A Tutorial

for the FHI-aims UK meeting

Sebastian Kokott
Konstantin Lion
Andrey Sobolev
James Green
Uthpala Herath
Min-ye Zhang
Dorothea Golze
Volker Blum

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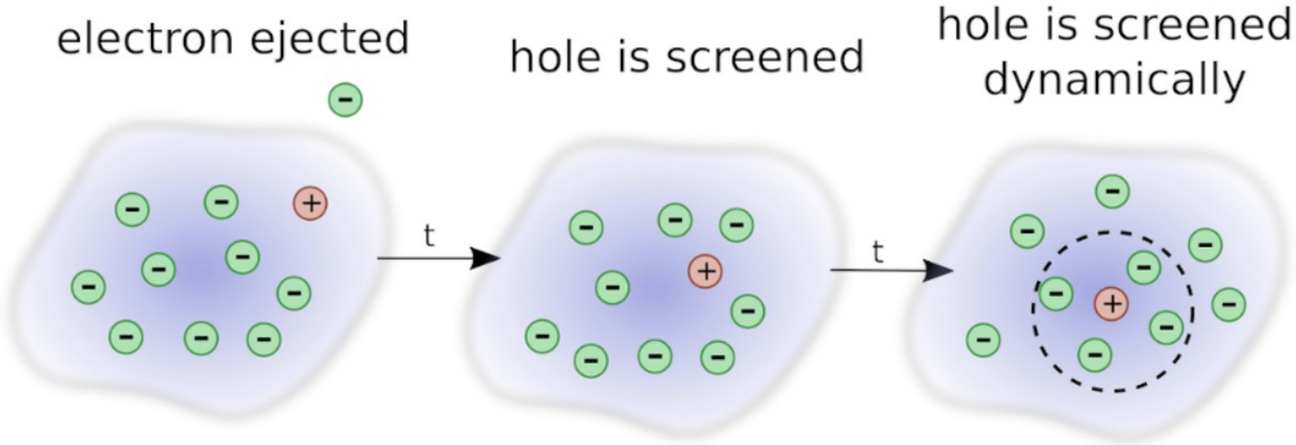
Part B: GW method for molecules and solids

What is the GW method?

- Accurate approach to calculate electron affinities/IPs/photoemission spectroscopy, band structures & gaps

- Think in terms of **quasiparticle** energy of an excitation = energy required to remove/add an electron from/to a many-particle system



D. Golze, M. Dvorak, and P. Rinke. “The GW Compendium: A Practical Guide to Theoretical Photoemission Spectroscopy”. In: Front. Chem. 7 (2019), p. 377.

- Perturbative expansion of **self-energy** Σ (interaction of QP with itself) in terms of the single particle Green’s function *G* and the screened Coulomb interaction *W*

$$\Sigma(\mathbf{r},\mathbf{r}',\omega) = \frac{i}{2\pi}\int d\omega' G(\mathbf{r},\mathbf{r}',\omega+\omega')W(\mathbf{r},\mathbf{r}',\omega')\,\mathrm{e}^{i\omega'\eta}$$

G_0W_0 and self-consistent GW

G_0W_0:

- Most commonly used GW flavour
- Single shot perturbation after preceding DFT calculation
- Compute QP energies as correction to KS DFT orbital energies

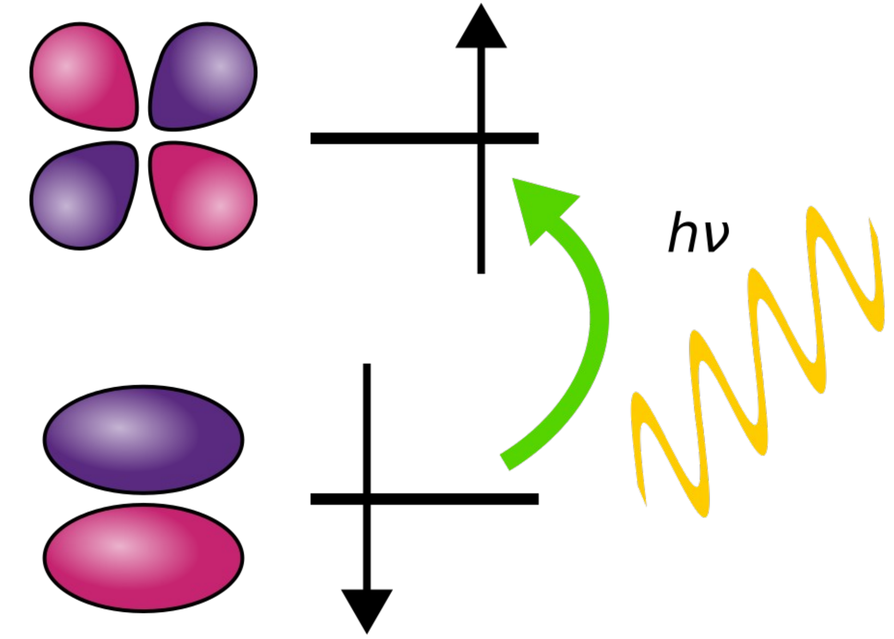
$$\epsilon_i^{QP} = \epsilon_i^{KS} - \left\langle \psi_i^{KS} \middle| \hat{V}_{xc}^{KS} - \hat{\Sigma}_{\mathrm{c}}^{GW}(\epsilon_i^{QP}) - \hat{\Sigma}_{\mathrm{x}} \middle| \psi_i^{KS} \right\rangle$$

- **Self-Consistent GW:**
  - **evGW$_0$** iterate eigenvalues in G
  - **evGW** iterate eigenvalues in G and W
  - **scGW** fully self-consistent GW, solve Dyson equation for G

GW + Bethe-Salpeter equation

- Alternative to TD-DFT for molecular excitation energies
- Uses prior GW calculation
- Solve the eigenvalue problem

$$\begin{bmatrix} A & B \\ -B^\dagger & -A^\dagger \end{bmatrix} \begin{bmatrix} X_s \\ Y_s \end{bmatrix} = E_s \begin{bmatrix} X_s \\ Y_s \end{bmatrix}$$



- Or use Tamm-Dancoff approximation

$$\mathbf{A}\mathbf{X}_s = E_s \mathbf{X}_s$$

GW in FHI-aims

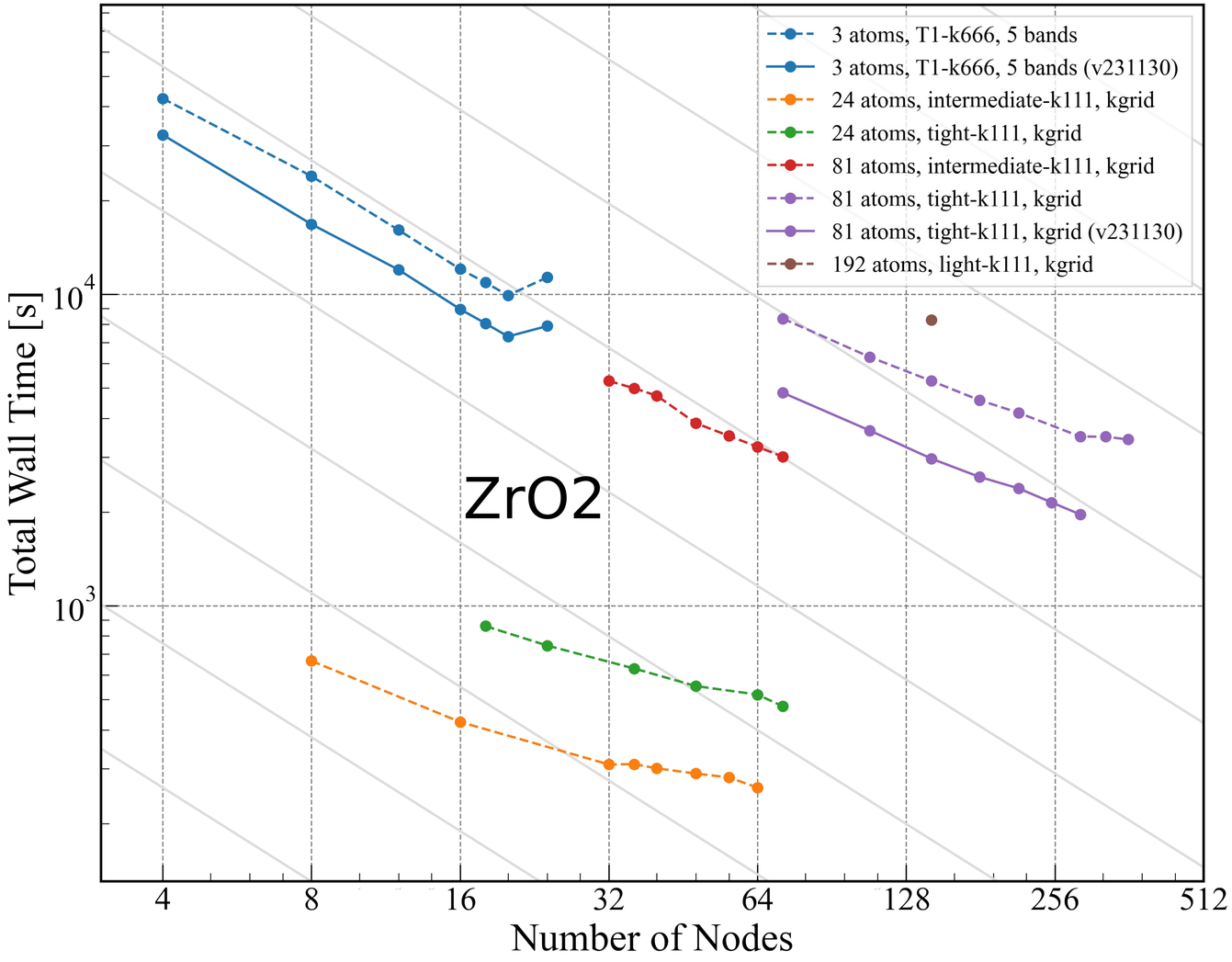
- **Single shot G_0W_0**
  - Molecular valence + core states
  - Periodic systems
- **Eigenvalue self-consistent GW**
  - Molecular valence + core states
- **Fully self-consistent GW**
  - Molecular valence states
- **GW + BSE**
  - Molecules only, excitation energies

Literature Summary

- **GW for molecular valence states**
  - Ren et al., New J. Phys., 14 (2012), 053020
  - Setten et al., JCTC, 11 (2015), 5665
- **GW for molecular core levels**
  - Golze et al., JCTC, 14 (2018), 4856
  - Golze et al., JPCL, 11 (2020), 1840
  - Keller et al. JCP, 153 (2020), 114110
- **Self-consistent GW**
  - Caruso et al., PRB, 88 (2013), 075105
  - Caruso et al., JCTC, 12 (2016), 5076
- **Periodic G_0W_0 for solid-state materials**
  - Ren et al., PRB, 5 (2021), 013807
- **BSE+GW**
  - Liu et al., JCP, 152 (2020), 044105

Recent GW Developments in FHI-aims

- **GreenX Library:**
  - M. Azizi *et. al.* Phys. Rev. B, 2024 (accepted, arXiv:2403.06709)
  - M. Azizi *et. al.*, JOSS, 2023, 8(90), 5570
- **New species defaults (_gw):**
  - Minye Zhang and Uthpala Herath
  - Should be used by default for GW
- **Optimization of periodic GW:**
  - Minye Zhang and Florian Merz
  - Calculations of 50-100 atoms feasible with GW



Practical Guidelines

- Need to choose frequency integration technique (Analytic Continuation for valence states, Contour Deformation for deep core)
- For AC, choose between 2-pole model (should work most of the time), or Padé model (more accurate, but can be numerically unstable)
- Which density functional to use for G_0W_0, or use self-consistent GW (more expensive)
- Check convergence
  - Basis set (FHI-aims has specialized basis sets for GW in the species defaults folder)
  - Number of frequency points
  - k-grid (for solids)

Where to find the material

Go to fhi-aims.org

FHI-aims version (special release)

Download fhi-aims.240507

Install it

(see “Building the FHI-aims code”)

Online Tutorial Material

- Click Resources>Introduction-tutorials
- “RPA, GW, and BSE for Molecules and Solids”
- Part 1: GW and BSE for molecules
  - Run all parts locally
  - Skip Counterpoise Correction
- Part 2: GW for solids
  - Read through and survey input/output files if you do not have access to a cluster
- At a later date – watch the lectures