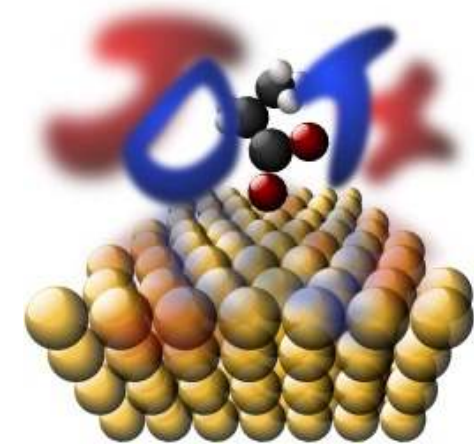
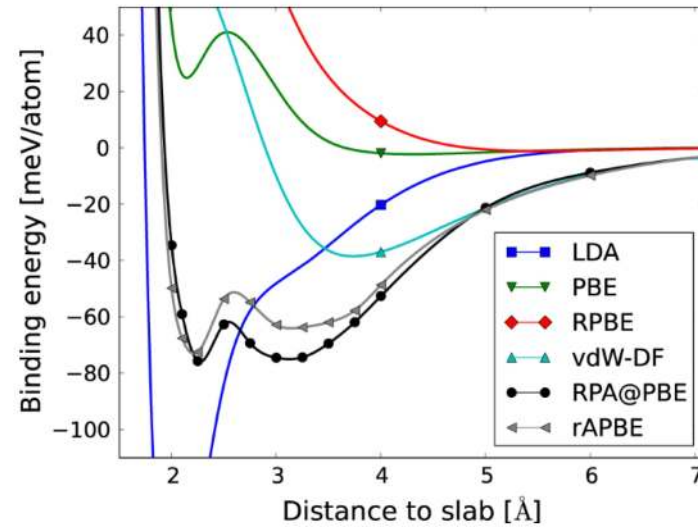
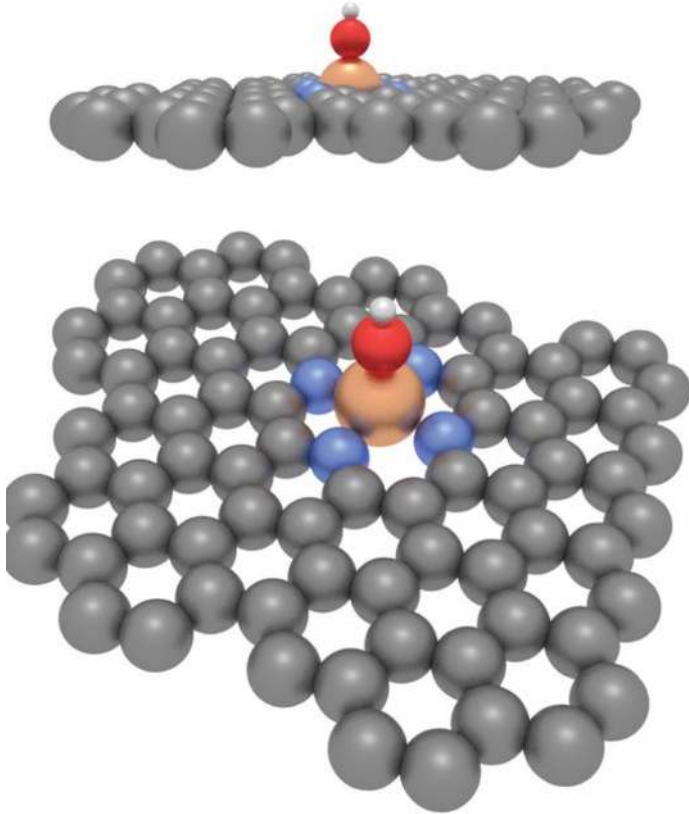


The Random Phase Approximation (RPA) for electrochemistry



BerkeleyGW

Derek Vigil-Fowler

National Renewable Energy Laboratory



Overview

- RPA: brief introduction
- RPA: results on selection of chemical properties
- RPA for electrochemistry
- ACFDT and RPA: deeper dive



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Density functional theory

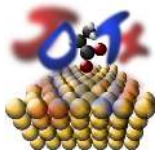


Density functional theory (Kohn-Sham)

- Predict ground state properties without empirical input

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

- Properties : structure, charge density, reaction energetics
- Thousands of practitioners world wide (16k citations on Hohenberg, Kohn)
 - JDFTx, Quantum ESPRESSO, VASP, ABINIT, EXCITING, Fleur, Octopus, ELK



Density functional theory (Kohn-Sham)

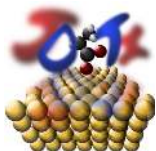
- Predict ground state properties without empirical input



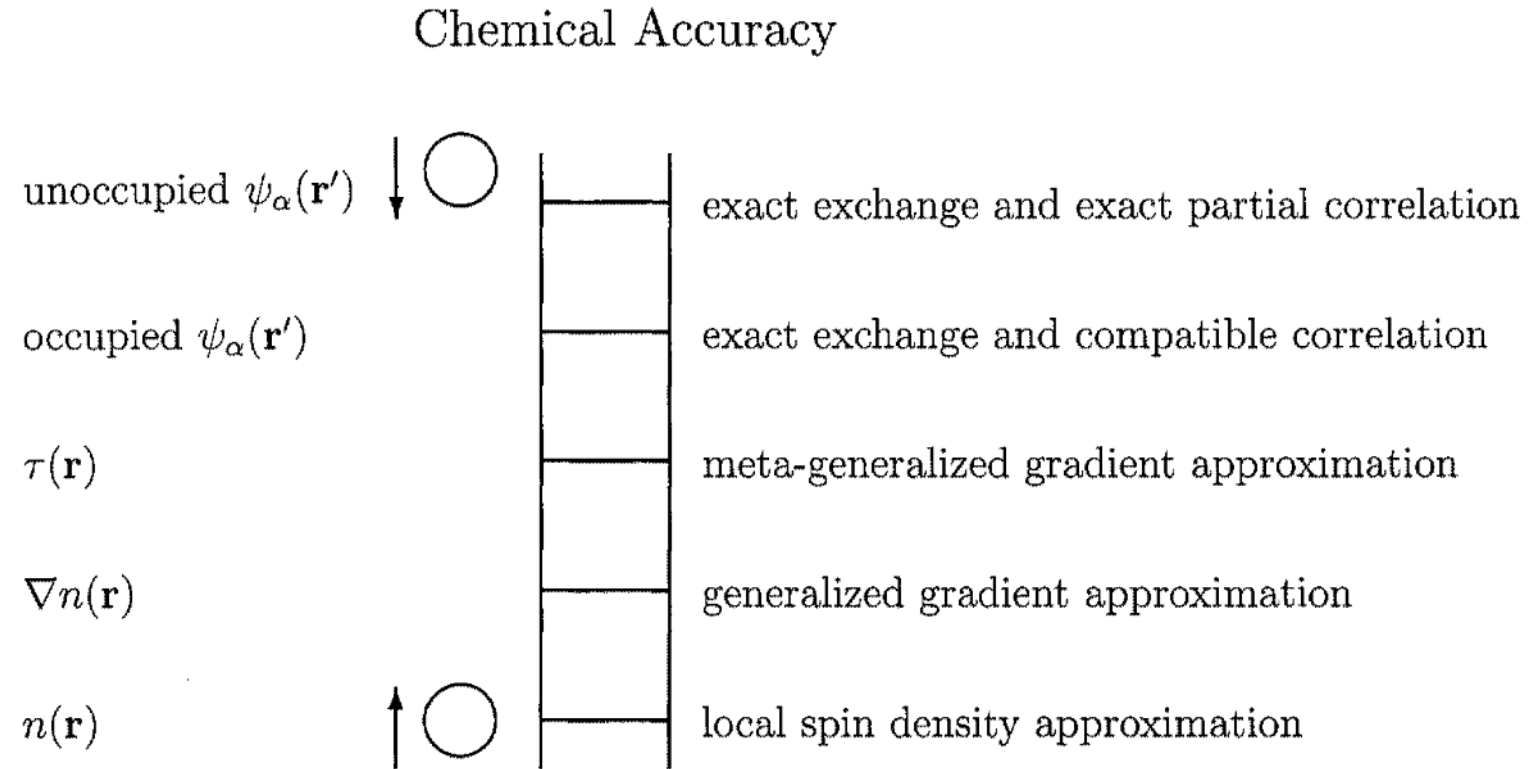
Walter Kohn (1998)

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

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Jacob's ladder



Hartree World



What is the random phase approximation (RPA)?



What is the random phase approximation (RPA)?

“We distinguish between two kinds of response of the electrons to a wave. One of these is **in phase** with the wave, so that the phase difference between the particle response and the wave producing it **is independent of the position of the particle**. This is the response which contributes to the **organized behavior of the system**. The other response has a **phase difference** with the wave producing it...Because of the general random location of the particle, this second response tends to **average out to zero**...This procedure we call the *random-phase approximation*.”



What is the RPA?

- More meaningful definitions:
 - Orbital-dependent DFT functional using linearized time-dependent Hartree density response
 - Coupled cluster doubles (CCD) with only ring diagrams

$$E_c^{\text{RPA}} = -\frac{1}{4} \text{ (ring diagram)} - \frac{1}{6} \text{ (ring diagram)} - \dots$$

- Infinite summation of direct term in MP perturbation theory



Overview

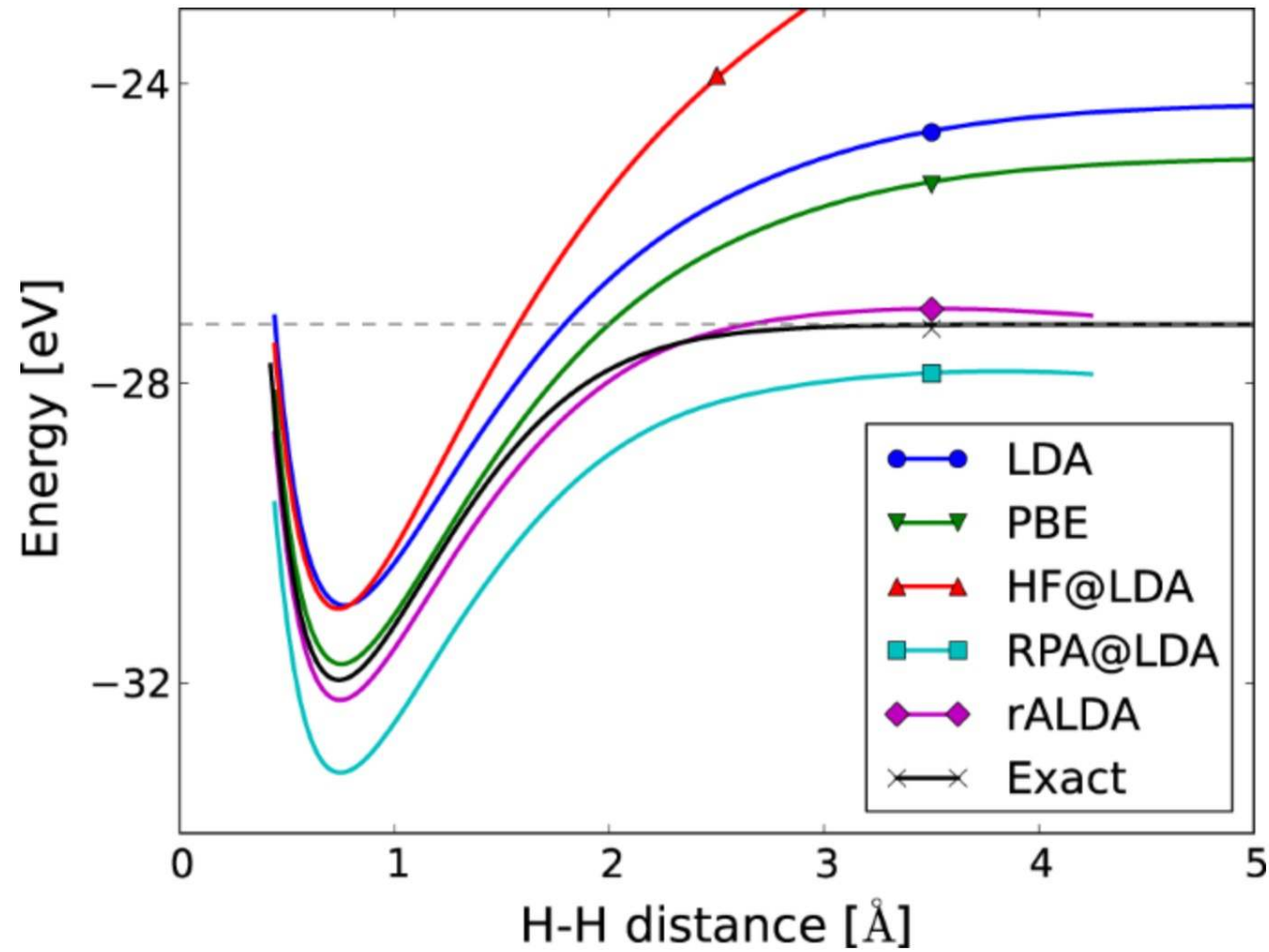
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How good is RPA?

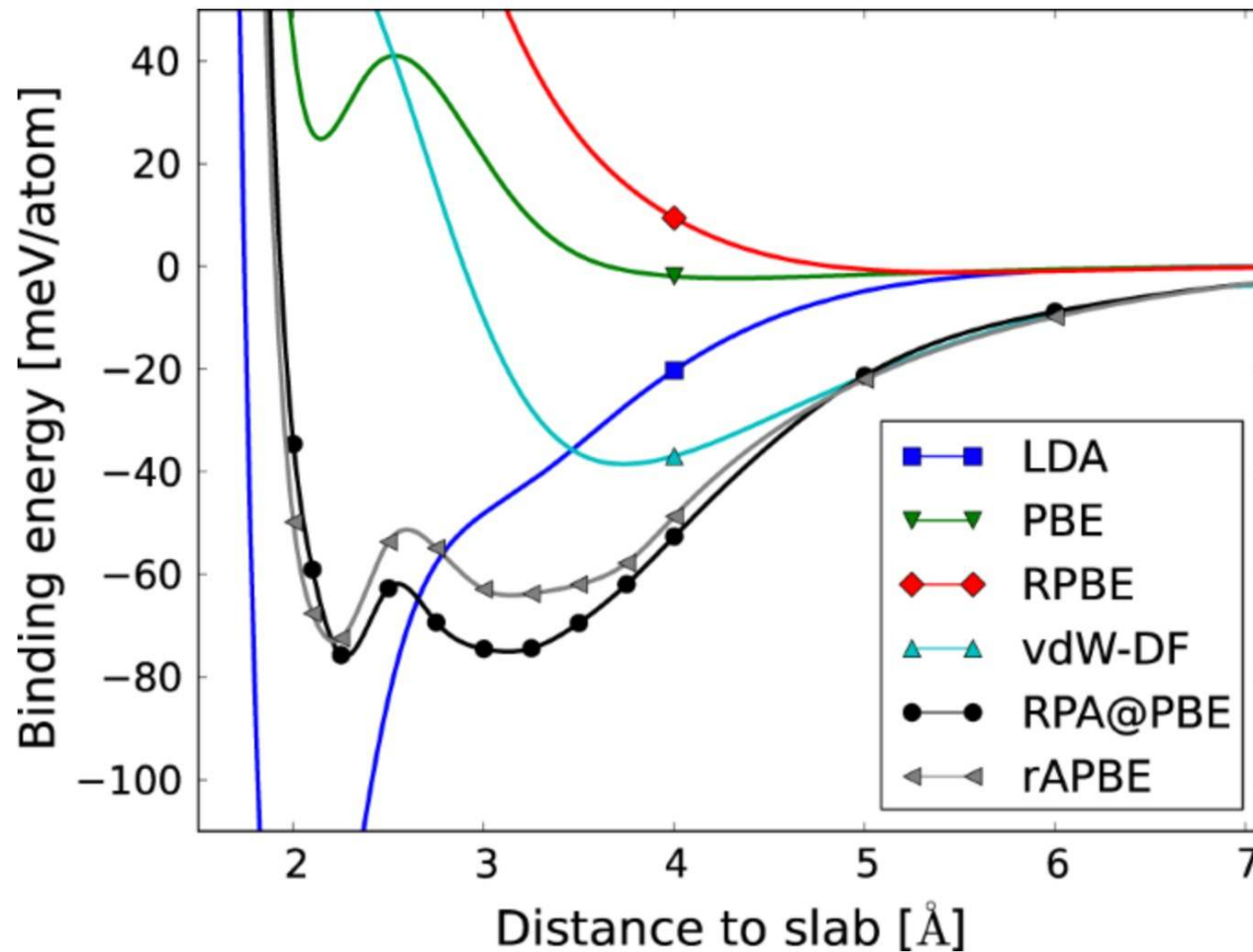


H₂ dissociation: RPA good



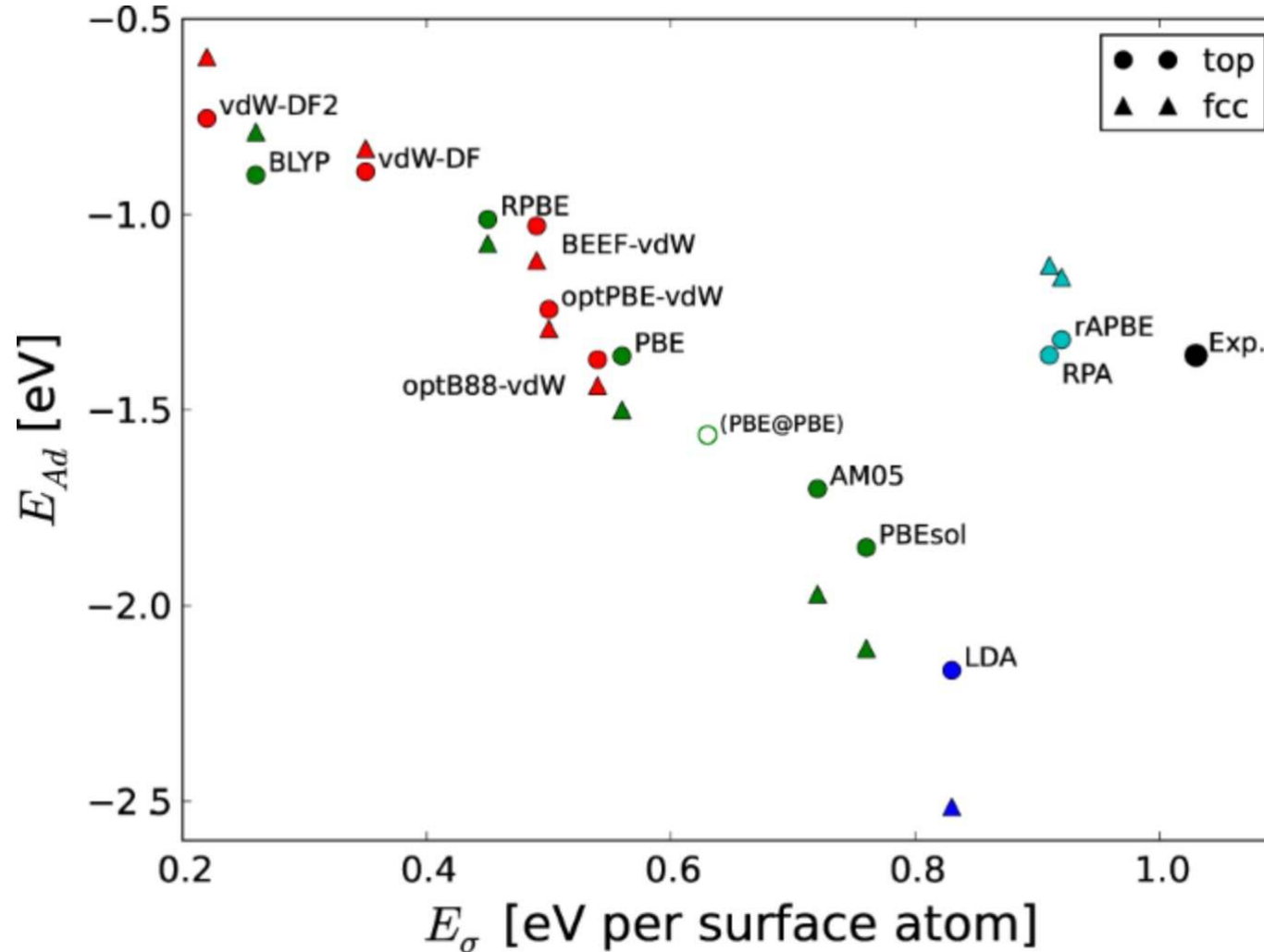
Binding of 2D materials: RPA

Graphene on Ni(111)

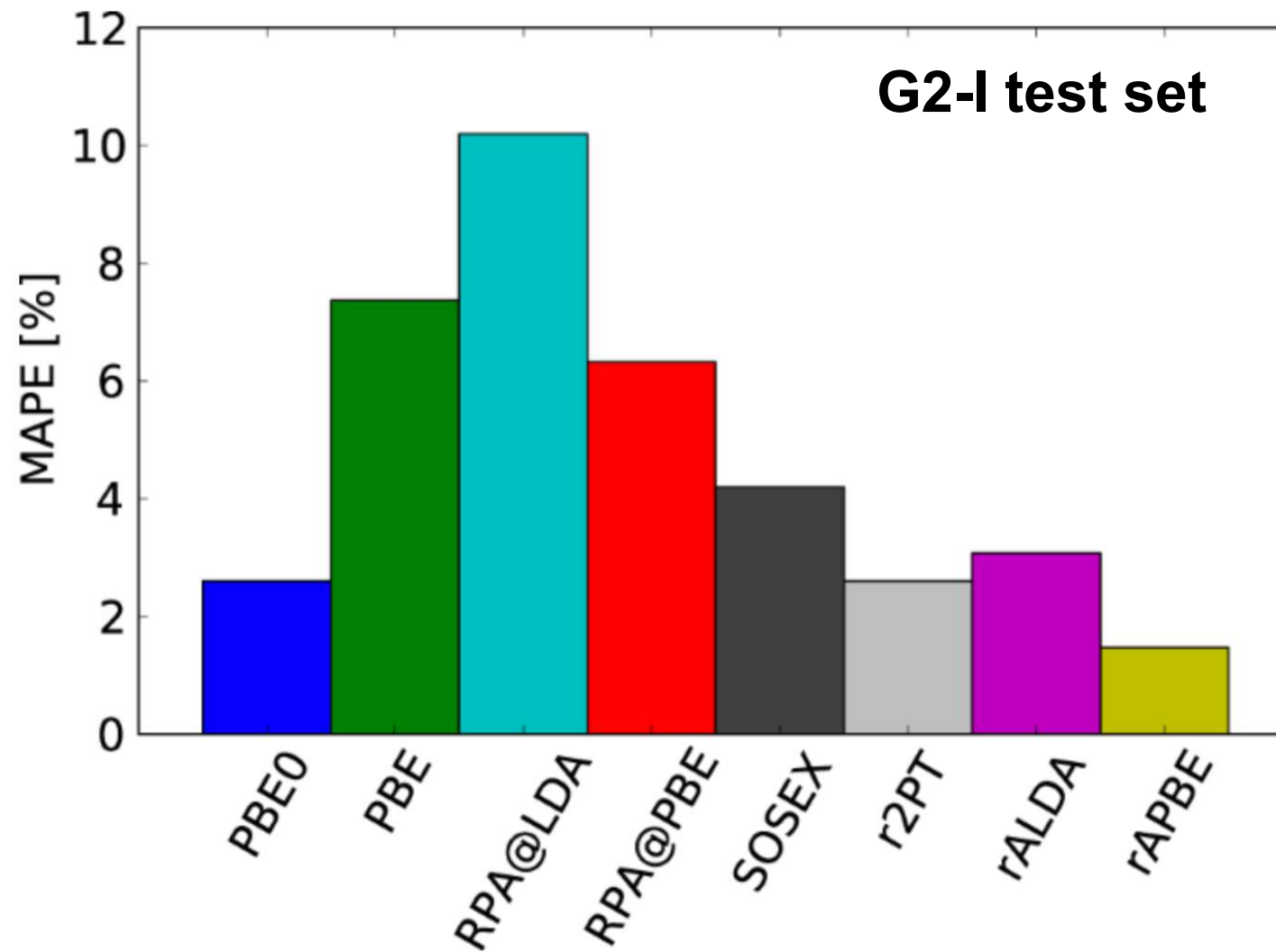


Adsorption and surface energies: RPA

CO on Pt(111)

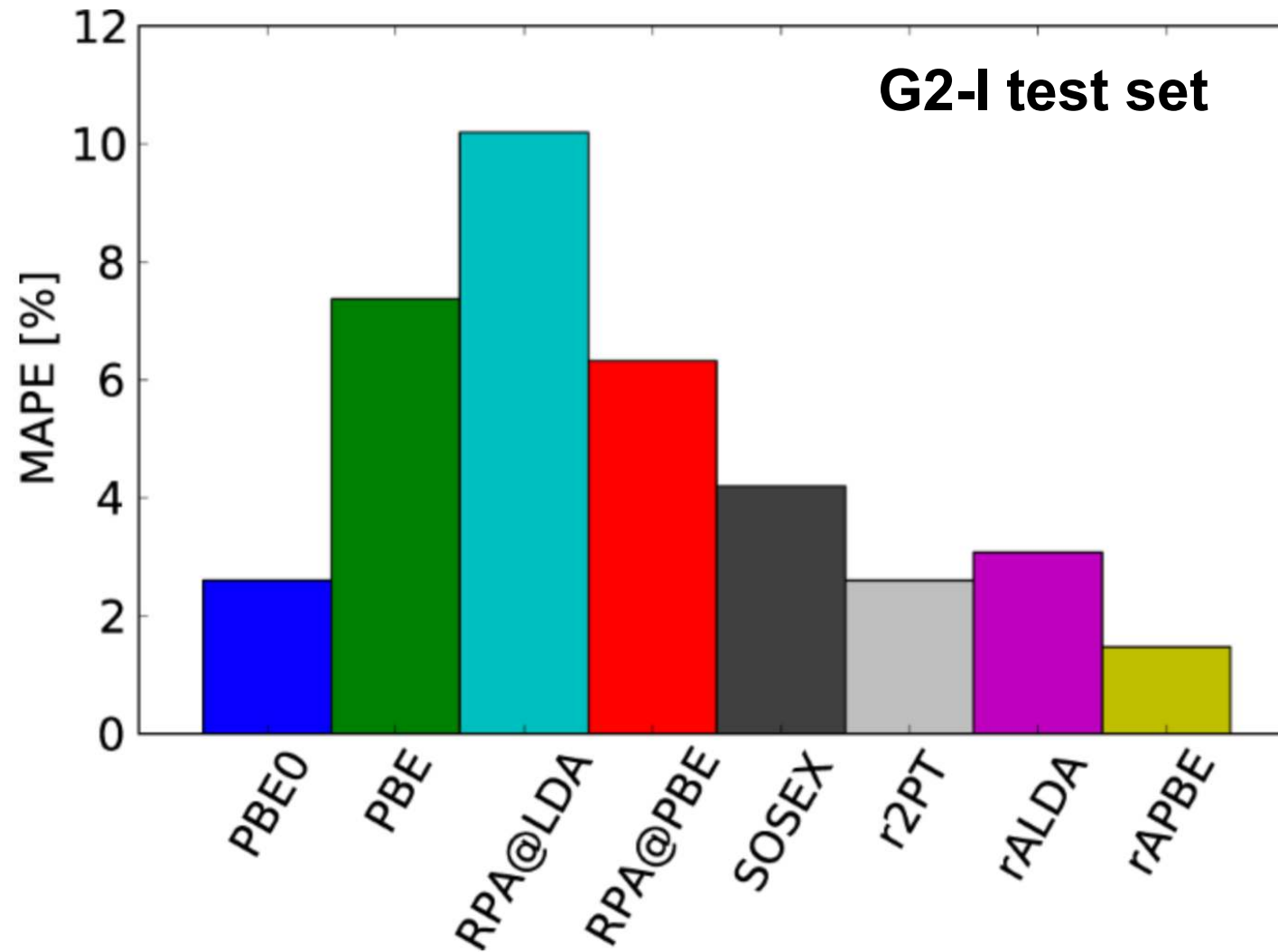


Atomization energies: RPA ok

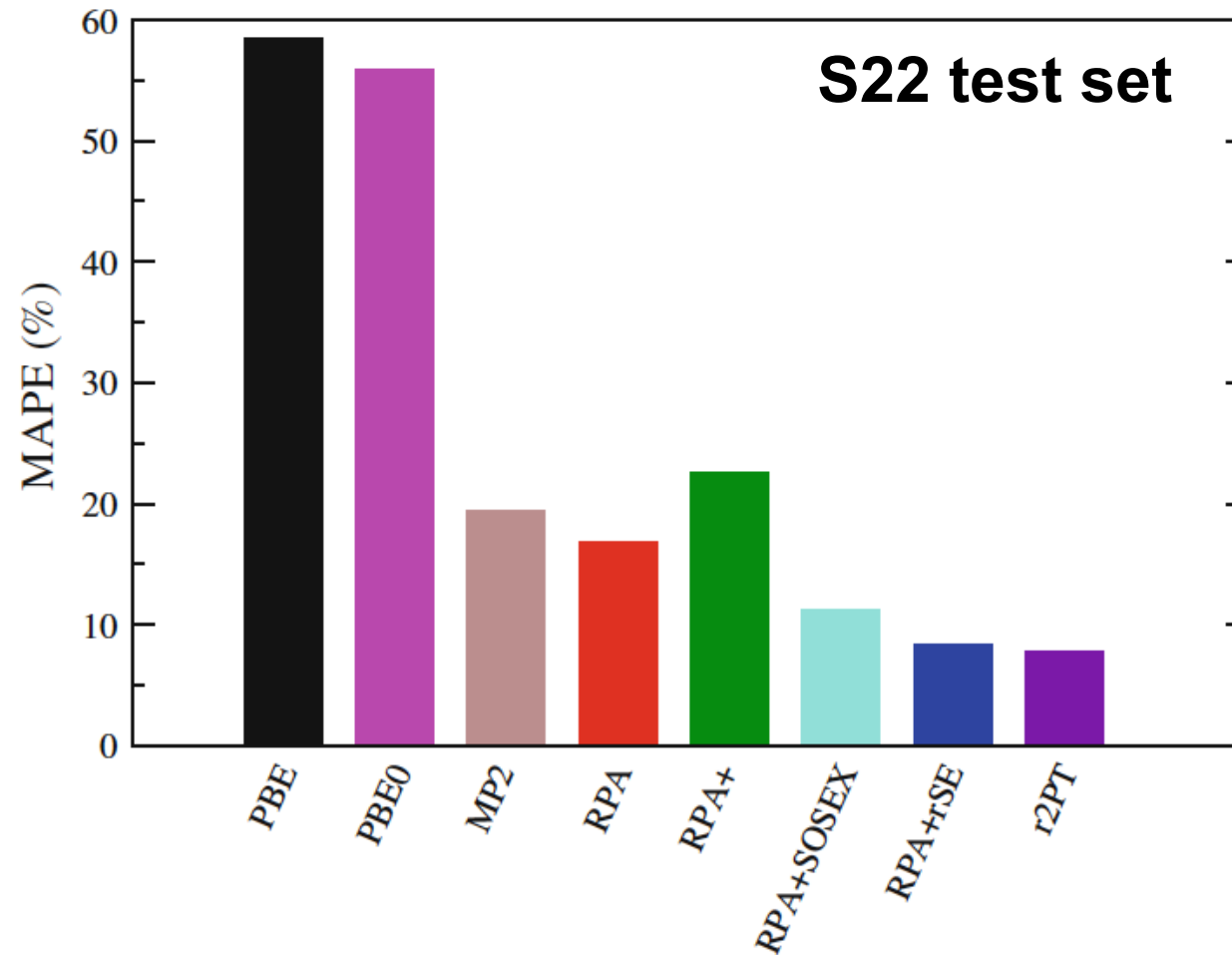


Atomization energies: RPA ok

G2-I: atomization energies of small organic molecules

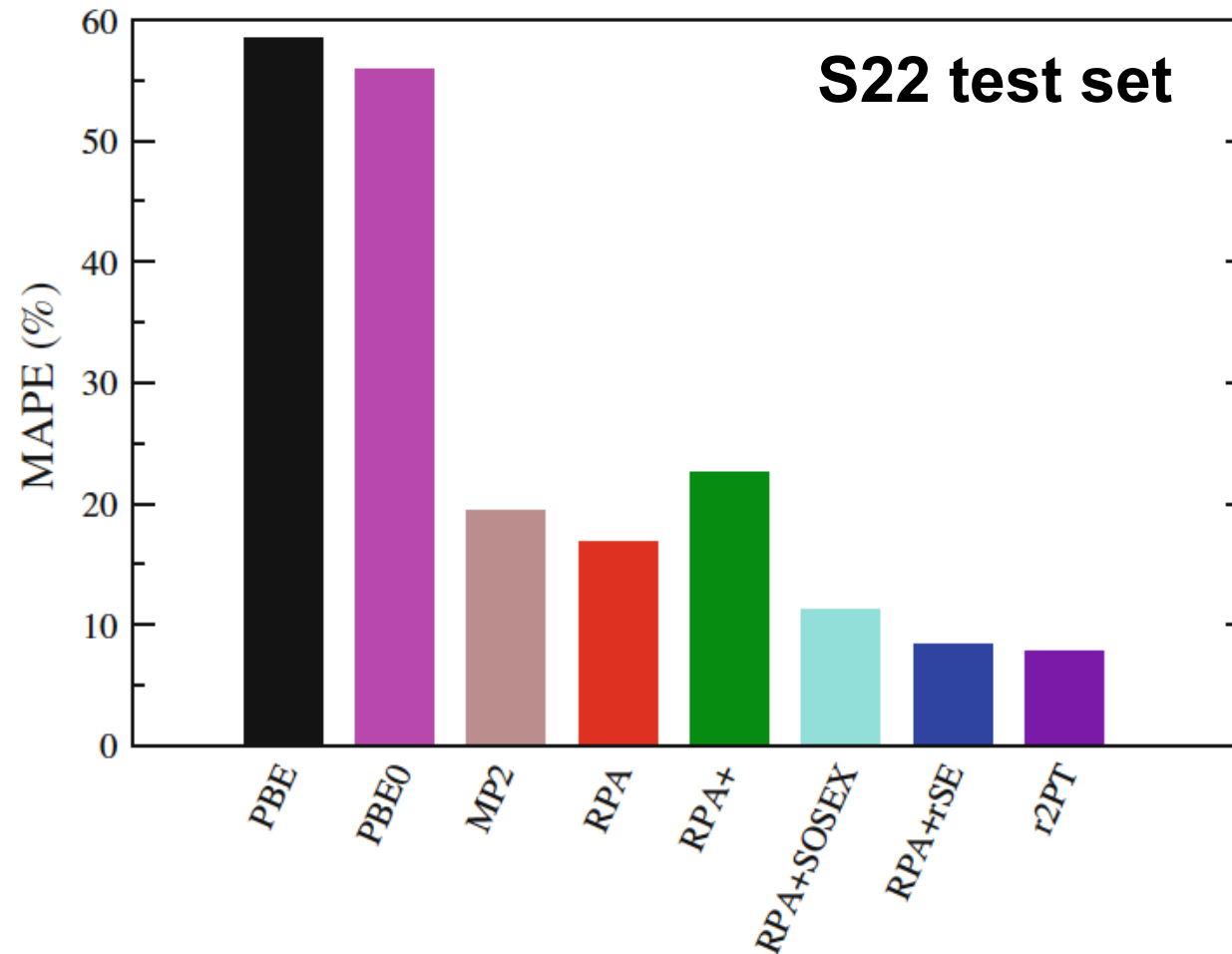


Dispersion and Hydrogen bonding: RPA very good

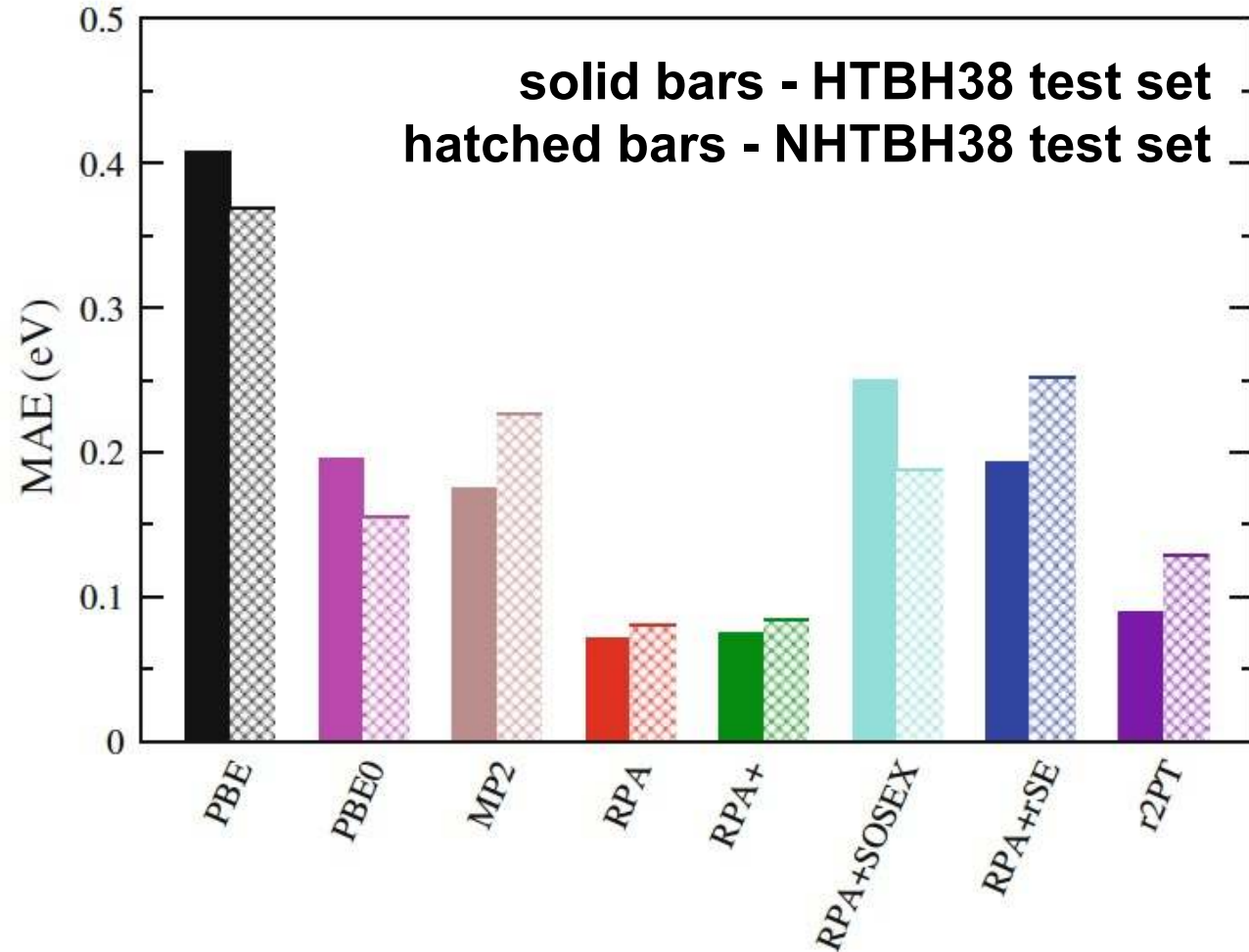


Dispersion and Hydrogen bonding: RPA very good

S22: 22 weakly bound molecular complex of different size and bonding type (seven of hydrogen bonding, eight of dispersion bonding, and seven of mixed nature).

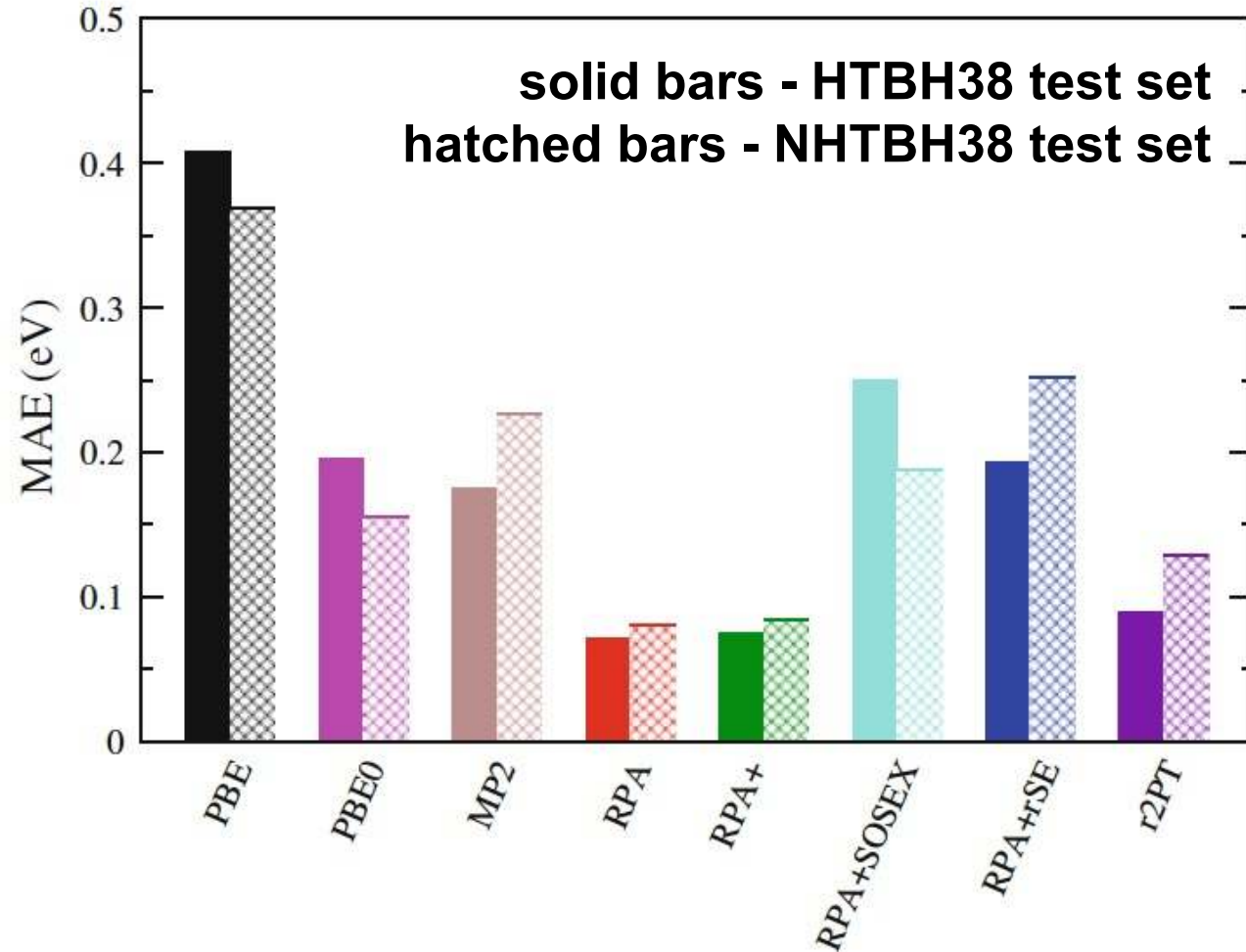


Reaction Barriers: RPA excellent



Reaction Barriers: RPA excellent

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



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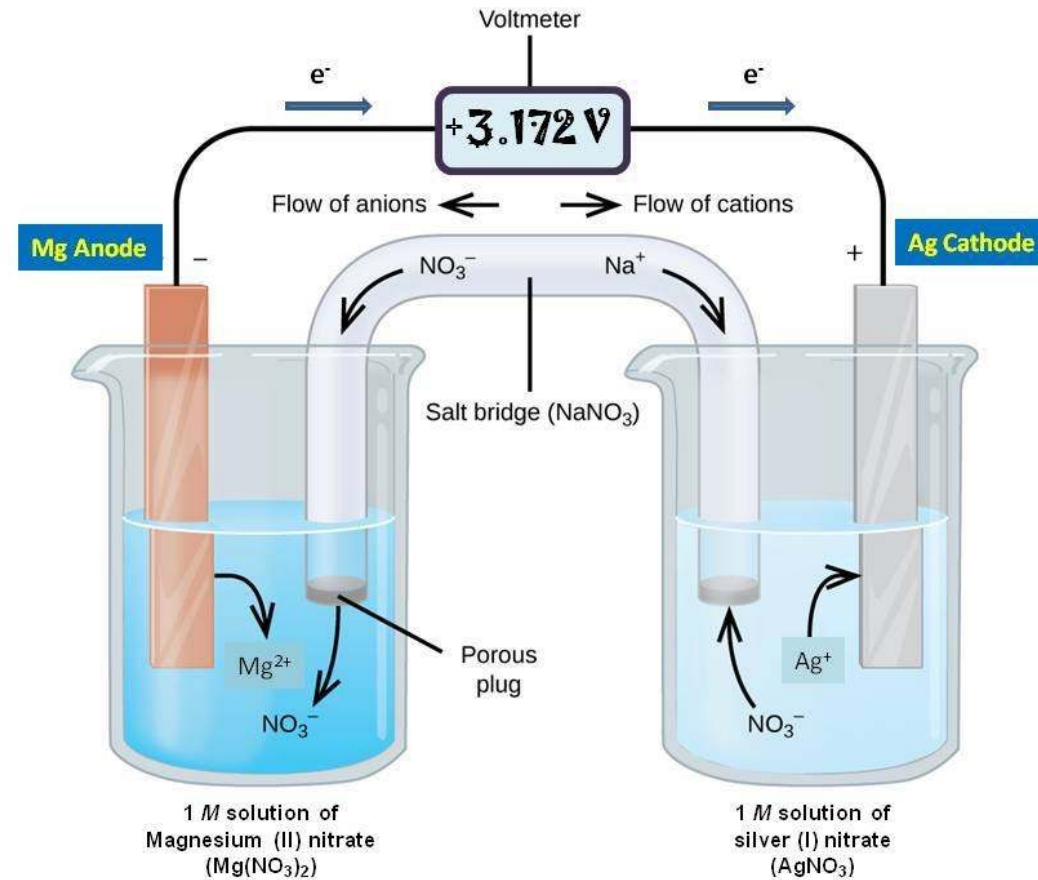


Electrochemistry



Electrochemistry

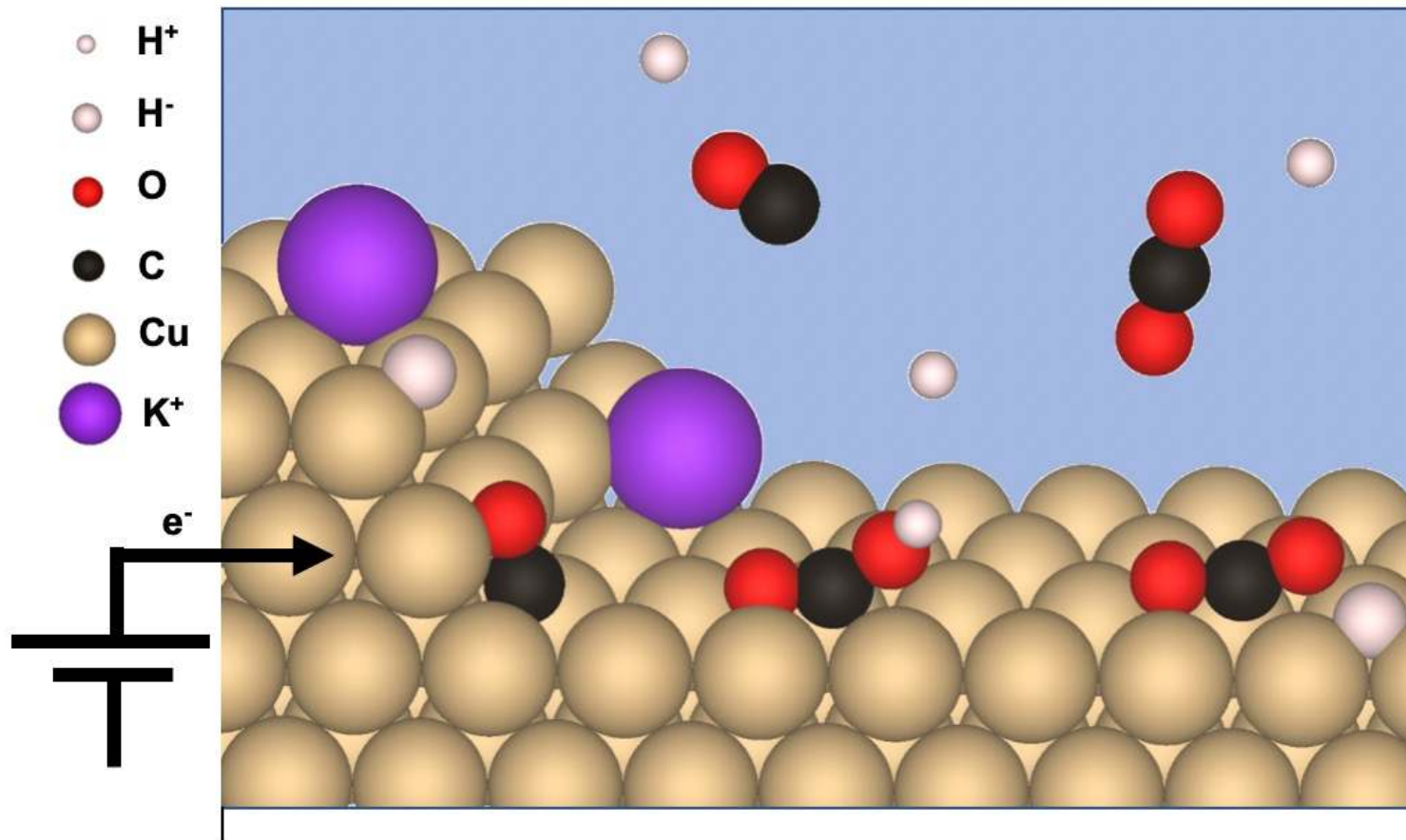
- Chemistry in the presence of applied potential, occurring in aqueous solution



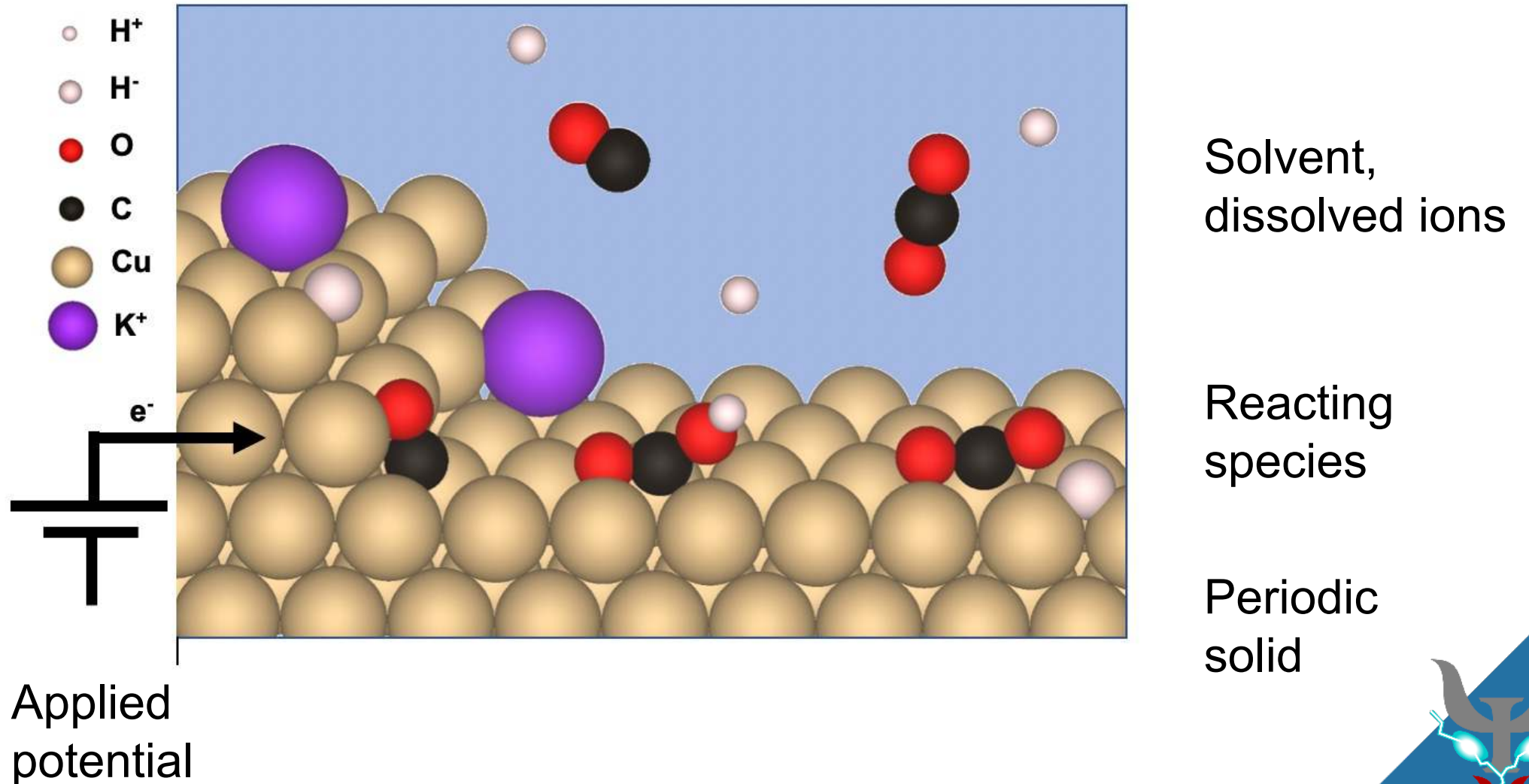
Electrochemical system in real space (theorist's depiction)



Electrochemical system in real space (theorist's depiction)



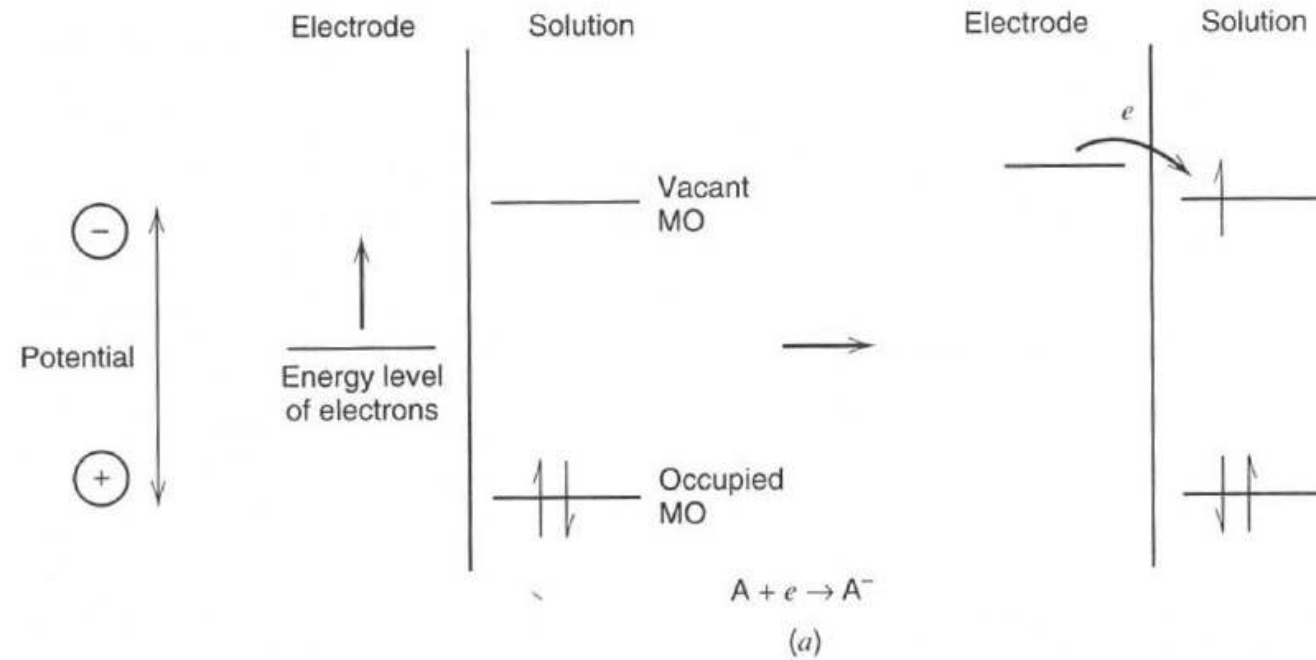
Electrochemical system in real space (theorist's depiction)



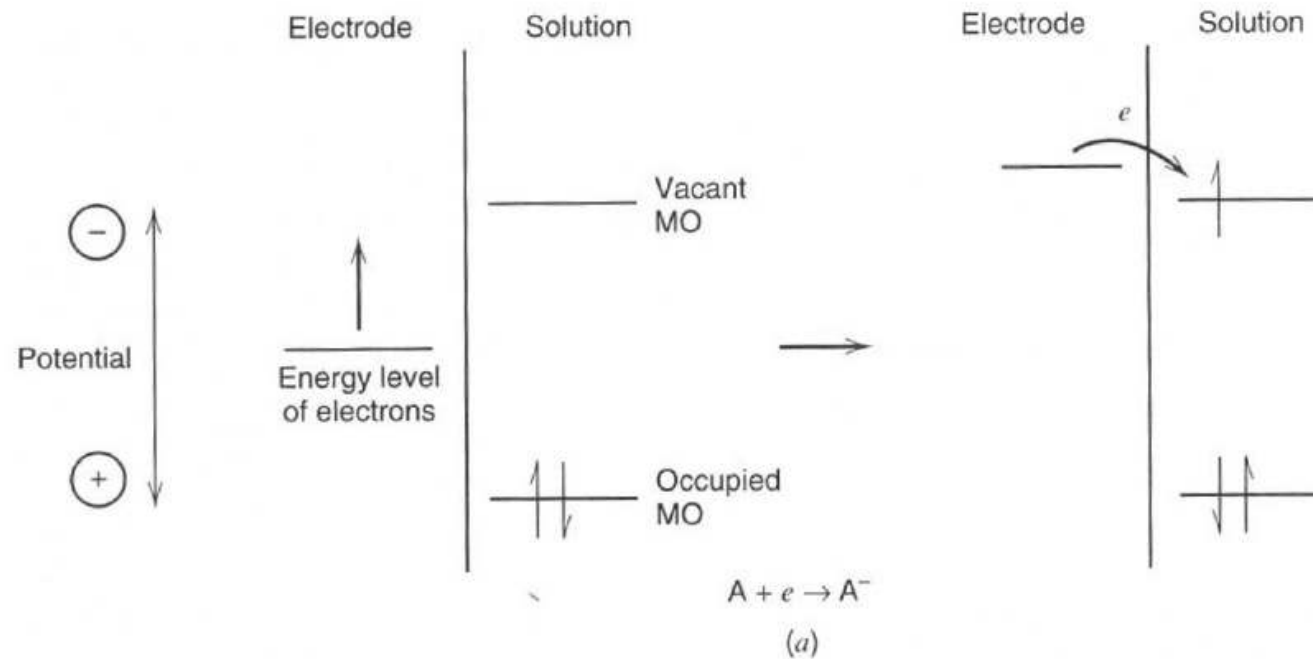
Electrochemical system to a theorist: energy space



Electrochemical system to a theorist: energy space



Electrochemical system to a theorist: energy space



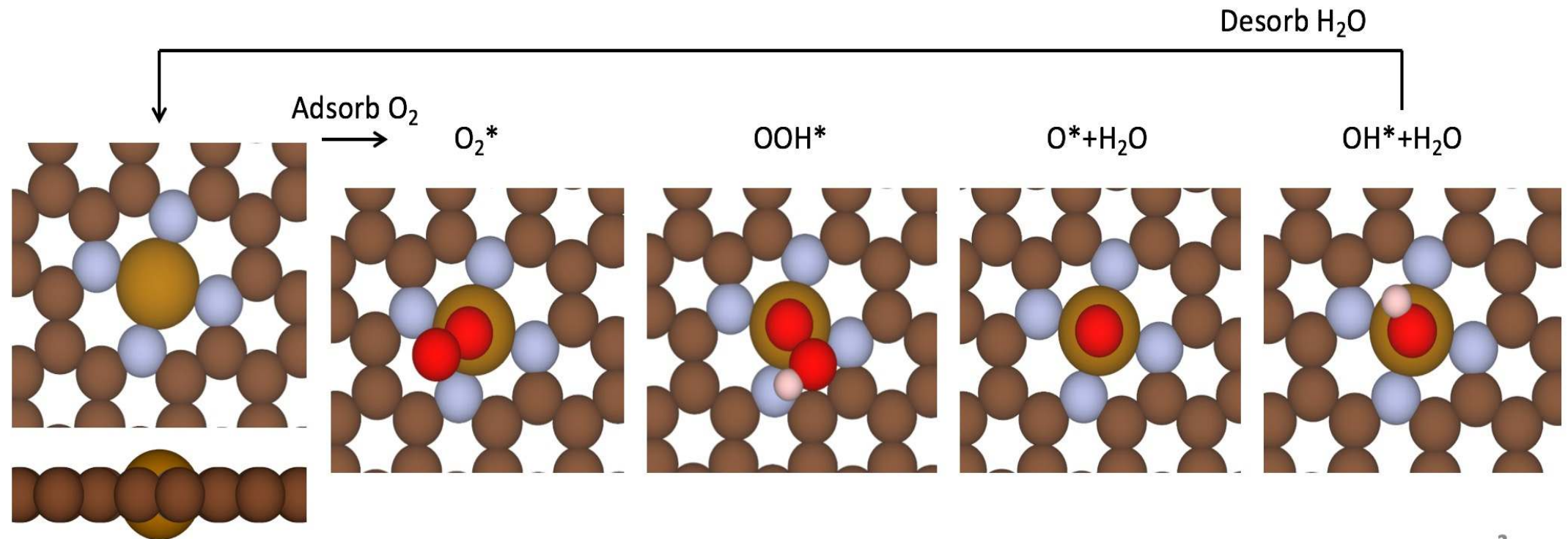
Simplification!

- **Electrified interface**
 - **complex rearrangements of atoms in response (double layer)**
 - **non-rigid shift of energy levels**

Carl Koval, NREL Fall 2019 Electrochemical Tutorial Series;
Electrochemical Methods, Bard and Faulkner

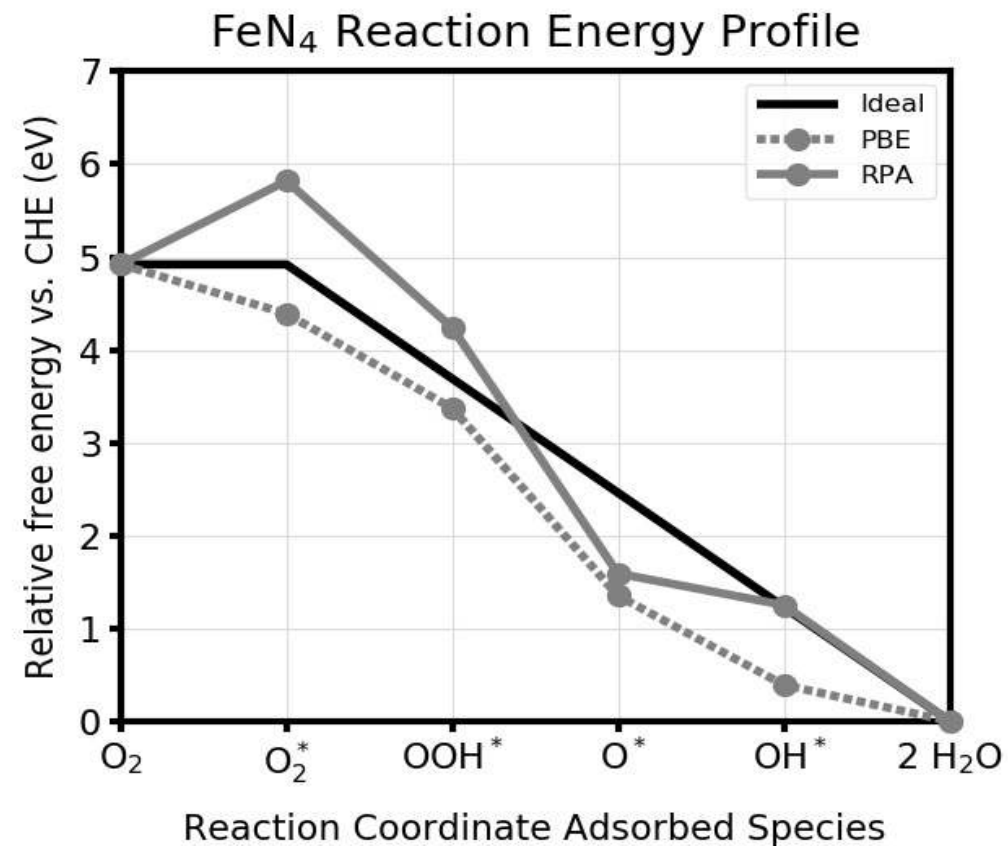


ORR on FeN₄ in graphene

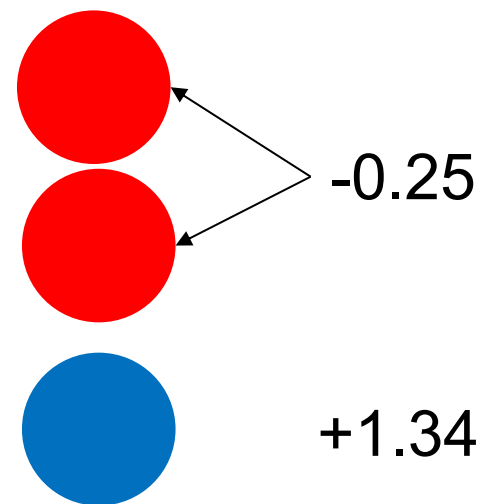
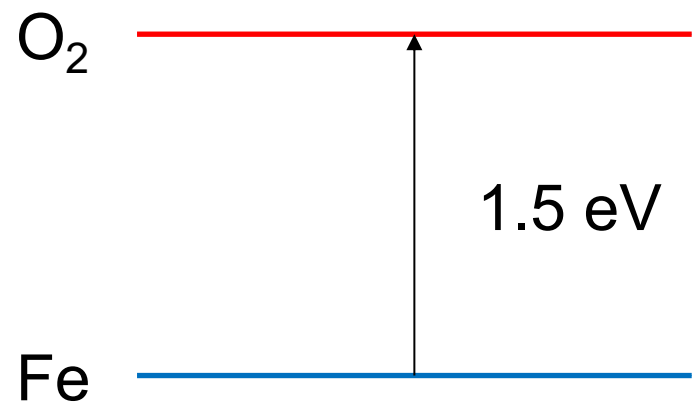


RPA insights on FeN₄ in graphene

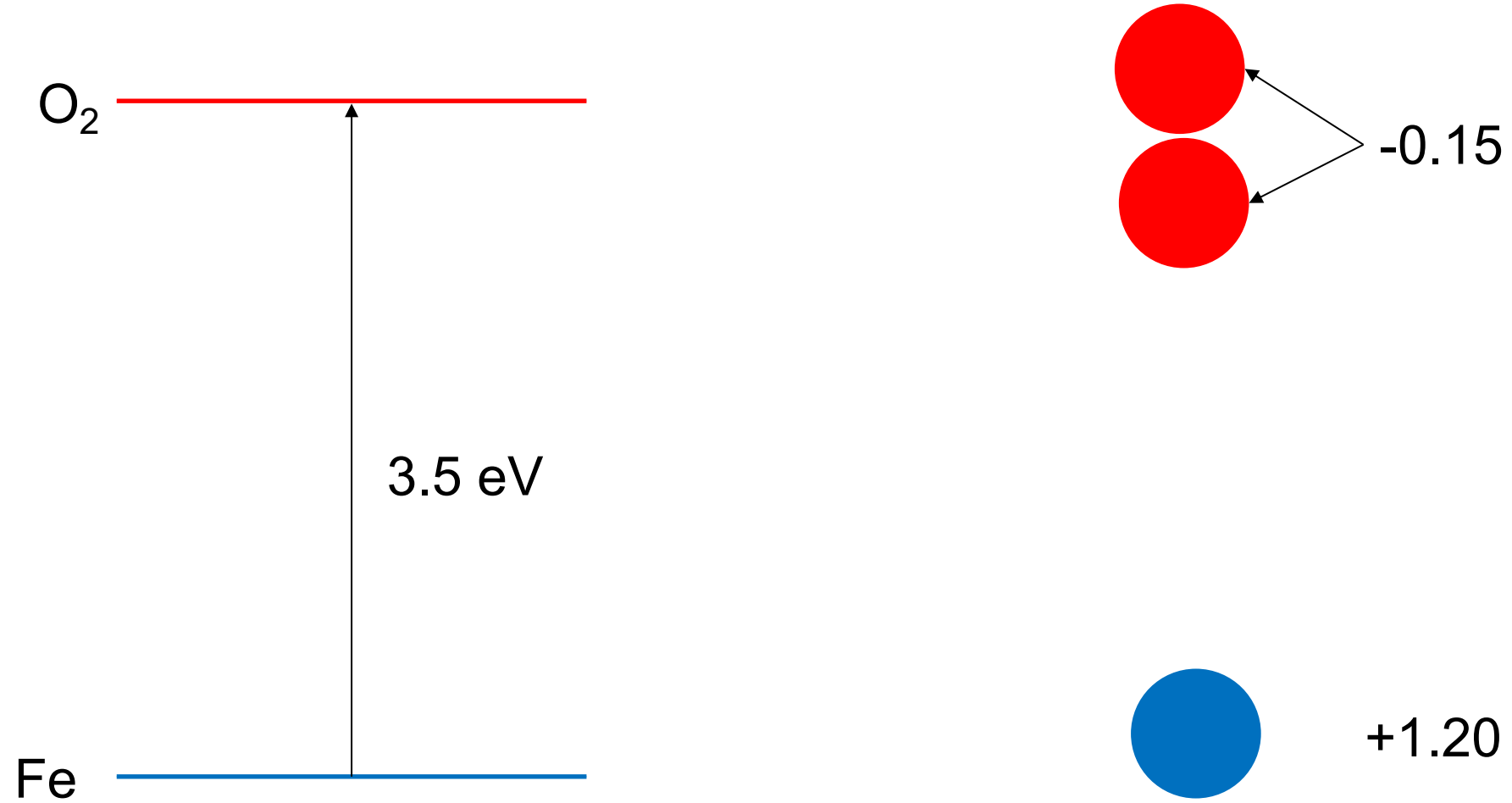
- O₂ adsorption uphill in RPA, downhill in DFT, ~1.5 eV difference



DFT picture



HSE picture



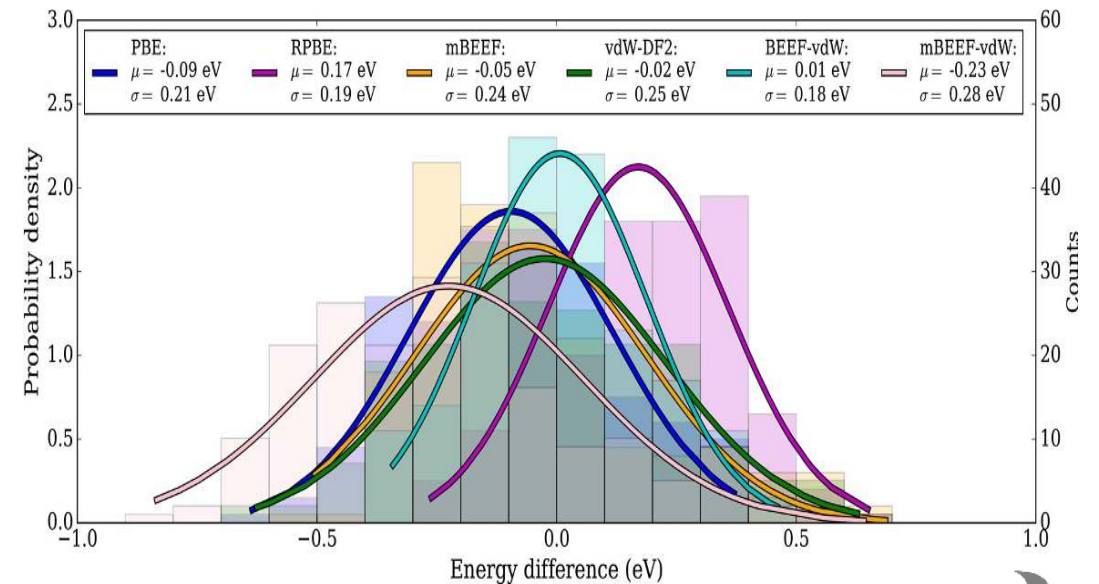
RPA insights into electrochemical systems



RPA insights into electrochemical systems

- In general, for small, oxygen-containing molecules, DFT underestimation of energy gaps leads to prediction of overbinding/ too much charge transfer on FeN_4 in graphene
 - Similar effect likely in catalysts that aren't bulk metals

- Effect is small in bulk metals, e.g. Pt



- DFT for charge-transfer phenomena: be careful!



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Kohn-Sham DFT

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



Adiabatic Connection Fluctuation Dissipation Theorem (ACFDT)

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

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

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

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



Key quantity: interacting polarizability χ^λ

- Solve Dyson equation

$$\chi^\lambda(\omega) = \chi_{\text{KS}}(\omega) + \chi_{\text{KS}}(\omega) [\lambda v_c + f_{\text{xc}}^\lambda(\omega)] \chi^\lambda(\omega).$$



Key quantity: interacting polarizability χ^λ

- Solve Dyson equation

$$\chi^\lambda(\omega) = \chi_{KS}(\omega) + \chi_{KS}(\omega) [\lambda v_c + f_{xc}^\lambda(\omega)] \chi^\lambda(\omega).$$

where

$$\chi_{GG'}^{KS}(\mathbf{q}, i\omega) = \frac{1}{V} \sum_{nn'\mathbf{k}} 2g_{\mathbf{k}}(f_{n'\mathbf{k}+\mathbf{q}} - f_{n\mathbf{k}}) \frac{\langle \psi_{n'\mathbf{k}+\mathbf{q}} | e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}} | \psi_{n\mathbf{k}} \rangle \langle \psi_{n\mathbf{k}} | e^{-i(\mathbf{q}+\mathbf{G}')\mathbf{r}'} | \psi_{n'\mathbf{k}+\mathbf{q}} \rangle}{\epsilon_{n'\mathbf{k}+\mathbf{q}} - \epsilon_{n\mathbf{k}} - i\omega}$$

$$f_{xc}(\mathbf{r}, \mathbf{r}', t - t') = \frac{\delta v_{xc}(\mathbf{r}, t)}{\delta n(\mathbf{r}', t')}$$



How do we compute E_c ?



How do we compute E_c ?

$$E_c = - \int_0^1 d\lambda \int_0^\infty \frac{d\omega}{2\pi} \langle\langle v_c \chi_\lambda(i\omega) - v_c \chi_0(i\omega) \rangle\rangle.$$



How do we compute E_c ?

$$E_c = - \int_0^1 d\lambda \int_0^\infty \frac{d\omega}{2\pi} \langle\langle v_c \chi_\lambda(i\omega) - v_c \chi_0(i\omega) \rangle\rangle.$$

- RPA: $f_{xc}^\lambda = 0 \rightarrow$ do integral analytically

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



RPA summary

- Features
 - RPA gives correlation energy, compute EXX using input orbitals
 - Exactly cancels self-interaction from Hartree term (some self-interaction in correlation)
 - $O(N^4)$ 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@GC-DFT

- The liquid polarizability χ_{liquid}^0 within JDFT framework for local response models is:

$$\hat{\chi} \cdot \phi(\mathbf{r}) \equiv \underbrace{\nabla \cdot \left(\frac{\epsilon_b - 1}{4\pi} s(\mathbf{r}) \nabla \phi(\mathbf{r}) \right)}_{\text{Dielectric}} - \underbrace{\frac{\kappa^2}{4\pi} s(\mathbf{r}) \phi(\mathbf{r})}_{\text{Ionic}}.$$

- This can be added to the electronic polarizability to give the total polarizability

$$\chi_{total}^0 = \chi_{liquid}^0 + \chi_{electronic}^0$$

- Solvated RPA, including with applied potential, can be computed from χ_{total}^0



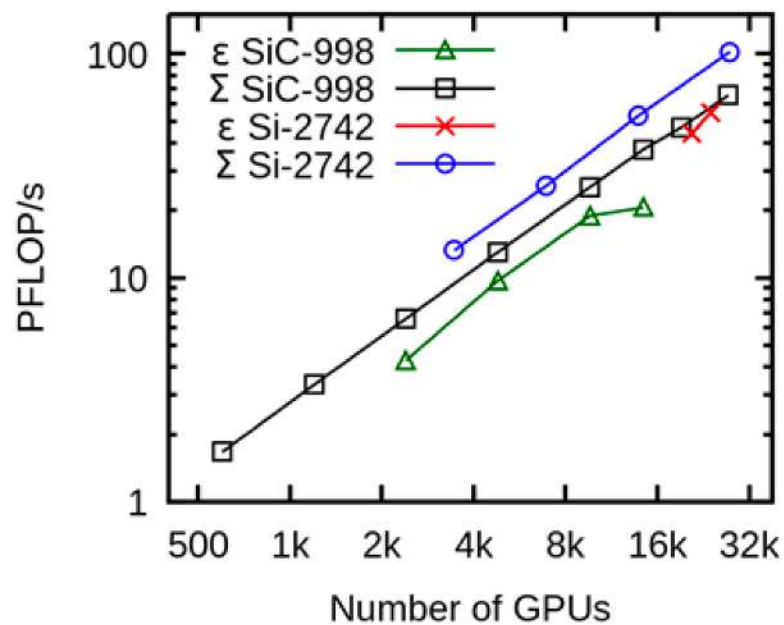


BerkeleyGW On the Path to Exascale

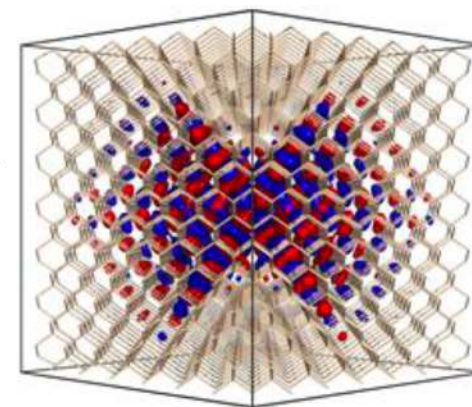
Foreseen exascale HPC systems will be GPU accelerated architectures

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.

