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PERSPECTIVE

Single molecule charge transport: from a quantum mechanical to a classical description

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This paper explores charge transport at the single molecule level. The conductive properties of both small organic molecules and conjugated polymers (molecular wires) are considered. In particular, the reasons for the transition from fully coherent to incoherent charge transport and the approaches that can be taken to describe this transition are addressed in some detail. The effects of molecular orbital symmetry, quantum interference, static disorder and molecular vibrations on charge transport are discussed. All of these effects must be taken into account (and may be used in a functional way) in the design of molecular electronic devices. An overview of the theoretical models employed when studying charge transport in small organic molecules and molecular wires is presented.

1. Introduction: the quantum mechanical and the classical

One of the smallest scales that can be imagined for functional electronic devices is that of a single molecule.[1] For this reason, charge transport in single molecules has been the subject of numerous experimental and theoretical studies over the last few decades.[2–9] There are some similarities, but also many fundamental differences between charge transport in a molecule and an electrical current in a macroscopic wire. On the small scale, many effects that originate from the quantum mechanical nature of matter are observed explicitly, while such effects are mostly averaged out in macroscopic wires at room temperature.

Charge transport in, for instance, a short conjugated molecule generally occurs by a single step tunneling process, which implies a coherent (quantum mechanical) mechanism. Such a single-step tunneling process infers an exponential dependence of the current or the charge transfer rate on the length of the molecule. An exponential dependence has been observed in experiments that can roughly be divided into two categories: spectroscopic experiments of charge transfer in donor–bridge–acceptor systems[10,11] and measurements on molecules between electrodes.[12,13] From both experimental

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methods there are many examples in which the rate or the current decays exponentially, although the strength of this dependence may vary depending on the energetics of a particular system.[14]

Interestingly, when increasing the length of the molecule in which charge transport is measured, deviations are observed from a simple exponential distance dependence. Such deviations have been observed in studies of charge transfer in donor–bridge–acceptor systems where the bridge consists of a π-stack of DNA bases. For short bridges the rate of charge transfer decays exponentially with the distance between the donor and the acceptor, but beyond a certain length the rate is almost independent of the distance.[15–17] A very similar observation has also been made in single molecule conductance experiments for a series of conjugated chains of varying length.[11,18] The chain length dependence of the conductance was found to be exponential for short chains but at a certain length the decrease with distance became much weaker.[19] These deviations from exponential behavior have been explained by a transition in the mechanism of charge transfer from coherent single-step tunneling to incoherent hopping where the distance dependence is much weaker than for tunneling.[20–22] Such an incoherent hopping mechanism would imply that the charge actually becomes localized on the bridge between the donor and acceptor or between the electrodes. However, charge localization on the bridge has not been observed experimentally until now.

Alternative experiments have been performed in which charges were directly generated on conjugated molecular wires by irradiation with short electron pulses.[23–26] Charge transport could subsequently be studied directly by microwave conductivity experiments[25] or indirectly by spectroscopically probing the movement of the charges to appended traps at the chain ends.[23] Interestingly, also in these experiments it is not always straightforward to predict whether charge transport occurs by a partially coherent (band-like) mechanism or by incoherent hopping.[27]

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It is clear from these examples that the transition from a purely quantum mechanical description of charge transport to a purely classical model is of considerable interest, especially in longer molecular wires where mobile charges can interact with vibrational degrees of freedom.

Our universe is inherently quantum mechanical in nature—at least there is currently no experimental evidence to suggest otherwise. However, many physical phenomena can be readily described classically, and it is not always obvious whether a specific case calls for a quantum mechanical or a classical description. In the context of charge transport this means that sometimes charge carriers may be treated as particles, while other times they must be described by their wavefunctions. In the former case it is, in principle, possible to follow the trajectory of a charge carrier, while in the latter case only a time-dependent probability of finding the charge carrier in any given spatial region can be defined. More generally, any property of a classical particle has a well-defined state, while a quantum mechanical particle resides in a superposition of states (until an observable is measured and the wavefunction "collapses" into a specific eigenstate of that observable).

One can imagine that the propagation of a quantum mechanical charge carrier through space (and particularly through a medium, where interactions with the environment are present) may be substantially different from that of its classical counterpart. In the following sections the models that were developed to treat both of these cases will be discussed in some detail. However, it is interesting to first consider the reasons behind the transition from a quantum mechanical to a classical description (beyond the superficial, albeit intuitive, connection that follows from the Ehrenfest theorem[28,29] or from the WKB approximation).[29–32] This issue was originally treated in the context of quantum measurement and quantum information theory. While a detailed consideration of the subject is beyond the scope of this paper (comprehensive reviews can be found in ref. 33 and 34), a summary of the reasoning and of the relevant conclusions is in order.

Consider a system with a state vector $|\psi_s\rangle$ and an observable corresponding to a Hermitian operator $\boldsymbol{A}_s$ with a discrete spectrum acting on the Hilbert space of the system. Let $\{|a_n\rangle\}$ be the set of normalized eigenvectors of $\boldsymbol{A}_s$, and $\{a_n\}$ be the set of corresponding eigenvalues, for simplicity assumed to be non-degenerate: $\boldsymbol{A}_s|\psi_s\rangle = a_n|a_n\rangle$. The set of eigenvectors $\{|a_n\rangle\}$ forms a basis in the Hilbert space of the system: $|\psi_s\rangle = \sum_n |a_n\rangle\langle a_n|\psi_s\rangle$.

As long as no measurement is performed on the system, its state vector evolves according to the time-dependent Schrödinger equation:

$$i\hbar\frac{\mathrm{d}|\psi_s\rangle}{\mathrm{d}t} = \boldsymbol{H}_s|\psi_s\rangle, \qquad (1)$$

where $\boldsymbol{H}_s$ is the Hamiltonian of the system. However, once $\boldsymbol{A}_s$ is measured, the state vector of the system "collapses" into one of the eigenstates of $\boldsymbol{A}_s$ with probability $P(a_n) = P(|\psi_s\rangle \rightarrow |a_n\rangle) = |\langle a_n|\psi_s\rangle|^2$ for each eigenstate. It is clear that with respect to the observable $\boldsymbol{A}_s$ not all states are created equal: if the system is *already* in an eigenstate of $\boldsymbol{A}_s$, the measurement will not alter its state, $P(a_n) = P(|a_n\rangle \rightarrow |a_n\rangle) = |\langle a_n|a_n\rangle|^2 = 1$. Measuring a complete set of commuting observables specifies the quantum state of the system.

A measurement is nothing else than an interaction of the system with a measuring device. During the measurement the system does not evolve independently anymore: together with the device it forms a *larger* system (which will be from now on referred to as "complex") with state vector $|\Psi\rangle$ and Hamiltonian

$$\boldsymbol{H} = \boldsymbol{H}_{\mathrm{s}} \otimes \boldsymbol{I}_{\mathrm{e}} + \boldsymbol{I}_{\mathrm{s}} \otimes \boldsymbol{H}_{\mathrm{e}} + \boldsymbol{H}_{\mathrm{i}}, \qquad (2)$$

where $\boldsymbol{H}_{\mathrm{s}}$ is the system part, $\boldsymbol{H}_{\mathrm{e}}$ is the device (environment) part, $\boldsymbol{H}_{\mathrm{i}}$ is the system–environment interaction part and $\boldsymbol{I}_{\mathrm{e}}$ and $\boldsymbol{I}_{\mathrm{s}}$ are the identity operators in the environment and system Hilbert spaces, respectively.

During the measurement event, the time-dependent Schrödinger equation holds for the system–device complex as a whole:

$$i\hbar\frac{\mathrm{d}|\Psi\rangle}{\mathrm{d}t} = \boldsymbol{H}|\Psi\rangle. \qquad (3)$$

However, eqn (1) for the system separately is no longer valid: within the timeframe of the measurement the state vector "collapse" $|\psi_{\mathrm{s}}\rangle \rightarrow |a_n\rangle$ occurs. It should be noted here that although measurements in quantum mechanics are typically assumed to be instantaneous, in reality they are not. However, it can be shown that the characteristic timescale of the state vector collapse, known as the "decoherence time", is much shorter than any other characteristic dynamic timescale of the system.[33]

A logical conclusion is that the state vector "collapse" $|\psi_{\mathrm{s}}\rangle \rightarrow |a_n\rangle$ of the system is a consequence of the system–device interaction. During the measurement process the system and environment wave vectors become entangled and no longer evolve independently.[33] However, information transfer usually associated with measurements is a common result of almost any interaction of the system with its environment. Thus, one can imagine that the environment constantly "measures" any non-isolated system, and any system state $|\psi_{\mathrm{s}}\rangle$ that is *not* an eigenstate of an observable quickly collapses into one that *is*. This is the basis of *e*nvironment-*in*duced super-*selection* of states, nicknamed "*einselection*", and einselected states are referred to as "pointer states". It is obvious now that, save the classical dynamics, nothing happens to pointer states, even though they are immersed in the environment.[33]

A subsequent measurement of an observable already "measured" by the environment will produce a predefined result, which means that the system behaves as if it were classical. Thus, classical behavior is a consequence of the "openness" of the systems observed. Therefore, in order to decide whether a quantum mechanical description of a system is necessary or a classical description will suffice, it is necessary to consider the interactions of the system with its environment.

2. Interference effects on charge transport: a fully quantum mechanical case

Purely coherent quantum mechanical phenomena can only occur in isolated systems. However, in the microworld, interactions with the environment are often sufficiently weak for the system to be considered nearly isolated, and thus for its evolution to be considered quantum mechanical on a sufficiently long timescale. Any measurement performed on the system inevitably leads to the collapse of the system's state vector into an eigenstate of the measured observable, $|\psi_{\mathrm{s}}\rangle \rightarrow |a_n\rangle$. However, if the system is isolated between measurement events, the probabilities of possible outcomes, $P(a_n) = |\langle a_n|\psi_{\mathrm{s}}\rangle|^2$, are determined by its quantum mechanical evolution history.

One of the most striking effects predicted by quantum theory is particle interference. Interference effects have been known for over 300 years (Newton's rings were first described by Hooke in 1665).[35] A consistent theory of interference, based on Huygens' wave theory of light, was developed by Fresnel in the first quarter of the nineteenth century.[36] With the emergence of quantum mechanics and the concept of the particle–wave duality, it was expected that interference could occur not just for weightless photons, but also for heavier particles. However, the first experimental observation of interference for anything other than photons was not made until 1961, when Jönsson performed Young's double-slit experiment with electrons.[37] In recent years, quantum interference experiments have also been extended to composite nanoparticles, such as fullerenes,[38] helium clusters[39] and large fluorinated molecules.[40,41]

In double-slit experiments with electrons arriving at the slits one at a time, Merli and coworkers demonstrated that the position of every electron upon interaction with the detector is well-defined, but the interference pattern is retained for a statistical ensemble of electrons.[42] This means that there is no need for an interaction between several electrons in order for quantum interference to occur. The probability $P(\boldsymbol{r}) = |\psi_{\mathrm{e}}(\boldsymbol{r})|^2$ of being registered at position $\boldsymbol{r}$ exhibits an interference pattern even for a single electron with state vector $|\psi_{\mathrm{e}}\rangle$ (or wavefunction $\psi_{\mathrm{e}}(\boldsymbol{r}) = \langle \boldsymbol{r}|\psi_{\mathrm{e}}\rangle$ in the position representation):[29] in effect, the electron "interferes with itself".

This result has important implications for charge transport. An electron moving in free space is described by a plane wave: $\psi_{\mathrm{e}}(\boldsymbol{r},t) = \exp[i(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t + \varphi_0)]$, where ω is the frequency, $\boldsymbol{k}$ is the wavevector and φ_0 is the initial phase. However, the wavefunction of an electron travelling in a static potential, $V(\boldsymbol{r})$, experiences partial reflections at every point where $\nabla V(\boldsymbol{r}) \neq 0$. The incident and reflected waves are coherent (have a constant phase difference), and their interference may result in the formation of a standing wave pattern. For example, the wavefunction of an electron in a periodic potential, $V(\boldsymbol{r} + \sum_{n=1}^{3} m_n\boldsymbol{a}_n) = V(\boldsymbol{r})$, of a crystal lattice with primitive vectors $\boldsymbol{a}_n$, $m_n \in Z$, is a Bloch wave:[43]

$$\psi_{\mathrm{e}}(\boldsymbol{r}) = u_k(\boldsymbol{r})\exp(i\boldsymbol{k}\cdot\boldsymbol{r}), \qquad (4)$$

where $u_k(\boldsymbol{r})$ is a function with the same periodicity as $V(\boldsymbol{r})$.

The wavefunction given by eqn (4) does not depend on time; it is a standing wave resulting from an electron "interfering with itself" in the periodic potential of the crystal. Similarly, atomic or molecular orbitals are standing waves formed by an electron "interfering with itself" in the potential of an atom or molecule or, effectively, in a potential well. The square of the electron wavefunction $|\psi_{\mathrm{e}}(\boldsymbol{r})|^2$ determines the probability of finding an electron at position $\boldsymbol{r}$ (in effect, the electron density). According to the Hohenberg–Kohn theorem, a one to one correspondence exists between a potential field $V(\boldsymbol{r})$, defined up to a constant, and the ground state electron density $\rho(\boldsymbol{r})$ or the ground state wavefunction $\psi_{\mathrm{e}}(\boldsymbol{r})$, defined up to a phase

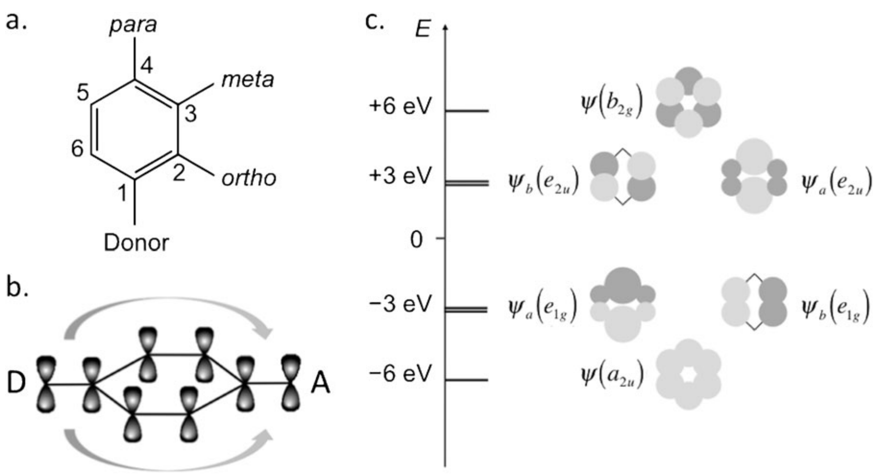

Fig. 1 (a) A benzene molecule with a donor and an acceptor coupled to it in either the *ortho*, *meta* or *para* configuration; (b) p_z-orbitals on the carbon atoms in the benzene ring, on the donor and on the acceptor, with two possible "spatial" pathways between the donor and the acceptor; (c) the molecular orbitals of benzene.

factor.[44] Thus, interference effects determine the electronic structure (band or orbital) and local electron density in perfect crystals and molecules—and, consequently, charge transport!

An interesting example to consider in this context is that of charge transport from a donor to an acceptor coupled to a benzene molecule in either the *ortho*, *meta* or *para* configuration (Fig. 1a). It is well-known that charge transport in organic molecules is mediated primarily by the conjugated π-electron system, and thus it is reasonable to consider only the atomic orbitals contributing to this system—in benzene, these are the p_z orbitals on carbon atoms (Fig. 1b).[45,46] In the Hückel approximation, the molecular orbitals (Fig. 1c), formed by these atomic orbitals, can be written as:[47]

$$\begin{aligned}
\psi(a_{2u}) &= \tfrac{\sqrt{6}}{6}(p_1+p_2+p_3+p_4+p_5+p_6),\\
\psi_a(e_{1g}) &= \tfrac{\sqrt{3}}{6}(2p_1+p_2-p_3-2p_4-p_5+p_6),\\
\psi_b(e_{1g}) &= \tfrac{1}{2}(p_2+p_3-p_5-p_6),\\
\psi_a(e_{2u}) &= \tfrac{\sqrt{3}}{6}(2p_1-p_2-p_3+2p_4-p_5-p_6),\\
\psi_b(e_{2u}) &= \tfrac{1}{2}(p_2-p_3+p_5-p_6),\\
\psi(b_{2g}) &= \tfrac{\sqrt{6}}{6}(p_1-p_2+p_3-p_4+p_5-p_6),
\end{aligned} \tag{5}$$

where p_n, $n = \overline{1,6}$ is the p_z orbital on the n-th carbon atom in the benzene ring (Fig. 1a).

If the donor and the acceptor are assumed to be coupled to benzene by just a single p_z-orbital, it is easy to calculate the

Table 1 Electronic couplings (charge transfer integrals) between a single p_z orbital of a donor and an acceptor and the molecular orbitals of benzene; J_0 = 2.3 eV is the electronic coupling between two carbon atoms at 0.14 nm distance, the equilibrium length of an aromatic bond[46]

	Donor	Acceptor (*ortho*)	Acceptor (*meta*)	Acceptor (*para*)
$\psi(a_{2u})$	$+\frac{J_0}{\sqrt{6}}$	$+\frac{J_0}{\sqrt{6}}$	$+\frac{J_0}{\sqrt{6}}$	$+\frac{J_0}{\sqrt{6}}$
$\psi(b_{2g})$	$+\frac{J_0}{\sqrt{6}}$	$-\frac{J_0}{\sqrt{6}}$	$+\frac{J_0}{\sqrt{6}}$	$-\frac{J_0}{\sqrt{6}}$
$\psi_a(e_{1g})$	$+\frac{J_0}{\sqrt{3}}$	$+\frac{J_0}{2\sqrt{3}}$	$-\frac{J_0}{2\sqrt{3}}$	$-\frac{J_0}{\sqrt{3}}$
$\psi_a(e_{2u})$	$+\frac{J_0}{\sqrt{3}}$	$-\frac{J_0}{2\sqrt{3}}$	$-\frac{J_0}{2\sqrt{3}}$	$+\frac{J_0}{\sqrt{3}}$
$\psi_b(e_{1g})$	0	$-\frac{J_0}{2}$	$-\frac{J_0}{2}$	0
$\psi_b(e_{2u})$	0	$-\frac{J_0}{2}$	$+\frac{J_0}{2}$	0

electronic couplings of the donor and the acceptor (at *ortho*, *meta* or *para* position) to each of the molecular orbitals of benzene given by eqn (5). These electronic couplings (also referred to as charge transfer integrals) are presented in Table 1, in terms of the electronic coupling J_0 between p_z orbitals on two carbon atoms. From Fig. 1c and Table 1 it is immediately obvious that the orbitals $\psi_b(e_{1g})$ and $\psi_b(e_{2u})$ do not contribute to charge transport from the donor to the acceptor coupled to benzene in any configuration, since the electronic coupling between the donor and each of these orbitals is zero. However, the remaining four orbitals may contribute to charge transport.

The Hamiltonian of the total donor–benzene–acceptor system in the energy representation can be written as

$$\boldsymbol{H}_\mathrm{s} = \begin{bmatrix}
0 & J_{p_\mathrm{D}\psi(a_{2u})} & J_{p_\mathrm{D}\psi(b_{2g})} & J_{p_\mathrm{D}\psi_a(e_{1g})} & J_{p_\mathrm{D}\psi_a(e_{2u})} & 0\\
J_{p_\mathrm{D}\psi(a_{2u})} & \varepsilon_{\psi(a_{2u})} & 0 & 0 & 0 & J_{p_\mathrm{A}\psi(a_{2u})}\\
J_{p_\mathrm{D}\psi(b_{2g})} & 0 & \varepsilon_{\psi(b_{2g})} & 0 & 0 & J_{p_\mathrm{A}\psi(b_{2g})}\\
J_{p_\mathrm{D}\psi_a(e_{1g})} & 0 & 0 & \varepsilon_{\psi_a(e_{1g})} & 0 & J_{p_\mathrm{A}\psi_a(e_{1g})}\\
J_{p_\mathrm{D}\psi_a(e_{2u})} & 0 & 0 & 0 & \varepsilon_{\psi_a(e_{2u})} & J_{p_\mathrm{A}\psi_a(e_{2u})}\\
0 & J_{p_\mathrm{A}\psi(a_{2u})} & J_{p_\mathrm{A}\psi(b_{2g})} & J_{p_\mathrm{A}\psi_a(e_{1g})} & J_{p_\mathrm{A}\psi_a(e_{2u})} & i\hbar/\tau
\end{bmatrix}, \tag{6}$$

where the diagonal elements are molecular orbital energies (Fig. 1c), with the energy of the donor set to zero, and the energy of the acceptor taken to be imaginary to ensure that the charge is irreversibly trapped when it arrives at the acceptor.[48] The value of $\tau = 1.3$ (small enough to ensure that the charge disappears from the acceptor site instantaneously, and sufficiently large to avoid severe reflections of the wavefunction on the acceptor site) was assumed in the calculations described below. Varying τ within reasonable limits has no effect on the calculated results. The off-diagonal elements of the Hamiltonian (eqn (6)) are electronic couplings between the orbitals involved in charge transport. The electronic couplings of the benzene molecular orbitals, given by eqn (5), to the donor and acceptor orbitals can be found in Table 1. Electronic couplings between different molecular orbitals of benzene are assumed to be zero.

The wavefunction of a charge carrier on the donor–benzene–acceptor system in the energy representation is

$$\psi_s(t) = C_D(t)p_D + C_1(t)\psi(a_{2u}) + C_2(t)\psi(b_{2g}) + C_3(t)\psi_a(e_{1g}) + C_4(t)\psi_a(e_{2u}) + C_A(t)p_A, \quad (7)$$

where C_D, C_A and $C_n(t)$, $n = 1,2,3,4$, are complex time-dependent coefficients. Introducing the Hamiltonian given by eqn (6) and the wavefunction given by eqn (7) into the time-dependent Schrödinger equation for an isolated system, eqn (1), produces a set of equations for the coefficients $C_n(t)$.

Solving the obtained equations for $C_n(t)$ with the initial condition of a charge carrier localized on the donor,

$$C_D(0) = 1, \quad (8)$$

and all other coefficients in the expansion of the wavefunction being zero, allows one to estimate the rate of charge transfer from the donor to the acceptor. Since $|C_n(t)|^2$ gives the probability of finding the charge carrier in a given orbital, $|C_D(t)|^2 + \sum_{n=1}^{4}|C_n(t)|^2 + |C_A(t)|^2$ gives the total probability of finding the charge in the donor–benzene–acceptor system.

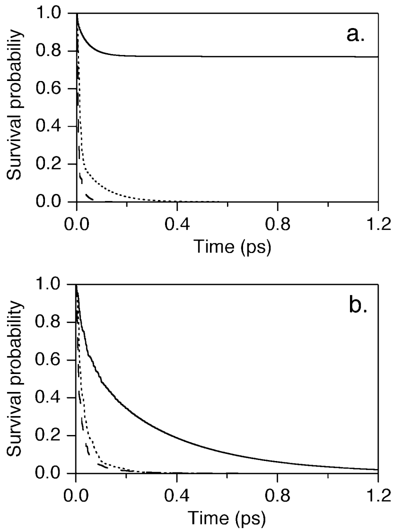

Fig. 2 Decay of the survival probability for a charge in a system consisting of a donor and an acceptor coupled to a benzene molecule in an *ortho* (dotted), *meta* (solid) and *para* (dashed) configuration: (a) Hückel approximation; (b) electronic couplings between p_z orbitals on all atoms included.

The initial conditions make this probability unity at $t = 0$. However, once the charge reaches the acceptor, it is removed from the system due to the imaginary component in the Hamiltonian, eqn (6). This leads to the decay of the total probability of finding the charge in the system, with a rate given by the rate of charge transfer from the donor to the acceptor.

The (numerical) solutions of the time-dependent Schrödinger equation, eqn (1), with the Hamiltonian, wavefunction and initial condition given by eqn (6)–(8), respectively, are shown in Fig. 2a for the donor and acceptor coupled to the benzene ring in an *ortho*, *meta* or *para* configuration (Fig. 1a). Charge transfer between a donor and an acceptor in a *para* or *ortho* configuration is found to be efficient: it only takes a fraction of a picosecond. On the contrary, for an acceptor at the *meta* position charge transport is inefficient. After a short equilibration time, during which charge transfer may occur with a probability of approximately 20%, the system reaches a steady state. The probability of charge transfer to the acceptor at later times is zero.

This phenomenon can be understood in terms of the molecular orbital structure of benzene. It turns out that the contribution of the orbitals $\psi(a_{2u})$ and $\psi(b_{2g})$ to charge transport is negligible because of the large energy difference of these orbitals with the donor and acceptor sites (Fig. 1c). Charge transport is thus fully determined by the orbitals $\psi_a(e_{1g})$ and $\psi_a(e_{2u})$. Due to symmetry, the contributions of these orbitals to the amplitude of the wavefunction on the acceptor at the *meta* position are equal in magnitude, but opposite in sign, resulting in zero net charge transport in equilibrium.[49,50]

It is more illustrative, however, to look at charge transport through the benzene ring in terms of the p_z orbitals on individual carbon atoms, rather than in terms of molecular orbitals.[46] The wavefunction of the charge carrier can in this case be written as

$$\psi_s(t) = C_D(t)p_D + \sum_{n=1}^{N} c_n(t)p_n + C_A(t)p_A, \quad (9)$$

where $c_n(t)$, $n = \overline{1, N}$, are complex time-dependent coefficients, N is the number of atoms in the bridge molecule ($N = 6$ in the case of benzene). This representation of the wavefunction can be obtained from eqn (7) by a (unitary) transformation of the orbital basis set, inverse to the transformation given by eqn (5). The system Hamiltonian (in the Hückel approximation) written in the basis set of molecular orbitals, eqn (6), should be transformed accordingly.[45,46] The initial condition for the charge carrier wavefunction is still given by eqn (8).

Since the p_z orbitals are localized on individual atoms, one can imagine that there are two possible "spatial" pathways from the donor to the acceptor, as shown by arrows in Fig. 1b. This notion is purely illustrative: using atomic orbitals still implies working in the energy, rather than the coordinate, representation. One can now think of a component of the wavefunction travelling along each of the two "spatial" pathways. As the two components are coherent, after a short equilibration time, they form an interference pattern—a standing wave, with a node at the *meta* position. Because the probability of finding a charge at a node is zero, charge transfer to an acceptor coupled to the benzene ring at the

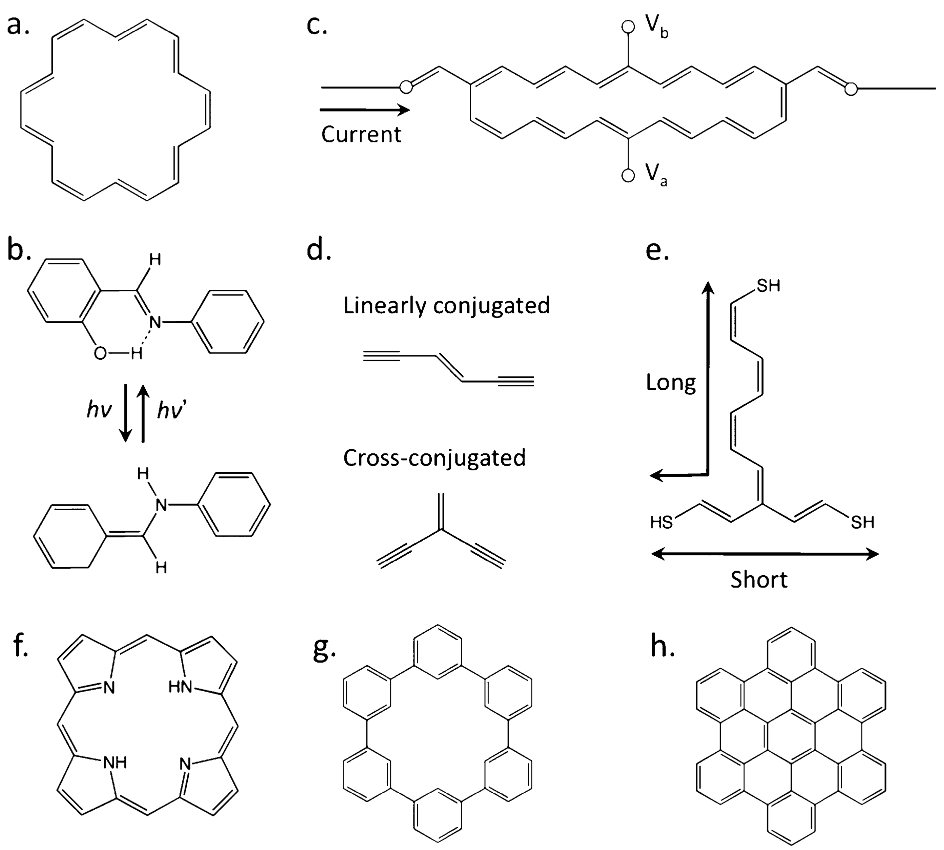

Fig. 3 Some molecules with strongly pronounced quantum interference effects and devices based on such molecules: (a) annulene;[55,58] (b) *N*-salicylideneaniline molecular switch;[59] (c) interference-based XOR switch;[60,61] (d) linearly- and cross-conjugated acyclic molecules;[62] (e) branched molecule with linearly conjugated "long" pathway and cross-conjugated "short" pathway;[63] (f) porphyrin;[64] (g) davidene;[46,65] (h) hexabenzocoronene.[46]

meta position does not occur. This also accounts for the well-known chemical fact that it is much more difficult to couple a substituent at the *meta* than at the *para* or *ortho* position, where there is an appreciable electron density.[51]

This description offers an intuitive understanding of charge transport in molecules.[46,52] Keeping to it, one can go as far as formulating a mnemonic rule, stating that charge transport between two sites in a molecule is inefficient if all possible pathways between these sites are cross-conjugated (have two adjacent single bonds).[53,54] For aromatic molecules this rule holds whichever way the single and double bonds are drawn (Fig. 1a).

The significant difference in the rate of charge transfer through a benzene molecule to the *meta* and *para* positions has led to a suggestion that this molecule may be used as a molecular transistor.[55] However, the performance of such a transistor may be significantly impaired by the contribution of charge transfer "through space" rather than "through bonds". The Hückel approximation, which was used in the calculations above, neglects the possibility of direct charge transport between atoms that are not covalently bound. When applied to a benzene molecule, this assumption is hardly reasonable, since quantum chemical calculations show a significant electronic coupling of the p_z orbitals on non-nearest carbon atoms, which has important consequences for the orbital structure of the molecule.[56]

The result of a charge transfer calculation for benzene with non-nearest neighbor couplings included in the Hamiltonian is shown in Fig. 2b. One can see a significant increase in the charge transfer rate to an acceptor at the *meta* position, although charge transfer to an acceptor at the *ortho* or *para* position is still an order of magnitude faster.[46] It has been shown that through-space, rather than through-bond terms dominate charge transfer in a surprising number of cases.[57] A related problem with using benzene as a molecular transistor is that if it were connected to electrodes, the distance would be small enough for the charge to tunnel from one electrode to the other directly, without ever going onto the benzene ring. This issue can be resolved by replacing benzene with a larger cyclic molecule (Fig. 3a).[58]

It is surprising that a molecule as simple and common as benzene already exhibits pronounced quantum interference effects that could, in principle, be used in a functional way. Even though benzene is probably more of a model system than an actual working molecular device, there is clear potential for exploiting quantum interference effects as a mechanism to control charge transport.

Since quantum interference effects were first considered as such by Sautet and Joachim in 1988 (curiously, for a benzene ring embedded in a polyacetylene chain),[66] a large number of molecules were considered that would allow to tune and optimize these effects. Already in 1989 Sautet and Joachim showed that quantum interference was the operational mechanism in the *N*-salicylideneaniline molecular switch activated by photoexcited intramolecular proton transfer (Fig. 3b), and proposed optimizations of this switch.[59] Other device-concepts exploiting interference effects have been proposed since (for example, Fig. 3c).[60,61]

In order for quantum interference to have a significant impact on charge transport the molecule need not be aromatic or even cyclic. In branched molecules (for example, Fig. 3d and e) charge transfer is much more efficient along linearly conjugated pathways, than along cross-conjugated pathways.[62] Under normal circumstances the conductance of a "wire" is proportional to its length. However, the conductance of a linearly conjugated pathway in a branched molecule can be higher than for a cross-conjugated pathway even when the latter is shorter (Fig. 3e).[63] One can also think of charge transport in branched molecules in terms of "spatial" pathways. The interference pattern is then formed by two components of the charge carrier wavefunction: the one that travels directly along the pathway from electrode to electrode (or from donor to acceptor) and the one that goes into the side branch, encounters a "dead end" and is reflected.

Quantum interference effects were also predicted to influence charge transport in heterocyclic molecules (such as porphyrin, Fig. 3f),[64] molecules that are non-planar in their equilibrium conformation (such as davidene, Fig. 3g),[46,65] and fused-ring molecules (such as hexabenzocoronene, Fig. 3h),[46] among others.

There are several theoretical approaches to studying the effects of quantum interference on charge transfer through molecules. One possibility is to solve the time-dependent Schrödinger equation, eqn (1), for the wavefunction of the charge and look at the rate of the charge arriving at the acceptor site, as discussed above.[46] Equivalently, one may solve the von Neumann (quantum Liouville) equation[67]

$$i\hbar\frac{\mathrm{d}\rho_\mathrm{s}}{\mathrm{d}t} = [\boldsymbol{H}_\mathrm{s}, \rho_\mathrm{s}], \tag{10}$$

for the density operator of the charge, $\rho_\mathrm{s} = |\psi_\mathrm{s}\rangle\langle\psi_\mathrm{s}|$. If the charge is removed from the system by using an imaginary term in the Hamiltonian, see eqn (6), then Tr ρ_s decays as the charge arrives at the acceptor. The rate of this decay can be equated to the charge transfer rate. Alternatively, the charge transfer rate through a molecule *in the steady state* can be defined as $k_\mathrm{SS} = \kappa\rho_\mathrm{AA}/\rho_\mathrm{DD}$, where ρ_AA and ρ_DD are the steady-state populations of the donor and acceptor sites and κ is a system constant with the dimension of inverse time.[65]

It is also possible to obtain a charge transfer rate without directly solving the quantum mechanical equations of motion, eqn (1) or (10), for the charge carrier. This approach is taken particularly often when charge transfer through a molecule between electrodes, rather than through a molecular bridge in a donor–bridge–acceptor system, is studied. It is then possible to apply the Landauer linear response theory.[68,69] The transmission function $\eta(E)$, which characterizes charge scattering within the molecule and, consequently, the molecular conductance, is then calculated using either the electron scattering quantum chemistry technique[66,70] or the Green's function approach.[52,71]

3. Decoherence: emergence of classical reality from quantum mechanics

Real molecules in solid state, solution or gas phase are far from being isolated. Charge carriers on such molecules can experience decoherence effects, induced by the environment. This leads to a complete or partial loss of quantum mechanical behavior and could have important consequences for charge transport.

Consider a system interacting with its environment, forming together a complex that can be assumed to be isolated from the outside world. The system-environment complex as a whole is described by the state vector $|\Psi\rangle$ or density operator $\rho = |\Psi\rangle\langle\Psi|$. The state vector $|\Psi\rangle$ obeys the time-dependent Schrödinger equation, eqn (3), and the density operator evolves as prescribed by the von Neumann equation[67]

$$i\hbar\frac{\mathrm{d}\rho}{\mathrm{d}t} = [\boldsymbol{H}, \rho], \tag{11}$$

where $\boldsymbol{H}$ is given by eqn (2). A density operator that satisfies eqn (11) can be written in the form

$$\rho(t) = \exp\left(-i\frac{\boldsymbol{H}}{\hbar}t\right)\rho(0)\exp\left(i\frac{\boldsymbol{H}}{\hbar}t\right). \tag{12}$$

To elucidate the contribution of the system–environment interaction to the evolution of the density operator $\rho(t)$ it is convenient to work in the Dirac (interaction) picture. Operators in the Dirac picture are related to operators in the Schrödinger picture by a unitary transformation[72,73]

$$\begin{aligned} &\boldsymbol{A}^{(I)}(t) = \boldsymbol{U}^{+}(t)\boldsymbol{A}(t)\boldsymbol{U}(t),\\ &\text{with } \boldsymbol{U}(t) = \exp\left(-i\frac{\boldsymbol{H}_\mathrm{s}\otimes\boldsymbol{I}_\mathrm{e} + \boldsymbol{I}_\mathrm{s}\otimes\boldsymbol{H}_\mathrm{e}}{\hbar}t\right). \end{aligned} \tag{13}$$

The density operator in the Dirac picture then becomes

$$\begin{aligned} \rho^{(I)}(t) &= \boldsymbol{U}^{+}(t)\rho(t)\boldsymbol{U}(t)\\ &= \exp\left(-i\frac{\boldsymbol{H}_\mathrm{i}}{\hbar}t\right)\rho(0)\exp\left(i\frac{\boldsymbol{H}_\mathrm{i}}{\hbar}t\right). \end{aligned} \tag{14}$$

where eqn (2), (12) and (13) have been used, and the Hamiltonian becomes

$$\boldsymbol{H}^{(I)}(t) = \boldsymbol{U}^{+}(t)\boldsymbol{H}\boldsymbol{U}(t). \tag{15}$$

It is obvious from eqn (14) that in the Dirac picture the density operator $\rho^{(I)}(t)$ changes with time only due to the interaction part of the Hamiltonian $\boldsymbol{H}_\mathrm{i}$; at initial time $\rho^{(I)}(0) = \rho(0)$. The internal evolution of the system and the environment, described by $\boldsymbol{H}_\mathrm{s}$ and $\boldsymbol{H}_\mathrm{e}$, respectively, in the Dirac picture does not affect the density operator $\rho^{(I)}(t)$, but gives the Hamiltonian $\boldsymbol{H}^{(I)}(t)$ explicit time dependence, eqn (15); at initial time $\boldsymbol{H}^{(I)}(0) = \boldsymbol{H}$. Note that the Hamiltonian $\boldsymbol{H}$ in the Schrödinger picture is time-independent, since explicit time dependence would violate energy conservation in the isolated system–environment complex. The evolution of the system with time is completely described in the Schrödinger picture by $\rho(t)$.

Differentiating eqn (14) with respect to time yields

$$\frac{\mathrm{d}\rho^{(I)}}{\mathrm{d}t} = \frac{1}{i\hbar}[\boldsymbol{H}_{\mathrm{i}}^{(I)}, \rho^{(I)}]. \tag{16}$$

Formally integrating eqn (16) and introducing the obtained expression for $\rho^{(I)}(t)$ back into eqn (16) produces an expression of the second-order in system–environment coupling:

$$\frac{\mathrm{d}\rho^{(I)}}{\mathrm{d}t} = \frac{1}{i\hbar}\left[\boldsymbol{H}_{\mathrm{i}}^{(I)}(t), \rho^{(I)}(0)\right] - \frac{1}{\hbar^2}\int_0^t [\boldsymbol{H}_{\mathrm{i}}^{(I)}(t), [\boldsymbol{H}_{\mathrm{i}}^{(I)}(t'), \rho^{(I)}(t')]]\mathrm{d}t'. \tag{17}$$

If only the evolution of the system, and not of the environment, is of interest, eqn (17) can be reduced to an equation for the density operator of the system alone, $\rho_{\mathrm{s}}^{(I)} = |\psi_{\mathrm{s}}^{(I)}\rangle\langle\psi_{\mathrm{s}}^{(I)}|$.

At initial time, $t = 0$, the system and the environment are typically taken to be uncorrelated: $\rho^{(I)}(0) = \rho_{\mathrm{s}}^{(I)}(0) \otimes \rho_{\mathrm{e}}^{(I)}(0)$; this is known as the factorization assumption and its validity must be verified for each specific system.[74,75] If it is further assumed that the environment is much larger than the system, and that the coupling between the two is sufficiently weak so that the influence of the system on the evolution of the environment is negligible, and the environment can be assumed to remain in an equilibrium state at all times: $\rho_{\mathrm{e}}^{(I)}(t) = \rho_{\mathrm{e}}^{(I)}(0), \forall t$. Then,

$$\rho^{(I)}(t) = \rho_{\mathrm{s}}^{(I)}(t) \otimes \rho_{e}^{(I)}(0). \tag{18}$$

The assumption that the environment remains in equilibrium at all times is sufficient, but not necessary, as long as the Born approximation is valid.[76,77]

From eqn (18) it follows that the density operator of the system is a partial trace of the total density operator of the system–environment complex over environmental states: $\mathrm{Tr}_{\mathrm{e}}\, \rho^{(I)} = \rho_{\mathrm{s}}^{(I)}(t)\mathrm{Tr}\, \rho_{\mathrm{e}}^{(I)}(0) = \rho_{\mathrm{s}}^{(I)}(t)$, since $\mathrm{Tr}\, \rho_{\mathrm{e}}^{(I)}(0) = 1$ is the normalization condition. Introducing eqn (18) into eqn (17) and taking a partial trace over environmental states results in

$$\frac{\mathrm{d}\rho_{\mathrm{s}}^{(I)}}{\mathrm{d}t} = -\frac{1}{\hbar^2}\int_0^t \mathrm{Tr}_{\mathrm{e}}[\boldsymbol{H}_{\mathrm{i}}^{(I)}(t), [\boldsymbol{H}_{\mathrm{i}}^{(I)}(t'), \rho_{\mathrm{s}}^{(I)}(t') \otimes \rho_{\mathrm{e}}^{(I)}(0)]]\mathrm{d}t', \tag{19}$$

where the first term in eqn (17) was eliminated by setting $\mathrm{Tr}_{\mathrm{e}}[\boldsymbol{H}_{\mathrm{i}}^{(I)}(t), \rho_{\mathrm{e}}^{(I)}(0)] = 0$, this is true if the coupling of the environment to the system has a zero mean value in the state $\rho_{\mathrm{e}}^{(I)}(0)$, which can always be arranged by simply including $\mathrm{Tr}_{\mathrm{e}}[\boldsymbol{H}_{\mathrm{i}}^{(I)}(t), \rho_{\mathrm{e}}^{(I)}(0)]$ in the system Hamiltonian.

Since the environment is assumed to always remain in the equilibrium state $\rho_{\mathrm{e}}^{(I)}(0)$, it cannot retain any information about the system's evolution history. Assuming that the system's density operator $\rho_{\mathrm{s}}^{(I)}(t + \mathrm{d}t)$ is only determined by $\rho_{\mathrm{s}}^{(I)}(t)$, and not by $\rho_{\mathrm{s}}^{(I)}(t' < t)$ (Markov approximation),[78] one can replace $\rho_{\mathrm{s}}^{(I)}(t')$ in eqn (19) by $\rho_{\mathrm{s}}^{(I)}(t)$:

$$\frac{\mathrm{d}\rho_{\mathrm{s}}^{(I)}}{\mathrm{d}t} = -\frac{1}{\hbar^2}\int_0^t \mathrm{Tr}_{\mathrm{e}}[\boldsymbol{H}_{\mathrm{i}}^{(I)}(t), [\boldsymbol{H}_{\mathrm{i}}^{(I)}(t'), \rho_{\mathrm{s}}^{(I)}(t) \otimes \rho_{\mathrm{e}}^{(I)}(0)]]\mathrm{d}t'. \tag{20}$$

Eqn (20) is the master equation for the density operator of the system, $\rho_{\mathrm{s}}^{(I)}(t)$, in the Born and Markov approximations. Since it is written in the Dirac picture, it only accounts for the changes of the system state resulting from interaction with the environment. Several approaches are available to estimate the commutators in eqn (20).[72,73,79] There are also numerous non-Markovian generalizations of the master equation.[80–83]

In the above derivation it was assumed that the system is weakly coupled to the environment. Indeed, for practical purposes this is the most interesting case: if the coupling of the system to the environment is strong, the system behaves classically and can be described with classical equations of motion, while if the coupling is absent altogether, eqn (1) is valid. In the case of weak coupling, the interaction with the environment can be considered a perturbation of the system. A consequence of this is, for example, the fact that in systems weakly coupled to the environment transition rates obtained from Markovian master equations coincide with those calculated using Fermi's golden rule (which can also be derived using perturbation theory).[84]

There are several approaches to describing the dynamics of Markovian open quantum systems, most notably, Redfield theory[85,86] and the semigroup formalism developed by Lindblad[87] and Gorini, Kossakowski and Sudarshan.[88]

The Redfield equations were derived for the matrix elements of the density operator in the energy representation: $\rho_{nm}^{\mathrm{s}} = \langle E_n|\rho_{\mathrm{s}}|E_m\rangle$, where $|E_n\rangle$, $|E_m\rangle$ are eigenstates of the system Hamiltonian $\boldsymbol{H}_{\mathrm{s}}$. In the Schrödinger picture the equation of motion for each matrix element takes the form

$$\frac{\mathrm{d}\rho_{nm}^{\mathrm{s}}}{\mathrm{d}t} = -i\hbar\omega_{nm}\rho_{nm}^{\mathrm{s}}(t) + \sum_{kl}\boldsymbol{R}_{nm,kl}\rho_{kl}^{\mathrm{s}}(t), \tag{21}$$

where $\hbar\omega_{nm} = E_n - E_m$ is the energy difference between $\boldsymbol{H}_{\mathrm{s}}$ eigenstates $|E_n\rangle$ and $|E_m\rangle$, and $\boldsymbol{R}_{nm,kl}$ is the Redfield tensor, $\mathrm{rank}(\boldsymbol{R}_{nm,kl}) = [\mathrm{rank}(\rho_{nm})]^2$.

In the derivation of eqn (21) Redfield combines projection operator techniques[89] with perturbation theory,[29] thus limiting the applicability of his approach to the weak coupling regime. Outside the applicability limits of perturbation theory, as well as on timescales smaller than the correlation time of the environment, Redfield theory does not retain the density operator completely non-negative.[90] Thus, for an arbitrary Hermitian operator $\boldsymbol{A}_{\mathrm{s}}$ with a set of eigenvectors $\{|a_n\rangle\}$, the expression $\langle a_n|\rho_{nm}^{\mathrm{s}}|a_n\rangle$ cannot be interpreted as the probability of finding the system in state $|a_n\rangle$.

Lindblad takes a more generic approach, showing that, in the Schrödinger picture, the general form of Markovian evolution of the system density operator $\rho_{\mathrm{s}}(t)$ is[87]

$$\frac{\mathrm{d}\rho_{\mathrm{s}}}{\mathrm{d}t} = \frac{1}{i\hbar}[\boldsymbol{H}_{\mathrm{s}}, \rho_{\mathrm{s}}] - \sum_{n>0}\frac{\gamma_n}{2}([\boldsymbol{F}_n\rho_{\mathrm{s}}, \boldsymbol{F}_n^{+}] + [\boldsymbol{F}_n, \rho_{\mathrm{s}}\boldsymbol{F}_n^{+}]), \tag{22}$$

where γ_n are real, positive scalar interaction parameters with the dimension of frequency and $\boldsymbol{F}_n$ are the so-called Lindblad or "quantum jump" operators,[91] defined by $\boldsymbol{H}_{\mathrm{i}} = \hbar\sum_n\gamma_n\boldsymbol{F}_n \otimes \boldsymbol{B}_n$, with $\boldsymbol{B}_n$ being environmental operators (remember, the environment constantly "measures" the system). The first term on the right accounts for the unitary evolution of the system, described by the von Neumann equation, eqn (10); the second term accounts for the system–environment interaction. Eqn (22) is known as the Lindblad equation and can be used to treat a variety of dissipative processes: dephasing,[92] collisions,[93] bond breaking,[94] electron transfer,[95] *etc.*

Dissipative processes can be classified into two major types. The first type involves energy exchange between the system and the environment and changes the populations of the system's energy states. For example, if the system is initially not in thermal equilibrium with its environment, then the interaction in the system–environment complex will cause energy transfer and will lead to eventual equilibration. The second type is pure dephasing, a quasielastic interaction that leads only to a loss of phase coherence between quantum levels. Since pure dephasing conserves the energy state of the system, the Lindblad operators in this case must commute with the system Hamiltonian: $[\boldsymbol{H}_s, \boldsymbol{F}_n] = 0, \forall n$.[96] Both inelastic and quasielastic interactions lead to wave function decoherence.

An alternative approach is not to use one of the more formal relaxation theories,[87,88,97–101] but to incorporate the system–environment coupling in a phenomenological way. In this case the density operator ρ_s of the system is propagated with the von Neumann equation, eqn (10), with additional relaxation terms.[102] These dephasing terms can be handled explicitly, although there are also attempts to incorporate them directly into the system Hamiltonian in the framework of time-dependent density functional theory.[103,104] When charge transport in donor–bridge–acceptor systems is described, the additional terms that have to be included are a charge injection rate on the donor, a charge decay rate on the acceptor and dephasing rates γ on bridge sites. The latter describe how much time is required for the phases of the charge carrier wavefunction at different atoms in a molecule to lose correlation, which makes components of the wavefunction travelling along different spatial pathways incoherent and the charge transport, by definition, classical.

In ref. 65 a model with a Hückel type Hamiltonian was used to calculate the steady-state charge transfer rate k_{CT} through a benzene molecule with a donor and an acceptor coupled to it in *ortho*, *meta* and *para* configurations (Fig. 1a). The result of the calculation is shown schematically in Fig. 4. It can be seen that the charge transfer rate from a donor to an acceptor coupled in the *meta* configuration is zero if there is no dephasing, while for an acceptor coupled in the *ortho* or *para* configuration charge transfer is efficient (the rate of electron transfer in benzene is as high as 150 ps^{-1}). This is in agreement with the calculation results presented in Fig. 2a. As dephasing gets stronger, the difference between charge transfer from a donor to an acceptor coupled in different configurations is diminished. Thus, in the classical regime the absence of interference effects leads to charge transfer to all sites in the molecule being equally probable.

A strong point of the above-described approach is the possibility of easily varying the magnitude of the dephasing rate γ, as well as the possibility of applying dephasing locally (at a specific site or a group of sites within the molecule). These features were used, for example, to study the scaling laws in molecules with multiple spatial pathways for charge transfer. The dependence of the charge transfer rate k_{CT} through a molecule on the number and length of available spatial pathways was found to change significantly with both the magnitude of γ and the sites at which dephasing was applied.[105]

The dephasing rate γ is an empirical parameter and estimating its value for a specific molecule in a specific environment is not straightforward. Experimental estimates have been performed for some systems using spectral hole burning, photon echo, or resonance Raman techniques among others.[106] It would be interesting, however, to directly observe the effects of dephasing stemming from vibrations within the molecule or its environment on charge transport in a simulation, without having to invoke additional experiments. This can be achieved by simultaneously simulating the (quantum mechanical) charge transfer from a donor to an acceptor through a molecular bridge and the (classical) dynamics of the bridge molecule.[46]

The results of such simulations for bridges consisting of a benzene and a hexabenzocoronene molecule in gas phase at 0 K and at 300 K are shown in Fig. 5. In these simulations the charge carrier wavefunction was assumed to be given by eqn (9), with the initial conditions given by eqn (8). Electronic couplings between the p_z orbitals on all atoms were included in

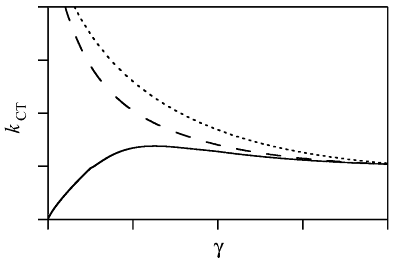

Fig. 4 The coalescence of charge transmission rates for a donor and an acceptor coupled to benzene in the *ortho* (dotted), *meta* (solid) and *para* (dashed) configuration, adapted from ref. 65.

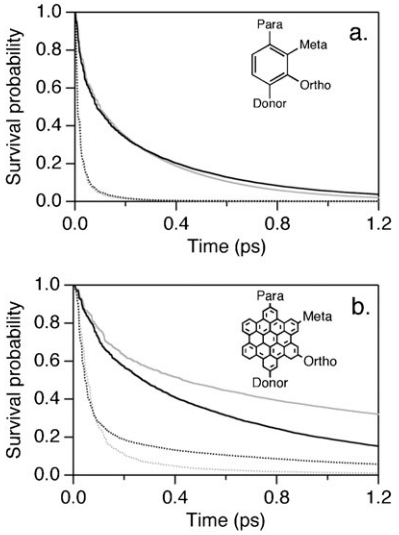

Fig. 5 Decay of the survival probability of the charge in a donor–bridge–acceptor system at 0 K (gray) and 300 K (black), with the acceptor at the *meta* (solid) or *para* (dotted) position with respect to the donor. The bridge consists of: (a) benzene; (b) hexabenzocoronene.

the Hamiltonian. The charge carrier was removed from the system once it arrived at the acceptor site, and the survival probability of the charge in the system was calculated as discussed in Section 2.

One can see that in the case of benzene the intramolecular vibrations have no noticeable effect on the quantum mechanical evolution of the system at room temperature. In the case of hexabenzocoronene charge transfer at 300 K retains the quantum mechanical character only partially. The difference between the transfer rates from a donor to an acceptor in the *meta* and *para* configurations is still evident, but it is significantly smaller than in the absence of vibrations. This agrees well with the result shown in Fig. 4.

In general, for small molecules quantum interference effects are expected to be largely retained at room temperature. Charge transfer through such molecules can be described quantum mechanically. In larger molecules with more vibrational degrees of freedom (and particularly in flexible molecules with rotational and out-of-plane bending degrees of freedom present) dephasing is likely to be non-negligible. At room temperature these molecules may be in the intermediate regime between quantum mechanical and classical charge transfer, or even exhibit fully classical behavior.

If a molecule interacts strongly with its environment, such as in solution or in the solid state, the environmental degrees of freedom may additionally contribute to dephasing and the loss of quantum mechanical behavior. One should keep in mind, however, that the characteristic timescales of these degrees of freedom are typically large as compared to the timescales of intramolecular vibrations. Thus, if charge transfer in a molecule is fast with respect to environmental fluctuations, dephasing effects can be expected to be relatively weak.

Although dephasing can be a significant hurdle to designing molecular electronic devices based on quantum interference effects, it could also be used in a functional way. If specific vibrational modes in a molecular system were controlled, both pure dephasing and energy dissipation due to vibrations would provide a mechanism of switching charge transfer through molecules on and off. Several designs of molecular switches and interferometers based on these effects have been proposed.[107,108]

4. Polymers: from band-like to incoherent hopping charge transport

Ever since the discovery of electrically conductive polymers by MacDiarmid, Shirakawa and Heeger *et al.*,[109,110] these materials have enjoyed growing attention of researchers. Studying charge transport in polymers is interesting both from the fundamental and the practical viewpoints. Thiophene-,[111–114] phenylene-,[115–117] fluorene-,[118] naphthalene-based polymers,[119] among others, are currently considered promising materials for applications in solar cells, light-emitting diodes and other (opto)electronic devices.

Charge transport properties of conducting polymers are typically characterized by the charge carrier mobility $\mu = v_d/E$, where E is the applied electric field and v_d is the drift velocity of the charge carrier induced by the applied electric field. Generally, in anisotropic materials μ is a tensor. In quasi-one-dimensional materials, such as polymers, one is interested in the mobility along the contour of the chain. Many polymers have been shown to possess sufficiently high intrachain charge carrier mobilities to be used in electronic applications, with values up to 600 cm^2 V^{-1} s^{-1} reported.[26] However, the charge transport mechanism in polymers is still not fully understood.

A major difficulty when describing charge transport in polymers is that it often falls into the intermediate regime between the quantum mechanical and the classical. Charge transport in some polymers has been successfully described as quantum mechanical, or bandlike,[26,45,120] while in others it has been described as classical incoherent hopping.[27,45,121] However, both bandlike and hopping models are nothing more than approximations for a charge transport regime that is neither fully coherent nor fully incoherent.

Conceptually, charge transport in polymers is no different from charge transport in small molecules. The main difficulties that should be dealt with are of computational nature. Representing the wavefunction of a charge carrier in the form given by eqn (9) would involve a very large number of atomic orbitals, N. Finding the wavefunction coefficients $c_n(t)$, $n = \overline{1, N}$, requires a large amount of computational power for large N, since numerical methods for solving a system of linear differential equations always scale superlinearly with the number of variables.[122] It would thus be practical to reduce the size of the basis set used to represent the charge carrier wavefunction.

In Section 2 it was shown that only two molecular orbitals, $\psi_a(e_{1g})$ and $\psi_a(e_{2u})$, contribute to charge transfer through a benzene molecule. The other four molecular orbitals, composed of the p$_z$ orbitals on carbon atoms, see eqn (5), can be discarded without sacrificing the accuracy of the calculation. Using a basis set of two, rather than six, orbitals reduces the computational power requirements by a factor of 3^r, $r > 1$. Thus, a good choice of a basis set offers the possibility of performing charge transport simulations more efficiently.

An infinitely long polymer chain is a quasi-one-dimensional periodic structure and can be described in terms of band theory. The bands are formed as a result of the interaction between the discrete energy levels of monomer units. Thus, the valence (highest occupied) band of a polymer is largely composed of monomer unit HOMOs and the conduction (lowest unoccupied) band is largely composed of the monomer unit LUMOs. The valence and conduction bands are typically the only energy bands that contribute to charge transport in intrinsic semiconductors; all other bands can be taken out of the consideration.[43] The monomer unit HOMOs and LUMOs then form natural basis sets for the wavefunction of a charge carrier in the valence band or conduction band, respectively. Since the monomer unit can consist of a significant number of atoms, using monomer unit orbitals rather than atomic orbitals as the basis set in charge transport simulations results in considerably reduced computational power requirements.[27,117,118]

A further simplification can be achieved by reconsidering the initial conditions. In the case of donor–bridge–acceptor systems it has been assumed that the charge carrier is initially generated on the donor site; the initial condition was thus taken in the form of eqn (8). Then, in the absence of decoherence, in order for energy to be conserved during charge transfer through the bridge molecule, both the HOMO and LUMO of the bridge must contribute to charge transfer.

In the case of polymers the situation is somewhat different. For the sake of specificity, consider hole transport. A hole on a polymer chain is most often created by exciting a valence band electron—over the bandgap, to an impurity or defect energy level, or to the vacuum level (in the case of ionization). The hole is created in the valence band, and is then transported *via* states belonging to the valence band only. Similarly, an electron created in the conduction band is transported *via* states belonging to the conduction band only. This means that the basis set used to represent the charge carrier wavefunction can be reduced further: a hole wavefunction can be represented in terms of monomer unit HOMOs and an electron wavefunction can be represented in terms of monomer unit LUMOs only.

The wavefunction of a hole (electron) on a polymer can be written in the energy representation as

$$\psi_s(t) = \sum_{n=-\infty}^{\infty} c_n(t)\varphi_n, \tag{23}$$

where φ_n is the HOMO (LUMO) of the n-th monomer unit, and $c_n(t)$ are complex time-dependent coefficients. As discussed in ref. 45, it can be assumed that the charge carrier is initially localized on a single monomer unit:

$$\psi_s(0) = \varphi_m. \tag{24}$$

Although this is a crude approximation, it allows making a reasonable estimate of the charge carrier mobility along the polymer chain in the case of band-like (quantum mechanical) charge transport.

The summation in eqn (23) runs over all monomer units in an infinite polymer chain. However, it is sufficient to consider a finite chain with negligible reflection of the charge carrier wavefunction at the chain ends within the timeframe of the charge transport simulation. Since all monomer units in a periodic infinite chain are equivalent, the charge carrier in this case should simply be initially localized as far as possible from the chain ends: in the middle of the long finite polymer chain. It is also possible to simulate charge transport along oligomers, but the initial charge distribution that is assumed in this case should reflect the process by which the charge carrier is created on the oligomer chain.

The Hamiltonian of the charge carrier in the Hückel approximation is[45]

$$\boldsymbol{H}_s = \begin{bmatrix} \varepsilon_1 & J_{12} & 0 & \ldots & 0 & 0 \\ J_{12} & \varepsilon_2 & J_{23} & \ldots & 0 & 0 \\ 0 & J_{23} & \varepsilon_3 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \ldots & \varepsilon_{(N-1)} & J_{(N-1)N} \\ 0 & 0 & 0 & \ldots & J_{(N-1)N} & \varepsilon_N \end{bmatrix}, \tag{25}$$

where $\varepsilon_n = \langle\varphi_n|\boldsymbol{H}_s|\varphi_n\rangle$ is the energy of a charge carrier localized on the n-th monomer unit, and $J_{nm} = \langle\varphi_n|\boldsymbol{H}_s|\varphi_m\rangle - \frac{1}{2}\langle\varphi_n|\varphi_m\rangle(\varepsilon_n + \varepsilon_m)$ is the effective charge transfer integral between the n-th and m-th monomer units, with the first term being the exact charge transfer integral (electronic coupling) and the second term being a correction accounting for orbital spatial overlap.[45,123,124]

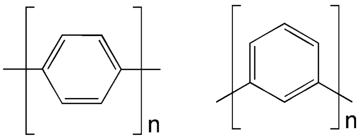

Fig. 6 Poly(*para*)phenylene (left) and poly(*meta*)phenylene (right).

The components of the Hamiltonian given by eqn (25) can be found from quantum chemical calculations. It is often a good approximation to assume that ε_n is a monomer property and J_{nm} is a dimer property. It is then sufficient to perform the calculations for a monomer and a dimer, respectively. It is particularly convenient to calculate these parameters using the ADF program, which implements the possibility of using the orbitals of arbitrarily defined molecular fragments (such as monomer units) as a basis set.[125] However, when the components of the Hamiltonian are obtained from calculations on monomers and dimers, care should be taken to make sure that the electronic structure of the monomer (dimer) is not altered by the electronic coupling to other units along the polymer chain. For example, from Fig. 6 it is evident that both the monomer and the dimer of poly(*para*)phenylene and poly(*meta*)phenylene are identical. Still, these are different polymers that may be expected to have distinct conductive properties.

The quantum mechanical evolution of the charge carrier follows the time-dependent Schrödinger equation, eqn (1), with the wavefunction given by eqn (23), the Hamiltonian given by eqn (25) and initial conditions given by eqn (24).

In the absence of an applied electric field, the mean displacement of a charge carrier from its initial position is zero at all times. On the other hand, the mean squared displacement increases with time, and can generally be expressed as

$$\langle\Delta x^2(t)\rangle = \sum_{n,m} f(m)|c_n(t,m)|^2(n-m)^2a^2, \tag{26}$$

where $f(m)$ describes the initial distribution of the charge, a is the distance between neighboring monomer units, $(n - m)a$ is the distance between the orbitals localized on monomer units n and m, and $c_n(t,m)$ is the coefficient of the orbital on monomer unit n at time t for the case of the hole wavefunction being initially localized on monomer unit m.

According to the work of Kubo, the frequency-dependent (one-dimensional) mobility of charge carriers is given by[126–128]

$$\mu(\omega) = -\frac{e\omega^2}{2k_BT}\int_0^{\infty}\langle\Delta x^2(t)\rangle\cos(\omega t)\mathrm{d}t, \tag{27}$$

where e is the elementary charge, ω is the (radial) frequency of the probing electric field, and the mean squared displacement of the charge carrier $\langle\Delta x^2(t)\rangle$ is given by eqn (26). An implicit convergence factor $\exp(-ot)$ ($\lim o \to 0$) is understood in the integral.[127,128] For normal Gaussian diffusion the mean squared displacement of charge carriers moving along an infinitely long one-dimensional chain increases linearly with time:

$$\langle\Delta x^2(t)\rangle = 2Dt, \tag{28}$$

where D is the diffusion constant. In this special case, the mobility is frequency independent, and eqn (27) reduces to the Einstein relation

$$\mu_{\mathrm{dc}} = \frac{e}{k_{\mathrm{B}}T}D. \qquad (29)$$

In the presence of structural disorder, eqn (28) and (29) are not valid. In that case the charge carrier mobility μ must be calculated from the mean squared displacement $\langle \Delta x^2(t)\rangle$ found on the basis of a numerical simulation, eqn (26), using eqn (27).

It is possible to account for decoherence effects on charge transport along polymer chains by simultaneously propagating the degrees of freedom that define the geometry of the chain in a (classical) molecular mechanics simulation, as described in ref. 46. However, if the monomer HOMOs (LUMOs), φ_n, are to remain time-independent, only those degrees of freedom that do not change the internal geometry of the monomer units can be propagated. For example, for the polymers depicted in Fig. 6 such degrees of freedom include the dihedral angles between neighboring monomer units (which turn out to strongly influence the electronic couplings between them).[26] Alternatively, decoherence can be included in charge transport simulations in a more formal manner, for example, by employing the Redfield equation, eqn (21).[45]

For an infinitely long periodic polymer chain, the charge carrier mobility in the limit of weak scattering can also be estimated directly from band theory (for oligomers its applicability is somewhat limited). The width of the conduction (valence) band in the case of an unperturbed periodic one-dimensional lattice is $W = 4|J|$, here the electronic couplings $J_{mn} = J, \forall m,n$, since all monomer units in the periodic chain are equivalent.[45,129] In wide-band materials, $W \gg k_{\mathrm{B}}T$, mobile charges are found at the bottom of the conduction band (electrons) or at the top of the valence band (holes). Near the band extremum the harmonic approximation for the dispersion relation, $E(\boldsymbol{k})$, is valid. Within this approximation the mobility of charge carriers is given by the well-known expression, derived within the framework of the Drude free electron model:[130–132]

$$\mu(\omega) = \frac{e\tau}{m^*}\left(\frac{1 - i\omega\tau}{1 + \omega^2\tau^2}\right), \qquad (30)$$

where e is the elementary charge, τ is the average time between scattering events (scattering time), ω is the driving field frequency and the free-electron mass has been replaced by the effective mass of the charge carrier $m^* = \hbar^2(\mathrm{d}^2E/\mathrm{d}k^2)^{-1}$. For the dc mobility, $\mu_{\mathrm{dc}} = e\tau/m^*$ trivially follows from eqn (30). The band structure and scattering time can be calculated with standard solid state theory methods.[43,131]

As long as perturbations of the periodic polymer chain remain negligible, reducing the band width W simply increases the effective mass m^* of the charge carrier.[129] According to eqn (30), this reduces the charge carrier mobility μ, but up to a certain point the description of charge transport does not change qualitatively. However, once the bandwidth becomes comparable to the thermal energy, $W \approx k_{\mathrm{B}}T$, the situation changes significantly.

It has been shown by Anderson that introducing static disorder in charge carrier localization energies, the diagonal elements of the Hamiltonian given by eqn (25), leads to charge carrier localization.[133] Lifshitz showed that the same is true if disorder is introduced in electronic couplings, the off-diagonal elements in eqn (25).[134,135] Charge carrier localization due to the presence of (static) disorder in a system is known as "Anderson localization".[136] This effect is purely coherent: the localized wavefunction of the mobile charge carrier is the interference pattern formed by wavefunction components reflected from the varying potential $V(\boldsymbol{r})$ of the atomic cores at every point where $\nabla V(\boldsymbol{r}) \neq 0$, as discussed in Section 2. The interference pattern is a localized state, rather than a Bloch wave, eqn (4), since the potential $V(\boldsymbol{r})$ is no longer strictly periodic.

The criterion for a state being localized is not trivial to define mathematically, and a number of criteria have been proposed.[133,137–140] However, qualitatively the behavior of a localized wavefunction is the same for all definitions. The original criterion proposed by Anderson is that a wavefunction given by eqn (23) could be considered localized if

$$\exists n : |c_n(0)|^2 \neq 0 \Rightarrow \lim_{t\to\infty} |c_n(t)|^2 \neq 0. \qquad (31)$$

Eqn (31) may hold for more than one n; localization in this sense does not imply that the charge carrier stays on a given monomer unit. Rather, if eqn (31) holds for an arbitrarily large (but finite) number of neighboring monomer units, often termed a "cluster", the charge carrier is considered "localized" on that cluster. The periodic boundary conditions used to obtain the Bloch wave, eqn (4), are replaced by the condition of the wavefunction coefficients becoming zero at the boundaries of a cluster that is not equivalent to other clusters along the polymer chain.

For a one-dimensional chain the presence of even weak disorder always leads to the formation of localized states.[129] However, the number of sites in the cluster, on which the charge carrier wavefunction is localized, is very large if the electronic coupling along the polymer chain is strong. Strong electronic coupling means that the electronic couplings J in the Hamiltonian given by eqn (25), or the bandwidth $W = 4|J|$, are large as compared to the magnitude of disorder. In the case when the cluster size is comparable to the polymer (oligomer) chain length, charge transport along the chain may be considered band-like.[45]

The variations in the energies and electronic couplings along the polymer chain may be induced by electrostatic interaction of the mobile charge carrier with its environment (polarization, which may include nuclear rearrangement within the polymer chain and/or the surrounding medium). In this case one speaks of a *polaron*, a self-induced localized state of the charge carrier. The degree of localization, in the sense of eqn (31), depends on the relative magnitude of the electronic couplings J and the reorganization energy λ of the environment due to polarization by the charge carrier. If $\lambda \gg J$, the charge carrier is almost completely localized on a single molecular unit and is referred to as a "small" polaron. If $\lambda \approx J$, the charge carrier is localized on a considerably larger cluster, and is called a "large" polaron.[120,121] Since polarization of the environment is always present, all charge transport is polaronic to some extent.

If disorder in the charge carrier localization energies on monomer units and in the electronic couplings is static, no charge transport outside the boundaries of the localization cluster is possible. However, dynamic disorder, such as thermal vibrations, perturbs the localization cluster, so the coefficients of the charge carrier wavefunction, eqn (23), are no longer zero at its boundaries. Interactions with phonons allow the polaron to absorb or dissipate energy and momentum necessary to "hop" to a new site on the polymer chain.[141,142] Also, interaction with the environment always leads to wavefunction decoherence, as has been discussed in Section 3. If the decoherence time is shorter than the time spent at a localization site, the charge carrier loses all memory of its quantum mechanical evolution after each hop to a new site. Thus, subsequent hopping events can be considered independent, and the overall motion of the charge is diffusive. This transport regime is known as "incoherent hopping".[45]

Incoherent hopping transport is realized for small polarons, since their lifetime at each localization site is large. In most polymers the electronic couplings between neighboring monomer units are sufficiently large for intrachain charge transport to be described as band-like.[26,117,118] However, incoherent hopping is the acting charge transport mechanism in some polymers with weaker electronic couplings.[27] Hopping transport is also commonly assumed when charge transfer between different molecules is described (polymer chains in a film, individual molecules in a discotic liquid crystal).[143,144] It should be noted that the transition from band-like to hopping transport is not well defined, and in many cases contributions of both mechanisms can be expected.[145,146]

A large number of models have been proposed to describe hopping transport. Among the most popular is the Miller–Abrahams model, which neglects polaronic effects.[147,148] The Miller–Abrahams rate from an initial site n with energy ε_n to a final site m with energy ε_m is expressed as

$$w_{nm} = w_0 \exp(-2\alpha R_{nm}) \begin{cases} \exp[-(\varepsilon_m - \varepsilon_n)/k_\mathrm{B}T] & \text{if } \varepsilon_m > \varepsilon_n \\ 1 & \text{if } \varepsilon_m \le \varepsilon_n \end{cases}, \qquad (32)$$

where w_0 is a pre-factor, which is proportional to the square of the magnitude of the electronic coupling J_{nm}; R_{nm} is the distance between the initial and the final sites; α is a decay factor, which takes into account the decay of the electronic coupling with intersite distance. Incoherent charge transport with a Miller–Abrahams hopping rate, eqn (32), can be studied with Monte-Carlo simulations, for example, employing a Metropolis–Hastings algorithm.[149,150] Miller–Abrahams hopping is a special case of the more general Holstein–Emin equation.[141,142,151]

In the presence of a charge induced lattice deformation the hopping rate of a charge carrier can be described by the Marcus (small polaron hopping) theory. The classical expression for the hopping rate, originally derived by Marcus,[152] has the form[45]

$$w_{nm} = \frac{2\pi |J_{nm}|^2}{\hbar} \sqrt{\frac{1}{4\pi\lambda k_\mathrm{B}T}} \exp\left[-\frac{(\varepsilon_m - \varepsilon_n + \lambda)^2}{4\lambda k_\mathrm{B}T}\right], \qquad (33)$$

where λ is the reorganization energy of the environment of the charge carrier. This expression is only valid in the high-temperature limit, where charge transport is purely classical. It has been generalized to other temperature regimes by Jortner and Bixon[153,154] and Schatz and Ratner.[155]

For recent reviews of modeling charge transport by hopping in organic materials, see ref. 156–158.

5. Summary and outlook

Charge transfer processes in materials on all length scales are largely determined by the electronic structure: orbital structure in molecules and band structure in crystals. Orbitals and energy bands in perfectly regular molecules and crystals are standing waves, or interference patterns of the electron wavefunction in a static potential. Thus, coherent charge transport is largely governed by quantum interference effects.

Real systems at room temperature are not static. Consequently, the charge carrier Hamiltonian $\boldsymbol{H}(t)$ is time-dependent. If the variation of the Hamiltonian relative to equilibrium is small, it can be considered a time-dependent perturbation: $\boldsymbol{H}(t) = \boldsymbol{H}_0 + \boldsymbol{H}'(t)$, where the equilibrium Hamiltonian $\boldsymbol{H}_0$ accounts for the unitary evolution of the charge carrier wavefunction, while the perturbation $\boldsymbol{H}'(t)$ is responsible for wavefunction decoherence. If the interaction of the charge carrier with the environment (phonons) is strong enough, different components of its wavefunction are no longer coherent and do not form an interference pattern (standing wave). The charge carrier then behaves classically and its motion is described by classical equations of motion.

It is obvious that the more degrees of freedom a system possesses, the stronger the perturbations that a charge carrier in it experiences. Thus, in large and flexible molecules, such as polymers, purely quantum mechanical interference effects are likely to be suppressed, at least partially. However, a comprehensive investigation of quantum interference survival as a function of the molecular size and other parameters is still to be carried out. An in-depth study of interference and decoherence effects in molecules would allow us to design molecular electronic devices in which both of these phenomena could be used in a functional way.

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