Collective Excitations and Stability of the Excitonic Phase in the Extended Falicov–Kimball model

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• Falicov–Kimball model and the excitonic state
  – Excitonic state as a mean field solution
  – Excitonic insulator in a conventional semi-metal

• Extending the Falicov–Kimball model
  – Degeneracy of the excitonic state
  – Stabilising the excitonic state by the perturbation

• Collective excitations in the Falicov–Kimball model
  – Nature of the instability of the excitonic state at weak perturbation
  – Beyond the leading order: stabilising the spectrum

• Implications for the critical temperature.
  – Phase-disordered state at finite temperature?

• Electronic ferroelectricity: how and when.
Spinless Falicov–Kimball Model and the Excitonic State

- Localised and itinerant fermions, on-site interaction $U$, half-filling, $T = 0$.

$$\mathcal{H} = -\frac{t}{2} \sum_{\langle ij \rangle} (c_i^\dagger c_j + c_j^\dagger c_i) + E_d \sum_i d_i^\dagger d_i + U \sum_i c_i^\dagger d_i^\dagger d_i c_i,$$

- Introduced in 1969 to describe mixed-valence phenomena and metal-insulator transitions.
- Uniform Hartree–Fock mean field solution (A. N. Kocharyan, D. I. Khomskii, 1976; H. J. Leder, 1978):
  - Mixed-valence regime: two partially filled bands.
  - Interaction-induced spontaneous hybridisation $\Delta = \langle c_i^\dagger d_i \rangle$ – excitonic phase.
  - Filled and empty quasiparticle bands:
    $$\epsilon_k^{(1,2)} = \frac{1}{2} \left\{ (E_d + U n_c) + (\epsilon_k^c + U n_d) \mp \sqrt{[(E_d + U n_c) - (\epsilon_k^c + U n_d)]^2 + 4U|\Delta|^2} \right\}$$
    where
    $$n_c = 1 - n_d, \quad \epsilon_k^c = -\cos k_x - \cos k_y(-\cos k_z), \quad t = 1.$$
  - Gap equation: at $T = 0$
    Narrow-band occupancy:
    $$\Delta = \frac{1}{N} \sum_k \Delta_k^c, \quad \Delta_k^c \equiv \langle c_k^\dagger d_k \rangle = \frac{U \Delta}{\sqrt{\xi_k^2 + 4U^2|\Delta|^2}}; \quad n_d = \frac{1}{N} \sum_k n_k^d, \quad n_k^d \equiv \langle d_k^\dagger d_k \rangle = \frac{1}{2} - \frac{\xi_k^c}{2\sqrt{\xi_k^2 + 4U^2|\Delta|^2}}.$$ 
    Notation: $\xi_k^c = (E_d + Un_c) - (\epsilon_k^c + Un_d)$, and $E_{rd} = E_d + Un_c - Un_d$. 
Electronic Ferroelectricity

- Ferroelectricity which does not involve the lattice. \( \text{(T. Portengen et al., 1996)} \)
- Requires opposite-parity bands and \( \text{Re} \Delta \neq 0 \): 

\[
\begin{align*}
\text{Electronic Ferroelectricity} \\
\text{Single Atom} \\
\begin{aligned}
\alpha e^{i\varphi} + & \text{ hybridized orbital} \\
& \text{s-orbital} \\
& \text{p-orbital}
\end{aligned}
\end{align*}
\]

\( \varphi = 0 \) 
\( \varphi = \pi \) 

(from a 2006 talk by J. E. Gubernatis)

Experimental Search for Excitonic Insulator or Electronic Ferroelectric

- No generally recognised excitonic insulators at present.
- Large number of candidates: \( \text{SmB}_6, \text{SmS}, \text{TmSe}, \text{TiSe}_2, \text{TmSe}_{0.45}\text{Te}_{0.55}, \text{LuFe}_2\text{O}_4, \ldots \)
  Typically, a narrow band involved. Review: J. Neuenschwander and P. Wachter (1990)
- Suggested relevance for CMR manganates and \( \text{URu}_2\text{Si}_2 \).
- Theory models of specific compounds: T. A. Kaplan, S. D. Mahanti, 1970s; K. A. Kikoin (1993); S. Curnoe, K. A. Kikoin (2000),...
Degeneracy of Excitonic Insulator in the Falicov – Kimball Model

\[ H_0 = -\frac{t}{2} \sum_{\langle ij \rangle} (c_i^\dagger c_j + c_j^\dagger c_i) + E_d \sum_i d_i^\dagger d_i + U \sum_i c_i^\dagger d_i^\dagger d_i c_i, \]

- Local continuous degeneracy of the excitonic state: \( d_i \to d_i \exp(i \varphi_i) \), phase of \( \langle c_i^\dagger d_i \rangle \).

⇒ Instability of the excitonic state (Elitzur’s theorem) (V. Subrahmanyam and M. Barma, 1988)

- An infinitesimal perturbation of \( H_0 \) restores excitonic insulator at \( T = 0 \) ???
  J. K. Freericks and V. Zlatić, (2003)

Extending the Falicov – Kimball Model

- Different kinds of perturbations break the degeneracy:
  - hopping \( t' \ll t \) in the narrow zone.
  - hybridisation: \( V_0 \) on-site, \( V_1 \) nearest-neighbour (same parity bands), \( V_2 \) (opposite parity).

\[ \delta H = -\frac{t'}{2} \sum_{\langle ij \rangle} d_i^\dagger d_j - V_0 \sum_i c_i^\dagger d_i - \frac{V_1}{2} \sum_{\langle ij \rangle} (c_i^\dagger d_j + c_j^\dagger d_i) - \frac{V_2}{2} \sum_{\langle ij \rangle} \left\{ (\vec{R}_i - \vec{R}_j) \cdot \vec{\Xi} \right\} (c_i^\dagger d_j - c_j^\dagger d_i) + \text{H.c.}, \]

( \( \vec{R}_i \) is the radius-vector of a site \( i \), \( a \vec{\Xi} = \{1, 1(1), 1\} \), lattice period \( a \to 1 \)).

- Extended FKM - no longer exactly soluble.
  - literature: mean field, numerical (C. Czycholl, P. Farkašovský, C. D. Batista, P. M. R. Brydon...)
  - mean field solution corresponding to the excitonic phase is still present: \( \Delta = \langle c_i^\dagger d_i \rangle \neq 0 \).
• Example: small but finite $t'$ stabilises the excitonic solution:

\[ -t' \]

\[ 2E_d \]

$\beta$ - uniform excitonic phase, $\gamma$, $\beta'$ – charge ordered, $\alpha, \epsilon$ - no mixed valence

• **Stabilisation** of the excitonic phase on increasing $|t'|$ via **2nd order phase transition**.

$\Rightarrow$ **contradicts** suggested **more exotic behaviour**

(the latter expected if the instability of the excitonic phase for pure FKM is due to **local degeneracy**.)
Collective Excitations in the Excitonic State of the Falicov–Kimball Model

• Hamiltonian of the pure FKM:

$$H_0 = -\frac{t}{2} \sum_{\langle ij \rangle} (c_i^\dagger c_j + c_j^\dagger c_i) + E_d \sum_i d_i^\dagger d_i + U \sum_i c_i^\dagger d_i^\dagger d_i c_i,$$

• Weak perturbation, $t'$, $V_i$ small:

$$\delta H = \sum_\vec{k} \left\{ t' \epsilon_\vec{k} d_\vec{k}^\dagger d_\vec{k} + V_\vec{k} c_\vec{k}^\dagger d_\vec{k} + V_\vec{k}^* d_\vec{k}^\dagger c_\vec{k} \right\}, \quad V_\vec{k} = \begin{cases} V_0 + V_1 \epsilon_\vec{k}, & \text{same parity bands,} \\ iV_2 \lambda_\vec{k}, & \text{opposite parity,} \end{cases}$$

where $\epsilon_\vec{k} = -\sum_{\alpha=1}^d \cos k_\alpha$ and $\lambda_\vec{k} = -\sum_{\alpha=1}^d \sin k_\alpha$.

• Generic particle-hole excitation in the excitonic phase:

$$X_\vec{q} = \frac{1}{\sqrt{N}} \sum_\vec{k} \left\{ F_+ (\vec{k}, \vec{q}) c_\vec{k}^\dagger d_{\vec{k}+\vec{q}} + F_- (\vec{k}, \vec{q}) d_\vec{k}^\dagger c_{\vec{k}+\vec{q}} + F_c (\vec{k}, \vec{q}) c_\vec{k}^\dagger c_{\vec{k}+\vec{q}} + F_d (\vec{k}, \vec{q}) d_\vec{k}^\dagger d_{\vec{k}+\vec{q}} \right\}.$$

• Eigenstate in the mean field sense:

$$[X_\vec{q}, H + \delta H]^{\text{eff}} = \omega_\vec{q} X_\vec{q}.$$

(Hartree-Fock decoupling in the $[\ldots]$)

• Pure FKM ($t' = V_i = 0$) - degenerate, hence solution, $X_\vec{q}^{(0)} = \frac{1}{\sqrt{N}} \sum_\vec{k} d_\vec{k}^\dagger d_{\vec{k}+\vec{q}}$, with $\omega_\vec{q} \equiv 0$.

• In general, decoupling and collecting terms in the secular equation.
Spectrum in the Pure FKM (no perturbation)

- A branch that vanishes identically throughout BZ:
  \[ \omega \vec{q} = 0 \text{ for any } \vec{q} \]

- A consequence of local continuous degeneracy
  cf. Kagomé antiferromagnet

Leading Order in Perturbation: the Instability

- Weak perturbation → Keep leading order in \( t', V_{0,1} \) (linear), or \( V_2 \) (quadratic), linearise in \( \omega^2 \),

\[
(\omega \vec{q}/U \Delta)^2 \cdot D_{\omega}(\vec{q}) + M_{11}(\vec{q}) \cdot D_0(\vec{q}) = 0.
\]

- \( \omega^2 \vec{q} \) always changes sign in the BZ ⇒ instability! \( \omega^2 \vec{q} < 0 \) for some \( \vec{q} \).

- The instability is conventional, due to the presence of a lower-energy state.
  – Not due to the local continuous degeneracy of the pure FKM.
  – Not visible in the spectrum unless small perturbation included. (this, due to degeneracy)

Beyond the Linear Order: Stabilising the Spectrum

- Numerically, a very small perturbation stabilises the excitonic phase. Can we see this in our spectrum?

- Technically, leading order instability is due \( D_0(\vec{q}) \) changing sign in the BZ.

- \( D_0(\vec{q}) \) is not large numerically.

- The next-order correction \( D_0(\vec{q}) \Rightarrow D_1(\vec{q}) + D_0(\vec{q}) \)

- Stabilisation if \( D_1(\vec{q}) + D_0(\vec{q}) < 0 \) for all \( \vec{q} \).
Spectrum of Excitonic Phase a 2D EFKM, $U = 2$ and $E_d = 0.4$.

$$\mathcal{H} = -\frac{t}{2} \sum_{\langle ij \rangle} (c_i^\dagger c_j + c_j^\dagger c_i) + E_d \sum_i d_i^\dagger d_i + U \sum_i c_i^\dagger d_i^\dagger d_i c_i,$$

- Stabilised by the perturbation:

$$\delta \mathcal{H} = -\frac{t'}{2} \sum_{\langle ij \rangle} d_i^\dagger d_j - V_0 \sum_i c_i^\dagger d_i - \frac{V_1}{2} \sum_i (c_i^\dagger d_j + c_j^\dagger d_i) - \frac{V_2}{2} \sum_{\langle ij \rangle} \{ (\vec{R}_i - \vec{R}_j) \cdot \vec{\Xi} \} (c_i^\dagger d_j - c_j^\dagger d_i) + \text{H.c.},$$

- **Solid lines**: effect of $t'$
  - Bottom to top: $t' = -0.04, -0.0565, -0.07$
- **Dashed lines**: effect of $V_0$
  - Bottom to top: $V_0 = -0.06, -0.074, -0.09$
- **Dotted lines**: effect of $V_2$
  - Bottom to top: $V_2 = 0.115, 0.249, 0.35$

- In all cases, $\omega_{\vec{q}}$ within the quasiparticle gap

**Surviving Degeneracies of the Excitonic Phase**

- **Effect of $t' < 0$:** Goldstone mode at $\vec{q} = (0, 0)$  
  $$d_i \rightarrow d_i \exp (i \varphi) \text{ globally}$$

- **Effect of $V_2 \neq 0$:** Goldstone mode at $\vec{q} = (\pi, \pi)$  
  $$d_i \rightarrow d_i \exp (\pm i \varphi) \text{ in a checkerboard pattern, globally}$$
Phase Diagram of the Excitonic Insulating State in EFKM

- Critical values of perturbations in a 2D EFKM at $T = 0$ for different $U$:
  - Solid lines: $t'_{cr}(E_d)$
  - Dashed lines: $V_{0,cr}(E_d)$
  - Dashed-dotted lines: $V_{1,cr}(E_d)$
  - Dotted lines: $V_{2,cr}(E_d)$

- $U = 0.5$ – weak coupling regime
  - $U = 4$ – strong coupling

- Expected critical temperature for excitonic insulator in EFKM:
  \[ T_C \propto \sqrt{|t'|(|t'| - |t'_{cr}|)} , \sqrt{V_2\sqrt{V_2^2 - V_{2,cr}^2}}, \sqrt{|V_0|(|V_0| - V_{0,cr})}, \text{or} \sqrt{|V_1|(|V_1| - V_{1,cr})} \] (roughly)

- This is much lower than critical temperature $T_\Delta$ from the gap equation:
  \[ T_\Delta \sim k_B\Delta , \quad \frac{1}{N} \sum_k \frac{U}{\sqrt{\xi_k^2 + 4U^2|\Delta|^2}} = 1 \]

- What happens at $T_C < T < T_\Delta$? V. A. Apinian & T. K. Kopec, 2013:
  \[ \langle c_i^\dagger d_i \rangle = \Delta_i \exp(i\phi_i) \]
  - $T < T_C$ – both $\Delta_i$ and $\phi_i$ ordered, excitonic insulator.
  - $T_C < T < T_\Delta$ – only $\Delta_i$ ordered, $\phi_i$ disordered, novel phase.
  - $T > T_\Delta$ – all $\Delta_i \equiv 0$, conventional semiconductor or semimetal.
Conditions for Electronic Ferroelectricity at $T = 0$

**Electronic Ferroelectricity**

*Single Atom*

\[
\begin{align*}
\mathcal{H} &= \frac{-t}{2} \sum_{\langle ij \rangle} \left( c_i^\dagger c_j + c_j^\dagger c_i \right) + E_d \sum_i d_i^\dagger d_i + U \sum_i c_i^\dagger d_i^\dagger d_i c_i, \\
\text{Perturbation terms allowed for opposite-parity bands:} \\
\delta \mathcal{H} &= \frac{-t'}{2} \sum_{\langle ij \rangle} d_i^\dagger d_j - \frac{V_2}{2} \sum_{\langle ij \rangle} \left\{ (\vec{R}_i - \vec{R}_j) \cdot \vec{\Xi} \right\} (c_i^\dagger d_j - c_j^\dagger d_i) + \text{H.c.}, \\
\text{Polarisation density:} \\
\vec{P} &= 2\mu \Re \left( \frac{1}{N} \sum_k \langle c_k^\dagger d_k \rangle \right)
\end{align*}
\]

- $\mu$ – interband element of the dipole moment operator, direction determined by the orbital structure

(from a 2006 talk by J. E. Gubernatis)
• Including the electrostatic dipole-dipole interaction:

\[ E_{tot} = H + \delta H - \int_{\text{sample}} \left( \vec{E} \cdot \vec{P} + \frac{1}{2} \vec{E}_{\text{int}} \cdot \vec{P} \right) dV \]

\( \vec{E} \) – external, \( \vec{E}_{\text{int}} \) – created by \( \vec{P}(r) \)

• \( \vec{E} = 0 \), no free charges, hence

\[ \int \vec{E}_{\text{int}} \cdot \vec{D} dV = 0 \Rightarrow \frac{1}{2} \int_{\text{sample}} \vec{E}_{\text{int}} \cdot \vec{P} dV = \frac{1}{8\pi} \int_{\text{entire space}} E_{\text{int}}^2 dV \]

– positive quantity, \( \propto P^2 \) (usual cause of domain formation)

• \(-t' > |t'_c|\) and \( V_2 = 0 \) – micro degeneracy (global) with respect to the phase of \( \langle c_i^\dagger d_i \rangle \)

\( H + \delta H \) have same value for \( \vec{P} = 0 \) and \( \vec{P} \neq 0 \) states

• \( \vec{P} = 0 \) at \( \vec{E} = 0 \), no spontaneous polarisation

• \( \vec{P}(E) \) linear, \( E_{\text{int}} = -E \) – divergent dielectric constant

• \( \vec{P}(E) \) saturates for \( |\vec{E} \cdot \vec{p}/\mu| > 8\pi|\mu|\langle c_i^\dagger d_i \rangle|/3 \) (spherical sample).

• \(|V_2| > V_{2,cr}\) and \(-t' = 0\) – similar behaviour, \( \vec{P} = 0 \) at \( E = 0 \).

(degeneracy associated with Goldstone at \( \vec{q} = (\pi, \pi) \))

• \( V_2 \neq 0, t' < 0 \) – no degeneracy; excitonic insulator stable

\( \Rightarrow \) spontaneous polarisation.

• when either \( t' \) or \( V_2 \) too small, \( \vec{P} \) destroyed by dipole-dipole interaction.
Conclusions

• An insight into the instability of the excitonic phase in the pure FKM.
  – A lower-energy ground state of the pure FKM (not the fluctuations in the degenerate excitonic phase).
  – On an increase of the perturbation, stabilising the excitonic state via the 2nd order phase transition.

• In the literature, $T_C$ of excitonic insulator (in the EFKM or otherwise) is calculated from the gap equation:
  – Transition due to thermal excitations of the electron-hole continuum.
  – Effect of collective excitations on $T_C$ not considered.

• We calculated the low-lying excitation energy in the excitonic state of the extended Falicov–Kimball model.
  – New low energy scale, related to $T_C$ of the excitonic insulator.
  – When the pure FKM limit is approached (narrow band), $T_C$ is strongly suppressed.
  – Expected: 2nd order transition mediated by excitations at $T_C$.
  – Novel phase-disordered state above $T_C$?

• The quest for electronic ferroelectricity:
  – Both narrow-band hopping and hybridisation required for a robust spontaneous polarisation.

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Excitonic Insulator in a Conventional Semimetal (Semiconductor)

L. V. Keldysh and Yu. V. Kopaev (1964); the following is after W. Kohn (1967)

- Valence and conduction bands of identical shape, nested Fermi surface:
  \[ \varepsilon_a(\vec{k}) = -\frac{G}{2} - \frac{k^2}{2m_a}, \quad \varepsilon_b(\vec{k}) = \frac{G}{2} + \frac{(\vec{k} - \vec{k}_0)^2}{2m_b} \]

- Interaction \( V(\vec{q}) \equiv V_0 \), gap function \( \Delta = \left( \frac{V_0}{N} \right) \Sigma_{\vec{k}} \langle a_{\vec{k}}^\dagger b_{\vec{k}} \rangle \), gap equation for \( T = 0 \):
  \[ 1 = \frac{V_0}{2N} \sum_{\vec{k}} \left\{ \frac{1}{4} \left[ \varepsilon_a(\vec{k}) - \varepsilon_b(\vec{k}) \right]^2 + \Delta^2 \right\}^{1/2} \quad \Rightarrow \quad \Delta = \Delta(G) \quad \Rightarrow \quad T_c(G) \sim \Delta(G)/k_B \]

(assuming \( \vec{k}_0 = 0 \); on the semiconducting side, \( V \) is \( \vec{q} \)-dependent \( \rightarrow \) quantitative change)

- Hybridised bands: “The Snail:”

slave boson MF (dots Hartree–Fock):

\[ \text{(a) } G > 0 \quad \text{(b) } G = 0 \quad \text{(c) } G < 0 \]

Critical temperature, \( T_c(G) \)

\[ \uparrow \text{ B. Zenker et al. (2010a)} \]