Quantum plasmonics with adatoms on graphene flakes

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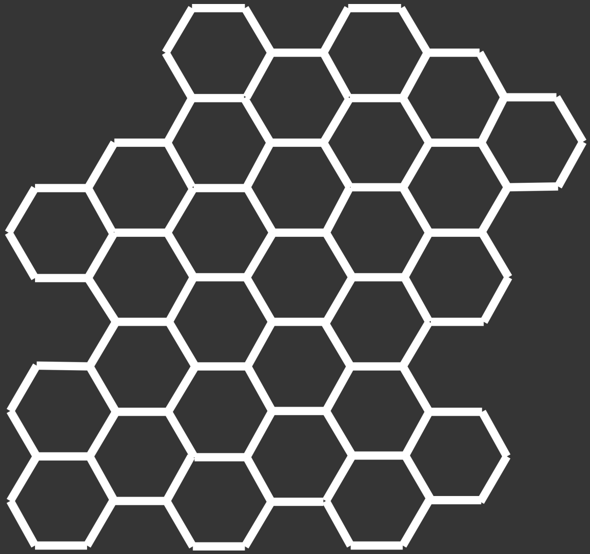
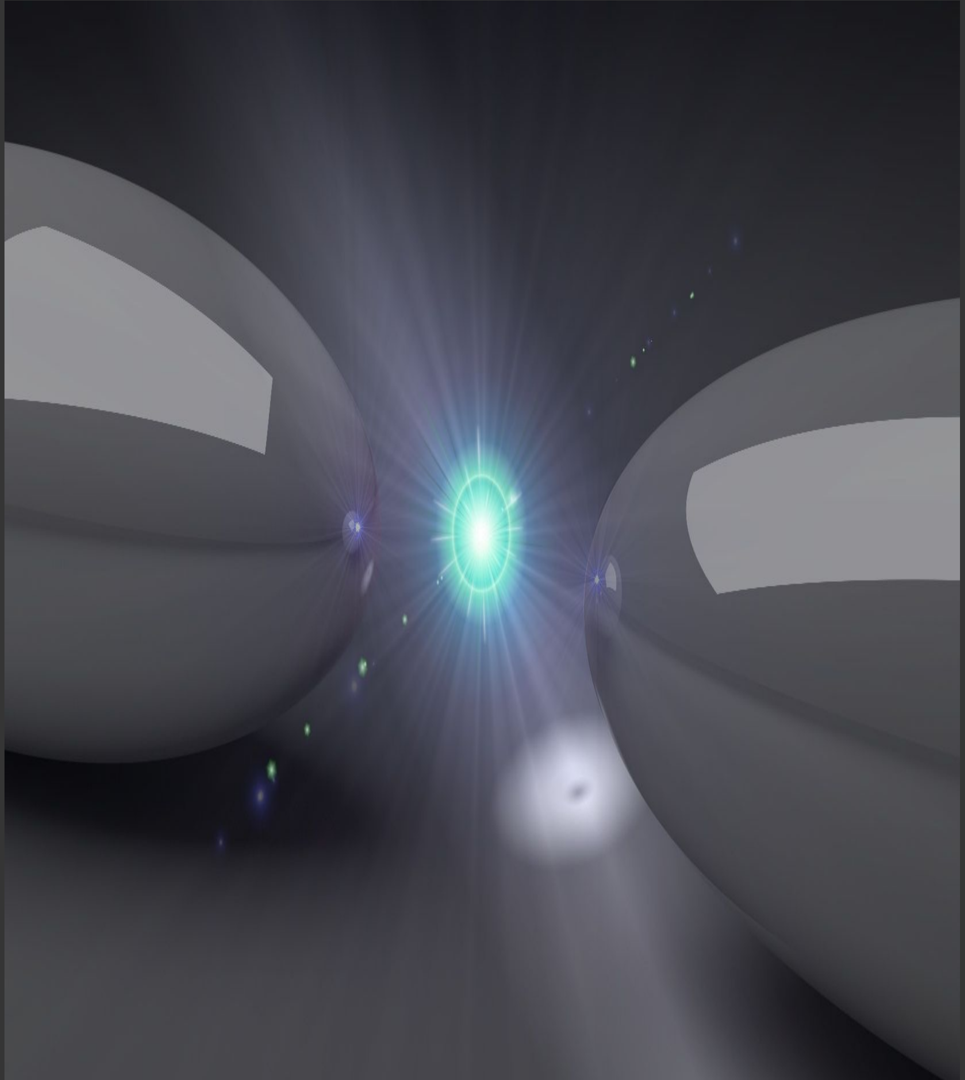


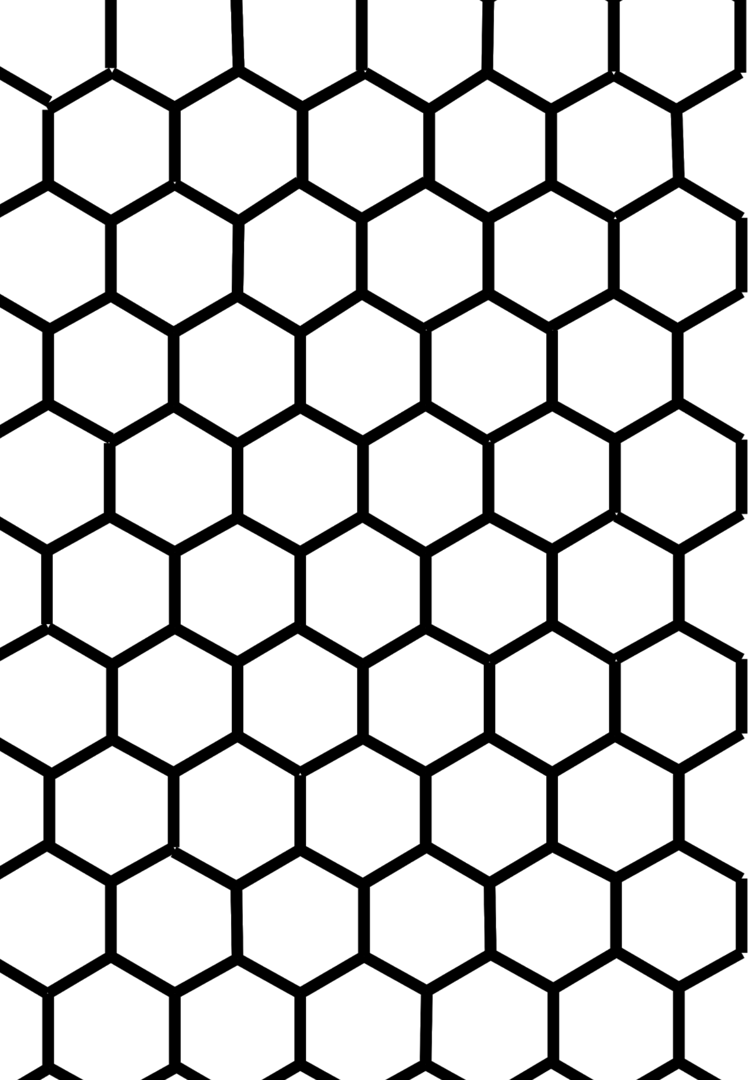
Quantum plasmonics

Quantum emitters
placed near nanoantennas

Emitter - light interactions
- strong coupling
- fast dynamics

- absorption losses
- limited tunability





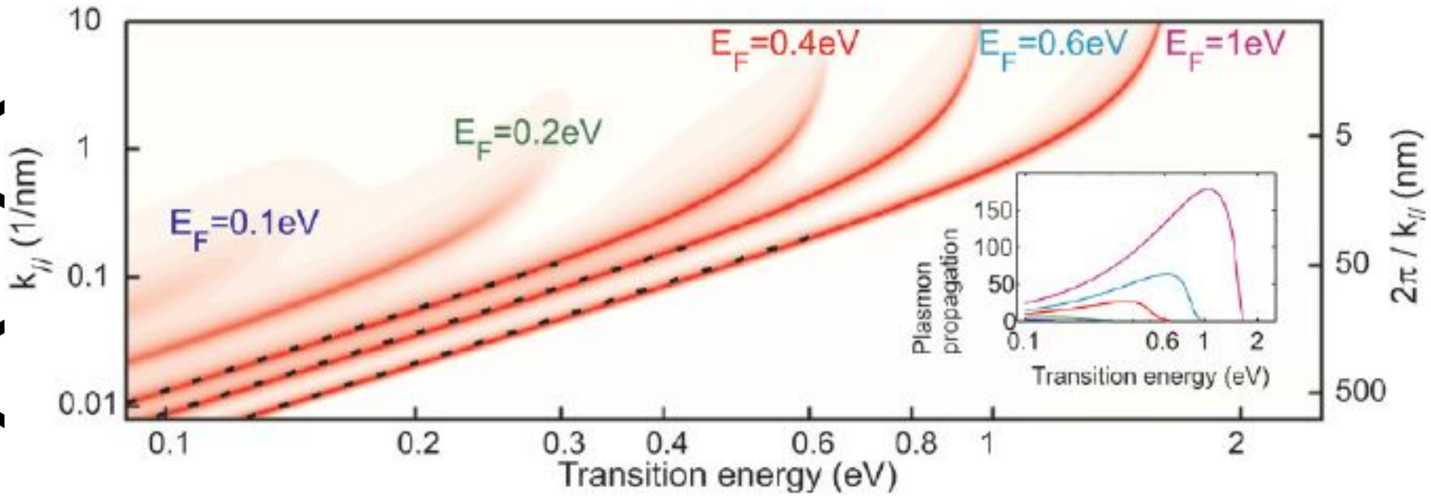
Graphene plasmonics

extreme platform for plasmonics

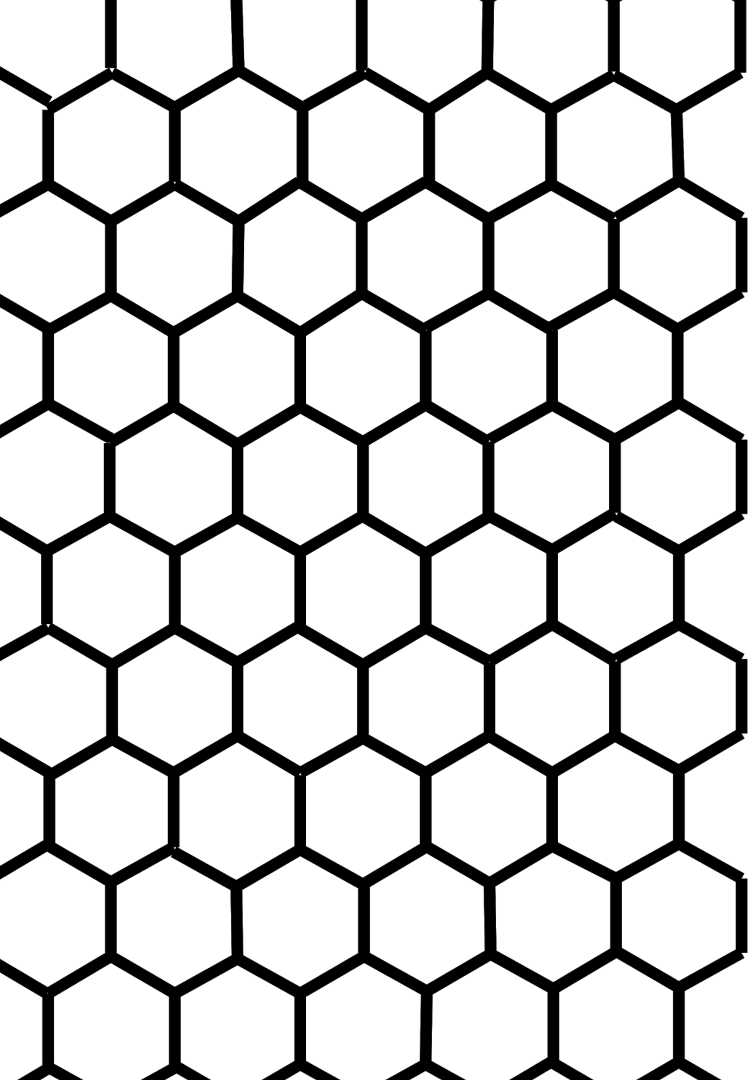
tunability

Graphene plasmonics

extreme platform for plasmonics



Koppens et al. Nano Letters (2011)



Graphene plasmonics

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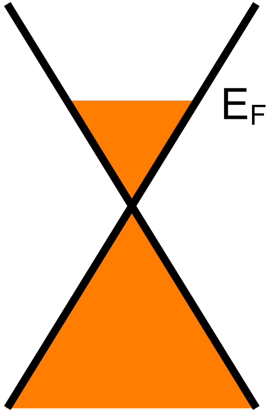
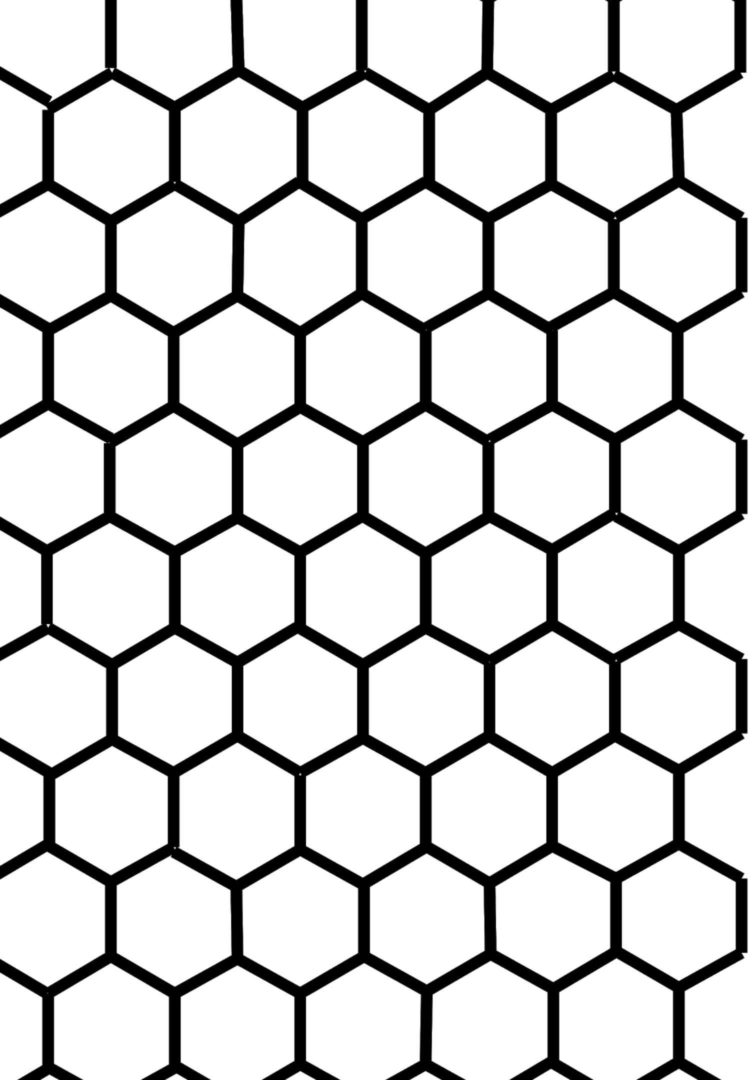
tunability

$$\omega_{res} \sim E_F^{1/2}$$



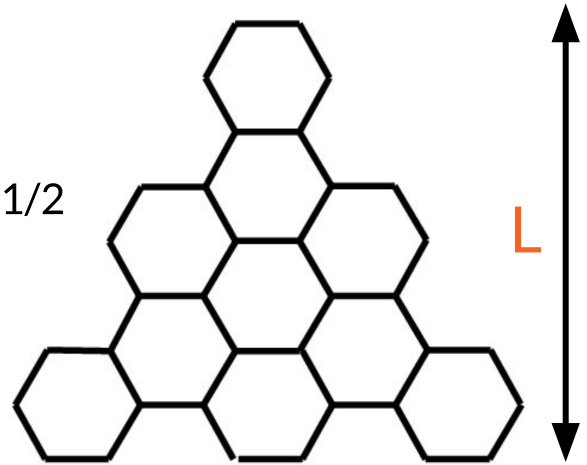


Graphene plasmonics

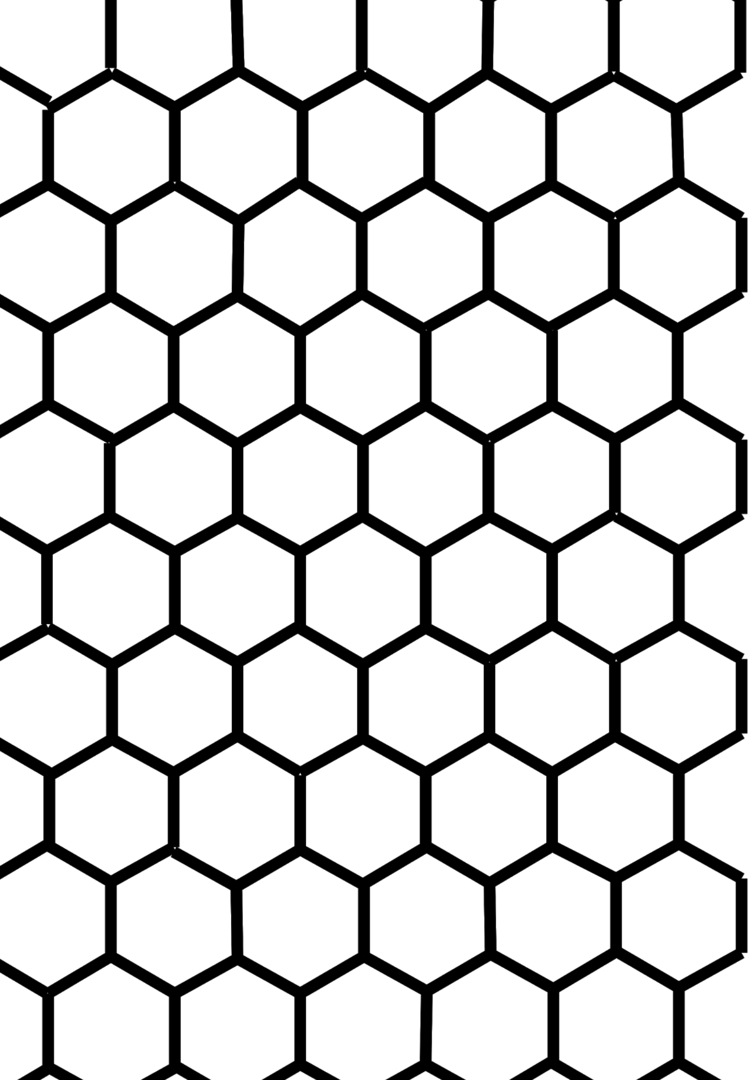
extreme platform for plasmonics

tunability

$$\omega_{res} \sim (E_F / L)^{1/2}$$



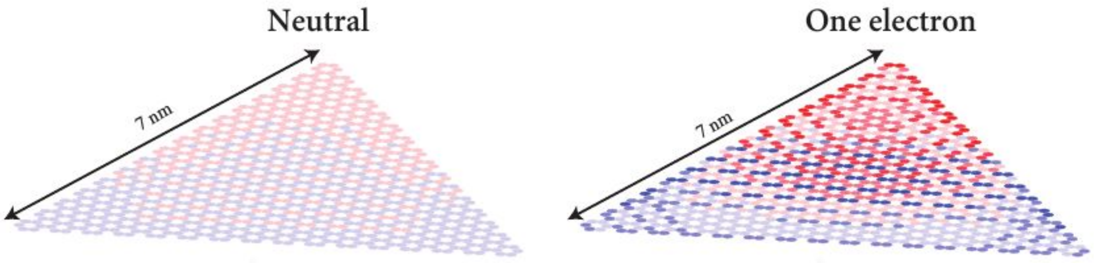
Renwen Yu et al. ACS Photonics (2017)



Graphene plasmonics

extreme platform for plasmonics

tunability



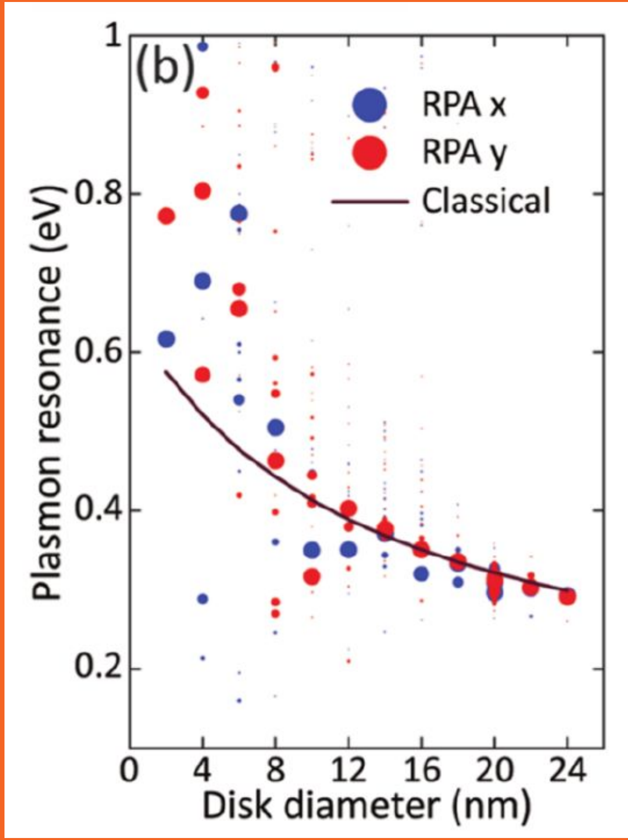
Manjavacas et al. Nanophotonics (2013)

Graphene flakes

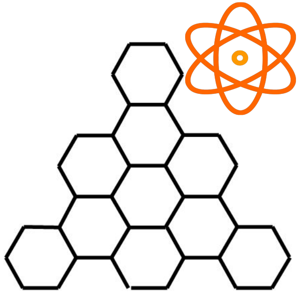
resonances in optical range

quantum model required
for size < 20 nm

Thongrattanasiri et al. ACS Nano (2012)



Outline

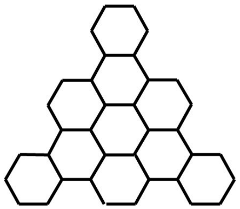


Model

Applications

Ingredients

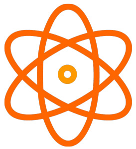
Graphene flake



arbitrary shape
and edge type

small: <1000 C atoms
(computation time,
resonance in visible)

Adatom

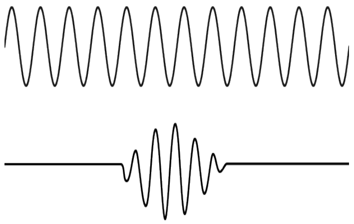


one or more

Anderson model of one-,
two- or few-level
defects

coupled to selected
carbon sites

Laser beam

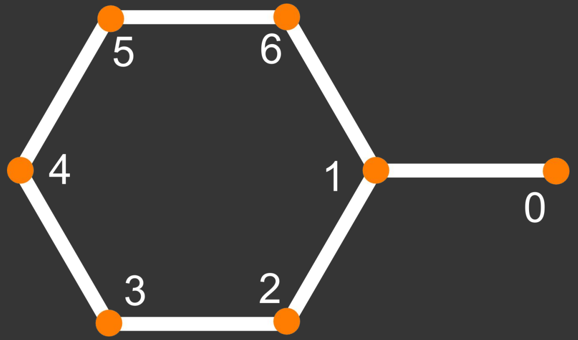


arbitrary temporal shape
cw, Gaussian, $\delta(t)$, ...

classical, no feedback
from atoms

Hamiltonian: flake

t = - 2.66 eV

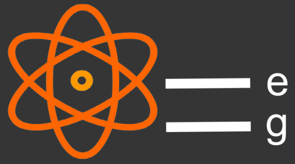


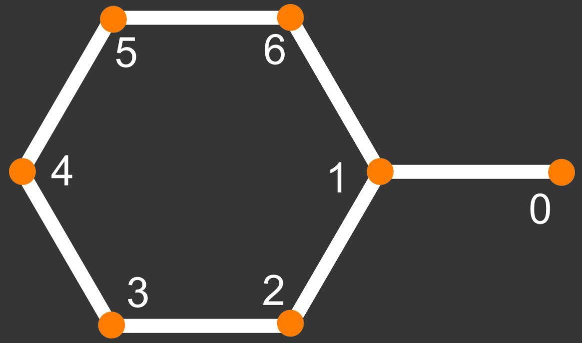
site basis

	0	1	2	3	4	5	6
0		t					
1	t		t				t
2		t		t			
3			t		t		
4				t		t	
5					t		t
6		t				t	

Hamiltonian: flake + atom

$t = -2.66$ eV



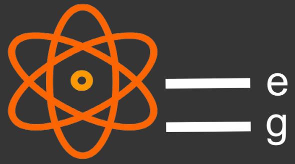


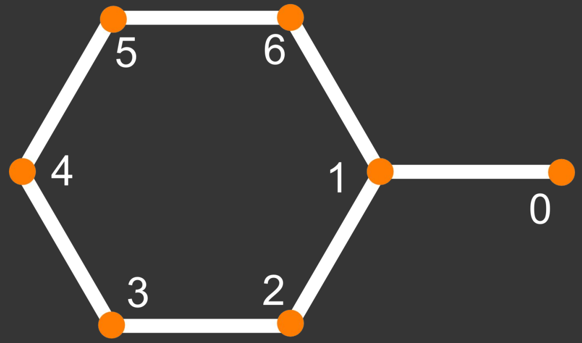
site basis

	0	1	2	3	4	5	6	e	g
0		t							
1	t		t				t		
2		t		t					
3			t		t				
4				t		t			
5					t		t		
6		t				t			
e								ω_e	
g									ω_g

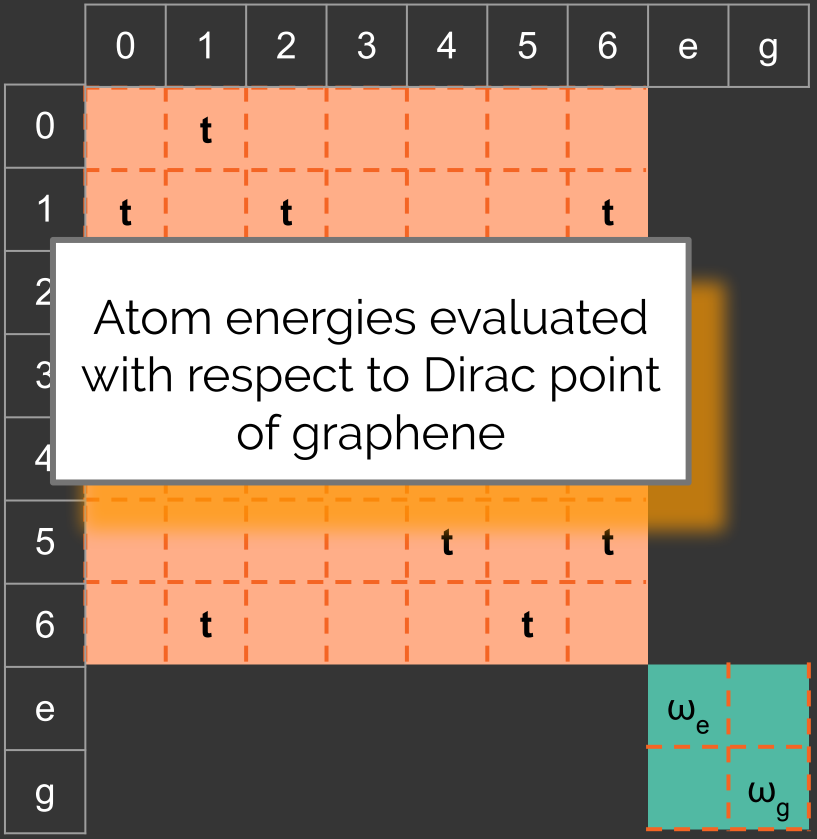
Hamiltonian: flake + atom

t = - 2.66 eV





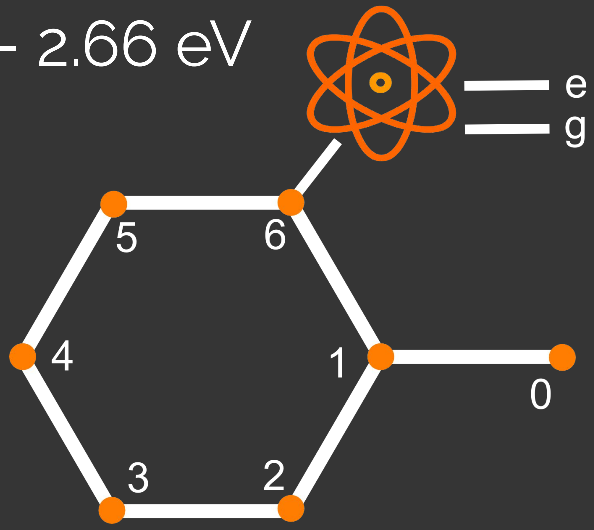
site basis



Atom energies evaluated with respect to Dirac point of graphene

Hamiltonian: flake + atom

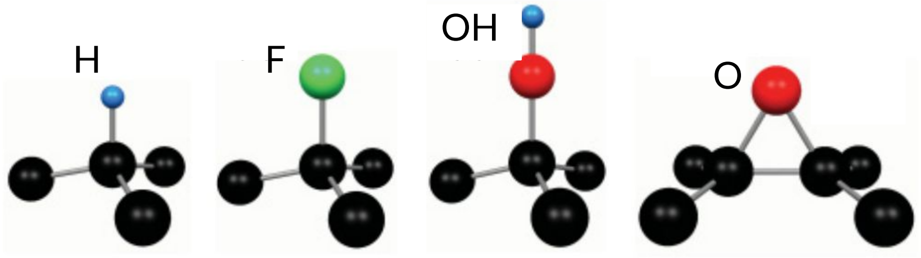
$t = -2.66$ eV



site basis

	0	1	2	3	4	5	6	e	g
0		t							
1	t		t				t		
2		t		t					
3			t		t				
4				t		t			
5					t		t		
6		t				t		t_e	t_g
e							t_e	ω_e	
g							t_g		ω_g

Real - system parameters



adatom	Ψ	ω_k	t_k	Δt_0
H	$1s$	-0.81	1.89	0.79
F	$2s$	-10.59	4.70	0.79
	$2p_z$	-2.48	1.45	
OH	$2s^{\mathrm{O}}$	-7.74	4.10	0.73
	$2p_z^{\mathrm{O}}$	-1.26	1.24	
	$1s^{\mathrm{H}}$	-0.81	0.36	
OH	ψ_1	-8.17	3.75	0.73
	ψ_2	-1.64	1.81	
	ψ_3	7.39	1.69	
O	$2s$	-7.74	3.47	0.92
	$2p_z$	-1.26	0.76	0.89
	$2p_x$	-1.26	± 0.80	

all quantities in units of t

Ihnatsenka & Kirczenow, PRB (2011)

Eigenstate basis

$$H \Psi_j = E_j \Psi_j$$

$$\Psi_j = \Sigma_l \, c_{jl} \, \varphi_l$$

$$\begin{bmatrix}
 & t & & & & & & & \\
t & & t & & & & t & & \\
 & t & & t & & & & & \\
 & & t & & t & & & & \\
 & & & t & & t & & & \\
 & & & & t & & t & & \\
 & t & & & & t & & t_e & t_g \\
 & & & & & & t_e & \omega_e & \\
 & & & & & & t_g & & \omega_g
\end{bmatrix}$$

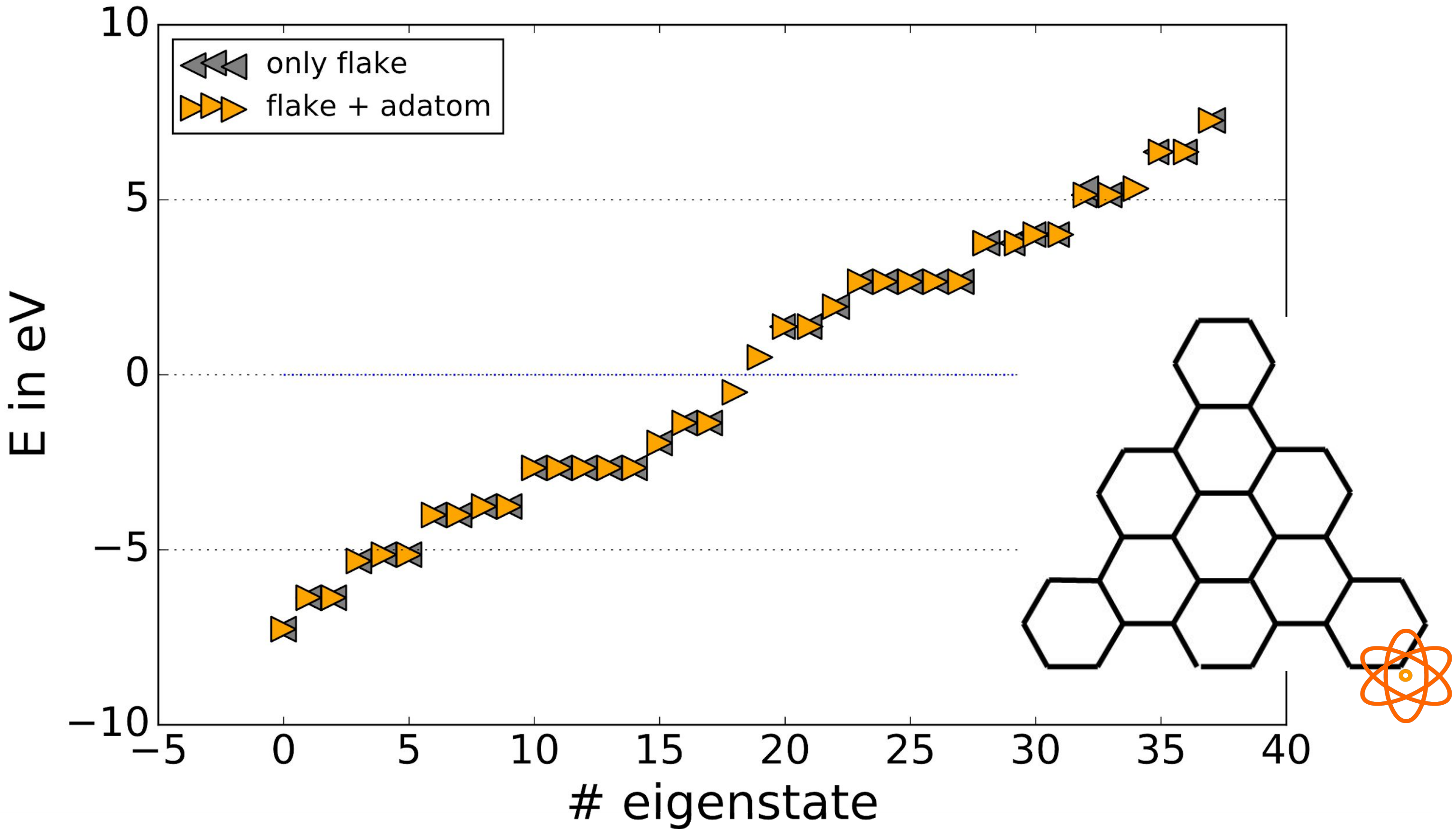
Eigenstate basis

$$H\,\Psi_j = E_j\,\Psi_j$$

$$\Psi_j = \Sigma_l\, c_{jl}\,\varphi_l$$

E_1								
	E_2							
		E_3						
			E_4					
				E_5				
					E_6			
						E_7		
							E_8	
								E_9

Energy landscape



Field

$$H(t) = H_{\text{flake+adatom}} + H_{\text{adatom+field}} + \Phi_{\text{ext}} + \Phi_{\text{ind}}$$

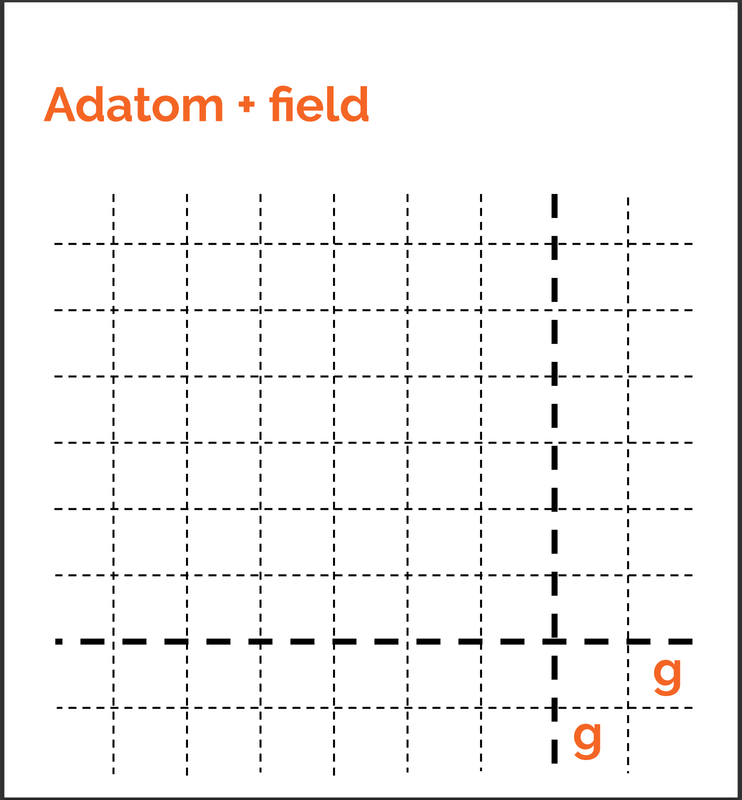
Flake + adatom

tight - binding Hamiltonian

$$H_{\text{atom+flake}} = t \sum_{\langle l,k \rangle} c_l^\dagger c_k + \sum_{i=\text{e,g}} \left(\omega_i c_i^\dagger c_i + t_i c_i^\dagger c_0 + \text{H.c.} \right)$$

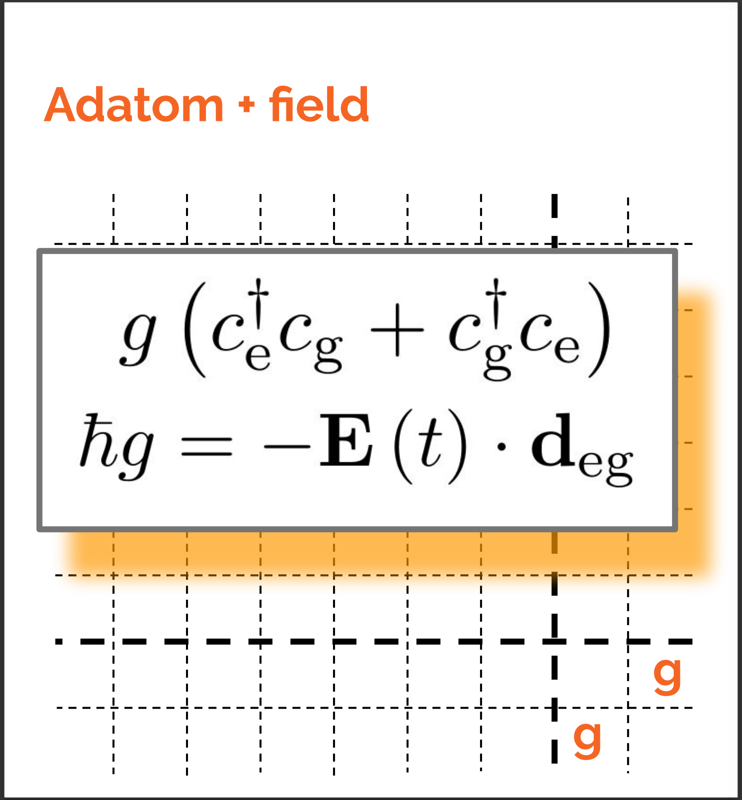
Field

$$H(t) = H_{\text{flake+adatom}}$$
$$+\ H_{\text{adatom+field}}$$
$$+\ \Phi_{\text{ext}}$$
$$+\ \Phi_{\text{ind}}$$



Field

$$H(t) = H_{\text{flake+adatom}} + H_{\text{adatom+field}} + \Phi_{\text{ext}} + \Phi_{\text{ind}}$$



Field

$H(t) = H_{\text{flake+adatom}}$

$+ H_{\text{adatom+field}}$

$+ \Phi_{\text{ext}}$

$+ \Phi_{\text{ind}}$

External potential

coupling of flake and field

$$(\Phi_{\text{ext}})_{kk} = -e\mathbf{r}_k \cdot \mathbf{E}(t)$$

$\mathbf{r}_k$ - position of site k

$\mathbf{E}(t)$ - laser field

diagonal in site basis

Cox et al. Nature Communications (2014)

Field

$$H(t) = H_{\text{flake+adatom}} + H_{\text{adatom+field}} + \Phi_{\text{ext}} + \Phi_{\text{ind}}$$

Induced potential

$$(\Phi_{\text{ind}})_{ll} = -Ne \sum_m v_{lm} \left(\rho_{mm} - \rho^0_{mm} \right)$$

v_{lm} **Coulomb** interaction + **exchange** integrals

on flake
on atom if ≠ 1 electron
inbetween scaled with t_e, t_g

Potasz et al. PRB (2012)

Field

$$H(t) = H_{\text{flake+adatom}} + H_{\text{adatom+field}} + \Phi_{\text{ext}} + \Phi_{\text{ind}}$$

Induced potential

$$(\Phi_{\text{ind}})_{ll} = -Ne \sum_m v_{lm} \left(\rho_{mm} - \rho^0_{mm} \right)$$

doping with electrons or holes

on flake
on atom if ≠ 1 electron
inbetween scaled with t_e, t_g

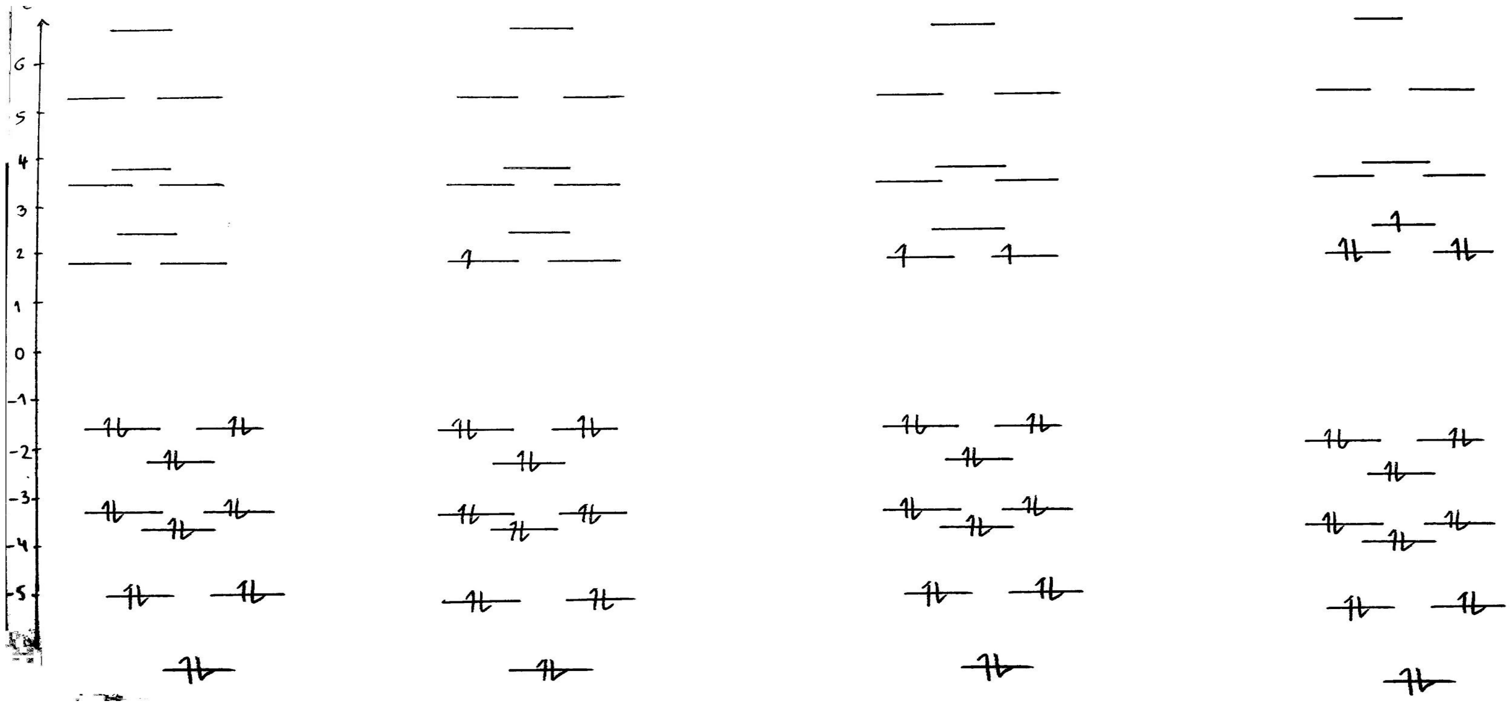
Equilibrium state

no doping

1 doping electron

2 doping electrons

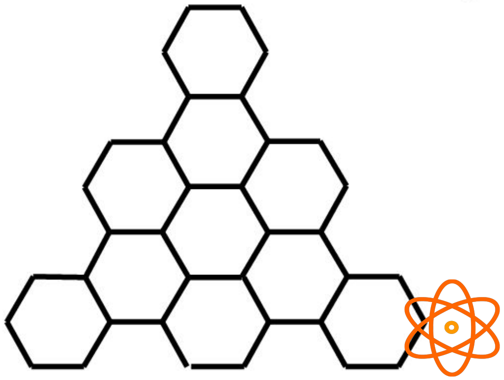
5 doping electrons

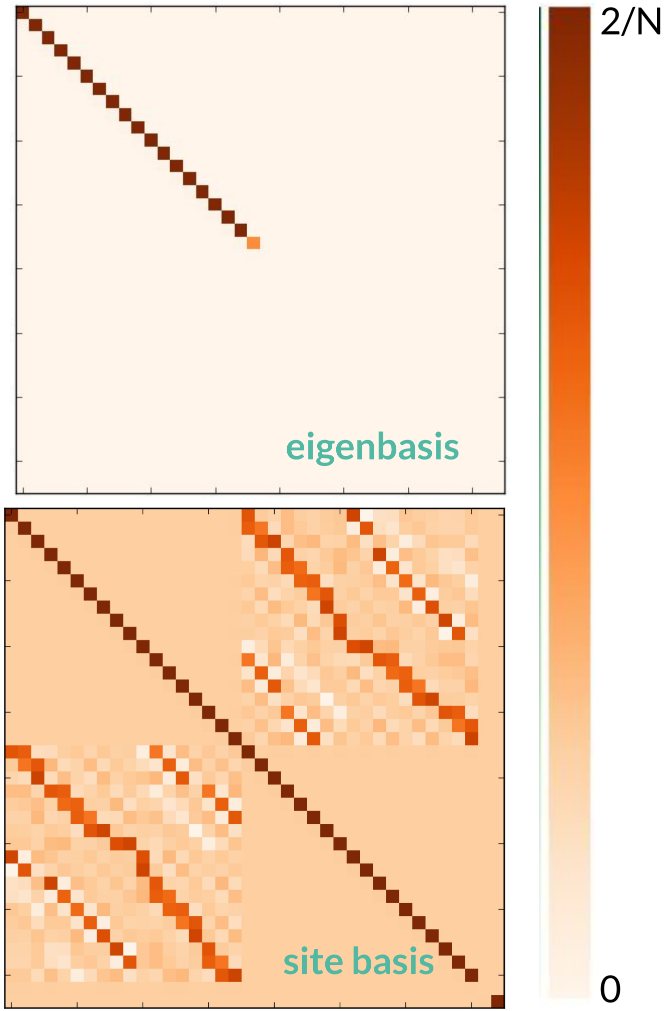


Equilibrium state

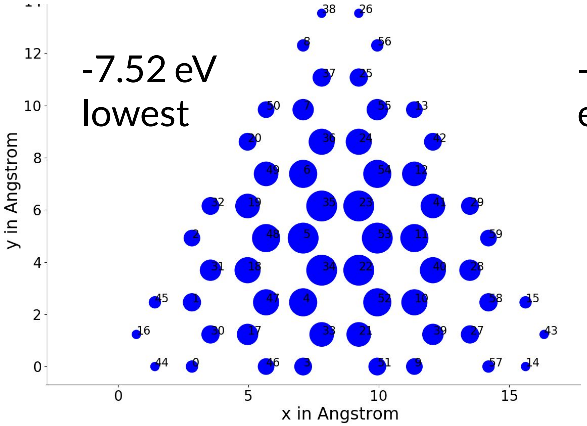
$$\rho_0 = \frac{1}{N}\sum_j f_j(N)\,|\psi_j\rangle\langle\psi_j|$$

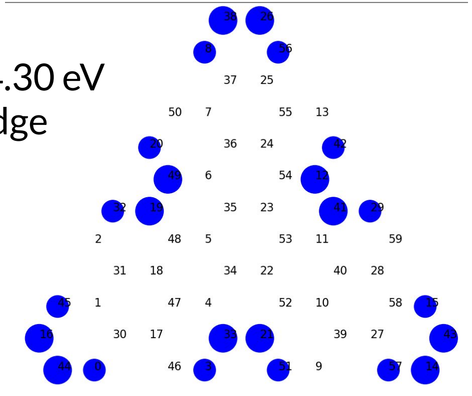
$$f_j(N) = \frac{1}{\exp\left(\frac{E_j - E_F(N)}{k_B T} + 1\right)}$$

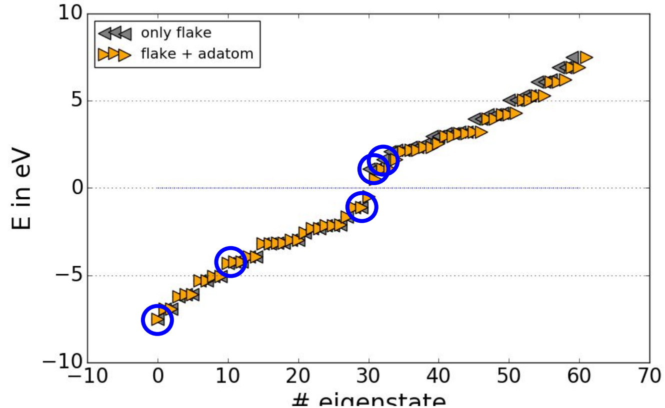


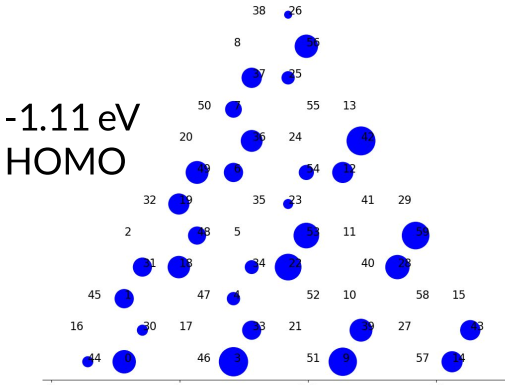


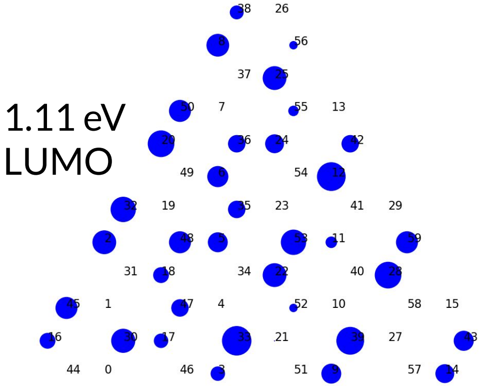
Eigenstate charge distributions

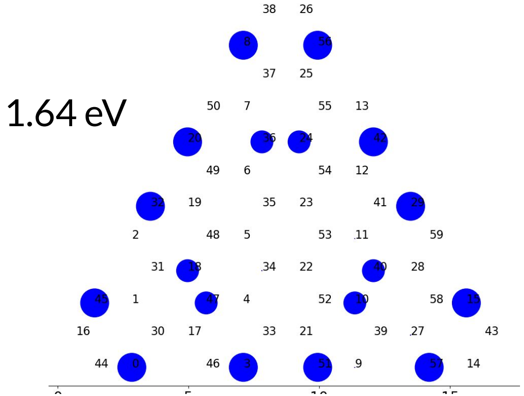




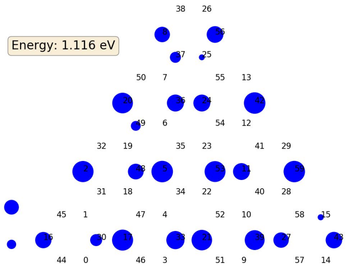


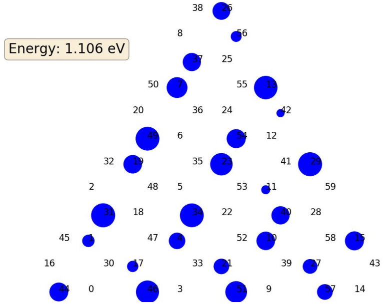


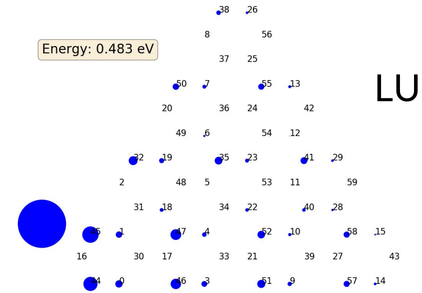




Eigenstates with adatom

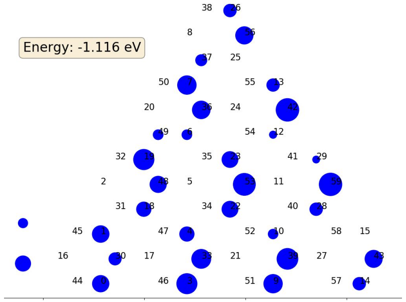


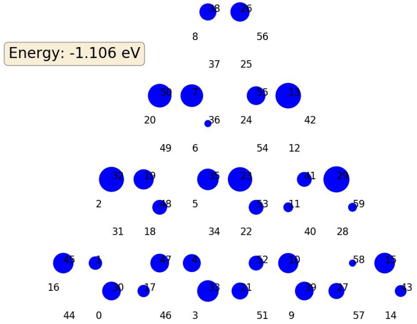


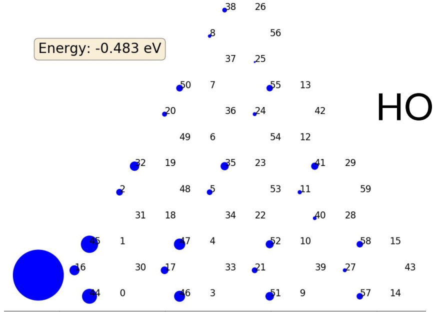


LUMO

$t_{e,g} = 0.5$ eV

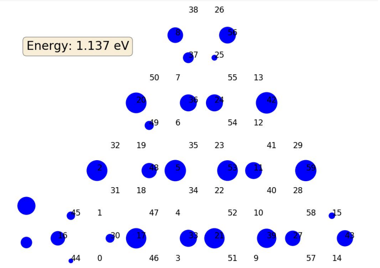


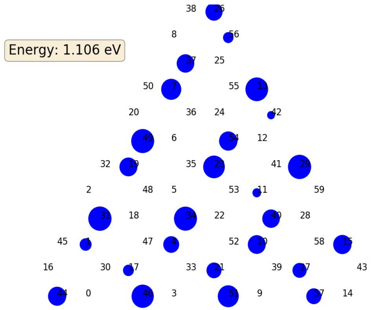


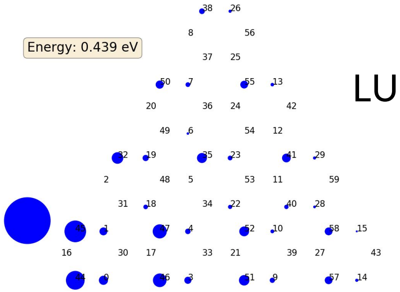


HOMO

Eigenstates with adatom

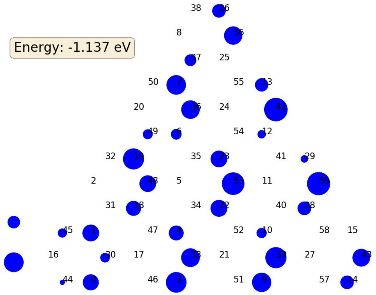


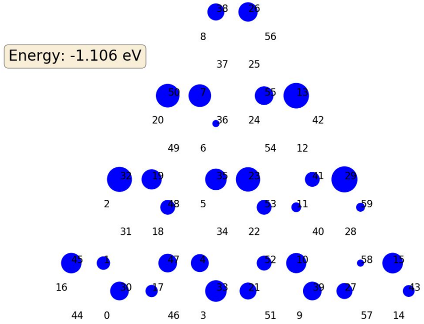


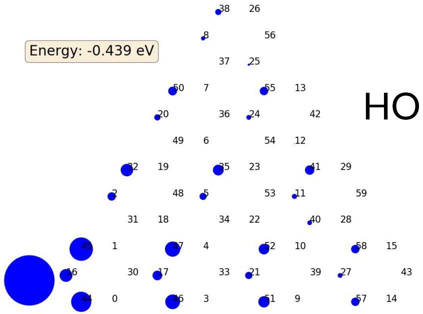


LUMO

$t_{e,g} = 1.0$ eV







HOMO

Density matrix dynamics

master equation

$$\dot{\rho} = -\frac{i}{\hbar}\left[H,\rho\right] + D\left(\rho\right)$$

Density matrix dynamics

master equation

$$\dot{\rho} = -\frac{i}{\hbar}\left[H,\rho\right] + D\left(\rho\right)$$

decoherence

$$D\left(\rho\right) = \sum_p 2\gamma_p\left(\sigma_p\rho\sigma_p^\dagger - \left\{\rho,\sigma_p^\dagger\sigma\right\}\right)$$

via Lindblad terms

Density matrix dynamics

master equation

$$\dot{\rho} = -\frac{i}{\hbar}\left[H, \rho\right] + D\left(\rho\right)$$

decoherence

$$D\left(\rho\right) = \sum_{p} 2\gamma_p \left(\sigma_p \rho \sigma_p^{\dagger} - \left\{\rho, \sigma_p^{\dagger}\sigma\right\}\right)$$

via Lindblad terms

decoherence between selected pair of states

Density matrix dynamics

master equation

$$\dot{\rho} = -\frac{i}{\hbar}\left[H, \rho\right] + D\left(\rho\right)$$

decoherence

$$D\left(\rho\right) = \sum_{p} 2\gamma_p \left(\sigma_p \rho \sigma_p^\dagger - \left\{\rho, \sigma_p^\dagger \sigma\right\}\right)$$

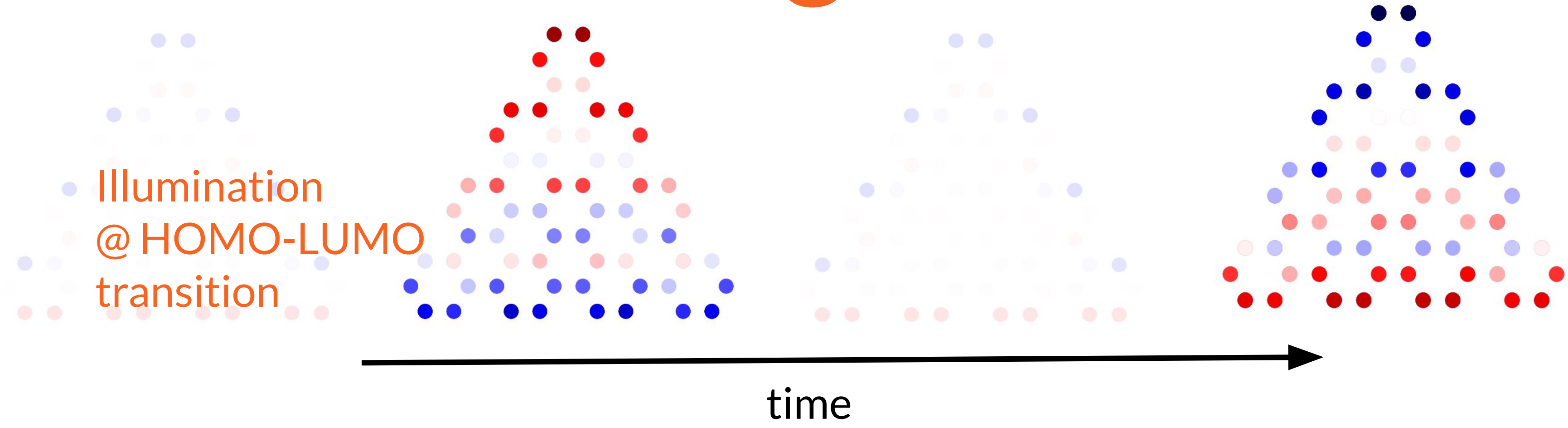
via Lindblad terms

decoherence between selected pair of states

$$D\left(\rho\right) = \frac{-1}{2\tau}\left(\rho - \rho_0\right)$$

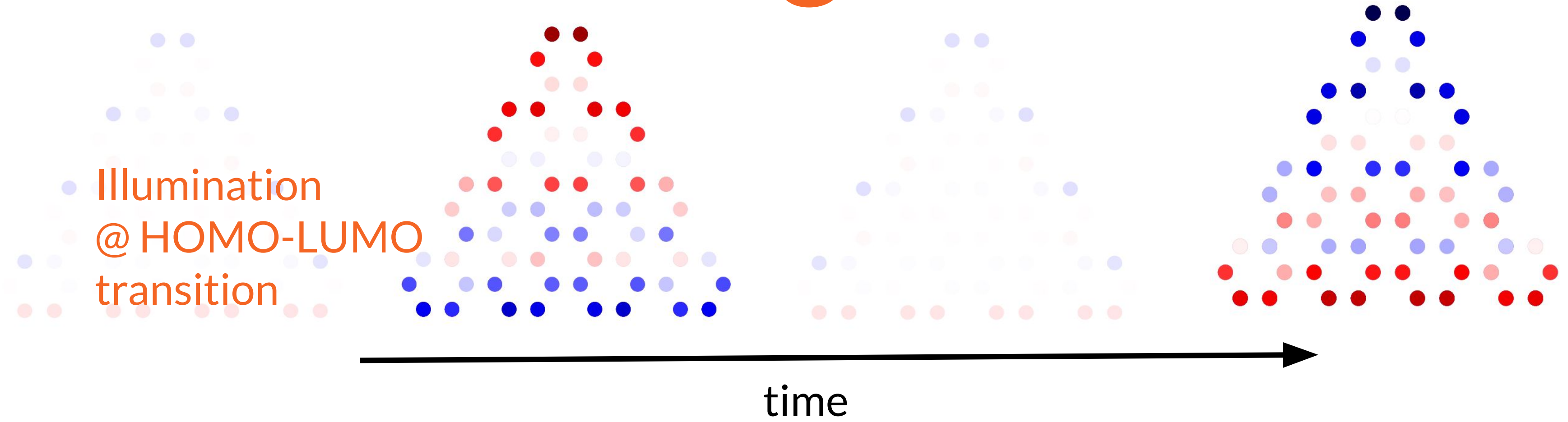
phenomenologically

Induced charge

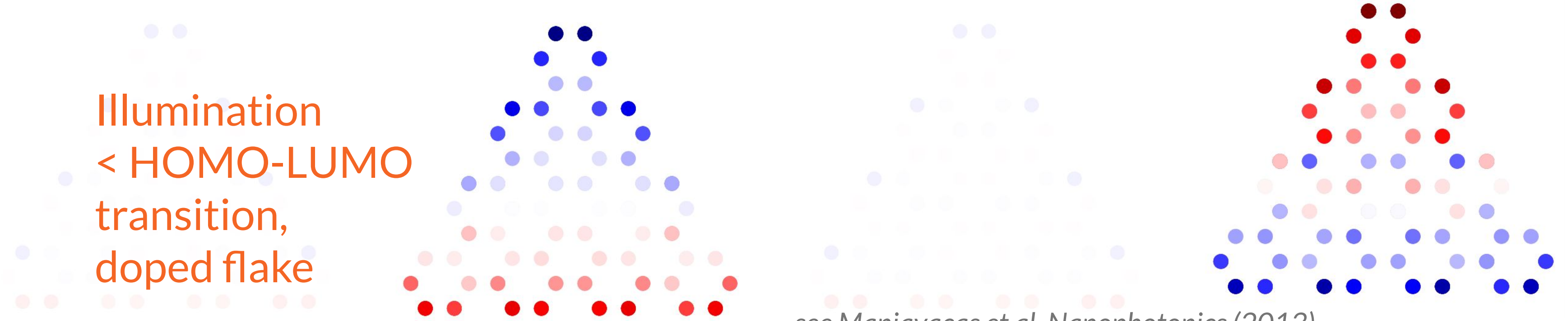


Induced charge

Illumination
@ HOMO-LUMO
transition

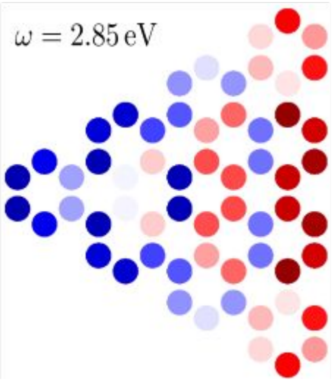


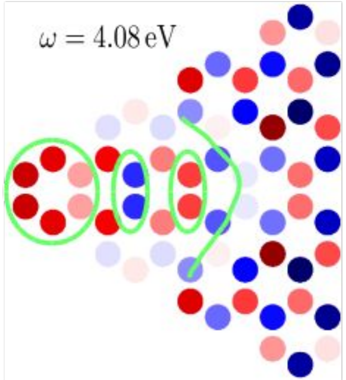
Illumination
< HOMO-LUMO
transition,
doped flake

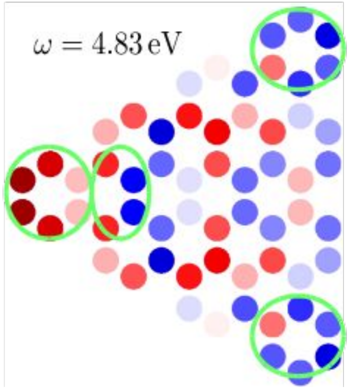


see Manjavacas et al. Nanophotonics (2013)

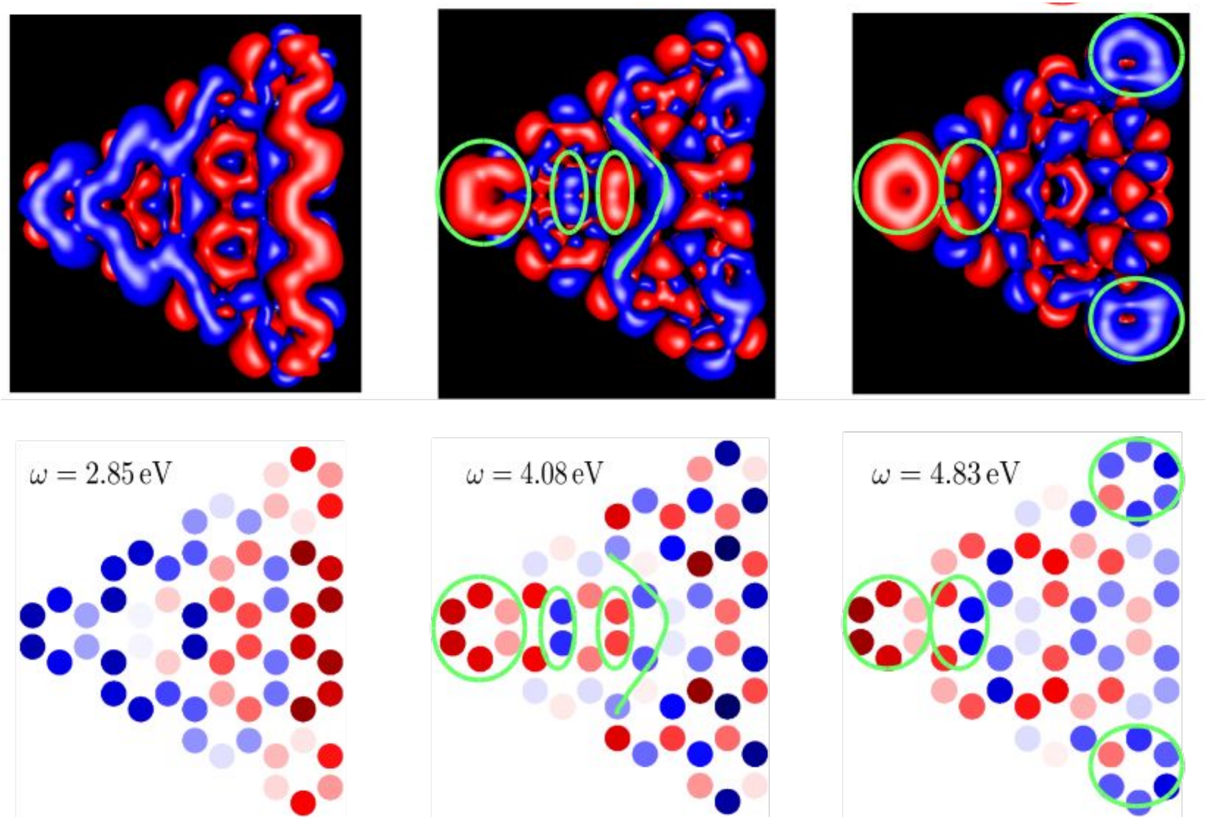
Induced charge







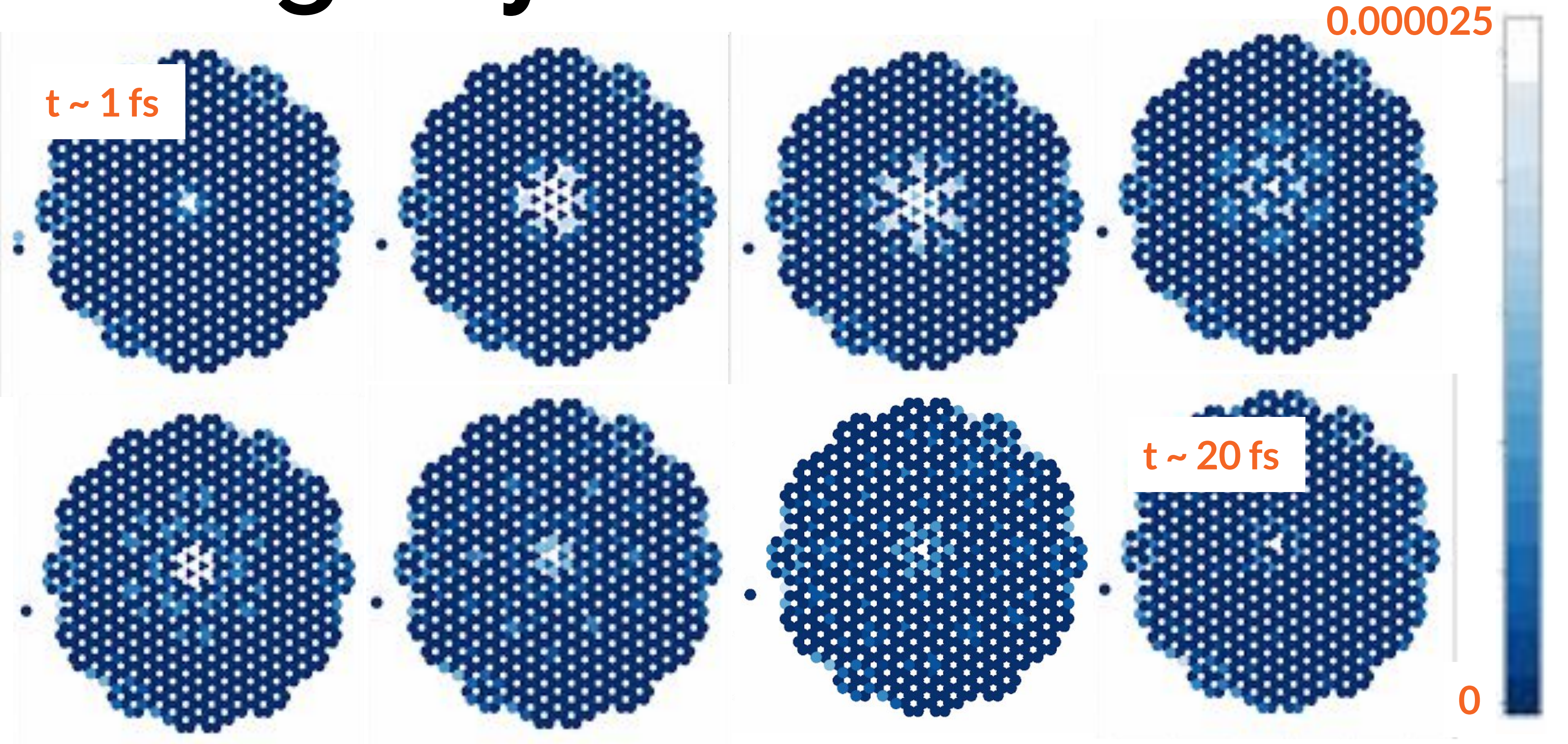
Induced **charge**



DFT simulations by Giulia Giannone (Istituto Italiano di Tecnologia, Lecce)

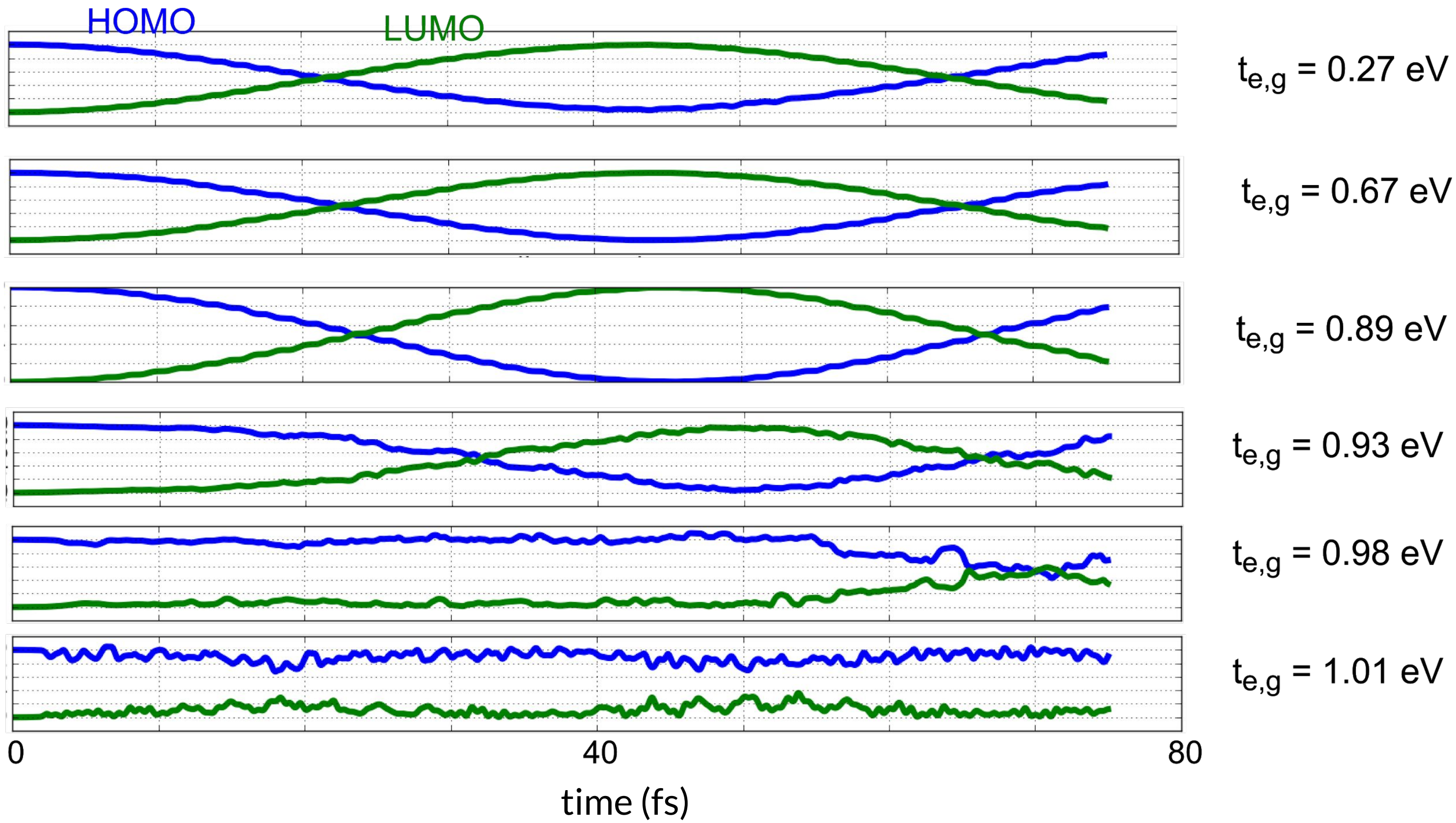
Comparison of **induced charge distribution plots** obtained from DFT and our code.

Charge dynamics with atom

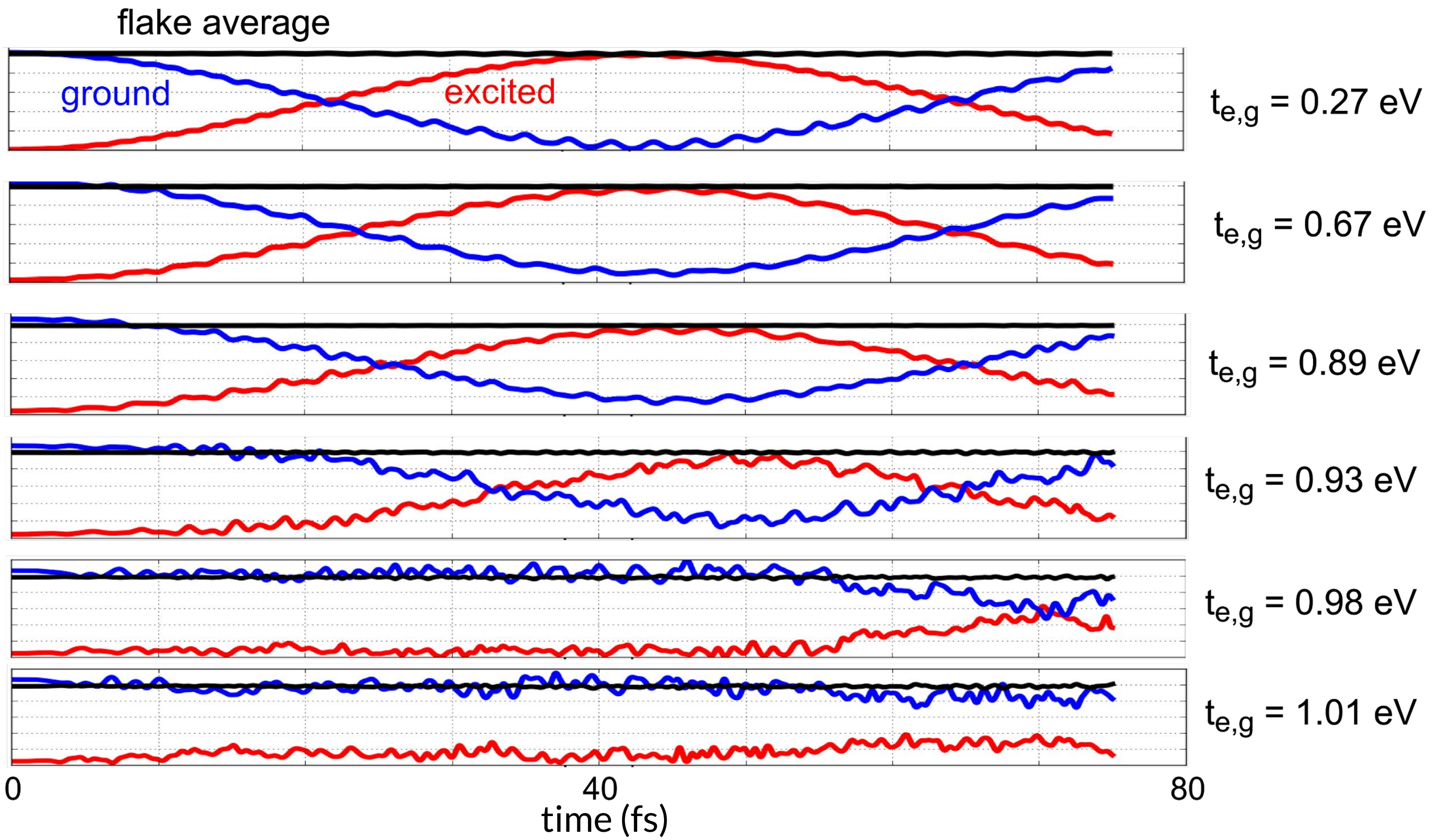


Coupling flakes to adatoms

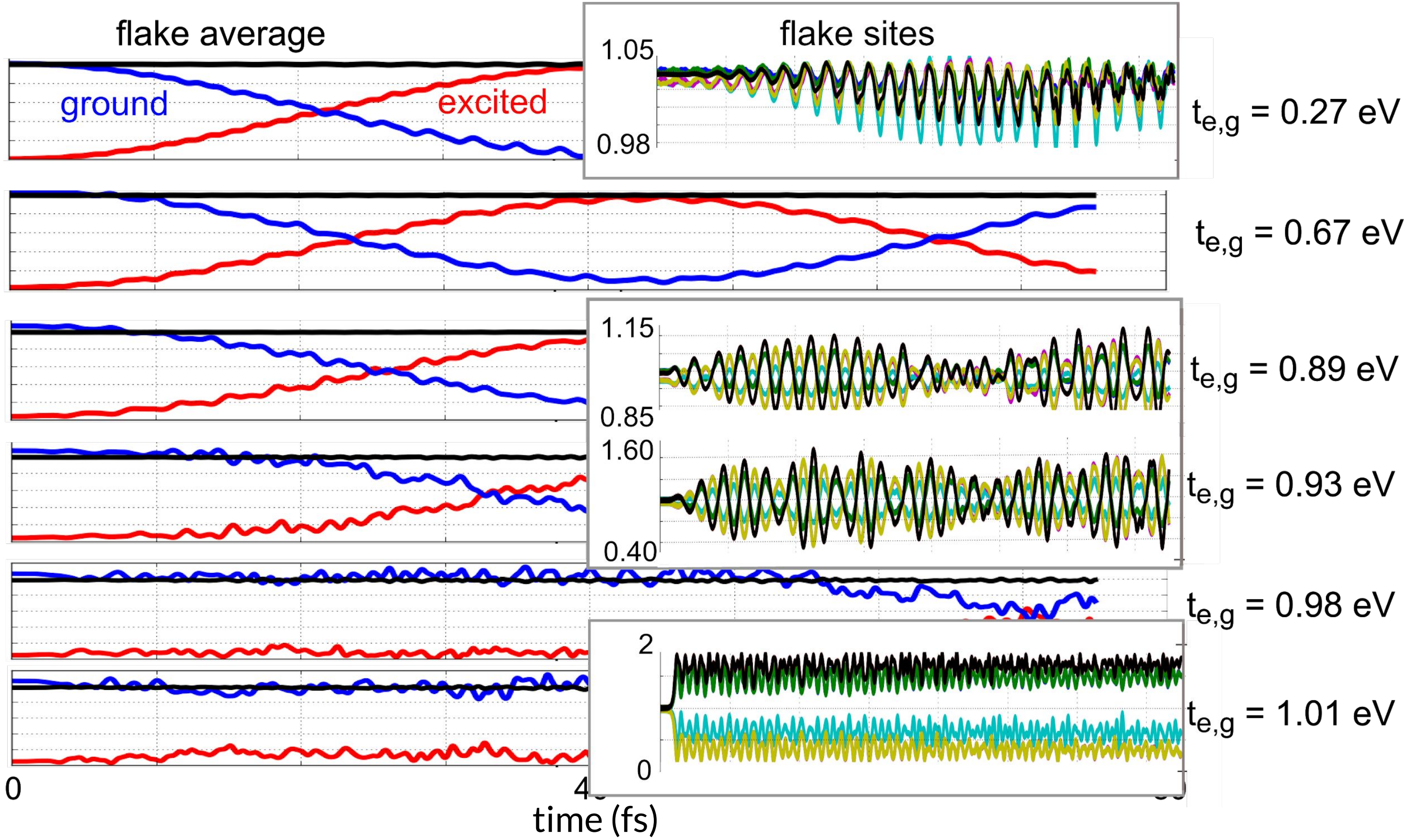
$$\Omega = E\, d_{HL}$$



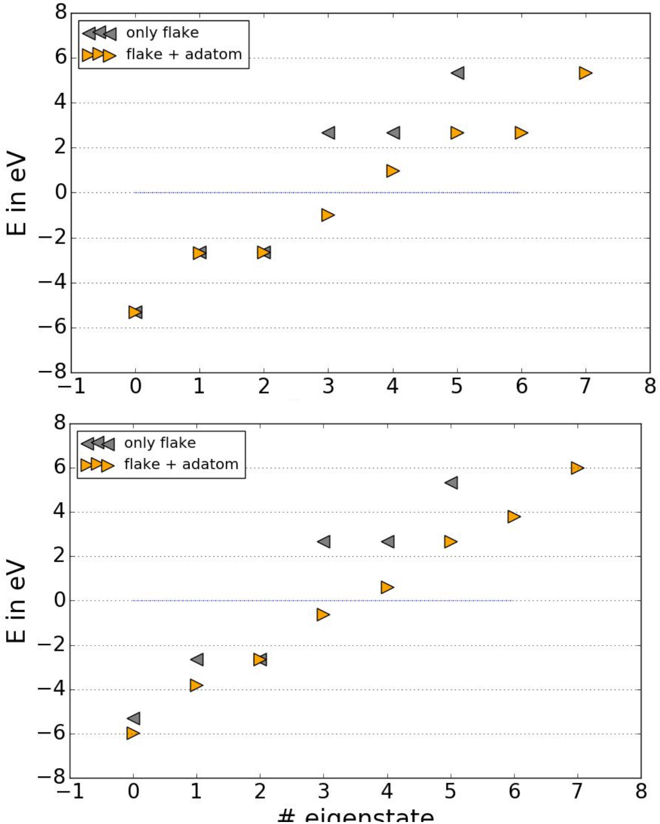
Coupling flakes to adatoms

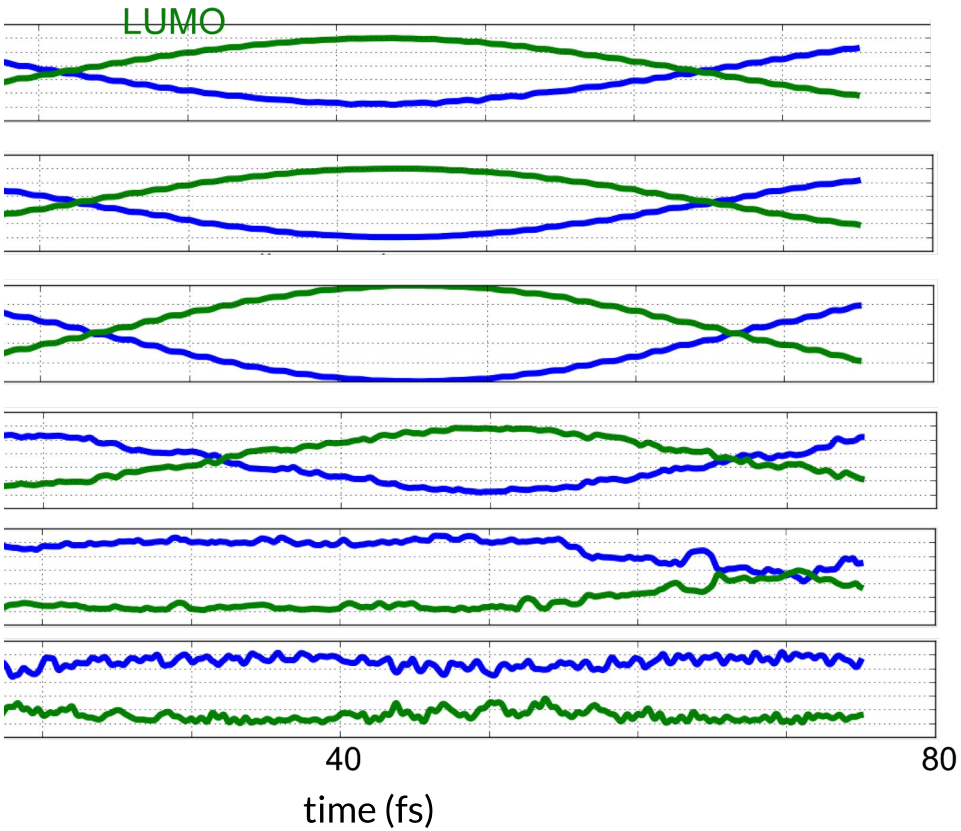


Coupling flakes to adatoms



Coupling flakes to adatoms





$t_{e,g}$ = 0.27 eV

$t_{e,g}$ = 0.67 eV

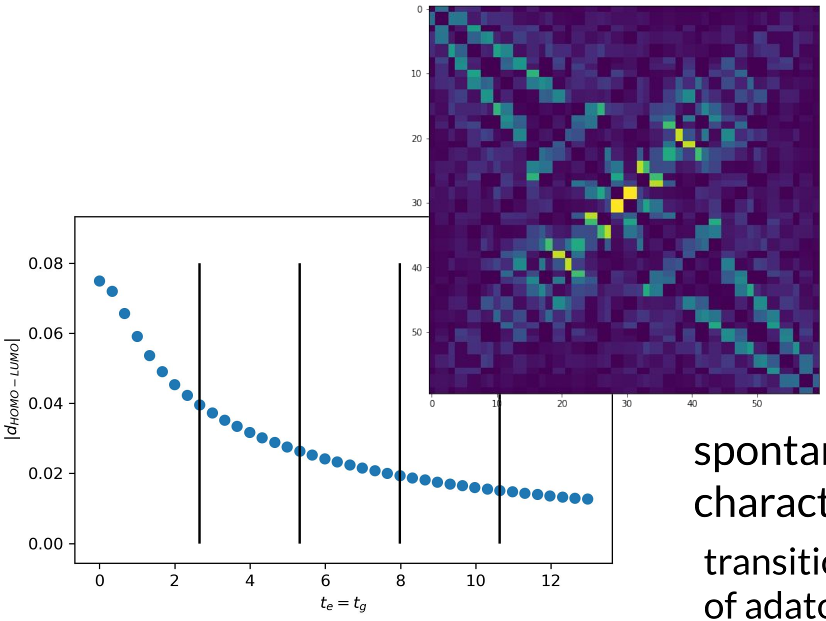
$t_{e,g}$ = 0.89 eV

$t_{e,g}$ = 0.93 eV

$t_{e,g}$ = 0.98 eV

$t_{e,g}$ = 1.01 eV

Poster advertisement



Rabi oscillations in flake + adatom

spontaneous emission characteristics

transition dipole moment of adatom, flake & combined

Miriam

Interaction of a graphene nanoflake with an adatom under optical illumination

M. Kosik et al., poster

Decoherence dynamics

via Lindblad terms

$$\sum_p 2\gamma_p \left(\sigma_p \rho \sigma_p^\dagger - \{\rho, \sigma_p^\dagger \sigma\}\right)$$

$\overset{?}{=}$

phenomenologically

$$- \frac{1}{2\tau}(\rho - \rho_0)$$

not known, but scalable

known for pristine graphene

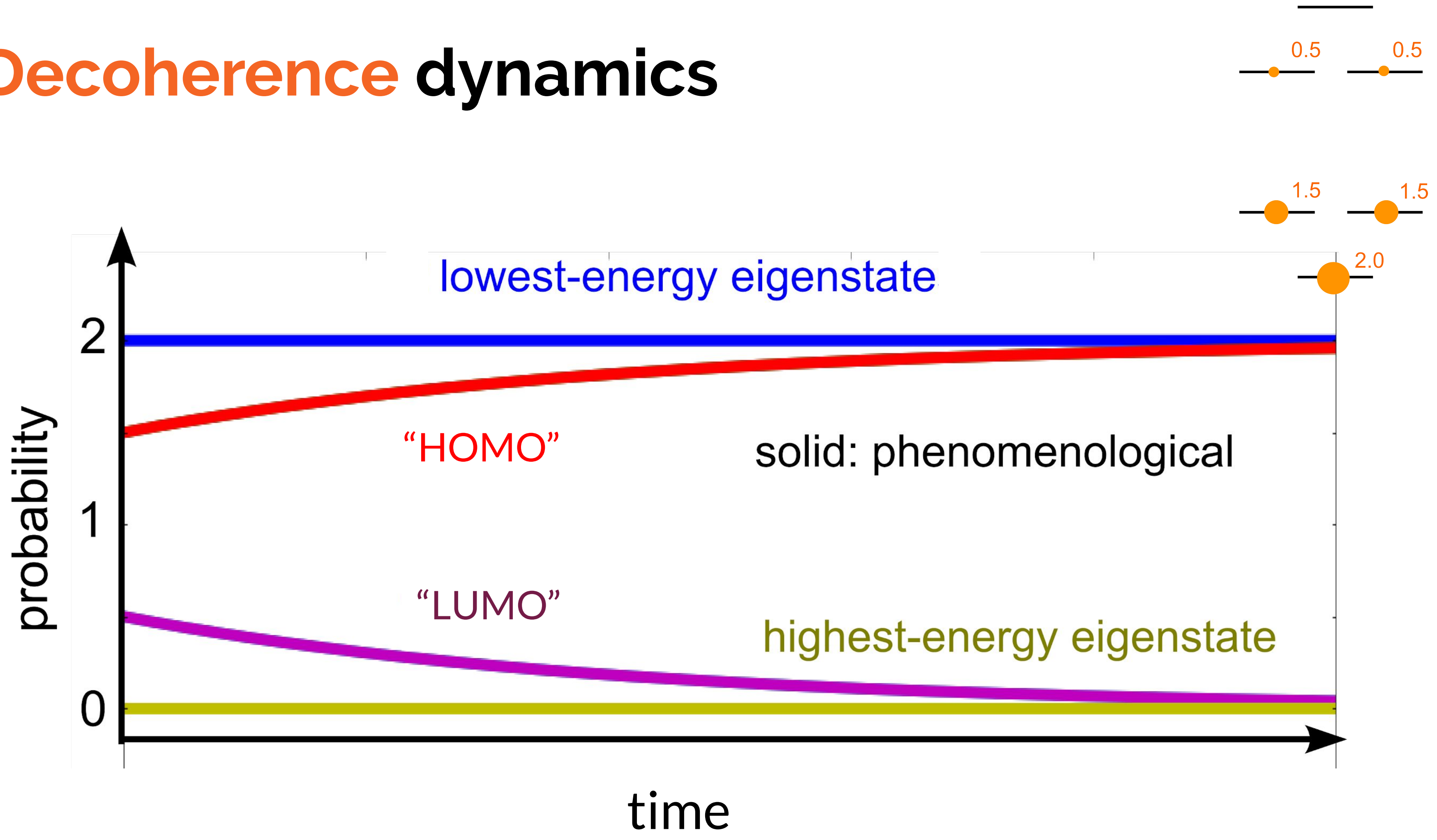
2+ free parameters γ_p

1 parameter τ

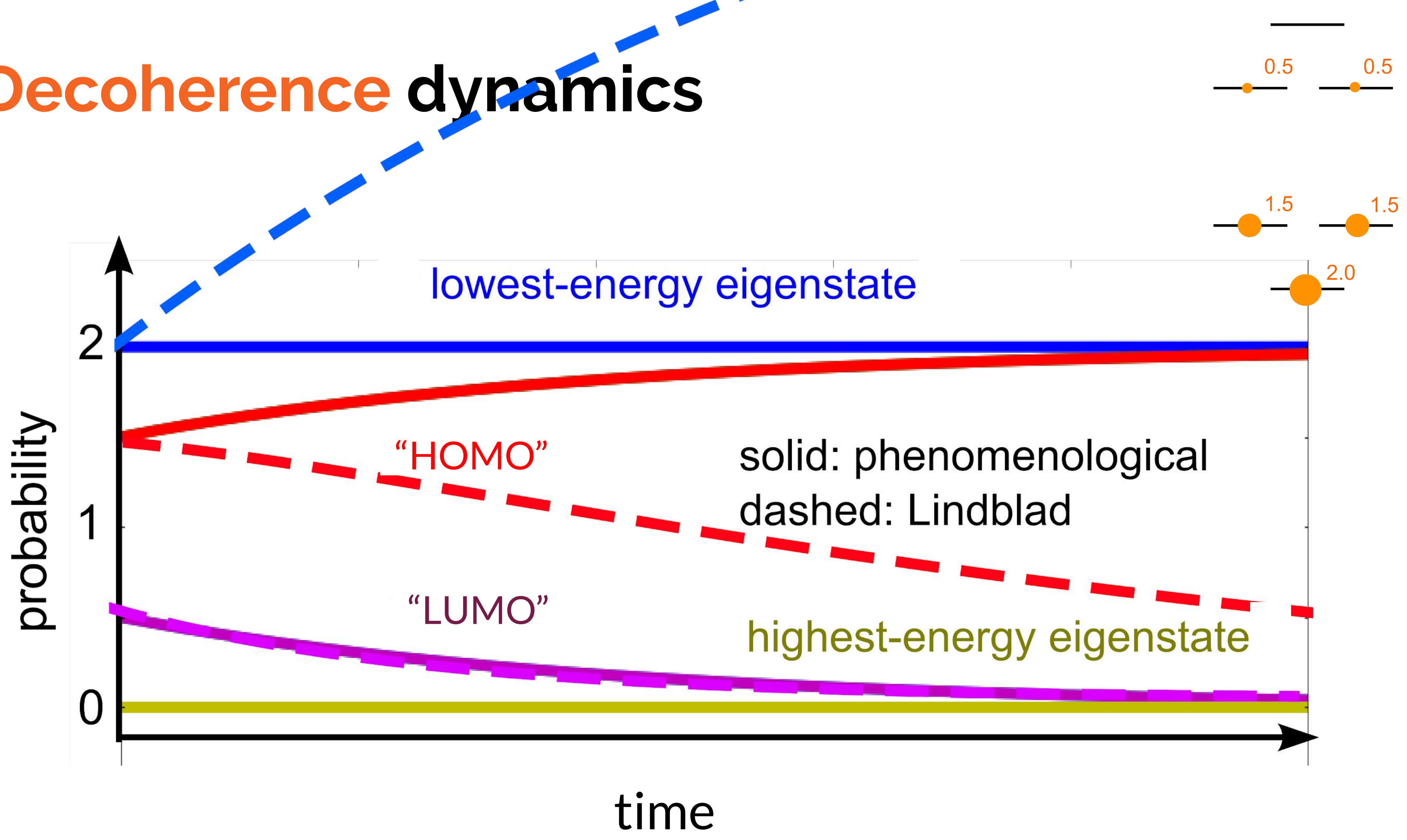
not protected against Pauli principle breaking

decay to predefined stationary state

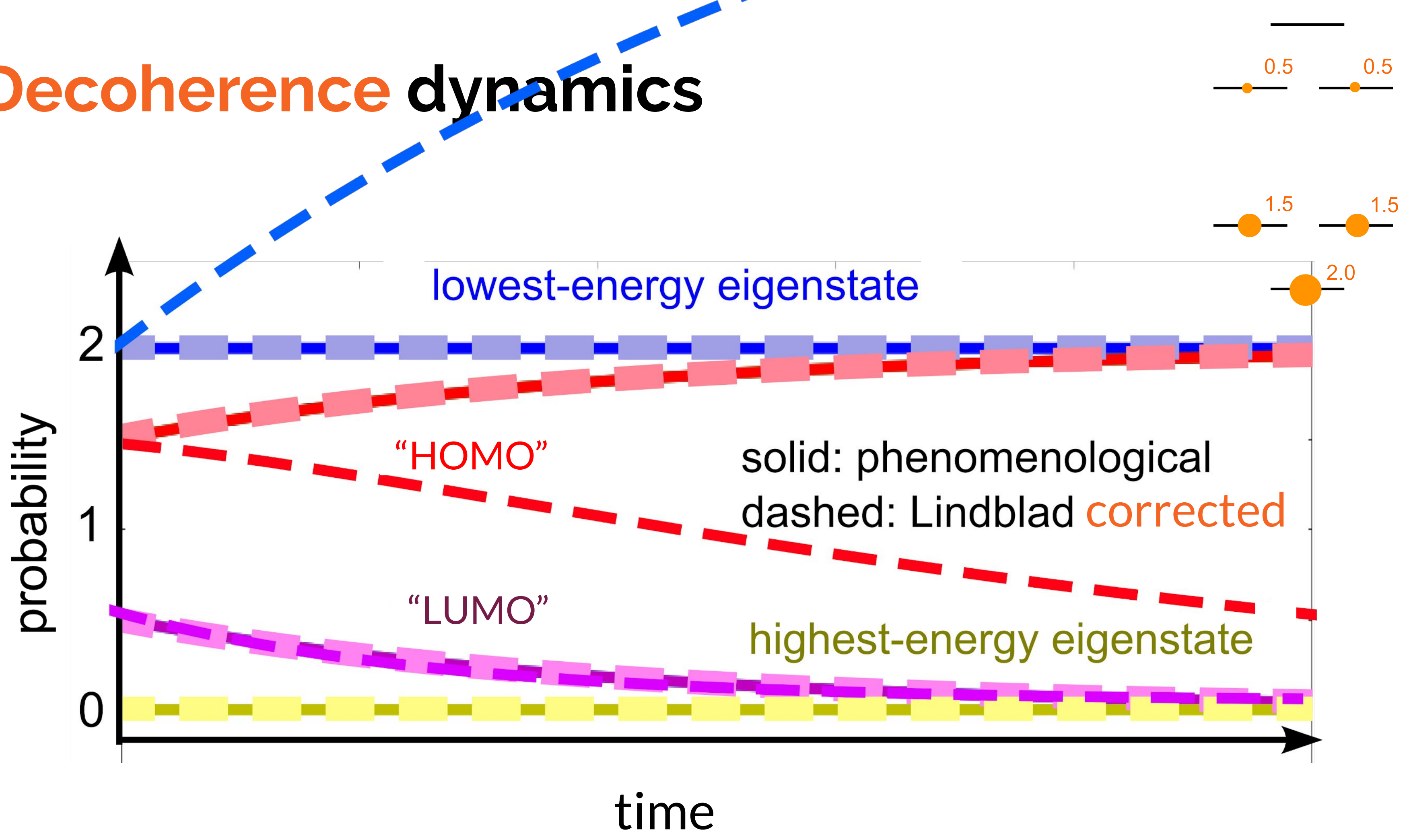
Decoherence dynamics



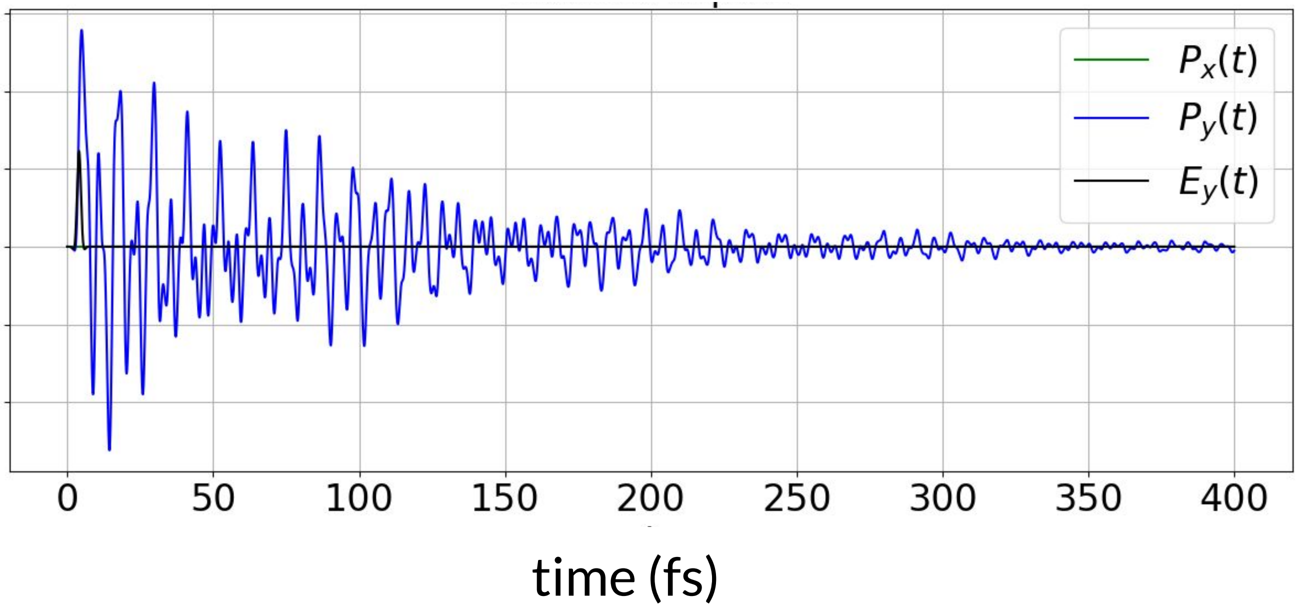
Decoherence dynamics

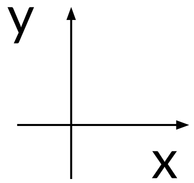


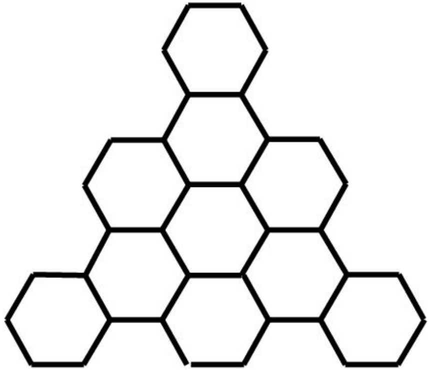
Decoherence dynamics



Polarizability

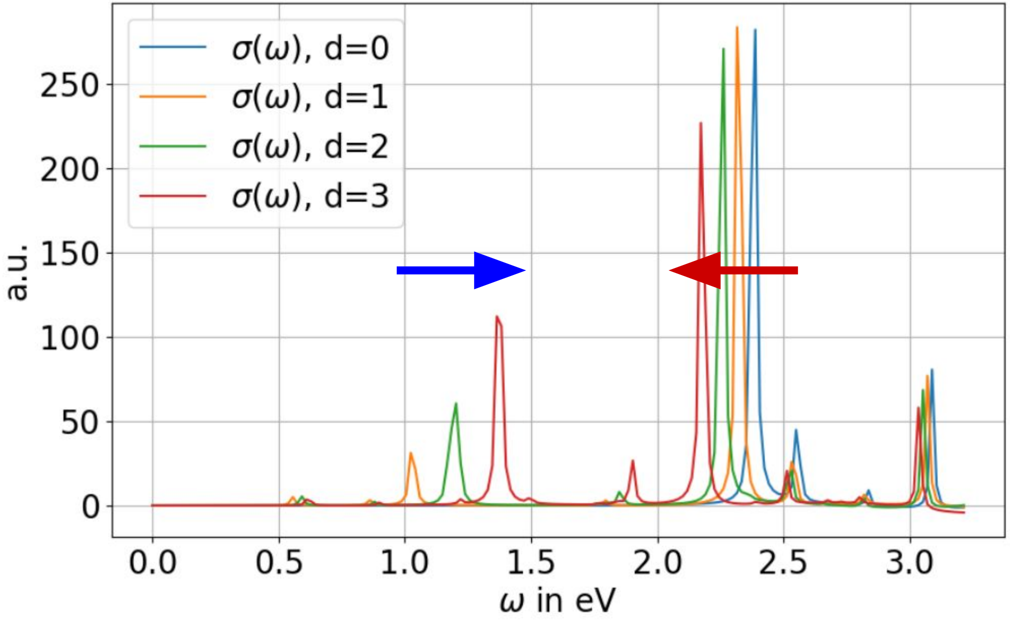






$$\mathbf{P}(t) = -eN\sum_l \left[\rho_{ll}(t) - \rho_{ll}^0\right]\boldsymbol{r}_l$$

Absorption spectrum

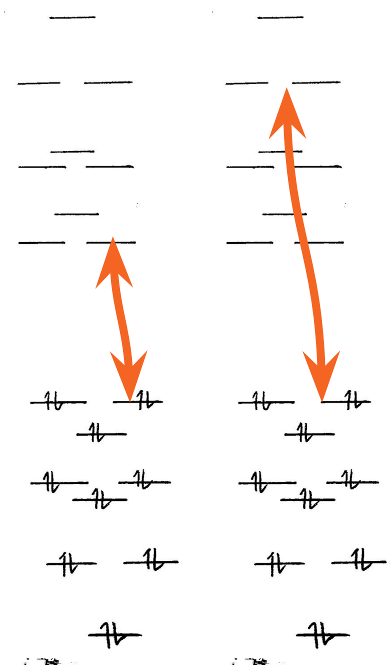


$$\sigma(\omega) \sim \omega \mathrm{Im}\left[\alpha(\omega)\right]$$

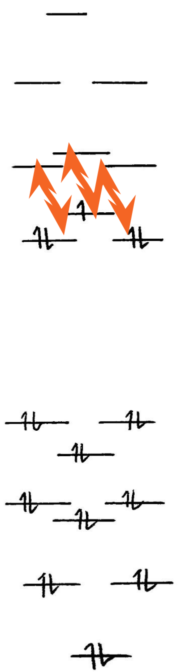
Blue shifting resonances
➔ require doping
➔ lower energy

Red shifting resonances
➔ do not require doping
➔ higher energy

Excitons or plasmons

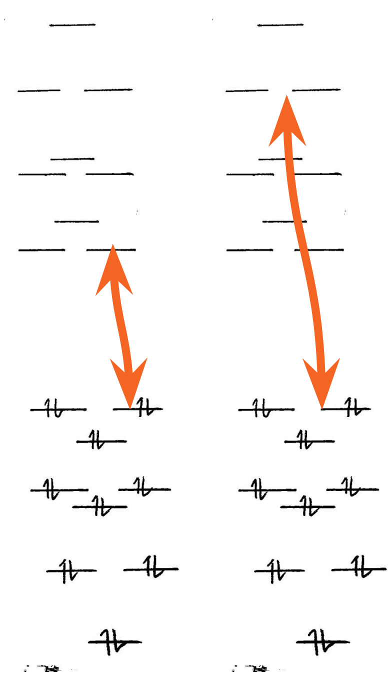


- ➔ creation of an electron-hole pair
- ➔ single-particle process
- ➔ appear without doping
- ➔ might disappear with doping
- ➔ “Interband” → higher energy



- ➔ motion of electron cloud
- ➔ collective process
- ➔ ± doping required
- ➔ shift with doping ~$n^{1/2}$
- ➔ nonlinear optical response
- ➔ “intraband” → lower energy

Excitons or plasmons



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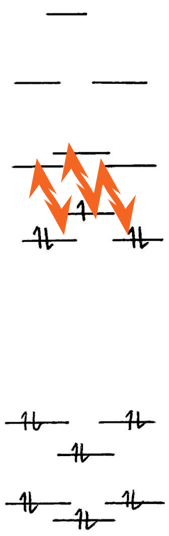

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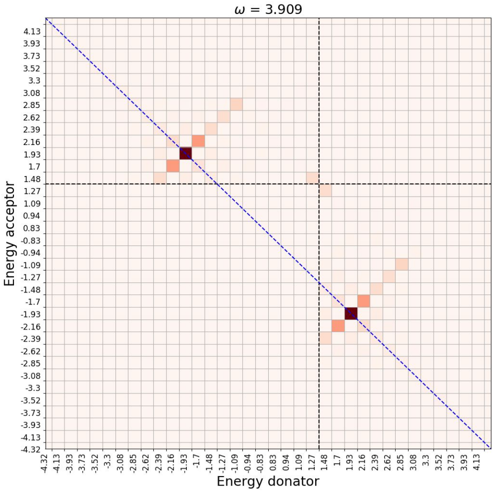
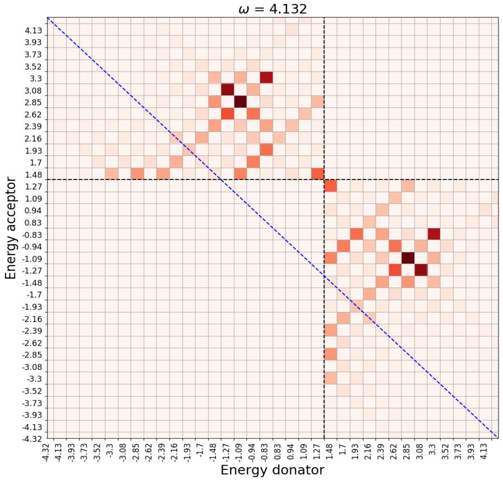
Bernadotte et al. *J. Phys. Chem. C* (2013)
Townsend& Bryant *J.Opt.* (2014)
G. Bryant *J. Opt.* (2016)
Zhang et al. *ACS nano* (2017)
….

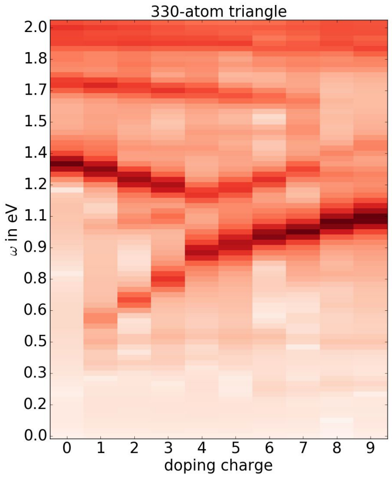
Poster advertisement

mostly excitonic transition

predominantly plasmonic transition







Co-Existence of Tunable Plasmons and Excitons in Graphene Nanoantennas
M. Müller et al., poster

Summary & outlook

- ➔ Tool to study dynamics of illuminated graphene flakes with adatoms
  - ◆ Spectral properties (eigenenergies and states)
  - ◆ Dynamics of density matrix
  - ◆ Induced charges & optical response
- ➔ Distinction of plasmonic & excitonic resonances
- ➔ Influence of flake on adatom's optical response & vice-versa

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DFG Deutsche Forschungsgemeinschaft

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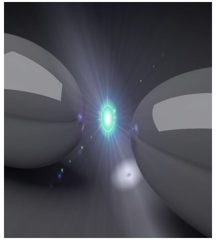
- ➔ more atoms
- ➔ back-action on field



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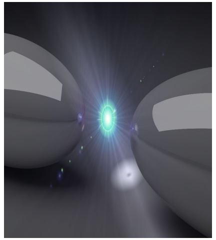

thank you

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