

Condensation of Frontier Molecular Orbital Fukui Functions

Felipe A. Bulat,[†] Eduardo Chamorro,[‡] Patricio Fuentealba,[§] and Alejandro Toro-Labbé^{*,†}

Laboratorio de Química Teórica Computacional (QTC), Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Correo 22, Santiago, Chile, Departamento de Ciencias Químicas, Facultad de Ecología y Recursos Naturales, Universidad Andres Bello (UNAB), República 217, Santiago, Chile, and Departamento de Física, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago de Chile, Chile

Received: August 13, 2003; In Final Form: October 24, 2003

A comparison of the regional Fukui index evaluation within the frontier molecular orbital (FMO) Fukui functions is presented. The atoms-in-molecules (AIM) real space-based condensation scheme is compared against a basis set-based condensation scheme and the reliability of the produced reactivity trends is compared. The AIM condensation scheme turns out to give the best results. Furthermore, the AIM atom condensed Fukui indexes can be formally proven to be nonnegative.

1. Introduction

Within Fukui's Frontier Molecular Orbital (FMO) theory^{1,2} the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) play fundamental roles in the interpretation of chemical reactivity, particularly toward nucleophiles or electrophiles.³ In general, an electrophilic reaction is more likely to take place where the HOMO electron density is the largest within the substrate. Likewise, a nucleophilic reaction will take place preferably in the molecular sites with the largest values for the LUMO density.

Density Functional Theory (DFT), based on the Hohenberg–Kohn theorems,⁴ has provided along its development formal basis to a number of chemical concepts and ideas on reactivity. Indeed, concepts such as electronic chemical potential, μ , and global hardness, η ,⁵ have proved successful in the rationalization of chemical processes.⁶ In particular, and in connection with Fukui's theory, the so-called Fukui function has been formally defined as:⁷

$$f(\mathbf{r}) = \left[\frac{\delta\mu}{\delta\nu(\mathbf{r})} \right]_N \quad (1)$$

where $\nu(\mathbf{r})$ is the external potential and the functional derivative must be taken at a constant number of electrons N . Alternatively, the Fukui function can be written as:

$$f(\mathbf{r}) = \left(\frac{\partial\rho(\mathbf{r})}{\partial N} \right)_{\nu(\mathbf{r})} \quad (2)$$

which is the most common expression for it. An important feature of the Fukui function is that it integrates to unity.

Although an analytic expression for the Fukui function is not available, its evaluation is usually done by using the so-called

finite difference approximation, which yields the following working formulas:

$$f^-(\mathbf{r}) = [\rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r})] \quad (3)$$

$$f^+(\mathbf{r}) = [\rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r})] \quad (4)$$

$$f^0(\mathbf{r}) = [f^-(\mathbf{r}) + f^+(\mathbf{r})]/2 = [\rho_{N+1}(\mathbf{r}) - \rho_{N-1}(\mathbf{r})]/2 \quad (5)$$

where $\rho_N(\mathbf{r})$ is the electron density for the N -electron species. Alternatively, and yielding simpler expressions, Senet has shown⁸ that the derivative of the chemical potential with respect to the Kohn–Sham potential is simple to calculate and it is the leading term in an exact expression for the Fukui function. Hence, one can write:

$$f^-(\mathbf{r}) \approx |\phi^h(\mathbf{r})|^2 \quad (6)$$

$$f^+(\mathbf{r}) \approx |\phi^l(\mathbf{r})|^2 \quad (7)$$

$$f^0(\mathbf{r}) \approx [f^-(\mathbf{r}) + f^+(\mathbf{r})]/2 = [|\phi^h(\mathbf{r})|^2 + |\phi^l(\mathbf{r})|^2]/2 \quad (8)$$

with $\phi^h(\mathbf{r})$ and $\phi^l(\mathbf{r})$ are the HOMO and LUMO frontier orbitals, respectively. Note that through these expressions the relationship with Fukui's theory is made evident, and under a frozen orbital regime such an approximation is quite a useful result. Indeed, note also that if the Frozen Orbital Approximation (FOA) is imposed on eqs 3–5, eqs 6–8 are obtained.^{9,10}

There are evidently major advantages in applying the FOA regime, from both the computational and theoretical standpoint. The estimation of eqs 3 and 4 requires three quantum mechanical calculations (at the $(N-1)$ -, N -, and $(N+1)$ -electron species), meanwhile eqs 6–8 are readily evaluated from a single calculation with the additional advantage that the spin multiplicity is not altered. Furthermore, eqs 6–8 are nonnegative ($|\phi^{h/l}(\mathbf{r})|^2 \geq 0 \forall \mathbf{r}$), which is not always the case for the finite difference approximation to Fukui functions, eqs 3–5. Although there is no formal proof that the Fukui function always should be positive, it is a desirable property and there are physical arguments suggesting so.^{11–13} While for a one-electron step

* Author to whom correspondence should be addressed. E-mail: atola@puc.cl.

[†] Pontificia Universidad Católica de Chile.

[‡] Universidad Andres Bello.

[§] Universidad de Chile.

discarding the orbital relaxation is drastic, within Senet's derivation although some strong conditions are imposed, there is no reference to a step size in the differentiation process.

A widely used method to obtain interesting and easy-to-handle information from Fukui functions is to obtain the so-called atom-condensed indexes, which for the finite difference Fukui functions, eqs 3–5, yields:

$$f_x^- = [q_x(N) - q_x(N-1)] \quad (9)$$

$$f_x^+ = [q_x(N+1) - q_x(N)] \quad (10)$$

$$f_x^0 = [f_x^- + f_x^+]/2 = [q_x(N+1) - q_x(N-1)]/2 \quad (11)$$

where f_x^- , f_x^+ , and f_x^0 are the electrophilic, nucleophilic, and radical Fukui indexes which indicate the susceptibility of atom labeled x under interaction toward electrophiles, nucleophiles, and radicals; $q_x(N)$ represents the atomic charges associated to atom x within the N -electron species. These formulas have been widely used and there exist vast literature that discusses its benefits and drawbacks (for recent reviews the reader is referred to ref 11).

Possible negative values for the Fukui indexes have been discussed in the literature and considered as artifacts coming from the condensation procedure¹² or due to strong structural distortions¹⁴ (see also refs 13 and 15–17).

Thanikaivelan et al.¹⁸ have thoroughly studied the effects of the population scheme and the basis set dependency of the Fukui indexes within the finite difference approximation eqs 9–11. The most stable schemes upon basis set modification turn out to be the Atoms in Molecules (AIM)¹⁹ and the CHELPG (charges from electrostatic potentials, using a grid-based method),²⁰ this last one being based on the molecular electrostatic potential (MESP) to derive the atomic charges. Interestingly enough, these two schemes provide also very similar Fukui indexes and they both predict appropriate reactivity sites for all kinds of attacks (nucleophilic, electrophilic, and radical). Although they note that Hirshfeld partitioning provides in all studied cases nonnegative Fukui indexes, as also stated by Roy et al.,¹² this fact cannot be generally extended since the allowance of negative values is in part a consequence of the finite difference approximation. Indeed, eqs 3–5 might be negative at some points since $\rho_{N+1}(\mathbf{r})$ might be smaller than $\rho_N(\mathbf{r})$ and $\rho_N(\mathbf{r})$ might be smaller than $\rho_{N-1}(\mathbf{r})$. Hence, regardless of the condensation scheme chosen negative Fukui indexes might appear. Furthermore, Hirshfeld partitioning fails to predict the correct reactivity trends in some cases.^{12,18}

The FMO Fukui functions given in eqs 6–8 can be condensed to produce the atomic Fukui indexes according to a basis set-based scheme proposed by Contreras et al.⁹ Although very appealing for its simplicity, it unfortunately predicts negative and/or out of scale Fukui indexes when large basis sets are used. This is clearly an artifact of the condensation procedure, since FMO Fukui functions are nonnegative. To overcome this difficulty and to take full advantage of the desirable properties of FMO Fukui functions, a real space-based condensation scheme can be performed on eqs 6–8 so as to produce well-behaved Fukui indexes. The aim of this paper is to prove the AIM condensation scheme for FMO Fukui functions in comparison to the scheme of Contreras et al., and to investigate whether the atom-condensed indexes produce the correct reactivity trends.

This article is organized as follows. After briefly introducing, in the next section, the theoretical background of both the real

space-based (AIM) and Contreras et al. basis set-based (BSB) condensation schemes for FMO Fukui functions, we succinctly present the computational methodologies used throughout this work. In section 4 we present the results for the electrophilic f_x^- and nucleophilic f_x^+ indexes along the torsional coordinate of three rotational systems. Phenol's *OH* rotation is thoroughly studied within a wide range of double- and triple- ζ basis sets to study the effects of basis sets modifications, in comparison to the BSB scheme of Contreras et al. Aniline's *NH*₂ internal rotation is studied within a range of augmented triple- ζ basis sets, to study the individual effects of the inclusion of diffuse functions on heavy atoms as well as on hydrogens. Finally, glyoxal is studied along the torsional coordinate of the *C–C* rotation to further illustrate the conclusions drawn from the above system, and also to illustrate the drastic changes that may occur within the BSB scheme in contrast to the well-behaved AIM scheme. The systems have been chosen to illustrate aromatic as well as nonaromatic systems containing the most common atoms within organic chemistry.

2. Calculation of Fukui Indexes

When expanding the HOMO and LUMO frontier molecular orbitals (FMO) of eqs 6 and 7 for an N -electron molecule in terms of the atomic basis function and integrating over space coordinates, one obtains the following normalization conditions for the FMO Fukui functions:

$$\int f^\alpha(\mathbf{r}) \, d\mathbf{r} = \sum_\mu \sum_\nu c_{\mu h(l)}^* c_{\nu h(l)} S_{\mu\nu} = 1 \quad (12)$$

with $S_{\mu\nu}$ the overlap integral between the atomic orbitals $\chi_\mu(\mathbf{r})$ and $\chi_\nu(\mathbf{r})$, $c_{\nu h(l)}$ the ν th expansion coefficient for HOMO (h) or LUMO (l), and $\alpha = -, +$ accordingly. Equation 12 allows the definition of an atomic orbital component of the total Fukui function as

$$f_\mu^\alpha = \sum_\nu c_{\mu h(l)}^* c_{\nu h(l)} S_{\mu\nu} \quad (13)$$

from where the atom condensed Fukui index is readily defined by summing over the atomic orbitals centered on atom x ⁹

$$f_x^\alpha = \sum_{\mu \in x} f_\mu^\alpha \quad (14)$$

Note that eq 14 is defined in terms of HOMO and LUMO populations on each atomic center. Evidently, the normalization condition remains valid.

The definition of the condensed-to-atom Fukui indexes given by eq 14 has been extensively used^{13,21,22} and has been shown to be quite reliable and stable when calculated with relatively small basis sets, or more precisely, without diffuse functions. Unfortunately, diffuse functions are generally needed to investigate nucleophilic susceptibilities.

Much discussion has arisen from the fact that AIM theory divides the total electron density into nonoverlapping atomic densities. Within the present framework this is truly an advantage, since overlapping atomic densities are not strictly real space partitions into atomic subdomains, and hence they might produce ill-behaved indexes (negative atom condensed indexes out of nonnegative functions). Bader's theory is then perfectly suited for an analysis of chemical reactivity from an atomic viewpoint, as atomic quantities might be readily available which are associated with clearly distinguishable subdomains

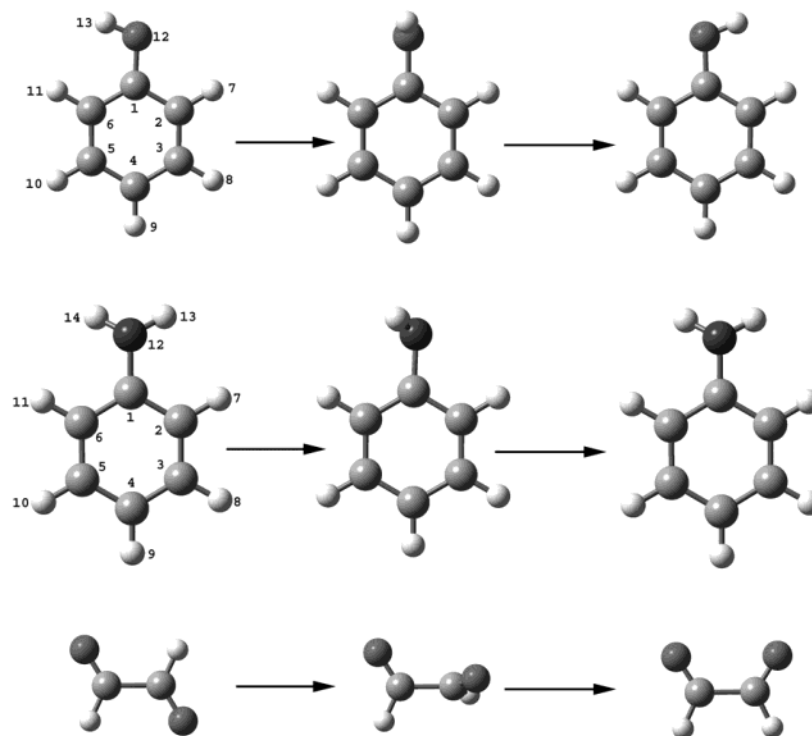


Figure 1. Sketch of the rotational isomerization of phenol, aniline, and glyoxal. The figure also shows the atom numbering.

of the real space. Indeed, atom condensed FMO Fukui indexes might be defined as

$$f_x^\alpha = \int_x |\phi^{h(l)}(\mathbf{r})|^2 d\mathbf{r} \quad (15)$$

where the subscript x under the integration sign indicates that the integration has to be performed only within the particular atomic domain of atom x . As in AIM the sum of all atomic domains comprises the full real space, it follows that

$$\sum_x f_x^\alpha = \sum_x \int_x |\phi^{h(l)}(\mathbf{r})|^2 d\mathbf{r} = \int |\phi^{h(l)}(\mathbf{r})|^2 d\mathbf{r} = \int f^\alpha(\mathbf{r}) d\mathbf{r} = 1 \quad (16)$$

One immediately notices that the atomic contributions to the total atomic Fukui index necessarily obey the condition $0 \leq f_x^\alpha \leq 1$.

It must be stressed that the condensed Fukui functions so defined within the AIM topological partitioning correspond to elements of the Atomic Overlap Matrix in the MO basis. Indeed, the elements of such a matrix are atomic integrals of $\phi^{*r}(\mathbf{r})\phi^s(\mathbf{r})$ with r and s ranging along all the MOs. When $r = s = \text{HOMO}$ (LUMO) such elements correspond to the electrophilic (nucleophilic) Fukui indexes. This very same definition of the real space-condensed Fukui function has already been proposed by Cioslowski et al.,¹⁰ who derived such expressions applying the FOA regime within a finite difference approximation procedure.

3. Computational Details

The Gaussian 98 program²³ has been used to obtain fully optimized geometries for all the studied systems, wave function files, and the Contreras et al. Fukui indexes through a modified version of link 601. The LUMO is included in the wave function files through a minor modification of link 9999. The Hartree–Fock level of theory was used throughout. The AIMPACK suite

of programs²⁴ was used to perform Bader's topological analysis for each wave function, which were slightly modified so that the *proaimv* module includes the atomic overlap matrix (AOM) elements in the MO basis up to the LUMO orbital. The appropriate elements of such a matrix for atomic basin x are identified, as shown previously, with the real space-condensed FMO Fukui indexes f_x^α . For all AIM calculations an atomic Laplacian $-c f_x \nabla^2 \rho(\mathbf{r}) d\mathbf{r}$ (c being a numerical constant) smaller than 10^{-3} was required as a criteria for the reliability of atomic integrations.¹⁹

4. Results and Discussion

Three rotational systems have been exhaustively studied along the appropriate rotational coordinates to evaluate the evolution of the atomic Fukui indexes. The processes herein studied are illustrated in Figure 1 along with the atom labeling.

The atomic Fukui indexes along the internal rotation of phenol are exhaustively studied within both condensation schemes and using a wide range of double- and triple- ζ quality basis sets at the HF level of theory (6-31G, 6-31G(d,p), 6-31++G(d,p), 6-311G, 6-311G(d,p), and 6-311++G(d,p)). The results are used to study the stability of both electrophilic and nucleophilic Fukui indexes at both condensation schemes. This example also illustrates how the AIM condensation scheme corrects the observed misbehaviors of the BSB scheme.

The internal rotation of aniline is studied, at the HF/6-311G(d,p), HF/6-311+G(d,p), and HF/6-311++G(d,p) levels, to further illustrate the reliability and stability of the topological partitioning and to study the effects of diffuse functions on the heavy atoms, as well as on hydrogen atoms. Furthermore this system has been chosen to include nitrogen atoms.

Finally, the evolution of the Fukui indexes along the reaction coordinate of the internal rotation of glyoxal at the HF/6-311++G(d,p) level of theory has been fully characterized, using both condensation schemes. As the basis set is quite extended

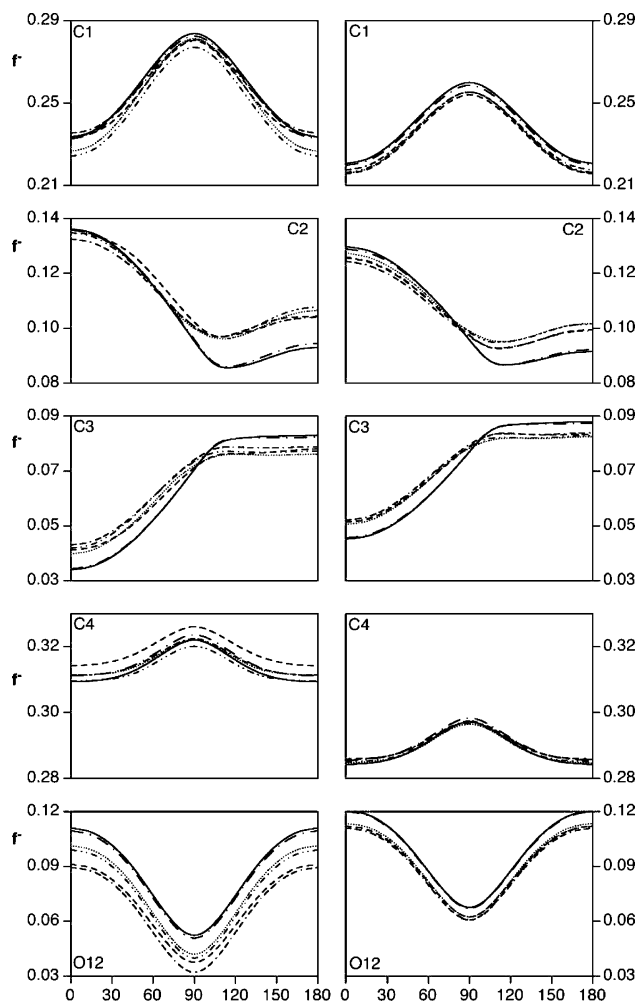


Figure 2. Atomic electrophilic Fukui indexes (atoms with $f_x^- < 0.01$ not shown) for the rotational isomerization of phenol at the HF level of theory with a series of double- and triple- ζ quality basis sets (—, HF/6-31G; ···, HF/6-31G(d,p); ---, HF/6-31++G(d,p); -·-, HF/6-311G; - - -, HF/6-311G(d,p); and - - · - -, HF/6-311++G(d,p)) at both BSB (left side) and AIM (right side) condensation schemes.

and augmented with diffuse functions, this case is used to illustrate the flaws in the BSB partition and how the AIM partition with Bader's topological analysis corrects and re-scales the values to fit the right numerical range. A general discussion of the origin of the misbehaviors in the BSB scheme is presented in terms of a few working formulas for this example.

4.1. Phenol. It can be seen from Figure 2, which shows the f_x^- Fukui indexes within the BSB and AIM condensation schemes, the remarkable similarity that the f_x^- indexes present along the reaction coordinate of the OH internal rotation in phenol, regardless of the basis set used and of the condensation scheme chosen. The observed stability of the electrophilic Fukui indexes is most probably a consequence of a well-defined HOMO encountered by the Hartree-Fock variational procedure. Furthermore, the preferred sites for electrophilic attacks are, in decreasing order, C₄, C₁, O₁₂, C₂, and C₃, in accordance with what is expected. Almost all such trends are followed along the rotational coordinate, but they vary more strongly within the BSB scheme. The hydrogen atoms present near-zero f_x^- indexes, since they do not react toward electrophiles.

From Figure 3a it can be noted that the f_x^+ indexes along the torsional coordinate, using the BSB condensation scheme, present also, within the basis set that do not include diffuse

functions, a remarkable similarity with the values encountered within the AIM condensation scheme. Nevertheless, the reactivity trends are not correct, since they assign the highest reactivity toward nucleophiles to the C₂ and C₃ atoms. Upon inclusion of diffuse functions within the basis set, as seen in Figure 3b, the BSB scheme produces negative and out-of-scale values for the Fukui indexes, while the real space-based scheme values remain, at least, within the physically correct $0 \leq f_x^\alpha \leq 1$ range. Clearly, a positive definite and normalized function, as the FMO Fukui function is, must upon regional condensation produce values within such a range; in other cases it is evident that the partition does not mimic or even resemble a regional condensation. While the BSB scheme is reliable for electrophilic Fukui functions and nucleophilic Fukui functions with no diffuse function within the basis sets, the AIM scheme has been shown to produce correct values for the Fukui indexes in all cases. Furthermore, while the BSB indexes with diffuse containing basis sets cannot be interpreted, the AIM scheme assigns the highest reactivity to the oxygen and hydrogen atoms.

It is generally accepted that diffuse functions need to be included to study chemical processes on which hydrogens react toward nucleophiles. If this is the case, then the general reactivity trends produced within basis sets that do not contain diffuse functions should not be considered as reliable no matter the condensation scheme used. Indeed, while chemical intuition tells us that the hydrogens on phenol should be more reactive toward nucleophiles than carbon atoms, the general trends produced by basis sets with no diffuse functions (regardless of the condensation scheme used) indicate that, in general, the carbon atoms are more reactive. Upon inclusion of diffuse functions within the basis sets, the BSB scheme becomes unreliable and no conclusions can be drawn from such results, while the AIM scheme indicates that the hydrogens are the most reactive, in accordance with what is expected from chemical grounds.

It has been seen, and will be further supported in the following sections, that although the f_x^+ values within the BSB scheme at diffuse containing basis sets are out of range, their general trends are quite similar to those produced by the AIM scheme (see section 4.3). Note in Figure 3b that the f_{O12}^+ trend along the reaction coordinate at the BSB scheme is quite similar to those of f_{H13}^+ at the AIM scheme. Note also that the f_{H13}^+ trends at the BSB scheme are quite similar to the f_{O12}^+ trends in the AIM scheme. This fact indicates that somehow the diffuse functions centered at the oxygen nuclei are describing the electron densities of the hydrogen attached to it, and the trends are governed by the corresponding diffuse function expansion coefficients of the neighboring atom. While the BSB scheme incorrectly describes such a situation, the AIM scheme corrects it.

A discussion of the importance of the diffuse functions when describing nucleophilic susceptibility and of the relevance of the condensation scheme will be further analyzed in the next section, since important information can be drawn from the basis set study performed for aniline.

4.2. Aniline. Although not shown, the electrophilic Fukui indexes for all atoms of aniline, at all levels studied and at both condensation schemes, show a remarkable coincidence as is seen also for phenol above. Figure 4 shows the nucleophilic Fukui indexes for aniline at the HF/6-311G(d,p), HF/6-311++G(d,p), and HF/6-311++G(d,p) levels of theory, estimated through both partition schemes. It is readily seen that within the BSB scheme the inclusion of diffuse functions only at the heavy atoms (HF/6-311++G(d,p)) is enough to produce unreasonable Fukui indexes, although those values are not similar to those produced

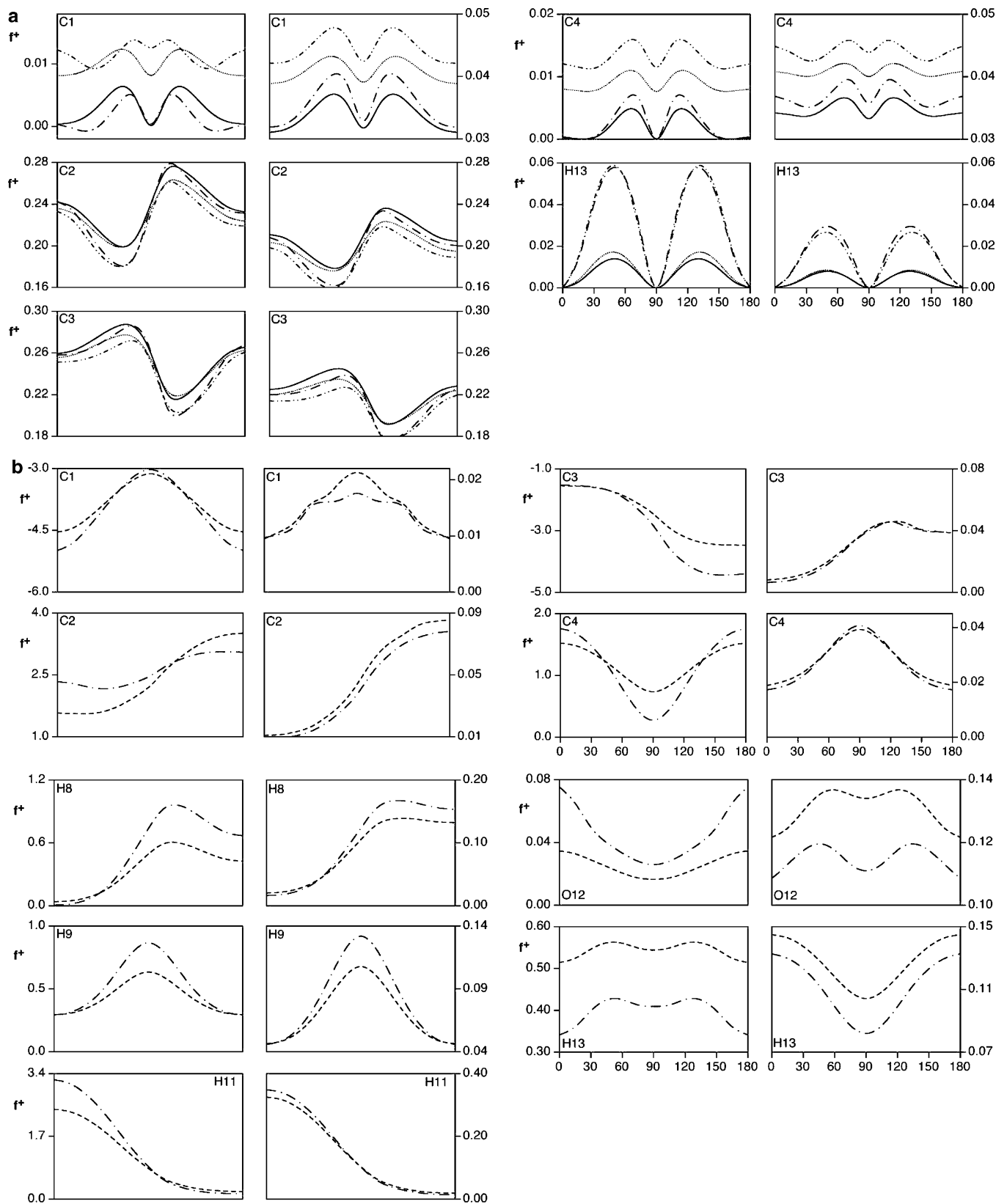


Figure 3. Atomic nucleophilic Fukui indexes (atoms with $f_x^+ < 0.01$ not shown) for the rotational isomerization of phenol at the HF level of theory with a series of double- and triple- ζ quality basis sets ((a) —, HF/6-31G; \cdots , HF/6-31G(d,p); $- \cdot -$, HF/6-311G; and $- \cdot \cdot -$, HF/6-311G(d,p); (b) —, HF/6-31++G(d,p), and $- \cdot \cdot -$, HF/6-311++G(d,p)) at both BSB (left side) and AIM (right panel) condensation schemes.

at the HF/6-311++G(d,p) level. Note that while the f_x^+ indexes for the heavy atoms at the HF/6-311+G(d,p) level change dramatically with respect to the HF/6-311G(d,p) level, the hydrogens are almost unaffected, a result that is quite

intuitive within the BSB scheme. Note that, in contrast, within the AIM scheme the inclusion of the heavy atom diffuse functions does modify the tendency of hydrogens also, and it is quite interesting to see that these results are actually closer

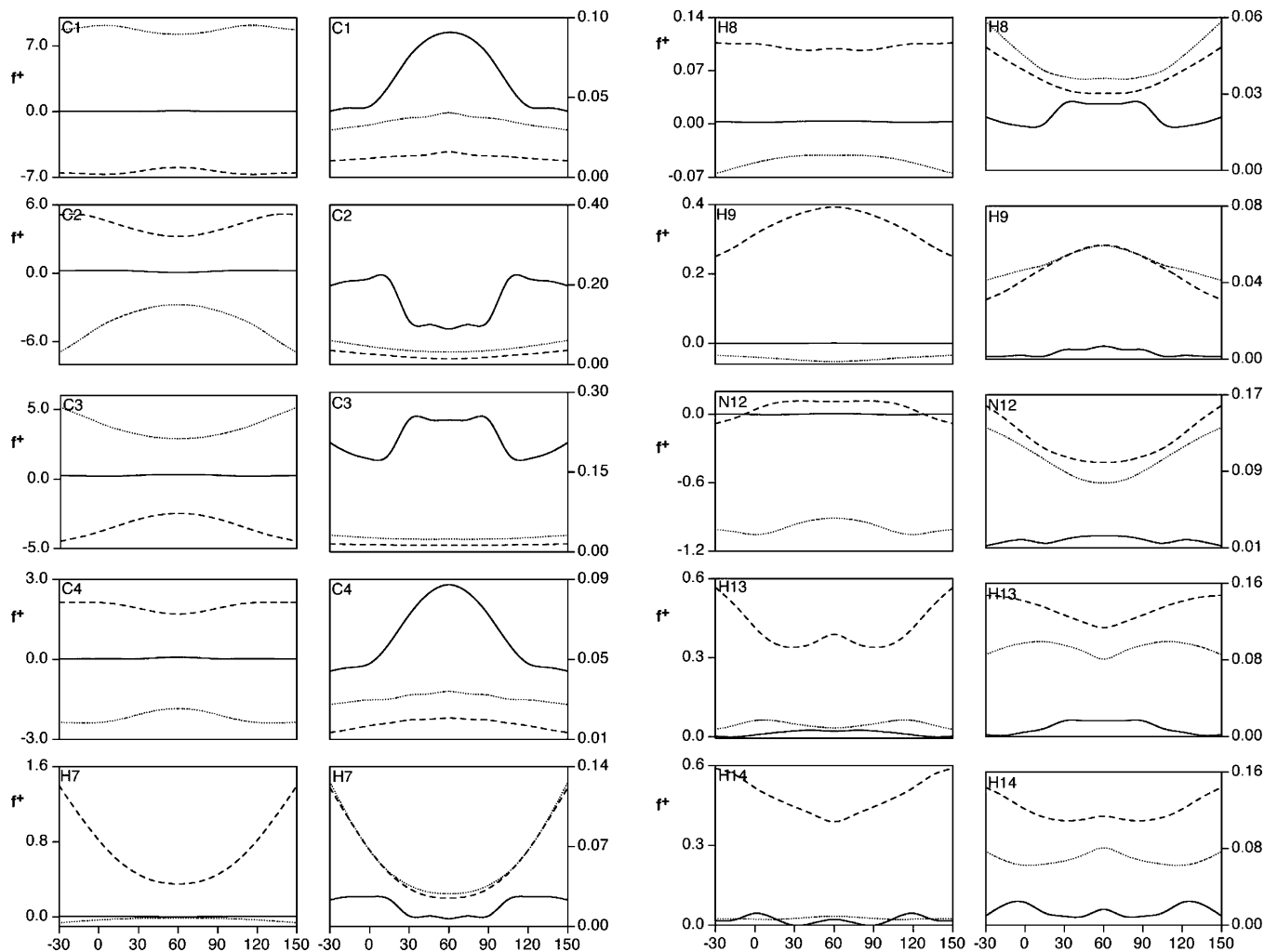


Figure 4. Atomic nucleophilic Fukui indexes for the rotational isomerization of aniline at the HF level of theory with a series of triple- ζ quality basis sets (—, HF/6-311G(d,p); \cdots , HF/6-311+G(d,p); and - - -, HF/6-311++G(d,p)) at both BSB (left panel) and AIM (right panel) condensation schemes.

to those at the 6-311++G(d,p) basis set. Indeed, in the HF/6-311++G(d,p) level at the BSB scheme the f_x^+ indexes are again heavily modified, while the AIM results are quite stable. The instability of the BSB scheme is made evident, while it is also interesting to note that the presence of diffuse functions on the heavy atoms only is enough to produce the correct reactivity trends: hydrogens are more reactive than carbons. This fact can be well understood when considering that diffuse functions at the heavy atoms, as they are spatially big, also describe electron density at the hydrogens. While the BSB sums these contributions to the heavy atoms neighboring the hydrogens, the AIM scheme correctly identifies that density as belonging to the hydrogen atoms.

It has been seen for phenol that, within the AIM condensation scheme, the inclusion of diffuse functions modifies the qualitative trends of reactivity, since in general protons have higher Fukui functions than carbons. This is also the case for aniline, for which it is seen that this modification is produced when diffuse functions are included at the heavy atoms, and the values for the HF/6-311+G(d,p) and HF/6-311++G(d,p) levels are very similar. The reader should keep in mind that, when considering reaction coordinates along which hydrogens are moved apart from the neighboring atom, hydrogen-centered diffuse functions must be used.

Figure 5, which shows the AIM f_x^+ indexes at the HF/6-311G(d,p) level along with those produced by the BSB scheme

at the same level, shows the similarities of such indexes at both condensation schemes when the basis sets has no diffuse functions. This fact has also been emphasized for phenol, see Figure 3a, in the previous section. Note that at this level the results are counterintuitive, since bigger values for f_x^+ are obtained for the carbon atoms, while hydrogens are expected to be more reactive toward nucleophiles.

4.3. Glyoxal. Although not shown, it has been seen that for the f_x^- index the condensation schemes seem to be immaterial, as both produce virtually the same results. This is indeed a surprising result when considering the very different nature of both condensation schemes; however, it indicates that the atomic basis set is well localized and that the BSB partition closely resembles the AIM partition. Moreover, it must be stressed that the BSB f_x^- atomic indexes are well behaved along the torsional coordinate in the sense that their values are always positive and smaller than one.

When analyzing the f_x^+ Fukui indexes, shown in Figure 6, it is readily seen that within the BSB scheme the values lie outside the correct range, the f_C^+ is virtually always negative (except at the stable configurations located at 0° and 180°), and it presents very large negative values. As evidently the normalization is obeyed, and the f_O^+ index behaves correctly, the f_H^+ index presents unphysical high values near 2.0. When analyzing the coefficients of the LUMO it is seen (data not

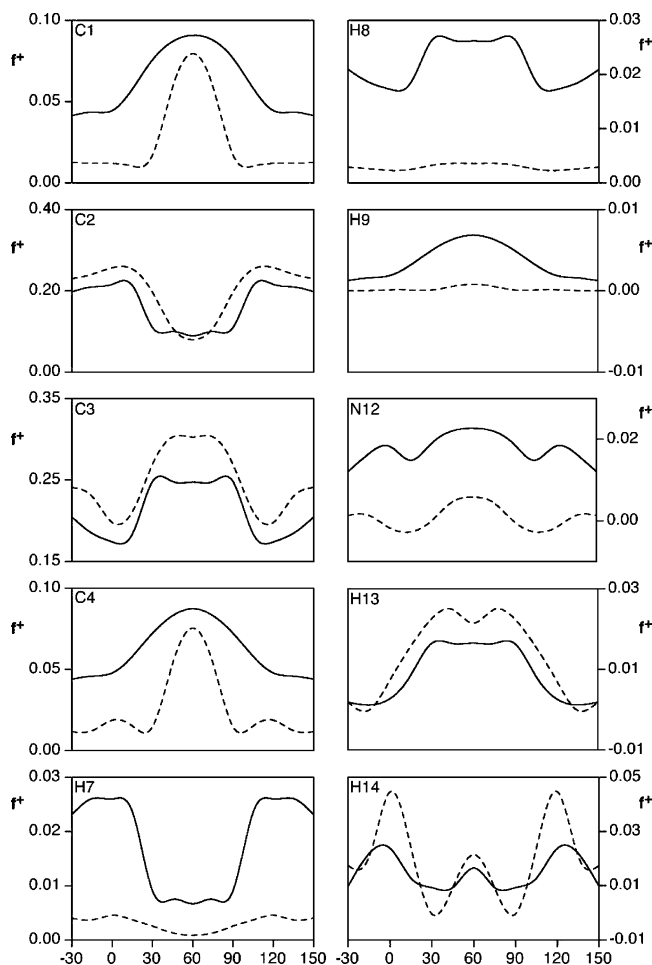


Figure 5. Comparison of the AIM (—) and BSB (---) HF/6-311(d,p) atomic nucleophilic Fukui indexes for the rotational isomerization of aniline.

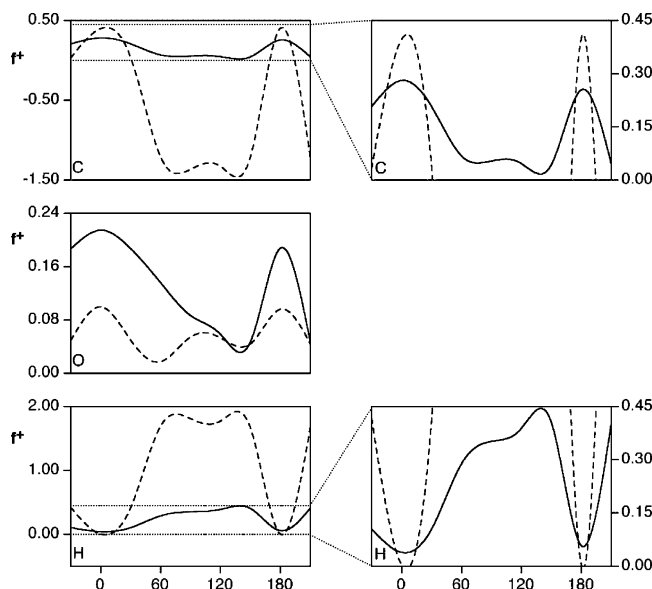


Figure 6. AIM (—) and BSB (---) HF/6-311++G(d,p) atomic nucleophilic Fukui indexes for the rotational isomerization of glyoxal.

shown) that the diffuse functions which present quite large coefficients are responsible for such misbehavior.

It must be noted that while the AIM partitioning corrects the misbehavior of the BSB calculations, it shows very similar qualitative trends along the coordinate as can be seen by comparing the BSB results on the left-hand side of Figure 6

with the AIM values on the re-scaled graphs shown on the right-hand side of Figure 6. See that the trends along the torsional coordinate are quite similar. Also note that at both stable configurations the BSB scheme produces virtually the same results as the real space-based scheme, but small movements along the torsional coordinate result in unphysically large values for f_x^+ ($x = C, H$) within the BSB scheme.

4.4. Rationalization of the Fukui Indexes. Let us examine the working formulas to understand the behavior of the different condensation schemes. Assuming that the basis set is real, but not necessarily orthogonal, the BSB Fukui indexes can be expressed as

$$f_x^\alpha = \sum_{\mu \in x} f_\mu^\alpha = \sum_\nu c_{\mu h(l)}^* c_{\nu h(l)} S_{\mu\nu} = |c_{\mu h(l)}|^2 + c_{\mu h(l)}^* \sum_{\nu \neq \mu} c_{\nu h(l)} S_{\mu\nu} \quad (17)$$

Note that the first term in the rightmost expression is always positive; negative values of the Fukui indexes can then be attributed to the contributions of the second term, which allows negative values but has been considered by Contreras et al. as generally small. This is truly the case when considering relatively small basis sets with no diffuse functions, but in the cases herein studied it appears to be quite large. Indeed, by examining the orbital contributions to the hydrogen nucleophilic Fukui index at an intermediate structure of the rotation of glyoxal (dihedral = 80°), whose value is $f_H^+ = 1.79$, we note that the contribution from the $4s$ atomic orbital is as large as $f_{4s(H)}^+ = 1.76$. The $f_{4s(H)}^+$ index is calculated as follows:

$$f_{4s(H)}^+ = |c_{4s(H),l}|^2 + c_{4s(H),l} \sum_{\nu \neq 4s(H)} c_{\nu,l} S_{4s(H),\nu} \quad (18)$$

where $c_{4s(H),l}$ is the $4s(H)$ atomic orbital coefficient for the LUMO (l). In particular, the quadratic term is quite big because $c_{4s(H),l} \approx 2.99$, while the coefficients for $4s(H)$ at the occupied MOs are $c_{4s(H),occ} < 0.06$ (which explains the reliability observed for f_x^-). It must be noted also that the overlap elements $S_{4s(H),\nu}$ present some large values (when the overlap is between $4s(H)$ and the s and p_y orbitals of the adjacent carbon atom with principal quantum number $n = 3, 4, 5$), indeed $S_{4s(H),5s(C)} \approx 0.9$. Therefore the presence of diffuse functions within the basis sets makes it difficult for the BSB condensation scheme to be accurate and reliable. The problem in general is that the diffuse functions describe electron density belonging to other atoms, as they are spatially big functions, so they will have in general small coefficients when describing occupied orbitals. Although the topology and general shape of the virtual MOs with diffuse functions might be correct, a partition based on the basis function space will not be reliable.

Consider now the expression for the evaluation of the AIM Fukui indexes, which performs integrations in subdomains of the full real space of the Fukui function $f^\alpha(\mathbf{r})$:

$$f_x^\alpha = \int_x |\phi^{h(l)}(\mathbf{r})|^2 d\mathbf{r} \quad (19)$$

As noted earlier, the Fukui function so defined is a positive definite function and as so, any integration of it within subdomains of real space will be positive. Furthermore, as it is also normalized, only the integration within the full space will give a value of exactly 1. Evidently, as the sum of all atomic subdomains of the real space comprises the full space, the normalization condition statement expressed in terms of the Fukui indexes will be correct. As the AIM partition is a real space partition, it will indeed give values of any condensed-

local index as those of true regions of the real space, a characteristic that any BSB partition fails to provide because of its very nature.

5. Concluding Remarks

The AIM condensation scheme for FMO Fukui functions, as proposed by Cioslowski et al.,¹⁰ has been studied in comparison with the BSB scheme of Contreras et al.⁹ To the best of our knowledge, these are the only two condensations schemes that have been used or proposed for this kind of Fukui functions.

It has been seen that the f_x^- index is almost unaltered upon variations on the basis sets, and the condensation scheme chosen seems to be immaterial. The amazing coincidence of the AIM results and the BSB counterpart suggests that, at least within the HOMO, the atomic orbitals are well localized and the BSB scheme closely resembles a true regional condensation as is the AIM scheme.

The reliability of the nucleophilic AIM-condensed Fukui indexes f_x^+ has been illustrated and compared, again, to the BSB condensation scheme. It has been seen that, when the basis sets do not contain diffuse functions, the BSB and AIM schemes produce almost identical results, not necessarily producing correct reactivity trends. However, upon inclusion of diffuse functions, the AIM scheme produces well-behaved f_x^+ indexes but the BSB scheme fails, producing f_x^+ values that lie outside the correct range. Furthermore, when diffuse functions are included to describe the reactivity behavior of hydrogens toward nucleophiles, only the AIM scheme produces the physically correct reactivity trends.

In light of the study by Thanikaivelan et al.¹⁸ within the finite differences approximation, the AIM scheme, along the CHELPG, turns out to produce the best indexes, although sometimes present negative values and three calculations are needed. In analogy, we have formally shown and illustrated that the AIM scheme produces nonnegative Fukui indexes out of a single calculation in the framework of FMO Fukui functions, producing also chemically correct reactivity trends. In light of our study AIM condensed FMO Fukui indexes are a simple and reliable choice for the study of chemical reactivity.

It must be stressed that only within FMO Fukui functions is it possible to ensure nonnegativity of Fukui indexes and only with real space partitioning, since the finite difference Fukui functions might produce negative indexes as they might be negative at some points. Basis set based partitioning, performed on whichever definition of Fukui functions, might produce negative values. In this context, it is interesting to note that Hirshfeld partitioning produces nonnegative values, although no formal proof can be given.

Acknowledgment. The authors are thankful for financial support from FONDECYT through projects 1030173 (E.C.), 1010649 (P.F.) and 1020534 (A.T.L.). E.C. also is thankful for financial support from the Universidad Andres Bello through grant UNAB-DI No. 11-02. F.A.B. thanks CONICYT for a

graduate fellowship and for financial support through Beca de Ayuda de Tesis (AT-403061).

References and Notes

- (1) Fukui, K.; Yonezawa, T.; Shingu, H. *J. Chem. Phys.* **1952**, *20*, 722.
- (2) Fukui, K.; Yonezawa, T.; Nagata, C.; Shingu, H. *J. Chem. Phys.* **1954**, *22*, 1433.
- (3) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Chemie: Weinheim, Germany, 1970.
- (4) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864.
- (5) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, UK, 1989.
- (6) Gutiérrez-Oliva, S.; Jaque, P.; Toro-Labbé, A. In *Reviews of Modern Quantum Chemistry. A Celebration of the Contributions of Robert G Parr*; World Scientific: Singapore, 2002; p 966. Chamorro, E.; Toro-Labbé, A.; Fuentealba, P. *J. Phys. Chem. A* **2002**, *106*, 3891. Chattaraj, P.; Pérez, P.; Zevallos, J.; Toro-Labbé, A. *J. Mol. Struct. (THEOCHEM)* **2002**, *580*, 171. Jaque, P.; Toro-Labbé, A. *J. Chem. Phys.* **2002**, *117*, 3208. Pérez, P.; Toro-Labbé, A. *Theor. Chem. Acc.* **2001**, *105*, 422. Gutiérrez-Oliva, S.; Jaque, P.; Toro-Labbé, A. *J. Phys. Chem. A* **2000**, *104*, 8955. Pérez, P.; Toro-Labbé, A. *J. Phys. Chem. A* **2000**, *104*, 1557. Jaque, P.; Toro-Labbé, A. *J. Phys. Chem. A* **2000**, *104*, 995. Pérez, P.; Toro-Labbé, A.; Contreras, R. *J. Phys. Chem. A* **1999**, *103*, 11246. Toro-Labbé, A. *J. Phys. Chem. A* **1999**, *103*, 4398.
- (7) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049.
- (8) Senet, P. *J. Chem. Phys.* **1997**, *107*, 2516.
- (9) Contreras, R. R.; Fuentealba, P.; Galván, M.; Pérez, P. *Chem. Phys. Lett.* **1999**, *304*, 405.
- (10) Cioslowski, J.; Martinov, M.; Mixon, S. T. *J. Phys. Chem.* **1993**, *97*, 10948.
- (11) Fuentealba, P.; Contreras, R. In *Reviews of Modern Quantum Chemistry. A Celebration of the Contributions of Robert G Parr*; World Scientific: Singapore, 2002; p 1013. Chermette, H.; Boulet, P.; Portmann, S. In *Reviews of Modern Quantum Chemistry. A Celebration of the Contributions of Robert G Parr*; World Scientific: Singapore, 2002; p 992.
- (12) Roy, R. K.; Pal, S.; Hirao, K. *J. Chem. Phys.* **1999**, *110*, 8236.
- (13) Fuentealba, P.; Pérez, P.; Contreras, R. *J. Chem. Phys.* **2000**, *113*, 2544.
- (14) Bultnick, P.; Carbó-Dorca, R.; Langenaeker, W. *J. Chem. Phys.* **2003**, *118*, 4349.
- (15) Roy, R. K.; Tajima, N.; Hirao, K. *J. Phys. Chem. A* **2001**, *105*, 2117.
- (16) Ayers, P. W.; Morrison, R. C.; Roy, R. K. *J. Chem. Phys.* **2002**, *116*, 8731.
- (17) Roy, R. K. *J. Phys. Chem. A* **2003**, *106*, 397.
- (18) Thanikaivelan, P.; Padmanabhan, J.; Subramanian, V.; Ramasami, T. *Theor. Chem. Acc.* **2002**, *107*, 326.
- (19) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Oxford University Press: Oxford, UK, 1990.
- (20) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361.
- (21) Pérez, P.; Contreras, R. *Chem. Phys. Lett.* **1998**, *239*, 239.
- (22) Pérez, P.; Contreras, R.; Aizman, A. *J. Mol. Struct. (THEOCHEM)* **1999**, *493*, 267.
- (23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (24) AIMPAC suite, developed by R. F. W. Bader and co-workers, available from the author.