Electronic excitations, spectroscopy and quantum transport from \textit{ab initio} theory

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Résumé

• Motivation: Spectroscopy and Quantum Transport
• The many-body problem
• TDDFT from EELS to optical spectra
• MBQFT, GW approximation and beyond
• Quantum Transport beyond DFT-Landauer
• Conclusions and Perspectives
Optical Spectroscopy

incident photon → sample → reflected photon → transmitted photon → detector

Cardona et al.
Optical Spectroscopies

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Dielectric, Energy-Loss Spectroscopy (EELS)

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Synchrotron Radiation Spectroscopy (IXSS)

X rays

Sample

Detector

Silicon

IXSS, Dynamic Structure Factor

Sturm et al.
PRL 48, 1425 (1982),
(ESRF, Grenoble)

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Photoemission (ARPES)

Direct photoemission

\[ A = \frac{1}{\pi} |\Im G| \]

Inverse photoemission

LURE, Orsay

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Quantum Transport
Spectroscopy

provides informations on:

Atomic Structure
Electronic Structure

Knowledge (calculation) of:

Atomic Structure
Electronic Structure

allows to derive:

Excitations

1) To understand and explain observed phenomena;
2) To offer experimentalists reference data;
3) To predict properties before the synthesis, the experiment.
Schrödinger Equation (1926)

\[ h = -\frac{1}{2} \partial_r^2 + v(r) \]

\[ h \phi(r) = \epsilon \phi(r) \]

P. Dirac: “Chemistry has come to an end!”
But so far Chemistry has not come to an end ... because of:

The Many-Body problem

\[ H = -\frac{1}{2} \sum_{n=1}^{N} \partial_{r_n}^2 + \sum_{n=1}^{N} v(r_n) + \frac{1}{2} \sum_{n \neq m=1}^{N} \frac{1}{|r_n - r_m|} \]

where \( N \) can be up to the Avogadro number \( 10^{23} \)!!!

\[ H \Phi(r_1, \ldots, r_N) = E \Phi(r_1, \ldots, r_N) \]

many-body wavefunction

many-body e-e interaction

kinetic

external potential

e-ions interaction

\[ w(r, r') = \frac{1}{|r - r'|} \]
The many-body non-interacting system

\[ H = -\frac{1}{2} \sum_{n=1}^{N} \partial^2_{r_n} + \sum_{n=1}^{N} \nu(r_n) + \frac{1}{2} \sum_{n \neq m=1}^{N} \frac{1}{|r_n - r_m|} \]

\[ H = -\frac{1}{2} \sum_{n=1}^{N} h(r_n) \quad h(r) = -\frac{1}{2} \partial^2_r + \nu(r) \quad \text{Factorizable Hamiltonian} \]

\[ h \phi_i(r) = \epsilon_i \phi_i(r) \quad \text{Solvable single-particle Schrödinger equation} \]

\[ E_0 = \sum_{i=1}^{N} \epsilon_i \quad \text{Many-body ground-state total energy} \]

\[ \Phi_0(r_1, \ldots, r_N) = \phi_1(r_1) \cdot \phi_2(r_2) \cdots \phi_N(r_N) \quad \text{Total many-body ground state wavefunction} \]
First Attempts: Thomas-Fermi and Hartree-Fock

- Thomas-Fermi: does not predict bonding among atoms (molecules and solids cannot form)
  - LDA too crude approximation on the kinetic energy
  - Oversimplified e-e classical interaction (and the quantistic exchange?)
- Hartree-Fock: too large band dispersions, too large band gaps, singularities at the Fermi level (density of states \( \rightarrow 0 \) logarithmically, against conductivity, superconductivity; electron velocity logarithmically infinite)
  - Misses what is by now on defined as the correlation among the electrons

\[ E_c = E - E_{HF} \]
Condensed Matter Theory

Models
- simplify and search analytical solutions
- Anderson, Hubbard model
- renounce to exact analytical solutions even on models and address to numerical

Numerical
- numerical solution but keeping all degrees of freedom

Semi-Empirical
- Phenomenological

Ab Initio
- Microscopical

CI
- DFT
- QMC
- GW, BSE
- DMFT

Tight-binding
**DFT, Density-Functional Theory**

**Hohenberg-Kohn Theorem (1964):**
The electronic density is one-to-one with the external potential.

\[ \nu(\mathbf{r}) \iff \rho(\mathbf{r}) \]

\[ \rho(\mathbf{x}) \text{ instead of } \Psi(x_1, \ldots, x_N) \]

\[ \bar{o} = \langle \Psi | \hat{O} | \Psi \rangle = o[\rho(\mathbf{r})] \]

\[ E[\rho(\mathbf{r})] \quad \frac{\delta E[\rho(\mathbf{r})]}{\delta \rho} = 0 \to \rho_0(\mathbf{r}), \quad E_0 = E[\rho_0(\mathbf{r})] \]

\[ E[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + V[\rho(\mathbf{r})] + E_H[\rho(\mathbf{r})] + E_{xc}[\rho(\mathbf{r})] \]
DFT, Kohn-Sham scheme

Kohn-Sham (1965):

\[
-\frac{\partial^2 r^2}{2} + v_{KS}(r) \phi_i(r) = \epsilon_i \phi_i(r)
\]

\[
v_{KS}(r) = v(r) + \int dr' \frac{\rho(r')}{|r-r'|} + v_{xc}[\rho](r)
\]

\[
\rho(r) = \sum_i^{occ} |\phi_i(r)|^2
\]

let's introduce a ficticious non-interacting \((W=0)\) system KS whose density is the same \(\rho(r)\) of the interacting real system.

Kohn-Sham system

Kohn-Sham equations

Exchange and Correlation? -> LDA using \(e_c^{\text{HEG}}\)

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What DFT can predict

(normal error 1~2% in the 99% of cond-mat systems)

- Lattice Parameters, Atom Positions (XRD)
- Total Energy, Phase Stability
- Electronic Density (SEM, XRS, STM)
- Elastic Constants
- Phonon Frequencies (IR, Neutron scattering)

that is, all **Ground State** Properties!
DFT and the Atomic Structure of strongly correlated VO$_2$

- DFT is an in principle exact theory for ground-state properties even on strongly correlated systems

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>
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<tbody>
<tr>
<td>a</td>
<td>5.659 Å</td>
<td>5.549 Å</td>
<td>5.7517 ± 0.0030 Å</td>
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<tr>
<td>b</td>
<td>4.641 Å</td>
<td>4.522 Å</td>
<td>4.5378 ± 0.0025 Å</td>
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<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>α</td>
<td>121.46</td>
<td>121.73°</td>
<td>122.646° ± 0.096</td>
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Monoclinic Insulator (T < 340 K)

M. Gatti et al., PRL 2007
Citation Statistics from 110 years of Physical Review


Table 1. Physical Review Articles with more than 1000 Citations Through June 2003

<table>
<thead>
<tr>
<th>Publication</th>
<th># cites</th>
<th>Av. age</th>
<th>Title</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>
</tr>
<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>
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<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>
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<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>

DFT = Standard Model of Cond-Mat

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What DFT cannot predict

- Bandplot
- Bandgap (Metal/Insulator/Semiconductor)
- Optical and Dielectric properties
  that is, all *Excited State* Properties!

You can use DFT to predict all such properties but it cannot be blamed if it does not succeed.
Possible *ab-initio* Theories for the Excited States

- **TDDFT** (Time-Dependent Density-Functional Theory) in the Approximations:
  - RPA
  - TDLDA
  - beyond
- **MBPT** (Many-Body Theory) in the Approximations:
  - GW
  - BSE (Bethe-Salpeter Equation approach)
TDDFT
What is TDDFT?

- TDDFT is an extension of DFT
- TDDFT is a DFT with time-dependent external potential:

\[
v(r) \iff \rho(r)
\]

Static Ionic Potential

\[
\begin{align*}
\rho(r,t) \text{ instead of } \Psi(r_1, \ldots, r_N, t)
\end{align*}
\]

\text{time-dependent density as fundamental degree of freedom}

\rightarrow \text{ no need for } \Psi

Valerio Olevano, Introduction to TDDFT
<table>
<thead>
<tr>
<th>DFT</th>
<th>VS</th>
<th>TDDFT</th>
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</thead>
<tbody>
<tr>
<td>Hohenberg-Kohn:</td>
<td>Runge-Gross:</td>
<td></td>
</tr>
<tr>
<td>$v(r) \Leftrightarrow \rho(r)$</td>
<td></td>
<td>$v(r,t) \Leftrightarrow \rho(r,t)$</td>
</tr>
<tr>
<td><strong>The Total Energy:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\langle \Phi</td>
<td>\hat H</td>
<td>\Phi \rangle = E[\rho]$</td>
</tr>
<tr>
<td>are unique functionals of the density.</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>The extrema of the:</strong></td>
<td><strong>The stationary points of the:</strong></td>
<td></td>
</tr>
<tr>
<td>Total Energy</td>
<td>Action</td>
<td></td>
</tr>
<tr>
<td>$\frac{\delta E[\rho]}{\delta \rho(r)} = 0$</td>
<td>$\frac{\delta A[\rho]}{\delta \rho(r,t)} = 0$</td>
<td></td>
</tr>
<tr>
<td>give the exact density of the system:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\rho(r)$</td>
<td>$\rho(r,t)$</td>
<td></td>
</tr>
</tbody>
</table>

Valerio Olevano, Introduction to TDDFT
DFT vs TDDFT

Kohn-Sham:

\[ \rho(r) = \sum_{i=1}^{N} |\phi_{i}^{KS}(r)|^2 \]

\[ v^{KS}(r) = v(r) + \int dr' \frac{\rho(r')}{|r-r'|} + \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \]

\[ H^{KS}(r) \phi_{i}^{KS}(r) = \epsilon_{i}^{KS} \phi_{i}^{KS}(r) \]

Runge-Gross:

\[ \rho(r,t) = \sum_{i=1}^{N} |\phi_{i}^{KS}(r,t)|^2 \]

\[ v^{KS}(r,t) = v(r,t) + \int dr' \frac{\rho(r',t)}{|r-r'|} + \frac{\delta A_{xc}[\rho]}{\delta \rho(r,t)} \]

\[ i\partial_t \phi_{i}^{KS}(r,t) = H^{KS}(r,t) \phi_{i}^{KS}(r,t) \]

Valerio Olevano, Introduction to TDDFT
Linear Response TDDFT: fundamental equations

\[ \epsilon^{-1} = 1 + v_c \chi \]

Dielectric Function \( \epsilon \) → Observables

ABS = \( \text{Im} \, \epsilon \)

EELS = \(-\text{Im} \, \epsilon^{-1}\)

\[ \chi = \chi^{KS} + \chi^{KS}(v_c + f_{xc}) \chi \]

Polarizability \( \chi \)

Coulombian (Local-Fields)

Exchange-Correlation Kernel

\[ \chi^{KS}(r, r', \omega) = \sum_{ij} (f_i - f_j) \frac{\phi_i(r) \phi_j^*(r') \phi_i^*(r') \phi_j(r')}{\omega - (\epsilon_i - \epsilon_j) - i\delta} \]

Independent-Particle Polarizability (Adler-Wiser)

\[ f_{xc} = \frac{\delta v_{xc}}{\delta \rho} = ? \]

Exchange-Correlation Kernel

approximations required
Exchange-Correlation kernel $f_{xc}$ approximations

- **RPA**: Random Phase Approximation = neglect of the exchange-correlation effects (in the response)

$$f_{xc}^{RPA} = 0$$

- **ALDA**: Adiabatic Local Density Approximation

$$f_{xc}^{ALDA} = \frac{\delta V_{xc}^{LDA}}{\delta \rho} \omega = 0$$
dp code
(dielectric properties)

• **Linear-Response TDDFT** code in **Frequency-Reciprocal** Space on **PW** basis.
• **Purpose:** Dielectric and Optical Properties (Absorption, Reflectivity, Refraction, EELS, IXSS, CIXS,..)
• **Systems:** bulk, surfaces, clusters, molecules, atoms (through supercells) made of insulator, semiconductor and metal elements.
• **Approximations:** RPA, ALDA, GW-RPA, LRC, non-local kernels, …, with and without LF (Local Fields).
• **Machines:** Linux, Compaq, IBM, SG, Nec (6GFlop) , Fujitsu.
• **Libraries:** BLAS, Lapack, CXML, ESSL, IMSL, ASL, Goedecker, FFTW.
• **Interfaces:** ABINIT, Milan-CP, PWSCF, SPHINGx

http://www.dp-code.org
TDDFT and EELS in Solids

- TDLDA (but also RPA) in good agreement with experiment;
- Importance of Local-Field (LF) effects.
Local-Fields Effects (LF)

\[ \delta \mathbf{v}_G^{tot} = \sum_{G'} \varepsilon_{GG'}^{-1} \delta \mathbf{v}_{G'}^{ext} \]

Effect of the \( \varepsilon \) non diagonal elements (density inhomogeneities ~ atomic structure)

\[ \delta \mathbf{v}_{ext} \quad + \quad \varepsilon^{-1} \sim \rho \quad \rightarrow \quad \delta \mathbf{v}_{tot} \]

\[ \varepsilon^{NLF}_M(q, \omega) = \varepsilon_{00}(q, \omega) \]

Macroscopic Dielectric Function \( \varepsilon \) without local-fields effects (NLF)

Valerio Olevano, Introduction to TDDFT
Atomic Structure and Local-Field Effects

- RPA is enough. But when inhomogeneities are present, Local-Field effects should be absolutely taken into account.
- Quantitative Agreement

A. Marinopoulos et al. PRL 89, 76402 (2002)
LFE in Reduced-Dimensionality Atomic Structures

- LF explain depolarization effects both for Nanotubes and Graphene in perpendicular polarization optical spectra
In Solids all Dielectric Properties related to the Energy-Loss function are well described by TDDFT in RPA with an improvement in ALDA.

Weissker et al.
Optical Properties in Solids: Si

- The TDLDA cannot reproduce Optical Properties in Solids.
- We miss both:
  1. **Self-Energy (electron-electron) effects** (red shift of the entire spectrum)
  2. **Excitonic (electron-hole) effects** (underestimation of the low-energy part)
New Approximations:

LRC
(Long Range Contribution only)

Nanoquanta kernel
(or mapping BSE on TDDFT)
LRC Approximation

\[ \chi = \chi^{(0)} + \chi^{(0)} \left( v_c + f_{xc} \right) \chi \]

long-range coulombian

ALDA: local kernel

\[ f_{xc}^{LRC} = \frac{\alpha}{q^2} \] Long Range Contribution only

\[ \alpha = -4.6 \varepsilon^{-1} \] Inversely proportional to the screening
The LRC approximation makes TDDFT work also on Optical Properties in Solids.
Nanoquanta kernel

\[ f_{xc} = G \quad W \quad \chi_0^{-1} \]

Solid Argon: Bound Excitons

The Nanoquanta kernel makes TDDFT reproduce even **Bound Excitons**

- The Nanoquanta kernel makes TDDFT reproduce even **Bound Excitons**
Conclusions on TDDFT

- TDDFT can today reproduce both EELS and Optical spectra
- Careful choice of the approximation needed:
  - LF are crucial in reduced dimensionality atomic structure systems
  - TDLDA beyond RPA on EELS/IXSS spectra at high $q$
  - Beyond TDLDA (LRC, Nanoquanta) for optical properties

Perspectives

- Improve the algorithms
- Search for a truly density-functional kernel
Photoemission (ARPES)

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$A = \frac{1}{\pi} |\tilde{G}|$

Direct photoemission

Inverse photoemission

LURE, Orsay

Detector

Sample

Sample
What is MBQFT?

• It is a Quantum Field Theory, based on second quantization of operators and a Green’s function formalism, addressed to the solution of the many-body problem.

• 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.

\[ G(x_1, x_2) \text{ instead of } \Psi(x_1, \ldots, x_N) \]
The Green's function or propagator

\[ G(x_1, x_2) = -i \langle \Psi_0 | T \{ \psi(x_1) \psi^\dagger(x_2) \} | \Psi_0 \rangle \]  
\text{definition}

\[ \rho(x) = i G(x, x) \quad \text{G provides all ground-state observables} \]

\[ G(r_1, r_2, \omega) = \sum_s \frac{\psi_s(r_1) \psi^*_s(r_2)}{\omega - \epsilon_s \pm i \eta} \quad \text{G contains the excitations energies} \]

\[ A(k, \omega) = -\pi^{-1} \Im G(k, \omega) \quad \text{G provides the spectral function observable in photoemission} \]
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;
- Iterative solution of Hedin equations = exact solution of the problem!
Hedin Equations (PR 139, 3453 (1965))

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

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

\[ G = G^{(0)} + G^{(0)} \sum G \]
\[ W = \nu + \nu \Pi W \]
\[ \sum_M = iGW \Gamma \]
\[ \Pi = -iGG \Gamma \]
\[ \Gamma = 1 + \frac{\delta \sum_M}{\delta G} GG \Gamma \]

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

Valerio Olevano, CNRS Grenoble
Hedin's GW Approximation

\[ \Gamma(x_1, x_2 ; x_3) = \delta(x_1, x_2) \delta(x_1, x_3) \]

GW Self-Energy

\[ \Sigma^{GW}(x_1, x_2) = i G(x_1, x_2) W(x_1, x_2) \]

Dynamical Screened Interaction \( W \)

Green Function or Electron Propagator \( G \)

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Hedin's GW Approximation for the Self-Energy

\[ \Sigma_{GW}(x_1, x_2) = iG(x_1, x_2)W(x_1, x_2) \]

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 \( v \)

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Quasiparticle Energies

DFT Kohn-Sham equation

\[ -\frac{1}{2} \nabla^2 \phi_i(r) + v_{\text{ext}}(r) + v_H(r) \phi_i(r) + v_{\text{xc}}(r) \phi_i(r) = \epsilon_i^{\text{KS}} \phi_i(r) \]

KS energies (no physical meaning)

Hartree-Fock equation

\[ -\frac{1}{2} \nabla^2 \phi_i(r) + v_{\text{ext}}(r) + v_H(r) \phi_i(r) + \int dr' \Sigma_x(r, r') \phi_i(r') = \epsilon_i^{\text{HF}} \phi_i(r) \]

Exchange (Fock) operator (non-local)

Quasiparticle equation

\[ -\frac{1}{2} \nabla^2 \phi_i(r) + v_{\text{ext}}(r) + v_H(r) \phi_i(r) + \int dr' \Sigma(r, r', \omega = \epsilon_i^{\text{QP}}) \phi_i(r') = \epsilon_i^{\text{QP}} \phi_i(r) \]

QP energies

Self-Energy (non-local and energy dependent)

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Calculating the Band-Gap: inadequacy of HF or DFT

- **HF always overestimates** the bandgap.
- The **DFT** 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.

<table>
<thead>
<tr>
<th>Material</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>
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<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>
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</table>

A. Svane, PRB 1987
GW and the Photoemission Band Gap

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
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<tr>
<td>α-Sn</td>
<td>2.60</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Our calculation but reproducing:
M.S. Hybertsen and S.G. Louie (1986)

• 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).
GW and the Photoemission Band Gap

The graph shows a comparison between the calculated and experimental (ARPES) gap values for various materials. The calculated gap values are represented by different symbols for different methods: HF, LDA, and $G^0W^0$. The experimental gap values are shown along the x-axis, while the calculated gap values are plotted on the y-axis. The materials plotted include $\alpha$-Sn, InSb, InAs, Ge, GaSb, InP, GaAs, AlSb, CdS, CdSe, CdTe, AlAs, SiC, GaP, AIP, AlP, Si, ZnSe, ZnS, GaN, and ZnTe, with some materials having a change in their gap values depicted with arrows (e.g., AlAn, Li$_2$O, MgO, LiCl). The blue dashed line indicates the correlation between calculated and experimental gaps.
GW band plot

Graphene band plot

Energy [eV]

Γ K M Γ

P. E. Trevisanutto, PRL 2008
GW spectral function

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

\[
\begin{align*}
\Gamma_{1v} & \rightarrow \Gamma'_{25v} & 11.73 & \quad 12.5 \pm 0.6 \\
\Gamma'_{25v} & \rightarrow \Gamma_{15c} & 3.23 & \quad 3.40 \\
\Gamma'_{25v} & \rightarrow \Gamma'_{2c} & 3.96 & \quad 4.2
\end{align*}
\]
Vanadium Oxide ($\text{VO}_2$)

Phase transition at $T_c = 340 \text{ K}$

- Monoclinic
- Insulator
- Paramagnetic

- Rutile
- Metal
- Paramagnetic

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

Monoclinic $\text{VO}_2$

Bandgap

$\text{VO}_2$

<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></td>
<td>7.6</td>
<td>0</td>
<td>0.8</td>
<td>0.7</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Conclusions on MBQFT GW

• *Ab initio* GW describe fairly well excited state properties and photoemission spectroscopy.

• The GW approximation is in good agreement with ARPES bandplots/bandgaps.

Perspectives

• Is GW working well on strongly correlated systems?

• In case of limits (for example, satellite descptions), how to go beyond GW? : vertex corrections.

• Beyond MBQFT
Quantum Transport problem

\[ V = \mu_L - \mu_R \]

**Nanoscale Conductor:**
finite number of states, out of equilibrium, dissipative effects

**Mesoscopic Leads:**
large but finite number of states, partial equilibrium, ballistic

Macroscopic Reservoirs:
continuum of states, thermodynamic equilibrium

We need:
- a First Principle description of the **Atomic** and **Electronic Structure**
Landauer Theory

\[ C(\epsilon) = \frac{2e^2}{h} M(\epsilon) T(\epsilon) \]

Landauer Formula

Left Contact \( \mu_L \)

Right Contact \( \mu_R \)

\[ T(\epsilon) \]

Conductance \[ \left[ \frac{2e^2}{h} \right] \]

\[ \epsilon [eV] \]

R. Landauer, IBMJ. Res. Dev. (1957)
Landauer formalism and Fisher-Lee formula in the Principal Layers approach

\[
\begin{pmatrix}
G_L & G_{LC} & G_{LCR} \\
G_{CL} & G_C & G_{CR} \\
G_{RCL} & G_{RC} & G_R
\end{pmatrix} = \begin{pmatrix}
(\epsilon - H_L) & -H_{LC} & 0 \\
-H_{LC}^\dagger & (\epsilon - H_C) & -H_{CR} \\
0 & -H_{CR}^\dagger & (\epsilon - H_R)
\end{pmatrix}^{-1}
\]

\[G_C = (\epsilon - H_C - \Sigma_L - \Sigma_R)^{-1}\] conductor Green's functions

\[\Sigma_L = H_{LC}^\dagger g_L H_{LC}\] lead self-energies

\[\Sigma_R = H_{CR} g_R H_{CR}^\dagger\]

\[g_{L,R} = (\epsilon - H_{L,R})^{-1}\] lead bulk Green's functions

\[\Gamma_{L,R} = i[\Sigma_{L,R}^r - \Sigma_{L,R}^a]\] lead injection rate

\[\bar{T} = tr[\Gamma_L G_C^r \Gamma_R G_C^a]\] Fisher-Lee formula (transmittance)
Landauer on top of DFT

What to take for the hamiltonian? \[ H = \begin{pmatrix} H_L & H_{LC} & 0 \\ H_{LC}^\dagger & H_C & H_{CR} \\ 0 & H_{CR}^\dagger & H_R \end{pmatrix} \]

DFT Kohn-Sham hamiltonian! But projected in Real Space!
Landauer approach

Correctly describes:

✔ Contact Resistance
✔ Scattering on Defects, Impurities
✔ Non-commensurability patterns
DFT-Landauer drawbacks

✗ The DFT KS electronic structure is in principle **unphysical**.
✗ DFT, no Open Systems, no Out-of-Equilibrium Theory:
  ✓ only **linear response**, **small bias**.
✗ Non interacting quasiparticles:
  ✓ only **coherent** part of transport.

← Need to go Beyond!
Why GW?

Direct and Exchange terms:

- Band Structure Renormalization

Self-consistent Hartree-Fock

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

\[ \sum\{>_<\} = 0 \]

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

\[ \sum\{>_<\} \neq 0 \]

Collisional Term:

Band structure renormalization for Electronic Correlations + e-e Scattering -> Conductance Degrading Mechanisms, Resistance, non-coherent transport
GW conductance

- Loss of Conductance:
  - Appearance of Resistance

- Broadening of the peaks:
  - QP lifetime
C / V characteristics: GW vs EXP

Effective 1D system
i.e., restoring the True Dimensionality (1D) of the quantum transport problem

1D System built by Recursion Algorithm

\[ H |\psi_n\rangle = a_n |\psi_n\rangle + b_n^* |\psi_{n-1}\rangle + b_{n+1} |\psi_{n+1}\rangle \]

\[ \psi_0 \]

We start from the central costriction (effective channels are issued from the central part)

\[ a_0 = \langle \psi_0 | H | \psi_0 \rangle \]

\[ \psi_1 = \frac{1}{b_1} (H \psi_0 - a_0 \psi_0) \]

We build the next state

\[ b_1 = \langle \psi_1 | H | \psi_0 \rangle \]

Renormalization constant and hopping coefficient

\[ a_1 = \langle \psi_1 | H | \psi_1 \rangle \]

Orthonormal Basis Set

Effective Tridiagonal Hamiltonian

\[ H = \begin{pmatrix}
    a_0 & b_0 & 0 & 0 & \ldots \\
    b_0 & a_1 & b_1 & 0 & \ldots \\
    0 & b_1 & a_2 & b_2 & \ldots \\
    0 & 0 & b_2 & a_3 & \ldots \\
    \vdots & \vdots & \vdots & \vdots & \ddots
\end{pmatrix} \]

\[ \ldots \ a_{-\infty} \ldots \ldots \ldots \ldots \ a_{-2} \ a_{-1} \ a_1 \ a_2 \ a_3 \ a_4 \ \ldots \ \ldots \ \ldots \ \ldots \ a_{\infty} \ \ldots \]

\[ b_{-\infty} \]

effective 1D system

\[ b_{-2} \ b_{-1} \ b_1 \ b_2 \ b_3 \ b_4 \]

\[ b_{\infty} \]
Generalized Fisher-Lee formula

\[ T = Tr \left[ \Gamma_L G_C^r \Gamma_R G_C^a \right] \]

\[ T = Tr \left[ \tilde{\Gamma}_L G_C^r \tilde{\Gamma}_R G_C^a \right] \]

Renormalized injection rates:
- Refer to both ballistic and non-ballistic lead sections;
- Include contact resistance.

Physically more intuitive
More clear interpretation
Extension to NEGF

\[ i_T = \frac{e}{\hbar} Tr \left[ \tilde{\Sigma}_T^< G^> - \tilde{\Sigma}_T^> G^< \right] \quad \text{Meir-Wingreen} \]

\[ i_{t_{noncoh}} = \frac{e}{\hbar} Tr \left[ \tilde{\Sigma}_t^< G_c^r \Sigma_{corr} G_c^a - \tilde{\Sigma}_t^> G_c^r \Sigma_{corr} G_c^a \right] \quad \text{Generalized Meir-Wingreen} \]

\[ \tilde{\Sigma}_t = H_{ct} \tilde{g}_r \Sigma_T \tilde{g}_r H_{tc} \quad \text{Contact resistance dressed lead } t \text{ scattering function: Accounts for contact resistance} \]

Extension to non-coherent transport and correlations
Graphene slits: Kirchhoff and Bethe Diffraction

Graphene Nanoribbons as Fabry-Perot Interferometers

\[ T_{FP}(\omega) = \frac{1}{1 + F(\omega) \sin^2(k(\omega)L)} \]

Conclusions

• The Landauer – Fisher-Lee Principal-Layers DFT quantum transport formalism presents some drawbacks

• The \textbf{GW self-energy} beyond the DFT KS better reproduces the real situation and the resistance mechanisms due to the e-e scattering

• Beyond the Principal-Layers, the \textbf{effective 1D formalism} relying on \textbf{effective channels} is better suited to quantum transport calculations, numerically \textbf{more efficient} and physically \textbf{more intuitive}

Perspectives

• \textbf{GW on organic molecules} -> T. Rangel PhD thesis at Louvain la Neuve

• Implement a true out-of-equilibrium \textbf{NEGF-GW} formalism
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Pierre Darancet

GDR-DFT
GW: optical properties in Solids

- GW corrects the red-shift but still misses the Excitonic Effects
MBQFT: GW, BSE and Excitonic Effects

\[ P = \text{RPA} + \text{GW} + \text{BSE} + O(2) \]

Valerio Olevano, CNRS, Introduction to TDDFT
Bethe-Salpeter Equation: optical properties in Solids

- Almost quantitative agreement of BSE with the experiment