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

The BEAST collaboration

2nd Annual BEAST Workshop

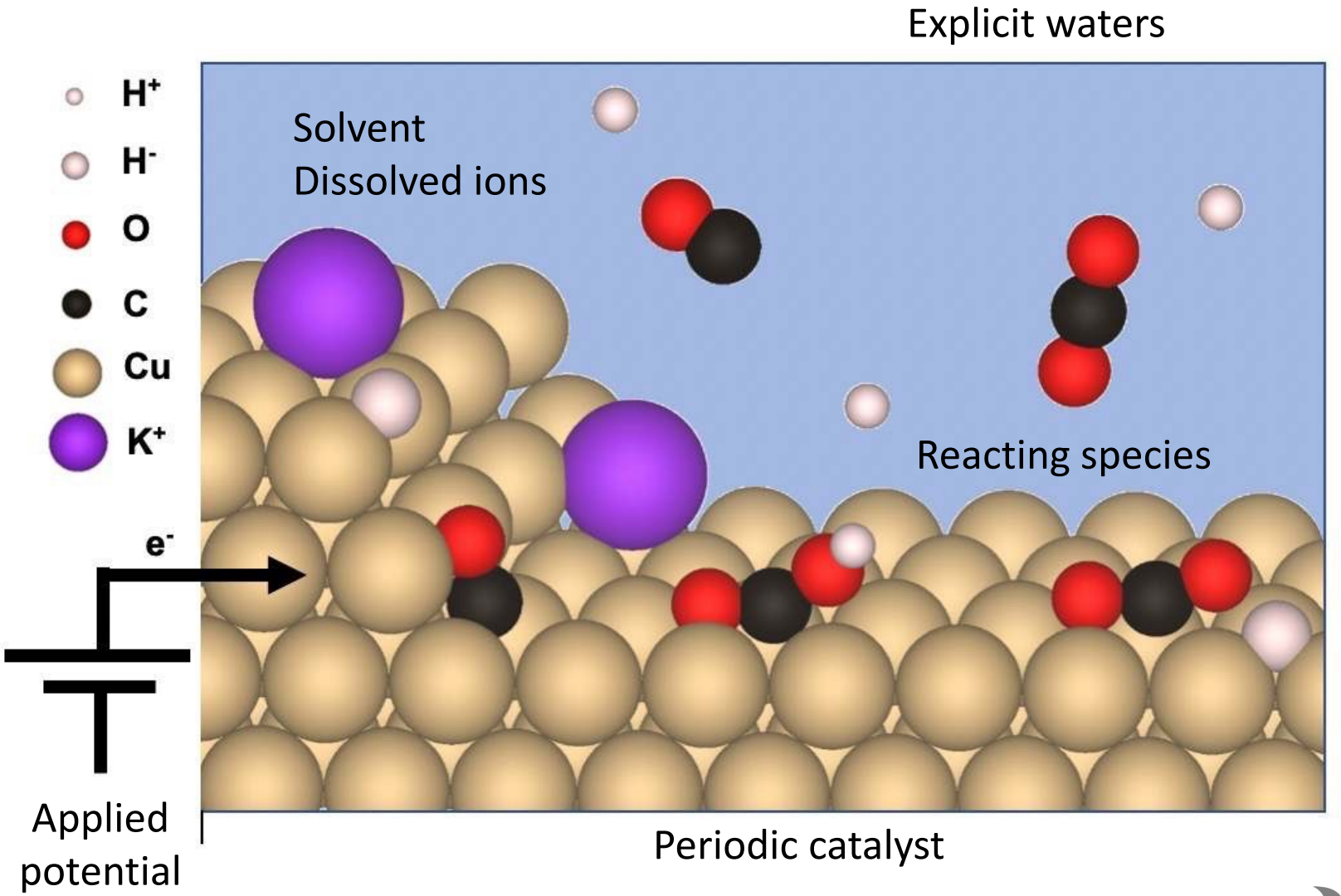
August 18, 2023

U.S. DEPARTMENT OF ENERGY

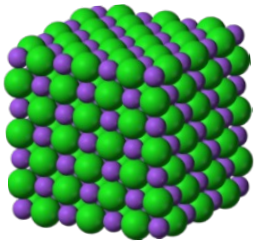
Office of Science

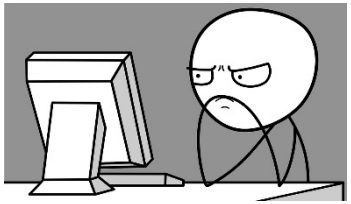
Award # DE-SC0022247

Electrochemical systems are complex

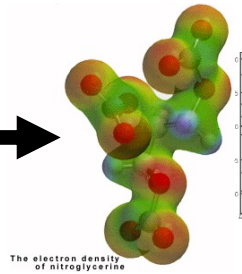


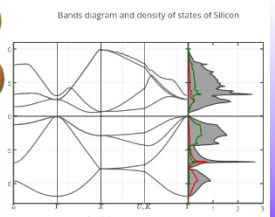
Density functional theory (Kohn-Sham)

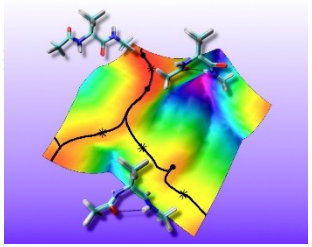




(J)DFT, RPA-GW

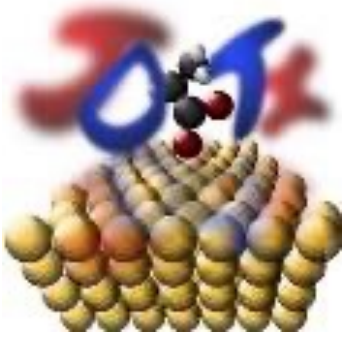






- Predict ground state properties without empirical input
- Properties: structure, charge density, reaction energetics

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



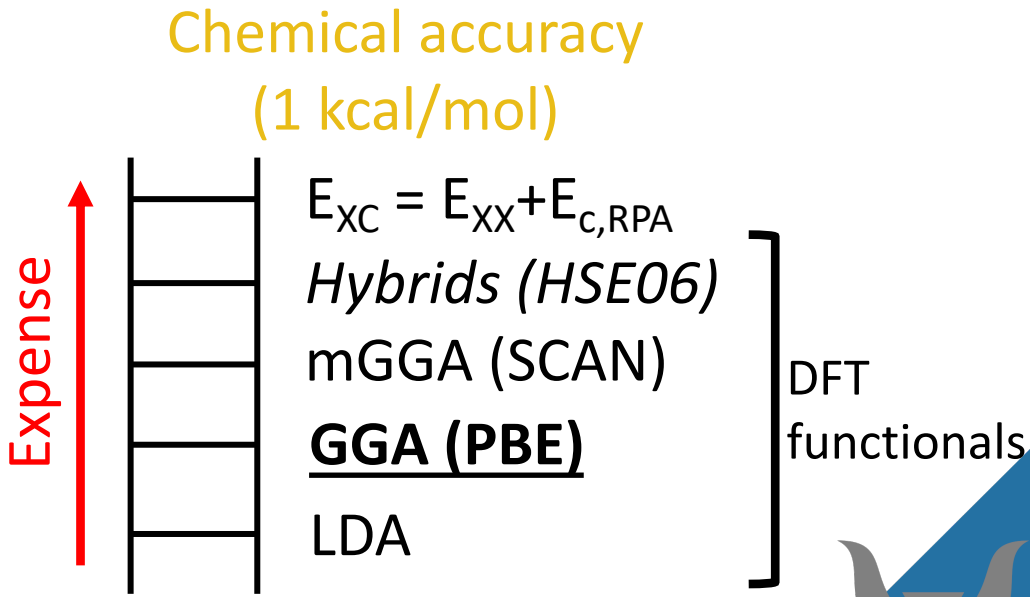
Density functional theory (Kohn-Sham)

- Describing exchange-correlation term is key

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

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

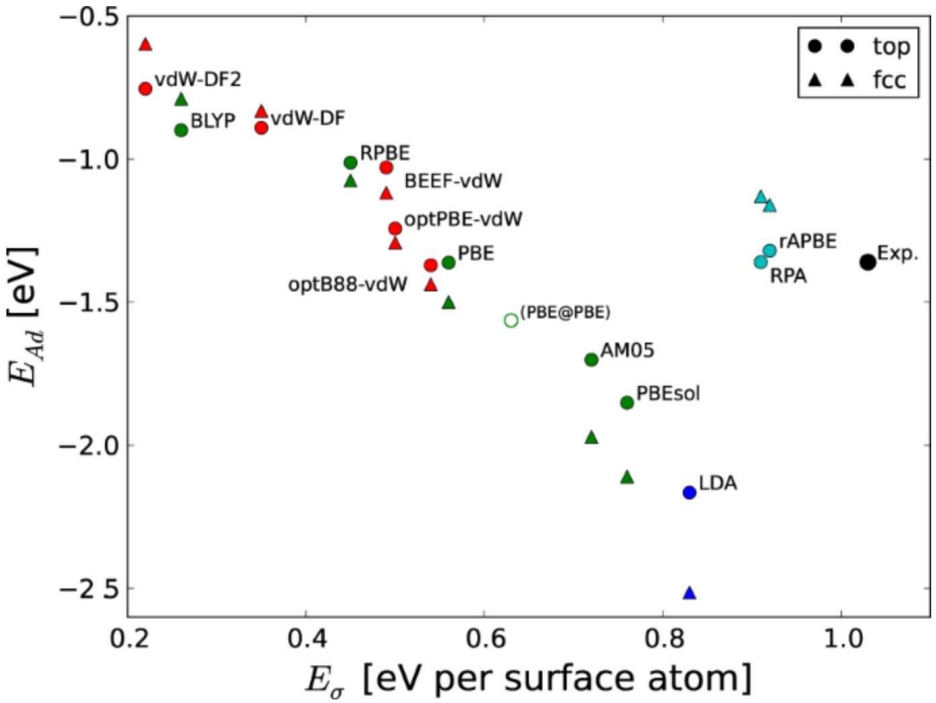
- Calculate E_{XC} with varying degrees of accuracy/expense
  - 0 K, vacuum conditions

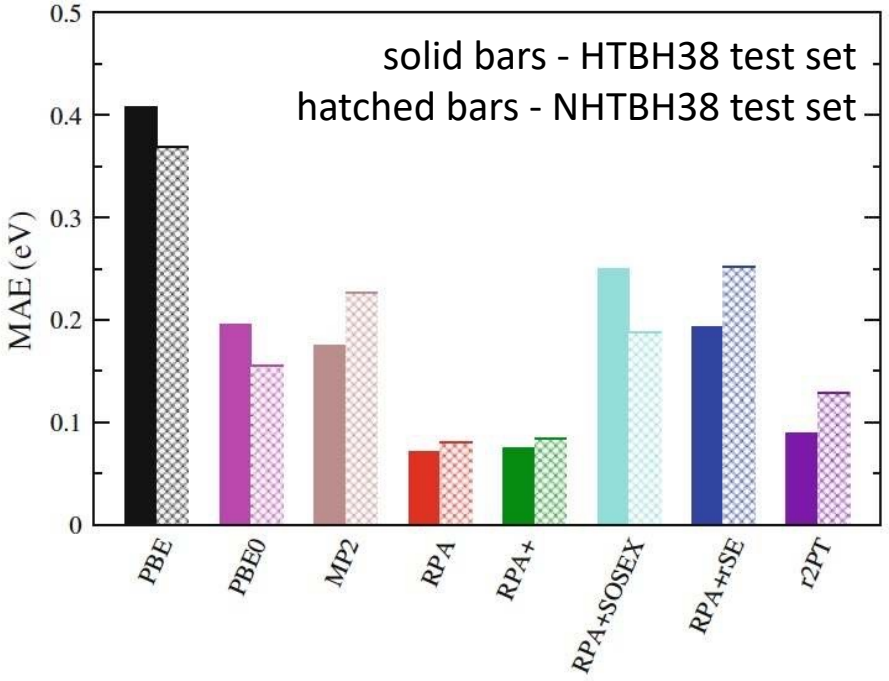


What functional gives accurate energies and electronic structure… generally?

RPA can predict accurate properties relevant to catalysis

CO adsorption to Pt(111)

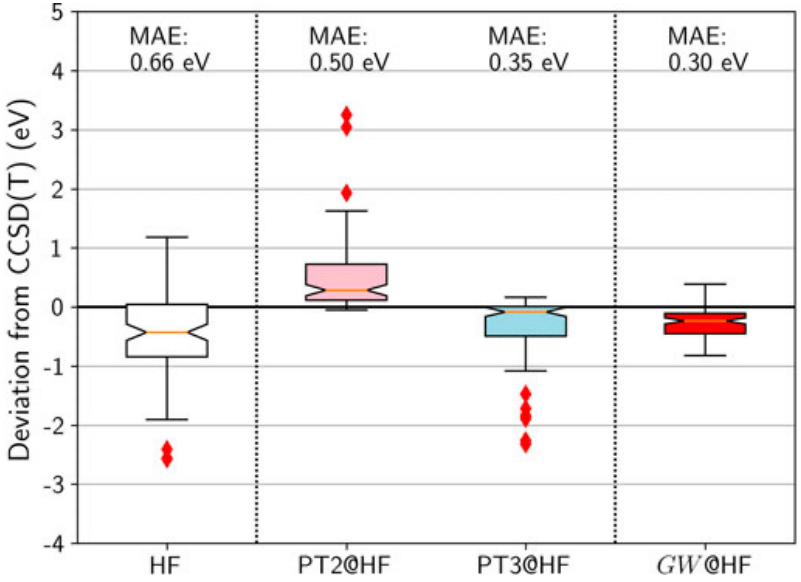


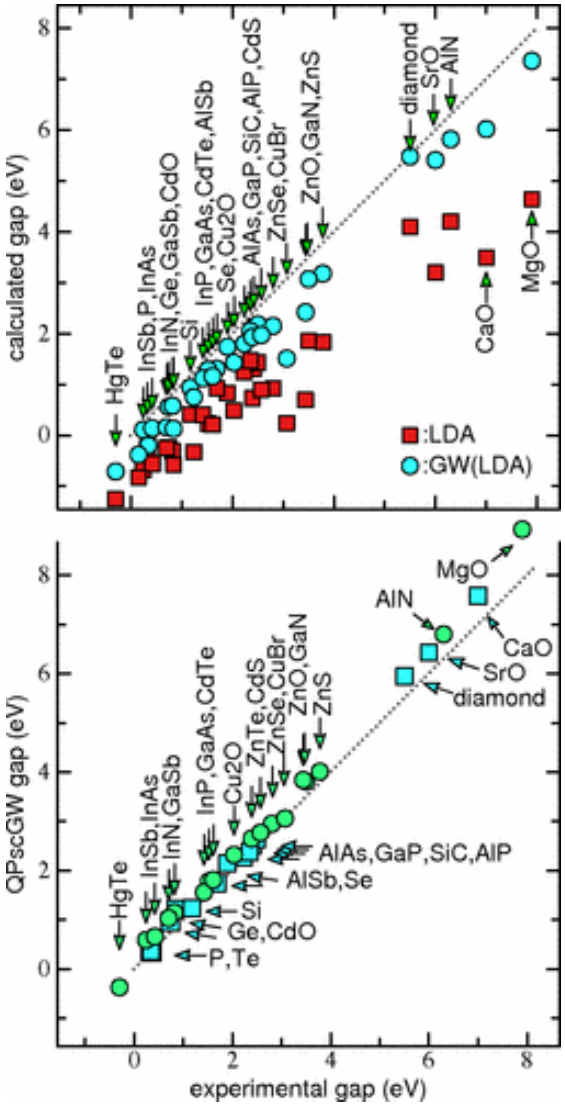


HTBH38: forward, inverse barrier heights of 19 hydrogen-transfer reactions, NHTBH38: 19 reactions involving heavy atom transfers, nucleophilic substitutions, association, unimolecular processes.

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

GW can predict accurate IPs and band gaps





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

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

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

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

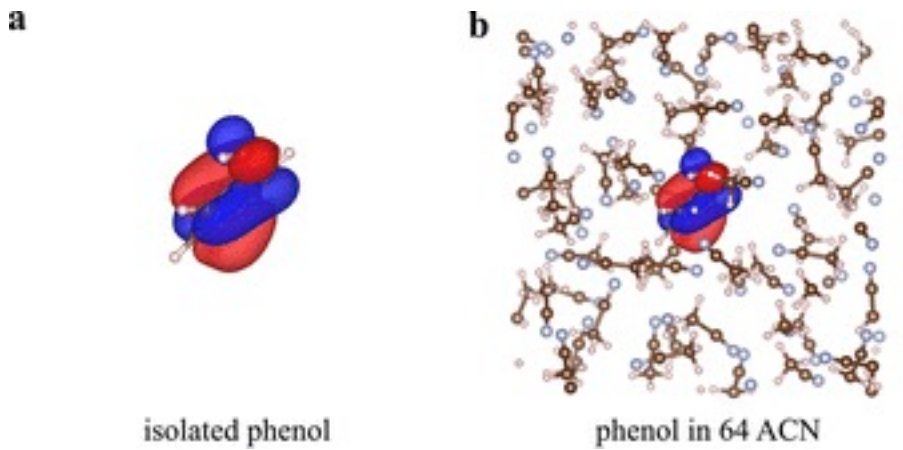
- The RPA: $f_{xc}^{\lambda} = 0$

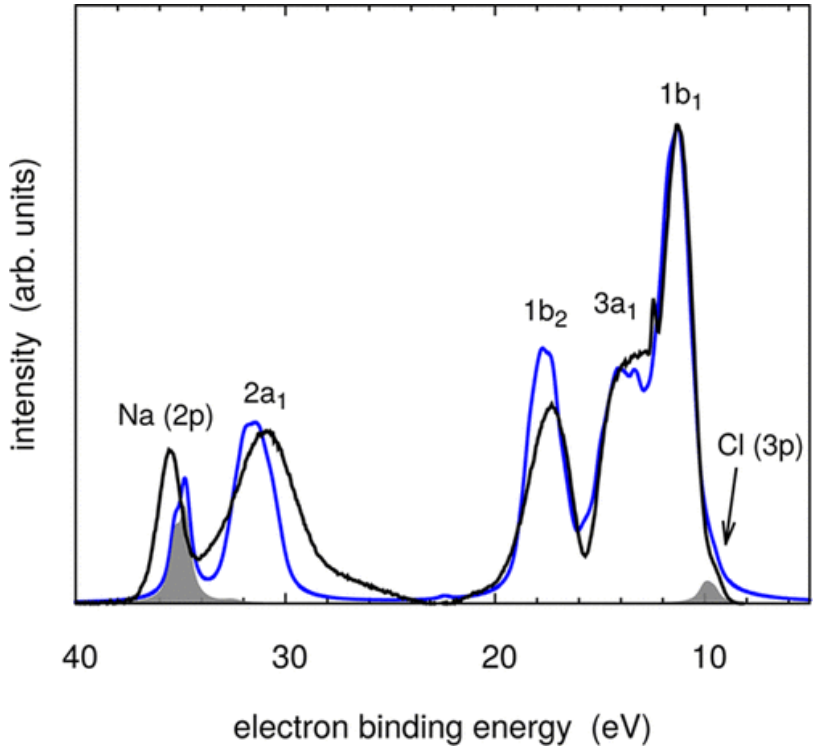
- Obtain polarizability
- Can calculate RPA correlation energy analytically

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

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



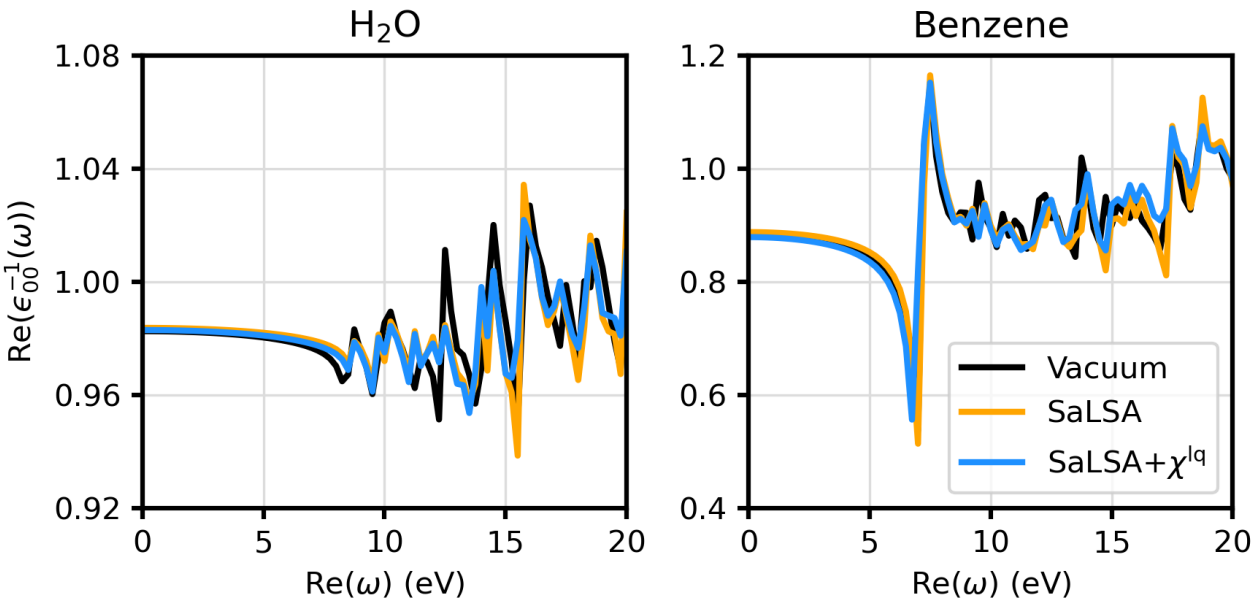


Weng, et al., J. Phys. Chem. Lett., 14 (2023)
Gaiduk, et al., JACS, 138 (2016)

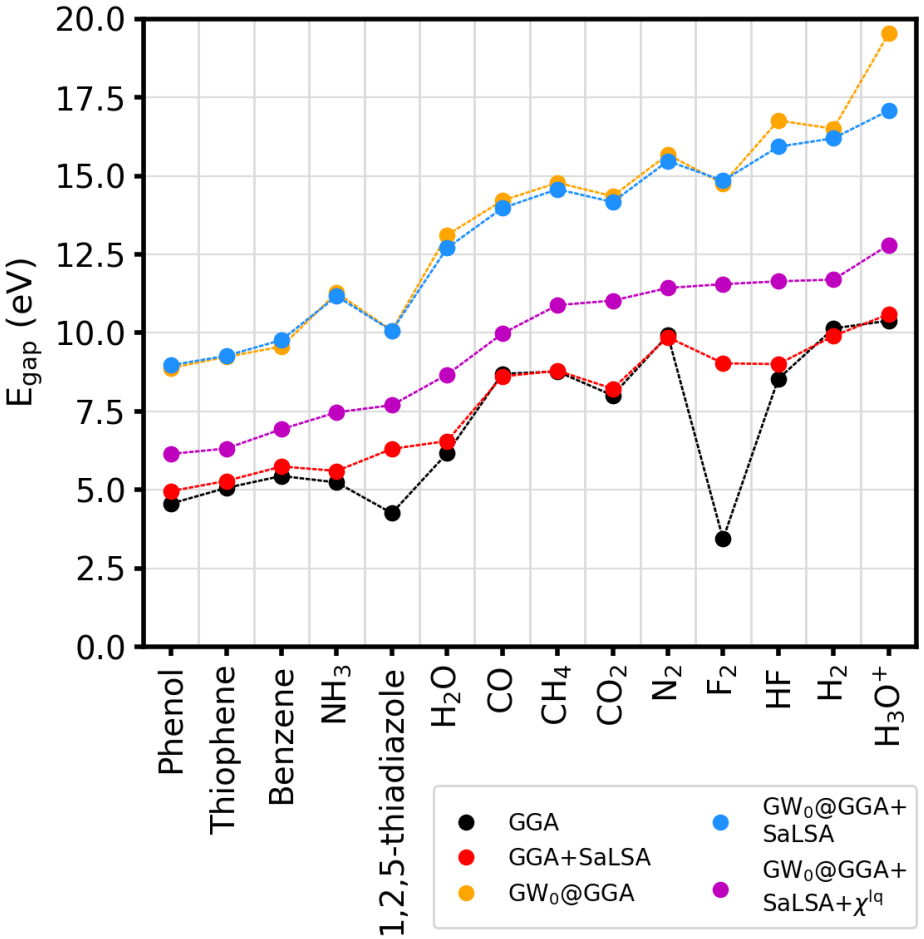
Merging GW with advanced implicit solvation models

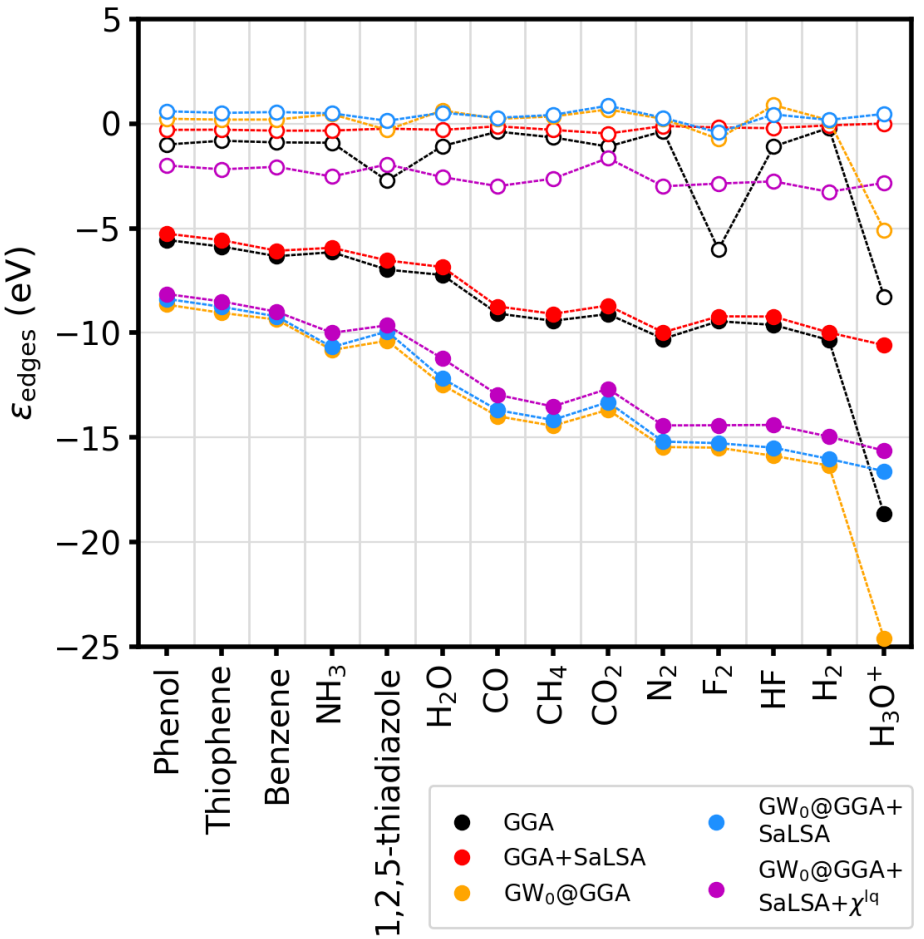
- We published a formalism merging GW with SaLSA model
  - Accepted paper should be available online soon
  - *Impact of solvation on the GW quasiparticle spectra of molecules*
- Use wavefunctions from solvated DFT calculation
- Combine fluid polarizability with electronic polarizability from SaLSA

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



Get lowering of HOMO-LUMO gap in molecules



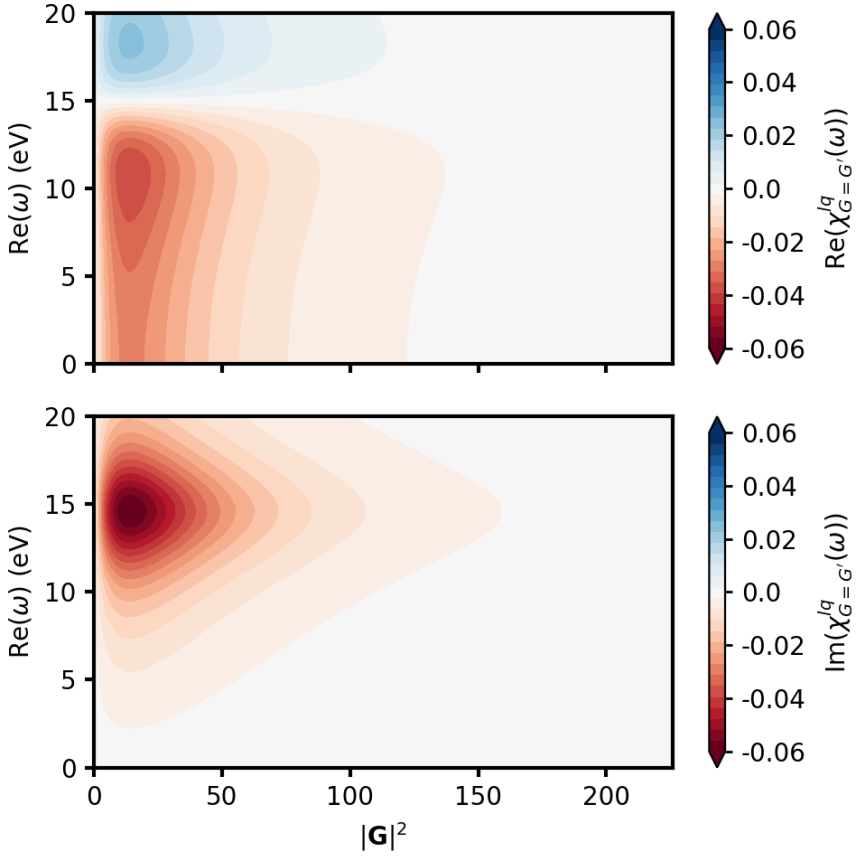


Get IP agreement with experiment where available

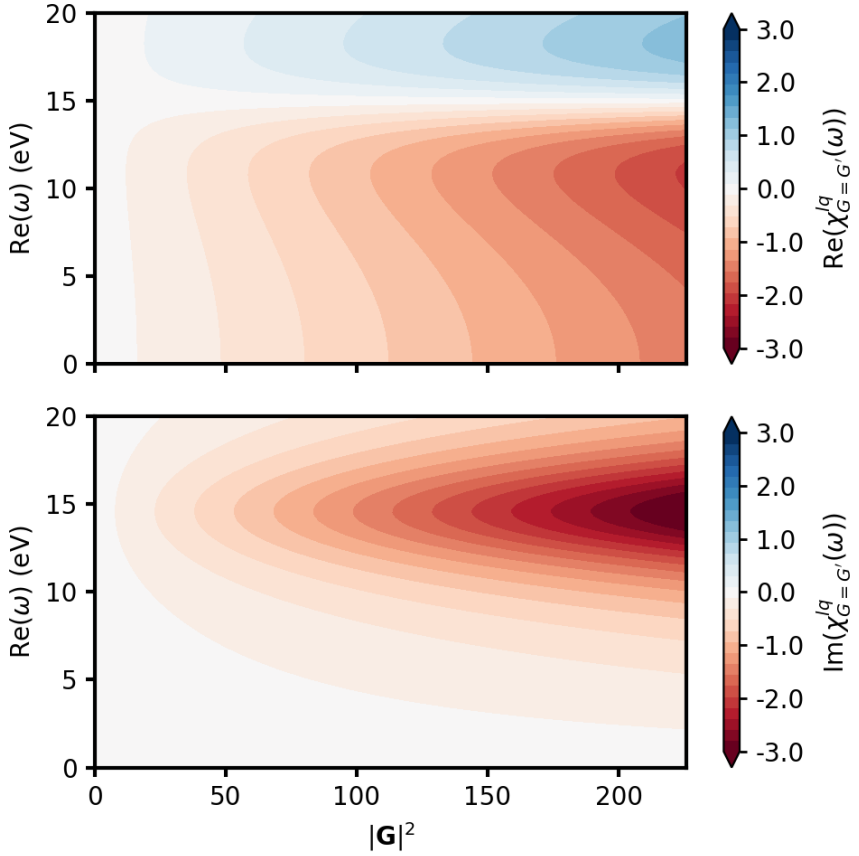
Molecule	IP	GW_0@GGA+ SaLSA+χ^{lq} IP (eV)	Experimental IP (eV)
H_2O	1^{st}	11.224	$11.1 - 11.5^{58–61}$
H_2O	2^{nd}	13.468	$13.5 - 13.8^{59–61}$
H_2O	3^{rd}	17.339	$17.3 - 17.4^{59,61}$
H_3O^+	2^{nd}	20.619	$20 - 21^{62}$
Phenol	1^{st}	8.141	$7.8 - 8.3^{63,64}$
Phenol	2^{nd}	8.924	8.6^{63}

Have to use SaLSA currently to avoid divergence

SaLSA



GLSSA13

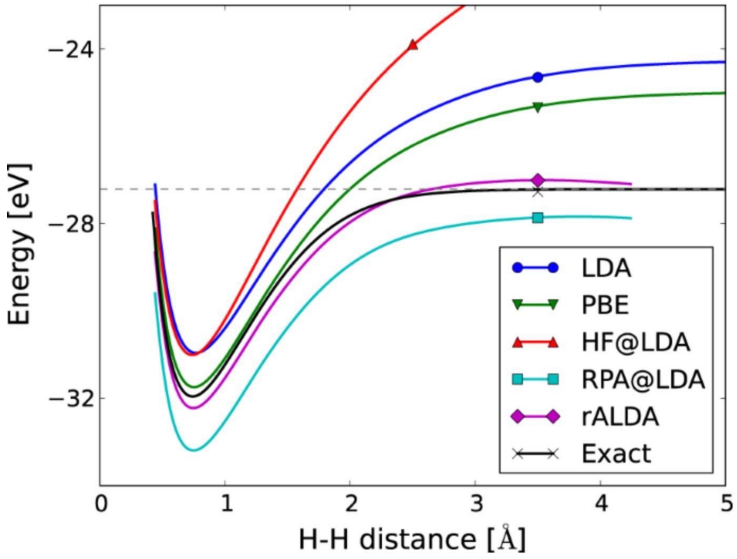


Current work: can we extend this to RPA?

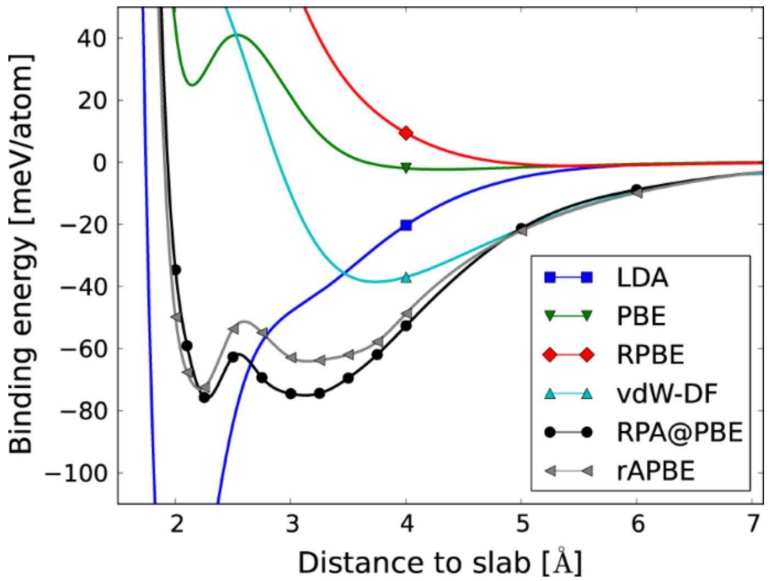
- Features
  - RPA gives correlation energy, compute EXX using input orbitals
  - Exactly cancels self-interaction from Hartree term (some self-interaction in correlation)
  - O(N4) complexity: between DFT and high-fidelity MP2, CCSD, CCSD(T)
  - Parameter-free dispersion forces: key for surface chemistry,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

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

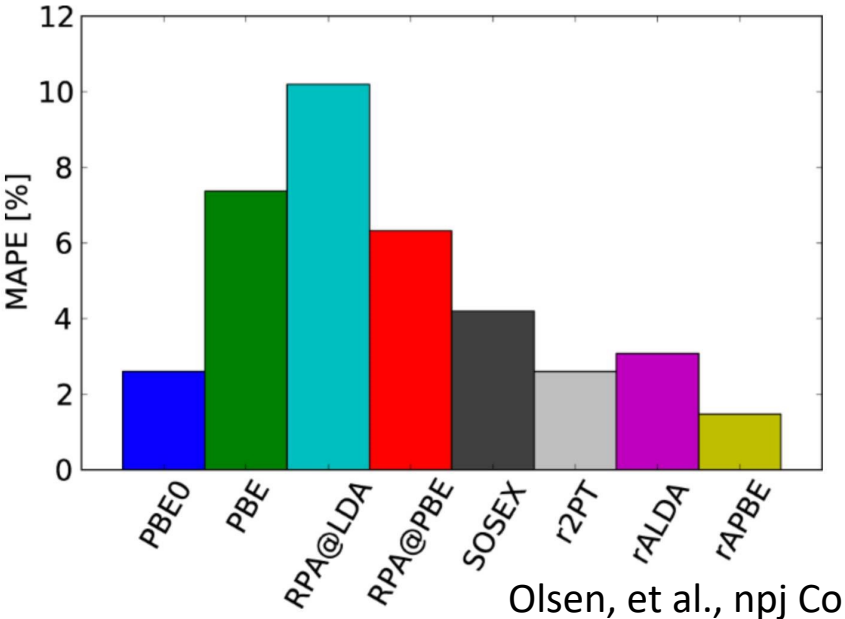
H_2 dissociation: RPA good



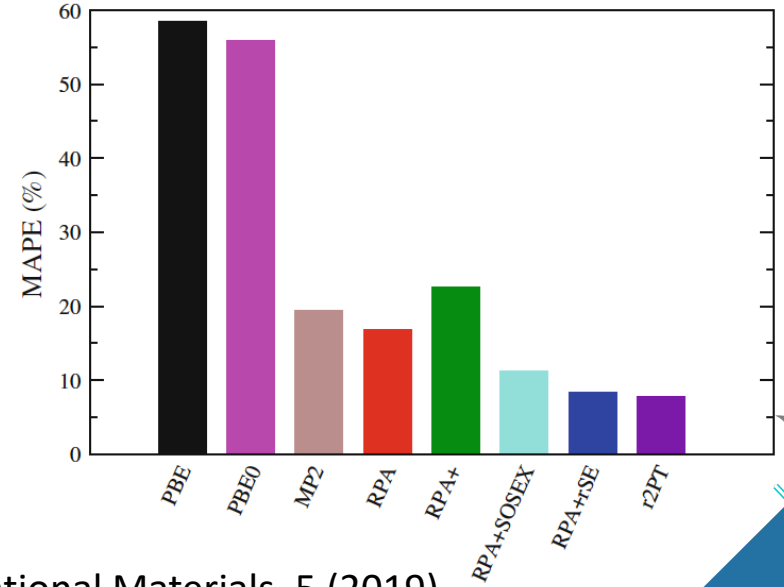
Graphene*+Ni(111): RPA good



Atomization energies: RPA ok



vdW/H-bonding: RPA very good



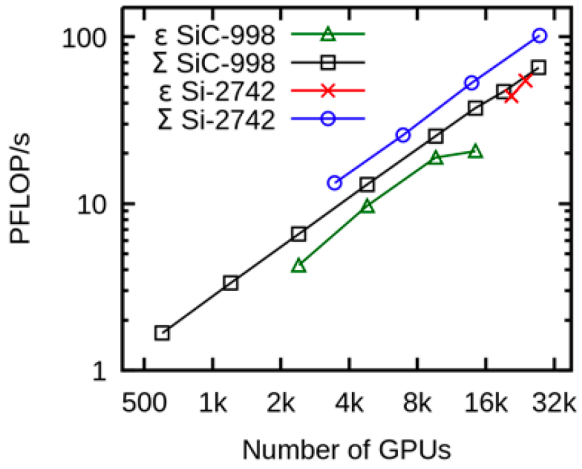
Olsen, et al., npj Computational Materials, 5 (2019)

BerkeleyGW On the Path to Exascale

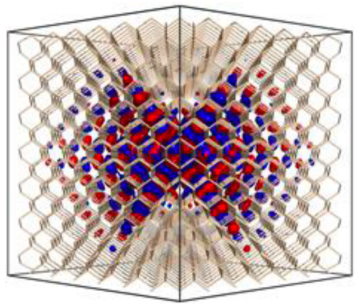
Foreseen exascale HPC systems will be GPU accellerated architectures

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.