

Interference and interaction in molecular electronics: a density matrix approach

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# **TR** Double slit experiment: (London, 1801)

#### PHILOSOPHICAL

#### TRANSACTIONS.

 The Bakerian Lecture. Experiments and Calculations relative to physical Optics. By Thomas Young, M. D. F.R.S.

Read November 24, 1803.

I. EXPERIMENTAL DEMONSTRATION OF THE GENERAL LAW OF THE INTERFERENCE OF LIGHT.





Phil. Trans. R. Soc. Lon., 94, 12 (1804)



# Double slit with electrons: (Tübingen, 1961)

Aus dem Institut für Angewandte Physik der Universität Tübingen

#### Elektroneninterferenzen an mehreren künstlich hergestellten Feinspalten

Von

CLAUS JÖNSSON

Mit 14 Figuren im Text (Eingegangen am 17. Oktober 1960)

A glass plate covered with an evaporated silver film of about 200 Å thickness is irradiated by a line-shaped electron-probe in a vacuum of  $10^{-4}$  Torr. A hydro-carbon polymerisation film of very low electrical conductivity is formed at places subjected to high electron current density. An electrolytically deposited copper film leaves these places free from copper. When the copper film is stripped a grating with slits free of any material is obtained.  $50 \,\mu$  long and  $0.3 \,\mu$  wide slits with a grating constant of  $1 \,\mu$  are obtained. The maximum number of slits is five.

The electron diffraction pattern obtained using these slits in an arrangement analogous to Young's light optical interference experiment in the Fraunhofer plane and Fresnel region shows an effect corresponding to the well-known interference phenomena in light optics.

C.Jönsson





Zeitschrift für Physik, 161, 454 (1961)

# **CR** Single electron interference (Bologna, 1974)

#### On the statistical aspect of electron interference phenomena

P. G. Merli CNR-LAMEL, Bologna, Italy

G. F. Missiroli and G. Pozzi CNR-GNSM, Istituto di Fisica, Laboratorio Microscopia Elettronica, Bologna, Italy (Received 29 May 1974; revised 17 October 1974)



Am. J. Phys., 44, 306 (1976)

### **TR** Single electron interference (Tokyo, 1987)

#### Demonstration of single-electron buildup of an interference pattern

A. Tonomura, J. Endo, T. Matsuda, and T. Kawasaki Advanced Research Laboratory, Hitachi, Ltd., Kokubunji, Tokyo 185, Japan

H. Ezawa Department of Physics, Gakushuin University, Mejiro, Tokyo 171, Japan

(Received 17 December 1987; accepted for publication 22 March 1988)

The wave-particle duality of electrons was demonstrated in a kind of two-slit interference experiment using an electron microscope equipped with an electron biprism and a positionsensitive electron-counting system. Such an experiment has been regarded as a pure thought experiment that can never be realized. This article reports an experiment that successfully recorded the actual buildup process of the interference pattern with a series of incoming single electrons in the form of a movie.



A. Tonomura



Am. J. Phys., 57, 117 (1989)





#### In mesoscopic rings (Rehovot, 1995)

VOLUME 74, NUMBER 20

TR

PHYSICAL REVIEW LETTERS

15 May 1995

#### Coherence and Phase Sensitive Measurements in a Quantum Dot

A. Yacoby, M. Heiblum, D. Mahalu, and Hadas Shtrikman Braun Center for Submicron Research, Department of Condensed Matter Physics, Weizmann Institute of Science, Rehovor 76100, Israel (Received 10 November 1994)

Via a novel interference experiment, which measures magnitude and *phase* of the transmission coefficient through a quantum dot in the Coulomb regime, we prove directly, for the first time, that transport through the dot has a coherent component. We find the same phase of the transmission coefficient at successive Coulomb peaks, each representing a different number of electrons in the dot; however, as we scan through a single Coulomb peak we find an *abropt* phase change of #. The observed behavior of the phase cannot be understood in the single particle framework.

PACS numbers: 73.20.Dx, 71.45.-d, 72.80.Ey, 73.40.Gk



M. Heiblum





Phys. Rev. Lett., 74, 4047 (1995)

#### ... counting single electrons (Zürich, 2008)

#### Time-Resolved Detection of Single-Electron Interference

S. Gustavsson,\* R. Leturcq, M. Studer, T. Ihn, and K. Ensslin

Solid State Physics Laboratory, ETH Zürich, CH-8093 Zürich, Switzerland

#### D. C. Driscoll and A. C. Gossard

Materials Departement, University of California, Santa Barbara, California 93106

Received June 13, 2008

**U**R

#### NANO LETTERS 2008 Vol. 8, No. 8 2547-2550



K. Ensslin

#### ABSTRACT

We demonstrate real-time detection of self-interfering electrons in a double quantum dot embedded in an Aharonov – Bohm interferometer, with visibility approaching unity. We use a quantum point contact as a charge detector to perform time-resolved measurements of singleelectron tunneling. With increased bias voltage, the quantum point contact exerts a back-action on the interferometer leading to decoherence. We attribute this to emission of radiation from the quantum point contact, which drives noncoherent electronic transitions in the quantum dots.





Nano Lett., 8, 2547 (2008)

## Intramolecular interference



**T**R

P. Sautet and C. Joachim *Chem. Phys. Lett.* **153**, 511 (1988)



R. Baer and D. Neuhauser *JACS*, **124**, 4200 (2002)



R. Stadler, et al. Nanotechnology, **14**, 138 (2003)



D. V. Cardamone, et al. Nano Lett., **6**, 2422 (2006)



G. Solomon, et al. *JACS* **130**, 17307 (2008)



S.H. Ke, et al. Nano Lett., **8**, 3257 (2008)



T. Markussen, et al. Nano Lett., **10**, 4260 (2010)

### Interference and dephasing

**T**R



### Interference in weak coupling

**T**R



G. Begemann, D. Darau, A. Donarini, M. Grifoni, *Phys. Rev. B* 77, 201406(R) (2008)



## Interference Single Electron Transistors







## (Benzene) ISET...









**T**R

$$|1'\rangle = a|1\rangle + b|2\rangle$$
  $\longrightarrow$   $\gamma_{1'L} = a\gamma_{1L} + b\gamma_{2L}$ 

More degenerate states? See A. Donarini , G. Begemann and M. Grifoni *Phys. Rev. B*, **82**, 125451 (2010) for the general theory.



## ... with a magnetic flavour

۶R



#### Are this conditions **achievable** in today experiments ?





### Coulomb blockade





- Gating of 2 nm sized molecule
- Weak coupling realization with specific anchor groups

A. Danilov, S. Kubatkin, et al. Nano Lett. 8, 1 (2008)

# **TR** Symmetry breaking contacts





### Contacts with atomic control



J. Repp and G. Meyer, *Phys. Rev. Lett.* **94**, 026803 (2005)



G. Schull, T. Frederiksen, A. Arnau, D. Sánchez-Portal and R.Berndt *Nature Nanotechnology* **6**, 23 (2011)





### The Hamiltonian



### Interacting isolated benzene

• The Pariser-Parr-Pople Hamiltonian for isolated benzene reads:

$$H_{\text{ben}}^{0} = \xi_{0} \sum_{i\sigma} d_{i\sigma}^{\dagger} d_{i\sigma} + b \sum_{i\sigma} \left( d_{i\sigma}^{\dagger} d_{i+1\sigma} + d_{i+1\sigma}^{\dagger} d_{i\sigma} \right)$$
$$+ U \sum_{i} \left( n_{i\uparrow} - \frac{1}{2} \right) \left( n_{i\downarrow} - \frac{1}{2} \right)$$
$$+ V \sum_{i} \left( n_{i\uparrow} + n_{i\downarrow} - 1 \right) \left( n_{i+1\uparrow} + n_{i+1\downarrow} - 1 \right)$$

R



- The size of the Fock space for the many-body system 4<sup>6</sup> = 4096 since for each site there are 4 possibilities: |0⟩, |↑⟩, |↓⟩, |↑↓⟩
- Within this Fock space we diagonalize exactly the Hamiltonian.

# Symmetry of the ground states

Ν	Degeneracy	GS energy[eV]	GS symmetry
		$(at \xi = 0)$	representation
0	1	0	$A_{1g}$
1	2	-22	$A_{2u}$
2	1	-42.25	$A_{1g}$
3	4	-57.42	$E_{1g}$
4	3	-68.875	$A_{2g}$
5	4	-76.675	$E_{1g}$
6	1	-81.725	$A_{1g}$
7	4	-76.675	$E_{2u}$
8	3	-68.875	$A_{2g}$
9	4	-57.42	$E_{2u}$
10	1	-42.25	$A_{1g}$
11	2	-22	$B_{2g}$
12	1	0	$A_{1g}$

#### Rotation phase factors

Under rotation of an angle  $\phi = \frac{n\pi}{3}$ 

•  $\mathcal{R}_{\phi}|6_g
angle=|6_g
angle$  No phase acquired

• 
$$\mathcal{R}_{\phi}|7_{g}\,\ell\rangle = e^{-i\ell\phi}|7_{g}\,\ell\rangle$$
  $\ell = \pm 2$ 

$$\ell = +2 \qquad \exp\left(+i\frac{2\pi}{3}\right)$$
$$\ell = -2 \qquad \exp\left(-i\frac{2\pi}{3}\right)$$

# **Generalized Master Equation**

 $\sigma$ 

- We start with the Liouville equation:  $\dot{\rho} = -\frac{i}{\hbar}[\mathcal{H}, \rho]$
- We define the reduced density matrix σ = Tr<sub>Leads</sub>{ρ} which is block-diagonal in

particle number spin energy

- We keep the coherences between orbitally degenerate states.
- The Generalized Master Equation is the equation of motion for  $\sigma$ :

$$\dot{\sigma} = -\frac{i}{\hbar}[H_{\rm sys}, \sigma] - \frac{i}{\hbar}[H_{\rm eff}, \sigma] + \mathcal{L}_{\rm tun}\sigma$$

$$\begin{array}{c} \mathbf{Coherent} \\ \text{dynamics} \end{array} \quad \begin{array}{c} \text{Effective} \\ \text{internal} \end{array} \quad \begin{array}{c} \text{Tunnelling} \\ \text{dynamics} \end{array}$$

**>ip**C

dynamics

# Generalized Master Equation

The reduced density matrix is decomposed in particle number and energy subblocks by means of projection operators:

 $\sigma^{\rm NE} = \mathcal{P}_{\rm NE} \sigma \mathcal{P}_{\rm NE}$  where  $\mathcal{P}_{\rm NE} := \sum_{\ell \tau} |N E \ell \tau \rangle \langle N E \ell \tau |$ 

The generalized master equation for these subblocks reads

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$$\begin{split} \sigma^{\rm NE} &= -\sum_{\alpha\tau} \frac{\Gamma_{\alpha}}{2} \Biggl\{ \mathcal{P}_{\rm NE} d_{\alpha\tau} \left[ f_{\alpha}^{+} (H_{\rm ben}^{0} - E) - \frac{i}{\pi} p_{\alpha} (H_{\rm ben}^{0} - E) \right] d_{\alpha\tau}^{\dagger} \sigma^{\rm NE} + \\ &+ \mathcal{P}_{\rm NE} d_{\alpha\tau}^{\dagger} \left[ f_{\alpha}^{-} (E - H_{\rm ben}^{0}) - \frac{i}{\pi} p_{\alpha} (E - H_{\rm ben}^{0}) \right] d_{\alpha\tau} \sigma^{\rm NE} + h.c. \Biggr\} + \\ &+ \sum_{\alpha\tau E'} \Gamma_{\alpha} \mathcal{P}_{\rm NE} \Biggl\{ d_{\alpha\tau}^{\dagger} f_{\alpha}^{+} (E - E') \sigma^{\rm N-1E'} d_{\alpha\tau} + d_{\alpha\tau} f_{\alpha}^{-} (E' - E) \sigma^{\rm N+1E'} d_{\alpha\tau}^{\dagger} \Biggr\} \mathcal{P}_{\rm NE}, \end{split}$$



### The effective Hamiltonian

The effective Hamiltonian is expressed in terms of angular momentum operators and renormalization frequencies:

 $L_L$ 

$$H_{
m eff} = \sum_{lpha\sigma} \omega_{lpha\sigma} L_{lpha}$$

In particular in the Hilbert space of the 7 particle ground states

**T**R

$$L_{\alpha} = \frac{\hbar}{2} \begin{pmatrix} 1 & e^{i2|\ell|\phi_{\alpha}} \\ e^{-i2|\ell|\phi_{\alpha}} & 1 \end{pmatrix}$$

$$\omega_{\alpha\sigma} = \frac{1}{\pi} \sum_{\sigma'\{E\}} \Gamma^{0}_{\alpha\sigma'} \begin{bmatrix} \langle 7_g \ell \sigma | d_{M\sigma'} | 8\{E\} \rangle \langle 8\{E\} | d_{M\sigma'}^{\dagger} | 7_g m \sigma \rangle p_{\alpha} (E - E_{7_g}) + \\ \langle 7_g \ell \sigma | d_{M\sigma'}^{\dagger} | 6\{E\} \rangle \langle 6\{E\} | d_{M\sigma'} | 7_g m \sigma \rangle p_{\alpha} (E_{7_g} - E) \end{bmatrix}$$
 Bias and gate dependent



### Para vs. Meta



G. Begemann, D. Darau, A. Donarini, M. Grifoni, *Phys. Rev. B* 77, 201406(R) (2008)



### Conductance suppression ----



### Destructive interference

$$\Lambda = \left| \sum_{nm\tau} \langle N, n | d_{\mathrm{L}\tau} | N+1, m \rangle \langle N+1, m | d_{\mathrm{R}\tau}^{\dagger} | N, n \rangle \right|^{2}$$

۶R

Interference factor

In particular for the transition 6 -7 in the meta configuration:

$$\Lambda = \left| |\langle 6_g | d_{\mathrm{L}\tau} | 7_g, +2, \tau \rangle |^2 e^{+i\frac{2\pi}{3}} + |\langle 6_g | d_{\mathrm{L}\tau} | 7_g, -2, \tau \rangle |^2 e^{-i\frac{2\pi}{3}} \right|^2$$

**2** = **(b)** 
$$e^{+i\frac{2\pi}{3}}$$
 + **(b)**  $e^{-i\frac{2\pi}{3}}$ 





# Physical basis

- The 7 particle ground state has spin and orbital degeneracies;
- Physical basis: the basis that diagonalizes the stationary density matrix;
- •The physical basis depends on the bias: in whatever reference basis, coherences are essential for a correct description of the system;
- The visualization tool: position resolved transition probability to the physical basis:

$$P(x,y;\ell\tau) = \lim_{L \to \infty} \sum_{\sigma} \frac{1}{2L} \int_{-L/2}^{L/2} \mathrm{d}z |\langle 7_g \,\ell\tau |\psi_{\sigma}^{\dagger}(\vec{r}) | 6_g \rangle|^2$$



## Interference blockade



#### Geometry

#### I-V for transition 6 -7

#### Energetics

#### **Blocking state**

TR



#### Non-blocking state







#### current onset



# **Tr** Normal vs. ferromagnetic leads

Polarization = 0.85



# **TR** Selective Interference Blocking



Minority blocking



Majority blocking D

A. Donarini, G. Begemann, and M. Grifoni Nano Lett. 9, 2897 (2009)

# **T**<sub>R</sub> Normal vs ferromagnetic leads



**Si** 

# **Tr** Level renormalization in presence of polarized leads

We obtain a difference in the renormalization frequencies for the 2 spin directions linear in the **polarization of the leads**:

$$\begin{split} \boldsymbol{\omega}_{\alpha\uparrow} - \boldsymbol{\omega}_{\alpha\downarrow} &= \left[ \widehat{\Gamma}_{\alpha}^{0} P_{\alpha} \frac{1}{\pi} \right]_{\{E\}} \\ & \left[ \langle 7_{g}\ell \uparrow | d_{M\uparrow} | 8\{E\} \rangle \langle 8\{E\} | d_{M\uparrow}^{\dagger} | 7_{g}m \uparrow \rangle p_{\alpha}(E - E_{7_{g}}) \right. \\ & \left. + \langle 7_{g}\ell \uparrow | d_{M\uparrow}^{\dagger} | 6\{E\} \rangle \langle 6\{E\} | d_{M\uparrow} | 7_{g}m \uparrow \rangle p_{\alpha}(E_{7_{g}} - E) \right. \\ & \left. - \langle 7_{g}\ell \uparrow | d_{M\downarrow} | 8\{E\} \rangle \langle 8\{E\} | d_{M\downarrow}^{\dagger} | 7_{g}m \uparrow \rangle p_{\alpha}(E - E_{7_{g}}) \right. \\ & \left. - \langle 7_{g}\ell \uparrow | d_{M\downarrow}^{\dagger} | 6\{E\} \rangle \langle 6\{E\} | d_{M\downarrow} | 7_{g}m \uparrow \rangle p_{\alpha}(E_{7_{g}} - E) \right] \end{split}$$

The splitting of the level renormalization depends crucially on the Coulomb interaction on the molecule and vanishes in absence of exchange.





#### The triple dot ISET

 $H = H_{\rm sys} + H_{\rm leads} + H_{\rm tun}$ 

$$H_{\text{sys}} = \xi_0 \sum_{i\sigma} d^{\dagger}_{i\sigma} d_{i\sigma} + b \sum_{i\sigma} \left( d^{\dagger}_{i\sigma} d_{i+1\sigma} + d^{\dagger}_{i+1\sigma} d_{i\sigma} \right)$$
$$+ U \sum_i \left( n_{i\uparrow} - \frac{1}{2} \right) \left( n_{i\downarrow} - \frac{1}{2} \right)$$
$$+ V \sum_i \left( n_{i\uparrow} + n_{i\downarrow} - 1 \right) \left( n_{i+1\uparrow} + n_{i+1\downarrow} - 1 \right)$$

Extended Hubbard Hamiltonian with on-site and nearest neighbors Coulomb interaction

 $H_{\rm tun} = t \sum_{\alpha k\sigma} (c^{\dagger}_{\alpha k\sigma} d_{\alpha\sigma} + d^{\dagger}_{\alpha\sigma} c_{\alpha k\sigma})$ 

Tunnelling restricted to the dot closest to the corresponding lead

*H*<sub>leads</sub> Ferromagnetic leads with equal parallel polarization







### Many-body spectrum



### Excited state blocking

**T**R





TR



**Dip**C

### Excited state blocking



Three linear combinations of 2-particle excited states are coupled ONLY to the source.

TR





### Triplet splitting

The states decoupled from the right lead are eigenstates of  $L_R$ . They are eigenstates of  $H_{\text{eff}}$  only if





## The "two paths" in the ISET





### Robustness

- We have tested the robustness of the effects against:
  - Residual potential drop on the (artificial) molecule (in weak coupling to the leads the potential drop is concentrated at the contacts)
  - On-site energy renormalization of the contact atom due to different anchor groups
  - Lifting of the electronic degeneracy due to deformation (static Jahn-Teller effect)
- The minimal necessary condition is quasi-degeneracy:

 $\delta E \ll \hbar \Gamma$ 

D. Darau, G. Begemann, A. Donarini, and M. Grifoni, PRB, 79, 235404 (2009)





### **Blocking conditions**

The interference blocking state:

- is a linear combination of (quasi-)degenerate system eigenstates
- is achievable from the global minimum via a finite number of allowed transitions
- has vanishing tunnelling amplitudes for all energetically allowed outgoing transitions

$$\mathcal{L}_{tun}\sigma_{\rm B}=0$$

• is an eigenstate of the effective Hamiltonian

$$[H_{\rm eff},\sigma_{\rm B}]=0$$





### Conclusions

• Interference does occur even in the single-electron tunnelling regime when energetically equivalent paths involving **degenerate states** contribute to the dynamics.



2.75

• Interference effects dominates the transport characteristics of ISET both in the linear and non linear regime producing selective **suppression of the conductance** and inferference **current blocking**.



 In the presence of ferromagnetic leads, the interplay between interference and exchange on the ISET allows to achieve all-electrical spin control of the junction.



### Thanks



**Georg Begemann** 

Milena Grifoni



Dana Darau



#### in the research programs



SPP 1243 Quantum Transport at the Molecular Scale



SFB 689 Spinphänomene in reduzierten Dimensionen



Donostia - 3,10,2011



# Other systems

#### Vibronic effects in transport through conjugated molecules

Phys. Rev. Lett., 97, 166801 (2006)

Transport through suspended single wall carbon nanotube quantum dots *Phys. Rev. B*, **84**, 115432 (2011)

Interference effects in transport through single molecules in the STM set-up





K. Richter



A. Yar





S. Kolmeder

J. Repp

Transport through double dot structures with multiple gates







D. Preusche



Donostia - 3.10.2011

Vb -



# Thank you for your attention!





### Conclusions

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## Supplementary material





# The 8 electrons "anomaly"



The tunnelling preserves this mirror symmetry: the lowest 8 electron state involved in transport is the mirror-symmetric (first excited) state with  $E_{2g}$  symmetry.