The GW approximation

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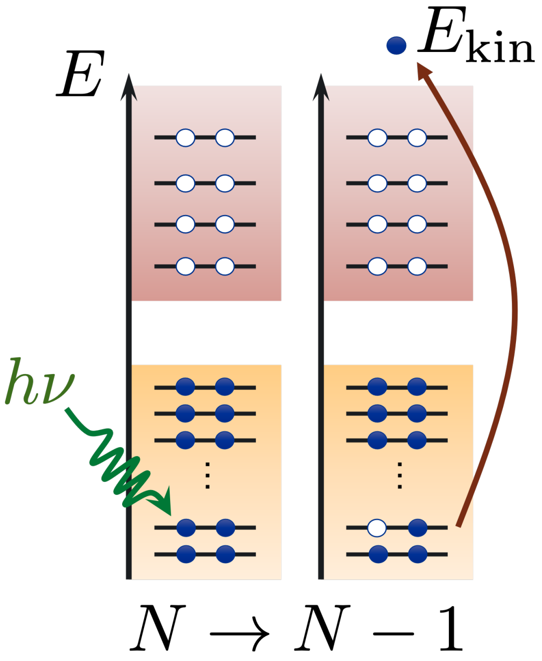
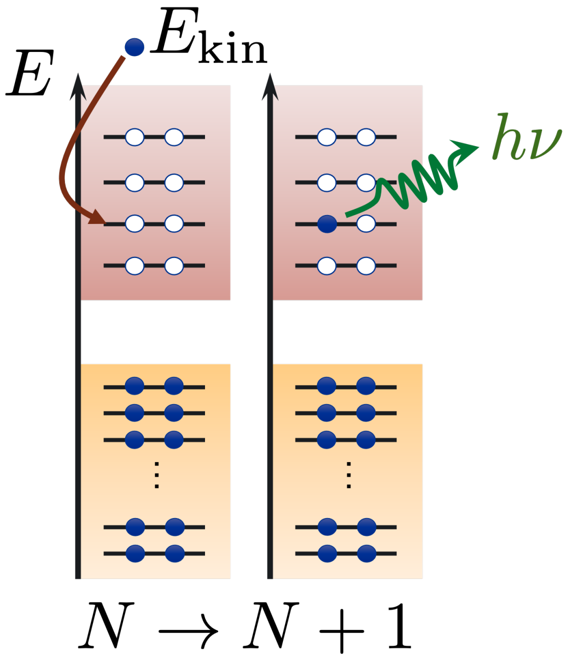
2023 CyberWorkshop

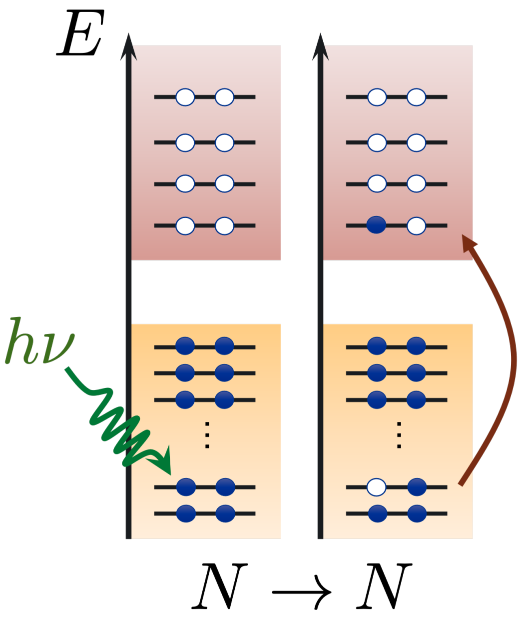
How do we study electronic excitations?



Photoemission

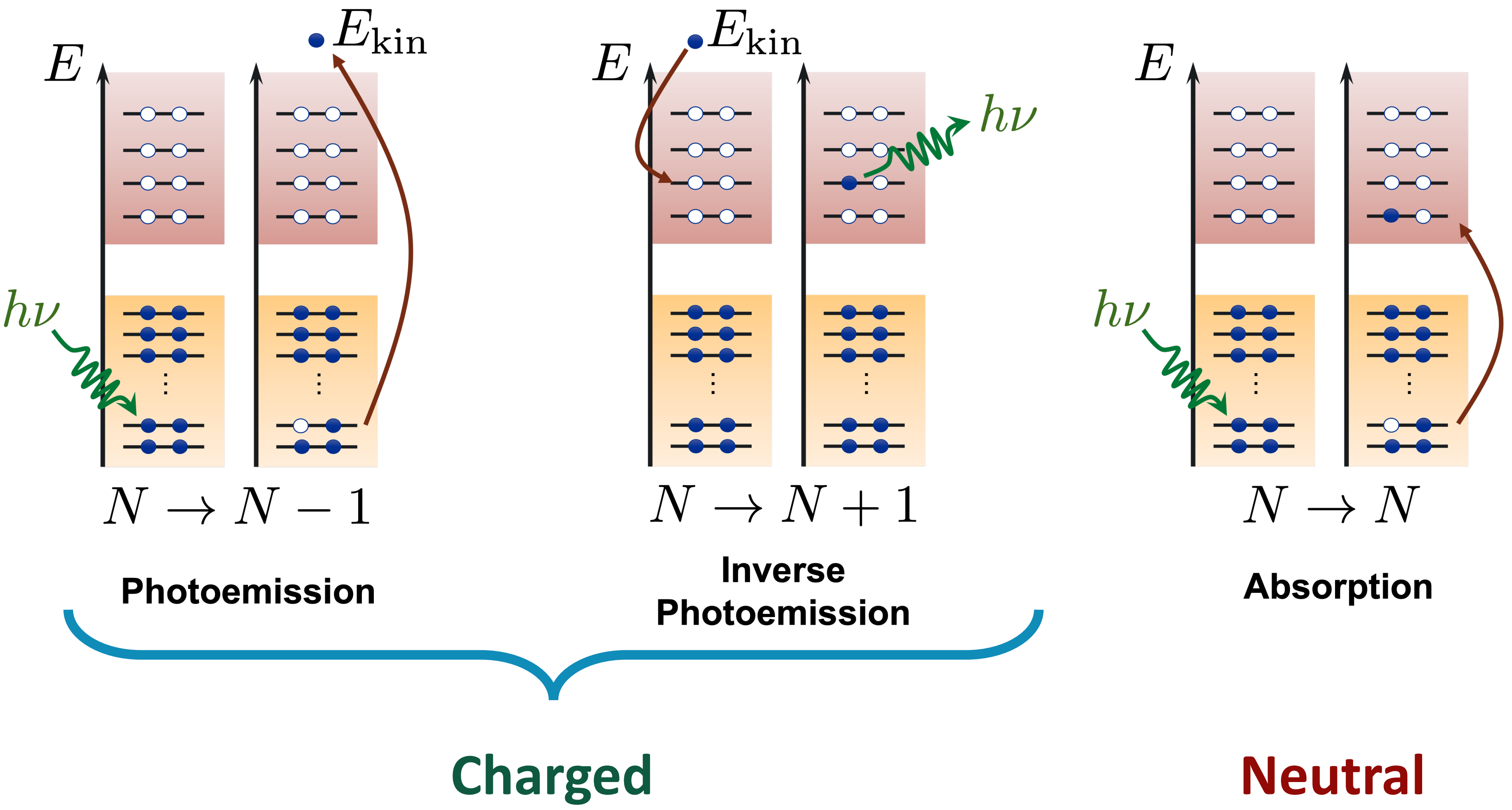


Inverse Photoemission



Absorption

How do we study electronic excitations?



Photoemission

Inverse Photoemission

Absorption

Charged

Neutral

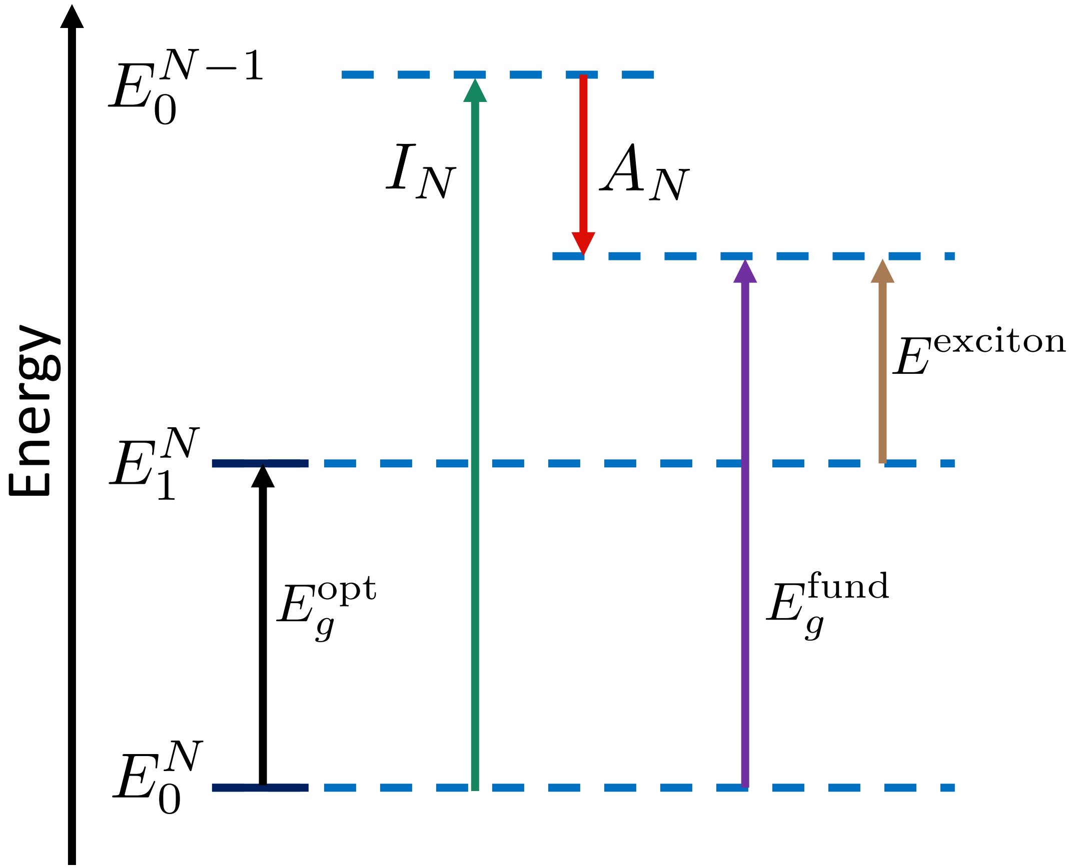
How do we study electronic excitations?

In a quantum mechanical framework that describes interacting electrons and nuclei in the presence of a time-dependent external field.

- Wavefunctions-based methods (HF, CASSCF, CC, …)
- Green's-function-based methods (*GW*, GFCC, …)
- Density-based methods (DFT, TD-DFT)

Compromise between the **accuracy of results** and **computational effort**

Optical gap, fundamental gap, and orbital gap



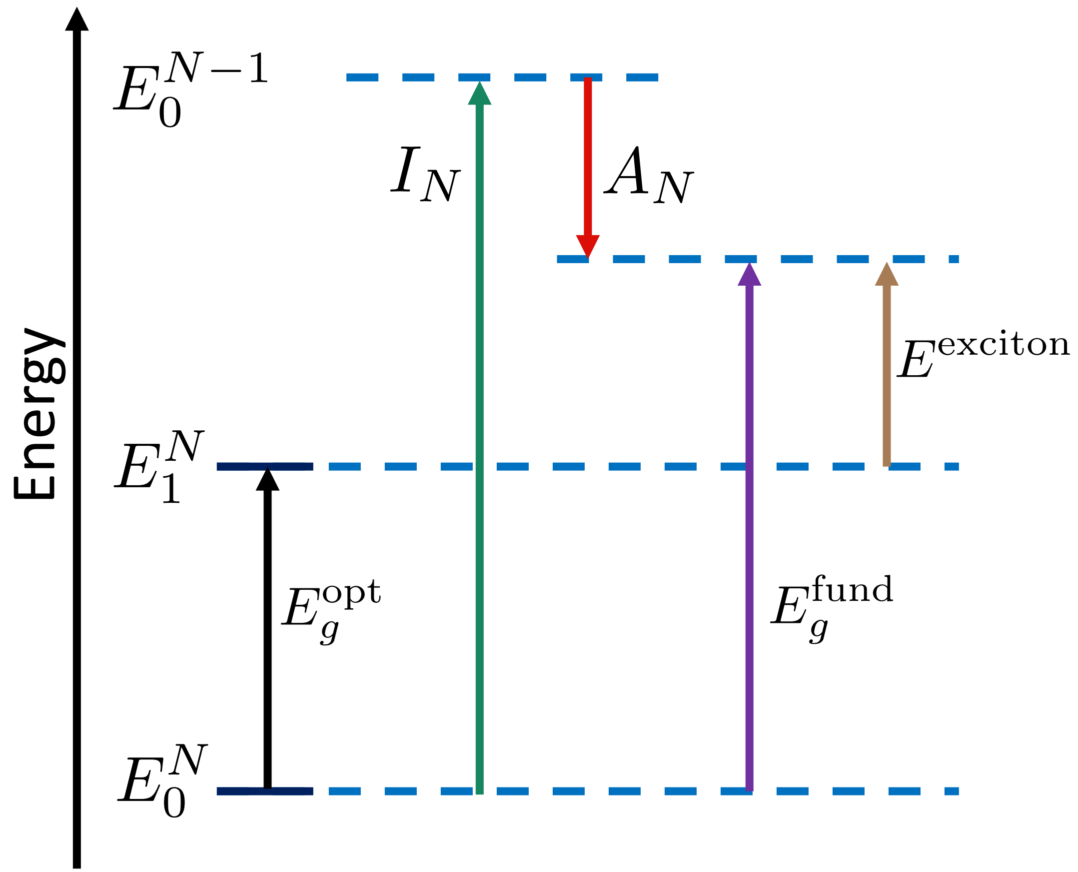
$$E_g^{\mathrm{fund}} = I_N - A_N$$

$$E^{\mathrm{exciton}} = E_g^{\mathrm{fund}} - E_g^{\mathrm{opt}}$$

$$E_g^{\mathrm{fund}} \approx \epsilon_{\mathrm{HF}}^{\mathrm{LU}} - \epsilon_{\mathrm{HF}}^{\mathrm{HO}} = E_g^{\mathrm{orb(HF)}}$$

Koopman’s theorem

Optical gap, fundamental gap, orbital gap, and derivative discontinuities



$$E_g^{\text{fund}} = \epsilon_{\text{KS}}^{\text{LU}} - \epsilon_{\text{KS}}^{\text{HO}} + \Delta = E_g^{\text{orb(KS)}} + \Delta$$

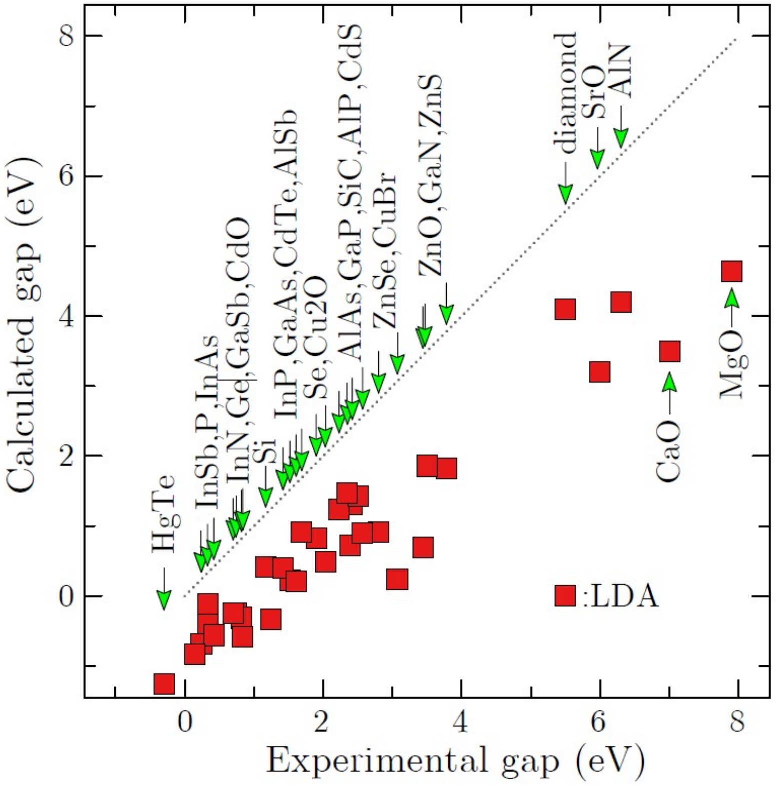
$$E_g^{\text{opt}} = \epsilon_{\text{KS}}^{\text{LU}} - \epsilon_{\text{KS}}^{\text{HO}} + \Delta_{og} = E_g^{\text{orb(KS)}} + \Delta_{og}$$

Perdew, Parr, Levy, Balduz
PRL **49**, 1691 (1982)

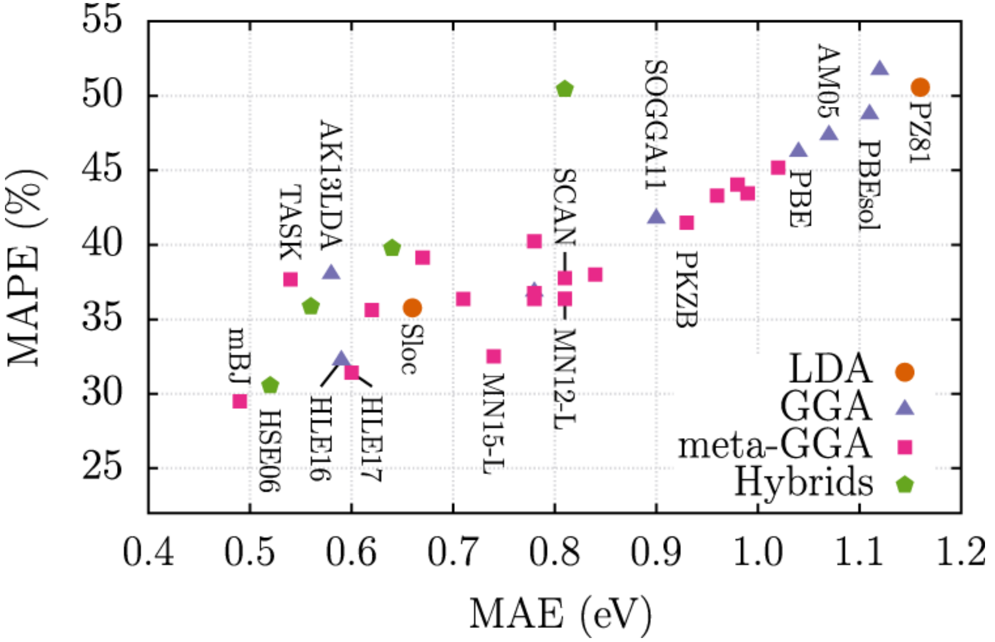
Levy
PRA **52**, R4313 (1995)

Kraisler, Hodgson, Gross
JCTC **17**, 1390 (2021)

Orbital gaps in DFT



Adapted from PRL **96** 226402 (2008)



npj Computational Materials **6**, 96 (2020)

How to improve within DFT?

- Include effects of the derivative discontinuity

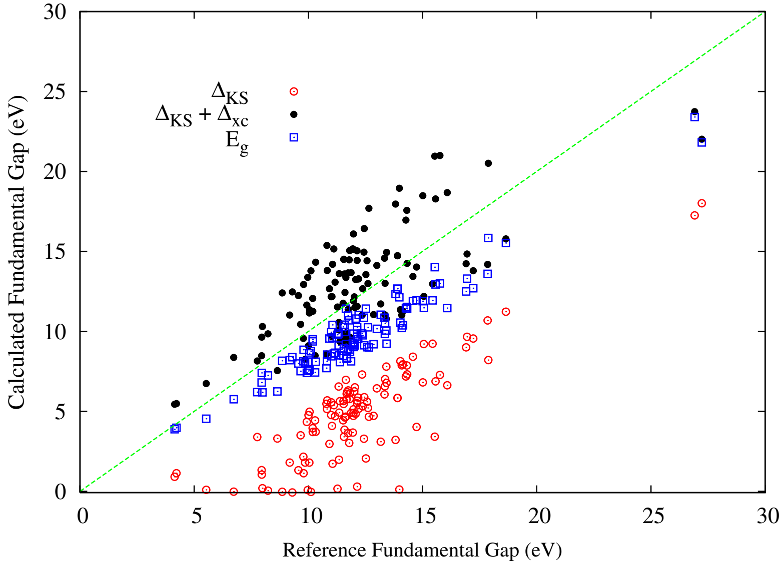


FIG. 1 (color online). Calculated versus reference fundamental gaps for the FG115 database [20]. The fundamental gaps are calculated by three schemes (see the text for details) using the LDA functional.

PRL **110**, 033002 (2013)

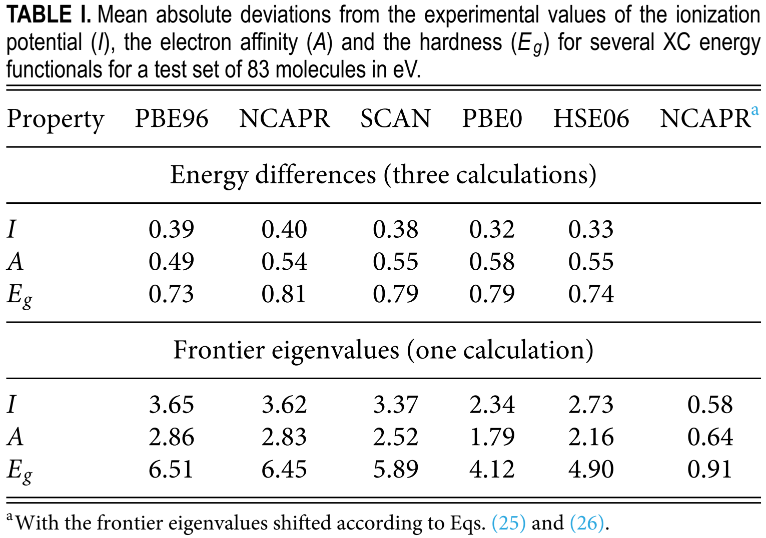


TABLE I. Mean absolute deviations from the experimental values of the ionization potential (*I*), the electron affinity (*A*) and the hardness (E_g) for several XC energy functionals for a test set of 83 molecules in eV.

Property	PBE96	NCAPR	SCAN	PBE0	HSE06	NCAPR[a]
Energy differences (three calculations)						
I	0.39	0.40	0.38	0.32	0.33	
A	0.49	0.54	0.55	0.58	0.55	
E_g	0.73	0.81	0.79	0.79	0.74	
Frontier eigenvalues (one calculation)						
I	3.65	3.62	3.37	2.34	2.73	0.58
A	2.86	2.83	2.52	1.79	2.16	0.64
E_g	6.51	6.45	5.89	4.12	4.90	0.91

[a] With the frontier eigenvalues shifted according to Eqs. (25) and (26).

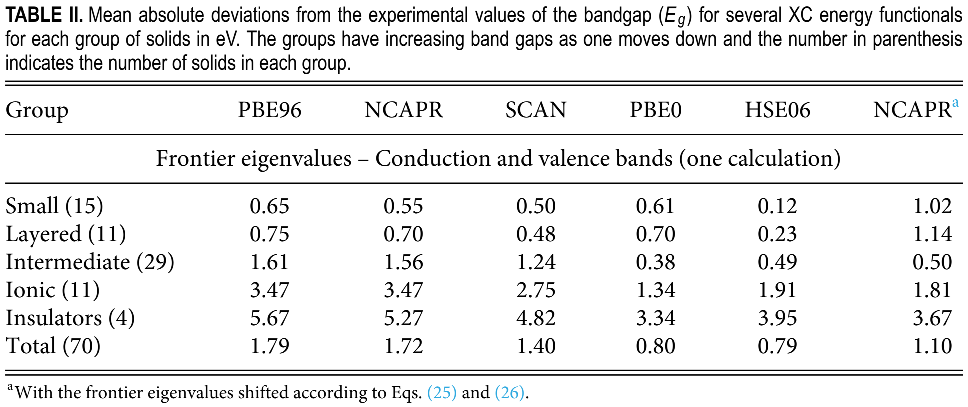


TABLE II. Mean absolute deviations from the experimental values of the bandgap (E_g) for several XC energy functionals for each group of solids in eV. The groups have increasing band gaps as one moves down and the number in parenthesis indicates the number of solids in each group.

Group	PBE96	NCAPR	SCAN	PBE0	HSE06	NCAPR[a]
Frontier eigenvalues – Conduction and valence bands (one calculation)						
Small (15)	0.65	0.55	0.50	0.61	0.12	1.02
Layered (11)	0.75	0.70	0.48	0.70	0.23	1.14
Intermediate (29)	1.61	1.56	1.24	0.38	0.49	0.50
Ionic (11)	3.47	3.47	2.75	1.34	1.91	1.81
Insulators (4)	5.67	5.27	4.82	3.34	3.95	3.67
Total (70)	1.79	1.72	1.40	0.80	0.79	1.10

[a] With the frontier eigenvalues shifted according to Eqs. (25) and (26).

JCP **157**, 114109 (2022)

Beyond DFT:

Green’s Function Many Body Theory

Green's Function

- Historically older than Hohenberg-Kohn theorems
- The Green's function is a natural generalization of the density and the one-body density matrix:

$$n(x) = \left\langle \Psi \left| \hat{\psi}(x,t)\hat{\psi}^\dagger(x,t) \right| \Psi \right\rangle$$

+ spin-space non-locality

$$\rho(x;x') = \left\langle \Psi \left| \hat{\psi}(x,t)\hat{\psi}^\dagger(x',t) \right| \Psi \right\rangle$$

+ time non-locality

$$G(x,t;x',t') = -i \left\langle \Psi \left| T\left[\hat{\psi}(x,t)\hat{\psi}^\dagger(x',t') \right] \right| \Psi \right\rangle$$

Green's Function

$$G(x,t;x',t') = -i\left\langle \Psi \middle| T\left[\hat{\psi}(x,t)\hat{\psi}^\dagger(x',t')\right] \middle| \Psi \right\rangle$$

- The field operators in the Heisenberg picture are related to those in the Schrödinger picture

  $$\hat{\psi}(x,t) = e^{i\hat{H}t}\hat{\psi}(x)e^{-i\hat{H}t}$$

- T orders the operators from left to right in decreasing time (earliest on the right) with a -1 factor for each permutation (fermions)

- Let $1=(x_1,t_1)$, $2=(x_2,t_2)$, and $t_1>t_2$:

$$iG(1,2) = \theta(t_1-t_2)\left\langle \Psi \middle| e^{i\hat{H}t_1}\hat{\psi}(x_1)e^{-i\hat{H}(t_1)}e^{i\hat{H}t_2}\hat{\psi}^\dagger(x_2)e^{-i\hat{H}t_2} \middle| \Psi \right\rangle$$

$$iG(1,2) = \theta(t_1-t_2)\left\langle \Psi(t_1) \middle| \hat{\psi}(x_1)e^{-i\hat{H}(t_1-t_2)}\hat{\psi}^\dagger(x_2) \middle| \Psi(t_2) \right\rangle$$

Green's Function

$$iG^p(1,2) = \theta(t_1 - t_2) \left\langle \Psi(t_1) \middle| \hat{\psi}(x_1) e^{-i\hat{H}(t_1-t_2)} \hat{\psi}^\dagger(x_2) \middle| \Psi(t_2) \right\rangle$$

$\hat{\psi}^\dagger(x_2) \middle| \Psi(t_2) \right\rangle$	represents a state with one electron added in x_2 to the N-electron ground-state at time t_2.
$e^{-i\hat{H}(t_1-t_2)}$	Propagates the N+1-electron state from time t_2 to t_1.
$\left\langle \Psi(t_1) \middle| \hat{\psi}(x_1)$	represents the bra of the state with one electron added in x_1 to the N-electron ground-state at time t_1.

The final projection measures the overlap between the two N+1 states after a (t1-t2) time delay

The **Green's function** describes the *propagation* of electrons and holes (i.e. missing electrons)

Green's function

Lehman amplitudes

$$iG^p(1,2) = \theta(t_1 - t_2) \left\langle \Psi(t_1) \middle| \hat{\psi}(x_1) e^{-i\hat{H}(t_1-t_2)} \hat{\psi}^\dagger(x_2) \middle| \Psi(t_2) \right\rangle$$

Using the spectral decomposition of H

$$e^{-i\hat{H}(t_1-t_2)} = \sum_n e^{-iE_n^{N+1}(t_1-t_2)} \left| \Psi_n^{N+1} \right\rangle \left\langle \Psi_n^{N+1} \right|$$

$$|\Psi(t)\rangle = e^{-i\hat{H}t} |\Psi(t)\rangle = e^{-iE_0^N t} |\Psi\rangle$$

$$iG^p(1,2) = \sum_n f_n^{N+1}(x_1) \bar{f}_n^{N+1}(x_2) e^{-i\varepsilon_n^{N+1}(t_1-t_2)}$$

$$f_n^{N+1}(x_1) = \left\langle \Psi \middle| \hat{\psi}(x_1) \middle| \Psi_n^{N+1} \right\rangle$$

Addition Lehman amplitude

$$\varepsilon_n^{N+1} = E_n^{N+1} - E_0^N$$

Addition energy

Green's function

Lehman amplitudes

We can proceed similarly with the hole-related part and obtain:

$$iG(1,2) = \theta(t_1 - t_2) \sum_n f_n^{N+1}(x_1) \bar{f}_n^{N+1}(x_2) e^{-i\varepsilon_n^{N+1}(t_1 - t_2)}$$
$$-\theta(t_2 - t_1) \sum_n f_n^{N-1}(x_1) \bar{f}_n^{N-1}(x_2) e^{-i\varepsilon_n^{N-1}(t_2 - t_1)}$$

The Fourier transform of $G(1,2)$ leads to

$$G(x_1, x_2; \omega) = \sum_n \frac{f_n(x_1)\bar{f}_n(x_2)}{\omega - \varepsilon_n + i\eta \, \mathrm{sgn}(\varepsilon_n - \mu)}$$

where μ is the Fermi level (chemical potential), and f_n, ε_n are the addition/removal Lehman amplitudes and energies depending on the sign of $\varepsilon_n - \mu$.

Green's function

The **poles** of the **Green's function** are the **true** addition/removal electronic energies of the N-electron system!

$$G(x_1, x_2; \omega) = \sum_n \frac{f_n(x_1)\bar{f}_n(x_2)}{\omega - \varepsilon_n + i\eta\,\mathrm{sgn}(\varepsilon_n - \mu)}$$

For non-interacting systems, Ψ is given by a single Slater determinant and the Lehman amplitudes and energies reduce to single orbitals:

$$G_0(x_1, x_2, \omega) = \underbrace{\sum_i \frac{\phi_i(x_1)\bar{\phi}_i(x_2)}{\omega - \epsilon_i - i\eta}}_{\text{removal}} + \underbrace{\sum_a \frac{\phi_a(x_1)\bar{\phi}_a(x_2)}{\omega - \epsilon_a + i\eta}}_{\text{addition}}$$

Equation of motion for the Green's Function

- The change of G with respect to one of its time arguments is

$$\left[i\frac{\partial}{\partial t_1} - \hat{h}(1)\right] G(1,2) + i\int d(3)v(1,3)G_2(1,3^+;2,3^{++}) = \delta(1,2)$$

$$\left[i\frac{\partial}{\partial t_1} - \hat{h}(1)\right] G(1,2) + i\int d(3)\Sigma_{HXC}(1,3)G(3,2) = \delta(1,2)$$

$$\Sigma_{HXC}(1,3) = -i\int d(24)v(1,4)G_2(1,4^+;2,4^{++})G^{-1}(2,3)$$

All Hartree and exchange-correlation effects can be described by an effective two-body time-dependent operator Σ

Equation of motion for the Green's Function

- The Fourier transform of the equation of motion for the Green's function leads to

$$\left[\omega - \hat{h}(r_1)\right] G(r_1, r_2; \omega) - \int dr_3\, \Sigma_{HXC}(r_1, r_3; \omega) G(r_3, r_2; \omega) = \delta(r_1 - r_2)$$

- Introducing the Lehman representation of G, and solving term by term at $\omega = \varepsilon_n$ leads to the following eigenvalue equation:

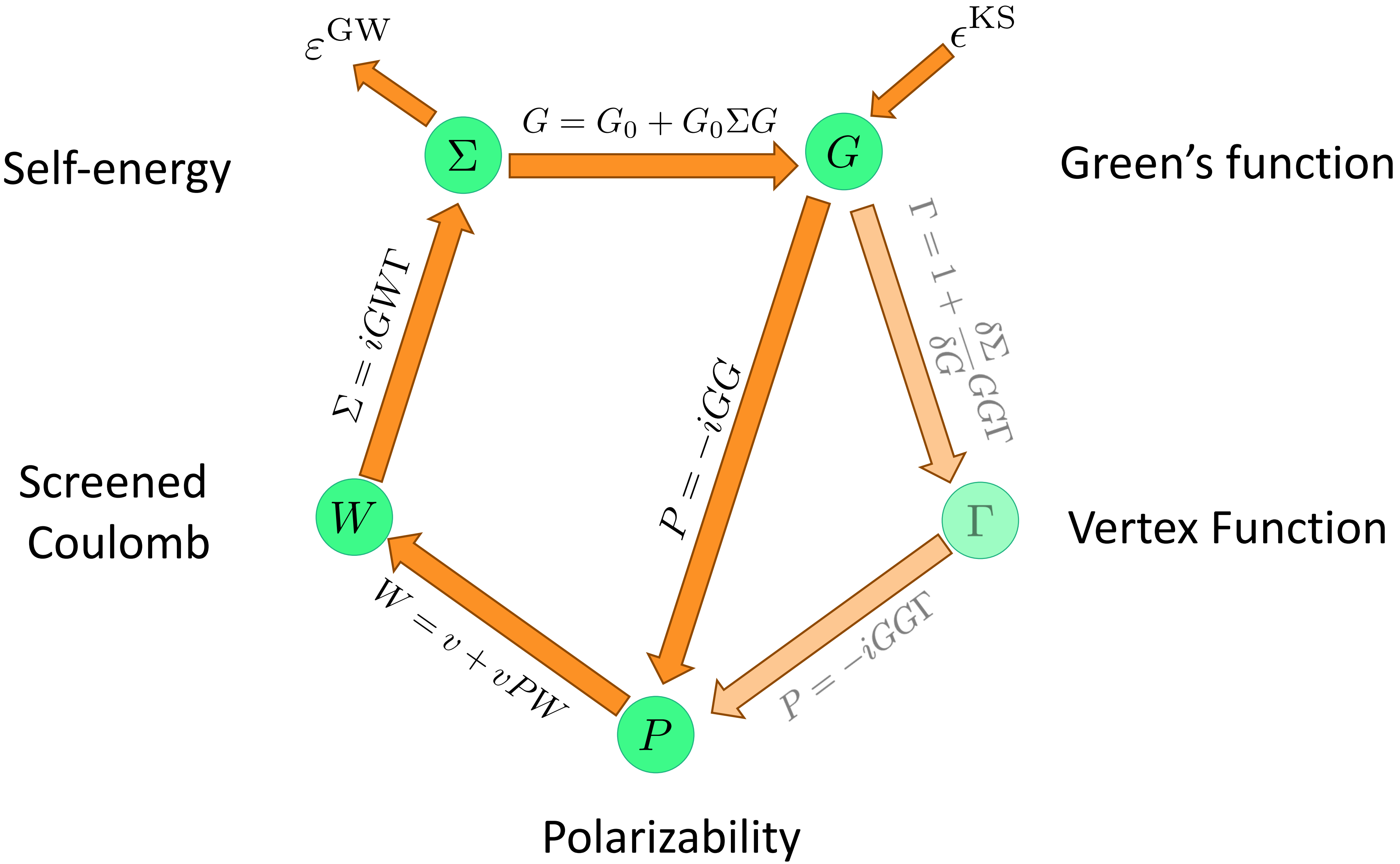
$$\hat{h}(r) f_n(r) + \int dr' \Sigma_{HXC}(r, r', \varepsilon_n) f_n(r') = \varepsilon_n f_n(r)$$

The true addition/removal energies are solutions of a simple one-body equation, but now the HXC operator depends on the energy of the state it is acting on

The *GW* approximation

ε^{GW}

$W = v + vPW$



Self-energy

Green's function

Screened Coulomb

Vertex Function

Polarizability

Phys. Rev. **139**, A796 (1965)

GW calculations in practice

- The input Green's functions is built from Kohn-Sham eigenstates and eigenvalues.
- The screened Coulomb interaction is obtained using either
  - The independent-particle polarizability

$$P(1,2) = -iG(1,2)G(2,1)$$

$$\varepsilon(1,2) = \delta(1,2) - \int d(3)v(1,3)P(3,2)$$

$$W(1,2) = \int d(3)\varepsilon^{-1}(1,3)v(3,2)$$

  - The interacting polarizability (neglecting exchange-correlation kernel)

$$\Pi(1,2) = \frac{\delta n(1)}{\delta v_{ext}(2)}$$

$$W(1,2) = v(1,2) + \int d(34)v(1,3)\Pi(3,4)v(4,2)$$

GW calculations in practice

GW flavours

- Perturbative GW, one-shot GW, G_0W_0
  - One loop through Hedin’s pentagon
  - Output: quasiparticle energies
- evGW or eigenvalue-only (partially) self-consistent GW
  - Several loops through Hedin’s pentagon
  - Lehman amplitudes are kept frozen
  - Output: quasiparticle energies
- qsGW or quasiparticle (partially) self-consistent GW
  - Several loops through Hedin’s pentagon
  - Lehman amplitudes are updated using a Hermitian self-energy
  - Output: quasiparticle energies and amplitudes
- scGW or (fully) self-consistent GW
  - Several loops through Heding’s pentagon
  - Lehman amplitudes are updated using the non-Hermitian self-energy
  - Output: quasiparticle energies and amplitudes

GW calculations in practice

One-shot G_0W_0

$$\hat{h}^{MF} = -\frac{1}{2}\nabla^2 + v_{ext} + v_H + v_\sigma^{MF}$$

$$\hat{h}^{MF}(\mathbf{r})\psi_{s\sigma}(\mathbf{r}) - \int d\mathbf{r}' v_\sigma^{MF}(\mathbf{r},\mathbf{r}')\psi_{s\sigma}(\mathbf{r}') + \int d\mathbf{r}'\Sigma_\sigma(\mathbf{r},\mathbf{r}',\varepsilon_{s\sigma})\psi_{s\sigma}(\mathbf{r}') = \varepsilon_{s\sigma}\psi_{s\sigma}(\mathbf{r})$$

$$\Sigma_\sigma(\mathbf{r},\mathbf{r}',\omega) = \frac{i}{2\pi}\int d\omega' e^{i\omega'\eta} G_0^\sigma(\mathbf{r},\mathbf{r}',\omega+\omega')W_0(\mathbf{r},\mathbf{r}',\omega')$$

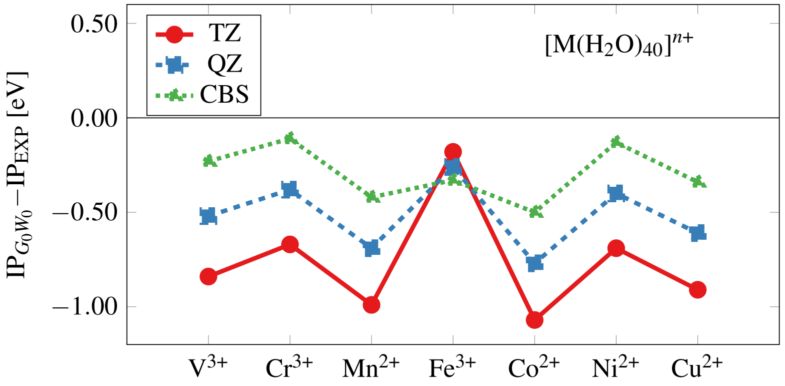
$$\varepsilon_{s\sigma} = \varepsilon_{s\sigma}^{MF} + \langle\phi_{s\sigma}^{MF}\left|\Sigma_\sigma(\varepsilon_{s\sigma}) - v_\sigma^{MF}\right|\phi_{s\sigma}^{MF}\rangle$$

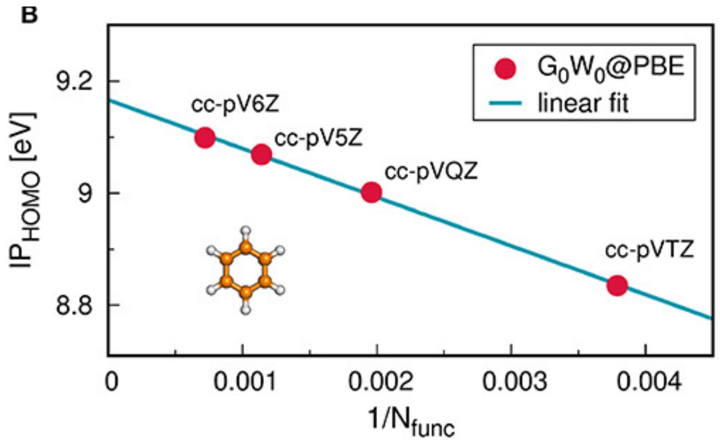
Quasiparticle energies are updated

Lehman amplitudes are kept **frozen**

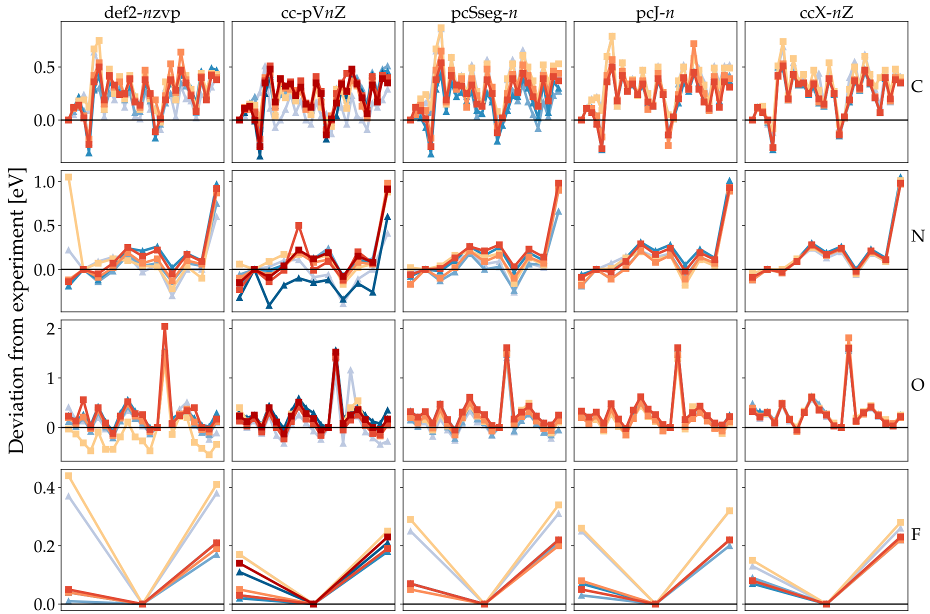
Convergence with basis set size

- Convergence with respect to the number of occupied levels can be slow:





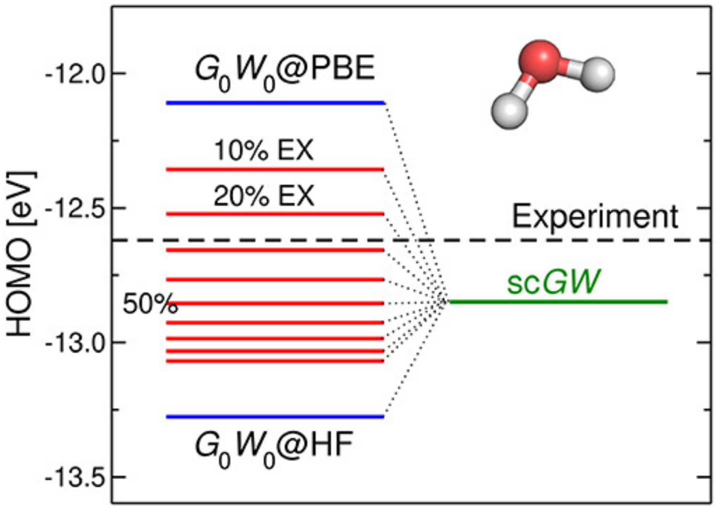
- Chemical shifts converge rather fast (removal energies)



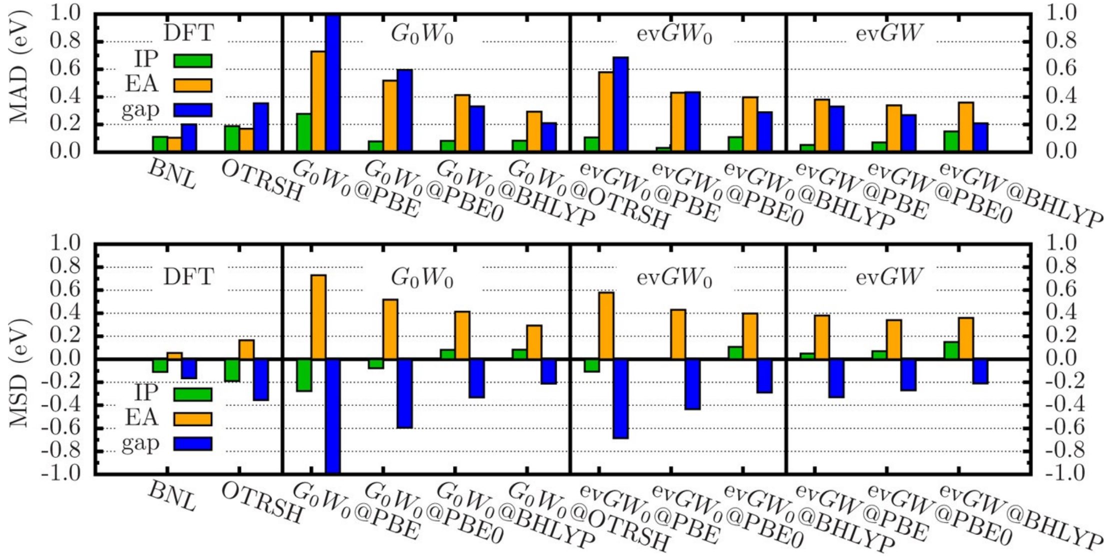
JCTC **18**, 4919 (2022)

Starting-point-dependence

- G0W0 has a strong starting-point dependence since G0 and W0 are built from Kohn-Sham inputs
- Partially self-consistent schemes alleviate the issue but does not solve it

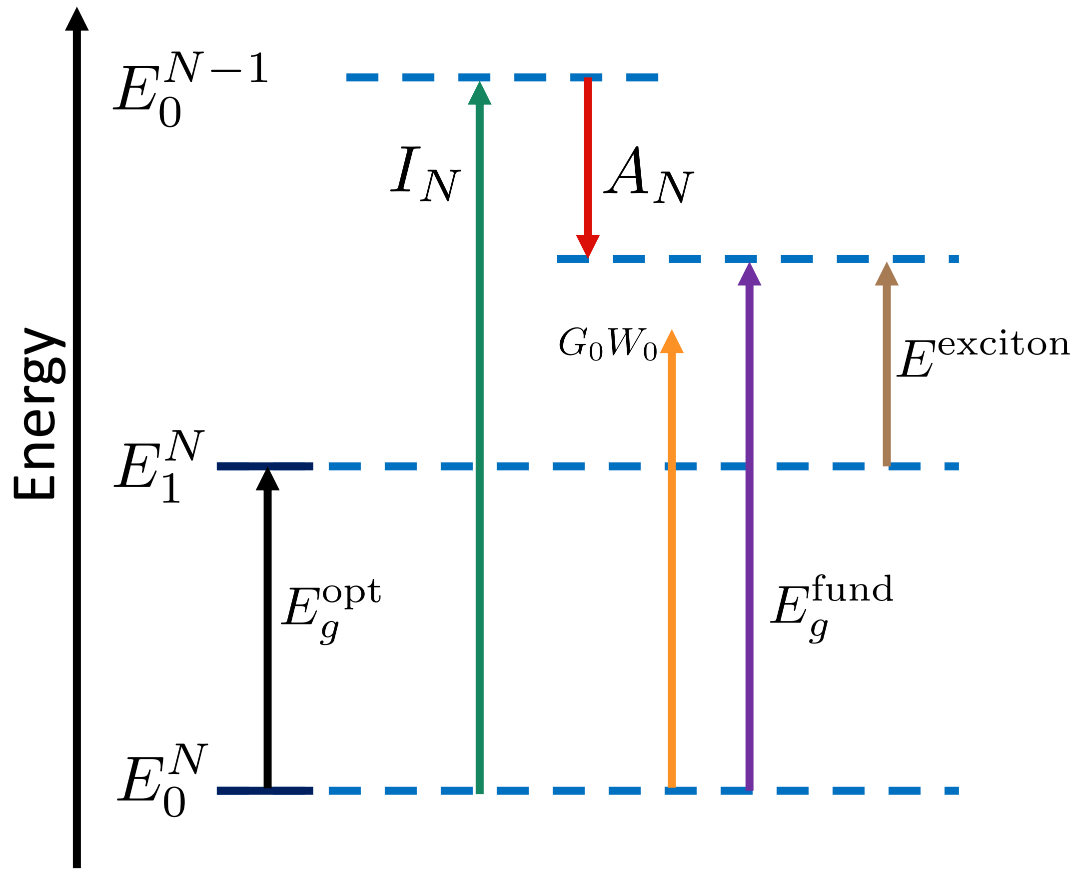


Front. Chem. **7**, 00377 (2019)



JCTC **12**, 2834 (2016)

Gaps



The GW method gives approximate fundamental gaps

It misses excitonic binding effects

GW Implementation

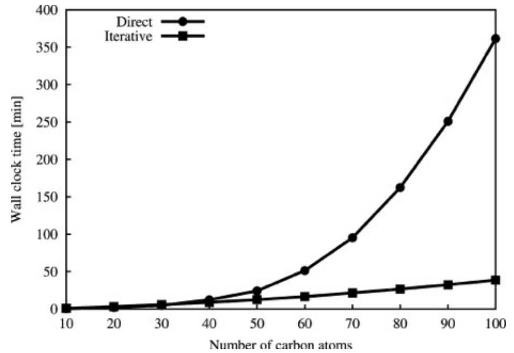
CD-*GW*

Contour Deformation

$$\sim \mathcal{O}(N^3)$$

MINRES

SIAM J. Numer. Anal. ***12***, 617-629, (1975)
J. Chem. Theory Comput. ***11***, 1493 (2015)



NWCHEM
HIGH-PERFORMANCE COMPUTATIONAL CHEMISTRY SOFTWARE

Variational Fitting

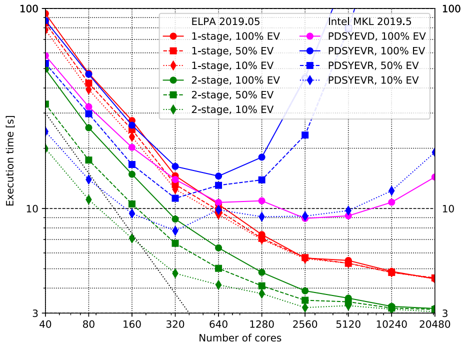
AFF-*GW*

Analytical Full Frequency

$$\mathcal{O}(N^6)$$

ELPA

Parallel Computing ***37***, 783 (2011)

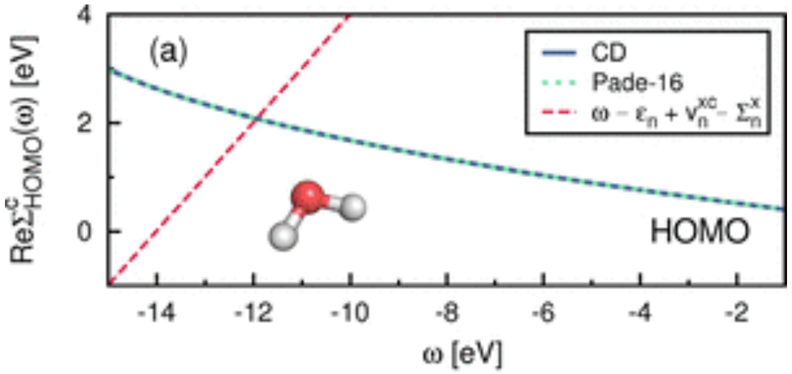


JCTC **17**, 7504 (2021)

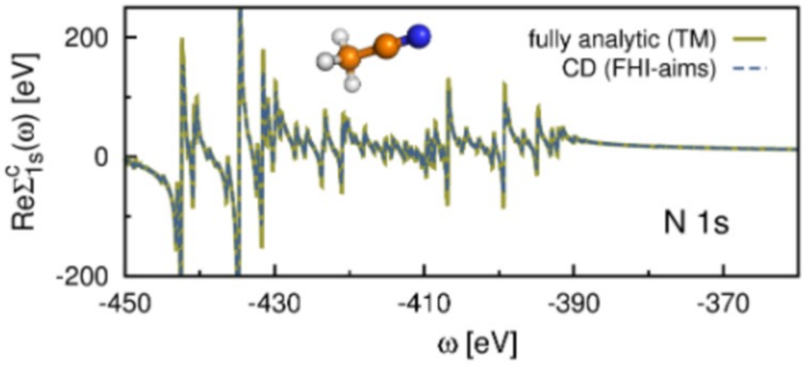
GW Implementation

Numerical stability

Valence



Core

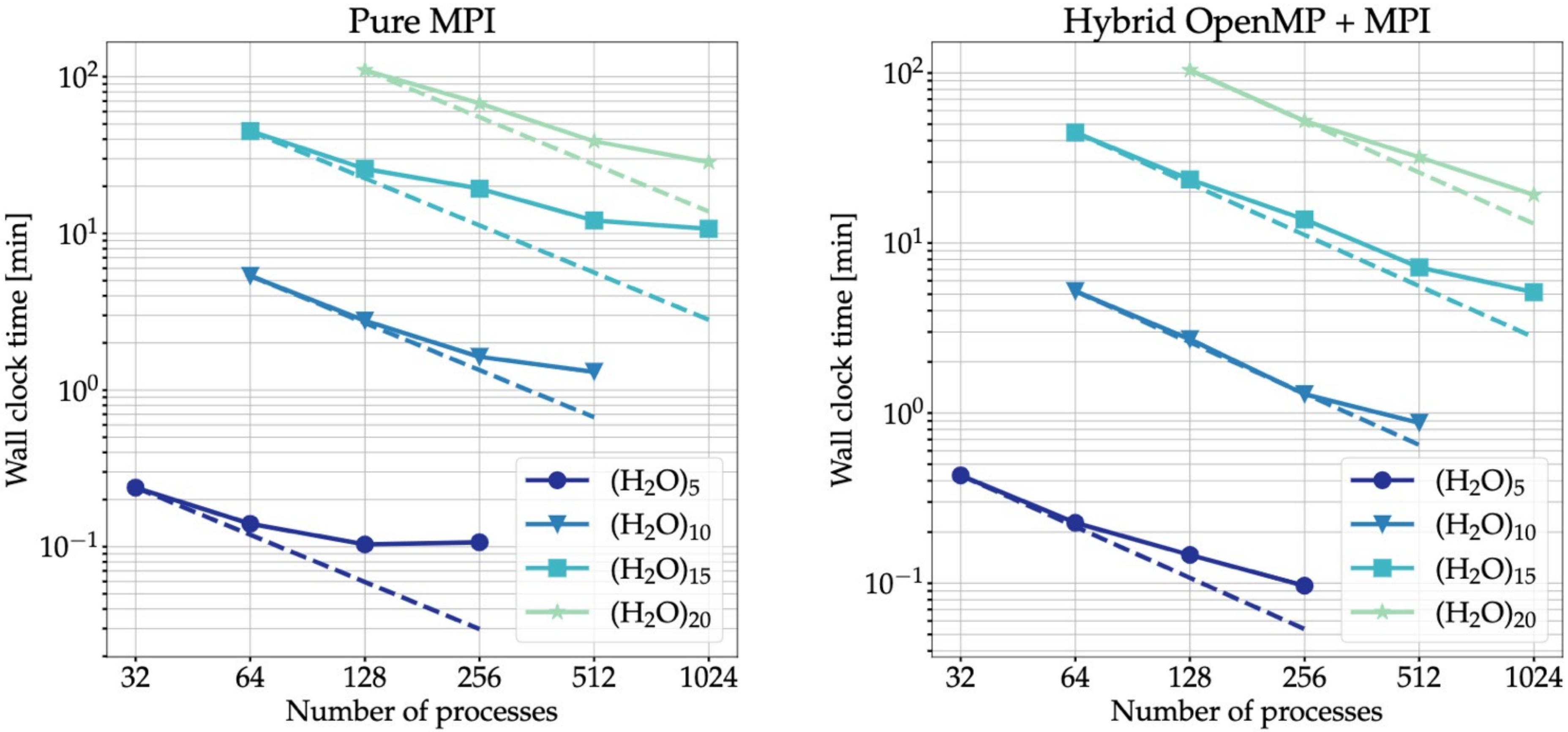


$$\varepsilon_{s\sigma} = \varepsilon_{s\sigma}^{MF} + \langle \phi_{s\sigma}^{MF} \left| \Sigma_\sigma(\varepsilon_{s\sigma}) - v_\sigma^{MF} \right| \phi_{s\sigma}^{MF} \rangle$$

GW implementation

Performance

Core + Valence



JCTC **17**, 7504 (2021)

Examples

N_2 Ionization potential with GW

```
geometry
  N 0.0 0.0 -0.545
  N 0.0 0.0  0.545
  symmetry c1
end

basis "ao basis" spherical
 * library def2-qzvp
end

basis "cd basis" spherical bse
 * library def2-universal-jkfit
end

dft; xc mgga_x_r2scan mgga_c_r2scan; end

task dft gw
```

This input directs NWChem to compute the N_2 ionization potential using GW with default options:

- Analytical
- Newton solver
- Only HOMO

GW needs a fitting basis

- cd basis --> used during SCF and GW
- ri basis --> used only in GW

Explore the starting point dependence by using different exchange-correlation approximations

GW input block options

```
gw
  [rpa]                                # Computes RPA energy
  [first <integer ifirst, default 1>]  # Start counting from orbital <ifirst>
  [core]                               # Count from orbital <ifirst> upwards
  [eta <float>]                        # Imaginary infinitesimal
  [convergence <float thresh, default 0.005> [eV || hartree]]
  [evgw <integer maxiter, default 4>]  # Perform evGW partial self-consistent
                                       # calculation
  [evgw0 <integer maxiter, default 4>] # Perform evGW0 partial
                                       # self-consistent calculation
  [method [cdgw || analytic]]          # Method to obtain Sigma = GW
                                       # convolution
  [solver [newton || graph]]           # Quasiparticle equation solver
  [states [alpha [occ <integer, default 1>] [vir <integer, default 0>]]
  [states [beta  [occ <integer, default 0>] [vir <integer, default 0>]]
end
```

N_2 Ionization potential with GW

```
geometry
  N 0.0 0.0 -0.545
  N 0.0 0.0  0.545
  symmetry c1
end

basis "ao basis" spherical
 * library def2-qzvp
end

basis "cd basis" spherical bse
 * library def2-universal-jkfit
end

dft; xc mgga_x_r2scan mgga_c_r2scan; end

task dft gw
```

Add a GW input block to request the calculation of 5 occupied quasiparticle energies and 5 virtual quasiparticle energies.

Modify the input to compute both 1s core-level binding energies only

Modify the input to perform an evGW0 calculation with 5 iterations. Use the option –1 to compute all occupied and all virtual orbitals

Analytical vs CDGW

```
geometry
  C  -1.2131   -0.6884    0.0000
  C  -1.2028    0.7064    0.0000
  C  -0.0103   -1.3948    0.0000
  C   0.0104    1.3948   -0.0000
  C   1.2028   -0.7063    0.0000
  C   1.2131    0.6884    0.0000
  H  -2.1577   -1.2244    0.0000
  H  -2.1393    1.2564    0.0000
  H  -0.0184   -2.4809   -0.0000
  H   0.0184    2.4808    0.0000
  H   2.1394   -1.2563    0.0000
  H   2.1577    1.2245    0.0000
  symmetry c1
end
```

Use the PBE0 hybrid functional with the def2-tzvp basis set to compute the ionization potential of benzene with both the analytical and the CDGW methods

Questions?

Thank you