Why should I study more than Kohn-Sham DFT?

Fatema Mohamed[1,2,3], Maram Ali Ahmed[1,2,4], Matteo Gatti[1,2], and you all present here

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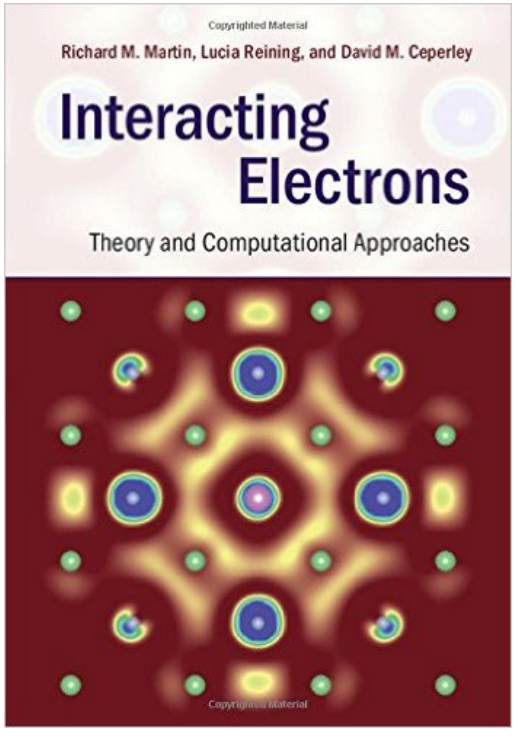
(2) LSI - CNRS Ecole Polytechnique - France
(3) University of Khartoum, Sudan
(4) National Ribat University, Sudan

ASESMA 2025 - University of Ghana

Books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Interacting Electrons
Theory and Computational Approaches
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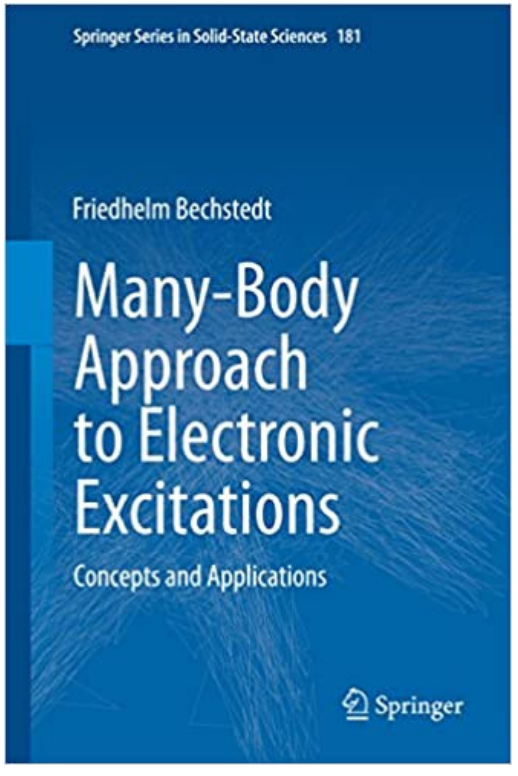
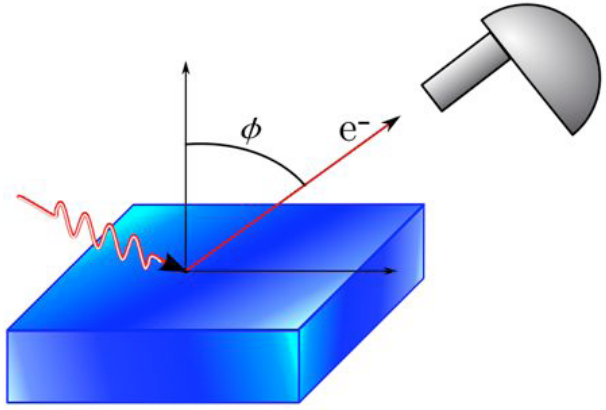

Springer Series in Solid-State Sciences 181
Friedhelm Bechstedt
Many-Body Approach to Electronic Excitations
Concepts and Applications
Springer

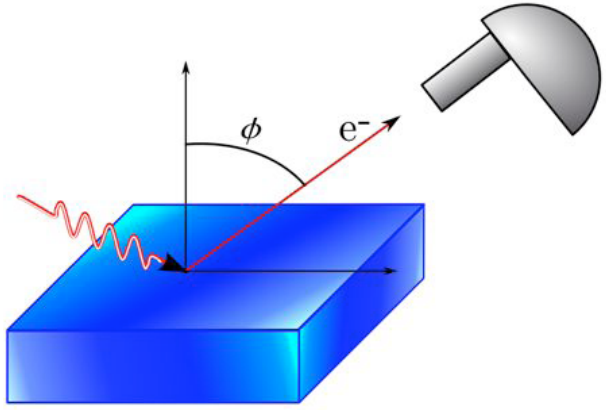
Outline

Direct Photoemission



photon in - electron out

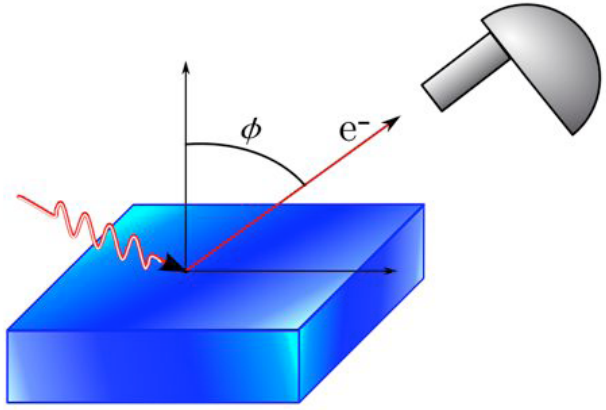
Direct Photoemission



photon in - electron out

$$E(N) + h\nu = E(N-1, i) + E_{kin}$$

Direct Photoemission



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$$E(N) + h\nu = E(N-1, i) + E_{kin}$$

$$E_i = E(N) - E(N-1, i) = E_{kin} - h\nu$$

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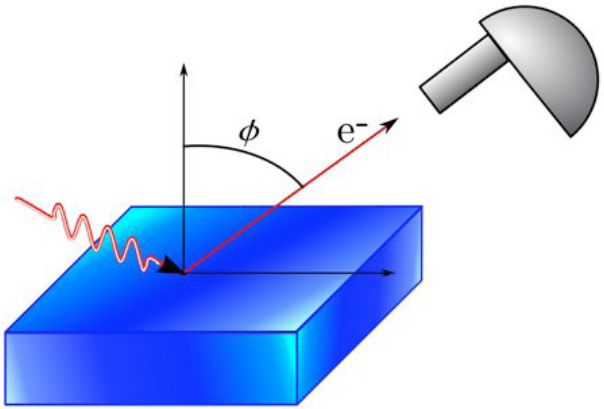

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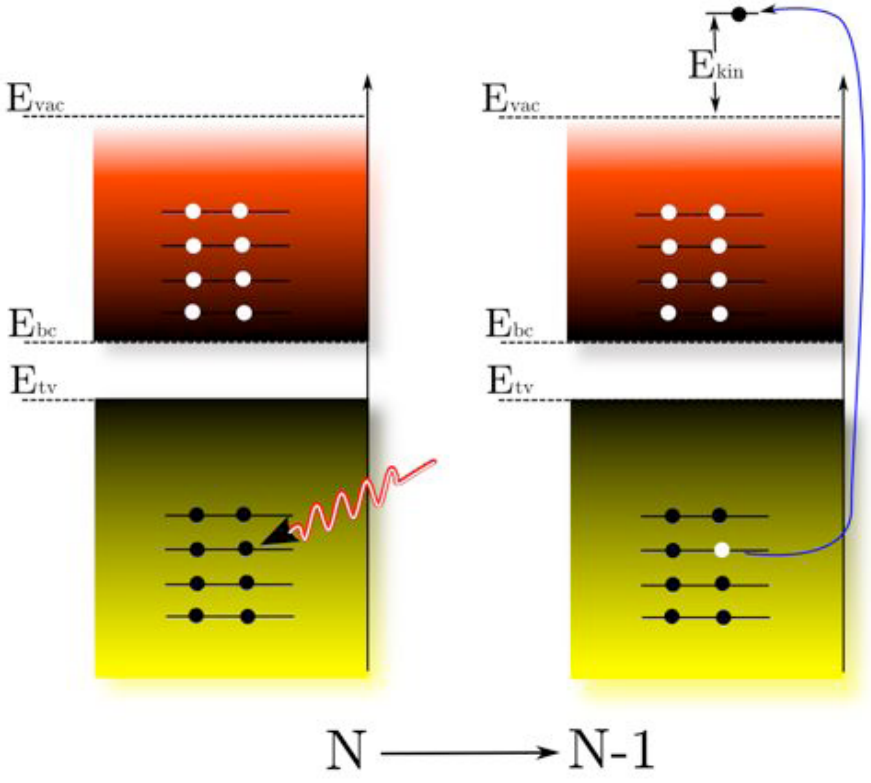
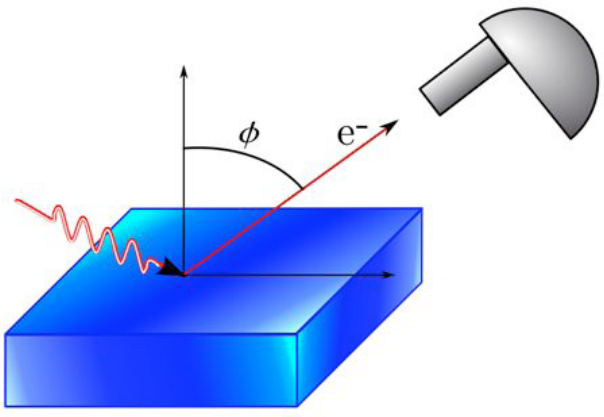


occupied states

S. Hüfner, Photoelectron spectroscopy

Direct Photoemission



photon in - electron out

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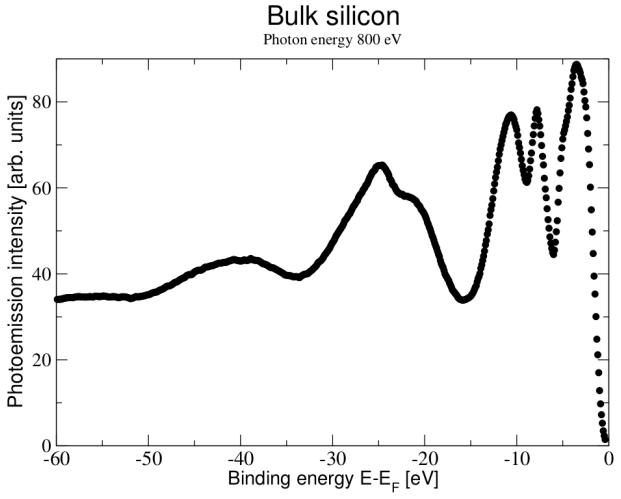
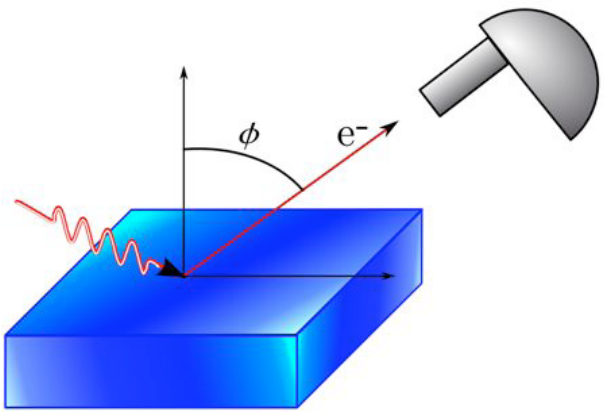


M. Guzzo *et al.*, PRL 107 (2011).

Direct Photoemission



photon in - electron out

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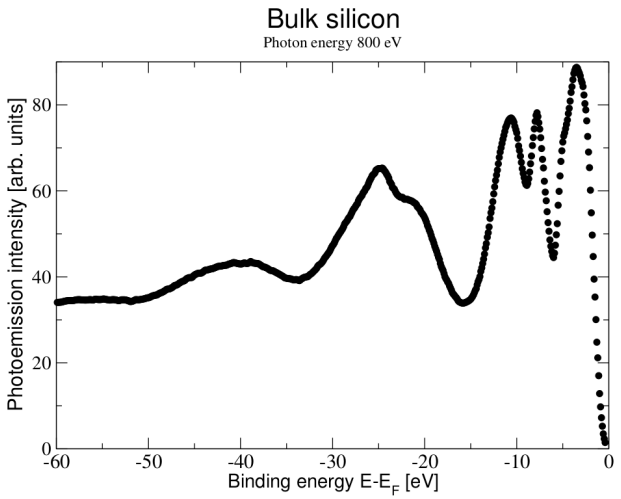
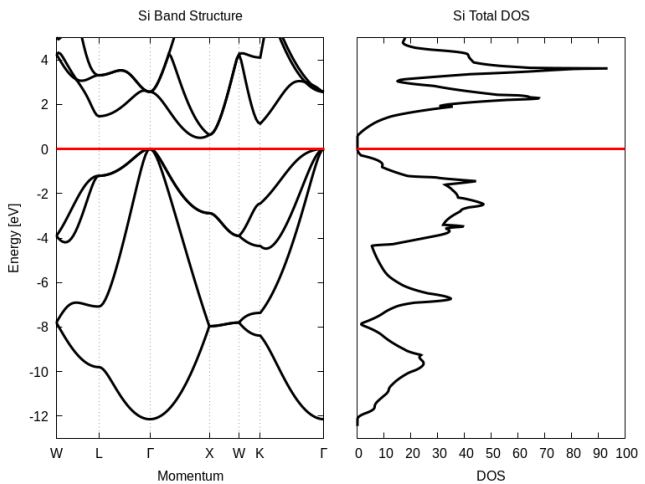
$$E_i = E(N) - E(N-1, i) = E_{kin} - h\nu$$

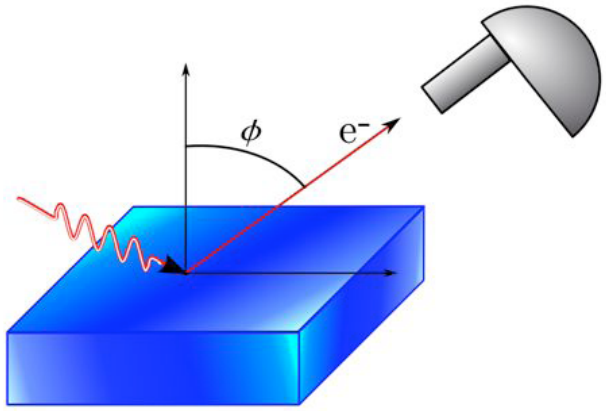


M. Guzzo *et al.*, PRL 107 (2011).



Courtesy of Mohamed Hamid - AIMS Cameroon.

Angle-resolved photoemission (ARPES)

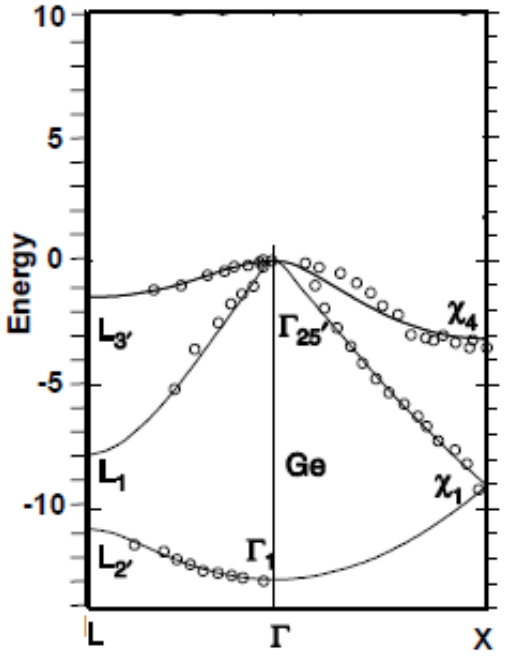


photon in - electron out

$$E(N) + h\nu = E(N-1, i) + E_{kin}$$

$$E_i = E(N) - E(N-1, i) = E_{kin} - h\nu$$

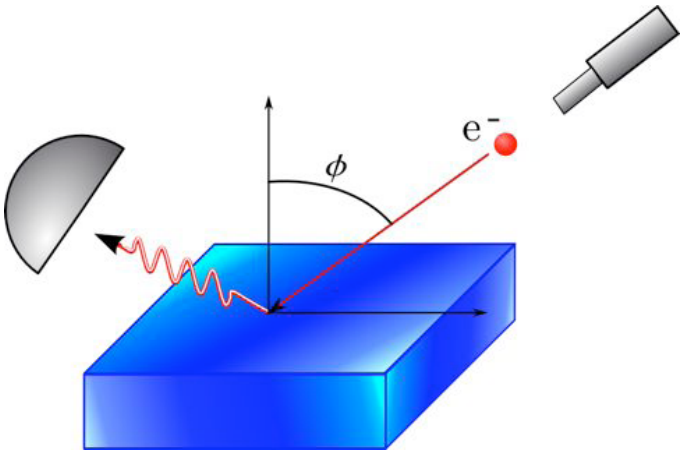
...plus momentum conservation $\Rightarrow$ ARPES



Germanium:

PRB **32** 2326 (1985); PRB **47** 2130 (1993).

Inverse Photoemission

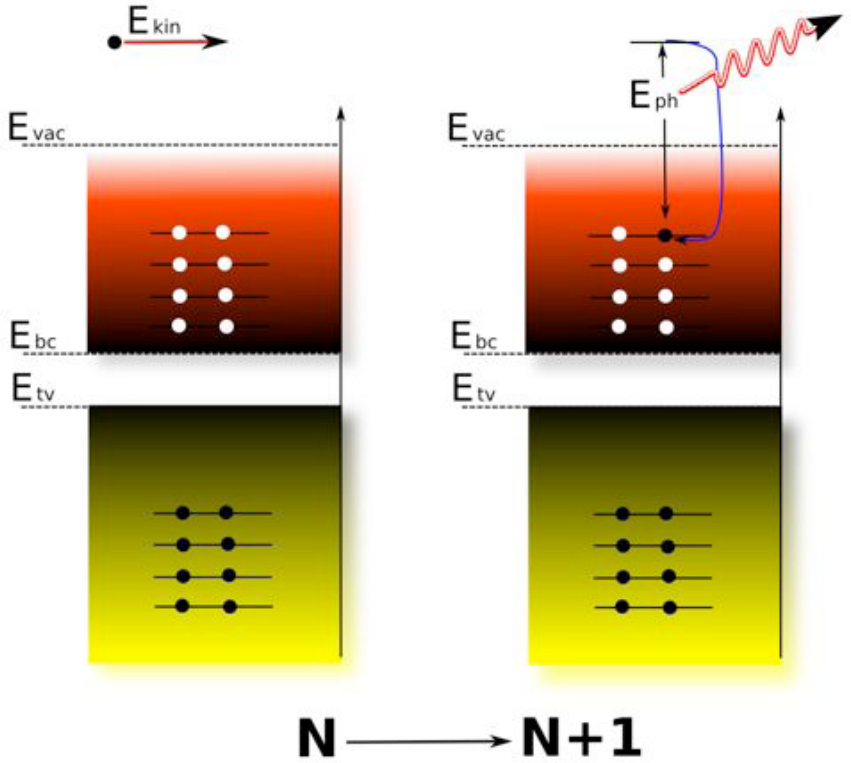


electron in - photon out

$$E(N) + E_{kin} = E(N+1, i) + h\nu$$

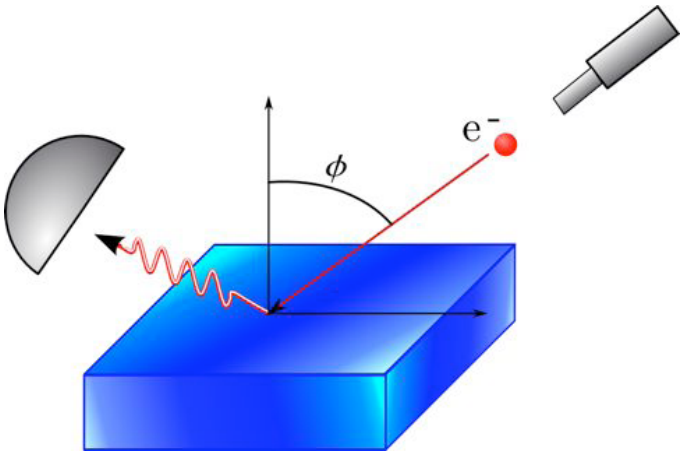
$$E_i = E(N+1, i) - E(N) = E_{kin} - h\nu$$

aka Bremsstrahlung
isochromat spectroscopy (BIS)

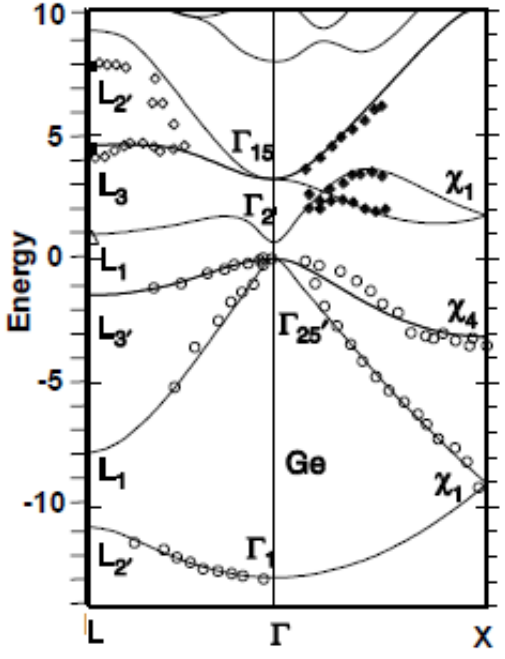


empty states

Inverse Photoemission



electron in - photon out



Germanium:

PRB **32** 2326 (1985); PRB **47** 2130 (1993)

$$E_g = \min_{c,v}\{E_c - E_v\} = \min_{c,v}\{[E(N+1,c) - E(N)] - [E(N) - E(N-1,v)]\}$$

Why more than Kohn-Sham?

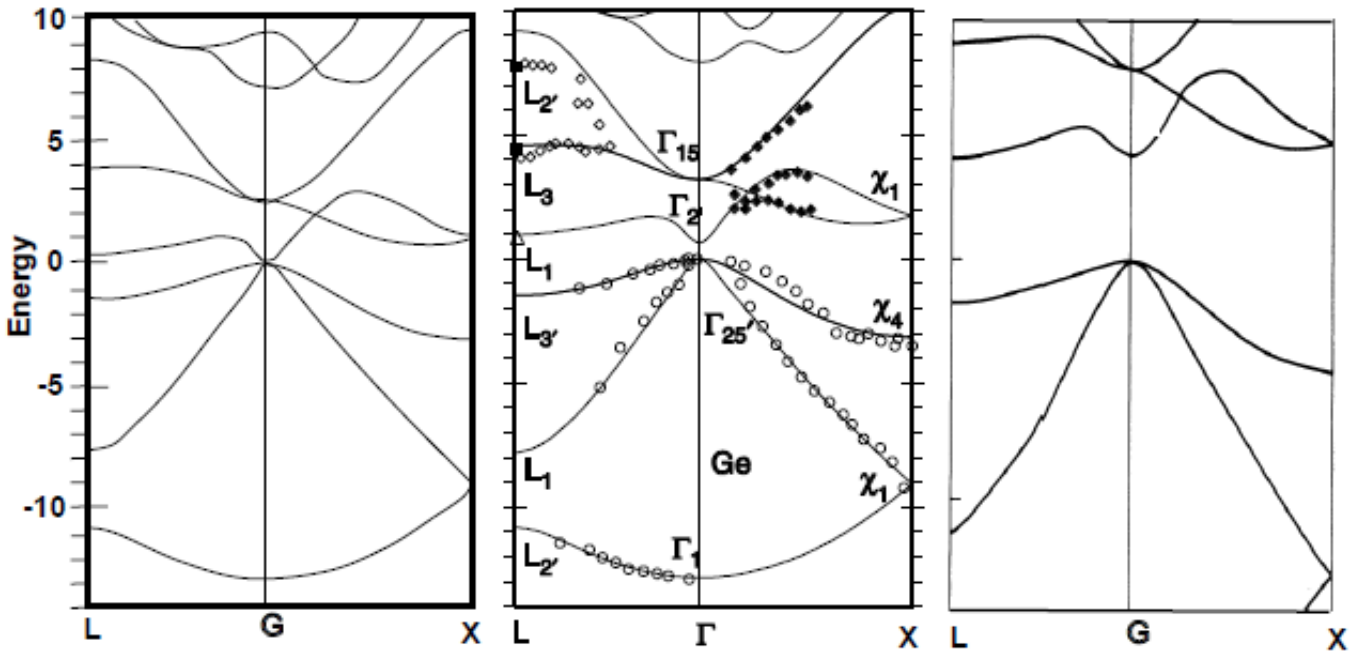
Kohn Sham gaps

	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).

Why more than independent electrons?

LDA Hartree-Fock



Germanium band structure

Exp. from PRB **32** (1985); PRB **47** (1993);
GW from PRB **48** (1993); Hartree-Fock from PRB **35** (1987)

What are the differences???

Kohn-Sham

$$\left[-\frac{\nabla^2}{2} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right]\varphi_i(\mathbf{r}) + V_{xc}(\mathbf{r})\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r})$$

Hartree-Fock

$$\left[-\frac{\nabla^2}{2} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right]\phi_i(\mathbf{r}) + \int d\mathbf{r}' V_x^F(\mathbf{r},\mathbf{r}')\phi_i(\mathbf{r}') = E_i\phi_i(\mathbf{r})$$

$$V_{\mathrm{H}}[\rho](\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Hartree-Fock

$$V_x^F(\mathbf{r}, \mathbf{r}') = -\frac{\gamma(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_i^{\mathrm{occ}} \phi_i(\mathbf{r}) \phi_i^*(\mathbf{r}')$$

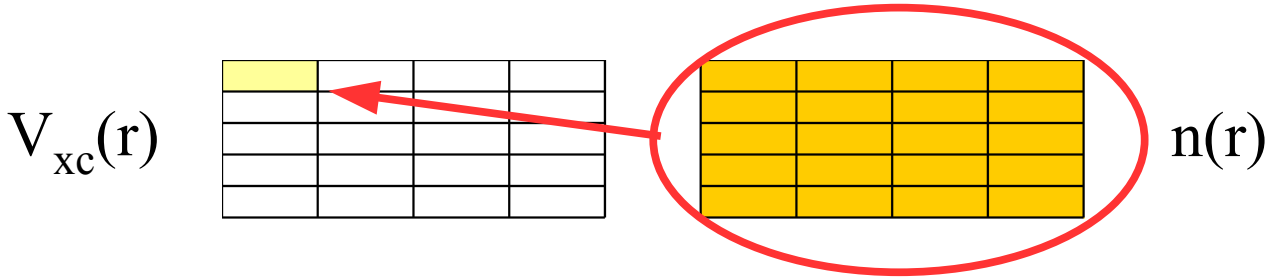
$$\gamma(\mathbf{r}, \mathbf{r}) = \rho(\mathbf{r})$$

Kohn-Sham

$$V_{\mathrm{xc}}[\rho](\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}}{\delta \rho(\mathbf{r})}$$

$$E_{\mathrm{xc}}[\rho] = T[\rho] - T_s[\rho] + E_{ee}[\rho] - E_H[\rho]$$

$V_{\mathrm{xc}}[n](\mathbf{r})$ (non-local) functional



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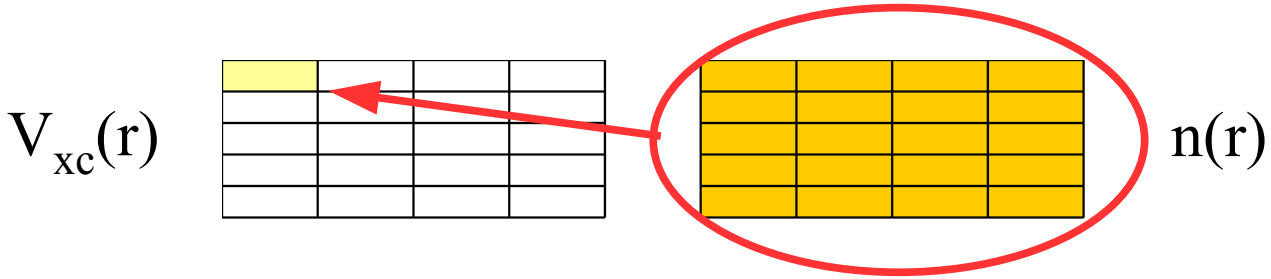
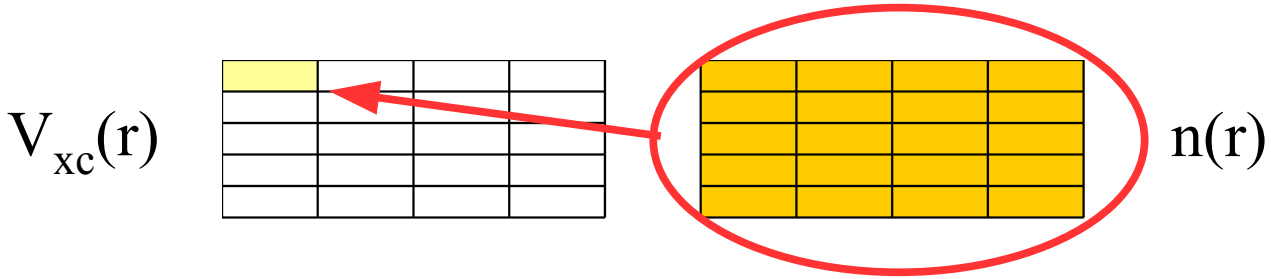


homogeneous density n^h → the same density everywhere

$V_{\mathrm{xc}}^h(n^h)$ ...becomes a function

$V_{\mathrm{xc}}[n](\mathbf{r})$ (non-local) functional



homogeneous density n^h → the same density everywhere

$V_{\mathrm{xc}}^h(n^h)$ ...becomes a function

..and the same for any density functional $E_{\mathrm{xc}}[n]$

DFT : A “multiverse” theory

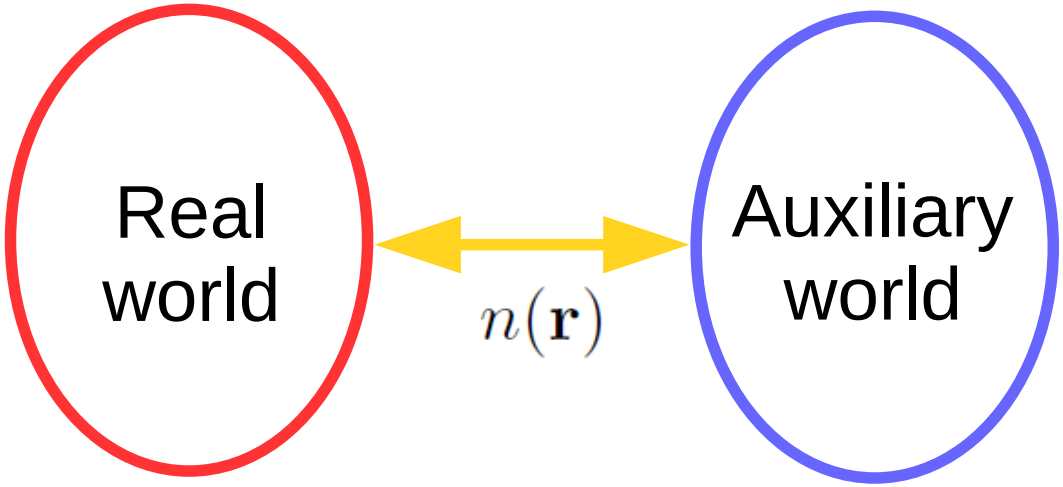
$$H\Psi = E\Psi$$

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

All observables

Kohn-Sham

$V_{\mathrm{xc}}[n](\mathbf{r})$?



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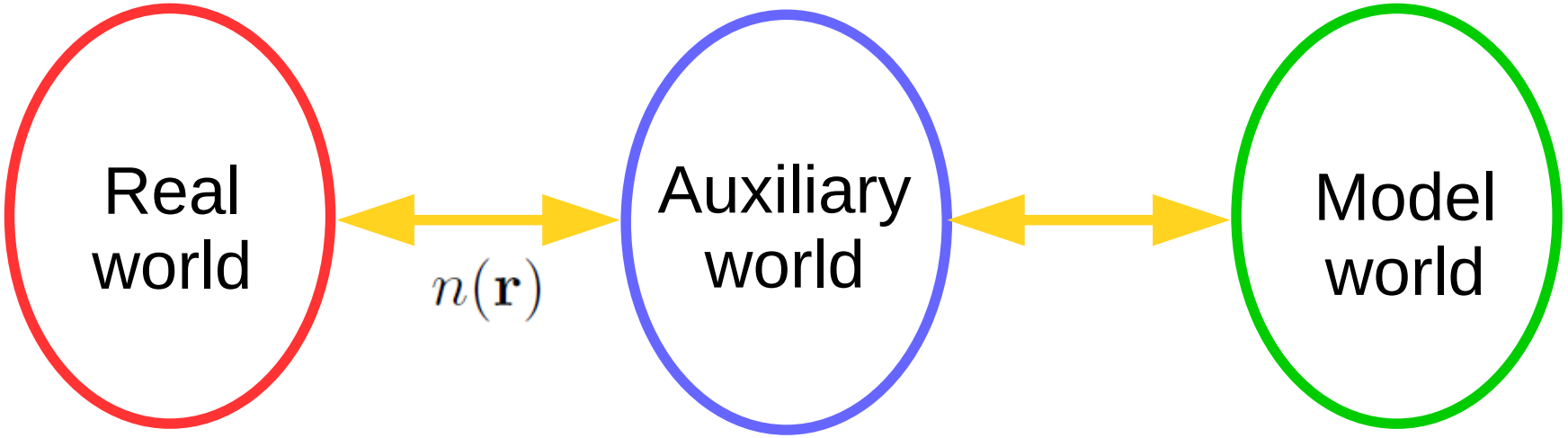
Kohn-Sham

$V_{\mathrm{xc}}[n](\mathbf{r})$?

Homogeneous electron gas

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



DFT : A “multiverse” theory

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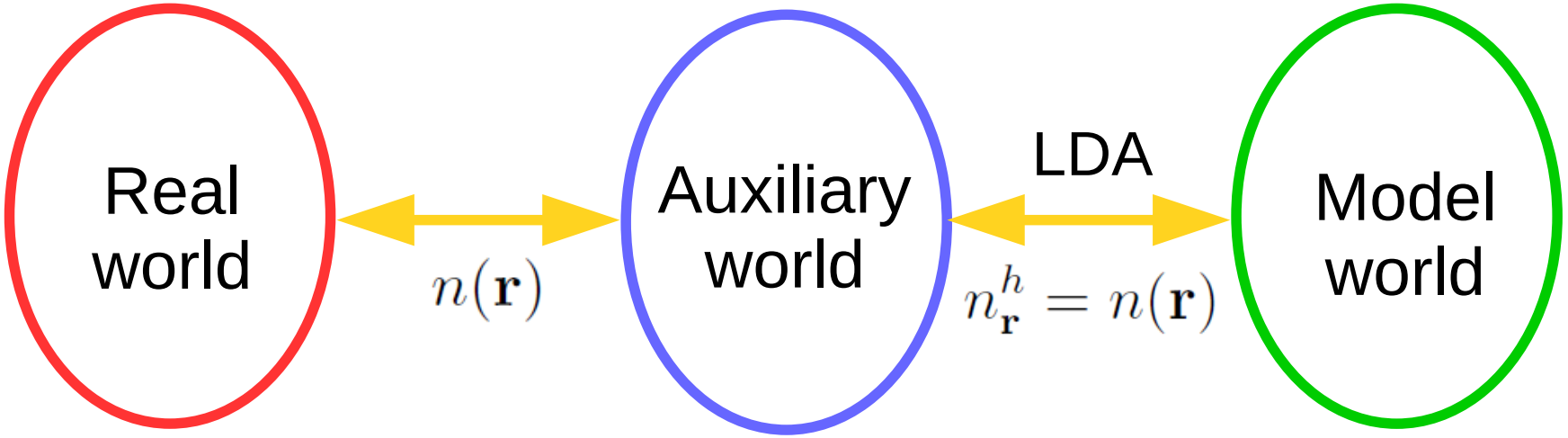
$V_{\mathrm{xc}}[n](\mathbf{r})$?

Homogeneous electron gas

$n^h \;\; V^h_{\mathrm{xc}}(n^h)$



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

DFT : A “multiverse” theory

$$H\Psi = E\Psi$$

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

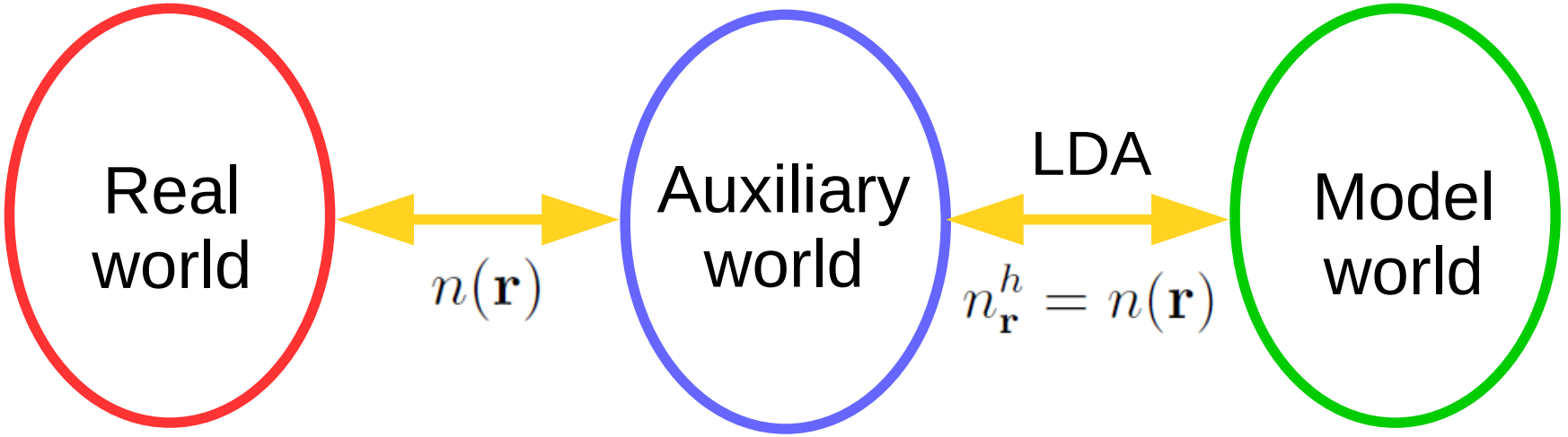
All observables

Kohn-Sham

$V_{\rm xc}[n](\mathbf{r})$?

Homogeneous electron gas

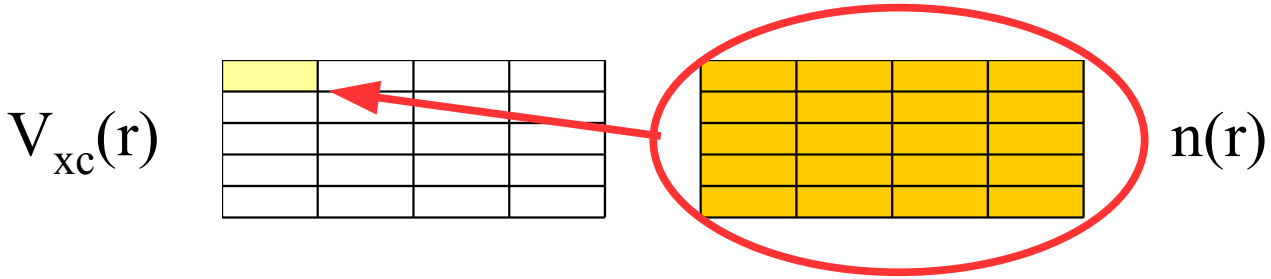
$n^h \;\; V^h_{\rm xc}(n^h)$



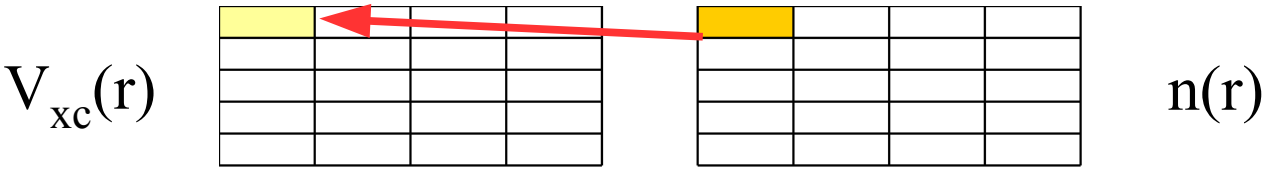
$$V_{\rm xc}[n](\mathbf{r}) = V^h_{\rm xc}(n^h_{\mathbf{r}} = n(\mathbf{r}))$$

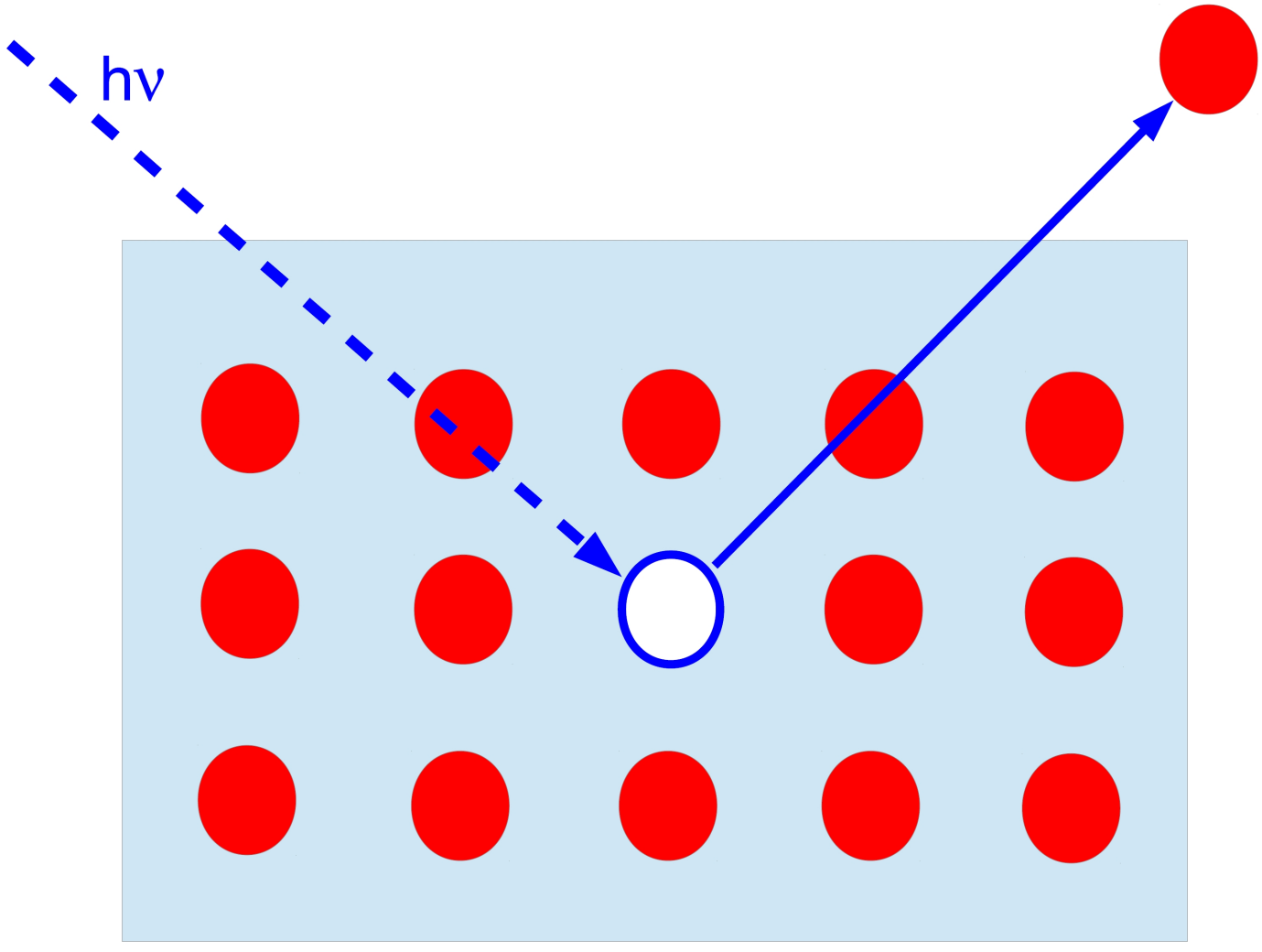
$$E_{\rm xc}[n] = \int d\mathbf{r}\, n(\mathbf{r}) \epsilon^h_{xc}(n^h_{\mathbf{r}} = n(\mathbf{r}))$$

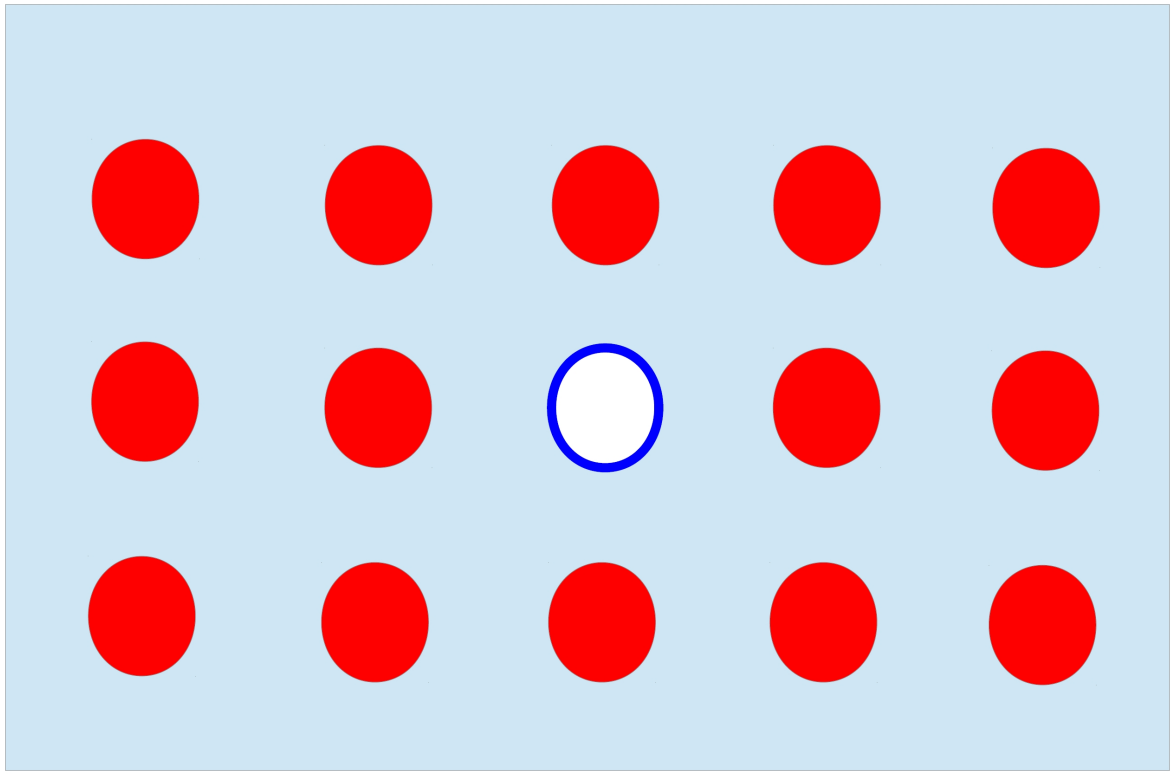
$V_{\mathrm{xc}}[n](\mathbf{r})$ (non-local) functional



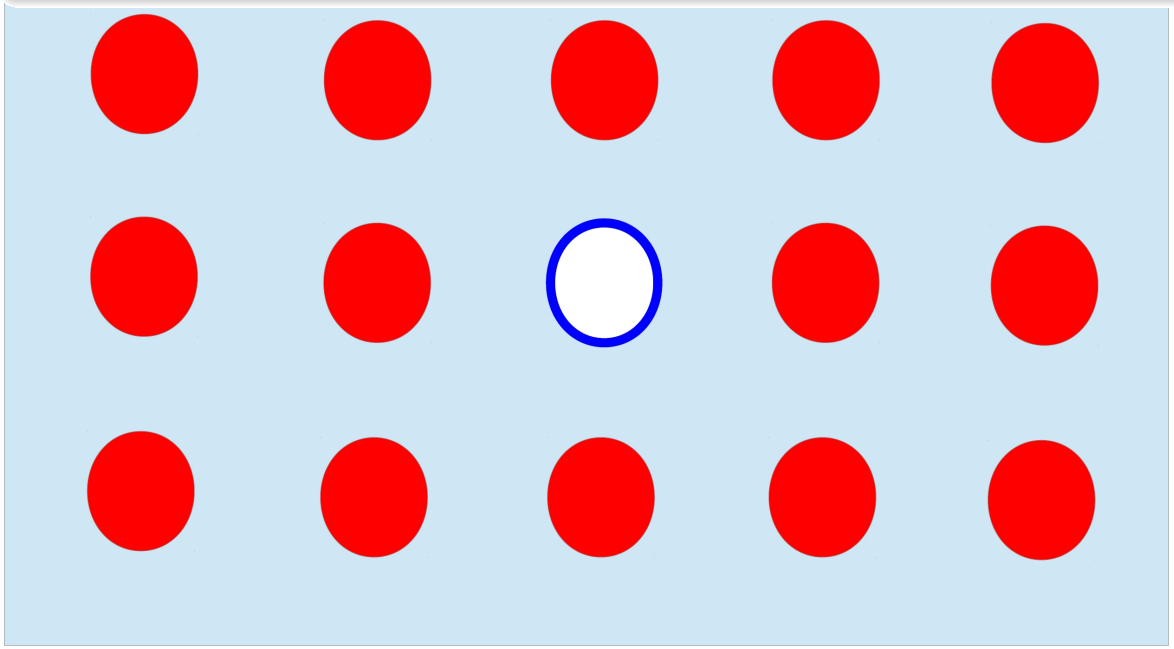
$V_{\mathrm{xc}}[n](\mathbf{r})$ LDA: it becomes a local functional



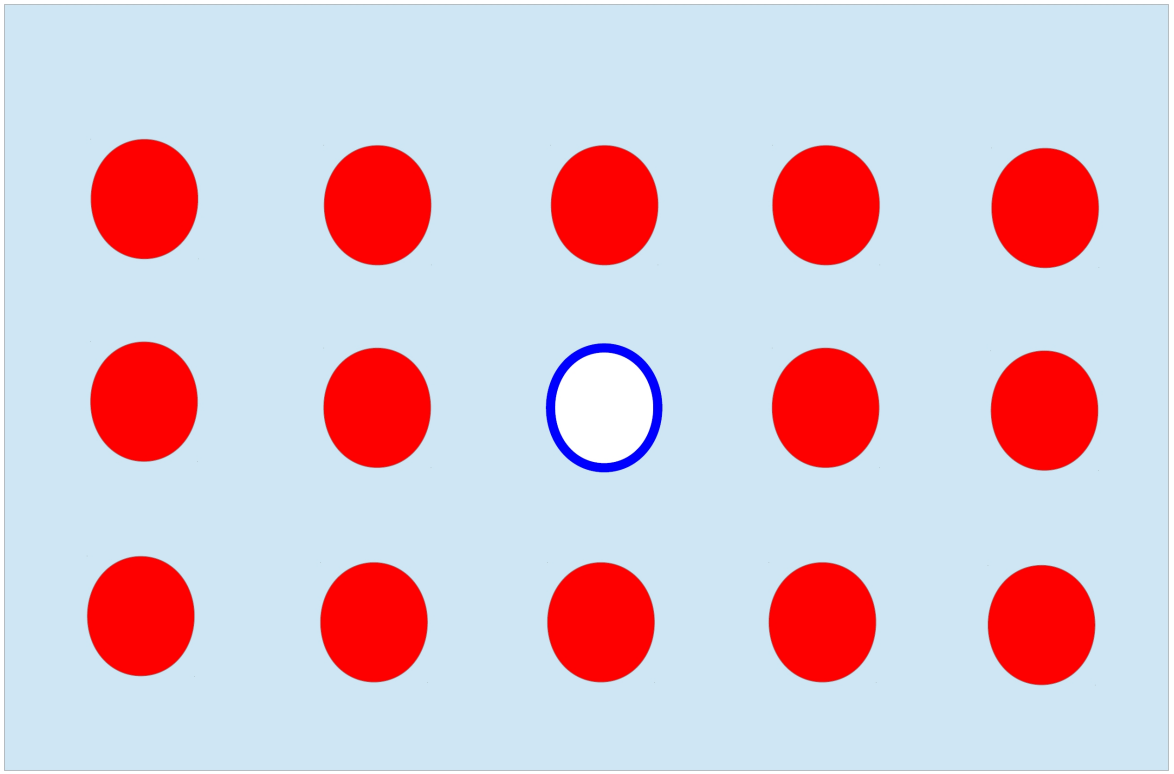

hν



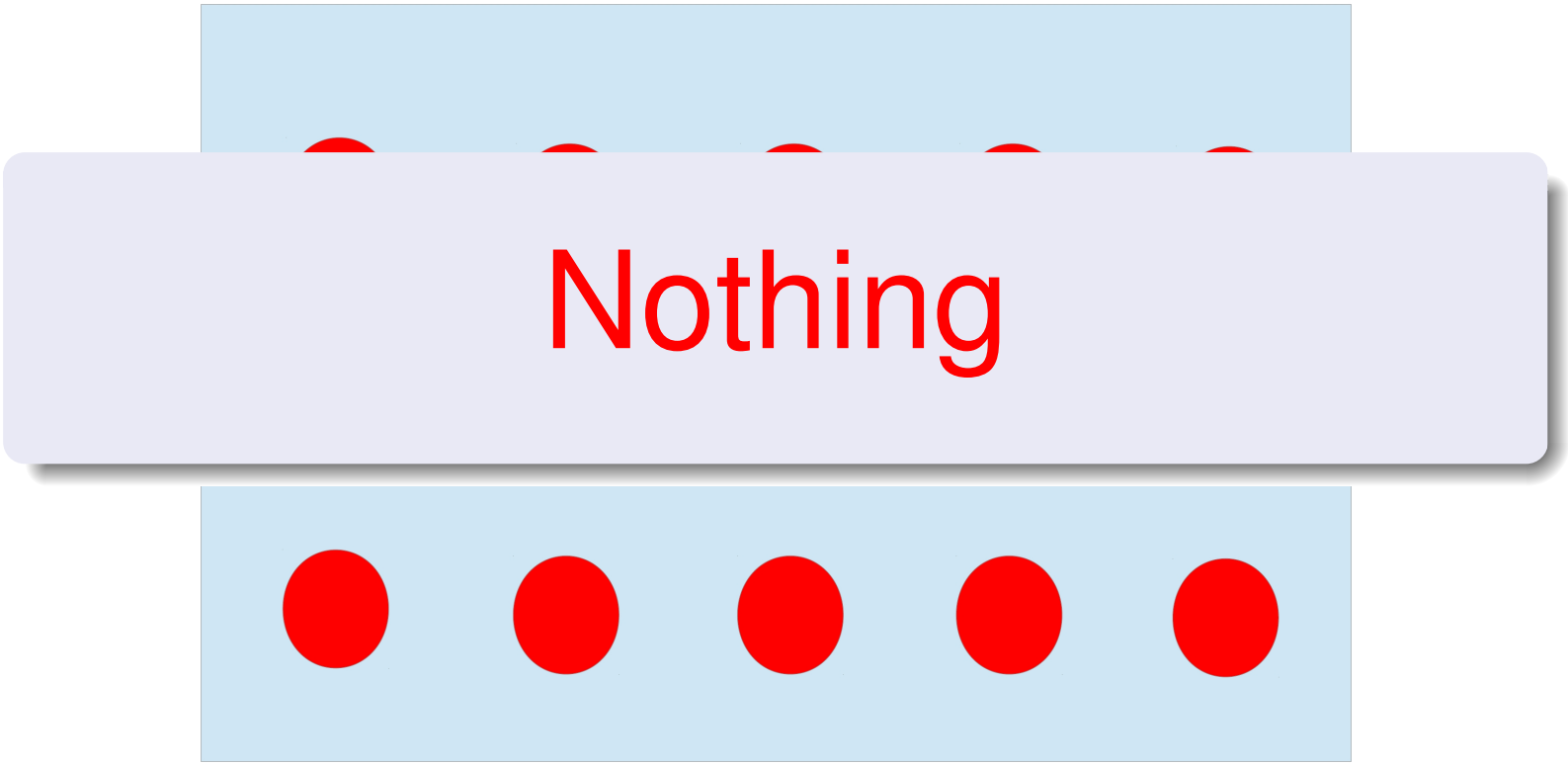
What happens?



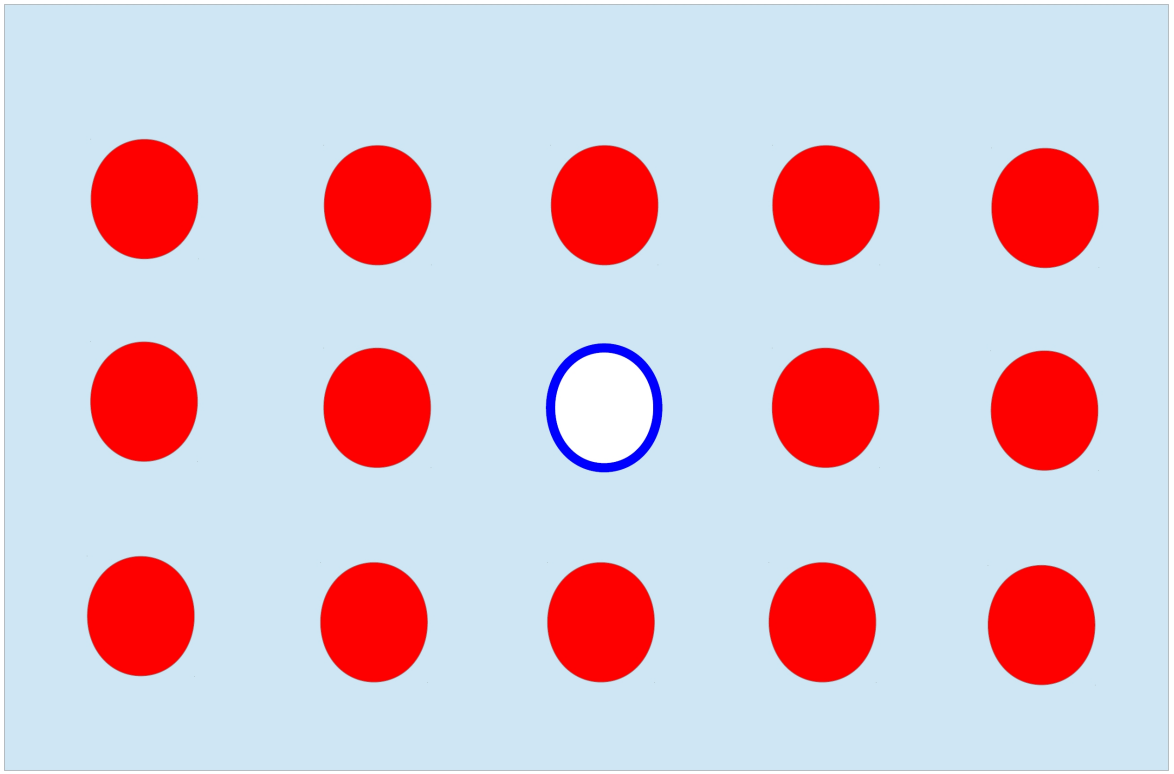
Non-interacting particles



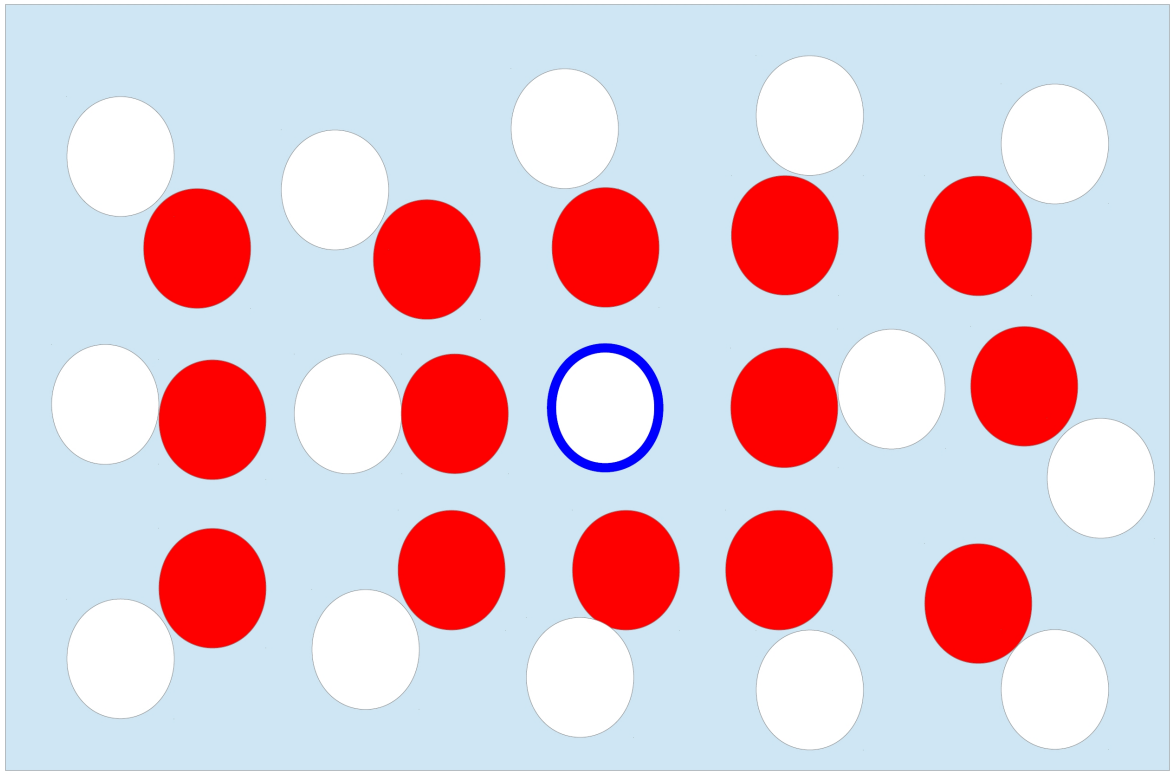
Non-interacting particles



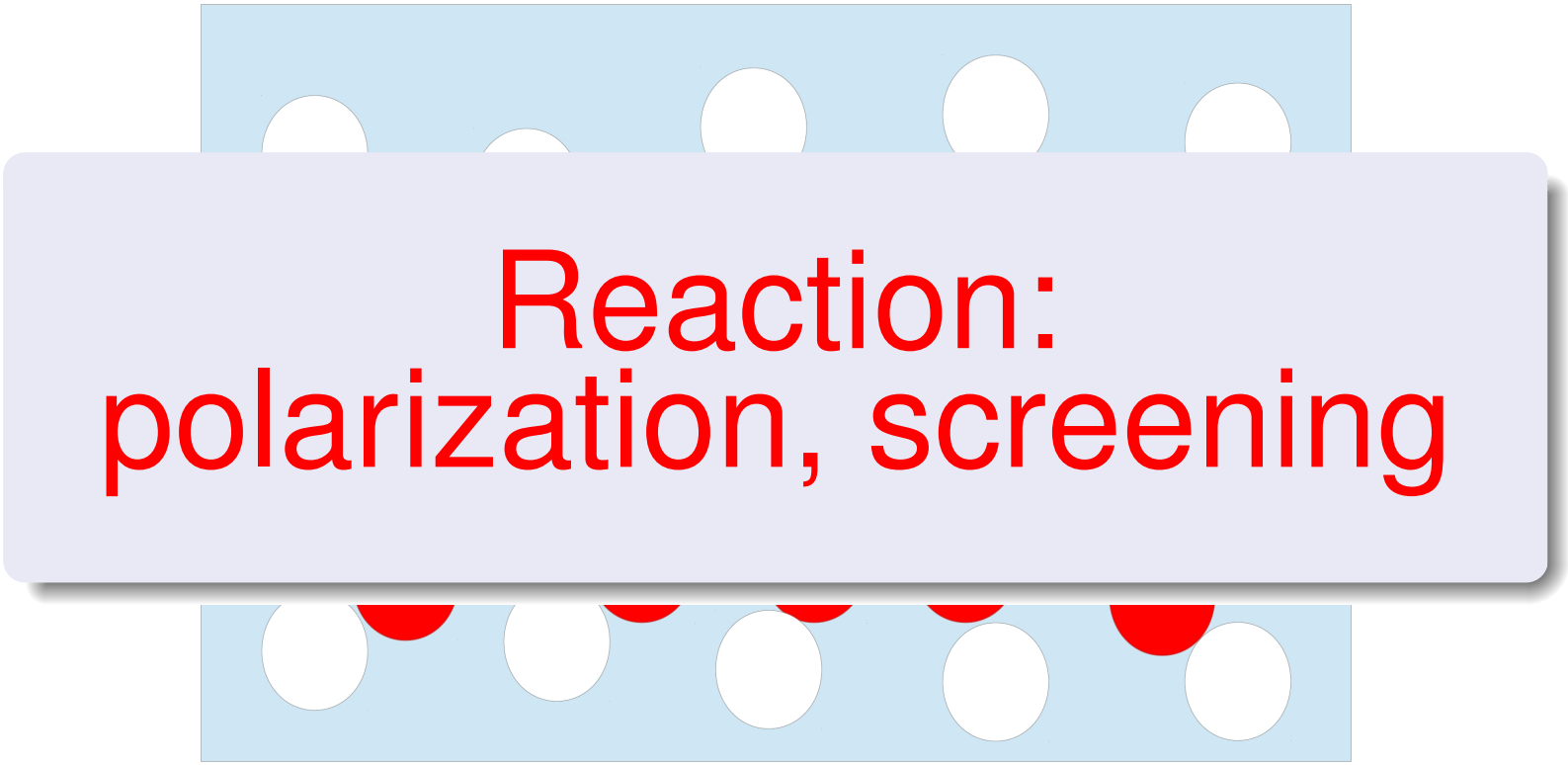
Interacting particles



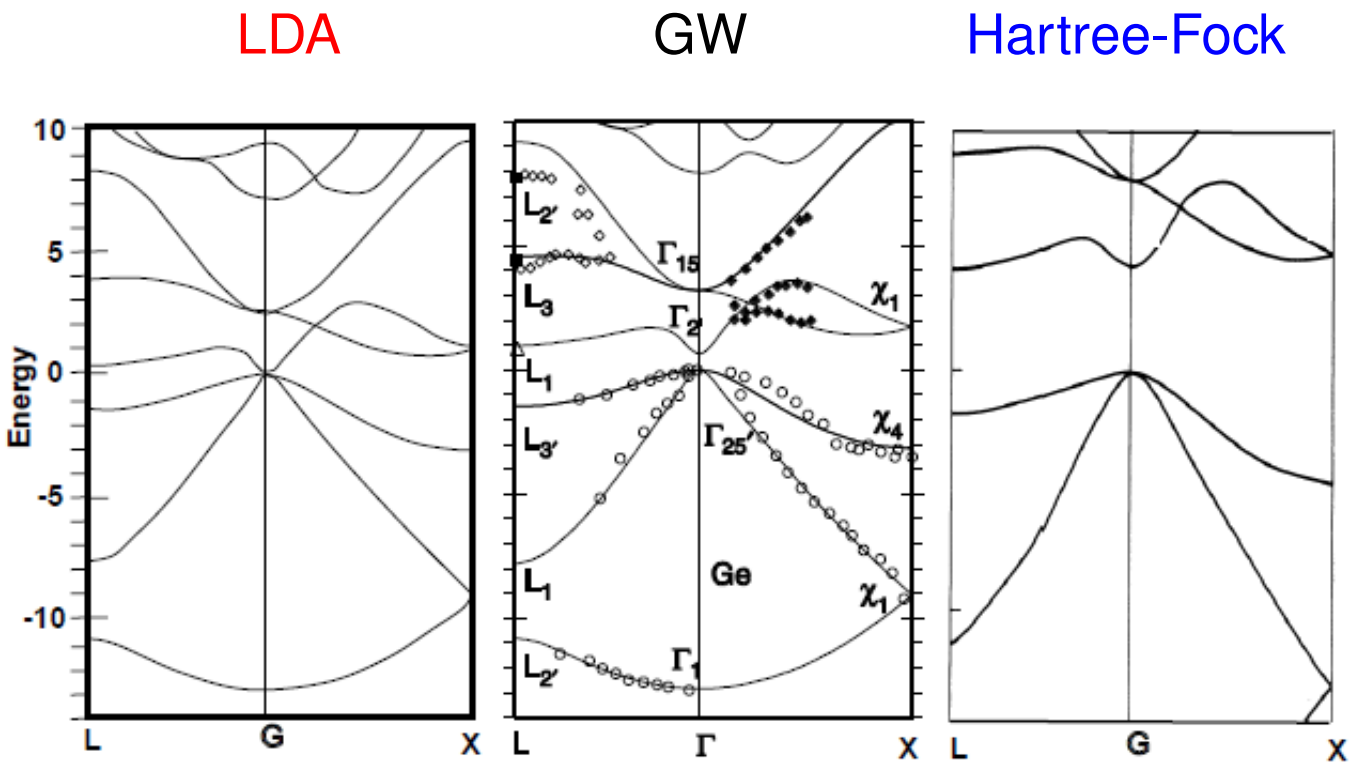
Interacting particles



Interacting particles



Why more than independent electrons?



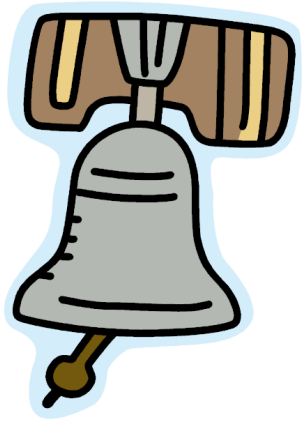
Germanium band structure

Exp. from PRB **32** (1985); PRB **47** (1993);
GW from PRB **48** (1993); Hartree-Fock from PRB **35** (1987)

Outline

Spectroscopy

A first example

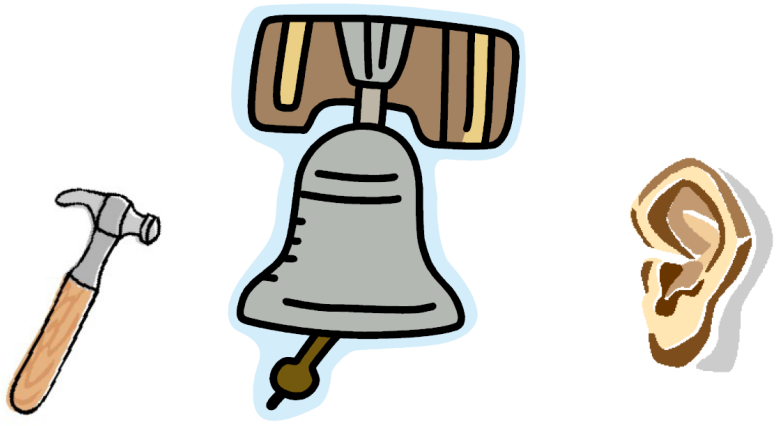


Spectroscopy

A first example

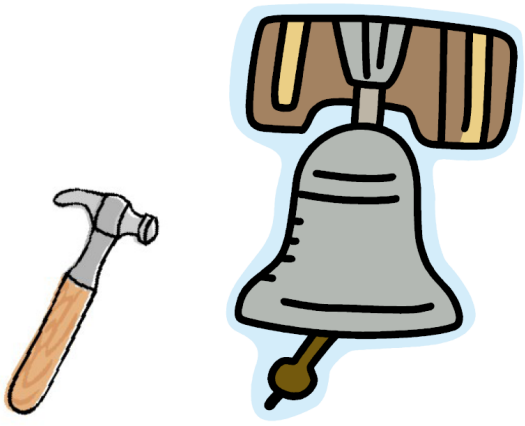
Spectroscopy

A first example



Spectroscopy

A first example

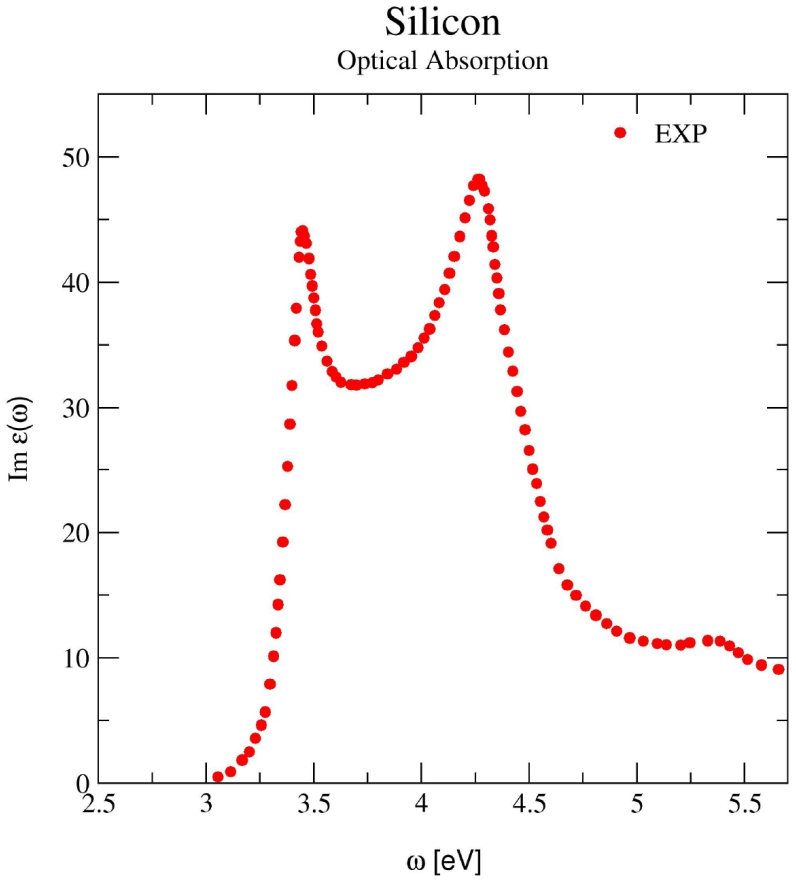


Perturbation

Excitation

Response

Theoretical spectroscopy



Exp. at 30 K from: P. Lautenschlager *et al.*, Phys. Rev. B **36**, 4821 (1987).

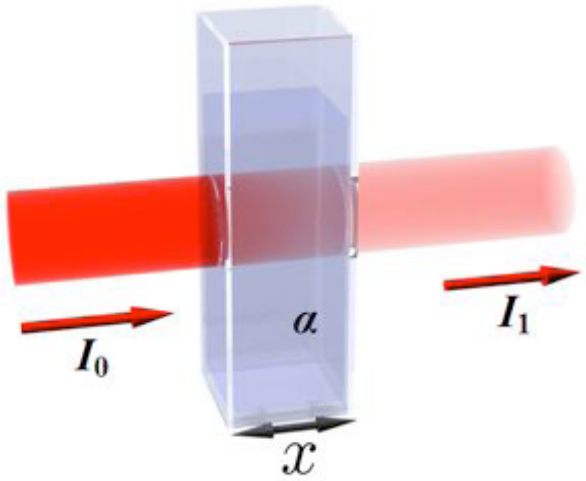
Theoretical spectroscopy

- Calculate and reproduce
- Understand and explain
- Predict

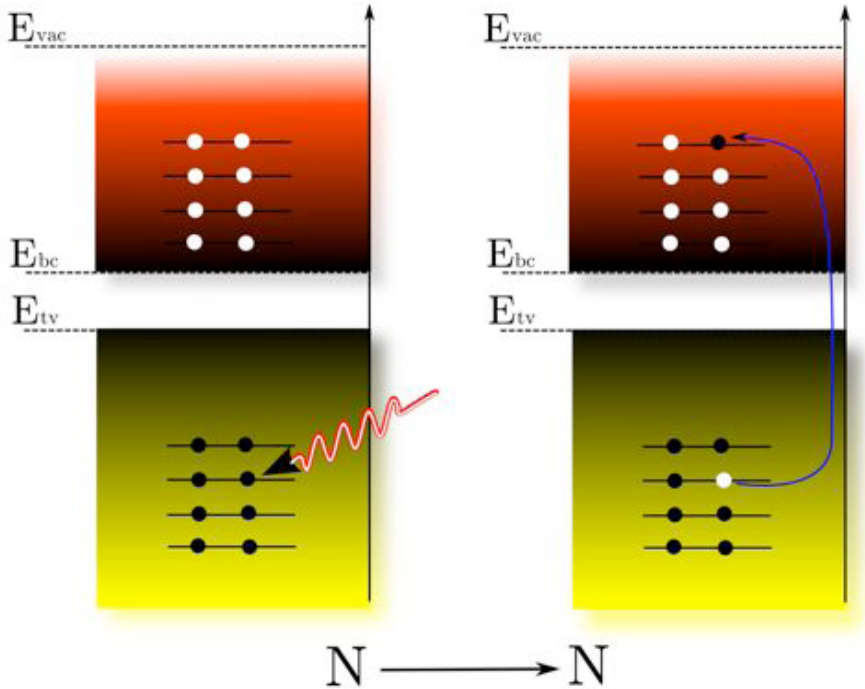
Theoretical Spectroscopy

- Which kind of spectra?
- Which kind of tools?

Absorption



Beer-Lambert law: $I = I_0 e^{-\alpha x}$



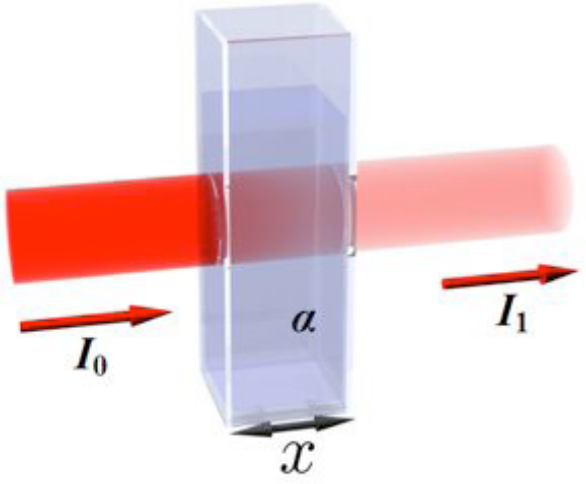
$\alpha(\omega) \propto \mathrm{Im}\epsilon_M(\mathbf{q} \to 0, \omega) \quad \Rightarrow \quad$ (extended system) absorption coefficient

$\sigma(\omega) \propto \mathrm{Im}\epsilon_M(\mathbf{q} \to 0, \omega) \quad \Rightarrow \quad$ (finite system) photoabsorption cross section

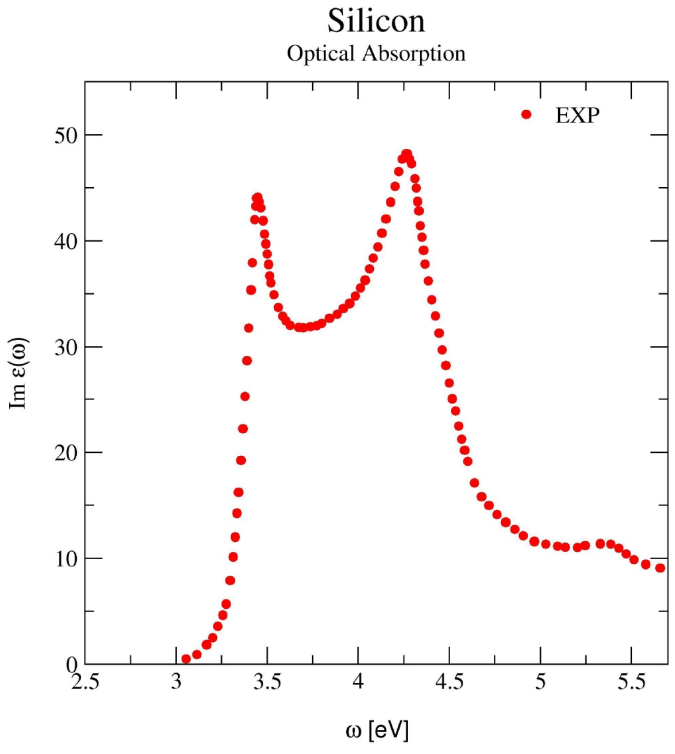
$$E(x,t) = E_0 e^{i\frac{\omega\tilde{n}}{c}x} e^{-i\omega t} \qquad \tilde{n} = \sqrt{\epsilon_M} = n + ik \qquad \epsilon_M = \epsilon_1 + i\epsilon_2$$

J. D. Jackson, Classical Electrodynamics

Absorption



Beer-Lambert law: $I = I_0 e^{-\alpha x}$



$\alpha(\omega) \propto \mathrm{Im}\epsilon_M(\mathbf{q} \to 0, \omega) \quad \Rightarrow \quad$ (extended system) absorption coefficient

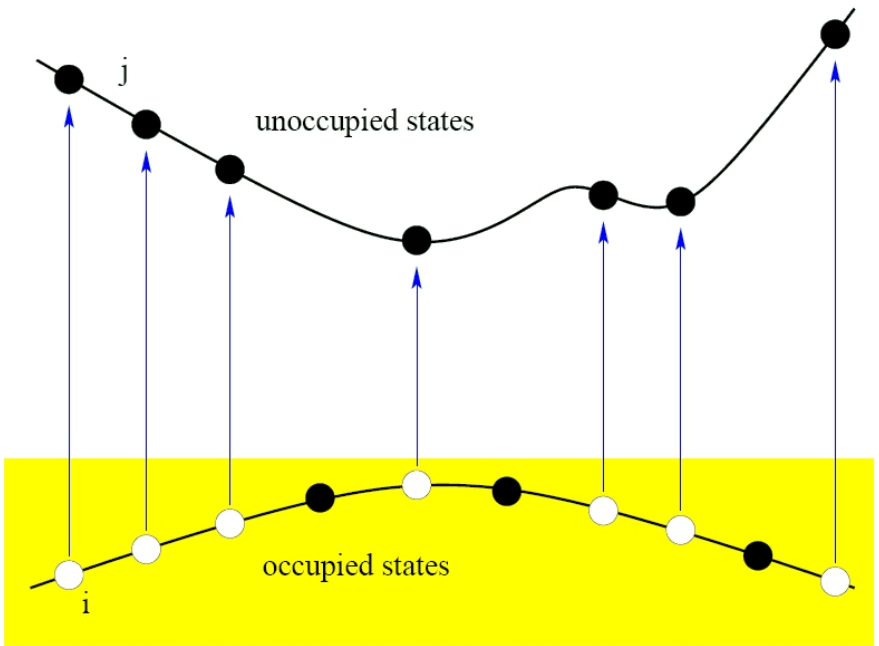
$\sigma(\omega) \propto \mathrm{Im}\epsilon_M(\mathbf{q} \to 0, \omega) \quad \Rightarrow \quad$ (finite system) photoabsorption cross section

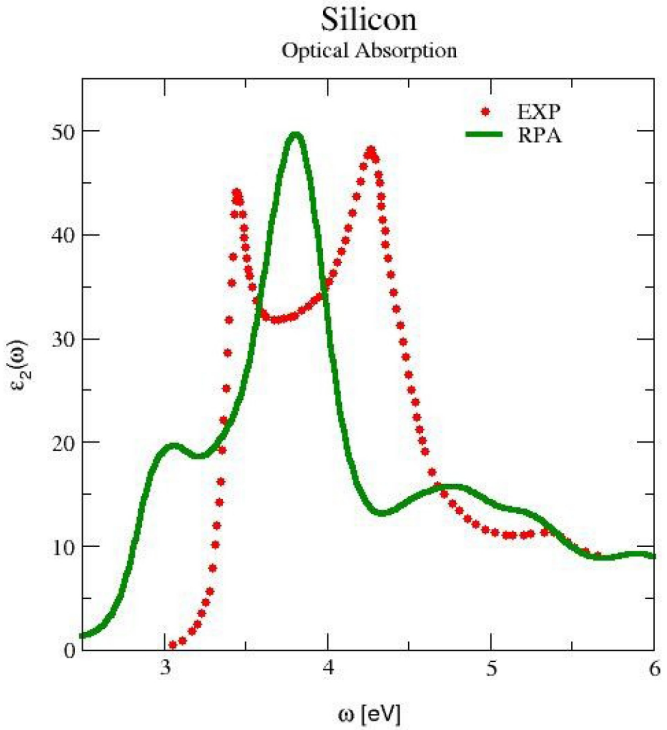
$$\mathrm{Im}\epsilon_M(\omega) \equiv \epsilon_2(\omega)$$

More than LDA band structure

Independent transitions:

$$\epsilon_2(\omega) = \lim_{\mathbf{q}\to 0} \frac{8\pi^2}{\Omega q^2} \sum_{ij\mathbf{k}} |\langle \varphi_{j\mathbf{k}-\mathbf{q}} | e^{-i\mathbf{qr}} | \varphi_{i\mathbf{k}} \rangle|^2 \delta(\varepsilon_{j\mathbf{k}-\mathbf{q}} - \varepsilon_{i\mathbf{k}} - \omega)$$





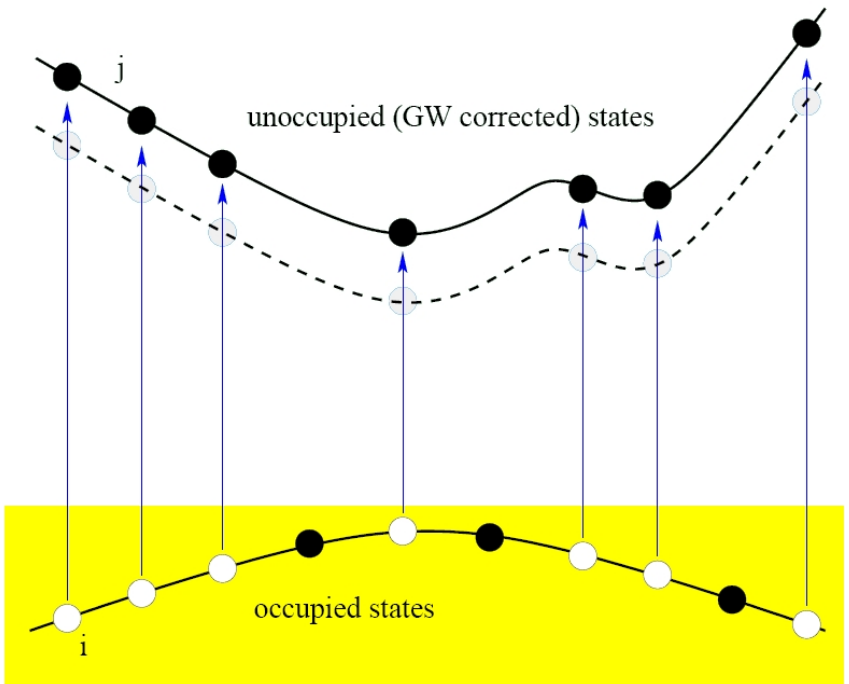
What is wrong?

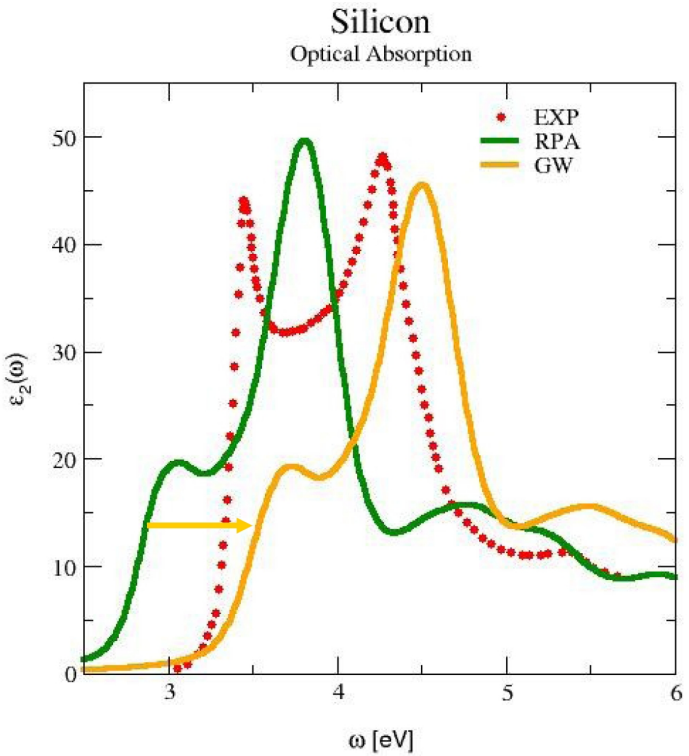
What is missing?

More than GW band structure

Independent transitions:

$$\epsilon_2(\omega) = \lim_{\mathbf{q}\to 0} \frac{8\pi^2}{\Omega q^2} \sum_{ij\mathbf{k}} |\langle \varphi_{j\mathbf{k}-\mathbf{q}} | e^{-i\mathbf{qr}} | \varphi_{i\mathbf{k}} \rangle|^2 \delta(E_{j\mathbf{k}-\mathbf{q}} - E_{i\mathbf{k}} - \omega$$

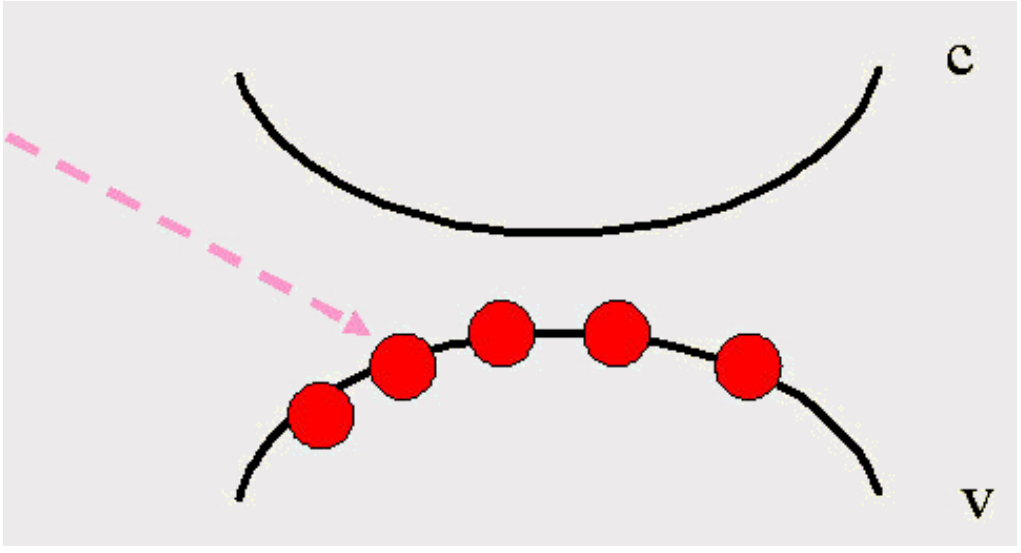




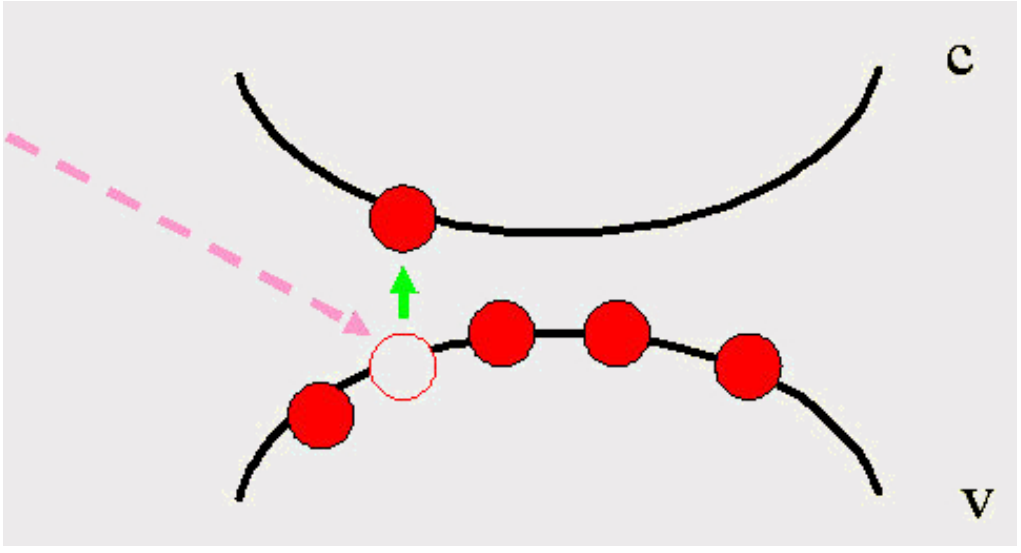
What is wrong?

What is missing?

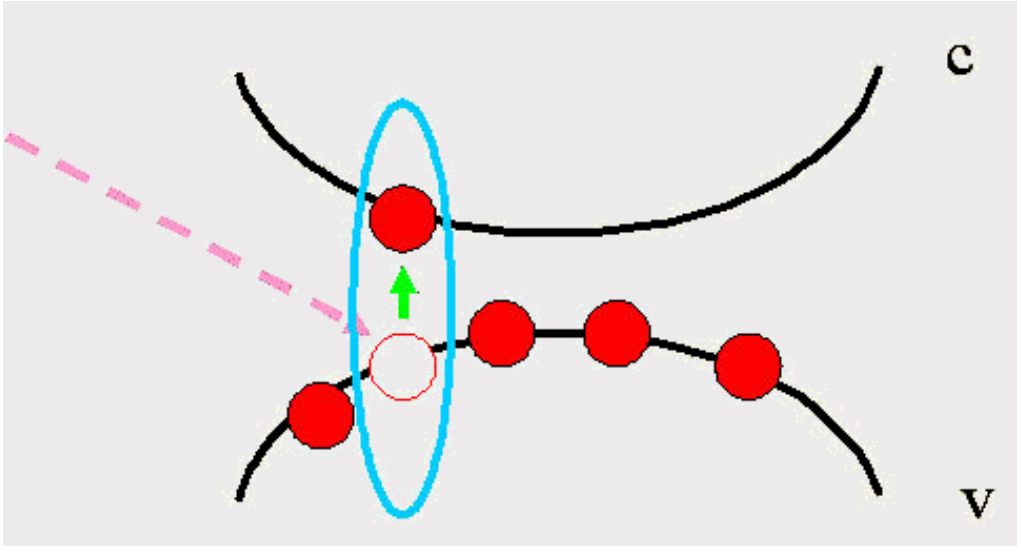
Absorption



Absorption



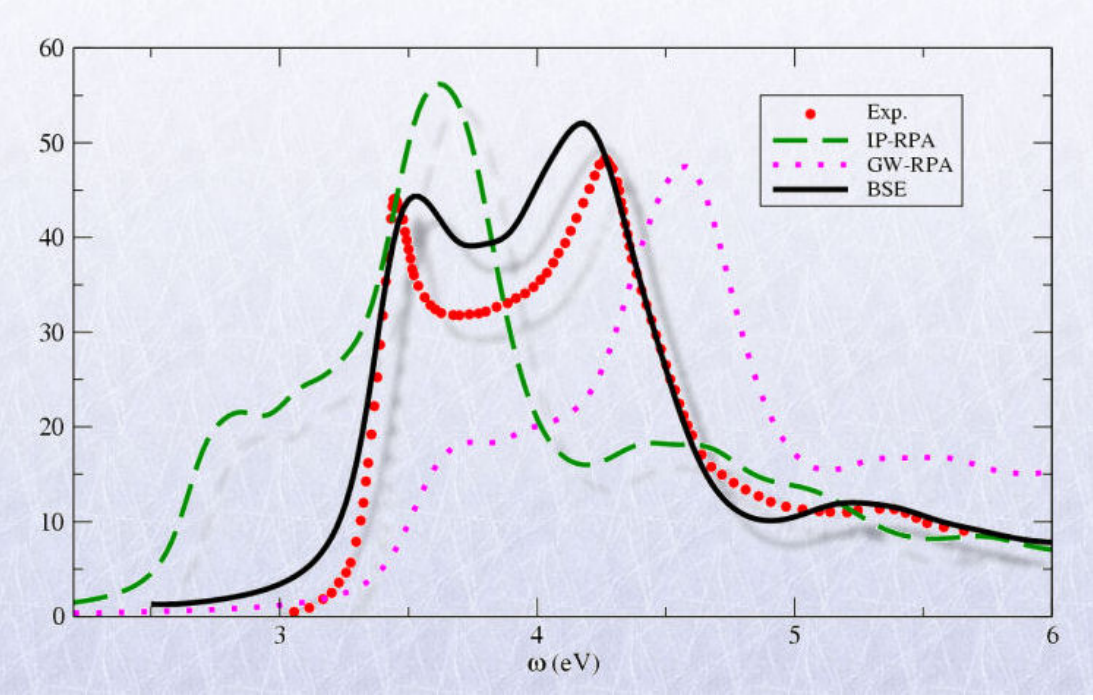
Absorption



Excitonic effects = electron - hole interaction

Absorption spectrum

Bulk silicon

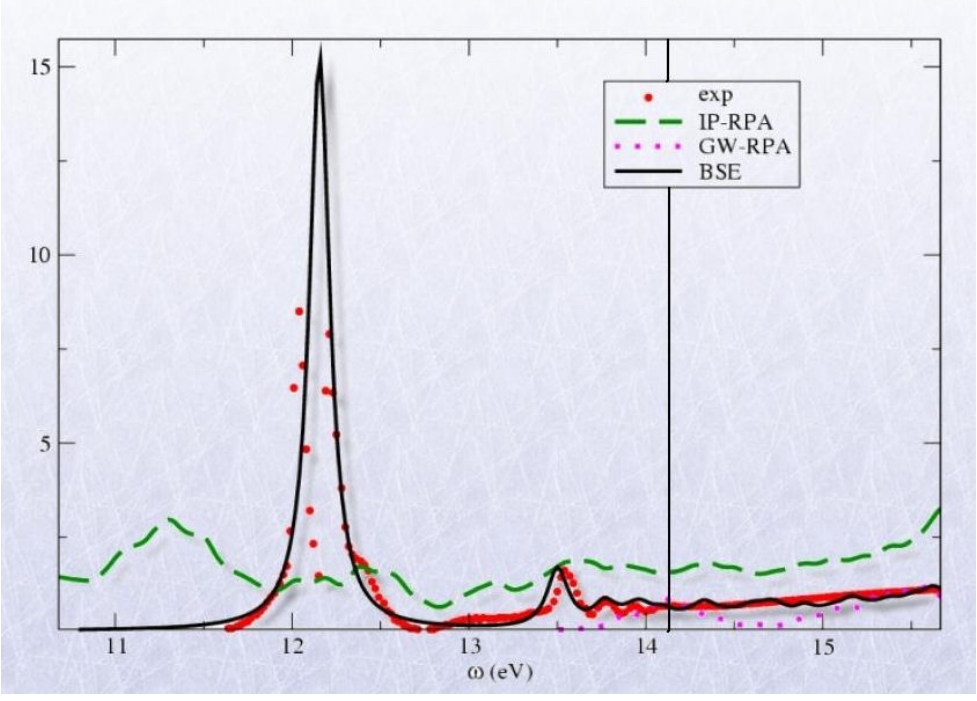


G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74** (2002).

Bound excitons

E_{abs} = Optical gap $<$ Photoemission (fundamental) gap = E_{pes}

Binding energy = $E_{\text{pes}} - E_{\text{abs}}$



Solid argon: F. Sottile *et al.* PRB **76** (2007).

Outline

Spectroscopy is exciting!!!

Many thanks!