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Optical vibrations on microscopic rings in a magnetic field

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We show that on microscopic rings, such as cyclic polymer molecules, or on quantum dots the frequency of some vibrations depends on the magnetic field and on the electron filling factor. The effect is related to the existence of orbital currents on the ring, which induce a frequency change of the vibrational mode. Each increase in single-electron current induces a change in the vibrational frequency. The magnetic field may also create an equilibrium distortion of atoms. The extent of atomic distortions changes with the magnetic field. The latter effect is characterized by a huge electric polarizability and hyperpolarizability of cyclic molecules, discovered recently. The relation of persistent current on rings and on quantum dots to the frequency-change effect is discussed; possible experiments are proposed.

I. INTRODUCTION

Recently, considerable progress has been made in preparation techniques of complex polymeric molecules. Various macromolecules of ring-chain shape have been synthesized. One example is the C_{60} fullerene molecule. When intercalated with alkali-metal atoms to form the fullerides A_xC_{60}, the material with $x=3$ becomes superconducting below temperatures 18 and 28 K for $A=\mathrm{K}$ (Ref. 1) and for $A=\mathrm{Rb}$,[2] respectively. The unusual features of this high-temperature superconductivity may be connected with the creation of so-called flux phase states.[3–9] The idea of flux phase states is based on the existence of orbital electron currents (see Ref. 9 and references therein). On the nearly spherical C_{60} molecule there may exist molecular orbital currents.

Another relevant problem is the origin of the large diamagnetic anisotropy and huge polarizability discovered in some aromatic molecules and analogous compounds.[10] For example, these effects sometimes appear in single crystals of polycyclic hydrocarbons. The magnetic susceptibility measured normal to the plane of these molecules is several times greater than that measured parallel to the plane. Such an anisotropy has been explained by the existence of orbital currents.[10] Recently there has been increasing interest in the use of conjugated organic materials for nonlinear-optics applications.[10–12] These compounds also have a large polarizability, which has been attributed to the mobility of their π electrons.

In a related area, carbon clusters have recently received much attention from both the theoretical and experimental communities.[11] Clusters ranging from C_2 to C_{200} have been studied. The theory, which agrees with an experiment, claims that with a large number of carbon atoms the monocyclic structures are more stable than the corresponding linear forms. Such monocyclic structures are also important on the basis of aromaticity considerations.

With the advent of nuclear magnetic resonance (NMR) spectroscopy, there was renewed interest in orbital-current theories.[12] The protons in polycyclic hydrocarbons and related compounds show large chemical shifts of the NMR lines at lower fields. This effect is due to large contributions to the local magnetic field at proton sites arising from electron ring currents. Nevertheless, at the present time there are no satisfactory experimental methods for the detection of such orbital currents. In the presence of orbital currents, the resulting local magnetic field can still be very small. If the ring contains a trapped vortex, it also contains one quantum of flux, which creates its own magnetic field. As a result, there may be a total cancellation of the local field, as in the Meissner effect for superconductors. Such an analogy with the Meissner effect is, however, valid only for a macroscopic specimen.

With the aim to develop a method as an alternative to local-magnetic-field measurements (or NMR), we have studied vibrational spectra within a simplified model. We found that the frequency of some vibrations of atoms on microscopic rings depends strongly on the presence or absence of orbital currents along the ring. The magnitude of orbital currents depends on the magnetic field. Thus, by changing the magnetic field, we may change the vibrational frequency. This influence of the magnetic field on the vibrational spectrum is a general phenomenon. The effect will appear for all systems having large anisotropy in the diamagnetic susceptibility, which is associated with orbital currents. For example, this effect is expected to exist in aromatic molecules. However, the presence of this effect does not necessarily imply the presence of a magnetic field. It is nonetheless important that the existence of such orbital currents, or any electrical current whatsoever, be recognized.

This effect is particularly important for theories of spontaneous orbital moments in small particles.[13–20] Periodic magnetoconductance oscillations can occur in systems of singly connected geometry, such as a point contact[21] or a disk-shaped region in a two-dimensional electron gas ("quantum dot").[22,23] As is well known, the Aharonov-Bohm effect in such systems is due to transport via the edge states. In the quantum Hall-effect regime, such states are the current-carrying states at the Fermi level. Sivan and Imry[24] have shown that edge states of a quantum dot make the geometry effectively doubly connected, in which case the quantum dot traps flux quanta equally well as a ring and the orbital current flows through the edge states. For two identical small particles (e.g., quantum dots) with and without orbital magnetic moments (currents), this phonon spectra are then different.

II. MODEL

Next we discuss how the motion of electrons influences the vibrational spectrum. In order to study such an effect, we consider an N-atom chain forming a ring similar to a cyclic molecule. We put such a cyclic molecule in a transverse magnetic field and consider the spectrum of vibrations. This model is introduced simply as illustration of a more general principle and as a means of extracting typical, though not necessarily correct, numbers characterizing the system. Atoms of mass M_0 with only one orbital are coupled by elastic forces governed by the Hamiltonian

$$H_L=4M_0\sum_{n=1}^{N}\dot{u}_n^2+K\sum_{n=1}^{N}(u_n-u_{n+1})^2\ , \tag{1}$$

where K is the elastic constant and u_n is the displacement of the nth atom along the ring measured from the equilibrium point. For the Hamiltonian of electrons on an N-site ring in a magnetic field, we choose, for simplicity, the Hamiltonian of free spinless fermions, which, in the presence of magnetic field, has the form

$$H_e=-\sum_{\langle i,j\rangle}^{N}t_{ij}a_i^{\dagger}a_j\ . \tag{2}$$

Where $a_i^{\dagger}$ and a_j are the fermion creation and annihilation operators, respectively, the sum is over nearest-neighbor bonds $\langle ij\rangle$,

$$t_{ij}=t\exp(iA_{ij})\ , \tag{3}$$

where t is the hopping constant. The phase A_{ij} is equal to

$$A_{ij}=2\pi\int_i^j\mathbf{A}\cdot d\mathbf{s}\ . \tag{4}$$

In the symmetrical gauge $\mathbf{A}=(-y,x,0)B/2$ we obtain for nearest-neighbor bonds, in units of elementary flux ϕ_0 (we use units in which $\phi_0=\hbar=1$),

$$A_{ij}=\frac{2\pi f}{N}\ , \tag{5}$$

where f is the flux of the magnetic field through the ring: $f=B\pi R^2$. Here, for simplicity, we have neglected the spin, since it does not change qualitatively the final result. The Hamiltonian for the electron-phonon coupling has the usual deformation-potential form

$$H_{\text{int}}=D\sum_{n=1}^{N}\exp(iA_{n,n+1})a_n^{\dagger}a_{n+1}(u_n-U_{n+1})+\text{c.c.}\ , \tag{6}$$

where D is the deformation potential.

Let us consider the longitudinal oscillation of atoms, along the ring, in the presence of the magnetic field. This problem can be solved in two steps. First, we proceed to find the electronic spectrum, at a specific displacement, of a collection of atoms in the adiabatic approximation. We consider the so-called Peierls distortion, i.e., a displacement of the nth atom by the amount $\Delta/2D$ and of the $(n+1)$th atom correspondingly by the amount $-\Delta/2D$, where

$$\Delta=D\begin{cases}u_n-u_{n+1} & \text{if } n \text{ is odd}\\ -u_n+u_{n+1} & \text{if } n \text{ is even}\ .\end{cases} \tag{7}$$

In the limit $N\rightarrow\infty$, such displacements correspond to an acoustical branch of spectrum at a specified value of momentum. In other words, we consider the top of the dispersion curve in the acoustic spectrum. In the case of a two-atom chain of infinite length, the vibrations correspond to the optical branch of the vibrational spectrum. Generally speaking, for a ring of finite size, such terminology is not correct, since here the dispersion curve disappears. In the adiabatic approximation, the electronic spectrum for the Peierls distortion has the form[25]

$$E_m=\pm\left[2t^2+2\Delta^2+2(t^2-\Delta^2)\cos\left[\frac{4\pi}{N}(m+f)\right]\right]^{1/2}\ , \tag{8}$$

where $m=0,+1,+2,\ldots$. As one can see from Eq. (8), in the continuum limit $N\rightarrow\infty$ the parameter 2Δ plays the role of the gap associated with the splitting of the electronic band into two. The width of each band is $t-\Delta$, where $\Delta<t$. Such a splitting is usually called the Peierls transition.

III. THE FREQUENCY CHANGE IN A MAGNETIC FIELD

The dependence of the total energy of the system on the magnetic flux is qualitatively different for even and odd number of fermions on the ring. This qualitative difference has already been found for $\Delta=0$.[18] For an odd number of fermions, the total energy increases as the flux f through the ring increases from zero up to $f=\frac{1}{2}$. On the other hand, for an even number of fermions the total energy decreases, as the flux through the ring increases up to $f=\frac{1}{2}$. The latter property plays a crucial role in the existence of the flux phase state on a cylinder consisting of many rings with an even number of fermions.[18] The total energy of $2M+1$ electrons (provided that $2M+1\leq N/2$) is equal to

$$\begin{aligned}E=&-2\sum_{n=0}^{M}\left[t^2\cos^2\left[\frac{2\pi}{N}(f+n)\right]\right.\\&\qquad\left.+\Delta^2\sin^2\left[\frac{2\pi}{N}(f+n)\right]\right]^{1/2}\\&-2\sum_{n=1}^{M}\left[t^2\cos^2\left[\frac{2\pi}{N}(f-n)\right]\right.\\&\qquad\left.+\Delta^2\sin^2\left[\frac{2\pi}{N}(f-n)\right]\right]^{1/2}\ ,\end{aligned} \tag{9}$$

and there is an analogous expression for the case of even number of fermions. At small deviations $\Delta^2/\{t^2\cos^2[2\pi(f+n)/N]\} \ll 1$, we can use the approximation

$$E=E_0-\frac{\Delta^2}{t}K_1(f)+\frac{\Delta^4}{2t^3}K_2(f)\ , \tag{10}$$

where E_0 is the energy at $\Delta=0$ (see Ref. 18),

$$K_1(f)=\sum_{n=0}^{M}\frac{\sin^2\left[\frac{2\pi}{N}(f+n)\right]}{\cos\left[\frac{2\pi}{N}(f+n)\right]}+\sum_{n=1}^{M}\frac{\sin^2\left[\frac{2\pi}{N}(f-n)\right]}{\cos\left[\frac{2\pi}{N}(f-n)\right]} \tag{11}$$

and

$$K_2(f)=\sum_{n=0}^{M}\frac{\sin^4\left[\frac{2\pi}{N}(f+n)\right]}{\cos^3\left[\frac{2\pi}{N}(f+n)\right]}+\sum_{n=1}^{M}\frac{\sin^4\left[\frac{2\pi}{N}(f-n)\right]}{\cos^3\left[\frac{2\pi}{N}(f-n)\right]}\ . \tag{12}$$

Since $K_1(f)\neq 0$, the second term in the right-hand side of Eq. (10) will give a contribution to the elastic energy of the ring molecule.

Such a contribution can change the frequency of the vibrations. There are two different cases here: when the equilibrium positions are (1) $\Delta=0$ and (2) $\Delta\neq 0$. Let us consider the first case.

In the case when there exists only one free electron on the ring, the frequency changes from ω_0 at zero magnetic field to the value

$$\Omega=\omega_0\left[1-p\cos\left[\frac{2\pi f}{N}\right]\tan^2\left[\frac{2\pi f}{N}\right]\right]^{1/2}\ , \tag{13}$$

where $p=D^2/(tKN)$. As one can see from Eq. (13), the frequency decreases with f. The decrease of the frequency will occur for any odd number of fermions on the ring. The maximal effect of such a decrease is obtained in the case of half filling. Unfortunately, at half filling the expansion (10) is not valid, since in this case the denominator in (10)–(12) equals zero. Therefore in this case we should consider the complete nonlinear dependence $E(\Delta)$, as will be done in the next section.

Let the filling factor of electrons be lower than half as in the case, for example, if there is only one electron. For a simple estimate of this shift, we set $D=12$ eV and $t=1$ eV. For the number of sites on a ring we take $N=60$, i.e., the ring consists of 60 atoms, like C_{60}. Taking into account interatomic distances on the ring for the elastic constant K, we obtain $K\sim 24$ eV. Then (13) is simplified to the form $\Omega\sim\omega_0(1-0.002f^2)^{1/2}$. One sees that even for one electron there exists the effect of the frequency change with the magnetic flux.

The effect increases strongly with the filling of the ring by electrons. The frequency shift can be represented by the following general formula:

$$\Omega=\omega_0[1-pK_1(f)]^{1/2}\ . \tag{14}$$

Here with the filling appears a situation in which, at zero flux, the frequency Ω decreases and may be equal to zero. At this point, nonzero equilibrium positions of atoms $\Delta=\Delta_0\neq 0$ will appear. The effect of the frequency change for the case of nonzero equilibrium positions of atoms will be preserved. Now let us continue to study the first case, when $\Delta_0=0$. If we take the number of electrons on the ring as $2M+1=29$ at weaker electron-phonon interaction $p=0.01$, the frequency-shift dependence on the magnetic field is presented in Fig. 1(a). One sees a smooth decrease of this frequency with the magnetic flux f. For the other values of f ($|f|\geq 1/2$), this function is periodic.

On the other hand, for an even number of fermions the

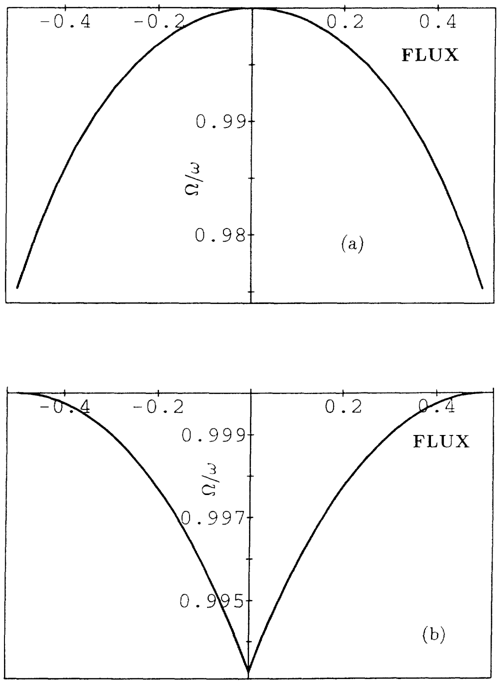

FIG. 1. The change of the vibrational frequency for a ring in a magnetic field with the following parameters: $D=4$ eV, $t=1$ eV, the number of sites on the ring, $N=60$, the constant $K\sim 24$ eV, i.e., the assumed value $p=\frac{1}{90}$. The magnitude f is an external magnetic flux through a ring in units of the elementary flux quantum. For other values of f ($|f|\geq\frac{1}{2}$) this function should be continued periodically. (a) For an odd number of fermions $N_e=29$. (b) For an even number of fermions $N_e=28$.

vibrational frequency increases with increasing magnetic flux through the ring. Let us estimate this shift with the flux f. For the number of fermions $2M=28$, we use the same values for parameters as we have used in the case of an odd number of electrons. In this case the frequency shift is described through an expression analogous to Eq. (14). The results of numerical calculation are presented in Fig. 1(b). One can see a drastic difference in comparison with the case of an odd number of fermions. The dependence of the frequency on the external flux has cuspidal minima at a y integer number of flux quanta through the ring. Each of the cuspidal minima corresponds to the trapping of a vortex by the ring. The total flux through the ring, after such trapping, changes by one unit.

One may see that even without a magnetic field the frequency is shifted with the filling of electrons. The reason for the effect is that, even without a magnetic field, electrons create orbital currents, i.e., they have orbital moments. Thus the effect may be observed by the change of electron filling, even at zero magnetic field.

The present calculation shows that the effect for simple aromatic molecules is very small for typical laboratory magnetic fields. In this case, the flux, which is of the order of a sizable fraction of a flux quantum, can only be obtained at enormous fields. The best place to look for the effect will probably be quantum dots (disks),[21–24] in which orbital currents are created through edge states. The size of a quantum dot may easily be changed so that, at laboratory magnetic fields, a sizable part of one flux quantum will penetrate into the dot. In this case, the frequency change may be observable in edge phonon states, which are analogous to surface vibrations. Even without a magnetic field, the frequency of some phonons will be softened with electron filling.

Any electron which creates current on the ring contributes to the change of the frequency, i.e., to the change of the elastic constant. It is very useful to consider here a single electron with current $J_i \neq 0$. From the expression for $K_1(f)$ [see formula (11)] it is obvious that only nonzero currents can cause a change of the frequency. If an electron has no orbital motion, there is no contribution to the change of frequency from this electron. This phenomenon is similar to the classical Doppler effect. One can see from Eqs. (13) and (14) that the frequency is changed by an extra multiplicative factor as in the case of the usual Doppler shift. The orbital current is created by moving electrons, which interact with oscillating atoms. Due to the nonzero velocity of the electron, the frequency changes according to the Doppler effect. Thus each moving electron contributes a Doppler shift of the frequency. As a result, we obtain the dependence of the average frequency on the magnetic field and/or on the electron filling. Of course, if the velocity of light is equal to infinity, the effect disappears.

IV. POLARIZABILITY

As one may see from Eq. (14), for some values of the parameters of the ring (for example, with an increase of the electron filling), the frequency Ω may be equal to zero. This point is critical for the appearance of nonzero displacements of atoms on the ring $\Delta_0 \neq 0$. The value of these displacements depends on the magnetic field and can be easily estimated from the expansion (10),

$$\Delta_0 = \pm \left[\frac{[pK_1(f)-1]}{p^2 K_2(f)} \right]^{1/2} . \tag{15}$$

The dependence of the distortion $x=\Delta_0/(\sqrt{p}\,t)$ on the magnetic flux is qualitatively different for the cases of an even and an odd number of fermions on the ring.

If we take the value $p=0.1$, the same as in the case of one electron, a nonzero Peierls distortions x, which will depend on the value of the magnetic flux, will appear on the ring. For 29 fermions on the C_{60} ring, the dependence of the equilibrium distortions x on the flux is presented in Fig. 2(a). Here the strong dependence on the magnetic field at half-integer flux quanta is changed by a weak dependence for small values of the flux. On the other hand, for an even number of fermions on the ring the strong dependence of the distortion x upon the magnetic field appears at integer values of the flux f. For 28 fermions on the C_{60} ring, the dependence of the distortion x on the magnetic flux is presented in Fig. 2(b). At integer values of flux, cuspidal minima have appeared [see Fig. 2(b)]. One notes that the Peierls transition discussed may be stimulated by a magnetic field.

The behavior of the vibrational frequency is similar to

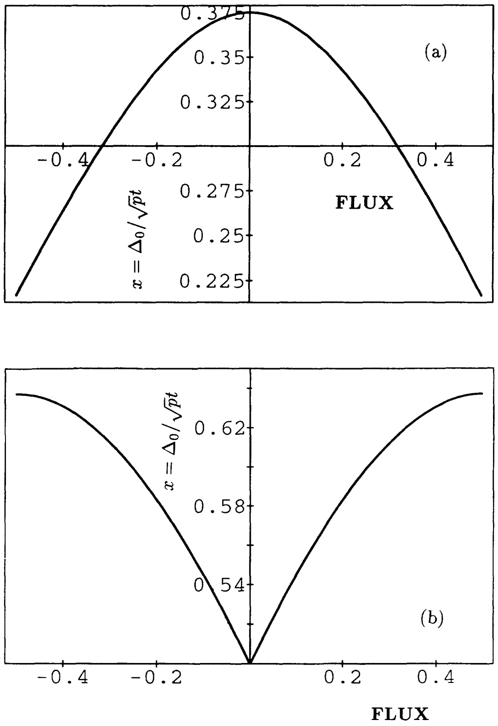

FIG. 2. The equilibrium distortion x of atoms from equidistant positions in a magnetic field on a C_{60} ring with the constant $p=0.1$ and f the value of an external magnetic flux through a ring in units of the elementary flux quantum. The gap $\Delta_0=\sqrt{p}\,xt$. (a) For an odd number of fermions $N_e=29$. (b) For an even number of fermions $N_e=28$.

the behavior of distortions. The dependencies of the frequency on the magnetic flux are presented in Figs. 3(a) and 3(b) for the cases of an even and an odd number of fermions, respectively. In contrast with the case of zeroth equilibrium displacement $x=0$ (see Sec. III), one sees that in the latter case the dependence on the magnetic flux is stronger. The change of the frequency may even reach 50%.

The effect will be huge at the point of the appearance of nonzero Peierls distortions x or Δ_0. In this case the vibrations will lose their harmonic character and become soft and nonlinear. Here it is important to notice that the predicted effect is related to polarizability of cyclic molecules. Let us estimate the change of the molecular electric polarizability in magnetic field. The dipole moment of a molecule is proportional to the shift Δ of nuclei of the molecule from their equidistant positions. Thus, the electric polarizability will depend strongly upon magnetic field in the same manner as described above for Peierls distortions.

The value $\Delta_0 \neq 0$ may also correspond to the equilibrium state of the molecule due to reasons other than Peierls instability as, for example, in the case of a molecule with two different types of chemical bonds. One can show within the present model that in this case the value Δ_0 in the magnetic field changes to $\Delta_0^* = \Delta_0/R$, where R is a relativistic factor, the same factor as in formula (14). Clearly, the polarizability will depend strongly on the magnetic field in the same way: $\alpha(H)=\alpha(0)/R$. Thus, the predicted effect can be measured by observing the change of the polarizability in a magnetic field. The related phenomena of hyperpolarizability and also the unusual electro-optics for symmetrical cyclic molecules[10] are connected with this anomaly of the vibrational spectra and with the appearance of nonzero Peierls distortions in a magnetic field, found in the present paper.

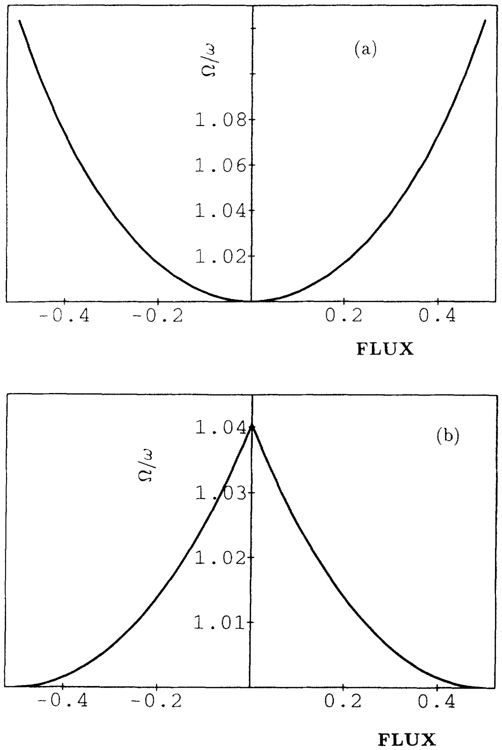

FIG. 3. The dependence of the vibrational frequency upon the magnetic flux through the ring. (a) For an odd number of fermions 29. (b) For an even number of fermions 28. We take here the values of all parameters the same as in Fig. 2.

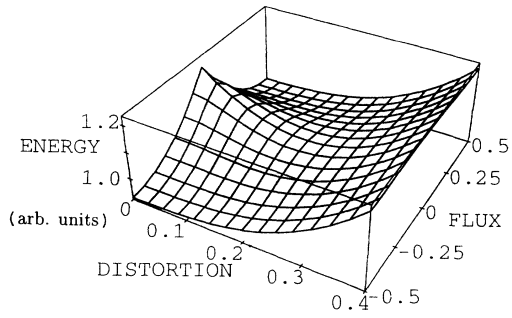

FIG. 4. The surface of potential energy for an even number of fermions at half filling in E-x-f (energy-distortion-flux) space. We choose $N_e=30$. The constant $p=0.025$. Cuspidal maximum corresponds to zeroth displacements of atoms. The extremal point at each fixed value of flux corresponds to equilibrium positions of atoms.

The case of half filling requires special attention, since in this case expansion (10) is not valid. Instead of (10) we should consider dependence (9). The dependencies of the potential energy on Δ and on the magnetic flux f are presented in Figs. 4 and 5 for the cases of an even and an odd number of fermions, respectively. For illustration we choose in the first case 30 fermions and the value $p=0.025$. In the second case the number of fermions is $N_e=31$ and $p=0.045$. The minima of the energy dependence on the distortion at constant flux (see Figs. 4 and 5) correspond to different equilibrium atomic displacements at different values of the flux. One sees that in this case there are stronger dependencies of the vibrational frequencies and of atomic distortion on the magnetic flux.

At half of the flux quantum the equilibrium distortion x_0 is practically equal to zero. On the other hand, at

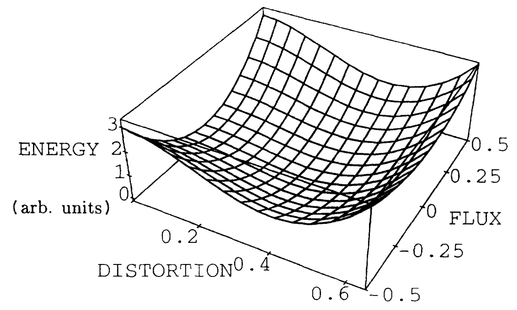

FIG. 5. The surface of potential energy for an odd number of fermions on the ring C_{60} near half filling in E-x-f (energy-distortion-flux) space. We choose $N_e=29$. The constant $p=0.045$.

zero flux x_0 is equal to 0.25 (see Fig. 4). The vibrational frequency, which is the curvature at the points of minima, increases with increasing flux from $f=-0.5$ until the value of the flux $f=0$ has been reached. Then the frequency again decreases with increasing flux (see Fig. 4). For the odd number of fermions the frequency behavior on the magnetic flux is shifted by half of a flux quantum (see Fig. 5). For the filling factor ρ_{large} which is larger than half filling the picture is the same as for the case of low filling ρ_{low}, hence displaying a symmetry: The system with ρ_{large} has the same properties as the system with $\rho_{\text{low}}=1-\rho_{\text{large}}$.

V. DISCUSSION

So far, we have considered the model of spinless fermions. The main results are unaffected if we will take into account the spin of electrons. The main difference is that there now will be four different cases instead of two for spinless fermions (cases of even and odd numbers of fermions). This means that in the case of real electrons the properties of the ring will be changed with period in filling factor, which is equal to 4.

For example, let us consider the case of vibrations at zero equilibrium distortions. For the case of one electron on the ring the vibrational frequency will decrease with magnetic field. For case of two electrons on the ring the frequency will also decrease with increasing magnetic field. The decrease in the latter case will be deeper than for the case of one electron on the ring. For three electrons on the ring we will have a linear increase of the frequency with increasing magnetic field. The maximum effect of this linear increase of the frequency will arise in the case of four electrons.[26] For the case of five electrons the vibrational frequency will also increase, but with the smaller slope than in the case of four electrons. For six electrons we recover the same situation as for the case of two electrons.

With increasing electron filling, the increase and the decrease of the vibrational frequency will occur periodically. As a result, this periodicity can be represented by the following simple formula: $N_e=4n+2$, where N_e is the number of electrons on a ring and n is the period number. This is reminiscent of the "Hückel rule." It is interesting that the properties of the carbon clusters C_n also satisfy this rule.[11] In this case the number n is the number of carbon atoms in the cluster C_n. This effect exists also for a ring with more complicated elementary cells (two-atom or multiatom cells). A similar classification exists also with the Peierls distortions $\Delta\neq0$.

Generally speaking this effect is similar to the Kohn effect in crystals.[27] For the Kohn anomaly, the frequency of the acoustic mode is softened when the quasimomentum of the phonon is equal to an extremal diameter of the Fermi surface. At this point the group velocity goes to infinity. In our case we do not have a Fermi energy, but an analogous role is played by the number of particles (in the grand-canonical ensemble). The change of the magnetic field induces transitions between states with different orbital quantum numbers. Such transitions are reflected in the dependence of the total energy on the magnetic field as cuspidal maxima and, correspondingly, in the dependence of phonon frequency on the magnetic field as cuspidal minima (see Figs. 1–4). On the other hand, from this analogy we may arrive at another important conclusion: With any current in the system there should be associated a change in the phonon frequency.

Excluding the magnetic field f from the dependencies of the current $j(f)$ and of the vibrational frequency shift $\Delta\Omega(f)$ with the aid of the method of dimensions, one may get the following rough estimate:

$$\Delta\Omega\sim j^2 r k_F/\sigma \ , \tag{16}$$

where j is an electron current through the sample, which is proportional to applied field E (Ohm's law: $j=\sigma E$), σ is the conductivity, which may be estimated with the Drude formula, k_F is the Fermi momentum, and τ is the collisional relaxation time. One sees that for systems with the Drude type conductivity, where σ is proportional to τ, the frequency shift depends only on electron density. The current's dependence obtained reminds one of a Stark effect. One see that the effect increases with increasing conductivity σ. Our estimations show that in the case of a linear current for copper metal at 6 K the effect of the frequency shift is too small but it may increase at the transition in a superconducting state. Thus, the effect may be observable at superconducting transitions.

For normal metals the effect means simply that under an electric field the Fermi energy will be shifted, inducing a change in the phonon spectrum. For a system of finite size, for example, for a polymeric chain, the optical frequency will depend on the current through the chain. The softening of the vibrational frequency will depend on the filling factor, i.e., on the total number of electrons on the chain.

For a symmetrical vibrational mode of the ring the frequency does not depend on the magnetic field. In this case there is a static nonzero displacement of atoms, which is proportional to the magnetic field. It can be explained by the presence of the Lorenz force acting on moving electrons.

For experimental investigation of the effect found it is important to understand the influence of the temperature. It is clear that the Peierls nonzero equilibrium distortions may disappear as the temperature increases. However, the frequency change under the magnetic field will still survive, as we have obtained in Sec. III. Therefore the observation of the present effect may be prevented only by the thermal dispersion of the phonon lines. On the other hand, the single ring is strictly not in the thermodynamic limit because of its finite size. The temperature, which may be introduced, is the temperature of some thermal reservoir, for example the substrate on which the ring is located, or this may be the temperature of a gas of cyclic molecules. The calculation of the partition function will depend on the system and how the temperature is introduced. This consideration is beyond the scope of the present work.

VI. RELATED EXPERIMENTS

There is a long-standing problem of a persistent current on a ring, which, in the past, has been studied theoretically very extensively. On the other hand, there is only one single experiment proving the existence of such persistent current.[15] In this experiment 10^7 mesoscopic copper rings have been located in a plane, in a transverse magnetic field. Based on the effect found in the present work, one may predict that a shift of optical-phonon frequencies for copper rings in magnetic field[15] should also oscillate with a change of external magnetic flux with period $T=\frac{1}{2}$ in units of the elementary flux quantum. Clearly half of these rings have an even number of electrons. The value of the phonon frequency on these rings will oscillate with period one unit, having cuspidal minima at integer flux quanta [see Figs. 1(b)–3(b)]. The other half of the rings will have an odd number of electrons. The phonon frequency will also oscillate with period one unit with increasing magnetic field, having cuspidal minima at half-odd integer flux quanta [see Figs. 1(a)–3(a)]. Therefore, on average, for the whole assembly of rings the period of the frequency change in magnetic field will be equal to $\frac{1}{2}$. Thus the existence of the persistent current can be proven by a measurement of the phonon frequencies in a magnetic field.

The effect of the change of the frequency of the vibrations in a magnetic field allows one to follow the value of the orbital currents on a ring by measuring the frequency shift in the Raman scattering. We propose the following experiment. First, place the cyclic molecules or quantum dots in a transverse magnetic field. It may be some plane with a lattice of quantum dots. The magnetic field will induce an orbital current. Next remove the field. Without the magnetic field the orbital current will be damped with a characteristic relaxation time, which is long in comparison with the frequency of vibrations. This relaxation time may be measured by Raman scattering. One should measure a line shift of frequency as a function of time after the removal of the magnetic field. The observation of a line shift would prove the existence of the persistent current, which has been proposed in many theoretical investigations (see Refs. 13, 14, 16–18, and references therein) but still there is only one single experiment giving evidence of its existence.[15]

Thus, we have observed a correlation between the value of the orbital current and the value of the frequency of the vibrations. We believe that this correlation can be a powerful tool for the detection of molecular and orbital currents, which are important, for example, in future molecular-electronics design work. Since we have limited our considerations to planar geometry, we have not considered in the present paper the spherical C_{60} fullerene molecule. Of course, there all the effects demonstrated are expected to exist also.

Note added. Very recently I became aware that the shift of the phonon frequency with filling factor x for some optical phonons in the fullerides A_xC_{60} that we discussed has been found independently also by Varma and already observed experimentally in Raman spectra.[28]

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[26] For electrons with spin, the situation is more complicated when electron-electron interactions are taken into account. For example, with four noninteracting electrons there are six degenerate ground states (two triplets and four singlets). For interacting electrons in the Hartree-Fock approximation, the

triplet, which has zero orbital current, will be the lowest and there will be zero first-order perturbation by an applied magnetic field. However, in many or most cases, one of the singlets may be the lowest when correlation effects are taken into account. It is clear that in any event, the energy splittings among these states due to electron-electron interactions will be dominant over magnetic-field effects if the magnetic field is weak enough. Therefore in the cases of electron-electron interactions, the qualitative picture of the dependence of the energy or the vibrational frequency on the magnetic flux and/or on filling will depend on factors that have not been thoroughly and systemically investigated.

[27] J. Hajdu (private communication).

[28] C. Varma (private communication).