Theoretical Analysis and Numerical Simulation of Intramolecular Barriers in Polyphenyl-Based Molecular Devices

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We report a detailed study of electron transfer in aromatic systems that have been suggested by Tour as basic elements for assembling simple molecular circuits. We simulated the behavior of electrons in response to an external perturbation by means of the Gaussian 98 quantum chemical package, and we carried out calculations for isolated molecules, consisting of an anionic system made up of two benzene rings bonded by an "insulator" methylene group. When point charges creating an external forcing field are placed close enough to one of the aromatic rings, a strongly nonlinear behavior is observed for the location of the highest energy electron, as a consequence of the presence of the methylene group acting as a barrier. Quantitative results on such a behavior are reported here for the first time.

I. Introduction

The steady trend toward further miniaturization of devices and circuits for information processing that we have been experiencing for more than three decades is now approaching physical limits. It appears to be very difficult to overcome such limits with the traditional scaling down process that has been at the basis of the success of current microelectronics. Traditional scaling rules for CMOS (complementary metal-oxide-semiconductor) transistors start failing when the channel length approaches a few tens of nanometers, due to unwanted tunneling between the source and drain electrodes and to a series of other problems.[1]

As a consequence, many proposals for devices based on molecular building blocks have appeared in the literature, relying on molecular equivalents of traditional circuit elements,[2,3] on the exploitation of specific properties of molecular monolayers[4,5] or on completely new architectural and operational concepts.[6] Besides such pioneering work on the design and fabrication of molecular devices and architectures, experiments have been performed on the electrical properties of single molecules,[7,8] and sophisticated simulation tools for charge transport through molecules sandwiched between metal electrodes have been developed.[9−12]

Several molecular device concepts are based on the existence of potential barriers within molecules, which prevent the free flow of electrons and create, as will be discussed in section II, the possibility for a strongly nonlinear bistable behavior, which is essential for the operation of many types of devices. Bistability is this particular context the property of switching abruptly between two well-defined states in response to a small electrostatic input perturbation.

This nonlinear response allows restoration of logical levels and their correct propagation through circuits made up of a very large number of individual components: otherwise signals representing logical values would quickly decay in amplitude while traveling across the circuit and would soon be lost below the noise floor. In other, more traditional terms, any circuit for information processing needs to exhibit signal gain (in the region of the response function around the origin), in order to be suitable for the implementation of architectures large enough to be useful for practical applications. Even revolutionary architectures such as those based on the QCA (quantum cellular automaton) concept[6,13] require gain (in this case for the quantity defined as "cell polarization"[13]), to be suitable for information processing.

Our investigation on barriers in molecular structures was actually prompted by the search of a molecular implementation for a QCA cell: such a cell should have four sites that can host an electron, located at the corners of a square and separated by large enough barriers as to strongly localize the two excess electrons added to the cell. Due to electrostatic repulsion, the two electrons will line up along a diagonal, either one with equal probability, in the absence of any external field. Application of a perturbing field, which can be produced by an already polarized neighboring cell, leads to polarization along one of the diagonals, with a very sharp response if the barriers are opaque enough.[14] It has been shown[15] that arbitrary combinatorial logic circuits can be implemented by means of two-dimensional arrays of such cells. With this approach, electrons would move only within each cell, without a net current flow along the circuit, thereby allowing a significant reduction in power consumption with respect to traditional electronics.

The presence of potential barriers is essential also in devices which are closer to traditional electronic components, and many molecular structures including barriers have been proposed. No detailed analysis of the properties of such intramolecular barriers has however been provided in the literature so far.

We have been interested in a quantitative investigation of molecular structures containing aliphatic chains acting as barriers inserted between aromatic π-conjugated rings, focusing on systems with a methylene group ($-CH_2-$) placed between two phenyl rings.

To test the barrier properties of the aliphatic groups, we have investigated, by means of a numerical simulation performed within the *Gaussian 98*[16] environment, the response of the

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electron density in molecular structures to the applied electric field. On the basis of the QCA concept, an excess electron has been added to the molecule that we have considered, which is representative of half a QCA cell: in the absence of a barrier group, its density shifts smoothly from one side to the other in response to a varying electric field. In the presence of a barrier, instead, the density associated with the excess electron exhibits a very abrupt transition for relatively small values of the applied field. From the response curves thus obtained, we can gain information on the characteristics of the barriers and provide quantitative evidence supporting their existence. These results can be of interest also for the analysis of situations characterized by a net current flow along the molecule, such as in the case of the mentioned experiments.[7,8] Since in these experiments the molecule is attached to metal electrodes, changes in its electronic structural parameters with respect to the free molecule case should be taken into consideration.[17] However, if one is specifically interested in the quantitative analysis of steady-state nonequilibrium transport across a metal-molecule-metal structure, methods such as those of refs 9−12 should be used.

In section II we present the model used for our calculations, as well as a simplified model that can be solved analytically and that is useful to understand the effect of barriers on the displacement of an electron as a function of the applied electric field. Some computational details for the more refined model are provided in section III, while numerical results are discussed in section IV, where we analyze also the discrepancies between the polarization curves obtained with different computational methods, and comment on the failure of a simple density functional approach in properly reproducing localization effects in bistable structures. Conclusions are finally presented in section V.

II. Model

In the past few years, several molecular systems have been proposed as building blocks for nanoelectronic devices,[18] often on the basis of the too optimistic conjecture that generic properties of electronic transport through the molecule could suffice to make it a good candidate for the implementation of information processing circuits. Following this assumption, molecular wires made up of conjugated aromatic rings (differently functionalized) have been considered one of the most suitable classes of molecules for this aim.[3,19]

The source of conductivity for a polyphenylene wire is a set of delocalized π-type molecular orbitals above and below the plane of a single benzene ring. This is also true when a triple chemical bond (e.g., an ethynyl group) is inserted between two contiguous rings, so long as conjugation among the π-bonded fragment is maintained throughout.

Aviram and Ratner,[20] in a pioneering article in the field, first indicated the focal point that aliphatic organic fragments σ-bonded to a benzene ring interrupt the extension of the π-orbital, and they, therefore, act as insulators.

Here we present a quantum mechanical analysis of the electron density behavior of the polyphenylene wire originally proposed by Tour et al.,[21] in which an aliphatic group (e.g., $-CH_2-$) is inserted between two aromatic rings and an external perturbation is added.

To analyze the characteristics of the barrier, we have computed the electron density of the molecular anion in the presence of a static electric field generated by a couple of point charges placed above and below the plane of one of the two benzene rings. We have chosen this particular type of external perturbation because, although the inclusion of a uniform electric field is in principle possible, the geometry of the two systems under investigation (especially the diphenylmethane, which does not lie in a plane as the diphenyle does) makes the choice of an appropriate orientation of the field nontrivial.

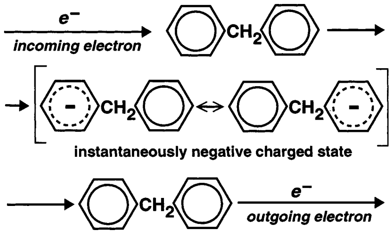

Figure 1. Schematic representation of the conduction process through a simple molecular wire.

The fact that the molecule has an excess electron is particularly useful for illustrating the motion of electrons across the barrier, since, being the last electron in an antibonding π^*-orbital, it is less involved in the formation of chemical bonds and therefore can be more easily driven through the barrier by the electric field. Investigation of the anion is justified also by the fact that a molecule can be considered as instantaneously charged during the conduction process, while each electron moves from one end to the other (Figure 1), as pointed out by Majumder and co-workers.[22]

If we take into account a system with an electron added to an isolated biphenylene molecule in which two aromatic rings are directly bonded to each other, we expect, in the absence of any external perturbation, that the excess electron is fully delocalized over the two phenyl rings.

The two point charges are placed above and below one of the two rings, at a distance of 2 Å from the ring plane: the highest occupied molecular orbital (which can be identified as the one occupied by the conduction electron) will tend to localize on the other phenyl ring, if the charges are negative, and on the same phenyl ring if they are positive. The greater the magnitude of the charges, the more shifted the electron density will be.

A suitable observable for our purpose can be obtained by computing the electron occupancies for the two aromatic rings, since their difference vanishes in the absence of any perturbation (e.g., when the magnitude of the point charges equals zero), and its dependence on the perturbation magnitude can clearly reveal properties of bistability.

We have considered the charge densities on the two aromatic rings Φ_1 and Φ_2, and integrated them on the regions defined in Figure 2, to compute the total charge on each ring, $\rho(\Phi_1)$ and $\rho(\Phi_2)$. We then define the polarization $\Delta\rho$, whose value is directly related to the localization of the excess electron, as

$$\Delta\rho = \frac{\rho(\Phi_1) - \rho(\Phi_2)}{-q}, \tag{1}$$

where q is the elementary electron charge.

From a chemical point of view, when an aliphatic fragment like a methylene group is inserted between the two rings through two σ-bonds, it destroys the conjugation of the π-orbitals of the rings: in the absence of an external perturbation, this gives rise to two degenerate states accessible for the highest energy electron and substantially localized on each ring.

Electron motion across a the barrier between the two aromatic rings resembles an electron-transfer reaction, which is one of the most studied chemical processes, with practical applications in nature in a large number of biological, physical, inorganic and organic chemical systems. Modeling of two-state systems

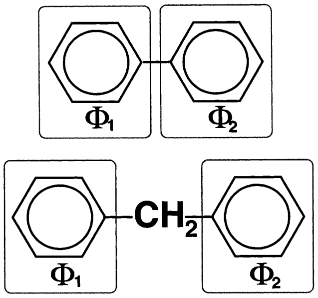

Figure 2. Regions over which the electron density of the biphenyle and the biphenylmethane molecules is integrated in order to determine the polarization $\Delta\rho$.

has been investigated in detail, and useful references on this topic can be found in the articles of Hush, Newton, and coworkers.[23,24]

The simple quantum mechanical model presented below provides an intuitive understanding of the role played by the aliphatic fragment in a biphenylene system.

The Hamiltonian for a single electron in a system with two levels, E_1 and E_2, coupled through an external perturbation, can be written, in second quantization formalism, as

$$\hat{H} = \sum_{i=1,2} n_i E_i + t({b^\dagger}_1 b_2 + {b^\dagger}_2 b_1) + \sum_{i=1,2} n_i q V_i \tag{2}$$

where n_1 and n_2 are the occupation numbers of the two levels accessible to the electron, ${b^\dagger}_i$ and b_i are the creation and annihilation operators for an electron in the ith level, t represents the interlevel coupling, and the last term in the sum takes into account the perturbing potential V, through its value V_i in the location corresponding to the ith level. If this Hamiltonian is expanded over a simple basis ($|\,0\rangle(n_1 = 1, n_2 = 0)$, $|1\rangle(n_1 = 0, n_2 = 1)$) and written in matrix form, it reads, in atomic units, as

$$\mathbf{H} = \begin{pmatrix} E_1 + V_1 & t \\ t & E_2 + V_2 \end{pmatrix} \tag{3}$$

We now refer to the energies as $E_1 + V_1$, and we define $\epsilon \equiv (E_2 + V_2) - (E_1 + V_1)$, obtaining

$$\mathbf{H} = \begin{bmatrix} 0 & t \\ t & \epsilon \end{bmatrix} \tag{4}$$

with eigenvalues

$$e_1 = \frac{1}{2}\left(\epsilon - \sqrt{\epsilon^2 + 4t^2}\right) \tag{5}$$

$$e_2 = \frac{1}{2}\left(\epsilon + \sqrt{\epsilon^2 + 4t^2}\right) \tag{6}$$

In Figure 3 we plot the square c_1 of the first coefficient of the eigenvector of the ground state, i.e., the occupancy of the first level, as a function of the perturbation V, for different values of the coupling energy t. The analytical expression for c_1 is

$$c_1 = \frac{\left(\epsilon - \sqrt{\epsilon^2 + 4t^2}\right)^2}{2\left(\epsilon^2 + 4t^2 + \epsilon\sqrt{\epsilon^2 + 4t^2}\right)} \tag{7}$$

If we translate the model to describe the behavior of the highest energy electron in the biphenylmethane or biphenyle anion, the parameter t corresponds to the effective interaction between the orbitals of the two aromatic rings and therefore will be smaller when an aliphatic group breaks the π-conjugation and spaces the rings.

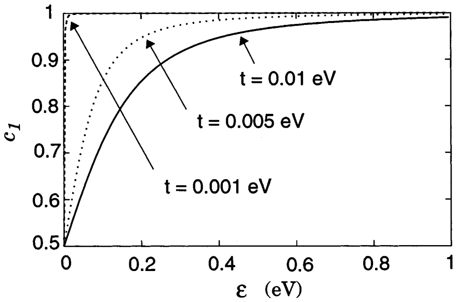

Figure 3. Occupancy of the first level of the analytically solvable model as a function of the perturbation V, for three different values of the coupling term: $t = 1 \times 10^{-2}$ eV (solid line), $t = 5 \times 10^{-3}$ eV (dotted line), and $t = 1 \times 10^{-3}$ eV (dashed line).

Results for larger t could then represent the behavior of a molecular wire without any internal barrier, in which the aromatic fragments are closer together and strongly interacting, as a consequence of the complete delocalization of the π-systems. In such a case, the response of the electron to the external perturbation will be continuous and smooth, as a function of the driver field. Smaller values of t correspond instead to a reduced interaction between the aromatic rings, i.e., to the case of the biphenylmethane anion in which the methylene group creates an obstacle to the interaction between the orbitals, and from the point of view of electronic transport, effectively separates the rings.

The curve in Figure 3 for the lowest value of t (weak interaction between the two accessible electronic states) exhibits the desired nonlinear behavior, corresponding to a sudden transfer of the excess electron between the two phenyl rings as the perturbing charges change sign.

III. Computational Details

A detailed simulation of the molecular structure we are discussing has yielded results that are qualitatively similar to those obtained from the simple model analyzed above. Such a detailed simulation has been performed by means of the *Gaussian 98* package,[16] and its results are discussed in section IV.

Particular attention was initially paid to the determination of the correct geometry of the molecular structures. Geometry optimizations have been performed for both biphenylene and biphenylmethane anions at different levels of theory with various sets of basis functions. The uncorrelated Hartree−Fock (HF) method as well as the Gaussian density functional theory (DFT) and the Møller−Plesset many-body perturbation theory (MP)[25] have all given similar results for the equilibrium geometries calculated for limit values of the perturbing charges ($Q = 0$, -1, and $+1$).

Since no experimental data are available for bond lengths of anionic systems in a vacuum, the choice of the basis sets for the calculations was performed mainly on the assumption that the addition of one electron makes the charge distribution more delocalized. We have therefore used diffuse basis functions in the atomic basis sets, to account for the spatial extent of the outer orbitals. For this reason, all of the calculations were performed adding two sets of diffuse functions to the common 6-311G basis set.[26]

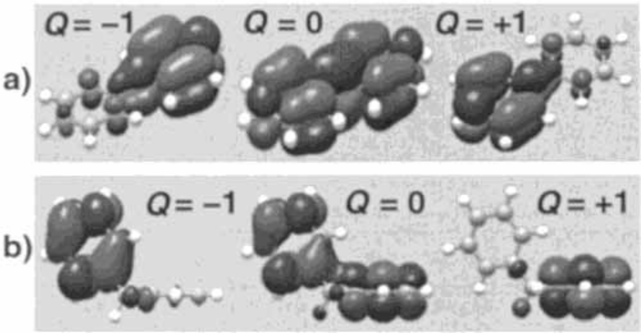

Figure 4. Shape of the HOMO orbitals for biphenyle (a) and biphenylmethane (b) for different values of the driver charges Q, in terms of elementary electron charges.

The Becke-style three-parameter density functional with the Lee−Yang−Parr correlation functional (B3LYP)[27,28] has been used for the final optimization of the anion geometries.

IV. Results

As specified in section II, the external perturbation that induces charge transfer is obtained by placing two point charges at a distance of 2.0 Å above and below the center of the plane defined by the first (leftmost) phenyl ring of the system under investigation. This distance was set large enough (greater than a typical bond distance) to prevent a strong modification of the atomic wave functions by the proximity of the point charge.

The perturbing field due to the charges can be modulated by varying their value Q between -1 and $+1$ electron charges: effects on the system are different, depending on the possibility of the highest occupied molecular orbital (HOMO) to delocalize all over the two phenyl rings. In the case of the diphenylic anion, there is no disruption of the conjugation of the twelve π-orbitals (six for each aromatic ring in the biphenyl structure); hence, the orbital corresponding to the highest energy electron can progressively shift from one side of the molecule to the other.

The HOMO orbital for the optimized geometry of the diphenylic anion was calculated in limit cases using the Møller−Plesset technique, and as shown in Figure 4a for values of the driver charges $Q = -1$, 0, or $+1$ (in electron units), it has nonvanishing components at the carbon atoms of both rings, even for a large external perturbation. A similar behavior has been observed when the neutral diphenyle molecule was considered. In this case, the shift of the electron density is obviously less pronounced, since all the π-electrons are strongly involved in chemical bonds and transfer of an electron from one ring to the other becomes clearly much harder to achieve.

Looking at the HOMO orbital of the anionic system phenyl-methylene-phenyl (Figure 4b), it is clear that the localization of the excess electron is almost complete when the driver charges reach their maximum value. In any case, the atomic orbitals contributing to the HOMO are only those of the aromatic carbon atoms, while the contribution of methylene fragments is almost negligible.

Incidentally, we notice that the shape of the highest occupied orbitals is clearly different in the two cases, even in the absence of any external perturbation. The HOMO of the system without barriers is strongly delocalized all over the two rings, as a consequence of the complete conjugation of the π-orbitals of the two phenyl rings.

A shift of the orbital is however not sufficient to demonstrate the existence of bistability: we need to verify whether a sharp transition takes place as a function of the external perturbation. For this purpose, it is convenient to look at the polarization $\Delta\rho$, already defined in eq 1, versus the value of the driver charges: $\Delta\rho$ varies between -1 and 1, corresponding to full localization of the excess electron on one or the other ring.

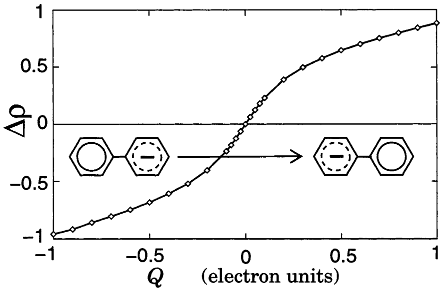

Figure 5. Polarization $\Delta\rho$ for the diphenyle anion as a function of the magnitude of the driver charges.

We have computed the electron density for optimized structures of the molecular systems discussed above, using a 6-311G basis with diffuse functions added to the hydrogen atoms. The full electron density has been decomposed in terms of atomic orbitals (according to the natural bond orbital formalism[29]), and we have therefore been able to obtain the electron distributions relative to selected areas of the molecule, according to the schematic representation of Figure 2.

In Figure 5, $\Delta\rho$ is plotted versus the magnitude Q (in electron units) of the point charges. for the diphenylic anion. Calculations carried out with the Hartree−Fock, density functional (B3LYP), and Møller−Plesset levels of approximation yield in this case similar results, corresponding to the response of a system in which the π-orbital of the two phenyl rings are strongly interacting and no obstacle to the smooth migration of the electron density is present. The result is in good qualitative agreement with the simplified model of section II for large values of the coupling term t (see Figure 3). In other words, in the absence of any insulating group between the two rings, electrons can move freely across the entire structure and therefore the response curve is rather smooth.

An extended interpretation of the electronic correlation effects in these systems goes beyond the aims of the present article, but resort to a more rigorous quantum chemical technique, such as the Møller−Plesset second-order perturbative scheme (MP2), appears to be necessary if an intermolecular barrier is added, due to the small energy differences between the states involved, and on the basis of the authors' experience in performing calculations on model bistable systems, like the Quantum Cellular Automata.[14] The major limitation of the Hartree−Fock method is indeed its failure to include electron correlation; MP2 calculations, on the other hand, begin with the Hartree−Fock wave function, but then perturb this wave function to the second order to calculate a more accurate energy of the system. In such a way, the MP2 method incorporates some of the effects of dynamic electron−electron interactions, and therefore, results are expected to be more accurate.

When an insulator spacer like $-CH_2-$ is inserted between the aromatic systems Φ_1 and Φ_2, the situation varies radically. In Figure 6a, the methylene bridge between the phenyl rings produces a sharp step in the polarization curve when the driving charge Q varies from -1 to 1. The results from the Møller−Plesset perturbative approach are represented with a solid line, those from Hartree−Fock with a dashed line and those from a density functional approach with a dotted line.

We notice that both the Hartree−Fock and the MP2 calculations yield a sharp transition and therefore a nonlinear behavior for the polarization. This corresponds exactly to the bistable effect that was expected on the basis of considerations on the

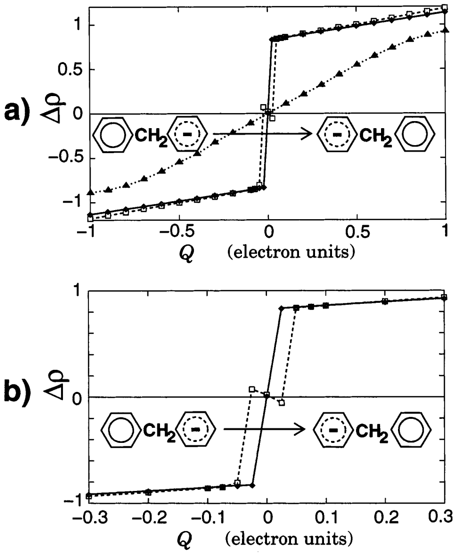

Figure 6. (a) Polarization $\Delta\rho$ for the anionic biphenylmethane as a function of the magnitude of the driver charges, computed with three different approaches: MP2 (solid line), Hartree−Fock (dashed line), and density functional approximation (dotted line). In (b) we show an enlargement of the region around the origin, where the Hartree−Fock approach yields an unphysical result.

orbitals or of the application of the simplified analytical model (Figure 3) for small values of the coupling energy t.

We also notice that neglecting the electron correlation leads to the unphysical behavior of the HF curve, i.e., the kink around the origin of Figure 6a, which is more clearly visible in the enlargement of Figure 6b. This effect is probably enhanced by the fact that the energy levels become almost degenerate when the perturbing charges are very small.

To include a more detailed representation of the effect of electronic correlation, we have chosen to perform calculations also beyond the so-called monodeterminantal domain, moving to a configuration−interaction approach.

In particular, keeping in mind that variations in our systems, as a function of the magnitude of the driver charges, concern only few electrons, we have used the complete active space (CAS) method, one of the commonly used multiconfiguration techniques, in which the spin−orbitals of the system are divided into two groups: *inactive* and *active*. Spin−orbitals in the first group are kept doubly occupied, while the remaining electrons are distributed among the active orbitals in all possible ways compatible with the total spin (and symmetry) of the state of interest.[30,31] The polarization curves resulting from CAS calculations are practically coincident with those from the MP2 calculations, for the case of anionic biphenylmethane, thereby further validating their results, and confirming that the MP2 approach correctly represents electron correlations, at least for the systems under consideration.

On the other hand, we notice that results obtained with the density functional approach do not exhibit any strong nonlinearity: they are quite smooth and far from the correct solution. This is not surprising if one considers that the density functional approach fails to reproduce bistability also in QCA calculations, due to the lack of a proper construction and antisymmetrization of the many-electron wave function, which plays a fundamental role in the nonlinear transition.[14]

V. Conclusion

Motivated by the currently widespread interest in the development of alternatives to traditional electron devices, and by the lack of detailed studies of polarization bistability in molecular structures, we have investigated, by means of numerical simulations based on the Gaussian 98 quantum chemical package, the effect of the presence of a barrier, consisting in a methylene group, on the transfer of an excess electron between two phenyl rings. Our results confirm previous conjectures according to which the methylene group breaks the conjugation of the π-orbitals of the two rings responsible for the relatively good conductivity across the molecule.

In particular, we have considered the response of the charge unbalance between the two aromatic rings to the perturbation due to two driver charges placed next to one of the aromatic rings, for anionic biphenylmethane. We observed that, as the value of the driver charges is varied, a sharp transition occurs, with the excess electron moving suddenly from one ring to the other for a small change of the driver charges around the origin. As a comparison, we have investigated also an anionic biphenyl molecule, i.e., without a methylene barrier, in which the electron transfer takes place very smoothly as a function of the external perturbation. A qualitative explanation of the behavior resulting from the detailed model has been provided by means of a simple, analytically solvable model, representing the molecular structure as a two-level system with an adjustable coupling between the two levels: decreased coupling between the two levels (as in the case of the presence of a potential barrier) produces an effective localization of electrons, which leads to an abrupt transition in response to externally induced asymmetries.

Our results also show that a correct representation of the behavior of molecular polarization in the presence of a barrier requires the usage of sophisticated computational tools: a Møller−Plesset second order perturbative scheme or a configuration−interaction approach appear to be necessary to correctly reproduce the nonlinear behavior, while a Hartree−Fock calculation exhibits some instability and yields a completely unphysical solution around the origin. On the other hand, a simple density functional method is unable to reproduce the nonlinear behavior at all, yielding similar results for systems with or without an interruption in the π-conjugation.

Nonlinear properties such as the one investigated in this study are relevant for the implementation of molecular devices applicable to information processing, because they are key to restoration of logic levels and therefore to the successful operation of circuits containing a very large number of logic gates.

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