Strong Correlation Effects in Fullerene Molecules and Solids

Fei Lin

Physics Department, Virginia Tech, Blacksburg, VA 24061

Collaborators:

- **Erik Sorensen**, McMaster University, Canada
- **Catherine Kallin**, McMaster University, Canada
- **John Berlinsky**, McMaster University and Perimeter Institute for Theoretical Physics, Canada

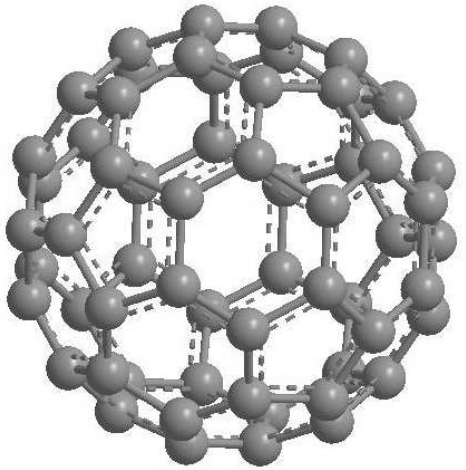
Outline:

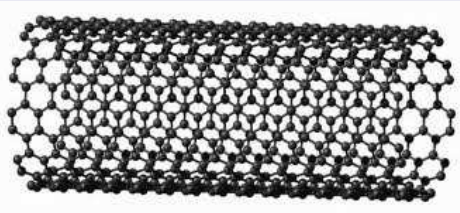
- Introduction to Fullerene molecules and solids.
- Effective tight-binding Hubbard model for the molecules.
- C_{20} molecule and solid: pair-binding energies; magnetic properties; density of states, etc.
- C_{60} molecule and solid: Single-particle excitation spectrum for solid; molecular orientations; comparison with ARPES.
- Some recent experimental developments.
- Summary.

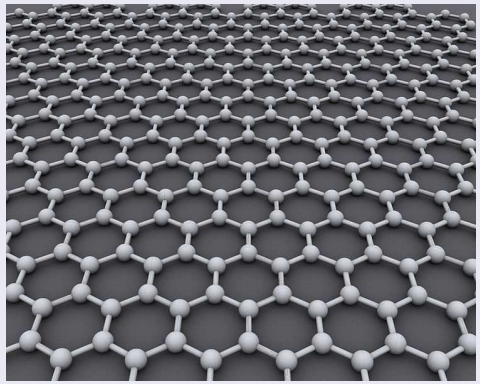
Introduction

Carbon based nano materials

- 0D: cage structures: C_{60}, C_{20}, etc. (Nobel Prize in 1996)
- 1D: rod structures: nanotube.
- 2D: planar sheet structure: graphene (Nobel prize 2010)







Introduction

Intensive researches in the past

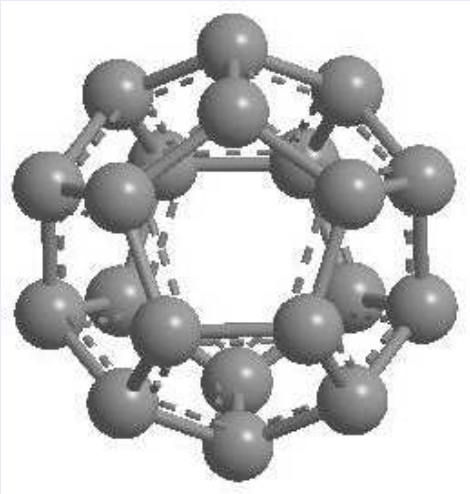
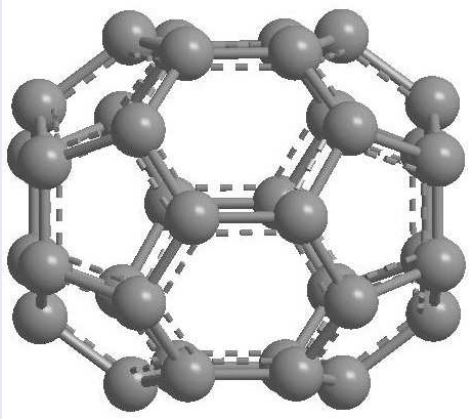
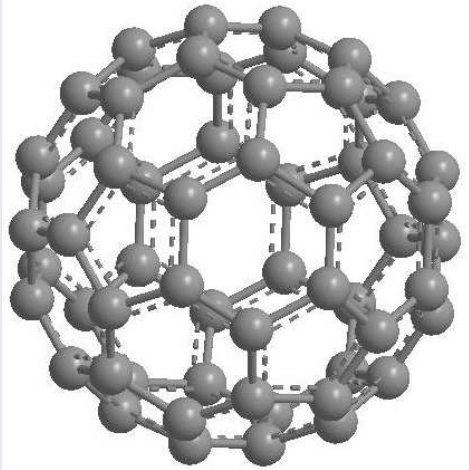
- 21,000 derivatives of fullerene found by the end of 2002;
- 23,000 papers published by the end of 2002;
- Amazing properties: superconducting, ferromagnetic, antiferromagnetic, spin density wave, ...
- Crystal structures seems relatively simpler than cuprates;
- However, after 20 years' research superconducting mechanism still unclear.

Introduction.

What are Fullerene molecules?

Carbon cage molecules with exactly 12 pentagons and varying number of hexagons. A consequence of Euler's polyhedral formula: $V - E + F = 2$. Three examples:

- C_{20}: $V = 20$, $E = 30$, $F = 12$;
- C_{36}: $V = 36$, $E = 54$, $F = 20$;
- C_{60}: $V = 60$, $E = 90$, $F = 32$.

Introduction.

Synthesis and properties.

- C_{60} discovered by Kroto, Curl, and Smalley [Nature, 1985] (Nobel Prize in 1996).
- K_3C_{60} molecular superconductor (Tc=18K) found by Hebard et al [Nature, 1991].
- "Pentagon separation rule", Kroto [Nobel lecture, 1997].
- Solid C_{36} first produced by Zettl group [Nature, 1998].
- Gas phase C_{20} first produced by Prinzbach et al [Nature, 2000].
- Solid C_{20} synthesized by Wang et al [Phys. Lett. A , 2001] and Iqbal et al [Eur. Phys. J. B, 2003].

Outline:

- Introduction to Fullerene molecules and solids.
- Effective tight-binding Hubbard model for the molecules.
- C_{20} molecule and solid: pair-binding energies; magnetic properties; density of states, etc.
- C_{60} molecule and solid: Single-particle excitation spectrum for solid; molecular orientations; comparison with ARPES.
- Some recent experimental developments.
- Summary.

Effective Hamiltonian Approach

Importance of Carbon radial p_r orbitals

Fullerene molecules electronic properties are mainly determined by the electrons from Carbon atom radial p_r orbitals. Eg. for C_{60} molecule, 94% of bonds around Fermi energy are made of p_r orbitals as shown by Satpathy [Chem. Phys. Lett., 1985].

$\rightarrow$ Conjugated π bonds: electron delocalization

$\rightarrow$ **One-band tight-binding** Hamiltonian description can be successful.

Effective Hamiltonian: Hubbard Model

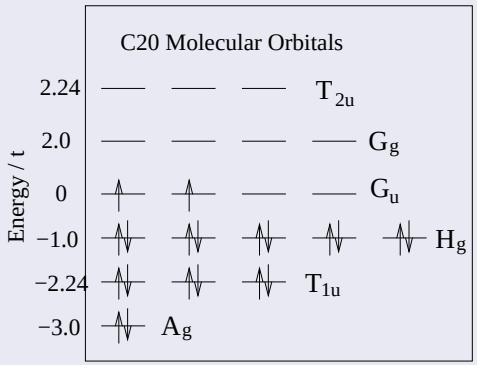
$$H = -\sum_{\langle ij\rangle\sigma} t_{ij}(c^{\dagger}_{i\sigma}c_{j\sigma} + h.c.) + U\sum_{i} n_{i\uparrow}n_{i\downarrow}, \quad (1)$$

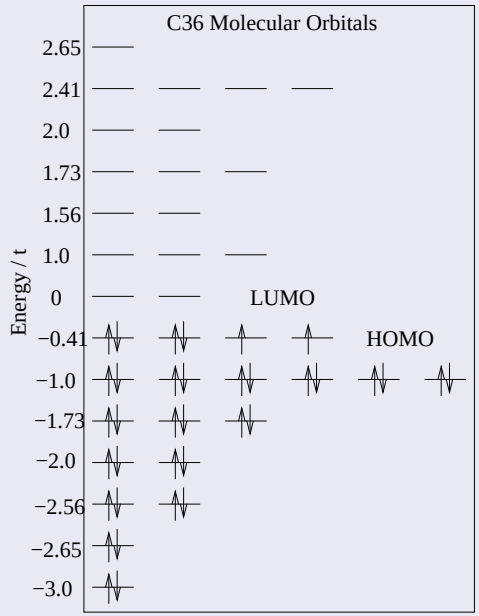
- What are U/t values?
- Solve by quantum Monte Carlo (QMC) and exact diagonalization (ED).

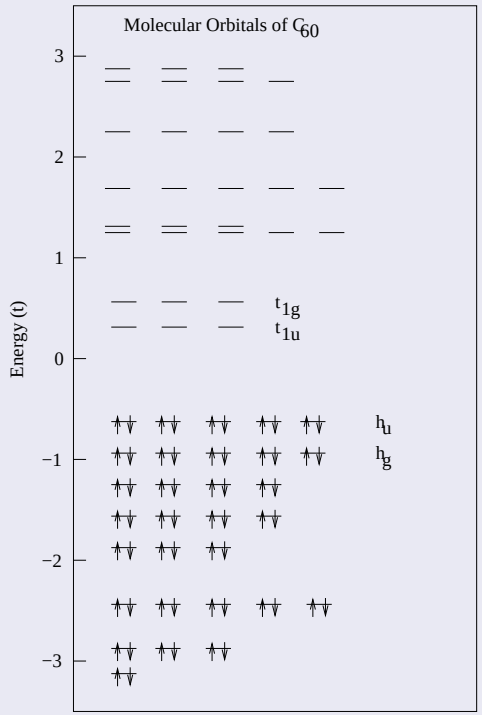
Effective Hamiltonian Approach

Huckel energy level diagrams

For $U = 0$ (non-interacting), we can easily diagonalize Hamiltonian:

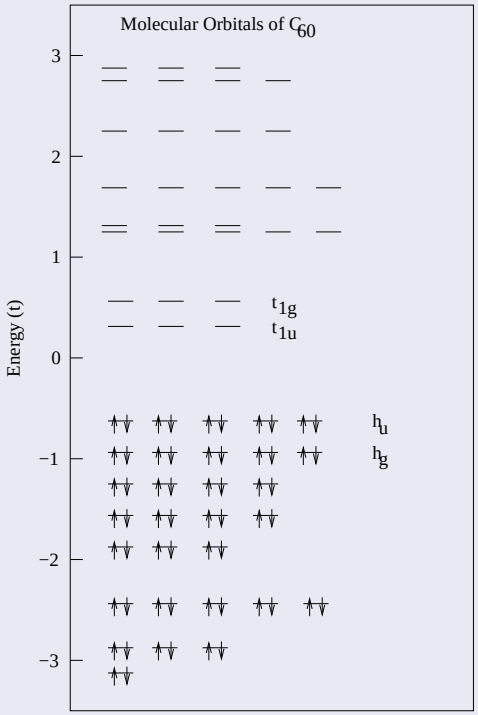






Effective Hamiltonian Approach

Huckel energy level diagrams: electron dopings



- C_{60}^{-}: quasi 1D lattice, phase transition at 50K from 1D conductor to spin density wave ground state; Chauvet et al [Phys. Rev. Lett. 1994], Stephens et al [Nature 1994].
- C_{60}^{2-}: no; not yet realized.
- C_{60}^{3-}: yes; discuss this later.
- C_{60}^{4-}: insulator; Fleming et al [Nature 1991]
- C_{60}^{5-}: metal monolayer; Crommie group [Science 2005, Phys. Rev. Lett. 2007]
- C_{60}^{6-}: insulator; Zhou et al [Nature 1991], Stephens et al [Phys. Rev. B 1992]

Effective Hamiltonian Approach

Parameters Determination

- Hopping t_{ij} can be determined by fitting Huckel energy levels around Fermi energy to those from DFT calculations.
- U can be determined by comparison to some experiments:
  Electron affinity energy
  Wang et al [J. Chem. Phys., 1999] for C_{60}
  Prinzbach et al [Nature, 2000] for C_{20}.

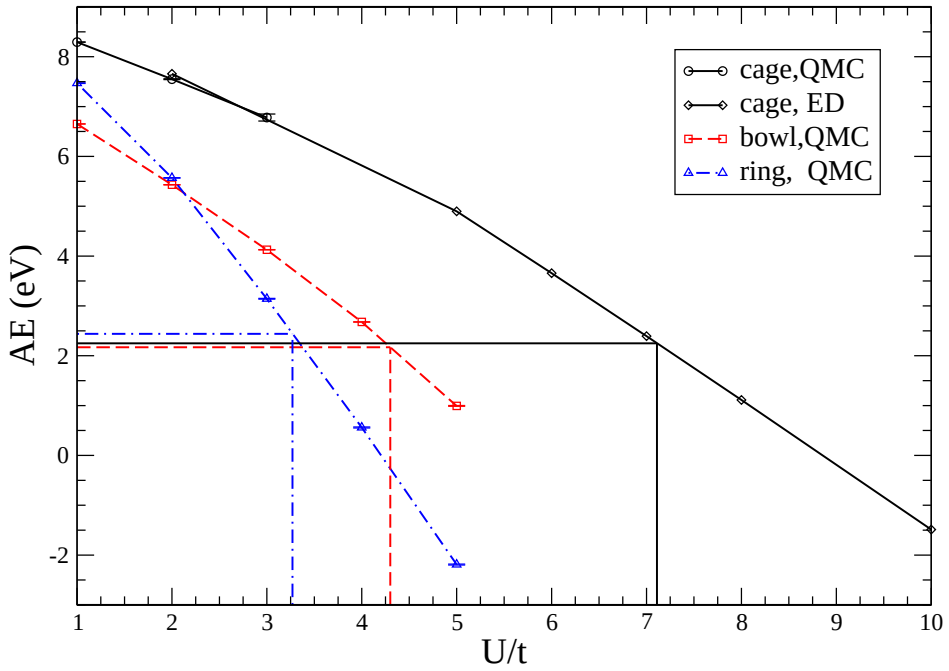
$$\mathrm{AE} = E(C_N) - E(C_N^-). \tag{2}$$

  X-ray scattering
  Chow and Friedman [Phys. Rev. B, 2008]
  Dynamic structure factor: $S(k, \omega)$.

Effective Hamiltonian Approach

Parameters for C_{20} molecule

- By matching energy gaps from DFT and Huckel energy levels, we can determine the hopping $t \sim 1.36$ eV.
- By matching $\mathrm{AE} = E(20) - E(21)$ to experimental value of 2.25 eV, we find $U/t \sim 7.1$. Consistent with U values assumed in some literatures.



Parameters for C_{60} molecule

$t \sim 2.5$ eV

$U/t \sim 4$

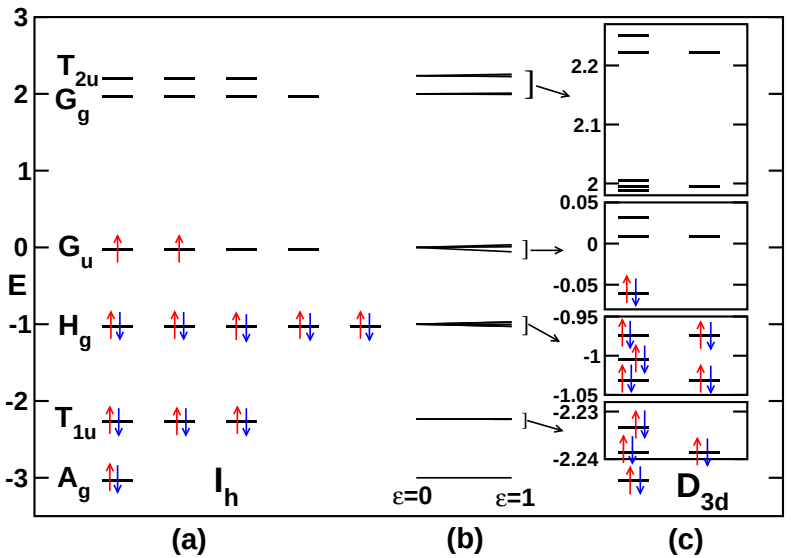
Outline:

- Introduction to Fullerene molecules and solids.
- Effective tight-binding Hubbard model for the molecules.
- C_{20} molecule and solid: pair-binding energies; magnetic properties; density of states, etc.
- C_{60} molecule and solid: Single-particle excitation spectrum for solid; molecular orientations; comparison with ARPES.
- Some recent experimental developments.
- Summary.

Single C_{20} molecule

Magnetic properties

- Magnetic from Huckel energy diagram;
- With ED and QMC:
  - Spin triplet (magnetic) for $U/t < U_c/t \sim 4.10$ (3-fold orbital degeneracy);
  - Spin singlet for $U > U_c$ (non-degenerate); Hund's rule violation;
  - Jahn-Teller is suppressed for $U > U_c$.
- Above for I_h symmetry; similar for D_{3d} symmetry (except at $U = 0$ and $U_c \sim 4.19$).

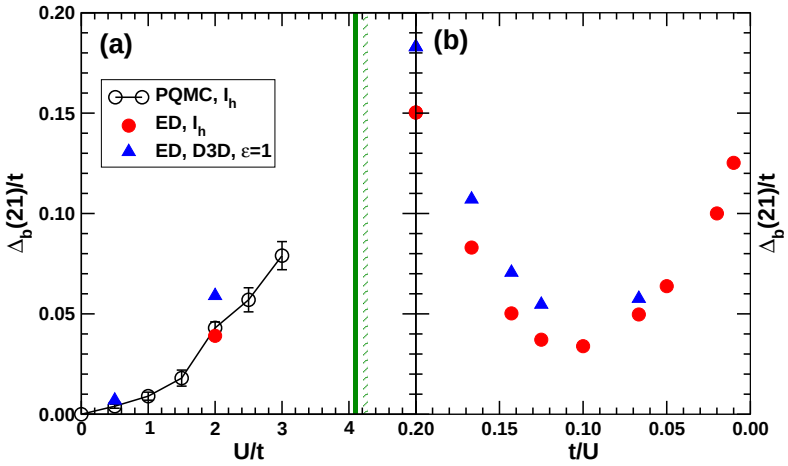


Single C_{20} molecule

Pair-binding energy

$$\Delta_b(N+1) = E(N+2) - 2E(N+1) + E(N). \quad (3)$$

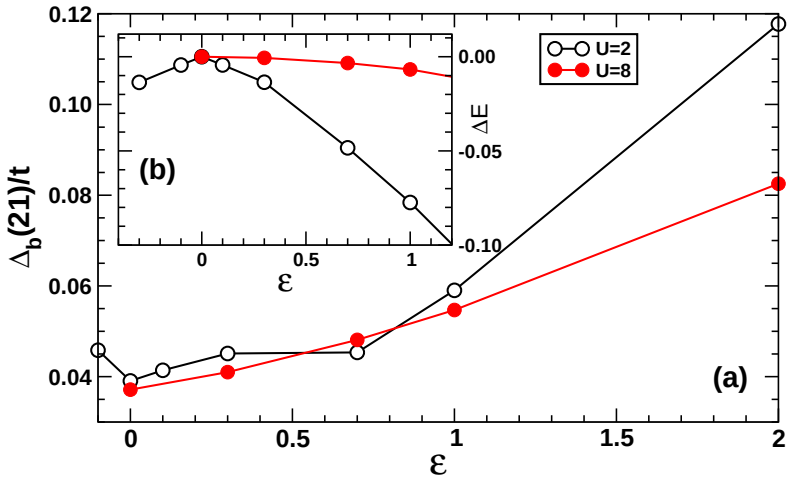
- Importance of mesoscale structure in electronic mechanism of superconductivity, Chakravarty and Kivelson [Science, 1991; Phys. Rev. B, 2001];
- Δ_b always positive $\rightarrow$ absence of pair binding.



Single C_{20} molecule

Jahn-Teller distortion of C_{20} with I_h symmetry

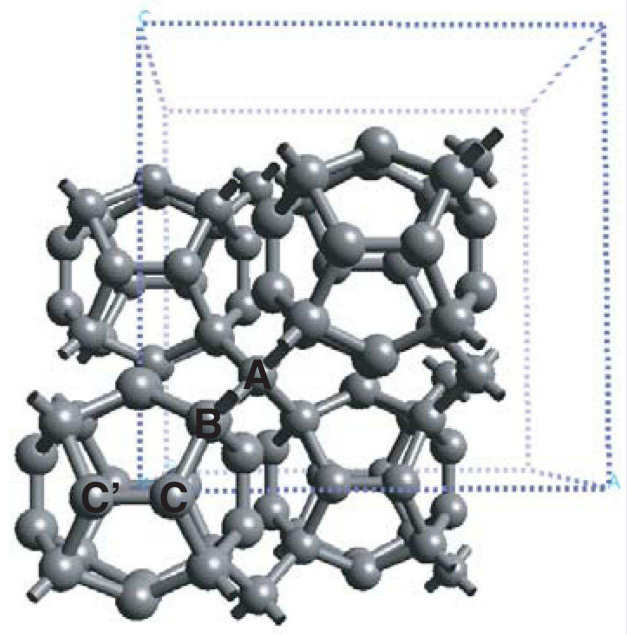
- D_{3d} has 4 bond lengths: $a_{ab} = 1.464$Å, $a_{bc} = 1.469$Å, $a_{cc'} = 1.519$Å, and $a_{cc''} = 1.435$Å, Yamamoto et al [Phys. Rev. Lett., 2005];
- $t_a/t = 1 - \varepsilon(a - \bar{a})/\bar{a}$, where I_h ($\varepsilon = 0$) and D_{3d} ($\varepsilon = 1$);
- Jahn-Teller suppressed for $U > U_c$.



C_{20} solid

Lattice structure

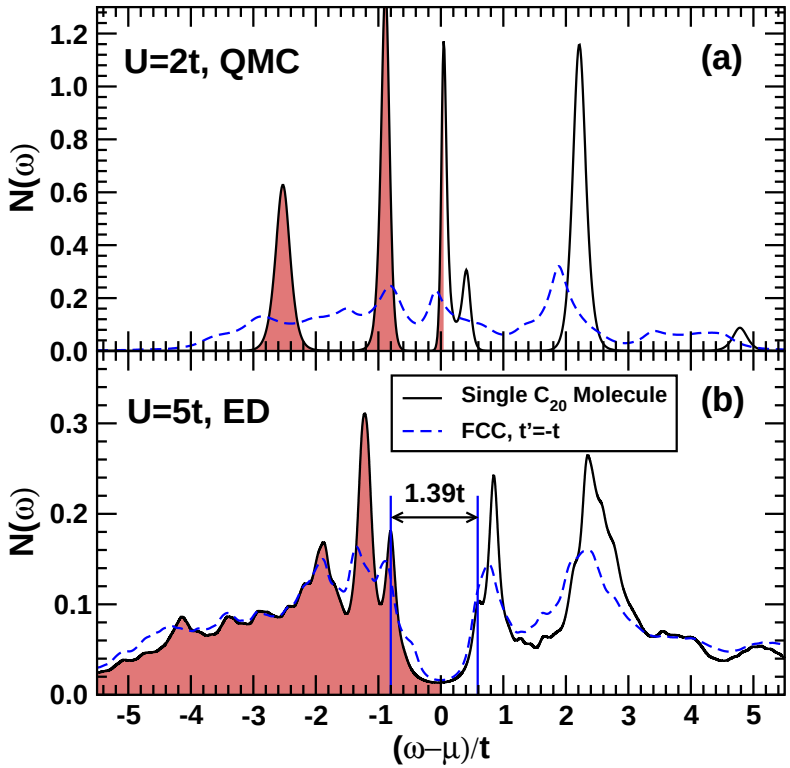
- Solid C_{20} synthesized by Wang et al [Phys. Lett. A, 2001] and Iqbal et al [Eur. Phys. J. B, 2003].
- fcc structure; 1 additional carbon between 4 C_{20} molecules.
- t intra-molecular hopping; $t^{'}$ inter-molecular hopping.
- Cluster perturbation theory, with exact diagonalization (ED) by Sénéchal et al [Phys. Rev. Lett., 2000]; with QMC by Lin et al [HPC06, p.27].



C_{20} solid

Metal-insulator transition

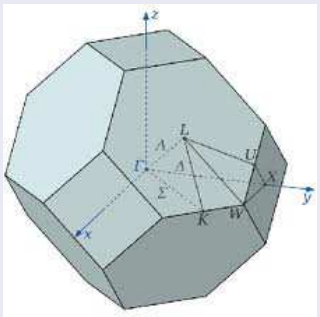
- Magnetic to nonmagnetic transition at $U = U_c$;
- Metal to insulator transition at $U = U_c$, too;
- Appearance of gap in DOS.

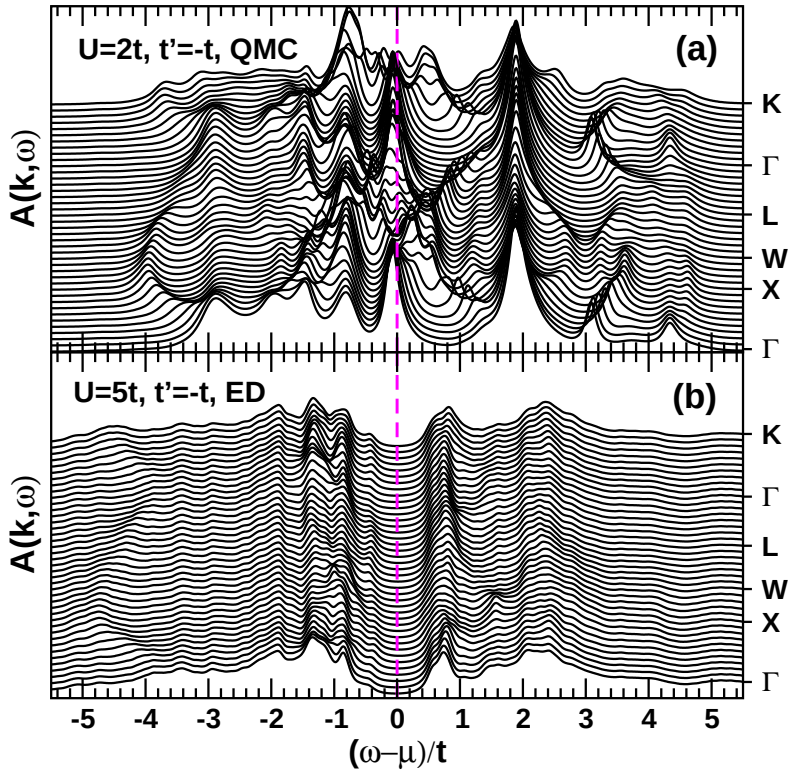


C_{20} solid

Metal-insulator transition

- Spectral dispersions:





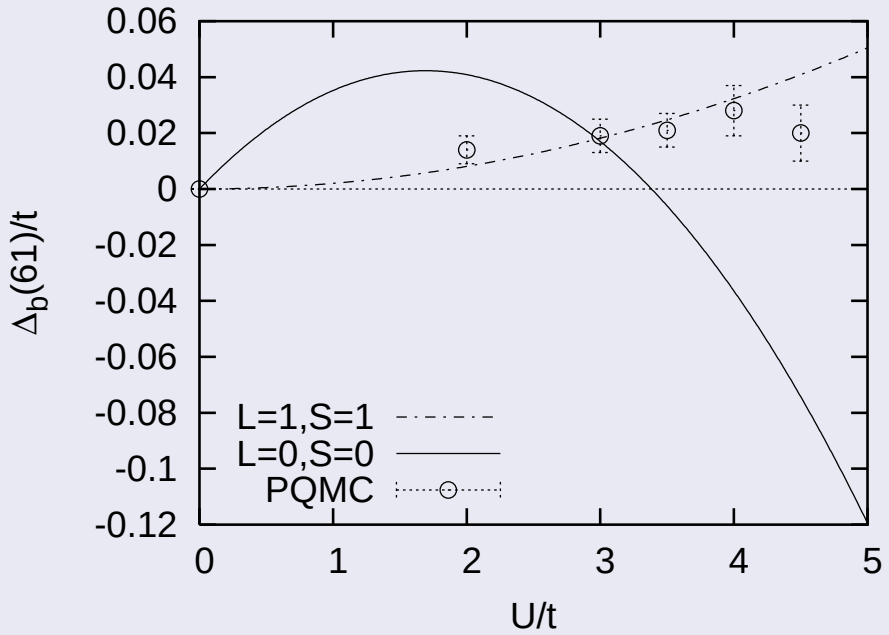
Outline:

- Introduction to Fullerene molecules and solids.
- Effective tight-binding Hubbard model for the molecules.
- C_{20} molecule and solid: pair-binding energies; magnetic properties; density of states, etc.
- C_{60} molecule and solid: Single-particle excitation spectrum for solid; molecular orientations; comparison with ARPES.
- Some recent experimental developments.
- Summary.

Single C_{60} molecule

Pair-binding energy

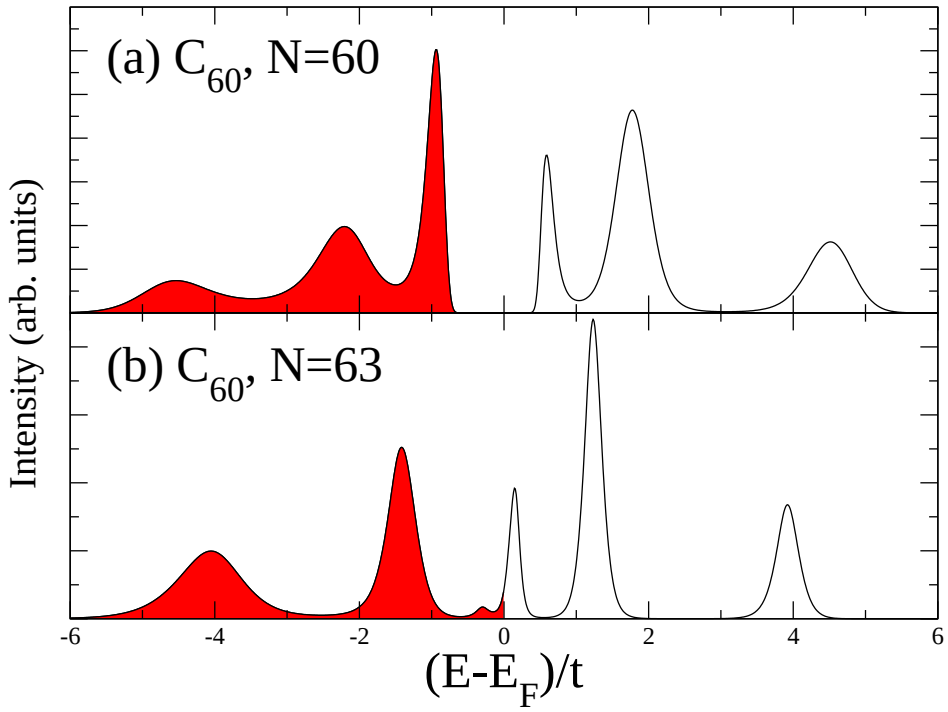
- **Perturbation calculations**
  Chakravarty et al [Science 1992];
  Ground state of C_{60}^{2-} is in spin-singlet channel at $U/t > 3$;
  $\Delta_b < 0$ for $U/t > 3.3$.
- **QMC calculations**
  Ground state of C_{60}^{2-} is in spin triplet channel;
  $\Delta_b > 0$ for $U/t \leq 4.5$



Single C_{60} molecule

Density of states (DOS)

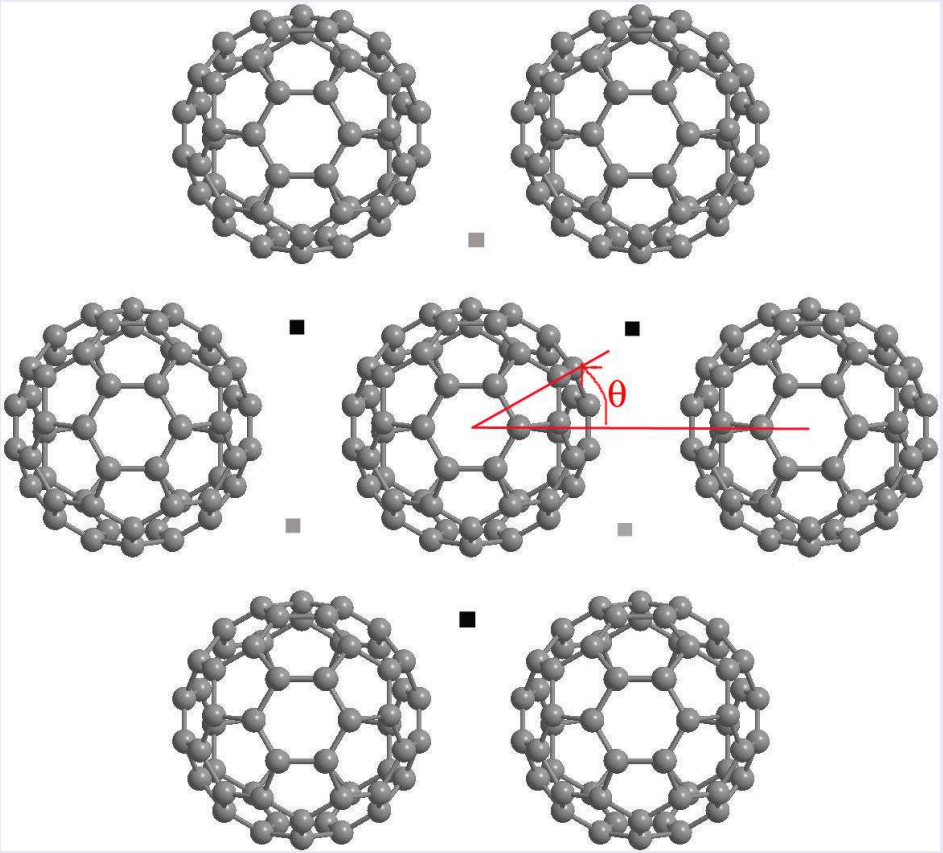
- Neutral C_{60} molecule is insulating;
- Three electron doped C_{60} molecule is metallic.



C_{60} monolayer

Monolayer setup

- 2D hexagonal C_{60} superlattice: Z.X. Shen's group [Science, 2003; Phys. Rev. B, 2005]
- Orientation dependent band dispersion.



C_{60} monolayer

Intermolecular hopping matrix

$$V = -\sum_{\langle Ii,Jj\rangle\sigma} (t^{'}\alpha_{Ii,Jj} + t^{\text{ind}}_{Ii,Jj})(c^{\dagger}_{Ii\sigma}c_{Jj\sigma} + h.c.), \tag{4}$$

where **direct hoppings** between NN molecules are given by

$$\alpha_{Ii,Jj} = [V_{\sigma}(d) - V_{\pi}(d)](\hat{\mathbf{R}}_{Ii}\cdot\hat{\mathbf{d}})(\hat{\mathbf{R}}_{Jj}\cdot\hat{\mathbf{d}}) + V_{\pi}(d)(\hat{\mathbf{R}}_{Ii}\cdot\hat{\mathbf{R}}_{Jj}), \tag{5}$$

Satpathy et al [Phys. Rev. B, 1992], and **indirect hoppings** via K^+ ions are given by

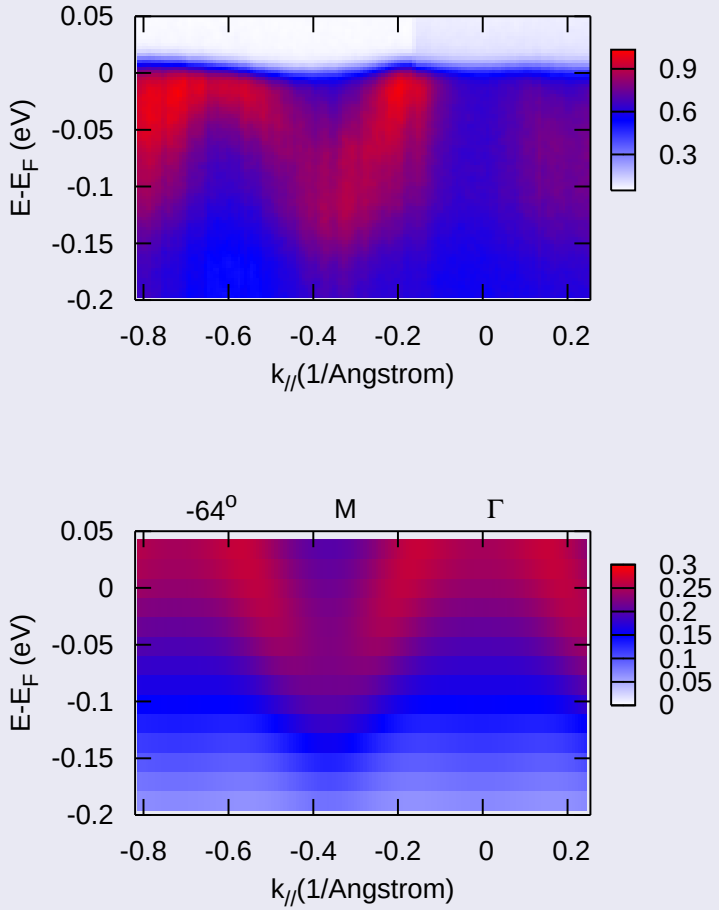
$$t^{\text{ind}}_{Ii,Jj} = \sum_{\gamma} \frac{t_{Ii,\gamma}t_{Jj,\gamma}}{\epsilon_C - \epsilon_K}, \tag{6}$$

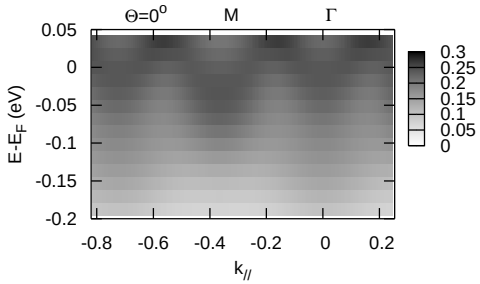
$$t_{Ii,\gamma} = 1.84D\frac{\hbar^2}{md^2}e^{-3(d-R_{\text{min}})}. \tag{7}$$

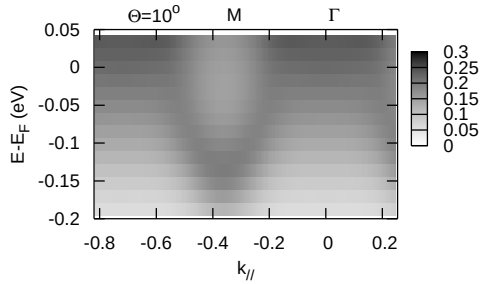
Gunnarsson et al [Phys. Rev. B, 1998].

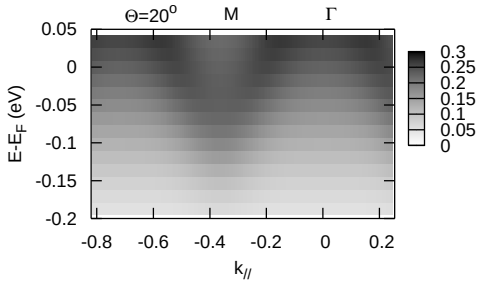
Band dispersion matching

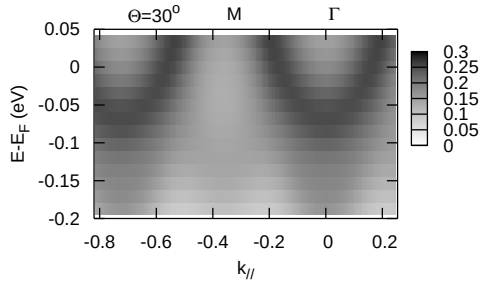
- Intermolecular hopping $t^{'}$ and molecular orientation angle θ are variational parameters.
- Cluster perturbation theory.
- Best fit gives $t' = -0.3t$, $\theta = 64^{\circ}$.

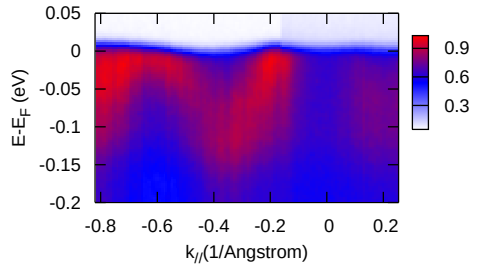


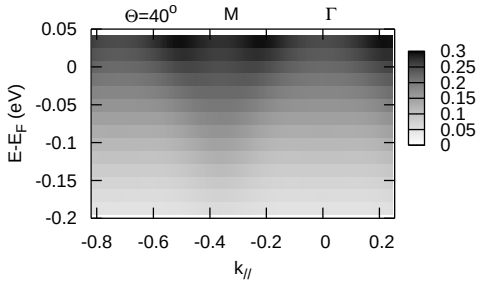

Θ=0° M Γ
E-E_F (eV)
k_//

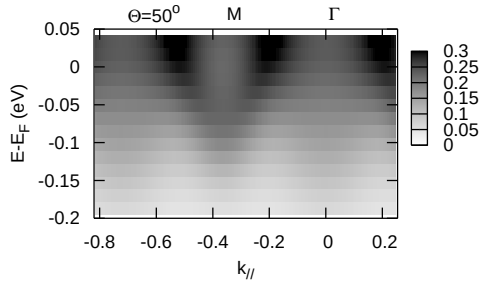

Θ=10° M Γ
E-E_F (eV)
k_//

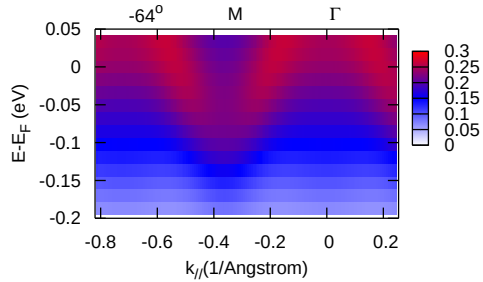

Θ=20° M Γ
E-E_F (eV)
k_//

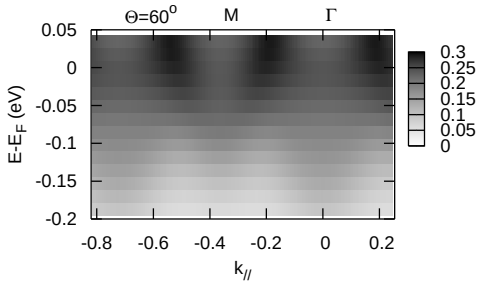

Θ=30° M Γ
E-E_F (eV)
k_//

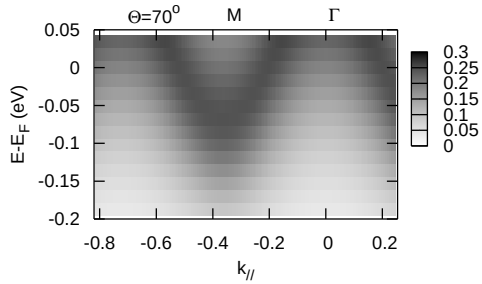

E-E_F (eV)
k_//(1/Angstrom)


Θ=40° M Γ
E-E_F (eV)
k_//


Θ=50° M Γ
E-E_F (eV)
k_//

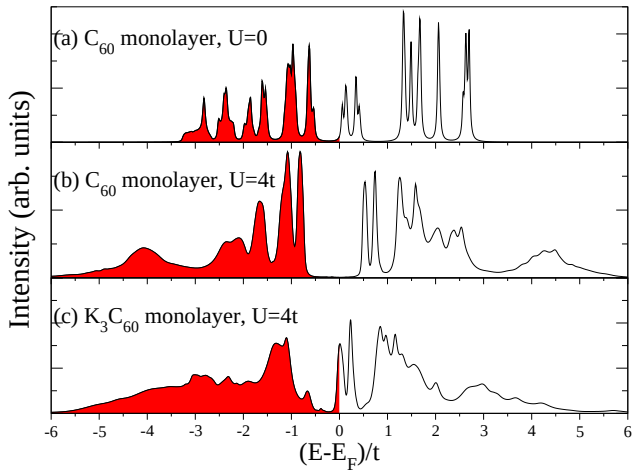

-64° M Γ
E-E_F (eV)
k_//(1/Angstrom)


Θ=60° M Γ
E-E_F (eV)
k_//

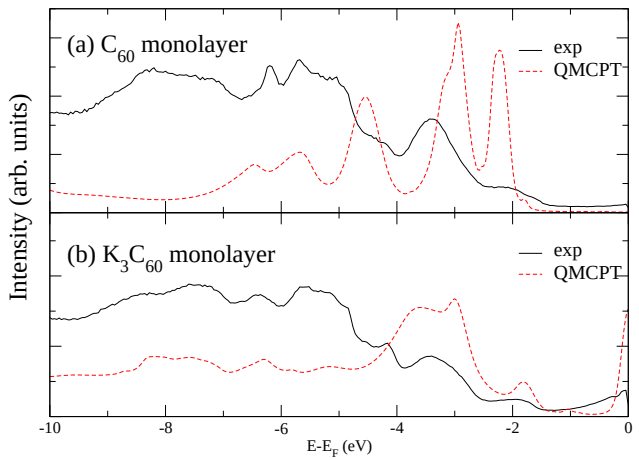

Θ=70° M Γ
E-E_F (eV)
k_//

Monolayer DOS

- Evolution of DOS with U and electron doping.



- Comparison with experimental PES.



Recent developments in experiments

Future projects

- K_4C_{60} monolayer, Crommie group [Science, 2005]; K_xC_{60} monolayers $3 \leq x \leq 5$, Crommie group [Phys. Rev. Lett., 2007];
  - Why is K_4C_{60} insulating? Jahn-Teller?
  - Role of orientational ordering?
- Cs_3C_{60} superconductor, Rosseinsky group [Science, 2009]
  - $T_c = 38$K; disorder-free
  - parent state: AF insulator; pressure-inudced SC
  - unconventional superconductor
- Single molecule transistors: Winkelmann et al [Nature Physics 2009], Yu et al [Nano Lett. 2004], etc.
  - Can we calculate transport property?
- Carbon is light. Intramolecular vibration frequency up to 0.2 eV; $E_F = 0.3$ eV.
  - Can we include Carbon dynamics in QMC?

Summary

- Effective tight-binding Hubbard model can capture most of the physics of Fullerene molecules;
- U/t increases with molecular curvature: C_{20} is the most correlated molecule;
- C_{20} molecule/solid undergoes magnetic metal to nonmagnetic insulator transition at $U_c/t \sim 4.1$;
- Neutral C_{20} is an insulator;
- Jahn-Teller distortion is suppressed in C_{20} molecule since $U/t \sim 7.1$;
- Neutral C_{60} is an insulator; K_3C_{60} a metal;
- Not able to find favorable pair binding from Δ_b calculations.
- Able to compare with ARPES for molecular orientation dependent band dispersion.