Electronic Squeezing by Optically Pumped Phonons: Transient Superconductivity in $K_3C_{60}$

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Background: Mean-Field Theory of Simple Superconductivity

• If the effective electron-electron interaction is attractive (negative), then it is easy to show that starting from the non-interacting Fermi sea, 2 electrons with energies above the Fermi energy will form a bound state with a wave function \( \psi(\vec{r}_1 - \vec{r}_2)e^{i\mathbf{q}(\vec{r}_1 + \vec{r}_2)/2} \). At q=0 this is just 
\[
\sum_k \psi(k)e^{ik\vec{r}_1}e^{-ik\vec{r}_2},
\]

namely a pairing (if made into singlet) of \((k\uparrow,-k\downarrow)\) plane wave functions together.

• For real metals, the effective e-e interaction is indeed attractive for states within shell \( \sim \hbar\omega_p \) around the Fermi level (surface) due to over-screening of ions via phonons. Important to note-electron-phonon interaction taken to be linear in phonon coordinate.

\[
\sum_{\mathbf{r}} \psi^\dagger(k)\psi(-k)e^{i\mathbf{q}(\mathbf{r} - \mathbf{r})}.
\]

• Together, motivates guess for the ground state wave function of the form 
\[
|\Psi_g\rangle \propto \prod (u_k + v_k c_k^\dagger c_{-k\downarrow}^\dagger) |0\rangle.
\]

Can then show by minimization that this variational guess gives lower energy than non-interacting Slater determinant.
Consequences:

• Find within variational calculation that energy difference between normal metal and superconducting state is \( E_N - E_S = \frac{1}{2}VN(0)\Delta_0^2 \), where \( \Delta_0 \) is the energy gap, \( \Delta_0 \approx 2\omega_p \frac{1}{N(0)V} \). \( V \) strength of e-e attraction, \( \omega_p \) is characteristic phonon frequency.

• Same calculations can easily be performed at finite T. Find a transition at to superconducting state \( k_BT_c \sim \Delta_0 \). Gap is T-dependent-disappears at \( T_c \).

• Meaning of gap-minimum energy to create single particle excitation from superconducting ground state is \( 2\Delta_0 \): \( \Delta_0 \) for removing it from one state and \( \Delta_0 \) for placing it in another. Finite energy to break up pairs-protected from scattering.
Background: Primer on Optical Conductivity

Consider simple model for motion of electrons in a metal:

$$m \frac{d\vec{v}(t)}{dt} = e\vec{E}(t) - \frac{m\vec{v}(t)}{\tau}, \quad \vec{E}(t) = \vec{E}e^{i\omega t}.$$ 

Then

$$\vec{v}(t) = \frac{\tau e/m}{1 + i\omega\tau} \vec{E}(t), \quad \vec{j} = ne\vec{v} \rightarrow \vec{j} = \sigma(\omega)\vec{E}, \quad \sigma(\omega) = \frac{(\tau ne^2/m)}{1 + i\omega\tau}.$$ 

This defines the frequency dependent (optical) conductivity. It can be microscopically and quantum mechanically computed from Kubo relation (current-current correlator). Real part of above is Lorentzian centered at $\omega=0$. 

![Graph showing real part of conductivity as a function of frequency]
In a superconductor, no dissipation so expect $\tau \to \infty$ and the Lorentzian should become a delta function with weight $\frac{\pi n_e^2}{m}$. But this should only be for the fraction of pairs formed, not the rest of the “normal” electrons which should only be visible in optical conductivity at frequencies corresponding to twice the gap and higher.

As well by the Kramers-Kronig relation, the imaginary part

$$\text{Im} \sigma(\omega) \sim \frac{\pi n_s e^2}{m} \cdot \frac{1}{\omega}$$
Background: Superconductivity in $K_3C_{60}$

- Parent FCC lattice insulator
- Doping 3 electrons per $C_{60}$ metallic.
- $T_c$ high: -20-30K.
- Generally thought to be “standard” superconductivity mediated by linearly-coupled phonons (albeit with strong couplings).
- Recent evidence—this is not quite the case (but will ignore here).
Possible light-induced superconductivity in $K_3C_{60}$ at high temperature


Equilibrium ($T_c \sim 20K$)
EMERGENT PHENOMENA
Light-induced superf conductivity

Intense light pulses irradiating a sample of $\text{K}_3\text{C}_6\text{O}_6$ result in dramatic changes of its high-frequency (terahertz) conductivity. Could these be signatures of fleeting superf conductivity at 100 K and beyond?

Jure Demšar

Superconductivity is a phenomenon that occurs in certain materials below their $T_c$ (critical temperature). $T_c$ depends on external pressure, superf conductivity below $143 \text{ K} (\approx 120 \text{ K})$. Alternatively, in addition to testing the properties by varying chemical structure, superfconducting properties can be tuned externally, for instance, by applying pressure or by irradiating with light. Whereas resonances chosen for the design of superf conductors are expected to be suppressed more than the $T_c$ of the order of milli-electrons (3.2 – 4.3 meV) corresponds to a gap frequency $2.5 \times 10^{14}$ Hz, superf conductors are used as sensitive far-infrared detectors. However, the latest experiments performed by N. M. Tzvetkov and colleagues suggest that in $\text{K}_3\text{C}_6\text{O}_6$ superf conductivity can be induced at temperatures up to 100 K, when excited with intense mid-infrared optical pulses.

Non-equilibrium superf conductivity — when a material is exposed to a continuous or a time-varying stimulus — has been studied since the 1960s. One of the most fascinating observations was that upon exposure to light, the superfconducting gap $\Delta_c$ and even the critical temperature, were enhanced in this film of metallic aluminium and tin when illuminated with electromagnetic radiation at mid-infrared frequencies (below $25 \text{ K}$). Although the superfconducting enhancement effects were small (typical changes in $T_c$ or the order of a percent were demonstrated), thus of little practical significance, these results nonetheless represented a significant theoretical implication. The first 

“Superconductivity enhancement effects were small (typical changes in $T_c$ or the order of a percent were demonstrated)”

Cavalleri understands and points out that the team was careful to describe the behavior as superfcondutctor-like. But he adds that his group is working to achieve long-term superf conductivity using continuous-wave lasers, rather than pulsed light.

Figure 1] The proposed mechanism for light-induced superf conductivity in $\text{K}_3\text{C}_6\text{O}_6$ includes mid-infrared pulses (light pink) at 4.2 THz. This resonantly excites the $T_c$ molecular orbitals of $\text{K}_3\text{C}_6\text{O}_6$ (red), creating charge carriers that move through the material to heat the sample. The addition of mid-infrared pulses can therefore increase the superfconducting gap by exciting the molecular orbitals of the material, leading to enhanced conductivity.

This is interesting work, says physicist David Tománek of Michigan State University, who was among the first to study electron-phonon coupling in superfconducting fullerenes. But because of the short lifetime of the excited state, the physics community will be unlikely to accept the association of this effect with superf conductivity,” he tells C&EN.
Building a Model Hamiltonian

• The phonon modes that mediate equilibrium superconductivity in $K_3C_{60}$ are well characterized. These modes are linearly coupled to the electronic degrees of freedom.

• However the modes that are IR active (the 4 triply degenerate $T_{1u}$ modes) by symmetry can only couple quadratically to the electronic degrees of freedom. These are the modes pumped in the experiment. Strength of quadratic coupling order of magnitude smaller than linear. Generally ignored in equilibrium.

• In model with just linear coupling can remove coupling with polaron transformation. Will make band narrower and $U$ negative (favoring pairing). We assume the band and $U$ terms are effective parameters and already have absorbed this transformation. Take values consistent with known $T_c$.

• Have worked out full tensor structure of couplings but will ignore that and keep simple here.
We have not included the interaction of the vibrations with the laser field. For simplicity here-we will assume this merely leads to a time dependence in the amplitude of the phonon modes...
In particular....

We consider decoupled interaction of $T_{1u}$ phonons with the laser field:

$$\hat{H}_{boson} = \omega_0 \sum_i \left( \beta_i \beta_i^\dagger + \frac{1}{2} \right) + F(t) \sum_i \left( \beta_i \beta_i^\dagger + \beta_i^\dagger \beta_i \right),$$

$$\hat{X}_i = \sqrt{2(MK)} \frac{1}{2} \left( \beta_i \beta_i^\dagger + \beta_i^\dagger \beta_i \right), \quad \omega_0 = \sqrt{\frac{K}{M}}.$$
Physical Role of Quadratic Coupling: Squeezing

\[ U_{\text{eff}} = E(2, m) + E(0, m) - 2E(1, m) = \tilde{U} - (m + \frac{1}{2})\sqrt{\frac{K}{M}}\left(2\sqrt{1+2g} - 1 - \sqrt{1+4g}\right) \]

Always >0!

Thus-high amplitude phonon excitation leads to an increasingly negative (attractive) interaction between electrons!
Physical Role of Quadratic Coupling: Squeezing

Note-density dependent change in oscillator stiffness requires $g > -1/4$. A change in stiffness without change in mass: change in uncertainty ellipse for oscillator-squeezing in phase space!

$$\hat{S} = e^{(i/2)\sum_j \zeta_j (\hat{X}_j \hat{P}_j + \hat{P}_j \hat{X}_j)}$$

$$\zeta_i = -(1/4) \ln[1 + 2g (\hat{n}_{i\uparrow} + \hat{n}_{i\downarrow})]$$

$$\hat{S} \hat{H} \hat{S}^{-1} = -\sum_{\langle i,j \rangle} \hat{S} (\tilde{J}_{ij} (\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + h.c.)) \hat{S}^{-1} + \tilde{U} \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \sum_{i\sigma} \omega(\hat{n}_{i\sigma}) (\beta_i^\dagger \beta_i + \frac{1}{2})$$

$$\omega(\hat{n}_{i\sigma}) = \sqrt{\frac{K}{M}} (1 + 2g \hat{n}_{i\sigma})^{1/2}, \quad \hat{X}_i = \sqrt{2(MK)^2} \left( \beta_i^\dagger + \beta_i \right)$$
Approximation: simplify hopping (kinetic energy) and drop inelastic terms.

Remaining model interesting: 

\[
\tilde{H} = -\tilde{J}^* \sum_{\langle i,j \rangle \sigma} (\hat{c}_{i\sigma} \hat{c}_{j\sigma}^\dagger + h.c.) + \left( \tilde{U} - \frac{g^2 \omega_0}{2} \sum_i (2\langle \beta_i^\dagger \beta_i \rangle + 1) \right) \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \\
+ \omega_0 \sum_i (\beta_i^\dagger \beta_i + \frac{1}{2}) + (\frac{g}{2} - \frac{g^2}{4}) \omega_0 \sum_{i\sigma} (2\beta_i^\dagger \beta_i + 1) \hat{n}_{i\sigma}
\]

From known distortion caused by optical pumping can estimate mean occupancy of boson mode \( \langle \beta^\dagger \beta \rangle (t \to \infty) > 10 \)

Disorder weak but not so far from boundary of localization.

Higher occupancy of phonon mode DECREASES U-stronger attraction

Higher occupancy of phonon modes INCREASES site disorder and kills all conductivity!
How good is our approximate Hamiltonian?

Can test with a 2-site model which we can (numerically) solve exactly:

Spectral Function
How good is our approximate Hamiltonian?

• Phonon properties:
The Hamiltonian suggests a “phase diagram” of system under driving:
Putting in numbers: Optical Conductivity

![Graphs showing optical conductivity for different temperatures and lifetimes.](image-url)
Putting in numbers: “transition” temperatures.
Some Comments (I)

• We have some numerical evidence from exact (1D) DMRG simulations (Wilner et al, to be published) that the field-induced disorder effect is real-and the induction of collective behavior competes with this.

• The couplings we have used are on the high end but not unrealistic. On the other hand, we have ignored many features of the true band structure (multi-orbital character, phonon multiplicity, Hund’s coupling, etc) and have used a BCS-like calculation.
Some Comments (II)

• There are at least 2 other recent explanations for these non-equilibrium effects. Demler et al. have a theory similar in spirit but focusing on different couplings, Georges et al. have a theory based on excitonic cooling that actually does not involve enhanced pairing at all.

• Still need to be able to explain similar effects seen in cuprates...
Conclusions:

• The notion that coherent excitation may induce transient collective electronic effects is actually not as implausible as seems at first sight.

• The mechanism put forward here is general-applies to other systems. Predict distinct transient changes (“phase transitions”) other than superconductivity as well...

• On other hand-see no way to make these effects long lasting-phonon dephasing, relaxation will always kill behavior at longer times.
Thx-E.Wilner, D.Kennes and A.Millis

• Kennes, Wilner, Reichman and Millis, Nature Physics, online publication (DOI 10.1038/NPHYS4024) January 2017.

• Kennes, Wilner, Reichman and Millis, arXiv 1703.07248 (2017)

• Wilner, Kennes, Reichman, Millis (to be submitted).