Magnetic resonance on a ring of aromatic molecules

1991 J. Phys.: Condens. Matter 3 3199

(http://iopscience.iop.org/0953-8984/3/18/014)

J. Phys.: Condens. Matter 3 (1991) 3199–3204. Printed in the UK

LETTER TO THE EDITOR

Magnetic resonance on a ring of aromatic molecules

F V Kusmartsev

Institut für Theoretische Physik der Universität zu Köln, D-5000 Köln 41, Federal Republic of Germany
and
L D Landau Institute for Theoretical Physics, Moscow, 117940, GSP-1, Kosygina 2, V-334, USSR

Received 4 January 1991

Abstract. We have calculated exactly the spectrum of electrons on a ring in a magnetic field for the case of the Hubbard interaction between electrons. We have found that very unusual resonances occur when the flux through the ring changes. The appearance of these resonances strongly depends on the total number of electrons N. They appear when the flux changes by $\Delta f = 1/N$. In analogy with two-particle bound states one can think that on a ring with strong interactions between electrons, N-particle bound states appear. Such resonances may be found in aromatic molecules and on a ring system of singly connected quantum dots for 'Coulomb blockade' conditions.

In our previous work we have calculated the spectrum of spinless fermions located on a ring without interaction [1,2] and with interaction [3] in a transverse magnetic field. We found that for an even number of fermions on a ring there exists a flux phase state [4–10]. On the other hand interacting electrons can have a different behaviour. Namely, spin-flip processes may destroy the non-zero orbital moment which exists in the case of spinless fermions [1,2]. We show in the present letter that such processes exist and have an amusing character. They completely destroy the orbital moment so that it becomes zero. In order to demonstrate this phenomenon we will solve, using the Bethe ansatz, the Hubbard Hamiltonian having the form

$$H = -t \sum_{\langle i,j\rangle,\sigma} a^+_{i\sigma} a_{j\sigma} + U \sum_{i=1}^{L} n_{i+} n_{i-} \tag{1}$$

involving as parameters the electron hopping integral t, the on-site repulsive Coulomb potential U, and L which is the number of sites on a ring. The operator $a^+_{i\sigma}$ ($a_{i\sigma}$) creates (destroys) an electron with spin projection σ ($\sigma = +$ or $-$) at a ring site i, and $n_{i\sigma}$ is the occupation number operator $a^+_{i\sigma} a_{i\sigma}$. The summations in (1) extend over the ring sites i or—as indicated by $\langle i,j\rangle, \sigma$—over all distinct pairs of nearest-neighbour sites along the ring with the spin projection σ.

The Hamiltonian (1) models a system of M electrons with spin projection up $\sigma = +$ and $N - M$ electrons with down spin $\sigma = -$.

0953-8984/91/183199+06$03.50

For the case of the magnetic field we will use the same form of the wavefunction as has been proposed in previous works [11–18]:

$$\psi(x_1,\ldots,x_N)=\sum_P[Q,P]\exp\left(\mathrm{i}\sum_{j=1}^{N}k_{Pj}x_{Qj}\right) \tag{2}$$

where $P=(P_1,\ldots,P_N)$ and $Q=(Q_1,\ldots,Q_N)$ are two permutations of $(1,2,\ldots,N)$. The coefficients $[Q,P]$ as well as $(K_1,\ldots,K_N)$ are determined from the Bethe equations which in a magnetic field are changed by the addition of the flux phase $2\pi f$ [19, 20]

$$\exp[\mathrm{i}(k_jL-2\pi f)]=\prod_{\beta=1}^{M}\left(\frac{\mathrm{i}t\,\sin k_j-\mathrm{i}\lambda_\beta-U/4}{\mathrm{i}t\,\sin k_j-\mathrm{i}\lambda_\beta+U/4}\right) \tag{3}$$

$$-\prod_{j=1}^{N}\left(\frac{\mathrm{i}t\,\sin k_j-\mathrm{i}\lambda_\beta-U/4}{\mathrm{i}t\,\sin k_j-\mathrm{i}\lambda_\beta+U/4}\right)=\prod_{\alpha=1}^{M}\left(\frac{\mathrm{i}\lambda_\alpha-\mathrm{i}\lambda_\beta+U/2}{\mathrm{i}\lambda_\alpha-\mathrm{i}\lambda_\beta-U/2}\right). \tag{4}$$

These equations are greatly simplified in the limit $U\to\infty$. As a result we have the following equations:

$$Lk_j=2\pi\left(I_j+\frac{1}{N}\sum_\alpha J_\alpha\right)+2\pi f \tag{5}$$

where the quantum numbers I_j and J_α are connected with charge and spin degrees of freedom, respectively [21, 22]. The sets of these quantum numbers, of course, strongly depend on the magnetic flux f. They are different for even and odd numbers of particles. One can have the following classification for sets (I_j) and (J_α). For even numbers of electrons, N, and for even numbers of the up spins, M, the numbers I_j should be integer and the numbers J_α should be half-odd integer. For even numbers of electrons, N, and for odd numbers of the up spins, M, the numbers I_j should be half-odd integer and J_α should be integer. For odd numbers of electrons, N, and for even numbers of the up spins, M, the numbers I_j and the numbers J_α should also be integer. For odd numbers of electrons, N, and for odd number of up spins, M, the numbers I_j and J_α should be half-odd integer.

For example at zero magnetic field they have the following form [21, 22]: when $N=2K$ (an even number), then

$$I_1,\ldots,I_{2K}=-K,-(K-1),\ldots,-1,0,1,\ldots,K-1 \tag{6}$$

$$J_1,\ldots,J_M=-\tfrac{1}{2}(M-1),\ldots,-\tfrac{1}{2},\tfrac{1}{2},\ldots,\tfrac{1}{2}(M-1) \tag{7}$$

where M is also an even number; and

$$I_1,\ldots,I_{2K}=-K+\tfrac{1}{2},\ldots,-\tfrac{1}{2},\tfrac{1}{2},\ldots,K-\tfrac{1}{2} \tag{8}$$

$$J_1,\ldots,J_M=-\tfrac{1}{2}(M-1),\ldots,-1,0,1,\ldots,\tfrac{1}{2}(M-1) \tag{9}$$

where M is an odd number.

If $N = 2K + 1$ (an odd number) then

$$I_1, \ldots, I_{2K+1} = -K, \ldots, -1, 0, 1, \ldots, K \tag{10}$$

$$J_1, \ldots, J_M = -\tfrac{1}{2}M, \ldots, -1, 0, 1, \ldots, \tfrac{1}{2}M - 1 \tag{11}$$

where M is an even number; and

$$I_1, \ldots, I_N = -\tfrac{1}{2}N, \ldots, -\tfrac{1}{2}, \tfrac{1}{2}, \ldots, \tfrac{1}{2}N \tag{12}$$

$$J_1, \ldots, J_M = -\tfrac{1}{2}M, \ldots, -\tfrac{1}{2}, \tfrac{1}{2}, \ldots, \tfrac{1}{2}M \tag{13}$$

where M is an odd number.

In a magnetic field these sets of numbers are shifted. The optimal set is determined from the principle of the minimum of the total energy of N electrons with M up spins. Using such a principle for an even number of electrons one may obtain the following expressions for the total energy:

$$E^{\text{even } M}_{\text{even } N} = -D \cos\left[\frac{2\pi}{L}\left(f - \frac{M}{2N} + \frac{N-M}{2N} + l + \frac{M}{N}k\right)\right] \tag{14}$$

and

$$E^{\text{odd } M}_{\text{even } N} = -D \cos\left[\frac{2\pi}{L}\left(f + l + \frac{M}{N}k\right)\right] \tag{15}$$

where l and k are arbitrary integer numbers; the magnitude D is the positive constant:

$$D = 2t \frac{\sin(\pi N/L)}{\sin(\pi/L)}. \tag{16}$$

For an odd number of electrons the expressions for the total energy have the form

$$E^{\text{even } M}_{\text{odd } N} = -D \cos\left[\frac{2\pi}{L}\left(f - \frac{M}{2N} + l + \frac{M}{N}k\right)\right] \tag{17}$$

and

$$E^{\text{odd } M}_{\text{odd } N} = -D \cos\left[\frac{2\pi}{L}\left(f - \frac{N-M}{2N} + l + \frac{M}{N}k\right)\right] \tag{18}$$

when the values of M are even and odd, respectively. It is worth noting that all these expressions, as functions of f, are periodic functions with periods $f_T = L$, $f_T = LM/N$ and, of course, $f_T = L(N-M)/N$. The quantum numbers l and k describe the charge and spin vortices.

Let us consider the case of an odd number of particles N. For the ground state the *quantum numbers k, l and M are not independent and are governed by the equation* which can be obtained from (17):

$$l + \frac{m}{N}k = \frac{M}{2N}. \tag{19}$$

Let all spins be down, i.e. $M = 0$. Then a simple solution of (19) is $k = l = 0$. Then from (17) the ground state energy is given by

$$E^0_{\mathrm{odd}\ N} = -D\cos\left(\frac{2\pi}{L}f\right). \tag{20}$$

For $k = l = 0$ at the point $f = 1/2N$ a transition will exist in the state with $M = 2$ where, for the ground state energy from (17), we have:

$$E^2_{\mathrm{odd}\ N} = -D\cos\left[\frac{2\pi}{L}\left(f - \frac{1}{N}\right)\right]. \tag{21}$$

Then upon further increasing the magnetic flux f to $f = 3/2N$ a transition in the state with $M = 4$ will occur and so on. That is, at the point $f = (2p-1)/2N$ there is a transition in the state with $M = 2p$, where here k and l are equal to zero and p is an integer number. The ground state energy in this state has the form:

$$E^{2p}_{\mathrm{odd}\ N} = -D\cos\left[\frac{2\pi}{L}\left(f - \frac{p}{N}\right)\right]. \tag{22}$$

This expression describes the ground state energy only in the interval of flux f: $(2p-1)/2N \leqslant f \leqslant (2p+1)/2N$. If in the initial state all spins are up, then the energy should be described by equation (18). At $k = l = 0$ we again have transitions with M changing by $\Delta M = 2$. Here the ground state energy has smooth minima when

$$f_{\mathrm{min}} = \frac{p}{N} \tag{23}$$

where p is an arbitrary integer number. The ground state energy has cuspoidal maxima at

$$f_{\mathrm{max}} = \frac{p}{N} + \frac{1}{2N}. \tag{24}$$

When the magnetic flux increases from zero the total current decreases. At the point $f = 1/2N$ this diamagnetic current changes sign, but conserves its absolute value. The expression describing the total current at arbitrary f has the form

$$J = -\frac{2\pi D}{L}\sin\left[\frac{2\pi}{L}\left(f - \frac{p}{N}\right)\right] \qquad \frac{2p-1}{2N} \leqslant f \leqslant \frac{2p+1}{2N}. \tag{25}$$

One can see from this formula that at $f = (2p+1)/2N$ the current makes a jump from $J_{\mathrm{min}} = -(2\pi D/L)\sin(\pi/L)$ to $J_{\mathrm{max}} = (2\pi D/L)\sin(\pi/L)$. This jump has a deep meaning in that it characterizes the phase transition. The abrupt changing of the diamagnetic current at the point of transition helps the ring to trap a new fractional quantum of the total flux $f = 1/N$ which characterizes the spin–charge vortex. In this case the diamagnetic current screens the magnetic flux only before the transition; after the transition it does not screen the external magnetic flux, but, vice versa, the diamagnetic current generates the additional fractional quantum of the flux $f = 1/N$.

The dependence of the diamagnetic current on the magnetic flux behaves qualitatively like the dependence of the current associated with a single particle with an effective charge $e^* = Ne$ in the ground state on the flux through the hole in a superconducting ring. The diamagnetic current does not have a direction which brings the total flux to zero. The direction of the orbital current is such that it brings the total flux closer to the nearest fractional number of flux quantum $f = p/N$. The direction of the diamagnetic current alters suddenly at each transition. It is amusing that at each of these transitions there is the generation of the spin–charge vortex, described by the quantum numbers k, l and M. These quantum numbers are not independent. At $k = l = 0$ the transition is simply the flip of two spins which can even be in the opposite direction to the magnetic field. This can be explained by the fact that the changing of the sign of the current at the points of the transitions means a flip of the orbital momentum. As a result we have spin–orbital momentum flip or, in other words, the generation of a spin–charge vortex. If we take into account the Zeemann interaction then in high magnetic field $f \gg 1$ this ideal physical picture may be changed.

The same behaviour can be obtained with an even number of particles. In this case the ground state is also strongly degenerate. The quantum numbers l, k and M for ground state energy are governed by an analogous equation to (19):

$$l + \frac{M}{N} k = 0.$$

At $k = l = 0$ without a field the ground state is singlet. Thus, we have obtained results which are equivalent to the 'Nagaoka' theorem. That is, for the quantum numbers $l = k = 0$ and an odd number of particles in the ring, the ferromagnetic state is favoured, while for even number of particles the antiferromagnetic singlet state is favoured. However it is worth noting that all states with different M may give the same energy dependence at an appropriate choice of the values of the quantum numbers l and k, i.e. the ground state energy is strongly degenerate.

Let, for example, $l = k = 0$ then for an even number of particles in the region $-1/2N \leqslant f \leqslant 1/2N$ the ground state energy is described by equations (14) with $M = N/2$ (it coincides with (20)); in the region $1/2N \leqslant f \leqslant 3/2N$ it is described by equation (14) with $M = N/2 + 2$ (it coincides with (21)) and so on. One general conclusion that can be drawn here is that the ground state energy is a periodic function of the flux f through the ring with period $f_{\mathrm{T}} = 1/N$.

This phenomenon has a simple explanation that is related to the multi-valued wavefunction of the hole on the ring (see, for comparison, [23]). If we take the hole around the ring once, we have, in effect, changed the entire ring from one ground state phase to the other (all electrons have moved only one site). Only by taking the hole around N times do we restore the system to its original state. The total change of the Aharonov–Bohm phase due to this process is Nf_{T}. For the periodicity of the total wavefunction this change, according to gauge invariance, equals one unit. Whence the ground state energy as a function of the flux f has the period $f_{\mathrm{T}} = 1/N$. The strong Coulomb site–site repulsion prevents a free one-electron motion over the ring ('Coulomb blockade') but it allows the motion of all N electrons together.

The magnetization and susceptibility of this ring are also periodic functions with this universal period $f_{\mathrm{T}} = 1/N$.

For the ring system of singly connected quantum dots [24] such a phenomenon may also be readily observed. There is an experiment in which the oscillation of the magnetization with period $f = 1/2$ on copper rings has been observed [25]. If instead of a copper ring we take a ring consisting of one of the transition metals (Mn, Fe, Co or Ni) then on such a ring it should be possible to observe the oscillation of the magnetization and magnetic sucseptibility with period $f_T = 1/N$, i.e. the period of the oscillation is inversely proportional to the density of electrons on the ring. At intermediate values of $U \sim t$ the period of the oscillation may be equal to an arbitrary fractional number. An analogous system, where we have found a similar '$1/N$' oscillation, is the free electrons on a ring with one magnetic 'Kondo' impurity [26]. The phenomenon found in the present work may also be observed when studying aromatic molecules in a transverse magnetic field. Of special importance may be the optical experiments.

I wish to thank F Woynorovich, S Kivelson, B Spivak and G Kohring for fruitful discussions and also M L Ristig for hospitality. This work was supported by the Alexander von Humboldt Foundation.

References

[1] Kusmartsev F V 1990 Flux phase states on a ring *University of Cologne Preprint*; 1991 *Pis. Eksp. Teor. Fiz.* **53** 27
[2] Wohlleben D, Esser E, Zipper E and Szopa M 1990 *Possibility of orbital magnetic phase transitions in mesoscopic metallic rings* University of Cologne preprint
[3] Kusmartsev F V 1990 University of Cologne preprint; 1991 *Proc. Miami Workshop on Electronic Structure and Mechanisms for High T_c Superconductivity* ed J Ashkenazi *et al* (New York: Plenum)
[4] Kalmeyer V and Laughlin R B 1987 *Phys. Rev. Lett.* **59** 2095
[5] Affleck J and Manston J B 1988 *Phys. Rev.* B **37** 3774
[6] Wen X G, Wilczek Fr and Zee A 1989 *Phys. Rev.* B **39** 11413
[7] Anderson P W 1989 *Phys. Scr.* T **27** 60
[8] Wiegmann P 1989 *Phys. Scr.* T **27** 160
[9] Hasegawa Y, Lederer P, Rice T M and Wiegmann P B 1989 *Phys. Rev. Lett.* **63** 907
[10] Montambaux G 1989 *Phys. Rev. Lett.* **63** 1657
[11] Bethe H 1931 *Z. Phys.* **71** 205
[12] Lieb E, Schultz T and Mattis D 1961 *Ann. Phys., NY* **16** 407
[13] Yang C N and Yang C P 1966 *Phys. Rev.* **147** 303; *Phys. Rev.* **150** 321, 327; *Phys. Rev.* **151** 258
[14] des Cloizeaux J and Gaudin M 1966 *J. Math. Phys.* **7** 1384
[15] Hamer C J, Quispel G R W and Batchelor M T 1987 *J. Phys. A: Math. Gen.* **20** 5677
[16] Woynarovich F and Eckle H P 1987 *J. Phys. A: Math. Gen.* **20** L97
[17] Woynarovich F 1987 *Phys. Rev. Lett.* **59** 259, 1264 (erratum)
[18] Sutherland B and Shastry B S 1990 *Phys. Rev. Lett.* **65** 1833
[19] Bayers N and Yang C N 1961 *Phys. Rev. Lett.* **46** 7
[20] Yang C N 1962 *Rev. Mod. Phys.* **34** 694
[21] Lieb E and Wu F 1968 *Phys. Rev. Lett.* **20** 1445
[22] Woynarovich F 1989 *J. Phys. A: Math. Gen.* **22** 4243
[23] Kivelson S and Rocek M 1985 *Phys. Lett.* **156B** 85
[24] Demel T, Heitmann D, Grambow P and Ploog K 1990 *Phys. Rev. Lett.* **64** 788
[25] Levy L P, Dolan G, Dunsmeir J and Bouchiat H 1990 *Phys. Rev. Lett.* **64** 2074
[26] Kusmartsev F V 1991 to be published