Methods and code developments for many body perturbation theory calculations

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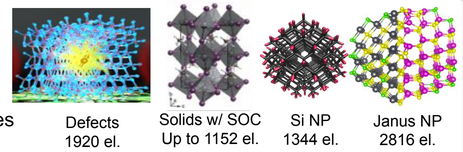
We describe method developments and their implementation in the WEST code; WEST is a massively parallel code for large-scale many-body perturbation theory calculations (GW and BSE) with scalar and fully relativistic pseudopotentials.

Large-scale many-body perturbation theory

Distinctive features

- Low-rank decomposition of dielectric matrices (no explicit diagonalization and storage of the full matrix)
- No explicit calculation of virtual electronic states
- GW with full frequency integration
- GW starting from semi-local and hybrid DFT
- Parallelization demonstrated over 500k cores on ANL Mira and 200k cores on ANL Theta



New Features

- **Electron-phonon** self-energy evaluated without computing virtual electronic states
- GW calculations with **spin-orbit coupling**
- Novel **hybrid functionals** derived from GW
- Implementation of **k-point sampling**
- **WEST-Qbox coupling** for BSE and GWΓ
- **Restructured I/O** in JSON format, enabling seamless integration with WESTPy and compatibility with Jupyter notebooks

Software development

- A dedicated GitLab server is operational (http://greatfire.uchicago.edu)
- Public releases are mirrored on GitHub
- Continuous Integration is used to verify the integrity of the code at every step of the development
- Documentation is automatically generated using Sphinx
- Licensed under the open-source GPLv3

WESTpy and REST API tutorials

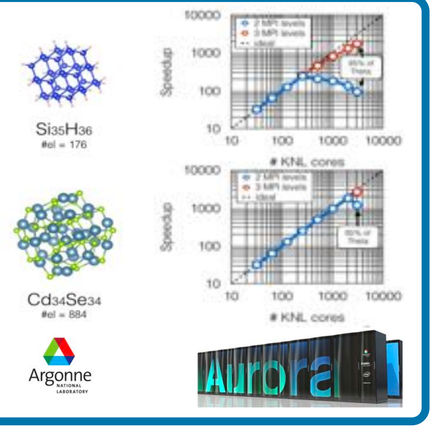
- WESTpy is a python package designed to assist users of the WEST code **in pre- and post-processing operations**
- REST API tutorials allow users to **run the codes *as-a-service*,** without learning how to install it

http://www.west-code.org/doc/westpy/latest/

WEST porting to new platforms

WEST was ported to Intel Xeon Phi KNL platforms:
- Theta at ALCF
- Cori at NERSC

Code optimization & parallelization paves the way to an efficient utilization of the Aurora platform at ALCF

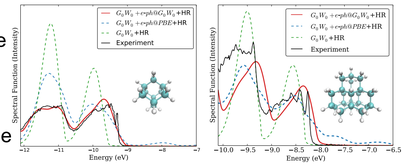


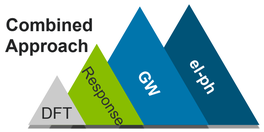
Ongoing and future work

- Investigate the accuracy of pseudopotentials for MBPT calculations
- Develop and implement new algorithms to investigate ultrafast time-resolved processes
- Enable on-the-fly calculations of spectroscopic properties

Electron-phonon coupling

- Efficient evaluation of e-ph self-energies using GW quasi-particle energies
- No virtual electronic states
- Lanczos algorithm is utilized to compute all self-energies over the full frequency spectrum



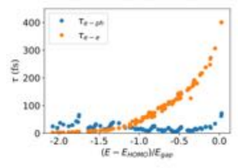


- Temperature dependent computational spectroscopy
- Lifetimes to be used in Boltzmann Transport Equation (BTE)

Electron-electron and electron-phonon lifetimes

$$\left(\tau_n^{e-e}\right)^{-1} = 2|Im\Sigma_n^{G_0W_0}(E_n^{tot})|$$
$$\left(\tau_n^{e-ph}\right)^{-1} = 2|Im\Sigma_n^{ep}(E_n^{tot})|$$

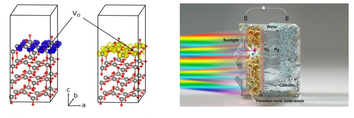
- Computation of electron-electron and electron-phonon self-energies are combined
- Lifetimes can be efficiently computed in nanoparticles with more than several hundred electrons and phonon modes



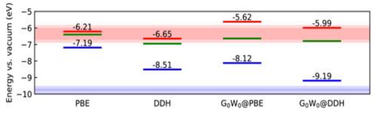
R. McAvoy, M. Govoni, G Galli JCTC, under review (2018)

Liquids and solid/liquid interfaces

Solvated WO_3 surface



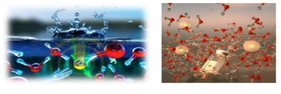
- Studied a realistic model of non-stoichiometric WO_3 surfaces with oxygen vacancies using FPMD (Qbox code)



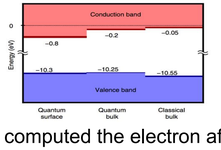
- Band offsets and flat-band potentials computed using G_0W_0 calculations (WEST code) starting from FPMD trajectories and wavefunctions generated with hybrid functionals

M. Gerosa, F. Gygi, M Govoni, G Galli, Nature Materials *accepted* (2018)

Liquid Water and Aqueous Solutions



- FPMD (DFT & hybrid-DFT)
- GW calculations from snapshots extracted from FPMD trajectories



- We computed the electron affinity (EA) of bulk water and its surface.
- We revisited the experimental literature on the EA of water.

A. P. Gaiduk, T.A. Pham, M. Govoni, F. Paesani & G. Galli , Nature communication (2018)

Verification

G_0W_0 for solids: comparison between results obtained with West and those reported by D.Nabok et al, PBR 2016 (G_0W_0 @LDA with the **exciting** code).

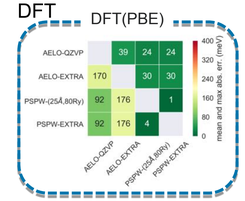
Material	Γ_v	L_v	L_c	X_v	X_c
C-dc	7.56(7.43)	-2.99(-2.94)	10.55(10.38)	-6.67(-6.58)	6.32(6.26)
Si-zb	7.39(7.37)	-1.14(-1.11)	6.67(6.63)	-3.38(-3.31)	2.48(2.45)
Si-dc	3.35(3.24)	-1.23(-1.22)	2.30(2.09)	-2.91(-2.86)	1.44(1.25)
BN-zb	11.34(11.28)	-2.12(-2.04)	12.28(12.32)	-5.30(-5.13)	6.49(6.47)
AlP-zb	4.28(4.10)	-0.77(-0.78)	3.87(3.69)	-2.14(-2.14)	2.61(2.41)
GaN-zb	2.21(3.00)	-1.17(-0.94)	5.23(6.10)	-3.15(-2.64)	4.13(4.71)
GaAs-zb	0.71(1.16)	-1.30(-1.16)	1.26(1.60)	-2.94(-2.71)	1.82(1.95)
MgO-rs	7.36(7.63)	-0.74(-0.71)	10.78(10.91)	-1.49(-1.45)	11.86(12.11)
ZnS-zb	3.30(3.38)	-0.89(-0.85)	4.67(4.73)	-2.26(-2.16)	4.73(4.64)
CdS-zb	1.90(2.09)	-0.82(-0.78)	3.95(4.14)	-2.01(-1.91)	4.49(4.54)
Ar-fcc	13.57(13.20)	-0.17(-0.17)	16.94(16.36)	-0.50(-0.50)	16.68(16.06)
Ne-fcc	19.91(20.31)	-0.10(-0.09)	25.92(26.06)	-0.27(-0.25)	26.93(27.18)
LiF-rs	14.10(14.09)	-0.27(-0.26)	15.87(15.90)	-1.15(-1.10)	20.60(20.24)

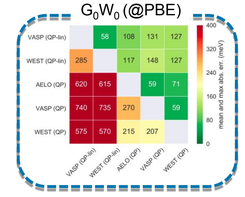
Ongoing work: impact of semi-core states in G_0W_0 calculations

Two PP for WO_3: PP1 (28 VE for W), PP2 (14 VE for W) yield the same results at the DFT level but different results for CBM and band gap at the G_0W_0 level of theory

K Points	PP1 (eV)	PP1-soc (eV)	PP2 (eV)	PP2-soc (eV)
Γ_v	8.41(9.21)	8.47(9.29)	4.45(5.37)	4.87(5.46)
Γ_c	9.88(10.95)	9.68(10.78)	7.28(7.15)	7.95(6.98)
R_v	9.42(10.27)	9.43(10.28)	5.57(6.43)	5.87(6.45)
R_c	15.37(16.04)	15.21(15.88)	12.53(12.23)	14.25(12.07)
Gap	0.46(0.68)	0.25(0.50)	1.71(0.72)	2.08(0.53)

G_0W_0 for molecules
- GW100 test set
- Compared All Electron and Pseudopotential codes
- Agreement between MBPT results is ~2x worse than in DFT





M. Govoni, G. Galli, JCTC (2018)

Hybrid functional for interfaces

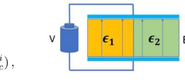
- Dielectric properties of interfaces expressed in terms of those of sub- systems
- Design of local hybrid functional for modeling heterogeneous systems

Local hybrid functional

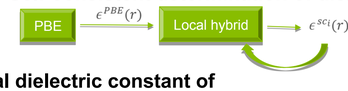
$$E_x = -\sum_{i<j}\int d\boldsymbol{r}d\boldsymbol{r}'\frac{1}{\sqrt{\epsilon(\boldsymbol{r})\epsilon(\boldsymbol{r}')}}\frac{\psi_i^*(\boldsymbol{r})\psi_j^*(\boldsymbol{r}')\psi_j(\boldsymbol{r})\psi_i(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$
$$+\int d\boldsymbol{r}\left[1-\frac{1}{\epsilon(\boldsymbol{r})}\right]\rho(\boldsymbol{r})\epsilon_x^{\mathrm{PBE}}[\rho(\boldsymbol{r})].$$

Dielectric constant evaluated using a finite field method (with Qbox)

$$\epsilon_{ij} = \delta_{ij} + 4\pi\frac{\delta P_i}{\delta E_j},$$
$$\delta\boldsymbol{P}(\boldsymbol{r}) = \sum_i \Delta\boldsymbol{r}_c^i\delta(\boldsymbol{r}-\boldsymbol{r}_c^i),$$

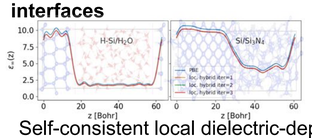


Self-consistent determination of dielectric constant

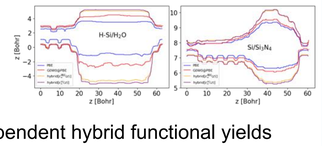


H. Zheng et al, in preparation

Local dielectric constant of solid/liquid and solid/solid interfaces



Band offsets



Self-consistent local dielectric-dependent hybrid functional yields accurate dielectric constants of solids and band offsets of interfaces.