MECHANISM OF HIGH-TEMPERATURE SUPERFLUORESCENCE IN HYBRID PEROVSKITE THIN FILMS

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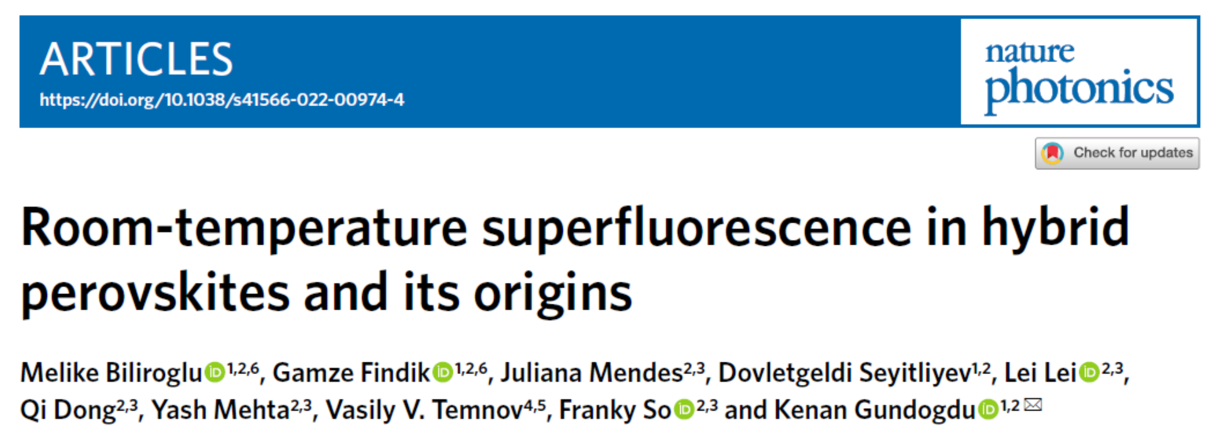
Superfluorescence in hybrid perovskites



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Room-temperature superfluorescence in hybrid perovskites and its origins

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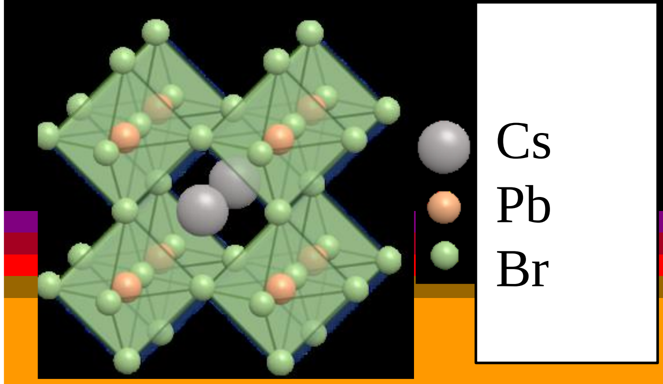


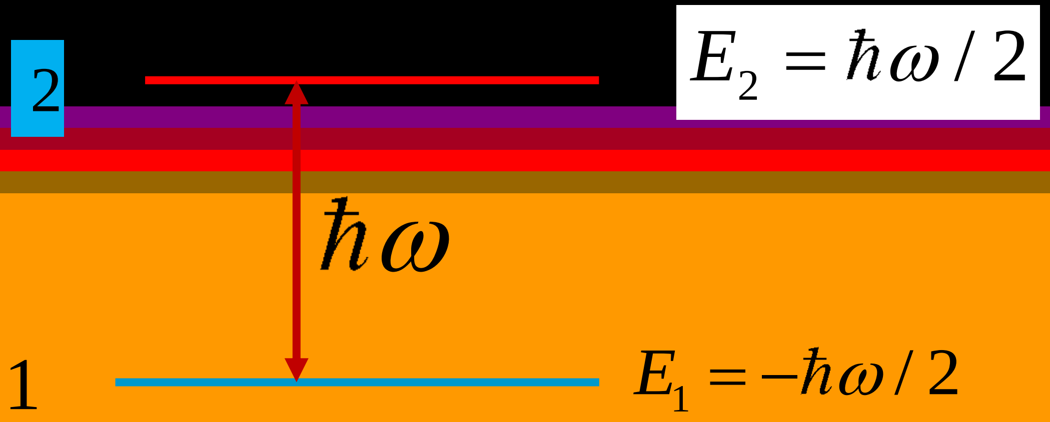
Phenethylammonium cesium lead bromide **quasi-2D CsPbBr3 thin films**

Experiments by Gundogdu et al. suggest that **large polarons** in these systems protect electronic excitation from dephasing even at room temperature. We aim to elucidate the mechanism enabling SF in hybrid perovskites at high temperatures.

Outline

1. Dicke model of superradiance
2. Wannier excitons in polar crystals interacting with LO phonons
3. Equations of motion for vibration-assisted single-exciton wave-function
4. Small deviations from the coherent superradiant state
5. Multiple excited states
6. Solution of nonlinear equations for any value of the wave vector
7. Conclusion

Dicke model of superradiance



2

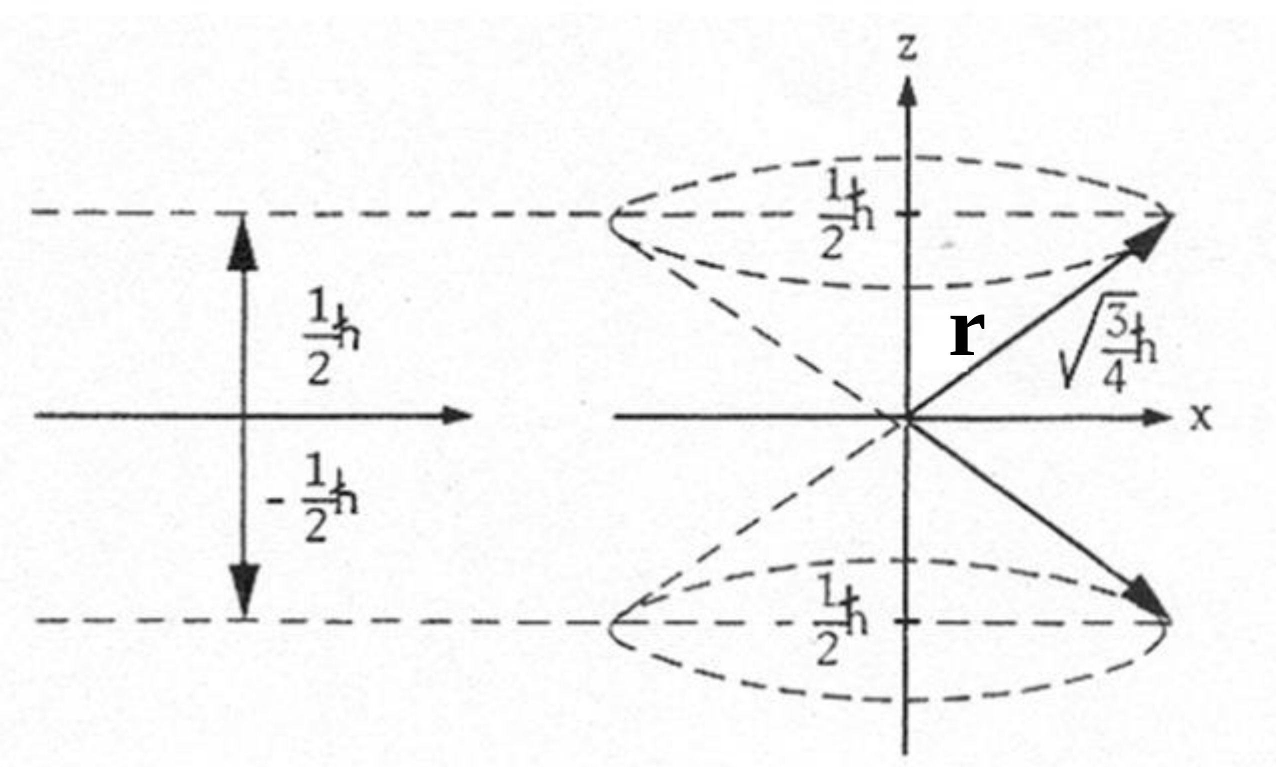
$E_2 = \hbar\omega / 2$

$\hbar\omega$

1

$E_1 = -\hbar\omega / 2$

$$H_0 = \hbar\omega r_3$$



$$N = N_1 + N_2$$

$$R_i = \sum_{m=1}^{N} r_{mi}, \quad i = 1, 2, 3$$

$$R^2 = R_1^2 + R_2^2 + R_3^2$$

$$H = \tilde{H} + \hbar\omega R_3$$

$\tilde{H}$ acts on the center–of–mass coordinates and represents the translational and intermolecular interaction energies

Eigenstates of H are eigenstates $|R,M\rangle$ of R^2 and R_3.

According to the theory of angular momentum,

$$|M| \le \mathrm{R} \le \mathrm{N}/2$$

Spontaneous radiation probabilities are

$$I = I_0 (R+M)(R-M+1)$$

If $M=R=N/2$ (i.e., all N molecules excited), $I = I_0 N$ (I_0 – radiation rate of one excited molecule).

Coherent radiation is emitted when R is large but $|M|$ small.

For example, if $R=N/2$ and $M=0$,

$$I = I_0 \frac{N}{2}\left(\frac{N}{2}+1\right) \sim N^2 \text{ for large } N$$

This is the largest rate at which a gas of molecules can radiate spontaneously.

The Dicke model undergoes the superradiant phase transition. It is possible to distinguish between static and **dynamic critical phenomena** that characterize time-dependent behavior like relaxation times. We will focus on studying a dynamical critical phenomenon - **the decay of the superradiant state** in the presence of vibrations - which allows us to restrict the models to collective emission from **single excitation states** ($R=N/2$, $M=-N/2+1$). Then

$$\boxed{I = I_0 (R+M)(R-M+1) = I_0 N}$$

The coherent state decays at an enhanced superradiance rate $N\Gamma$, which is N times larger than the single-molecule emission rate Γ.

Wannier excitons in polar crystals interacting with LO phonons

$$\hat{H}_I^{pol(W)} = -i\hbar \sum_{nn'\mathbf{kq}} D_l^{pol}(\mathbf{k};nn')B^{\dagger}_{n,\mathbf{q}+\mathbf{k}}B_{n'\mathbf{q}}(b_{\mathbf{k}} - b^{\dagger}_{-\mathbf{k}})$$

$$D_l^{pol}(\mathbf{k};nn') = \omega_l \sqrt{\frac{4\pi\alpha}{uV}}\frac{1}{k}[Q_e(\mathbf{k};nn') - Q_h(\mathbf{k};nn')]$$

α – the Frohlich coupling constant

$$Q_{e,h}(\mathbf{k};nn') \equiv \int \psi_n^*(\mathbf{r})\psi_{n'}(\mathbf{r})\exp(\pm i p_{e,h}\mathbf{kr})dr$$

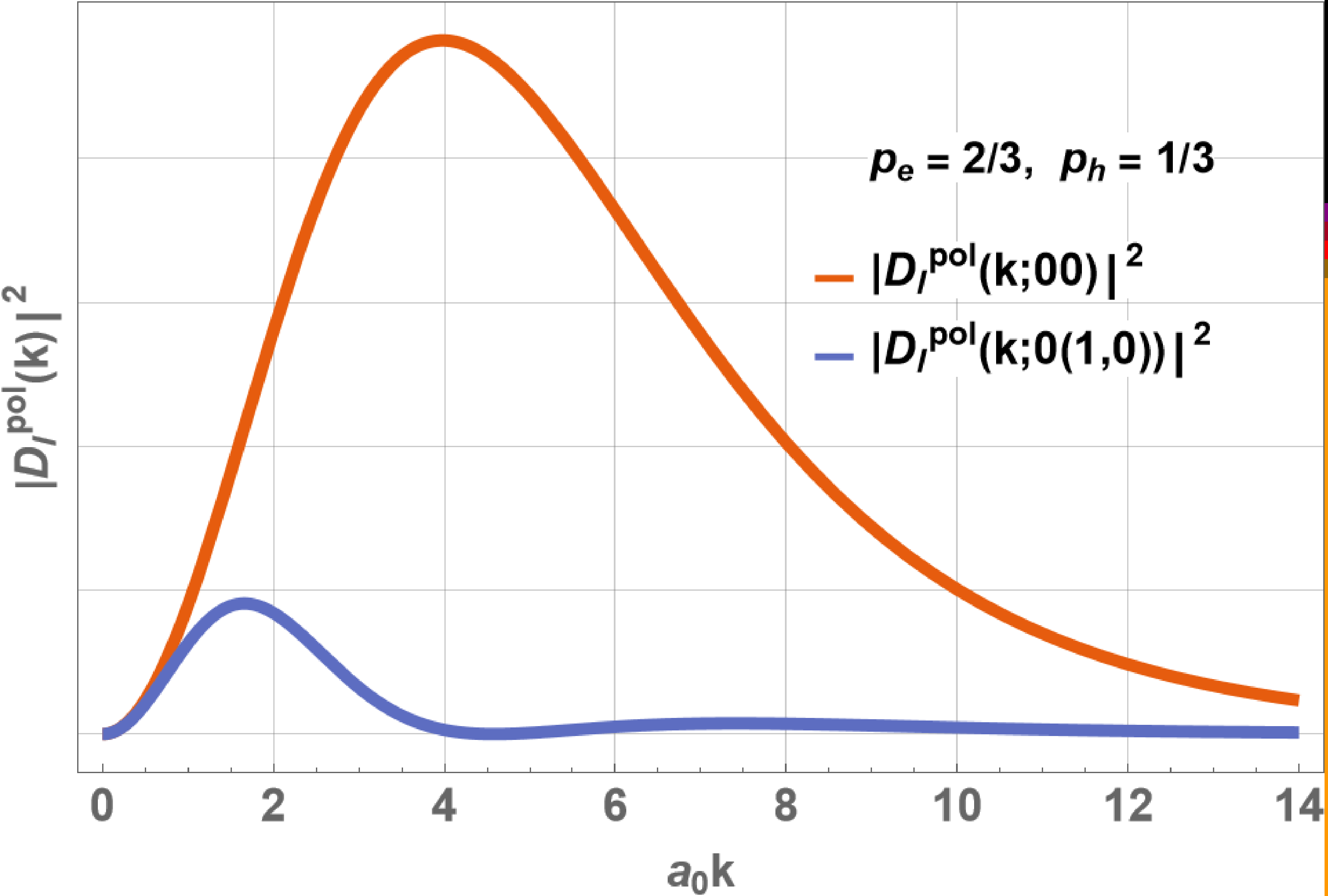
- the Fourier transform of the charge distributions of the electron (hole) in the internal motion. $\pm p_{e,h}\mathbf{r} = \mathbf{r}_{e,h} - \mathbf{R}$. It represents the effectivity of the electron (hole) charge for a particular phonon **k**:

$$\lim_{k\to 0} Q_{e,h}(\mathbf{k};nn') = \begin{cases} 1, n = n' \\ 0, n \neq n' \end{cases}; \quad Q_{e,h}(\mathbf{k};nn') \to 0 \text{ if } \frac{2\pi}{k} < a_0$$

$$D_l^{pol}(\mathbf{k};00) = \omega_l \sqrt{\frac{4\pi\alpha}{uV}}\frac{1}{k}\left[\left(1+(\frac{p_e k a_0}{4})^2\right)^{-3/2} - \left(1+(\frac{p_h k a_0}{4})^2\right)^{-3/2}\right]$$

- for quasi-2D

For $k < 1/a_0$, $D_l^{pol}(\mathbf{k};00) \sim k$



for quasi-2D

$$D_l^{pol}(\mathbf{k};0(1,0)) = \omega_l \sqrt{\frac{4\pi\alpha}{uV}}\,\frac{27\sqrt{3}}{512}\,a_0^2 k \left[\frac{p_e^{\;2}}{[(\frac{3a_0 p_e k}{8})^2+1]^{5/2}} - \frac{p_h^2}{[(\frac{3a_0 p_h k}{8})^2+1]^{5/2}} \right]$$

Equations of motion for vibration-assisted single-exciton wave-function

TIME-DEPENDENT COHERENT STATES BASIS & MULTISCALE HARTREE APPROACH

We use coherent states $|\sigma\rangle$ basis as the basis for the phonon states:

$$|\sigma\rangle = \exp\left(-\frac{1}{2}|\sigma|^2\right)\exp\left(ab^+\right)|0\rangle$$

Dirac-Frenkel variation principle allows one to separate time evolution of vibrational subsystem and evolution of exciton wave function expansion coefficients.

The correspondence to the original description by the Schrödinger equation is exact.

V.Al. Osipov, B.D. Fainberg, Phys. Rev. B, 2023, 107, 075404.

Equations of motion for a single-exciton wave-function

$$\dot{\sigma}_{\mathbf{k}} = -(i\omega_l + \gamma)\sigma_{\mathbf{k}} + Tr[\hat{D}_l^{pol}(-\mathbf{k})\hat{F}(\mathbf{k}\,|\,t)]$$

$$F_{nn'}(\mathbf{k}\,|\,t) = \sum_{\mathbf{q}} \rho_{n,\mathbf{q}+\mathbf{k};n'\mathbf{q}}(t)$$

-Hartree term

$$\dot{C}_0(\mathbf{q}\,|\,t) = -i\{W_0(\mathbf{q}) - \frac{1}{2}\sum_{\mathbf{k}} Tr[i\tilde{\alpha}_l(\mathbf{k})\hat{F}^{\dagger}(\mathbf{k}\,|\,t)]\}C_0(\mathbf{q}\,|\,t) + \sum_{n\mathbf{k}} \tilde{\alpha}_l(\mathbf{k};n0)C_n(\mathbf{q}+\mathbf{k}\,|\,t) - \frac{1}{2}\Gamma_{\mathbf{q}}C_0(\mathbf{q}\,|\,t)$$

$$\tilde{\alpha}_l(\mathbf{k};nn') = D_l^{*\,pol}(\mathbf{k};nn')(\sigma_{\mathbf{k}}^{*} - \sigma_{-\mathbf{k}})$$

$\Gamma_{\mathbf{q}=0} = 24\pi\left(\frac{\lambda}{a_0}\right)^2 \gamma_s$ - the radiative decay rate is enhanced by a factor of $24\pi\left(\frac{\lambda}{a_0}\right)^2$

Small deviations from the coherent superradiant state

Under perpendicular incidence of the pump field, excitons with **q**=0 are created. This **q**=0 state having the lowest energy is a coherent superradiant state. $\tilde{\alpha}_l(k)$ equals 0 when k=0. This behavior arises because **for k=0, the macroscopic electric field of the LO phonon is uniform in space. The exciton is neutral, so its energy cannot be changed by a uniform field. Thus,** $for\ k < 1/a_0,\ D_l^{pol}(\mathbf{k};00) \sim k$ **similar to the matrix element for optical quadrupole transitions. Therefore a state with a specific wave vector q behaves like metastable state in optics when there is no dipole transition.**

$$C_0(\mathbf{q}\,|\,t) = C_0(\mathbf{q}\,|\,0)\exp\{-i[W_0(\mathbf{q}) - \frac{\omega_l}{\gamma^2+\omega_l^2}\sum_{\mathbf{k},k<K=1/a_0} |\,D_l^{pol}(\mathbf{k};00)\,|^2]t - \frac{1}{2}\Gamma_{\mathbf{q}}t\}$$

Procedure for limiting possible wave vector values, *k*<*K*, is similar to deriving a block Hamiltonian using the Kadanoff transformation in the theory of phase transitions. The last equation demonstrates that even for nonzero *k*, the "vibrational" contribution to the superradiant state attenuation is absent up to order k^2 terms. This is true on a scale greater than $2\pi/K = 2\pi a_0$.

What happens in case of multiple excited state？

Semiclassical Hamiltonian: $b_{\mathbf{k}} \to \sigma_{\mathbf{k}}$

$$\hat{H}^{SC} = \hat{H}^{W}_{ex} + \hat{H}^{W}_{I} = \hbar \sum_{n\mathbf{q}} W_n(\mathbf{q}) B^{\dagger}_{n\mathbf{q}} B_{n\mathbf{q}} - i\hbar \sum_{nn'\mathbf{kq}} \tilde{\alpha}^{*}_{l}(\mathbf{k}; nn') B^{\dagger}_{n,\mathbf{q}+\mathbf{k}} B_{n'\mathbf{q}}$$

Exactly solvable model for long-wave excitons – LMG model that assumes the same interaction between different sites:

$$\hat{H}_{LMG} = \hbar \sum_{m} \Big(B^{\dagger}_{m} B_{m} \bar{W} - |J| \sum_{m' \neq m} B^{\dagger}_{m} B_{m'}\Big)$$ where m number various sites.

$$\begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix} = \begin{pmatrix} B^{\dagger} + B \\ i(B - B^{\dagger}) \\ B^{\dagger}B - BB^{\dagger} \end{pmatrix} \to \hat{H}^{iso}_{LMG} = -\hbar |J| \Big(R_1^2 + R_2^2 - \frac{N}{2} I\Big) - \hbar \bar{W} R_3; \quad \sum_{m} r_{mi} = R_i, \quad i = 1, 2, 3$$

Eigenstates of $\hat{H}^{iso}_{LMG}$ are eigenstates $|R,M\rangle$ of R^2 and $R3$. The ground state of $\hat{H}^{iso}_{LMG}$ is the **totally symmetric Dicke state** with $R=N/2$ and $M<<N$. In the theory of PTs, the wave number expansion is used. Up to terms of order k^2

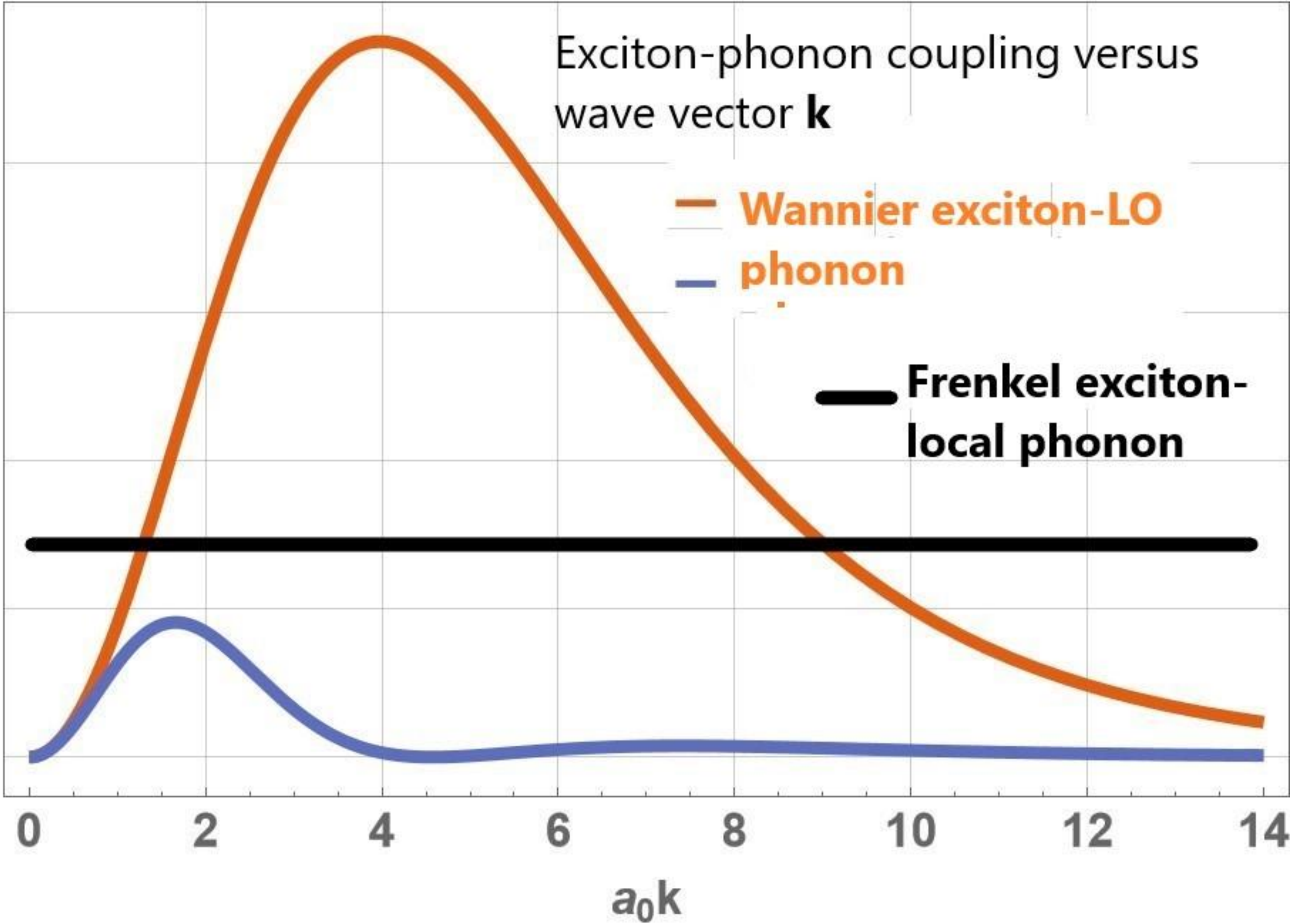
$$-i\hbar \sum_{\mathbf{kq}} \tilde{\alpha}^{*}_{l}(\mathbf{k}; 00) B^{\dagger}_{\mathbf{q}+\mathbf{k}} B_{\mathbf{q}} = \frac{-2\omega_l}{\gamma^2 + \omega_l^2} \hbar \tilde{B} \sum_{\mathbf{q}} B^{\dagger}_{\mathbf{q}} B_{\mathbf{q}} \sum_{\mathbf{k}, k<K} k^2 \ \text{ where } \sum_{\mathbf{q}} B^{\dagger}_{\mathbf{q}} B_{\mathbf{q}} = \tfrac{N}{2} I + R_3$$

Presence of the vibrational coupling does not violate the isotropic LMG model up to terms of order k^2.

This is due to $\boxed{for\ k < 1/a_0,\ D_l^{pol}(\mathbf{k};00) \sim k}$ Such an approximation is analogous to the decay $\tilde{\Gamma}_k$ for systems where certain conservation laws require the constant part of the decay to be zero. For an isotropic Heisenberg ferromagnet, the total spin, (**k**=0 mode) is conserved due to spin rotational invariance. Thus, noise cannot change magnetization for **k**=0 at any temperature, requiring $\tilde{\Gamma}_{\mathbf{k}} = ak^2 + bk^4 + O(k^6)$ if total spin is conserved. $\tilde{\Gamma}_{\mathbf{k}} \sim |D_l^{pol}(\mathbf{k};00)|^2$.

Perturbation theory calculations illustrate this rule well:

1) Electron-vibrational interactions in a model of *N* identical two-level molecules, where $|D_l^{pol}(\mathbf{k};00)|^2 = const$ independent of *k*, lead to destroying the coherence of the collective molecular excitation and suppressing SF [Nitzan et al. PRA(2022)].
2) In contrast, LO phonon-exciton Frohlich interactions, for which $|D_l^{pol}(\mathbf{k};00)|^2$ has no a constant component, do not disrupt the superradiant coherent state *q=0*.


Exciton-phonon coupling versus wave vector **k**
Wannier exciton-LO phonon
Frenkel exciton-local phonon
0
2
4
6
8
10
12
14
a_0k

Solution of nonlinear equations for $k>1/a_0$

New manifestations of the exciton-phonon interaction, which are associated with nonlinearity (e.g., soliton formation, instability, etc.).

Significant difference between the case of the LO phonon-Wannier exciton Fröhlich interaction and that of the Frenkel exciton-local phonon interaction. In the latter case, the nonlinearity is local, leading to the formation of Davydov's soliton in 1D molecular aggregates. In contrast, the LO phonon-Wannier exciton Fröhlich interaction results in an essentially nonlocal nonlinearity reflecting a significant increase in the range of interaction.

V.Al. Osipov and B.D. Fainberg, Phys. Rev. B, 2023, 107, 075404.

B.D. Fainberg and V.Al. Osipov, J. Chem. Phys., 2024, 161, 114705.

Conclusion

1. Hartree approach for the exciton wave function, where vibrations interact with the exciton quantum field.

2. Application to the high-temperature superfluorescence in hybrid perovskite thin films.

3. Nonlinear Hartree equations in the real space (for any value of the wave vector) with nonlocal non-linearity.

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