Electronic Properties of Buckminsterfullerenes: Degeneracies and Surprises

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Abstract

Buckminsterfullerene compounds exhibit remarkable physics at low temperatures, e.g. high temperature superconductivity in alkali-fullerenes, and ferromagnetism in TDAE- C$_{60}$. Here we review recent theoretical studies of electron correlations in these compounds. In particular, we discuss models of electron-vibron interactions, electron-electron interactions, and intermolecular hopping. We show that the origin of novel electronic phases lies in local degeneracies of C$_{60}$; a direct consequence of the high molecular symmetry.

1 Introduction

The synthesis of buckminsterfullerene (C$_{60}$) into molecular crystals with electron donors has resulted in materials with surprising electronic properties[1].

C$_{60}$ is a truncated icosahedron. From a physicist’s standpoint, the charged molecule is fundamentally interesting, because the high molecular symmetry gives rise to degeneracies in both electronic and vibrational systems. Thus,

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the molecule is very sensitive to perturbations. In particular, electron–phonon and electron–electron interactions are expected to produce highly correlated ground states and excitations.

First, superconductivity was discovered in alkali-fullerenes, $A_3C_{60}$, ($A=K, Cs, Rb$) at relatively high temperatures ($T_c \leq 33^\circ K$ [2]), compared, say, to intercalated graphite. Soon thereafter ferromagnetism was found in TDAE-$C_{60}$ at $T_c \approx 16^\circ K$ [3, 4, 5], where TDAE is tetrakis(dimethylamino)ethylene, $C_2N_4(CH_3)_8$ (the stoichiometry is a 1:1 ratio of TDAE to $C_{60}$).

Some striking aspects of TDAE-$C_{60}$ are its relatively large value of $T_c$—for an organic ferromagnet—and its nonmetallic conductivity, suggestive of Mott-Hubbard localization[6]. Ferromagnetism is thus particularly unusual, since superexchange na"ively predicts antiferromagnetic interactions between localized spins in many such systems.

An obvious question is raised: Are superconductivity in $A_3C_{60}$ and ferromagnetism in TDAE-$C_{60}$ related? While superconductivity involves effectively attractive interactions, magnetism is usually believed to result from repulsive Coulomb forces.[4] The similarity between the materials is that both involve partially filled conduction bands made of $t_{1u}$-orbitals of $C_{60}$. Also one expects similar intramolecular electron-vibron and electron-electron interactions.

The primary differences between the two systems are in their crystalline symmetries and $C_{60}$ ionizations. While $A_3C_{60}$ is an FCC crystal with cubic symmetry in which the $C_{60}$ molecules are triply ionized ($C_{60}^{3-}$), TDAE-$C_{60}$ has a $c$-centered monoclinic unit cell[4], which gives rise to preferred hopping along the $c$-axis, and singly ionized $C_{60}$.

Here we review recent work on the local molecular interactions which are separated into two major contributions: the electron-electron pseudopotentials (Section 2), and the electron-vibron interactions (Section 3). The latter

\[ ^{1} \text{A similar mystery underlies the proximity of high } T_c \text{ superconductivity to antiferromagnetism in the high- } T_c \text{ cuprates.} \]
exhibit, in the semiclassical limit, interesting dynamical Jahn Teller effects accompanied by non trivial Berry phases \cite{8,9,10}. We show that this effect enhances the attractive interaction due to electron-vibron interactions by a significant factor. This analysis, though admittedly qualitative, points at a plausible cause for the relatively high $T_c$'s of $A_3C_{60}$.

In Section 4 we discuss TDAE- $C_{60}$. We derive an effective model for the low excitations of TDAE- $C_{60}$ using a muticomponent superexchange expansion about the Mott-Hubbard insulating phase \cite{11}. As a result, we obtain a rich phase diagram which includes spin ferromagnetism, spin density waves, and orbital ferromagnetism depending on the ratios of interaction pseudopoten-

\section{The electron-electron pseudopotentials}

We consider a system of $N$ $\pi$-electrons hopping on the truncated icosahedron (the soccer-ball) lattice of $C_{60}$. The single particle Hamiltonian is

$$H^0 = \sum_\lambda \epsilon_\lambda \sum_\mu \sum_{s=\uparrow\downarrow} c_{\lambda\mu s}^\dagger c_{\lambda\mu s}$$

(1)

$\lambda\mu$ denote the irreducible representations of the icosahedral group $\chi_{\lambda\mu}(\hat{\Omega})$ where $\hat{\Omega}$ is a unit vector pointing at one of the soccer ball vertices. At low $\lambda$, $\chi_{\lambda\mu}(\hat{\Omega})$ are closely related to the angular momentum functions $Y_{lm}(\hat{\Omega})$. However, the structure of the states near the Fermi level of 60 electrons is different. The soccer-ball lattice splits the degenerate spherical $l = 5$ multiplet, and the Fermi level lies in the semiconducting gap between the 5-fold and 3-fold degenerate $\lambda = h_g, t_{1u}$ orbitals respectively.

The Coulomb interactions on a metallic spherical shell is parametrized by two dimensionless variables $g, \alpha$.

$$H^{e-e} = \frac{1}{2} \int d\hat{\Omega}_1 d\hat{\Omega}_2 V(\hat{\Omega}_1 - \hat{\Omega}_2) : \rho(\hat{\Omega}_1) \rho(\hat{\Omega}_2) :$$
\[ V = g \ 2\pi r_{\text{min}} \sum_{LMss'} \left( \frac{2}{r_{\text{min}}(2L+1)} \right)^{\alpha} Y^{*}_{LM}(\hat{\Omega}_1)Y_{LM}(\hat{\Omega}_2), \quad (2) \]

\[ \rho = \sum_{s} \psi_{s}^{\dagger} \psi_{s} \text{ is the density operator where } \psi_{s}^{\dagger} = \sum_{\lambda\mu} \chi_{\lambda\mu}(\hat{\Omega})c_{\lambda\mu s}^{\dagger}. \quad g = e^{2}/(\epsilon Re_{0}) \text{ is the strength of the screened interaction, and } R \text{ is the radius of the ball.} \]

The power law tail of \( V(r) \) depends on \( \alpha \) such that as \( \alpha \) decreases, the potential has shorter range. \( 0 \leq \alpha \leq 1 \) interpolates smoothly between a \( \delta \) function and an unscreened \( 1/r \) Coulomb potential:

\[ V^{\alpha=0} = g \ 2\pi r_{\text{min}} \delta(\hat{\Omega}_1 - \hat{\Omega}_2); \quad V^{\alpha=1} = \frac{g}{|\hat{\Omega}_1 - \hat{\Omega}_2|} \quad (3) \]

When \( \alpha \) changes from 0 to 1, the averaged interaction over an area of radius \( r_{\text{min}} \) (analogous to Hubbard’s U) is held fixed.

The interaction in the basis of \( H_{0} \) can thus be explicitly given in the second quantized form as

\[ H^{e-e} = g\pi r_{\text{min}} \sum_{L} \left( \frac{2}{r_{\text{min}}(2L+1)} \right)^{\alpha} \times (-1)^{m'+\mu} C_{LM\bar{\mu}' - \bar{\mu}}^{L \lambda, \lambda'} C_{M\lambda' - \mu'}^{L \lambda} \chi_{\lambda\mu}' c_{\lambda\mu s}^{\dagger} c_{\lambda\mu s} \chi_{\lambda\mu}'(\hat{\Omega}) \quad (4) \]

where summation of repeated indices is assumed.

For a molecule with \( N \) electrons in a closed shell (above which there is a gap larger than the interaction strength), the zero frequency interaction between two electrons in the open shell is given by

\[ u_{\lambda\mu} \equiv E^{\lambda\mu}_{N+2} - 2E_{N+1} + E_{N} \quad (5) \]

which we call “pseudopotentials”. \( \lambda\mu \) denote the representation of the \( N+2 \) electron state. The computation of \( u_{\lambda\mu} \) for the Hamiltonian \( H_{0} + H^{e-e} \) is a difficult task which was undertaken using second order perturbation theory[12, 13] and later using perturbative renormalization group up to three loops order[14].
For the real compounds however, estimation of the true pseudopotentials requires incorporating the electron-vibron interactions (see the following Section 3) as well as crystal fields, screening from neighboring molecules and polarization effects of $\sigma$ electrons. As we shall see, the electronic properties of the conduction bands in the solid are very sensitive to the combination of electron-electron and electron-vibron pseudopotentials. Thus even ab-initio calculations [15] (which involve certain approximations for the higher order effects of interactions) may not be accurate enough for precise predictions of the ground state phase diagram. Here we shall therefore look for \textit{qualitative} effects and leave the electron-electron pseudopotentials as free parameters within an acceptable range of magnitudes.

3 The electron-vibron problem and superconductivity

In this section we solve the problem of a single $H_g$ vibron coupled to $t_{1u}$ electrons in a $C_{60}^-$ molecule. The model is too simplified for quantitative predictions for $C_{60}$, but it contains interesting novel physics which will be important for further studies of this system.

Semiclassically, a dynamical Jahn–Teller effect occurs [16, 17, 18]. For $n = 1, 2, 4, 5$, the molecule distorts unimodally, giving rise to a pseudo-angular momentum spectrum, plus three harmonic oscillators. For $n = 3$, there is a bimodal distortion, which generates a spectrum of a symmetric top rotator, plus two harmonic oscillators. The pseudo-rotations are subject to non trivial Berry phase effects [19], which determine the pseudo-angular momenta $L$, and thus the degeneracies and level ordering of the low lying states. Strong Berry phase effects seem to survive even at moderate and weak coupling as shown by the exact diagonalization results.

We find at weak coupling that the pair binding energy is a factor of
5/2 larger than the classical JT effect, and a factor of three larger than the pairing interaction of Migdal–Eliashberg theory of superconductivity. This enhancement can be interpreted semiclassically as due to large zero point energy reduction of the pseudo–rotations. From the weak coupling point of view, this effect is due to degeneracies in both electronic and vibronic systems.

Migdal’s approximation neglects vertex corrections in the resummation of two–particle ladder diagrams. This is justified only in the retarded limit \( \omega << \epsilon_F \). Here we have considered the opposite limit, where the molecular ground state energies are solved first, assuming that the JT relaxation time is of the same order, or faster than the inter molecular hopping time. In this regime, we have found therefore that Migdal’s approximation substantially underestimates the pairing interaction, and \( T_c \), for these ideal molecular solids [20]. This large effect suggests that some of the enhancement is likely to carry over to the real case of \( \text{A}_3\text{C}_{60} \) metals, where electron hopping \( t \) and vibron frequencies are of similar strength.

### 3.1 The Model

We consider a single \( H_g \) (five dimensional) vibrational multiplet which couples to \( n = 1, \ldots 5 \) electrons in an open \( t_{1u} \) shell. \( t_{1u} \) and \( H_g \) are the icosahedral group counterparts of the spherical harmonics \( \{Y_{1m}\}_{m=-1}^1 \), and \( \{Y_{2M}\}_{M=-2}^2 \) respectively. By replacing the truncated icosahedron (soccer ball) symmetry group by the spherical group, we ignore lattice corrugation effects. These are expected to be small since they do not lift the degeneracies of the \( L = 1, 2 \) representations.

The Hamiltonian is thus defined as\[10\]

\[
H = H^0 + H^{e-v} ,
\]
where,
\[
H^0 = \hbar \omega \sum_M \left( b_M^\dagger b_M + \frac{1}{2} \right) + (\epsilon - \mu) \sum_{ms} c_{ms}^\dagger c_{ms} .
\]

\( b_M^\dagger \) creates a vibron with azimuthal quantum number \( M \), and \( c_{ms}^\dagger \) creates an electron of spin \( s \) in an orbital \( Y_{1m} \). By setting \( \mu \to \epsilon \) we can discard the second term.

The \( H_g \) vibration field is
\[
u(\hat{\Omega}) = \frac{1}{\sqrt{2}} (Y_{2M}^* (\hat{\Omega}) b_M^\dagger + Y_{2M} (\hat{\Omega}) b_M) ,
\]
where \( \hat{\Omega} \) is a unit vector on the sphere. The \( t_{1u} \) electron field is
\[
\psi_s^\dagger (\hat{\Omega}) = \sum_{m=-1}^1 \psi_{1m} (\hat{\Omega}) c_{ms}^\dagger .
\]
The electron–vibron interaction is local and rotationally invariant. Its form is completely determined (up to an overall coupling constant \( g \)) by symmetry:
\[
H_{e-v} \propto g \int d\hat{\Omega} \nu(\hat{\Omega}) \sum_{s} \psi_s^\dagger (\hat{\Omega}) \psi_s (\hat{\Omega}) .
\]
Using the relation
\[
\int d\hat{\Omega} \ Y_{LM} (\hat{\Omega}) Y_{lm_1} (\hat{\Omega}) Y_{lm_2} (\hat{\Omega}) \propto (-1)^M \langle L, -M | lm_1; lm_2 \rangle ,
\]
where \( \langle \cdots \rangle \) is a Clebsch-Gordan coefficient \cite{21}, yields the second quantized Hamiltonian
\[
H_{e-v} = \frac{\sqrt{3}}{2} g \hbar \omega \sum_{s,M,m} (-1)^m \left( b_M^\dagger + (-1)^M b_{-M} \right) \psi_s^\dagger \psi_s \times \langle 2, M|1,-m; 1, M + m \rangle c_{ms}^\dagger c_{M+ms} .
\]
The coupling constant \( g \) is fixed by the convention of O’Brien, who studied first this kind of dynamical JT problem \cite{22}. Representation (12) is convenient for setting up an exact diagonalization program in the truncated Fock space.
3.2 The Real Representation

The semiclassical expansion is simpler to derive in the real coordinates representation. The vibron coordinates are

\[ q_\mu = \frac{6}{\sqrt{10}} \sum_{m=-2}^{2} M_{\mu m} \left( b_m^\dagger + (-1)^m b_{-m} \right) , \]  

where

\[ M_{\mu,\mu \neq 0} = (2 \text{sign}(\mu))^{-\frac{1}{2}} (\delta_{\mu,m} + \text{sign}(\mu) \delta_{\mu,-m}) , \]

\[ M_{\mu,0} = \delta_{\mu,0} . \]  

\{q_\mu\} are coefficients of the real spherical functions

\[ f_\mu (\hat{\Omega}) = \frac{6}{\sqrt{5}} \sum_m M_{\mu,m} Y_{2m}(\hat{\Omega}) \]

\[ = \begin{cases} 
\frac{6}{\sqrt{10}} \text{Re} \left( Y_{2\mu}(\hat{\Omega}) \right) & \mu = 1, 2 \\
\frac{6}{\sqrt{5}} Y_{20}(\hat{\Omega}) & \mu = 0 \\
\frac{6}{\sqrt{10}} \text{Im} \left( Y_{2\mu}(\hat{\Omega}) \right) & \mu = -1, -2
\end{cases} . \]  

We also choose a real representation for the electrons

\[ c^\dagger_{x s} = \frac{1}{\sqrt{2}} (c^\dagger_{1 s} + c^\dagger_{-1 s}) \]

\[ c^\dagger_{y s} = \frac{1}{i\sqrt{2}} (c^\dagger_{1 s} - c^\dagger_{-1 s}) \]

\[ c^\dagger_{z s} = c^\dagger_{0 s} . \]  

Thus the Hamiltonian in the real representation is given by

\[ H = H^0 + H^{e-v} \]

\[ H^0 = \frac{\hbar \omega}{2} \sum_\mu \left( -\partial^2_\mu + q_\mu^2 \right) \]

\[ H^{e-v} = g \frac{\hbar \omega}{2} \sum_s (c^\dagger_{x s} c^\dagger_{y s} c^\dagger_{z s}) \begin{pmatrix}
q_0 + \sqrt{3}q_2 & -\sqrt{3}q_{-2} & \sqrt{3}q_1 \\
-\sqrt{3}q_{-2} & q_0 - \sqrt{3}q_2 & -\sqrt{3}q_{-1} \\
-\sqrt{3}q_1 & \sqrt{3}q_{-1} & -2q_0
\end{pmatrix} \begin{pmatrix}
c_{x s} \\
c_{y s} \\
c_{z s}
\end{pmatrix} \]  

\[ (17) \]
This form of the JT hamiltonian is well known \cite{22,17}. Since the Hamiltonian is rotationally invariant, its eigenvalues are invariant under simultaneous O(3) rotations of the electronic and vibronic representations.

### 3.3 Jahn–Teller Distortions

In the classical limit, one can ignore the vibron derivative terms in \( (17) \), and treat \( \vec{q} = \{q_\mu\} \) as frozen coordinates in \( H^{e-v} \). The coupling matrix in \( H^{e-v} \) is diagonalized by \cite{23}:

\[
T^{-1}(\varpi) \begin{pmatrix} z - \sqrt{3}r & 0 & 0 \\ 0 & z + \sqrt{3}r & 0 \\ 0 & 0 & -2z \end{pmatrix} T(\varpi),
\]

(18)

where

\[
T = \begin{pmatrix} \cos \psi & \sin \psi & 0 \\ -\sin \psi & \cos \psi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos \theta & 0 & \sin \theta \\ 0 & 1 & 0 \\ \sin \theta & 0 & \cos \theta \end{pmatrix} \begin{pmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{pmatrix}.
\]

(19)

\( \varpi = (\phi, \theta, \psi) \) are the three Euler angles of the O(3) rotation matrix \( T \). In the diagonal basis of \( (18) \), the electron energies depend only on two vibron coordinates:

\[
\vec{q}(0) = \begin{pmatrix} r \\ 0 \\ z \\ 0 \end{pmatrix}.
\]

(20)

By rotating the vibron coordinates \( \vec{q} \) to the diagonal basis using the \( L = 2 \) rotation matrix \( D^{(2)} \) \cite{21}, one obtains

\[
\vec{q}_\mu(r, z, \varpi) = \sum_{m, m', \mu'}^{2} M_{\mu, m} D^{(2)}_{m, m'}(\varpi) M_{m' \mu}^{-1} \vec{q}_{\mu'}(0),
\]

(21)

where \( M_{\mu, m} \) was defined in \( (14) \).
By (21), and the unitarity of $D$ and $M$, $|q|^2$ is invariant under rotations of $\varpi$. Thus, the adiabatic potential energy $V$ depends only on $r$, $z$, and the occupation numbers of the electronic eigenstates $n_i$, where $\sum_i n_i = n$.

$$V(z, r, [n_i]) = \frac{\hbar \omega}{2} (z^2 + r^2) + \frac{\hbar \omega g}{2} \left( n_1 (z - \sqrt{3}r) + n_2 (z + \sqrt{3}r) - n_3 2z \right).$$

$V$ is minimized at the JT distortions $(\bar{z}_n, \bar{r}_n, \bar{n}_i)$, at which the classical energy is given by

$$E_n^{cl} = \min V(\bar{z}_n, \bar{r}_n, \bar{n}_i).$$

The JT distortions at different fillings are given in Table I. We define $\tilde{\phi}, \tilde{\theta}$ as the longitude and latitude with respect to the diagonal frame ("principal axes") labelled $(1, 2, 3)$ (3 is at the north pole). $\bar{z}, \bar{r}$ parametrize the Jahn-Teller distortion in the real representation (8), as

$$\langle u^{JT}(\hat{\Omega}) \rangle = \frac{\bar{z}}{2} (3 \cos^2 \tilde{\theta} - 1) + \frac{\sqrt{3}}{2} \sin^2 \tilde{\theta} \cos(2\tilde{\phi}).$$

In Table I we present the values of the ground state JT distortions at all electron fillings. We see that electron fillings $n = 1, 2, 4, 5$ have unimodal distortions which are symmetric about the 3 axis, while $n = 3$ has a bimodal, about the 3 and 1 axes. The two types of distortions are portrayed in Fig. 1. We depict the distortions of (24) for the unimodal and bimodal cases.

### 3.4 Semiclassical Quantization

At finite coupling constant $g$, quantum fluctuations about the frozen JT distortion must be included. In order to carry out the semiclassical quantization, we define a natural set of five dimensional coordinates $r, z, \varpi$. $\varpi$ parametrize the motion in the JT manifold (the valley in the "mexican hat" potential $V$) and $r, z$ are transverse to the JT manifold, since $V$ depends on them explicitly.
For the unimodal cases the kinetic energy is given by
\[
\frac{1}{2} |\dot{q}|^2 \approx \frac{1}{2} \left( z^2 + r^2 + r^2 (2\dot{\psi})^2 + 3z^2 \left( \dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2 \right) \right) .
\] (25)
and the semiclassical Hamiltonian is thus
\[
H_{\text{uni}} \approx H_{\text{rot}} + H_{\text{ho}}
\]
\[
H_{\text{rot}} = \frac{\hbar \omega}{6z^2} \vec{L}^2
\]
\[
H_{\text{ho}} = \hbar \omega \sum_{\gamma=1}^{3} (a^\dagger_{\gamma} a_{\gamma} + \frac{1}{2}) ,
\] (26)
where \(\vec{L}\) is an angular momentum operator, and \(H_{\text{ho}}\) are the three harmonic oscillator modes of \(r\). The energies are given by
\[
E_{\text{uni}} = \hbar \omega \left( \frac{1}{6z^2} L(L+1) + \sum_{\gamma=1}^{3} (n_\gamma + \frac{1}{2}) \right) .
\] (27)
The rotational part of the eigenfunctions is
\[
\Psi_{Lm}^{\text{rot}}(\vec{q}) = Y_{Lm}(\hat{\Omega}) \left| [n_{is}] \right\rangle_{\hat{\Omega}} ,
\] (28)
where \(\hat{\Omega} = (\theta, \phi)\) is a unit vector, and \(\left| [n_{is}] \right\rangle_{\hat{\Omega}}\) is the electronic adiabatic ground state. It is a Fock state in the principal axes basis. In terms of the stationary Fock basis \(\left| [n_{\alpha s}] \right\rangle\) where \(\alpha = x, y, z\), the adiabatic ground state is
\[
\left| [n_{is}] \right\rangle_{\hat{\Omega}} = \sum_{[n_{as}]} \langle [n_{as}] | [n_{is}] \rangle_{\hat{\Omega}} \left| [n_{as}] \right\rangle .
\] (29)
Each overlap is a Slater determinant which is a sum of \(n\) products of spherical harmonics
\[
\langle [n_{as}] | [n_{is}] \rangle_{\hat{\Omega}} = \sum_{[\nu]} C_{[\nu]} \ Y_{1\nu_1}(\hat{\Omega})Y_{1\nu_2}(\hat{\Omega}) \cdots Y_{1\nu_n}(\hat{\Omega}) ,
\] (30)
where \(C_{[\nu]}\) are constants.
Now we discuss how boundary conditions determine the allowed values of $L$. A reflection on the JT manifold is given by

$$\hat{\Omega} \rightarrow -\hat{\Omega}. \quad (31)$$

Spherical harmonics are known to transform under reflection as

$$Y_{Lm} \rightarrow (-1)^L Y_{Lm}. \quad (32)$$

Thus, by (29) and (30), the electronic part of the wave function transforms as

$$|n_{is}\rangle_{\hat{\Omega}} \rightarrow (-1)^n |n_{is}\rangle_{-\hat{\Omega}}. \quad (33)$$

The reflection (31) can be performed by moving on a continuous path on the sphere from any point to its opposite. It is easy to verify, using (21) that this path is a closed orbit of $\vec{q} \in \mathbb{R}^5$:

$$\vec{q}(\hat{\Omega}) \rightarrow \vec{q}(-\hat{\Omega}) = \vec{q}(\hat{\Omega}). \quad (34)$$

Thus we find that the electronic wave function yields a Berry phase factor of $(-1)^n$ for rotations between opposite points on the sphere which correspond to closed orbits of $\vec{q}$. In order to satisfy (28) using the invariance of the left hand side under reflection, the pseudorotational $Y_{Lm}$ wavefunction must cancel the electronic Berry phase. This amounts to a selection rule on $L$:

$$(-1)^{L+n} = 1. \quad (35)$$

Thus, the ground state for $n = 1$ and 5 electrons has pseudo-angular momentum $L = 1$ and finite zero point energy due to the non trivial Berry phases.

3.4.1 Bimodal Distortion

The analysis of the bimodal distortions $n = 3$ proceeds along similar lines. The quantization of the pseudo-rotational part is the quantum symmetric
top Hamiltonian. Fortunately, it is a well-known textbook problem (see e.g. Ref. [24, 21]). The eigenfunctions of a rigid body rotator are the rotational matrices

$$D^{(L)}_{mk}(\varpi),$$  \hspace{1cm} (36)

where \(L, m, k\) are quantum numbers of the commuting operators \(\vec{L}^2, L^z, L^1\) respectively. \(L^z\) and \(L^1\) are defined with respect to the fixed \(z\) axis and the co-rotating \(1\) axis respectively. The quantum numbers are in the ranges

$$\begin{align*}
L &= 0, 1, \ldots \infty \\
m, k &= -L, -L + 1, \ldots L .
\end{align*}$$  \hspace{1cm} (37)

The remaining coordinates are two massive harmonic oscillators modes

$$\mathbf{r} = (r - \bar{r}, z - \bar{z}).$$  \hspace{1cm} (38)

The semiclassical Hamiltonian is thus

$$H^{bi} \approx H^{rot} + H^{ho},$$

$$H^{rot} = \frac{\hbar \omega}{4z^2} \hat{L}^2 - \frac{3\hbar \omega}{16z^2} (L^1)^2,$$

$$H^{ho} = \hbar \omega \sum_{\gamma=1}^{2} (a_{\gamma}^\dagger a_{\gamma} + \frac{1}{2}),$$  \hspace{1cm} (39)

and its eigenvalues are

$$E^{bi} = \hbar \omega \left( \frac{1}{4z^2} L(L + 1) - \frac{3}{16z^2} k^2 + \sum_{\gamma=1}^{2} (n_{\gamma} + \frac{1}{2}) \right).$$  \hspace{1cm} (40)

The rotational eigenfunctions are explicitly dependent on \(\varpi\) as

$$\Psi^{rot}_{Lmk}[\vec{q}] = D^{(L)}_{mk}(\varpi) \prod_{is} |n_{is}\rangle \varpi .$$  \hspace{1cm} (41)

Unlike the unimodal case, in the bimodal case no single reflection fully classifies the symmetry of the wavefunction. However, one can obtain definite
sign factors by transporting the electronic ground state in certain orbits. We define the rotations of $\pi$ about principle axis $L^i$ as $C_i$. The Berry phases associated with these rotations can be read directly from the rotation matrix $T$ in Eq. (19). For example: for $\psi \rightarrow \psi + \pi$ ($C_3$), the states $|1\rangle$ and $|2\rangle$ get multiplied by $(-1)$.

Since $D_{m,k}^{(L)}$ transform as $Y_{Lk}$ under $C_i$, it is easy to determine the sign factors of the pseudorotational wavefunction. The results are given below:

\begin{align*}
C_1 : |1, 0, 2\rangle_\varphi & \rightarrow |1, 0, 2\rangle_\varphi' & C_1 : D_{m,k}^{(L)} & \rightarrow (-1)^k D_{m,k}^{(L)} \\
C_2 : |1, 0, 2\rangle_\varphi & \rightarrow -|1, 0, 2\rangle_\varphi' & C_2 : D_{m,k}^{(L)} & \rightarrow (-1)^{L+k} D_{m,-k}^{(L)} \\
C_3 : |1, 0, 2\rangle_\varphi & \rightarrow -|1, 0, 2\rangle_\varphi' & C_3 : D_{m,k}^{(L)} & \rightarrow (-1)^L D_{m,-k}^{(L)} .
\end{align*}

$q$ are coefficients in an $L=2$ representation, and therefore are invariant under $C_1, C_2, C_3$. $C_i$ describe continuous closed orbits in $R^5$. In order to satisfy (12) and using the degeneracy of $E^{bi}$ for $k \rightarrow -k$, we find that

$$L = \text{odd}, \quad k = \text{even}. \quad (43)$$

In particular, the ground state of (11) is given by $L=1$, and $k=0$.

### 3.5 Exact Diagonalization

The above semiclassical scheme gives a clear and intuitive picture of the behaviour of the system in a strong coupling limit[9]. This limit is appropriate for describing, e.g., Na$_3$ [25]. However, in C$_{60}$ the actual range of the coupling parameter - $g \approx 0.3$ for a typical mode [26, 27] - suggests that the electron–vibron coupling is actually in the weak to intermediate regime.

In Ref. (14) we have diagonalized the electron–vibron Hamiltonian (12) for single $H_g$ mode in a truncated Fock space. This approach yields accurate results weak to moderate values of the coupling strength. The eigenenergies match the semiclassical approximation (27) and (10) at large $g$, as expected.
The electron-vibron pseudopotentials are defined as

\[ u_{LM} = E_{n+1}^{LM} + E_{n-1} - 2E_n, \]  

(44)

where \( E_n \) are the fully relaxed ground state energies of \( n \) electrons, which ignore the effects of electron-electron interactions. For odd values of \( n \), this is an effective pairing interaction often called “pair binding” in the literature[12]. In Section 3.4 we found that for all odd \( n \), the pair energies are negative, and given by the large \( g \) asymptotic expression

\[ u_{n=1,3,5} \sim -g^2 + 1 - \frac{2}{3g^2} + \mathcal{O}(g^{-4}). \]  

(45)

The first term is the classical energy. The second term is due to reduction of zero point energy along the JT manifold, since only radial modes remain hard. This term is independent of \( g \) and positive. The last term is due to the quantum pseudo-rotator Hamiltonian, and the Berry phases which impose a finite ground state energy associated with odd \( L \) for odd numbers of electrons. This term, although nominally small at large \( g \), becomes important at weaker coupling. If (45) is extrapolated to the weak coupling regime the last term would dominate the pair binding energy. The exact diagonalization indeed shows a significant enhancement of the pair binding energy over the classical value in the weak coupling regime.

In the weak coupling limit, we can obtain analytical expressions for \( u_n(g) \) for \( g << 1 \) by second order perturbation theory. The unperturbed Hamiltonian is the non interacting part \( H^0 \). The perturbing Hamiltonian is \( H^{e-v} \) of Eq. (12), which connects Fock states differing by one vibron occupation. All diagonal matrix elements vanish, and the leading order corrections to any degenerate multiplet are of order \( g^2 \). These are given by diagonalization of the matrix [29],

\[ \Delta_{n_{ms},n'_{ms}}^{(2)} = \langle 0, n_{ms} | H^{e-v} \frac{1}{E_a^{(0)} - H^0} H^{e-v} | 0, n'_{ms} \rangle. \]  

(46)
in the degenerate 0-vibrons subspace. The sum implied by the inverse operator \((E_a^{(0)} - H^0)^{-1}\) extends just to the \(N_e=1\) states. The eigenvalues of \(\Delta^{(2)}\) yield the ground state energies and splittings for different electron fillings. These results, for all \(H_g\) and also \(A_g\) modes, and extended to the \(N_e=1\) multiplet, are discussed more extensively in Ref. [27].

Here we refer only to ground state energetics. In particular, using the perturbative expressions, we obtain, for a single \(H_g\), mode the small \(g\) pair binding energy

\[
\frac{\mu_{n=1,3,5}}{\hbar \omega} = -\frac{5}{2}g^2 + \mathcal{O}(g^4).
\]  

(47)

The origin of the \(5/2\) factor that characterizes the perturbative result (47) is group theoretical [28, 27].

The molecular pair binding energy can be considered as an effective negative-U Hubbard interaction for the lattice problem, provided that the Fermi energy \(\epsilon_F\) is not much larger than the JT frequency scale \(\omega\). A mean field estimate of the transition temperature for the negative-\(U\) Hubbard model in the weak coupling regime is

\[
T_c \approx \epsilon_F \exp \left[\left(-N(\epsilon_F)|U|\right)^{-1}\right].
\]  

(48)

In Refs. [32] and [33], the results of Migdal–Eliashberg approximation for the superconducting transition temperature was given. Without the Coulomb pseudopotentials this approach yields

\[
T_c \approx \omega \exp \left[\left(-N(\epsilon_F)|V|\right)^{-1}\right]
\]

\[
V = -\frac{5}{6}g^2.
\]  

(49)

By comparing (47) to (49) we find a striking discrepancy between the values of the effective pairing interaction:

\[
U = 3V.
\]  

(50)
That is to say: in the weak coupling regime, the correct molecular calculation yields a pairing interaction which is \textit{three times larger} than the results of Migdal–Eliashberg theory!

\section{TDAE- \textit{C}\textsubscript{60}: Mott-ferromagnetism}

The fullerene compound TDAE- \textit{C}\textsubscript{60}, where \textit{C}\textsubscript{60} is buckminsterfullerene and TDAE is tetrakis(dimethylamino)ethylene \textit{C}\textsubscript{2}N\textsubscript{4}(CH\textsubscript{3})\textsubscript{8}, exhibits ferromagnetism at \textit{T}\textsubscript{c} \approx 16^\circ\text{K} \cite{3,4}. The striking aspects of this discovery are (i) the magnitude of \textit{T}\textsubscript{c}– relatively large for a material with no transition metals – and (ii) its nonmetallic conductivity, suggestive of Mott-Hubbard localization\cite{6}.

ESR studies \cite{34} show that TDAE donates an electron to \textit{C}\textsubscript{60}. Furthermore, no ESR signature of TDAE\textsuperscript{+} is observed, suggesting that the TDAE radical spins are somehow paired. The monoclinic structure makes for a relatively short \textit{C}\textsubscript{60} separation along the \textit{c}-axis. We are then led to consider a model of \textit{C}\textsuperscript{1}\textsubscript{60} chains whose conduction electrons interact via superexchange.

Superexchange in a one-band model is always antiferromagnetic, since the intermediate state |\textit{↑\downarrow}\rangle is a spin singlet. The molecular degeneracy of the \textit{t}\textsubscript{1u} \textit{C}\textsubscript{60} LUMO leads to interesting possibilities not realized in an orbitally nondegenerate model. Indeed, Seshadri \textit{et al.}\cite{5} have discussed how ferromagnetism naturally arises via superexchange through intermediate states with a negative singlet-triplet splitting (\textit{e.g.} Hund’s rule) in \textit{C}\textsubscript{2}\textsubscript{60}\textsuperscript{−}. We introduce here what we believe to be a ‘minimal model’, based on the structure of TDAE- \textit{C}\textsubscript{60}, which leads to insulating ferromagnetic behavior.

The main result in this section is the full multicomponent superexchange Hamiltonian for the Mott insulator and the analysis of its phase diagram. The model is characterized by only three pseudopoentials for the intermediate states of \textit{C}\textsubscript{2}\textsubscript{60}\textsuperscript{−} in an axially symmetric crystal field. In the limit where all the intermediate states are degenerate there is an accidental symmetry which
leads to the SU(4) Heisenberg antiferromagnetic model in its fundamental representation. This model, coincidentally, was solved by Sutherland using Bethe’s Ansatz. In the case of large singlet-triplet splitting, the ground state is a fully polarized spin ferromagnet and an orbital antiferromagnet whose correlations are given by n by Bethe’s wavefunction. Full details of the calculations below were given in Ref. [11].

4.1 The Hopping Model

We consider tight binding hopping on a lattice of C_{60} molecules with a filling of one electron per site. In general, a tetragonal or monoclinic crystalline symmetry will resolve the triply degenerate t_{1u} orbital into three distinct levels. Better details could be obtained ab-initio once the precise structure and orientations of the C_{60} molecules are experimentally ascertained. In our model, we shall retain only what we believe may be the essential microscopic physics undelying the ferromagnetism in TDAE-C_{60}: (a) The hopping is quasi-one dimensional along the c-axis. (b) We assume that the crystal field resolves the t_{1u} orbital triplet into a lower doublet (l = ±) and a higher singlet l = 0 at higher energy, as if the crystal fields are cylindrically symmetric about an axis which pierces the center a pentagonal face of C_{60}. (c) Hopping along the chains is assumed to preserve the orbital magnetization l.

Thus we investigate the Hamiltonian $\mathcal{H} = \mathcal{H}_{\text{hop}}^\parallel + \mathcal{H}_{\text{hop}}^\perp + \mathcal{H}_{\text{ion}}$, where

$$\mathcal{H}_{\text{hop}}^\parallel = -t^\parallel \sum_{i,l,\sigma} \left( c_{l\sigma}^\dagger (i) c_{l\sigma} (i + c) + \text{H.c.} \right)$$

$$\mathcal{H}_{\text{hop}}^\perp = -\frac{1}{2} \sum_{i,\delta,\sigma} t_{\delta}^\perp \left( c_{l\sigma}^\dagger (i) c_{l\sigma} (i + \delta) + \text{H.c.} \right)$$

$$\mathcal{H}_{\text{ion}} = \sum_{i,\Lambda} \bar{u}_\Lambda \left| \Lambda (i) \right\rangle \left\langle \Lambda (i) \right| . \tag{51}$$

Here $c_{l\sigma}^\dagger (i)$ creates, at site $i$, an electron of spin polarization $\sigma = \uparrow, \downarrow$ and “isospin” $l = +, -, c$ and $\delta$ denote nearest neighbor lattice vectors in the $c$
direction and the $a$-$b$ plane respectively. $t_{\mu\nu}$ are the hopping matrix elements between orbitals $l$ and $l'$ on neighboring chains.

$H_{\text{ion}}$ is the interaction Hamiltonian which discourages multiple electron occupancy on any C$_{60}$ molecule. It is parametrized by pseudopotentials $\bar{u}_\Lambda$ which correspond to the following C$_{60}^2$ multiplets,

$$
\bar{u}_0 : \frac{1}{\sqrt{2}}(c^\dagger_{l\uparrow}c_{l\downarrow} - c^\dagger_{l\downarrow}c_{l\uparrow})|0\rangle \\
\bar{u}_1 : c^\dagger_{l\uparrow}c_{l\downarrow}|0\rangle , \frac{1}{\sqrt{2}}(c^\dagger_{l\uparrow}c_{l\downarrow} + c^\dagger_{l\downarrow}c_{l\uparrow})|0\rangle , c^\dagger_{l\downarrow}c_{l\uparrow}|0\rangle \\
\bar{u}_2 : c^\dagger_{l\uparrow}c_{l\downarrow}|0\rangle , c^\dagger_{l\downarrow}c_{l\uparrow}|0\rangle 
$$

The relations between $\bar{u}_\Lambda$ and the isotropic pseudopotentials $u_L$ of angular momenta $L$ are: $\bar{u}_1 = u_1$, $\bar{u}_2 = u_2$, but $\bar{u}_0 = \frac{2}{3}u_0 + \frac{1}{3}u_2$ due to projecting out the “$l = 0$” orbital state. Thus, while in an isotropic environment there might be pair binding ($u_0 < 0$) due to electron-electron [12] and electron-vibron [10] interactions, it does not preclude a repulsive $\bar{u}_0 > 0$ in the monoclinic crystal field environment. This may help to explain why TDAE-C$_{60}$ is not a CDW, nor a superconductor as is A$_3$C$_{60}$.

### 4.2 Multicomponent Superexchange Hamiltonian

Experiments have shown that TDAE-C$_{60}$ is insulating at low temperatures, consistent with the existence of a gap to charge fluctuations (i.e. all $\bar{u}_\Lambda > 0$) [1]. The low-lying excitations can be described by a superexchange Hamiltonian, formally obtained as a second order expansion in small $t_{\parallel}/\bar{u}$. Since charge excitations are gapped, a renormalized version of the superexchange Hamiltonian is expected to describe the low energy excitations also for $t_{\parallel}/\bar{u} \gtrsim 1$.

The zeroth order states of the superexchange Hamiltonian are four singly occupied states enumerated by $l, \sigma$. The operators which act on these states can be represented by spin operators, $S^\mu_i = \frac{1}{2} \sum_{l,\sigma,\sigma'} c^{l\sigma\dagger}(i) \tau^\mu_{\sigma\sigma'} c_{l\sigma'}(i)$ and “isospin” operators, $I^\nu_i = \frac{1}{2} \sum_{l,l',\sigma} c^{l\sigma\dagger}(i) \tau^\nu_{ll'} c_{l\sigma}(i)$ where $\tau$ are the Pauli ma-
trices. Taking into account the constraint $\sum_\alpha c_\alpha^* c_\alpha = 1$, the 15 independent elements of the SU(4) generators $S_\beta^\alpha = c_\alpha^* c_\beta$ can be expressed in terms of the 15 operators $\{S^\mu, I^\nu, S^\mu I^\nu\}$.

For simplicity we consider the purely one-dimensional limit where $t_{l'i} = 0$. There are three superexchange constants defined as

$$J_M \equiv \frac{2(t^\parallel)^2}{\bar{u}_M} \quad M = 0, 1, 2 \ , \quad (53)$$

A straightforward, though cumbersome, leads to an effective Hamiltonian given by

$$\tilde{\mathcal{H}} = \sum_n \left( A s_n \cdot s_{n+1} + B I_n \cdot I_{n+1} + C I^n_z I^z_{n+1} + D s_n \cdot I_{n+1} + E s_n \cdot s_{n+1} I^n_z I^z_{n+1} + F \right) , \quad (54)$$

where

$$A = -\frac{1}{2} J_1 + J_2 + \frac{1}{2} J_0, \quad B = \frac{3}{2} J_1 - \frac{1}{2} J_0, \quad C = J_0 - J_2, \quad D = 2 J_1 + 2 J_0, \quad E = 4 J_2 - 4 J_0, \quad F = -\frac{3}{8} J_1 - \frac{1}{4} J_2 - \frac{1}{8} J_0 \ . \quad (55)$$

This model possesses a global SU(2)$\times$U(1) symmetry, i.e. $\tilde{\mathcal{H}}$ commutes with $\sum_n s_n$ and with $\sum_n I^n_z$. Enlarged symmetries occur when $J_0 = J_2$, where the symmetry group is SU(2)$\times$SU(2), and when $J_0 = J_1 = J_2$, where the symmetry group is SU(4).

**SU(4) Point** - At the point $\bar{u}_1 = \bar{u}_2 = \bar{u}_0 \equiv \bar{u}$ (54) acquires full SU(4) symmetry. For each $c$-chain the Hamiltonian is

$$\mathcal{H}_{SU(4)} = J \sum_n \sum_{\alpha,\beta} S^\beta_\alpha(n) S^\alpha_\beta(n+1) \ , \quad (56)$$

where $J = 2(t^\parallel)^2 / \bar{u}$.

The SU($P$) Heisenberg antiferromagnet in the fundamental representation has been solved by Sutherland for general $P$ using Bethe’s Ansatz [34].
This model exhibits $P - 1$ gapless elementary excitation branches. We presume, based on what happens in the SU(2) model \[36\], that for a chain of $N$ sites where $N$ is an integer multiple of $P$, the ground state is an SU($P$) singlet and the low-lying excitations transform according either to the singlet or the adjoint representation. This is essentially what happens in the fermion mean field (large $P$) theory of the SU($P$) antiferromagnet \[37, 38, 39\]. The mean field has four degenerate quarter-filled ($k_F = \frac{1}{4}\pi$) bands for $P = 4$. Although there it has no true long-ranged order, the spin and isospin susceptibilities diverges at the nesting wavevector $2k_F = \frac{1}{2}\pi$, which describes a commensurate spin density wave of period four. The period four arises because the spin chain is in its fundamental representation, and by ‘4-ality’ one needs four sites to make a singlet \([40]\). The mean field theory also predicts a constant uniform (Pauli) susceptibility, and a linear specific heat as in a Fermi liquid\[38\].

**Ferro-Antiferromagnetic points** – Along the surface $\bar{u}_2 = \bar{u}_0$, our Hamiltonian possesses an SU(2)×SU(2) symmetry. There are then two special limits in which we can determine the exact ground state. (i) The “F × A model” at $\bar{u}_0 \to \infty$, with $J_\parallel = 2(t\parallel)^2/\bar{u}_1$,

$$\mathcal{H}_{F \times A} = -\frac{4(t\parallel)^2}{\bar{u}_1} \sum_n (S_n \cdot S_{n+1} + \frac{3}{4})(\frac{1}{4} - I_n \cdot I_{n+1})$$

(57)
where the interactions are ferromagnetic in the spin channel and antiferromagnetic in the isospin channel, and (ii) the “A × F model” for $\bar{u}_1 \to \infty$, with $J_\parallel = 2(t\parallel)^2/\bar{u}_0$, and the roles of $I$ and $S$ interchanged.

It is possible to prove that the ground state of $\mathcal{H}_{F \times A}$ is the fully polarized ferromagnet $|F\rangle_S$ for the spin variables, and Bethe’s ground of the spin-half antiferromagnet for the isospin variables $i.e.$

$$\Psi_0^{F \times A} = |F\rangle_S \otimes |\text{Bethe}\rangle_I.$$  

(58)

A corresponding result holds for $\mathcal{H}_{A \times F}$, with spin and isospin variables exchanged. Due to the SU(2) ⊗ SU(2) symmetry the total spin $S_{tot}$, total
isospin $I_{\text{tot}}$, and their polarizations along the $\hat{z}$ axis ($M_S$ and $M_I$, respectively) are good quantum numbers. Following Lieb and Mattis’ proof of the Marshall theorem for the Heisenberg model\cite{lieb1961}, we perform a $\pi$ rotation about the $\hat{z}$ axis of the isospin operators on odd-numbered sites. The Hamiltonian transforms into a non-positive (‘negative semidefinite’) operator in the product Ising basis

$$
\mathcal{H}_{F \times A} \rightarrow J \sum_n \left( I_n^z I_n^z - \frac{1}{2} I_n^+ I_{n+1}^+ - \frac{1}{2} I_n^- I_{n+1}^- - \frac{1}{4} \right) \times (S_n \cdot S_{n+1} + \frac{3}{4}) \equiv \mathcal{H}'_{F \times A}.
$$

(59)

The accessibility of all states within a given magnetization sector by repeated application of the Hamiltonian, implies (see Ref.\cite{lieb1961}) that the ground state of $\mathcal{H}'_{F \times A}$ in the sector $(M_S, M_I) = (0, 0)$ can be chosen to be positive definite in the sublattice-rotated Ising basis, \textit{i.e.} it obeys Marshall’s sign rule. Since the same Marshall signs hold for the state on the right hand side of Eq. 58, which has $S_{\text{tot}} = \frac{1}{2} N$, and $I_{\text{tot}} = 0$, the two sides of Eq. 58 have finite overlap hence the same $S_{\text{tot}}$ and $I_{\text{tot}}$. We are free to choose $M_S = \frac{1}{2} N$ as a representative of the ground state manifold. Note that $|\Psi_{0}^{F \times A}\rangle$ is indeed an eigenstate of the spin triplet projection operator $(S_n \cdot S_{n+1} + \frac{3}{4})$ with eigenvalue one. It follows from Eq. 57 that the isospin part of the wavefunction is the ground state of the spin-half antiferromagnetic Heisenberg chain, given by Bethe’s \textit{Ansatz}.

Exact excitations of $\mathcal{H}_{F \times A}$ within the isospin sector (retaining full spin polarization) with dispersion $\frac{1}{2} \pi J |\sin k|$ can be constructed as in Refs.\cite{lieb1961, baxter1968}. The gapless ferromagnetic magnons, which exist due to Goldstone’s theorem, can be approximated within the Single Mode Approximation (SMA): $|k\rangle \equiv S_k^- |\Psi_{0}^{F \times A}\rangle$. The trial state dispersion is

$$
\omega(k) \leq 2 \ln(2) J (1 - \cos k)
$$

(60)

from which we see that the ferromagnon bandwidth is decreased due to the
antiferromagnetic nearest-neighbor isospin correlations, i.e. \( \langle \frac{1}{4} - \mathbf{I}_n \cdot \mathbf{I}_{n+1} \rangle = \ln(2) \).

### 4.3 Classical Phase Diagram

The ground state depends on the dimensionless ratios \( \bar{u}_0/\bar{u}_1 \) and \( \bar{u}_2/\bar{u}_1 \). The classical approximation (justified at \( S, I >> 1 \)) is given by minimizing the bond energies of Eq. (54) as function of vectors \( \mathbf{S}_i \) and \( \mathbf{I}_i \) of magnitude \( \frac{1}{2} \). The results are plotted in Fig. 2).

It is interesting to note that the SU(4) symmetry point is at the border of 4 distinct ordered phases of different symmetries, where the energy is degenerate along the lines \( \langle \mathbf{I}_n \cdot \mathbf{I}_{n+1} \rangle = -\frac{1}{4} \) and \( \langle \mathbf{S}_n \cdot \mathbf{S}_{n+1} \rangle = \frac{1}{4} \). The large degeneracy of the classical SU(4) model is reduced by quantum fluctuations.

The classical regime of Heisenberg spin–ferromagnetism and isospin-antiferromagnetism extends throughout \( \bar{u}_0, \bar{u}_2 > \bar{u}_1 \), although quantum fluctuations break the SU(2) isospin symmetry away from the isotropic line \( \bar{u}_0 = \bar{u}_2 \) (marked as a dashed line in Fig. 2).

**3D Ordering in the F \times A Model** – As shown by Scalapino et al. [13], one can treat the interchain interactions by mean field theory and thereby derive an expression for the full susceptibility \( \chi_{ab}(q_\perp, q_z, \omega) \) in terms of \( \chi_{1D}^{ab}(q_z, \omega) \), the susceptibility for the one-dimensional chains. The general result is

\[
\chi(q_\perp, q_z, \omega) = \left[ 1 - J_\perp(q_\perp) \chi_{1D}(q_z, \omega) \right]^{-1} \chi_{1D}(q_z, \omega), \tag{61}
\]

where \( J_\perp(q_\perp) = \sum_{\delta_\perp} J_\perp(\delta_\perp) e^{-i q_\perp \cdot \delta_\perp} \) is the spatial Fourier transform of the interchain coupling matrix. (Note that the quantities \( \chi, J_\perp \), and \( \chi_{1D} \) in Eq. (61) are matrices.) This approximation also may be employed at finite temperature.

Consider now the F × A model discussed above. At finite temperature \( T \), long-ranged ferromagnetic order is destroyed and the global SU(2)×SU(2) symmetry is restored. The uniform susceptibility of the ferromagnetic chain
is given by

$$\chi_F'(0,0;T) = \frac{J_\parallel}{24T^2} + \ldots,$$

(62)
as was first derived by Takahashi in Ref. [44] (see also Refs. [38, 46]).

For the antiferromagnetic susceptibility, we appeal to the bosonization results of Schulz and of Eggert and Affleck [47], who have computed the dynamic susceptibility of the $S = \frac{1}{2}$ antiferromagnetic Heisenberg chain. Performing a Fourier transform of their result and taking the low frequency and wavevector limit near the antiferromagnetic point we obtain the staggered isospin susceptibility

$$\chi_A \approx \frac{a_0^2}{\pi T},$$

(63)

where $a_0 \simeq 4.44$.

For mixed interchain coupling operators e.g. $O = S^x I^y$, we may use the assumed independence of ferromagnetic and antiferromagnetic magnons to obtain at low temperatures $\chi_{FA}'(\pi,0;T) \sim (J_\parallel T)^{-1/2}$, which diverges even more slowly than $\chi_A$ in the $T \to 0$ limit.

The interchain interaction is given by $J_\perp = J_\parallel ((t_1^\perp)^2 + (t_2^\perp)^2)/4(t^\parallel)^2$, where $t_1^\perp, t_2^\perp$ are the transverse hopping integrals (see Ref. [13]). Thus, as the temperature is lowered, a transition from paramagnetic to ferromagnetic state should set in when $J_\perp \chi_F' = 1$. This yields $T_C \simeq \sqrt{J_\parallel J_\perp}/24$. The relation $T_C \propto \sqrt{J_\parallel J_\perp}$ was also found by Scalapino et al. (ref. [43]) in their studies of anisotropic Heisenberg magnets. It is conceivable that at still lower temperatures a Néel ordering of the isospin variables occurs at a Néel temperature $T_N \simeq 3a_0^2 J_\perp/\pi$.

4.4 Experimental notes

(a) The lower isospin transition, to our knowledge, has not been resolved experimentally. Perhaps it is not very well separated from the ferromagnetic transition which would help explain the mysterious excessive entropy
of transition found by Ref. [34].

(b) Alternatively, the isospin ordering might be preempted by a isospin-Peierls ordering (orbital dimerization) aided by the electron-phonon coupling. In that case, a signature for the isospin-Peierls effect should be present in X-ray scattering or in the phonon spectrum.

(c) The role of a possible orientational disordered ground state [48] has not been considered here although it might help explain the observed weak ferromagnetism [3]. In addition, Bloch’s $T^{3/2}$ temperature dependence of the ordered moment found in Ref. [4] which holds upto $T \approx T_C$ is hard to reconcile with quasi-one dimensionality where $J_\perp \ll T_C$.

In summary, this section has described a model of quasi-one dimensional interacting electrons with doubly degenerate orbitals motivated by the structure of TDAE-$C_{60}$. At occupancy of one electron per site, we obtain a Mott-insulator with multicomponent superexchange between spins and isospins at neighboring sites. At special values of the interactions we identify exactly solvable points, including the SU(4) antiferromagnet, and spin-ferromagnet, isospin-antiferromagnet limit. The classical ground state diagram also contains a large region of spin ferromagnetism and orbital antiferromagnetism which we believe is relevant for TDAE-$C_{60}$. A mean field analysis of the interchain coupling in this regime predicts two transition temperatures: ferromagnetic spin ordering at $T_C \propto \sqrt{J_\parallel J_\perp}$, and orbital (isospin) antiferromagnetic ordering at $T_N \propto J_\perp$. This lower transition, to our knowledge, has not yet been resolved experimentally.

5 Concluding remark

In this review we have seen that it is possible to understand some of the unusual electronic properties of buckminsterfullerene compounds by relating them to the high molecular symmetry, and local degeneracies of the partially filled $t_{1u}$ orbitals. We have investigated in detail some simplified models with
local degeneracies, which exhibit enhanced superconductivity, and ferromagnetism, as well as other possible phases not yet observed experimentally. This suggests that continual experimenting with the family of fullerene compounds would most probably produce further surprises.

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Table 1: Semiclassical ground state distortions and energies for a single $H_g$

coupled mode of frequency $\omega$. $n$ is the electron number, $S$ is the total spin, $\bar{z}_n, \bar{r}_n$ are the JT distortions, $\bar{n}_i$ is the occupation of orbital $i$, $E_n$ is the ground state energy and, and $u_n$ is the pair energy (Eq.(44)). Energies are calculated for strong coupling to order $g^{-2}$.

| $n$ | $S$ | $(\bar{z}_n, \bar{r}_n)$ | $(\bar{n}_1, \bar{n}_2, \bar{n}_3)$ | $E_n/\langle h\omega \rangle$ | $U_n/\langle h\omega \rangle$ |
|-----|-----|-----------------|-----------------|-----------------|-----------------|
| 0   | 0   | (0,0)           | (0,0,0)         | $-\frac{5}{2}g^2 + \frac{3}{2} + \frac{1}{3g^2}$ | $-g^2 + 1 - \frac{2}{3g^2}$ |
| 1   | $\frac{1}{2}$ | $(g, 0)$         | (0,0,1)         | $-2g^2 + \frac{3}{2}$                          | $-g^2 + 1 - \frac{2}{3g^2}$ |
| 2   | 0   | $(2g, 0)$       | (0,0,2)         | $-\frac{5}{2}g^2 + 1 + \frac{1}{3g^2}$        | $-g^2 + 1 - \frac{2}{3g^2}$ |
| 3   | $\frac{1}{2}$ | $(\frac{3}{2}g, \frac{\sqrt{3}}{2}g)$ | (1,0,2)         | $-2g^2 + \frac{3}{2}$                          | $-g^2 + 1 - \frac{2}{3g^2}$ |
| 4   | 0   | $(-2g, 0)$      | (2,2,0)         | $-\frac{5}{2}g^2 + \frac{3}{2} + \frac{1}{3g^2}$ | $-g^2 + 1 - \frac{2}{3g^2}$ |
| 5   | $\frac{1}{2}$ | $(-g, 0)$       | (2,2,1)         | $-2g^2 + \frac{3}{2}$                          | $-g^2 + 1 - \frac{2}{3g^2}$ |
| 6   | 0   | (0,0)           | (2,2,2)         | $-\frac{5}{2}g^2 + \frac{3}{2} + \frac{1}{3g^2}$ | $-g^2 + 1 - \frac{2}{3g^2}$ |

Figure 1: A polar representation of the Jahn-Teller distortions $u^{JT}(\bar{\theta}, \bar{\phi})$, Eq.(24). The distortion is measured relative to a sphere. (a) The unimodal distortion for the ground states of $n = 1, 2, 4, 5$ electrons (b) The bimodal distortion for $n = 3$ electrons.

Figure 2: TDAE- $C_{60}$: Classical ground state phase diagram