

Chapter 5

Excited States

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Abstract: In this chapter, inclusion of excited states in Conceptual DFT is discussed. We focus on the study of reactivity, along two axes: either looking for reactivity and selectivity in the excited states themselves, or using excited states as a mere tool to delineate ground state chemical properties.

Keywords: Conceptual DFT, excited states, perturbation theory

5.1. Introduction

Conceptual DFT[1–3], by its explicit dependence over the first Hohenberg-Kohn theorem[4], is a ground-state theory. Therefore, the very purpose of this chapter may then seem out of scope of conceptual DFT. How can one include excited states in a ground-state only representation? And for which aim?

Several approaches were undertaken in the past years to embrace this topic,

which we propose to revisit here. Broadly speaking, two axes can be drawn: either one is interested in characterizing the excited states properties, by studying them or conjecturing their properties from the ground state, or either one is interested in using the excited states to improve the representation of the ground state. Illustrations of both ideas are provided in sections 1 and 2, respectively. Note however this chapter does not aim at being exhaustive. Noticeably, many developments were proposed over the years, especially at times when no efficient computational framework for excited states was available (before the advent of TDDFT, so to say). Additionally, some works focused on the development of time-independent DFT models, looking for the definition and construction of either state-specific or generic energy density functionals.[5, 6] We believe such developments, though precious and meaningful, fall out of the scope of the chapter, and for the sake of clarity and concision we decided not to include them in the following.

5.2. Reactivity and Selectivity of Excited States

5.2.1. Photochemical reactivity

Study of excited states properties is particularly interesting for photochemical reactions (reactions performed under photoexcitation).[7] Experimentally, it is indeed often observed that the course of a chemical reaction is altered when this reaction is performed under exposition to light. This is for instance the case of the electrocyclic reactions, whose reactivity is explained by the famous

Woodward-Hoffmann rules.[8]

In such photochemical reactions one reactant is electronically excited to one of the very first excited states. Following Kasha’s rule,[9] light absorption may indeed lead to high excited singlet states, which quickly decay to the lowest excited one (S_1). This singlet state may also convert to a lower energy triplet state T_1 through inter system crossing (ISC). Hence, among the excited states manifold, one may restrict the study to states S_1 and T_1 only to explain photochemical reactivity and selectivity.

The case of triplet state T_1 is noteworthy. Formally speaking, this excited state is indeed a ground state for the triplet spin multiplicity. Hence many photochemical reactions can be straightforwardly studied by the means of genuine ground-state conceptual DFT tools. This has been nicely illustrated by a series of publication from Geerlings and de Proft group in the case of photochemical cycloadditions.[10, 11] They showed that the sign of the hardness variation at the onset of the reaction is a reliable indicator of the feasibility of the reaction (in connection with Woodward-Hoffmann rules).[12] They also demonstrated, by deriving original spin-polarised descriptors (spin donicity and philicity), that selectivity in the [2+2] photochemical cycloaddition of enones with substituted alkenes is better explained by the differential spin-coupling between reactive sites than by standard charge-transfer arguments.[13]

5.2.2. Insight from frontier MO theory

Nonetheless, how can one address cases for which ISC is not active, or not leading to chemical reactivity? In such a case, a genuine excited state (S_1) needs to be studied and a model for predicting their chemical behavior should

be proposed.

At first, one may rely on the formalism of MO theory, and employ "usual" approximations to delineate the chemical behaviour of the first excited state. If one neglects orbital relaxation, the first excitation may be seen as arising from the promotion of one electron from the HOMO to the LUMO. The resulting excited state configuration can then be written as $(HO)^1(LU)^1$.

This approximate electron configuration can then be used to express usual conceptual-DFT (C-DFT) descriptors. Let us for instance consider the electrophilic Fukui function.[14] Under the finite difference approximation, it is expressed as the following electron density difference

$$f_{ex}^+(\mathbf{r}) = \rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r}) \quad (5.1)$$

where the indices refer to the total number of electrons in the system. Here one has to consider the neutral excited configuration, and a configuration with one additional electron (N+1). Keeping the frozen orbital hypothesis, the lowest N+1 configuration in energy is $(HO)^2(LU)^1$. Hence, in the excited state and under the previous approximations the electrophilic Fukui function will equal the HOMO density

$$f_{ex}^+(\mathbf{r}) = \rho_{HO}(\mathbf{r}) = f_{gs}^-(\mathbf{r}) \quad (5.2)$$

which is itself equal to the nucleophilic ground state Fukui function. Using the same line of arguments, one has $f_{ex}^-(\mathbf{r}) = f_{gs}^+(\mathbf{r})$. Ultimately one may infer that the dual descriptor (DD)[15] in the excited state will be the opposite of that

of the ground state:

$$\Delta f_{ex}(\mathbf{r}) = f_{ex}^+(\mathbf{r}) - f_{ex}^-(\mathbf{r}) = \rho_{HO}(\mathbf{r}) - \rho_{LU}(\mathbf{r}) = -\Delta f_{gs}(\mathbf{r}) \quad (5.3)$$

Sites with positive (resp. negative) values of $\Delta f(\mathbf{r})$ will be nucleophilic (resp. electrophilic) in S_1 and electrophilic (resp. nucleophilic) in the ground state. Such a simple development was used and allowed to retrieve the regio-selectivity of photo-chemically induced cycloaddition (Woodward-Hoffmann rules).[16] Even though this naive model holds and provides results in agreement with experiments, there is room for an improved and more grounded theory.

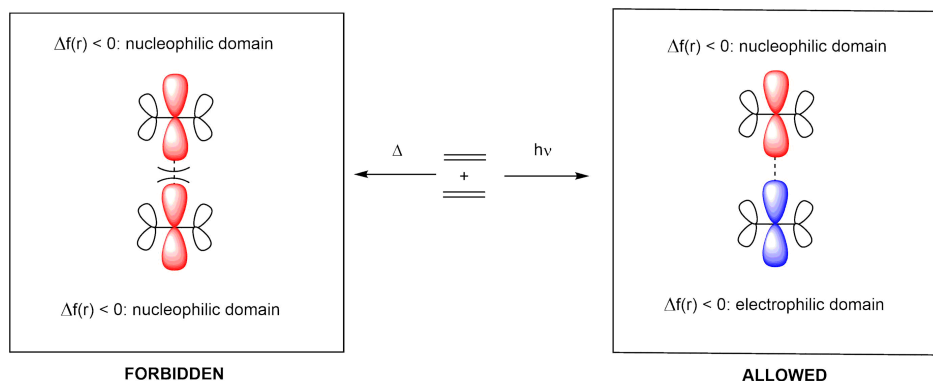


Figure 5.1: [2+2] cycloaddition of ethylene explained by the Dual descriptor. Molecules in the ground state are depicted in red, while molecules in the first excited state are depicted in blue.

5.2.3. Chemical potential locality

So, how can one derive more general knowledge on the excited states, thus without the need to rely on the rather drastic frozen orbital hypothesis? One of the very few proposal relies upon the electronic chemical potential.

Let us recall that the electronic chemical potential μ is defined, according to Parr, as the functional derivative of the energy with respect to the electron density:

$$\mu = \left(\frac{\delta E}{\delta \rho(\mathbf{r})} \right)_N = v(\mathbf{r}) + \frac{\delta F_{HK}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}. \quad (5.4)$$

This global quantity interestingly arises from the sum of two local quantities, namely the external potential and the Hohenberg-Kohn universal functional derivative against the density. Actually, μ is constant because the ground state electron density is stationary (it minimises E). In 2009, it was proposed to use a vertical excited state density $\rho_k(\mathbf{r})$ (thus at constant external potential) instead of the ground state electron density in this derivative:[17]

$$\lambda_k(\mathbf{r}) = \left(\frac{\delta E}{\delta \rho_k(\mathbf{r})} \right)_N = v(\mathbf{r}) + \frac{\delta F_{HK}[\rho_k(\mathbf{r})]}{\delta \rho_k(\mathbf{r})}. \quad (5.5)$$

The excited state concerned in the above equation is called Hot Excited State as it is both electronically and vibrationally excited. In this approach, λ_k is a local quantity, since the excited density does not minimize the ground state energy functional. Indeed, the above formulation uses the universal Hohenberg-Kohn functional that only works for ground states. This non constant chemical potential is thus fitted to translate the tendency of the electron density to relax to the ground state configuration, at fixed geometry through the integrated equation:

$$dE \approx \int \lambda_k(\mathbf{r}) \delta \rho(\mathbf{r}) d\mathbf{r} \quad (5.6)$$

Levy and Nagy have proposed an excited state formulation of DFT in which

the Hohenberg-Kohn functional is no longer universal, in the sense that it is a functional of both the electron density and the external potential.[18] To reach a stationary state, the external potential need to evolve (geometry relaxation).

$$E_k = \int \rho_k(\mathbf{r}) \delta v(\mathbf{r}) d\mathbf{r} + F_k[\rho_k(\mathbf{r}), v(\mathbf{r})] \quad (5.7)$$

λ_k would have been global should this excited state formulation has been used.

After some developments, it could be shown that for the low lying excited states one may write

$$\lambda_k(\mathbf{r}) = \mu + \int \frac{\rho_k(\mathbf{r}') - \rho_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = \mu + \int \frac{\Delta f_k(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (5.8)$$

with ρ_k the k^{th} excited state electron density (0 meaning ground state), and Δf_k the so-called kth state-specific dual descriptor (SSDD). Hence, the difference between the global and local potentials is equal to the difference in the electrostatic potential induced by the electron density distributions in the ground and excited states. A site that lost electron density under excitation will then become attractive to electrons in the excited state (thus become electrophilic). Conversely a site that gained electron density will become repulsive to electrons, thus bear some nucleophilicity.

If we now focus only on the first excited state, then we retrieve our previous results on the signification of the DD sign in the excited states. Indeed, it is often assumed that the first SSDD is equal to the "usual" C-DFT and ground-state DD (*vide infra*). Thus the ground state DD may indeed be used to retrieve the reactivity and selectivity in the first excited state, but the relation between the sign of the DD and the philicities is reversed (see figure 5.2). Nucleophilic regions will be characterised by a positive sign of the DD in

the excited state, while electrophilic regions are associated to a negative DD. Eventually, this model grounds the naive view that the opposite of the ground state dual descriptor can ascribe the electro/nucleophilicity of molecular regions. This approach has been successful to recover the Woodward-Hoffmann rules, predict the regioselectivity of Paterno-Buchi reactions,[17] and has also been used for explaining DNA photo-chemically induced lesions.[19]

5.2.4. In summary

Very few attempts have been made to propose a theory able to predict the reactivity and selectivity of excited states. Generally, the proposed approaches intend to only tackle the low-lying excited states, which are expected to be the major player in photoreactivity. In fact, in several cases these excited states are formally ground states for the triplet multiplicity, hence ground-state descriptors are perfectly working.

Otherwise, the electron densities can be described from a Taylor's expansion of the ground state density, allowing to delineate excited state properties using "standard" C-DFT developments. In this spirit a descriptor based on a local chemical potential was proposed, and successfully applied to predict the regioselectivity of various [2+2] photochemical cycloadditions.

5.3. Excited states used to describe the ground state

The use of excited states to understand the reactivity of a ground state electron system goes back to a publication by Walsh in the 1940's.[20] At that time Walsh was arguing that ethylene oxide and ethylene are more reactive than ethane because the first excited state wavelengths of the former are lower (resp. 1950 Å and 1745 Å) than that of the latter. After this first rough approach, the subject was left almost untouched till Pearson,[21] Bader[22] and Salem[23] revived it up in the 1960's. In three different papers they provided a series of conditions for an excited state to favor a chemical reaction. In this part, starting from their development, it is shown that lot of information about the ground state reactivity, regio and stereoselectivity can be obtained from the excited states.

5.3.1. Reactivity from excitation energy: an early formulation of the Maximum Hardness Principle

In the late 1980's Pearson was working on the physical meaning of the chemical potential and the absolute hardness. His main concern was chemical reactivity and how to compare the stability of molecules. In the following years he was about to propose the Maximum Hardness Principle. In this context he published an article in the journal of the American Chemical Society entitled "Electronic spectra and chemical reactivity".[24] In this paper, actually a

follow up of the series of original papers published by Bader, Salem and himself, he proposed a reactivity model based upon the wave-function and energy perturbation of a molecular fragment experiencing a modification of its surrounding, due for instance to the approach of another molecule or an internal reorganisation (isomerisation). Its perturbed wave function, as it is common in this theory, was expanded through the set of the unperturbed eigenfunctions.

Following Pearson’s notation, let U be the nuclear-nuclear and nuclear-electron potential energy, and Q be the reaction coordinate. The molecular (total) Hamiltonian can be expanded as a Taylor series:

$$H = H_0 + \left(\frac{\partial U}{\partial Q}\right) Q + \frac{1}{2} \left(\frac{\partial^2 U}{\partial Q^2}\right) Q^2 + \dots \quad (5.9)$$

and according to Rayleigh-Schrödinger perturbation theory ground state energy and wavefunction vary according to the perturbation as

$$E = E_0 + \left\langle \psi_0 \left| \frac{\partial U}{\partial Q} \right| \psi_0 \right\rangle Q + \left\langle \psi_0 \left| \frac{\partial^2 U}{\partial Q^2} \right| \psi_0 \right\rangle \frac{Q^2}{2} + \sum_{k \neq 0} \frac{\left[\left\langle \psi_0 \left| \frac{\partial U}{\partial Q} \right| \psi_k \right\rangle Q \right]^2}{E_0 - E_k} \quad (5.10)$$

$$\psi = \psi_0 + \sum_{k \neq 0} \frac{\left\langle \psi_0 \left| \frac{\partial U}{\partial Q} \right| \psi_k \right\rangle Q}{E_0 - E_k} \psi_k \quad (5.11)$$

where (E_0, ψ_0) and (E_k, ψ_k) are the unperturbed solutions of the Schrödinger equation for, respectively, the ground and k^{th} excited state.

Pearson then used equations 5.10 and 5.11 to deduce simple rules to evaluate the reactivity of a given compound. In the energy response, he noticed that the two first terms basically translate how the energy changes when nuclei move while electron density remains frozen. Obviously, if the refer-

ence geometry is a minimum, this contribution is positive (destabilisation). On the other hand, the last contribution is stabilising, since the numerator is by construction positive, while denominator is negative. This term translates the energy change experienced by the system as the electronic configuration is changed along the perturbation. As such, chemical reaction will take place only in cases where the last term has non negligible values. This will be more likely to occur if transition energies $E_k - E_0$ are small, thus easily excitable compounds are expected to be rather reactive. Lot of examples were provided to support Pearson statement that *the lower the excitation energy, the more reactive the molecule*. As for instance the nucleophilic attack of carbonyl compounds that turn out to be easier in the following order: $\text{HCOF}(45.5 \times 10^3 \text{cm}^{-1}) > \text{CH}_3\text{COCl}(42.6 \times 10^3 \text{cm}^{-1}) > \text{CH}_3\text{COCH}_3(35 \times 10^3 \text{cm}^{-1}) > \text{CH}_3\text{CHO}(34 \times 10^3 \text{cm}^{-1}) > \text{CH}_2=\text{CHCHO}(26.5 \times 10^3 \text{cm}^{-1})$. Another example given was the decreasing bond strength of the following alkylhalides: $\text{CH}_3\text{F}(75.4 \times 10^3 \text{cm}^{-1}) > \text{CH}_3\text{Cl}(59 \times 10^3 \text{cm}^{-1}) > \text{CH}_3\text{Br}(50 \times 10^3 \text{cm}^{-1}) > \text{CH}_3\text{I}(38.5 \times 10^3 \text{cm}^{-1})$. The numbers between brackets are the first excitation wavenumbers. Later, it has been shown by Nagy[25] that the first excitation energy is very likely the best way to measure the hardness of a molecule. As a consequence Pearson article can be retrospectively regarded as an early formulation of the Principle of Maximum Hardness. A question naturally follows: would it be possible to get regioselectivity information by pursuing this research axis?

5.3.2. States Specific Dual Descriptors

At the core of Pearson and Bader approaches, one finds perturbation theory, which basically states that response to perturbation of a given system can be developed on the basis of its unperturbed eigenstates. Then, treating chemical interaction as a perturbation, and identifying eigenstates as the set of ground and excited states, it is possible to account for the ground state chemical properties through a careful analysis of the excited states.

In a related approach, it was proposed in 2013 that evolution of the electron density along a chemical process, that is, following a reaction coordinate, could also be extrapolated from a set of excited states electron densities.[26] More specifically, it was proposed that ground state electron density at a given point P on the potential energy surface, closer to the transition state of interest than the reagent R is, reads

$$\rho_{P,0}(\mathbf{r}) = \sum_{i \geq 0} \alpha_i \rho_{R,i}(\mathbf{r}) \quad (5.12)$$

where indices P and R refer to the geometry, and i to the energy state (ith excited state, 0 meaning ground state). From the conservation of the electron number we directly obtain that

$$\sum_{i \geq 0} \alpha_i = 1 \quad (5.13)$$

from which we see that electron density reorganisation from R to P is

$$\Delta \rho_{R \rightarrow P}(\mathbf{r}) = \sum_{i \geq 1} \alpha_i [\rho_{R,i}(\mathbf{r}) - \rho_{R,0}(\mathbf{r})] = \sum_{i \geq 1} \alpha_i \Delta f_{R,i}(\mathbf{r}) \quad (5.14)$$

Thus one gets that electron density reorganisation along a chemical process

can be expressed thanks to the electron density reorganisation under excitation of the reagent. Analytical formulas for the coefficients α are unknown, but following Pearson’s arguments it may be expected that high lying excited states will not contribute significantly to the ground state reactivity. Following Fukui’s development, one may even expect that the first excited state, likely stemming from a $\text{HO} \rightarrow \text{LU}$ excitation, will be the principal player. Under a frozen orbital hypothesis, such a transition will indeed yield

$$\Delta f_{R,1}(\mathbf{r}) = \rho_{R,1}(\mathbf{r}) - \rho_{R,0}(\mathbf{r}) = \rho_{R,LU}(\mathbf{r}) - \rho_{R,HO}(\mathbf{r}) \approx \Delta f(\mathbf{r}) \quad (5.15)$$

thus the electron density reorganisation from R to P will be roughly equal to the FMO approximation of the dual descriptor. From this identification, it was proposed to coin $\Delta f_i = \rho_i - \rho_0$ the i^{th} state specific dual descriptor (SSDD).

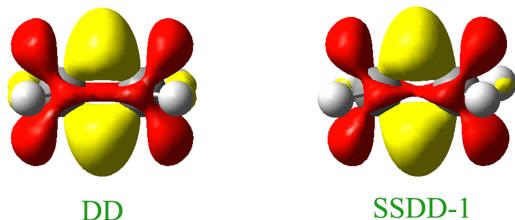


Figure 5.2: The ground state DD and the first SSDD of ethylen.

Interestingly, though in most cases the correct reactivities and selectivities are grasped by the first SSDD (see Figure 5.2), situations arise where higher excitations are required (in line with Pearson’s observation). This is obviously expected for cases where Frontier Molecular Orbital theory itself is failing. But more interestingly, this is also often the case when one studies reactant complexes at the onset of a chemical reaction – thus with a rather large separation between reagents.[27]. An illustrative example is given below. In figure 5.3 are

represented on the top and bottom left both the second and third SSDD, and on the top and bottom right the first and second NOCV for a butadiene-ethylene complex. NOCV is an acronym that stands for Natural Orbital for Chemical Valence. Basically the NOCVs describe the electron density deformation of the most relevant orbital during a chemical reaction. The first SSDD actually consists on an intra-fragment excitation located on butadiene that quite likely suggest that butadiene is more prone to react with itself than with ethylene. It is in perfect line with the Frontier Molecular Orbital theory as both butadiene HOMO and LUMO are located in between those of ethylene making the [4+2] cyclo-adduct of butadiene with itself the major product of the reaction. Nonetheless, the first density reshuffling located on one reagent alone does not necessarily bring relevant information about reactivity or selectivity. On the other hand, charge transfers from one reagent to the other may be observed in higher excited states, and thus translate how electron density is likely to distort along the reaction path, especially regarding the direction of the easiest electron flow. SSDD may then ascertain the reagents relative philicities and site selectivities, as expected for a Dual Descriptor avatar. Still on the example of cycloaddition between butadiene and ethylene it can be observed on figure 5.3 that the 1stSSDD describes the electron donation from the ethylene to butadiene while the 2ndSSDD pictures the back donation from ethylene to butadiene. Interestingly, these inter-fragment state specific dual descriptors uncannily look like the 1st and 2nd ETS-NOCVs density deformations calculated at the transition state structure.[27]

Dewar, [28] pointed out in his critic of isoquinoline as a usual heterocycle for which the use of Frontier Molecular Orbital Theory (FMOT) fails to predict the correct orientation of Electrophilic Aromatic Substitution (EAS). Using

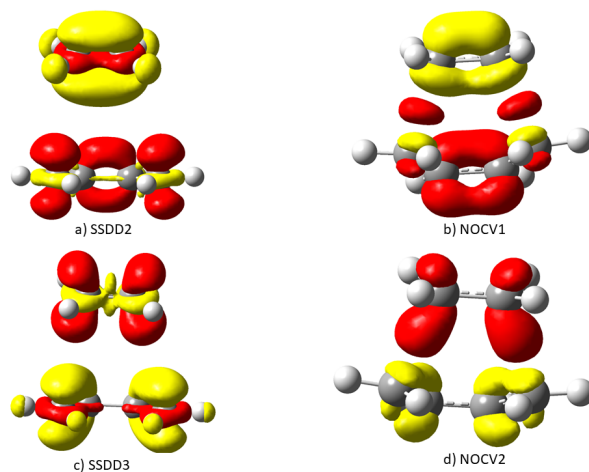


Figure 5.3: SSDD and NOCV 3D maps pertaining to the $[4+2]$ cycloaddition between ethylene (top) and butadiene (bottom) a) 2^{nd} SSDD b) 1^{st} NOCV c) E^{rd} SSDD and d) 2^{nd} NOCV, in red regions where both functions are positive, in yellow regions where both functions are negative.

HOMO coefficients, FMOT suggests that the order of reactivity is $C4 < C5 < C8$, and is not in good agreement with the experimental data. Indeed, the 4-derivative has never been observed. All the experimental results are consistent with a high reactivity of carbon C5 followed closely by carbon C8.

Concerning the region-selectivity of the Electrophilic Aromatic Substitution (EAS), it seems that the DFT-based descriptors, such as Fukui functions or the usual dual descriptor, are not better than FMOTs. As can be seen in Figure 5.4, the usual DD and the first SSDD calculated for isoquinoline are different. As can be seen, the usual DD does not give the correct prediction of regio-selectivity. Therefore, for the usual DD, EAS should occur at carbons 3 and 7, the positions known to be non-reactive with respect to EAS. The first SSDD provides an alternative prediction. It indicates that the electrophiles should target the nitrogen lone pair. This example underline the advantage

of calculating the dual descriptor using excited states. Once protonated, the dual descriptor and the 1stSSDD of isoquinolin become identical.

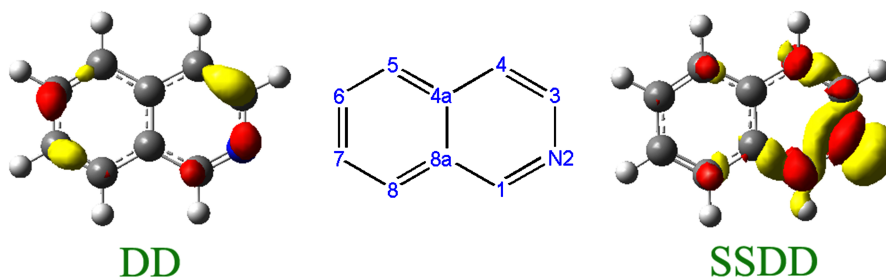


Figure 5.4: The usual DD and SSDD for isoquinoline, in red regions where both functions are positive, in yellow regions where both functions are negative (Isovalue=0.005)

In a final note, it is interesting to note that resorting to explicit evaluation of excited states has two significant advantages. First, since excited states are not restricted to single MO excitations, SSDDs are expected to incorporate fine details about the electron density reorganisation, *e.g.* σ relaxation for a reaction involving unsaturated compounds. MO relaxation may thus be grasped, at least partially. Second, as a "side-product" of the excited state calculations, one ends up with charge-transfer excitation energies. These energies could serve as quantitative reactivity indicators, as long as one is interested in comparable chemical systems. Interestingly, this point was overlooked so far.

5.3.3. Electron Polarization rationalized with Excited States

In 2020, some of the present authors retraced Pearson’s, Walsh’ and Bader’s footsteps, and used explicit Rayleigh Schrödinger perturbation theory to study the response of a chemical system.[29] The premises are thus known: let \mathcal{H}_{pert} a perturbation Hamiltonian, acting on a system whose quantum states $(E_n, |n\rangle)$ are known. From the first order development of the ground state wavefunction,

$$|\psi\rangle = c_0 \left(|0\rangle + \sum_{k \neq 0} \frac{\langle k | \mathcal{H}_{pert} | 0 \rangle}{E_0 - E_k} |k\rangle \right) = c_0 \left(|0\rangle + \sum_{k \neq 0} c_k |k\rangle \right) \quad (5.16)$$

it is possible to express the perturbed electron density

$$\rho_{pert}(\mathbf{r}) = \langle \psi | \hat{\rho}(\mathbf{r}) | \psi \rangle \approx \rho_0(\mathbf{r}) + 2 \sum_{k \neq 0} c_k \rho_k^0(\mathbf{r}). \quad (5.17)$$

In the previous expressions, c_0 is a normalisation constant, which is assumed to be close to unity (small perturbation), and $\rho_k^0 = \langle k | \hat{\rho}(\mathbf{r}) | 0 \rangle$ is the transition density from the ground state to the excited state k .¹

Electron density reshuffling under perturbation will thus be

$$\delta\rho(\mathbf{r}) = \rho_{pert}(\mathbf{r}) - \rho_0(\mathbf{r}) = 2 \sum_{k \neq 0} c_k \rho_k^0(\mathbf{r}) \quad (5.18)$$

hence be expressed as a weighted sum of transition densities, which can themselves be obtained from any TD-DFT calculation. Several features of $\delta\rho$ deserve to be delineated. First, if the perturbation is designed to mimic the approach

¹Note this quantity is different from the k^{th} SSDD, $\Delta f_k(\mathbf{r}) = \langle k | \hat{\rho}(\mathbf{r}) | k \rangle - \langle 0 | \hat{\rho}(\mathbf{r}) | 0 \rangle$

of a reagent, then this quantity translates the electron density polarisation caused by this approach. This is a missing term in usual reactivity developments (Klopman-Salem[30, 31] for instance), and relates to soft/hard interactions in the nomenclature of Pearson. Interestingly, it proves more relevant than expected to describe chemical reactivity and selectivity, as various known chemical properties can be grasped from such a quantity.

Second, since transition densities integrate to zero, so does $\delta\rho$: we indeed work at constant electron count. Regarding the c_k coefficients, it may be noted that they are decreasing as excitation energy increases, thus only the lowest excited states need to be computed. Nevertheless, and in perfect line with Pearson, one cannot rely on the very first excited states alone, since the numerator may be negligible for these states (poor overlap between unperturbed states through the perturbation). In fact, in the case of a simple point charge perturbation, it could be shown that the largest contribution could stem from rather high excited states – up to the 33rd excitation in the case of a cobalt complex!

Similarly, energy responses can be defined, up to the second order:

$$E^{(1)} = \langle 0 | \mathcal{H}_{pert} | 0 \rangle \quad (5.19)$$

$$E^{(2)} = - \sum_{k \neq 0} \frac{|\langle k | \mathcal{H}_{pert} | 0 \rangle|^2}{E_k - E_0} = - \sum_{k \neq 0} c_k^2 (E_k - E_0). \quad (5.20)$$

If the perturbation Hamiltonian is the electrostatic potential induced by a point charge at point \mathbf{r} , $E^{(1)}$ will then simply be proportional to the electronic component of the molecular electrostatic potential (MEP) at point \mathbf{r} . It will be stabilising if the point charge is positive, and destabilising otherwise.

On the other hand, $E^{(2)}$ will always be a stabilising contribution, translat-

ing the stabilisation undergone by the system by distorting its electron density within the perturbing potential. Following Pearson, if we consider a perturbation potential mimicking the approach of a reagent, the favored geometry of approach should be associated to the most negative (stabilising) value of $E^{(2)}$. Hence polarisation energy can bring valuable information on reactivity and selectivity. And indeed, studying the evolution of $E^{(2)}$ for carbonyl compounds perturbed by a negative point charge placed at a constant distance from the C and for various angles of attack on the C=O function, the well-known Bürgi-Dunitz angle of attack can be retrieved, see Figure 5.5. According to the density polarisation sign, the main excited state involved in this charge transfer is associated to the promotion of a small fraction of electron of the $\pi(C-O)$ bonding orbital to the $\pi^*(C-O)$ anti-bonding orbital. The transition density that allows this electron excitation is represented in Figure 5.5

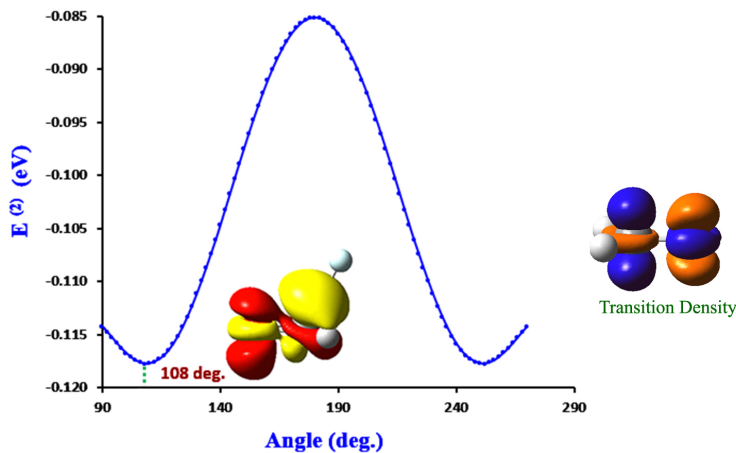


Figure 5.5: 7th formol transition density and electron density response for formaldehyde perturbed by a -0.5 a.u. point charge placed at 2 Å from the C atom, represented by the light blue sphere. Colour scheme: $\delta\rho > 0$, red; $\delta\rho < 0$, yellow. Isodensity: 0.0004 a.u.

In a further study, it could furthermore be shown that the more the system can spread its electron density reorganisation, both through space and among the excited states manifold, the larger the second-order stabilisation.[32] This could in fact be quantified. Recalling equation 5.16 and considering we now study a large number of replicas of the molecule under study, one may see that c_k^2 will provide the proportion of molecules reaching excited state k as a consequence of perturbation. Thus the collection of c_k^2 values (including $c_0^2 = 1 - \sum c_k^2$) is a statistical distribution of excited states populations induced by perturbation. According to Gibbs and Shannon, an entropy can be associated to this statistical distribution:

$$S = -k_B \sum_k c_k^2 \ln c_k^2. \quad (5.21)$$

It may be noted that the same entropy can be defined for the unperturbed system ($c_k = \delta_{0k}$) but it equals zero. Hence S here can be alternatively seen as the entropy of the perturbed configuration or the entropy change induced by the perturbation.

Strong correlations were observed between $E^{(2)}$ and S values for a given system, confirming that most reactive positions in molecules lead to a maximal response in terms of excited states population.

This is for instance illustrated in the case of furan in Figure 5.6: placing a 0.1 e point charge perturber on carbon atom $C\alpha$ results in a much larger polarisation response, translated either in the transition probabilities for each excited state or in the total entropy, than placing the same charge on carbon atom $C\beta$. At the same time, polarisation energy is significantly more stabilising in the case of a perturbation at $C\alpha$, in the line with the expected higher reactivity on this position.

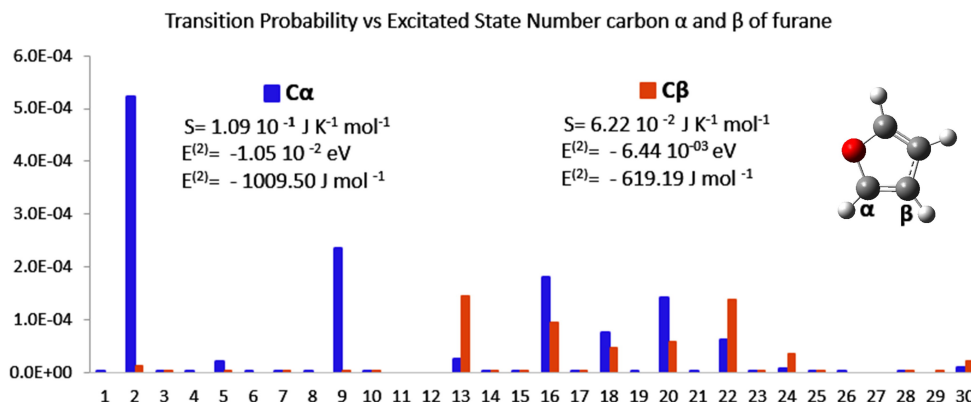


Figure 5.6: Polarisation spectrum when $C\alpha$ and $C\beta$ are perturbed by a 0.1e point charge.

In fact, successively perturbing all nuclei in the furan molecule allows to draw a clear linear relation between entropy and energy, as shown on Figure 5.7. This linearity suggests that a statistical temperature,

$$T = \left(\frac{\partial E}{\partial S} \right) \quad (5.22)$$

could be constructed, if not rigorously defined. Here one obtains $T = 9300 \text{ K}$, which is interestingly in agreement with the calculated temperature necessary to excite 1 percent of the total population of a collection of molecules in the first excited state.

Linearity in the $E=f(S)$ plots was also shown in various other examples, suggesting this is a general feature. In the end, external perturbation can be seen as interaction with a "heat source", and polarisation as a heat exchange between the perturber and the system. Said otherwise, interaction of two reagents along a chemical reaction could be understood in terms of heating and cooling; it is then possible to say "how hot" or "how cool" an electron density is

expected to become as a consequence of the approach of a reagent.

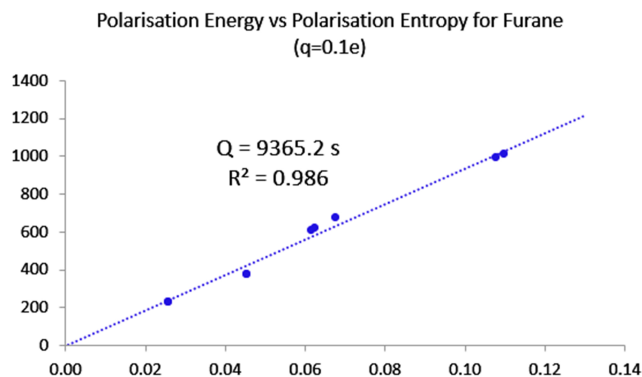


Figure 5.7: Absolute polarisation energy versus entropy for furane; $q=0.1e$.

5.3.4. In summary

To summarise, by its very vocabulary and concepts, chemistry invites to study chemical reactions through a "perturbation perspective". As such, it is not surprising that mathematical expressions derived in this context rely explicitly on excited states. But this is not a mere mathematical coincidence. In fact, as pointed out first by Walsh, a formal connection between reactivity and excitability is expected, since both properties are linked to the propensity of the electron distribution in a system to reorganise under external stress. It is also not surprising that Pearson came to the same idea, since he proposed to analyse reactivity through polarisability, which is also another way to describe the plasticity of the electron distribution. Overall, reactivity can then be conceived as "states-specific" excitation of a molecule induced by the approach of a reagent, or conversely excitation can be seen as a "reagent-specific" distortion of the electron cloud in view of a reaction.

5.4. Conclusion and Perspectives

In a more general conclusion, although C-DFT is usually conceived as a ground-state theory, extensions to excited states are possible. As retraced previously, one can either focus on the properties of excited states themselves, or try to extract ground state properties from excitations (through a perturbation framework). Formally speaking, both ideas were already present in early theoretical developments (in Walsh, Bader, Fukui and Pearson papers for instance). Nevertheless, it is only rather recently – say in the last twenty years or so – that they bloomed, owing to the developments of more and more efficient tools to compute excited states. Nowadays, excited state calculations are rather cheap, and computer developments allows the simultaneous calculation of large sets of excited states for relatively large systems – hence ”brute force” evaluations are now feasible.

Because of this, it could be tempting to declare that the perspectives are rather limited, since equations are known and can now be evaluated. Yet, the case of the electron density polarisation illustrates that there is always room for more development. First, this phenomenon proved to be more relevant than expected, although polarisation is the fifth wheel of usual reactivity model.

Second, a quantity displaying the features of a temperature could be constructed from polarisation. What is the actual meaning and extent of this temperature? Could it be used to help developing T-dependent DFT models?

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