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Dynamical Mean Field Theory of the Mott transition in A_4C_{60}

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Chapter 1

The alkali doped fullerides

The alkali metal doped fullerides A_nC_{60}, based on tightly bound C_{60} molecules, are relatively simple molecular conductors where strong electron-electron correlations, orbital degeneracy and Jahn-Teller effect intervene at the same time, leading to remarkable physical properties[1]. The three-fold degenerate t_{1u} state of the isolated molecule, icosahedral counterpart of a p state, leads to three bands hosting the valence electrons provided by the alkali metals. Hence all compounds A_nC_{60} with $0 < n < 6$ should in principle be metallic if, as one expects, the bandwidth (of order 0.5 eV), is larger than the relatively small crystal field splittings. The $n = 3$ fullerides are in fact generally metals, and become superconducting with T_c as high as 40 K [2]. Among the $n = 4$ compounds, however, Na_4C_{60}, a stable fcc structure at high temperature[3], is the only one which is also a paramagnetic metal, whereas K_4C_{60} and Rb_4C_{60}, stable bct structures down to low temperatures, are instead paramagnetic narrow-gap insulators. Understanding in detail this insulating state proves nontrivial, and constitues the main scope of this thesis. Known experimental parameters for K_4C_{60} are a minimum band gap (probably indirect) between 0.05 and 0.2 eV[4, 5, 6], and a direct, optical gap of 0.5-0.6 eV[7]. The insulating state is *non magnetic* with a spin gap to the lowest triplet exciton of 0.1-0.14 eV[6, 8]. Transition to a metal can be provoked by pressure[6], which rationalizes why Na_4C_{60} should be metallic, Na being the smaller cation.

One can invoke at least two possible scenarios for the insulating behavior of A_4C_{60}: a) a band insulator, due to a strong splitting of the t_{1u} bands, arising for example from the bct distortion, or else from a collective static Jahn-Teller (JT) distortion of the C_{60} molecules, or alternatively b) a Mott-Jahn-Teller insulator[9], where the hopping between adjacent molecules is first of all suppressed by a strong Coulomb

repulsion, an intra-molecular JT effect subsequently optimizing the state of the four localized electrons. In this work we first study the molecular ion C_{60}^{4-}, and then the possible origin of the insulating behavior of A_4C_{60} by several theoretical approaches, tight-binding Hartree-Fock, density functional, and Dynamical Mean Field Theory (DMFT). This latter tecnique has been proven to be a powerful method to treat the Mott transition[10], and has the advantage to allow the study of the Mott transition for states without symmetry breaking.

Chapter 2

The C_{60}^{4-} molecular ion

We start considering the single C_{60}^{4-} molecular ion. Within the t_{1u} orbital, assuming rotational (icosahedral) symmetry, a general interaction among electrons can be written as

$$H_{int} = \frac{U}{2}n^2 + \frac{U_2}{6}\left[3\left(n_1 - n_2\right)^2 + 3\sum_{i<j}\Delta_{ij}^2 + \left(n_1 + n_2 - 2n_3\right)^2\right], \qquad (2.1)$$

where $n_i = \sum_\sigma c_{i,\sigma}^\dagger c_{i,\sigma}$, is the electron number on each orbital ($i = 1, 2, 3$), and $n = n_1 + n_2 + n_3$; $\Delta_{ij} = \sum_\sigma c_{i,\sigma}^\dagger c_{j,\sigma} + H.c.$. Working at fixed n, the second term is responsible for the multiplet splitting. For $n = 2, 4$, the lowest energy state is the ${}^3T_{1g}$ Hund's rule triplet, followed at energy $2U_2$ by a ${}^1H_g$ singlet, and at $5U_2$ by a ${}^1A_g$ singlet. The exchange coupling U_2 is expected not to be significantly screened by the t_{1u} electrons, so that a reasonable estimate can be obtained by optical measurement on solid C_{60}, which give $U_2 \simeq 0.05$eV[11]. Next, we consider the JT coupling to the eight H_g vibrational modes. In the adiabatic limit, one can use a single-mode approximation[12]

$$\begin{aligned} H_{JT} &= \frac{\hbar\omega_* g_*^2}{2}\left\{\left(z^2 + r^2\right) + \right. \\ &\left. z\left(n_1 + n_2 - 2n_3\right) + r\sqrt{3}\left(n_1 - n_2\right)\right\}. \end{aligned} \qquad (2.2)$$

By using vibrational frequencies and couplings extracted from gas phase $C_{60}^{(-)}$ photoemission[13] we obtain $\hbar\omega_* = 0.117$eV, and a dimensionless coupling $g_* = 1.204$, so that $E_{JT} = \hbar\omega_* g_*^2 = 0.169$eV. Instead of attempting an exact solution of $H_{int} + H_{JT}$, we consider

two opposite limits, antiadiabatic (the vibronic frequency is assumed to be larger than the electron energy scale) and adiabatic (the vibronic energy scale is much smaller than the electronic energy). Although neither of them strictly applies, for $\hbar\omega_*$ is comparable to all splittings and the coupling is of medium strength, the former limit will yield the right symmetries, while the latter will be quantitatively much more accurate.

In the anti-adiabatic limit, the JT term (2.2) gives rise to a non-retarded electron-electron interaction, which can be absorbed into $U_2 \longmapsto U_2 - (3/4)E_{JT}$, with a change of sign of U_2 from 0.05 to -0.076eV. The lowest energy state is now the ${}^1A_g$ singlet, followed at 0.23eV by the ${}^1H_g$ singlet, and at 0.38eV by the ${}^3T_{1g}$ triplet. The overall JT energy gain in this limit is very large, 0.84eV, about a factor three larger than the bare adiabatic JT energy (see below). This signals a true enhancement, due to the gain in zero point energy corresponding to the frequency collapse of the tangential vibron modes, first pointed out in Ref.[14], as a possible mechanism for explaining the high critical temperature of A_3C_{60} compounds.

In the adiabatic limit we diagonalize (2.1) plus (2.2) for $n = 4$, minimizing successively the eigenvalues with respect to z and r treated as classical variables. We find a lowest energy singlet at a classical distortion $z = -1.9867$ and $r = 0$, gaining $E_{JT} = 0.293$eV. Adding the zero point energy gain $\hbar\omega_*$[14], we obtain a total gain of 0.41eV, the zero-point enhancement still sizable. (A similar total gain of 0.42eV was obtained by uncorrelated eight-mode calculations[13, 12].) The lowest triplet state has instead $z = 1.0$ and $r = 0$ and lies above the ground state by $E_t = 0.108$eV (spin gap). The lowest singlet, (with $z = 1.0$ and $r = 0$), is at $E_s = 0.208$eV above the ground state. The *single-particle (optical) gap*, identified with the JT orbital splitting, is $\Delta = (3/2)zE_{JT} \simeq 0.504$eV.

In both limits therefore *the isolated C_{60}^{4-} ion is predicted to be a singlet.* We now turn to the solid, in order to study how the hybridazation between molecules affects the molecular physics.

Chapter 3

Bandstructure for A_4C_{60}

3.1 Hartree-Fock

Since the C_{60}^{4-} ion is a singlet, if hybridization between adjacent molecules were much smaller than all the molecular gaps involved, then a lattice of C_{60}^{4-} molecules would indeed be a non magnetic insulator, moreover with an optical gap Δ and a spin gap E_t remarkably close to the experimental ones. In that case, an electronic structure calculation and total energy minimization for the A_4C_{60} lattice should yield a narrow t_{1u} band split by an insulating gap, in turn supported by a static (uniform or staggered) collective JT distortion of all molecules (scenario (a)).

A tight-binding Hartree-Fock (HF) approximation yields precisely that. The Hamiltonian which we use is

$$H = \sum_{i,j,a,b,\sigma} t_{ij}^{ab} c_{ia\sigma}^{\dagger} c_{jb\sigma} + H_{int} + H_{JT}, \tag{3.1}$$

where the hopping amplitudes t_{ij}^{ab} are evaluated along the lines outlined in Ref.[15], and the vibronic terms are treated in the adiabatic approximation, as in Eq.(2.2). We look for a HF state with a non-zero uniform average of $n_1 = n_2 \neq n_3$ (collective JT state) and find a stable band insulator with direct gap and spin gap of ~ 1.48eV and an indirect gap of ~ 1.03eV, all of which are much larger than the experimental values. The calculated HF bandstructure is shown in Fig. 3.1. This indicates that this method, known to overestimate insulating tendencies, is unreliable for this problem, and more realistic first principles calculations are called for in this case.

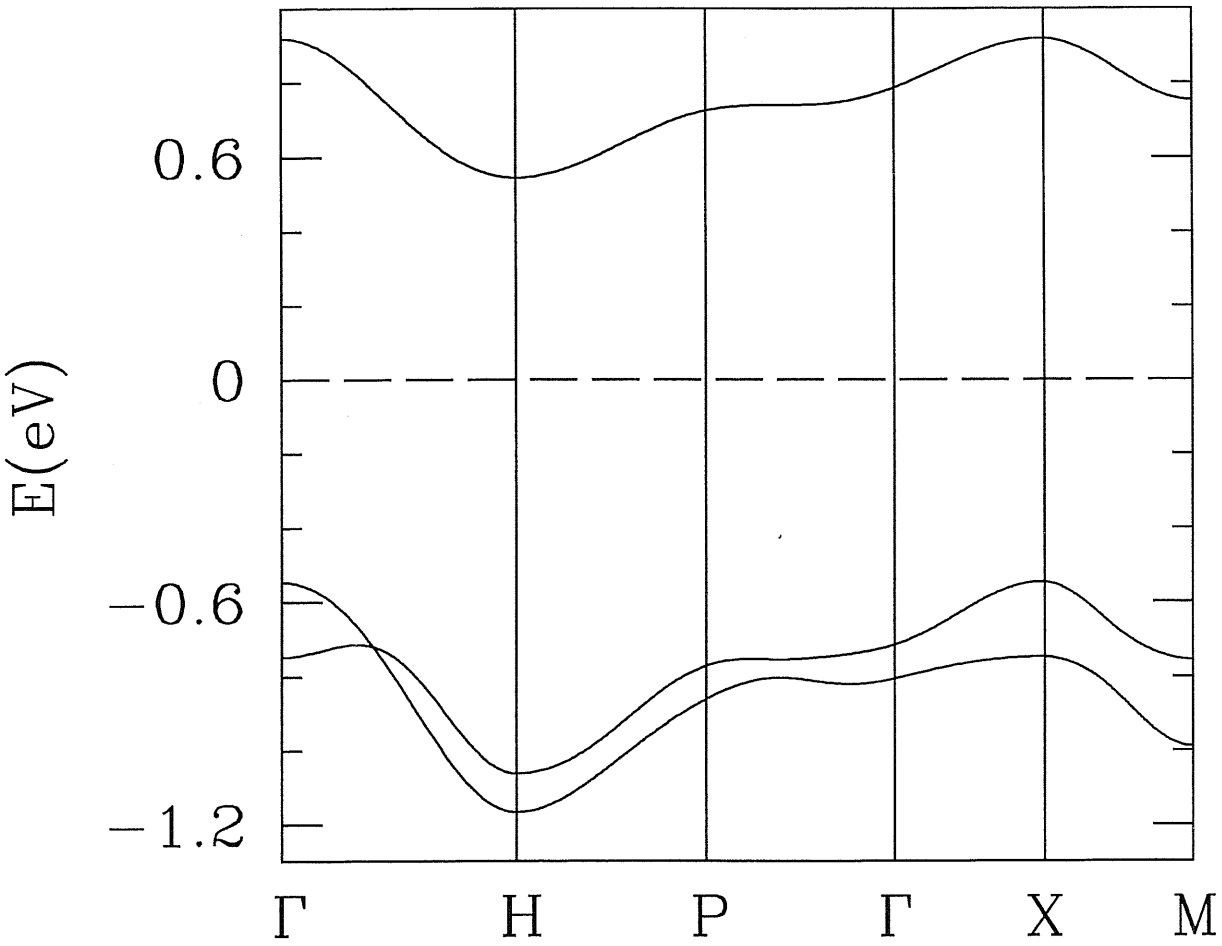

Figure 3.1: The t_{1u} bands for K_4C_{60} according to Hartree-Fock. The chemical potential is shown as a dashed line.

3.2 Density Functional theory: Local Density Approximation

We report the results of a series of such calculations for K_4C_{60}, starting with bct configurations compatible with X-ray data[16], and using state-of the-art pseudopotential plane-wave density functional techniques [17], with E_{cut} = 35 Ry (55 Ry for refinements), and careful k-point summations. Confirming previous results[18], it has been found first of all that intermolecular electron hopping is not small, yielding metallic t_{1u} bands of width $W \simeq 0.6$eV, as shown in Fig. 3.2. We searched next for a spontaneous collective JT distortion by relaxing atomic positions based on Hellmann-Feynman forces. In order to check that the calculation could in principle yield such a delicate JT distortion, and also reproduce the molecular limit, we performed test calculations at an artificially enhanced intermolecular spacing of 13.3Å. In that case a distortion appeared spontaneosly, leading to a distribution of carbon distances from the C_{60} center between 3.511 and 3.553Å. This distortion magnitude $\Delta R = 0.042$Å, although small, is very close to that reported for $[PPN(+)]_2C_{60}(2\text{-})$ salts[19], namely 0.043Å, and that is very gratifyng since JT distortions of C_{60}^{-2} and C_{60}^{4-} should be essentially the same. The single-particle gap was only about 0.1 eV, instead of the expected 0.5 eV, a standard density functional shortcoming of no consequence for this case. When carried out for the true structure (bct,intermolecular spacing 9.97Å) however, an extensive search for a JT distortion with one molecule/cell yielded no result, and the system remained undistorted and metallic. Notably, X-rays fail to find a static JT distortion[16], however within a resolution of precisely 0.04Å, which is inconclusive. Selected trial calculations with two molecules/cell also failed to yield a doubling, as would be caused, e.g., by charge-density-waves [18] or by a staggered collective JT state. We temporarily conclude that, since accurate density functional calculations cannot account for its insulating behavior, K_4C_{60} is probably not a band insulator. In the following section we will show the crucial role played by the electron-electron correlation in turning these systems to insulators.

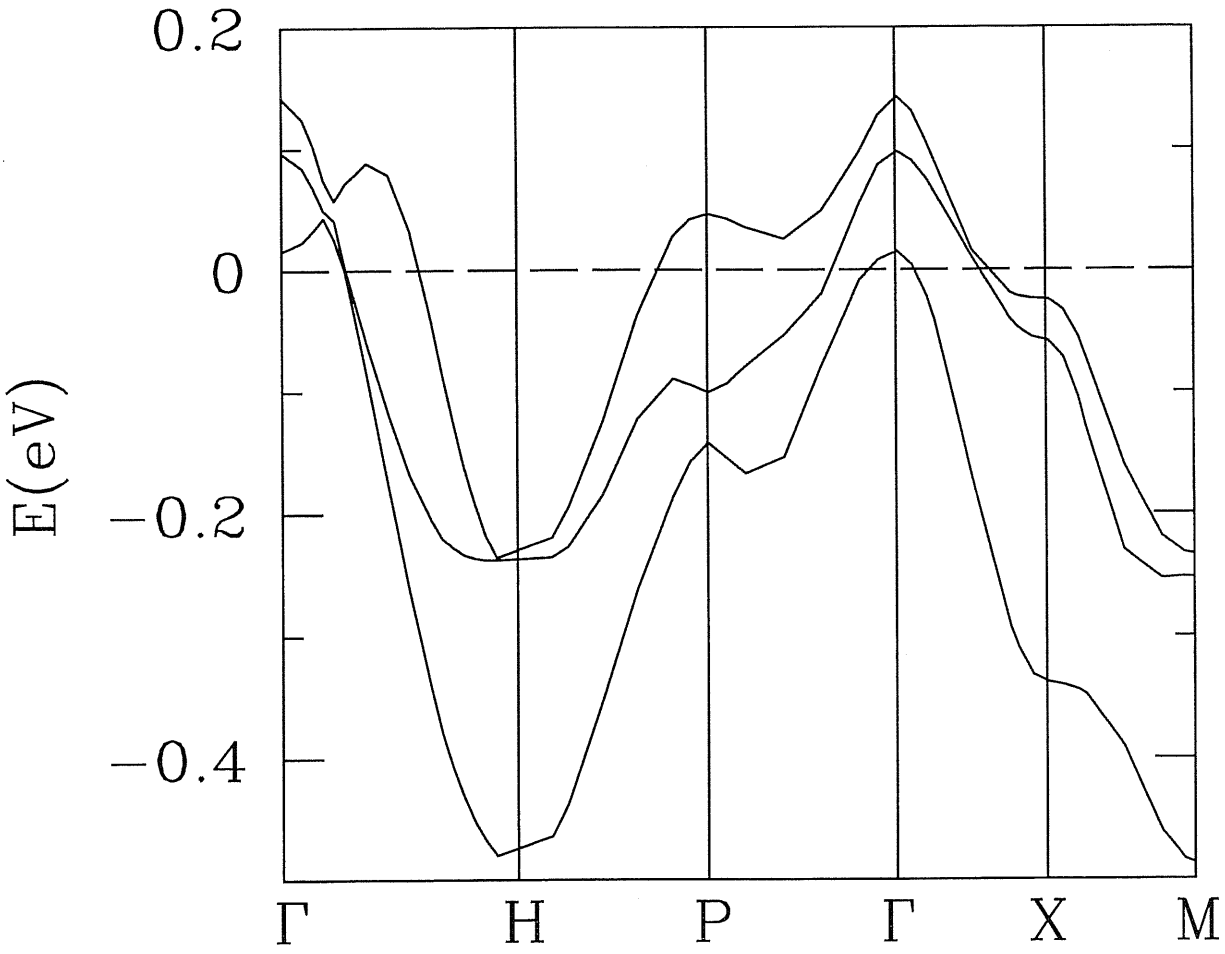

Figure 3.2: The t_{1u} bands for K_4C_{60} according to Density Functional Theory (LDA). The chemical potential is shown as a dashed line.

Chapter 4

Dynamical Mean Field Theory (DMFT)

4.1 The DMFT formalism

Electron correlations can be strong in these compounds. A realistic estimate[1, 11], of the intra-molecular Hubbard U of Eq.(2.1) is $\simeq$ 1.0–1.6eV, which is larger than the full bandwidth. The failure of density functional calculations does not appear surprising in this light. To get a description of the insulating state, and of the insulator-metal transition, we resort to dynamical mean-field theory (DMFT)[10], which is exact in the limit of infinite coordination lattices, and has proved quantitatively successful in describing the Mott transition.

Within DMFT, the Hamiltonian (3.1) is associated with a single-site effective dynamics, which can be described in terms of an imaginary-time action for the single-site fermionic degrees of freedom ($c_{0i\sigma}$, $c^{\dagger}_{0i\sigma}$):

$$S_{eff} = -\int_0^\beta d\tau \int_0^\beta d\tau' \sum_{i\sigma} c^{\dagger}_{0i\sigma}(\tau) G^{-1}_{0i}(\tau - \tau') c_{0i\sigma}(\tau') + S^{(0)}_{int}, \tag{4.1}$$

where $S^{(0)}_{int}$ is the interaction (electron-electron + electron-vibron) action for the electrons on the "impurity" site 0. The main difference with classical mean-field theory is that the generalized "Weiss field" $G^{-1}_{0i}(\tau - \tau')$ is a function of time. While spatial fluctuations are frozen, local quantum fluctuations are fully taken into account. To obtain a closed set of mean-field equations, a self-consistency equation relating $G^{-1}_{0i}(\tau - \tau')$ to quantities computable from S_{eff} must be supplemented. It can be

shown that such a relation is given by

$$G_{0i}^{-1}(i\omega_n) = i\omega_n + \mu + G(i\omega_n)^{-1} - R[G(i\omega_n)]. \tag{4.2}$$

$G(i\omega_n)$ is the Green's function evaluated from S_{eff}, and $R[G]$ is the reciprocal function of the Hilbert transform of free density of states (DOS) of the lattice at hand. For the case of the infinite coordination Bethe-lattice with bandwidth $W = 4t$ (semi circular DOS), the self-consistency equation (4.2) reads

$$G_{0i}^{-1}(i\omega_n) = \omega_n + \mu + G(i\omega_n)^{-1} - t^2 G(i\omega_n). \tag{4.3}$$

Due to the dynamical nature of the Weiss field, no single-site Hamiltonian form can be found, and an Hamiltonian formulation can be used only reintroducing auxiliary degrees of freedom ($a_{li\sigma}^{\dagger}$,$a_{li\sigma}$) describing a counduction "bath" which interacts with the impurity site. In such a way the action (4.1) can be associated with a three-fold degenerate impurity Anderson model,

$$H_{AM} = \sum_{li\sigma} \tilde{\epsilon}_{li} a_{li\sigma}^{\dagger} a_{li\sigma} + \sum_{li\sigma} V_{li}(a_{li\sigma}^{\dagger} c_{0i\sigma} + h.c.) + H_{int}^{(0)}, \tag{4.4}$$

where $H_{int}^{(0)}$ is the interaction Hamiltionian limited to the impurity site. This Hamiltonian is quadratic in the conduction bath degrees of freedom; integrating them out gives rise to an action of the form (4.1) with

$$G_{0i}^{-1}(i\omega_n) = i\omega_n + \mu - \sum_{il\sigma} \frac{V_{li}^2}{i\omega_n - \tilde{\epsilon}_{li}}, \tag{4.5}$$

where the parameters V_{li} and $\tilde{\epsilon}_{li}$ are chosen such as to reproduce the actual solution of G_{0i} of the mean-field equations. Band structure enters the calculations via the density of states (DOS) in the self-consistency equations. We approximate the realistic DOS of our problem with a semicircular DOS of same bandwidth W, appropriate for a tight-binding model on an infinite-coordination Bethe lattice. This approximation does not change the qualitative behavior of the model and is not expected to significantly influence the value of the gap.

4.2 Results for A_4C_{60}

The Anderson model, eq.(4.4), is solved by means of exact diagonalization with a finite number (n_s) of conduction electron degrees of freedom[20], checking convergence as a

function of n_s by finite-size scaling. The density is fixed to $n = 4$ by suitably tuning the chemical potential. We should look for either orbital symmetry broken ($V_{il} \neq V_{jl}$ for $i \neq j$) and unbroken ($V_{il} = V_l$) phases, as the capability to describe a true Mott insulator without any symmetry breaking is a unique feature of DMFT, which is not shared by HF or density functional-based calculations, always implying symmetry breaking at metal-insulator transitions. For simplicity, we have restricted our search for insulating solutions either without orbital symmetry breaking or with uniform JT ordering. In order to locate the metal-insulator transition (MIT), we calculate the quasiparticle residue Z given by

$$\frac{1}{Z} = 1 - \frac{\partial}{\partial\omega} Re\Sigma(\omega + i0^+)|_{\omega=0}, \tag{4.6}$$

where the self-energy Σ is given by

$$\Sigma(i\omega_n) = G_0^{-1}(i\omega_n) - G^{-1}(i\omega_n). \tag{4.7}$$

The vanishing of Z identifies the critical U/W above which a paramagnetic insulator is stable, and the metallic one is not. Notice that, within DMFT, $Z = m/m^*$, being m^* the effective electron mass. Again, we limit our analysis to limiting cases:

1. No JT coupling;

2. Antiadiabatic JT effect;

3. Adiabatic JT effect.

Case 1 – The three-fold degenerate Hubbard model without JT coupling, is well studied for $U_2 = 0$[1, 21]. In the presence of a finite $U_2/W = 0.08$ we find a MIT at $U/W \simeq 1.414$ for symmetric solutions, much reduced with respect to $U/W \simeq 1.98$ with $U_2 = 0$.

Case 2 – The JT coupling renormalizes the dipolar integral, leading to an effective $U_2/W = -0.127$. The critical MIT U/W is shifted to a much lower value $U/W \simeq 0.707$.

Case 3 – Solution of DMFT equations is more involved, since the self-consistency must be required only after averaging over the classical vibrational (five-dimensional) variable $\vec{Q}$ [22, 23]. In the broken-symmetry case the average simplifies, at $T = 0$, as the probability distribution of $\vec{Q}$ becomes a single δ-function. We obtain a critical $U/W \simeq 0.9 - 1.0$ (the uncertainty due to convergence difficulty). The orbitally

symmetric insulating solution, which becomes stable at $U/W \simeq 1.237$, is of particular interest since it describes a molecular insulator where each molecule is distorted with equal probability in all possible directions and independently from any other molecule. This state has therefore a very large entropy which could be reduced by including quantum fluctuations, for instance in the form of tunnelling between the equivalent local distortions, a way of describing a dynamical JT effect, not included at the adiabatic level. It should be noted that our adiabatic limit does not now include the vibron zero-point energy gain. Because it is present in the symmetric case only, it could lower the true critical U/W value of this phase, which could in reality prevail over the broken symmetry case. Moreover, temperature would also favor the symmetric state, where entropy is higher.

We can now compare critical U/W's with the true ones. As before, we expect the adiabatic values to be quantitatively more accurate. The calculated critical values are in all cases substantially smaller than the actual U/W value, i.e. 1.7–2.7. In such a way the electronic on-site repulsion has been identified as the dirving force to the insulating state. We conclude that the insulator is best explained as a Mott-Jahn-Teller state, where orbital degeneracy has becomes split, giving rise to an essentially intra-molecular C_{60}^{4-} Jahn-Teller state whose calculated gaps (optical, spin) agree very closely with experimental data. In the adiabatic limit the orbital symmetry is broken, but that is likely to change when zero-point energy and temperature are included.

The close agreement between the adiabatic gaps of C_{60}^{4-} and experimental optical and spin gaps in A_4C_{60} is perhaps the strongest piece of evidence in favor of a Mott state. Suppose one could even find, by some other band calculation, such as GW[24], a stable static collective JT state as in scenario (a). By necessity, the collective JT distortion magnitude would have to be substantially smaller than that of the isolated molecular ion, since electrons leaving the molecule very frequently to hop on other molecules weaken the on-site JT effect. But, in that case, it should not be possible to observe optical and spin gaps of exactly the right molecular magnitude, as one does. They would be much smaller, corresponding to the delocalization, or spillout, of the band Wannier function. In the Mott state, the electron spillout to neighboring molecules is reduced to order t/U, which is very small. Hence this is the only state that can explain why JT electronic gaps are essentially intra-molecular. When the Mott insulator state is destroyed, for example by pressure-induced increase of W and decrease of U, this intra-molecular physics is expected to disappear rather suddenly (giving way to a density functional-like metal), instead of gradually as in a band MIT transition.

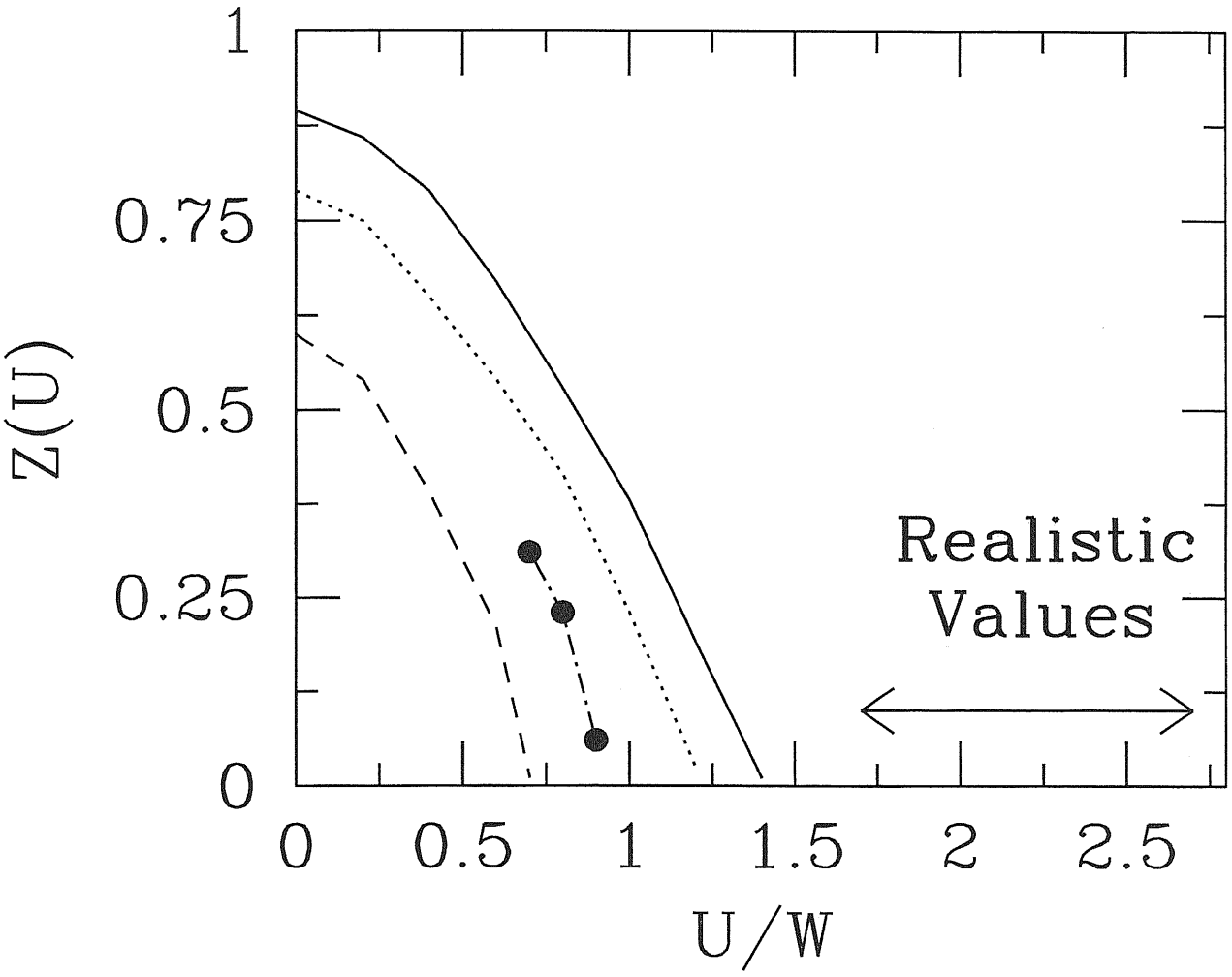

Figure 4.1: Quasiparticle residue Z as a function of U/W for the purely electronic model-symmetric solution (solid line), the adiabatic limit-symmetric solution (dotted line), the adiabatic limit-broken symmetry solution (dot-dashed line + dots), and the antiadiabatic limit-symmetric solution (dashed line).

Chapter 5

Conclusions

In this thesis the unconventional insulating state in A_4C_{60} has been studied with a variety of approaches, ranging from density functional calculations and dynamical mean-field theory. While the density functional theory (in local density approximation) predicts a metallic state, in disagreement with experiment, and a simple Hartree-Fock approach provides unrealistic values for the band gaps, the dynamical mean field approach yields a (paramagnetic) Mott-Jahn-Teller insulator, in extremely good agreement with experimental evidence. In that state, conduction between molecules is suppressed by on-site Coulomb repulsion (Mott insulator), and magnetism is suppressed by intra-molecular Jahn-Teller effect. In the Mott state the most relevant excitations (such as optical and spin gap) should then be essentially intra-molecular. It is not surprising that the experimental gaps of 0.5 eV and 0.1 eV respectively compare well with molecular ion values, in agreement with the picture described above. Therefore, a full understanding of the insulating state in these systems can be obtained only considering both the strong correlation effects driving the system to a Mott insulator, and the splitting of the orbital degeneracy due to the electron-vibron interaction (Jahn-Teller effect).

This finding incidentally suggests that also the n=3 fullerides, whose bandwidth is quite similar, are most likeky close to a strongly correlated state [11], (the same physics would predict in that case a Mott-Jahn-Teller spin 1/2 antiferromagnetic insulator), with the implication that strong correlations should probably not be ignored when discussing superconductivity in these compounds.

Chapter 6

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