New approaches for treating correlation in molecules and solids

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Outline

- Clifford boundary conditions for the study of periodic Coulomb systems
- Photoemission from the three-body Green's function
- Photoemission from the many-body effective energy theory

Clifford boundary conditions

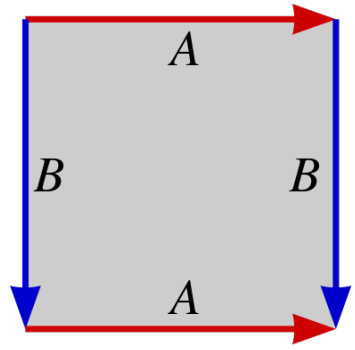
Stefano Evangelisti

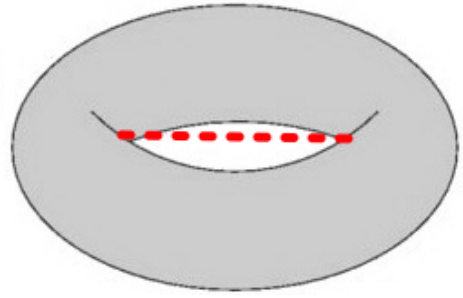
Clifford periodic boundary conditions

Motivation: efficient and general method for the description of periodic systems with an explicit two-body Coulomb interaction

Strategy:

- Isolate a fragment of the system.
- Modify the topology of this supercell to that of a Clifford torus (flat)
- Use the Euclidean distance of the embedding space in the Coulomb potential
- Converge result with respect to the size of the supercell.

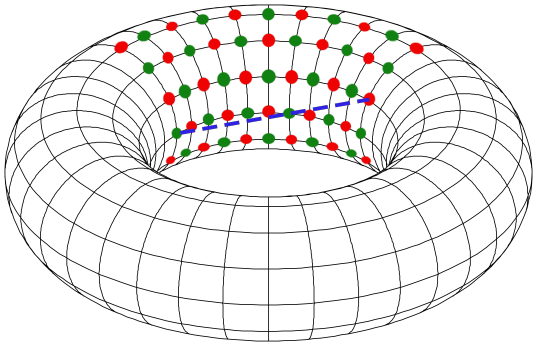




Madelung constants

A classical problem with a two-body Coulomb interaction. Applying Clifford periodic boundary conditions allows for a direct-sum solution.

We construct a Clifford supercell (CSC) with K ions per side.



2D NaCl on a 2-torus

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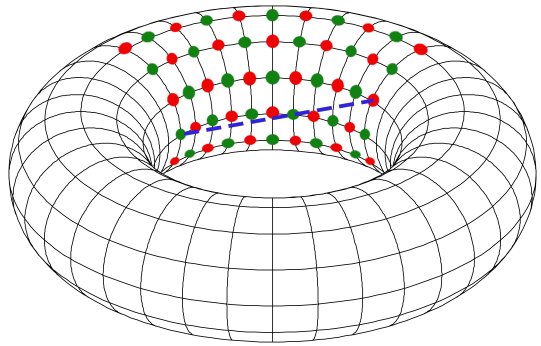


2D NaCl on a 2-torus

Example: CsCl (3D)

K	ESC	Evjen	CSC
40	-165.1951301706	-3.1228159774	-1.7613129129
41	-172.8428945898	-0.4025235314	-1.7613786888
42	-173.4399599212	-3.1228353436	-1.7614398086
43	-181.0877243486	-0.4025055166	-1.7614967019
60	-247.6434281092	-3.1229317065	-1.7620703281
80	-330.0917264008	-3.1229722138	-1.7623349348
100	-412.5400247666	-3.1229909632	-1.7624573245
120	-494.9883231553	-3.1230011482	-1.7625237851
∞			-1.7626748322

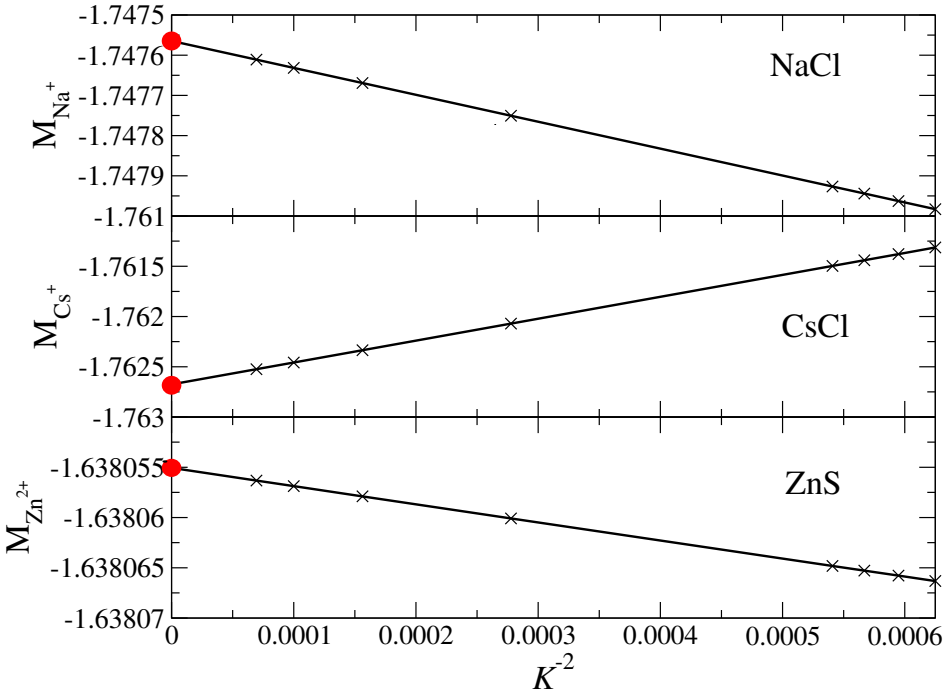
Reference value:[21] -1.7626747731

CSC results converge monotonically to the reference value

Tavernier *et al.*, J. Phys. Chem. Lett. 11, 7090 (2020)

Madelung constants

Results are linear as a function of K^{-2}.



We can extrapolate using

$$M(K) = M_\infty + CK^{-2},$$

Other crystal structures

	CSC	Reference
h-BN	-1.542219721703	-1.542219721707 [17]
$CaTiO_3$	-24.7549360589	-24.7549 [23]

Tavernier *et al.*, J. Phys. Chem. Lett. 11, 7090 (2020)

Wigner crystals: Ground-state energies

Ground-state energy per electron of a Wigner crystal :

$$E_{WC} \sim \frac{\eta_0}{r_s} + \frac{\eta_1}{r_s^{3/2}} + \frac{\eta_2}{r_s^2} + \frac{\eta_3}{r_s^{5/2}} + \ldots$$

η_0: energy of a classical Wigner crystal
η_1: zero-point correction in the harmonic approximation.

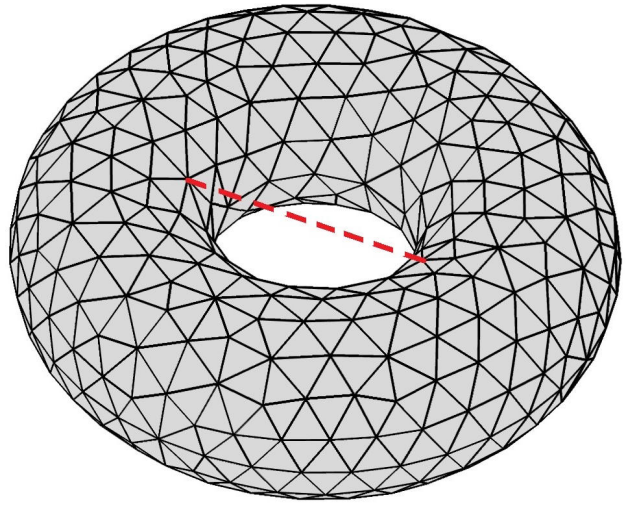
Most accurate literature values before our work.

	1D linear lattice	2D triangular lattice	3D bcc lattice
η_0	-	-1.106 103	-0.895 929
η_1	0.359 933	0.795	1.328 62

Wigner crystals: Clifford approach

We now use our Clifford PBC approach.

$$\frac{\eta_0}{r_s} = \frac{U_0}{N}$$



triangular lattice on a 2-torus

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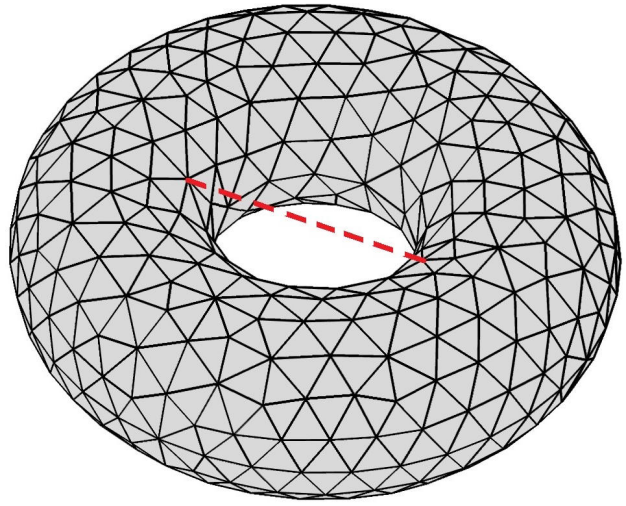


triangular lattice on a 2-torus

Lattice	η_0^{2D}	
	this work	literature
square	-1.100 244 420	-1.100 244
triangle	-1.106 102 587	-1.106 103

Lattice	η_0^{3D}	
	this work	literature
simple cubic	-0.880 059 440	-0.880 059
body-centered cubic	-0.895 929 255	-0.895 929
face-centered cubic	-0.895 873 614	-0.895 874
hexagonal close packed	-0.895 838 120	-0.895 838

Alves *et al.*, Phys. Rev. B 103, 245125 (2021)

Wigner crystals: zero-point correction

Using a normal mode transformation we can also calculate η_1.

$$\frac{\eta_1}{r_s^{3/2}} = \frac{1}{2N} \sum_{k=1}^{N} \sum_{\alpha=1}^{d} \omega_{k,\alpha}.$$

Lattice	η_1	
	this work	literature
1D (linear)	0.359 933	0.359 933
2D (triangular)	0.813 686	0.795
3D (body-centered cubic)	1.328 624	1.328 62

All our results in agreement with literature values except η_1 in 2D.

Alves *et al.*, Phys. Rev. B 103, 245125 (2021)

Quantum applications

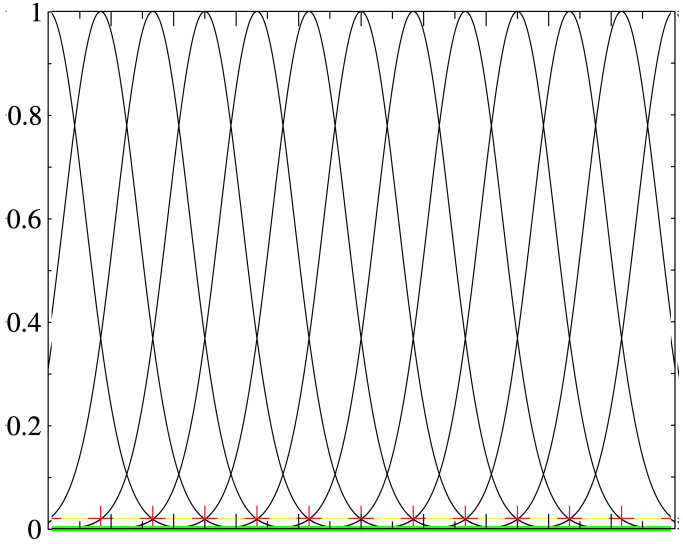
We also applied our Clifford approach to quantum systems.

Wigner localisation at (very) low density with 2 electrons in the Clifford supercell

Miguel Escobar Azor

Summary

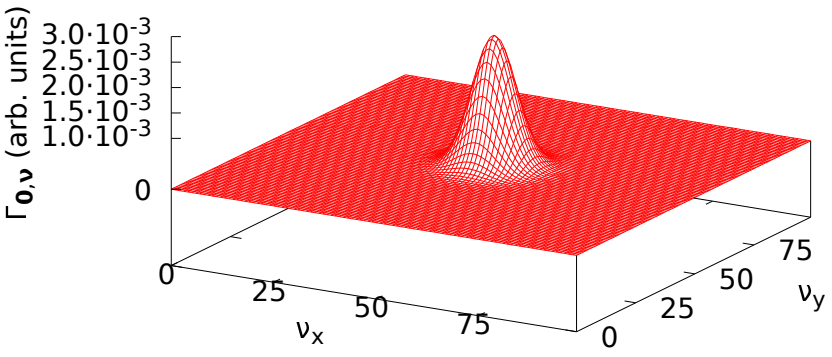
- 1s gaussians on a regular grid in the CSC
- create symmetry adapted orbitals (SAO)
- calculate the 1- and 2-electron integrals in the SAO basis
- exact diagonalization



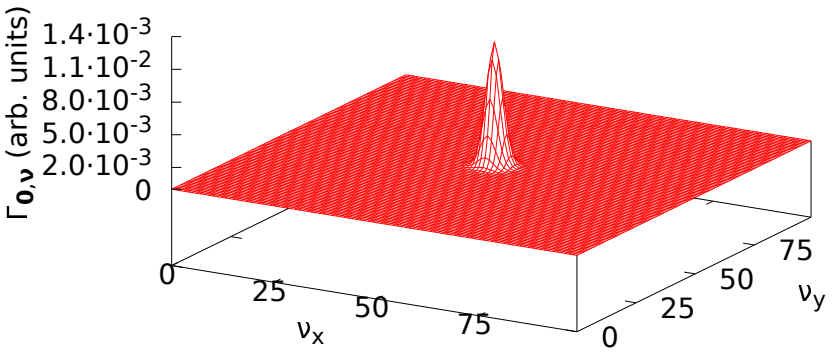
Escobar Azor *et al.*, J. Chem. Phys. 155, 124114 (2021)

Results: 2-RDM

We can characterize the Wigner localization using the 2-RDM ($\Gamma^{(2)}$) in the local gaussian basis.



$L = 10^4$ Bohr



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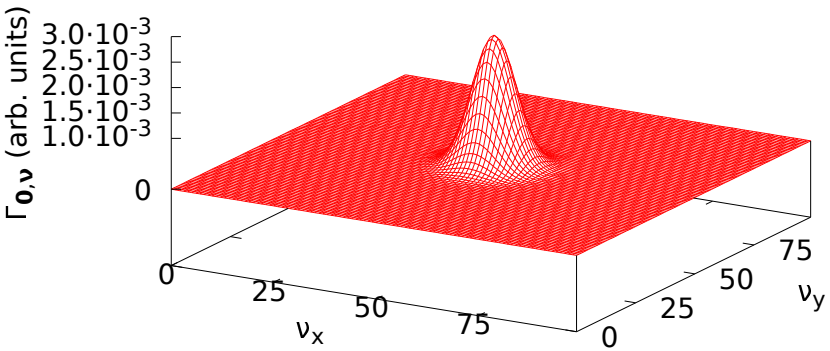

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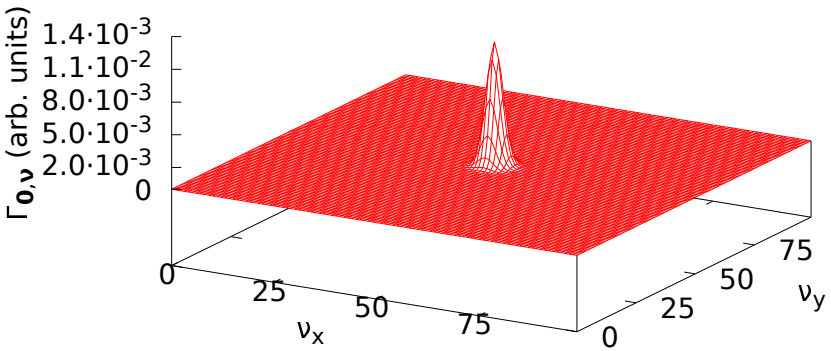

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Outlook

- more electrons
- configuration interaction, coupled cluster
- solids

A periodic position operator

Another way to characterize Wigner localisation is to look at the total position spread (TPS) of the electrons

$$\mathbf{\Lambda} = \langle\Psi|\hat{\mathbf{R}}^2|\Psi\rangle - \langle\Psi|\hat{\mathbf{R}}|\Psi\rangle^2$$

where $\hat{\mathbf{R}}$ is defined as

$$\hat{\mathbf{R}} = \sum_{i=1}^{N} \mathbf{r}_i$$

The TPS per electron $\mathbf{\Lambda}/N$ is known as the localisation tensor.

However $\mathbf{r}$ is incompatible with PBC, so we cannot calculate the TPS within our periodic Clifford formalism.

Can we define a one-body position operator that is consistent with PBC?

A periodic position operator

In 1D a one-body position $q_L(x)$ compatible with PBC should satisfy the following 4 conditions.

1. translational invariance
$$q_L(x+L) = q_L(x) \;\; \forall x.$$
2. one-to-one correspondence between x and $q_L(x)$.
$$x \neq 0 \;\; \Rightarrow \;\; q_L(x) \neq q(0).$$
3. the distance between $q(x)$ and $q(x+d)$ is independent of x.
$$|q_L(x+d) - q_L(x)| = |q_L(d) - q_L(0)|.$$
4. for $L \to \infty$ we must obtain the OBC distance.
$$\lim_{L\to\infty} |q_L(d) - q_L(0)| = d.$$

Only one possibility (modulo a phase factor and additive constant)

$$q_L(x) = \frac{L}{2\pi i}\left[\exp\left(\frac{2\pi i}{L}x\right) - 1\right]$$

The distance $|q_L(x_1) - q_L(x_2)|$ is the Euclidean distance in the embedding space of the CSC.

Valenca *et al.*, PRB 99, 205144 (2019)

Evangelisti *et al.*, arXiv:2111.12538

Photoemission from the 3-body Green's function

Gabriele Riva

Pina Romaniello

Photoemission from the 1-body Green's function

The spectral function $A(\omega)$ of $G_1(\omega)$ is linked to photoemission spectroscopy (sudden approximation)

$$A(\omega) = \frac{1}{\pi}|\mathrm{Im}\, G_1(\omega)|$$

Lehmann representation

$$G_1(\omega) = \sum_n \frac{\langle \Psi_0^N | \hat{\psi} | \Psi_n^{N+1} \rangle \langle \Psi_n^{N+1} | \hat{\psi}^\dagger | \Psi_0^N \rangle}{\omega - (E_n^{N+1} - E_0^N) + i\eta} + \sum_n \frac{\langle \Psi_0^N | \hat{\psi}^\dagger | \Psi_n^{N-1} \rangle \langle \Psi_n^{N-1} | \hat{\psi} | \Psi_0^N \rangle}{\omega - (E_0^N - E_n^{N-1}) - i\eta}$$

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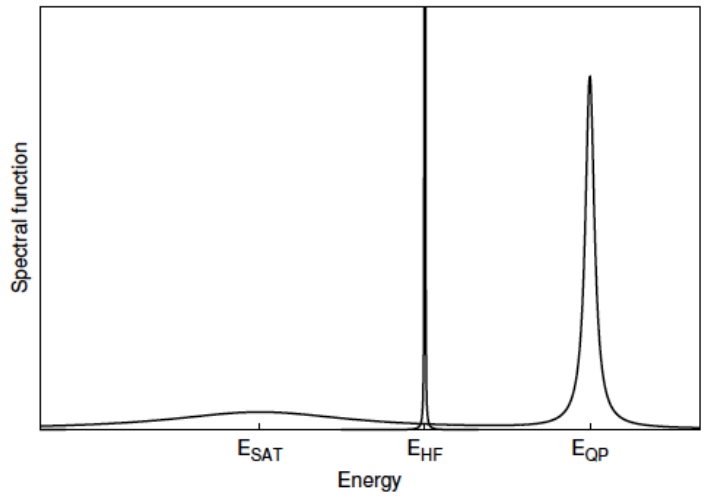
It is convenient to express G_1 in a basis

$$G_{1,ij}(\omega) = \iint dx dx' G_1(x, x', \omega)\phi_i^*(x)\phi_j(x') \qquad (\phi = \phi^{KS/HF})$$

One component $G_{1,ii}(\omega)$:



The one-body self-energy

In practice G_1 is obtained by solving a Dyson equation

$$G_1(\omega) = G_{01}(\omega) + G_{01}(\omega)\Sigma_1(\omega)G_1(\omega)$$

G_{01} is a noninteracting Green's function (G_{KS}, G_{HF} in practice)

$$G_{01}(\omega) = \sum_n \frac{\phi_n \phi_n^*}{\omega - \epsilon_n^0 + i\eta \text{sign}(\epsilon_n^0 - \mu)} \qquad \epsilon_n^0 = \epsilon_{KS/HF}$$

G_{01} only contains (approximate) QP poles $\rightarrow \Sigma_1(\omega)$ has to create all satellites.

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In the diagonal approximation

$$G_{1,ii}(\omega) = \frac{1}{\omega - \epsilon_i^0 - \Sigma_{1,ii}(\omega)}$$

one sees we need a dynamical $\Sigma_1(\omega)$ to obtain satellites.

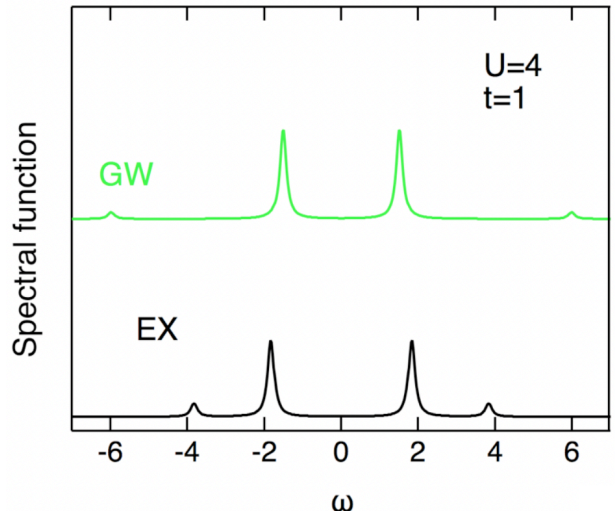
Self-energy: static or dynamical?

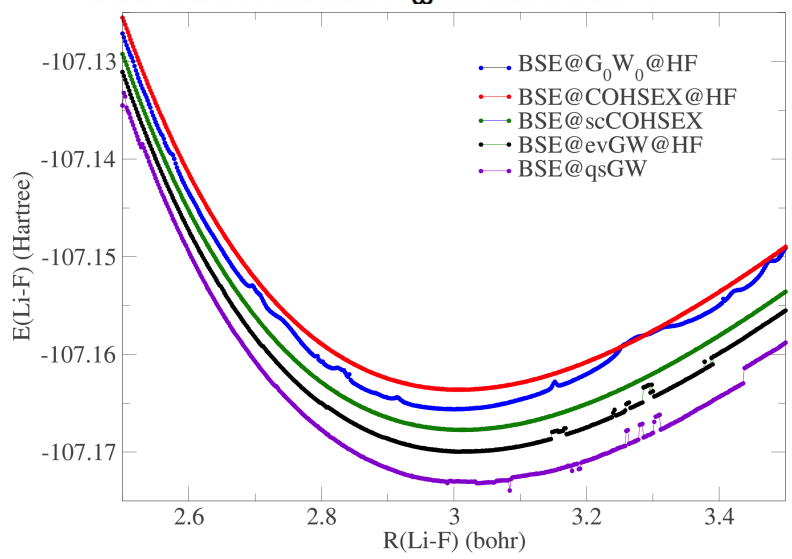
static Σ_1

- no satellites
- QP energies not always accurate
- self-consistency simple

dynamical $\Sigma_1(\omega)$

- satellites
- accurate QP energies
- self-consistency cumbersome
- satellites not always accurate
- multiple solutions



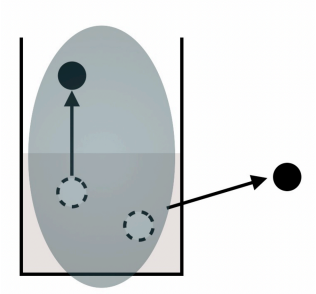


AB *et al.* JCTC 17, 191 (2021)

Can we have the best of both worlds?
(not worrying too much about computational time for now)

Photoemission from the 3-body Green's function

Photoemission can be seen as a 3 particle process (1).



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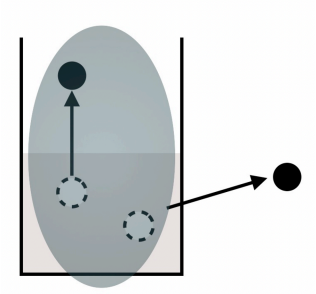

$$Q(\omega) \rightarrow \begin{pmatrix} Q & C_1 \\ C_2 & S \end{pmatrix}$$

We can build a non-interacting three-body GF (G^h_{03}) of one hole plus an electron-hole pair.

$$G^h_{03}(\omega) = \sum_{v,v'} \sum_{c} \frac{\phi_v \phi^*_v \phi_{v'} \phi^*_{v'} \phi_c \phi^*_c}{\omega - \epsilon_v + (\epsilon_c - \epsilon_{v'}) - i\eta} + \cdots$$

and similar one for G^e_{03} (one electron plus an electron-hole pair)

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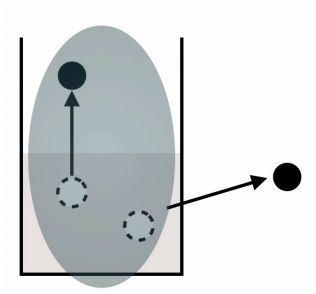

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Since $G^{e+h}_{03}(\omega)$ contains satellites we solve a Dyson equation with a static Σ_3

$$G^{e+h}_3(\omega) = G^{e+h}_{03}(\omega) + G^{e+h}_{03}(\omega)\Sigma_3 G^{e+h}_3(\omega)$$

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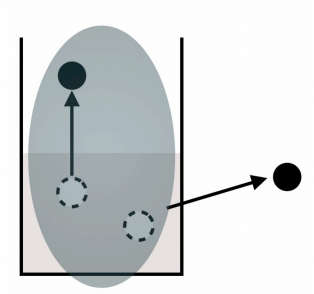

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Finally, we contract $G^{e+h}_3(\omega)$ to obtain $G_1(\omega)$ (and $A(\omega)$)

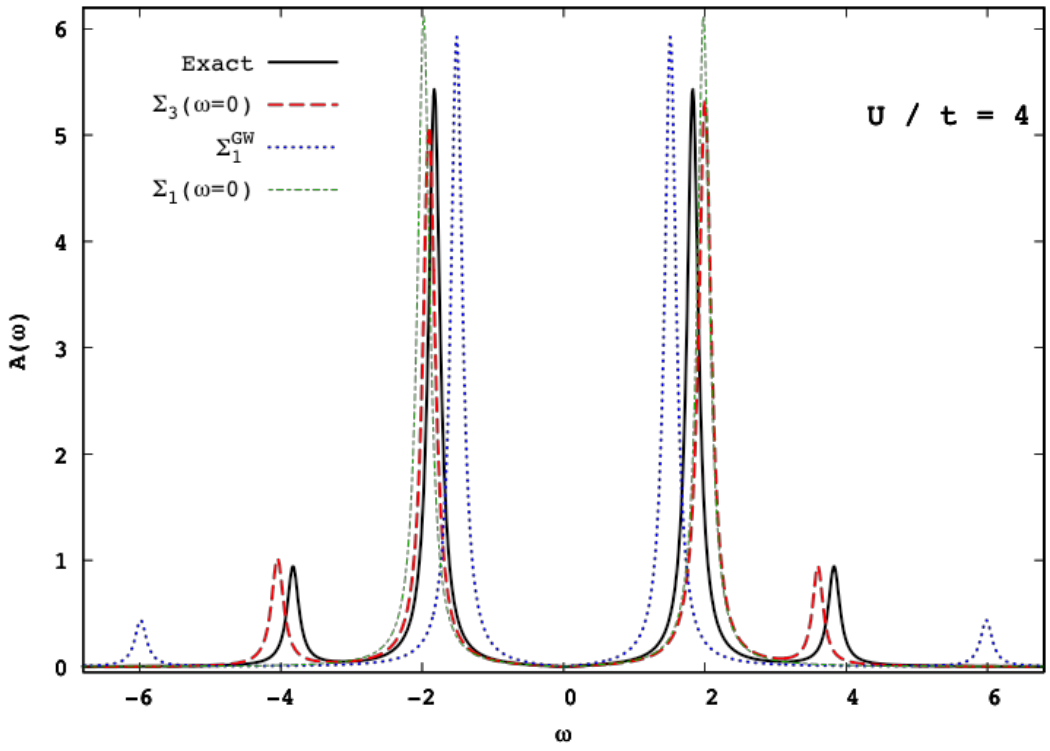
$$G^e_1(x_1, x_{1'}, \omega) = \frac{1}{N^2} \iint dx_2 dx_3 \, G^e_3(x_1, x_2, x_3, x_{1'}, x_3, x_2, \omega)$$

$$G^h_1(x_1, x_{1'}, \omega) = \frac{1}{(N-1)^2} \iint dx_2 dx_3 \, G^h_3(x_1, x_2, x_3, x_{1'}, x_3, x_2, \omega)$$

Proof-of-principle: Hubbard dimer

1/4 filling (1 electron): The exact Σ_3 is static.

1/2 filling (2 electrons)



Conclusion: a static Σ_3 can reproduce both QP and satellites.

Riva et al. arXiv:2110.05623

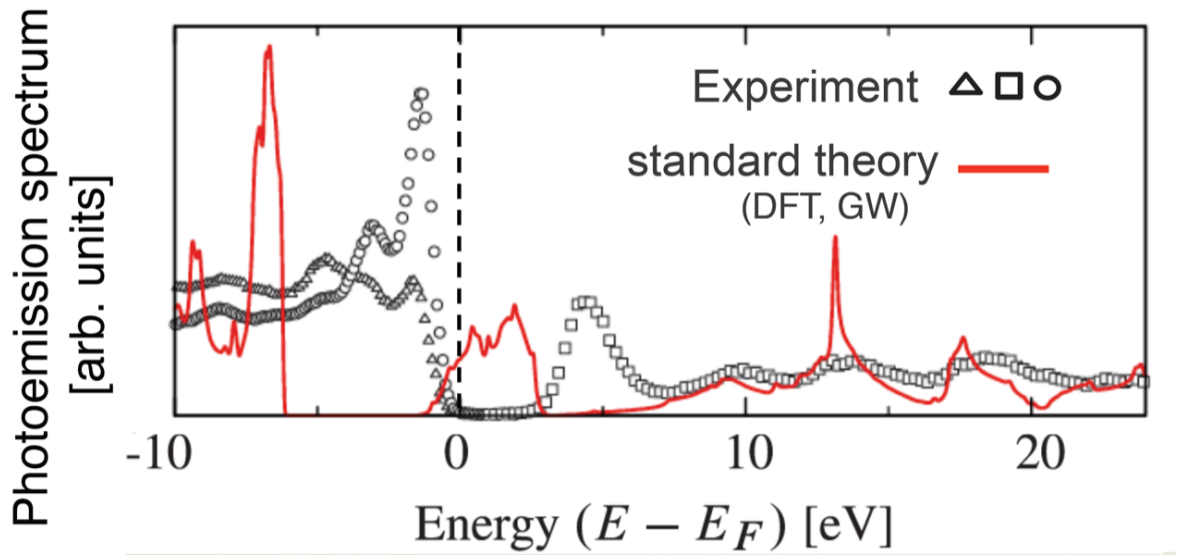
Many-body effective energy theory

Stefano Di Sabatino

Pina Romaniello

NiO

Bulk NiO in its paramagnetic phase. Metal or insulator?



Standard theories wrongly predicts NiO (PM) to be a metal.

Many-body Effective Energy Technique (MEET)

Introduce occupation numbers n_i, i.e., eigenvalues of the 1-RDM.
Fractional $n_i \rightarrow$ correlation.

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1. Spectral representation of $G^R(\omega)$ in the basis of natural orbitals.

$$G^R_{ii}(\omega) = \sum_k \frac{\overbrace{\langle \Psi_0 | c_i^\dagger | \Psi_k^{N-1} \rangle \langle \Psi_k^{N-1} | c_i | \Psi_0 \rangle}^{B^k_{ii}}}{\omega - \epsilon_k} \qquad \epsilon_k = E_k^{N-1} - E_0$$

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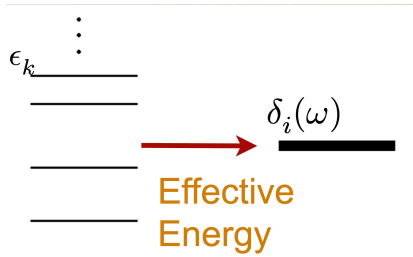
2. Introduce an effective energy $\delta_i(\omega)$

$$G^R_{ii}(\omega) = \sum_k \frac{B^k_{ii}}{\omega - \epsilon_k} = \sum_k \frac{B^k_{ii}}{\omega - \delta_i(\omega)} = \frac{n_i}{\omega - \delta_i(\omega)}$$



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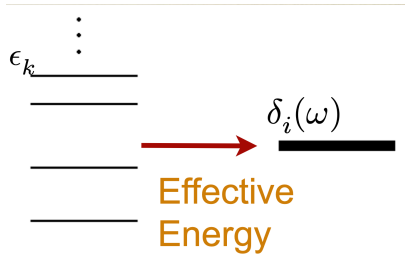


3. Do the same "trick" for $\delta_i(\omega)$

$$\delta_i(\omega) = \frac{1}{G^R_{ii}(\omega)} \sum_k \frac{B^k_{ii}\epsilon_k}{\omega - \epsilon_k} = \frac{1}{G^R_{ii}(\omega)} \sum_k \frac{\langle \Psi_0 | c_i^\dagger | \Psi_k^{N-1} \rangle \langle \Psi_k^{N-1} | [\hat{H}, c_i] | \Psi_0 \rangle}{\omega - \tilde{\delta}_i(\omega)}$$

Many-body Effective Energy Technique (MEET)

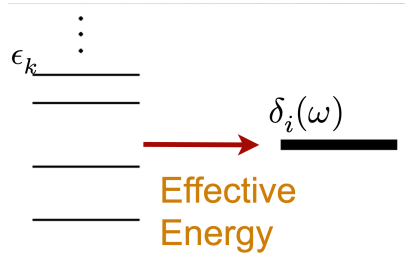
Introduce occupation numbers n_i, i.e., eigenvalues of the 1-RDM.
Fractional $n_i \rightarrow$ correlation.

1. Spectral representation of $G^R(\omega)$ in the basis of natural orbitals.

$$G^R_{ii}(\omega) = \sum_k \frac{\overbrace{\langle \Psi_0 | c_i^\dagger | \Psi_k^{N-1} \rangle \langle \Psi_k^{N-1} | c_i | \Psi_0 \rangle}^{B^k_{ii}}}{\omega - \epsilon_k} \qquad \epsilon_k = E_k^{N-1} - E_0$$

2. Introduce an effective energy $\delta_i(\omega)$

$$G^R_{ii}(\omega) = \sum_k \frac{B^k_{ii}}{\omega - \epsilon_k} = \sum_k \frac{B^k_{ii}}{\omega - \delta_i(\omega)} = \frac{n_i}{\omega - \delta_i(\omega)}$$



3. Do the same "trick" for $\delta_i(\omega)$

$$\delta_i(\omega) = \frac{1}{G^R_{ii}(\omega)} \sum_k \frac{B^k_{ii}\epsilon_k}{\omega - \epsilon_k} = \frac{1}{G^R_{ii}(\omega)} \sum_k \frac{\langle \Psi_0 | c_i^\dagger | \Psi_k^{N-1} \rangle \langle \Psi_k^{N-1} | [\hat{H}, c_i] | \Psi_0 \rangle}{\omega - \tilde{\delta}_i(\omega)}$$

4. Truncate the series

RDMFT

Working out the commutators yields reduced density matrices.
For example, $\langle \Psi_k^{N-1} | [\hat{H}, c_i] | \Psi_0 \rangle$ yields $\Gamma^{(2)}$

RDMFT

Working out the commutators yields reduced density matrices.
For example, $\langle \Psi_k^{N-1} | [\hat{H}, c_i] | \Psi_0 \rangle$ yields $\Gamma^{(2)}$

Use RDMFT to calculate n_i and approximate $\Gamma^{(2)}$.

The unknown part of the energy is E_{xc}

$$E_{xc} = \iint dx dx' v_c(x, x') \Gamma_{xc}^{(2)}[\gamma](x, x'; x, x')$$

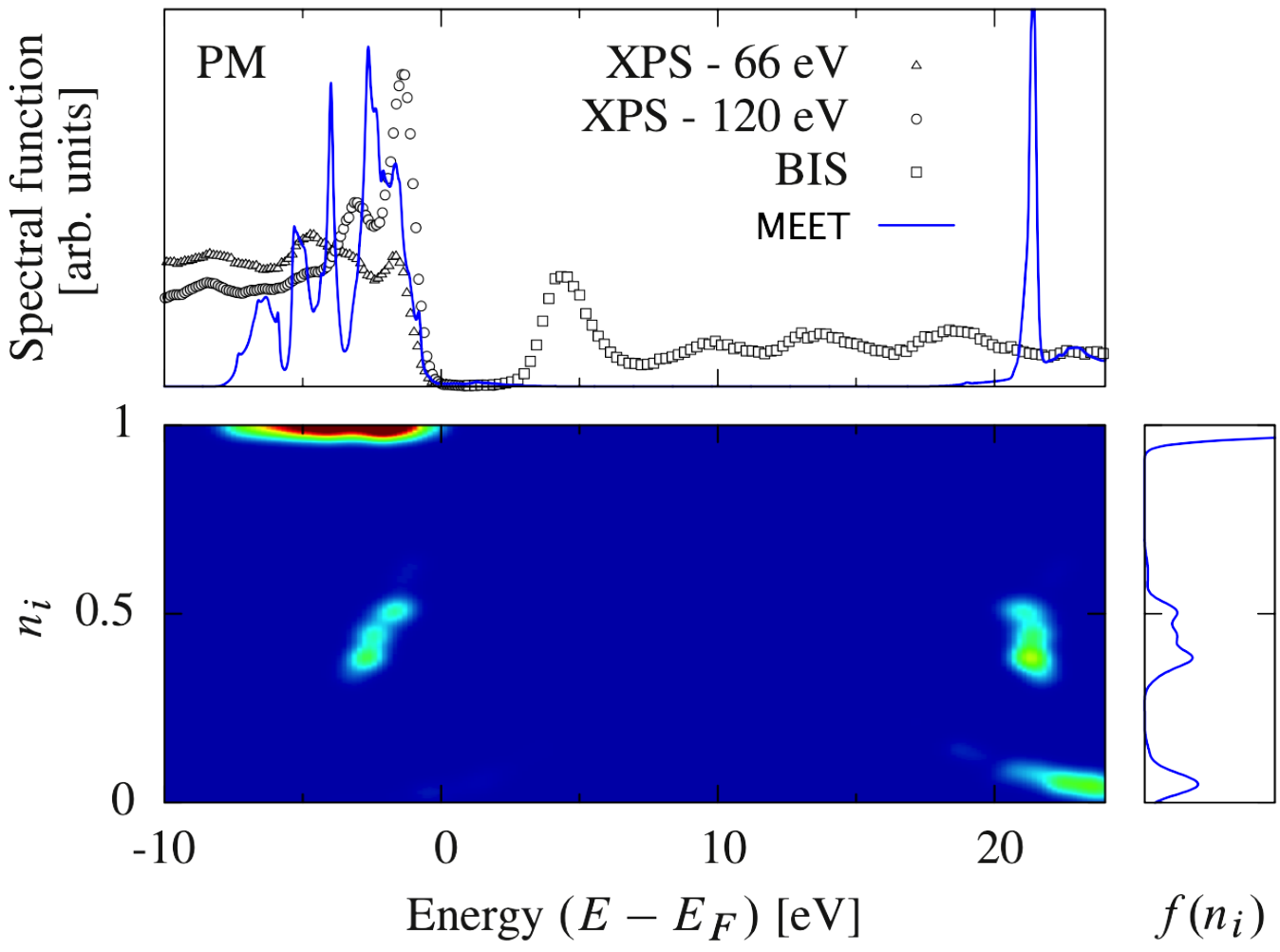
We need approximations for $\Gamma_{xc}^{(2)}$

$$E_{xc} = \iint dx dx' v_c(x, x') \gamma^{\alpha}(x, x') \gamma^{\alpha}(x', x)$$

Power functional (PF): $\alpha = 0.65$

S. Sharma et al. PRB 78 (2008); A. M. K. Müller, Phys Lett A 105 (1984)

MEET: Silicon



We have a gap !
... but it is much too big

S. Di Sabatino *et al.*, PRB 94, 155141 (2016)

S. Di Sabatino *et al.*, JCTC 15, 5080 (2019)

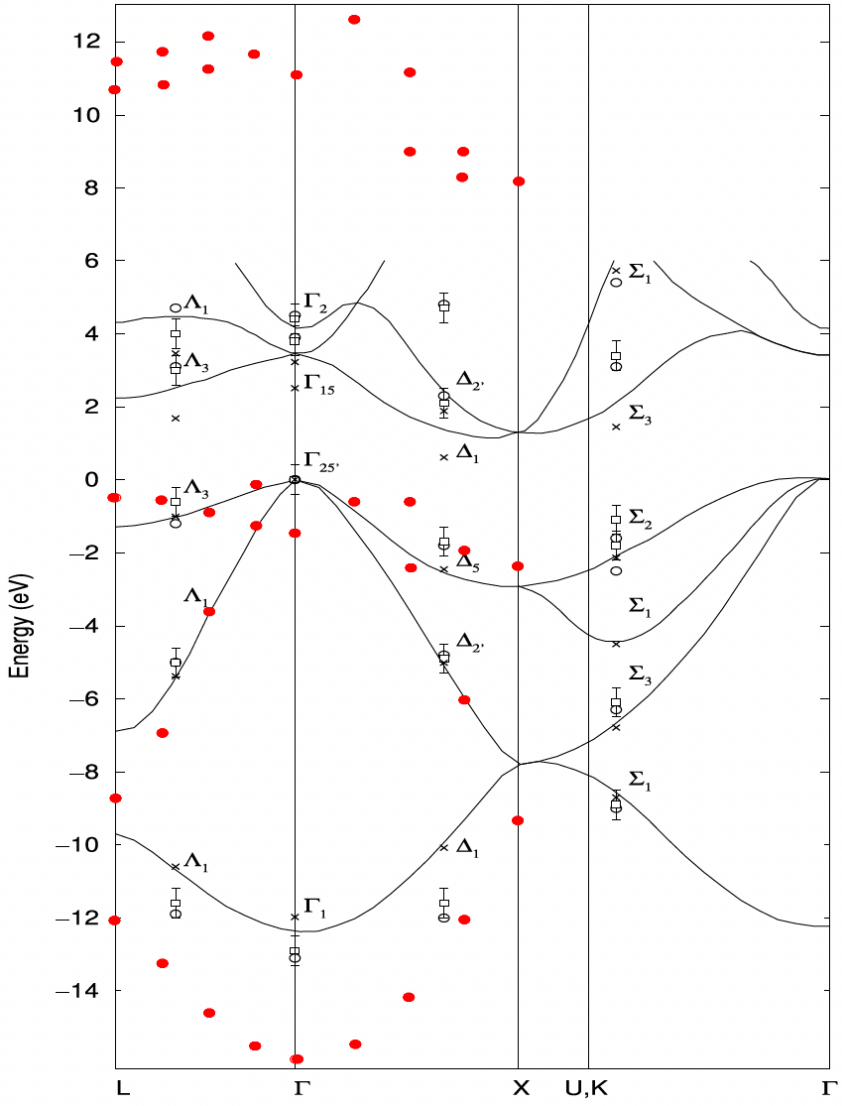
MEET: NiO

Two possible source of error

- truncation of the MEET series
- RDMFT functional (PF)

We compare MEET@PF(red dots) with MEET@QMC (open symbols) for the band structure of silicon.

Influence of the functional on the error is significant.



Kent *et al.* PRB 57, 15293

Extended Koopmans' theorem

MEET at lowest order is equivalent to the extended Koopmans' theorem (EKT) in the diagonal approximation

Everything about the EKT for photoemission spectroscopy can be found in Stefano Di Sabatino's recent ETSF seminar :

https://www.youtube.com/watch?v=m5an9J1QzlY

S. Di Sabatino *et al.*, Frontiers in Chem. 9, 746735 (2021)

Thanks!

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MEET/EKT

Stefano Di Sabatino
Jaakko Koskelo
Lucia Reining
Pina Romaniello

Conclusions

- Clifford periodic boundary conditions are efficient to describe periodic Coulomb systems.
- Using the 3-GF we can describe satellites with a static self-energy.
- MEET/EKT promising for (strongly) correlated materials but better occupation numbers are needed