantum Atoms scheme^[47–50] considers domains
8 bounded by zero-flux surfaces of the density as defined by
9 Bader.^[46] However, other nonoverlapping partition schemes,
10 such as *ELF* basins,^[51] can be considered at the expense of the
11 determination of the fragment kinetic energies. Methods for
12 fuzzy atom partitioning have been developed by Salvador and
13 Mayer.^[52,53]

14 Finally, Experimental Quantum Chemistry (EQC) is an energy-
15 based partitioning unique in that it can interchangeably rely on
16 the quantum chemical calculation, at any level of theory, as
17 well as on experimental thermochemical data, vibrational and
18 photoelectron, and X-ray diffraction and absorption measure-
19 ments.^[54,55] Developed by Rahm and Hoffmann, EQC makes
20 use of observable “reference frames.” For example, when study-
21 ing chemical bonding, the EQC partitioning refers to the bond
22 dissociation process. EQC is, in principle, applicable to any
23 chemical or physical transformations yet consists of relatively
24 few energetic terms. One of these terms is defined as the elec-
25 tronegativity of the system.^[56]

26 EDA methods are multipurpose methods used to quantify,
27 characterize, and explain interactions between fragments of
28 quantum systems. Whereas we have not mentioned all varieties
29 here, most EDAs can provide important pieces of informa-
30 tion on chemical interactions. This class of methods can also
31 have other practical uses, maybe most notably for the design
32 of molecular mechanics force fields.^[14,57,58] The explanations
33 offered by EDAs are seldom “chemical explanations” in the
34 sense that interactions are not directly described in terms of
35 “atom in molecules” chemical properties, such as electronega-
36 tivity, valence, ionic, and covalent radii. The latter properties
37 being determined by the location of the constituent atoms in
38 the periodic table. Most EDA methods instead rely on either
39 physical or quantum chemical concepts. In EDAs, interaction
40 energies are described as the sum of contributions arising
41 from a sequence of equations that typically are specific to
42 each method. The physical (or quantum chemical) interpreta-
43 tions of these equations, and the balance of the resulting
44 energy contributions, yields a deterministic explanation
45 focused on the dominant terms. Challenges for EDA method-
46 ology and future development of the field are what we will
47 discuss in this article.

48 Alston Misquitta and Krzysztof Szalewicz

51 We will address the nine questions from the perspective of
52 SAPT, sometimes also called exchange perturbation theory.
53 SAPT has been presented in detail in many original
54 papers,^[15,59–68] reviews,^[16,18] and textbooks.^[20,69,70] Thus, there
55 is no need for its extensive description here. However, we will
56 briefly lay out the main features of SAPT, particularly those that
57 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 article.

SAPT is a perturbation theory that calculates interaction
energy directly, starting from isolated monomers. Thus, in con-
trast to the supermolecular approach, no subtractions are
involved and, in consequence, SAPT is free of basis-set superposi-
tion error. The interaction operator V is the sum of all Coulomb
interactions between particles of different monomers. The sim-
plest 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, that is, enforce Pauli’s exclusion principle,
resulting in SAPT. There are several ways to perform such adap-
tation, 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 text-
books discussing intermolecular interactions use SAPT concepts
even if the SAPT acronym is not mentioned. SAPT is also known
under several other names, for example, 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 interac-
tions). This is because SAPT by design defines the interaction
energies in terms of electrostatic, induction (polarization and
charge-transfer, or charge-delocalization), 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 mono-
mers, 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 , possi-
bly with selective summations to infinite order applying the
coupled-cluster (CC) method. A version of SAPT, denoted as
SAPT (DFT), uses monomers described at the Kohn–Sham
(KS) density-functional (DFT) level (however, interaction ener-
gies 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 the truth. In particular, it is sometimes stated that
SAPT is “just” one more EDA method, useful only for inter-
preting 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 assem-
bles it from well-defined components. What is important, if this
assembly is performed up to sufficiently high order (second

1 order in V and fourth order in W are adequate for most pur- 58
2 poses), SAPT gives interaction energies similarly accurate to 59
3 those given by the supermolecular approach in the fourth order 60
4 (MP4) or the CC method with single, double, and non- 61
5 perturbative triple excitations [CCSD(T)]. 62

6 SAPT, in fact, is an exact method in the sense that it repro- 63
7 duces the exact interaction energy as the order in V goes to 64
8 infinity provided that appropriate symmetry-enforcing tech- 65
9 niques and exact monomer wave functions are used (or the 66
10 number of excitations in the CC method used to describe 67
11 monomers approaches the number of electrons in each 68
12 monomer). These statements are based on high-order calcula- 69
13 tions for small systems, see Ref. [65] for a review of 70
14 this work. 71

15 Since SAPT is a perturbation expansion in powers of V , one 72
16 may expect that SAPT will start to diverge as R becomes small 73
17 and consequently V is no longer a small perturbation. Appar- 74
18 ently, with proper symmetry enforcing, this divergence is not 75
19 observed even for interactions as strong as those characteristics 76
20 of chemical bonds.^[65] Also, low-order SAPT calculations for 77
21 larger systems show only a minimal worsening of convergence 78
22 when one goes to small R 's, see Ref. [72] for an analysis of 79
23 Ar_2 SAPT results at $R = 1.5 \text{ \AA}$, where the interaction energy is 80
24 more than three orders of magnitude larger than the absolute 81
25 value of this quantity at the van der Waals minimum, 82
26 $R = 3.76 \text{ \AA}$. 83

27 Another myth is that the programmed general version of 84
28 SAPT^[73–75] is at the best equivalent to MP2. In fact, the version 85
29 of SAPT that is applicable to interactions of arbitrary closed- 86
30 shell molecules and some open-shell ones includes terms up to 87
31 third-order in V and a high-order treatment of electron correla- 88
32 tion in monomers. By analyzing individual terms, one can show 89
33 that this version of SAPT is approximately equivalent to the 90
34 CCSD(T). This is confirmed by the agreement between these 91
35 two methods to within a few percent found in most calcula- 92
36 tions. In particular, for the helium dimer, the calculations of 93
37 Refs. [76,77] performed at CBS limits and including also a 94
38 benchmark all-order calculation estimated to be accurate to 95
39 about 0.01% show that the potential from SAPT at the level 96
40 available in the SAPT codes^[73] and the CCSD(T) potential are 97
41 similarly accurate, although SAPT is slightly more accurate at 98
42 the van der Waals minimum. 99

43 A broader comparison of SAPT with CCSD(T) was performed 100
44 in Ref. [78] In this work, CCSD(T)/CBS benchmarks were com- 101
45 puted for 10 dimers, containing up to 28 atoms, varying R from 102
46 asymptotic to repulsive configurations. The median unsigned 103
47 percentage error of SAPT(DFT) is only about 1% larger than that 104
48 of CCSD(T), both methods computed in the same basis set [the 105
49 CCSD(T) error here is, of course, entirely due to basis set incom- 106
50 pleteness]. SAPT (DFT) performs significantly better than all 107
51 other DFT-based methods investigated in Ref. [78] 108

52 The next myth is that SAPT (DFT) is an approximation to the 109
53 KS DFT supermolecular approach. While it should be already 110
54 clear from the discussion above that this is not the case, a dra- 111
55 matic illustration is presented in Refs. [72,79] Figure 1 in Ref. 112
56 [72] shows that CCSD(T) and SAPT [SAPT(DFT) is almost indistin- 113
57 guishable from SAPT] potential energy curves for Ar_2 are very 114

close to each other. In stark contrast, supermolecular DFT calcu-
lations 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 as 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, for example, 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 “nonequivalent” definitions of a chemical concept; the mentioned bonding and aromaticity indices belong to this category (although sometimes it is tried to sell this nonequivalence 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 a large number of proposed energy partitioning schemes in the last decades. Therefore, the reverse question is more legitimate to me: “Is the coexistence of many partitioning schemes the reason for lack

1 of precision in the definition of many chemical concepts?". As I
2 stressed elsewhere,^[80] as far as one does not have a compre-
3 hensive theory for the concept of interest and just tries to make
4 the qualitative to quantitative transition intuitively, the problem
5 of over-quantification will be prevailed.

6 **István Mayer**

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

27 **Martin Rahm**

28 I think so, yes. However, I do not see an inherent problem with
29 trying to quantify the same "fuzzy" concepts in several different
30 ways. Future cross-comparison efforts, discussed in questions
31 six and seven, will hopefully indicate which precise EDA defini-
32 tions are more predictive and chemically useful.

34 **Frank Weinhold**

36 On the contrary, we contend that the dubious physical assump-
37 tions underlying EDA partitions (i.e., existence of mutually
38 exclusive and simply additive "components" whose labels corre-
39 spond to chemical concepts as broadly understood) are the
40 issue. This is particularly so when the partition is formulated in
41 terms of nonorthogonal "reference fragment" orbitals and their
42 attendant conceptual ambiguities. Dubious premises lead inevi-
43 tably to a multiplicity of (equally dubious) EDA partitions.

45 **Ángel Martín Pendás**

47 In a sense, the lack of precision in defining concepts will inevi-
48 tably lead to different partition schemes. However, there are
49 several levels at which differences will arise, and much as in
50 other fields of Chemistry, a set of minimal rules for an EDA to
51 be acceptable for the community should be given. Are there
52 references? If so, are they well defined, or may they be chosen
53 at will by the user? Similarly, are there intermediate states from
54 which particular energy components are defined? If so, are they
55 well behaved, that is, are they compliant with the quantum
56 mechanical framework? It is my opinion that, in many cases, it
57 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.

61 **Julien Pilmé**

63 Yes, it can be argued that the lack of precision or the lack of
64 physical basis of some simple chemical concepts such as the
65 "lone pair" concept, promotes the coexistence of numerous par-
66 tition schemes. However, even if these concepts were better
67 defined, one might think that the abundance of partition
68 schemes will be sustained due to the difficulty to build a rigor-
69 ous bridge between a unique definition of an atom and the
70 quantum mechanics. Therefore, the lack of clear relationship
71 between the chemical concepts and the quantum mechanics
72 leads to an arbitrary character in the definition of partitions dic-
73 tated by a compelling need to rationalize the diversity of inter-
74 actions observed in the matter at the microscopic level.

75 **Carlo Gatti**

77 In my view, rather than the lack of precision in the definition of
78 many chemical concepts, it is the quite different perspective of
79 the various partitioning schemes that lead to and motivate, to
80 some extent, their coexistence. Indeed, broadly speaking,
81 energy decomposition analyses (EDAs) may be grouped in two
82 main categories, according to whether the decomposition is
83 performed in Fock (orbital) space or in the position space R³,
84 using some convenient partitioning of R³ in subdomains
85 (e.g., QTAIM). Advantages and shortcomings of the two
86 approaches have been masterfully analyzed and discussed by
87 Martín Pendás et al.^[82] In the former, attention is directed to
88 the composing energies of the (often fictitious) intermediate
89 steps through which the analyzed system is formed from some
90 initial moieties, whereas in the second kind of approaches,
91 attention is focused on dissecting intra and intersubdomains
92 energy contributions for the very final step of such system (and
93 with a similar analysis performed on a given initial step of the
94 system, if the approach is applied to the interaction energy
95 also). The proposers of the real space EDAs are like a film direc-
96 tor or a mystery writer which focus and analyze the last scene
97 of the movie or of the murder based only on what they see,
98 using unbiased scissors and zooming lenses. Instead, those of
99 the orbital space EDAs are eager to reconstruct a sequence of
100 Gedanken facts which have led the actors to the final outcome.
101 Actors keep changing (and often losing) their identity through
102 this process and in most cases, represent purely imaginary char-
103 acters. Clearly, in the case of "orbital space" EDAs, the film
104 directors or mystery writers enjoy more freedom in their work
105 and their products may more largely differ among each other
106 and raise more vibrant, yet often nonsense, debates.

108 **Paul Popelier**

110 Yes, is the short answer. I can think of one important example
111 of a chemical concept that causes a proliferation of EDAs. The
112 concept is that of the molecule itself and, in particular, the
113 identity of a molecule when in close contact with other mole-
114 cules. More precisely, nontopological EDAs suffer from an

1 unclear definition of a molecule at short range. At close inter-
2 molecular distances, the separation of charge transfer and
3 polarization then becomes increasingly ill-defined. Of course, at
4 long range, the identity of a molecule is not problematic. RS
5 perturbation theory is based on this clear idea of a molecule at
6 long range but this theory's vulnerability is that it breaks down
7 at short range. In that regime, molecules stop "owning" their
8 electrons and strong delocalization (i.e., exchange) start spoiling
9 the classical picture of what a given molecule is within a molec-
10 ular assembly. In other words, if one is uncomfortable with
11 finite (bounded) subsystems (i.e., the "real space" approach)
12 then the challenge is to determine where a given molecule
13 stops and starts. On the other hand, if one is inclined toward
14 infinite and overlapping subsystems (i.e., the "fuzzy" or "orbital"
15 or "Hilbert space" approach) then the challenge is to determine
16 which orbital or basis function still belong to the molecule in
17 question. In any event, without a clear decision on the matter
18 of how to carve out a molecule from a molecular assembly, one
19 will face ambiguities down the line, such as the one mentioned
20 above. It is important to make the right decision upfront in
21 order to avoid issue that needs fixing later. I still like to think
22 that the topological partitioning offers a clear definition of a
23 molecule at short range and is thus a good starting point for an
24 EDA. Indeed, IQA defines charge transfer and polarization in a
25 well-defined way.

26 Finally, I had to comment on Carlo's nice metaphor. Of
27 course, at first sight, it is true that IQA does not invoke any
28 intermediate steps unlike nontopological EDAs. However,
29 strictly speaking, this is not really true, depending on one's
30 starting point. Granted, IQA does not introduce a state that vio-
31 lates the Pauli principle but it could do this, and still apply its
32 topological partitioning to it. To me, how one partition and
33 which reference states one brings in are two independent
34 things. In fact, one can argue that IQA also refers to an artificial
35 reference state, by the fine structure of the second-order
36 reduced density matrix. This object contains an electrostatic
37 part, an exchange part, and an electron correlation part. The lat-
38 ter is a by-product of the fictitious Hartree-Fock state, while the
39 exchange part can be seen as a by-product of the fictitious Har-
40 tree state. So maybe the last scene of the IQA movie had some
41 predecessor scenes after all...

42 43 **Pedro Salvador**

44
45 To some extent, yes. But, I think it is worth to start by pointing
46 out that we are referring here to two main families of energy
47 decomposition schemes, as the reason for not having a unique,
48 unambiguously defined, scheme is different in each case. I do
49 not consider either of these two approaches superior from a
50 conceptual point of view, they merely provide different insight.

51 On one hand, there are approaches that decompose the total
52 energy into a number of global contributions that bear some
53 physical/chemical significance. In this case, the main issue
54 appears to be that some of these global energy contributions
55 are defined with respect to a reference. Another family of
56 methods decomposes the total energy into domain contribu-
57 tions, 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 over-
lapping AIM approaches. Furthermore, there is no need to fur-
ther 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, for example, for plane-wave calcula-
tions^[85]). Hence, the arbitrariness in this scheme comes solely
from the definition of AIM, as is the case of many other descrip-
tors such as partial atomic charges or, to some extent, bond
orders.

However, it is also worth to point out that, contrary to, for
example, electron population analyses, energy decomposition
schemes may differ from one particular electronic structure
method to another, just because the way the total energy is deter-
mined 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.

42 43 **Jerzy Cioslowski**

44 The coexistence of many schemes is a direct consequence of
45 the concept of energy partitioning being replete with ambigu-
46 ities. To begin with, it encompasses two very different
47 approaches, namely, (1) partitioning into contributions due to
48 physical phenomena and (2) partitioning into contributions due
49 to subsystems and clusters comprising them. This observation,
50 already made by Pedro Salvador in his answer above, deserves
51 further elaboration.

52 In the first case, the interaction between two subsystems is
53 analyzed by application of a sequence of contrived processes
54 such as geometry relaxation, charge transfer, polarization,
55 etc..., each giving rise to a particular energy component. It is
56 important to understand the distinction between the terms
57 "sequence" and "superposition" in this context as the contribu-
58 tions of these processes to the total energy are not commuta-
59 tive. To further complicate matters, not all permutations among
60 the members of the sequence in question are allowed. Thus, for
61 example, one can relax the nuclear and electronic degrees of
62 freedom in arbitrary order (by unfreezing the geometries of
63 subsystems while keeping their electron densities frozen, or
64 vice versa), each time obtaining different values of the respec-
65 tive energy components. On the other hand, if one defines
66 polarization as complete relaxation of the electron density and
67 charge transfer as relaxation of the total charges of the subsys-
68 tems, then obviously that the latter has to precede the former.
69 To summarize, the plethora of the possible energy partitioning
70 schemes of the first kind arises not only from certain degree of
71 arbitrariness in the definitions of the individual physical pro-
72 cesses (polarization, charge transfer, etc...) but also from the
73 (limited) arbitrariness of the order in which they are applied.
74 Another layer of ambiguity is added by the necessity of

1 specifying the definition of the partitioning of the electronic
2 properties into subsystem contributions that underlie the entire
3 energy partitioning scheme.

4 In the second case, one attempts to write the total energy as
5 a sum of contributions due to individual subsystems, pairs of
6 subsystems, clusters of three subsystems, and so on. Usually,
7 these subsystems are atoms or functional groups. Again, all of
8 such schemes derive from particular definitions of properties of
9 atoms in molecules. However, there is another conceptual diffi-
10 culty that has to be considered. The electronic Hamiltonian is
11 composed of one- and two-particle terms that give rise to the
12 respective one- and two-electron energy densities. Integration
13 of these densities over the entire Cartesian space produces the
14 corresponding energy components (i.e., kinetic, electron-
15 nuclear attraction, and electron-electron repulsion) whose
16 atomic and diatomic contributions are obtained by analogy
17 upon multiplication of the integrands by atomic projection
18 functions (whose sum over all atoms equals one; the functions
19 themselves can be smooth or not). Consequently, the atomic
20 contributions can be defined for all the three energy compo-
21 nents, whereas the diatomic contributions arise strictly from the
22 electron-electron repulsion energy (though one may further
23 partition the electron-nuclear attraction energy by separating it
24 into terms due to individual nuclei). Thus, the “many-body”
25 energy contributions due to clusters of more than two atoms
26 cannot be defined in a meaningful way, which runs contrary to
27 expectations from chemists (who would often prefer to deal
28 with atomic and diatomic energies transferable from one sys-
29 tem to another, the residual energy is accounted for by interac-
30 tions involving more than two atoms) and physicists (who are
31 inspired by the cluster expansions of energies of systems com-
32 posed of noble gas atoms, etc...). Even worse, this observation
33 appears to contradict at the first glance the results of
34 perturbative treatments of the dispersion interactions that pro-
35 duce closed-form expressions for, for example, three-body
36 interactions (the AxilrodTeller potential).

37 38 39 **Gernot Frenking**

40 The coexistence of many partition schemes is due to the fact
41 that different concepts and bonding models exist, which come
42 from different viewpoints and which address different questions.
43 Chemical bonding is a very complex phenomenon, which can be
44 interpreted in various ways. There will always be several chemical
45 concepts in chemical research, which consider diverse aspects of
46 chemical phenomena. Chemical concepts and bonding models
47 are not right or wrong, but they are more or less useful and the
48 usefulness depends on the question that is asked. Partition
49 schemes are tools in the arsenal of bonding models, which serve
50 as a bridge between the numerical results of quantum chemical
51 calculations and the human desire to understand them in terms
52 of classical concepts. Chemistry has rather a problem with the
53 coexistence of (1) historically developed and poorly defined heu-
54 ristic concepts and (2) more recently suggested quantum chemi-
55 cal partitioning schemes. The conclusions of the two models
56 may contradict each other. In such cases, it is important to exam-
57 ine 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 mol-
ecule or the point-wise energy in a molecule. However, I
completely disagree there is no physics behind. There are phys-
ics behind from the moment people have been able to find pat-
terns 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 neither 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 fol-
lowing a very simple principle: “as simple as it can be, but not
simpler”. Just like many models coexist for describing other prob-
lems 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 defini-
tions is 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 phe-
nomena 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 toward 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 the-
ory. This “unification” could be an objective in itself for the

1 community, leading to a simplification of concepts and descrip-
2 tions. Shant Shahbazian proposed another question: "Is the
3 coexistence of many partitioning schemes the reason for lack
4 of precision in the definition of many chemical concepts?" I
5 think that the development of a "universal" partition scheme
6 could lead to a simplification of chemical concepts and an eas-
7 ier dialogue between theoretical and experimental chemists.

9 Laurent Joubert and Vincent Tognetti

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

18 Paul W. Ayers

19 Yes and no. Insofar as people cannot agree on the precise defi-
20 nition of induction, or dispersion, or electron transfer, or polari-
21 zation, there can never be a unique EDA. (As a pernicious
22 example, electron transfer energy can always be viewed as an
23 extreme form of polarization, where the electron density of a
24 fragment becomes extremely delocalized. Similarly, the mere
25 idea of a local or regional kinetic energy is mathematically ill-
26 defined.) So yes. However, the existence of many partitioning
27 methods leads to ambiguity in chemical concepts, since differ-
28 ent EDA methods give qualitatively different explanations of
29 chemical phenomena in many cases. So no—it is not fair to
30 "blame", the coexistence of many partition systems on the
31 ambiguity in chemical concepts any more than it is fair to
32 blame the ambiguity of chemical concepts on the existence of
33 myriad partitioning schemes.

35 Farnaz Heidar-Zadeh

37 Given that chemical concepts are nonempirical, any attempt
38 toward quantifying them is doomed to be nonunique. Parti-
39 tioning schemes are no exception! Considering the fact that
40 partitioning schemes cannot be defined accurately, putting too
41 much effort into the precision of various definitions is futile. Each
42 scheme starts from a different set of assumptions (some of
43 which may be unknown or not carefully laid out at the begin-
44 ning) and consequently gives a different set of results. The best
45 one can hope for is having a rigorous mathematical definition of
46 partitioning schemes (and other concepts) which confirms chem-
47 ical trends and aids us in rationalizing the behavior of molecules
48 and materials. So, even though it is interesting to quantitatively
49 compare various schemes (i.e., the so-called precision of various
50 schemes), only their qualitative comparison can truly testify to
51 their value (i.e., assessing how various schemes comply with or
52 improve chemical reasoning is the closest thing to an accuracy
53 check we can dream of). As G. Frenking clearly explained, these
54 schemes are tools for making sense of numerical results of quan-
55 tum chemistry calculations in terms of familiar classical chemical
56 concepts and depending on the problem at hand, some of these
57 tools will be more/less useful than the others.

		System	
		Same	Different
Code	Same	Reproducible	Replicable
	Different	Robust	Generalizable

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 of how chemical concepts (in this case, atomic charge and oxidation state) can achieve progressively improved operational definition. Unfortunately, their concepts are not observables, that is, 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 nonobservable; 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 to use approximations and set up rules within one's field (e.g., 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 (sometimes conflicting) outcomes. For instance, we often regard charge transfer as a process occurring from one monomer to another

1 monomer, or from one fragment to another fragment of one
2 molecule, or approximately from one fragmental HOMO to
3 another fragmental LUMO. But, in computations, we need to
4 define the fragmental orbitals. Here the disparity comes up
5 because we usually get only canonical MOs which are extended
6 over the whole system. Approximations are introduced to get
7 fragmental orbitals and different approaches lead to different
8 solutions and eventually different energy terms.

9 10 **Eduard Matito**

11 Yes, but in my opinion, it is actually one particular chemical
12 concept that is most responsible for the proliferation of energy
13 partitions. Since an atom in a molecule (AIM) is a fuzzy chemical
14 concept, it is only natural that many partition schemes coexist.
15 This most evident in the case of real-space energy partitions:
16 we can have as many such energy partitions as definitions of
17 AIMs. In this sense, one way to reduce the number of energy
18 partitions would be to focus on the reliability of the AIM defini-
19 tion. For instance, we have found that some AIMs do not pro-
20 vide correct predictions when they are used to analyze certain
21 properties (see my answer to question 4).

23 **Eloy Ramos-Cordoba**

24 Since traditional chemical concepts are not observables, they
25 are not well defined in the context of quantum mechanics. As a
26 consequence, a given chemical concept can, in principle, be
27 described by many different mathematically rigorous partition
28 schemes. The number of reasonable schemes can be reduced
29 by imposing a series of physical constraints on the partition for-
30 malism. For instance, in variational EDA, one can impose that all
31 the intermediate wavefunctions must be antisymmetrized.

33 **W. H. Eugen Schwarz**

35 Many chemical concepts should not only comply with the general
36 laws of basic physics, but at best also match the set of specific
37 chemical materials of interest, the properties, and reactions of main
38 interest, and the ways different chemists are trained to understand
39 and intuitively guess and predict them. The chemical concepts
40 should be designed in a clear, unique, rational, consistent, and pur-
41 positive manner. Accordingly, there will and shall emerge related,
42 slightly different concepts, without lack of conceptual quality. A
43 simple example is the partitioning of interatomic distances,
44 modeled by sums of various types of "atomic radii" (van der Waals
45 radii opposite and orthogonal to a bond, ionic radii for different
46 formal charges and coordination numbers, covalent radii for differ-
47 ent formal bond orders, hydrogen bond radii, etc.). The richness of
48 chemistry requires a richness of concepts and schemes.

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

In principle, physics is more distinct and chemistry is fuzzier. 58
That is, "lack of precision" may exist in cases where one is still 59
in the phase of development of the chemical concepts, but it 60
is misleading and biased discrediting the principle of *fuzziness* 61
as a lack of some improper requirement in *mature scientific* 62
cases. Also note that the clear physical concept of, for exam- 63
ple, an electronic particle (in a molecule) in the low-energy 64
approximation fades away in the high energy regime (near 65
heavy nuclei), where it must be replaced by the electron- 66
positron matter field of noncoinciding charge, mass and spin 67
distributions. Or the clear physical concept of a sharp spatial 68
boundary (sometimes postulated between "atoms" in a mole- 69
cule) in the low-velocity approximation fades away in the real- 70
istic relativistic regime. 71

Therefore, many chemical concepts cannot be that general 72
and unique as most of the basic physical concepts. They have 73
to be appropriately adjusted to the ranges of materials, to the 74
typical conditions and to the useful purposes, which the 75
researchers want them to apply to. Experienced researchers 76
with some special interest in some field of chosen materials will 77
search for useful parameters as a quantification of their *experi-* 78
ence-guided fuzzy ideas. Related concepts of different scholars 79
may be analyzed with the help of statistical techniques, see 80
below. 81

Finally, we must distinguish between *descriptive, analytic,* and 82
explanative concepts. Description is the qualitative or quantita- 83
tive specification of the interactions of some specimen with its 84
surrounding, as given by nature and its laws. (The specimen 85
may be a molecule or nanoparticle or droplet or crystallite or 86
surface layer etc. of some material or compound. The interac- 87
tion properties may be described by mass, charge, polarizabil- 88
ity, color, chirality, various specific reactivity parameters, etc.) 89
Respective probability distributions and source functions of 90
these interaction properties can be analyzed in spatial detail, as 91
for instance in the QTAIM. As long as no restraints of the 92
description are imposed, such as monopole approximations, or 93
same average values for whole sets of specimens or homolo- 94
gous series, the descriptive parameters should be comparatively 95
unique. 96

There are then two further steps toward a deeper *under-* 97
standing of WHY is WHAT is. First, there is the question of the 98
internal structure of the data, and relations between them. That 99
is so to say an "autonomous" intrachemical approach. One 100
approach is by additive increment systems, approximating the 101
property parameters of compounds by sums over atomic, 102
diatomic, and possibly multi-atomic (three-center or ring) 103
contributions. Examples are effective atomic radii, effective atomic 104
charges, ionic conductivities, diamagnetic (Pascal) increments, 105
diatomic bond energy increments, spectroscopic ligand field 106
parameters, stereospecific ligand parameters, and so 107
on. Depending on the chosen set of compounds, the chosen 108
types of properties, and the perspectives of the researchers, 109
related alternative partition schemes may emerge, where the 110
increments may have different meanings. As long as observable 111
properties P_j of specimens j can reasonably well be approxi- 112
mated by different sets of increments b_k and d_l as in eq. (1), it 113
is fine. 114

$$P_j \approx \sum_{k \text{ for } j} b_k \approx \sum_{l \text{ for } j} d_l \quad (1)$$

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* interphysicochemical 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 respond 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 the 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 *nonidentical 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-delocalization, one should include E_{indx} computed to third order in V , as well as the $\delta_{\text{int}}^{\text{HF}}$ term. This term is defined as the difference between the supermolecular interaction energy $E_{\text{int}}^{\text{HF}}$ 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 does not. The impression is that the great number of partition schemes worsens 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

1 interest is also precisely defined within the “context” of each
2 given partitioning scheme. The problematic situation appears
3 when one tries to compare the nonequivalent definitions not
4 within, but between various partitioning schemes. As I stressed
5 also in answer to question 1, this is the result of “over-quantifi-
6 cation”. At a personal level, one may simply dismiss all available
7 partitioning schemes but a single one and adopt the preferred
8 scheme trying to avoid the dilemma though, at the level of
9 community the problem retains (the relevant literature however
10 hardly supports that even at a personal level this is the pre-
11 ferred strategy). Since part of what we mean by precise defini-
12 tion is the “consensus” of a scientific “community”, not a single
13 person, to use the “preferred” partitioning scheme, without a
14 consensus the above-mentioned formal mathematical view-
15 point on the precise definition is at best handicap. These are
16 the motivations to address questions 8 and 9.

17 **István Mayer**

18 Any partition scheme is based on a selected well-defined defini-
19 tion of the atoms within the molecule.

20 **Martin Rahm**

21 In one way of looking at it, yes. Chemical concepts are what we
22 make of them. Different chemists can and will have different
23 opinions on the best definition of what is covalence, electro-
24 negativity, etc. Differences in such definitions are also a conse-
25 quence of the development of the concepts over time.
26 Different partition schemes will naturally be a reflection of this.
27 As such, different EDA schemes can provide precise definitions
28 within their respective frameworks. If a particular incarnation is
29 chemically useful is another question.

30 **Frank Weinhold**

31 Not in any rational process of advancing science. Any EDA com-
32 ponent “label” is a language construct, not a “concept” per
33 se. The correlations (if any) between EDA component labels
34 and more broadly understood chemical concepts should be
35 demonstrated, not assumed.

36 **Ángel Martín Pendás**

37 If an EDA is seen as a way to compress (or to compact) the
38 complex energy information content of a wavefunction (or set
39 of wavefunctions if references are needed), different EDAs
40 should provide different readings of the same physical
41 (or mathematical) objects. In this sense, all EDAs should be
42 compatible among themselves (and that is why I advocate par-
43 titions which can be applied to any or at least to a large class
44 of wavefunctions). By understanding how different methods
45 read the same function providing different answers, the limits
46 and windows of applicability of the underlying chemical con-
47 cepts might probably be sharpened.

48 **David L. Cooper**

49 There are indeed senses in which the adoption of a particular
50 partitioning scheme leads to more precise definitions of

51 particular EDA “labels” within that scheme, but such “labels” are
52 likely to have somewhat different meanings in equally valid
53 alternative approaches. I agree with Frank Weinhold that sup-
54 posed correlations with underlying chemical concepts need to
55 be demonstrated, without any such links simply being
56 assumed. I am also struck by a point that is reiterated in a
57 recent perspective article^[89]: the use of models (including EDA
58 schemes) can risk blurring the distinction between what is
59 really mathematical modeling and what is, at least in some
60 sense, an underlying chemical/physical “reality” or a “meaning-
61 ful set of concepts”. [That particular article classifies exchange,
62 Pauli repulsion, and orbital interactions as being part of the
63 mathematical model, and it also addresses the extent to which
64 there is really any proper distinction between charge transfer
65 and polarization. Then again, picking (say) exchange, it can be
66 important to remember that not everyone agrees as to what
67 such entities really signify even in a *qualitative* sense.^[90]

68 **Carlo Gatti**

69 Not necessarily and surely not in the present state of affairs.
70 Chemical concepts are in general very much intertwined in the
71 energetic terms of the various EDAs based on orbital space
72 decompositions and they may be so to a different extent,
73 depending on the given scheme adopted. A clear and enlight-
74 ening analysis of this rather convoluted problem is presented in
75 82. I’m personally in favor of retaining only those energy par-
76 titioning schemes where each energy component has a clearly
77 defined physical basis and then of possibly observing whether
78 and which of these components may be roughly related to
79 chemical concepts, if any. This is the typical situation one is fac-
80 ing with position space EDAs, like IQA. To make an example,
81 charge transfer, which is a typical chemical concept, may be
82 clearly defined and easily evaluated with all these approaches.
83 However, it is not possible to isolate its energetic impact in
84 standard real space EDA schemes. One should make recourse
85 to the theory of resonance structures in real space to estimate
86 such energy component.^[91]

87 **Paul Popelier**

88 According to the way I answered question 1, the current ques-
89 tion sounds almost like the opposite of question 1, and thus I
90 am inclined to answer yes. As a fan of IQA (a sentiment to be
91 updated when something better comes along) I am happy
92 (hopefully not naively) with the way this EDA defines the fol-
93 lowing chemical concepts: covalency (via exchange), ionicity
94 and polarity (via electrostatics), dispersion (via electron correla-
95 tion), and steric effects^[92] (via the intra-atomic or self-energy).
96 Because IQA is able to also provide intra-atomic “dispersion” it
97 has the potential to perhaps define a new chemical concept,
98 which focuses on stability of weakly bound van der Waals com-
99 plexes but then from an (intra)atomic point of view.

100 **Pedro Salvador**

101 If we assume an atom-in-molecule definition being a partition
102 scheme, I think the answer is yes. Not only the numerical results
103 differ from one AIM to another (sometimes quite dramatically),
104

1 but some particular chemical concepts may only be achieved
2 by making use of a given AIM. This is, for instance, the case of
3 the so-called “overlap population”, which can only be
4 accounted for with “fuzzy” atomic domains. This, however, com-
5 promises this particular concept, which probably should be
6 considered deprecated. In a way, one should stick to chemical
7 concepts that can be achieved, at least quantitatively, with any
8 reasonable (see question 7) partition scheme.

9 Jerzy Cioslowski

11 As put succinctly by István Mayer in his answer above, “any par-
12 tition scheme is based on a selected well-defined definition of
13 the atoms within the molecule.” However, in the case of energy
14 partitioning schemes formulated in terms of (imaginary) physi-
15 cal processes, specification of the order of their application is
16 equally important (see my response to question 1). Thus, the
17 implication is always one way, namely definitions of
18 chemical/physical concepts) energy partitioning.

20 Gernot Frenking

21 I agree with Martin Rahm that “Chemical concepts are what we
22 make of them.” A useful partitioning scheme should indeed
23 lead to a more precise definition of the underlying chemical
24 concept. Five conditions are to be fulfilled by a reasonable par-
25 titioning scheme: (1) it should be based on accurate quantum
26 chemical calculations; (2) it should be mathematically unambig-
27 uously defined; (3) the results should be largely independent of
28 the level of theory used; (4) the different terms should lead to a
29 plausible interpretation; (5) it should be useful for chemical
30 problems. The adoption of a particular partition scheme comes
31 from its usefulness. The agreement with chemical concepts is a
32 fuzzy condition because chemical concepts are fuzzy. I think
33 that this comes out of the necessity to bring the pandemonium
34 of chemical facts into an ordering scheme in terms of rules and
35 models, which are accessible to the human mind. I was puzzled
36 by the statement in Ref. [82], that the use of bonding models
37 “sometimes leads to a blurring of the distinction between
38 mathematical modeling and physical reality.” In the quantum
39 world, physical reality of an electron is not entirely assigned to
40 its electronic charge distribution, which represents only a pro-
41 jection onto a space of lower information content; its complete-
42 ness is only provided by its wave function Ψ . The wave
43 function Ψ contains more information about the behavior of
44 the electron than ρ . In chemistry, this comes to the fore for
45 example in the outcome of pericyclic reactions, or in any spec-
46 troscopic investigation, which can only be explained when the
47 symmetry and sign pattern of Ψ are considered.

49 Émilie-Laure Zins

51 Most of the current chemical concepts are based on the obser-
52 vations, interpretations, and intuitions of experimental chemists.
53 One of the roles of theoretical chemistry is to explain and
54 develop chemical concepts based on the fundamental equa-
55 tions of quantum physics and to link these concepts to those of
56 the experimental chemists. Thus, the use of any partition
57 scheme to explain any empirical chemical concept should lead

to more precise definitions of the underlying chemical concepts 58
from the perspective of our community, provided that the 59
energy partition is based on variables that have physical signifi- 60
cance. However, experimental chemists will not necessarily be 61
immediately convinced by the increase in precision that we can 62
bring to empirical concepts they work with on a daily. 63
64

65 Miquel Solà

66 It is an advantage, not a problem, to have different partitions 67
schemes as far as they prove to be useful, to be rooted in quan- 68
tum mechanics, to be mathematically unambiguous, to provide 69
physically meaningful energy terms, to give insight, and to pos- 70
sess predictive power. Let me quote Dewar who said: “the only 71
criterion of a model is usefulness, not its *truth*”.^[93] 72

73 Paul W. Ayers

74 In a narrow sense, once one chooses a partitioning method 75
(either for the atom-in-molecule or the energy-into-fragments) 76
then those choices can be profitably used as a “model chemis- 77
try” to elucidate chemical phenomena, to observe trends, and 78
to draw inferences. In this sense, all computed quantities within 79
the selected partitioning are “precise” (in the sense of being 80
exactly defined) within the context. However, a different par- 81
titioning method might reveal different trends and different 82
insights that are not less precise, but merely more or less useful 83
(as a matter of preference and opinion). 84

85 Farnaz Heidar-Zadeh

86 A well-defined scheme is based on a rigorous set of physical 87
assumptions, consequently, it consistently prescribes the defini- 88
tion of underlying chemical concepts. So, I would use the term 89
“consistent” instead of “precise.” This gives an elegant and 90
unambiguous framework for further developing concepts. Even 91
if a concept was proposed on heuristic grounds, but proved to 92
be useful, establishing a framework within which it is mathe- 93
matically justified is essential. 94

95 Juan Andrés

96 As Solà remarked recently^[94]: “My usual answer is that the most 97
fruitful concepts in chemistry share the same lack of strict defi- 98
nition.”^[95] In addition, there is not a unique way to compute 99
quantities related with such intuitive chemical concepts and 100
therefore, partition schemes. As Martín Pendás et al. write^[96] “A 101
chemical bond has an energetic strength (its bond energy) that 102
is somehow connected to a particular electron count (its bond 103
order). Interestingly, neither bond energies nor bond orders are 104
(Dirac) observables. The former vanish into thin air once we 105
pass from diatomics to polyatomics, whereas the latter too 106
often rely on the orbital approximation. Notwithstanding, 107
chemists feel comfortable with such an edifice otherwise built 108
on shifting sands”. Therefore, the different partition schemes 109
need to be rooted in quantum mechanics, to be mathematically 110
unambiguous, in order to provide physical basis of the underly- 111
ing chemical concepts. 112
113
114

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 agreements 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 behavior. The exchange components should decay purely exponentially, that is, 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, 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 the best of our knowledge, no relation to experiment is possible in these methods.

While all acceptable variants of SAPT must have the same asymptotic behavior 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

1 dispersion energies. The nonuniqueness appears only in the
2 second-order exchange corrections. Of those, the exchange-
3 dispersion energies are relatively small so the potential differ-
4 ences can usually be safely ignored. The differences in
5 exchange-induction corrections are eliminated by the $\delta_{\text{int}}^{\text{HF}}$ term.
6 Also, some variants that perform best in all orders are equiva-
7 lent or very close to SRS in low order. In conclusion, whereas
8 there is a small nonuniqueness in definitions of physical contri-
9 butions resulting from the flavors of SAPT, differences between
10 best theories can be ignored.

12 **Question 3: How Can One Use the Results of a** 13 **Partition Scheme to Improve the Clarity of** 14 **Definitions of Concepts?**

16 **Ramon Carbó-Dorca**

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

26 **Shant Shahbazian**

27 In my opinion, there is no direct relationship between the
28 results of a partitioning scheme and the clarity of chemical con-
29 cepts. As I stressed in answer to question 1, to have a well-
30 defined concept, a comprehensive theory for the concept of
31 interest must be developed. Let me give an example. While
32 humans had always an intuitive qualitative understanding of
33 temperature, since the time of Galileo people tried to quantify
34 this intuition through constructing various thermometers. In
35 one sense, in this period, temperature was an index of
36 hotness/coldness but temperature only conceived as a physical
37 "observable" when thermodynamics was formulated and the
38 absolute temperature was introduced independently from ther-
39 mometers, based on its relationship with internal energy and
40 entropy. In other words, thermodynamics is an organized web
41 of connections between various thermal concepts and the posi-
42 tion of each concept, for example, temperature, in the web
43 makes it a well-defined and clarified concept.^[98] What currently
44 lacks in theoretical chemistry is a similar comprehensive theory
45 (or theories) that not only introduce each chemical concept
46 quantitatively but also makes a web of relationships between
47 various concepts. Index-based view in computational chemistry
48 that focuses only on quantitative definition of a single concept
49 lacks such capability and, in my opinion, current partitioning
50 schemes are also no exceptions.

52 **Martin Rahm**

53 It would depend on the concept in question. For example, I
54 have, together with Roald Hoffmann, redefined the chemical
55 concept of electronegativity within the framework of the
56 "Experimental Quantum Chemistry"-partitioning.^[54] Together
57

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 toward clarifying such concepts
is to use EDA-descriptors and creates maps of chemical interac-
tions. 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 def-
initions of chemical concepts.

Frank Weinhold

Reference [99] serves as an example of 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 illus-
trated in this work?

Roberto A. Boto

On the one hand, a partition scheme is built from some theo-
retical 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 unifor-
mity 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 com-
mented 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 "signa-
ture" which can be identified through several partition

1 schemes, the confrontation of results arising from numerous
2 partition schemes would be useful to improve the definition of
3 the concept. I think for example that the case of the covalent
4 bond, already reported by Ángel, falls into this category.

6 Carlo Gatti

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

27 Paul Popelier

28 An example of how to use the results of a partition scheme is
29 that of the EDA called IQA being combined with the newly pro-
30 posed Relative Energy Gradient (REG) method.^[100] The REG
31 method is able to handle, automatically and exhaustively, the typ-
32 ically hundreds of individual energy contributions that IQA gener-
33 ates. REG ranks atoms to the degree that they act like the total
34 system they are part of, in terms of energy changes. This minimal
35 method can handle competing for energy contributions, which
36 may appear contradictory and thereby fuelled ongoing debates.
37 For example, in our very recent biphenyl case study,^[101] we use
38 REG-IQA to explain its planar rotation barrier. The central torsion
39 angle in biphenyl prefers to be 45° and when at 0°, biphenyl's
40 total energy profile reaches a local maximum. REG shows that
41 IQA's intra-atomic energies of the orthohydrogens dominate the
42 barrier, which is compatible with the textbook explanation of a
43 steric clash. However, at the same time, the exchange energy
44 between these two orthohydrogens becomes most stabilizing at
45 0°, indicative of the formation of a covalent bond. REG is not con-
46 fused by these two opposing effects and concludes that, while
47 they largely cancel out, it is the energy behavior of the ortho-
48 carbons that causes the rotation barrier. This is an example of the
49 Dutch expression "als twee honden vechten om een been loopt
50 de derde er mee heen." (Note: just in case you GoogleTranslate
51 this then know that "been" actually means "bot").

53 Pedro Salvador

54 As Martin stated, that would depend on the particular concept.
55 For instance, the concept of Oxidation State has lacked a clear
56 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 sat-
isfactory 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 undesir-
able. 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 defini-
tion 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 con-
ditions given in my answer to question 2, which should be ful-
filled 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 do not. Both Hilbert and real
space energetic decompositions have been focused on describ-
ing what we know, plaguing the literature with different views
of things for what we have an intuition. However, in my view-
point, more efforts should be paid in describing things for
which we do not have an intuition (e.g., high pressure) and pre-
dict 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 con-
cepts that were born without the need for 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 chemi-
cal concepts as suggested by the question. In the case of defini-
tions 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

1 use for deciphering chemistry. To expand this point, it is impor-
2 tant to recall that (as already stated by Jerzy Cioslowski in dis-
3 cussion for question 1) EDAs can be divided into two main
4 categories: those obtained during the generation of
5 wavefunction or molecular energy, and those coming from a
6 subsequent post-treatment. Let us, for instance, consider a MPn
7 calculation: it will naturally provide a decomposition into vari-
8 ous additive contributions, from the zeroth to the n -th pertur-
9 bation orders. Alternatively, KS energy is by definition split into
10 the KS kinetic energy, the interaction energy between electrons
11 and nuclei and the Hartree and exchange-correlation contribu-
12 tions. One can then wonder whether such decompositions may
13 convey chemical information. For instance, the second-order
14 correction in MP treatments is often linked to dispersion
15 (London) effects. Conversely, the chemical meaning of KS
16 kinetic energy (related to the fictitious noninteracting system,
17 and not to the real one) is far from being obvious, as well as
18 exchange-correlation since it involves corrections to kinetic
19 energy and electron repulsion. KS thus provides direct energy
20 decomposition without meaningful chemical information. Note
21 that a second exact additive KS decomposition could be
22 straightforwardly obtained from first principles with the orbital
23 energies and exchange-correlation potential. However, it is not
24 deprived of drawbacks: (1) what is the meaning of KS orbital
25 energies? (2) how to interpret the other terms? For the first
26 point, the only exact result is that the HOMO energy is opposite
27 to the vertical ionization potential if the exact exchange-
28 correlation functional is used. The second problem can be
29 cured using Mel Levy's recent potential shift^[104] that allows for
30 expressing the total energy as the only sum of orbital energies.
31 Such a scheme would certainly simplify energy decompositions,
32 but it is still in the youth age.

34 Paul W. Ayers

35 If the "clarity of definition" of a concept was dependent on the
36 "results of a [one specific] partitioning scheme" then I am reluc-
37 tant to embrace that definition. On the other hand, if the "clar-
38 ity of definition" of a concept is supported by the "results of a
39 [many nonspecific] partitioning schemes", then that concept is
40 well-founded and defined qualitatively (even if the partitionings
41 might give different quantitative results).

43 Farnaz Heidar-Zadeh

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

52 Juan Andrés

53 An underlying theme of the above questions has been the gap
54 that exists, in general, between quantitative quantum theory
55 and chemical concepts. In this context, we agree with the com-
56 ment by Grunenberg^[95] "I am not writing against the use of

57 qualitative chemical concepts per se, but against their quantifi-
58 cation. In many cases, qualitative concepts even in combination
59 with nonperfect experiments led to real progress in chemistry.
60 However, one striking attribute of the aforementioned disputes
61 in the literature is the fact, that many of these quantifications
62 are triggered by a conceptual farrago and by this, most of these
63 scientific quarrels are inherently insoluble. Some even resemble
64 mock discussions. (Interestingly, in the course of such discus-
65 sions, usually one side is referring to a medieval scholastic
66 "questio." Therefore, we need partition schemes precisely
67 defined mathematically from the underlying physics to reach
68 clarity on the definitions of concepts.

70 Yirong Mo

71 The conflicting results from different partition schemes certainly
72 will certainly attract attentions and stimulate discussion and fur-
73 ther research work. In this way, the definitions of concepts can
74 be progressively clarified and eventually quantified.

75 Eduard Matito

76 I refer to my answer to question 2: I believe this can only be
77 achieved in the case of concepts that lack consistency. In these
78 cases, there must be a consensus among different partitions
79 (and within the community) before walking the dangerous path
80 of changing (clarifying, if you prefer) the definition of concepts.
81 Again, I believe the concept of aromaticity serves as a nice exam-
82 ple. In the 1990s, the definition of aromaticity given by the
83 IUPAC applied only to ground-state pi-aromatic compounds and,
84 although the current definition of aromaticity is not less blurry
85 than it used to be, now recognizes different aspects of aromati-
86 city such as electron delocalization, particular reactivity, thermody-
87 namic stability, and certain structural features. Many of the latter
88 features have been repeatedly confirmed by the corresponding
89 computational measures/models of aromaticity. In fact, the work
90 still continues. The "Aromaticity" conference organized in Riviera
91 Maya in 2018 by Gabriel Merino, Miquel Solà, and Henrik
92 Ottosson included a round-table session to find a consensus
93 among the members of this community (experimental and theo-
94 retical) about an updated definition of the concept.

95 W. H. Eugen Schwarz

96 Yes, for instance: statistical correlations and factor and cluster
97 analyses can work out whether one or more conceptual main-
98 components are behind a group of related empirical or theoret-
99 ical concepts, and how narrow the relations between them are.
100 Theoretical schemes may need revision in the case of poor rela-
101 tion to well-proven empirical concepts.

102 Alston Misquitta and Krzysztof Szalewicz

103 The SAPT partition scheme gives indeed a clear definition of
104 concepts. Consider two polar systems. One of the main con-
105 cepts appearing in many undergraduate courses is that at large
106 separations this interaction is determined by the simple interac-
107 tion of the permanent dipole moments with its $1/R^3$ decay. As
108 R decreases, contributions from higher multipole moments
109 become important. The sum of all these contributions agrees to
110
111
112
113
114

1 a high accuracy with the SAPT electrostatic energy. Once R is so
2 small that the $1/R^6$ terms matter, contributions from induction
3 and dispersion energies are becoming important. At these R ,
4 such contributions can be expressed in terms of dipole
5 moments and of the static and dynamics polarizabilities. Again,
6 both components are very accurately reproduced by SAPT. As
7 R decreases further, overlap and exchange effects come into
8 play. This does not mean any loss of physical insight despite
9 things getting a bit more complicated. For example, the electro-
10 static energy is still just the Coulomb interaction of two charge
11 distributions. For the induction and dispersion energies, we
12 have to use the concept of density–density response function
13 which also has a clear physics meaning. As the distance
14 between monomers is now of the order of a few angstroms,
15 electrons can tunnel through the potential barrier. Tunneling is
16 one of the main concepts of quantum mechanics, with a clear
17 interpretation. Such clarity of definitions of concepts as outlined
18 above cannot be achieved if a decomposition starts from the
19 dimer wave function.

21 **Question 4: Are Partition Schemes Subject to** 22 **Scientific Darwinism? If So, What Is the** 23 **Influence of a community's Sociological** 24 **Pressure in the "Natural Selection" Process?**

25 **Ramon Carbó-Dorca**

26 A chemically and physically bound piece of research cannot be
27 influenced by anything but the theoretical scheme itself. A par-
28 tition scheme, if it really conforms according to quantum
29 mechanics, shall be appropriate to any electronic system. If a
30 system influences the construction of a partition scheme, then
31 there cannot be any hope to obtain a general procedure.

32 **Shant Shahbazian**

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

49 **István Mayer**

50 Yes, I think so. One needs results that help interpret the calcu-
51 lated and/or experimental quantities. The observation that Mul-
52 liken's gross populations often fail to provide chemically

53 reasonable results, motivated the quest for alternative schemes
54 of population analysis. (This was the case although Mulliken's
55 gross population is that definition which is consistent with the
56 internal mathematical structure of the LCAO formalism.^[105])
57 When EDA methods are concerned, I have experienced a pres-
58 sure from chemists to produce a scheme in which the diatomic
59 bonding energies are on the "chemical scale", that is, not equal
60 but comparable with the accepted bonding energies. (Also see
61 my answer to question 6.)

62 **Martin Rahm**

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

75 **Frank Weinhold**

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

80 **Roberto A. Boto**

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

90 **Ángel Martín Pendás**

91 Like anything in Science, partition schemes are subjected to
92 Darwinism. Whether Darwinism in Science chooses the best
93 solution or only the fanciest one is another problem, since, as a
94 human activity, Science does not escape fashion. Since, unfortu-
95 nately, many EDAs are intimately associated with particular
96 electronic structure paradigms (e.g., molecular orbital or
97 valence bond descriptions), the waves in the former are clearly
98 conditioned by those in the latter.

99 **David L. Cooper**

100 Experience suggests that the partitioning schemes that are
101 likely to be the most widely used in the scientific literature will
102 not necessarily be the "best" ones, as determined by cross-
103

1 comparison and “benchmarking”, nor indeed those that are
2 best suited to impact the practice and teaching of Chemistry by
3 nontheoreticians. Although “fashion” can indeed be an impor-
4 tant factor, ultimately it is the availability of particular methods
5 in certain “standard packages” that could end up being the
6 deciding factor. This could, of course, be ameliorated to some
7 extent by the availability of free and easy-to-use facilities that
8 implement other schemes.

9 Carlo Gatti

10 Yes, they probably do, but are we sure that the more fitted to
11 survive are those schemes with largest scientific rigor? The
12 sociological pressure of the community may largely bias the
13 selection process. Factors like ease of use, simplicity of analysis
14 (few composing energetic terms rather than a potential pleth-
15 ora of progressively finer dissections like in the real space
16 EDAs), adoption by large and numerically dominant communi-
17 ties, may clearly bias the game, offsetting the purely scientific
18 selection process. Other counterweighting and disturbing fac-
19 tors might be the implementation of given schemes rather than
20 others in popular quantum-mechanical codes.

23 Julien Pilmé

24 Yes, I agree with that. In my opinion, the “natural” selection pro-
25 cess, which should be conducted according to scientific
26 requirements, is hardly efficient owing to the lack of the
27 straight forward link with the experimental data. Maybe, this
28 process becomes more “fashion-driven” and more sensitive to a
29 sociological pressure. Yes, it seems also that the selection pro-
30 cess is flawed by the ready availability (or not) of EDA methods
31 in the quantum chemistry software.

34 Paul Popelier

35 The metaphor of natural selection is useful to think about
36 where the zoo of EDAs is at, and where it should head for. The
37 answer to question 4 is yes because natural selection is already
38 happening. For example, the recent review by Skylaris et al.^[2]
39 compares and discusses six test sets. The authors conclude that
40 “Overall the ALMO EDA scheme is shown to provide the most
41 chemically sensible EDA results for our systems relevant to drug
42 optimization.” Unfortunately, this comparative study was con-
43 fined to nontopological EDAs. Building on the Darwinistic meta-
44 phor, this means that topological EDAs happily live on some
45 island or disconnected continent that has had no contact yet
46 with nontopological EDAs (although Ángel and co-workers have
47 published such a comparative study.^[107]

48 We should keep in mind how natural selection actually works.
49 Ultimately, it is the interaction between the creature (i.e., a given
50 EDA) and its environment (the other EDAs and the community
51 of users) that determines if the creature survives or not. I think
52 that as a community we should be a more demanding environ-
53 ment, even if that means that an EDA becomes extinct. Experi-
54 mentalists can only take the work of theoreticians seriously if it
55 provides future-proof insight or correct predictions. There is no
56 harm in two different EDAs coming to the same conclusion; what
57 is a problem is if they contradict each other. Although I do not

58 have precise references in mind my feeling is that the commu-
59 nity allows contradiction to exist, and even worse, allow them to
60 thrive under the false banner of diversity and richness. This is
61 dangerous for Science. I am still dreaming of a consistent world
62 of interpretations and predictions, one where $F = ma$ is the only
63 equation that puts a person on the moon rather than $F = m/a$ or
64 $F = ma^2$. However, equivalent theories (e.g., Matrix Mechanics
65 and Wave Mechanics, or Valence Bond and Molecular Orbital, or
66 String Theory and Quantum Gravity) can coexist as long as they
67 make the same predictions.

68 Jerzy Cioslowski

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

83 A simple prescription to avoid this undesirable status quo
84 would be axiomatization of chemical concepts. Spelling out a
85 set of axioms that all the concepts have to satisfy would greatly
86 reduce the room for personal preferences and thus diminish
87 the importance of the “human factor in interpretation of elec-
88 tronic wavefunctions.”

91 Gernot Frenking

92 Darwinism means the survival of the fittest. In that sense, I do
93 think that those concepts will eventually be adopted by the
94 community, which are considered as the most useful ones.
95 However, I see an ongoing preference for simple models that
96 are intuitively easy to accept even when the underlying
97 assumptions are incorrect, instead of a more complicated
98 model, which agrees with a thorough quantum chemical analy-
99 sis. There seems to be a human tendency even in science to
100 prefer a known disease to unknown health because one is
101 afraid of the work that comes along with the cure. The great
102 acceptance of the NBO method is at least partly due to the
103 smoothing tranquilizer effect for addicts of the Lewis model
104 who do not want to be bothered by the complexity of the elec-
105 tronic structure. The sociological pressure could lead to a situa-
106 tion where the well-known illness is preferred over the
107 unknown health. With other words, the frequent use of NBO
108 results may lead to the acceptance of the method even when
109 the shortcomings are well known.

111 Julia Contreras

112 Absolutely. I see that there are two main trends: mathematical
113 and physical Darwinism and I totally advocate for physical
114

1 Darwinism. Theories can be very elegant, but what I really
2 expect from an energetic partition (or as well any other theory),
3 is to describe the physics of the system. To provide a descrip-
4 tive and predictive framework. What should not be interpreted
5 as social pressure (and we have seen much of these lobbies in
6 this community): MY method is BETTER than the others (and I
7 reject papers otherwise).

8 **Henry Chermette**

10 Darwinism..., yes or no: selection of the survival scheme(s) can
11 be biased by factors like ease of use, availability in (the widely
12 used) software, and simplicity of analysis. And a scheme can be
13 "rediscovered" 20 or 30 later after its (first) description in a (spe-
14 cialized, not popular) journal.

16 **Émilie-Laure Zins**

17 This question suggests a comparison between the theory of
18 evolution and the description of the chemical bond. This com-
19 parison seems to me to be particularly relevant and deserves a
20 short comment. Experimental chemists, during their observa-
21 tions or interpretations, have proposed and developed many
22 concepts, which can be compared (metaphorically) to different
23 living species: they can appear, persist, evolve, or disappear. It
24 can be hypothesized that some chemical concepts could be
25 merged, in particular, through the use and development of
26 adapted partition schemes. It seems to me that a "massive
27 extinction" in the zoo of chemical concepts, caused by a "uni-
28 versal" partition scheme, or by a limited number of partition
29 schemes based on the fundamental theorems of quantum
30 physics, would be beneficial to chemistry.

32 **Laurent Joubert and Vincent Tognetti**

34 We think that different communities may have preferences
35 guided by some historical reasons or, let us say, some traditions
36 in interpreting the same results. Assume that we are interested
37 in the energy difference between two conformations (that can
38 be measured experimentally in some cases). The virial theorem
39 actually brings us two explanations: (1) it is due to the electron
40 kinetic energy, (2) it is due to the potential energy. No one is
41 preferable, being both correct, since, quoting Godard, "The
42 essential difference between classical mechanics and quantum
43 mechanics is that in classical mechanics the kinetic energy and
44 the potential energy are independent (one is determined by
45 momentum, the other by position), whereas in quantum
46 mechanics T and V are simultaneously determined by the
47 wavefunction." However, an experimental chemist is much
48 more accustomed to think of potential energy (linked to inter-
49 actions between atoms) than of kinetic energy, and we are thus
50 facing different habits in various chemical communities. T fea-
51 tures the advantage of being derived from a one-body opera-
52 tor, while V involves a two-body operator. When decomposed
53 into N atoms, it thus generates about N^2 values, a number that
54 may make the analysis inextricable. Noteworthy, Popelier
55 recently proposed a powerful relative energy gradient approach
56 to select the most relevant contributions.^[100] Certainly, such
57 analyses will clearly benefit from the big data and artificial

intelligence fields. Maybe, they will thus lead to favor some par- 58
titions to the detriment of others. However, from our point of 59
view, there is nowadays rather coexistence of various theories, 60
within different frameworks (real-space analysis, wavefunction 61
analysis). The fact that there is such a debate indicates that 62
there is currently no natural selection process at work... One 63
can also say that natural selection actually requires a very long 64
evolution time, much more than the age of quantum 65
chemistry... 66

67 **Paul W. Ayers**

68 Yes, but in a strange way. Science is both "red in tooth and claw"
69 in the sense that the most vociferous, forceful, ruthless, and
70 prominent researchers (and referees) have an advantage. It is
71 also true that people who write/convey their ideas most clearly
72 (and forcefully) have an advantage. Yet (fortunately) vehemence
73 and salesmanship is not everything (though I do feel we often
74 underestimate its importance). Most scientists possess an ideal-
75 ism and thus the drive toward utility and simplicity is strong. I
76 think many of us seek decompositions/partitionings that "can fit
77 on a T-shirt" (Occam's razor). And all of us seek definitions that
78 are helpful to experimentalists. That is, while I often call my work
79 on concepts "chemical philosophy," just like traditional episte-
80 mology, the goal is to find precepts/concepts that have broad
81 and practical utility for everyone. 82

83 **Farnaz Heidar-Zadeh**

84 There is no doubt that partitioning schemes (and other con-
85 cepts) evolve over time and the fittest survive, that is, the ones
86 which are well-defined and make better predictions. However,
87 this natural selection is commonly disturbed by our biases and
88 prejudices as humans, which makes the scientific discourse not
89 very scientific. (This was a very disappointing realization for me
90 as a young scientist!) 91

92 **Juan Andrés**

93 As Ayala wrote^[108] "There is a contradiction between Darwin's
94 methodology and how he described it for public consumption."
95 Darwin claimed that he proceeded "on true Baconian [induc-
96 tive] principles and without any theory collected facts on a
97 wholesale scale." He also wrote, "How odd it is that anyone
98 should not see that all observation must be for or against some
99 view if it is to be of any service!" The scientific method includes
100 two episodes. The first consists of formulating hypotheses; the
101 second consists of experimentally testing them. What differenti-
102 ates science from other knowledge is the second episode: sub-
103 jecting hypotheses to empirical testing by observing whether
104 or not predictions derived from a hypothesis are the case in
105 relevant observations and experiments. A hypothesis is scientific
106 only if it is consistent with some but not other possible states
107 of affairs not yet observed, so that it is subject to the possibility
108 of falsification by reference to experience" But, the more impor-
109 tant yet is that Darwin discovered natural selection, the process
110 that accounts for the adaptations of organisms and their com-
111 plexity and diversification, in a wide range of research fields,
112 including biology, geology, and also chemistry and physics. In
113 114

1 our case, it is necessary to remember that theories such Lewis,
2 Valence Shell Electron Pair Repulsion (VSEPR), molecular orbital
3 (MO), its extension to natural bond orbital (NBO), frontier
4 molecular orbital (FMO) of Fukui, valence bond (VB), or even
5 conceptual density functional (CDF). These theories have their
6 advantages and shortcomings, work in some cases but not in
7 another, and are still used in the current bibliography. There-
8 fore, it is expected that in the partition schemes occurs the
9 same and that many of these are still used. The important and
10 desirable thing is to know if they are used correctly and as far
11 as you can get with the results obtained. A large dose of self-
12 criticism is necessary to overcome the sociological pressure.

13 Yirong Mo

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

22 Eduard Matito

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

50 W. H. Eugen Schwarz

51 Yes. *First, some sociological pressure* may be induced by charis-
52 matic colleagues and their followers influencing the fashions of
53 a time. We all know it, concerning "overlapping VB concepts" vs
54 "orthogonal MO concepts," concerning aromaticity as a single-
55 dimensional concept best represented by the NICS parameter,
56 concerning QTAIM based molecular partition schemes, or that
57 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 com-
munity. *Third, the availability of technical options:* an analysis
scheme will best survive if it can be applied with little invest-
ment 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 sup-
ports analyses of densities in three-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 interac-
tion 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 cor-
rection is included. As discussed above, SAPT satisfies this con-
dition very well. The second condition 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 mecha-
nisms 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 sepa-
rate 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, that
is, 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 $\delta_{\text{int}}^{\text{HF}}$ 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) interac-
tion 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 the differences between SAPT and CCSD(T), one may
assign an uncertainty of ± 0.3 kcal/mol to this value. However,
the noncharge-transfer part of induction energy, that is, the
polarization energy, is not negligible and it is by definition neg-
ative. This energy can be estimated from the classical polariza-
tion 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 addi-
tional -0.2 kcal/mol from the further iterations. Thus, the total
polarization energy amounts to -1.0 kcal/mol, giving an

1 estimate for the infinite-order charge-transfer energy of
2 -1.2 ± 0.3 kcal/mol. Values much larger in magnitude, often
3 found in literature (see a discussion in Refs. [116,117]), cannot
4 be considered to represent true charge-transfer energies. Some
5 EDA schemes are consistent with our estimate, for example, the
6 ALMO method based on CCSD^[118] gives -0.8 kcal/mol.
7 The method of estimating charge-transfer terms based on the
8 regularized-SAPT(DFT) approach, developed by one of us,^[119]
9 gives a smaller in magnitude value of -0.4 kcal/mol (however,
10 this estimate includes only the second-order terms and would
11 increase in magnitude if higher-order corrections were
12 accounted for).

14 **Question 5: To What Extent Does/Can/Should** 15 **Investigated Systems Influence the Choice of** 16 **a Particular Partition Scheme?**

18 **Ramon Carbó-Dorca**

19 It seems difficult to foresee how partition schemes clarify any-
20 thing, being somehow (or quite) arbitrary. Perhaps they could
21 add more obscurity to the certainly not very clear usual chemi-
22 cal concepts.

24 **Shant Shahbazian**

25 In principle, a mathematically rigorous partitioning scheme must
26 be applied to any molecular system regardless of the size, type
27 of atoms, or complexity of its electronic structure. However, in
28 practice, the "interpretational" problems emerging from applying
29 a scheme to certain systems may have a strong influence on
30 favoring or dismissing the scheme. As an example, the popular
31 "misinterpretation" of the (3, -1) critical points (CPs) emerging
32 from the topological analysis of the molecular electron densities
33 as indicator of bonds has been a source of confusion.^[120,121]
34 There are certain systems that if one insists that (3, -1) CPs are
35 "bond" CPs, that is, BCPs, then inevitably there would be a clash
36 between the quantum theory of atoms in molecules (QTAIM)
37 analysis and most of the other partitioning schemes on the pre-
38 sence/absence of bonds between certain atoms. In such prob-
39 lematic cases, people usually try to avoid the use of the QTAIM
40 analysis, though a proper reinterpretation may fix the prob-
41 lem.^[96] However, such problems are not confined to just misin-
42 terpretations and there are cases where a partitioning scheme
43 does not support (or is at odds with) an established viewpoint
44 regarding a system and people try to avoid the scheme. Such
45 "expectational bias" regarding what "must" emerge for a system
46 may unconsciously (or even consciously) affect the
47 preference/dismissal of a partitioning scheme. For me, this is an
48 unpleasant element of "subjectively"....

51 **Martin Rahm**

52 I suspect it often does not. This is in large part because most
53 EDA methods require quite some expertise to execute and
54 interpret. There are also a lot of methods out there, and it is
55 not always easy to evaluate pros and cons in an objective man-
56 ner. Publishing work addressing chemical validation and cross-

57 validation of EDA methods, discussed in questions six and
58 seven, should help in this respect.

61 **Frank Weinhold**

62 In principle, the EDA method of choice should be independent
63 of the problem. To the extent that such influence exists (i.e., for
64 possible subjective choice of EDA method or "reference frag-
65 ments"), it seems to represent a particularly dangerous aspect
66 of the partitioning approach.

68 **Roberto A. Boto**

69 A well-defined partition scheme should be valid for any chemi-
70 cal system. Energy partitions are based on chemical concepts
71 such as covalency, ionicity, and polarizability. These concepts
72 should be well-defined regardless of the nature of the system.
73 Otherwise, we may create a chaotic scenario with a panoply of
74 partitions, one for each chemical system.

76 **Ángel Martín Pendás**

77 Ideally, it should not. However, it is usually the case that, as it
78 happens with density functionals, basis sets, or many other of
79 our computational knobs, ideas propagate that advise the use
80 of this or that method to deal with these or those problems. In
81 many cases, the partition scheme is chosen a posteriori, a prac-
82 tice that should not be allowed.

84 **Carlo Gatti**

85 Generally speaking, if someone believes that his or her favorite
86 partitioning scheme is suited for some classes of compounds
87 and (much) less for others, he/she should probably make a step
88 back and ask himself or herself what prevent his or her favorite
89 method to be general enough to be applied equally well to any
90 chemical system. This is an important exercise that may lead to
91 an improvement of the scheme or to abandon it in favor of a
92 more general one. I also believe that more than the investi-
93 gated system, it is the chemical question to be addressed that
94 may influence the choice of a particular partition scheme.

96 **Paul Popelier**

97 I agree with the general consensus building up here, which is
98 that the nature of a system should not influence the choice of
99 the partition scheme used, in the end. Unfortunately, this is not
100 the case at the moment. For example, anionic systems or sys-
101 tems with large rings need diffuse Gaussian primitives in order
102 for their wave functions to be properly described. Partitioning
103 schemes that depend on the location of the center of these
104 primitives suffer from the use of diffuse functions (because the
105 mapping between center and ownership starts breaking down).
106 Hence such partitioning schemes cannot be used in that case
107 or they have to be modified. Anthony Stone did the latter by
108 injecting some real-space partitioning character into his original
109 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 nontopological 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 analyzed 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. However, it is often only the combination of several methods (charge and 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 strongly 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 physicochemical components (charge transfer, polarization, and induction) whose definitions are in general not unique, and/or into subsystems (atoms, substituents...) for which various partitions also exist. All these energy decompositions 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 a 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 on whether the fragments considered in the EDA are Li^+ and F^- ions or Li. and F. 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 of 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

- 1 on a specific electronic structure ansatz, and would not be
2 applicable, for example, to a diffusion quantum Monte Carlo
3 calculation, or to a calculation that use nonatom-centered basis
4 sets (e.g., plane waves). Others could not be applied to a lattice
5 (e.g., a Hubbard or Pariser–Parr–Pople model for an aromatic
6 system), or to a periodic solid. Even among the few methods
7 that are universal in scope (and there are very few such
8 methods), their utility is unlikely to be universal.
9
- 10 **Farnaz Heidar-Zadeh**
11
12 In theory, a partitioning scheme should be applicable to any
13 system, because the same physical laws apply to them all. Any
14 deviation from universal applicability is a warning sign that
15 should give one-second thoughts about using the scheme. If a
16 scheme is suitable for only a specific class of systems, it is very
17 unlikely to be physically sound.
18
- 19 **Juan Andrés**
20
21 It is not appropriate or desirable to investigate a system in
22 order to choose a particular partition scheme. We must remem-
23 ber that history tells us that opening this path can cause great
24 confusion with the proliferation of different methods. One has
25 to remember the extensive number of semiempirical methods,
26 basis sets, functional hybrids, and so on, as also have pointed
27 by Profs. Martin-Pendás, Cioslowski, and Ayers.
28
- 29 **Yirong Mo**
30
31 May be not much. See question 3.
32
- 33 **Eduard Matito**
34
35 I believe it depends on the motivation. Making a choice of the
36 partition based on the premise that it provides the answer you
37 are looking for is obviously scientific misconduct. As Jerzy
38 points out, a scenario in which a large collection of energy par-
39 titions is available, each being adequate for a particular prob-
40 lem is highly undesirable. Ideally, any method should be
41 universally valid and provide a correct and complete descrip-
42 tion of the system. However, in practice, they are not. If valida-
43 tion tests (see questions 6 and 7) offer us some hints of flaws
44 and boundaries of current energy partitions, I find adequate to
45 use these results to select (or discard) an energy partition
46 scheme. For instance, a method having a slow convergence
47 with the basis set size should probably be discarded in situa-
48 tions where we cannot afford a sufficiently large basis set.
49
- 50 **Eloy Ramos-Cordoba**
51
52 Ideally, the molecular system under study or the electronic
53 structure method employed should not influence the choice of
54 a particular EDA scheme. In practice, the system dependency
55 seems to be unavoidable since there are EDAs which are only
56 defined for some electronic structure methods, and some of
57 them are restricted to be used in conjunction with atomic-
centered basis sets. In this sense, topological energy decom-
positions 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 parti-
tion schemes should be intuitively understandable, that is, sim-
pler 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 prac-
tical 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 3 years since this publication, possi-
bly, 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, that is, they analyze a
given electronic structure and provide a picture of the bonding
situation. There are many elegant EDA definitions that can pro-
vide detailed information about 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 toward “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 the 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 “consen-
sus” what is the “standard” reference set for such chemical

1 validation? I am currently pessimistic about the whole idea
2 (please also check my answer to question 9).

3 **István Mayer**

4 Ideally, the energy decomposition produces diatomic energy
5 components representing the interatomic bonding
6 (or repulsion) at the actual configuration of the molecule, and
7 one center ones describing the promotion of the atoms when
8 the molecule is formed. However, in several EDA schemes
9 (including semiempirical, e.g., MNDO ones) one encounters the
10 difficulty, that delocalizations responsible for bond formation
11 also give rise to ionic wave function components (in VB termi-
12 nology) that increase the intra-atomic electron repulsion ener-
13 gies, thus also the apparent atomic promotion energies. As
14 compensation, one obtains very negative diatomic energy com-
15 ponents, that are not on the “chemical scale.” No doubt, such a
16 straightforward energy decomposition may be quite useful for
17 comparing different bonds, etc., or even making some predic-
18 tions. However, chemists are inclined “not to buy” these large
19 (in absolute values) numbers. This reservation of colleagues
20 chemists served for me as a strong stimulus to introduce a
21 corrected scheme.^[129] The ionic terms are due to the bond for-
22 mation, so their interelectronic energy was distributed between
23 the different bonds in accordance with partial bond orders
24 formed by different “effective atomic orbitals.”

27 **Frank Weinhold**

28 Yes (see question 3).

31 **Ángel Martín Pendás**

32 I tend to agree with the need of validation to properly screen
33 the different methods available, but I also acknowledge the dif-
34 ficulty in finding a suitable set of quantities that might be taken
35 as a reference validation set. To focus just a bit, let us simply
36 take the Pauling repulsion term of many EDAs. What chemical
37 relevant observable (In Martin’s words) does it correlate with?
38 In the absence of a consensus on what types of energetic terms
39 should be allowed/not-allowed in a partitioning scheme, valida-
40 tion is desirable but difficult.

42 **Paul Popelier**

43 Yes, I believe so. I come back to this question in question
44 7 because the latter question overlaps with question 6, in which
45 the word “focused” pops out. I had like to interpret this word in
46 a sociological sense. The community of interpretative theoret-
47 ical chemistry, especially that of Quantum Chemical Topology
48 (which is younger and somewhat lags behind), should scour
49 more for “hot case studies” and work on them. These regularly
50 appear in the popular scientific magazines (e.g., Chemistry
51 World of the Royal Society of Chemistry). We can then to test
52 (and showcase) partitioning methods. In the medium and long-
53 er term we can find out what we can do for experimentalists
54 (e.g., material scientists and synthetic chemists). After all, there
55 is a reason why the largest scientific funding body in Britain,
56 called EPSRC, launched as one of its main research themes the

Grand Challenge of “Directed Assembly” (short title). The associ-
ated 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 experimental-
ists 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.

70 **Jerzy Cioslowski**

71 In my opinion, “chemical validation” should be limited to check-
72 ing whether energy components (and other descriptors) com-
73 puted for similar systems are themselves similar. This may also
74 include the “chemical scale” argument of István Mayer, that is,
75 that diatomic (bond) contributions should have values similar in
76 order to those encountered experimentally (bond dissociation
77 energies, etc...). Anything more than that amounts to falling
78 back into the trap of “chemical intuition”, which is what one
79 presumably hoped to avoid from the start.

82 **Gernot Frenking**

83 “Chemical validation” is an ill-defined fuzzy expression. I agree
84 with Jerzy Cioslowski that chemical validation leads to the dan-
85 ger of using “chemical intuition” as measure for the validity of
86 the EDA results, which is one step toward alchemy. A useful
87 partitioning scheme should provide a self-consistent ordering
88 scheme for the pandemonium of chemical facts. The physical
89 interpretation of the energy terms will always be debatable.

92 **Julia Contreras**

93 YES! In this direction, chemical interpretation has always been
94 too much influenced by pre-QM concepts, trying to reproduce
95 what was already there. However, these concepts were intro-
96 duced to predict composition, reactivity. I think we should go
97 back to these roots. Just like in many other fields where
98 theoretical/computational answers are difficult and the field is
99 still at a strong development stage (e.g., solvation energies,
100 molecular solid structure), we could propose “games” to predict
101 the outcome of a given molecular change (not easy to calcu-
102 late). Extremely naive, but double-blind tests are a wonderful
103 way of testing methods! Of course, this means being able to
104 predict the behavior or energy terms upon perturbations, a
105 point that has not been paid much attention..., and which
106 chemists overcame long ago. However, it would provide a
107 clear-cut (and fun) way of taking the next step in energy
108 decomposition.

109 **Paul W. Ayers**

110 Hell yes. We should be careful about what we mean by “valida-
111 tion.” There are a few molecules that might be proposed as
112 such canonical examples of a concept that any EDA/partitioning
113 that disagrees with them should at least be heavily scrutinized,
114

1 and probably discarded outright. (For example, a method that
2 did not predict that benzene has an “aromatic stabilization
3 energy,” however one might define that, has questionable util-
4 ity.) There are more sequences of molecules for which a clear
5 chemical trend may be asserted, and EDA can be validated
6 against that.

7
8 **Farnaz Heidar-Zadeh**

9 Definitely, and this is long overdue! The systematic study of
10 partitioning schemes in order to put them on equal footing is
11 necessary and gives us a better understanding of their
12 strengths and shortcomings. However, we first need to agree
13 on this “validation protocol”. As elaborated by many contribu-
14 tors, as a community, we need to make a comprehensive list of
15 desirable axioms/features (distancing ourselves from intuitive
16 measures) to assess and scrutinize various schemes and con-
17 cepts. The five conditions suggested by G. Frenking are a great
18 starting point.

19
20 **Juan Andrés**

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

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

35 On the other hand, we also need descriptors/terms in gen-
36 eral, but many of these descriptors/terms derived from chemi-
37 cal concepts that can be considered fuzzy concepts, compared
38 to unicorns or even noumenons. This is because there exists no
39 physical observable associated with them. Therefore, is a very
40 challenging task to reach this aim, we need to, first, clarify EDA
41 methodology and descriptors/terms in order to obtain a chemi-
42 cal validation of both subjects.

43
44 **Yirong Mo**

45 Absolutely.

46
47 **Eduard Matito**

48 Indeed! This is probably a quite arduous task but is certainly
49 needed in the field. Given the proliferation of energy partitions,
50 “outsiders” from the chemical bonding community need guid-
51 ance and, therefore, benchmarks (see question 7) and “chemical
52 validation tests” are essential. However, as many people
53 pointed out before, it is not straightforward to design a chemi-
54 cal validation test. In this sense, it is important putting the focus
55 on the reliability of the tests (for which we need consensus
56 within the community) rather than on having extensive tests

57 that cover the many facets of energy partitions. Indeed, some
58 aspects of energy partitions cannot be easily tested (for
59 instance, the Pauli repulsion term mentioned by Ángel) and,
60 hence, the validation test is deemed to be incomplete. How-
61 ever, this should not preclude the search for such validation
62 tests because they do not only help in classifying and assessing
63 energy partitions, they also provide important hints to modify
64 and improve current energy partition schemes. Maybe a chal-
65 lenge for our community in the next editions of ECCB con-
66 ferences (and bond slams) could be suggesting chemical
67 validation tests that would be subsequently debated openly in
68 a forum like this until a consensus test set is obtained.

69
70
71 **W. H. Eugen Schwarz**

72 Yes. Statistical data analyses (cluster analyses, factor analyses)
73 can clarify what is behind a group of related concepts, and
74 quantify the correspondence of different partition schemes.

75
76 **Alston Misquitta and Krzysztof Szalewicz**

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

81 82 83 **Question 7: Is there any Interest in** 84 **Developing Common Benchmarks and Test** 85 **Sets for Cross-Validation of Methods?**

86
87 **Ramon Carbó-Dorca**

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

96
97 **Martin Rahm**

98 I very much hope so. Reasons for validation against experiment
99 are outlined in the answer to the previous question. Bench-
100 marks can help in this by including experimental data but could
101 additionally serve another important service to the community:
102 facilitating for more straightforward comparison of EDA
103 methods. This is beneficial for several reasons. Benchmarks will
104 allow newcomers to the field to more easily get acquainted
105 with advantages and drawbacks with the different methods,
106 which is of relevance to question four. Benchmarks will also
107 help the community to come to better terms with issues raised
108 in all previous questions, 1–6, and question nine. For example,
109 by revealing which EDA-terms and descriptors that do or might
110 relate to the same chemical concepts. In other words,
111 which terms that show the same trends in relation to relevant
112 chemistry. Ultimately, the ability to cross-correlate different
113 approaches should help highlight complementarities between
114

1 EDA methods and aid future development of them. One suc-
2 cessful example of EDA-term comparison is work of Racioppi
3 et al.^[130]

5 Shant Shahbazian

6 As I stressed in my answer to question 6, I find it extremely
7 unlikely that a standard set of data (I mean a set of numbers)
8 may be proposed that all scientists find them equally objective
9 and reliable. Think about the concept of bond energy
10 (or something similar to this concept) that probably most peo-
11 ple would agree that a good EDA method must deliver as its
12 output. How we may find the proper set of bond energies to
13 start the cross-validation? If there is no such standard set then
14 any cross-validation study will simply reveal the similarities and
15 differences between the applied EDA methods, not the “objec-
16 tivity” of any EDA method (please also check my answer to
17 question 9).

19 István Mayer

20 Yes, it could be of interest to have a selection of different mole-
21 cules with fixed geometries and a few different basis sets, for
22 which the results of each method are tabulated. Results
23 obtained with different wave functions (HF, DFT, CAS-SCF, CCA,
24 etc.) could be included as well. For the Hilbert space analysis,
25 basis sets of sufficiently atomic character (as e.g., STO-NG,
26 6-31G**, or cc-pVTZ) should be considered and no diffuse func-
27 tions (augmented basis sets) should be admitted.

30 Frank Weinhold

31 Self-correlation among closely related EDA variants is of little
32 value. Tests with experimental data (such as those suggested in
33 the reply to question 3) could give a more effective reality
34 check to cull the ranks of proposed partitions. The development
35 of the field would benefit from some common benchmarks that
36 are well chosen to represent a diversity of phenomena and spe-
37 cies (cf. question 9). Only then can meaningful differences in
38 methods be illuminated and discussed.

40 Ángel Martín Pendás

41 An interesting initiative might be choosing a selection of mole-
42 cules, basis sets and methods to construct an EDA
43 benchmarking data set. Although, in agreement with Shant, it
44 would be difficult to find a proper set of values for the chemical
45 concepts that would then be cross-validated, a simple cross-
46 correlation among the different EDA energetic terms would
47 provide relevant data about their similarities and differences.

50 Carlo Gatti

51 Since aims might be quite diverse from method to method (see
52 my answer to question 1), I envisage complementary insights,
53 more than cross-validation from the suggested procedure.
54 However, common benchmarks and test sets could be useful to
55 observe which concepts and conclusions survive the various
56 methods. If concepts and conclusions were found to vary signif-
57 icantly 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, that is, “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 molecu-
lar 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 bond-
ing and $\pi\pi$ stacking interactions).

Pedro Salvador

Coming back to my answer to Q1, topological EDAs only differ
on the underlying atom-in-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 for-
ward by Feixas et al.^[131] in order to grade the different aroma-
ticity indicators. Some work along this line has already been
attempted. For instance, the harpoon effect expected in the dis-
sociation 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] Semiquantitative 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 nonzero. Is the
diatomic electron-nuclear attraction contribution of X-H bonds
reasonable?

Jerzy Cioslowski

The only reason for embarking upon cross-validation of differ-
ent 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 lan-
guage) 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, that is, it encompasses two sets of
values that are linearly independent. Thus, if one insists upon
cross-validation of energy partitioning schemes, it should be

1 carried out with a set comprising a large number of “unusual”
2 molecules, the results being subject to the principal component
3 analysis.

5 Gernot Frenking

6 It is a good idea to have a test set of species, which are then
7 used to explore the performance of a method for different
8 types of electronic structures. For molecules, this should
9 include, for example, compounds with polar and nonpolar as
10 well as localized and delocalized bonds and it should encom-
11 pass transition metal complexes as well as main group com-
12 pounds with “normal” valency and “hypervalent” compounds.

14 Miquel Solà

15 Benchmarks to prove the reliability of the different energy
16 decomposition analysis (EDA) approaches are highly desirable.
17 While the dissociation energy is an observable, the components
18 of the dissociation energy obtained from an EDA are not
19 observables. To validate concepts or quantities that cannot be
20 precisely defined mathematically from the underlying physics,
21 such as the components of the EDA, Ayers et al.^[87] proposed to
22 take an axiomatic approach, which consists on listing the chem-
23 ical, mathematical, and computational properties that one
24 desires for a concept to possess. In our group, we followed this
25 approach to prove the reliability of a series of descriptors used
26 to quantify aromaticity, a quantity that is not observable, either.
27 To this end, we designed benchmarks containing a series of
28 tests.^[131–133] The chosen tests fulfilled two requirements: first
29 and most important, they were based on the accumulated
30 chemical experience in such a way that one expects most
31 chemists agree about the expected aromaticity trend and, sec-
32 ond, the size of the systems involved were relatively small to
33 facilitate a fast application. As an example, we considered dif-
34 ferent deformations of benzene, such as the bond length alter-
35 nation (BLA). Any good indicator of aromaticity should detect a
36 reduction of aromaticity of the benzene ring when BLA
37 increases. Or, for instance, when going from benzene to pyr-
38 idine (one heteroatom in the ring), pyrazine (two heteroatoms
39 in the ring) and triazine (three heteroatoms in the ring), aroma-
40 ticity should decrease. In the case of EDA, one may proceed
41 similarly. It is probably not a good idea to consider results for a
42 particular molecule instead of analyzing particular trends in a
43 series of molecules. Let us consider for instance LiF. According
44 to IQA calculations,^[96] covalency, defined as the percentage
45 between orbital interaction and the sum of electrostatic plus
46 orbital interactions, is 14 the other hand, for the same molecule,
47 a Morokuma-like EDA considering Li⁺ and F⁻ as fragments indi-
48 cates that covalency represents an 8% of the total stabilizing
49 interactions.^[124] It is not possible to know which of these two
50 results is the correct one. To make things more complicated, if
51 fragments considered in the Morokuma-like EDA are F. and
52 Li. radicals, covalency of LiF increases to 91%. The reader could
53 ask whether the ionic or the radical fragments is the best
54 option to discuss bonding in LiF. One may argue that radical
55 fragments should be preferred because, for the gas-phase LiF
56 molecule, the homolytic dissociation costs less energy than the

heterolytic one, the latter being favored only if one includes at
least five water molecules, that is, for the LiF(H₂O)₅ species.^[134]
However, in the equilibrium geometry, the electronic distribu-
tion 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 mat-
ter 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 mol-
ecule, except in some particular cases (like LiH, vide infra), I con-
sider that an EDA benchmark should discuss trends and not
particular molecules. For instance, for alkali metal 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 H₂ < 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 H₂ from two H atoms, Pauli repul-
sion should be the main component of the interaction between
two RH molecules to form the RH...HR complex. These are pos-
sible 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 neces-
sary to have consensus on all the systems (even things as sim-
ple as the interaction energy in the water dimer or the
energetic barrier to rotation in ethane are interpreted differ-
ently 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 bat-
tleground 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 bench-
marks 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 for-
ward! These give us a better understanding of current par-
titioning 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

1 also very important, even though less discussed, results gener-
2 ated for a specific schemes' implementation (code) and mole-
3 cule (system) need to be reproducible, robust, replicable, and
4 generalizable as depicted in the image below.

6 Reliability of a given Scheme's results

7
8 **Juan Andrés**

9 It is desirable to develop common benchmarks and test sets for
10 cross-validation of methods. Ayers et al.^[87] propose an axiom-
11 atic approach, as it was previously noted by us (see question 1)
12 and by Prof. Solá (see question 7).

14 **Yirong Mo**

15 Not sure about this. Experimental evidences are always the gold
16 standards.

18 **Eduard Matito**

20 The short answer is yes, there is a large interest in designing
21 validation tests. There is some overlap between questions
22 6 and 7. I decided to comment on "chemical validation tests"
23 on question 6 and here, I will comment on another kind of vali-
24 dation tests. Benchmarking should also consider other essential
25 features of energy partitions such as basis set dependency (and
26 convergence toward CBS), size extensivity, and method depen-
27 dency. Some of these features might be easy to anticipate from
28 the construction of some energy partition schemes (e.g., size
29 extensivity) but other require the design of tests that are appro-
30 priate to this purpose.

32 **W. H. Eugen Schwarz**

33 Yes, it would be very deserving. However, at first, a set of useful
34 decomposition methods and a set of empirical, valid, reliable
35 data must be agreed upon.

38 **Alston Misquitta and Krzysztof Szalewicz**

39 The only test that can be conducted are those outlined in the
40 answer to question 4, so each method can be tested individu-
41 ally since this is a pass/fail test.

43 Question 8: Is it Possible to Contemplate a 44 Unified Partition Scheme (Let Us Call it the 45 "Standard Model" of Partitioning), that Is 46 Proper for all Applications in Chemistry, in the 47 Foreseeable Future or Even in Principle?

49 **Ramon Carbó-Dorca**

51 The previous question leads to the present one. One can
52 answer it like: if EDA techniques are somehow arbitrary, then it
53 seems difficult to obtain a unified universal partitioning
54 scheme. However, perhaps research on this topic is missing
55 something, which could transform the EDA problem into a pre-
56 cise description. I must confess that I cannot imagine what
57 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 inter-
ested 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 ulti-
mate unique definition of an individual atom within the mole-
cule. However, the 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, sep-
arate 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 toward development of as generally applica-
ble 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 phe-
nomena 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 uni-
fied theory of chemical bonding, something that as far as I
know, is far from being achieved. From a more pragmatism
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 enter-
prise. 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

1 methodology. In the end, this ultimately leads, in agreement
2 with István Mayer, to the atom-in-the-molecule conundrum.

3 David L. Cooper

4 I remains very deeply skeptical that a utopian model of par-
5 titioning could ever emerge that not only is applicable to but
6 also (almost) universally agreed to be the “best” choice for, all
7 applications in Chemistry. There is even a sense in which it
8 would be more than a little disappointing if no new Chemistry
9 could ever be discovered for which such a “standard” model
10 might not be the most appropriate.

11 Carlo Gatti

12 Perhaps yes, but I doubt it would be the most appealing one
13 for most of the chemists. In principle, I would be highly in favor
14 of a unified approach and I fully agree with Ángel Martín
15 Pendás that it should rely on orbital invariant quantities. How-
16 ever, as I discussed in my answer to question 1, the aims
17 behind the present partitioning methods are different. There-
18 fore, adoption of a standard model, while favoring scientific
19 rigor, could also result in a significant loss of richness of
20 interpretation.

21 Paul Popelier

22 I want to be optimistic about a “standard model of partitioning”
23 and indeed strive for it although it could be a long process. As
24 explained in question 4, schemes that make the same predic-
25 tions can co-exist, but if they produce contradictory outcomes
26 then they cannot. Allow me to comment on the related and
27 perhaps less sensitive topic of population analyses. In the pletho-
28 ra of population analyses, the (original) Hirshfeld method and
29 the QTAIM typically produced answers at the two opposite
30 extremes: Hirshfeld was judged to give too small an answer
31 and QTAIM too large. The community often regarded both as
32 suspicious. However, over time Hirshfeld was modified
33 (in response to a theoretical deficiency related to the reference
34 state it invokes) and then gave less extreme values. This is an
35 example of convergence, which is a weaker form of unification.
36 A further step toward convergence would be to finally ditch
37 the Mulliken population analysis, which has been heavily criti-
38 cized for decades but still regularly pops up. In my PhD thesis,
39 Mulliken charges served the purpose of creating a sufficiently
40 reliable crystal field in which solid state molecular geometries
41 could be obtained. However, when I saw a few years later that
42 the Mulliken population analysis assigned a non-negligible neg-
43 ative net charge (i.e., -0.26) to a boron atom^[135] then I am
44 happy to ditch Mulliken because its answer violates any of the
45 dozen electronegativity scales. In terms of Darwinian selection,
46 a harsher environment consisting of the now more demanding
47 user results in Mulliken not surviving ultimately. To make the
48 main point again: diversity is good provided it leads to a stron-
49 ger end product. However, diversity for its own sake, in terms
50 of wallowing in contradictory interpretations and lauding this
51 situation as the richness of Chemistry is wrong. Yes, chemistry
52 is a complex science, which is we should do an utmost effort to
53 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 physicalization process: they
become better and better connected with an underlying phys-
ical and indeed quantum mechanical reality. Whereas a typical
biochemistry textbook of today is still nave in its typically intro-
ductory 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.

24 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 suffi-
cient number of “stress tests” for the existing partition schemes
as I suggest in question 7, one can probably narrow the search
to a handful of them, which hopefully will produce similar out-
puts for most purposes. On the other hand, in the present con-
text of energy decomposition schemes, unification in the
formulation applied to different levels of theory is also desir-
able. In particular, a rigorous topological EDA for KS DFT that is
able to provide energy contributions comparable to those
obtained for correlated wavefunction methods is still lacking, in
my opinion.

28 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 separa-
tion 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.

32 Gernot Frenking

No! The complexity and diversity of electronic structures in mol-
ecules and solids requests partitioning schemes that are appro-
priate 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 descrip-
tion of the bonding situation is made.

- 1 **Paul W. Ayers** 58
2 It is useful to contemplate, but it is a bit like contemplating nirvana. Useful, but it is best to live in the real (imperfect) world 59
3 most of the time. I tend to feel that while unified partitioning 60
4 schemes may exist (in the sense that there may be atom-in- 61
5 molecule partitioning schemes and energy decomposition anal- 62
6 ysis methods with broad utility and applicability and, indeed, 63
7 some of our current tools approach this lofty standard) there 64
8 will always be room for improvement. At some point, though, 65
9 the “improvements” one might make will be achieved only by 66
10 adding complexity (“engineering” the model in a way that risks 67
11 overfitting), and some convergence may occur. However, as 68
12 every person has a different tolerance for model complexity 69
13 (in a different context, some prefer PBE, some BLYP, and some 70
14 M06L), the idea that our community could ever agree upon a 71
15 “standard model” seems...unfathomable. Indeed, it seems we 72
16 cannot even agree whether such a standard model should be 73
17 pursued! 74
18
19
20 **Farnaz Heidar-Zadeh** 75
21 Having a unified partitioning scheme is the holy grail. As such, 76
22 it is not possible to find a universal definition or even get close 77
23 to one. However, this should not lead one to underestimate the 78
24 usefulness and value of partitioning schemes (and other con- 79
25 cepts) and the need for improving/validating the existing 80
26 approaches. 81
27
28 **Juan Andrés** 82
29 It is possible to contemplate a unified partition scheme, but it 83
30 must be recognized that this is still a pretension. In the current 84
31 state, I do not see a possible way to reach it. 85
32
33
34 **Yirong Mo** 86
35 I am not optimistic about this. Researchers always intend to be 87
36 unique and propose something different from others. So there 88
37 will be a constant endeavor to propose “novel” and “for the first 89
38 time” kind of partition schemes. 90
39
40 **Eduard Matito** 91
41 I highly doubt that an energy partition “to unite them all” will 92
42 ever be found. In the best case scenario, I would expect that 93
43 we find a partition (or a set of them) that gives reasonable pre- 94
44 dictions for “chemical validation tests”. 95
45
46 **Eloy Ramos-Cordoba** 96
47 I also agree that it is unlikely that a unique “standard model” 97
48 can be defined. However, as Prof. Cioslowski stated above, I 98
49 also think it would be convenient to establish a set of axiom or 99
50 requirements (e.g., well-defined basis set limit), based on math- 100
51 ematical or quantum mechanical arguments that every EDA has 101
52 to fulfill. 102
53
54 **W. H. Eugen Schwarz** 103
55 No: The various partition schemes yielding a few small numbers 104
56 to explain a given class of molecules w.r.t. a given type of 105
57 questions (e.g., concerning stability or reactivities) are quite 106
58 diverse. The universal cover approach consists of general quan- 107
59 tum mechanics combined with a comprehensive set of ques- 108
60 tions, which is too demanding to be useful. 109
61
62 **Alston Misquitta and Krzysztof Szalewicz** 110
63 Not only contemplate, SAPT already provides the standard 111
64 model and we believe this has been generally recognized in 112
65 recent years. 113
66
67 **Question 9: In the End, Science Is about 114
68 Experiments and the Real World. Can One
69 Therefore Use any Experiment or
70 Experimental Data Be Used to Favor One
71 Partition Scheme over another?**
72
73 **Ramon Carbó-Dorca**
74 If experimental data could relate to EDA, then possibly the pre-
75 cise description of the theoretical scheme might be solved. The
76 adequate (ultimate) EDA will be the one adapting better to this
77 kind of experiment. Can one imagine any experiment of this
78 kind to be performed soon? However, if there is an experiment
79 which can be (completely) adapted to some EDA, this will mean
80 that the EDA terms will become observables. Therefore, a quan-
81 tum mechanical operator (or operators) might be constructed
82 to describe the experiment. Can one foresee this observable
83 nature of the EDA partition terms?
84
85 **Martin Rahm**
86 Aside from valiant efforts toward X-ray constrained
87 wavefunctions,^[136] which might move all EDA’s closer to experi-
88 ment, most of what we do in the field requires a quantum
89 mechanical calculation to approximate a wave function or den-
90 sity. My personal preference is toward concepts and quantities
91 that are, at least in principle, experimentally measurable. For
92 this reason, I am exploring the possibilities of an EDA that can
93 interchangeably rely on both measurements and quantum
94 chemical calculations.^[54] Of course, plenty of nonobservable
95 quantities are conceptually valuable. Time will tell when and
96 where an “Experimental Quantum Chemistry” EDA approach is
97 more advantageous in some respects. Experimental comparison
98 and cross-validation, discussed in questions six and seven,
99 should help to highlight complementarities between EDA
100 methods and be a good basis for making more informed
101 choices for particular sets of systems and questions.
102
103 **Shant Shahbazian**
104 This question is tightly connected to questions 6 and 7. Without
105 any reference to experimental data, which are free from subjec-
106 tive judgments and chemical prejudice, it is hard to see how a
107 positive operational answer may be given to questions 6 and
108 7. I am interested to see if someone have any clue or proposal
109 on how a partitioning scheme may, in a nontrivial way, to be
110 connected to quantitative experimental data. However, if there
111 is no link, I see no way of real progress. 112
113
114

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 question 3 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] 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 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 B₂H₆ where IQA states that the interatomic exchange energy between the bridging hydrogen atoms is about three 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

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

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 judgments (see table 2) sound like: "Observed overestimation of polarization and underestimation of charge transfer." or "Presence of the DEMIX energy unascrivable 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 questions 7 and 8 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 the 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.

1 Gernot Frenking

2 The preference of a particular partitioning scheme is not
3 decided by an experiment, but by the interpretation of the
4 experimental results. This is done by the human mind of the
5 observer. "Real world" implies a definition of physical reality in
6 a region where quantum theory is valid but not classical phys-
7 ics. The outcome of a Diels–Alder reaction can only be
8 explained when the symmetry (sign) of the wave functions of
9 the interactions species is considered. This gives the wave func-
10 tion the status of physical reality. Three statements at the end:
11 (1) Physical reality becomes a fuzzy concept when quantum
12 effects are considered. (2) When chemical facts are reduced to
13 physical laws alone, they become mere stamp collection. Fuzzy
14 concepts are an integral part of chemistry. (3) Historically devel-
15 oped concepts must be examined with quantum chemical calcu-
16 lations, because they may be based on assumptions that are
17 not correct.

20 Julia Contreras

21 My answer to this is pretty similar to question 6.

24 Émilie-Laure Zins

25 I agree with the general opinion of the previous contributors: a
26 comparison and a dialogue between theoretical and experi-
27 mental chemists are essential. But what experimental tools
28 could be used in comparison with theoretical studies on energy
29 partition schemes? Do the existing partition schemes allow a
30 comparison with observable or deductible quantities from
31 experiments? Would it be possible to develop new partition
32 schemes allowing an easier comparison with experimental
33 data? I think the answer to the latter question is "yes", and that
34 it would be interesting to move in this direction, probably by
35 using a combination of complementary experimental
36 approaches, or even by developing new experimental
37 approaches. Of course, experimental techniques do not allow
38 an energetic decomposition, but in-depth investigations involv-
39 ing complementary experimental techniques allow to deduce
40 information on polarization and polarizability, the contribution
41 of the spin...Among the most versatile tools, we can mention
42 the technique of isolation of the investigated species in a
43 matrix (rare gas, para-hydrogen,...at cryogenic temperatures
44 (typically below 20 K). This technique allows to characterize
45 weak interactions, such as hydrogen bonds or agostic interac-
46 tions. This technique is also useful to probe the spin state of a
47 metal atom in an organometallic complex, or even to induce
48 changes in spin states by photo-excitation. Isomerizations
49 between different inter or intramolecular complexes can also
50 be detected by annealing. This isolation technique is often
51 coupled with vibrational spectroscopy. One could imagine the
52 development of such an experimental set-up allowing to apply
53 a magnetic field. The use of such advanced experimental
54 approaches to deduce some of the physical components of an
55 energy partition scheme would need to be discussed with the
56 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 not 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 chemistry where the experimental selectiv-
ity in dipolar cycloadditions is governed by such factors). As
well known, entropy can be decomposed into electronic, trans-
lational, 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 accu-
rate 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
properties.^[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 reason-
able, 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 is obtained experimentally.

1 Yirong Mo

2 It is the only way. Even there is little direct experimental data for
3 partition schemes, there are many indirect evidences to examine
4 individual energy terms. Structural and spectral parameters are
5 good indicators for partition schemes. In the study of inter-
6 molecular interaction, distance-dependent energy profiles are
7 often instructive for the verification of partition schemes. For
8 instance, in the void of orbital (electron transfer) interactions, the
9 optimal intermolecular distances should be comparable to regu-
10 lar van der Waals distances (unless strong electrostatic interac-
11 tions exist). Unfortunately, so far, very few partition schemes can
12 perform geometry optimization. But at least numerical test calcu-
13 lations with small systems can be done for all partition schemes.
14

15 Eduard Matito

16 Maybe, but I doubt we will generate numbers that can be directly
17 compared to the experimental ones and, at the same time, pro-
18 vide undeniable chemical insight. For instance, in the future, per-
19 haps we can obtain reliable electron density data that leads to
20 accurate prediction of, let us say, QTAIM atomic energies. How-
21 ever, the fact that we can measure these energies does not make
22 them any more useful to provide chemical insight. On the other
23 hand, I believe experimental evidence can provide qualitative
24 information that is useful in assessing energy partitions.
25

26 Eloy Ramos-Cordoba

27 In principle since energy components are not observables, it
28 seems not possible to quantify them by direct observation.
29 However, some energetic information can be extracted from
30 experiments. For instance, molecular-beam scattering experi-
31 ments have been used to indirectly quantify the charge-transfer
32 stabilization energy.
33

34 W. H. Eugen Schwarz

35 Yes. Ultimately, the purposes of theory and partition schemes
36 are creating models that help to intuitively understand and
37 extrapolate (predict) the experimental facts. The answer to this
38 last question 9 therefore depends on three points: *First*, the par-
39 tition scheme should appropriately *explain the experimental*
40 *trends* as seen by the chemists. If a theoretical model cannot
41 reproduce differences chemists are commonly talking about
42 (such as nonbonded repulsion vs chemical bonding attraction,
43 or strong vs very strong ionic or covalent interactions) then
44 probably the theoretical scheme should be modified. *Second*,
45 the observation of a positive value may be theoretically repre-
46 sented by the sum of one or two positive terms and several
47 small corrections, or as a sum of several large numbers of differ-
48 ent signs. The latter model is not satisfactory. It may then help
49 to combine some numbers to get only medium-sized contribu-
50 tions of same sign, for instance summing large positive Pauli
51 repulsion and large negative quasi-classical electric attraction to
52 construct the "steric interaction" (or some other combination,
53 *depending on the case*). Namely, not only the values of a specific
54 partitioning characterize the real system, but also which type of
55 partitioning is simple in the given case. *Third*, whether a

partitioning is useful and efficient also depends on the cogni- 58
tive *competences and preferences of the users*. Some experimen- 59
talists and theoreticians focus on the observable numbers only; 60
some other ones also consider the process of relaxation that 61
results in the observed outcome. Different partition schemes 62
may be required for different addresses. 63
64

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66 Indirectly, due to SAPT-based PESs providing close interplay 67
with experiments and due to the fact that SAPT interaction 68
energy is built up from components (rather than decomposed), 69
comparisons with experiments provide a real-world connection 70
for these components. SAPT has been used to develop pPESs 71
for a large number of dimers. SAPT PESs are among the most 72
accurate ones published and if used in nuclear dynamics calcu- 73
lations predict observables in excellent agreement with experi- 74
ment, for example, for the water dimer spectra.^[141,142] Also, 75
SAPT PESs allow precise predictions of crystal structures.^[143] 76
Thus, there is a strong connection between SAPT and experi- 77
ment. Although these comparisons involve the total PESs, there 78
is a weaker connection to SAPT components as well. For exam- 79
ple, to predict correctly crystal densities, one has to have the 80
repulsive walls at the right places, which tests the exchange- 81
repulsion energy. Crystals of monomers dominated by disper- 82
sion interactions, like for example the argon crystal,^[144] indi- 83
rectly test this component of SAPT. There is a further broad 84
connection to the real world: construction of force fields based 85
on SAPT components and using forms of the fitting functions 86
that reflect the behavior of SAPT components.^[88,145] One can fit 87
intermolecular interaction energies by several types of analytic 88
functions or even use methods such as neural networks, but 89
fitting with physically relevant forms enables such PES to be 90
transferable. Use of SAPT to develop biomolecular force fields 91
has become increasingly popular.^[146] A particular example is 92
water clusters. There is experimental data available for such 93
clusters, for example, the authors of Ref. [147] performed mea- 94
surements on hexamer, heptamer, and nonamer. A very accu- 95
rate force field developed in Ref. [148] was fitted to CCSD(T) 96
calculations for the water dimer and trimer. Predictions of prop- 97
erties of clusters from this force field agree very well with accu- 98
rate *ab initio* data available for some clusters. Thus, component- 99
based force fields enable calculations for water clusters of 100
essentially arbitrary size, whereas reasonably accurate *ab initio* 101
calculations are limited to about 20 water molecules. In Ref. 102
^[148], not only the form of the fitting function was designed 103
based on the behavior of SAPT components, but also the long- 104
range asymptotics was computed *ab initio* using SAPT codes. In 105
contrast, while damping and exchange-repulsion parameters 106
are also consistent with SAPT, the parameters in these terms 107
are just free parameters of the fit. This can be improved by per- 108
forming SAPT calculations for close-range separations and 109
fitting component-by-component (as done for water in Ref. 110
[141]). While such direct fits can currently be done for dimers 111
and for small trimers, there remains an issue with higher than 112
three-body contributions. Reference ^[148] approximated such 113
contributions by a damped classical polarization model iterated 114

1 to convergence over the whole cluster. While the polarization
2 model alone is a poor approximation to three-body interaction
3 energies, it was shown in Ref. [148] that this model recovers
4 the four- to six-body interaction energies surprisingly well. Since
5 the many-body polarization models is so critical for clusters
6 and condensed phases, work on improved forms of this
7 model is essential. Here the work of Refs. [115,119] is important
8 since it both extends the model beyond the isotropic dipole-
9 dipole polarizability case and designs better damping functions
10 which are essential at shorter separations. Furthermore, the
11 decomposition of induction energy into polarization (including
12 a part of the exchange components) and charge-transfer terms
13 may lead to improved models of damping.

16 Concluding Remarks

17 Bernard Silvi

19 For this article, I tried to collect a large panel of opinions on the
20 use of EDA methods in Quantum Chemistry. I had no
21 preconceived ideas about the outcome and therefore, I have
22 been surprised by the diversity of points of view often appar-
23 ently contradictory. Whereas some contributors reject EDA
24 methods, many others consider them as a fundamental contri-
25 bution of Quantum Chemistry. The origin of this dispersion of
26 opinions is not a crisis of our discipline announcing the advent
27 of a new paradigm but rather a consequence of its good health.
28 As we wrote in the introduction, EDAs are tools (not theories)
29 providing pieces of information enabling to set up explan-
30 ations. They belong to normal science processes and as tools,
31 they have not to strictly satisfy demarcation criteria. They are
32 mostly used to understand geometries and stabilities of mole-
33 cules and molecular complexes on the basis of quantum chemi-
34 cal and physical arguments. Here *quantum chemical* is related
35 to systems of explanations based on quantum chemical con-
36 cepts such as those of orbital, valence-bond structure, etc...
37 whereas *physical* concerns arguments rooted in the theory of
38 intermolecular forces. These systems of explanation may be
39 interdependent and complementary, never contradictory: they
40 address different meanings of a given question and are
41 intended for different scientific (sub)communities. Each system
42 corresponds to its own representation of the microscopic mat-
43 ter, adopts its own point of view and uses its own vocabulary.

44 Moreover, there is an inherent source of difficulty in our
45 attempt to explain the microscopic matter because we try to
46 understand the behavior of quantum objects which is not
47 deterministic in a deterministic fashion. Most explanations in
48 science belong to the deductive-nomological account^[149]
49 which provides a scheme for any deterministic explanation of a
50 particular event and consists in a deductive derivation of the
51 occurrence of the event from a set of true propositions involv-
52 ing at least a scientific law or principle. The choice of rules and
53 principles leaves additional degrees of freedom.

55 **Keywords:** energy decomposition analysis · interaction
56 energy · partitioning · chemical bonding · status of the
57 methods

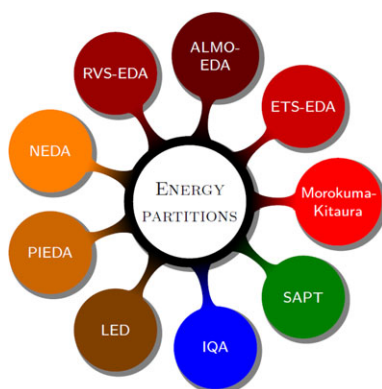
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Many methods enable the calculation of contributions to the interaction energy between two fragments of a molecular or complex system.

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