



## Interacting Quantum Atoms: A Correlated Energy Decomposition Scheme Based on the Quantum Theory of Atoms in Molecules

M. A. Blanco,\* A. Martín Pendás, and E. Francisco

*Departamento de Química Física y Analítica, Facultad de Química,  
Universidad de Oviedo, 33006-Oviedo, Spain*

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**Abstract:** We make use of the Quantum Theory of Atoms in Molecules (QTAM) to partition the total energy of a many-electron system into intra- and interatomic terms, by explicitly computing both the one- and two-electron contributions. While the general scheme is formally equivalent to that by Bader et al., we focus on the separation and computation of the atomic self-energies and all the interaction terms. The partition is ultimately performed within the density matrices, in analogy with McWeeny's Theory of Electronic Separability, and then carried onto the energy. It is intimately linked with the atomistic picture of the chemical bond, not only allowing the separation of different two-body contributions (point-charge-like, multipolar, total Coulomb, exchange, correlation, ...) to the interaction between a pair of atoms but also including an effective many-body contribution to the binding (self-energy, formally one-body) due to the deformation of the atoms within the many-electron system as compared to the free atoms. Many qualitative ideas about the chemical bond can be quantified using this scheme.

### I. Introduction

Quantum chemistry is a successful theory, able to predict global properties of molecular species, such as binding energies, molecular geometries, spectra, etc., very accurately. However, its main results, the wave function of the molecule and its associated energy, are difficult to correlate to such cornerstone chemical concepts as individual atoms, functional groups, and the bonds and interactions among them. To build a connection between quantum results and chemical concepts, there have been proposed many different a posteriori analyses of these results that extract chemical information with different degrees of success: concepts such as atomic charges, bond orders, bond energies, ... have already reached textbook status.<sup>1</sup> Particularly, the partition of the total molecular energy into chemically meaningful components has deserved a lot of attention over the years<sup>2–8</sup> and is still today a rather active research topic.<sup>9–15</sup>

Among the many energy partitioning schemes already proposed in the literature, some rely on orbital descriptions

and the characteristics of the LCAO method to define the fragments, so that the components of the energy can be either directly extracted or else computed from the intermediate properties that have to be evaluated in this type of calculation. However, this makes them dependent on the particular model elements used on the calculations (basis sets, for example). Some partitions define unphysical intermediate states to be used as a reference to compare with the global calculation, so that the binding process can be conceptually divided into different steps.<sup>3,4,6,9,10</sup> There is an ongoing controversy about this point, whether to focus on the final, bonded state or on the evolution from an initial, unbonded state, to understand the chemical bond. They can be considered to provide complementary views of the same concept, although it is difficult to compare them and understand the origin of the different terms on physical grounds.

These analyses suggest that the energy partition of a molecular system should fulfill some key conditions to be of general interest. We propose the following.

A good energy partition should be a useful tool for chemists and must be theoretically sound. It has to provide

\* Corresponding author phone: +34 985105017; e-mail: miguel@carbono.quimica.uniovi.es.

a means to identify the atoms and functional groups within the molecule, which have to be transferable. This requirement will make it consistent with the fact that atoms and functional groups retain, albeit partially, their identity in the molecule. This fact also points to the molecular binding energy as a better chemical indicator than the total energy, which contains large atomic contributions. To describe the chemical bond, the partition should also give detailed definitions of the interactions among atoms, functional groups, and molecules. Finally, the partition should be derived from the molecular wave function without resort to the approximations involved in its calculation. It must be unique and exhaustive and should recover the exact quantum chemical energy of the system.

In this article, we propose an energy partition scheme according to the requirements posed above. Thus, we partition the energy of the molecule with atoms as chemically meaningful fragments. Each atom consists of its nucleus and its 3D atomic basin as defined in the Quantum Theory of Atoms in Molecules (QTAM) of Bader and co-workers.<sup>8</sup> This induces a partition of the one- and two-electron density matrices, which is carried onto an exhaustive partition of the total energy. The elements of this partition were already proposed by Bader<sup>8</sup> and have been used in different ways by others.<sup>16,14</sup> However, the recent development of a fast algorithm to compute the two-electron integrals ( $\mathcal{O}(N^4)$  instead of  $\mathcal{O}(N^6)$  for the numerical quadrature of the two-center case),<sup>17</sup> together with a means to simplify them for correlated calculations ( $\mathcal{O}(N^2)$  instead of  $\mathcal{O}(N^4)$  in the two-electron density matrix expansion),<sup>18</sup> have made it now less computationally intensive to perform this analysis in practice. In addition, the arrangement of the terms in our partition differs from the previous ones: in order to avoid having large, mutually canceling energy terms, we have rearranged them following the spirit of McWeeny's Theory of Electronic Separability (TES),<sup>19</sup> a Hilbert-space (as opposed to real-space) approximate partitioning of the energy into strongly orthogonal interacting electron groups. We note here that we need not restrict ourselves to QTAM's partition, not even to space partitions, and we can talk about general 1- and 2-matrix partitions, as pointed by the work of Ruedenberg.<sup>2</sup> Such a generalization and the comparison of different partitioning schemes will be the subject of a forthcoming article.

The scheme of this paper is as follows. First, we introduce the energy partition in section II. Then, we present a thorough energy analysis of the hydrogen molecule, to introduce the concepts within a particular example, followed by a comparison of the different contributions in several molecules representative of different traditional bonding types. Finally, in section IV we give our conclusions and a plan for future work.

## II. Energy Partition: Theory

In this section we present the theoretical aspects of the QTAM energy partition that we propose. First, we partition the density matrices and show how the different contributions can be evaluated. Then, we show how the rearrangement of

these contributions into one-atom and two-atom terms gives an appealing chemical image with strong physical grounds. Later, we examine the one-atom terms and their relation to binding, and we will finish this section with a further decomposition of the two-atom terms through the second-order density matrix.

**A. Density Matrices and Energy Partition.** Let us assume that we know the many-electron wave function  $\Psi_e$  with the desired accuracy, and from it we construct the first- (nondiagonal) and second-order (diagonal) density matrices

$$\rho_1(1;1') = N_e \int \Psi_e(1, \dots, N_e) \Psi_e^*(1', 2, \dots, N_e) d\mathbf{x}_2 \cdots d\mathbf{x}_{N_e} \quad (1)$$

$$\rho_2(1, 2) = N_e(N_e - 1) \int \Psi_e(1, \dots, N_e) \Psi_e^*(1, \dots, N_e) d\mathbf{x}_3 \cdots d\mathbf{x}_{N_e} \quad (2)$$

where the  $\mathbf{x}$  vectors include spatial and spin coordinates, 1, 2, ... represent  $\mathbf{x}_1, \mathbf{x}_2, \dots$  within density matrices and  $\Psi_e$ , and  $N_e$  is the number of electrons. These density matrices suffice to compute the expectation value of the electronic wave function within the Coulomb Hamiltonian scheme (atomic units)

$$E_e = h + V_{ee} = \int_{\infty} \hat{h} \rho_1(1;1') d\mathbf{x}_1 + \frac{1}{2} \int_{\infty} \int_{\infty} \rho_2(1, 2) r_{12}^{-1} d\mathbf{x}_1 d\mathbf{x}_2 \quad (3)$$

Here is understood that the prime superscript is removed after the operators act on functions but before performing the integrations.  $\hat{h}$  is the usual monoelectronic operator containing kinetic energy ( $\hat{T}$ ) and nuclear attraction ( $\hat{U}$ ) operators, while  $r_{12}^{-1}$  is the interelectronic repulsion, thus defining the global properties  $h$  and  $V_{ee}$ . To obtain the total Born–Oppenheimer energy of the molecule, we have to add the internuclear repulsion,  $E = E_e + V_{nn}$ , which can be easily computed as

$$V_{nn} = \frac{1}{2} \sum_{A \neq B} V_{nn}^{AB} = \frac{1}{2} \sum_A \sum_{B \neq A} \frac{Z^A Z^B}{r_{AB}} \quad (4)$$

where  $Z^X$  is the nuclear charge of atom X and  $r_{AB}$  is the distance between atoms A and B.

Since  $V_{nn}$  has a quite clear two-body partition, the partitioning of  $E$  requires that of  $E_e$ , which we will carry on through a partition of the density matrices. To this end, we introduce QTAM's partition of real space:<sup>8</sup> atomic basins  $\Omega$  are defined as the 3D attraction basins of the gradient field of the electron density,  $\nabla \rho(\mathbf{r})$ , which are bounded by a zero local flux surface of this field ( $\nabla \rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0$  for  $\mathbf{r} \in S(\Omega)$ , where  $\mathbf{n}(\mathbf{r})$  is a vector normal to the surface  $S(\Omega)$ ). These basins usually contain one and only one nucleus and are easier to handle by defining a Heaviside-like basin step function

$$\Theta_{\Omega}(1) = \begin{cases} 1 & \text{if } r_1 \in \Omega \\ 0 & \text{elsewhere} \end{cases} \quad (5)$$

Notice that, since QTAM's partition is exhaustive,  $\sum_A \Theta_A = 1$ . Using this identity, we partition the first-order density

matrix into atomic contributions

$$\rho_1(1;1') = \sum_A \rho_1^A(1;1') = \sum_A \rho_1(1;1') \Theta_A(1') \quad (6)$$

This induces a partition in all monoelectronic properties, since

$$O = \int_{\infty} \hat{O} \rho_1(1;1') d\mathbf{x}_1 = \sum_A \int_{\infty} \hat{O} \rho_1^A(1;1') d\mathbf{x}_1 = \sum_A \int_{\infty} \Theta_A(1') \hat{O} \rho_1(1;1') d\mathbf{x}_1 = \sum_A \int_{\Omega_A} \hat{O} \rho_1(1;1') d\mathbf{x}_1 = \sum_A O^A \quad (7)$$

In particular, since  $\hat{h} = \hat{T} + \hat{U}$

$$h = \sum_A h^A = T + U = \sum_A T^A + \sum_A U^A \quad (8)$$

The atomic kinetic energy,  $T^A$ , is at the origin of QTAM's partition.<sup>8</sup> The zero-flux definition of the atomic basins ensures that both kinetic energy operators ( $-\nabla^2/2$  and  $\nabla\nabla/2$ ) have the same expectation value (by making the momentum operator hermitian within the bounded region),<sup>20</sup> giving a kinetic energy,  $T^A$ , which is transferable<sup>21</sup> and that fulfills an atomic virial theorem.<sup>22</sup> Bader<sup>8</sup> used this theorem to partition the total energy in atomic (one-body) contributions,  $E = -T = -\sum_A T^A = \sum_A E(A)$  in his notation. The use of this one-body partition, while successful, is at the core of many criticisms of the theory. Particularly, this is only valid at equilibrium (where  $2T + V = 0$ ), unnecessarily restricting the scope of the partition. It also hides the interatomic interactions within a single additive contribution, interpreting atomic energies as kinetic energies only. Thus, we will not use this scheme in what follows, allowing for nonequilibrium geometries and interaction contributions.

Regarding the electron–nucleus attraction, its operator is defined as

$$\hat{U} = \sum_B \hat{V}_{\text{en}}^B = -\sum_B Z^B/r_{1B} \quad (9)$$

and thus

$$U = \sum_A U^A = \sum_A \sum_B V_{\text{en}}^{AB} \quad (10)$$

where

$$V_{\text{en}}^{AB} = \int_{\Omega_A} \hat{V}_{\text{en}}^B \rho_1(1;1') d\mathbf{x}_1 = -\int_{\Omega_A} \frac{\rho(\mathbf{r}_1) Z^B}{r_{1B}} d\mathbf{r}_1 \quad (11)$$

is the electrostatic interaction energy between electrons in basin A and the nucleus of atom B. When  $A = B$ , this is an intra-atomic (one-center/body) nuclear attraction, whereas when  $A \neq B$  this is an interatomic (two-center/body) nuclear attraction, monoelectronic in both cases. It is to be noticed that, since it involves different types of particles, it does not include the 1/2 prefactor of eq 4 and also that  $V_{\text{en}}^{AB} \neq V_{\text{en}}^{BA}$  in general, since both  $Z$  and  $\rho(\mathbf{r}_1)$  within each basin can be different for the two atoms. Note that the order of sub- and superscripts does matter, i.e.,  $V_{\text{en}}^{AB} \equiv V_{\text{ne}}^{BA} \neq V_{\text{en}}^{BA} \equiv V_{\text{ne}}^{AB}$ .

Unfortunately, a monoelectronic  $\rho_1(1;1')$  partition does not provide a partition for the bielectronic  $\rho_2(1, 2)$ . However, Li and Parr<sup>23</sup> showed that if  $\rho = \rho_A + \rho_B = \Theta_A \rho + \Theta_B \rho$  (with arbitrary  $\Theta_X$  weighting factors in their general case), then a partition for the second-order density matrix that preserves the physical meaning of all energy contributions in the global and both in the intra- and interatomic cases is  $\rho_2^{AB}(1, 2) = \rho_2(1, 2) \Theta_A(1) \Theta_B(2)$  or, symmetrizing,  $\rho_2^{AB}(1, 2) = \rho_2(1, 2) \cdot (1/2) [\Theta_A(1) \Theta_B(2) + \Theta_B(1) \Theta_A(2)]$ . Both expressions give the same symmetric energy results, since the  $r_{12}^{-1}$  operator is hermitian, but only the latter fulfills  $\rho_2^{AB}(1, 2) = \rho_2^{BA}(1, 2)$ . Let us notice that within McWeeny's scheme,<sup>19</sup>  $\rho_2^{AA}(1, 2)$  is allowed to include as much correlation as needed, but  $\rho_2^{AB}(1, 2)$  is restricted to Coulomb and exchange terms only, making it approximately valid only in the case of weakly correlated electron groups. In this regard, our partition makes no approximation or assumption beyond those needed to obtain the wave function, and thus  $\rho_2^{AB}(1, 2)$  can be fully correlated.

Using this partition,  $\rho_2 = \sum_{A,B} \rho_2^{AB}$ , we can partition the two-electron energy as

$$V_{\text{ee}} = \frac{1}{2} \int_{\infty} \int_{\infty} \sum_{A,B} \rho_2^{AB}(1, 2) r_{12}^{-1} d\mathbf{x}_1 d\mathbf{x}_2 = \sum_A V_{\text{ee}}^{AA} + \frac{1}{2} \sum_A \sum_{B \neq A} V_{\text{ee}}^{AB} \quad (12)$$

Here we have defined, on one hand

$$V_{\text{ee}}^{AA} = \frac{1}{2} \int_{\Omega_A} \int_{\Omega_A} \rho_2(1, 2) r_{12}^{-1} d\mathbf{x}_1 d\mathbf{x}_2 \quad (13)$$

the total intrabasin interelectronic repulsion, coincident with Bader's  $V_{\text{ee}}(\Omega_A, \Omega_A)$ , but on the other hand

$$V_{\text{ee}}^{AB} = \int_{\Omega_A} \int_{\Omega_B} \rho_2(1, 2) r_{12}^{-1} d\mathbf{x}_1 d\mathbf{x}_2 \quad (14)$$

the total interbasin interelectronic repulsion interaction, which is twice the  $V_{\text{ee}}(\Omega_A, \Omega_B)$  defined by Bader (see ref 8). In this way, intrabasin components represent total contributions, but the interbasin components represent interaction contributions, which have to be halved afterward to avoid double-counting in the global properties. This completes the partition of the total energy using QTAM's zero-flux atomic basins, which we have recast into a density matrix partitioning scheme so that it can be easily compared with other atomic partitions.<sup>19,23</sup> The next subsection is devoted to rearrange all of these energy terms into chemically meaningful contributions.

**B. QTAM Energy Partition.** We have several contributions to the total energy:  $T^A$ ,  $V_{\text{nn}}^{AB}$ ,  $V_{\text{en}}^{AB}$ , and  $V_{\text{ee}}^{AB}$  ( $A = B$  or  $A \neq B$ ). All of them have in fact been previously described in the literature, although only the first three have been widely used due to the extremely high computational resources needed to evaluate the two-electron integrals. The situation has changed with the recent development of a fast algorithm to evaluate these integrals,<sup>17</sup> and thus all of the contributions can now be used in the partition of the total energy. However, they convey a much finer partition than needed and present an important drawback: these properties

have very large values when compared with the binding energy of the molecule, which can be several orders of magnitude smaller. This comes from an almost exact cancellation of the different contributions and has a clear physical meaning, as we shall shortly see.

Instead of using these terms as such, we will reorganize them according to McWeeny's ideas. Thus, we first gather all of the monatomic (effective one-body) contributions in what we call the atomic net energy

$$E_{\text{net}}^A = T^A + V_{\text{en}}^{\text{AA}} + V_{\text{ee}}^{\text{AA}} \quad (15)$$

containing all of the contributions from the particles ascribed to atom A. Then, we define an interatomic interaction energy by collecting all of the two-atom (two-body) contributions

$$E_{\text{int}}^{\text{AB}} = V_{\text{nn}}^{\text{AB}} + V_{\text{en}}^{\text{AB}} + V_{\text{ne}}^{\text{AB}} + V_{\text{ee}}^{\text{AB}} \quad (A \neq B) \quad (16)$$

This includes all interaction potential energies of particles ascribed to atom A with particles ascribed to atom B and is symmetric with respect to the  $A \leftrightarrow B$  interchange (notice that  $V_{\text{ne}}^{\text{AB}} = V_{\text{en}}^{\text{BA}}$ ).

Using these net and interaction energies, the total energy of the molecule can be written as

$$E = \sum_A E_{\text{net}}^A + \frac{1}{2} \sum_A \sum_{B \neq A} E_{\text{int}}^{\text{AB}} \quad (17)$$

This is the main equation in our partition scheme, which states that the total energy of a molecule can be exactly partitioned in net energy contributions, one-body self-energy terms which carry all of the intra-atomic contributions (kinetic, nuclear attraction, and two-electron repulsion within the atom), and interaction energy contributions, two-body pairwise additive terms including all interparticle potentials (nucleus–nucleus, nucleus–electron, electron–nucleus, and electron–electron). Although they are not going to be used in this study, it is also interesting to define, following McWeeny, the effective energy of a given atom

$$E_{\text{eff}}^A = E_{\text{net}}^A + \sum_{B \neq A} E_{\text{int}}^{\text{AB}} \quad (18)$$

which contains all the A-dependent terms in eq 17, and also what we call the additive energy of an atom

$$E_{\text{add}}^A = E_{\text{net}}^A + \frac{1}{2} \sum_{B \neq A} E_{\text{int}}^{\text{AB}} \quad (19)$$

whose value is in the recovery of the total energy by a simple sum,  $E = \sum_A E_{\text{add}}^A$ .

Equation 17 has many interesting properties. First, it is equally valid for molecules and extended systems, where the energy per unit formula will be just computed by summing up the additive energies of the atoms in this unit formula; thus, the only infinite (but convergent) summation involved is the one over interactions with all  $B \neq A$  atoms in eq 19. Moreover, eq 17 is the same one successfully used in semiempirical atomistic simulations (solid and liquid state, but also gas phase) over the years,<sup>24–26</sup> in which the focus is in the pairwise terms, assuming that the self-energies of

the atoms do not change much within the particular simulation and can thus be ignored as a constant. In fact, this partition includes also the many-body effects through the electron density matrices, derived from the many-body wave function, so that the net and interaction terms should be more properly called effective one- and two-body. It is also behind the size extensiveness of the total energy, which is at the heart of order- $N$  scaling algorithms: the net energies are local and simply additive, while the interaction energies are usually of short-range, mainly with the nearest neighbors, and thus half of their sum (their contribution to the additive energies) for a given atom also represents a local term to the energy of an extensive system. This equation is also equivalent to eq 2 in ref 14, although these authors used a Hartree–Fock scheme.

Compared with other partition schemes, eq 17 has also the same form as those derived from McWeeny's energy of interacting electron groups<sup>19</sup> when they are variationally optimized,<sup>27</sup> and it can also be shown to be equivalent to that by Li and Parr,<sup>23</sup> as we shall see below. Let us also recall that, unlike Bader's original scheme based in kinetic energies only, our scheme is not linked to the equilibrium nuclear geometry and can be used to analyze any point in the potential energy surface, thus being very valuable in understanding kinetics and reaction barriers, for example.

Given the simple form of eq 17, we can also group together several atoms to form functional groups. Let us consider the system formed by several groups of atoms,  $\mathcal{G}, \mathcal{H}, \dots$ . We can define the net energy of a group by adding the net energies of its constituents and their intragroup interactions (counted once each)

$$E_{\text{net}}^{\mathcal{G}} = \sum_{A \in \mathcal{G}} E_{\text{net}}^A + \frac{1}{2} \sum_{A \in \mathcal{G}} \sum_{\substack{B \neq A \\ B \in \mathcal{G}}} E_{\text{int}}^{\text{AB}} \quad (20)$$

We can also define the interaction between two groups by adding all the interactions of atoms in one group with atoms in the other

$$E_{\text{int}}^{\mathcal{GH}} = \sum_{A \in \mathcal{G}} \sum_{B \in \mathcal{H}} E_{\text{int}}^{\text{AB}} \quad (21)$$

In this way, the total energy can be recovered from these net and interaction group energies as

$$E = \sum_{\mathcal{G}} E_{\text{net}}^{\mathcal{G}} + \frac{1}{2} \sum_{\mathcal{G}} \sum_{\mathcal{H} \neq \mathcal{G}} E_{\text{int}}^{\mathcal{GH}} \quad (22)$$

an expression completely equivalent to that for atomic contributions, eq 17. Thus, inasmuch as a functional group is unchanged from system to system, its net energy will remain constant, and it will be its interaction energy with other groups the one governing the combined system behavior. In covalent, organic molecules, the intergroup interaction will be typically dominated by a single bond between the group and the backbone of the molecule, and whenever this bond is more or less equivalent to those of other possible substituents, we have the classical additive character of the energy with respect to the interchange of functional groups.<sup>28</sup> Another important possibility is for the



groups to be entire molecules, in which case the net energies will be the proper energies of each molecule, and the interaction will be the intermolecular interaction, thus treating on equal footing the intra- and intermolecular interactions.

Up to this point, we have mostly fulfilled the program stated in the Introduction for a good energy partition. We are able to identify atoms and functional groups, which are transferable (as shown by Bader<sup>8</sup>). The energy contains a clear description of interactions, very intuitive since it is given in terms of the Coulombic interactions of the constituent particles of each atom, and which is equally capable of describing intermolecular interactions. In practice, the partition only needs the nuclear geometry and a wave function (or, equivalently, the nondiagonal first-order and the diagonal second-order density matrices), and thus it is a physical property of the system, as accurate as the wave function being used. A final point remains to be fully justified, that is, how the binding energy arguments can be cast into this new language. This will be addressed in the next subsection.

**C. Atomic Self-Energy and Deformation Energy.** It is clear that the net energy is the quantity carrying the atomic identity from system to system: the core and the internal valence are not going to change much for a given atom in different systems, and thus their kinetic energies, the attraction by its atomic nucleus, and the electron–electron repulsion (including correlation) are going to be largely the same. Thus, we could take the net energy of an atom (or functional group) in a given environment as a reference when comparing the same atom in different environments, and its changes will be very small, while those in the interaction energy will be larger. This can be beautifully explained using an argument by Li and Parr.<sup>23</sup> For a given atom or functional group, we can see the influence of the rest of the system as a nonlocal potential acting over it. When the chemical environment changes (provided there is not a large charge transfer), we can estimate the effective energy change through the Hellmann–Feynman theorem as

$$\Delta E_{\text{eff}}^A \approx \int_A \Delta \hat{V} \rho_0^A \quad (23)$$

up to first order, where  $\rho_0^A$  is the atomic density in the original environment. Since the potential change only affects the interaction energy, the net energy will remain mostly constant (up to first order) for small and moderate changes in the environment of a given atom or functional group. However, if the environment change is large, there are several factors through which the net energy can change: (i) charge transfer, (ii) electronic reorganization within the atomic basin, and (iii) a change in the interatomic surface.

The net energy contains all of the energy contributions that are already present in an isolated atom, and so the free atomic energies are comparable in order of magnitude. This fact can be exploited by taking our net energy reference as that of the atoms in vacuo, thus defining what we call the atomic deformation or reorganization energy

$$E_{\text{def}}^A = E_{\text{net}}^A - E_{\text{vac}}^A \quad (24)$$

We label this as deformation since it takes into account the deformations in the atomic density on going from the free

state into the combined system. This labeling is appropriate when there is a change in shape of the density or the atomic basin, but its larger component, by far, comes from charge transfer when this is present. For very ionic systems, the reference can be set in the isolated ions, for example, but for intermediate systems (partially ionic) there is usually no isolated-atom system that can be taken as a faithful reference. Nevertheless, the net energy does not change between similar environments even for cases where there is no close enough reference, and this constancy can always be exploited by taking as reference a nonisolated atomic net energy. However, there is an important property to be drawn from the deformation energy with respect to the isolated atoms: using eq 17, the binding energy can be computed as

$$E_{\text{bind}} = E - \sum_A E_{\text{vac}}^A = \sum_A E_{\text{def}}^A + \frac{1}{2} \sum_A \sum_{B \neq A} E_{\text{int}}^{\text{AB}} \quad (25)$$

In this way, all the contributions are usually of the same order of magnitude as the binding energy itself, since the large cancellation of the atomic contributions is already included in the deformation energy, and so the origin of stability can be easier to rationalize. Thus, one can see the binding of the molecule as the sum of a deformation energy, which can be shown to be necessarily positive in homodiatomics and is usually positive (depending on the reference) in any other case, and an interaction energy, that is usually negative. This can be described as the following virtual process: the atoms have to raise their energy in order to form the molecule, but this energy gain is compensated by a larger energy lowering due to their interaction.

Equation 25 is equivalent to that given in Li and Parr's partition scheme,<sup>23</sup> where they label the deformation energy as a promotion energy, in view of the mental process of molecule formation just mentioned. However, our scheme differs mainly in two points from theirs. First, their  $\Theta_A$  weighting factors defining the density matrices' partition are diffuse, continuous functions in the general case, instead of being step functions (they can be analytically shown to coincide with QTAM's partition for the  $\text{H}_2^+$  case, but that is no longer true when the electron–electron interaction comes in). Second, they put an a priori requirement into the atomic partition, namely that it gives the lowest possible sum of the promotion energies (deformation energies in our language). This is done so that the atoms in the molecule are energetically as close as possible to the free atoms, but it really amounts to minimizing the net energy sum (or maximizing the interaction energy). This requirement defines the partition into atomic densities, in the same way that the zero-flux condition defines ours. Many other partitioning schemes can be introduced by selecting different definitions for the atomic density weighting factors. In the case of Li and Parr's scheme, while the partition can be reasonable for homonuclear and low polarity systems, it will fail to meet chemical intuition for highly polar or ionic compounds: since the promotion energy into ions is very large, the minimization of the net energies will tend to make all of the atoms in the molecule neutral, and so the traditional understanding of the chemistry of these compounds as coming from a large charge-transfer compensated by a larger electrostatic energy

lowering will be lost. This is not the case in our partition, where we choose the atomic weighting functions according to the topology of the electron density. Thus, a charge transfer will be predicted whenever the electron density rearranges in that way and not through an energy criterion.

A final word on the energy references is necessary. It is the behavior of the net energy, which should not change much for an atom across similar compounds, that gives the partition its meaning, and not the reference used to define the deformation energy. The effect of the reference is to shift the atomic energies by a constant, and it is only introduced for convenience in comparing the net energies of an atom in different compounds with a common level and in understanding binding energies.

**D. Interatomic Interaction Energy.** As already mentioned, the interaction energy provides a very intuitive definition of the interaction between two atoms, including all of the pairwise interparticle contributions:  $V_{nn}^{AB}$ ,  $V_{ne}^{AB}$ ,  $V_{en}^{AB}$ ,  $V_{ee}^{AB}$ . It is thus based on the physical interaction between the two systems, fully taking into account the quantum nature of the electrons through the use of the second-order density matrix in the electron–electron repulsion. It also does not make any a priori distinction between bonded (i.e. atoms connected by a chemical bond), non-bonded, or even intermolecular interactions, treating all of them on the same basis. Of course, the ranges of interaction energy values will be different for each of these cases and also for different kinds of bonds. To better understand the interactions, it is desirable to make a different arrangement of its components: although the final atomic charges are usually small, and close to zero in many cases, the nuclear charges are usually much higher, and also the total number of electrons. Thus, the above-mentioned terms will be several orders of magnitude larger than the interaction energy, while an approximate application of the Gauss theorem ensures that they will mostly cancel out for neutral systems.

The second-order density matrix admits a natural partition that facilitates a meaningful rearrangement, as presented in ref 18. We define the Coulomb term of  $\rho_2$  as  $\rho_2^C(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)$  and the Fock-Dirac exchange term as  $\rho_2^X(\mathbf{r}_1, \mathbf{r}_2) = -\rho_1(2;1)\rho_1(1;2)$ . The remainder then defines the correlation density,  $\rho_2^{\text{corr}} = \rho_2 - \rho_2^C - \rho_2^X$ , and we can also define an exchange-correlation term as  $\rho_2^{\text{xc}} = \rho_2^X + \rho_2^{\text{corr}}$ , so that  $\rho_2 = \rho_2^C + \rho_2^{\text{xc}}$ . The total electron–electron interaction in eq 14 can be then partitioned in Coulomb, exchange, and correlation terms

$$V_\tau^{AB} = \int_{\Omega_A} \int_{\Omega_B} \rho_2^\tau(1, 2) r_{12}^{-1} d\mathbf{x}_1 d\mathbf{x}_2 \quad (26)$$

where  $\tau = C, X, \text{corr}$ . In this way

$$V_{ee}^{AB} = V_C^{AB} + V_X^{AB} + V_{\text{corr}}^{AB} \quad (27)$$

where  $V_C^{AB}$  coincides with the  $J^{AB}$  integral and  $V_X^{AB}$  with  $-K^{AB}$  in eqs 10 and 11 of ref 17. Now we can collect all the classical electrostatic terms in what we call the classical interaction energy

$$V_{\text{cl}}^{AB} = V_{nn}^{AB} + V_{ne}^{AB} + V_{en}^{AB} + V_C^{AB} \quad (28)$$

and thus the interaction energy becomes

$$E_{\text{int}}^{AB} = V_{\text{cl}}^{AB} + V_{\text{xc}}^{AB} \quad (29)$$

since  $V_{\text{xc}}^{AB} = V_X^{AB} + V_{\text{corr}}^{AB}$ .

The  $V_{\text{cl}}^{AB}$  classical term is the one where the interaction cancellations occur. Our atoms include both nucleus and electrons, and they tend to preserve their core and only partially share, donate, or accept their valence electrons, thus being neutral or having small charges. In this way,  $V_{\text{cl}}^{AB}$  for neutral atoms will be negligible if they are well separated, and it will be positive and larger if they are closer together (bonded, one could say). Of course, if the atoms are heavily charged, the charge–charge classical interaction will be the leading contribution to  $V_{\text{cl}}^{AB}$ , positive or negative for same or oppositely charged atoms, respectively. In any case,  $V_{\text{cl}}^{AB}$  will always be much smaller than the individual terms in eq 28.

It should be recalled here that, as shown in ref 17, all of the two-electron interactions can be efficiently computed through an exact and convergent multipolar expansion of the energy, and the same scheme is used here for consistency for the one-electron terms. So, each of the potential energy contributions, one- and two-electron but also one- and two-body, can always be written as a multipolar sum. This is most important for the classical electrostatic terms, where we can define approximate energy contributions based on the point multipoles ( $Q_l^A$  are the order- $l$  spherical multipoles of the electron density as defined in eq 26 of ref 17). In this way, given the total charge of the atom,  $Q^A = Z^A - Q_0^A$ , the leading point-charge (monopolar) term is  $V_Q^{AB} = Q^A Q^B / r_{AB}$ . Joining all of the electronic point multipole contributions, we define the long-range Coulomb term  $V_{C,\text{lr}}$  (equivalent to  $J_{\text{lr}}^{AB}$  as defined in eq 24 of ref 17). If we substitute  $Q_0^A \rightarrow Q^A$  within  $V_{C,\text{lr}}$ , thus including the point multipole contributions to the electron–nucleus and the nucleus–nucleus interaction, we obtain the long-range part of the classical interaction,  $V_{\text{cl},\text{lr}}^{AB}$ , an approximation to  $V_{\text{cl}}^{AB}$ . These long-range approximations will be especially useful in understanding intermolecular interactions, where they account for most of the interaction, but they are also valuable when discussing some intramolecular interactions.

The exchange–correlation contribution to the AB interaction,  $V_{\text{xc}}^{AB}$ , contains all of the quantum terms in the interaction, and it will typically be smaller than the Coulomb term,  $V_C^{AB}$ . However, its importance when compared with the classical interaction,  $V_{\text{cl}}^{AB}$ , will depend on the type of interaction between A and B. Although we have further split the exchange–correlation interaction into exchange and correlation terms, it should be kept in mind that any such separation is arbitrary and can produce misleading results. Nevertheless, our Fock-Dirac-like exchange, based on the first-order density matrix that can be derived from the second-order one, is uniquely defined, independent of any orbital representation, and coincides with the usual exchange (with zero correlation) in the monodeterminantal limit.

The partition into classical and quantum terms, and into exchange- and correlation-only terms, can also be carried on within the intra-atomic contributions by splitting

$\rho_2$  as above, thus defining

$$V_{\tau}^{AA} = \frac{1}{2} \int_{\Omega_A} \int_{\Omega_A} \rho_2^{\tau}(1, 2) r_{12}^{-1} d\mathbf{x}_1 d\mathbf{x}_2 \quad (30)$$

where  $\tau = C, X, \text{corr}$ . This is analogous to eq 13, but it should be noticed that  $V_C^{AA}$  and  $V_X^{AA}$  so defined are half of the integrals  $J^{AA}$  and  $-K^{AA}$  as defined in eqs 10 and 11 of ref 17 when  $A = B$ . In this way,  $V_{ee}^{AA} = V_C^{AA} + V_X^{AA} + V_{\text{corr}}^{AA}$ , and we can define  $V_{\text{cl}}^{AA} = V_{\text{ne}}^{AA} + V_C^{AA}$  and  $V_{\text{xc}}^{AA} = V_X^{AA} + V_{\text{corr}}^{AA}$ , so that  $E_{\text{net}}^A = T^A + V_{\text{cl}}^{AA} + V_{\text{xc}}^{AA}$ . However, this partitioning will not be as useful as that in the interaction energy, since there will not be any cancellation within the single basin. Furthermore, the net energy also contains the electronic kinetic energy, another quantum term with a much larger value than the exchange-correlation one.

### III. Energy Analysis

In this section, we will present the results of our energy partition scheme for several chemically representative systems. In the first subsection, we will give a thorough analysis of the hydrogen molecule, a well understood benchmark with which to compare any new idea. Then, we will perform a comparative analysis of  $\text{N}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{LiF}$ , and  $\text{He}_2$ , molecules representing apolar covalent, polar covalent, ionic, and van der Waals bonding types, respectively. Bonding in the molecules of metallic atoms is not qualitatively different from covalent bonding, and so we will not include any example, while hydrogen bonding is a complicated enough issue as to warrant a separate study.

All of the calculations have used the *gamess* code<sup>29</sup> to obtain the wave function and our code *promolden* to do the QTAM analysis and energy partition. The wave functions have been computed using Hartree–Fock (HF, for  $\text{H}_2$  and  $\text{N}_2$ ), different levels of complete active space multiconfiguration calculations (CAS[ $n, m$ ],  $n$  active electrons and  $m$  active orbitals: CAS[2,2] for  $\text{H}_2$ , CAS[10,10] for  $\text{N}_2$ , CAS[6,5] for  $\text{H}_2\text{O}$ , and CAS[10,10] for  $\text{LiF}$ ), and full configuration interactions (FCI, for  $\text{H}_2$  and  $\text{He}_2$ ). The basis sets used were Pople’s 6-311G(d,p), except for He, in which a cc-PVTZ Dunning basis set was used. The numerical integrations in *promolden* used  $\beta$ -spheres for all of the atoms, with radii between 0.3  $a_0$  (H in  $\text{H}_2\text{O}$ ) and 1.6  $a_0$  (F in  $\text{LiF}$ ). Inside these spheres, a 600 points Gauss-Chebyshev second kind radial quadrature and a Lebedev angular quadrature with 74 points were used, considering generalized energy multipoles up to  $L = 6$ . Outside the  $\beta$ -spheres, a trapezoidal radial quadrature with 500 points and a 1202 angular points Lebedev quadrature were used, with generalized energy multipoles up to  $L = 10$  (see ref 17 for the definition of the computational parameters and the integration algorithm). These integrations are enough to obtain the so-called chemical accuracy, since the errors with respect to the analytical energies as given by *gamess* were always smaller than 0.33 kcal/mol. All of the calculations were performed at the respective experimental equilibrium geometries (except for  $\text{He}_2$ , where an accurate theoretical value is used instead<sup>30</sup>), to better compare calculations with different approximate wave functions.<sup>31</sup> We want to stress once more that our QTAM energy partition does not rely on the virial theorem,

**Table 1:** QTAM Energy Partition for  $\text{H}_2$  at the Experimental Equilibrium Distance (0.74144 Å), as Described by Three Different Wave Functions<sup>a</sup>

Prop	HF	CAS[2,2]	FCI
$Q^A$	16 $\mu e$	15 $\mu e$	16 $\mu e$
$Q_1^A$	−0.1021	−0.1068	−0.1064
$Q_2^A$	−0.3617	−0.3452	−0.3488
$T^A$	0.5608	0.5805	0.5849
$V_{\text{en}}^{AA}$	−1.2153	−1.2277	−1.2251
$V_{\text{ee}}^{AA}$	0.1979	0.1628	0.1532
$V_{\text{cl}}^{AA}$	−0.8196	−0.8283	−0.8267
$V_{\text{xc}}^{AA}$	−0.1979	−0.2366	−0.2452
$V_C^{AA}$	0.3957	0.3994	0.3984
$V_X^{AA}$	−0.1979	−0.1988	−0.1967
$V_{\text{corr}}^{AA}$	0.0000	−0.0378	−0.0486
$E_{\text{net}}^A$	−0.4566	−0.4844	−0.4871
$\Delta T^A$	0.0610	0.0807	0.0851
$\Delta V_{\text{en}}^A$	−0.2157	−0.2281	−0.2255
$\Delta V_{\text{ee}}^A$	0.1979	0.1628	0.1532
$E_{\text{def}}^A$	0.0432	0.0154	0.0128
$V_{\text{nn}}^{AB}$	0.7137	0.7137	0.7137
$V_{\text{en}}^{AB}$	−0.5974	−0.5975	−0.5975
$V_{\text{ee}}^{AB}$	0.2619	0.2993	0.2871
$V_{\text{cl}}^{AB}$	0.0426	0.0423	0.0423
$V_{\text{xc}}^{AB}$	−0.2619	−0.2244	−0.2365
$V_C^{AB}$	0.5238	0.5237	0.5236
$V_X^{AB}$	−0.2619	−0.2522	−0.2510
$V_{\text{corr}}^{AB}$	0.0000	0.0279	0.0145
$E_{\text{int}}^{AB}$	−0.2193	−0.1820	−0.1942
$E$ (integ)	−1.1324	−1.1509	−1.1683
$E$ (analy)	−1.1325	−1.1509	−1.1683
$\Delta E$	41 $\mu E_h$	40 $\mu E_h$	42 $\mu E_h$
$E_{\text{bind}}$	−0.1328	−0.1513	−0.1687

<sup>a</sup> Atomic units are used throughout.

and thus can be used outside of the equilibrium geometry of the corresponding Hamiltonian. This allows us to obtain the partition at any point of the potential energy surface, and we will use it to follow the behavior of the different components when varying the distance in the  $\text{H}_2$  molecule in the next subsection.

**A. The Hydrogen Molecule.** All of the  $\text{H}_2$  QTAM energy partition contributions and their energy components as defined in section II are gathered in Table 1. The different columns refer to wave functions of increasing accuracy: single-determinant Hartree–Fock, two-determinant CAS[2,2], and multideterminantal full CI. The first block corresponds to the atomic charge ( $Q^A$ ), dipole ( $Q_1^A$ ), and quadrupole ( $Q_2^A$ ) of atom A (the one in the negative  $z$  axis). The second one contains the different one-atom contributions to the net energy,  $E_{\text{net}}^A$ , together with the atomic deformation energy,  $E_{\text{def}}^A$  (the change in net energy of the atom with respect to the in vacuo reference), and its  $\Delta X^A = X^A(\text{H}_2) - X^A(\text{H}_{\text{vac}})$  ( $X^A = T^A, V_{\text{en}}^{AA}, V_{\text{ee}}^{AA}$ ) components. The third block lists the interatomic interaction energy,  $E_{\text{int}}^{AB}$ , and its decomposition according to the various schemes proposed in the previous subsection. Finally, the last block lists the total energy as



recovered by the sum of the integrated QTAM contributions, the analytical value as obtained from *gamess*, the total energy integration error  $\Delta E = E(\text{integ}) - E(\text{analy})$ , and the binding energy with respect to the free atom reference.

Let us first address the precision of the numerical integration: the total charge is always smaller than  $2 \times 10^{-5} e$ , while the error in the total energy sum is on the order of  $4 \times 10^{-5} E_h$ . We have found that both absolute errors are usually related, as one should expect. The main source of error in the energy lies in its largest term, the intra-atomic nuclear attraction, and it is related to the discontinuity in the integrand at the atomic surface: the angular integration of a discontinuous function introduces a noise related to the jump in the value of the function at the discontinuity. We have observed that any error in the estimation of the charge introduces a proportional error in the nuclear attraction integral. Thus, one could perform previous exploratory charge integrations, of order  $N^3$  complexity, to estimate the order of magnitude of the error in the energy, whose calculation has an  $N^4$  complexity with a much higher prefactor (also growing with the square of the number of atoms).

As could also be expected for  $H_2$ , in which the HF approximation gives qualitatively correct geometrical results, the three calculations give a qualitatively consistent picture. However, HF fails to give accurate enough values for the kinetic and electron–electron contributions. Simply allowing the mixing with the  $(\sigma_u)^2$  configuration (introducing the antibonding orbitals coming from  $1s$  AOs in the simple orbital picture) generates a wave function in much better agreement with the FCI result for this basis set. The deformation energy in HF is three times larger than in CAS and FCI, due to two complementary facts: the well-known dissociation error of HF, which is partially translated into the equilibrium situation, and the lack of correlation energy (which in fact mainly corrects for the latter error), of the same order of magnitude of the overestimation.

The atomic dipoles ( $Q_1^A$ ) correspond to an outward displacement of the electronic charge, while the quadrupolar deformation ( $Q_2^A$ ) shifts charge outside from the inter-nuclear axis. The values are fairly insensitive to the type of calculation, being almost identical for the CAS and FCI calculations.

Let us focus on the second block of Table 1, including intra-atomic contributions. First of all, let us notice that  $V_{ee}^{AA} \neq 0$ : although there is one electron on average on each atom, there is a non-negligible probability of having two electrons on a given atomic basin. Regarding the net energy (see eq 15) it is clearly seen that it stems from the balance of the large, negative electron–nuclear attraction, and the somewhat smaller kinetic (on the order of half the absolute value of  $V_{en}^{AA} + V_{ee}^{AA}$ , even though no virial theorem applies to them) and electron repulsion positive contributions, all of them of the same order of magnitude as the net energy itself. The situation does not change if we define the classical and exchange–correlation contributions: both are negative but still of the same order of magnitude as the kinetic energy. This is inherent to the intra-atomic energies, which always bear large cancellations. However, as pointed out in the previous

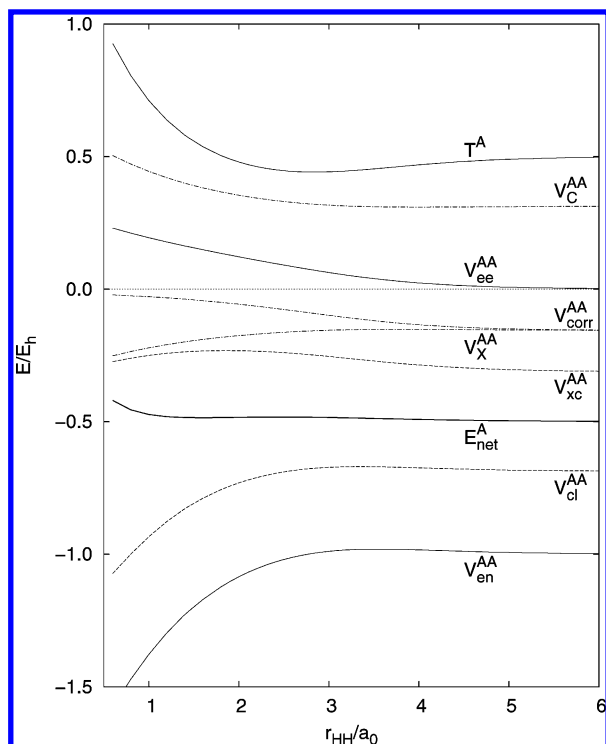
subsection, these large contributions are similar to the free atom ones, as we can see from the  $\Delta X^A$  contributions: they are an order of magnitude smaller than the  $X^A(H_2)$  values, except for  $\Delta V_{ee}^A$ . This is due to the special character of the mono-electronic H atom, with no electron–electron repulsion, and does not happen in many-electron atoms, as we shall see below. The increase in kinetic energy, decrease in the nucleus–electron attraction, and increase in the electron–electron repulsion are consistent with Slater's ideas on covalent bonding:<sup>32</sup> electrons in the molecule go faster and are closer to the nuclei, and the sharing puts them closer together so that they repel each other more (this will also be true when the free atom  $V_{ee}^{AA}$  is not zero). The intra-atomic balance still gives a positive deformation energy, which is almost an order of magnitude smaller than the  $\Delta X^A$  values. This is general and reveals that the deformation energy is a hard to partition property, coming from a very delicate interplay of large magnitudes.

Regarding the third block in Table 1, containing the interatomic interaction contributions, we can see that the positive and negative (there are two, symmetrical in this homonuclear case, electron–nucleus interactions) contributions have all of them the same order of magnitude, and they mostly cancel to give the interaction energy, smaller than any of them (see eq 16). However, we see that  $V_{cl}^{AB}$  is quite small and very similar in the three calculations (as they are its components,  $V_{nn}^{AB}$ ,  $V_{en}^{AB}$ , and  $V_{C}^{AB}$ ), while the exchange–correlation quantum contribution is larger in absolute value and varies with the amount of correlation energy included. In fact, it is remarkable that the Fock–Dirac exchange contribution in correlated wave functions is within 1% (intra-) and 5% (interatomic, and almost equal for CAS and FCI) the HF one. Due to this, the correlation interaction energy,  $V_{corr}^{AB}$ , is the main contribution to the differences in the interaction energies when varying the correlation energy scheme. This did not happen with the intra-atomic contributions, where the variations in the density matrices introduced changes in the kinetic energy and nuclear attraction.

Finally, the total energy, the sum of the net energies of both H atoms plus their interaction (see eq 17), is clearly a large number, mainly dominated by the net energies sum. However, when the binding energy is computed (eq 25), its value is an order of magnitude smaller than the total energy, and we also see that its main contribution comes from the interaction:  $E_{int}^{AB}$  is about 2.5 times the sum of deformation energies in the HF case, and about 6 times larger for the correlated cases. Thus, binding in  $H_2$  can be understood through a small deformation of the H atoms (8 kcal/mol each in the FCI calculation), compensated by a much larger interaction energy (−122 kcal/mol), which in turn is dominated by the pure quantum mechanical exchange–correlation part (−148 kcal/mol versus 26 kcal/mol for the classical interaction).

It is interesting to compare our HF results with those of Salvador et al. in ref 14. Although they used a somewhat poorer basis set (6-31G(d,p), double- $\zeta$  in the valence instead of our triple- $\zeta$ ), the main results are equivalent within the basis set errors. The numerical precision is similar as well as the net, interaction, and total energies, differing in less



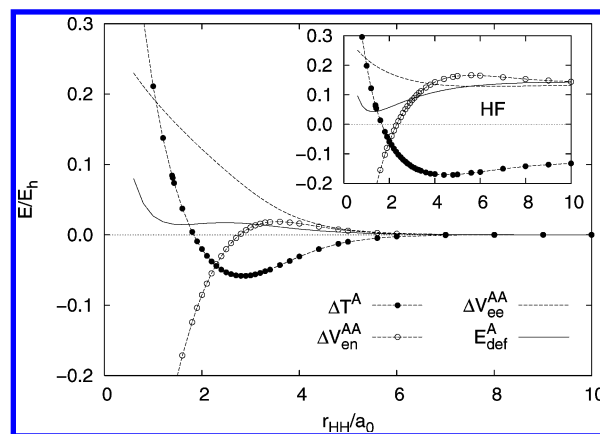


**Figure 1.** CAS[2,2] net energy ( $E_{\text{net}}^A$ , intra-atomic) and its components for H<sub>2</sub> as functions of internuclear distance ( $r_{\text{HH}}$ ).

than 2  $mE_h$ . The main difference lies in the kinetic energies, since our calculation is away from equilibrium to better compare with the correlated cases, but is nevertheless of about 4  $mE_h$ .

Let us now examine the behavior of the partition for a wide range of distances using the CAS wave function. In Figure 1 we have included the net energy, together with its several components and their possible rearrangements, as functions of the internuclear distance. The net energy appears to be flat in this energy scale, with a value of  $-0.5 E_h$  for distances above 1  $a_0$ . It is clearly seen that all of its components are large, and not much insight can be extracted from them. In fact, the main components  $T^A$  and  $V_{\text{en}}^{\text{AA}}$  stand out from the rest above and below, respectively, while  $V_{\text{ee}}^{\text{AA}}$  is only important at short distances.

It is interesting to follow the independent behavior of exchange and correlation: the latter seems to go to zero at short distances, while at large distances exchange and correlation tend to the same limit. This result is clearly related to the simple, two-determinantal wave function. At short distances, with the He atom as limit, the antibonding orbital goes into a united atom  $p$  state, with a quite small contribution to correlation and hence the wave function will behave as a single-determinant one, with  $V_{\text{corr}}^{\text{AA}} \approx 0$ . On the other hand, at large distances the singlet is in fact a 50% superposition of two independent doublets, leading to this artificial exchange-correlation partition. So, the separation into exchange and correlation only makes sense when there is a dominant determinant, and the correlation contribution comes from a partial (but not negligible) mixing with other configurations. In any case, one must remember that this separation is not uniquely defined. Also, the meaning of the exchange-correlation term is distorted in the long-distance

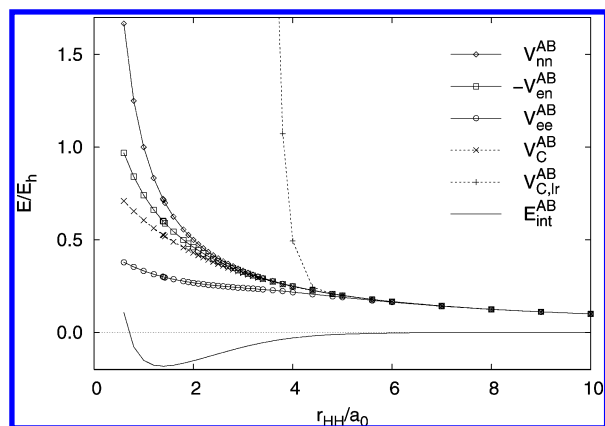


**Figure 2.** CAS[2,2] deformation energy ( $E_{\text{def}}^A$ ) and its contributions for H<sub>2</sub> as functions of internuclear distance ( $r_{\text{HH}}$ ). The inset shows the corresponding HF values.

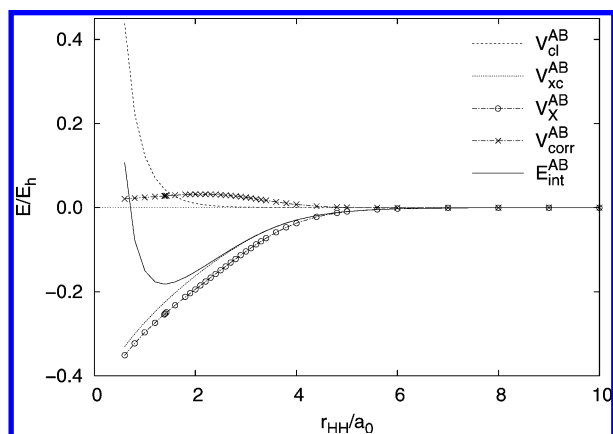
regime of covalent (i.e., electron pairing) bonds. In this regime the system should be properly treated as two separate and independent subsystems. The dependence introduced to make a singlet from the two doublets is related to the quantum entanglement between them: if one of the H atoms is spin-up, the other is certainly spin-down. It should be stressed that this is not solvable with a better wave function: the CAS[2,2] gives the exact solution for this system in the  $r_{\text{HH}} \rightarrow \infty$  limit within the basis set chosen, since the 1s HF orbital is the exact solution for H.

Although the individual components of  $E_{\text{net}}^A$  are widely separated, subtracting the infinite distance limit values (free atoms) transforms these components into the  $\Delta X^A$  values, and the net energy into  $E_{\text{def}}^A$ , as shown in Figure 2. Notice that the energy scale is much smaller than that in Figure 1 and that all of the curves go to zero as  $r_{\text{HH}} \rightarrow \infty$ , but  $E_{\text{def}}^A$  is still almost an order of magnitude smaller than these components. Let us stress again that  $E_{\text{def}}^A$  is very small whenever the charge transfer is small, and in general that  $E_{\text{net}}^A$  tends to maintain its value for a given atom up to first order in the variations of its environment (this fails under large compression here and also when there is a significant charge transfer). Figure 2 shows that, at long distances, the kinetic energy decreases, while the nuclear attraction increases, with respect to the free atom limit. Both trends are reversed at smaller distances, so that at the equilibrium geometry (1.4  $a_0$ ) the kinetic energy is larger and the nuclear attraction smaller than the free atom limit. On the other hand, the electron–electron repulsion increases monotonically from zero (one-electron separated atoms) when decreasing the distance. Adding up all of these contributions, the deformation energy varies as follows: for distances larger than 5  $a_0$ , there are large cancellations and its value is almost zero; in going from 5 to 3  $a_0$ , its value increases slightly; between 3 and 1  $a_0$  it is almost flat; and finally, below 1  $a_0$  it increases sharply due to the increase of the kinetic energy (that becomes even steeper than  $\Delta V_{\text{en}}^{\text{AA}}$ ) and the steady increase of the electron repulsion energy. The HF results, shown in the inset, have a completely different behavior, owing to the wrong dissociation limit.

Figure 3 represents the H–H interaction energy,  $E_{\text{int}}^{\text{AB}}$ , and its main contributions. All of the  $V_{\text{nn}}^{\text{AB}}$ ,  $-V_{\text{en}}^{\text{AB}}$ , and  $V_{\text{ee}}^{\text{AB}}$



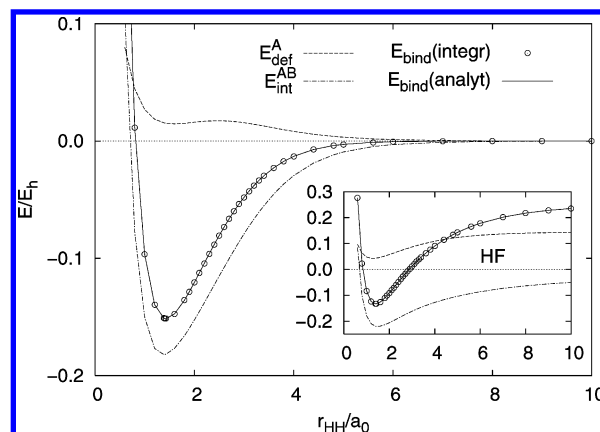
**Figure 3.** CAS[2,2] interaction energy ( $E_{\text{int}}^{\text{AB}}$ , interatomic) and its components for  $\text{H}_2$  as functions of internuclear distance ( $r_{\text{HH}}$ ).



**Figure 4.** Alternative partition of the CAS[2,2] interaction energy ( $E_{\text{int}}^{\text{AB}}$ ) into classical ( $V_{\text{cl}}^{\text{AB}}$ ) and exchange-correlation ( $V_{\text{xc}}^{\text{AB}}$ ) contributions for  $\text{H}_2$  as functions of internuclear distance ( $r_{\text{HH}}$ ).

components are monotonic and much larger than the interaction energy itself, with a large cancellation that is most evident at long distances: all of them fall as  $1/r_{\text{HH}}$  with distance, as expected, but their sum goes to zero much faster, being the interaction energy negligible above  $5 a_0$ . This is precisely the limit in which  $V_{\text{nn}}^{\text{AB}}$  is equivalent to  $V_{\text{ee}}^{\text{AB}}$  and to  $-V_{\text{en}}^{\text{AB}}$  and also to  $V_{\text{C}}^{\text{AB}}$ : at long distance, the point multipolar approach is exact, and the long-range (point multipole) component of the Coulomb interaction,  $V_{\text{C,lr}}^{\text{AB}}$ , becomes meaningful and equivalent to the overall  $V_{\text{C}}^{\text{AB}}$  value, its leading monopole term being the product of the number of electrons of each atom (1  $e$ ) over their distance,  $1/r_{\text{HH}}$ .

Figure 4 shows the alternative partition of the interaction energy into classical and exchange-correlation terms, which gives more chemical insight: the  $V_{\text{cl}}^{\text{AB}}$  term is almost zero for distances larger than  $2 a_0$  and largely repulsive below this point, while the exchange-correlation term is monotonically attractive. Thus, the interaction energy resembles  $V_{\text{xc}}^{\text{AB}}$  on its attractive part, while its repulsive contribution is dominated by the classical part at small distances. At the experimental equilibrium distance of  $1.4 a_0$ , almost at the minimum of the  $E_{\text{int}}^{\text{AB}}$  curve, the classical part is still small, and the interaction is dominated by the exchange-correlation part.



**Figure 5.** CAS[2,2] binding energy ( $E_{\text{bind}}$ ) partition for  $\text{H}_2$  as a function of internuclear distance ( $r_{\text{HH}}$ ). The inset shows the corresponding HF values. Notice the coincidence of the numerically integrated (circles) and analytically computed (solid line) values in both cases.

Moreover, Figure 4 also includes the separation of the exchange-correlation interaction energy into exchange-only and correlation-only contributions. Since the correlation part is much smaller than the exchange part, it is the latter which dominates  $V_{\text{xc}}^{\text{AB}}$ , and through it the attractive part of  $E_{\text{int}}^{\text{AB}}$  and also of  $E_{\text{bind}}$  (since  $E_{\text{def}}^{\text{A}}$  is positive and almost flat, Figure 2). Thus, we may say that  $\text{H}_2$  is mainly bound by the exchange interaction between the two atoms, in the same spirit of the Heitler-London original treatment and in accordance with the traditional ideas of covalent bonding. It is important to notice that the  $V_{\text{X}}^{\text{AB}}$  integral is in fact equivalent to the Heitler-London resonance integral: it is an exchange integral in which each of the electrons is restricted to a different atom (eq 26), through the density matrix contribution  $\rho_2^{\text{X,AB}}(1, 2) = -\rho_1(2;1)\rho_1(1;2)\Theta_{\text{A}}(1)\Theta_{\text{B}}(2)$ . The energy lowering acquired through this delocalization is responsible for the attractive force, compensating the electrostatic classical repulsion and the intra-atomic (deformation) energy increase.

Finally, let us compare the two main components of binding, the deformation and the interaction energies. Figure 5 presents the binding energy of  $\text{H}_2$  as computed by numerical integration of its components within QTAM (symbols) and analytically within *gamess* (solid line). They are almost indistinguishable, the integration error being always smaller than 0.1 kcal/mol and mostly independent of the distance. Notice the depth of the well, about  $0.15 E_{\text{h}}$ , and that the energy scale is much smaller than in previous figures. As already mentioned, the deformation (net) energy is almost flat between 1 and  $3 a_0$ , precisely the region of the minimum, and thus the binding energy minimum is almost coincident with the minimum of the interaction energy. On the other hand, since the deformation energy is smaller, interaction dominates the overall binding behavior above  $1 a_0$ , while the repulsion below this point is the sum of both deformation and interaction.

This picture is not clear at all in the HF results, shown in the inset of Figure 5. This is again due to the dissociation problem, which makes the three curves to have different  $r_{\text{HH}} \rightarrow \infty$  limits. Notice how the deformation energy is always

**Table 2:** QTAM Energy Partition on Several Molecules at Their Equilibrium Geometries: Experimental for N<sub>2</sub> (1.09768 Å), H<sub>2</sub>O (0.95781 Å, 104.4776°), and LiF (1.563864 Å), Theoretical for He<sub>2</sub> (5.6 ± 0.05 a<sub>0</sub>)<sup>a</sup>

properties	N <sub>2</sub> (HF)	N <sub>2</sub> (CAS)	H <sub>2</sub> O(CAS)		LiF(CAS)		He <sub>2</sub> (FCI)
atomic	N	N	O	H	F	Li	He
$Q^A$	1.4e-4	1.3e-4	-1.0903	0.5448	-0.9299	0.9299	0.000009
$Q_1^A$	-0.6218	-0.6269	0.1828	-0.1705	0.3415	-0.0147	-0.000727
$Q_2^A$	-0.7014	-0.6608	0.5876	0.0084	-0.1726	-0.0330	-0.004062
$T^A$	54.3857	54.5993	75.3874	0.3968	99.8543	7.3589	2.900972
$V_{en}^{AA}$	-129.3892	-129.6904	-184.4199	-0.7517	-243.8116	-16.3471	-6.751391
$V_{ee}^{AA}$	20.8630	20.7466	34.3837	0.0447	44.3978	1.7518	0.950394
$V_{cl}^{AA}$	-102.4366	-102.5803	-141.5102	-0.6397	-188.8937	-12.9159	-4.702448
$V_{xc}^{AA}$	-6.0895	-6.3635	-8.5259	-0.0673	-10.5201	-1.6794	-1.098549
$V_C^{AA}$	26.9525	27.1101	42.9096	0.1120	54.9179	3.4312	2.048943
$V_X^{AA}$	-6.0895	-6.0899	-8.4137	-0.0519	-10.2325	-1.6483	-1.013100
$V_{corr}^{AA}$	0.0000	-0.2736	-0.1122	-0.0154	-0.2876	-0.0310	-0.085449
$\Delta T^A$	-0.0140	0.1852	0.5678	-0.1030	0.2985	-0.0732	0.000052
$\Delta V_{en}^A$	-1.0352	-1.3133	-6.3206	0.2479	-5.1238	0.7989	-0.000189
$\Delta V_{ee}^A$	1.3036	1.1861	5.9043	0.0447	4.7557	-0.5300	0.000464
$E_{net}^A$	-54.1405	-54.3445	-74.6487	-0.3102	-99.5595	-7.2364	-2.900025
$E_{def}^A$	0.2543	0.0579	0.1515	0.1896	-0.0696	0.1956	0.000326
interaction	N-N	N-N	O-H	H-H	Li-F		He-He
$V_{nn}^{AB}$	23.6222	23.6222	4.4199	0.3494	9.1362		0.712697
$V_{en}^{AB}$	-22.1174	-22.1327	-4.8922	-0.1434	-10.0462		-0.712554
$V_{ne}^{AB}$	-22.1174	-22.1327	-1.6458	-0.1434	-6.2778		-0.712554
$V_{ee}^{AB}$	19.9235	20.1843	1.6449	0.0539	6.8579		0.711748
$V_{cl}^{AB}$	0.2348	0.2294	-0.2751	0.1225	-0.2836		0.000001
$V_{xc}^{AB}$	-0.9239	-0.6883	-0.1981	-0.0059	-0.0463		-0.000664
$V_C^{AB}$	20.8474	20.8726	1.8430	0.0598	6.9042		0.712412
$V_{C,lr}^{AB}$	1.51e3	1.29e3	4.96e4	0.1238	6.8241		0.712412
$V_X^{AB}$	-0.9239	-0.8642	-0.2112	-0.0012	-0.0456		-0.000646
$V_{corr}^{AB}$	0.0000	0.1760	0.0131	-0.0048	-0.0007		-0.000018
$E_{int}^{AB}$	-0.6891	-0.4589	-0.4732	0.1166	-0.3299		-0.000664
global							
$E$ (integ)	-108.9700	-109.1479	-76.0991		-107.1258		-5.800713
$E$ (analy)	-108.9696	-109.1480	-76.0986		-107.1258		-5.800702
$\Delta E$	-0.0004	0.0001	-0.0005		1.8e-5		-0.000011
$E_{bind}$	-0.1800	-0.3432	-0.2988		-0.2039		-1.323e-7

<sup>a</sup> Dipoles are positive when the electrons displace toward the internuclear region, quadrupoles correspond to the  $z^2$  spherical component along the bond (the only nonzero one) except for water in which the main component is written ( $x^2 - y^2$  for O with  $z$  the molecular axis,  $yz$  for H with  $z$  the H-O line and  $yz$  the molecular plane). Atomic units are used for all properties.

positive, as mentioned in subsection IIC for homodiatomics, but it falls below its apparent long-distance energy. This is because its value is worse at a very long distance, but not so much near equilibrium, where the HF determinant dominates within the exact wave function. On the other hand, the interaction energy goes to zero much more slowly than with the CAS wave function: this is due to the exchange part, which forces a  $1/r_{HH}$  behavior instead of the cancellation shown by the CAS wave function results. These problems are the main source of error for the HF wave function, which nevertheless can give qualitatively correct results when the depth of the binding energy well is larger (masking the singlet limit dissociation error) or for noncovalent bonding cases. Also, the dominant contributions to either the deformation or the interaction energies can usually be correctly guessed within the HF scheme.

**B. Representative Molecules.** We will now analyze the QTAM energy partition on some molecules representative

of different kinds of bonding. The results for N<sub>2</sub> (both HF and CAS[10,10]), H<sub>2</sub>O, LiF (at their experimental equilibrium distances), and He<sub>2</sub> (at its theoretically predicted<sup>30</sup> equilibrium distance) are gathered in Table 2. Once again, the total charge integration errors are small (the largest is the one in water, with a 0.7 me excess), as are the total energy integration errors (the largest corresponds again to water, with a 0.5 mE<sub>h</sub> defect).

The HF dissociation problem displayed by H<sub>2</sub> persists in N<sub>2</sub>: the HF binding energy is half its CAS value, the deformation more than four times larger, and the interaction is 50% larger in absolute value. In addition, the experimental geometry is away from the HF equilibrium geometry, and so the HF calculation is far from being virial-consistent. This is the reason behind the negative value of  $\Delta T^N$  (-0.0140 E<sub>h</sub>), since the quantum mechanical molecular calculation gives  $2T + V = -0.2 E_h$ , with a clear lack of kinetic energy, whereas the calculation of the isolated atom gives  $2T_{vac} +$

$V_{\text{vac}} = 0.005 E_h$ . On the other hand, the rest of the HF values are surprisingly good, being that the correlation energy (both intra- and interatomic) is the main source of error for this method. Thus, the HF calculation can indeed be used as a qualitative guide of the partition results. Overall, the binding in  $N_2$  shows again a relatively small deformation energy (notice that, in the CAS calculation, it is 36 kcal/mol, 3 orders of magnitude smaller than the net energy), with a large interaction energy ( $-288$  kcal/mol). This interaction is again dominated by the exchange-correlation term, although in this case the classical term is of comparable magnitude (144 kcal/mol versus  $-432$  kcal/mol for the former). This is probably due to the much larger polarization of the N atoms when compared with the H atoms (see the corresponding  $Q_1^A$  dipole values), which is also responsible for the fact that  $E_{\text{def}}^N \gg E_{\text{def}}^H$ .

Compared with Salvador et al. results,<sup>14</sup> our integration accuracy is here an order of magnitude better, due to the considerably denser integration grids we used, but the overall results again agree within the basis set differences (less than  $26 mE_h$  for net, interaction, and total energies) for the HF case.

Let us turn to the  $H_2O$  molecule. Here, the charge transfer as obtained by QTAM is quite large, each H atom having donated more than half an electron to the O atom (notice that there is a  $0.7 m_e$  integration excess, the largest on these calculations, accompanied by a  $-0.5 mE_h$  total energy error, also the largest in absolute value). Surprisingly, atomic dipoles are not very large, nor the  $Q_2^H$  quadrupole, but the  $Q_2^O x^2 - y^2$  component is quite large due to the asymmetry of the molecule. The large charge transfer is responsible for the large deformation energies (about three times the CAS entry for  $N_2$ , for example). In the case of O, the electron increase induces a large energy lowering through  $\Delta V_{\text{en}}^{OO}$ , but this is compensated by a large increase in the interelectronic repulsion and in the kinetic energy. As mentioned before, this behavior is consistent with the traditional ideas of covalent bonding, where there is a charge concentration in the bonding region, and is also displayed here by the O atom, which increases its total charge. However, the behavior is much different in the H atoms, which lose charge. For them, the kinetic energy decreases and the electron–nucleus attraction increases from the free atoms situation, owing to the decrease in the number of electrons, while the electron repulsion increases slightly from its separated atoms zero limit.

Regarding the interaction contributions, there is a clear distinction between the bonded, polar O–H interaction and the nonbonded, nonpolar H–H interaction. The first one displays a large and negative exchange-correlation contribution, as the previous ones considered, but here the classical interaction is also negative and even larger, in contrast with the results for  $H_2$  and  $N_2$ . Clearly, this classical interaction arises from the charge transfer, with a leading point-charge term  $V_Q^{OH} = -0.328 E_h$ . However, the long-range multipolar series does not converge, as shown by the  $V_{C,\text{lr}}^{OH}$  unphysically large value: there is a multipolar overlap (MPOV) contribution,<sup>33</sup> since this is a covalent bond, which makes necessary the use of the proper short-range accounting

in the  $r_{12}^{-1}$  multipolar expansion. The overall O–H interaction energy is thus negative and very large, as much as the one for the traditionally much stronger N–N bond. However, one must remember that, to get the strongly binding classical contribution, the atoms have to suffer a charge transfer and pay a price in an also high deformation energy, so that overall the N–N bond is indeed stronger even than the two O–H bonds together.

On the other hand, the nonbonded H–H interaction has a very different behavior. The exchange-correlation contribution is almost negligible, while the classical term is larger and positive. Once again, this is due to the charge transfer, with the point charge term ( $V_Q^{HH} = 0.104 E_h$ ) accounting for most of the interaction. Nevertheless, the short distance between the H atoms ( $1.51 \text{ \AA}$ ) still induces a poor convergence of the long-range series, and  $V_{C,\text{lr}}^{HH}$ , although not divergent, is still twice the real value of the interatomic  $V_C^{HH}$ . Of course, nonbonded intramolecular interactions at larger distances will eventually display a pure long-range behavior. The sum of the positive classical term and the small negative exchange-correlation term gives a moderately positive H–H interaction, as one would expect.

The final balance of binding in the water molecule is then as follows. The charge transfer induces large and positive deformation energies (95 kcal/mol for O and 119 kcal/mol for H) and a repulsion between the positively charged H atoms (73 kcal/mol) that is mostly of classical origin. However, these positive contributions are more than compensated by the two very strong O–H negative interactions ( $-297$  kcal/mol each): to a relatively large negative exchange-correlation contribution ( $-124$  kcal/mol), proper of covalent systems, it adds a larger negative classical contribution ( $-173$  kcal/mol), coming from the polar nature of the bond.

To increase further the polarity of the bond, we have considered LiF as a molecule widely accepted as ionic. Here, the QTAM charge transfer is almost the purely ionic one, with  $0.93 e$ . The fluorine atom (almost a fluoride anion) polarizes toward the lithium atom (almost a  $\text{Li}^+$  cation), which in turn has a very slight outward polarization. This is consistent with the classical images of polarizable anions and hard, spherical-like cations.<sup>27</sup> In addition,  $\text{F}^-$  is the least polarizable anion, hence its not so large dipole, and  $\text{Li}^+$  is one of the least polarizable cations. There is also a small quadrupolar distortion along the bond.

The large charge-transfer puts so many electrons into the F atom that its deformation energy is *negative*: the electron–nucleus energy decrease more than compensates for the small kinetic energy increase and the electron–electron repulsion increase. However,  $E_{\text{def}}^F$  is small ( $-44$  kcal/mol) when compared with the much larger positive deformation energy of the Li atom (123 kcal/mol). The atom losing charge has negative  $\Delta T^{\text{Li}}$  and  $\Delta V_{\text{ee}}^{\text{LiLi}}$  but a much larger and positive  $\Delta V_{\text{en}}^{\text{LiLi}}$  value (in analogy with the H results in water). In contrast, both deformation energies are small if we take the separated ions as reference: the deformation of the fluoride will be  $-0.019 E_h$  ( $-12$  kcal/mol), that for  $\text{Li}^+$  will be  $0.013 E_h$  (8 kcal/mol), and the binding energy will be  $-0.3361 E_h$  ( $-211$  kcal/mol, which is larger than the nonionic reference



$E_{\text{bind}} = -128$  kcal/mol, since the separated ions are higher in energy than the separated atoms). In fact, their roles are inverted:  $\text{F}^-$  loses charge in entering the molecule, and so  $\Delta T^{\text{F}^-}$  and  $\Delta V_{\text{ee}}^{\text{F}^-}$  are negative for it, with positive  $\Delta V_{\text{en}}^{\text{F}^-}$ , while  $\text{Li}^+$  gains charge upon formation of the molecule, and the increments are opposite. The usefulness of each of these two energy references will depend, of course, on the context, but the ionic image is more appealing, with smaller deformations that hint at a more faithful description of the binding when considering ions as the components to bind. Notice, however, that the interaction energy ( $-207$  kcal/mol) does not depend on this choice, since it is computed for the atoms already within the molecule.

Regarding the partition of the interaction energy, the exchange-correlation contribution is very small ( $-29$  kcal/mol), while the classical interaction is large and negative ( $-178$  kcal/mol). This is the expected behavior in an ionic compound, and in fact the purely point-charge interaction,  $V_{\text{Q}}^{\text{LiF}} = -0.2926 E_{\text{h}}$  ( $-184$  kcal/mol), is within 3% of the total classical value. In this case, this is indeed because of a correct long-range behavior, since  $V_{\text{C,lr}}^{\text{LiF}}$  is also within 2% of  $V_{\text{C}}^{\text{LiF}}$ , and points out that both atoms are almost non-MPOV and also almost spherical, as seen by their small dipoles. Hence, the point charge term is a very good approximation for the classical interaction energy. Overall, the picture for this molecule is that of mostly spherical ions, with a large classical interaction very well approximated by the point charge term. The large energy penalty due to ionization (paid through the deformation energy if we use the neutral atom reference and through the already high reference in the ionic case) is still smaller than the interaction energy gain.

Finally, as an example of a van der Waals bonded system, we have performed a full CI calculation on  $\text{He}_2$  and partitioned its energy. The FCI calculation, using a moderate-size correlation-consistent basis set, displays a very shallow minima, with a binding energy of  $0.042$  K (the FCI, complete basis set extrapolation in ref 30 is  $11$  K). This very low binding energy,  $0.13 \mu E_{\text{h}}$ , is beyond the precision attainable with the numerical integration in a reasonable time. However, using the same numerical integration parameters as in the rest of the calculations (but taking much more time, given the number of active orbitals and determinants), we obtain an error in the total energy of  $11 \mu E_{\text{h}}$ , the lowest in this series of compounds. This is an order of magnitude smaller than most of the partition components, particularly deformation and interaction, and hence we can reliably say that the low binding energy comes from the cancellation of these much larger components. This reliability has two causes: the density matrices are essentially non-MPOV (faster convergence), and the interatomic surface discontinuity lies in a low- $\rho$  region.

$\text{He}_2$  is possibly the worst-case scenario for the cancellation of properties problem: the monatomic components are of the order of units of  $E_{\text{h}}$ , while the deformation is 4 orders of magnitude smaller; the interaction components are of the order of  $0.7 E_{\text{h}}$  (even for this large distance,  $2.97 \text{ \AA}$ , they still decrease as  $1/r$ ), while the total interaction is 3 orders of magnitude smaller. Nevertheless, the  $\Delta X^{\text{He}}$  intra-atomic components display the familiar pattern for homonuclear

systems, being of the same order of magnitude as the deformation energy. In the case of the interaction,  $V_{\text{cl}}^{\text{HeHe}}$  is smaller than  $1 \mu E_{\text{h}}$ , displaying a 6 orders of magnitude cancellation of the electrostatic interactions. This is not so surprising, if we look at the accuracy of the long-range multipolar approximation  $V_{\text{C,lr}}^{\text{HeHe}}$ , exactly matching the complete  $V_{\text{C}}^{\text{HeHe}}$  integral: both He atoms are non-MPOV and neutral, and hence the  $V_{\text{Q}}^{\text{HeHe}}$  point-charge contribution has to be zero, while the other multipolar components fall much faster with distance (the classical point dipole–point dipole interaction will be about  $3 \text{ nE}_{\text{h}}$ ). On the other hand, the exchange-correlation component comprises most of the interaction energy in  $\text{He}_2$ . The image is, then, that of a very small polarization of the two atoms, having a negligible effect in the classical energy, with a small but non-negligible deformation energy; the binding component in the interaction is the exchange-correlation, as expected for a dispersion-bound system, although the binding energy value comes after the 3 orders of magnitude cancellation of these two (interaction and deformation) terms.

#### IV. Conclusions and Perspectives

An energy partition based on QTAM but using ideas from McWeeny's TES is proposed that splits the total energy exhaustively into atomic contributions, both intra- and interatomic. The partition recovers many chemical concepts and an atomistic intuition about binding, by recognizing the importance of the large contributions of the intra-atomic energy, which should show little variation from compound to compound for a given atom, and the smaller interatomic components that vary with the different types of interactions. In particular, this partition can fully account for the definition and maintained identity of functional groups and can treat on the same footing bonded and nonbonded interactions and even intermolecular ones. Being based on QTAM, its atoms have well-defined kinetic energies and are transferable while at the same time making the partition independent of any arbitrariness in the wave function calculation: everything (including the atomic basins) is derived from the first- and second-order density matrices, and hence it is truly a physical property of the system. It can be applied both to single-determinant (HF) and multideterminant approximate wave functions.

The partition acknowledges the existence of large cancellations to recover the binding energy, both in the intra-atomic and in the classical interatomic terms, coming from the essentially unchanged and neutral atoms that form the molecules in many cases of interest. The resulting terms are not so small when there is charge transfer, since varying the number of electrons undoubtedly changes the intra-atomic energies, while the electrostatic interaction between charged systems is quite large. Usually, the intra-atomic deformation terms are positive, and they are larger in absolute value for atoms with stronger and shorter bonds and whenever there is a large charge transfer. Homopolar-bonded and negatively charged atoms generally suffer a kinetic and electron repulsion energy increase which is partially compensated by a corresponding decrease in the nucleus–electron attraction energy, while the opposite happens with atoms losing

electron density. The interaction energy is usually larger than the deformation terms, and hence binding can be seen as the tradeoff of a small intra-atomic deformation energy increase by a much larger decrease due to the interatomic interaction energy. The interaction energies in bonded pairs are generally negative and large, while nonbonded interactions (either intramolecular or intermolecular) are much smaller and can often be approximated by point multipolar series, neglecting both short-range classical and exchange-correlation contributions.

Regarding the different patterns for different kinds of bonds, we have found the covalent homopolar bonds to have a small deformation energy, with a large and negative exchange-correlation interaction contribution as mainly responsible for binding. Their classical interaction is usually small and positive, as it should be for neutral, nonpenetrating charge systems; however, they display MPOV, and hence the point-multipole long-range contributions diverge and cannot be properly used. Ionic bonds have atoms with large deformation energies due to the charge transfer, but they are more than compensated by the large and negative classical interactions, where the point-charge term already accounts for 90% of the interaction energy. For them, the long-range multipolar approach is convergent and accurate to reproduce the classical energy, due to their small MPOV, and the exchange-correlation interaction is very small. The case of polar covalent bonds is intermediate: the deformation is dependent on the charge transfer extent, and both the covalent-like exchange-correlation and the ionic-like classical attraction terms are present and comparable in value. For them, the point-charge estimation gives the correct trend for the classical interaction, but the long-range multipolar series does not converge due to the covalent-like MPOV. Finally, van der Waals interactions are exceedingly weak when compared with bonded ones; in a dispersion-bound system like He<sub>2</sub>, the classical interaction is negligible, and only exchange-correlation constitutes an attractive term.

In summary, we have presented a powerful tool to quantitatively analyze both the intra- and interatomic components of the molecular energy and relate them to the chemical concepts of bonding. Our results in selected molecules give plausible trends, which we have also seen in other preliminary calculations, making a consistent and appealing image of the physical atomistic components in the different chemical bonds. We plan to expand this study to other chemical systems of interest, on one hand, and to generalize it to different atomic partitions and compare their results, on the other.

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### References

- (1) Jensen, F. *Introduction to Computational Chemistry*; Wiley: Chichester, 1999.
- (2) Ruedenberg, K. *Rev. Mod. Phys.* **1962**, *34*, 326.
- (3) Kitaura, K.; Morokuma, K. *Int. J. Quantum Chem.* **1976**, *10*, 325.
- (4) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558 and 1755.
- (5) Bagus, P. S.; Hermann, K.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1984**, *80*, 4378.
- (6) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
- (7) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
- (8) Bader, R. F. W. *Atoms in Molecules*; Oxford University Press: Oxford, 1990.
- (9) Glendening, E. D.; Streitwieser, A. *J. Chem. Phys.* **1994**, *100*, 2900–2909.
- (10) Mo, Y.; Gao, J.; Peyerimhoff, S. D. *J. Chem. Phys.* **2000**, *112*, 5530.
- (11) Pophristic, V.; Goodman, L. *Nature* **2001**, *431*, 565.
- (12) Bickelhaupt, F. M.; Baerends, E. J. *Angew. Chem., Int. Ed.* **2003**, *115*, 4315.
- (13) Frenking, G.; et al. *Coord. Chem. Rev.* **2003**, *238–239*, 55.
- (14) Salvador, P.; Duran, M.; Mayer, I. *J. Chem. Phys.* **2001**, *115*, 1153–57.
- (15) Salvador, P.; Mayer, I. *J. Chem. Phys.* **2004**, *120*, 5046.
- (16) Popelier, P. L. A.; Kosov, D. S. *J. Chem. Phys.* **2001**, *114*, 6539–47.
- (17) Martín Pendás, A.; Blanco, M. A.; Francisco, E. *J. Chem. Phys.* **2004**, *120*, 4581–92.
- (18) Martín Pendás, A.; Francisco, E.; Blanco, M. A. *J. Comput. Chem.* **2005**, *26*, 344–351.
- (19) McWeeny, R. *Methods of Molecular Quantum Mechanics*, 2nd ed.; Academic Press: London, 1992.
- (20) Bader, R. F. W.; Preston, H. J. T. *Int. J. Quantum Chem.* **1969**, *3*, 327.
- (21) Bader, R. F. W.; Beddall, P. M. *J. Chem. Phys.* **1972**, *56*, 3320.
- (22) Srebrenik, S.; Bader, R. F. W. *J. Chem. Phys.* **1975**, *63*, 3945.
- (23) Li, L.; Parr, R. G. *J. Chem. Phys.* **1986**, *84*, 1704.
- (24) Born, M.; Huang, K. *Dynamical Theory of Crystal Lattices*; Oxford University Press: Oxford, 1954.
- (25) Hirschfelder, J. O.; Curtis, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1954.
- (26) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Clarendon Press: Oxford, 1987.
- (27) Luaña, V.; Pueyo, L. *Phys. Rev. B* **1990**, *41*, 3800–3814.
- (28) Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419.
- (29) Schmidt, M. W.; et al. *J. Comput. Chem.* **1993**, *14*, 1347.
- (30) van Mourik, T.; Dunning, T. H., Jr. *J. Chem. Phys.* **1999**, *111*, 9248.
- (31) Costales, A.; Blanco, M. A.; Mori-Sánchez, P.; Luaña, V.; Martín Pendás, A. *J. Phys. Chem. A* **2004**, *108*, 2794–801.
- (32) Slater, J. C. *Quantum Theory of Molecules and Solids*; McGraw-Hill: New York, 1963; Vol. 1.
- (33) As discussed in ref 17, an overlap contribution in the sense of the multipolar expansion occurs when the sum of the maximum radii of both atomic basins surpasses the interatomic distance,  $R_A + R_B > r_{AB}$ , making invalid the long-range multipolar approximation; see Figure 2 of that paper.