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2*e* or not 2*e*: Flux Quantization in the Resonating Valence Bond State.

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Abstract. – The «resonating valence bond» (RVB) state has been proposed as the basis for an explanation of high-temperature superconductivity. Recently, we have described the charge and spin excitations about this state, and have shown that they are solitons, precisely analogous to those found in polyacetylene. Since the charged solitons are $+e$ bosons, it is natural to ask whether flux quantization will occur in units of $hc/2e$, as in traditional BCS superconductivity, or will come only in larger units of hc/e. We show here that flux quantization in units of $hc/2e$ will occur unless a condensation of cooperative ring exchanges occurs analogous to that found in the fractional quantized Hall effect.

Resonance, the description of the quantum ground state of a system (say benzene) as a superposition of several bond configurations, has been the chemist's way of incorporating some of the delocalization energy which is naturally described using electronic energy bands. L. Pauling originally introduced the «resonating valence bond» (RVB) state in the hope of describing simple metals. This state, a quantum liquid of valence bonds, is kept from crystallizing into a Peierls state by its «zero point» or resonance energy. Anderson [1] has recently proposed that it may be realized in the recent high-temperature ceramic superconductors.

Here we consider a tight-binding model on a square lattice, with M electrons occupying $N > M$ sites. Since we are interested in topological properties (rather than energetics), we need not examine the true ground state—any state that is adiabatically connected to the ground state will do. The states we will examine will be coherent superpositions of nearest-neighbor singlet bond configurations, where each electron participates in a singlet bond with one neighboring electron. We define RVB states as those which can be constructed perturbatively from one of these superpositions (1).

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(1) We should caution that this definition probably excludes the states discussed by Anderson and collaborators, which have no gap to spin excitations. Such states will have a large density of neutral solitons, while the unperturbed states we discuss have none.

There are two ways to describe the valence bond configurations: one can pay attention to either the singlet bonds or the empty space between them. The latter description becomes preferable near half-filling $M \approx N$, where the unoccupied sites are dilute: we have shown [2] that these sites act as charge $+e$ spinless bosons. Because of the close analogy between these excitations and the domain walls in polyacetylene, we call them charged solitons. There are disadvantages to each of these points of view. The soliton description is incomplete: many bond configurations are compatible with a given arrangement of solitons. The description in terms of singlet bonds is complicated, because the various valence bond configurations are not orthogonal. (For example, on a 2×2 square, the overlap between the state with two horizontal bonds and the state with two vertical bonds is 1/2.)

This paper will use both of these descriptions. First, we shall use the singlet bond description to investigate the Aharonov-Bohm (microscopic) periodicity in the energy. Since the elementary units in this description have charge $-2e$, one might imagine that the energy must be rigorously periodic in the enclosed flux with periodicity $hc/2e$. We shall see that the lack of orthogonality ([2]) between configurations makes the Aharonov-Bohm energy periodicity hc/e. The Aharonov-Bohm effect is microscopic in the sense that the magnitude of the periodic terms decays with the size of the ring. (The argument applies equally to metals and insulators.) Second, we shall use the soliton description to investigate flux quantization. Flux quantization is given by the *macroscopic* energy periodicity in large annuli, *i.e.* the stiffness caused by the off-diagonal long-ranged order. The Aharonov-Bohm flux periodicity is only an upper bound on the flux quantum: even in ordinary superconductors, extremely small annuli will have energy periodic only with period hc/e. It may be possible to prove ([3]) that flux quantization in a system of electrons must occur in even multiples of e, but we do not know of a compelling argument. (The flux quantum has been measured by several groups to be $hc/2e$ in both $La_{2-x}Sr_xCuO_{4-y}$ and in YBa_2CuO_{7-y} ([4]).) We shall show that a condensation of cooperative ring exchanges [5] is a necessary condition for flux quantization in units of hc/e.

Aharonov and Bohm showed that in a system of particles of charge q contained in an annulus with magnetic flux Φ passing through, the total free energy is periodic in Φ with period hc/q. The standard argument is made by constructing wave functions with the same energy at fluxes Φ and $\Phi + hc/q$. Choose the vector potential to lie in the azimuthal direction: $\boldsymbol{A} = \nabla_\theta(\Phi\theta/2\pi)$. Since the Hamiltonian depends only on $(\hbar/i)\nabla_j - (q/c)\boldsymbol{A}$, the wave function

$$\Psi_{\Phi + hc/q} = \exp\left[i \sum_j \theta_j\right] \Psi_\Phi \tag{1}$$

has the same energy at flux $\Phi + hc/q$ as Ψ_Φ had at flux Φ. (The θ_j are the angular coordinates of the particle positions R_j.) This argument also works if the particles are molecules with

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([2]) After completing this work, we received a preprint from David Thouless on the same topic; he finds the energy has period $hc/2e$ regardless of the size of the system. In his two-dimensional models, his treatment ignores the nonorthogonality of the bond configurations; his work should be interpreted as a generalization of the topological constraint to nonbipartite lattices. We agree with his conclusion that strictly localized singlet bonds in single chain annuli have period $hc/2e$; however, realistic models will have exponentially falling tails to the singlet bond wave functions which produce a small contribution to the energy with period hc/e.

([3]) There are hints of a general argument in Yang's work on off-diagonal long-range order [3].

([4]) Many of these measurements were of periodicities in Josephson junctions, which could disrupt the bonds. Recently, the flux lattice period has been measured by P. L. Gammel *et al.* [4].

internal degrees of freedom, so long as their extent is small compared to the hole in the annulus (so that their angular center of charge θ_j is well defined).

What goes wrong when we apply this argument to valence bond configurations? We can imagine writing a many-body wave function Ψ^b_Φ for the bonds as a superposition of bond configurations, and label each configuration in terms of the center θ_j and orientation of each of the singlet bonds. Can we use eq. (1) to create a new wave function for flux $\Phi + hc/2e$? The lack of orthogonality between the bond configuration «position eigenstates» prevents us from doing so. Changing the relative phase of two overlapping pieces of the wave function changes the normalization and the potential energy as well as the kinetic energy. Two bond configurations are orthogonal if the solitons are in different places, but the center of charge can move (and the relative phase can change) without moving the solitons: as shown in fig. 1, rearrangements of bonds with enclose the hole in the annulus can change the center of charge $\sum_j \theta_j$ by π.

Thus exchange rings which encircle the hole (fig. 1) change the microscopic Aharonov-Bohm flux periodicity of the energy from $hc/2e$ to hc/e. Does this extend to flux quantization? For large annuli, the rearrangements which span the hole have exponentially small overlaps with the original configuration ($\sim 2^{-L}$, where L is the circumference); each of their contributions to the flux-dependent energy is also exponentially small([5]). There are, however, many distinct rearrangements which encircle the hole—if they are important to the wave function, then the periodicity of the macroscopic energy could also be hc/e. This is precisely analogous to the physics of the fractional quantum Hall effect, where exponentially small contributions from an exponentially large number of exchange loops add coherently to the energy.

To make this analogy more precise, we turn to the soliton description of the resonating valence bond state. First, let us establish some conventions. It is useful to distinguish a red and a black sublattice with a checkerboard convention: our singlet bonds always connect a red site to a neighboring black site. Vacant sites can lie on either sublattice, so there are red and black charged solitons. We will be interested in ordered pairs $\{A, B\}$ of singlet bond configurations; the first element can be considered as a bra and the second as a ket in a matrix element $\langle A|\hat{O}|B\rangle$. It is also useful to give a direction([6]) to each bond: the bonds in the A configuration are directed from red to black, in the B configuration from black to red.

Suppose first that the empty sites (charged solitons) are in the same places in the two configurations. Draw both configurations on the same lattice. Since any occupied site shares exactly one A bond and one B bond, the drawing will decompose into nonintersecting loops [6]. (If a particular bond is part of both configurations, it will form a trivial loop of no enclosed area.) The directions of the bonds give orientations to each of the loops, and allow one to reconstruct the original pair of configurations from the oriented loops.

These loops represent the electronic degrees of freedom left after the positions of the charge solitons are set. We would like to define a quasi-particle wave function $\Psi^s(R_1, \ldots, R_{N-M})$ for the solitons, where the electronic degrees of freedom are considered

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([5]) In the large-U limit, it is easy to see that it goes like t^L/U^{L-1}.

([6]) Many of the arguments presented here, distinguishing red and black sublattices and directions of bonds, work only on bipartite lattices (*e.g.* square and cubic). The conclusions presented here are also valid for triangular lattices; however, the arguments are a bit different—since the loops are no longer oriented, the winding number is only defined modulo two. Also, we should note that an annular region with an edge dislocation through the hole also has winding number defined modulo two (if there are an odd number of sites on a loop, it can change a red soliton to a black one). Again, simple modifications of the arguments give the same answer.

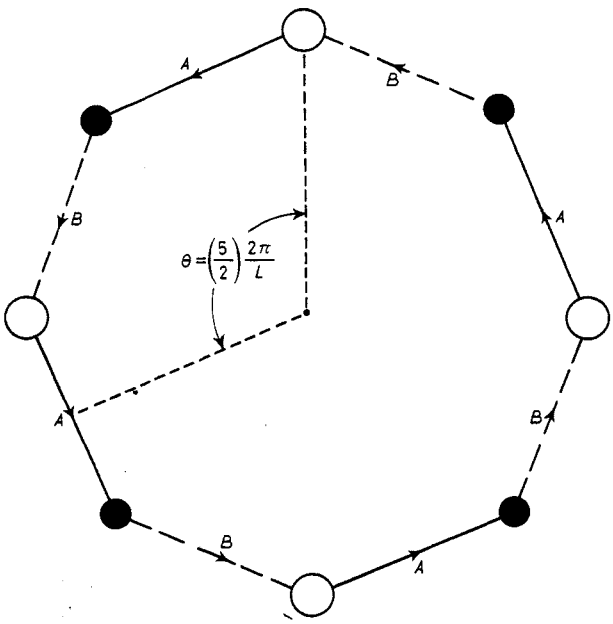

Fig. 1.

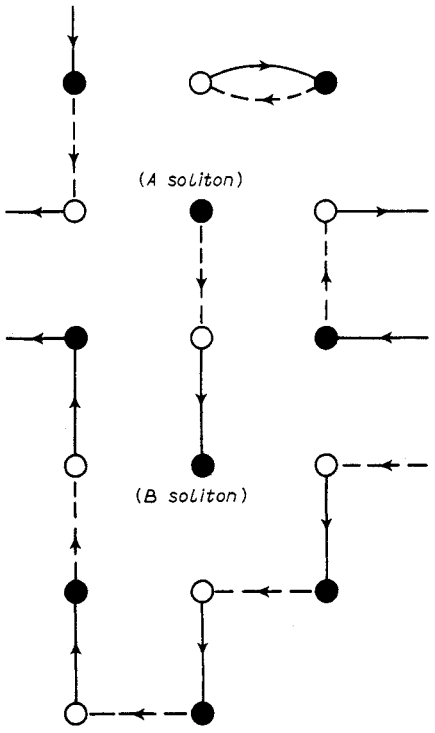

Fig. 2.

Fig. 1. – Loop around the hole. Two valence bond configurations are shown, encircling a hole of circumference $L = 8$. If we lump the charges into bonds of charge $-2e$, the A configuration has bonds centered at $\theta = ((1/2)(2\pi/L), (5/2)(2\pi/L), \ldots, ((2L-3)/2)(2\pi/L)))$, while the B configuration has bonds centered at $\theta = ((3/2)(2\pi/L), (7/2)(2\pi/L), \ldots, ((2L-1)/2)(2\pi/L))$. The charges actually sit in the same places in the two configurations; nonetheless, the center of bond charges $\sum_j \theta_j$ changes by π as one shifts from A to B.

Fig. 2. – Solitons act as sources and sinks for «bond-string». One vacant site is different between the A and B configurations. The black soliton in the A sublattice acts as a source, and the black soliton in the B sublattice acts as a source. As the B soliton encircles the hole in the annulus, it leaves behind a loop as shown in fig. 1.

slaves to the soliton positions (just as they are slaves to the nuclear positions in helium). The problem ([7]) in this approach is the assumption that there is a unique «best» electronic state for each soliton configuration in a multiply-connected geometry.

([7]) There is another less subtle but more serious problem of which the reader should be aware. In helium, the electrons can be removed using the Born-Oppenheimer approximation: the electrons relax fast compared to the nuclear motions. At least for the simplest models for high T_c, quite the reverse is true. The solitons move with hopping matrix element t and the bonds rearrange via exchange interactions $t^2/U \ll t$: the solitons move fast, and the bonds adjust slowly. This may not be the final answer (the quasi-particles may behave somewhat differently from «bare» vacant sites), but it seems for now that a soliton quasi-particle description is not the obvious one. On the other hand, we are interested in topological questions which should not change as we make the solitons heavy. Especially since this paper answers why the flux quantum given by the soliton charge is wrong, it seems natural to examine the limit in which the solitons are the only important degrees of freedom.

To see this, consider moving one black soliton in the B configuration, keeping the A configuration fixed (fig. 2). The original black site for the soliton has one bond pointing out of it (the B bond) and no A bond pointing into it (since the A configuration has a soliton there). The final position for the soliton has one bond pointing in, and none out—it is a sink for «bond-string», where the original site is a source. As we carry the soliton around the hole in the annulus and back to its original position, we leave behind a loop encircling the hole (fig. 1). Clearly, this nonlocal effect is missed in the quasi-particle description. In the bond description, the solitons have fractional charge; nonlocal effects of this kind are typical of fractionally charged quasi-particles [7].

For fixed soliton positions, we can classify the bond configurations by a topological winding number W. The difference in winding number between two configurations is the net number of loops enclosing the hole counterclockwise. We also want to assign relative values of W for configurations with differing soliton positions; clearly, configurations in which only a few solitons have moved short distances and only local bond configurations have changed should have nearly the same winding number. However, because moving a soliton completely around the hole changes the winding number by one, we must add to W a factor involving the center of charge to make a winding angle Ω which changes continuously as the solitons move around.

Let us imagine setting $\Omega = 0$ for some initial configuration of bonds (say, unstaggered vertical bonds everywhere, with all the solitons symmetrically disposed in one angular slice around $\theta = 0$). Any state can be produced by suitable local rearrangements of the bonds and solitons. Let θ_j^{R} and θ_j^{B} denote the angular positions of the red and black solitons, including the net number of times they encircle the hole from their original positions. We can define the winding angle Ω for a general rearrangement to be the net angular motion of solitons needed to produce the final configuration

$$\Omega = \sum_j \theta_j^{\mathrm{B}} - \sum_j \theta_j^{\mathrm{R}} . \tag{2}$$

If the solitons in two configurations are in the same places, the winding number W defined above equals the difference in Ω between the two configurations, divided by 2π.

Thus the bond configurations «remember» the net number of solitons that have circled the annulus. The quasi-particle wave function can depend on Ω in addition to the soliton positions. Now, *half* the angular center of charge for all the solitons

$$\frac{1}{2}\sum_{j,C} \theta_j^{\mathrm{C}} = \frac{1}{2}\left\{\sum_j \theta_j^{\mathrm{B}} + \sum_j \theta_j^{\mathrm{R}}\right\} = \Omega/2 + \sum_j \theta_j^{\mathrm{R}}$$

is a single-valued function of Ω and $R_1, \ldots, R_{N-M}$, so

$$\Psi^{\mathrm{s}}_{\Phi + hc/2e} = \exp\left[i \sum_{j,C} \theta_j^{\mathrm{C}}/2\right] \Psi^{\mathrm{s}}_{\Phi}(R_1, \ldots, R_{N-M}; \Omega) =$$

$$= \exp\left[i\left(\Omega/2 + \sum_j \theta_j^{\mathrm{R}}\right)\right] \Psi^{\mathrm{s}}_{\Phi}(R_1, \ldots, R_{N-M}; \Omega) \tag{3}$$

is a single-valued quasi-particle wave function.

Do these two wave functions have the same energy, for large annuli? Roughly speaking, we want to know the energy cost of changing the relative phase of the even and odd winding number sectors: flux will not be quantized in the larger units hc/e unless that energy cost

grows with the system size. We have seen (using both the bond and soliton descriptions) that if the energy cost is ε, then time evolution for a time $\hbar/\varepsilon$ will introduce significant bond rearrangements which encircle the hole in the annulus without a next flux of solitons (the mixing states with different winding numbers). If the Hamiltonian is local (*i.e.* not involving products of creation and annihilation operators linking for distant sites), then a loop of shifted bonds of length L involves powers of the Hamiltonian of order L. For a loop to form without moving a soliton around, the system has to go through higher-energy intermediate states around the perimeter; the contribution of such a loop to the time evolution will go as $\exp[-\alpha L]$ for some constant α. The number of paths around the hole grows with a similar form, and one might imagine a phase transition (as is found in the fractional quantized Hall effect [5]) when large loops begin to dominate. Otherwise, it will take an exponentially large time to excite large loops, and the hc/e periodicity to the energy will therefore be exponentially small.

We have examined this question in two dimensions, using both a mean-field theory and by approximately mapping the 2-d lattice onto a $1+1$ dimensional continuum field theory [8]. Both approaches suggest that condensation of ring exchanges does not occur in two dimensions. We have no constructive argument that flux quantization in units of hc/e is impossible in a hypothetical resonating-valence-bond states with 3-d connectivity ([8]).

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([8]) If the experiment is not difficult, we suggest measuring the flux quantum in $Ba(Pb/Bi)O_3$.

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