TDAE-C\textsubscript{60}: Can a Mott insulator be a ferromagnet?

Assa Auerbach and Daniel P. Arovas
Physics Department, Technion-IIT, Haifa 32000, Israel
(February 4, 2018)

Motivated by the structure of TDAE-C\textsubscript{60}, we derive a multicomponent superexchange Hamiltonian for the spins and orbital (“isospin”) degrees of freedom in the Mott-insulating phase. We explore its phase diagram and identify points of special interest: an SU(4) antiferromagnet (solved by Sutherland) and two ferromagnet+antiferromagnet points where the ground state is known. For the ferromagnetic regime, we apply interchain mean field theory and derive an expression for the Curie temperature where spin ordering occurs and a lower Neél temperature for a conjectured isospin ordering.

PACS numbers: 33.10.Lb, 71.38.+i, 74.20.-z, 71.10.+x

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

ESR studies [3] show that TDAE donates an electron to C\textsubscript{60}. Furthermore, no ESR signature of TDAE+ is observed, suggesting that the TDAE radical spins are somehow paired. The monoclinic structure makes for some interesting possibilities not realized in a orbitally nondegenerate model. Indeed, Seshadri et al. [5] have discussed how ferromagnetism naturally arises via superexchange through intermediate states with a negative exchange through intermediate states with a negative

$$V = -J \sum_{\langle i,j \rangle} \langle \sigma_i (\downarrow, \uparrow) \sigma_j (\uparrow, \uparrow) \rangle$$

This latter case, which we think relevant to TDAE-C\textsubscript{60}, is a rare example where ferromagnetism can be proven in a microscopic model of localized electrons [3]. The three-dimensional susceptibilities can be expressed in terms of the exact one-dimensional functions following Scalapino et al. [6]. For the ferromagnetic model we find the spin Curie temperature and the orbital Neél temperature as a function of interchain couplings.

Full details of the calculations below will be soon available in a longer paper [5].

The Hopping Model: We consider tight binding hopping on a lattice of C\textsubscript{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\textsubscript{60} molecules are experimentally ascertained. In our model, we shall retain only what we believe may be the essential microscopic physics underlying the ferromagnetism in TDAE-C\textsubscript{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\textsubscript{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

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

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

$$\mathcal{H}_{\text{ion}} = \sum_{i,A} \bar{U}_{A} | A(i) \rangle \langle A(i) | .$$

Here $c_{i,\sigma}^\dagger (i)$ creates, at site $i$, an electron of spin polar-
After a straightforward calculation, we derive the general Hamiltonian which discourages multiple electron occupancy on any $C_60$ molecule. It is parametrized by pseudopotentials $u_A$ which correspond to the following $C_60$ multiplets,

$$
\begin{align*}
\bar{u}_0 : & \frac{1}{\sqrt{2}} (c_{i+}^{\dagger} c_{i-} - c_{i-}^{\dagger} c_{i+}) |0\rangle \\
\bar{u}_1 : & c_{i+}^{\dagger} c_{i-} |0\rangle, \frac{1}{\sqrt{2}} (c_{i+}^{\dagger} c_{i-} + c_{i-}^{\dagger} c_{i+}) |0\rangle, c_{i+}^{\dagger} c_{i-} |0\rangle \\
\bar{u}_2 : & c_{i+}^{\dagger} c_{i-} |0\rangle, c_{i-}^{\dagger} c_{i+} |0\rangle 
\end{align*}
$$

(2)

The relations between $\bar{u}_A$ and the isotropic pseudopotentials $u_L$ of angular momenta $L$ are: $\bar{u}_1 = u_1$, $\bar{u}_2 = u_2$, but $\bar{u}_0 = \frac{1}{2} u_0 + \frac{1}{2} u_2$ 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 [1] and electron-vibron [12] 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 in A$_3$C$_{60}$.

**Multicomponent Supercorrelation 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 $\bar{u}_A > 0$ [4]). 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, $S^\alpha_l = \frac{1}{2} \sum_{l,\sigma,\sigma'} c^\dagger_{l\sigma} (i) \tau^\alpha_{\sigma\sigma'} c_{l\sigma'} (i)$ and “isospin” operators, $P^\alpha_l = \frac{1}{2} \sum_{l,l',\sigma} c^\dagger_{l\sigma} (i) \tau^\alpha_{ll'} c_{l'\sigma} (i)$ where $\tau$ are the Pauli matrices. Taking into account the constraint $\sum_\alpha c^\dagger_{l\sigma} c_{l\sigma} = 1$, the 15 independent elements of the SU(4) generators $S^\alpha_l = c^\dagger_{l\sigma} c_{l\sigma}$ can be expressed in terms of the 15 operators $[S^\mu, P^\nu, S^\mu P^\nu]$.

**One-Dimensional Limit.** We first consider the purely one-dimensional case, where $t^\perp_l = 0$. There are three superexchange constants defined as

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

(3)

After a straightforward calculation, we derive the general spin/isospin representation of the effective Hamiltonian as

$$\hat{\mathcal{H}} = \sum_n \left( A S_n \cdot S_{n+1} + B I_n \cdot I_{n+1} + C I^\dagger_n I^\perp_{n+1} + D S_n \cdot S_{n+1} I_n \cdot I_{n+1} + E S_n \cdot S_{n+1} I^\dagger_n I^\dagger_{n+1} + F \right),$$

(4)

where

$$A = -\frac{1}{2} J_1 + \frac{1}{2} J_2, \quad B = \frac{3}{2} J_1 - \frac{1}{2} J_0,$$

$$C = J_0 - J_2, \quad D = 2 J_1 + 2 J_0,$$

$$E = 4 J_2 - 4 J_0, \quad F = -\frac{3}{4} J_1 - \frac{1}{4} J_2 - \frac{1}{8} J_0. \quad (5)$$

This model possesses a global SU(2)$\times$U(1) symmetry, i.e. $\hat{\mathcal{H}}$ commutes with $\sum_n S_n$ and with $\sum_n I^\perp_n$. 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 $\bar{u}_1 = \bar{u}_2 = \bar{u}_0 \equiv \bar{u}$ [2] acquires full SU(4) symmetry. For each $c$-chain the Hamiltonian is

$$\hat{\mathcal{H}}_{SU(4)} = J \sum_n \sum_{\alpha, \beta} S^\alpha_n (n) S^\beta_n (n+1),$$

(6)

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 [3]. This model exhibits $P - 1$ gapless elementary excitation branches. We assume, based on what happens in the SU(2) model [4], 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 theory [1] of the SU(P) antiferromagnet [4,5]. The mean field has four degenerate quarter-filled ($k_F = \frac{1}{2} \pi$) bands for $P = 4$. Although there it no true long-ranged order, the spin and isospin susceptibilities diverges at the nesting wavevector $2k_F = \frac{1}{4} \pi$, 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 [6]. The mean field theory also predicts a constant uniform (Pauli) susceptibility, and a linear specific heat as in a Fermi liquid [5].

**Ferro-Antiferromagnetic points.** Along the surface $\bar{u}_2 = \bar{u}_0$, our Hamiltonian possesses an SU(2)$\times$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 $J_{||} = 2(t^\parallel)^2/\bar{u}_1$,

$$\hat{\mathcal{H}}_{F\times A} = -\frac{4(t^\parallel)^2}{u_1} \sum_n (S_n \cdot S_{n+1} + \frac{3}{4}) (I_n \cdot I_{n+1})$$

(7)

where the interactions are ferromagnetic in the spin channel and antiferromagnetic in the spin channel, and (ii) the “A×F model” for $\bar{u}_1 \to \infty$, with $J_{||} = 2(t^\parallel)^2/\bar{u}_0$, 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 $|F\rangle$ for the spin variables, and Bethe’s ground of the spin-half antiferromagnet for the isospin variables i.e.

$$\Psi_0^{F \times A} = |F\rangle_S \otimes |\text{Bethe}\rangle_I.$$  \hspace{1cm} (8)

A corresponding result holds for $\mathcal{H}_{A \times F}$, with spin and isospin variables exchanged. Due to the $SU(2) \otimes SU(2)$ symmetry the total spin $S_{\text{tot}}$, 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 [19], 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

$$\mathcal{H}_{F \times A} \to J \sum_n (I_n^I I_{n+1}^I - \frac{1}{2} I_n^I I_{n+1}^I - \frac{1}{2} I_n^I I_{n+1}^I - \frac{1}{4})$$

$$\times (S_n \cdot S_{n+1} + \frac{1}{2}) \equiv \mathcal{H}'_{F \times A}$$  \hspace{1cm} (9)

The accessibility of all states within a given magnetization sector by repeated application of the Hamiltonian, implies (see Ref. [19]) 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, i.e. it obeys Marshall’s sign rule. Since the same Marshall signs hold for the state on the right hand side of Eq. (8) which has $S_{\text{tot}} = \frac{1}{2} N$, and $I_{\text{tot}} = 0$, the two sides of Eq. (8) 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 $(S_n \cdot S_{n+1} + \frac{1}{2})$ with eigenvalue one. It follows from Eq. (6) that the isospin part of the wavefunction is the ground state of the spin-half antiferromagnetic Heisenberg chain, given by Bethe’s 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. [13, 21]. 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

$$\omega(k) \leq 2 \ln(2) J(1 - \cos k)$$  \hspace{1cm} (10)

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

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 $S, I \gg 1$) is given by minimizing the bond energies of Eq. (4) as function of vectors $S_I$ and $I_I$ of magnitude $\frac{1}{2}$. The results are plotted in Fig. [4].

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 $\langle I_n \cdot I_{n+1} \rangle = -\frac{1}{4}$ and $\langle S_n \cdot S_{n+1} \rangle = \frac{1}{4}$. 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 $u_0, u_2 > u_1$, although quantum fluctuations break the SU(2) isospin symmetry away from the isotropic line $u_0 = u_2$ (marked as a dashed line in Fig. [4]).

3D Ordering in the $F \times A$ Model – As shown by Scalapino et al. [8], one can treat the interchain interactions by mean field theory and thereby derive an expression for the full susceptibility $\chi_{ab}(q, z, \omega)$ in terms of $\chi_{1D}^{ab}(q, z, \omega)$, the susceptibility for the one-dimensional chains. The general result is

$$\chi(q, z, \omega) = [1 - J_\perp(q) \chi_{1D}(q, z, \omega)]^{-1} \chi_{1D}(q, \omega),$$  \hspace{1cm} (11)

where $J_\perp(q) = \sum_{\delta} J_\perp(\delta) e^{-iq \cdot \delta}$ is the spatial Fourier transform of the interchain coupling matrix. (Note that the quantities $\chi, J_\perp$, and $\chi_{1D}$ in Eq. (11) are matrices.) This approximation also may be employed at finite temperature.

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

$$\chi_F(0, 0; T) = \frac{J_0}{24 T^2} + \ldots,$$  \hspace{1cm} (12)

as was first derived by Takahashi in Ref. [21] (see also Refs. [13, 22]).

For the antiferromagnetic susceptibility, we appeal to the bosonization results of Schulz and of Eggert and Affleck [23], 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

$$\chi_A \approx \frac{a_0^2}{\pi T},$$  \hspace{1cm} (13)

where $a_0 \approx 4.44$.

For mixed interchain coupling operators e.g. $\mathcal{O} = S^z I^z$, we may use the assumed independence of ferromagnetic
and antiferromagnetic magnons to obtain at low temperatures $\chi^{-1}_T(\pi, 0; T) \sim (J_\parallel T)^{-1/2}$, which diverges even more slowly than $\chi_\perp$ in the $T \to 0$ limit.

The interchain interaction is given by $J_{\perp} = J_{\parallel} (t_{\perp}^2 + (t_{\perp}^2)/d(t_{\parallel}^2)$, where $t_{\perp}^2$, $t_{\parallel}^2$ are the transverse hopping integrals (see Ref. [18]). Thus, as the temperature is lowered, a transition from paramagnetic to ferromagnetic state should set in when $J_{\perp} J_{\parallel} = 1$. 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. [4]) 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 $T_N \simeq 3a^2_0 J_{\perp}/\pi$.

**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. [3].

(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 [24] has not been considered here although it might help explain the observed weak ferromagnetism [1]. In addition, Bloch’s $T^{3/2}$ temperature dependence of the ordered moment found in Ref. [2] which holds up to $T \approx T_C$ is hard to reconcile with quasi-one dimensionality where $J_{\perp} \ll T_C$.

In summary, we have introduced a new 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.

Acknowledgements We thank Ian Affleck, Amnon Aharony, Brooks Harris, and Ganpathy Murthy for useful discussions. The support of US-Israeli Binational Science Foundation, the Israeli Academy of Sciences and the Fund for Promotion of Research at Technion is gratefully acknowledged. DPA thanks the Institute for Theoretical Physics at Technion, where this work was performed, and the Lady Davis Fellowship Trust for partial support.

---

1. P.M. Allemans et al., *Science* 253, 301 (1991).
2. A. Lappas et al., *Science* (in press, 1995).
3. K. Tanaka, *Chem. Phys. Lett.* 230, 271 (1994).
4. A. Schilder et al., *Phys. Rev. Lett.* 73, 1299 (1994).
5. R. Seshadri et al., *Sol. State. Comm.* 85, 971 (1993);
   C.N.R. Rao and R. Seshadri, *MRS Bulletin* 19, 28 (1994).
6. B. Sutherland, *Phys. Rev. B* 12, 3795 (1975).
7. W. Marshall, *Proc. R. Soc. A* 232, 48 (1955).
8. Other examples are: the Nagaoka ferromagnet of one hole in the infinite $U$ Hubbard model, and the Hubbard model on a bipartite lattice with unequal sublattice sizes. Neither is easy to realize physically.
9. D. J. Scalapino, Y. Imry, and P. Pincus, *Phys. Rev. B* 11, 2042 (1975).
10. D.P. Arovos and A. Auerbach, preprint (1995).
11. S. Chakravarty, M. Gelfand and S. Kivelson, *Science* 254, 970 (1991); G. N. Murthy and A. Auerbach, *Phys. Rev. B* 46, 331 (1992).
12. C. M. Varma, J. Zaanen, and K. Raghubavachari, *Science* 254, 989 (1991); A. Auerbach, N. Manini, and E. Tosatti, *Phys. Rev. B* 49, 12998 (1994).
13. L. D. Faddev and L. A. Takhtajan, *Phys. Lett. A* 85, 375 (1981).
14. G. Baskaran, Z. Zou, and P.W. Anderson, *Solid State Comm.* 63, 973 (1987); I. Affleck and J. B. Marston, *Phys. Rev. B* 37, 3774 (1988).
15. D. Arovos and A. Auerbach, *Phys. Rev. B* 38, 316 (1988).
16. N. Read and S. Sachdev, *Nucl. Phys. B* 316, 609 (1989).
17. A separate class of SU(3) models in which sites on alternating sublattices transform according to fundamental and anti-fundamental allow a singlet to be formed within any consecutive pair of sites, and such models exhibit long-ranged order via dimerization.
18. D.P. Arovos and A. Auerbach, preprint (1995).
19. E. Lieb and D.C. Mattis, *J. Math. Phys.* 3, 749 (1962).
20. J. des Cloizeaux and J. J. Pearson, *Phys. Rev. B* 135, A640 (1964).
21. M. Takahasi, *Prog. Theor. Phys. Suppl.* 87, 233 (1986).
22. A. Auerbach, “Interacting Electrons and Quantum magnetism” (Springer-Verlag, NY, 1994).
23. H. J. Schulz, *Phys. Rev. B* 34, 6372 (1986); S. Eggert and I. Affleck, preprint (1995).
24. A. B. Harris, *Physica A* 205, 154 (1994).
25. I. Affleck, *Phys. Rev. Lett.* 54, 966 (1985).
FIG. 1. Ground state phase diagram for the Hamiltonian $\tilde{\mathcal{H}}$ of Eq. 8.