# Supplemental Material for:
# Exciton-Phonon Interactions and Relaxation Times from First Principles

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## I. DERIVATION OF THE EXCITON-PHONON MATRIX ELEMENTS

We provide a detailed derivation of the ex-ph matrix elements. Sec. I A briefly reviews electron-phonon ($e$-ph) interactions in first-order perturbation theory and introduces an formalism to obtain the standard $e$-ph interaction. The same formalism is used in Sec. I Bto derive the exciton-phonon (ex-ph) interaction and matrix elements.

### A. Electron-Phonon Interaction in First-Order Perturbation Theory

A system with static atomic displacements $\{\mathbf{u}_{is}\}$ from the equilibrium positions provides a perturbed Kohn-Sham potential, given by a Taylor expansion about the equilibrium positions ($i$ labels the unit cell and $s$ the atom):

$$V^{KS}(\{\mathbf{u}_{is}\}) = V_0^{KS} + \sum_{is\alpha} \frac{\partial V^{KS}}{\partial \mathbf{u}_{is\alpha}} \mathbf{u}_{is\alpha} + \mathcal{O}(\{\mathbf{u}_{is}\}^2) \tag{1}$$

where $V_0^{KS}$ is the unperturbed Kohn-Sham potential, for which all $\mathbf{u}_{is} = 0$. The electronic wave functions and eigenvalues of the perturbed system depend on the atomic displacements $\{\mathbf{u}_{is}\}$. To obtain their change in the perturbed system, we apply first-order perturbation theory by keeping terms linear in $\{\mathbf{u}_{is}\}$. To first-order, the correction to the eigenvalues vanishes, while the correction to the wave functions $\phi_i$ can be written as:

$$\delta|\phi_i\rangle = \sum_{j\neq i} \frac{\langle\phi_j|\Delta V|\phi_i\rangle}{\epsilon_i - \epsilon_j}|\phi_j\rangle, \qquad \text{with} \quad \Delta V = \sum_{is\alpha} \frac{\partial V^{KS}}{\partial \mathbf{u}_{is}} \cdot \mathbf{u}_{is} \tag{2}$$

where$|\phi_i\rangle$ are the unperturbed Kohn-Sham wave functions satisfying:

$$\left(\frac{-\hbar^2\nabla^2}{2m} + V_0^{KS}\right)|\phi_i\rangle = \epsilon_i|\phi_i\rangle. \tag{3}$$

In the following, we use the tilde for physical quantities of the perturbed system, and write the perturbed wave function as

$$|\tilde{\phi}_i\rangle = |\phi_i\rangle + \delta|\phi_i\rangle = |\phi_i\rangle + \sum_{j\neq i} \Delta_{ij}|\phi_j\rangle \tag{4}$$

with

$$\Delta_{ij} \equiv \frac{\langle\phi_j|\Delta V|\phi_i\rangle}{\epsilon_i - \epsilon_j}. \tag{5}$$

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To obtain the $e$-ph interaction, we second quantize the perturbed Hamiltonian, introducing unperturbed electron creation and annihilation operators, $\hat{c}^\dagger$ and $\hat{c}$, and rewrite the perturbed Hamiltonian as

$$\tilde{H} = H_0 + \Delta V, \quad \text{where } H_0 = \sum_i \epsilon_i \hat{c}_i^\dagger \hat{c}_i \text{ and } \hat{c}_i^\dagger|0\rangle = |\phi_i\rangle. \tag{6}$$

In addition, we project the perturbed Hamiltonian onto the unperturbed basis states $|\phi_i\rangle$:

$$\begin{aligned}\tilde{H} &= \sum_{ij} \langle\phi_i|\tilde{H}|\phi_j\rangle \hat{c}_i^\dagger \hat{c}_j = \sum_{ij,kl} \langle\phi_i|\tilde{\phi}_k\rangle\langle\tilde{\phi}_k|\tilde{H}|\tilde{\phi}_l\rangle\langle\tilde{\phi}_l|\phi_j\rangle \hat{c}_i^\dagger \hat{c}_j \\ &= \sum_{ij,k} \tilde{\epsilon}_k \langle\phi_i|\tilde{\phi}_k\rangle\langle\tilde{\phi}_k|\phi_j\rangle \hat{c}_i^\dagger \hat{c}_j \approx \sum_{ij,k} \epsilon_k \langle\phi_i|\tilde{\phi}_k\rangle\langle\tilde{\phi}_k|\phi_j\rangle \hat{c}_i^\dagger \hat{c}_j\end{aligned} \tag{7}$$

where in the first line we insert the complete perturbed basis set, $\sum_k |\tilde{\phi}_k\rangle\langle\tilde{\phi}_k| = 1$, with basis elements satisfying $\tilde{H}|\tilde{\phi}_k\rangle = \tilde{\epsilon}_k|\tilde{\phi}_k\rangle$, and in the second line we neglect the electronic eigenvalue correction due to the real part of the e-ph self-energy and approximate the perturbed eigenvalues as $\tilde{\epsilon}_k \approx \epsilon_k$ to first order.

Next, we use Eq. (4) to expand the inner product of the unperturbed and perturbed wave functions to first order, $\langle\phi_i|\tilde{\phi}_k\rangle \approx \delta_{ik} + \sum_{\alpha\neq k} \Delta_{k\alpha}\delta_{i\alpha}$, and dropping terms of order $\mathcal{O}(\Delta^2)$ we obtain:

$$\tilde{H} \approx \sum_{ij,k} \epsilon_k \left(\delta_{ik} + \sum_{\alpha\neq k} \Delta_{k\alpha}\delta_{i\alpha}\right)\left(\delta_{jk} + \sum_{\beta\neq k} \Delta^*_{k\beta}\delta_{j\beta}\right) \hat{c}_i^\dagger \hat{c}_j = \sum_k \epsilon_k \hat{c}_k^\dagger \hat{c}_k + {\sum_{ij}}' \left(\epsilon_i \Delta^*_{ij} + \epsilon_j \Delta_{ji}\right) \hat{c}_i^\dagger \hat{c}_j, \tag{8}$$

where the prime in the summation $\sum'_{ij}$ indicates $i \neq j$. Using Eq. (5), we obtain the perturbed Hamiltonian in a form that will be useful below:

$$\tilde{H} = \sum_k \epsilon_k \hat{c}_k^\dagger \hat{c}_k + {\sum_{ij}}' \left(\epsilon_i \frac{\langle\phi_i|\Delta V|\phi_j\rangle}{\epsilon_i - \epsilon_j} + \epsilon_j \frac{\langle\phi_i|\Delta V|\phi_j\rangle}{\epsilon_j - \epsilon_i}\right) \hat{c}_i^\dagger \hat{c}_j = \sum_k \epsilon_k \hat{c}_k^\dagger \hat{c}_k + {\sum_{ij}}' \langle\phi_i|\Delta V|\phi_j\rangle \hat{c}_i^\dagger \hat{c}_j. \tag{9}$$

By expanding $\Delta V$ as a sum of phonon modes, one can also derive the usual $e$-ph interaction Hamiltonian.

As we show next, this result holds true also in the presence of degenerate electronic states. Taking the possibility of degenerate states into account, the perturbation expansion in Eq. (4) is modified as:

$$|\tilde{\phi}_i\rangle = \sum_{j\in\mathcal{D}} \alpha_{ij} \left(|\phi_j\rangle + \sum_{k\notin\mathcal{D}} \Delta_{jk}|\phi_k\rangle\right) \quad \text{with} \quad \sum_{k\in\mathcal{D}} \alpha_{ik}\langle\phi_j|\Delta V|\phi_k\rangle = \epsilon_i^{(1)}\alpha_{ij}, \tag{10}$$

where $\mathcal{D}$ is the degenerate subspace containing the unperturbed state $\phi_i$, $\alpha_{ij}$ is the unitary transformation mixing states within the subspace, and $\epsilon_i^{(1)}$ is the first-order correction to the energy eigenvalue, which is proportional to the intra-subspace coupling $\langle\phi_j|\Delta V|\phi_k\rangle$ and can no longer be neglected. Substituting Eq. (10) into Eq. (7) and using the unitarity condition $\sum_k \alpha_{ik}\alpha^*_{jk} = \delta_{ij}$, we obtain the same formula as in Eq. (8) for inter-subspace scattering:

$$H_{\text{inter-subspace}} = {\sum_{\mathcal{D}\mathcal{D}'}}' \sum_{i\in\mathcal{D}} \sum_{j\in\mathcal{D}'} \left(\epsilon_i \Delta^*_{ij} + \epsilon_j \Delta_{ji}\right) \hat{c}_i^\dagger \hat{c}_j = {\sum_{\mathcal{D}\mathcal{D}'}}' \sum_{i\in\mathcal{D}} \sum_{j\in\mathcal{D}'} \langle\phi_i|\Delta V|\phi_j\rangle \hat{c}_i^\dagger \hat{c}_j, \tag{11}$$

where the prime in the summation $\sum'_{\mathcal{D}\mathcal{D}'}$ indicates $\mathcal{D} \neq \mathcal{D}'$, while intra-subspace scattering adds new terms:

$$\begin{aligned}H_{\text{intra-subspace}} &= \sum_{\mathcal{D}} \sum_{ijk\in\mathcal{D}} \epsilon_k^{(1)} \alpha_{ki}\alpha^*_{kj} \hat{c}_i^\dagger \hat{c}_j = \sum_{\mathcal{D}} \sum_{ijkk'\in\mathcal{D}} \alpha_{kk'}\alpha^*_{kj} \langle\phi_i|\Delta V|\phi_{k'}\rangle \hat{c}_i^\dagger \hat{c}_j \\ &= \sum_{\mathcal{D}} \sum_{ijk'\in\mathcal{D}} \delta_{jk'} \langle\phi_i|\Delta V|\phi_{k'}\rangle \hat{c}_i^\dagger \hat{c}_j = \sum_{\mathcal{D}} \sum_{ij\in\mathcal{D}} \langle\phi_i|\Delta V|\phi_j\rangle \hat{c}_i^\dagger \hat{c}_j,\end{aligned} \tag{12}$$

where the $i = j$ term contributes only to second order. After combining Eq. (12), Eq. (11) and the diagonal term $\sum_k \epsilon_k \hat{c}_k^\dagger \hat{c}_k$, we obtain the $e$-ph interaction Hamiltonian in the same form as Eq. (9), which therefore is valid also in the presence of degenerate electronic states.

### B. Exciton-Phonon Interaction

We now turn to the ex-ph interaction. We define the unperturbed BSE Hamiltonian $H \equiv H(\{\mathbf{u}_{is}\}=0)$ and the perturbed BSE Hamiltonian $\tilde{H} \equiv H(\{\mathbf{u}_{is}\})$. The unperturbed BSE Hamiltonian is solvable and gives the exciton energies and wave functions. The perturbed BSE Hamiltonian is not solved directly, but to first order it provides the ex-ph interactions we aim to derive. Using the known form of the BSE Hamiltonian, we write:

$$H_{vc,v'c'} = \langle vc|H|v'c'\rangle = (\epsilon_c - \epsilon_v)\,\delta_{vv'}\delta_{cc'} + K_{vc,v'c'} \tag{13}$$

and

$$\tilde{H}_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'} = \langle \tilde{v}\tilde{c}|\tilde{H}|\tilde{v}'\tilde{c}'\rangle = (\tilde{\epsilon}_{\tilde{c}} - \tilde{\epsilon}_{\tilde{v}})\,\delta_{\tilde{v}\tilde{v}'}\delta_{\tilde{c}\tilde{c}'} + \tilde{K}_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'}. \tag{14}$$

Here, $K_{vc,v'c'}$ is the BSE kernel, defined as:

$$K_{vc,v'c'} = \langle vc|K|v'c'\rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}_3 d\mathbf{x}_4\ \psi_v(\mathbf{x}_2)\psi_c^*(\mathbf{x}_1)K(\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\mathbf{x}_4)\psi_{v'}^*(\mathbf{x}_3)\psi_{c'}(\mathbf{x}_4), \tag{15}$$

where

$$K(\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\mathbf{x}_4) = -i\delta(\mathbf{x}_1,\mathbf{x}_2)\delta(\mathbf{x}_3,\mathbf{x}_4)v(\mathbf{x}_1,\mathbf{x}_4) + i\delta(\mathbf{x}_1,\mathbf{x}_4)\delta(\mathbf{x}_2,\mathbf{x}_3)W(\mathbf{x}_1,\mathbf{x}_2) \tag{16}$$

includes the bare Coulomb potential $v$ and the screened Coulomb interaction $W$. In addition, $\tilde{K}_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'}$ is the corresponding BSE kernel in the perturbed system with the phonon displacement frozen in:

$$\tilde{K}_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'} = \langle \tilde{v}\tilde{c}|\tilde{K}|\tilde{v}'\tilde{c}'\rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}_3 d\mathbf{x}_4\ \tilde{\psi}_{\tilde{v}}(\mathbf{x}_2)\tilde{\psi}_{\tilde{c}}^*(\mathbf{x}_1)\tilde{K}(\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\mathbf{x}_4)\tilde{\psi}_{\tilde{v}'}^*(\mathbf{x}_3)\tilde{\psi}_{\tilde{c}'}(\mathbf{x}_4) \tag{17}$$

where

$$\tilde{K}(\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\mathbf{x}_4) = -i\delta(\mathbf{x}_1,\mathbf{x}_2)\delta(\mathbf{x}_3,\mathbf{x}_4)v(\mathbf{x}_1,\mathbf{x}_4) + i\delta(\mathbf{x}_1,\mathbf{x}_4)\delta(\mathbf{x}_2,\mathbf{x}_3)\tilde{W}(\mathbf{x}_1,\mathbf{x}_2). \tag{18}$$

Solving the BSE Hamiltonian in Eq. (13) gives the exciton wave functions $|S_n\rangle$ and energies $E^{S_n}$:

$$\sum_{v'c'} H_{vc,v'c'} A_{v'c'}^{S_n} = E^{S_n} A_{vc}^{S_n} \quad \text{with the exciton wave function} \quad |S_n\rangle = \sum_{vc} A_{vc}^{S_n}|vc\rangle. \tag{19}$$

While we do not solve Eq. (14) directly, our strategy will mimic the one we discussed above in Sec. I A for the $e$-ph interaction. We project the perturbed BSE Hamiltonian onto the unperturbed basis set and keep terms of first-order in the phonon perturbation; by comparing the result with the unperturbed BSE Hamiltonian in Eq. (13), the additional terms will define the ex-ph interaction. Also, since as mentioned above the correction to the electron energies is of second order, we will use $\tilde{\epsilon}_i = \epsilon_i$.

We first write the perturbed BSE Hamiltonian in the unperturbed exciton basis:

$$\tilde{H}_{mn} = \langle S_m|\tilde{H}|S_n\rangle = \sum_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'} \langle S_m|\tilde{v}\tilde{c}\rangle\langle\tilde{v}\tilde{c}|\tilde{H}|\tilde{v}'\tilde{c}'\rangle\langle\tilde{v}'\tilde{c}'|S_n\rangle = \sum_{vc,v'c'}\sum_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'} \langle S_m|vc\rangle\langle vc|\tilde{v}\tilde{c}\rangle\langle\tilde{v}\tilde{c}|\tilde{H}|\tilde{v}'\tilde{c}'\rangle\langle\tilde{v}'\tilde{c}'|v'c'\rangle\langle v'c'|S_n\rangle \tag{20}$$

where we inserted twice the complete unperturbed and perturbed basis sets, $\sum_{vc}|vc\rangle\langle vc| = 1$ and $\sum_{\tilde{v},\tilde{c}}|\tilde{v}\tilde{c}\rangle\langle\tilde{v}\tilde{c}| = 1$, respectively. Using the BSE wave function $\langle v'c'|S_n\rangle = A_{v'c'}^{S_n}$, we write Eq. (20) as

$$\tilde{H}_{mn} = \langle S_m|\tilde{H}|S_n\rangle = \sum_{vc,v'c'} A_{vc}^{S_m*}A_{v'c'}^{S_n} \times \left[\sum_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'} \langle vc|\tilde{v}\tilde{c}\rangle\langle\tilde{v}\tilde{c}|\tilde{H}|\tilde{v}'\tilde{c}'\rangle\langle\tilde{v}'\tilde{c}'|v'c'\rangle\right] \tag{21}$$

We focus on the term in brackets and separate it into two parts:

$$\sum_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'} \langle vc|\tilde{v}\tilde{c}\rangle\langle\tilde{v}\tilde{c}|\tilde{H}|\tilde{v}'\tilde{c}'\rangle\langle\tilde{v}'\tilde{c}'|v'c'\rangle = \sum_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'} \langle vc|\tilde{v}\tilde{c}\rangle\left[(\tilde{\epsilon}_{\tilde{c}} - \tilde{\epsilon}_{\tilde{v}})\,\delta_{\tilde{v}\tilde{v}'}\delta_{\tilde{c}\tilde{c}'} + \tilde{K}_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'}\right]\langle\tilde{v}'\tilde{c}'|v'c'\rangle$$
$$= \sum_{\tilde{v}\tilde{c}} \langle vc|\tilde{v}\tilde{c}\rangle\,(\epsilon_{\tilde{c}} - \epsilon_{\tilde{v}})\,\langle\tilde{v}\tilde{c}|v'c'\rangle + \sum_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'} \langle vc|\tilde{v}\tilde{c}\rangle\tilde{K}_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'}\langle\tilde{v}'\tilde{c}'|v'c'\rangle. \tag{22}$$

As discussed in the main text, we approximate the perturbed kernel with the unperturbed one, $\tilde{K}_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'} \approx \langle\tilde{v}\tilde{c}|K|\tilde{v}'\tilde{c}'\rangle$, since the effect of the atomic displacements on the bare and screened Coulomb interactions can be neglected, $\tilde{W} \approx W$ [1], consistent with the Born-Oppenheimer approximation. With this approximation, we have:

$$\sum_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'} \langle vc|\tilde{v}\tilde{c}\rangle \tilde{K}_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'} \langle\tilde{v}'\tilde{c}'|v'c'\rangle \approx \sum_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'} \langle vc|\tilde{v}\tilde{c}\rangle\langle\tilde{v}\tilde{c}|K|\tilde{v}'\tilde{c}'\rangle\langle\tilde{v}'\tilde{c}'|v'c'\rangle = \langle vc|K|v'c'\rangle = K_{vc,v'c'} \tag{23}$$

and thus the term in brackets in Eq. (21) becomes

$$\sum_{\tilde{v}\tilde{c},\tilde{v}'\tilde{c}'} \langle vc|\tilde{v}\tilde{c}\rangle\langle\tilde{v}\tilde{c}|\tilde{H}|\tilde{v}'\tilde{c}'\rangle\langle\tilde{v}'\tilde{c}'|v'c'\rangle = \sum_{\tilde{v}\tilde{c}}\langle vc|\tilde{v}\tilde{c}\rangle\left(\epsilon_{\tilde{c}} - \epsilon_{\tilde{v}}\right)\langle\tilde{v}\tilde{c}|v'c'\rangle + K_{vc,v'c'}. \tag{24}$$

Next, we use Eq. (4) to expand $\sum_{\tilde{v}\tilde{c}}\langle vc|\tilde{v}\tilde{c}\rangle\left(\epsilon_{\tilde{c}} - \epsilon_{\tilde{v}}\right)\langle\tilde{v}\tilde{c}|v'c'\rangle$ to order $\mathcal{O}(\Delta)$. We work within the Tamm-Dancoff approximation and keep only the resonant part of the BSE Hamiltonian; as a consequence, only valence-valence and conduction-conduction $e$-ph scattering will take place, namely, $\Delta_{vc} = \Delta_{cv} = 0$.

Using Eq. (4), we get:

$$\begin{aligned}
\langle vc|\tilde{v}\tilde{c}\rangle = \langle v|\tilde{v}\rangle\langle c|\tilde{c}\rangle &= (\delta_{v\tilde{v}} + \sum_{v''\neq\tilde{v}} \Delta_{\tilde{v}v''}\delta_{vv''})(\delta_{c\tilde{c}} + \sum_{c''\neq\tilde{c}} \Delta_{\tilde{c}c''}\delta_{cc''}) & (25)\\
&= \left(\delta_{v\tilde{v}}\delta_{c\tilde{c}} + \delta_{v\tilde{v}}\sum_{c''\neq\tilde{c}} \Delta_{\tilde{c}c''}\delta_{cc''} + \delta_{c\tilde{c}}\sum_{v''\neq\tilde{v}} \Delta_{\tilde{v}v''}\delta_{vv''}\right) + \mathcal{O}(\Delta^2) & (26)
\end{aligned}$$

and similarly

$$\langle\tilde{v}\tilde{c}|v'c'\rangle = \langle v'|\tilde{v}\rangle^*\langle c'|\tilde{c}\rangle^* = \left(\delta_{v'\tilde{v}}\delta_{c'\tilde{c}} + \delta_{v'\tilde{v}}\sum_{c''\neq\tilde{c}} \Delta^*_{\tilde{c}c''}\delta_{c'c''} + \delta_{c'\tilde{c}}\sum_{v''\neq\tilde{v}} \Delta^*_{\tilde{v}v''}\delta_{v'v''}\right) + \mathcal{O}(\Delta^2). \tag{27}$$

Using these results, we find five first-order terms in $\sum_{\tilde{v}\tilde{c}}\langle vc|\tilde{v}\tilde{c}\rangle\left(\epsilon_{\tilde{c}} - \epsilon_{\tilde{v}}\right)\langle\tilde{v}\tilde{c}|v'c'\rangle$, which we simplify using the $\delta$'s:

$$\begin{aligned}
&\sum_{\tilde{v}\tilde{c}}\langle vc|\tilde{v}\tilde{c}\rangle\left(\epsilon_{\tilde{c}} - \epsilon_{\tilde{v}}\right)\langle\tilde{v}\tilde{c}|v'c'\rangle \\
&\approx \left(\epsilon_c - \epsilon_v\right)\delta_{vv'}\delta_{cc'} + \delta_{cc'}\sum_{\tilde{v}}\left(\epsilon_c - \epsilon_{\tilde{v}}\right)\sum_{v''\neq\tilde{v}}\left(\Delta^*_{\tilde{v}v''}\delta_{vv''}\delta_{v'\tilde{v}} + \Delta_{\tilde{v}v''}\delta_{v'v''}\delta_{v\tilde{v}}\right) \\
&\qquad + \delta_{vv'}\sum_{\tilde{c}}\left(\epsilon_{\tilde{c}} - \epsilon_v\right)\sum_{c''\neq\tilde{c}}\left(\Delta_{\tilde{c}c''}\delta_{cc''}\delta_{c'\tilde{c}} + \Delta^*_{\tilde{c}c''}\delta_{c'c''}\delta_{c\tilde{c}}\right) \\
&= \left(\epsilon_c - \epsilon_v\right)\delta_{vv'}\delta_{cc'} + \delta_{cc'}\left[\sum_{v''\neq v'}\left(\epsilon_c - \epsilon_{v'}\right)\Delta^*_{v'v''}\delta_{vv''} + \sum_{v''\neq v}\left(\epsilon_c - \epsilon_v\right)\Delta_{vv''}\delta_{v'v''}\right] \\
&\qquad + \delta_{vv'}\left[\sum_{c''\neq c'}\left(\epsilon_{c'} - \epsilon_v\right)\Delta_{c'c''}\delta_{cc''} + \sum_{c''\neq c}\left(\epsilon_c - \epsilon_v\right)\Delta^*_{cc''}\delta_{c'c''}\right] \\
&= \left(\epsilon_c - \epsilon_v\right)\delta_{vv'}\delta_{cc'} + \delta_{cc'}\left(\epsilon_{v'} - \epsilon_v\right)\Delta_{vv'} + \delta_{vv'}\left(\epsilon_c - \epsilon_{c'}\right)\Delta^*_{cc'} \qquad (28)
\end{aligned}$$

where we used $\Delta_{ij} = -\Delta^*_{ji}$ to obtain the last line. Finally, the perturbed Hamiltonian in the exciton basis in Eq. (21) becomes:

$$\begin{aligned}
\tilde{H}_{mn} &= \sum_{vc,v'c'} A^{S_m*}_{vc}A^{S_n}_{v'c'} \times \{\ [\left(\epsilon_c - \epsilon_v\right)\delta_{vv'}\delta_{cc'} + K_{vc,v'c'}] + \delta_{cc'}\left(\epsilon_{v'} - \epsilon_v\right)\Delta_{vv'} + \delta_{vv'}\left(\epsilon_c - \epsilon_{c'}\right)\Delta^*_{cc'}\ \} \\
&= E^{S_m}\delta_{mn} + \sum_{vc,v'c'} A^{S_m*}_{vc}A^{S_n}_{v'c'} \cdot \left(\delta_{cc'}\left(\epsilon_{v'} - \epsilon_v\right)\Delta_{vv'} + \delta_{vv'}\left(\epsilon_c - \epsilon_{c'}\right)\Delta^*_{cc'}\right) \qquad (29)
\end{aligned}$$

where we use the fact that the unperturbed Hamiltonian is diagonalized by the Tamm-Dancoff exciton eigenvectors:

$$E^{S_m}\delta_{mn} = \sum_{vc,v'c'} A^{S_m*}_{vc}A^{S_n}_{v'c'} \times \left(\left(\epsilon_c - \epsilon_v\right)\delta_{vv'}\delta_{cc'} + K_{vc,v'c'}\right). \tag{30}$$

Therefore, the first term in the second line of Eq. (29) is the unperturbed Hamiltonian, while the second term is the ex-ph interaction,

$$\tilde{H}_{\text{ex}-\text{ph}} = \sum_{vc,v'c'} A_{vc}^{S_m*} A_{v'c'}^{S_n} \cdot \left(\delta_{cc'} \left(\epsilon_{v'} - \epsilon_v\right) \Delta_{vv'} + \delta_{vv'} \left(\epsilon_c - \epsilon_{c'}\right) \Delta_{cc'}^*\right). \tag{31}$$

To obtain the final result, we relabel all quantities in the ex-ph Hamiltonian for a periodic system. The wave functions are Bloch states

$$|\phi_i\rangle \to |\phi_{n\mathbf{k}}\rangle,$$

and the transition basis set for an exciton with center of mass momentum $\mathbf{Q}$ is $|vc\rangle = |v\mathbf{k}_v, c\mathbf{k}_c\rangle = |v\mathbf{k}_v, c\mathbf{k}_v + \mathbf{Q}\rangle$. We write the change in potential due to atomic displacements as a sum of phonon interactions:

$$\Delta V = \sum_{\nu\mathbf{q}} \left(\frac{\hbar}{2\omega_{\nu\mathbf{q}}}\right)^{1/2} \Delta_{\nu\mathbf{q}} V^{\text{KS}} (\hat{b}_{\nu\mathbf{q}} + \hat{b}_{\nu-\mathbf{q}}^\dagger) \tag{32}$$

where $\hat{b}_{\nu\mathbf{q}}^\dagger$ and $\hat{b}_{\nu\mathbf{q}}$ are phonon creation and annihilation operators. That the $\Delta_{ij}$ describing the transition from $i$-th state to $j$-th state becomes:

$$\Delta_{n\mathbf{k}n'\mathbf{k}'} = \frac{\langle n'\mathbf{k}'|\Delta V|n\mathbf{k}\rangle}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}'}} = \sum_{\nu\mathbf{q}} \frac{g_{nn'\nu}(\mathbf{k},\mathbf{q})\delta(\mathbf{k}' - \mathbf{k} - \mathbf{q})}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}'}} (\hat{b}_{\nu\mathbf{q}} + \hat{b}_{\nu-\mathbf{q}}^\dagger). \tag{33}$$

where $g_{nn'\nu}(\mathbf{k},\mathbf{q}) = (\hbar/2\omega_{\nu\mathbf{q}})^{1/2} \langle n'\mathbf{k}'|\Delta_{\nu\mathbf{q}} V^{\text{KS}}|n\mathbf{k}\rangle$ is the usual $e$-ph matrix element, namely the probability amplitude for an electron in band $n$ with crystal momentum $\mathbf{k}$ to transition to a final state in band $n'$ and momentum $\mathbf{k}' = \mathbf{k}+\mathbf{q}$, by absorbing or emitting a phonon with mode index $\nu$ and wave vector $\mathbf{q}$.

By introducing exciton creation and annihilation operators, $\hat{a}_{S_n(\mathbf{Q})}^\dagger$ and $\hat{a}_{S_n(\mathbf{Q})}$, we rewrite the ex-ph Hamiltonian in Eq. (31) as:

$$\tilde{H}_{\text{ex}-\text{ph}} = \sum_{nm\nu,\mathbf{Qq}} \mathcal{G}_{nm\nu}(\mathbf{Q},\mathbf{q}) \hat{a}_{S_m(\mathbf{Q}+\mathbf{q})}^\dagger \hat{a}_{S_n(\mathbf{Q})} (\hat{b}_{\nu\mathbf{q}} + \hat{b}_{\nu-\mathbf{q}}^\dagger). \tag{34}$$

where we defined the exciton-phonon matrix elements as:

$$\mathcal{G}_{nm\nu}(\mathbf{Q},\mathbf{q}) = \sum_{\substack{vcv'c' \\ \mathbf{k}_v\mathbf{k}_c\mathbf{k}'_{v'}\mathbf{k}'_{c'}}} A_{v\mathbf{k}_v,c\mathbf{k}_c}^{S_m(\mathbf{Q}+\mathbf{q})*} A_{v'\mathbf{k}'_{v'},c'\mathbf{k}'_{c'}}^{S_n(\mathbf{Q})} \left[\delta_{vv'} g_{c'c\nu}(\mathbf{k}'_{c'},\mathbf{q})\delta(\mathbf{k}_c - \mathbf{k}'_{c'} - \mathbf{q}) - \delta_{cc'} g_{vv'\nu}(\mathbf{k}_v,\mathbf{q})\delta(\mathbf{k}'_{v'} - \mathbf{k}_v - \mathbf{q})\right]. \tag{35}$$

Let us make momentum conservation explicit to obtain the expression given in Eq. (5) of the main text. The exciton-phonon coupling constant $\mathcal{G}_{nm\nu}(\mathbf{Q},\mathbf{q})$ is the probability amplitude for scattering from an exciton with band index $n$ with center-of-mass momentum $\mathbf{Q}$ to an exciton with band index $m$ and center-of-mass momentum $\mathbf{Q}+\mathbf{q}$. Since $A_{v\mathbf{k}_v,c\mathbf{k}_c}^{S(\mathbf{Q})} \neq 0$ only for $\mathbf{k}_c - \mathbf{k}_v = \mathbf{Q}$, in Eq. (35) we can impose three constraints, $\mathbf{k}_c - \mathbf{k}_v = \mathbf{Q}$, $\mathbf{k}'_c - \mathbf{k}'_v = \mathbf{Q}+\mathbf{q}$ and $\mathbf{k}'_c - \mathbf{k}_c = \mathbf{q}$ (or $\mathbf{k}'_v - \mathbf{k}_v = \mathbf{q}$). As a consequence, we drop three $\mathbf{k}$-point Brillouin zone (BZ) summations, and the final result for the ex-ph matrix element for a given exciton momentum $\mathbf{Q}$ and phonon momentum $\mathbf{q}$ is Eq. (5) in the main text:

$$\boxed{\mathcal{G}_{nm\nu}(\mathbf{Q},\mathbf{q}) = \sum_{\mathbf{k}} \left[\sum_{vcc'} A_{v\mathbf{k},c(\mathbf{k}+\mathbf{Q}+\mathbf{q})}^{S_m(\mathbf{Q}+\mathbf{q})*} A_{v\mathbf{k},c'(\mathbf{k}+\mathbf{Q})}^{S_n(\mathbf{Q})} g_{c'c\nu}(\mathbf{k}+\mathbf{Q},\mathbf{q}) - \sum_{cvv'} A_{v(\mathbf{k}-\mathbf{q}),c(\mathbf{k}+\mathbf{Q})}^{S_m(\mathbf{Q}+\mathbf{q})*} A_{v'\mathbf{k},c(\mathbf{k}+\mathbf{Q})}^{S_n(\mathbf{Q})} g_{vv'\nu}(\mathbf{k}-\mathbf{q},\mathbf{q})\right].} \tag{36}$$

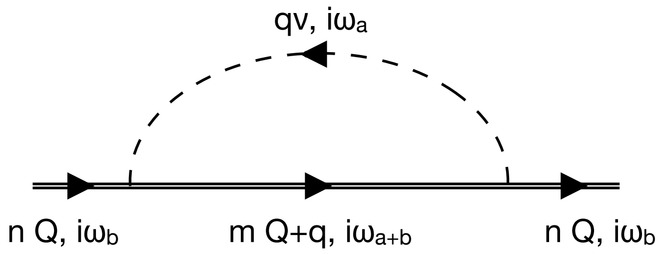


FIG. S1: One-loop exciton self-energy due to the ex-ph interaction

## II. DERIVATION OF THE EXCITON-PHONON SCATTERING RATE

In this section, we derive the ex-ph scattering rate using the optical theorem, which relates the scattering rate (inverse of the relaxation time $\tau$) and the imaginary part of the self-energy $\Sigma$:

$$\frac{1}{\tau} = -(2/\hbar)\mathrm{Im}\Sigma. \tag{37}$$

To compute the ex-ph scattering rate, we consider the one-loop exciton self-energy, and utilize the method of Matsubara frequency summation to calculate the Feynman diagram in Fig. S1. Using the imaginary time coordinate and imaginary frequency, as is usual in the Matsubara technique, the propagator for a boson (here, an exciton or a phonon) is written as:

$$\mathcal{D}_n(i\omega_a, \mathbf{k}) = \frac{1}{i\omega_a - E_{n\mathbf{k}}} - \frac{1}{i\omega_a + E_{n\mathbf{k}}}, \tag{38}$$

where $n$ is the band index for excitons or the mode index for phonons, $E_{n\mathbf{k}}$ is the on-shell energy, and the Matsubara frequency is defined as:

$$\omega_a = \frac{2\pi}{\beta}a \qquad \text{with} \;\; a \in \mathbb{Z},\; \beta = \frac{1}{k_B T}. \tag{39}$$

For details on the optical theorem and Matsubara's method, we refer the reader to Ref. [2]. The self-energy diagram in Fig. S1 can be evaluated as follows:

$$\begin{aligned}
\Sigma_n(i\omega_b, \mathbf{Q}) &= \frac{-1}{\beta\mathcal{N}_\mathbf{q}} \sum_{m\mathbf{q}\nu a} |\mathcal{G}_{nm\nu}(\mathbf{Q},\mathbf{q})|^2 \mathcal{D}_m(i\omega_{a+b}, \mathbf{Q}+\mathbf{q}) \mathcal{D}_\nu(i\omega_a, \mathbf{q}) \\
&= \frac{-1}{\beta\mathcal{N}_\mathbf{q}} \sum_{m\mathbf{q}\nu a} |\mathcal{G}_{nm\nu}(\mathbf{Q},\mathbf{q})|^2 \cdot \left[\frac{1}{i\omega_{a+b} - E_{m\mathbf{Q+q}}} - \frac{1}{i\omega_{a+b} + E_{m\mathbf{Q+q}}}\right]\left[\frac{1}{i\omega_a - E_{\nu\mathbf{q}}} - \frac{1}{i\omega_a + E_{\nu\mathbf{q}}}\right] \\
&= \frac{-1}{\beta\mathcal{N}_\mathbf{q}} \sum_{m\mathbf{q}\nu a} |\mathcal{G}_{nm\nu}(\mathbf{Q},\mathbf{q})|^2 \cdot \Bigg[\left(\frac{1}{i\omega_{a+b} - E_{m\mathbf{Q+q}}} - \frac{1}{i\omega_a - E_{\nu\mathbf{q}}}\right) \times \frac{1}{E_{m\mathbf{Q+q}} - E_{\nu\mathbf{q}} - i\omega_b} \\
&\qquad - \left(\frac{1}{i\omega_{a+b} - E_{m\mathbf{Q+q}}} - \frac{1}{i\omega_a + E_{\nu\mathbf{q}}}\right) \times \frac{1}{E_{m\mathbf{Q+q}} + E_{\nu\mathbf{q}} - i\omega_b} \\
&\qquad + \left(\frac{1}{i\omega_{a+b} + E_{m\mathbf{Q+q}}} - \frac{1}{i\omega_a + E_{\nu\mathbf{q}}}\right) \times \frac{1}{-E_{m\mathbf{Q+q}} + E_{\nu\mathbf{q}} - i\omega_b}\Bigg].
\end{aligned} \tag{40}$$

To simplify the expression, we apply the identity for the Bose-Einstein statistics:

$$\mathcal{N}(\epsilon) = \frac{1}{e^{\beta\epsilon} - 1} = -\frac{1}{2} - \frac{1}{\beta}\sum_{n=-\infty}^{\infty} \frac{1}{2ni\pi/\beta - \epsilon}, \tag{41}$$

and get:

$$\begin{aligned}\Sigma_n(i\omega_b,\mathbf{Q}) &= \frac{-1}{\mathcal{N}_\mathbf{q}}\sum_{m\mathbf{q}\nu}|\mathcal{G}_{nm\nu}(\mathbf{Q},\mathbf{q})|^2\left[\frac{-\mathcal{N}(E_{m\mathbf{Q}+\mathbf{q}})+\mathcal{N}(E_{\nu\mathbf{q}})}{E_{m\mathbf{Q}+\mathbf{q}}-E_{\nu\mathbf{q}}-i\omega_b}-\frac{-\mathcal{N}(E_{m\mathbf{Q}+\mathbf{q}})+\mathcal{N}(-E_{\nu\mathbf{q}})}{E_{m\mathbf{Q}+\mathbf{q}}+E_{\nu\mathbf{q}}-i\omega_b}\right.\\
&\qquad\left.-\frac{-\mathcal{N}(-E_{m\mathbf{Q}+\mathbf{q}})+\mathcal{N}(E_{\nu\mathbf{q}})}{-E_{m\mathbf{Q}+\mathbf{q}}-E_{\nu\mathbf{q}}-i\omega_b}+\frac{-\mathcal{N}(-E_{m\mathbf{Q}+\mathbf{q}})+\mathcal{N}(-E_{\nu\mathbf{q}})}{-E_{m\mathbf{Q}+\mathbf{q}}+E_{\nu\mathbf{q}}-i\omega_b}\right]\\
&= \frac{-1}{\mathcal{N}_\mathbf{q}}\sum_{m\mathbf{q}\nu}|\mathcal{G}_{nm\nu}(\mathbf{Q},\mathbf{q})|^2\left[(N_{\nu\mathbf{q}}-F_{m\mathbf{Q}+\mathbf{q}})\times\left(\frac{1}{E_{m\mathbf{Q}+\mathbf{q}}-E_{\nu\mathbf{q}}-i\omega_b}-\frac{1}{-E_{m\mathbf{Q}+\mathbf{q}}+E_{\nu\mathbf{q}}-i\omega_b}\right)\right.\\
&\qquad\left.-(N_{\nu\mathbf{q}}+1+F_{m\mathbf{Q}+\mathbf{q}})\times\left(\frac{1}{-E_{m\mathbf{Q}+\mathbf{q}}-E_{\nu\mathbf{q}}-i\omega_b}-\frac{1}{+E_{m\mathbf{Q}+\mathbf{q}}+E_{\nu\mathbf{q}}-i\omega_b}\right)\right],\end{aligned} \tag{42}$$

where we changed the notation to distinguish the exciton and phonon sectors by re-naming $\mathcal{N}(E_{\nu\mathbf{q}})\to N_{\nu\mathbf{q}}$ for phonons and $\mathcal{N}(E_{m\mathbf{Q}+\mathbf{q}})\to F_{m\mathbf{Q}+\mathbf{q}}$ for excitons. Lastly, we use analytical continuation to extend the complex function $\Sigma$ from the imaginary exciton energy to full complex plane, by setting $i\omega_b\to E_{n\mathbf{Q}}+i\epsilon$ with infinitesimal positive deviation $\epsilon$ from the real exciton energy axis. The ex-ph scattering rate is obtained by applying the optical theorem in Eq. (37) and computing the imaginary part of the self-energy through the identity:

$$\frac{1}{x+i\epsilon}=P\frac{1}{x}-i\pi\delta(x), \tag{43}$$

where $\epsilon$ is a positive infinitesimal and $P$ takes the principal value of $1/x$. The total exciton scattering rate obtained this way consists of multiple terms, in which we denote the exciton energies as $E$ and the phonon energies as $\hbar\omega$:

$$\begin{aligned}\Gamma_{n\mathbf{Q}}(T) &= \frac{2\pi}{\hbar}\frac{1}{\mathcal{N}_\mathbf{q}}\sum_{m\mathbf{q}\nu}|\mathcal{G}_{nm\nu}(\mathbf{Q},\mathbf{q})|^2\left[(N_{\nu\mathbf{q}}-F_{m\mathbf{Q}+\mathbf{q}})\times(\delta(E_{n\mathbf{Q}}-E_{m\mathbf{Q}+\mathbf{q}}+\hbar\omega_{\nu\mathbf{q}})-\delta(E_{n\mathbf{Q}}+E_{m\mathbf{Q}+\mathbf{q}}-\hbar\omega_{\nu\mathbf{q}}))\right.\\
&\qquad\left.+(N_{\nu\mathbf{q}}+1+F_{m\mathbf{Q}+\mathbf{q}})\times(\delta(E_{n\mathbf{Q}}-E_{m\mathbf{Q}+\mathbf{q}}-\hbar\omega_{\nu\mathbf{q}})-\delta(E_{n\mathbf{Q}}+E_{m\mathbf{Q}+\mathbf{q}}+\hbar\omega_{\nu\mathbf{q}}))\right].\end{aligned} \tag{44}$$

The four terms in Eq. (44) correspond to phonon absorption, two excitons combining into a phonon, phonon emission, and 3-particle annihilation, respectively. We ignore the two terms due to two excitons combining into a phonon and annihilation of two excitons and a phonon since they are not relevant here (the 3-particle annihilation process is also prohibited by energy conservation), keeping only the phonon emission and absorption terms. We thus obtain the ex-ph scattering rate given in Eq. (6) of the main text:

$$\begin{aligned}\Gamma^{\text{ex}-\text{ph}}_{n\mathbf{Q}}(T) = \frac{2\pi}{\hbar}\frac{1}{\mathcal{N}_\mathbf{q}}\sum_{m\nu\mathbf{q}}|\mathcal{G}_{nm\nu}(\mathbf{Q},\mathbf{q})|^2&\left[(N_{\nu\mathbf{q}}+1+F_{m\mathbf{Q}+\mathbf{q}})\times\delta(E_{n\mathbf{Q}}-E'_{m\mathbf{Q}+\mathbf{q}}-\hbar\omega_{\nu\mathbf{q}})\right.\\
&\left.+(N_{\nu\mathbf{q}}-F_{m\mathbf{Q}+\mathbf{q}})\times\delta(E_{n\mathbf{Q}}-E'_{m\mathbf{Q}+\mathbf{q}}+\hbar\omega_{\nu\mathbf{q}})\right],\end{aligned} \tag{45}$$

where $N$ and $F$ are phonon and exciton occupations, $\mathcal{N}_\mathbf{q}$ is the number of **q**-points, and the first and second terms in bracket correspond, respectively, to an exciton emitting or absorbing one phonon.

## III. NUMERICAL DETAILS

In our calculations, the same set of electronic wave functions are employed in the $e$-ph and BSE calculations, so that the ex-ph matrix elements in Eq. (5) of the main text are not affected by the random phase of the electronic wave functions. The quasiparticle energies are corrected using a one-shot plasmon-pole GW calculation (with a 10 Ry cutoff and 100 bands) before solving the BSE at finite center-of-mass exciton momenta. For the BSE, we use a 10 Ry cutoff for the statically screened Coulomb interaction and the two highest valence and two lowest conduction bands to obtain the lowest 8 excitonic states, of which 2 are bright and 6 are dark excitons at $\mathbf{Q}=0$. The ex-ph matrix elements are computed without interpolation or symmetry, using full Brillouin zone grids to converge the sum over **k**-points in Eq. (5) of the main text. The delta function in the scattering rate equation is approximated by a Gaussian with a small broadening of 4 meV.

## IV. PHONON DISPERSION

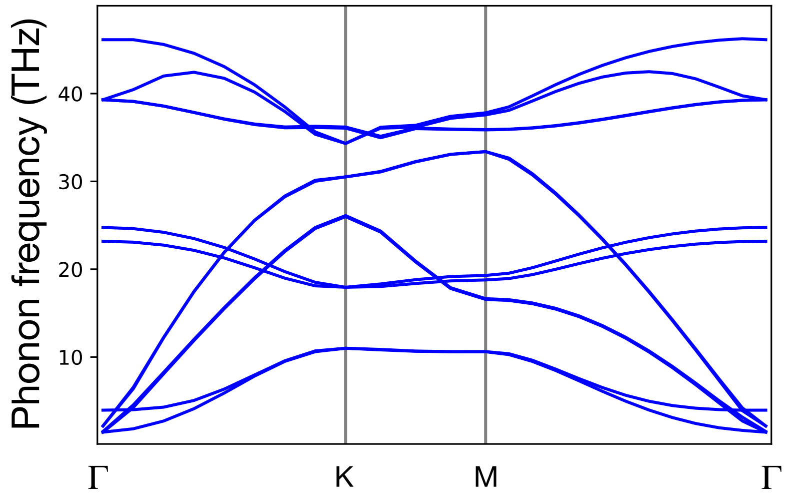


FIG. S2: Phonon dispersion curves in bulk h-BN, computed using DFPT.

## V. CONVERGENCE OF THE SCATTERING RATE

Here we show the convergence of the ex-ph scattering rate for the lowest-energy exciton band (the one with slowest convergence) by comparing results obtained with Brillouin zone grids of $24 \times 24 \times 4$ and $18 \times 18 \times 4$. It is seen that the scattering rates obtained with the two grids are in good agreement, so the values shown in the main text (for a $24 \times 24 \times 4$ grid) are expected to be reasonably well converged (say, within $\sim 10-20\%$ of the infinite-grid limit). Note that the same grid is used for **k**-points (for electrons), **q**-points (for phonons) and **Q**-points (for excitons).

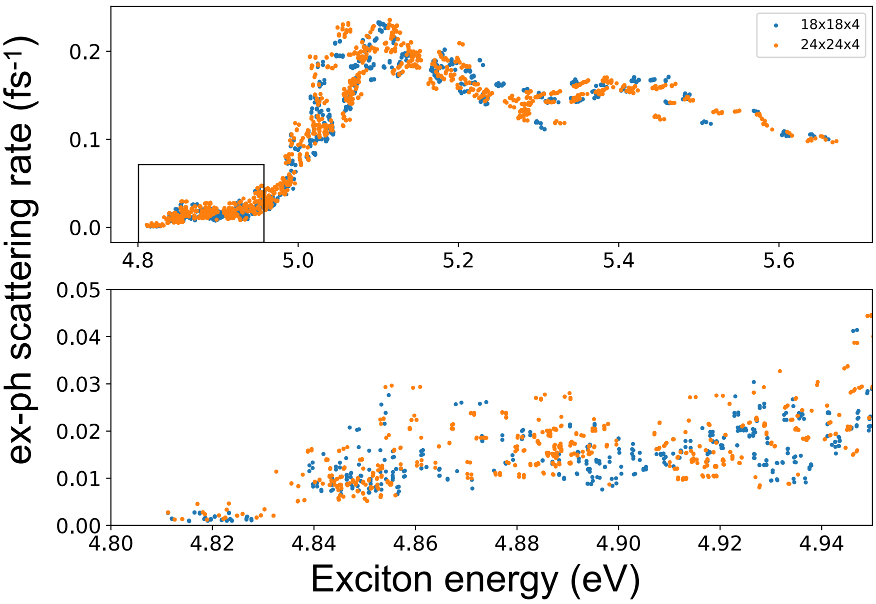


FIG. S3: The ex-ph scattering rate for the lowest exciton band, computed with two Brillouin zone grids of $24 \times 24 \times 4$ (orange) and $18 \times 18 \times 4$ (blue). The lower panel zooms in the low-energy region (below the LO emission threshold) marked by a rectangle in the upper panel.

## VI. PHOTOLUMINESCENCE

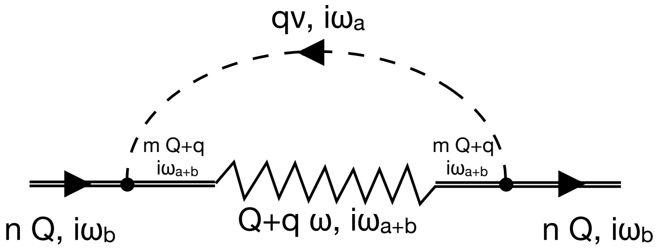


FIG. S4: One-loop exciton self-energy due to ex-ph processes involving photon emission. From left to right, the exciton (double solid line) emits or absorbs a phonon with momentum $\mathbf{q}$ (dashed line), and then emits a photon (zigzag line) with momentum $\mathbf{Q}+\mathbf{q}\approx 0$. The process then rewinds to form the self-energy loop.

Here we derive the formula used for calculating the phonon-assisted photoluminescence in Fig. 5 of the main text. The photoluminescence intensity $I(\omega)$ is defined as the number of photons with frequency $\omega$ emitted per unit time. The source of emitted photons is the radiative decay of excitons, and thus we can write:

$$I(\omega)=\frac{dn_\omega}{dt}=-\sum_n\int d\mathbf{Q}\frac{dN_{n\mathbf{Q}}}{dt}=\sum_n\int d\mathbf{Q}\Gamma_n(\mathbf{Q},\omega)N_{n\mathbf{Q}} \tag{46}$$

where $n_\omega$ is the number of photons with energy $\omega$, $N_{n\mathbf{Q}}$ is the number of excitons in a given state (with exciton band n and momentum $\mathbf{Q}$), which follows the Bose-Einstein distribution at low exciton density, and $\Gamma_n(\mathbf{Q},\omega)$ is the radiative rate of the same exciton state for emitting a photon with frequency $\omega$. Due to momentum conservation, excitons with a large enough finite momentum cannot emit a photon directly. The next-order emission processes is phonon-assisted luminescence, in which an exciton can emit or absorb a phonon and change its momentum before emitting the photon. We again derive the process rate using the optical theorem, by computing the imaginary part of the self-energy diagram in Fig. S4 as:

$$\Sigma_n(i\omega_b,\mathbf{Q})=\frac{-1}{\beta\mathcal{N}_\mathbf{q}}\sum_{m\mathbf{q}\nu a}|\mathbf{A}\cdot\mathbf{p}_m(\mathbf{Q}+\mathbf{q})|^2\cdot|\mathcal{G}_{nm\nu}(\mathbf{Q},\mathbf{q})|^2\left[\mathcal{D}_m(i\omega_{a+b},\mathbf{Q}+\mathbf{q})\right]^2\mathcal{D}_\nu(i\omega_a,\mathbf{q})\mathcal{D}_\omega(i\omega_{a+b},\mathbf{Q}+\mathbf{q}), \tag{47}$$

where $\mathbf{q}$ is the phonon momentum and $|\mathbf{A}\cdot\mathbf{p}|$ is the standard exciton-photon interaction within minimal coupling. We impose several conditions to compute the physical process we are interested in. First, the photon momentum is negligible compared to the crystal momentum, and thus we can set $\mathbf{Q}+\mathbf{q}\approx 0$ (see Fig. S4 ). In h-BN, we take the lowest two bright excitons (with zero momentum) for the optically active exciton states; these two states are degenerate, with equal-in-magnitude but perpendicular dipole moment $\mathbf{p}$. Since we focus on photon emission in a temperature range where phonon absorption is negligible compared to phonon emission, we use only the emission part of the photon and phonon propagators:

$$\mathcal{D}_\nu(i\omega_a,\mathbf{q})\approx-\frac{1}{i\omega_a+\hbar\omega_{\nu\mathbf{q}}},\qquad \mathcal{D}_\omega(i\omega_a,\mathbf{q})\approx\frac{1}{i\omega_a-\hbar\omega} \tag{48}$$

Note that the different sign in the photon and phonon propagators is due to the opposite directions of the propagation arrows in the self-energy diagram in Fig. S4. For the same reason, since only the emission process is considered, the intermediate exciton state propagator becomes:

$$\mathcal{D}_m(i\omega_a,\mathbf{Q})\approx\frac{1}{i\omega_a-E_{m\mathbf{Q}}}. \tag{49}$$

As a result, the self-energy takes a simpler expression, which with constants neglected reads:

$$\begin{aligned}\Sigma_n(i\omega_b,\mathbf{Q}) &\propto \frac{-1}{\beta\mathcal{N}_\mathbf{q}}\sum_{m\nu a}|\mathcal{G}_{nm\nu}(\mathbf{Q},-\mathbf{Q})|^2\left[\frac{1}{i\omega_{a+b}-E_{m\Gamma}}\right]^2\frac{-1}{i\omega_a+\hbar\omega_{\nu\mathbf{Q}}}\frac{1}{i\omega_{a+b}-\hbar\omega}\\ &= \frac{-1}{\beta\mathcal{N}_\mathbf{q}}\sum_{m\nu a}\left(I^{(1)}+I^{(2)}+I^{(3)}\right),\end{aligned} \tag{50}$$

where with some algebra we separate the self-energy into three terms:

$$\begin{aligned}
I^{(1)} &= \frac{-1}{(E_{m\Gamma}-\hbar\omega)^2}\frac{1}{i\omega_b-\hbar\omega-\hbar\omega_{\nu\mathbf{Q}}}\left(\frac{1}{i\omega_{a-b}+\hbar\omega_{\nu\mathbf{Q}}}-\frac{1}{i\omega_a-\hbar\omega}\right)\\
I^{(2)} &= \frac{1}{(i\omega_b-E_{m\Gamma}-\hbar\omega_{\nu\mathbf{Q}})^2}\frac{1}{E_{m\Gamma}-\hbar\omega}\left(\frac{1}{i\omega_a-E_{m\Gamma}}-\frac{1}{i\omega_{a-b}+\hbar\omega_{\nu\mathbf{Q}}}\right)\\
I^{(3)} &= \frac{1}{i\omega_b-E_{m\Gamma}-\hbar\omega_{\nu\mathbf{Q}}}\times\left[\frac{1}{E_{m\Gamma}-\hbar\omega}\frac{1}{(i\omega_a-E_{m\Gamma})^2}\right.\\
&\qquad\left.+\frac{1}{(E_{m\Gamma}-\hbar\omega)^2}\left(\frac{1}{i\omega_a-E_{m\Gamma}}+\frac{1}{i\omega_{a-b}+\hbar\omega_{\nu\mathbf{Q}}}-\frac{2}{i\omega_a-\hbar\omega}\right)\right]. \qquad (51)
\end{aligned}$$

The terms $I^{(1)}$, $I^{(2)}$ and $I^{(3)}$ are arranged according to their pole behavior. In particular, $I^{(1)}$ has pole at $i\omega_b-\hbar\omega-\hbar\omega_{\nu\mathbf{Q}}=0$, while $I^{(2)}$ and $I^{(3)}$ have a double and simple pole, respectively, at $i\omega_b-E_{m\Gamma}-\hbar\omega_{\nu\mathbf{Q}}=0$. After setting $i\omega_b\to E_{n\mathbf{Q}}+i\epsilon$, only the first pole at $i\omega_b-\hbar\omega-\hbar\omega_{\nu\mathbf{Q}}=0$ is associated with our process of interest, in which the initial exciton emits a phonon and transitions to a virtual bright state before emitting light. The other pole corresponds to an on-shell intermediate state (rather than a virtual one) and is negligible at low temperature since there are no excitons with a high enough energy for this process to occur. Therefore, we keep only the $I^{(1)}$ term. Using the identity in Eq. (41) and ignoring overall constant factors, we obtain the phonon-assisted radiative rate:

$$\Gamma_n(\mathbf{Q},\omega)\propto\sum_{m\in\text{bright exciton}}\left[\sum_{\nu}|\mathcal{G}_{nm\nu}(\mathbf{Q},-\mathbf{Q})|^2\cdot\frac{1+N(\hbar\omega_{\nu\mathbf{Q}})}{(\hbar\omega-E_m)^2}\cdot\delta\left(\hbar\omega+\hbar\omega_{\nu\mathbf{Q}}-E_{n\mathbf{Q}}\right)\right]. \qquad (52)$$

Substituting this rate in Eq. (46), we finally obtain phonon-assisted photoluminescence formula used to compute the spectra in Fig. 5 of the main text:

$$\boxed{I(\omega)=\sum_n\int d\mathbf{Q}\Gamma_n(\mathbf{Q},\omega)N_{n\mathbf{Q}}\propto\sum_{nm\nu}|p_{S_m}|^2\int d\mathbf{Q}\,|\mathcal{G}_{nm\nu}(\mathbf{Q},-\mathbf{Q})|^2\cdot N_{n\mathbf{Q}}\frac{1+N(\hbar\omega_{\nu\mathbf{Q}})}{(\hbar\omega-E_m)^2}\cdot\delta\left(\hbar\omega+\hbar\omega_{\nu\mathbf{Q}}-E_{n\mathbf{Q}}\right).} \qquad (53)$$


[1] Z. Li, G. Antonius, M. Wu, H. Felipe, and S. G. Louie, Phys. Rev. Lett. **122**, 186402 (2019).
[2] G. D. Mahan, *Many-particle physics* (Springer Science & Business Media, 2013).