Longitudinal Gauge Theory of Surface Second Harmonic Generation

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Abstract

We present a theoretical review of surface second harmonic generation (SHG) from semiconductor surfaces based on the longitudinal gauge. This layer-by-layer analysis is carefully presented in order to show how a surface SHG calculation can be readily evaluated. The nonlinear susceptibility tensor $\boldsymbol{\chi}$ is split into two terms relating to inter-band and intra-band one-electron transitions.

Contents

I. INTRODUCTION

Second harmonic generation (SHG) is a powerful spectroscopic tool for studying the optical properties of surfaces and interfaces since it has the advantage of being surface sensitive. Within the dipole approximation, inversion symmetry forbids SHG from the bulk of controsymmetric materials. SHG is allowed at the surface of these materials where the inversion symmetry is broken and should necessarily come from the localized surface region. SHG allows the study of the structural atomic arrangement and phase transitions of clean and adsorbate covered surfaces. Since it is also an optical probe it can be used out of UHV conditions and is non-invasive and non-destructive. Experimentally, new tunable high intensity laser systems have made SHG spectroscopy readily accessible and applicable to a wide range of systems.[1,2]

However, theoretical development of the field is still an ongoing subject of research. Some recent advances for the cases of semiconducting and metallic systems have appeared in the literature, where the use of theoretical models with experimental results have yielded correct physical interpretations for observed SHG spectra.[1,3–10]

In a previous article[11] we reviewed some of the recent results in the study of SHG using the transverse gauge for the coupling between the electromagnetic field and the electron. In particular, we demonstrated a method to systematically analyze the different contributions to the observed SHG peaks.[12] This approach consists of separating the different contributions to the nonlinear susceptibility according to 1ω and 2ω transitions, and the surface or bulk nature of the states among which the transitions take place.

To compliment those results, in this article we review the calculation of the nonlinear susceptibility using the longitudinal gauge. We show that it is posible to clearly obtain the "layer-by-layer" contribution for a slab scheme used for surface calculations.

II. LONGITUDINAL GAUGE

We follow the article by Aversa and Sipe[13] to calculate the optical properties of a given system within the longitudinal gauge. More recent derivations[14,15] can also be found. Assuming the long-wavelength approximation which implies a position independent electric field, $\mathbf{E}(t)$, the Hamiltonian in the length gauge approximation is given by

$$\hat{H} = \hat{H}_0^S - e\hat{\mathbf{r}} \cdot \mathbf{E}, \tag{1}$$

with

$$\hat{H}_0^S = \hat{H}_0^{\rm LDA} + \hat{S}(\mathbf{r},\mathbf{p}). \tag{2}$$

The LDA Hamiltonian can be expressed as follows,

$$\begin{aligned} \hat{H}_0^{\rm LDA} &= \frac{\hat{p}^2}{2m_e} + \hat{V}^{\rm ps}(\mathbf{r},\mathbf{r}') \\ \hat{V}^{\rm ps}(\mathbf{r},\mathbf{r}') &= \hat{V}^l(\mathbf{r}) + \hat{V}^{\rm nl}(\mathbf{r},\mathbf{r}'), \end{aligned} \tag{3}$$

where $\hat{V}^l(\mathbf{r})$ and $\hat{V}^{\rm nl}(\mathbf{r},\mathbf{r}')$ are the local and the non-local parts of the crystal $\hat{V}^{\rm ps}(\mathbf{r},\mathbf{r}')$ pseudopotential. The Schrödinger equation reads

$$\left(\frac{-\hbar^2}{2m_e}\nabla^2 + \hat{V}^l(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) + \int d\mathbf{r}'\hat{V}^{\rm nl}(\mathbf{r},\mathbf{r}')\psi_{n\mathbf{k}}(\mathbf{r}') = E_i\psi_{n\mathbf{k}}(\mathbf{r}), \tag{4}$$

where $\psi_{n\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r}|n\mathbf{k}\rangle = \sqrt{\Omega/8\pi^3}e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$, are the real space representations of the Bloch states $|n\mathbf{k}\rangle$ labelled by the band index n. The crystal momentum $\mathbf{k}$ and $u_{n\mathbf{k}}(\mathbf{r})$ are cell periodic. m_e is the bare mass of the electron and Ω is the unit cell volume. The nonlocal scissors operator is given by

$$S(\mathbf{r},\mathbf{p}) = \hbar\Delta\sum_n\int d^3k'(1-f_n)|n\mathbf{k}'\rangle\langle n\mathbf{k}'|, \tag{5}$$

where f_n is the Fermi-Dirac factor. We have that

$$\begin{aligned} H_0^{\rm LDA}|n\mathbf{k}\rangle &= \hbar\omega_n^{\rm LDA}(\mathbf{k})|n\mathbf{k}\rangle \\ H_0^S|n\mathbf{k}\rangle &= \hbar\omega_n^S(\mathbf{k})|n\mathbf{k}\rangle, \end{aligned} \tag{6}$$

where

$$\hbar\omega_n^S(\mathbf{k}) = \hbar\omega_n^{\rm LDA}(\mathbf{k}) + \Delta(1-f_n), \tag{7}$$

is the $\mathbf{k}$-independent scissored energy. Here, $\Delta = E_g - E_g^{\rm LDA}$ where E_g could be the experimental or GW band gap. We used the fact that $|n\mathbf{k}\rangle^{\rm LDA} \approx |n\mathbf{k}\rangle^S$, thus negating the need to label the Bloch states with the LDA or S superscripts. The matrix elements of $\mathbf{r}$ are split between the *intraband* ($\mathbf{r}_i$) and *interband* ($\mathbf{r}_e$) parts , where $\mathbf{r} = \mathbf{r}_i + \mathbf{r}_e$ and[13,16,17]

$$\langle n\mathbf{k}|\hat{\mathbf{r}}_i|m\mathbf{k}'\rangle = \delta_{nm}\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nn}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right], \tag{8}$$

$$\langle n\mathbf{k}|\hat{\mathbf{r}}_e|m\mathbf{k}'\rangle = (1-\delta_{nm})\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nm}(\mathbf{k}), \tag{9}$$

and

$$\boldsymbol{\xi}_{nm}(\mathbf{k}) \equiv i\frac{(2\pi)^3}{\Omega}\int_\Omega d\mathbf{r}\, u_{n\mathbf{k}}^*(\mathbf{r})\nabla_{\mathbf{k}}u_{m\mathbf{k}}(\mathbf{r}). \tag{10}$$

The interband part $\mathbf{r}_e$ can be obtained as follows. We start by introducing the velocity operator

$$\hat{\mathbf{v}}^{\Sigma} = \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{H}_0^S], \tag{11}$$

and calculating its matrix elements

$$i\hbar\langle n\mathbf{k}|\mathbf{v}^{\Sigma}|m\mathbf{k}\rangle = \langle n\mathbf{k}|[\hat{\mathbf{r}}, \hat{H}_0^S]|m\mathbf{k}\rangle = \langle n\mathbf{k}|\hat{\mathbf{r}}\hat{H}_0^S - \hat{H}_0^S\hat{\mathbf{r}}|m\mathbf{k}\rangle = (\hbar\omega_m^S(\mathbf{k}) - \hbar\omega_n^S(\mathbf{k}))\langle n\mathbf{k}|\hat{\mathbf{r}}|m\mathbf{k}\rangle, \tag{12}$$

thus defining $\omega_{nm\mathbf{k}}^S = \omega_n^S(\mathbf{k}) - \omega_m^S(\mathbf{k})$ we get

$$\mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}_{nm}^{\Sigma}(\mathbf{k})}{i\omega_{nm}^S(\mathbf{k})} \qquad n \neq m, \tag{13}$$

which can be identified as $\mathbf{r}_{nm} = (1 - \delta_{nm})\boldsymbol{\xi}_{nm} \to \mathbf{r}_{e,nm}$. When $\mathbf{r}_i$ appears in commutators we use[13]

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}_i, \hat{\mathcal{O}}]|m\mathbf{k}'\rangle = i\delta(\mathbf{k} - \mathbf{k}')(\mathcal{O}_{nm})_{;\mathbf{k}}, \tag{14}$$

with

$$(\mathcal{O}_{nm})_{;\mathbf{k}} = \nabla_{\mathbf{k}}\mathcal{O}_{nm}(\mathbf{k}) - i\mathcal{O}_{nm}(\mathbf{k})\left(\boldsymbol{\xi}_{nn}(\mathbf{k}) - \boldsymbol{\xi}_{mm}(\mathbf{k})\right), \tag{15}$$

where $;\mathbf{k}$ denotes the generalized derivative (see Appendix A).

As can be seen from Eq. (2) and (3), both $\hat{S}$ and $\hat{V}^{\mathrm{nl}}$ are nonlocal potentials. Their contribution in the calculation of the optical response has to be taken with care. We proceed as follows; from Eqs. (11) and (2) we find

$$\begin{aligned}\hat{\mathbf{v}}^{\Sigma} &= \frac{\hat{\mathbf{p}}}{m_e} + \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{V}^{\mathrm{nl}}(\mathbf{r}, \mathbf{r}')] + \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{S}(\mathbf{r}, \mathbf{p})] \\ &\equiv \mathbf{v} + \mathbf{v}^{\mathrm{nl}} + \mathbf{v}^S = \mathbf{v}^{\mathrm{LDA}} + \mathbf{v}^S,\end{aligned} \tag{16}$$

where we have defined

$$\begin{aligned}\mathbf{v} &= \frac{\hat{\mathbf{p}}}{m_e} \\ \mathbf{v}^{\mathrm{nl}} &= \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{V}^{\mathrm{nl}}(\mathbf{r}, \mathbf{r}')] \\ \mathbf{v}^S &= \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{S}(\mathbf{r}, \mathbf{p})] \\ \mathbf{v}^{\mathrm{LDA}} &= \mathbf{v} + \mathbf{v}^{\mathrm{nl}}\end{aligned} \tag{17}$$

with $\hat{\mathbf{p}} = -i\hbar\boldsymbol{\nabla}$ the momentum operator. Using Eq. (5), we obtain that the matrix elements of $\mathbf{v}^S$ are given by

$$\mathbf{v}_{nm}^S = i\Delta f_{mn}\mathbf{r}_{nm}, \tag{18}$$

with $f_{nm} = f_n - f_m$, where we see that $\mathbf{v}^S_{nn} = 0$, then

$$\begin{aligned}
\mathbf{v}^{\Sigma}_{nm} &= \mathbf{v}^{\mathrm{LDA}}_{nm} + i\Delta f_{mn}\mathbf{r}_{nm} \\
&= \mathbf{v}^{\mathrm{LDA}}_{nm} + i\Delta f_{mn}\frac{\mathbf{v}^{\Sigma}_{nm}(\mathbf{k})}{i\omega^S_{nm}(\mathbf{k})} \\
\mathbf{v}^{\Sigma}_{nm}\frac{\omega^S_{nm} - \Delta f_{mn}}{\omega^S_{nm}} &= \mathbf{v}^{\mathrm{LDA}}_{nm} \\
\mathbf{v}^{\Sigma}_{nm}\frac{\omega^{\mathrm{LDA}}_{nm}}{\omega^S_{nm}} &= \mathbf{v}^{\mathrm{LDA}}_{nm} \\
\frac{\mathbf{v}^{\Sigma}_{nm}}{\omega^S_{nm}} &= \frac{\mathbf{v}^{\mathrm{LDA}}_{nm}}{\omega^{\mathrm{LDA}}_{nm}},
\end{aligned} \tag{19}$$

since $\omega^S_{nm} - \Delta f_{mn} = \omega^{\mathrm{LDA}}_{nm}$. Therefore, Eq. (13) gives

$$\mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}^{\Sigma}_{nm}(\mathbf{k})}{i\omega^S_{nm}(\mathbf{k})} = \frac{\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k})}{i\omega^{\mathrm{LDA}}_{nm}(\mathbf{k})} \qquad n \neq m. \tag{20}$$

The matrix elements of $\mathbf{r}_e$ are the same whether we use the LDA or the scissored Hamiltonian and there is no need to label them with either LDA or S superscripts. Thus, we can write

$$\mathbf{r}_{e,nm} \to \mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k})}{i\omega^{\mathrm{LDA}}_{nm}(\mathbf{k})} \qquad n \neq m, \tag{21}$$

which gives the interband matrix elements of the position operator in terms of the matrix elements of $\mathbf{v}^{\mathrm{LDA}}$. These matrix elements include the matrix elements of $\mathbf{v}^{\mathrm{nl}}_{nm}(\mathbf{k})$ which can be readily calculated[18] for fully separable nonlocal pseudopotentials in the Kleinman-Bylander form.[19–21]

In Appendix B we outline how this can be accomplished.

III. TIME-DEPENDENT PERTURBATION THEORY

In the independent particle approximation, we use the electron density operator $\hat{\rho}$ to obtain the expectation value of any observable $\mathcal{O}$ as

$$\mathcal{O} = \mathrm{Tr}(\hat{\mathcal{O}}\hat{\rho}) = \mathrm{Tr}(\hat{\rho}\hat{\mathcal{O}}), \tag{22}$$

where Tr is the trace and is invariant under cyclic permutations. The dynamic equation of motion for ρ is given by

$$i\hbar\frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}], \tag{23}$$

where it is more convenient to work in the interaction picture. We transform all operators according to

$$\hat{\mathcal{O}}_I = \hat{U}\hat{\mathcal{O}}\hat{U}^{\dagger}, \tag{24}$$

where

$$\hat{U} = e^{i\hat{H}_0 t/\hbar}, \tag{25}$$

is the unitary operator that shifts us to the interaction picture. Note that $\hat{\mathcal{O}}_I$ depends on time even if $\hat{\mathcal{O}}$ does not. Then, we transform Eq. (23) into

$$i\hbar \frac{d\hat{\rho}_I(t)}{dt} = [-e\hat{\mathbf{r}}_I(t) \cdot \mathbf{E}(t), \hat{\rho}_I(t)], \tag{26}$$

that leads to

$$\hat{\rho}_I(t) = \hat{\rho}_I(t = -\infty) + \frac{ie}{\hbar} \int_{-\infty}^{t} dt' [\hat{\mathbf{r}}_I(t') \cdot \mathbf{E}(t'), \hat{\rho}_I(t')]. \tag{27}$$

We assume that the interaction is switched-on adiabatically and choose a time-periodic perturbing field, to write

$$\mathbf{E}(t) = \mathbf{E} e^{-i\omega t} e^{\eta t} = \mathbf{E} e^{-i\tilde{\omega} t}, \tag{28}$$

with

$$\tilde{\omega} = \omega + i\eta, \tag{29}$$

where $\eta > 0$ assures that at $t = -\infty$ the interaction is zero and has its full strength $\mathbf{E}$ at $t = 0$. After computing the required time integrals one takes $\eta \to 0$. Also, $\hat{\rho}_I(t = -\infty)$ should be time independent and thus $[\hat{H}, \hat{\rho}]_{t=-\infty} = 0$, This implies that $\hat{\rho}_I(t = -\infty) = \hat{\rho}(t = -\infty) \equiv \hat{\rho}_0$, where $\hat{\rho}_0$ is the density matrix of the unperturbed ground state, such that

$$\langle n\mathbf{k}|\hat{\rho}_0|m\mathbf{k}'\rangle = f_n(\hbar\omega_n^S(\mathbf{k}))\delta_{nm}\delta(\mathbf{k} - \mathbf{k}'), \tag{30}$$

with $f_n(\hbar\omega_n^S(\mathbf{k})) = f_{n\mathbf{k}}$ as the Fermi-Dirac distribution function.

We solve Eq. (27) using the standard iterative solution, for which we write

$$\hat{\rho}_I = \hat{\rho}_I^{(0)} + \hat{\rho}_I^{(1)} + \hat{\rho}_I^{(2)} + \cdots, \tag{31}$$

where $\hat{\rho}_I^{(N)}$ is the density operator to order N in $\mathbf{E}(t)$. Then, Eq. (27) reads

$$\hat{\rho}_I^{(0)} + \hat{\rho}_I^{(1)} + \hat{\rho}_I^{(2)} + \cdots = \hat{\rho}_0 + \frac{ie}{\hbar} \int_{-\infty}^{t} dt' [\hat{\mathbf{r}}_I(t') \cdot \mathbf{E}(t'), \hat{\rho}_I^{(0)} + \hat{\rho}_I^{(1)} + \hat{\rho}_I^{(2)} + \cdots], \tag{32}$$

where, by equating equal orders in the perturbation, we find

$$\hat{\rho}_I^{(0)} \equiv \hat{\rho}_0, \tag{33}$$

and

$$\hat{\rho}_I^{(N)}(t) = \frac{ie}{\hbar}\int_{-\infty}^{t} dt'[\hat{\mathbf{r}}_I(t')\cdot\mathbf{E}(t'), \hat{\rho}_I^{(N-1)}(t')]. \tag{34}$$

It is simple to show that matrix elements of Eq. (34) satisfy $\langle n\mathbf{k}|\rho_I^{(N+1)}(t)|m\mathbf{k}'\rangle = \rho_{I,nm}^{(N+1)}(\mathbf{k})\delta(\mathbf{k}-\mathbf{k}')$, with

$$\rho_{I,nm}^{(N+1)}(\mathbf{k};t) = \frac{ie}{\hbar}\int_{-\infty}^{t} dt'\langle n\mathbf{k}|[\hat{\mathbf{r}}_I(t'), \hat{\rho}_I^{(N)}(t')]|m\mathbf{k}\rangle\cdot\mathbf{E}(t'). \tag{35}$$

We now work out the commutator of Eq. (35). Then,

$$\begin{aligned}\langle n\mathbf{k}|[\hat{\mathbf{r}}_I(t), \hat{\rho}_I^{(N)}(t)]|m\mathbf{k}\rangle &= \langle n\mathbf{k}|[\hat{U}\hat{\mathbf{r}}\hat{U}^\dagger, \hat{U}\hat{\rho}^{(N)}(t)\hat{U}^\dagger]|m\mathbf{k}\rangle \\ &= \langle n\mathbf{k}|\hat{U}[\hat{\mathbf{r}}, \hat{\rho}^{(N)}(t)]\hat{U}^\dagger|m\mathbf{k}\rangle \\ &= e^{i\omega_{nm\mathbf{k}}^S t}\left(\langle n\mathbf{k}|[\hat{\mathbf{r}}_e, \hat{\rho}^{(N)}(t)] + [\hat{\mathbf{r}}_i, \hat{\rho}^{(N)}(t)]|m\mathbf{k}\rangle\right).\end{aligned} \tag{36}$$

We calculate the interband term first, so using Eq. (21) we obtain

$$\begin{aligned}\langle n\mathbf{k}|[\hat{\mathbf{r}}_e, \hat{\rho}^{(N)}(t)]|m\mathbf{k}\rangle &= \sum_\ell\Big(\langle n\mathbf{k}|\hat{\mathbf{r}}_e|\ell\mathbf{k}\rangle\langle\ell\mathbf{k}|\hat{\rho}^{(N)}(t)|m\mathbf{k}\rangle \\ &\quad -\langle n\mathbf{k}|\hat{\rho}^{(N)}(t)|\ell\mathbf{k}\rangle\langle\ell\mathbf{k}|\hat{\mathbf{r}}_e|m\mathbf{k}\rangle\Big) \\ &= \sum_{\ell\neq n,m}\left(\mathbf{r}_{n\ell}(\mathbf{k})\rho_{\ell m}^{(N)}(\mathbf{k};t) - \rho_{n\ell}^{(N)}(\mathbf{k};t)\mathbf{r}_{\ell m}(\mathbf{k})\right) \\ &\equiv \mathbf{R}_e^{(N)}(\mathbf{k};t),\end{aligned} \tag{37}$$

and from Eq. (14),

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}_i, \hat{\rho}^{(N)}(t)]|m\mathbf{k}'\rangle = i\delta(\mathbf{k}-\mathbf{k}')(\rho_{nm}^{(N)}(t))_{;\mathbf{k}} \equiv \delta(\mathbf{k}-\mathbf{k}')\mathbf{R}_i^{(N)}(\mathbf{k};t). \tag{38}$$

Then Eq. (35) becomes

$$\rho_{I,nm}^{(N+1)}(\mathbf{k};t) = \frac{ie}{\hbar}\int_{-\infty}^{t} dt' e^{i(\omega_{nm\mathbf{k}}^S-\tilde{\omega})t'}\left[R_e^{\mathrm{b}(N)}(\mathbf{k};t') + R_i^{\mathrm{b}(N)}(\mathbf{k};t')\right]E^{\mathrm{b}}, \tag{39}$$

where the roman superindices $\mathrm{a}, \mathrm{b}, \mathrm{c}$ denote Cartesian components that are summed over if repeated. Starting from the linear response and proceeding from Eq. (30) and (37),

$$\begin{aligned}R_e^{\mathrm{b}(0)}(\mathbf{k};t) &= \sum_\ell\left(r_{n\ell}^{\mathrm{b}}(\mathbf{k})\rho_{\ell m}^{(0)}(\mathbf{k}) - \rho_{n\ell}^{(0)}(\mathbf{k})r_{\ell m}^{\mathrm{b}}(\mathbf{k})\right) \\ &= \sum_\ell\left(r_{n\ell}^{\mathrm{b}}(\mathbf{k})\delta_{\ell m}f_m(\hbar\omega_m^S(\mathbf{k})) - \delta_{n\ell}f_n(\hbar\omega_n^S(\mathbf{k}))r_{\ell m}^{\mathrm{b}}(\mathbf{k})\right) \\ &= f_{mn\mathbf{k}}r_{nm}^{\mathrm{b}}(\mathbf{k}),\end{aligned} \tag{40}$$

where $f_{mn\mathbf{k}} = f_{m\mathbf{k}} - f_{n\mathbf{k}}$. From now on, it should be clear that the matrix elements of $\mathbf{r}_{nm}$ imply $n \neq m$. We also have from Eq. (38) and Eq. (15) that

$$R_i^{\mathrm{b}(0)}(\mathbf{k}) = i(\rho_{nm}^{(0)})_{;k^{\mathrm{b}}} = i\delta_{nm}(f_{n\mathbf{k}})_{;k^{\mathrm{b}}} = i\delta_{nm}\nabla_{k^{\mathrm{b}}} f_{n\mathbf{k}}. \tag{41}$$

For a semiconductor at $T = 0$, $f_{n\mathbf{k}}$ is one if the state $|n\mathbf{k}\rangle$ is a valence state and zero if it is a conduction state; thus $\nabla_{\mathbf{k}} f_{n\mathbf{k}} = 0$ and $\mathbf{R}_i^{(0)} = 0$ and the linear response has no contribution from intraband transitions. Then,

$$\begin{aligned}
\rho_{I,nm}^{(1)}(\mathbf{k};t) &= \frac{ie}{\hbar} f_{mn\mathbf{k}} r_{nm}^{\mathrm{b}}(\mathbf{k}) E^{\mathrm{b}} \int_{-\infty}^{t} dt' e^{i(\omega_{nm\mathbf{k}}^{S} - \tilde{\omega})t'} \\
&= \frac{e}{\hbar} f_{mn\mathbf{k}} r_{nm}^{\mathrm{b}}(\mathbf{k}) E^{\mathrm{b}} \frac{e^{i(\omega_{nm\mathbf{k}}^{S} - \tilde{\omega})t}}{\omega_{nm\mathbf{k}}^{S} - \tilde{\omega}} \\
&= e^{i\omega_{nm\mathbf{k}}^{S} t} B_{mn}^{\mathrm{b}}(\mathbf{k}) E^{\mathrm{b}}(t) \\
&= e^{i\omega_{nm\mathbf{k}}^{S} t} \rho_{nm}^{(1)}(\mathbf{k};t).
\end{aligned} \tag{42}$$

We generalize this result since we need it for the non-linear response. In general we could have several perturbing fields with different frequencies, i.e. $\mathbf{E}(t) = \mathbf{E}_{\omega_\alpha} e^{-i\tilde{\omega}_\alpha t}$, then

$$\rho_{nm}^{(1)}(\mathbf{k};t) = B_{mn}^{\mathrm{b}}(\mathbf{k},\omega_\alpha) E_{\omega_\alpha}^{\mathrm{b}} e^{-i\tilde{\omega}_\alpha t}, \tag{43}$$

with

$$B_{nm}^{\mathrm{b}}(\mathbf{k},\omega_\alpha) = \frac{e}{\hbar} \frac{f_{mn\mathbf{k}} r_{nm}^{\mathrm{b}}(\mathbf{k})}{\omega_{nm\mathbf{k}}^{S} - \tilde{\omega}_\alpha}. \tag{44}$$

Now, we calculate the second-order response. Then, from Eq. (37)

$$\begin{aligned}
R_e^{\mathrm{b}(1)}(\mathbf{k};t) &= \sum_{\ell} \left(r_{n\ell}^{\mathrm{b}}(\mathbf{k}) \rho_{\ell m}^{(1)}(\mathbf{k};t) - \rho_{n\ell}^{(1)}(\mathbf{k};t) r_{\ell m}^{\mathrm{b}}(\mathbf{k}) \right) \\
&= \sum_{\ell} \left(r_{n\ell}^{\mathrm{b}}(\mathbf{k}) B_{\ell m}^{\mathrm{c}}(\mathbf{k},\omega_\beta) - B_{n\ell}^{\mathrm{c}}(\mathbf{k},\omega_\beta) r_{\ell m}^{\mathrm{b}}(\mathbf{k}) \right) E_{\omega_\beta}^{\mathrm{c}}(t),
\end{aligned} \tag{45}$$

and from Eq. (38)

$$R_i^{\mathrm{b}(1)}(\mathbf{k};t) = i(\rho_{nm}^{(1)}(t))_{;k^{\mathrm{b}}} = iE_{\omega_\beta}^{\mathrm{c}}(t)(B_{nm}^{\mathrm{c}}(\mathbf{k},\omega_\beta))_{;k^{\mathrm{b}}}. \tag{46}$$

Using Eqs. (45) and (46) in Eq. (39), and generalizing to two different perturbing fields, we obtain

$$
\begin{aligned}
\rho^{(2)}_{I,nm}(\mathbf{k};t) &= \frac{ie}{\hbar}\bigg[\sum_\ell \Big(r^{\mathrm{b}}_{n\ell}(\mathbf{k})B^{\mathrm{c}}_{\ell m}(\mathbf{k},\omega_\beta) - B^{\mathrm{c}}_{n\ell}(\mathbf{k},\omega_\beta)r^{\mathrm{b}}_{\ell m}(\mathbf{k})\Big) \\
&+ i(B^{\mathrm{c}}_{nm}(\mathbf{k},\omega_\beta))_{;k^{\mathrm{b}}}\bigg]E^{\mathrm{b}}_{\omega_\alpha}E^{\mathrm{c}}_{\omega_\beta}\int_{-\infty}^{t} dt' e^{i(\omega^S_{nm\mathbf{k}}-\tilde{\omega}_\alpha-\tilde{\omega}_\beta)t'} \\
&= \frac{e}{\hbar}\bigg[\sum_\ell \Big(r^{\mathrm{b}}_{n\ell}(\mathbf{k})B^{\mathrm{c}}_{\ell m}(\mathbf{k},\omega_\beta) - B^{\mathrm{c}}_{n\ell}(\mathbf{k},\omega_\beta)r^{\mathrm{b}}_{\ell m}(\mathbf{k})\Big) \\
&+ i(B^{\mathrm{c}}_{nm}(\mathbf{k},\omega_\beta))_{;k^{\mathrm{b}}}\bigg]E^{\mathrm{b}}_{\omega_\alpha}E^{\mathrm{c}}_{\omega_\beta}\frac{e^{i(\omega^S_{nm\mathbf{k}}-\tilde{\omega}_3)t}}{\omega^S_{nm\mathbf{k}}-\tilde{\omega}_3} \\
&= e^{i\omega^S_{nm\mathbf{k}}t}\rho^{(2)}_{nm}(\mathbf{k};t).
\end{aligned} \tag{47}
$$

Now, we write $\rho^{(2)}_{nm}(\mathbf{k};t) = \rho^{(2)}_{nm}(\mathbf{k};\omega_3)e^{-i\tilde{\omega}_3 t}$, with

$$
\begin{aligned}
\rho^{(2)}_{nm}(\mathbf{k};\omega_3) = \frac{e}{i\hbar}\frac{1}{\omega^S_{nm\mathbf{k}}-\tilde{\omega}_3}\bigg[&-(B^{\mathrm{c}}_{nm}(\mathbf{k},\omega_\beta)_{;k^{\mathrm{b}}} \\
&+ i\sum_\ell \Big(r^{\mathrm{b}}_{n\ell}B^{\mathrm{c}}_{\ell m}(\mathbf{k},\omega_\beta) - B^{\mathrm{c}}_{n\ell}(\mathbf{k},\omega_\beta)r^{\mathrm{b}}_{\ell m}\Big)\bigg]E^{\mathrm{b}}_{\omega_\alpha}E^{\mathrm{c}}_{\omega_\beta}
\end{aligned} \tag{48}
$$

where $\tilde{\omega}_3 = \tilde{\omega}_\alpha + \tilde{\omega}_\beta$ and $\mathbf{E}_{\omega_i}$ is the amplitude of the perturbing field with ω_i for $i = \alpha, \beta$, and $B^{\mathrm{a}}_{\ell m}(\mathbf{k},\omega_\alpha)$ are given by Eq. (44). We remark that $\mathbf{r}_{nm}(\mathbf{k})$ for $n \neq m$ are the same whether calculated with the LDA or the scissored Hamiltonian. We chose the former in this article.

IV. LAYERED CURRENT DENSITY

In this section, we derive the expressions for the macroscopic current density of a given layer in the unit cell of the system. The approach we use to study the surface of a semi-infinite semiconductor crystal is as follows. Instead of using a semi-infinite system, we replace it by a slab (see Fig. 1). The slab consists of a front and back surface, and in between these two surfaces is the bulk of the system. In general the surface of a crystal reconstructs as the atoms move to find equilibrium positions. This is due to the fact that the otherwise balanced forces are disrupted when the surface atoms do not find their partner atoms that are now absent at the surface of the slab.

To take the reconstruction into account, we take "surface" to mean the true surface of the first relaxed layer of atoms, and some of the relaxed atomic sub-layers adjacent to it. Since the front and the back surfaces of the slab are usually identical the total slab is centrosymmetric. This (see Sec. IV) implies that $\chi^{slab}_{\mathrm{abc}} = 0$, and thus we must find a way to bypass this characteristic of a centrosymmetric slab in order to have a finite χ^{s}_{abc} representative of the surface. Even if the front and back surfaces of the slab are different, breaking the centrosymmetry and therefore giving an overall $\chi^{slab}_{\rm abc} \neq 0$, we still need a procedure to extract the front surface $\chi^f_{\rm abc}$ and the back surface $\chi^b_{\rm abc}$ from the non-linear susceptibility $\chi^{slab}_{\rm abc}$ of the entire slab.

A convenient way to accomplish the separation of the SH signal of either surface is to introduce a "cut function", $\mathcal{C}(z)$, which is usually taken to be unity over one half of the slab and zero over the other half. In this case $\mathcal{C}(z)$ will give the contribution of the side of the slab for which $\mathcal{C}(z) = 1$. We can generalize this simple choice for $\mathcal{C}(z)$ by a top-hat cut function $\mathcal{C}^\ell(z)$ that selects a given layer,

$$\mathcal{C}^\ell(z) = \Theta(z - z_\ell + \Delta^{\rm b}_\ell)\Theta(z_\ell - z + \Delta^f_\ell), \tag{49}$$

where Θ is the Heaviside function. Here, $\Delta^{f/b}_\ell$ is the distance that the ℓ-th layer extends towards the front (f) or back (b) from its z_ℓ position. $\Delta^f_\ell + \Delta^b_\ell$ is the thickness of layer ℓ (see Fig. 1).

Now, we show how this "cut function" $\mathcal{C}^\ell(z)$ is introduced in the calculation of $\chi_{\rm abc}$. The microscopic current density is given by

$$\mathbf{j}(\mathbf{r}, t) = \mathrm{Tr}(\hat{\mathbf{j}}(\mathbf{r})\hat{\rho}(t)), \tag{50}$$

where the operator for the electron's current is

$$\hat{\mathbf{j}}(\mathbf{r}) = \frac{e}{2}\left(\hat{\mathbf{v}}^\Sigma|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}^\Sigma\right), \tag{51}$$

where $\hat{\mathbf{v}}^\Sigma$ is the electron's velocity operator to be dealt with below. We define $\hat{\mu} \equiv |\mathbf{r}\rangle\langle\mathbf{r}|$ and use

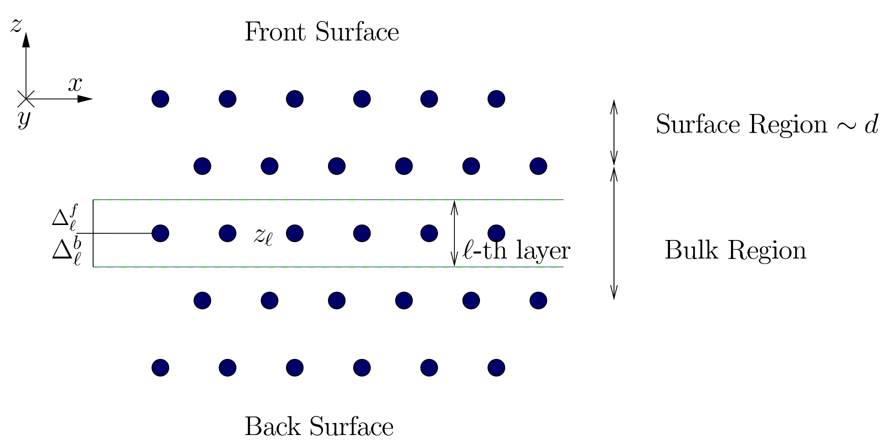

FIG. 1: A sketch of a slab where the circles represent atoms.

the cyclic invariance of the trace to write

$$
\begin{aligned}
\mathrm{Tr}(\hat{\mathbf{j}}(\mathbf{r})\hat{\rho}(t) &= \mathrm{Tr}(\hat{\rho}(t)\hat{\mathbf{j}}(\mathbf{r})) = \frac{e}{2}\left(\mathrm{Tr}(\hat{\rho}\hat{\mathbf{v}}^{\Sigma}\hat{\mu}) + \mathrm{Tr}(\hat{\rho}\hat{\mu}\hat{\mathbf{v}}^{\Sigma})\right) \\
&= \frac{e}{2}\sum_{n\mathbf{k}}\left(\langle n\mathbf{k}|\hat{\rho}\hat{\mathbf{v}}^{\Sigma}\hat{\mu}|n\mathbf{k}\rangle + \langle n\mathbf{k}|\hat{\rho}\hat{\mu}\hat{\mathbf{v}}^{\Sigma}|n\mathbf{k}\rangle\right) \\
&= \frac{e}{2}\sum_{nm\mathbf{k}}\langle n\mathbf{k}|\hat{\rho}|m\mathbf{k}\rangle\left(\langle m\mathbf{k}|\hat{\mathbf{v}}^{\Sigma}|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle + \langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}^{\Sigma}|n\mathbf{k}\rangle\right) \\
\mathbf{j}(\mathbf{r},t) &= \sum_{nm\mathbf{k}}\rho_{nm}(\mathbf{k};t)\mathbf{j}_{mn}(\mathbf{k};\mathbf{r}),
\end{aligned}
\tag{52}
$$

where

$$
\mathbf{j}_{mn}(\mathbf{k};\mathbf{r}) = \frac{e}{2}\left(\langle m\mathbf{k}|\hat{\mathbf{v}}^{\Sigma}|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle + \langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}^{\Sigma}|n\mathbf{k}\rangle\right), \tag{53}
$$

are the matrix elements of the microscopic current operator, and we have used the fact that the matrix elements between states $|n\mathbf{k}\rangle$ are diagonal in $\mathbf{k}$, i.e. proportional to $\delta(\mathbf{k}-\mathbf{k}')$.

Integrating the microscopic current $\mathbf{j}(\mathbf{r},t)$ over the entire slab gives the total macroscopic current density. If we want the contribution from only one region of the unit cell towards the total current, we can integrate $\mathbf{j}(\mathbf{r},t)$ over the desired region. The contribution to the current density from the ℓ-th layer of the slab is given by

$$
\frac{1}{\Omega}\int d^3r\,\mathcal{C}^{\ell}(z)\,\mathbf{j}(\mathbf{r},t) \equiv \mathbf{J}^{\ell}(t), \tag{54}
$$

where $\mathbf{J}^{\ell}(t)$ is the microscopic current in the ℓ-th layer. Therefore we define

$$
e\boldsymbol{\mathcal{V}}^{\Sigma,\ell}_{mn}(\mathbf{k}) \equiv \int d^3r\,\mathcal{C}^{\ell}(z)\,\mathbf{j}_{mn}(\mathbf{k};\mathbf{r}), \tag{55}
$$

to write

$$
J^{(N,\ell)}_{a}(t) = \frac{e}{\Omega}\sum_{mn\mathbf{k}}\mathcal{V}^{\Sigma,a,\ell}_{mn}(\mathbf{k})\rho^{(N)}_{nm}(\mathbf{k};t), \tag{56}
$$

as the induced macroscopic current of the ℓ-th layer, to order N in the external perturbation. The matrix elements of the density operator for $N = 1, 2$ are given by Eqs. (44) and (48) respectively. The Fourier component of macroscopic current of Eq. (56) is given by

$$
J^{(N,\ell)}_{\mathrm{a}}(\omega_3) = \frac{e}{\Omega}\sum_{mn\mathbf{k}}\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}(\mathbf{k})\rho^{(N)}_{nm}(\mathbf{k};\omega_3). \tag{57}
$$

We proceed to give an explicit expression of $\boldsymbol{\mathcal{V}}^{\Sigma,\ell}_{mn}(\mathbf{k})$. From Eqs. (55) and (53) we obtain

$$
\boldsymbol{\mathcal{V}}^{\Sigma,\ell}_{mn}(\mathbf{k}) = \frac{1}{2}\int \mathrm{d}^3r\,\mathcal{C}^{\ell}(z)\Big[\langle m\mathbf{k}|\mathbf{v}^{\Sigma}|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle + \langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\mathbf{v}^{\Sigma}|n\mathbf{k}\rangle\Big], \tag{58}
$$

and using the following property

$$\langle\mathbf{r}|\hat{\mathbf{v}}^{\Sigma}(\mathbf{r},\mathbf{r}')|n\mathbf{k}\rangle = \int d^3r''\langle\mathbf{r}|\hat{\mathbf{v}}^{\Sigma}(\mathbf{r},\mathbf{r}')|\mathbf{r}''\rangle\langle\mathbf{r}''|n\mathbf{k}\rangle = \hat{\mathbf{v}}^{\Sigma}(\mathbf{r},\mathbf{r}'')\int d^3r''\langle\mathbf{r}|\mathbf{r}''\rangle\langle\mathbf{r}''|n\mathbf{k}\rangle = \hat{\mathbf{v}}^{\Sigma}(\mathbf{r},\mathbf{r}')\psi_{n\mathbf{k}}(\mathbf{r}), \tag{59}$$

that stems from the fact that the operator $\mathbf{v}^{\Sigma}(\mathbf{r},\mathbf{r}')$ does not act on $\mathbf{r}''$, we can write

$$\begin{aligned}
\boldsymbol{\mathcal{V}}^{\Sigma,\ell}_{mn}(\mathbf{k}) &= \frac{1}{2}\int \mathrm{d}^3r\,\mathcal{C}^{\ell}(z)\Big[\psi_{n\mathbf{k}}(\mathbf{r})\hat{\mathbf{v}}^{\Sigma*}\psi^*_{m\mathbf{k}}(\mathbf{r}) + \psi^*_{m\mathbf{k}}(\mathbf{r})\hat{\mathbf{v}}^{\Sigma}\psi_{n\mathbf{k}}(\mathbf{r})\Big] \\
&= \int \mathrm{d}^3r\,\psi^*_{m\mathbf{k}}(\mathbf{r})\left[\frac{\mathcal{C}^{\ell}(z)\mathbf{v}^{\Sigma} + \mathbf{v}^{\Sigma}\mathcal{C}^{\ell}(z)}{2}\right]\psi_{n\mathbf{k}}(\mathbf{r}) \\
&= \int \mathrm{d}^3r\,\psi^*_{m\mathbf{k}}(\mathbf{r})\boldsymbol{\mathcal{V}}^{\Sigma,\ell}\psi_{n\mathbf{k}}(\mathbf{r}).
\end{aligned} \tag{60}$$

We used the hermitian property of $\mathbf{v}^{\Sigma}$ and defined

$$\boldsymbol{\mathcal{V}}^{\Sigma,\ell} = \frac{\mathcal{C}^{\ell}(z)\mathbf{v}^{\Sigma} + \mathbf{v}^{\Sigma}\mathcal{C}^{\ell}(z)}{2}, \tag{61}$$

where the superscript ℓ is inherited from $\mathcal{C}^{\ell}(z)$ and we supress the dependance on z from the increasingly crowded notation. We see that the replacement

$$\hat{\mathbf{v}}^{\Sigma} \to \hat{\boldsymbol{\mathcal{V}}}^{\Sigma,\ell} = \left[\frac{\mathcal{C}^{\ell}(z)\hat{\mathbf{v}}^{\Sigma} + \hat{\mathbf{v}}^{\Sigma}\mathcal{C}^{\ell}(z)}{2}\right], \tag{62}$$

is all that is needed to change the velocity operator of the electron $\hat{\mathbf{v}}^{\Sigma}$ to the new velocity operator $\boldsymbol{\mathcal{V}}^{\Sigma,\ell}$ that implicitly takes into account the contribution of the region of the slab given by $\mathcal{C}^{\ell}(z)$. From Eq. (11),

$$\begin{aligned}
\boldsymbol{\mathcal{V}}^{\Sigma,\ell} &= \boldsymbol{\mathcal{V}}^{\mathrm{LDA},\ell} + \boldsymbol{\mathcal{V}}^{S,\ell} \\
\boldsymbol{\mathcal{V}}^{\mathrm{LDA},\ell} &= \boldsymbol{\mathcal{V}}^{\ell} + \boldsymbol{\mathcal{V}}^{\mathrm{nl},\ell} = \frac{1}{m_e}\boldsymbol{\mathcal{P}}^{\ell} + \boldsymbol{\mathcal{V}}^{\mathrm{nl},\ell}.
\end{aligned} \tag{63}$$

The matrix elements of $\boldsymbol{\mathcal{V}}^{S,\ell}$ and $\boldsymbol{\mathcal{V}}^{\mathrm{LDA},\ell}$ are given in Appendix C.

To limit the response to one surface, the equivalent of Eq. (61) for $\boldsymbol{\mathcal{V}}^{\ell} = \boldsymbol{\mathcal{P}}^{\ell}/m_e$ was proposed in Ref. 22 and later used in Refs. 3 and 23 for SHG. The layer-by-layer analysis of Refs. 24 and 25 used Eq. (49), limiting the current response to a particular layer of the slab and used to obtain the anisotropic linear optical response of semiconductor surfaces. However, the first formal derivation of this scheme is presented in Ref. 26 for the linear response and now here for the non-linear optical response of semiconductors.

V. NON-LINEAR SURFACE SUSCEPTIBILITY

In this section we obtain the expressions for the second order non-linear surface susceptibility tensor for the perturbing fields. We start with the non-linear polarization $\mathbf{P}$ written as

$$\begin{aligned}P_{\mathrm{a}}(\omega_3) &= \chi_{\mathrm{abc}}(-\omega_3;\omega_1,\omega_2)E_{\mathrm{b}}(\omega_1)E_{\mathrm{c}}(\omega_2)\\ &\quad + \chi_{\mathrm{abcl}}(-\omega_3;\omega_1,\omega_2)E_{\mathrm{b}}(\omega_1)\nabla_{\mathrm{c}}E_{\mathrm{l}}(\omega_2) + \cdots ,\end{aligned} \tag{64}$$

where χ_{abc} and χ_{abcl} correspond to the dipolar and quadrupolar susceptibilities. The sum continues with higher multipolar terms. If we consider a semi-infinite system with a centrosymmetric bulk, the equation above can be separated into two contributions from symmetry considerations alone; one from the surface of the system and the other from the bulk of the system. We take

$$P_{\mathrm{a}}(\mathbf{r}) = \chi_{\mathrm{abc}}E_{\mathrm{b}}(\mathbf{r})E_{\mathrm{c}}(\mathbf{r}) + \chi_{\mathrm{abcl}}E_{\mathrm{b}}(\mathbf{r})\frac{\partial}{\partial \mathbf{r}_{\mathrm{c}}}E_{\mathrm{l}}(\mathbf{r}) + \cdots , \tag{65}$$

as the polarization with respect to the original coordinate system, and

$$\begin{aligned}P_{\mathrm{a}}(-\mathbf{r}) &= \chi_{\mathrm{abc}}E_{\mathrm{b}}(-\mathbf{r})E_{\mathrm{c}}(-\mathbf{r})\\ &\quad + \chi_{\mathrm{abcl}}E_{\mathrm{b}}(-\mathbf{r})\frac{\partial}{\partial(-\mathbf{r}_{\mathrm{c}})}E_{\mathrm{l}}(-\mathbf{r}) + \cdots ,\end{aligned} \tag{66}$$

as the polarization in the coordinate system where inversion is taken, i.e. $\mathbf{r} \to -\mathbf{r}$. Note that we have kept the same susceptibility tensors, and they must be invariant under $\mathbf{r} \to -\mathbf{r}$ since the system is centrosymmetric. Recalling that $\mathbf{P}(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$ are polar vectors[27], we have that Eq. (66) reduces to

$$\begin{aligned}-P_{\mathrm{a}}(\mathbf{r}) &= \chi_{\mathrm{abc}}(-E_{\mathrm{b}}(\mathbf{r}))(-E_{\mathrm{c}}(\mathbf{r})) - \chi_{\mathrm{abcl}}(-E_{\mathrm{b}}(\mathbf{r}))(-\frac{\partial}{\partial \mathbf{r}_{\mathrm{c}}})(-E_{\mathrm{l}}(\mathbf{r})) + \cdots ,\\ P_{\mathrm{a}}(\mathbf{r}) &= -\chi_{\mathrm{abc}}E_{\mathrm{b}}(\mathbf{r})E_{\mathrm{c}}(\mathbf{r}) + \chi_{\mathrm{abcl}}E_{\mathrm{b}}(\mathbf{r})\frac{\partial}{\partial \mathbf{r}_{\mathrm{c}}}E_{\mathrm{l}}(\mathbf{r}) + \cdots ,\end{aligned} \tag{67}$$

that when compared with Eq. (65) leads to the conclusion that

$$\chi_{\mathrm{abc}} = 0 \tag{68}$$

for a centrosymmetric bulk.

If we move to the surface of the semi-infinite system our assumption of centrosymmetry breaks down, and there is no restriction in χ_{abc}. We conclude that the leading term of the polarization in a surface region is given by

$$\begin{aligned}\int d\mathbf{R}\int dz P_{\mathrm{a}}(\mathbf{R},z) &\approx \mathcal{S}dP_{\mathrm{a}}\\ &= \mathcal{S}P^{s}_{\mathrm{a}}\\ &= \chi_{\mathrm{abc}}E_{\mathrm{b}}E_{\mathrm{c}},\end{aligned} \tag{69}$$

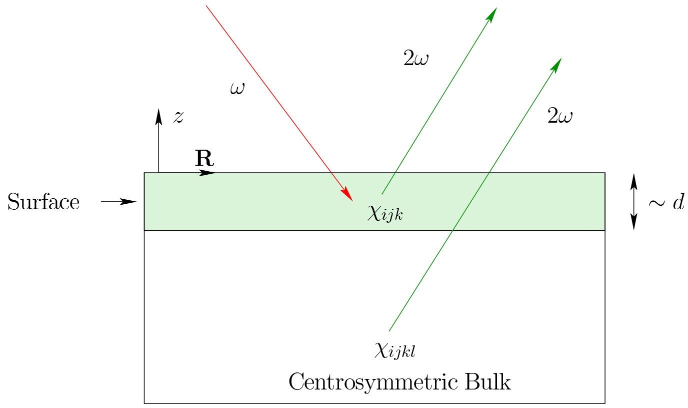

FIG. 2: (Color Online) Sketch of the semi-infinite system with a centrosymmetric bulk. The surface region is of width $\sim d$. The incoming photon of frequency ω is represented by a downward red arrow, whereas both the surface and bulk created second harmonic photons of frequency 2ω are represented by upward green arrows. The red color suggests an incoming infrared photon with a green second harmonic photon. The dipolar ($\chi_{\rm abc}$), and quadrupolar ($\chi_{\rm abcl}$) susceptibility tensors are shown in the regions where they are different from zero. The axis has z perpendicular to the surface and $\mathbf{R}$ parallel to it.

where $\mathbf{R}$ is a vector parallel to the surface which is perpendicular to z, $\mathcal{S}$ is the surface area of the unit cell that characterizes the surface of the system, and d is the surface region from which the dipolar signal of $\mathbf{P}$ is different from zero (see Fig. 2). $d\mathbf{P} \equiv \mathbf{P}^s$ is the surface SH polarization given by

$$P^s_{\rm a} = \frac{1}{\mathcal{S}}\chi_{\rm abc}E_{\rm b}E_{\rm c} = \chi^s_{\rm abc}E_{\rm b}E_{\rm c}, \tag{70}$$

with $\chi^s_{\rm abc} = \chi_{\rm abc}/\mathcal{S}$ the non-linear surface susceptibility. On the other hand,

$$P^b_{\rm a}(\mathbf{r}) = \chi_{\rm abcl}E_{\rm b}(\mathbf{r})\nabla_{\rm c}E_{\rm l}(\mathbf{r}), \tag{71}$$

gives the bulk polarization. We immediately recognize that the surface polarization is of dipolar order while the bulk polarization is of quadrupolar order. The surface ($\chi_{\rm abc}$) and bulk ($\chi_{\rm abcl}$) susceptibility tensor ranks are three and four, respectively. We will only concentrate on surface SHG in this article even though nulk generated SH is also a very important optical phenomenon. In centrosymmetric systems for which the quadrupolar bulk response is much smaller than the dipolar surface response, SH is readily used as a very useful and powerful optical surface probe.[1]

To calculate $\chi^s_{\rm abc}$, we start with the basic relation $\mathbf{J} = d\mathbf{P}/dt$ with $\mathbf{J}$ the current calculated in Sec. IV. From Eq. (57) we obtain

$$J^{(2,\ell)}_{\rm a}(\omega_3) = -i\omega_3 P_{\rm a}(\omega_3) = \frac{e}{\Omega}\sum_{mn\mathbf{k}} \mathcal{V}^{\Sigma,{\rm a},\ell}_{mn}(\mathbf{k})\rho^{(2)}_{nm}(\mathbf{k};\omega_3), \tag{72}$$

and using Eqs. (48) and (70) leads to

$$\chi^{s,\ell}_{\mathrm{abc}}(-\omega_3;\omega_1,\omega_2) = \frac{ie}{\Omega E^{\mathrm{b}}_1 E^{\mathrm{c}}_2 \mathcal{S}\omega_3} \sum_{mn\mathbf{k}} \mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}(\mathbf{k}) \rho^{(2)}_{nm}(\mathbf{k};\omega_3)$$
$$= \frac{e^2}{\mathcal{S}\Omega\hbar\omega_3} \sum_{mn\mathbf{k}} \frac{\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}(\mathbf{k})}{\omega^S_{nm\mathbf{k}} - \tilde{\omega}_3} \Bigg[-\left(B^{\mathrm{c}}_{nm}(\mathbf{k},\omega_\beta)\right)_{;k^{\mathrm{b}}}$$
$$+ i \sum_\ell \left(r^{\mathrm{b}}_{n\ell} B^{\mathrm{c}}_{\ell m}(\mathbf{k},\omega_\beta) - B^{\mathrm{c}}_{n\ell}(\mathbf{k},\omega_\beta) r^{\mathrm{b}}_{\ell m} \right) \Bigg], \tag{73}$$

which gives the surface susceptibility of ℓ-th layer, where $\boldsymbol{\mathcal{V}}^\Sigma$ is given in Eq. (63). Using Eq. (44) we split this equation into two contributions from the first and second terms on the right hand side,

$$\chi^{s,\ell}_{i,\mathrm{abc}}(-2\omega;\omega,\omega) = -\frac{e^3}{\Omega\hbar^2\omega_3} \sum_{mn\mathbf{k}} \frac{\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}}{\omega^S_{nm} - \omega_3} \left(\frac{f_{mn} r^{\mathrm{b}}_{nm}}{\omega^S_{nm} - \omega_\beta} \right)_{;k^{\mathrm{c}}}, \tag{74}$$

and

$$\chi^{s,\ell}_{e,\mathrm{abc}}(-2\omega;\omega,\omega) = \frac{ie^3}{\Omega\hbar^2\omega_3} \sum_{\ell mn\mathbf{k}} \frac{\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}}{\omega^S_{nm} - \omega_3} \left(\frac{r^{\mathrm{c}}_{n\ell} r^{\mathrm{b}}_{\ell m} f_{m\ell}}{\omega^S_{\ell m} - \omega_\beta} - \frac{r^{\mathrm{b}}_{n\ell} r^{\mathrm{c}}_{\ell m} f_{\ell n}}{\omega^S_{n\ell} - \omega_\beta} \right), \tag{75}$$

where $\boldsymbol{\chi}^{s,\ell}_i$ is related to intraband transitions and $\boldsymbol{\chi}^{s,\ell}_e$ to interband transitions. We warn the reader not to be confused by the already busy notation; lower case s refers to the $s$urface, whereas the capital case S referes to the Scissors correction. For the generalized derivative in Eq. (74) we use the chain rule

$$\left(\frac{f_{mn} r^{\mathrm{b}}_{nm}}{\omega^S_{nm} - \omega_2} \right)_{;k^{\mathrm{c}}} = \frac{f_{mn}}{\omega^S_{nm} - \omega} \left(r^{\mathrm{b}}_{nm} \right)_{;k^{\mathrm{c}}} - \frac{f_{mn} r^{\mathrm{b}}_{nm} \Delta^{\mathrm{c}}_{nm}}{(\omega^S_{nm} - \omega)^2}, \tag{76}$$

and

$$\left(\omega^S_{nm}\right)_{;k^{\mathrm{a}}} = \left(\omega^{\mathrm{LDA}}_{nm}\right)_{;k^{\mathrm{a}}} = v^{\mathrm{LDA,a}}_{nn} - v^{\mathrm{LDA,a}}_{mm} \equiv \Delta^{\mathrm{a}}_{nm}, \tag{77}$$

as shown in Appendix D.

In order to calculate the nonlinear susceptibility of any given layer ℓ we simply add the above terms $\boldsymbol{\chi}^{s,\ell} = \boldsymbol{\chi}^{s,\ell}_e + \boldsymbol{\chi}^{s,\ell}_i$ and then calculate the surface susceptibility as

$$\boldsymbol{\chi}^s \equiv \sum_{\ell_0}^{\ell_d} \boldsymbol{\chi}^\ell, \tag{78}$$

where ℓ_0 represents the first layer right at the surface, and ℓ_d the layer at a distance $\sim d$ from the surface (see Fig. 2). We can use Eq. (78) for either the front or the back surface. Likewise

$$\boldsymbol{\chi}^{\ell_f} \equiv \sum_{\ell_d}^{\ell_f} \boldsymbol{\chi}^\ell, \tag{79}$$

is a dipolar bulk susceptibility with the property

$$\boldsymbol{\chi}^{\ell_f} \stackrel{\ell_f \to \ell_b}{=} 0, \tag{80}$$

where ℓ_b is a bulk layer such that the bulk centrosymmetry is fully established and the dipolar non-linear susceptibility is identically zero in accordance to Eq. (68). We note that ℓ_d is not universal and ℓ_b should be found according to Eq. (80).

We can see from the prefactors of Eqs. (74) and (75) that they diverge as $\omega \to 0$. To remove this apparent divergence of $\boldsymbol{\chi}^s$, we perform a partial fraction expansion over ω. As shown in Appendix E, we use time-reversal invariance to remove these divergences and obtain the following expressions for $\boldsymbol{\chi}$,

$$\mathrm{Im}[\chi^{s,\ell}_{e,\mathrm{abc},\omega}] = -\frac{\pi|e|^3}{2\hbar^2} \sum_{vc\mathbf{k}} \sum_{l\neq(v,c)} \frac{1}{\omega^S_{cv}} \left[\frac{\mathrm{Im}[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{lc}\{r^{\mathrm{b}}_{cv} r^{\mathrm{c}}_{vl}\}]}{(2\omega^S_{cv} - \omega^S_{cl})} - \frac{\mathrm{Im}[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vl}\{r^{\mathrm{c}}_{lc} r^{\mathrm{b}}_{cv}\}]}{(2\omega^S_{cv} - \omega^S_{lv})} \right] \delta(\omega^S_{cv} - \omega), \tag{81}$$

$$\mathrm{Im}[\chi^{s,\ell}_{e,\mathrm{abc},2\omega}] = -\frac{\pi|e|^3}{2\hbar^2} \sum_{vc\mathbf{k}} \frac{4}{\omega^S_{cv}} \left[\sum_{v'\neq v} \frac{\mathrm{Im}[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc}\{r^{\mathrm{b}}_{cv'} r^{\mathrm{c}}_{v'v}\}]}{2\omega^S_{cv'} - \omega^S_{cv}} - \sum_{c'\neq c} \frac{\mathrm{Im}[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc}\{r^{\mathrm{c}}_{cc'} r^{\mathrm{b}}_{c'v}\}]}{2\omega^S_{c'v} - \omega^S_{cv}} \right] \delta(\omega^S_{cv} - 2\omega), \tag{82}$$

$$\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{abc},\omega}] = -\frac{\pi|e|^3}{2\hbar^2} \sum_{cv\mathbf{k}} \frac{1}{(\omega^S_{cv})^2} \left(\mathrm{Re}\left[r^{\mathrm{b}}_{cv} \left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc} \right)_{;k^{\mathrm{c}}} \right] + \frac{\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc} r^{\mathrm{b}}_{cv} \right] \Delta^{\mathrm{c}}_{cv}}{\omega^S_{cv}} \right) \delta(\omega^S_{cv} - \omega), \tag{83}$$

and

$$\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{abc},2\omega}] = -\frac{\pi|e|^3}{2\hbar^2} \sum_{vc\mathbf{k}} \frac{4}{(\omega^S_{cv})^2} \left(\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc} \left(r^{\mathrm{b}}_{cv} \right)_{;k^{\mathrm{c}}} \right] - \frac{2\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc} r^{\mathrm{b}}_{cv} \right] \Delta^{\mathrm{c}}_{cv}}{\omega^S_{cv}} \right) \delta(\omega^S_{cv} - 2\omega). \tag{84}$$

We have split the interband and intraband 1ω and 2ω contributions. The real part of each contribution can be obtained through a Kramers-Kronig transformation,[28] and then $\chi^{s,\ell}_{\mathrm{abc}} = \chi^{s,\ell}_{e,\mathrm{abc},\omega} + \chi^{s,\ell}_{e,\mathrm{abc},2\omega} + \chi^{s,\ell}_{i,\mathrm{abc},\omega} + \chi^{s,\ell}_{i,\mathrm{abc},2\omega}$. To fulfill the required intrinsic permutation symmetry,[29] the $\{\}$ notation symmetrizes the bc Cartesian indices, i.e. $\{u^{\mathrm{b}} s^{\mathrm{c}}\} = (u^{\mathrm{b}} s^{\mathrm{c}} + u^{\mathrm{c}} s^{\mathrm{b}})/2$, and we show that $\chi^{s,\ell}_{\mathrm{abc}} = \chi^{s,\ell}_{\mathrm{acb}}$. In Appendices F and C we demonstrate how to calculate the generalized derivatives of $\mathbf{r}_{nm;\mathbf{k}}$ and $\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm;\mathbf{k}}$. We find that

$$(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{a}}} = -i\mathcal{T}^{\mathrm{ab}}_{nm} + \frac{r^{\mathrm{a}}_{nm}\Delta^{\mathrm{b}}_{mn} + r^{\mathrm{b}}_{nm}\Delta^{\mathrm{a}}_{mn}}{\omega^{\mathrm{LDA}}_{nm}} + \frac{i}{\omega^{\mathrm{LDA}}_{nm}} \sum_{\ell} \left(\omega^{\mathrm{LDA}}_{\ell m} r^{\mathrm{a}}_{n\ell} r^{\mathrm{b}}_{\ell m} - \omega^{\mathrm{LDA}}_{n\ell} r^{\mathrm{b}}_{n\ell} r^{\mathrm{a}}_{\ell m} \right), \tag{85}$$

where

$$\mathcal{T}^{\mathrm{ab}}_{nm} = [r^{\mathrm{a}}, v^{\mathrm{LDA,b}}] = \frac{i\hbar}{m_e}\delta_{ab}\delta_{nm} + \mathcal{L}^{\mathrm{ab}}_{nm}, \tag{86}$$

and

$$\mathcal{L}^{\rm ab}_{nm} = \frac{1}{i\hbar}[r^{\rm a}, v^{\rm nl,b}]_{nm}, \tag{87}$$

is the contribution to the generalized derivative of $\mathbf{r}_{nm}$ coming from the nonlocal part of the pseudopotential. In Appendix G we calculate $\mathcal{L}^{\rm ab}_{nm}$. $\mathcal{L}^{\rm ab}_{nm}$, is a term with very small numerical value but with a computational time at least an order of magnitude larger than for all the other terms involved in the expressions for $\chi^{s,\ell}_{\rm abc}$.[30] Therefore, we neglect it throughout this article and take

$$\mathcal{T}^{\rm ab}_{nm} \approx \frac{i\hbar}{m_e}\delta_{ab}\delta_{nm}. \tag{88}$$

Finally, we also need the following term (Eq. (F10))

$$\begin{aligned}(v^{\rm LDA,a}_{nn})_{;k^{\rm b}} = \nabla_{k^{\rm a}} v^{\rm LDA,b}_{nn}(\mathbf{k}) &= -i\mathcal{T}^{\rm ab}_{nn} - \sum_{\ell\neq n}\omega^{\rm LDA}_{\ell n}\Big(r^{\rm a}_{n\ell}r^{\rm b}_{\ell n} + r^{\rm b}_{n\ell}r^{\rm a}_{\ell n}\Big)\\ &\approx \frac{\hbar}{m_e}\delta_{\rm ab} - \sum_{\ell\neq n}\omega^{\rm LDA}_{\ell n}\Big(r^{\rm a}_{n\ell}r^{\rm b}_{\ell n} + r^{\rm b}_{n\ell}r^{\rm a}_{\ell n}\Big),\end{aligned} \tag{89}$$

among other quantities for $\mathcal{V}^{\Sigma,\rm a,\ell}_{nm;\mathbf{k}}$, where we also use Eq. (88). Above is the standard effective-mas sum rule.[31] In Appendix I, we list all the quantities that should be coded in order to calculate the previous expressions for $\boldsymbol{\chi}$.

VI. CONCLUSIONS

We have presented a complete derivation of the required elements to calculate the surface SHG susceptibility tensor $\boldsymbol{\chi}^s(-2\omega;\omega,\omega)$ using a layer-by-layer approach. We have done so for semiconductors using the length gauge for the coupling of the external electric field to the electron.

Appendix A: $\mathbf{r}_e$ and $\mathbf{r}_i$

In this appendix, we derive the expressions for the matrix elements of the electron position operator $\mathbf{r}$. The r representation of the Bloch states is given by

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r}|n\mathbf{k}\rangle = \sqrt{\frac{\Omega}{8\pi^3}}e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r}), \tag{A1}$$

where $u_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R})$ is cell periodic, and

$$\int_\Omega d^3r\, u^*_{n\mathbf{k}}(\mathbf{r})u_{m\mathbf{k}'}(\mathbf{r}) = \delta_{nm}\delta_{\mathbf{k},\mathbf{k}'}, \tag{A2}$$

with Ω the volume of the unit cell.

The key ingredient in the calculation are the matrix elements of the position operator $\mathbf{r}$, so we start from the basic relation

$$\langle n\mathbf{k}|m\mathbf{k}'\rangle = \delta_{nm}\delta(\mathbf{k}-\mathbf{k}'), \tag{A3}$$

and take its derivative with respect to $\mathbf{k}$ as follows. On one hand,

$$\frac{\partial}{\partial \mathbf{k}}\langle n\mathbf{k}|m\mathbf{k}'\rangle = \delta_{nm}\frac{\partial}{\partial \mathbf{k}}\delta(\mathbf{k}-\mathbf{k}'), \tag{A4}$$

on the other,

$$\begin{aligned}\frac{\partial}{\partial \mathbf{k}}\langle n\mathbf{k}|m\mathbf{k}'\rangle &= \frac{\partial}{\partial \mathbf{k}}\int d\mathbf{r}\langle n\mathbf{k}|\mathbf{r}\rangle\langle \mathbf{r}|m\mathbf{k}'\rangle \\ &= \int d\mathbf{r}\left(\frac{\partial}{\partial \mathbf{k}}\psi^*_{n\mathbf{k}}(\mathbf{r})\right)\psi_{m\mathbf{k}'}(\mathbf{r}),\end{aligned} \tag{A5}$$

the derivative of the wavefunction is simply given by

$$\frac{\partial}{\partial \mathbf{k}}\psi^*_{n\mathbf{k}}(\mathbf{r}) = \sqrt{\frac{\Omega}{8\pi^3}}\left(\frac{\partial}{\partial \mathbf{k}}u^*_{n\mathbf{k}}(\mathbf{r})\right)e^{-i\mathbf{k}\cdot\mathbf{r}} - i\mathbf{r}\psi^*_{n\mathbf{k}}(\mathbf{r}). \tag{A6}$$

We take this back into Eq. (A5), to obtain

$$\begin{aligned}\frac{\partial}{\partial \mathbf{k}}\langle n\mathbf{k}|m\mathbf{k}'\rangle &= \sqrt{\frac{\Omega}{8\pi^3}}\int d\mathbf{r}\left(\frac{\partial}{\partial \mathbf{k}}u^*_{n\mathbf{k}}(\mathbf{r})\right)e^{-i\mathbf{k}\cdot\mathbf{r}}\psi_{m\mathbf{k}'}(\mathbf{r}) \\ &- i\int d\mathbf{r}\psi^*_{n\mathbf{k}}(\mathbf{r})\mathbf{r}\psi_{m\mathbf{k}'}(\mathbf{r}) \\ &= \frac{\Omega}{8\pi^3}\int d\mathbf{r}\, e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}\left(\frac{\partial}{\partial \mathbf{k}}u^*_{n\mathbf{k}}(\mathbf{r})\right)u_{m\mathbf{k}'}(\mathbf{r}) \\ &- i\langle n\mathbf{k}|\hat{\mathbf{r}}|m\mathbf{k}'\rangle.\end{aligned} \tag{A7}$$

Restricting $\mathbf{k}$ and $\mathbf{k}'$ to the first Brillouin zone, we use the following result valid for any periodic function $f(\mathbf{r}) = f(\mathbf{r}+\mathbf{R})$,

$$\int d^3r\, e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}}f(\mathbf{r}) = \frac{8\pi^3}{\Omega}\delta(\mathbf{q}-\mathbf{k})\int_\Omega d^3r\, f(\mathbf{r}), \tag{A8}$$

to finally write,[17]

$$\begin{aligned}\frac{\partial}{\partial \mathbf{k}}\langle n\mathbf{k}|m\mathbf{k}'\rangle &= \delta(\mathbf{k}-\mathbf{k}')\int_\Omega d\mathbf{r}\left(\frac{\partial}{\partial \mathbf{k}}u^*_{n\mathbf{k}}(\mathbf{r})\right)u_{m\mathbf{k}}(\mathbf{r}) \\ &- i\langle n\mathbf{k}|\hat{\mathbf{r}}|m\mathbf{k}'\rangle.\end{aligned} \tag{A9}$$

where Ω is the volume of the unit cell. From

$$\int_\Omega u_{m\mathbf{k}}u^*_{n\mathbf{k}}d\mathbf{r} = \delta_{nm}, \tag{A10}$$

we easily find that

$$\int_\Omega d\mathbf{r}\left(\frac{\partial}{\partial \mathbf{k}}u_{m\mathbf{k}}(\mathbf{r})\right)u^*_{n\mathbf{k}}(\mathbf{r}) = -\int_\Omega d\mathbf{r}\, u_{m\mathbf{k}}(\mathbf{r})\left(\frac{\partial}{\partial \mathbf{k}}u^*_{n\mathbf{k}}(\mathbf{r})\right). \tag{A11}$$

Therefore, we define

$$\boldsymbol{\xi}_{nm}(\mathbf{k}) \equiv i\int_\Omega d\mathbf{r}\, u^*_{n\mathbf{k}}(\mathbf{r})\nabla_{\mathbf{k}}u_{m\mathbf{k}}(\mathbf{r}), \tag{A12}$$

with $\partial/\partial\mathbf{k} = \nabla_{\mathbf{k}}$. Now, from Eqs. (A4), (A7), and (A12), we have that the matrix elements of the position operator of the electron are given by

$$\langle n\mathbf{k}|\hat{\mathbf{r}}|m\mathbf{k}'\rangle = \delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nm}(\mathbf{k}) + i\delta_{nm}\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}'), \tag{A13}$$

Then, from Eq. (A13), and writing $\hat{\mathbf{r}} = \hat{\mathbf{r}}_e + \hat{\mathbf{r}}_i$, with $\hat{\mathbf{r}}_e$ ($\hat{\mathbf{r}}_i$) the interband (intraband) part, we obtain that

$$\langle n\mathbf{k}|\hat{\mathbf{r}}_i|m\mathbf{k}'\rangle = \delta_{nm}\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nn}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right], \tag{A14}$$

$$\langle n\mathbf{k}|\hat{\mathbf{r}}_e|m\mathbf{k}'\rangle = (1-\delta_{nm})\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nm}(\mathbf{k}). \tag{A15}$$

To proceed, we relate Eq. (A15) to the matrix elements of the momentum operator as follows.

For the intraband part, we derive the following general result,

$$\begin{aligned}\langle n\mathbf{k}|[\hat{\mathbf{r}}_i,\hat{\mathcal{O}}]|m\mathbf{k}'\rangle &= \sum_{\ell,\mathbf{k}''}\Big(\langle n\mathbf{k}|\hat{\mathbf{r}}_i|\ell\mathbf{k}''\rangle\langle\ell\mathbf{k}''|\hat{\mathcal{O}}|m\mathbf{k}'\rangle \\ &\quad -\langle n\mathbf{k}|\hat{\mathcal{O}}|\ell\mathbf{k}''\rangle\langle\ell\mathbf{k}''|\hat{\mathbf{r}}_i|m\mathbf{k}'\rangle\Big) \\ &= \sum_\ell\left(\langle n\mathbf{k}|\hat{\mathbf{r}}_i|\ell\mathbf{k}'\rangle\mathcal{O}_{\ell m}(\mathbf{k}')\right. \\ &\quad \left.-\mathcal{O}_{n\ell}(\mathbf{k})|\ell\mathbf{k}\rangle\langle\ell\mathbf{k}|\hat{\mathbf{r}}_i|m\mathbf{k}'\rangle\right),\end{aligned} \tag{A16}$$

where we have taken $\langle n\mathbf{k}|\hat{\mathcal{O}}|\ell\mathbf{k}''\rangle = \delta(\mathbf{k}-\mathbf{k}'')\mathcal{O}_{n\ell}(\mathbf{k})$. We substitute Eq. (A14), to obtain

$$\begin{aligned}&\sum_\ell\Big(\delta_{n\ell}\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nn}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right]\mathcal{O}_{\ell m}(\mathbf{k}') \\ &\quad -\mathcal{O}_{n\ell}(\mathbf{k})\delta_{\ell m}\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{mm}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right]\Big) \\ &\quad = \Big(\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nn}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right]\mathcal{O}_{nm}(\mathbf{k}') \\ &\quad -\mathcal{O}_{nm}(\mathbf{k})\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{mm}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right]\Big) \\ &\quad = \delta(\mathbf{k}-\mathbf{k}')\mathcal{O}_{nm}(\mathbf{k})\left(\boldsymbol{\xi}_{nn}(\mathbf{k}) - \boldsymbol{\xi}_{mm}(\mathbf{k})\right) + i\mathcal{O}_{nm}(\mathbf{k}')\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}') \\ &\quad + i\delta(\mathbf{k}-\mathbf{k}')\nabla_{\mathbf{k}}\mathcal{O}_{nm}(\mathbf{k}) - i\mathcal{O}_{nm}(\mathbf{k}')\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}') \\ &\quad = i\delta(\mathbf{k}-\mathbf{k}')\Big(\nabla_{\mathbf{k}}\mathcal{O}_{nm}(\mathbf{k}) - i\mathcal{O}_{nm}(\mathbf{k})\left(\boldsymbol{\xi}_{nn}(\mathbf{k}) - \boldsymbol{\xi}_{mm}(\mathbf{k})\right)\Big) \\ &\quad \equiv i\delta(\mathbf{k}-\mathbf{k}')(\mathcal{O}_{nm})_{;\mathbf{k}}.\end{aligned} \tag{A17}$$

Then,

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}_i, \hat{\mathcal{O}}]|m\mathbf{k}'\rangle = i\delta(\mathbf{k}-\mathbf{k}')(\mathcal{O}_{nm})_{;\mathbf{k}}, \tag{A18}$$

with

$$(\mathcal{O}_{nm})_{;\mathbf{k}} = \nabla_{\mathbf{k}}\mathcal{O}_{nm}(\mathbf{k}) - i\mathcal{O}_{nm}(\mathbf{k})\left(\boldsymbol{\xi}_{nn}(\mathbf{k}) - \boldsymbol{\xi}_{mm}(\mathbf{k})\right), \tag{A19}$$

the generalized derivative of $\mathcal{O}_{nm}$ with respect to $\mathbf{k}$. Note that the highly singular term $\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')$ cancels in Eq. (A17), thus giving a well defined commutator of the intraband position operator with an arbitrary operator $\hat{\mathcal{O}}$. We use Eq. (21) and (A18) in the next section.

Appendix B: Matrix elements of $\mathbf{v}^{\mathrm{nl}}_{nm}(\mathbf{k})$

We obtain the matrix elements of $\mathbf{v}^{\mathrm{nl}}_{nm}(\mathbf{k})$ by using the following commutator in a real-space basis

$$\begin{aligned}
\langle\mathbf{R}'|[\hat{\mathbf{r}}, \hat{V}(\hat{\mathbf{r}},\hat{\mathbf{r}}')]|\mathbf{R}\rangle &= \langle\mathbf{R}'|(\hat{\mathbf{r}}\hat{V}(\hat{\mathbf{r}},\hat{\mathbf{r}}') - \hat{V}(\hat{\mathbf{r}},\hat{\mathbf{r}}')\hat{\mathbf{r}})|\mathbf{R}\rangle \\
&= \int d\mathbf{R}''\langle\mathbf{R}'|\hat{\mathbf{r}}|\mathbf{R}''\rangle\langle\mathbf{R}''|\hat{V}(\hat{\mathbf{r}},\hat{\mathbf{r}}')|\mathbf{R}\rangle - \int d\mathbf{R}''\langle\mathbf{R}'|\hat{V}(\hat{\mathbf{r}},\hat{\mathbf{r}}')|\mathbf{R}''\rangle\langle\mathbf{R}''|\hat{\mathbf{r}}|\mathbf{R}\rangle \\
&= \int d\mathbf{R}''\mathbf{R}''\delta(\mathbf{R}'-\mathbf{R}'')\langle\mathbf{R}''|\hat{V}(\hat{\mathbf{r}},\hat{\mathbf{r}}')|\mathbf{R}\rangle - \int d\mathbf{R}''\langle\mathbf{R}'|\hat{V}(\hat{\mathbf{r}},\hat{\mathbf{r}}')|\mathbf{R}''\rangle\mathbf{R}\delta(\mathbf{R}''-\mathbf{R}) \\
&= \mathbf{R}'\langle\mathbf{R}'|\hat{V}(\hat{\mathbf{r}},\hat{\mathbf{r}}')|\mathbf{R}\rangle - \langle\mathbf{R}'|\hat{V}(\hat{\mathbf{r}},\hat{\mathbf{r}}')|\mathbf{R}\rangle\mathbf{R} \\
&= \mathbf{R}'V(\mathbf{R},\mathbf{R}') - V(\mathbf{R},\mathbf{R}')\mathbf{R} = \mathbf{R}'V(\mathbf{R},\mathbf{R}') - \mathbf{R}V(\mathbf{R},\mathbf{R}') \\
\langle\mathbf{R}'|[\hat{V}(\hat{\mathbf{r}},\hat{\mathbf{r}}'), \hat{\mathbf{r}}]|\mathbf{R}\rangle &= \mathbf{R}V(\mathbf{R},\mathbf{R}') - \mathbf{R}'V(\mathbf{R},\mathbf{R}') \\
\langle\mathbf{R}|[\hat{V}(\hat{\mathbf{r}},\hat{\mathbf{r}}'), \hat{\mathbf{r}}]|\mathbf{R}'\rangle &= \mathbf{R}'V(\mathbf{R},\mathbf{R}') - \mathbf{R}V(\mathbf{R},\mathbf{R}'),
\end{aligned} \tag{B1}$$

where we used $\hat{\mathbf{r}}|\mathbf{R}\rangle = \mathbf{R}|\mathbf{R}\rangle$, and the matrix elements of the non-local operator $\langle\mathbf{R}'|\hat{V}(\hat{\mathbf{r}},\hat{\mathbf{r}}')|\mathbf{R}\rangle = V(\mathbf{R},\mathbf{R}')$ just a function, no longer an operator, and thus it commutes with $\mathbf{R}$ and $\mathbf{R}'$. Now we distinguish operators and non-operators by the carate symbol, $\hat{}$, on top. We want to calculate

$$\begin{aligned}
\langle n\mathbf{k}|[\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}},\hat{\mathbf{r}}'), \hat{r}^a]|m\mathbf{k}'\rangle &= \int d\mathbf{r}d\mathbf{r}'\langle n\mathbf{k}||\mathbf{r}\rangle\langle\mathbf{r}|[\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}},\hat{\mathbf{r}}'), \hat{r}^a]|\mathbf{r}'\rangle\langle\mathbf{r}'||m\mathbf{k}'\rangle \\
&= \int d\mathbf{r}d\mathbf{r}'\psi^*_{n\mathbf{k}}(\mathbf{r})(r'^a V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}') - r^a V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}'))\psi_{m\mathbf{k}'}(\mathbf{r}'),
\end{aligned} \tag{B2}$$

where due to the fact that the integrand is periodic in real space, $\mathbf{k} = \mathbf{k}'$ where $\mathbf{k}$ is restricted to the Brillouin Zone. In plane waves we have that

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}}\sum_{\mathbf{K}} C_{n\mathbf{k}}(\mathbf{K})e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}, \tag{B3}$$

where Ω is the volume of the unit cell. Then,

$$\langle n\mathbf{k}|[\hat{V}^{\rm nl}(\hat{\mathbf{r}},\hat{\mathbf{r}}'),\hat{r}^a]|m\mathbf{k}\rangle = \frac{1}{\Omega}\sum_{\mathbf{K},\mathbf{K}'} C^*_{n\mathbf{k}}(\mathbf{K})C_{m\mathbf{k}}(\mathbf{K}')\int d\mathbf{r}d\mathbf{r}' e^{-i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}(r'^a V^{\rm nl}(\mathbf{r},\mathbf{r}') - r^a V^{\rm nl}(\mathbf{r},\mathbf{r}'))e^{i(\mathbf{k}+\mathbf{K}')\cdot\mathbf{r}'}. \tag{B4}$$

Using the following identity

$$\begin{aligned}(\nabla_{\mathbf{K}}+\nabla'_{\mathbf{K}})\int e^{-i\mathbf{K}\cdot\mathbf{r}}V^{\rm nl}(\mathbf{r},\mathbf{r}')e^{i\mathbf{K}'\cdot\mathbf{r}'}\,d\mathbf{r}d\mathbf{r}' &= -i\int e^{-i\mathbf{K}\cdot\mathbf{r}}\left(\mathbf{r}V^{\rm nl}(\mathbf{r},\mathbf{r}') - V^{\rm nl}(\mathbf{r},\mathbf{r}')\mathbf{r}'\right)e^{i\mathbf{K}'\cdot\mathbf{r}'}\,d\mathbf{r}d\mathbf{r}' \\ &= i\int e^{-i\mathbf{K}\cdot\mathbf{r}}\left(\mathbf{r}'V^{\rm nl}(\mathbf{r},\mathbf{r}') - \mathbf{r}V^{\rm nl}(\mathbf{r},\mathbf{r}')\right)e^{i\mathbf{K}'\cdot\mathbf{r}'}\,d\mathbf{r}d\mathbf{r}',\end{aligned} \tag{B5}$$

then, we obtain

$$\begin{aligned}\langle n\mathbf{k}|[\hat{V}^{\rm nl}(\hat{\mathbf{r}},\hat{\mathbf{r}}'),\hat{r}^a]|m\mathbf{k}\rangle &= -\frac{i}{\Omega}\sum_{\mathbf{K},\mathbf{K}'} C^*_{n\mathbf{k}}(\mathbf{K})C_{m\mathbf{k}}(\mathbf{K}')(\nabla_{K^{\rm a}}+\nabla_{K'^{\rm a}})\int e^{-i\mathbf{K}\cdot\mathbf{r}}V^{\rm nl}(\mathbf{r},\mathbf{r}')e^{i\mathbf{K}'\cdot\mathbf{r}'}\,d\mathbf{r}d\mathbf{r}' \\ &= -\frac{i}{\Omega}\sum_{\mathbf{K},\mathbf{K}'} C^*_{n\mathbf{k}}(\mathbf{K})C_{m\mathbf{k}}(\mathbf{K}')(\nabla_{K^{\rm a}}+\nabla_{K'^{\rm a}})\langle\mathbf{K}|V^{\rm nl}|\mathbf{K}'\rangle,\end{aligned} \tag{B6}$$

where

$$\langle\mathbf{K}|V^{\rm nl}|\mathbf{K}'\rangle = \int e^{-i\mathbf{K}\cdot\mathbf{r}}V^{\rm nl}(\mathbf{r},\mathbf{r}')e^{i\mathbf{K}'\cdot\mathbf{r}'}\,d\mathbf{r}d\mathbf{r}'. \tag{B7}$$

For fully separable pseudopotentials in the Kleinman-Bylander form,[19–21] above matrix elements can be readily calculated.[18] Therefore,

$$\frac{i}{\hbar}\langle n\mathbf{k}|[\hat{V}^{\rm nl}(\hat{\mathbf{r}},\hat{\mathbf{r}}'),\hat{r}^{\rm a}]|m\mathbf{k}'\rangle = \delta(\mathbf{k}-\mathbf{k}')\mathbf{v}^{\rm nl}_{nm}(\mathbf{k}), \tag{B8}$$

where $\mathbf{v}^{\rm nl}_{nm}(\mathbf{k})$ are known quantities.

Appendix C: Generalized derivative $\left(\mathcal{V}^{\Sigma,{\rm a},\ell}_{nm}\right)_{;k^{\rm b}}$

From Eq. (63)

$$\left(\mathcal{V}^{\Sigma,{\rm a},\ell}_{nm}\right)_{;k^{\rm b}} = \left(\mathcal{V}^{{\rm LDA},{\rm a},\ell}_{nm}\right)_{;k^{\rm b}} + \left(\mathcal{V}^{S,{\rm a},\ell}_{nm}\right)_{;k^{\rm b}}. \tag{C1}$$

For the LDA term we have

$$
\begin{aligned}
\mathcal{V}_{nm}^{\mathrm{LDA,a},\ell} &= \frac{1}{2}\left(v^{\mathrm{LDA,a}}\mathcal{C}^{\ell} + \mathcal{C}^{\ell}v^{\mathrm{LDA,a}}\right)_{nm} \\
&= \frac{1}{2}\sum_{q}\left(v_{nq}^{\mathrm{LDA,a}}\mathcal{C}_{qm}^{\ell} + \mathcal{C}_{nq}^{\ell}v_{qm}^{\mathrm{LDA,a}}\right) \\
\left(\mathcal{V}_{nm}^{\mathrm{LDA,a}}\right)_{;k^{\mathrm{b}}} &= \frac{1}{2}\sum_{q}\left(v_{nq}^{\mathrm{LDA,a}}\mathcal{C}_{qm}^{\ell} + \mathcal{C}_{nq}^{\ell}p_{qm}^{\mathrm{LDA,a}}\right)_{;k^{\mathrm{b}}} \\
&= \frac{1}{2}\sum_{q}\left((v_{nq}^{\mathrm{LDA,a}})_{;k^{\mathrm{b}}}\mathcal{C}_{qm}^{\ell} + v_{nq}^{\mathrm{LDA,a}}(\mathcal{C}_{qm}^{\ell})_{;k^{\mathrm{b}}} + (\mathcal{C}_{nq}^{\ell})_{;k^{\mathrm{b}}}v_{qm}^{\mathrm{LDA,a}} + \mathcal{C}_{nq}^{\ell}(v_{qm}^{\mathrm{LDA,a}})_{;k^{\mathrm{b}}}\right), \quad \text{(C2)}
\end{aligned}
$$

where we omitted $\mathbf{k}$ in all quantities. From Eq. (B8) we know that $\mathbf{v}_{nm}^{\mathrm{nl}}(\mathbf{k})$ can be readily calculated, and from Appendix H, both v_{nm}^{a} and $\mathcal{C}_{nm}^{\ell}$ are also known quantities, and thus the $\mathbf{v}_{nm}^{\mathrm{LDA}}(\mathbf{k})$ are known, which in turns means that $\mathcal{V}_{nm}^{\mathrm{LDA,a},\ell}$ are also known. For the generalized derivative $(\mathbf{v}_{nm}^{\mathrm{LDA}}(\mathbf{k}))_{;\mathbf{k}}$ we use Eq. (21) to write

$$
\begin{aligned}
(v_{nm}^{\mathrm{LDA,a}})_{;k^{\mathrm{b}}} &= im_e(\omega_{nm}^{\mathrm{LDA}}r_{nm}^{\mathrm{a}})_{;k^{\mathrm{b}}} \\
&= im_e(\omega_{nm}^{\mathrm{LDA}})_{;k^{\mathrm{b}}}r_{nm}^{\mathrm{a}} + im_e\omega_{nm}^{\mathrm{LDA}}(r_{nm}^{\mathrm{a}})_{;k^{\mathrm{b}}} \\
&= im_e\Delta_{nm}^{b}r_{nm}^{\mathrm{a}} + im_e\omega_{nm}^{\mathrm{LDA}}(r_{nm}^{\mathrm{a}})_{;k^{\mathrm{b}}} \quad \text{for} \quad n \neq m, \qquad \text{(C3)}
\end{aligned}
$$

where we used Eq (77) and $(r_{nm}^{\mathrm{a}})_{;k^{\mathrm{b}}}$ is given in Eq. (F12).

Likewise, For the S term we have

$$
\begin{aligned}
\mathcal{V}_{nm}^{S,\mathrm{a},\ell} &= \frac{1}{2}\left(v^{S,\mathrm{a}}\mathcal{C}^{\ell} + \mathcal{C}^{\ell}v^{S,\mathrm{a}}\right)_{nm} \\
&= \frac{1}{2}\sum_{q}\left(v_{nq}^{S,\mathrm{a}}\mathcal{C}_{qm}^{\ell} + \mathcal{C}_{nq}^{\ell}v_{qm}^{S,\mathrm{a}}\right) \\
\left(\mathcal{V}_{nm}^{S,\mathrm{a}}\right)_{;k^{\mathrm{b}}} &= \frac{1}{2}\sum_{q}\left(v_{nq}^{S,\mathrm{a}}\mathcal{C}_{qm}^{\ell} + \mathcal{C}_{nq}^{\ell}p_{qm}^{S,\mathrm{a}}\right)_{;k^{\mathrm{b}}} \\
&= \frac{1}{2}\sum_{q}\left((v_{nq}^{S,\mathrm{a}})_{;k^{\mathrm{b}}}\mathcal{C}_{qm}^{\ell} + v_{nq}^{S,\mathrm{a}}(\mathcal{C}_{qm}^{\ell})_{;k^{\mathrm{b}}} + (\mathcal{C}_{nq}^{\ell})_{;k^{\mathrm{b}}}v_{qm}^{S,\mathrm{a}} + \mathcal{C}_{nq}^{\ell}(v_{qm}^{S,\mathrm{a}})_{;k^{\mathrm{b}}}\right), \qquad \text{(C4)}
\end{aligned}
$$

where $v_{nm}^{S,\mathrm{a}}(\mathbf{k})$ are given in Eq. (18) and $(v_{nm}^{S,\mathrm{a}})_{;k^{\mathrm{b}}}$ is given in Eq. A(6) of Ref. 32,

$$
(v_{nm}^{S,\mathrm{a}})_{;k^{\mathrm{b}}} = i\Delta f_{mn}(r_{nm}^{\mathrm{a}})_{;k^{\mathrm{b}}}. \qquad \text{(C5)}
$$

To evaluate $(\mathcal{C}_{nm}^{\ell})_{;k^{\mathrm{a}}}$, we use the fact that as $\mathcal{C}^{\ell}(z)$ is only a function of the z coordinate, its commutator with $\mathbf{r}$ is zero, then,

$$
\langle n\mathbf{k}|\left[r^{\mathrm{a}},\mathcal{C}^{\ell}(z)\right]|m\mathbf{k}'\rangle = \langle n\mathbf{k}|\left[r_e^{\mathrm{a}},\mathcal{C}^{\ell}(z)\right]|m\mathbf{k}'\rangle + \langle n\mathbf{k}|\left[r_i^{\mathrm{a}},\mathcal{C}^{\ell}(z)\right]|m\mathbf{k}'\rangle = 0. \qquad \text{(C6)}
$$

The interband part reduces to,

$$\begin{aligned}
\left[r_e^{\mathrm{a}}, \mathcal{C}^\ell(z)\right]_{nm} &= \sum_{q\mathbf{k}''} \Big(\langle n\mathbf{k}|r_e^{\mathrm{a}}|q\mathbf{k}''\rangle\langle q\mathbf{k}''|\mathcal{C}^\ell(z)|m\mathbf{k}'\rangle - \langle n\mathbf{k}|\mathcal{C}^\ell(z)|q\mathbf{k}''\rangle\langle q\mathbf{k}''|r_e^{\mathrm{a}}|m\mathbf{k}'\rangle \Big) \\
&= \sum_{q\mathbf{k}''} \delta(\mathbf{k}-\mathbf{k}'')\delta(\mathbf{k}'-\mathbf{k}'') \Big((1-\delta_{qn})\xi^{\mathrm{a}}_{nq}\mathcal{C}^\ell_{qm} - (1-\delta_{qm})\mathcal{C}^\ell_{nq}\xi^{\mathrm{a}}_{qm} \Big) \\
&= \delta(\mathbf{k}-\mathbf{k}') \left(\sum_q \Big(\xi^{\mathrm{a}}_{nq}\mathcal{C}^\ell_{qm} - \mathcal{C}^\ell_{nq}\xi^{\mathrm{a}}_{qm} \Big) + \mathcal{C}^\ell_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn}) \right),
\end{aligned} \tag{C7}$$

where we used Eq. (A15), and the $\mathbf{k}$ and z dependence is implicitly understood. From Eq. (A18) the intraband part is,

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}_i, \mathcal{C}^\ell(z)]|m\mathbf{k}'\rangle = i\delta(\mathbf{k}-\mathbf{k}')(\mathcal{C}^\ell_{nm})_{;\mathbf{k}}, \tag{C8}$$

then from Eq. (C6)

$$\begin{aligned}
&\left((\mathcal{C}^\ell_{nm})_{;\mathbf{k}} - i\sum_q \Big(\xi^{\mathrm{a}}_{nq}\mathcal{C}^\ell_{qm} - \mathcal{C}^\ell_{nq}\xi^{\mathrm{a}}_{qm} \Big) - i\mathcal{C}^\ell_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn}) \right) i\delta(\mathbf{k}-\mathbf{k}') = 0 \\
\frac{1}{i}(\mathcal{C}^\ell_{nm})_{;\mathbf{k}} &= \sum_q \Big(\xi^{\mathrm{a}}_{nq}\mathcal{C}^\ell_{qm} - \mathcal{C}^\ell_{nq}\xi^{\mathrm{a}}_{qm} \Big) + \mathcal{C}^\ell_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn}) \\
&= \sum_{q\neq nm} \Big(\xi^{\mathrm{a}}_{nq}\mathcal{C}^\ell_{qm} - \mathcal{C}^\ell_{nq}\xi^{\mathrm{a}}_{qm} \Big) + \Big(\xi^{\mathrm{a}}_{nn}\mathcal{C}^\ell_{nm} - \mathcal{C}^\ell_{nn}\xi^{\mathrm{a}}_{nm} \Big)_{q=n} + \Big(\xi^{\mathrm{a}}_{nm}\mathcal{C}^\ell_{mm} - \mathcal{C}^\ell_{nm}\xi^{\mathrm{a}}_{mm} \Big)_{q=m} \\
&+ \mathcal{C}^\ell_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn}) \\
(\mathcal{C}^\ell_{nm})_{;\mathbf{k}} &= i\sum_{q\neq nm} \Big(\xi^{\mathrm{a}}_{nq}\mathcal{C}^\ell_{qm} - \mathcal{C}^\ell_{nq}\xi^{\mathrm{a}}_{qm} \Big) + i\xi^{\mathrm{a}}_{nm}(\mathcal{C}^\ell_{mm} - \mathcal{C}^\ell_{nn}) \\
&= i\sum_{q\neq nm} \Big(r^{\mathrm{a}}_{nq}\mathcal{C}^\ell_{qm} - \mathcal{C}^\ell_{nq}r^{\mathrm{a}}_{qm} \Big) + ir^{\mathrm{a}}_{nm}(\mathcal{C}^\ell_{mm} - \mathcal{C}^\ell_{nn}),
\end{aligned} \tag{C9}$$

since in every ξ^{a}_{nm}, $n \neq m$, thus we replace it by r^{a}_{nm}. The matrix elements $\mathcal{C}^\ell_{nm}(\mathbf{k})$ are calculated in Appendix H.

For the general case of

$$\langle n\mathbf{k}| \left[\hat{r}^{\mathrm{a}}, \hat{\mathcal{G}}(\mathbf{r},\mathbf{p})\right] |m\mathbf{k}'\rangle = \mathcal{U}_{nm}(\mathbf{k}), \tag{C10}$$

above result would lead to a more general expression,

$$(\mathcal{G}_{nm}(\mathbf{k}))_{;k^{\mathrm{a}}} = \mathcal{U}_{nm}(\mathbf{k}) + i\sum_{q\neq(nm)} \big(r^{\mathrm{a}}_{nq}(\mathbf{k})\mathcal{G}_{qm}(\mathbf{k}) - \mathcal{G}_{nq}(\mathbf{k})r^{\mathrm{a}}_{qm}(\mathbf{k}) \big) + ir^{\mathrm{a}}_{nm}(\mathbf{k})(\mathcal{G}_{mm}(\mathbf{k}) - \mathcal{G}_{nn}(\mathbf{k})), \tag{C11}$$

notice that the last term is zero for $n = m$.

Appendix D: Generalized derivative $(\omega_n(\mathbf{k}))_{;\mathbf{k}}$

We obtain the generalized derivative $(\omega_n(\mathbf{k}))_{;\mathbf{k}}$. We start from

$$\langle n\mathbf{k}|\hat{H}_0^S|m\mathbf{k}'\rangle = \delta_{nm}\delta(\mathbf{k}-\mathbf{k}')\hbar\omega_m^S(\mathbf{k}), \tag{D1}$$

then Eq. (A19) gives for $n = m$

$$\begin{aligned}(H_{0,nn}^S)_{;\mathbf{k}} &= \nabla_{\mathbf{k}} H_{0,nn}^S(\mathbf{k}) - iH_{0,nn}^S(\mathbf{k})\left(\boldsymbol{\xi}_{nn}(\mathbf{k}) - \boldsymbol{\xi}_{nn}(\mathbf{k})\right)\\ &= \hbar\nabla_{\mathbf{k}}\omega_m^S(\mathbf{k}),\end{aligned} \tag{D2}$$

where from Eq. (A18),

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}_i, \hat{H}_0]|m\mathbf{k}\rangle = i\delta_{nm}\hbar(\omega_m^S(\mathbf{k}))_{;\mathbf{k}} = i\delta_{nm}\hbar\nabla_{\mathbf{k}}\omega_m^S(\mathbf{k}), \tag{D3}$$

then

$$(\omega_n^S(\mathbf{k}))_{;\mathbf{k}} = \nabla_{\mathbf{k}}\omega_n^S(\mathbf{k}). \tag{D4}$$

From Eq. (11)

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}, \hat{H}_0]|m\mathbf{k}\rangle = i\hbar\mathbf{v}_{nm}^{\Sigma}, \tag{D5}$$

therefore, substituting above into

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}, \hat{H}_0]|m\mathbf{k}\rangle = \langle n\mathbf{k}|[\hat{\mathbf{r}}_i, \hat{H}_0]|m\mathbf{k}\rangle + \langle n\mathbf{k}|[\hat{\mathbf{r}}_e, \hat{H}_0]|m\mathbf{k}\rangle, \tag{D6}$$

we get

$$i\hbar\mathbf{v}_{nm}^{\Sigma} = i\delta_{nm}\hbar\nabla_{\mathbf{k}}\omega_m^S(\mathbf{k}) + \omega_{mn}^S\mathbf{r}_{e,nm}, \tag{D7}$$

from where

$$\begin{aligned}\nabla_{\mathbf{k}}\omega_n^S(\mathbf{k}) &= \mathbf{v}_{nn}^{\Sigma}\\ \nabla_{\mathbf{k}}(\omega_n^{\mathrm{LDA}}(\mathbf{k}) + \frac{\Delta}{\hbar}(1-f_n)) &= \nabla_{\mathbf{k}}\omega_n^{\mathrm{LDA}}(\mathbf{k})\\ \nabla_{\mathbf{k}}\omega_n^{\mathrm{LDA}}(\mathbf{k}) &= \mathbf{v}_{nn}^{\Sigma},\end{aligned} \tag{D8}$$

where we used Eq. (7), but from Eq. (18), $v_{nn}^S = 0$, and then $\mathbf{v}_{nn}^{\Sigma} = v_{nn}^{\mathrm{LDA}}$. Thus, from Eq. (D4)

$$(\omega_n^S(\mathbf{k}))_{;k^{\mathrm{a}}} = (\omega_n^{\mathrm{LDA}}(\mathbf{k}))_{;k^{\mathrm{a}}} = v_{nn}^{\mathrm{LDA,a}}(\mathbf{k}), \tag{D9}$$

the same for the LDA and scissored Hamiltonians; $\mathbf{v}_{nn}^{\mathrm{LDA}}(\mathbf{k})$ are the LDA velocities of the electron in state $|n\mathbf{k}\rangle$.

Appendix E: Deriving Expressions for $\chi^s_{\rm abc}$ in terms of $\mathcal{V}^{\Sigma,\mathbf{a},\ell}_{mn}$

As can be seen from the prefactor of Eqs. (74) and (75), they diverge as $\omega \to 0$. To remove this apparent divergence of $\boldsymbol{\chi}^s$, we perform a partial fraction expansion in ω.

1. Intraband Contributions

For the intraband term of Eq. (74) we obtain

$$
\begin{aligned}
I = C &\left[-\frac{1}{2(\omega^S_{nm})^2}\frac{1}{\omega^S_{nm}-\omega} + \frac{2}{(\omega^S_{nm})^2}\frac{1}{\omega^S_{nm}-2\omega} + \frac{1}{2(\omega^S_{nm})^2}\frac{1}{\omega}\right] \\
- D &\left[-\frac{3}{2(\omega^S_{nm})^3}\frac{1}{\omega^S_{nm}-\omega} + \frac{4}{(\omega^S_{nm})^3}\frac{1}{\omega^S_{nm}-2\omega} + \frac{1}{2(\omega^S_{nm})^3}\frac{1}{\omega} - \frac{1}{2(\omega^S_{nm})^2}\frac{1}{(\omega^S_{nm}-\omega)^2}\right],
\end{aligned}
\tag{E1}
$$

where $C = f_{mn}\mathcal{V}^{\Sigma,\rm a}_{mn}(r^{\rm LDA,b}_{nm})_{;k^{\rm c}}$, and $D = f_{mn}\mathcal{V}^{\Sigma,\rm a}_{mn} r^{\rm b}_{nm}\Delta^{\rm c}_{nm}$.

Time-reversal symmetry leads to the following relationships:

$$
\begin{aligned}
\mathbf{r}_{mn}(\mathbf{k})|_{-\mathbf{k}} &= \mathbf{r}_{nm}(\mathbf{k})|_{\mathbf{k}}, \\
(\mathbf{r}_{mn})_{;\mathbf{k}}(\mathbf{k})|_{-\mathbf{k}} &= (-\mathbf{r}_{nm})_{;\mathbf{k}}(\mathbf{k})|_{\mathbf{k}}, \\
\mathcal{V}^{\Sigma,\rm a,\ell}_{mn}(\mathbf{k})|_{-\mathbf{k}} &= -\mathcal{V}^{\Sigma,\rm a,\ell}_{nm}(\mathbf{k})|_{\mathbf{k}}, \\
(\mathcal{V}^{\Sigma,\rm a,\ell}_{mn})_{;\mathbf{k}}(\mathbf{k})|_{-\mathbf{k}} &= (\mathcal{V}^{\Sigma,\rm a,\ell}_{nm})_{;\mathbf{k}}(\mathbf{k})|_{\mathbf{k}}, \\
\omega^S_{mn}(\mathbf{k})|_{-\mathbf{k}} &= \omega^S_{mn}(\mathbf{k})|_{\mathbf{k}}, \\
\Delta^a_{nm}(\mathbf{k})|_{-\mathbf{k}} &= -\Delta^a_{nm}(\mathbf{k})|_{\mathbf{k}}.
\end{aligned}
\tag{E2}
$$

For a clean cold semiconductor, $f_n = 1$ for an occupied or valence ($n = v$) band, and $f_n = 0$ for an empty or conduction ($n = c$) band independent of $\mathbf{k}$, and $f_{nm} = -f_{mn}$. Using above relationships, we can show that the $1/\omega$ terms cancel each other out. Therefore, all the remaining non-zero terms in expressions (E1) are simple ω and 2ω resonant denominators well behaved at zero frequency.

To apply time-reversal invariance, we notice that the energy denominators are invariant under $\mathbf{k} \to -\mathbf{k}$, and then we only look at the numerators, then

$$
\begin{aligned}
C \to f_{mn}\mathcal{V}^{\Sigma,\rm a,\ell}_{mn}\left(r^{\rm LDA,b}_{nm}\right)_{;k^{\rm c}}|_{\mathbf{k}} &+ f_{mn}\mathcal{V}^{\Sigma,\rm a,\ell}_{mn}\left(r^{\rm LDA,b}_{nm}\right)_{;k^{\rm c}}|_{-\mathbf{k}} \\
&= f_{mn}\left[\mathcal{V}^{\Sigma,\rm a,\ell}_{mn}\left(r^{\rm LDA,b}_{nm}\right)_{;k^{\rm c}}|_{\mathbf{k}} + \left(-\mathcal{V}^{\Sigma,\rm a,\ell}_{nm}\right)\left(-r^{\rm LDA,b}_{mn}\right)_{;k^{\rm c}}|_{\mathbf{k}}\right] \\
&= f_{mn}\left[\mathcal{V}^{\Sigma,\rm a,\ell}_{mn}\left(r^{\rm LDA,b}_{nm}\right)_{;k^{\rm c}} + \mathcal{V}^{\Sigma,\rm a,\ell}_{nm}\left(r^{\rm LDA,b}_{mn}\right)_{;k^{\rm c}}\right] \\
&= f_{mn}\left[\mathcal{V}^{\Sigma,\rm a,\ell}_{mn}\left(r^{\rm LDA,b}_{nm}\right)_{;k^{\rm c}} + \left(\mathcal{V}^{\Sigma,\rm a,\ell}_{mn}\left(r^{\rm LDA,b}_{nm}\right)_{;k^{\rm c}}\right)^*\right]
\end{aligned}
$$

$$= 2 f_{mn} \, \mathrm{Re} \left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} \left(r^{\mathrm{LDA,b}}_{nm} \right)_{;k^{\mathrm{c}}} \right], \tag{E3}$$

and likewise,

$$\begin{aligned} D \to f_{mn} \mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm} \Delta^{\mathrm{c}}_{nm}|_{\mathbf{k}} &+ f_{mn} \mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm} \Delta^{\mathrm{c}}_{nm}|_{-\mathbf{k}} \\ &= f_{mn} \left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm} \Delta^{\mathrm{c}}_{nm}|_{\mathbf{k}} + \left(-\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm} \right) r^{\mathrm{LDA,b}}_{mn} \left(-\Delta^{\mathrm{c}}_{nm} \right) |_{\mathbf{k}} \right] \\ &= f_{mn} \left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm} + \mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm} r^{\mathrm{LDA,b}}_{mn} \right] \Delta^{\mathrm{c}}_{nm} \\ &= f_{mn} \left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm} + \left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm} \right)^* \right] \Delta^{\mathrm{c}}_{nm} \\ &= 2 f_{mn} \, \mathrm{Re} \left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm} \right] \Delta^{\mathrm{c}}_{nm}. \end{aligned} \tag{E4}$$

The last term in the second line of Eq. (E1) is dealt with as follows.

$$\begin{aligned} \frac{D}{2(\omega^S_{nm})^2} \frac{1}{(\omega^S_{nm} - \omega)^2} &= \frac{f_{mn}}{2} \frac{\mathcal{V}^{\Sigma,\mathrm{a}}_{mn} r^{\mathrm{b}}_{nm}}{(\omega^S_{nm})^2} \frac{\Delta^{\mathrm{c}}_{nm}}{(\omega^S_{nm} - \omega)^2} = -\frac{f_{mn}}{2} \frac{\mathcal{V}^{\Sigma,\mathrm{a}}_{mn} r^{\mathrm{b}}_{nm}}{(\omega^S_{nm})^2} \left(\frac{1}{\omega^S_{nm} - \omega} \right)_{;k^{\mathrm{c}}} \\ &= \frac{f_{mn}}{2} \left(\frac{\mathcal{V}^{\Sigma,\mathrm{a}}_{mn} r^{\mathrm{b}}_{nm}}{(\omega^S_{nm})^2} \right)_{;k^{\mathrm{c}}} \frac{1}{\omega^S_{nm} - \omega}, \end{aligned} \tag{E5}$$

where we used Eqs. (77) and for the last line, we performed an integration by parts over the Brillouin zone, where the contribution from the edges vanishes.[31] Now, we apply the chain rule, to get

$$\left(\frac{\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}}{(\omega^S_{nm})^2} \right)_{;k^{\mathrm{c}}} = \frac{r^{\mathrm{LDA,b}}_{nm}}{(\omega^S_{nm})^2} \left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} \right)_{;k^{\mathrm{c}}} + \frac{\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}}{(\omega^S_{nm})^2} \left(r^{\mathrm{LDA,b}}_{nm} \right)_{;k^{\mathrm{c}}} - \frac{2 \mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}}{(\omega^S_{nm})^3} \left(\omega^S_{nm} \right)_{;k^{\mathrm{c}}}, \tag{E6}$$

and work the time-reversal on each term. The first term is reduced to

$$\begin{aligned} \frac{r^{\mathrm{LDA,b}}_{nm}}{(\omega^S_{nm})^2} \left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} \right)_{;k^{\mathrm{c}}} |_{\mathbf{k}} + \frac{r^{\mathrm{LDA,b}}_{nm}}{(\omega^S_{nm})^2} \left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} \right)_{;k^{\mathrm{c}}} |_{-\mathbf{k}} &= \frac{r^{\mathrm{LDA,b}}_{nm}}{(\omega^S_{nm})^2} \left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} \right)_{;k^{\mathrm{c}}} |_{\mathbf{k}} + \frac{r^{\mathrm{LDA,b}}_{mn}}{(\omega^S_{nm})^2} \left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm} \right)_{;k^{\mathrm{c}}} |_{\mathbf{k}} \\ &= \frac{1}{(\omega^S_{nm})^2} \left[r^{\mathrm{LDA,b}}_{nm} \left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} \right)_{;k^{\mathrm{c}}} + \left(r^{\mathrm{LDA,b}}_{nm} \left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} \right)_{;k^{\mathrm{c}}} \right)^* \right] \\ &= \frac{2}{(\omega^S_{nm})^2} \mathrm{Re} \left[r^{\mathrm{LDA,b}}_{nm} \left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} \right)_{;k^{\mathrm{c}}} \right], \end{aligned} \tag{E7}$$

the second term is reduced to

$$\begin{aligned} \frac{\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}}{(\omega^S_{nm})^2} \left(r^{\mathrm{LDA,b}}_{nm} \right)_{;k^{\mathrm{c}}} |_{\mathbf{k}} + \frac{\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}}{(\omega^S_{nm})^2} \left(r^{\mathrm{LDA,b}}_{nm} \right)_{;k^{\mathrm{c}}} |_{-\mathbf{k}} &= \frac{\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}}{(\omega^S_{nm})^2} \left(r^{\mathrm{LDA,b}}_{nm} \right)_{;k^{\mathrm{c}}} |_{\mathbf{k}} + \frac{\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm}}{(\omega^S_{nm})^2} \left(r^{\mathrm{LDA,b}}_{mn} \right)_{;k^{\mathrm{c}}} |_{\mathbf{k}} \\ &= \frac{1}{(\omega^S_{nm})^2} \left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} \left(r^{\mathrm{LDA,b}}_{nm} \right)_{;k^{\mathrm{c}}} + \left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} \left(r^{\mathrm{LDA,b}}_{nm} \right)_{;k^{\mathrm{c}}} \right)^* \right] \\ &= \frac{2}{(\omega^S_{nm})^2} \mathrm{Re} \left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} \left(r^{\mathrm{LDA,b}}_{nm} \right)_{;k^{\mathrm{c}}} \right], \end{aligned} \tag{E8}$$

and by using (77), the third term is reduced to

$$
\begin{aligned}
\frac{2\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell} r_{nm}^{\mathrm{LDA,b}}}{(\omega_{nm}^S)^3}\left(\omega_{nm}^S\right)_{;k^{\mathrm{c}}}|_{\mathbf{k}} + \frac{2\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell} r_{nm}^{\mathrm{LDA,b}}}{(\omega_{nm}^S)^3}\left(\omega_{nm}^S\right)_{;k^{\mathrm{c}}}|_{-\mathbf{k}} &= \frac{2\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell} r_{nm}^{\mathrm{LDA,b}}}{(\omega_{nm}^S)^3}\Delta_{nm}^{\mathrm{c}}|_{\mathbf{k}} + \frac{2\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell} r_{nm}^{\mathrm{LDA,b}}}{(\omega_{nm}^S)^3}\Delta_{nm}^{\mathrm{c}}|_{-\mathbf{k}} \\
&= \frac{2\mathcal{V}_{nm}^{\Sigma,\mathrm{a},\ell} r_{mn}^{\mathrm{LDA,b}}}{(\omega_{nm}^S)^3}\Delta_{nm}^{\mathrm{c}}|_{\mathbf{k}} + \frac{2\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell} r_{nm}^{\mathrm{LDA,b}}}{(\omega_{nm}^S)^3}\Delta_{nm}^{\mathrm{c}}|_{\mathbf{k}} \\
&= \frac{2}{(\omega_{nm}^S)^3}\left[\mathcal{V}_{nm}^{\Sigma,\mathrm{a},\ell} r_{mn}^{\mathrm{LDA,b}} + \left(\mathcal{V}_{nm}^{\Sigma,\mathrm{a},\ell} r_{mn}^{\mathrm{LDA,b}}\right)^*\right]\Delta_{nm}^{\mathrm{c}} \\
&= \frac{4}{(\omega_{nm}^S)^3}\mathrm{Re}\left[\mathcal{V}_{nm}^{\Sigma,\mathrm{a},\ell} r_{mn}^{\mathrm{LDA,b}}\right]\Delta_{nm}^{\mathrm{c}}. \qquad \text{(E9)}
\end{aligned}
$$

Combining the results from (E7), (E8), and (E9) into (E6),

$$
\begin{aligned}
&\frac{f_{mn}}{2}\left[\left(\frac{\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell} r_{nm}^{\mathrm{LDA,b}}}{(\omega_{nm}^S)^2}\right)_{;k^{\mathrm{c}}}|_{\mathbf{k}} + \left(\frac{\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell} r_{nm}^{\mathrm{LDA,b}}}{(\omega_{nm}^S)^2}\right)_{;k^{\mathrm{c}}}|_{-\mathbf{k}}\right]\frac{1}{\omega_{nm}^S-\omega} = \\
&\left(2\,\mathrm{Re}\left[r_{nm}^{\mathrm{LDA,b}}\left(\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell}\right)_{;k^{\mathrm{c}}}\right] + 2\,\mathrm{Re}\left[\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell}\left(r_{nm}^{\mathrm{LDA,b}}\right)_{;k^{\mathrm{c}}}\right] - \frac{4}{\omega_{nm}^S}\mathrm{Re}\left[\mathcal{V}_{nm}^{\Sigma,\mathrm{a},\ell} r_{mn}^{\mathrm{LDA,b}}\right]\Delta_{nm}^{\mathrm{c}}\right)\frac{f_{mn}}{2(\omega_{nm}^S)^2}\frac{1}{\omega_{nm}^S-\omega}.
\end{aligned} \qquad \text{(E10)}
$$

We substitute (E3), (E4), and (E10) in (E1),

$$
\begin{aligned}
I = \Bigg[&-\frac{2f_{mn}\,\mathrm{Re}\left[\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell}\left(r_{nm}^{\mathrm{LDA,b}}\right)_{;k^{\mathrm{c}}}\right]}{2(\omega_{nm}^S)^2}\frac{1}{\omega_{nm}^S-\omega} + \frac{4f_{mn}\,\mathrm{Re}\left[\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell}\left(r_{nm}^{\mathrm{LDA,b}}\right)_{;k^{\mathrm{c}}}\right]}{(\omega_{nm}^S)^2}\frac{1}{\omega_{nm}^S-2\omega}\Bigg] \\
&+\left[\frac{6f_{mn}\,\mathrm{Re}\left[\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell} r_{nm}^{\mathrm{LDA,b}}\right]\Delta_{nm}^{\mathrm{c}}}{2(\omega_{nm}^S)^3}\frac{1}{\omega_{nm}^S-\omega} - \frac{8f_{mn}\,\mathrm{Re}\left[\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell} r_{nm}^{\mathrm{LDA,b}}\right]\Delta_{nm}^{\mathrm{c}}}{(\omega_{nm}^S)^3}\frac{1}{\omega_{nm}^S-2\omega}\right. \\
&\left.+\frac{f_{mn}\left(2\,\mathrm{Re}\left[r_{nm}^{\mathrm{LDA,b}}\left(\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell}\right)_{;k^{\mathrm{c}}}\right] + 2\,\mathrm{Re}\left[\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell}\left(r_{nm}^{\mathrm{LDA,b}}\right)_{;k^{\mathrm{c}}}\right] - \frac{4}{\omega_{nm}^S}\,\mathrm{Re}\left[\mathcal{V}_{nm}^{\Sigma,\mathrm{a},\ell} r_{mn}^{\mathrm{LDA,b}}\right]\Delta_{nm}^{\mathrm{c}}\right)}{2(\omega_{nm}^S)^2}\frac{1}{\omega_{nm}^S-\omega}\right].
\end{aligned}
$$

If we simplify,

$$
\begin{aligned}
I = &-\frac{2f_{mn}\,\mathrm{Re}\left[\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell}\left(r_{nm}^{\mathrm{LDA,b}}\right)_{;k^{\mathrm{c}}}\right]}{2(\omega_{nm}^S)^2}\frac{1}{\omega_{nm}^S-\omega} + \frac{4f_{mn}\,\mathrm{Re}\left[\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell}\left(r_{nm}^{\mathrm{LDA,b}}\right)_{;k^{\mathrm{c}}}\right]}{(\omega_{nm}^S)^2}\frac{1}{\omega_{nm}^S-2\omega} \\
&+\frac{6f_{mn}\,\mathrm{Re}\left[\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell} r_{nm}^{\mathrm{LDA,b}}\right]\Delta_{nm}^{\mathrm{c}}}{2(\omega_{nm}^S)^3}\frac{1}{\omega_{nm}^S-\omega} - \frac{8f_{mn}\,\mathrm{Re}\left[\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell} r_{nm}^{\mathrm{LDA,b}}\right]\Delta_{nm}^{\mathrm{c}}}{(\omega_{nm}^S)^3}\frac{1}{\omega_{nm}^S-2\omega} \\
&+\frac{2f_{mn}\,\mathrm{Re}\left[r_{nm}^{\mathrm{LDA,b}}\left(\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell}\right)_{;k^{\mathrm{c}}}\right]}{2(\omega_{nm}^S)^2}\frac{1}{\omega_{nm}^S-\omega} \\
&+\frac{2f_{mn}\,\mathrm{Re}\left[\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell}\left(r_{nm}^{\mathrm{LDA,b}}\right)_{;k^{\mathrm{c}}}\right]}{2(\omega_{nm}^S)^2}\frac{1}{\omega_{nm}^S-\omega} \\
&-\frac{4f_{mn}\mathrm{Re}\left[\mathcal{V}_{nm}^{\Sigma,\mathrm{a},\ell} r_{mn}^{\mathrm{LDA,b}}\right]\Delta_{nm}^{\mathrm{c}}}{2(\omega_{nm}^S)^3}\frac{1}{\omega_{nm}^S-\omega},
\end{aligned} \qquad \text{(E11)}
$$

we conveniently collect the terms in columns of ω and 2ω. We can now express the susceptibility in terms of ω and 2ω. Separating the 2ω terms and substituting in above equation

$$\begin{aligned} I_{2\omega} &= -\frac{e^3}{\hbar^2}\sum_{mn\mathbf{k}}\left[\frac{4f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right]}{(\omega^S_{nm})^2} - \frac{8f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}\right]\Delta^{\mathrm{c}}_{nm}}{(\omega^S_{nm})^3}\right]\frac{1}{\omega^S_{nm}-2\omega} \\ &= -\frac{e^3}{\hbar^2}\sum_{mn\mathbf{k}}\frac{4f_{mn}}{(\omega^S_{nm})^2}\left[\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right] - \frac{2\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}\right]\Delta^{\mathrm{c}}_{nm}}{\omega^S_{nm}}\right]\frac{1}{\omega^S_{nm}-2\omega}. \end{aligned} \tag{E12}$$

We can express the energies in terms of transitions between bands. Therefore, $\omega^S_{nm}=\omega^S_{cv}$ for transitions between conduction and valence bands. We analyze the limit,

$$\lim_{\eta\to 0}\frac{1}{x\pm i\eta} = P\frac{1}{x}\mp i\pi\delta(x), \tag{E13}$$

and can finally rewrite (E12) in the desired form,

$$\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{a},\ell\mathrm{bc},2\omega}] = -\frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\frac{4}{(\omega^S_{cv})^2}\left(\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc}\left(r^{\mathrm{LDA,b}}_{cv}\right)_{;k^{\mathrm{c}}}\right] - \frac{2\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc}r^{\mathrm{LDA,b}}_{cv}\right]\Delta^{\mathrm{c}}_{cv}}{\omega^S_{cv}}\right)\delta(\omega^S_{cv}-2\omega). \tag{E14}$$

where we added a 1/2 from the sum over $\mathbf{k}\to-\mathbf{k}$.

We do the same for the ω terms in (E11) to obtain

$$\begin{aligned} I_{\omega} = -\frac{e^3}{2\hbar^2}\sum_{nm\mathbf{k}}\Bigg[&-\frac{2f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right]}{(\omega^S_{nm})^2} + \frac{6f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}\right]\Delta^{\mathrm{c}}_{nm}}{(\omega^S_{nm})^3} \\ &+\frac{2f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right]}{(\omega^S_{nm})^2} - \frac{4f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm}r^{\mathrm{LDA,b}}_{mn}\right]\Delta^{\mathrm{c}}_{nm}}{(\omega^S_{nm})^3} \\ &+\frac{2f_{mn}\,\mathrm{Re}\left[r^{\mathrm{LDA,b}}_{nm}\left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\right)_{;k^{\mathrm{c}}}\right]}{(\omega^S_{nm})^2}\Bigg]\frac{1}{\omega^S_{nm}-\omega}. \end{aligned} \tag{E15}$$

We reduce in the same way as (E12),

$$I_{\omega} = -\frac{e^3}{2\hbar^2}\sum_{nm\mathbf{k}}\frac{f_{mn}}{(\omega^S_{nm})^2}\left[2\,\mathrm{Re}\left[r^{\mathrm{LDA,b}}_{nm}\left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\right)_{;k^{\mathrm{c}}}\right] + \frac{2\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}r^{\mathrm{LDA,b}}_{nm}\right]\Delta^{\mathrm{c}}_{nm}}{\omega^S_{nm}}\right]\frac{1}{\omega^S_{nm}-\omega}, \tag{E16}$$

and using (E13) we obtain our final form,

$$\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{a},\ell\mathrm{bc},\omega}] = -\frac{\pi|e|^3}{2\hbar^2}\sum_{cv\mathbf{k}}\frac{1}{(\omega^S_{cv})^2}\left(\mathrm{Re}\left[r^{\mathrm{LDA,b}}_{cv}\left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc}\right)_{;k^{\mathrm{c}}}\right] + \frac{\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc}r^{\mathrm{LDA,b}}_{cv}\right]\Delta^{\mathrm{c}}_{cv}}{\omega^S_{cv}}\right)\delta(\omega^S_{cv}-\omega), \tag{E17}$$

where again we added a 1/2 from the sum over $\mathbf{k}\to-\mathbf{k}$.

2. Interband Contributions

We follow the equivalent procedure for the int$E$rband contribution. From Eq. (75) we get

$$E = A\left[-\frac{1}{2\omega^S_{lm}(2\omega^S_{lm}-\omega^S_{nm})}\frac{1}{\omega^S_{lm}-\omega}+\frac{2}{\omega^S_{nm}(2\omega^S_{lm}-\omega^S_{nm})}\frac{1}{\omega^S_{nm}-2\omega}+\frac{1}{2\omega^S_{lm}\omega^S_{nm}}\frac{1}{\omega}\right] - B\left[-\frac{1}{2\omega^S_{nl}(2\omega^S_{nl}-\omega^S_{nm})}\frac{1}{\omega^S_{nl}-\omega}+\frac{2}{\omega^S_{nm}(2\omega^S_{nl}-\omega^S_{nm})}\frac{1}{\omega^S_{nm}-2\omega}+\frac{1}{2\omega^S_{nl}\omega^S_{nm}}\frac{1}{\omega}\right], \tag{E18}$$

where $A = f_{ml}\mathcal{V}^{\Sigma,\mathrm{a}}_{mn} r^{\mathrm{c}}_{nl} r^{\mathrm{b}}_{lm}$ and $B = f_{ln}\mathcal{V}^{\Sigma,\mathrm{a}}_{mn} r^{\mathrm{b}}_{nl} r^{\mathrm{c}}_{lm}$.

Appendix F: Generalized derivative $(\mathbf{r}_{nm}(\mathbf{k}))_{;\mathbf{k}}$ for non-local potentials

We obtain the generalized derivative $(\mathbf{r}_{nm}(\mathbf{k}))_{;\mathbf{k}}$ for the case of a non-local potential in the Hamiltonian. We start from (see Eq. (17))

$$[r^{\mathrm{a}}, v^{\mathrm{LDA,b}}] = \frac{i\hbar}{m_e}\delta_{ab} + \frac{1}{i\hbar}[r^{\mathrm{a}}, v^{\mathrm{nl,b}}] \equiv \mathcal{T}^{\mathrm{ab}}, \tag{F1}$$

where the matrix elements of $\mathcal{T}^{\mathrm{ab}}$ are calculated in Appendix G. Then,

$$\langle n\mathbf{k}|[r^{\mathrm{a}}, v^{\mathrm{LDA,b}}]|m\mathbf{k}'\rangle = \langle n\mathbf{k}|\mathcal{T}^{\mathrm{ab}}|m\mathbf{k}'\rangle = \mathcal{T}^{\mathrm{ab}}_{nm}(\mathbf{k})\delta(\mathbf{k}-\mathbf{k}'), \tag{F2}$$

so

$$\langle n\mathbf{k}|[r^{\mathrm{a}}_i, v^{\mathrm{LDA,b}}]|m\mathbf{k}'\rangle + \langle n\mathbf{k}|[r^{\mathrm{a}}_e, v^{\mathrm{LDA,b}}]|m\mathbf{k}'\rangle = \mathcal{T}^{\mathrm{ab}}_{nm}(\mathbf{k})\delta(\mathbf{k}-\mathbf{k}'). \tag{F3}$$

From Eq. (A18) and (A19)

$$\langle n\mathbf{k}|[r^{\mathrm{a}}_i, v^{\mathrm{b}}_{\mathrm{LDA}}]|m\mathbf{k}'\rangle = i\delta(\mathbf{k}-\mathbf{k}')(v^{\mathrm{LDA,b}}_{nm})_{;k^{\mathrm{a}}} \tag{F4}$$

$$(v^{\mathrm{LDA,b}}_{nm})_{;k^{\mathrm{a}}} = \nabla_{k^{\mathrm{a}}} v^{\mathrm{LDA,b}}_{nm}(\mathbf{k}) - i v^{\mathrm{LDA,b}}_{nm}(\mathbf{k})\left(\xi^{\mathrm{a}}_{nn}(\mathbf{k}) - \xi^{\mathrm{a}}_{mm}(\mathbf{k})\right), \tag{F5}$$

and

$$\begin{aligned}
\langle n\mathbf{k}|[r_e^{\mathrm{a}}, v^{\mathrm{LDA,b}}]|m\mathbf{k}'\rangle &= \sum_{\ell\mathbf{k}''}\Big(\langle n\mathbf{k}|r_e^{\mathrm{a}}|\ell\mathbf{k}''\rangle\langle\ell\mathbf{k}''|v^{\mathrm{LDA,b}}|m\mathbf{k}'\rangle \\
&- \langle n\mathbf{k}|v^{\mathrm{LDA,b}}|\ell\mathbf{k}''\rangle\langle\ell\mathbf{k}''|r_e^{\mathrm{a}}|m\mathbf{k}'\rangle\Big) \\
&= \sum_{\ell\mathbf{k}''}\Big((1-\delta_{n\ell})\delta(\mathbf{k}-\mathbf{k}'')\xi^{\mathrm{a}}_{n\ell}\delta(\mathbf{k}''-\mathbf{k}')v^{\mathrm{LDA,b}}_{\ell m} \\
&- \delta(\mathbf{k}-\mathbf{k}'')v^{\mathrm{LDA,b}}_{n\ell}(1-\delta_{\ell m})\delta(\mathbf{k}''-\mathbf{k}')\xi^{\mathrm{a}}_{\ell m}\Big) \\
&= \delta(\mathbf{k}-\mathbf{k}')\sum_{\ell}\Big((1-\delta_{n\ell})\xi^{\mathrm{a}}_{n\ell}v^{\mathrm{LDA,b}}_{\ell m} \\
&- (1-\delta_{\ell m})v^{\mathrm{LDA,b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m}\Big) \\
&= \delta(\mathbf{k}-\mathbf{k}')\Bigg(\sum_{\ell}\Big(\xi^{\mathrm{a}}_{n\ell}v^{\mathrm{LDA,b}}_{\ell m} - v^{\mathrm{LDA,b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m}\Big) \\
&+ v^{\mathrm{LDA,b}}_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn})\Bigg).
\end{aligned} \tag{F6}$$

Using Eqs. (F4) and (F6) into Eq. (F3) gives

$$\begin{aligned}
i\delta(\mathbf{k}-\mathbf{k}')\Bigg((v^{\mathrm{LDA,b}}_{nm})_{;k^{\mathrm{a}}} - i\sum_{\ell}\Big(\xi^{\mathrm{a}}_{n\ell}v^{\mathrm{LDA,b}}_{\ell m} - v^{\mathrm{LDA,b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m}\Big) \\
- iv^{\mathrm{LDA,b}}_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn})\Bigg) = \mathcal{T}^{\mathrm{ab}}_{nm}(\mathbf{k})\delta(\mathbf{k}-\mathbf{k}'),
\end{aligned} \tag{F7}$$

then

$$(v^{\mathrm{LDA,b}}_{nm})_{;k^{\mathrm{a}}} = -i\mathcal{T}^{\mathrm{ab}}_{nm} + i\sum_{\ell}\Big(\xi^{\mathrm{a}}_{n\ell}v^{\mathrm{LDA,b}}_{\ell m} - v^{\mathrm{LDA,b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m}\Big) + iv^{\mathrm{LDA,b}}_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn}), \tag{F8}$$

and from Eq. (F5),

$$\nabla_{k^{\mathrm{a}}}v^{\mathrm{LDA,b}}_{nm} = -i\mathcal{T}^{\mathrm{ab}}_{nm} + i\sum_{\ell}\Big(\xi^{\mathrm{a}}_{n\ell}v^{\mathrm{LDA,b}}_{\ell m} - v^{\mathrm{LDA,b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m}\Big). \tag{F9}$$

Now, there are two cases. We use Eq. (21).

Case $n = m$

$$\begin{aligned}
\nabla_{k^{\mathrm{a}}}v^{\mathrm{LDA,b}}_{nn} &= -i\mathcal{T}^{\mathrm{ab}}_{nn} + i\sum_{\ell}\Big(\xi^{\mathrm{a}}_{n\ell}v^{\mathrm{LDA,b}}_{\ell n} - v^{\mathrm{LDA,b}}_{n\ell}\xi^{\mathrm{a}}_{\ell n}\Big) \\
&= -i\mathcal{T}^{\mathrm{ab}}_{nn} - \sum_{\ell\neq n}\Big(r^{\mathrm{a}}_{n\ell}\omega^{\mathrm{LDA}}_{\ell n}r^{\mathrm{b}}_{\ell n} - \omega^{\mathrm{LDA}}_{n\ell}r^{\mathrm{b}}_{n\ell}r^{\mathrm{a}}_{\ell n}\Big) \\
&= -i\mathcal{T}^{\mathrm{ab}}_{nn} - \sum_{\ell\neq n}\omega^{\mathrm{LDA}}_{\ell n}\Big(r^{\mathrm{a}}_{n\ell}r^{\mathrm{b}}_{\ell n} - r^{\mathrm{b}}_{n\ell}r^{\mathrm{a}}_{\ell n}\Big),
\end{aligned} \tag{F10}$$

since the $\ell = n$ cancels out. This would give the generalization for the inverse effective mass tensor $(m_n^{-1})_{ab}$ for nonlocal potentials. Indeed, if we neglect the commutator of $\mathbf{v}^{\rm nl}$ in Eq. (F1), we obtain $-i\mathcal{T}^{\rm ab}_{nn} = \hbar/m_e\delta_{\rm ab}$ thus obtaining the familiar expression of $(m_n^{-1})_{ab}$.[31]

Case $n \neq m$

$$
\begin{aligned}
(v^{\rm LDA,b}_{nm})_{;k^{\rm a}} &= -i\mathcal{T}^{\rm ab}_{nm} + i\sum_{\ell\neq m\neq n}\left(\xi^{\rm a}_{n\ell}v^{\rm LDA,b}_{\ell m} - v^{\rm LDA,b}_{n\ell}\xi^{\rm a}_{\ell m}\right) \\
&+ i\left(\xi^{\rm a}_{nm}v^{\rm LDA,b}_{mm} - v^{\rm LDA,b}_{nm}\xi^{\rm a}_{mm}\right) \\
&+ i\left(\xi^{\rm a}_{nn}v^{\rm LDA,b}_{nm} - v^{\rm LDA,b}_{nn}\xi^{\rm a}_{nm}\right) + iv^{\rm LDA,b}_{nm}(\xi^{\rm a}_{mm} - \xi^{\rm a}_{nn}) \\
&= -i\mathcal{T}^{\rm ab}_{nm} - \sum_{\ell}\left(\omega^{\rm LDA}_{\ell m}r^{\rm a}_{n\ell}r^{\rm b}_{\ell m} - \omega^{\rm LDA}_{n\ell}r^{\rm b}_{n\ell}r^{\rm a}_{\ell m}\right) + i\xi^{\rm a}_{nm}(v^{\rm LDA,b}_{mm} - v^{\rm LDA,b}_{nn}) \\
&= -i\mathcal{T}^{\rm ab}_{nm} - \sum_{\ell}\left(\omega^{\rm LDA}_{\ell m}r^{\rm a}_{n\ell}r^{\rm b}_{\ell m} - \omega^{\rm LDA}_{n\ell}r^{\rm b}_{n\ell}r^{\rm a}_{\ell m}\right) + ir^{\rm a}_{nm}\Delta^{\rm b}_{mn},
\end{aligned}
\tag{F11}
$$

where we use $\Delta^{\rm a}_{mn}$ of Eq. (77). Now, for $n \neq m$, Eqs. (21), (D9) and (F11) and the chain rule, give

$$
\begin{aligned}
(r^{\rm b}_{nm})_{;k^{\rm a}} &= \left(\frac{v^{\rm LDA,b}_{nm}}{i\omega^{\rm LDA}_{nm}}\right)_{;k^{\rm a}} = \frac{1}{i\omega^{\rm LDA}_{nm}}\left(v^{\rm LDA,b}_{nm}\right)_{;k^{\rm a}} - \frac{v^{\rm LDA,b}_{nm}}{i(\omega^{\rm LDA}_{nm})^2}\left(\omega^{\rm LDA}_{nm}\right)_{;k^{\rm a}} \\
&= -i\mathcal{T}^{\rm ab}_{nm} + \frac{i}{\omega^{\rm LDA}_{nm}}\sum_{\ell}\left(\omega^{\rm LDA}_{\ell m}r^{\rm a}_{n\ell}r^{\rm b}_{\ell m} - \omega^{\rm LDA}_{n\ell}r^{\rm b}_{n\ell}r^{\rm a}_{\ell m}\right) + \frac{r^{\rm a}_{nm}\Delta^{\rm b}_{mn}}{\omega^{\rm LDA}_{nm}} \\
&- \frac{r^{\rm b}_{nm}}{\omega^{\rm LDA}_{nm}}\left(\omega^{\rm LDA}_{nm}\right)_{;k^{\rm a}} \\
&= -i\mathcal{T}^{\rm ab}_{nm} + \frac{i}{\omega^{\rm LDA}_{nm}}\sum_{\ell}\left(\omega^{\rm LDA}_{\ell m}r^{\rm a}_{n\ell}r^{\rm b}_{\ell m} - \omega^{\rm LDA}_{n\ell}r^{\rm b}_{n\ell}r^{\rm a}_{\ell m}\right) + \frac{r^{\rm a}_{nm}\Delta^{\rm b}_{mn}}{\omega^{\rm LDA}_{nm}} \\
&- \frac{r^{\rm b}_{nm}}{\omega_{nm}}\frac{v^{\rm LDA,a}_{nn} - v^{\rm LDA,a}_{mm}}{m_e} \\
&= -i\mathcal{T}^{\rm ab}_{nm} + \frac{r^{\rm a}_{nm}\Delta^{\rm b}_{mn} + r^{\rm b}_{nm}\Delta^{\rm a}_{mn}}{\omega^{\rm LDA}_{nm}} + \frac{i}{\omega^{\rm LDA}_{nm}}\sum_{\ell}\left(\omega^{\rm LDA}_{\ell m}r^{\rm a}_{n\ell}r^{\rm b}_{\ell m} - \omega^{\rm LDA}_{n\ell}r^{\rm b}_{n\ell}r^{\rm a}_{\ell m}\right),
\end{aligned}
\tag{F12}
$$

where the $-i\mathcal{T}_{nm}$ term, generalizes the usual expresion of $\mathbf{r}_{nm;\mathbf{k}}$ for local Hamiltonians,[13,29,32,33] to the case of a nonlocal potential in the Hamiltonian.

Appendix G: Matrix elements of $\mathcal{T}^{\rm ab}_{nm}(\mathbf{k})$

To calculate $\mathcal{T}^{\rm ab}_{nm}$, first we need to calculate

$$
\mathcal{L}^{\rm ab}_{nm}(\mathbf{k}) = \frac{1}{i\hbar}\langle n\mathbf{k}|[\hat{r}^{\rm a}, \hat{v}^{\rm nl,b}]|m\mathbf{k}'\rangle\delta(\mathbf{k}-\mathbf{k}') = \frac{1}{\hbar^2}\langle n\mathbf{k}|\big[\hat{r}^{\rm a}, [\hat{V}^{\rm nl}(\hat{\mathbf{r}}, \hat{\mathbf{r}}'), \hat{r}^{\rm b}]\big]|m\mathbf{k}'\rangle\delta(\mathbf{k}-\mathbf{k}'),
\tag{G1}
$$

for which we need the following triple commutator

$$\big[\hat{r}^{\mathrm{a}},[\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}},\hat{\mathbf{r}}'),\hat{r}^{\mathrm{b}}]\big]=\big[\hat{r}^{\mathrm{b}},[\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}},\hat{\mathbf{r}}'),\hat{r}^{\mathrm{a}}]\big], \tag{G2}$$

where the r.h.s follows form the Jacobi identity, since $[\hat{r}^{\mathrm{a}},\hat{r}^{\mathrm{b}}]=0$. We expand the triple commutator as,

$$\begin{aligned}\big[\hat{r}^{\mathrm{a}},[\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}},\hat{\mathbf{r}}'),\hat{r}^{\mathrm{b}}]\big] &= \big[\hat{r}^{\mathrm{a}},\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}},\hat{\mathbf{r}}')\hat{r}^{\mathrm{b}}\big]-\big[\hat{r}^{\mathrm{a}},\hat{r}^{\mathrm{b}}\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}},\hat{\mathbf{r}}')\big]\\ &= \big[\hat{r}^{\mathrm{a}},\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}},\hat{\mathbf{r}}')\big]\hat{r}^{\mathrm{b}}-\hat{r}^{\mathrm{b}}\big[\hat{r}^{\mathrm{a}},\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}},\hat{\mathbf{r}}')\big]\\ &= \hat{r}^{\mathrm{a}}\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}},\hat{\mathbf{r}}')\hat{r}^{\mathrm{b}}-\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}},\hat{\mathbf{r}}')\hat{r}^{\mathrm{a}}\hat{r}^{\mathrm{b}}-\hat{r}^{\mathrm{b}}\hat{r}^{\mathrm{a}}\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}},\hat{\mathbf{r}}')+\hat{r}^{\mathrm{b}}\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}},\hat{\mathbf{r}}')\hat{r}^{\mathrm{a}}.\end{aligned} \tag{G3}$$

Then,

$$\begin{aligned}\frac{1}{\hbar^2}\langle n\mathbf{k}|\big[\hat{r}^{\mathrm{a}},[\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}},\hat{\mathbf{r}}'),\hat{r}^{\mathrm{b}}]\big]|m\mathbf{k}'\rangle &= \frac{1}{\hbar^2}\int d\mathbf{r}d\mathbf{r}'\langle n\mathbf{k}||\mathbf{r}\rangle\langle\mathbf{r}|\big[\hat{r}^{\mathrm{a}},[\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}},\hat{\mathbf{r}}'),\hat{r}^{\mathrm{b}}]\big]|\mathbf{r}'\rangle\langle\mathbf{r}'||m\mathbf{k}'\rangle\delta(\mathbf{k}-\mathbf{k}')\\ &= \frac{1}{\hbar^2}\int d\mathbf{r}d\mathbf{r}'\psi^*_{n\mathbf{k}}(\mathbf{r})\Big(r^{\mathrm{a}}V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')r'^{\mathrm{b}}-V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')r'^{\mathrm{a}}r'^{\mathrm{b}}\\ &-r^{\mathrm{b}}r^{\mathrm{a}}V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')+r^{\mathrm{b}}V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')r'^{\mathrm{a}}\Big)\psi_{m\mathbf{k}}(\mathbf{r}')\delta(\mathbf{k}-\mathbf{k}')\\ &= \frac{1}{\hbar^2\Omega}\sum_{\mathbf{K},\mathbf{K}'}C^*_{n\mathbf{k}}(\mathbf{K})C_{m\mathbf{k}}(\mathbf{K}')\int d\mathbf{r}d\mathbf{r}'e^{-i\mathbf{K}\cdot\mathbf{r}}\Big(r^{\mathrm{a}}V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')r'^{\mathrm{b}}-V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')r'^{\mathrm{a}}r'^{\mathrm{b}}\\ &-r^{\mathrm{b}}r^{\mathrm{a}}V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')+r^{\mathrm{b}}V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')r'^{\mathrm{a}}\Big)e^{i\mathbf{K}'\cdot\mathbf{r}'}\delta(\mathbf{k}-\mathbf{k}').\end{aligned} \tag{G4}$$

We use the following identity

$$\begin{aligned}&\Big(\frac{\partial^2}{\partial K^{\mathrm{a}}\partial K'^{\mathrm{b}}}+\frac{\partial^2}{\partial K'^{\mathrm{a}}\partial K'^{\mathrm{b}}}+\frac{\partial^2}{\partial K^{\mathrm{a}}\partial K^{\mathrm{b}}}+\frac{\partial^2}{\partial K^{\mathrm{b}}\partial K'^{\mathrm{a}}}\Big)\int d\mathbf{r}d\mathbf{r}'e^{-i\mathbf{K}\cdot\mathbf{r}}V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')e^{i\mathbf{K}'\cdot\mathbf{r}'}\\ &=\int d\mathbf{r}d\mathbf{r}'e^{-i\mathbf{K}\cdot\mathbf{r}}\Big(r^{\mathrm{a}}V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')r'^{\mathrm{b}}-V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')r'^{\mathrm{a}}r'^{\mathrm{b}}-r^{\mathrm{b}}r^{\mathrm{a}}V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')+r^{\mathrm{b}}V^{\mathrm{nl}}(\mathbf{r},\mathbf{r}')r'^{\mathrm{a}}\Big)e^{i\mathbf{K}'\cdot\mathbf{r}'}\\ &=\Big(\frac{\partial^2}{\partial K^{\mathrm{a}}\partial K'^{\mathrm{b}}}+\frac{\partial^2}{\partial K'^{\mathrm{a}}\partial K'^{\mathrm{b}}}+\frac{\partial^2}{\partial K^{\mathrm{a}}\partial K^{\mathrm{b}}}+\frac{\partial^2}{\partial K^{\mathrm{b}}\partial K'^{\mathrm{a}}}\Big)\langle\mathbf{K}|V^{\mathrm{nl}}|\mathbf{K}'\rangle,\end{aligned} \tag{G5}$$

to write

$$\mathcal{L}^{\mathrm{ab}}_{nm}(\mathbf{k})=\frac{1}{\hbar^2\Omega}\sum_{\mathbf{K},\mathbf{K}'}C^*_{n\mathbf{k}}(\mathbf{K})C_{m\mathbf{k}}(\mathbf{K}')\Big(\frac{\partial^2}{\partial K^{\mathrm{a}}\partial K'^{\mathrm{b}}}+\frac{\partial^2}{\partial K'^{\mathrm{a}}\partial K'^{\mathrm{b}}}+\frac{\partial^2}{\partial K^{\mathrm{a}}\partial K^{\mathrm{b}}}+\frac{\partial^2}{\partial K^{\mathrm{b}}\partial K'^{\mathrm{a}}}\Big)\langle\mathbf{K}|V^{\mathrm{nl}}|\mathbf{K}'\rangle \\ . \tag{G6}$$

The double derivatives with respect to $\mathbf{K}$ and $\mathbf{K}'$ can be worked out as it is done in Appendix B to obtain the matrix elements of $[\hat{V}^{\mathrm{nl}}(\hat{\mathbf{r}},\hat{\mathbf{r}}'),\hat{r}^{\mathrm{b}}]$,[34] and thus we could have the value of the matrix elements of the triple commutator.[30]

With above results we can proceed to evaluate the matrix elements $\mathcal{T}_{nm}(\mathbf{k})$. From Eq. (F1)

$$
\begin{aligned}
\langle n\mathbf{k}|\mathcal{T}^{\mathrm{ab}}|m\mathbf{k}'\rangle &= \langle n\mathbf{k}|\frac{i\hbar}{m_e}\delta_{ab}|m\mathbf{k}'\rangle + \langle n\mathbf{k}|\frac{1}{i\hbar}[r^{\mathrm{a}}, v^{\mathrm{nl,b}}]|m\mathbf{k}'\rangle \\
\mathcal{L}^{\mathrm{ab}}_{nm}(\mathbf{k})\delta(\mathbf{k}-\mathbf{k}') &= \delta(\mathbf{k}-\mathbf{k}')\Big(\frac{i\hbar}{m_e}\delta_{ab}\delta_{nm} + \mathcal{L}^{\mathrm{ab}}_{nm}(\mathbf{k})\Big) \\
\mathcal{T}^{\mathrm{ab}}_{nm}(\mathbf{k}) = \mathcal{T}^{\mathrm{ba}}_{nm}(\mathbf{k}) &= \frac{i\hbar}{m_e}\delta_{ab}\delta_{nm} + \mathcal{L}^{\mathrm{ab}}_{nm}(\mathbf{k}),
\end{aligned}
\tag{G7}
$$

which is an explicit expression that can be numerically calculated.

Appendix H: Explicit expressions for $\mathcal{V}^{a,\ell}_{nm}(\mathbf{k})$ and $\mathcal{C}^{\ell}_{nm}(\mathbf{k})$

Expanding the wave function in plane waves we obtain

$$
\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} A_{n\mathbf{k}}(\mathbf{G})e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}},
\tag{H1}
$$

where $\{\mathbf{G}\}$ are the reciprocal basis vectors satisfying $e^{\mathbf{R}\cdot\mathbf{G}} = 1$, with $\{\mathbf{R}\}$ the translation vectors in real space, and $A_{n\mathbf{k}}(\mathbf{G})$ are the expansion coefficients. Using $m_e\mathbf{v} = -i\hbar\boldsymbol{\nabla}$ into Eq. (62) we obtain,[26]

$$
\boldsymbol{\mathcal{V}}^{\ell}_{nm}(\mathbf{k}) = \frac{\hbar}{2m_e}\sum_{\mathbf{G},\mathbf{G}'} A^*_{n\mathbf{k}}(\mathbf{G}')A_{m\mathbf{k}}(\mathbf{G})(2\mathbf{k}+\mathbf{G}+\mathbf{G}')\delta_{\mathbf{G}_\parallel\mathbf{G}'_\parallel} f_\ell(G_\perp - G'_\perp),
\tag{H2}
$$

where

$$
f_\ell(g) = \frac{1}{L}\int_{z_\ell-\Delta^b_\ell}^{z_\ell+\Delta^f_\ell} e^{igz}dz,
\tag{H3}
$$

where the reciprocal lattice vectors $\mathbf{G}$ are decomposed into components parallel to the surface $\mathbf{G}_\parallel$, and perpendicular to the surface $G_\perp\hat{z}$, so that $\mathbf{G} = \mathbf{G}_\parallel + G_\perp\hat{z}$. Likewise we obtain that

$$
\begin{aligned}
\mathcal{C}_{nm}(\mathbf{k}) &= \int \psi^*_{n\mathbf{k}}(\mathbf{r})f(z)\psi_{m\mathbf{k}}(\mathbf{r})\,\mathrm{d}\mathbf{r} \\
&= \sum_{\mathbf{G},\mathbf{G}'} A^*_{n\mathbf{k}}(\mathbf{G}')A_{m\mathbf{k}}(\mathbf{G})\int f(z)e^{-i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} \\
&= \sum_{\mathbf{G},\mathbf{G}'} A^*_{n\mathbf{k}}(\mathbf{G}')A_{m\mathbf{k}}(\mathbf{G}) \underbrace{\int e^{-i(\mathbf{G}_\parallel-\mathbf{G}'_\parallel)\cdot\mathbf{R}_\parallel}\,\mathrm{d}\mathbf{R}_\parallel}_{\delta_{\mathbf{G}_\parallel\mathbf{G}'_\parallel}} \underbrace{\int e^{-i(g-g')z}f(z)\,\mathrm{d}z}_{f_\ell(G_\perp-G'_\perp)},
\end{aligned}
$$

which we can express compactly as,

$$
\mathcal{C}^{\ell}_{nm}(\mathbf{k}) = \sum_{\mathbf{G},\mathbf{G}'} A^*_{n\mathbf{k}}(\mathbf{G}')A_{m\mathbf{k}}(\mathbf{G})\delta_{\mathbf{G}_\parallel\mathbf{G}'_\parallel} f_\ell(G_\perp - G'_\perp).
\tag{H4}
$$

The double summation over the $\mathbf{G}$ vectors can be efficiently done by creating a pointer array to identify all the plane-wave coefficients associated with the same $G_\parallel$. We take z_ℓ at the center of an atom that belongs to layer ℓ, and thus above equations gives the ℓ-th atomic-layer contribution to the optical response.[26]

If $\mathcal{C}^\ell(z) = 1$ from Eqs. (H2) and (H4) we recover the well known result

$$v_{nm}(\mathbf{k}) = \frac{\hbar}{m_e}\sum_{\mathbf{G}} A^*_{n\mathbf{k}}(\mathbf{G})A_{m\mathbf{k}}(\mathbf{G})(\mathbf{k}+\mathbf{G})$$
$$\mathcal{C}^\ell_{nm} = \delta_{nm}, \tag{H5}$$

since for this case $f_\ell(g) = \delta_{g0}$.

1. Time–reversal relations

The following relations hold for time–reversal symmetry.

$$A^*_{n\mathbf{k}}(\mathbf{G}) = A_{n-\mathbf{k}}(\mathbf{G}),$$

$$\mathbf{P}_{n\ell}(-\mathbf{k}) = \hbar\sum_{\mathbf{G}} A^*_{n-\mathbf{k}}(\mathbf{G})A_{\ell-\mathbf{k}}(\mathbf{G})(-\mathbf{k}+\mathbf{G}),$$

$$(\mathbf{G}\to-\mathbf{G}) = -\hbar\sum_{\mathbf{G}} A_{n\mathbf{k}}(\mathbf{G})A^*_{\ell\mathbf{k}}(\mathbf{G})(\mathbf{k}+\mathbf{G}) = -\mathbf{P}_{\ell n}(\mathbf{k}),$$

$$\begin{aligned}\mathcal{C}_{nm}(L;-\mathbf{k}) &= \sum_{\mathbf{G}_\parallel,g,g'} A^*_{n-\mathbf{k}}(\mathbf{G}_\parallel,g)A_{m-\mathbf{k}}(\mathbf{G}_\parallel,g')f_\ell(g-g') \\ &= \sum_{\mathbf{G}_\parallel,g,g'} A_{n\mathbf{k}}(\mathbf{G}_\parallel,g)A^*_{m\mathbf{k}}(\mathbf{G}_\parallel,g')f_\ell(g-g') \\ &= \mathcal{C}_{mn}L;\mathbf{k}.\end{aligned}$$

Appendix I: Coding

In this Appendix we reproduce all the quantities that should be coded.

Eqs. (81), (82), and (83) (84)

$$\mathrm{Im}[\chi^{s,\ell}_{e,\mathrm{abc},\omega}] = -\frac{\pi|e|^3}{2\hbar^2}\sum_{v c\mathbf{k}}\sum_{l\neq(v,c)}\frac{1}{\omega^S_{cv}}\left[\frac{\mathrm{Im}[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{lc}\{r^{\mathrm{b}}_{cv}r^{\mathrm{c}}_{vl}\}]}{(2\omega^S_{cv}-\omega^S_{cl})} - \frac{\mathrm{Im}[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vl}\{r^{\mathrm{c}}_{lc}r^{\mathrm{b}}_{cv}\}]}{(2\omega^S_{cv}-\omega^S_{lv})}\right]\delta(\omega^S_{cv}-\omega), \tag{I1}$$

$$\mathrm{Im}[\chi^{s,\ell}_{e,\mathrm{abc},2\omega}] = -\frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\frac{4}{\omega^S_{cv}}\left[\sum_{v'\neq v}\frac{\mathrm{Im}[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc}\{r^{\mathrm{b}}_{cv'}r^{\mathrm{c}}_{v'v}\}]}{2\omega^S_{cv'}-\omega^S_{cv}} - \sum_{c'\neq c}\frac{\mathrm{Im}[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc}\{r^{\mathrm{c}}_{cc'}r^{\mathrm{b}}_{c'v}\}]}{2\omega^S_{c'v}-\omega^S_{cv}}\right]\delta(\omega^S_{cv}-2\omega), \tag{I2}$$

$$\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{abc},\omega}] = -\frac{\pi|e|^3}{2\hbar^2}\sum_{cv\mathbf{k}}\frac{1}{(\omega^S_{cv})^2}\left(\mathrm{Re}\left[r^{\mathrm{b}}_{cv}\left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc}\right)_{;k^{\mathrm{c}}}\right] + \frac{\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc}r^{\mathrm{b}}_{cv}\right]\Delta^{\mathrm{c}}_{cv}}{\omega^S_{cv}}\right)\delta(\omega^S_{cv}-\omega), \tag{I3}$$

and

$$\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{abc},2\omega}] = -\frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\frac{4}{(\omega^S_{cv})^2}\left(\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc}\left(r^{\mathrm{b}}_{cv}\right)_{;k^{\mathrm{c}}}\right] - \frac{2\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc}r^{\mathrm{b}}_{cv}\right]\Delta^{\mathrm{c}}_{cv}}{\omega^S_{cv}}\right)\delta(\omega^S_{cv}-2\omega). \tag{I4}$$

Eq. (21)

$$\mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k})}{i\omega^{\mathrm{LDA}}_{nm}(\mathbf{k})} \qquad n\neq m, \tag{I5}$$

where $\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k})$ include the local and nonlocal parts of the pseudopotential.

Eq. (C1) and (C2)

$$\begin{aligned}\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm} &= \mathcal{V}^{\mathrm{LDA},\mathrm{a},\ell}_{nm} + \mathcal{V}^{S,\mathrm{a},\ell}_{nm}\\ \left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm}\right)_{;k^{\mathrm{b}}} &= \left(\mathcal{V}^{\mathrm{LDA},\mathrm{a},\ell}_{nm}\right)_{;k^{\mathrm{b}}} + \left(\mathcal{V}^{S,\mathrm{a},\ell}_{nm}\right)_{;k^{\mathrm{b}}}.\end{aligned} \tag{I6}$$

For the LDA term we have

$$\begin{aligned}\mathcal{V}^{\mathrm{LDA},\mathrm{a},\ell}_{nm} &= \frac{1}{2}\sum_q\left(v^{\mathrm{LDA},\mathrm{a}}_{nq}\mathcal{C}^{\ell}_{qm} + \mathcal{C}^{\ell}_{nq}v^{\mathrm{LDA},\mathrm{a}}_{qm}\right)\\ \left(\mathcal{V}^{\mathrm{LDA},\mathrm{a}}_{nm}\right)_{;k^{\mathrm{b}}} &= \frac{1}{2}\sum_q\left((v^{\mathrm{LDA},\mathrm{a}}_{nq})_{;k^{\mathrm{b}}}\mathcal{C}^{\ell}_{qm} + v^{\mathrm{LDA},\mathrm{a}}_{nq}(\mathcal{C}^{\ell}_{qm})_{;k^{\mathrm{b}}} + (\mathcal{C}^{\ell}_{nq})_{;k^{\mathrm{b}}}v^{\mathrm{LDA},\mathrm{a}}_{qm} + \mathcal{C}^{\ell}_{nq}(v^{\mathrm{LDA},\mathrm{a}}_{qm})_{;k^{\mathrm{b}}}\right).\end{aligned} \tag{I7}$$

Eqs. (C3), (C4) and (C5)

$$(v^{\mathrm{LDA},\mathrm{a}}_{nm})_{;k^{\mathrm{b}}} = im_e\Delta^{b}_{nm}r^{\mathrm{a}}_{nm} + im_e\omega^{\mathrm{LDA}}_{nm}(r^{\mathrm{a}}_{nm})_{;k^{\mathrm{b}}} \quad \text{for} \quad n\neq m. \tag{I8}$$

Eqs. (77) and (F12),

$$\Delta^{\mathrm{a}}_{nm} = v^{\mathrm{LDA},\mathrm{a}}_{nn} - v^{\mathrm{LDA},\mathrm{a}}_{mm}, \tag{I9}$$

$$(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{a}}} = -i\mathcal{T}^{\mathrm{ab}}_{nm} + \frac{r^{\mathrm{a}}_{nm}\Delta^{\mathrm{b}}_{mn} + r^{\mathrm{b}}_{nm}\Delta^{\mathrm{a}}_{mn}}{\omega^{\mathrm{LDA}}_{nm}} + \frac{i}{\omega^{\mathrm{LDA}}_{nm}}\sum_{\ell}\left(\omega^{\mathrm{LDA}}_{\ell m}r^{\mathrm{a}}_{n\ell}r^{\mathrm{b}}_{\ell m} - \omega^{\mathrm{LDA}}_{n\ell}r^{\mathrm{b}}_{n\ell}r^{\mathrm{a}}_{\ell m}\right), \tag{I10}$$

with $\mathcal{T}^{\rm ab}_{nm}\approx 0$ for $n\neq m$. Also, Eq. (89)

$$
\begin{aligned}
(v^{\rm LDA,a}_{nn})_{;k^{\rm b}} &= -i\mathcal{T}^{\rm ab}_{nn} - \sum_{\ell\neq n}\omega^{\rm LDA}_{\ell n}\Big(r^{\rm a}_{n\ell}r^{\rm b}_{\ell n}+r^{\rm b}_{n\ell}r^{\rm a}_{\ell n}\Big)\\
&\approx \frac{\hbar}{m_e}\delta_{\rm ab} - \sum_{\ell\neq n}\omega^{\rm LDA}_{\ell n}\Big(r^{\rm a}_{n\ell}r^{\rm b}_{\ell n}+r^{\rm b}_{n\ell}r^{\rm a}_{\ell n}\Big),
\end{aligned} \tag{I11}
$$

since $\mathcal{T}^{\rm ab}_{nn}\approx(\hbar/m_e)\delta_{\rm ab}$ for $n=m$.

Eq. (C4) , (C5) and (18)

$$
\begin{aligned}
\mathcal{V}^{S,{\rm a},\ell}_{nm} &= \frac{1}{2}\sum_q\Big(v^{S,{\rm a}}_{nq}\mathcal{C}^{\ell}_{qm}+\mathcal{C}^{\ell}_{nq}v^{S,{\rm a}}_{qm}\Big)\\
\big(\mathcal{V}^{S,{\rm a}}_{nm}\big)_{;k^{\rm b}} &= \frac{1}{2}\sum_q\Big((v^{S,{\rm a}}_{nq})_{;k^{\rm b}}\mathcal{C}^{\ell}_{qm}+v^{S,{\rm a}}_{nq}(\mathcal{C}^{\ell}_{qm})_{;k^{\rm b}}+(\mathcal{C}^{\ell}_{nq})_{;k^{\rm b}}v^{S,{\rm a}}_{qm}+\mathcal{C}^{\ell}_{nq}(v^{S,{\rm a}}_{qm})_{;k^{\rm b}}\Big)\,,
\end{aligned} \tag{I12}
$$

with (Eqs. (18) and (C5))

$$
v^{S,{\rm a}}_{nm} = i\Delta f_{mn}r^{\rm a}_{nm}, \tag{I13}
$$

$$
(v^{S,{\rm a}}_{nm})_{;k^{\rm b}} = i\Delta f_{mn}(r^{\rm a}_{nm})_{;k^{\rm b}}. \tag{I14}
$$

Eq. (H4) and (C9)

$$
\mathcal{C}^{\ell}_{nm}(\mathbf{k}) = \sum_{\mathbf{G},\mathbf{G}'}A^*_{n\mathbf{k}}(\mathbf{G}')A_{m\mathbf{k}}(\mathbf{G})\delta_{\mathbf{G}_\parallel\mathbf{G}'_\parallel}f_\ell(G_\perp-G'_\perp). \tag{I15}
$$

$$
(\mathcal{C}^{\ell}_{nm})_{;\mathbf{k}} = i\sum_{q\neq nm}\Big(r^{\rm a}_{nq}\mathcal{C}^{\ell}_{qm}-\mathcal{C}^{\ell}_{nq}r^{\rm a}_{qm}\Big)+ir^{\rm a}_{nm}(\mathcal{C}^{\ell}_{mm}-\mathcal{C}^{\ell}_{nn}). \tag{I16}
$$

Δ is the value of the scissors shift, not to be confused with Δ_{nm}. $\mathcal{C}^{\ell}_{nm}(\mathbf{k})$ must be coded in the same subroutine of $\boldsymbol{\mathcal{V}}^{\ell}_{nm}$ calculated with Eq. (H2)

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