International workshop on

Local Correlation Methods: from Molecules to Crystals

Dresden, Sept. 12 - 15, 2007

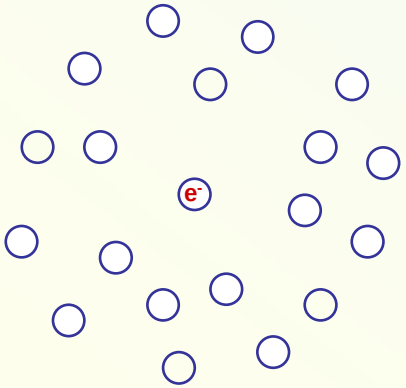
The correlation hole of an electron

Two competing effects on electron motion

- Coulomb repulsion: keeps eletrons apart

- kinetic energy: wants to have them moving as freely as possible

⟶ compromise depending on relative strengths of the two



correlation hole

- electron gas: $E_{kin} = \frac{(\Delta p)^2}{2m}$; $\Delta p \Delta x = 1$ with $\Delta x = d$

⟶ $E_{kin} \sim \frac{1}{d^2}$ $E_{coul} \sim \frac{1}{d}$

extreme cases: high density ⟶ $d \to 0$ ⟶ $E_{kin} \gg E_{coul}$

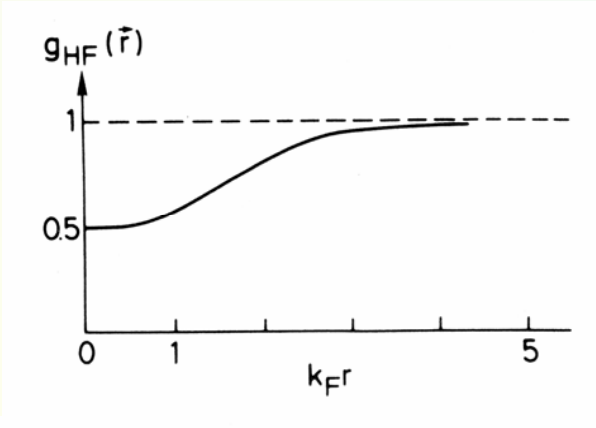
low density ⟶ $d \to \infty$ ⟶ $E_{coul} \gg E_{kin}$

Wigner crystal

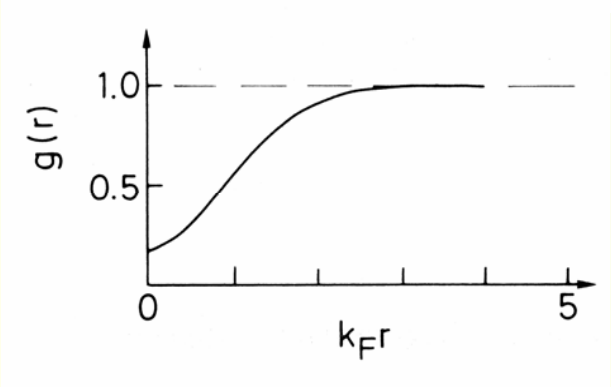
basic problem: description of the correlation hole

pair-distribution fct. $$g(\mathbf{r},\mathbf{r}') = \frac{1}{\rho(\mathbf{r})\rho(\mathbf{r}')}\left\langle \psi_0 \left| \sum_{i\neq j} \delta(\mathbf{r}-\mathbf{r}_i)\,\delta(\mathbf{r}'-\mathbf{r}_j) \right| \psi_0 \right\rangle$$

due to Pauli principle ➡ already structure in HF



$$g_{HF}(\mathbf{r}) = 1 - \frac{9}{2}\left[\frac{\sin k_F r - k_F r \cos k_F r}{(k_F r)^3}\right]^2$$



for large r ➡ $$g_{HF}(\mathbf{r}) \to 1 - \frac{\alpha \cdot \cos^2 k_F r}{(k_F r)^4}$$

small r ➡ $$g(\mathbf{r}) < g_{HF}(\mathbf{r})$$

screening of the long-range Coulomb interactions

→ plasma oscillations must include zero-point motion of plasmons in $|\psi_0\rangle$

$$|\psi_0\rangle = e^{\sum_q \tau_q \rho_q^+ \rho_q} |\Phi_{SCF}\rangle \qquad \text{RPA}$$

$$\rho_{\mathbf{q}} = \sum_{\mathbf{p}\sigma} c^+_{\mathbf{p}-\mathbf{q}\sigma} c_{\mathbf{p}\sigma} \qquad \text{density fluctuation}$$

Fourier transf. $$|\psi_0\rangle = \exp\left[\int d\mathbf{r} d\mathbf{r}' \tau(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r})\rho(\mathbf{r}')\right]|\Phi_0\rangle$$

1-st quantized form $$\psi_0(\mathbf{r}_1,...,\mathbf{r}_N) = \exp\left[\sum_{ij} \tau(\mathbf{r}_i - \mathbf{r}_j)\right]\Phi_0(\mathbf{r}_1,...,\mathbf{r}_N)$$

inhomogen. system

Jastrow function

$$\psi_0(\mathbf{r}_1,...,\mathbf{r}_N) = \exp\left[\sum_i g(\mathbf{r}_i) + \sum_{ij} \tau(\mathbf{r}_i - \mathbf{r}_j)\right]\Phi_0(\mathbf{r}_1,...,\mathbf{r}_N)$$

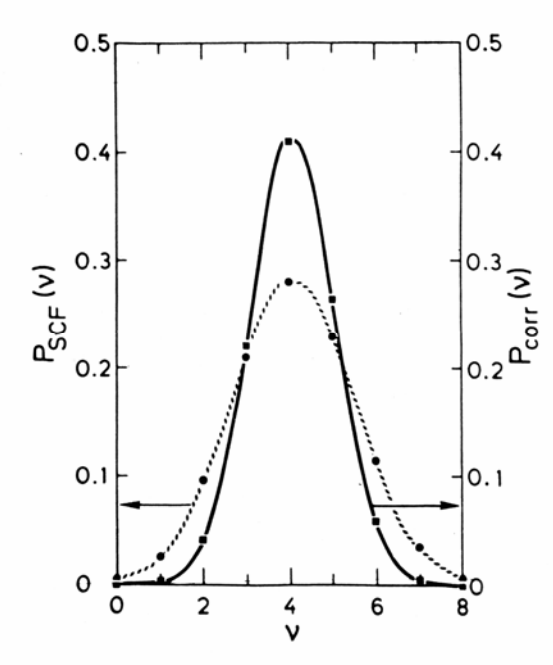
has been applied to semiconductors (S. Louie et al.)

Short-range correlations

distinction between interatomic and intra-atomic correlations

1) interatomic correlations

reduce charge fluctuations on a given site compared with SCF



C atom in C_2H_2
correlat. strength

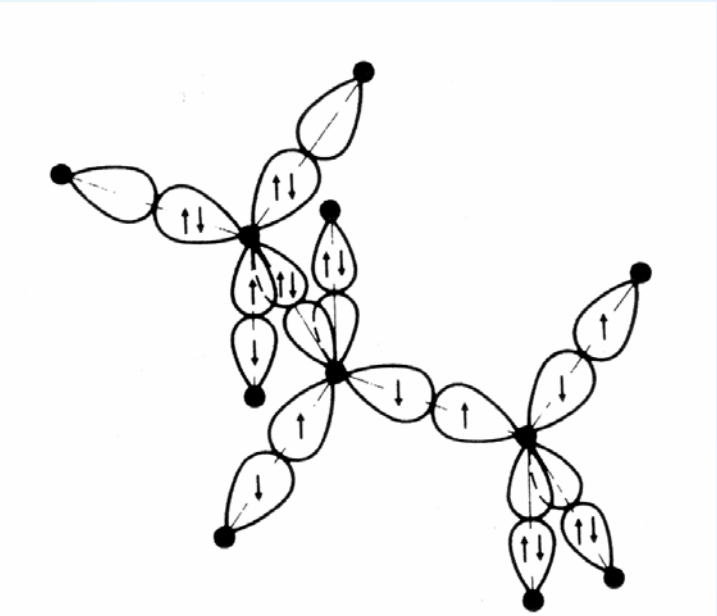
extreme case: Gd^{3+} $4f^7$ *no* $4f^6$ *or* $4f^8$

not so extreme:

Ce^{3+} : $4f^1$ *and small part* $4f^0$

singlet Kondo effect

when applied to bonds



→ van der Waals interactions

2) intra-atmic correlations

Hund‘s rule correl., in case of 4f shell $J = L - S$ for f^n $n < 7$

e.g., Pr^{3+} → $4f^2$ → $J = 4$

but also important in paramagn. Fe, even in C in C_2H_2

Description of the correlation hole

starting point: SCF calculations, e.g., CRYSTAL or WANNIER

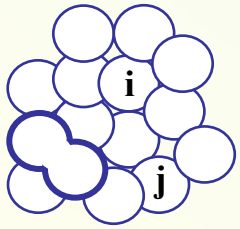
choice of basis set of GTO's

optimal description: construct (nonorthog.) wavelets from basis set

different coarse graining

⟹ introduce operator $n_\sigma(i)$, $\mathbf{s}(i)$ referring to wavelet i

$$n_\sigma(i) = b_\sigma^+(i) b_\sigma(i) \qquad \mathbf{s}(i) = \frac{1}{2}\sum_{\alpha\beta} b_\alpha^+(i)\,\boldsymbol{\sigma}_{\alpha\beta}\, b_\beta(i)$$



$$O(i,j) = \begin{cases} n_\sigma(i)\, n_{-\sigma}(i) \\ n(i)\, n(j) \\ \mathbf{s}(i)\,\mathbf{s}(j) \end{cases} \qquad O(i,j)\left|\Phi_{SCF}\right\rangle$$

reduce (or enhance) configurations

(Stollhoff + P.F., '80)

advantage: reduce number of configur. to be corrected to a minimum

applicable also to metals

disadvantage: nonorthogonality of wavelets

alternative: use orthogonal destruction operators $c_{i\sigma}, c_{j\sigma'}$ in

$H_{res} = H - H_{SCF}$, localized occupied SCF orbitals

⟹ Wannier (or Foster-Boys) centered at atoms

i and j and create electrons in (non-orthog.) virtual

orbitals $a^{+}_{\alpha\sigma}, a^{+}_{\beta\sigma'}$ (atomic like orbitals) "near" sites

i and j (P. Pulay '83, H.-J. Werner and M. Schütz '95)

advantage: much simpler to implement, e.g., into MOLPRO

disadvantage: not a priori applicable to metals like Na

How to apply this to solids?

(a) size extensivity: applying perturb. theory (Moeller-Plesset)

⟶ not a problem

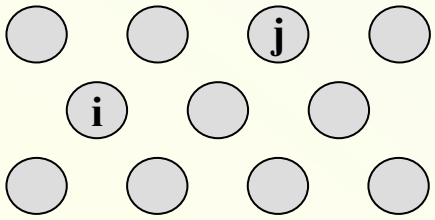
going beyond (e.g., CI or variational) ⟶ problem

solution: use exponent. form e^S, e.g., coupled cluster method

like Jastrow factor

much more elegant: use cumulants ⟶ need not use exponent. form

(b) method of increments (H. Stoll '92)



atoms (or bonds)

$$E_{corr} = \sum_i \varepsilon_{corr}(i) + \sum_{\langle ij \rangle} \delta\varepsilon_{corr}(i,j) + \ldots$$

like Bethe-Goldstone cluster expansion

achievements:

many-body wavefunction for ground state of many insulators and semicond.

recently also some metals, lattice constants, binding energies, bulk moduli

(see, e.g., review B. Paulus, including early work of Kiel et al., Horsch et al.,

more recent: Dolg, Doll, Rosciszewski, Birkenheuer et al.)

at present: improved new attempt by R. Bartlett, V. Staemmler,

G. Scuseria, C. Pisani and M. Schütz et al.

open problem: strongly correlated systems with d and f electrons

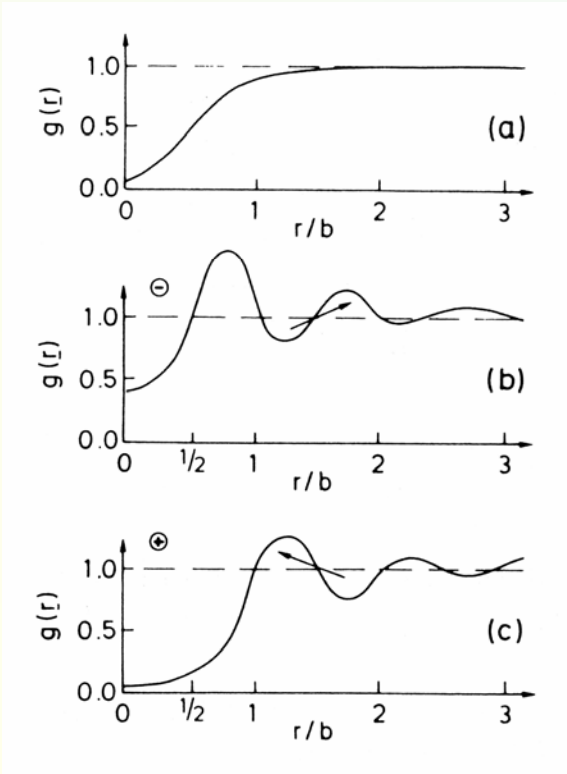
MC-SCF as starting point

room for much work

Correlation holes of excited states

➡ relevant for energy bands

example semiconductors: add an electron ➡ long ranged polarization cloud but also relaxation and loss of ground-state correlations



different to van der Waals correlations

in ground state

(reason for failure of LDA to describe energy gap)

quasiparticle: electron (hole) + correl. hole

move together though system in form of

Bloch wave

example: hole state SCF: $\left|\mathbf{k}\nu\sigma\right\rangle = \frac{1}{\sqrt{N_0}} \sum_{\mathbf{Rn}} \alpha_{\nu n}(\mathbf{k})\, e^{i\mathbf{kR}} \left|\mathbf{Rn}\sigma\right\rangle$

$$\left|\mathbf{Rn}\sigma\right\rangle = c_{\mathbf{Rn}\sigma} \left|\Phi_{SCF}\right\rangle$$

$$\left|\psi^{N-1}_{\mathbf{k}\nu\sigma}\right\rangle = \frac{1}{\sqrt{N_0}} \sum_{n\mathbf{R}} \alpha_{\nu n}(\mathbf{k})\, e^{i\mathbf{kR}} \left|\mathbf{Rn}\sigma\right\}$$

wave operator Ω: $\left|\mathbf{Rn}\sigma\right\} = \Omega \left|\mathbf{Rn}\sigma\right\rangle$

scatter. matrix S: $S = \Omega - 1$

contains 1- and 2-particle excitations

applications: keep hole state frozen and do new SCF calculation

⟹ relaxat. + polarizat.; for long-range part

use ε (diel. const.)

$$\Delta\varepsilon_{\mathbf{k}\nu\sigma} = \sum_{\mathbf{R}nn'} \alpha^{*}_{\nu n}(\mathbf{k})\, \alpha_{\nu n'}(\mathbf{k})\, e^{i\mathbf{kR}} \left\langle c_{on\sigma} \left| H_{res} S c_{\mathbf{Rn}'\sigma} \right\rangle_c \right.$$

similar procedure for conduction band

recent example: MgO (L. Hozoi et al.) , TZ basis set

SCF: gap	16.2 eV	
includ. correl.	8.1 eV	(somewhat fortuitous)
experiment	7.9 eV	
LDA	5.0 eV	

large contribut. from on-site and n.n.-site relaxation

surprise: width of valence band increases due to correlat.

Green's function: $$G_\nu(\mathbf{k},\omega) = \frac{1}{\omega - \varepsilon_\nu(\mathbf{k}) - \Sigma_\nu(\mathbf{k},\omega)}$$

quasiparticle representation:

$$G(\mathbf{k},\omega) = \frac{Z}{\omega - \varepsilon_{qp}(\mathbf{k}) - i\gamma_k \operatorname{sgn}\omega} + G_{inc}(\mathbf{k},\omega)$$

$G_{inc}(\mathbf{k},\omega)$ from excitations involving internal degrees of freedom

of the correlation hole (think of drum head)

- can be strongly damped

- simplest example: satellite peaks in PEs

Formalism:

retard. Green fct. $$G_\sigma(\mathbf{k},t) = -i\Theta(t)\left\langle \psi_0 \left| \left[c_\sigma(\mathbf{k},t), c_\sigma^+(\mathbf{k}) \right]_+ \right| \psi_0 \right\rangle$$

notation: $$\left(A\middle|B\right)_+ = \left\langle \psi_0 \left| \left[A^+, B \right]_+ \right| \psi_0 \right\rangle$$

choose most important operators which generate the correlation hole: $$c_\sigma^+(i), A_n(i) \Rightarrow \left\{ A_\nu(i) \right\}$$

$$\Rightarrow \quad \left\{ A_\nu(\mathbf{k}) \right\}$$

Green's function matrix: $$G_{\mu\nu}(\mathbf{k},t) = -i\Theta(t)\left(A_\mu(\mathbf{k},t) \middle| A_\nu(\mathbf{k}) \right)_+$$

with: $$LO = \left[H, O \right]_- = i\frac{dO}{dt} \quad \Rightarrow \quad O(t) = e^{iLt} O$$

$$G_{\mu\nu}(\mathbf{k},z) = \left(A_\mu \left| \frac{1}{z - L} A_\nu \right. \right)_+$$

(Pickup, Goscinski)

remain within the space of $\{A_\nu(\mathbf{k})\}$ ⟶ projection method (Löwdin)

example: Ni (paramagn.)

choice of $\{A_\nu\}$

$$A_\nu^{(0)}(\mathbf{k}) = c_{\nu\uparrow}^{+}(\mathbf{k})$$

$$A_{ij}^{(1)}(\ell) = \begin{cases} c_{i\uparrow}^{+}(\ell)\, n_{i\downarrow}(\ell) & i = j \\ c_{i\uparrow}^{+}(\ell)\, n_{j}(\ell) & i \neq j \end{cases}$$

$$A_{ij}^{(2)}(\ell) = c_{i\uparrow}^{+}(\ell)\, s_j^{z}(\ell) + c_{i\downarrow}^{+}(\ell)\, s_j^{+}(\ell)$$

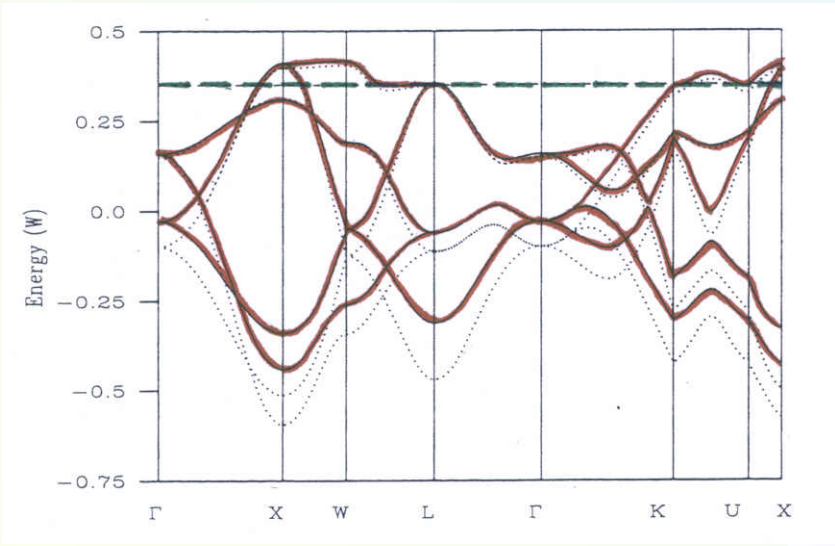
$$A_{ij}^{(3)}(\ell) = c_{j\downarrow}^{+}(\ell)\, c_{j\uparrow}^{+}(\ell)\, c_{i\downarrow}(\ell)$$

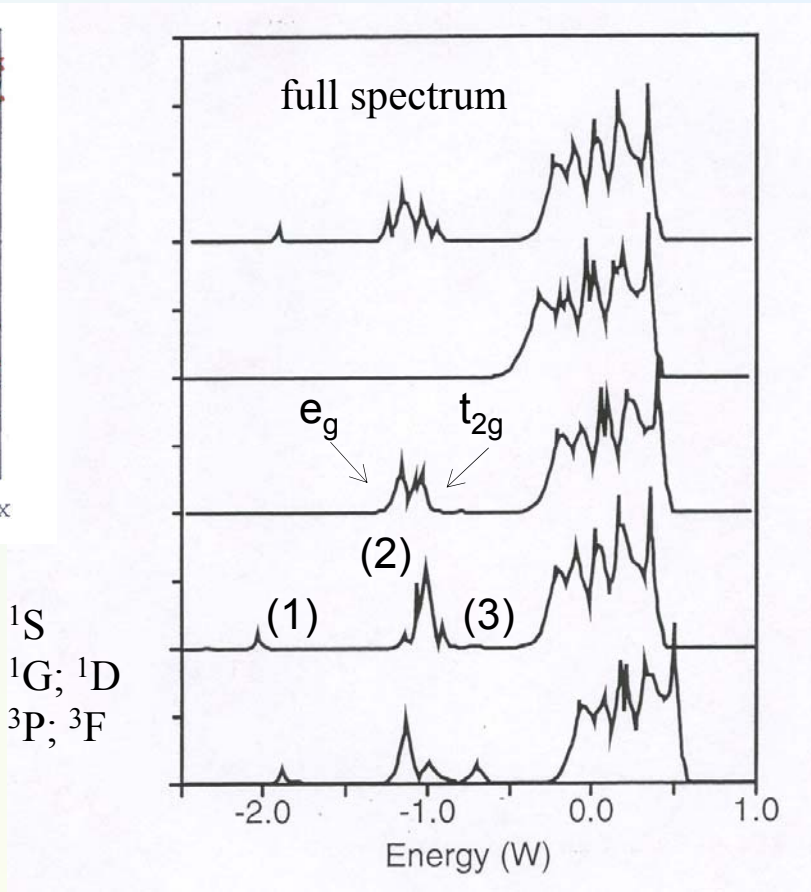
$$A_{ij}^{(\alpha)}(\mathbf{k}) = \frac{1}{\sqrt{N_0}} \sum_{\ell} A_{ij}^{(\alpha)}(\ell)\, e^{i\mathbf{k}\mathbf{R}_\ell}$$

total#: $1 + 25 + 20 + 20 = 66$

Results for paramagnetic Ni

n_d=9.4





U = 0.56
J = 0.22
ΔJ = 0.031

HF result

J = ΔJ = 0

J = 0.22

full spectr.
but with
Ω = 1

reduction of bandwidth

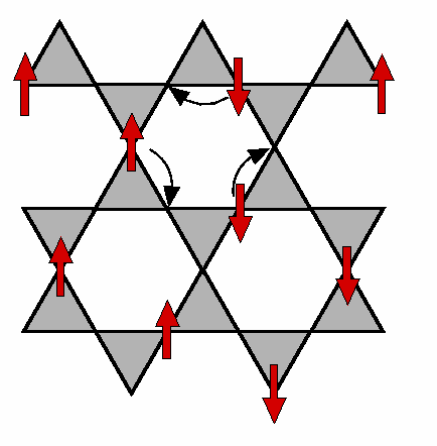
(1) ^{1}S
(2) ^{1}G; ^{1}D
(3) ^{3}P; ^{3}F

(Unger, Igarashi)

breakdown of the quasiparticle picture

one-dimensional systems:	spin-charge separation
	Luttinger liquid instead of Fermi liquid
fractional Quantum-Hall effect:	excitations with fractional charges
	strong coupling limit due to a high
	magnetic field
electrons on frustrated lattices:	fractional charges at special filling
	factors in the strong correlation limit, even
	in 3 dimensions

kagomé lattice



$$H = -t\sum_{\langle ij\rangle\sigma}\left(c^{+}_{i\sigma}c_{j\sigma} + \text{h.c.}\right) + U\sum_{i} n_{i\uparrow}n_{i\downarrow} + V\sum_{\langle ij\rangle} n_i n_j$$

1/6 filling, i.e., one electron per triangle

$U \to \infty \quad |t| \ll V$ strong correlations

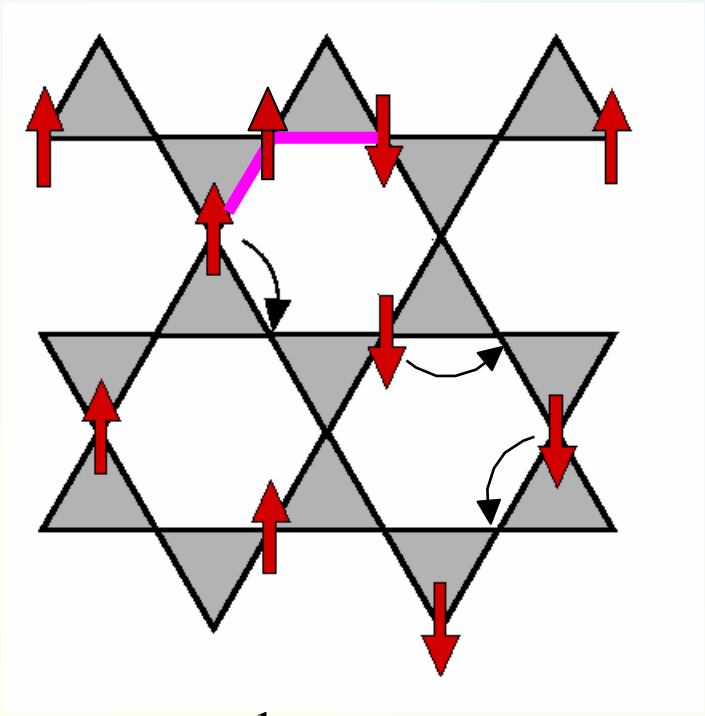
(1) $t = 0$ → ground state is macroscop. degenerate

(2) $t \neq 0$ →

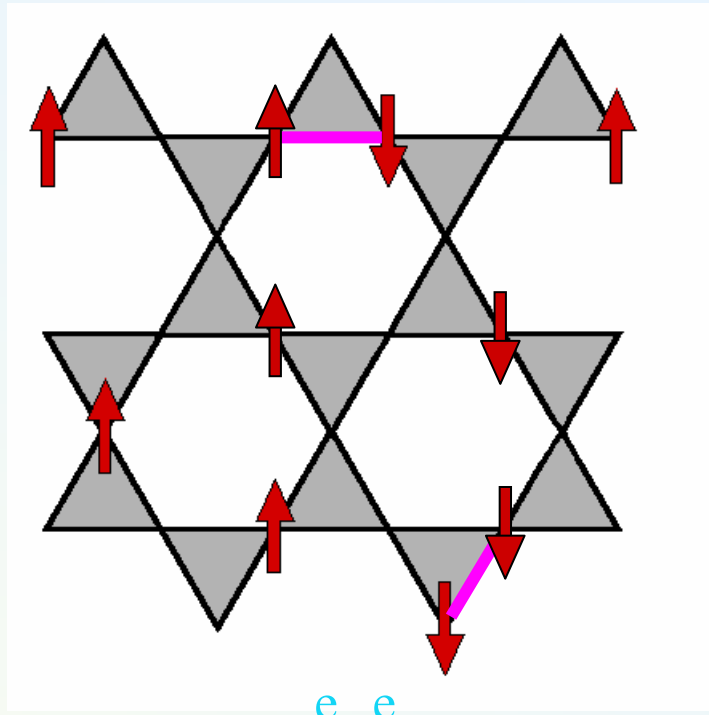
$$H_{\text{hex}} = -g \sum_{\{\hexagon\}\{\blacktriangle\blacksquare\bullet\}} \left(|\hexagon\rangle\langle\hexagon| + |\hexagon\rangle\langle\hexagon| + \text{H.c.} \right)$$

$$g = \frac{6t^3}{V^2}$$

add now a particle ⟶ $\Delta E = 2V$



charge e



charge $\frac{e}{2}, \frac{e}{2}$

correlation hole has fallen apart.

if there is a weak restoring force ⟶ correlation hole is very extended