Tuning the range separation parameter in periodic systems

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Kohn-Sham DFT with optimally tuned range-separated hybrid (RSH) functionals provides accurate and nonempirical fundamental gaps for a wide variety of finite-size systems. The standard tuning procedure relies on calculation of total energies of charged systems and thus cannot be applied to periodic solids. Here, we develop a framework for tuning the range separation parameter that can be used for periodic and open boundary conditions. The basic idea is to choose the range parameter that results in a stationary point where the fundamental gap obtained by RSH matches the gap obtained from a $G_0W_0$ over RSH calculation. The proposed framework is therefore analogous to eigenvalue self-consistent GW (scGW). We assess the method for various solids and obtain very good agreement with scGW results.

Due to its high accuracy and low computational cost, Kohn-Sham DFT (KS-DFT) is one of the most prevalent tools for probing the electronic structure of both molecular and periodic systems. However, KS-DFT with local and semilocal (LDA and GGA) functionals often severely underestimate the fundamental band gap. Several alternative frameworks have been developed to tackle the problem. One is the GW approximation, where the quasiparticle excitation energies are obtained by solving a Dyson equation. In practice, calculations are typically carried out with the $G_0W_0$ approximation, where the self energy is applied as a perturbative correction to KS-DFT orbital energies. For many systems this approach provides quasiparticle gaps that are in good agreement with experimental band gaps.

Another route is the generalized Kohn-Sham DFT (GKS-DFT) method where instead of a local exchange-correlation potential, the effective Hamiltonian is nonlocal. DFT with hybrid functionals, in either the original fractional exchange (e.g., B3LYP) or range-separated flavor, are all part of the GKS framework.

In hybrid functionals, certain fraction of Fock exchange is incorporated, and this choice can be justified by considering two facts. First, in semilocal approximations, due to the existence of self interaction the exchange-correlation functional does not have the correct asymptotic form, while in Hartree-Fock theory the one-particle self interaction is eliminated through the balance between the Hartree and Fock exchange terms. Therefore, inclusion of Fock exchange helps achieving the desired asymptotic behavior of exchange-correlation functionals.

A second, related, aspect of the self-interaction problem is that for the exact exchange-correlation functional the total energy curve, as a function of particle number, should be composed of line segments joining the energies at integer electron numbers. However, DFT with local and semilocal approximations is convex at fractional charge, while Hartree-Fock is concave. Therefore, by incorporating Fock exchange, hybrid functionals provide a way of enforcing piecewise linearity. In fact, studies have shown that optimally tuned range separated hybrid (OT-RSH) functionals produce total energy curves that are almost piecewise linear.

In OT-RSH the Coulomb interaction between electrons is separated into short-range and long-range parts. The short range part is then approximated using local or semilocal approximations, which preseve the cancellation of errors between the exchange and the correlation functional. In long-range exchange functionals, the long-range part is calculated with Fock exchange to offset the self-interaction error and enforce the correct long-range asymptotic behavior of the functional. The range-separation parameter $\gamma$ is chosen to maintain a balance between the long-range and short-range exchange, and $\gamma^{-1}$ is an effective screening length.

With this partition, the overall exchange-correlation energy becomes $E_{XC} = E_C + E_F^l + E_F^s$, where $E_F^l$, $E_F^s$ are the long range Fock exchange and short-range local/semilocal exchange, and the superscripts "l" and "s" refer to long-range and short-range respectively. The action of the exchange-correlation part of the Hamiltonian is then:

$$\tilde{V}_{XC}\psi(r) = \tilde{K}^l \psi(r) + [v_C(r) + v_C^s(r)] \psi(r)$$

$$= - \int dr' u'(|r - r'|) \rho(r', r') \psi(r') + v_C^s(r) \psi(r)$$

(1)

where $\rho(r, r')$ is the density matrix of the system, $u'(r) = \frac{\text{erf}(\gamma |r|)}{|r|}$ is the long-range part of the Coulomb interaction,

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while \( v^\ast_{XC} \) is the short range exchange-correlation potential.

The one unknown is then the range-separation parameter. For finite sized systems, a self-consistent optimal tuning procedure chooses \( \gamma \) to ensure that Koopman’s theorem is obeyed, i.e., to minimize the target function:

\[
J(\gamma) = |\epsilon_H^\gamma + IP\gamma|, \tag{2}
\]

where \( \epsilon_H^\gamma \) is the HOMO energy of the electron system, and the ionization potential is given by \( IP\gamma = [E^\gamma(N) - E^\gamma(N - \delta)]/\delta \), where \( N \) is the number of electrons in the neutral system, and \( \delta \) is a small fractional charge. Optimally tuned RSH (OT-RSH) functionals have been applied to study various molecular systems and nanocrystals, yielding band gaps in good agreement with GW and/or experimental results. However, this procedure is not applicable to periodic solids, where total energy calculations of charged systems are problematic.

There are several ways of obtaining \( \gamma \) for solids. For molecular solids, satisfactory results can be obtained with \( \gamma \) tuned for isolated molecules. For solids in general, various attempts were made to connect \( \gamma \) with the optical dielectric constant \( \epsilon^\infty \).

Here we devise instead an approach for systematically tuning the range-separation parameter for periodic systems solely based on first principle calculations. The idea is to perform RSH calculations as well as \( G_0W_0 \) calculations with RSH as starting points. Two sets of band gaps will then be obtained, each being functions of the parameter \( \gamma \). The optimal \( \gamma \) is determined such that the two gaps agree with each other.

We emphasize that this proposed technique is not just a modified \( G_0W_0 \), but is closely related to the self-consistent GW (scGW) method. In previous work, we have shown that perhaps the simplest self-consistent GW method is ev-scGW with scissors operator; namely, self-consistently, updating the \( G \) operator through a scissors shift of the occupied vs. virtuals states; this amounts to repeatedly writing:

\[
\hat{\Sigma}(t) \propto \hat{\Sigma}(t)e^{-i\Delta \theta(t)t},
\]

where we introduce the time domain self-energy \( \hat{\Sigma}(t) \), \( \Delta \) is the difference between the quasiparticle band gap and the DFT band gap, and \( \theta(t) \) is the Heaviside step function. We demonstrated that such a self-consistent procedure can open up the fundamental band gap and improve the accuracy of calculated gaps over one-shot \( G_0W_0 \). The current approach for finding \( \gamma \) gives \( \Delta = 0 \), and thus amounts to finding a stationary point for this self-consistent procedure.

In the following discussions, we will refer to this tuning procedure as OT-GW/RSH.

OT-GW/RSH can be implemented with any conventional GW code, such as VASP. Since many of the OT-GW/RSH applications are envisioned to eventually take place for large (potentially disordered) systems, we have also studied here the use of the method with our recent linear-scaling stochastic GW (sGW) approach, which has been successfully applied to systems of 10,000 electrons and more. To carry out sGW calculations with RSH, we also applied here a stochastic method for applying and propagating long-range Fock exchange.

In sGW, the quasiparticle energy in \( G_0W_0 \) formulation is obtained as first-order perturbation to the Kohn-Sham orbital energies:

\[
\epsilon_{QP}(r) = \epsilon_{KS}(r) + \langle \phi_F | \hat{\Sigma}_P(\epsilon_{QP}) + \hat{K} - \hat{V}_{XC} | \phi_F \rangle \tag{3}
\]

where \( \phi_F(r) \) is typically the HOMO or LUMO. \( \hat{\Sigma}_P \) is the dynamical polarization self energy, \( \hat{K} \) is the full Fock exchange operator, and \( \hat{V}_{XC} \) is the exchange-correlation part of the GKS-Hamiltonian as in equation (1). In sGW, we calculate the matrix elements of \( \hat{\Sigma}_P \) in the time domain. Detailed accounts of the sGW method are found in previous works.

One important issue is that the Generalized Kohn-Sham Hamiltonian \( \hat{h} \) contains the long-range exchange potential, which depends on the density matrix:

\[
\rho(r,r') = \sum_{i,\text{occ}} \psi_i^\ast(r) \psi_i(r'),
\]

For large systems, the number of occupied orbitals is large, making the application of long-range exchange computationally demanding. To solve this problem, we implemented stochastic long-range Fock exchange in the sGW code, as done recently. Detailed explanation of the method can be found in references. In short, we use for the purpose of stochastic exchange a total number of \( N_\zeta \) stochastic orbitals, each being a linear combination of occupied states that are obtained by a low-band-pass filter of a white-noise function, \( |\zeta\rangle = \sqrt{\Theta(\mu - \hat{h})}|\zeta_0\rangle \). Here, we introduced the chemical potential \( \mu \), the white noise function is chosen as \( \zeta_0(r) \propto \pm 1 \), and the application of \( \Theta \) operator is carried out by a Chebyshev expansion. The density matrix is then approximated by:

\[
\rho(r,r') \approx |\zeta(r)\zeta^\ast(r')\rangle. \tag{4}
\]

Further, the long-range Coulomb potential is approximated as \( u(|r - r'|) = |\chi(r)\chi^\ast(r')| \), where \( \chi(r) \) is constructed by Fourier transforming a stochastic combination of the square root of the Fourier components of the long-range potential, \( \sqrt{u(|k|)} \). These two random representations make the long range exchange operator a sum of separable terms. Then, the action of the long-range exchange operator becomes:
We note that a part of the GW calculation, the action of the short-time $e^{-iK\gamma dt}$ is required; a one-term Taylor expansion is used, in conjunction with re-normalization of the orbitals after the short-time propagator is applied. Finally, in calculating the final quasiparticle energy according to equation (3), we note that the difference $\hat{K} - \hat{V}_{XC}$ involves the term $\hat{K}^s = \hat{K} - \hat{K}^t$. In our code, this term is calculated in a similar manner to $\hat{K}^t$, but now using the Fourier transform of the short range potential.

\[ \hat{K}^t \psi = -[\zeta(r)\chi(r) \int dr'\zeta^*(r')\chi^*(r')\psi(r')] \]  
\[ = -\frac{1}{N_{\xi}} \sum_{\zeta} \zeta(r)\chi(r) \int dr'\zeta^*(r')\chi^*(r')\psi(r') \]

We assessed the tuning procedure for several solids using VASP. For two of the systems, we additionally performed sGW calculations. As an illustration of the tuning procedure, we plot the fundamental gaps calculated from sGW/RSH and RSH, as functions of the range-separation parameter $\gamma$ for a LiF $5 \times 5 \times 5$ supercell.

It is evident from Fig. 1 that the RSH DFT results are more sensitive to $\gamma$ than the GW gaps. This is expected, as $\gamma$ affects the GW gap only indirectly by changing the DFT starting point. A summary of the calculated fundamental band gaps are given in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>OT-GW/RSH</th>
<th>scGW</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>VASP</td>
<td>3.8$^a$</td>
<td>3.8$^b$</td>
<td>3.44$^c$</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.12</td>
<td>3.14$^d$</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.292</td>
<td>0.019</td>
<td>11.68$^e$</td>
</tr>
<tr>
<td>LiF</td>
<td>0.286</td>
<td>0.2</td>
<td>1.92$^d$</td>
</tr>
<tr>
<td>CdO</td>
<td>0.1</td>
<td>0.15</td>
<td>2.34$^d$</td>
</tr>
</tbody>
</table>

Table I: Fundamental band gaps with OT-GW/RSH using VASP and sGW, in eV. Results from self-consistent GW (scGW) as well as experiments (Exp.) are also reported. References: a)$^{45}$ b)$^{46}$ c)$^{11}$

Possible ways to fix the situation were proposed $^{45,49}$ and this will be explored in our future work.

As for the present work, we emphasize that OT-GW/RSH provides a way of tuning the range-separation parameter for periodic systems, and it produces good results. To see this, the fitted optimal $\gamma$ are reported in Table 2. For reference, we compare the optimal $\gamma$ obtained from OT-GW/RSH with that calculated using the empirical formula of Baer et al.$^{11}$ The two methods give results that are overall consistent though not identical. This indicates that OT-GW/RSH is an effective method for obtaining the range-separation parameter in periodic systems from first principles only.

\[ \gamma(VASP) = \gamma(sGW) - \gamma(Fitted) \]  
\[ \epsilon_{\infty} \]

Table II: Optimally tuned $\gamma$ in Bohr$^{-1}$, obtained from OT-GW/RSH with VASP and sGW. We also report values fitted from dielectric constant using the empirical formula from the work of Baer et al.$^{11}$ References: a)$^{45,46}$ c)$^{11}$

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I. RESULTS AND DISCUSSIONS

We assessed the tuning procedure for several solids using VASP. For two of the systems, we additionally performed sGW calculations. As an illustration of the tuning procedure, we plot the fundamental gaps calculated from sGW/RSH and RSH, as functions of the range-separation parameter $\gamma$ for a LiF $5 \times 5 \times 5$ supercell.
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