The *GW* Method for Quantum Chemistry applications: Theory, Implementation, and Benchmarks

M.J. van Setten
plan

- $G_0W_0$

- As little approximations as possible, i.e., exact frequency treatment

- Molecular systems and clusters

- Local (Gaussian) basis-set

- “general” approach, portable to other codes
Theory and implementation
KS v.s. Quasi-Particle equation

- Electron density parameterized by KS single particle states

\[ \rho(r) = \sum_{\text{nooc}} \psi_{n}^{KS}(r) \psi_{n}^{KS*}(r) \]

\[ V_{xc} : \text{exchange correlation potential} \]

\[ \left( -\frac{1}{2} \nabla^{2} + V_{H}(r) + V_{\text{ext}}(r) + V_{XC}(r) \right) \psi_{n}^{KS}(r) = \epsilon_{n}^{KS} \psi_{n}^{KS}(r) \]

- Greens function in spectral representation, expressed in terms of quasi-particle states leads to the quasi particle equation:

\[ G(r, r'; z) = \sum_{p} \frac{\Psi_{r, p}^{qp}(r, z) \Psi_{l, p}^{qp*}(r', z)}{z - \epsilon_{p}^{\text{qp}}(z) + i\eta \text{sign}(\epsilon_{p}^{\text{qp}}(z) - \mu)} \]

\[ \Sigma : \text{self-energy} \]

\[ \left( -\frac{1}{2} \nabla^{2} + V_{H}(r) + V_{\text{ext}}(r) \right) \Psi_{r, p}^{qp}(r, z) + \int dr' \Sigma(r, r'; \epsilon_{p}^{\text{qp}}(z)) \Psi_{r, p}^{qp}(r', z) = \epsilon_{p}^{\text{qp}}(z) \Psi_{r, p}^{qp}(r, z) \]

- The quasi-particle energies are the electron removal and addition energies

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$G_0 W_0$ and linearized QP equation

- Calculate the self-energy only once from KS-DFT energies and orbitals

\[
G_0(r, r'; E) = \sum_n \frac{\psi_n^{KS}(r) \psi_n^{KS}(r')}{E - \varepsilon_n^{KS} + i\eta \text{sign}(\varepsilon_n^{KS})}
\]

\[
\chi(r, r', \omega) = -\sum_m \rho_m(r) \rho_m(r') \left( \frac{1}{\Omega_m - \omega - i\eta} + \frac{1}{\Omega_m + \omega - i\eta} \right)
\]

\[
W(\omega) = v + v \cdot \chi(\omega) \cdot v
\]

\[
A \cdot B \equiv \int dr'' A(r, r'') B(r'', r')
\]
$G_0W_0$ and linearized QP equation

- Calculate the self-energy only once from KS-DFT energies and orbitals

$$G_0(r, r'; E) = \sum_n \frac{\psi_n^{KS}(r) \psi_n^{KS*}(r')}{E - \epsilon_n^{KS} + i\eta \text{sign}(\epsilon_n^{KS})}$$

- Spectral representation of the reducible polarization function from TD-KS response equation

$$\chi(r, r', \omega) = -\sum_m \rho_m(r)\rho_m(r') \left( \frac{1}{\Omega_m - \omega - i\eta} + \frac{1}{\Omega_m + \omega - i\eta} \right)$$

$$W(\omega) = v + v \cdot \chi(\omega) \cdot v$$

$$A \cdot B \equiv \int dr'' A(r, r'') B(r'', r')$$
Reducible response function

\[ \rho_m (r) = \sum_{i,a} (X_m + Y_m) \phi_i (r) \phi_a (r) \]

\[ (\Lambda - \Omega_m \Delta) X_m, Y_m \rangle = 0 \]
\[ \langle X_m, Y_m \mid \Delta \mid X_{m'}, Y_{m'} \rangle = \delta_{m,m'} \]

\[ \Lambda = \begin{pmatrix} A & B \\ B & A \end{pmatrix}, \quad \Delta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \]

\[ (A + B)_{iab} = (\varepsilon_a - \varepsilon_i) \delta_{i,j} \delta_{ab} + 2 \langle ij \mid ab \rangle \]
\[ (A - B)_{iab} = (\varepsilon_a - \varepsilon_i) \delta_{i,j} \delta_{ab} \]

\[ \langle ij \mid ab \rangle = \int \text{d}r \text{d}r' \phi_i (r) \phi_j (r') \frac{1}{|r - r'|} \phi_a (r) \phi_b (r') \]

- transition densities
- Generalized Dyson equation
- As used in TDHF and TDDFT
- RPA or TDDFT version of the orbital rotation Hessians
\( G_0W_0 \) and linearized QP equation

- Calculate the self-energy only once from KS-DFT energies and orbitals

\[
G_0(r, r'; E) = \sum_n \frac{\psi_n^{KS}(r) \psi_n^{KS*}(r')}{E - \varepsilon_n^{KS} + i\eta \text{ sign}(\varepsilon_n^{KS})}
\]

\[
\chi(r, r', \omega) = -\sum_m \rho_m(r)\rho_m(r') \left( \frac{1}{\Omega_m - \omega - i\eta} + \frac{1}{\Omega_m + \omega - i\eta} \right)
\]

\[
W(\omega) = v + v \cdot \chi(\omega) \cdot v
\]

\[
\Sigma(r, r', E) = \frac{i}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega\eta} G(r, r', E - \omega)W(r, r', \omega) d\omega
\]

- Linearized Quasi-Particle equation

\[
\varepsilon_n^{G_0W_0} = \varepsilon_n^{KS} + Z_n \text{ Re} \left[ \left\langle \psi_n^{KS} \left| \Sigma(\varepsilon_n^{KS}) - V_{XC} \right| \psi_n^{KS} \right\rangle \right]
\]

\[
Z_n(\varepsilon_n^{KS}) = \left[ 1 - \left\langle \psi_n^{KS} \left| \frac{d\Sigma(E)}{dE} \right|_{E=\varepsilon_n^{KS}} \psi_n^{KS} \right\rangle \right]^{-1}
\]
Matrix elements

Matrix elements to be calculated

\[
\langle n | \Sigma^x (\varepsilon_n) | n \rangle = - \sum_{i}^{\text{occ}} (ni|in)
\]

\[
\text{Re}\left( \langle n | \Sigma^c (\varepsilon_n) | n \rangle \right) = \sum_{m}^{\text{occ}} \left[ \sum_{i}^{\text{occ}} \left| (in|\rho_m) \right|^2 \frac{\varepsilon_n - \varepsilon_i + \Omega_m}{(\varepsilon_n - \varepsilon_i + \Omega_m)^2 + \eta^2} \right] + \sum_{a}^{\text{unocc}} \left| (an|\rho_m) \right|^2 \frac{\varepsilon_n - \varepsilon_a - \Omega_m}{(\varepsilon_n - \varepsilon_a - \Omega_m)^2 + \eta^2}
\]

\[
\varepsilon_n^{G_0W_0} = \varepsilon_n^{\text{KS}} + Z_n \text{ Re} \left[ \langle \psi_n^{\text{KS}} | \Sigma(\varepsilon_n^{\text{KS}}) - V_{XC} | \psi_n^{\text{KS}} \rangle \right]
\]

Implemented in TURBOMOLE (escf)

Very efficient evaluation of electron-electron integrals:

- (Contracted) Gaussian basis sets
- Resolution of the Identity (RI) method

MVS, F. Weigend, F Evers  JCTC in press
doi:10.1021/ct300648t
Test results for molecules
Test results and Benchmarking

- Test set including:
  - $H_2$, $N_2$, $F_2$, $Li_2$, $Na_2$, $Cs_2$
  - $NH_3$, $SiH_4$, $SF_4$
  - $LiH$, $BF$, $CO_2$, $H_2O$
  - $Au_2$, $Au_4$
  - Acetone, Acrolein, Ethylene, Isobutane
  - Methane – Butane, Benzene – Naphthacene

- Method comparison
- Basis-set convergence
- Functional dependence
Method comparison ionization potentials

-5\text{HOMO} (eV) vs Experimental (vertical) I_p (eV)

- HF (TZVPP)
- B3LYP (TZVPP)
- PBE (TZVPP)
- PBE G_0 W_0 (TZVPP)
Method comparison electron affinities

- HF (TZVPP)
- B3LYP (TZVPP)
- PBE (TZVPP)
- PBE $G_0W_0$ (TZVPP)

Experimental (non-adiabatic) $E_A$ (eV)

$\epsilon_{\text{LUMO}}$
Higher Ionization potentials benzene

![Graph showing ionization potentials for benzene with different calculations methods: HF, B3LYP, PBE, PBE G_0 W_0, and SCF PBE. The graph compares the calculated values against experimental values for vertical ionization potential.]
\( G_0W_0 \) basis-set convergence

- Tested for all molecules
- In general linear extrapolation possible especially to the DEF2 results
- TZVPP in this test set converged within 0.25 eV

Extrapolated results

\[
\begin{align*}
\text{QZVP} & \quad \text{TZVP} & \quad \text{SVP} \\
\text{TZVPP} & \quad & \\
\text{cc-pV5Z} & \quad \text{cc-pVTZ} & \quad \text{cc-pVDZ} & \quad \text{cc-pVQZ}
\end{align*}
\]
Basis set convergence

Deviation from the extrapolated results

\[ \varepsilon - \varepsilon_{\text{Extrapolated}} \text{ (eV)} \]

\[ \text{Experimental (vertical) } I^*_p \text{ (eV)} \]

QZVP
TZVPP
TZVP
SVP
$G_0W_0$ Functional dependence

- Differences between $G_0W_0$ results ($\Delta$) are much smaller than deviations between the respective DFT results.

- Largest differences for LiH, H$_2$O and hydrocarbons with OH groups.
Approximations within $G_0W_0$

- Plasmon pole / model response
- Analytic continuation / numerical integration
- Neglect of semi-core state contributions / pseudo potentials

- Linearized quasi particle equation (< 0.1 eV)
- RI approximation (< 0.1 eV)
- Difference RPA / TDDFT response (~ 0.1 eV)

- Off-diagonal elements
  - > Perturbative correction
- Neglect of self-consistency
  - > Partial self-consistency in the energies
Method testing

- New method, much testing needed
  - Basis sets
  - Approximations within GW

- Collaboration with FHI Berlin and Berkeley Lab US DoE
  - F. Caruso and P. Rinke
  - S. Sharifhades and J. Neaton
  - TURBOMOLE complementary to FHI-aims:
    - Moderate v.s. Massive parallelization
    - Gaussian v.s. numerical basis-sets
    - Analytic v.s. numerical energy integration / analytic continuation
  - BerkeleyGW: plane waves, supercell, periodic boundary conditions
  - 100 molecule benchmark set: GW100

- Open shell systems

- Metal cluster benchmark set:
  - alkali, alkaline earth, transition, noble
100 closed shell molecules
- Simple dimers, noble gas atoms
- Oxides, hydrides, fluorides
- Small metal clusters
- Hydrocarbons, Aromatic molecules,

Comparison between FHI-aims and TURBOMOLE with identical basis sets
GW100

- 100 closed shell molecules
  - Simple dimers, noble gas atoms
  - Oxides, hydrides, fluorides
  - Small metal clusters
  - Hydrocarbons, Aromatic molecules,

- Comparison between FHI-aims and TURBOMOLE with identical basis sets
Open shell systems

- Collinear case
  - Matrices are spin-diagonal
  - Screening is comes from both spin channels
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- Prof. F. Evers
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Summarizing

- Formulation of the matrix elements for a $G_0W_0$ calculation in a format practical for evaluation in a Gaussian basis set.

- Effectiveness relies on the efficient evaluation of four-center-integrals.

- Basis set convergence similar to that of DFT.

- Already with $G_0W_0$ much reduced functional dependence.

- Medium sized molecules are already feasible (without parallelization and symmetry exploitation).