Parameter-free calculation of response functions in time dependent density functional theory

Francesco Sottile, Valerio Olevano and Lucia Reining

Laboratoire des Solides Irradiés, CNRS-CEA,
École Polytechnique 91128 Palaiseau cedex, France

francesco.sottile@polytechnique.fr

EPS CMD 20th
Mini-Colloquium

Prague, July 19-23, 2004

LaTeX 2ε - JAVA powered

Outline

- How to calculate a response function
  - → Quasiparticle approach
  - → Density functional approach
- *Mapping theory* to describe spectra of solids in TDDFT
- Towards an efficient (fast) theory
- Conclusions

Dielectric function of the material

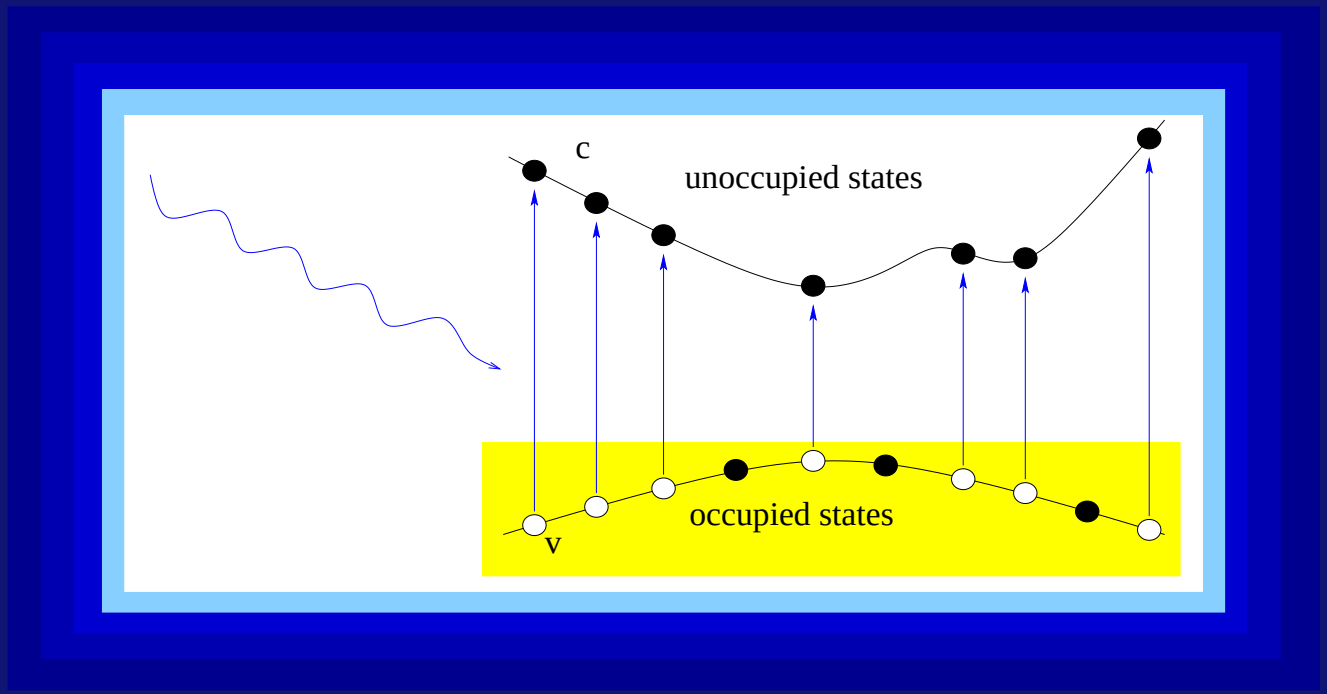
$$V_{tot} = \varepsilon^{-1} V_{ext}$$

Non polarizable system $\Rightarrow$ $V_{ext} = V_{tot}$ $\Rightarrow$ $\varepsilon = 1$

Polarizable system $\Rightarrow$ $V_{ext} = \varepsilon V_{tot}$ $\Rightarrow$ $\varepsilon \neq 1$

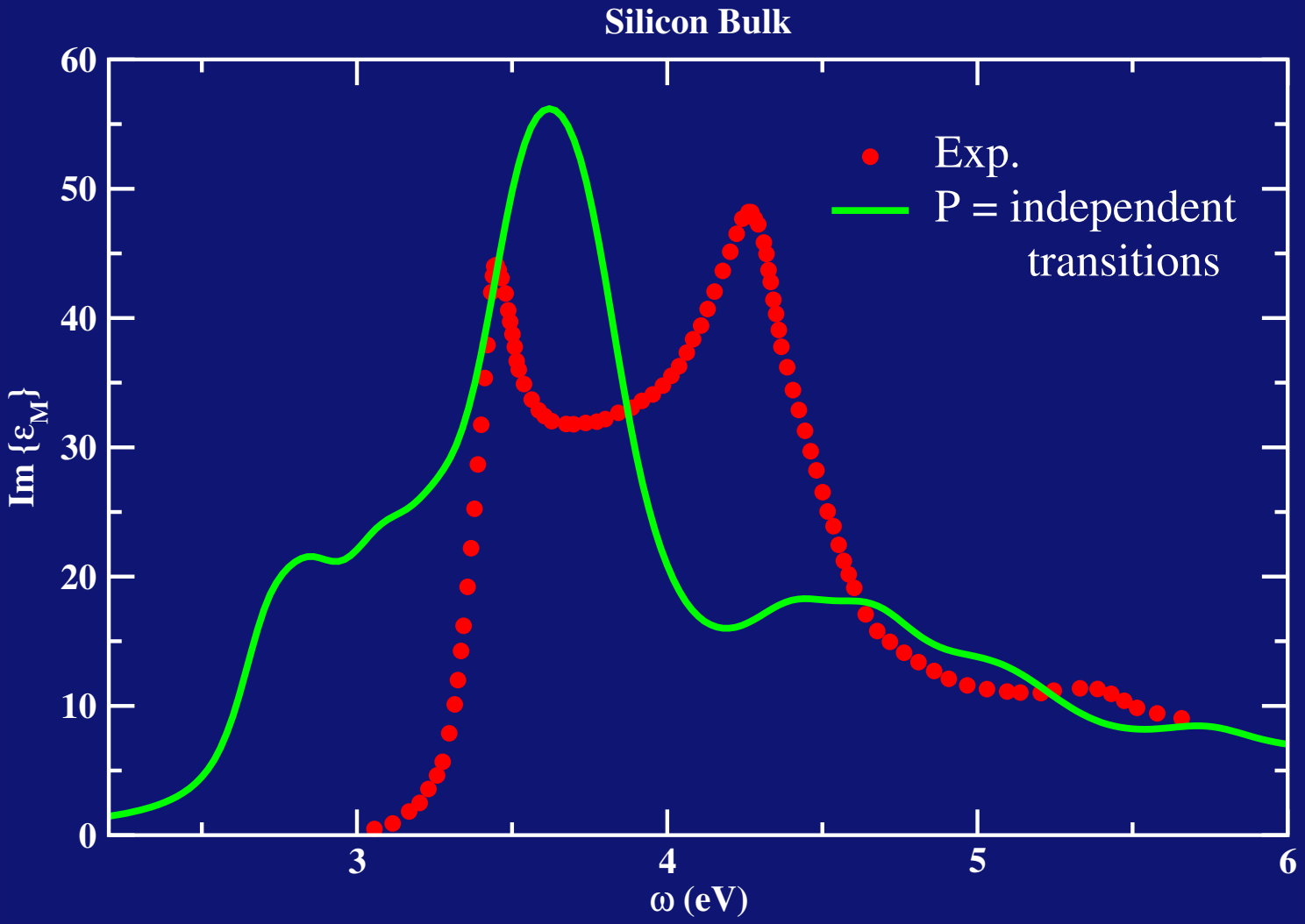
Response: dielectric function of the system

$$\varepsilon(\omega) = 1 - v\,P(\omega)$$



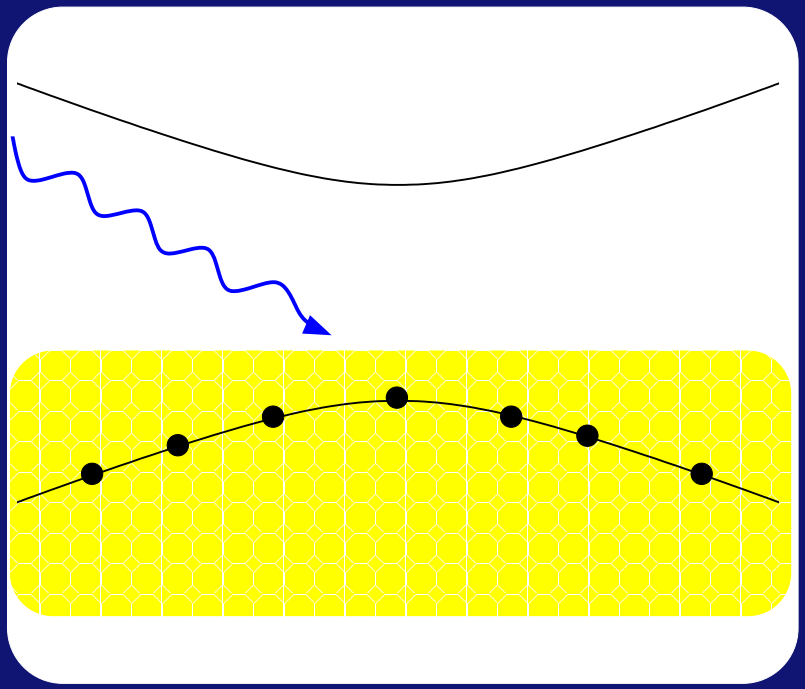
$\varepsilon(\omega)$ $\left\{\begin{array}{l} \text{Absorption spectrum} \\ \\ \text{(Electron}\|\text{X-ray) energy loss spectrum} \end{array}\right.$

Absorption Spectrum

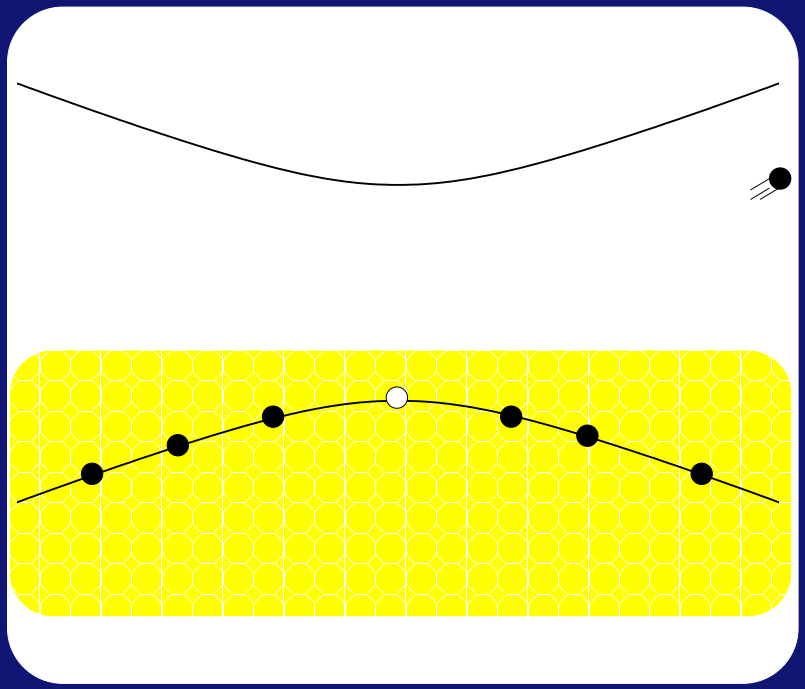


How do we *really* calculate the polarizability ?

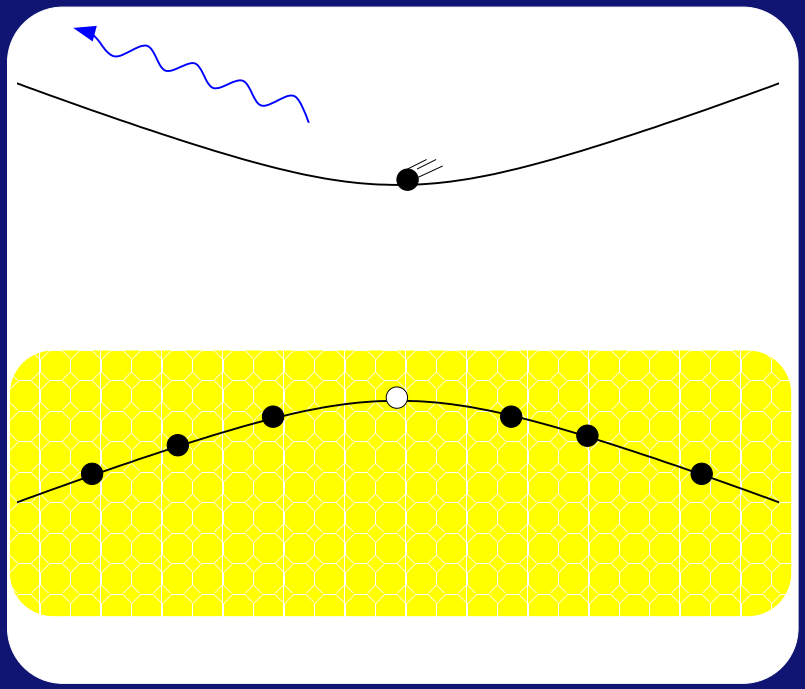
Quasiparticle approach



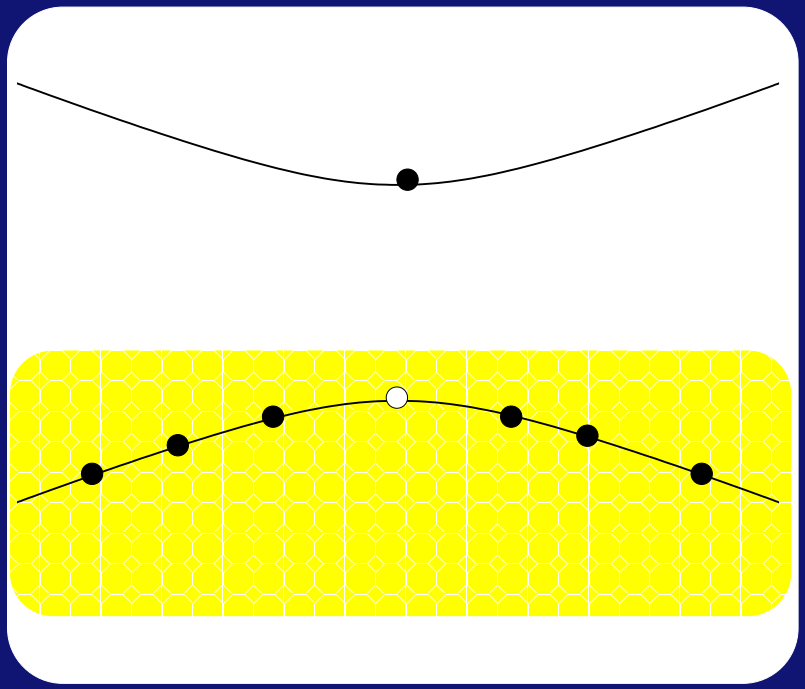
Quasiparticle approach



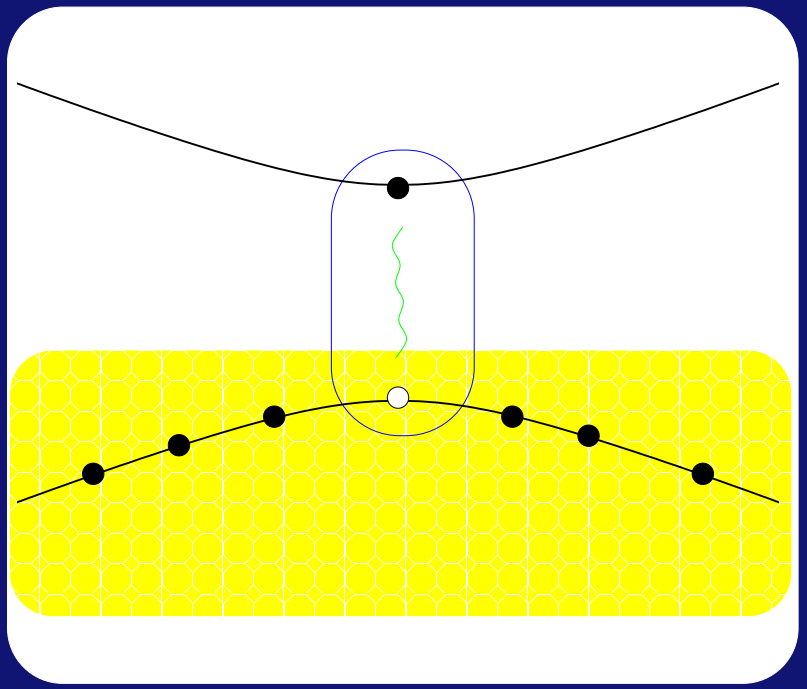
Quasiparticle approach



Quasiparticle approach

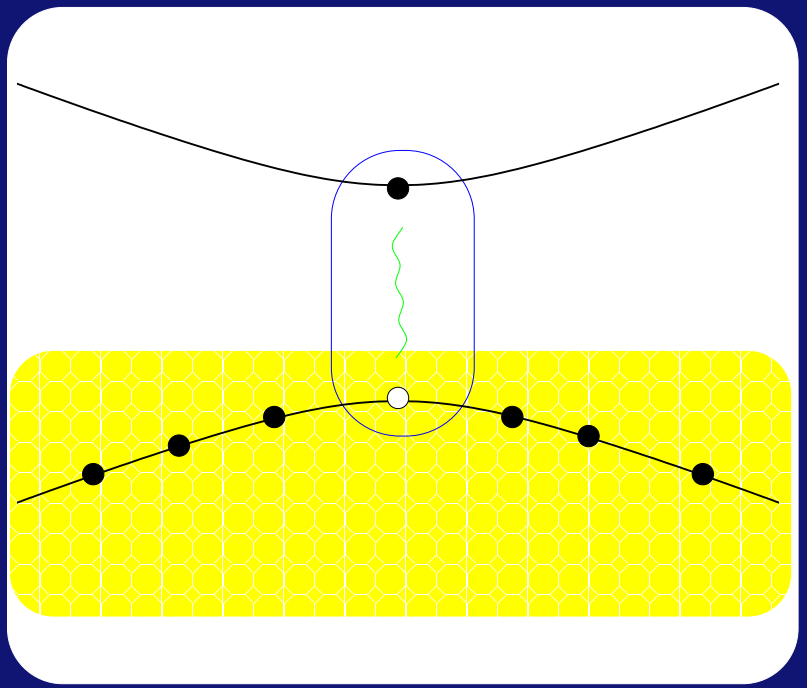


Quasiparticle approach



Electron-hole
interaction

The Bethe-Salpeter equation (BSE)



Electron-hole interaction

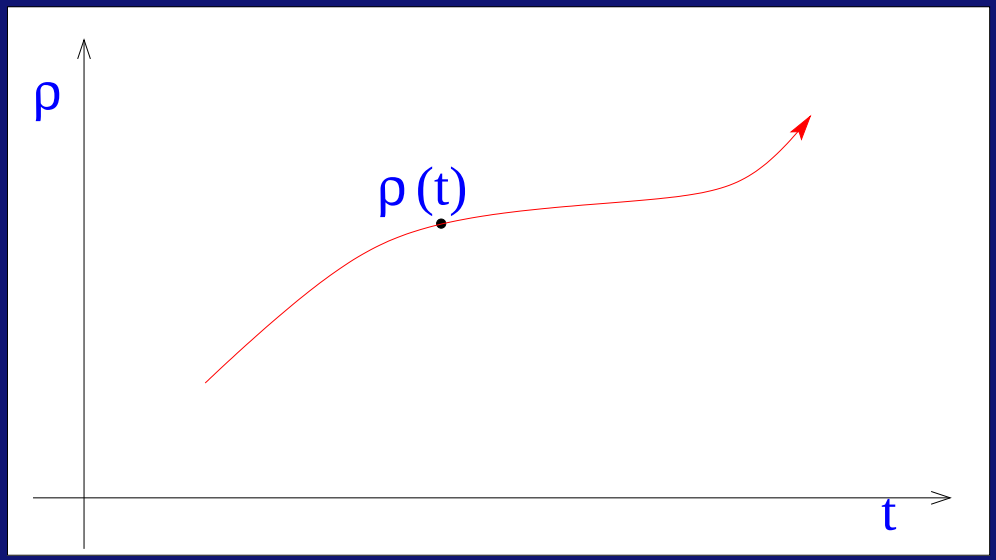
$$P^{\text{BSE}}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2, \mathbf{r}_3, t_3, \mathbf{r}_4, t_4) = P^0 + P^0 \, (v - W) \, P^{\text{BSE}}$$

Electron density based methods :

Density Functional Theory (DFT)

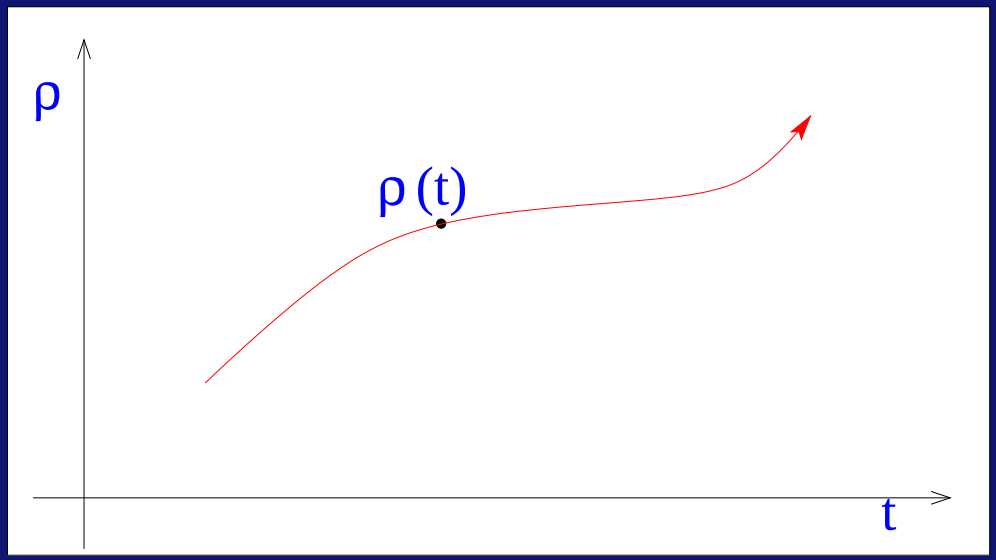
Time Dependent Density Functional Theory (TDDFT)

Time Dependent Density Functional Theory



E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
E. K. U. Gross and W. Kohn, Phys. Rev. Lett. **55**, 2850 (1985).

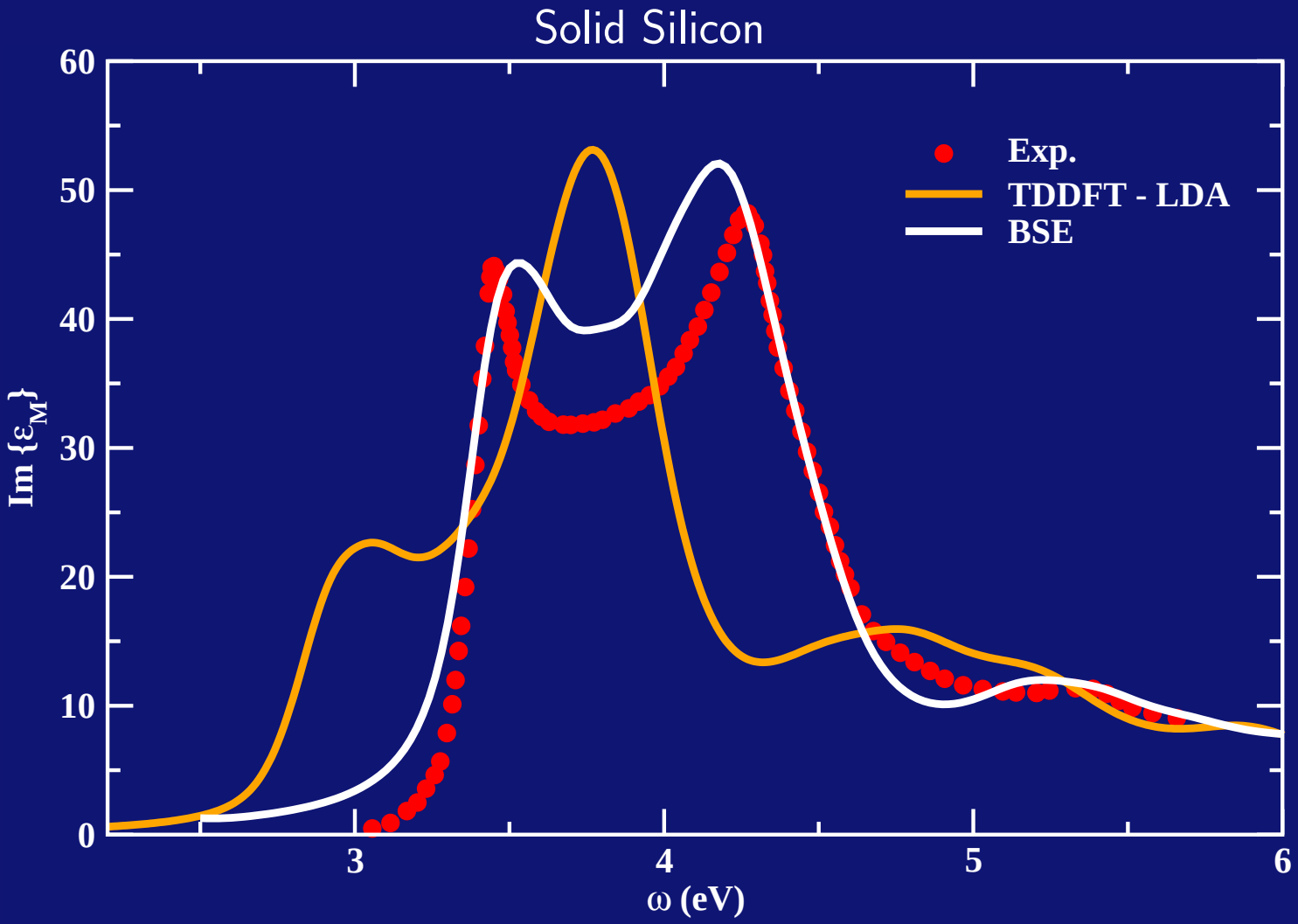
Time Dependent Density Functional Theory



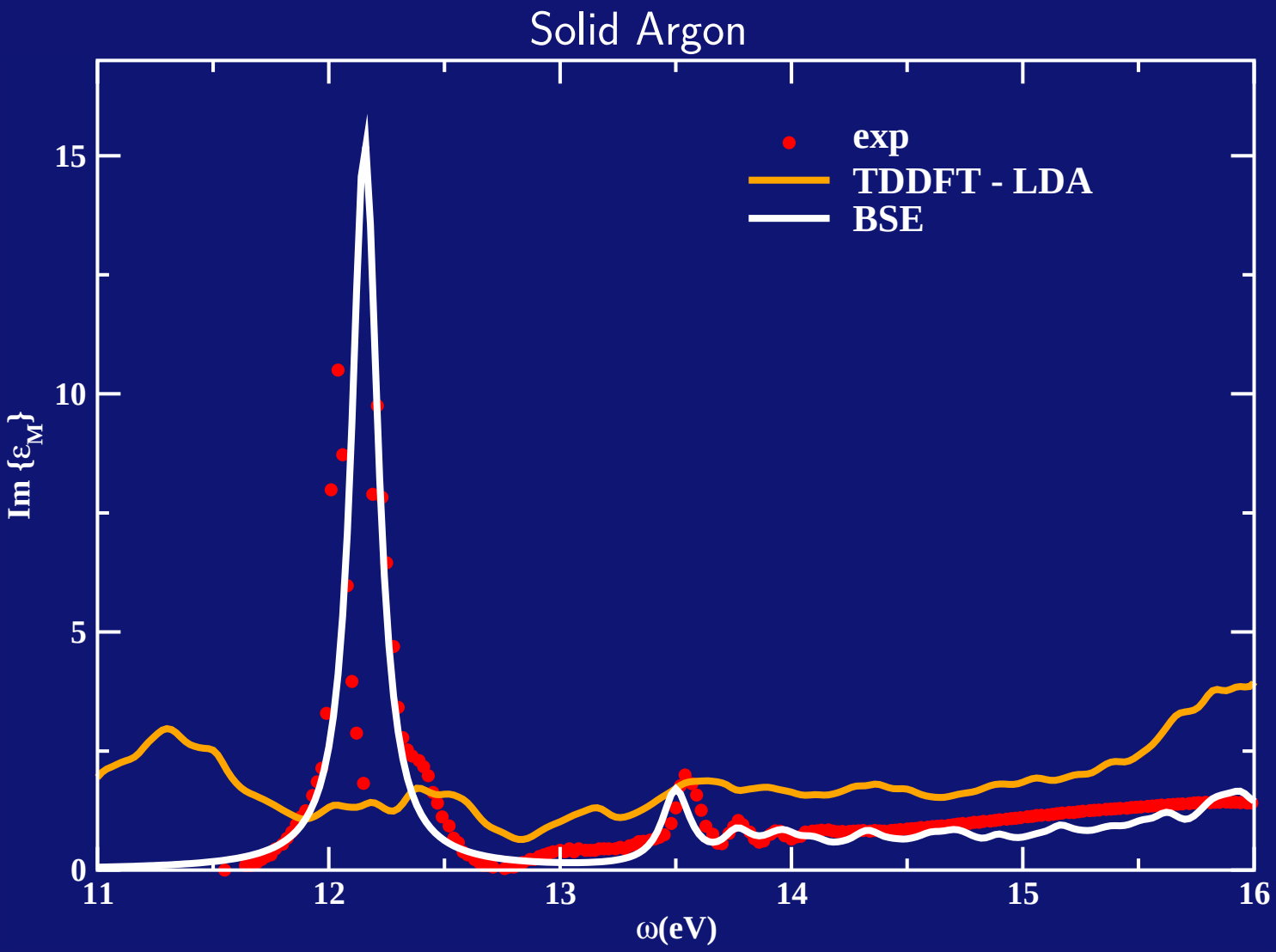
$$P_{\text{TDDFT}}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2) = P^0 + P^0 \left(v + f_{xc}\right) P_{\text{TDDFT}}$$

E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
E. K. U. Gross and W. Kohn, Phys. Rev. Lett. **55**, 2850 (1985).

Absorption Spectra in solids - Up to 2000



Absorption Spectra in solids - Up to 2000



Absorption Spectra in solids - Up to 2000

- BSE:
  - it "works"
  - unfavorable "scaling" $\propto N_{\text{atoms}}^6$

    $^4P(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2, \mathbf{r}_3, t_3, \mathbf{r}_4, t_4) = {}^4P^0 + {}^4P^0 \left({}^4v - {}^4W\right) {}^4P$

- TDDFT
  - suitable and elegant theory
  - poor approximations
  - more favorable "scaling" $\propto N_{\text{atoms}}^2$

Absorption Spectra in solids - Up to 2000

- BSE:
  - it "works"
  - unfavorable "scaling" $\propto N_{\text{atoms}}^6$

  $${}^4P(\mathbf{r}_1,t_1,\mathbf{r}_2,t_2,\mathbf{r}_3,t_3,\mathbf{r}_4,t_4) = {}^4P^0 + {}^4P^0\left({}^4v - {}^4W\right){}^4P$$

- TDDFT
  - suitable and elegant theory
  - poor approximations
  - more favorable "scaling" $\propto N_{\text{atoms}}^2$

How can we find better approximations in TDDFT for solids?

Comparison BSE $\leftrightarrow$ TDDFT

Several attempts, trying to exploit BSE↔TDDFT ...

- 2002 Reining, Olevano, Rubio, Onida $f_{xc} = \frac{\alpha}{q^2}$
- 2003 Del Sole, Adragna, Olevano, Reining $f_{xc} = \frac{\alpha(\omega)}{q^2}$
- 2003 Marini, Del Sole, Rubio $f_{xc} = o(W)$ *ab initio*
- 2003 this work $< f_{xc} > \rightarrow < W >$ *ab initio*

... or not

- 2002 de Boeij,Koostra,Berger,van Leeuwen,Snijders, td-current-dft
- 2002 Kim, Görling, exact-exchange

Comparison between BSE and TDDFT

- BSE $\leftrightarrow$ TDDFT

$$ {}^4P_{\text{BSE}} = {}^4P^0 + {}^4P^0 \left({}^4v - {}^4W \right) {}^4P_{\text{BSE}} $$

$$ P_{\text{TDDFT}} = P^0 + P^0 (v + f_{xc}) P_{\text{TDDFT}} $$

Transition framework

$$(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2, \mathbf{r}_3, t_3, \mathbf{r}_4, t_4) \quad \Longrightarrow (vc, v'c', \omega)$$

$$\text{BSE} \Leftrightarrow \Big[\Delta E + < v > - < W > \Big] \; A_\lambda = E_\lambda A_\lambda$$

$$\text{TDDFT} \Leftrightarrow \Big[\Delta E + < v > + < f_{xc} > \Big] \; A_\lambda = E_\lambda A_\lambda$$

$$< f_{xc} > \longrightarrow \; - < W >$$

Mapping Theory

How can we use $< W >$ in a *2-point* equation ??

$$
\begin{aligned}
P_{\text{TDDFT}} &= P^0 + P^0 \left(v + f_{xc}\right) P_{\text{TDDFT}} = \\
&= P^0 \left(P^0 - P^0 v P^0 - P^0 f_{xc} P^0\right)^{-1} P^0 \\
&= P^0 \left(P^0 - P^0 v P^0 - T\right)^{-1} P^0
\end{aligned}
$$

$$
T = \sum_{tt'} \frac{\tilde{\rho}_t^*(\mathbf{r})}{\omega - \Delta E_t} < f_{xc} > \frac{\tilde{\rho}_{t'}}{\omega - \Delta E_{t'}}
$$

$$
< f_{xc} > \longrightarrow \; - < W >
$$

How can we use $< W >$ in a *2-point* equation ??

$$
\begin{aligned}
P_{\mathsf{TDDFT}} &= P^0 + P^0 \left(v + f_{xc}\right) P_{\mathsf{TDDFT}} = \\
&= P^0 \left(P^0 - P^0 v P^0 - P^0 f_{xc} P^0\right)^{-1} P^0 \\
&= P^0 \left(P^0 - P^0 v P^0 - T\right)^{-1} P^0
\end{aligned}
$$

$$
T = \sum_{tt'} \frac{\tilde{\rho}_t^*(\mathbf{r})}{\omega - \Delta E_t} < W > \frac{\tilde{\rho}_{t'}}{\omega - \Delta E_{t'}}
$$

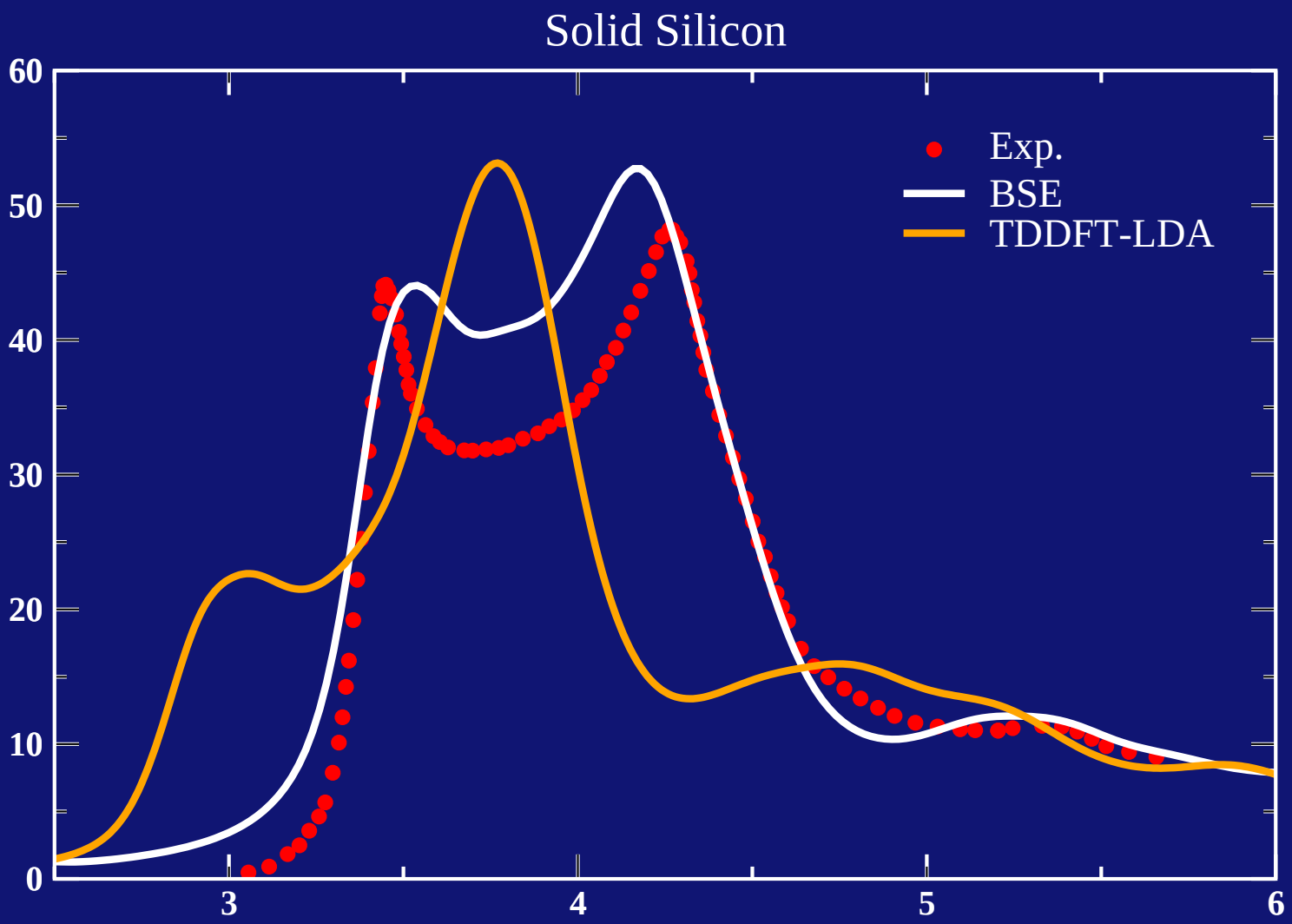
$$P_{\mathsf{TDDFT}}(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2) = P^0 \left(P^0 - P^0 v P^0 - T \right)^{-1} P^0$$

$$\mathsf{Abs}(\omega) = \Im\mathfrak{s}\{1 - v P_{\mathsf{TDDFT}}(\omega)\}$$

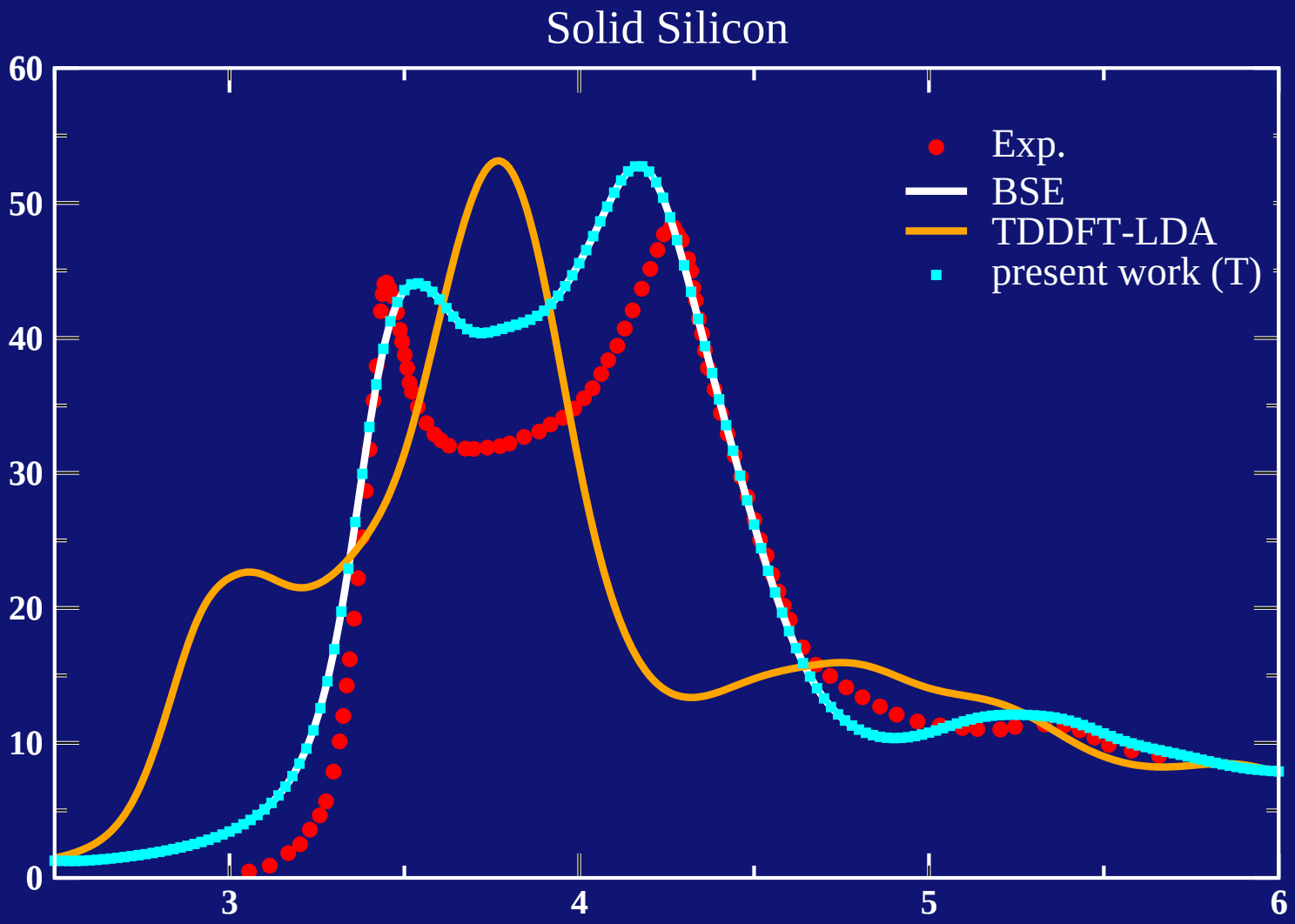
Does it work ?

Realistic applications

Solid Silicon - 256k

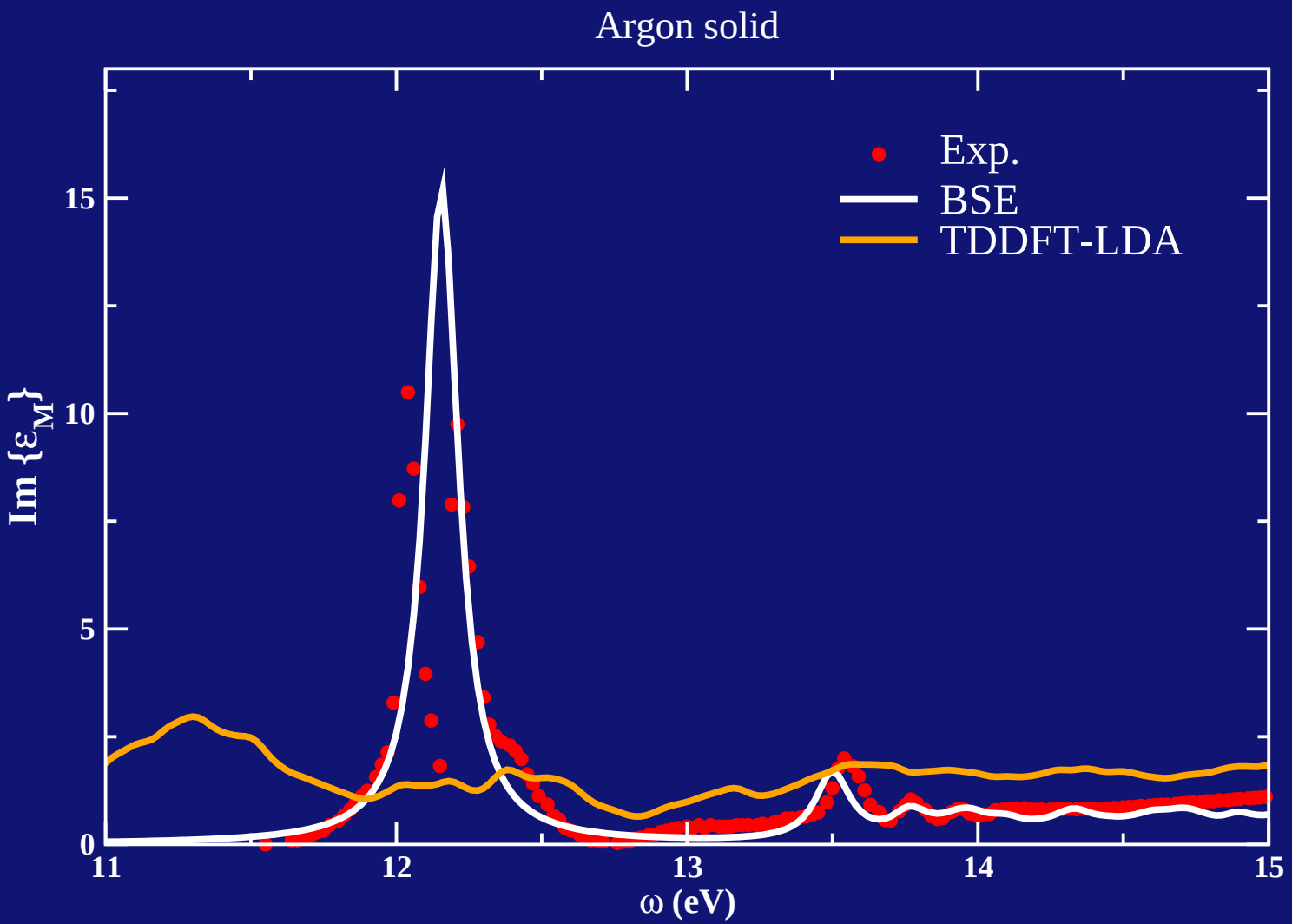


Solid Silicon - 256k

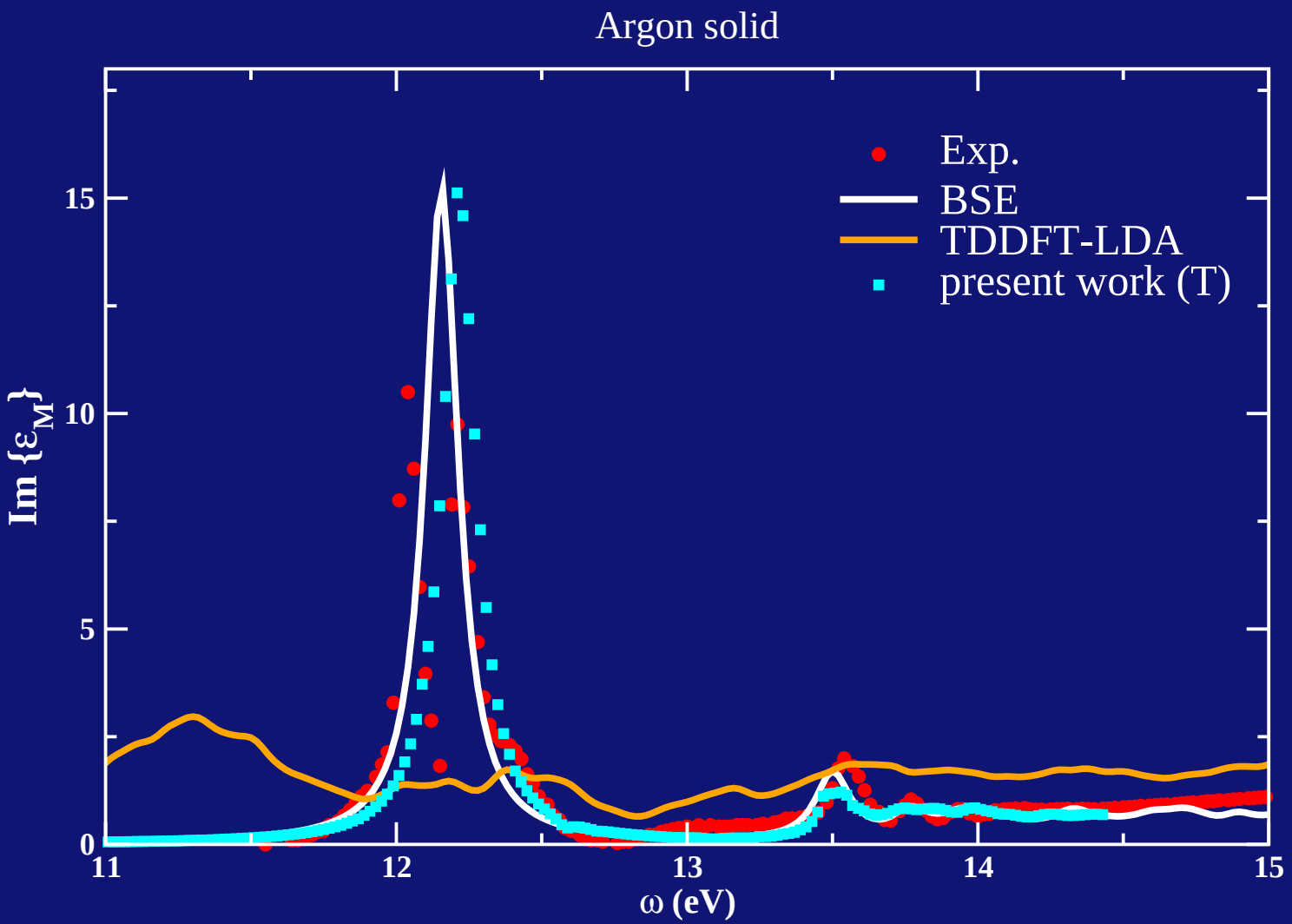


Sottile, Olevano and Reining, PRL (2003)

Solid Argon - 2048k



Solid Argon - 2048k



Good results:

TDDFT with the same precision as the BSE.

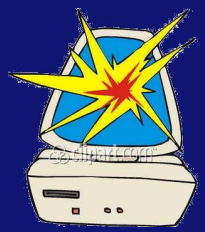
absorption and (electron | X-ray) energy loss

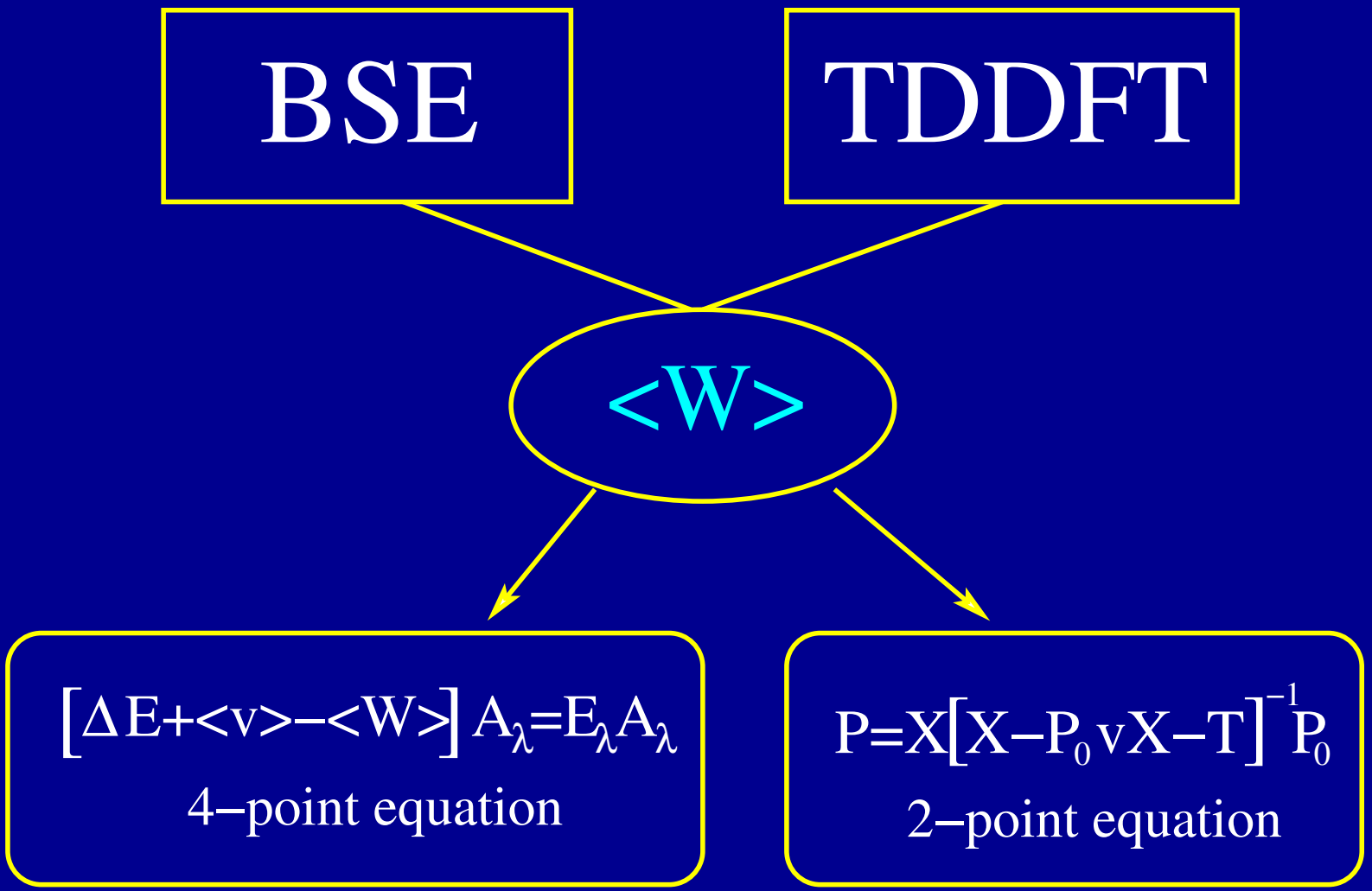
semiconductors and insulators

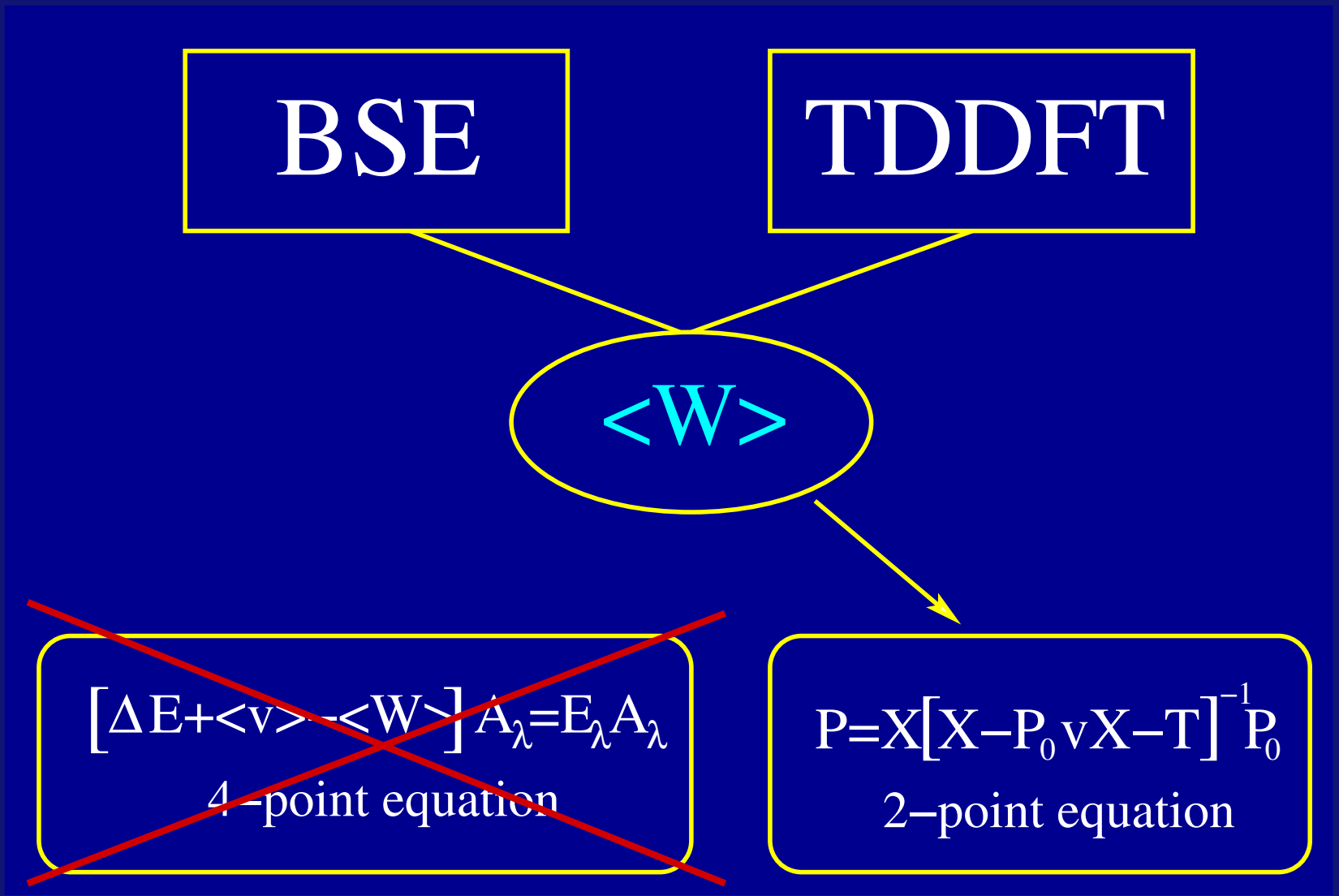
Very important achievements, BUT ...

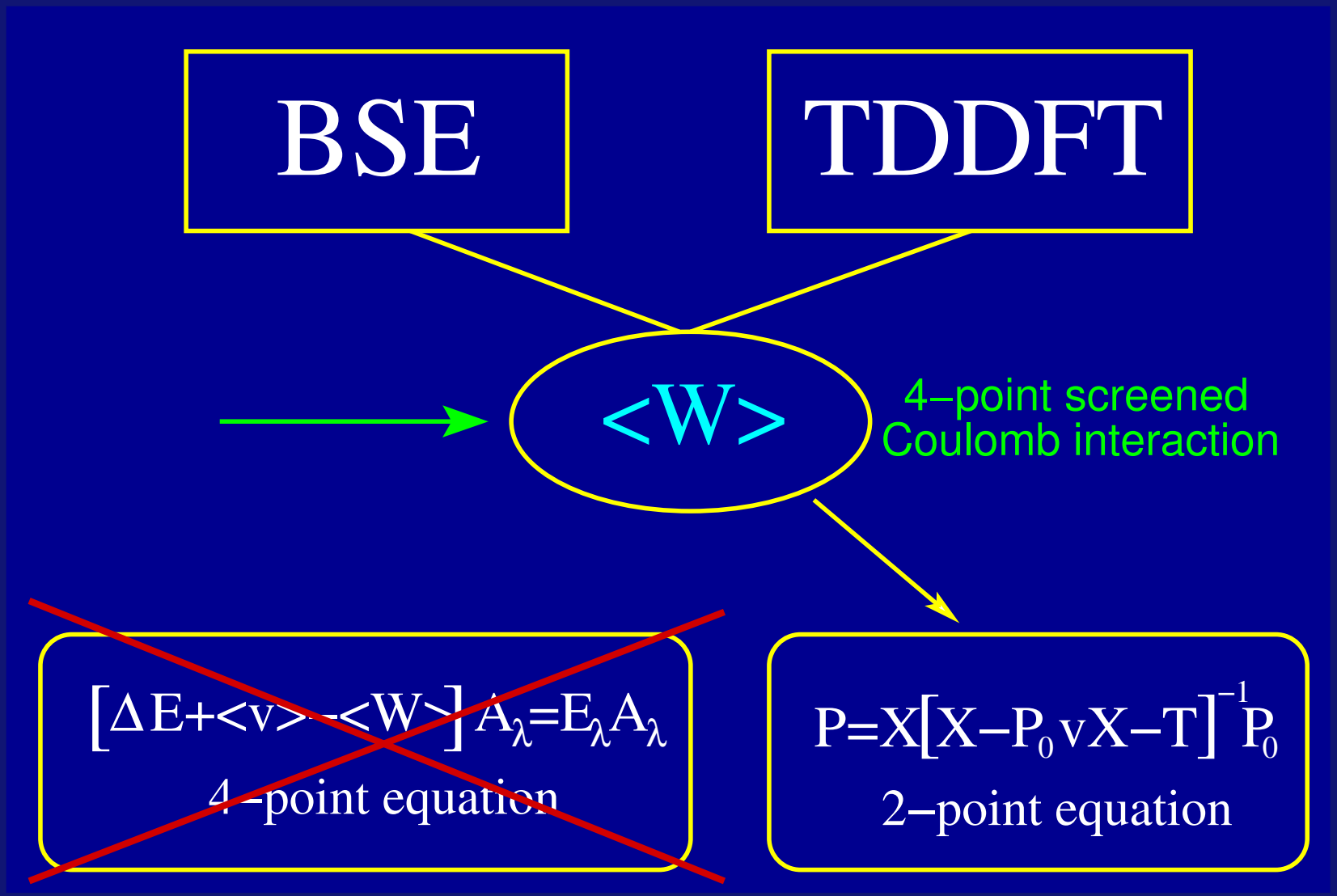
The approach still remains

CUMBERSOME




BSE
TDDFT
<W>
$[\Delta E+<v>-<W>]\,A_\lambda=E_\lambda A_\lambda$
4–point equation
$P=X[X-P_0 vX-T]^{-1}P_0$
2–point equation


BSE
TDDFT
<W>
$[\Delta E+<v>-<W>]A_\lambda=E_\lambda A_\lambda$
4–point equation
$P=X[X-P_0 vX-T]^{-1}P_0$
2–point equation


BSE
TDDFT
<W>
4–point screened
Coulomb interaction
$[\Delta E+<v>-<W>]A_\lambda=E_\lambda A_\lambda$
4–point equation
$P=X[X-P_0 vX-T]^{-1}P_0$
2–point equation

Exploit the Mapping Theory

to find a better algorithm

$$P = P^0 \left(P^0 - P^0 v P^0 - P^0 f_{xc} P^0 \right)^{-1} P^0$$

$$P = X\left(X - P^0 vX - P^0 f_{xc} X\right)^{-1} P^0$$

1) $$X = \sum_t \tilde{\rho}_t(\mathbf{r}) f_t(\mathbf{r}') \quad \Rightarrow \quad P^0 = \sum_t \frac{\tilde{\rho}_t(\mathbf{r})\tilde{\rho}_t^*(\mathbf{r}')}{\omega - \Delta\epsilon_t}$$

2) $$X = \sum_t \tilde{\rho}_t(\mathbf{r}) f_t(\mathbf{r}') \quad \Rightarrow \quad X = \sum_t \frac{\tilde{\rho}_t(\mathbf{r})\tilde{\rho}_t^*(\mathbf{r}')}{\Delta\epsilon_t}$$

3) $$X = \sum_t \tilde{\rho}_t(\mathbf{r}) f_t(\mathbf{r}') \quad \Rightarrow \quad X = \sum_t \tilde{\rho}_t(\mathbf{r})\tilde{\rho}_t^*(\mathbf{r}')$$

$$P = X \left(X - P^0 v X - P^0 \qquad\qquad f_{xc} X \right)^{-1} P^0$$

$$P = X\left(X - P^0 vX - P^0 X^{-1} X f_{xc} X\right)^{-1} P^0$$

$$X = \sum_t \tilde{\rho}_t(\mathbf{r})\tilde{\rho}_t^*(\mathbf{r}')$$

$$X f_{xc} X = \sum_{tt'} \tilde{\rho}_t(\mathbf{r}) < W > \tilde{\rho}_{t'}^*(\mathbf{r}')$$

$$P = X\left(X - P^0 vX - P^0 X^{-1} X f_{xc} X\right)^{-1} P^0$$

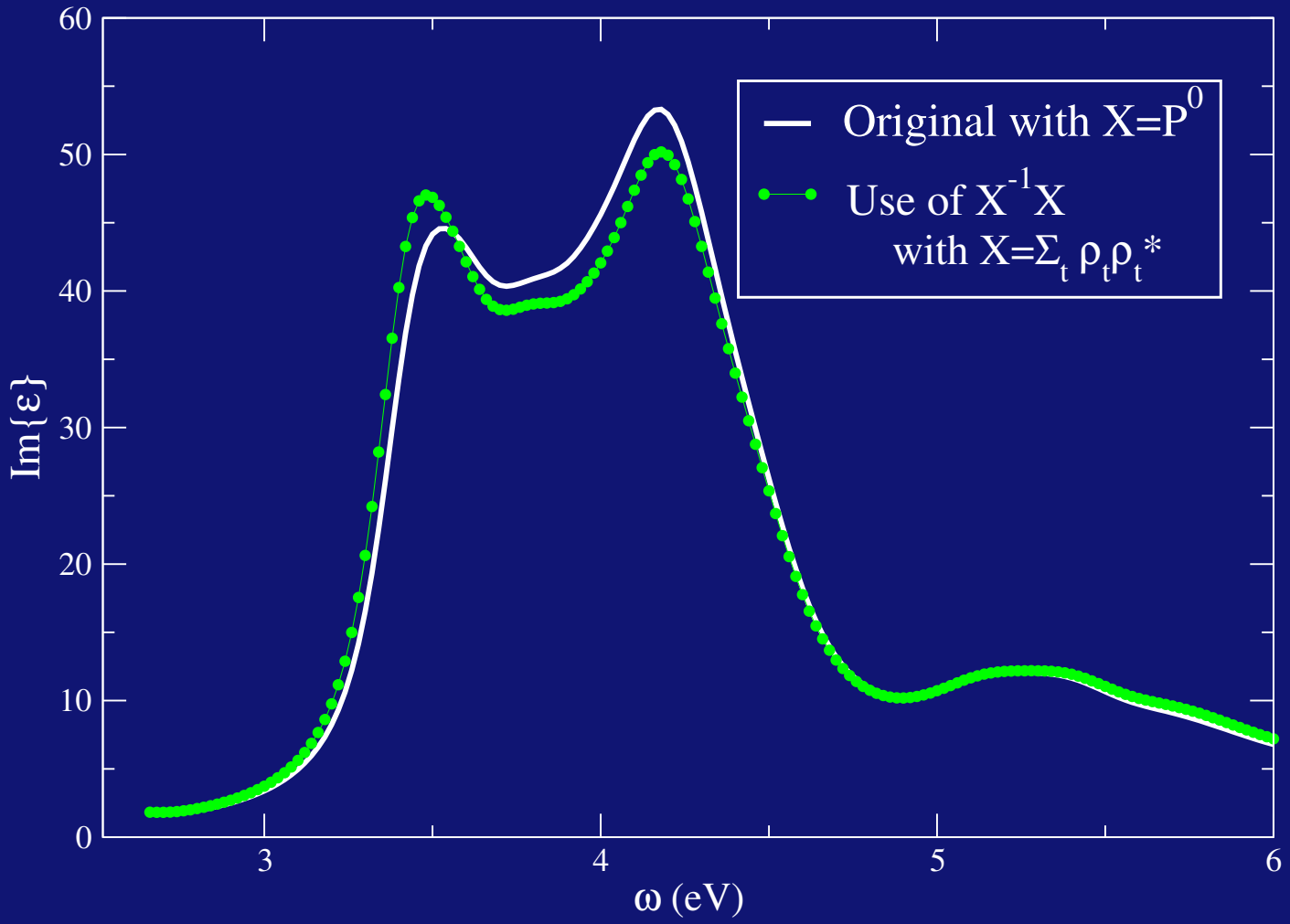
$$X = \sum_t \rho_t(\mathbf{r})\rho_t^*(\mathbf{r}')$$

$$X f_{xc} X = \sum_{tt'} \tilde{\rho}_t(\mathbf{r}) \int d\mathbf{r} d\mathbf{r}' \tilde{\rho}_t^*(\tilde{\mathbf{r}}) W(\tilde{\mathbf{r}}, \tilde{\mathbf{r}}') \tilde{\rho}_{t'}(\tilde{\mathbf{r}}') \cdot \tilde{\rho}_{t'}^*(\mathbf{r}')$$

not worse than RPA !!

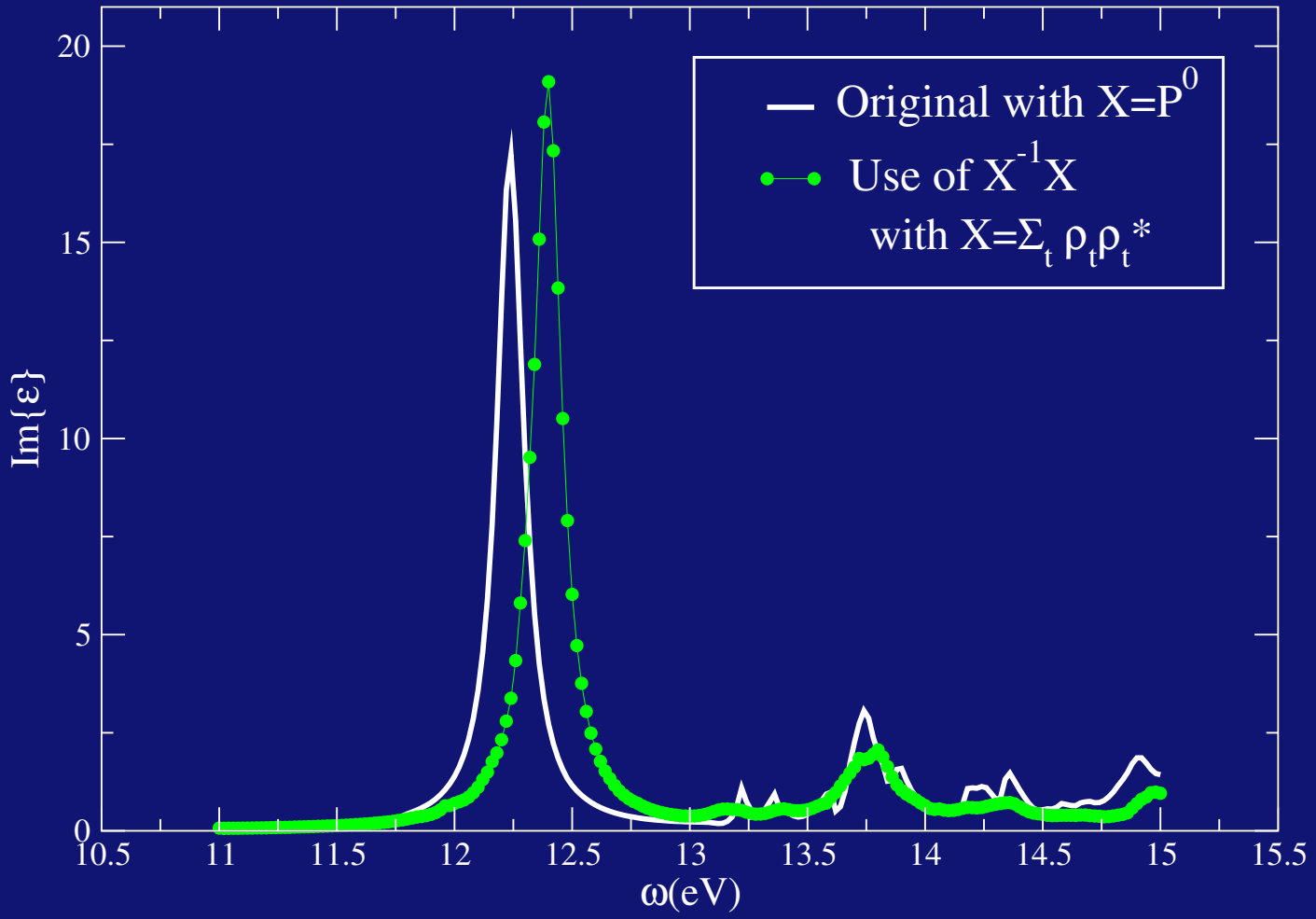
Absorption of Si

$$P = X\left(X - P^0 \upsilon X - P^0 X^{-1} X f_{xc} X\right)^{-1} P^0 \quad ; \quad X = \sum_t \tilde{\rho}_t \tilde{\rho}_t^*$$



Preliminary result for Solid Ar

$$P = X\left(X - P^0 v X - P^0 X^{-1} X f_{xc} X\right)^{-1} P^0 \quad ; \quad X = \sum_t \tilde{\rho}_t \tilde{\rho}_t^*$$



Conclusions

- *Ab initio* determination of the exchange-correlation contribution in the framework of the TDDFT, from a comparison with the BSE.
  - $T(\omega)$ dynamic exchange-correlation contribution
  - Static T exchange-correlation contribution
  - the approach works for semiconductors ...

    ...as well as for insulators
- Very efficient. Potential RPA-like difficulty

  but BSE-like quality

  Very promising!