Quantum interference in monocyclic molecules: A novel and straightforward phase wave model

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Abstract

We have proposed by far the simplest model, so-called phase wave model (PWM), to predict quantum interference states in monocyclic molecules. Meanwhile, transmission coefficient calculations were also performed using Green's function method incorporated with Hückel (Tight Binding) approximation. An impressive agreement has been obtained between the results of the phase wave model and the ones from transmission coefficient calculations for the chosen model systems, namely benzene, cycloheptatriene, cyclooctatetraene, and [10]annulene. PWM represents the phase of wave functions of the incoming electrons by a wave and associates a single wavelength of the phase with five atoms/sites. Hence, the electrical conductance would range from the highest to lowest when the phase shift between the interacting phase waves ranges from 0 to $\pi/2$. We believe that the present approach would develop a very swift intuition of quantum interference states in monocyclic molecules.

Keywords

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1. Introduction

Quantum interference (QI) rules are very essential in molecular electronics, for predicting conductance states of individual molecules [1,2]. Thus, investing these rules can seriously reduce the costs and endeavors of fabrication. Meanwhile, QI can be construed as the interaction between the incoming electronic de Broglie waves with multiple phases from multiple paths at a specific point. Thus, waves with the same phases result in constructive interference with a high (ON) conductance state; while waves with opposite phases produce destructive interference with a low (OFF) conductance state [3,4]. Therefore, anticipating theories, such as graphical rules [5], orbital rule [6], circuit rules [7], and magic ratio rules [8,9], as well as analytical formulae, have been proposed to predict the occurrence and behaviors of QI [10−14]. However, some of these theories have been found to languish when certain conditions are applied for specific and simple systems. As an example of such failures, Xia and co-workers demonstrated that atom counting rules are invalid in predicting QI in azulene derivatives, where the counting rules predicted a destructive QI in contrast to experimental and GW theoretical calculations [15]. Similarly, Lambert's team has also shown that curly arrow rules break down in predicting the proper QI state in cross-conjugated anthraquinone molecule; it is found that curly arrow rules predict destructive QI while the team's Green's function based method illustrates a constructive interference [16]. It should be confirmed that these deteriorations do not underestimate the brilliant work of the developing teams or the successful predictions of the rules but they only confined the implementations of these rules to specific systems. Nevertheless, theoretical rules still guide researchers to exploit the manifestation of QI for enhancing the electrical and thermal properties of single−molecule junctions.

Monocyclic molecules are interesting candidates as specific model systems, for clearly manifesting of QI signatures. For instance, the benzene ring illustrates three fundamental conductance states. High conductance when the benzene ring is attached to two electrodes at sites 1 and 4 named as para connection, as shown in Fig. 1. The figure also shows the other two states: meta (ortho) connection with low (high) conductance state when the ring is connected to the leads at sites 1 and 3 (1 and 2). In addition, cyclic molecules have developed from simple molecules like benzene to novel and sophisticated ones like cyclo [18] carbon [17], cyclic porphyrin hexamers [18], and cycloparaphenylenes (CPPs) [19]. They can also compose loops or belt-like molecules [20] as it was called by Tahara and Tobe [21]. The evolution from simple to intricate molecular structure reflects the lucrative applications of cyclic molecules in both technology and science. For example, the CPPs and their derivative represent perfect candidates for building electrodes in molecular junctions [22], and they also show potentials for electronic applications as the basic building blocks of carbon nanotubes [23]. Hence, we have suggested a very simple model that can be successfully performed on the back of an envelope to predict the QI of cyclic molecules.

The present work aims to provide a very easy to use QI predicting method; so-called phase wave rules (PWR), even though it can be applied for specific systems. The idea of the phase of the moving electrons in the molecules is not a new one as it was mentioned decades ago in the work, for example, of Sautet and Joachim [24]. They and others [25,26] studied the benzene molecule as a model system and attributed the resultants conductance states to the interactions of the phases in different branches. More recent work by Solomon et al. has formulated the total phase of the transmission as a sum of the mini-phase contributions associated with each molecular orbital. Although the energy-dependent "transmission phase" successfully describes QI patterns in the benzene ring, the interactions of the constituent mini-phases are rather complex [27]. These patterns were found to be sensitive (insensitive) to a point charge approaching the plane of the benzene ring horizontally (perpendicularly) [28]. Strange et al. tuned the QI in quinoid-type molecules to enhance their thermoelectric properties by attaching side groups [29]. In contrast, Nozaki and Toher detached the QI effects from the paths in the meta-connected benzene ring and attributed them to the suppression due to interactions of molecular orbital [30], which needs a discussion that is out of the scope of this paper.

However, the researchers did not put a clear and applicable rule as we do here. Besides, PWR is a response to a statement described molecular electronics, in general, and QI especially as a complicated and painful discipline. There is no doubt that molecular electronics from the theory point of view is not a naïve
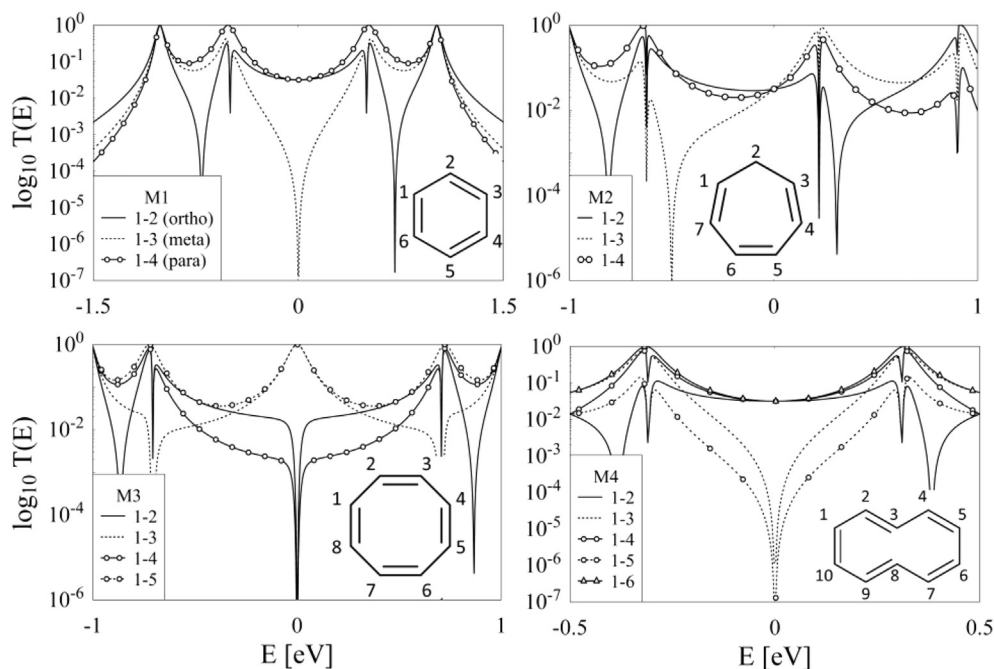
Fig. 1. The behavior of the transmission coefficient according to the location of the electrodes. The model systems are benzene (M1), cyclo-heptatriene (M2), cyclooctatetraene (M3), and [10]annulene (M4).

field; however, it is built on basic and elementary rules that can give impressive results. To prove such an idea of simplicity, we present the PWM approach, which depends on the phase of the incoming de Broglie waves of the electrons by assuming that the total phase of the wave can be divided over a series of atoms resembling Bloch waves in solid state materials. As far as we know, this is the first try in molecular electronics that correlates the phase of the electronic wave with space, location of the sites, rather than energy. The proposed approach can successfully be applied to cyclic hydrocarbon molecules with any size. Our results show that PWR auspiciously predicts the QI behaviors in benzene-like molecules and offers a good agreement with tight binding calculations. Such coherence supports the cogency of PWR assumptions and approves it is an indispensable tool to investigate QI.

2. Methodology

Similar to the Bloch wave in periodic solid materials, we have associated a specific phase of the electronic wave with each site throughout the moving path, see Fig. 2. The incoming wave enters the molecule at a single point/atom, which is attached to the first electrode, and splits into two sub-waves. Each of the two emergent sub-waves flows through one of the two branches of the molecule. Then they recombine again at another single point/atom, which is attached to the second electrode, to form the outgoing wave. As the two sub-waves arise from the same source, we assumed they hold the same phase along the molecular branches. However, the coherence of the phases may or may not be conserved at the outgoing point depending on the lengths of the individual paths. The resulting phase coherence or phase interference intensity (λ) defines the strength of the constructive interaction between the two sub-waves. When the interference is constructive, λ would be high or one but λ would be low or zero when the interference is destructive. The so-called phase interference intensity quantity can be calculated using the following formula,

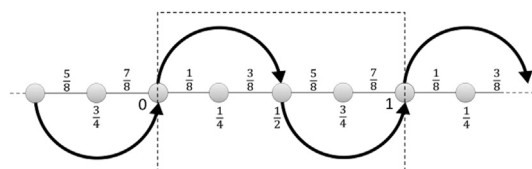$$\lambda = |cos(\Delta\pi)|. \tag{1}$$

Fig. 2. The phase of a single de Broglie wave passing through a chain of atoms represented by grey circles. The dashed rectangle confines single phase unit.

where λ takes the values between zero (the lowest) and one (the highest), $\Delta = |P_> - P_<|$, $P_>$ and $P_<$ represent the highest and lowest phases at the same point, respectively. For molecules with a total number of atoms N, we simply assume that the first electrode is attached to the first site of the molecule and the second electrode is attached to site number n. Thus, the total number of sites in branch one will equal to n and the total number of sites contained in branch two will equal to m (=N−n+2). Number two in the previous formula results from the fact that we have two electrodes. When the phases of the two recombining sub-waves are the same (0 or π), the phase interference intensity will equal to 1. In other words, constructive interference occurs and the conductance is supposed to be high. On the contrary, destructive interference with low conductance manifests if the phase difference between the interacting phase waves is equal to $\pi/2$. As a result, we have distributed the phase wave over five sites because they represent the smallest number of atoms that (i) capture these two main conditions and (ii) represent the main reduced five angles, namely 0, $\pi/4$, $\pi/2$, $3\pi/4$, π, of the unit circle to complete a full wave length. The reason for the angle reduction is that each unit circle corresponds to *one* wave length. For example, half phase cycle (half wave length) corresponds to π in the unit circle and a full phase cycle (full wave length) corresponds to 2π in the unit circle. Hence, we scaled the unit circle by the factor of ½. Furthermore, we have chosen the cosine function to represent the phase wave because it fulfills the above mentioned boundaries. In other words, the cosine is equal to one (zero) when the phase difference is zero (half). Besides, the cosine was placed under the absolute bars to ensure positive phase interference intensity. All the above-mentioned PWM rules are clearly described in the cases of four molecules with different sizes: benzene, cycloheptatriene, cyclooctatetraene, and [10]annulene.

Moreover, the electronic transmission of the model system was calculated using Olife code [31] that is incorporated Hückel Hamiltonians with Green's function method [32,33]. Hückel Hamiltonians mainly consist of the diagonal onsite elements and off-diagonal hoping elements. Olife can also calculate the electrical conductance, $\sigma = (2e^2/h) \int dE\, T(E) (-\partial f_E)$, using Landauer formula [34]. Where e is the electron charge, h is Plank's constant, E is the energy, $T(E) = |t|^2$, is the transmission coefficient, $f(E)$ is the Fermi-Dirac distribution function $= [1+\exp^{-\beta \Delta E}]^{-1}$, $\Delta E = E - E_F$, E_F is the Fermi energy, $\beta = k_B T$, k_B is Boltzman's constant, T is the temperature, and t is transmission amplitude for one allowed channel since

we allocated a single energy for each site. Finally, the transmission amplitude is calculated from Green's function, $G_{\delta,\mu} = (1/i\hbar v)te^{ik}$, using Fisher−Lee relation [35]. Where $G_{\delta,\mu}$ is the Green's function, the susceptibility of site δ to the perturbation on site μ, $\hbar = h/2\pi$, v is the "group velocity" in the input contact, and k is the wave number of the output contact.

3. Results and discussion

The first case to be discussed is the benzene molecule. The benzene, due to the symmetry, can only offer three configurations associated with three corresponding conductance states, as shown in M1 panel of Fig. 1. The first configuration, so-called ortho, offers high electrical conductance and emerges when the external electrodes are attached to the sites with the number one and two of the molecule. Fig. 3a demonstrates the ortho connectivity of the benzene in addition to the associated PWM pattern. In the ortho-associated-PWM pattern, the molecule was divided into two paths, where the first path is the direct connection between sites 1 and 2; the second path is defined by the atoms 1, 6, 5, 4, 3, and 2. As it is shown, the final phases at point 2 coming from the two branches are similar which means a constructive interference pattern and high conductance ($\lambda = 1$). The case of similar phases repeated as well in the para connectivity, where the second electrode is attached to the forth site of the molecule. However, when the second lead is attached to the site number 3, the meta connectivity established. The recombined waves in the meta formation show opposite phases. Hence, they destructively interfere with each other and the electrical conductance declines as $\lambda = 0$. The same discussion can also be applied to cyclooctatetraene (M3), and [10]annulene (M4) molecules.

Unlike the above three cases with even number of atoms, the transmission coefficient of cycloheptatriene that is a molecule with odd number atoms exhibits anomalous behavior. The conductance of cycloheptatriene is unique with a single value regardless of the positions of the two electrodes. This behavior can clearly be explained according to the PWM, which predicts a constant phase difference (=$\pi/4$) between the interacting sub-waves at the outgoing point no matter where the electrodes are connected to the molecule. As a result, phase interference intensity will equal to 0.707, which means that approximately 70% of the electronic wave flows out of the second electrode.
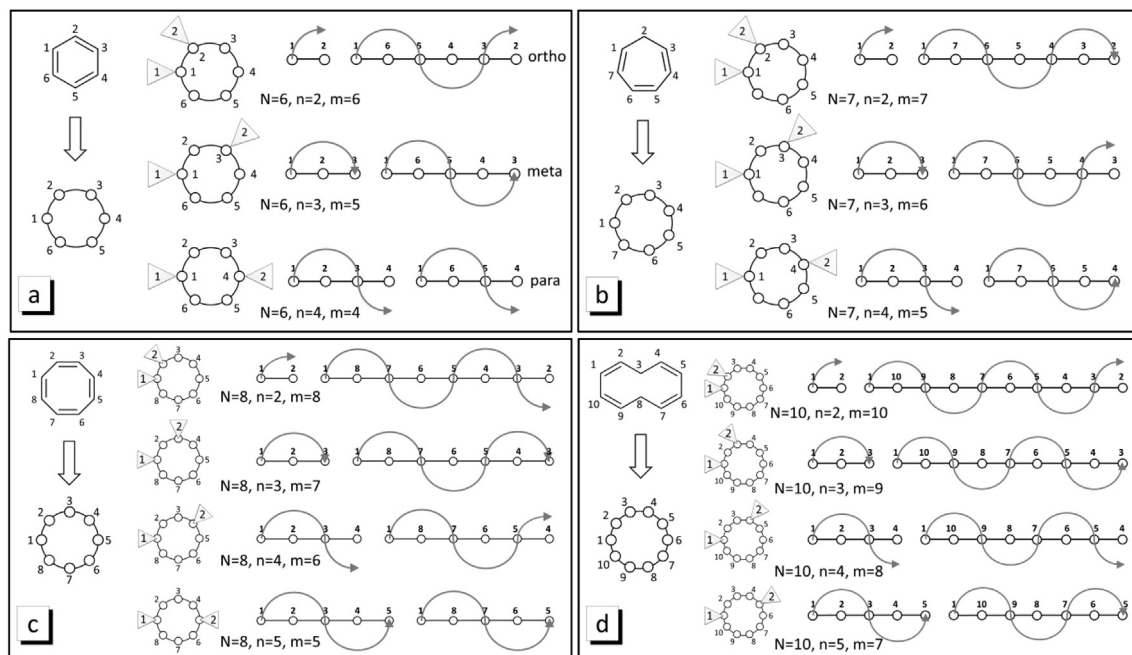
Fig. 3. Application of PWM on benzene (a), cycloheptatriene (b), cyclooctatetraene (c), and [10]annulene (d). In each connection configuration, the molecule is divided into two branches. N represents the total number or atoms in the molecule, n and m are the numbers of atoms in the first and second branch, respectively. For the sake of elegance, we did not show the 1—6 connectivity pattern in (d) panel.

4. Conclusions

A novel and easy to apply approach, phase wave model (PWM), has been developed to predict quantum interference (QI) signatures of monocyclic single molecule junctions. The predictions of QI patterns can be done on the back of an envelope in a few seconds without any hard complications. The PWM results of benzene, cycloheptatriene, cyclooctatetraene, and [10] annulene model systems were in impressive agreement with transmission coefficient calculations obtained from incorporating Hückel approximation with Green's function method. Hence, we believe that this model will strongly help developing fast and trustworthy intuitions of QI behaviors in the nominated type of molecules.

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