Density Functional Approach

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CAPACITIES

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ETSF European Theoretical Spectroscopy Facility

Density Functional Theory

1. Any observable of a quantum system can be obtained from the density of the system **alone**.

$$< O >= O[n]$$

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

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Density Functional ... Why ?

Basic ideas of DFT

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Importance of the density

Example: atom of Nitrogen (7 electron)

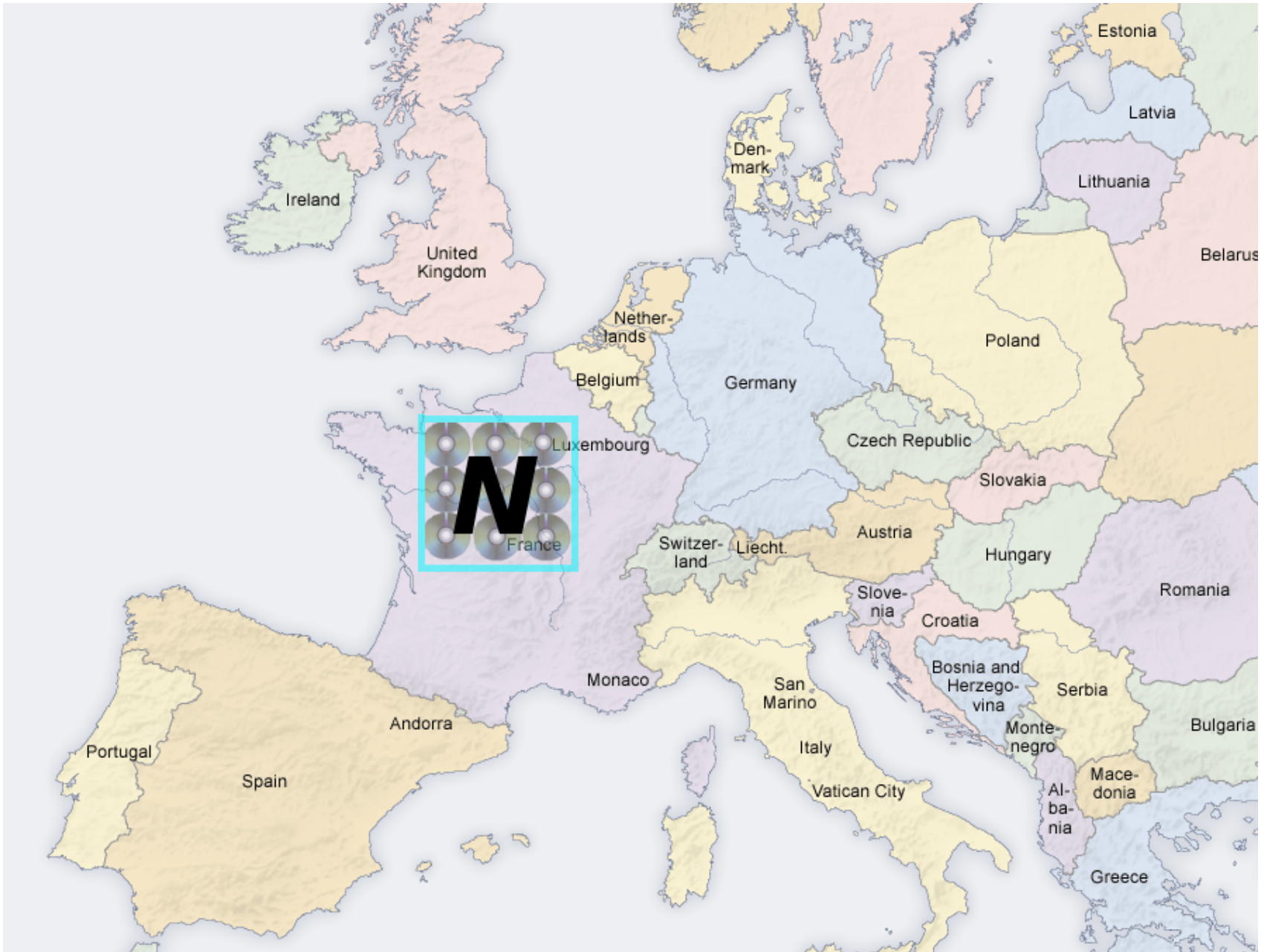
$$\Psi(\mathbf{r}_1, .., \mathbf{r}_7) \quad 21 \text{ coordinates}$$

10 entries/coordinate $\Rightarrow 10^{21}$ entries

8 bytes/entry $\Rightarrow 8 \cdot 10^{21}$ bytes

4.7×10^9 bytes/DVD $\Rightarrow 2 \times 10^{12}$ DVDs

Density Functional ... Why ?



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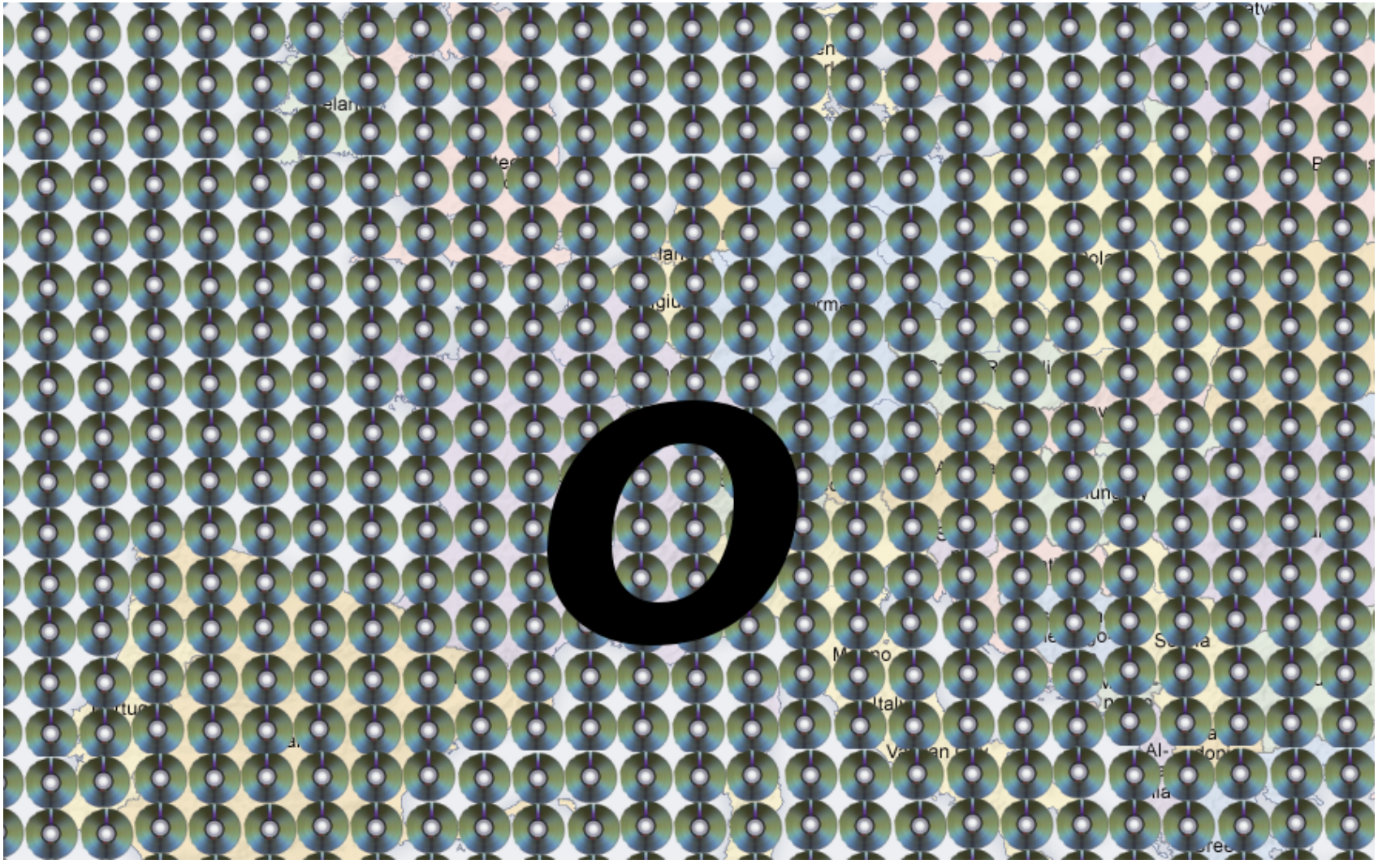

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Example: atom of Oxygen (8 electron)

$\Psi(\mathbf{r}_1, .., \mathbf{r}_8)$ 24 coordinates

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Importance of non-interacting

The Kohn-Sham one-particle equations

$$H_i(\mathbf{r})\psi_i(\mathbf{r}) = \epsilon_i(\mathbf{r})\psi_i(\mathbf{r})$$

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Density Functional Theory - Kohn-Sham

$$\left[\nabla_i^2 + V_{ext}(\mathbf{r}) + \int d\mathbf{r} \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{xc}[n](\mathbf{r})\right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i^{occ} |\psi_i(\mathbf{r})|^2 = \text{Exact density}$$

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Density Functional ... Hierarchy of approximation

- LDA (local)
- GGA (still local, but with a gradient expansion)
- MetaGGA (non-local)
- OEP (non local, orbital dependent)
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Density Functional ... Successfull ?

TABLE I: *Physical Review* articles with more than 1000 citations through June 2003. *PR, Physical Review; PRB, Physical Review B; PRD, Physical Review D; PRL, Physical Review Letters; RMP, Reviews of Modern Physics.*

Publication	# cites	Av. Age	Title	Author(s)
PR **140**, A1133 (1965)	3227	26.7	Self-Consistent Equations Including Exchange and Correlation Effects	W. Kohn, L. J. Sham
PR **136**, B864 (1964)	2460	28.7	Inhomogeneous Electron Gas	P. Hohenberg, W. Kohn
PRB **23**, 5048 (1981)	2079	14.4	Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems	J. P. Perdew, A. Zunger
PRL **45**, 566 (1980)	1781	15.4	Ground State of the Electron Gas by a Stochastic Method	D. M. Ceperley, B. J. Alder
PR **108**, 1175 (1957)	1364	20.2	Theory of Superconductivity	J. Bardeen, L. N. Cooper, J. R. Schrieffer
PRL **19**, 1264 (1967)	1306	15.5	A Model of Leptons	S. Weinberg
PRB **12**, 3060 (1975)	1259	18.4	Linear Methods in Band Theory	O. K. Andersen
PR **124**, 1866 (1961)	1178	28.0	Effects of Configuration Interaction on Intensities and Phase Shifts	U. Fano
RMP **57**, 287 (1985)	1055	9.2	Disordered Electronic Systems	P. A. Lee, T. V. Ramakrishnan
RMP **54**, 437 (1982)	1045	10.8	Electronic Properties of Two-Dimensional Systems	T. Ando, A. B. Fowler, F. Stern
PRB **13**, 5188 (1976)	1023	20.8	Special Points for Brillouin-Zone Integrations	H. J. Monkhorst, J. D. Pack

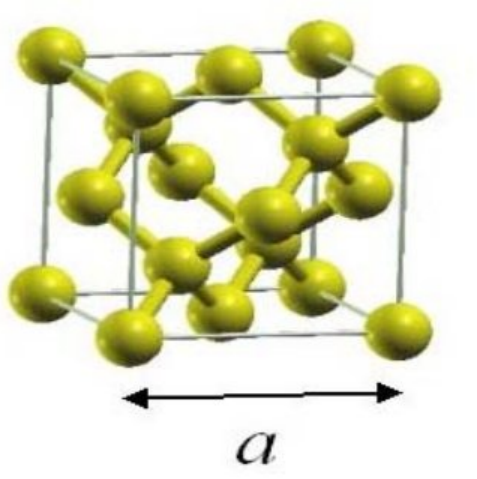
S. Redner `http://arxiv.org/abs/physics/0407137`

Density Functional Theory - Codes

- Abinit
- ADF
- AIMPRO
- Atomistix
- CADPAC
- CASTEP
- CPMD
- CRYSTAL06
- DACAPO
- DALTON
- deMon2K
- DFT++
- DMol3
- EXCITING
- Fireball
- FSatom
- GAMESS (UK)
- GAMESS (US)
- GAUSSIAN
- JAGUAR
- MOLCAS
- MOLPRO
- MPQC
- NRLMOL
- NWChem
- OCTOPUS
- OpenMX
- ORCA
- ParaGauss
- PLATO
- PWscf
- ESPRESSO
- Q-Chem
- SIESTA
- Spartan
- S/PHI/nX
- TURBOMOLE
- VASP
- WIEN2k

Density Functional Theory - Kohn-Sham

- total energy $E[n]$
  - ionic structure (lattice parameter)
  - surface reconstruction
  - molecular bonding
  - ...



- "pseudo" band-structure $\epsilon_{n\mathbf{k}}$
  - $\surd$ photoemission energies ??
  - $\times$ interpretation problem
  - $\times$ results (band-gap) problem

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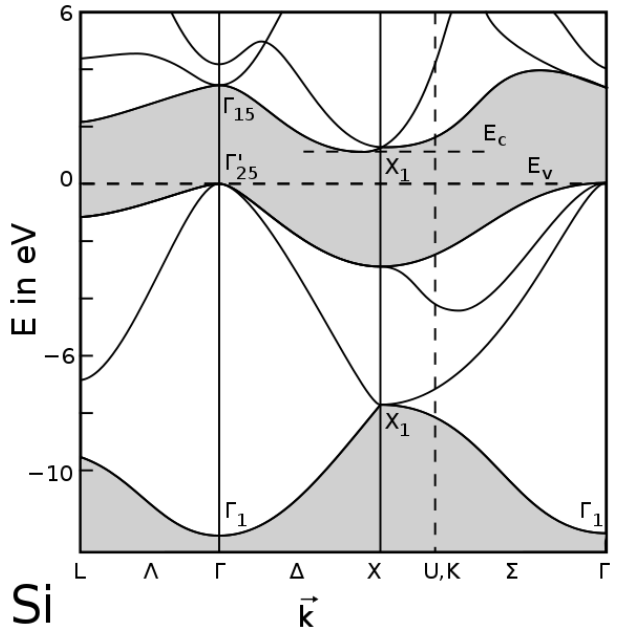

Linear Response Approach

Definition of polarizability

$$\varepsilon^{-1} = 1 + v\chi$$

χ is the polarizability of the system

Linear Response Approach

Polarizability

$$\text{interacting system} \quad \delta n = \chi \delta V_{ext}$$

$$\text{non-interacting system} \quad \delta n_{n-i} = \chi^0 \delta V_{tot}$$

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$$\chi^0(\mathbf{r}, \mathbf{r}', \omega) = \sum_{ij} \frac{\phi_i(\mathbf{r})\phi_j^*(\mathbf{r})\phi_i^*(\mathbf{r}')\phi_j(\mathbf{r}')}{\omega - (\epsilon_i - \epsilon_j)} \qquad :: \text{IPA}$$

hartree, hartree-fock, dft, etc.

G.D. Mahan *Many Particle Physics* (Plenum, New York, 1990)

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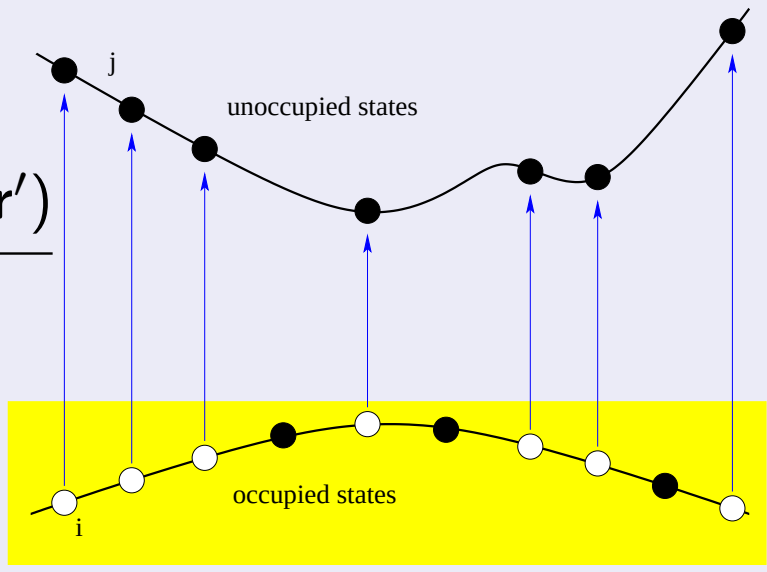
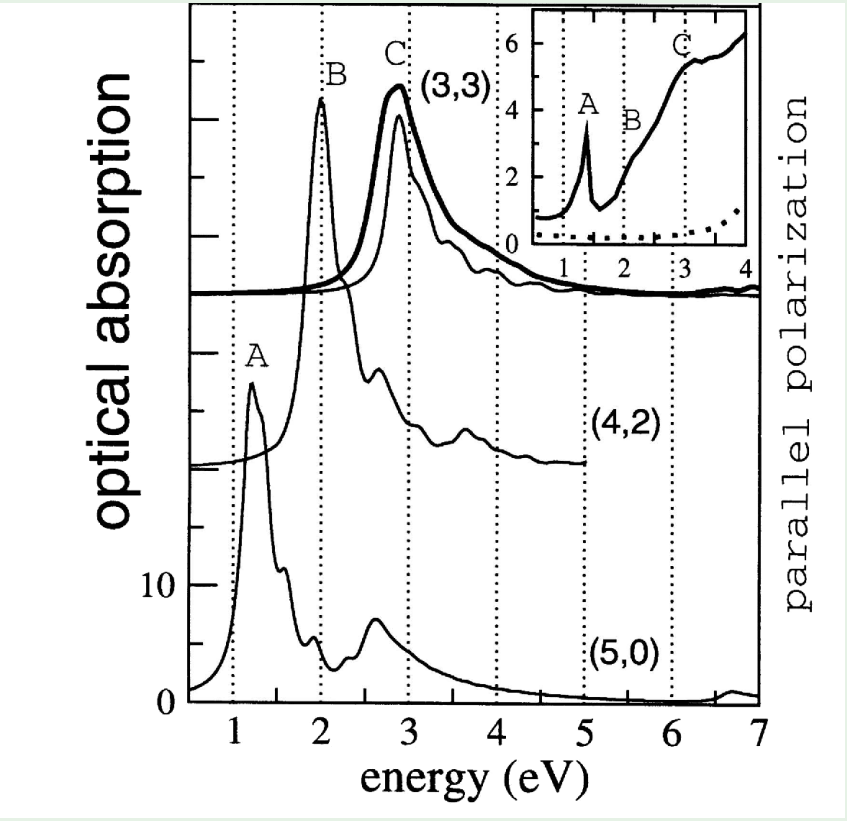
from a DFT calculation



Independent Particle Polarizability

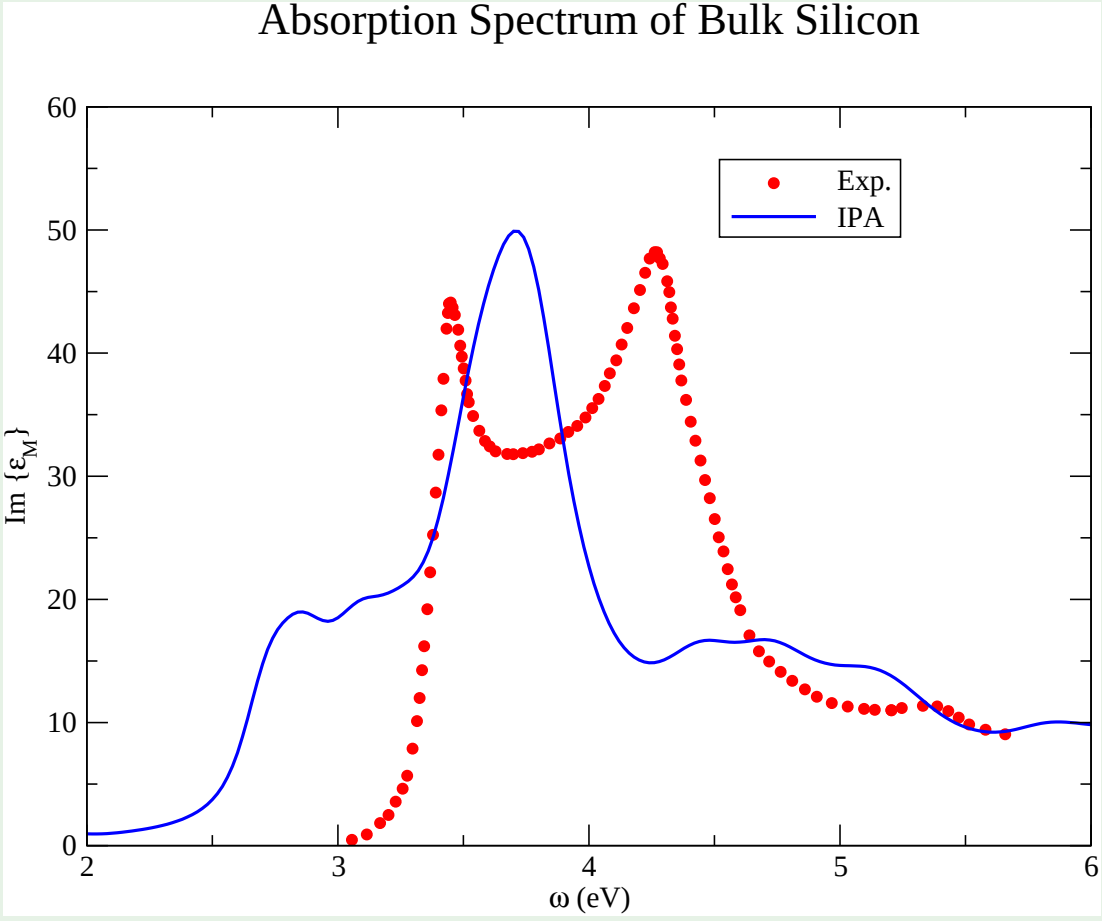
Some good results ... (carbon nanotube)



A.Marinopoulos *et al.* Appl. Phys. A, **78**, 1157 (2004)

Independent Particle Polarizability

... but it doesn't always work! (silicon)



Polarizability

$$\chi \neq \chi^0$$

$$\chi = \chi^0 + \text{something else}$$

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Time Dependent Density Functional Theory

Polarizability

interacting system $\quad \delta n = \chi \delta V_{ext}$

non-interacting system $\quad \delta n_{n-i} = \chi^0 \delta V_{tot}$

$\Updownarrow$

Density Functional Formalism

$$\delta n = \delta n_{n-i}$$

$$\delta V_{tot} = \delta V_{ext} + \delta V_H + \delta V_{xc}$$

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Polarizability

$$\chi \delta V_{ext} = \chi^0 \left(\delta V_{ext} + \delta V_H + \delta V_{xc} \right)$$

$$\chi = \chi^0 \left(1 + \frac{\delta V_H}{\delta V_{ext}} + \frac{\delta V_{xc}}{\delta V_{ext}} \right)$$

$$\frac{\delta V_H}{\delta V_{ext}} = \frac{\delta V_H}{\delta n} \frac{\delta n}{\delta V_{ext}} = v\chi$$

$$\frac{\delta V_{xc}}{\delta V_{ext}} = \frac{\delta V_{xc}}{\delta n} \frac{\delta n}{\delta V_{ext}} = f_{xc}\chi$$

with $\mathbf{f_{xc}}$ = **exchange-correlation kernel**

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$$\chi = \chi^0 + \chi^0 \left(v + f_{xc} \right) \chi$$

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Polarizability χ in TDDFT

1. DFT ground-state calc. $\rightarrow$ ϕ_i, ϵ_i
   - $E_{\text{cutoff}} = \frac{G_{\max}^2}{2}$
   - psedo-potential approach (norm-conserving)
   - $V_{xc}(LDA, GGA)$
2. $\phi_i, \epsilon_i \rightarrow \chi^0 = \sum_{ij} \frac{\phi_i(\mathbf{r})\phi_j^*(\mathbf{r})\phi_i^*(\mathbf{r}')\phi_j(\mathbf{r}')}{\omega - (\epsilon_i - \epsilon_j)}$
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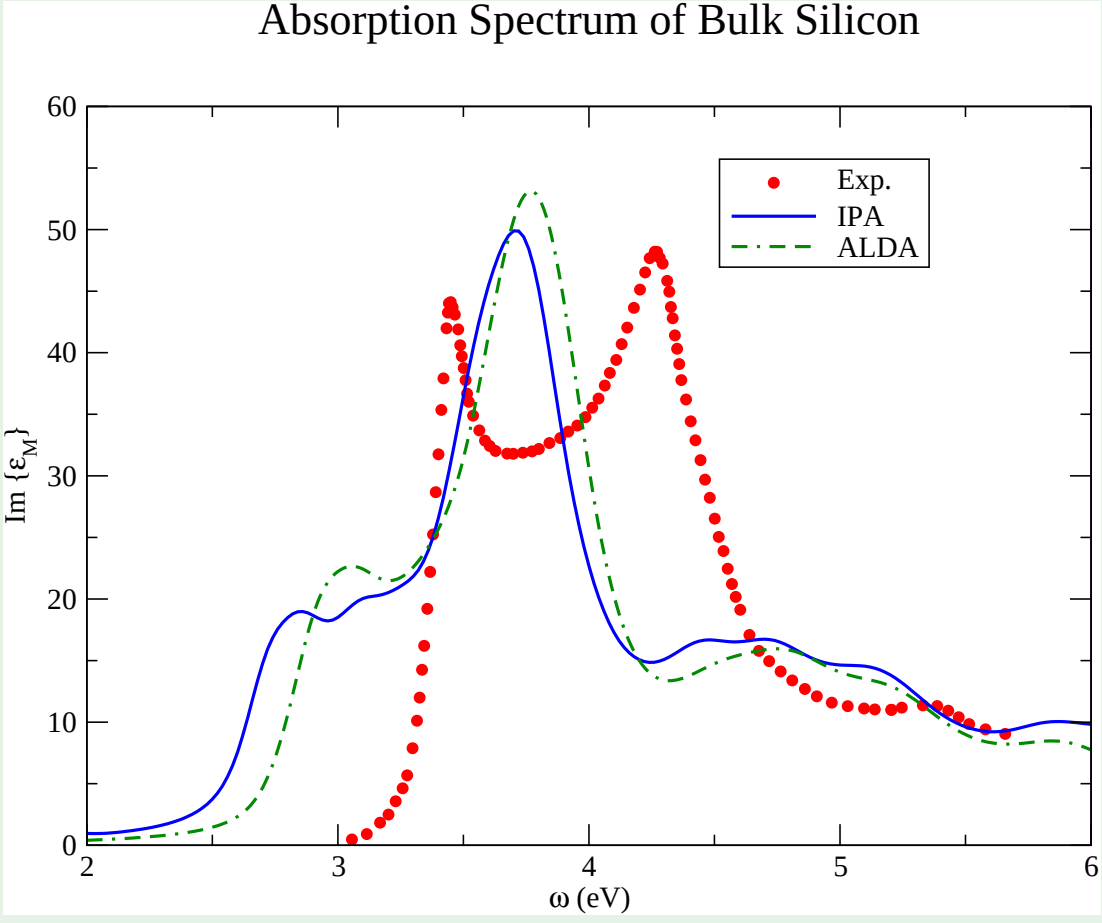
TDDFT - hierarchy for f_{xc}

- $f_{xc} = 0$ RPA
- $f_{xc} = \frac{dV_{xc}^{lda}}{\delta n}$ TD-LDA (ALDA)
- $f_{xc} = \frac{dV_{xc}^{gga}}{\delta n}$ TD-GGA
- TD-OEP
- ...

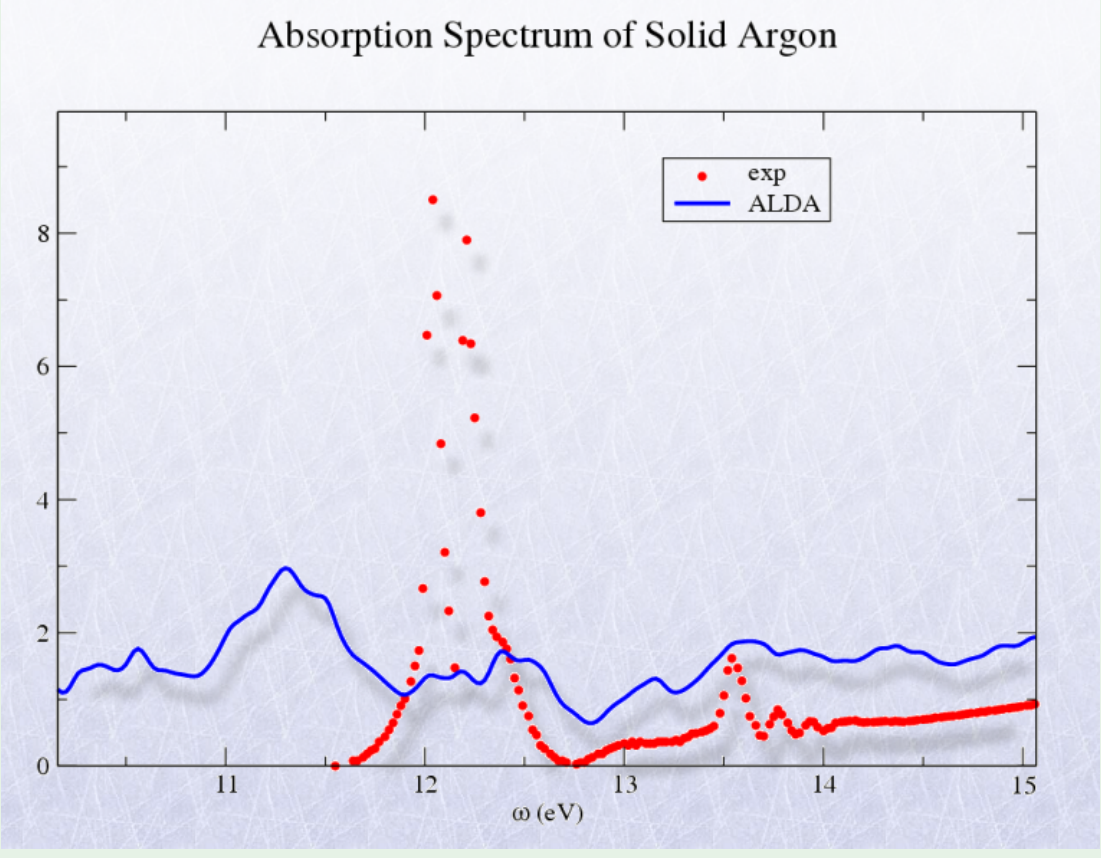
Time Dependent Density Functional Theory

TD-LDA on Absorption of Silicon



Time Dependent Density Functional Theory

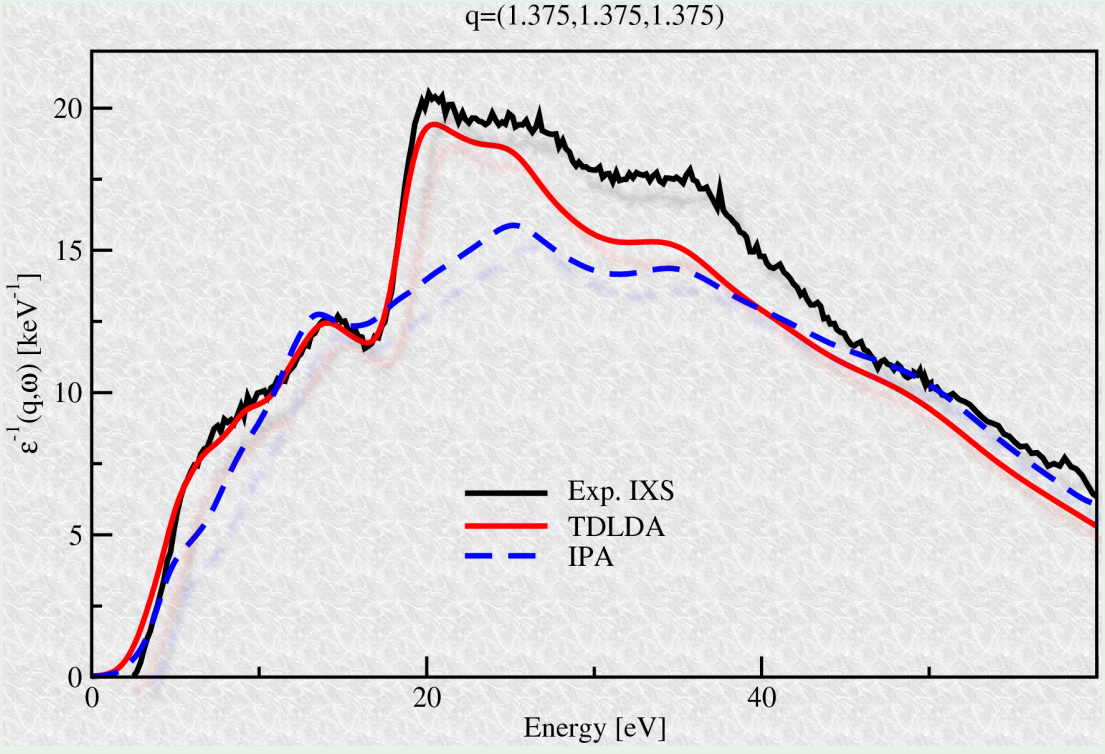
TD-LDA on Absorption of Argon



F.Sottile *et al.* PRB **76**, 161103 (2007).

Time Dependent Density Functional Theory

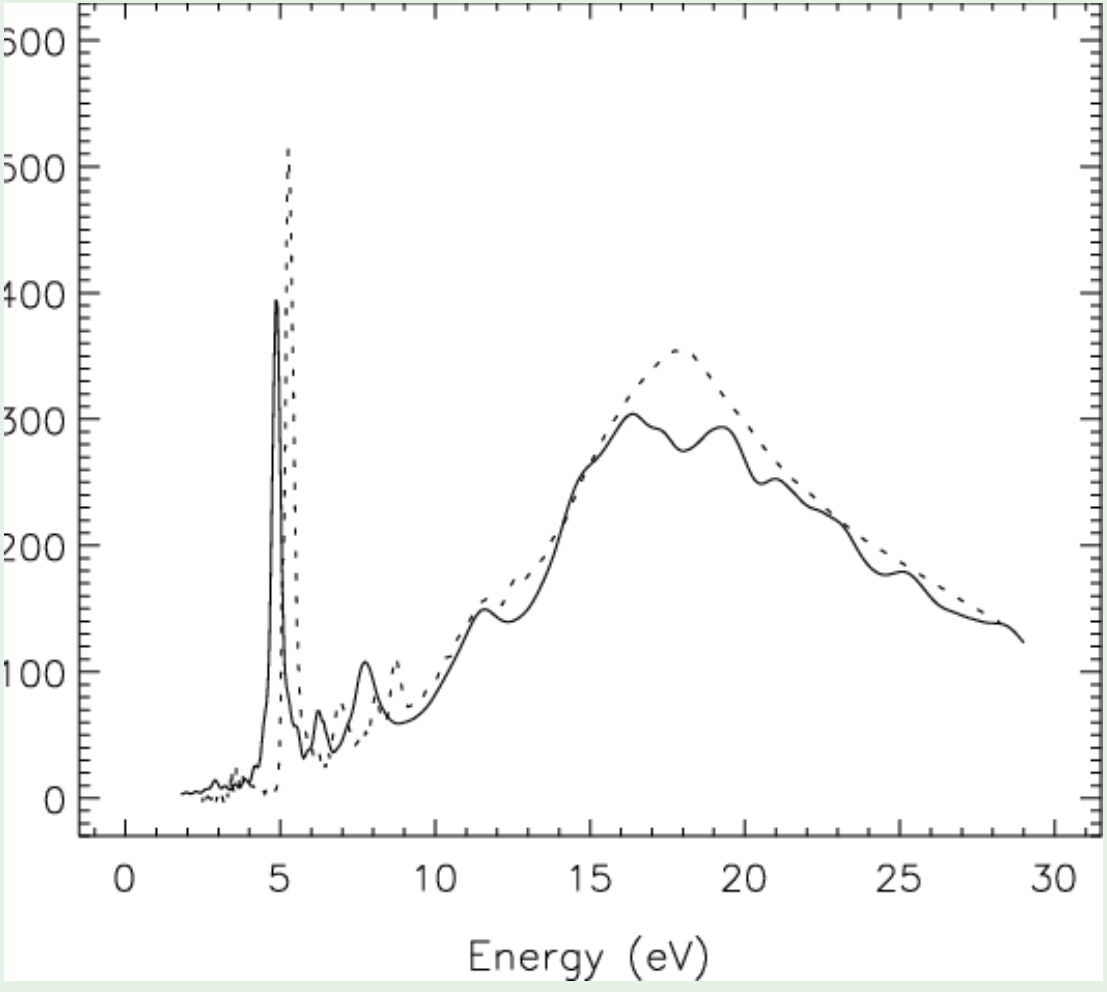
TD-LDA on IXS of Silicon



H-C.Weissker it et al., Physical Review Letters **97**, 237602 (2006)

Time Dependent Density Functional Theory

TD-LDA on Absorption of Anthracene ($C_{14}H_{10}$)



Malloci *et al.* A&A 426, 105-117 (2004)

Important Messages

- DFT (very) useful tool for the ground state properties
- DFT even used to construct an IPA polarizability
- TDDFT for electronic excitations and response functions
  - $\surd$ simple functionals (LDA, GGA) very good for (many) finite systems
  - $\times$ absorption spectrum of solids is bad
  - $\surd$ loss spectra ok

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