The Random Phase Approximation (RPA) and GW approximation for electrochemistry

The BEAST collaboration

3rd Annual BEAST Workshop

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U.S. DEPARTMENT OF ENERGY
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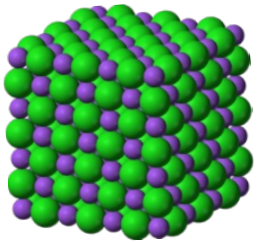
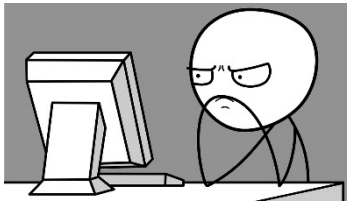
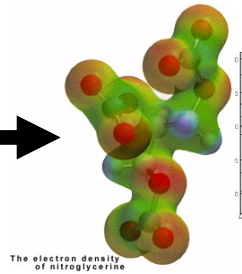
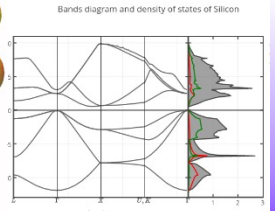
Density functional theory (Kohn-Sham)

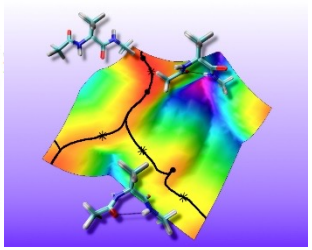




(J)DFT, RPA-GW

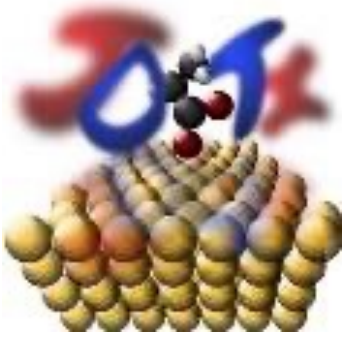






- Predict ground state properties without empirical input
- Properties: structure, charge density, reaction energetics

- Thousands of practitioners worldwide (16k citations on Hohenberg, Kohn)
  - JDFTx, Quantum ESPRESSO, VASP, ABINIT, EXCITING, Fleur, Octopus, ELK



Density functional theory (Kohn-Sham)

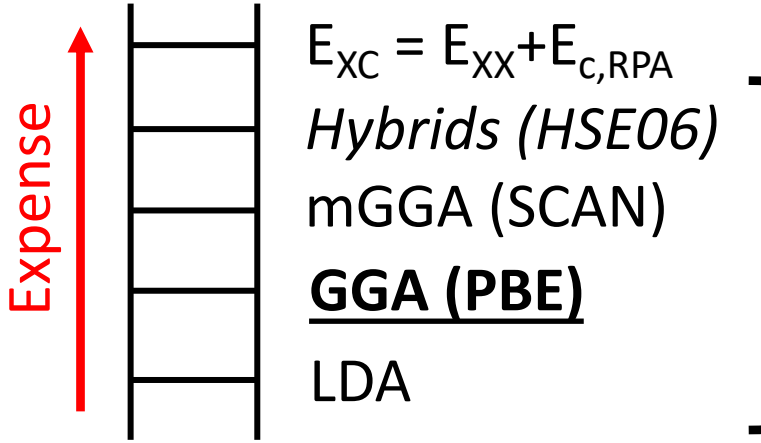
- Describing exchange-correlation term is key

$$\left(-\frac{1}{2}\nabla^2 + V_{ion} + V_{hartree}[n] + V_{xc}[n]\right)\psi_{nk} = \varepsilon\psi_{nk}$$

$$E_{DFT} = T_{KS} + E_{ion-el} + E_H + E_{XC}$$

- Calculate E_{XC} with varying degrees of accuracy/expense
  - 0 K, vacuum conditions

Chemical accuracy (1 kcal/mol)



What functional gives accurate energies and electronic structure… generally?

Adiabatic Connection Fluctuation Dissipation Theorem (ACFDT)

- Non-interacting Hamiltonian constructed such that its ground state Slater determinant $|\phi_0\rangle$ gives same density as true ground state wavefunction $|\psi_0\rangle$

- Generalization of Kohn-Sham DFT: scale the coulomb interaction

$$v_c \rightarrow \lambda v_c \qquad\qquad 0 \leq \lambda \leq 1$$

and obtain ground state wavefunction wavefunction $|\psi_0^{\lambda}\rangle$ gives same density as true ground state wavefunction $|\psi_0\rangle$

$$|\psi_0^{\lambda=0}\rangle = |\phi_0\rangle \qquad \text{and} \qquad |\psi_0^{\lambda=1}\rangle = |\psi_0\rangle$$

Key quantity: interacting polarizability χ^{λ}

- Solve Dyson equation

$$\chi^{\lambda}(\omega) = \chi_{\mathrm{KS}}(\omega) + \chi_{\mathrm{KS}}(\omega)\left[\lambda v_{\mathrm{c}} + f_{\mathrm{xc}}^{\lambda}(\omega)\right]\chi^{\lambda}(\omega)$$

- The RPA: $f_{xc}^{\lambda} = 0$

- Obtain polarizability
- Can calculate RPA correlation energy analytically

$$E_c^{RPA} = \int_0^{\infty} \frac{d\omega}{2\pi} \mathrm{Tr}\left[\ln\{1 - \chi^0(i\omega)v\} + \chi^0(i\omega)v\right]$$

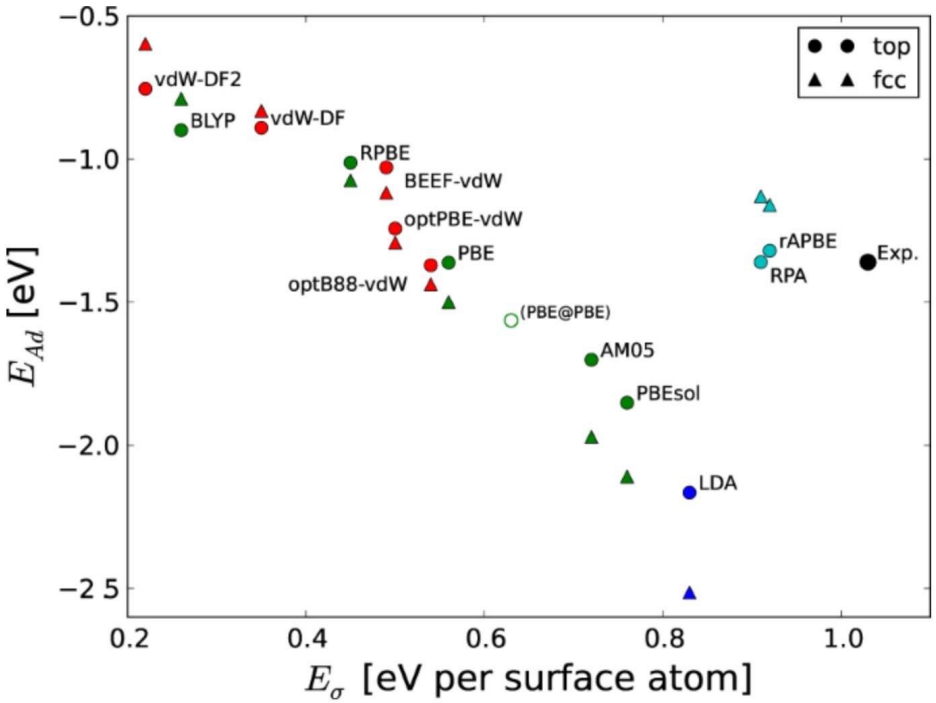
RPA

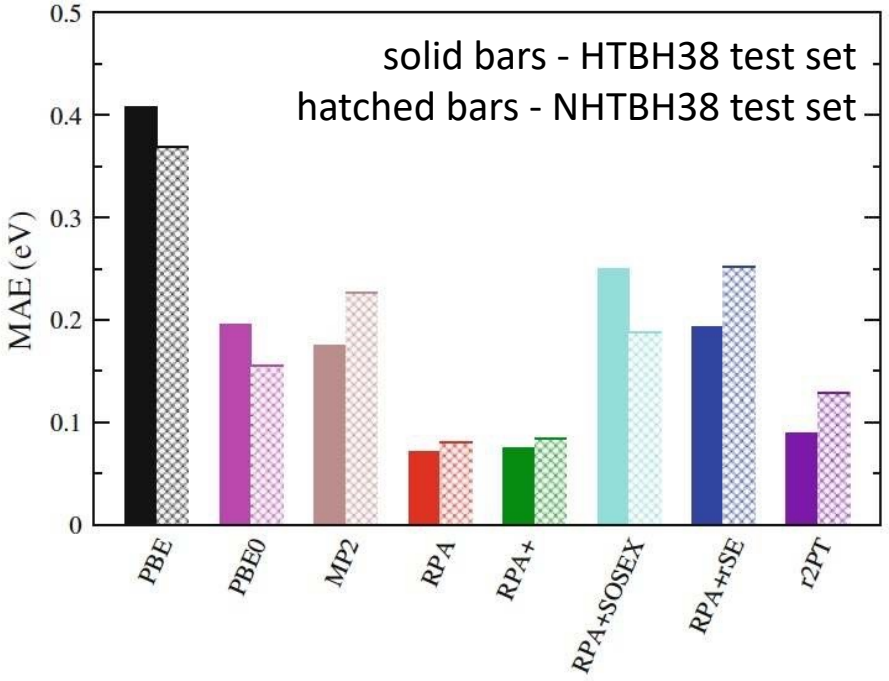
- Features
  - RPA gives correlation energy, compute EXX using input orbitals
  - Exactly cancels self-interaction from Hartree term (some self-interaction in correlation)
  - O(N4) complexity: between DFT and high-fidelity MP2, CCSD, CCSD(T)
  - Parameter-free dispersion forces: key for surface chemistry, binding of 2D materials

- Shortcomings
  - So-so short-range correlation: inaccurate cohesive energies, atomization energies
  - Slow convergence with kinetic energy cutoff (wavefunction cusp condition)

RPA can predict accurate properties relevant to catalysis

CO adsorption to Pt(111)

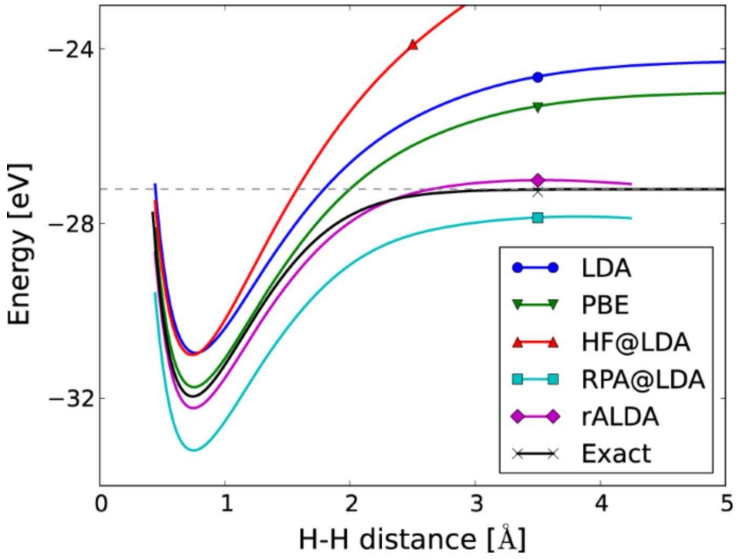




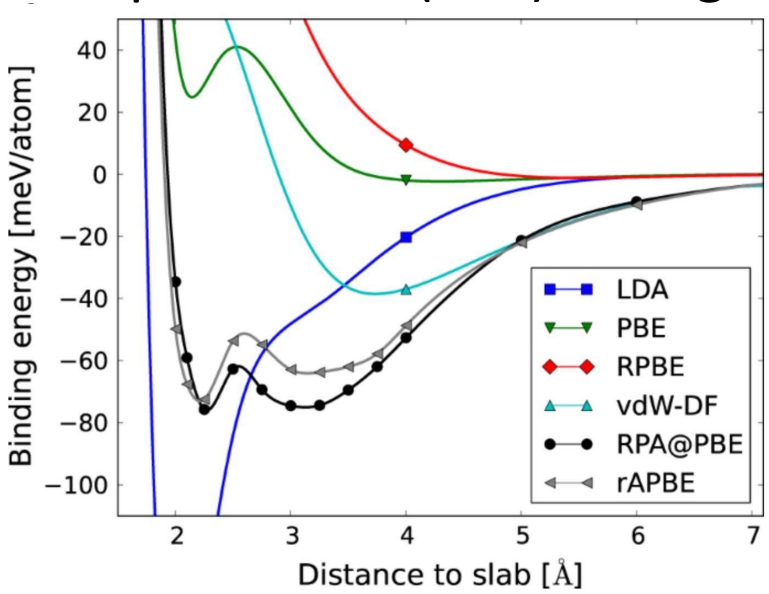
HTBH38: forward, inverse barrier heights of 19 hydrogen-transfer reactions, NHTBH38: 19 reactions involving heavy atom transfers, nucleophilic substitutions, association, unimolecular processes.

Olsen, et al., npj Computational Materials, 5 (2019)
Ren, et al.. J. Mat. Sci., 47 (2012)

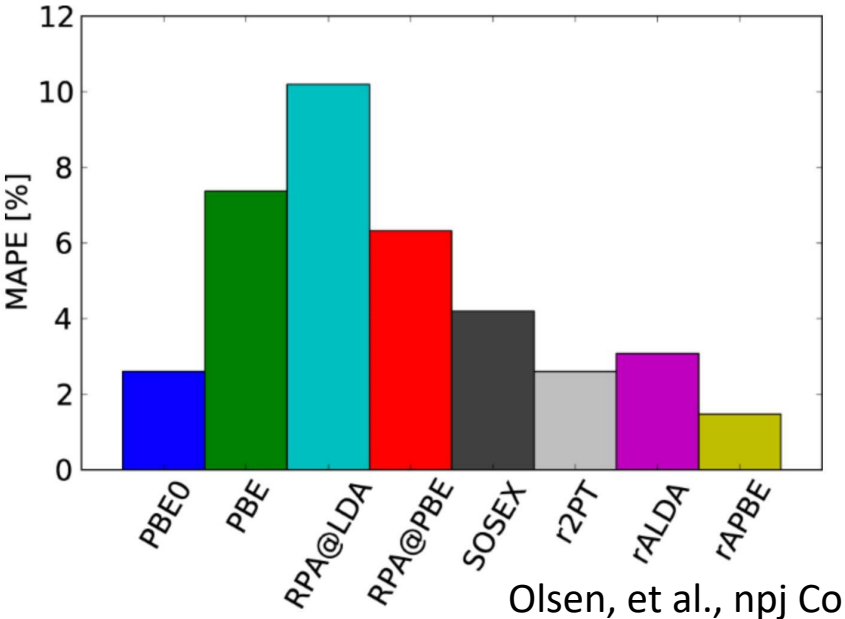
H_2 dissociation: RPA good



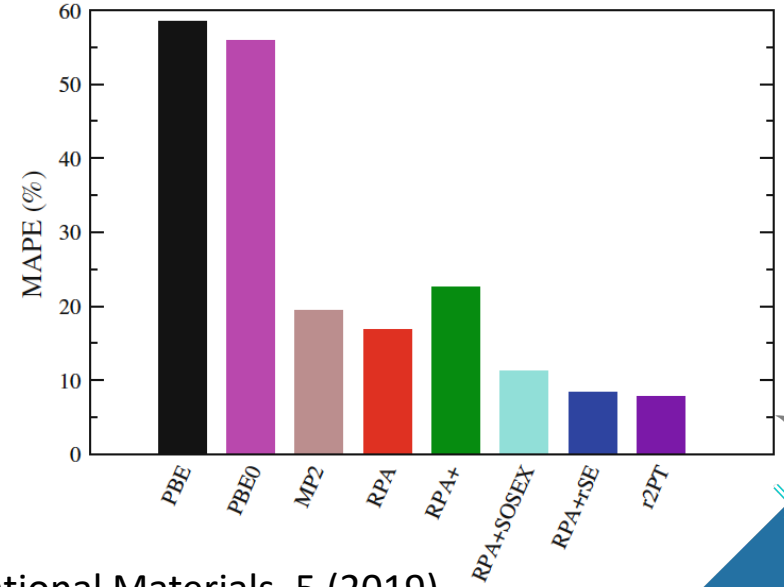
Graphene*+Ni(111): RPA good



Atomization energies: RPA ok



vdW/H-bonding: RPA very good



Olsen, et al., npj Computational Materials, 5 (2019)

What is the GW approximation?

- Dyson equation: replace exchange-correlation potential with many-body self-energy

$$\left[\frac{\nabla^2}{2} + V_{ion} + V_H + \Sigma\left(E_{nk}^{QP}\right)\right]\psi_{nk}^{QP} = E_{nk}^{QP}\psi_{nk}^{QP}$$

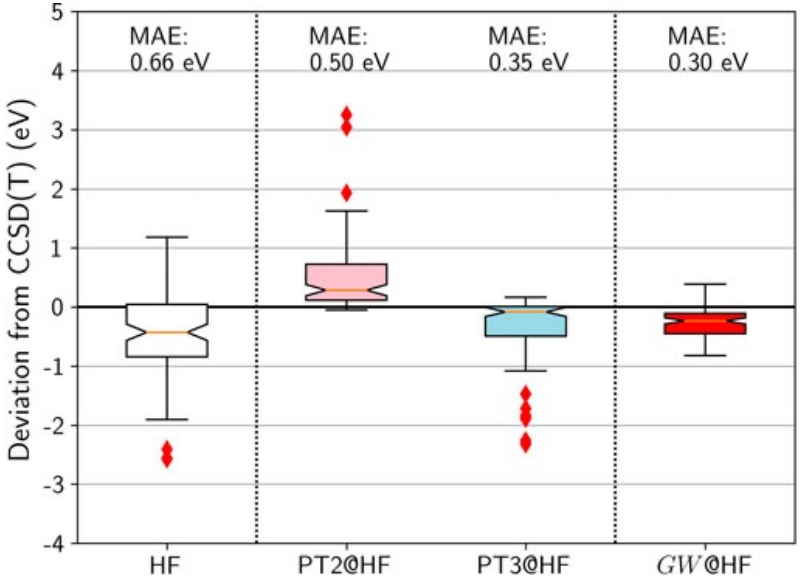
$$\Sigma = iGW$$

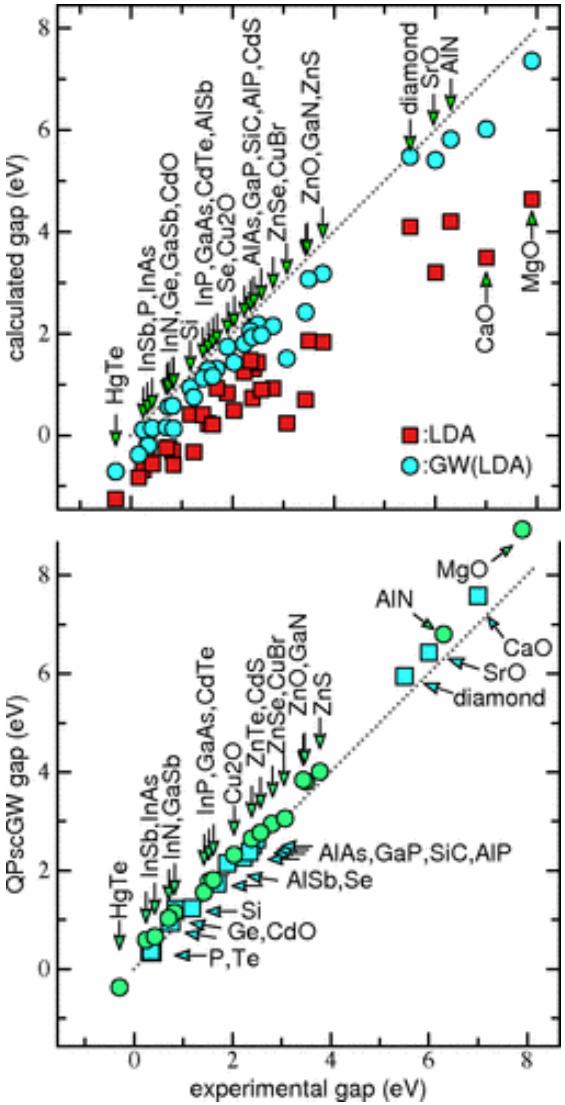
$$W_{GG'}(q;\omega) = \epsilon_{GG'}^{-1}(q;\omega)v(q+G')$$

$$\epsilon_{GG'}(q;\omega) = \delta_{GG'} - v(q+G)\chi_{GG'}^{0}(q;\omega)$$

- Polarizability calculated within random phase approximation

GW can predict accurate IPs and band gaps

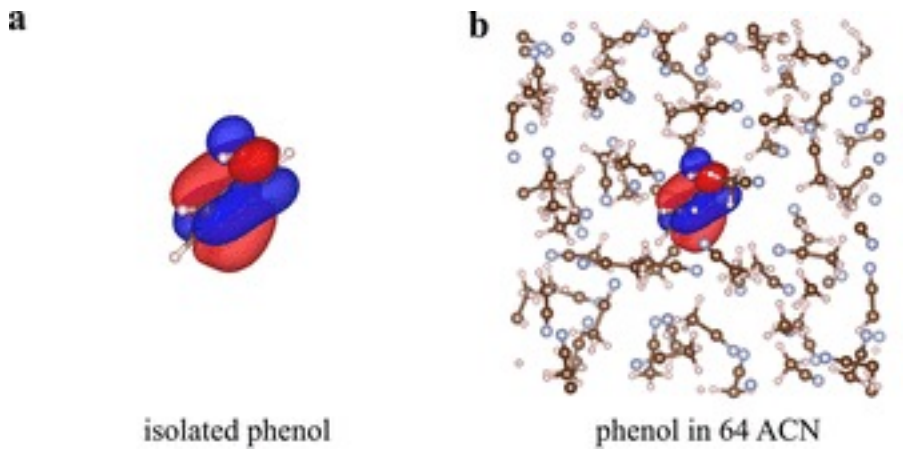


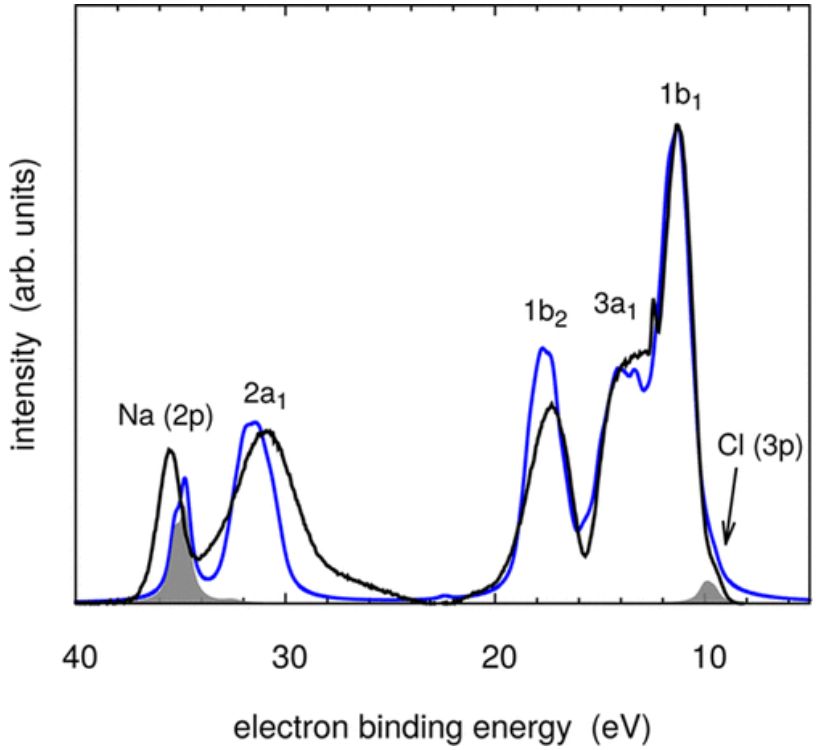


Bruneval, et al., Front. Chem. 9 (2021)
van Schilfgaarde, et al., PRL, 96, 226402 (2006)

Solvated beyond-DFT calculations are non-trivial

- Solvated GW calculations have previously used AIMD sampling of explicit waters or simplified implicit solvation models
  - 1 M NaCl = 1 Na + 1 Cl + 52 H_2O



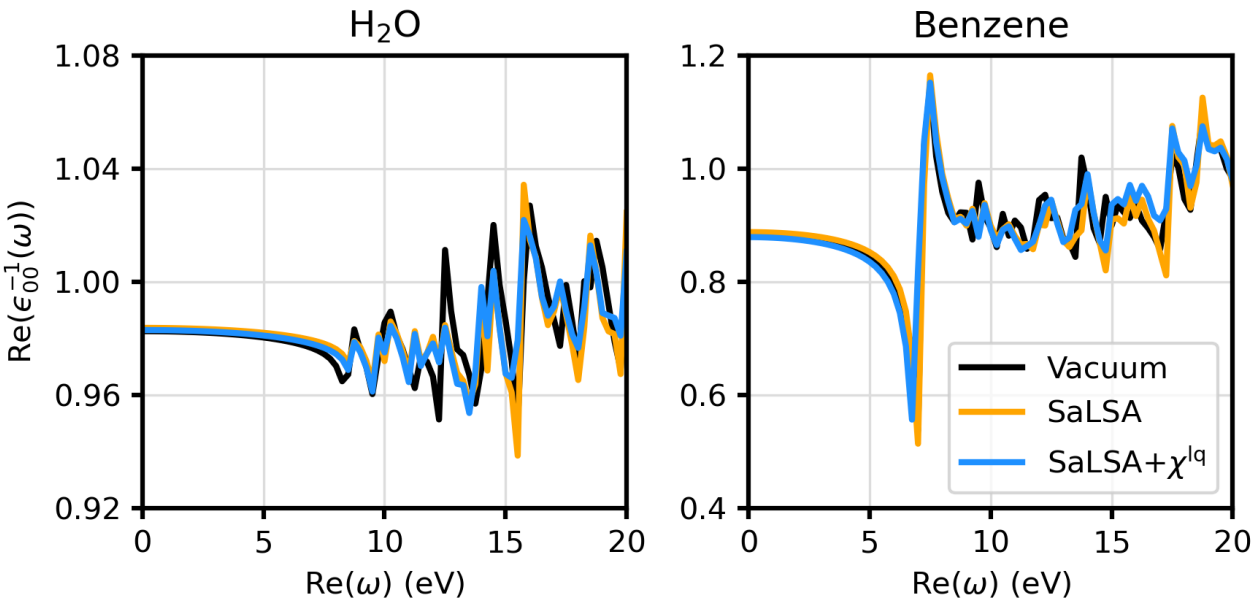


Weng, et al., J. Phys. Chem. Lett., 14 (2023)
Gaiduk, et al., JACS, 138 (2016)

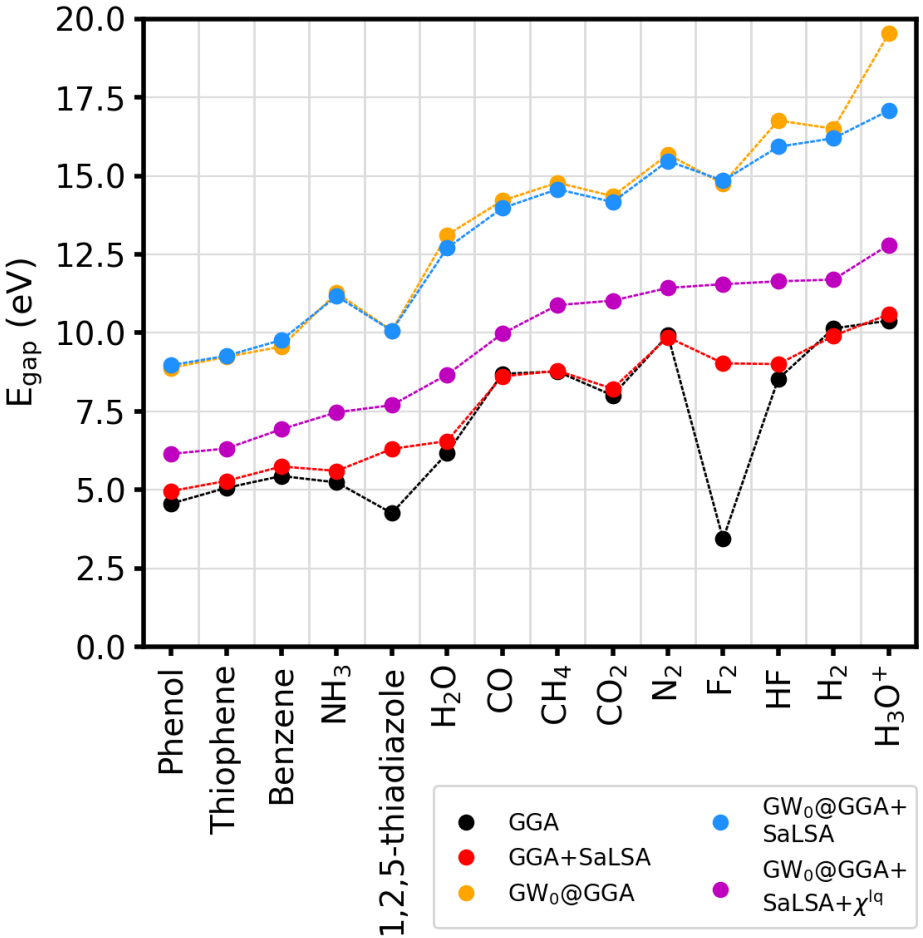
Merging GW with advanced implicit solvation models

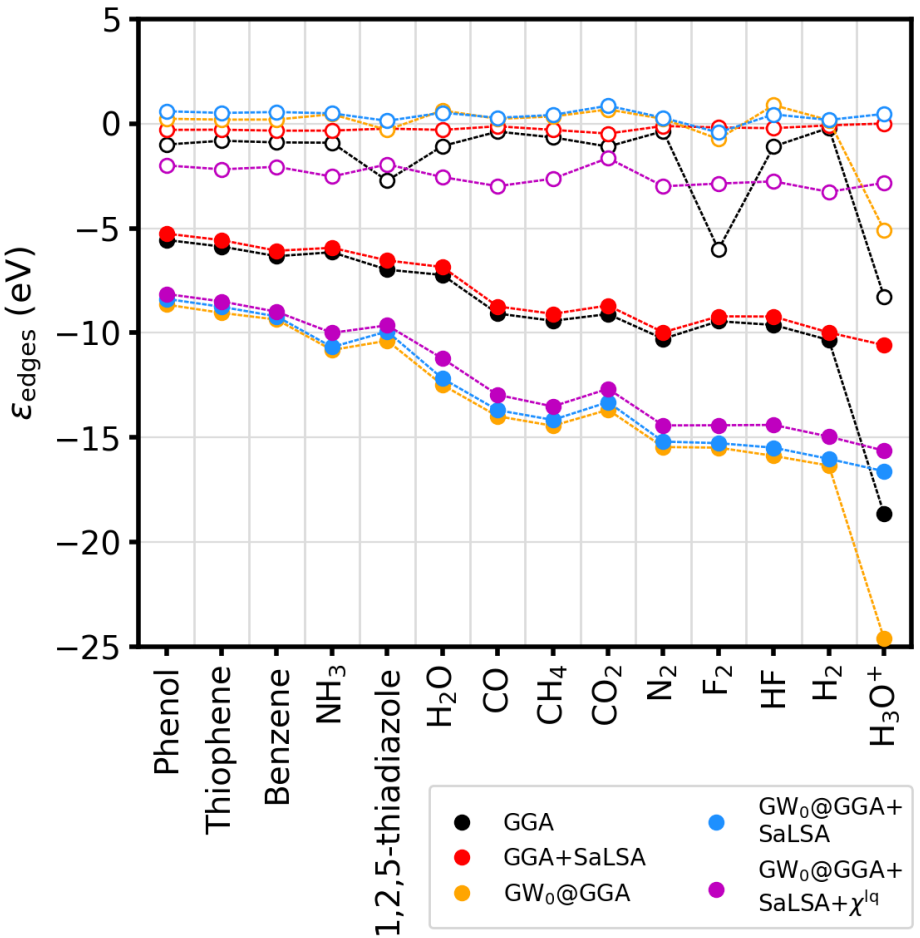
- We published a formalism merging GW with SaLSA model
  - J Clary, M Del Ben, R Sundararaman, D Vigil-Fowler, "Impact of solvation on the GW quasiparticle spectra of molecules",*J. Appl. Phys.* **134**, 085001 (2023)
- Use wavefunctions from solvated DFT calculation
- Combine fluid polarizability with electronic polarizability from SaLSA

$$\chi^{solv} = \chi^{0} + \chi^{lq}$$



Get lowering of HOMO-LUMO gap in molecules



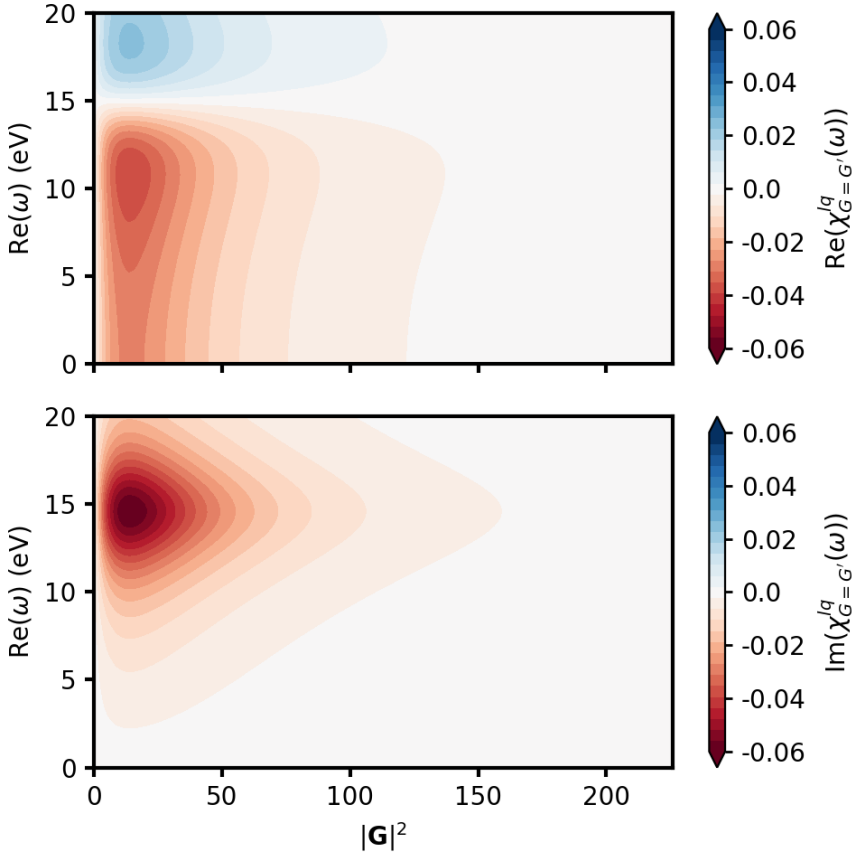


Get IP agreement with experiment where available

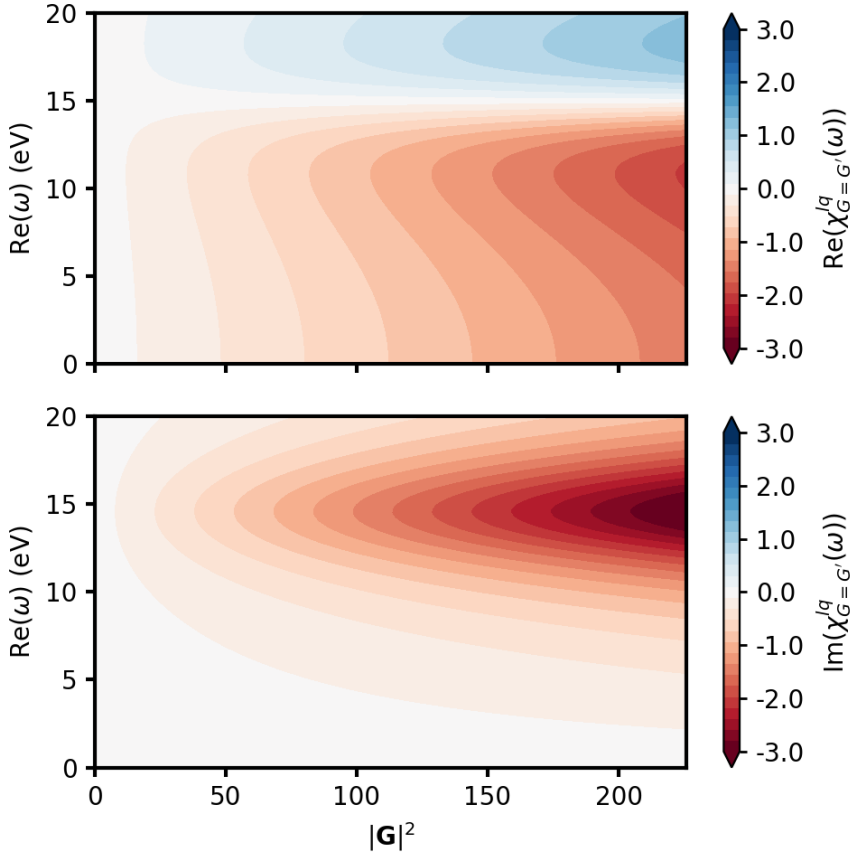
Molecule	IP	GW_0@GGA+ SaLSA+χ^{lq} IP (eV)	Experimental IP (eV)
H_2O	1^{st}	11.224	$11.1 - 11.5^{58–61}$
H_2O	2^{nd}	13.468	$13.5 - 13.8^{59–61}$
H_2O	3^{rd}	17.339	$17.3 - 17.4^{59,61}$
H_3O^+	2^{nd}	20.619	$20 - 21^{62}$
Phenol	1^{st}	8.141	$7.8 - 8.3^{63,64}$
Phenol	2^{nd}	8.924	8.6^{63}

Have to use SaLSA currently to avoid divergence

SaLSA



GLSSA13

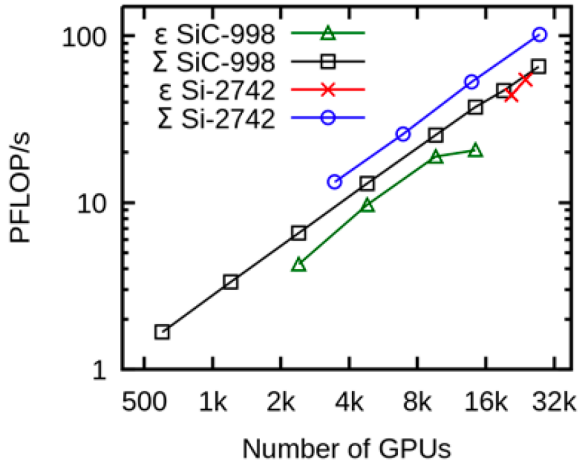


BerkeleyGW On the Path to Exascale

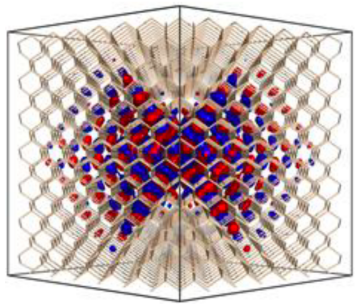
Foreseen exascale HPC systems will be GPU accellerated architectures

Optimized version of BerkeleyGW on GPU accelerated systems:

- Scale up to the full Summit machine at OLCF: **>27k GPUs**
- Reach nearly 53% of the peak performance at **106 PFLOP/s**
- Time to solution of **~10 mins for 11k electrons** system



M. Del Ben, C. Yang, Z. Li, F. H. da Jornada, S. G. Louie and J. Deslippe, "Accelerating Large-Scale Excited-State GW Calculations on Leadership Class HPC Systems" in Proceedings of the International Conference for High Performance Computing, Networking, Storage and Analysis, ser. SC '20 No.4 pp.1 (2020), ACM Gordon-Bell Finalist



Divacancy defect in semiconductor (such as Si and SiC) are proxy for solid state Qubits. For silicon shown is the 2742-atoms Si supercell, 10,968 electrons.