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How much can donor/acceptor-substitution change the responses of long push–pull systems to DC fields?

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Abstract

Mathematical arguments are presented that give a unique answer to the question in the title. Subsequently, the mathematical analysis is extended using results of detailed model calculations that, in addition, throw further light on the consequences of the analysis. Finally, through a comparison with various recent studies, many of the latter are given a new interpretation.

1. Introduction

The response to external electric and magnetic fields provides a fundamental tool for studying and altering the properties of materials with numerous attendant applications. In particular higher-order responses allow for 'manipulating light with light'. Thus, there is considerable interest in identifying molecular systems with large non-linear responses.

One approach in this direction is based on push–pull systems, i.e. chain-like molecules with an electron-donor group at one end and an electron-acceptor group at the other (see Fig. 1). When the backbone is a π-conjugated oligomer the π electrons of the backbone may respond easily to perturbations like those of the substituents and/or external fields. Due to the donor and acceptor groups a large electron transfer, and accordingly, a large dipole moment can occur and one may hope for large responses of the dipole moment to external fields. For these π-conjugated systems, each circle in Fig. 1 could be, for example, a vinylene group, a phenylene group, a methinimine group, or combinations of those.

If the push–pull system is sufficiently large, we may split it into three parts, i.e. a left (L), a central (C), and a right (R) part as shown in Fig. 1. Electrons of the central part are assumed to be so far from the terminations that they do not feel the latter (or, more precisely, the effects of the terminations are exponentially decaying in the central part).

The dipole moment, $\vec{\mu}$, is useful in quantifying the response of the system to an external electric field

$$\begin{aligned}\mu_i(\omega) = {} & \mu_i^{(0)}(\omega) + \sum_j \sum_{\omega_1} \alpha_{ij}(\omega;\pm\omega_1)\cdot E_j(\omega_1) \\ & + \frac{1}{2}\sum_{jk}\sum_{\omega_1,\omega_2}\beta_{ijk}(\omega;\pm\omega_1,\pm\omega_2)\cdot E_j(\omega_1)E_k(\omega_2) \\ & + \frac{1}{6}\sum_{jkl}\sum_{\omega_1,\omega_2,\omega_3}\gamma_{ijkl}(\omega;\pm\omega_1,\pm\omega_2,\pm\omega_3) \\ & \cdot E_j(\omega_1)E_k(\omega_2)E_l(\omega_3)+\cdots.\end{aligned} \tag{1}$$

Here, $E_m(\omega_s)$ is the mth component (i.e. x, y, or z) of the external field with the frequency ω_s and ω is the frequency of the response of the molecule to the field. The ω_n summations go over all the frequencies of the applied field. $\mu_i^{(0)}(\omega)$ is the dipole moment in the absence of the field which vanishes for $\omega \neq 0$. Moreover, $\alpha_{ij}(\omega;\pm\omega_1)$ is the linear polarizability, and $\beta_{ijk}(\omega;\pm\omega_1,\pm\omega_2)$, $\gamma_{ijkl}(\omega;\pm\omega_1,\pm\omega_2,\pm\omega_3),\ldots$ are the first, second, …hyperpolarizability. Sum rules

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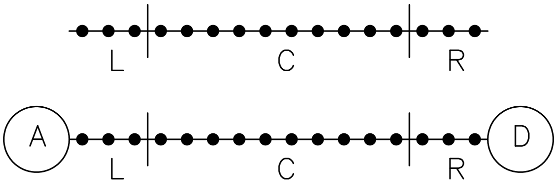

Fig. 1. Schematic representation of a long finite chain separated into a central region and two terminal regions. The lower chain shows what happens when a donor and an acceptor group have been added at the terminations. Each dot represents a group of atoms.

require that these quantities can be non-zero only if the frequency of the response, ω, equals the sum of the frequencies (eventually multiplied by -1), i.e. for $\gamma_{ijkl}(\omega; \pm\omega_1, \pm\omega_2, \pm\omega_3)$ we require $\omega = \pm\omega_1 \pm \omega_2 \pm \omega_3$.

In the present Letter, we focus on static external fields, in which case $\omega_i = 0$. Furthermore, we shall study a neutral system, although our arguments also are valid for charged systems as long as the extra charge is localized to the terminations. We let $\rho(\vec{r})$ be the (field-dependent) total charge density (i.e. the sum of the nuclear and electronic charge densities), and choose the long axis to be z. Then the component of the total dipole moment that is of interest here, namely z, is given by (omitting its argument, ω)

$$\begin{aligned}\mu_z &= \int \rho(\vec{r}) z \mathrm{d}\vec{r} \\ &= \int_{\mathrm{L}} \rho(\vec{r}) z \mathrm{d}\vec{r} + \int_{\mathrm{C}} \rho(\vec{r}) z \mathrm{d}\vec{r} + \int_{\mathrm{R}} \rho(\vec{r}) z \mathrm{d}\vec{r}, \end{aligned} \tag{2}$$

where we have split the integral into contributions from the left, central, and right regions of the chain. The central region consists of identical neutral units. We can, therefore, write

$$\int_{\mathrm{C}} \rho(\vec{r}) z \mathrm{d}\vec{r} = K_{\mathrm{C}} \mu_{\mathrm{C}}, \tag{3}$$

where K_{C} is the number of units in C and μ_{C} is the z component of the dipole moment of one of these units. In order to evaluate the other two contributions to the total dipole moment in Eq. (2) we define a 'typical' center for each term, i.e. $\vec{R}_{\mathrm{R}}$ and $\vec{R}_{\mathrm{L}}$ (these could, e.g. be the center of mass of the right and left parts, respectively), and let Z_{R} and Z_{L} be the z components of these vectors. Since the chain is neutral we, then, obtain

$$\begin{aligned}\int_{\mathrm{L}} \rho(\vec{r}) z \mathrm{d}\vec{r} + \int_{\mathrm{R}} \rho(\vec{r}) z \mathrm{d}\vec{r} &= (Z_{\mathrm{R}} - Z_{\mathrm{L}}) \int_{\mathrm{R}} \rho(\vec{r}) \mathrm{d}\vec{r} \\ &\quad + \int_{\mathrm{L}} \rho(\vec{r})(z - Z_{\mathrm{L}}) \mathrm{d}\vec{r} \\ &\quad + \int_{\mathrm{R}} \rho(\vec{r})(z - Z_{\mathrm{R}}) \mathrm{d}\vec{r}. \end{aligned} \tag{4}$$

The first term on the right hand side describes the contribution to the dipole moment associated with electron transfer from one end to the other. This term grows linearly with chain length (due to $Z_{\mathrm{R}} - Z_{\mathrm{L}}$) as does the term in Eq. (3). On the other hand, the last two terms in Eq. (4) describe local dipole moments that arise from the electron distributions within the two terminal regions and they are independent of the chain length.

This discussion suggests that donor/acceptor (=D/A) substitution at the ends of long chains may change the charge distribution in R and L so as to strongly enhance the dipole moment and, consequently, produce a particularly large change in the dipole moment when the system is exposed to an external electric field. Therefore, very many studies have been devoted to push–pull systems as a function of increasing length (see, e.g. [1–18]).

Not only the electrons but also the structure (phonons) will respond to a static electric field. We will demonstrate that, for sufficiently long chains, the electronic response per unit of a push–pull system (with structural relaxation taken into account) becomes independent of the donor and acceptor groups, implying that the materials properties cannot be improved upon substitution. Our mathematical arguments for this finding are presented in the next section, and in Section 3 we illustrate and analyse the results through calculations on a model system. The particular case of inversion symmetry is discussed in Section 4 where we also make a comparison with previous results. Finally, a summary is provided in Section 5.

The arguments we present are related to those originally given by Vanderbilt and King-Smith for an extended system in the absence of an external field. They argued that the permanent polarization (i.e. dipole moment per unit length) is a bulk property [19]. Very recently, Kudin et al. [20] proved that the permanent polarization is quantized for D/A substituted systems. Neither of these works considered the induced polarization or the structural relaxation due to an external field. Finally, in a recent Letter we presented some of the arguments behind the present work but did not analyze the predictions as we do here using a model system [21].

2. Changes in the charge distribution upon substitution

By replacing some (groups of) atoms with others at the chain ends, the electronic orbitals with components near the ends will change. Since the set of electronic orbitals is orthonormal, all other orbitals will change as well. Accordingly, the charge distribution may change everywhere due to the substitutions.

When an electrostatic field is applied as well, each orbital will respond to the field. Since the orbitals will have changed due to the substitution, so will their responses to the field. Furthermore, the structural responses due to the field will also depend on the substitution at the ends. Therefore, the dipole moment can depend upon both the substitution and the field. From these arguments there is no reason to believe that $\mu^{(0)}/N$, α/N, β/N, γ/N, ... (with N being the number of repeated units) will be independent of the substitution. However, we shall argue here that the charge