Future directions in electronic structure methods

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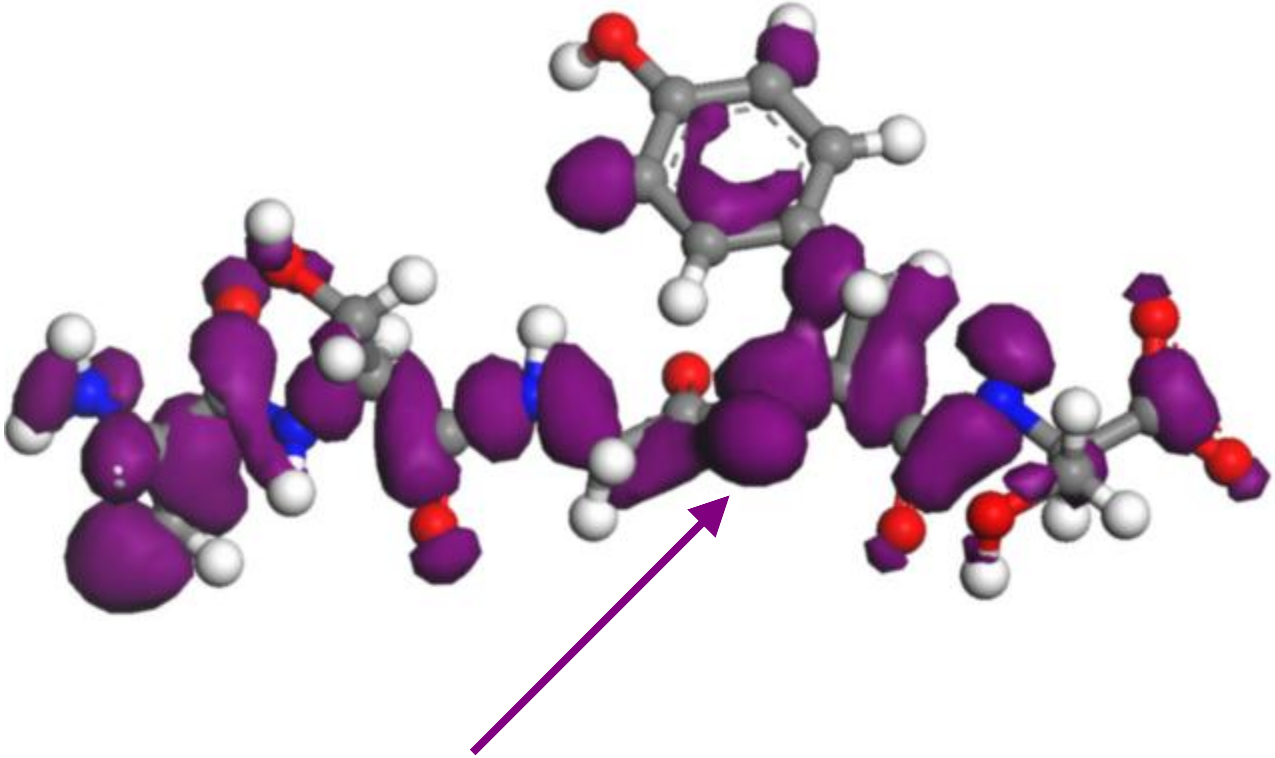
Outline

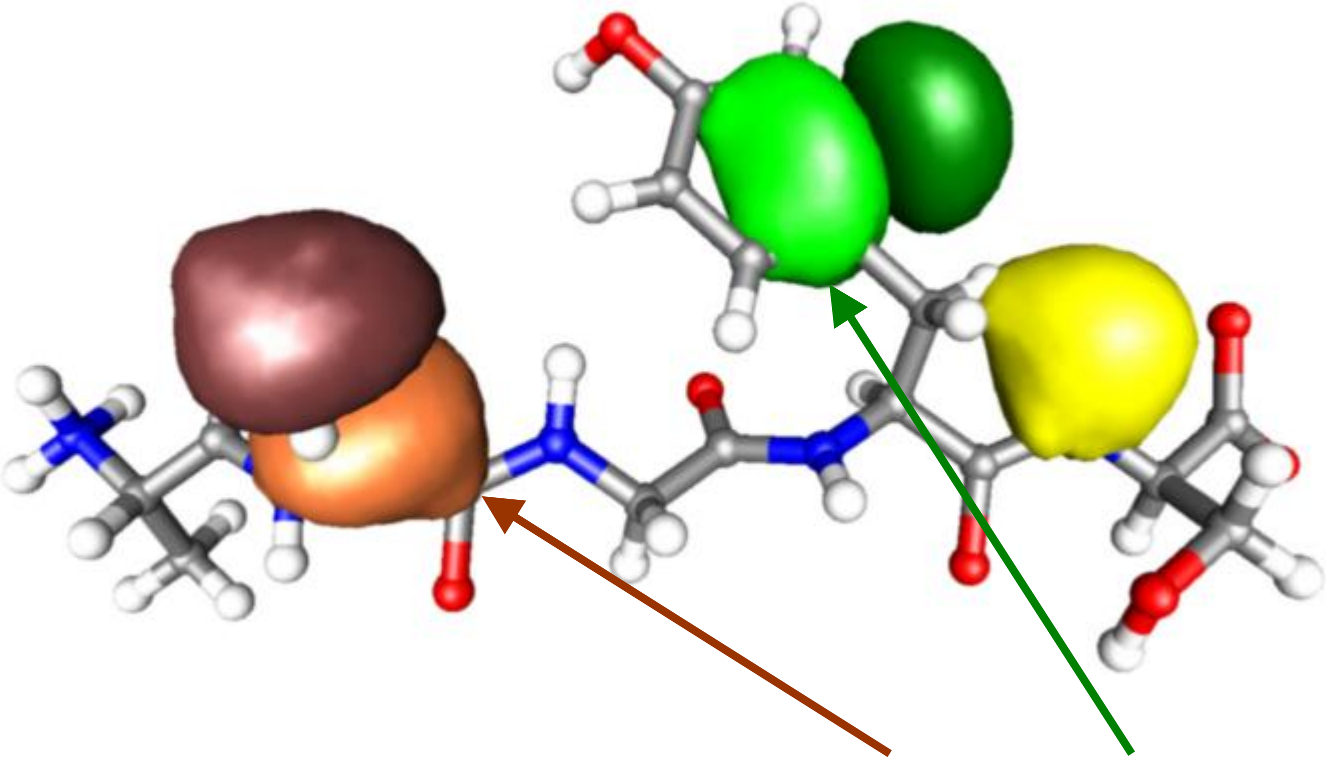
- Linear-scaling DFT
- Time-dependent DFT
- *GW* approximation
- Bethe-Salpeter equation
- Quantum Monte Carlo

Density-matrix formulation



$$\rho(\mathbf{r},\mathbf{r}') = \sum_n f_n\, \psi_n(\mathbf{r})\, \psi_n^*(\mathbf{r}')$$

Density-matrix formulation



$$\rho(\mathbf{r},\mathbf{r}') = \sum_n f_n \, \psi_n(\mathbf{r}) \, \psi_n^*(\mathbf{r}') = \sum_{\alpha\beta} \phi_\alpha(\mathbf{r}) \, K^{\alpha\beta} \, \phi_\beta^*(\mathbf{r}')$$

Galli & Parrinello, *Phys. Rev. Lett.* **69**, 3547 (1992)
Hernández & Gillan, *Phys. Rev. B* **51**, 10157 (1995)

Density-matrix properties

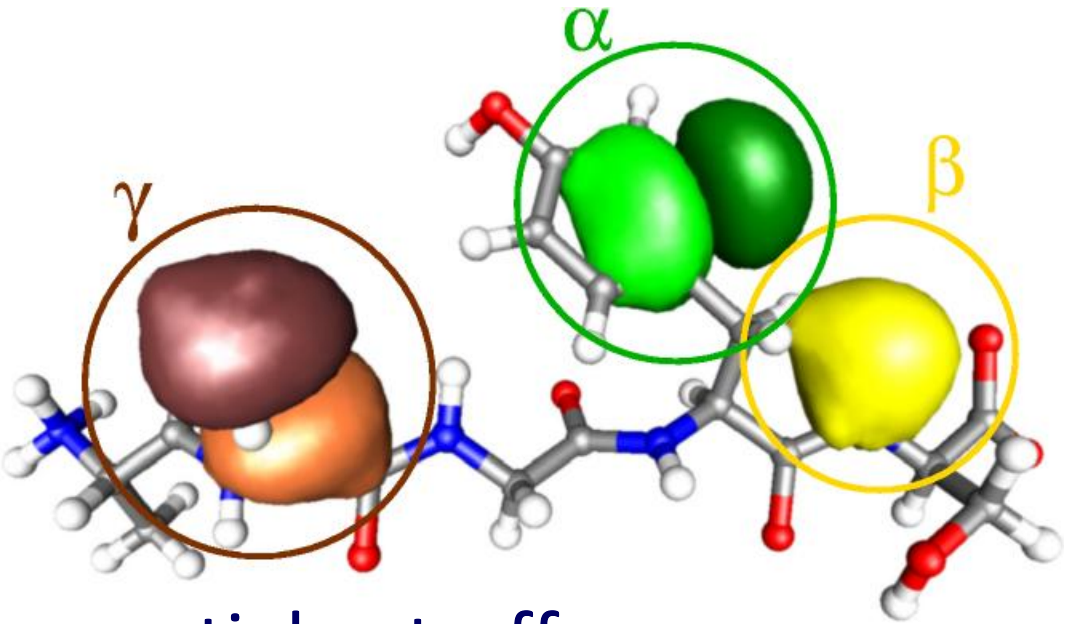
- Compatibility: $[\rho, H] = 0$
- Normalisation: $\mathrm{Tr}[\rho] = N$
- Idempotent: $\rho^2 = \rho$
- Short-ranged (nearsighted):

$$\rho(\mathbf{r}, \mathbf{r}') \longrightarrow 0 \quad \text{as} \quad |\mathbf{r} - \mathbf{r}'| \longrightarrow \infty$$

  - exponentially in insulators
  - algebraically in metals

Density-matrix formulation

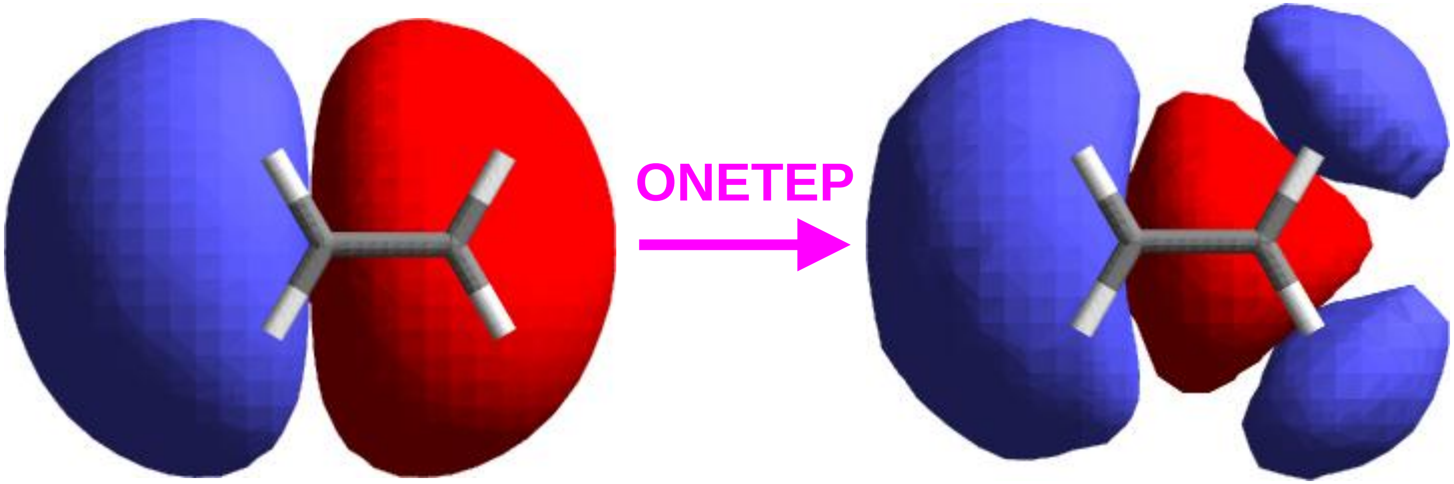
$$\rho(\mathbf{r},\mathbf{r}') = \sum_{\alpha\beta} \phi_\alpha(\mathbf{r}) K^{\alpha\beta} \phi_\beta(\mathbf{r}')$$



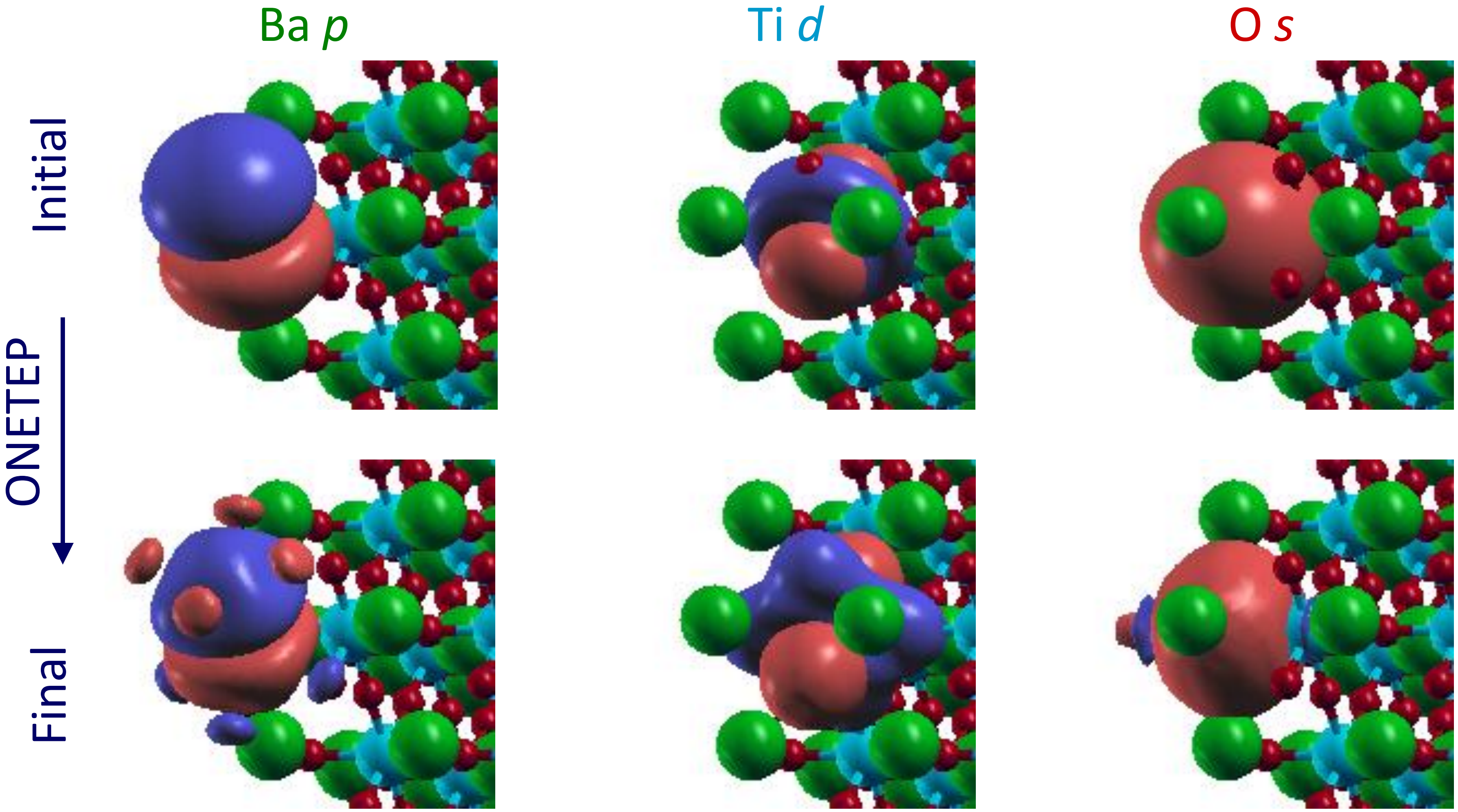
- Impose spatial cut-offs:
  - Non-orthogonal generalised Wannier functions
  - Sparse density kernel K

Local orbitals

1. Optimise local orbitals for isolated atoms
   - PLATO, SIESTA, $DMol^3$
   - increase size of orbital set to improve accuracy
2. Adapt local orbitals to each environment
   - greatest accuracy
   - minimal orbital set



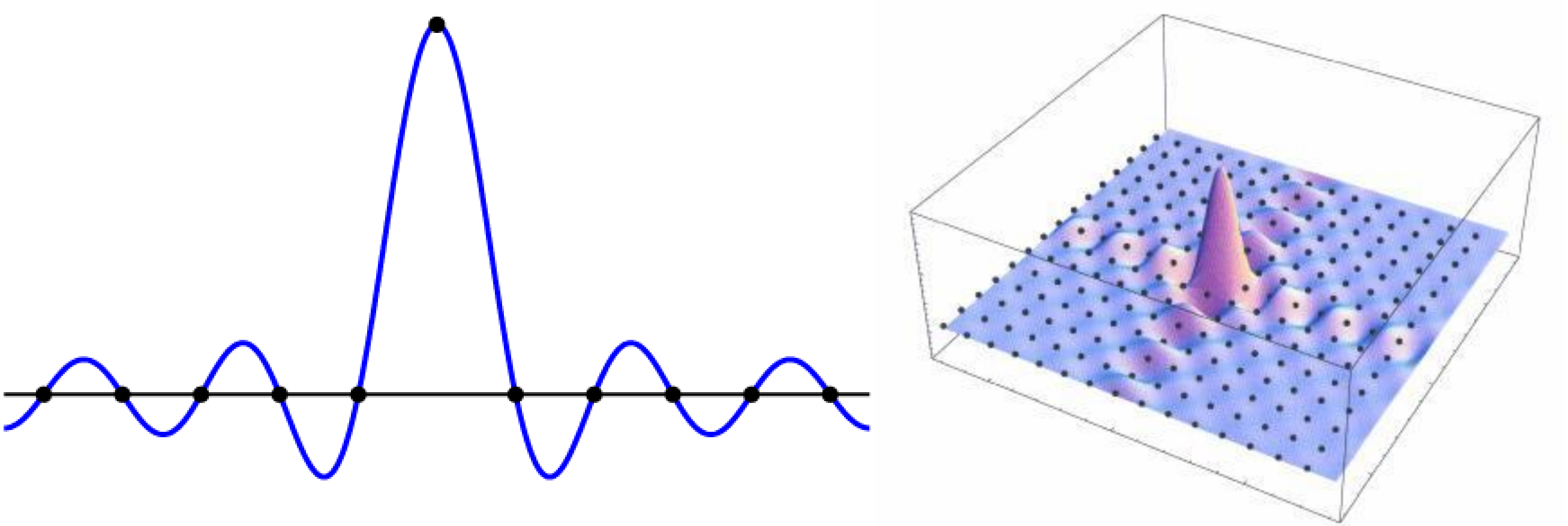
Local orbital optimisation



On-site rotation from Foster & Weinhold, *J. Am. Chem. Soc.* **102**, 7211 (1980)

Basis set: psincs

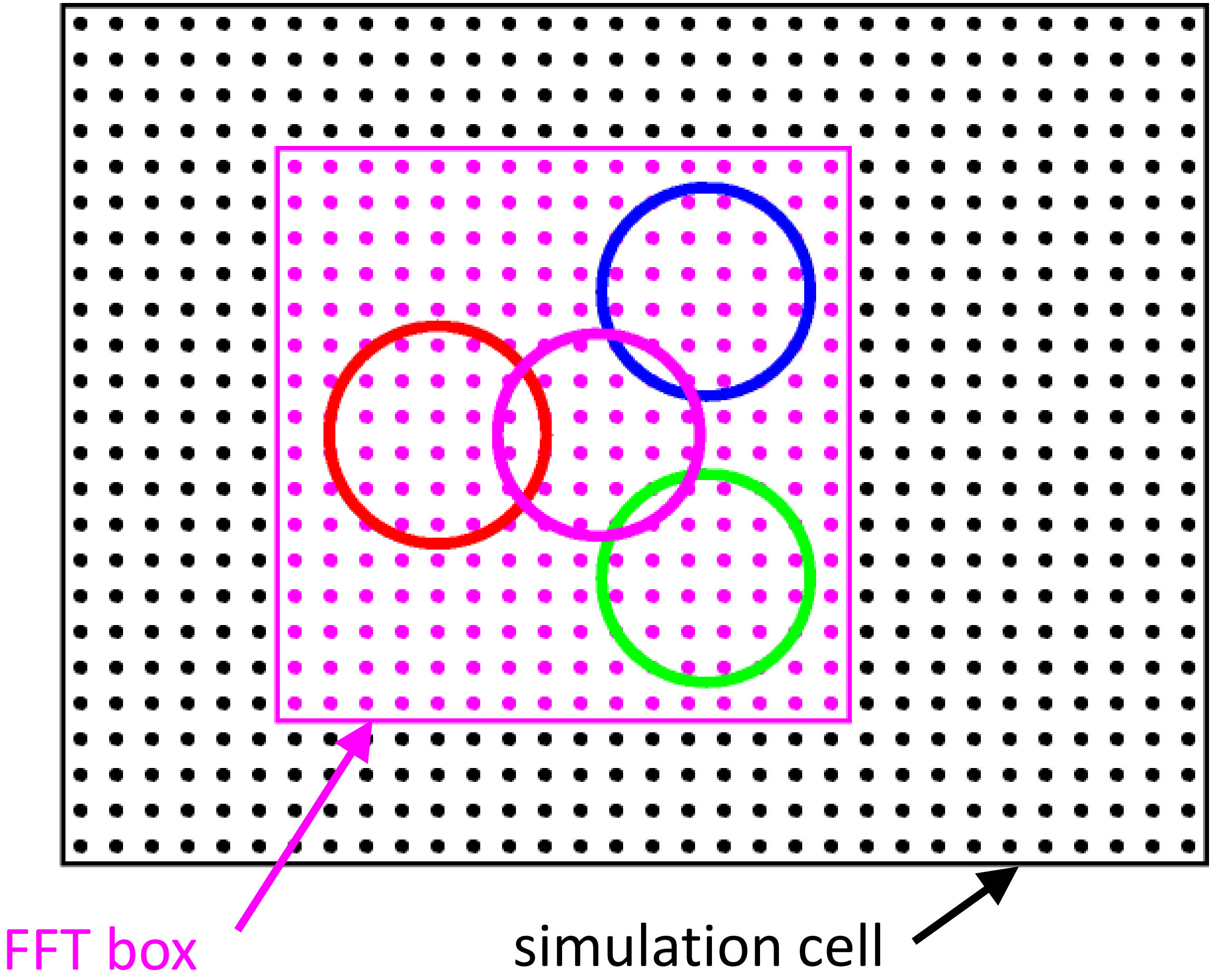
- “Periodic Cardinal Sine” or Dirichlet functions:



- Real linear combinations of plane-waves
- Localised
- Orthogonal

Mostofi, Haynes, Skylaris & Payne, *J. Chem. Phys.* **119**, 8842 (2003)

FFT box technique

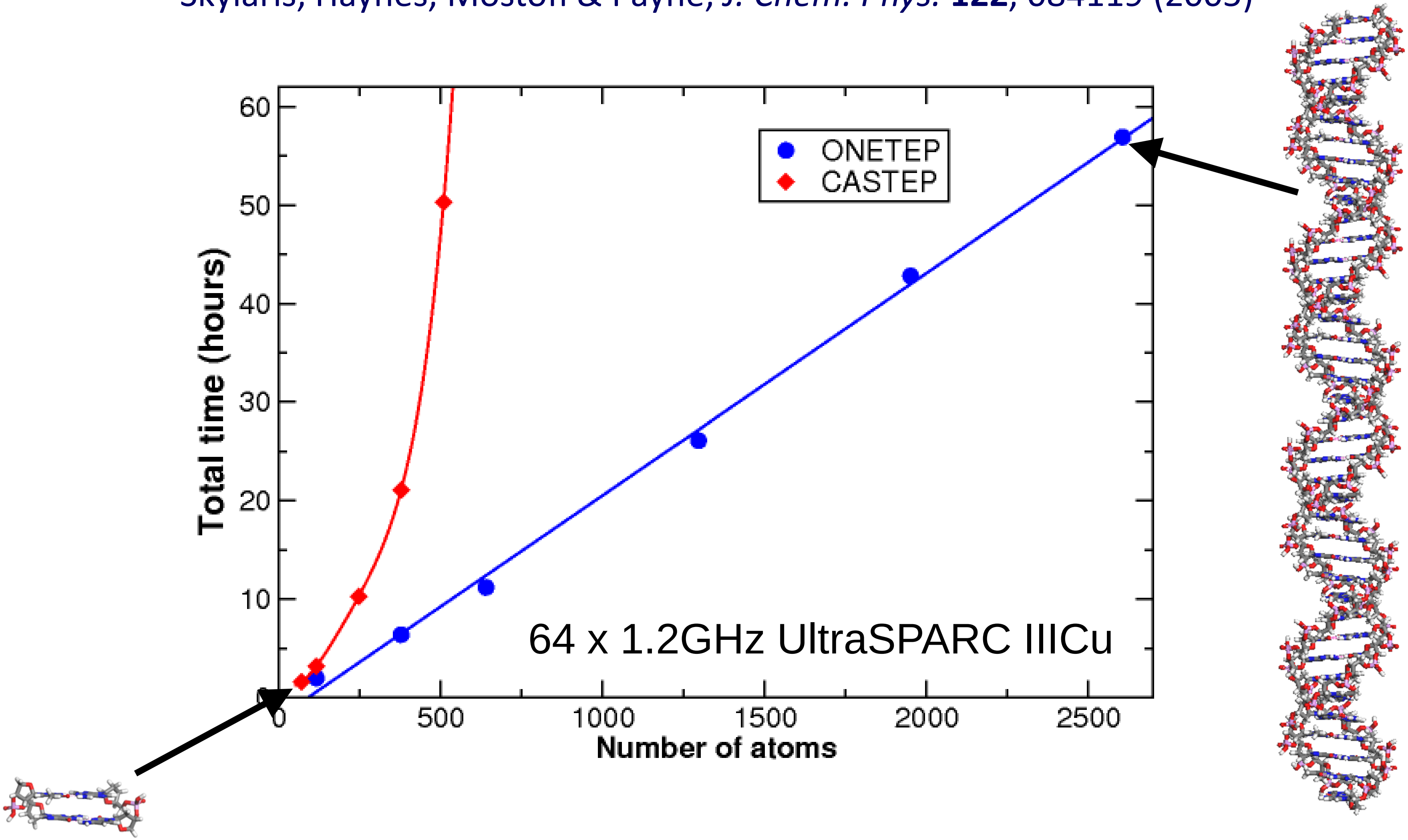


FFT box

simulation cell

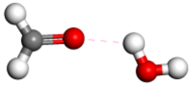
Linear scaling: DNA

Skylaris, Haynes, Mostofi & Payne, *J. Chem. Phys.* **122**, 084119 (2005)

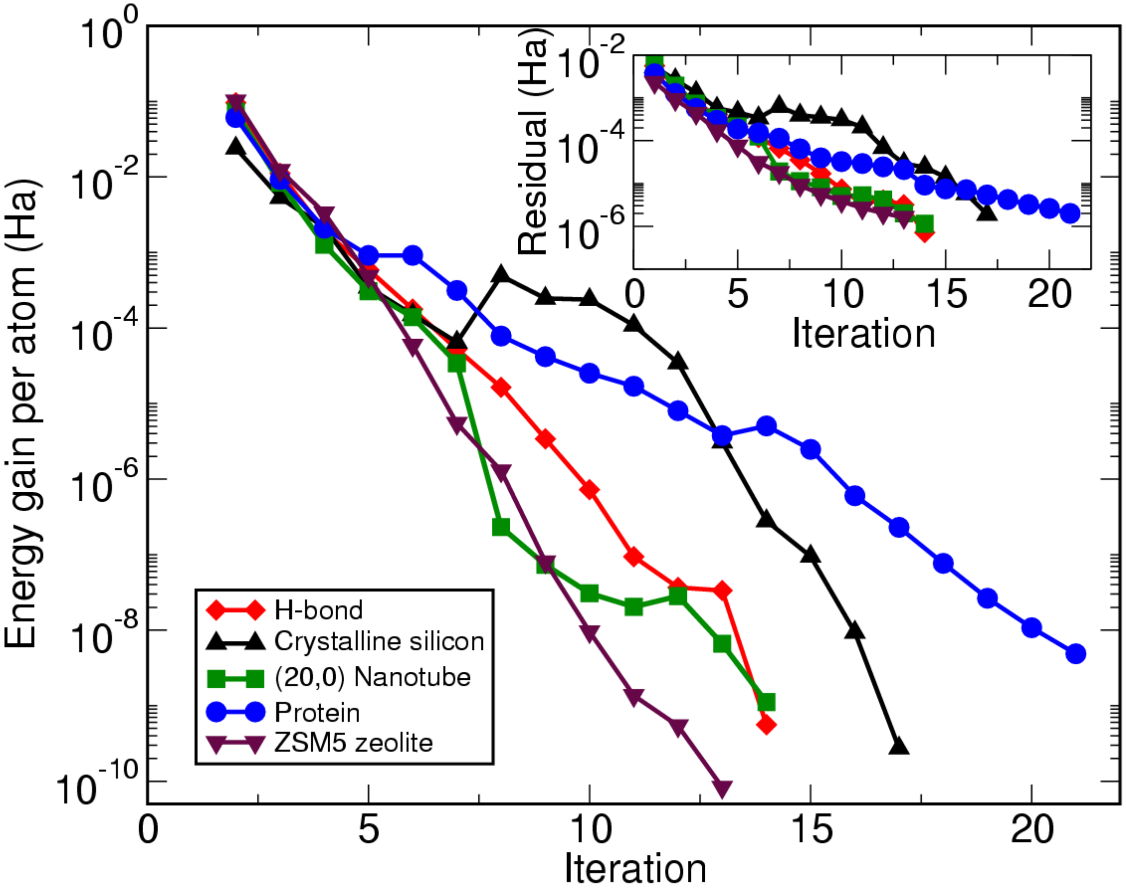


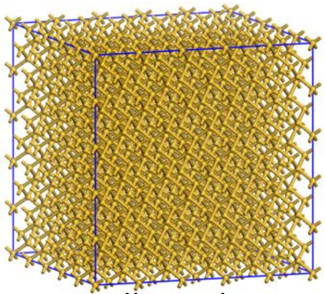
64 x 1.2GHz UltraSPARC IIICu

True linear scaling

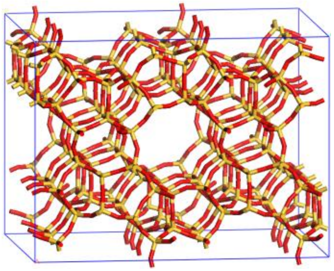


H-bond (7 atoms)

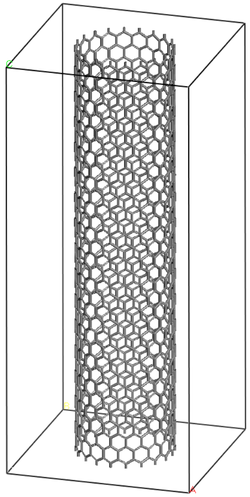




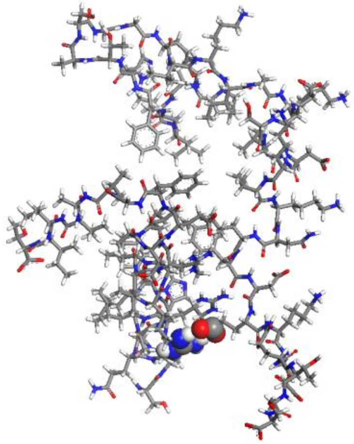
Crystalline silicon (1000 atoms)



ZSM5 zeolite (576 atoms)



(20, 0) Nanotube (1280 atoms)



Protein (988 atoms)

Skylaris, Haynes, Mostofi & Payne, *J. Phys.: Condens. Matter* **17**, 5757 (2005)

Band structure

- Compare bandstructure in detail:
  - generate Bloch functions from NGWFs:

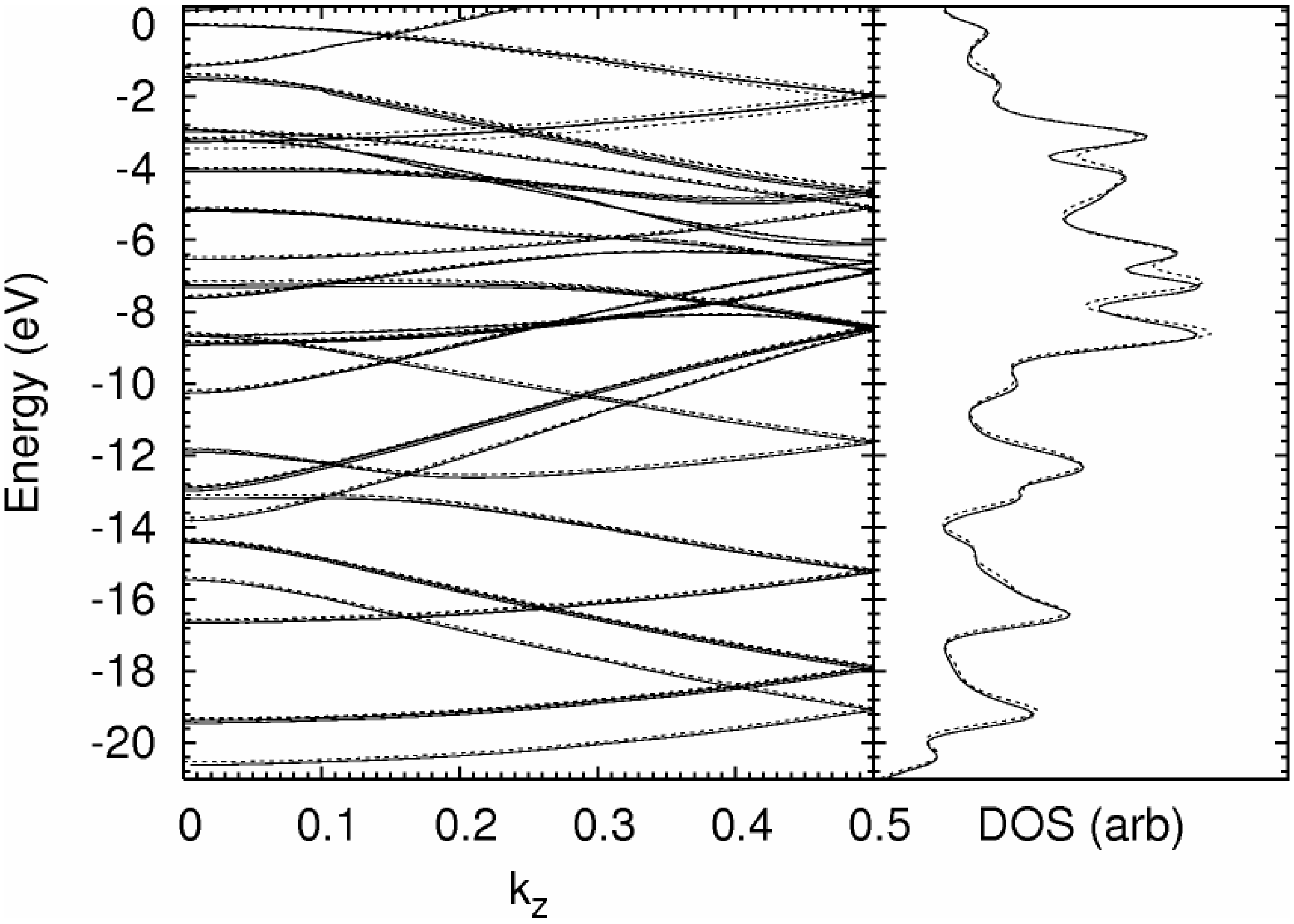
$$\psi_{n\mathbf{k}}(\mathbf{r}) = \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \sum_{\alpha} c_{n\mathbf{k}\alpha} \phi_{\alpha}(\mathbf{r})$$

  - diagonalise a modified Hamiltonian for each **k**-point:

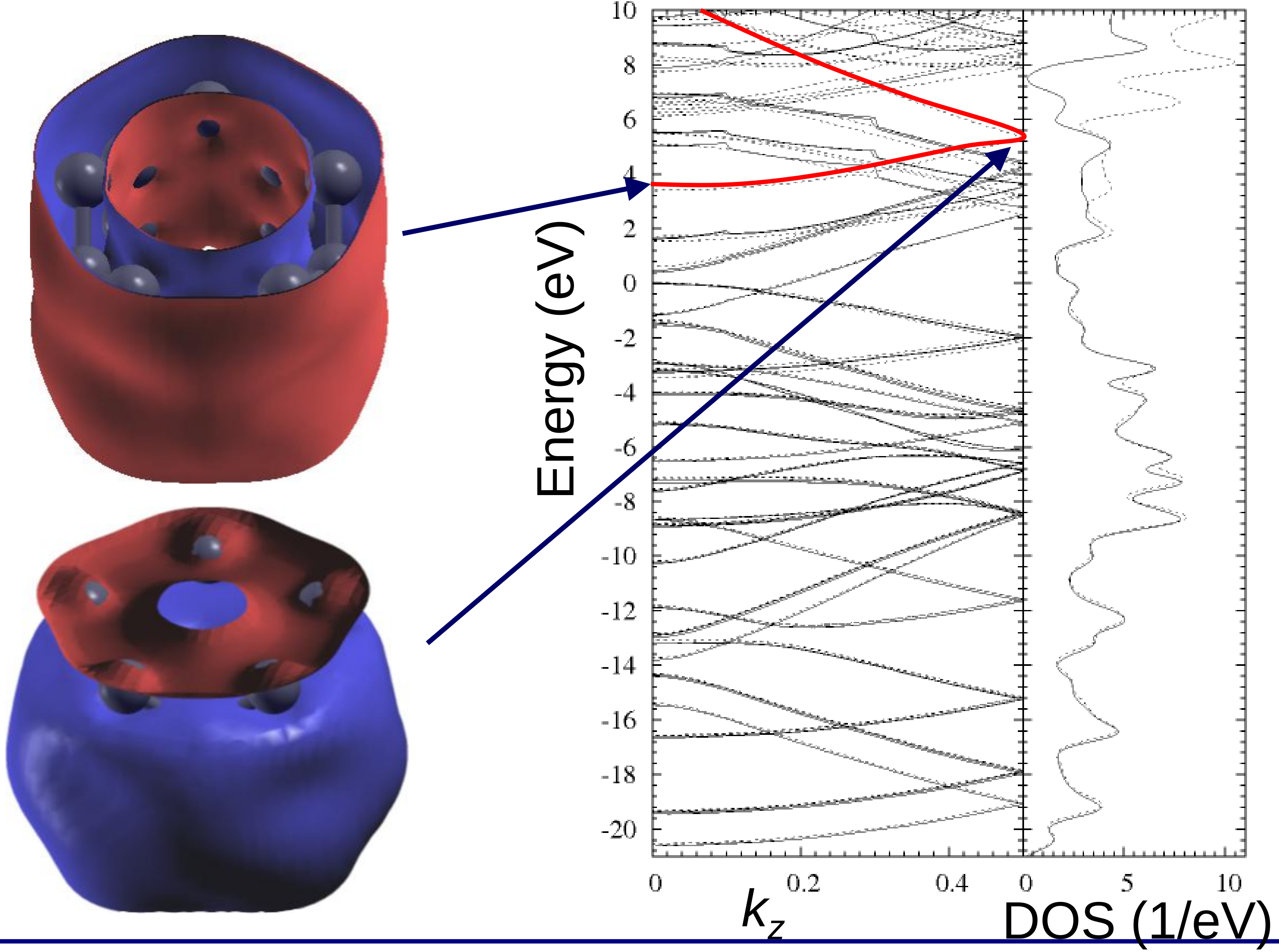
$$H(\mathbf{k}) = H(\Gamma) + \mathbf{k}\cdot\mathbf{p} + \tfrac{1}{2}k^2 S + \Delta V_{\mathrm{NL}}(\mathbf{k})$$

Nanotube band structure

(5,0) nanotube

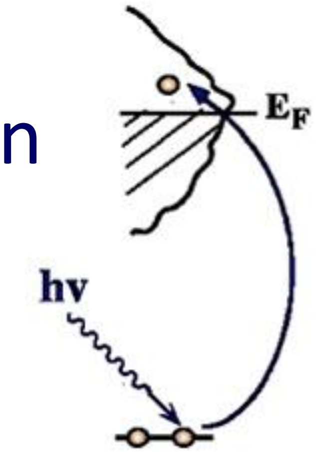


Nanotube band structure

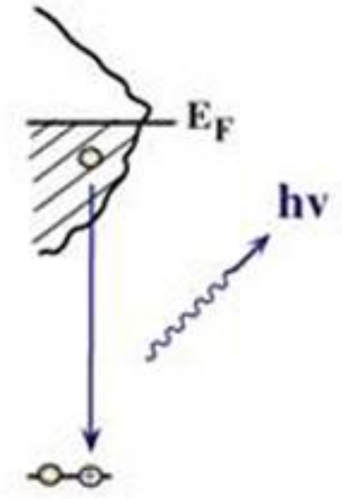


X-ray spectroscopy

Absorption
(XAS)

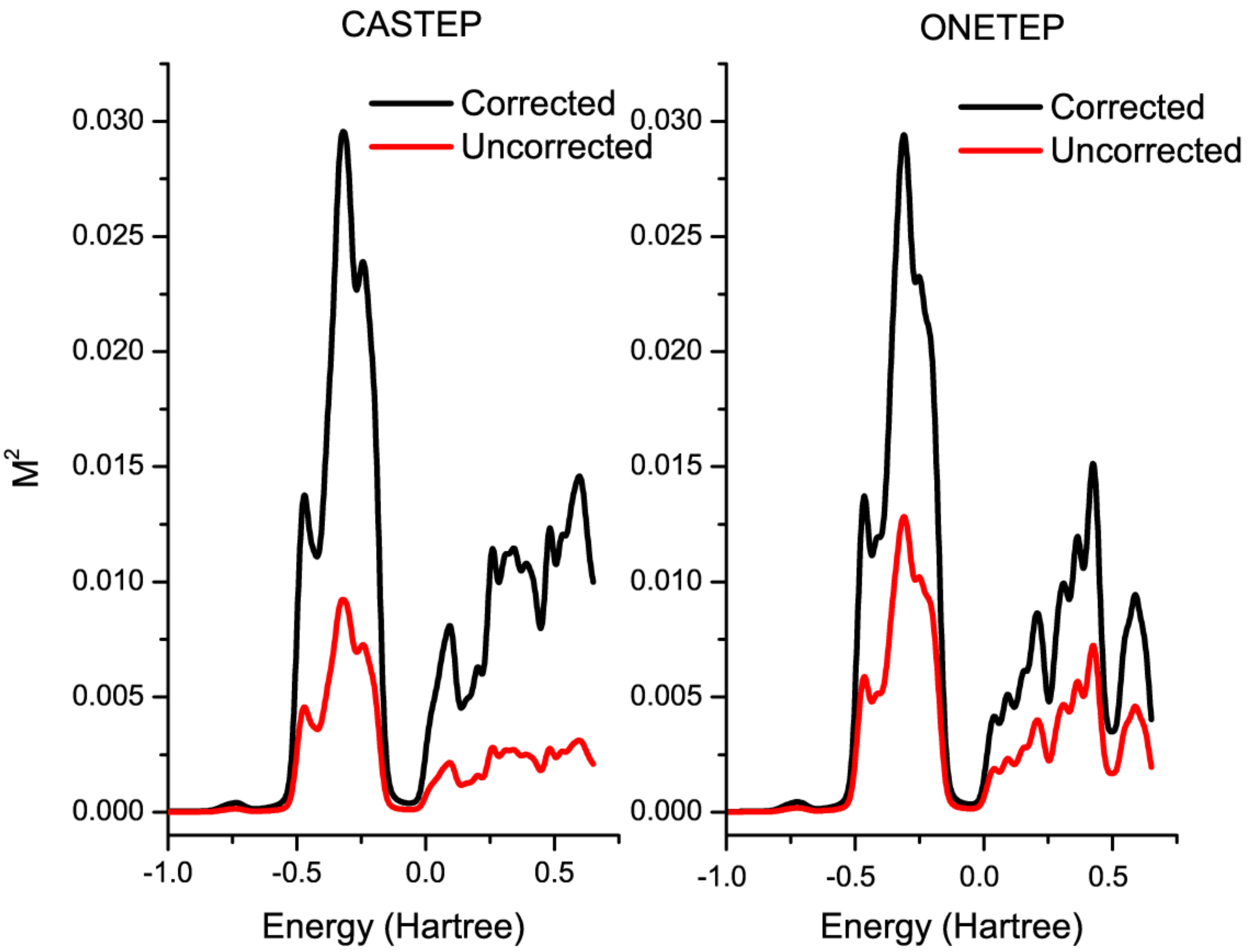


Emission
(XES)



$$
\begin{aligned}
\sigma(\omega) &= \frac{\pi e^2}{\epsilon_0 m_e^2 \omega c} \sum_n \left| \langle \psi_n | \mathrm{e}^{\mathrm{i}(\omega/c)\mathbf{n}\cdot\mathbf{r}} \varepsilon \cdot \mathbf{p} | \psi_\mathrm{c} \rangle \right|^2 \delta(E_n - E_\mathrm{c} - \hbar\omega) \\
&= -\frac{1}{\pi} \mathrm{Im} \sum_{\alpha\beta} \langle \psi_\mathrm{c} | \hat{O} | \phi_\alpha \rangle \left[\{ (\hbar\omega + E_\mathrm{c}) S - H \}^{-1} \right]^{\alpha\beta} \langle \phi_\beta | \hat{O} | \psi_\mathrm{c} \rangle
\end{aligned}
$$

X-ray spectroscopy



Summary of linear-scaling DFT

- True linear scaling
- Plane-wave accuracy
- Parallel scaling

✓ Insulators and semiconductors
✗ Metals

✓ Total energies
✓ Valence band
✗ Conduction band

Outlook for linear-scaling DFT

- General purpose total energy and force codes now available
- ONETEP is similar to CASTEP in some principles and operation
  - www.onetep.org
- Work in progress:
  - generate local orbitals for conduction bands
  - time-dependent DFT
  - NMR spectroscopy

Time-dependent DFT

- One-to-one correspondence:

$$V_{\text{ext}}(\mathbf{r},t) \leftrightarrow n(\mathbf{r},t)$$

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

- Time-dependent Kohn-Sham:

$$i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r},t) + V_{\text{eff}}[n](\mathbf{r},t)\psi(\mathbf{r},t)$$

$$V_{\text{eff}}[n](\mathbf{r},t) = V_{\text{ext}}(\mathbf{r},t) + \int\frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d^3r' + V_{\text{xc}}[n](\mathbf{r},t)$$

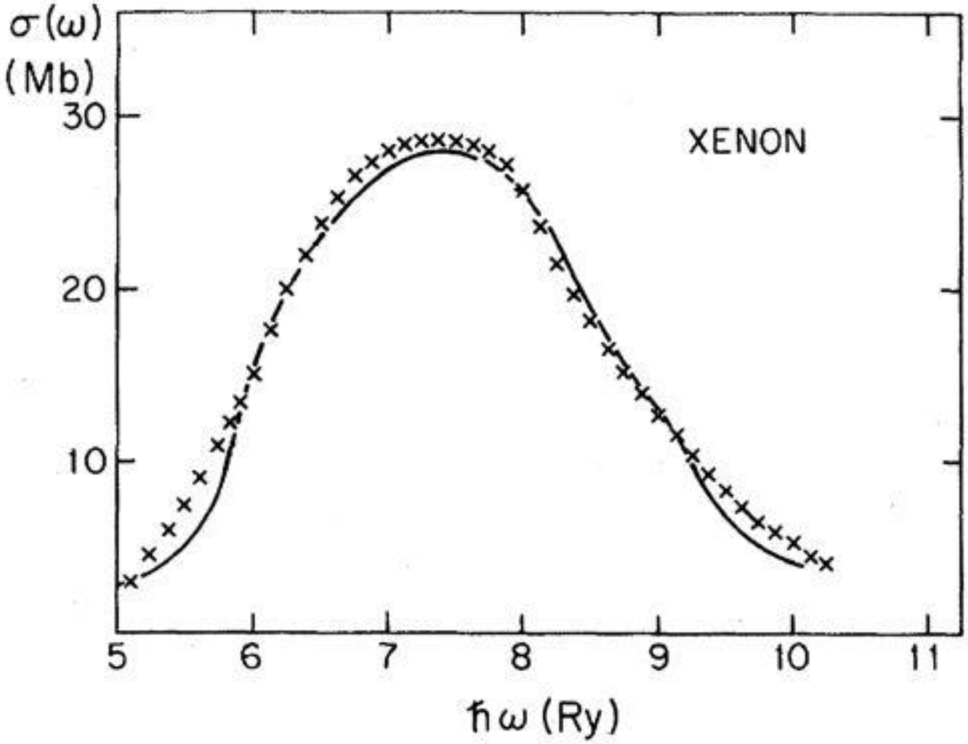
Exchange-correlation potential

$$V_{\text{eff}}[n](\mathbf{r},t) = V_{\text{ext}}(\mathbf{r},t) + \int \frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} d^3r' + V_{\text{xc}}[n](\mathbf{r},t)$$

- Simplest: *adiabatic* local density approximation:
  - Local in space
  - *and* ‘local’ in time

Time evolution

- Integrate the TD Kohn-Sham equations in the presence of a time-dependent potential e.g. field due to an intense laser pulse



Total photoabsorption cross section of the Xe atom versus photon energy.
Line (theory): Zangwill and Soven, *Phys. Rev. A* **21**, 1561 (1980)
Crosses (expt): Hänsel *et al.*, *Phys. Rev.* **188**, 1375 (1969)

Linear response

- Calculate first order change in density due to perturbation in external potential
  - poles in the density-density response function correspond to excited states

$$\Delta E = \varepsilon_j - \varepsilon_k + \iint \psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_k(\mathbf{r}')\psi_k^*(\mathbf{r})\left[\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}';\omega)\right] d^3r\, d^3r'$$

$$\frac{\delta V_{\mathrm{xc}}(\mathbf{r},t)}{\delta n(\mathbf{r}',t')}$$

Atomic excitation energies

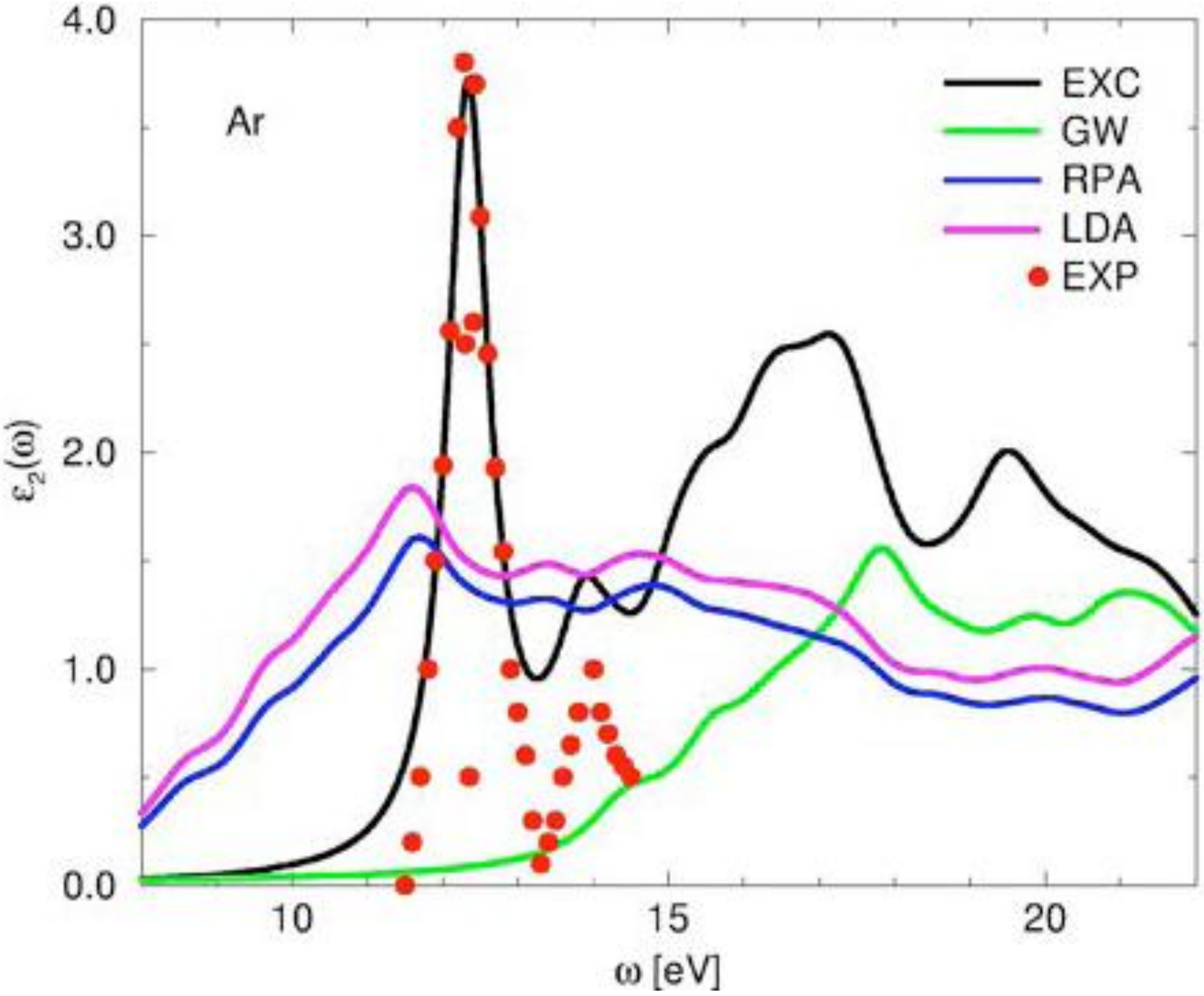
Atom	Experiment (Ry) $^1S \rightarrow {}^1P$	KS eigenvalues (Ry)	TDDFT-ALDA (Ry)
Be	0.388	0.257	0.399
Mg	0.319	0.249	0.351
Ca	0.216	0.176	0.263
Zn	0.426	0.352	0.477
Sr	0.198	0.163	0.241
Cd	0.398	0.303	0.427

Petersilka, Gossmann & Gross, *Phys. Rev. Lett.* **76**, 1212 (1996)

Failures of the ALDA

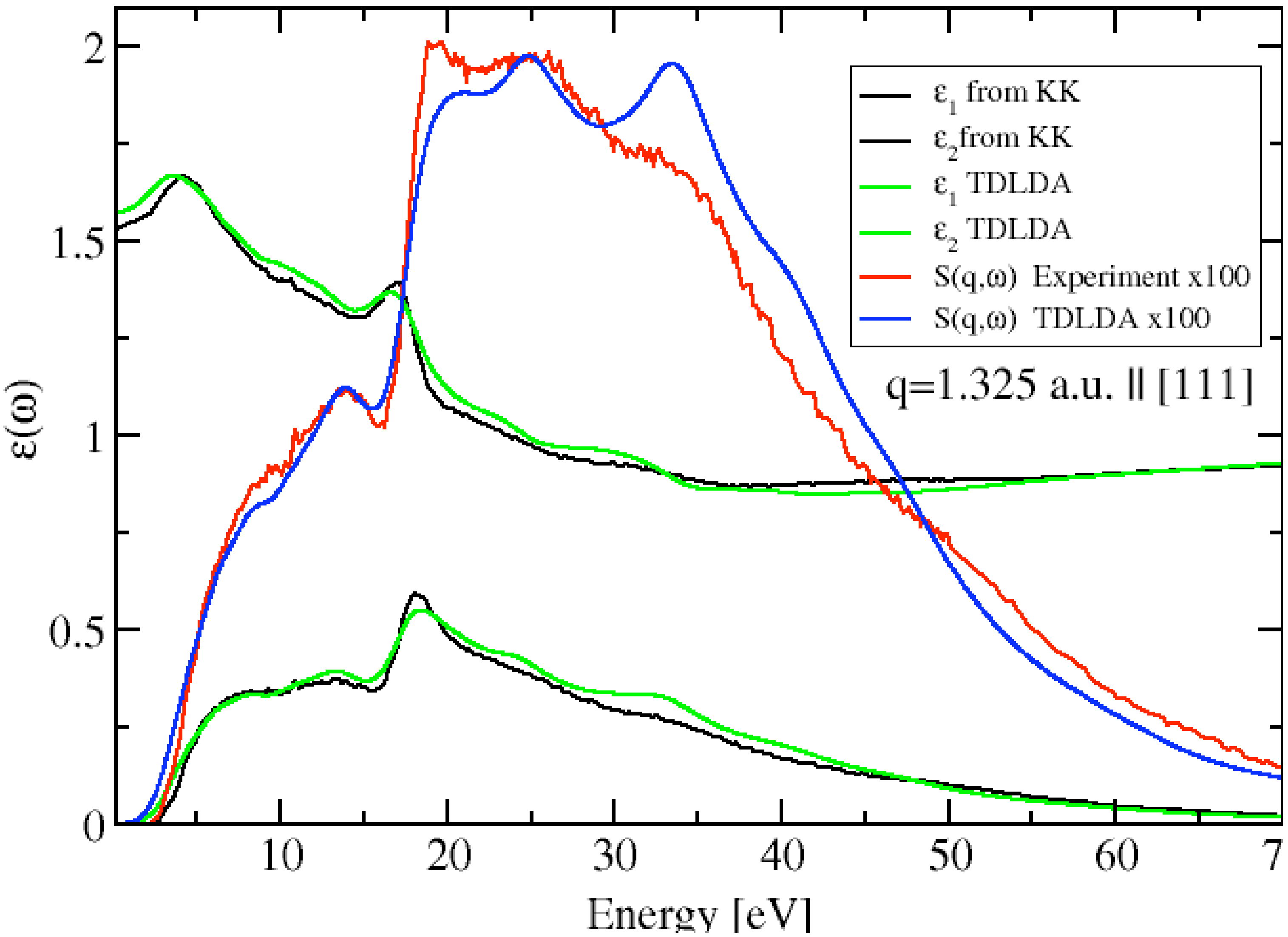
- H_2 dissociation wrong
- Response of long chains overestimated
- Charge transfer excitations incorrect
- In solids, f_{xc} lacks the correct $1/q^2$ divergence

Failure of the ALDA in solids



Optical absorption (q=0) of solid argon
Reining, Olevano, Rubio & Onida,
Phys. Rev. Lett. **88**, 066404 (2002)

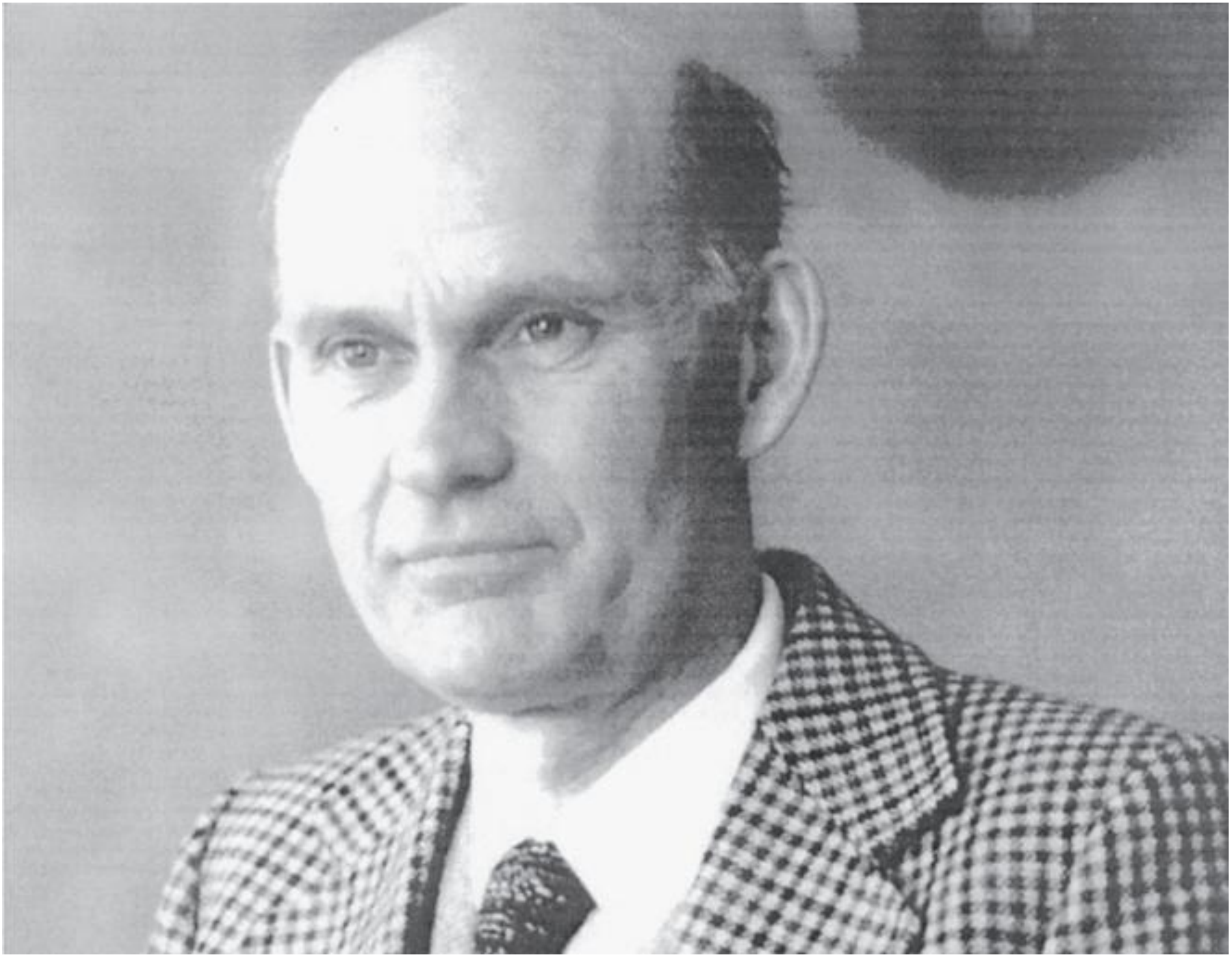
Dielectric function of Si



Outlook for TDDFT

- Relatively inexpensive
- Good for atoms and molecules
- Simple ALDA poor for solids as $q \rightarrow 0$
  - more sophisticated XC kernels with $1/q^2$ divergence required
- Similar problem to DFT in approximating exchange and correlation
- Widely available and coming to CASTEP...

GW approximation



GW approximation

- Many-body perturbation theory approach
- Hedin's coupled equations: *Phys. Rev.* **139,** A796 (1965)

$$\begin{aligned}
\Sigma(1,2) &= \mathrm{i}\int W\left(1^{+},3\right) G(1,4)\,\Gamma\cancel{(4,2,3)}\,\mathrm{d}(3,4)\\
P(1,2) &= -\mathrm{i}\int G(2,3)\,G(4,2)\,\Gamma\cancel{(3,4,1)}\,\mathrm{d}(3,4)\\
W(1,2) &= v(1,2)+\int W(1,3)\,P(3,4)\,v(4,2)\,\mathrm{d}(3,4)\\
\Gamma(1,2,3) &= \delta(1,2)\,\delta(1,3)\\
&\quad \xcancel{+\int \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6)\,G(7,5)\,\Gamma(6,7,3)\,\mathrm{d}(4,5,6,7)}
\end{aligned}$$

$\Sigma=0$

Quasiparticles

- Kohn-Sham equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V_{\text{ext}}(\mathbf{r})+V_{\text{H}}(\mathbf{r})\right]\psi_i(\mathbf{r})+V_{\text{xc}}(\mathbf{r})\psi_i(\mathbf{r})=\varepsilon_i\,\psi_i(\mathbf{r})$$

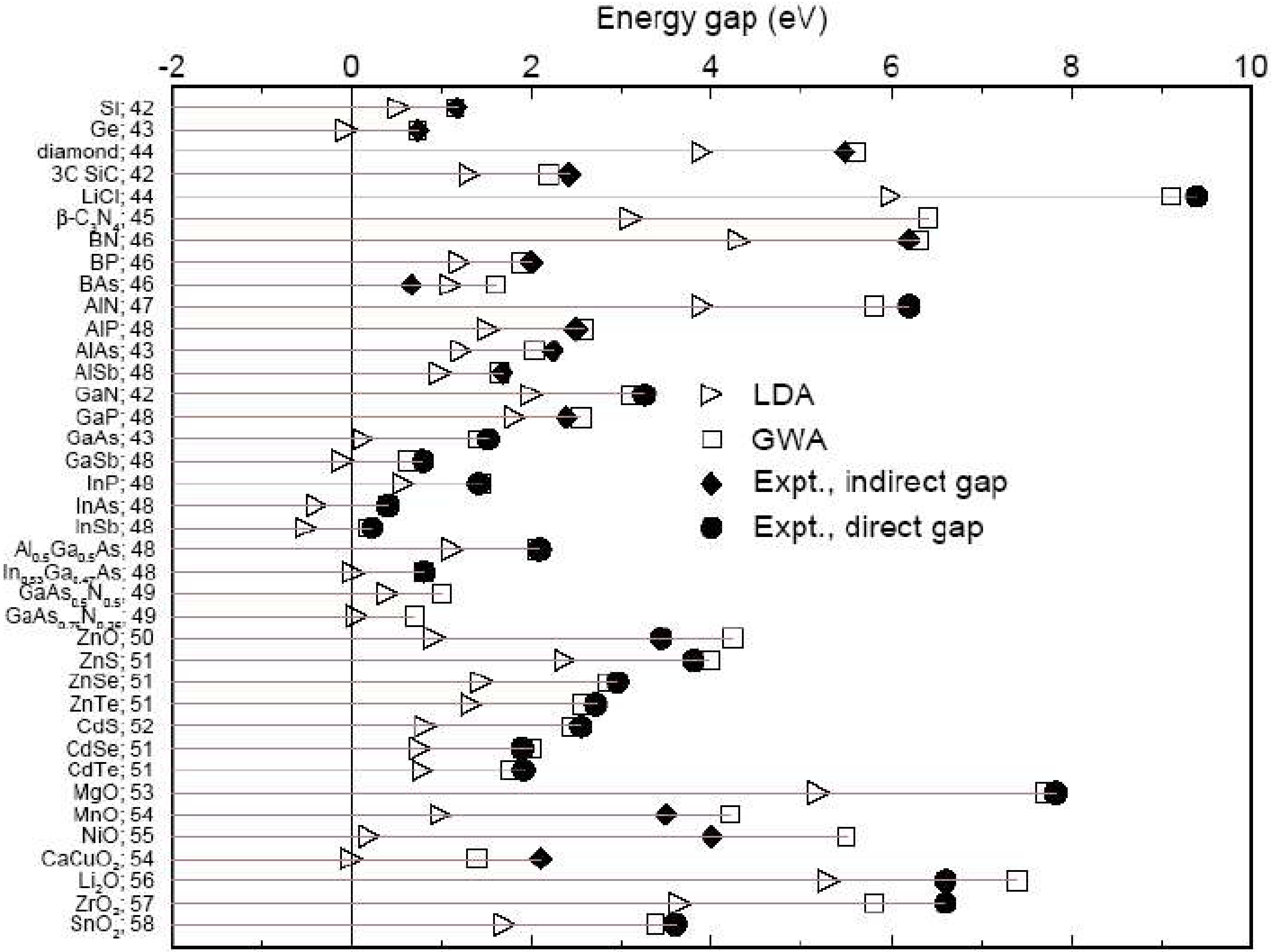
- Quasiparticle equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V_{\text{ext}}(\mathbf{r})+V_{\text{H}}(\mathbf{r})\right]\psi(\mathbf{r})+\int\Sigma(\mathbf{r},\mathbf{r}';\varepsilon)\psi(\mathbf{r}')d^3r'=\varepsilon\psi(\mathbf{r})$$

↑

nonlocal, energy-dependent

Quasiparticle gaps



Aulbur, Jönsson and Wilkins, *Solid State Physics* **54**, 1 (2000)

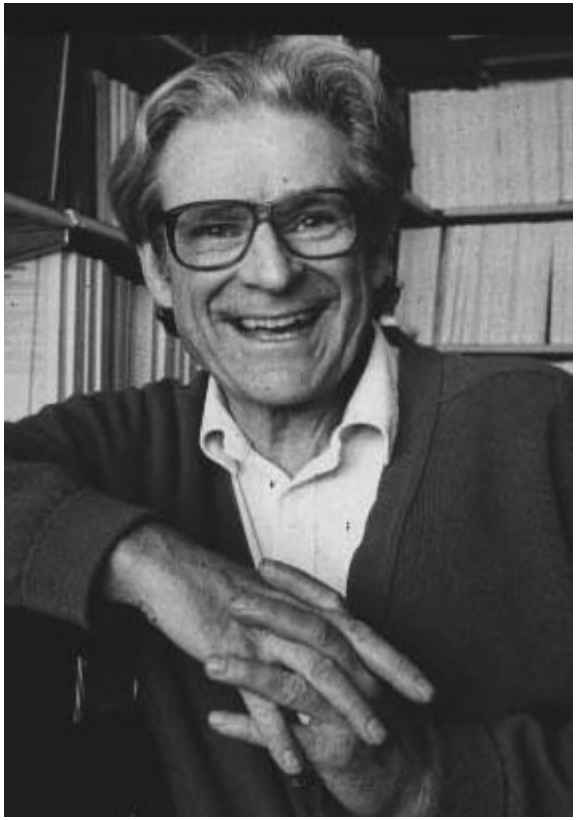
Outlook for *GW*

- Better behaved than (TD)DFT
- Provides more information than TDDFT
- More accurate
- More expensive
  - use Wannier functions to represent polarization: Umari, Stenuit & Baroni, *Phys. Rev. B* **79**, 201104(R) (2009)

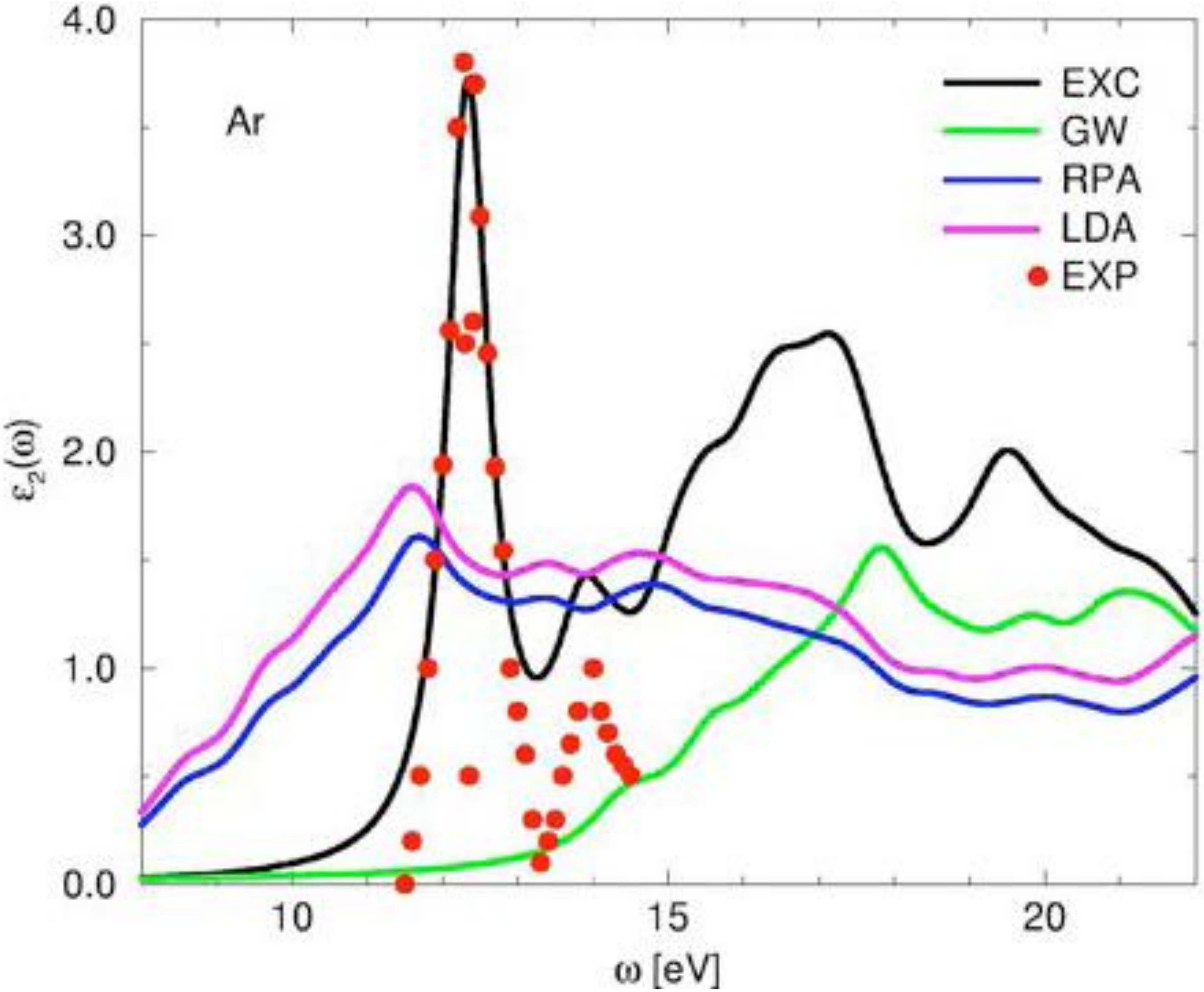
$$P(\mathbf{r},\mathbf{r}';\omega)=\sum_{\mu\nu}\Phi_{\mu}(\mathbf{r})P_{\mu\nu}(\omega)\Phi_{\nu}(\mathbf{r}')$$

  - approximate dielectric function using maximally localised eigenmodes: Lu, Gygi & Galli, *Phys. Rev. Lett.* **100**, 147601 (2008)

Bethe-Salpeter equation



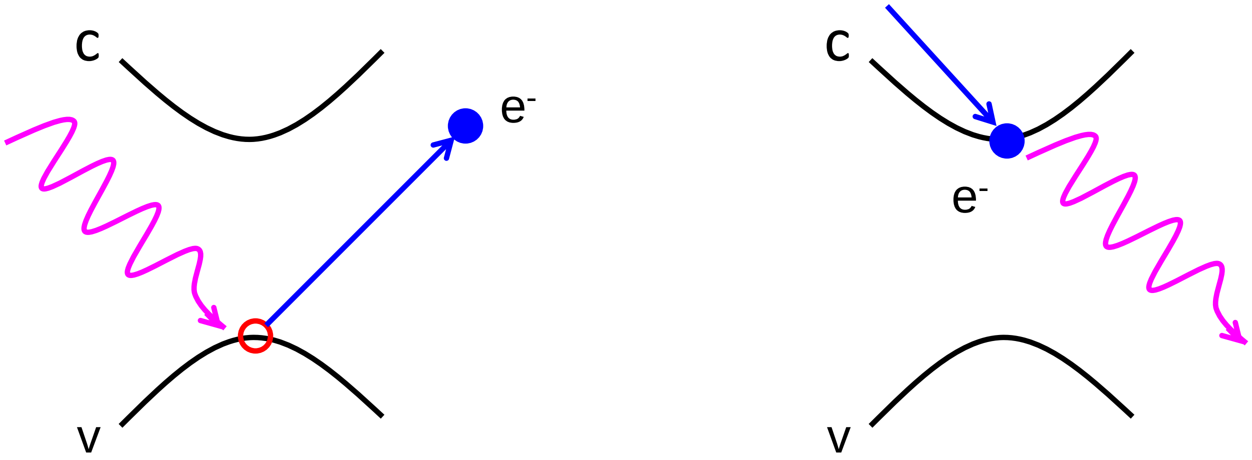
Optical absorption



Optical absorption (q=0) of solid argon
Reining , Olevano, Rubio & Onida,
Phys. Rev. Lett. **88**, 066404 (2002)

What is missing?

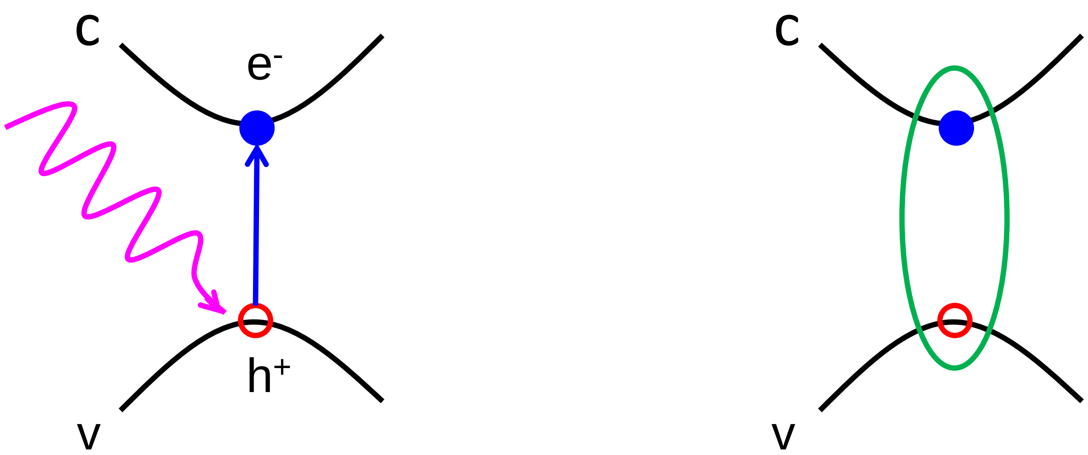
- *GW* approximation describes non-interacting one-particle excitations e.g. photoemission:



- Pole in one-particle Green's function *G*

What is missing?

- Absorption involves a two-particle excitation:



- Pole in two-particle Green’s function *L*
- Electron-hole interaction → excitons

Vertex corrections

- Need to go beyond RPA for polarization

$$
\begin{aligned}
\Sigma(1,2) &= \mathrm{i}\int W\left(1^+,3\right)G(1,4)\,\Gamma(4,2,3)\,\mathrm{d}(3,4)\\
P(1,2) &= -\mathrm{i}\int G(2,3)\,G(4,2)\boxed{\Gamma(3,4,1)}\,\mathrm{d}(3,4)\\
W(1,2) &= v(1,2)+\int W(1,3)\,P(3,4)\,v(4,2)\,\mathrm{d}(3,4)\\
\Gamma(1,2,3) &= \delta(1,2)\,\delta(1,3)\\
&+ \int\frac{\delta\Sigma(1,2)}{\delta G(4,5)}G(4,6)\,G(7,5)\,\Gamma(6,7,3)\,\mathrm{d}(4,5,6,7)
\end{aligned}
$$

Bethe-Salpeter equation

- Exact:

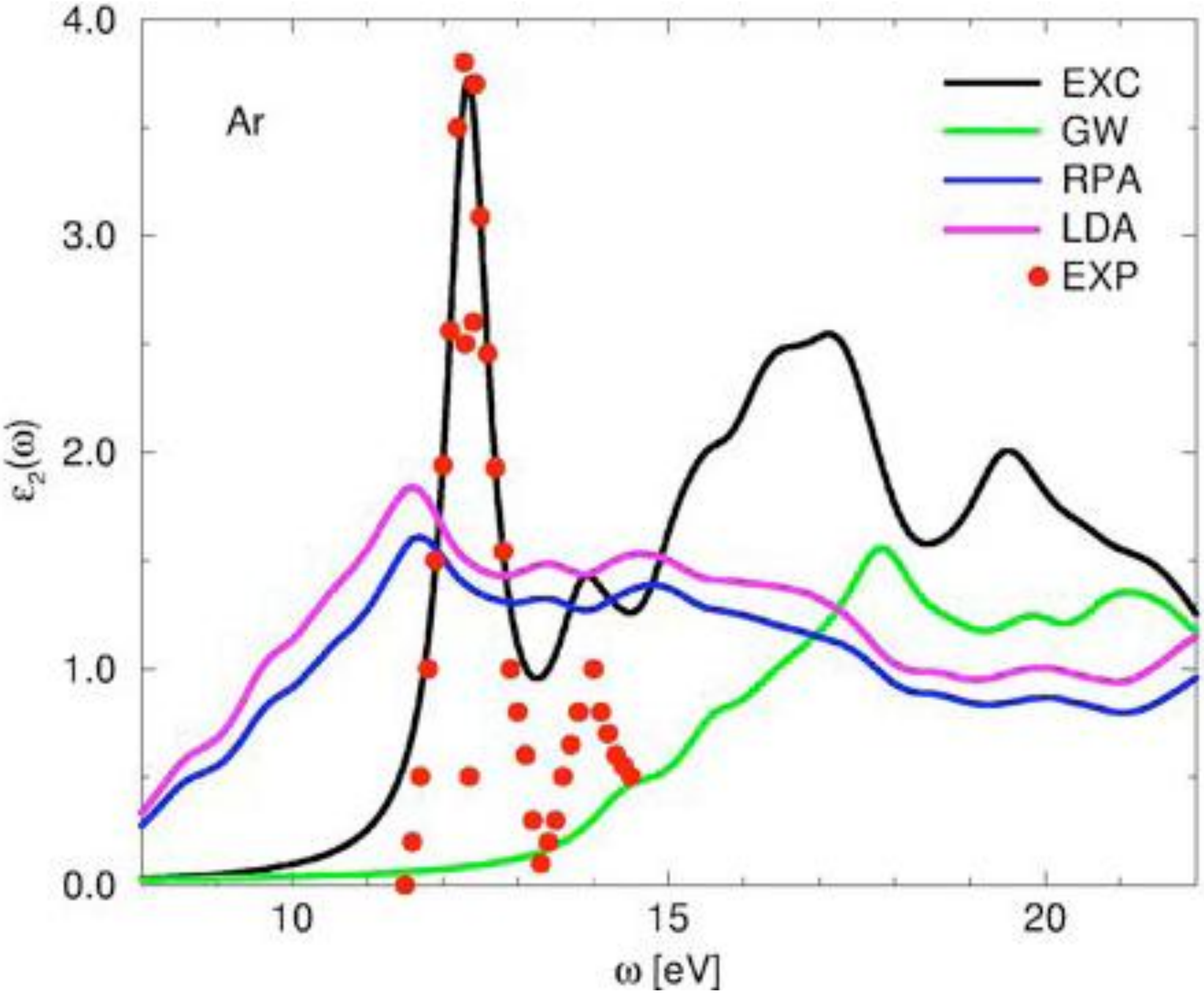
$$L = L_0 + L_0\left(v + \mathrm{i}\frac{\delta\Sigma}{\delta G} \right)L$$

- Approximation:

$$\Sigma \approx \mathrm{i}GW \;\Rightarrow\; L = L_0 + L_0\left(v - W\right)L$$

- Static *W*

Optical absorption



Optical absorption (q=0) of solid argon
Reining , Olevano, Rubio & Onida,
Phys. Rev. Lett. **88**, 066404 (2002)

Outlook for BSE

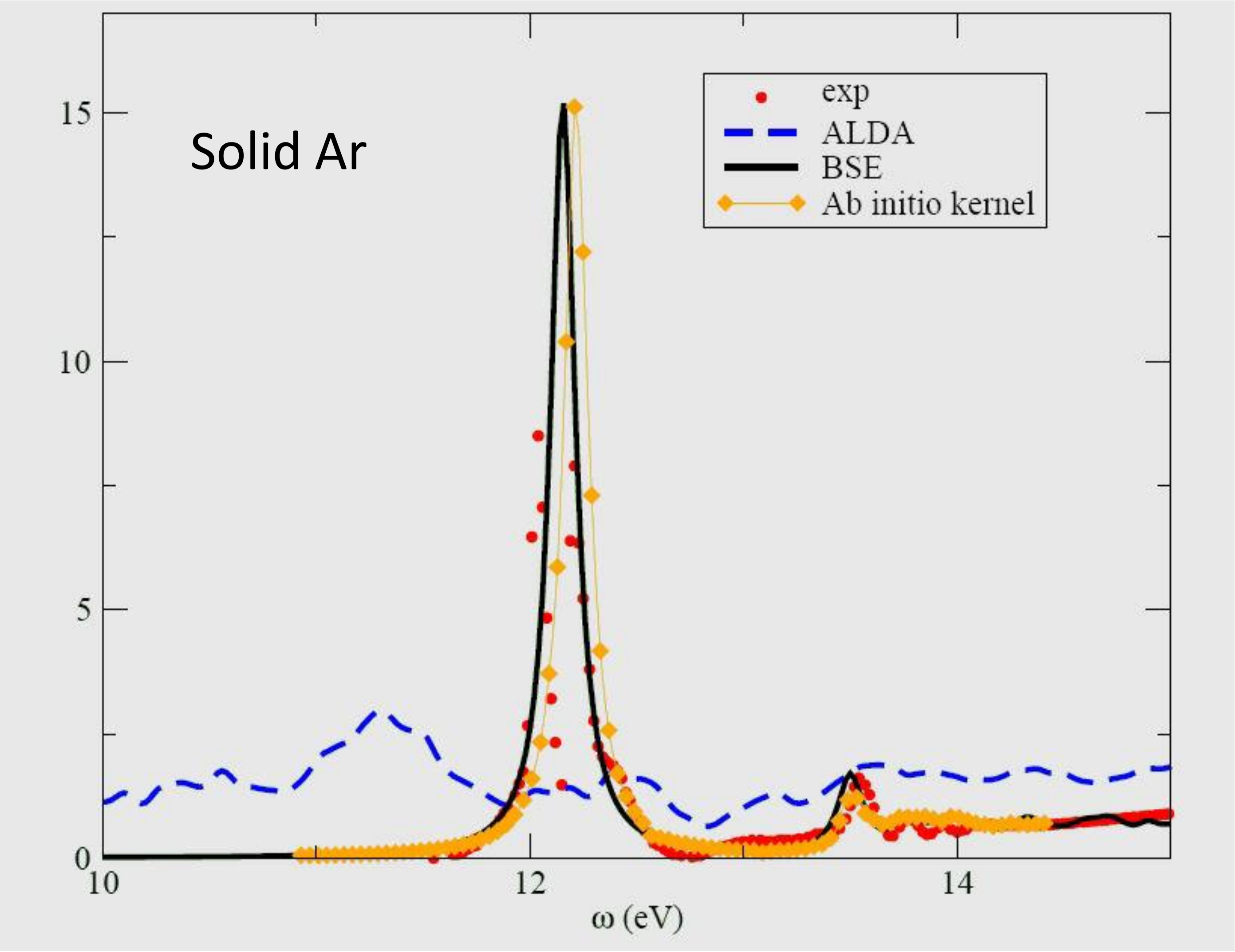
- Runs on top of *GW* calculation
- Efficient algorithms have been developed e.g. $O(N^2)$ algorithm: Fuchs *et al.*, *Phys. Rev. B* **78**, 085103 (2008)
- Extensions
  - EELS: Olevano & Reining, *Phys. Rev. Lett.* **86**, 5962 (2001)
  - dynamic *W*: Marini & Del Sole, *Phys. Rev. Lett.* **91**, 176402 (2003)
  - forces: Ismail-Beigi & Louie, *Phys. Rev. Lett.* **90**, 076401 (2003)
  - finite temperature (exciton-phonon coupling): Marini, Phys. Rev. Lett. **101**, 106405 (2008)
  - spin-polarization: C. Rödl *et al.*, *Phys. Rev. B* **77**, 184408 (2008)

MBPT vs TDDFT

	TDDFT	MBPT
Based on	Density	Green's functions
Excitations	Neutral	One and two particle
Advantage	Efficient	Transparent

- Can the advantages of both be combined i.e. extract f_{xc} from *GW*-BSE that both
  - – opens up gaps (*GW*)
  - – describes excitonic effects (BSE)

Optical absorption



Sottile *et al.*, *Phys. Rev. B* **76**, 161103 (2007)

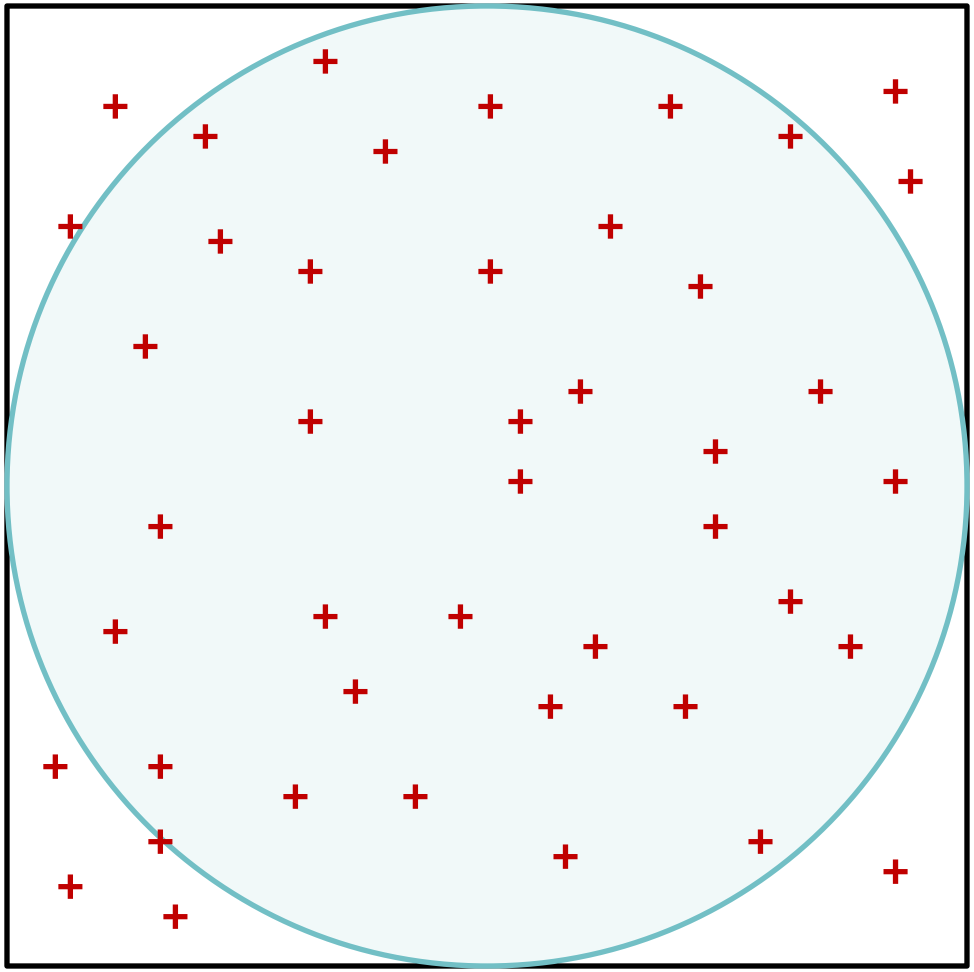
Quantum Monte Carlo

Monte Carlo

- Generate points in the square at random
- Count the number of points falling inside the circle $x^2 + y^2 < 1$

$\pi \approx 4 \text{ x } 34 / 44$

$\approx 3.1 \pm 0.2$



Numerical integration

Dimensions	Uniform	Monte Carlo
1	N^{-1}	$N^{-1/2}$
2	$N^{-1/2}$	$N^{-1/2}$
3	$N^{-1/3}$	$N^{-1/2}$
d	$N^{-1/d}$	$N^{-1/2}$

Monte Carlo wins for $d > 2$

Quantum Monte Carlo

- System of *n* electrons
  - *n* three-dimensional positions vectors
  - 3*n*-dimensional integrals:

$$E = \frac{\int \Psi \hat{H} \Psi \, d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_n}{\int \Psi \Psi \, d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_n}$$

- Exploit the efficiency of Monte Carlo methods

Foulkes *et al.*, *Rev. Mod. Phys.* **73**, 33 (2001)

Variational Monte Carlo

$$E_{\mathrm{V}} = \frac{\int \Psi_{\mathrm{T}}(\mathbf{R})\hat{H}(\mathbf{R})\Psi_{\mathrm{T}}(\mathbf{R})\,d\mathbf{R}}{\int \Psi_{\mathrm{T}}(\mathbf{R})\Psi_{\mathrm{T}}(\mathbf{R})\,d\mathbf{R}}$$

$$= \frac{\int \Psi_{\mathrm{T}}(\mathbf{R})^2 E_{\mathrm{L}}(\mathbf{R})\,d\mathbf{R}}{\int \Psi_{\mathrm{T}}(\mathbf{R})^2\,d\mathbf{R}}$$

$$\mathbf{R} \in \mathbb{R}^{3n} \qquad E_{\mathrm{L}}(\mathbf{R}) = \frac{\hat{H}\Psi_{\mathrm{T}}}{\Psi_{\mathrm{T}}}$$

Diffusion Monte Carlo

- Schrödinger equation:

$$\begin{tikzcd}
\hat{H}\Phi = i\frac{\partial \Phi}{\partial t} \arrow[dr, bend left] & \\
& \tau = it \arrow[dl, bend left] \\
\hat{H}\Phi = -\frac{\partial \Phi}{\partial \tau} &
\end{tikzcd}$$

- Projects out ground state:

$$\lim_{\tau \to \infty} \Phi \sim \Phi_0$$

Outlook for QMC

- Very accurate total energies
- Accurate forces now possible
  - Badinski *et al.*, *Phys. Rev. B* **77**, 085111 (2008)
- Excitation energies possible
  - Kent *et al.*, *Phys. Rev. B* **57**, 15293 (1998)
- Optical gaps and Stokes shifts but not spectra
- CASINO code available
  - www.tcm.phy.cam.ac.uk/~mdt26/casino2.html

Conclusions

- TDDFT is available for routine calculations, but improvements to treatment of XC ongoing
- *GW* and BSE are growing in popularity and will become routine over next decade
- Future is a combination of the above
- QMC is accurate but its future role in computational spectroscopy is unclear
- *O(N)* DFT is emerging and local orbital formulations fit well with new MBPT methods