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Cyclic hydrocarbons: nanoscopic (π)-SQUIDs?

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Abstract. A nonperturbative method for calculating persistent currents in molecules and nanoscopic quantum rings is presented. Starting from the extended Hubbard model on a ring threaded by an Aharonov-Bohm flux, a feedback term through which the current can generate magnetic flux is added. Another extension of the Hamiltonian describes the energy stored in the internally generated field. This model is evaluated using exact diagonalization and an iterative scheme to find the minima of the free energy with respect to the current. The magnetic properties due to electron delocalization of conjugated hydrocarbons like benzene [magnetic anisotropy, magnetic susceptibility exaltation, nucleus-independent chemical shift (NICS)] — that have become important criteria for aromaticity — can be examined using this model. A possible novel mechanism for a permanent orbital magnetic moment in quantum rings analogous to the one in π-SQUIDs is found in the framework of the proposed model. The quantum rings must satisfy two conditions to exhibit this kind of permanent orbital magnetic moment: a negative Drude weight and an inductivity above the critical level.

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1 Introduction

1.1 Aromaticity and ring currents

Organic semiconductors have gained a lot of attention during recent years. Organic thin film transistors with the highest mobilities of electrons can be built from pentacene [1], an aromatic molecule that consists of five benzene rings. For the development of molecular electronics [2], molecules with delocalized π-systems seem most promising [3]. The objective of this article is to investigate the magnetic properties of these aromatic molecules, specifically those properties originating from ring currents.

There is no unique definition of the property "aromaticity". Several physical, geometrical and chemical criteria (e.g., magnetic properties, equality of bond lengths, a particularly pleasant smell, a predisposition to nitration and sulphonation and a strong delocalization of spin) have been used to classify molecules as aromatic at different times. Therefore, there has been much confusion over the precise meaning and definition. For a review on aromaticity and its relation to ring currents see the recent articles of Lazzeretti [4], Gomes, and Mallion [5].

The ring-current model was proposed in 1936 by Pauling [6] to explain the experimental fact that the magnetic "susceptibility ellipsoids of the aromatic molecules are found to be approximately prolate ellipsoids of revolution, with the long axis normal to the plane of the molecule". In 1961, the effect of the ring current on the chemical shift of proton resonance spectra [7] led to the suggestion that this effect should be a criterion of aromaticity [8]. The magnetic field that the ring current in an aromatic ring generates enhances the magnetic field at the proton locations outside the ring and diminishes the field inside the ring. These substances are called "diatropic", in contrast to paratropic rings that enhance the magnetic field in their interior [9]. There is a clear correlation between diatropic and aromatic substances on the one hand and paratropic and antiaromatic substances on the other.

Today there is overwhelming evidence that aromaticity can be uniquely defined through magnetic properties. For example, the magnetic anisotropy [10] and the magnetic susceptibility exaltation [11,12] (defined as the difference between the magnetic susceptibility for the observed compound and the value estimated for the hypothetical system without cyclic electron delocalization) are used as a criterion along with the nucleus-independent chemical shift (NICS) [13] that has been proposed as the major criterion for aromaticity [14]. However, the NICS is a theoretical criterion that is by definition not observable.

There are many ab-initio methods for calculating chemical shifts for NMR spectroscopy; for a good review see, e.g., reference [15]. All of these methods are linear approximations for small fields. Of course, a linear response

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current cannot describe the system's behavior in arbitrarily high external magnetic fields. The response current should show a periodicity with respect to the number of flux quanta threading the ring [16]. This periodicity will be destroyed due to Zeeman splitting of the electronic energies and spin flipping. Therefore, a highly nonlinear dependence of the current with respect to large enough external fields is expected. To force a flux quantum inside a benzene molecule — a hexagon with a side length of 140 pm — one would need an extremely high magnetic field of 8×10^4 T. However, we do not intend to describe such high values of magnetic field within the approximation scheme discussed in this paper. The Zeeman interaction of the electron spins with the magnetic field is neglected, which is rigorously correct for a quantum ring threaded by a flux tube but is an approximation for quantum rings in homogeneous magnetic fields. In this paper we are primarily interested in the orbital magnetic effects of quantum rings.

1.2 The connection to SQUIDs

The comparison between superconductors and aromatic molecules has been made very frequently in the literature. F. London was the first to compare the diamagnetism of aromatic molecules to the diamagnetism of superconductors [17]. Haddon called for a combined effort of chemists and physicists to explain the precise similarities between superconducting currents and the persistent currents in aromatic molecules [18].

There is an interesting similarity between the phase coherence of the superconducting wave function in a ring and the wave function of the π-electrons in aromatic molecules. The reaction of the superconducting wave function in a superconducting ring with a Josephson junction and the wave function of the π-electrons in aromatic molecules to a magnetic flux through the ring is essentially the same. While the superconducting wave function accumulates a phase

$$\phi = 2\pi \frac{2e}{h} \Phi \tag{1}$$

due to the flux Φ it encloses, the wave function of the electrons in an aromatic molecule gathers a phase shift of

$$\phi = 2\pi \frac{e}{h} \Phi. \tag{2}$$

Another similarity between superconducting rings with a junction and molecules with delocalized π-systems is the shape of the free energy with respect to the external magnetic flux. Whereas superconducting rings with a conventional Josephson junction and aromatic molecules possess a minimum of the free energy at zero external flux, superconducting rings with a π-junction [19,20] and antiaromatic molecules possess a maximum of the free energy at zero external flux. Going through a π-junction, the supercurrent accumulates a phase shift of π. In d-wave superconductors, a π-junction can be realized by joining differently oriented grain boundaries.

1.3 The Hubbard model and its extensions

The electrons in (anti)aromatic hydrocarbons move through a delocalized π-system. However, due to the Coulomb interaction of the positively charged cores of the carbon atoms, the probability of finding an electron is peaked at the sites of the carbon atoms. This leads to an effective tight-binding model. In combination with a local interaction, this leads to the semi-empirical descendants of the Hubbard model that are used in this paper.

According to Hückel, a planar, monocyclic, completely conjugated system is aromatic if the ring contains $4n + 2$ delocalized π-electrons [21]. Antiaromatic rings contain $4n$ π-electrons. This effect occurs in the Hubbard model, where half-filled finite rings with $4n$ lattice sites possess a negative Drude weight, leading to paramagnetic ring currents, and half-filled rings with $4n + 2$ lattice sites are diamagnetic [22].

We present a nonperturbative method for calculating ring currents in the framework of strongly correlated electronic systems. For reasons of simplicity, we neglect the effect of the interaction of the spins of the electrons with the magnetic field itself (anomalous Zeeman effect) and only consider an Aharonov-Bohm type vector potential threading the ring. The vector potential just generates a phase shift of the wave function.

We extend the kinetic energy part of the model to include a feedback of the ring current to the magnetic flux in Section 2.1. The total magnetic flux through the ring is thus evaluated as the sum of the external flux and the internal flux generated by the ring current. The strength of the feedback can be adjusted by the inductivity of the ring. In Section 2.2 an iterative solution scheme for the model is developed. This scheme minimizes the free energy with respect to the current in the ring (Sect. 2.3). In Section 2.4 we determine the critical inductivity above which a system can in principle have a permanent orbital magnetic moment. The theory of Section 2 is applied to physical systems in Section 3. A test of the developed model is the application to benzene in Section 3.2. The magnetic susceptibility due to ring currents is evaluated. Another example shows a possible new mechanism for the occurrence of a permanent orbital magnetic moment in Section 3.3.

2 Method

2.1 The model Hamiltonian

We use semi-empirical one-band models with only nearest-neighbor hybridization t to describe the π-electrons of cyclic hydrocarbons, for example, the Hubbard model, the extended Hubbard model, or the Pariser-Parr-Pople (PPP) model. These models are described by the Hamiltonian

$$\mathrm{H} = -t \sum_{l\sigma} \left(\mathrm{c}^{\dagger}_{l+1,\sigma}\, \mathrm{c}_{l,\sigma} + \mathrm{c}^{\dagger}_{l,\sigma}\, \mathrm{c}_{l+1,\sigma} \right) + U \sum_{l} \mathrm{n}_{l\uparrow}\, \mathrm{n}_{l\downarrow} + \frac{1}{2} \sum_{l \neq m} V_{lm}\, \mathrm{n}_l\, \mathrm{n}_m, \tag{3}$$

where $\mathrm{c}^\dagger_{l\sigma}$ creates an electron with spin σ on site l, $\mathrm{n}_{l\sigma} = \mathrm{c}^\dagger_{l\sigma}\,\mathrm{c}_{l\sigma}$, and $\mathrm{n}_l = \mathrm{n}_{l\uparrow} + \mathrm{n}_{l\downarrow}$. The sums are taken over all N sites, and periodic boundary conditions are used. The Coulomb interaction between the electrons is modeled by an on-site repulsion U and by a long-range repulsion V_{lm} (which is zero for the Hubbard model). The extended Hubbard model also includes a nearest-neighbor repulsion ($V_{lm} \neq 0$ for $|l-m| = 1$). In the PPP model, the Coulomb repulsion can be parameterized by the Ohno [23] potential with a dielectric constant $\epsilon_r > 1$ [24]:

$$V_{lm} = \frac{U}{\epsilon_r \sqrt{1+\zeta r_{lm}^2}}, \tag{4}$$

where we choose

$$\zeta = \left(\frac{U}{1.4397\,\mathrm{nm\ eV}}\right)^2, \tag{5}$$

in order that $V_{lm} \to e^2/4\pi\epsilon_0\epsilon_r r_{lm}$ as $r_{lm} \to \infty$ [25]. The dielectric constant originates from the screening of the π-electrons by the σ-electrons and from screening effects from the environment.

In these models, the twist of the phase in the wave function in the presence of an Aharonov-Bohm flux can be partitioned into phase shifts for every hopping process. Therefore, the kinetic energy part of the Hamiltonian is modified with the usual Peierls phase factor $\exp(\frac{2\pi i}{N\phi_0}\phi_{\mathrm{ext}})$, where $\phi_0 = h/|e|$ is the flux quantum. In natural units ($e = c = \hbar = k_B = 1$) the unit of energy is 1 eV and the flux quantum equals 2π. The Hamiltonian presented in equation (10) below is the Hamiltonian needed to calculate the Drude weight D, which is identical to the *dc* conductivity of an electronic system in the thermodynamic limit. However, for small rings, the quantum nature of the system could lead to equilibrium persistent currents, leading the concept of conductivity ad absurdum. Persistent currents may occur in systems with two minima in the ground-state energy E_0, with respect to the external flux. The curvature of the ground-state energy between those minima is negative, leading to a negative Drude weight [22,26].

If the system is given the opportunity to generate an internal flux itself, by letting a persistent current

$$j = -\frac{\partial \mathrm{H}}{\partial \phi_{\mathrm{ext}}} \tag{6}$$

flow, the system falls into the minimum of the ground-state energy with respect to the internally generated flux

$$\phi_{\mathrm{int}} = Lj. \tag{7}$$

In order to be able to formulate a simple model Hamiltonian for ring currents, we assume the inductivity L — which depends only upon the geometry of the system — to be a valid concept down to the scale of organic molecules. This approximation corresponds to the neglect of quantum fluctuations in the calculation of the internally generated flux. The inductivity is a fit parameter in our calculations; it can only be roughly estimated for molecules. The internal flux leads to an additional phase shift represented by the unitary phase-shift operator

$$P \equiv e^{-\frac{i}{N}L\,j}. \tag{8}$$

The current operator appears in the exponential because the eigenstates carry different quantities of current, leading to a different phase shift for different eigenstates.

The energy that is stored in the internal magnetic field of an electronic quantum ring, e.g., a cyclic hydrocarbon,

$$\frac{L}{2}\,j^2, \tag{9}$$

must be added to the model under consideration. This term boosts the eigenenergies of the current carrying eigenstates.

The complete Hamiltonian is now given by:

$$\begin{aligned}\mathrm{H} = -t\sum_{l\sigma}\Big[&e^{\frac{i}{N}(\phi_{\mathrm{ext}}+L\,j)}\,\mathrm{c}^\dagger_{l+1,\sigma}\,\mathrm{c}_{l,\sigma}\\ &+\mathrm{c}^\dagger_{l,\sigma}\,\mathrm{c}_{l+1,\sigma}\,e^{-\frac{i}{N}(\phi_{\mathrm{ext}}+L\,j)}\Big]\\ &+U\sum_l \mathrm{n}_{l\uparrow}\,\mathrm{n}_{l\downarrow} + \tfrac{1}{2}\sum_{l\neq m} V_{lm}\,\mathrm{n}_l\,\mathrm{n}_m + \tfrac{1}{2}L\,j^2\,.\end{aligned} \tag{10}$$

This Hamiltonian is motivated by the free energy of superconducting rings with a conventional or a π-junction given in reference [19]. The approach of reference [19] is based on earlier work by Silver and Zimmermann (1967) and by Bulaevskii et al. (1977) [27,28]. We reemphasize that our model (10) is semi-phenomenological (i.e., not fully microscopic) in nature, since it is based on the concept of an inductivity, see equation (7). Note that the Hamiltonian depends explicitly on ϕ_{ext} and on the current operator: $\mathrm{H} = \mathrm{H}(\phi_{\mathrm{ext}}, j)$. Accordingly, we will in the following calculate partial derivatives of H with respect to ϕ_{ext} or j, while keeping the other variable fixed. Once the Hamiltonian is known, the free energy of the ring follows as $F = -\beta^{-1}\ln\mathrm{tr}(e^{-\beta\mathrm{H}})$.

Let us simplify the notation by introducing operators for the sum of leftward hopping and the sum of rightward hopping terms as well as for the interaction:

$$\begin{aligned}C &\equiv -te^{-\frac{i}{N}\phi_{\mathrm{ext}}}\sum_{l\sigma}\mathrm{c}^\dagger_{l,\sigma}\,\mathrm{c}_{l+1,\sigma}\\ &= -te^{-\frac{i}{N}\phi_{\mathrm{ext}}}\sum_{k\sigma}e^{ik}\,\mathrm{n}_{k\sigma},\\ C^\dagger &= -te^{\frac{i}{N}\phi_{\mathrm{ext}}}\sum_{l\sigma}\mathrm{c}^\dagger_{l+1,\sigma}\,\mathrm{c}_{l,\sigma},\\ W &\equiv U\sum_l \mathrm{n}_{l\uparrow}\,\mathrm{n}_{l\downarrow} + \tfrac{1}{2}\sum_{l\neq m}V_{lm}\,\mathrm{n}_l\,\mathrm{n}_m\,.\end{aligned} \tag{11}$$

The kinetic energy can then be expressed as

$$K = C\,P + P^\dagger\,C^\dagger \tag{12}$$

and the current operator is

$$j = -\frac{\partial \mathrm{H}}{\partial \phi_{\mathrm{ext}}} = \frac{i}{N}\left(C\,P - P^\dagger\,C^\dagger\right), \tag{13}$$

so that the entire Hamiltonian can be written as $H = K + W + \frac{1}{2}Lj^2$. The kinetic energy and the current are obviously Hermitian operators. Although it is difficult to prove rigorously, it is physically obvious that the kinetic energy and the current are diagonal in momentum space. Consequently, any two operators from the set $\{C, C^\dagger, P, P^\dagger, j, K\}$ commute with each other.

2.2 Iterative scheme

The current operator is defined implicitly to be the current operator that minimizes the free energy resulting from the model Hamiltonian (10) for fixed ϕ_{ext}. The metastable current states are found as the local minima of the free energy. We will derive a solution scheme of the model in this section. The current operator will be determined iteratively. We first state the iterative scheme and afterwards prove that it minimizes the free energy with respect to the current operator.

Before starting the iteration ($n = 1$), we choose the current to be

$$j_{(0)} = 0. \tag{14}$$

The iterative scheme is the search for a fixed point of the current operator:

$$\begin{aligned} P_{(n)} &= e^{-\frac{i}{N} L\, j_{(n-1)}} \\ j_{(n)} &= -\frac{\partial\, \mathrm{H}}{\partial \phi_{\text{ext}}} = \frac{i}{N}\left(C\, P_{(n)} - P^\dagger_{(n)}\, C^\dagger\right). \end{aligned} \tag{15}$$

The corresponding fixed-point equation is

$$j = G(j) \equiv \frac{i}{N}\left[C\, P(j) - P^\dagger(j)\, C^\dagger\right]. \tag{16}$$

Thus, the current operator is determined without linearizing the Hamiltonian with respect to the external field. In momentum space, we may think of the above equations as $\dim(\mathcal{H})$ uncoupled equations for the eigenvalues of the operators instead of the operators themselves, because of diagonality.

In the following, we show that the free energy is minimized with respect to the current operator by the iterative scheme. In fact, every single energy eigenvalue is minimized. In momentum space, the alternation of the eigenvalues due to a change in the current operator is determined by the diagonal elements of the matrix representing the Hamiltonian. The off-diagonal matrix elements correspond to the interaction of the electrons and are independent of the current operator.

2.3 Minimization of the free energy

The iterative solution scheme of the last subsection would be useless, if it were to minimize the diagonal elements of the Hamiltonian matrix in momentum space. Here, we will show that the current operator, minimizing the diagonal elements of the Hamiltonian in momentum space, also minimizes the eigenvalues of the Hamiltonian and therefore the free energy, provided the Hamiltonian is nondegenerate.

Assuming the minimal diagonal elements of the Hamiltonian matrix in momentum space were found, every other possible Hamiltonian matrix could be described by the sum of the minimal Hamiltonian matrix and a positive semidefinite matrix. Any deviation from the minimal Hamiltonian matrix would lead to an increase of some eigenvalues while others remain constant. In Section 2.4 we develop a criterion under which the iterative scheme converges and minimizes the diagonal elements of the Hamiltonian in momentum space.

In the notation defined above, the Hamiltonian can be written as:

$$\mathrm{H} = C\, P + P^\dagger\, C^\dagger + \frac{1}{2} L\, j^2 + W\,. \tag{17}$$

The first three terms are diagonal in momentum space with diagonal entries composed of the eigenvalues of the hopping, phase-shift, and current operator (C^κ, P^κ, j^κ). Let the eigenstates of the noninteracting many-particle system in momentum space be $|p^\kappa\rangle$ with $\kappa \in \{1, \ldots, \dim\mathcal{H}\}$. The derivative

$$\frac{\partial\, \mathrm{H}_{\kappa\xi}}{\partial\, j^\zeta} = \delta_{\kappa\xi}\delta_{\xi\zeta} L \left\{\frac{i}{N}\left[(P^\kappa)^*(C^\kappa)^* - C^\kappa\, P^\kappa\right] + j^\kappa\right\} \tag{18}$$

of the Hamiltonian with respect to the current eigenvalues j^ζ must vanish:

$$\frac{\partial\, \mathrm{H}_{\kappa\xi}}{\partial\, j^\zeta} = 0, \quad \forall \kappa, \xi, \zeta \in \{1, \ldots, \dim\mathcal{H}\}. \tag{19}$$

This condition is necessary for the elements of the Hamiltonian matrix in this representation to have minima and is automatically fulfilled if the iterative scheme converges, see equations (15) and (16). It is sufficient for the existence of minima that the second derivatives of $\mathrm{H}_{\kappa\xi}$ with respect to the current eigenvalues are positive:

$$\begin{aligned} \frac{\partial^2\, \mathrm{H}_{\kappa\xi}}{\partial (j^\zeta)^2} &= \delta_{\kappa\xi}\delta_{\xi\zeta} L \left\{1 - \frac{L}{N^2}\left[C^\kappa\, P^\kappa + (P^\kappa)^*(C^\kappa)^*\right]\right\} \\ &> 0, \quad \forall \kappa = \xi = \zeta \in \{1, \ldots, \dim\mathcal{H}\}. \end{aligned} \tag{20}$$

Since the off-diagonal elements of the Hamiltonian are independent of the current eigenvalues, the second derivative (20) is diagonal in the indices ($\kappa\xi$).

We assume that the current $j_{(\infty)}$ minimizes the diagonal elements of the Hamiltonian. Any deflection of the current from this position corresponds to a small perturbation of the Hamiltonian with a positive semidefinite matrix M. The Hamiltonians from previous iterations in general exhibit larger diagonal elements than the converged Hamiltonian $\mathrm{H}_{(\infty)}$ in momentum space:

$$\mathrm{H}_{(n)} = C\, P_{(n)} + P^\dagger_{(n)}\, C^\dagger + \frac{L}{2}\, j^2_{(n)} + W \tag{21}$$

$$\begin{aligned} \mathrm{H}_{(n)} - \mathrm{H}_{(\infty)} = M &= \operatorname{diag}\left(d^1, \ldots, d^{\dim\mathcal{H}}\right), \\ &\forall 1 \le l \le \dim\mathcal{H}\colon d^l \ge 0. \end{aligned} \tag{22}$$

Adding a diagonal matrix to a normal matrix changes the eigenvalues within well-defined boundaries. So for every eigenvalue $E^{\kappa}_{(\infty)}$ of $\mathrm{H}_{(\infty)}$ there is an eigenvalue $E^{\kappa}_{(n)}$ of $\mathrm{H}_{(n)}$ with

$$|E^{\kappa}_{(\infty)} - E^{\kappa}_{(n)}| \leq \|M\| = \max_{l} |d^{l}|. \tag{23}$$

Therefore, the eigenvalues of the Hamiltonian lie within disks around the eigenvalues of the nth approximation to the Hamiltonian, if the iterative scheme converges. For the special case of the Hermitian Hamiltonian and the *real* diagonal perturbation M, these disks are simple intervals. Furthermore, if the Hamiltonian is nondegenerate (so that the eigenvectors and eigenvalues are differentiable functions with respect to a small perturbation), it can be proven that the energy eigenvalues are minimal at the current $j_{(\infty)}$ because a perturbation with a *positive* semidefinite matrix M to a Hermitian matrix $\mathrm{H}_{(\infty)}$ makes the eigenvalues larger [29]. Consequently we obtain that

$$E^{\kappa}_{(\infty)} \equiv E^{\kappa}(j_{(\infty)}) \leq E^{\kappa}(j), \tag{24}$$

for all κ and for all possible current operators in some finite neighborhood of $j_{(\infty)}$. We can now partition the current space into small finite neighborhoods and extend the above calculation to a larger neighborhood of $j_{(\infty)}$. If the minimum of the diagonal matrix elements is global, the minimum of the eigenvalues is also global. The above relation (24) is only strictly valid if the Hamiltonian is nondegenerate near $j_{(\infty)}$. However, if we look at the maximally degenerate case of zero interaction, the eigenvalues of the Hamiltonian are identical to the diagonal matrix elements. Equation (24) also holds trivially in that case. Therefore, there is strong evidence that the following statement is always true: the minima of the eigenenergies of the system with respect to the current are the eigenvalues of the Hamiltonian whose diagonal matrix elements are minimized in momentum space. The minimal diagonal matrix elements are found if the two criteria (19) and (20) are matched.

2.4 The critical inductivity

The convergence of the iterative scheme is investigated here. Below a certain bound of the inductivity, the critical inductivity, the iterative solution scheme converges to one fixed point of the current operator. Above the critical inductivity, more than one fixed point for the current operator can be found. The critical inductivity is therefore a very important point at which the physical characteristics of quantum rings change dramatically.

The condition (19) is automatically fulfilled if the iterative scheme (15) converges. A criterion for the convergence of the sequence of currents is the Banach fixed-point theorem. We apply it to determine the parameter range for which there is only one stable current state for each external flux.

The operator G in the fixed-point equation (16) fulfills a Lipschitz condition:

$$\|\mathrm{G}(j_2) - \mathrm{G}(j_1)\| \leq g\,\|j_2 - j_1\|. \tag{25}$$

It is called a contraction if $0 \leq g < 1$. The operator G is diagonal and Hermitian in momentum space. Therefore it is considered as a simple continuously differentiable function G: $\mathbb{R}^{\dim \mathcal{H}} \longrightarrow \mathbb{R}^{\dim \mathcal{H}}$. We derive an estimation for the smallest possible Lipschitz constant of G in the following. Let $\frac{\partial \mathrm{G}}{\partial j}$ be the Jacobian matrix of the operator G:

$$\begin{aligned} \left(\frac{\partial \mathrm{G}}{\partial j}\right)_{\kappa\xi} &\equiv \frac{\partial \mathrm{G}^{\kappa}}{\partial j^{\xi}} \\ &= \delta_{\kappa\xi} \frac{L}{N^2} \left[C^{\kappa}\, P^{\kappa} + (P^{\kappa})^{*} (C^{\kappa})^{*}\right], \end{aligned} \tag{26}$$

with

$$\begin{aligned} \|\mathrm{G}(j + \Delta j) - \mathrm{G}(j)\| &= \left\| \int_0^1 \frac{\partial \mathrm{G}}{\partial j}(j + t\Delta j) \cdot \Delta j \, dt \right\| \\ &\leq \int_0^1 \left\| \frac{\partial \mathrm{G}}{\partial j}(j + t\Delta j) \right\| \|\Delta j\| dt \\ &\leq \left(\sup_{0 \leq t \leq 1} \left\| \frac{\partial \mathrm{G}}{\partial j}(j + t\Delta j) \right\| \right) \|\Delta j\|. \end{aligned} \tag{27}$$

The smallest possible global Lipschitz constant can be estimated as:

$$\begin{aligned} g &= \sup \|\frac{\partial \mathrm{G}}{\partial j}\| \\ &= \frac{L}{N^2} \sup \|C\,P(j) + P^{\dagger}(j)\; C^{\dagger}\| \\ &\leq \frac{L}{N^2} \left(\|C\| + \|C^{\dagger}\|\right) \\ &= \frac{2L}{N^2} |\lambda_{\max}(C)|. \end{aligned} \tag{28}$$

The Hermiticity of j, unitarity of P, normality of C, and the triangle inequality have been used. Here $\lambda_{\max}(C)$ denotes the complex eigenvalue of the operator C with the largest absolute value. It follows that G is a contraction ($g < 1$) if the condition

$$L < L_c = \frac{N^2}{2|\lambda_{\max}(C)|} \tag{29}$$

is satisfied. The hopping operator is diagonal in momentum space. Thus we obtain

$$L_c = \frac{N^2}{2t \max_{\kappa} |\sum_{k\sigma} e^{ik} \langle p^{\kappa}| \, \mathrm{n}_{k\sigma} \, |p^{\kappa}\rangle \, |}, \tag{30}$$

where the maximum is taken over all normalized configurations of the electrons in momentum space $|p^{\kappa}\rangle$.

The sufficient criterion (20) is also fulfilled. The supremum g of the norm of the Jacobian matrix of G is smaller than one, therefore the entries in the Jacobian matrix are also smaller than one. In terms of the Jacobian matrix the criterion (20) reads

$$\begin{aligned} \frac{\partial^2 \mathrm{H}_{\kappa\xi}}{\partial (j^{\zeta})^2} &= \delta_{\kappa\xi}\delta_{\xi\zeta} \left\{ 1 - \left(\frac{\partial G}{\partial j}\right)_{\kappa\kappa} \right\} \\ &> 0, \quad \forall \kappa = \xi = \zeta \in \{1, \ldots, \dim \mathcal{H}\}. \end{aligned} \tag{31}$$

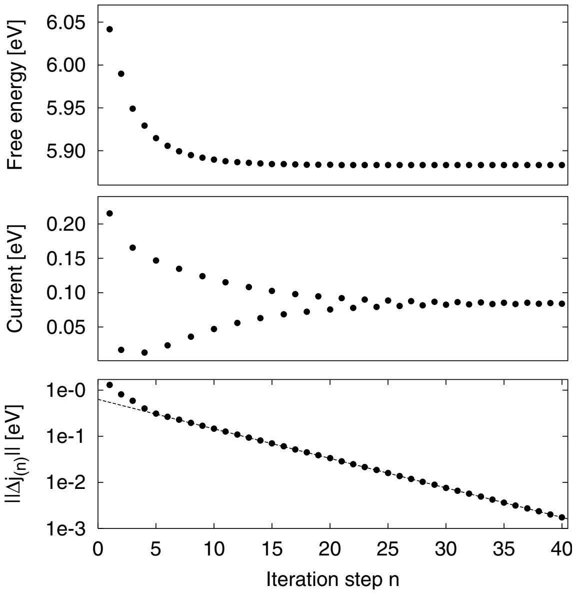

Fig. 1. Free energy, current and the difference of the norm of successive current operators on a logarithmic scale were obtained for the extended Hubbard model on 4 sites with 2 up and 2 down electrons with $t = 1$ eV, $U = 4$ eV, $V = 3$ eV, $L = 2.5$/eV, $\phi_{\text{ext}} = 1.5$ at $T = 0.01$ eV. The critical inductivity for this model is $L_c = 2\sqrt{2}/\text{eV} \approx 2.8284/\text{eV}$.

The physical essence of this result is that for inductivities smaller than the critical inductivity L_c, the current is a unique, single valued function of the external flux.

Furthermore, the expectation value of the current is an antisymmetric function of the external flux. The current operator is antisymmetric in ϕ_{ext}. This can be verified by looking at the eigenvalues of the current operator. The eigenvalues are proportional to the imaginary part of $e^{i\phi_{\text{ext}}/N}$, which is clearly antisymmetric. The density matrix of the problem is symmetric because the external flux enters the Hamiltonian only through the kinetic energy operator and the square of the current operator. Both are symmetric in ϕ_{ext}. Therefore, there is no persistent current for zero external flux [$\langle j(\phi_{\text{ext}})\rangle = 0$ for $\phi_{\text{ext}} = 0$] and for inductivities $L \leq L_c$. States with a spontaneous orbital magnetic moment without external magnetic field are only possible for inductivities $L > L_c$.

The convergence of the scheme can be tested numerically by the operator norm of the difference of current operators of two successive iteration steps:

$$\|\Delta j_{(n)}\| \equiv \|j_{(n)} - j_{(n-1)}\| \overset{n\to\infty}{\longrightarrow} 0. \tag{32}$$

The iterative procedure may be considered to have reached convergence once the spectral norm $\|\Delta j_{(n)}\|$ drops below a certain bound. The convergence for very small rings becomes exponential in n after sufficiently many steps (see Fig. 1). The expectation value of the free energy is seen to be lowered in each iteration step while the expectation value of the current reaches its equilibrium value.

2.5 Modification for large inductivities

Above the critical inductivity, the iterative scheme does not converge in general. This can occur for certain values of the external flux. In this case, there is more than one stable current state. Since the current operator and the phase-shift operator in equation (15) are diagonal, it is possible to reduce the scheme to $\dim\mathcal{H}$ one-dimensional searches for fixed points. For fixed points of one-dimensional functions, Hillam's theorem [30] provides an iterative scheme to find a fixed point for every single eigenvalue of the current operator. Let g^κ be the Lipschitz constant for the κth eigenvalue of the current operator [analog to Eq. (28)]:

$$g^\kappa = \frac{2L|\,C^\kappa\,|}{N^2}. \tag{33}$$

Hillam's theorem states that the iterative scheme

$$\begin{aligned} P^\kappa_{(n)} &= e^{-\frac{i}{N}L\,j^\kappa_{(n-1)}} \\ j^\kappa_{(n)} &= -\frac{2}{N}\,\mathrm{Im}(C^\kappa\,P^\kappa_{(n)}) \\ j^\kappa_{(n)} &= \lambda^\kappa\,j^\kappa_{(n)} + (1-\lambda^\kappa)\,j^\kappa_{(n-1)} \\ \Delta j^\kappa_{(n)} &= \frac{1}{\lambda^\kappa}\left(j^\kappa_{(n)} - j^\kappa_{(n-1)}\right) \end{aligned} \tag{34}$$

will converge when $\lambda^\kappa = \frac{1}{g^\kappa+1}$. The iteration starts with $n = 1$. The current eigenvalues $\{j^\kappa_{(0)}\}$ can be set in order to find different branches of the solution. A criterion for the convergence of the scheme is $\max_\kappa\left(\Delta j^\kappa_{(n)}\right) < \epsilon$. After the convergence criterion is satisfied, it still has to be verified that the current minimizes the energy eigenvalues. Consequently, the criterion

$$\min_\kappa \left|1 - \frac{2L}{N^2}\,\mathrm{Re}(C^\kappa\,P^\kappa_{(\infty)})]\right| > 0 \tag{35}$$

needs to be checked, in analogy to equation (20).

2.6 Asymptotic expansion for large inductivities, approximate solutions

We now show that asymptotically exact results for the eigenvalues of the current operator can be obtained in the limit of large inductivities ($L \to \infty$). These asymptotic results can also be extended to yield approximate expressions for the eigenvalues of the current operator, valid both for $L \to \infty$ and (at finite L) if the current is small.

From equations (11) and (13) we deduce that the implicit equations, determining the eigenvalues of the current operator, are given by

$$j^\kappa = \frac{2t\tilde{n}}{N}\sin\left[K - \frac{1}{N}(Lj^\kappa + \phi_{\text{ext}})\right]. \tag{36}$$

Here $\tilde{n}$ and K are defined by the equation

$$e^{iK}\tilde{n} = \sum_{k\sigma} e^{ik}\,\langle p^\kappa|\,\mathrm{n}_{k\sigma}\,|p^\kappa\rangle\,, \tag{37}$$

where $\tilde{n}$ is a positive real number. The kets $|p^\kappa\rangle$ denote the eigenstates of the noninteracting Hamiltonian in momentum space. We define $J^\kappa = Lj^\kappa$ so that

$$\frac{J^\kappa}{L} = \frac{2t\tilde{n}}{N}\sin\left[K - \frac{1}{N}\left(J^\kappa + \phi_{\text{ext}}\right)\right]. \qquad (38)$$

The reason for the introduction of J^κ (rather than j^κ) is that J^κ remains finite in the limit $L \to \infty$. Expanding the solution of (38) in a power series in L^{-1}, we find that there are, in fact, infinitely many solutions for the lowest order coefficient J_0^κ in the expansion, which we label by an index m:

$$J_0^{\kappa,m} = N\left(K + 2m\pi\right) - \phi_{\text{ext}}, \quad m \in \frac{1}{2}\mathbb{Z}. \qquad (39)$$

From equations (10–12) we see that the energy eigenvalues of the non-interacting model ($U = V_{lm} = 0$) have the form

$$E^\kappa = -2t\tilde{n}\cos\left[K - \frac{1}{N}\left(J^{\kappa,m} + \phi_{\text{ext}}\right)\right] + \frac{1}{2}\frac{(J^{\kappa,m})^2}{L}, \qquad (40)$$

and it is evident from equation (39) that $J_0^{\kappa,m}$-values with $m \in \mathbb{Z}$ correspond to *minima* of the kinetic energy eigenvalues, whereas $J_0^{\kappa,m}$-values with $m - \frac{1}{2} \in \mathbb{Z}$ correspond to maxima. We focus on solutions with $m \in \mathbb{Z}$. Starting from (40), it is easy to expand the rescaled current eigenvalues $J^{\kappa,m}$ about the $L \to \infty$ limit $J_0^{\kappa,m}$. To second order in L^{-1} one finds the following remarkably simple result:

$$J^{\kappa,m}/J_0^{\kappa,m} = \sum_{n=0}^{2}\left(-\frac{N^2}{2tL\tilde{n}}\right)^n + \mathcal{O}\left(\frac{1}{L^3}\right) \qquad (L \to \infty). \qquad (41)$$

This asymptotically exact result shows that, apart from correction terms of order L^{-3}, the $J^{\kappa,m}$ are proportional to $J_0^{\kappa,m}$ and, hence, are linear functions of the external flux ϕ_{ext}.

The form of equation (41) suggests another asymptotic expansion, namely for small $J_0^{\kappa,m}$, i.e., for $\phi_{\text{ext}} \to N(K + 2m\pi) \equiv \phi_{\text{ext}}^{\kappa,m}$. The inductivity L is kept finite in this limit. The hope is to be able to complete the geometric series, the first three terms of which appear in the right hand side of equation (41). Indeed, one finds from (38):

$$J^{\kappa,m}/J_0^{\kappa,m} = \frac{2tL\tilde{n}}{N^2 + 2tL\tilde{n}} + \mathcal{O}\left[(J_0^{\kappa,m})^2\right] \quad (\phi_{\text{ext}} \to \phi_{\text{ext}}^{\kappa,m}). \qquad (42)$$

An extension of (41) and (42), valid for both $L \to \infty$ and $\phi_{\text{ext}} \to \phi_{\text{ext}}^{\kappa,m}$, is

$$J^{\kappa,m} = \frac{2tL\tilde{n}}{N^2 + 2tL\tilde{n}}J_0^{\kappa,m} - \frac{N^3(J_0^{\kappa,m})^3}{48t^3L^3\tilde{n}^3} + \mathcal{O}\left[\frac{(J_0^{\kappa,m})^3}{L^4}\right].$$

For the current eigenvalues $j^{\kappa,m} = J^{\kappa,m}/L$, this implies:

$$j^{\kappa,m} = \frac{2t\tilde{n}}{N^2 + 2tL\tilde{n}}\left[\phi_{\text{ext}}^{\kappa,m} - \phi_{\text{ext}}\right] - \frac{N^3\left[\phi_{\text{ext}}^{\kappa,m} - \phi_{\text{ext}}\right]^3}{48t^3L^4\tilde{n}^3} + \ldots, \qquad (43)$$

where the correction terms are of order L^{-5} for large inductivities ($L \to \infty$) and of order $\left[\phi_{\text{ext}}^{\kappa,m} - \phi_{\text{ext}}\right]^3$ for $\phi_{\text{ext}} \to \phi_{\text{ext}}^{\kappa,m}$. The solutions $j^{\kappa,m}$ as functions of ϕ_{ext} are sketched in Figure 2, where the leading linear behavior in (45) is indicated by solid lines and the actual solution by the dashed curves.

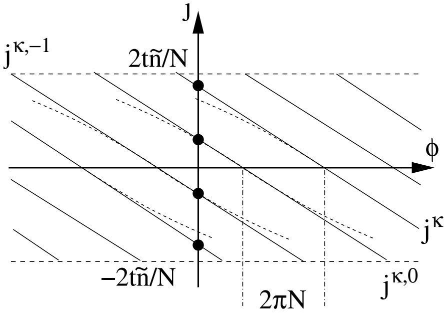

Fig. 2. Sketch of the asymptotic expansion (solid lines) and the real solution (dashed curves).

Equation (36) shows that the current eigenvalues are bounded from above and below by $|j^\kappa| \leq \frac{2t}{N}$. We thus obtain the following interpretation of Figure 2: the closer the solutions lie to the line $j = 0$, the lower is their energy, because of the $\frac{1}{2}L(j^\kappa)^2$ contribution. The real solutions jump from one m-level $j^{\kappa,m}$ to the next $j^{\kappa,m\pm1}$ or interpolate between them continuously at low inductivities.

The number of solutions N_s for $j^\kappa(\phi_{\text{ext}})$ at a given value of ϕ_{ext} can be approximated as the number of lines $j^{\kappa,m}$ intersecting the line $\phi_{\text{ext}} = 0$ in the interval $j \in [-2t/N, 2t/N]$ (circles in Fig. 2), which can be evaluated to be roughly

$$N_s = \frac{1}{2\pi}\left(2 - K + \frac{4tL\tilde{n}}{N^2}\right) + 1 \\ \overset{L\to\infty}{\approx} \frac{2tL\tilde{n}}{\pi N^2}. \qquad (44)$$

We can draw the following conclusion from the above calculations: the ring current is a finite-size effect that decreases with the reciprocal system size for all $L > 0$. The possibility to find several stable current states decreases proportionally to $1/N^2$ while growing linearly with the inductivity. The value of one particular solution $j^{\kappa,m}$ goes to zero like $1/L$ for high inductivities.

3 Numerical examination and physical consequences

In this section, we apply the proposed method to physical systems. Realistic parameters for cyclic hydrocarbon, especially the π-electrons in benzene are given and applied. The magnetic properties of benzene due to ring-current effects are evaluated.

In the last part of this section, we exhibit a system with a hysteresis loop in the magnetization with respect to the external field. The hysteresis loop is centered around the external field value of half a flux quantum in the ring. The system is a half-filled four-site Hubbard ring. The phenomenon of the hysteresis loop is not restricted to this system; it should be found in any system with a negative Drude weight. Apart from half-filled Hubbard rings, rings of noninteracting electrons with a band structure that cannot be approximated by a straight line around the Fermi points can possess a negative Drude weight. In a system with a negative Drude weight and six lattice sites, the hysteresis loop would be centered around zero external flux. Thus there would exist a spontaneous orbital magnetic moment without external magnetic field.

3.1 Realistic parameters

The work of Castleton, Bursill, and Barford [24,25] makes it seem reasonable to choose the parameters of the PPP model for benzene as follows:

$$t = 2.64\ \text{eV},\ U = 8.9\ \text{eV},\ \epsilon_r = 1.28. \tag{45}$$

This means that the on-site interaction U between electrons is actually *strong*, of the order of the bandwidth, so that non-perturbative methods (like the ones we use in this paper) must be used. We estimate the inductivity of a molecule as follows. If we take a look at the inductivity of a non-ferromagnetic classical conducting ring in vacuum of the size of a benzene molecule, we find that the inductivity

$$L = \mu_0 R \left\{ \frac{1}{4} + \left[\ln\left(\frac{8R}{r}\right) - 2 \right] \right\} \tag{46}$$

will be very small. The radius of the ring R in the above equation is about 140 pm. If the radius r of the conductor itself were about $R/5$, the inductivity would be about $L \approx 0.02/\text{eV}$ in natural units. However, the inductivity is a phenomenological parameter that has to be fitted to experiments. We try a large range of inductivities to show what kind of effects might arise because of the inductivity of a molecule or a ring of coupled quantum dots.

3.2 Benzene

The magnetic susceptibility of aromatic compounds is anisotropic. In benzene, the diamagnetic susceptibility perpendicular to the molecular plane ($\chi_\perp^{\text{mol}} = -119 \times 10^{-11}\,\text{m}^3\,\text{mol}^{-1}$) is about three times larger than the diamagnetic susceptibility parallel to the molecular plane ($\chi_\parallel^{\text{mol}} = -43.8 \times 10^{-11}\,\text{m}^3\,\text{mol}^{-1}$) [31]. With the proposed model, the total magnetic susceptibility cannot accurately be described because the influence of the core electrons is neglected. Moreover, the π-electrons are not able to move perpendicular to the plane of the molecule. Therefore, the orbital magnetic susceptibility in the plane of the benzene molecules is zero within our model. However, the part of the magnetic susceptibility that stems from the delocalization of the π-electrons — and this is the part that is important to determine the degree of aromaticity — is extracted.

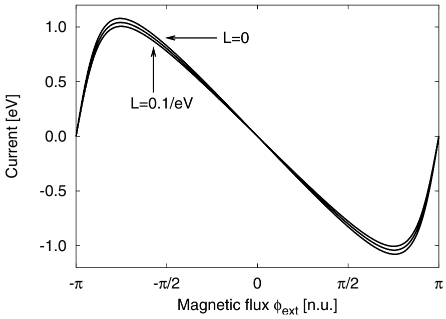

Fig. 3. Current as a function of the magnetic flux for the PPP model on 6 sites with 3 up and 3 down electrons, $t = 2.64$ eV, $U = 8.9$ eV, $\epsilon_r = 1.28$, $T = 0.025$ eV, $L = 0.0$, $0.05/\text{eV}$, $0.1/\text{eV}$ was used to model benzene.

If only the ring-current effect in benzene were anisotropic, the magnetic susceptibility anisotropy,

$$\begin{aligned} \Delta\chi^{\text{mol}} &\equiv \chi_\perp^{\text{mol}} - \chi_\parallel^{\text{mol}} \\ &= 75.2 \times 10^{-11}\,\text{m}^3\,\text{mol}^{-1}, \end{aligned} \tag{47}$$

would be a good number to test the model. But according to Pople, the ring current effect makes up only 30% of the anisotropy [32,33]. The rest is caused by van Vleck paramagnetism. Other calculations have produced different results [34]. The van Vleck paramagnetism is a local contribution that can be captured by incremental schemes that ascribe a certain amount of the total magnetic susceptibility to every atom or bond in the molecule.

This observation has led to the definition of the magnetic susceptibility exaltation as the difference between the measured susceptibility (averaged over all orientations of the molecule) and the susceptibility calculated from incremental schemes:

$$\Lambda \equiv \bar{\chi}^{\text{mol}} - \left(\sum \chi_{\text{atom,i}}^{\text{mol}} + n\chi_{C=C}^{\text{mol}} \right). \tag{48}$$

Another method to determine the magnetic susceptibility exaltation is to take the difference between the measured magnetic susceptibility of the aromatic molecule and the susceptibility of molecules built from the same atoms but without cyclic delocalization. The magnetic susceptibility exaltation should therefore be a good measure for the delocalization of electrons in a molecule. In current magnetochemistry textbooks, the value

$$\Lambda = -17.2 \times 10^{-11}\,\text{m}^3\,\text{mol}^{-1} = -13.7\,\text{ppm}\,\text{cgs} \tag{49}$$

is found for the ring-current contribution to the total susceptibility in benzene [31]. This value stems from the articles of Dauben [11,12]. It was calculated using the incremental schemes that were developed by Haberditzl, Pacault, and Hoarau. We compare it in the following with the susceptibility of our model.

The response current of benzene to an externally applied Aharonov-Bohm flux would look like that displayed in Figure 3. The data was obtained with the parameters in equation (45) and including the electron-electron interaction according to the Ohno potential in equation (4). The

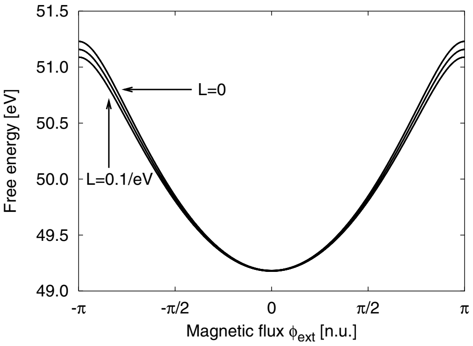

Fig. 4. The free energy as a function of the magnetic flux for the system shown in Figure 3.

diamagnetic response of benzene and the shape of the free energy in Figure 4 is reminiscent of superconducting rings with a conventional junction. The existence of a large almost linear regime around zero flux clarifies why linear approximations were so successful in explaining the magnetic response. The critical inductivity is ($t = 2.64$ eV)

$$L_c = \frac{9}{2t} \approx 1.70455/\text{eV}. \tag{50}$$

Since this inductivity is very high, we expect the effect of the inductivity to be rather small in benzene rings. The slope of the curves at zero magnetic flux was determined as $j_{L=0}(\phi_{\text{ext}}) = -\frac{1.73\ \text{eV}}{\pi}\phi_{\text{ext}}$, $j_{L=0.05/eV}(\phi_{\text{ext}}) = -\frac{1.68\ \text{eV}}{\pi}\phi_{\text{ext}}$, $j_{L=0.1/eV}(\phi_{\text{ext}}) = -\frac{1.63\ \text{eV}}{\pi}\phi_{\text{ext}}$. It should be noted that the plots are not intended to be representative of the real ring current in benzene over the whole range of flux shown in the figures. This would only be true if it were possible to create a thin flux tube threading the molecule. In that case, the anomalous Zeeman effect for the quantum ring would be rigorously zero, in accordance with our model. On the other hand, in a homogeneous magnetic field the Zeeman interaction of the electron spins with the magnetic field would be relevant; for a detailed comparison with experiment it needs to be added to the model Hamiltonian (10). However, even in this case, the spins are not polarized in the benzene molecule if the homogeneous field is sufficiently small, so that our results can still be used to extract the ring-current effect and compare this to experiment.

The molar magnetic susceptibility

$$\chi^{\text{mol}} \equiv \frac{\chi}{\rho} M_r, \tag{51}$$

is the magnetic susceptibility divided by the density of the material and multiplied by the molecular weight. In the framework of the model proposed above, the magnetic susceptibility is equal to the magnetic susceptibility exaltation

$$\Lambda = \bar{\chi}^{\text{mol}} = \frac{\mu_0}{3} \frac{jA^2}{\phi_{\text{ext}}}. \tag{52}$$

With the values of $\frac{j}{\phi_{\text{ext}}} \approx -\frac{1.73\ \text{eV}}{\pi}$ and $A = \frac{3\sqrt{3}}{2}(140\,\text{pm})^2$ we obtain

$$\Lambda = -13.3 \times 10^{-11}\,\text{m}^3\,\text{mol}^{-1}, \tag{53}$$

which agrees reasonably well with the value that was cited above [see Eq. (49)].

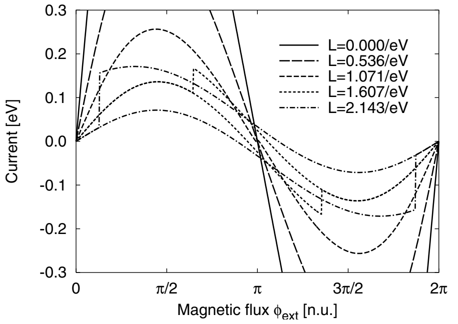

Fig. 5. Current for the Hubbard model on 4 sites with 2 up and 2 down electrons, $t = 2.64$ eV, $U = 8.9$ eV, $V_{lm} = 0$, $T = 0.01$ eV, at inductivities $L = 0, \frac{1}{2}, 1, \frac{3}{2}, 2L_c$.

3.3 Systems with negative Drude weight

Systems with a negative Drude weight were first found by Stafford [22] and Fye [26]. These systems are finite, half-filled Hubbard rings with a multiple of 4 lattice sites. As the ring reaches the thermodynamic limit, the Drude weight becomes positive semidefinite. These rings are paramagnetic and correspond to [$4n$] annulenes. The negative Drude weight is related to the paramagnetism of these substances. However, we cannot expect to capture every property of the [$4n$] annulenes with the simple Hubbard model. Bond length alternation and the long-range Coulomb interaction counteract such an oversimplified description.

In this section we simply examine the new physical features that emerge from the proposed model. There can be states with a permanent orbital magnetic moment for these systems if the inductivity is tuned to values above the critical inductivity. We have calculated a hysteresis loop centered around half a flux quantum of the external field. There are two current states reached by entering the hysteresis loop from above or below. This is shown in Figure 5. For small fields and small inductivities, the response is paramagnetic, and the overall characteristics are reminiscent of a π-SQUID, although for large inductivities, the response current of the 4-site system differs from that of a π-SQUID. The magnitude of the current becomes smaller for larger inductivities. The critical inductivity is ($t = 2.64$ eV)

$$L_c = \frac{2\sqrt{2}}{t} \approx 1.07137/\text{eV}. \tag{54}$$

States with a permanent orbital magnetic moment occur above the critical inductivity. They evolve around half a flux quantum. The free energy at $T = 0.01$ eV is plotted in Figure 6. The current in a ring that is exposed to a magnetic field is the negative first derivative of the free energy with respect to the external flux.

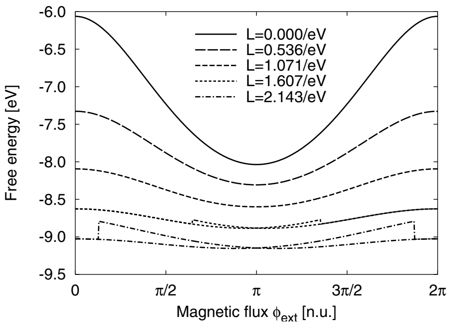

Fig. 6. Here the free energy for the current curves shown in Figure 5 is illustrated.

Although the electron interaction plays a subordinate role in the iterative scheme for the fixed point of the current operator, it is important for the occurrence of a permanent orbital magnetic moment in the 4-site system. We can ask which energy eigenstate of the noninteracting system is the first to cross from a single minimum with respect to the corresponding eigenvalue of the current operator to two minima. For the noninteracting system, the eigenenergies are

$$\mathrm{H}^{\kappa} = 2\,\mathrm{Re}\left[e^{-\frac{i}{N}Lj^{\kappa}}\,C^{\kappa}\right] + \frac{1}{2}L(j^{\kappa})^{2}. \tag{55}$$

Most of all, we are interested in the properties of the state that crosses first from one minimum to two minima as the inductivity is increased (see Fig. 7). The crossover takes place at L_c. This state has to be the state that produces the highest amplitude of the exponential term in equation (55). Occupying the single particle states $-\frac{\pi}{2}$ and π in momentum space with two electrons each yields the highest real part of the hopping operator in equation (55). Let us call this state $|\psi\rangle$. The state $|\psi\rangle$ is the state with the highest energy for the noninteracting system. Hence we expect the expectation value of the current at low temperatures not to exhibit a spontaneous orbital magnetic moment. The interaction of the electrons plays a vital role in mixing the state $|\psi\rangle$ with the ground state and thus adding a spontaneous orbital magnetic moment to the ground state (see Fig. 8). The hysteresis loop of the spontaneous orbital magnetic moment is seen to evolve for high interaction strengths. There is no hysteresis for the noninteracting system.

4 Conclusion

Based upon a model for superconducting rings with a conventional or a π-junction, we have presented a model and a nonperturbative solution scheme for one-dimensional strongly correlated electronic rings in magnetic fields. The model includes a feedback term through which the current in the ring can generate magnetic flux. Current and generated magnetic flux are coupled linearly by an inductivity. The energy of the generated magnetic field is quadratic in the current. An iterative scheme for the solution of the model has been developed.

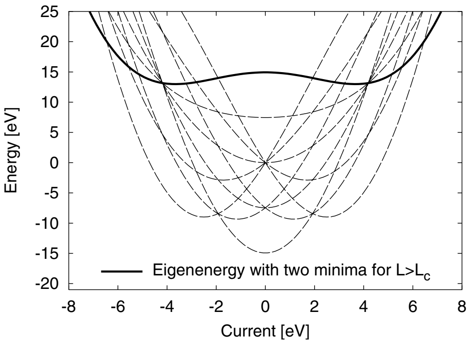

Fig. 7. The eigenenergies for the noninteracting model on four lattice sites with two up and two down electrons with respect to the corresponding eigenvalues of the current operator. The state with the highest energy is nondegenerate and crosses first from one to two minima. The inductivity chosen for the graph is $L = 1.5$ eV ($U = 0$, all other parameters taken from Fig. 5). The eigenvalues of the current operator will be adjusted by the fixed-point method so as to minimize the eigenenergies.

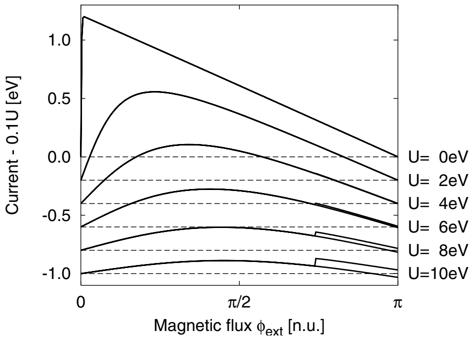

Fig. 8. The expectation value of the current at $T = 0.01$ eV for the Hubbard model on four lattice sites with two up and two down electrons. The inductivity is held constant at $L = 1.5$ eV. The on-site interaction varies from $U = 0$ eV to $U = 10$ eV in steps of 2 eV.

We have shown an example system with negative Drude weight that is paramagnetic within the framework of this solution. The paramagnetism of antiaromatic substances can thus be explained. A state with a permanent orbital magnetic moment has been found for high inductivities. This is a state where at zero external field there is a persistent current flowing through the ring, generating a magnetic moment. It is not clear whether the critical inductivities we estimated can be reached in molecules; however, it should be possible to tune the inductivity of a ring of coupled quantum dots to the desired values.

Systems with a positive Drude weight exhibit diamagnetism. These systems are, e.g., aromatic hydrocarbons. They are comparable to superconducting rings with one conventional junction.

The ring-current effect contributes to the anisotropy of the magnetic susceptibility in benzene. It has been found that the inductivity of a benzene ring should be almost negligible due to the extremely small diameter (240 pm) of the molecule. However, for an exact determination of the inductivity of the π-system of benzene, the part of the anisotropy of the magnetic susceptibility that is induced by ring currents would have to be clearly separated from the part of the anisotropy that stems from Van Vleck paramagnetism.

The proposed model has been applied to extract the ring-current contribution to the magnetic susceptibility in benzene. It should be possible to apply this method to other substances and thus establish a theoretical criterion for aromaticity. The advantage over the theoretical predictions of aromaticity from DFT calculations is the full consideration of the Coulomb interaction.

In closing, we reemphasize that our model Hamiltonian (10), despite its foundation on sound physical arguments and the analogy to superconducting rings, is semi-phenomenological in nature and not fully microscopic. Clearly, a microscopic justification of the model (10) would be both interesting and very valuable. One possible way to proceed would be to start from a microscopic action for charged matter, coupled to the radiation field, integrate out the electromagnetic field (with the exception of the external flux), and derive an effective action for interacting charges and currents in an external flux. This would be very much in the spirit of Loss's work [35,36], with one crucial difference, since one has to keep the ring finite and cannot make a Luttinger liquid assumption. A microscopic foundation of our model along these lines would clearly be a highly non-trivial undertaking and has to be set aside at this stage for future research.

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