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Enhanced electron pairing in a lattice of Berry-phase molecules

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We show that electron hopping in a lattice of molecules possessing a Berry phase naturally leads to pairing. Our building block is a simple molecular site model inspired by C_{60}, but realized in closer similarity with Na_3. In the resulting model electron hopping must be accompanied by orbital operators, whose function is to switch on and off the Berry phase as the electron number changes. The effective Hamiltonians (electron-rotor and electron-pseudospin) obtained in this way are then shown to exhibit a strong pairing phenomenon, by means of one-dimensional linear-chain case studies. This emerges naturally from numerical studies of small-N-site rings, as well as from a BCS-like mean-field theory formulation. The pairing may be explained as resulting from the exchange of singlet pairs of orbital excitations, and is intimately connected with the extra degeneracy implied by the Berry phase when the electron number is odd. The relevance of this model to fullerides, to other molecular superconductors, as well as to present and future experiments, is discussed.

I. INTRODUCTION

A significant feature of the physics of unconventional superconductors such as the cuprates is the constraint imposed on the motion of the charge carriers by the background degrees of freedom, i.e., the spins in the case of the cuprate superconductors. In this paper we focus attention on a class of constraints imposed on the motion of conduction electrons by the Berry phase,[1] or molecular Aharonov-Bohm phase,[2] which can arise in molecular crystals with large on-site degeneracies. In general, for this to be the case, the symmetries of electron and vibron states must match appropriately and, moreover, the number of electrons needs to be odd.

As an explicit example, we have demonstrated elsewhere[3] the presence of a Berry phase in negatively charged fullerene ions C_{60}^{-}, C_{60}^{3-}, C_{60}^{5-} ensuing from a dynamic Jahn-Teller (DJT) effect arising from the coupling between the partly occupied t_{1u} orbital and the H_g vibron modes.

In such a situation a physical electron (or hole) may be regarded as a composite particle, made up of the bare electron plus the geometrical phase that accompanies it when sitting, unpaired (or more generally in a state with an odd number of electrons), on a given molecule. By contrast, either the absence of electrons or the presence of a pair of electrons will eliminate the Berry phase on that molecule. We argue below that the kinematical constraints imposed by the Berry phase can be a factor capable of tilting the balance in favor of pairing, even in the presence of repulsive interactions.[4] The way this works is for a pair of electrons on one molecule to gain energy by each tunneling off onto neighbors with accompanying vibron excitations before coming together again. A single electron, on the other hand, will tunnel accompanied by its vibron excitations, so the electrons will gain less energy by tunneling as individuals than will be gained by tunneling as pairs.

In this paper, we propose a class of simple coupled electron-rotor models, which we believe capture the essential physics introduced by the Berry-phase constraint. Omitting at this stage the complications of real C_{60}^{n-} anions, our model lattice Hamiltonian is instead directly inspired by the simpler and well-known[5] strong-coupling Berry-phase molecule Na_3.

In general, there are an infinite number of rotor states on each molecular site. To simplify further, we shall truncate to a three-state model for the rotors. The resulting many-site Hamiltonian will be shown to take the form

$$H = -\frac{t}{2} \sum_{\langle i,j\rangle,\sigma} c_{i,\sigma}^{\dagger} c_{j,\sigma} (S_i^{+} S_j^{-} + \text{H.c.}) \qquad (1)$$

where S^{+}, S^{-} are raising and lowering operators for a spin-1 vibron manifold for each molecule, and $\langle i,j\rangle$ denote first neighbors.

To test the pairing properties of (1), we include a Hubbard repulsion term

$$H_U = U \sum_i n_{i\uparrow} n_{i\downarrow}. \qquad (2)$$

We then study the half-filled state of the model numerically for small systems (4–8 site rings), and also by a mean-field BCS-type calculation for the one-dimensional (1D) chain.

The final conclusion is that the Berry-phase coupling is found to be greatly beneficial to electron pairing, at least within the simple 1D lattice studied so far. Pairing, in particular, appears to prevail and to survive even in presence of a repulsive Hubbard U, up to values $U \approx t$.

In Sec. II we will introduce the main concepts and build our working Hamiltonian, representing an idealized lattice of Berry-phase molecules. Section III is devoted to a numerical study of the four, six, and eight-site 1D chain clusters, where correlations can be studied exactly, and the presence of pairing is demonstrated. Section IV discusses a mean-field BCS-type formulation for the infinite 1D chain. We close with a discussion section, where a number of interesting open issues are also briefly presented.

II. THE MODEL

Our model system is a regular lattice of molecules. Each molecule possesses initially a degenerate orbital, an odd number of electrons, and a dynamical Jahn-Teller (DJT) coupling (with the Berry phase) to a local vibration, also degenerate, of the pseudorotational type. For simplicity, we stick to the case of one electron in a doubly degenerate orbital and one rotor, which provides the simplest case of Berry-phase coupling. The electron can hop from a molecule to the next one in the usual fashion, conserving ordinary spin. We will generally also include an on-site ("intramolecular") electron-electron repulsion U, so that, for a nondegenerate level and no rotor coupling, we would have just an ordinary Hubbard model. Berry-phase coupling to the rotors is the ingredient giving rise to peculiar selection rules for electron hopping between two molecules in different rotor states. In the following, we describe successively the on-site Hamiltonian and the full lattice Hamiltonian inclusive of electron hopping.

A. On-site Hamiltonian: Modeling a Berry phase molecule

We consider at each site a molecule with a partly occupied doubly degenerate electronic state. Suppose this orbital interacts via linear DJT coupling with a doubly degenerate vibration. A practical example (not relevant for superconductivity) of such a situation is the Na_3 molecule. A single unpaired electron occupies the doubly degenerate electronic molecular orbital $E \equiv (E_x, E_y)$, and the doubly degenerate vibron is a pseudorotation of the Na_3 triangular structure. Direct spectroscopical evidence has been found,[5] showing that the formalism we present here (supplemented by quadratic couplings, which are omitted here for simplicity) correctly describes the dynamics of this system.

The single-molecule, one-electron, linear coupling case is a classic textbook Jahn-Teller problem.[6] When only one electron occupies the degenerate state, the lowest-order electron-vibron Hamiltonian can be written

$$H = \frac{\hbar\omega}{2}\left[\frac{\partial^2}{\partial q_1^2} + \frac{\partial^2}{\partial q_2^2} + q_1^2 + q_2^2\right]\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + g\frac{\hbar\omega}{2}\begin{pmatrix} -q_1 & q_2 \\ q_2 & q_1 \end{pmatrix}, \tag{3}$$

where the 2 × 2 matrices span the twofold E electronic level, and q_i are the vibrational normal coordinates in the vibron space; the second term is the coupling between vibron and electron, of dimensionless strength g.

The problem is rotationally invariant in the $(q_1,\, q_2)$ space. It is therefore conveniently rewritten by introducing polar coordinates q, ϕ in the vibron space and a pseudospin $\frac{1}{2}$ representation in the electron space:

$$\left|\mp \frac{1}{2}\right\rangle = \pm\frac{i}{\sqrt{2}}\left(|E_x\,\rangle \mp i\,|E_y\,\rangle\right). \tag{4}$$

In terms of these quantities the Hamiltonian is expressed as

$$H = \frac{\hbar\omega}{2}\left[-\frac{\partial^2}{\partial q^2} - \frac{1}{q}\frac{\partial}{\partial q} - \frac{1}{q^2}\frac{\partial^2}{\partial\phi^2} + q^2\right] + \frac{g\hbar\omega}{2}\begin{pmatrix} 0 & qe^{+i\phi} \\ qe^{-i\phi} & 0 \end{pmatrix}. \tag{5}$$

A new total angular momentum j, defined as

$$j = \hbar^{-1}\left(q_1 p_2 - q_2 p_1\right) - \frac{1}{2}\sigma_z = -i\frac{\partial}{\partial\phi} - \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}, \tag{6}$$

is found to commute with H.[6] Note that σ_z is only a *pseudospin* $\frac{1}{2}$ spanning in reality the twofold *orbital* state and should not be confused with the *true* spin, which is ignored at this stage. Because of this pseudospin $\frac{1}{2}$ term, the eigenvalues of j are a half-odd integer, an amusing anomaly pointed out by Herzberg and Longuet-Higgins[7] for the case of the triangular molecule. This fractionalization can be seen as a manifestation of a Berry phase[1] of π, which the vibrons pick up from the electron degeneracy.[5]

Diagonalization of (5) must, in general, be done numerically.[6,8] In the limit of strong coupling ($g >> 1$), however, the massive radial q motion can be approximately separated from the ϕ pseudorotation quantized by j, and both can be solved analytically in the form of an oscillator and a free rotor, respectively. The resulting spectrum is classified according to j and ν, the quantum number coming from the quantization of the radial massive motion:

$$E(v,j) = \hbar\omega\left(\nu + \frac{1}{2}\right) + \frac{2\hbar\omega}{g^2}\left(j^2 + \frac{1}{4} \pm \sqrt{j^2 + \frac{g^8}{64}}\right),$$

$$\nu = 0, 1, 2, \ldots\,, \quad j = \pm\frac{1}{2}, \pm\frac{3}{2}, \ldots\,. \tag{7}$$

Since we shall be concerned only with the low-lying rotor states, we can forget the massive boson ladder. Furthermore, we will express all energies in units of the pseudorotational quantum $\Omega := \frac{2\hbar\omega}{g^2}$.

The corresponding wave functions in the strong-coupling limit are

$$\psi_{\nu,j}(q,\phi) = \psi_\nu(q) \begin{pmatrix} \cos\theta_j e^{i(j+\frac{1}{2})\phi} \\ \sin\theta_j e^{i(j-\frac{1}{2})\phi} \end{pmatrix} \qquad (j \text{ half-odd integer}), \quad (8)$$

where $\psi_\nu(q)$ is the appropriate harmonic oscillator wave function and θ_j is a pseudospin mixing angle,

$$\tan\theta_j = 8\frac{-j \pm \sqrt{j^2 + g^8/64}}{g^4}. \quad (9)$$

In the $g \to \infty$ (strong-coupling) limit, θ_j tends to $\pm\frac{\pi}{4}$. The energy can be expanded as

$$E(j) = \pm\frac{g^4}{8} + j^2 + \frac{1}{4} \pm 4\frac{j^2}{g^4} + \cdots . \quad (10)$$

At low energies, we consider only the rotor states

$$\psi_j(\phi) = 2^{-\frac{1}{2}} \begin{pmatrix} e^{i(j+\frac{1}{2})\phi} \\ -e^{i(j-\frac{1}{2})\phi} \end{pmatrix}, \quad j = \pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}, \ldots \quad (11)$$

with energy

$$E(j) = j^2 \ , \quad j = \pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}, \ldots \ , \quad (12)$$

where we have omitted, as usual, the $-\frac{g^4}{8}$ offset contribution (polaron energy shift), but also the extra zero-point energy 1/4 required by the Berry phase.[3] This is our simplified model for the one-electron Berry molecule.

To study electron hopping among different molecules, we also need an equivalent description for molecular occupancy different from one. When two electrons occupy the molecular orbital in a singlet state, the DJT distortion is still present. However, the orbital phases for the two electrons cancel each other and a Berry phase is no longer present.

For uniformity with the one-electron case, we will still label for n=2 the pseudorotational levels with j. Cancellation of the geometrical phase now requires j to be an integer. The assumed spectrum is simply that of a standard free pseudorotor:

$$E(j) = j^2 \ , \ j = 0, \pm 1, \pm 2, \ldots \quad (13)$$

with wave functions

$$\psi_j(\phi) = e^{ij\phi} \ , \ j = 0, \pm 1, \pm 2, \ldots \ . \quad (14)$$

In the energy eigenvalue (13) we are again omitting the polaron energy gain $-\frac{g^4}{2}$ (units of Ω).

In the n=0 case, where no electron is present, no Jahn-Teller effect occurs and thus no pseudorotor either. However, we really would like to mimic an electron-hole symmetric situation, such as, for example, going to C_{60}^{2-} or C_{60}^{4-} with respect to C_{60}^{3-}. For this reason we assume even for zero electrons a pseudorotation [(13) and (14)] identical to that of the two electron case. We finally discard occupancies higher than two; for instance, we may suppose that, if the average occupancy is one, states with $n > 2$ are strongly suppressed by Coulomb repulsions.

To summarize, if n is the number of electrons present in the degenerate orbital, $2j$ assumes even or odd values according to whether n is even or odd. The j dependence of the energy eigenvalues is quadratic, as in a free (pseudo)rotor. The full quantum state of such a molecule, in the limit considered, is described by a set of three quantum numbers, which for convenience we define as integers:

$$\begin{aligned} &n \text{ (occupancy)}, \\ m &= 2j \text{ (rotor state)}, \\ \sigma &= 2m_s \text{ (spin state)}, \end{aligned} \quad (15)$$

where $m_s = \pm\frac{1}{2}$ is the z component of the true electron spin. Their allowed values are constrained in the form

$$\begin{aligned} n &= 0, 1, 2, \\ m &= 2l + \sin(\pi n) \ , \quad l = 0, \pm 1, \pm 2, \pm 3, \ldots \ , \\ \sigma &= \pm\sin(\pi n) \ . \end{aligned} \quad (16)$$

With reference to the physics of C_{60}^{n-}, discussed in Ref. 3, the similarity with the present model should be clear. In that case, in particular, the ground state has even L for even n, and odd L for odd n.

B. Intersite Hamiltonian → hopping between Berry molecules

To allow electrons to move among sites, we need to specify how the hopping process is affected by the j quantum numbers on each site. Therefore, we begin considering one electron hopping between two neighboring molecules. With sufficiently high point symmetry, such as one has for the linear chain, we will have hopping between $|E_{x,1}\rangle$ and $|E_{x,2}\rangle$ and between $|E_{y,1}\rangle$ and $|E_{y,2}\rangle$ only, with amplitude t_x and t_y, respectively.[9] If, for instance, the twofold degenerate state is associated to a p orbital, then $t_x = t_{pp\sigma}$, $t_y = t_{pp\pi}$, in Slater-Koster's notation.[10] The hopping Hamiltonian then is

$$\begin{aligned} H_{\mathrm{kin}} = \sum_\sigma \big[& t_x (c^\dagger_{x,\sigma,1} c_{x,\sigma,2} + \mathrm{H.c.}) \\ & + t_y (c^\dagger_{y,\sigma,1} c_{y,\sigma,2} + \mathrm{H.c.}) \big]. \end{aligned} \quad (17)$$

To characterize its behavior, suppose we have on site 2 a spin-up electron, with m_2 (odd) molecular pseudospin, and we want the hopping amplitude of this electron to site 1 with final spin up, and pseudospin m_1 (also odd). We need to invert relation (4) to express the fermionic operators in the pseudospin basis:

$$c^\dagger_{x,s} = \frac{c^\dagger_{+,s} - c^\dagger_{-,s}}{-i\sqrt{2}}, \quad c^\dagger_{y,s} = \frac{c^\dagger_{+,s} + c^\dagger_{-,s}}{\sqrt{2}}. \quad (18)$$

The matrix element we compute depends also on the (even) pseudospin of the empty sites l_2 (final state) and l_1 (initial state) in the following way:

$$\left\langle \begin{array}{cc|} 1 & 0 \\ m_1 & l_2 \\ \uparrow & 0 \end{array} H_{\rm kin} \begin{array}{|cc} 0 & 1 \\ l_1 & m_2 \\ 0 & \uparrow \end{array} \right\rangle = \frac{t_x+t_y}{2}\left(\frac{\delta_{m_1+1,l_1}\delta_{l_2,m_2+1}+\delta_{m_1-1,l_1}\delta_{l_2,m_2-1}}{2}\right) + \frac{t_x-t_y}{2}\left(\frac{\delta_{m_1+1,l_1}\delta_{l_2,m_2-1}+\delta_{m_1-1,l_1}\delta_{l_2,m_2+1}}{2}\right) . \tag{19}$$

The Kronecker deltas here originate through trivial orthogonality of angular-momentum wave functions [(11) and (14)], while the overall $\frac{1}{2}$ factors originate from the $\sqrt{2}$ factors in (18) and in (11).

If we limit ourselves to the special case of intermolecular interaction with $t_y = t_x$ ($t_y = -t_x$), then we have an additional conservation $l_1 + m_2 = m_1 + l_2$ ($l_1 - m_2 = m_1 - l_2$) of the total pseudospin, as shown by Eq. (19). In this case, the spectrum separates into different independent manifolds. For $t_y = t_x$, they correspond to different values of total pseudospin. Even if somewhat unrealistic (for a real p state, t_x is larger and positive, t_y smaller and negative) this is a very convenient choice, and we shall adopt it in the following. We have made a check, to be described in Sec. III, releasing this restriction, which have satisfied us that the physics is not fundamentally different in the more general case $t_y \neq t_x$. Accordingly, we define a single effective hopping

$$t = \frac{t_x + t_y}{2}, \tag{20}$$

which in the absence of direct electron-electron interactions is the only independent parameter of our model, the rotor energy quantum Ω being unity.

Similar considerations and selection rules to those discussed above for the process $|0,1\rangle \to |1,0\rangle$ apply to the case involving doubly occupied sites, namely $|0,2\rangle \to |1,1\rangle$ or $|1,2\rangle \to |2,1\rangle$. Now we have all the ingredients to place these "Berry molecules" on a lattice to see the effect of local rotor coupling on electron hopping.

C. Lattice of Berry molecules: The working Hamiltonian

As a first attempt to study this model on a lattice we consider a linear chain of N sites, with $N_{\rm el}$ electrons moving on them. The basis we consider is labeled by the set of all the n_i, m_i, σ_i, for $i = 1, \ldots, N$, so that an arbitrary state is expandable on states:

$$\left| \begin{array}{cccc} n_1 & n_2 & \cdots & n_N \\ m_1 & m_2 & \cdots & m_N \\ \sigma_1 & \sigma_2 & \cdots & \sigma_N \end{array} \right\rangle . \tag{21}$$

These basis states are obtained by ordered applications of $N_{\rm el}$ local fermionic creation operators $c^\dagger_{j,\sigma}$ on a vacuum state, where no electrons are present, and setting the m_i rotational quantum numbers to values allowed by the Berry constraint (16).

The hopping of an electron between site i and site j is, in this space, a composite operation, since it implies $n_i \to n_i - 1$, $n_j \to n_j + 1$, but also $m_i \to m_i \pm 1$, $m_j \to m_j \mp 1$ [(16), Eq. (19)]. Hence, we write a general hopping Hamiltonian in second quantized language as

$$H_{\rm kin} = -\frac{t}{2} \sum_{\langle i,j\rangle,\sigma} c^\dagger_{i,\sigma} c_{j,\sigma} (L_i^+ L_j^- + L_i^- L_j^+) \tag{22}$$

where the action of the operator $L_j^\pm$ is to raise (lower) the pseudospin m_j (really an orbital angular momentum) by one unit:

$$L_j^\pm \left| \begin{array}{ccccc} n_1 & \cdots & n_j & \cdots \\ m_1 & \cdots & m_j & \cdots \\ \sigma_1 & \cdots & \sigma_j & \cdots \end{array} \right\rangle = \left| \begin{array}{ccccc} n_1 & \cdots & n_j & \cdots \\ m_1 & \cdots & m_j \pm 1 & \cdots \\ \sigma_1 & \cdots & \sigma_j & \cdots \end{array} \right\rangle . \tag{23}$$

To the hopping Hamiltonian $H_{\rm kin}$, we add an on-site rotor Hamiltonian $H_{\rm rot}$, as well as an additional on-site electron-electron Hubbard interaction term H_U

$$H_{\rm rot} = \sum_{j=1}^{N} \frac{1}{4} \left(L_j^z\right)^2 , \quad H_U = U \sum_{j=1}^{N} n_{j,\uparrow} n_{j,\downarrow} , \tag{24}$$

the rotor energy contribution is at site j due in the rotor state m_j being

$$H_{{\rm rt}\ j} = \frac{1}{4} m_j^2 , \tag{25}$$

as in Eqs. (12), (13), and having introduced a third operator

$$L_j^z \left| \begin{array}{ccccc} n_1 & \cdots & n_j & \cdots \\ m_1 & \cdots & m_j & \cdots \\ \sigma_1 & \cdots & \sigma_j & \cdots \end{array} \right\rangle = m_j \left| \begin{array}{ccccc} n_1 & \cdots & n_j & \cdots \\ m_1 & \cdots & m_j & \cdots \\ \sigma_1 & \cdots & \sigma_j & \cdots \end{array} \right\rangle . \tag{26}$$

The commutation relations for these operators are $[L^+, L^-] = 0$, $[L^z, L^\pm] = \pm L^\pm$. We stress here that the kinetic term $H_{\rm kin}$ alone in Eq. (22) is the relevant part of the Hamiltonian we want to study.

The new electron operators $c^\dagger_{i,\sigma} L_i^\pm$ are different from the original ones, $c^\dagger_{x,\sigma,i}$, $c^\dagger_{y,\sigma,i}$, of Eq. (17). In particular, we now have a single band instead of the original double-band problem. However, with the exclusion of all site occupancies higher than 2, all matrix elements are the same in the two descriptions.

By construction, the Hamiltonian (22) conserves the constraints (16) among the quantum numbers, and can therefore be diagonalized in the Hilbert space of states defined in (21). The matrix elements of the kinetic term $H_{\rm kin}$ (off diagonal) and of $H_{\rm rot} + H_U$ (diagonal) on the basis (21) are trivial, once periodic boundary conditions (PBC's) are applied to indices. In some cases we shall, however, need antiperiodic boundary conditions

(ABC's), replacing t with $-t$ in the kinetic term involving sites 1 and N.

The Hilbert space of the problem is infinite dimensional even for finite N, due to the m_i rotor quantum numbers, which are boundless. In the numerical computations, we shall truncate the basis (21) by choosing a cutoff energy E_{cut}, including only states having some local energy smaller than this E_{cut}. Unfortunately, the choice $H_{\text{rot}} \leq E_{\text{cut}}$ is unfair with respect to singly occupied states, having larger energy (at least by 1/4) than the unoccupied and doubly occupied lowest-j ones. To achieve better convergence even at relatively small E_{cut}, we subtract this contribution and retain those states satisfying

$$H_{\text{rot}} + \sum_j \left(\frac{n_{j,\uparrow} n_{j,\downarrow}}{2} - \frac{n_{j,\uparrow} + n_{j,\downarrow}}{4} \right) \leq E_{\text{cut}} \ . \qquad (27)$$

The special case $E_{\text{cut}} = 0$ is of very strong interest. Physically, this corresponds to the limiting case $t \ll \Omega$, where the intramolecular rotor energy is much larger than the hopping energy. In this limit, the only allowed values for m_j are 0 (even occupancy) and ± 1 (odd occupancy). The resulting model has six states per site, two corresponding to even (0 and 2) occupancies, and four to the 2×2 combinations of spin σ_j and pseudospin m_j values allowed for one electron. It is possible and convenient to rewrite this simplified version of the model in terms of fictitious spin-1 states, the m_j quantum number becoming the z projection of a pseudospin $S = 1$. For this simplified version we can rewrite the Hamiltonian (22) replacing the free rotor operators L^+, L^-, L^z with the generators of the spin-1 algebra[11] S^+, S^-, S^z, respectively,

$$H'_{\text{kin}} = -\frac{t}{2} \sum_{\langle i,j \rangle, \sigma} c^\dagger_{i,\sigma} c_{j,\sigma} (S^+_i S^-_j + \text{H.c.}). \qquad (28)$$

The full ladder of rotational states [(11) and (14)] has now disappeared, being replaced just by the double degeneracy of the n=1 sites (S_z=± 1), with $H_{\text{rot}} \equiv 0$ for all n.

The extra terms (24) would still need to be added to H'_{kin}. However, H_{rot} has the simple effect of giving an energy shift of $\Omega/4$ per each singly occupied site. As suggested above, this has the same effect as an operator such as

$$\Omega \sum_j \left(\frac{n_{j,\uparrow} n_{j,\downarrow}}{2} - \frac{n_{j,\uparrow} + n_{j,\downarrow}}{4} \right) , \qquad (29)$$

i.e., it is the same as a positive Hubbard U term with $U = \frac{\Omega}{2}$, apart from a chemical potential. For $t \ll \Omega$, this term amounts to a divergent shift of the Hubbard U. Such a diverging term has no physical origin [the JT energy gains we have neglected in (12) and (13) are also infinite and have the opposite sign]. Therefore, we will omit it, and simply work with the Hamiltonian (28), with the only *caveat* that we need to remember the shift in Hubbard U when comparing the results of this low-cutoff model (28) with the fully converged one.

Both Hamiltonians (22) and (28) show a significant degree of symmetry, which we can take advantage of. Each of them conserves the number of electrons N_{el}, the total pseudo-angular momentum $2J = M = \sum_i m_i$ (i.e., the total S_z in the S=1 pseudospin version), and total electron spin. For a linear chain, the lattice translational symmetry is also obvious. Pseudospin conservation is a result of our approximation $t_x = t_y$. The others are exact. We choose to study the problem (22) in the manifold at half filling ($N_{\text{el}} = N$) and at $M = 0$ (even N) because of the higher symmetry present in this case, which includes electron-hole symmetry. Although we have not yet carried out a complete study of the model away from half filling, we believe that the basic physics will be (at least for U=0) the same, due to a suggestive analogy with the negative-U Hubbard model, which will finally emerge.

At this point, we are set with two alternative working models. The electron-rotor (ER) model

$$H_{\text{ER}} = H_{\text{kin}} + H_{\text{rot}} + H_U \ , \qquad (30)$$

where H_{kin}, H_{rot}, and H_U are given by (22) and (24), is more realistic, and is characterized by two parameters, the hopping energy t and the rotor energy Ω. This latter quantity, in turn, contains the ionic mass, and will therefore make the model sensitive to isotopic changes. The second, electron-pseudospin (EP) model

$$H_{\text{EP}} = H'_{\text{kin}} + H_U \ , \qquad (31)$$

where H'_{kin} is given by (28), represents the extreme molecular limit and is more idealized, the hopping energy t being the only parameter. Clearly, there will be no isotope effect in this model.

Although the important terms are H_{kin} and H'_{kin}, both models are endowed with the Hubbard term H_U, which can describe additional repulsive interactions, and is also convenient as a gauge of the effective attractions that will arise. Having taken Ω as the energy unit, the physical results in the ER model will depend on the two dimensionless ratios t/Ω and U/Ω. Those in the EP model will depend only upon U/t, making direct comparison with the simple Hubbard model particularly straightforward.

As will be shown, there is numerical evidence that the two models, ER and EP, lead to qualitatively similar effects, at least when t is not too large. Hence, it will be possible for many purposes to focus on the simpler EP model.

In the next two sections, we propose to study these models on a 1D linear chain, as follows. First, we will study numerically some very small clusters, by direct diagonalization. This will permit a first crude comparison between ER and EP, and also between them and the simple Hubbard model. Next, we will introduce a mean-field theory for the EP model on the infinite 1D linear chain. Here, the S=1 pseudospin variables can be approximately integrated out, giving rise to negative effective electron-electron forward and backward couplings, again suggesting singlet pairing.

III. NUMERICAL STUDIES FOR SMALL LINEAR CHAIN CLUSTERS (RINGS)

We consider here small N-site linear chain clusters (rings), in particular N=4,6,8, accessible to numerical diagonalization using conventional Lanczos method. While these sizes are admittedly small, we find that the qualitative results for small N are clear enough at this initial stage.[12]

We define useful equal-time correlation functions for singlet superconductivity (SC) and spin density wave (SDW) in the standard form of q-space "structure factors:"

$$S_{\rm SC}(q) = \frac{1}{N}\sum_{j,l}^{N} e^{iq(j-l)} \left\langle c^\dagger_{j,\downarrow} c^\dagger_{j,\uparrow} c_{l,\uparrow} c_{l,\downarrow}\ \mathbf{I}_m \right\rangle , \qquad (32)$$

$$S_{\rm SDW}(q) = \frac{1}{N}\sum_{j,l}^{N} e^{iq(j-l)} \left\langle c^\dagger_{j,\uparrow} c_{j,\downarrow} c^\dagger_{l,\downarrow} c_{l,\uparrow}\ \mathbf{I}_m \right\rangle . \qquad (33)$$

We ignore alternative channels, such as charge density waves (CDW's) or triplet superconductivity,[13] which can also be probed, but whose behaviour is not relevant at this stage. In particular, a CDW will be definitely disfavored in the more general case away from half filling. The property of correlations (32) and (33) is that they transform into one another under the transformation $c_{j,\uparrow} \rightarrow \tilde{c}_{j,\uparrow}$, $c^\dagger_{j,\downarrow} \rightarrow (-1)^j \tilde{c}_{j,\downarrow}$, which, remarkably, amounts simply to the transformation $U \rightarrow -U$ (Ref. 14) in the Hubbard model. Hence in that model $S_{\rm SC}(q)$ and $S_{\rm SDW}(q)$ are perfectly symmetric around U=0, where their values must cross, the SC instability prevailing for $U<0$, the SDW for $U>0$. This of course is confirmed for the N-site rings, as shown in Fig. 1. In the upper panel we choose a PBC, so that the free system ($U = 0$) is in a closed shell configuration of six electrons. In the lower panel, instead, ABC's are applied. Here, the resulting shift of the single-particle k states yields an open shell for free fermions at half filling. Open-shell and closed-shell calculations must finally converge to the same answer for $N \rightarrow \infty$, and their systematic comparison at finite N provides a rough but useful measure of finite-size corrections.

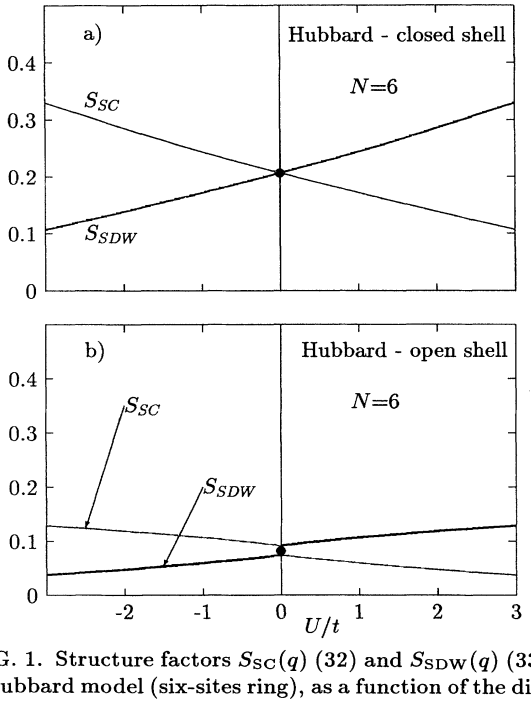

FIG. 1. Structure factors $S_{\rm SC}(q)$ (32) and $S_{\rm SDW}(q)$ (33) for the Hubbard model (six-sites ring), as a function of the dimensionless parameter U/t. In the upper panel periodic boundary conditions (PBC's) are applied to indexes, so that for U=0 the ground state is nondegenerate ("closed shell"), while in the lower panel antiperiodic boundary conditions (ABC's) make the noninteracting ground state degenerate ("open shell"). In panel (a) $q = 0$, while in panel (b) $q = \pi/N$, as appropriate to the boundary conditions applied. Solid dots mark crossings, where the switching from superconductivity to spin-density waves takes place.

Our strategy is therefore to calculate $S_{\rm SC}$ and $S_{\rm SDW}$ for our Hamiltonian $H_{\rm ER}$ and $H_{\rm EP}$, as a function of U/t, and to *find the value of* $U = U^*$ *where they cross*, so that superconducting pairing prevails at all $U < U^*$. The finding that U^* is finally positive will in turn imply that the bare U=0 model is approximately equivalent to a *negative* Hubbard U model, with $U = U_{\rm eff}$, where a crude linear estimate is

$$U_{\rm eff} \approx -U^* , \qquad (34)$$

so long as U^* is small.

Figure 2 shows results for the EP model, obtained for N=4,6,8 sites, at half filling ($N_{\rm el} = N$) as a function of U. The two panels (a) and (b) correspond to the different

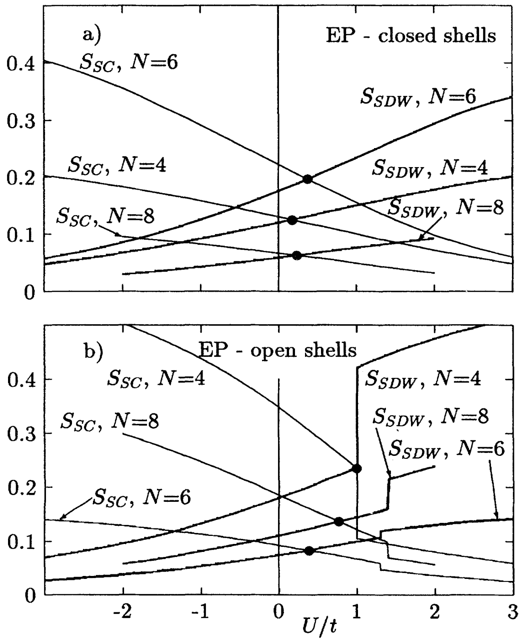

FIG. 2. Structure factors $S_{\rm SC}$ (32) and $S_{\rm SDW}$ (33) for the EP model, plotted as a function of U/t. In panel (a) we report the result for the closed-shell case, while panel (b) has the result for the open-shell case, as discussed in the text. Solid dots mark crossings defining U^*, indicating that superconductive pairing prevails even at positive U.

choices of closed shells and open shells, respectively. For instance, $N = 4$ and 8 correspond to closed shells generated with antiperiodic boundary conditions (ABC's), while $N = 6$ does that with periodic boundary conditions (PBC's). Conversely $N = 4$ and 8 yield open shells with PBC's and $N = 6$ with ABC's. The condensation wave vector q is correspondingly zero with PBC's and $q = \frac{\pi}{N}$ for ABC's.

These results show, strikingly, that in the EP model, a *finite positive* U^*/t is needed to suppress superconductivity in favor of SDW's. Roughly, the EP model (28) behaves therefore like a negative-U Hubbard model, with $U_{\rm eff} \propto -t$ For small N, the value of $U_{\rm eff}$ varies with N, and also depends on whether the shell is closed or open. Although we have not tried a systematic finite-size scaling extrapolation for $U_{\rm eff}$ to the $N = \infty$ limit, the result up to N=8 suggests that

$$-0.8t < U_{\rm eff} < -0.2t \ . \qquad (35)$$

In particular, at N=6 both ABC's and PBC's yield $U_{\rm eff} = -0.37|t|$, which may therefore be a likely value.

We have also studied the full ER model (30). For this model, the Hilbert space is that of states (21), with an upper cutoff in the rotor states $E_{\rm cut}$. Due to the larger Hilbert space, we have restricted calculations to $N = 4, 6$. We proceed by calculating $S_{\rm SC}$ and $S_{\rm SDW}$ for fixed t/Ω as a function of U/Ω, and we look for the value U^*/Ω where they cross. This again defines, via (35), a value for $U_{\rm eff}$. Typical results are shown in Fig. 3.

Now t is an independent parameter. The effective interaction $U_{\rm eff}$ can be recalculated by varying t, and the results are given in Fig. 4. The main feature is that the negative $U_{\rm eff}$ at small t, already found in the EP model, is confirmed. Hence, the ER model also leads to superconductive pairing for t/Ω not too large. This fully confirms our expectations that kinematical restrictions imposed by the switching of orbital states are important in that regime. For larger values of t, these restrictions gradually become irrelevant, until, for $t \to \infty$ we recover the value $U_{\rm eff} \to 0$. In other words, when the hopping energy is too large, the DJT effect does not work any more, and Fig. 4 describes how its "phase" part is quenched (the JT distortion magnitude is held constant in our model). The pair attraction $U_{\rm eff}$ of Fig. 4 does, as anticipated, depend on the ionic mass M, since it has the form $U_{\rm eff} = -\Omega/2 - \alpha t$ for $t \to 0$, and $\Omega \propto M^{-1}$.

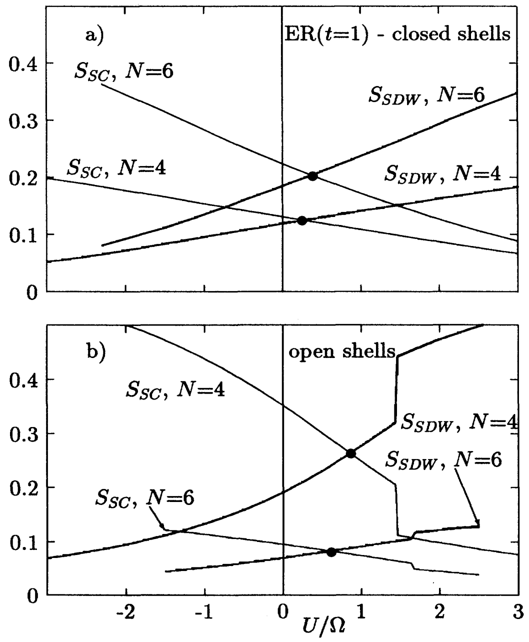

FIG. 3. Structure factors $S_{\rm SC}$ (32) and $S_{\rm SDW}$ (33) for the ER model (N=4,6), plotted as a function of U/Ω, with $t = 1$. In panel (a) we report the result for the closed-shell case, while panel (b) has the result for the open-shell case. $E_{\rm cut} = 6$ for N=4, and $E_{\rm cut} = 3$ for N=6. Solid dots mark crossings defining U^*, again indicating pairing even at positive U.

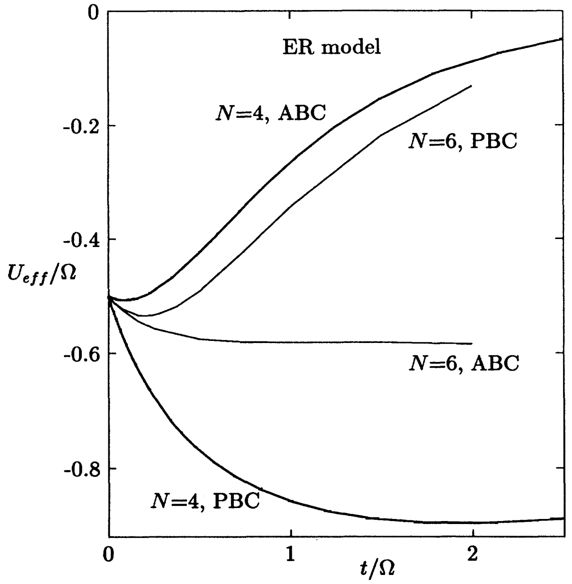

FIG. 4. The effective Hubbard term $U_{\rm eff}$ (35) for the ER model (N=4,6), plotted as a function of t/Ω. The N=4 ABC's and N=6 PBC's are closed shells, while N=4 PBC's and N=6 ABC's are open-shell cases. $E_{\rm cut} = 8$ for N=4, and $E_{\rm cut} = 4$ for N=6. For $t/\Omega \ll 1$, the slope of $U_{\rm eff}$ coincides with $U_{\rm eff}/t$ of the EP model (Fig. 2). For $t/\Omega \gg 1$, the dynamical Jahn-Teller effects are suppressed, whence $U_{\rm eff} \to 0$.

One may suspect that the pairing we are demonstrating is just a consequence of the exact symmetry between the x and y degenerate molecular orbitals that we enforce by the assumption of having equal intermolecular hopping matrix elements t_x, t_y, defined in (17), as discussed in Sec. II. A simple test releasing this assumption shows that this is actually not the case. If $t_x \neq t_y$, the hitherto missing term corresponding to unequal t_x, t_y contributions is the following kinetic additive contribution:

$$H'_{\rm kin} = -\frac{t'}{2} \sum_{\langle i,j\rangle,\sigma} c^\dagger_{i,\sigma} c_{j,\sigma} (L^+_i L^+_j + L^-_i L^-_j) \ , \qquad (36)$$

where t' is the independent hopping amplitude $t' = (t_x - t_y)/2$. This term violates the conservation of total m

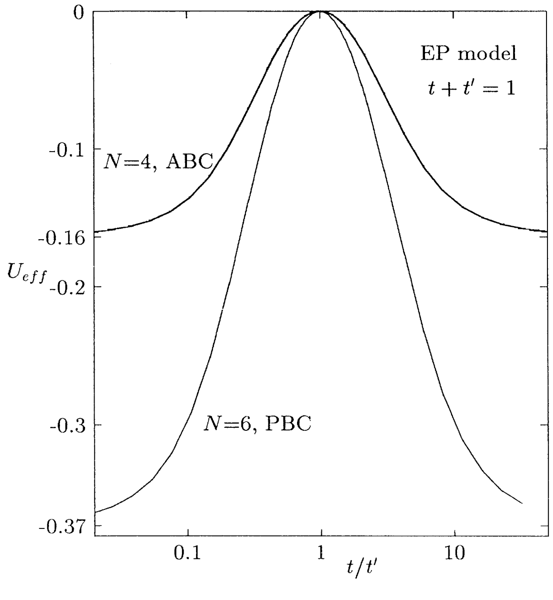

FIG. 5. The effective Hubbard term $U_{\rm eff}$ (35) for the EP model (N=4,6, in closed shells) with the addition of the term (36), describing $t_x \neq t_y$, plotted as a function of t/t', at fixed $t+t'=t_x=1$. The effective interaction survives everywhere except at the isolated point $t/t'=1$, corresponding to the unphysical case $t_y=0$ (or $t_x=0$).

(equivalent to complete x-y symmetry). By adding to the symmetric Hamiltonian (30) a term like (36) we can break this symmetry continuously, monitoring the effects of this on pairing, and, in particular, on the $U_{\rm eff}$ that was defined above.

In Fig. 5 we plot $U_{\rm eff}$ for the EP model (for simplicity) in the closed-shell configurations for four and six sites, as a function of t/t', at fixed $t+t'=t_x$. This figure shows that although the negative effective attractive $U_{\rm eff}$ is maximum for $t_x=t_y$ and $t_x=-t_y$, it is not cancelled in the general case $t_x \neq t_y$, except for the very special case $t_y=0$ (or $t_x=0$). The cancellation of pairing interaction in this limit is due to the complete breaking of the rotational symmetry, creating two separate bands from the x and y orbitals, the x-originated band being a regular tight-binding band, the y one being made of localized degenerate states. Anyway, this is indeed a very special case, in which no t_y term is present. In a more realistic situation having, say, $t_y \approx -t_x/2$, the pairing effect fully survives.

IV. THE INFINITE-CHAIN–MEAN-FIELD BCS APPROACH

In order to get a qualitative idea of the effects of the Berry-phase constraints on the infinite system, we first integrate out the vibron degrees of freedom in the simple spin-1 model Hamiltonian (1). To do this, we make the further approximation of replacing the spin operators by pseudofermion operators representing the vibron excitations. We can then integrate out the vibron degrees of freedom and apply the BCS equations to the resulting interacting fermion system.

Introducing an auxiliary spin-$\frac{1}{2}$ fermion $B^\dagger_{i\alpha}$, we classify the $m=+1$ vibron state as an "α-up" state, and the $m=-1$ state as an "α-down" state. The $m=0$ state is treated as a vacuum state for the B fermions, which we will call "berryons":

$$|m=1\rangle \equiv B^\dagger_\uparrow|0\rangle \ , \ |m=-1\rangle \equiv B^\dagger_\downarrow|0\rangle. \qquad (37)$$

Using this representation, we express the spin-1 operators by

$$S^+ \equiv B^\dagger_\uparrow + B_\downarrow \ , \ S^- \equiv B_\uparrow + B^\dagger_\downarrow \ , \ S^z \equiv B^\dagger_\uparrow B_\uparrow - B^\dagger_\downarrow B_\downarrow \ . \qquad (38)$$

This representation is overcomplete (in particular, it does not exclude unphysical states with n_i, m_i of different parity) and will therefore not allow a strictly variational treatment. Still, it is of use in exploring whether the model does or does not display tendencies toward pairing at the simplest mean-field level.

We rewrite the Hamiltonian (1) in this fermion representation as

$$H_{\rm kin} = -\frac{t}{2}\sum_{\langle i,j\rangle,\sigma} c^\dagger_{i,\sigma}c_{j,\sigma}(B^\dagger_{i\uparrow}B_{j\uparrow} + B^\dagger_{i\downarrow}B_{j\downarrow} + B^\dagger_{i\uparrow}B^\dagger_{j\downarrow} + B_{i\downarrow}B_{j\uparrow} + \text{H.c.}) \qquad (39)$$

or, in Fourier representation,

$$H_{\rm kin} = -\frac{t}{2N}\sum_{k_1,k_2,q,\sigma} \cos(k_1+q)c^\dagger_{k_1,\sigma}c_{k_2,\sigma} \times(B^\dagger_{q\uparrow}B_{k_1-k_2+q\uparrow} + B^\dagger_{q\downarrow}B_{k_1-k_2+q\downarrow} + B^\dagger_{q\uparrow}B^\dagger_{-k_1+k_2-q\downarrow} + B_{-q\downarrow}B_{k_1-k_2+q\uparrow} + \text{H.c.}) \ . \qquad (40)$$

We take as a zeroth-order mean-field Hamiltonian just free fermions (note that this term was missing in the original problem)

$$H_{\rm MF} = \sum_{k,\sigma}\epsilon_k c^\dagger_{k,\sigma}c_{k,\sigma} + \sum_{k,\alpha}\eta_k B^\dagger_{k,\alpha}B_{k,\alpha} \qquad (41)$$

such that

$$E_{\rm MF} = \langle 0_{\rm MF}|H|0_{\rm MF}\rangle \qquad (42)$$

is minimum. $|0_{\rm MF}\rangle$ is the direct product of a half-filled Fermi sea of c electrons and of a Fermi sea of berryons filled up to $x \equiv N_B/N$. Here, x can be regarded as an adjustable variational parameter [although $H_{\rm MF}$ is not truly variational, as it violates the constraints required by Eq. (16)]. The precise value of x is, however, immaterial, since the qualitative results we will find appear to be independent of N_B.

Direct substitution gives

$$E_{\rm MF} = -\frac{8tN}{\pi^2}\sin\left(\frac{\pi}{2}x\right) \ , \qquad (43)$$

which is minimum for $x = 1$. The single-particle excitation energies are

$$\epsilon_k = -2\theta \cos k, \tag{44}$$

$$\eta_k = -\frac{4t}{\pi} \cos k \ , \tag{45}$$

where $\theta \equiv \frac{2t}{\pi} \sin(\pi x/2)$ is the effective mean-field hopping amplitude for c electrons.

The next step is the determination of the first nontrivial correction to the mean field due to the actual interaction (40) between c electrons and berryons. These corrections are achieved through an expansion in the interaction $(H - H_{\rm MF})$ around the free dynamics $H_{\rm MF}$. For this purpose, we write the full many-body partition function at temperature $1/\beta$:[15]

$$\begin{aligned} Z &= Z_{\rm MF}\left\langle \left\langle e^{-S} \right\rangle_B \right\rangle_c \\ &\approx Z_{\rm MF}\left\langle \exp\left(-\langle S\rangle_B + \frac{1}{2}[\langle S^2\rangle_B - \langle S\rangle_B^2] + ...\right) \right\rangle_c \ , \end{aligned} \tag{46}$$

with

$$\begin{aligned} Z_{\rm MF} &= Z^c_{\rm MF} Z^B_{\rm MF}, \\ S &= \int_0^\beta d\tau [H(c(\tau), ...B(\tau)) - H_{\rm MF}(c(\tau), ...B(\tau))], \\ \langle O[c_{k\sigma}]\rangle_c &= \int \frac{D[c^\dagger_{k\sigma} c_{k\sigma}]}{Z^c_{\rm MF}} \exp\left(-\int_0^\beta d\tau \sum_{k,\sigma} c^\dagger_{k\sigma}(\tau)(\partial_\tau + \epsilon_k) c_{k\sigma}(\tau)\right) O[c_{k\sigma}(\tau)], \\ \langle O[B_{k\alpha}]\rangle_B &= \int \frac{D[B^\dagger_{k\alpha} B_{k\alpha}]}{Z^B_{\rm MF}} \exp\left(-\int_0^\beta d\tau \sum_{k,\alpha} B^\dagger_{k\alpha}(\tau)(\partial_\tau + \eta_k) B_{k\alpha}(\tau)\right) O[B_{k\alpha}(\tau)], \end{aligned} \tag{47}$$

where $O[\,]$ is any operator, and

$$Z^c_{\rm MF} = \int D[c^\dagger_{k\sigma} c_{k\sigma}] \exp\left(-\int_0^\beta d\tau \sum_{k,\sigma} c^\dagger_{k\sigma}(\tau)(\partial_\tau + \epsilon_k) c_{k\sigma}(\tau)\right) \tag{48}$$

and a similar expression for $Z^B_{\rm MF}$.

Averaging over the noninteracting many body B fields in the cumulant expansion in (46) leaves an effective Hamiltonian operator for the c electrons. That expansion contains a first term $\langle S\rangle_B$, whose form is $\int_0^\beta d\tau \sum c^\dagger_{k\sigma}(\tau) c_{k\sigma}(\tau)$. It simply renormalizes the mean-field parameters. The lowest-order nontrivial action correction belongs to $-\langle S^2\rangle_B$, having the form of an effective electron-electron interaction term

$$S_{\rm eff} = \frac{1}{N} \int d\tau \int d\tau' \sum_{\sigma,\sigma'} \sum_{k_1,k_2,k_3,k_4} c^\dagger_{k_1\sigma}(\tau) c_{k_2\sigma}(\tau) c^\dagger_{k_3\sigma'}(\tau') c_{k_4\sigma'}(\tau') K_{k_1,k_2,k_3,k_4}(\tau - \tau'). \tag{49}$$

This term has a very simple significance. It corresponds to the exchange of a berryon particle-hole pair with singlet total pseudospin between the two electrons, as in the diagram of Fig. 6.

The imaginary time integration can be recast in a Matsubara frequency summation, in terms of a kernel

$$\begin{aligned} K_{k_1,k_2,k_3,k_4}(i\omega_B) = \delta_{k_1+k_3,k_2+k_4} \frac{t^2}{2N} \sum_k \cos(k_1 + k) \cos(k_3 + k + q) \frac{1}{\beta} \sum_{\omega_n} [&-2\tilde{g}_{k\uparrow}(\omega_n) \tilde{g}_{k\uparrow}(\omega_n + \omega_B) \\ &+ \tilde{g}_{k\uparrow}(\omega_n) \tilde{g}_{k\downarrow}(-\omega_n - \omega_B) \tilde{g}_{k\downarrow}(\omega_n) \tilde{g}_{k\uparrow}(-\omega_n + \omega_B)] \ , \end{aligned} \tag{50}$$

where $q := k_2 - k_1$, ω_n are fermionic Matsubara frequencies, and $\tilde{g}_{k\alpha}(\omega_n)$ is the free fermion propagator in Matsubara space as defined in Ref. 15. The sum over the Matsubara frequencies can be performed to recast Eq. (50) in form

$$\begin{aligned} K_{k_1,k_2,k_3,k_4}(i\omega_B) = \delta_{k_1+k_3,k_2+k_4} \frac{t^2}{2N} &\sum_k \cos(k_1 + k) \cos(k_3 + k + q) \\ &\times [2\Sigma(i\omega_B; \xi_k, \xi_{k-q}) - \Sigma(i\omega_B; \xi_k, -\xi_{k-q}) - \Sigma(i\omega_B; -\xi_k, \xi_{k-q})] \ , \end{aligned} \tag{51}$$

where $\Sigma(z, a, b) := [f_F(a) - f_F(b)]/[z - (b - a)]$, $f_F(\,)$ are Fermi occupation factors, and $\xi_k := \eta_k - \mu = -\frac{4t}{\pi}[\cos(k) - \cos(\frac{\pi x}{2})]$ are the single-particle excitation energies for the berryons reduced by the corresponding chemical potential.

We would now like to extract physical conclusions from this calculation. Since we deal with an effective 1D electron system, we wish to use the calculated effective electron-electron scattering as a guide to understanding which one of the standard 1D Lüttinger model fixed points will prevail. In particular, for that model, an estimate of the forward and backward coupling constants g_1 and g_2 (Ref. 13) will determine what kind of ground state to expect.

The pair-scattering amplitude we have obtained is obviously time (or frequency) dependent, i.e., non-Hamiltonian in nature. In this sense, straight identification with true Hamiltonian parameters, such as g_1 and g_2,[13] is not automatically correct. However, we see no physical reason preventing us from using our derived amplitudes as effective coupling constants so long as we stay sufficiently close to the Fermi surface.

We therefore identify

$$g_1 \propto K_{-k_F,k_F,k_F,-k_F}(i\omega_B) \quad (q=\pi) \ , \ g_2 \propto K_{k_F,k_F,-k_F,-k_F}(i\omega_B) \quad (q=0) \ . \tag{52}$$

Direct computation of K for these special momenta gives

$$\begin{aligned} K_{-k_F,k_F,k_F,-k_F}(i\omega) &= K_{k_F,k_F,-k_F,-k_F}(i\omega) \\ &= -\frac{t^2}{2N}\int_0^\pi \frac{dk}{\pi}\sin^2(k)[f_F(-\xi_k)-f_F(\xi_k)]\frac{2}{2\xi_k - i\omega} \\ &= -\frac{t}{8N}\int_{-1}^{1} dv\sqrt{1-v^2}\tanh\left(\frac{4}{\pi}\beta t v\right)\frac{1}{v-\frac{i\pi\omega}{8t}} \ . \end{aligned} \tag{53}$$

Interestingly, these two couplings arise from different terms in the Hamiltonian. The former is due to the $B^\dagger B$, $BB^\dagger$ terms in (40), whereas the latter is due to the $B^\dagger B^\dagger$ and BB terms.

In the zero frequency limit $z \to 0$, the two quantities are negative and coincide. In terms of the Lüttinger model phase diagram,[13] this corresponds to a spin singlet superconducting state, which is therefore found to prevail. This is in very good agreement with the effective negative U of the preceding section, with the additional remark that the alternative possibility of charge-density waves is now explicitly ruled out.

Actually, the zero-frequency limit is singular at zero temperature, when the Fermi functions become step functions and the k integration diverges logarithmically for vanishing frequency around k_F^B, the Fermi momentum for the berryons. In other words, in this approximation $g_1 = g_2$ diverge as $\ln|z|$ at small z. This is a singular feature, due to our assuming the exchange of a bare, unrenormalized particle-hole pair as in Fig. 6. Higher-order diagrams will modify that. More importantly, in the presence of a finite pairing amplitude, for example, this divergence will disappear, due to a pairing gap in the berryon spectrum. There is, in fact, an exact symmetry between fermions and pseudofermions, and the two Cooper channels are also identical.

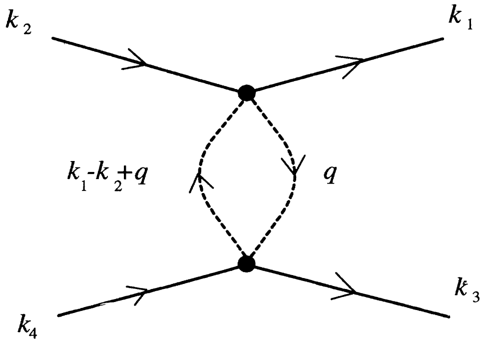

FIG. 6. The second-order effective interaction between electrons is due to the exchange of a pair of berryons.

V. DISCUSSION

A very important property of our Berry-phase-constrained tunneling Hamiltonian is the fact that the constraint operates at the energy scale of the tunneling matrix element t. Thus the pairing tendency induced by the constraints is not dictated directly by the strength of the intramolecular electron–vibron coupling, but rather by the indirect effect of this coupling in the semiclassical limit on the relative phase space available for single electron tunnelling versus that for pair tunnelling. Thus the enforcing of the Berry-phase constraint effectively separates the energy scale of the tunneling t from that of the internal degrees of freedom of the constituent molecules. In this sense, the resulting part of the attractive pairing interaction is unretarded. The ensuing superconducting state, which we expect in a 3D case, is not yet fully worked out, but does not appear to be Eliashberg-like.

In the case of C_{60} itself, the model is in too extreme a semiclassical limit to give a reasonable representation of the physics of K_3C_{60}, since, in that case, the dimensionless electron-vibron coupling strength g is of order ~ 0.4, whereas the strong-coupling limit, where the Berry-phase representation becomes useful, is for $g \gtrsim 1$.

Nevertheless, the model does illustrate a new physical principle for superconductivity in strongly constrained systems. It is tempting to make an analogy with the physics of the t-J model of interest for describing the physics of doped Mott insulators. In that case, the hopping Hamiltonian may be rewritten as

$$H_t = -t\sum_{\langle ij\rangle}(S_i^+ c_{i\downarrow}^\dagger c_{j\downarrow} S_j^- + S_i^- c_{i\uparrow}^\dagger c_{j\uparrow} S_j^+ + \text{H.c.}), \tag{54}$$

where S_i^+, S_j^- are spin raising and lowering operators. A number of recent studies[16] suggest that pairing of holes close to the half-full insulating state occurs as a result of kinematical constraints in this model.

Although the present model does not have the ordered or quasiordered background of the antiferromagnetic state in the t-J model, it does have the feature that pair tunneling proceeds by each partner causing a vibron excitation when executing a tunneling step, which then annihilates when the pair of carriers come together again on the same site. Similarly, in the t-J model case, individual hole hopping is accompanied by a spin flip, which can be cancelled by the hopping of its partner.

It is of interest to consider whether our Berry-phase considerations could also apply to the Chevrel-phase class of superconductors such as $LaMo_6Se_8$ or $PbMo_6S_ySe_{8-y}$.[17] In these materials the Mo_6Se_8 cluster has a set of degenerate lowest unoccupied molecular orbitals (LUMO's) analogous to those in C_{60}. Measurements of the doping dependence of T_c indicate a sharp maximum as a function of doping in the unfilled LUMO shell. Thus, there is the possibility of a general class of constraint-driven superconductors with distinctly different dependence of T_c on material parameters than those of the conventional BCS-type electron-phonon superconductors.[18]

Although, as stated above, we do not expect our model to be a realistic representation of the physics of K_3C_{60}, it would nevertheless be interesting to test experimentally whether the kind of electron-vibron coupling we have proposed could be observed in this compound. One way to do this would be through the two-vibron Raman spectrum. Our coupling mechanism would naturally lead to a direct electron-hole pair channel coupling to a pair of vibron modes. This channel would open up a gap of 2Δ, in the vibron spectrum, where Δ is the superconducting gap, on lowering the temperature of the material below T_c.

More generally, we observe that the pseudorotor Berry-phase mechanism sketched here, ties together electron hopping with the hopping of quanta of *orbital* molecular angular momentum, which is unquenched in the free-molecule limit we start from. In the paired state, orbital quanta are also paired, whereby the orbital excitation branch will *also develop a gap* at $q = 2k_F$. The gap will follow identically the superconducting gap at $T = T_c$. The staggered orbital susceptibility should therefore be maximum at T_c. In turn, the uniform $q = 0$ orbital susceptibility may also develop a maximum, although weaker, via momentum nonconserving or local field effects. It is possible that orbital effects of this kind, even if weaker than suggested by this extreme picture, could be detectable, e.g., by NMR. In particular, the relaxation time $1/T_1$ could be enhanced at low temperature, and peak up around T_c due to large susceptibility fluctuations.[19]

It would be of considerable interest to see if these new effects could be observed in K_3C_{60} and Rb_3C_{60}. Encouragingly, in this latter compound, very recent NMR data[20] seem to indicate a behavior of the relaxation time, which is anomalous precisely in the way suggested above. The anomaly at T_c, in particular, is seen in the Rb ion, but not on the carbon, as we would expect for a C_{60} orbital effect.

Finally, it is of interest to speculate that T_c would be enhanced by doping our model system away from half filling. Because of the nature of our pairing mechanism, the carriers would have more phase space for pairing if each partner in a pair could find many empty neighboring sites to hop on to before pairing again. Thus the doping dependence of T_c might be expected to have a maximum away from half filling in systems for which this mechanism is driving the superconductivity. In this sense the case of half filling is probably the least favorable. There are indications from an exact solution for the two-electron state that in the EP model, $U_{\rm eff}$ is one order of magnitude more attractive near zero filling.[21]

In the fullerides, exact half filling appears to be required by chemical stability.[22] In the Chevrel systems, however, where continuous doping is feasible, one indeed finds a maximum of T_c for a hole density close to one per molecular unit.[17] This corresponds to only 1/6 filling of the narrow Γ_{25} molecular band in that case.[23] A second observation is that the correlation length should tend to be short, of the order of the intermolecular distance a, since this is the scale where the energy gain takes place. In K_3C_{60}, this expectation is well borne out, with a correlation length of order $\equiv 2a$.

Experimentally, it would be of interest to consider building new molecular solids where high-symmetry Jahn-Teller molecules can exchange electrons. Larger molecules may be better ones because of a weaker intramolecular Coulomb repulsion U. Relatively weak JT coupling may provide an additional favorable circumstance, since in that case the effective Ω is larger (although our treatment does not strictly apply there) and DJT quantum effects are more important. Both these conditions are met in the fullerides, but it might be possible to find other systems where they apply.

VI. CONCLUSIONS

We have proposed a model for constrained tunneling of charge carriers in a lattice of Berry-phase molecules, inspired by the physics of the fullerides. The general model [Eq. (22)] is based on an electron-quantum rotor Hamiltonian, which includes a (in principle, infinite) manifold of vibron states on each site. Although we have been able to investigate the effects of a large number of vibron states on the pairing tendency, it is clear that the effect is strongest when only the lowest are important. For the extreme case where only the lowest vibron state is important ($S = 1$ pseudospin model), both our numerical studies on small clusters (Sec. III) and our BCS-type mean-field treatment (Sec. IV) indicate a strong pairing tendency for a half-filled band. The fact that the model exhibits intrinsic pairing even in the presence of Hubbard repulsion U of the order of the tunneling matrix element t is understood readily from the form of the model Hamiltonian [Eqs. (1) and (22)]. On integrating out the vibron degrees of freedom, we obtain an effective BCS attraction of order t^2/W, where W is a vibron bandwidth of order t. Thus the Berry-phase constraint leads to an electron-electron attraction whose energy scale is not directly related to the strength of the intramolecular electron-vibron coupling in the semiclassical limit.

In physical terms, our model is based on the entanglement of the orbital angular momentum of the individual molecules with electron hopping between molecules. Pairing of electrons is generated by an accompanying ("singlet") pairing of orbital momenta on neighboring molecules, suggesting short correlation lengths in the order of the intermolecular spacing. It has been argued that this mechanism might be relevant also in such other molecular superconductors, such as the Chevrel compounds.

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