ARTICLES

Nonmagnetic molecular Jahn-Teller Mott insulators

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Narrow-band conductors may turn insulating and magnetic as a consequence of strong electron-electron correlation. In molecular conductors, the concomitance of a strong Jahn-Teller coupling may give rise to the alternative possibility of a nonmagnetic insulator, with or without a static cooperative Jahn-Teller distortion. In the latter case the insulator has Mott-like properties, with an interesting interplay between electron-electron repulsion and the Jahn-Teller effect, which is dynamical. We study this kind of nonmagnetic insulator in a very simple $E \otimes e$ Jahn-Teller model and we discuss its general properties in a more general context, also in connection with the insulating state of K_4C_{60} and Rb_4C_{60}. [S0163-1829(97)03919-2]

I. INTRODUCTION

The existence of a model of conducting electrons which turns into a nontrivial paramagnetic Mott insulator at zero temperature is a long-standing question. The problem can be formulated in the following way. Let us consider a model which is supposed to be a metal if some kind of correlation (among the electrons or between the electrons and the ions) is neglected. Can these correlations turn the model into a Mott insulator, as opposed to a band insulator? (For a band insulator we mean a system which fits all the standard one-electron criteria of an insulator, i.e., an even number of valence electrons per unit cell, an integer number of filled band, and a band gap.) In fact, in spite of many efforts, many of the models which have been proposed to this end become insulating by enlarging the unit cell and consequently reducing the Brillouin zone so to fit those criteria. Typical examples are the Hubbard model in $D>1$ or the one-dimensional Su-Schrieffer-Hegger (SSH) models at half filling. In these cases the density corresponds to one valence electron per unit cell, so the models should be in principle metallic. However, the electron-electron interaction in the Hubbard model and the electron-phonon coupling in the SSH model force on the system a staggered order parameter which doubles the unit cell, so that the systems acquire the prerequisite for being insulators, and in fact they become insulating.

In this paper we are going to describe an alternative kind of Mott insulator. Let us consider a lattice made of molecules which have unfilled degenerate valence orbitals occupied by an *even* number of electrons. Let us briefly discuss how the lattice of such molecules might be insulating. A first trivial possibility is that the crystal field and the electron hopping split the degeneracy so to give rise to a band insulator once filled by the available electrons. We are not going to consider this case. That is we will assume that, even after the crystal field and the hopping are duly taken into account, the resulting band structure still implies a metallic state. In such a situation, considering electron-electron repulsion, a Mott insulating behavior may still occur because the energy cost to change the valence of a molecule by ± 1 electron overcomes the gain in energy due to the electron hopping. Specifically, if the isolated molecule has $2n$ valence electrons and we define an effective Hubbard U_{eff} as

$$2U_{\text{eff}} = E(2n+1) + E(2n-1) - 2E(2n), \quad (1)$$

where $E(m)$ is the molecular ground state energy with m valence electrons, a Mott state can be expected for $U_{\text{eff}} \gg W$, where W is the electron bandwidth.

However, in this case we still have two possible routes to an insulating state. If the molecular ground state has a non-zero spin due to a prevailing Hund's rule coupling, the insulator will likely be magnetic, similarly to the previously discussed Hubbard model at half filling. In particular, the neighboring molecules will couple either ferromagnetically or antiferromagnetically depending upon the detailed properties of the system.

In the alternative case where the molecular ground state is a singlet, we expect instead a nonmagnetic Mott insulator. A possible mechanism for a Hund's rule violation, leading to a singlet in a molecule with partially filled orbitals, is of course provided by the Jahn-Teller (JT) effect. Let us therefore assume that the coupling to some vibrational mode is able to split the degeneracy of the molecular orbitals favoring, in the absence of Coulomb repulsion, a nondegenerate singlet state. In the following we will consider a coupling to a local vi-

bron, driving the single molecule to a Jahn-Teller distortion. Then, if the JT energy splitting $\Delta E_{\rm JT}$ between the nondegenerate singlet and the high-spin states overcomes the Hund's rule (Coulomb) splitting $\Delta E_{\rm Hund}$, then the molecular ground state is the nondegenerate singlet and the insulator is nonmagnetic.[1] [Notice that the JT effect will in general also contribute to an increase of $U_{\rm eff}$ in Eq. (1).]

Now, there are still two possibilities for both the magnetic and nonmagnetic insulators. If the intramolecular coordinates can be treated as classical, we can fix them at each site to some values and then solve the electron problem in the external potential provided by the static molecular distortions. The ground state lattice configuration is found by minimizing the total energy given by the vibrational energy plus the electron energy (in the presence of the molecular deformation), and in general consists of a periodic arrangement of statically distorted molecules (cooperative JT effect). Note that a commensurate distortion might turn the metallic state into an insulator even if $U_{\rm eff} \sim W$ as a consequence of a nested Fermi surface.

A second and newer possibility arises if the quantum fluctuations of the intramolecular coordinates cannot be neglected. This is the case, for example, with a large spacing between the lowest rotational levels in the Jahn-Teller trough potential (or the tunnel splitting in a warped one) compared with the intermolecular coupling. In this case a static collective molecular distortion may become disadvantageous and the rotational (or cubic, or bct, etc.) symmetry of each molecule dynamically restored (dynamic JT effect). This would be a quite interesting situation in which the Jahn-Teller effect plays a crucial role in making the insulating state nonmagnetic without revealing itself by a cooperative distortion. We will define this insulator as a Jahn-Teller-Mott (JTM) insulator.

Hence, a lattice of molecules with this kind of property can in principle display a variety of behavior depending upon the relative strengths of the parameters which come into play. If $U_{\rm eff} \gg W$, we expect an insulating behavior to be either magnetic, if $\Delta E_{\rm Hund} \gg \Delta E_{\rm JT}$, or nonmagnetic, if $\Delta E_{\rm JT} \gg \Delta E_{\rm Hund}$. On the contrary, if $W \gg U_{\rm eff}$, a metallic state should be favored. A cooperative JT effect may or may not be present depending on the value of the lowest rotational frequencies compared to the intermolecular coupling. In the particular case of $\Delta E_{\rm JT} \gg \Delta E_{\rm Hund}$ we expect that, as the bandwidth increases, a transition should take place from a nonmagnetic insulator to a metal.

A source of inspiration for this work has been the fullerides K_4C_{60} and Rb_4C_{60}, which, as we discuss in Sec. IV, have many features in common with the general model we have previously discussed, although in these materials it is still unclear from the experimental and theoretical point of views which of the above introduced scenarios is effectively realized. However, our main purpose here is to introduce and discuss a mechanism for the occurrence of a nonmagnetic Mott insulator, which may, in way of principle, be realized in a different system, even though not yet found or studied. Therefore, since the situation in fullerenes is still open, we have postponed the discussion of the possible realization of this insulating state in those materials to Sec. IV. We instead use the following two sections to study a prototype simple model which does show all the interesting features we have

previously foreshadowed, depending on the values of the different parameters in the Hamiltonian. Specifically, this model consists of a lattice of ''molecules,'' each with two degenerate orbitals coupled to a doubly degenerate vibron ($E \otimes e$ Jahn-Teller problem[2]). Different molecules are then coupled via a single particle electron hopping term, and, in addition, an intramolecule Coulomb interaction is taken into account.

II. SINGLE MOLECULE

We start by describing our modeling of the isolated molecule. We take the following molecular Hamiltonian ($\hbar = 1$):

$$\hat{H} = \frac{\omega_0}{2}(\vec{p}^2 + \vec{r}^2) + \omega_0 g \vec{r} \cdot \vec{\tau} + \hat{H}_{\rm int}, \tag{2}$$

where $\vec{r}$ is a two-dimensional vibrational coordinate, $\vec{p}$ its conjugate momentum, and $\vec{\tau}$ are pseudospin-1/2 matrices acting in the space of the two-degenerate electronic orbitals, i.e.,

$$\tau^+ = \sum_\sigma c_{1\sigma}^\dagger c_{2\sigma}, \tag{3}$$

$$\tau_z = \frac{1}{2}\sum_\sigma (c_{1\sigma}^\dagger c_{1\sigma} - c_{2\sigma}^\dagger c_{2\sigma}). \tag{4}$$

The interaction part $\hat{H}_{\rm int}$ of the Hamiltonian can be written in the form

$$\hat{H}_{\rm int} = Un^2 + V(\tau_x^2 + \tau_y^2), \tag{5}$$

which takes into account the planar symmetry of the model. Here $n = \sum_\sigma c_{1\sigma}^\dagger c_{1\sigma} + c_{2\sigma}^\dagger c_{2\sigma}$ is the total occupation number, and U,V are positive interaction parameters. In particular U will limit fluctuations of total charge of the molecule, while V controls the internal spin and orbital state.

By rewriting in polar coordinates $\vec{r} = (r\cos\phi, r\sin\phi)$ the coupling between the vibron mode and the electrons, we get

$$\vec{r} \cdot \vec{\tau} = \frac{1}{2} r e^{i\phi} \tau^- + \text{H.c.} \tag{6}$$

The angular coordinate dependence can be partly eliminated via the (non-Abelian) gauge transformation:

$$\hat{H} \mapsto \hat{U}\hat{H}\hat{U}^\dagger,$$

where

$$\hat{U} = e^{i\phi\tau_z}. \tag{7}$$

Under this transformation

$$c_{1\sigma} \mapsto c_{1\sigma} e^{-i\phi/2},$$

$$c_{2\sigma} \mapsto c_{2\sigma} e^{i\phi/2}, \tag{8}$$

so that the Hamiltonian (2) simplifies into

TABLE I. Electronic eigenstates and eigenvalues at fixed r, for occupation numbers $n=1,2,3$.

n	Quantum numbers	$E(r)$
1	$s=1/2,\ \tau_x=-1/2$	$U+V/2-\omega_0 g r/2+\omega_0/(8r^2)$
1	$s=1/2,\ \tau_x=1/2$	$U+V/2+\omega_0 g r/2+\omega_0/(8r^2)$
2	$s=0,\ \tau_x^2=1$	$4U+3V/2+\omega_0/(4r^2)-\sqrt{V^2/4+\omega_0^2 g^2 r^2}$
2	$s=1,\ \tau=0$	$4U$
2	$s=0,\ \tau_x^2=0$	$4U+V+\omega_0/(2r^2)$
2	$s=0,\ \tau_x^2=1$	$4U+3V/2+\omega_0/(4r^2)+\sqrt{V^2/4+\omega_0^2 g^2 r^2}$
3	$s=1/2,\ \tau_x=-1/2$	$9U+V/2-\omega_0 g r/2+\omega_0/(8r^2)$
3	$s=1/2,\ \tau_x=1/2$	$9U+V/2+\omega_0 g r/2+\omega_0/(8r^2)$

$$\hat{H}=-\frac{\omega_0}{2r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right)-\frac{\omega_0}{2r^2}\left(\frac{\partial}{\partial\phi}+i\tau_z\right)^2$$

$$+\frac{\omega_0}{2}r^2+\omega_0 g r\tau_x+\hat{H}_{\text{int}}. \qquad (9)$$

The angular part of Eq. (9) is simply diagonalized by eigenfunctions $\exp(i\lambda\phi)$. Moreover, since the total wave function must not change upon varying ϕ by 2π, as a consequence of the gauge transformation (7) λ has to be an integer for an even electron number and a half odd integer for an odd electron number. Due to the symmetry $\lambda\rightarrow-\lambda$ and to the spin degeneracy, each level for odd electron number is at least four times degenerate (in this case the dynamic JT effect does not split the orbital degeneracy). On the contrary, for two electrons (the states with zero or with four electrons are trivial) the degeneracy is lifted and the ground state is nondegenerate. Let us now assume a strong JT coupling, $g\gg1$, and calculate the ground state and lowest energy spectrum with an accuracy of order g^{-2}. In this limit, we can adopt a Born-Oppenheimer (BO) approximation scheme for the transformed Hamiltonian (9). In fact, the ''electronic'' states (notice that the transformed electrons are indeed a mixing of purely electronic and vibrational degrees of freedom), which are not orbital singlets, will be split by the electron-vibron coupling of terms of order $\omega_0 g\langle r\rangle$, where $\langle r\rangle$ is the average value of the vibron displacement in the BO approximation, which is different for different electronic configurations. If $g\gg1$, the energy differences between different electronic configurations will be much larger than the lowest excitation energies within the Jahn-Teller trough potential, thus justifying the BO approximation.

We therefore start by calculating the electronic energies and eigenstates at fixed r. These are listed in Table I for different occupation numbers $n=1,2,3$, where each eigenstate is identified by a set of quantum numbers. In particular, when the total orbital momentum is not zero, the appropriate orbital quantization axis is x.[3] It is therefore useful to introduce the rotated orbitals which diagonalize τ_x, defined by

$$d_{1\sigma}=\frac{1}{\sqrt{2}}(c_{1\sigma}+c_{2\sigma}), \qquad (10)$$

$$d_{2\sigma}=\frac{1}{\sqrt{2}}(c_{1\sigma}-c_{2\sigma}). \qquad (11)$$

The next step is to diagonalize the Hamiltonian for the vibrational coordinates using the electronic eigenvalues $E(r)$'s of Table I as effective potentials. We are going to discuss the final result only for the lowest energy states.

For two electrons, the molecule has two sets of low energy states. The first one is spin singlets which take more advantage from the JT effect (see Table I). Notice, however, that the vibrational potential energy of this state shows a minimum at finite r only if $2\omega_0 g^2>V$, otherwise the minimum stays at $r=0$. This describes the competition on the single molecule between Hund's rule, which is related to V of Eq. (5), against a JT effect. If the latter is strong enough, so that $2\omega_0 g^2>V$, then a distorted potential energy minimum develops at

$$r_*=g\sqrt{1-\left(\frac{V}{2\omega_0 g^2}\right)^2},$$

and the low energy spectrum of singlets is

$$^1E_{l,\lambda}^{(2)}\simeq\left(l+\frac{1}{2}\right)\omega_*+\frac{\omega_0}{2}\left(\frac{\lambda}{r_*}\right)^2$$

$$-\frac{\omega_0}{2}g^2-\frac{V^2}{8\omega_0 g^2}+4U+\frac{3}{2}V, \qquad (12)$$

where $l=0,1,2,\ldots$ is the quantum number labeling the small oscillations in the JT potential well, whose frequency ω_* is

$$\omega_*=\omega_0\sqrt{1-\frac{V^2}{4\omega_0^2 g^4}}, \qquad (13)$$

and $\lambda=0,1,2,\ldots$ is the angular momentum eigenvalue. In Eq. (12) we have omitted constant terms of order $\geq\omega_0/g^2$ as well as l- and λ-dependent terms of higher order.

The second set of states for the two-electron molecule consists of spin triplets. Since these are orbital singlets, the JT coupling is ineffective and the low energy spectrum is simply

$$^3E_{n_1,n_2}^{(2)}=(n_1+n_2+1)\omega_0+4U. \qquad (14)$$

If the JT energy gain overcomes the Hund's rule gain, that is if

$$\frac{\omega_0}{2}g^2+\frac{V^2}{8\omega_0 g^2}>\frac{3}{2}V, \qquad (15)$$

then the ground state is a spin-singlet belonging to the set (12), and the lowest singlet excitations in the $g \gg 1$ limit are obtained by increasing the angular momentum λ.

When the molecule is occupied by one or three electrons, on the other hand, the low energy spectrum is simply

$$^2E_{l,\lambda}^{(1,3)} \simeq \left(s+\frac{1}{2}\right)\omega_0 + 2\omega_0\left(\frac{\lambda}{g}\right)^2 - \frac{\omega_0}{8}g^2 + Un^2 + \frac{V}{2}, \quad (16)$$

where $n=1$ or $n=3$, respectively, and λ is half an odd integer.

When condition (15) is fulfilled, i.e., when the $n=2$ molecular ground state is a spin singlet, the effective Hubbard U_{eff} is given by

$$2U_{eff} = {}^2E_{1/2,0}^{(1)} + {}^2E_{1/2,0}^{(3)} - 2\,{}^1E_{0,0}^{(2)}$$
$$\simeq \frac{3}{4}\omega_0 g^2 + 2U + \frac{V^2}{4\omega_0 g^2} - V. \quad (17)$$

We are interested in the case where the above U_{eff} is much bigger than the electron bandwidth W.

III. A LATTICE OF MOLECULES WITH TWO ELECTRONS PER SITE

Let us now consider a lattice of molecules, each of them described by the molecular Hamiltonian (2), with an average electron density of two electrons per site (half filling). As previously discussed, we assume that for $n=2$ the molecular ground state is a singlet due to the Jahn-Teller effect prevailing the Hund's rule. If the molecules were uncoupled, the system would be a trivial insulator made of independent dynamic Jahn-Teller molecules each doubly occupied and nondegenerate. An intermolecular coupling is introduced via a single particle hopping of the general form

$$\hat{T} = -\sum_{ij}\sum_{\sigma}\sum_{a,b=1}^{2} t_{ij}^{ab} c_{ia\sigma}^{\dagger} c_{jb\sigma}. \quad (18)$$

We will assume that the hopping energy is smaller enough than the effective Hubbard U_{eff} of Eq. (17), so that the addition of Eq. (18) into the Hamiltonian does not automatically turn the system into a metal. Nevertheless the interplay between the on site energy and the hopping can in principle lead to different situations, as anticipated in the Introduction.

A. Effective model in the strong Jahn-Teller coupling limit

In this section we are going to derive an effective model valid in the limit $U_{eff} \gg W$ and $g \gg 1$. In the absence of the hopping term (18), each molecule would be in its ground state with quantum numbers $(l,\lambda)=(0,0)$ and total spin $S=0$ [see Eq. (12)]. The hopping mixes the molecular ground state with the excited states. We will concentrate only on singlet excitations which do not change the values of l, i.e., we will keep only the excitations to larger λ's. To be consistent, we must consider only excitations up to $\lambda \sim g$. Within these approximations, the second order perturbation theory in Eq. (18) provides, as we are going to show, an effective intermolecular contribution $\hat{J}$ to the Hamiltonian which only acts on the subspace with molecular quantum

numbers $l=0$ and $S=0$ but different λ's. The matrix elements of this term are formally given by

$$\langle a'|\hat{J}|a\rangle = \sum_{b} \langle a'|\hat{T}|b\rangle\langle b|\hat{T}|a\rangle \frac{1}{E_a - E_b}, \quad (19)$$

where in the states $|a\rangle$ and $|a'\rangle$ all the molecules are in eigenstates belonging to the set of Eq. (12) with $l=0$. After the gauge transformation (7) is performed, Eq. (18) is transformed into

$$\hat{T} = -\sum_{ij}\sum_{\sigma} t_{ij}^{11}e^{i(\phi_i-\phi_j)/2}c_{1i\sigma}^{\dagger}c_{1j\sigma} + t_{ij}^{22}e^{-i(\phi_i-\phi_j)/2}c_{2i\sigma}^{\dagger}c_{2j\sigma}$$
$$+ t_{ij}^{12}e^{i(\phi_i+\phi_j)/2}c_{1i\sigma}^{\dagger}c_{2j\sigma} + t_{ij}^{21}e^{-i(\phi_i+\phi_j)/2}c_{2i\sigma}^{\dagger}c_{1j\sigma},$$

which, in terms of the orbitals d_1 and d_2 of Eqs. (10) and (11), becomes

$$\hat{T} = -\sum_{ij}\sum_{\sigma}\sum_{a,b=1}^{2} T_{ij}^{ab}d_{ai\sigma}^{\dagger}d_{jb\sigma}. \quad (20)$$

The hopping matrix elements in the above equation are

$$2T_{ij}^{ab} = (t_{ij}^{11}e^{i(\phi_i-\phi_j)/2} + t_{ij}^{22}e^{-i(\phi_i-\phi_j)/2})\delta_{ab}$$
$$+ (t_{ij}^{11}e^{i(\phi_i-\phi_j)/2} - t_{ij}^{22}e^{-i(\phi_i-\phi_j)/2})\sigma_{ab}^{x}$$
$$+ (t_{ij}^{12}e^{i(\phi_i+\phi_j)/2} + t_{ij}^{21}e^{-i(\phi_i+\phi_j)/2})\sigma_{ab}^{z}$$
$$- i(t_{ij}^{12}e^{i(\phi_i+\phi_j)/2} - t_{ij}^{21}e^{-i(\phi_i+\phi_j)/2})\sigma_{ab}^{y}. \quad (21)$$

Both our initial and final molecular states, $|a\rangle$ and $|a'\rangle$ in Eq. (19), have the orbitals d_2 of Eq. (11) doubly occupied at each site. Therefore the only processes allowed at second order by the hopping correspond to move an electron from an orbital d_2 at site i into a d_1 orbital at site j (which is the only one available) or vice versa, and then move it back. The sum over the intermediate states $|b\rangle$ in Eq. (19) only runs over molecular configurations in which two molecules are in a state with an odd number of particles and in general with $l \geq 0, \lambda \geq 0$. In the $U_{eff} \gg (W,\omega_0)$ limit, the energy denominator in Eq. (19) can be taken as a constant $\simeq -2U_{eff}$ for any $|b\rangle$. Consequently the sum over $|b\rangle$ becomes unity for completeness, which implies, for instance, that the hopping is not renormalized by any Ham reduction factor. Under all the previous assumptions, the explicit expression of Eq. (19) reads

$$\hat{J} = -\frac{1}{2U_{eff}}\sum_{ij} (T_{ij}^{12})^*T_{ij}^{12} + T_{ij}^{21}(T_{ij}^{21})^*, \quad (22)$$

which, through Eq. (21) and apart from constant terms, is equal to

$$\hat{J} = \frac{1}{8U_{eff}}\sum_{ij} (t_{ij}^{11*}t_{ij}^{22}e^{-i(\phi_i-\phi_j)} + \text{c.c.})$$
$$+ (t_{ij}^{12*}t_{ij}^{21}e^{-i(\phi_i+\phi_j)} + \text{c.c.}). \quad (23)$$

Notice that an analogous intermolecular phase coupling would also arise from multipolar forces among the molecules. We will not take these forces explicitly into account,
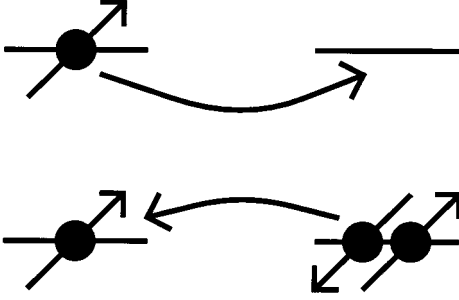
FIG. 1. Second-order process responsible of the motion of the $S = 1$ excitation.

even though they are as well important, since their inclusion does not modify the following qualitative discussion.

In addition to the intermolecular interaction (23), we must add the intramolecular orbital energy $\hat{H}_0$, which in the same $g \gg 1$ limit is

$$\hat{H}_0 = -\frac{\omega_0}{2 r_*^2} \sum_i \frac{\partial^2}{\partial \phi_i^2}. \tag{24}$$

The sum of Eqs. (23) and (24) thus represents the effective Hamiltonian acting on the *phases* of the molecular vibrons at a leading order in $1/U_{\text{eff}}$ and $1/g^2$. On one hand, the intersite coupling (23) tends to fix statically the phase of each molecule to get an advantage from the electron hopping (cooperative Jahn-Teller effect). On the other hand, the on site rotational energy favors a state in which the angular momentum is fixed and consequently the phase is indeterminate (dynamical Jahn-Teller effect).

From the above discussion we expect that, as the intermolecular interaction increases with respect to the lowest rotational frequency, the model should undergo a transition from a state where the vibron phase is disordered to a state where it orders. In both cases the system is insulating. The transition to a metallic phase cannot be described in this scheme, which is valid only in the limit of bandwidth much smaller than U_{eff}.

B. Excitations in the insulating phase

A possible way of discriminating among the two kinds of nonmagnetic insulator states, one which is accompanied by a cooperative JT effect and another one which is not, is through the study of the low energy excitations. Let us start with the dynamical case, i.e., let us assume that the rotational frequency overcomes the intermolecular coupling.

The first kind of excitation that we consider is a neutral spin-1 exciton. A single molecule is in a triplet state with, for instance, $S_z = 1$ and it has both orbitals singly occupied with a spin up electron. No JT effect occurs in this case. All the other molecules are in the singlet molecular ground state with $l = \lambda = 0$ [see Eq. (12)]. This state is obviously degenerate since any of the molecules can be in the triplet state. This degeneracy can be lifted by the single particle hopping via a second order process (see Fig. 1). As a consequence the triplet excitation moves coherently with an exciton hopping Hamiltonian given by

$$\frac{\Gamma}{2 U_{\text{eff}}} \sum_{ij} \langle T_{ij}^{11} T_{ji}^{22} \rangle |i\rangle\langle j|, \tag{25}$$

where the average $\langle\ \rangle$ is over molecular states with $\lambda = 0$, and gives

$$\langle T_{ij}^{11} T_{ji}^{22} \rangle = \tfrac{1}{4}(|t_{ij}^{11}|^2 + |t_{ij}^{22}|^2 - |t_{ij}^{12}|^2 - |t_{ij}^{21}|^2).$$

The constant Γ in Eq. (25) is a Ham's factor reducing the bandwidth of the spin-1 excitations and comes from the overlap of the vibronic wave functions with and without Jahn-Teller distortion. In conclusion, there are triplet excitations which can move coherently throughout the lattice.

The second coherent excitation that we consider is charged. Let us suppose that we add (or remove) one electron, as in a photoemission experiment. First let us neglect electron hopping. The additional electron modifies the occupancy of a single molecule leading to a degenerate ground state with $l = 0$, two electrons in the d_2 orbital, one in the d_1, and $\lambda = \pm 1/2$. As for the exciton, also this charged excitation can move coherently, i.e., without changing the total energy during the hopping process, and gives rise to two bands resulting from the molecular degeneracy $\lambda = \pm 1/2$. The general Bloch wave function is

$$|\vec{k}_{\pm}\rangle = \frac{1}{\sqrt{2N}} \sum_{\vec{R}} (|\vec{R}, \lambda = +1/2\rangle \pm |\vec{R}, \lambda = -1/2\rangle) e^{-i\vec{k}\cdot\vec{R}},$$

$\vec{R}$ being the position of the added electron and N the number of sites. The energy of this state is obtained by applying the hopping Hamiltonian (20) and is simply

$$\epsilon_{\pm}(\vec{k}) = \frac{\Gamma}{2} \sum_{\vec{r}} (t_{\vec{r}}^{11} \pm t_{\vec{r}}^{12}) e^{-i\vec{k}\cdot\vec{r}},$$

where $t_{ij}^{ab} = t_{i-j}^{ab}$. We note that these bands look exactly the same as those in the absence of electron-vibron coupling, although with a bandwidth reduced by the factor Γ. This is a clear manifestation of the dynamical JT effect. Moreover, it is important to notice that the bandwidth which results from such an ideal photoemission experiment should not be identified with the energy scale which competes against the intramolecular orbital energy Eq. (24) in deciding whether the Jahn-Teller distortion is static rather than dynamic. In fact, in the $U_{\text{eff}} \gg W$ limit we are considering, that energy scale is instead $\propto W^2/U_{\text{eff}}$. For smaller values of U_{eff} (smaller, but still enough to make the system a Mott insulator), the value of this energy scale is expected to be perhaps larger than W^2/U_{eff} but still smaller than W. This point will be relevant to our discussion of Sec. IV. Moreover, we stress that this result relies on a sort of adiabatic assumption, that is, we have assumed that the molecule after the addition of the electron flows into the corresponding ground state. Other configurations have been neglected since they are energetically disadvantageous even though they might have larger matrix elements.[4]

What is the spectrum of these charged excitations, instead, for a cooperative JT state? In the same adiabatic assumption we expect that the additional electron locally modifies the Jahn-Teller deformation. It should then move

coherently with this deformation, likely forming a single narrow polaron band instead of two as in the dynamical JTM state.

Finally, a third class of coherent excitations involves only the rotational degrees of freedom. In the limit $\omega_0 \gg t_{ij}^{ab}$ each molecule is in a state with $\lambda = 0$. The lowest excitations consist of larger angular momentum eigenvalues. Let us excite a single molecule into a state with $\lambda = 1$. This excitation is highly degenerate since $\lambda = -1$ has the same energy and also because we can choose any of the molecules. These degeneracies are lifted by the inclusion of the intermolecular exchange (23). If we stay restricted to the subspace where all molecules are in the $\lambda = 0$ state but one, with $\lambda = \pm 1$, and diagonalize Eq. (23) in this subspace, we again find two dispersive bands for this orbital excitation. Orbital angular momentum is quenched instead in the cooperative Jahn-Teller state. The presence of orbital excitations would be strong evidence of the dynamical nature of the Jahn-Teller effect, and of the JTM state.

IV. ARE FULLERENES A_4C_{60} POSSIBLE CANDIDATES?

A possible candidate for the scenario we have presented could be, at least in principle, the tetravalent fullerides K_4C_{60} and Rb_4C_{60}. In fact, as we pointed out in the Introduction, this was the original source of inspiration of this work, even though, as we shall see, it could still be that the Jahn-Teller effect in these fullerides is, in fact, static and collective, rather than dynamical. In these compounds the threefold-degenerate molecular orbital t_{1u} of C_{60} is partly occupied by the four electrons provided by the alkali atoms. In a purely band picture, and a rigid undistorted lattice, this would imply a metal. In particular, the noncubic bct crystal field is not predicted to split sufficiently the degeneracy so as to produce a band insulator.[5] Yet these compounds are nonmagnetic insulators at ambient pressure[6–10] and also undergo an insulator-to-metal transition under pressure.[11] A possible explanation of this behavior might just rely on the mechanism we have until now discussed, that is, a strong Coulomb repulsion which drives the system into a Mott insulating phase, and a Jahn-Teller splitting which overcomes the Hund rule and makes the insulator nonmagnetic (see also Refs. 11 and 12). The estimated values of the relevant physical parameters are not in contradiction with this scenario. In fact, the bandwidth W measured by photoemission is of order 0.5–0.7 eV,[10] while the Coulomb interaction U may be a factor 1.5–2.5 larger than W.[13] Moreover, single molecule calculations predict that the ground state of C_{60}^{4-} is indeed a singlet due to prevailing Jahn-Teller effect, with an energy difference between the ground state singlet and the lowest triplet of the order of 0.14 eV.[14] Recent NMR measurements on K_4C_{60} (Ref. 11) show evidence of an exponential temperature dependence of the relaxation rate T_1^{-1} with an activation energy comparable to the above mentioned splitting. Therefore, it seems that some of the properties of a single molecule persist in the lattice, which is not incompatible with a Mott insulating state.[15]

A. Isolated C_{60}^{-n} molecules

It is worthwhile to present a brief overview of some properties of the C_{60}^{-n} molecular ions to point out the analogies

with the simple model we have studied in the preceding sections (we mostly follow Ref. 14). Let us start by neglecting the intramolecular Coulomb repulsion. In the C_{60}^{-n} molecule, the threefold-degenerate t_{1u} lowest unoccupied molecular orbital is Jahn-Teller coupled to eight fivefold degenerate H_g vibrational modes. We will discuss here the low energy picture at strong coupling ($g \gg 1$), even though the realistic estimate is $g \sim 1$. As discussed in Ref. 14, the strong coupling analysis gives a qualitatively good description of the lowest energy excitations also at $g \sim 1$, since no level crossing occurs above this value. For strong coupling the lowest energy modes correspond to those of a rigid body rotator for $n = 3$ and of a point particle moving on a sphere for $n = 1,2,4,5$. Moreover, analogously to the model previously discussed, the condition that the vibronic wave function be single valued generates ''Berry's phase''[16,14] constraints on the quantum numbers of those lowest excitations. Specifically, for $n = 3$ the rigid body rotator eigenfunctions are identified by the quantum numbers L, L_z, and k, where L and L_z are the eigenvalues of the rotator top angular momentum $\vec{L}^2$ and its z component, respectively, and k the eigenvalue of the rotation around the corotating axis. These quantum numbers are subject to the constraint $L = $ odd and $k = $ even.[14] This implies, for instance, that for $n = 3$ the molecular ground state is sixfold degenerate ($L = 1$ and $S = 1/2$). Here, the JT effect does not remove completely the original orbital degeneracy. On the other hand, for $n = 1,2,4,5$ the eigenfunctions are simply spherical harmonics with quantum numbers L and L_z subject to the constraint $(-1)^{L+n} = 1$.[14] Specifically for $n = 4$, which is the relevant case for Rb_4C_{60} and K_4C_{60}, the ground state is nondegenerate ($L = 0$ and $S = 0$). The Jahn-Teller effect fully removes in this case the orbital degeneracy. This JT energy gain is predicted to overcome the Hund's rule energy (favoring a high spin state) thus giving a nondegenerate ground state for $n = 4$. The lowest singlet excitations in the limit of strong JT effect correspond to the motion of a particle on a sphere. They are therefore parametrized by solid angle coordinates (θ, ϕ), and are diagonalized in terms of spherical harmonics $Y_{LM}(\theta, \phi)$ with L even. Their typical energy scale is of an order of 0.02 eV.[17] The ground state configuration of each molecule is nondegenerate with $L = M = 0$, in spite of the degeneracy in the absence of electron-vibron coupling.

B. The lattice of C_{60}^{-n} molecules

As we said, the ratio of $U_{eff} = 0.5[E(C_{60}^{3-}) + E(C_{60}^{5-}) - 2E(C_{60}^{4-})]$ and electron bandwidth W is likely above the critical value for the onset of the Mott insulating phase.[18] In this case, the hopping is expected to produce just an intermolecular coupling which, as before, tends to fix the angles (θ, ϕ) of each molecule, thus contrasting the intramolecular energy which favors the conjugate angular momentum operator to acquire a finite eigenvalue. Moreover, one should take into account additional effects which tend to fix the phases, like the crystal field and multipolar forces among the molecules. The interplay of all these terms to the total Hamiltonian might give rise in this case too to the two different kinds of insulating states just discussed, i.e., the collective static Jahn-Teller and the dynamical Jahn-Teller Mott insulators. However, the order of magnitude of the vari-

ous relevant parameters seem at present to point more in favor of a static and collective distortion. In fact, the inter-molecule coupling arising from the electron hopping is expected to be of the order $W^2/U_{\mathrm{eff}} \sim 0.2$ eV, that is an order of magnitude larger than the rotational lowest excitation energy. In addition, one has to consider the crystal field, which also favors a static distortion. In the end, in the tetravalent fullerides, this issue will have to be resolved experimentally. In fact, at least to our knowledge, there is so far no clear experimental evidence in favor either of a cooperative and static, or of a dynamical Jahn-Teller Mott-like insulator. Statically, the bct lattice being bipartite, we might expect a staggered molecular distortion doubling the lattice unit cell to be more favorable than a homogeneous one. In fact, Erwin has predicted on the basis of a band structure local density approximation calculation a charge density wave instability with wave vector $\vec{Q} = (0,0,\pi/c)$, due to a Fermi surface quasiperfect nesting.[5] This would lead to a doubling of the bct unit cell along the c axis, for which there is as yet no evidence in x-ray diffraction experiments.[19] In the Jahn-Teller-Mott state, no such doubling is required.

V. CONCLUSION

In this paper we have investigated the properties of a prototypical Jahn-Teller insulator, consisting of a lattice of molecules. Each molecule has a degenerate electronic orbital (the degeneracy being bigger than half the number of valence electrons, which is taken as even), coupled to a degenerate vibron, and can undergo a Jahn-Teller distortion. For the case of degeneracy two, which we treated explicitly, the molecular ground state with two electrons is nondegenerate due to the Jahn-Teller effect overcoming the Hund's rule splitting, which would favor a high-spin state instead. If a lattice of such doubly occupied molecules is constructed, and if the effective Hubbard repulsion overcomes the electron hopping matrix elements, the system is insulating. However the insulating state has different properties depending on whether a cooperative and static Jahn-Teller distortion is realized or whether instead a dynamical, nonmagnetic Jahn-Teller-Mott state prevails. By analyzing the low lying excitations, we

have identified some characteristic features which could discriminate between the two insulators. Specifically we have shown that these excitations have some reminiscences of the original degeneracy of the electronic as well as of the vibronic degrees of freedom in the dynamical case which are lost if a cooperative Jahn-Teller effect takes place.

We have also briefly discussed the possible occurrence of this Jahn-Teller Mott insulator in the fullerides K_4C_{60} and Rb_4C_{60}. Apart from the obvious differences arising from the larger degeneracy of the electronic orbitals and of the vibronic modes involved, we believe that the qualitative picture obtained in the simpler doubly degenerate model is useful to understand this case. Although the order of magnitude of the relevant physical parameters seems to favor a scenario in which a static and cooperative Jahn-Teller distortion takes place, so far there are to our knowledge no experimental data which clearly point in favor of this situation rather than a dynamic Jahn-Teller effect. Therefore the question for these systems remains open and, in our opinion, is interesting enough to deserve further experimental investigations.

Note added in proof. A very recent x-ray diffraction study [C. A. Kuntscher, G. M. Bendele, and P. W. Stephens, Phys. Rev. B **55**, R3366 (1997)] appears to rule out a *uniform* cooperative JT state for K_4Co_{60}, thus suggesting that they should be viewed as Mott insulators. Since the JT effect is inevitably present in the nonmagnetic and insulating ground state, this directly suggests a JTM dynamic state. One possible alternative would be a cooperative, static, but *staggered* distortion, where neighboring C_{60} molecules distort along different directions. Such a state would have at least two molecules per unit cell, and should therefore possess additional diffraction spots with respect to simple bct. If the absence of any such extra spots could be rigorously proven, then we would conclude that K_4C_{60} and Rb_4C_{60} definitely have a JTM ground state.

[1] Even though the high-spin state is energetically favorable, the role played by the Jahn-Teller effect may be still relevant in determining both the structural and the magnetic properties of the insulator (see, e.g., K.I. Kugel and D.I. Khomskii, Usp. Fiz. Nauk **136**, 621 (1982) [Sov. Phys. Usp. **25**, 231 (1982)]).

[2] R. Englman, *The Jahn-Teller Effect in Molecules and Crystals* (Wiley, New York, 1973).

[3] The τ_z dependent term in Eq. (9) can be approximated at order g^{-2} by

$$\left(\frac{\partial}{\partial\phi} + i\tau_z\right)^2 \simeq \frac{\partial^2}{\partial\phi^2} - \frac{1}{2}(\vec{\tau}\cdot\vec{\tau} - \tau_x^2).$$

[4] A more proper inclusion of higher excited states has been considered for the quarter filling case by N. Manini, E. Tosatti, and S. Doniach, Phys. Rev. B **51**, 3731 (1995).

[5] S.C. Erwin, in *Buckminsterfullerenes*, edited by W.E. Billups and M.A. Ciufolini (VCH, New York, 1992).

[6] For resistivity measurements see F. Stepniak, P.J. Benning, D.M. Poirier, and J.H. Weaver, Phys. Rev. B **48**, 1899 (1993); R.C. Haddon, A.S. Perel, R.C. Morris, S.-H. Chang, A.T. Fiory, A.F. Hebard, T.T.M. Palstra, and G.P. Kochanski, Chem. Phys. Lett. **218**, 100 (1994).

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[15] Notice that a simple uniform Jahn-Teller distortion cannot explain the insulating behavior, since the bandwidth is larger than the Jahn-Teller contribution to U_{eff} (the latter being estimated of the order 0.2–0.4 eV). Therefore the Coulomb repulsion has to play a relevant role in making the system insulating (see also Note added in proof).

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