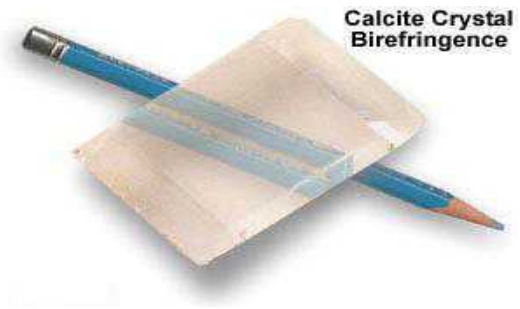
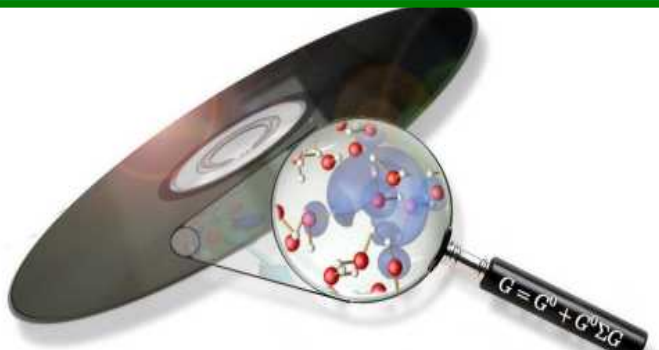
La mécanique quantique dans les systèmes à N corps

Lucia Reining

Palaiseau Theoretical Spectroscopy Group & Friends

Theoretical Spectroscopy





La mécanique quantique dans les systèmes à N corps
ou comment chercher la solution d'un problème insoluble

→ What is our job?

→ We are physicists: the quantum many-body problem

→ Re-writing: functionals

→ Approximating: many-body perturbation theory

→ the synchrotron, back and forth

→ …..and coding: a quantum video camera

→ motivated by a museum

→ Less petrol in the pipeline: Connector approach

→ an ecological use of models

→ Remarks

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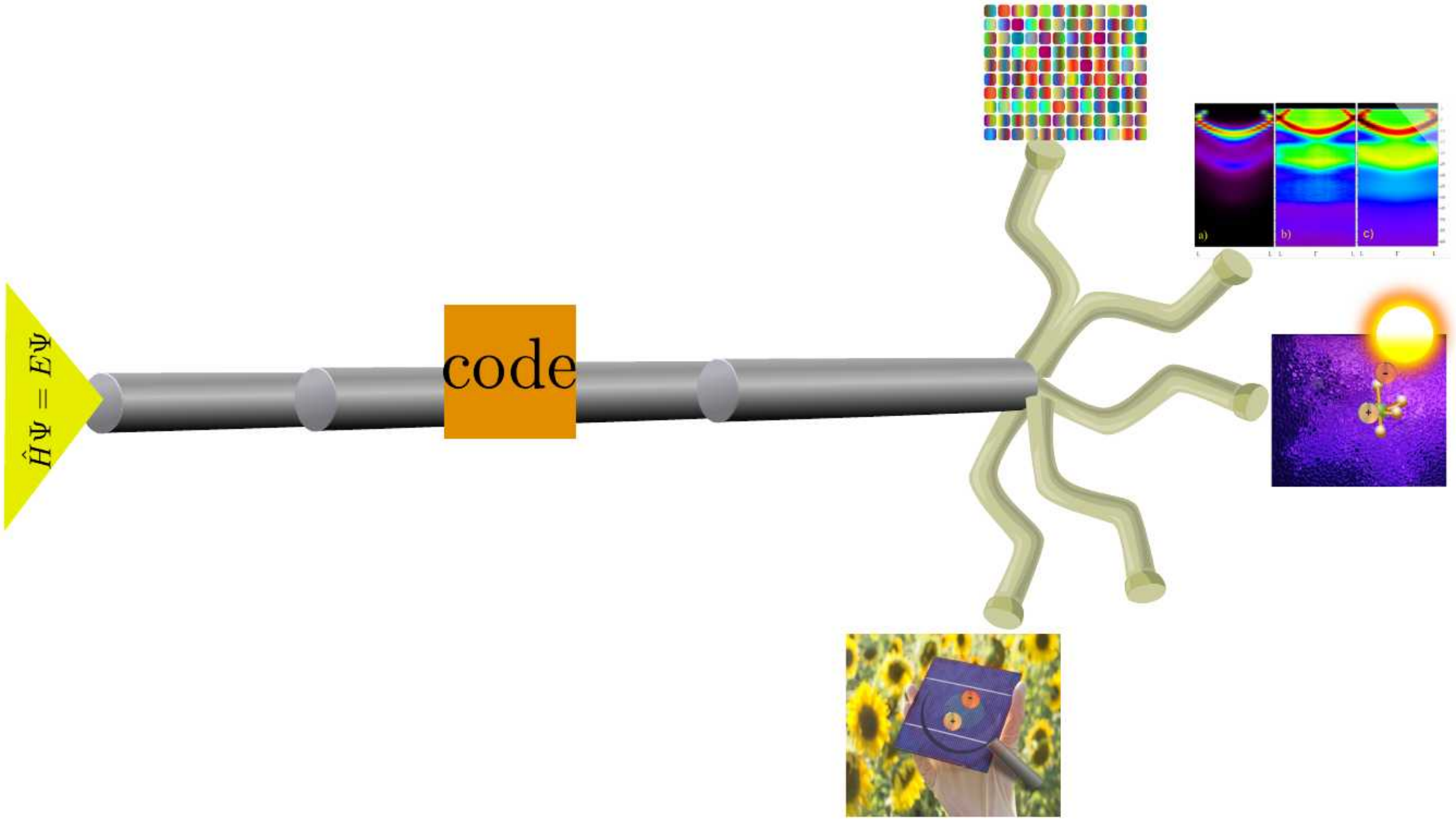
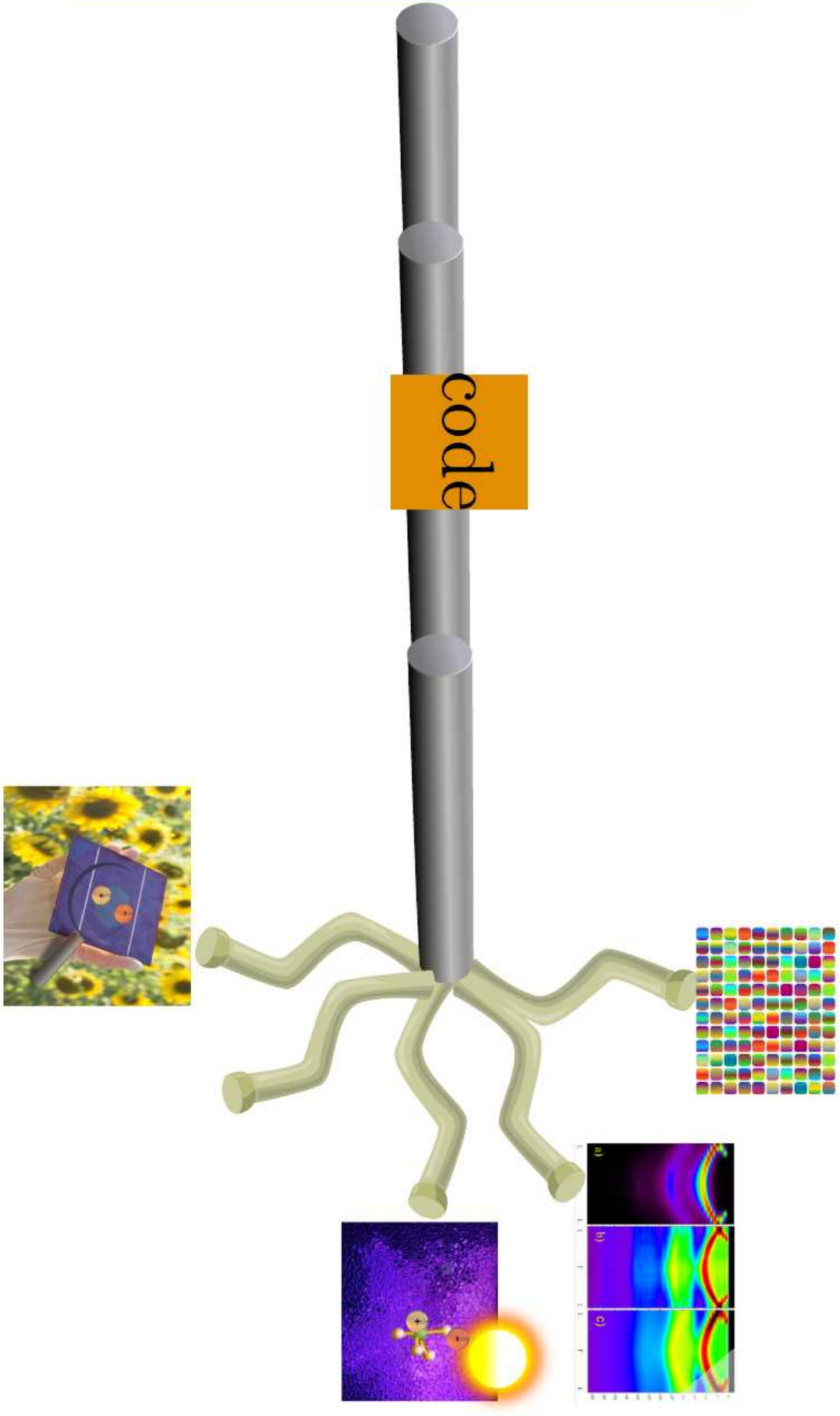
$$\hat{H}\Psi_\lambda(x_1, x_2, ..., x_N) = E_\lambda \Psi_\lambda(x_1, x_2, ..., x_N)$$


$\hat{H}\Psi = E\Psi$
code
a)
b)
c)

$$\hat{H}\Psi(x_1, x_2, ..., x_N) = E\Psi(x_1, x_2, ..., x_N)$$



$$\hat{H}\Psi_\lambda(x_1, x_2, ..., x_N) = E_\lambda \Psi_\lambda(x_1, x_2, ..., x_N)$$

$(3n_x \text{ points})^N$

$$\hat{H}\Psi_\lambda(x_1, x_2, \ldots\ldots, x_N) = E_\lambda \Psi_\lambda(x_1, x_2, \ldots\ldots, x_N)$$

Not (exactly) solvable
Not storable

$$\hat{H}\Psi_\lambda(x_1, x_2, ..., x_N) = E_\lambda \Psi_\lambda(x_1, x_2, ..., x_N)$$

The quantum many-body problem

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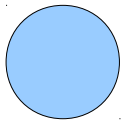
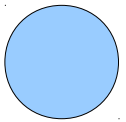
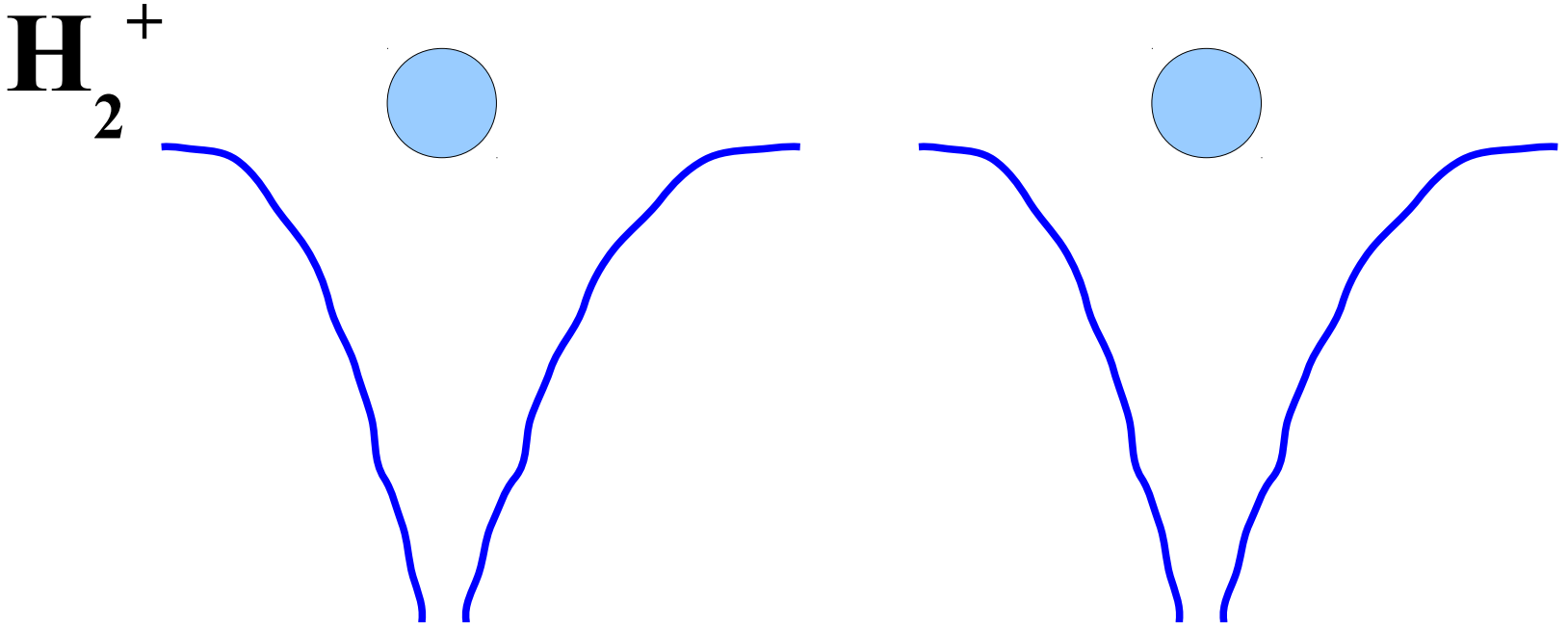
H_2^+

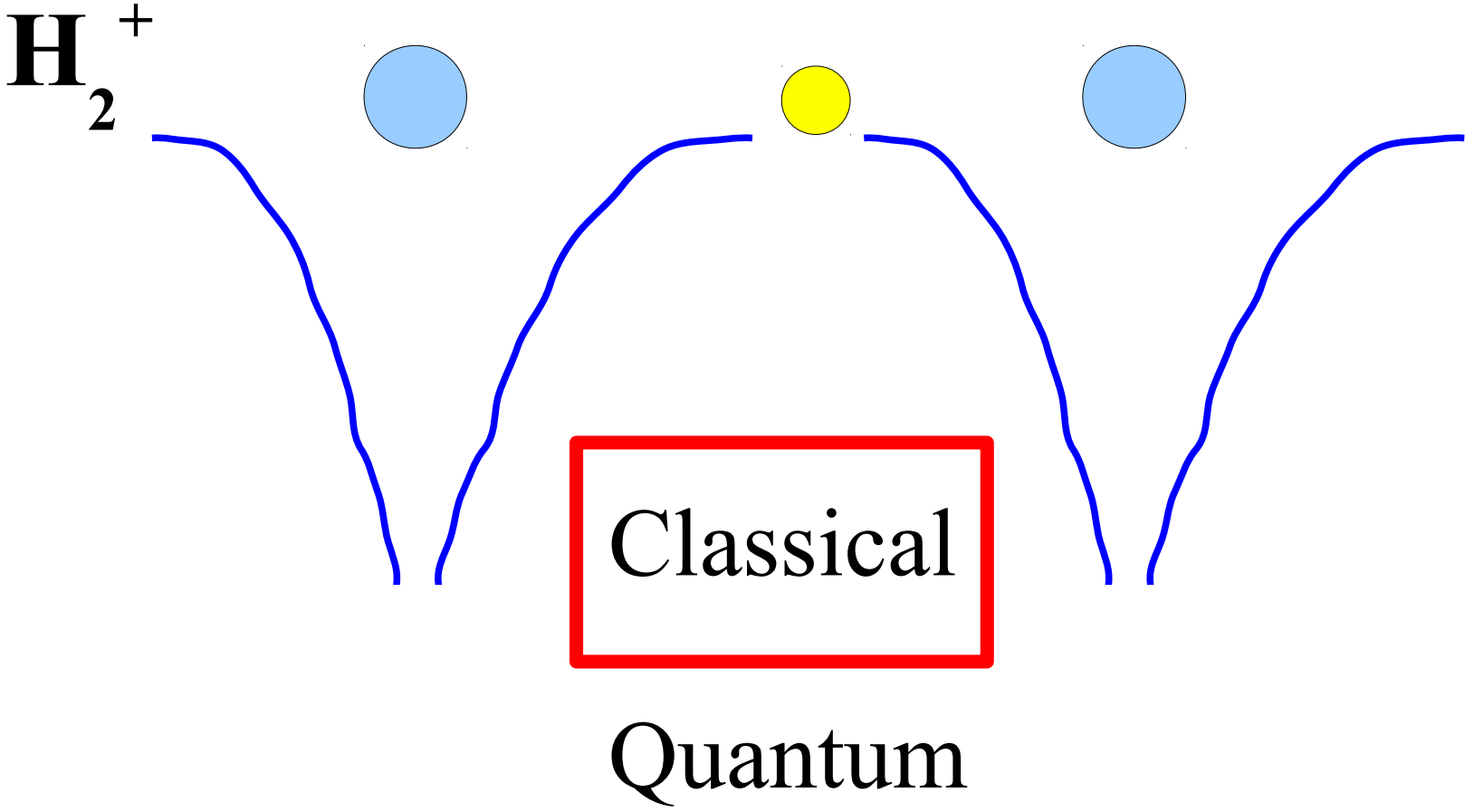


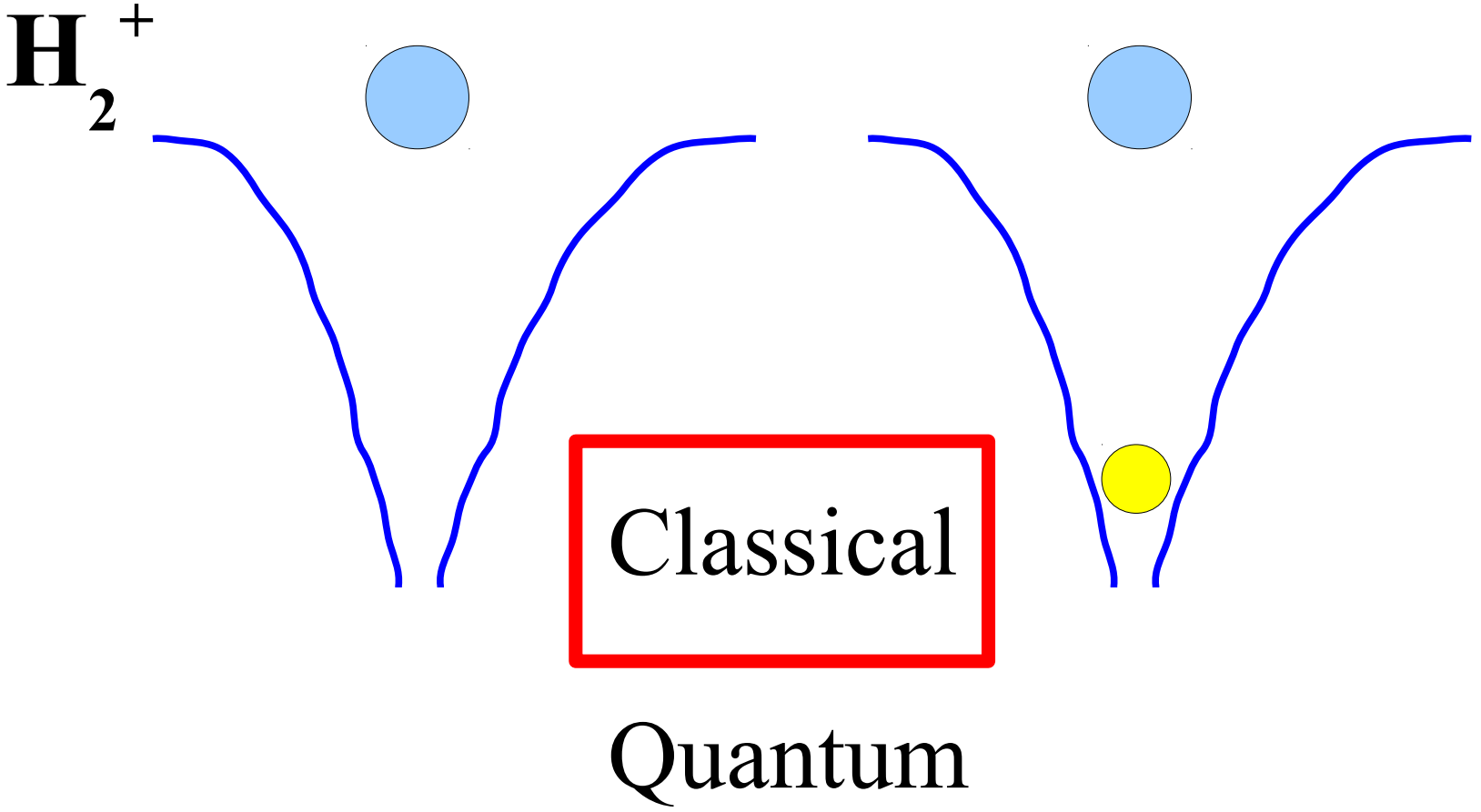


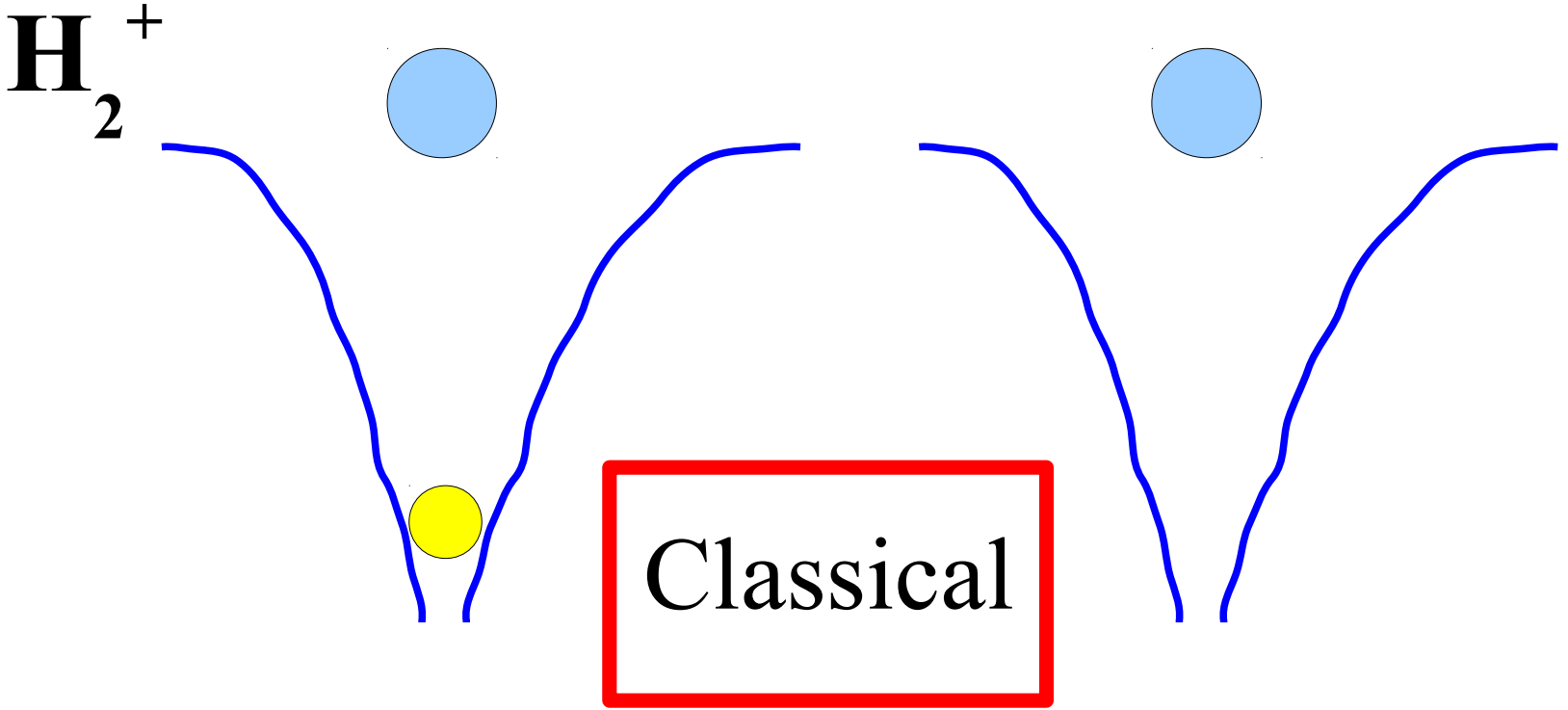
Quantum

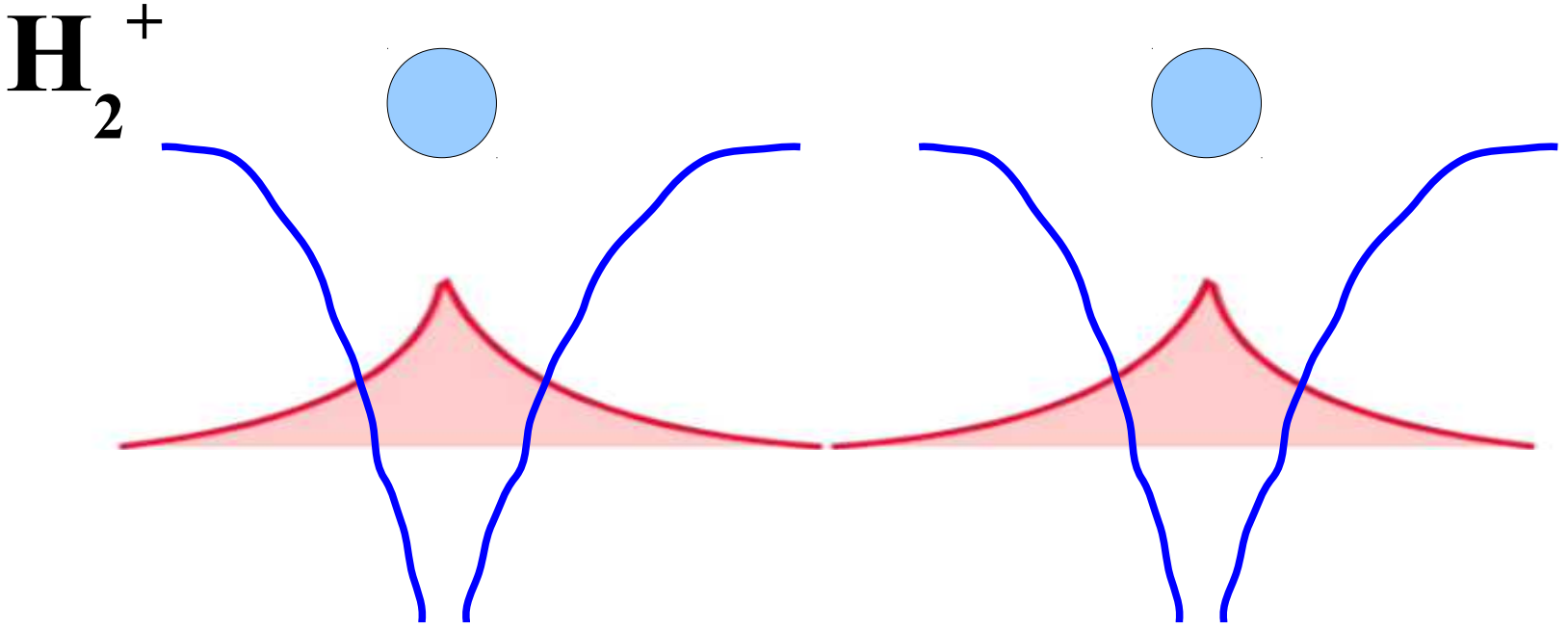


Quantum

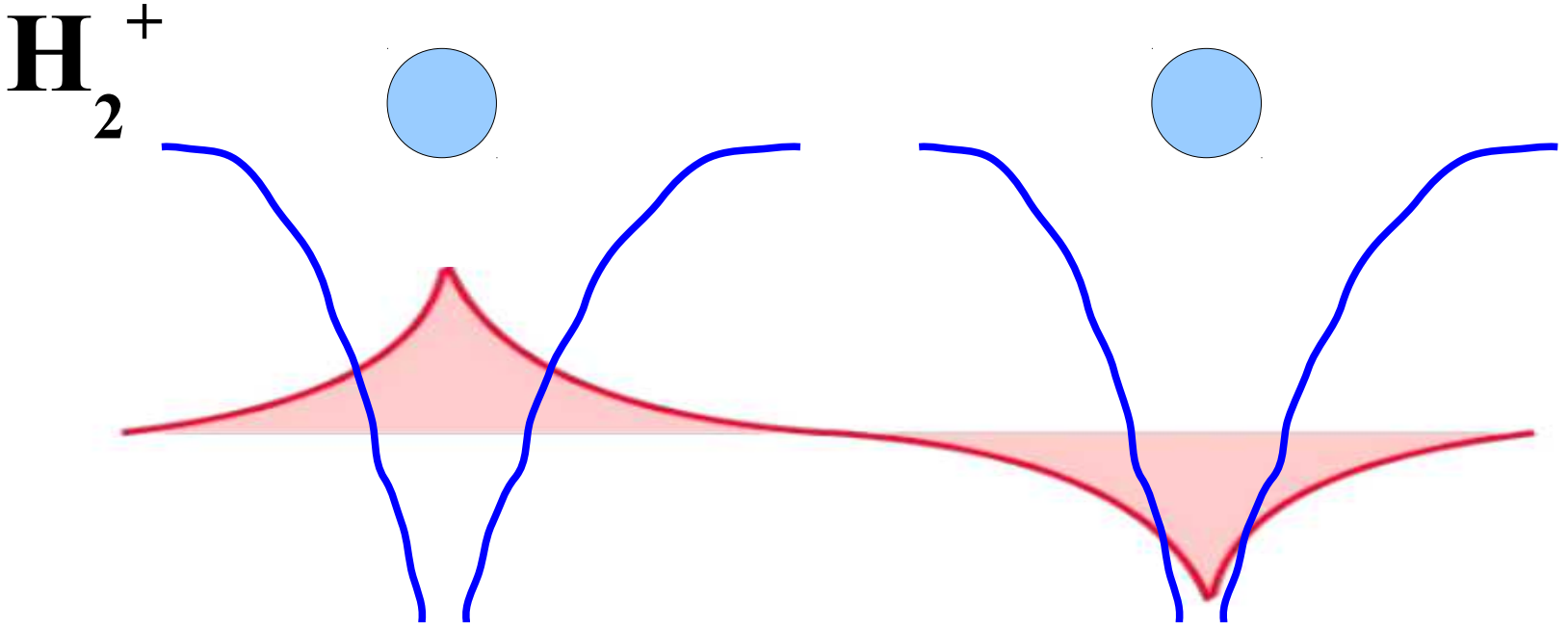

H_2^+
Classical
Quantum


H_2^+
Classical
Quantum


H_2^+
Classical
Quantum

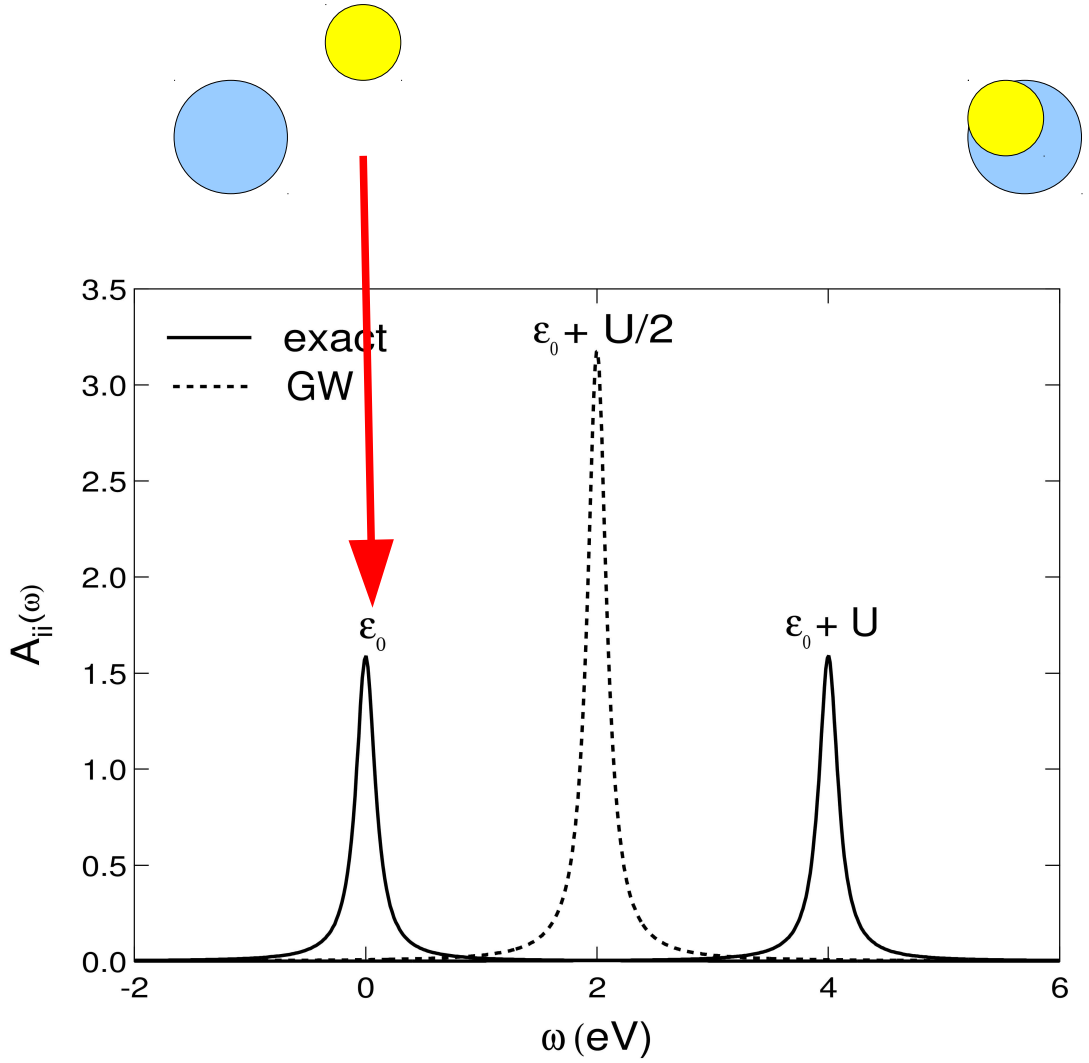


Quantum

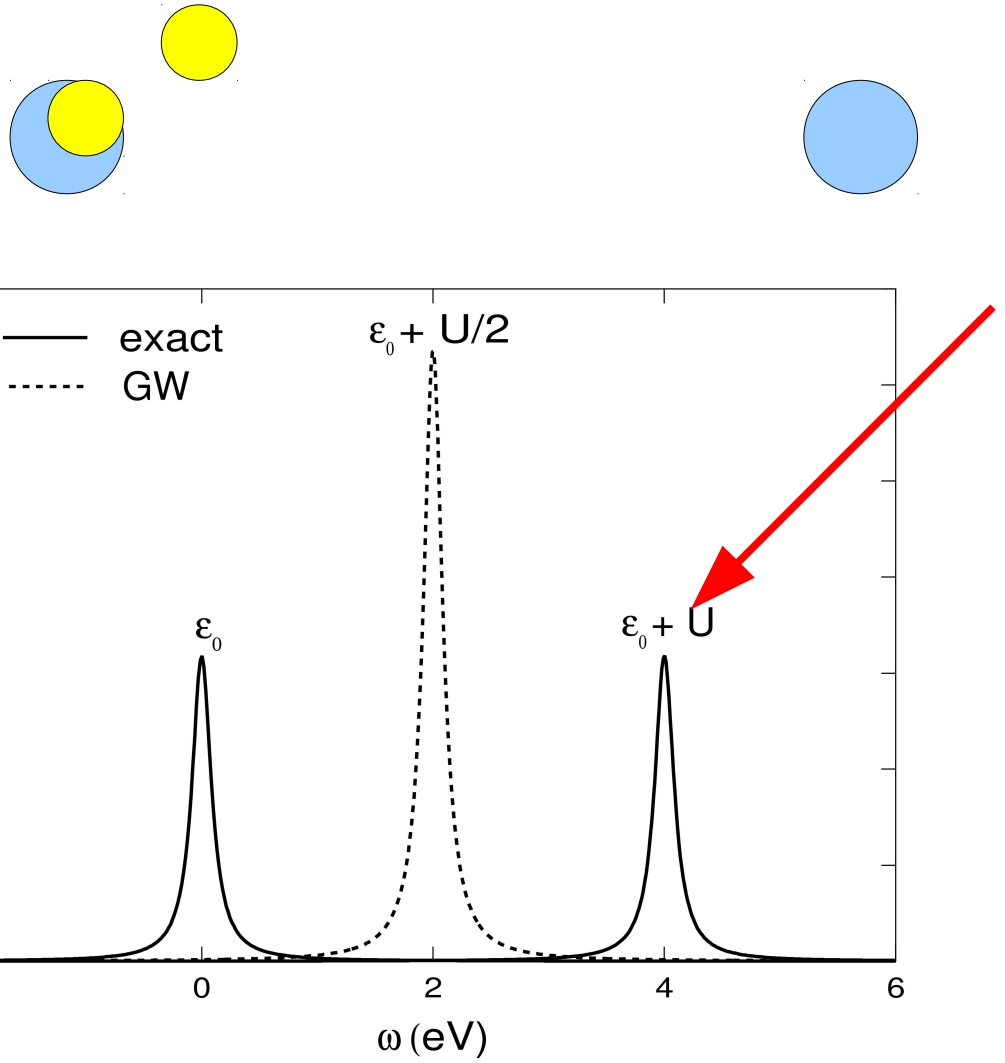


Quantum

H_2^+


exact
GW
ε_0 + U/2
ε_0
ε_0 + U
$A_{ii}(\omega)$
ω (eV)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-2
0
2
4
6

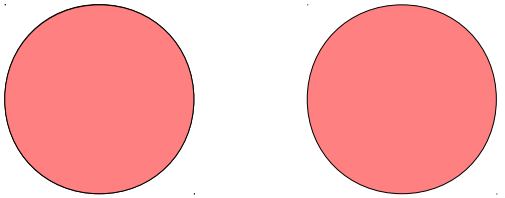
H_2^+



→ Translated into our world,
our theory must take care of the possible stories
instead of working with averages

Quantum

For example:



Quantum

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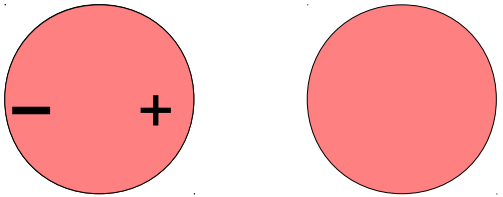

Quantum

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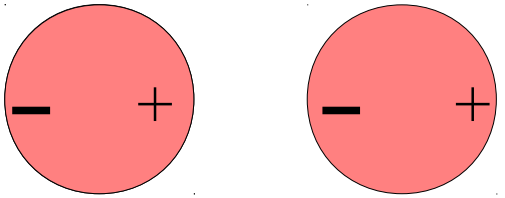
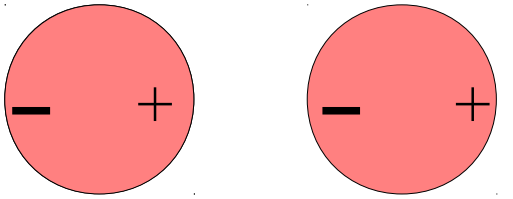
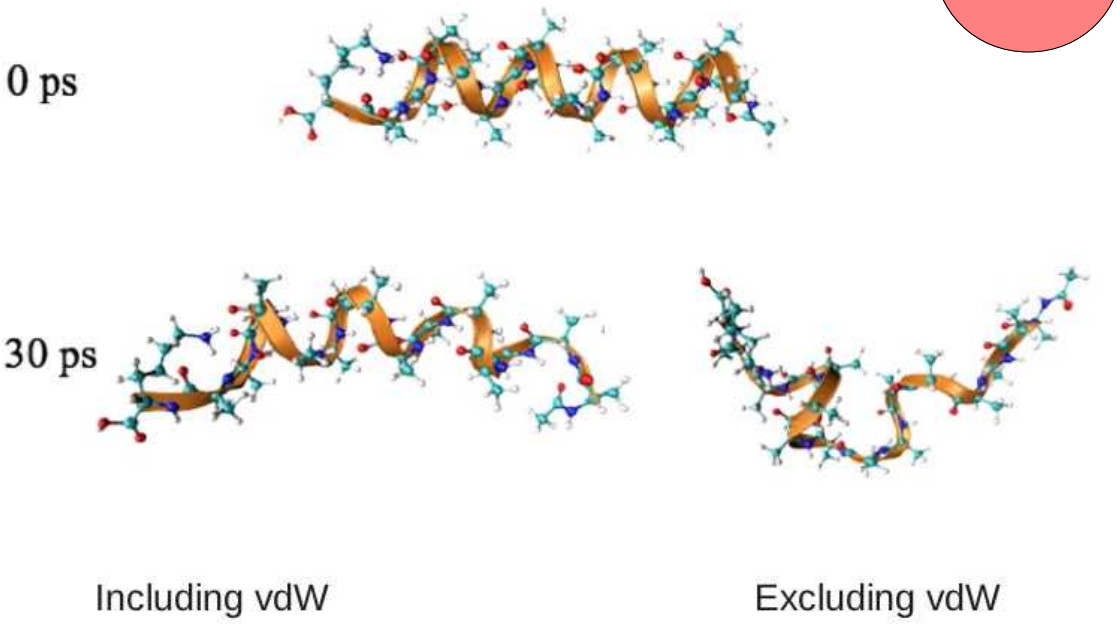


Van der Waals dispersion interaction

Quantum

Why is this important?





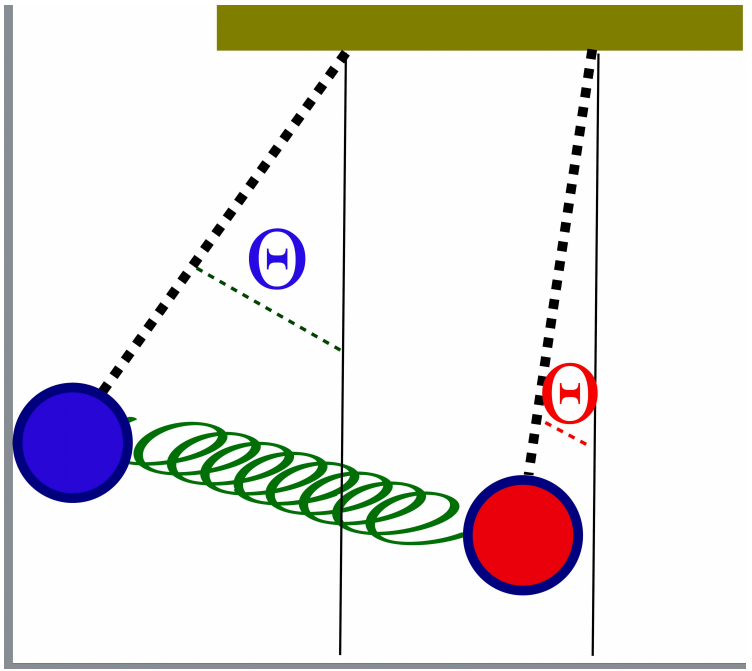
Alanine helix structures in alanine polypeptides:

→ α-helix structure is stable in experiment up to 725 K.

→ At 700 K inclusion of van der Waals contribution crucial

A. Tkatchenko, et al., Phys. Rev. Lett. 106:118102, 2011.
Figure provided by Mariana Rossi,
adapted in "Interacting Electrons", Martin, Reining, Ceperley (Cambridge 2016).

More-than-one-body problem



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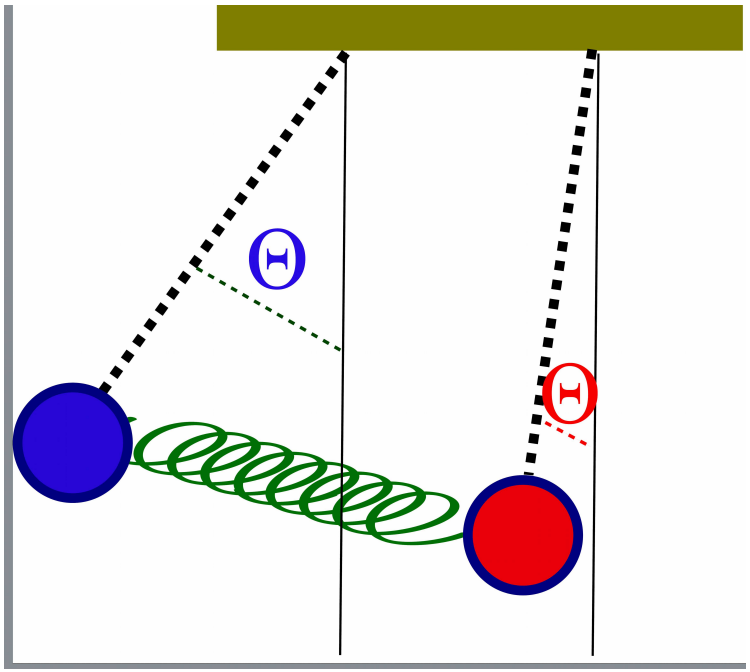
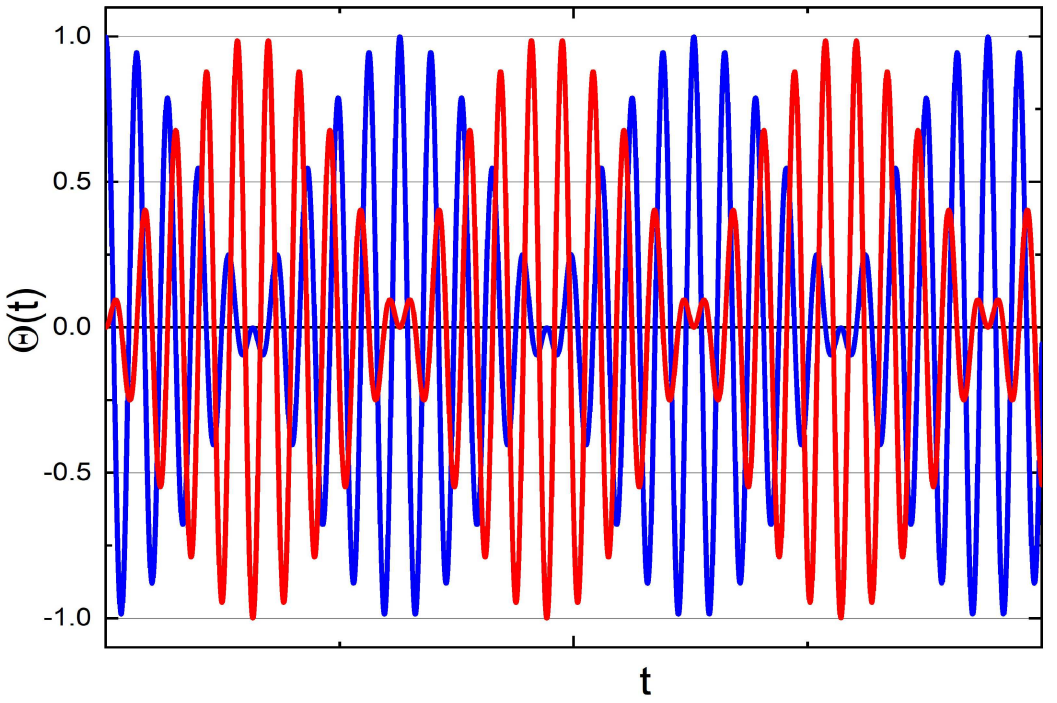


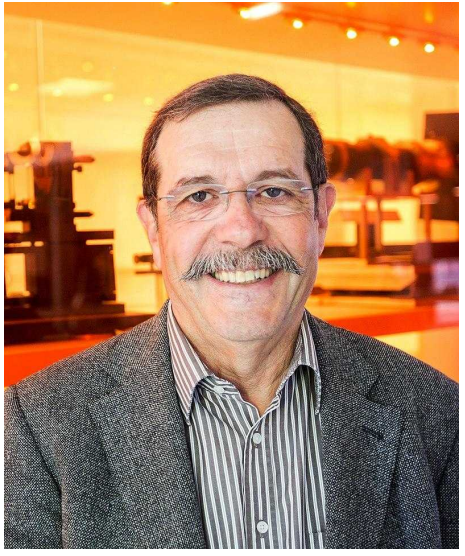


More-than-one-body problem

$$\hat{H}\Psi_\lambda(x_1, x_2, ..., x_N) = E_\lambda \Psi_\lambda(x_1, x_2, ..., x_N)$$

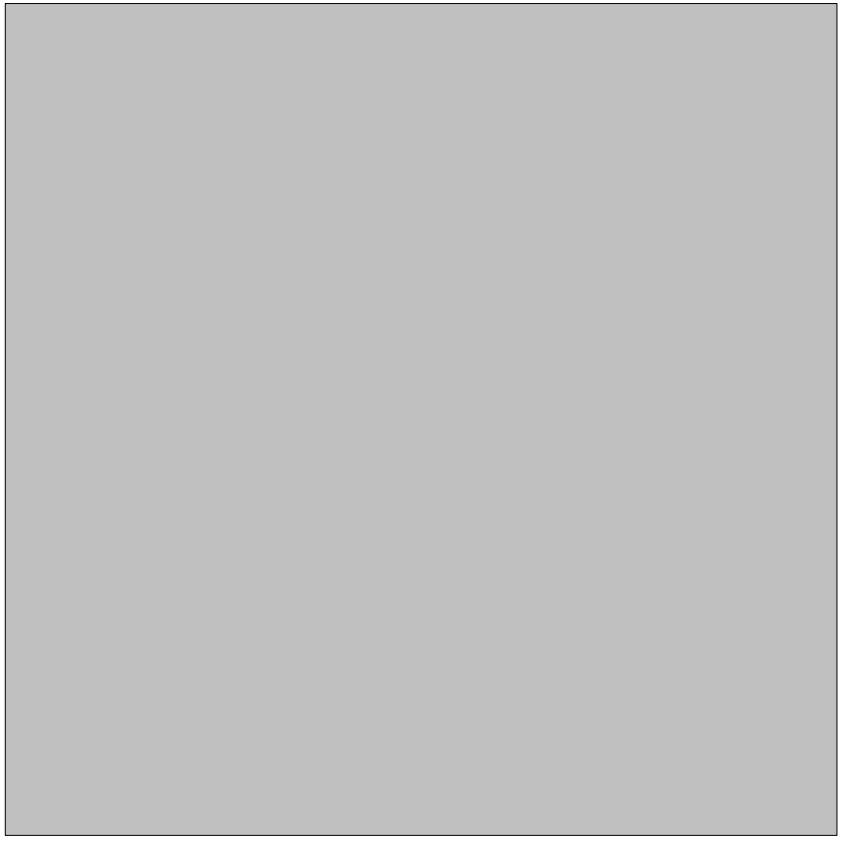
Entanglement

Alain Aspect, Nobel Prize 2022
(avec John Clauser and Anton Zeilinger)



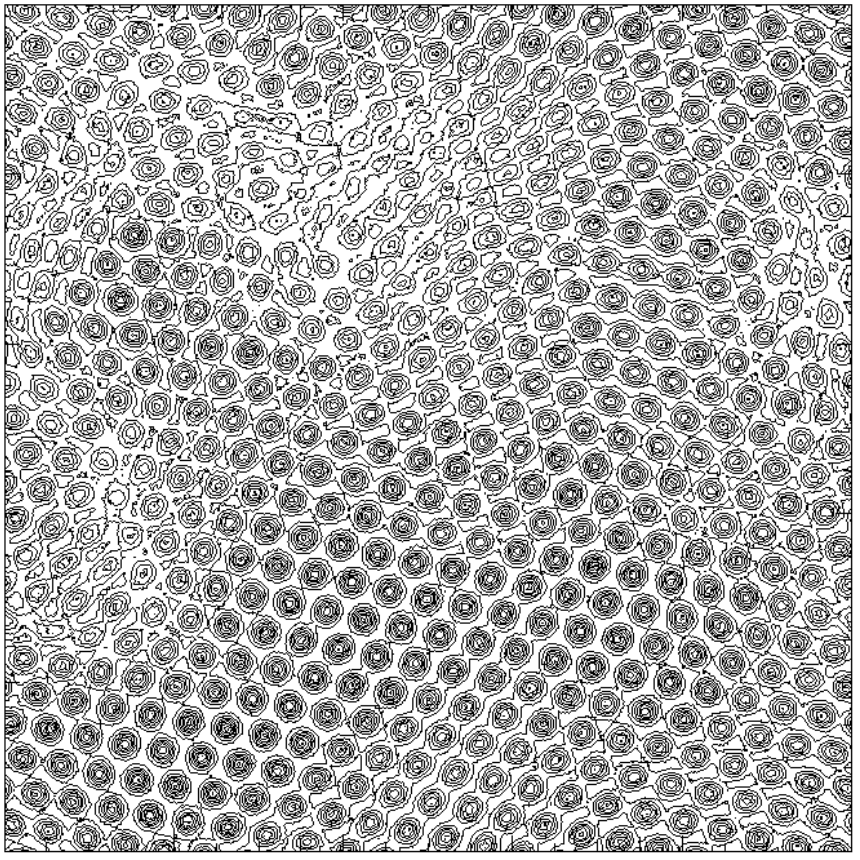
Quantum

The homogeneous electron gas on paper



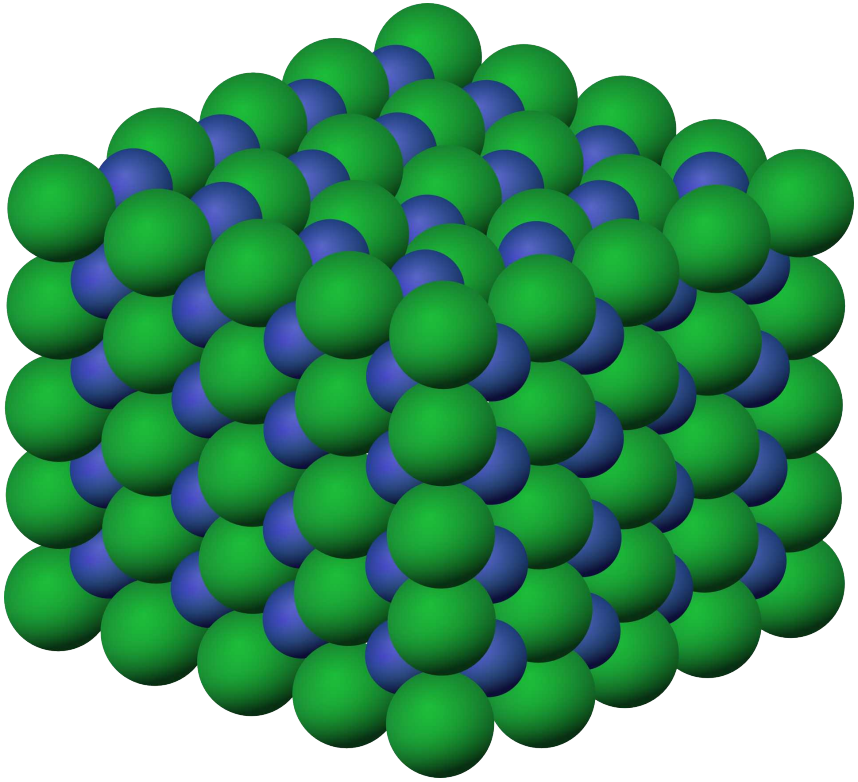
Many-body problem

When electrons decide to form an ordered structure: Wigner crystal



Path-integral Monte Carlo for a 2D Wigner crystal
From R.M. Martin, L. Reining, D.M. Ceperley, Interacting electrons, Cambride (2016)

The mere existence of crystals is an intriguing many-body effect



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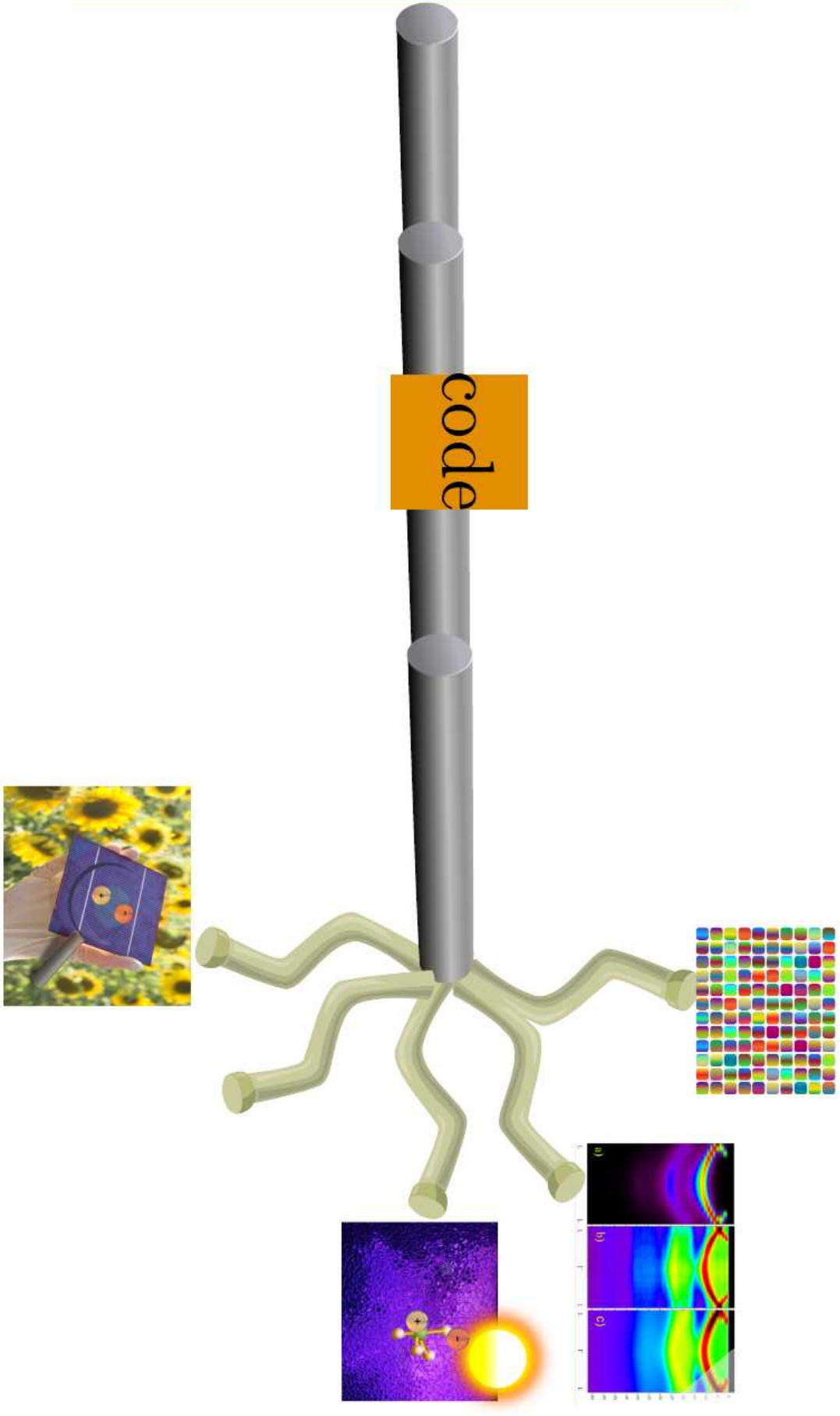

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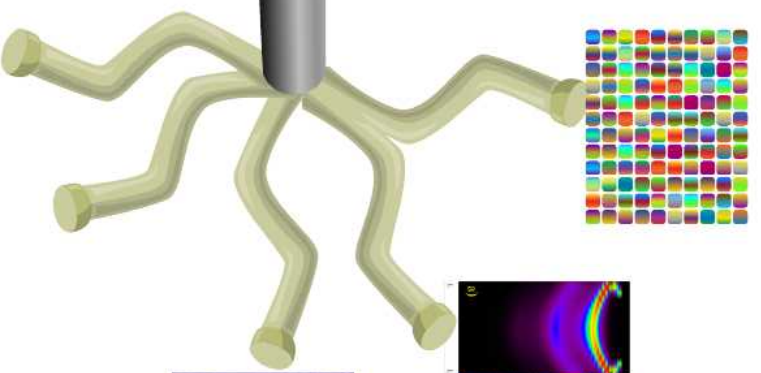
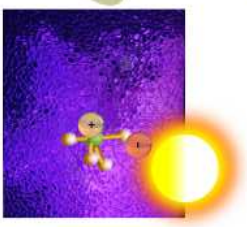
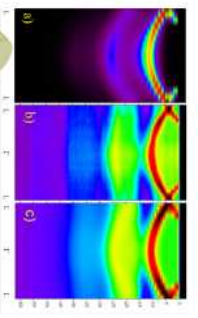
code







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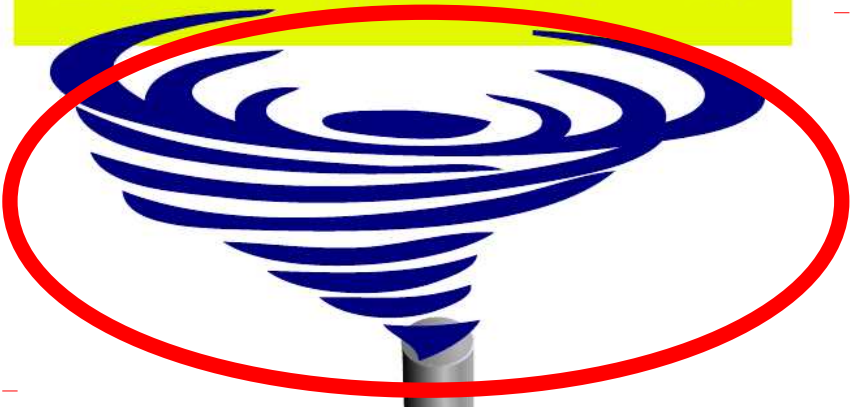
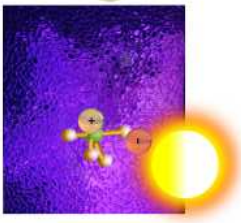
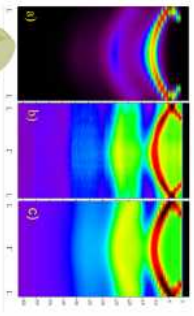
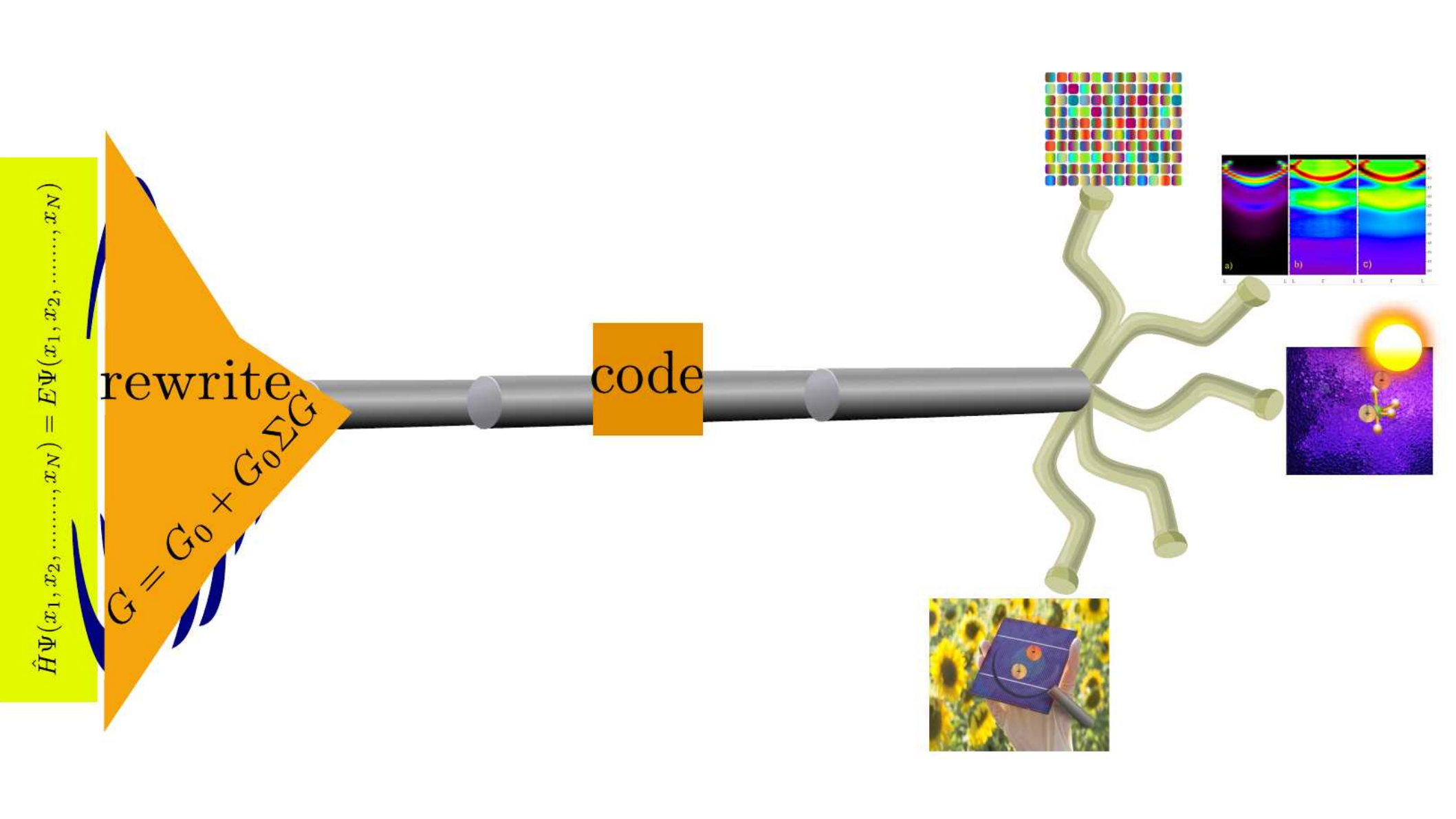


code






$\hat{H}\Psi(x_1, x_2, \ldots\ldots, x_N) = E\Psi(x_1, x_2, \ldots\ldots, x_N)$
rewrite
$G = G_0 + G_0 \Sigma G$
code

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Observation:

We are not interested in the full solution of the many-body problem

(we do not want the answer to all questions)

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$$\int dx_1 dx_2 .....dx_N \Psi^*(x_1, x_2, ..., x_N) O(.....) \Psi(x_1, x_2, ..., x_N)$$

$$O = O[\Psi]$$

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$$O = O[\Psi]$$

* well-known expression

* difficult to use

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* difficult to use

Idea: maybe we do not need Ψ in all detail

maybe a simpler quantity Q would also contain enough info

$$O = \tilde{O}[Q]$$ → e.g., type and position of all atoms?

$$O = O[\Psi]$$

* well-known expression $\int dx_1 dx_2 ..... dx_N \Psi^*(x_1, x_2, ..., x_N) O(.....) \Psi(x_1, x_2, ..., x_N)$

* difficult to use

Idea: maybe we do not need Ψ in all detail

maybe a simpler quantity Q would also contain enough info

$$O = \tilde{O}[\underbrace{Q}_{n}]$$

→ e.g., type and position of all atoms?

→ prominent choice: electron density $n(\mathbf{r})$

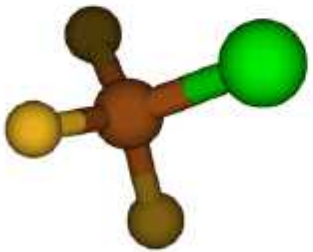
Density Functional Theory, Nobel prize Walter Kohn 1998 (chemistry)

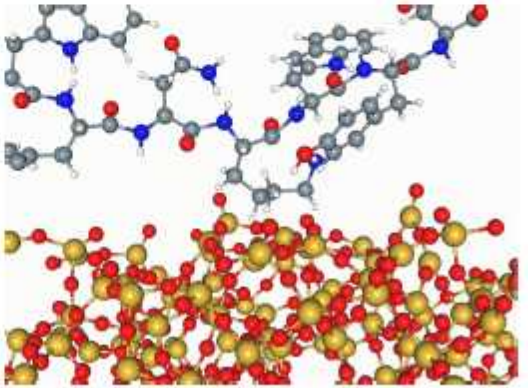
$$\Psi(x_1, x_2, ..., x_N; t)$$

$$n(\mathbf{r}; t)$$

CI, QMC

Density Functionals

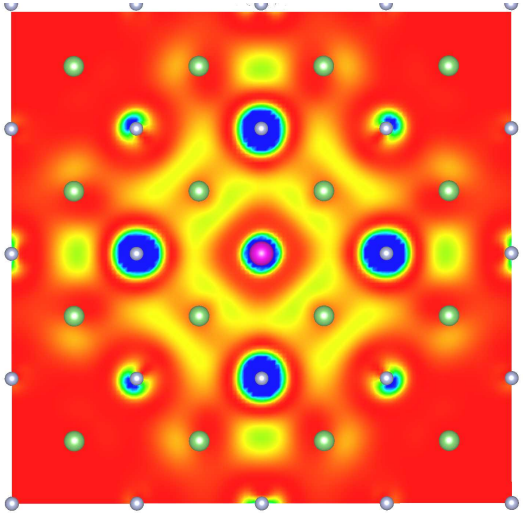




Descriptor

DFT: $n(\mathbf{r})$

But how to get Q ?



Density of excited electron in LiF
Picture: Francesco Sottile

P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964)

Descriptor

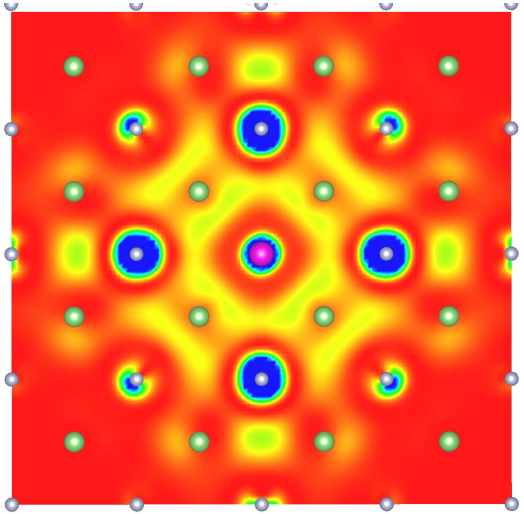
DFT: $n(\mathbf{r})$

$n(\mathbf{r})$

But how to get Q ?

Build a simplified world that gives same Q

(here: without interaction)



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W. Kohn and L. J. Sham, Phys. Rev. 140, A113 (1965)

Descriptor

Auxiliary "potential"

DFT: $n(\mathbf{r})$ $v_{\mathrm{xc}}(\mathbf{r};[n])$

But how to get Q ?

Build a simplified world that gives same Q

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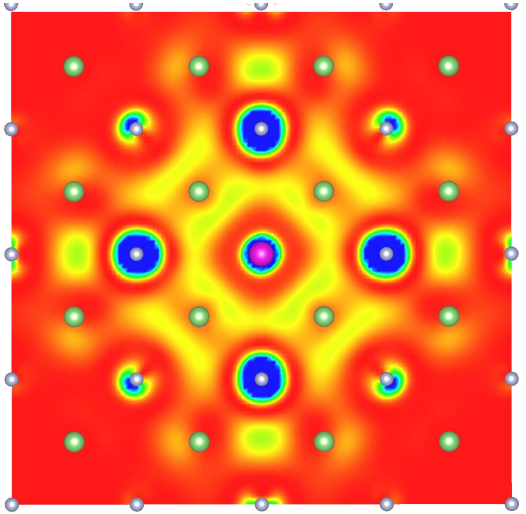

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Picture: Francesco Sottile

P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964)

W. Kohn and L. J. Sham, Phys. Rev. 140, A113 (1965)

Auxiliary system=simulation chamber

Image from pixabay:
www.noft-traders.com/establish-zero-gravity-zones-with-supply-and-demand/

Auxiliary system=simulation chamber

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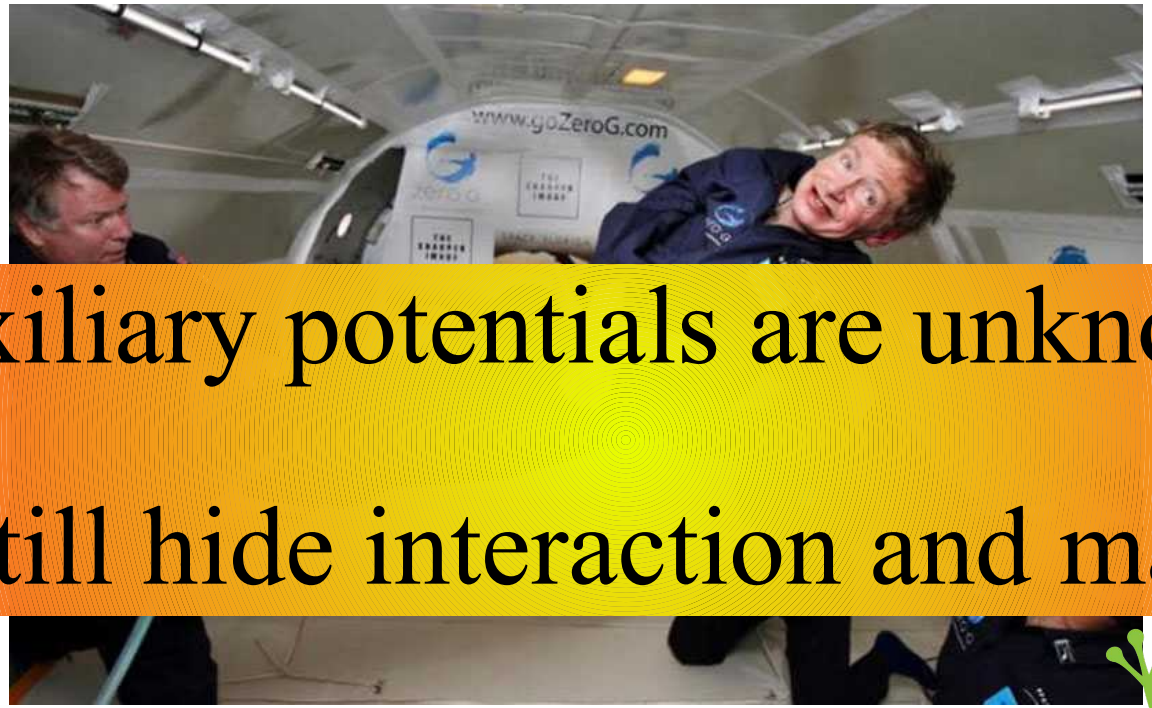


All auxiliary potentials are unknown

They still hide interaction and material

Image from pixabay:
www.noft-traders.com/establish-zero-gravity-zones-with-supply-and-demand/

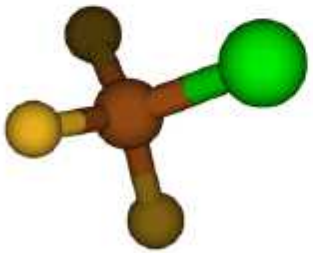
Choose a descriptor Q
to calculate $O = \tilde{O}[Q]$

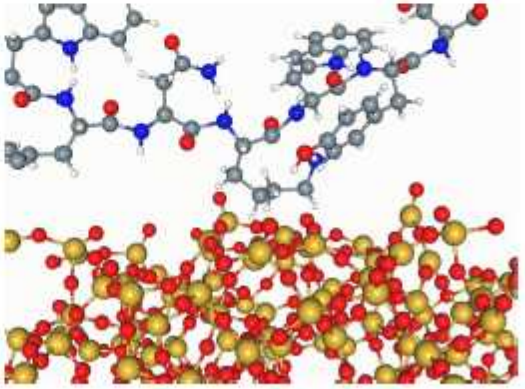
$\Psi(x_1, x_2, ..., x_N; t)$

$n(\mathbf{r}; t)$

CI, QMC

Density Functionals





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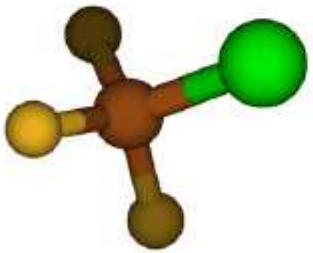
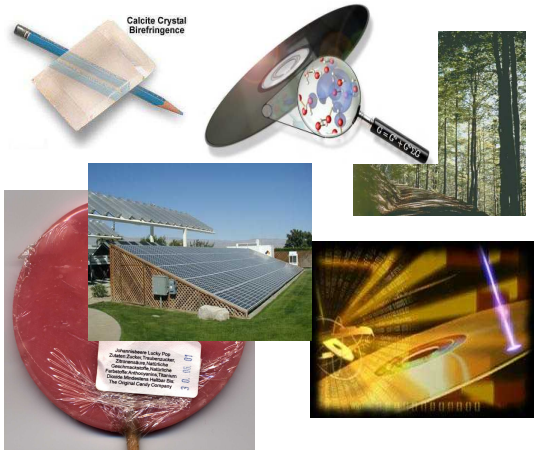
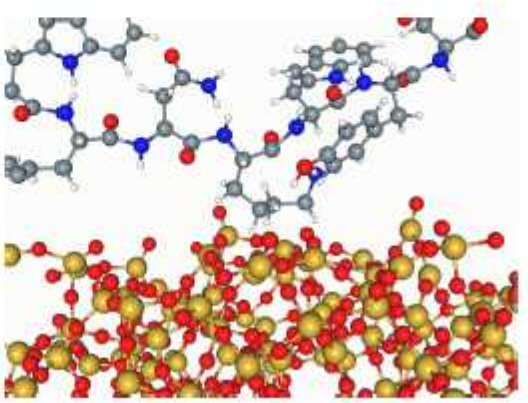
$\Psi(x_1, x_2, ..., x_N; t)$??? $n(\mathbf{r}; t)$

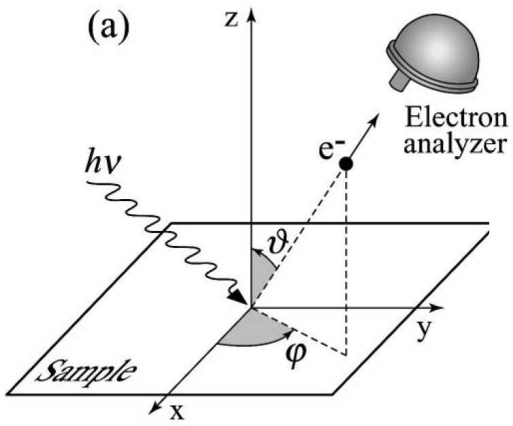
CI, QMC





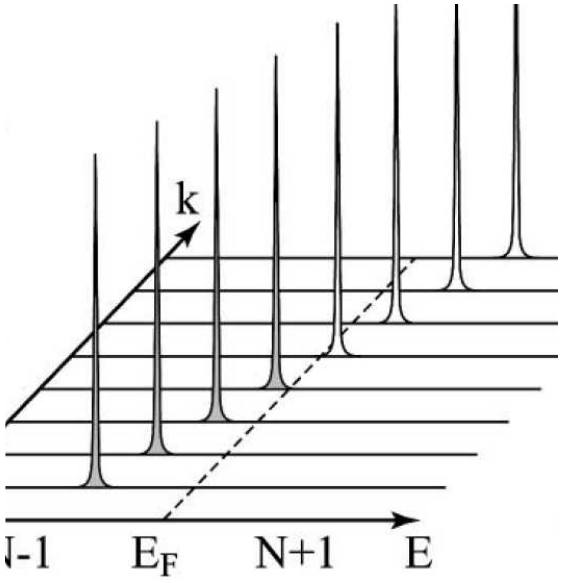
Density Functionals

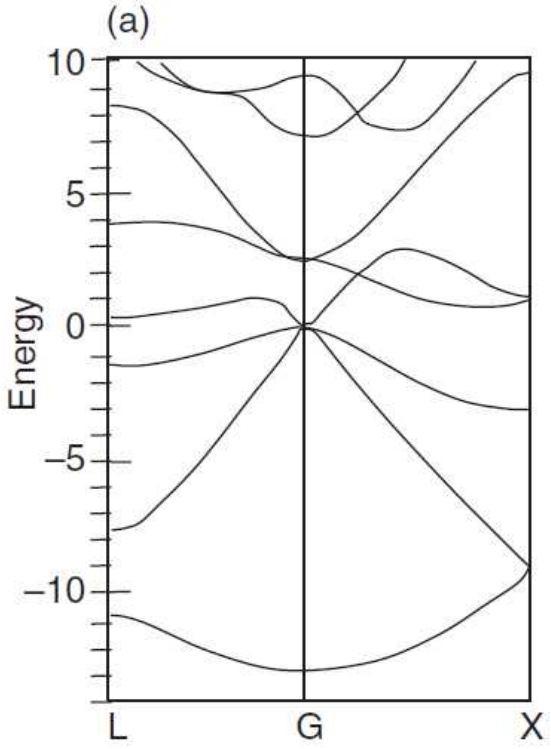




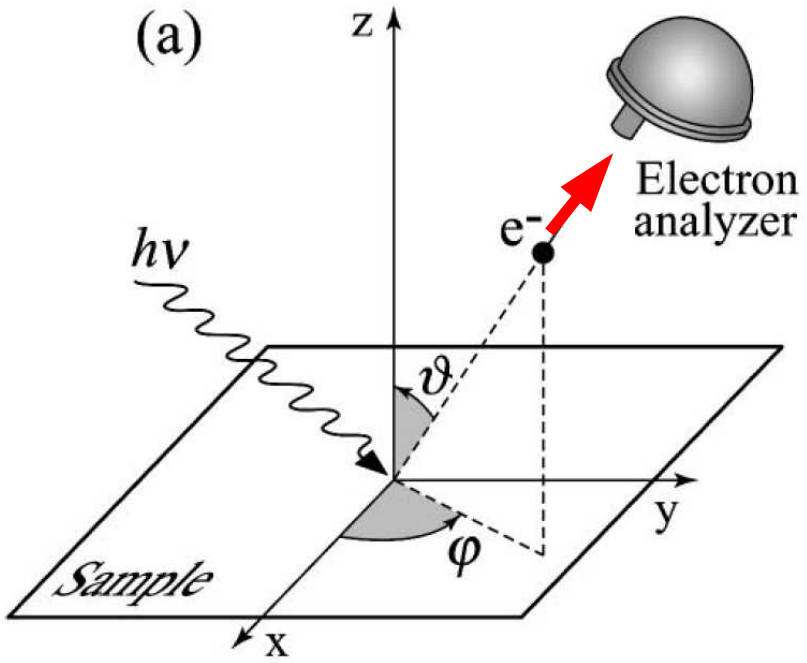
Photoemission geometry

From Damascelli et al., RMP 75, 473 (2003)





Can we use this approximation for photoemission spectra?



Photoemission geometry

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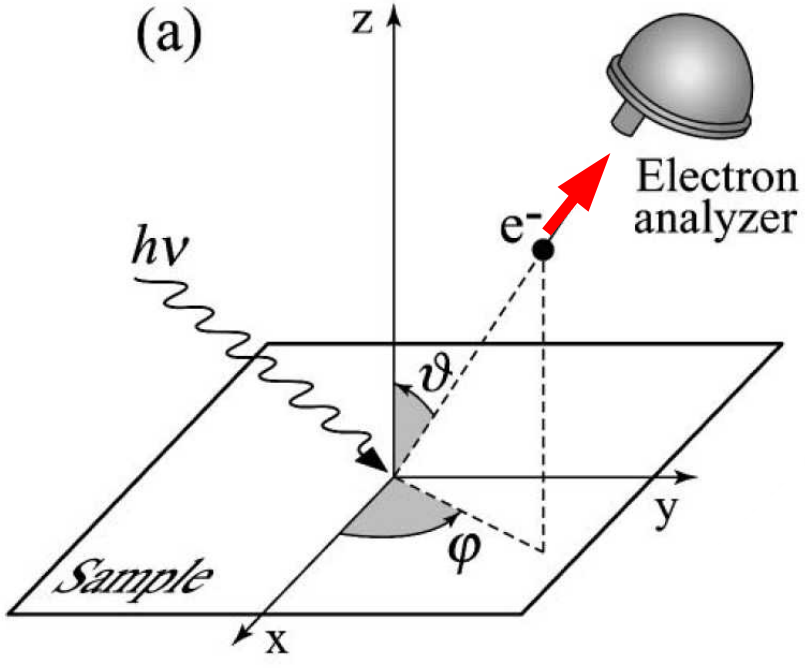

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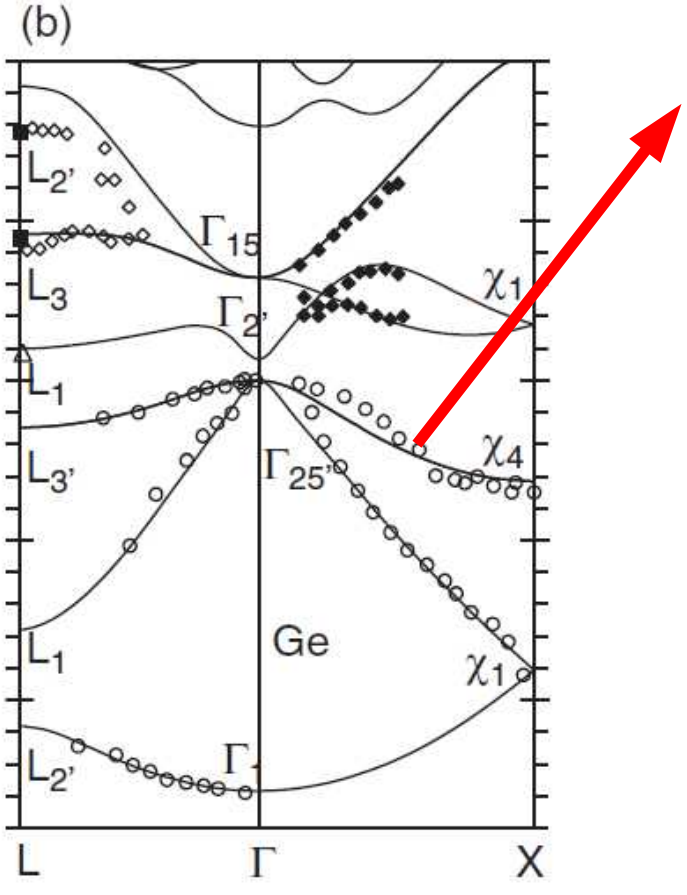

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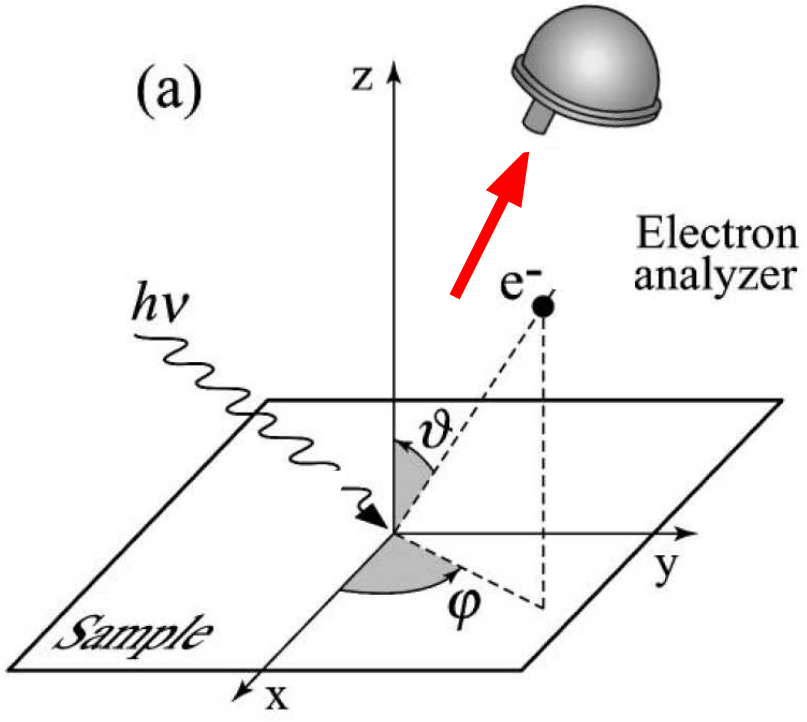

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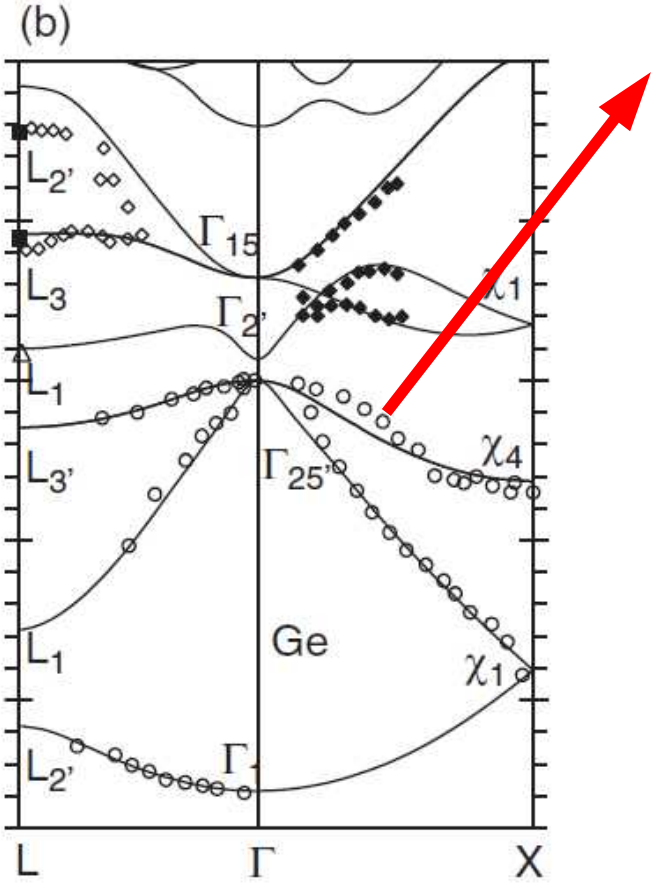

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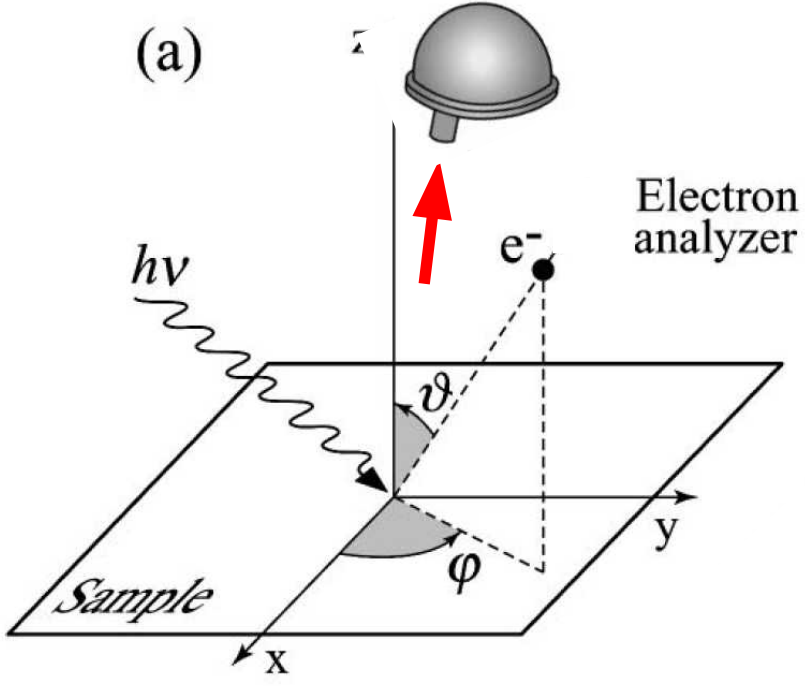
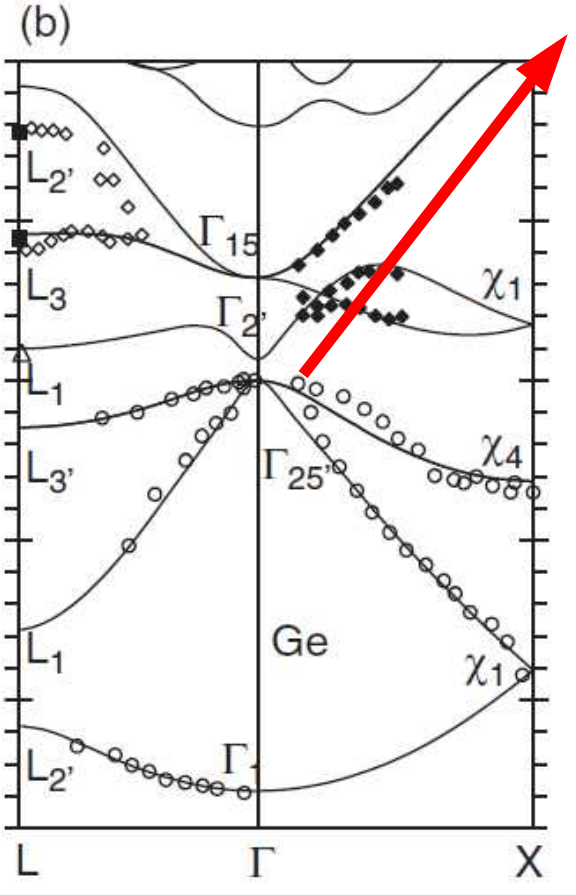


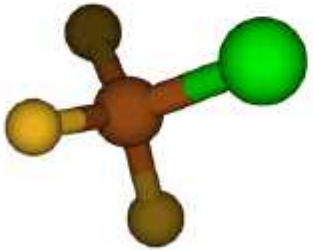
Photoemission geometry



We know how to calculate spectra: $A_{\mathbf{k}}(\omega;[G]) = \frac{1}{\pi}|\mathrm{Im}\, G_{\mathbf{kk}}(\omega)|$

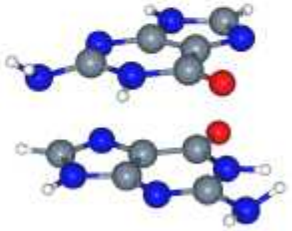
$\Psi(x_1, x_2, ..., x_N; t)$

CI, QMC



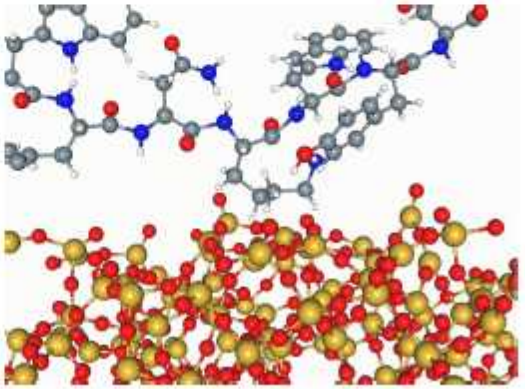
$G(x_1, x_1', t, t')$

Green's Functions



$n(\mathbf{r}; t)$

Density Functionals



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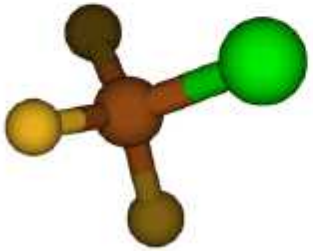

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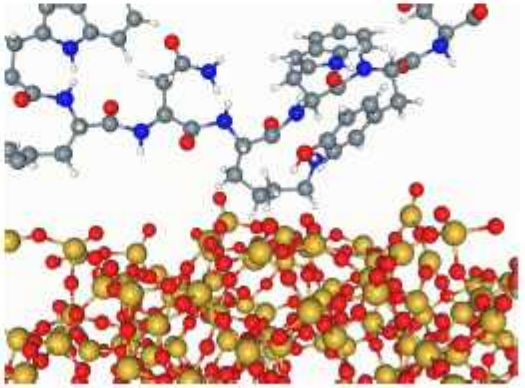
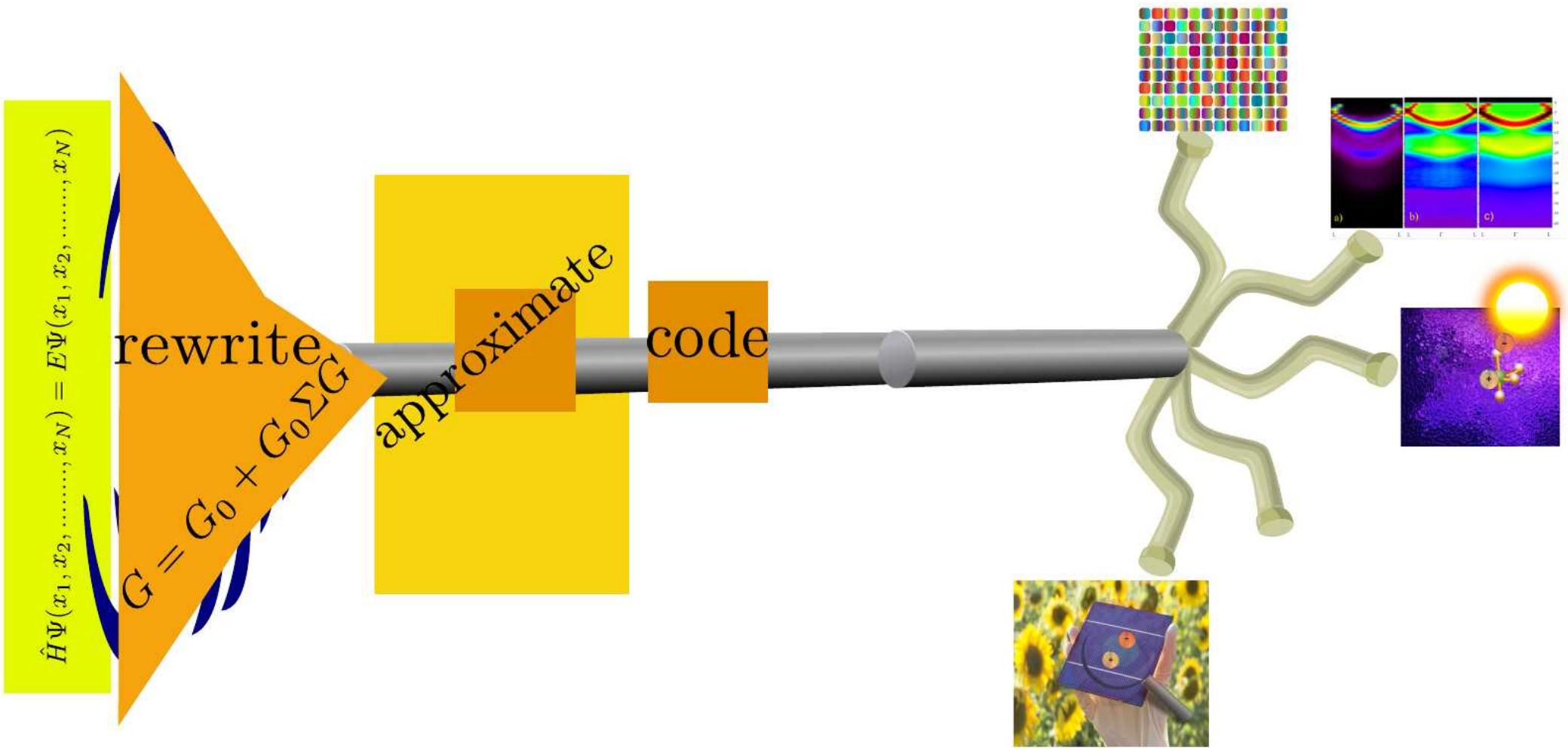



$\hat{H}\Psi(x_1, x_2, \ldots\ldots, x_N) = E\Psi(x_1, x_2, \ldots\ldots, x_N)$
rewrite
$G = G_0 + G_0 \Sigma G$
approximate
code

La mécanique quantique dans les systèmes à N corps

→ What is our job?

→ We are physicists: the quantum many-body problem

→ Re-writing: functionals

→ Approximating: many-body perturbation theory

→ the synchrotron, back and forth

→ …..and coding: a quantum video camera

→ motivated by a museum

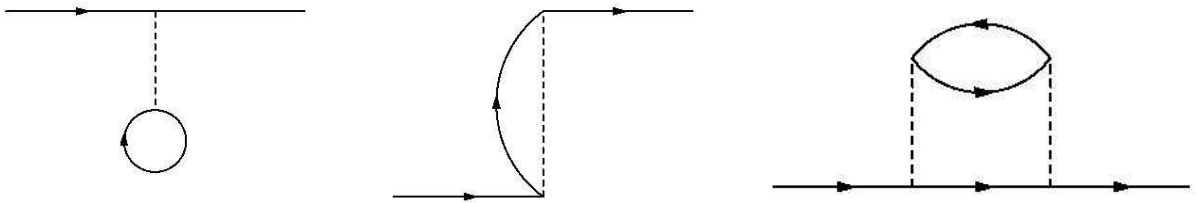
→ Less petrol in the pipeline: Connector approach

→ an ecological use of models

→ Remarks

Typical GFFT approximation strategy

$$G(x_1, x_1', t, t') = -i\langle N|T[\hat{\Psi}(x_1, t)\hat{\Psi}^{\dagger}(x_1', t')]|N\rangle$$



Many-body perturbation theory = story writing

$$\hat{H}\Psi_{\lambda}(x_1, x_2, ..., x_N) = E_{\lambda}\Psi_{\lambda}(x_1, x_2, ..., x_N)$$

Typical GFFT approximation strategy

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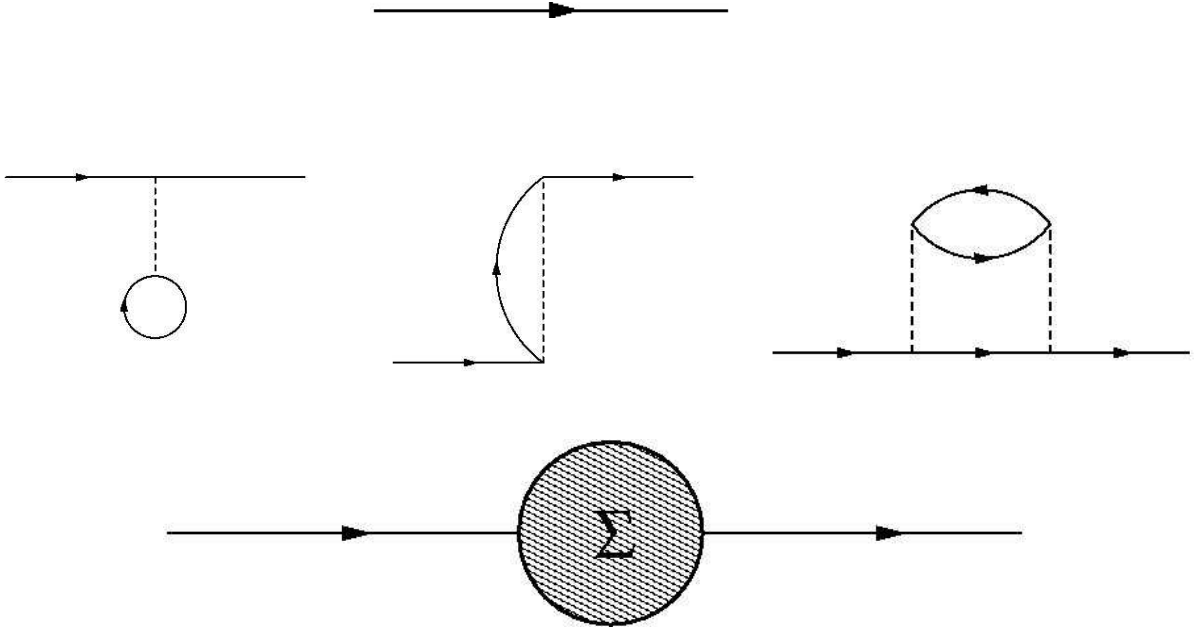

Dyson equation: $G = G_0 + G_0 \Sigma G$

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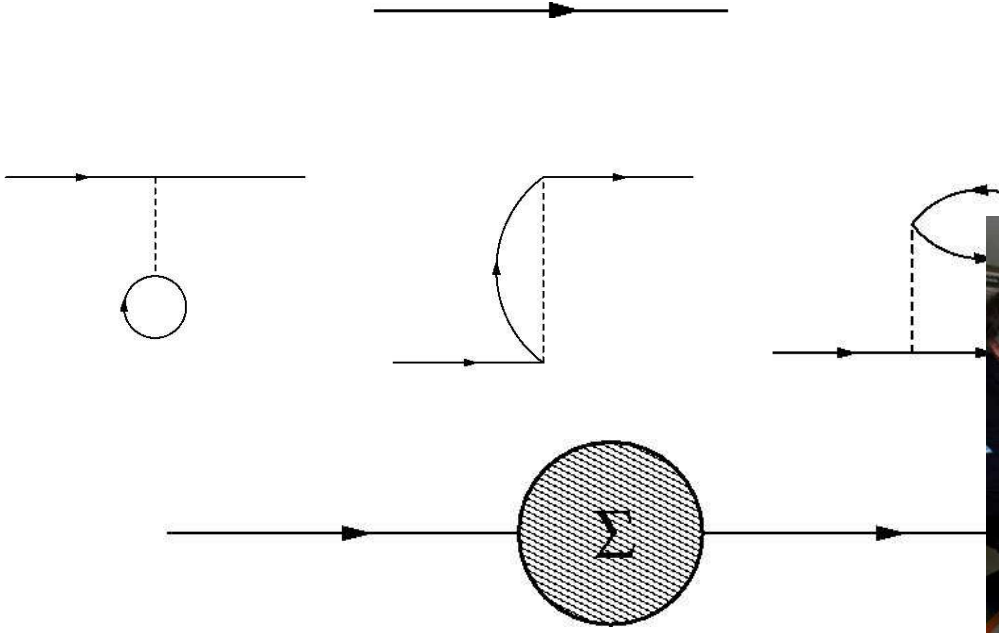

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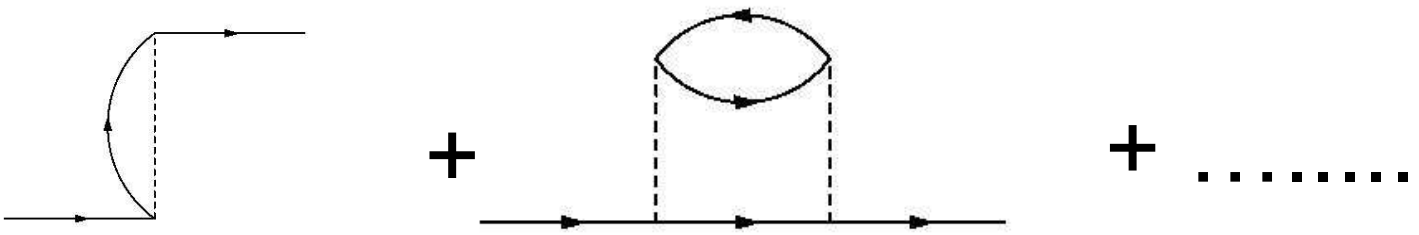
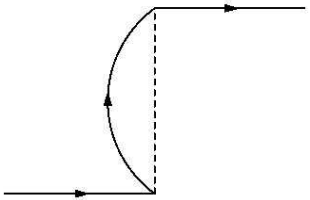


$\rightarrow \Sigma \sim i\,WG$ “GW”

$W = \varepsilon^{-1}(\omega)\, v$

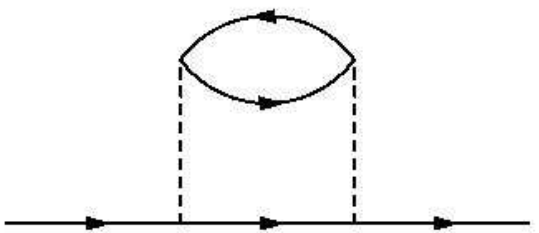
L. Hedin, Phys. Rev. 139:A796–823, 1965

Hartree-Fock



GW

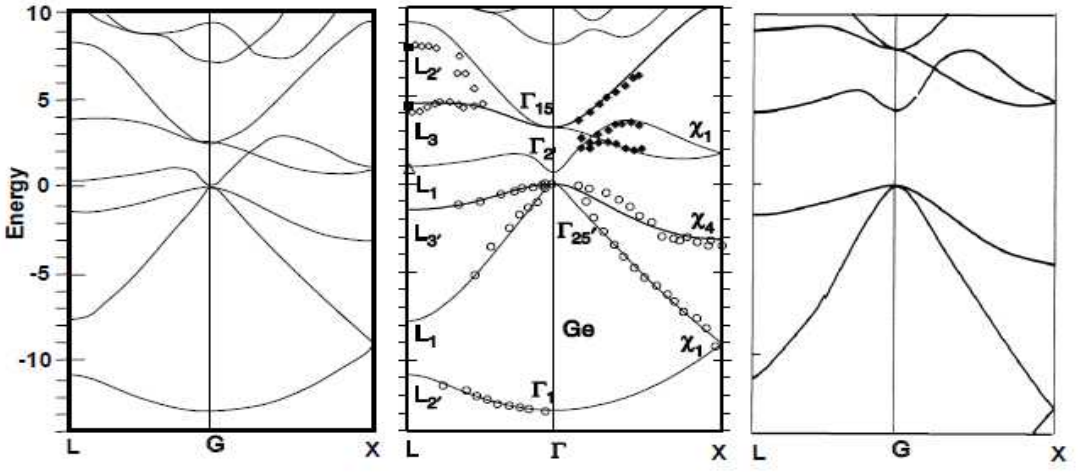
“electronic polaron”

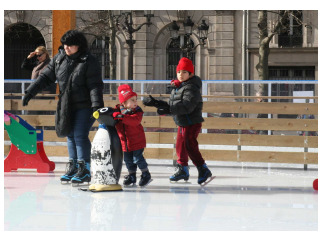


+ .....

GW today: standard for bandstructures

DFT GW HF





GW calculations, Rohlfing et al., PRB 48, 17791 (1993)

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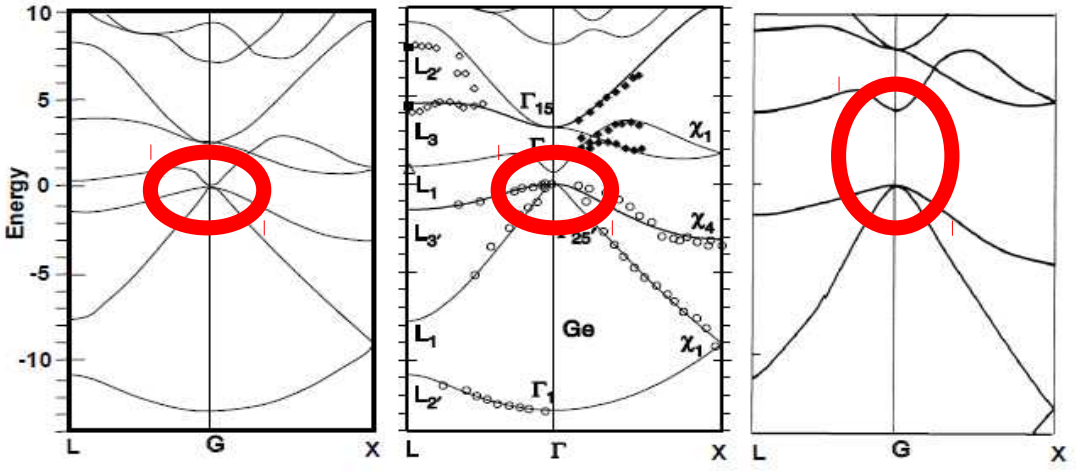

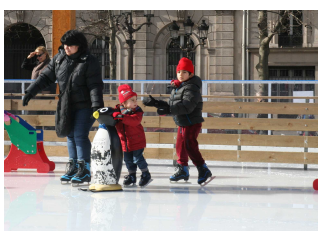

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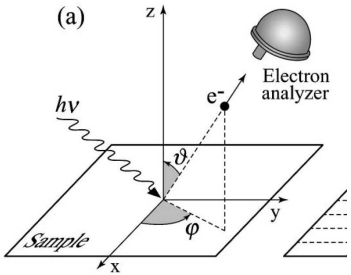
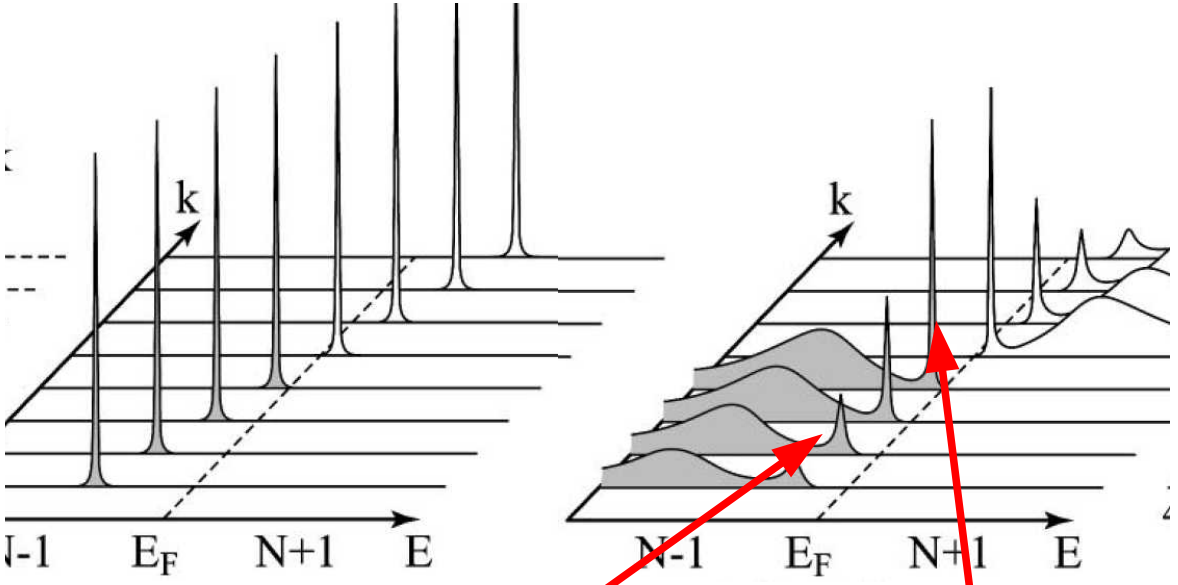
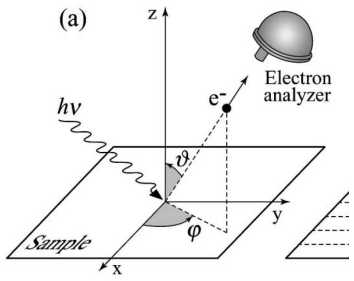


Photoemission geometry



Broadening

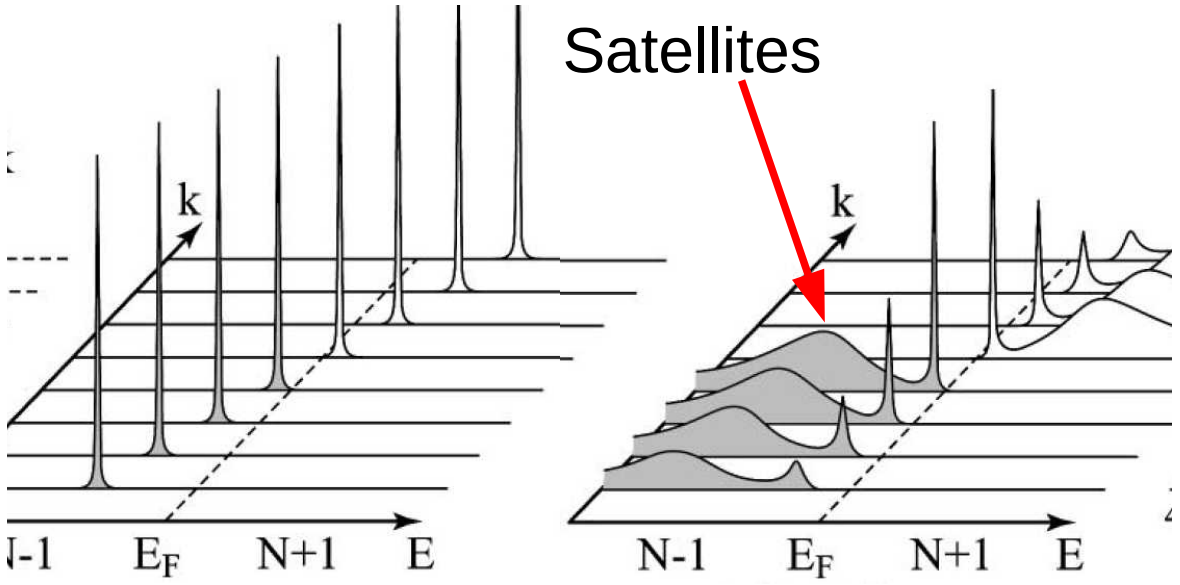
Renormalization



Photoemission geometry

Satellites: long story…..

Matteo Gatti, Matteo Guzzo, Giovanna Lani, Pina Romaniello, Francesco Sottile, J. Sky Zhou Josh Kas & John Rehr



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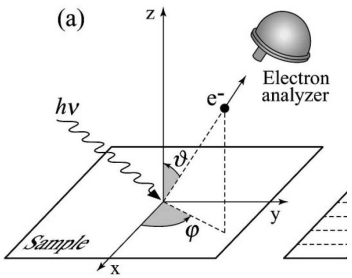

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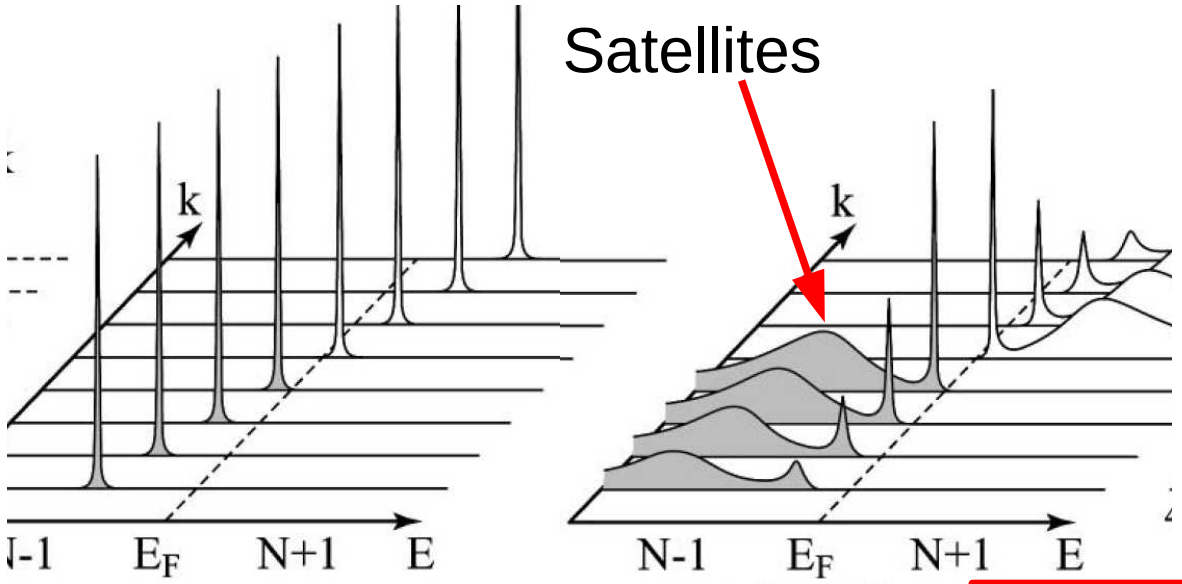
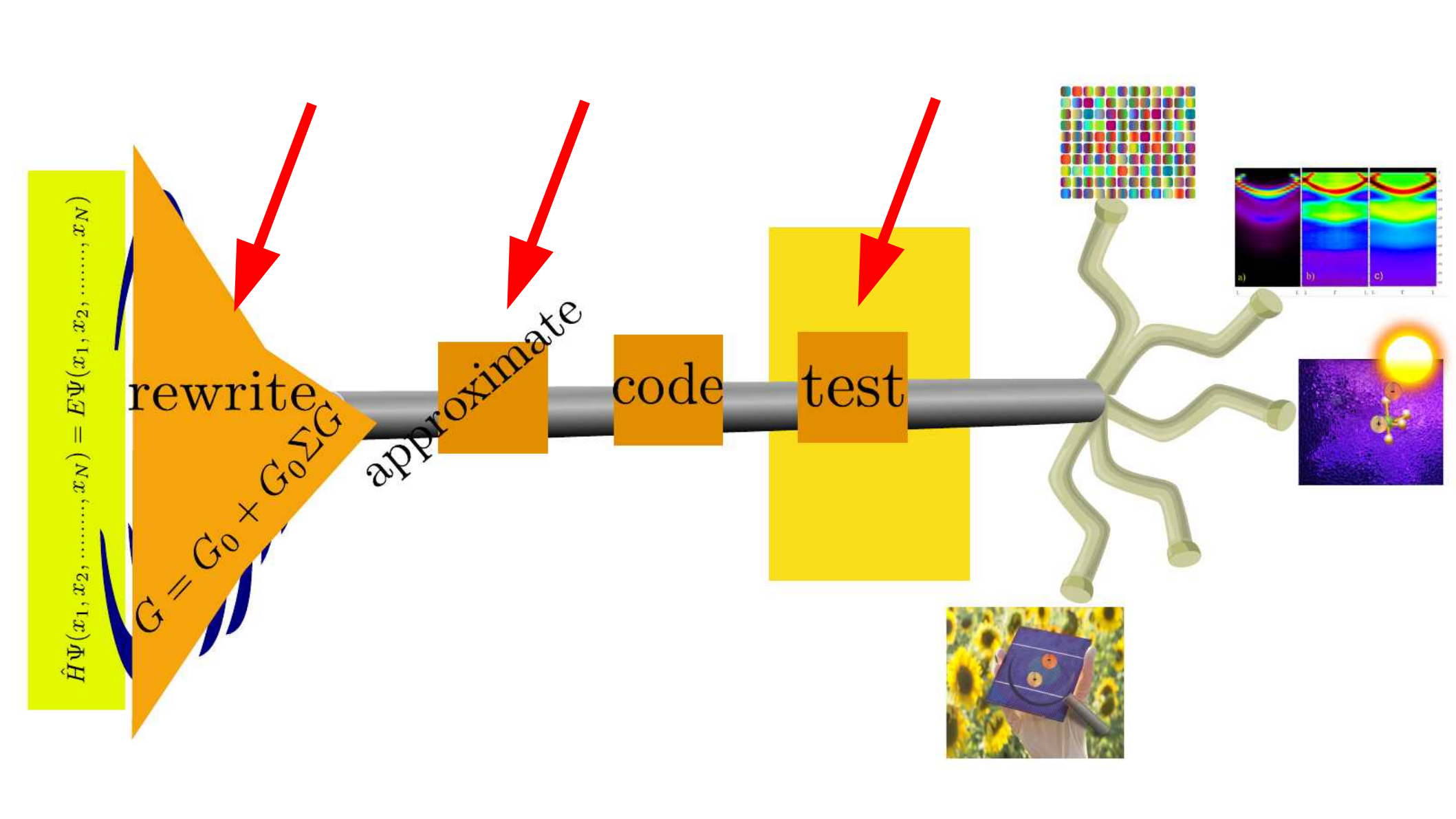


We had to change the auxiliary system

$$G(t_1, t_2) = G_{\mathrm{cl}}(t_1, t_2) e^{C(t_1, t_2)}$$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rewrite
$G = G_0 + G_0 \Sigma G$
approximate
code
test

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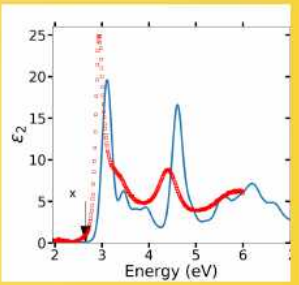
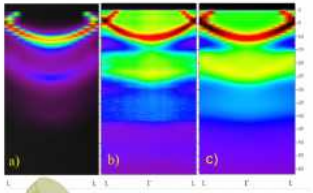
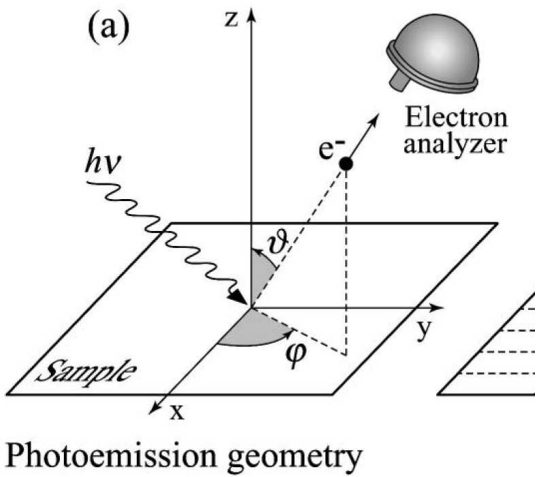




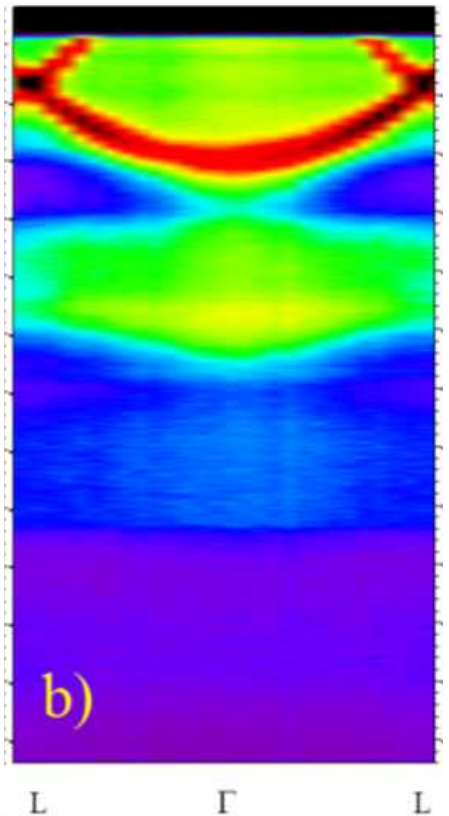
Photoemission of bulk aluminum

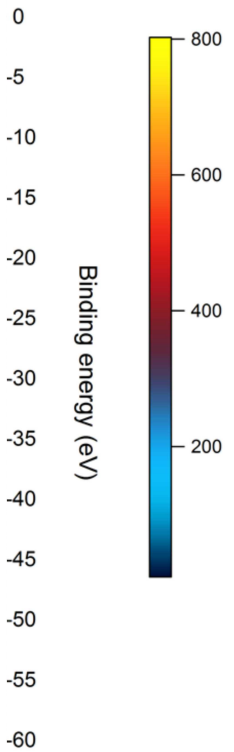
Experiment → the synchrotron, back and forth



Photoemission geometry

From Damascelli et al., RMP 75, 473 (2003)





Zhou, Reining, Nicolaou, Bendounan, Ruotsalainen, Vanzini, Kas, Rehr, Muntwiler, Strocov, Sirotti, Gatti, PNAS 117 (46), 28596 (2020)

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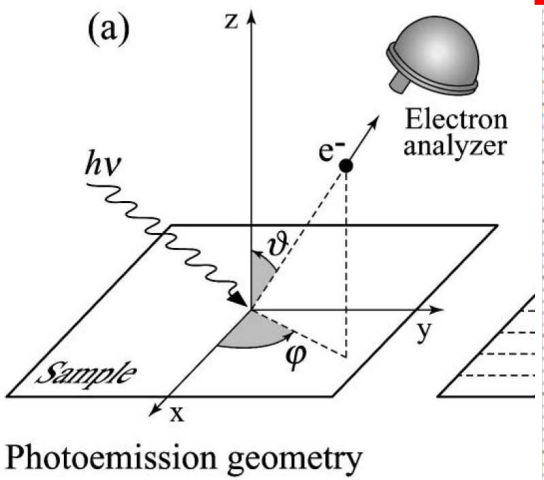

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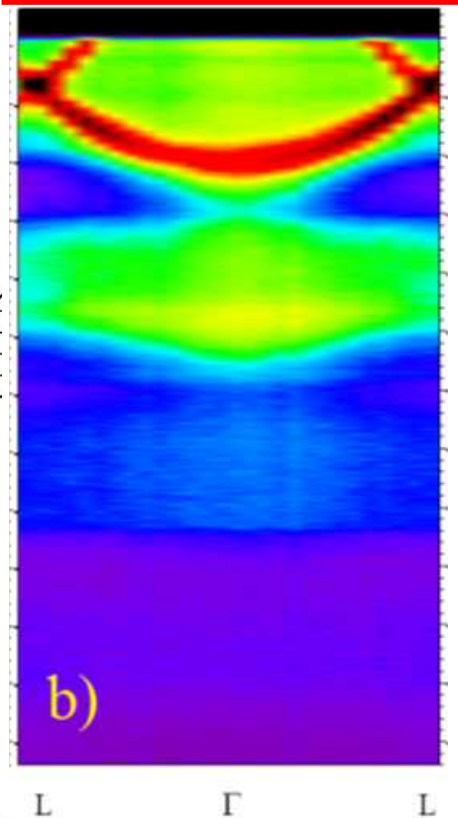
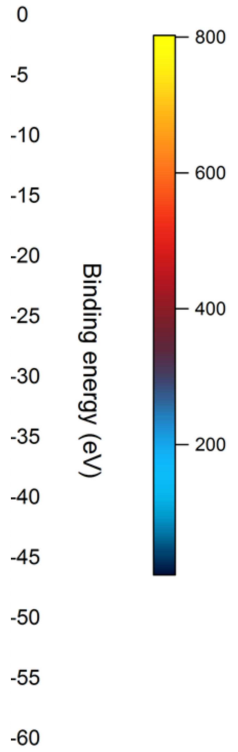
From Damascelli et al., RMP 75, 473 (2003)



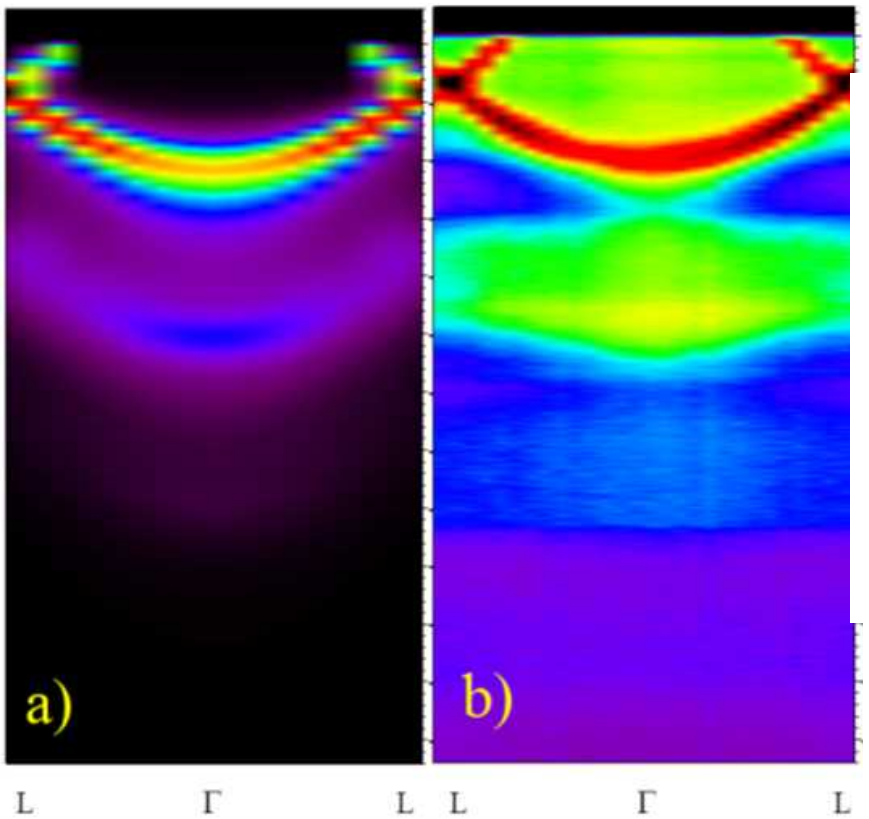


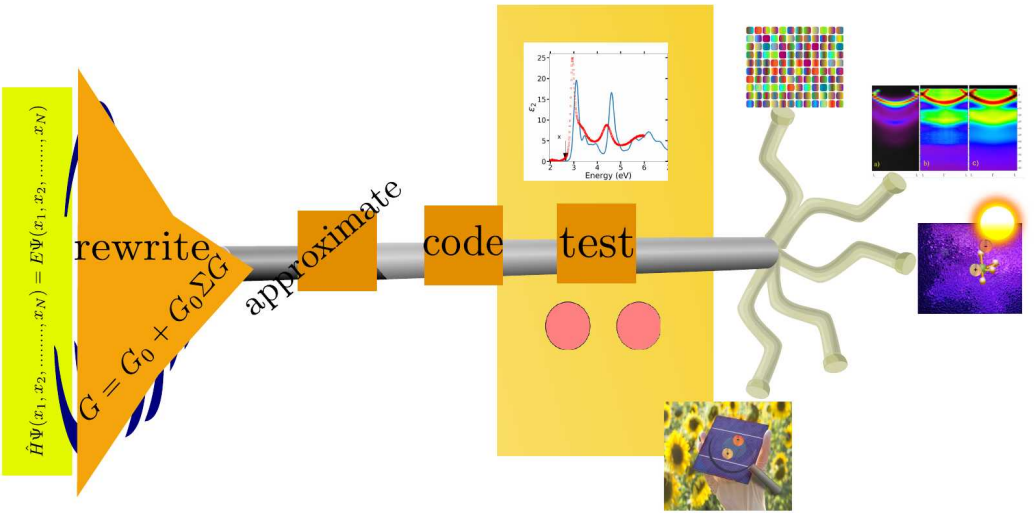
Zhou, Reining, Nicolaou, Bendounan, Ruotsalainen, Vanzini, Kas, Rehr, Muntwiler, Strocov, Sirotti, Gatti, PNAS 117 (46), 28596 (2020)

Photoemission of bulk aluminum

GW+C spectrum

Experiment





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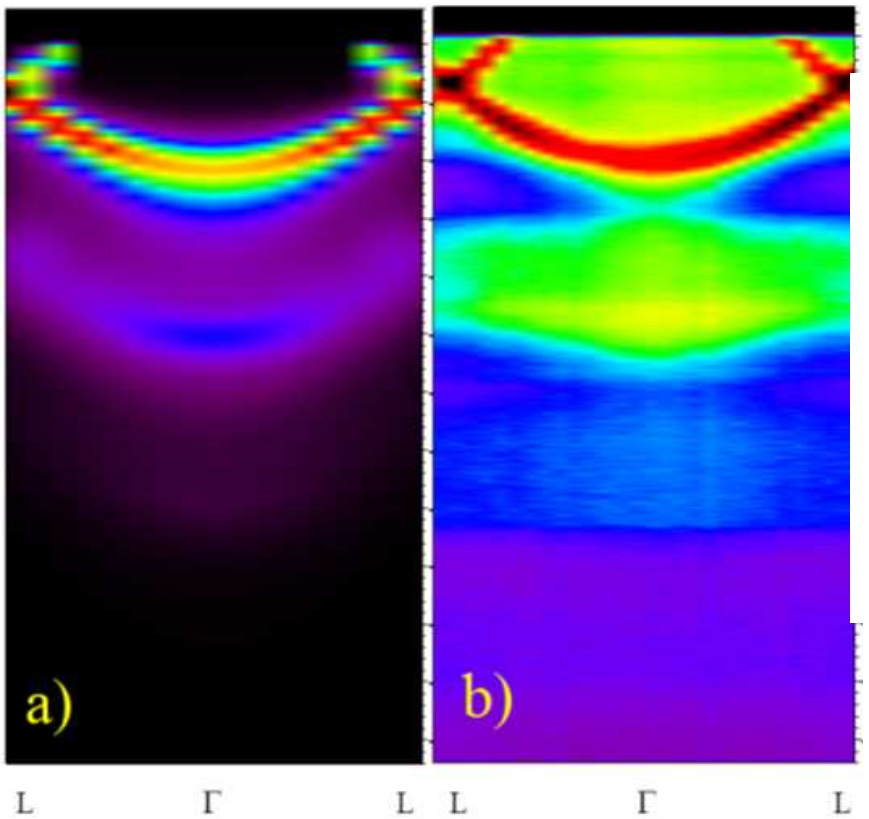

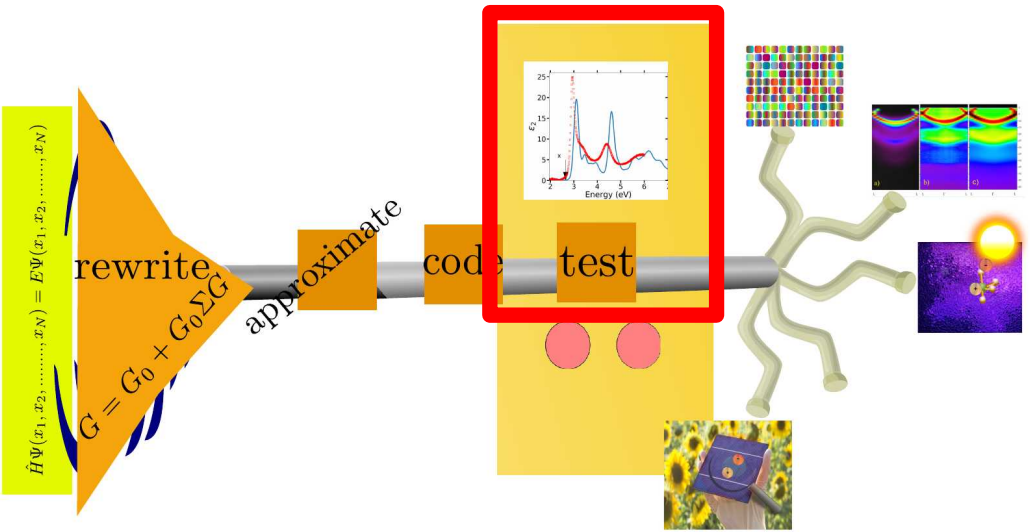

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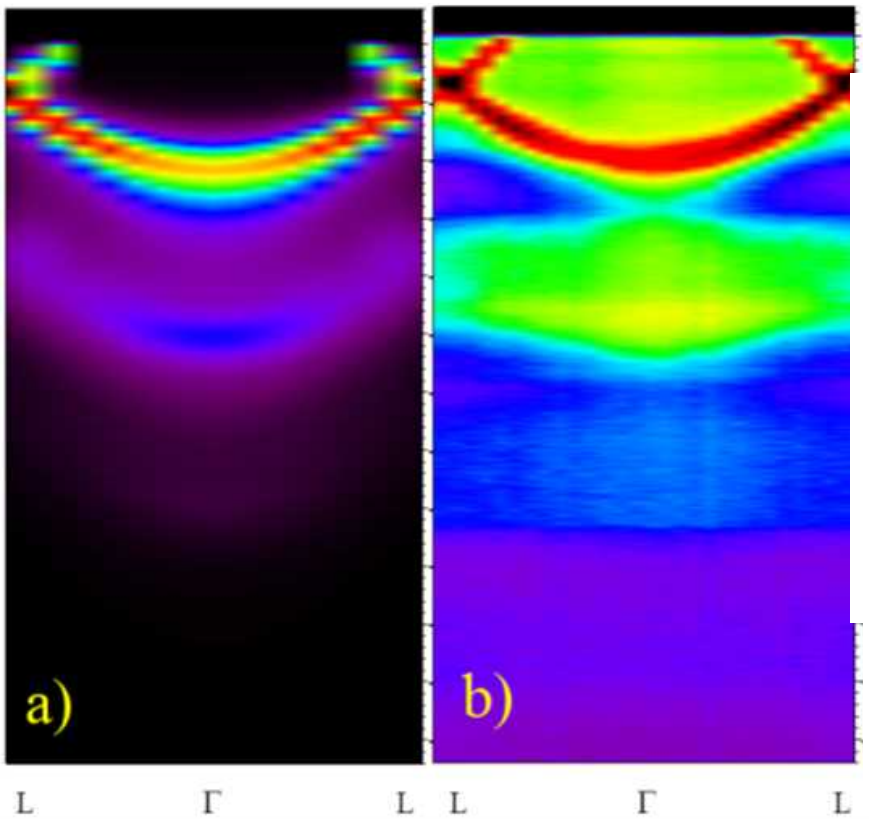
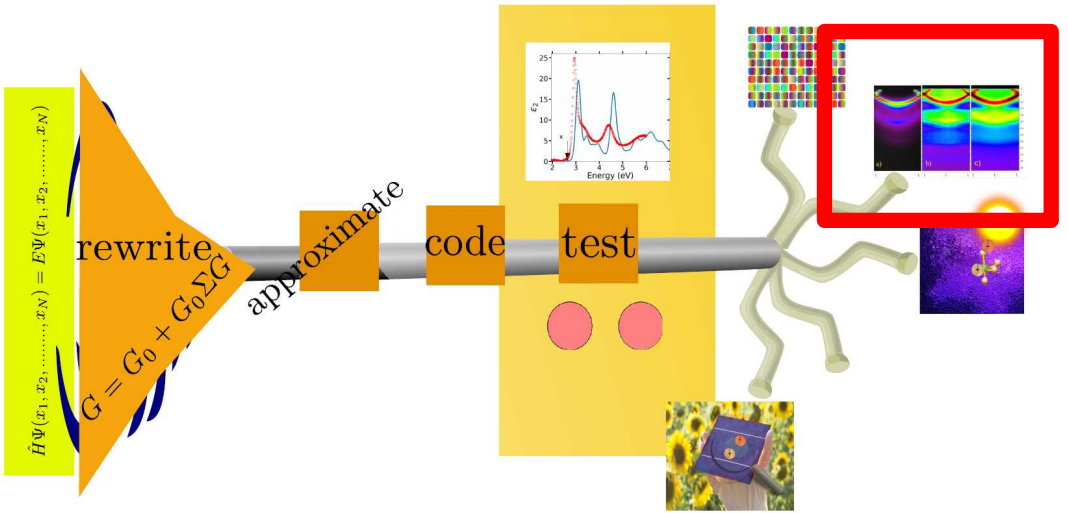


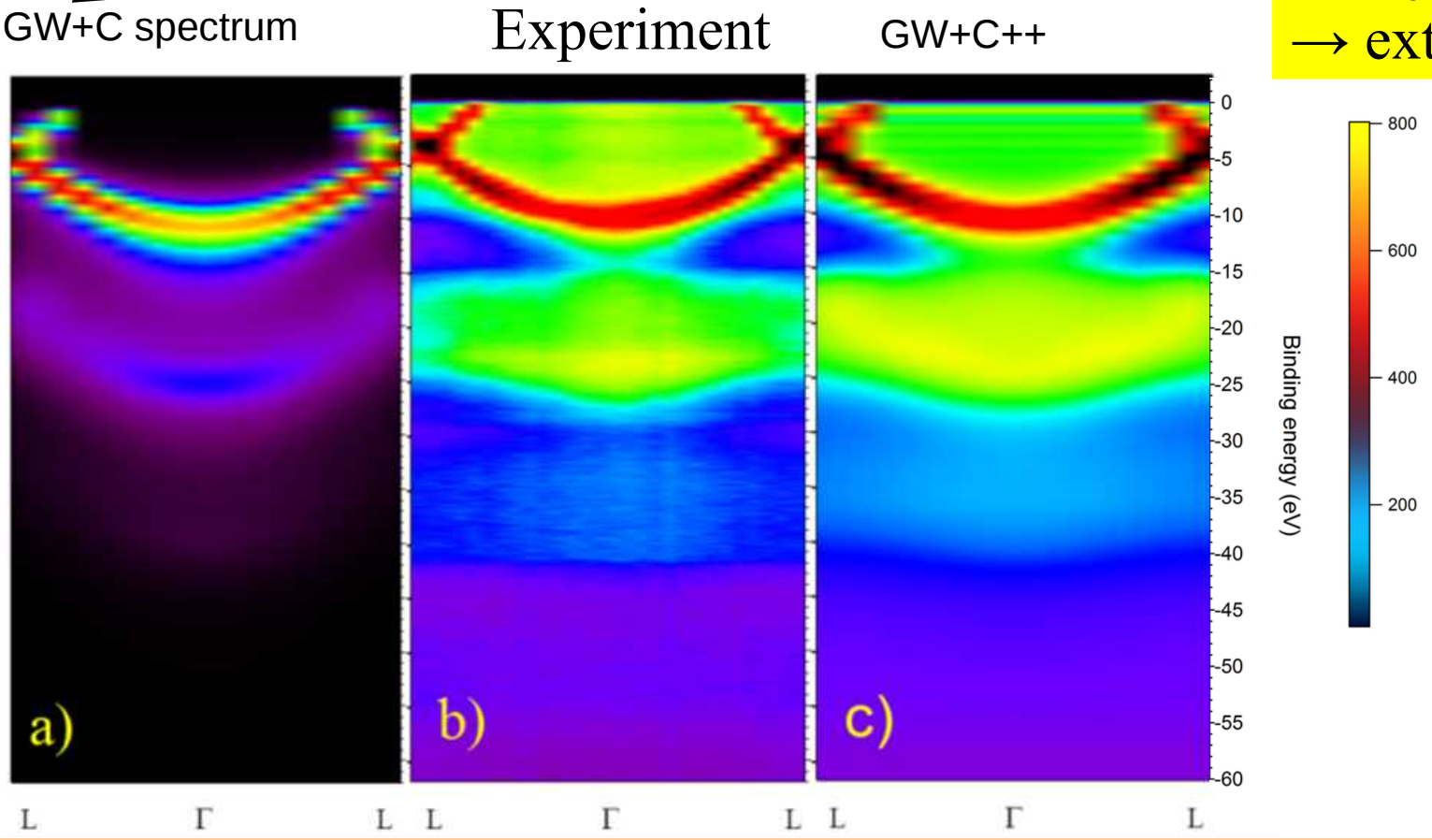


Zhou, Reining, Nicolaou, Bendounan, Ruotsalainen, Vanzini, Kas, Rehr, Muntwiler, Strocov, Sirotti, Gatti, PNAS 117 (46), 28596 (2020)

Photoemission of bulk aluminum

cumulant → GW+C spectrum

→ Temperature
→ extrinsic scattering



Zhou, Reining, Nicolaou, Bendounan, Ruotsalainen, Vanzini, Kas, Rehr, Muntwiler, Strocov, Sirotti, Gatti, PNAS 117 (46), 28596 (2020)

Mathematics

Quantum chemistry

Nuclear physics

Experiment

Synchrotron

Computers

$\hat{H}\Psi(x_1, x_2, \ldots, x_N) = E\Psi(x_1, x_2, \ldots, x_N)$

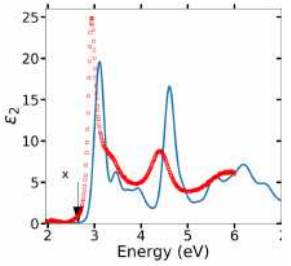
rewrite

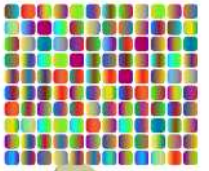
$G = G_0 + G_0 \Sigma G$

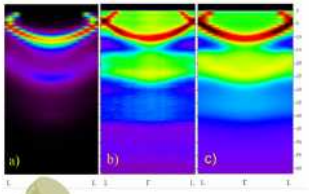
approximate

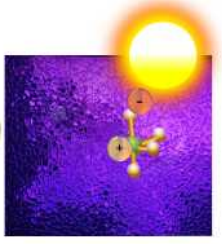
code

test









Technology

Modeling

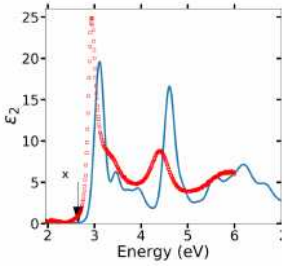
Mathematics

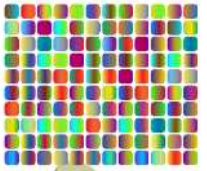
Quantum chemistry

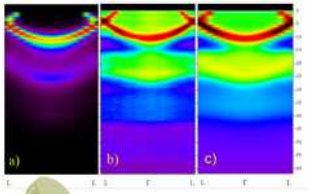
Nuclear physics

Experiment

Synchrotron







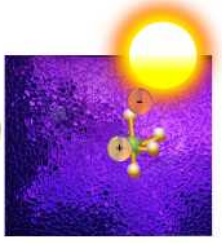
Computers

rewrite

approximate

code

test



Technology

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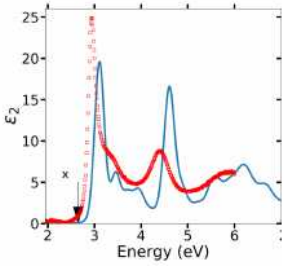
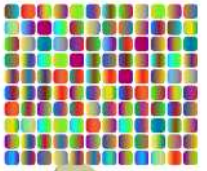
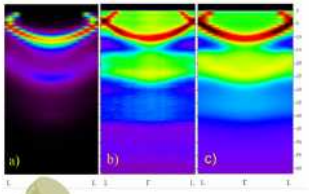






Technology

Modeling

Medicine

Museum

……..

La mécanique quantique dans les systèmes à N corps

→ What is our job?

→ We are physicists: the quantum many-body problem

→ Re-writing: functionals

→ Approximating: many-body perturbation theory

→ the synchrotron, back and forth

→ …..and coding: a quantum video camera

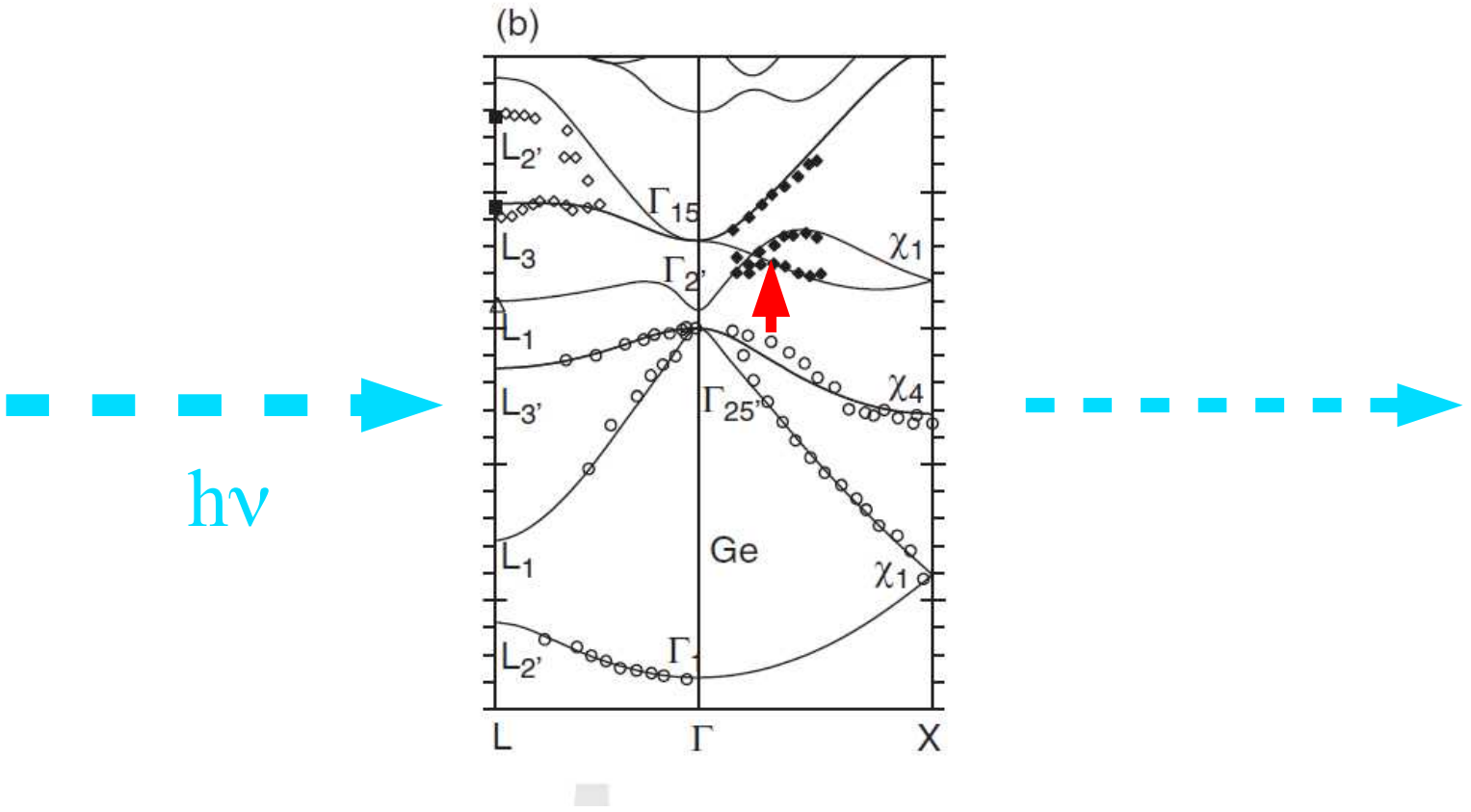
→ motivated by a museum

→ Less petrol in the pipeline: Connector approach

→ an ecological use of models

→ Remarks

Absorption: measuring electron-hole pairs



25 years of developments

$\hat{H}\Psi(x_1, x_2, \ldots, x_N) = E\Psi(x_1, x_2, \ldots, x_N)$

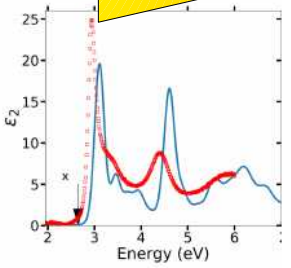
rewrite

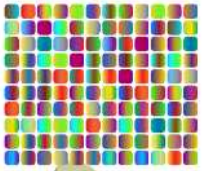
$G = G_0 + G_0 \Sigma G$

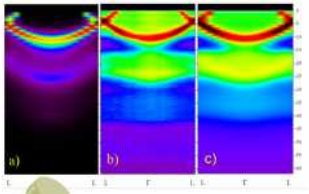
approximate

code

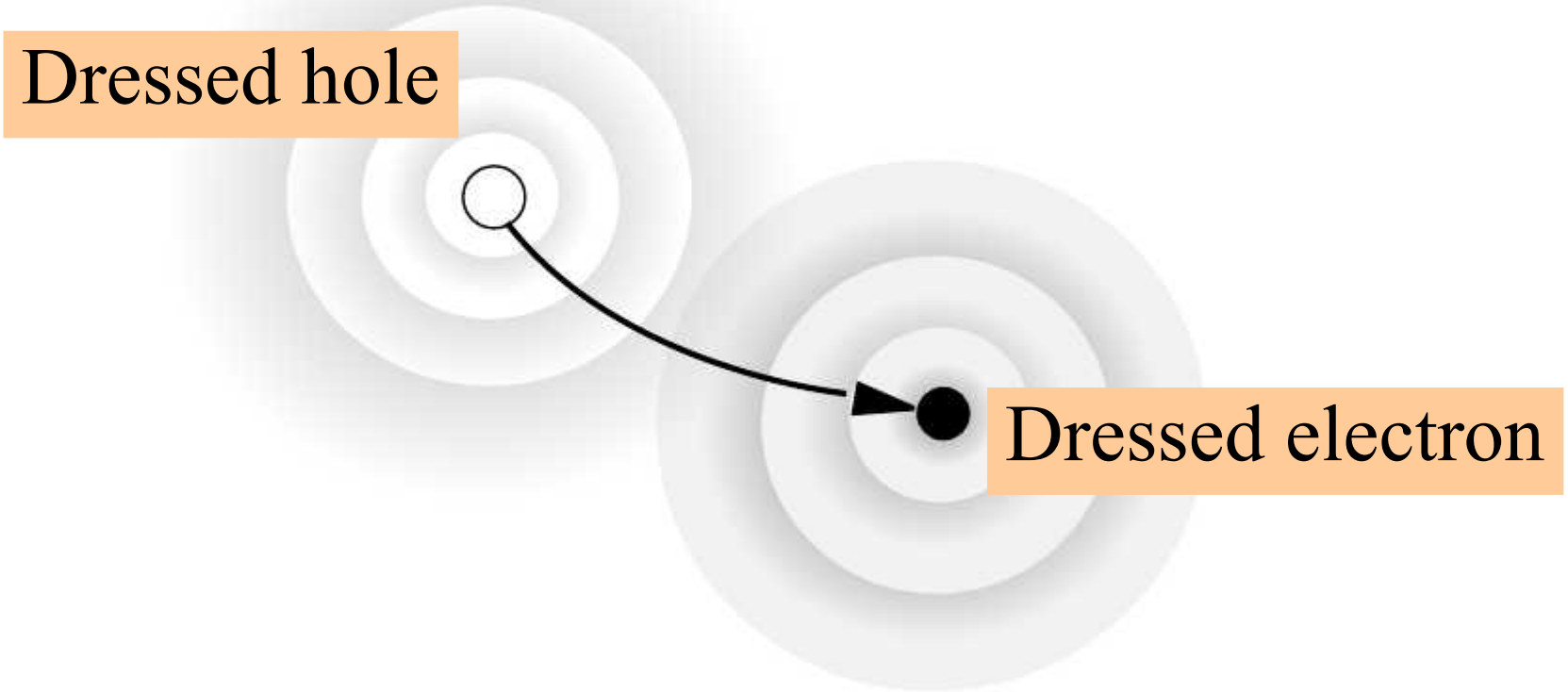
test







$$L_0 = GG$$



$$L = L_0 + L_0 \Xi L$$

$$L_0 = GG$$

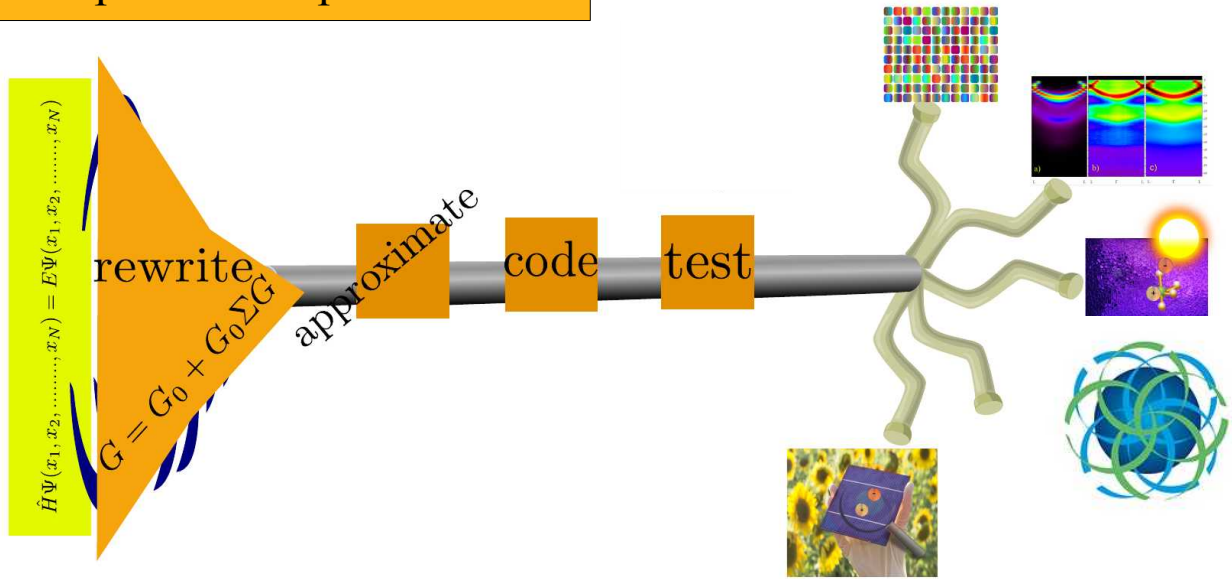
Dressed hole

e-h interaction

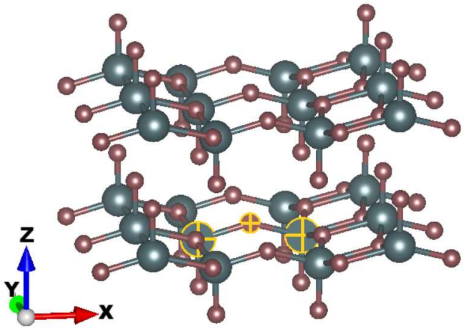
Dressed electron

Hanke & Sham, Phys. Rev. Lett. 43, 387 (1979)
Strinati, Nuovo Cimento 11, 1 (1988)
Onida, et al., Phys. Rev. Lett. 75, 818 (1995)
Albrecht, Onida, Reining Phys. Rev. B 55, 10278 (1997); Albrecht et al. PRL 80, 4510 (1998)
Benedict, Shirley, Bohn, PRL 80, 4514 (1998)
Rohlfing & Louie, PRL 80, 3320 (1998); PRL 81, 2312 (1998)

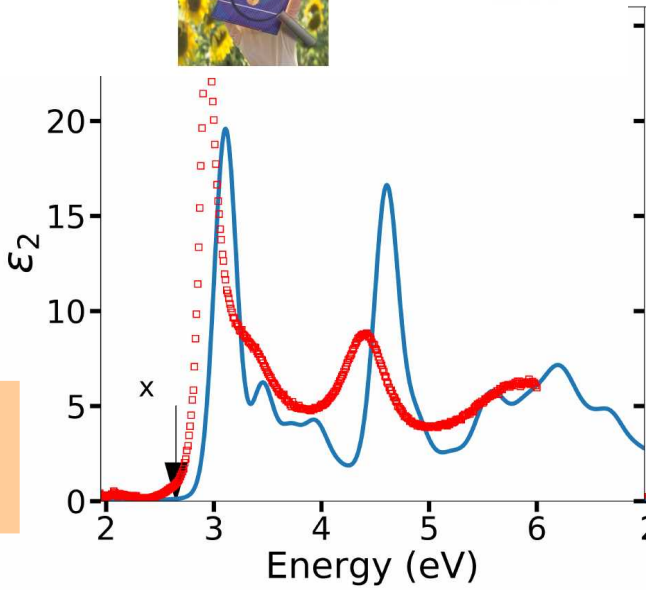
Optical absorption



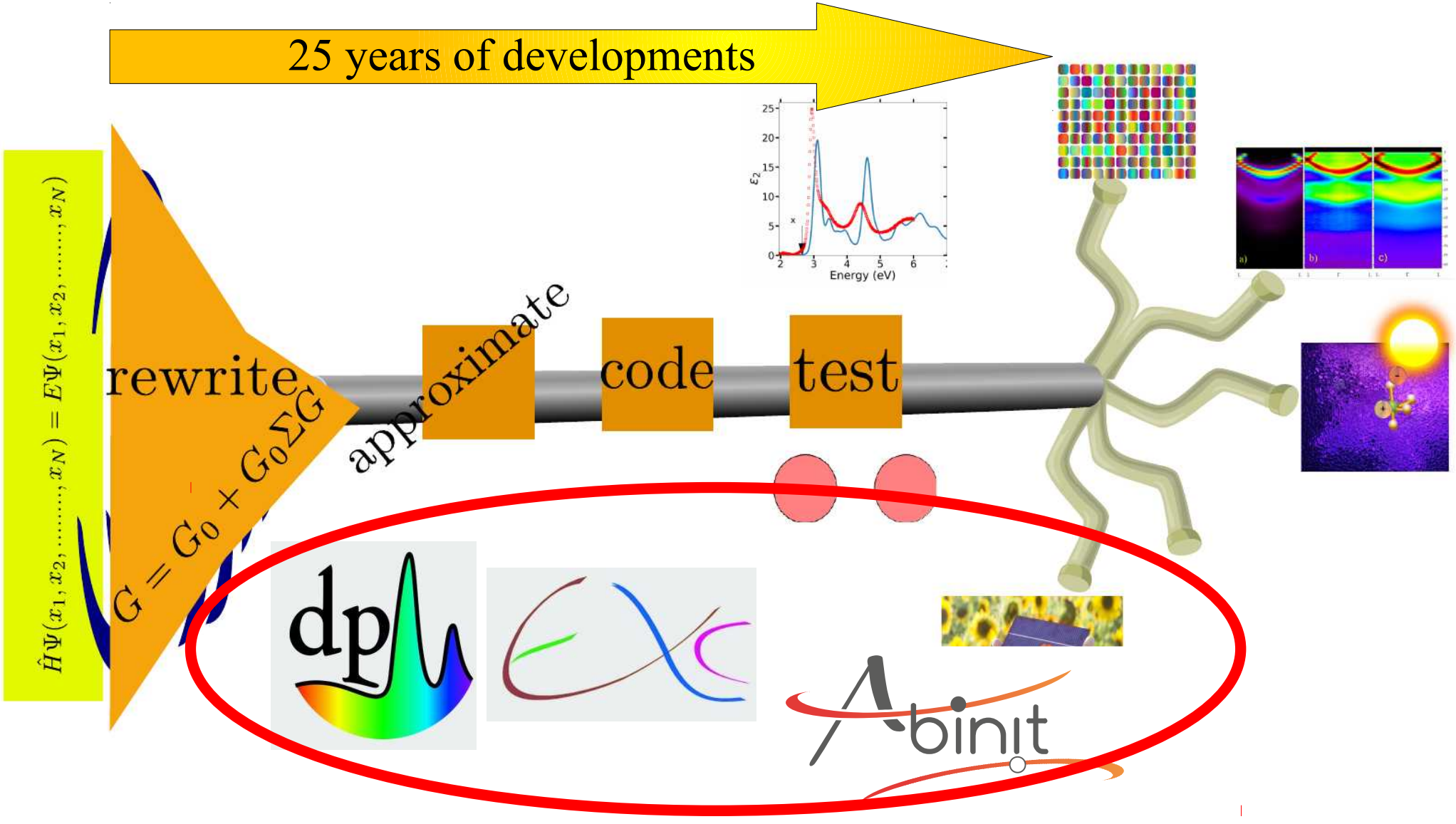
Chaire Énergies Durables
École polytechnique - EDF



V_2O_5: a layered bulk material



Vitaly Gorelov
Reining, Feneberg, Goldhahn, Schleife, Lambrecht, Gatti
npj Comp Mat 8:94 (2022)


25 years of developments
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rewrite
$G = G_0 + G_0 \Sigma G$
approximate
code
test
Energy (eV)
ε_2
dp
Abinit

But what happens really in the material?

$\hat{H}\Psi(x_1, x_2, \ldots\ldots, x_N) = E\Psi(x_1, x_2, \ldots\ldots, x_N)$

rewrite

$G = G_0 + G_0 \Sigma G$

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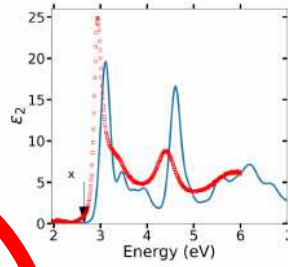
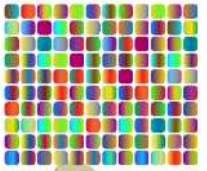
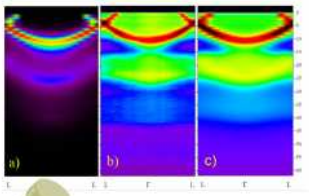
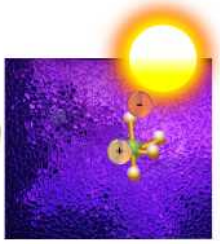








Giulia Pegolotti, Ralph Hambach,
Claudia Roedl, Igor Reshetnyak,
Matteo Gatti, Francesco Sottile,
Arnaud Lorin,….Alam Orsorio, Vitaly Gorelov

But what happens really in the material?

Motivation: cultural heritage - photography

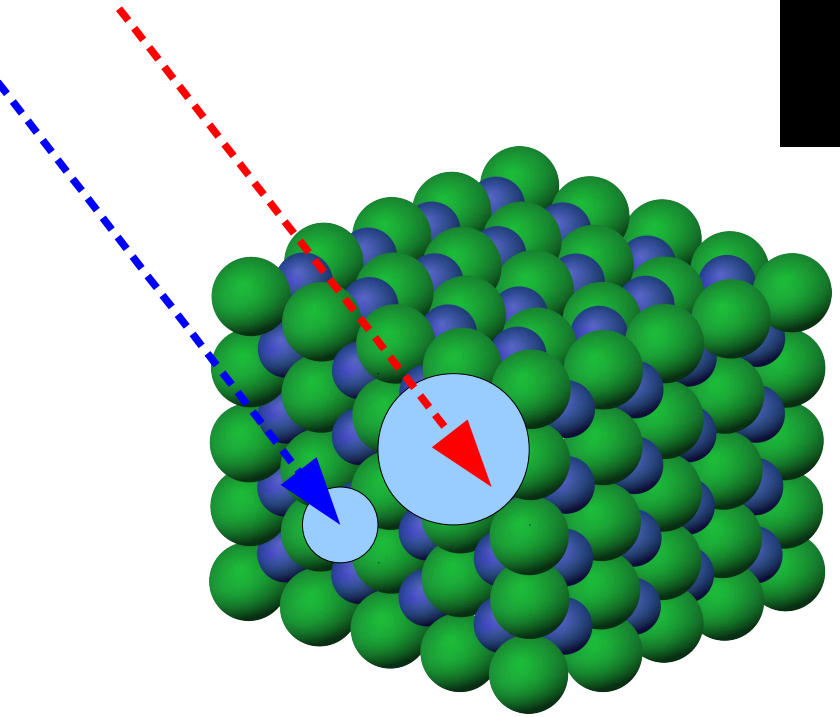
1839 : BW Photography by Daguerre
1848 : First colour photography by Edmond Becquerel

Collaboration with the Muséum national d'histoire naturel, Paris

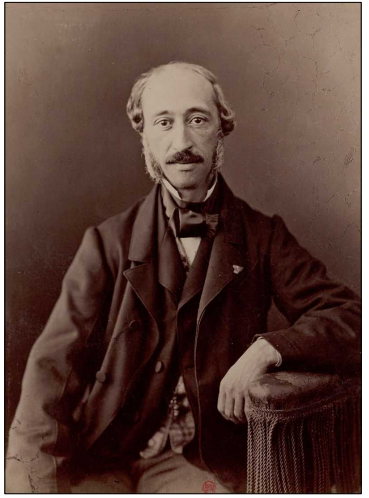
Cultural heritage - photography

Silver chloride, AgCl, with silver inclusions

Muséum national d'histoire naturel, Paris (V. de Seauve et al.)



V. de Seauve, et al, Angew. Chem. Int. Ed. 2020, 59, 9113.



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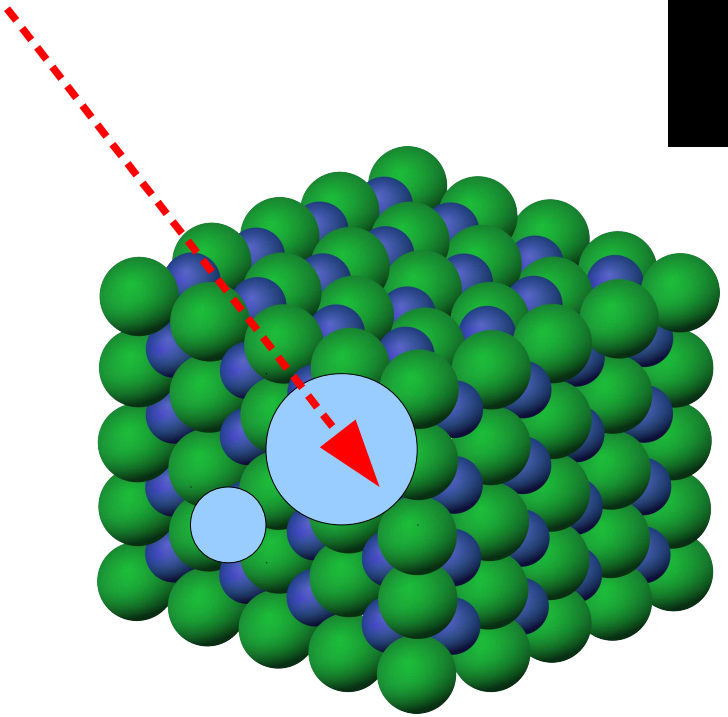

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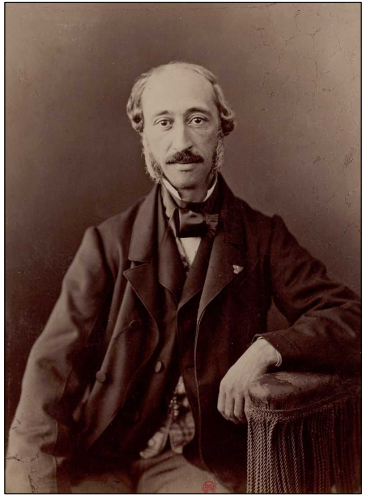

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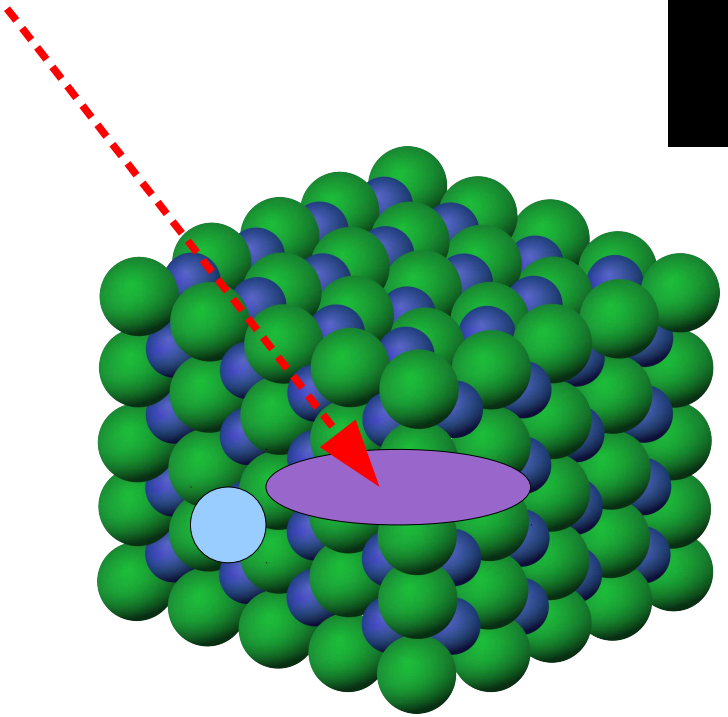

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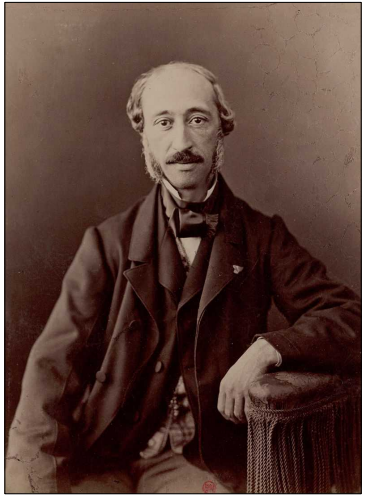

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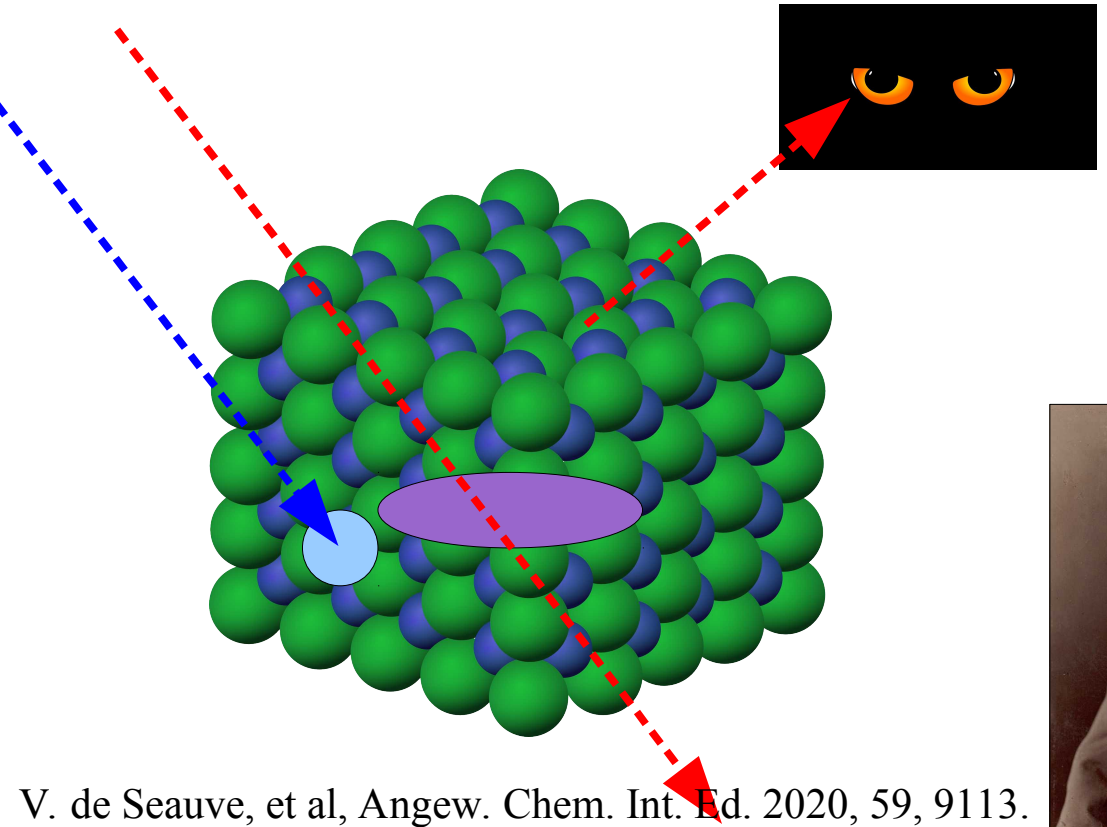

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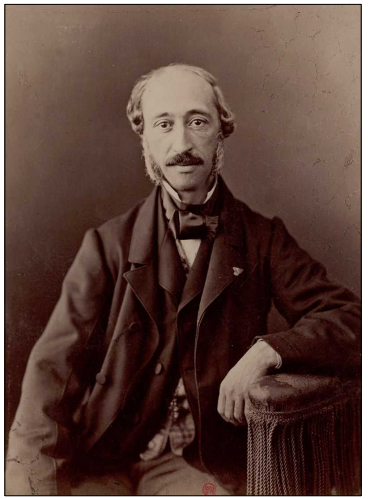

Cultural heritage - photography

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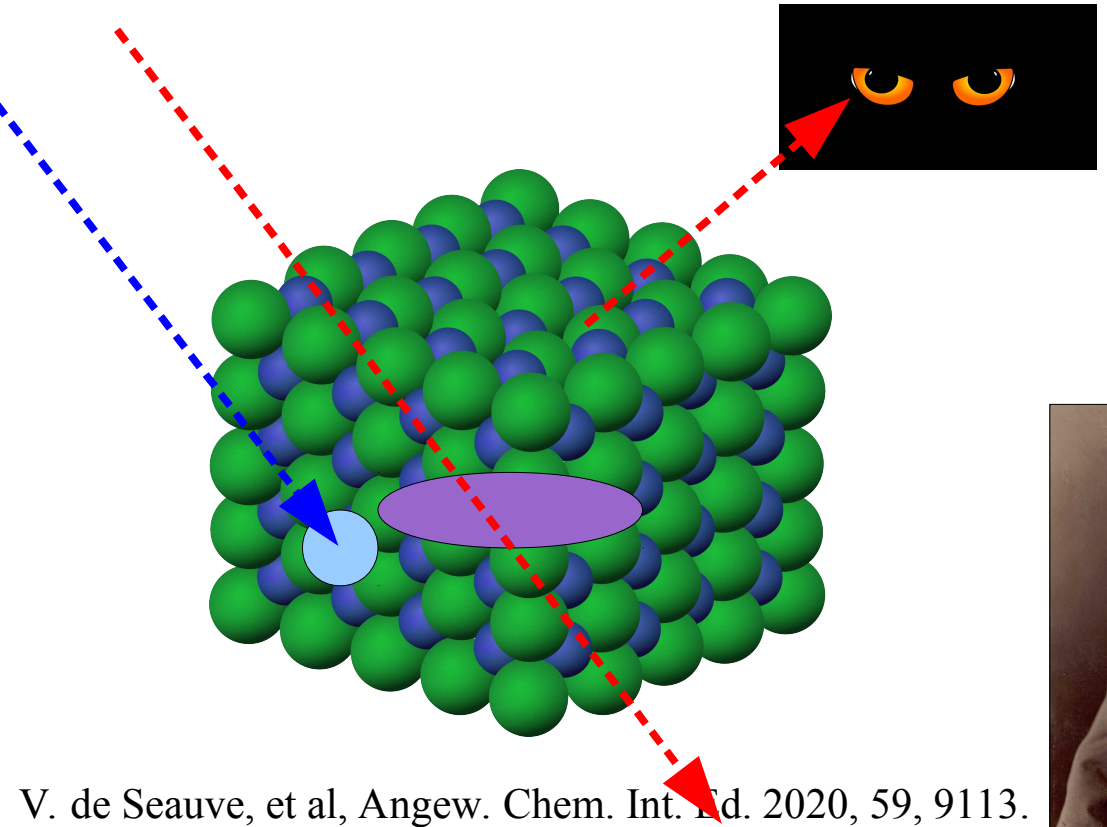
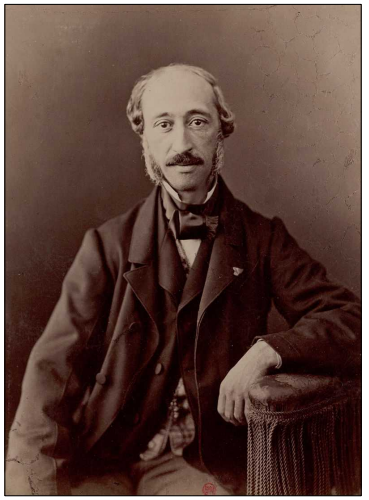
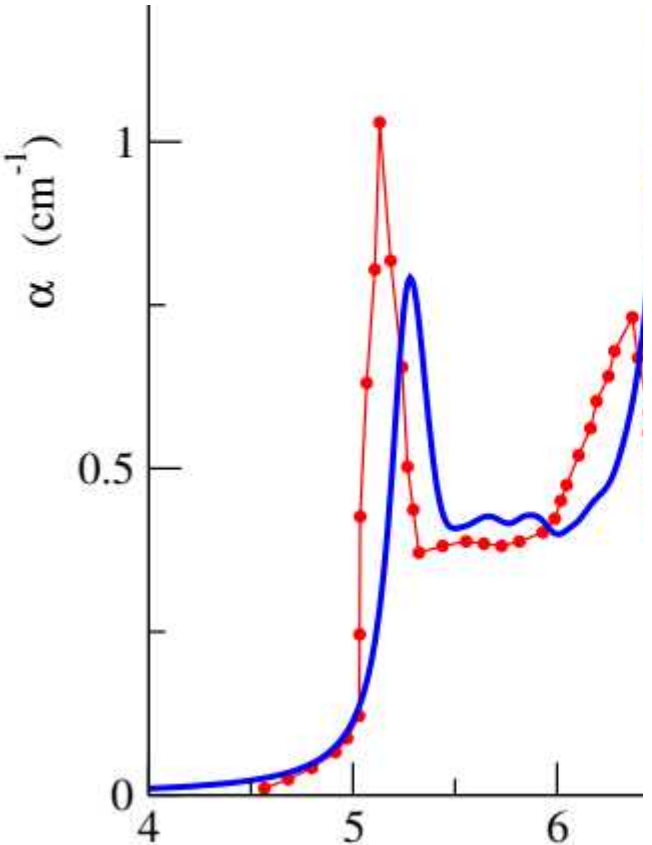


V. de Seauve, et al, Angew. Chem. Int. Ed. 2020, 59, 9113.

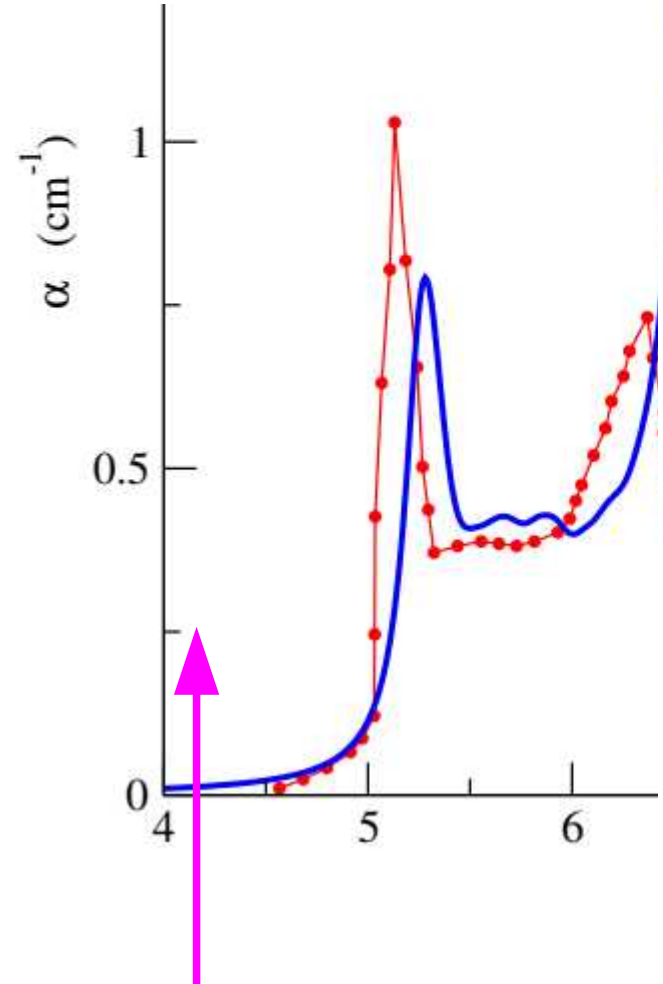


Use this to study charge dynamics in silver chloride, AgCl

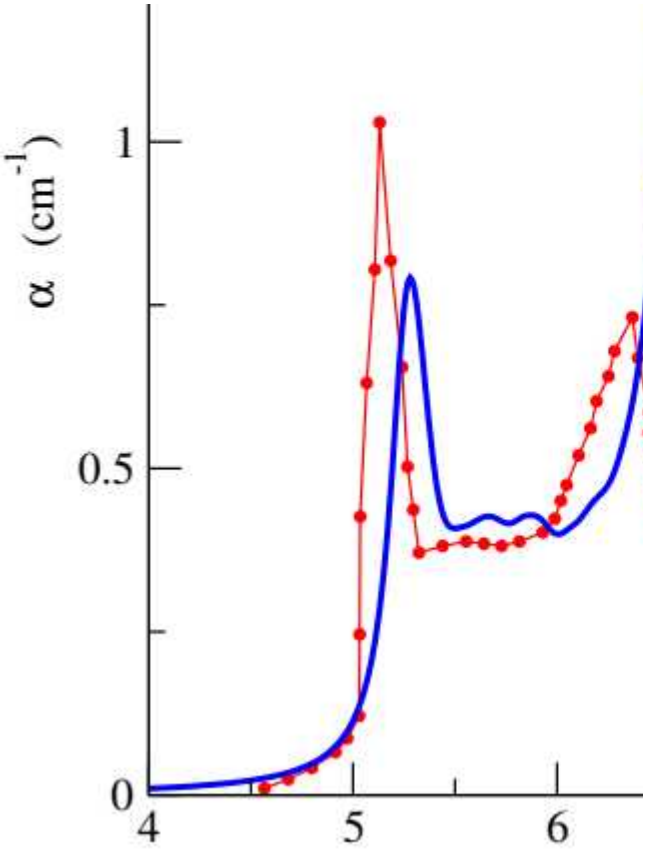


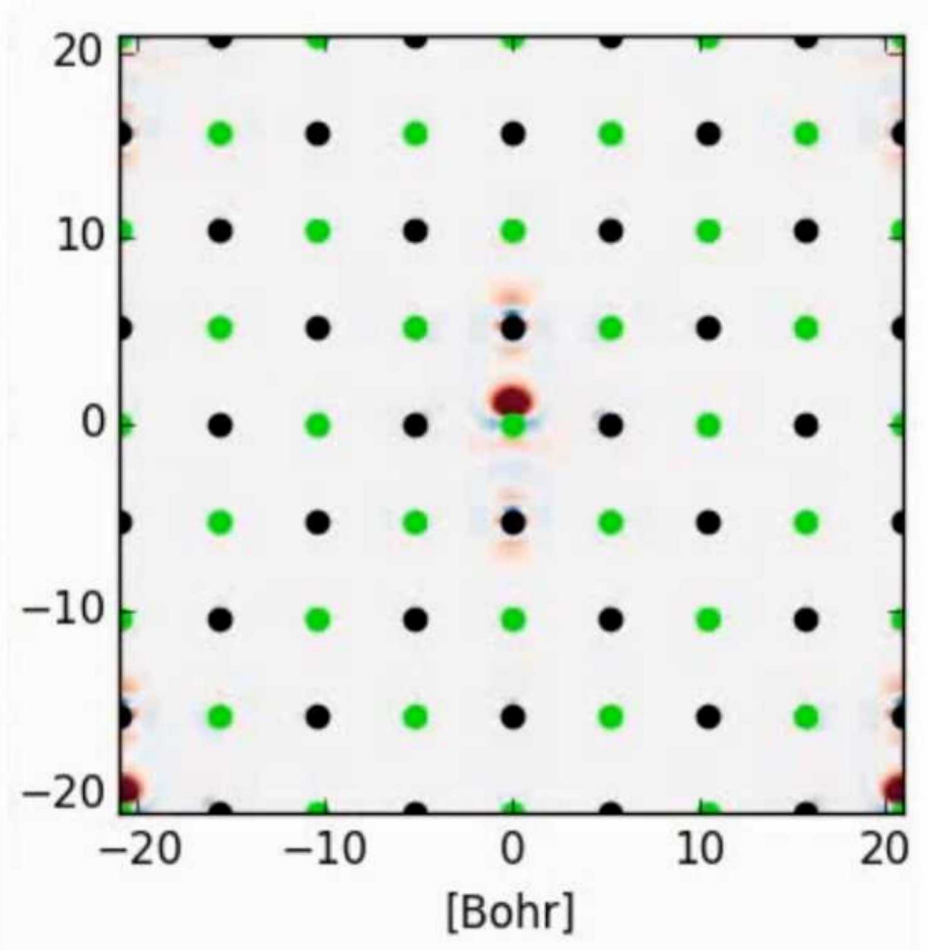
Arnaud Lorin, Matteo Gatti, Lucia Reining, Francesco Sottile, PRB 104, 235149 (2021)

Frequency in gap:



Frequency in gap:





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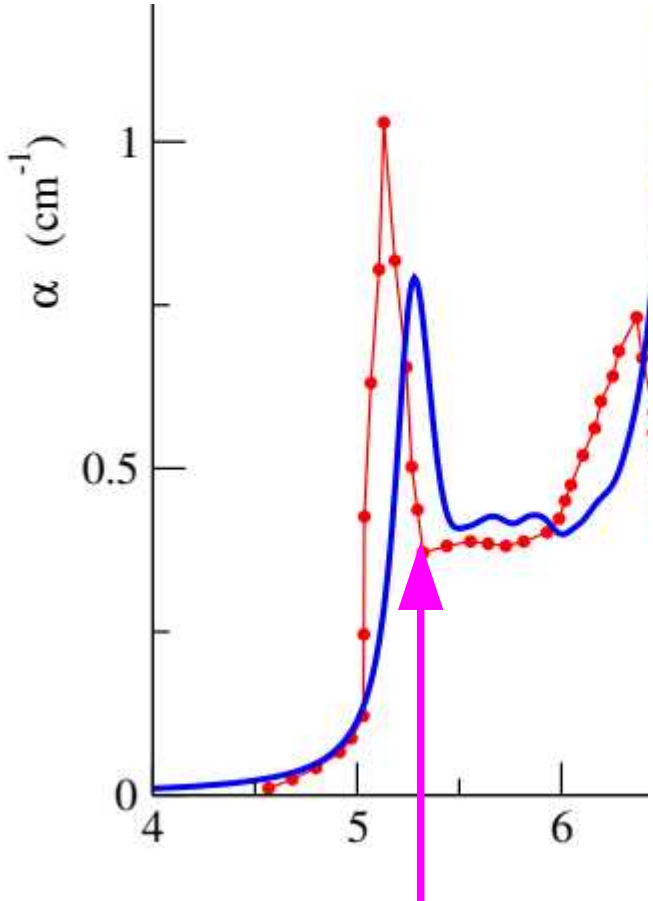
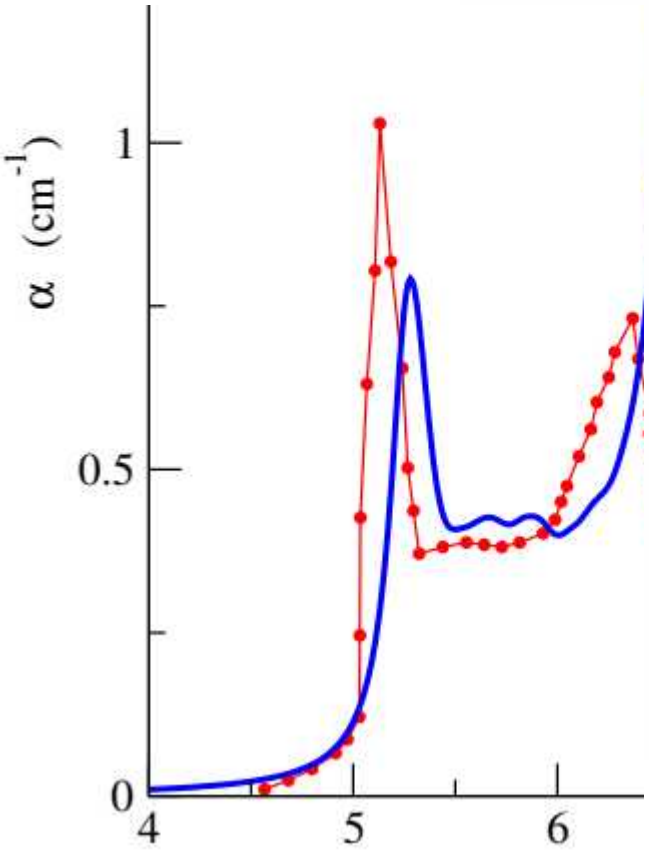
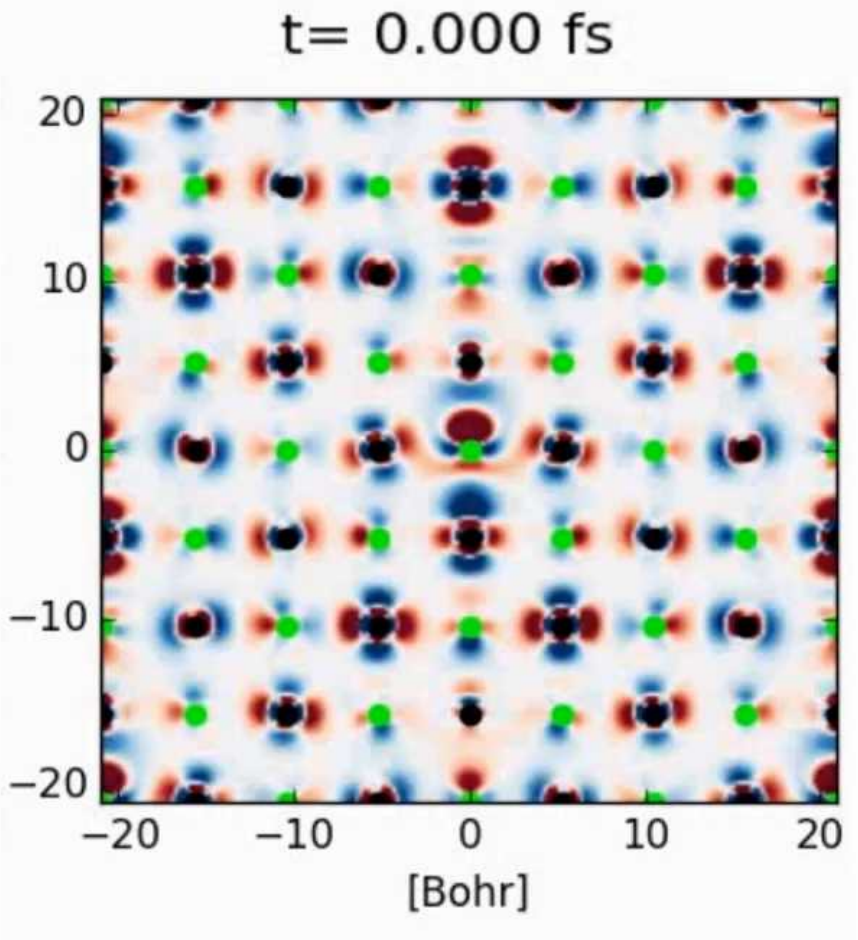
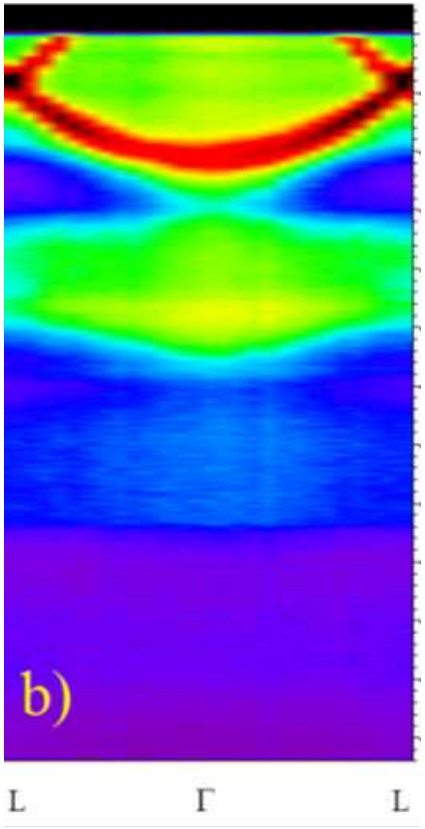


Frequency on exciton:



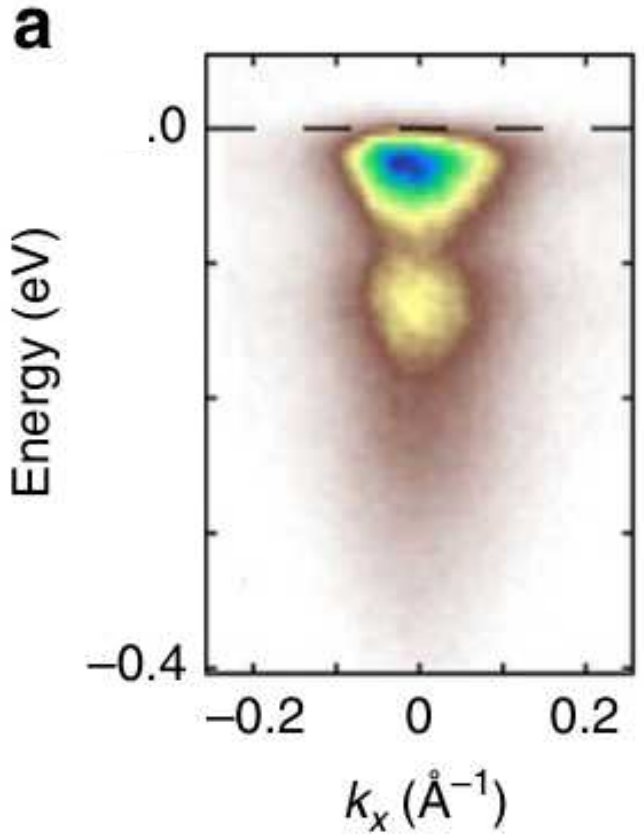


Bulk aluminum



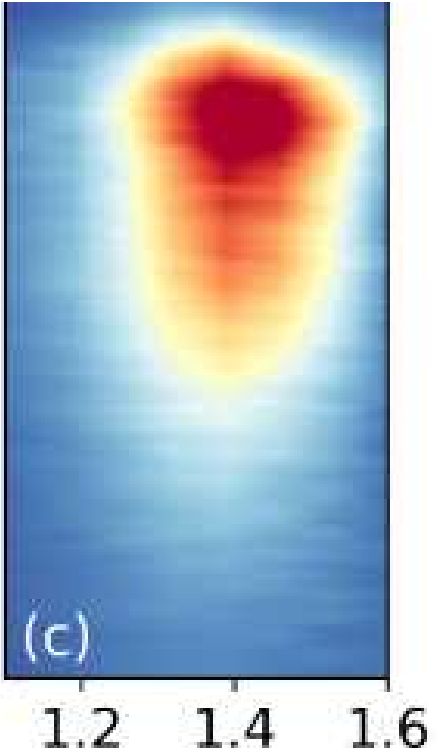
Zhou, et al.,
PNAS 117 (46), 28596 (2020)

Polarons in TiO2



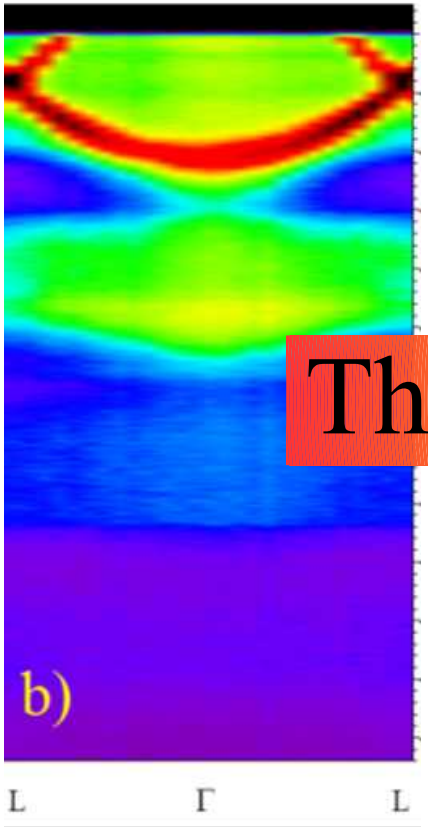
Verdi, Caruso, Giustino,
Nat. Comm. 8:15769 (2017)

n-doped MoS2



Caruso, et al.,
Phys. Rev. B 103, 205152

Bulk aluminum



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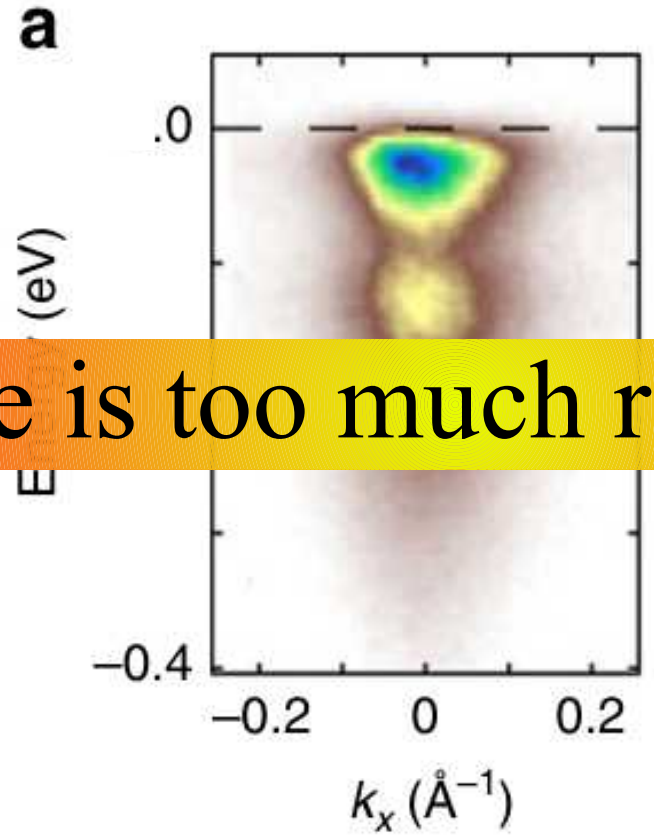


Verdi, Caruso, Giustino,
Nat. Comm. 8:15769 (2017)

n-doped MoS2

Caruso, et al.,
Phys. Rev. B 103, 205152

There is too much redundancy

La mécanique quantique dans les systèmes à N corps

→ What is our job?

→ We are physicists: the quantum many-body problem

→ Re-writing: functionals

→ Approximating: many-body perturbation theory

→ the synchrotron, back and forth

→ …..and coding: a quantum video camera

→ motivated by a museum

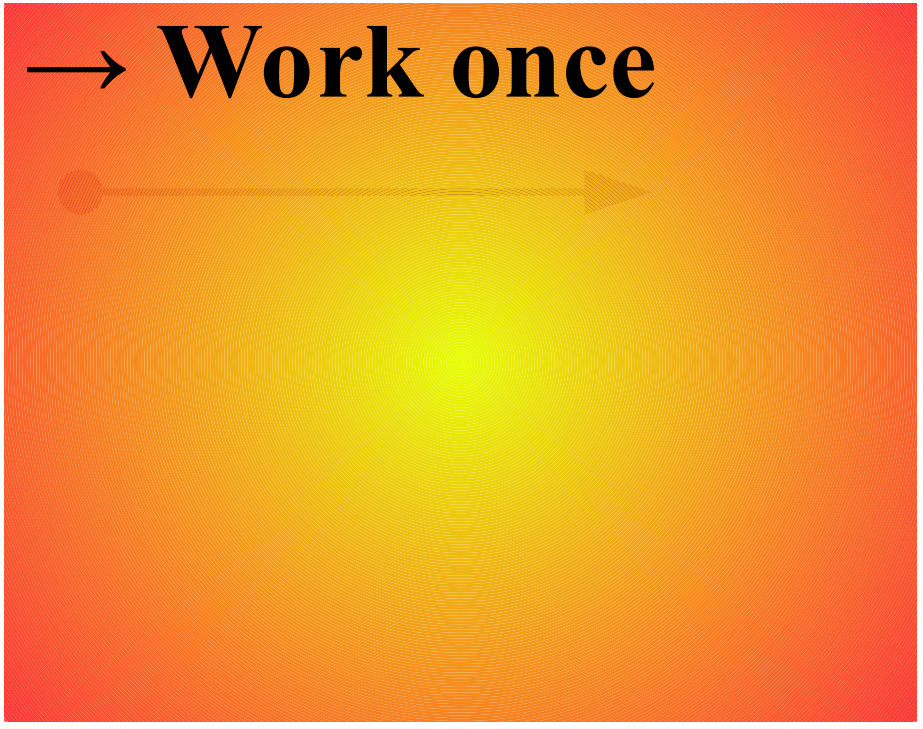
→ Less petrol in the pipeline: Connector approach

→ an ecological use of models

→ Remarks

Extract universal pieces

Extract universal pieces



Extract universal pieces

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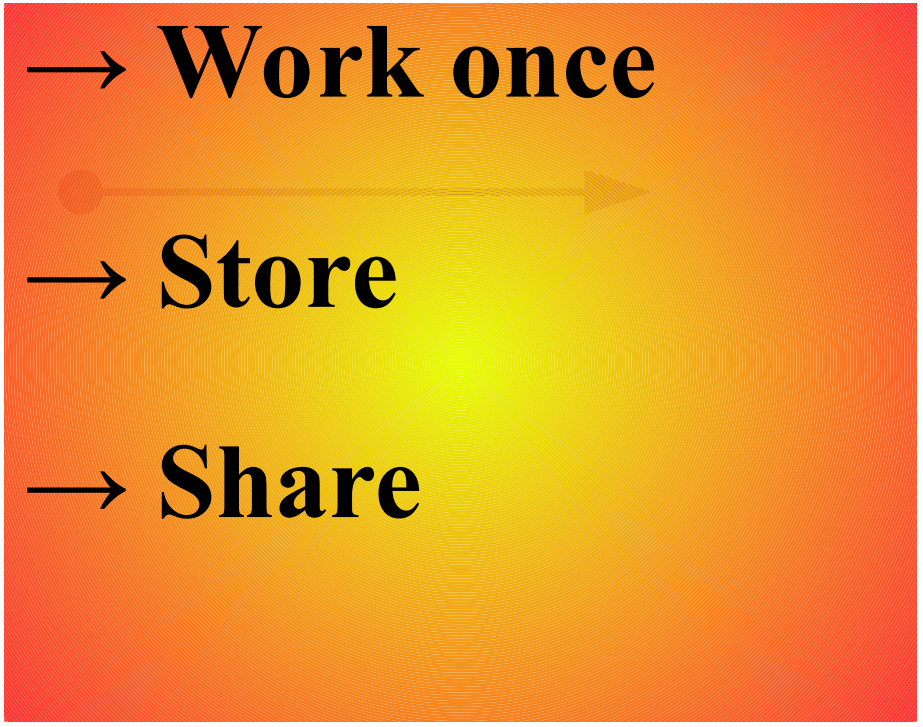
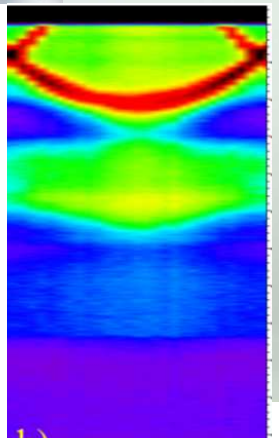


$$\hat{H}\Psi_\lambda(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N) = E_\lambda \Psi_\lambda(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N)$$

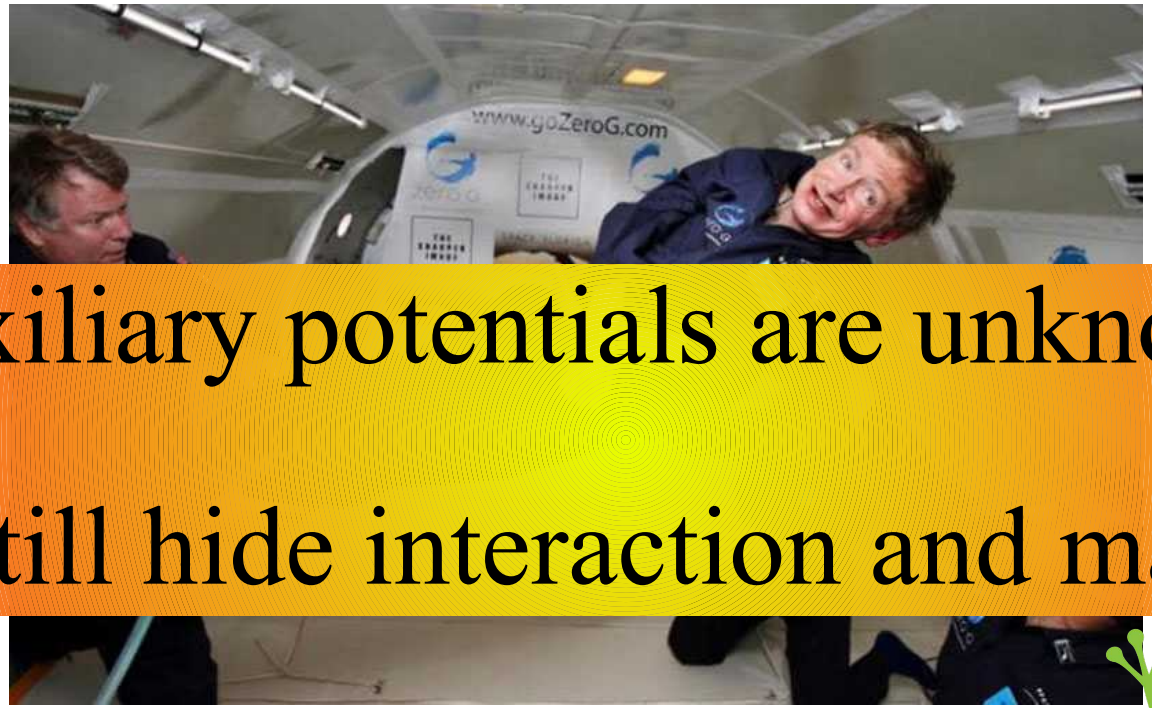


Faster

Faster

Better understanding

Auxiliary system=simulation chamber



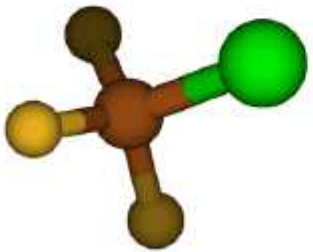
All auxiliary potentials are unknown

They still hide interaction and material

Image from pixabay:
www.noft-traders.com/establish-zero-gravity-zones-with-supply-and-demand/

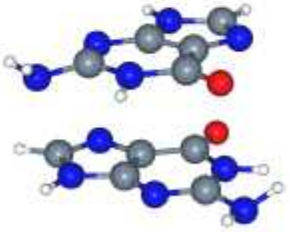
$\Psi(x_1, x_2, ..., x_N; t)$

CI, QMC



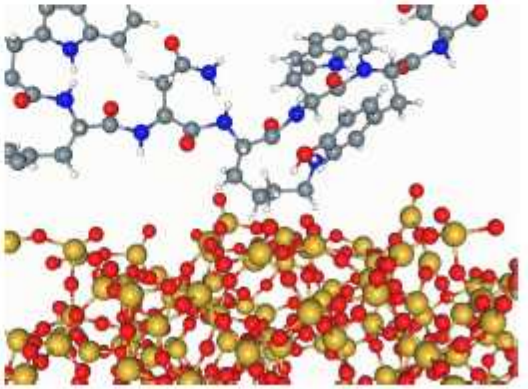
$G(x_1, x_1', t, t')$

Green's Functions



$n(\mathbf{r}; t)$

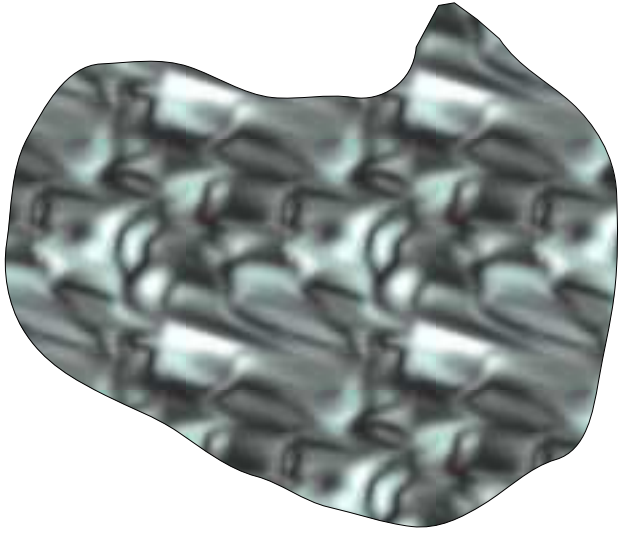
Density Functionals



Density Functional Theory

$v_{\mathrm{xc}}(\mathbf{r})$???

Material

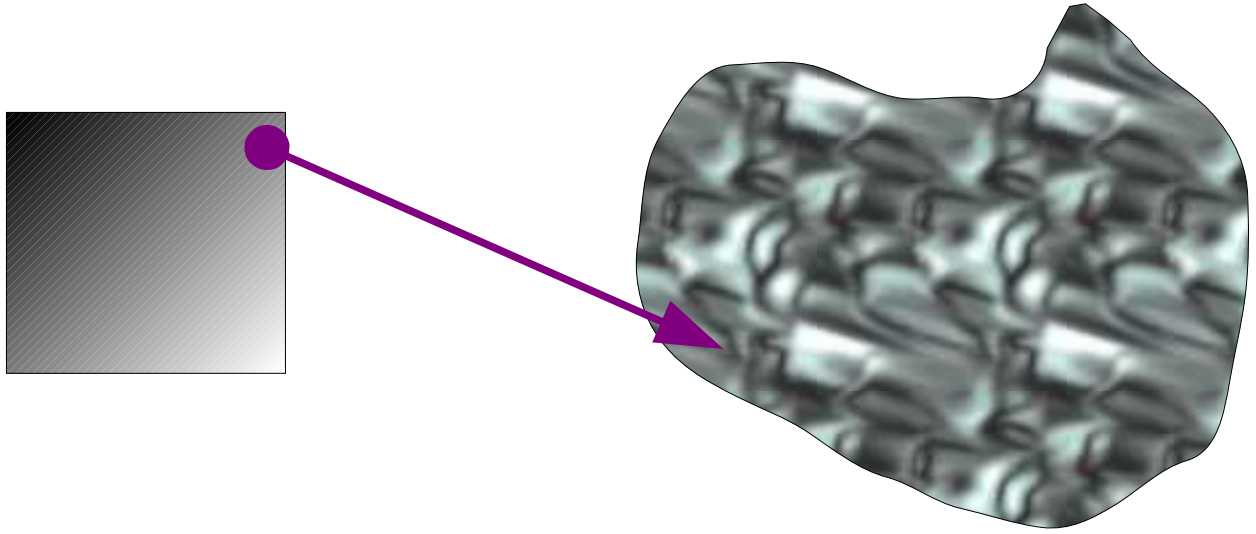


Typical DFT approximation strategy

$v_{\mathrm{xc}}(\mathbf{r})$???

Material

Homogeneous electron gas



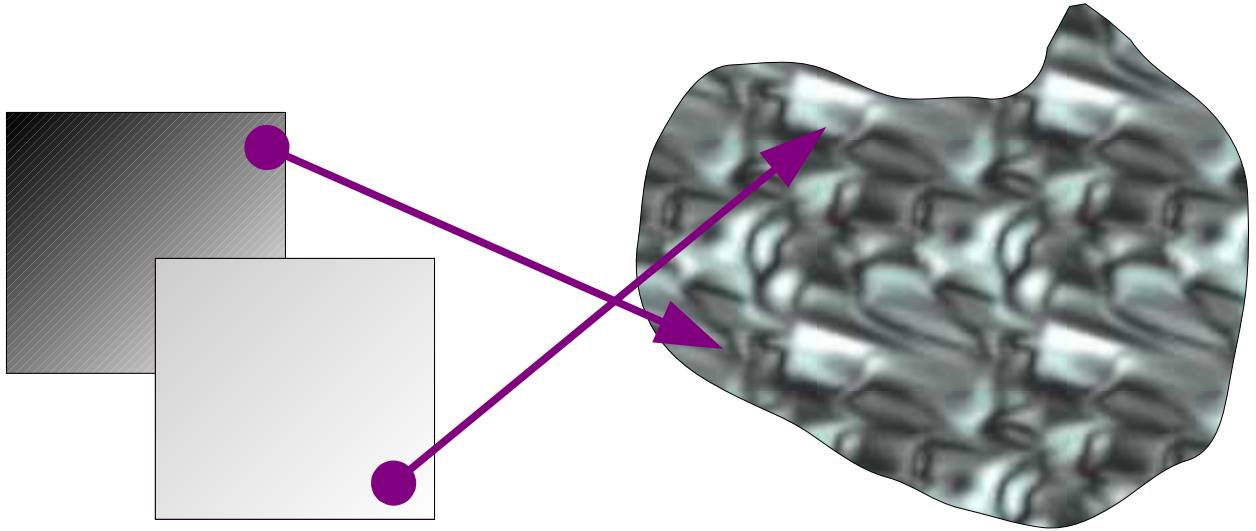
W. Kohn and L. J. Sham, Phys. Rev. 140:A1133–1138, 1965

Typical DFT approximation strategy

$v_{\mathrm{xc}}(\mathbf{r})$ of different HEG in each point

Material

Homogeneous electron gas



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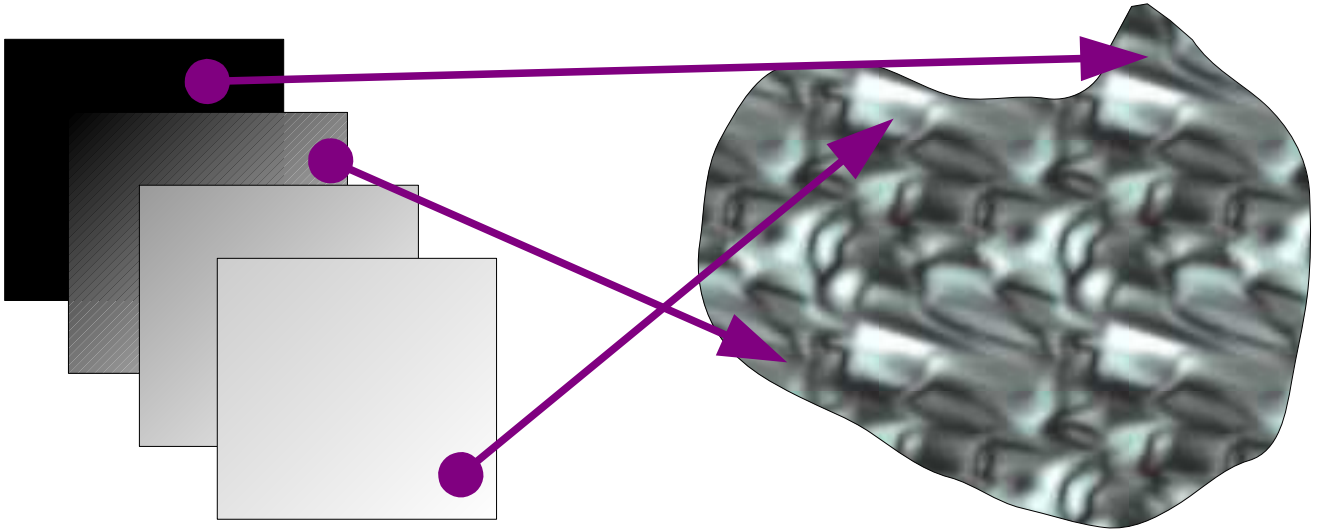
Typical DFT approximation strategy

Local Density Approximation (LDA)

Homogeneous electron gas

Material



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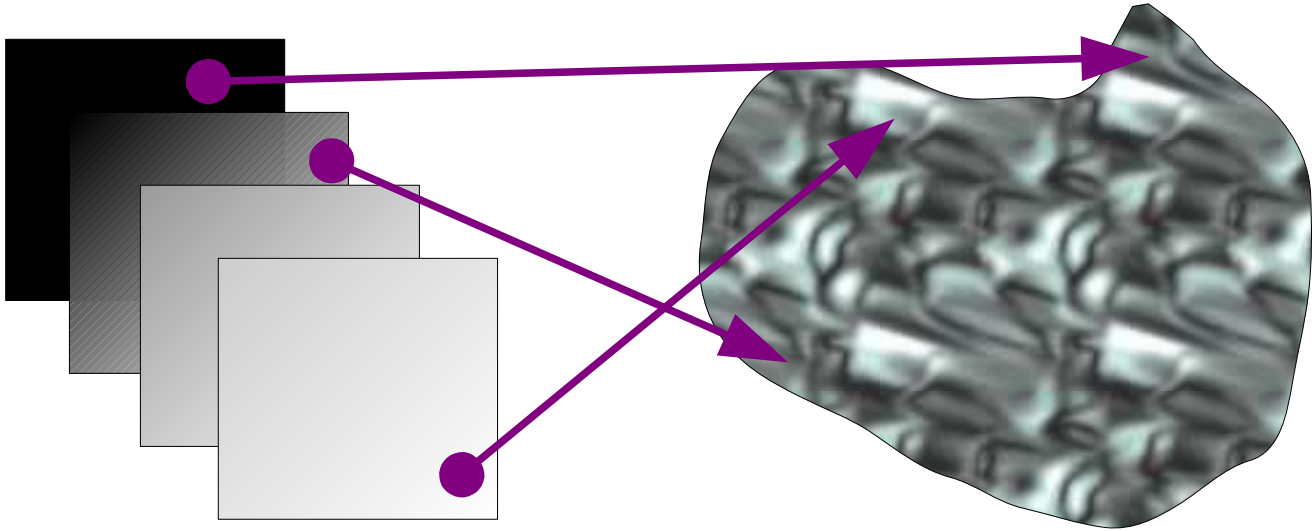

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D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566(1980)

$\hat{H}\Psi(x_1, x_2, \ldots\ldots, x_N) = E\Psi(x_1, x_2, \ldots\ldots, x_N)$

QMC

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Typical DFT approximation strategy

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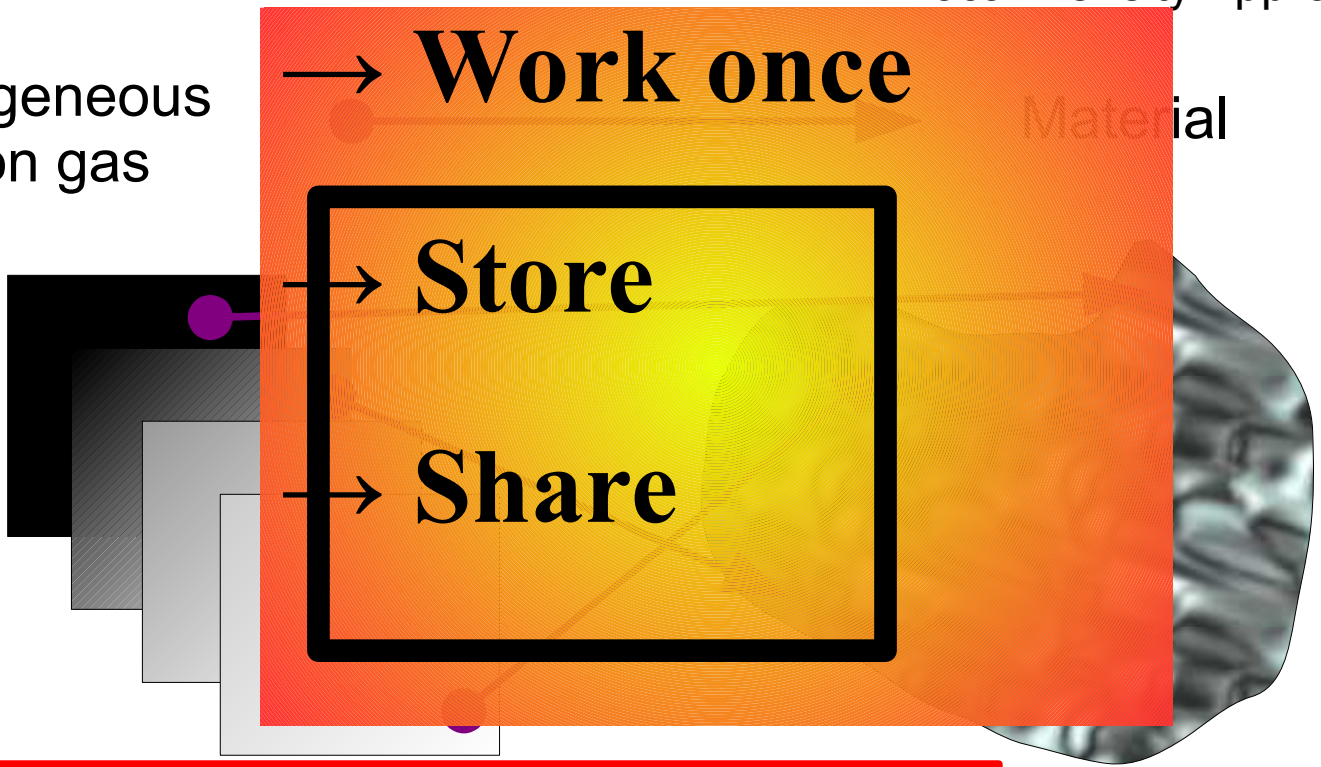

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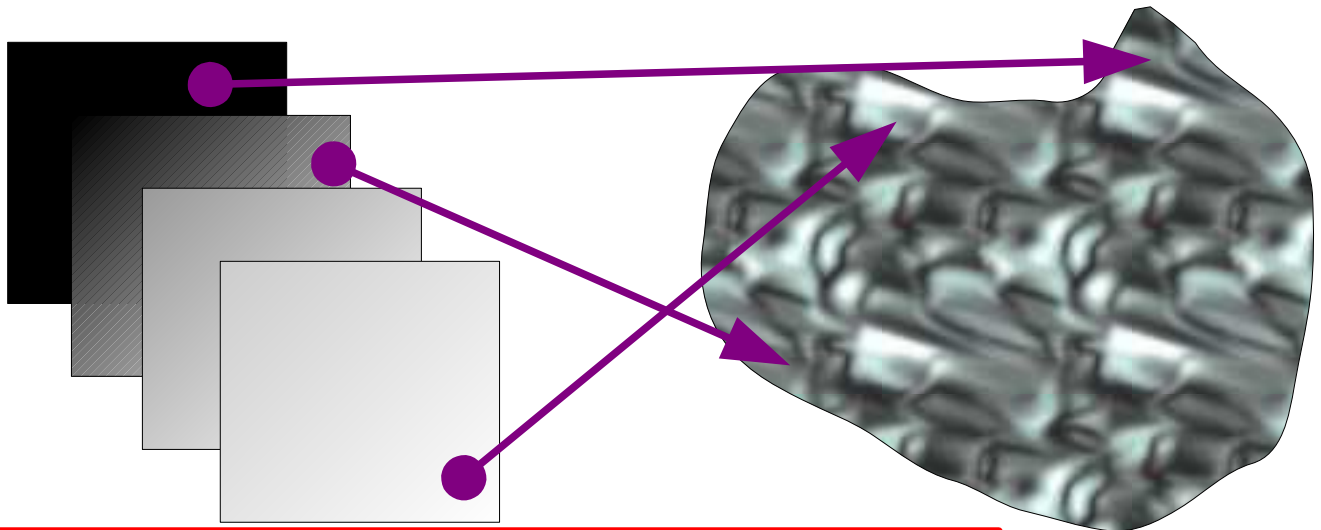

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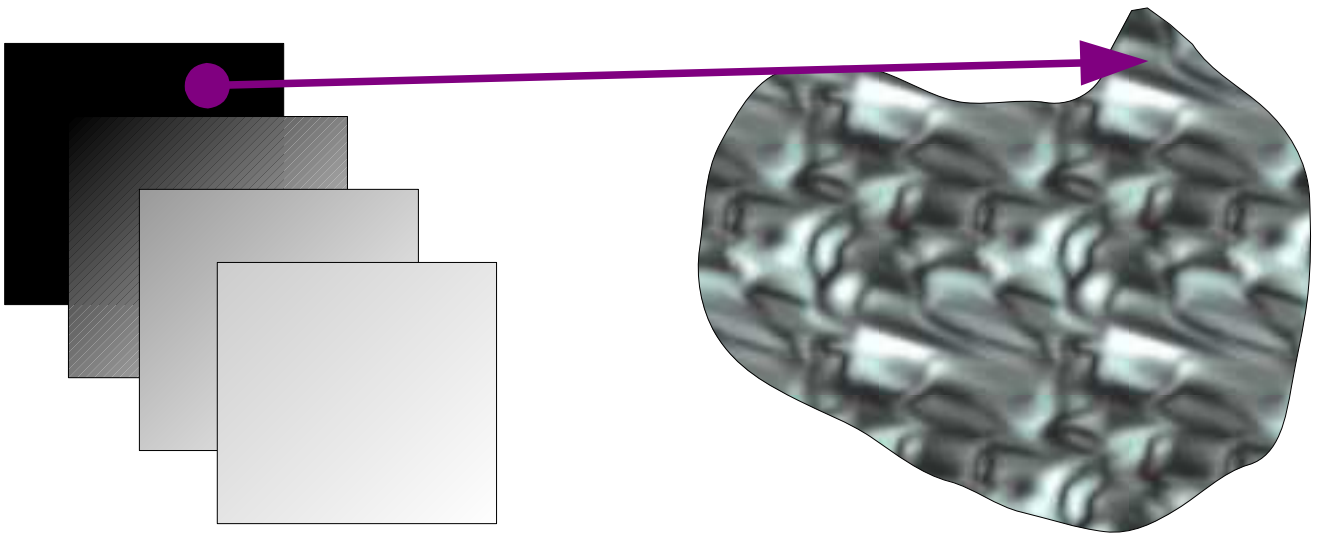
E. Fermi, Rend. Accad. Naz. Lincei 6, 602 (1927); L. Thomas, Proc. Cambridge Phil. Soc. 33, 542 (1927); S.-K. Ma and K. A. Brueckner, Phys. Rev. 165, 18 (1968); S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. 58, 1200 (1980); O. Gunnarsson, M. Jonson, and B. Lundqvist, Solid State Commun. 24, 765 (1977); J. A. Alonso and L. Girifalco, Solid State Commun. 24, 135 (1977); J. A. Alonso and L. A. Girifalco, Phys. Rev. B 17, 3735 (1978); O. Gunnarsson, M. Jonson, and B. I. Lundqvist, Phys. Rev. B 20, 3136 (1979); O. Gunnarsson and R. Jones, Phys. Scr. 21, 394 (1980); R. Cuevas-Saavedra, D. Chakraborty, S. Rabi, C. Crdenas, and P. W. Ayers, J. Chem. Theory Comput. 8, 4081 (2012); D. C. Langreth and J. P. Perdew, Phys. Rev. B 21, 5469 (1980); J. P. Perdew and W. Yue, Phys. Rev. B 33, 8800 (1986); J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996); J. P. Perdew, S. Kurth, A. Zupan, and P. Blaha, Phys. Rev. Lett. 82, 2544 (1999); J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Phys. Rev. Lett. 100, 136406 (2008); J. Sun, A. Ruzsinszky, and J. P. Perdew, Phys. Rev. Lett. 115, 036402 (2015); J. F. Dobson, in Electronic Density Functional Theory, Recent Progress and New Directions, edited by J. F. Dobson, G. Vignale, and M. P. Das (Springer, Boston, MA,New York, 1998) pp. 261–284.J. Jung, P. Garcıa-Gonzalez, J. F. Dobson, and R. W. Godby, Phys. Rev. B 70, 205107 (2004); P. Garcıa-Gonzalez, J. E. Alvarellos, and E. Chacon, Phys. Rev. A 54, 1897 (1996); T. Olsen and K. S. Thygesen, Phys. Rev. B 86, 081103 (2012); T. Olsen and K. S. Thygesen, Phys. Rev. Lett. 112, 203001 (2014); C. E. Patrick and K. S. Thygesen, J. Chem. Phys. 143, 102802 (2015); P. S. Schmidt, C. E. Patrick, and K. S. Thygesen, Phys. Rev. B 96, 205206 (2017); D. Lu, J. Chem. Phys. 140, 18A520 (2014); G. Vignale and M. Rasolt, Phys. Rev. Lett. 59, 2360 (1987); A. Zangwill and P. Soven, Phys. Rev. A 21, 1561 (1980); E. K. U. Gross and W. Kohn, Phys. Rev. Lett. 55, 2850 (1985); J. F. Dobson, M. J. Buenner, and E. K. U. Gross, Phys. Rev. Lett. 79, 1905 (1997); T. K. Ng, Phys. Rev. Lett. 62, 2417 (1989); G. Vignale and W. Kohn, Phys. Rev. Lett. 77, 2037 (1996); G. Vignale, C. A. Ullrich, and S. Conti, Phys. Rev. Lett. 79, 4878 (1997); I. V. Tokatly, Phys. Rev. B 75, 125105 (2007); X. Gao, J. Tao, G. Vignale, and I. V. Tokatly, Phys.
Rev. B 81, 195106 (2010); V. U. Nazarov, I. V. Tokatly, S. Pittalis, and G. Vignale, Phys. Rev. B 81, 245101 (2010); P. E. Trevisanutto, A. Terentjevs, L. A. Constantin, V. Olevano, and F. D. Sala, Phys. Rev. B 87, 205143 (2013); M. Panholzer, M. Gatti, and L. Reining, Phys. Rev. Lett. 120, 166402 (2018); G. Giuliani and G. Vignale, Quantum Theory of the Electron Liquid (Cambridge University Press, 2005);
R. M. Martin, Electronic Structure: Basic Theory and Practical Methods (Cambridge University Press, 2004)

Exact choice possible?

Homogeneous
electron gas

Material



Aouina, Gatti, Reining, Faraday Discussions 224, 27 (2020)
Vanzini, Aouina, Panholzer, Gatti, Reining, npj Comp Mat 8:98 (2022)

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electron gas

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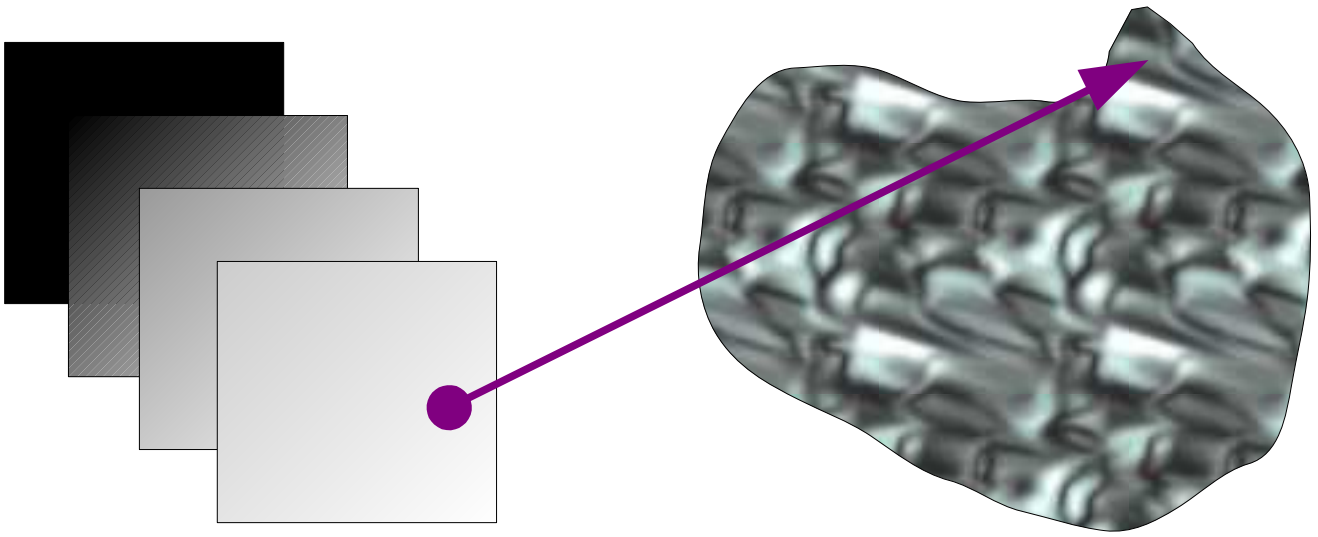

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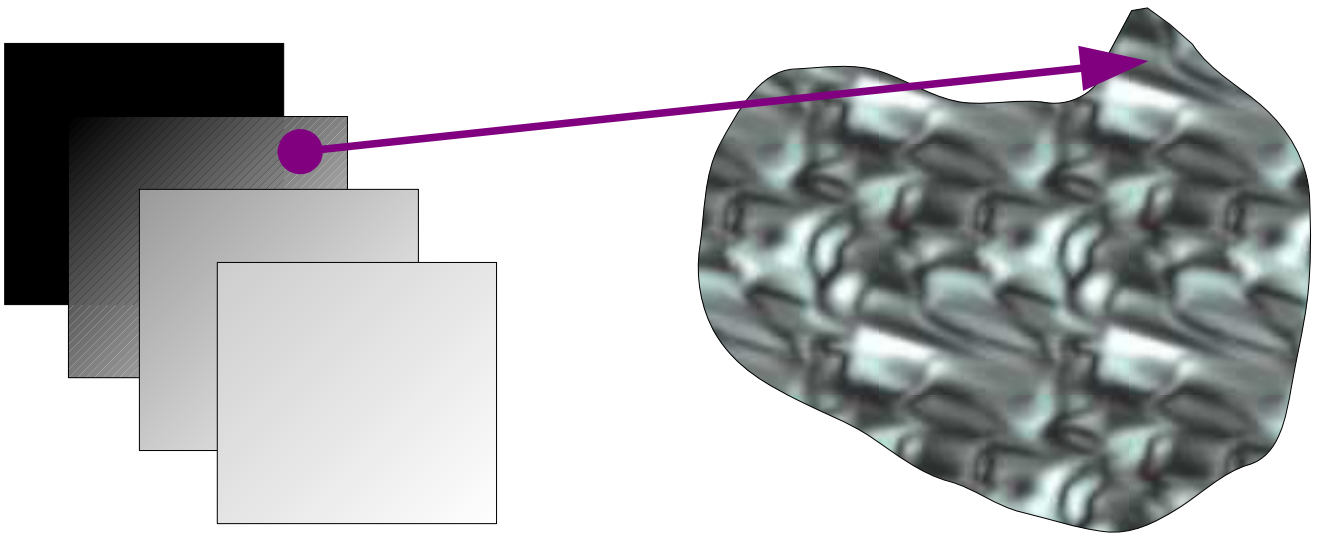

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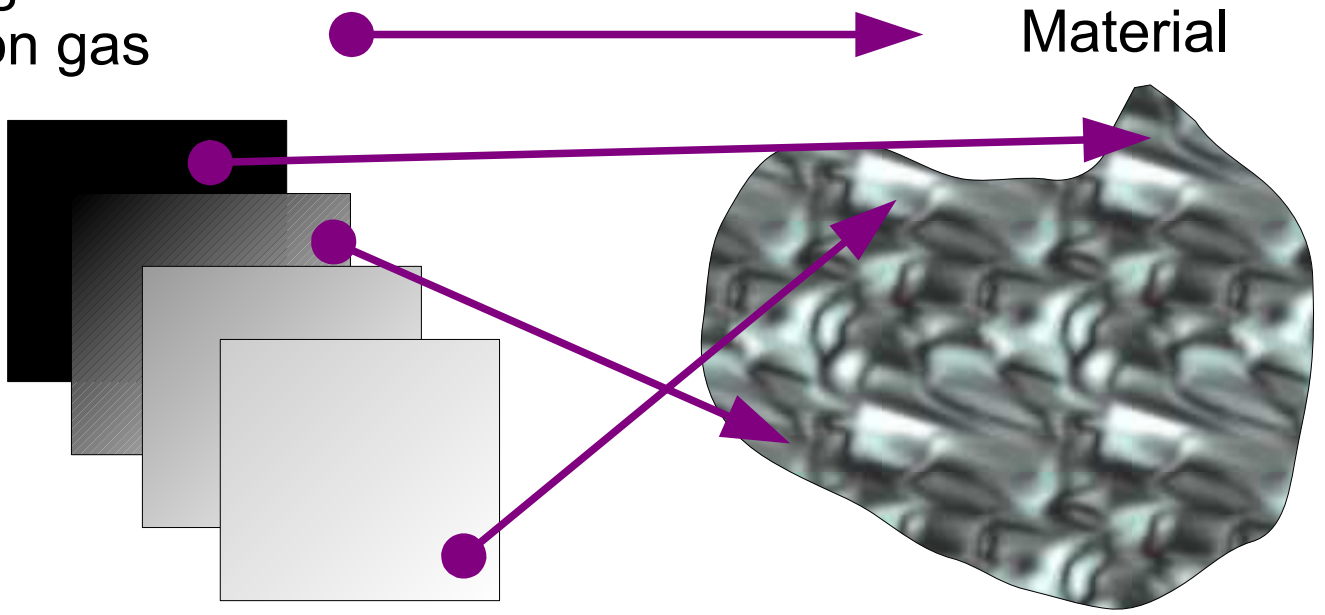
Exact: $v_{\mathrm{xc}}(n^h_{\mathbf{r}}) = v_{\mathrm{xc}}(\mathbf{r}; [n])$

Homogeneous electron gas



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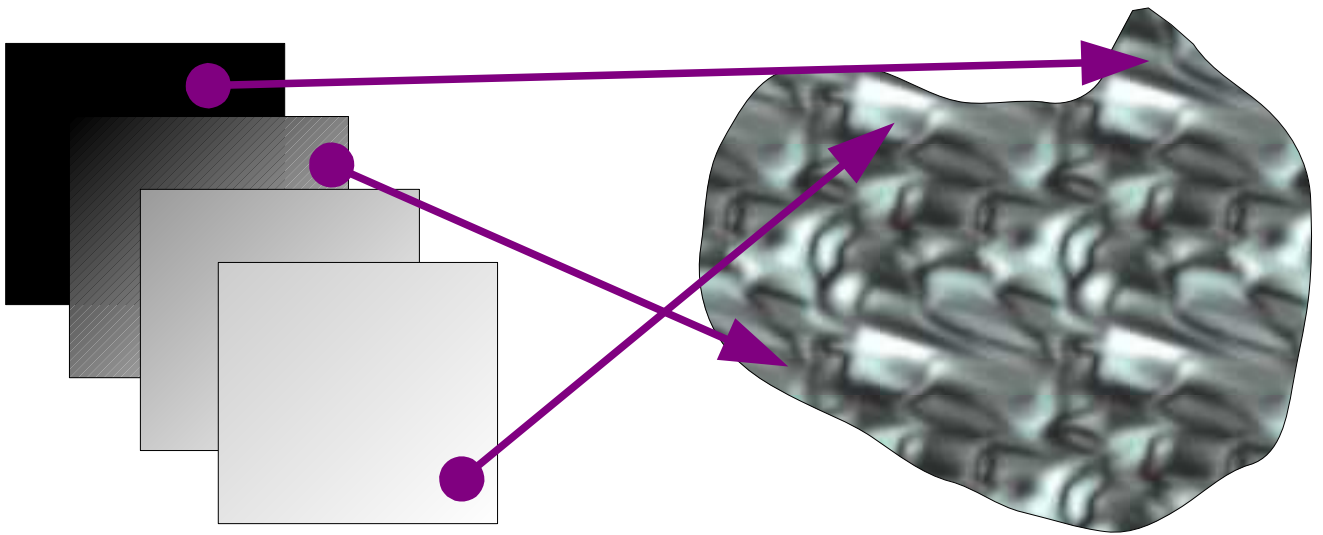
"Connector"

Homogeneous electron gas

Material



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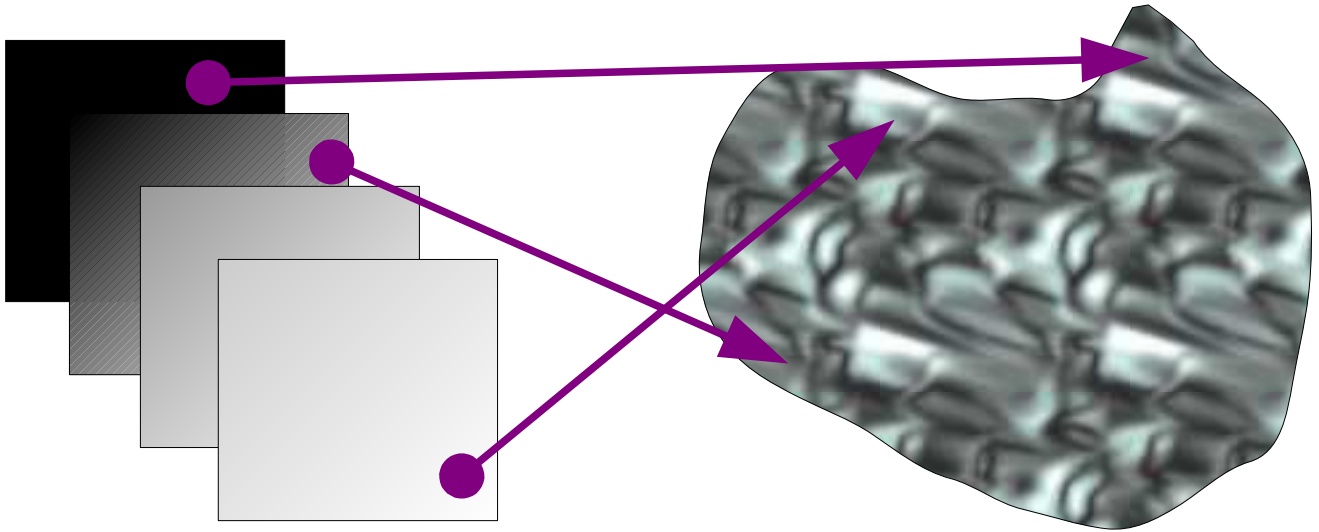

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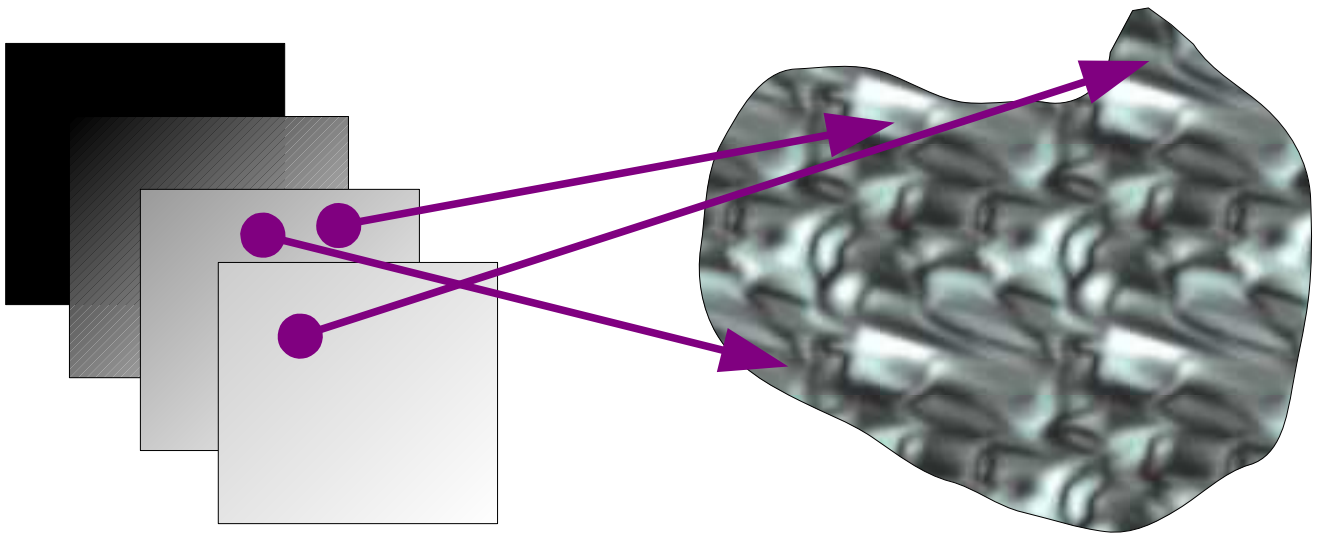

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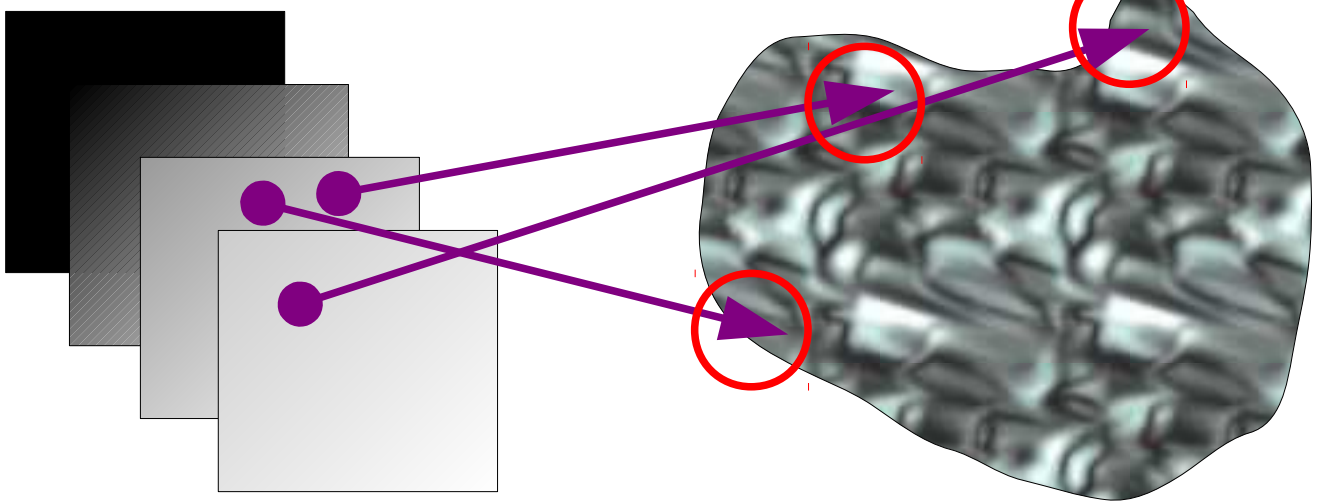
"Connector"

Homogeneous electron gas

Material



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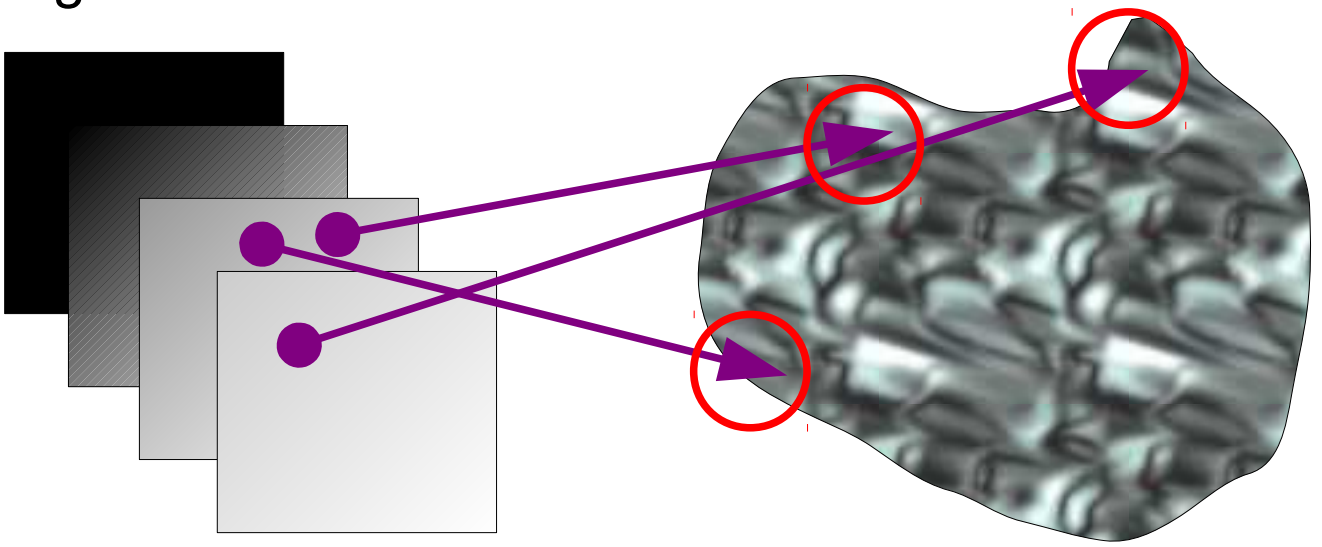
$$v_{\mathrm{xc}}\left(n_{\mathbf{r}}^{h}\right) = v_{\mathrm{xc}}(\mathbf{r};[n])$$

"Connector"

???

Homogeneous electron gas

Material



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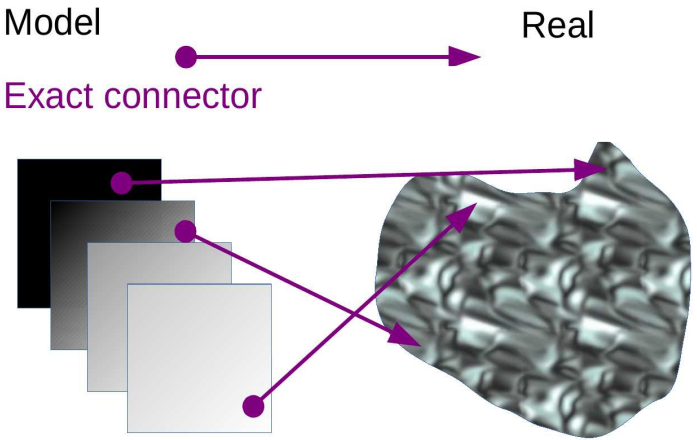
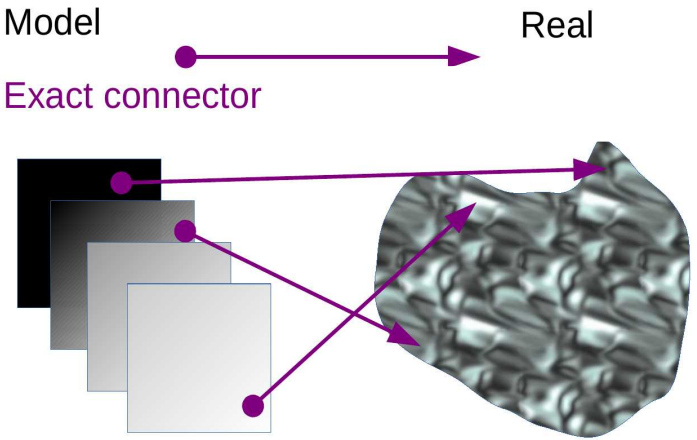
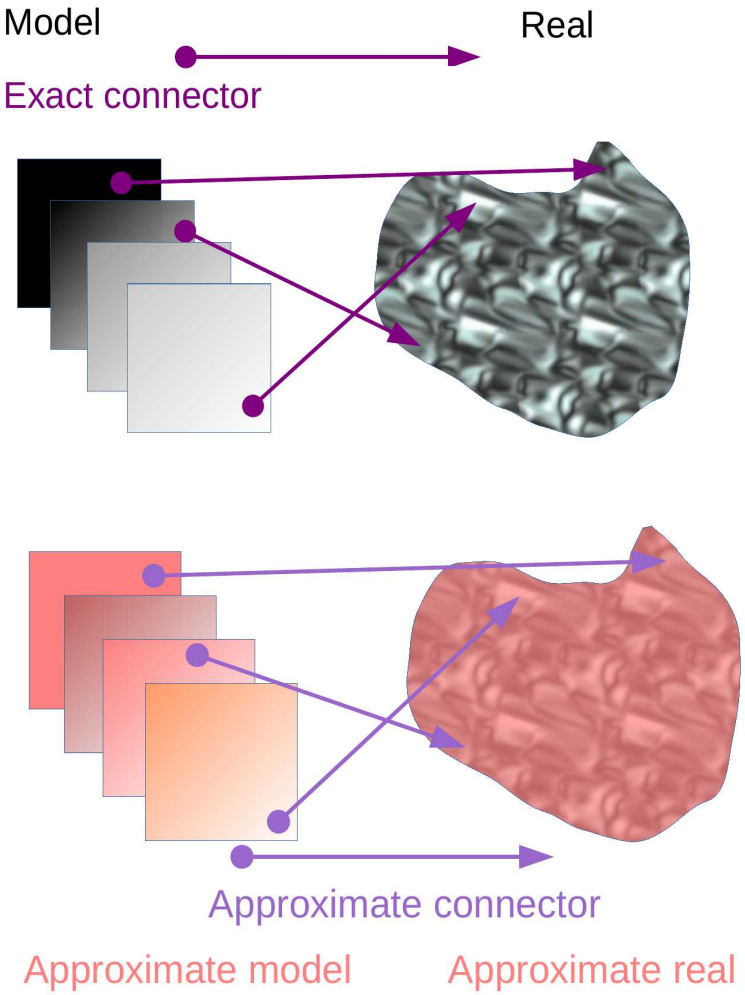


Aouina, Gatti, Reining, Faraday Discussions 224, 27 (2020)
Vanzini, Aouina, Panholzer, Gatti, Reining, NPJ Comp Mat (2022)

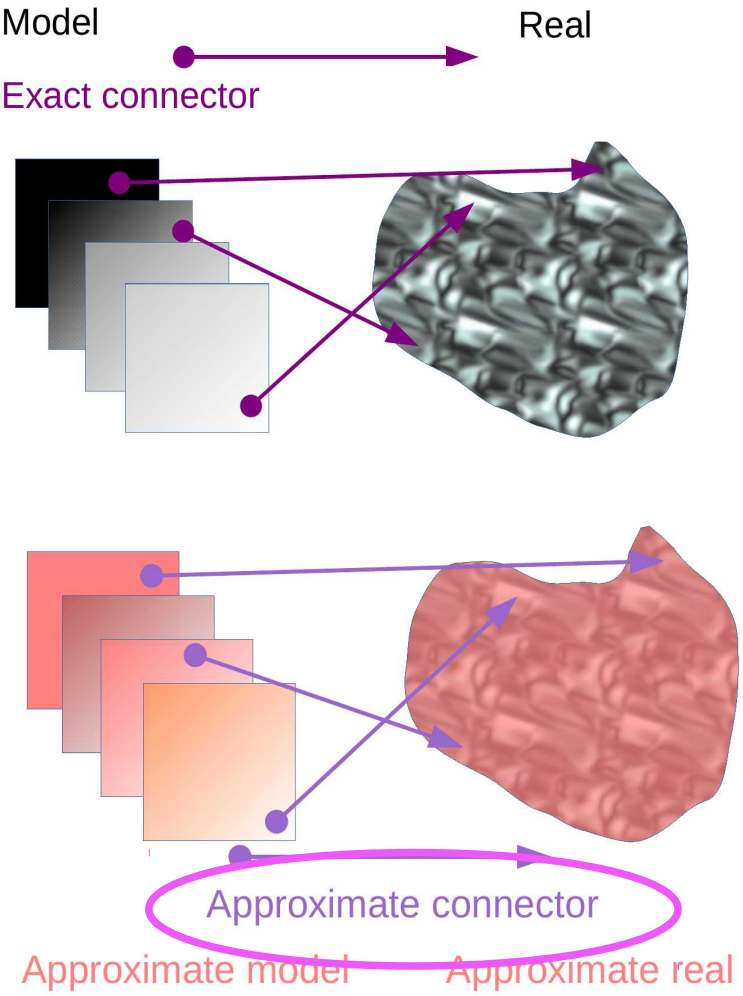


Approximation strategy

Aouina, Gatti, Reining, Faraday Discussions 224, 27 (2020)
Vanzini, Aouina, Panholzer, Gatti, Reining, NPJ Comp Mat (2022)



Aouina, Gatti, Reining, Faraday Discussions 224, 27 (2020)
Vanzini, Aouina, Panholzer, Gatti, Reining, NPJ Comp Mat (2022)



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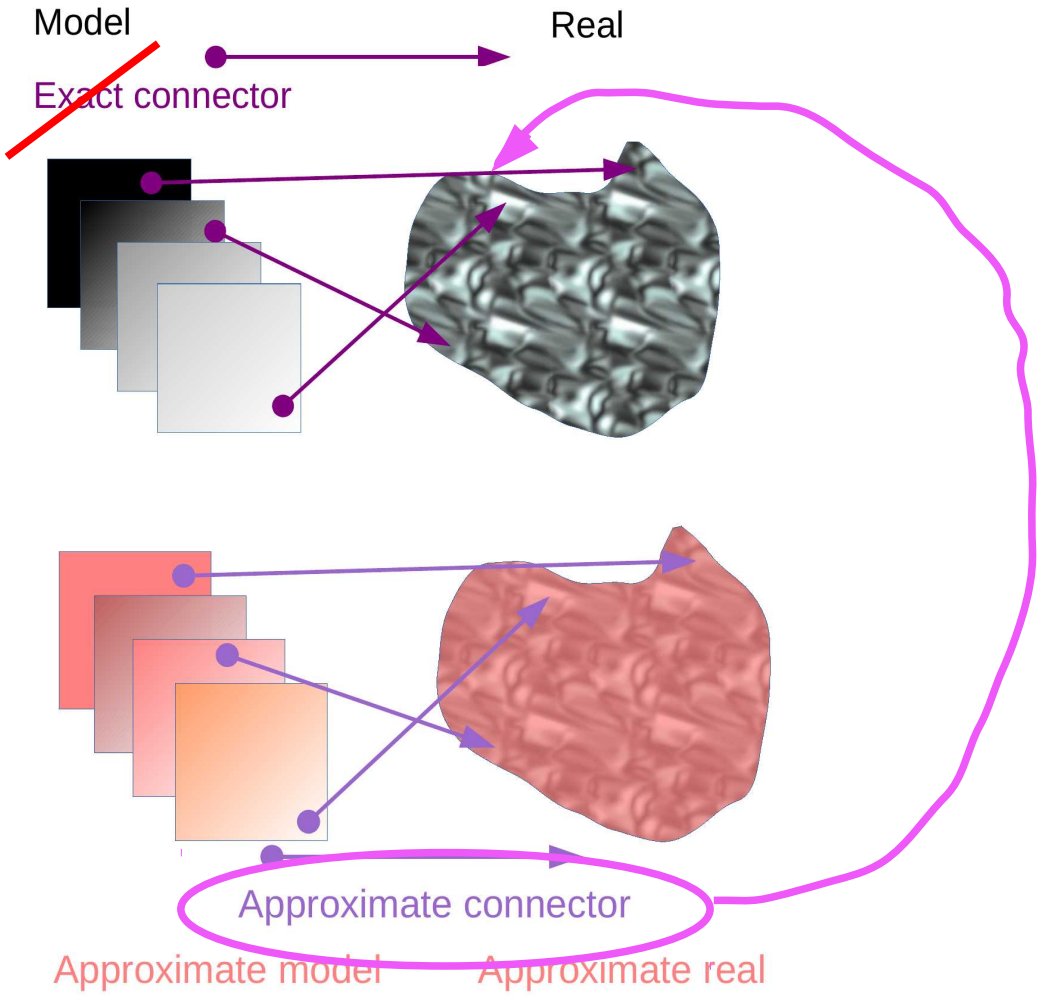
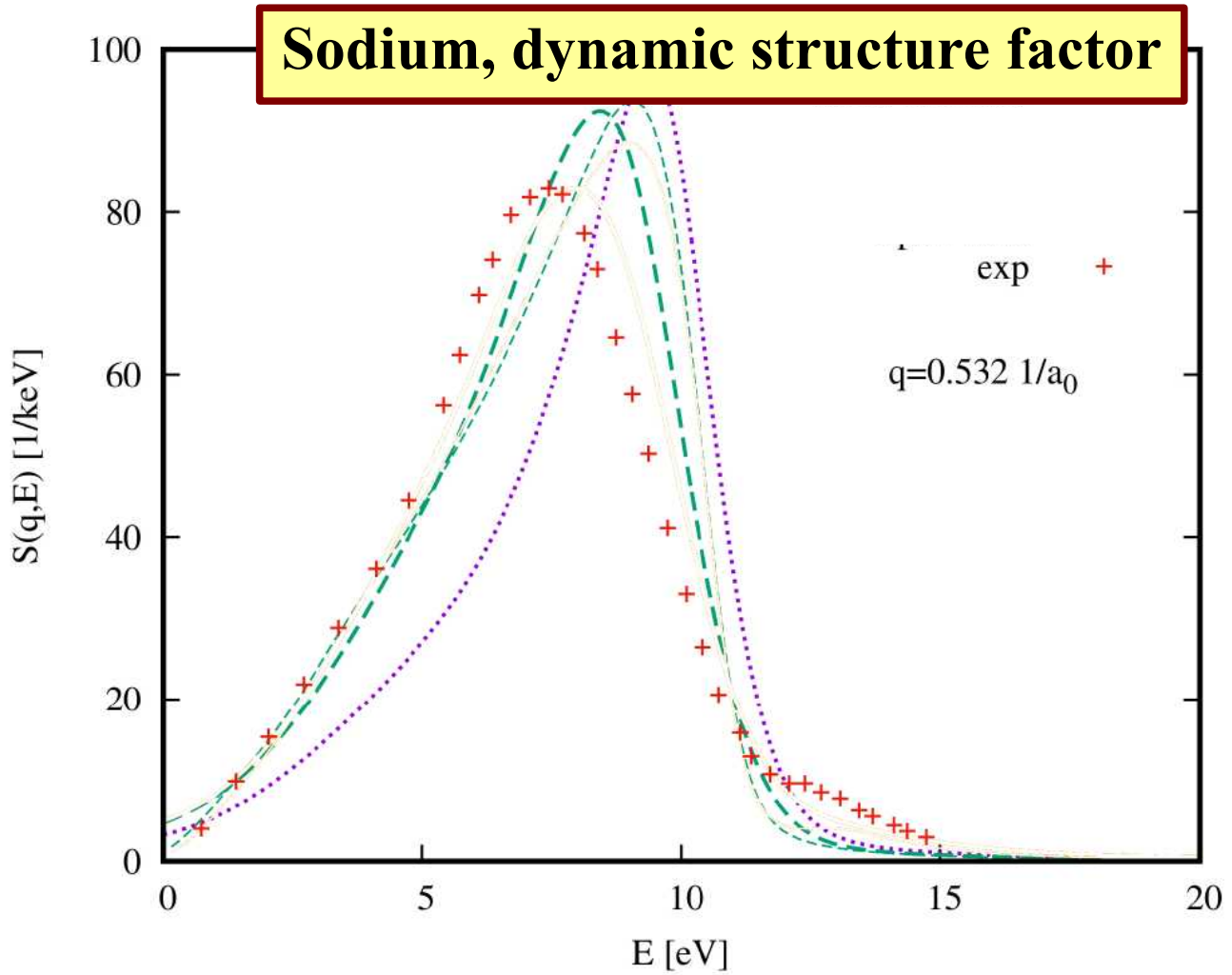
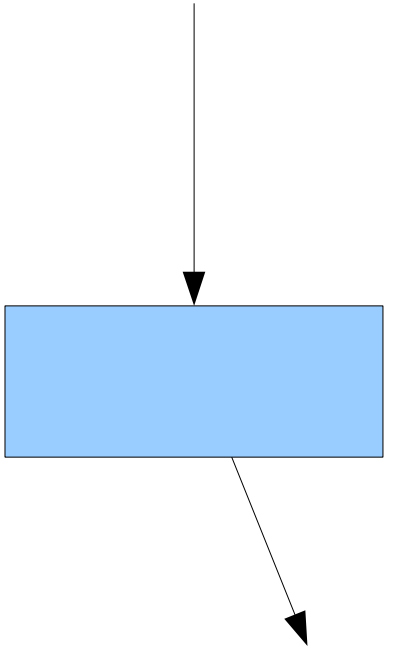


Aouina, Gatti, Reining, Faraday Discussions 224, 27 (2020)
Vanzini, Aouina, Panholzer, Gatti, Reining, NPJ Comp Mat (2022)

Sodium, dynamic structure factor



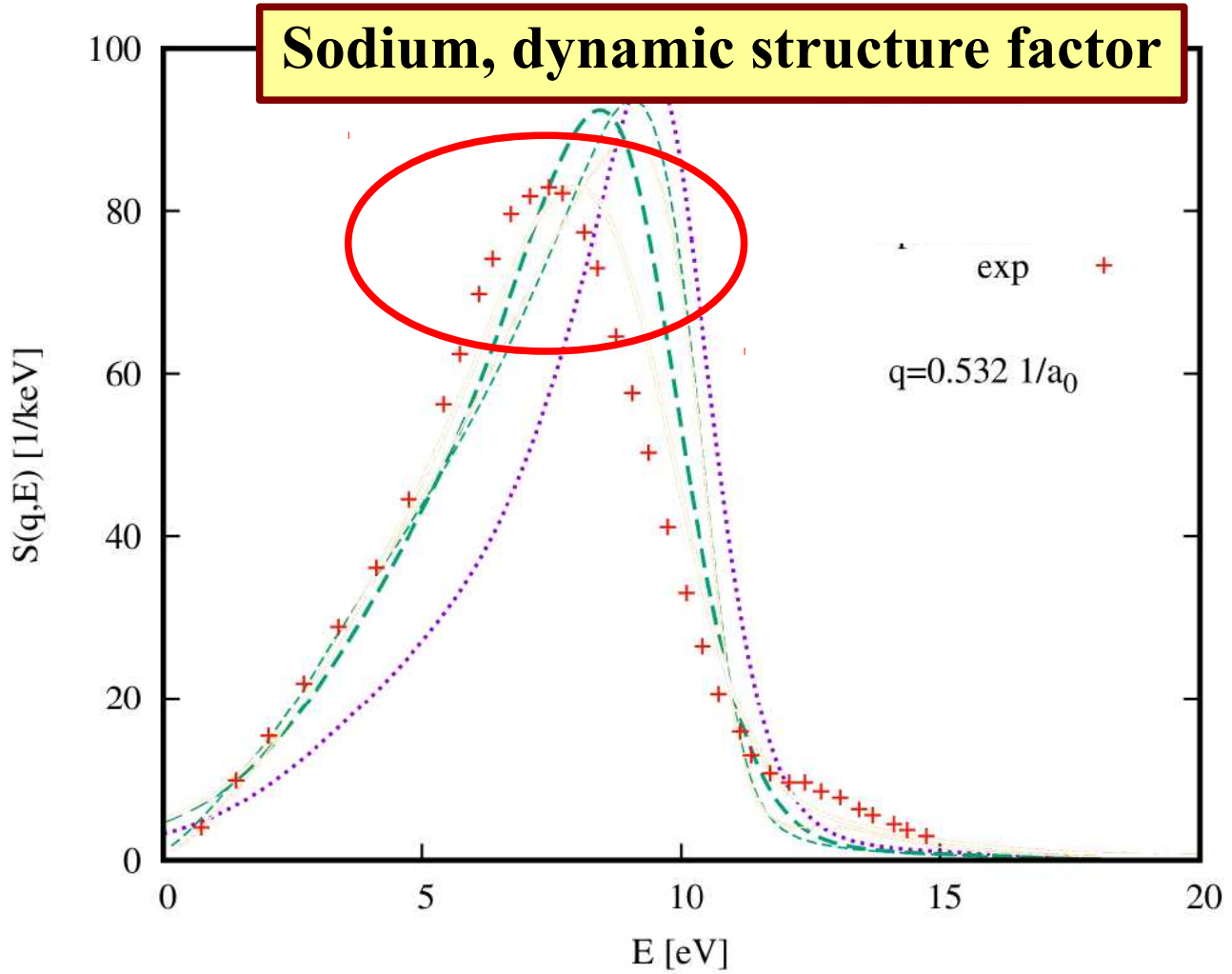
Inelastic x-ray scattering



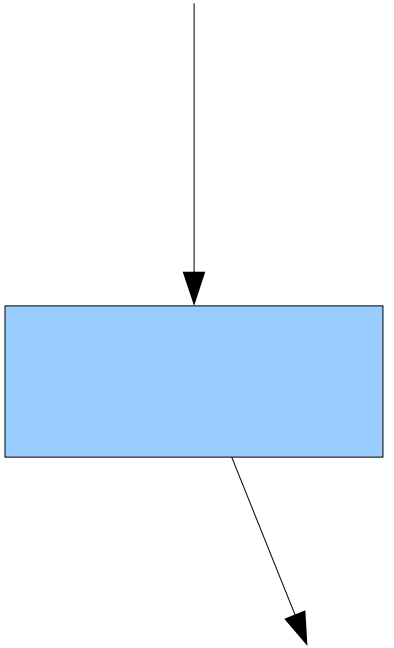
S. Huotari et al.,
PRB 84, 075108 (2011)

Cazzaniga et al.,
PRB 84, 075109 (2011)

Sodium, dynamic structure factor



Inelastic x-ray scattering



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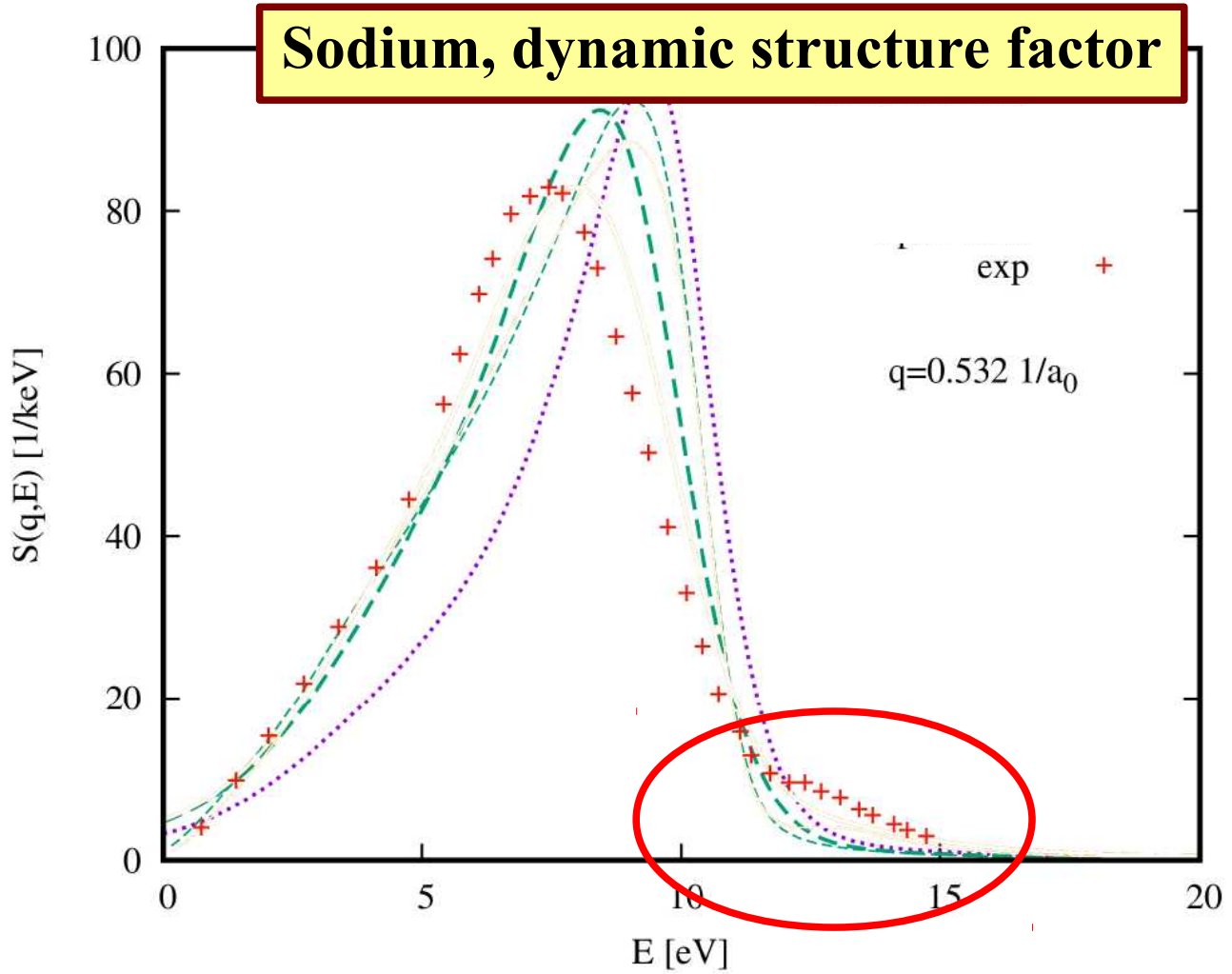
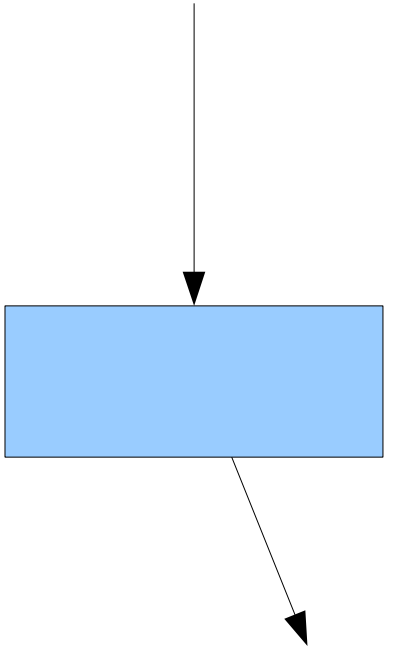


Inelastic x-ray scattering



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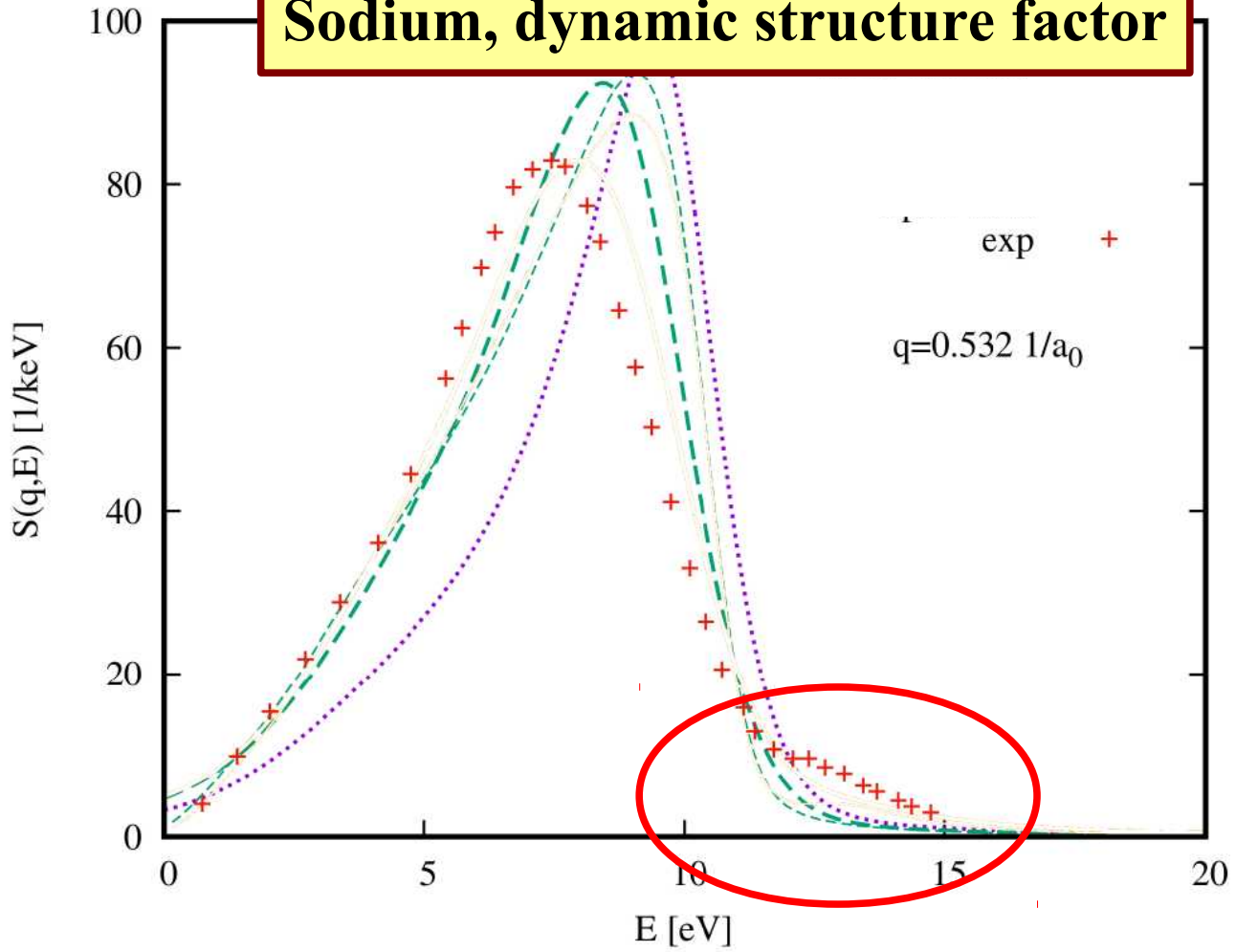

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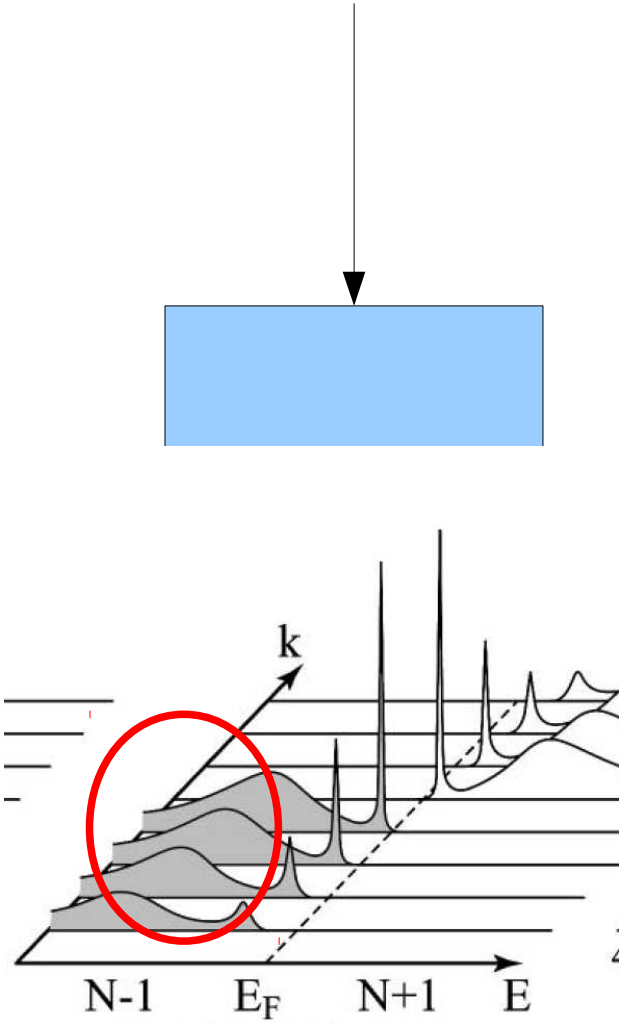
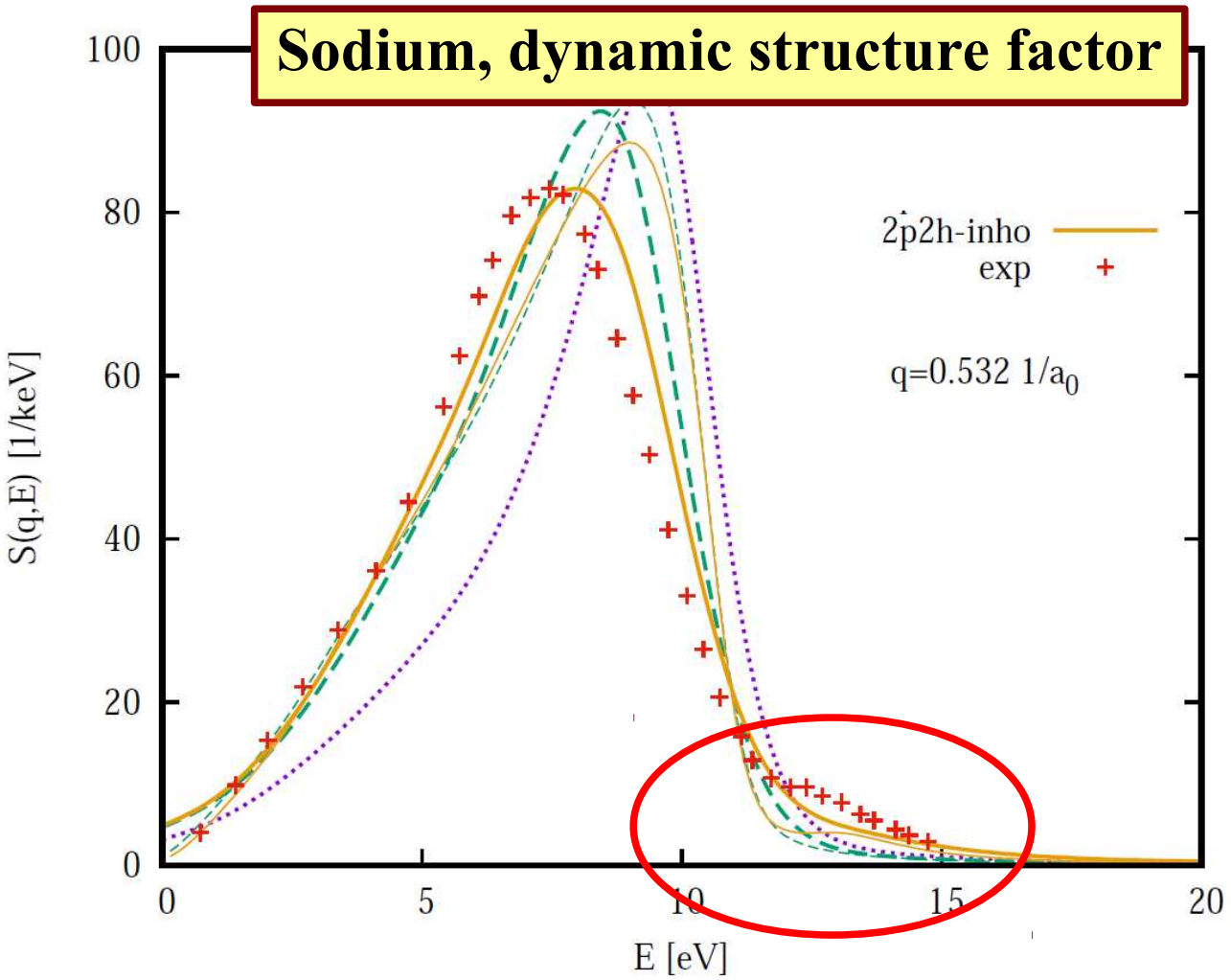
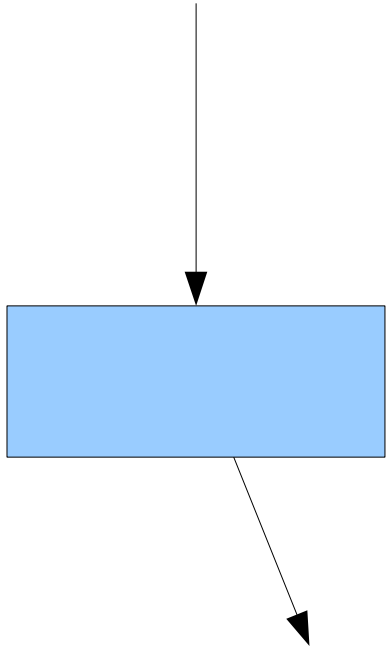


Sodium, dynamic structure factor



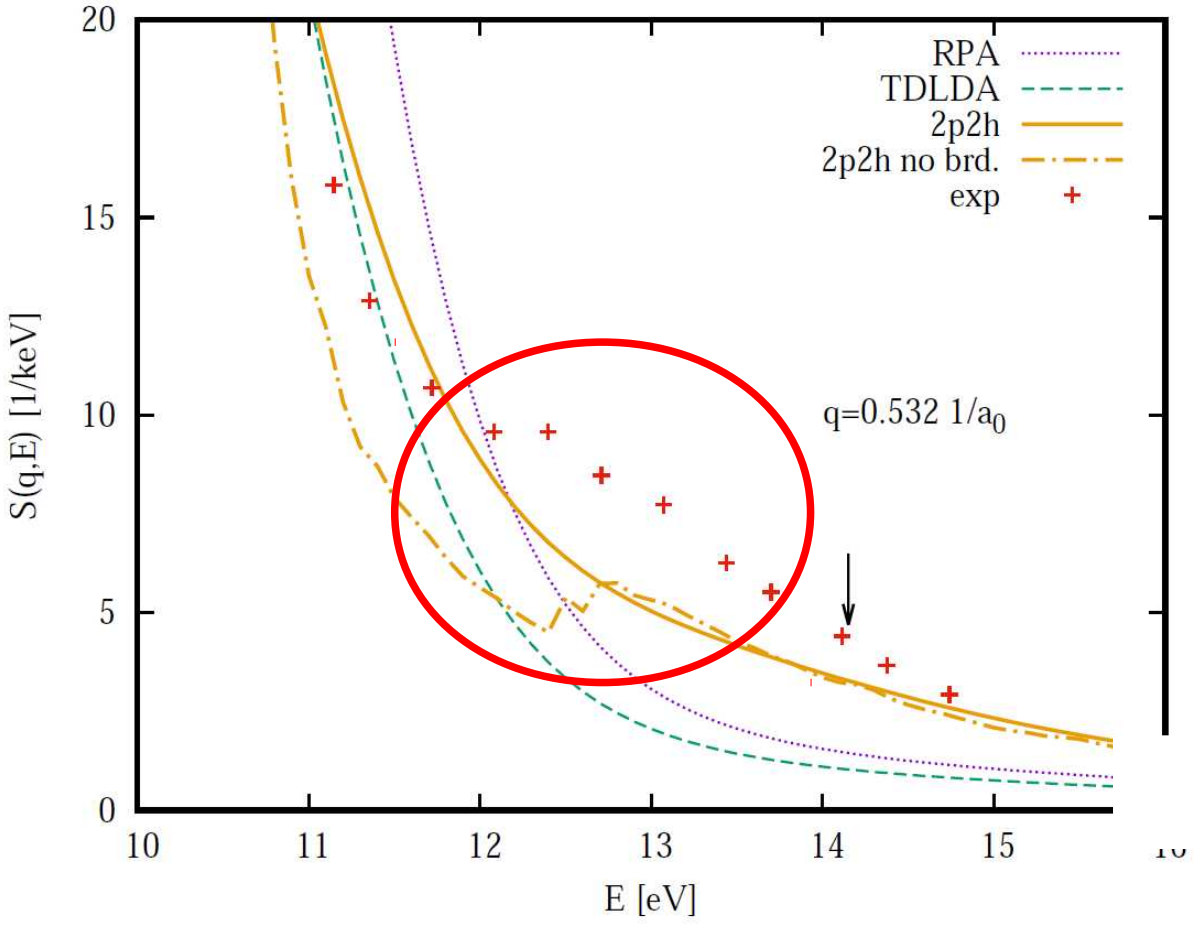
Inelastic x-ray scattering



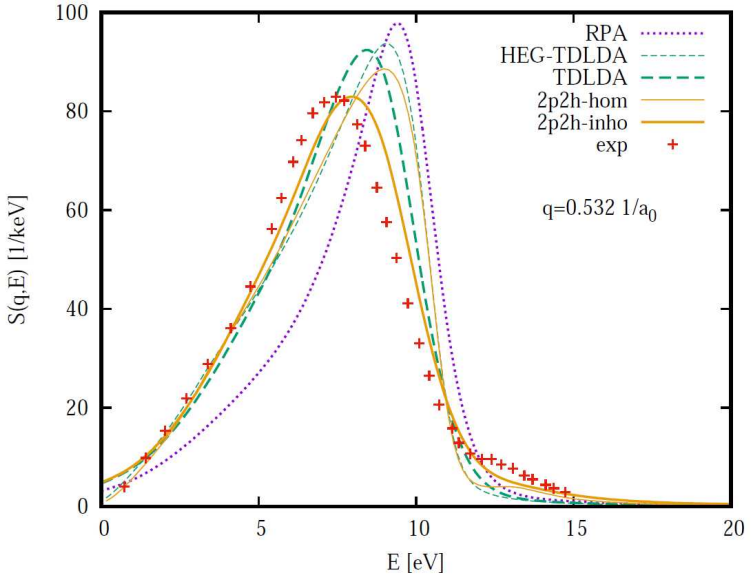
S. Huotari et al.,
PRB 84, 075108 (2011)

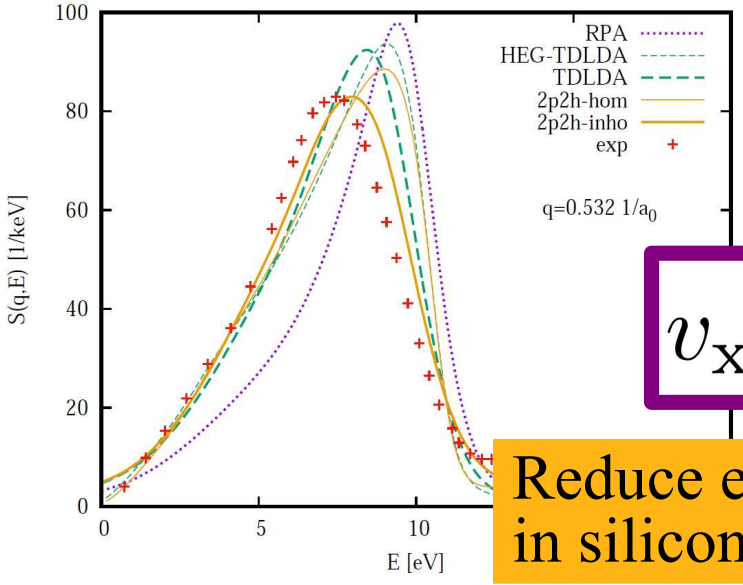
Cazzaniga et al.,
PRB 84, 075109 (2011)

Panholzer, Gatti, Reining, PRL 120, 166402 (2018)



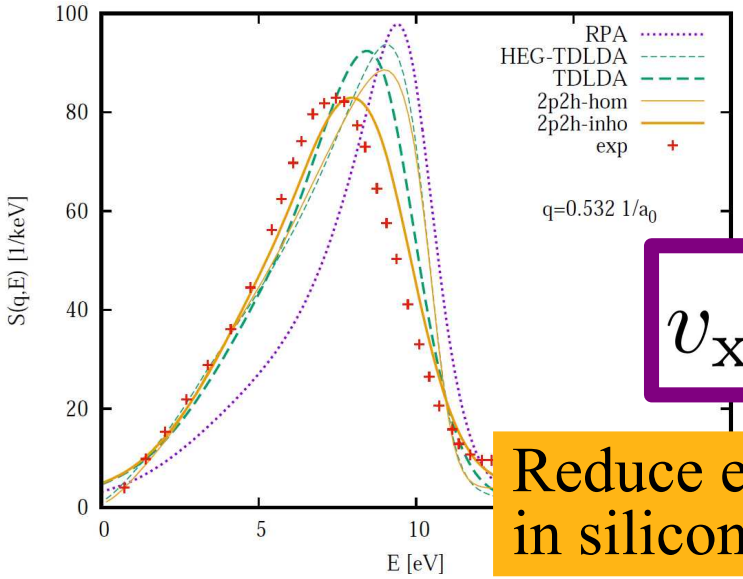
Panholzer, Gatti, Reining, Phys. Rev. Lett. 120, 166402 (2018)


RPA
HEG-TDLDA
TDLDA
2p2h-hom
2p2h-inho
exp
q=0.532 1/a0
S(q,E) [1/keV]
E [eV]
0
20
40
60
80
100
0
5
10
15
20



$$v_{\mathrm{xc}}(\mathbf{r}, [n])$$

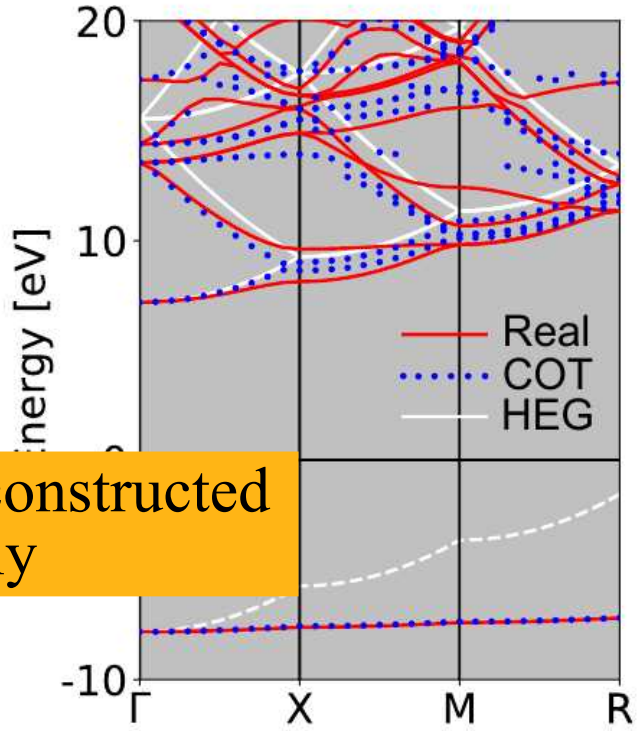
Reduce error of charge density
in silicon by factor of 2 w.r.t. LDA



Panholzer, Gatti, Reining, PRL 120, 166402 (2018)

$$v_{\mathrm{xc}}(\mathbf{r}, [n])$$

Reduce error of char
in silicon by factor c



Band structure reconstructed
from 1 k-point only

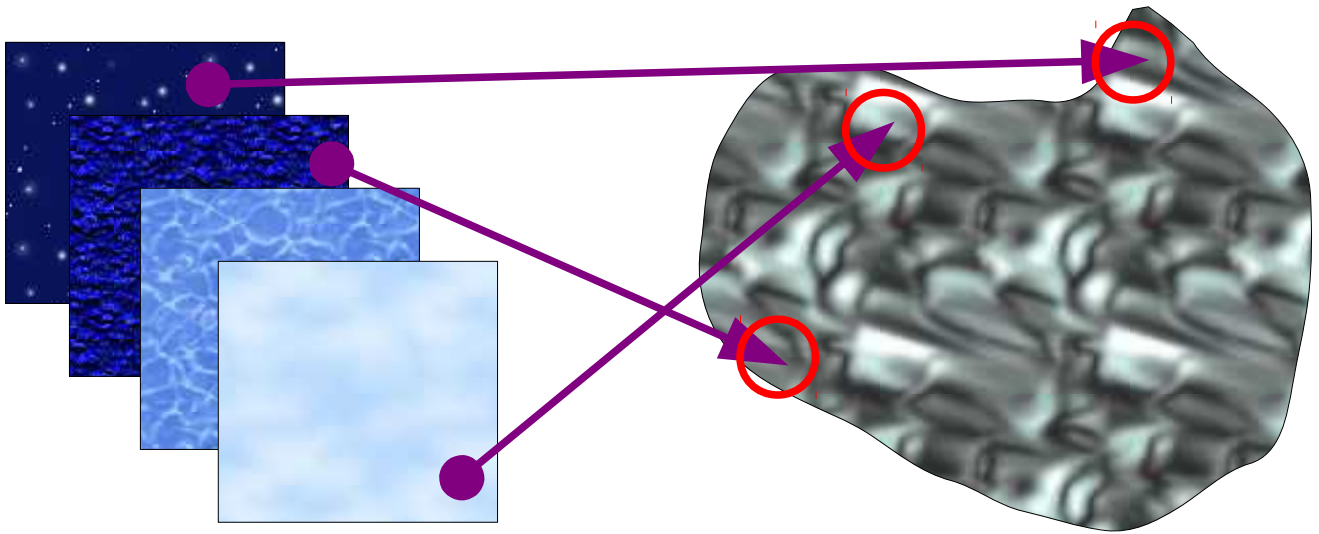
Aouina, Gatti, Reining, Faraday Discussions 224, 27 (2020)
Vanzini, Aouina, Panholzer, Gatti, Reining, npj Comp Mat 8:98 (2022)

The future: inhomogeneous model +ML

Multiple Connector Approximation

Inhomogeneous model

Material

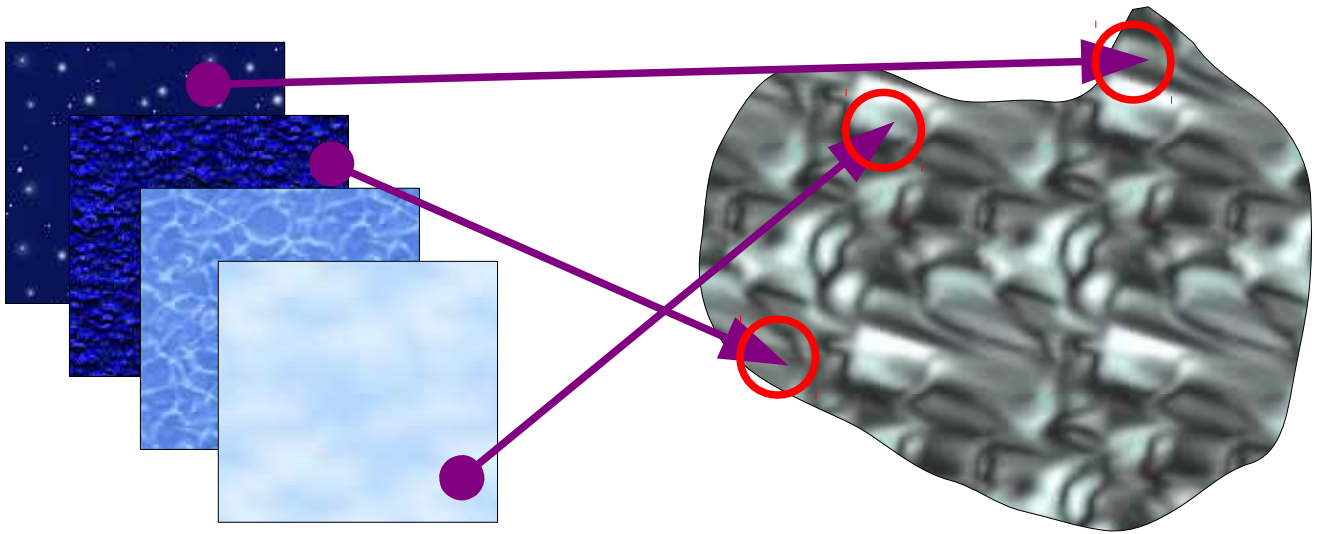


Aouina, Gatti, Reining, Faraday Discussions 224, 27 (2020)

The future:

→ will be frugal (work once, store)

Inhomogeneous model → Material



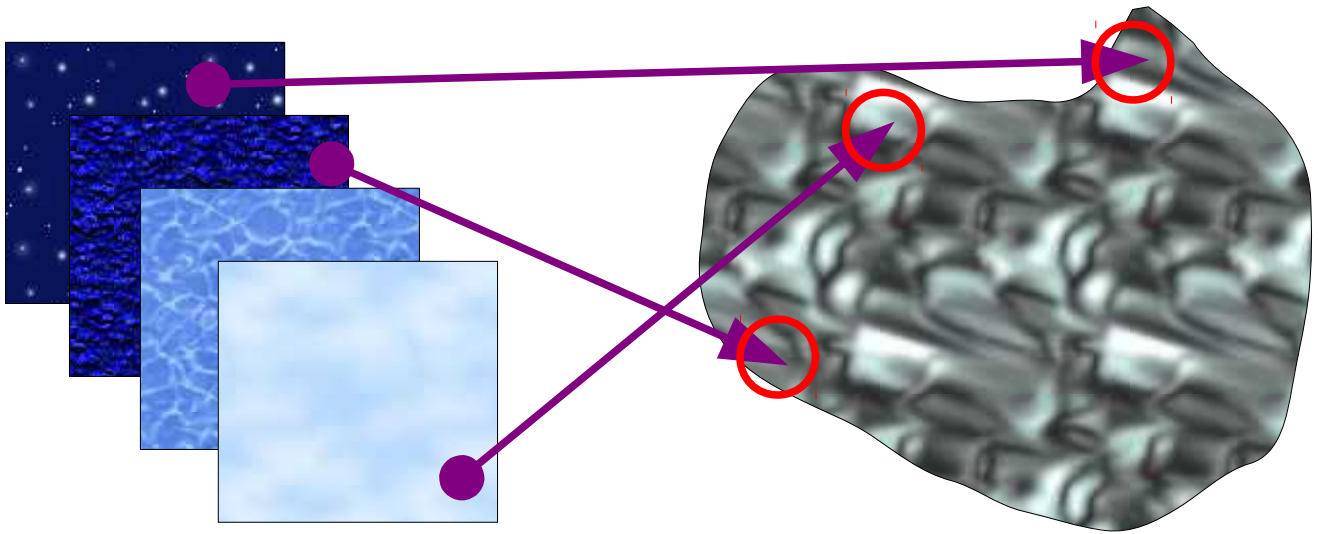
Aouina, Gatti, Reining, Faraday Discussions 224, 27 (2020)

The future:

→ will be frugal (work once, store)

→ will be collective (share)

Inhomogeneous model → Material



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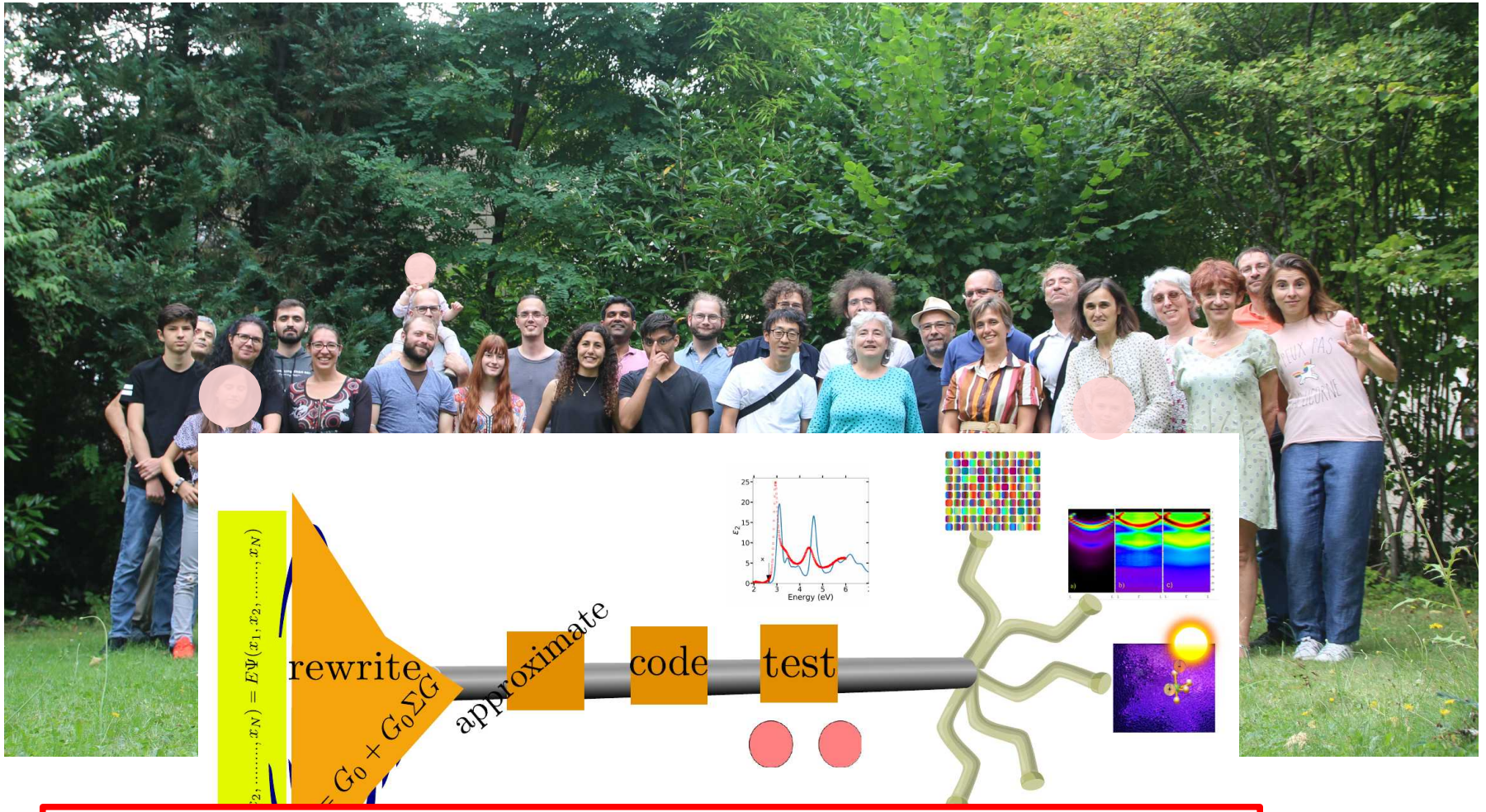

https://etsf.polytechnique.fr/
https://de.coursera.org/learn/density-functional-theory

La mécanique quantique dans les systèmes à N corps
ou comment **chercher** la solution d'un problème insoluble

Lucia Reining

Palaiseau Theoretical Spectroscopy Group & Friends

Put one after the other

Challenges: → higher precision

→ wider pipeline (change pipeline)

→ new output (change color and new tube d /dt)

→ new understanding *(c'est quoi la comprehension)*

→ allow for surprises (new output little green woman)

(here add comment ML)

Circular pipeline and work once….collective

The quantum many-body problem: unsolvable but keeping us busy!

Palaiseau Theoretical Spectroscopy Group & Friends

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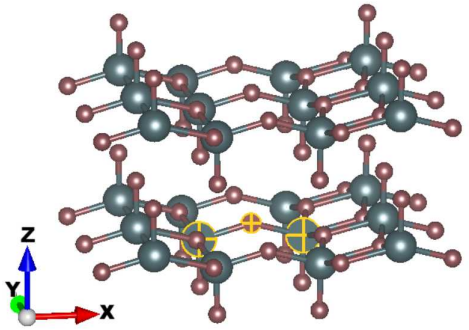
http://etsf.polytechnique.fr

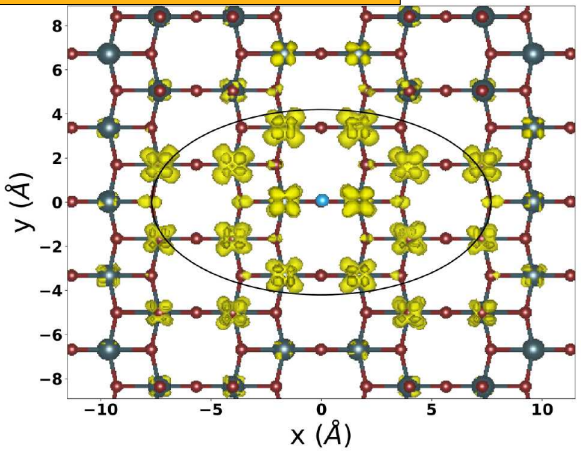
State-of-the-art Bethe-Salpeter

Chaire Énergies Durables
École polytechnique - EDF

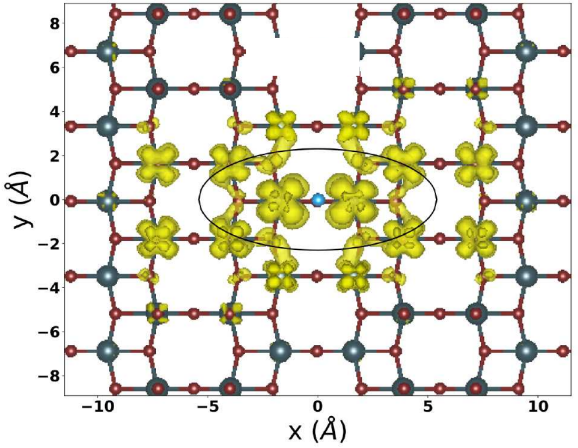
V_2O_5: a layered bulk material



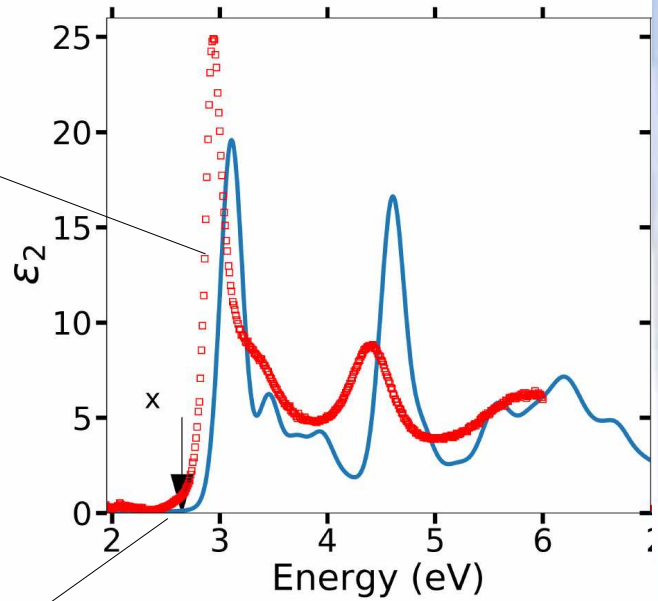
(a)



(b)



(d)

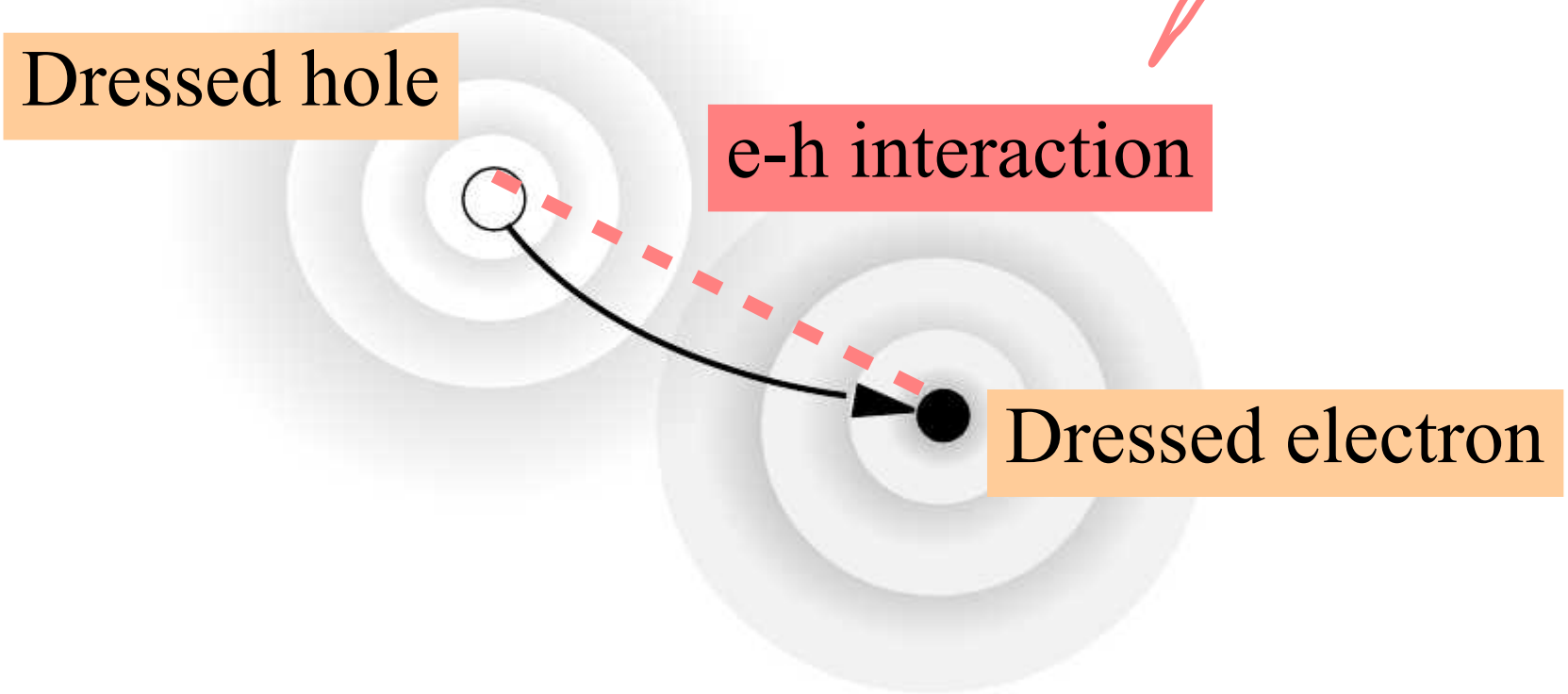


Vitaly Gorelov et al.,
npj comp mat (2022)

Bethe-Salpeter Equation

$$L = L_0 + L_0 \frac{\delta(v_H + \Sigma_{xc})}{\delta G} L$$

$$L_0 = GG$$

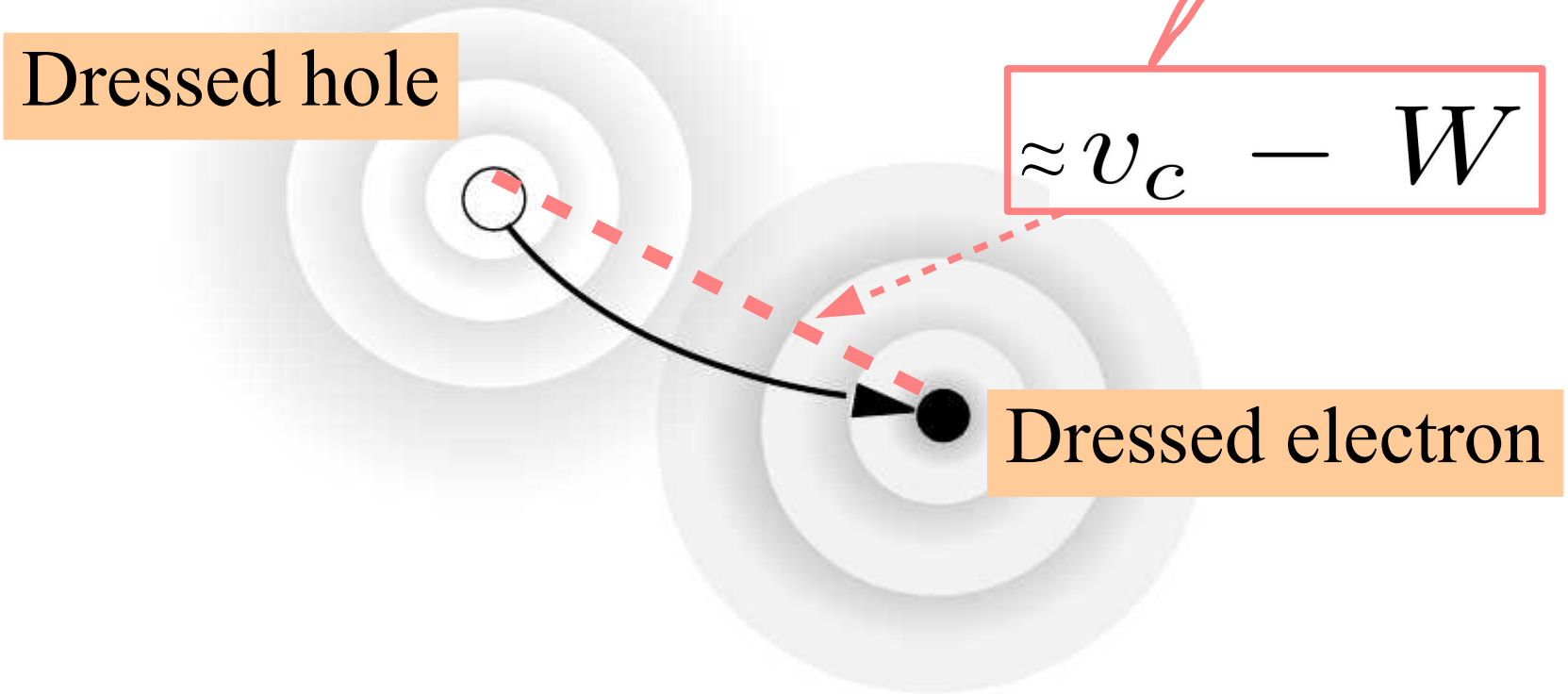


Bethe-Salpeter Equation

$$L = L_0 + L_0 \frac{\delta(v_H + \Sigma_{xc})}{\delta G} L$$

$$L_0 = GG$$

$$\approx v_c - W$$



Bethe-Salpeter Equation

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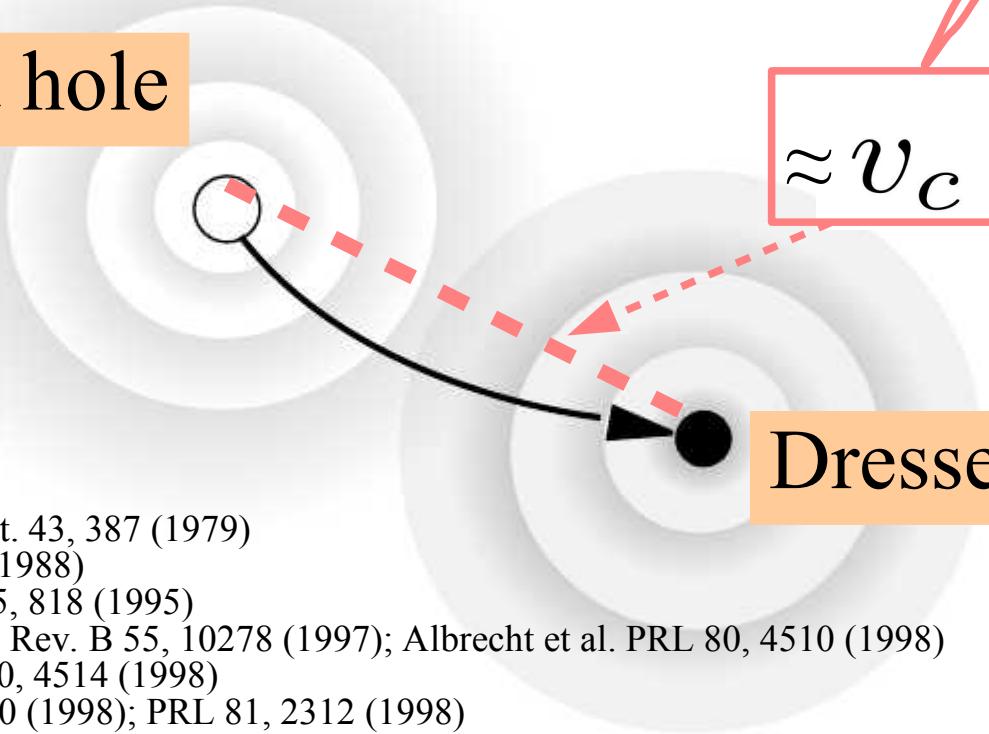


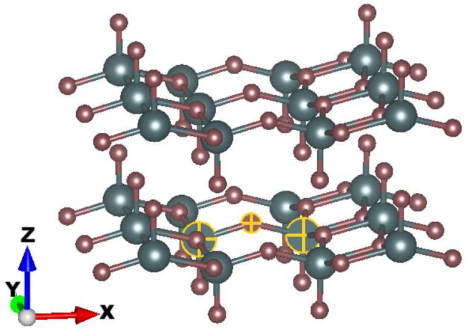
Dressed hole

Dressed electron

Hanke & Sham, Phys. Rev. Lett. 43, 387 (1979)
Strinati, Nuovo Cimento 11, 1 (1988)
Onida, et al., Phys. Rev. Lett. 75, 818 (1995)
Albrecht, Onida, Reining Phys. Rev. B 55, 10278 (1997); Albrecht et al. PRL 80, 4510 (1998)
Benedict, Shirley, Bohn, PRL 80, 4514 (1998)
Rohlfing & Louie, PRL 80, 3320 (1998); PRL 81, 2312 (1998)

Optical absorption

V_2O_5: a layered bulk material



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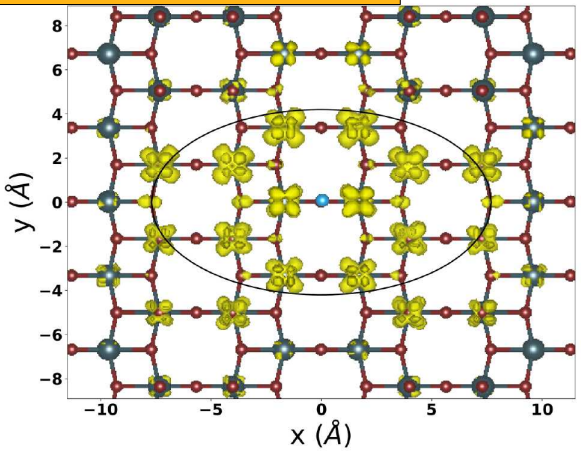
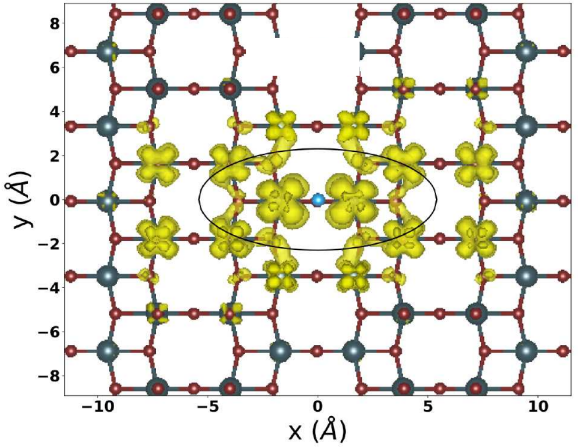
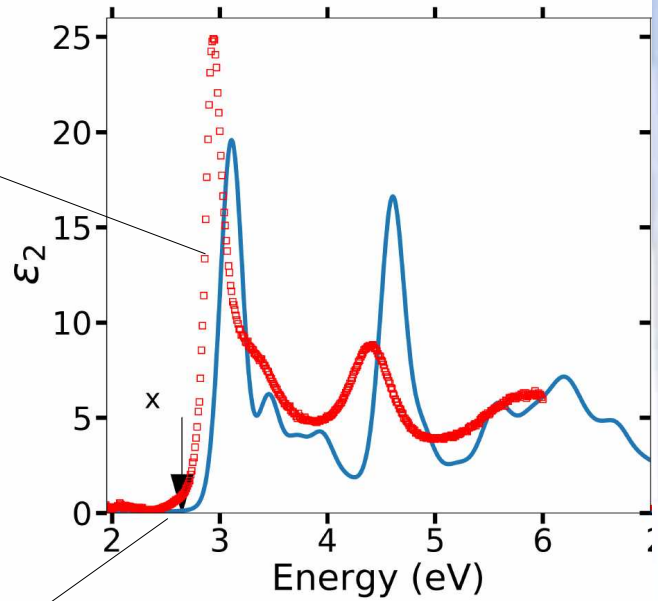


(b)



(d)

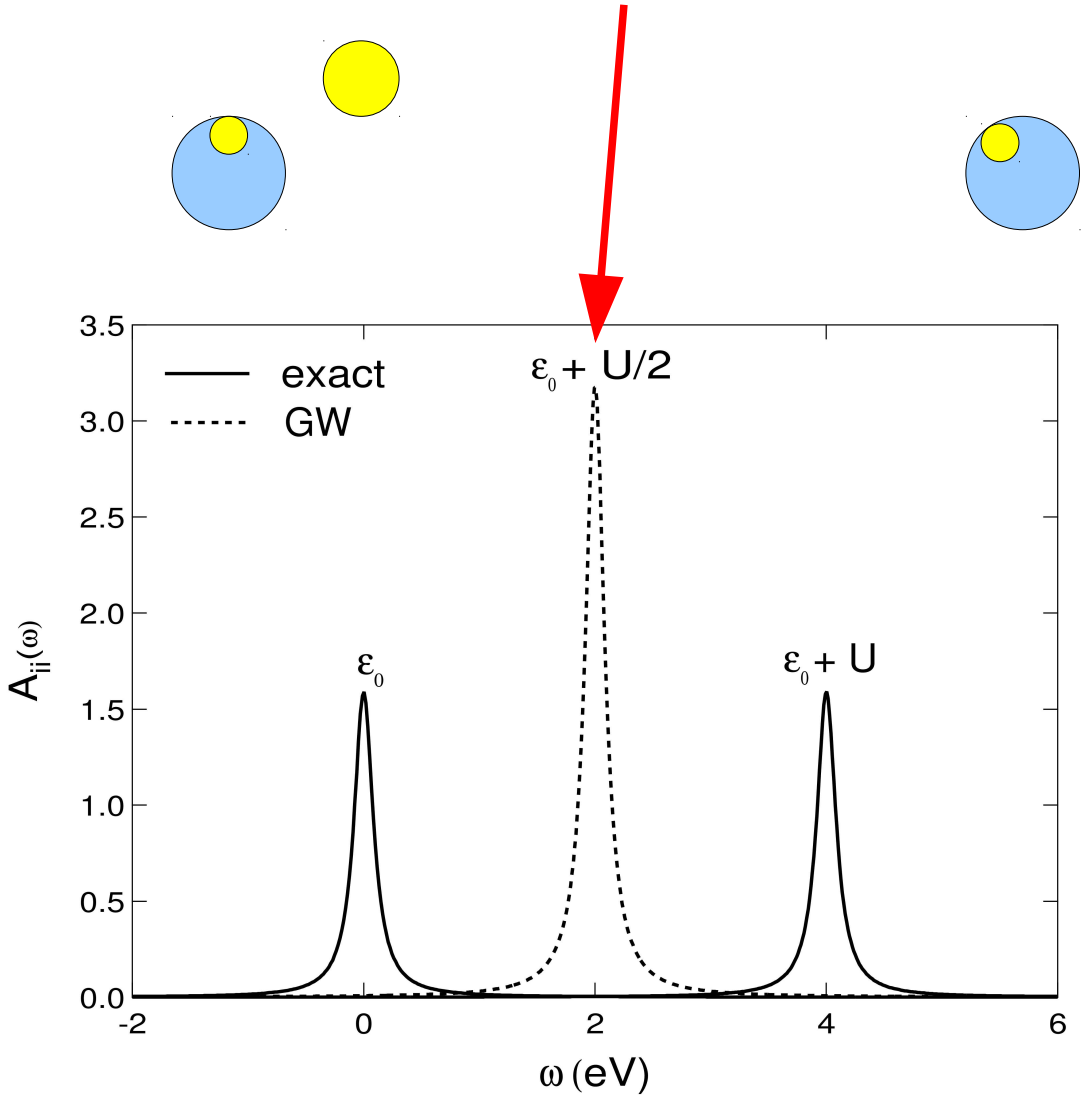


Vitaly Gorelov et al.,
npj comp mat (2022)

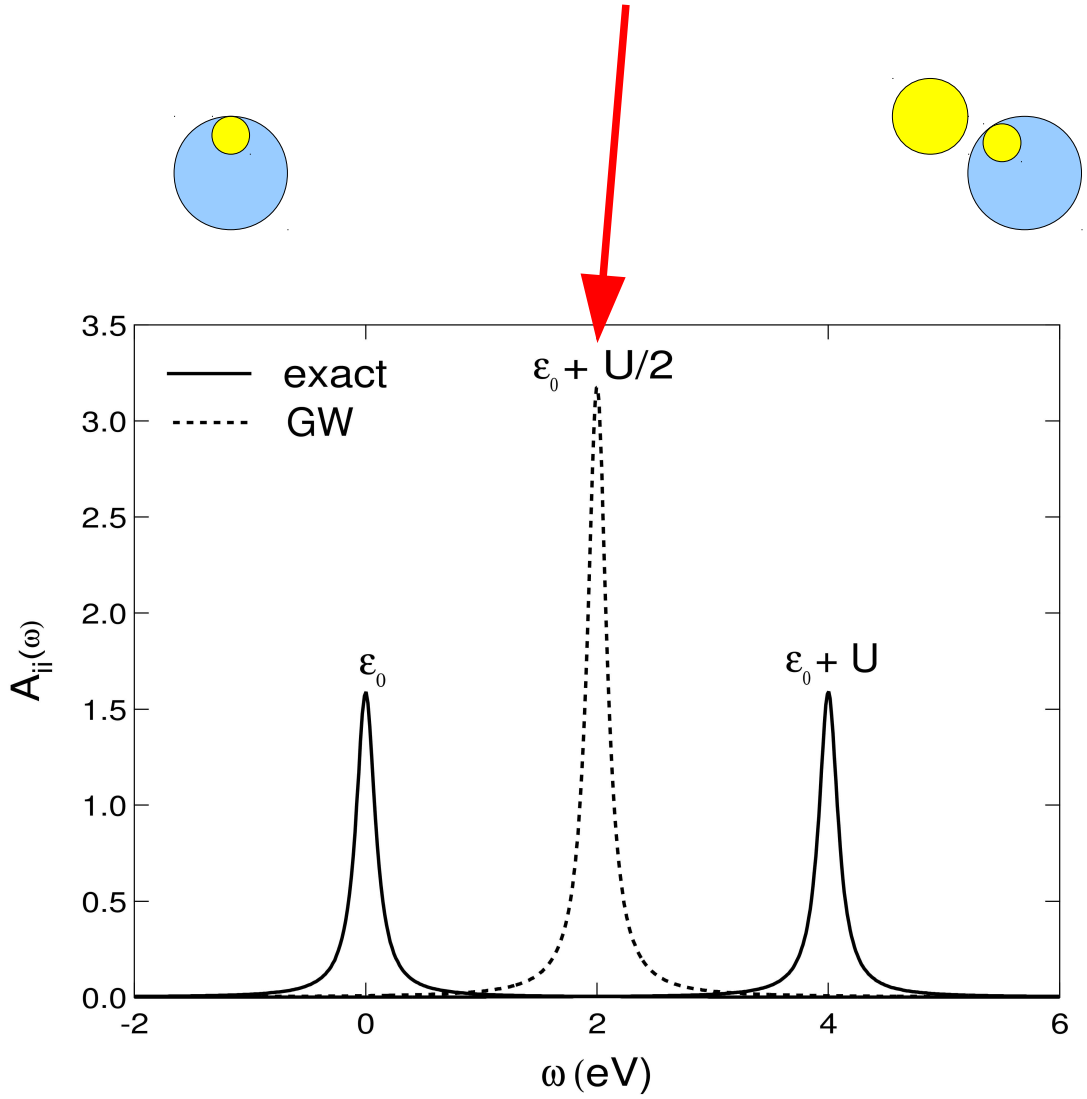
H_2^+

H_2^+

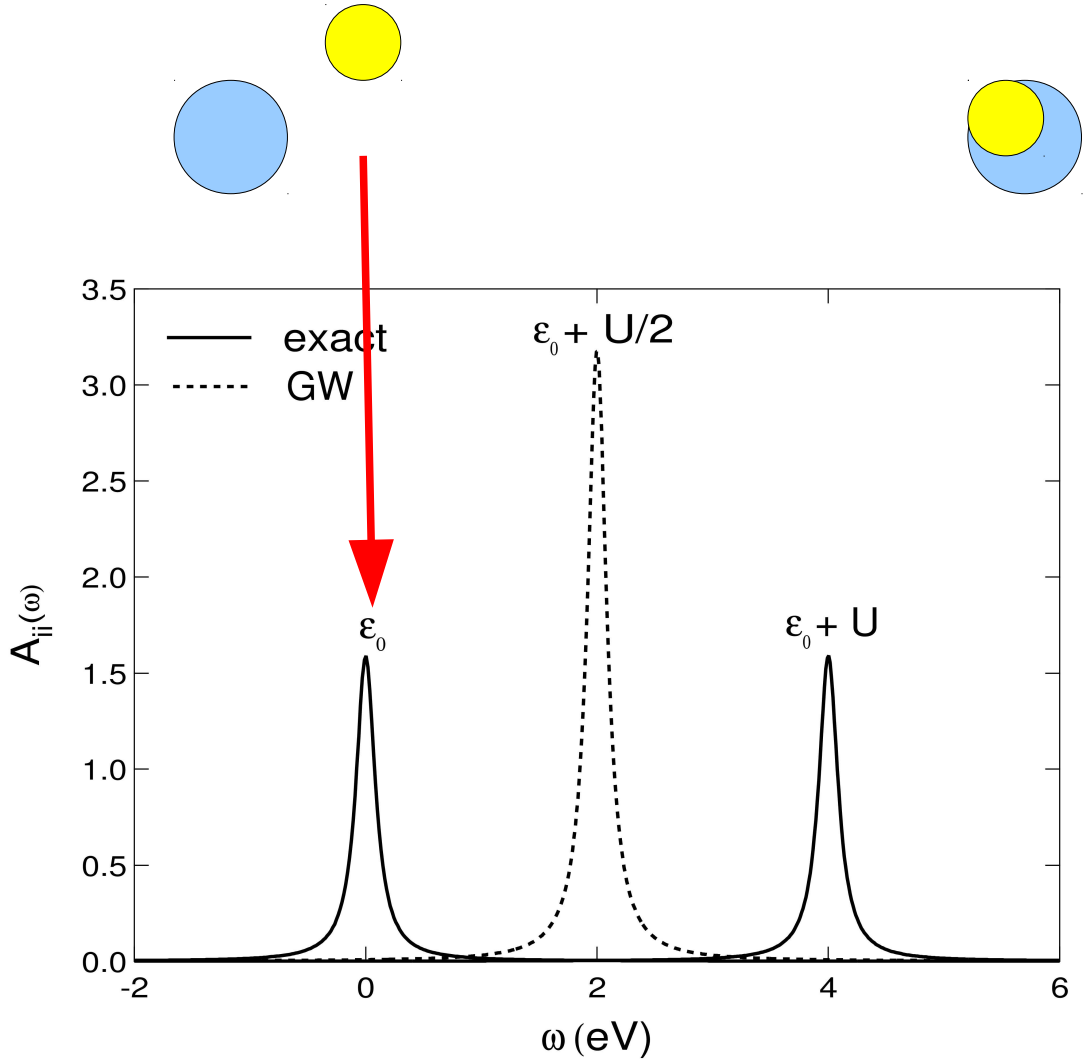
H_2^+


exact
GW
$\varepsilon_0 + U/2$
ε_0
$\varepsilon_0 + U$
$A_{ii}(\omega)$
ω (eV)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-2
0
2
4
6

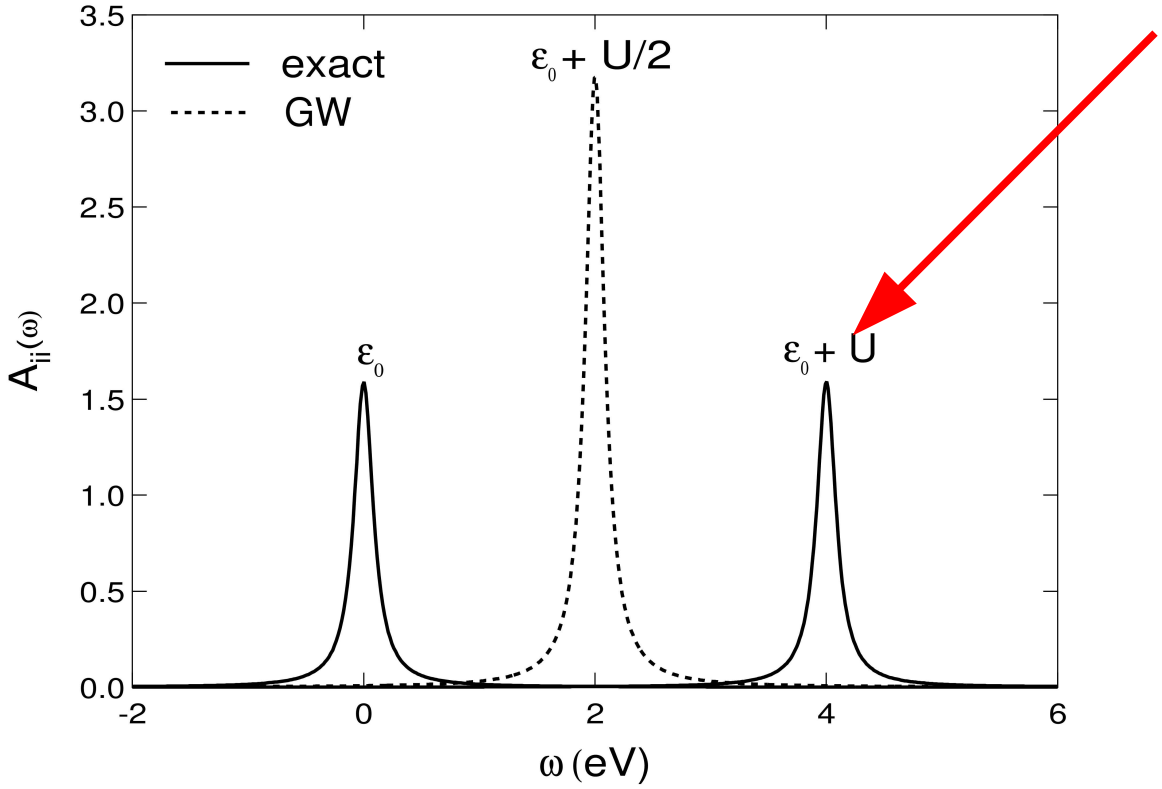
H_2^+


exact
GW
$\varepsilon_0 + U/2$
ε_0
$\varepsilon_0 + U$
$A_{ii}(\omega)$
ω (eV)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-2
0
2
4
6

H_2^+


exact
GW
ε_0 + U/2
ε_0
ε_0 + U
$A_{ii}(\omega)$
ω (eV)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-2
0
2
4
6

H_2^+


exact
GW
$\varepsilon_0 + U/2$
ε_0
$\varepsilon_0 + U$
$A_{ii}(\omega)$
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-2
0
2
4
6
ω (eV)

The quantum many-body problem: unsolvable but keeping us busy!

Palaiseau Theoretical Spectroscopy Group & Friends **P8**

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Synchrotron SLS: Matthias Muntwiler, Vladimir Strocov

Descriptor	Auxiliary "potential"	
$n(\mathbf{r})$	$v_{\mathrm{xc}}(\mathbf{r};[n])$	
$G(\mathbf{r},\mathbf{r}',\omega)$	$\Sigma(\mathbf{r},\mathbf{r}',\omega;[G])$	
$G_{\ell\ell}(\omega)$	$\Sigma^{loc}_{\ell}(\omega;[G^{loc}])$	DMFT

Give color to
Slides for insiders

→ Known functional $A_{\ell\ell}(\omega;[G_{\ell\ell}])$

→ Often approximate $A_{\mathbf{k}}(\omega;[G^{loc}])$

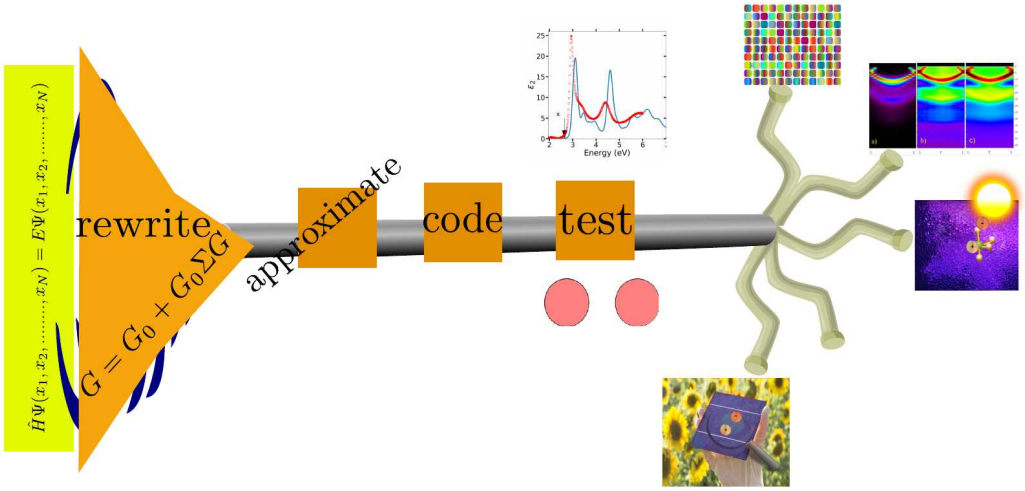
A. Georges et al., Rev. Mod. Phys. 68, 13 (1996)
S. Y. Savrasov and G. Kotliar, Phys. Rev. B 69, 245101 (2004)

Descriptor	Auxiliary "potential"	
$n(\mathbf{r})$	$v_{\mathrm{xc}}(\mathbf{r};[n])$	
$G(\mathbf{r},\mathbf{r}',\omega)$	$\Sigma(\mathbf{r},\mathbf{r}',\omega;[G])$	
$G_{\ell\ell}(\omega)$	$\Sigma^{loc}_{\ell}(\omega;[G^{loc}])$	DMFT

$\rightarrow$ Known functional $A_{\ell\ell}(\omega;[G_{\ell\ell}])$

$\rightarrow$ Often approximate $A_{\mathbf{k}}(\omega;[G_{\ell\ell}])$

Generalization: see M. Gatti, et al., PRL 99, 057401 (2007);
M. Vanzini, et al., Faraday Discussions 224, 424-447 (2020)



Challenges: → higher precision

→ wider pipeline (more complex systems)

→ new output

→ new understanding

→ allow for surprises

$$\hat{H}\Psi_\lambda(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N) = E_\lambda \Psi_\lambda(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N)$$

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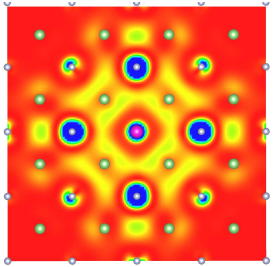
$$(\hat{h} + \hat{V})\varphi_s(\mathbf{r}) = \varepsilon_s \varphi_s(\mathbf{r})$$

$$\hat{H}\Psi_\lambda(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) = E_\lambda \Psi_\lambda(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$$

$$(\hat{h} + \hat{V})\varphi_s(\mathbf{r}) = \varepsilon_s \varphi_s(\mathbf{r})$$

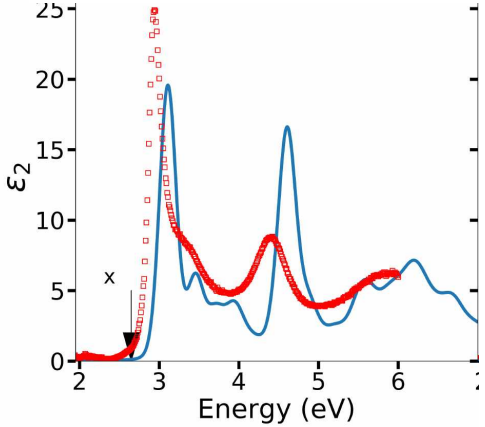
$$v_{\mathrm{xc}}(\mathbf{r})$$



W. Kohn and L. J. Sham, Phys. Rev. 140:A1133–1138, 1965

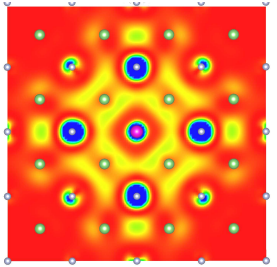
$$\hat{H}\Psi_\lambda(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_N)=E_\lambda\Psi_\lambda(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_N)$$

$$(\hat{h}+\hat{V})\varphi_s(\mathbf{r})=\varepsilon_s\varphi_s(\mathbf{r})$$



$$v_{SF}(\mathbf{r},\omega)$$

$$v_{\mathrm{xc}}(\mathbf{r})$$



Gatti, Olevano, Reining, Tokatly, Phys. Rev. Lett. 99, 057401 (2007)

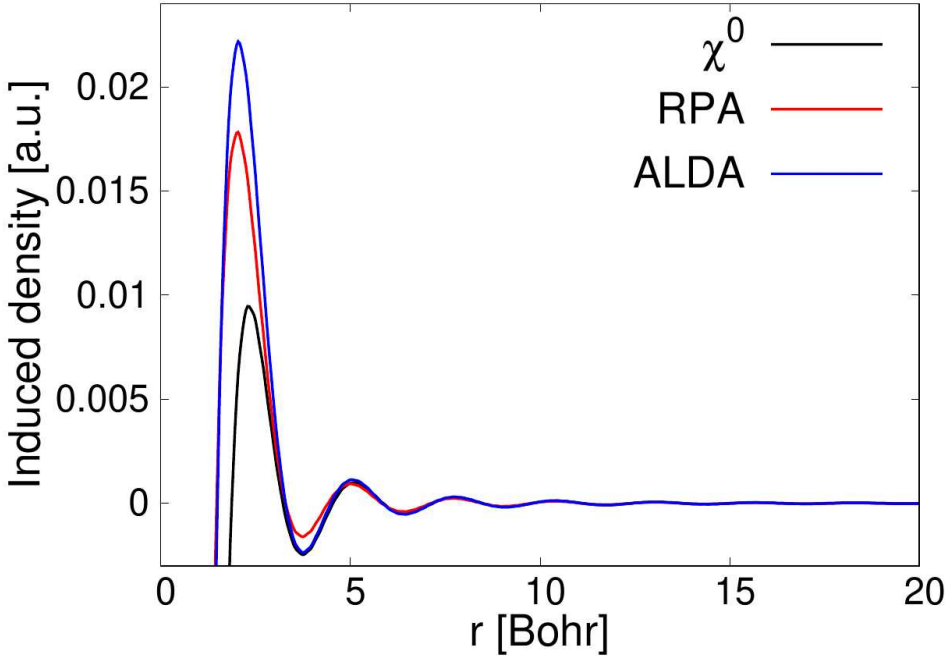
Descriptor	Auxiliary "potential"
$n(\mathbf{r})$	$v_{\mathrm{xc}}(\mathbf{r};[n])$
$G(\mathbf{r},\mathbf{r}',\omega)$	$\Sigma(\mathbf{r},\mathbf{r}',\omega;[G])$

→ Known functionals $A_{\mathbf{k}}(\omega;[G]) = \frac{1}{\pi}|\mathrm{Im}\, G_{\mathbf{kk}}(\omega)|$

$$E = \tilde{E}[G]$$

→Often try to approximate $\epsilon(\mathbf{q},\omega;[G])$

Martin, Richard M., Reining, Lucia, Ceperley, David M.:
Interacting Electrons: Theory and Computational Approaches (Cambridge 2016)

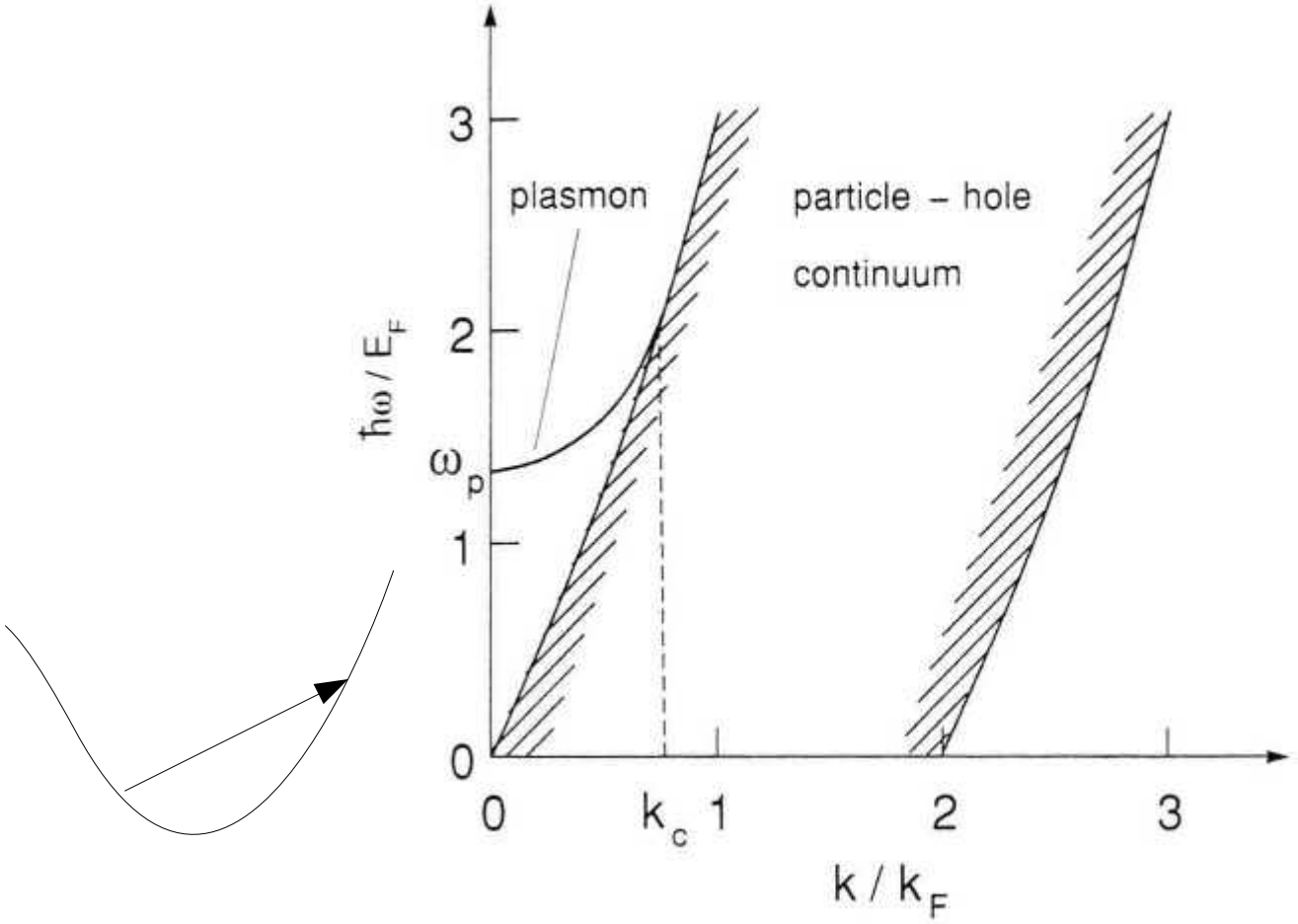


Static response
(Friedel oscillations)

HEG, rs=1.6
(silver chloride, AgCl)

$$n(\mathbf{r}) = \int d\mathbf{r}'\, \chi(\mathbf{r},\mathbf{r}')v_{\text{ext}}(\mathbf{r}')$$

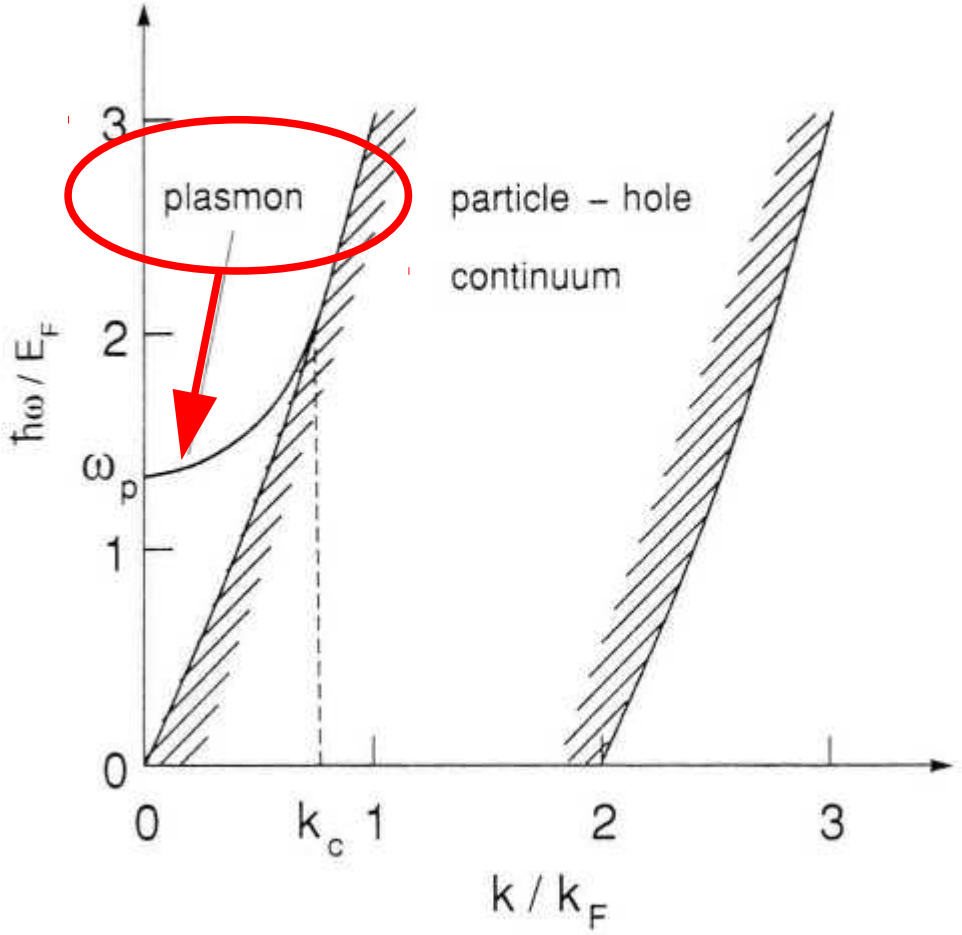
Excitations in the homogeneous electron gas



from K. Sturm, "Dynamic Structure Factor: an Introduction", Zeitschrift für Naturforschung A (1993)

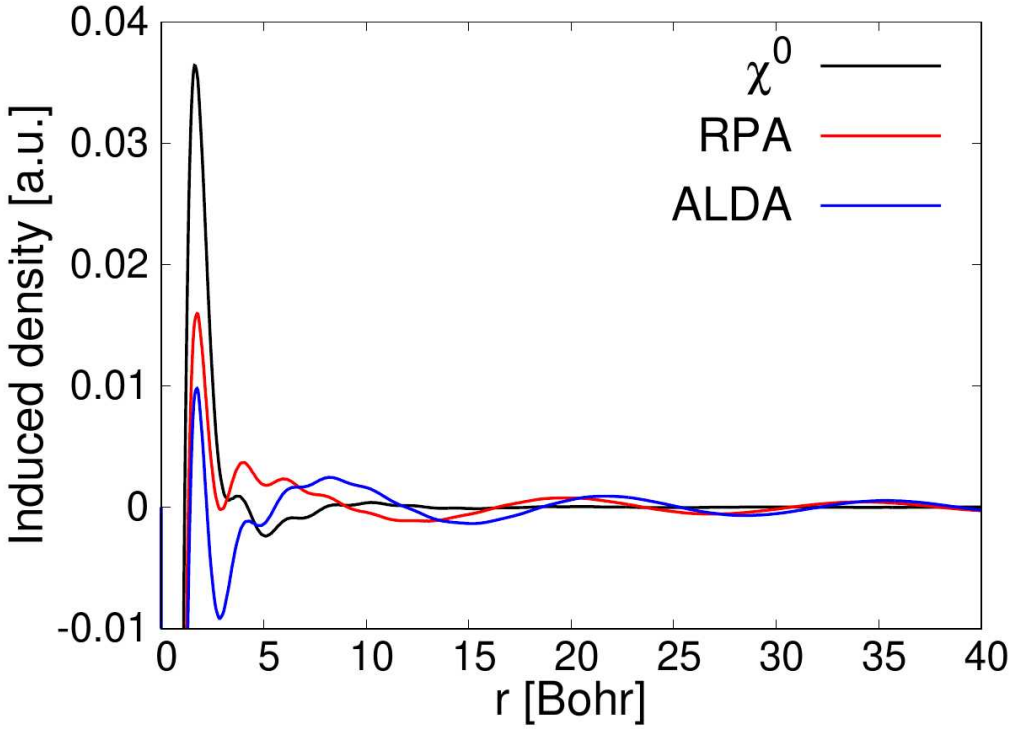
Excitations in the homogeneous electron gas

collective

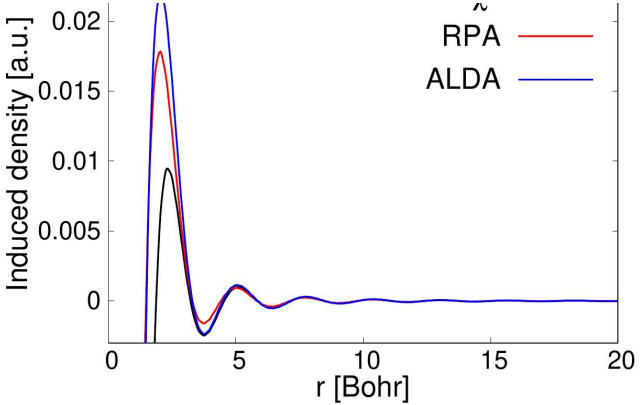


from K. Sturm, "Dynamic Structure Factor: an Introduction", Zeitschrift für Naturforschung A (1993)

HEG, rs=1.6 (silver chloride)

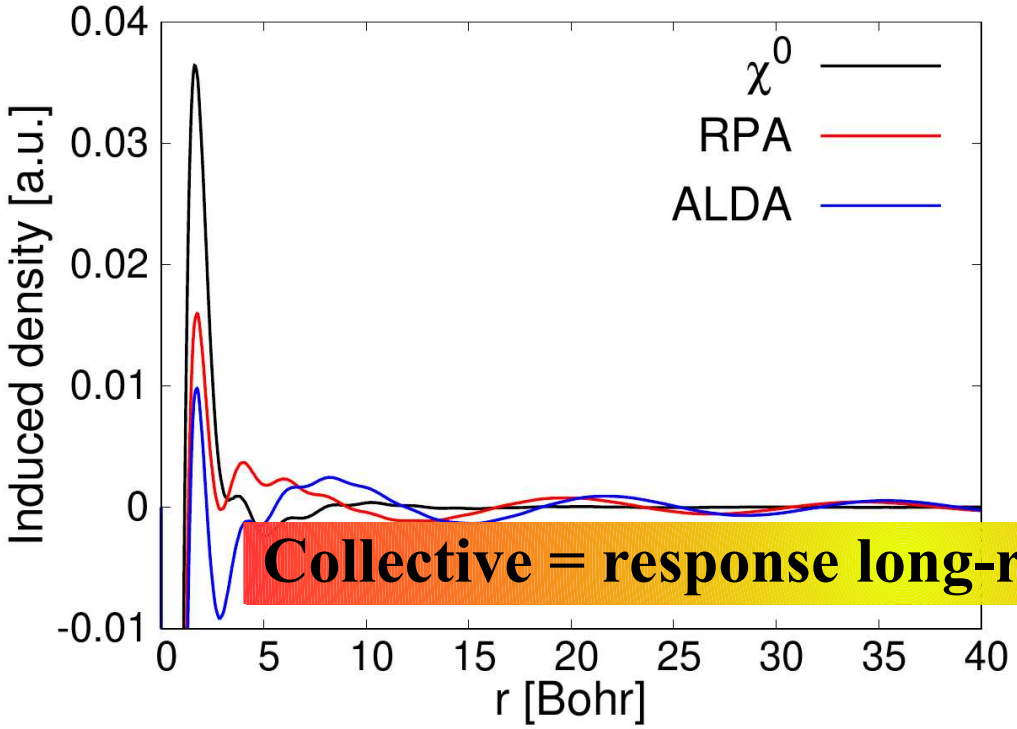


Plasmon resonance (26 eV)



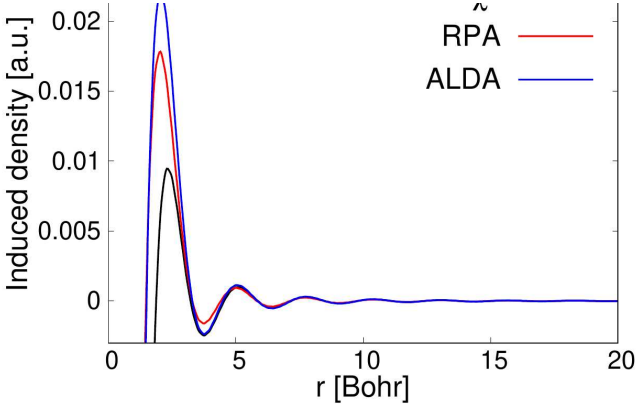
Static response
(Friedel oscillations)

HEG, rs=1.6 (silver chloride)



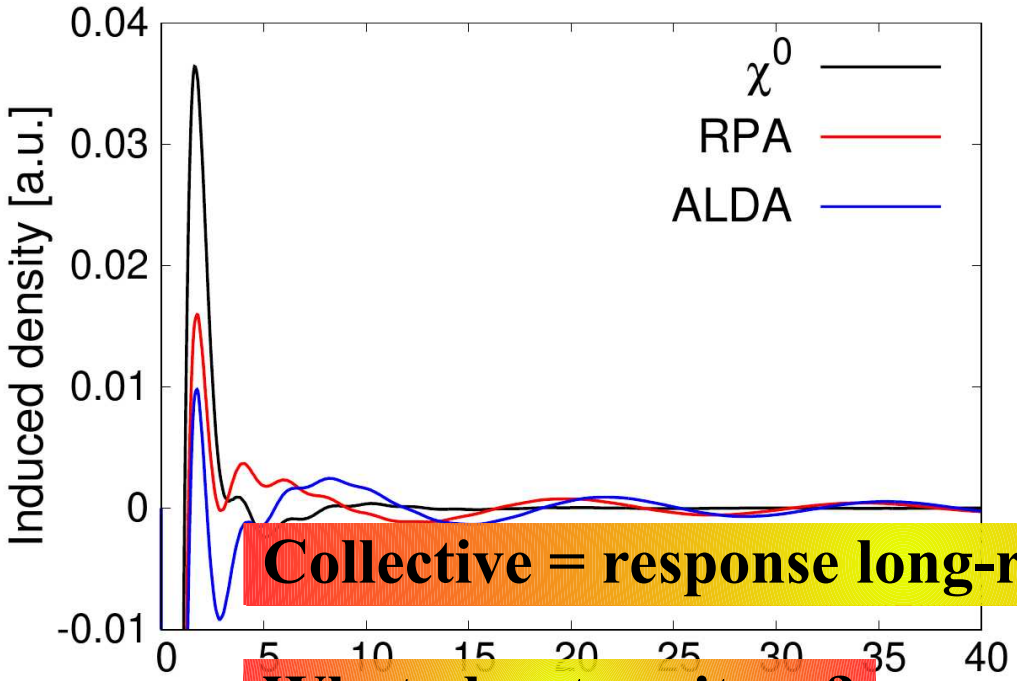
Plasmon resonance (26 eV)

Collective = response long-ranged in real space



Static response
(Friedel oscillations)

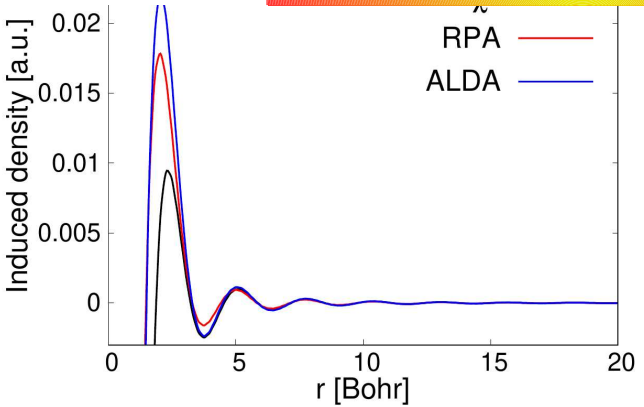
HEG, rs=1.6 (silver chloride)



Plasmon resonance (26 eV)

Collective = response long-ranged in real space

What about excitons?



Static response
(Friedel oscillations)

Spectrum = linear response

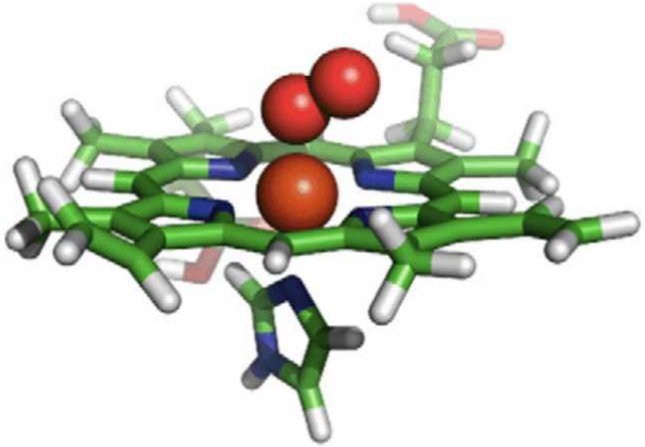
Add elements from becquerel video

$$n(\mathbf{r},t) = \int d\mathbf{r}'dt'\,\chi(\mathbf{r},\mathbf{r}',t-t')v_{\mathrm{ext}}(\mathbf{r}',t')$$

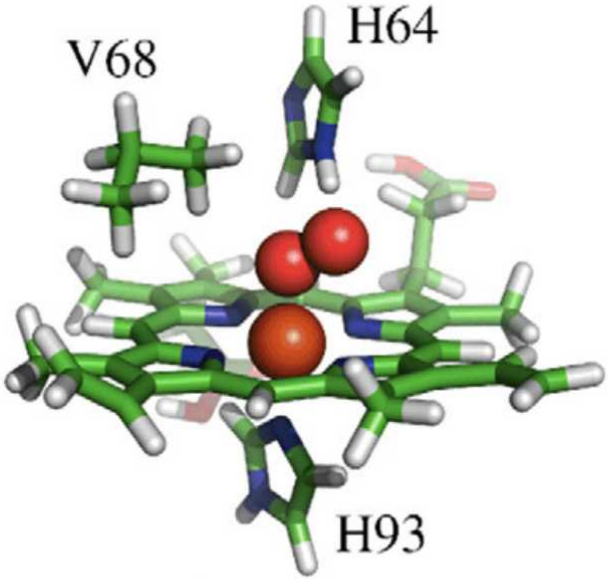
Full microscopic response needed

Igor Reshetnyak, Matteo Gatti, Francesco Sottile, and Lucia Reining, Phys. Rev. Research 1, 032010(R) (2019)

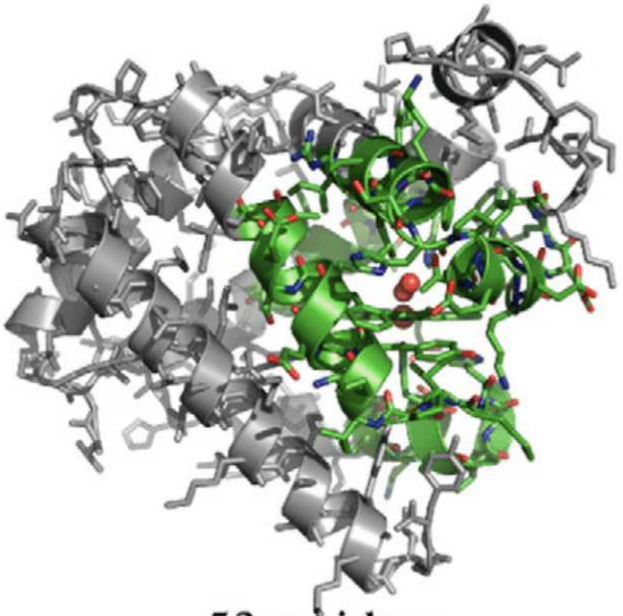
Myoglobin



1 residue



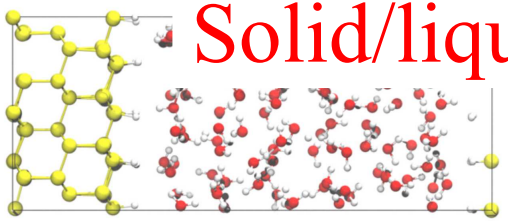
3 residues

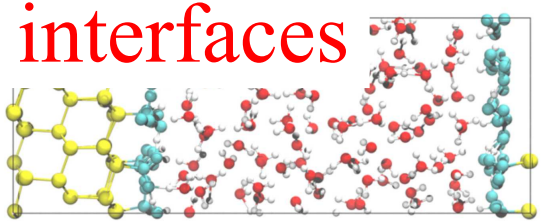


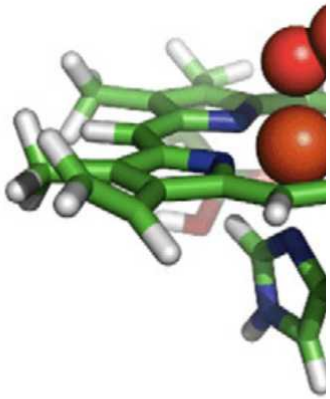
53 residues

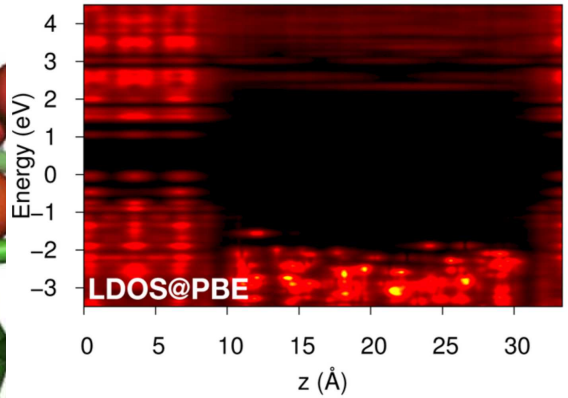
Cole D J, O'Regan D D and Payne M C 2012 Ligand discrimination in myoglobin from linear-scaling DFT+U J. Phys. Chem. Lett. 3 1448–52

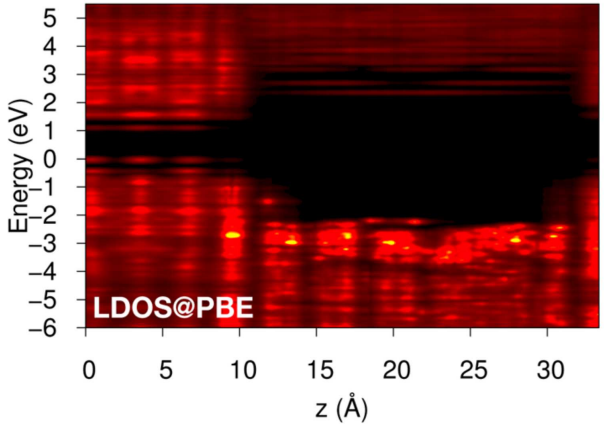
Solid/liquid interfaces

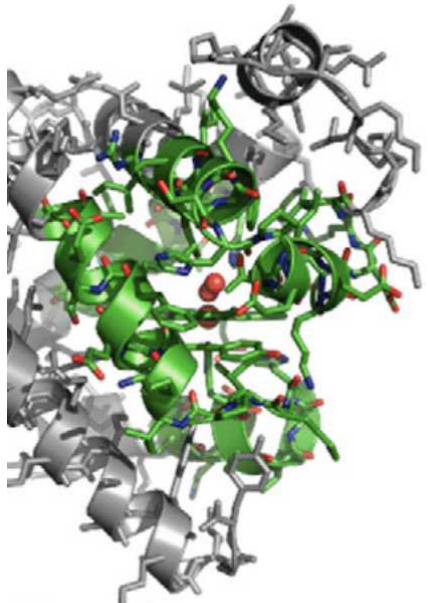






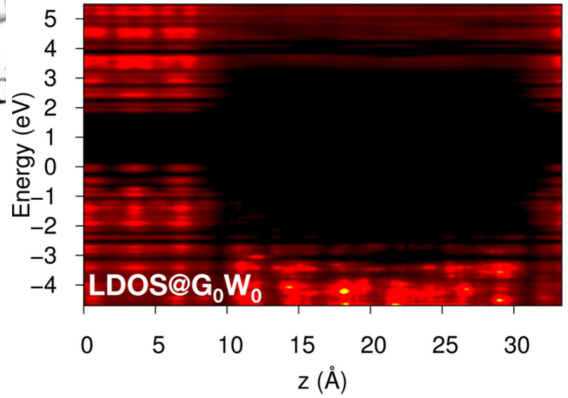


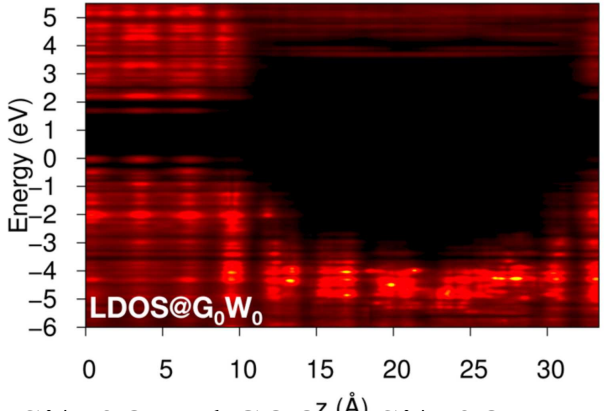




1 resic

53 residues





Local density of states of two solid/liquid interfaces: H−Si/H2O and COOH−Si/H2O, Govoni&Galli, JCTC 11, 2680 (2015)

“The field is mature”

“The field is mature”

“The field is boaring”

“The field is mature”

“The field is boaring”

“These people are number crunchers”

1. No, because we still need a lot of development

2. No, because we still have to understand the numbers

“These people are number crunchers”

1. No, because we still need a lot of development

2. No, because we still have to understand the numbers

3. A bit yes, because……..

“These people are number crunchers”