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Binding Energies of First Row Diatomics in the Light of the Interacting Quantum Atoms Approach

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Binding energies of first row diatomics are revisited within the interacting quantum atoms (IQA) approach. This is a formalism in chemical bonding theory based upon the quantum theory of atoms in molecules. It is characterized by the preservation of the energetic identity of atoms within molecules. Quantum mechanically computed binding energies are recovered in IQA as a sum of small atomic deformation energies and large pairwise interaction terms. We show how this partition responds faithfully to chemical intuition, and how the different evolution of deformations and interactions accounts in a unified manner for the subtle variations of the binding energy of these molecules.

I. Introduction

Developments in quantum chemistry over the last twenty years have provided us with a set of tools that allows for the calculation of the electronic structure of small molecules to chemical accuracy.[1] This qualitative computational jump has not been followed by similar changes at the interpretive level. The origin of this dichotomy lies in the intrinsic nonseparability of quantum objects, for many of the basic problems in bonding and binding rest in understanding the change suffered by a number of chemical entities upon interaction. This need of partitioning an interacting system into components is well supported by simple molecular orbital (MO) models,[2] where electrons occupy independent energy levels, and has contributed to the success of theories of orbital interactions.[3] Other theoretical schemes like the valence bond (VB) method,[4] which dominated early quantum mechanical interpretations in chemistry, have proven much more difficult both to implement algorithmically and to further provide quantitative partitionings. As of today, we may say that interpretive quantum chemistry is still dominated by orbital reasonings, more so after the initial reticence regarding the use of Kohn−Sham orbitals within density functional theory (DFT) has mostly dissipated.[5]

A characteristic of many of the methods of analysis of molecular binding has been with quantum chemistry since its inception: binding energies are only a small fraction of the total molecular energies, so it is very difficult to devise energetic partitions that do not lead to almost exact cancellations among large opposite components. As an example, Ziegler−Rauk energetic decompositions,[6,7] very popular these days due to their generality, wide computational scope, and chemical insight,[8−10] define energetic components (i.e., Pauli energy, electrostatic energy) which are, at most, of the same order of magnitude as the final molecular binding energy. And this final goal is only achieved after subtracting even larger terms (i.e., kinetic, potential energies) from largely arbitrary reference fragments.

Interpretive problems abound even in the simplest first row homodiatomics. Here, the gap between the naïve proportionality of atomization energies with the number of bonding electrons and the actual experimental values is large and difficult to close by means of simple explanations. For instance, a simple plot of atomization energies versus the atomic number shows a triangular evolution of the former on filling the *p* shell and going from B_2 to F_2. However, the binding energies of O_2 and F_2 are smaller than those of C_2 and B_2, respectively. This sequence has been rationalized within independent electron models as due to the difference between increasing bond order by filling bonding states and decreasing it by filling antibonding MO's. Nevertheless, this simple image cannot be held after noticing how badly Hartree−Fock (HF) binding energies perform in these systems. Actually, difluorine is unstable with respect to dissociation at the HF level, so its low binding energy is exclusively due to correlations among its electrons. This special place of F_2 was very soon recognized,[11,12] for a number of known relationships fulfilled by the rest of the dihalogen molecules fail when they are extrapolated to the head of the group. Since then, a large number of possible mechanisms for this anomalous behavior have been proposed,[13−16] going from the dispersion energy argument suggested by Pitzer,[13] to the excessive lone-pair repulsions of Jolly and Eyermann.[15] Moreover, it was the study of this and other anomalous systems that led to the charge-shift bond concept developed by Shaik et. al.,[17] a distinguished example showing us that there is still plenty of room for new, unexpected ideas even in very simple chemical systems.

A way out to the general quantum-mechanical nonseparability as applied to chemical problems is exemplified by topological approaches to chemical bonding. Because chemists talk about atoms interacting with each other, forming and breaking bonds, we should try to leave Hilbert space in favor of the physical space. These statements have evolved into a number of theories, among which we single out the quantum theory of atoms in molecules (QTAM), developed by Bader and co-workers.[18] It provides a generalization of the rules of quantum mechanics to real space subsystems. A recent account of its underlying philosophy in comparison to conventional MO theory may be found in ref 19. The topological method has contributed to connect the physical world of chemists with quantum mechanics by providing mathematically rigorous recipes to associate the

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objects of chemistry (atoms, electron pairs, lone pairs, etc.) to regions of space derivable from wave functions in an orbital independent manner. However, most known applications of these ideas to binding have used the immediate one-body energetic partition provided by topology. This leads to defining additive atomic energies that may only be used at equilibrium configurations, on one hand, and that are subject to the same cancellation problems just discussed, on the other.

We have recently shown[20−22] how a chemically meaningful theory of interacting quantum atoms (IQA) may be constructed from topologically derived partitions of the physical space. Its natural, most successful niche is the QTAM, but this ascription is not compulsory, because our basic arguments hold for general partitions of the molecular electron density into atomic components.[23] The basic tenet of the formalism preserves the core of our chemical intuition by translating into a quantum mechanical compliant language the following idea: atoms are entities that keep their individuality upon interaction to form molecules. Thus molecular binding energies must contain two clearly different ingredients: the changes suffered by the self-energies of the atoms in the interaction process, on one hand, and the interaction energies by themselves, on the other.

This intuitive notion, so near conventional wisdom, and so many times explored in the literature under different theoretical umbrellas (let us just recall McWeeny's theory of electronic separability,[24] or the atoms in molecules of Li and Parr[25]), has not previously found its way further into the topological theories of the chemical bond.

The purpose of this paper is to show how the straightforward application of the IQA/QTAM approach to the decomposition of the binding energy of first row diatomics into self-and interaction components provides a complementary new way to rationalize the experimental facts. According to the view that emerges from our analysis, the variation of the atomic self-energies along the row is responsible for much of the observed trends, and displays the familiar double-hump shape related to the half-filling of atomic shells. Our other factor, the interaction energy, shows a much smoother evolution and depends basically on the number of electrons that are shared between the interacting atoms. Overall, this image, which we stress is independent of the orbital model, is compatible with a growing importance of intra-atomic repulsions on moving along the period. Similar ideas have been proposed repeatedly.[15,16]

In the rest of the paper we will first introduce a minimal set of concepts from the IQA approach, followed by a succinct description of the calculations made in the first row diatomics to further discuss thoroughly our results.

II. Results and Discussion

A. IQA/QTAM Approach. The IQA/QTAM approach starts from a partition of the physical space into the atomic domains provided by the QTAM.[18] These domains are separated by interatomic surfaces that satisfy a zero local-flux condition for the gradient field of the electron density. We want to notice, however, that, in the case of homonuclear diatomics, the QTAM partition coincides with the only one exhaustive atomic partition compatible with symmetry: a plane bisecting the internuclear axis separates both atomic domains.[26] Using the common nonrelativistic molecular Hamiltonian, we may write the energy for a general molecule as follows:

$$E = \sum_A \int_{\Omega \mathrm{A}} \mathrm{d}\mathbf{r}_1 \left(\hat{T} - \sum_B \frac{Z_\mathrm{B}}{r_{1\mathrm{B}}}\right)\rho_1(\mathbf{r}_1;\mathbf{r}_1') + \frac{1}{2}\sum_{\mathrm{A,B}} \int_{\Omega \mathrm{A}} \mathrm{d}\mathbf{r}_1 \int_{\Omega \mathrm{B}} \mathrm{d}\mathbf{r}_2 \frac{\rho_2(\mathbf{r}_1,\mathbf{r}_2)}{r_{12}} + \sum_{\mathrm{A>B}} \frac{Z_\mathrm{A} Z_\mathrm{B}}{R_\mathrm{AB}} \quad (1)$$

A common notation in which capital letters mark nuclei (atoms), small letters electron coordinates, and Ω_A denotes the atomic domain of atom A has been used. ρ_1 and ρ_2 are the first and second-order reduced density matrices, respectively.[24] If we now gather all monocentric and bicentric terms together, we get

$$E = \sum_A (T_\mathrm{A} + V_\mathrm{en}^\mathrm{AA} + V_\mathrm{ee}^\mathrm{AA}) + \sum_{\mathrm{A>B}} (V_\mathrm{nn}^\mathrm{AB} + V_\mathrm{en}^\mathrm{AB} + V_\mathrm{en}^\mathrm{BA} + V_\mathrm{ee}^\mathrm{AB}) \quad (2)$$

where we have introduced the kinetic energy of atom A, T_A; the electron−nucleus potential energy between electrons of atom A and the nucleus of atom B, $V_\mathrm{en}^\mathrm{AB}$; the electron repulsion between the electrons of A and those of B, $V_\mathrm{ee}^\mathrm{AB}$; and the nuclear repulsion between nuclei A and B, $V_\mathrm{nn}^\mathrm{AB}$. The expressions for all these magnitudes are straightforwardly obtained from eq 1. Notice that similar partitions have been used in a DFT context by Li and Parr.[25]

As we may see, the IQA decomposition does not contain any extraneous physical force, nor does it depend on reference quantum mechanical states, so common in other procedures. It just provides a partition of every physical interaction present in the Coulomb Hamiltonian into one-center (atomic), and two-center (interaction) terms. All quantum effects (i.e., antisymmetry, confinement, etc.) are extracted from the wave function used in the analysis. Much of the power of our approach comes from the neat separation between atomic energies and interactions. The molecular energy is just a sum of atomic self-energies, $E_\mathrm{self}^\mathrm{A}$, and pair interaction potential energies, $V_\mathrm{int}^\mathrm{AB}$:

$$E = \sum_A E_\mathrm{self}^\mathrm{A} + \sum_{\mathrm{A>B}} V_\mathrm{int}^\mathrm{AB} \quad (3)$$

If binding energies with respect to free atoms are the main object under study, we may compare directly the changes experimented by each $E_\mathrm{self}^\mathrm{A}$ with the chosen atomic reference energy, E_0^A. The binding energy is, then, a sum of atomic energy changes $E_\mathrm{self}^\mathrm{A} - E_0^\mathrm{A}$ (we call them atomic deformation energies), and pairwise interactions:

$$E_\mathrm{bind} = \sum_A E_\mathrm{def}^\mathrm{A} + \sum_{\mathrm{A>B}} V_\mathrm{int}^\mathrm{AB} \quad (4)$$

Notice that we can gather several atoms together, define a functional group, and write an equivalent expression, this time with deformations measured with respect to the reference group, and interactions being computed between pairs of groups. It is also illuminating[21] to split $V_\mathrm{int}^\mathrm{AB}$ into a classical contribution, the purely Coulombic interaction of the joint electron-nucleus charge distribution of atomic domains A and B, and a quantum mechanical or exchange-correlation one: $V_\mathrm{int}^\mathrm{AB} = V_\mathrm{cl}^\mathrm{AB} + V_\mathrm{xc}^\mathrm{AB}$.

If atoms (or functional groups) may be recognized within molecules, as is customarily assumed by the science of chemistry, then most of the cancellations of quantum chemistry should be hidden in deformation energies, which will then be small or, at least, similar, when compared to total binding energies.[27]

Let us end this brief summary by pointing out another simple byproduct of our procedure. Domain integrations of ρ_2 itself

TABLE 1: IQA Analysis for the Diatomics Considered in This Work[a]

	R_e(c)	R_e(e)	D_e(c)	D_e(e)	E_{def}^A	V_{int}^{AB}	V_{cl}^{AB}	ΔV_{en}^{AA}	ΔV_{ee}^{AA}	δ^{AB}
H_2	0.741	0.741	107.9	109.5	8.0	−124.0	26.4	−140.2	95.1	0.851
He_2	2.875	2.96	0.0	0.0	0.3	−0.6	0.0	0.1	0.3	0.005
Li_2	2.674	2.673	27.7	24.6	16.8	−61.2	0.8	−53.7	65.2	0.835
Be_2	2.523	2.45	4.1	2.3	26.4	−56.9	2.5	−33.5	57.0	0.589
B_2	1.601	1.590	72.9	71.2	47.6	−168.0	29.8	−247.0	257.7	1.368
C_2	1.254	1.243	147.5	145.9	48.4	−244.3	87.4	−524.2	502.6	1.805
N_2	1.106	1.098	224.3	228.4	35.7	−295.7	137.4	−822.7	747.5	1.952
O_2	1.219	1.208	122.7	120.2	51.0	−224.8	86.2	−559.7	544.7	1.541
F_2	1.399	1.412	42.2	38.3	45.6	−133.3	33.1	−255.3	285.2	0.925
Ne_2	2.728	3.2	0.6	0.1	1.3	−3.2	0.0	2.2	0.4	0.034

[a] See the text for computational details. R_e and $D_e = -E_{bind}$ are the equilibrium internuclear distance and the binding energy, respectively, with (c) and (e) indicating calculated and experimental magnitudes. All distances in Å, and all energetic quantities in kcal/mol. Experimental quantities are taken from ref 33, except those for He_2, Be_2, and Ne_2, which are taken from the high quality calculations of refs 34−36, respectively. Atomic energetic variations (in E_{def}, ΔV_{ee}^{AA}, and ΔV_{en}^{AA}) have been computed with respect to free ground-state atoms. Numerical integrations do not exceed the tenth of kcal/mol accuracy, so all energies have been truncated to the first decimal place.

give information about the number of pairs of electrons contained in an atomic basin, or *shared* between two basins. This has been used to define a delocalization index,[28,29] δ^{AB}, that measures the number of shared pairs of electrons for a given bond:

$$\delta^{AB} = 2|\int_{\Omega_A} d\mathbf{r}_1 \int_{\Omega_B} d\mathbf{r}_2 \, (\rho_2(\mathbf{r}_1,\mathbf{r}_2) - \rho_1(\mathbf{r}_1)\, \rho_1(\mathbf{r}_2))| \quad (5)$$

This magnitude plays in orbital-free theories of the chemical bond a role similar to that for bond orders in conventional MO treatments. For instance, it turns out to be very nearly the expected figure associated with standard bond orders if calculated from HF wave functions.

B. Computational Details. Wave functions for first row homodiatomics from Li_2 to Ne_2 have been calculated with the GAMESS[30] code in their respective ground states. Given both our aim and the rather high computational cost of IQA decompositions,[20] we have chosen complete active space calculations (CASSCF) with an active space comprising all of the valence (2s, 2p) orbitals plus the σ s and p MO's coming from the M atomic shells. This amounts to including almost all the static correlation needed to improve the poor HF performance, and a bit of dynamical correlation which is essential to describe reasonably well both O_2 and F_2. A full valence CI calculation is presented in Be_2 to cope with the delicate 2s−2p quasidegeneracy. Standard GAMESS TZV(2d,f) basis sets were used except in Be_2 and F_2, where cc-PVTZ bases have been used. Only theoretical equilibrium distances will be discussed, and as we can see from Table 1, both geometries and binding energies are reasonable for our interests. We have also included full CI//cc-PVTZ calculations in the H_2 and He_2 molecules for comparative purposes.

IQA analyses have been performed by numerically integrating the reduced density matrices output by GAMESS over the atomic basins[26] using our PROMOLDEN code. Computational parameters[20] have been chosen so that the integrated net atomic charges are smaller than 10^{-3} electrons in every case. This has been shown to be a good indicator of the global numerical accuracy of the procedure.

C. IQA Analysis in First Row Diatomics. Table 1 gathers all the basic data provided by the IQA analysis. The overall agreement between experiments and calculations is sufficient for our purposes, allowing us to draw trustworthy conclusions about trends in the energetic decomposition.

Let us start considering the atomic deformations in detail. As found and rationalized previously,[22] deformation energies in systems without net charge transfer, and homodiatomics belong certainly to this class, are necessarily positive. This translates the physically intuitive notion that an atom should find itself at its best when isolated. Any perturbation caused by interaction should increase its self-energy, so binding in these systems is exclusively due to the attractive interaction potential, which opposes the repulsive atomic deformations. This is the first noteworthy result from the IQA decomposition.

According to our eqs 2−4, deformation energies are made up of the changes that atomic kinetic, electron-own-nucleus attraction, and intra-atomic electron repulsion energies suffer upon interaction: $E_{def}^A = \Delta T_A + \Delta V_{en}^{AA} + \Delta V_{ee}^{AA}$. All these quantities may be obtained from the table. It is important to recall that the individual free atomic values for these components are very large. For instance, V_{en} evolves from −628 to about −195 000 kcal/mol when going from H to Ne. The ability of the IQA theory to reconstruct, *inside* molecules, magnitudes with the same physical interpretation used in their atomic counterparts is the most important source of preservation of atomic identities in molecules. Because the intra-atomic IQA magnitudes dominate the total molecular energy, the comparison of mostly unchanged atoms is at the root of the energetic cancellations of quantum chemistry.

In N_2, the worst of the systems considered as these sort of cancellations are regarded, $\Delta V_{en}^{AA} \simeq -800$ kcal/mol, a number to be compared with V_{en}(in vacuo) $\simeq -$ 80 000 kcal/mol. Similar results are obtained for the other intra-atomic quantities, and this first step washes out 2 orders of magnitude in energies, at least. A second source of cancellation emerges as the individual energy variations are added together to form the atomic deformation energy. On average, final E_{def}'s hide an almost 3 orders of magnitude annihilation when compared to their free atomic components, and top at about 50 kcal/mol in the molecules under scrutiny, the latter being a typically sized chemical energetic magnitude. As previously put forward,[22] there are physical forces trying to maintain the self-energy of an atom close to its in vacuo value. They work as far as the interaction with other atoms may be considered as a kind of perturbation. If this holds, the energy change upon interaction will not affect the self-energies. It must also be taken into consideration that the nonnegligible values of ΔV_{ee}^{AA} play an essential role in the final small magnitude of deformations. This is shown in the H_2 case,[22] where free monocentric electron repulsions are absent. Thus, the 95 kcal/mol electron repulsions are a consequence of the electron delocalization between the atoms and, were it not present, the deformation energy of each hydrogen atom would be negative and large, darkening most of our arguments.

Figure 1 shows the evolution of our monocentric energies with *Z*. Although some of the magnitudes depicted are also found in Table 1, several facts are uncovered by representing them graphically. In the first place, we observe the double-hump shape of E_{def}^A, which accounts for the many thermochemical effects of half-filled shells.[31] These are seen to arise from the change of purely atomic properties as quantum atoms keep track of their free electron structure upon molecular formation. This behavior is in sharp contrast with that of each of the components of E_{def}^A, which show a triangular evolution centered at N_2. Notice that the double-hump is not present in any of the large components, so it is to be considered a global effect.

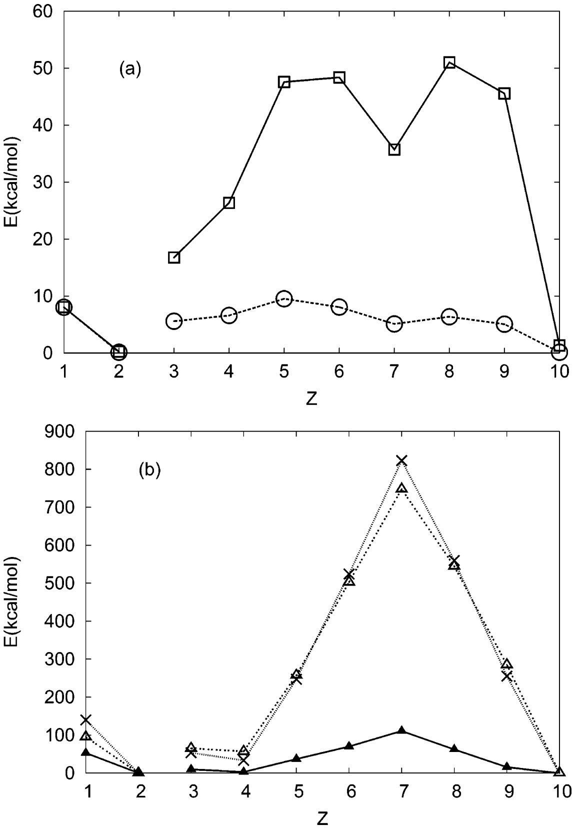

Figure 1. Variation of the atomic deformation energy and its components with atomic number, Z: (a) total deformation energy, $E_{\rm def}^{\rm A}$ (□), and its share per electron, $E_{\rm def}^{\rm A}/Z$ (○); (b) $-\Delta V_{\rm en}^{\rm AA}$ (×), $\Delta V_{\rm ee}^{\rm AA}$ (△), and $\Delta T^{\rm A}$ (▲). Notice the double-hump shape of $E_{\rm def}$, and the order of magnitude energy difference in the two energy scales.

The two humps in $E_{\rm def}$ are not exactly symmetric. We find a group of molecules that includes C_2, N_2, O_2 (and also H_2) with $|\Delta V_{\rm en}^{\rm AA}| > |\Delta V_{\rm ee}^{\rm AA}|$. And a second family formed by Li_2, Be_2, B_2, and F_2 with the opposite behavior, signaling probably too large intra-atomic electron repulsions. This is consistent with the accepted role of lone pair repulsions in first row diatomics.[15]

Let us also mention two other facts that reveal the compliance of deformations with chemical thinking. Noble gas molecules (He_2, Ne_2) display very small deformation energies, and the negligible value found in He_2 is in agreement with a practically noninteracting system. Be_2, on the other hand, has a rather high $E_{\rm def}$ that might be traced back to the need of 2s, 2p mixing for efficient bonding, and to its associated intra-atomic promotion energy. In no way can it be considered a weakly closed-shell interacting system.

A final remark concerning the atomic deformations is put forward by considering the electronic share in $E_{\rm def}$. Figure 1 seems to indicate that the deformation energy per electron is a much more slowly varying quantity than $E_{\rm def}$ itself, pointing toward a certain extensivity of deformations that deserves further investigation. Should the generality of this result be confirmed, the role of intra-atomic electron crowding (repulsion) upon molecular formation might need a revision.

Turning now to the interaction potential, $V_{\rm int}^{\rm AB}$ is proportional to the classical number of bonding electrons. This is not a surprise but clarifies its role in bonding. Because this is the attractive term in our partition, it must reflect the strength of the bond.

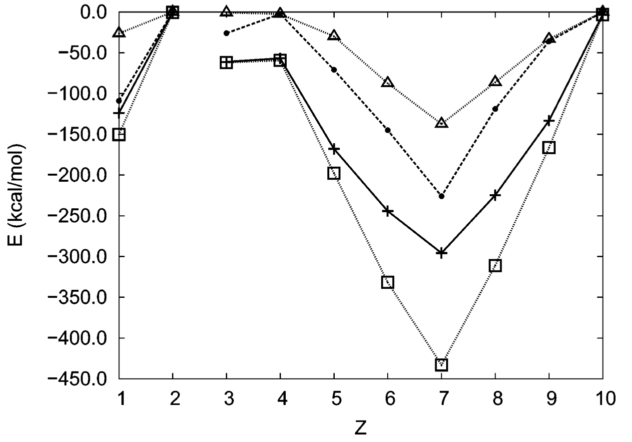

Figure 2. Variation of the interaction potential and its components with atomic number, Z: total interaction, $V_{\rm int}^{\rm AB}$ (×); $-V_{\rm cl}^{\rm AB}$ (△); $V_{\rm xc}^{\rm AB}$ (□). The experimental binding energies, $-D_{\rm e}$(e), are also shown (●) for comparison purposes.

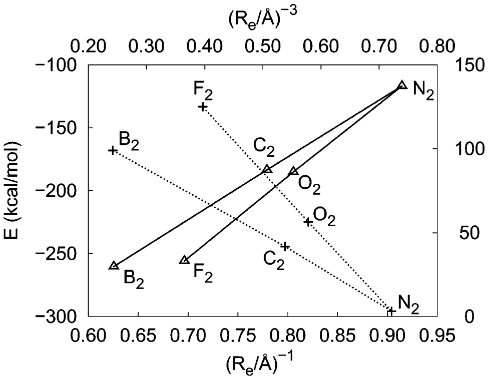

Figure 3. Evolution of the interaction energy components with the internuclear distance from B_2 to F_2. The full line corresponds to $V_{\rm cl}$ and must be read on the top-right scales. The dotted one is $V_{\rm int}$ and is to be read on the left-bottom scales. Individual systems may be located in conjunction with Table 1, noting that N_2 is located at the vertex of both lines.

A gross examination of Figure 2 shows that both the exchange-correlation ($V_{\rm xc}$) and the classical ($V_{\rm cl}$) contributions to the interaction potential display a triangular evolution on filling the 2p shell, much as the final binding energies, and in sharp contrast with the behavior of the atomic deformations. However, both $V_{\rm cl}$ and $V_{\rm xc}$ are much more symmetric with respect to N_2 than to $D_{\rm e}$. For $V_{\rm cl}$ this follows from its classical nature, which does not discriminate much B_2 from F_2, or C_2 from O_2. It is noticeable how its magnitude is not negligible at all. Actually, its origin is very easy to grasp: the first nonzero multipole of the atomic charge distribution in a homodiatomic is a dipole. In this way, the classical interaction of two head to head facing dipoles is repulsive and scales as R^{-3}. This is clearly seen in Figure 3.

The high symmetry exhibited in the classical contributions is lost in $V_{\rm xc}$, which is appreciably more stabilizing in diboron and dicarbon than in their counterparts, dioxygen and difluorine. In a MO language we might say that $|V_{\rm xc}|$ increases from Be_2 to N_2 by means of new bonding contributions and decreases back to F_2 by adding antibonding electrons, the latter effect being more destabilizing than stabilizing is the former. After the data in Figure 3, we have a clear distinction between the behavior of atomic-like deformations and interaction-like energies. Most of the reasonings that are made from the examination of orbitals in MO treatments are mapped here into $V_{\rm int}$, and this is a particularly satisfying feature of the present procedure. Figure 3 also shows how $V_{\rm int}$ seems to scale as the inverse power of the internuclear equilibrium distance on filling the 2p shell. We have not found an easy way to rationalize this fact, which deserves future consideration.

The final V_{int} values correlate rather neatly with the computed delocalization indices, δ^{AB}. It is noteworthy that all the three systems to which we would blindly assign a bond order of about one, H_2, Li_2, and F_2, do actually have δ^{AB} values only a little bit smaller than 1.0, this decrease being a consequence of electron correlations acting as a localizing force that diminishes the interatomic charge fluctuations of covalent bonds.[32] Some other trends are also quite visible. For instance, correlation decreases electron sharing more intensely in multiple than in single bonds, though our N_2 value is perhaps too small in view of the somewhat greater than 2 δ^{AB} value reported by Fradera[29] using a CISD wave function. It is also to be noticed how noble gas diatomics display negligible δ^{AB} values, and how bonding in Be_2 cannot be considered a van der Waals-like interaction.

Total V_{int}'s are proportional to δ^{AB}'s, as one can extract from Table 1. Actually, all our systems seem to group into different sets that satisfy a $V_{int} = \alpha\delta^{AB}$ correlation. One of such groups is made up of H_2, He_2, Ne_2, F_2, O_2, and N_2, and another is composed of Be_2, B_2, and C_2. Li_2 has no partner. The accuracy and generality of this assertion still need further confirmation but signal the existence of different types of bonding energetics. For instance, H_2 and Li_2 have a very similar electron sharing, $\delta^{AB} = 0.84 \pm 0.01$, but completely different interaction energies. This means that sharing a (mainly) 2s electron pair in Li_2 generates a much smaller attraction in Li_2 than sharing a 1s pair in H_2. In other words, the single bond in Li_2 is weaker than in H_2.

Final binding energies result from adding the deformation suffered by both interacting atoms to the interaction energy. As has become clear at this point, we have two possible extreme behaviors. In one of them the deformation energy is negligible with respect to the interaction. In the other, as large as, or even larger than V_{int}^{AB}. The first limit is difficult to attain, but the second turns out to be quite general. It is satisfying that common chemical intuition may be used predictively here. "Difficult to deform", for instance, is a term that many chemists would associate to noble gas atoms. Because interaction is not possible without deformation, it is not at all surprising that more than 90% of V_{int} is canceled out by deformation in He_2 and Ne_2, leaving very small residual binding energies. Similar arguments, this time taking into account the necessary 2s−2p promotion in the Be atom, may be used to rationalize the small binding energy of Be_2. D_e is not small due to a weak interaction. On the contrary, its magnitude at the large Be_2 equilibrium distance, around 60 kcal/mol, is as stabilizing as in Li_2. It is the large deformation energy that decreases this value. These systems display throttled bonds, because the way toward their natural internuclear distances and binding energies dictated by interactions is strangled by a large rise in atomic self-energies as both atoms approach each other.

The overall trend toward greater deformation on increasing the number of electrons explains the rest of the numbers. Let us just consider in some detail the difluorine case. On going from N_2 to O_2, and finally to F_2, we face a shrinking interaction energy as δ^{AB} values decrease, together with a coupled rise in deformation. This is not very important in O_2, for its interaction energy is still large. But in F_2, the total E_{def} is 70% the absolute value of the interaction, leaving only 30% of it as D_e. Though the actual value of D_e in F_2 is really small, we understand it as the result of two clear competing trends, and not as an anomaly. The relation of all these ideas with known explanatory models of the difluorine binding energy is of great interest and will be the object of future studies.

III. Conclusions

There is a simple lemma that summarizes our results: atoms have to deform and increase their self-energies to interact efficiently. Were the sphericity of their densities conserved upon interaction, for instance, no binding would take place. Therefore, binding energies behave in the way we see because there are two basically uncoupled contributions to them. An energetic deformation, which is atomic in nature and keeps memory of the electronic structure of the atoms that interact, and an interaction component, which is attractive at equilibrium and depends on the binding abilities of the atoms. Both components depend on fundamentally different (though related) properties and evolve in a different (but related) manner. We are able to understand very simply their trends when taken separately, and it is only when they combine that an apparent complexity appears. These are common qualitative notions that receive here an energetically quantitative and rigorous quantum-mechanical foundation thanks to the chemically meaningful partition of space provided by the QTAM.

We believe that the ideas explored in this paper provide a fresh description of the energetic phenomena that characterize the formation of chemical bonds. The ability of the IQA approach to generate sensible atomic self-energies that hide all the important cancellations of the usual energetic terms of quantum chemistry may well be used to introduce new complementary ways of understanding a wealth of chemical phenomena.

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References and Notes

(1) Martin, J. M. L.; de Oliveira, G. *J. Chem. Phys.* **1999**, *111*, 1843.

(2) Gimarc, B. M. *Molecular structure and bonding. The qualitative molecular orbital approach*; Academic Press: New York, 1979.

(3) Albright, T. A.; Burdett, J. K.; Whangbo, M. *Orbital Interactions in Chemistry*; Wiley & Sons: New York, 1985.

(4) Cooper, D. L., Ed. *Valence Bond Theory*; Elsevier: Amsterdam, 2002.

(5) Baerends, E. J.; Gritsenko, O. V. *J. Phys. Chem. A* **1997**, *101*, 5383.

(6) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558.

(7) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1755.

(8) Bickelhaupt, F. M.; Baerends, E. J. *Rev. Comput. Chem.* **2000**, *15*, 1.

(9) Frenking, G.; Wichmann, F.; Frölich, N.; Loschen, C.; Lein, M.; Frunzke, J.; Rayón, V. M. *Coord. Chem. Rev.* **2003**, *238−239*, 55.

(10) Lein, M.; Frenking, G. *Coord. Chem. Rev.* **2003**, *238−239*, 55.

(11) Pitzer, K. S. *J. Chem. Phys.* **1955**, *23*, 1735.

(12) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press.: Ithaca, NY, 1960.

(13) Caldow, G. L.; Coulson, C. A. *Trans. Fraday Soc.* **1962**, *58*, 633.

(14) Mulliken, R. S. *J. Am. Chem. Soc.* **1955**, *77*, 884.

(15) Jolly, W. L.; Eyermann, C. J. *Inorg. Chem.* **1983**, *22*, 1566.

(16) Forslund, L. E.; Kaltsoyannis, N. *New. J. Chem.* **2003**, *27*, 1108.

(17) Shaik, S.; Maitre, P.; Sini, G.; Hiberty, P. C. *J. Am. Chem. Soc.* **1992**, *114*, 7861.

(18) Bader, R. F. W. *Atoms in Molecules*; Oxford University Press: Oxford, U.K., 1990.

(19) Cortés-Guzman, F.; Bader, R. F. W. *Coord. Chem. Rev.* **2005**, *249*, 633.

(20) Martín Pendás, A.; Blanco, M. A.; Francisco, E. *J. Chem. Phys.* **2004**, *120*, 4581.

(21) Martín Pendás, A.; Francisco, E.; Blanco, M. A. *J. Comput. Chem.* **2005**, *26*, 344.

(22) Blanco, M. A.; Martín Pendás, A.; Francisco, E. *J. Chem. Theory Comput.* **2005**, *1*, 1096.

(23) Francisco, E.; Martín Pendás, A.; Blanco, M. A. *J. Chem. Theory Comput.* **2006**, *2*, 90.

(24) McWeeny, R. *Methods of Molecular Quantum Mechanics*, 2nd ed.; Academic Press: London, 1992.

(25) Li, L.; Parr, R. G. *J. Chem. Phys.* **1986**, *84*, 1704.

(26) Li_2 shows a non-nuclear attractor at its equillibrium geometry. Because our purpose in this paper is to compare quantities across systems, we have apportioned half the attractor's basin to each of the Li atoms by using the plane bisecting the internuclear axis. This is indeed a zero-flux surface, so we do not leave the QTAM in the procedure.

(27) Calculated with respect to appropriate references. The choice of reference is an important issue when large charge transfers among different quantum atoms are in effect.

(28) Bader, R. F. W.; Stephens, M. E. *J. Am. Chem. Soc.* **1975**, *97*, 7391.

(29) Fradera, X.; Austen, M. A.; Bader, R. F. W. *J. Phys. Chem. A* **1999**, *103*, 304.

(30) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(31) Shriver, D. F.; Atkins, P. W. *Inorganic Chemistry*, 3rd ed.; Oxford University Press: London, 1999.

(32) Yu, M.; Dolg, M.; Fulde, P. *Int. J. Quantum Chem.* **1998**, *67*, 157.

(33) Huber, K.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV Constants of Diatomic Molecules*; Van Nostrand: Princeton, NJ, 1979.

(34) van Mourik, T.; Dunning, T. H., Jr. *J. Chem. Phys.* **1999**, *111*, 9248.

(35) Martin, J. M. L. *Chem. Phys. Lett.* **1999**, *303*, 344.

(36) van Mourik, T.; Wilson, A. K.; Dunning, T. H., Jr. *Mol. Phys.* **1999**, *96*, 529.