

Dielectric-dependent hybrid functionals for accurate electronic structure of Materials and Molecules

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Global Dielectric-dependent Hybrid functional

Improving hybrids without empiricism

Electronic properties obtained with DFT can be improved if hybrid functionals (e.g. PBE0, HSE) are employed instead of semilocal functionals. Hybrid functionals are defined using a parameter (α) that determines the amount of exact exchange that is to be admixed to the semilocal exchange in the exchange-correlation potential.

(Eq. 1) $v_{xc}^{hyb}(\mathbf{r}, \mathbf{r}') = \alpha v_x(\mathbf{r}, \mathbf{r}') + (1 - \alpha) v_x(\mathbf{r}) + v_c(\mathbf{r})$

Hybrids with a fixed value for the mixing parameter are an improvement over semilocal functionals for materials but description of electronic properties for a wide range of materials is still not satisfactory.

Desire is to have GW level reliability in description of electronic structure, but at a reduced cost. We achieve this by defining the exact-exchange parameters entering the hybrid functional through relation with many-body perturbation theory in the GW approximation.

Dielectric Dependent Hybrid (DDH)

An approximated form of the screened-exchange $W(\mathbf{r}, \mathbf{r}')$ energy term of the self-energy in many body perturbation theory is related to the mixing fraction (α) of a hybrid density functional.

Self energy in COHSEX approx: $\Sigma(\mathbf{r}, \mathbf{r}', \omega = 0) = \Sigma_{COH}(\mathbf{r}, \mathbf{r}') + \Sigma_{SEX}(\mathbf{r}, \mathbf{r}')$

$$\Sigma_{COH}(\mathbf{r}, \mathbf{r}') = -\frac{1}{2}\delta(\mathbf{r} - \mathbf{r}') [v(\mathbf{r}, \mathbf{r}') - W(\mathbf{r}, \mathbf{r}')] \quad \Sigma_{SEX}(\mathbf{r}, \mathbf{r}') = -\sum_{i=1}^{N_{occ}} \phi_i(\mathbf{r}) \phi_i^*(\mathbf{r}') W(\mathbf{r}, \mathbf{r}')$$

Approximate microscopic inverse dielectric response function by the inverse macroscopic dielectric constant: $W(\mathbf{r}, \mathbf{r}') = \int d\mathbf{r}'' \epsilon^{-1}(\mathbf{r}, \mathbf{r}'') v(\mathbf{r}'', \mathbf{r}') \approx \frac{\epsilon_\infty^{-1}}{|\mathbf{r} - \mathbf{r}'|}$

(Eq. 2) $\Sigma_{COH}(\mathbf{r}, \mathbf{r}') \approx -(1 - \epsilon_\infty^{-1}) \frac{1}{2} \delta(\mathbf{r} - \mathbf{r}') v(\mathbf{r}, \mathbf{r}')$

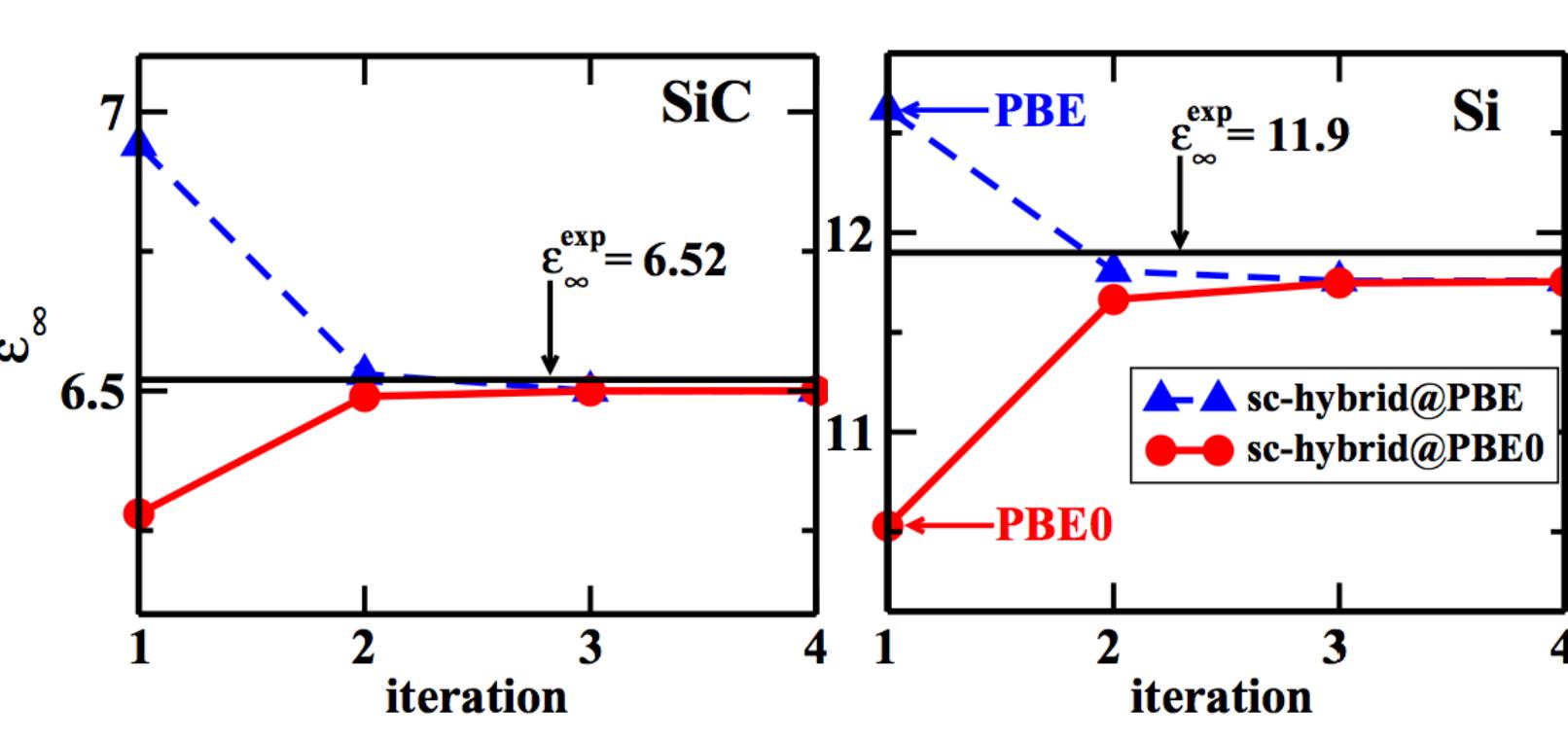
(Eq. 3) $\Sigma_{SEX}(\mathbf{r}, \mathbf{r}') \approx -\epsilon_\infty^{-1} \sum_{i=1}^{N_{occ}} \phi_i(\mathbf{r}) \phi_i^*(\mathbf{r}') v(\mathbf{r}, \mathbf{r}')$

Prefactors of the local and nonlocal exchange potentials in (Eq. 1) can be compared to the prefactors of the energies in the COHSEX approximation when neglecting microscopic components of dielectric screening (Eq. 2) and (Eq. 3), thus arriving at $\alpha = \epsilon_\infty^{-1}$ and the resulting dielectric-dependent exchange-correlation potential expression:

$$v_{xc}^{hyb}(\mathbf{r}, \mathbf{r}') = \epsilon_\infty^{-1} v_x(\mathbf{r}, \mathbf{r}') + (1 - \epsilon_\infty^{-1}) v_x(\mathbf{r}) + v_c(\mathbf{r})$$

Self-consistent hybrid (sc-hybrid)

Since the dielectric constant ϵ_∞^{-1} depends on the fraction of exact-exchange, the dielectric screening should be self-consistently determined in a DDH functional so that it does not depend on the

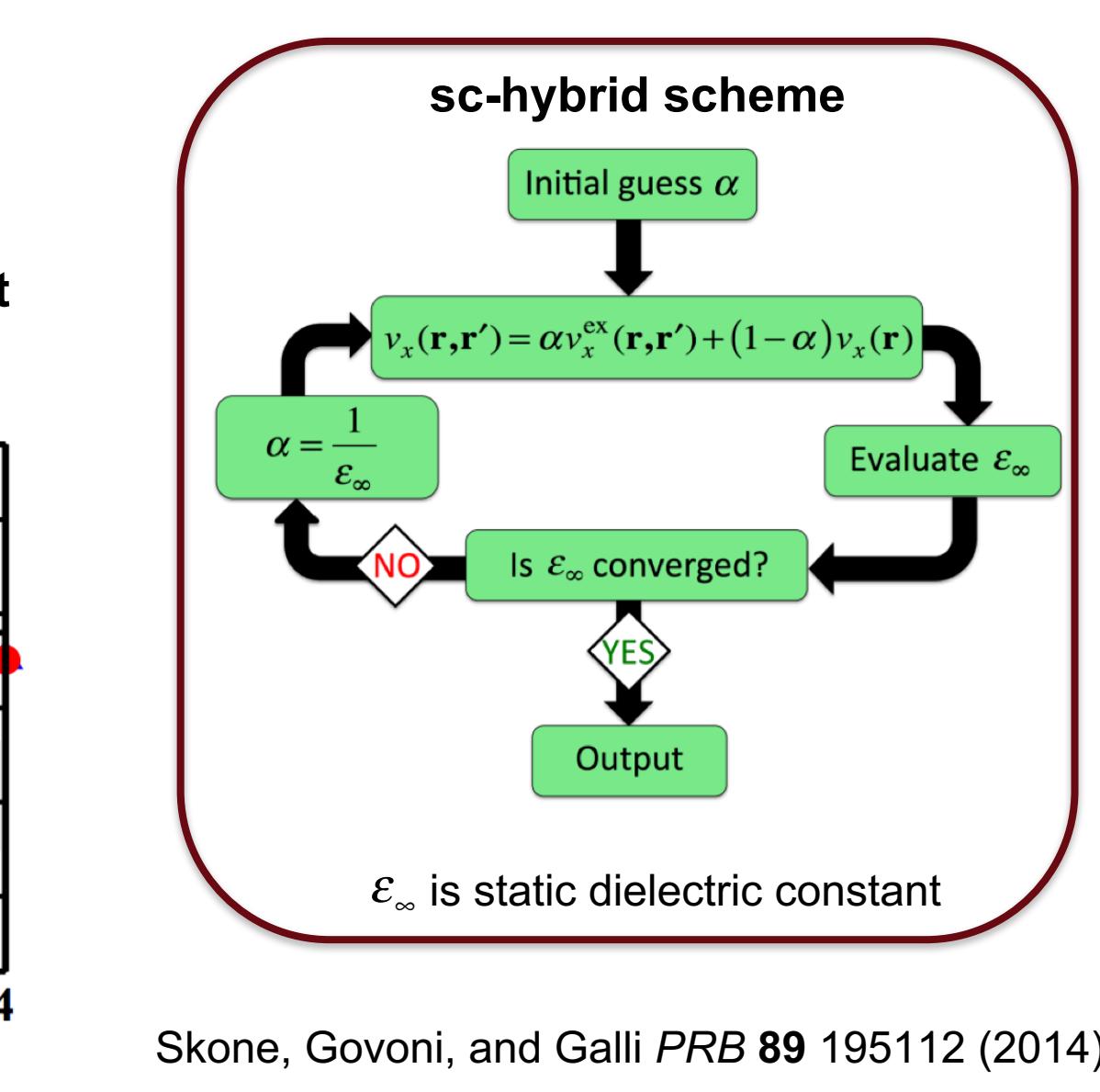


The self-consistent procedure leads to the same converged electronic dielectric constant, regardless of the initial value of α .

The sc-hybrid functional is a simple and accurate global hybrid functional for the electronic properties, including band gaps, band structures, dielectric constants, and lattice constants, of a wide variety of solids and liquids.

Generally only one or two iterations of the self-consistent cycle are necessary to obtain a converged dielectric screening.

The computational cost of the sc-hybrid scheme is similar to that of hybrid calculations, making it a computationally cheaper alternative to GW calculations.



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Range-separated DDH functional

A Range-Separated (RS) Dielectric Dependent Hybrid

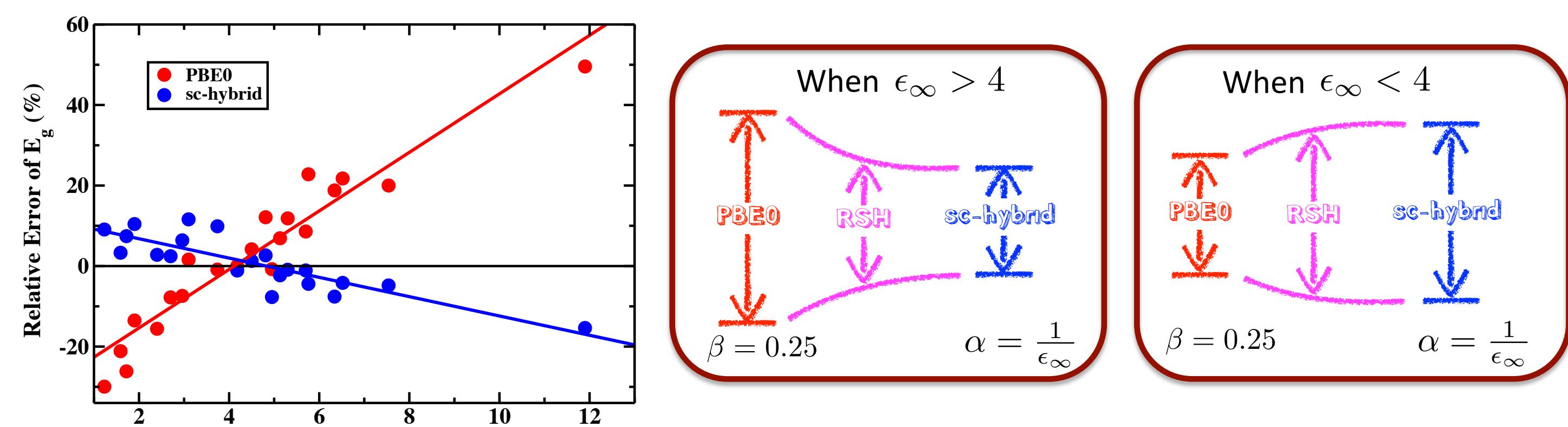
Global dielectric-dependent hybrid functionals approximate the dielectric screening as constant for all inter-electronic distances.

To better approximate the dielectric screening entering the definition of a dielectric-dependent hybrid functional, range-separation can be introduced to provide a better description of the screened coulomb interaction $W(\mathbf{r}, \mathbf{r}')$:

$$W(\mathbf{r}, \mathbf{r}') \approx \frac{\epsilon_\infty^{-1}}{|\mathbf{r} - \mathbf{r}'|} + (\beta - \epsilon_\infty^{-1}) \text{erfc}(\mu |\mathbf{r} - \mathbf{r}'|)$$

$$v_{xc}^{hyb}(\mathbf{r}, \mathbf{r}') = \epsilon_\infty^{-1} v_x^{lr-ex}(\mathbf{r}; \mu) + \beta v_x^{sr-ex}(\mathbf{r}, \mathbf{r}'; \mu) + (1 - \epsilon_\infty^{-1}) v_x^{lr}(\mathbf{r}; \mu) + (1 - \beta) v_x^{sr}(\mathbf{r}; \mu) + v_c(\mathbf{r})$$

This leads to two additional parameters, a short-range fraction of exchange (β) and a screening length (μ) that bridges the inter-electronic short-range and long-range limits of electronic screening.



For systems with $\epsilon_\infty^{-1} = \alpha < (>) 0.25$ increasing (lowering) α from 0.25 may further improve electronic gaps. We use the PBE0 functional value $\beta = 0.25$ in the short-range. Though this does not correspond to the asymptotic short-range limit, which should be unscreened ($\beta = 1$), the attenuated value of 0.25 introduces an approximate form of short-range correlation into the functional.

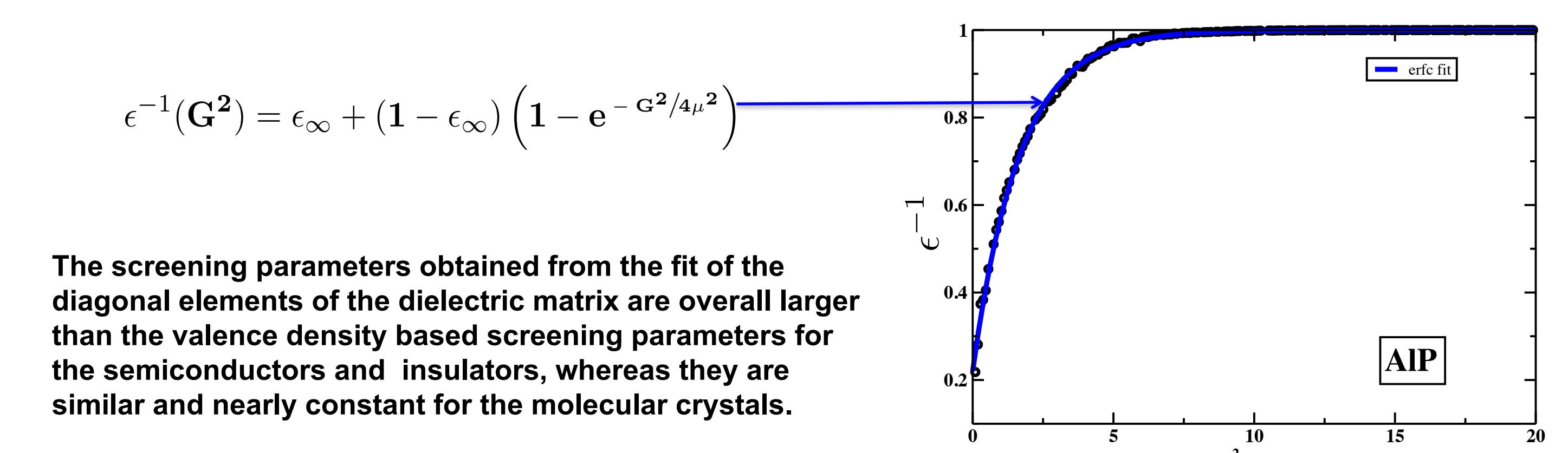
Screening Parameter

For periodic systems the screening parameter can be determined nonempirically from the valence density.

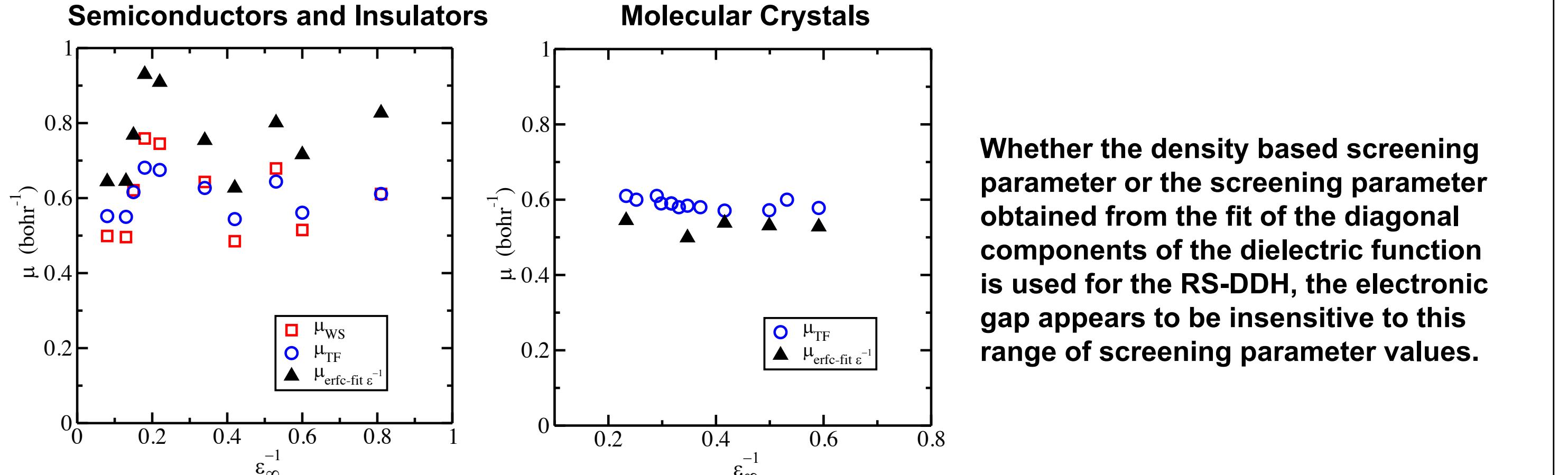
The Wigner-Seitz radius:

$$\frac{4\pi r_s^3}{3} = n^{-1} \quad \mu_{WS} = \frac{1}{r_s} = \left(\frac{4\pi n}{3} \right)^{1/3}$$

Can also extract μ by fitting the diagonal elements of the dielectric matrix using the WEST code. We use the complimentary error function to fit $\epsilon^{-1}(G, G')$ with the resulting screening parameter $\mu_{erfc-fit}$

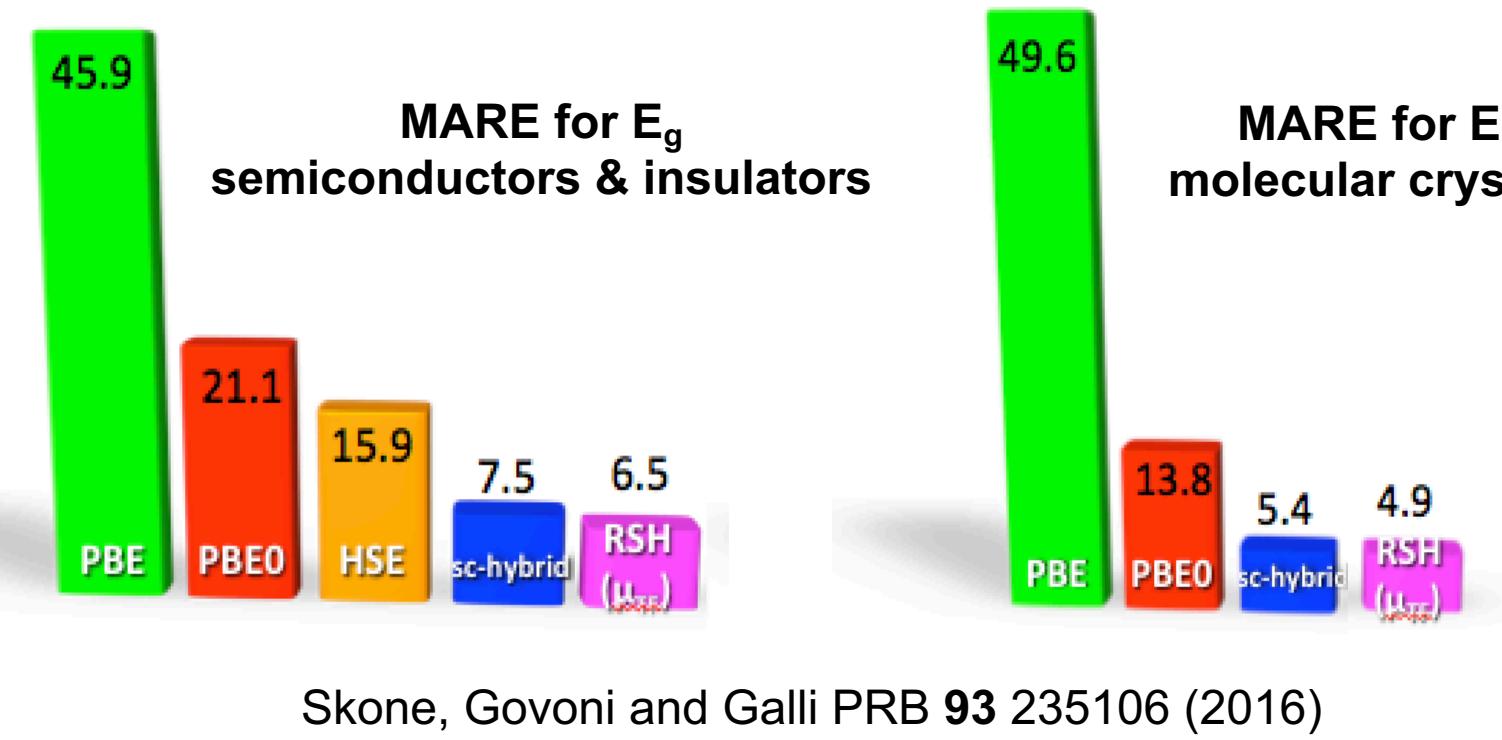


The screening parameters obtained from the fit of the diagonal elements of the dielectric matrix are overall larger than the valence density based screening parameters for the semiconductors and insulators, whereas they are similar and nearly constant for the molecular crystals.



Application of RS DDH to Materials and Molecules

Electronic gap of Materials



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Both full-range and range-separated DDH functionals provide a substantial improvement in the electronic gap as compared to other commonly used hybrid functionals (PBE0 and HSE) for materials.

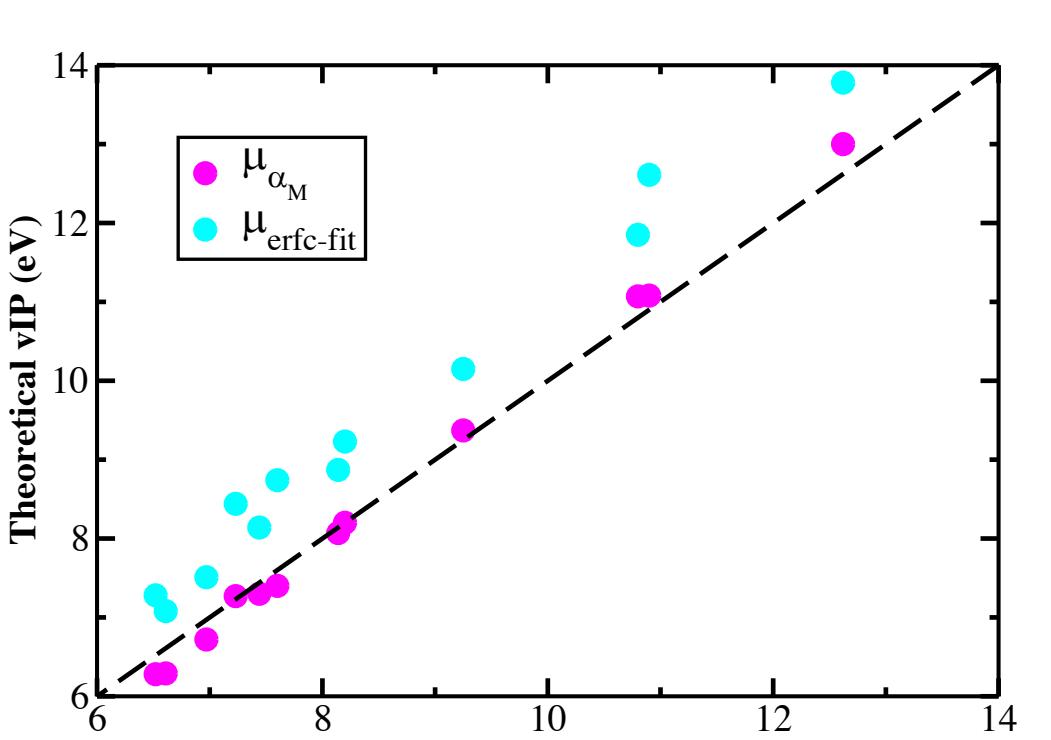
Electronic gaps evaluated with the range-separated dielectric-dependent hybrid show a small, but statistically significant improvement over the full-range dielectric dependent hybrid (sc-hybrid).

Range-separated DDH for Finite Systems

For finite systems μ can be obtained from linear response theory:

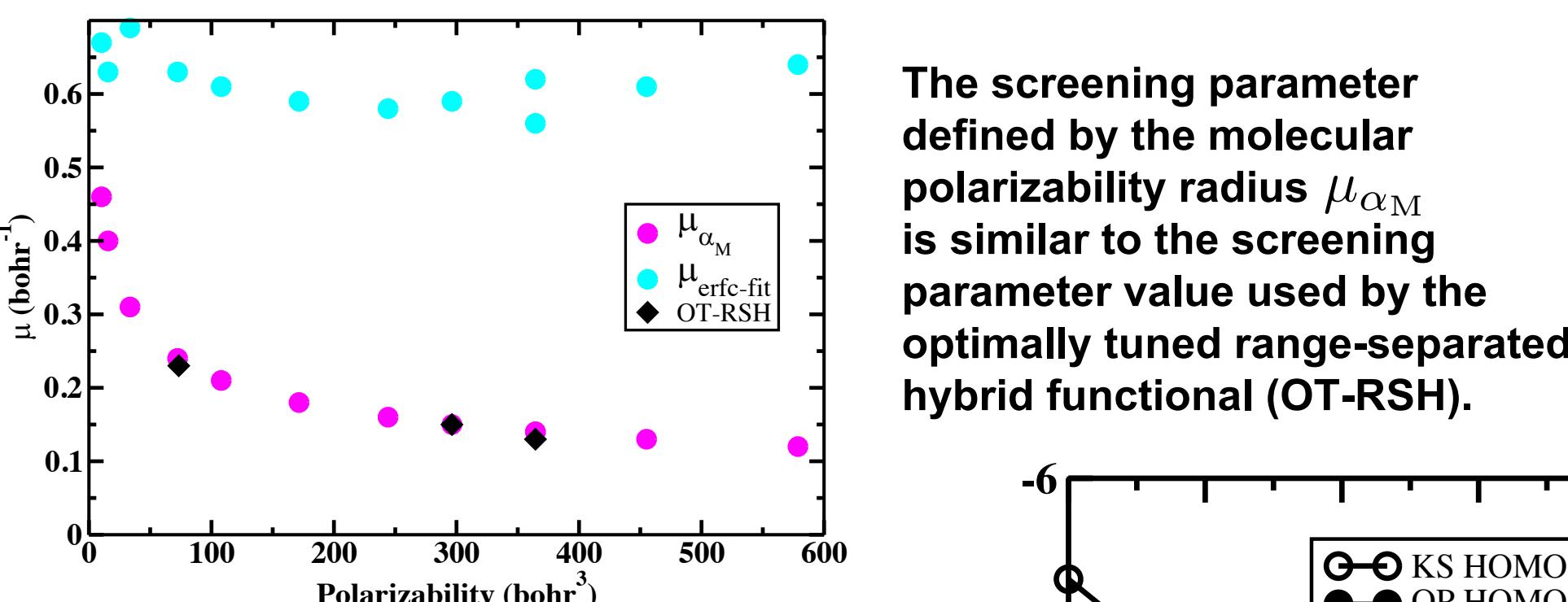
$$\mu_{\alpha_M} = \left(\frac{1}{\alpha_M} \right)^{1/3} \quad \alpha_M = \frac{\Omega}{4\pi} \lim_{q \rightarrow 0} \frac{1}{q^2} \chi_{00}(q, \omega = 0)$$

Can also extract μ by fitting the diagonal elements of the dielectric matrix using the WEST code. We use the complimentary error function to fit $\epsilon^{-1}(G, G')$ with the resulting screening parameter referred to as $\mu_{erfc-fit}$

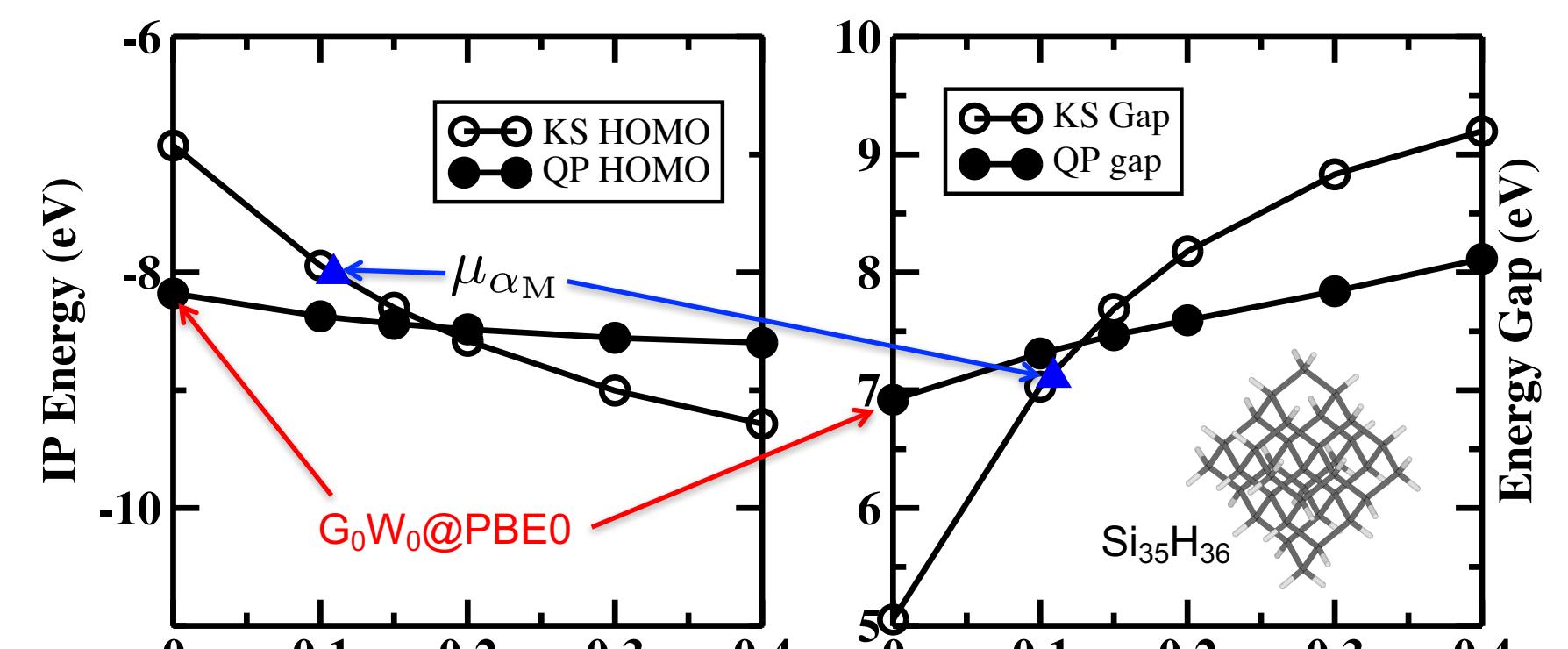


Unlike with solids, for molecules, the electronic gap and VIP are sensitive to the screening parameter μ .

The RSH functional more accurately predicts energy states below the HOMO in the photoelectron spectrum of finite systems as compared to a full-range hybrid.



The screening parameter defined by the molecular polarizability radius μ_{α_M} is similar to the screening parameter value used by the optimally tuned range-separated hybrid functional (OT-RSH).



The range-separated DDH with screening parameter μ_{α_M} provides similar accuracy to $G_0W_0@PBE0$.

Computational Details

Dielectric constant computed at level of RPA + f_{xc} (inclusion of local field effects) $\delta v_{GKS} = \frac{\delta v_H}{\delta n} + \frac{\delta v_{xc}}{\delta n}$. Calculations done at experimental geometries and T = 0K without consideration of zero point vibrational effects.

All-electron calculations employ def2-TZVPP basis.

Norm-conserving pseudopotentials used for all plane-wave calculations.



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