CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200700365

Understanding the Woodward–Hoffmann Rules by Using Changes in Electron Density

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Abstract: The Woodward-Hoffmann rules for pericyclic reactions are explained entirely in terms of directly observable physical properties of molecules (specifically changes in electron density) without any recourse to model-dependent concepts, such as orbitals and aromaticity. This results in a fundamental explanation of how the physics of molecular interactions gives rise to the chemistry of pericyclic reactions. This construction removes one of the key outstanding problems in the qualitative density-functional theory of chemical reactivity (the so-called conceptual DFT). One innovation in this paper is that the link between molecular-orbital theory and conceptual DFT is treated very explicitly, revealing how molecular-orbital theory can be used to provide "back-of-the-envelope" approximations to the reactivity indicators of conceptual DFT.

Keywords: conceptual density-functional theory • density functional calculations • dual descriptor • Fukui function • pericyclic reaction

Introduction

The language of chemistry is filled with orbitals, whether they be hybrid orbitals (in valence-bond models) or linear combinations of atomic orbitals (in molecular-orbital models). The power of the orbital concept cannot be disputed: almost everything in chemistry can be described, at a qualitative level, by appropriate use of an orbital model. And yet the orbital model is not entirely satisfactory. On the one hand, orbitals are not experimental observables: one can only observe expectation values for the total wavefunction (however, those expectation values can be used, after the fact, to parameterize an orbital model[1]). Second, the orbital models that are most useful for conceptual purposes (Hartree–Fock or semiempirical methods with minimal basis sets) are not quantitatively accurate. Conversely, the orbital models that are useful for quantitative calculations of chemical processes (valence-bond calculations with thousands of resonance structures; molecular-orbital calculations with thousands of configurations) are not conceptually facile. Increasing the accuracy of the orbital model obscures its interpretation.

This stimulates interest in using DFT to describe chemical reactions.[2] DFT is exact, in principle, and yet it is based on the electron density which, like an orbital, is a simple three-dimensional quantity. The electron density, $\rho(r)$, is the probability of observing an electron at the point r. It can be computed from the exact N-electron wavefunction:

$$\rho(r) = N \int \int \cdots \int |\Psi(r, r_2, \cdots, r_N)|^2 \mathrm{d}r_2 \cdots \mathrm{d}r_N \tag{1}$$

or as the sum of the squares of the occupied Kohn–Sham orbitals:

$$\rho(r) = \sum_{i=1}^{N} |\phi_i(r)|^2 \tag{2}$$

The Kohn–Sham orbitals can be computed by using common approximations[3,4] or, alternatively, by using the results of accurate ab initio electronic structure calculations.[5,6] Unlike orbitals, the electron density is experimen-

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tally observable by using, for example, X-ray crystallography.[7,8] Unlike orbital models, the conceptual utility of density functional theory methods does not decrease as the level of accuracy increases. The chemical concepts obtained from "exact" implementations of DFT[9,10] have the same conceptual utility as those obtained from simple approximations.

Chemical reactivity is related to how a molecule changes in response to an approaching reagent. Changes that lower the molecule's energy are favorable and indicate possible reactive channels. Changes that raise the molecule's energy (or do not lower it very much) indicate that a reaction is unlikely to occur.[11,12] In conceptual density-functional theory,[13,14] these changes are quantified by using "response functions" of the electronic energy and the electron density; various types of response functions play key roles in describing different sorts of reactivity.[15,16] The change in energy due to electron transfer is quantified by response functions, such as the electronic chemical potential (equal to minus the electronegativity)[17] and the chemical hardness.[18,19] Other response functions quantify how the electron density changes due to electron transfer[20,21] and due to the electrostatic forces of the approaching reagent.[11]

Although it is almost thirty years old, conceptual DFT is still an active and growing field of research. It has had many successes, both practical (in toxicology, biology, catalysis, and materials characterization) and fundamental. At a fundamental level, conceptual DFT works very well when describing the vast regime of chemistry that falls under the heading "reactions of a Lewis acid with a Lewis base". This category includes not only classic inorganic acid/base chemistry, but also Brønsted–Lowry acidity/basicity, electrophilic/nucleophilic substitution/elimination reactions, and redox reactions. Most chemical processes are well-described by conceptual density functional theory.[14] One can make formal mathematical arguments that conceptual DFT can describe all of chemistry,[16] though it is certainly true that some processes are harder to describe than others.

But how is this done? When one constructs the electron density, one loses all the "phase" information in the wavefunction/orbitals, and we know that the phase of orbitals is important for describing chemical reactions. Moreover, the electron density always transforms as the totally symmetric representation of the molecular symmetry group. But orbital symmetry is also important for describing chemical reactions. It seems impossible, then, for a theory that uses the electron density alone to successfully describe the whole gamut of chemical reactivity.

If one wants to attack conceptual DFT, then one should apply it to reactions for which 1) the orbitals' phase and 2) the orbitals' symmetry is decisive. The most famous and important examples are pericyclic reactions. According to the treatment of Woodward and Hoffmann, the symmetry of highest occupied and lowest unoccupied molecular orbitals is decisive in determining whether a given reaction is allowed or forbidden.[22–26] One can also formulate reactivity rules for pericyclic reactions by using the "orbital phase continuity principle" from valence-bond theory.[27–29] In that case, it is the relative phase of the atomic orbitals that is decisive.

The Dual Descriptor

In this paper, we want to show that pericyclic reactions can be described by using the appropriate response function of the electron density and, moreover, that the resulting theory is so simple and conceptually transparent that it can be used for "back-of-the-envelope" calculations. The key reactivity indicator is the second-order response of the electron density to changes in the number of electrons,[30–32]

$$f^{(2)}(r) = \left(\frac{\partial^2 \rho(r)}{\partial N^2}\right)_{v(r)} \tag{3}$$

In performing this derivative the molecular geometry (and consequently, the nuclear-electron potential $v(r)$) is held fixed. $f^{(2)}(r)$ is the second-order Fukui function;[15] it is often called the "dual descriptor".[30–32] The meaning of $f^{(2)}(r)$ is made clear if we consider the finite difference approximation:

$$f^{(2)}(r) \approx \rho_{N+1}(r) - 2\rho_N(r) + \rho_{N-1}(r) \tag{4}$$

Here $\rho_M(r)$ denotes the electron density of the M-electron system. We now introduce the first-order Fukui functions for electron addition:[21]

$$f^{+}(r) = \rho_{N+1}(r) - \rho_N(r) \tag{5}$$

and electron removal:

$$f^{-}(r) = \rho_N(r) - \rho_{N-1}(r) \tag{6}$$

The dual descriptor is related to the Fukui functions by

$$f^{(2)}(r) \approx f^{+}(r) - f^{-}(r) \tag{7}$$

For a system at zero temperature with a nondegenerate ground state, Equations (5) and (6) are exact.[33–35]

Parr and Yang introduced the Fukui functions as the DFT analogue of the frontier orbitals.[21,34] $f^{+}(r)$ measures how a molecule's electron density changes when an electron is added to the system; it is big in places at which the molecule readily accepts electrons. Conversely, $f^{-}(r)$ measures how a molecule's electron density changes when an electron is removed from the system; it is big in places at which the molecule readily donates electrons. Thus, $f^{(2)}(r)$ will be positive in regions of a molecule that are better at accepting electrons than they are at donating electrons. $f^{(2)}(r)$ will be negative in regions that are better at donating electrons than they are at accepting electrons. *Favorable chemical reactions occur when regions that are good electron acceptors* ($f^{(2)}(r) >$

0) *are aligned with regions that are good electron donors* ($f^{(2)}(r) < 0$).[30,31] The preceding principle is intuitively obvious, but it can be derived by making a detailed analysis using density functional perturbation theory.[12,16] In that approach, one observes that if two molecules, A and B, are aligned so that the Coulomb interaction between the molecules' dual descriptors is attractive,

$$\int\int \frac{f_A^{(2)}(r) f_B^{(2)}(r')}{|r-r'|} \mathrm{d}r\mathrm{d}r' < 0 \tag{8}$$

then the interaction between the molecules is favorable. In practice, this requires that the positive regions of $f_A^{(2)}(r)$ are aligned with the negative regions of $f_B^{(2)}(r)$ and vice versa. A similar integral to Equation (8), involving the ordinary Fukui functions (not the second-order Fukui functions) plays a key role in the regioselectivity of Lewis acids and bases.[36]

Before showing how $f^{(2)}(r)$ is used to rederive the Woodward–Hoffmann rules, we want to show how this quantity is related to the frontier molecular orbitals. In a simple molecular orbital model in which electron correlation and orbital relaxation is neglected, the electron-density change from adding an electron to a molecule is given by the density of the lowest-unoccupied molecular orbital (LUMO):[20]

$$f^+(r) \approx |\phi_{\mathrm{LUMO}}(r)|^2 \tag{9}$$

Similarly, electrons are removed from the highest-occupied molecular orbital (HOMO), and so the density change due to electron removal is given by[20]

$$f^-(r) \approx |\phi_{\mathrm{HOMO}}(r)|^2 \tag{10}$$

Neglecting orbital relaxation and electron correlation, then

$$f^{(2)}(r) \approx |\phi_{\mathrm{LUMO}}(r)|^2 - |\phi_{\mathrm{HOMO}}(r)|^2 \tag{11}$$

The orbitals in Equation (11) can be computed at any level of approximation, though for "back-of-the-envelope" calculations Hückel-type models will be preferred.

Pericyclic Reaction Rules

As an example of how these rules work, we will start with the simple Diels–Alder reaction. Table 1 contains a pictorial representation of the frontier orbitals and the second-order Fukui function, as computed by using Equation (11). Because electron density builds up in the center of a bonding orbital and diminishes in the center of an antibonding orbital, $f^{(2)}(r)$ tends to be negative (dark regions in figures) in the center of the ethene molecule and positive (light regions in figures) at the ends. This coincides with conventional wisdom: ethene will donate electrons from the double bond (in which $f^{(2)}(r) < 0$) and accept electrons on the ends (at the ever-so-slightly acidic hydrogens). Butadiene and hexatriene are similar, if forced to accept an electron, the molecule will place that electron where it does not have a double bond. If forced to donate an electron, the molecule will forfeit an electron from one of the double bonds.

It is now clear that ethene and butadiene are appropriately matched (Figure 1). If an ethene molecule approaches from below (or above) the plane of the butadiene molecule, regions with opposite signs for the dual descriptor align; this is energetically favorable (cf. Equation (8)). The [2+2] addition reaction (ethene + ethene) is predicted to be unfavorable for the same reason. If one examines a hypothetical [2+6] addition reaction (ethene + hexatriene), one observes that the best alignment of $f_{\mathrm{ethene}}^{(2)}(r)$ and $f_{\mathrm{hexatriene}}^{(2)}(r)$ occurs when the molecules orient themselves so that a [2+4] cycloaddition can occur. One infers that, in the ground state, [2+4] cycloaddition reactions are allowed while [2+2] and [2+6] cycloaddition reactions are forbidden.[25]

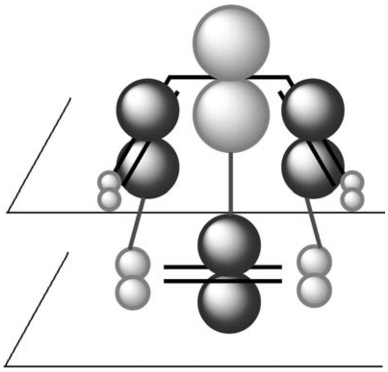
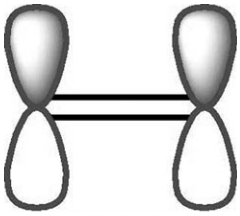
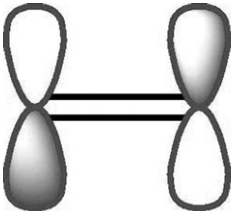
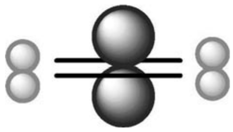
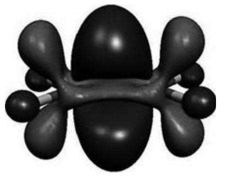
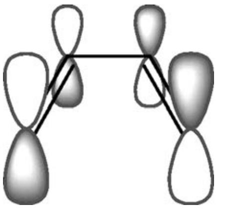
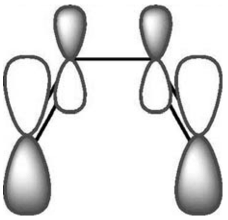
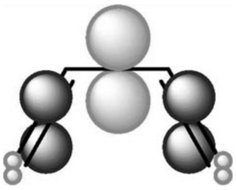
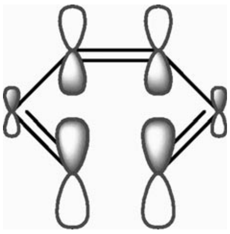
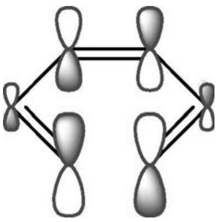
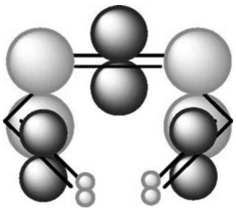
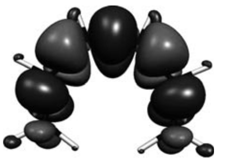
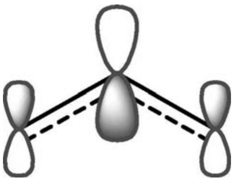
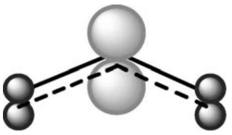


Figure 1. The interaction between the dual descriptors in the [4+2] suprafacial/suprafacial addition of butadiene to ethene. Notice that the molecules align so that there are favorable interactions (represented with the green lines) between their dual descriptors. Acidic sites ($f^{(2)}(r) > 0$) are denoted light and basic sites ($f^{(2)}(r) < 0$) are dark.

One way to interpret the selection rules for other types of pericyclic reactions is to regard them as "generalized" Diels–Alder reactions.[37] So it is unsurprising that other pericyclic reactions can also be described by using the dual descriptor. Recall that favorable reactions will be associated with small (and preferably negative) values of the electrostatic interaction energy between the two molecules' dual descriptors (cf. Equation (8)). Thus, if two ethene molecules are oriented so that their double bonds are parallel (cf. Figure 2a), then there is a large repulsive energy between them (this is why the [2+2] suprafacial/suprafacial cycloaddition is forbidden). This repulsive interaction will be reduced if the ethene molecules rotate so that their double bonds are perpendicular, as shown in Figure 2c. In the resulting suprafacial/antarafacial orientation, the interactions between the ethene molecules are relatively favorable. This also agrees with orbital symmetry considerations: [2+2] suprafacial/an-

Table 1. The frontier orbitals and the dual descriptors for the example molecules considered in this paper. Acidic sites ($f^{(2)}(r)>0$) are light and basic sites ($f^{(2)}(r)<0$) are dark. The last column presents the dual descriptor computed from finite differences of molecular densities [Eq. (4)] at the B3LYP/6-31G** level. Note that the dual descriptor in butadiene has a different shape than the dual descriptors in ethene and hexatriene. This explains why [2+4] cycloadditions are allowed but [2+2] and [2+6] cycloadditions are not.

Molecule	$\varphi_{\mathrm{HOMO}}(r)$	$\varphi_{\mathrm{LUMO}}(r)$	$f^{(2)}(r) \approx \lvert\varphi_{\mathrm{LUMO}}(r)\rvert^2 - \lvert\varphi_{\mathrm{HOMO}}(r)\rvert^2$	$f^{(2)}(r) \approx \rho_{N+1}(r) - 2\rho_N(r) + \rho_{N-1}(r)$
ethene				
butadiene				
hexatriene				
allyl radical				

tarafacial cycloaddition would be allowed, but are not observed because the attacking ethene molecule isn't floppy enough to "reach around" the other molecule.

Such considerations become more important, however, when one considers electrocyclizations.[26] As shown in Figures 3 and 4, electrocyclizations can be considered "generalized" Diels–Alder reactions in which the two fragments are tethered together at their ends. Thus, electrocyclization of hexatriene (Figure 3a) is related to the [4+2] cycloaddition reaction and it will be favorable for the ethene fragment and the butadiene fragment to "twist towards each other" (disrotatory motion) as if to align for suprafacial–suprafacial attack. This is clear in Figure 3a, the attraction of the ethene fragment for the butadiene fragment causes the ring to buckle inwards; this disrotatory motion improves the overlap between the dual descriptors of the fragments, as shown in Figure 3b. Electrocyclization of butadiene (Figure 4a) is related to the [2+2] cycloaddition reaction; in this case, the ethene fragments will twist away from each other (conrotatory motion) as if aligning for suprafacial–antarafacial attack. This is clear if one compares Figures 4a and 2a; the ethene fragments will twist away from each other to reduce the repulsion between the dual descriptors. One fragment will twist above the molecular plane and the other will twist below the molecular plane, as shown in Figure 4b. This twist brings the top of one of the ethene fragments in a position to interact with the bottom of the other ethene fragment and corresponds to a conrotatory process.

Sigmatropic shifts are described similarly. For example, to characterize the migration of a methyl group, one first models the transition state of the reaction by rehybridizing the methyl to sp^2 (replacing the σ-bond of the molecule with a weaker π-bond). After rehybridization, the molecule resembles an ethene-type fragment (consisting of the migrating methyl group and the neighboring carbon atom) and a remnant (see Table 2). If the remnant has four carbons (1,5-sigmatropic shift), then the attraction between the dual descriptors of the molecular fragments causes the ring to buckle inwards, just as it did in the disrotatory electrocyclization of cyclohexatriene. The movement along this reaction coordinate corresponds to a suprafacial sigmatropic shift. If the remnant has two carbons (1,3-sigmatropic shift), the reaction resembles the electrocyclization of butadiene. This antarafacial sigmatropic shift can be identified with a conrotatory mode in the electrocyclization. These analogies are in line with the observed similarity of the transition states in

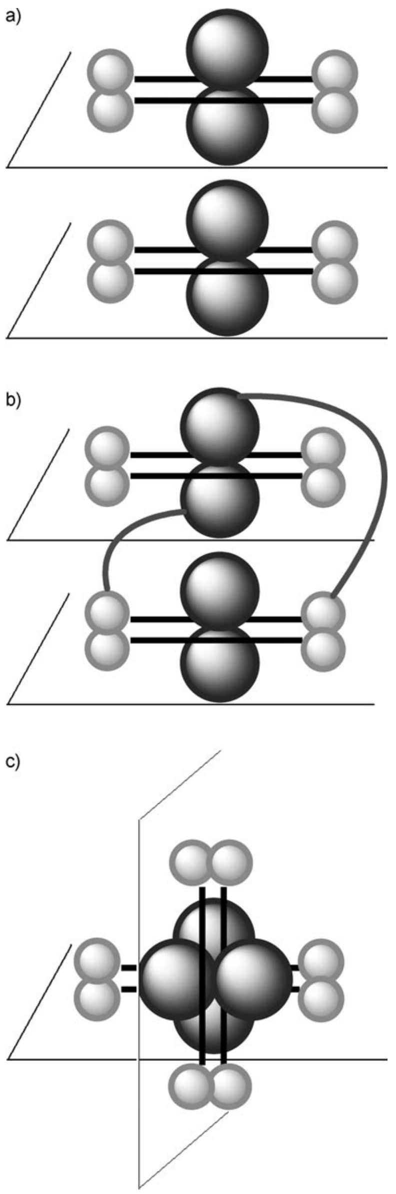


Figure 2. The interaction between the dual descriptors of two ethene molecules is repulsive (a). Suprafacial/antarafacial interactions (b) can be exploited if the ethene molecules rotate so that the double bounds are perpendicular (c). The curved lines represent attractive interactions, and can be imagined as rubber bands that pull the molecule into an energetically favorable alignment.

sigmatropic hydrogen shifts and protonated electrocyclizations.[38]

Finally, as a more challenging example, we consider whether the Cope rearrangement occurs through a boatlike intermediate or a chairlike intermediate. If we consider the transition state of this reaction to be approximately modeled by two allyl radicals, then the repulsion between their dual descriptors will be smaller in the chair structure than in the boat structure (Figure 5). This prediction agrees with experiment.[39] The reader will recognize that this type of argument can be generalized to provide guidance on whether the *endo* or *exo* product forms in a Diels–Alder reaction.

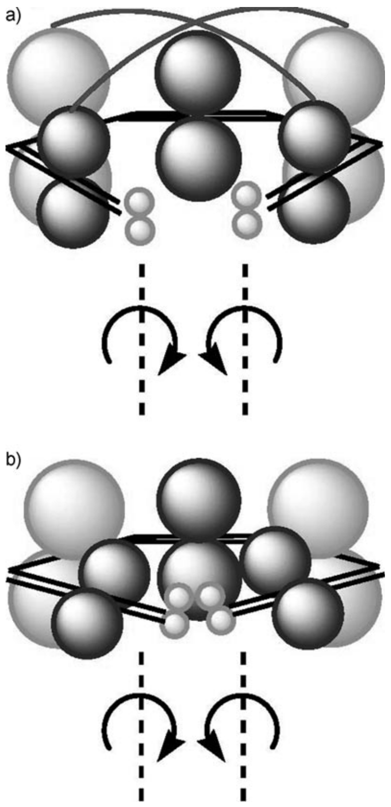


Figure 3. a) The [2+4] electrocyclization can be conceived as a butadienyl group tethered to (and interacting with) an ethenyl group. b) The favorable [2+4] interaction tends to make the ring buckle inward in a disrotatory fashion.

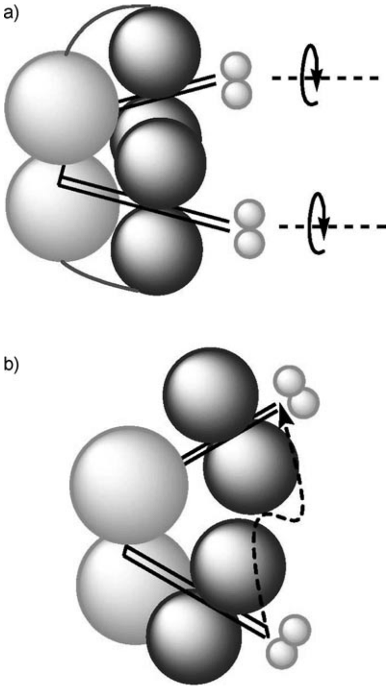
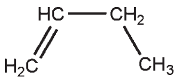
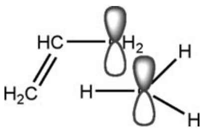
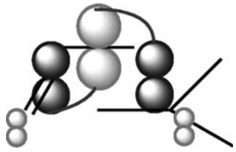
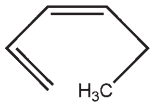
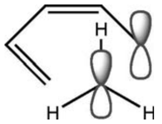
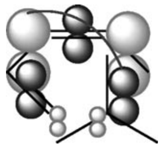


Figure 4. a) The [2+2] electrocyclization can be conceived as two ethenyl groups interacting. b) In order to minimize the repulsion between the dual descriptors on the two sides of the molecule, the molecule twists into an orientation that facilitates suprafacial/antarafacial attack, with the top of one side of the molecule moving into a position to attack the bottom of the other side of the molecule, as indicated by the arrow. This corresponds to a conrotatory motion.

Table 2. The sigmatropic shift can be described if one recalls that rehybridization occurs as one approaches the transition state of this reaction. In the rehybridized state, sigmatropic shifts can be explained as generalized electrocylizations/cycloadditions. The curved lines represent attractive interactions, and can be imagined as rubber bands that pull the molecule into an energetically favorable alignment.

Shift	Structure	Rehybridization	Dual descriptor
1,3-methyl			
1,5-methyl			

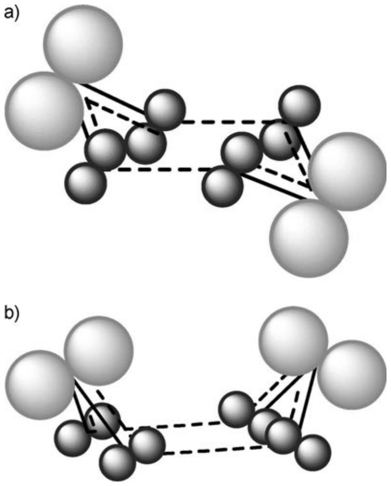


Figure 5. For a diyl intermediate in the Cope rearrangement, the chair structure (a) is more favorable than the boat structure (b). The repulsion between the dual descriptors of the two allylic fragments is minimized in the chair structure. The repulsion in the boat structure is very large.

Excited-state reactivity can also be predicted. If one promotes an electron from $\varphi_{\mathrm{HOMO}}(r)$ to $\varphi_{\mathrm{LUMO}}(r)$, and subsequently adds an electron to the system, the additional electron will occupy the (now singly-occupied) $\varphi_{\mathrm{HOMO}}(r)$:

$$f^{+}_{\mathrm{e.s.}}(r) = \rho_{e.s.;N+1}(r) - \rho_{e.s.;N}(r) \approx |\phi_{\mathrm{HOMO}}(r)|^2 \tag{12}$$

Similarly if one removes an electron from the excited state, it will come from $\varphi_{\mathrm{LUMO}}(r)$:

$$f^{-}_{\mathrm{e.s.}}(r) = \rho_{e.s.;N}(r) - \rho_{e.s.;N-1}(r) \approx |\phi_{\mathrm{LUMO}}(r)|^2 \tag{13}$$

When one moves beyond the orbital model, the appropriate formulas for the Fukui functions are the differences between the densities of the N-electron excited state and the $N-1$ and $N+1$ electron ground states, as shown in Equations (12) and (13).[40] Inserting Equations (12) and (13) into the equation for the dual descriptor [Eq. (7)], we find that the dual descriptor for the first excited state is approximately equal to minus one times the ground-state dual descriptor:

$$f^{(2)}_{\mathrm{e.s.}}(r) \approx f^{+}_{\mathrm{e.s.}}(r) - f^{-}_{\mathrm{e.s.}}(r) \approx |\phi_{\mathrm{HOMO}}(r)|^2 - |\phi_{\mathrm{LUMO}}(r)|^2 \approx -f^{(2)}_{\mathrm{g.s.}}(r) \tag{14}$$

Consequently, reactivity preferences in the excited state are exactly reversed from those in the ground state. That which is thermochemically forbidden is photochemically allowed. That which is photochemically allowed is thermochemically forbidden.

Moving past the orbital model, one can return to the finite difference approximation [Eq. (4)] or the exact definition [Eq. (3)]. The last column in Figure 1 plots $f^{(2)}(r)$ at the B3LYP/6–31G** level.[41–43] The results are the same except for the small differences due to orbital relaxation effects that are observed near the nodal surfaces of the frontier orbitals, as expected.[44–46]

Perspective

The dual descriptor does not require information about the frontier orbitals and provides, in this sense, a true “no orbitals necessary” alternative to the usual formulations of the Woodward–Hoffmann rules. While orbitals might be used to facilitate the computation of the electron density, orbitals are not required to compute the dual descriptor. Consequently, the dual descriptor could be computed from accurate orbital-free methods, such as reduced-density matrix theory[47] or quantum Monte–Carlo;[48] it could even be constructed from high-resolution X-ray data. The overall picture provided by the dual descriptor will be insensitive to the type and accuracy of the underlying calculations of the electron density except, of course, in cases for which lower levels of theory are qualitatively incorrect. This is the power of the approach based on density functional theory: all of the old results are recovered when they should be and, in cases for which the simple orbital models fail, the density-functional theory approach will not. It is also worth noting that our results do not invoke symmetry and can therefore be applied to asymmetric reagents. As most large molecules lack symmetry, this is an important advantage of the dual descriptor approach.

It seems that a large part of chemistry can be predicted by using the dual descriptor and the general principle that, when two molecules approach each other, the electrophilic regions of the first reagent align with the nucleophilic regions of the second reagent, and vice versa. This principle suffices to derive the Woodward–Hoffmann rules, but the dual descriptor can also be used to predict the regioselectivity of conventional electrophilic/nucleophilic attack.[30–32] Finally, one can use a Maxwell relation to rewrite the dual descriptor as the functional derivative of the chemical hardness[18] with respect to the electron-nuclear potential:[31]

$$f^{(2)}(r) = \left(\frac{\delta\eta}{\delta\nu(r)}\right)_N \tag{15}$$

In this way, the dual descriptor makes contact with the response of the chemical hardness to changes in molecular geometry and elucidates the origins of the maximum hardness principle[12,49–51] and the initial hardness response criterion.[52] Given this fundamental link, it is unsurprising that the maximum hardness principle and the initial hardness response have been invoked in computational studies of the Woodward–Hoffmann rules.[52,53] In particular, it is found that for allowed Diels–Alder reactions, the hardness increases as the reagents proceed along the reaction coordinate from the separated reagent limit to the transition state.

The dual descriptor is a powerful local reactivity indicator for regioselectivity but, like the Fukui function, it is not expected to provide an accurate indication of the overall reactivity of a molecule. In particular, neither the Fukui function nor the dual descriptor is size extensive. When a reactivity indicator that reflects overall reactivity is needed, workers in conceptual DFT usually work in the grand canonical ensemble.[54] Reactivity indicators in the grand canonical ensemble are obtained by replacing derivatives with respect to the number of electrons, N, with derivatives with respect to the electronic chemical potential, μ (the electronic chemical potential measures the intrinsic strength of Lewis acids and bases, so reactivity indicators in the grand canonical ensemble represent how a molecule's reactivity changes as its electron-withdrawing power or electronegativity decreases).[17,55]) In the grand canonical ensemble, the Fukui function is replaced by the local softness[56]

$$s(r) = \left(\frac{\partial\rho(r)}{\partial\mu}\right)_{\nu(r)} = \frac{f(r)}{\eta} \tag{16}$$

which augments the regioselectivity information from the Fukui function, $f(r)$, with the overall reactivity information associated with the maximum hardness principle. The Fukui function in this equation can be identified with the Fukui function from above [Eq. (5)], the Fukui function from below [Eq. (6)], or the average of the two. Similarly, the grand canonical dual descriptor is as follows:

$$s^{(2)}(r) = \left(\frac{\partial^2\rho(r)}{\partial\mu^2}\right)_{\nu(r)} = \frac{f^{(2)}(r)}{\eta^2} - \frac{f(r)}{\eta^3}\left\{\left(\frac{\partial\eta}{\partial N}\right)_{\nu(r)}\right\} \tag{17}$$

and augments the regioselectivity information from the dual descriptor with the overall molecular reactivity information from the maximum hardness principle. The second term in Equation (17) should be negligible because the term in brackets (the hyper-hardness) is usually small.[57] Other workers in conceptual DFT have proposed dual-descriptor-based measures for the overall reactivity of molecules (e.g., the dual local softness,[31] $f^{(2)}(r)/\eta$ and the excess electrophilicity,[58–61] $\mu^2 f^{(2)}(r)/2\eta$), but those reactivity indicators are not size extensive and so they are not appropriate for comparing the relative reactivity of molecules with different sizes.

Conceptual DFT is a powerful and general approach for predicting chemical reactivity, but we do not believe that orbital-based descriptions of chemical reactivity are obsolescent. Orbitals certainly have a role to play in the conceptual analysis of molecules, not least because an orbital analysis has a more direct link with how calculations are actually performed (as almost every modern quantum chemistry technique is based on an orbital-based independent electron model, with possible corrections added to it). But it is reassuring that the richness and breadth of chemical reactions can be described by using only physical observables, specifically, the response of the energy to various sorts of perturbations. These quantities can be observed experimentally or computed by using anything from simple back-of-the-envelope Hückel-type models to the most accurate ab initio techniques. For this reason, conceptual density-functional theory allows one to describe chemistry in a way that fully accounts for the effects of orbital relaxation and electron correlation. It does not replace simple orbital-based conceptual models, but coincides with them when they work, and supersedes them when they do not.

Acknowledgements

P.W.A. acknowledges helpful discussions with Professor R. Parr and Dr. S. Liu (Univ. North Carolina, Chapel Hill), Professor A. Toro-Labbe (Pontificia Universidad Católica de Chile), and Professor P. Chattaraj (IIT-Kharagpur) and financial support from the NSERC and the Canada Research Chairs. C.M. thanks CEA-Grenoble for financial support. P.G. and F.D.P. thank the Fund for Scientific Research Flanders (FWO) and the VUB for continuous support of their research group.

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Received: March 4, 2007