Magnetic vacancies in Graphene: Disordered impurity physics within the variational cluster approach

Martin Nuss[1]

Institute of Theoretical and Computational Physics, Graz University of Technology, Austria

May 21, 2012

[1] supervision: Prof. Wolfgang von der Linden, Prof. Enrico Arrigoni

Table of contents

Many Body Cluster Group at Technical University Graz

Anna Fulterer

Prof. Wolfgang von der Linden

Christoph Heil

Prof. Enrico Arrigoni

itp cp

Quantum many body cluster methods for strongly correlated systems

TUG

Michael Knap

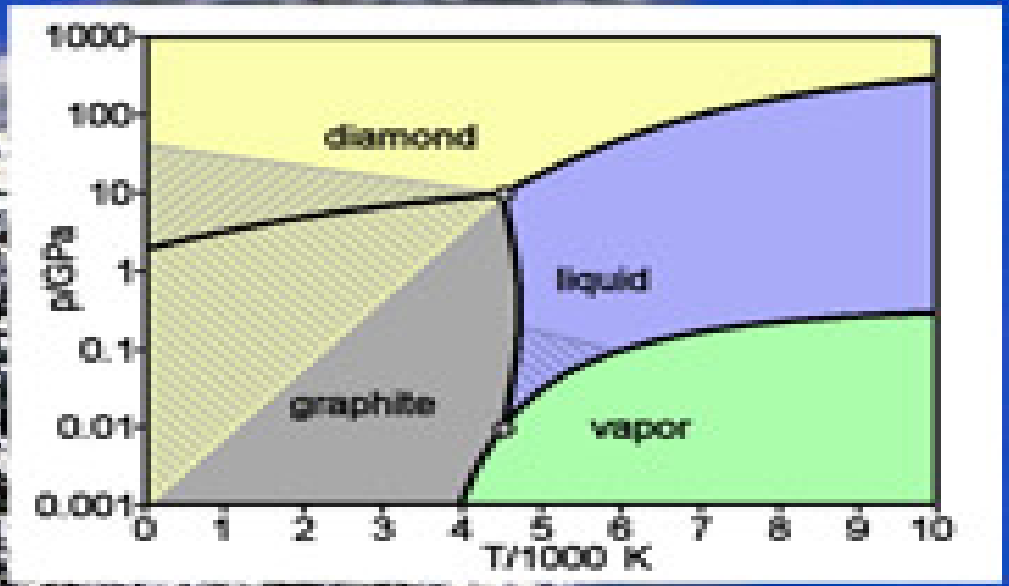
Markus Aichhorn

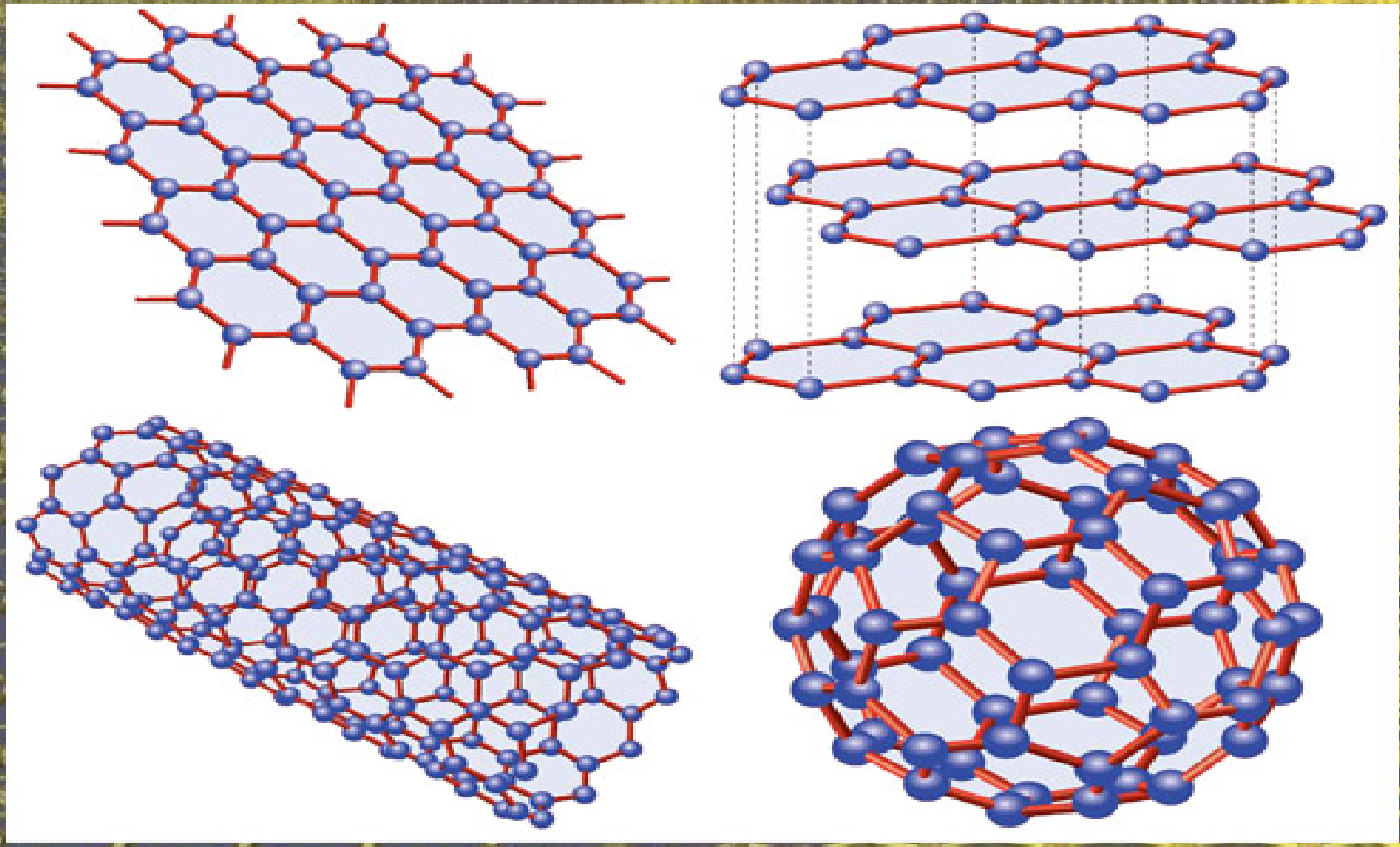
Martin Nuss

Faruk Geles

Outline

Graphite (natural allotrope of Carbon)





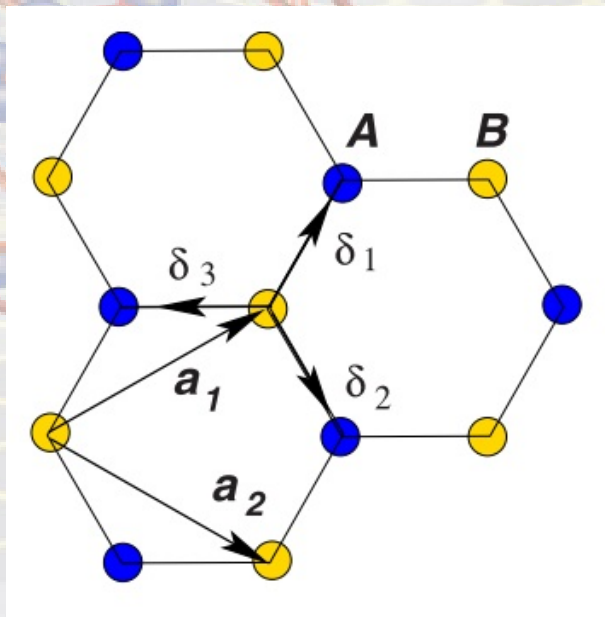
1 nm

Castro Neto A.H., Peres N.M.R., Novoselov K.S., Geim A. K., Rev. Mod. Phys. 81, 1, 109-162 (2009)

Graphene - basic properties

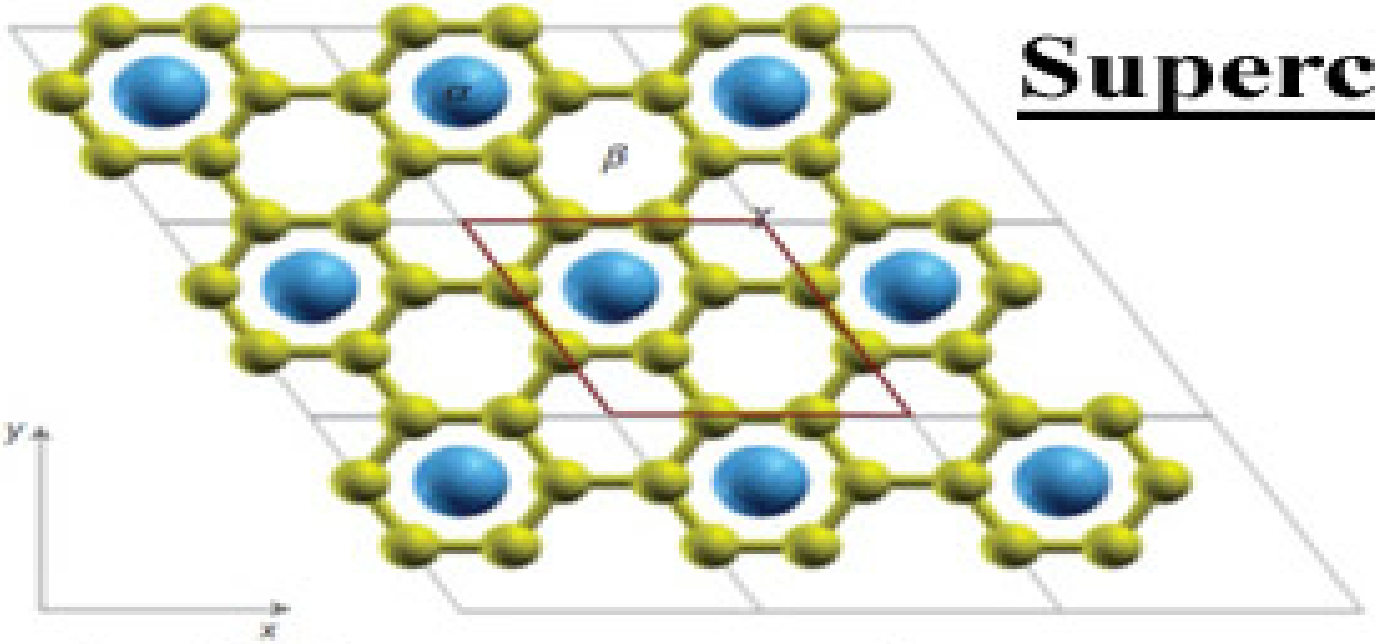
- very high electrical + thermal conductivity (transparent conductor)
- mechanically very strong + stretchable
- Dirac-like Fermions (QED)
- anomalous integer quantum hall effect
- Klein tunneling
- spin injection, valleytronics, nano electronics

$$\vec{a}_1 = \frac{a}{2}(3, \sqrt{3}), \vec{a}_2 = \frac{a}{2}(3, -\sqrt{3})$$



Castro Neto A.H., Peres N.M.R., Novoselov K.S., Geim A. K.,

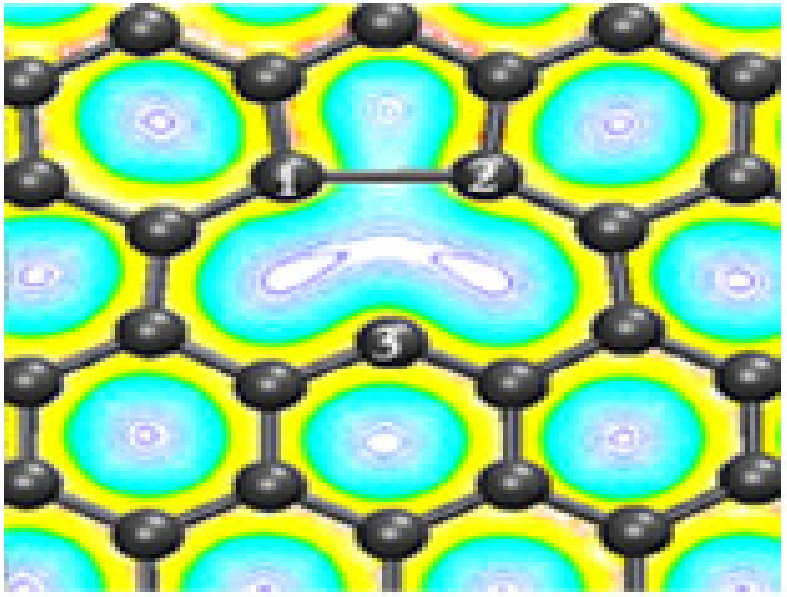
Superconductivity



Profeta G., Calandra M. and Mauri F. Nat. Phys. 8, 2, 131-134 (2012).

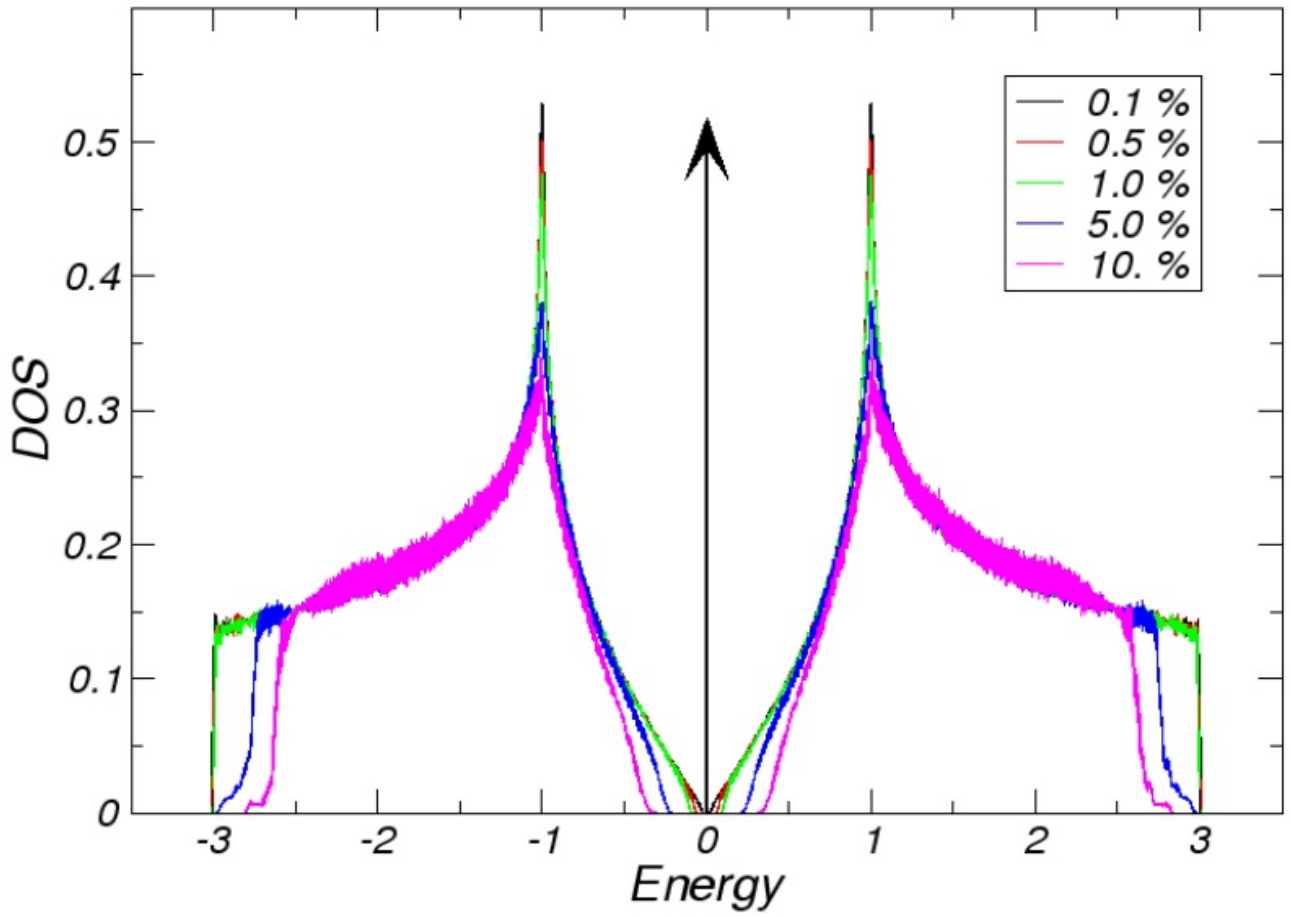
Magnetism

lattice defects: vacancies



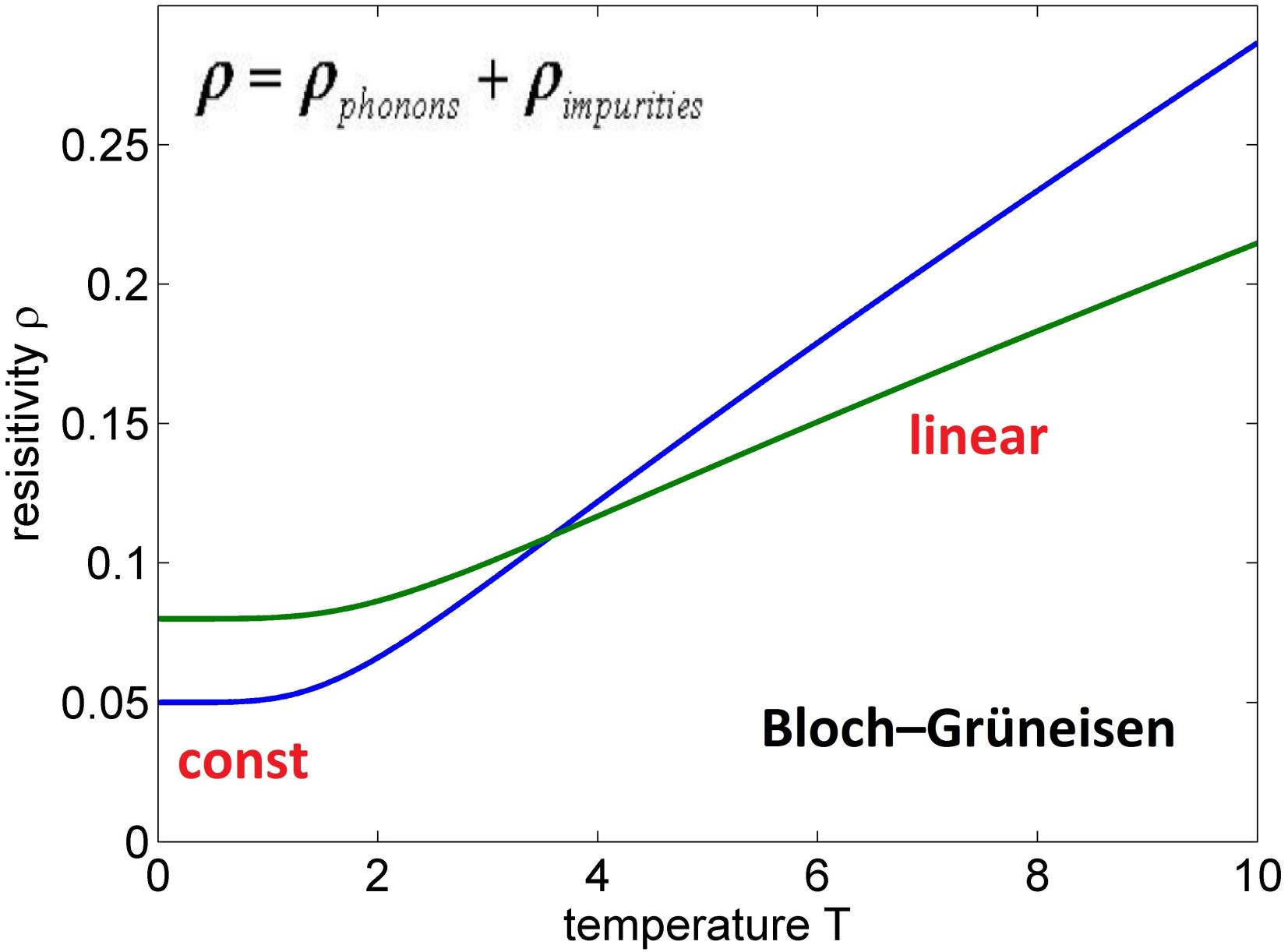
Lehtinen P.O., Foster A.S., Ma Y., Krasheninnikov A.V. and Nieminen R.M., Phys. Rev. Lett. 93, 18 , 1-4 (2004).

Disorder

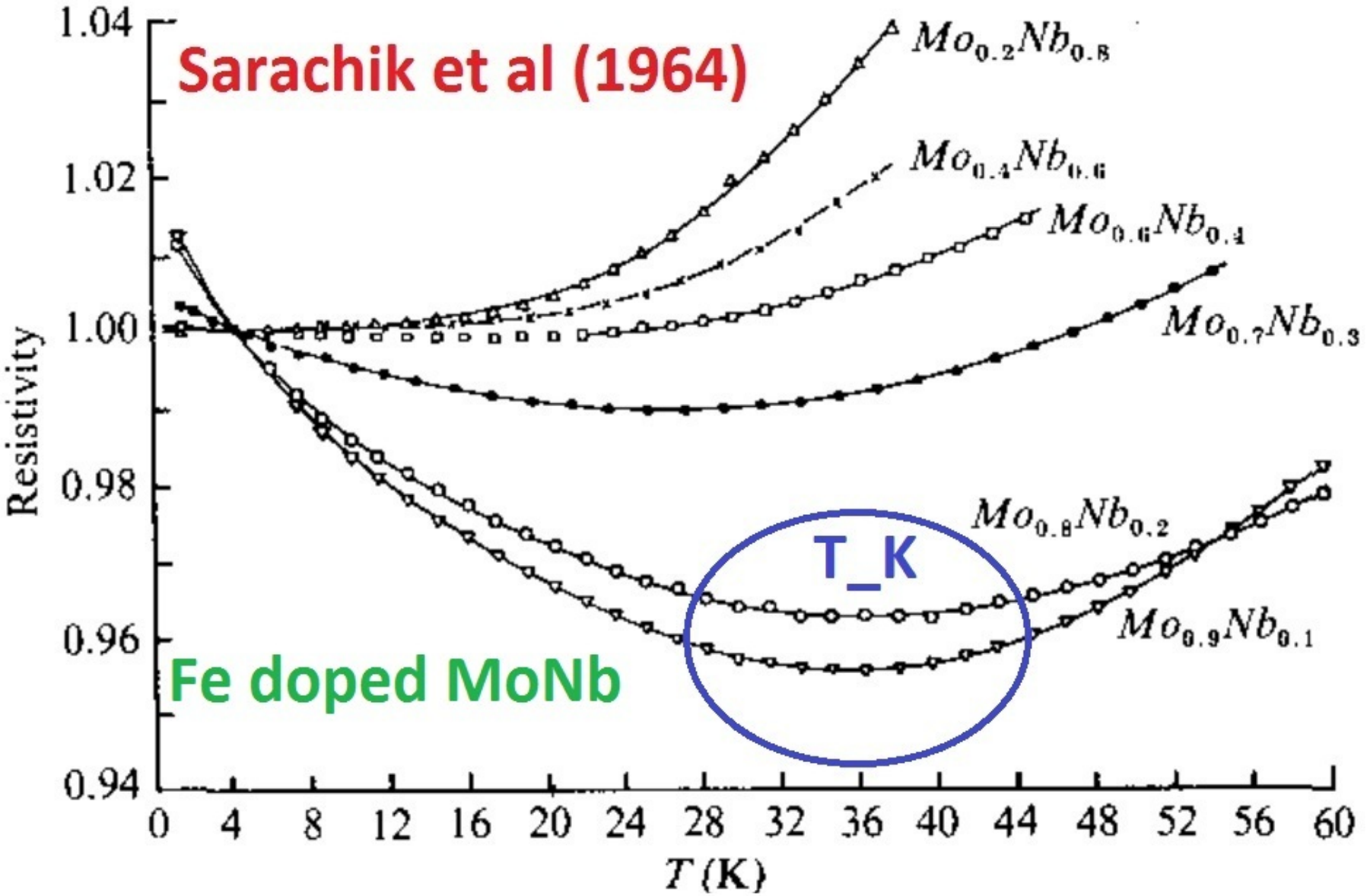


V. M. Pereira, J. M. B. Lopes dos Santos and A. H. Castro Neto, Modeling disorder in graphene, Phys. Rev. B 77, 115109 (2008)

Resistivity in metals (I)

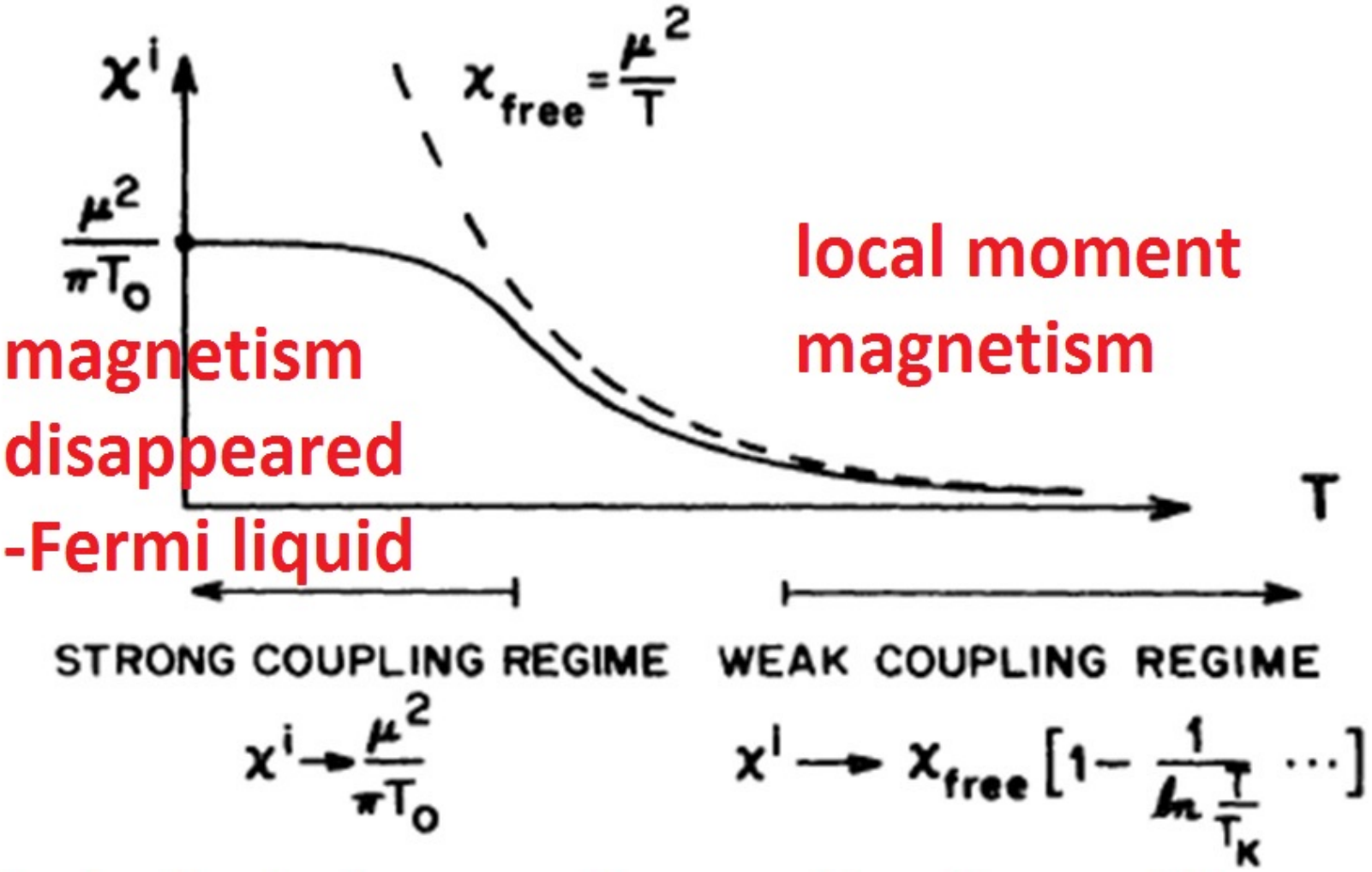


Resistivity in metals (II)



increased scattering at low T

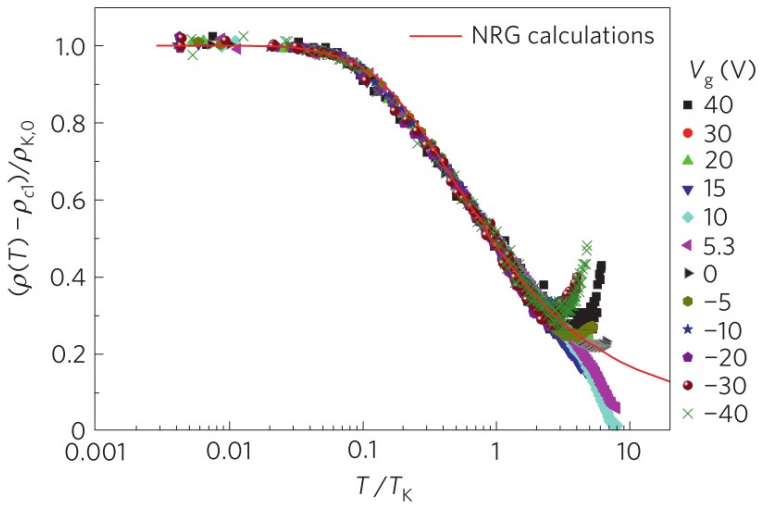
What about susceptibility?



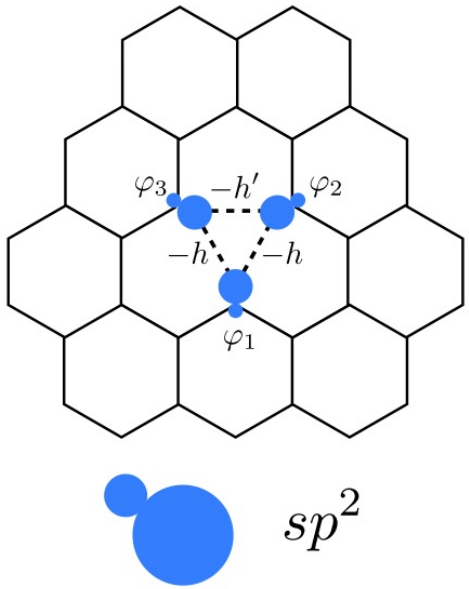
J.Mydosh: lecture notes on Kondo problem

Kondo effect in Graphene

- Proton irradiation -> (single) vacancies
  - STM:
    Ugeda MM, Brihuega I and Go JM, Missing Atom as a Source of Carbon Magnetism, 096804, 1-4 (2010).
  - DFT:
    Lehtinen PO, Foster AS, Ma Y, Krasheninnikov AV and Nieminen RM, Irradiation-Induced Magnetism in Graphite: A Density Functional Study. Phys. Rev. Lett. 93, 18, 1-4 (2004).
    Yazyev OV and Helm L, Defect-induced magnetism in graphene, Phys. Rev. B 75, 125408 1-5 (2007).



Chen J-H, Li L, Cullen WG, Williams ED and Fuhrer MS, Tunable Kondo effect in graphene with defects, Nat.Phys. 7, 7, 535-538 (2011).



Kanao T, Matsuura H and Ogata M, Theory of Defect-Induced Kondo Effect in Graphene: Numerical Renormalization Group Study. J. Phys. Soc. Jpn. (2012)

Dilute problem so single impurity picture valid.

- Disorder is a complicated problem
- Correlations are a complicated problem
- What about disorder + correlations?

Outline

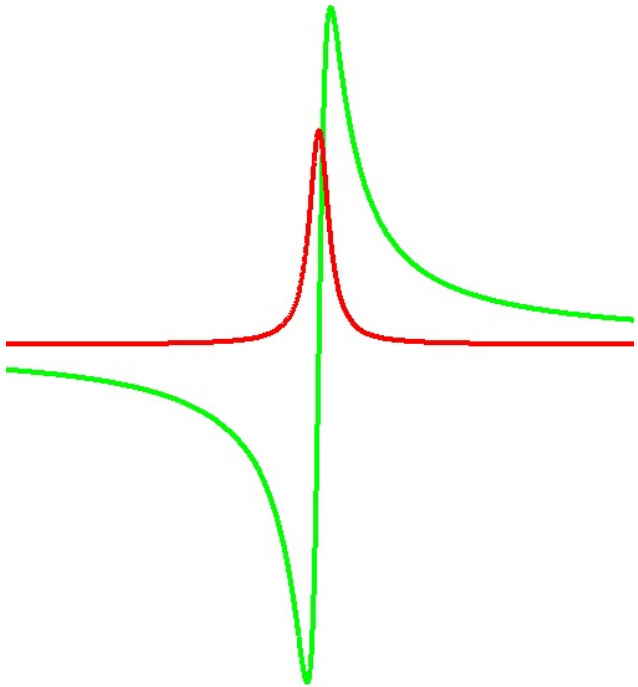
Generic lattice model

$$\begin{aligned}\hat{\mathcal{H}} &= \sum_{ij} t_{ij}\, c_i^\dagger\, c_j + \sum_{ijkl} U_{ijkl}\, c_i^\dagger\, c_j^\dagger\, c_k\, c_l \\ &= \hat{\mathcal{H}}_I(t) + \hat{\mathcal{H}}_{II}(U)\end{aligned}$$

To apply a perturbative method one has to expand in some parameter. Usually the hopping (strong coupling) or the interaction (weak coupling) are considered.

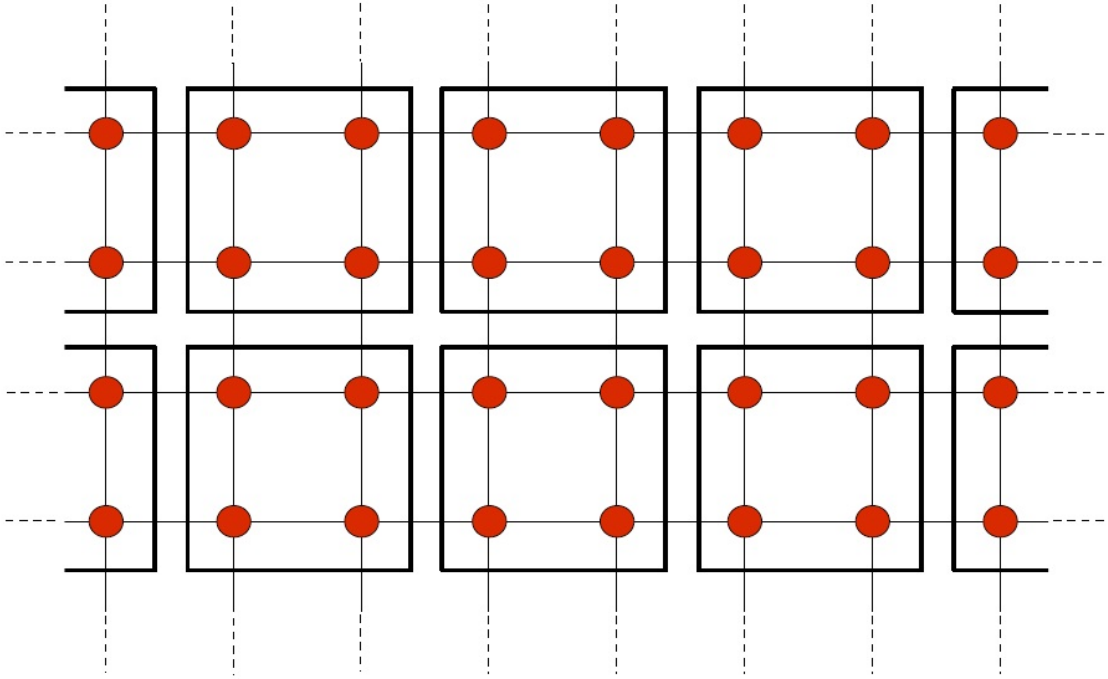
Atomic limit

$$G(z;t,U) = \left\langle \frac{1}{z - \hat{\mathcal{H}}(t,U)} \right\rangle$$



- strong coupling perturbation theory (in hopping t)
- consider G$(t = 0)$ as starting point

Manybody Cluster Methods

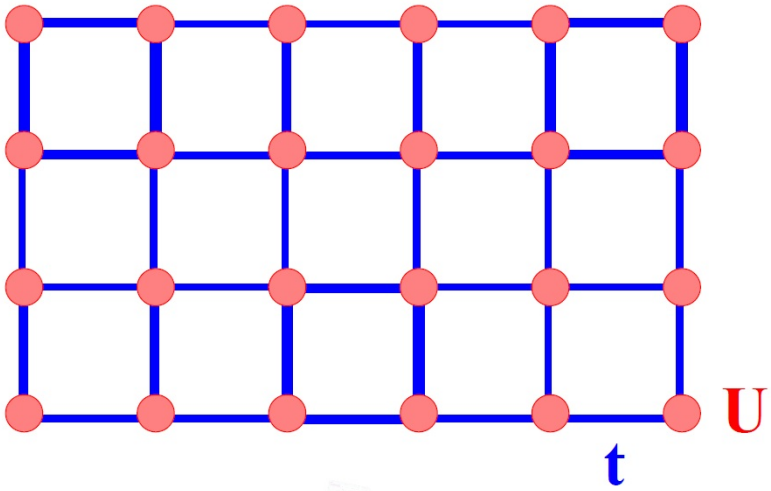


Extrapolate cluster to thermodynamic limit:

- Cluster Perturbation Theory (**CPT**)
- Variational Cluster Approach (**VCA**)
- Cluster/Cellular Dynamical Mean-Field Theory (**CDMFT**)
- Dynamical Cluster Approximation (**DCA**)

Illustration of Cluster Perturbation Theory

Correlated lattice model



given: Hamiltonian e.g. Hubbard model

$\hat{\mathcal{H}}$

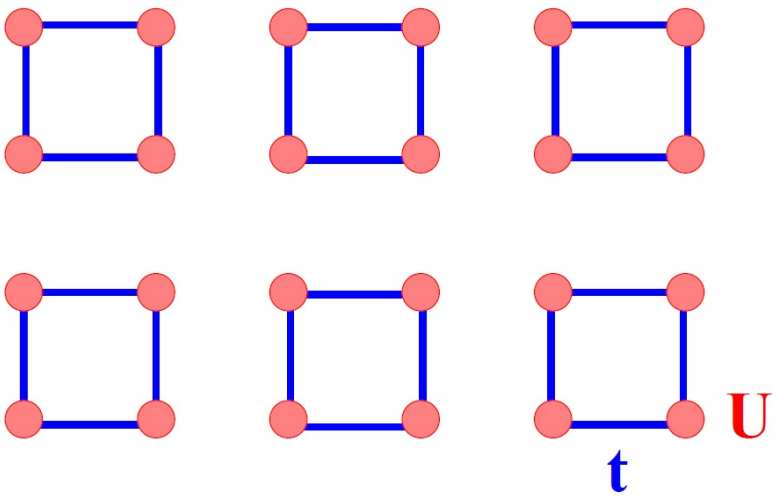
ask for: Green's function

$\mathbf{G} = ?$

in general intractable ... :(

Illustration of Cluster Perturbation Theory

Cluster Tiling



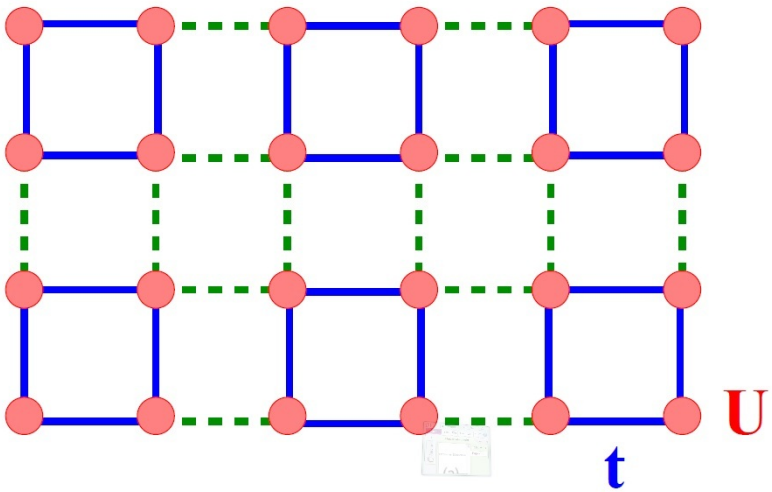
$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{\text{cluster}}$$

$$\mathbf{G}^{-1} = \mathbf{G}^{-1}_{\text{cluster}}$$

(numerically) exactly solvable ... :)

... but isn't this quite different from original system ... :(

Cluster Perturbation Theory[2] [3]



$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{\text{cluster}} + \hat{\mathcal{H}}_{\text{inter-cluster}}$$

$$\mathbf{G}^{-1}_{\mathbf{CPT}}(\omega, \mathbf{k}) = \mathbf{G}^{-1}_{\mathbf{cluster}}(\omega) - \mathbf{T}(\mathbf{k})$$

First order result for the lattice Green function G

- $G_{cluster}$ = exact Green's function of the **cluster**
- T = **inter**-cluster off diagonal one particle terms (i.e. hopping)

[2] C. Gros and R. Valenti, Phys. Rev. B 48, 418 (1993)

[3] D. Sénéchal, D. Perez, and M. Pioro-Ladriére, Phys. Rev. Lett. 84, 522 (2000)

Cluster Perturbation Theory - Motivation

Heuristic derivation using **Dyson's equation**:

$$\mathsf{G}^{-1} = \mathsf{G}_0^{-1} - \Sigma$$
$$\mathsf{G}_{\text{cluster}}^{-1} = \mathsf{G}_{\text{cluster},0}^{-1} - \Sigma_{\text{cluster}}$$

- $_0$ = non-interacting Green's functions

$$\mathsf{G}_0^{-1} = \omega + \mu - V$$

  - V = hopping matrix
- Σ = self-energy

Cluster Perturbation Theory - Motivation

$$
\begin{aligned}
\mathsf{G}^{-1} &= \mathsf{G}_0^{-1} - \Sigma \\
&\approx \mathsf{G}_0^{-1} - \Sigma_{\text{cluster}} \\
&= \mathsf{G}_0^{-1} - \left(\mathsf{G}_{\text{cluster},0}^{-1} - \mathsf{G}_{\text{cluster}}^{-1} \right) \\
&= \mathsf{G}_{\text{cluster}}^{-1} - \left(\mathsf{G}_{\text{cluster},0}^{-1} - \mathsf{G}_0^{-1} \right) \\
&= \mathsf{G}_{\text{cluster}}^{-1} - \mathsf{T}
\end{aligned}
$$

- Approximation: take **self-energy of the cluster**
- T = inter-cluster hopping:

$$
\begin{aligned}
\left(\mathsf{G}_{\text{cluster},0}^{-1} - \mathsf{G}_0^{-1} \right) &= (\omega + \mu - V_{\text{cluster}}) - (\omega + \mu - V) \\
&= V - V_{\text{cluster}} = \mathsf{T}
\end{aligned}
$$

Cluster Perturbation Theory - Limits

CPT is exact for

- $t \to 0$,
- $U \to 0$,
- $L \to \infty$.

CPT captures **short-range correlations** exactly, long-range correlations are neglected.

CPT is usually improved not by considering higher order expansions in the inter-cluster hopping but by **increasing the cluster** size.

Variational Cluster Approach[4]

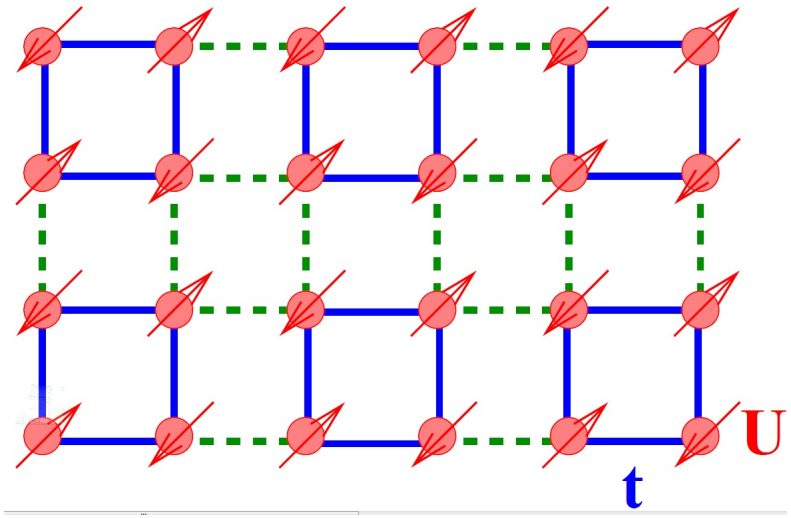
- VCA = variational extension to CPT - rigorously developed within the **Self-Energy Functional Approach** (SFA)[ab],
- does **not** implement a variational principle in the sense of a Rayleigh-Ritz variational principle,
- is applicable to **broken-symmetry/ordered** phases.

[a] M. Potthoff, Eur. Phys. J. B 32, 429 (2003)
[b] M. Potthoff, Eur. Phys. J. B 36, 335 (2003)

[4] M. Potthoff, M. Aichhorn, and C. Dahnken, Phys. Rev. Lett. 91, 206402 (2003)

Illustration of the Variational Cluster Approach

VCA = Variational CPT: **Optimize the initial state**



$$\hat{\mathcal{H}} = \hat{\mathcal{H}}'_{\text{cluster}} + \hat{\mathcal{H}}'_{\text{inter-cluster}}$$

$$\mathbf{G}^{-1}_{\mathbf{CPT}}(\omega, \mathbf{k}) = \mathbf{G}'^{-1}_{\mathbf{cluster}}(\omega) - \mathbf{T}'(\mathbf{k})$$

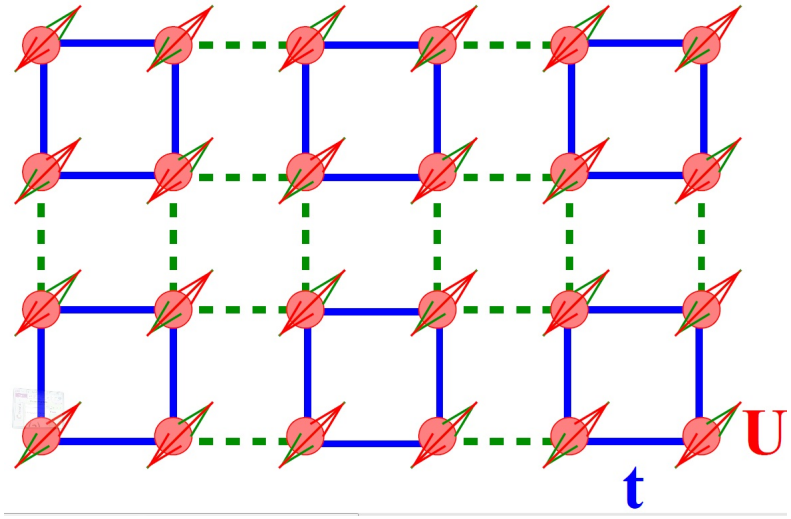
Variational aspect: Add **virtual field** to cluster Hamiltonian

$$\hat{\mathcal{H}}'_{\text{cluster}} = \hat{\mathcal{H}}_{\text{cluster}} + \hat{h}_{\text{field}}$$

field: **any single particle terms** of original Hamiltonian + bath sites

Illustration of the Variational Cluster Approach

Adding and subtracting single-particle terms



$$\hat{\mathcal{H}} = \hat{\mathcal{H}}'_{\text{cluster}} + \hat{\mathcal{H}}'_{\text{inter-cluster}}$$

$$\mathbf{G}^{-1}_{\mathbf{CPT}}(\omega, \mathbf{k}) = \mathbf{G}'^{-1}_{\mathbf{cluster}}(\omega) - \mathbf{T}'(\mathbf{k})$$

Variational aspect: Add **virtual field** to cluster Hamiltonian

$$\hat{\mathcal{H}}'_{\text{cluster}} = \hat{\mathcal{H}}_{\text{cluster}} + \hat{h}_{\text{field}}$$

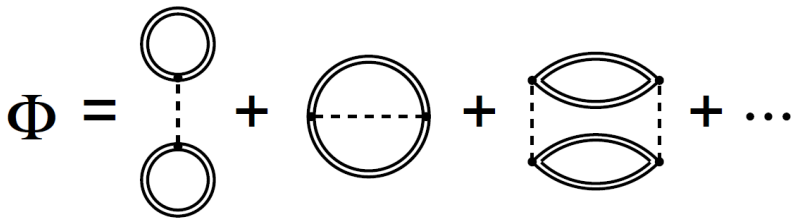
subtract field again via CPT

$$\hat{\mathcal{H}}'_{\text{inter-cluster}} = \hat{\mathcal{H}}_{\text{inter-cluster}} - \hat{h}_{\text{field}}$$

field: **any single particle terms** of original Hamiltonian + bath sites

Luttinger-Ward functional $\Phi[G]$

- $\Phi[G]$ = sum of all **two-particle irreducible** diagrams



- The **functional derivative** of $\Phi[G]$ is the self-energy:

$$\beta \frac{\delta \Phi[G]}{\delta G} = \Sigma$$

- It is a **universal functional** of G.

Legendre Transform of $\Phi[\mathsf{G}]$

It can be shown that

$$\beta \frac{\delta \Phi[\mathsf{G}]}{\delta \mathsf{G}} = \Sigma \,,$$

is **locally invertible**.
Legendre Transform of the Luttinger-Ward functional:

$$F[\Sigma] = \Phi[\Sigma] - \mathrm{Tr}\left\{\Sigma \mathsf{G}\right\} \,.$$

It can be shown that the generalized **grand potential functional** is given by:

$$\Omega[\Sigma, \mathsf{G}_0] = F[\Sigma] - \mathrm{Tr}\ln\left(-\mathsf{G}_0^{-1} + \Sigma\right) .$$

Grand Potential Functional $\Omega[\Sigma]$

Dyson's equation is recovered at the stationary point of the grand potential functional $\Omega[\Sigma]$

$$\beta \frac{\delta F[\Sigma]}{\delta \Sigma} = -\mathsf{G}$$
$$\beta \frac{\delta \Omega[\Sigma, \mathsf{G}_0]}{\delta \Sigma} = -\mathsf{G} + \left(\mathsf{G}_0^{-1} - \Sigma\right)^{-1} \stackrel{!}{=} 0\,.$$

VCA Reference System (I)

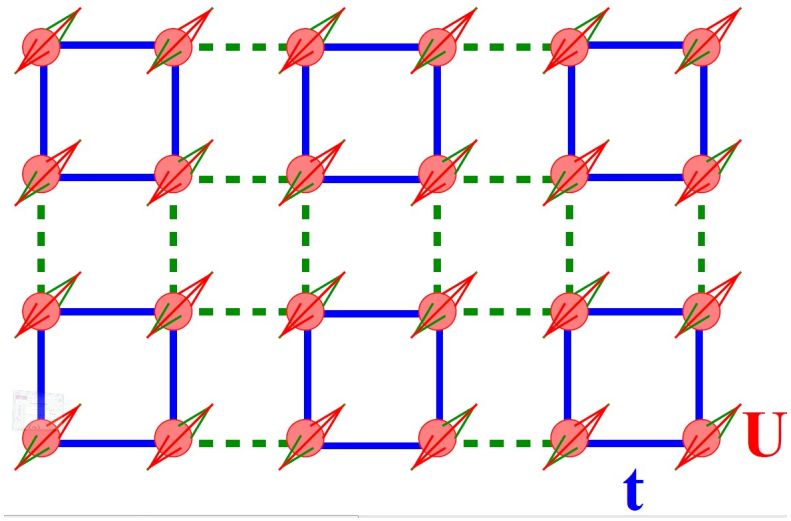
Since systems which share the same interaction part $\hat{\mathcal{H}}_{II}(U)$ have the same $\Phi[\mathrm{G}]$ (or $F[\Sigma]$) we construct a **reference system**:

$$\hat{\mathcal{H}}' = \hat{\mathcal{H}}_I(t') + \hat{\mathcal{H}}_{II}(U)$$

- defined on the **same lattice**,
- having the **same interaction** as the original system,
- but may have entirely different **single-particle** operators / **parameters**.

Illustration of the Variational Cluster Approach

How is $\hat{h}_{\text{field}}$ determined?



$$\hat{\mathcal{H}} = \hat{\mathcal{H}}'_{\text{cluster}} + \hat{\mathcal{H}}'_{\text{inter-cluster}}$$

$$\mathbf{G}^{-1}_{\mathbf{CPT}}(\omega, \mathbf{k}) = \mathbf{G}'^{-1}_{\text{cluster}}(\omega) - \mathbf{T}'(\mathbf{k})$$

The self energy functional approach (SFA) provides a variational principle:

Stationary point of the grand potential:

$$\frac{\delta \Omega}{\delta h_{\text{field}}} \stackrel{!}{=} 0$$

VCA = CPT + variational principle

VCA Reference System (II)

The reference system $\hat{\mathcal{H}}'$ may be used to **eliminate the Luttinger-Ward functional**: (This is still exact!)

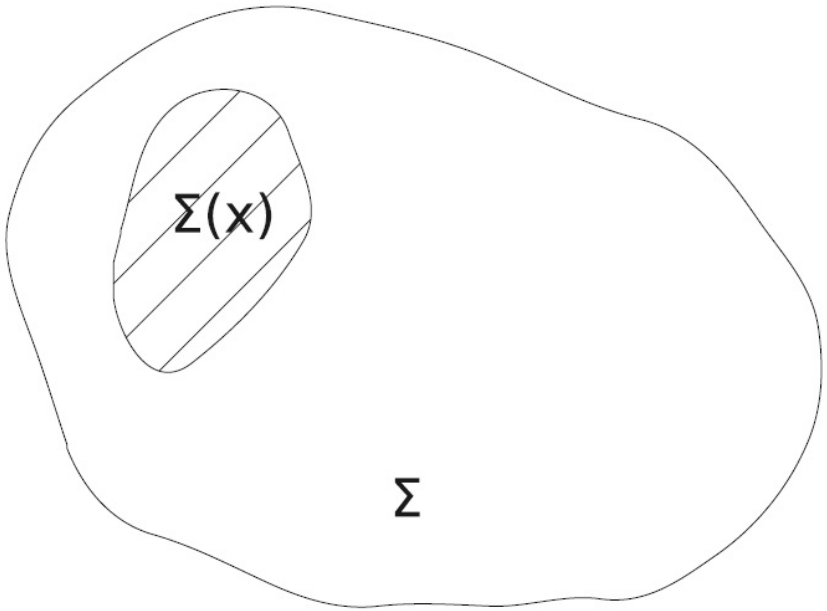
$$\Omega[\Sigma] = F[\Sigma] - \mathrm{Tr}\left\{\ln\left(-\mathsf{G}_0^{-1} + \Sigma\right)\right\}$$
$$\Omega'[\Sigma] = F[\Sigma] - \mathrm{Tr}\left\{\ln\left(-\mathsf{G}_0'^{-1} + \Sigma\right)\right\}$$

$$-\sum$$

$$\begin{aligned}\Omega[\Sigma] &= \Omega'[\Sigma] + \mathrm{Tr}\left\{\ln\left(-\mathsf{G}_0'^{-1} + \Sigma\right)\right\} - \mathrm{Tr}\left\{\ln\left(-\mathsf{G}_0^{-1} + \Sigma\right)\right\} \\ &= \Omega'[\Sigma] + \mathrm{Tr}\left\{\ln\left(-\mathsf{G}'[\Sigma]\right)\right\} - \mathrm{Tr}\left\{\ln\left(-\mathsf{G}[\Sigma]\right)\right\}\end{aligned}$$

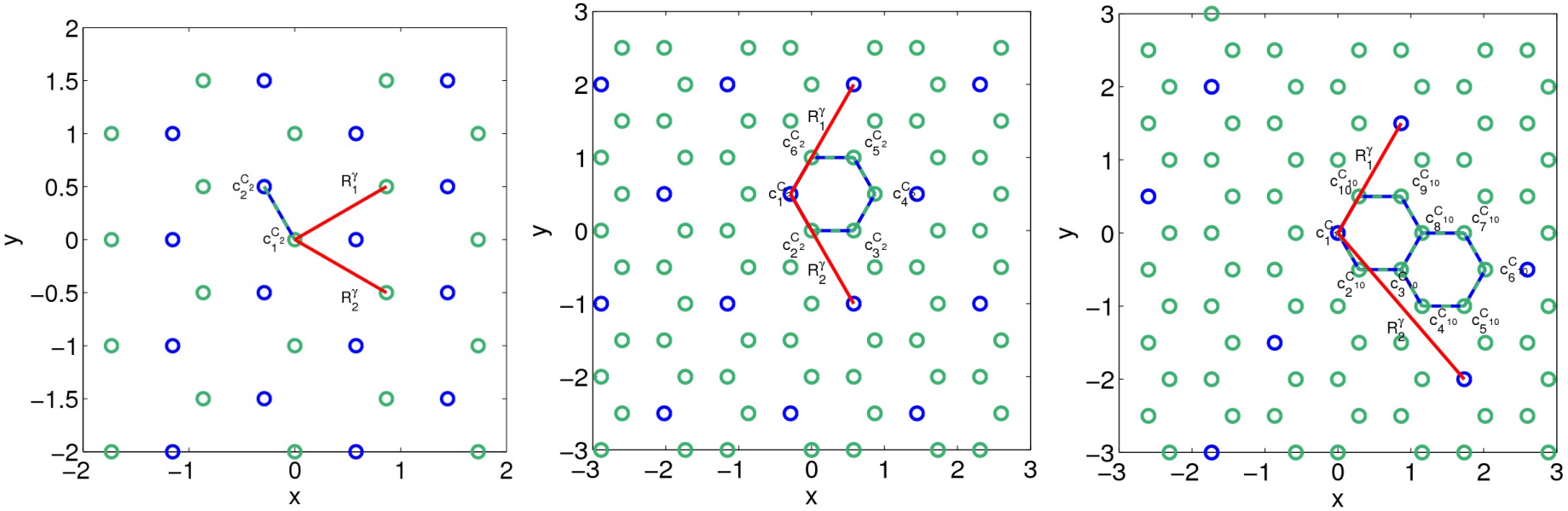
Restriction of self-energies

Self-energy $\Sigma(x)$ = self-energy of the reference system $\Sigma(x')$
x = single particle parameters, **restricting the space of available self-energies**.



VCA Basic quantity: single-particle Green's function

Cluster decompositions of Graphene



Introduce **disorder configurations** η

- η might be on-site energies $\epsilon_i \in \mathcal{U}$, with some distribution $\mathcal{U}$

We need to **average** over these disorder configurations!

Averaging the final single particle Green's function

Consider **CPT**-equation **for each** disorder configuration

$$G_\eta^{-1} = G_{\text{cluster},\eta}^{-1} - T_\eta$$

$G_{\textbf{cluster},\eta}$ may be calculated within CPT or VCA

Average the **final** Green's function G_η

$$\bar{G}_{II} = \frac{1}{w} \sum G_\eta$$

Why is this **not** the way to go?

Averaging the cluster single particle Green's function

Calculate a cluster Green's function G_{cluster} with **excitations from all** disorder configurations

$$\bar{G}_{\text{cluster}} = \frac{1}{w} \sum \text{excitations of configuration } \eta$$

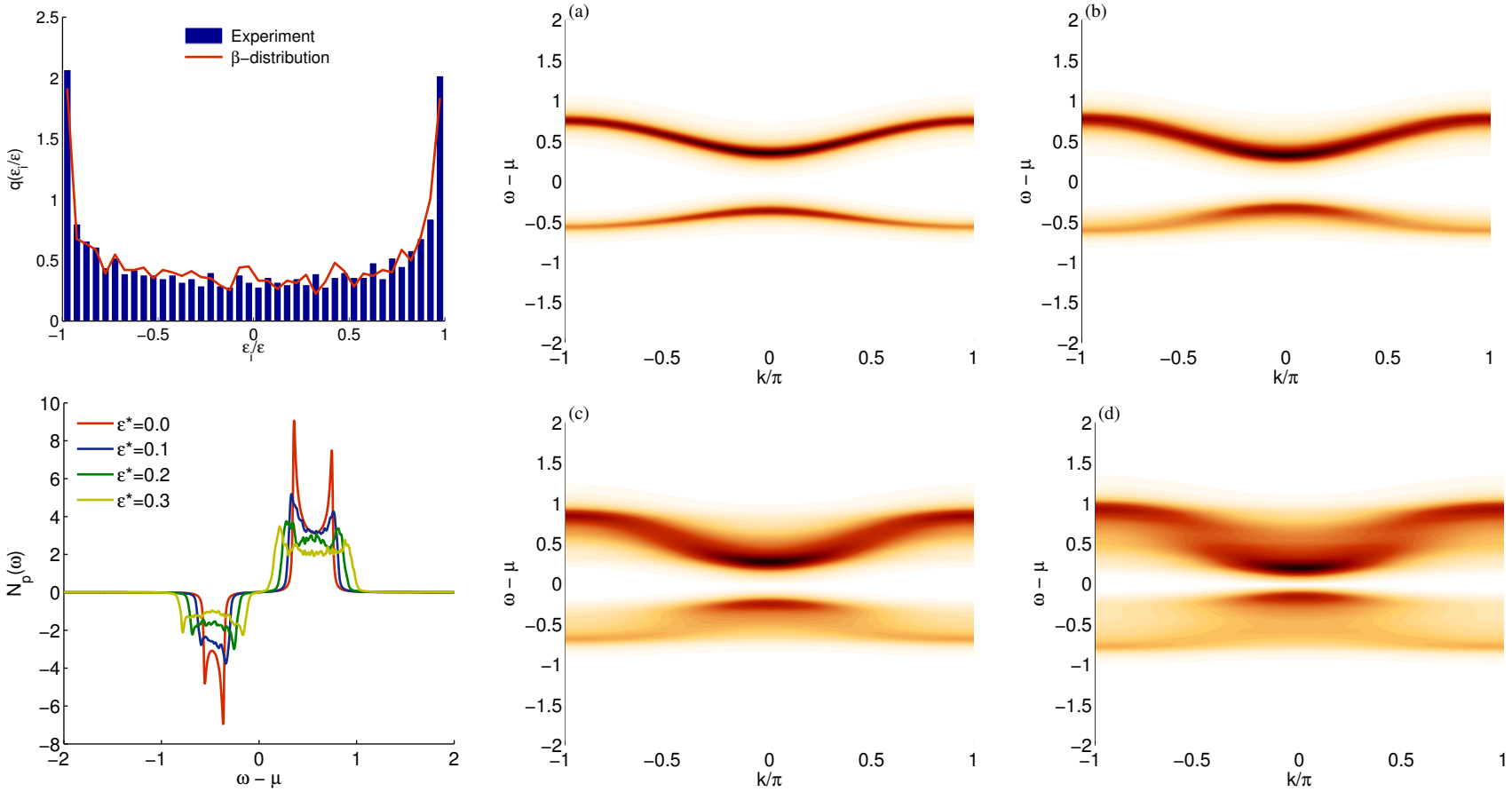
Average on **cluster level**

$$\bar{G}_I = \left(1 - \bar{G}_{\text{cluster}}\, T\right)^{-1} \bar{G}_{\text{cluster}}$$

Why is this the way to go?

Potthoff M and Balzer M, Self-energy-functional theory for systems of interacting electrons with disorder, Phys. Rev. B. 75, 12 1-22 (2007).

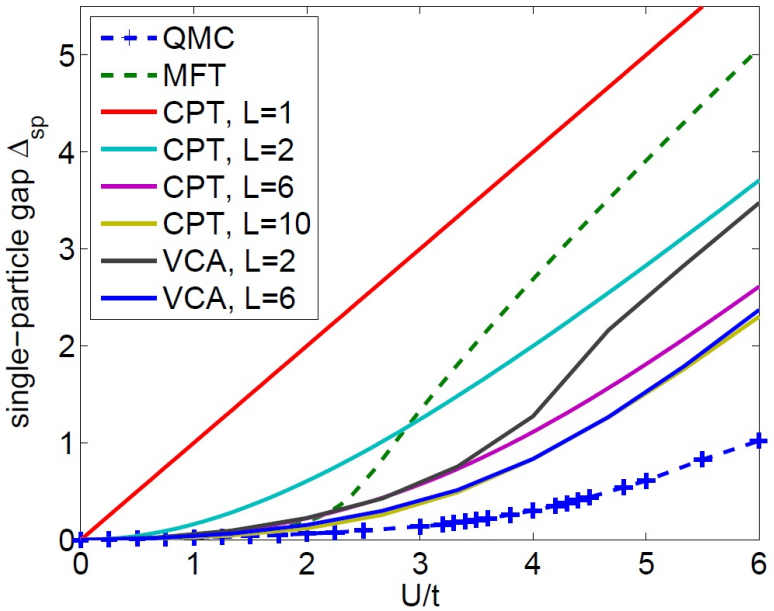
Excitations in disordered bosonic optical lattices



Knap M, Arrigoni E and von der Linden W, Excitations in disordered bosonic optical lattices, Phys. Rev. A. 81 1-16 (2009).

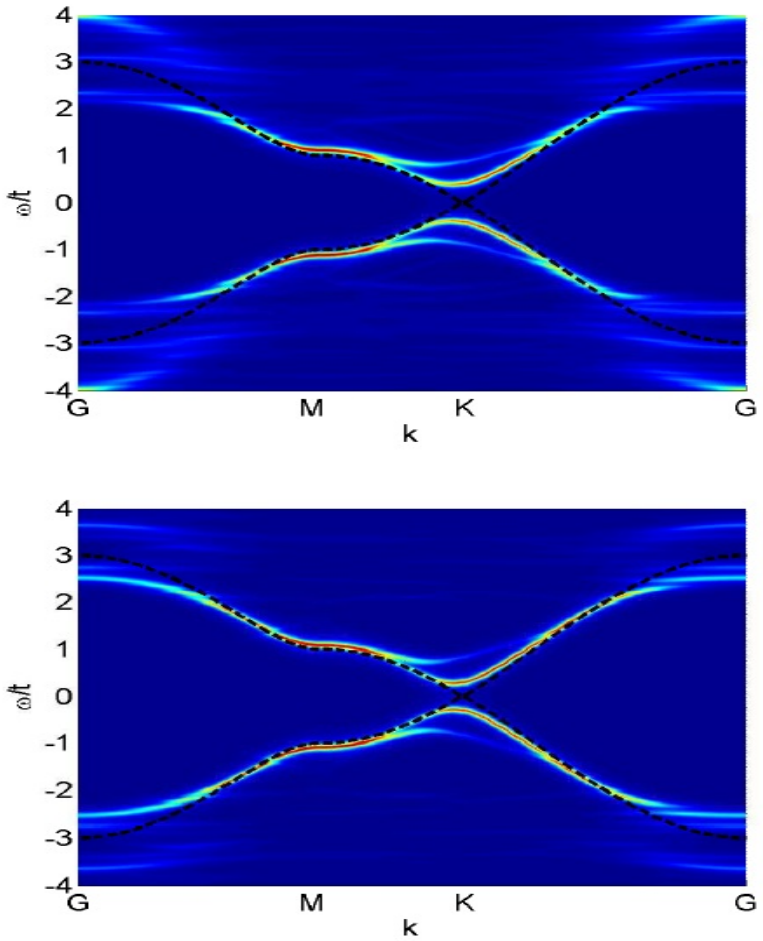
Outline

Graphene + on-site interaction



$U = 4t$

CPT (top), VCA (bottom)

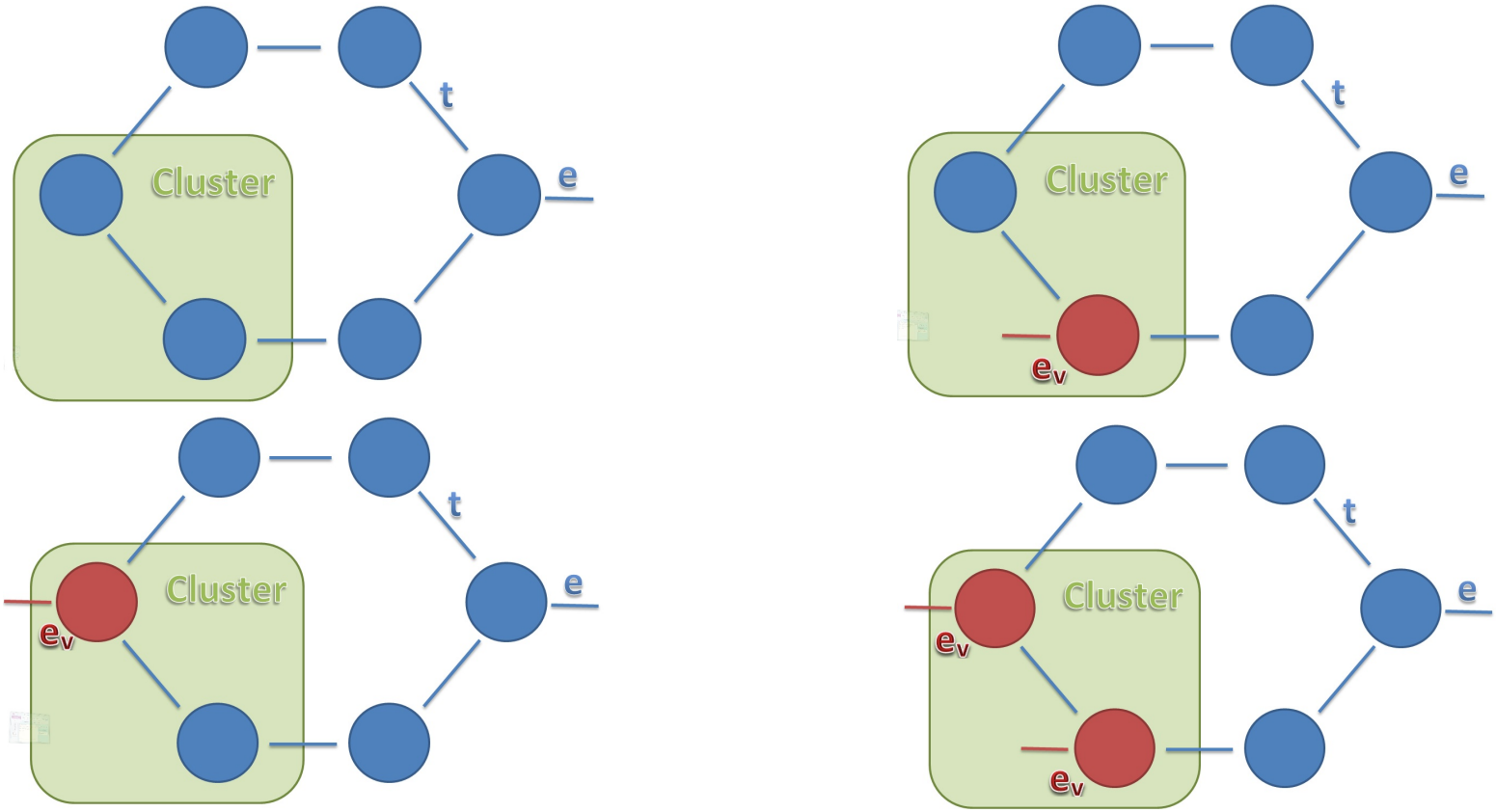


Disordered vacancy model

- vacancy model, by high on-site energy:

$$\epsilon_v >> t, U, \epsilon, \ldots$$

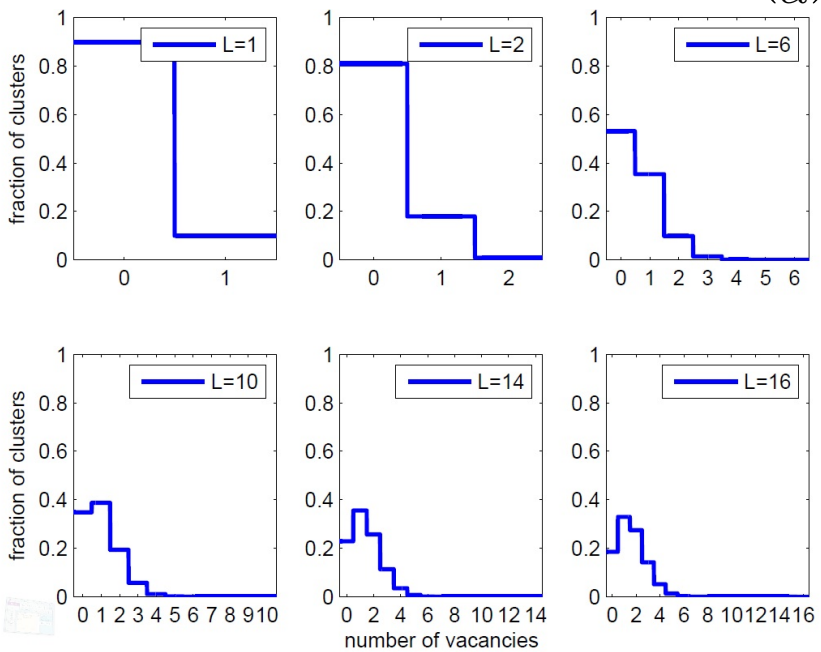
- generate disorder configurations η, vacancies in any possible arrangement (symmetry!)



Disordered vacancy model

- weigh (number of vacancies) according to binomial distribution to reach desired vacancy concentration:

$$w_\alpha(L, P_v) = P_v^\alpha (1 - P_v)^{(L-\alpha)} \binom{L}{\alpha}$$

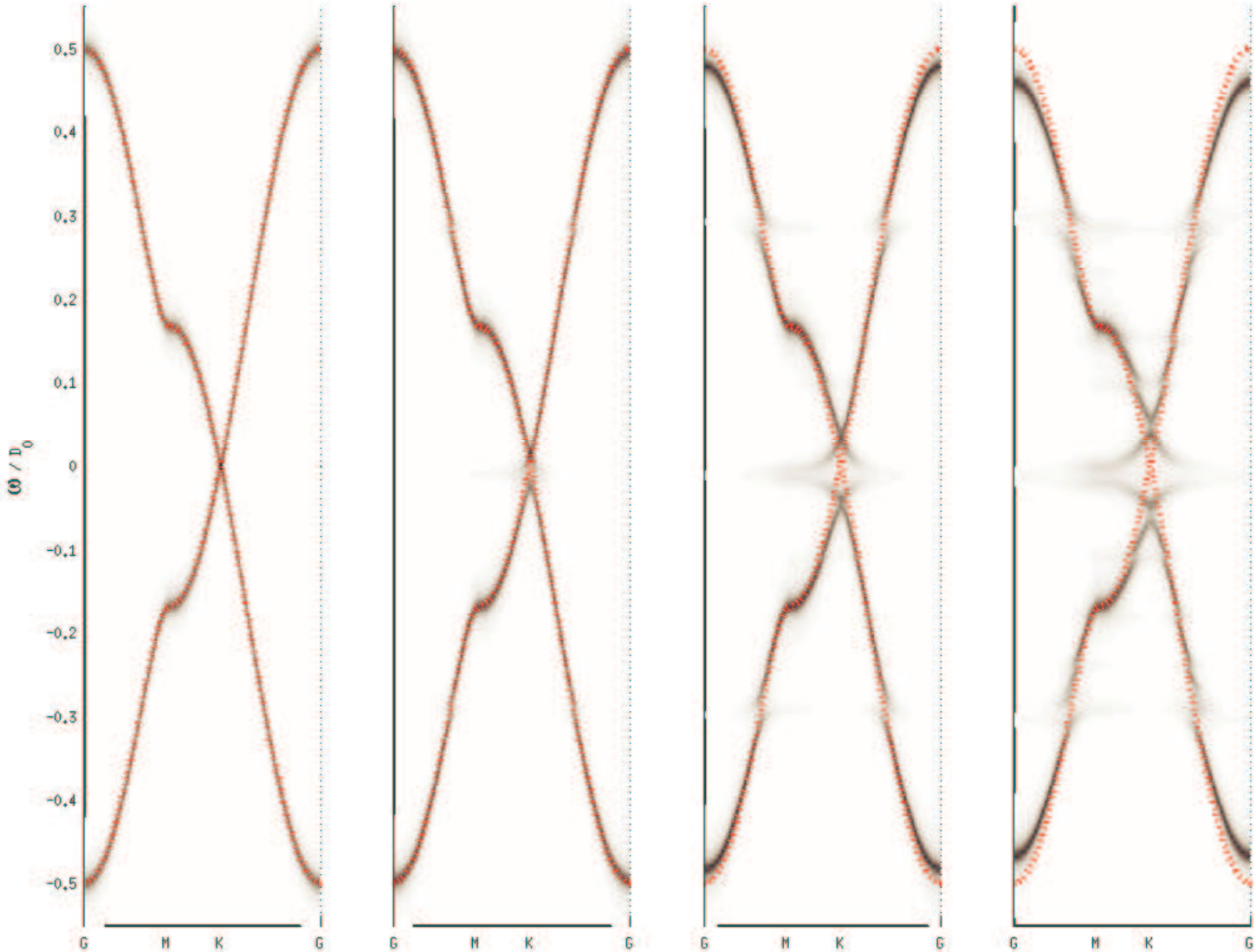


Haverkort MW, Elfimov IS and Sawatzky GA, Electronic structure and self energies of randomly substituted solids using density functional theory and model calculations, arXiv:1109.4036 (2011).

- $\Rightarrow$ (non-magnetic) vacancies = diagonal single-particle disorder

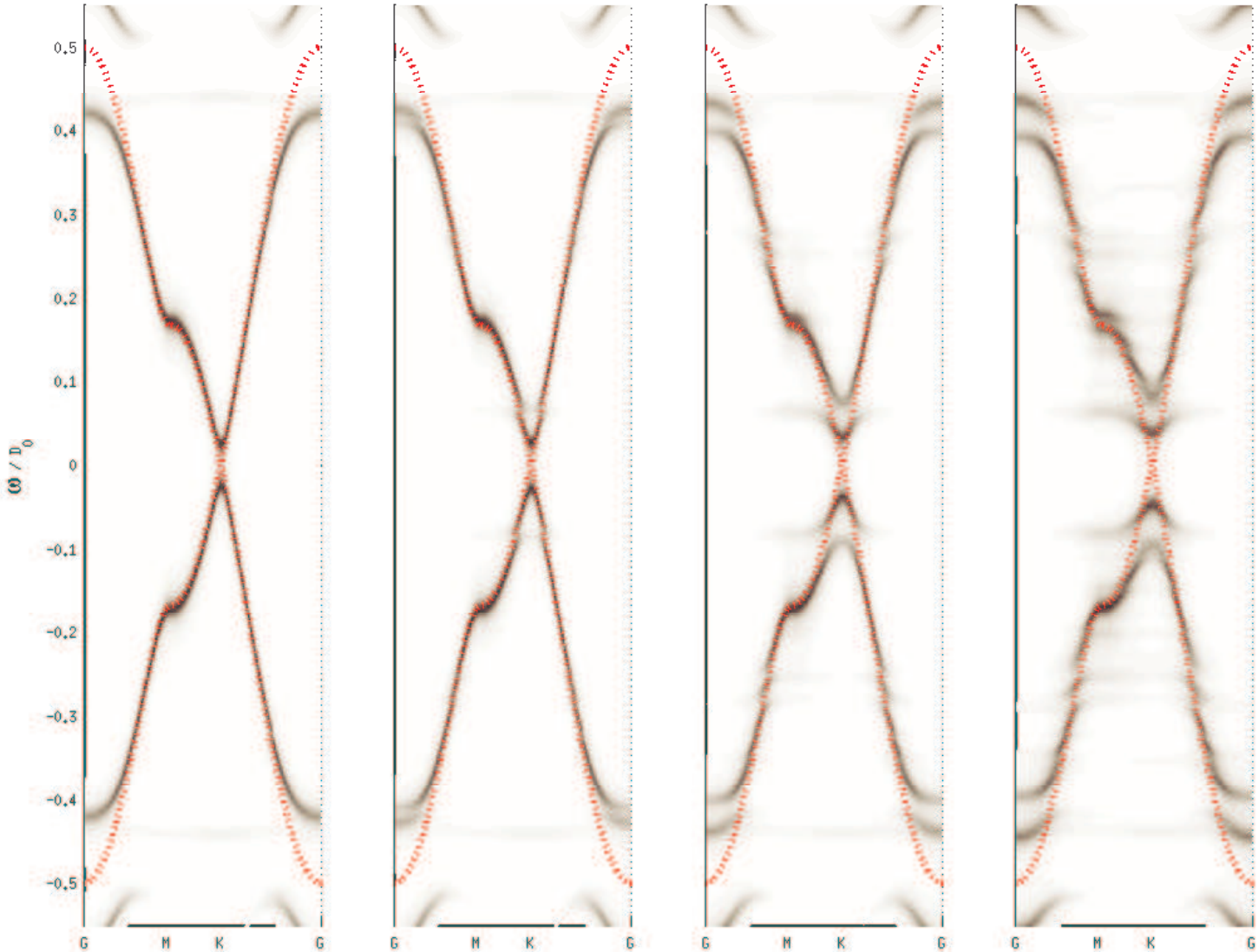
(Non-magnetic) vacancies in Graphene, non-interacting

vacancy concentration $D = [0.0, 0.01, 0.05, 0.1]$



(Non-magnetic) vacancies in Graphene, $U = 3eV$

vacancy concentration $D = [0.0, 0.01, 0.05, 0.1]$

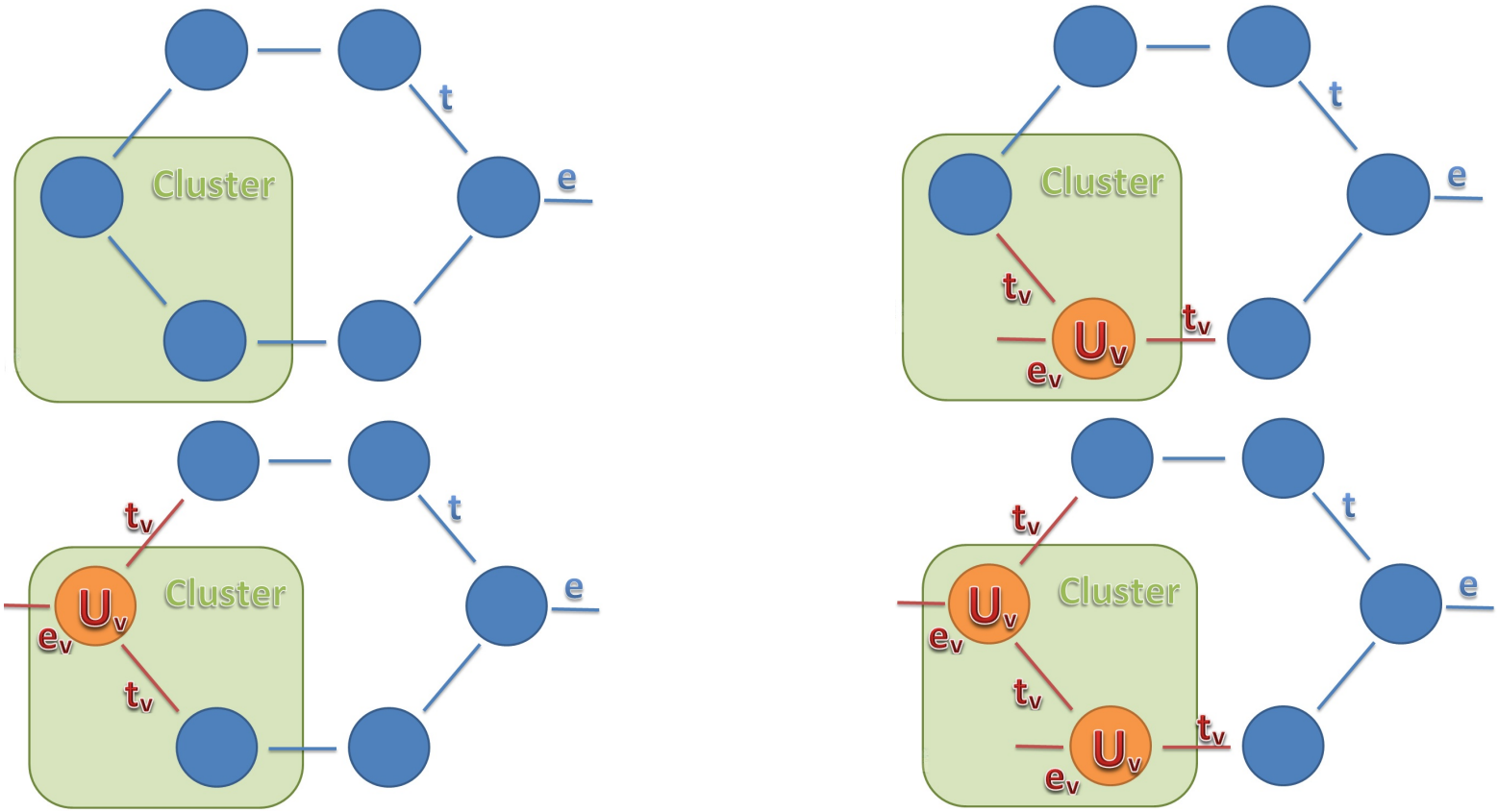


Magnetic vacancies - Model

- vacancy magnetism by on-site interaction:

$$\epsilon_v + U_v + t_v$$

- generate disorder configurations η, vacancies in any possible arrangement (symmetry!)



Magnetic vacancies - Model

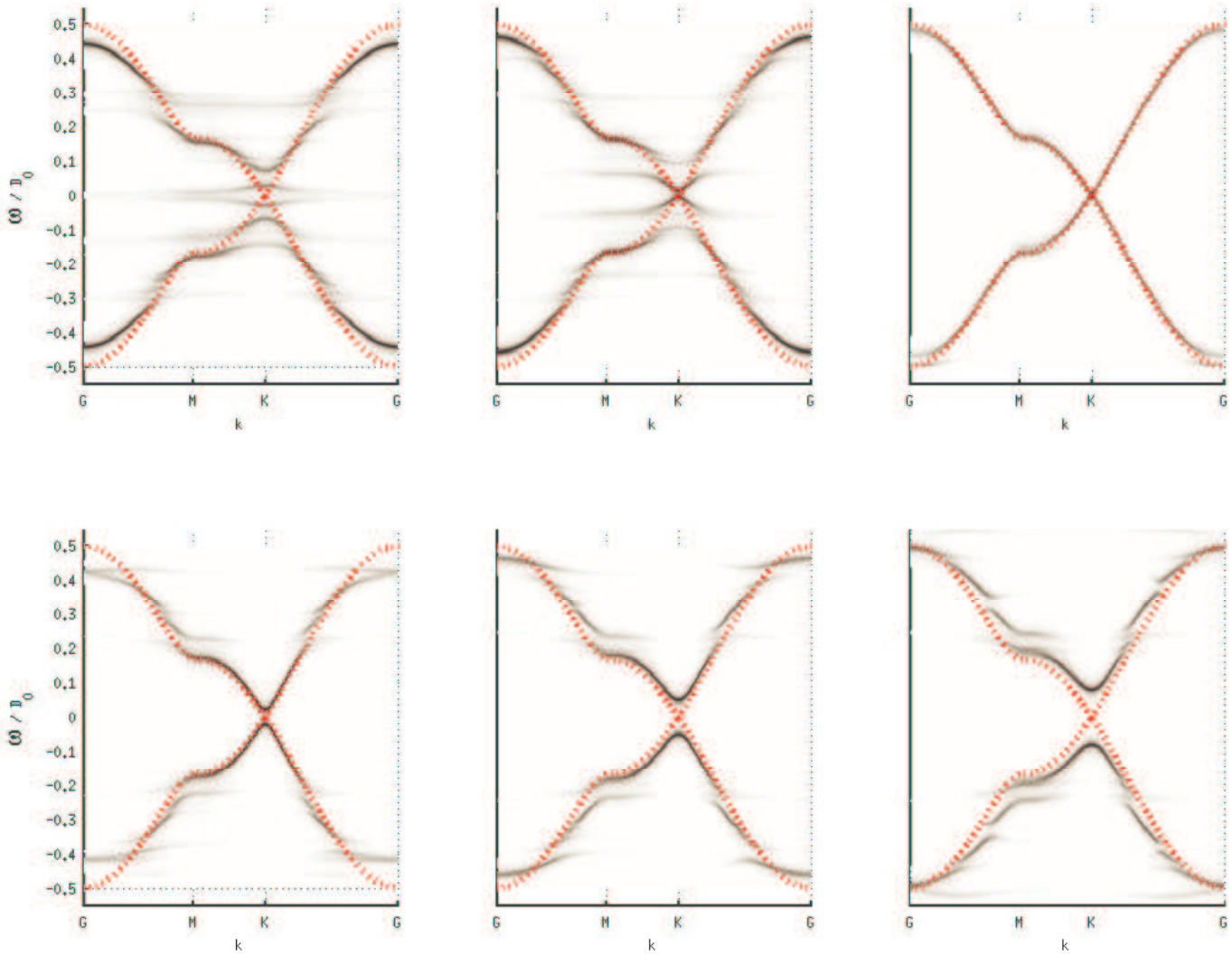
- $\Rightarrow$ magnetic vacancies =
  diagonal single-particle disorder
  + two-particle disorder
  + off-diagonal single-particle disorder
- substantially more difficult:
  1. two-particle disorder (U_v): self-energy for each η different $\Rightarrow$ additional approximation needed!
  2. off-diagonal single-particle disorder (t_v): T for each η different $\Rightarrow$ additional averaging needed!

$$\bar{G}_I = \left(1 - \bar{G}_{\text{cluster}}\, \bar{T}\right)^{-1} \bar{G}_{\text{cluster}}$$

$$G_{\text{cluster}}{}^{-1}(\eta) = G^{-1}_{0,\text{cluster}}(\eta) - \Sigma(\eta)$$

Magnetic vacancies in Graphene

From left to right $t_v = [0.1, 6.4]eV$, vacancy concentration $D = 5\%$



Conclusion

- (disordered) CPT/VCA $\longrightarrow$ disorder + correlations
- further approximations $\longrightarrow$ disorder in interaction

- vacancies induce localized low energy states
- which seem to be destroyed by correlations

Outlook

- finding more sophisticated ways to treat complex forms of disorder
- combine with ab-initio calculations
- study out of equilibrium phenomena

Thank You!

Thank you for your attention!

contact: martin.nuss@student.tugraz.at

I acknowledge financial support from the Förderungsstipendium of the TU Graz and the Austrian Science Fund (FWF) P24081-N16 and P18551-N16.