Matteo Gatti

African connections

Laboratoire des Solides Irradiés – CNRS – Ecole Polytechnique (France)
European Theoretical Spectroscopy Facility (ETSF)
Synchrotron SOLEIL

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ASESMA 2023 – EAIFR Kigali (Rwanda)

Outline

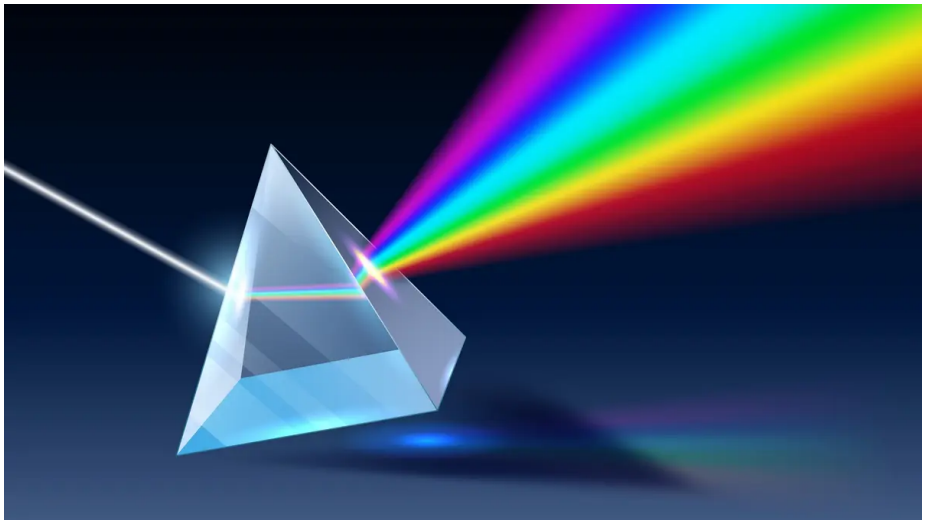
- Projects summary: Electronic excitations in materials
  - Plasmons in Dirac materials
  - Excitons in compressed helium

- Challenge: Advanced questions on DFT
  - What is the exact Kohn-Sham gap in silicon?
  - Can we make the LDA in principle “exact”?

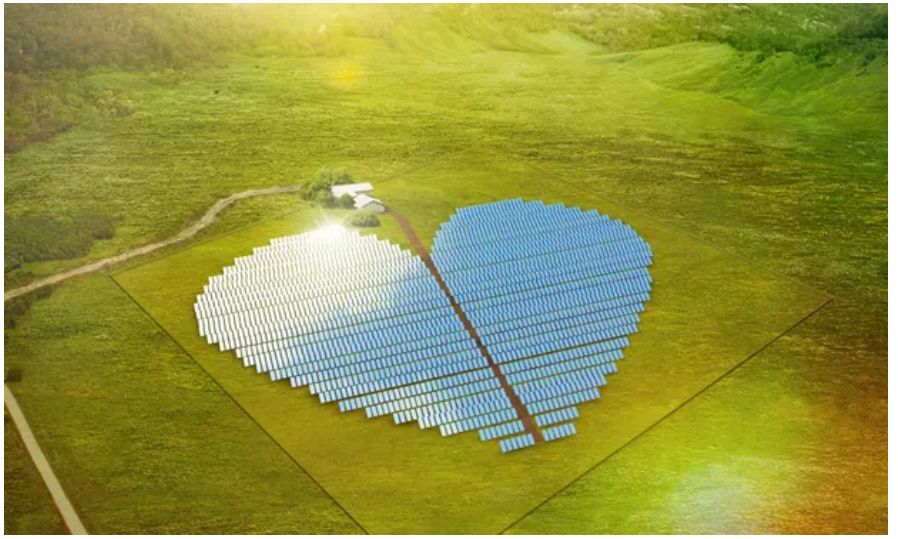
Part 1: Electronic excitations in materials

Theoretical spectroscopy

- Many materials properties and functionalities are due to electronic excitations (e.g. color, solar cells, …)



Pink Floyd – The Dark side of the Moon



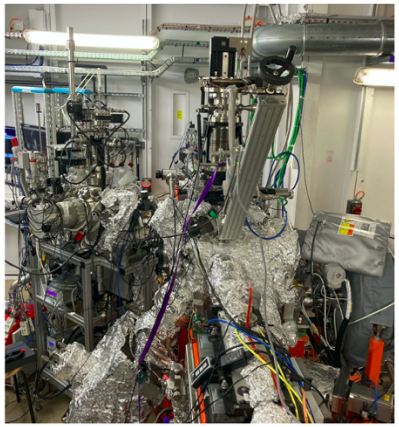
Solar farm in New Caledonia

Theoretical spectroscopy

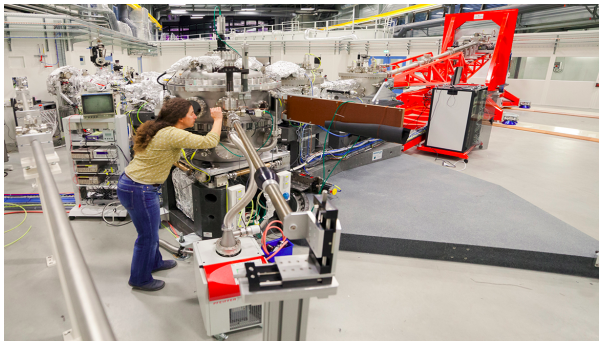
- Many materials properties and functionalities are due to electronic excitations (e.g. color, solar cells, …)
- Spectroscopy experiments measure excitation spectra (e.g. absorption, inelastic scattering of electrons/photons)

ALBA synchrotron

Hall of SOLEIL



GALAXIES@SOLEIL



ID32@ESRF

Theoretical spectroscopy

- Many materials properties and functionalities are due to electronic excitations (e.g. color, solar cells, …)
- Spectroscopy experiments measure excitation spectra (e.g. absorption, inelastic scattering of electrons/photons)
- Theoretical spectroscopy: calculate, interpret and predict

Your next equation?

Mare Nostrum @ BSC

Theoretical spectroscopy

- Many materials properties and functionalities are due to electronic excitations (e.g. color, solar cells, …)
- Spectroscopy experiments measure excitation spectra (e.g. absorption, inelastic scattering of electrons/photons)
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- Identification of elementary excitations is challenging. Collective excitations result from the Coulomb interaction.

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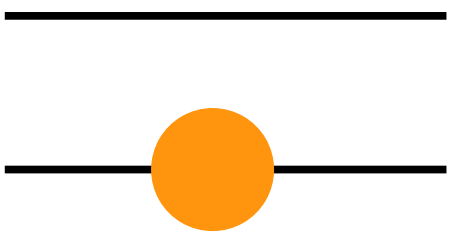
- Identification of elementary excitations is challenging. Collective excitations result from the Coulomb interaction.
- Here excitations of the electronic charge. Plasmons & excitons.

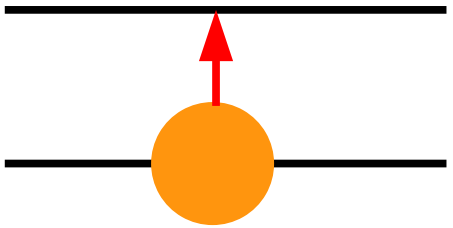
Plasmons: collective charge excitations

A two-level atom…



Plasmons: collective charge excitations

A two-level atom…
...gets excited



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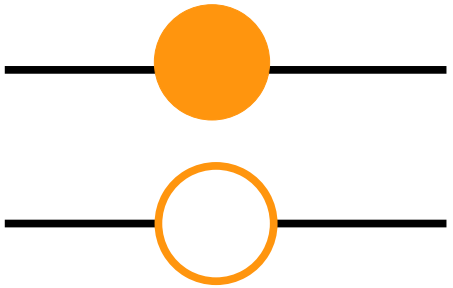
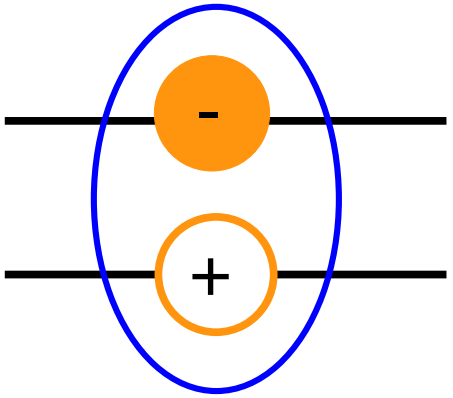


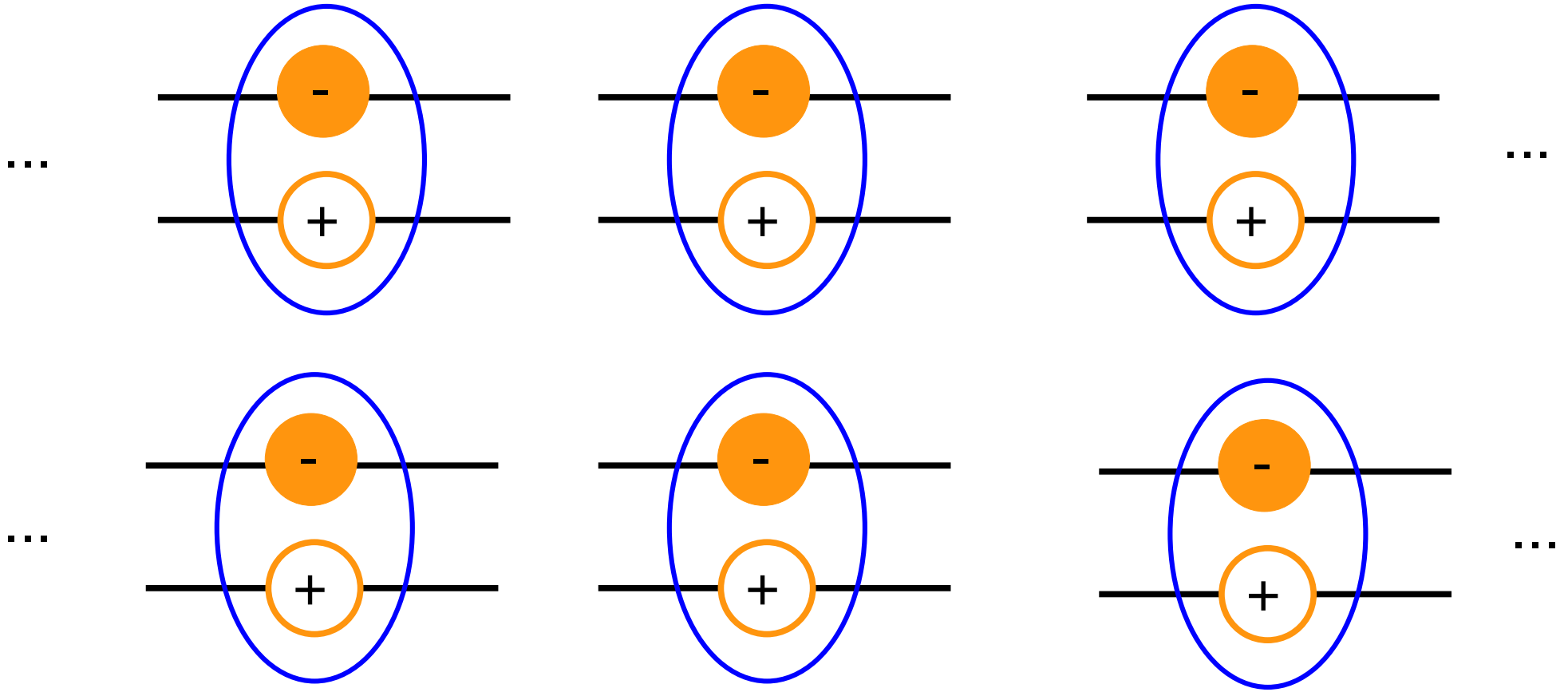
Plasmons: collective charge excitations

Excitation ~ “dipole”



Plasmons: collective charge excitations

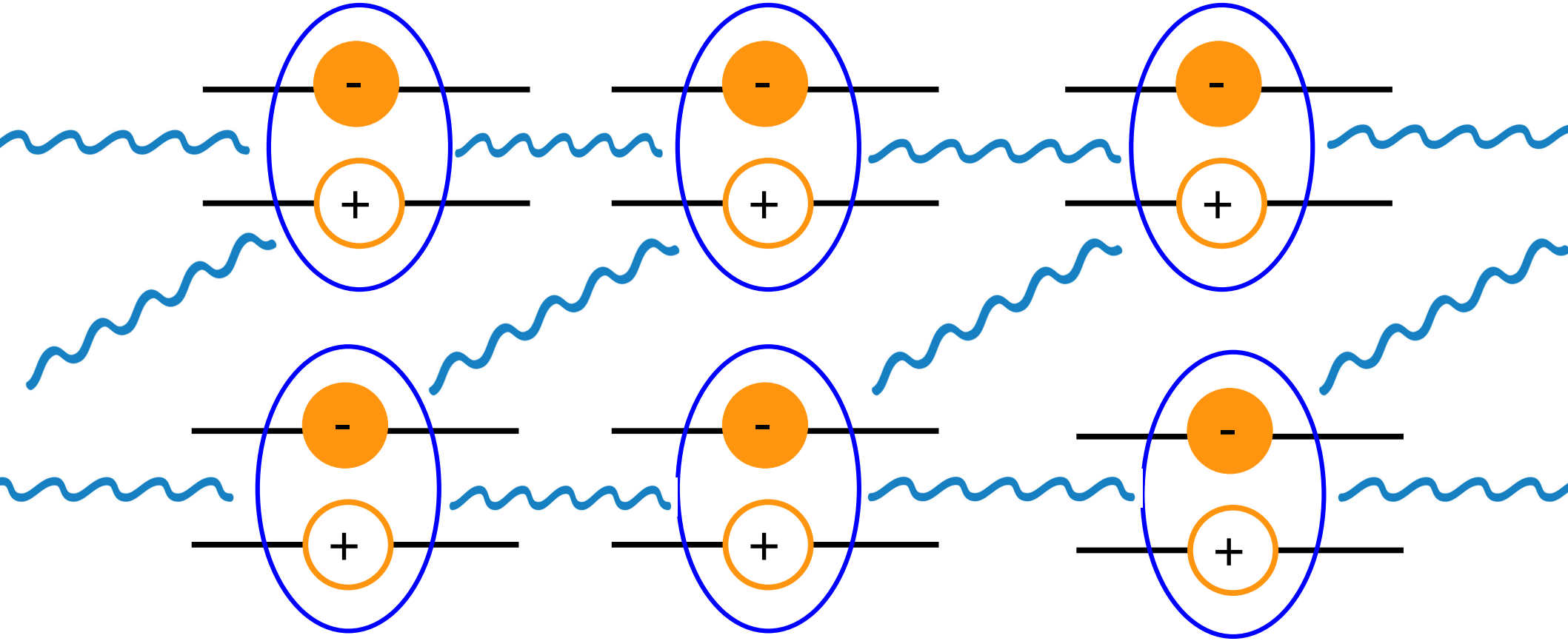
Extended system : many atoms, many dipoles



Plasmons: collective charge excitations

Extended system : many atoms, many dipoles

Coulomb interaction gives rise
to collective oscillations = plasmons



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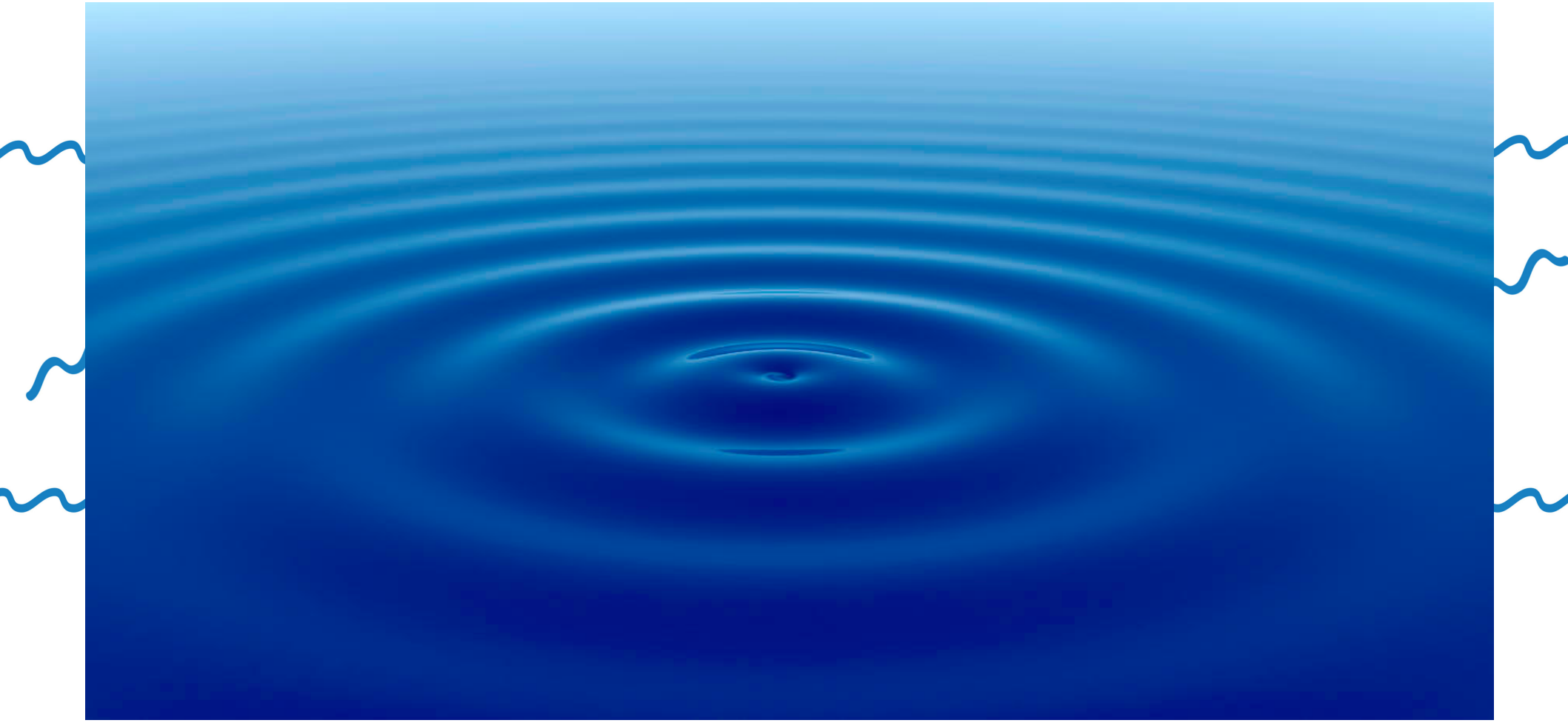


Plasmons: collective charge excitations

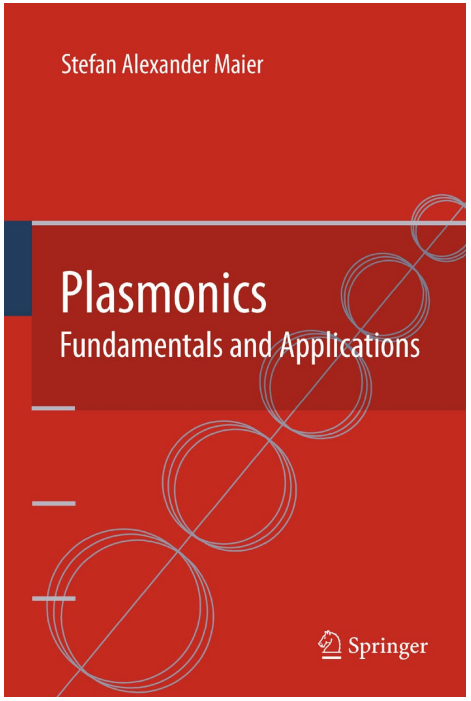
- Measurable! By means of electron energy loss spectroscopy (EELS) or Inelastic X-ray scattering (IXS)
- Peaks in loss function spectra

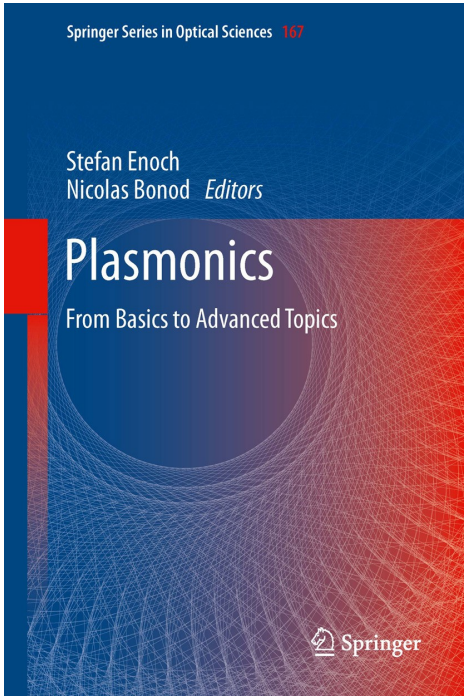
$$-\mathrm{Im}\epsilon^{-1}(q,\omega)$$

- They can be calculated within linear response:
  - Time-dependent density-functional theory (TDDFT)
  - Green's function theory (MBPT)

Plasmons: collective charge excitations

- Useful!
  Plasmonics = nanostructured optoelectronic devices

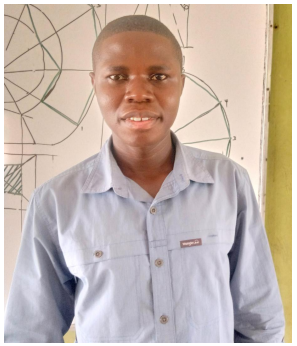




Plasmons in Dirac materials

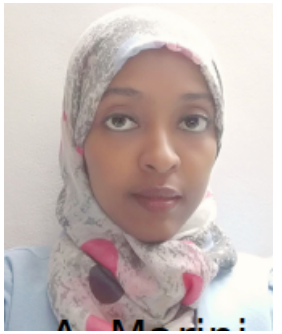
R. Agbaoye
(Nigeria)

M. Ali Ahmed
(Sudan)

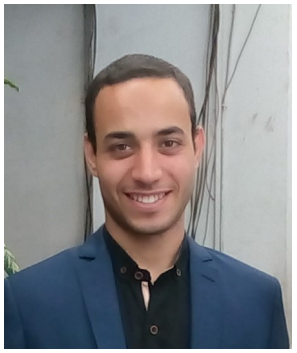


T. Ashani
(Nigeria)

B. Dandogbessi
(Benin)



W. Elsayed
(Rwanda)



M. Kinawy
(Egypt)

F. Mohamed
(Sudan)

M. Woldemariam
(Ethiopia)

A. Marini
(Italy)

M. Gatti
(France)

Plasmons in Dirac materials

- We have studied!
  Fundamental concepts of DFT, linear response, TDDFT,
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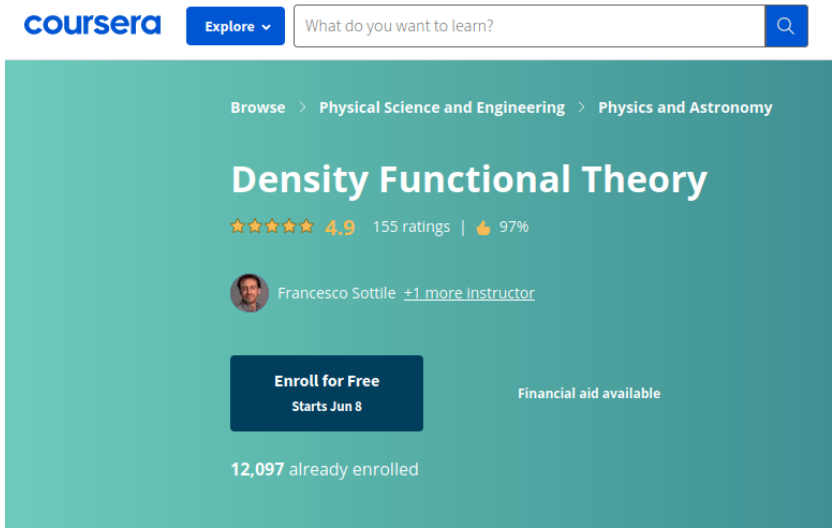

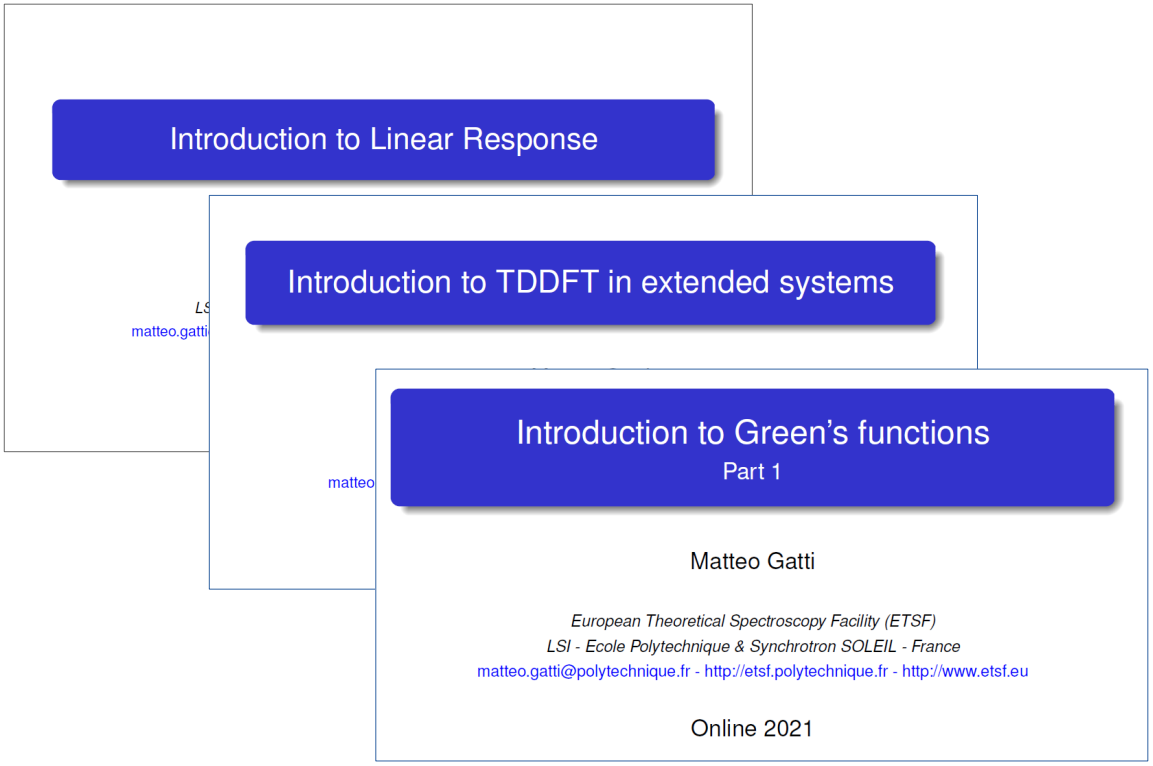

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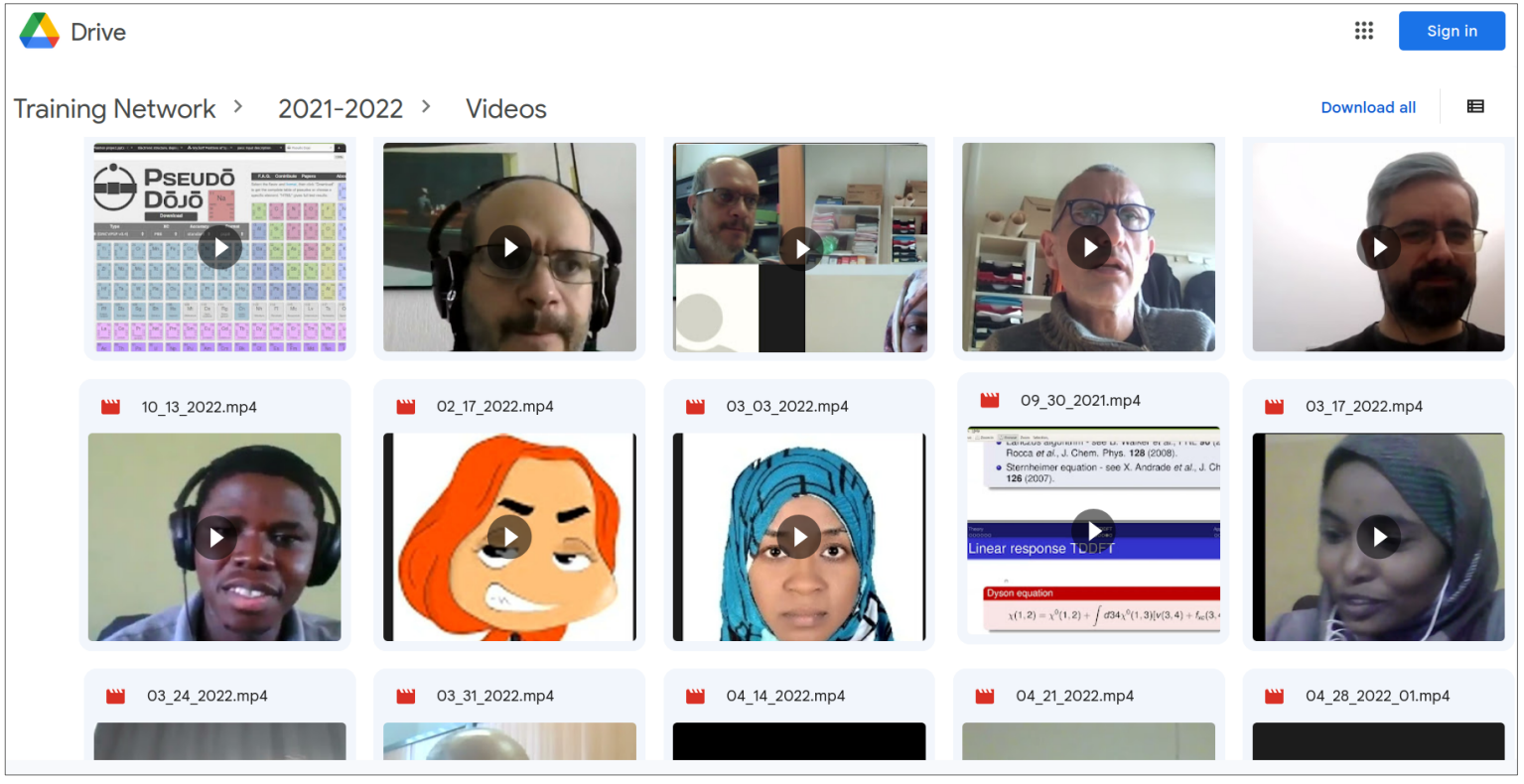

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- Joint article in preparation...

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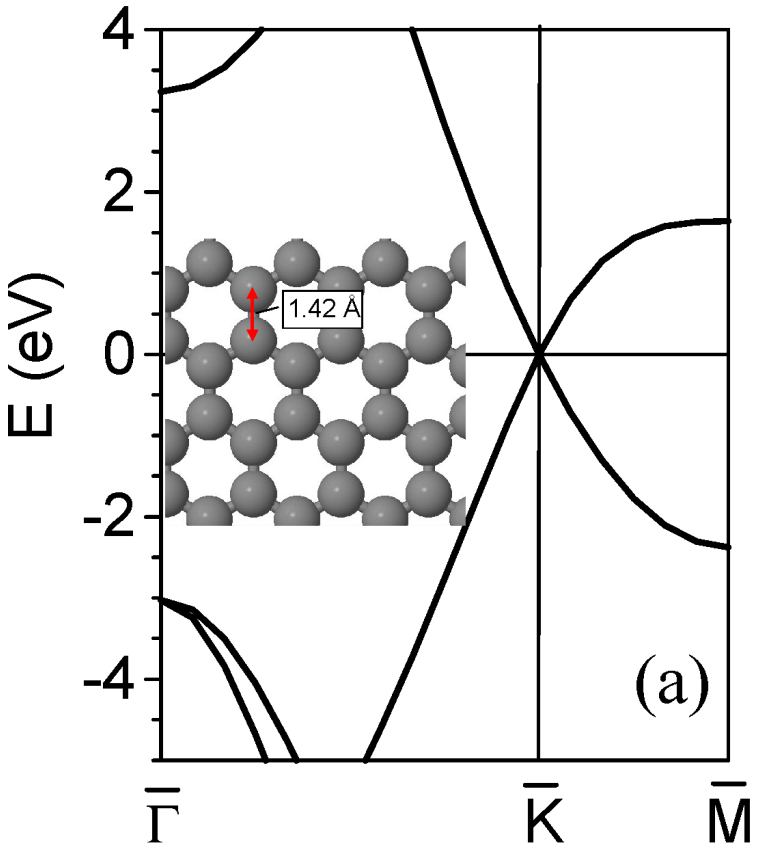
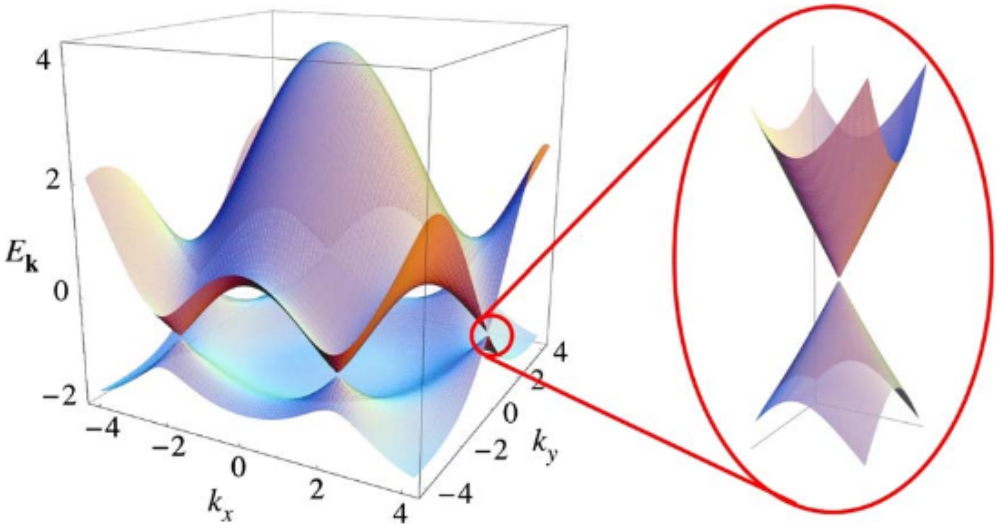
A lot of work.
And... a lot of fun!

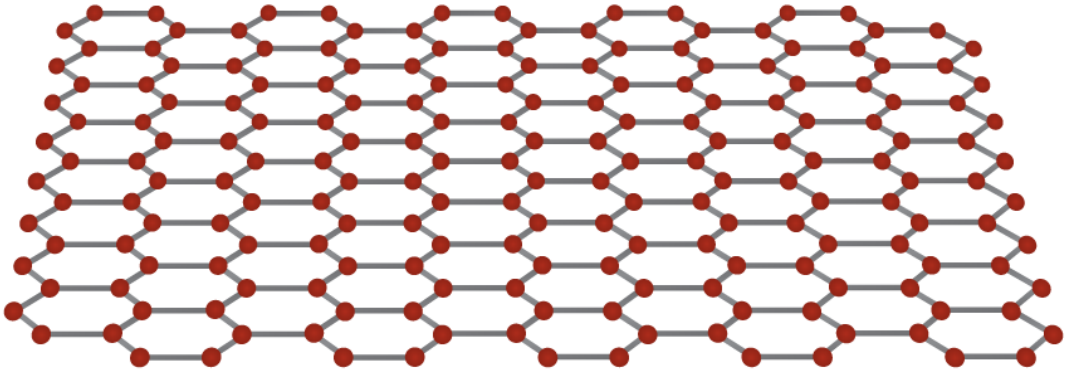
2D Dirac materials: graphene

Ideal graphene



Dirac cone



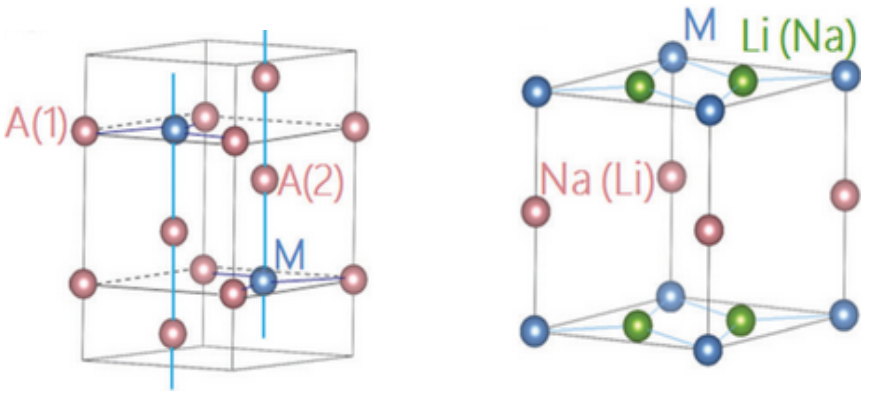


Graphene sheet

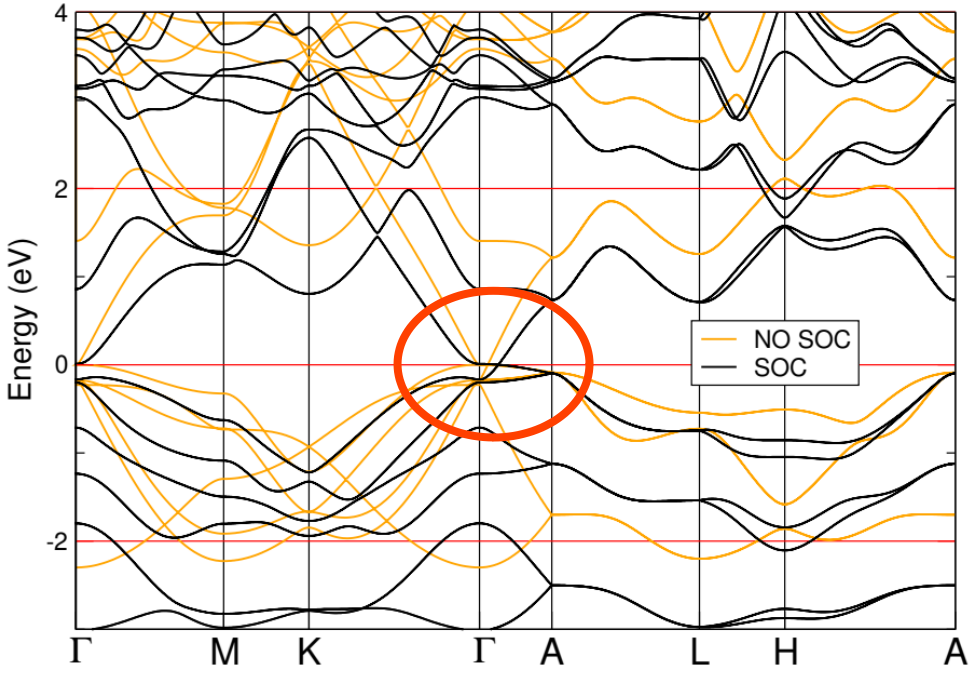
3D Dirac materials: alkali pnictides

Dirac topology near the Fermi level also in 3D materials

$Li_{3-x}Na_xM$ (M=N,Bi)



Layered structure



Band structure of Na_3Bi

Z. Wang, et al., Phys. Rev. 85, 195320 (2012); Z. K. Liu, et al., Science 343, 864 (2014);
L. Jin, et al., Phys. Chem. Chem. Phys. 22, 5847 (2020)

3D Dirac materials: alkali pnictides

Drive

Sign in

Training Network › 2021-2022 › Plasmon_project

Download all

Bruno

Bruno

Na3N

CINECA HOW TO

CINECA

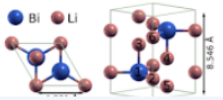
How to use Marconi-100

See:https://www.hpc.cineca.it/hardware/marconi100

Fatema

Fatema

Lithium Bismuth alloy (Li3Bi)



Maram

MARAM

Li2NaN

Matteo

Matteo

Na3Bi

Menberu

Menberu Mengesh

LiNa2N

Mohamed

Mohamed

Lithium Nitride (Li3N)

Ridwan

baoye Ridwan Olar

Li2NaBi

Timothy

Timothy

LiNa2Bi

Wala

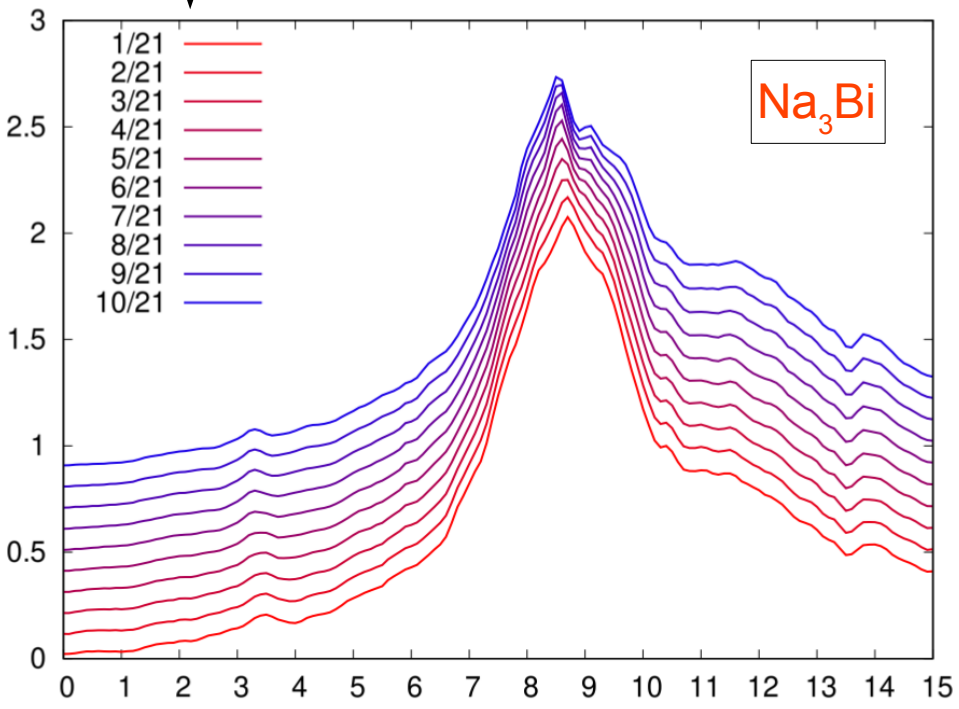
Wala

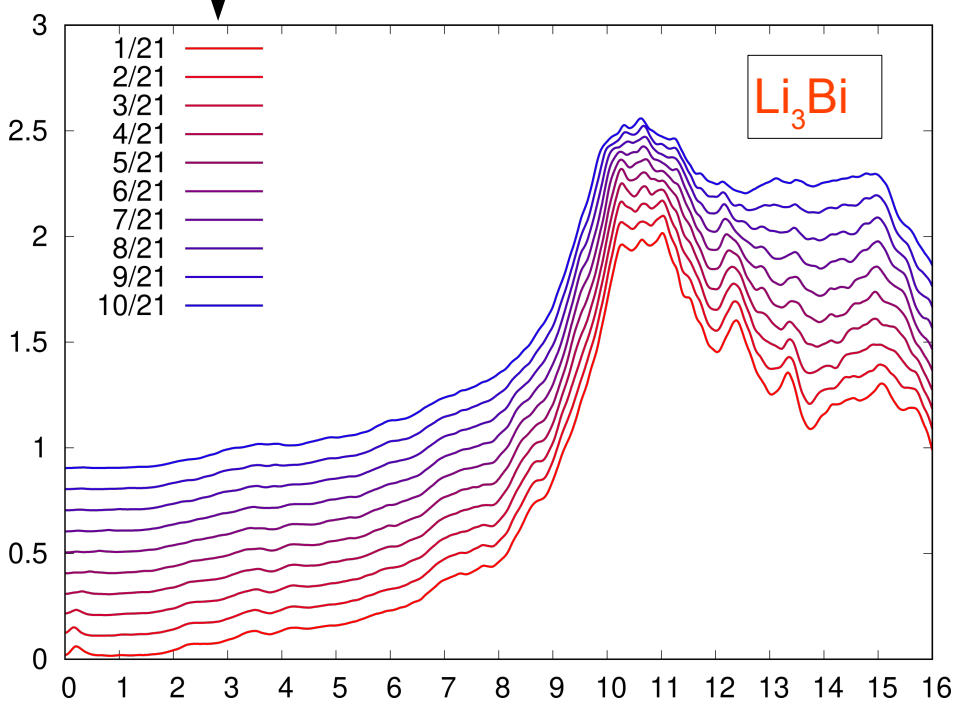
Sodium antimonide Na_3Sb

Plasmons in 3D Dirac materials

wavevector q along z (rlu)

$$-\mathrm{Im}\epsilon^{-1}(q,\omega)$$

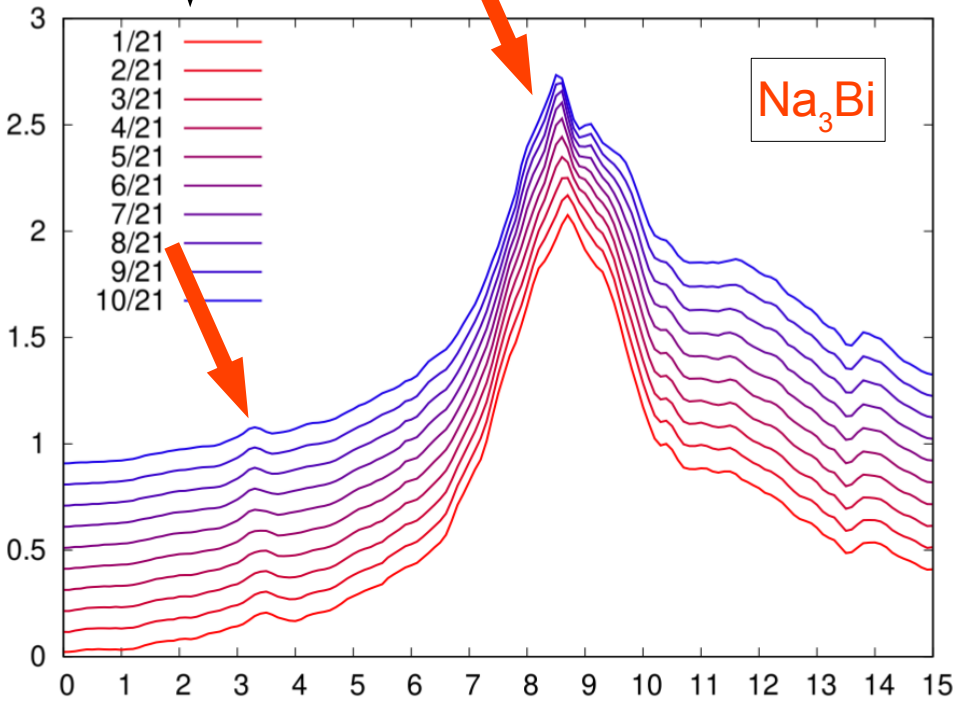


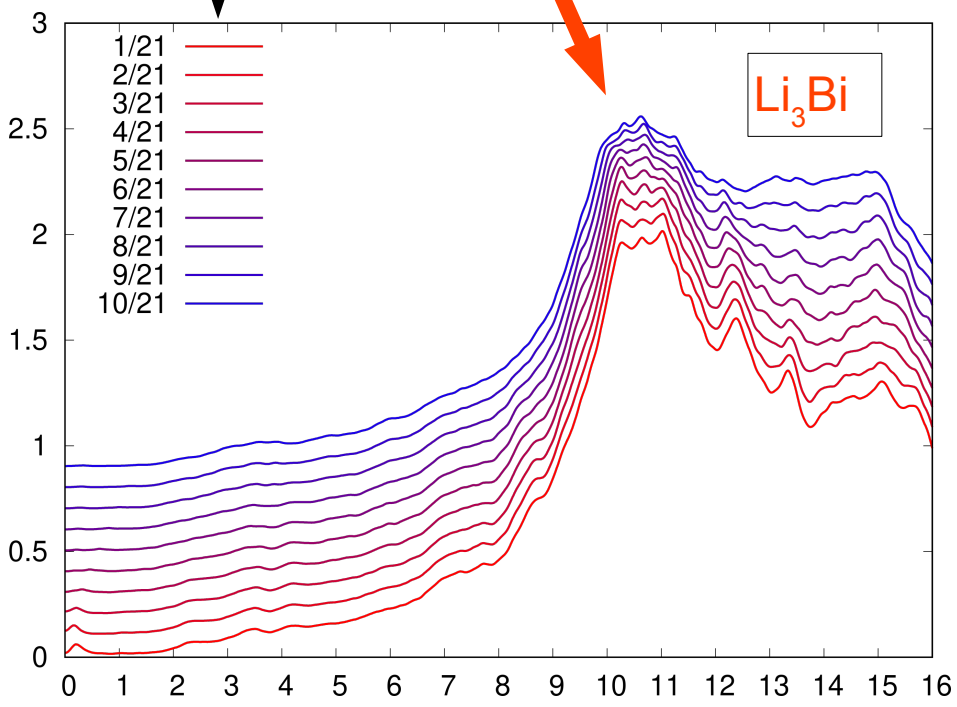


Plasmons in 3D Dirac materials

wavevector q along z (rlu)

$$-\mathrm{Im}\epsilon^{-1}(q,\omega)$$





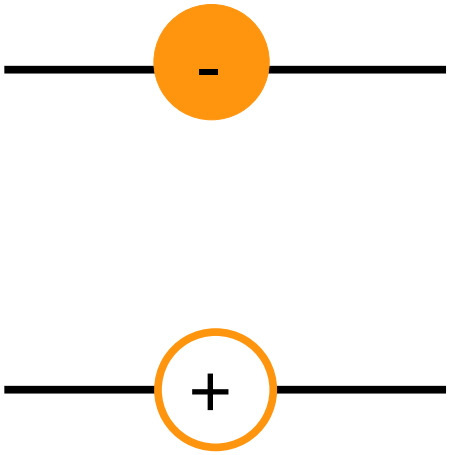
- Plasmons are not dispersing (unusual behavior).
- Important to take into account whole band structure (not only Dirac cone)

- Fatema: excitons in compressed helium
  “Eurotech” Marie-Curie postdoc (since January 2023)

- Maram: plasmons in cubic antimony
  “Faculty of the Future” fellowship - Schlumberger foundation (since September 2023)

Excitons: interacting electron-hole pairs

Electron-hole pair



Excitons: interacting electron-hole pairs

Interacting
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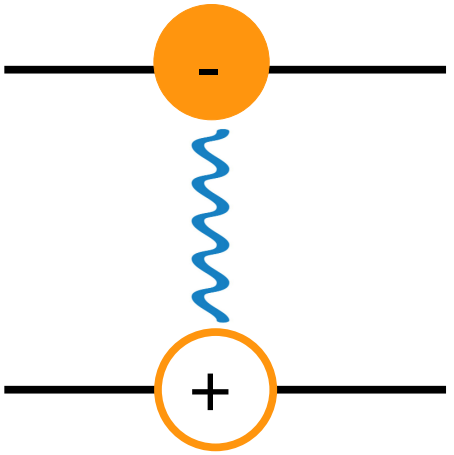
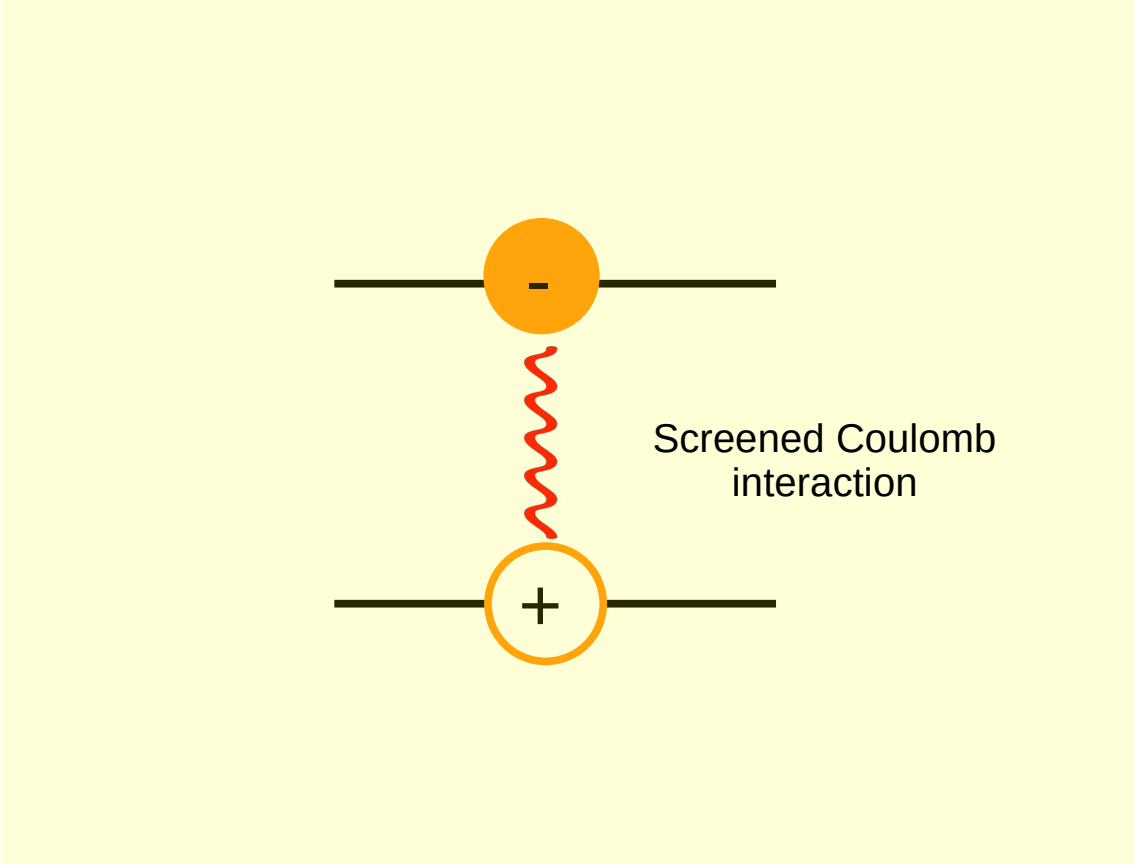
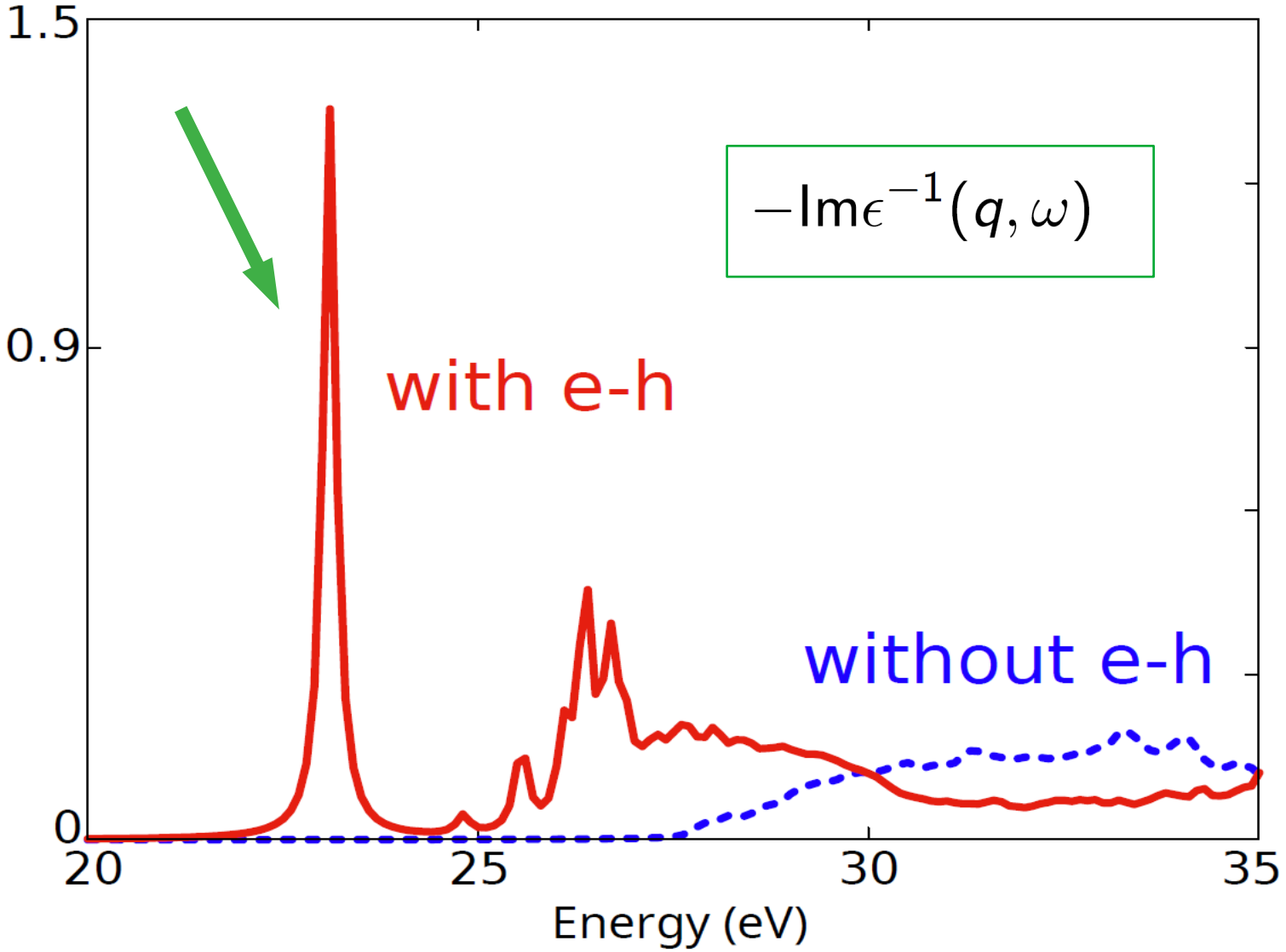


Excitons: interacting electron-hole pairs

Interacting
Electron-hole pair
Embedded in a dielectric medium



Excitons in compressed helium

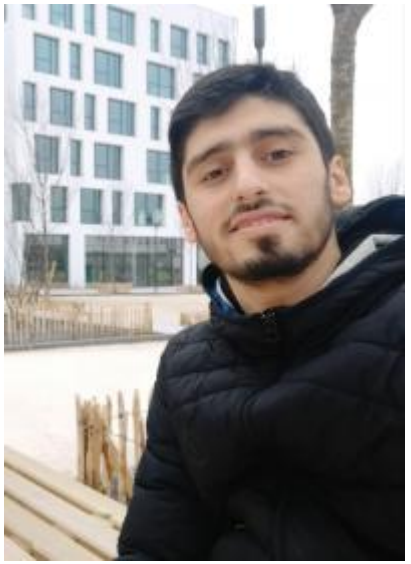


Part 2: Research questions on DFT

(…with 1 cpu only!)

Together with:

Ayoub Aouina



Lucia Reining

(Algeria → France → Germany)

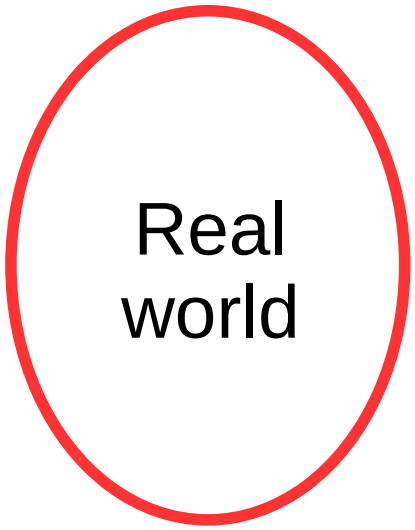
And Palaiseau Theoretical Spectroscopy group & friends

DFT : A “multiverse” theory

$$H\Psi = E\Psi$$

$$\Psi = \Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$$

All observables



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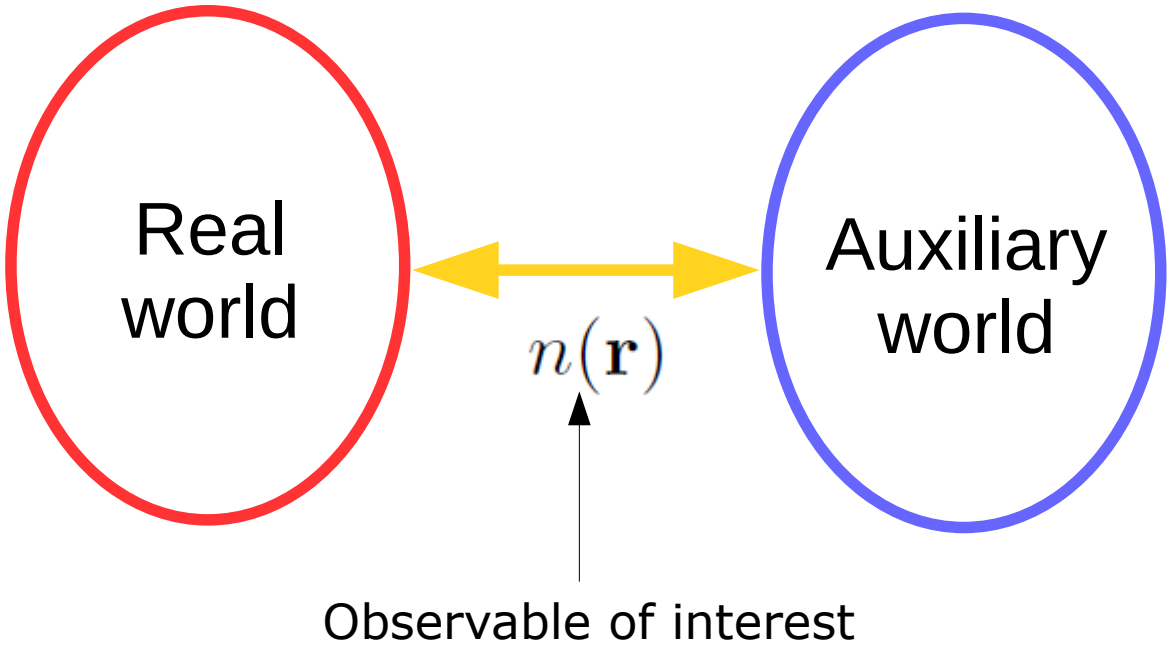
Kohn-Sham

$V_{xc}(\mathbf{r})$?



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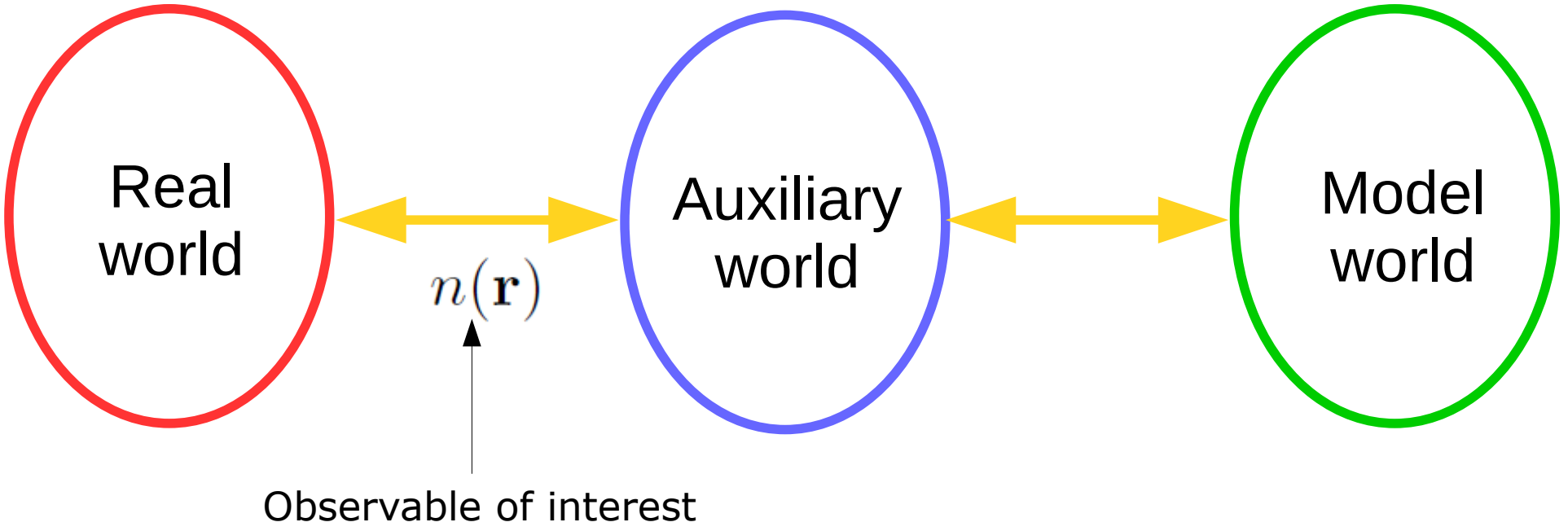
Homogeneous electron gas

$n^h \;\; V_{xc}^h$



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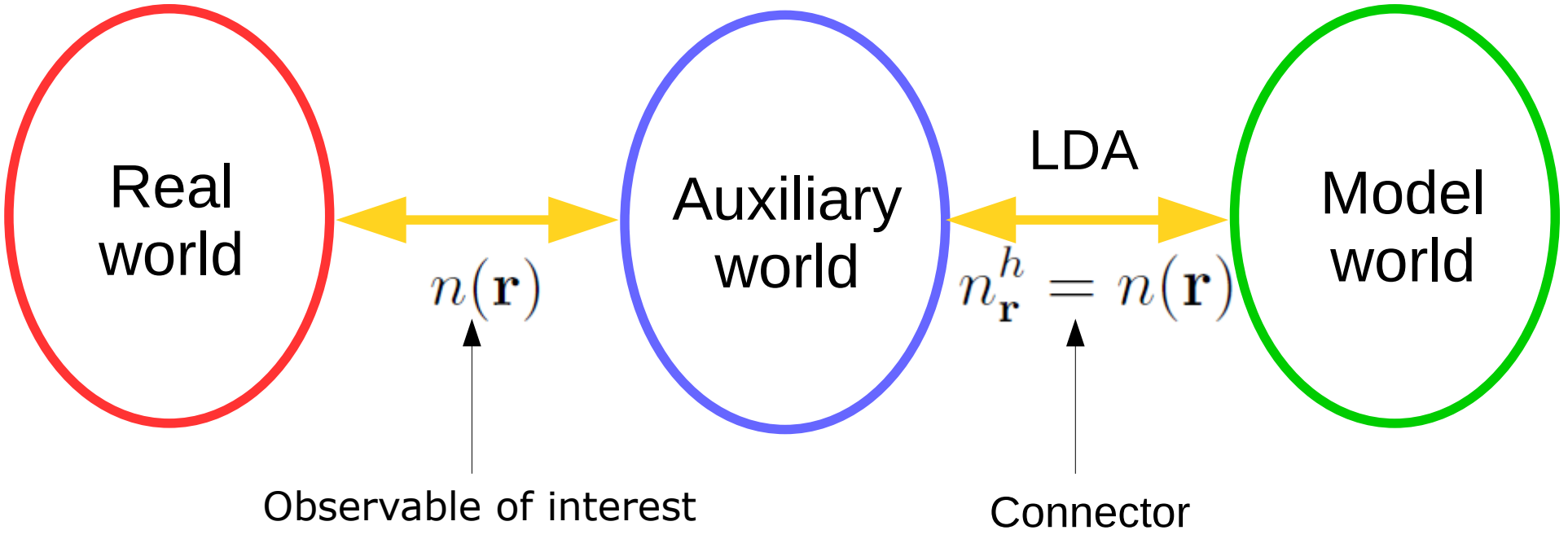

$$E_{\rm xc}[n] = \int d\mathbf{r}\, n(\mathbf{r}) \epsilon_{xc}^h(n^h_{\mathbf{r}} = n(\mathbf{r}))$$

$$V_{\rm xc}(\mathbf{r}) = V_{\rm xc}^h(n^h_{\mathbf{r}} = n(\mathbf{r}))$$

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- Big advantage 2: Difficult calculation has been done once for all in the model and the results have been shared.

D. M. Ceperley and B. J. Alder Phys. Rev. Lett. 45, 566 (1980)

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- Big advantage 2: Difficult calculation has been done once for all in the model and the results have been shared.
- Note: our first target is n(r).
  Other question is E=E[n].

Error in the density vs. Error in the energy functional:

PRL **111,** 073003 (2013) PHYSICAL REVIEW LETTERS week ending 16 AUGUST 2013

Understanding and Reducing Errors in Density Functional Calculations

Min-Cheol Kim and Eunji Sim*

Department of Chemistry and Institute of Nano-Bio Molecular Assemblies, Yonsei University, 50 Yonsei-ro Seodaemun-gu, Seoul 120-749, Korea

Kieron Burke

Department of Chemistry, University of California, Irvine, California 92697, USA

(Received 12 December 2012; published 15 August 2013)

We decompose the energy error of any variational density functional theory calculation into a contribution due to the approximate functional and that due to the approximate density. Typically, the functional error dominates, but in many interesting situations the density-driven error dominates. Examples range from calculations of electron affinities to preferred geometries of ions and radicals in solution. In these abnormal cases, the error in density functional theory can be greatly reduced by using a more accurate density. A small orbital gap often indicates a substantial density-driven error.

Approximations are biased towards “good” energies sacrificing “good” densities

Density functional theory is straying from the path toward the exact functional

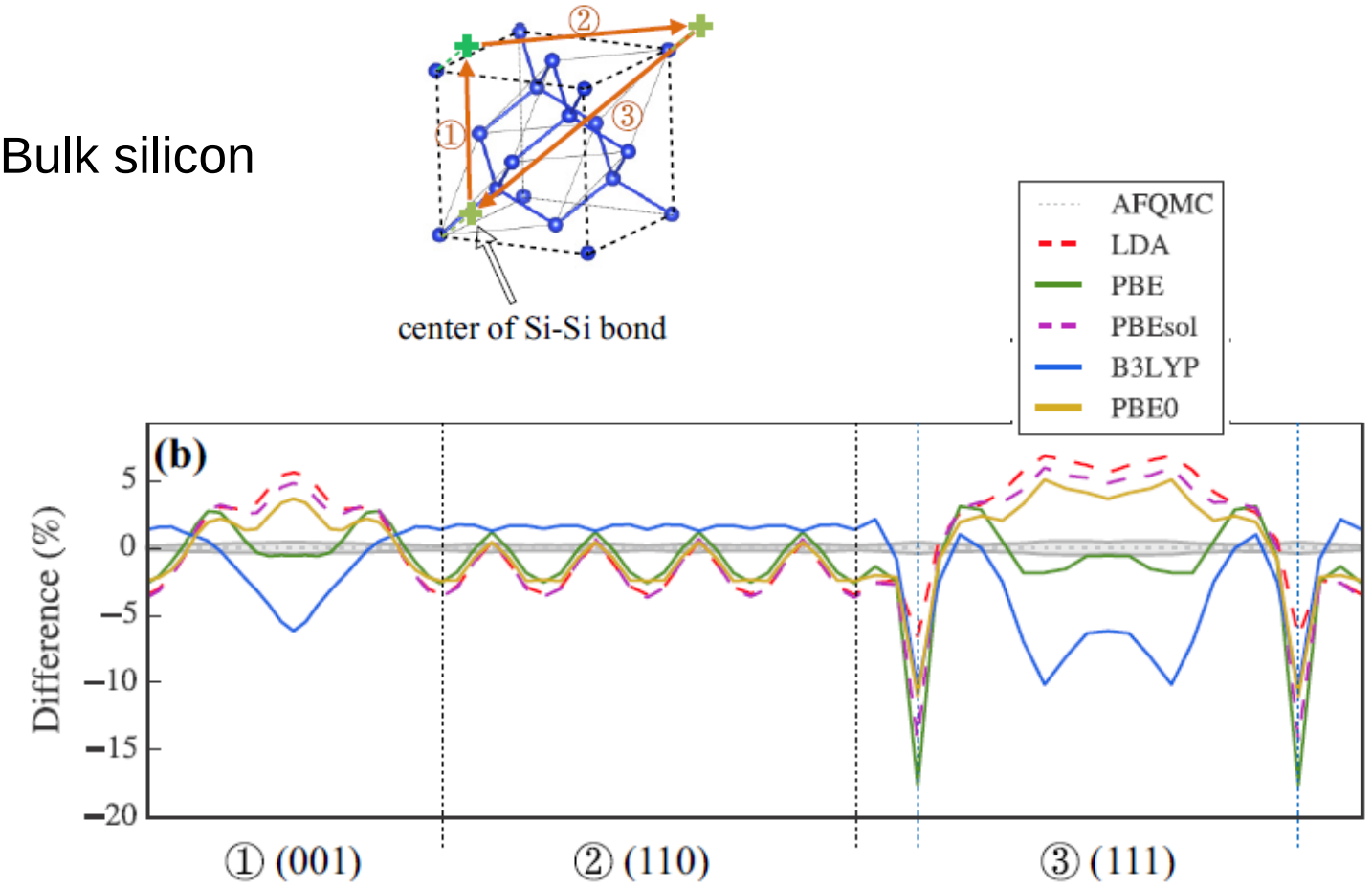
Michael G. Medvedev,[1,2,3]*† Ivan S. Bushmarinov,[1]*† Jianwei Sun,[4]‡ John P. Perdew,[4,5]† Konstantin A. Lyssenko[1]†

The theorems at the core of density functional theory (DFT) state that the energy of a many-electron system in its ground state is fully defined by its electron density distribution. This connection is made via the exact functional for the energy, which minimizes at the exact density. For years, DFT development focused on energies, implicitly assuming that functionals producing better energies become better approximations of the exact functional. We examined the other side of the coin: the energy-minimizing electron densities for atomic species, as produced by 128 historical and modern DFT functionals. We found that these densities became closer to the exact ones, reflecting theoretical advances, until the early 2000s, when this trend was reversed by unconstrained functionals sacrificing physical rigor for the flexibility of empirical fitting.

Medvedev *et al.*, *Science* **355**, 49–52 (2017)

Density: DFT approximations vs. accurate QMC

Bulk silicon



Siyuan Chen, et al. PRB 103, 075138 (2021).

- Big advantage 1: It is easier to use the model to approximate the effective potential of the auxiliary system rather than approximating the real system directly.
- Big advantage 2: Difficult calculation has been done once for all in the model and the results have been shared.
- Note: our first target is n(r).
  Other question is E=E[n].

- Big advantage 1: It is easier to use the model to approximate the effective potential of the auxiliary system rather than approximating the real system directly.
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- Note: our first target is n(r).
  Other question is E=E[n].
- More generally: the auxiliary system is not supposed to directly yield other observables of interest.

$$O = O[\Psi] \neq O[\Phi_{\mathrm{KS}}]$$

The density functional is often unknown:

$$O = \tilde{O}[n] \quad ???$$

Question 1: What is the “exact” Kohn-Sham gap in a solid?

Ordinary Kohn-Sham problem

$$V_{xc}(\mathbf{r}) \longrightarrow n(\mathbf{r})$$

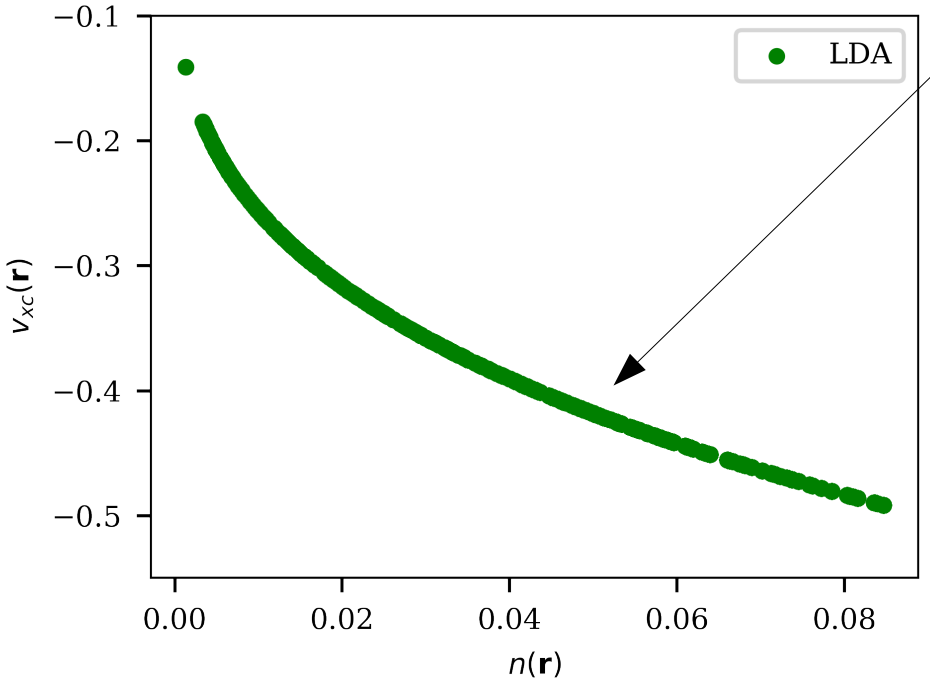
Inverse Kohn-Sham problem

$$n(\mathbf{r}) \longrightarrow V_{xc}(\mathbf{r})$$

...from accurate QMC density

Vxc potential: DFT approximations vs. accurate QMC

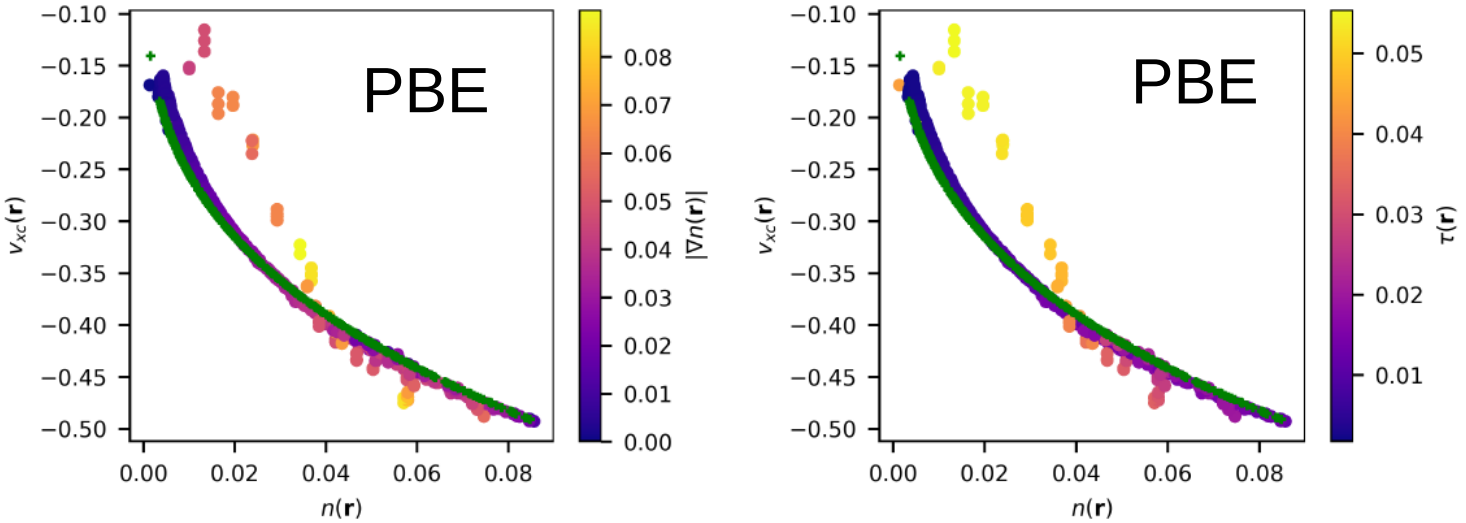
Bulk silicon



At each ***r***: $n(\mathbf{r})$, $v_{xc}(\mathbf{r})$

LDA: universal function of $n(\mathbf{r})$

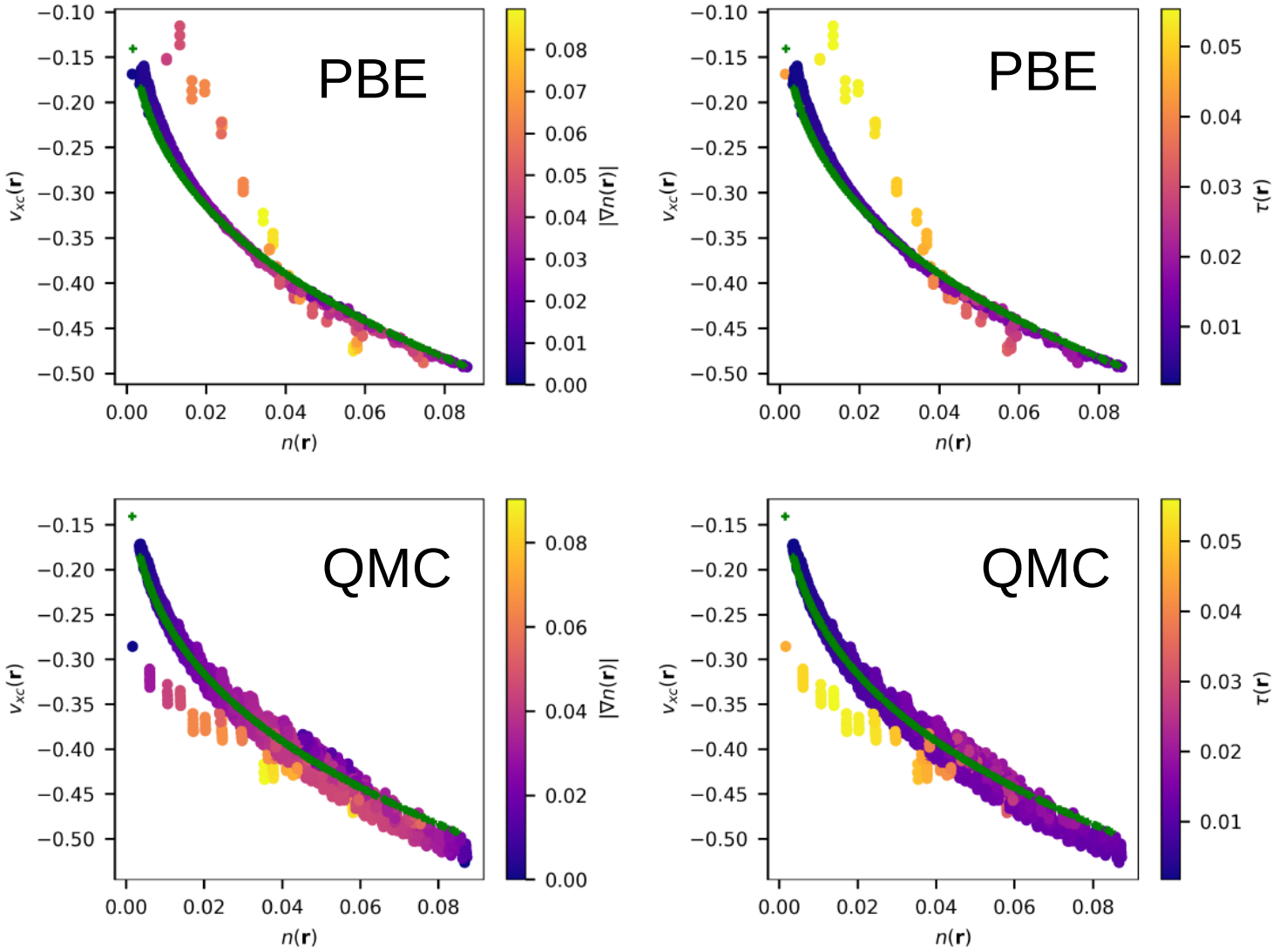
Vxc potential: DFT approximations vs. accurate QMC



Non locality and environment dependence

A. Aouina, M. Gatti, S. Chen, S. Zhang, and L. Reining, PRB 107, 195123 (2023)

Vxc potential: DFT approximations vs. accurate QMC



Non locality and environment dependence

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Kohn-Sham band gaps: DFT approximations vs. accurate QMC

	Si		NaCl
	indirect	direct at Γ	direct at Γ
QMC derived	0.69	2.72	5.25
PBE	0.66	2.60	5.08
LDA	0.49	2.55	4.59
Exp.	1.17 [85]	3.05[87]	8.5[86]
		3.40[85]	

A. Aouina et al, PRB 107 (2023)

See also: R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. Lett. 56, 2415 (1986)

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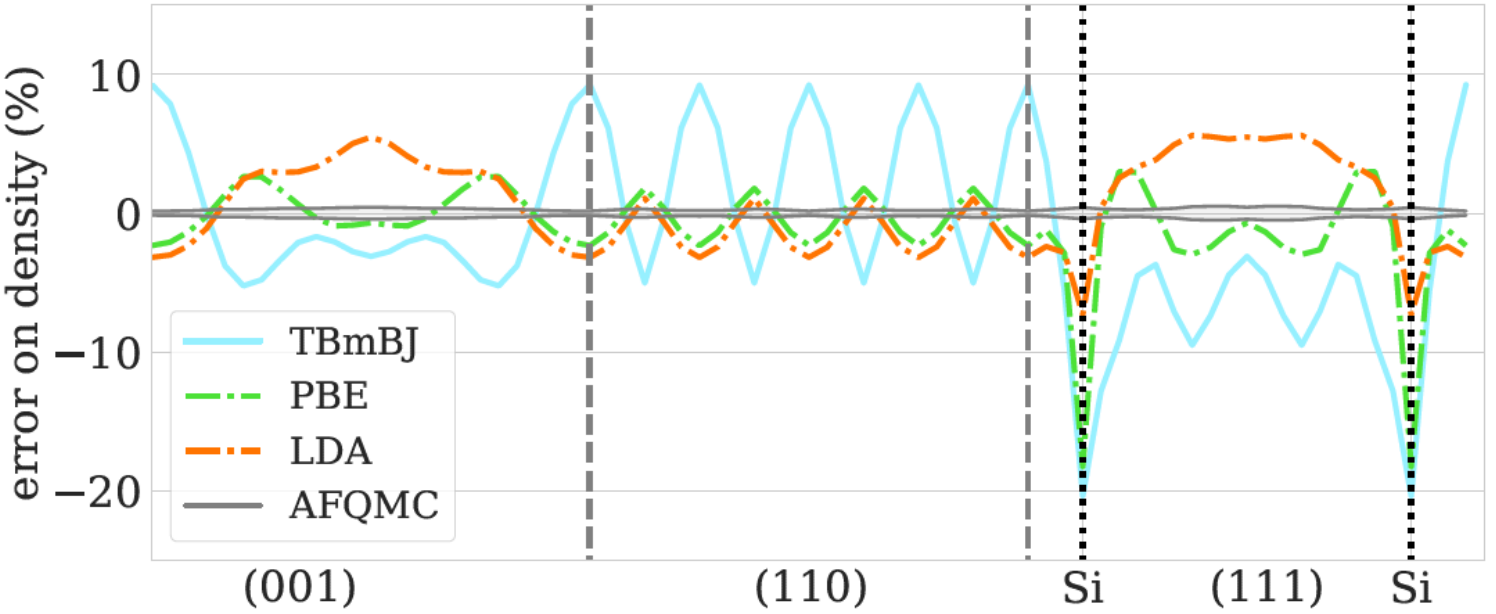
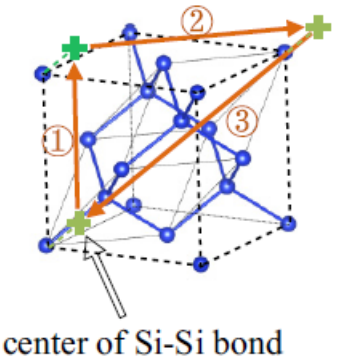
We shouldn't blame the LDA or PBE...

Note: Several common DFT approximations (hybrids, SCAN, LDA+U,…) don't use a local multiplicative Kohn-Sham potential → band gap can be larger ("Generalised Kohn-Sham" with non-local potential)

Question 1b: Can the KS gap agree with experiment?

Modified Becke Johnson MGGA:
Tuned for “Good gaps” (e.g. 3.09 eV at Γ), but bad density!





Bulk silicon: error with respect to QMC

Question 2: Can we make the LDA “exact” ?

DFT : A “multiverse” theory

$$H\Psi = E\Psi$$

$$\Psi = \Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$$

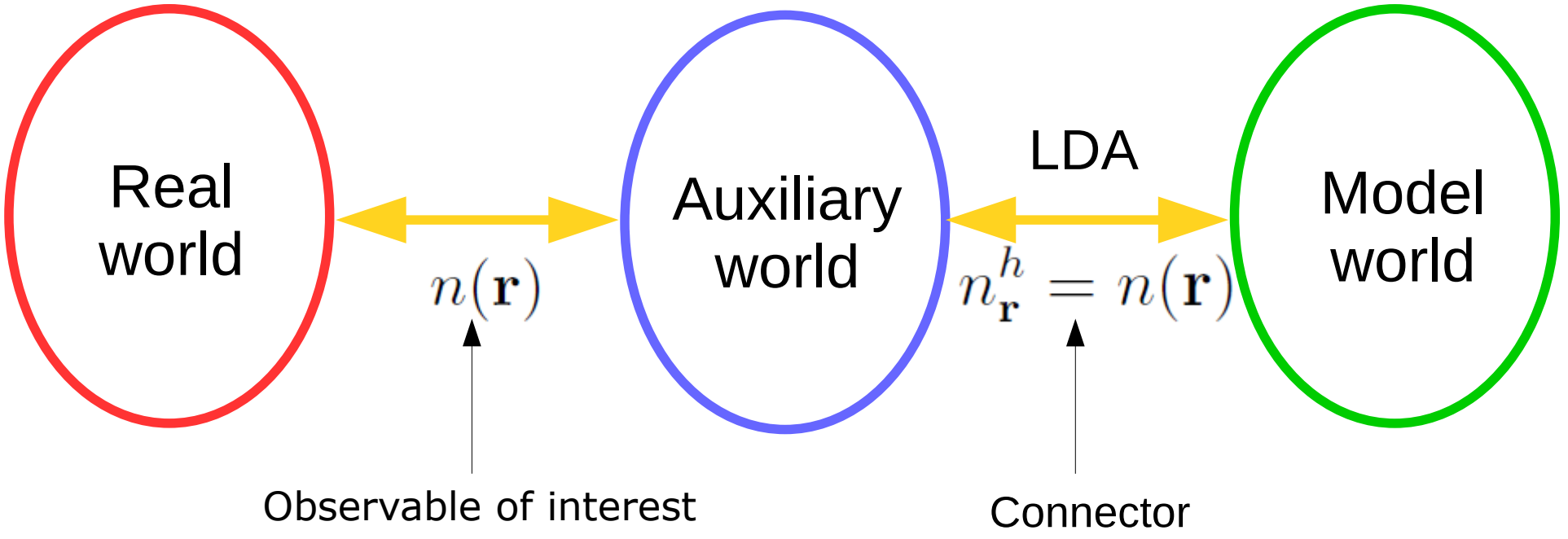
All observables

Kohn-Sham

$V_{xc}(\mathbf{r})$?

Homogeneous electron gas

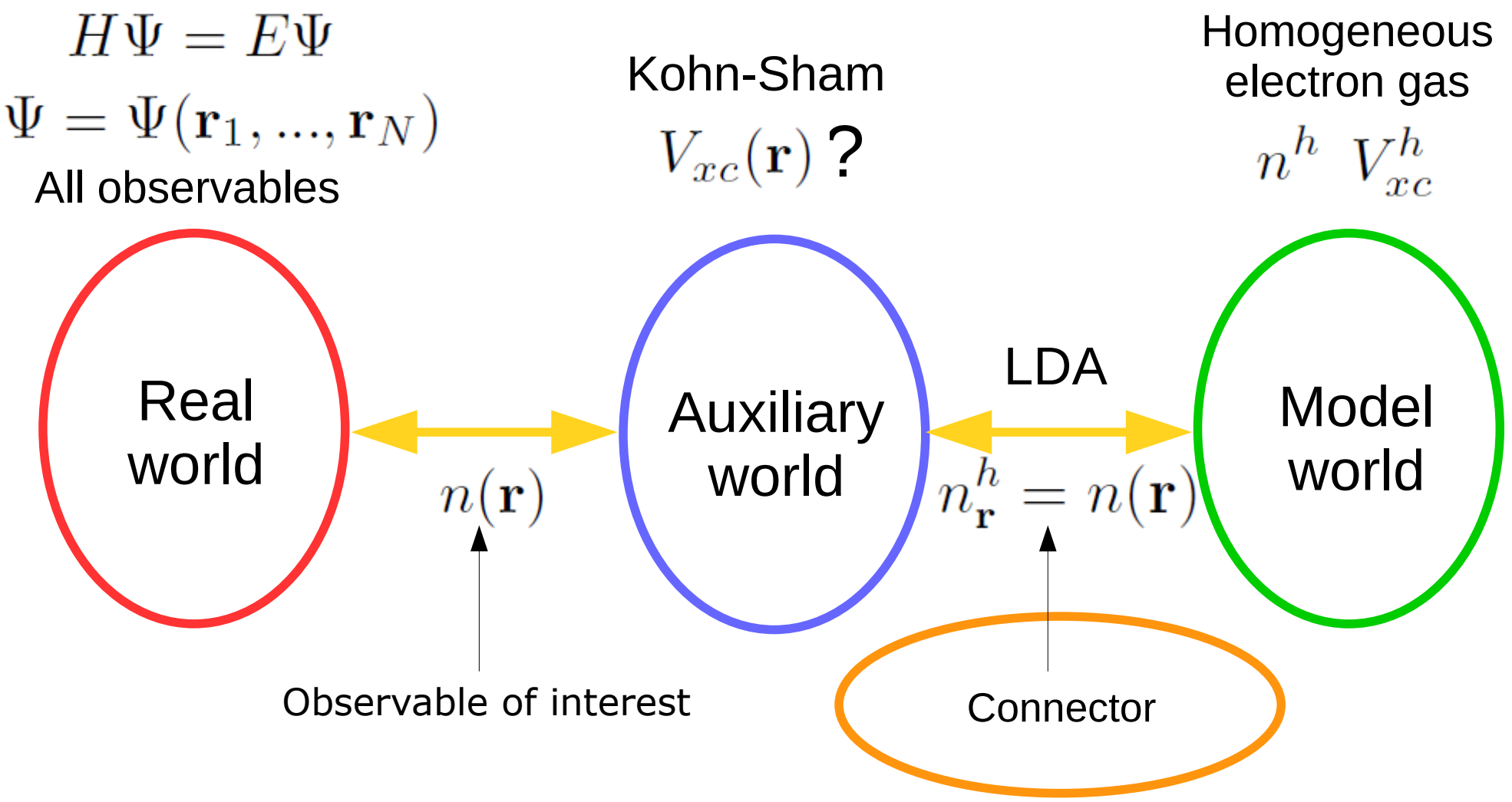
$n^h \;\; V_{xc}^h$



$$E_{\rm xc}[n] = \int d\mathbf{r}\, n(\mathbf{r}) \epsilon_{xc}^h(n^h_{\mathbf{r}} = n(\mathbf{r}))$$

$$V_{\rm xc}(\mathbf{r}) = V_{\rm xc}^h(n^h_{\mathbf{r}} = n(\mathbf{r}))$$

DFT : A successful tale of 3 worlds



Generalize??? **Exactify???**

The connector theory

Kohn-Sham $V_{\mathrm{xc}}(\mathbf{r},[n])$

Model (HEG) $V_{\mathrm{xc}}^{h}(n^{h})$

The connector theory

Kohn-Sham $V_{\rm xc}(\mathbf{r},[n])$ Model (HEG) $V^h_{\rm xc}(n^h)$

n^h ? $V_{\rm xc}(\mathbf{r},[n]) = V^h_{\rm xc}(n^h)$ (if share same values)

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$$n^h = (V_{\rm xc}^h)^{-1}\{V_{\rm xc}(\mathbf{r},[n])\} \equiv n^h_{\mathbf{r}}[n]$$ (if inversion possible)

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Connector

$V_{\rm xc}^h(n^h_{\mathbf{r}}[n]) \longrightarrow V_{\rm xc}$

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Connector

So far nothing gained!

$V_{\rm xc}^h(n^h_{\mathbf{r}}[n]) \longrightarrow V_{\rm xc}$

The connector theory

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Connector

$$n^h_{\mathbf{r}}[n] = (V^h_{\rm xc,approx})^{-1}\{V_{\rm xc,approx}(\mathbf{r},[n])\}$$

$$V_{\rm xc}^h(n^h_{\mathbf{r}}[n]) \longrightarrow V_{\rm xc}$$

Exchange-correlation potential

Kohn-Sham $V_{\mathrm{xc}}(\mathbf{r},[n])$ HEG $V_{\mathrm{xc}}^{h}(n^{h})$

LDA $n_{\mathbf{r}}^{h}[n]=n(\mathbf{r})$ $V_{\mathrm{xc}}^{h}(n(\mathbf{r}))$

Connector $n_{\mathbf{r}}^{h}[n]=(V_{\mathrm{xc,approx}}^{h})^{-1}\{V_{\mathrm{xc,approx}}(\mathbf{r},[n])\}$

$V_{\mathrm{xc}}^{h}(n_{\mathbf{r}}^{h}[n])$ Non-local density functional!

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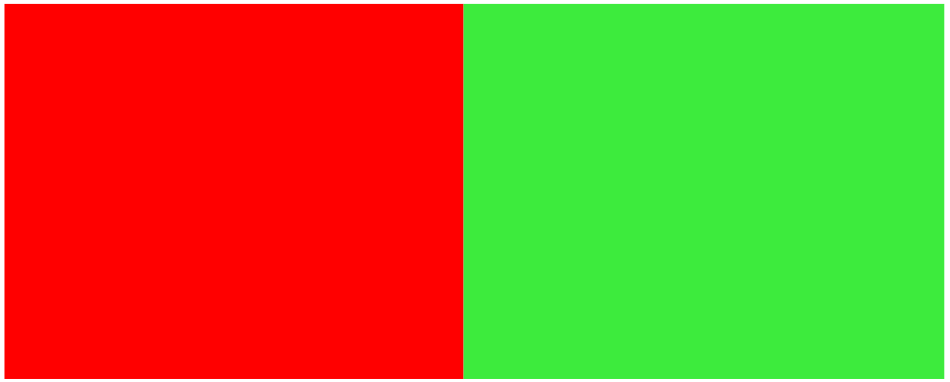
Why advantageous???

The connector theory

Direct approximation

$$V_{\mathrm{xc,approx}}$$

Good if approximation is good



The connector theory

Direct approximation

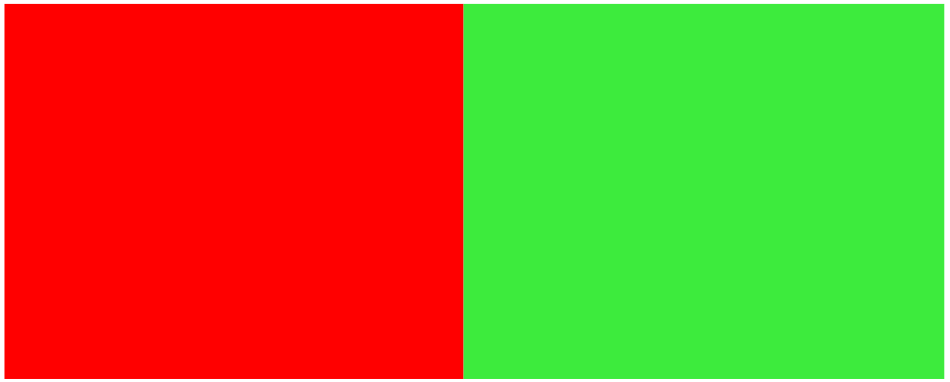
$$V_{\mathrm{xc,approx}}$$

Connector approximation

$$V_{\mathrm{xc}}^{h}\{V_{\mathrm{xc,approx}}^{h,-1}[V_{\mathrm{xc,approx}}]\}$$

Error canceling!

Good if approximation is good



Bad ⟷ Good

Approximation

The connector theory

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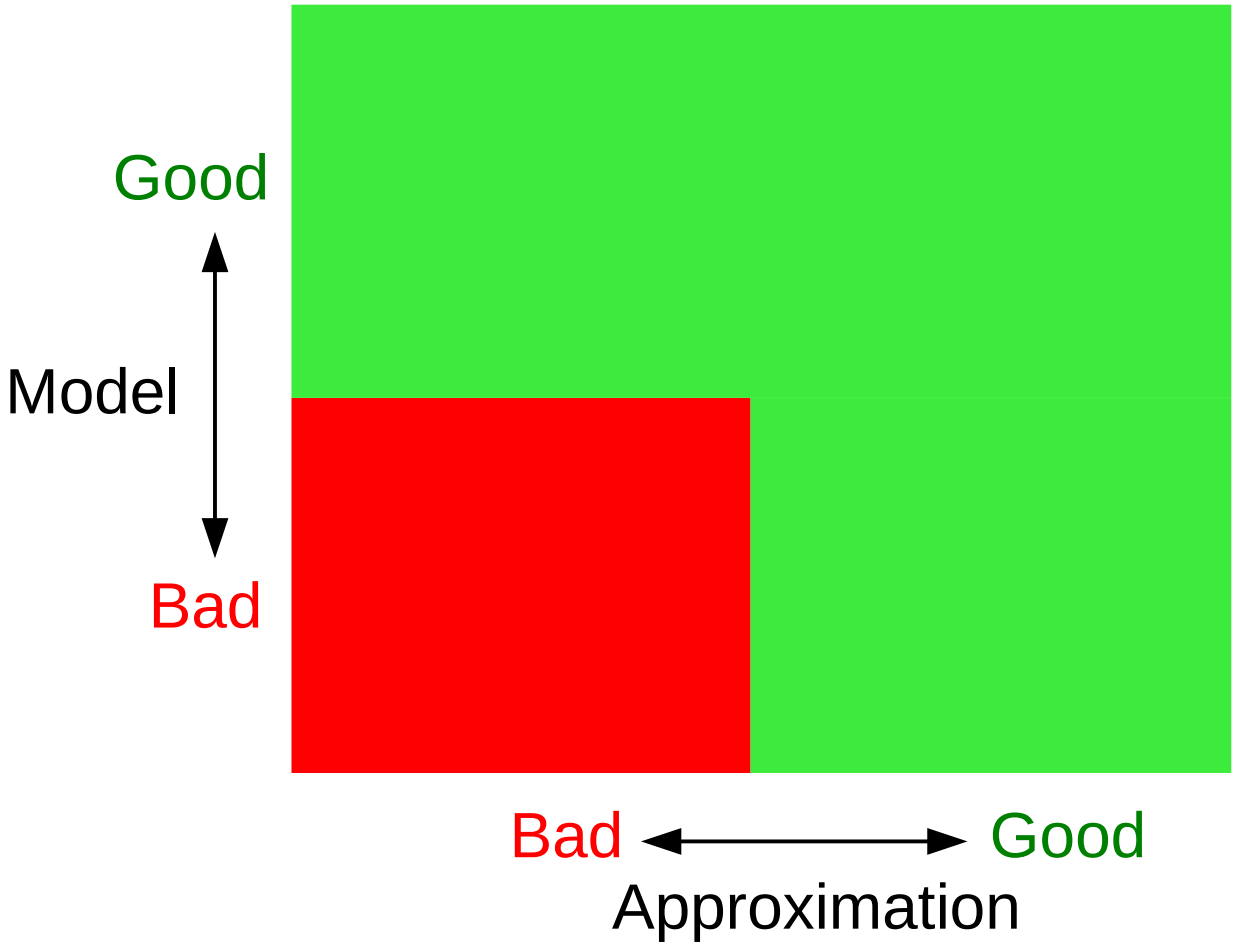

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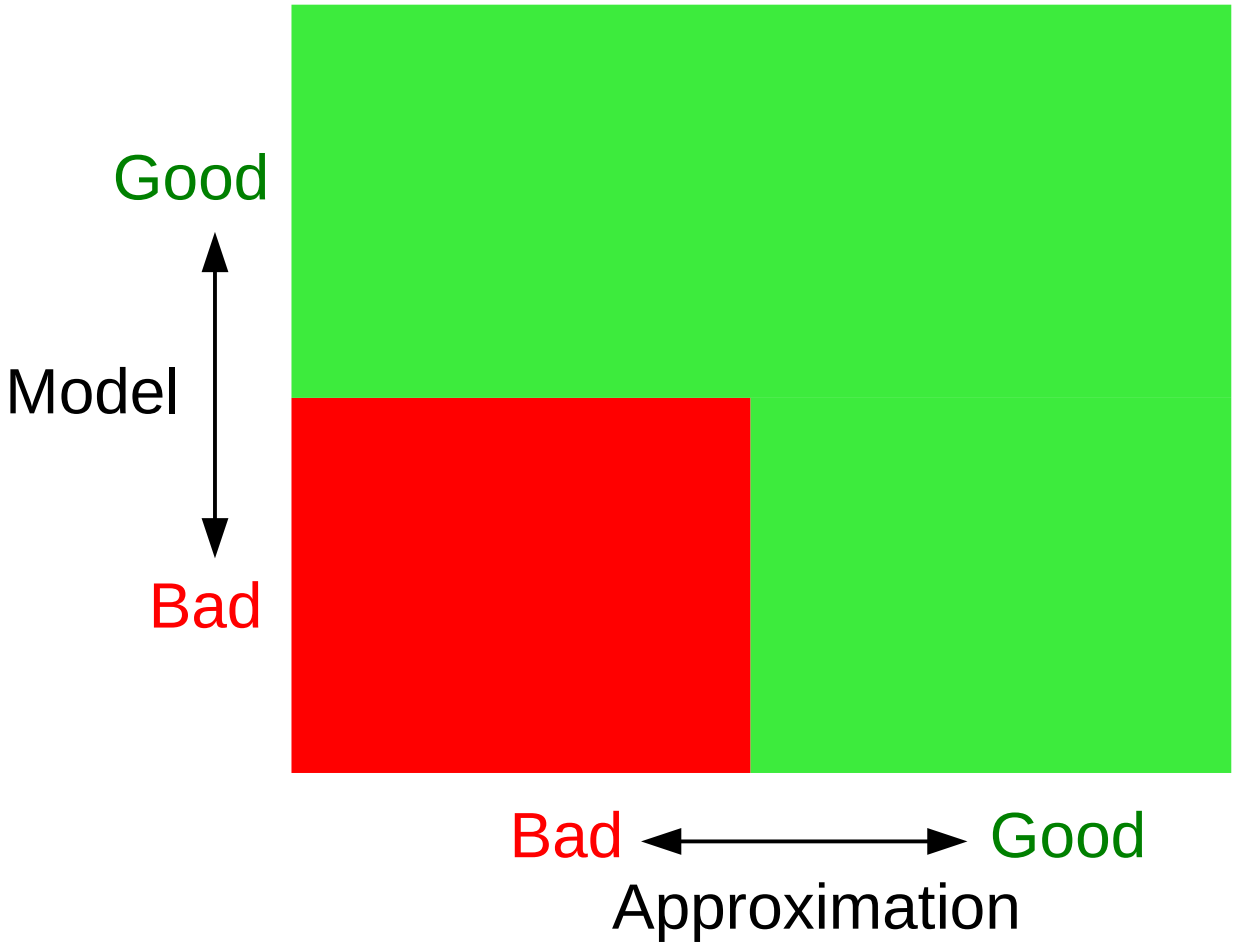

Error canceling!

Good if approximation is good
(even if model is bad)

Good if model is good
(even if approximation is bad)

Calculate
once and forever!

An ecological approach!!!

Exchange-correlation potential

Simple approximation : Linearization around homogeneous density

Kohn-Sham $$V_{\rm xc}(\mathbf{r},[n]) \approx V_{\rm xc}(\bar{n}) + \int d\mathbf{r}' f_{\rm xc}(|\mathbf{r}-\mathbf{r}'|;\bar{n})(n(\mathbf{r}')-\bar{n})$$

HEG $$V^h_{\rm xc}(n^h) \approx V^h_{\rm xc}(\bar{n}) + f^h_{\rm xc}(\bar{n})(n^h-\bar{n})$$

Connector $$n^h_{\mathbf{r}}[n] = \frac{1}{f^h_{\rm xc}(\bar{n})} \int d\mathbf{r}' f_{\rm xc}(|\mathbf{r}-\mathbf{r}'|;\bar{n}) n(\mathbf{r}')$$

LDA $$n^h_{\mathbf{r}}[n] = n(\mathbf{r})$$

fxc known from M. Corradini, R. Del Sole, G. Onida, and M. Palummo, Phys. Rev. B 57, 14569 (1998)

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LDA $$n^h_{\mathbf{r}}[n] = n(\mathbf{r})$$

Test on inhomogeneous system: $$n(\mathbf{r}) = \mathbf{A}\cos(\mathbf{a}\cdot\mathbf{r}) + \mathbf{B}$$

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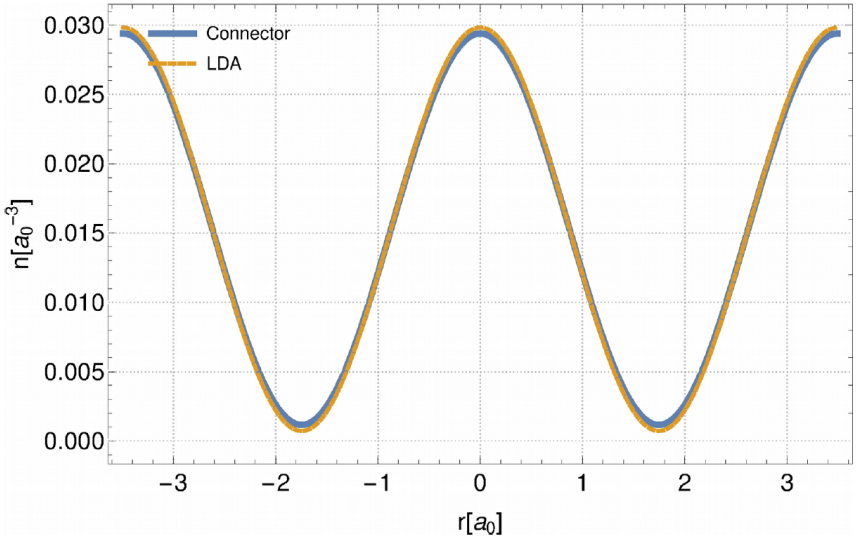
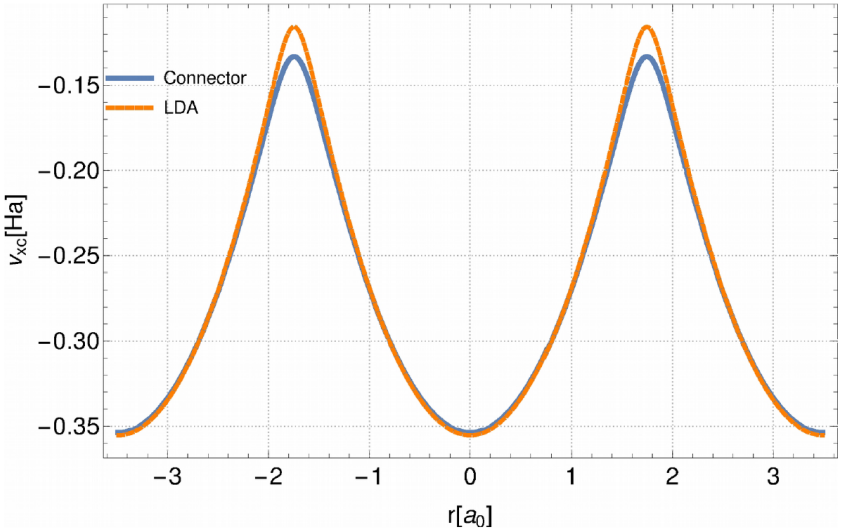
Slowly varying density:

Connector ~ LDA

$$n^h_{\mathbf{r}}[n]$$



$$V^h_{\mathbf{xc}}(n^h_{\mathbf{r}}[n])$$

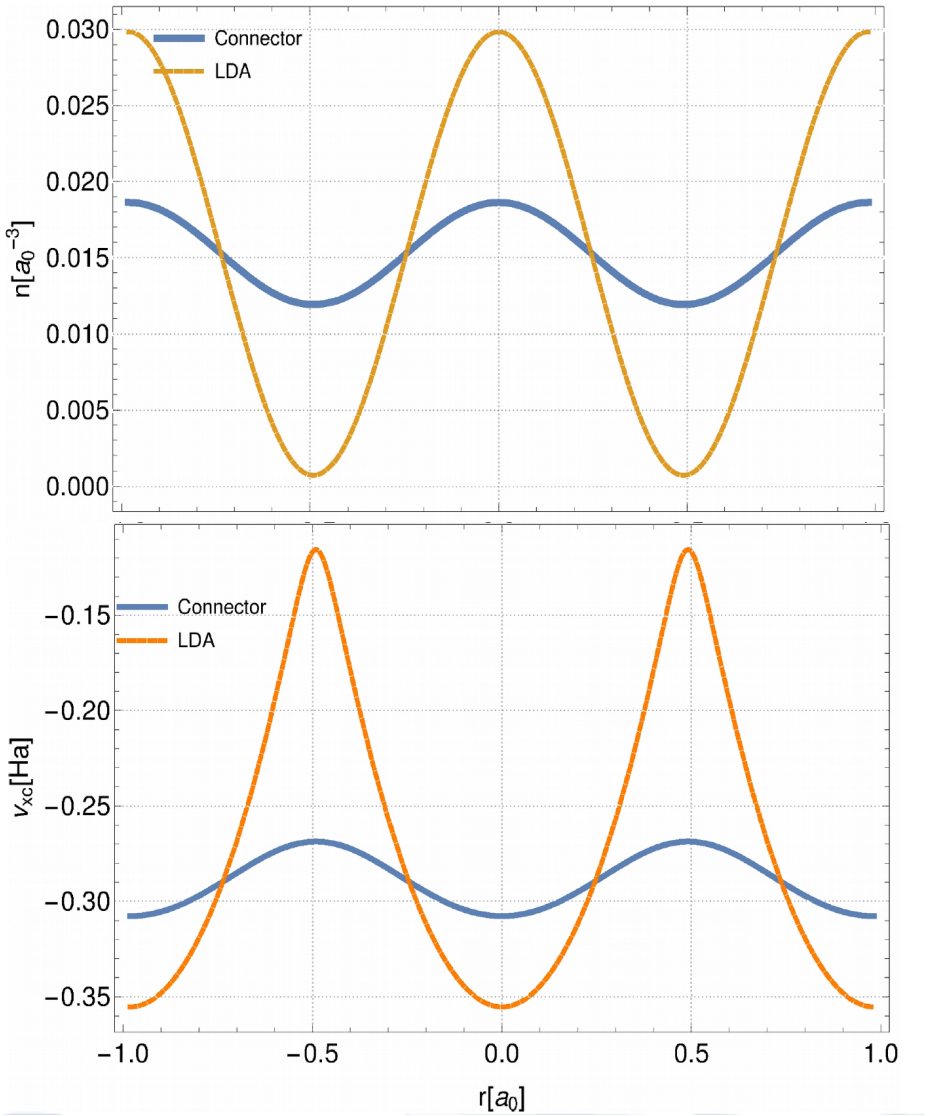


Rapidly varying density:

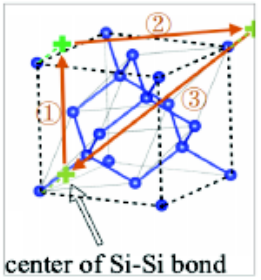
Connector ~ Mean density

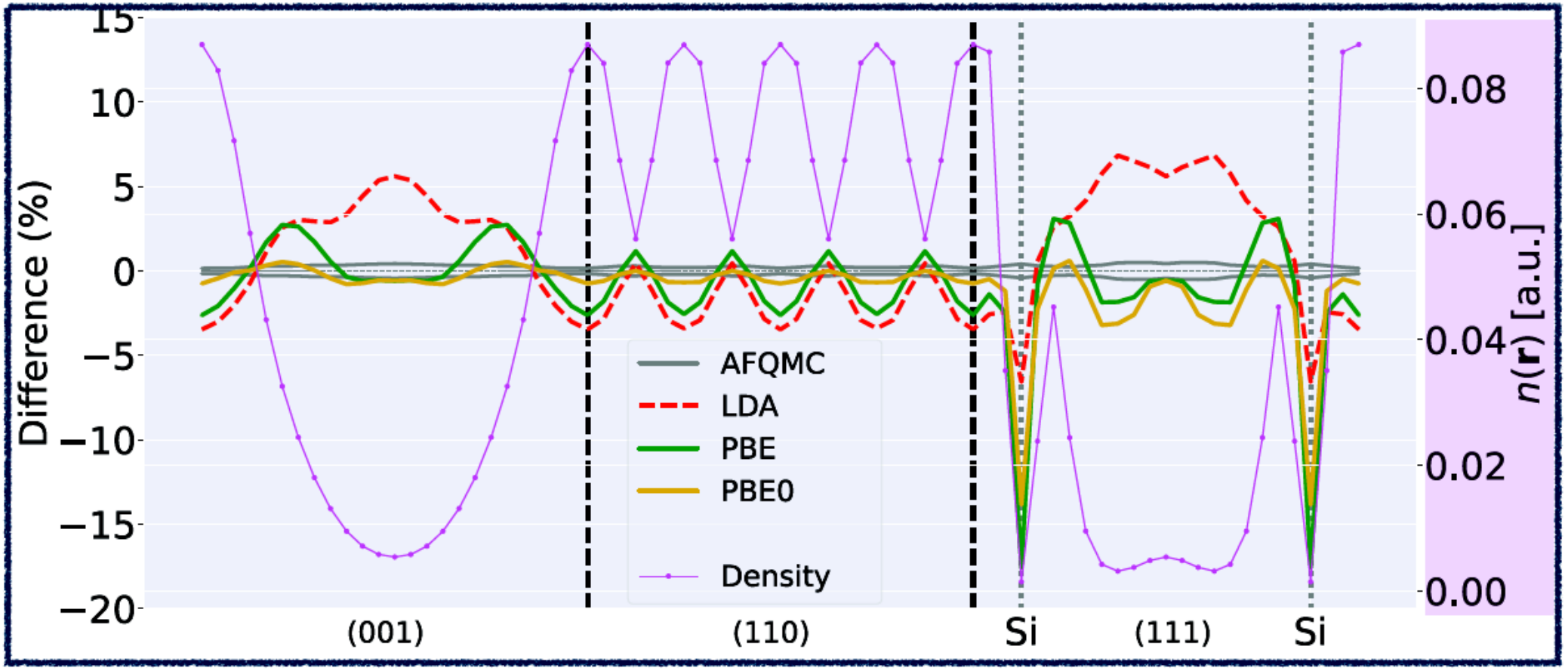
$$n^h_{\mathbf{r}}[n]$$

$$V^h_{\mathbf{xc}}(n^h_{\mathbf{r}}[n])$$



Charge density of Silicon





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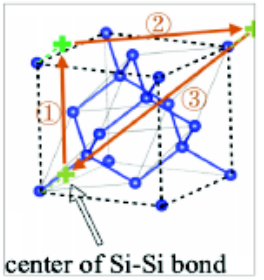

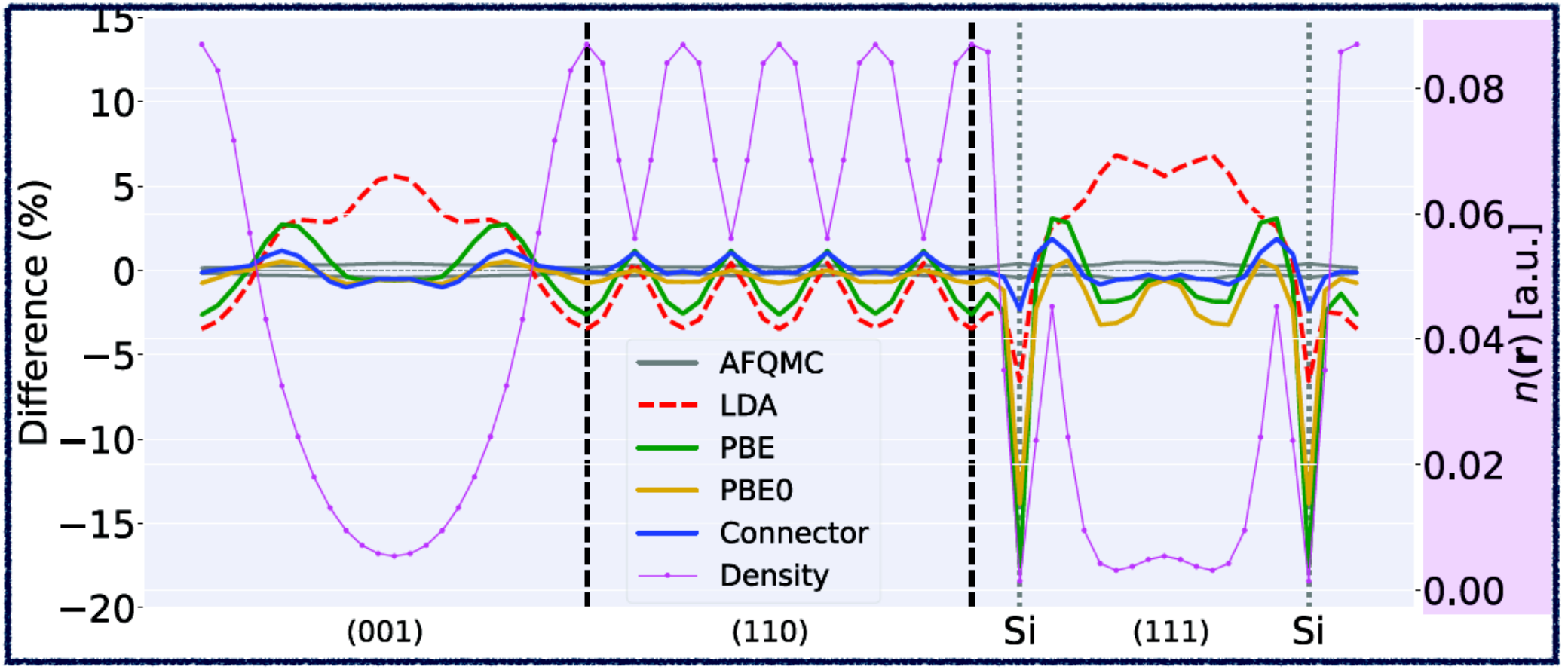

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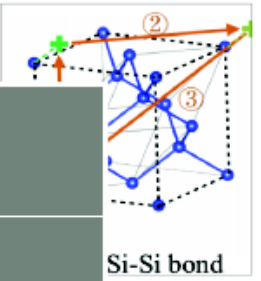
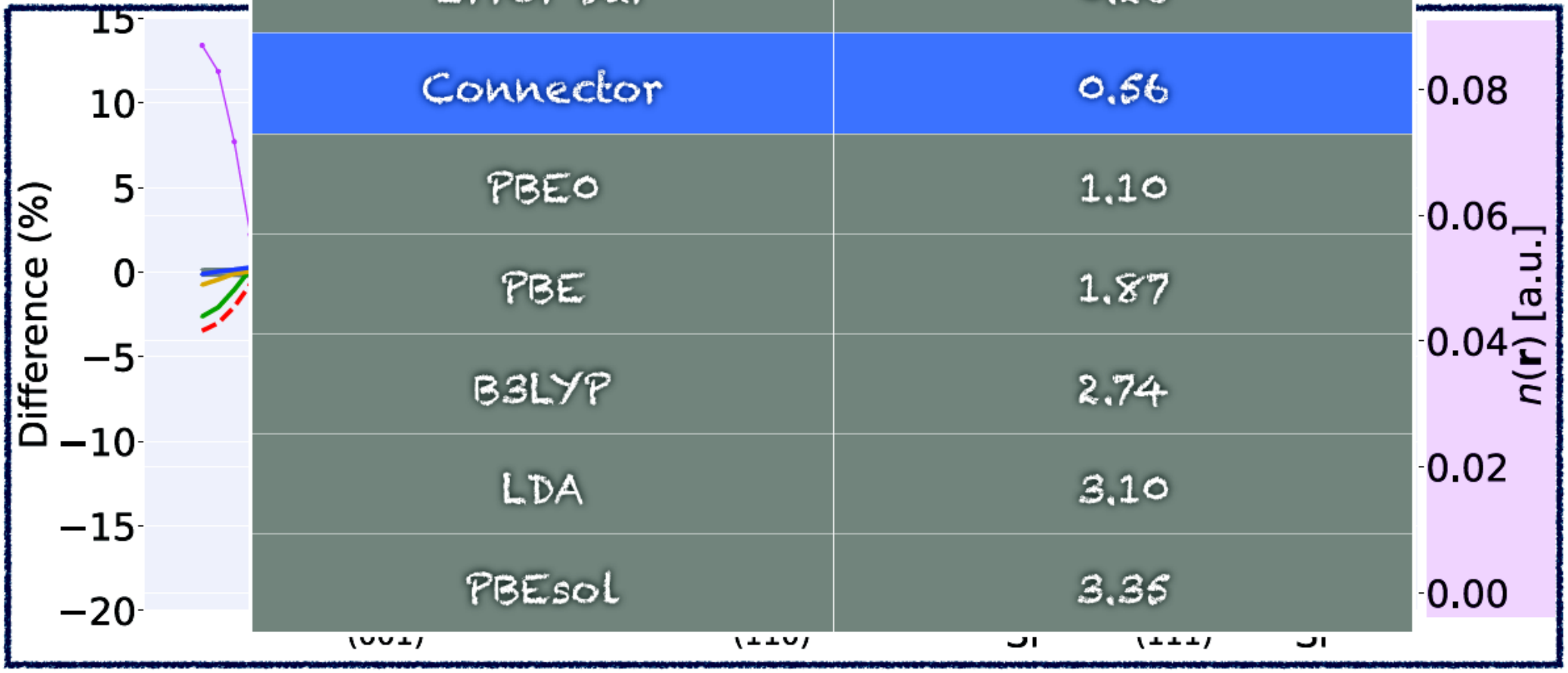
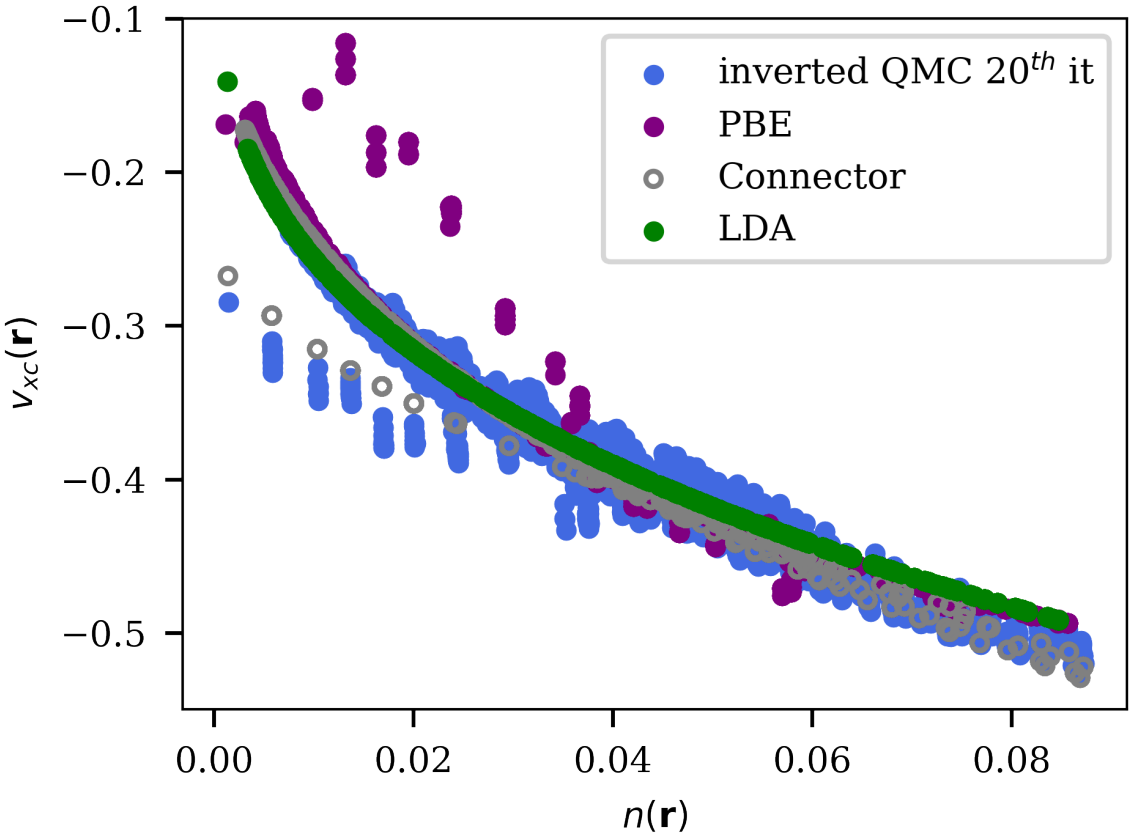


Approximation	Error (%)
Error bar	0.26
Connector	0.56
PBE0	1.10
PBE	1.87
B3LYP	2.74
LDA	3.10
PBEsol	3.35



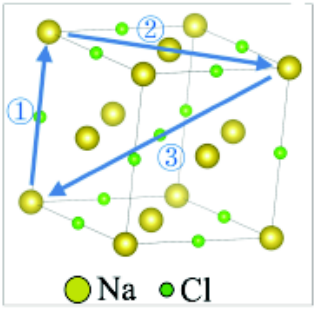
Vxc potential: DFT approximations vs. accurate QMC

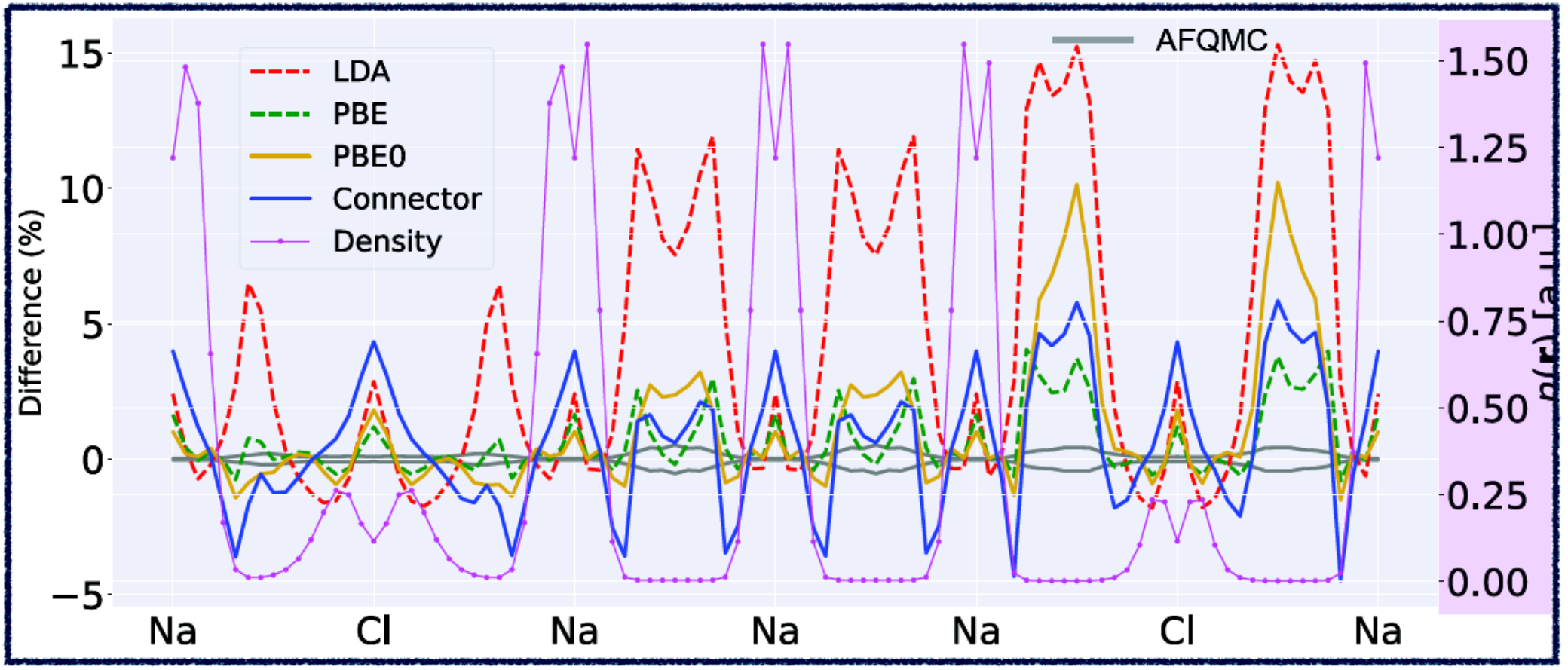


Kohn-Sham band gaps: DFT approximations vs. accurate QMC

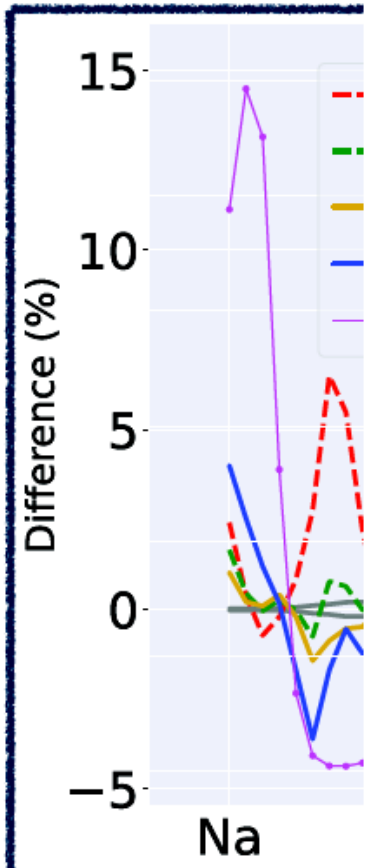
v_{xc}	KS gap Si (ev)	KS gap NaCl
AFQMC	0.82	5.25
PBE	0.80	5.08
Connector	0.86	4.87
LDA	0.63	4.59

Charge density of NaCl





Charge density of NaCl



Approximation	Error (%)
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B3LYP	0.68
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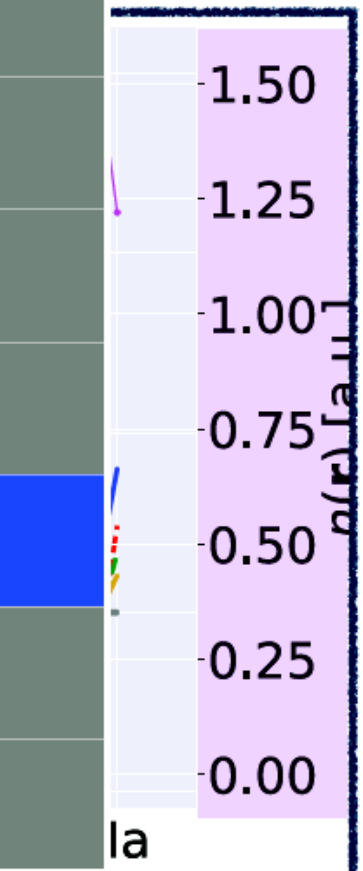
PBE0	1.61
Connector	2.06
PBEsol	2.39
LDA	4.45



The connector theory

Very general strategy of approximation

Choose:

- A quantity of interest (an observable, a potential, ...)
- A model (HEG, inhomogeneous model, …)
- An approximation (linearization, ...)

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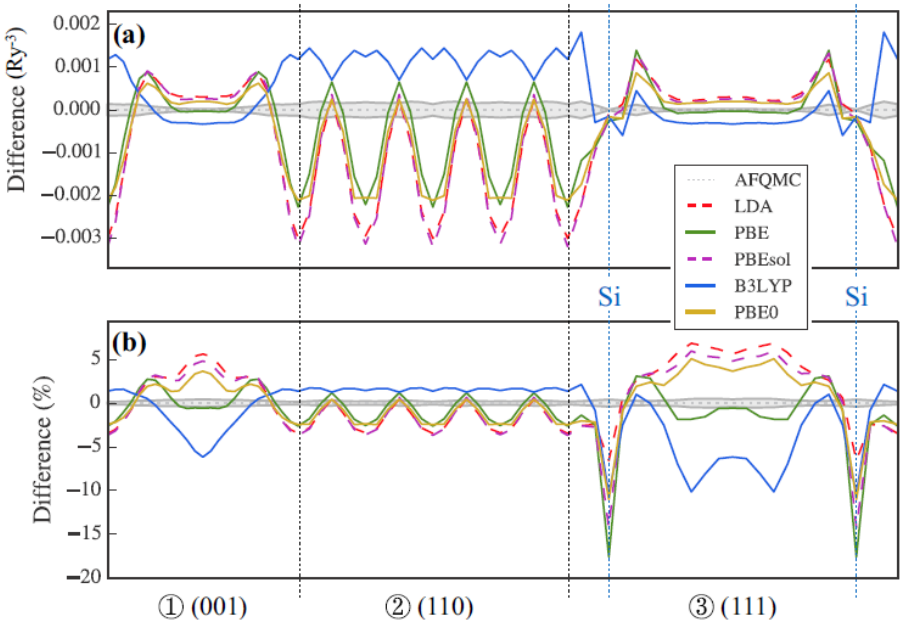
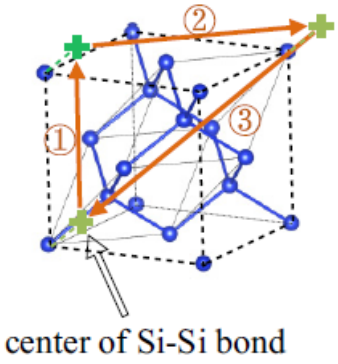
To know more:

- M. Vanzini, A. Aouina, M. Panholzer, M. Gatti & L. Reining, npj Computational Materials 8, 98 (2022).
- A. Aouina, PhD thesis (Ecole Polytechnique, 2022)

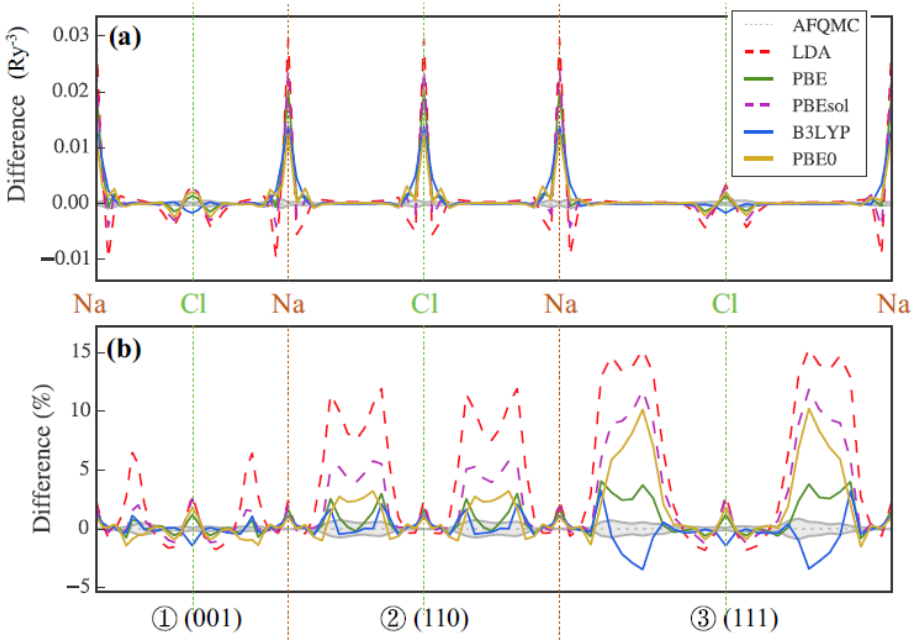
Many thanks!

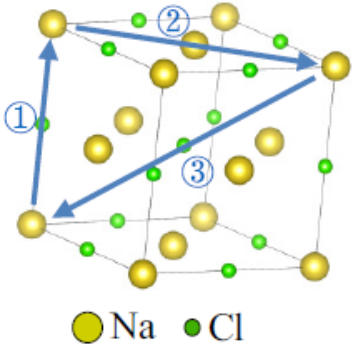
n(r) in bulk silicon:





n(r) in bulk NaCl:





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