

Supplementary Material for “Interplay between classical and quantum dissipation in light-matter dynamics”

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1 Master equation for an electronic system coupled to a photon bath

The total Hamiltonian \hat{H} that describes a many-electron system coupled to a photon bath can be expressed as:

$$\hat{H} = \hat{H}_S + \sum_{\mathbf{k}} \sum_{\lambda=1}^2 \hbar\omega_{\mathbf{k}} \left(\hat{a}_{\mathbf{k},\lambda}^\dagger \hat{a}_{\mathbf{k},\lambda} + \frac{1}{2} \right) + \frac{e}{m} \sum_{\mathbf{k}} \hat{\mathbf{A}}_{\mathbf{k}} \cdot \hat{\mathbf{p}}, \quad (1)$$

where λ denotes the two possible indices for the orthogonal polarization states, $\hat{a}_{\mathbf{k},\lambda}^\dagger$ and $\hat{a}_{\mathbf{k},\lambda}$ are the creation and annihilation operators for photons with wavevector $\mathbf{k} = (k_x, k_y, k_z)$ and angular frequency $\omega_{\mathbf{k}} = c|\mathbf{k}|$, $\hat{\mathbf{p}}$ is the electron’s momentum operator and $\hat{\mathbf{A}}_{\mathbf{k}}$ is the vector potential operator:

$$\hat{\mathbf{A}}_{\mathbf{k}} = \sum_{\lambda=1}^2 \epsilon_{\mathbf{k},\lambda} \left(\frac{\hbar}{2\omega_{\mathbf{k}} V \epsilon_0} \right)^{1/2} \left(\hat{a}_{\mathbf{k},\lambda}^\dagger + \hat{a}_{\mathbf{k},\lambda} \right). \quad (2)$$

where we have used the dipole approximation, i.e., $e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$. Here, V stands for the system’s volume, ϵ_0 is the vacuum permittivity, and $\epsilon_{\mathbf{k},\lambda}$ are the two polarization vectors, which satisfy the following conditions:

$$\begin{aligned} \epsilon_{\mathbf{k},1} &= \frac{\mathbf{e}_1 \times \mathbf{k}}{|\mathbf{e}_1 \times \mathbf{k}|}, \\ \epsilon_{\mathbf{k},2} &= \epsilon_{\mathbf{k},1} \times \frac{\mathbf{k}}{|\mathbf{k}|}, \end{aligned} \quad (3)$$

where \mathbf{e}_1 stands for the unit vector in the x direction. These polarization vectors allow us to simplify the interaction term if we consider a one-dimensional electronic system with $\hat{\mathbf{p}} = \hat{p}_x \mathbf{e}_1$:

$$\hat{\mathbf{A}}_{\mathbf{k}} \cdot \hat{\mathbf{p}} = -\frac{(k_y^2 + k_z^2)^{1/2}}{|\mathbf{k}|} \left(\frac{\hbar}{2\omega_{\mathbf{k}} V \epsilon_0} \right)^{1/2} \left(\hat{a}_{\mathbf{k}}^\dagger + \hat{a}_{\mathbf{k}} \right) \hat{p}_x. \quad (4)$$

Here, for simplicity, we have omitted the λ index from the $\hat{a}_{\mathbf{k}}$ and $\hat{a}_{\mathbf{k}}^\dagger$ operators.

Since we are interested in the electronic subsystem, we will obtain the evolution of its reduced density operator by tracing the full Liouville-von Neumann equation over the photonic degrees of freedom:

$$i\hbar \frac{d}{dt} \hat{\rho}(t) = \left[\hat{H}_S, \hat{\rho}(t) \right] + \sum_{\mathbf{k}} \left[\hat{p}_x, \text{Tr}_{\text{ph}} \left(\hat{A}_{\mathbf{k},x} \hat{\rho}_T(t) \right) \right], \quad (5)$$

where $\hat{\rho}$ is the reduced density operator of the electronic subsystem, $\hat{\rho}_T$ is the density operator of the total system, Tr_{ph} implies the partial trace over the photonic degrees of freedom, and $\hat{A}_{\mathbf{k},x}$ is the x -component of $\hat{\mathbf{A}}_{\mathbf{k}}$, which we will denote simply as $\hat{A}_{\mathbf{k}}$ from now on, since in our treatment it is the only relevant component. We can formally integrate the total density matrix in the interaction picture to obtain:

$$\hat{\rho}_T(t) = e^{-i\hat{H}_0 t/\hbar} \hat{\rho}(0) e^{i\hat{H}_0 t/\hbar} + \frac{1}{i\hbar} \sum_{\mathbf{k}} \frac{e}{m} \int_0^t e^{i\hat{H}_0(\tau-t)/\hbar} \left[\hat{A}_{\mathbf{k}} \hat{p}_x, \hat{\rho}_T(\tau) \right] e^{-i\hat{H}_0(\tau-t)/\hbar} d\tau, \quad (6)$$

where

$$\hat{H}_0 = \hat{H}_S + \hat{H}_B = \hat{H}_S + \sum_{\mathbf{k}} \sum_{\lambda=1}^2 \hbar \omega_{\mathbf{k}} \left(\hat{a}_{\mathbf{k},\lambda}^\dagger \hat{a}_{\mathbf{k},\lambda} + \frac{1}{2} \right), \quad (7)$$

is the unperturbed Hamiltonian.

Using equation 6, we can write:

$$\text{Tr}_{\text{ph}} \left(\hat{A}_{\mathbf{k}} \hat{\rho}_T(t) \right) = \frac{e}{mi\hbar} \text{Tr}_{\text{ph}} \left\{ \sum_{\mathbf{k}'} \left(\int_0^t \hat{p}_x^{\tau-t} \hat{A}_{\mathbf{k}} \hat{A}_{\mathbf{k}'}^{\tau-t} \hat{\rho}_T^{\tau-t}(\tau) d\tau - \int_0^t \hat{\rho}_T^{\tau-t}(\tau) \hat{A}_{\mathbf{k}'}^{\tau-t} \hat{A}_{\mathbf{k}} \hat{p}_x^{\tau-t} d\tau \right) \right\}, \quad (8)$$

where we have used the notation $\hat{Q}^t = e^{i\hat{H}_0 t/\hbar} \hat{Q} e^{-i\hat{H}_0 t/\hbar}$. Applying the decomposition $\hat{A}\hat{B} = (1/2)[\hat{A}, \hat{B}] + (1/2)\{\hat{A}, \hat{B}\}$ gives:

$$\begin{aligned} \text{Tr}_{\text{ph}} \left(\hat{A}_{\mathbf{k}} \hat{\rho}_T(t) \right) &= \frac{e}{2mi\hbar} \text{Tr}_{\text{ph}} \left(\sum_{\mathbf{k}'} \int_0^t [\hat{p}_x^{\tau-t}, \hat{\rho}_T^{\tau-t}(\tau)] \left\{ \hat{A}_{\mathbf{k}}, \hat{A}_{\mathbf{k}'}^{\tau-t} \right\} d\tau \right) \\ &\quad + \frac{e}{2mi\hbar} \text{Tr}_{\text{ph}} \left(\sum_{\mathbf{k}'} \int_0^t \left\{ \hat{p}_x^{\tau-t}, \hat{\rho}_T^{\tau-t}(\tau) \right\} \left[\hat{A}_{\mathbf{k}}, \hat{A}_{\mathbf{k}'}^{\tau-t} \right] d\tau \right). \end{aligned} \quad (9)$$

Since we have:

$$\hat{A}_{\mathbf{k}}^{\tau-t} = -\frac{(k_y^2 + k_z^2)^{1/2}}{|\mathbf{k}|} \left(\frac{\hbar}{2\omega_{\mathbf{k}} V \varepsilon_0} \right)^{1/2} \left(\hat{a}_{\mathbf{k}}^\dagger e^{i\omega_{\mathbf{k}}(\tau-t)} + \hat{a}_{\mathbf{k}} e^{-i\omega_{\mathbf{k}}(\tau-t)} \right), \quad (10)$$

we can use:

$$\sum_{\mathbf{k}'} \left[\hat{A}_{\mathbf{k}}, \hat{A}_{\mathbf{k}'}^{\tau-t} \right] = i \frac{k_y^2 + k_z^2}{|\mathbf{k}|^2} \frac{\hbar}{\omega_{\mathbf{k}} V \varepsilon_0} \sin(\omega_{\mathbf{k}}(\tau-t)). \quad (11)$$

and, under the assumption that the coupling between the electronic system and the photons is weak enough to consider harmonic behaviour:

$$\text{Tr}_{\text{ph}} \left(\sum_{\mathbf{k}'} \left\{ \hat{A}_{\mathbf{k}}, \hat{A}_{\mathbf{k}'}^{\tau-t} \right\} \hat{\rho}_{\text{ph}}^{\tau-t}(\tau) \right) \approx \frac{k_y^2 + k_z^2}{|\mathbf{k}|^2} \frac{\hbar}{\omega_{\mathbf{k}} V \varepsilon_0} (2N_{\mathbf{k}}(\tau) + 1) \cos(\omega_{\mathbf{k}}(\tau-t)), \quad (12)$$

we finally get:

$$\begin{aligned} \text{Tr}_{\text{ph}} \left(\hat{A}_{\mathbf{k}} \hat{\rho}_T(t) \right) &= \frac{e}{2m\omega_{\mathbf{k}} i \varepsilon_0 V} \frac{k_y^2 + k_z^2}{|\mathbf{k}|^2} \int_0^t [\hat{p}_x^{\tau-t}, \hat{\rho}_T^{\tau-t}(\tau)] (2N_{\mathbf{k}}(\tau) + 1) \cos(\omega_{\mathbf{k}}(\tau-t)) d\tau \\ &\quad + \frac{e}{2m\omega_{\mathbf{k}} \varepsilon_0 V} \frac{k_y^2 + k_z^2}{|\mathbf{k}|^2} \int_0^t \left\{ \hat{p}_x^{\tau-t}, \hat{\rho}_T^{\tau-t}(\tau) \right\} \sin(\omega_{\mathbf{k}}(\tau-t)) d\tau. \end{aligned} \quad (13)$$

Now, we will assume that the distribution of photon modes is isotropic and dense enough to replace the summation over the wavevectors \mathbf{k} by an integral. We additionally introduce the operators $\hat{\chi}^A$ and

$\hat{\chi}^B$, whose matrix elements in the basis of eigenstates of \hat{H}_S are given by:

$$\chi_{nn'}^A(k, k') = \int_0^\infty \frac{e\omega_{\mathbf{k}}}{6i\pi^2 m \varepsilon_0 c^3} (2N_{\mathbf{k}} + 1) \int_0^t p_{nn'}^{\tau-t}(k, k') \cos(\omega_{\mathbf{k}}(\tau - t)) d\tau d\omega_{\mathbf{k}}, \quad (14)$$

$$\chi_{nn'}^B(k, k') = \int_0^\infty \frac{e\omega_{\mathbf{k}}}{6\pi^2 m \varepsilon_0 c^3} \int_0^t p_{nn'}^{\tau-t}(k, k') \sin(\omega_{\mathbf{k}}(\tau - t)) d\tau d\omega_{\mathbf{k}}. \quad (15)$$

Let's first consider the following integral:

$$\chi_{nn'}^A(k, k') = \int_0^\infty \frac{e\omega_{\mathbf{k}}}{12i\pi^2 m \varepsilon_0 c^3} (2N_{\mathbf{k}} + 1) \int_0^t p_{nn'}(k, k') e^{i\omega_{nn'}(k, k')(\tau-t)} \left(e^{i\omega_{\mathbf{k}}(\tau-t)} + e^{-i\omega_{\mathbf{k}}(\tau-t)} \right) d\tau d\omega_{\mathbf{k}}, \quad (16)$$

where the integration as a function of τ can be solved by replacing $s = \tau - t$ with the following limits:

$$\begin{aligned} & \lim_{\epsilon \rightarrow 0^+} \lim_{s \rightarrow -\infty} p_{nn'}(k, k') \int_s^0 e^{i(\omega_{nn'}(k, k') + \omega_{\mathbf{k}} - i\epsilon)s} + e^{i(\omega_{nn'}(k, k') - \omega_{\mathbf{k}} - i\epsilon)s} ds \\ &= \lim_{\epsilon \rightarrow 0^+} \frac{p_{nn'}(k, k')}{i} \left(\frac{1}{\omega_{nn'}(k, k') + \omega_{\mathbf{k}} - i\epsilon} + \frac{1}{\omega_{nn'}(k, k') - \omega_{\mathbf{k}} - i\epsilon} \right) \\ &= \lim_{\epsilon \rightarrow 0^+} \frac{p_{nn'}(k, k')}{i} \left(\frac{\omega_{nn'}(k, k') + \omega_{\mathbf{k}} + i\epsilon}{(\omega_{nn'}(k, k') + \omega_{\mathbf{k}})^2 + \epsilon^2} + \frac{\omega_{nn'}(k, k') - \omega_{\mathbf{k}} + i\epsilon}{(\omega_{nn'}(k, k') - \omega_{\mathbf{k}})^2 + \epsilon^2} \right) \\ &= \frac{p_{nn'}(k, k')}{i} \left(\frac{1}{\omega_{nn'}(k, k') + \omega_{\mathbf{k}}} + \frac{1}{\omega_{nn'}(k, k') - \omega_{\mathbf{k}}} + \pi i \delta(\omega_{nn'}(k, k') + \omega_{\mathbf{k}}) + \pi i \delta(\omega_{nn'}(k, k') - \omega_{\mathbf{k}}) \right). \end{aligned} \quad (17)$$

Therefore, we can write:

$$\begin{aligned} \chi_{nn'}^A(k, k') &= - \int_0^\infty \frac{ep_{nn'}(k, k')\omega_{\mathbf{k}}}{12\pi^2 m \varepsilon_0 c^3} (2N_{\mathbf{k}} + 1) \\ &\times \left(\frac{1}{\omega_{nn'}(k, k') + \omega_{\mathbf{k}}} + \frac{1}{\omega_{nn'}(k, k') - \omega_{\mathbf{k}}} + \pi i \delta(\omega_{nn'}(k, k') + \omega_{\mathbf{k}}) + \pi i \delta(\omega_{nn'}(k, k') - \omega_{\mathbf{k}}) \right) d\omega_{\mathbf{k}}. \end{aligned} \quad (18)$$

Following the same rationale, the expression for the matrix elements of $\hat{\chi}^B$ yields:

$$\begin{aligned} \chi_{nn'}^B(k, k') &= - \int_0^\infty \frac{ep_{nn'}(k, k')\omega_{\mathbf{k}}}{12\pi^2 m \varepsilon_0 c^3} \\ &\times \left(\frac{1}{\omega_{nn'}(k, k') + \omega_{\mathbf{k}}} + \frac{1}{\omega_{nn'}(k, k') - \omega_{\mathbf{k}}} + \pi i \delta(\omega_{nn'}(k, k') + \omega_{\mathbf{k}}) - \pi i \delta(\omega_{nn'}(k, k') - \omega_{\mathbf{k}}) \right) d\omega_{\mathbf{k}}. \end{aligned} \quad (19)$$

We retain only the Dirac delta functions, discarding the Lamb shift terms, resulting in the final expressions for the matrix elements:

$$\begin{aligned} \chi_{nn'}^A(k, k') &\approx - \int_0^\infty \frac{ep_{nn'}(k, k')\omega_{\mathbf{k}}}{12\pi^2 m \varepsilon_0 c^3} (2N_{\mathbf{k}} + 1) (\pi i \delta(\omega_{nn'}(k, k') + \omega_{\mathbf{k}}) + \pi i \delta(\omega_{nn'}(k, k') - \omega_{\mathbf{k}})) d\omega_{\mathbf{k}} \\ &= - \frac{ie p_{nn'}(k, k') |\omega_{nn'}(k, k')|}{12\pi m \varepsilon_0 c^3} (2N(|\omega_{nn'}(k, k')| + 1)), \end{aligned} \quad (20)$$

$$\begin{aligned} \chi_{nn'}^B(k, k') &\approx - \int_0^\infty \frac{ep_{nn'}(k, k')\omega_{\mathbf{k}}}{12\pi^2 m \varepsilon_0 c^3} (\pi i \delta(\omega_{nn'}(k, k') + \omega_{\mathbf{k}}) - \pi i \delta(\omega_{nn'}(k, k') - \omega_{\mathbf{k}})) d\omega_{\mathbf{k}} \\ &= \frac{ie p_{nn'}(k, k') \omega_{nn'}(k, k')}{12\pi m \varepsilon_0 c^3}. \end{aligned} \quad (21)$$

Thus, we can rewrite equation 5 as:

$$i\hbar \frac{d}{dt} \hat{\rho} = [\hat{H}_S, \hat{\rho}] + \frac{e}{m} [\hat{p}, [\hat{\chi}^A, \hat{\rho}] + \{\hat{\chi}^B, \hat{\rho}\}]. \quad (22)$$

In order to get the master equation for the one-electron density operator, we need to trace over the degrees of freedom of the electrons, denoted as Tr_{2,\dots,N_e} , where N_e is the total number of electrons. Since we consider $\hat{H}_S, \hat{\chi}^A$ and $\hat{\chi}^B$ as single electron operators, tracing over the related commutators leads to the same expression. For the anticommutator, we have:

$$\text{Tr}_{2,\dots,N_e} (\{\hat{\chi}^B, \hat{\rho}\}) = \{\hat{\chi}^{B,oe}(1), \hat{\rho}^{oe}(1)\} + 2 \text{Tr}_2 (\hat{\chi}^{B,te}(2) \hat{\rho}^{te}(1, 2)), \quad (23)$$

where the superscripts *oe* and *te* indicate one- and two-electron operators, respectively, with the numbers in parentheses specifying the electrons on which the operators act. Assuming a basis of independent electrons, we can write:

$$2 \text{Tr}_2 (\hat{\chi}^{B,te}(2) \hat{\rho}^{te}(1, 2)) = -2 \hat{\rho}^{oe}(1) \hat{\chi}^{B,oe}(1) \hat{\rho}^{oe}(1) + 4 \hat{\rho}^{oe}(1) \text{Tr} (\hat{\chi}^{B,oe}(1) \hat{\rho}^{oe}(1)). \quad (24)$$

In this way, we arrive at the final master equation for the single-electron density operator:

$$i\hbar \frac{d}{dt} \hat{\rho} = [\hat{H}_S, \hat{\rho}] + \frac{e}{m} [\hat{p}, [\hat{\chi}^A, \hat{\rho}]] + \frac{e}{m} [\hat{p}, \{\hat{\chi}^B, \hat{\rho}\}] + 4 \hat{\rho} \text{Tr} (\hat{\rho} \hat{\chi}^B) - 2 \hat{\rho} \hat{\chi}^B \hat{\rho} \quad (25)$$

2 Matrix elements of the velocity operator

Before deriving the matrix elements of the velocity operator, we need to establish some additional properties of our system. We are dealing with a linear chain of dimers, with each atom corresponding to the same element. The atomic basis functions in the unit cell with index j are designated by $|L_j\rangle, |R_j\rangle$. The distance between the atoms L_j and R_j inside cell j is d_1 while that between R_j and L_{j+1} is d_2 . The lattice parameter is given by $a = d_1 + d_2$. The electronic structure is described by the Su-Schrieffer-Heeger (SSH) model, using the tight-binding Hamiltonian in real space:

$$\hat{H}_S = \beta_1 \sum_j^N |R_j\rangle \langle L_j| + \beta_2 \sum_j^N |L_{j+1}\rangle \langle R_j| + \text{h.c.}, \quad (26)$$

where β_1 and β_2 represent the hopping energies and N is the number of unit cells. Since our system is periodic, the eigenstates of \hat{H}_S can be written as Bloch states:

$$|nk\rangle = \frac{1}{\sqrt{N}} \sum_j^N e^{ikaj} [c_{L,n}(k) |L_j\rangle + c_{R,n}(k) |R_j\rangle], \quad (27)$$

where n is the band index and k the wavevector. The expansion coefficients $c_{L,n}(k)$ and $c_{R,n}(k)$ can be obtained by solving the eigenvalue problem:

$$\begin{pmatrix} 0 & \beta_1 + \beta_2 e^{-iak} \\ \beta_1 + \beta_2 e^{iak} & 0 \end{pmatrix} \begin{pmatrix} c_{L,n}(k) \\ c_{R,n}(k) \end{pmatrix} = E_n(k) \begin{pmatrix} c_{L,n}(k) \\ c_{R,n}(k) \end{pmatrix}. \quad (28)$$

After diagonalizing, the eigenvalues obtained are:

$$\begin{aligned} E_1(k) &= -\sqrt{(\beta_1 - \beta_2)^2 + 4\beta_1\beta_2 \cos^2\left(\frac{ka}{2}\right)}, \\ E_2(k) &= \sqrt{(\beta_1 - \beta_2)^2 + 4\beta_1\beta_2 \cos^2\left(\frac{ka}{2}\right)}. \end{aligned} \quad (29)$$

The normalized coefficients for the band with index $n = 1$ are given by:

$$\begin{aligned} c_{L,1}(k) &= \frac{f(k)}{\sqrt{1 + |f(k)|^2}}, \\ c_{R,1}(k) &= \frac{1}{\sqrt{1 + |f(k)|^2}}, \end{aligned} \quad (30)$$

where we have defined the complex function $f(k)$:

$$f(k) = -\frac{\sqrt{(\beta_1 - \beta_2)^2 + 4\beta_1\beta_2 \cos^2\left(\frac{ka}{2}\right)}}{\beta_1 + \beta_2 e^{iak}}. \quad (31)$$

For the band with index $n = 2$ we have:

$$\begin{aligned} c_{L,2}(k) &= \frac{g(k)}{\sqrt{1 + |g(k)|^2}}, \\ c_{R,2}(k) &= \frac{1}{\sqrt{1 + |g(k)|^2}}, \end{aligned} \quad (32)$$

where now we defined $g(k)$ as:

$$g(k) = \frac{\sqrt{(\beta_1 - \beta_2)^2 + 4\beta_1\beta_2 \cos^2\left(\frac{ka}{2}\right)}}{\beta_1 + \beta_2 e^{iak}}. \quad (33)$$

The electronic position operator, \hat{x} , of a linear, non-periodic chain can be defined as:

$$\hat{x} = \sum_j \left(ja\hat{I}_j^+ + \frac{d_1}{2}\hat{I}_j^- \right), \quad (34)$$

where

$$\hat{I}_j^\pm = |R_j\rangle\langle R_j| \pm |L_j\rangle\langle L_j|. \quad (35)$$

Now, we define the velocity operator, \hat{v} , as:

$$\hat{v} = \frac{1}{i\hbar} [\hat{x}, \hat{H}]. \quad (36)$$

It is important to note that, even if the position operator becomes ill-defined when applying periodic boundary conditions, the velocity operator remains meaningful since it is translationally invariant. Therefore, in the following, \hat{x} serves merely as a tool for the matrix elements of the velocity operator, which holds actual physical relevance.

The matrix elements of \hat{v} are computed in the space spanned by the eigenstates $|nk\rangle$ of the Hamiltonian \hat{H}_S . Within this representation, we have

$$\begin{aligned} \langle nk|\hat{v}|n'k'\rangle &= \frac{1}{i\hbar} \langle nk| [\hat{x}, \hat{H}] |n'k'\rangle \\ &= \frac{1}{i\hbar} \sum_j \left(ja\langle nk|\hat{I}_j^+|n'k'\rangle + \frac{d_1}{2}\langle nk|\hat{I}_j^-|n'k'\rangle \right) (E_{n'}(k') - E_n(k)). \end{aligned} \quad (37)$$

Each term can be worked out separately. For the first one, we have:

$$\begin{aligned} & \frac{1}{i\hbar} (E_{n'}(k') - E_n(k)) \sum_j ja \langle nk | \hat{I}_j^+ | n'k' \rangle \\ &= \frac{\delta_{k,k'}}{\hbar} \left[\delta_{n,n'} \frac{dE_{n'}(k)}{dk} + (E_{n'}(k') - E_n(k)) \langle \phi_n(k) | \frac{d\phi_{n'}(k)}{dk} \rangle \right], \end{aligned} \quad (38)$$

where we have defined

$$|\phi_n(k)\rangle = c_{L,n}(k)|L\rangle + c_{R,n}(k)|R\rangle. \quad (39)$$

For the second term, we have:

$$\begin{aligned} & \frac{d_1}{2i\hbar} (E_{n'}(k') - E_n(k)) \sum_j \langle nk | \hat{I}_j^- | n'k' \rangle \\ &= \delta_{k,k'} \frac{d_1}{2i\hbar} (E_{n'}(k) - E_n(k)) [c_{R,n}^*(k)c_{R,n'}(k) - c_{L,n}^*(k)c_{L,n'}(k)]. \end{aligned} \quad (40)$$

3 Master equation for an electronic system coupled to a phonon bath

Since we will define the matrix elements of the force operator for our electronic system—a linear chain of dimers composed of same-element atoms—in close analogy to the simpler case of a chain with one atom per unit cell, we begin the analysis with this system. Under the nearest-neighbor orthornormal tight-binding approximation, the Hamiltonian is defined as:

$$\hat{H}_S = \beta \sum_j^N (|j+1\rangle\langle j| + |j-1\rangle\langle j|) + \text{h.c.}, \quad (41)$$

where $\{|j\rangle\}$ correspond to the atomic basis states, \hat{H}_S is the electronic Hamiltonian operator, and β is the hopping integral. Due to the system's translational symmetry, the eigenstates of the Hamiltonian can be expressed as Bloch states of the form:

$$|k\rangle = \frac{1}{\sqrt{N}} \sum_j^N e^{ijk a} |j\rangle. \quad (42)$$

Here, N represents the number of unit cells, and a the lattice parameter. The force operator over atom j can be defined, in our nearest-neighbor approximation, as:

$$\hat{F}_j = -\beta' (|j\rangle\langle j-1| - |j\rangle\langle j+1|) + \text{h.c.}, \quad (43)$$

where β' is a parameter that sets the magnitude of the force. Thus, the matrix elements of \hat{F}_j in the basis of eigenstates of \hat{H}_S are given by:

$$\langle k | \hat{F}_j | k' \rangle = -\frac{2i\beta' e^{ij(k'-k)a}}{N} (\sin(ka) - \sin(k'a)). \quad (44)$$

In the case of the dimerized chain, we will define the matrix elements of the force operator analogously to the monoatomic scenario:

$$\langle nk | \hat{F}_j | n'k' \rangle = F_{j,nn'}(k, k') = -\frac{2i}{N} \delta_{nn'} \beta'_n e^{ij(k'-k)a} (\sin(ka) - \sin(k'a)), \quad (45)$$

where j is the cell index. This model assumes that the force operator has non-zero matrix elements only within the same band, allowing us to define two parameters β'_n , one for the valence band and another for the conduction band.

The total Hamiltonian of the electronic system coupled to the phonon bath is given by

$$\hat{H} = \hat{H}_S + \hat{H}_P + \hat{H}_C, \quad (46)$$

where \hat{H}_P is the Hamiltonian of the phonon bath, corresponding to a set of uncoupled harmonic oscillators:

$$\hat{H}_P = \sum_j \hbar \Omega_j \left(\hat{N}_j + \frac{1}{2} \right), \quad (47)$$

where, as usual, \hat{N}_j denotes the particle number operator associated with mode j , with angular frequency Ω_j . The electron-phonon coupling Hamiltonian, \hat{H}_C , is linear with respect to the displacement of ions from their equilibrium positions:

$$\hat{H}_C = \sum_j \hat{F}_j \hat{X}_j. \quad (48)$$

where \hat{X}_j corresponds to a configuration coordinate for displacement of ions in cell j , and \hat{F}_j is the force operator, which couples first-neighbors.

The derivation of the master equation is analogous to the procedure detailed in *Bustamante et al., J. Chem. Phys. 158, 144104 (2023)*, resulting in:

$$i\hbar \frac{d}{dt} \hat{\rho} = \left[\hat{H}_S, \hat{\rho} \right] - \sum_j \left[\hat{F}_j, [\hat{\eta}_j^A, \hat{\rho}] + \{ \hat{\eta}_j^B, \hat{\rho} \} - 2\hat{\rho} \hat{\eta}_j^B \hat{\rho} \right], \quad (49)$$

where the matrix elements of the operators $\hat{\eta}_j^A$ and $\hat{\eta}_j^B$ in the basis of eigenstates of \hat{H}_S are given by:

$$\eta_{j,nn'}^A(k, k') = \frac{i\pi F_{j,nn'}(k, k')(2N(|\omega_{nn'}(k, k')|) + 1)}{4M|\omega_{nn'}(k, k')|\Delta\Omega}, \quad (50)$$

$$\eta_{j,nn'}^B(k, k') = -\frac{i\pi F_{j,nn'}(k, k')}{4M\omega_{nn'}(k, k')\Delta\Omega}. \quad (51)$$

Here, $\omega_{nn'}(k, k')$ represents the frequency associated with the transition from electronic state $|nk\rangle$ to $|n'k'\rangle$, where $\hbar\omega_{nn'}(k, k') = E_n(k) - E_{n'}(k')$, with $E_n(k)$ being the energy of the electronic levels. Additionally $N(|\omega_{nn'}(k, k')|) = (e^{\hbar|\omega_{nn'}(k, k')|/k_B T} - 1)^{-1}$ with T the bath temperature, M an effective nuclear mass, and $\Delta\Omega = \Omega_{\max} - \Omega_{\min}$ the range of phonon bath frequencies. We assume a uniform density of states for the phonon modes of angular frequency Ω , which is $1/\Delta\Omega$ in the range $\Omega_{\min} \leq \Omega \leq \Omega_{\max}$ and zero outside this range. Consequently, if $|\omega_{nn'}(k, k')| < \Omega_{\min}$ or $|\omega_{nn'}(k, k')| > \Omega_{\max}$, the corresponding matrix elements $\eta_{j,nn'}^A(k, k')$ and $\eta_{j,nn'}^B(k, k')$ are zero.

Equation 49 involves summations over products between the operators \hat{F}_j and $\hat{\eta}_j^i$ (for $i = A, B$). Since different phonon modes are uncorrelated, we have:

$$\sum_j F_{j,nn'}(k, k') \eta_{j,n''n'''}^{(i)}(k'', k''') \propto \frac{1}{N^2} \sum_j e^{ij(k'-k)a} e^{ij(k'''-k'')a} = \frac{\delta_{k'-k, k''-k'''}}{N}. \quad (52)$$

Therefore, these products will be non-zero only when:

$$k' - k + k''' - k'' = 0. \quad (53)$$

Finally, we define the phonon driving term, $\hat{\Lambda}_{\text{vib}}$ as:

$$\hat{\Lambda}_{\text{vib}} = - \sum_j \left[\hat{F}_j, [\hat{\eta}_j^A, \hat{\rho}] + \{ \hat{\eta}_j^B, \hat{\rho} \} - 2\hat{\rho}\hat{\eta}_j^B\hat{\rho} \right]. \quad (54)$$

4 Semiclassical and QED-based emitted powers

The radiated power by an electronic system with a time-independent Hamiltonian \hat{H}_S following a master equation of the type

$$i\hbar \frac{d}{dt} \hat{\rho} = \left[\hat{H}_S, \hat{\rho} \right] + \hat{\Lambda}_{\text{rad}}, \quad (55)$$

is given by

$$P = -\frac{2}{i\hbar} \text{Tr} \left(\hat{H}_S \hat{\Lambda}_{\text{rad}} \right). \quad (56)$$

where the factor of 2 arises from spin degeneracy. In our case:

$$\hat{\Lambda}_{\text{rad}} = \frac{e}{m} [\hat{p}, [\hat{\chi}^A, \hat{\rho}]] + \frac{e}{m} [\hat{p}, \{ \hat{\chi}^B, \hat{\rho} \} + 4\hat{\rho} \text{Tr} (\hat{\rho} \hat{\chi}^B) - 2\hat{\rho} \hat{\chi}^B \hat{\rho}], \quad (57)$$

with the $\hat{\chi}^A$ and $\hat{\chi}^B$ operators given according to

$$\chi_{nn'}^A(k, k') = -\frac{ie p_{nn'}(k, k') |\omega_{nn'}(k, k')|}{12\pi \epsilon_0 m c^3} (2N(|\omega_{nn'}(k, k')|) + 1), \quad (58)$$

$$\chi_{nn'}^B(k, k') = \frac{ie p_{nn'}(k, k') \omega_{nn'}(k, k')}{12\pi \epsilon_0 m c^3}. \quad (59)$$

$\hat{\Lambda}_{\text{rad}}$ can be separated into two contributions:

$$\hat{\Lambda}_{\text{SC}} = \frac{e}{m} [\hat{p}, 4\hat{\rho} \text{Tr} (\hat{\rho} \hat{\chi}^B)], \quad (60)$$

$$\hat{\Lambda}_{\text{QED}} = \frac{e}{m} [\hat{p}, [\hat{\chi}^A, \hat{\rho}]] + \frac{e}{m} [\hat{p}, \{ \hat{\chi}^B, \hat{\rho} \} - 2\hat{\rho} \hat{\chi}^B \hat{\rho}]. \quad (61)$$

Working in the state space spanned by the $|nk\rangle$, the eigenstates of \hat{H}_S , we can think of each k -point as a different emitter, and therefore compute the total emitted power as a sum of the power of each k -point:

$$\begin{aligned} P &= \sum_k [P_{\text{SC}}(k) + P_{\text{QED}}(k)] \\ &= -\frac{2}{i\hbar} \sum_k \sum_n \left(\langle nk | \hat{H}_S \hat{\Lambda}_{\text{SC}} | nk \rangle + \langle nk | \hat{H}_S \hat{\Lambda}_{\text{QED}} | nk \rangle \right). \end{aligned} \quad (62)$$

Using the previous formula for the semiclassical contribution yields:

$$P_{\text{SC}}(k) = -\frac{2}{i\hbar} \sum_n \langle nk | \hat{H}_S \hat{\Lambda}_{\text{SC}} | nk \rangle = -\frac{2}{i\hbar} \sum_n \langle nk | \hat{\Lambda}_{\text{SC}} | nk \rangle E_n(k), \quad (63)$$

where $\hat{H}_S |nk\rangle = E_n(k) |nk\rangle$. Considering expression 60, we obtain

$$\begin{aligned} P_{\text{SC}}(k) &= -\frac{8e}{i\hbar} \text{Tr} (\hat{\rho} \hat{\chi}^B) \sum_n \left(\sum_{n'} \langle nk | \hat{v} | n'k \rangle \langle n'k | \hat{\rho} | nk \rangle \right. \\ &\quad \left. - \sum_{n''} \langle nk | \hat{\rho} | n''k \rangle \langle n''k | \hat{v} | nk \rangle \right) E_n(k), \end{aligned} \quad (64)$$

where in the last equation we have made use of the fact that the momentum operator is diagonal in k . From expression 64, it can be seen that when $n = n' = n''$, the terms in the summations cancel out.

Therefore, the semiclassical power does not include a contribution arising from the diagonal elements of the density matrix (i.e., the populations), but only from the coherences.

In the particular case of a system with two bands, as the one studied in this work, expression 64 reduces to

$$P_{\text{SC}}(k) = \frac{8e^2\omega_{21}(k)}{3\pi\epsilon_0c^3}\text{Im}\left(\rho_{12}(k)v_{21}(k)\right) \sum_{k' \neq k} \omega_{21}(k')\text{Im}\left(\rho_{12}(k')v_{21}(k')\right) + \frac{2e^2\omega_{21}^2(k)}{3\pi\epsilon_0c^3} \left[2|\rho_{12}(k)|^2|v_{12}(k)|^2 - \rho_{12}^2(k)v_{21}^2(k) - \rho_{21}^2(k)v_{12}^2(k)\right], \quad (65)$$

where we have used the notation $f(k, k) = f(k)$ for the diagonal elements, to simplify the notation. In equation 65, we have separated the contribution to the semiclassical power into that independent of all k -points with $k' \neq k$ in the second line, and that including the effect of other excited k -points in the first line. In particular, for a system with only one k -point (i.e., a two-level system), only the second term survives.

The QED power can be computed in an analogous way. Again, for a system with only two bands, the result is:

$$P_{\text{QED}}(k) = \frac{e^2}{3\pi\epsilon_0c^3}\omega_{21}^2(k)|v_{21}(k)|^2 \left[(2N(|\omega_{21}(k)|) + 1)(\rho_{22}(k) - \rho_{11}(k)) + \rho_{22}(k) + \rho_{11}(k) - 2\rho_{11}(k)\rho_{22}(k) + \rho_{12}^2(k)\frac{v_{21}^2(k)}{|v_{21}(k)|^2} + \rho_{21}^2(k)\frac{v_{12}^2(k)}{|v_{21}(k)|^2} \right]. \quad (66)$$

5 Impact of chain length on subradiant transient states in emission dynamics

According to equation 64, the following proportional relationship exists for the emitted semiclassical power:

$$P_{\text{SC}} \propto -\text{Tr}(\hat{\rho}\hat{\chi}^B). \quad (67)$$

Using definition 59 for the matrix elements of the operator $\hat{\chi}^B$ in the $|nk\rangle$ basis of eigenstates of \hat{H}_S , we can write:

$$\begin{aligned} \chi_{nn'}^B(k, k') &= \langle nk|\hat{\chi}^B|n'k'\rangle = \frac{ie\langle nk|p|n'k'\rangle}{12\pi\hbar\epsilon_0mc^3} \left(\langle nk|\hat{H}_S|nk\rangle - \langle n'k'|\hat{H}_S|n'k'\rangle \right) \\ &= -\frac{ie}{12\pi\hbar\epsilon_0mc^3} \langle nk| [\hat{p}, \hat{H}_S] |n'k'\rangle. \end{aligned} \quad (68)$$

Therefore, the operator $\hat{\chi}^B$ can be expressed, using the definition of the velocity operator, as:

$$\hat{\chi}^B = \frac{e}{12\pi i\hbar\epsilon_0c^3} [\hat{v}, \hat{H}_S]. \quad (69)$$

On the other hand, the expectation value of the second derivative with respect to time of the electric dipole moment operator can be computed as:

$$\langle \ddot{\mu} \rangle = \frac{e}{(i\hbar)^2} \langle [[\hat{x}, \hat{H}_S], \hat{H}_S] \rangle = \frac{2e}{i\hbar} \text{Tr}(\hat{\rho} [\hat{v}, \hat{H}_S]). \quad (70)$$

Consequently:

$$P_{\text{SC}} \propto -\langle \ddot{\mu} \rangle. \quad (71)$$

Computing explicitly $\langle \ddot{\mu} \rangle$ with equation 70 for a system with two bands, we get:

$$\begin{aligned}
\langle \ddot{\mu} \rangle &= \frac{2e}{i\hbar} \sum_k \left(\langle 1k | \hat{\rho} [\hat{v}, \hat{H}_S] | 1k \rangle + \langle 2k | \hat{\rho} [\hat{v}, \hat{H}_S] | 2k \rangle \right) \\
&= \frac{2e}{i\hbar} \sum_k [E_1(k)(\langle 1k | \hat{\rho} \hat{v} | 1k \rangle - \langle 1k | \hat{v} \hat{\rho} | 1k \rangle) + E_2(k)(\langle 2k | \hat{\rho} \hat{v} | 2k \rangle - \langle 2k | \hat{v} \hat{\rho} | 2k \rangle)] \\
&= \frac{2e}{i\hbar} \sum_k E_1(k) (\rho_{11}(k)v_{11}(k) + \rho_{12}(k)v_{21}(k) - v_{11}(k)\rho_{11}(k) - v_{12}(k)\rho_{21}(k)) \\
&\quad + \frac{2e}{i\hbar} \sum_k E_2(k) (\rho_{22}(k)v_{22}(k) + \rho_{21}(k)v_{12}(k) - v_{22}(k)\rho_{22}(k) - v_{21}(k)\rho_{12}(k))
\end{aligned} \tag{72}$$

$$\langle \ddot{\mu} \rangle = \frac{2e}{i\hbar} \sum_k (E_2(k) - E_1(k))(\rho_{21}(k)v_{12}(k) - \rho_{12}(k)v_{21}(k)) = 4e \sum_k \omega_{21}(k) \text{Im}(\rho_{21}(k)v_{12}(k)). \tag{73}$$

Now, for a coherent system, we can write $\rho_{21}(k, t) = \sqrt{\rho_{11}(k)\rho_{22}(k)}e^{-i\omega_{21}(k)t}$, with t denoting time. Using the fact that the matrix elements $v_{12}(k)$ are purely imaginary in the $\{|nk\rangle\}$ representation, we finally obtain:

$$\langle \ddot{\mu}(t) \rangle = 4e \sum_k \sqrt{\rho_{11}(k, t)\rho_{22}(k, t)}\omega_{21}(k)|v_{21}(k, t)| \cos(\omega_{21}(k)t), \tag{74}$$

where we have made explicit which variables have time dependency. Equation 74 shows that the total semiclassical power radiated by the system is proportional to a sum of cosines for each k -point, where each term of the sum is modulated by distinct populations and frequency $\omega_{21}(k)$.

Although the previous summation in principle runs over all the reciprocal space, after irradiation with a monochromatic pulse, only a narrow range of k -points will have appreciable populations in the conduction band. Consequently, we can neglect those k -points whose excitation frequencies differ significantly to the pulse frequency, and restrict the summation to:

$$\langle \ddot{\mu}(t) \rangle \approx 8e \sum_{k_0 - \Delta k/2}^{k_0 + \Delta k/2} \sqrt{\rho_{11}(k, t)\rho_{22}(k, t)}\omega_{21}(k)|v_{21}(k, t)| \cos(\omega_{21}(k)t), \tag{75}$$

where k_0 is the k -point whose frequency is resonant with the laser, Δk denotes the range of reciprocal space that has a non-negligible conduction band population, and the additional multiplicative factor of 2 takes into account the symmetric nature for k and $-k$, since we are summing for only one of these pairs.

To gain additional insight into the implications of equation 75, we propose a series of assumptions, whose validity will be discussed later.

Firstly, we assume that the product $\sqrt{\rho_{11}(k, t)\rho_{22}(k, t)}\omega_{21}(k)|v_{21}(k, t)|$ varies slowly enough over the range $k_0 - \Delta k/2 \leq k \leq k_0 + \Delta k/2$, allowing us to approximate it by $\sqrt{\rho_{11}(k_0, t)\rho_{22}(k_0, t)}\omega_{21}(k_0)|v_{21}(k_0, t)|$. Secondly, we expand the excitation frequency $\omega_{21}(k)$ as a Taylor series around k_0 , retaining only the first-order term:

$$\omega_{21}(k) \approx \omega_{21}(k_0) + \left. \frac{d\omega_{21}}{dk} \right|_{k=k_0} (k - k_0). \tag{76}$$

Given that k -space is sampled uniformly, we can express k as $k = 2\pi j/(Na)$, where j is a non-negative integer, N is the number of k -points sampled, and a the lattice parameter. Using these assumptions, we

can write:

$$\langle \ddot{\mu}(t) \rangle \approx 8e \sqrt{\rho_{11}(k_0, t) \rho_{22}(k_0, t)} \omega_{21}(k_0) |v_{21}(k_0, t)| \sum_{j=j_{\min}}^{j=j_{\max}} \cos \left(\omega_{21}(k_0) t + \left. \frac{d\omega_{21}}{dk} \right|_{k=k_0} \left(\frac{2\pi j}{Na} - k_0 \right) t \right), \quad (77)$$

where j_{\min}, j_{\max} correspond to the values of j for $k_0 - \Delta k/2$ and $k_0 + \Delta k/2$, respectively.

Since each k -point has a slightly different frequency, the cosines in the sum can interfere constructively, leading to dissipation, or destructively, resulting in subradiant transient states. A period of this cycle will be completed when the argument of the cosine function for a given k -point equals that of its neighbors modulo 2π , i.e.:

$$\omega_{21}(k_0)T + \left. \frac{d\omega_{21}}{dk} \right|_{k=k_0} \cdot \left(\frac{2\pi j}{Na} - k_0 \right) T + 2\pi r = \omega_{21}(k_0)T + \left. \frac{d\omega_{21}}{dk} \right|_{k=k_0} \cdot \left(\frac{2\pi(j+1)}{Na} - k_0 \right) T, \quad (78)$$

where r is an integer and T is the period over which fully constructive interference is observed. Hence, we obtain:

$$T = rNa \left| \left. \frac{d\omega_{21}}{dk} \right|_{k=k_0} \right|^{-1}, \quad r \in \mathbb{N} \quad (79)$$

According to this result, the time intervals between subradiant steps should increase linearly with the numbers of k -points sampled (and therefore with the length of the linear chain). This trend is evident in Figure 1, where we plot the radiated energy as a function of time using the same laser parameters as in Section 3.2. of the main text ($E_0 = 1.3 \text{ V}\cdot\text{\AA}^{-1}$, $t_{\text{off}} = 50 \text{ fs}$ and $\omega = 11 \text{ fs}^{-1}$, corresponding to the excitation frequency at $k = \pi/2a$), but varied the number N of k -points sampled. In all cases, the excited state was evolved using the semiclassical driving term, $\hat{\Lambda}_{\text{SC}}$. As predicted by equation 79, the time needed to observe dissipation increases linearly with N .

Moreover, using equation 79 with the corresponding values for $d\omega_{21}/dk|_{k=-\pi/2a} = 15.75 \text{ eV fs}^{-1} \text{\AA}$, $a = 2.80 \text{ \AA}$, and $N = 400$, we predict a fundamental period of $T \approx 70 \text{ fs}$, which is in excellent agreement with the one observed in Figure 1 for the same value of N . This demonstrates that the first-order approximation of $\omega_{21}(k)$ is sufficient for the range of k -points with a non-negligible conduction band population.

The analysis leading to equation 79 not only correctly predicts the dependence of the period of the emission cycles on the length of the chain but also explains why the duration of the subradiant transient states (the plateaus that separate the periods of non-negligible dissipation) remains constant. This period is independent of any time-dependent quantity. On the other hand, the decrease in the radiated energy at each step can be understood from equation 77 as a consequence of the diminishing amplitude of the cosine functions, which occurs as the populations in the conduction band decrease over time.

The inclusion of the dependency of the amplitudes $\sqrt{\rho_{11}(k)\rho_{22}(k)}\omega_{21}(k)|v_{21}(k)|$ on k complicates the analysis. Despite the added complexity, equation 79 remains valid as long as the first-order expansion 76 holds over the range $k_0 \pm \Delta k/2$, since the amplitudes of the cosine functions are positive for all k . Therefore, the nature of the interference (constructive or destructive) is entirely determined by the dephasing of the cosines.

These results further suggest that for very dense grids in k -space, transient subradiant states should be long-lived. In the limit of a continuous number of k -points, summation 74 transforms into the integral:

$$\langle \ddot{\mu}(t) \rangle = \frac{4\pi e}{a} \int_{-\pi/a}^{\pi/a} \sqrt{\rho_{11}(k)\rho_{22}(k)} \omega_{21}(k) |v_{21}(k)| \cos(\omega_{21}(k)t) dk, \quad (80)$$

which asymptotically approaches zero for large t due to the destructive interference among a continuous

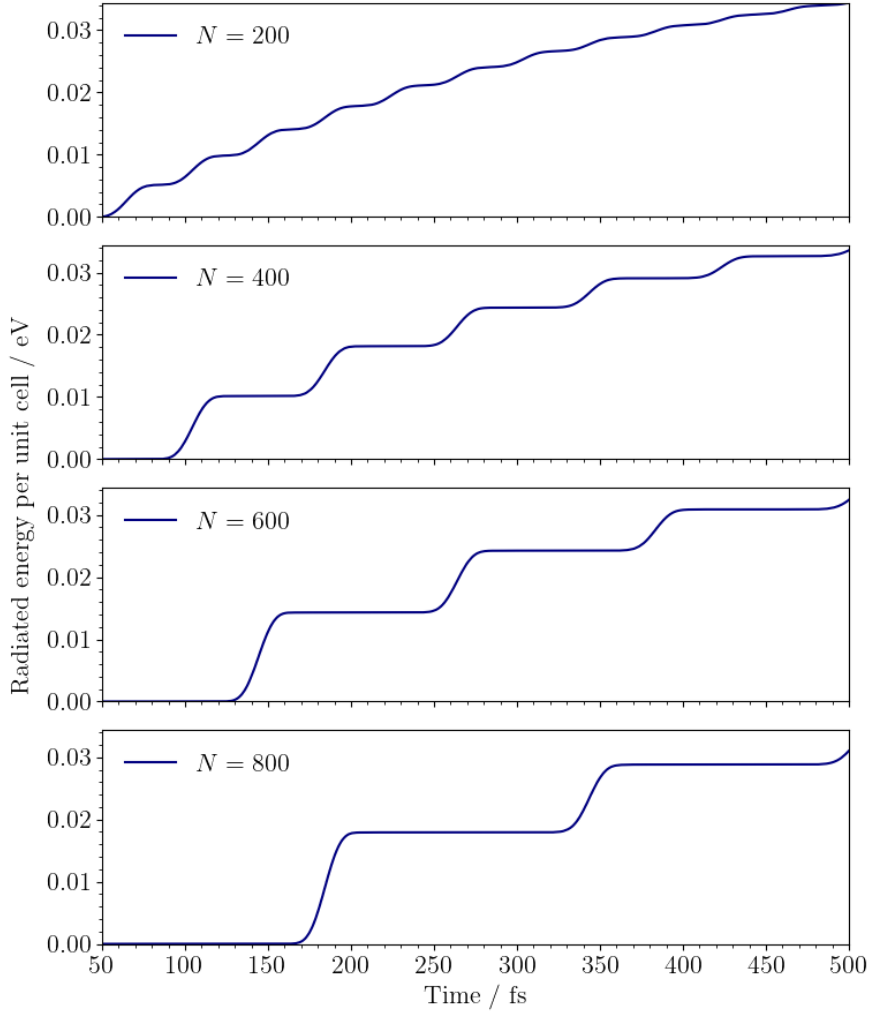


Figure 1: Radiated energy, computed as the time integral of the emitted power, for linear periodic systems with varying numbers of k -points sampled in reciprocal space, N . The initial excited states, prepared by irradiation with a laser pulse, were evolved using the semiclassical driving term scaled by an acceleration factor $f = 10^4$.

set of frequencies.