Ab Initio theories to predict ARPES
Hedin's GW and beyond

Valerio Olevano
Institut NEEL, CNRS, Grenoble, France and
European Theoretical Spectroscopy Facility
Many thanks to:

Matteo Gatti, Pierre Darancet,
Fabien Bruneval, Francesco Sottile
and Lucia Reining

Institut NEEL, CNRS, Grenoble, France and
LSI, CNRS - CEA Ecole Polytechnique, Palaiseau France
Résumé

- **Motivation:** Electronic Excitations and Spectroscopy
- Many-Body Perturbation Theory and the Hedin's GW approximation -> ARPES
- **Non-Equilibrium Green's Function (NEGF)** theory, GW approximation -> e-e in Quantum Transport
- MBPT using the Density-functional concept: vertex corrections beyond GW.
- Generalized Sham-Schlüter Equation and frequency-dependent effective local potentials.
- **Conclusions**
The Ground State

Ab initio DFT theory well describes (error 1~2%):

- Ground State Total Energy and Electronic Density
- Atomic Structure, Lattice Parameters
- Elastic Constants
- Phonon Frequencies

that is, all the **Ground State** Properties.

### Vanadium Oxide, VO$_2$

<table>
<thead>
<tr>
<th>Lattice Parameters</th>
<th>DFT-LDA nlcc</th>
<th>DFT-LDA semic</th>
<th>EXP [Longo et al.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>5.659 Å</td>
<td>5.549 Å</td>
<td>5.7517 ± 0.0030 Å</td>
</tr>
<tr>
<td>b</td>
<td>4.641 Å</td>
<td>4.522 Å</td>
<td>4.5378 ± 0.0025 Å</td>
</tr>
<tr>
<td>c</td>
<td>5.420 Å</td>
<td>5.303 Å</td>
<td>5.3825 ± 0.0025 Å</td>
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<tr>
<td>$\alpha$</td>
<td>121.46°</td>
<td>121.73°</td>
<td>122.646° ± 0.096°</td>
</tr>
</tbody>
</table>

M. Gatti et al.  
To be published

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Citation Statistics from 110 years of Physical Review


DFT Standard Model of Condensed Matter

<p>| Table 1. Physical Review Articles with more than 1000 Citations Through June 2003 |</p>
<table>
<thead>
<tr>
<th>Publication</th>
<th># cites</th>
<th>Av. age</th>
<th>Title</th>
<th>Author(s)</th>
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<tr>
<td>PR 140, A1133 (1965)</td>
<td>3227</td>
<td>26.7</td>
<td>Self-Consistent Equations Including Exchange and Correlation Effects</td>
<td>W. Kohn, L. J. Sham</td>
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<tr>
<td>PR 136, B864 (1964)</td>
<td>2460</td>
<td>28.7</td>
<td>Inhomogeneous Electron Gas</td>
<td>P. Hohenberg, W. Kohn</td>
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<tr>
<td>PR 108, 1175 (1957)</td>
<td>1364</td>
<td>20.2</td>
<td>Theory of Superconductivity</td>
<td>J. Bardeen, L. N. Cooper, J. R. Schrieffer</td>
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<tr>
<td>PRL 19, 1264 (1967)</td>
<td>1306</td>
<td>15.5</td>
<td>A Model of Leptons</td>
<td>S. Weinberg</td>
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<tr>
<td>PRB 12, 3060 (1975)</td>
<td>1259</td>
<td>18.4</td>
<td>Linear Methods in Band Theory</td>
<td>O. K. Anderson</td>
</tr>
<tr>
<td>PR 124, 1866 (1961)</td>
<td>1178</td>
<td>28.0</td>
<td>Effects of Configuration Interaction of Intensities and Phase Shifts</td>
<td>U. Fano</td>
</tr>
<tr>
<td>PRB 13, 5188 (1976)</td>
<td>1023</td>
<td>20.8</td>
<td>Special Points for Brillouin-Zone Integrations</td>
<td>H. J. Monkhorst, J. D. Pack</td>
</tr>
</tbody>
</table>

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Excited States

But can **DFT** describe the Excited States, such as:

- Band Gap, Band Plot
- Metal/Insulator character
- Spectral Function

![Diagram of Vanadium Oxide, VO$_2$]


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Excited States

**Answer:** NO! DFT *cannot* in principle describe excited states, band gap and so on!

(and it cannot be blamed if it does not succeed)

Nevertheless, be careful:
- DFT for electronic structure -> photoemission spectroscopy
- DFT for optical spectroscopy
- DFT of superconductivity -> superconductivity gap
- DFT-NEGF -> quantum transport

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Why we need *ab initio* theories to calculate spectra

1) To understand and explain observed phenomena
2) To offer experimentalists reference spectra
3) To predict properties before the synthesis, the experiment
Excited States *Ab initio* Theories

- **HF** (Hartree-Fock), **CI** (Configuration Interaction)
- **QMC** (Quantum Montecarlo)
- **TDDFT** (Time-Dependent Density-Functional Theory)
- **MBPT** (Many-Body Theory) in the Approximation:
  - **GW**
- **NEGF** (Non-Equilibrium Green's Functions Theory)

Photoemission

Quantum Transport

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MBPT and the \textbf{GW} approximation

\textbf{vs}

\textbf{ARPES} Photoemission Spectroscopy

(Band Gap, Band Plot, Spectral Function)
Photoemission

direct photoemission

inverse photoemission

\[ A = \frac{1}{\pi} |\Im G| \text{ band gap} \text{ band plot} \]

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Calculating the Band-Gap: inadequacy of HF or DFT

- HF always overestimates the bandgap.
- The Kohn-Sham energies have not an interpretation as removal/addition energies (Kopman Theorem does not hold). If we use them, however we see they are better than HF but the band gap is always underestimated.
- Need to go beyond: MBPT and GW!

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>DFT-LDA</th>
<th>EXP</th>
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<tbody>
<tr>
<td>Silicon</td>
<td>5,6</td>
<td>0,55</td>
<td>1,17</td>
</tr>
<tr>
<td>Germanium</td>
<td>4,2</td>
<td>0</td>
<td>0,7</td>
</tr>
<tr>
<td>Diamond</td>
<td>12,10</td>
<td>4,26</td>
<td>5,48</td>
</tr>
<tr>
<td>MgO</td>
<td></td>
<td>5,3</td>
<td>7,83</td>
</tr>
<tr>
<td>Sn</td>
<td>2,60</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

A. Svane, PRB 1987

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What is the MBPT?

• Many-Body “Perturbation” Theory is a Quantum Field Theory, based on second quantization of operators and a Green’s function formalism.

• Advantages of the Field-Theoretic treatment:
  1. Avoids indices running on the many particles;
  2. Fermionic antisymmetrization automatically imposed;
  3. Treats systems with varying number of particles;
  4. Opens to Green’s functions or Propagators which have condensed inside all the Physics (all the observables) of the system. Spectral Function \( A(k, \omega) = \text{Im} \, G(k, \omega) \)

\[ G(x_1, x_2) \text{ instead of } \Psi(x_1, \ldots, x_N) \]
MBPT in brief

- Many-Body “Perturbation” Theory does not work as a Perturbation Theory - the perturbation is not small -
- 1st order MBPT = Hartree-Fock;
- 2nd order not small, the series does not converge -> need to resort to complicated partial resummations of diagrams;
- Better functional and iterative methods: Hedin equations.
- Iterative solution of Hedin equations = exact solution of the problem!
Hedin Equations (PR 139, 3453 (1965))

\[ G = G^{(0)} + G^{(0)} \Sigma G \]
\[ W = v + v \Pi W \]
\[ \Sigma_M = iG W \Gamma \]
\[ \Pi = -iGG \Gamma \]
\[ \Gamma = 1 + \frac{\delta \Sigma_M}{\delta G} GG \Gamma \]

- So far, nobody has solved Hedin Equations for a real system
- Need for approximations
Hedin Equations: GW approximation

\[ G = G^{(0)} + G^{(0)} \Sigma G \]
\[ W = v + v \Pi W \]
\[ \Sigma_M = iGW\Gamma \]
\[ \Pi = -iGG\Gamma \]
\[ \Gamma = 1 + \frac{\delta \Sigma_M}{\delta G} GG\Gamma \]

Reviews on GW:
F. Aryasetiawan and O. Gunnarsson, RPP 1998
W.G. Aulbur, L. Jonsson and J.F. Wilkins, 1999

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Hedin's GW Approximation for the Self-Energy

GW Self-Energy

$$\Sigma^G_W(x_1, x_2) = iG(x_1, x_2)W(x_1, x_2)$$

Dynamical Screened Interaction $W$

Green Function or Electron Propagator $G$

Hartree-Fock Self-Energy

$$\Sigma_x(x_1, x_2) = iG(x_1, x_2)v(x_1, x_2)$$

Bare Coulombian Potential $v$
Quasiparticle Energies

Kohn-Sham equation

\[\begin{align*}
\left(-\frac{1}{2}\partial_r^2 + v_{\text{ext}}(r) + v_{\text{H}}(r)\right)\phi_1(r) + v_{\text{xc}}(r)\phi_1(r) &= \epsilon_i^{KS} \phi_1(r) \\
\end{align*}\]

KS energies (no physical meaning)

Hartree-Fock equation

\[\begin{align*}
\left(-\frac{1}{2}\partial_r^2 + v_{\text{ext}}(r) + v_{\text{H}}(r)\right)\phi_1(r) + \int dr' \Sigma_x(r, r')\phi_1(r') &= \epsilon_i^{HF} \phi_1(r) \\
\end{align*}\]

Exchange (Fock) operator (non-local)

Quasiparticle equation

\[\begin{align*}
\left(-\frac{1}{2}\partial_r^2 + v_{\text{ext}}(r) + v_{\text{H}}(r)\right)\phi_1(r) + \int dr' \Sigma(r, r', \omega = \epsilon_i^{QP})\phi_1(r') &= \epsilon_i^{QP} \phi_1(r) \\
\end{align*}\]

QP energies

Self-Energy (non-local and energy dependent)

Exchange-Correlation potential (local)

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The GW Approximation corrects the LDA band-gap problem (underestimation) and the HF overestimation and it is in good agreement with the Experiment.

The GW Approximation correctly predicts electron Addition/Removal excitations (Photoemission Spectroscopy).

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GW and the Photoemission Band Gap

Adapted from Schiffelgard et al. PRL 2006
GW band plot

Graphite

J. Serrano et al, unpublished

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GW spectral function

Silicon
GW (AC) Spectral Function (bands 1-8) at Γ

<table>
<thead>
<tr>
<th>Transition</th>
<th>GW</th>
<th>EXP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Γ1v -&gt; Γ'25v</td>
<td>11.73</td>
<td>12.5 ± 0.6</td>
</tr>
<tr>
<td>Γ'25v -&gt; Γ15c</td>
<td>3.23</td>
<td>3.40</td>
</tr>
<tr>
<td>Γ'25v -&gt; Γ'2c</td>
<td>3.96</td>
<td>4.2</td>
</tr>
</tbody>
</table>

V. Olevano, unpublished
Vanadium Oxide (VO$_2$)

Phase transition at $T_c = 340$ K

- Monoclinic
- Insulator
- Paramagnetic

- Rutile
- Metal
- Paramagnetic

Mechanism? Role of correlation? Peierls? or Mott-Hubbard?

Monoclinic VO$_2$

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>DFT-LDA</th>
<th>SC-COHSEX</th>
<th>GW on SC-COHSEX</th>
<th>EXP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap VO$_2$</td>
<td>7.6</td>
<td>0</td>
<td>0.8</td>
<td>0.7</td>
<td>0.6</td>
</tr>
</tbody>
</table>

M. Gatti et al, to be published
Vanadium Oxide (VO₂)

- Need for self-consistency
- But static GW (COHSEX) self-consistent already ok!

M. Gatti et al, to be published

From perturbative $G_0W_0$ corrections towards self-consistent calculations

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>DFT-LDA</th>
<th>GW on DFT</th>
<th>SC-COHSEX</th>
<th>GW on SC-COHSEX</th>
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<tbody>
<tr>
<td>VO₂</td>
<td>7.6</td>
<td>0</td>
<td>0 !!!</td>
<td>0.8</td>
<td>0.7</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Quantum Transport and NEGF

GW approximation
and e-e scattering effects
Quantum Transport: The Working Bench

We need:
- a First Principle description of the Electronic Structure

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Non-Equilibrium Green's Function Theory (NEGF)  
(improperly called Keldysh)

Much more complete framework, allows to deal with:

- **Many-Body** description of **incoherent** transport (electron-electron interaction, electronic correlations and also electron-phonon);
- **Out-of-Equilibrium** situation;
- Access to **Transient** response (beyond Steady-State);
- Reduces to Landauer-Buttiker for coherent transport.

The theory is due to the works of Schwinger, Baym, Kadanoff and Keldysh
Many-Body Finite-Temperature formalism

\[ \hat{H} = \hat{T} + \hat{V} + \hat{W} \]  

many-body

\[ \bar{O} = \frac{\sum_{i} e^{-\beta E_i} \langle \Psi_i | \hat{O} | \Psi_i \rangle}{\sum_{i} e^{-\beta E_i}} = \text{tr} \left[ \hat{\rho} (\hat{H}) \hat{O} \right] \]  

observable

\[ \hat{\rho} (\hat{H}) = \frac{e^{-\beta \hat{H}}}{\text{tr} \left[ e^{-\beta \hat{H}} \right]} \]  

statistical weight
Negf formalism

\[ \hat{H}(t) = \hat{H} + \hat{U}(t) = \hat{T} + \hat{V} + \hat{W} + \hat{U}(t) \]

Hamiltonian

many-body + time-dependence

\[ \bar{o}(t) = \text{tr} \left[ \hat{\rho}(\hat{H}) \hat{o}_H(t) \right] \quad t > t_0 \]

Observable

Statistical weight referred to the unperturbed Hamiltonian and the equilibrium situation before \( t_0 \)

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\[ \hat{o}_H(t) = \hat{s}(t_0, t) \hat{o}(t) \hat{s}(t, t_0) \]  
Heisenberg representation

\[ \hat{s}(t, t_0) = T \left[ \exp \left( -i \int_{t_0}^{t} dt' \hat{H}(t') \right) \right] \]  
evolution operator

\[ \hat{s}(t_0 - i \beta, t_0) = e^{-\beta \hat{H}} \]  
trick to put the equilibrium weight into the evolution

\[ \bar{o}(t) = \frac{\text{tr} [\hat{s}(t_0 - i \beta, t_0) \hat{s}(t_0, t) \hat{o}(t) \hat{s}(t, t_0)]}{\text{tr} [\hat{s}(t_0 - i \beta, t_0)]} \]

\[ \bar{o}(t) = \frac{\text{tr} [T_C [\exp (-i \int_C dt' \hat{H}(t')) \hat{o}(t)]]}{\text{tr} [T_C [\exp (-i \int_C dt' \hat{H}(t'))]]} \]

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NEG F Fundamental Kinetic Equations

\[ G^r = \left[ \omega - H_c - \Sigma^r \right]^{-1} \]

\[ G^< = G^r \Sigma < G^a \]

\[ G^> = G^r \Sigma > G^a \]

Caveat!: in case we want to consider also the transient, then we should add another term to these equations:

\[ G^< = G^r \Sigma < G^a + (1 + G^r \Sigma^r) G^0^< (1 + \Sigma^a G^a) \]

Keldysh equation

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Quantum Transport: composition of the Self-energy

\[ \Sigma^{r<} = \sum_p \Sigma_p^{r<} + \Sigma_{e\text{-}ph}^{r<} + \Sigma_{e\text{-}e}^{r<} \]

- Interaction with the leads
- Electron-phonon interaction
- Electron-electron interaction

Critical point:

- Choice of relevant approximations for the Self-Energy and the in/out scattering functions

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Our Self-Energy: GW. Why GW?

Selfconsistent Hartree Fock

\[ G^0W^0 \]

Direct and Exchange terms:
Band Structure Renormalization

\[ G_{2}^{HF} = G + \]
\[ G_{2}^{GW} = G^0 + W^0 \]

Collisional Term:
Band structure renormalization for Electronic Correlations +
e-e Scattering ->
Conductance Degrading Mechanisms, Resistance, non-coherent transport

\[ \sum{>,<} = 0 \]
\[ \sum{>,<} \neq 0 \]
GW and e-e scattering and correlation effects

Gold Atomic Infinite Chain

Loss of Conductance:
- Appearance of Resistance
- Appearance of Satellite Conductance Channels

Broadening of the peaks:
- QP lifetime

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P. Darancet et al, PRB 2007
C / V characteristics: GW vs EXP

Gold Atomic Infinite Chain

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MBPT quantities as density-functionals: vertex corrections beyond GW
Hedin Equations

\[ G = G^{(0)} + \Sigma_{M} \]

\[ W = w + \Pi \]

\[ \Sigma_{M} = 1 + \Gamma \]

\[ \Pi = 1 \]

\[ \Gamma = 1 + \frac{\delta \Sigma_{M}}{\delta V_{c}} + \frac{\delta \Sigma_{M}}{\delta G} \frac{\delta G}{\delta V_{c}} + \frac{\delta \Sigma_{M}}{\delta G} GG \Gamma \]

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MBPT quantities as density-functionals: local vertex corrections beyond GW

\[ \Gamma(1,2;3) = 1 + \frac{\delta \Sigma_{1,2}}{\delta V_c} + \frac{\delta G}{\delta \rho} + \frac{\delta \Sigma_{1,2}}{\delta V_c} G(5,7) G(6,8) G(7,8;3) \]

\[ \Gamma(1,2;3) = 1 + \frac{\delta \Sigma_{1,2}}{\delta V_c} + \frac{\delta G}{\delta \rho} + \frac{\delta \Sigma_{1,2}}{\delta V_c} \Pi(4,3) \]

\[ \Gamma(1,2;3) = 1 + \delta(1,2) f_{xc}^{\text{eff}}(2,4) \Pi(4,3) + \Delta \Gamma(1,2;3) \]

<table>
<thead>
<tr>
<th></th>
<th>Direct gap</th>
<th>LDA</th>
<th>GW</th>
<th>Local (\Delta)</th>
<th>EXP</th>
<th></th>
<th>Direct gap</th>
<th>COHSEX</th>
<th>GW</th>
<th>Local (\Delta)</th>
<th>EXP</th>
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</thead>
<tbody>
<tr>
<td>Si</td>
<td>2.53</td>
<td>3.27</td>
<td>3.28</td>
<td>3.40</td>
<td></td>
<td></td>
<td>Si</td>
<td>3.64</td>
<td>3.30</td>
<td>3.32</td>
<td>3.40</td>
</tr>
<tr>
<td>Ar</td>
<td>8.18</td>
<td>12.95</td>
<td>12.75</td>
<td>14.2</td>
<td></td>
<td></td>
<td>Ar</td>
<td>14.85</td>
<td>14.00</td>
<td>14.76</td>
<td>14.2</td>
</tr>
</tbody>
</table>

F. Bruneval et al., PRL (2005)
Generalized Sham-Schlüter Equation: link between non-locality and frequency dependence
Sham-Schlüter Equation

\[ G = G^{KS} + G^{KS}(\Sigma - V_{xc})G \]

AND

\[ G^{KS}(x, x) = G(x, x) = -i \rho(r) \]

Dyson Equation

The density of the Kohn-Sham system is by construction equal to the exact density

\[ V_{xc} = (G^{KS}G)^{-1}G^{KS}\Sigma G \]

Sham-Schlüter Equation, PRL (1983)

\[ V_{xc} = (GG)^{-1}G\Sigma G \]

Linearised SSE

\[ V_{x}^{EXX} = (GG)^{-1}G\Sigma_x G \]

Example: OEP EXact eXchange

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Generalize SSE

- Spectroscopy calls for the description of new quantities (ex. bandgap), beyond the ground-state density.
- I want the simpler one-body potential $V^{SF}$ able to provide the Green's function $G^{SF}$ of a Fictitious (Kohn-Sham-like) system such as by construction yields the exact density AND the exact photoemission bandgap.
- You can read the bandgap for example just only on the trace of the spectral function.
**Generalized Sham-Schlüter Equation**

\[ \mathbf{G} = \mathbf{G}^{\text{SF}} + \mathbf{G}^{\text{SF}}(\Sigma - V^{\text{SF}})\mathbf{G} \quad \text{Dyson Equation} \]

**AND**

\[ \mathbf{G}^{\text{SF}}(x, x) = \mathbf{G}(x, x) = -i\rho(r) \quad \text{The density of the SF system is equal to the exact density} \]

**AND**

\[ |\Im \mathbf{G}^{\text{SF}}(r, r, \omega)| = |\Im \mathbf{G}(r, r, \omega)| = A(r, r, \omega) \quad \text{The Trace of the spectral function is the exact one} \]

\[ V^{\text{SF}}(r, \omega) = \int \left( \Im \left[ \mathbf{G}^{\text{SF}}(r, r_1, \omega) \mathbf{G}(r_1, r, \omega) \right] \right)^{-1} \Im \left[ \mathbf{G}^{\text{SF}}(r_1, r_2, \omega) \Sigma(r_2, r_3, \omega) \mathbf{G}(r_3, r_1, \omega) \right] \]

This is the real local and dynamical potential that yields the correct density and the correct bandgap!
Transforming non-locality

Hartree-Fock self-energy
on Jellium \( r_s = 2.07 \)

into frequency-dependence

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Conclusions

- **GW** Quasiparticle band gaps and band plots are in *good agreement* with Photoemission spectroscopy. But the statistics is not yet quite large. We have still to see the role of self-consistence and to which extent GW works on strongly-correlated systems.

- **NEGF – GW** seems to introduce e-e scattering effects, correlation and lost-of-coherence in Quantum Transport.

- Setting MBPT quantities as *density-functionals* could be a good way to address *vertex corrections beyond GW*.

- Thank to Generalized SSE, we have introduced an effective framework which allows to get rid of the complicated *non-local self-energy* and have a simpler *on-body local potential* which yields the right bandgap. The effective potential is real but needs to be *frequency-dependent*.  

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The ABINIT-GW code in few words

- **The thing**: GW code in Frequency-Reciprocal space on a PW basis.
- **Purpose**: Quasiparticle Electronic Structure.
- **Systems**: Bulk, Surfaces, Clusters.
- **Approximations**: GW, Plasmon-Pole model and RPA on W, non Self-Consistent $G^0 W^{RPA}$, first step of self-consistency on W and G.

ABINIT is distributed **Freeware** and **Open Source**
under the terms of the GNU General Public Licence (GPL).
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(R.W. Godby, L. Reining, G. Onida, V. Olevano, G.M. Rignanese, F. Bruneval)