



The relation between delocalization, long bond order structure count and transmission: An application to molecular wires



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ABSTRACT

Pauling long bond orders have previously been used to obtain qualitative insight in the transmission through nanographenes. Here we show that this long bond order, the atom–atom polarizability (a measure for delocalization) and the transmission probability are intimately linked and that their relationships are valid for all alternant hydrocarbons. These relationships allow a simple rationalization of the transport properties of a variety of molecules considered in molecular electronics. As an example, some molecular wires such as oligo(*p*-phenylene) are studied, leading to a simple explanation for the experimentally observed exponential decay of the transmission probability with the number of phenyl units.

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1. Introduction

Over the past few years, several simplified models to predict transmission probability around the Fermi level have been developed. These models were respectively based on frontier orbitals [1–3], Kékulé structures [4] or long bond orders [5]. Others have tried to predict the transmission probability based on electron delocalization measures [6–9]. In this letter, the mathematical link between the long bond order model (and equivalently the Kekulé structure counting model) and a prototype delocalization index (the atom–atom polarizability) will be discussed and both properties will be theoretically connected to the transmission probability as it was derived in the Source-and-Sink-Potential (SSP) method [10,11]. With this knowledge, the transport properties of a wide range of alternant hydrocarbons can be discussed. Oligo(*p*-phenylene) chains and its quinodimethane-analogue will be studied in more detail, further illustrating the power of this long bond order structure counting method in the rationalization of both experimental and theoretical findings.

A lot of experimental and theoretical studies have already been performed on oligo(*p*-phenylene). When these molecules are incorporated in an electronic circuit by taking the end-chain para-carbons as contact atoms, an exponential decay of the

conductance as a function of the number of phenyl rings at the Fermi level has been observed [12,6,7,13,14]. It was also predicted very recently by Mandado and Ramos-Berdullas that the addition of a methylene carbon atom at each end of oligo(*p*-phenylene) (resulting in oligo(pheno)-*p*-quinodimethane, denoted as pX2 in the work of Mandado et al.) leads to a much better conduction, making poly(pheno)-*p*-quinodimethane an interesting potential candidate for a highly conducting polymer [6,7]. With the models at our disposal, we are able to explain the theoretically and experimentally observed exponential decay in transmission for oligo(*p*-phenylene) [12,6,7,13,14], the reason for the inverse behavior of oligo(pheno)-*p*-quinodimethane [6,7] and why delocalization measures can be used for these systems to predict their transport properties (Figure 1).

2. Methods

First, the link between the (Pauling) long bond order, the atom–atom polarizability (a prototype measure for delocalization) and transmission will be established.

The Pauling bond order between two adjacent atoms *r* and *s* of a conjugated carbon system, p_{rs}^p , as introduced by Pauling et al., can be defined as the fraction of the resonance structures in which a double bond is present between those atoms [15,16]. This can equivalently be expressed in a graph-theoretical way as [17]:

$$p_{rs}^p = \frac{K(G \ominus rs)}{K(G)} \quad (1)$$

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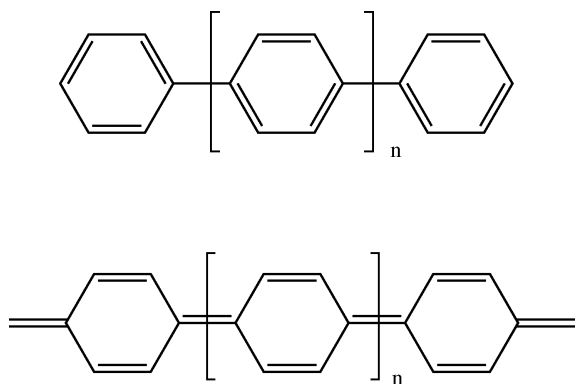


Figure 1. Poly(*p*-phenylene) (above) and poly(pheno)-*p*-quinodimethane (below).

where $K(G)$ is the number of Kekulé structures (KS) for graph G corresponding to the carbon skeleton of a hydrocarbon and $K(G \ominus rs)$ is the number of Kekulé structures when the vertices corresponding to atom r and atom s are deleted from graph G [18,19].

This bond order was then generalized to non-adjacent atoms by Morikawa et al. and they showed that the long bond order in graphene correlates nicely with the transmission probability [5]. For nanographenes, a theoretical explanation for this trend was offered by Fowler et al. [4]. More recently, the same qualitative valence bond (VB) model was used by Mandado et al. to rationalize the improved conductance of oligo(pheno)-*p*-quinodimethane compared to oligo(*p*-phenylene) [6].

It can be shown that the link between all these quantities centers around the complex function $\Delta_{r,s}/\Delta$, where Δ is the characteristic polynomial of the Hückel Hamiltonian matrix corresponding to the considered system and $\Delta_{r,s}$ is the characteristic polynomial of the same Hückel Hamiltonian matrix when row r and column s are deleted. It was previously established that this rational function can be identified with the propagator $G_{rs}^{(0)}$ between atoms r and s [20–22]. Coulson et al. derived that the Coulson bond order can be defined as the integral over the imaginary axis of this function [23,24]

$$p_{r,s}^c = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\Delta_{r,s}(iy)}{\Delta(iy)} dy \quad (2)$$

It was proven by Hosoya et al. that the Pauling bond order can be identified with this function evaluated at the origin [18,19]

$$p_{r,s}^p = \frac{\Delta_{r,s}(0)}{\Delta(0)} \quad (3)$$

On the other hand, the atom–atom polarizability (the Hückel equivalent of the linear response function in conceptual density functional theory (DFT) [25] and a measure for delocalization) [26,27] can be defined as the integral over the imaginary axis of the square of this function [23]

$$\pi_{r,s} = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\Delta_{r,s}^2(iy)}{\Delta^2(iy)} dy \quad (4)$$

In a previous contribution [9], the authors have shown the link between $\pi_{r,s}$ and the expression for the transmission probability around the Fermi level in the SSP method in the weak interaction limit, derived by Fowler et al. [10,28,4]

$$T(0) = 4\beta^2 \frac{\Delta_{r,s}^2(0)}{\Delta^2(0)} \quad (5)$$

When the Green's function approach is taken, exactly the same expression can be obtained in the limit of weak interaction [29].

As $\Delta_{r,s}(0)/\Delta(0)$ is real (or zero), since all of the coefficients of the characteristic polynomial of the Hamiltonian matrix are real, it

is evident that for any hydrocarbon for which Kekulé structures can be drawn, the limiting transmission is proportional to the square of the Pauling bond order. We should note that Fowler et al. already expressed the transmission at the Fermi level without the weak interaction limit as a non-linear function of the Pauling long-bond order specifically for benzenoids and nanographenes [4].

Conventionally, the (generalized) Pauling bond order is only defined for benzenoid graphs. However, it has to be stressed that, as the relations derived by Hosoya are very general and not limited to benzenoid molecules, the (generalized) Pauling bond order can be extended towards any conjugated hydrocarbon that (i) has no non-bonding molecular orbital (NBMO) (an energy level situated at the origin), (ii) has a bonding HOMO, (iii) has an anti-bonding LUMO.

Except for $4n$ membered rings, every possible even alternant hydrocarbon for which Kekulé structures can be drawn fulfills these criteria [19]. The reason why the Pauling bond order was never extended towards for example linear polyenes is quite obvious. As only one Kekulé structure can be drawn for a linear polyene, the Pauling bond order for such a system will alternate between 0 and 1, no fractional bond orders will arise. However, when studying transmission through linear polyenes, this realization allows us to rationalize for example the results presented recently by Hoffmann et al. in a non-mathematical way [30]. In that paper, the transport properties of alternant hydrocarbons are discussed by looking at the Green's function matrix elements ($G_{rs}^{(0)}$), where $\mathbf{G}^{(0)} = -\mathbf{H}^{-1}$. In simple Hückel theory, the zeroth order Green's function matrix element between atom r and atom s is (as already mentioned) $\Delta_{r,s}(0)/\Delta(0)$, so the absolute values of the elements in the Green's function matrices presented in that paper can be derived merely by drawing the required structures. We also would like to note that the method developed by Ernzerhof et al. for estimating the zero-voltage conductance of nanographenes is essentially equivalent to the method of the estimation of the conduction through determination of the (extended) Pauling bond order. Ernzerhof calculates the bond orders for the considered polycyclic rings in a very elegant way, avoiding the laborious work of drawing all possible structures of both the original molecule and the *contactless* states (the graphs corresponding to the molecule where atoms r and s have been deleted) [31].

The relationship between the zeroth order Green's function (the propagator) and the Pauling bond order is also evident when considering Ham's work where a molecular orbital expression for Pauling bond orders is derived [17]. One of the main steps in his derivation was the proof of the following equalities

$$p_{rs}^p = \frac{\text{number of KS having } rs \text{ as double bond}}{\text{number of KS}} \quad (6)$$

$$= H_{rs}^{-1} = \frac{\mathbf{H}^{rs}}{\det(\mathbf{H})} \quad (7)$$

where \mathbf{H}^{rs} is the cofactor of the element H_{rs} of the Hamiltonian matrix in the Hückel approximation. Eqs. (6) and (7) can be restated as

$$p_{rs}^p = \frac{K(G \ominus rs)}{K(G)} = H_{rs}^{-1} = G_{rs}^{(0)} = \frac{\Delta_{r,s}(0)}{\Delta(0)} \quad (8)$$

The link between both the transmission probability (see Eq. (5)) as well as the Pauling bond order (see Eq. (8)) and the atom–atom polarizability (see Eq. (4)) for alternant hydrocarbons can be established starting from the proof of the pairing theorem [9]. In the proof of this theorem [24,32], it is derived that for alternant hydrocarbons without non-bonding orbitals, the determinant is either even or odd, depending on the parity of the number of carbon atoms, n :

$$\Delta(z) = (-)^n \Delta(-z) \quad (9)$$

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