Supplementary material

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1 Pseudobands and the physics behind our model

A *GW* calculation under the generalized plasmon-pole (GPP) model involves the calculation of the zero-frequency dielectric matrix $\chi_{\mathbf{GG}'}(\mathbf{q}, \omega = 0)$ (done in `epsilon` in BerkeleyGW) and the calculation of the screened-exchange (SX) and Coulomb hole (CH) part of the single-electron self-energy (done in `sigma` in BerkeleyGW) [1]. Calculation of χ and Σ^{CH} involves summation over theoretically infinite bands, which is a bottleneck of the performance of the procedure. The problem is usually handled by the pseudobands technique [2], in which the empty bands are divided into one low-energy protected subspace and a series of pseudobands blocks; each of the blocks contain bands with comparable energies. The energies of each block are then replaced by a single energy, which is the average of the former, and for each $\mathbf{k}$ point, all $|n\mathbf{k}\rangle$ states in the block S is replaced by $\sum_n^S |n\mathbf{k}\rangle$. In this way each pseudobands block is replaced by a flat band, and at each $\mathbf{k}$ point we have an effective, unnormalized wave function; this band is known as a pseudoband. The protected bands and the pseudobands are then fed to `epsilon` and `sigma`. In this section, I briefly discuss why this seemingly crude approximation works.

The expression of the zero-frequency dielectric matrix is

$$\chi_{\mathbf{GG}'}(\mathbf{q}, \omega = 0) = \sum_{\mathbf{k}} \sum_{n}^{\mathrm{occ}} \sum_{n'}^{\mathrm{emp}} M_{nn'}(\mathbf{k}, \mathbf{q}, \mathbf{G}) M^*_{nn'}(\mathbf{k}, \mathbf{q}, \mathbf{G}') \frac{2}{E_{n\mathbf{k}+\mathbf{q}} - E_{n'\mathbf{k}}}, \tag{1}$$

where

$$M_{nn'}(\mathbf{k}, \mathbf{q}, \mathbf{G}) = \langle n\mathbf{k} + \mathbf{q} | \mathrm{e}^{\mathrm{i}(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | n'\mathbf{k} \rangle . \tag{2}$$

When pseudobands is used, the high-energy terms in $\chi_{\mathbf{GG}'}(\mathbf{q}, \omega = 0)$ are therefore replaced by (P.B. means pseudobands)

$$\chi^{\text{P.B. terms}}_{\mathbf{GG}'}(\mathbf{q}, \omega = 0) = \sum_{\mathbf{k}} \sum_{S}^{\text{P.B. blocks}} \frac{2}{E_{n\mathbf{k}+\mathbf{q}} - \bar{E}_S} \sum_{n_1', n_2'}^{S} \sum_{n}^{\mathrm{occ}} M_{nn_1'}(\mathbf{k}, \mathbf{q}, \mathbf{G}) M^*_{nn_2'}(\mathbf{k}, \mathbf{q}, \mathbf{G}'). \tag{3}$$

To justify the pseudobands technique, it is sufficient to show that the unwanted $n_1' \neq n_2'$ cross terms that do not appear in the definition of χ vanish after the summations over $\mathbf{k}$ and n.

Because the energies of states in each pseudobands block are comparable, in each pseudobands block, the states share the same set of predominant $\mathbf{G}$ vectors. Thus the states in pseudobands block S can be written as

$$\langle \mathbf{r} | n'\mathbf{k} \rangle = \frac{1}{\sqrt{V}} \sum_{i}^{N} c_{n'\mathbf{k}}(\mathbf{G}^{(i)}_{S\mathbf{k}}) \mathrm{e}^{\mathrm{i}(\mathbf{k}+\mathbf{G}^{(i)}_{S\mathbf{k}})\cdot\mathbf{r}}, \quad \sum_{i}^{N} c_{n_1'\mathbf{k}}(\mathbf{G}^{(i)}_{S\mathbf{k}}) c^*_{n_2'\mathbf{k}}(\mathbf{G}^{(i)}_{S\mathbf{k}}) = \delta_{n_1'n_2'}, \tag{4}$$

and therefore

$$M_{nn'}(\mathbf{k}, \mathbf{q}, \mathbf{G}) = \sum_{i}^{N} c_{n'\mathbf{k}}(\mathbf{G}^{(i)}_{S\mathbf{k}}) c^*_{n\mathbf{k}+\mathbf{q}}(\mathbf{G} + \mathbf{G}^{(i)}_{S\mathbf{k}}). \tag{5}$$

The pseudobands approximation of the diagonal $\chi_{\mathbf{GG}}$ components of the polarizability is proportional to

$$\begin{aligned}
&\sum_{n}^{\mathrm{occ}} M_{nn_1'}(\mathbf{k}, \mathbf{q}, \mathbf{G}) M^*_{nn_2'}(\mathbf{k}, \mathbf{q}, \mathbf{G}) \\
&= \sum_{i,j}^{N} c_{n_1'\mathbf{k}}(\mathbf{G}^{(i)}_{S\mathbf{k}}) c^*_{n_2'\mathbf{k}}(\mathbf{G}^{(j)}_{S\mathbf{k}}) \sum_{n}^{\mathrm{occ}} c^*_{n\mathbf{k}+\mathbf{q}}(\mathbf{G} + \mathbf{G}^{(i)}_{S\mathbf{k}}) c_{n\mathbf{k}+\mathbf{q}}(\mathbf{G} + \mathbf{G}^{(j)}_{S\mathbf{k}}) \\
&\propto \sum_{i,j}^{N} c_{n_1'\mathbf{k}}(\mathbf{G}^{(i)}_{S\mathbf{k}}) c^*_{n_2'\mathbf{k}}(\mathbf{G}^{(j)}_{S\mathbf{k}}) \delta_{ij} = \delta_{n_1'n_2'}.
\end{aligned} \tag{6}$$

In the third step we argue that the summation over the occupied states leads to an approximate, non-normalized orthogonal relation, because the subspace spanned by the dominant $\mathbf{G}$ components of the occupied states is expected to largely overlap with the subspace of the occupied states, and therefore although for $i = j$ terms, the summation over occupied n is usually far less than one, the fast oscillation of $i \neq j$ terms when n changes quickly brings the summation to zero. Therefore, the unwanted non-diagonal terms in (3) can be ignored when $\mathbf{G} = \mathbf{G}'$.

For the $\mathbf{G} \neq \mathbf{G}'$ terms we similarly have

$$\begin{aligned}
&\sum_{n}^{\text{occ}} M_{nn_1'}(\mathbf{k},\mathbf{q},\mathbf{G}) M^*_{nn_2'}(\mathbf{k},\mathbf{q},\mathbf{G}') \\
&= \sum_{i,j}^{N} c_{n_1'\mathbf{k}}(\mathbf{G}^{(i)}_{S\mathbf{k}}) c^*_{n_2'\mathbf{k}}(\mathbf{G}^{(j)}_{S\mathbf{k}}) \sum_{n}^{\text{occ}} c^*_{n\mathbf{k}+\mathbf{q}}(\mathbf{G}+\mathbf{G}^{(i)}_{S\mathbf{k}}) c_{n\mathbf{k}+\mathbf{q}}(\mathbf{G}'+\mathbf{G}^{(j)}_{S\mathbf{k}}) \\
&\propto \sum_{i,j}^{N} c_{n_1'\mathbf{k}}(\mathbf{G}^{(i)}_{S\mathbf{k}}) c^*_{n_2'\mathbf{k}}(\mathbf{G}^{(i)}_{S\mathbf{k}}+\mathbf{G}-\mathbf{G}').
\end{aligned} \tag{7}$$

Numerical experiments reveal that the unwanted $n_1' \neq n_2'$ terms in the $\mathbf{G} \neq \mathbf{G}'$ components in the above equation do not cancel each other; the summation over $\mathbf{k}$ however could eliminate these terms. We note that the $1/(E_\text{v} - E_\text{c})$ factor in (3) is approximately a constant as $\mathbf{k}$ varies, and therefore the summation over $\mathbf{k}$ in (3) contains the following factor

$$\sum_{\mathbf{k}} c_{n_1'\mathbf{k}}(\mathbf{G}^{(i)}) c^*_{n_2'\mathbf{k}}(\mathbf{G}^{(j)}) \propto \sum_{\mathbf{k}} \mathrm{e}^{\mathrm{i}\theta_{n_1'\mathbf{k}} - \mathrm{i}\theta_{n_2'\mathbf{k}}} \overset{N_\mathbf{k}\to\infty}{\longrightarrow} \delta_{n_1'n_2'}, \tag{8}$$

where $\mathrm{e}^{\mathrm{i}\theta_{n\mathbf{k}}}$ is the random global phase factor introduced in the diagonalization process, which changes much more rapidly than the rest part of $c_{n\mathbf{k}}$ as $\mathbf{k}$ runs over the Brillouin zone sampling. In conclusion, the validity of the pseudobands technique for high-energy bands is well-justified for the whole $\chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega=0)$ because of the summation over $\mathbf{k}$ and/or n.

The analysis of pseudobands in `sigma` is more complicated because in the Coulomb hole part of the GPP self-energy

$$\begin{aligned}
\langle n\mathbf{k}\,|\Sigma_{\text{C H}}(E)|\,n'\mathbf{k}\rangle = \frac{1}{2}\sum_{n''}\sum_{\mathbf{q}\mathbf{G}\mathbf{G}'} & M^*_{n''n}(\mathbf{k},-\mathbf{q},-\mathbf{G}) M_{n''n'}(\mathbf{k},-\mathbf{q},-\mathbf{G}') \\
& \times \frac{\Omega^2_{\mathbf{G}\mathbf{G}'}(\mathbf{q})\,(1-\mathrm{i}\tan\phi_{\mathbf{G}\mathbf{G}'}(\mathbf{q}))}{\tilde{\omega}_{\mathbf{G}\mathbf{G}'}(\mathbf{q})\,(E-E_{n''\mathbf{k}-\mathbf{q}}-\tilde{\omega}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}))} v\,(\mathbf{q}+\mathbf{G}')\,,
\end{aligned} \tag{9}$$

where $\Omega_{\mathbf{G}\mathbf{G}'}$, $\tilde{\omega}_{\mathbf{G}\mathbf{G}'}$ and $\phi_{\mathbf{G}\mathbf{G}'}$ are quantities calculated from $\chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega=0)$ and the momentum space ground state density $\rho(\mathbf{G})$. The right hand side contains complicated dependence on $\mathbf{q}$, $\mathbf{G}$ and $\mathbf{G}'$. However, note that when n'' is high and is within one of the pseudobands blocks, typically the magnitudes of $\mathbf{G}$ and $\mathbf{G}'$ are large enough to dominate $v(\mathbf{q}+\mathbf{G}) = 4\pi/|\mathbf{q}+\mathbf{G}|^2$, and therefore the rapid variation of the random phase factor in $|n''\mathbf{k}-\mathbf{q}\rangle$ compared with the relatively slow variance of second line of (9) as $\mathbf{q}$ runs over the Brillouin zone sampling again provides us with the opportunity to justify using pseudobands here: we have

$$\langle n\mathbf{k}|\Sigma^{\text{high energy bands}}_{\text{CH}}(E)|n'\mathbf{k}\rangle \propto \sum_{\mathbf{G},\mathbf{G}'} \sum_{n''}^{\text{high energy bands}} \sum_{\mathbf{q}} M^*_{n''n}(\mathbf{k},-\mathbf{q},-\mathbf{G}) M_{n''n'}(\mathbf{k},-\mathbf{q},-\mathbf{G}'), \tag{10}$$

and by applying the arguments in (8), the pseudobands estimation of the high-energy terms in Σ_{CH} is

$$\begin{aligned}
\langle n\mathbf{k}|\Sigma^{\text{P.B. terms}}_{\text{CH}}(E)|n'\mathbf{k}\rangle &\propto \sum_{\mathbf{G},\mathbf{G}'} \sum_{S}^{\text{P.B. blocks}} \sum_{n_1'',n_2''}^{S} \sum_{\mathbf{q}} M^*_{n_1''n}(\mathbf{k},-\mathbf{q},-\mathbf{G}) M_{n_2''n'}(\mathbf{k},-\mathbf{q},-\mathbf{G}') \\
&\propto \sum_{\mathbf{q}} |n_1''\mathbf{k}-\mathbf{q}\rangle\ \langle n_2''\mathbf{k}-\mathbf{q}| \overset{N_\mathbf{q}\to\infty}{\propto} \delta_{n_1''n_2''},
\end{aligned} \tag{11}$$

and the unwanted $n_1'' \neq n_2''$ cross terms that do not appear in (10) again vanish.

The aforementioned fact that the random phase factor in DFT diagonalization ensures the pseudobands technique can be further exploited by *intentionally* inserting random phase factors before $|n\mathbf{k}\rangle$ states for a given $\mathbf{k}$ point and replacing a pseudobands block by several flat unnormalized bands, instead of just one such band; under such a scheme the size of pseudobands blocks can be drastically increased, further improving the speed of the *GW* methodology; specifically, an empirical observation is that the valence bands can be pseudo-ized as well, and the protected subspace can be very small, without any real damage to accuracy (TODO: cite Altman et al. forthcoming).

The above discussion shows that there exists a relatively simple and smooth mapping from the protected bands, ground state density and pseudobands to the *GW* energies. Even after the pseudobands procedure, there are still hundred of (protected and pseudo) bands; in our model, we tentatively eliminate the protected subspace and pseudo-ize all bands, and also reduce the number of pseudobands subspaces to (TODO: 5??) for each material, hoping that given that the ground state electron density in principle contains all information of the material, as shown by the foundation of DFT [3], having the ground state electron density somehow compensates for the information loss.

References

[1] Jack Deslippe et al. "BerkeleyGW: A massively parallel computer package for the calculation of the quasiparticle and optical properties of materials and nanostructures". In: *Computer Physics Communications* 183.6 (2012), pp. 1269–1289.

[2] Mauro Del Ben et al. "Large-scale GW calculations on pre-exascale HPC systems". In: *Computer Physics Communications* 235 (2019), pp. 187–195.

[3] Pierre Hohenberg and Walter Kohn. "Inhomogeneous electron gas". In: *Physical review* 136.3B (1964), B864.