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Chemical Bonding in the N_2 Molecule and the Role of the Quantum Mechanical Interference Effect[†]

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The chemical bond in the N_2 molecule is analyzed from the perspective of the quantum mechanical interference effect by means of the recently developed generalized product function energy partitioning (GPF-EP) scheme. The analysis is carried out at the GVB-PP and SC levels, which constitute interpretable independent particle models, while ensuring the correct dissociation behavior for the molecule. The results suggest that some current ideas concerning the bond in the N_2 molecule should be revised. It is shown that, in the absence of the interference effect, there is no chemical bond in the N_2 molecule. The influence of the basis set on the energy partitioning is also evaluated. The interference contributions to the energy are substantially less sensitive to the choice of the basis set than the reference energy, making the investigation of the relative importance of inteference effects in larger systems feasible.

Introduction

The nature of chemical bonding in the nitrogen molecule has been the subject of much investigation and speculation.[1−7] A particularly widespread view is that the bond in the nitrogen molecule, which is homopolar in character, possesses an important electrostatic contribution to the stabilization of the molecule.[2−6]

On the other hand, it has been established, for quite some time now, that the formation of chemical bonds is associated in some extent with the quantum-mechanical interference effect.[2,4,5,8−14] The first general approach for calculating the interference and quasi-classical energy contributions of a given system, involving the decomposition of its reduced density matrices (RDMs) in interference and quasi-classical parts, was formulated by Ruedenberg.[8] To obtain such a partition, it was necessary to choose, by some criteria, a set of atomic orbitals among which the interference effect was to be evaluated, and possible ways to obtain such sets were proposed by the same author and co-workers.[15−19] Nevertheless, due to the arbitrariness involved in the choice of atomic orbitals, this approach was applied to only a few molecules.

We have recently developed a generalized product function energy partitioning (GPF-EP) approach which eliminates this arbitrariness while allowing the interference energy arising from different bonds to be separately calculated.[20] This approach is based on McWeeny's GPFs, whose RDMs are neatly blocked in electron group parts,[21] leading naturally to a partition in terms of individual bonds. By choosing modern valence bond wave functions (such as GVB[22] or SC[23]) for the description of the different electron groups, interpretable and uniquely defined (within a given basis set) atomic-like orbitals are automatically generated by self-consistent optimization, eliminating the need to arbitrarily partition the wave function in atomic orbitals.[11,20] Approaches closely related to GPFs have also been used in a different context for the investigation of the chemical bond.[24−26]

In this work, we apply the GPF-EP to the nitrogen molecule to determine the role that quantum mechanical interference plays in the formation of its chemical bond. It is shown that, as for the hydrogen molecule, the bonding in N_2 originates from the lowering in the kinetic energy associated with the change in the molecular electronic density which, in turn, arises from the interference effect among bonding orbitals. In the scope of the $\sigma-\pi$ separability approximation,[27,28] the relative importance of σ and π bonding in nitrogen is evaluated. The role of the nonbonding orbitals is also discussed. In addition, the influence of the basis set on the results of the energy partitioning is examined and discussed.

For the sake of comprehensiveness, a brief discussion of the GPF-EP method follows. A more thorough presentation can be found elsewhere.[20]

Generalized Product Function Energy Partitioning

A GPF is a special kind of approximate wave function exhibiting the general form

$$\Psi = \hat{A}\{\Psi^{(1)}\Psi^{(2)}...\} \tag{1}$$

where the superindexes (1), (2), ... refer to groups of $N^{(1)}$, $N^{(2)}$, ... electrons each, and $\Psi^{(1)}$, $\Psi^{(2)}$, ... are their respective wave functions, defined in spatial and spin coordinates. The wave function of each μth group will be taken as a normalized, antisymmetrized product of N_μ orbitals. $\hat{A}$ is the antisymmetrizing operator containing all intergroup permutations involving, at most, one coordinate index from each group. Orbitals pertaining to different groups are restricted to be mutually orthogonal.

The first- and second-order spinless RDMs for this kind of wave function can be expressed in a simple manner in terms of the spinless RDMs for the constituting electron groups:[21]

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$$\rho(\vec{r}_1, \vec{r}'_1) = \sum_{\mu=1}^{\eta} \rho^{\mu}(\vec{r}_1, \vec{r}'_1) \tag{2a}$$

$$\pi(\vec{r}_1\vec{r}_2) = \sum_{\mu=1}^{\eta} \pi^{\mu}(\vec{r}_1\vec{r}_2) + \frac{1}{2}{\sum_{\mu,\nu=1}^{\eta}}' \Big[\rho^{\mu}(\vec{r}_1)\,\rho^{\nu}(\vec{r}_2) - \frac{1}{2}\rho^{\mu}(\vec{r}_2, \vec{r}_1)\,\rho^{\nu}(\vec{r}_1, \vec{r}_2)\Big] \tag{2b}$$

where ρ and π denote, respectively, the first- and second-order RDMs for the whole system, ρ^{μ} and π^{μ} refer to the corresponding RDMs for each of the η individual electron groups, and r_i stands for the spatial coordinate of the ith electron.

The total electronic energy is, thus, determined by the RDM of all electron groups and the relative nuclear positions:

$$E[\text{tot}] = \sum_{\mu=1}^{\eta}\left\{\int dV_1[\hat{h}\rho^{\mu}(\vec{r}_1, \vec{r}'_1)]_{\vec{r}_1=\vec{r}'_1} + \frac{1}{2}\int dV_1 dV_2 \frac{\pi^{\mu}(\vec{r}_1, \vec{r}_2)}{r_{12}}\right\} + \frac{1}{2}{\sum_{\mu,\nu=1}^{\eta}}'\left\{\frac{1}{2}\int dV_1 dV_2 \frac{\rho^{\mu}(\vec{r}_1)\,\rho^{\nu}(\vec{r}_2)}{r_{12}}\right\} - \frac{1}{2}{\sum_{\mu,\nu=1}^{\eta}}'\left\{\frac{1}{4}\int dV_1 dV_2 \frac{\rho^{\mu}(\vec{r}_2, \vec{r}_1)\,\rho^{\nu}(\vec{r}_1, \vec{r}_2)}{r_{12}}\right\} + \frac{1}{2}{\sum_{\mathrm{A,B}}^{M}}'\frac{Z_{\mathrm{A}}Z_{\mathrm{B}}}{r_{\mathrm{AB}}} \tag{3}$$

where $\hat{h}$ is the one-electron operator, including the kinetic energy and the electron−nuclei potential energy operators and r_{12} is the interelectronic distance. Z_{A} is the nuclear charge of atom A, and r_{AB} is the distance between the nuclei of atoms A and B. It is noteworthy that the electronic energy for such a wave function is separable in a sum of intragroup energies (first bracket, eq 3) and intergroup contributions similar in character to Coulomb and exchange energies (second and third brackets, respectively).

We have recently shown that by choosing GVB or SC wave functions as the group wave functions and by expressing the RDMs of the GPF in terms of the optimized orbitals, it is possible to partition the energy in a manner similar to that proposed by Ruedenberg, obtaining

$$E[\text{tot}] = E[\text{ref}] + E[\text{I}] + E[\text{II}] + E[x] \tag{4}$$

where E[ref] is the total contribution to the energy associated with the quasiclassical (interference-free) group densities and pair-densities; E[I] and E[II] are the first- and second-order interference contributions to the energy, respectively; and $E[x]$ is the energy contribution due to the antisymmetrization of electron indexes pertaining to different groups. In the GPF-EP scheme, each of these contributions is readily separable into intragroup and intergroup contributions:

$$E[\text{ref}] = \sum_{\mu=1}^{\eta} E^{\mu}[\text{ref}] + \sum_{\mu<\nu}^{\eta} E^{\mu,\nu}[\text{ref}] \tag{5}$$

$$E[\text{I}] = \sum_{\mu=1}^{\eta} E^{\mu}[\text{I}] \tag{6}$$

$$E[\text{II}] = \sum_{\mu=1}^{\eta} E^{\mu}[\text{II}] + \sum_{\mu<\nu}^{\eta} E^{\mu,\nu}[\text{II}] \tag{7}$$

$$E[x] = \sum_{\mu<\nu}^{\eta} E^{\mu,\nu}[x] \tag{8}$$

When applicable, the above quantities can also be divided into their kinetic energy and potential energy contributions. As mentioned earlier, a thorough discussion of the equations can be found in ref 20.

It is sometimes convenient to describe one of the electron groups at a different level of calculation, which does not automatically generate atomic-like orbitals. This is usually the case when a group, such as the core electrons, are presumed to bear little to no influence on bonding, contributing only to E[ref] and $E[x]$. In this case, the group can be reasonably described, to a degree of approximation, by a restricted Hartree−Fock (RHF) wave function, and the remaining electron groups can be described at the GVB-PP or SC levels with no loss of interpretability.

Computational Details

The 14 electrons of the nitrogen molecule were separated into four groups: the first group, with eight electrons, consisting of core and nonbonding electrons, and three other groups, with two electrons each, describing the chemical bonds. A RHF wave function was chosen for the first group, and the three other groups were described at the GVB/SC level. To preserve the $\sigma-\pi$ separability, Jacobi rotations of the π-bond orbitals with orbitals from all other groups were not allowed. Henceforth, this choice of groups will be referred to as scheme I.

To determine the influence of the basis set on the results of the energy partitioning, calculations were performed with Pople's double- and triple-ζ basis sets 6-31G and 6-311G, with or without polarization and diffuse functions,[29−32] and Dunning's cc-pVTZ and cc-pVQZ basis sets.[33]

To investigate the role of the nonbonding orbitals, a different group selection was made, separating the electrons into five different groups: one group, with the four core electrons described at the RHF level; another group with the four nonbonding electrons, using a SC(4) wave function; and three GVB bond groups, with two electrons each. This choice of groups will be called scheme II. The calculations for scheme II were carried out only at the cc-pVQZ level.

All wave functions were constructed and optimized with the VB2000/GAMESS package.[34,35] A stand-alone code was devised to obtain the GPF-EP.[36]

Results and Discussion

In what follows, the results obtained for scheme I at the cc-PVQZ level are discussed. These results will be later used as reference for the basis set analysis. All potential energy surfaces (PESs) and the corresponding energy partitioning curves were constructed using 100 points in intervals of 0.04 Å. One should note that, in all cases, electrons from different groups are not allowed to change their spin coupling along the PES. This, of course, results in a dissociation energy slightly higher than would

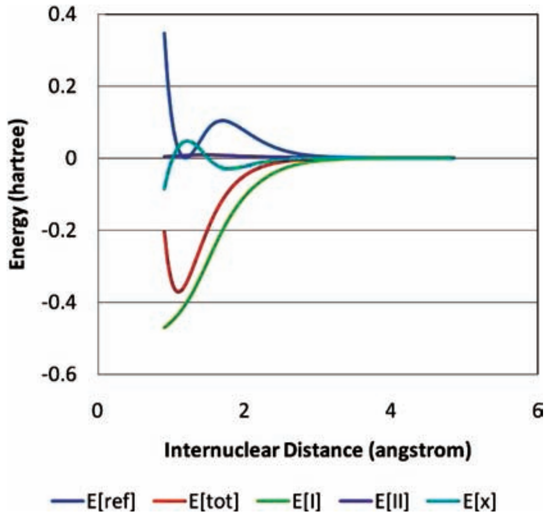

Figure 1. Partitioning of the total energy of N_2, E[tot], into reference energy E[ref], interference energy E[I], second-order interference energy E[II], and intergroup exchange energy $E[x]$.

be expected. One can always consider this energy difference as a promotion energy and proceed with the analysis, assuming the atoms to be in a valence state throughout.

Figure 1 shows the energy partitioning in terms of the reference, intergroup exchange, and interference contributions. To make the comparison easier, all curves are adjusted so that the corresponding quantities meet at the dissociated limit. Contrary to the reference and intergroup exchange energy, interference contributions really vanish at greater internuclear distances.

Among the quantities considered in scheme I, the first-order interference energy E[I] is the only one contributing to the formation of the chemical bond. The second-order interference contribution E[II] is very small through the whole PES (~5−0 millihartree). The intergroup exchange energy $E[x]$ is repulsive at the internuclear equilibrium distance. Although the reference energy E[ref] possesses a local minimum at the equilibrium distance, it is higher at the minimum than at the dissociation limit. It should be emphasized that the quantity $E[\mathrm{ref}] + E[x]$ would correspond to the energy of the N_2 molecule described by a quasi-classical density derived from a wave function with the correct permutational symmetry. It is seen that this quasi-classical description is completely unable to predict a chemical bond in the N_2 molecule and that interference is solely responsible for its formation. This seems to contradict some of the conclusions drawn by other authors concerning the nature of the bond in N_2, more specifically, the attribution of an important role to the electrostatic interaction between the atoms.[4−6] Differences should be expected, in part because the Morokuma-type partitioning schemes used by those authors do not separate the interference energy from the other contributions.[37,38] One should also be careful when making such comparisons, since the electrostatic description is not identical to a quasi-classical one. We do not mean by this that current theoretical estimations of the electrostatic contributions are wrong, only that these are, in practice, counteracted by the change in other energy components in this quasi-classical description. It will be seen that our analysis allows one to better understand the origin and relevance of the quasi-classical contributions in the nitrogen molecule.

The interference energy, E[I], can be further partitioned into its kinetic and potential energy contributions, as shown in Figure 2. It is clear from the figure that the kinetic energy part of the interference energy, T[I], is responsible for the energy lowering, which results in the formation of the potential well. On the other hand, the interference effect results in a potential energy rise.

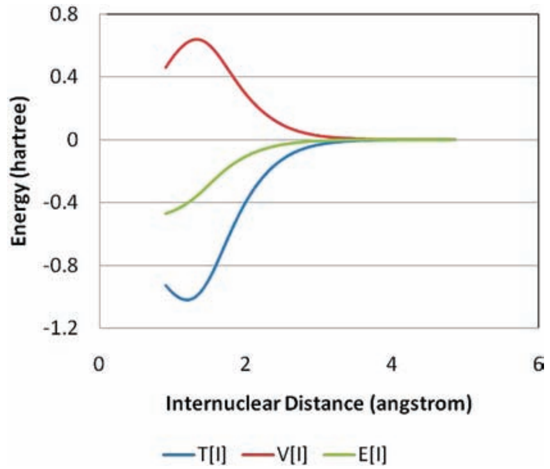

Figure 2. Partitioning of the interference energy E[I], into interference kinetic energy, T[I], and interference potential energy, V[I].

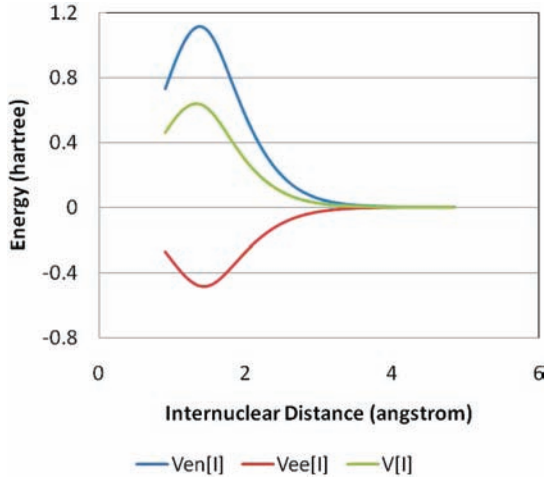

Figure 3. Partitioning of the interference potential energy V[I] into its electron−nucleus and electron−electron contributions (V_{en}[I] and V_{ee}[I], respectively).

The potential interference energy V[I] can be also partitioned into electron−nucleus and electron−electron contributions (V_{en}[I] and V_{ee}[I], respectively) and, as shown in Figure 3, V_{en}[I] increases and V_{ee}[I] decreases as the atoms approach each other. This agrees with the fact that the interference among orbitals from different centers whose electrons are singlet-coupled tends to remove electron density from regions near the nuclei toward the bond region. These results show that the mechanism for chemical bonding in the nitrogen molecule is completely analogous to that in the hydrogen molecule;[8] that is, the bond results from the lowering of the kinetic energy due to the electron density change that ensues from the quantum mechanical interference effect. The interference analysis, of course, in no way contradicts the virial relation, which predicts that the *total* potential energy lowers while the *total* kinetic energy rises as atoms approach to form molecules. The interference kinetic energy quantifies the softening of the kinetic energy pressure through electron coupling. The kinetic energy lowering through interference is an essential contributor in the context of the energy minimization that will establish the virial theorem, which is, in fact, valid to five significant figures in the present calculation. This particular role of the interference kinetic energy

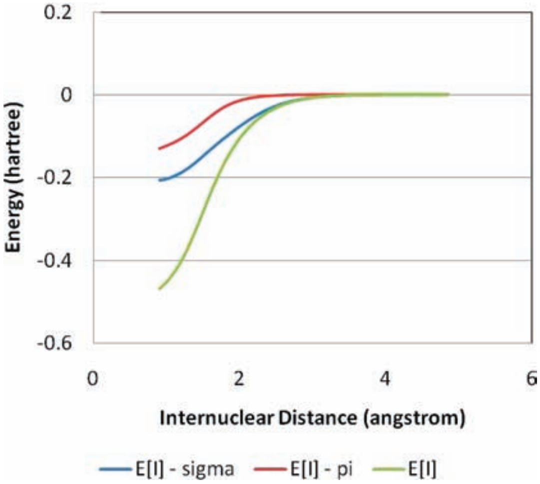

Figure 4. Partitioning of the interference energy E[I] into the σ and π bond contributions ($E[\mathrm{I}]_{-\mathrm{sigma}}$ and $E[\mathrm{I}]_{-\mathrm{pi}}$, respectively).

in bond formation has been exhaustively discussed in the literature[4,8−14,39] and will not be further examined.

As previously discussed, the same analysis can be carried out for the individual chemical bonds by means of the GPF-EP. Figure 4 shows the interference energy in a σ bond and in a π bond of the molecule.

Both σ and π bonds contribute significantly to the interference energy, the contribution of the σ bond being larger by ∼80 millihartrees, in comparison to that of a single π bond at the internuclear equilibrium distance. Should one proceed by further partitioning the interference energy arising from each bond in its kinetic and potential energy contributions, it becomes clear that there is no significant difference in the qualitative picture that emerges. In each bond, interference brings about a kinetic energy lowering and a potential energy rise, as can be seen in Figure 5a and b. The one significant difference that emerges is that the minima for the interference kinetic energy appear at different internuclear distances for the σ and π bonds. $T[\mathrm{I}]_{-\mathrm{pi}}$ has a minimum at an internuclear distance of ∼1.18 Å, close to the PES minimum, whereas $\mathrm{T[I]}_{-\mathrm{sigma}}$ shows a minimum at 1.34 Å. This furnishes a simple explanation for the known fact that multiple bonds are usually shorter than single bonds, if one observes that the largest contribution to the interference energy, and thus, to the potential well, comes from the kinetic energy of interference. In addition, this result mirrors the qualitative picture of the bond-breaking, where the π bonds are broken before the σ bond as the atoms separate, which can be derived either from inspection of the GVB orbitals involved or from more complicated types of analyses.[7]

The reference energy is composed of many different contributions, which vary greatly along the PES and combine to yield the curve E[ref] shown in Figure 1. Nevertheless, some interesting features of the components of the reference energy reveal important characteristics of the variational process of orbital optimization that eventually leads to the restoration of the virial relation between kinetic and potential energy.[8,10,39] This data is better discussed by considering the difference (Δvalue) between the value that a given component presents at the minimum of the PES and at the separated atom limit.

The small positive value for ΔE[ref] (∼0.020 hartree) results from the sum of ΔV[ref] and ΔT[ref], quantities that are almost 2 orders of magnitude larger (−1.312 and 1.331 hartree, respectively). This implies that the value of ΔE[ref] is a result of the mutual cancellation of the many terms that together compose each of ΔV[ref] and ΔT[ref]. It must be emphasized that both quantities should be taken into consideration when constructing a quasi-classical reference, which should not be mistaken for an electrostatic model. An electrostatic model disregards the change in the electronic density as the atoms approach and, thus, does not include the quasi-classical kinetic energy change, whereas a quasi-classical model, which includes this density modification, excludes only, and specifically, the density change due to the interference effect.

Partitioning of the reference potential energy difference, ΔV[ref] in intragroup and intergroup contributions does not reveal any particularly interesting features. All intragroup contributions have large modules and negative signs, meaning that, in all cases, the potential energy resulting from the interaction of the quasi-classical group charge with the nuclei surpasses by far the intragroup electron−electron repulsion. Tables containing this information are provided as Supporting Information.

A revealing feature of the reference energy partitioning is the contribution from each electron group to the behavior of the reference (i.e., quasi-classical) kinetic energy, T[ref], which is shown in Table 1. More to the point, the sole contribution from the "bond" groups to the steep rise of the reference kinetic energy as the atoms approach comes from the σ bond electrons. The π electron group contributes by reducing the reference

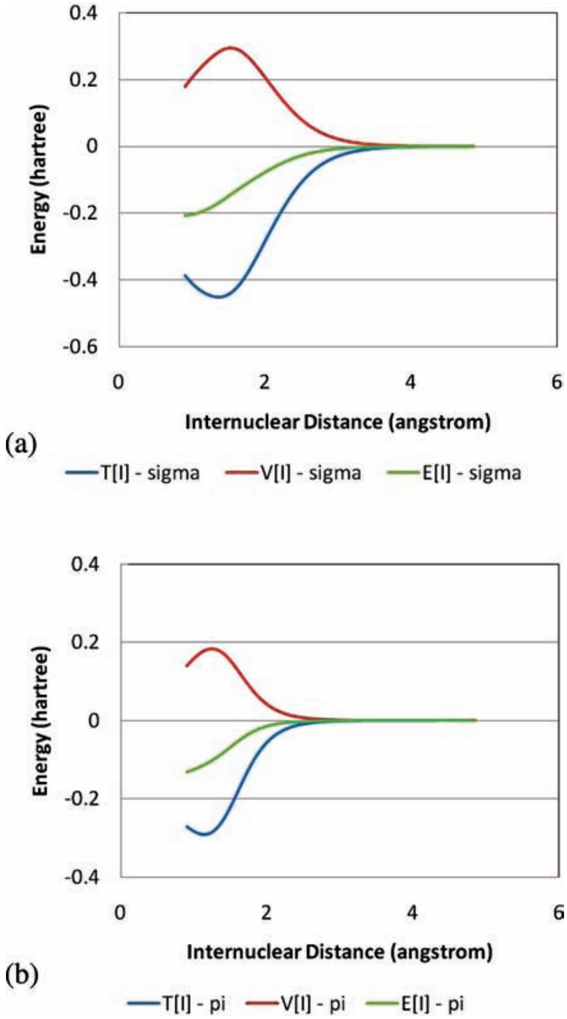

Figure 5. Partitioning of the interference energy contributions of each bond. (a) Partitioning of $E[\mathrm{I}]_{\mathrm{sigma}}$, into $T[\mathrm{I}]_{-\mathrm{sigma}}$ and $V[\mathrm{I}]_{-\mathrm{sigma}}$. (b) Partitioning of $E[\mathrm{I}]_{-\mathrm{pi}}$, into $T[\mathrm{I}]_{-\mathrm{pi}}$ and $V[\mathrm{I}]_{-\mathrm{pi}}$.

TABLE 1: Partitioning of the Reference Kinetic Energy for the N_2 Molecule

	energy (hartree)
ΔT[ref], (core + nb)	−0.4390
ΔT[ref], sigma	1.7887
ΔT[ref], pi	−0.0091
ΔT[ref]	1.3315

TABLE 2: Comparison of the Energy Partitioning for the Two Ways of Grouping the Electrons of the N_2 Molecule

	scheme I	scheme II	sch.II - sch.I
ΔE[I]	−0.4293	−0.4979	−0.0685
ΔE[II]	0.0058	0.0047	−0.0011
ΔE[ref]	0.0197	−0.3585	−0.3782
$\Delta E[x]$	0.0325	0.4708	0.4384
ΔE[tot]	−0.3714	−0.3809	−0.0095

TABLE 3: Comparison of the Interference Energy Partitioning for the Two Ways of Grouping the Electrons of the N_2 Molecule

	scheme I	scheme II	sch.II−sch.I
ΔE[I], nb		−0.0661	
ΔE[I], sigma	−0.1975	−0.2003	−0.0028
ΔE[I], pi	−0.1159	−0.1157	0.0002
ΔE[I], sigma + 2-pi	−0.4293	−0.4317	−0.0024

kinetic energy as the atoms approach the equilibrium internuclear distance. In the same way, the electrons that do not participate directly in bonding (i.e., the core and nonbonding electrons in the HF group) contribute, as a whole, to diminish the reference kinetic energy. It will be seen later that core and nonbonding electrons actually play different roles in the reference kinetic energy.

Two mechanisms could be invoked to explain this particular role of σ electrons. The first one is related to the contraction of the electron density from the bonding atomic (or quasi-atomic) orbitals, which would be variationally achieved by an increase in the contribution of less diffuse basis functions. A similar idea was first proposed by Ruedenberg to explain the quasi-classical kinetic energy rise in the formation of the bond in H_2 and H_2^+.8 It has been argued that bonding in those two species is unique and that this mechanism would not be able to explain the kinetic energy rise in the nitrogen molecule.[40] An alternative explanation for this result has to do with the fact that the nearly pure p_z-type orbitals of the isolated atoms start to acquire some s character as the atoms approach to form the σ bond. Given basis functions of similar exponents, the kinetic energy contribution of s-type orbitals are generally larger than that of p-type orbitals, which could explain the net kinetic energy rise. A rigorous analysis of the composition of the orbitals in terms of basis functions would surely help in solving this question.

The result of the energy partitioning applied to scheme II (Table 2), shows significant changes for ΔE[I], ΔE[ref], and $\Delta E[x]$, which, however, do not contradict the qualitative picture obtained in the previous analysis, as will be subsequently seen. The reference energy drops significantly at the equilibrium distance, which is accompanied by a sharp rise in the intergroup exchange energy. The difference between the interference energy change ΔE[I] calculated at the two different schemes presents a more modest, though significant, modification.

This lowering of ΔE[I] is easily explained if one looks at Table 3, which compares the interference energy contributions calculated for both schemes. In the following, $\Delta E[\mathrm{I}]_{-\mathrm{nb}}$ stands for the change in the interference energy for the group of the nonbonding electrons. It is seen that the modification that ΔE[I] undergoes with the change in description comes almost exclusively from the inclusion of $\Delta E[\mathrm{I}]_{-\mathrm{nb}}$, which accounts for ~96.5% of it. When considering exclusively the σ and π bond groups, scheme II yields an ΔE[I] only 2 millihartree lower than that obtained for scheme I. Thus, the previous interpretation of the role of the interference energy is preserved.

The sharp rise in the intergroup exchange energy, which was absent in the scheme I calculations, is in great part a consequence of separating the core and nonbonding electrons into two different groups. When this is done, it becomes possible to isolate the exchange terms involving the two different orbital types. $\Delta E[x]_{-\mathrm{core/nb}}$ accounts for ~80% of the change in $\Delta E[x]$.

The difference of ~378 millihartree for ΔE[ref] calculated at the two distinct schemes originates in the $\Delta E[\mathrm{ref}]_{-\mathrm{sigma}}$ term, which is lower by almost 580 millihartree in scheme II than in scheme I. Many other reference contributions oppose this lowering, the most important by far being the total contribution of the core and nonbonding electrons to the reference energy, $\Delta E[\mathrm{ref}]_{-(\mathrm{core+nb})}$, which is ~363 millihartree higher in scheme II than in scheme I.

As was seen before in the partitioning carried out for scheme I, the total, quasi-classical, kinetic energy change for the core and nonbonding orbitals ($\Delta T[\mathrm{ref}]_{-(\mathrm{core+nb})}$) was negative, valued at −439 millihartree. In scheme II, this increases to −454.7 millihartree and can be separated in each individual contribution. If this is done, one obtains $\Delta T[\mathrm{ref}]_{-\mathrm{core}} = +4199.0$ millihartree and $\Delta T[\mathrm{ref}]_{-\mathrm{nb}} = -4653.7$ millihartree. The change in the reference kinetic energy for the nonbonding orbitals is especially interesting, because it can be explained by the same mechanism proposed for understanding the kinetic energy rise in the σ bond in N_2: the nonbonding orbitals possess a predominant s character at the separated atom limit, and the σ bond orbitals are, practically, p_z orbitals. As the atoms approach, the σ bond orbitals acquire more s character (thus raising the reference kinetic energy), to which the nonbonding orbitals respond by acquiring greater p_z character, which lowers the reference kinetic energy. The increasing contribution of more diffuse functions might also play a role here.

The role of the nonbonding electrons in the formation of the chemical bond is, thus, made explicit in the preceding analysis. As the nonbonding orbitals are given sufficient variational freedom (by describing them with a SC wave function, effectively removing the double occupancy restriction), the σ orbitals are allowed to better adjust, leading to the significant decrease verified for $\Delta E[\mathrm{ref}]_{-\mathrm{sigma}}$. This energetic gain is, however, clearly tied to the changes undergone by the nonbonding orbitals and to the nonbonding/core separation. These changes appear more pointedly in the core/nonbonding exchange $\Delta E[x]_{-\mathrm{core/nb}}$ and in the total core and nonbonding reference energy $\Delta E[\mathrm{ref}]_{-(\mathrm{core+nb})}$, both of which are destabilizing in nature. These counteract almost completely the stabilizing contributions that are exclusive to scheme II, and as a result, the modification in the PES well depth with the change in description is of only 9.5 millihartree.

As noted before, the correct quasi-classical (i.e., without interference) description of a system must still include all the symmetries of the problem, and the quantity that best fulfills this requisite is $\Delta E[\mathrm{ref}] + \Delta E[x]$, valued at ~+112 millihartree. Thus, no matter the description chosen, the role and relative importance of the interference energy remains the same; that is, providing the kinetic energy drop that leads to the formation of the chemical bond.

We proceed now to investigate the influence of the basis set on the results of the energy partitioning. The results shown in

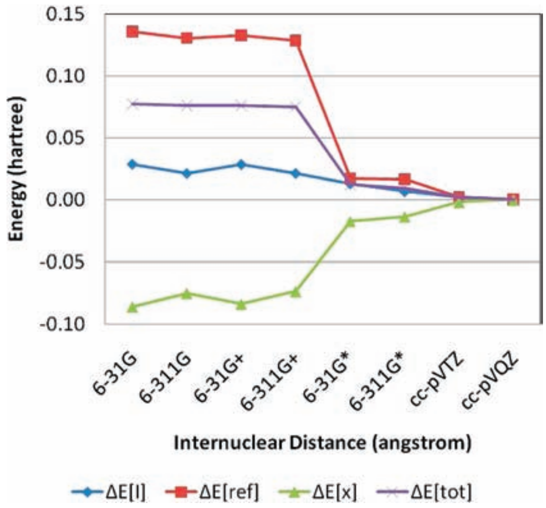

Figure 6. Influence of the basis set on the GPF-EP energy partitioning. All values are relative to the respective calculation with the cc-pVQZ basis set.

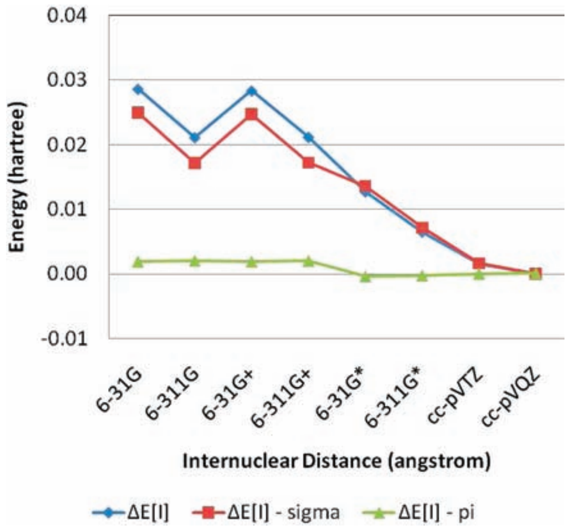

Figure 7. Influence of the basis set on the GPF-EP partitioning of the interference energy *E*[I]. All values are relative to the respective calculation with the cc-pVQZ basis set.

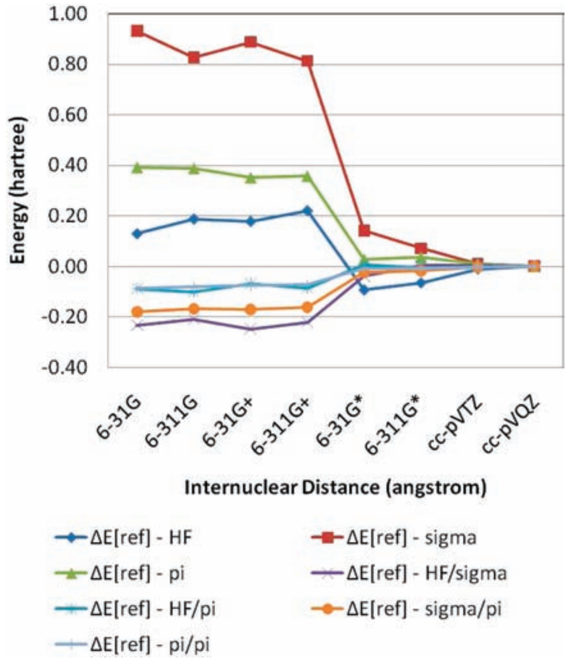

Figure 8. Influence of the basis set on the GPF-EP partitioning of the reference energy *E*[ref]. All values are relative to the respective calculation with the cc-pVQZ basis set.

Figures 6−9, for the different terms of the energy partitioning, represent the difference between the value of a given term at the equilibrium distance and that of the same term at the separated atom limit and are always expressed relative to the values obtained with the cc-pVQZ basis set.

It is clearly seen in Figure 6 that the presence of polarization functions in the basis is of utmost importance, whereas diffuse functions do not seem to play any important role. Both the intergroup exchange and reference contributions are particularly sensitive to the absence of polarization functions in the basis set. The reference energy difference, ΔE[ref], calculated without polarization functions (e.g., 6-31G) is more than 100 millihartrees greater than that obtained with the smallest basis set containing polarization functions(6-31G*). This is partly counteracted by the opposite trend in the intergroup exchange energy, for which the results obtained with no polarization functions are at least 70 millihartrees smaller than those calculated otherwise. In contrast, the interference contribution is considerably less sensitive to the absence of polarization functions, the calculated value being ∼16 millihartree larger than that containing polarization functions.

The use of Dunning's correlation consistent basis sets also improves the values obtained for the energy partitioning. Once again, the interference energy is less affected, with a difference of merely 5 millihartree between the 6-311G* and cc-pVTZ basis, whereas the reference energy and the intergroup exchange energy present differences of about 14 and 12 millihartree, respectively. It is seen that the choice of double, triple, or quadruple-ζ basis sets is less significant for all quantities.

Figure 7 shows the effect of the basis sets on the calculated interference energies for each individual bond. The interference energy calculated for the σ bond is clearly more affected by use of a poor basis set than that obtained for the π bond. Once again, polarization functions play a crucial role in the correct calculation of the energy components. Generally, the results show that poor basis sets lead to underestimated interference energies.

From all the contributions to the reference energy, the intragroup contributions are the most affected by the absence of polarization functions, as can be seen in Figure 8. For example, the results with the 6-31G and 6-31G* basis sets for the ΔE[ref]$_{-\mathrm{sigma}}$ differ by ∼800 millihartree. The difference between ΔE[ref]$_{-\mathrm{pi}}$ calculated with the 6-31G basis set and the cc-pVQZ basis set (about 390 millihartree) is in great part recouped by the simple addition of polarization functions, the difference between the calculations with 6-31G* and cc-pVQZ basis reducing to ∼28 millihartree. For ΔE[ref]$_{-\mathrm{sigma}}$, on the other hand, the presence of polarization functions reduces this difference to 141 millihartree, still too large by any criteria. Partitioning of ΔE[ref] is, thus, clearly dependent on the size and type of the basis set. The use of the triple-ζ 6-311G* improves this partially, but only by using correlation consistent basis sets do the results begin to approach a limit, the greatest difference between cc-pVTZ and cc-PVQZ coming from ΔE[ref]$_{-\mathrm{HF}}$ (a difference of approximately 11 millihartree).

The addition of diffuse functions to the basis set seems to improve somewhat the results obtained, though not by much. Whether this improvement is a consequence of the diffuse functions compensating for the lack of polarization functions

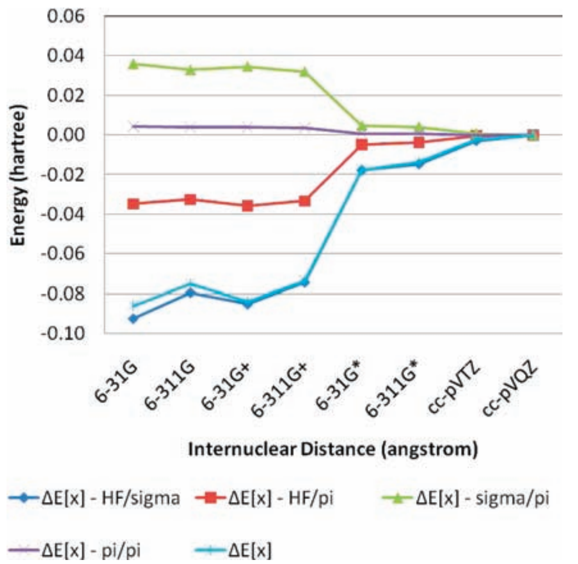

Figure 9. Influence of the basis set on the GPF-EP partitioning of the intergroup exchange energy $E[x]$. All values are relative to the respective calculation with the cc-pVQZ basis set.

or for the relatively small basis set size can only be determined by a more thorough study.

As in other cases, polarization functions are essential to obtain meaningful results for the intergroup exchange partitioning. It is seen in Figure 9 that, for all basis sets considered, there is a cancellation of errors from $\Delta E[x]_{-\mathrm{sigma/pi}}$ and from $\Delta E[x]_{-\mathrm{HF/pi}}$, whereas the $\Delta E[x]_{-\mathrm{HF/sigma}}$ has approximately the same value as the total intergroup exchange $\Delta E[x]$. As in other cases, going from Pople-type basis sets to correlation consistent basis sets is more important than merely increasing the basis set size.

The basis set analysis by means of the GPF-EP, albeit limited, offers some insight into the mathematical mechanisms underpinning the variational procedure of wave function optimization, which we think might help in the design of more compact and precise specialized basis sets. It is apparent that the interference energy, which responds for the formation of the chemical bond, is the least sensitive among the quantities obtained in the energy partitioning. The reference and exchange contributions are the most sensitive, especially those parts involving the σ bond. In fact, once polarization functions are included, quantities associated with the π bond are not much affected. As the basis set quality is increased, the more important adjustments to the wave function in N_2 occur in the σ bond and in the σ/HF intergroup quantities. If this analysis could be extended to other systems in the $\sigma-\pi$ bond separation approximation, problems concerning π electrons in planar molecules could, in principle, be investigated with quite modest basis sets containing polarization functions. This is now under investigation.

Conclusions

The qualitatively simple picture of the formation of the chemical bond as a result of the interference effect among one-electron states is shown to be valid for the N_2 molecule. The results obtained by the GPF-EP method indicate that the mechanism for bond formation in N_2 is equivalent to that reported by other authors for bonding in H_2 and H_2^+. More than that, the method makes it clear that the formation of σ and π bonds are achieved by the same common mechanism (i.e., the kinetic energy drop caused by the interference effect), although the σ bond contributes more to the interference energy.

The results also suggest that, although quasi-classical electrostatic contributions in the N_2 molecule can be quite large, they are necessarily accompanied by large increases in both the quasi-classical kinetic energy and the intergroup exchange energy. Hence, the quasi-classical density with the correct symmetry is unable to predict chemical bonding in the nitrogen molecule.

There is an important interplay between the σ bond electrons and the nonbonding electrons, which was revealed by extending the partitioning to the nonbonding orbitals. Small corrections to the PES of N_2, which arise from the use of a SC(4) wave function for the nonbonding electrons, are shown to result from large modifications in the reference energy of the σ bond and in the interference in the nonbonding electron group, balanced by an opposite trend in core/nonbonding energy terms.

The effect of the basis set on the GPF-EP was evaluated. It was shown that by using small basis sets with polarization functions, it should be possible to investigate the role of interference in other systems. The reference energy and intergroup exchange energy, on the other hand, demand larger basis sets, and the best results are obtained with correlation consistent sets, although qualitatively correct results should be obtained even with basis sets of modest size containing polarization functions. It is noteworthy that the π bond seems particularly unaffected by basis set size.

Supporting Information Available: We have included tables comparing all quantities calculated for the two-electron group schemes describing the N_2, obtained from the GPF-EP. Tables containing the partitioning of the total energy and of the interference energy are not included, since they already appear in the article. This material is available free of charge via the Internet at http://pubs.acs.org.

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