Metal-insulator transitions in systems with electron-phonon and Coulomb interactions

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We consider a model which includes the electron-phonon coupling to \(A_g\) or Jahn-Teller \(H_g\) phonons, the Coulomb interaction \(U\) and an exchange integral \(K\). We study the metal-insulator transition for the integer fillings \(n = 3\) and \(4\). We find that the coupling to \(A_g\) phonons increases the critical value \(U_c\) where the transition takes place, while the coupling to \(H_g\) phonons decreases \(U_c\). Without electron-phonon coupling the Hund’s rule coupling also decreases \(U_c\). There is, however, an interesting competition between the Hund’s rule coupling and the Jahn-Teller effect. Thus the reduction of \(U_c\) due to the \(H_g\) phonons becomes smaller when the Hund’s rule coupling is turned on. The implications of this is discussed in the context of \(A_nC_{60}\).

I. INTRODUCTION

The alkali-doped fullerenes, \(A_nC_{60}\) (\(A = K\), Rb), raise many interesting problems due to the important role played by both the electron-electron and the electron-phonon interaction \([1]\). For \(n = 3\) and \(n = 4\) each alkali atom is assumed to donate about one electron into a six-fold degenerate \(t_{1u}\) band. \(A_3C_{60}\) are metals and superconductors \([2,3]\), while \(A_4C_{60}\) are insulators \([4,5]\). The \(t_{1u}\) orbital is only partly filled for both systems, and band structure calculations predict both systems to be metallic \([1]\). \(A_4C_{60}\) must then be an insulator due to interaction effects neglected in band structure calculations. Under pressure \(A_3C_{60}\) becomes metallic \([7]\), while some fullerenes at normal pressure and with the doping \(n = 3\) \((\text{NH}_3\text{K}_3\text{C}_{60}, \text{C}_5\text{S}_3\text{C}_{60})\) are not superconductors and probably insulators, but become superconductors under pressure \([8,9]\). This suggest that these systems are relatively close to a metal-insulator transition. A metal-insulator transition is usually discussed in terms of the ratio between the Coulomb interaction \(U\) between two electrons on the same molecule and the one-particle band width \(W\). For \(A_3C_{60}\) and \(A_4C_{60}\) this ratio is, however, almost identical \([3,10]\). It is then interesting to ask which factors determine whether a system is on the metallic or insulating side.

These systems have been studied in a Hubbard-like model, and it was found that the three-fold degeneracy of the \(t_{1u}\) orbital plays an important role by increasing the ratio \(U/W\) where the metal-insulator transition takes place \([2,3]\). It was furthermore found that the lattice structure is important for the difference between \(A_3C_{60}\) (fcc) and \(A_4C_{60}\) (bct) \([4,11]\). Hubbard-like models predict, however, that \(A_4C_{60}\) is an anti-ferromagnetic insulator, while it is known experimentally that there are no moments in \(A_4C_{60}\) \([12]\). The electrons in \(A_nC_{60}\) have a relatively strong interaction with Jahn-Teller intramolecular phonons with \(H_g\) symmetry and a weaker interaction with \(A_g\) phonons. The interaction with the Jahn-Teller phonons favor a low spin state and might lead to a non-magnetic insulator \([7]\). At the same time there is, however, a Hund’s rule coupling, which favors a high spin state. This leads to an interesting competition between the Jahn-Teller effect and the Hund’s rule coupling. The purpose of this paper is therefore to study the influence of the Jahn-Teller effect and the Hund’s rule coupling on the metal-insulator transition. We do this in the context of the Fullerenes, but similar effects also occur in many other systems, e.g., transition metal compounds \([13]\).

In this paper we study a model of \(A_nC_{60}\) which includes the electron-phonon coupling and the electron-electron interaction. In \(A_nC_{60}\) partly occupied orbital \(t_{1u}\) couples to two nondegenerate phonons of \(A_g\) symmetry and to eight five-fold degenerate (Jahn-Teller) phonons of \(H_g\) symmetry. For \(A_nC_{60}\) the important coupling is believed to be to the \(H_g\) phonons \([14]\), and we therefore study a model with a coupling to one \(H_g\) phonon. To see the effect of having a Jahn-Teller phonon, we also compare with a model containing an \(A_g\) phonon. The models are solved in the dynamical mean-field theory (DMFT) \([15]\) or by using exact diagonalization. To interprete the results we also study analytically a single molecule and a simple two-site model. A brief summary of some aspects of this work are published elsewhere \([16]\).

In Sec. IV we present results for a free molecule and in Sec. II we discuss the typical parameter range. We present results for a two-site model in Sec. V and describe the DMFT calculation in Sec. VI. The results are given in Sec. VII and discussed in Sec. VIII.

II. ISOLATED MOLECULE

We first study an isolated molecule. We consider the case of the coupling to an \(A_g\) phonon and two cases of coupling to Jahn-Teller phonons, namely the \(E \times E\) case, where a two-fold degenerate level couples to a two-fold degenerate phonon, and the \(T \times H\) case, where a three-fold degenerate level couples to a five-fold degenerate phonon. The \(E \times E\) case is the simplest model with a Jahn-Teller effect, and the \(T \times H\) case is a simple model of a \(C_{60}\) molecule. Thus we consider the Hamiltonian

\[ H_{el-\text{ph}} = \varepsilon_0 \sum_m \sum_{\sigma} c_m^{\dagger} c_m \sigma + \omega_0 \sum_\nu b_\nu^\dagger b_\nu \]
The overall coupling strength is determined by $g$. In a metallic molecular solid with narrow bands, there is a simple relation between $g$ and the dimensionless coupling $\lambda \equiv \frac{g^2}{\omega_0}$.

$$\lambda_H = \frac{5}{3} N(0) \frac{g^2}{\omega_0}$$

for the $T \times H$ case and

$$\lambda_E = 2 N(0) \frac{g^2}{\omega_0}$$

for the $E \times E$ case. Here $N(0)$ is the electron density of states per spin. We also define a Jahn-Teller energy

$$E_{JT} = \frac{g^2}{\omega_0}.$$  

In addition we include the Coulomb interaction

$$H_U = U_{xx} \sum_m n_{m\uparrow} n_{m\downarrow} + U_{xy} \sum_{\sigma \sigma'} \sum_{m < m'} n_{\sigma m} n_{\sigma' m'} + \frac{1}{2} K \sum_{\sigma \sigma'} \sum_{m \neq m'} \psi_{m\sigma}^\dagger \psi_{m'\sigma} \psi_{m'\sigma'} \psi_{m\sigma'},$$

where $n_{m\sigma} = \psi_{m\sigma}^\dagger \psi_{m\sigma}$ is an occupation number, $U_{xx}$ and $U_{xy}$ are the Coulomb interactions between equal and unequal orbitals, respectively and $K$ is an exchange integral. The Coulomb integrals are related via

$$U_{xy} = U_{xx} - 2K.$$  

For $A_g$ phonons and a free molecule, the electron-phonon problem is reduced to a displaced oscillator, and we can easily obtain the electron-phonon contribution to the ground-state energy

$$E_{JT}(N) = -N^2 E_{JT}.$$
The tables show that in the low spin state the energy $E(N)$ is lowered by the electron-phonon coupling but is increased by the exchange integral $K$. In the high spin state, on the other hand, the exchange coupling lowers the energy, while the electron-phonon interaction lowers the energy less than in the low spin state or not at all.

This can be further illustrated by considering the case of two electrons in the $E \times E$ system. For $K < 2E_{JT}$, the important states are

$$|1\rangle = \psi_{1\uparrow}^i \psi_{1\downarrow}^i \left| \text{vac} \right> \quad |2\rangle = \psi_{2\uparrow}^i \psi_{2\downarrow}^i \left| \text{vac} \right>.$$  \hspace{1cm} (14)

These states couple directly via the exchange interaction and indirectly via the electron-phonon interaction. Thus we also include states where one phonon has been excited. In the corresponding Hamiltonian matrix the part corresponding to the states with one phonon are “folded” into the part corresponding to $|i\rangle$, $i = 1$ or 2, and we obtain the matrix

$$
\begin{pmatrix}
U_{xx} - 6E_{JT} & -2E_{JT} + K \\
-2E_{JT} + K & U_{xx} - 6E_{JT}
\end{pmatrix}
$$  \hspace{1cm} (15)

If $K < 2E_{JT}$ the corresponding energy is

$$U_{xx} - 6E_{JT} + (-2E_{JT} + K) = U_{av}(2) - 8E_{JT} + \frac{8}{3}K,$$

which clearly shows the competition between the Jahn-Teller coupling and the Hund’s rule coupling. For $K > 2E_{JT}$ a triplet state of the type $\psi_{1\uparrow}^i \psi_{2\downarrow}^i \left| \text{vac} \right>$ with the energy $U_{av}(2) - 4K/3$ becomes the lowest state.

III. PARAMETER RANGE

It is now important to establish the parameter range appropriate for $A_nC_{60}$. In particular, the relative size of $g$ and $K$ is important, since this determines whether the Jahn-Teller effect or the Hund’s rule coupling wins. The exchange integral $K$ has been estimated from an $ab\ initio$ SCF calculation \cite{25}. From the calculated multiplet splitting the result $K = 0.11$ eV was obtained. Correlation effects are expected to reduce this number, since correlation effects in particular lower the energies of the low spin states. The difference in Coulomb energy between the low spin states and the high spin states is then reduced and the effective $K$ becomes correspondingly smaller. For instance, for some atomic multiplets, correlation effects were found to reduce the multiplet splitting by about 25 \% \cite{26}. The electron-phonon coupling constants have been estimated from photoemission experiments for a free molecule \cite{27}. Here we replace the eight $H_g$ modes by one effective mode. The frequency of this mode is chosen as the logarithmically averaged frequency

$$\lambda = \sum_{\nu=1}^{8} \lambda_{\nu}; \quad \lambda \ln \omega_0 = \sum_{\nu=1}^{8} \lambda_{\nu} \ln \omega_{\nu}$$ \hspace{1cm} (17)

where $\lambda_{\nu}$ and $\omega_{\nu}$ are the electron-phonon couplings and frequencies, respectively. We have calculated the energies of the lowest singlet and triplet states for a free $C_{60}$ molecule. The results are shown in Fig. 1. Experimentally it is found that the low spin state wins for both $A_3C_{60}$ and $A_4C_{60}$. $A_3C_{60}$ being a nonmagnetic insulator \cite{14} and NH$_3$K$_3$C$_{60}$ being antiferromagnetic with a moment (0.7 $\mu_B$ per molecule) \cite{16} which corresponds to a spin 1/2 system. For $A_4C_{60}$ the triplet-singlet splitting is estimated to be 0.1 eV \cite{11}. In Fig. 1 this splitting is obtained for $K \sim 0.07$ eV. As expected this value is smaller than the value $K = 0.11$ eV deduced from the HF calculation. We observe that a change in the estimate of $g$ of course would also lead to a change in this empirical number of $K$. Since, however, the present estimate of $K$ seems reasonable relative the the HF value, this calculation also gives some support for the value of $g$ deduced from PES.

![Graph showing the triplet-singlet splitting of a C$_{60}$ molecule with one H$_g$ phonon and an exchange integral K. The arrows show the value of K deduced from a HF calculation and the empirical value deduced from the experimental triplet-singlet splitting.](image)

IV. A TWO-SITE MODEL

In this section we study a two-site model to gain understanding of a) the different influences of an $A_g$ and a Jahn-Teller phonon on the metal-insulator transition and b) the competition between the Jahn-Teller effect and the Hund’s rule coupling. We therefore compare the case of an $A_g$ phonon coupling to a two-fold degenerate level ($A \times E$ problem) with the Jahn-Teller $E \times E$ problem. Thus we study the model

$$H = \sum_{i=1}^{2} \left[ H_{el-phon}(i) + H_{U}(i) \right] + H_{hop},$$ \hspace{1cm} (18)
where $H_{el–phon}(i)$ (Eq. (1)) describes the electron-phonon interaction on site $i$, $H_U(i)$ (Eq. (3)) describes the Coulomb interaction on site $i$, and

$$H_{\text{hop}} = -t \sum_{m=1}^{g} \left( \psi_{1mσ}^\dagger \psi_{2mσ} + \psi_{2mσ}^\dagger \psi_{1mσ} \right), \quad (19)$$

describes the hopping between the two sites. We have assumed that there is only one hopping between equal $m$-quantum numbers.

The band gap $E_g(n)$ for the filling $n$ is given by

$$E_g(n) = E(2n - 1) + E(2n + 1) - 2E(2n) \quad (20)$$

for a two-site model, where $E(N)$ is the ground-state energy of a system with $N$ electrons. It is useful to consider $E_g$ in the limit when $U$ is very large, and then to extrapolate to intermediate values of $U$. The limit of a large $U$ is particular transparent, allowing for simple calculations and a qualitative understanding, but it is still relevant for the intermediate values of $U$ where the metal-insulator transition takes place [12]. The metal-insulator transition happens when $E_g = 0$, i.e., we find the critical value of $U$ for which this condition is satisfied. The two-site system is much too small for obtaining reliable quantitative estimates of the critical $U$ and the extrapolation of the large $U$ results is questionable. Nevertheless, this approach can give a qualitative understanding of more realistic calculations [12]. We consider the limit

$$g << \omega_0 << W << U \quad (21)$$

where the electron-phonon coupling and the exchange integral are just weak perturbations to the hopping and to the Coulomb interaction.

We first study the case of an $A_g$ phonon and calculate the gap for the filling $n = 1$. It is then convenient to transform the coupling term to the form

$$g \sum_{i=1}^{2} (n_i - 1)(b_i + b_i^\dagger), \quad (22)$$

where $n_i = \sum_{mσ} \psi_{1mσ}^\dagger \psi_{1mσ}$ and we have neglected an irrelevant term $(-g^2/\omega_0) \sum_i (2n_i - 1)$. For a system with two electrons and in the limit of a large $U$, hopping is almost completely suppressed, and each site has almost exactly one electron. The term (22) then has essentially zero coupling to this state, and we obtain

$$E_{A_g}(2) \approx 0. \quad (23)$$

Since there is only one electron per site, there are no multiplet effects. To obtain the energy of a system with one electron, it is convenient to transform to bonding and antibonding operators, e.g., $\psi_{±mσ} = (\psi_{1mσ} \pm \psi_{2mσ})$. This gives the interaction term

$$\frac{g}{\sqrt{2}} \left[ (\psi_{+mσ}^\dagger \psi_{+mσ} + \psi_{-mσ}^\dagger \psi_{-mσ})(b_+ + b_+^\dagger) + (\psi_{+mσ}^\dagger \psi_{-mσ} + \psi_{-mσ}^\dagger \psi_{+mσ})(b_- + b_-^\dagger) \right], \quad (24)$$

The bonding level is then occupied by one electron, giving the kinetic energy $-t$. The leading contribution to the energy due to the electron-phonon interaction is $-\frac{1}{2}E_{JT}$, giving

$$E_{A_g}(1) = -t - \frac{1}{2}E_{JT}. \quad (25)$$

In the limit studied here ($\omega_0 << W$), the phonons react to the average electronic charge, which gives rise to the factor $\frac{1}{2}$.

We next consider the system with three electrons. The wave function for $g = 0$ and $K = 0$ is

$$|0\rangle = \frac{1}{\sqrt{6}} (\psi_{11\uparrow}^\dagger \psi_{12\downarrow}^\dagger \psi_{22\uparrow}^\dagger + \psi_{11\uparrow}^\dagger \psi_{21\downarrow}^\dagger \psi_{12\downarrow}^\dagger + \psi_{21\uparrow}^\dagger \psi_{11\downarrow}^\dagger \psi_{12\downarrow}^\dagger + \psi_{21\uparrow}^\dagger \psi_{11\downarrow}^\dagger \psi_{22\uparrow}^\dagger + \psi_{21\uparrow}^\dagger \psi_{11\downarrow}^\dagger \psi_{22\uparrow}^\dagger + \psi_{11\uparrow}^\dagger \psi_{21\downarrow}^\dagger \psi_{22\uparrow}^\dagger) |\text{vac}\rangle. \quad (26)$$

The corresponding energy is $\langle 0 | H | 0 \rangle = -2t$. For a general lattice and for a state which is half-filled apart from one electron or one hole, we expect the hopping to be enhanced by roughly a factor $\sqrt{N_{\text{deg}}}$, where $N_{\text{deg}}$ is the orbital degeneracy [13]. However, for the two-site system this enhancement is $N_{\text{deg}} [12]$. The effects of the electron-phonon coupling are now included in perturbation theory. For the parameter range considered here ($\omega_0 << W$), there is only coupling to the states $b_i^\dagger |0\rangle$. Furthermore, the Coulomb energy is given by $\langle 0 | H_U | 0 \rangle$, since there are no states with the kinetic energy $-2t$ which couple to $|0\rangle$ via $H_U$. The energy is therefore

$$E_{A_g}(3) = U_{xx} - 2t - \frac{1}{2}E_{JT} - \frac{5}{3}K. \quad (27)$$

The corresponding band gap is given in Table (A × E), which also shows the result for the filling $n = 2$. The table shows that the band gap is reduced by the electron-phonon coupling. Extrapolating to intermediate values of $U$ then suggests that the electron-phonon coupling increases the critical value of $U$ where the metal-insulator transition takes place. The reason is that the electron-phonon interaction in the model (22) is not effective for integer filling in the large $U$ case, since the charge fluctuations are then suppressed. For the states with an extra electron or hole, on the other hand, there is a fluctuating charge due to the hopping of the electron or hole and a corresponding lowering of the energy due to the electron-phonon coupling.

The multiplet effects trivially reduce the gap for $n = 1$, since they are effective for the state with three electrons but not for the other two states. For $n = 2$, however, they
increase the gap. The reason is that in the integer occupation case \((N = 4)\), hopping plays no role for a large \(U\) and the state can adjust to use the multiplet effects optimally. This is not possible for the case of an extra hole \((N = 3)\) or an extra electron \((N = 5)\), since then the states first of all adjust to optimize hopping, and only in the second place adjust to optimize the multiplet effects. The increase of the gap due to the exchange integral has been observed earlier \([13]\).

We next consider the Jahn-Teller case of two-fold degenerate phonons. We first calculate the energy of the state with one electron per site in the large \(U\) limit. Perturbation theory shows that each phonon contributes an energy \(E_{JT}\). Since there are two phonons per site and two sites, the energy is

\[
E_{E^g}(2) = -4E_{JT},
\]

where \(E_g\) labels the Jahn-Teller case. Although charge fluctuations are completely suppressed in this case, the system can still gain energy by introducing a (dynamical) Jahn-Teller distortion. This is in strong contrast to the \(A_g\) phonons, which only couple to the net charge on a given site. In perturbation theory, the energies of the states with an extra electron or hole are

\[
\begin{align*}
E_{E^g}(1) &= -t - E_{JT} \\
E_{E^g}(3) &= U_{xx} - 2t - E_{JT} - \frac{5}{3}K.
\end{align*}
\]

(29)

The electron-phonon interaction lowers the energy twice as much as in the \(A_g\) case (Eqs. (22) and (27)), simply because the phonon is two-fold degenerate and the coupling therefore is to twice as many phonons as in the \(A_g\) case. The corresponding gap is shown in Table I, which also shows the gap for the filling \(n = 2\).

For \(n = 2\) and \(K < E_{JT}\) the Jahn-Teller effect dominates over the Hund’s rule coupling. In this case as well as for \(n = 1\) the gap is then increased by the electron-phonon interaction, while in the \(A_g\) case it is decreased. The reason is similar as for the multiplet effects in the \(A_g\) case, discussed in the second paragraph below Eq. (27). For the parameter range (Eq. (21)) we are considering and for integer filling, the hopping is very efficiently suppressed, and the Jahn-Teller system can therefore adjust efficiently to the electron-phonon interaction. With an extra electron or hole, however, the system cannot take advantage of the electron-phonon interaction to the same extent, since the wave function primarily optimizes the hopping of the electron or hole. According to Eq. (29), this leads to an increase of the gap. In the \(A_g\) case, on the other hand, the system cannot couple to the phonons in the integer filling case, and therefore even the reduced coupling to the phonons in the case of an extra electron or hole is sufficient to reduce the gap.

Table I furthermore illustrates the competition between the Jahn-Teller effect and the Hund’s rule coupling. For \(K < 2E_{JT}\) and \(n = 2\) an increase of \(K\) leads to a reduction of the gap. As \(K\) is further increased, the system instead tends to go into high spin states, and the gap is increased as \(K\) is increased.

It is interesting to compare the results with a different approach. We can calculate an effective on-site \(U_{eff}(n)\) for the filling \(n\) as

\[
U_{eff}(n) = E(n + 1) + E(n - 1) - 2E(n),
\]

(30)

where \(E(N)\) now refers to the energy of a free molecule, calculated in Sec. I. For \(K < 2E_{JT}\) and for the \(E \times E\) case, we then obtain

\[
\begin{align*}
U_{eff}(1) &= U_{av}(2) - 4E_{JT} + \frac{8}{3}K \\
U_{eff}(2) &= U_{av} + 12E_{JT} - \frac{16}{3}K.
\end{align*}
\]

(31)

It is then tempting to assume that for the filling \(n = 1\) and \(n = 2\) the gap is given by \(U_{eff}(1) - 3t\) and \(U_{eff}(2) - 4t\), respectively. Comparison with Table I shows that this is incorrect in the limit studied here (Eq. (21)). In particular, for \(n = 1\), this approach would even predict the wrong sign for the the electron-phonon contribution to the gap. The reason is that Eq. (31) assumes that the electron-phonon and Hund’s rule couplings can adjust to the instantaneous occupation of a given site. As we have seen above, this is not possible in the limit (Eq. (21)) for the states with an extra electron or hole. \(U_{eff}(2)\) may instead become relevant in the limit when the exchange coupling \(K\) and the Jahn-Teller energy \(E_{JT}\) are much larger than the hopping energy.

In a similar way we have calculated the gap for the \(T \times H\) two-site problem. The results are shown in Table IV. These results also illustrate the competition between the Jahn-Teller effect and the Hund’s rule coupling.

V. DYNAMICAL MEAN-FIELD CALCULATIONS

We now consider the \(T \times H\) problem in the dynamical mean-field theory (DMFT). We formulate the infinite dimensional limit on the Bethe lattice, where the nearest-neighbor hopping integral \(t_{im,jm'}\) is rescaled as \(t' / \sqrt{z}\) with the connectivity \(z\) going to infinity. We further simplify the hopping by setting \(t_{im,jm'} \propto \delta_{nm'}\) only allowing the diagonal hopping. The unit of energy is chosen such that the bandwidth, \(W\), is set to 2. The Jahn-Teller phonons embedded at each lattice sites of the bath can be easily incorporated into the effective medium of the impurity Anderson model \([23]\), since they are Einstein phonons without direct intersite couplings between them. Therefore the lattice contribution of phonons is implicitly included in the medium electron Green’s function.

We here focus on the problem where the exchange integral \(K = 0\). The effective impurity Anderson model is
solved using the quantum Monte Carlo (QMC) technique with the Fye-Hirsch algorithm \[30\], which has only mild “fermion sign-problems” with our Hamiltonian. Here we treat fully quantum mechanically the phonon fields which are updated together with the fermion auxiliary fields in each Monte Carlo step. Details of the implementation of the QMC technique in the DMFT can be found elsewhere in the literature \[14, 29\]. We have used the discretization step for the Trotter breakup, $\Delta \tau = 1/3$, throughout this paper unless mentioned otherwise and more than one million Monte Carlo sweeps are taken for each iteration of the self-consistency loop. For the case where the exchange integral $K > 0$ the QMC method has a serious “sign-problem”, and this case is treated in Sec. VI D using exact diagonalization.

VI. RESULTS

We study how the metal-insulator transition depends on the parameters, e.g., the ratio $U/W$ for different strengths of the electron-phonon coupling $\lambda$ and the exchange integral. When the system becomes insulating a gap is opened up in the electron spectral function $A(\omega)$. This shows up in the electron Green’s function $G(\tau)$ calculated for imaginary times $\tau$. For instance if

$$A(\omega) = 0 \quad \text{for} \quad |\omega| < \Delta,$$  \hspace{1cm} (32)

we obtain

$$G(\tau = \beta/2) \leq e^{-\Delta \beta/2},$$  \hspace{1cm} (33)

where $\beta = 1/T$. Thus $G(\beta/2)$ decays exponentially with $\beta$ for an insulator. We therefore use the behavior of $G(\beta/2)$ as a measure whether the system is a metal or an insulator. It is also interesting to study the charge fluctuation $\langle (n - n_0)^2 \rangle$, which is an average of $\langle (n_i - n_0)^2 \rangle$ and where $n_0$ is the average occupancy per site. This quantity is expected to become small but nonzero at the metal-insulator transition.

A. Jahn-Teller $H_g$ phonons

We first study the Jahn-Teller $H_g$ phonons and consider the case of half-filling, i.e., three electrons per site. Fig. 2 shows $G(\beta/2)$ as a function of $U/W$ for different values of $\lambda$. The figure illustrates that for a given $\lambda$, $G(\beta/2)$ is reduced as $U$ is increased and at some critical value $U_c$, $G(\beta/2)$ becomes very close to zero (not exactly equal to zero due to the finite temperature), where a metal insulator transition takes place. The figure also illustrates that the charge fluctuations $\langle (n - 3)^2 \rangle$ are strongly reduced in the insulating state. The critical $U_c/W$ is reduced as $\lambda$ grows. The reason for this was discussed extensively in Sec. IV.

It is interesting that $U_c$ as a function of $\lambda$ initially is reduced very strongly as $\lambda$ is increased, while for larger values of $\lambda$ the decrease is slower. This can be understood in terms of the results in Eq. (11, 13) for the Jahn-Teller energy in the weak- and strong-coupling limits. This shows that the electron-phonon energy increases much faster with $\lambda$ (by a factor of $5/2$) in the weak-coupling limit than in the strong-coupling limit. This is particularly relevant for the large $U$ integer filling case, where the electron-phonon interaction has a similar effect as in the free molecule, and it gives a qualitative explanation for the dependence of $U_c$ on $\lambda$.

FIG. 2. (a) $G(\beta/2)$ for $\beta = 16$ and (b) the charge fluctuation $\langle (n - 3)^2 \rangle$ as a function of $U/W$ for different values of $\lambda$ and coupling to $H_g$ phonons in $\Lambda_3 C_{60}$.

FIG. 3. $G(\beta/2)$ for $\beta = 16$ as a function of $U/W$ for $\lambda = 0.8$ and $\lambda = 0$ and coupling to $A_g$ phonons in $\Lambda_3 C_{60}$.
B. A₉ versus Jahn-Teller H₉ phonons

We next compare the Jahn-Teller H₉ phonons with A₉ phonons. Fig. 3 shows $G(\beta/2)$ in a system with coupling to A₉ phonons as a function of $U$ for $\lambda = 0$ and for $\lambda = 0.8$. Comparing the results for $\lambda = 0$ and $\lambda = 0.8$, we can see that the coupling to A₉ phonons increases the critical $U_c$ where the metal-insulator transition takes place, while in the case of H₉ phonons this value is decreased (see Fig. 2). The reason for this change was discussed extensively in Sec. IV.

It is interesting to observe that both the electron-phonon interaction and the electron-electron interaction by themselves would tend to reduce $G(\beta/2)$. In a weak-coupling theory where we simply add the lowest order contribution to the self-energy from each interaction, we would then predict that the two interactions work together in reducing $G(\beta/2)$. This is indeed what is found in Fig. 3 for $U/W = 0.5$. Not too surprisingly, the arguments presented below Eq. (21) and assuming the large $U$ limit are incorrect for $U/W = 0.5$. It is not surprising that these arguments become correct for large values of $U/W$, but it is important that they are qualitatively correct already for $U/W \sim 1.5$, which is on the metallic side of the metal-insulator transition.

For a system with only a Coulomb interaction $U$, the metal-insulator transition can be thought of as resulting from the competition between kinetic and potential energy. When the coupling to the phonons is introduced the hopping of the electrons is reduced, since an electron tends to drag a cloud of phonons along its path. It is then tempting to assume that the coupling to phonons will move the metal-insulator transition towards smaller values of $U$. Our results show that for the parameter range considered here, the effect is the opposite for the case of coupling to A₉ phonons.

The coupling to the A₉ phonons in A₃C₆₀ is weak [1], and the A₉ phonons should not play an important role. There is, however, a strong coupling to a charge carrying plasmon derived from the $t_{1u}$ electrons [31]. This plasmon couples in the same way as the A₉ phonons. Its energy (0.5eV) is larger than the phonon energies. However, whether we consider the plasmon energy to be small or large we arrive at the conclusion that it increases $U_c$. For small values of the plasmon energy this follows from the study of the A₉ phonons, and for large energies of the plasmon, we can introduce an effective $U_{eff}$ as in Eq. (34). The coupling to the plasmon reduces $U_{eff}$ and therefore the metal-insulator transition happens for a larger bare $U$.

C. A₃C₆₀ versus A₄C₆₀

Fig. 4 shows $G(\beta/2)$ for A₄C₆₀. The figure illustrates that $U_c$ is smaller at filling four than filling three (see Fig. 4). This is not surprising in view of Eq. (30) and Table IV, since the energy is lowered more by the electron-phonon coupling for filling four than for filling three. According to Eq. (20) this increases the gap of the insulating state more for filling four than for filling three, i.e., it makes $U_c$ smaller for filling four. As discussed in the next section, this result is, however, modified by the Jahn-Teller coupling.

D. Competition between Jahn-Teller and Hund’s rule coupling

We finally discuss the competition between the Jahn-Teller effect and the Hund’s rule coupling. Since there is a sign-problem in the dynamical mean-filed calculations if we use the full multiplet coupling in Eq. (3), we use an exact diagonalization technique. This requires that the system size is small. Therefore we consider a system with just four sites and we consider the $E \times E$ problem (Eq. (2)). We furthermore limit the Hilbert space by not allowing more than two phonons per site. To reduce the discreteness of the one-particle spectrum for such a small system, we pick the hopping integrals randomly. We calculate the gap according to Eq. (20) and add some finite size corrections [12]

$$E_g^{red}(U_{xx}) = E_g - \frac{U_{av}(2)}{N_{site}} - E_{g=0}$$

where $U_{av}(2)/N_{site}$ is a contribution to the gap from the electrostatic energy of a finite system, $N_{site}$ is the number of sites and $E_{g=0}$ is the gap of a system without any Coulomb interaction. Both these corrections go to zero for a large system. Assuming that that $E_g^{red}$ grows linearly with $U_{xx}$, we can then use

$$U_{xx} - E_g^{red}(U_{xx})$$

as a crude estimate of the critical $U_{xx}$. This quantity is shown in Fig. 4. The results can be qualitatively understood from the results in Table V for a two-site system,
although the parameter range considered here is outside the range where the results in the table are valid. For \( \lambda = 0 \), the critical value of \( U_{xx} \) is reduced as \( K \) is increased, as expected [13]. However, as \( \lambda \) is increased, the competition between the Jahn-Teller and Hund’s rule effects leads to an increase of the critical \( U_{xx} \). This is in agreement with Table I[11], although the increase is faster than for the parameter range of this table. For a particular value of \( \lambda \), the critical \( U_{xx} \) becomes comparable to the value for \( K = \lambda = 0 \). As \( \lambda \) is further increased, the Jahn-Teller effect becomes dominating and the critical value of \( U_{xx} \) decreases again. This critical value is, however, larger than for \( K = 0 \), due to the competition between the Jahn-Teller and Hund’s rule coupling.

VII. DISCUSSION

It is interesting to discuss these results in the context of \( A_3C_{60} \). Considering just the Hubbard \( U \) (\( g = K = 0 \)), it is found that the metal-insulator transition in \( A_3C_{60} \) takes place at the upper range of what is believed to be physical values of \( U/W \), while for \( A_4C_{60} \) this happens at the lower range of these parameters. This agrees nicely with the fact that \( A_3C_{60} \) is a metal but \( A_4C_{60} \) is an insulator. However, to explain why \( A_4C_{60} \) is not antiferromagnetic, we need to include the coupling to the Jahn-Teller \( H_g \) phonons. This substantially lowers the critical \( U_c \) for both systems, and it puts \( U_c/W \) of \( A_3C_{60} \) at the lower range of the physical parameters. This puts our understanding of \( A_3C_{60} \) being a metal into question. We find, however, that the competition between the Jahn-Teller effect and the Hund’s rule coupling increases \( U_c \) again. The coupling to the \( t_{1u} \) plasmons in \( A_4C_{60} \) should lead to an additional increase of \( U_c \) in this system. This makes it understandable that \( A_3C_{60} \) can be a metal.

VIII. ACKNOWLEDGEMENTS

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TABLE I. The ground-state energy $E(N)$ for $N$ electrons in the $E \times E$ case. The quantity $N(N-1)U_{av}(2)/2$ has been subtracted, where $U_{av}(2) = U_{xy} + K/3$ is the average interaction for a full shell.

| $N$ | $E(N) \equiv E(N) - N(N-1)U_{av}(2)/2$ |
|-----|--------------------------------------|
| 1   | $-2E_{JT}$                            |
| 2   | $-8E_{JT} + \frac{4}{3}K$            |

TABLE II. The ground-state energy $E(N)$ for $N$ electrons in the $T \times H$ case. The quantity $N(N-1)U_{av}(3)/2$ has been subtracted, where $U_{av}(3) = U_{xy}$ is the average interaction for a full shell.

| $N$ | $E(N) \equiv E(N) - N(N-1)U_{av}(3)/2$ |
|-----|--------------------------------------|
|     | Low spin                           |
| 1   | $-\frac{2}{3}E_{JT}$               |
| 2   | $-10E_{JT} + 4K$                    |
| 3   | $-\frac{16}{3}E_{JT} + 2K$         |
| 4   | $-10E_{JT} + 4K$                    |
| 5   | $-\frac{2}{3}E_{JT}$               |

TABLE III. $E_{g}(n) - U_{av}(2) - d_{2}(n)t$ for the $A \times E$ and the $E \times E$ two-site models as a function of the filling $n$, where $E_{g}$ is the band gap, $U_{av}(2)$ is the average Coulomb interaction and $d_{2}(n)t$ is the hopping contribution, with $d_{2}(n) = -3$ and -4 for $n = 1$ and 2, respectively. The results are symmetric around half-filling $n = 2$.

| Syst | $n$ | $E_{g}(n) - U_{av}(2) - d_{2}(n)t$ |
|------|-----|----------------------------------|
|      | $K \leq 2E_{JT}$                  |
| $A \times E$ | 1 | $-E_{JT}$                  |
| $A \times E$ | 2 | $-E_{JT} + \frac{16}{3}K$     |
| $E \times E$ | 1 | $6E_{JT}$              |
| $E \times E$ | 2 | $30E_{JT} - \frac{32}{3}K$    |
|      | $K > 2E_{JT}$                    |
| $A \times E$ | 1 | $2E_{JT} + \frac{16}{3}K$     |

TABLE IV. $E_{g}(n) - U_{av}(3) - d_{3}(n)t$ for the $T \times H$ two-site model as a function of the filling $n$. The hopping contribution to the gap is given by $d(n)t$, where $d_{3}(n) = -3, -5$ and -6 for $n = 1, 2$ and 3, respectively. The results are symmetric around half-filling $n = 3$.

| $E_{g}(n) - U_{av}(3) - d_{3}(n)t$ |
|-----|----------------------------------|
|     | $K \leq \frac{2}{3}E_{JT}$      |
| 1   | $5E_{JT} + \frac{4}{3}K$        |
| 2   | $5E_{JT} + \frac{16}{3}K$       |
| 3   | $\frac{25}{3}E_{JT} - 8K$      |

TABLE V. The ground-state energy $E(N)$ for $N$ electrons in the $T \times H$ case. The quantity $N(N-1)U_{av}(3)/2$ has been subtracted, where $U_{av}(3) = U_{xy}$ is the average interaction for a full shell.

| $N$ | $E(N) \equiv E(N) - N(N-1)U_{av}(3)/2$ |
|-----|--------------------------------------|
| 1   | $-2E_{JT}$                            |
| 2   | $-8E_{JT} + \frac{4}{3}K$            |