Light emission in real-time molecular simulations

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CMSP Seminar

Our Group

Molecular Simulation in Condensed Matter

Chemistry (Inorganic, Analytical, PhysChem)
Faculty of Sciences, University of Buenos Aires

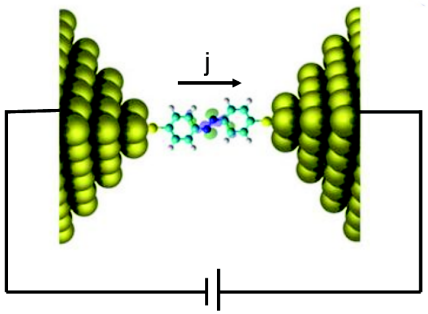
- Quantum dynamics for spectroscopy and transport
- Adsorption and reactivity on interfaces
- Water in nano-environments

Electron dynamics

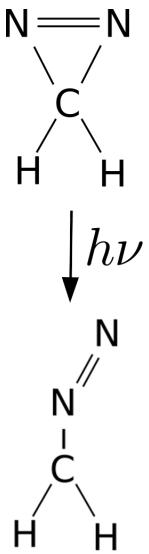
$$\frac{d}{dt}|\phi\rangle = -i\hat{H}|\phi\rangle \quad \textbf{or} \quad \frac{d\hat{\rho}}{dt} = -i[\hat{H},\hat{\rho}]$$

Real time simulations of:

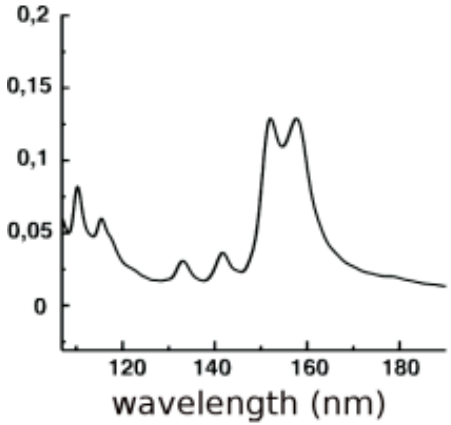
Transport



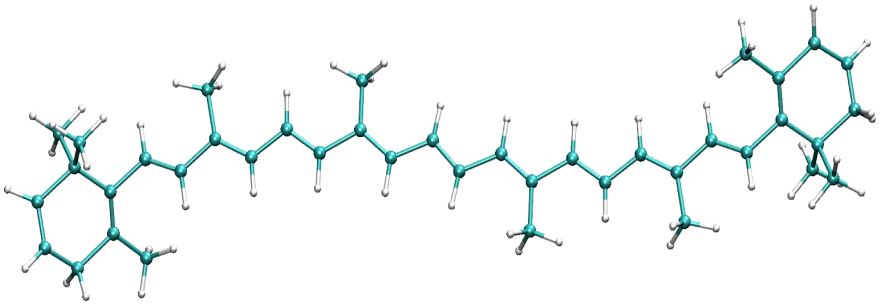
Photochemistry



Spectra



Electron density oscillations



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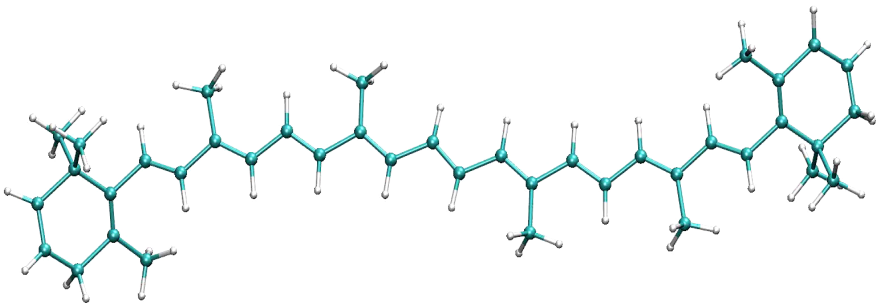
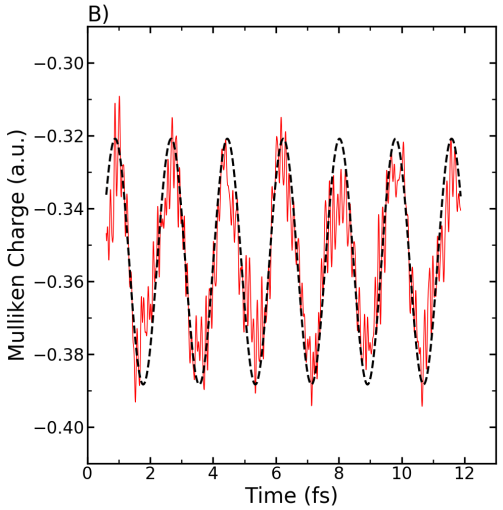
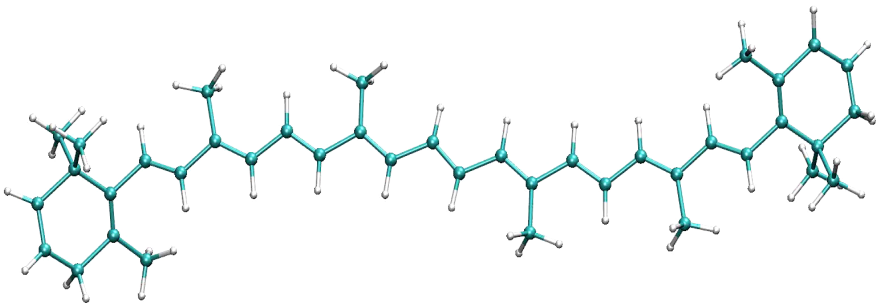
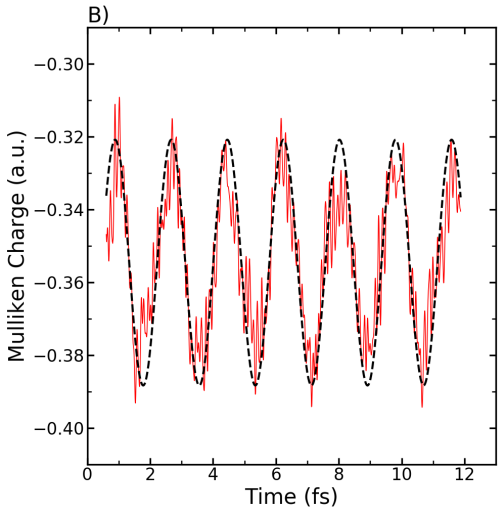




A perturbation leaves the charge density oscillating indefinitely in time, which is unphysical.

Electron density oscillations





A perturbation leaves the charge density oscillating indefinitely in time, which is unphysical.

$\frac{d\hat{\rho}}{dt} = -i[\hat{H}, \hat{\rho}]$ produces non-dissipative dynamics

Photons are missing

Radiative dissipation

$$\text{Radiative dissipation} \rightarrow \text{nanoseconds}$$

$$\left.\begin{array}{c}\text{Non-radiative dissipation} \\ \text{Typical electron dynamics simulations}\end{array}\right\} \rightarrow \text{picoseconds}$$

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Should we care about electromagnetic energy dissipation in atomistic simulations?

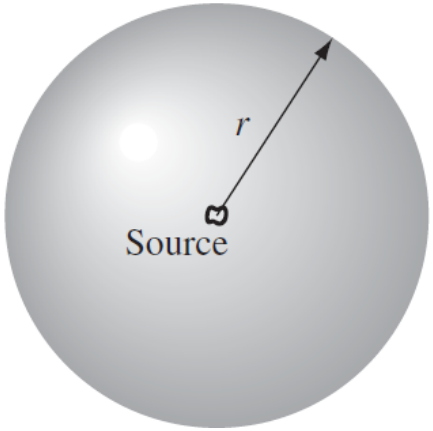
Well, in some cases, for example:

- Zero (nuclear) temperature dynamics
- Power from light-emitting systems
- Collective optical phenomena

Radiative dissipation in the classical picture

Let's assume that the charge density irradiates as a classical oscillating dipole emitting from an antenna.

$$P(r,t) = \oint \mathbf{S} \cdot d\mathbf{a} = \frac{1}{\mu_0} \oint (\mathbf{E} \times \mathbf{B}) \cdot d\mathbf{a}$$



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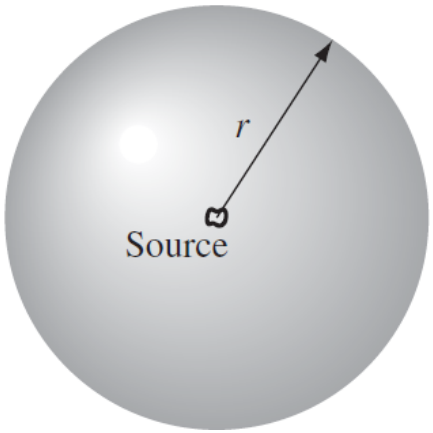

Under a few approximations, the power radiated by a moving dipole can be solved, to give the Larmor equation:

$$P_{rad} \cong \frac{\mu_0}{6\pi c}[\ddot{\mu}(t)]^2$$

Semiclassical approach: Lagrangian formulation

The time dependent Schrödinger equation for a set of single-particle wave-functions $|\phi_i\rangle$ is derivable from a Lagragian,

$$L = T(\dot{q}_1, \dot{q}_2, \cdots) - V(q_1, q_2, \cdots)$$

T: kinetic E ; V: potential E ; q: generalized coordinates

If:

$$T = \sum_j \langle \phi_j | i \frac{\partial}{\partial t} | \phi_j \rangle \quad ; \quad V = E_{electrons} \quad ; \quad q_i = |\phi_i\rangle$$

Then:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial |\dot{\phi}_j\rangle}\right) - \frac{\partial L}{\partial |\phi_j\rangle} = 0 \Rightarrow \quad \frac{d}{dt}|\phi_j\rangle = -i\hat{h}_j|\phi_j\rangle \quad \textbf{T.D.S.E.}$$

Lagrangian approach to the Schrödinger equation

In principle it must be possible to augment the Lagrangian with the radiative energy to get a dissipative EOM:

$$L = \sum_j \langle \phi_j | i \frac{\partial}{\partial t} | \phi_j \rangle + E_e + L_{rad}$$

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Using Larmor, $P_{rad} = \frac{\mu_0}{6\pi c}[\ddot{\mu}(t)]^2$:

$$L_{rad}(t) = \int_0^t P_{rad}\, dt = \frac{\mu_0}{6\pi c} \int_0^t \left[\frac{\partial^2 \mu}{\partial t^2}(t) \right]^2 dt$$

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Dissipative Lagrangian

An alternative pathway: Rayleigh dissipation function F

Lord Rayleigh (1870s'). Used in classical mechanics to introduce non-conservative forces, typically the friction:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} + \frac{\partial F}{\partial \dot{q}_i} = 0$$

F is half the energy dissipated per unit time.

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F is half the energy dissipated per unit time.

In the present case:

$$F = \frac{1}{2} P_{rad} \cong \frac{1}{2} \frac{\mu_0}{6\pi c} [\ddot{\mu}(t)]^2$$

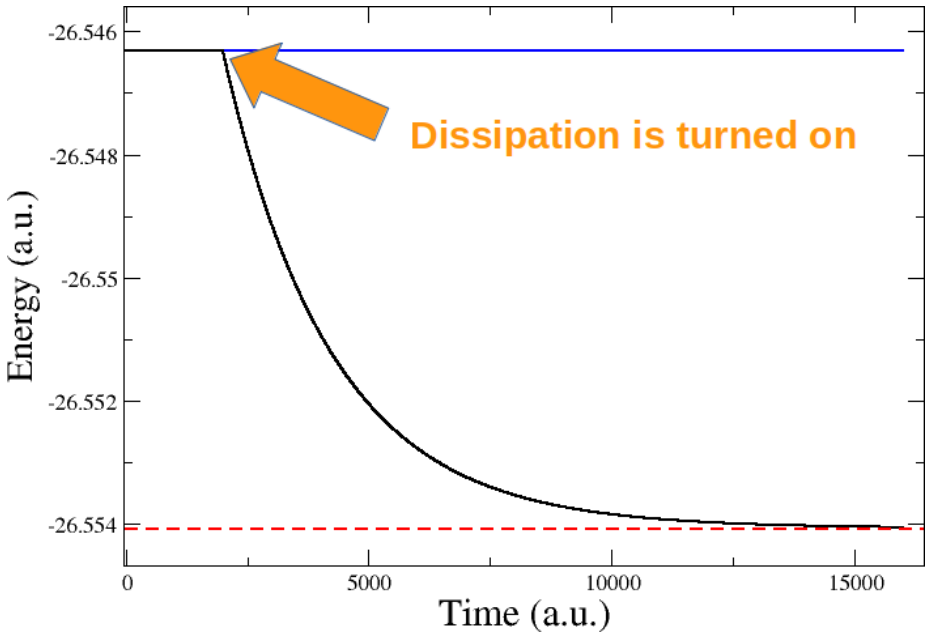
$$\frac{\partial F}{\partial |\dot{\phi}_n\rangle} = \frac{1}{2} \frac{\partial P_{rad}}{\partial |\dot{\phi}_n\rangle} = \frac{\mu_0}{6\pi c} \left(\frac{\partial^2 \langle \mu \rangle}{\partial t^2}\right) \frac{\partial \langle \ddot{\mu} \rangle}{\partial |\dot{\phi}_n\rangle}$$

Dissipative equation of motion

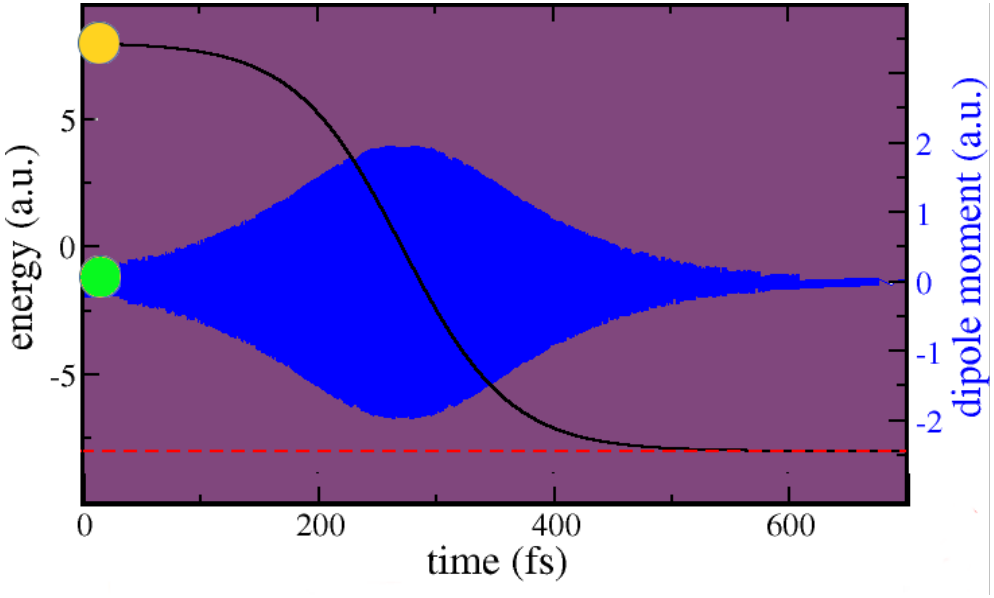
After some elaboration this leads to:

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}] - \frac{\mu_0}{6\pi c\hbar}\ddot{\mu}[[\hat{\mu}, \hat{H}], \hat{\rho}]$$

Tight-binding simulation in a two-level system: dissipative dynamics



Proof of concept



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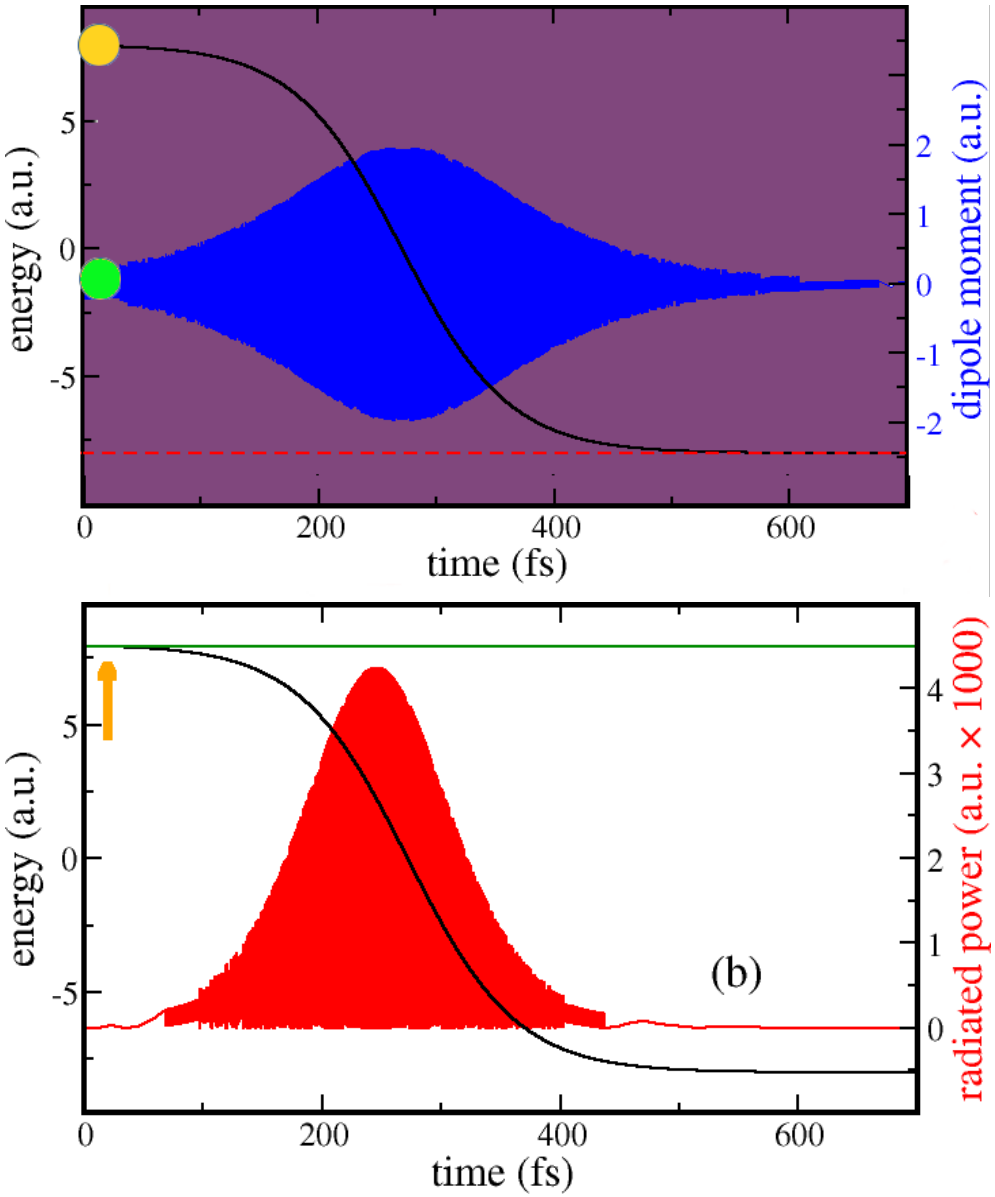

Power

$$P = -\frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{H}_S \rangle$$

Classical fingerprint of photon emission

Bustamante, Gadea, Horsfield, Todorov, Gonzalez-Lebrero, Scherlis
Phys. Rev. Lett. **2021** 126, 087401

Performance

For TB systems simulations predict:

- decay rates
- oscillator strengths
- width and shape of peaks consistently with natural broadening

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TDDFT implementation

Excitation lifetimes for the $2s2p$ state in atomic species

	$\mathbf{C^{2+}}$	$\mathbf{B^{+}}$	**Be**
Experimental (ns)	0.57 ± 0.02	0.86 ± 0.07	1.77 - 2.5
TDDFT (ns)	0.565	0.831	1.97

Bustamante, Gadea, Horsfield, Todorov, Gonzalez-Lebrero, Scherlis, *Phys. Rev. Lett.* **2021** 126, 087401

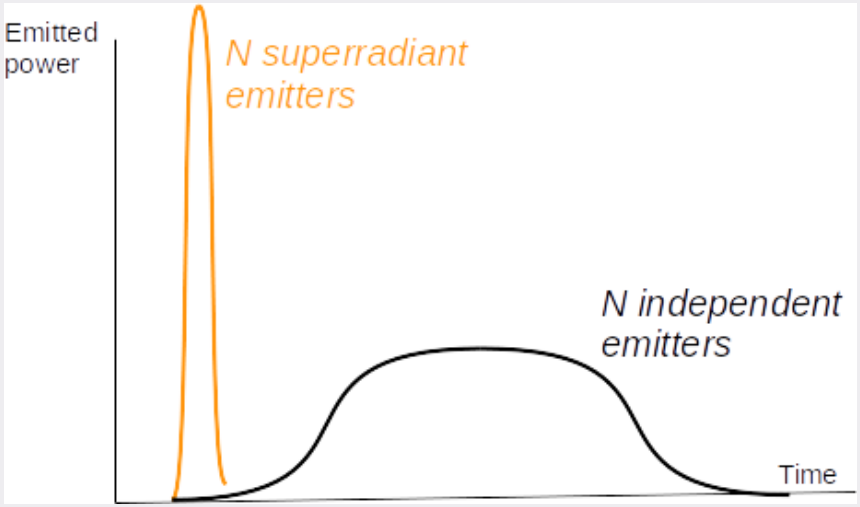
Application: cooperative emission in molecules

Superradiance

Coherent radiative relaxation of a set of identical emitters mutually coupled through their electromagnetic fields, producing a burst in the radiated power together with an acceleration of the emission rate.

$$\text{Power} \propto N_2(N_1 + 1)$$

$$\text{Lifetime} \propto \frac{1}{N}$$



Interesting for lasers and high-speed emitting devices

Application: cooperative emission in molecules

Subradiance

Antiphase coupling of the radiating dipoles that yields a destructive interference and switches off energy dissipation, allowing the system to survive indefinitely in an electronically excited state without emitting $\rightarrow$ “Dark States”

$$\text{Emission Probability} = \frac{N_{exc}}{N}$$

Optical energy storage

Superradiance in a molecular array of H_2

Simultaneous excitation of all monomers

The decay rate is linear with N

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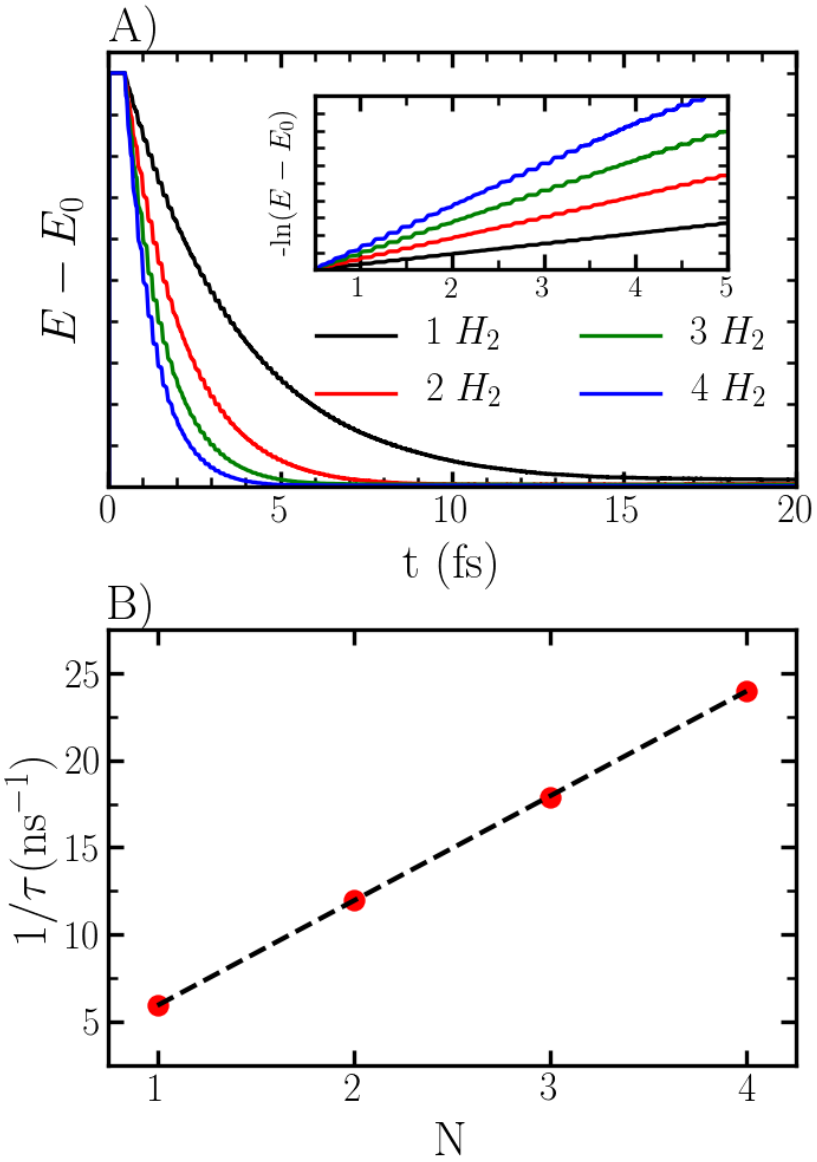
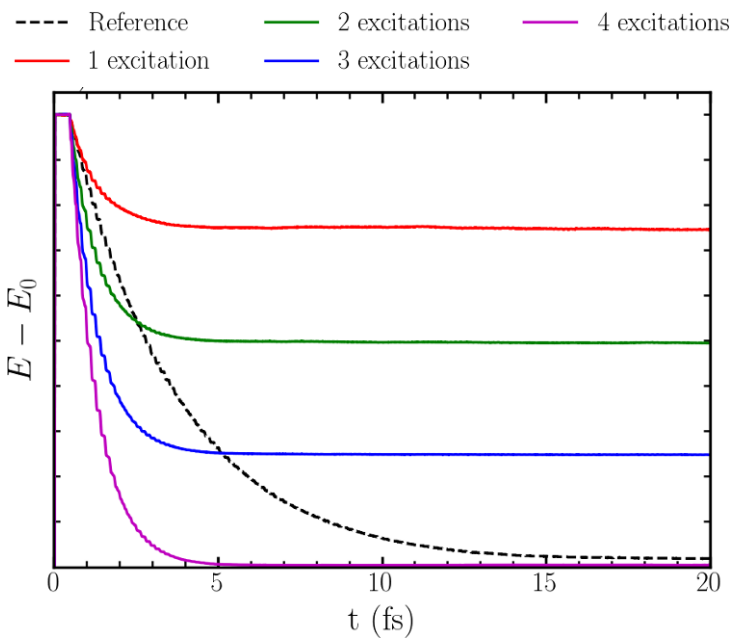


Bustamante, Gadea, Todorov, Scherlis, *J. Phys. Chem. Lett.* **2022** 13, 11601

Subradiance in a molecular array of H_2

Selective excitation of one, two, three or four molecules

$$P_e = \Delta E = \frac{N_{exc}}{N}$$



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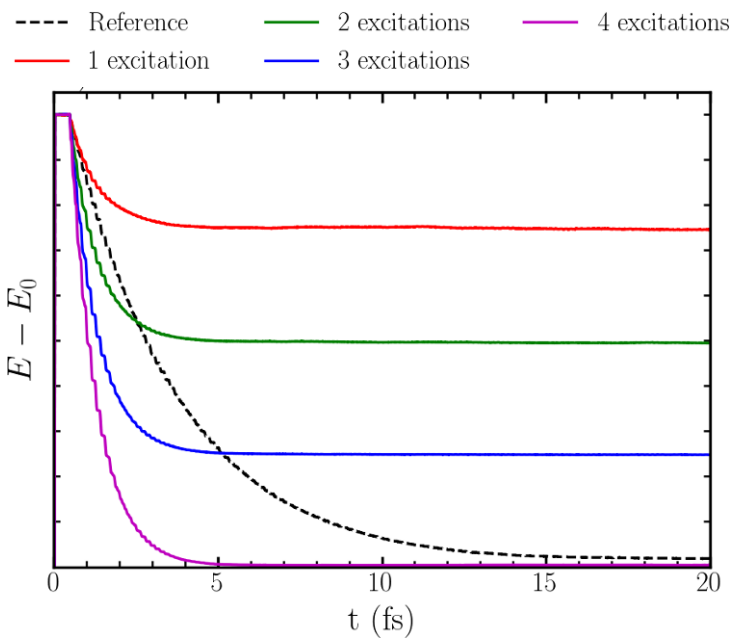

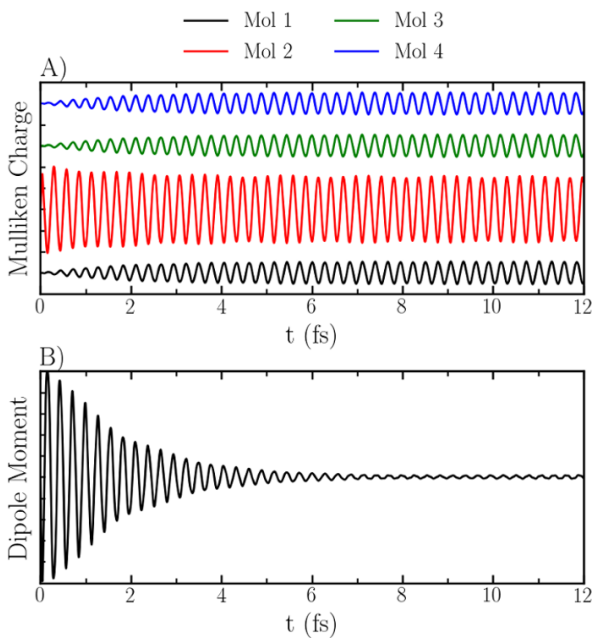

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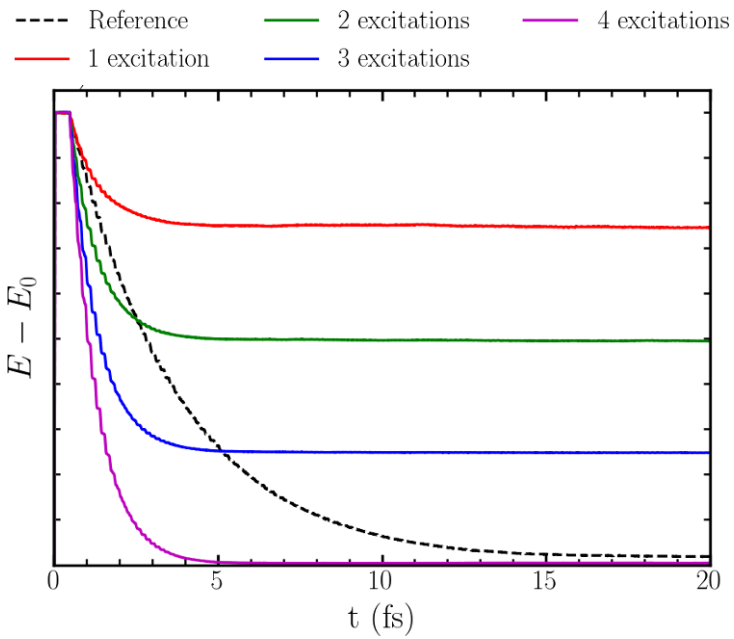

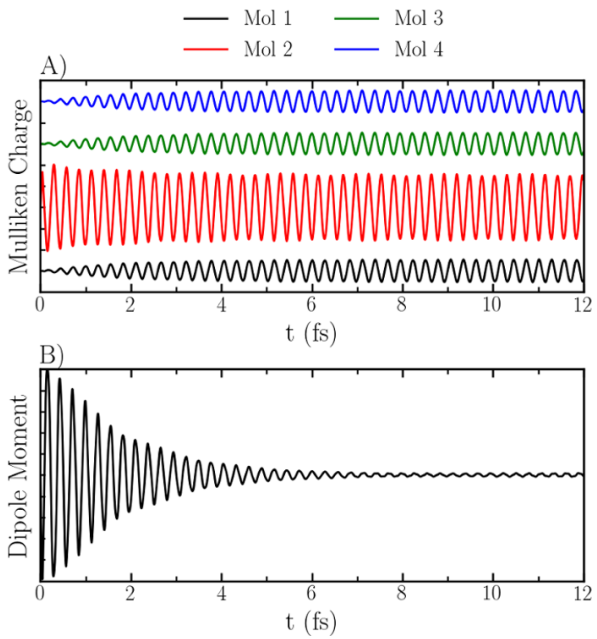

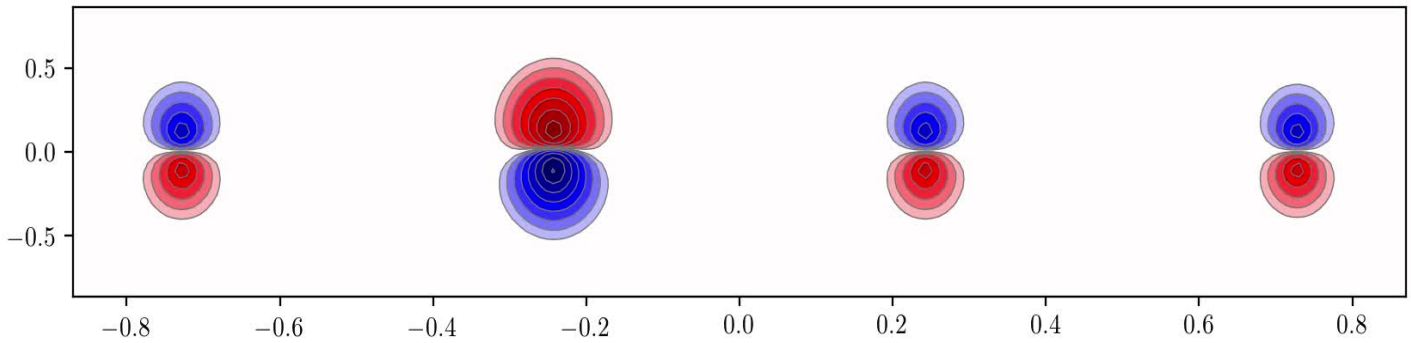

Semiclassical dynamics lacks spontaneous emission

Pure eigenstates remain stationary.

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}] - A\ddot{\mu}[[\hat{\mu}, \hat{H}], \hat{\rho}]$$

Larmor's fault.

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To go beyond the SC model we consider a QED treatment where the electrons are coupled to a photon bath:

$$\hat{H} = \hat{H}_e + \hat{H}_B + \hat{H}_I$$

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

QED approach based on a photon bath

In 1 D, applying the dipolar approximation and tracing over the photonic degrees of freedom:

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho} = \left[\hat{H}_S, \hat{\rho}\right] + \frac{e}{m}\Bigg(\left[\hat{p}, \left[\hat{\chi}^A, \hat{\rho}\right]\right] + \left[\hat{p}, \left\{\hat{\chi}^B, \hat{\rho}\right\}\right] + \left[\hat{p}, 4\hat{\rho}\,\mathrm{Tr}\left(\hat{\rho}\hat{\chi}^B\right)\right] - \left[\hat{p}, 2\hat{\rho}\hat{\chi}^B\hat{\rho}\right]\Bigg)$$

where

$$\chi^A_{nn'} = -\frac{\mathrm{i}ep_{nn'}|\omega_{nn'}|}{12\pi\varepsilon_0 mc^3}\left(2N(|\omega_{nn'}|, T) + 1\right)$$

$$\chi^B_{nn'} = \frac{\mathrm{i}ep_{nn'}\omega_{nn'}}{12\pi\varepsilon_0 mc^3}.$$

Tarasi, Todorov, Bustamante, Gadea, Todorov, Stella, Apostolova, Scherlis, *submitted.*

QED approach

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It can be shown that:

- $\mathrm{Tr}\left(\hat{\rho}\hat{\chi}^B\right) \propto \langle\ddot{\mu}\rangle$
- $\frac{e}{m}\left[\hat{p}, 4\hat{\rho}\,\mathrm{Tr}\left(\hat{\rho}\hat{\chi}^B\right)\right] = \frac{\mu_0}{6\pi i\hbar c}\langle\ddot{\mu}\rangle\left[\left[\hat{\mu}, \hat{H}_S\right], \hat{\rho}\right] = \hat{\Lambda}_{SC}$

QED approach

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

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Then:

SC Approach:

$$i\hbar\frac{d}{dt}\hat{\rho} = \left[\hat{H}_S, \hat{\rho}\right] + \hat{\Lambda}_{SC}$$

QED approach

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QED Approach:

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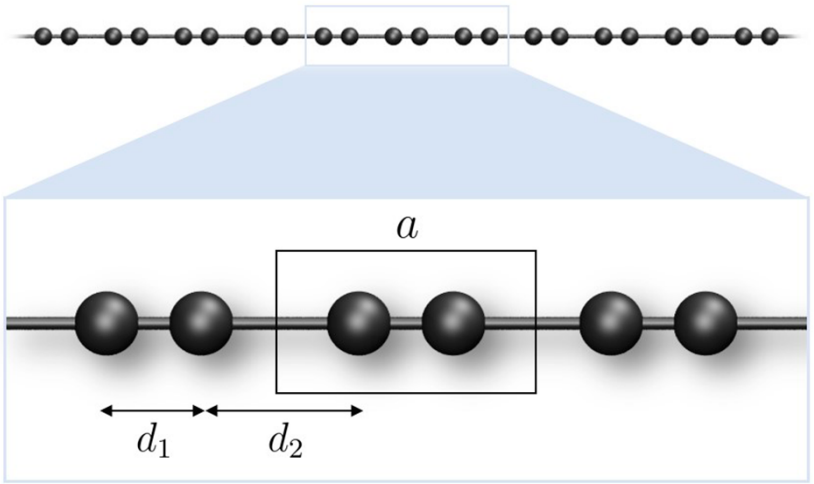
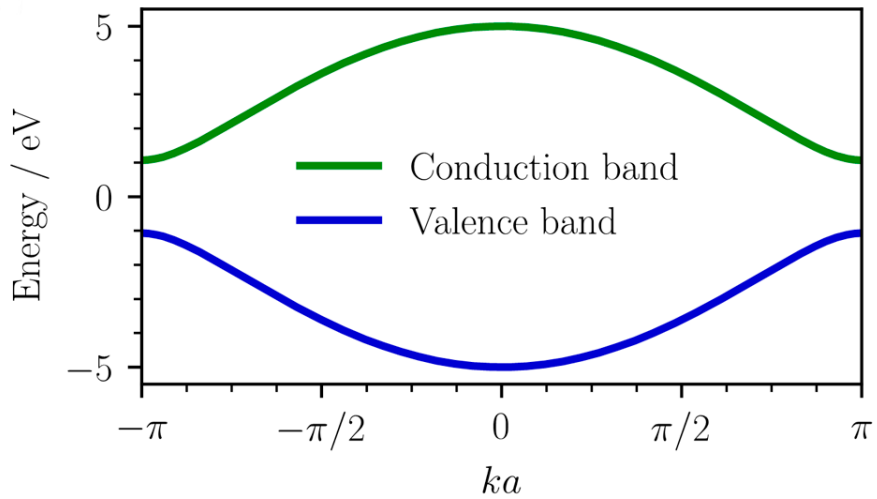
Model system

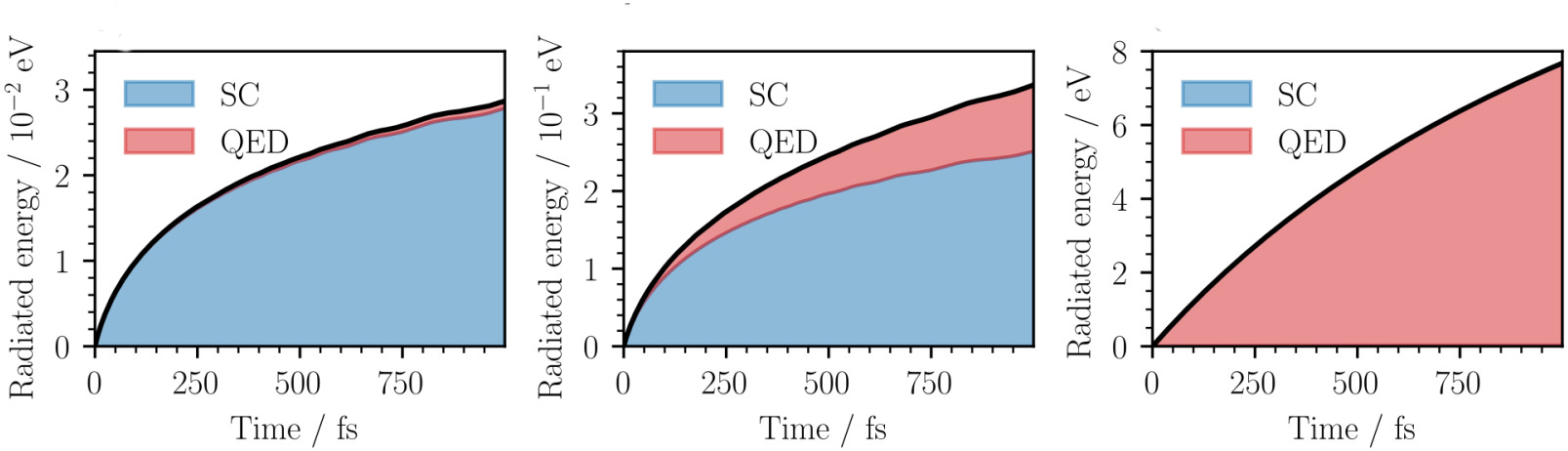
Su–Schrieffer–Heeger (SSH) model for polyacetylene
(First neighbors TB)





Interplay between classical and quantum dissipation

$\rho_{exc}(t=0) = 0.01$ $\rho_{exc}(t=0) = 0.1$ $\rho_{exc}(t=0) = 0.99$



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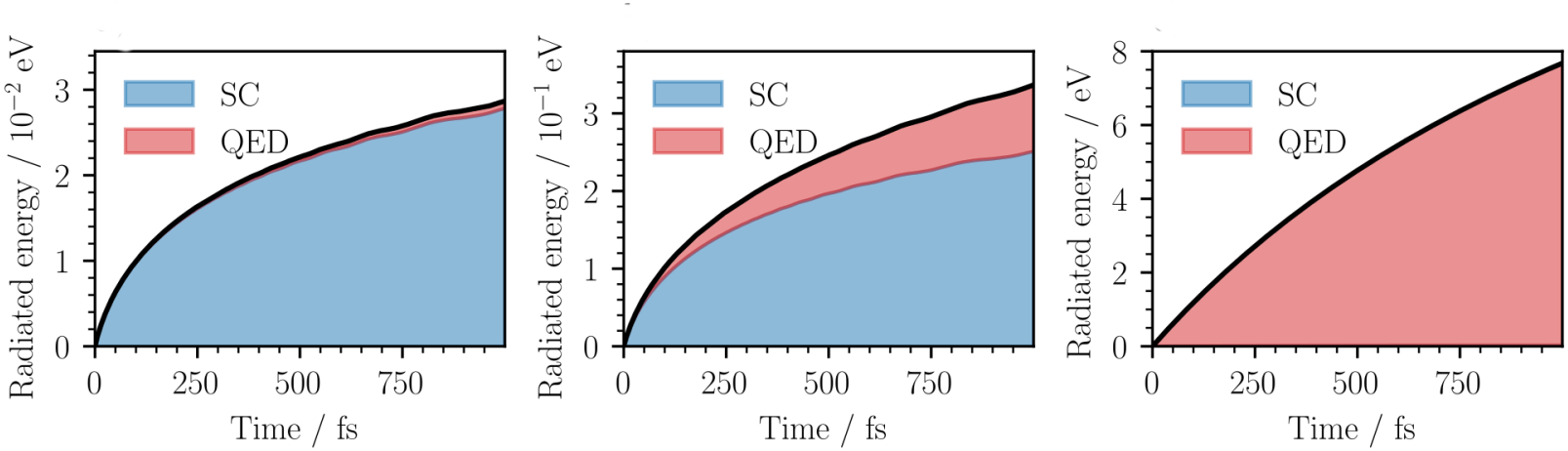
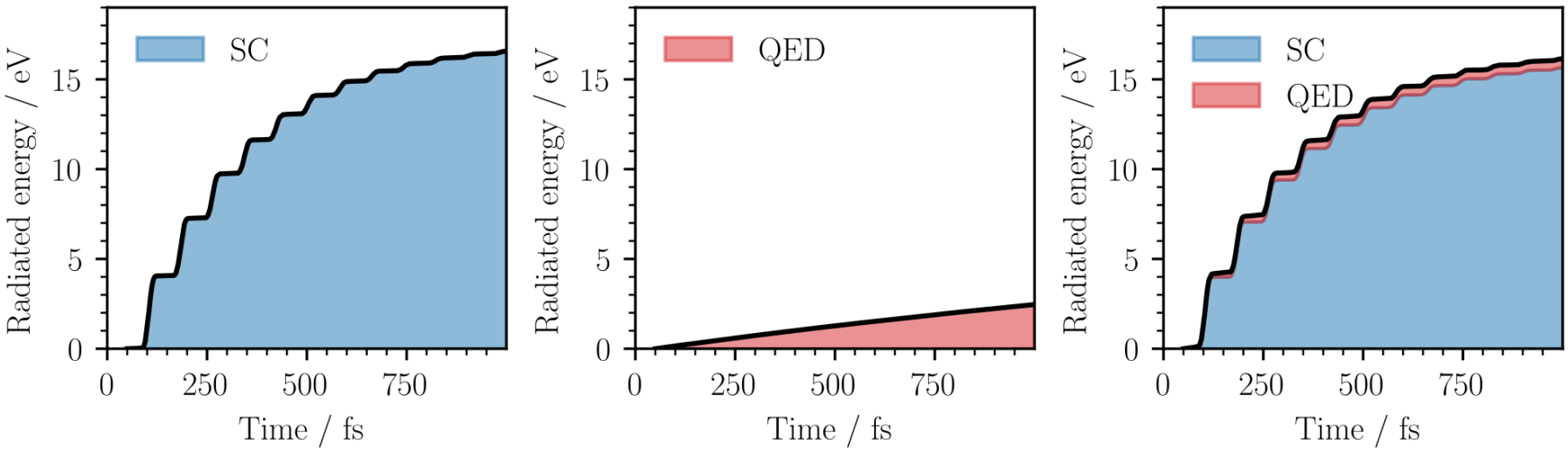


For a system of two bands it is possible to show:

$$P_{SC} \rightarrow \rho_{12}^2 \qquad P_{QED} \rightarrow \rho_{22}$$

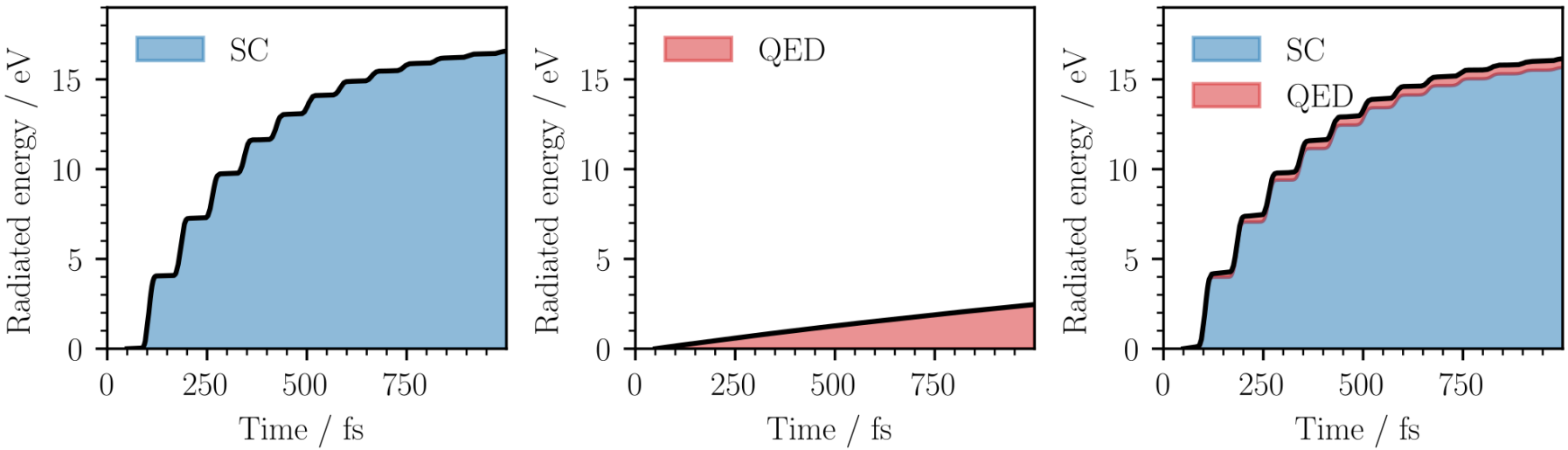
Interplay between classical and quantum dissipation

Excitation with a laser pulse resonant with $k = \frac{\pi}{2a}$



Interplay between classical and quantum dissipation

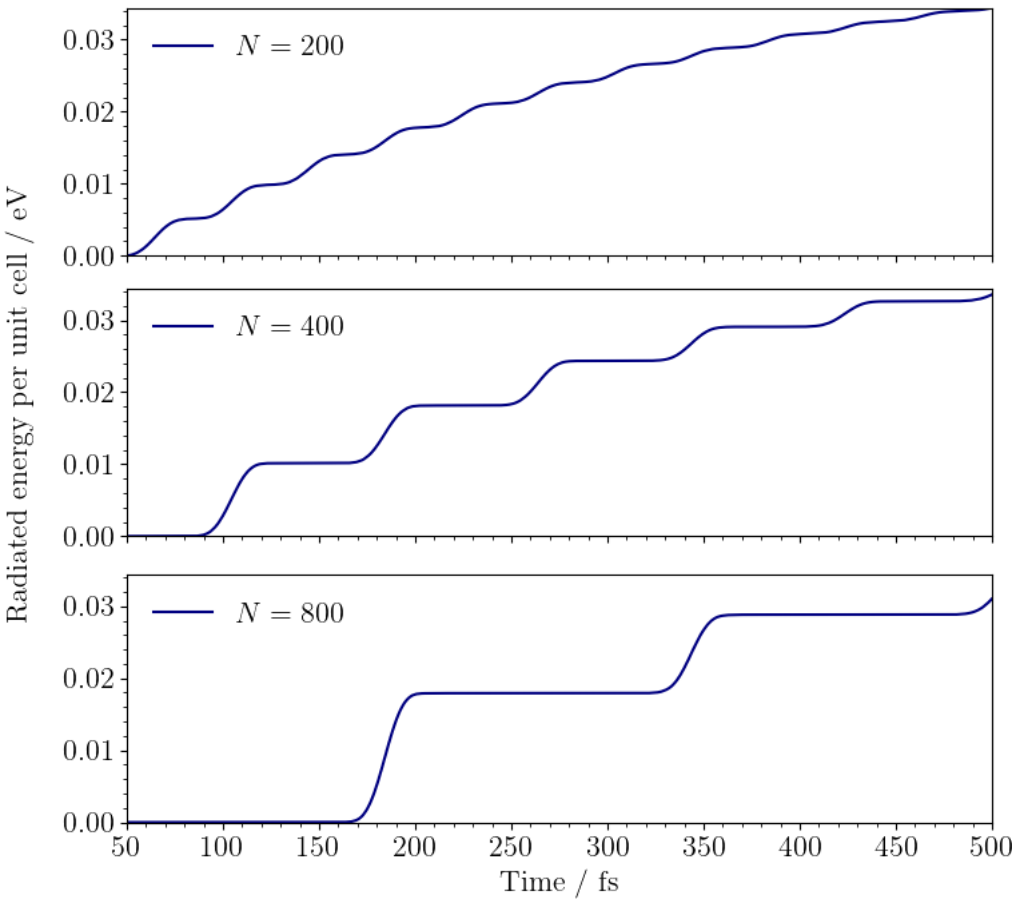
Excitation with a laser pulse resonant with $k = \frac{\pi}{2a}$



Λ_{SC} introduces stepwise relaxation through the subradiant coupling of different k-points

Interplay between classical and quantum dissipation

Effect of the number of k-points N (or number of cells) on the subradiant period T



Subradiant coupling between emitters of similar energies around $k = \pi/2a$, interfering destructively

Under a few assumptions it can be shown that:

$$T = \frac{N \cdot a}{\left[\frac{\mathrm{d}\omega_{21}}{\mathrm{d}k}\right]_{k=k_0}}$$

Electroluminescence of atomic chains

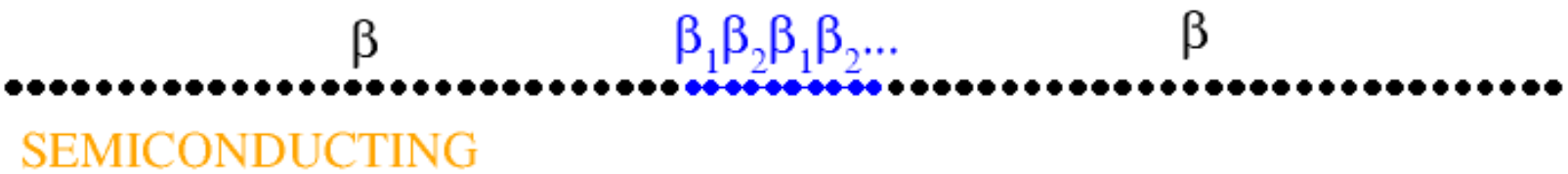
Model system

SOURCE

$$i\hbar\frac{d}{dt}\hat{\rho} = \left[\hat{H}_S, \hat{\rho}\right] - i\hbar\Gamma(\hat{\rho} - \hat{\rho}^-)$$

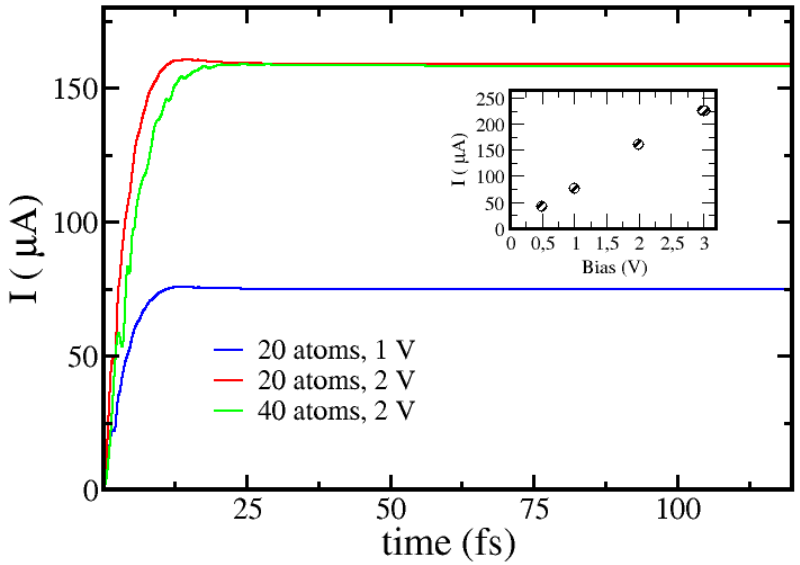
DRAIN

$$i\hbar\frac{d}{dt}\hat{\rho} = \left[\hat{H}_S, \hat{\rho}\right] - i\hbar\Gamma(\hat{\rho} - \hat{\rho}^+)$$



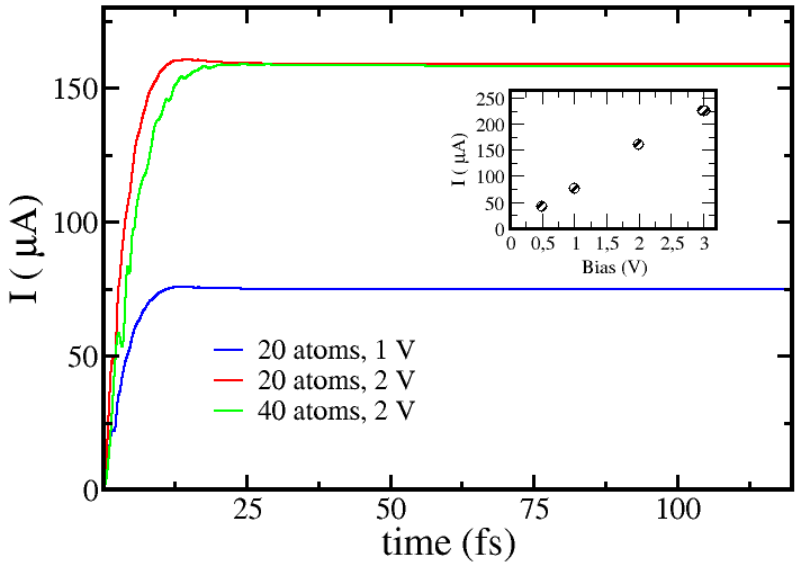
Electroluminescence of atomic chains

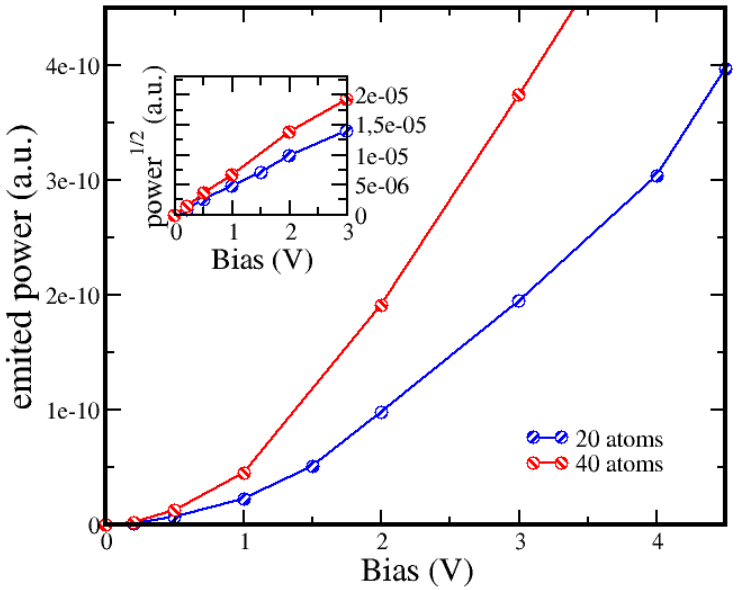
Metallic wires



Electroluminescence of atomic chains

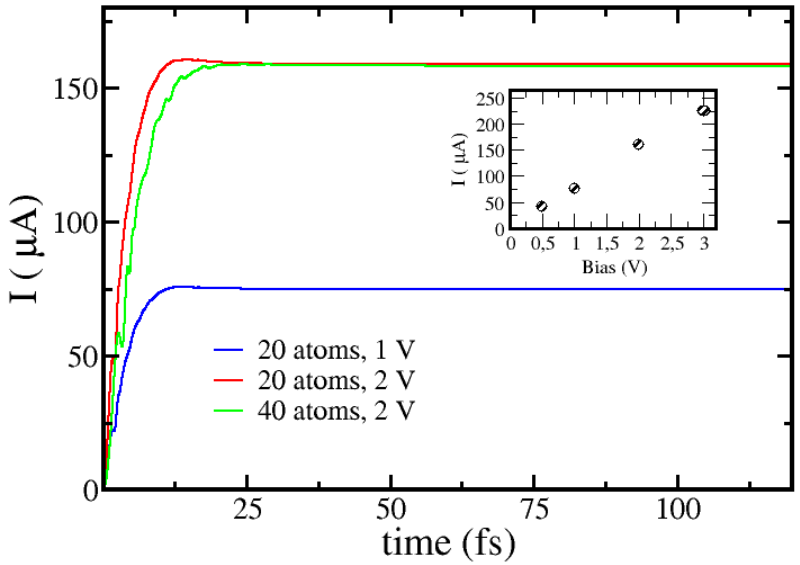
Metallic wires

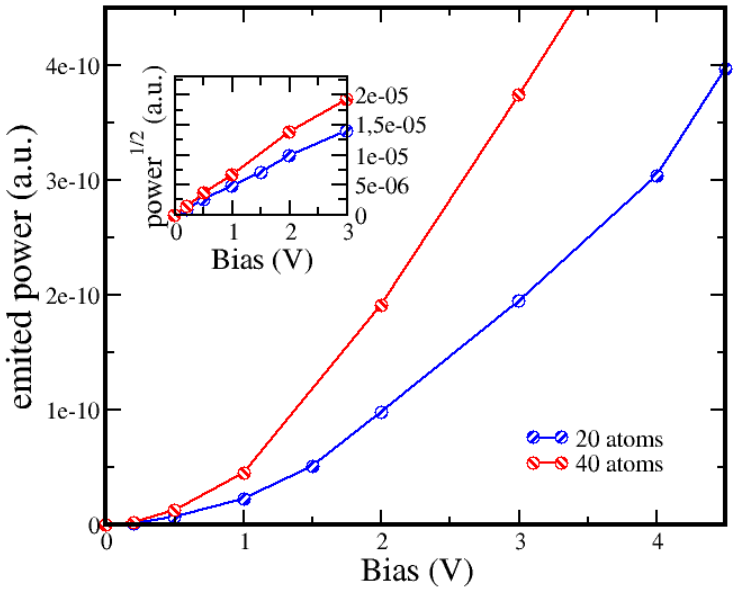




Electroluminescence of atomic chains

Metallic wires



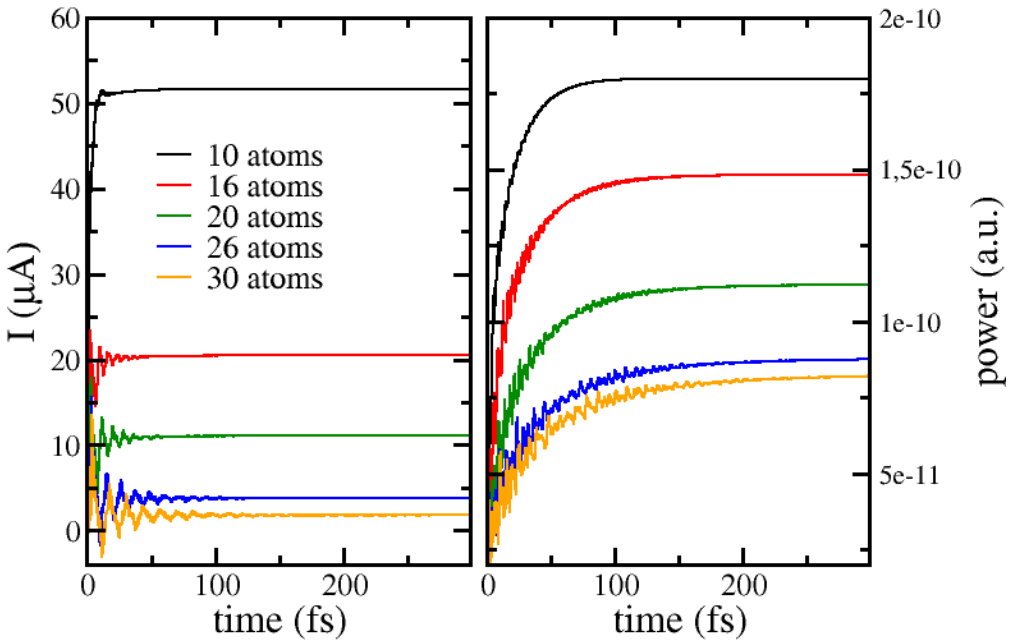


$$\text{Emitted power} \propto \begin{cases} L \\ V^2 \end{cases}$$

Bustamante, Todorov, Gadea, Tarasi, Stella, Horsfield, Scherlis, *J. Chem. Phys.* **2024** 160, 214102

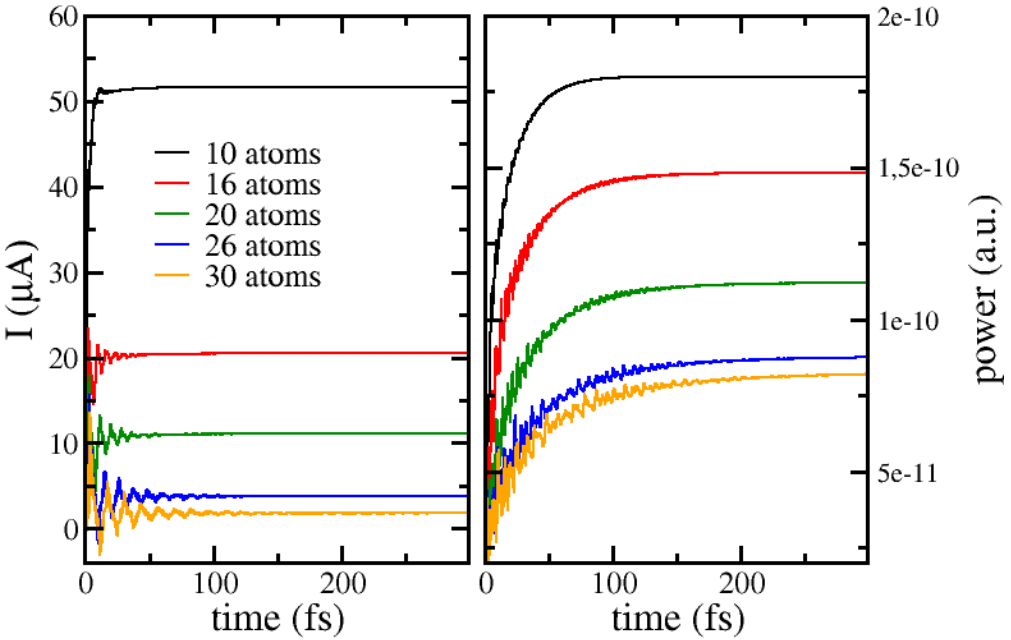
Electroluminescence of atomic chains

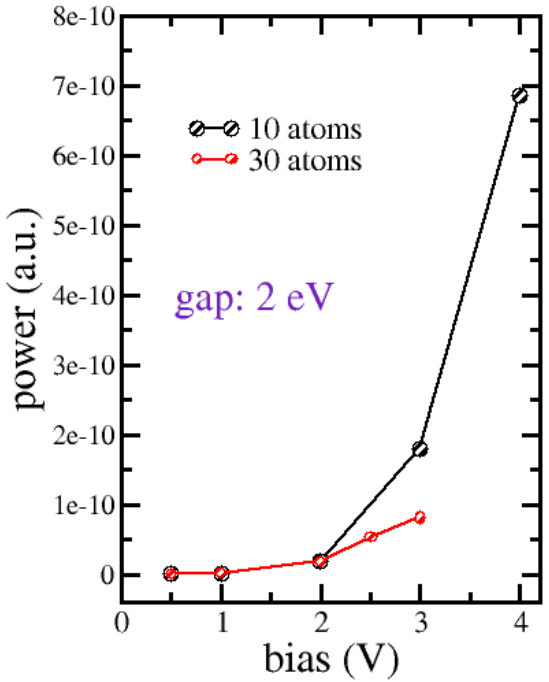
Semiconducting polymers



Electroluminescence of atomic chains

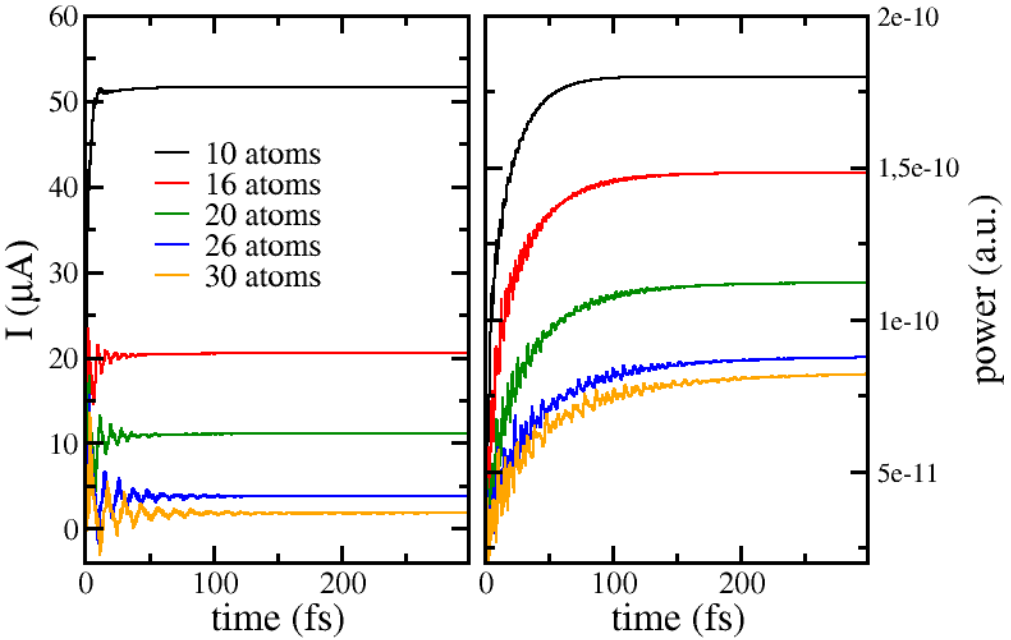
Semiconducting polymers

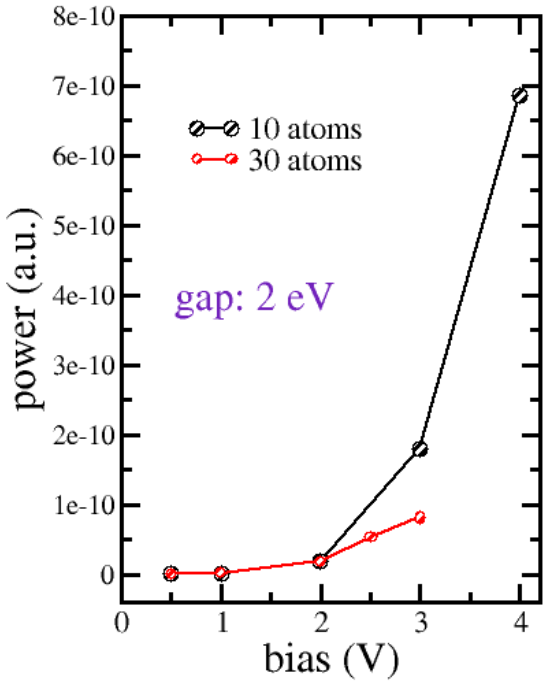




Electroluminescence of atomic chains

Semiconducting polymers

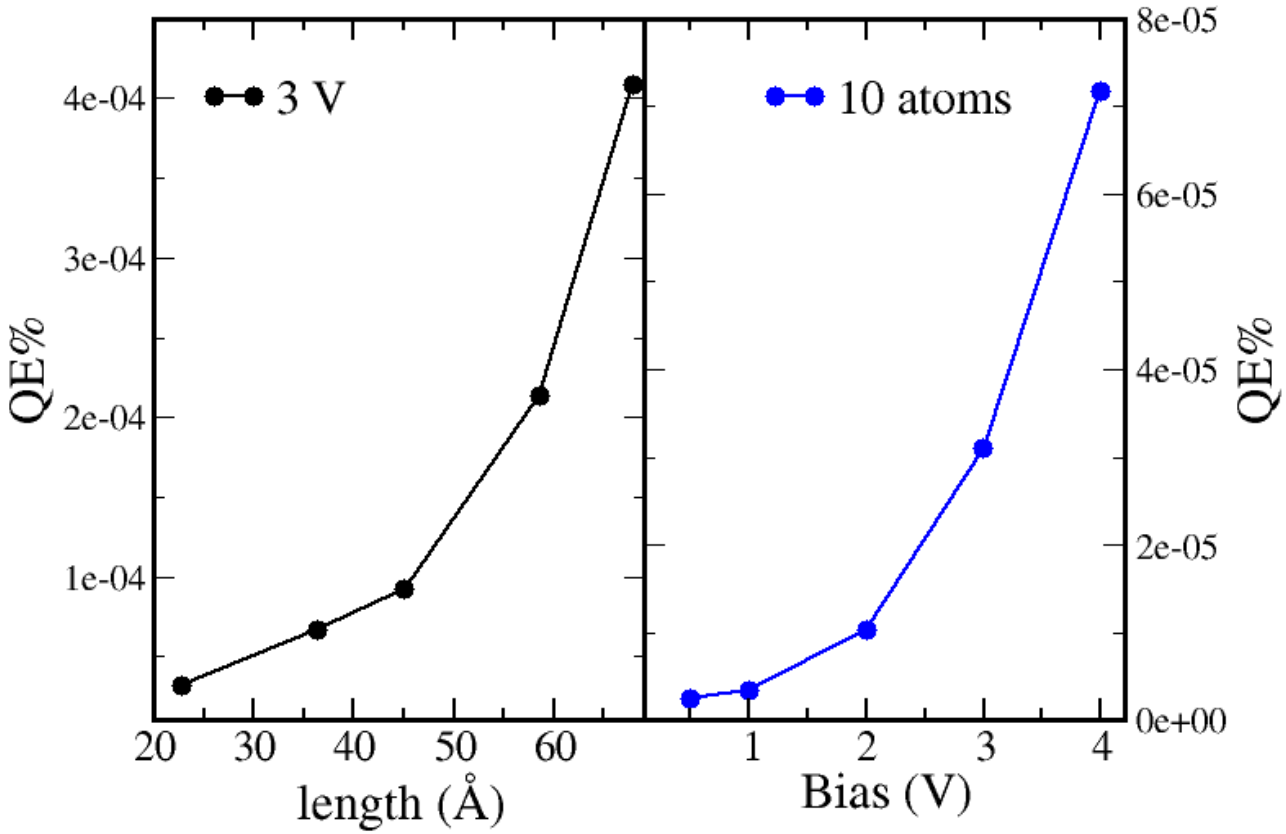




$$\left.\begin{array}{l} P \text{ and } I\downarrow \text{ with } L \\ P \text{ and } I\uparrow \text{ with } V \end{array}\right\} \Rightarrow \text{Q.E.} = \frac{\text{photons emitted}}{\text{electrons injected}} \text{?} \text{ with } L \text{ and } V$$

Electroluminescence of atomic chains

Quantum efficiencies of semiconducting polymers



Some conclusions

- Weakly excited systems: semiclassical contribution predominates, with the emission power controlled by the coherences.
- Strong excitations or excited eigenstates: semiclassical contribution becomes negligible, a fully quantum treatment is required. Power controlled by the populations.
- Periodic polymers: coupling between emitters with a continuum energy spectrum in k-space is a route to achieve subradiance in semiconductors. Interplay between band diagram topology and laser frequency.

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