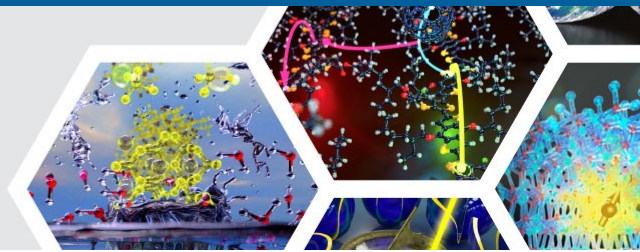

CENTER FOR MOLECULAR ENGINEERING
ARGONNE NATIONAL LABORATORY

# TUTORIAL: PHOTOEMISSION SPECTRA WITH WEST

**VICTOR YU, MARCO GOVONI**

Materials Science Division, Argonne National Lab, USA





MICCoM Workshop 2022
10/14/2022

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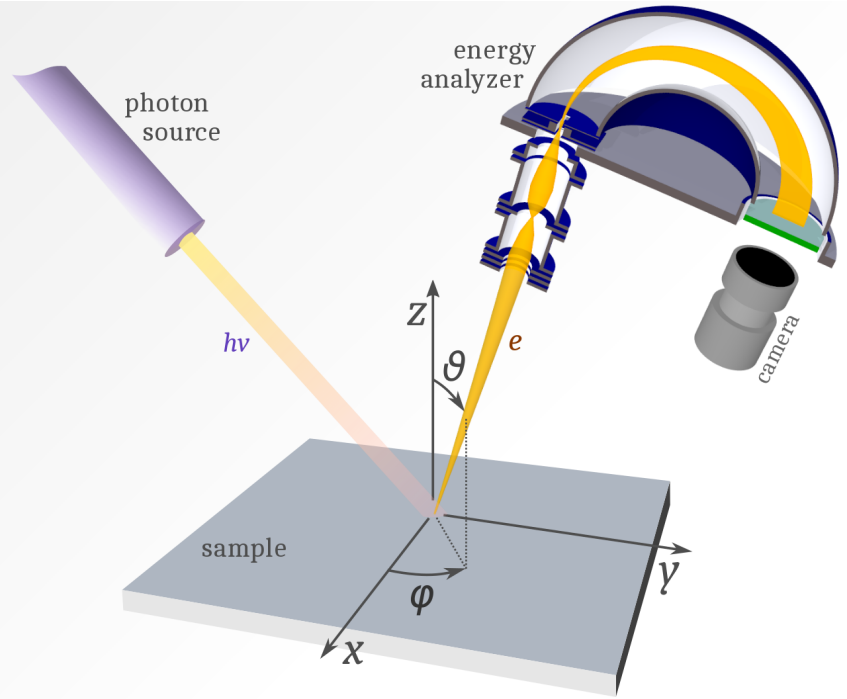
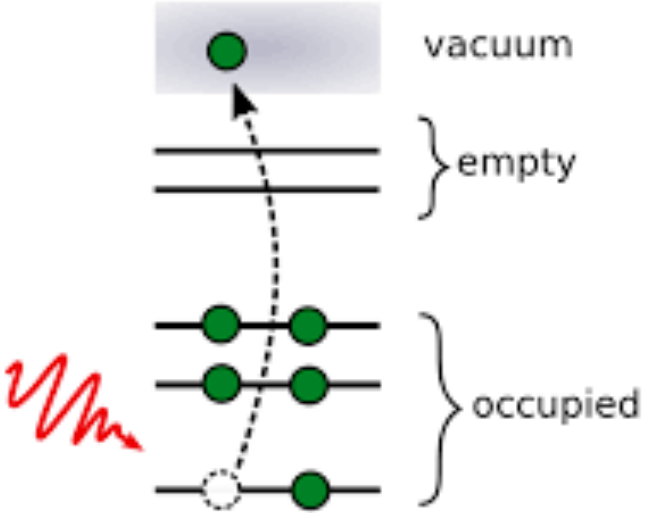
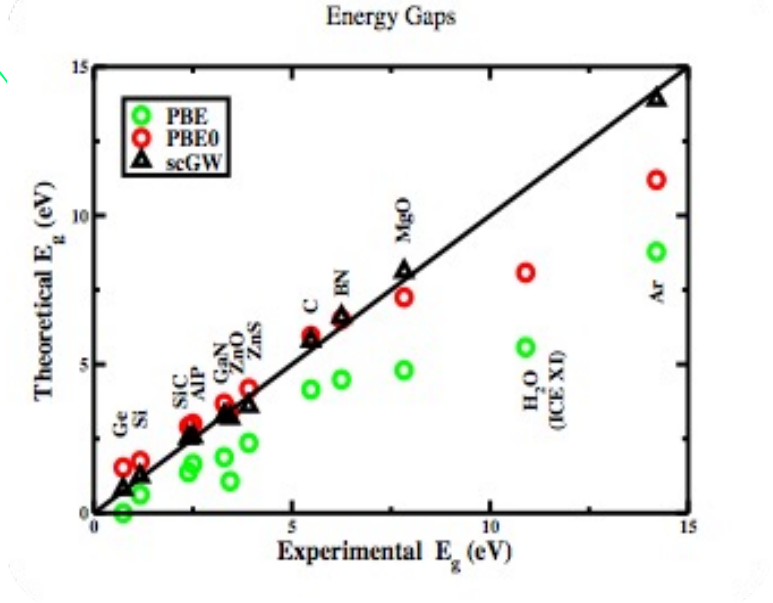
# PHOTOELECTRON SPECTROSCOPY



$$\hat{H}_{KS}^{\sigma}|\psi_{n\mathbf{k}\sigma}\rangle = \varepsilon_{n\mathbf{k}\sigma}|\psi_{n\mathbf{k}\sigma}\rangle$$ DFT



# MANY-BODY PERTURBATION THEORY

$$\hat{H}^{\sigma}_{\mathrm{KS}}|\psi_{n\mathbf{k}\sigma}\rangle = \varepsilon_{n\mathbf{k}\sigma}|\psi_{n\mathbf{k}\sigma}\rangle \quad \text{DFT}$$

$$\Sigma(\mathbf{r},\mathbf{r}';\omega) = \int \frac{d\omega}{2\pi} G(\mathbf{r},\mathbf{r}';\omega+\omega')W(\mathbf{r},\mathbf{r}';\omega')$$

$$G(\mathbf{r},\mathbf{r}';\omega) = \langle \mathbf{r}| \frac{1}{\omega - H} |\mathbf{r}'\rangle$$

$$W(\mathbf{r},\mathbf{r}';\omega) = \int d\mathbf{r}'' \epsilon^{-1}(\mathbf{r},\mathbf{r}'';\omega) v_c(\mathbf{r}'',\mathbf{r}')$$

GW

$$E^{\mathrm{QP}}_{n\mathbf{k}\sigma} = \epsilon_{n\mathbf{k}\sigma} + \langle \psi_{n\mathbf{k}\sigma}|\hat{\Sigma}^{\sigma}(E^{\mathrm{QP}}_{n\mathbf{k}\sigma})|\psi_{n\mathbf{k}\sigma}\rangle - \langle \psi_{n\mathbf{k}\sigma}|\hat{V}^{\sigma}_{\mathrm{xc}}|\psi_{n\mathbf{k}\sigma}\rangle$$

Correction

Onida et al., Rev. Mod. Phys. 74, 601 (2002)

# GW STARTED HERE 57 YEARS AGO!

PHYSICAL REVIEW VOLUME 139, NUMBER 3A 2 AUGUST 1965

## New Method for Calculating the One-Particle Green's Function with Application to the Electron-Gas Problem*

LARS HEDIN†
*Argonne National Laboratory, Argonne, Illinois*
(Received 8 October 1964; revised manuscript received 2 April 1965)

A set of successively more accurate self-consistent equations for the one-electron Green's function have been derived. They correspond to an expansion in a screened potential rather than the bare Coulomb potential. The first equation is adequate for many purposes. Each equation follows from the demand that a corresponding expression for the total energy be stationary with respect to variations in the Green's function. The main information to be obtained, besides the total energy, is one-particle-like excitation spectra, i.e., spectra characterized by the quantum numbers of a single particle. This includes the low-excitation spectra in metals as well as configurations in atoms, molecules, and solids with one electron outside or one electron missing from a closed-shell structure. In the latter cases we obtain an approximate description by a modified Hartree-Fock equation involving a "Coulomb hole" and a static screened potential in the exchange term. As an example, spectra of some atoms are discussed. To investigate the convergence of successive approximations for the Green's function, extensive calculations have been made for the electron gas at a range of metallic densities. The results are expressed in terms of quasiparticle energies $E(\mathbf{k})$ and quasiparticle interactions $f(\mathbf{k},\mathbf{k}')$. The very first approximation gives a good value for the magnitude of $E(\mathbf{k})$. To estimate the derivative of $E(\mathbf{k})$ we need both the first- and the second-order terms. The derivative, and thus the specific heat, is found to differ from the free-particle value by only a few percent. Our correction to the specific heat keeps the same sign down to the lowest alkali-metal densities, and is smaller than those obtained recently by Silverstein and by Rice. Our results for the paramagnetic susceptibility are unreliable in the alkali-metal-density region owing to poor convergence of the expansion for $f$. Besides the proof of a modified Luttinger-Ward-Klein variational principle and a related self-consistency idea, there is not much new in principle in this paper. The emphasis is on the development of a numerically manageable approximation scheme.

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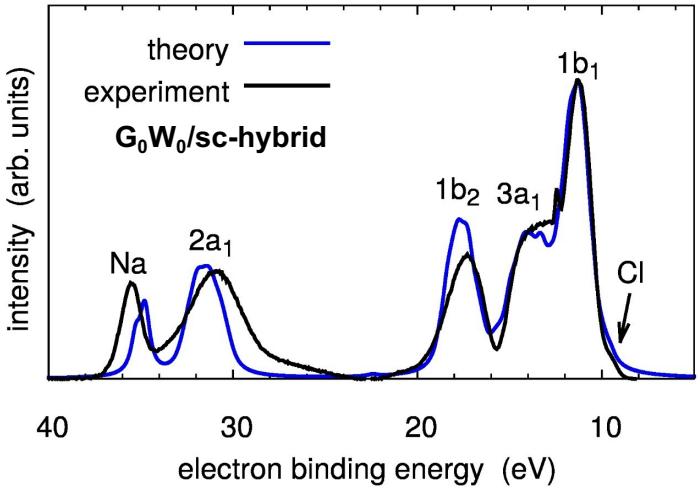
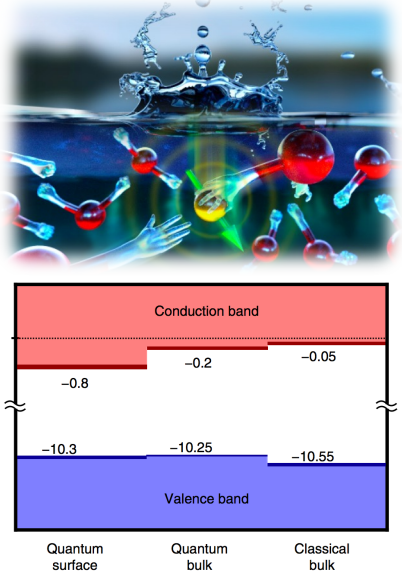
# PHOTOELECTRON SPECTRA OF AQUEOUS SOLUTIONS

The position of both ions and water peaks is greatly improved in **$G_0W_0$ on top of dielectric dependent hybrid functionals**




1M NaCl, 20ps simulation, PBE0, 128 snapshots average

- Linewidths are obtained from imaginary part of the $G_0W_0$ self-energy
- Easily generalizable to other non-metallic liquid electrolytes




Gaiduk et al., *Nature Comm*. 9, 247 (2018)

Gaiduk et al, *J. Am. Chem. Soc. Comm.* 138, 6912 (2016)
Pham et al, *Science Advances* 3, 1603210 (2017)

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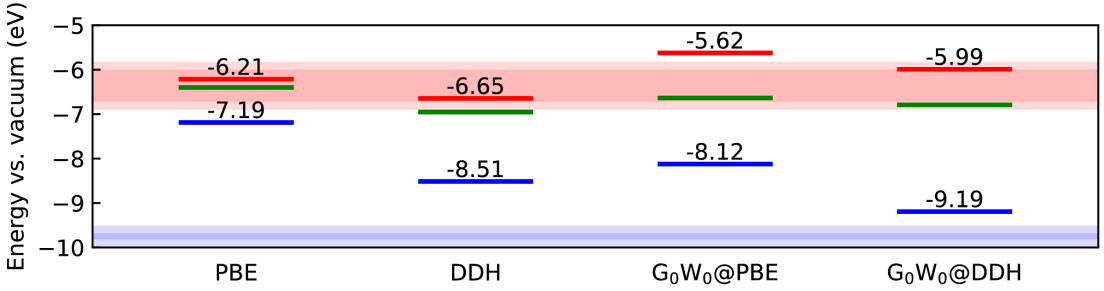
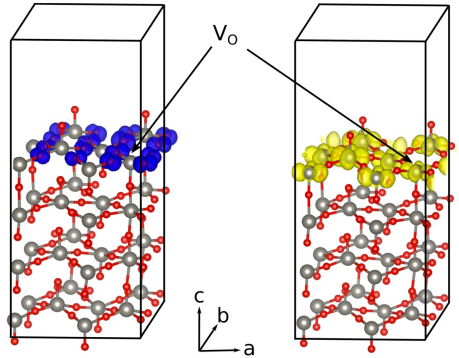
# GW SELF-ENERGY: OPTIMIZING OXIDE PHOTO-ABSORBERS

We investigated **realistic models of oxide ($WO_3$) surfaces**, with oxygen vacancies, and by coupling first principles molecular dynamics with hybrid functionals and many body electronic structure calculations



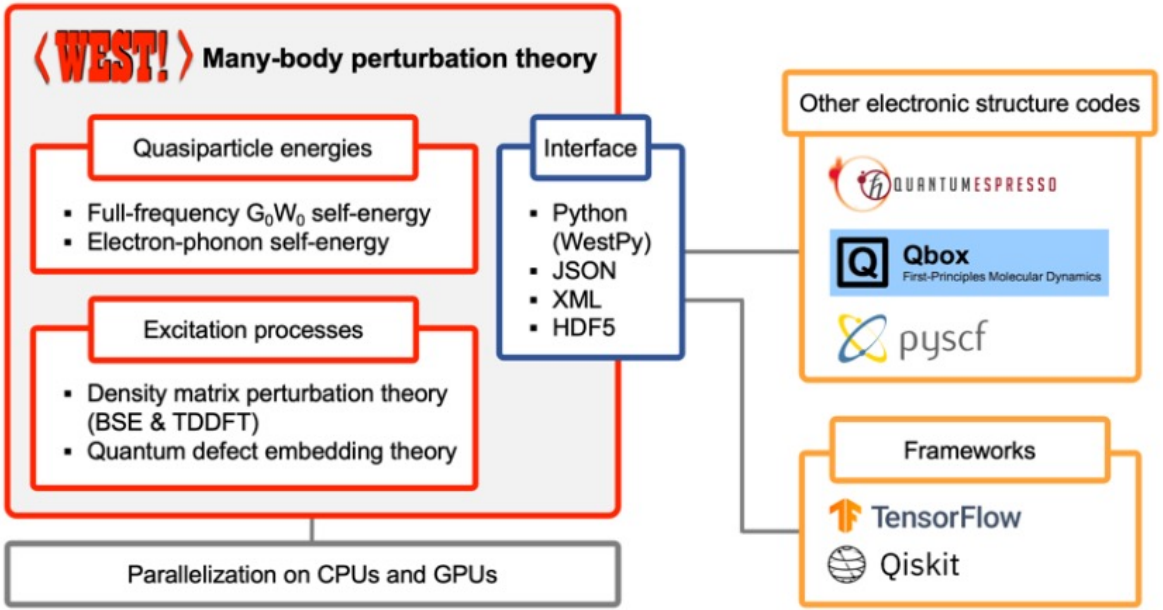




**$G_0W_0$ on top of dielectric dependent hybrid functionals** provided the best agreement with experiments

Gerosa, Gygi, Govoni, Galli, Nature Materials 17, 1122 (2018)

# WEST ENABLES COMPUTATIONAL SPECTROSCOPY OF LARGE SYSTEMS

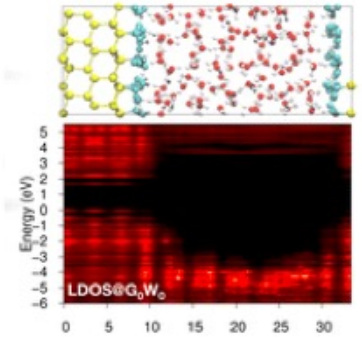
- WEST is an open-source software to perform large-scale many-body perturbation theory calculations



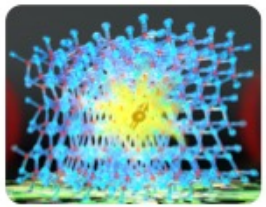

http://west-code.org

# WEST ENABLES COMPUTATIONAL SPECTROSCOPY OF LARGE SYSTEMS

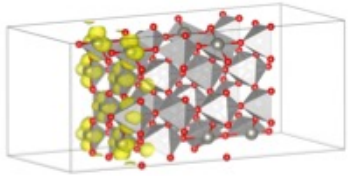
- **Range of applicability**:
  - Interfaces
  - Liquids/Solutions
  - Nanoparticles
  - Defects
  - Solids
  - Molecules




Solid/$H_2O$ interface
1560 el.

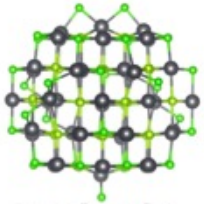


Defects in solids
1920 el.

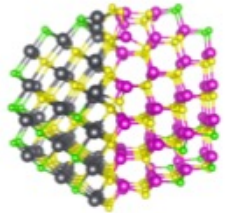


Defects at interfaces
1018 el.

Solids w/ SOC
Up to 1152 el.



PbSe NP
1236 el.

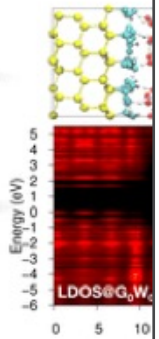


Janus NP
2816 el.

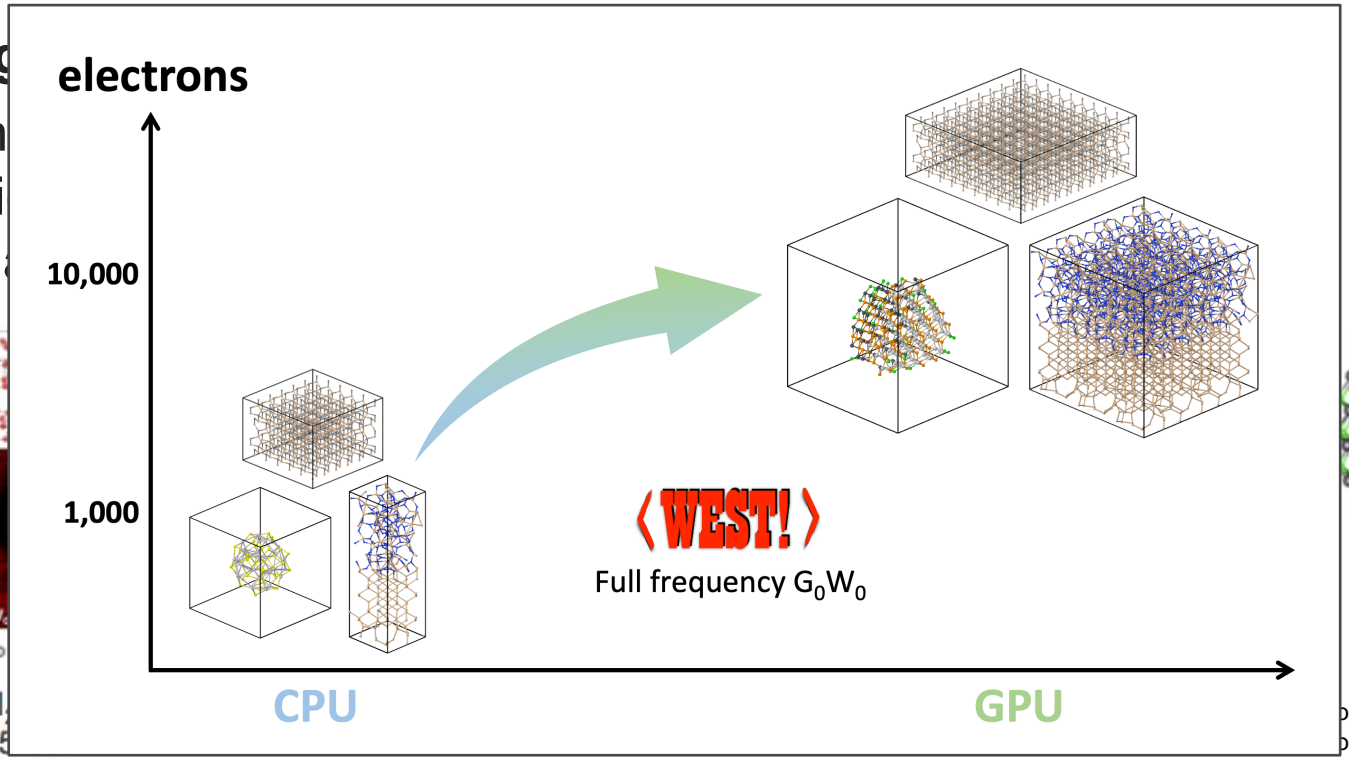

M. Govoni, G. Galli, J. Chem. Theory Comput. 11, 2680 (2015)
P. Scherpelz, I. Hamada, M. Govoni, G. Galli, J. Chem. Theory Comput. 12, 3523 (2016)
A. Gaiduk, M. Govoni, R. Seidel, J. Skone, B. Winter, G. Galli, JACS Comm. 138, 6912 (2016)
H. Seo, M. Govoni, G. Galli, Sci. Rep. 6, 20803 (2016)
M. Gerosa, M. Govoni, F. Gygi, G. Gall, Nature Materials 17, 1122 (2018)

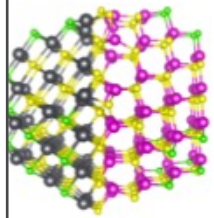
# WEST ENABLES COMPUTATIONAL SPECTROSCOPY OF LARGE SYSTEMS

- Rang
  - In
  - Li
  - N




Solid/H
15



Janus NP
2816 el.


ory Comput. 11, 2680 (2015)
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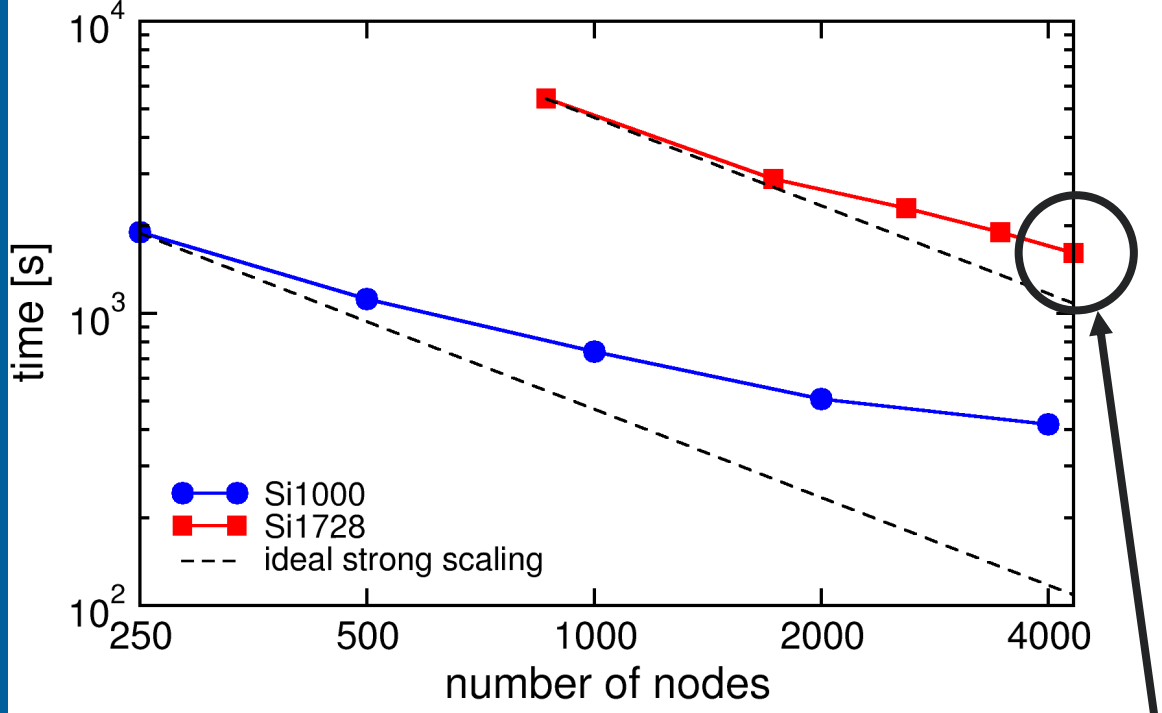
A. Gaiduk, M. Govoni, R. Seidel, J. Skone, B. Winter, G. Galli, JACS Comm. 138, 6912 (2016)
H. Seo, M. Govoni, G. Galli, Sci. Rep. 6, 20803 (2016)
M. Gerosa, M. Govoni, F. Gygi, G. Gall, Nature Materials 17, 1122 (2018)

# STRONG SCALING AT OLCF/SUMMIT




- WEST-GPU scales to the entire Summit supercomputer
- 80 quasi-particle energies of the 1,728-atom silicon supercell solved in ~30 min using **25,920 V100 GPUs** (94% of Summit)
- Better scalability observed for bigger system (1,728-atom silicon supercell) due to a higher computation-to-communication ratio

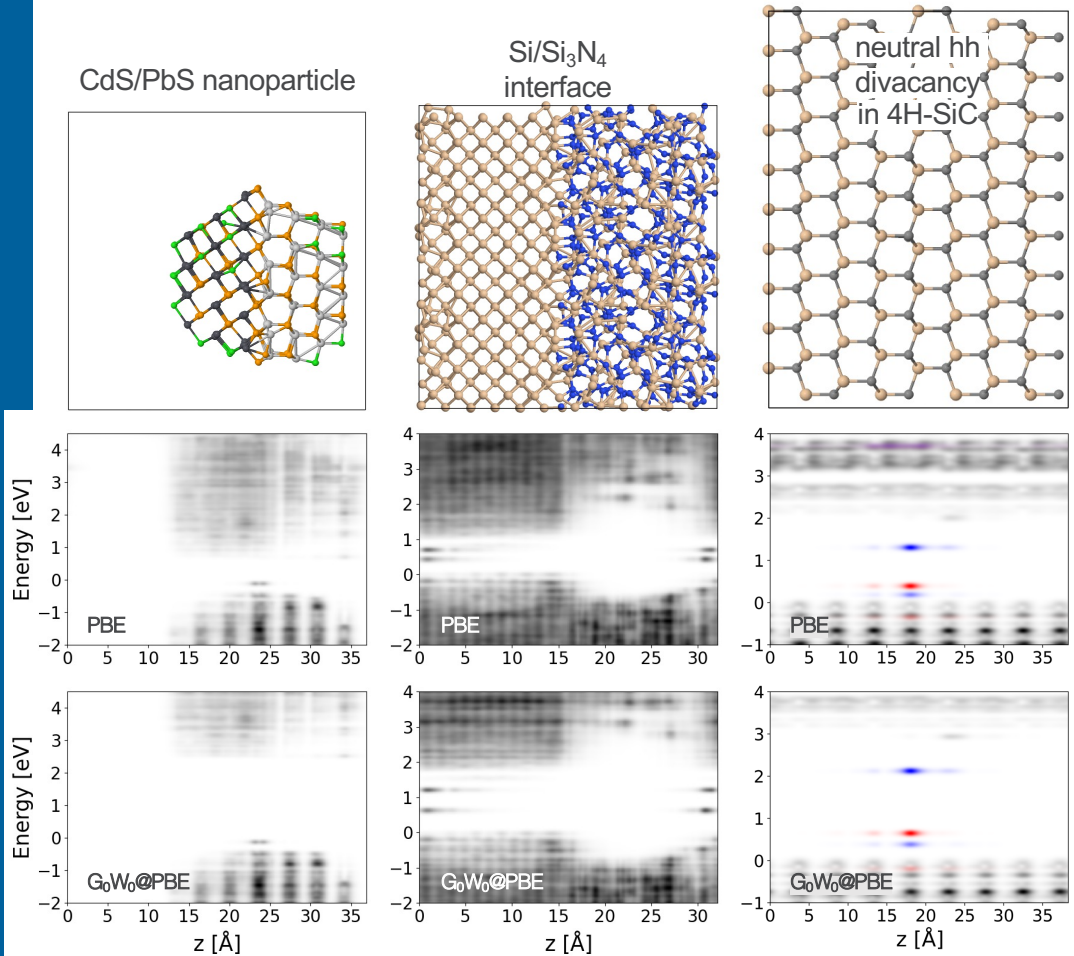
51 EF
4320 nodes
~60 PF/s

1 Summit node = 2 IBM POWER9 CPUs + 6 NVIDIA V100 GPUs

**Full-frequency $G_0W_0$** calculation of 4000 or 6912 electrons
Ground state DFT with Quantum ESPRESSO

Yu, Govoni, J. Chem. Theory Comput. 18, 4690 (2022)

# LARGE SCALE FULL-FREQUENCY GW CALC.




Local density of states computed for prototypical systems representing our target applications:

- Large nanoparticles and interfaces
  → materials for energy conversion
- Defects in semiconductors
  → quantum information science

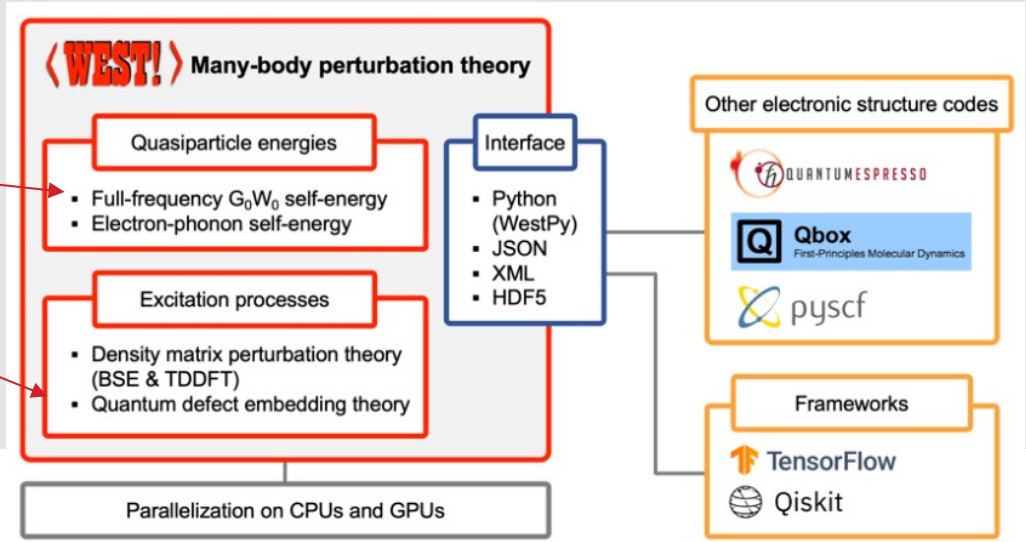
| system | $N_{atom}$ | $N_{electron}$ | $N_{spin}$ | $N_{PW}$ |
|---|---|---|---|---|
| CdS/PbS | 301 | 2,816 | 1 | 948,557 |
| $Si/Si_3N_4$ | 2,376 | 10,368 | 1 | 638,633 |
| $VV^0$ | 1,598 | 6,392 | 2 | 314,653 |

Yu, Govoni, J. Chem. Theory Comput. 18, 4690 (2022)

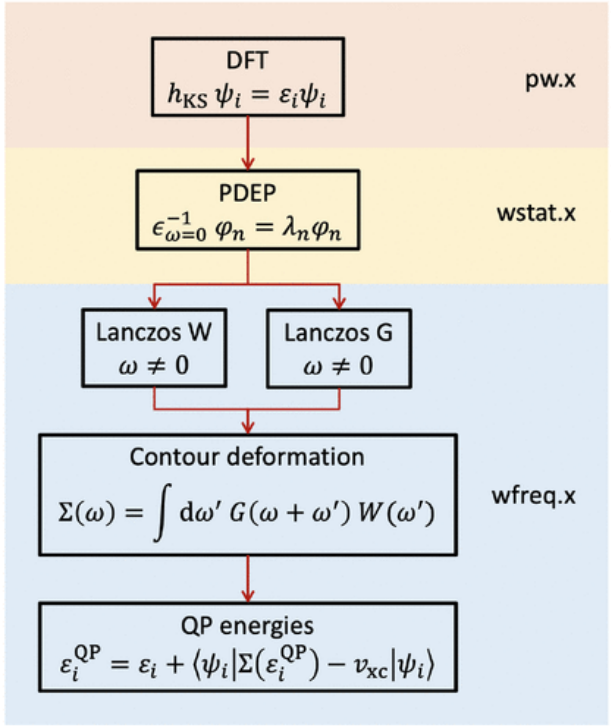
# PLAN FOR TODAY

10:30-noon

1:30-3pm



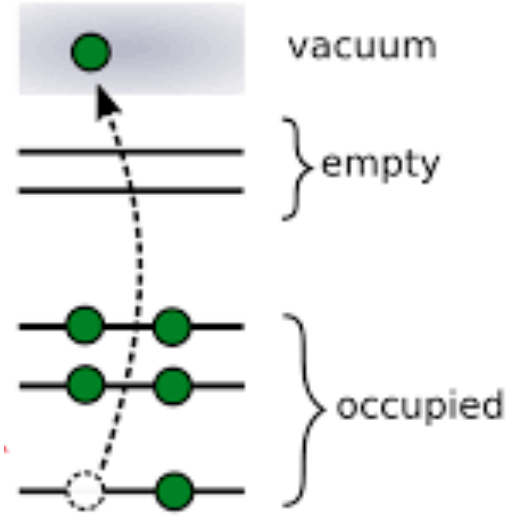
# FULL-FREQUENCY GW WORKFLOW




QUANTUMESPRESSO

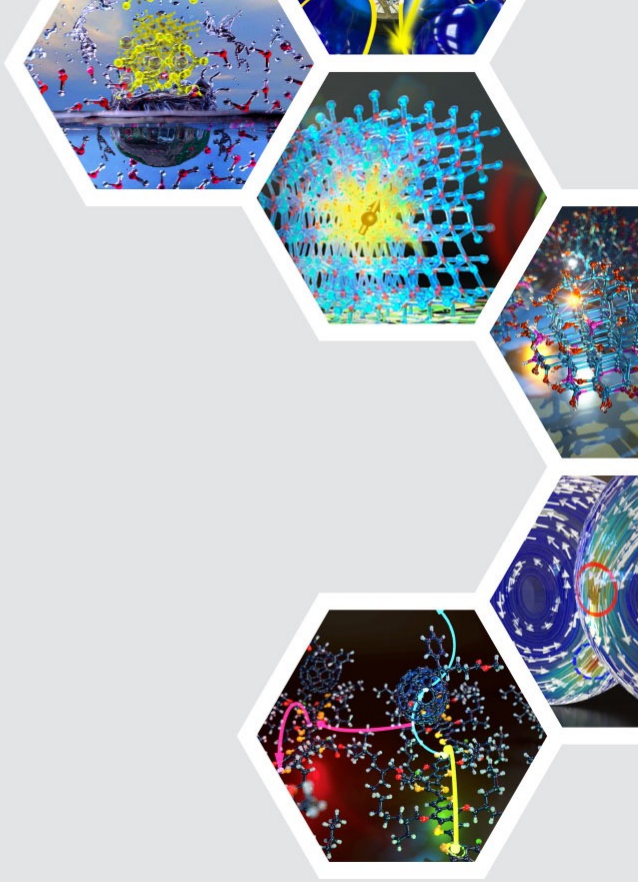
⟨ WEST! ⟩

⟨ WEST! ⟩

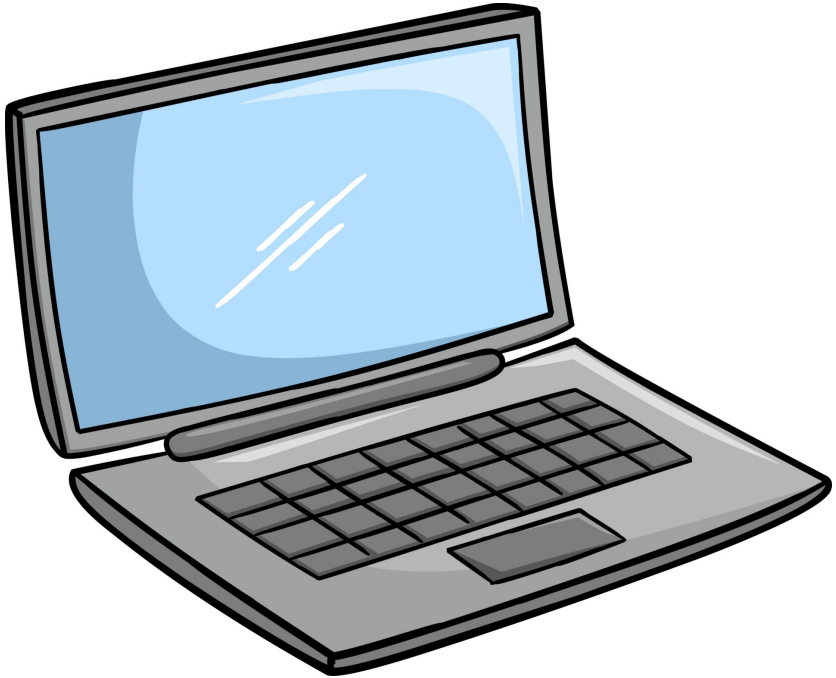


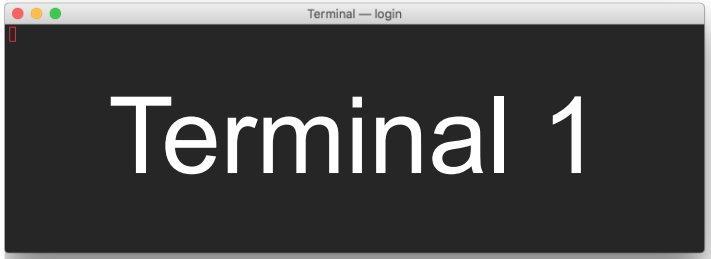

**Vertical Ionization Potential** (VIP):
minimum energy to remove an electron

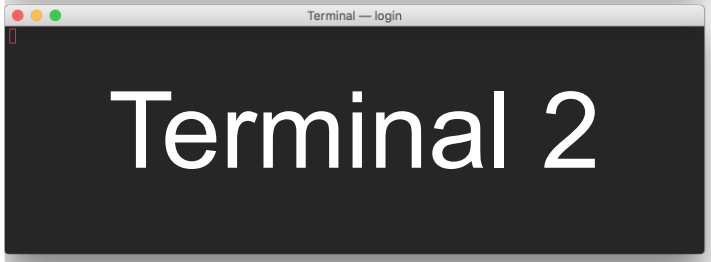
Govoni, Galli, J. Chem. Theory Comput. 11, 2680 (2015)

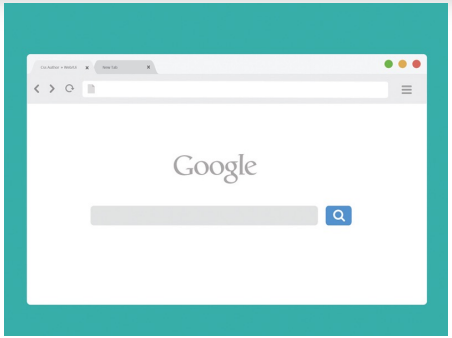



# LET'S CONNECT TO LCRC…




Terminal — login
Terminal 1


Terminal — login
Terminal 2


Google

Browser

# RESERVATION

**Day 2 – Oct 14, 2022**

| Computer | Time | Name of reservation | Nodes |
|---|---|---|---|
| **Bebop** | 10:15am – 12:15pm | `miccom_day2_am` | 75 |
| **Bebop** | 1:15pm – 5:15pm | `miccom_day2_pm` | 75 |
| **Swing** | 12:00pm – 6pm | `miccom_2` | 3 |

http://miccom-center.org/docs/MICCoM_Workshop_LCRC_instructions.pdf

# START Jupyter Notebooks

## Terminal #1 (1)

```
# ssh to Bebop
ssh <username>@bebop.lcrc.anl.gov

# set up environment
source /lcrc/project/MICCoM-train/load_bebop_env.sh

# get a compute node
srun --pty -A MICCOM-TRAIN --reservation miccom_day2_am
  -p knlall -N 1 -t 01:30:00 /bin/bash

# launch Jupyter notebook
miccom_start_jupyter

# each person gets a different node and port number

  Your compute node is :  knld-0019
  Your port number is  :  27055
  Starting Jupyter notebook ...

# (wait for several seconds...)

  To access the notebook, open this file in a browser:
     file:///gpfs/fs1/home/yuw/.local/...
  Or copy and paste one of these URLs:
     http://localhost:27055/?token=f86350...
  or http://127.0.0.1:27055/?token=f86350...
```

## Terminal #2 (2)

```
# ssh to Bebop (use the port number obtained in Terminal #1)
ssh -L 27055:localhost:27055 <username>@bebop.lcrc.anl.gov

# ssh to the compute node obtained in Terminal #1
ssh -L 27055:localhost:27055 knld-0019

# set up environment
source /lcrc/project/MICCoM-train/load_bebop_env.sh

# copy WEST tutorials to your home directory
cp -r /lcrc/project/MICCoM-train/west_tutorial $HOME
```

Do not copy **red** values from the slide!

If you have completed the instructions in Terminal #1 AND Terminal #2: (3)

**Open a browser** and visit this link


# YOU ARE GOOD TO GO!