Note for the calculation of phonon-induced electron self-energy using `PHonon`

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1 Introduction

The Allen-Heine-Cardona (AHC) theory [1, 2, 3] is one of the current state-of-the-art methods to study the effect of electron-phonon coupling (EPC) on electronic structures from first-principles density functional theory (DFT) and density functional perturbation theory (DFPT). In this note, we describe how to use the `PHonon` package to calculate electron self-energy within the AHC theory.

2 Formalism for the Allen-Heine-Cardona theory

In this section, we list the formulae needed to calculate the electron self-energy. For the derivation, consult the cited references.

2.1 Definitions

- M : number of bands in the "lower" subspace. Set by the number of bands in the NSCF calculation (can be different from `ahc_nbnd`)
- $\mathbf{k}$: electron crystal momentum
- $\mathbf{q}$: phonon crystal momentum
- $n,\ n',\ m$: index for electron bands
- $\kappa,\ \kappa'$: index for atoms
- $\alpha,\ \alpha'$: index for Cartesian directions (x, y, z)
- $\mu,\ \nu$: index for phonon eigenmodes
- $\varepsilon_{n\mathbf{k}}$: Kohn-Sham eigenvalue
- ε_{F} : Fermi energy
- $\omega_{\mathbf{q}\nu}$: Phonon frequency
- $U_{\kappa\alpha,\nu}(\mathbf{q})$: mass-scaled phonon eigenmodes

Quantity	Description	Definition	Output filename
$\varepsilon_{n\mathbf{k}}$	Electron energy at $\mathbf{k}$	-	ahc_etk_iq#.bin
$\varepsilon_{m\mathbf{k+q}}$	Electron energy at $\mathbf{k}+\mathbf{q}$	-	ahc_etq_iq#.bin
$g^{\kappa\alpha}_{mn}(\mathbf{k},\mathbf{q})$	First order e-ph matrix element	Eq. (2)	ahc_gkk_iq#.bin
$\widetilde{\mathcal{D}}^{\kappa\alpha\alpha'}_{nn'}(\mathbf{k})$	Debye-Waller matrix element	Eq. (3)	ahc_dw.bin
$\mathcal{F}^{\kappa\alpha\kappa'\alpha'}_{nn'}(\mathbf{k},\mathbf{q})$	Matrix element for upper Fan self-energy	Eq. (4)	ahc_upfan_iq#.bin

Table 1: Quantities calculated in a `ph.x` run with `electron_phonon='ahc'`.

Quantity	Description	Definition
$\Sigma^{\mathrm{OSA}}_{nn'\mathbf{k}}$	Total self-energy in the on-shell approximation (OSA)	$\Sigma^{\mathrm{DW,\,RIA}} + \Sigma^{\mathrm{Fan,\,OSA}}$
$\Sigma^{\mathrm{DW,\,RIA}}_{nn'\mathbf{k}}$	Debye-Waller self-energy in the RIA	Eq. (8)
$\Sigma^{\mathrm{Fan,\,OSA}}_{nn'\mathbf{k}}$	Total Fan self-energy in the OSA	$\Sigma^{\mathrm{Fan,\,upper}} + \Sigma^{\mathrm{Fan,\,lower,\,OSA}}$
$\Sigma^{\mathrm{Fan,\,upper}}_{nn'\mathbf{k}}$	Upper Fan self-energy	Eq. (11)
$\Sigma^{\mathrm{Fan,\,lower,\,OSA}}_{nn'\mathbf{k}}$	Lower Fan self-energy in the OSA	Eq. (10), Eq. (13)

Table 2: Self-energies calculated and printed by `postahc.x`.

The mass-scaled phonon eigenmodes $U_{\kappa\alpha,\nu}(\mathbf{q})$ are normalized to satisfy

$$\sum_{\kappa,\alpha}[U_{\kappa\alpha,\mu}(\mathbf{q})]^* U_{\kappa\alpha,\nu}(\mathbf{q}) M_\kappa = \delta_{\mu,\nu}. \tag{1}$$

2.2 Key equations

First, we define relevant matrix elements:

$$g^{\kappa\alpha}_{mn}(\mathbf{k},\mathbf{q}) = \langle u_{m\mathbf{k+q}} | \partial_{\mathbf{q}\kappa\alpha} \hat{v}_{\mathrm{KS}} | u_{n\mathbf{k}} \rangle \,, \tag{2}$$

$$\widetilde{\mathcal{D}}^{\kappa\alpha\alpha'}_{nn'}(\mathbf{k}) = i \,\langle u_{n\mathbf{k}} | [\partial_{\mathbf{\Gamma}\kappa\alpha} \hat{v}_{\mathrm{KS}}, \hat{p}_{\alpha'}] | u_{n'\mathbf{k}} \rangle \,, \tag{3}$$

and

$$\mathcal{F}^{\kappa\alpha\kappa'\alpha'}_{nn'}(\mathbf{k},\mathbf{q}) = \left\langle \hat{Q}_{M,\mathbf{k+q}} (\partial_{\mathbf{q}\kappa\alpha} u_{n\mathbf{k}}) \middle| \partial_{\mathbf{q}\kappa'\alpha'} \hat{v}_{\mathrm{KS}} \middle| u_{n'\mathbf{k}} \right\rangle . \tag{4}$$

In Eq. (4), $\hat{Q}_{M,\mathbf{k+q}}$ is a projection to the subspace of $M+1$-th or higher eigenstates:

$$\hat{Q}_{M,\mathbf{k+q}} = \hat{I} - \sum_{n=1}^{M} |u_{n\mathbf{k+q}}\rangle \langle u_{n\mathbf{k+q}}| \,. \tag{5}$$

In the dynamical AHC theory, the phonon-induced electron self-energy $\Sigma(\omega)$ which is a function of the frequency ω, is written as a sum of the Fan and the DW self-energies [6]:

$$\Sigma_{nn'\mathbf{k}}(\omega) = \Sigma^{\mathrm{Fan}}_{nn'\mathbf{k}}(\omega) + \Sigma^{\mathrm{DW}}_{nn'\mathbf{k}}, \tag{6}$$

$$\begin{aligned}\Sigma^{\mathrm{Fan}}_{nn'\mathbf{k}}(\omega) = \frac{1}{N_q} \sum_{\substack{\mathbf{q}\nu,m \\ \kappa\alpha\kappa'\alpha'}} \frac{1}{2\omega_{\mathbf{q}\nu}} [g^{\kappa\alpha}_{mn}(\mathbf{k},\mathbf{q})]^* g^{\kappa'\alpha'}_{mn'}(\mathbf{k},\mathbf{q}) U^*_{\kappa\alpha,\nu}(\mathbf{q}) U_{\kappa'\alpha',\nu}(\mathbf{q}) \\ \times \left[\frac{n_{\mathbf{q}\nu} + f_{m\mathbf{k+q}}}{\omega - \varepsilon_{m\mathbf{k+q}} + \omega_{\mathbf{q}\nu} + i\eta} + \frac{n_{\mathbf{q}\nu} + 1 - f_{m\mathbf{k+q}}}{\omega - \varepsilon_{m\mathbf{k+q}} - \omega_{\mathbf{q}\nu} + i\eta} \right],\end{aligned} \tag{7}$$

$$\Sigma^{\mathrm{DW,\,RIA}}_{nn'\mathbf{k}} = \frac{1}{N_q}\sum_{\substack{\mathbf{q}\nu\\ \kappa\alpha\alpha'}} \frac{1}{2\omega_{\mathbf{q}\nu}}\left(n_{\mathbf{q}\nu}+\frac{1}{2}\right)\widetilde{\mathcal{D}}^{\kappa\alpha\alpha'}_{nn'}(\mathbf{k},\mathbf{q})U^*_{\kappa\alpha,\nu}(\mathbf{q})U_{\kappa\alpha',\nu}(\mathbf{q}). \tag{8}$$

To calculate the Debye-Waller self-energy, we use the rigid-ion approximation(RIA).

To avoid a sum over a large number of high-energy empty bands, theFan self-energy is approximated as a sum of "lower" and "upper" Fan self-energy. The upper Fan self-energy is computed within the adiabatic approximation, ignoring the phonon frequency in the denominator. This approximation enables one to avoid the sum over infinite number of states using the solution of the Sternheimer equation [4].

$$\Sigma^{\mathrm{Fan}}_{nn'\mathbf{k}}(\omega) \approx \Sigma^{\mathrm{Fan,\,lower}}_{nn'\mathbf{k}}(\omega) + \Sigma^{\mathrm{Fan,\,upper}}_{nn'\mathbf{k}} \tag{9}$$

$$\Sigma^{\mathrm{Fan,\,lower}}_{nn'\mathbf{k}}(\omega) = \frac{1}{N_q}\sum_{\substack{\mathbf{q}\nu\\ \kappa\alpha\kappa'\alpha'}}\sum_{m=1}^{M}\frac{1}{2\omega_{\mathbf{q}\nu}}[g^{\kappa\alpha}_{mn}(\mathbf{k},\mathbf{q})]^* g^{\kappa'\alpha'}_{mn'}(\mathbf{k},\mathbf{q})U^*_{\kappa\alpha,\nu}(\mathbf{q})U_{\kappa'\alpha',\nu}(\mathbf{q}) \times\left[\frac{n_{\mathbf{q}\nu}+f_{m\mathbf{k}+\mathbf{q}}}{\omega-\varepsilon_{m\mathbf{k}+\mathbf{q}}+\omega_{\mathbf{q}\nu}+i\eta}+\frac{n_{\mathbf{q}\nu}+1-f_{m\mathbf{k}+\mathbf{q}}}{\omega-\varepsilon_{m\mathbf{k}+\mathbf{q}}-\omega_{\mathbf{q}\nu}+i\eta}\right], \tag{10}$$

$$\Sigma^{\mathrm{Fan,\,upper}}_{nn'\mathbf{k}} = \frac{1}{N_q}\sum_{\mathbf{q}\nu}\frac{1}{2\omega_{\mathbf{q}\nu}}(n_{\mathbf{q}\nu}+\frac{1}{2})\left[\sum_{\kappa\alpha\kappa'\alpha'}\mathcal{F}^{\kappa\alpha\kappa'\alpha'}_{nn'}(\mathbf{k},\mathbf{q})U^*_{\kappa\alpha,\nu}(\mathbf{q})U_{\kappa'\alpha',\nu}(\mathbf{q})+(n\leftrightarrow n')^*\right]. \tag{11}$$

In Eq. (11), $(n \leftrightarrow n')^*$ means switching n and n' and taking complex conjugate.

In `postahc.x`, we calculate the static self-energy using the on-the-mass-shell approximation (OSA) where ω is set to the bare Kohn-Sham electron eigenvalue [7]. For off-diagonal self-energy, the value of ω becomes ambiguous. In this case, we take the average of the two possible cases:

$$\Sigma^{\mathrm{OSA}}_{nn'\mathbf{k}} = \frac{1}{2}\left[\Sigma_{nn'\mathbf{k}}(\omega=\varepsilon_{n\mathbf{k}})+\Sigma_{nn'\mathbf{k}}(\omega=\varepsilon_{n'\mathbf{k}})\right]. \tag{12}$$

This approximation affects only the lower Fan self-energy because the Debye-Waller and upper Fan self-energy are static by definition.

$$\Sigma^{\mathrm{Fan,\,lower,\,OSA}}_{nn'\mathbf{k}} = \frac{1}{2}\left[\Sigma^{\mathrm{Fan,\,lower}}_{nn'\mathbf{k}}(\omega=\varepsilon_{n\mathbf{k}})+\Sigma^{\mathrm{Fan,\,lower}}_{nn'\mathbf{k}}(\omega=\varepsilon_{n'\mathbf{k}})\right] \tag{13}$$

3 Example: Electron-phonon renormalization of the indirect band gap of diamond

In this section, we describe how to calculate the phonon-induced renormalization of the indirect band gap of diamond using `PHonon`. The script and reference output files for this example can be found in `PHonon/example/example19`.

1. Run `pw.x` for the SCF calculation.
2. Run `ph.x` for a coarse q point grid.
3. Run `q2r.x` to calculate the force constants.

	Self-energy (Ry)			
	Debye-Waller ($N_q = 3$)	Upper Fan ($N_q = 3$)	Lower Fan ($N_q = 4$)	Total
CBM	0.0215548	-0.0229979	-0.0116025	-0.0130456
VBM	0.0827887	-0.0691964	-0.0053126	0.0082797
Indirect gap	-0.0612339	0.0461985	-0.0062899	-0.0213253

Table 3: Self-energy and indirect band gap renormalization of silicon at 300 K.

4. Run `dvscf_q2r.x` for inverse Fourier transformation of the phonon potential.

5. Run `pw.x` SCF calculation again for the next NSCF calculation.

6. Run `pw.x` for the NSCF calculation at k points to calculate the self-energy.

   To calculate both the indirect band gap, we need to calculate the self-energy for the VBM and the CBM state. So, we do the NSCF calculation for two k points: (0.0, 0.0, 0.0) and (0.365, 0.365, 0.0), in crystal coordinates.

   Also, we set `nosym=.true.` and `noinv=.true.` to sample the whole Brillouin zone, not the irreducible wedge, in the subsequent `ph.x` runs (See Sec. 4.1).

   The number of bands in this NSCF calculation (M defined in Sec. 2.1) is the number of bands in the "lower" subspace. High-energy bands that are not explicitly calculated consist of the "upper" subspace. The contribution of the high-energy bands to the Fan self-energy ("upper Fan" self-energy) is approximated using the solution of the Sternheimer equation [4].

7. Run `ph.x` with `electron_phonon='ahc'` and `ldvscf_interpolate=.true.`.

8. Run `matdyn.x`.

   The q points in the input of `matdyn.x` must be identical to the q points of the previous `ph.x` run. One can copy the q points from the `dyn0` output.

9. Run `postahc.x` to calculate the self-energies.

10. Run `ph.x` with `electron_phonon='ahc'` and `ldvscf_interpolate=.true.` at a finer q-point grid.

    Here, we set `skip_upperfan=.true.` to use the "double-grid technique" (See Sec. 4.2).

11. Run `matdyn.x` for a finer q-grid.

    The list of q points in the input of `matdyn.x` must be identical to the q points of the previous `ph.x` run. One can copy the q points from the `dyn0` output.

12. Run `postahc.x` with `skip_upperfan=.true.` and `skip_dw=.true.`.

The calculated self-energy and indirect band gap renormalization at T=300 K is summarized in Table 3. The Debye-Waller and the upper Fan self-energy is taken from the output of the first `postahc.x` run with a coarse q-grid, while the lower Fan self-energy is taken from the second `postahc.x` run with a finer q-grid. The calculated indirect band gap renormalization at T=300 K is $\Delta E_{\text{gap}} = -0.0213\,\text{Ry} = -290\,\text{meV}$.

Band gap renormalization at other temperatures can be obtained by setting `temp_kelvin` to different values and running `postahc.x`.

The parameters used in this example is far from convergence. To obtain a converged self-energy, one must converge the size of the q-point grid in all three runs of `ph.x` and the smearing `eta` used in `postahc.x`, as well as other usual convergence parameters in SCF calculations.

4 Technicalities related to the q-point sampling

4.1 Sampling only the irreducible wedge

One can calculate the diagonal self-energy at the Γ point using only the irreducible q points by assigning appropriate weights. To do so, one needs to edit the source code of `postahc.f90` where `wtq` (the weight of each q point) is hardcoded to $1/N_q$.

For k points other than the Γ point, the symmetry operation rotates not only the q but also the k vector. Hence, when sampling the q points only inside the irreducible wedge, one must calculate the diagonal self-energy for all symmetry-equivalent k points and take an average.

To calculate the off-diagonal part of the self-energy, one must sample q points in the full Brillouin zone. The reason is that the symmetry operation can change the phase of the wavefunctions.

Often, the most time-consuming step in calculating the electron self-energy is the self-consistent calculation of the phonon potential. For computational efficiency, one should avoid calculation of the phonon potential on the full q-grid by 1) performing DFPT calculations for q points in the irreducible wedge of a given q-grid, 2) Fourier interpolating the phonon potentials from q-grid to real space using `dvscf_q2r.x`, and 3) calculating matrix elements on the full q-grid (of the same size) using Fourier interpolation of phonon potential. This way, the potential at the full q-grid is accurately unfolded from the phonon potentials at the irreducible wedge. Note that `dvscf_q2r.x` internally uses symmetry operations to unfold the phonon potential from the irreducible wedge to the full grid.

4.2 Double-grid technique

The convergence of the self-energy with respect to the q-point sampling is known to be slow and is dominated by the convergence of the lower Fan self-energy [5].

The computational bottleneck in the calculation of the AHC matrix elements is the calculation of the upper Fan term, which involves solving the the Sternheimer equation. In contrast, calculation of $g^{\kappa\alpha}_{mn}(\mathbf{k},\mathbf{q})$ for the lower Fan self-energy only involves simple matrix element calculations.

Therefore, one can save considerable computational cost by calculating the rapidly-convergent upper Fan self-energy at a coarse q-point grid and the slowly-convergent lower Fan self-energy at a finer q-point grid. This method is called the "double-grid technique" for converging the electron self-energy.

Note that although the calculation of the Debye-Waller self-energy is also cheap, one should calculate it at the coarse grid, not the fine grid when using the double-grid technique. The reason is that the convergence of the sum of the DW and the upper Fan self-energies is much faster than the convergence of each term.

References

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