Density Functional Perturbation Theory

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I. THEORY

In the presence of lattice vibrations, the first order electron-phonon matrix elements can be written as [1]

$$g^{\mathbf{q}\lambda}_{n'n\mathbf{k}} = \sum_{\alpha s} \langle n, \mathbf{k} \left| \nabla_{\alpha s} \phi_{scf} \right| n', \mathbf{k}+\mathbf{q} \rangle \times \sum_{\mathbf{q}\lambda} \left(\frac{1}{2M_s \omega_{\mathbf{q}\lambda}} \right)^{\frac{1}{2}} e^{-iq\cdot\tau_s} \epsilon^* \left(\frac{\mathbf{q}\lambda}{s} \right) \tag{1}$$

where, $g^{\mathbf{q}\lambda}_{n'n\mathbf{k}}$ describes the scattering probability from $|\mathbf{n}, \mathbf{k}\rangle$ to $|\mathbf{n}', \mathbf{k}+\mathbf{q}\rangle$ as a result of emission or absorption of a phonon with momentum $\mathbf{q}$, frequency ω in branch λ. ϕ_{scf} is the self-consistent potential obtained by calculating the charge density from DFT. α are the atomic displacements and τ_s is the location of mass M of the s^{th} atomic species in the unit cell with the polarization vectors $\epsilon^* \left(\frac{\mathbf{q}\lambda}{s} \right)$. DFPT is then used to solve Eq. (A.1) taking 200 random $\mathbf{q}$ points in the irreducible Brillioun zone (BZ). The corresponding energy shift of the state $|\mathbf{n}, \mathbf{k}\rangle$ can now be obtained from the MBPT calculations. The single particle interacting Green's propagator in this case is $G_{n\mathbf{k}}(\omega) = \left[\omega - \epsilon_{n\mathbf{k}} - \sum^{Fan}_{n\mathbf{k}}(\omega) - \sum^{DW}_{n\mathbf{k}} \right]^{-1}$ in which $\epsilon_{n\mathbf{k}}$ is the bare energy. $\sum^{Fan}_{n\mathbf{k}}(\omega)$ and $\sum^{DW}_{n\mathbf{k}}$ are the Fan and the Debye-Waller self-energies respectively, that composed of all possible type of scatterings. The former is frequency dependent and can be written as [1]

$$\sum^{Fan}_{n\mathbf{k}}(\omega) = \sum_{n'\mathbf{q}\lambda} \left| g^{\mathbf{q}\lambda}_{n'n\mathbf{k}} \right|^2 \left[\frac{N(\omega_{\mathbf{q}\lambda}) + 1 - f_{n'\mathbf{k}-\mathbf{q}}}{\omega - \epsilon_{n'\mathbf{k}-\mathbf{q}} - \omega_{\mathbf{q}\lambda} - i0^+} + \frac{N(\omega_{\mathbf{q}\lambda}) + f_{n'\mathbf{k}-\mathbf{q}}}{\omega - \epsilon_{n'\mathbf{k}-\mathbf{q}} + \omega_{\mathbf{q}\lambda} - i0^+} \right] \tag{2}$$

in which N and f are the Bose and Fermi functions respectively. The later is the frequency independent and can be expressed as [2, 3]

$$\sum^{DW}_{n\mathbf{k}} = -\sum_{\mathbf{q}\lambda} \sum_{n'} \frac{\Lambda^{\mathbf{q}\lambda,-\mathbf{q}\lambda}_{nn'\mathbf{k}}}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}}} \left[2N(\omega_{\mathbf{q}\lambda}) + 1 \right] \tag{3}$$

The coefficients $\Lambda^{\mathbf{q}\lambda,-\mathbf{q}\lambda}_{nn'k}$ are the second order couplings $= \frac{1}{2}\sum_s \sum_{\alpha,\beta} \frac{\epsilon^*_\alpha\left(\frac{\mathbf{q}\lambda}{s}\right)\epsilon_\beta\left(\frac{-\mathbf{q}\lambda}{s}\right)}{2M_s\omega_{\mathbf{q}\lambda}} \langle n\mathbf{k}+\mathbf{q}+\mathbf{q}' \left| \nabla_{\alpha s}\nabla_{\beta s}\phi_{scf} \right| n\mathbf{k} \rangle$. We note here that in order to calculate the Debye-Waller term, a second-order derivative of the self-consistent potential within the perturbation theory is required. This is extremely computationally costly and is not provided by the DFPT calculation. Thus, in practice one uses the rigid-ion approximation and re-cast the Debye-Waller in terms of a product of Fan-like terms [4, 5]. Such modification needs Sternheimer linear solution [6] to avoid summation over empty electronic states. The MBPT Yambo code does not have such Sternheimer implementation. As a result the zero-point renormalization (ZPR) will converge very slowly with the number of bands.
Using $G_{n\mathbf{k}}(\omega)$ and Eqs. (A.2) and (A.3), it is now possible to write the energy shift $\Delta E_{n\mathbf{k}}$ of the state $|\mathbf{n}, \mathbf{k}\rangle$ as [7]

$$\Delta E_{n\mathbf{k}} - \epsilon_{n\mathbf{k}} \approx Z_{n\mathbf{k}} \Re \left[\sum^{Fan}_{n\mathbf{k}}(\omega) + \sum^{DW}_{n\mathbf{k}} \right] \tag{4}$$

in which $Z_{n\mathbf{k}} = \left[1 - \frac{\partial}{\partial\omega} \Re \sum^{Fan}_{n\mathbf{k}}(\omega) \Big|_{\omega=\epsilon_{n\mathbf{k}}} \right]^{-1}$ is the QP renormalized weight factor ($0 < Z_{n\mathbf{k}} \leq 1$) in this case. $Z_{n\mathbf{k}} \to 1$ for $\frac{\partial}{\partial\omega} \Re \sum^{Fan}_{n\mathbf{k}} \to 0$ is known as the static or the on-the-mass-shell approximation [7]. Once $G_{n\mathbf{k}}(\omega)$ is known, the spectral function can then be expressed as

$$A_{n,\mathbf{k}}(\omega, T) = \frac{1}{\pi} \frac{\left| \Im \sum^{ep}(\omega) \right|}{\left[\omega - \epsilon_{nk} - \Re \sum^{ep}(\omega) \right]^2 + \left[\Im \sum^{ep}(\omega) \right]^2} \tag{5}$$

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in which $\sum^{ep}(\omega) = \sum_{n\mathbf{k}}^{Fan}(\omega) + \sum_{n\mathbf{k}}^{DW}$. The shifts can be used to determine the Eliashberg function at each state $|\mathbf{n},\mathbf{k}\rangle$ as [8]

$$g^2_{n\mathbf{k}}F(\omega) = \sum_{q\lambda}\frac{\partial E_{n\mathbf{k}}}{\partial N(\omega_{q\lambda})}\delta(\omega-\omega_{q\lambda}) \tag{6}$$

Equation (A.6) can be computed at any state to get the required difference between conduction and valence energies.

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