

# The Longuet-Higgins phase and charge transport in molecular rings

J.E. Avron <sup>\*</sup>, J. Berger

*Department of Physics, Technion, 32000 Haifa, Israel*

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## Abstract

The Longuet-Higgins–Berry’s phase has remarkable consequences for charge transport in molecular rings. For generic (conical) crossing, where the phase is  $\pi$ , a vanishing cause can lead to a diverging response in the amount of charge transport. Away from level crossings, when the phase is 0, a vanishing cause leads to a vanishing response. The divergence of the response near crossing is related to, but distinct from, the divergence that occurs in the generalized susceptibility. We illustrate this behavior for quantum models of molecular rings driven by a running wave of small amplitude at zero and finite temperatures. © 1998 Elsevier Science B.V. All rights reserved.

Consider a molecular ring, such as a benzene or a triangular molecule  $X_3$ , such as  $\text{Na}_3$ . In the Born–Oppenheimer limit of heavy nuclei one can consider a cycle of deformations where each nucleus is displaced only slightly from its initial position and eventually returns to it. The question that we want to focus on is: What is the electronic charge transported around the molecular ring in one such cycle? As we shall explain below, there are two cases: If the cycle of atomic deformations can be shrunk to zero without trapping a point of level crossing (of the electronic energy levels) then one gets normal behavior in the sense that the weaker the deformation, the less the charge transported in one cycle. If, however, the cycle of atomic deformations pinches a point of level crossing, then the smaller the cycle, the larger the transported charge. We dub such anomalous behav-

ior, where the weaker the cause the larger the effect, homeopathic. We shall illustrate this for Hückel (tight binding) models of molecular rings at zero temperature.

Homeopathic charge transport is intimately related to the Longuet-Higgins [1] and Berry’s phase [2,3]: For time reversal invariant Hamiltonians level crossing is reflected in the sign of the electronic wave function undergoing a cycle of deformation. This sign is  $-1$  if the cycle pinches a (generic) crossing and  $1$  if it does not. The Longuet-Higgins phase has important consequences for (molecular) rovibronic spectra in Born–Oppenheimer and Jahn–Teller theory [4,5] and plays a role in molecular dynamics [6]. The theory of adiabatic transport adds the observation that Longuet-Higgins phase has direct consequences also for electronic properties, and not only to molecular properties. In particular, a phase  $-1$  implies homeopathic charge transport. There is both theoretical and experimental evidence that molecular trimers such as  $\text{Na}_3$  [7] and sym-tri-

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<sup>\*</sup> Corresponding author. E-mail: avron@physics.technion.ac.il

azine [8] as well as other trimers and systems have  $-1$  Longuet-Higgins phase.

Adiabatic charge transport near gap closures for infinite chains has been studied in [9]. For these there is no homeopathic divergence. Instead, a vanishing cause can lead to a finite and quantized charge transport when the Longuet-Higgins phase is  $-1$ . The charge transport in finite molecular rings is, therefore, more singular than that in infinite chains.

The homeopathic behavior that occurs for (out of equilibrium) charge transport is related to, but distinct from, the divergences that can occur in thermodynamic equilibrium of generalized susceptibilities at  $T=0$ . A necessary condition for either, at least for the simple model systems we consider below, is that quantum energy levels cross. But, while thermodynamic susceptibilities probe the singularity of the energy surface near crossing, non-equilibrium adiabatic transport probes the singularity of the surface of eigenstates near crossings. It is possible for one of these surfaces to be singular without the other being singular. We shall return to this issue below.

As we shall see, finite temperature introduces a cutoff of the homeopathic divergence. In some cases, a Jahn-Teller instability can censor the homeopathic divergence even at  $T=0$ .

Consider, for simplicity, the Hückel (tight-binding) model Hamiltonian for non-interacting electrons in a general triangular molecule of three identical atoms. Although the example of a molecular trimer is special, it turns out that it describes the generic situation near level crossing. The Hamiltonian is the  $3 \times 3$  Hermitian matrix

$$H(a, b, c, \phi) = E_0 \begin{pmatrix} 0 & a & \bar{\xi}c \\ a & 0 & b \\ \xi c & b & 0 \end{pmatrix}, \quad (1)$$

where  $E_0$  fixes the energy scale and  $a, b, c$  are (dimensionless, real) hopping amplitudes associated to the three bonds of the triangle. (The triangle is not necessarily equilateral.) We assume that  $a, b, c$  are all positive. We can, and shall, use  $a, b$ , and  $c$  as local coordinates in the space of (internal) configurations of a trimer.  $a, b$ , and  $c$  are actually not good coordinates globally. For good global coordinates see [4]. However, global subtleties need not concern us here since we consider only small deformations.

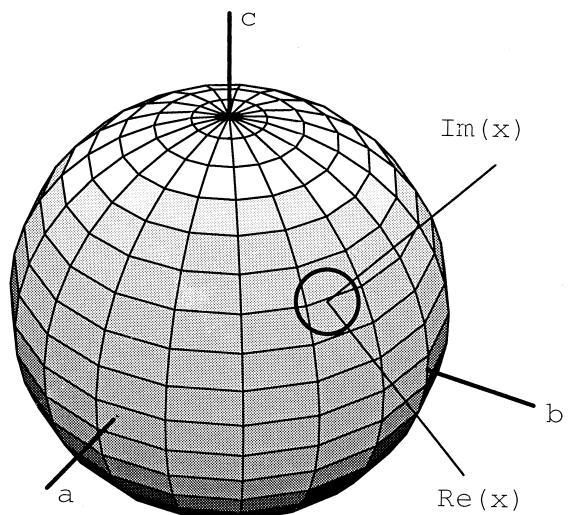


Fig. 1. A cycle of deformation for a molecule with three atoms.

$\xi = \exp i\phi$ , with  $\phi$  an auxiliary phase variable associated with a fictitious Aharonov-Bohm flux tube which carries flux  $\phi$  and threads the molecule. The explicit form of Eq. (1) involves a choice of gauge for the flux tube. (We shall consider observables that are independent of this choice.) The role of  $\phi$  will become clear below. Deformations of the molecule change the hopping amplitudes, and a closed cycle of deformations is a closed path in the three-dimensional space whose points are the hopping amplitudes  $(a, b, c) \in \mathcal{R}_+^3$ . Such a closed path is shown in Fig. 1. For notational convenience we denote by  $X$  the triplet  $(a, b, c)$ .

The reason for introducing the fictitious flux tube  $\phi$  is to define the current operator which circulates in such a ring. For the choice of gauge we have made for the Aharonov-Bohm flux, the current is associated with a single bond, the  $c$  bond, and is

$$(\partial_\phi H)(X, \phi) = cE_0 \begin{pmatrix} 0 & 0 & -i\bar{\xi} \\ 0 & 0 & 0 \\ i\xi & 0 & 0 \end{pmatrix}. \quad (2)$$

This is the sole role of  $\phi$  and in all our calculations we shall eventually set  $\phi = 0$ , which is the case with no flux at all. In this case the Hamiltonian  $H(X, 0)$  is real and therefore time reversal invariant. The observable associated to the circulating current, Eq. (2), is pure imaginary when  $\phi = 0$  and so odd under

time reversal. Because the model for  $\phi = 0$  is time reversal invariant, there are no diamagnetic (persistent) currents in any eigenstate. Let  $P(X, \phi)$  be a spectral projection for  $H(X, \phi)$ , i.e.  $H(X, \phi)P(X, \phi) = E(X, \phi)P(X, \phi)$  with  $E(X, \phi) \in \mathcal{R}$  an eigenvalue. The vanishing of the persistent currents is the statement  $\text{Tr}(P\partial_\phi H)|_{\phi=0} = 0$  for all  $X$ .

We are interested in the current that flows around the molecule when it is slowly driven so that  $X$  traces a closed path in parameter space, as e.g. in Fig. 1. In the theory of adiabatic transport this current is related to the adiabatic curvature. The basic equation for the expectation value of the current at time  $t$  and zero flux, reads [10–19]:

$$\text{Tr}(P_t \partial_\phi H) = \text{Tr}(\Omega_{\phi X}(P)) \cdot \dot{X} + O(1/\tau^2). \quad (3)$$

$X$  stands for the triplet  $a$ ,  $b$  and  $c$  and the dot denotes time derivative.  $P_t$  is a solution of the quantum evolution equation, with the (adiabatic) time-dependent Hamiltonian  $H(X, \phi)$  and with initial condition that  $P_{t=0}$  is an eigenstate.  $P(X, \phi)$  is an instantaneous spectral projection for the instantaneous  $H(X, \phi)$ .  $\Omega_{\phi X}(P) = -iP[\partial_\phi P, \partial_X P]P$  is the  $\phi X$  component of the adiabatic curvature [2,3].  $\tau$  is the time scale so that the adiabatic limit is  $\tau \rightarrow \infty$ . The charge transported around the ring in one cycle, in the adiabatic limit, is

$$Q = \int_0^\tau dt \text{Tr}(P_t \partial_\phi H) = \phi \text{Tr}(\Omega_{\phi X}(P)) dX. \quad (4)$$

Analysis of the characteristic equation of Eq. (1) shows that level crossing can occur only if  $a = b = c$  and  $\xi = \pm 1$ . For  $\xi = 1$ , the case we consider here, the simple eigenvalue is  $2aE_0$  (the top state if  $E_0$  is positive) and the corresponding eigenvector is  $|0\rangle = (\sqrt{3})^{-1}(1, 1, 1)$ . The twofold degenerate eigenvalue is  $-aE_0$  and the projection to its subspace is  $1 - |0\rangle\langle 0|$ . For  $\phi = 0$ , level crossings occur on a ray in  $X$  space.

The essence of homeopathic behavior is the following. Suppose first that the cycle of deformation does not pinch level crossing. (For the top state this holds for any closed cycle in the positive quadrant.) The adiabatic curvature is smooth and bounded along the path and the right-hand side of Eq. (4) is of the order of the area of the cycle of deformations (by Stokes formula).  $Q$  goes to zero when the cycle

shrinks to zero. Now suppose that the cycle of deformation pinches the ray of level crossing, e.g.

$$a(x) = 1 + \omega \bar{x} + \bar{\omega} x; \quad (5a)$$

$$b(x) = 1 + \bar{x} + x; \quad (5b)$$

$$c(x) = 1 + \bar{\omega} x + \omega x, \quad (5c)$$

where  $\omega$  is here a (complex) cube root of unity and  $x \in \mathcal{C}$  runs on a small circle in the complex plane surrounding the origin, see Fig. 1. As the cycle shrinks, the adiabatic curvature in Eq. (4) diverges quadratically, like a monopole [2,3,20], while the length of the cycle shrinks only linearly. It follows that now  $Q$  diverges as the cycle shrinks to zero, i.e.  $Q = O(|x|^{-1})$ .

In the simple case at hand the leading divergence characterizing homeopathic behavior can be calculated explicitly. The degeneracy splits in first order of perturbation theory, both in  $\phi$  and in  $x$ , and the local behavior near crossing of the two bottom states is given by the  $2 \times 2$  matrix

$$\frac{E_0}{3} \begin{pmatrix} -\sqrt{3} \phi & 6\omega \bar{x} \\ 6\bar{\omega} x & \sqrt{3} \phi \end{pmatrix}. \quad (6)$$

This matrix has the form of a Berry spin 1/2 model and the adiabatic curvature of its two states is explicitly computable. So, to leading order, the equation for the charge  $Q$ , Eq. (4), reduces to

$$Q = \pm \frac{\sqrt{3}}{12} \phi \frac{1}{|x|} d\text{Angle}, \quad (7)$$

where Angle is the angle swept by  $x$  as it moves around the origin in the complex plane. The  $\pm$  signs refer to the ground and first state respectively. A simple formula is obtained for a circular orbit,  $|x| = \text{const.}$ , where  $Q = \sqrt{3} \pi (6|x|)^{-1}$ . Evidently, the smaller the cycle that pinches the degeneracy, the more charge it transports and  $Q \rightarrow \pm \infty$  as  $|x| \rightarrow 0$ .

It may be worthwhile to explain which aspects of Eq. (7) are general and hold for any generic two-level crossing and what is special for the explicit model we consider. The overall constant  $\sqrt{3}/12$  is special for the model. What is general is that the divergence scales like an inverse power of the distance from crossing. This can be seen by noting that for any (generic) two-level crossing the adiabatic curvature diverges like the field of a monopole, i.e. like  $|x|^{-2}$ ,

and therefore a line integral on a loop of length  $O(|x|)$  will scale like the potential of a monopole.

It should be stressed that this result does not imply that the current is large. In Eq. (3) only the ratio of the current to the rate of driving is large. The current is not large because, as the circle is shrunk, the rate of driving must also decrease in order for the adiabatic theory to apply.

It may be worthwhile to point out that the charge  $Q$  in Eq. (7) even though a geometric, is not a Berry's phase (being a line integral, rather than a surface integral, of the curvature).

We now return to the question of how is homeopathic behavior of transport related to the divergence of the susceptibility near level crossing. At  $T = 0$  the generalized susceptibility matrix  $\chi$  of a family of Hamiltonians,  $H(X, \phi)$ , that depend parametrically on  $X$  and  $\phi$  is the symmetric matrix of second derivatives:

$$\chi_{XX}(X, \phi) = \frac{\partial E}{\partial x_i \partial x_j}(X, \phi);$$

$$\chi_{X\phi}(X, \phi) = \frac{\partial E}{\partial x_i \partial \phi}(X, \phi),$$

where  $E(X, \phi)$  is the ground state of  $H(X, \phi)$ .  $\chi$  is a thermodynamic (equilibrium) property and as such it depends only on the energy surface  $E(X, \phi)$ . The adiabatic curvature is associated with an anti-symmetric matrix whose components are

$$\text{Tr}\Omega_{XX}(X, \phi) = -i\text{Tr}\left(P\left[\partial_{x_i}P, \partial_{x_j}P\right]\right); \quad (8a)$$

$$\text{Tr}\Omega_{X\phi}(X, \phi) = -i\text{Tr}\left(P\left[\partial_{x_i}P, \partial_\phi P\right]\right). \quad (8b)$$

It describes transport coefficients which cannot be determined from the ground state energy (at  $T = 0$ ) or a thermodynamic potential (for  $T > 0$ ). This is evident from the formula for the adiabatic curvature, which is determined by the projection  $P(X, \phi)$  on the ground state and not on its energy  $E(X, \phi)$ .

Eigenenergies and eigenstates are, of course, related. Away from level crossings, both  $E$  and  $P$  are smooth functions of the parameters. However, besides that, the susceptibility and the curvature are essentially independent quantities. For example, from Eq. (6) the energy surface of the ground state is  $E(\phi, x) = -E_0(1 + \sqrt{\phi^2/3 + 4|x|^2})$ . So, while

$\Omega_{X,\phi}(X, \phi = 0)$  diverges at the crossing, the corresponding component of the susceptibility,  $\chi_{X,\phi}(X, \phi = 0)$  vanishes identically and, while  $\chi_{\phi\phi}$  diverges at crossing, the corresponding curvature  $\Omega_{\phi\phi}$  vanishes identically.

Finite temperature provides a cutoff to the homeopathic divergence. Two nearly crossing states, which are at distance  $\epsilon$  apart in energy, transport opposite charges  $Q = \pm O(1/\epsilon)$ . At finite temperature  $T$  the two nearly crossing states will be nearly equally populated with a bias of  $O(\epsilon/T)$  towards the lower state. For the triangular molecule undergoing a cycle of deformations, the leading behavior of the charge transport at low temperature is:

$$Q(T) = \frac{\pi E_0}{\sqrt{3} k_B T},$$

where  $k_B$  is Boltzmann's constant. The constants in this formula are special for the model. In general, for generic two level crossings, one can conclude that the total charge transport will approach a finite limit as one approaches the crossing so that:

$$Q(T) = O(1/T). \quad (9)$$

The  $1/T$  law is reminiscent of Curie's law.

Similar analysis can be made for a necklace of  $p$  equivalent atoms with  $p$  an arbitrary integer larger than 2. (For benzene  $p = 6$ .) The tight binding Hamiltonian is a  $p \times p$  Hermitian matrix with nearest neighbors hopping only. Now suppose that such a ring is deformed by means of a running sinusoidal wave of commensurate wavelength, i.e. the hopping amplitude between the  $k$ th and  $(k+1)$ th atom is time dependent and is given by  $1 + 2\kappa \cos[2\pi(jk/p - t/\tau)]$ , where  $\kappa$  (which is held fixed) stands for the amplitude of the distortion and  $j$  is a natural number smaller than  $p$ . (This is an analog of Eqs. (5a), (5b) and (5c).) When  $\phi = \kappa = 0$ , there are twofold degeneracies at energies  $2\cos(2m\pi/p)$  for  $m = \pm 1, \dots, \pm [p/2]$ . The new feature of this model is that the order of perturbation theory that splits the degeneracies depends on  $|m|$ ,  $p$  and  $j$ , and can be large if  $p$  is large. As a consequence, the singularity of the adiabatic curvature near crossing can be quite strong (without the susceptibilities being singular). The charge transported can be calculated here as well, but the details will be described elsewhere. The result is that the charge transported in the

pair of nearly crossing states near energy  $2\cos(2m\pi/p)$  is:

$$Q = \pm \frac{\pi q \sin m\theta}{p \kappa^q \cos(m - j/2)\theta} \\ \times \left( \prod_{k=1}^{q-1} \frac{\cos(m - jk)\theta - \cos m\theta}{\cos(m + j/2 - kj)\theta} \right). \quad (10)$$

$q \geq 1$  is the order of perturbation theory that splits the degeneracy.  $q$  is the smallest natural number such that  $qj \bmod p$  equals either  $2|m|$  or  $p - 2|m|$ . In the first case  $m = |m|$  in Eq. (10) and, in the second case,  $m = -|m|$ . The numerator and the denominator never vanish under the conditions that lead to this equation.  $\theta$  is shorthand for  $2\pi/p$ . We see that the amplitude of the perturbation  $k$  enters this expression with a negative exponent: this is the homeopathic effect. The sign of  $Q$  reflects the fact that each member of the pair of nearly crossing states transports charge in opposite sense. Under a complete cycle  $t \rightarrow t + \tau$  the electronic eigenstate acquires a phase factor  $(-1)^q$ . Eq. (9) is still obeyed.

The molecular models discussed so far are prototype models of finite quantum systems. It is natural to inquire what, if any, of the homeopathic behavior survives for infinite, macroscopic systems. A prototype of such a system is the infinite one-dimensional chain with finite electron density. When the Fermi energy lies in a gap such a chain is nominally an insulator and the theory of adiabatic transport applies. For non-interacting electrons and a periodic chain, the transport behavior can be analyzed using standard, single-electron techniques. It turns out that there is no homeopathic divergence of transport. What survives of the homeopathic behavior is that an arbitrarily small cycle of deformation can lead to a finite (nonzero) and quantized charge transport. This requires that the deformation pinches a gap closure. The quantization of transport (at  $T = 0$ ) comes as it does in charge pumps [15,17] and the Hall effect [10]. The theoretical framework presented above sheds light on the numerical findings of [9] who found divergence of the transport coefficients in Hubbard models of perovskite chains.

Until now we have only considered the electronic part of the Born–Oppenheimer theory. The inclusion of the rovibronic part is, in general, a formidable problem even for a molecular trimer where the intri-

cacies of the three-body problem come into play. We refer to [4] for what is known in general and to [6,21–24], for models. We shall content ourselves here with the classical limit for the nuclear dynamics.

If the ground state of the undeformed molecule is degenerate, the total energy may be decreased by deforming the molecule. This is the classical Jahn–Teller [23,24] instability. This is the case if the elastic energy is proportional to the square of the amplitude of the deformation (i.e., is harmonic) and if the degeneracy lifts to first order in the deformation. If the Jahn–Teller energy functional has a unique minimizer which breaks the degeneracy, then a sufficiently small cycle of deformations around the ground state will not encircle also the point of level crossings. In this case the homeopathic behavior (at  $T = 0$ ) is censored at the ground state by the Jahn–Teller instability and there is no divergence of the charge transport in the limit of an infinitesimal cycle of deformation.

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