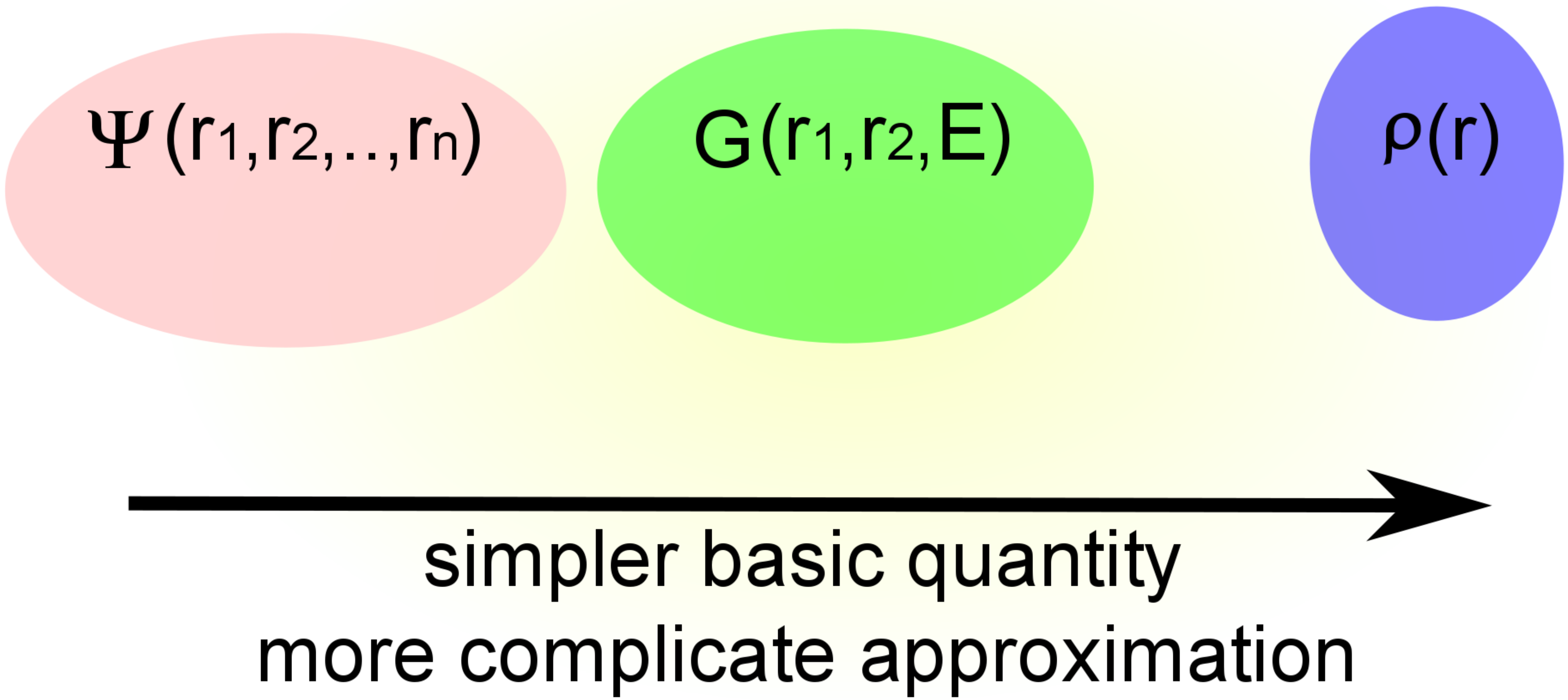
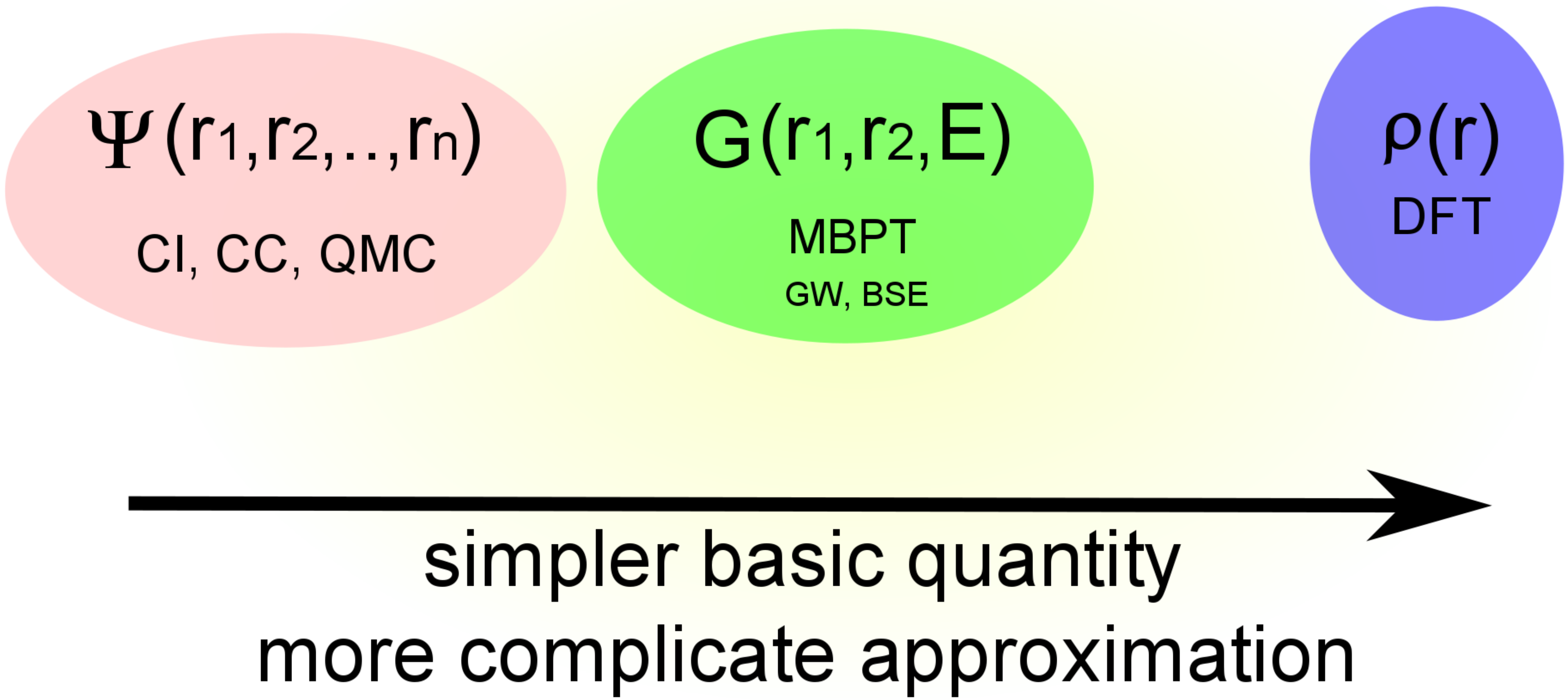
ISTPC 2017

TDDFT in Aussois

Francesco Sottile



Ψ(r1,r2,..,rn)
G(r1,r2,E)
ρ(r)
simpler basic quantity
more complicate approximation


$\Psi(r_1,r_2,..,r_n)$
CI, CC, QMC
$G(r_1,r_2,E)$
MBPT
GW, BSE
$\rho(r)$
DFT
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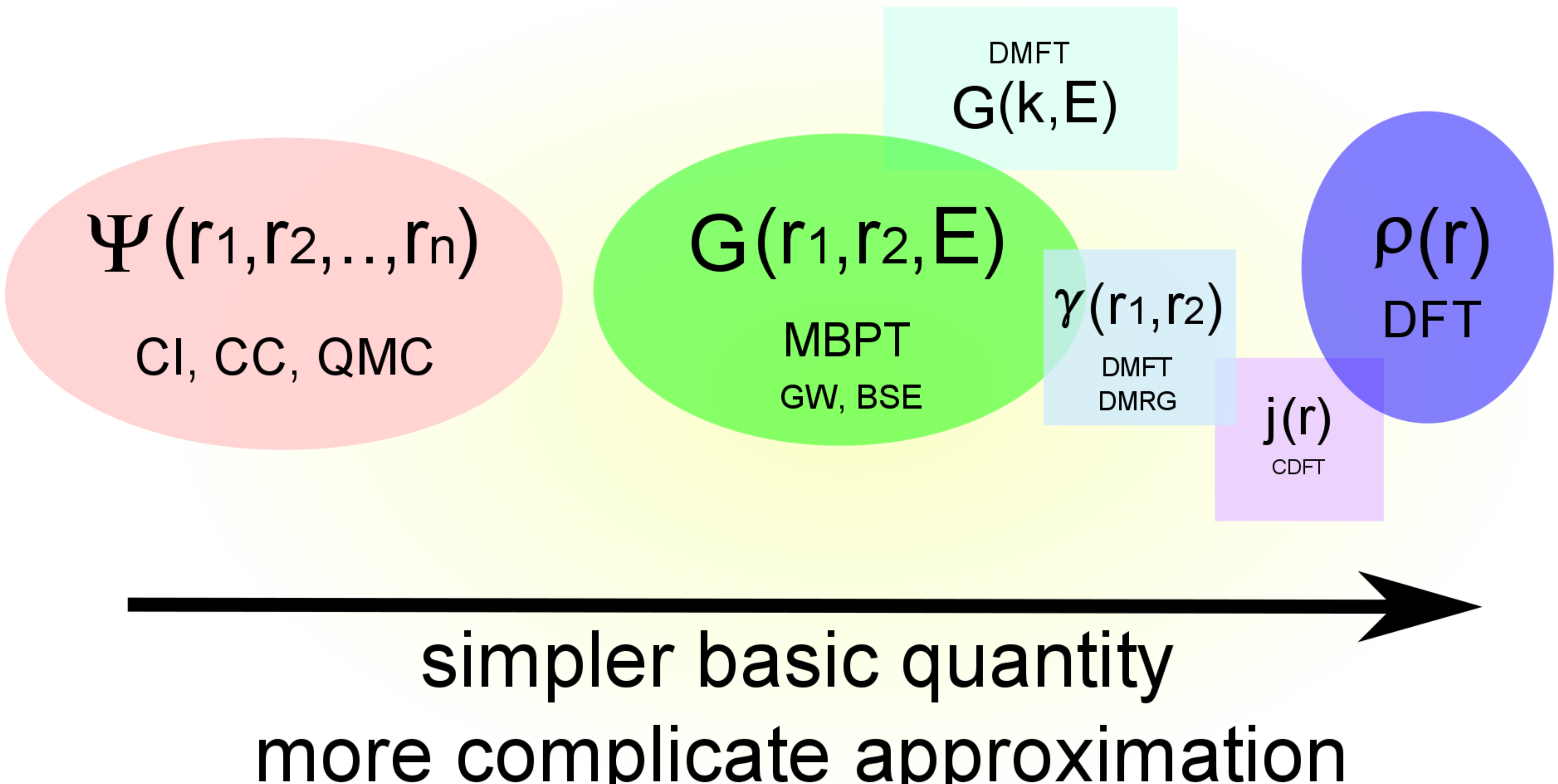

$\Psi(r_1,r_2,..,r_n)$
CI, CC, QMC
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DMFT
$G(k,E)$
$\gamma(r_1,r_2)$
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DMRG
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CDFT
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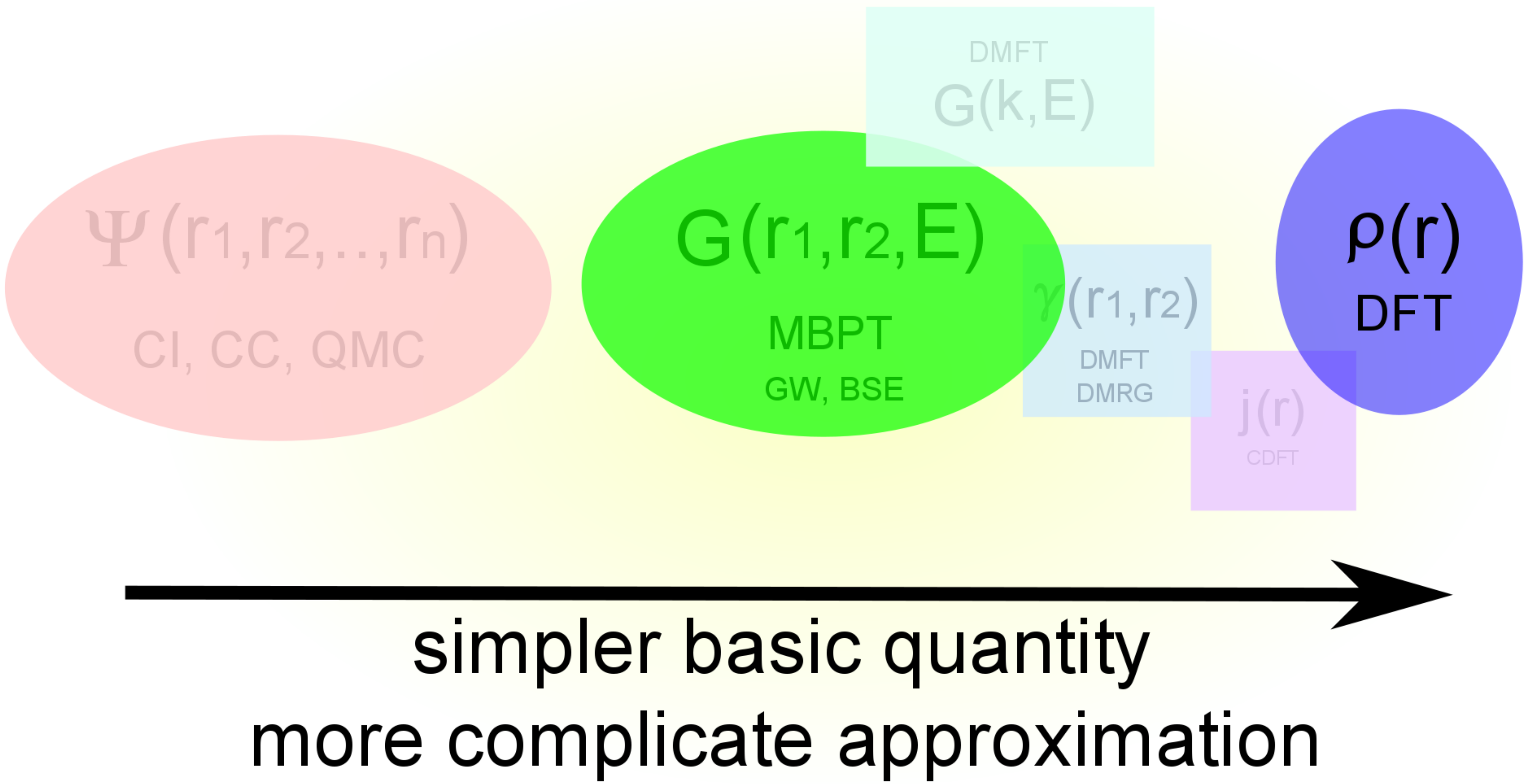
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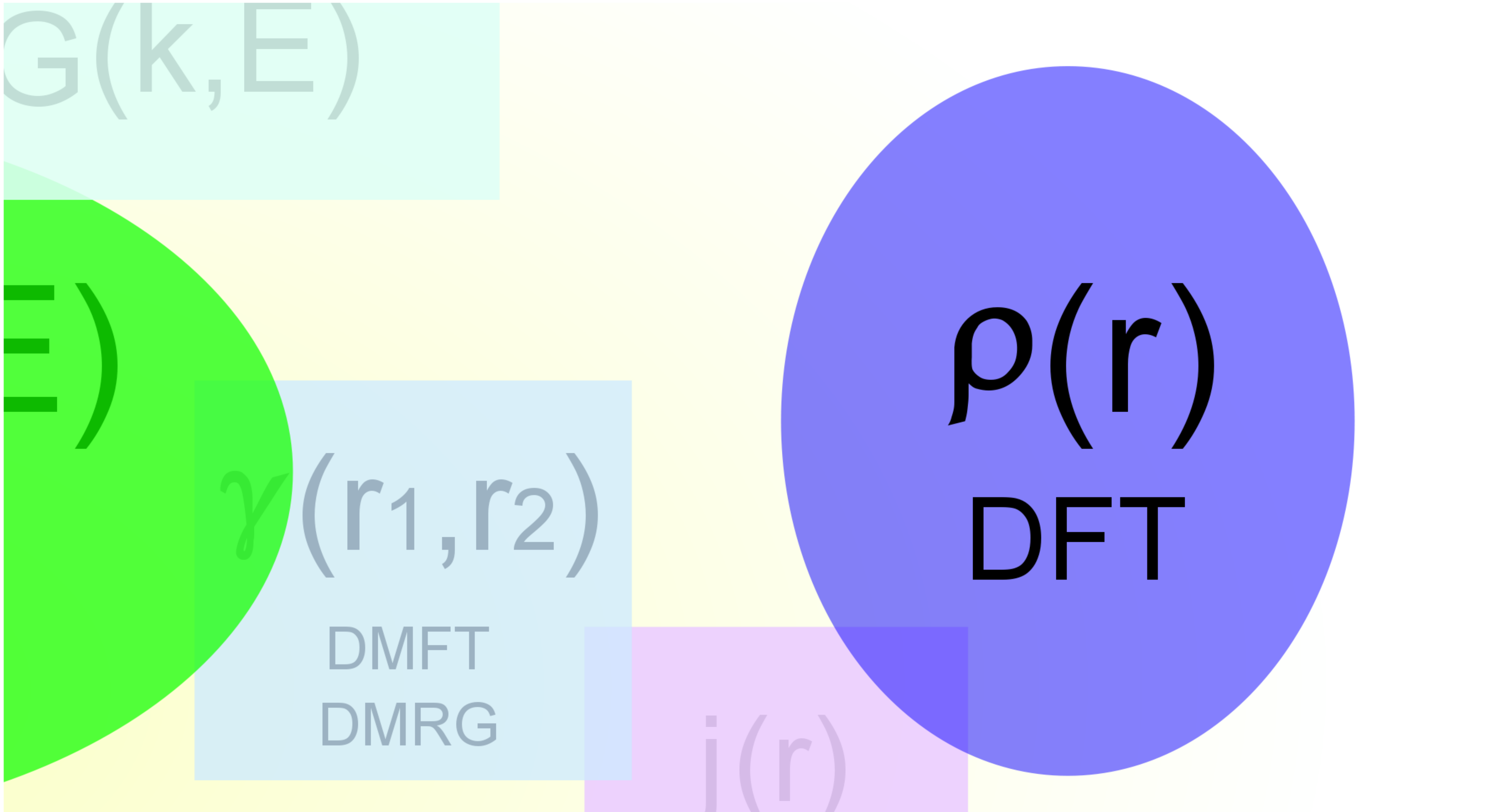
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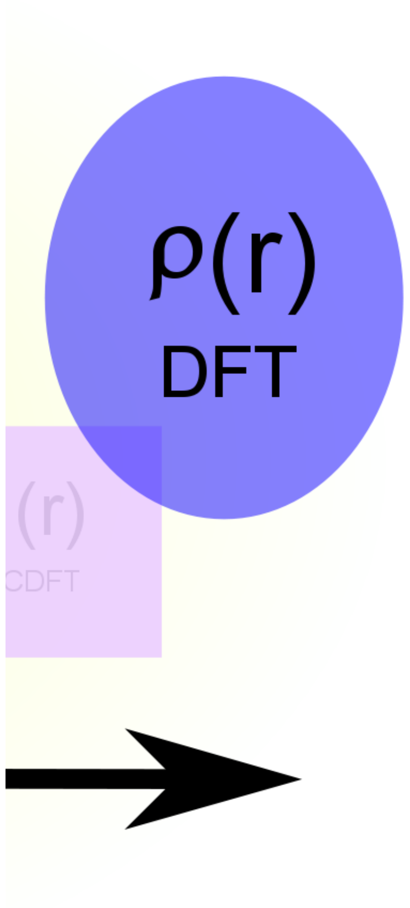
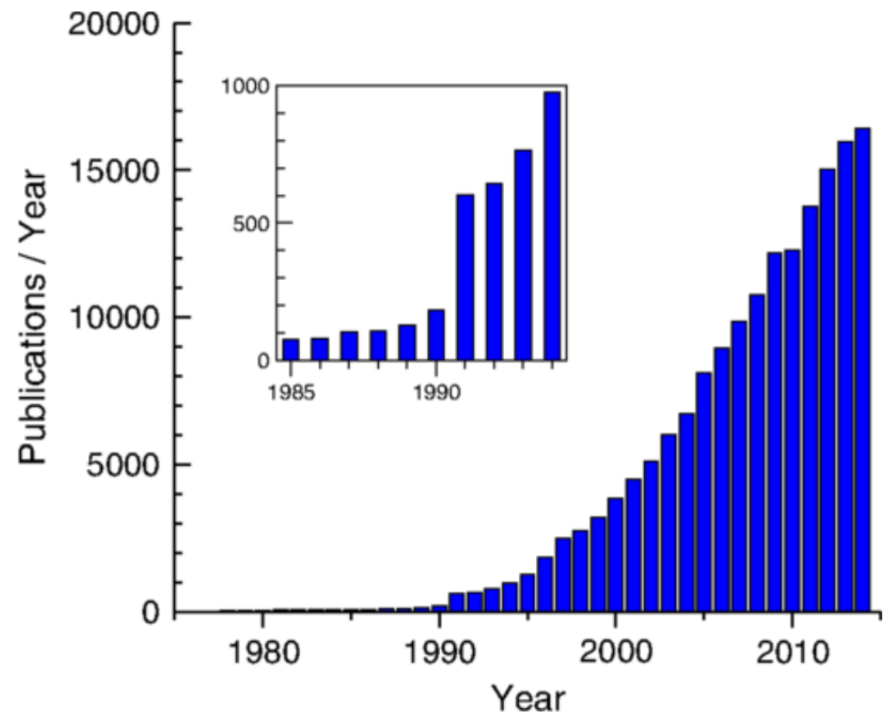


Success of DFT



R. O. Jones Rev. Mod. Phys. 87, 897 (2015)

Success of DFT

Ground-state properties

- lattice parameters
- intermolecular distance
- bulk modulus
- phonons / vibrations spectra
- total energies
- ......

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Excited-state energies

- ΔSCF
- ensemble DFT - see Killian's poster
- Variational Density-Functional Theory
  (Levy and Nagy PRL **83**, 4361 (1999))
- Adiabatic-connection formalism
  (Perdew and Levy PRB **31**, 6264 (1985))

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Excitation Spectra

- band structure calculation, via Kohn-Sham
- optical properties, via linear response

PES

Electron Energy Loss

Absorption

Success of DFT

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- intermolecular distance
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Excitation Spectra

- band structure calculation, via Kohn-Sham → **PES**
- optical properties, linear response → **Absorption**, **Electron Energy Loss**

DFT $\longrightarrow$ TDDFT

- Optical/dielectric properties
- system under strong laser impulses
- multiple harmonic generation
- relaxation
- convergence to steady state
- ....

$$[T + V_{e-e} + V_N + V_{\text{ext}}(t)]\,\Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_n, t) = i\hbar \frac{\partial \Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_n, t)}{\partial t}$$

Outline

- Time Dependent Density Functional Theory
  - introduction and derivation
  - thoughts and particularities
  - approximations, applications
- Linear Response approach
  - connection with spectroscopy
  - exchange-correlation kernel
  - beyond linear response
- Micro-macro connection

DFT

TDDFT

DFT

Hohenberg-Kohn theorem

$$V_{\text{ext}} \longleftrightarrow n$$

$$\langle \Psi | O | \Psi \rangle = O[n]$$

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

TDDFT

Runge-Gross theorem

$$V_{\text{ext}}(t) \longleftrightarrow n(t)$$

$$\langle \Psi(t) | O(t) | \Psi(t) \rangle = O[n, \Psi^0](t)$$

Runge and Gross, Phys. Rev. Lett. **52**, 997 (1984)

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$$V_{\rm ext}(t) \quad \longleftrightarrow \quad n(t)$$

Demonstration

Runge-Gross theorem

$$V_{\text{ext}}(t) \longleftrightarrow n(t)$$

Demonstration

1) $V_{\text{ext}}(\mathbf{r},t) \neq V'_{\text{ext}}(\mathbf{r},t) + c(t) \longleftrightarrow \mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t)$

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2) $\mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t) \longleftrightarrow n(\mathbf{r},t) \neq n'(\mathbf{r},t)$

DFT

Kohn-Sham equation

$$\left[-\frac{\nabla^2}{2} + v_{\mathrm{KS}}[n](\mathbf{r})\right]\psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

$$v_{\mathrm{KS}}[n](\mathbf{r}) = v_{\mathrm{ext}} + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + v_{\mathrm{xc}}[n](\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{\mathrm{occ}} |\psi_i(\mathbf{r})|^2$$

Kohn and Sham, Phys. Rev. **140**, A1133 (1965)

TDDFT

Kohn-Sham equation

$$\left[-\frac{\nabla^2}{2} + v_{\mathrm{KS}}[n;\Phi^0](\mathbf{r},t)\right]\psi_i(\mathbf{r},t) = i\frac{\partial\psi_i(\mathbf{r},t)}{\partial t}$$

$$v_{\mathrm{KS}}[n;\Phi^0](\mathbf{r},t) = v_{\mathrm{ext}}[n,\Psi_0](\mathbf{r},t) + \int \frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + v_{\mathrm{xc}}[n,\Psi_0,\Phi_0](\mathbf{r},t)$$

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TDDFT

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no self-consistency

local in space and time

functionally non-local

no variational from an energy functional

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$](\mathbf{r}, t)$

no self-consistency

local in space and time

functionally non-local

no variational from an energy functional

no (direct) derivation of the TDKS eqs.

less exact conditions known

Time propagation in practise

Time propagation in practise

$$\alpha(t) = \int \mathbf{r}\, n(\mathbf{r}, t) d\mathbf{r}$$

$$\sigma(\omega) = \frac{4\pi\omega}{c}\alpha(\omega)$$

Photo-absorption cross section

Time propagation in practise

$$\alpha(t) = \int \mathbf{r}\, n(\mathbf{r},t) d\mathbf{r}$$

$$\sigma(\omega) = \frac{4\pi\omega}{c}\alpha(\omega)$$

Photo-absorption cross section

$$M_{lm}(t) = \int r^l\, Y_{lm}(r)\, n(\mathbf{r},t)\, d\mathbf{r}$$

Multipoles

Time propagation in practise

$$\alpha(t) = \int \mathbf{r}\, n(\mathbf{r},t) d\mathbf{r}$$

$$\sigma(\omega) = \frac{4\pi\omega}{c}\alpha(\omega)$$

Photo-absorption cross section

$$M_{lm}(t) = \int r^l\, Y_{lm}(r)\, n(\mathbf{r},t)\, d\mathbf{r}$$

Multipoles

$$L_z(t) = \sum_i \int \psi_i(\mathbf{r},t) i(\mathbf{r}\times\nabla)_z \psi_i(\mathbf{r},t)\, d\mathbf{r}$$

Angular Momentum

Approximations

- ALDA

$$v_{xc}^{\mathrm{ALDA}}[n](\mathbf{r},t) = v_{xc}^{\mathrm{heg}}(n(\mathbf{r},t)) = \left.\frac{d}{dn}\left[n e_{xc}^{\mathrm{heg}}(n)\right]\right|_{n=n(\mathbf{r},t)}$$

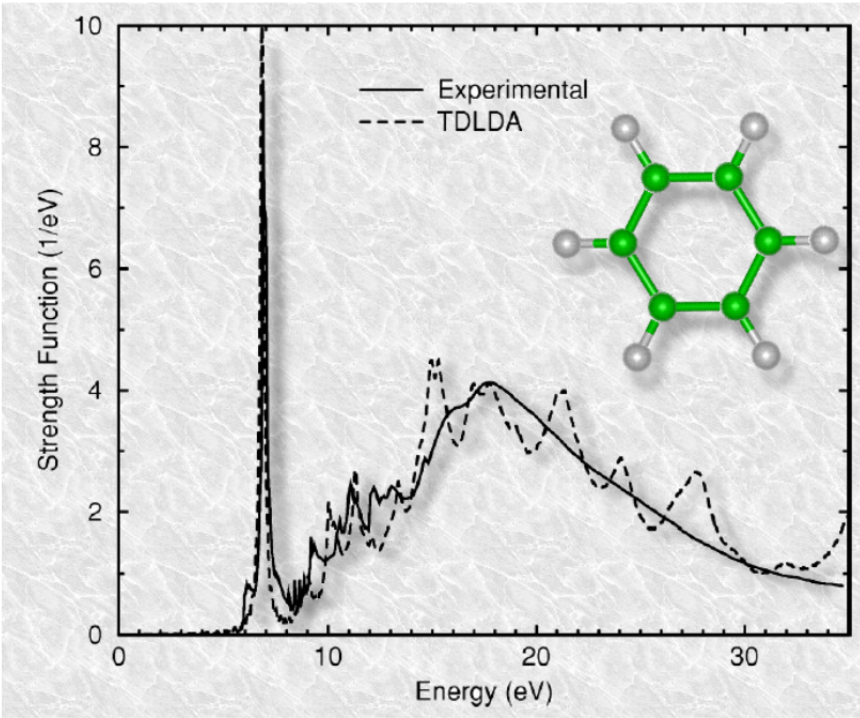
- AGGA

- Orbital dependent (OEP, TDEXX, hybrids, BSE-derived)

TDDFT applications

- Absorption spectra of simple molecules
- Loss function of metals and semiconductors

Benzene



Yabana and Bertsch Int.J.Mod.Phys.**75**, 55 (1999)

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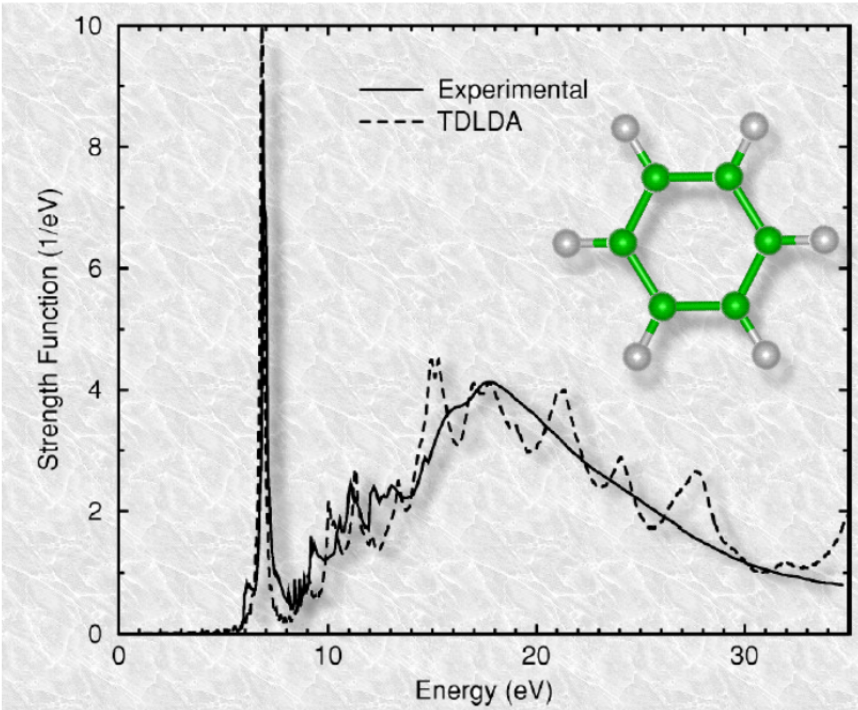
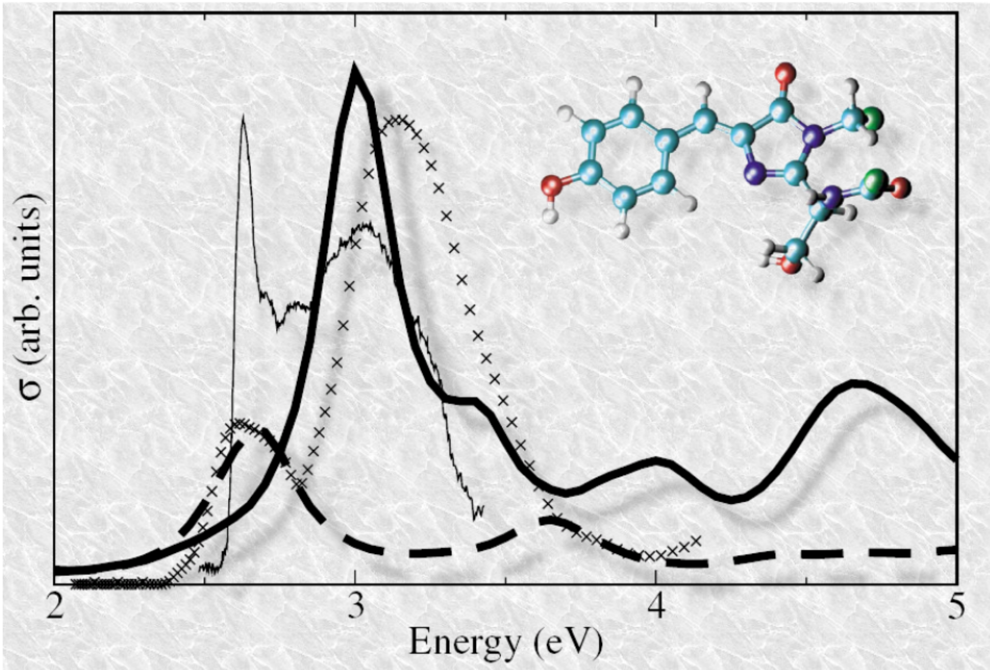


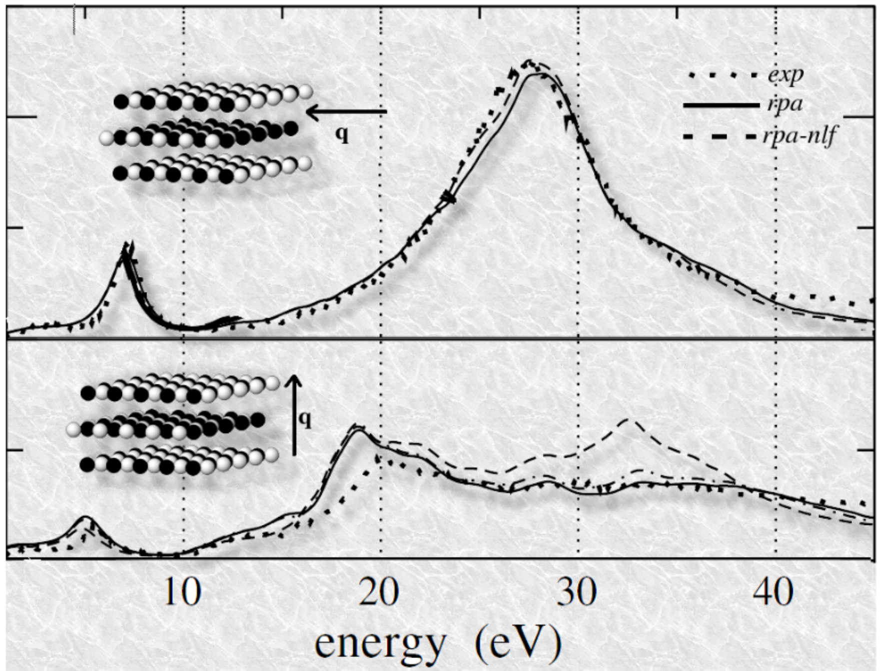
Yabana and Bertsch Int.J.Mod.Phys.**75**, 55 (1999)

GFP

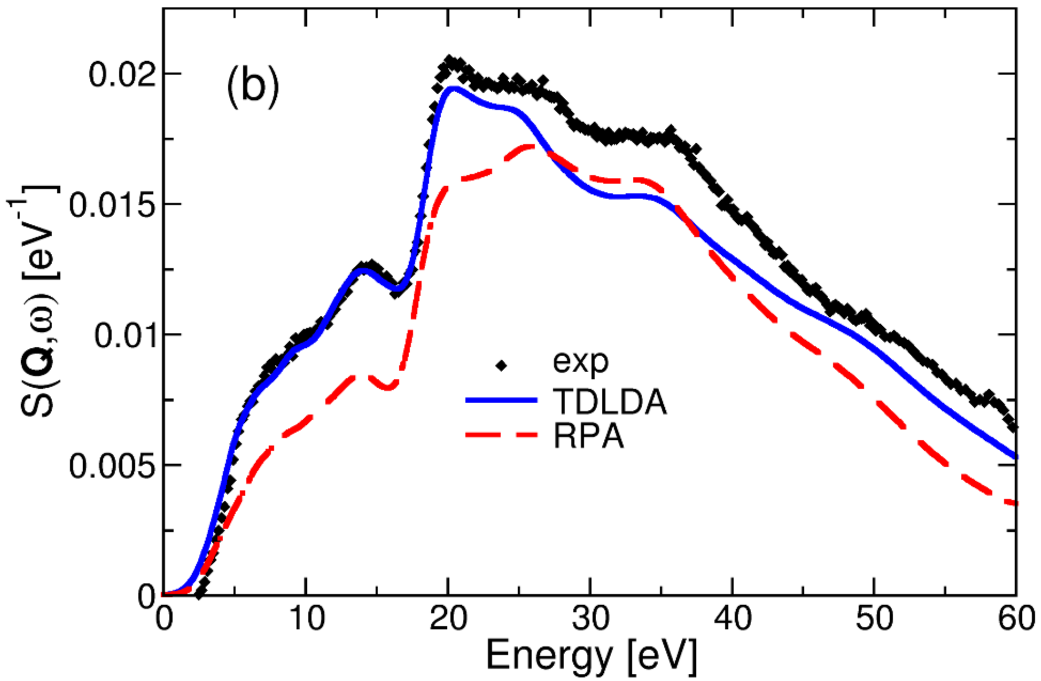


M.Marques *et al.* Phys.Rev.Lett. **90**, 258101 (2003)

Graphite



Silicon



A.Marinopoulos et al. Phys.Rev.Lett **89**, 76402 (2002)

Weissker *et al.* Phys. Rev. B **81**, 085104 (2010)

TDDFT applications

- Absorption spectra of simple molecules
- Loss function of metals and semiconductors
- Qualitatively first step

  → strong field phenomena

  → open quantum systems

  → superconductivity

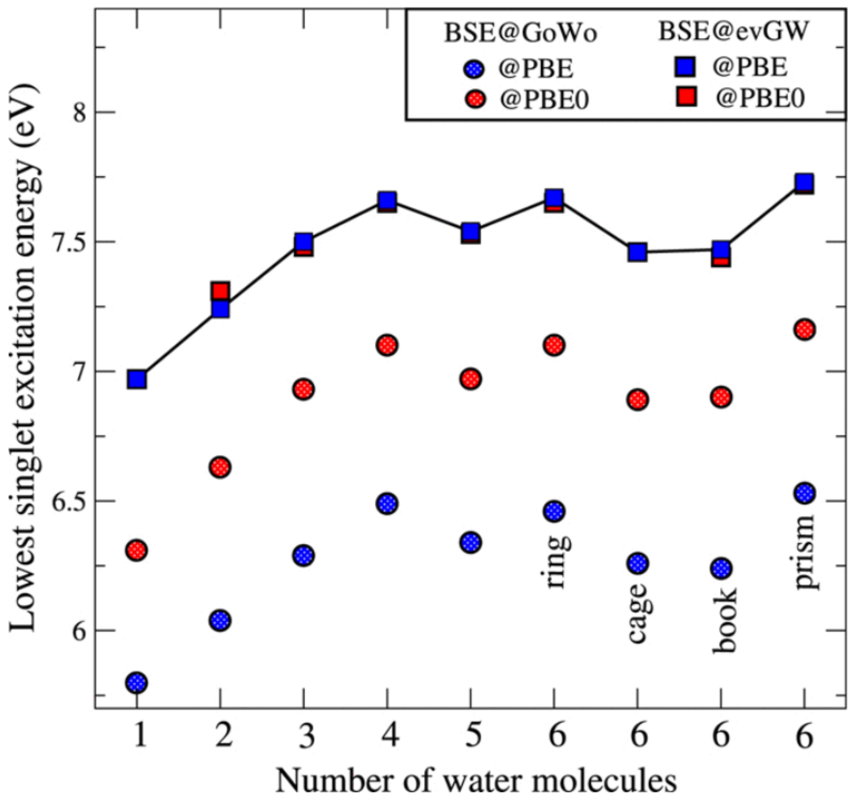
  → quantum optimal control

  → beyond BO dynamics

  → quantum transport

  → .....

Excitation energies of water clusters



Blase *et al.* . Chem. Phys. **144**, 034109 (2016)

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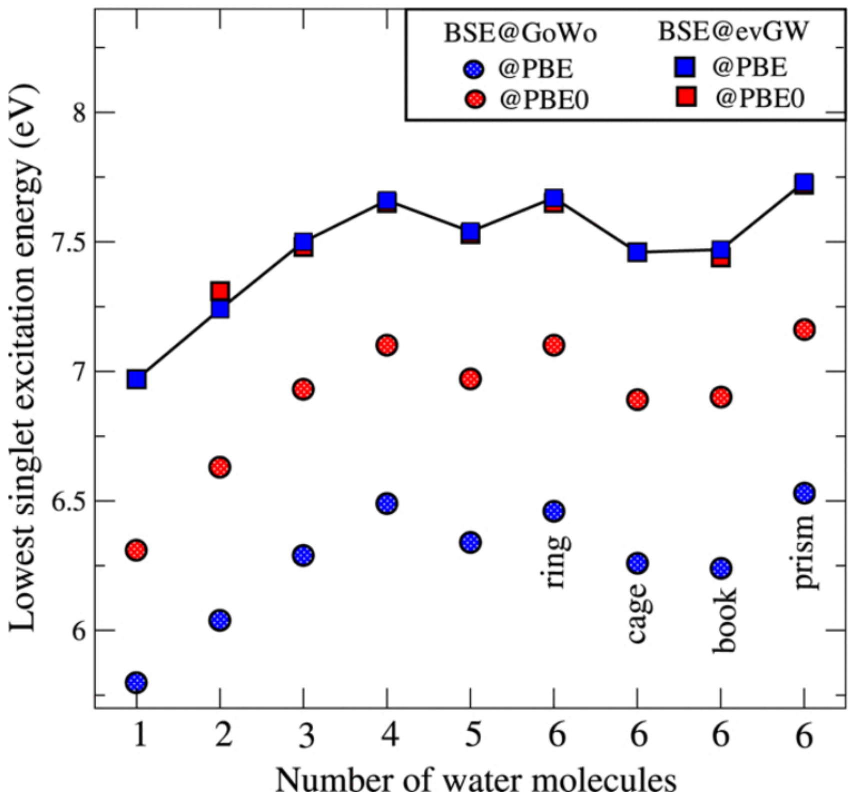
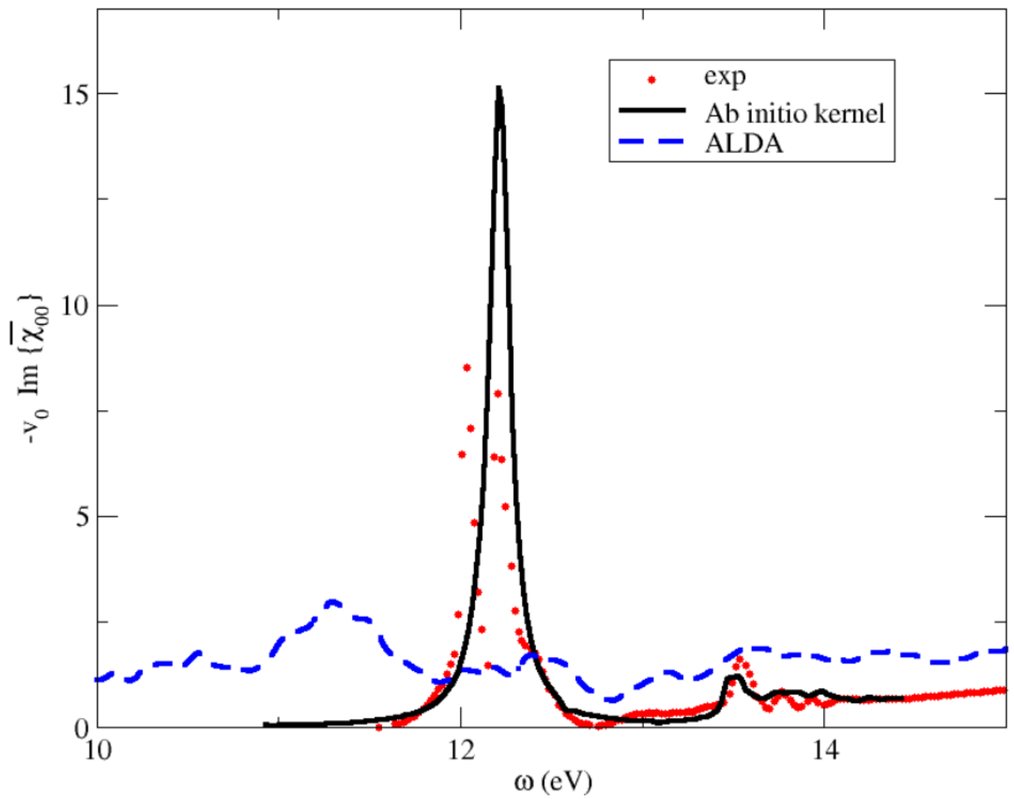


Blase *et al.* . Chem. Phys. **144**, 034109 (2016)

Abs of solid Argon



Marsili *et al.* Phys. Rev. B **76**, 161101(R) (2007)

TDDFT challenges

TDDFT challenges

$\frac{1}{r}$ tail

no memory

burden to v_{xc}, f_{xc}

operator in term of the density

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Demonstration of the Runge Gross theorem

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1) $V_{\mathrm{ext}}(\mathbf{r},t) \neq V'_{\mathrm{ext}}(\mathbf{r},t) + c(t) \quad \longleftrightarrow \quad \mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t)$

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$$= n_0(\mathbf{r})\nabla\left[v_{\rm ext}(\mathbf{r},0) - v'_{\rm ext}(\mathbf{r},0)\right]$$

if two potentials differ by more than a constant at t=0, they will generate two different current densities

$$i\frac{\partial\left[\mathbf{j}(\mathbf{r}),H(t)\right]}{\partial t} = \langle\Psi(t)|\Big[\left[\mathbf{j}(\mathbf{r}),H(t)\right],H\Big]|\Psi(t)\rangle$$

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$$\Big\Downarrow\ v_{\rm ext}\quad \text{Taylor expandable (in t)}$$

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$$\vdots$$

$$i\frac{\partial^{k+1}}{\partial t^{k+1}}\left[\mathbf{j}(\mathbf{r},t) - \mathbf{j}'(\mathbf{r},t)\right]\Big|_{t=t_0} = n_0(\mathbf{r})\nabla\,\frac{\partial^k}{\partial t^k}\left[v_{\mathrm{ext}}(\mathbf{r},t) - v'_{\mathrm{ext}}(\mathbf{r},t)\right]\Big|_{t=0}$$

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two different potentials will generate two different current densities

Demonstration of the Runge Gross theorem

2) $\mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t) \quad \longleftrightarrow \quad n(\mathbf{r},t) \neq n'(\mathbf{r},t)$

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2) $\mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t) \quad \longleftrightarrow \quad n(\mathbf{r},t) \neq n'(\mathbf{r},t)$

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Demonstration of the Runge Gross theorem

2) $\mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t) \quad \longleftrightarrow \quad n(\mathbf{r},t) \neq n'(\mathbf{r},t)$

$$i\frac{\partial^{k+2}}{\partial t^{k+2}}\left[n(\mathbf{r},t) - n'(\mathbf{r},t)\right]\Big|_{t=0} = \nabla \cdot \left[n_0(\mathbf{r})\nabla \frac{\partial^k}{\partial t^k}\left[v_{\text{ext}}(\mathbf{r},t) - v'_{\text{ext}}(\mathbf{r},t)\right]\Big|_{t=0}\right.$$

two different potentials will generate two different densities

provided that the surface integral does not vanish

Time evolution operator

$$i\frac{\partial\psi(\mathbf{r},t)}{\partial t} = H(t)\psi(\mathbf{r},t) \quad \longrightarrow \quad i\frac{dU(t,t_0)}{dt} = H(t)U(t,t_0)$$

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$$-i\int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \int_{t_0}^{\tau_2} d\tau_3 H(\tau_1)H(\tau_2)H(\tau_3) + \quad \ldots$$

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$$U(t,t_0) = 1 + \sum_{n=1}^{\infty} (-i)^n \int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \cdot\cdot \int_{t_0}^{\tau_{n-1}} d\tau_n H(\tau_1)H(\tau_2)\cdot\cdot H(\tau_n)$$

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time integrators problem

exponential operator

second-order differencing

Crank-Nicholson implicit midpoint

predictor-corrector (see Ivan's poster)

splitting techniques

Magnus expansion

exponential midpoint

$$U(t+\delta t, t) = e^{-i\delta t H(t+\delta t/2)}$$

Taylor expansion

Chebychev polynomials

Lanczos iterative scheme