# Aharonov-Bohm Effects in Entangled Molecules

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Molecules which are magnetic and conducting, if suitably entangled (e.g., catenanes and knots) could exhibit Aharonov-Bohm effects which can be viewed as particular examples of a Berry phase. The corrections to the quantum energy levels reflect the entangled geometry of the molecules and, while small (they are proportional to the square of the fine structure constant), may be observable. We illustrate these corrections for a number of catenated and knotted structures. For couplings between the components of a catenane (link), the Aharonov-Bohm corrections are determined by integer-valued linking numbers. For knots, the Aharonov-Bohm correction is proportional to the geometric writhe of the knot.

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Three characteristics of long chain molecules (including polymers or oligomers) are as follows: (i) Some form entangled loops and knots [1],[2]. (ii) Some can be electrically conducting [3]. (iii) Some have fairly large magnetic moments [4]. To simplify our treatment, we speculate that in some cases dipole-dipole and/or spin-orbit interactions orient the molecular magnetism parallel to the molecular chain. In views (i), (ii), and (iii), we consider the interplay between molecular magnetism and conduction when the molecules are entangled or knotted. Situations are described where the quantum-mechanical Aharonov-Bohm effect changes the electronic energy levels. Knotted or entangled mesoscopic systems could also exhibit the effects we discuss here (with some modifications). Additional relationships between knots and other physical effects, including electrostatics, fluid mechanics, gravity, chemical reactions, etc., are reviewed in [5,6].

Our simplest example of the relations between conduction, magnetization, and knotted geometry is just a restatement of the Aharonov-Bohm effect, which can be viewed as a particular example of a Berry phase [7]. Figure 1 shows two intertwined simple molecular loops (catenanes in chemistry and the Hopf link in mathematics). Assume one of these loops is magnetic with its magnetization aligned along the molecular chain (the chain axis), and the other loop is an electrical conductor.

The electrons on the conducting loop are taken to be free particles moving on a ring of length $L$. Ignoring magnetic coupling, the quantum energy levels for the electrons on the conducting loop are

$$E_n^0 = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 n^2, \tag{1}$$

where $m$ is the electron mass and $n$ is any integer.

When the loops are linked as is shown in Fig. 1, magnetic effects change the physics. A magnetic flux $\Phi$ produced by the magnetic molecule penetrates the plane of the conducting loop. This introduces an additional phase into the wave function of a conducting electron [via the incorporation of the vector potential $\vec{A}$ into the momentum operator $(\vec{p} \rightarrow \vec{p} + e\vec{A}/c)$]. This phase is associated with the Aharonov-Bohm effect. The resulting single-electron energy levels become

$$E_n^c = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2\left(n + \frac{e\Phi}{2\pi\hbar c}\right)^2, \tag{2}$$

where

$$\Phi = \oint \vec{A}(\vec{r}_1)\cdot d\vec{r}_1. \tag{3}$$

Here $d\vec{r}_1$ traces out the shape of the conducting loop. The equivalence of this flux expression to the standard

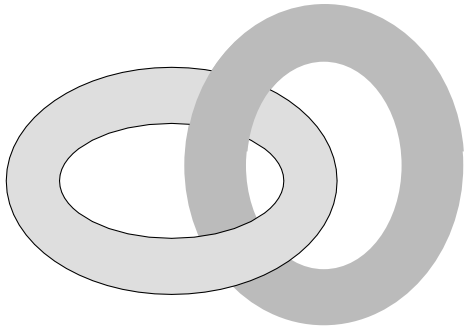

FIG. 1. A schematic of a catenane molecule. If one molecular loop is magnetic and the other is conducting, the Aharonov-Bohm effect will change the conduction electron energy levels. If both loops are conducting and magnetic, the conduction electron energies on each loop will be changed.

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$\Phi = \int \vec{B} \cdot d\vec{a}$ integrated over the surface bounded by the conducting loop follows from $\vec{B} = \vec{\nabla} \times \vec{A}$ and Stokes theorem [8].

To estimate the magnitude of the Aharonov-Bohm correction to the electronic energies, the magnetization per unit length on the magnetic loop is expressed in atomic units. Thus the magnetic moment of an infinitesimal length $d\vec{r}_2$ of the magnetic loop is

$$d\vec{m}_2 = \gamma \frac{e\hbar/(2mc)}{\hbar^2/(me^2)} d\vec{r}_2, \tag{4}$$

where $e\hbar/(2mc)$ is the Bohr magneton and $\hbar^2/(me^2)$ is the Bohr radius. In these scaled units, the dimensionless $\gamma$ could be of order unity, but examples from [4] suggest a value somewhat less than unity.

The vector potential resulting from the magnetization is obtained by treating each infinitesimal segment of the magnetic molecular loop as a tiny magnetic dipole aligned with the molecular loop axis. The total vector potential is then obtained by summing over the infinitesimal magnets, giving the integral

$$\vec{A}(\vec{r}_1) = \oint \frac{(\vec{r}_2 - \vec{r}_1) \times d\vec{m}_2}{|\vec{r}_2 - \vec{r}_1|^3}, \tag{5}$$

where this second path is defined by the geometry of the magnetic molecular loop. Combining these results yields the Aharonov-Bohm correction to the quantum number $n$ in the energy levels of Eq. (2),

$$\frac{e\Phi}{2\pi\hbar c} = \gamma\alpha^2[\mathrm{Lk}], \tag{6}$$

where $\alpha = e^2/(\hbar c) \cong 1/137$ is the fine structure constant and

$$\mathrm{Lk} = \frac{1}{4\pi} \oint_{r_1} \oint_{r_2} \left( \frac{(\vec{r}_2 - \vec{r}_1) \times d\vec{r}_2}{|\vec{r}_2 - \vec{r}_1|^3} \right) \cdot d\vec{r}_1 \tag{7}$$

is a "linking number" which characterizes the topology of the system [9]. The squared fine structure constant means Eqs. (2), (6), and (7) imply a very small Aharonov-Bohm correction to the electronic energy levels. However, such a small effect might be observable because the breaking of the $n \rightarrow -n$ symmetry yields a splitting of the excited state degeneracies. The detection method will depend on the knot geometry. For the example in Fig. 1, one could compare the fine details of spectra with the rings coupled and uncoupled. In principle, larger effects could be obtained from analogous mesoscopic systems.

Remarkably, the linking number of Eq. (7) is a topological invariant. It is the integer which specifies the (signed) number of times the magnetic loop passes through the plane of the conducting loop. The linking number does not change if the loops are arbitrarily deformed, provided they do not intersect. Thus the Aharonov-Bohm energy correction does not depend on the specific shapes of the linked molecular loops.

We next consider the case where *both* molecular loops are simultaneously magnetic and conducting. There will then be both interloop (one loop affecting the other) and intraloop (one loop affecting itself) Aharonov-Bohm corrections to the electron energies on each molecular loop. We first describe the interloop effects. The symmetry of the effect can be seen by rewriting Eq. (7) using the properties of the triple product

$$\mathrm{Lk} = \frac{1}{4\pi} \oint_{r_1} \oint_{r_2} \left( \frac{(\vec{r}_1 - \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|^3} \right) \cdot (d\vec{r}_1 \times d\vec{r}_2). \tag{8}$$

Letting $n_1$ and $n_2$ be the quantum numbers characterizing the electrons moving on the two molecular loops, and letting $\gamma_1$ and $\gamma_2$ characterize the magnetism on the two loops, the Aharonov-Bohm effects for two planar loops are

$$n_1 \rightarrow (n_1 + \gamma_2\alpha^2[\mathrm{Lk}]), \qquad n_2 \rightarrow (n_2 + \gamma_1\alpha^2[\mathrm{Lk}]). \tag{9}$$

For each quantum number modification, one must use the right-hand rule to obtain the correct sign. That is, a negative $n_1$ corresponds to current in loop #1 which produces a magnetic field parallel to the magnetism (from loop #2) which is threading it.

These interloop results extend to more complex geometries, and the Aharonov-Bohm energy corrections are additive. For example, three molecular loops entangled as Borromean rings [10] would exhibit no Aharonov-Bohm interloop energy shifts. (The rings are entangled, but they do not thread each other.)

Finally, we consider the intraloop corrections to the energy levels. For this aspect of the physics, we can consider a *single* magnetic and conducting molecule which has a complicated (perhaps knotted) shape. The magnetic flux of a single molecular loop can penetrate its own conducting path, leading to a self-induced Aharonov-Bohm energy shift. The expression for the intraloop Aharonov-Bohm shift is obtained using analogous reasoning, giving

$$n \rightarrow (n + \gamma\alpha^2[\mathrm{Wr}]), \tag{10}$$

where $n$ and $\gamma$ refer to the conducting state and the magnetism on the loop and

$$\mathrm{Wr} = \frac{1}{4\pi} \oint \oint \left( \frac{(\vec{r} - \vec{r}')}{|\vec{r} - \vec{r}'|^3} \right) \cdot (d\vec{r} \times d\vec{r}') \tag{11}$$

is the (geometric) "writhe" of the knot [11]. The integral for Wr is a double path integral over the single loop, and the integration variables $\vec{r}$ and $\vec{r}'$ are coordinates which *both* trace out the geometry of the loop. Unlike the linking number, this writhe is not a topological invariant but depends on the detailed geometry of the loop. The writhe Wr of Eq. (11) has the following characteristics:

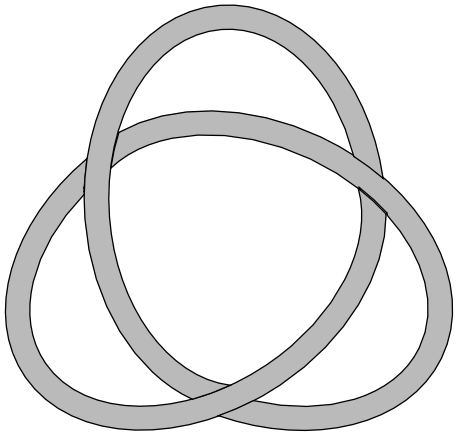

FIG. 2. If a conducting and magnetic molecule has the shape of this trefoil, the electronic energy levels are shifted by an Aharonov-Bohm term which is proportional to the writhe of the trefoil knot.

(i) For knots which lie nearly flat on a plane, Wr is the difference between the number of "positive" and "negative" crossings [10]. In general, writhe is the average of the difference between positive and negative crossings. Here "average" means consider projections of the loop onto an arbitrarily oriented plane, and average over all planes.

(ii) Despite the apparent divergence associated with $1/|\vec{r}_1 - \vec{r}_2|^3$, Wr is not singular when the molecule is "smooth."

(iii) Wr is dimensionless and does not change with the size of the molecule.

(iv) Wr vanishes for sufficiently symmetric molecules: any molecular shape which can be transformed into itself through translations, rotations, and a single inversion have $\mathrm{Wr} = 0$. This means all planar molecules are characterized by $\mathrm{Wr} = 0$, and thus there is no Aharonov-Bohm correction to the electronic energy levels.

The "unknot" is characterized by $\mathrm{Wr} = 0$ if it lies flat in a plane, but if the unknot is twisted to form a "figure eight," then $|\mathrm{Wr}| \cong 1$. Thus a magnetic and conducting molecule need not be knotted to exhibit an Aharonov-Bohm energy shift. However, positive and negative writhe numbers are equally likely for the unknot and one would expect fluctuations in the molecular shape to give a vanishing average for Wr. On the other hand, knotted molecules of short length will have restricted geometries which will produce a nonzero average Aharonov-Bohm correction to the energy levels.

Molecular knots which are tightly wound can be approximated by "ideal" knots. Ideal knots have a nonzero cross section and a minimum length. The Wr for a large number of such ideal knots has been tabulated in articles contained in [5]. For the simplest knot, the trefoil of Fig. 2, these tables show $|\mathrm{Wr}| \cong 3.4$ for the ideal trefoil. This is not a surprising value, since the simplest planar trefoil projection shows three crossings of the same sign. On the other hand, $\mathrm{Wr} \cong 0$ for the ideal figure eight knot (or $4_1$ knot or Listing's knot), probably because this knot can be transformed into its mirror image without being broken.

The ideal trefoil exhibits somewhat unphysical kinks in its shape, so we also considered the trefoil whose axis lies on a torus. The axis of this knot is described by the equations

$$x = [1 + \varepsilon \cos(\tfrac{3}{2}\phi)]\cos(\phi), \quad y = [1 + \varepsilon \cos(\tfrac{3}{2}\phi)]\sin(\phi), \quad z = \eta \sin(\tfrac{3}{2}\phi). \tag{12}$$

Our numerical calculations for the trefoil on a torus yield $|\mathrm{Wr}| \geq 3$ for a wide choice of the parameters $\varepsilon$ and $\eta$. The ideal trefoil on a torus (with minimum length for a fixed width) is characterized by $\varepsilon = \eta = 0.448$ [6]. For this case, we obtain the not surprising value $|\mathrm{Wr}| \cong 3.42$.

Aharonov-Bohm energy shifts are not the only physical consequence of knotted and entangled molecular geometry. Earlier work showed that the trefoil described by Eq. (12) has a nonzero optical activity [12] and estimates of the relative scattering functions of catenanes and trefoils are reviewed in [13].

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