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Electron transport via defect network

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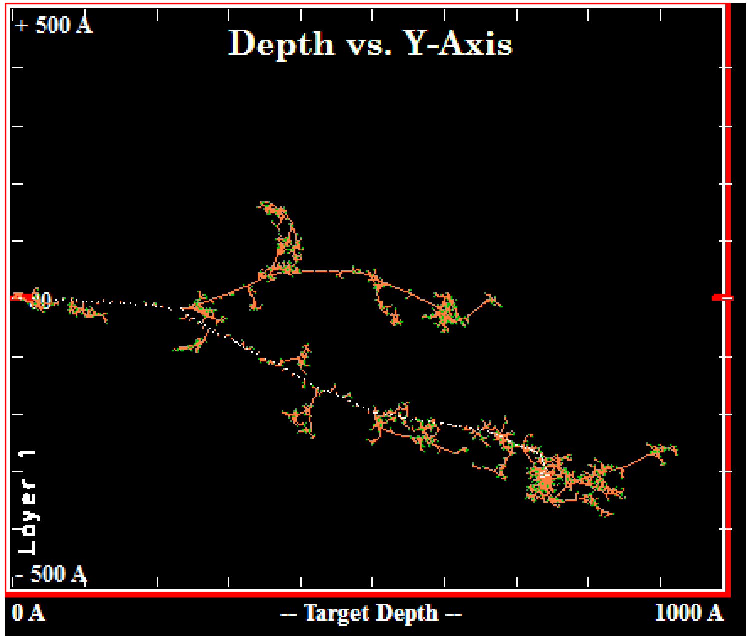
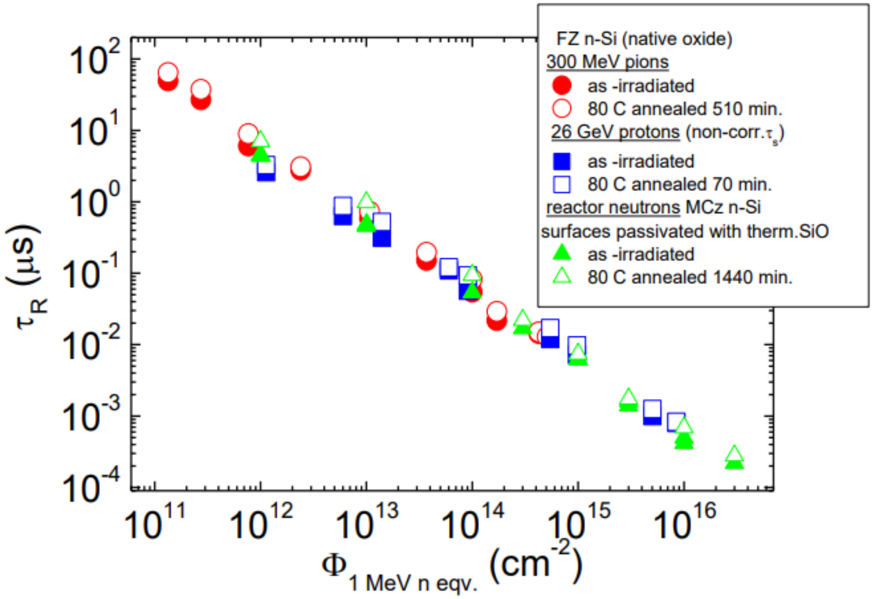
Motivation

1. Irradiation by high energy particles induced defect network
2. Electron lifetimes are sensitive to geometry
3. Defects form nano-size clusters
4. Bulk theory is not sufficient



24th RD50 workshop, Bucharest



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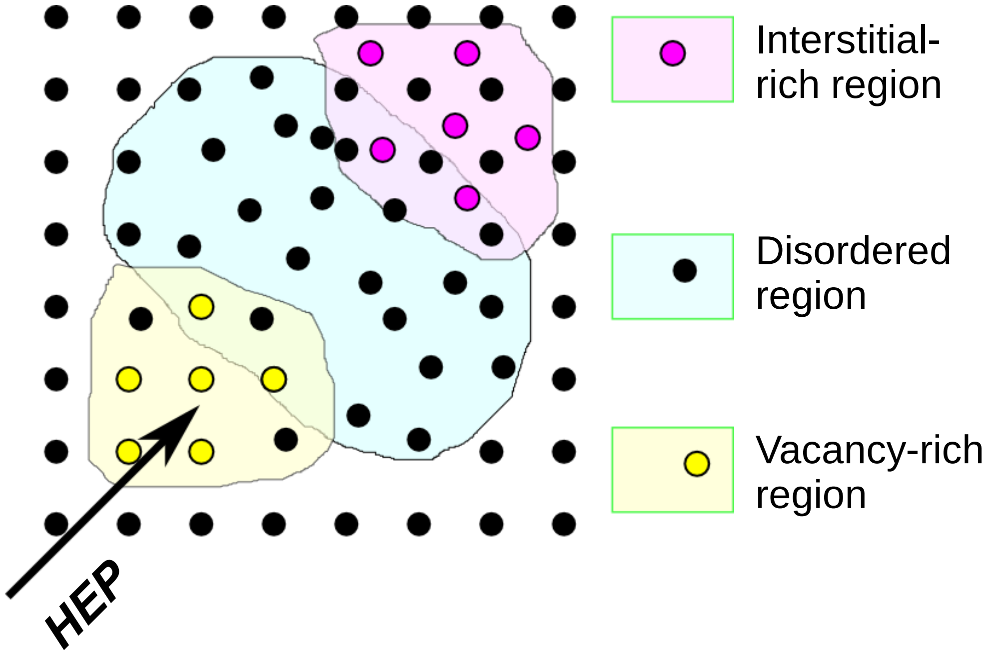
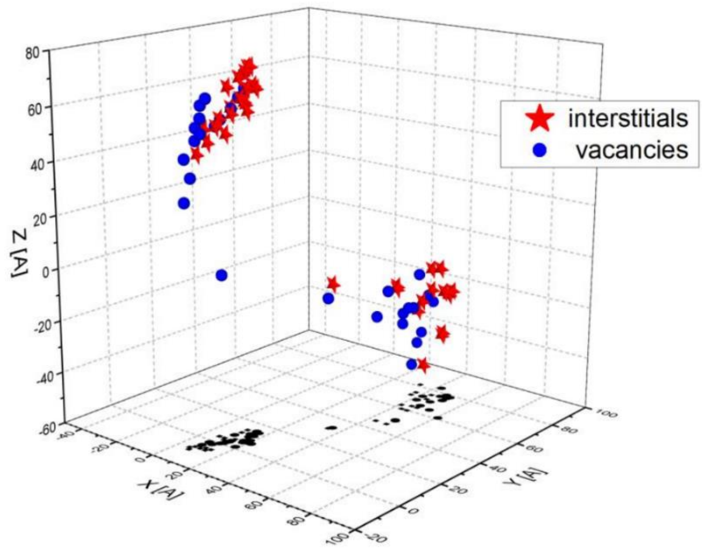
High Energy Particle (HEP) destroys the lattice:





36 V/I after recombination (20%)

TRIM and TCAS simulation results, presented by G. Lindstroem, 24th RD50 workshop, Bucharest, 2014.

After relaxation of cascade deffect and recombination of I-V pairs the rest of the vacancies and interstitials remain separated in space.

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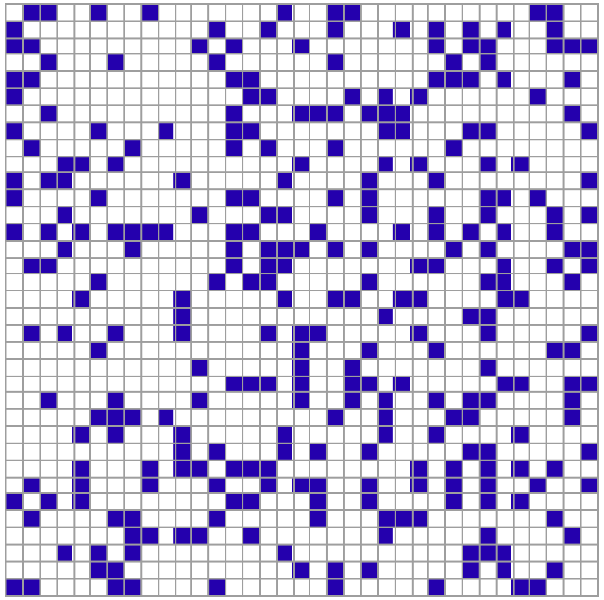
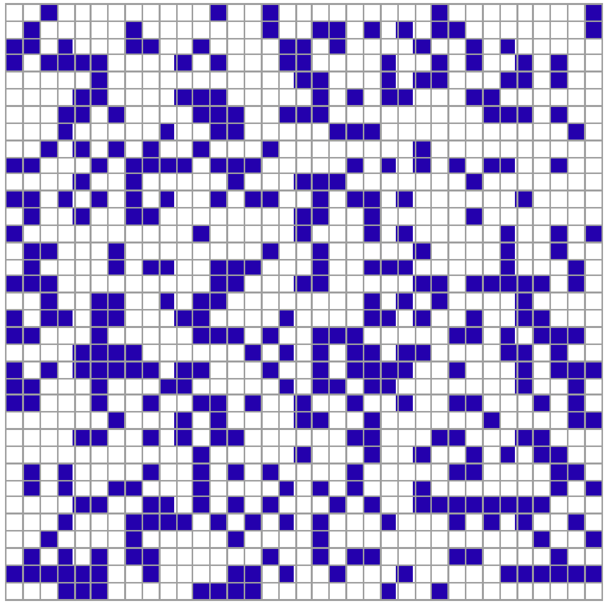
Percolation network



p=0.25



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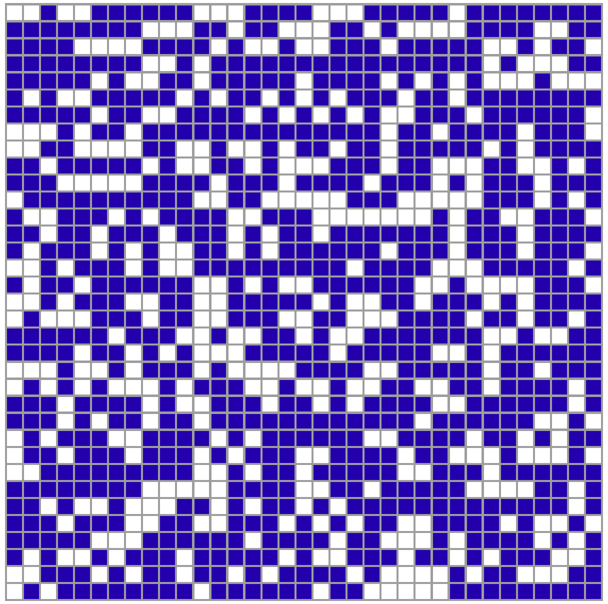
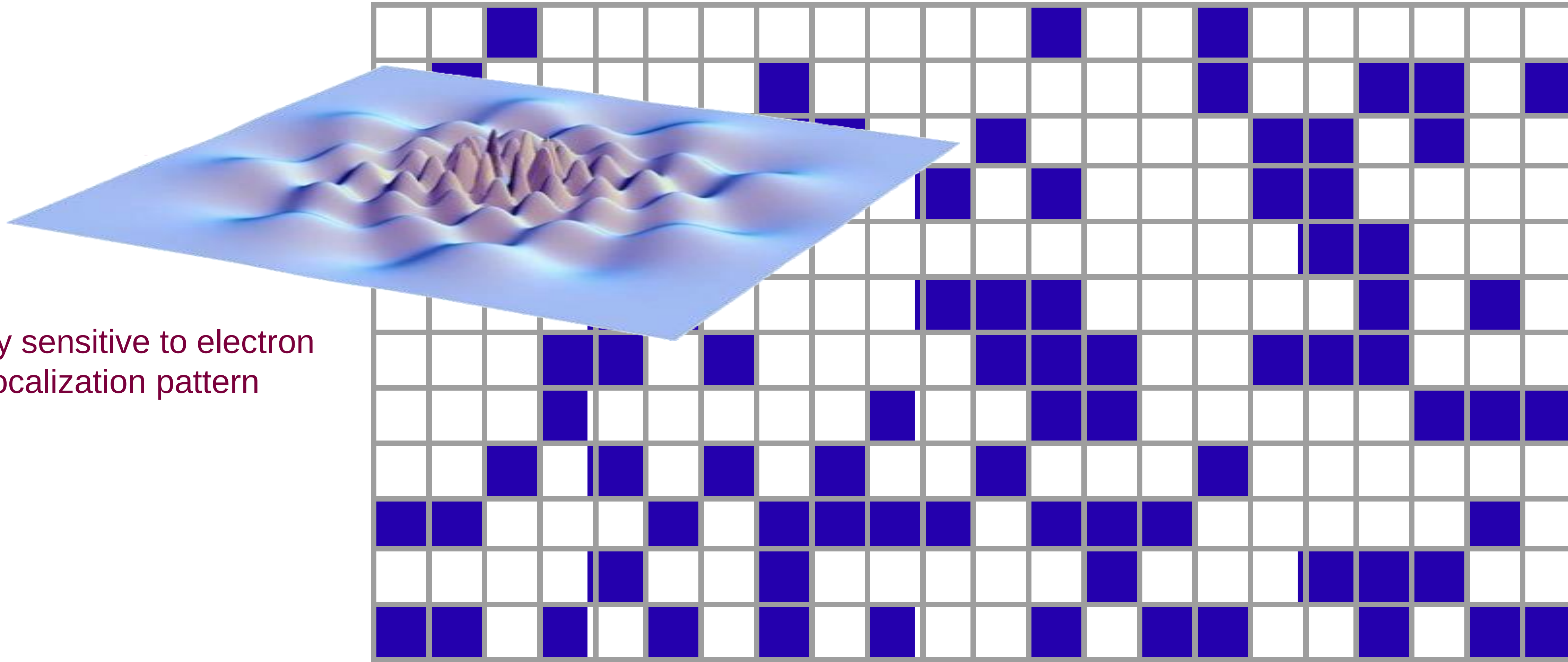


p=0.65

- Classical site percolation problem

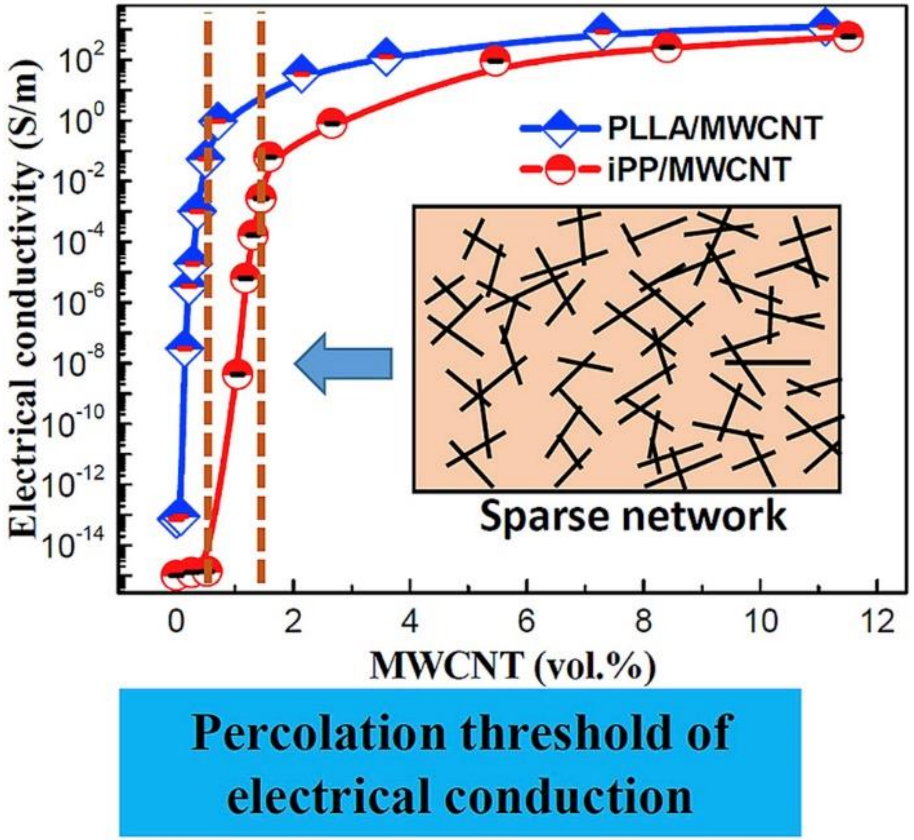
Quantum percolation network



- Very sensitive to electron delocalization pattern

Percolation network

- Percolation behavior of electrical conduction has been well demonstrated in conductive polymer composites (CPC), carbon nanotubes.



Composites Science and Technology, v 170, 20 January 2019, Pages 70-76

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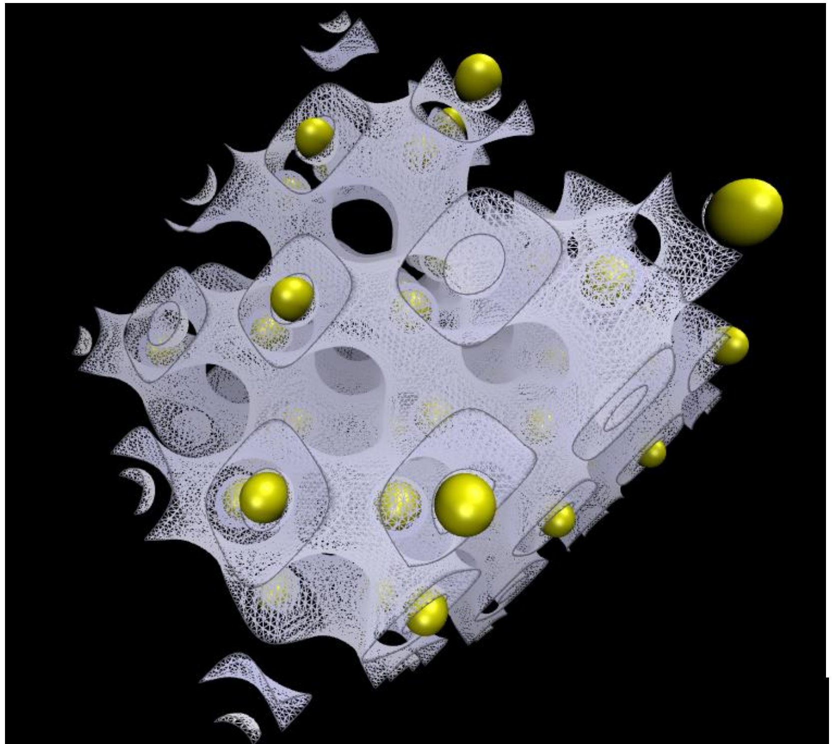
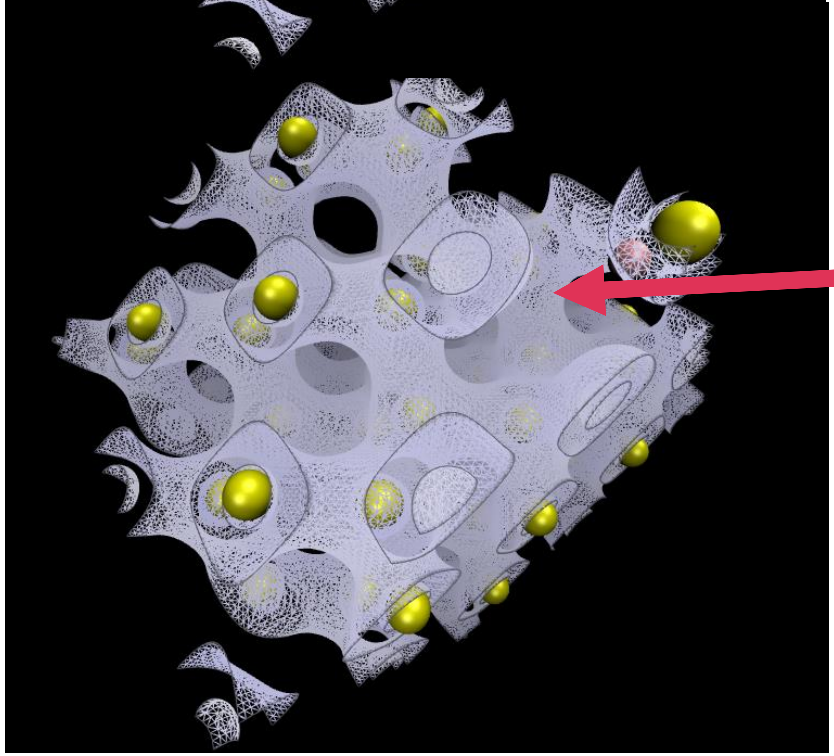
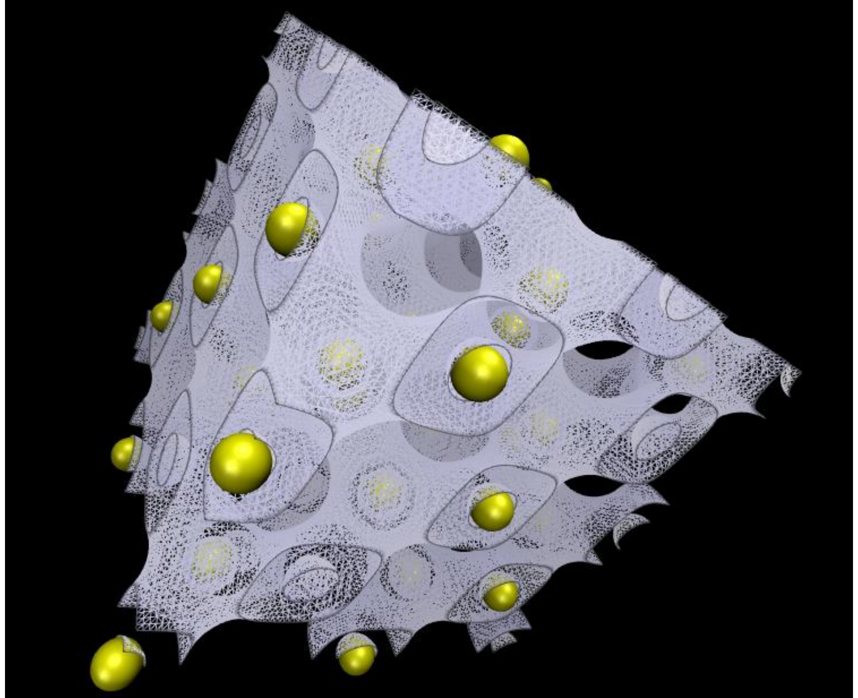
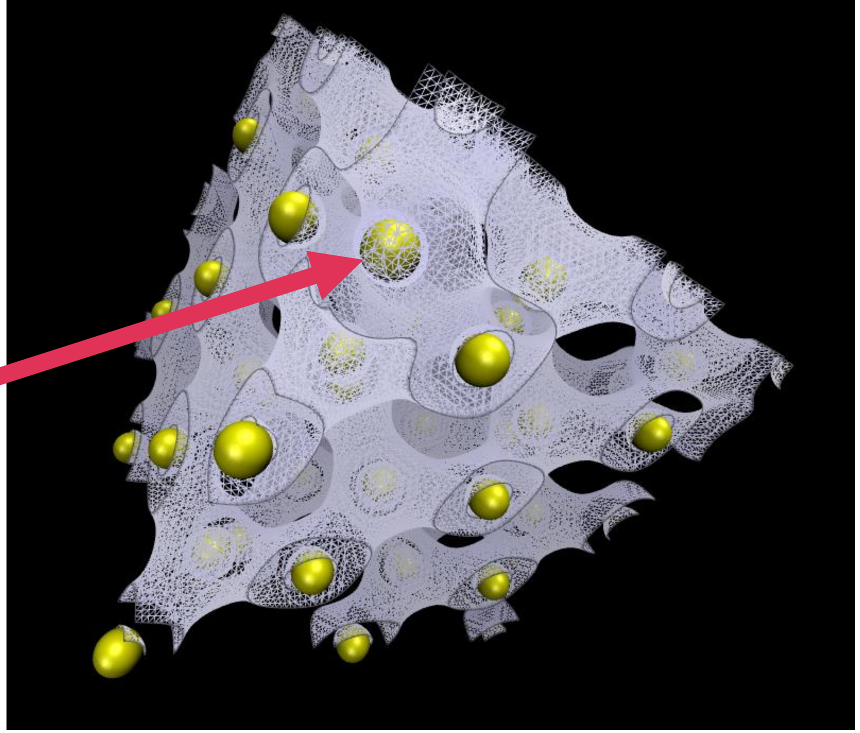
Electron density









vacancy

interstitial

Vacancy and Interstitial defect

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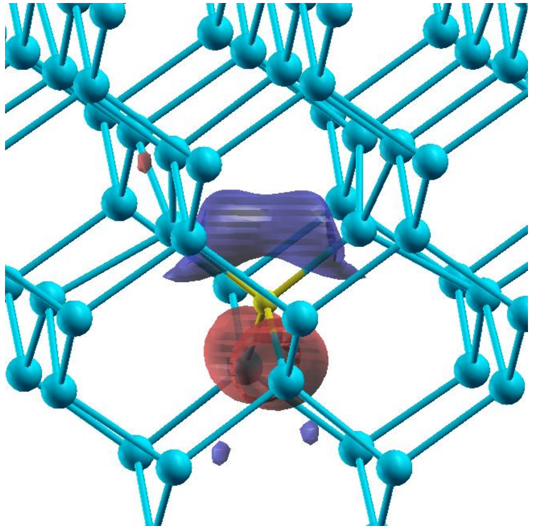
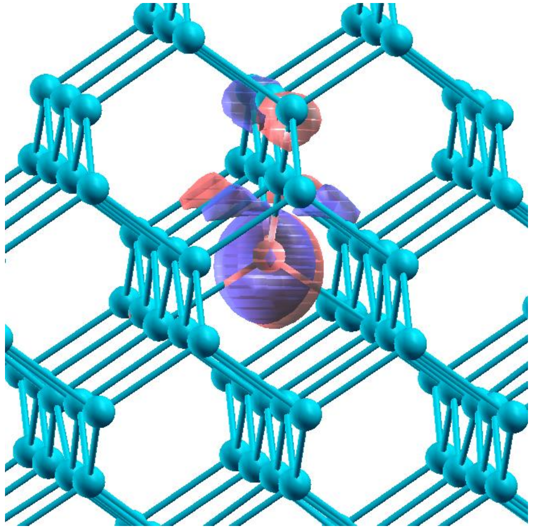




Vacancy defect, Td symmetry.
Wave function of a localized electron
in the acceptor site.

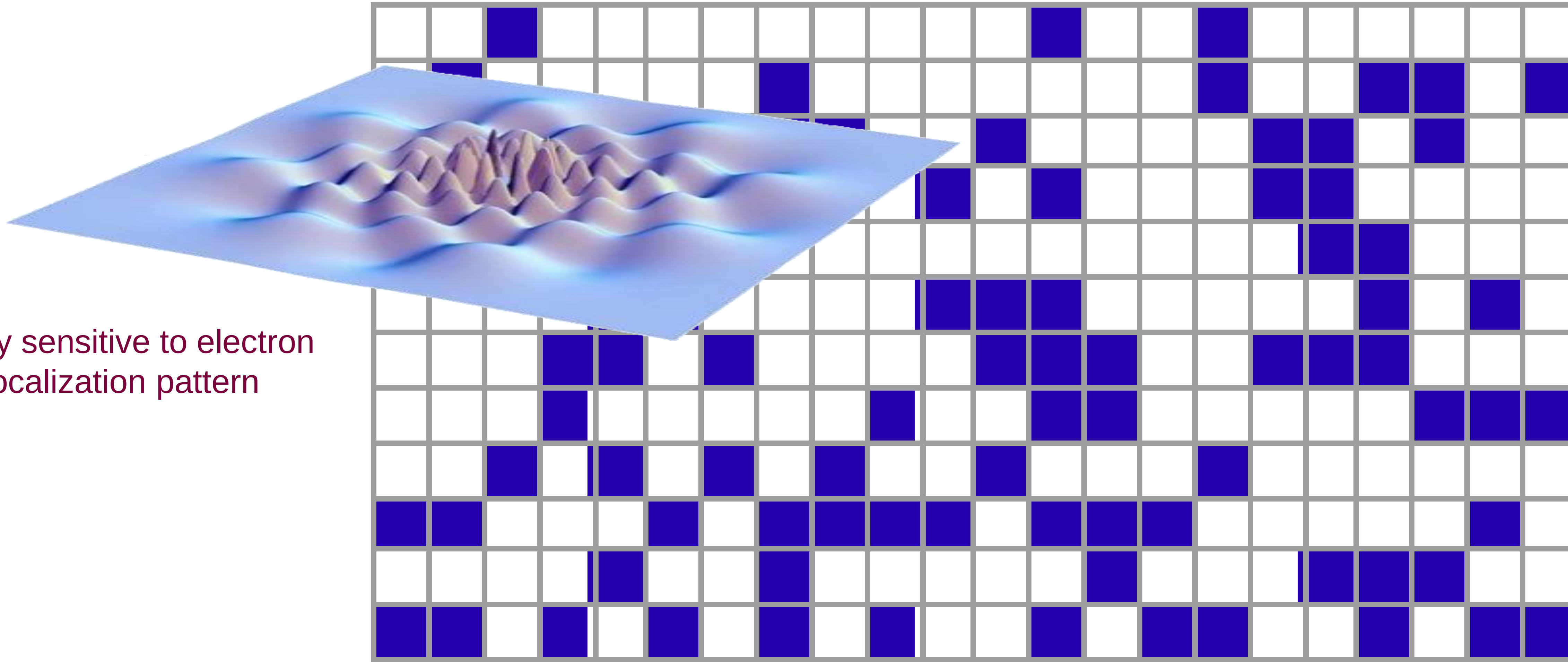
Neutral vacancy defect is known to be of
the **acceptor** type.

Interstitial defect, Td symmetry.
Wave function of a localized hole
in the donor site.

Interstitial defect in Td symmetry state is known
to be of the **donor** type (Ec – 0.39 eV)
Mukashev et al, Jpn. J. Appl. Phys. 21, 399 (1982).

simulations were performed by Ernestas Žąsinas (Vilnius University)

Quantum percolation network



- Very sensitive to electron delocalization pattern

Electron transport network

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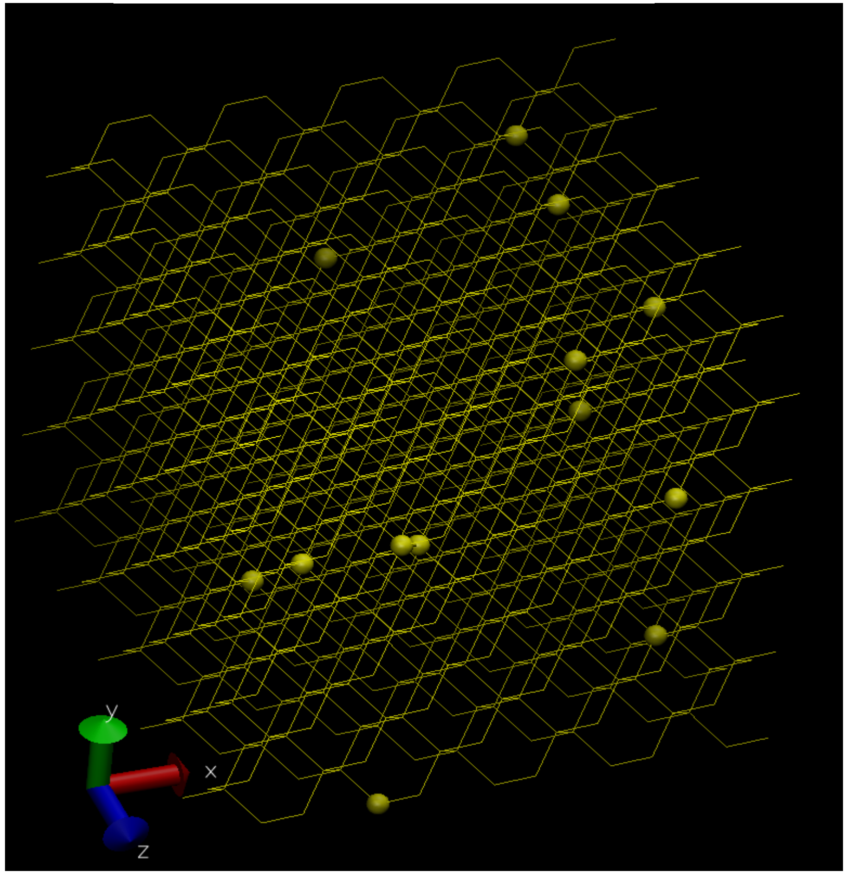
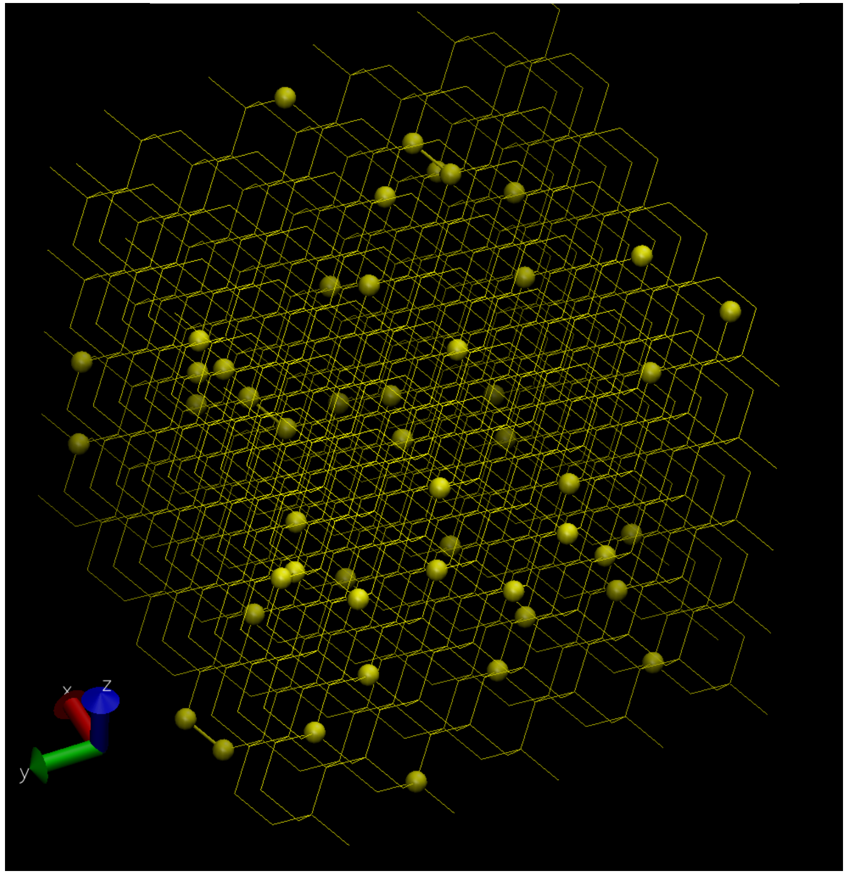
$n = 10^{20}\mathrm{cm}^{-1}$



$n = 5 \cdot 10^{20}\mathrm{cm}^{-1}$



Electron transport theory

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Tight binding Hamiltonian
(only defect sites)

Electron creation/annihilation operators

$$\hat{H} = \sum_{n} h_{nn}(\{\hat{x}_q\})\hat{c}_n^\dagger \hat{c}_n + \sum_{mn}^{n \neq n} h_{mn}(\{\hat{x}_q\})\hat{c}_m^\dagger \hat{c}_n + \sum_{q} \hbar\omega_q \left(\hat{p}_q^2 + \hat{x}_q^2\right) .$$

Phonon normal modes

Coherent processes

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Zero-order terms

$$\hat{H}_0 = \sum_{n} h^0_{nn}\hat{c}^\dagger_n\hat{c}_n + \sum_{mn}^{n\neq n} h^0_{mn}\hat{c}^\dagger_m\hat{c}_n$$

Stationary eigenstates $\left(\hat{H}_0\right)_{mn}\psi_{ne} = \varepsilon_e\psi_{ne}.$

Electron Green's function

$$G_{mn}(t,E) = \theta(t)\left(\exp(-i\hat{H}_0(E)t)\right)_{mn} = \theta(t)\sum_e \psi_{me}(E)\psi_{ne}(E)\exp\left(-i\varepsilon_e(E)t\right).$$

Transfer amplitude

$$T_{LR}(\omega,E) = \sum_m^{m\in L}\sum_n^{n\in R}|G_{mn}(\omega,E)|^2 = \lim_{\gamma\to+0}\sum_m^{m\in L}\sum_n^{n\in R}\left|\sum_e \frac{\psi_{me}(E)\psi_{ne}(E)}{\omega-\varepsilon_e(E)+i\gamma}\right|^2.$$

Incoherent processes

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$$h_{nn}(x_q) = h^0_{nn} + \sum_q b_{nnq} x_q$$

Electron scattering by phonons

$$h_{mn}(x_q) = h^0_{mn} + \sum_q b_{mnq} x_q$$

Quantum master equation

$$\frac{d\hat{\rho}(t)}{dt} = -\int_0^\infty d\tau \; Tr_{ph} \left[\hat{H}_{el-ph}(t), \left[\hat{H}_{el-ph}(\tau), \hat{W}(\tau) \right] \right]$$

Thermal equilibrium of phonons

$$\hat{\sigma}^{eq}_{ph}(T) = \frac{1}{Z_{ph}(T)} \exp\left(-\frac{\hat{H}_{ph}}{k_B T} \right)$$

Markovian Redfield equation

$$\frac{d\rho_{ab}(t)}{dt} = -i(\varepsilon_a - \varepsilon_b)\rho_{ab}(t) - \sum_{cd} \mathcal{K}_{ab,cd}\rho_{cd}(t).$$

The “observed” kinetics

$$\mathcal{G}_{nn,kk} = \sum_{e_1 e_2 e_3 e_4} \psi_{ne_1}\psi_{ne_2}\psi_{ke_3}\psi_{ke_4} \left[\exp\left(-\left(i\omega - \mathcal{K} \right) t \right) \right]_{e_1 e_2 e_3 e_4}$$

Acoustic phonons

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$$\mathcal{K}_{aa,cc} = \sum_{mnkl} \psi_{ma}\psi_{nc}\psi_{kc}\psi_{la}\left(\sum_{q_l} b_{mn,q_l} b_{kl,-q_l}\right)(1+\coth(\beta\omega_{ac}/2))$$

Hopping amplitude depends on distance

$$b_{mn}(\{x\}) \equiv b_{mn}(\sum_q x_q) \equiv B_{mn}\exp\left(-s\sqrt{\sum_\alpha \left(R^0_{m\alpha} - R^0_{n\alpha} + \sum_q (u_{m\alpha}(q) - u_{n\alpha}(q))\right)^2}\right)$$

$$b_{mnq} = -\frac{sb^0_{mn}}{R^0_{mn}}\left(\boldsymbol{R}^0_m - \boldsymbol{R}^0_n\right)\cdot\left(\boldsymbol{A}^q_m - \boldsymbol{A}^q_n\right)$$

For acoustic phonons dispersion relation is simple, wavevectors

$$\boldsymbol{A}^q_m = \frac{\boldsymbol{q}}{|\boldsymbol{q}|}\exp\left(-i\boldsymbol{q}\boldsymbol{r}_m\right)$$

Finally the electron transfer rate

$$\mathcal{K}_{aa,bb} = |\omega_{ab}|\,\omega_{ab}\left(\coth\left(\beta\omega_{ab}/2\right)+1\right)\left(\sum_{mnkl}\psi_{ma}h^0_{mn}\psi_{nb}\psi_{kb}h^0_{kl}\psi_{la}s^2\frac{x^2_{mn}x^2_{kl}+y^2_{mn}y^2_{kl}+z^2_{mn}z^2_{kl}}{r_{mn}r_{kl}}\right)$$

Relaxation pathways (energy representation)

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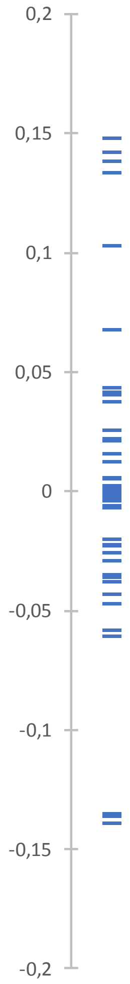

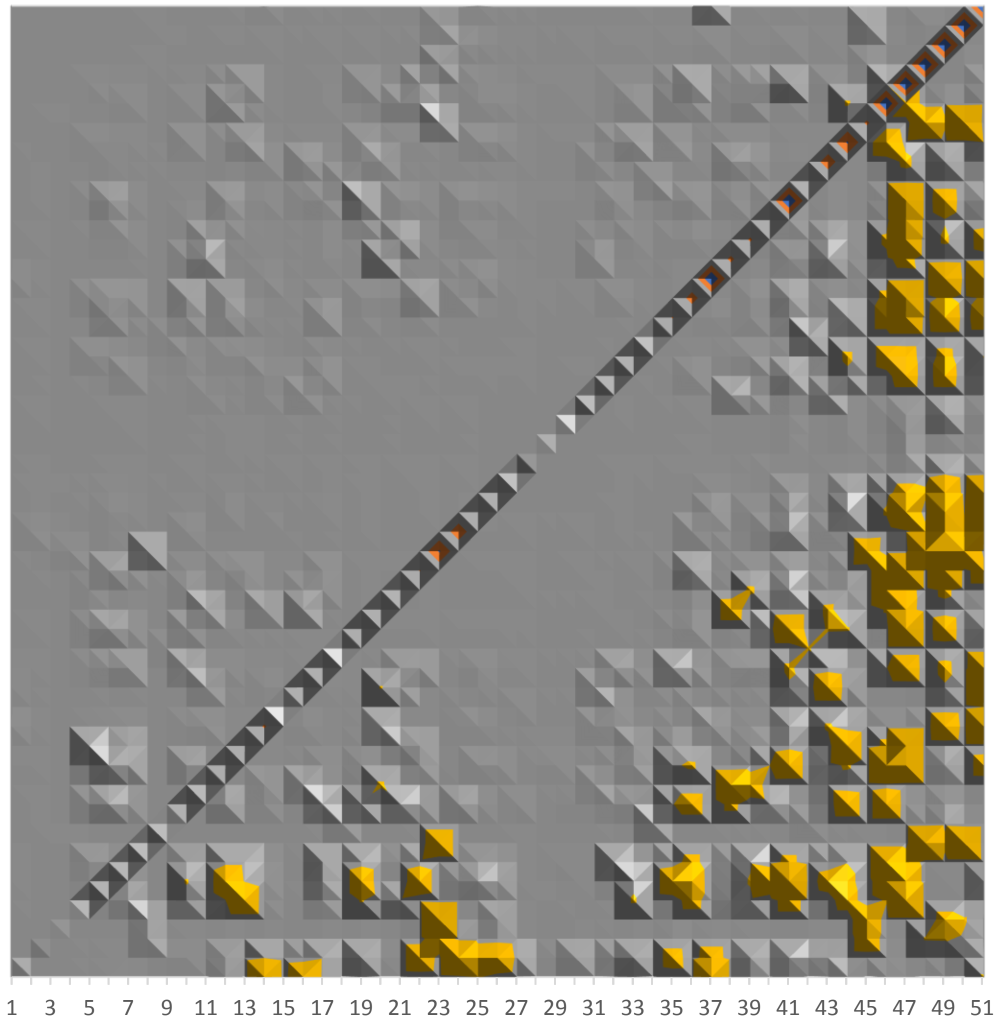

Relaxation pathways (energy representation)

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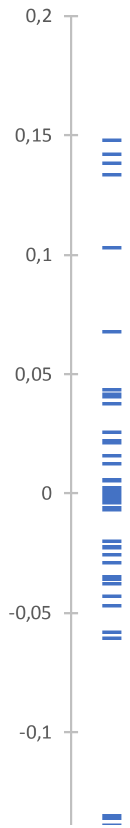

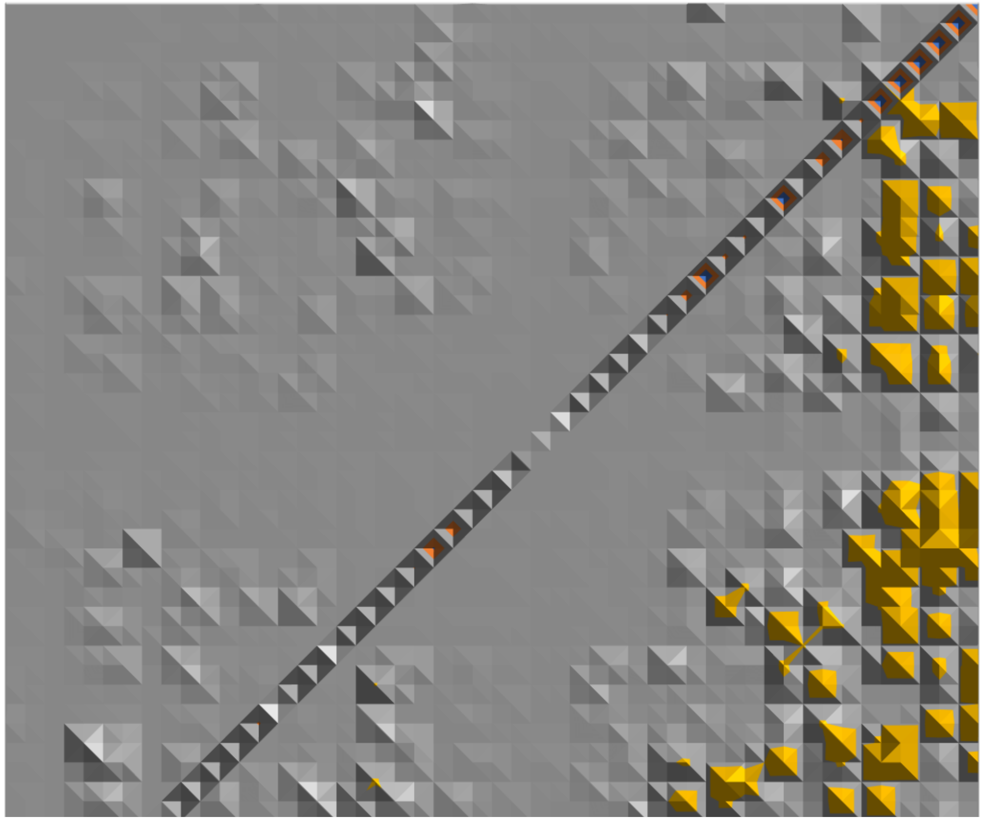

$$\mathcal{K}_{aa,bb} = |\omega_{ab}|\,\omega_{ab}\left(\coth\left(\beta\omega_{ab}/2\right)+1\right)\left(\sum_{mnkl}\psi_{ma}h^{0}_{mn}\psi_{nb}\psi_{kb}h^{0}_{kl}\psi_{la}s^{2}\frac{x^{2}_{mn}x^{2}_{kl}+y^{2}_{mn}y^{2}_{kl}+z^{2}_{mn}z^{2}_{kl}}{r_{mn}r_{kl}}\right)$$

Relaxation pathways (energy representation)

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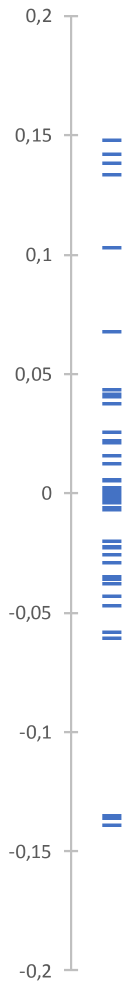

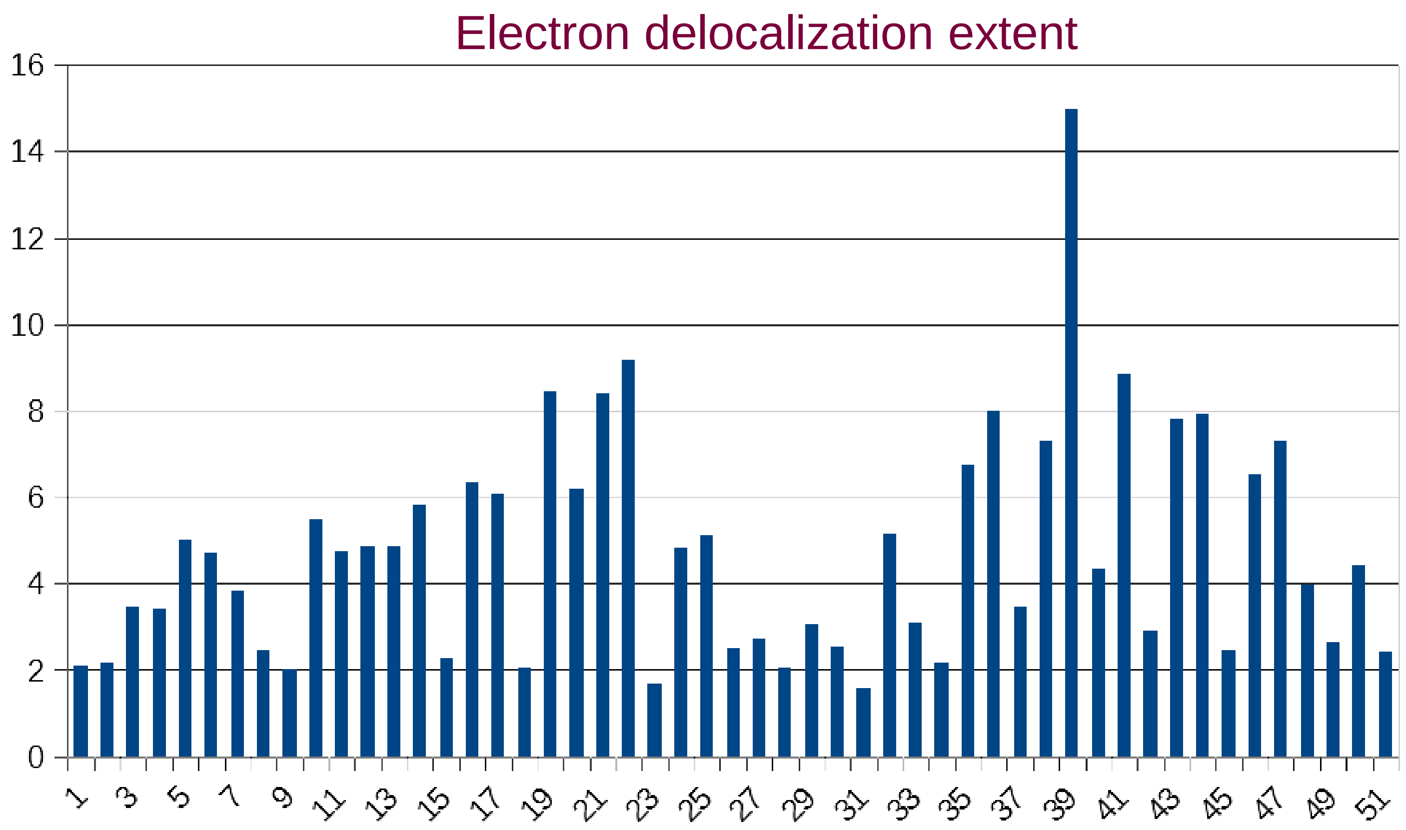

Poor correlation with electron energy

Short range transfer (27-th)

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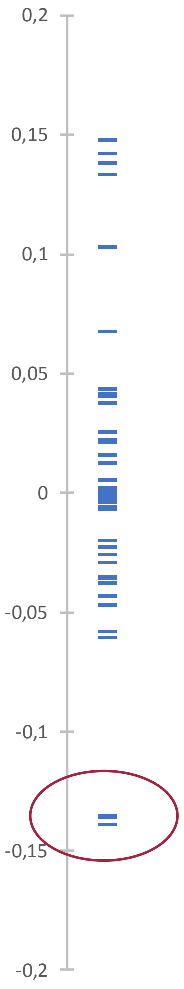
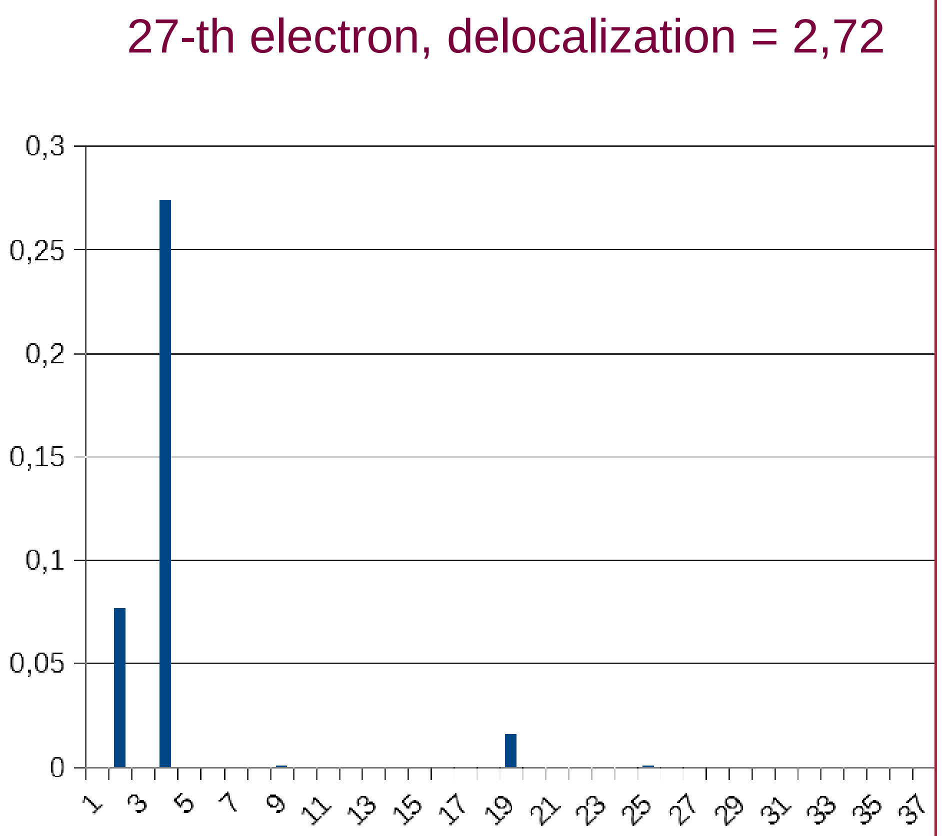
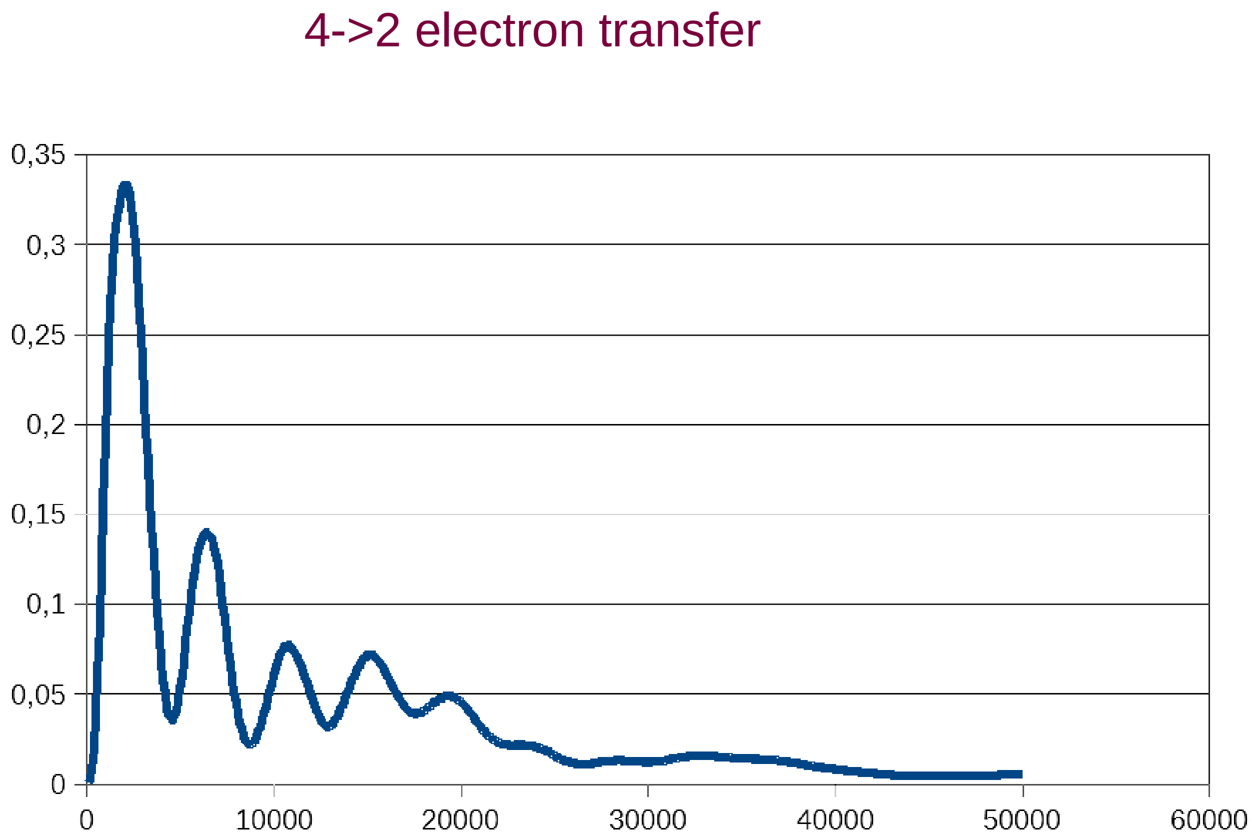




Composition in site-basis



Long range transfer (27-th)

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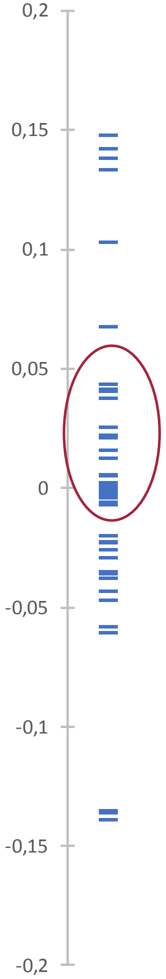
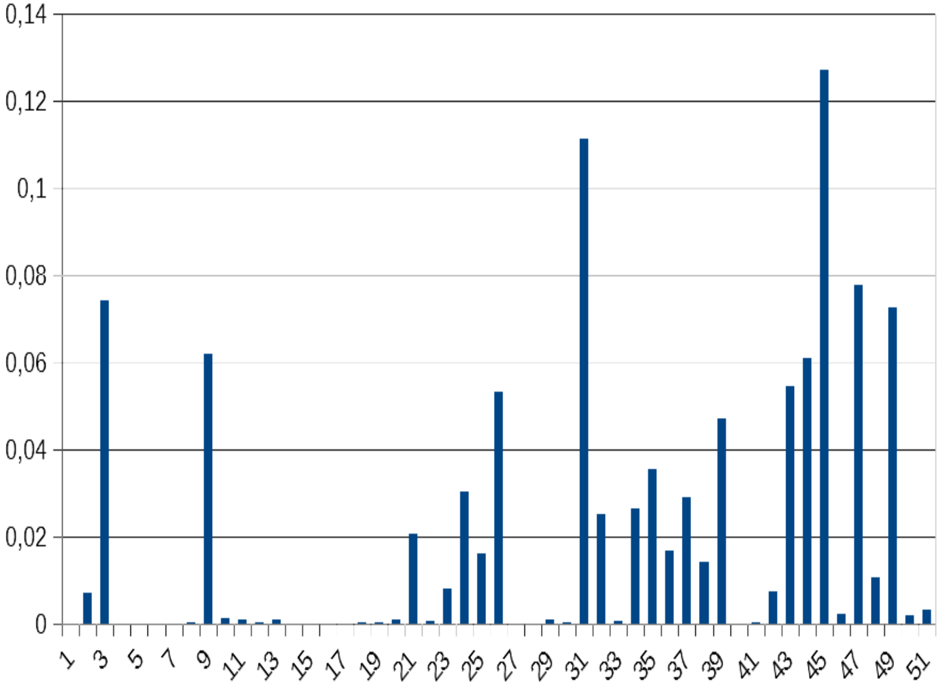
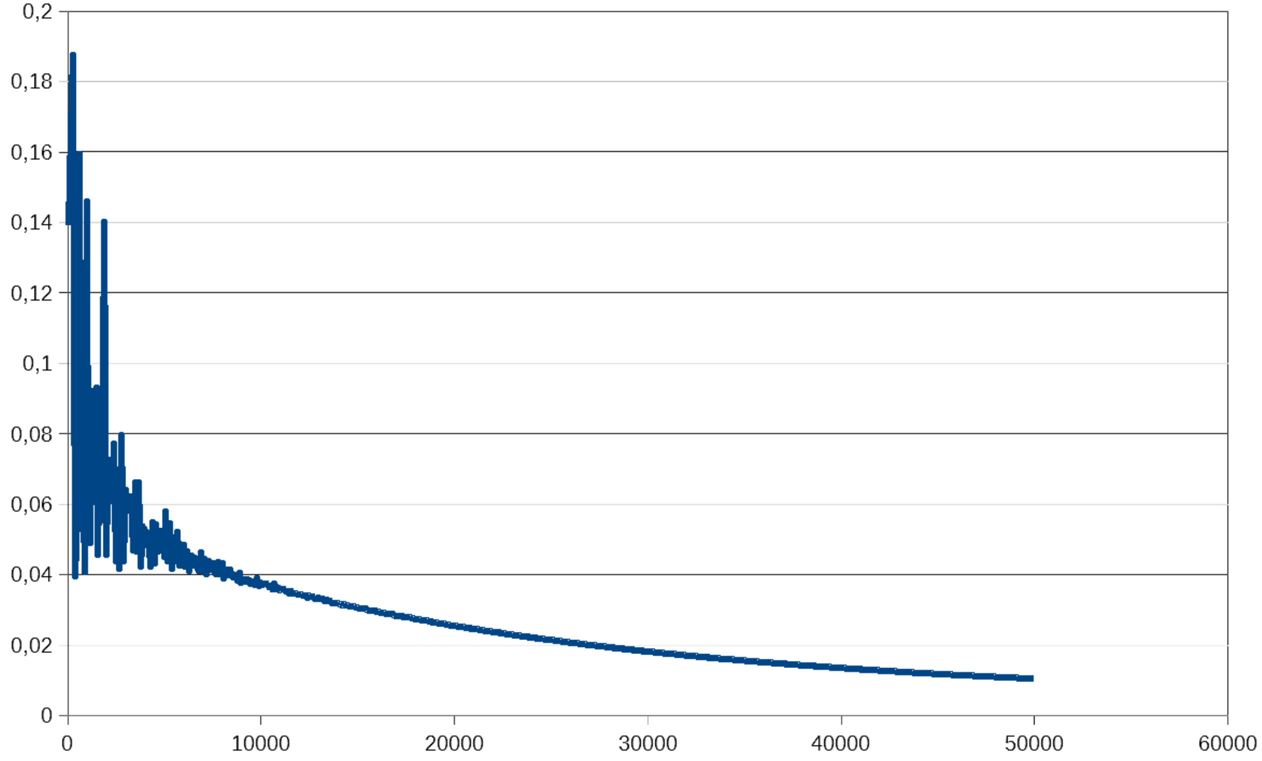


39-th electron, delocalization = 14,99



Composition in site-basis

31->45 electron transfer



Extensions

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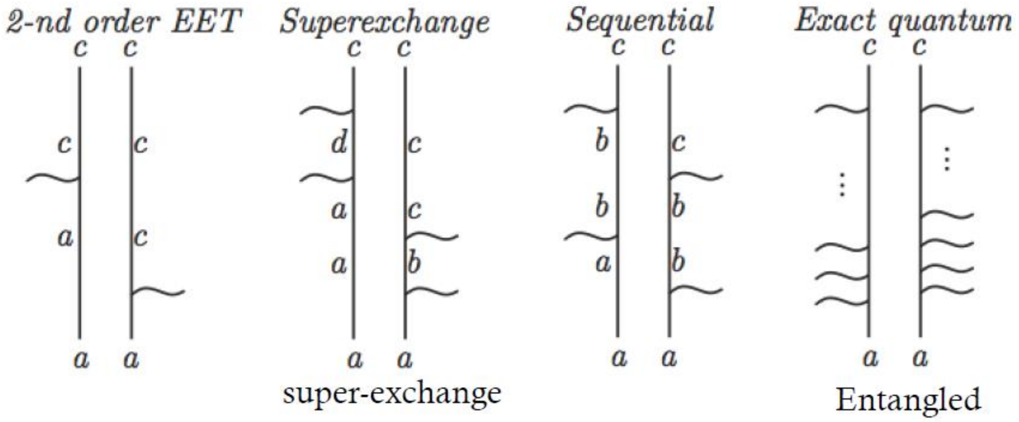
Lindblad equation approach

Non Markovian description

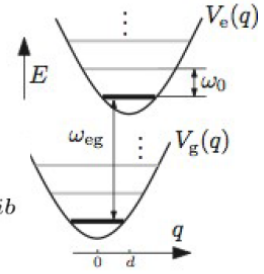
Time dependent variational approach



Variational approach
Davydov Ansatz
complete wave-function
approximate dynamics

Wave-like dynamics

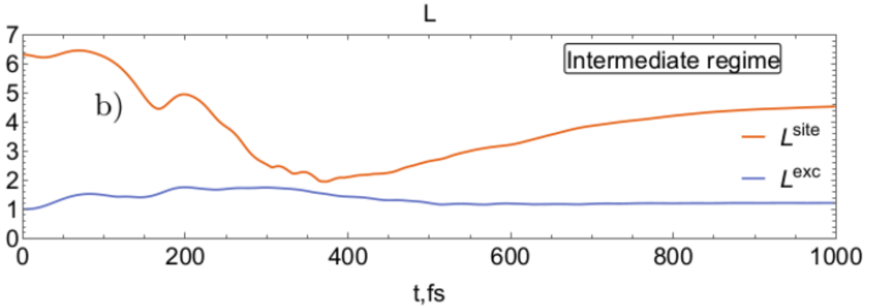
$$\Psi_{D2}(\ldots,t)=\sum_n a_n(t)|n\rangle \exp\left[\sum_q \lambda_q(t)\hat{b}_q^\dagger - h.c.\right]|0\rangle_{vib}$$



$$\Psi_{D2}(\ldots,t)=\sum_n a_n(t)|n\rangle \Pi_q \hat{D}_q(\lambda_q)|0\rangle_{vib}$$

$$\Psi_{SD2}(\ldots,t)=\sum_n a_n(t)|n\rangle \Pi_q \hat{D}_q(\lambda_q)\hat{S}_q(\zeta_q)|0\rangle_{vib}$$

Time dependent delocalization



Interstitials

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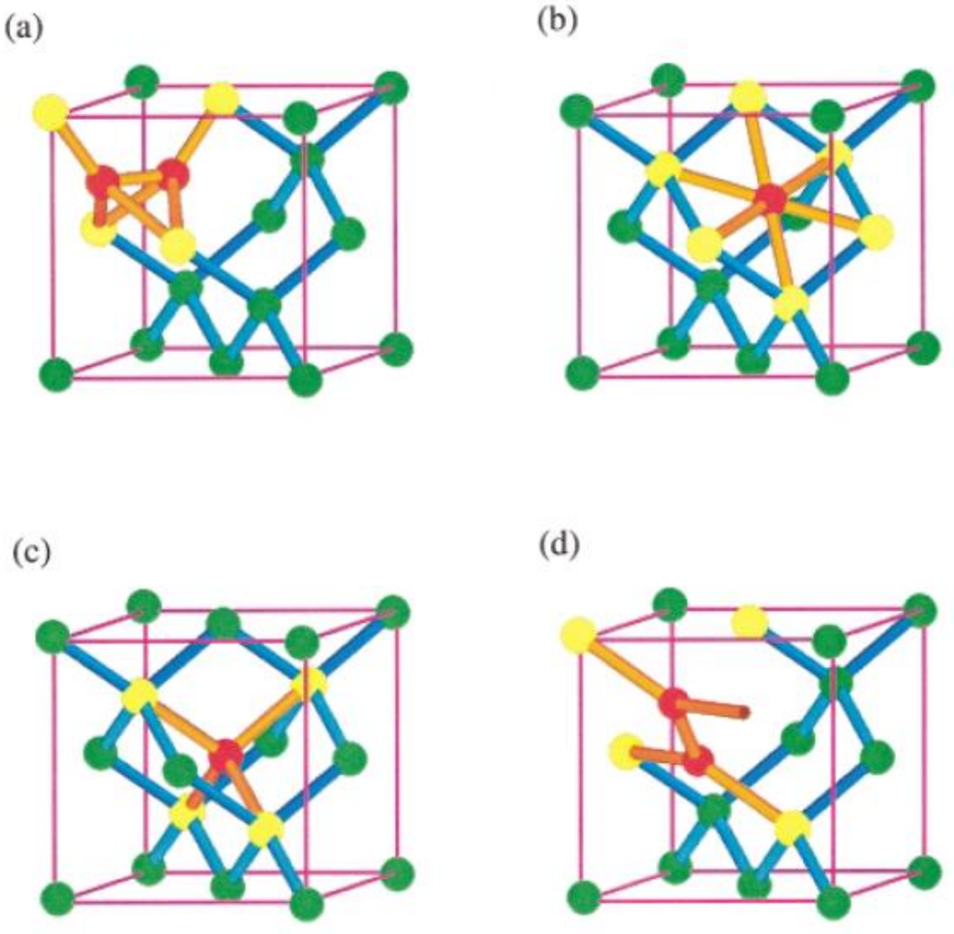

(a) The split-110,
(b) hexagonal,
(c) tetrahedral interstitial,
(d) the saddle point

Formation energies

Defect	LDA	GGA	DMC [a]	DMC [b]
Split-⟨110⟩	3.31	3.84	4.96(24)	4.96(28)
Hexagonal	3.31	3.80	4.70(24)	4.82(28)
“Caged”	3.34	3.85	5.26(24)	5.17(28)
Tetrahedral	3.43	4.07	5.50(24)	5.40(28)
Concerted exchange	4.45	4.80	5.85(23)	5.78(27)

Phys Rev Lett. 83, 2351, 1999

Vacancy – Interstitial pair (Frenkel pair) defect

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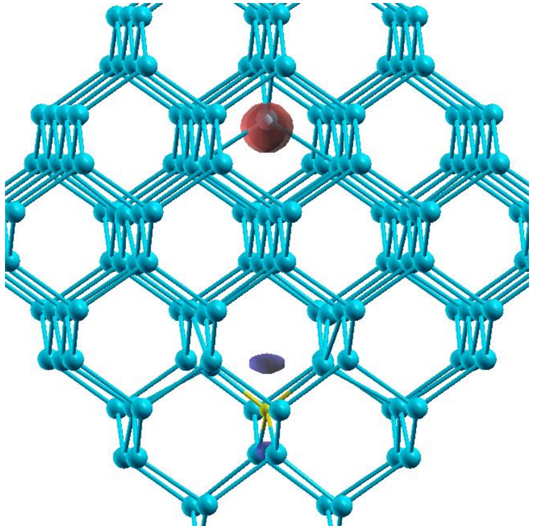
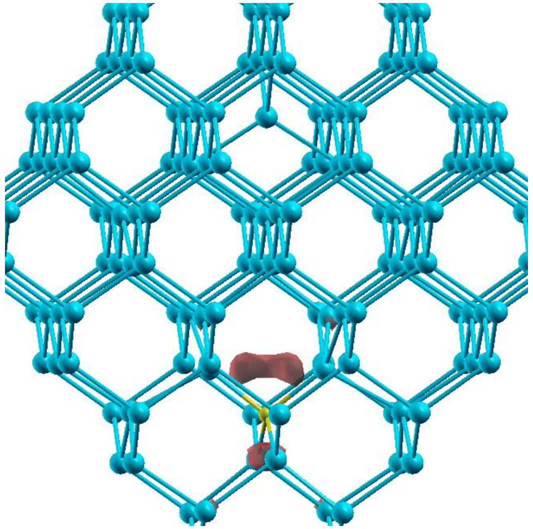
When vacancy and interstitial are approached to each other to form a pair then the extra electrons given by interstitial are “pumped” away from the interstitial site to the vacancy site. (Like in a ionic type molecule or crystal electrons mainly are located nearby more electronegative ion.)

! Interstitial and vacancy exchange their roles:
Interstitial turns into **acceptor** and vacancy into **donor**:



Charged (-) system, one electron added. The **electron** wave function (~80% of it) is located nearby interstitial site (or the electron is accepted by interstitial site).



Charged (+) system, one electron removed. The **hole** wave function is located nearby vacancy site (or the electron is donated away by vacancy site).

simulations were performed by Ernestas Žąsinas (Vilnius University)

Conclusions

1. Formation of clusters of the defect sites depends strongly on concentration of defects
2. Acoustic phonon description allows for simple model formulation for incoherent energy transport
3. Overlap of electron delocalized wavefunctions is necessary for electron transfer
4. Electron transport pathways can be visualized
5. Transition from coherent to diffusive transport may be important for various size clusters

Acknowledgement

Some simulations were performed by Ernestas Žąsinas

This work is coherent with CERN RD50 collaboration.

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