

Solitonic States in Organic Conducting Polymers

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Abstract

In a typical solitonic distribution, the soliton density is distributed over the entire molecule and the present work shows how its density can be decomposed into solitonic and antisolitonic components. It is found that there exists a unique electron as soliton over the anionic nanoconductor, while there are many other solitons and antisolitons. The solitonic states are further decomposed to the canonical molecule orbitals including the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), and it is concluded that LUMO is not necessarily occupied by one electron in the studied molecules. Also, analogous electrons were found to be responsible for spin separation which is revealed from distinct contributions in different molecular regions of the nanoconductor.

Keywords: Nanoconductor, Soliton, Spin

1. Introduction

The dynamics of solitons is closely related to the charge transport phenomena in nanoconductors which plays a cornerstone role in nanodevices and nanoelectronics technologies [1-3]. In general, a soliton is an electron free to move among the molecule whose mobility is governed by several chemical and physical factors. Polyacetylene and polymethine are the simplest nanoconductors consisting of conjugated double bonds whose conduction properties are widely studied. Fig. 1 displays a schematic electronic structure of polyacetylene in which

the soliton has induced a *misfit* in the conjugation pattern [4-7].

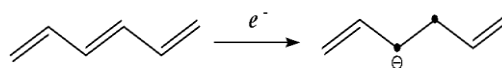


Fig. 1. A misfit induced by the excess electron in a conjugated system

In order to analyze the soliton in a nanoconductor, several theoretical schemes are available such as electron propagator (one-electron Green's function) method [8,9], density of states (DOS) and spin density wave (SDW) [7,10-13]. The SDW is mostly assigned to periodic conductors in which the canonical

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molecular orbitals (CMO) provide a wave-like charge density structure. In an open-shell electronic system, α and β electrons possess distinct densities and spin density is defined as the difference between α and β densities, i.e., $\Delta\rho_{\alpha-\beta} = \rho_{\alpha} - \rho_{\beta}$. Therefore, a negative spin density corresponds to β -spin density which is rarely noticed.¹⁴

Decomposition of $\Delta\rho$ for closed-shell systems has been conducted for different purposes including chemical bonding [15], van der Waals interaction [16] and quantification of kinetic energy pressure [17]. In general, a soliton is identified with the corresponding spin density; as the excess electron in a conductor carries its own spin. On the other hand, negative spin density is known as anti-soliton; since β -spin vanishes α -spin density. Ryabitsky et al. [13] and Kachkovsky et al. [18] has considered Δq (atomic charge alteration) to deeply inspect the solitonic nature in several nanoconductors.

Although a soliton naturally exhibits dynamic behavior, stationary states of solitons have been the subject of many researches in the past decades [13,18-20]. As a crude approximation, the lowest unoccupied molecular orbital (LUMO) of the neutral nanoconductor can be approximated as the soliton's single particle state when an excess electron appears in the system. However, such approximation is silent on the induced anti-soliton state(s). Kivelson [5] has pointed out the 'electron fractionalization' phenomenon in polyacetylene, which claims that the soliton(s) is not necessarily composed of integer number of electrons. In the present work, we aim to detect both solitonic and anti-solitonic stationary states via the spin density, theoretically, which support not only the presence of soliton fractionalization in nanoconductors, but also the presence of a

unique unfractionalized soliton and multiple fractionalized anti-solitons. In the next section, mathematical formulation of decomposition of the spin density is presented and section three discusses several systems for solitonic and anti-solitonic decompositions.

2. Theory

Suppose that the stationary state of i -th soliton is represented by $\theta_i(\mathbf{r})$. Therefore, the solitonic density can be obtained according to Eq. 1:

$$\rho^{(s)}(\mathbf{r}) = \sum_i n_i^{(s)} |\theta_i^{(s)}(\mathbf{r})|^2 \quad (1)$$

where, $\rho^{(s)}(\mathbf{r})$, $n_i^{(s)}$ and $\theta_i^{(s)}(\mathbf{r})$ stand for solitonic density, i -th occupancy and soliton orbital (SO), respectively. On the other hand, if the solitonic density is available, decomposition of $\rho^{(s)}(\mathbf{r})$ should reflect the (anti-)solitonic states. Decomposition of the total electronic density according to Eq. 1 results 'natural orbitals' [21] which are useful in identification of the molecular electronic structure [22].

Although the concept of soliton is equivalent to spin density, it has not yet been decomposed into its components as Eq. 1. In other words, we wish to extract (anti-)solitonic states from spin density (solitonic density) with regards to the reverse of Eq. 1.

Suppose Φ is a row vector consisting of basis elements, $\{\Phi_i\}$, according to Eq. 2:

$$\Phi = [\Phi_1 \quad \Phi_2 \quad \cdots \quad \Phi_m] \quad (2)$$

where m is the number of basis elements. The spin density can thus be written as Eq. 3:

$$\rho^{(s)}(\mathbf{r}) = \Phi(\mathbf{P}^{(\alpha)} - \mathbf{P}^{(\beta)})\Phi^\dagger = \Phi\mathbf{P}^{(s)}\Phi^\dagger \quad (3)$$

where, $\mathbf{P}^{(s)}$, $\mathbf{P}^{(\alpha)}$ and $\mathbf{P}^{(\beta)}$ are spin density matrix, α and β density matrices, respectively. If $\{\Phi_i\}$ provides an orthonormal set, diagonalization of $(\mathbf{P}^{(\alpha)} - \mathbf{P}^{(\beta)})$ matrix results in the n_i and $\theta_i^{(s)}$ mentioned in Eq. 1. Since $\{\Phi_i\}$ does not necessarily provide an orthonormal set, transformation of $\mathbf{P}^{(s)}$ to some orthonormal basis is required. Suppose that \mathbf{X} orthogonalizes $\{\Phi_i\}$ to $\{\Phi'_i\}$ via $\Phi' = \Phi\mathbf{X}$ transformation. To obtain $\mathbf{P}'^{(s)}$, $\mathbf{P}^{(s)}$ in the $\{\Phi'_i\}$ basis, Eq. 3 can be rewritten as Eq. 4:

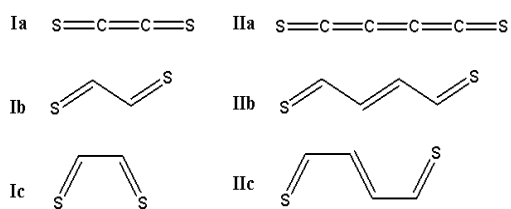
$$\rho^{(s)}(\mathbf{r}) = \Phi\mathbf{P}^{(s)}\Phi^\dagger = (\Phi\mathbf{X}^{-1})\mathbf{P}^{(s)}(\Phi\mathbf{X}^{-1})^\dagger = \Phi\mathbf{X}^{-1}\mathbf{P}^{(s)}\mathbf{X}^{-1\dagger}\Phi^\dagger \quad (4)$$

Eq. 4 suggests that $\mathbf{P}'^{(s)} = \mathbf{X}^{-1}\mathbf{P}^{(s)}\mathbf{X}^{-1\dagger}$. At this point, $\mathbf{P}'^{(s)}$ can be diagonalized as Eq. 5.

$$\mathbf{P}'^{(s)}\mathbf{C}'^{(s)} = \mathbf{C}'^{(s)}\mathbf{n}^{(s)} \quad (5)$$

The spin density can now be expressed as Eq. 1, where a row vector consisting of $\theta_i^{(s)}$ orbitals is related to the basis via Eq. 6:

$$\theta^{(s)} = \Phi\mathbf{X}\mathbf{C}'^{(s)} \quad (6)$$



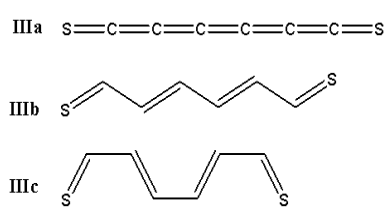
The diagonal elements of $\mathbf{n}^{(s)}$ represent the magnitude of solitons, where positive and negative $n_i^{(s)}$ stand for soliton and anti-soliton, respectively, whose state is represented by the corresponding $\theta_i^{(s)}(\mathbf{r})$. The $\theta_i^{(s)}$ orbitals can be further decomposed into the CMOs, $\{\chi_i\}$, of the neutral species.¹⁶ If $\{\chi_i\}$ is related to the basis via $\chi = \Phi\mathbf{C}^{(0)}$ transformation, $\mathbf{C}^{(0)}$ can be chosen as \mathbf{X} and consequently $\theta^{(s)} = \chi\mathbf{C}'^{(s)}$.

It has been known that eigenvalues of density difference matrix are symmetrically distributed, i.e., each positive eigenvalue has its corresponding negative eigenvalue and vice versa [15-17]. However, the above conclusion is shown for the cases in which the two matrices stand for equal number of electrons and consequently the trace of $\Delta\mathbf{P}$ equals zero. Therefore, it can not be hold for spin density matrix for an anion as its trace does not vanish and equals unity. In the next section, we will take a deeper look into the eigenvalues.

3. Numerical illustrations

In this section, decomposition of spin density is performed on several anionic conjugated systems as nanoconductor. The molecular electronic wave functions and geometries are obtained at UHF/6-31+G* level of theory utilizing Gaussian 03 suite of programs [23]. Vibrational frequency analysis is also

performed to make sure that the resultant



geometries are minimum structures. In order to

make plausible conclusions, a systematic group of nanoconductors are considered in this work. Since sulfur atom is generally used as terminal atom in nanoconductors, two sulfur atoms are also considered at the two ends of these systems. Fig. 2 displays the selected molecular systems and labels which are used throughout the text. As an example, isosurface of net spin density for anionic states of **IIIa** is shown in Fig. 3. The periodic colors for spin density in this figure represents the solitonic wave. Isosurfaces of the other systems had nearly the same periodic shape and are omitted to save space. The (anti-)solitonic orbitals as spin density components for **Ia-Ic**, **IIa-IIc** and **IIIa-IIIc** are plotted in Table 1. In this table, only the five highest significant soliton orbitals are plotted with respect to their eigenvalue square.

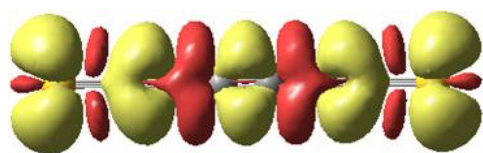


Fig. 3. Spin density wave of anionic state of **IIIa**. The yellow (light) and red (dark) colors correspond to α and β spins, respectively.

The five highest significant SO eigenvalues ($n^{(s)}$) for **Ia** were found to be +1.00, ± 0.17 and ± 0.07 . From now on, the SOs whose $n^{(s)}$ magnitude are the same but different spins (signs), will be called ‘analogous’ through this paper. In Table 1, the analogous SOs are plotted inside a box. Since a negative $n^{(s)}$ corresponds to β electron density, the negative sign is omitted from $n^{(s)}$ and their sign can be identified with respect to α (soliton) or β (anti-soliton) symbols in the table. Three interesting conclusions which can be realized from the eigenvalues are as follows. First, for all systems in Table 1, there exist a unique $n^{(s)} = 1.00\alpha$ with no analogous β one. It

reveals the existence of a *pure* soliton through the nanoconductor, i.e., *one* α electron. Second, there is a one-to-one correspondence between solitons and anti-solitons with respect to their $n^{(s)}$ signs, except for the first one (1.00α). Third, spin polarization is quite evident in the SOs, i.e., analogous α and β SOs are distributed in distinct regions. For instance, consider the two analogous 0.17α and 0.17β SOs of system **Ia**. The 0.17α SO is mainly located on the two sulfur atoms, while 0.17β SO is mainly located in the internuclear regions. Other systems also exhibit similar spin polarization with respect to their analogous α and β SOs.

At this point, one may ask that what the role of LUMO in these SOs is. Since the excess electron mainly occupies LUMO of neutral species, it is expected that the 1.00α SO is mainly composed of LUMO. Table 2 contains decompositions of some SOs in terms of CMOs of the corresponding neutral species. To keep clarity, only the three most significant coefficients are displayed in Table 2 except for 1.00α SOs. This table shows that the 1.00α SO is indeed the LUMO, except for **IIa** and **IIIa** in which the 1.00α SO is a mixture of LUMO and highest occupied molecular orbital (HOMO). Table 2 also shows that the analogous SOs are essentially composed of similar CMOs but different coefficients in sign, i.e., bonding or anti-bonding type mixing.

4. Summary and concluding remarks

The presence of soliton(s) in an anionic nanoconductor, induces anti-solitons whose density distribution can be decomposed into its components as anti-solitonic states. There is a one-to-one correspondence between solitons and anti-solitons with respect to the corresponding $n^{(s)}$ magnitude, except for one soliton whose magnitude is 1.00 electron. Spin polarization can be detected via the (anti-)solitonic distributions in Cartesian space as α

and β solitons are distributed in distinct spatial regions. However, decomposition of these solitons shows that their building blocks are the same but different types of mixing.

Table 1 Solitonic orbitals and their eigenvalues ($n^{(s)}$) of the anionic states

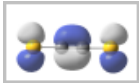
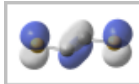

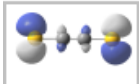
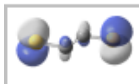
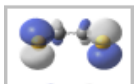
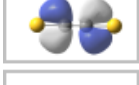

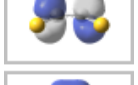






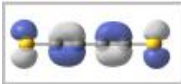


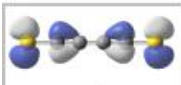
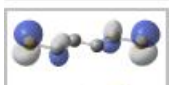

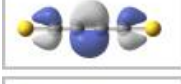
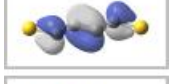




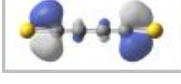


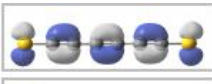
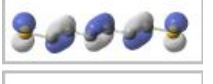

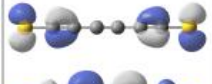
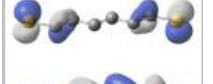
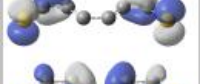
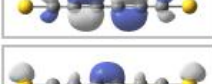

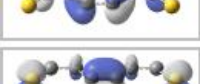


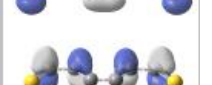



$n^{(s)}$	Ia	$n^{(s)}$	Ib	$n^{(s)}$	Ic
1.00 α		1.00 α		1.00 α	
0.17 α		0.20 α		0.23 α	
0.17 β		0.20 β		0.23 β	
0.07 α		0.06 α		0.06 α	
0.07 β		0.06 β		0.06 β	
$n^{(s)}$	IIa	$n^{(s)}$	IIb	$n^{(s)}$	IIc
1.00 α		1.00 α		1.00 α	
0.26 α		0.30 α		0.36 α	
0.26 β		0.30 β		0.36 β	
0.09 α		0.10 α		0.17 α	
0.09 β		0.10 β		0.17 β	
$n^{(s)}$	IIIa	$n^{(s)}$	IIIb	$n^{(s)}$	IIIc
1.00 α		1.00 α		1.00 α	
0.35 α		0.38 α		0.36 α	
0.35 β		0.38 β		0.36 β	
0.14 α		0.15 α		0.16 α	
0.14 β		0.15 β		0.16 β	

Table 2. Decomposition of (anti-)solitons to CMOs of the systems' neutral ground states.

system	$n^{(s)}$	CMO decomposition ^a
Ia	1.0 α	+ 1.0 (L)
	0.2 α	+ 0.7 (H - 1) - 0.7 (L + 12) + 0.2 (L + 5)
	0.2 β	+ 0.7 (H - 1) + 0.6 (L + 12) + 0.1 (L + 5)
Ib	1.0 α	+ 1.0 (L)
	0.2 α	+ 0.7 (H) - 0.5 (L + 2) + 0.4 (L + 13)
	0.2 β	+ 0.7 (H) + 0.4 (L + 2) - 0.4 (L + 13)
Ic	1.0 α	+ 1.0 (L)
	0.2 α	+ 0.7 (H - 1) - 0.6 (L + 5) - 0.4 (L + 8)
	0.2 β	- 0.7 (H - 1) - 0.5 (L + 5) - 0.4 (L + 8)
IIa	1.0 α	+ 0.8 (H) + 0.6 (L)
	0.3 α	+ 0.6 (H - 2) + 0.4 (H - 1) - 0.4 (L + 3)
	0.3 β	- 0.5 (H - 2) - 0.5 (H - 1) - 0.5 (L + 3)
IIb	1.0 α	+ 1.0 (L)
	0.3 α	+ 0.6 (H) - 0.7 (L + 2) - 0.3 (L + 15)
	0.3 β	+ 0.8 (H) + 0.5 (L + 2) + 0.3 (L + 15)
IIc	1.0 α	+ 1.0 (L)
	0.4 α	+ 0.4 (H - 3) + 0.5 (H) - 0.7 (L + 2)
	0.4 β	- 0.4 (H - 3) - 0.6 (H) - 0.6 (L + 2)
IIIa	1.0 α	+ 0.9 (L) - 0.4 (H)
	0.4 α	+ 0.3 (H - 2) - 0.5 (H - 1) + 0.7 (L + 3)
	0.4 β	- 0.3 (H - 2) + 0.7 (H - 1) + 0.5 (L + 3)
IIIb	1.0 α	+ 1.0 (L)
	0.4 α	+ 0.6 (H) + 0.8 (L + 1) + 0.2 (L + 12)
	0.4 β	+ 0.8 (H) - 0.6 (L + 1) - 0.1 (L + 12)
IIIc	1.0 α	+ 1.0 (L)
	0.4 α	+ 0.6 (H) + 0.8 (L + 1) + 0.2 (L + 18)
	0.4 β	+ 0.8 (H) - 0.6 (L + 1) - 0.2 (L + 18)

^a H and L stand for HOMO and LUMO, respectively

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