# Pauling Resonant Structures in Real Space through Electron Number Probability Distributions

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

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

*Received: July 20, 2006; In Final Form: November 6, 2006*

A general hierarchy of the coarsed−grained electron probability distributions induced by exhaustive partitions of the physical space is presented. It is argued that when the space is partitioned into atomic regions the consideration of these distributions may provide a first step toward an orbital invariant treatment of resonant structures. We also show that, in this case, the total molecular energy and its components may be partitioned into structure contributions, providing a fruitful extension of the recently developed interacting quantum atoms approach (*J. Chem. Theory Comput.* **2005**, *1*, 1096). The above ideas are explored in the hydrogen molecule, where a complete statistical and energetic decomposition into covalent and ionic terms is presented.

## I. Introduction

Real space analyses of wavefunctions have grown over the years into recognized alternatives to orbital theories of the chemical bond.[1] After all, chemistry is still being taught as something that takes place in the physical, not the Hilbert, space.

A central tenet of many of these techniques is the existence of regions in space that are to be identified with chemically meaningful concepts, i.e., atoms, bonds, cores, lone pairs, etc. In many of these descriptions, this is done by exhaustively partitioning the 3D space into appropriately defined domains. In others, these regions, usually atoms, are allowed to penetrate each other, and each point in space is shared by many of the elements according to well-defined rules (see ref 2, for instance, for a discussion of some particular implementations of exhaustive and fuzzy prescriptions).

Fuzzy atomic decompositions are not completely compatible with a pure real space viewpoint. Using only spatial requirements, once the position of a given electron is determined the indistinguishability principle should prevent us from recovering its original affiliation and assign it to atom A or atom B with given probabilities. To avoid these kinds of problems, electrons should be associated to spatial regions using geometrical criteria, leading to exhaustive partitions of the physical space.

These are usually obtained from the topologies induced by the gradient fields of appropriate scalar fields. Two well developed examples of nonfuzzy decompositions are based on the attraction basins of (i) the charge density $\rho$, an approach which becomes the quantum theory of atoms in molecules (QTAM), extensively developed by Bader and co-workers;[3] and (ii) the electron localization function (ELF) of Becke and Edgecombe[4] which has been thoroughly studied in the past decade by Savin,[5−10] Silvi,[11−13] and others.[14]

The aim of this paper is twofold. First we will show how to define coarse grained probability distributions from exhaustive topological partitions of $R^3$ in molecules. We think that they provide a first step in the investigation of Pauling's concept of resonance within an orbital invariant formalism. In order to do so, we will identify each possible partition of the $N$ electrons of the molecule into the $m$ nuclei as a resonant structure. This does not cover all of the resonance definitions proposed over the years, but we may consider the analogy as a good starting point. Second, we will show how to decompose the molecular energy into resonant contributions, a procedure not exempt from a certain degree of arbitrariness. Our work is reminiscent of the theory of loges proposed long ago by Daudel.[15−17] In fact, there are recent relevant developments along similar lines, as we will briefly comment on below.[18,19]

The rest of the paper is organized as follows. In section II, we define the coarse grained distributions and several magnitudes that are used throughout the paper. Section III deals with the resonant structure energetic decomposition, and section IV applies all of the former ideas to the simplest $H_2$ molecule, commenting upon the fruitful relationship between the present results and those of the interacting quantum atoms (IQA) approach to the chemical bond. The latter is a recently proposed energy decomposition scheme completely compatible with the QTAM.[20−22] We will end with some conclusions.

## II. Basic Definitions

Any exhaustive partition $P$ of the 3D space may be envisaged as a coarse−grained mapping of the set $\boldsymbol{r} \in R^3$ onto the set of mutually exclusive basins of the partition $\Omega_i$ such that $P: \boldsymbol{r} \rightarrow \Omega_i$, $\boldsymbol{r} \in \Omega_i$. All points belonging to a given basin are then replaced by the basin itself. This coarse−graining may be translated, either partially or totally, to the $N$−electron density matrix (DM), or probability density $\rho_N(1, ..., N) = \Psi^*(1, ..., N)\Psi(1, ..., N)$, to define coarse−grained density matrices (CGDMs). To that end, it is convenient to introduce $\bar{\Omega}_i$ (or simply $\bar{\imath}$) as the complement of the $\Omega_i$ (or simply $i$) basin. Coarse−graining the electrons of the system in real space is then equivalent to averaging the positions of some (partial condensation) or all (total condensation) of the electrons over a set of basins of the 3D partition. Total condensation provides a partition of the electron system into basins. If the latter are associated to nuclei, as done by using the QTAM,[3] the partition of the $N$ electrons into the $m$ nuclei of the molecule will provide our real space image of a resonant structure.

---

* To whom correspondence should be addressed.

10.1021/jp064600h CCC: $37.00

Let us then coarse-grain (or condense, or basin average) the general $\rho_N$. We will consider a finite number of basins 1, ..., $m$ ordered in some prescribed canonical way $\Omega_1, ..., \Omega_m$, such that $\Omega_1 \cup ... \cup \Omega_m = R^3$. The extension to an infinite number of basins (as is the case in crystals) is done easily. Now we will condense $c_1, ..., c_m$ electrons over each of the basins $\Omega_1, ..., \Omega_m$. Notice that any of these numbers may be zero, that all of the basins are mutually exclusive, and that the total number of condensed electrons needs not exhaust $N$, $c_1 + ... + c_m = \mathcal{N} \leq N$. The remaining non−condensed $i = N - \mathcal{N}$ electrons are situated at the $\boldsymbol{r}_1, ..., \boldsymbol{r}_i$ positions. Each of these positions necessarily belongs to a basin (save the null measure set formed by basin boundaries, with no consequences), and we will specify it by a superindex when necessary, for instance, $\boldsymbol{r}_1^{\alpha}$, $\boldsymbol{r}_2^{\beta}$, etc, where $\alpha$ needs not be $\Omega_1$, etc. The total number of electrons within a general basin $\alpha$ ($n^{\alpha}$) is given by the sum of the number of condensed ($c^{\alpha}$) and free ($f^{\alpha}$) electrons in it ($n^{\alpha} = c^{\alpha} + f^{\alpha}$). A coarse−graining or condensation $C$ is a partition of the $\mathcal{N} = N - i$ electron system into basins, determined by the vector of $m$ ordered integers $\boldsymbol{C} = (c_1, ..., c_m)$, with $c_j = c^{\Omega_j}$. Similarly, the basin adscription of the free electrons is specified by a $\boldsymbol{F}$ vector, $\boldsymbol{F} = (f_1, ..., f_m)$, with $f_j = f^{\Omega_j}$. The $\boldsymbol{S} = \boldsymbol{C} + \boldsymbol{F} = (n_1, ..., n_m)$ object, describing the total number of electrons in each basin is called a (resonant) structure. In these expressions, $c_j$, $f_j$, and $n_j$ refer to $c^{\Omega_j}$, $f^{\Omega_j}$, and $n^{\Omega_j}$, respectively, and no confusion between canonically ordered basins, associated with subindices, and general basins, labeled with superindices, should arise. For completeness, $\sum_j f_j = i$, $\sum_j c_j = \mathcal{N}$, and $\sum_j n_j = N$. Boldface symbols will only be used when their vector realization needs be highlighted.

Taken together, the CGDM describing the probability of such condensed configurations will be an $i$th order DM, and we will use a notation in which noncondensed electron positions are written in parenthesis, as usual, and the condensation inside brackets. If the basin asssociated to each free position is also specified, we will give the structure in brackets. In this notation $\rho_i(\boldsymbol{r}_1, ..., \boldsymbol{r}_i)[C]$ describes the probabiliy density that any set of $i$ electrons be located at $\boldsymbol{r}_1, ..., \boldsymbol{r}_i$, within condensation $\boldsymbol{C}$, and $\rho_i(\boldsymbol{r}_1^{\alpha}, ..., \boldsymbol{r}_i^{\iota})[C]$, the same object with respect to structure $\boldsymbol{S} = \boldsymbol{C} + \boldsymbol{F}$, where we should note that $\boldsymbol{F}$ is also determined by the $\boldsymbol{r}_1^{\alpha}$, ..., $\boldsymbol{r}_i^{\iota}$) set. Care should be taken on the physical interpretation of structure CGDMs. Each basin (e.g., $\alpha$) contains a fixed integer number of electrons, condensed and not condensed. This means that the apparently continuous variables $r_1, ..., r_i$ cannot cross the boundaries of their associated basins and enter others. When this happens, a change occurs in $\boldsymbol{F}$, and thus in $\boldsymbol{S}$, but not in the condensation $\boldsymbol{C}$, and that is why CGDMs are to be labeled with $\boldsymbol{C}$. Other definitions of CGDMs are possible, but as our interest in this paper is focused on resonant structures, we will stay with the above constraints.

Taking into account the indistinguishability of the full set of electrons, we may write

$$\rho_i(\boldsymbol{r}_1, ..., \boldsymbol{r}_i)[C] = I \int_{D_C} d\boldsymbol{r}_{i+1} \ldots d\boldsymbol{r}_N \, \rho_N(1, \ldots, N), \quad (1)$$

where $D_C$ is a domain such that electrons $(i + 1)$ to $(i + c_1)$ are integrated over basin $\Omega_1$, electrons $(i + c_1 + 1)$ to $(i + c_1 + c_2)$ over basin $\Omega_2$, etc, until each of the condensed electrons has been integrated over its associated basin. $I = N!/(i!c_1 \cdots c_m!)$ is the indistinguishability factor taking care of all permutations among equivalent groups of electrons.

Transition DMs may also be coarse−grained in a similar manner

$$\rho_i(\boldsymbol{r}_1', \ldots, \boldsymbol{r}_i'; \boldsymbol{r}_1, \ldots, \boldsymbol{r}_i)[\mathrm{C}] = I \int_{D_C} d\boldsymbol{r}_{i+1} \ldots d\boldsymbol{r}_N$$
$$\rho_N(1' \ldots, i', i + 1 \ldots N; 1 \ldots, i, i + 1 \ldots N) \quad (2)$$

Since all subsequent definitions regarding transition DMs may be obtained straightforwardly from the previous ideas, we will not comment further on them.

It may be shown that the traditional total reduced DMs are obtained by adding the above CGDMs over all possible condensations of $\mathcal{N} = N - i$ electrons

$$\rho_i(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_i) = \sum_{\{C\}} \rho_i(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_i)[C] \quad (3)$$

It is also to be noticed that any CGDM may be obtained by a suitable combination of the set here described.

The zeroth order total DM, obtained when only one basin is considered, and so with $C \equiv S = (N)$, and $\Omega_1 = R^3$, is $\rho_0()[N] = 1$, and keeps no relevant information, being a consequence of normalization or conservation of the number of electrons. Their equivalent zeroth-order CGDMs, however, provide the coarse−grained probability distributions (CGPDs) of the set of electrons into basins. We will use $p$ instead of $\rho_0()$ and will notice that condensations and structures are equivalent in this case. Thus

$$p(S) = \rho_0()[S \equiv C] = p(n_1, ..., n_m) \quad (4)$$

is the probability of finding the $N$ electrons distributed according to $S \equiv C$. Every CGDM may be normalized according to its associated CGPD to construct conditional measures. For instance

$$\rho(\boldsymbol{r}_1^{\alpha}|S) = \frac{\rho(\boldsymbol{r}_1^{\alpha})[\boldsymbol{S} - \boldsymbol{F}]}{p(S)} \quad (5)$$

is the conditional probability of finding any electron in basin $\alpha$ within structure $S$, with an $\boldsymbol{F}$ vector which has only one element different from zero (and equal to 1) for basin $\alpha$. This magnitude integrates to $n^{\alpha} = c^{\alpha} + 1$, the number of electrons in the basin.

It is many times relevant to consider only a subset of $k$ basins ($\alpha$, ...,$\kappa$) out of the $m$ basins in the original partition. This may be done by considering a new partitioning composed of $k + 1$ basins: the subset of interest plus a new basin formed by the union of the rest in the original set. For instance, indicating explicitly the number and basin occupied by each set of electrons

$$p(n^{\alpha}, ..., n^{\kappa}) = \rho_0[n^{\alpha}, ..., n^{\kappa}, (N - \mathcal{N}')^{\bar{A}}] \quad (6)$$

with $\mathcal{N}' = n\alpha + ... + n^{\kappa} < N$, and $A = \alpha \cup ... \cup \kappa$, is the probability that exactly $n^{\alpha}, ..., n^{\kappa}$ electrons lie within the $\alpha$, ..., $\kappa$ basins, $k < m$, respectively. It must be stressed again that the $n^{\alpha}, ..., n^{\kappa}$ labels do not necessarily keep the canonical order, and should therefore not be confused with the $n_i$'s used before, that do keep that order.

Particularly interesting are the one−basin electron distribution functions, $p(n^{\alpha})$, $0 \leq n^{\alpha} \leq N$. These have been studied by Savin and co-workers,[23−25] who have shown with clever algebraic rearrangements that they may be obtained easily from basin overlap matrices in monodeterminantal cases. The $p(n^{\alpha})$ values obtained in simple molecules behave in a Gaussian manner and, in some simple circumstances, correspond faithfully to binomial distributions that point toward the almost independency of the electrons under scrutiny. Once we have a full distribution function, any basin population average may be obtained from the $p(n^{\alpha})$ set. For instance, the average number of electrons in basin α, $\langle N\rangle_\alpha$, is $\langle N\rangle_\alpha = \sum_{n=0}^{n=N} np(n^\alpha)$. Relevant work related to these ideas is also found in more recent papers by Savin et al.[18,26] and by Ponec, Bochicchio, and co-workers.[19,27,28]

### III. Energy Decomposition Into Resonant Structures

Let us now further develop the concept of resonant structure in real space by considering atomic basins. As advanced, we will consider $S = (n_1, ..., n_m)$ as a partition of the $N = n_1 + ... + n_m$ electrons of a molecular system that assigns a given number of electrons (including possibly 0) to each of the $m$ nuclei of the molecule, which are supposed to be given in a certain canonical order 1, ..., $m$. As before, the basin of nucleus $i$ will be $\Omega_i$. There are $N_S = (N + m - 1)!/(N!(m - 1)!)$ of these structures, a combinatorial number equal to 3 in $H_2$, that rises to 66 in $H_2O$ or 286 in $NH_3$, and climbs to 76 223 753 060 in benzene. To construct such an object, we just need a theoretically sound partition of the physical space into atomic regions, which is standardly provided by the QTAM.[3] It is clear that

$$\sum_{\{S\}} p(S) \equiv \sum_{\{S\}} p(n_1, ..., n_m) = 1 \tag{7}$$

so we may consider $p(S)$ as an invariant definition of the weight of a given resonant structure, a figure that may be obtained from the wavefunction of a system, or a model of it. No assumptions or prescriptions coming from the particular origin of the wavefunctions are needed. Moreover, chemical intuition assures us that only a relatively small number of structures will significantly contribute to molecular properties. For instance, we may easily anticipate that the weights associated to structures containing all the 42 electrons of $C_6H_6$ condensed on one of the H atoms will be negligible.

Since the total molecular energy is determined under the usual Coulomb Hamiltonian by the first (diagonal and non−diagonal) and second order (diagonal) density matrices, all its expectation values may be obtained in terms of the (transition) CGDMs. Let us then decompose the expectation value of the electronic molecular Hamiltonian, $H_{\text{el}} = H_1 + H_2$ where $H_1 = \sum_i^N h_i$, and $H_2 = \sum_{i>j}^N r_{ij}^{-1}$, into coarse−grained components. There are $m^N$

$$E_{\text{el}} = \sum_{\underbrace{i,\ldots,k}_{N} = 1}^{m} \int_{\Omega_i} d1 \cdots \int_{\Omega_k} dN \; \Psi^*(1,\ldots,N) H_{\text{el}} \Psi(1,\ldots,N). \tag{8}$$

terms in the above sum, which may be grouped into classes corresponding to each of the $N_S$ resonant structures. Each structure $S = (n_1, n_2, \ldots, n_m)$ is represented by $n_S = N!/(n_1!, n_2!\ldots n_m!)$ terms obtained from the several ways in which the set of $N$ electrons may be distributed in $S$. This factor is a consequence of electron indistinguishability, and $\sum_{\{S\}} n_S = N_S$. As $H_{\text{el}}$ is symmetric with respect to electron permutations, each of these terms is equal, and a structure is characterized by a particular contribution to the expectation value, or *energy contribution of the structure*, $E_{\text{el}} = \sum_{\{S\}} \langle H_{\text{el}}\rangle_S$.

Let us consider one representant $R_S$ of the structure $S$, namely, any of the $n_S$ terms described above. A simple choice is that given by the natural ordering, in which electrons 1 to $n_1$ are within basin $\Omega_1$, electrons $n_1 + 1$ to $n_1 + n_2$ within basin $\Omega_2$, and so on. Then, $\langle H_{\text{el}}\rangle_S = n_S\langle H_{\text{el}}\rangle_{R_S}$, and it is sufficient to compute the expectation value of each of the structures' representants to reconstruct the energy. Using eqs 2 and 8, the monoelectronic component of $\langle H_{\text{el}}\rangle_{R_S}$ turns out to be a sum of $N$ terms

$$\langle H_1\rangle_{R_S} = \sum_{i=1}^{N} \Pi_{1i} \int_{W_1} \mathrm{d}1\, h_1 \rho_N(1, 2, ..., N; 1', 2, ..., N) \tag{9}$$

where $\Pi_{ij}$ exchanges electrons $i$ and $j$ together with their basins and $W_i$ is the basin of electron $i$ according to the above natural order. Since, in general, the $i$th basin contains $n_i$ electrons, the above sum is composed of $m$ groups with $\{n_i\}_{i=1,m}$ identical terms. Using our CGDMs

$$\langle H_1\rangle_S = \sum_{i=1}^{m} \int_{\Omega_i} \mathrm{d}\boldsymbol{r}\, h\, \rho(\boldsymbol{r}; \boldsymbol{r}'^{\Omega_i})[C_i] \tag{10}$$

where $C_i$ is the condensation associated to $S$ when a free electron lies in basin $\Omega_i$. Thus the monoelectronic component due to structure $S$ is a sum of atomic contributions, as it is for the complete system. Notice that when $\Omega_i$ changes in the above sum, the condensation $C$, and therefore the indistinguishability factors $I$ of eq 1, change even if the structure $S$ remains the same.

As $h$ is a sum of kinetic and potential terms, $h = t + \upsilon$, where $\upsilon$ is usually due exclusively to electron−nucleus terms $\upsilon = -\sum_i^m Z_i/r_i$, each atomic contribution to the electron−nucleus potential will be the sum of intra- and internuclear attractions, just as in the usual QTAM or IQA energetic partitions.[22] Separating these terms, we get

$$\langle H_1\rangle_S = \sum_{i=1}^{m} T^i(S) + \sum_{i,j=1}^{m} V_{en}^{ij}(S) \tag{11}$$

where $T^i(S)$ and $V_{en}^{ij}(S)$ are the contributions to the kinetic energy of atom $i$ and to the attraction between the electrons in atom $i$ and the nucleus of atom $j$ coming from structure $S$, respectively.

It is very important to notice that the Hermitian character of the kinetic energy operator in subsystems is only guaranteed when the boundary of the domain is a zero−flux surface for the gradient field that corresponds to the density upon which $t$ acts. This condition defines the QTAM basins, which are obtained from the total electron density $\rho$, but does not necessarily apply to each of the structure densities, $\rho(\boldsymbol{r}^{\Omega_i}|S)$. This means that each of the $T^i(S)$ kinetic energies are not well−defined, and that one will obtain slightly different expectation values by using different $t$ forms, like $k = (-\hbar^2/2m)\nabla^2$ or $g = (\hbar^2/4m)\nabla\cdot\nabla'$.

The above reasonings may be extended straightforwardly to the $H_2$ energetic component. Using now the two−basin second-order CGDMs, $\langle H_2\rangle_S$ becomes

$$\langle H_2\rangle_S = \sum_{i}^{m} \int_{\Omega_i} d\boldsymbol{r}_1 \int_{\Omega_i} \mathrm{d}\boldsymbol{r}_2\, r_{12}^{-1} \rho_2(\boldsymbol{r}_1^{\Omega_i}, \boldsymbol{r}_2^{\Omega_j})[C_{ii}] + 2\sum_{i>j}^{m} \int_{\Omega_i} d\boldsymbol{r}_1 \int_{\Omega_j} \mathrm{d}\boldsymbol{r}_2\, r_{12}^{-1} \rho_2(\boldsymbol{r}_1^{\Omega_i}, \boldsymbol{r}_2^{\Omega_j})[C_{ij}] \tag{12}$$

with $C_{ii}$, $C_{ij}$ the condensations coming from $S$ on freeing two electrons in basin $\Omega_i$, or in basins $\Omega_i$, $\Omega_j$, respectively. This is a straightforward decomposition of the contribution of structure $S$ to the total interelectron repulsion into intra− and interbasin terms. Joining terms we get

$$\langle H_{\mathrm{el}}\rangle_S = \sum_i^m \{T^i(S) + V_{ee}^{ii}(S) + V_{en}^{ii}(S)\} + \sum_{i>j}^m \{V_{ee}^{ij}(S) + V_{en}^{ij}(S) + V_{en}^{ji}(S)\} = \sum_i^m E_{\mathrm{self}}^i(S) + \sum_{i>j}^m V_{\mathrm{int,el}}^{ij}(S) \quad (13)$$

where we have defined the atomic self−energy contribution, and the electronic part of the interatomic potential. The definitions of $V_{ee}^{ii}$ and $V_{ee}^{ij}$ are obtained by directly comparing eqs 10, 12, and 13. Had we used the conditional densities of eq 5 instead of joint probability densities, we would have obtained the electronic energy of the structure. That is, its contribution to the energy, were the probability of $S$ be equal to one. Let us denote these normalized quantities with a tilde. For instance, $\tilde{T}^i(S) = T^i(S)/p(S)$, where $p(S)$ is the structure's probability of eq 7. We may further define the total normalized interbasin interaction potential of a structure by adding the corresponding nuclear repulsion term, $\tilde{V}_{\mathrm{int}}^{ij}(S) = \tilde{V}_{\mathrm{int,el}}^{ij}(S) + 1/R_{ij}$, and use it to construct the total normalized energy of the structure, such that the molecular total energy is a weighted sum of the normalized energies of the structures

$$\tilde{E}(S) = \sum_i^m \tilde{E}_{\mathrm{self}}^i(S) + \sum_{i>j}^m \tilde{V}_{\mathrm{int}}^{ij}(S)$$

$$E = \sum_{\{S\}} p(S)\tilde{E}(S) \quad (15)$$

## IV. Example. The $H_2$ Molecule

Let us apply the above proposed decomposition to the two−electron ground state dihydrogen molecule. We will examine both Hartree−Fock (HF) and correlated models to pinpoint the statistical signatures of electron correlation. Here, symmetry determines the QTAM basins of both atoms, $A$ and $B$, which are equivalent and whose separatrix is the plane orthogonal to the H−H axis that intersects the axis at its midpoint. All calculations have been performed with our PROMOLDEN code, which will be soon generalized in order to cope with resonant structures in multielectron systems.

As commented in the last section, $H_2$ has three possible resonant structures. If we choose the nuclei in the $A$, $B$ order, these are $S_1 = (1, 1)$, $S_2 = (2, 0)$, $S_3 = (0, 2)$, which clearly correspond to the covalent and the two ionic standard Lewis forms. Symmetry imposes that $S_2 \equiv S_3$, and all energetic magnitudes of both structures will be identical. We have selected three representative internuclear distances, $R_{AB} = 1.4$, 4.0, and 6.0 bohr to evaluate the evolution of magnitudes from the molecular to the isolated atoms limit. Since our purposes are illustrative, a simple 6-311G(p) basis set has been chosen except when explicitly stated. We will first comment on the total energy decomposition provided by IQA and then we will present the energy partition at the structure level.

**A. IQA Partition and General Comments.** Table 1 gathers the most important energetic magnitudes for the global IQA partition, both at the HF and complete active space (CAS)[2,2] levels. Just bearing in mind the idea of resonance in real space helps rationalize many interesting facts partially put forward in ref 22. If we start examining monocentric contributions, for instance, we immediately see that, despite considerable redistributions in each quantity with respect to the infinite distance limit, the self−energy of the hydrogen atom is very close to $-0.5\ E_h$ at the CAS level. The difference between the atomic self−energy in a molecule and a reference (usually in vacuo) is known as deformation energy, $E_{\mathrm{def}}^A = E_{\mathrm{self}}^A - E_{\mathrm{self}}^{A,0}$, and it is a basic tenet of the IQA approach that deformation energies are small magnitudes in the absence of large charge transfers. In IQA, binding results from a competition between (usually) repulsive deformations and overall attractive interactions. As we can see, it turns out necessary for $E_{\mathrm{def}}$ to be small that a non-negligible $V_{ee}^{AA}$ value be present. This is electron repulsion within one basin, that in $H_2$ has to be associated to the ionic structures, since in the covalent one there is one electron in each basin. $V_{ee}^{AA}$ is then exclusively due to structure $S_2$, and the origin of the failure of the HF model at large distances is made evident. $p(2, 0)$ is fixed at 1/4 in the HF solution (see below), and there is a 25% probability of finding the $S_2$ or $S_3$ structures at any distance that introduces a severe $V_{ee}^{AA}$ penalty. Even the simplest CAS[2,2] solution allows $p(2, 0)$ to vanish as the $R_{AB}$ distance increases, so the covalent structure is the correct infinite limit with $V_{ee}^{AA} = 0$.

**TABLE 1: Some Global IQA Magnitudes for 6-311G(p) $H_2$ at the HF (First Three Columns) and CAS[2,2] (Last Three Columns) Levels**[a]

| | HF | | | CAS | | |
|---|---|---|---|---|---|---|
| $R_{AB}$ | 1.4 | 4.0 | 6.0 | 1.4 | 4.0 | 6.0 |
| $T^A$ | 0.5611 | 0.3307 | 0.3386 | 0.5808 | 0.4689 | 0.4972 |
| $V_{en}^{AA}$ | −1.2161 | −0.8572 | −0.8344 | −1.2282 | −0.9837 | −0.9980 |
| $V_{ee}^{AA}$ | 0.1957 | 0.1348 | 0.1281 | 0.1629 | 0.0232 | 0.0021 |
| $V_C^{AA}$ | 0.3913 | 0.2696 | 0.2562 | 0.3996 | 0.3095 | 0.3121 |
| $V_{xc}^{AA}$ | −0.1957 | −0.1348 | −0.1281 | −0.2367 | −0.2863 | −0.3100 |
| $V_X^{AA}$ | −0.1957 | −0.1348 | −0.1281 | −0.1989 | −0.1518 | −0.1554 |
| $E_{self}^A$ | −0.4582 | −0.3917 | −0.3677 | −0.4845 | −0.4916 | −0.4986 |
| $V_{en}^{AB}$ | −0.5981 | −0.2529 | −0.1696 | −0.5980 | −0.2487 | −0.1664 |
| $V_{ee}^{AB}$ | 0.2861 | 0.1231 | 0.0833 | 0.2997 | 0.2179 | 0.1632 |
| $V_C^{AB}$ | 0.5723 | 0.2462 | 0.1665 | 0.5244 | 0.2476 | 0.1662 |
| $V_{xc}^{AB}$ | −0.2862 | −0.1231 | −0.0833 | −0.2247 | −0.0298 | −0.0030 |
| $V_X^{AB}$ | −0.2862 | −0.1231 | −0.0833 | −0.2526 | −0.0371 | −0.0024 |
| $V_{int}^{AB}$ | −0.1958 | −0.1327 | −0.0893 | −0.1820 | −0.0296 | −0.0030 |
| $p(1,1)$ | 0.5000 | 0.5000 | 0.5000 | 0.5832 | 0.9027 | 0.9877 |
| $p(2,0)$ | 0.2500 | 0.2500 | 0.2500 | 0.2084 | 0.0487 | 0.0062 |

[a] All magnitudes have been defined in the text for a given structure, except $V_C$, $V_{xc}$, and $V_X$, which are the Coulomb, exchange−correlation, and pure exchange components of the interelectron repulsion, respectively. All data are in a.u.

A similar analysis may be done for the interaction energetic components. One of the most interesting terms is $V_{ee}^{AB}$, which may only result this time from the covalent structure $S_1$. This number tends correctly to its Coulombic contribution (which in the infinite distance limit is $1/R_{AB}$) in the correlated description, but erroneously goes to $1/(2R_{AB})$ in the HF model. Again, a look at the constant $p(1, 1) = 1/2$ value clarifies this issue. A significant fact deserves due consideration. It regards the role of the quantum-mechanical $V_{xc}^{AB}$ term at large distances. As we see, it tends to be indistinguishable from the total interaction energy, $V_{int}^{AB}$, in the CAS description. This only means that all other classical interaction terms, $V_{en}^{AB} = V_{en}^{BA}$, $V_{nn}^{AB}$, and $V_{\mathrm{C}}^{AB}$ cancel among them, leaving non-classical behavior as the only source of cohesion at large distance.[22]

Let us proceed with the statistical features of the electron distribution in relation with our present motives. $H_2$ has no pure, equal−spin Fermi correlation, so at the HF level, i.e., without taking into account Coulomb correlation, all Fermi effects are due to improper electron counting, or self-interaction. From the statistical point of view, the two electrons are independent objects in HF $H_2$, this behavior not being affected by internuclear distance. At the density matrix level, $\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = \rho(\boldsymbol{r}_1)\rho'(\boldsymbol{r}_2)/2$, where $\rho' = (N - 1)\rho/N = \rho/2$ is the electron−number corrected density that integrates to $N - 1$, not to $N$. Given that both atomic basins are equivalent, the statistical independence of electrons must lead to a binomial distribution. This is characterized by the probability that a given basin be occupied by one of the independent electrons, $p = 1/2$, so $p(1, 1) = 0.5$, and $p(2, 0) = p(0, 2) = 0.25$, as numerically found. The average basin population is $\langle N^A \rangle = 0 \times p(0, 2) + 1 \times p(1, 1) + 2 \times p(2, 0) = 1$.

It is illuminating to examine the self−interaction problem from the point of view provided by considering resonant structures. In the standard textbook interpretation of the HF scheme, the problem is solved, as explained above, by properly counting electrons, so the $(N - 1)/N = 1/2$ factor introduced by the inclusion of the Fock−Dirac exchange transforms the incorrect Coulombic repulsions into the correct ones. Such a view may be recovered from Table 1, and $V_{xc} = V_X$ (for no correlation exists in HF) turns out to be minus half $V_C$. This stands both for the intra- and the interbasin contributions. If we think in terms of structures, $V_{ee}^{AA}$ is only due to $S_2$, so $\rho_2(\boldsymbol{r}_1^A, \boldsymbol{r}_2^A|S_2)$ determines it (eq 12), and we can ask ourselves about the Coulombic $\tilde{V}_C^{AA}(S_2)$ term that we may define with $\rho_1(\boldsymbol{r}^A|S_2)$, a density which integrates to 2 electrons. The answer will have to be corrected again for the proper number of electrons, so the monocentric self−interaction is as real a phenomenon as it may be.

The situation is very different as $V_{ee}^{AB}$ is regarded. Now only $S_1$ contributes, and $\rho_1(\boldsymbol{r}^A|S_1)$ as well as $\rho_1(\boldsymbol{r}^B|S_1)$ integrate to one electron in their respective basins. No self-interaction appears from computing repulsions with those densities, which refer to different electrons. Before analyzing the contributions of each structure in depth, we may confidently suppose that both $\rho_1(\boldsymbol{r}^B|S_1)$ and its $A$ counterpart will not depart in an essential way from the total $\rho$. $V_{ee}^{AB}$ may then be seen as the repulsion between two non-self-interacting atomic densities that has to be weighted with $p(1, 1)$, the probability that each electron occupies a different basin. Table 1 shows that $V_C^{AB}p(1, 1)$ is an excellent approximation to $V_{ee}^{AB}$. In this image, the Fock−Dirac exchange does not correct for the spurious self-interaction but for the existence of resonant structures in which different number of non-self-interacting electrons are located in each atomic basin. For each structure, electrons in different basins will now repel in a basically Coulombic manner, since correlations extinguish rapidly with distance in normal situations. We should then expect important correlation corrections *within* basins but rather uncorrelated descriptions among basins. We may then say that interbasin exchange energies, $V_X^{AB}$, are in fact resonance energies.

**B. Decomposition at the Structure Level.** Having only three different resonant structures and two electrons, CGDMs, CGPDs, and coarse−grained energetic magnitudes may be easily obtained in H$_2$. Let us call $C_1$, $C_2$, and $C_3$ the condensations leading to $S_1$, $S_2$, and $S_3$, respectively, upon considering free electrons. All CGPDs can be constructed from the data found in Table 1, and $p(0^A) = p(0^B) = p(2^A) = p(2^B) = p(2, 0) = p(0, 2)$, and $p(1^A) = p(1^B) = p(1,1)$. Similarly, we may use our previous formulas to derive different densities. Only one two−electron CGDM exists

$$\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = \Psi^*(1, 2)\Psi(1, 2) \tag{16}$$

since no condensed electrons remain. It can be condensed into the one−electron CGDMs

$$\rho(\boldsymbol{r}_1^A)[C_1] = 2\int_B d\boldsymbol{r}_2\, \Psi^*(1, 2)\Psi(1, 2)$$

$$\rho(\boldsymbol{r}_1^A)[C_2] = 2\int_A d\boldsymbol{r}_2\, \Psi^*(1, 2)\Psi(1, 2) \tag{17}$$

and their symmetry equivalent ones when the free electron is in $B$ and $S_2$ transforms into $S_3$.

This set of densities are immediately recovered from the HF model of H$_2$, as $\rho_2(1,2) = \rho(1)\rho(2)/4$ has separate electron coordinates. With this, $\rho(\boldsymbol{r}^A)[C_1] = \rho(\boldsymbol{r}^A)[C_2] = \rho(\boldsymbol{r})/2$, and the electron density within basin $A$, for instance, is partitioned equally into the $S_1$ and $S_2$ structures at any internuclear distance. Moreover, $p(S_1) = 0.5$, as well as $p(S_2) = 0.25$, are fixed weights that allow us to write $\rho(\boldsymbol{r}^A|S_1) = \rho(\boldsymbol{r})$ and $\rho(\boldsymbol{r}^A|S_2) = 2\rho(\boldsymbol{r})$, which clearly shows that there are 1 and 2 electrons within basin $A$ in the covalent and ionic structures, respectively. Notice that some structure specific CGDMs vanish. For instance, $\rho_2(\boldsymbol{r}_1^A, \boldsymbol{r}_2^B)[C_2]$ does not exist.

The energetic decomposition of the molecular energy into structure components at the HF level is therefore already contained in Table 1, so we will only comment briefly on it. For instance, $T^A = \tilde{T}^A(S_1) = \tilde{T}^A(S_2)/2$, and $V_{en}^{AA} = \tilde{V}_{en}^{AA}(S_1) = \tilde{V}_{en}^{AA}(S_2)/2$. As a true independent electron model, the normalized kinetic energy or electron−nuclear attraction of the $S_2$ structure is just twice that of a single electron. Also $V_{ee}^{AA} = \tilde{V}_{ee}^{AA}(S_2)/4$, and adding the intra−basin components we may get the normalized atomic self−energies for each structure. At $R_{AB} = 0.7$ bohr, $\tilde{E}_{\text{self}}^A$ is thus −0.6550 and −0.5272 a.u. for the $S_1$ and $S_2$ structures, respectively, and $E_{\text{self}}^A = p(S_1) \times \tilde{E}_{\text{self}}^A(S_1) + p(S_2) \times \tilde{E}_{\text{self}}^A(S_2)$, as previously proven. It is interesting to notice that the intrabasin Coulombic contribution $\tilde{V}_C^{AA}(S_2) = 2\tilde{V}_{ee}^{AA}(S_2)$, so $S_2$ behaves like an atomic HF scheme within the molecule, and we still need a self−interaction correction coming from intra−basin exchange contributions. On the contrary, $\tilde{V}_C^{AB}(S_1) = \tilde{V}_{ee}^{AB}(S_1)$, and the absence of self-interaction present in $S_1$, together with the statistical independence of both electrons, lead to a purely Coulombic interaction. Given the particularly simple structure of the conditional densities in the HF scheme, the atomic basins of $\rho$ are also basins of $\rho(\boldsymbol{r}^A|S_1)$ and $\rho(\boldsymbol{r}^A|S_2)$, so there are no problems with the hermitian character of $t$ within this approximation.

At the correlated level, the simplicity is lost. This, together with the ordinary second-order density $\rho_2$ are all we need to construct the CGDMs. Figure 1 displays a number of features of these densities at $R_{AB} = 4.0$ bohr in a full configuration interaction (FCI) calculation. First, it is interesting to notice that the probability density of finding an electron as it moves around the molecule with the other electron located within basin $B$, is a continuous function, equal to $\rho(\boldsymbol{r})[C_1]$ in $A$ and to $\rho(\boldsymbol{r})[C_3]$ in $B$. At this elongated internuclear distance, characterized by a low $p(S_3)$, $\rho(\boldsymbol{r})[C_3]$ is much smaller than $\rho(\boldsymbol{r})[C_1]$, but the small peak in $B$ grows when decreasing $R_{AB}$, at a similar pace as the weight of the ionic structures. Second, the total molecular density $\rho$, depicted only in basin $A$, is clearly dominated by the $S_1$ structure. Nevertheless, the traditional density increase in the bonding region, one of the alleged signatures of covalent interactions, is clearly due to the contribution of the ionic structures. Actually, to the possibility that two electrons be located in that bonding region, which in our basin separation corresponds to $S_2$ and $S_3$. A similar analysis using other space partitionings, i.e., that provided by the ELF, would assign this density increase to the electrons in the bonding valence basin.

The lower part of Figure 1 is particularly insightful. Here we plot the conditional (normalized) densities associated to $S_1$

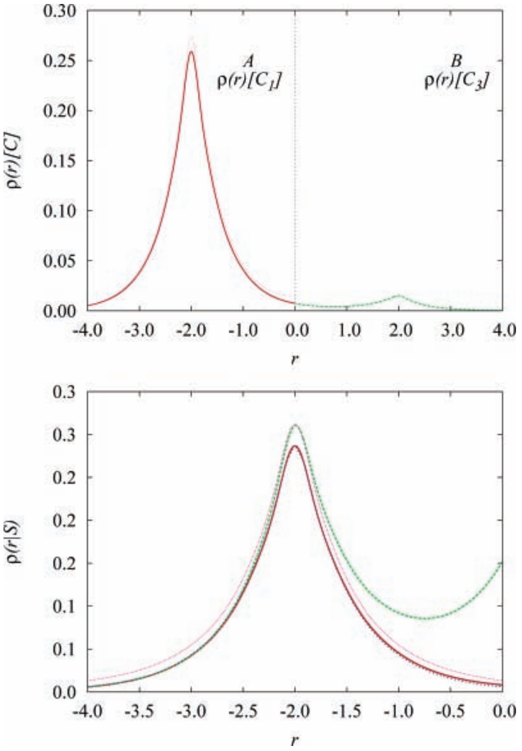

**Figure 1.** One electron densities along the internuclear axis for the covalent and ionic structures in $H_2$, as obtained from a full configuration interaction FCI//VTZ(d, f,2p) calculation at $R_{AB} = 4.0$ bohr. Nucleus $A$ is located at $r = -2.0$ bohr and nucleus $B$ at $r = 2.0$ bohr. In the top figure, we plot $\rho(\mathbf{r})[C_1]$ (full line) and the complete molecular density $\rho$ with dotted line within the $A$ (left) basin. Only $\rho(\mathbf{r})[C_3]$ (long-dashed line) is shown in the $B$ (right) basin. The dotted vertical line separates the $A$ and $B$ basins. In the bottom figure we present the conditional probabilities of $S_1$ (full line) and $S_2$ (dashed line) within basin $A$. They integrate to one and two electrons, respectively. We have also superimposed the total densities of the free H atom (short-dashed line) and the $H^-$ anion (dotted line). All data in atomic units.

and $S_2$ within basin $A$. It is clear that the two electrons in $S_2$ are very asymmetrically distributed with respect to the nucleus, much more likely to be found in the bonding region than in the rear nuclear part. As possibly expected, the $S_1$ density is almost indistinguishable from that of a free H atom, but interestingly enough, $\rho(\mathbf{r}|S_2)$ is very close to the density of a hydride anion near the nucleus. In the outer regions of this hydride ionic state, charge is pumped from the rear to the bonding region. It is tempting to rationalize this asymmetry in terms of the polarization induced by the naked $B$ proton. In fact, very simple attempts to simulate this polarization by means of a point charge electric field lead to a considerable enlargement of the region in which the $S_2$ density resembles the polarized hydride. We should take into account, however, that $H^-$ is a weakly bound system very difficult to simulate properly in a destabilizing positive field. For the time being, we simply state that $\rho(\mathbf{r}|S_2)$ has clear features that may be associated with a heavily polarized hydride. All of these considerations stand true in a wide range of internuclear distances, though the distortions/polarizations increase with decreasing $R_{AB}$.

Table 2 contains the energy decomposition into resonant structures obtained from the CAS[2,2]//6−311G(p) calculations. Since in $H_2$ intrabasin electron repulsions come from $S_2$, and inter−basin ones from $S_1$, the $V_{ee}$ terms are those of Table 1, though now their interpretation is different. For instance, $V_{ee}^{AA}(S_2)$ is equal to $V_{ee}^{AA}$ in Table 1, though now it is the whole electron repulsion coming from structure $S_2$.

**TABLE 2: CAS[2,2]//6−311G(p) Energetic Decomposition at the Structure Level[a]**

| | $S_1$ | | | $S_2$ | | |
|---|---|---|---|---|---|---|
| $R_{AB}$ | 1.4 | 4.0 | 6.0 | 1.4 | 4.0 | 6.0 |
| $G^A$ | 0.3483 | 0.4369 | 0.4922 | 0.2326 | 0.0320 | 0.0051 |
| $K^A$ | 0.3889 | 0.4528 | 0.4958 | 0.1919 | 0.0161 | 0.0014 |
| $V_{en}^{AA}$ | −0.7293 | −0.9096 | −0.9897 | −0.4988 | −0.0741 | −0.0083 |
| $V_{ee}^{AA}$ | | | | 0.1629 | 0.0232 | 0.0021 |
| $V_{ee}^{AB}$ | 0.2997 | 0.2179 | 0.1632 | | | |
| $V_{en}^{AB}$ | −0.3443 | −0.2215 | −0.1639 | −0.2532 | −0.0272 | −0.0026 |
| $E_{self}^A$ | −0.3810 | −0.4727 | −0.4975 | −0.1033 | −0.0189 | −0.0011 |
| $E$ | −0.7348 | −0.9448 | −0.9950 | −0.2074 | −0.0339 | −0.0027 |

[a] Magnitudes and internuclear distances correspond to those in Table 1, but we have included both the $g$ and $k$ forms of the kinetic energy operators. Here the first three columns correspond to the $S_1$ structure and the last three to the $S_2$ one. Both $E$ and $E_{\rm self}^A$ are obtained with $g$-based kinetic energy values. All data are in a.u.

The hermiticity problem of the kinetic energy operator manifests clearly in the correlated case, though the differences between the $g$ and $k$ descriptions are not large. If we compare the balance of the $S_1$ and $S_2$ components of $K^A$ and $G^A$ at $R_{AB} = 1.4$ a.u. with those coming from the HF model, it turns out that the $G^A$ data are clearly closer to the half and half HF partition than those of $K^A$. We will then use $G$, as is usually done when managing similar situations.

The evolution of the energetic components in $S_1$ and $S_2$ with increasing distance is interesting. At $R_{AB} = 1.4$ a.u, the covalent structure accounts for 64% the total molecular energy, though $p(S_1) = 0.5832$. This clearly means that $\tilde{E}(S_1) < \tilde{E}(S_2)$. In fact, both energies are −1.2599 and −0.9952 $E_h$, respectively. These covalent and ionic energies are in reasonable agreement with those found from other methods. As $R_{AB}$ increases, the energetic contribution of the covalent structure becomes dominant. It must be taken into proper account, however, that the energetic decomposition proposed here does not come from a state superposition of variational structures, like in the usual Heitler−London description in which structures are mixed at the state (wavefunction) level. If done so, no structure may have a lower energy than the molecular ground state, and the minimal energy of the latter is interpreted in terms of resonance between the states of each given structure. Our proposal comes from an a posteriori analysis of a system's state vector and is compatible with a statistical mixture of different electron arrangements in real space. No variational restriction about each structure's energy applies here.

The normalized atomic self−energies, $\tilde{E}_{\rm self}^A$ provide energetic counterparts to the atomic densities depicted in the inset of Figure 1. At $R_{AB} = 1.4$ bohr, these are easily computed as −0.6532 and −0.4957 $E_h$ for the $S_1$ and $S_2$ structures, respectively. The covalent H atom is almost 100 kcal/mol more stable than the free H atom, and this stability is due to an increase in kinetic energy more than compensated by the large electron−nucleus attraction, which indicates that $\rho(\mathbf{r}|S_1)$ is noticeably more compact than the free H density. The ionic $H^-$ energy is higher than the free H limit but lies 18 kcal/mol below the HF//6−311G description of the hydride. Its energetic balance is, however, very different from that of a free $H^-$, with $\tilde{K}^A(S_2) = 1.1161$ $E_h$ as compared with a HF//6−311G kinetic energy of 0.5741 a.u. These data are consistent with a very compressed $H^-$ moiety at $R_{AB}$ distances near $H_2$ equillibrium. Similar analyses may be done at the other internuclear distances. At $R_{AB} = 6.0$ bohr, $\tilde{E}_{\rm self}^A(S_1) = -0.4966$, which is the free H energy limit within 1 kcal/mol. Notice that all normalized magnitudes for $S_2$ near the dissociation limit suffer from a heavy loss of precision, so they should be taken with care.

It is interesting to compare energetic data across Table 1 and Table 2. We can see, for instance, how the $V_{ee}^{AB}(S_1)$ and $V_{en}^{AB}(S_1)$ values are much more similar than the global numbers found in Table 1. This is a sign of both the compactness of the $\rho(\boldsymbol{r}|S_1)$ density and the interference created in the electron−nucleus attraction by the ionic structures. Many other facts are easily rationalized by adopting a more or less classical image of the resonant structures. In this regard, the $V_{en}^{AB}(S_2)$ value is not very far from the classical value computed for a HF H$^-$ anion and a test proton separated by the internuclear distance, which is 0.2977, 0.0245, and 0.0021 $E_h$ at $R_{AB} = 1.4$, 4.0, and 6.0 bohr, respectively, the difference decreasing on increasing $R_{AB}$.

It is slightly surprising that a simple CAS[2,2] description, which does include static but a vanishing amount of dynamic correlation, gives rise to a considerable difference between $V_{ee}^{AA}$ and $V_{\mathrm{C}}^{AA}/2$, 23 kcal/mol at $R_{AB} = 1.4$ bohr, as calculated from Table 1. However, if we compute the Coulombic contribution of $S_2$, $V_{\mathrm{C}}^{AA}(S_2)$, we obtain 0.3288 $E_h$, which decreases the difference with respect to $V_{ee}^{AA}$ to a value smaller than 1 kcal/mol, since $V_{ee}^{AA} = V_{ee}^{AA}(S_2)$. The CAS[2,2] S$_2$model is therefore quasi-HF, with almost independent electrons. A similar 1 kcal/mol difference is obtained between $V_{ee}^{AB}(S_1)$ and $V_{\mathrm{C}}^{AB}(S_1)$. From the two electron statistical point of view, the CAS[2,2] $S_1$-structure thus corresponds to a very correlated electronic motion, for if one electron is in basin *A*, the other is in basin *B*. However, this correlation is actually very simple, for it corresponds to two sets of quasi-independent one-electron cages. The inability of the HF model to account for these two different kinds of statistical independece is the source of its failure upon dissociation conditions.

Finally, we should notice that a big part of the nonclassical energetic contributions contained in total $V_{ee}^{AA}$ and $V_{ee}^{AB}$ terms acquire a new meaning when decomposed at the resonant structure level. As our H$_2$ example has shown us, very small $V_{\mathrm{X}}^{AB}$ and $V_{\mathrm{corr}}^{AB}$ values in each of the relevant structures of a given molecule may conspire, after averaging, to provide much larger total apparent exchange or correlation energies. Further work will prove the generality of these ideas.

## V. Conclusions

The purpose of this paper has been twofold. On the one hand, we have shown how exhaustive partitions of the physical space may be used to obtain a whole hierarchy of coarse-grained density matrices and probability distributions from a general molecular wavefunction. These objects serve multiple purposes, and may be used, for instance, to construct the electron density in a given region, when we know that exactly *n* electrons lie within another region of space.

On the other hand, when the partition of space is into atomic regions, as in the quantum theory of atoms in molecules,[3] each possible distribution of electrons into atoms may be associated to a given resonant structure, in the sense of Pauling. We have shown that, in these conditions, the total molecular energy may be written as a weighted sum of structure energies, the weights being the probabilities with which each structure enters the total wavefunction.

We have used the H$_2$ molecule as a model to present some actual numerical data under the umbrella of the interacting quantum atoms approach.[2,20] The decomposition of the energy into the covalent and ionic structures sheds light on the self-interaction problem of interelectron repulsions, and the interbasin electron−electron potential energy, which is exclusively due to the covalent structure, has been shown to be free of self-interaction. Many energetic magnitudes in IQA acquire a new sense when examined at the structure level. Some of them turn out to behave more classically when separated into structures, and their complexity at the global level turns out to be the result of mixing quantities with different origins and trends.

We think that this work is a first step toward a general theory of resonance in real space, that may become a bridge between modern valence bond theory and the topological frameworks of the chemical bond. We are currently working to generalize our computer codes to multielectron cases so that more chemical examples may be dealt with.

**Acknowledgment.** The authors acknowledge financial support from the Spanish MEC, Project No. CTQ2006-02976.

## References and Notes

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

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

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

(4) Becke, A. D.; Edgecombe, K. E. *J. Chem. Phys.* **1990**, *92*, 5397−5403.

(5) Haussermann, U.; Wengert, S.; Hofmann, P.; Savin, A.; Jepsen, O.; Nesper, R. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2069−2073.

(6) Savin, A.; Silvi, B.; Colonna, F. *Can. J. Chem.* **1996**, *74*, 1088−1096.

(7) Kohout, M.; Savin, A. *J. Comput. Chem.* **1997**, *18*, 1431−1439.

(8) Marx, D.; Savin, A. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2077−2080.

(9) Savin, A.; Nesper, R.; Wengert, S.; Fassler, T. F. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1809−1832.

(10) Noury, S.; Colonna, F.; Savin, A.; Silvi, B. *J. Mol. Struct.* **1998**, *450*, 59−68.

(11) Silvi, B.; Savin, A. *Nature* **1994**, *371*, 683−686.

(12) Krokidis, X.; Noury, S.; Silvi, B. *J. Phys. Chem. A* **1997**, *101*, 7277−7282.

(13) Krokidis, X.; Silvi, B.; Alikhani, M. E. *Chem. Phys. Lett.* **1998**, *292*, 35−45.

(14) Burdett, J. K.; McCormick, T. A. *J. Phys. Chem. A* **1998**, *102*, 6366−6372.

(15) Daudel, R.; Brion, H.; Odiot, S. *J. Chem. Phys.* **1955**, *23*, 2080.

(16) Aslangui, C.; Constanciel, R.; Daudel, R.; Kottis, P. *Adv. Quantum Chem.* **1972**, *6*, 93.

(17) Daudel, R.; Bader, R. F. W.; Stephens, M. E.; Borrett, D. S. *Can. J. Chem.* **1974**, *52*, 1310.

(18) Savin, A. *J. Chem. Sci.* **2005**, *111*, 473.

(19) Bochicchio, R.; Ponec, R.; Lain, L.; Torre, A. *J. Phys. Chem. A* **2000**, *104*, 9130.

(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) Savin, A. *Reviews of Modern Quantum Chemistry*; Sen, K. D., Ed.; World Scientific Publishing: Singapore, 2002.

(24) Chamorro, E.; Fuentealba, P.; Savin, A. *Electron J. Comp. Chem.* **2003**, *24*, 496.

(25) Cancès, E.; Keriven, R.; Lodier, F.; Savin, A. *Theor. Chem. Acc.* **2004**, *111*, 373.

(26) Gallegos, A.; Carbó−Dorca, R.; Lodier, F.; Cances, E.; Savin, A. *J. Comput. Chem.* **2005**, *26*, 455.

(27) Bochicchio, R.; Ponec, R.; Torre, A.; Lain, L. *Theor. Chem. Acc* **2001**, *105*, 9130.

(28) Torre, A.; Lain, L.; Bochicchio, R. *J. Math. Chem.* **2002**, *32*, 241.