

## Metal-Insulator Transitions: Influence of Lattice Structure, Jahn-Teller Effect, and Hund's Rule Coupling

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We study the influence of the lattice structure, the Jahn-Teller effect, and the Hund's rule coupling on a metal-insulator transition in  $A_nC_{60}$  ( $A = K, Rb$ ). The difference in the lattice structure favors  $A_3C_{60}$  (fcc) being a metal and  $A_4C_{60}$  (bct) being an insulator, and the coupling to  $H_g$  Jahn-Teller phonons favors  $A_4C_{60}$  being nonmagnetic. The coupling to  $H_g$  ( $A_g$ ) phonons decreases (increases) the value  $U_c$  of the Coulomb integral at which the metal-insulator transition occurs. There is an important partial cancellation between the Jahn-Teller effect and the Hund's rule coupling.

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The competition between the Coulomb repulsion, the kinetic energy, the Jahn-Teller effect, and the Hund's rule coupling, leads to interesting physics. Examples are perovskites, e.g., the manganites [1], and alkali-doped fullerenes [2]. Here we focus on the metal-insulator transition for an integer number of electrons per site. This is particularly relevant for the fullerenes, since  $A_3C_{60}$  ( $A = K, Rb$ ) is a metal [3] while  $A_4C_{60}$  is a nonmagnetic insulator [4,5]. According to band theory both are metals [6], and  $A_4C_{60}$  must therefore be an insulator due to interactions left out in band structure calculations.

The metal-insulator transition in a correlated system is usually discussed in terms of the ratio  $U/W$  [7], where  $U$  is the Coulomb interaction between two electrons on the same molecule and  $W$  is the one-particle bandwidth. The ratio  $U/W$  is, however, almost identical for  $A_3C_{60}$  and  $A_4C_{60}$  [2,6,8]. The question is then why not both systems are either metals or insulators. To study this, we apply the dynamical mean-field theory (DMFT), projection quantum Monte Carlo (QMC) methods, and exact diagonalization techniques to models of  $A_nC_{60}$ .

For the fullerenes it is believed that  $U/W \sim 1.5-2.5$  [2]. In spite of this large ratio, these systems are close to a metal-insulator transition due to the orbital degeneracy  $N = 3$  of the partly occupied  $t_{1u}$  band [9,10]. The lattice structure is fcc for  $A_3C_{60}$  and bct for  $A_4C_{60}$ . The important electron-phonon coupling is to  $H_g$  Jahn-Teller phonons. We find that the difference in lattice structure alone can explain why  $A_3C_{60}$  is a metal but  $A_4C_{60}$  is an insulator and that the electron-phonon coupling can explain why  $A_4C_{60}$  is nonmagnetic. We find an important competition between the Jahn-Teller effect and the Hund's rule coupling. The  $H_g$  and  $A_g$  intramolecular phonons are found to have the opposite effect on the critical  $U_c$ , for which the metal-insulator transition occurs.

We consider a model of  $A_nC_{60}$  which includes a threefold degenerate  $t_{1u}$  level on each molecule and the hopping between different molecules

$$H_{\text{hop}} = \sum_{\sigma, m} \varepsilon_{t_{1u}} n_{i\sigma m} + \sum_{\langle ij \rangle \sigma m m'} t_{ij m m'} \psi_{i\sigma m}^\dagger \psi_{j\sigma m'}, \quad (1)$$

where  $\psi_{i\sigma m}^\dagger$  creates an electron on molecule  $i$  with the quantum number  $m$  and spin  $\sigma$ . The hopping matrix elements  $t_{ij m m'}$  [11] include the orientational disorder [12] and the lattice structure, with nearest neighbor hopping for the fcc structure and a weak second nearest neighbor hopping for the bct structure [8]. The Coulomb interaction is given by

$$\begin{aligned} H_U = & U_{xx} \sum_{im} n_{im\uparrow} n_{im\downarrow} + U_{xy} \sum_{i\sigma\sigma'} \sum_{m < m'} n_{i\sigma m} n_{i\sigma' m'} \\ & + \frac{1}{2} K \sum_{i\sigma\sigma'} \sum_{m \neq m'} \psi_{i\sigma m}^\dagger \psi_{i\sigma' m'}^\dagger \psi_{i\sigma' m} \psi_{i\sigma m} \\ & + \frac{1}{2} K \sum_{\sigma} \sum_{m \neq m'} \psi_{m\sigma}^\dagger \psi_{m-\sigma}^\dagger \psi_{m'-\sigma} \psi_{m'\sigma}, \quad (2) \end{aligned}$$

where  $U_{xx}$  and  $U_{xy}$  describe the interaction between equal and unequal orbitals, respectively.  $K$  is an exchange integral and  $U_{xx} = U_{xy} + 2K$ . Finally we include the interaction with a fivefold degenerate  $H_g$  phonon on each site

$$\begin{aligned} H_{\text{ph}} = & \omega_{\text{ph}} \sum_{i\nu} b_{i\nu}^\dagger b_{i\nu} \\ & + \frac{g}{2} \sum_{i\nu\sigma m m'} V_{m m'}^{(\nu)} c_{i\sigma m}^\dagger c_{i\sigma' m'} (b_{i\nu} + b_{i\nu}^\dagger), \end{aligned}$$

where  $b_{i\nu}$  creates a phonon with the quantum number  $\nu$  on the molecule  $i$ . The matrices  $V_{m m'}^{(\nu)}$  are determined by symmetry [13]. The coupling constant  $g$  is related to the dimensionless electron-phonon coupling  $\lambda = (5/3)N(0)g^2/\omega_{\text{ph}}$ . We also consider the coupling to  $A_g$  phonons, for which  $V_{m m'}^{(\nu)}$  is diagonal in  $m$  and  $m'$ .

In a first step we analyze the effect of the lattice structure alone, neglecting the electron-phonon coupling ( $g = 0$ ) and the multiplet effects ( $K = 0$  and  $U_{xx} = U_{xy} \equiv U$ ). We use a projection QMC  $T = 0$  method in the fixed node approximation [14], which gives quite accurate ground-state results for this model [9].  $A_3C_{60}$  and  $A_4C_{60}$  differ in the number  $n$  of conduction electrons per site and in the lattice structures. For a fcc lattice,  $n = 3$  and  $n = 4$  give Mott transitions at almost the same  $U_c$  [15]. We therefore focus on the difference in lattice structure, and consider

$n = 4$  for clusters with  $M$  molecules put on fcc or bct lattices. The band gap for filling  $n$  is

$$E_g = E(nM + 1) + E(nM - 1) - 2E(nM), \quad (3)$$

where  $E(N)$  is the energy of a system with  $N$  electrons. We want to extrapolate to  $M \rightarrow \infty$  and determine the  $U_c$  for which  $E_g$  is zero. To reduce the finite size effects [9], we add

$$\tilde{E}_g(U) = E_g(U) - \frac{U}{M} - E_g(U = 0), \quad (4)$$

where  $E_g(U = 0)$  is the band gap for  $U = 0$ . These corrections go to zero for large  $M$ , but they improve the extrapolation  $M \rightarrow \infty$ . Figure 1 shows that the metal-insulator transition happens for a substantially smaller  $U/W$  for the bct ( $U_c/W \sim 1.3$ ) than for the fcc structure ( $U_c/W \sim 2.3$ ). The insulating state is antiferromagnetic.

To understand these results, we note that on the fcc lattice it is possible to hop on a triangle, i.e., to return to the original site after three hops. On a bct lattice, on the other hand, this is not possible if the small second nearest neighbor hopping integrals are neglected. The simplest systems with these properties are a triangle and a square, each site having a level with spin but no orbital degeneracy. A nearest neighbor hopping integral  $t < 0$  connects the orbitals. The one-particle spectrum is  $\pm 2t$  for the square and  $-2|t|$  and  $t$  for the triangle. For the triangle there is a state with maximum bonding character ( $-2|t|$ ), but it is not possible to construct an optimally antibonding state, due to the presence of frustration. Thus the one-particle bandwidths are  $W = 3t$  and  $4t$  for the triangle and the square, respectively. The curves in Fig. 1 mainly differ in the large  $U$  limit and we therefore consider this limit. We construct the many-body states of the triangle with two, three, and four electrons, which determine the band gap [Eq. (3)]. The energy  $E(3) = O(t^2/U)$ , since hopping is suppressed to order  $t/U$ . For the case of four electrons, we construct all states with the minimum (one) double occupancy and  $S_z = 0$ . These states describe how the double occupancy hops around the triangle. The original state is, however,

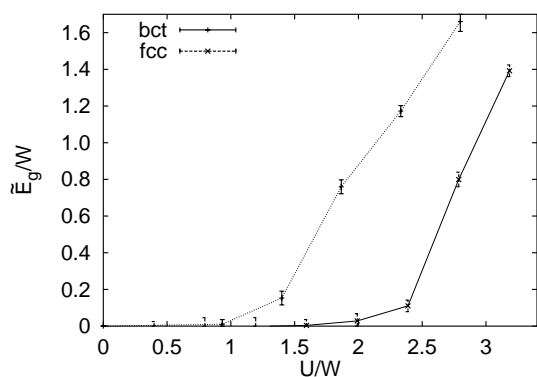


FIG. 1. The energy gap  $\tilde{E}_g$  [Eq. (4)] as a function of  $U/W$  for  $M = 32$  molecules on fcc and bct lattices and the filling  $n = 4$ . The lines are guides for the eye.

not recovered after one loop, since the spins on the sites with a single occupancy have been flipped. Moving the double occupancy around the triangle a second time restores the spins and the original state is recovered after six moves. The corresponding  $6 \times 6$  matrix has the extreme eigenvalues  $\pm 2t$ . In the lowest many-body state of the triangle with four electrons, it is therefore not possible to restore the state in an odd number of hops, and the frustration does not show up. In a similar way we obtain the lowest energy  $-2t$  for the two-electron state. The square has the same energies. Thus

$$E_g = U - 4|t| = U - \frac{4}{3}W \quad \text{for a triangle,}$$

$$E_g = U - 4|t| = U - W \quad \text{for a square.} \quad (5)$$

Both the triangle and the square have no frustration in their many-body states, and for fixed  $t$  the gaps are the same. The one-particle bandwidth  $W$ , however, is reduced by the frustration in the triangle, and expressing  $E_g$  in terms of  $W$  requires a larger prefactor in the frustrated case. These results give a qualitative explanation of Fig. 1.

Although the calculation above can explain why  $A_4C_{60}$  is an insulator while  $A_3C_{60}$  is a metal, it incorrectly predicts  $A_4C_{60}$  to be antiferromagnetic. The calculation neglects, however, the coupling to the Jahn-Teller phonons, which tends to make  $A_4C_{60}$  a nonmagnetic insulator [16]. The electron-phonon interaction has been estimated from photoemission experiments for a free molecule [17]. We describe the eight  $H_g$  phonons by an effective mode, with the logarithmically averaged frequency  $\omega_{\text{ph}} = 0.089$  eV, and the effective coupling  $g = 0.089$  eV. For a free molecule this leads to a singlet being 0.29 eV below the lowest triplet. This triplet-singlet splitting is larger than an

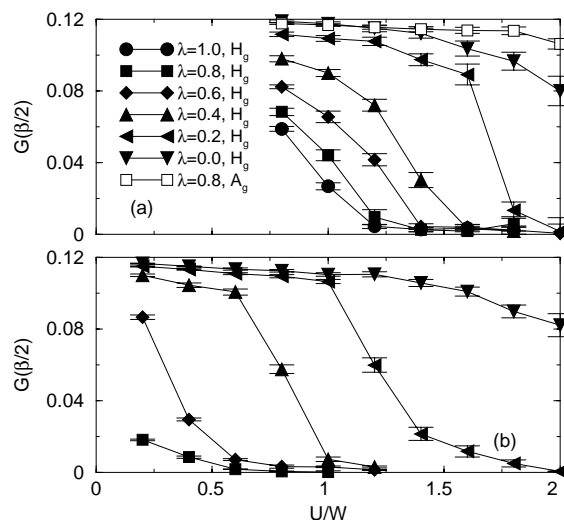


FIG. 2. (a) The electron Green's function  $G(\tau = \beta/2)$  as a function of  $U/W$  for the filling  $n = 3$  and different values of the electron-phonon coupling  $\lambda$ . The figures compare the couplings to  $A_g$  and  $H_g$  phonons. (b)  $G(\beta/2)$  for coupling to  $H_g$  phonons and  $n = 4$ .  $G(\beta/2) \approx 0$  implies an insulator.

TABLE I. The ground-state energy  $E(n)$  of an isolated molecule for  $n$  electrons. The quantity  $n(n-1)U_{xy}/2$  has been subtracted. The results are symmetric around  $n=3$ .

$n$	$\tilde{E}(N) \equiv E(N) - N(N-1)U_{xy}/2$	
	Low spin ( $K < \frac{3}{2}E_{JT}$ )	High spin ( $K \geq \frac{3}{2}E_{JT}$ )
1		$-\frac{5}{2}E_{JT}$
2	$-10E_{JT} + 4K$	$-\frac{5}{2}E_{JT} - K$
3	$-\frac{15}{2}E_{JT} + 2K$	$-3K$

experimental estimate of 0.1 eV for  $A_4C_{60}$  [5]. The splitting is, however, reduced by the competition with the Hund's rule coupling. An estimate of the exchange integral  $K$  based on an *ab initio* self-consistent field calculation [18] gave  $K = 0.11$  eV [19]. This number is, however, expected to be reduced by correlation effects. For instance, for atomic multiplets a reduction by 25% has been found [20]. Indeed, we find that the experimental triplet-singlet splitting is reproduced by using  $K = 0.07$  eV.

Since the metal-insulator transition depends on a competition between the kinetic and Coulomb energies, and since we may expect the electron-phonon coupling to reduce the hopping, we may expect this to reduce  $U_c$  [21]. We therefore study the effect of phonons on  $U_c$  (for  $K = 0$ ).

For this purpose we apply the DMFT [7]. We use hopping integrals for a Bethe lattice in the infinite dimensional limit  $t_{ijm'l} \sim t^* \delta_{mm'}/\sqrt{z}$ , where  $z \rightarrow \infty$  is the connectivity. The impurity model, resulting in the DMFT, is solved with a QMC method [22]. The phonon fields are treated fully quantum mechanically, and they are updated together with the Fermion auxiliary fields in each Monte Carlo step [23]. We use the one-particle bandwidth  $W = 2$ , the phonon frequency  $\omega_{ph} = 0.5$ , and a Trotter breakup  $\Delta\tau = 1/3$ .

For an insulator  $G(\tau = \beta/2)$  decays exponentially with  $\beta$ , where  $G(\tau)$  is the electron Green's function on the imaginary time axis. We therefore use  $G(\beta/2)$  to determine whether the system is a metal or an insulator.

We first compare the coupling to  $A_g$  and  $H_g$  phonons for  $n = 3$ . Figure 2a shows that  $G(\beta/2)$  is reduced as  $U/W$  is increased, since the system gets closer to a metal-insulator transition. For  $\lambda = 0$  extrapolation suggests a rather large

$U_c/W$ . For  $H_g$  phonons an increase in  $\lambda$  leads to a rapid reduction of  $G(\beta/2)$  and  $U_c$ , while for  $A_g$  phonons this leads to an *increase* in  $G(\beta/2)$  and  $U_c$ .

To understand these results we study a free molecule (Table I) and a system consisting of two molecules (dimer) (Table II) in the limit

$$K \sim \frac{g^2}{\omega_{ph}} \equiv E_{JT} \ll \omega_{ph} \ll W \ll U. \quad (6)$$

Table II shows the energy gap of the dimer. In agreement with the full DMFT results ( $K = 0$  and  $n = 3$ ) the gap is increased by a coupling to  $H_g$  but decreased by a coupling to  $A_g$  phonons. We first consider the  $A_g$  case. Since  $V_{mm'} = \delta_{mm'}V_{mm}$  we can transform the electron-phonon coupling to the form

$$g \sum_i (n_i - n)(b_i + b_i^\dagger), \quad (7)$$

where  $n_i$  is the total occupation number operator for site  $i$  and  $n$  is the (integer) filling. An irrelevant constant has been neglected. We first study the state with  $2n$  electrons. In the limit  $W \ll U$  hopping is suppressed, and  $n_i - n \approx 0$ . The coupling [Eq. (7)] is then negligible, and the electron-phonon contribution to the energy is small. In the case of an extra electron or hole, however, this additional charge can hop even for  $W \ll U$ . The coupling to the phonons then lowers the energy, and according to Eq. (3) this reduces the gap.

For coupling to  $H_g$  phonons, the state with  $2n$  electrons can lower its energy via the (dynamic) Jahn-Teller effect. Since hopping is very efficiently suppressed, the energy gain is accurately given as twice the energy for a free molecule (Table I). In the case of an extra electron or hole, on the other hand, hopping dominates over the Jahn-Teller effect in the limit (6). The system can then only take advantage of this effect to the extent that it does not interfere with the hopping. The electron-phonon coupling then gives a much smaller lowering of the energy than for the state with  $2n$  electrons, which increases the gap [Eq. (3)].

Figure 2b shows results for coupling to  $H_g$  phonons and filling  $n = 4$ .  $U_c/W$  is smaller than for  $n = 3$ , although the lattice structure is the same as for  $n = 3$ . This can be

TABLE II.  $E_g(n) - U_{xy} - d_3(n)t$  for a two-site model as a function of the filling  $n$ . The hopping contribution to the gap is  $d(n)t$ , where  $d_3(n) = -3, -5$ , and  $-6$  for  $n = 1, 2$ , and  $3$ , respectively. The coupling is to one  $A_g$  (A) or one  $H_g$  (H) phonon per site. The results are symmetric around  $n = 3$ .

Phonon	$n$	$E_g(n) - U_{xy} - d_3(n)t$		
		$K \leq \frac{3}{2}E_{JT}$	$\frac{3}{2}E_{JT} < K \leq \frac{9}{4}E_{JT}$	$K > \frac{9}{4}E_{JT}$
A	1		$-E_{JT} - K$	
A	2		$-E_{JT} + 3K$	
A	3		$-E_{JT} + 12K$	
H	1		$5E_{JT} + \frac{2}{3}K$	$\frac{35}{4}E_{JT} - K$
H	2	$35E_{JT} - \frac{46}{3}K$	$5E_{JT} + \frac{14}{3}K$	$\frac{35}{4}E_{JT} + 3K$
H	3	$\frac{55}{2}E_{JT} - 8K$		$-\frac{5}{2}E_{JT} + 12K$

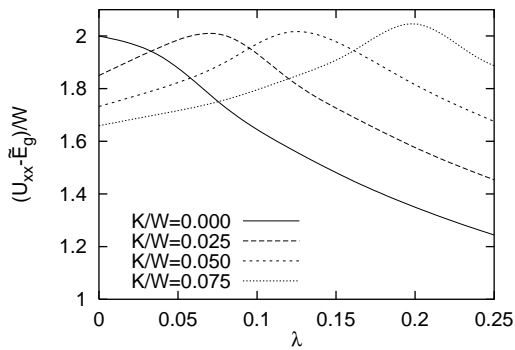


FIG. 3. The estimate  $U_{xx} - \tilde{E}_g$  of the critical  $U_{xx}$  as a function of  $\lambda = 4g^2/(\omega_{ph}W)$  for different values of  $K$  and  $U_{xx}/W = 3$ .

understood from Table I, which shows that the energy gain in the free molecule due to the electron-phonon coupling is larger for  $n = 4$ . This enters in  $E(nM)$ , while the electron-phonon coupling plays a smaller role for  $E(nM \pm 1)$ . The electron-phonon coupling *alone* would then tend to favor  $A_4C_{60}$  being an insulator and  $A_3C_{60}$  being a metal. As we will see below, this effect is, however, partly canceled by the Hund's rule coupling.

The coupling to the  $H_g$  phonons pushes  $U_c$  for  $A_3C_{60}$  to the lower end of the physical range of  $U/W$ , raising some questions of why not also  $A_3C_{60}$  is an insulator. Although, the  $A_g$  phonons tend to increase  $U_c$ , this should not be important due to the weak coupling to the  $A_g$  phonons [24]. However, there is a substantial coupling to a plasmon in  $A_3C_{60}$  [25]. This should tend to increase  $U_c$ , since it couples to the electrons in the same way as the  $A_g$  phonons. Below we show that the Hund's rule coupling also plays an important role in this context.

We next consider the effects of the Hund's rule coupling ( $K > 0$ ). Since these terms in Eq. (2) lead to a sign problem in the DMFT QMC calculation, we use exact diagonalization. To reduce the size of the Hilbert space we consider a four-site system with twofold orbital and phonon degeneracies. The nearest neighbor hopping  $t_{im,jm'} = t_{ij}\delta_{mm'}$  is chosen randomly, thus reducing the degeneracy and the one-particle spacing. We limit the size of the Hilbert space by allowing a maximum of two phonons per site. Because of this limitation, the calculation is not fully converged for the larger coupling constants considered below. From the finite size corrected band gap  $\tilde{E}_g(U_{xx})$  we estimate the critical  $U_{xx}$  as  $U_{xx} - \tilde{E}_g(U_{xx})$ , shown in Fig. 3. The figure illustrates that for  $\lambda = 0$  an increase in  $K$  leads to a decrease in  $U_c$  [10]. In analogy to the discussion for the Jahn-Teller effect, the Hund's rule coupling can effectively lower the energy of the state with  $nM$  electrons while for the states with  $nM \pm 1$  electrons, the stronger interference with hopping leads to a smaller lowering of the energy. For  $\lambda > 0$  the competition between the Jahn-Teller effect and the Hund's rule coupling tends to reduce the influence of either effect on  $U_c$ . This is shown in Tables I and II and in Fig. 3.

To summarize, we have found that the difference in lattice structure favors  $A_3C_{60}$  being a metal and  $A_4C_{60}$  being

an insulator. The Jahn-Teller effect wins over the Hund's rule coupling, making  $A_4C_{60}$  a nonmagnetic insulator. The coupling to the  $H_g$  phonons tends to strongly reduce the critical  $U$  for a metal-insulator transition, raising questions about why not also  $A_3C_{60}$  is an insulator. This effect is, however, partially canceled by the Hund's rule coupling. The coupling to plasmons tends to further increase the critical  $U$ .

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