QUANTUM INTERFERENCE AND DECOHERENCE

AN INTRODUCTION

Aleksey Kocherzhenko
Talking about theory...
I. Quantum interference: a reminder
Two-slit experiments and what we learn from them

An electron can “interfere with itself”

Interference patterns can only be observed for coherent waves

Voted “most beautiful experiment” by readers of *Physics World* in 2002

Electrically conducting organic molecules

trans-polyacetylene  cis-polyacetylene  poly(para-phenylene)  poly(para-pyridine)
polythiophene  polypyrrole  poly(para-phenylene vinylene)  poly(para-pyridiyyl vinylene)

Alan J. Heeger  Alan G. MacDiarmid  Hideki Shirakawa  2000 Nobel Prize (Chemistry)

Which charge transfer pathway is more efficient?

DTP < SHORT < LONG

Where does the acceptor want to go?
Which are the best pathways for charge transfer?

Why?
Particle in a box

Electron in free space:

\[
\psi_e(r, t) = \exp[i(k \cdot r - \omega t + \varphi_0)]
\]

(plane wave)

Particle in a box:

3D:
Hydrogen atom

Particle in a 3D box:
Crystalline solid

$E_g = 1.12 \text{ eV}$
$E_L = 2.0 \text{ eV}$
$E_x = 1.2 \text{ eV}$
$E_{\infty} = 0.044 \text{ eV}$
$E_{T1} = 3.4 \text{ eV}$
$E_{T2} = 4.2 \text{ eV}$

Energy bands of Si

Split-off band

Wave vector

Heavy holes

Light holes
Quantum interference

Potential step:

Particle in a box  Hydrogen atom  Crystalline solid

\( n = 1 \) \( n = 2 \) \( n = 3 \) \( n = 4 \)
There is a pattern...

...quantum interference shapes the world as we know it!

(What is not defined by quantum interference is defined by decoherence. But we will get to that...)

II. Quantum interference and decoherence in molecules
Reactivity and charge transfer in molecules with multiple “spatial pathways”

Benzene

Hexabenzocoronene

Charge transfer rate is the decay rate of the survival probability $P(t)$:

probability that a charge placed on the donor at $t = 0$ has not reached the acceptor at time $t$.

Simulation results: Benzene

Couplings between all atoms

Nearest-neighbor couplings

0 K   RT

Para  Meta  Ortho
Donor
Simulation results: Hexabenzocoronene

Couplings between all atoms

Nearest-neighbor couplings
Quantum interference in polymers

Dimer:

\[
\begin{align*}
&\text{a)} \quad \begin{array}{c}
\text{R} \\
\text{R} \\
\text{R} \\
\text{R}
\end{array} \\
&\text{b)} \quad \begin{array}{c}
\text{R} \\
\text{R} \\
\text{R} \\
\text{R}
\end{array}
\end{align*}
\]
Coherent vs. incoherent charge (energy) transport

The advantage: Coherent (band-like) transport is more efficient

The challenge: Understanding when it occurs and engineering it
III. Some applications
Using quantum interference in a functional way

Controlling Quantum Transport through a Single Molecule

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ABSTRACT

We investigate multiterminal quantum transport through single monocyclic aromatic amine molecule and their derivatives, using the nonequilibrium Green function approach within the self-consistent Hartree–Fock approximation. We propose a new device concept, the quantum interference effect transistor, that exploits perfect destructive interference stemming from molecular symmetry and controls current flow by introducing decoherence and/electronic scattering that breaks the symmetry. This approach overcomes the fundamental problems of power dissipation and environmental sensitivity that beset nanoscale device proposals.

Figure 2. Schematic diagram of a QuET based on benzene. Here $\Gamma_1$ and $\Gamma_2$ are the coupling strengths of metallic leads 1 and 2, connected in the meta orientation, to the corresponding $\pi$-orbitals of benzene. $\Sigma_3$, determined by a control variable $x$, is the retarded self-energy induced by lead 3. The real part of $\Sigma_3$ introduces elastic scattering, while the imaginary part introduces decoherence.

Figure 1. Artist’s conception of a quantum interference effect.

A quantum-interference-based transistor

Molecular transistor:

[Graphical representations of molecular structures and graphs showing transfer probability over time]
An example from nature: photosynthesis

Fenna-Matthews-Olson complex
Conclusions

• Quantum interference is a very fundamental phenomenon that, largely, shapes the world as we know it (unless decoherence interferes).

• In molecules, quantum interference is responsible for the formation of orbitals and orbital symmetry.

• Coherence of wave function components travelling along different spatial pathways can be destroyed by time-dependent fluctuations (vibrations).

• However, interference effects are retained in many systems even at RT and can be used in a functional way (in molecular devices).
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Model of charge transport in molecules

Simultaneous classical molecular dynamics

\[
\begin{align*}
\mathbf{r}_i &= [x_i(t), y_i(t), z_i(t)] ,
\mathbf{v}_i &= [v_i^x(t), v_i^y(t), v_i^z(t)]\}
\end{align*}
\]

\( i = 1, n \)

- Start with equilibrium geometry and a set of velocities corresponding to a given temperature
- Propagate long enough to get away from equilibrium geometry
- (Classical) forces from TINKER, MM2/MM3 force field

\[
F_q = -\frac{d J_{mn}(l_{mn})}{d l_{mn}} (c_m c_n^* + c_m^* c_n)
\]

quantum mechanical charge propagation

\[
\begin{align*}
\hbar \frac{\partial \Psi(t)}{\partial t} &= \mathbf{H}(\mathbf{r}_i)\Psi(t) \\
\Psi(t) &= c_D(t) \varphi_D + \sum_{n} c_n(t) \varphi_n + c_A(t) \varphi_A \\
\mathbf{H} &= \sum_i \varepsilon_i a_i^+ a_i + \sum_{i \neq j} J_{i,j} a_i^+ a_j, \quad \text{or}
\end{align*}
\]

\[
\begin{bmatrix}
\varepsilon_1 & J_{12} & J_{13} & \cdots & J_{1n} \\
J_{12} & \varepsilon_2 & J_{23} & \cdots & J_{2n} \\
J_{13} & J_{23} & \varepsilon_3 & \cdots & J_{3n} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
J_{1n} & J_{2n} & J_{3n} & \cdots & \varepsilon_{nn} - i \hbar \tau
\end{bmatrix}
\]
“Shouldn’t you use molecular orbitals instead?”

\[
\begin{align*}
\psi(b_{2g}) &= \frac{\sqrt{6}}{6} (p_1 - p_2 + p_3 - p_4 + p_5 - p_6) \\
\psi_b(e_{2u}) &= \frac{1}{2} (p_2 - p_3 + p_5 - p_6) \\
\psi_a(e_{1g}) &= \frac{\sqrt{3}}{6} (2p_1 + p_2 - p_3 - 2p_4 - p_5 + p_6) \\
\psi_a(e_{2u}) &= \frac{\sqrt{3}}{6} (2p_1 - p_2 - p_3 + 2p_4 - p_5 - p_6) \\
\psi_b(e_{1g}) &= \frac{1}{2} (p_2 + p_3 - p_5 - p_6) \\
\psi(a_{2u}) &= \frac{\sqrt{6}}{6} (p_1 + p_2 + p_3 + p_4 + p_5 + p_6)
\end{align*}
\]