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Longitudinal Gauge Theory of Surface Second Harmonic Generation

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Abstract

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

Contents

I. INTRODUCTION

intro

Second harmonic generation (SHG) has become a powerful spectroscopic tool to study optical properties of surfaces and interfaces since it has the advantage of being surface sensitive. For centrosymmetric materials inversion symmetry forbids, within the dipole approximation, SHG from the bulk, but it is allowed at the surface, where the inversion symmetry is broken. Therefore, SHG should necessarily come from a localized surface region. SHG allows to study the structural atomic arrangement and phase transitions of clean and adsorbate covered surfaces, and since it is an optical probe, it can be used out of UHV conditions, and is non-invasive and non-destructive. On the experimental side, the new tunable high intensity laser systems have made SHG spectroscopy readily accessible and applicable to a wide range of systems.[1,2] However, the theoretical development of the field is still an ongoing subject of research. Some recent advances for the case of semiconducting and metallic systems have appeared in the literature, where the confrontation of theoretical models with experiment has yield correct physical interpretations for the 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 showed a method to systematically investigate the different contributions to the observed peaks in SHG.[12] The approach consisted in the separation of the different contributions tothe nonlinear susceptibility according to 1ω and 2ω transitions and tothe surface or bulk character of the states among which the transitions take place. To complement above results, on this article we review the calculation of the nonlinear susceptibility using the longitudinal gauge, and show that it is posible to clearly obtain the "layer-by-layer" contribution for a slab scheme, used for a surface calculation.

II. LONGITUDINAL GAUGE

To calculate the optical properties of a given system within the longitudinal gauge, we follow the article by Aversa and Sipe.[13] A more recent derivation can also be found in Ref. [14] and [15]. Assuming the long-wavelength approximation, which implies a position independent electric field, $\mathbf{E}(t)$, the hamiltonian in the so called length gauge approximation is given by

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

with

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

and

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

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

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

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

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

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with f_n the Fermi-Dirac factor. We have that

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

where

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

is the $\mathbf{k}$-independent scissored energy, with $\Delta = E_g - E_g^{\mathrm{LDA}}$, where E_g could be the experimental or GW band gap. In above we used the fact that $|n\mathbf{k}\rangle^{\mathrm{LDA}} \approx |n\mathbf{k}\rangle^{S}$, and thus there is no need to label the Bloch states with LDA or S, superscripts. The matrix elements of $\mathbf{r}$ are split between its *interband* part $\mathbf{r}_i$ and *interband* part $\mathbf{r}_e$, where $\mathbf{r} = \mathbf{r}_i + \mathbf{r}_e$ and adamsJCP53,blountSSP62,aversaPRB95 [13,16,17]

$$\begin{aligned} \langle n\mathbf{k}|\hat{\mathbf{r}}_i|m\mathbf{k}'\rangle &= \delta_{nm}\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nn}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right], \qquad (8) \\ \langle n\mathbf{k}|\hat{\mathbf{r}}_e|m\mathbf{k}'\rangle &= (1-\delta_{nm})\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nm}(\mathbf{k}), \qquad (9) \end{aligned}$$

where

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

zetann

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

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

conhrnm

thus defining $\omega^S_{nm\mathbf{k}} = \omega^S_n(\mathbf{k}) - \omega^S_m(\mathbf{k})$ we get

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

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, which contribution in the calculation of the optical response has to be taken with care. Then, 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

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

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

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

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

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

which gives the interband matrix elements of the position operator in terms of the matrix elements of $\mathbf{v}^{\rm LDA}$. These matrix elements do include the matrix elements of $\mathbf{v}^{\rm nl}_{nm}(\mathbf{k})$ that for fully separable nonlocal pseudopotentials in the Kleinman-Bylander form,[18–20] can be readily calculated.[21] In Appendix B we outline how this can be done.

III. TIME-DEPENDENT PERTURBATION THEORY

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

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

where Tr is the trace, that is invariant under cyclic permutations. The dynamical 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, for which we transform all the 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 take 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

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

intrho2

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

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

efield

with

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

got

where $\eta > 0$ assures that at $t = -\infty$ the interaction is zero and has its full strength, $\mathbf{E}$, at $t = 0$. After the required time integrals are done, one takes $\eta \to 0$. Also, $\hat{\rho}_I(t=-\infty)$ should be independent of time, and thus $[\hat{H}, \hat{\rho}]_{t=-\infty} = 0$, which 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

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

nrhon

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

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

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

rhop

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

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

intrho3

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

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

rho0

and

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

rhoN

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

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

rtilde

Now we work out the commutator of Eq. (35). Then,

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

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

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

Now, from Eq. (14) we simply obtain,

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

conmri4

Then Eq. (35) becomes,

$$
\rho^{(N+1)}_{I,nm}(\mathbf{k};t)=\frac{ie}{\hbar}\int_{-\infty}^{t}dt'e^{i(\omega^S_{nm\mathbf{k}}-\tilde{\omega})t'}\left[R^{\mathrm{b}(N)}_e(\mathbf{k};t')+R^{\mathrm{b}(N)}_i(\mathbf{k};t')\right]E^{\mathrm{b}}, \tag{39}
$$

rtilde2

where, the roman superindices a, b, c denote Cartesian components that are summed over if repeated. We start with the linear response, then from Eq. (30) and (37),

$$
\begin{aligned}
R^{\mathrm{b}(0)}_e(\mathbf{k};t) &= \sum_\ell\Big(r^{\mathrm{b}}_{n\ell}(\mathbf{k})\rho^{(0)}_{\ell m}(\mathbf{k})-\rho^{(0)}_{n\ell}(\mathbf{k})r^{\mathrm{b}}_{\ell m}(\mathbf{k})\Big) \\
&= \sum_\ell\Big(r^{\mathrm{b}}_{n\ell}(\mathbf{k})\delta_{\ell m}f_m(\hbar\omega^S_m(\mathbf{k}))-\delta_{n\ell}f_n(\hbar\omega^S_n(\mathbf{k}))r^{\mathrm{b}}_{\ell m}(\mathbf{k})\Big) \\
&= f_{mn\mathbf{k}}r^{\mathrm{b}}_{nm}(\mathbf{k}),
\end{aligned}
\tag{40}
$$

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 $n\neq m$. Also, from Eq. (38) and Eq. (15)

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

R0i

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 $\mathbf{R}^{(0)}_i=0$. Therefore the linear response has no contribution from intraband transitions. Then,

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

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

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

rhonoi1

with

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

rho1

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

$$
\begin{aligned}
R^{\mathrm{b}(1)}_{e}(\mathbf{k};t) &= \sum_{\ell} \Big(r^{\mathrm{b}}_{n\ell}(\mathbf{k}) \rho^{(1)}_{\ell m}(\mathbf{k};t) - \rho^{(1)}_{n\ell}(\mathbf{k};t) r^{\mathrm{b}}_{\ell m}(\mathbf{k}) \Big) \\
&= \sum_{\ell} \Big(r^{\mathrm{b}}_{n\ell}(\mathbf{k}) B^{\mathrm{c}}_{\ell m}(\mathbf{k},\omega_\beta) - B^{\mathrm{c}}_{n\ell}(\mathbf{k},\omega_\beta) r^{\mathrm{b}}_{\ell m}(\mathbf{k}) \Big) E^{\mathrm{c}}_{\omega_\beta}(t),
\end{aligned}
\tag{45}
$$

and from Eq. (38)

$$
R^{\mathrm{b}(1)}_{i}(\mathbf{k};t) = i(\rho^{(1)}_{nm}(t))_{;k^{\mathrm{b}}} = iE^{\mathrm{c}}_{\omega_\beta}(t)(B^{\mathrm{c}}_{nm}(\mathbf{k},\omega_\beta))_{;k^{\mathrm{b}}}.
\tag{46}
$$

R1i

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

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

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

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

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 $i = \alpha, \beta$, where $B^{\mathrm{a}}_{\ell m}(\mathbf{k},\omega_\alpha)$ 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, and 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 two surfaces, say the front and the back surface, and in between these two surfaces 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 any more their bulk partner atoms, since these, by definition, are absent above (below) the front (back) surface of the slab. Therefore, to take the reconstruction into account, by surface we really mean the true surface that consists of the very first relaxed layer of atoms, and some of the sub-true-surface relaxed atomic layers. Since the front and the back surfaces of the slab are usually identical, the total slab is centrosymmetric. This fact (see Sec. IV), will imply $\chi^{slab}_{\mathrm{abc}} = 0$, and thus we must device a way in which this artifact of a centrosymmetric slab is bypassed 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, thus breaking the centrosymmetry and therefore giving an overall $\chi^{slab}_{\mathrm{abc}} \neq 0$, we need a procedure to extract the front surface χ^{f}_{abc} and the back surface χ^{b}_{abc} from the slab non-linear susceptibility $\chi^{slab}_{\mathrm{abc}}$.

A convenient way to accomplish the separation of the SH signal of either surface is to introduce the so called "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 $\mathcal{C}(z) = 1$. However, 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,

$$
\mathcal{C}^{\ell}(z) = \Theta(z - z_\ell + \Delta^{\mathrm{b}}_\ell)\Theta(z_\ell - z + \Delta^{f}_\ell), \qquad (49)
$$

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

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

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

jmic

where the operator for the electron's current is

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

hatjmic

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 the cyclic invariance of the trace to write

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

where

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

jmic3

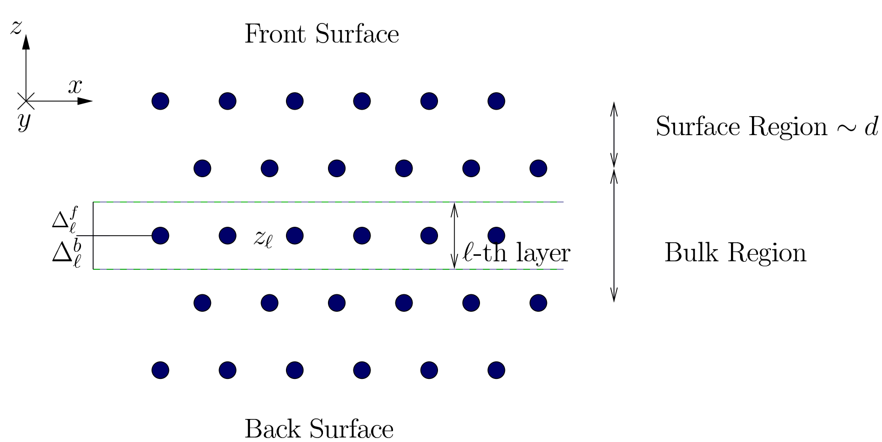

FIG. 1: We show a sketch of the slab, where the small circles represent the atoms. See the text for the details.

fslab

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, however, 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

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

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

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

to write

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

as the induced macroscopic current of the ℓ-th layer, to order N-th 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

$$J^{(N,\ell)}_{\mathrm{a}}(\omega_3) = \frac{e}{\Omega}\sum_{mn\mathbf{k}} \mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}(\mathbf{k})\rho^{(N)}_{nm}(\mathbf{k};\omega_3). \tag{57} \qquad \boxed{\texttt{jmac2}}$$

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

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

and using the following property

$$\langle\mathbf{r}|\hat{\mathbf{v}}^\Sigma(\mathbf{r},\mathbf{r}')|n\mathbf{k}\rangle = \int d^3r''\langle\mathbf{r}|\hat{\mathbf{v}}^\Sigma(\mathbf{r},\mathbf{r}')|\mathbf{r}''\rangle\langle\mathbf{r}''|n\mathbf{k}\rangle = \hat{\mathbf{v}}^\Sigma(\mathbf{r},\mathbf{r}'')\int d^3r''\langle\mathbf{r}|\mathbf{r}''\rangle\langle\mathbf{r}''|n\mathbf{k}\rangle = \hat{\mathbf{v}}^\Sigma(\mathbf{r},\mathbf{r}')\psi_{n\mathbf{k}}(\mathbf{r}), \tag{59} \qquad \boxed{\texttt{nl.2}}$$

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

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

where 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 supres the dependance on z form the crowded notation. Then, 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 what it takes 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.

Actually, 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 latter used in Refs. 3 and 23 in the context of SHG. Then, the layer-by-layer analysis of Refs. 24 and 25 actually used Eq. (49) thus limiting the current response to a particular layer of the slab, and used it 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 optical response, and here for the non-linear optical response of semiconductors.

V. NON-LINEAR SURFACE SUSCEPTIBILITY

In this section we obtain the expressions for the non-linear surface susceptibility tensor to second order in 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, respectively, and the sum continues with higher multipolar terms. If we consider a semi-infinite system with a centrosymmetric bulk, above equation splits, due to symmetry considerations alone, into two contributions, one from the surface of the system and the other from the bulk of the system. Indeed, let's take

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

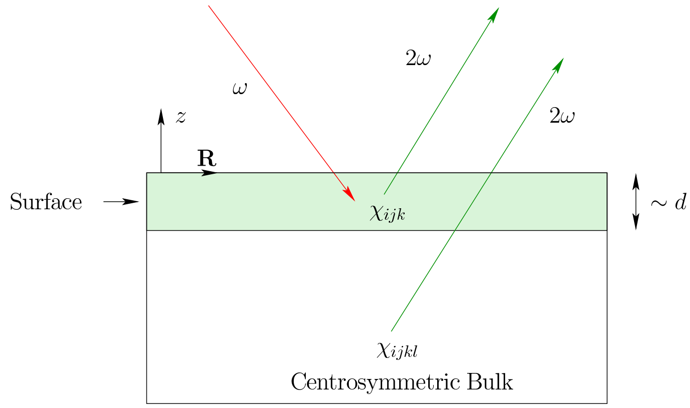

FIG. 2: (color online) We show a sketch of the semi-infinite system with a centrosymmetric bulk. The surface region is of width $\sim d$. The incoming photon of frequency ω is represented by a downward red arrow, whereas both the surface and bulk created second harmonic photons of frequency 2ω are represented by an upward green arrow. The red color suggests an infrared incoming photon whose second harmonic generated photon is in the green. 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 are also shown, with z perpendicular to the surface and $\mathbf{R}$ parallel to it.

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

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

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, since as the system is centrosymmetric, they must be invariant under $\mathbf{r}\to-\mathbf{r}$. Recalling that $\mathbf{P}(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$, are polar vectors,[27] we have that Eq. (66) reduces to

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

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

$$\chi_{\rm abc}=0 \qquad \text{for a centrosymmetric bulk.} \tag{68}$$

Therefore, if we move to the surface of the semi-infinite system, the assumption of centrosymmetry necessarily breaks down, and there is no restriction in $\chi_{\rm abc}$. Thus, we conclude that the leading term of the polarization in a surface region is given by

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

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). Also, $d\mathbf{P} \equiv \mathbf{P}^{s}$ is the surface SH polarization, given by

$$P_{\mathrm{a}}^{s} = \frac{1}{\mathcal{S}} \chi_{\mathrm{abc}} E_{\mathrm{b}} E_{\mathrm{c}} = \chi_{\mathrm{abc}}^{s} E_{\mathrm{b}} E_{\mathrm{c}}, \tag{70}$$

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

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

gives the bulk polarization. Immediately we see that the surface polarization is of dipolar order, whereas the bulk polarization is of quadrupolar order, and that the rank of the susceptibility tensors is 3 for the surface, i.e. χ_{abc}, and 4 for the bulk, i.e. χ_{abcl}. Although the bulk generated SH is in itself a very important optical phenomena, in here we concentrate only in the surface generated SH. Indeed, in centrosymmetric systems for which the quadrupolar bulk response is much smaller that the dipolar surface response, SH is readily used as a very useful and powerful optical surface probe.[1]

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

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

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

$$\begin{aligned}
\chi_{\mathrm{abc}}^{s,\ell}(-\omega_3;\omega_1,\omega_2) &= \frac{ie}{\Omega E_1^{\mathrm{b}} E_2^{\mathrm{c}} \mathcal{S} \omega_3} \sum_{mn\mathbf{k}} \mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell}(\mathbf{k}) \rho_{nm}^{(2)}(\mathbf{k};\omega_3) \\
&= \frac{e^2}{\mathcal{S}\Omega\hbar\omega_3} \sum_{mn\mathbf{k}} \frac{\mathcal{V}_{mn}^{\Sigma,\mathrm{a},\ell}(\mathbf{k})}{\omega_{nm\mathbf{k}}^{S} - \tilde{\omega}_3} \Big[- (B_{nm}^{\mathrm{c}}(\mathbf{k},\omega_\beta))_{;k^{\mathrm{b}}} \\
&\quad + i \sum_{\ell} \Big(r_{n\ell}^{\mathrm{b}} B_{\ell m}^{\mathrm{c}}(\mathbf{k},\omega_\beta) - B_{n\ell}^{\mathrm{c}}(\mathbf{k},\omega_\beta) r_{\ell m}^{\mathrm{b}} \Big) \Big],
\end{aligned} \tag{73}$$

which gives the surface susceptibility of layer ℓ-th, where $\boldsymbol{\mathcal{V}}^{\Sigma}$ is given in Eq. (63). Using Eq. (44), we split above equation into two contributions, one coming from the first term and the other from the second term on the r.h.s.,

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

chii

and

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

chie

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 confusing 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

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

gene2

and

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

eli.13

as shown in Appendix D.

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

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

chiijksur

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). Of course we can use Eq. (78) for either the front or the back surface. Likewise

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

chiijklf

is a dipolar bulk susceptibility, with the property that,

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

chiijkbul

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

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. As shown in the Appendix E using time-reversal invariance these divergences can be removed, and the following expressions for $\boldsymbol{\chi}$ are obtained

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

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

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

and

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

where 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 Cartesian indices bc, i.e. $\{u^{\mathrm{b}}s^{\mathrm{c}}\} = (u^{\mathrm{b}}s^{\mathrm{c}} + u^{\mathrm{c}}s^{\mathrm{b}})/2$, from where we obtain that $\chi^{s,\ell}_{\mathrm{abc}} = \chi^{s,\ell}_{\mathrm{acb}}$. In Appendices F and C we show how to calculate the generalized derivatives of $\mathbf{r}_{nm;\mathbf{k}}$ and $\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm;\mathbf{k}}$, respectively. Indeed, 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

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

with

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

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

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

Finally, for $\mathcal{V}^{\Sigma,{\rm a},\ell}_{nm;\mathbf{k}}$, among other quantities we also need the following term

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

where we also use Eq. (tau.69 88). Above is the standard effective-mas sum rule. ashcroft_solid_1976 [31]

VI. CONCLUSIONS

con

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 the "layer-by-layer" approach. We have done so for a semiconductor using the length gauge for the coupling of the external electric field to the electron.

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

reri

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

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

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

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

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

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

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

$$\frac{\partial}{\partial\mathbf{k}}\langle n\mathbf{k}|m\mathbf{k}'\rangle = \delta_{nm}\frac{\partial}{\partial\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}'), \tag{A4}$$ ddk1

on the other,

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

the derivative of the wavefunction is simply given by

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

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

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

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

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

to finally write,[blountSSP62 17]

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

where Ω is the volume of the unit cell. From

$$\int_\Omega u_{m\mathbf{k}}u^*_{n\mathbf{k}}d\mathbf{r} = \delta_{nm}, \tag{A10}$$ dnm1

we easily find that

$$\int_\Omega d\mathbf{r}\left(\frac{\partial}{\partial \mathbf{k}}u_{m\mathbf{k}}(\mathbf{r})\right)u^*_{n\mathbf{k}}(\mathbf{r}) = -\int_\Omega d\mathbf{r}\, u_{m\mathbf{k}}(\mathbf{r})\left(\frac{\partial}{\partial \mathbf{k}}u^*_{n\mathbf{k}}(\mathbf{r})\right). \tag{A11}$$ dnm2

Therefore, we define

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

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

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

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,

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

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

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

Then,

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}_i,\hat{\mathcal{O}}]|m\mathbf{k}'\rangle = i\delta(\mathbf{k}-\mathbf{k}')(\mathcal{O}_{nm})_{;\mathbf{k}}, \tag{A18}$$ $\boxed{\texttt{conmri3}}$

with

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

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 $\mathbf{v}^{\rm nl}_{nm}(\mathbf{k})$

We obtain the matrix elements of $\mathbf{v}^{\rm nl}_{nm}(\mathbf{k})$ 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, ˆ, on top. We want to calculate

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

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,

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

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,[18–20] above matrix elements can be readily calculated.[21] 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

$$
\begin{aligned}
\mathcal{V}^{{\rm LDA},{\rm a},\ell}_{nm} &= \frac{1}{2}\left(v^{\rm LDA,a}\mathcal{C}^\ell+\mathcal{C}^\ell v^{\rm LDA,a}\right)_{nm} \\
&= \frac{1}{2}\sum_q\left(v^{\rm LDA,a}_{nq}\mathcal{C}^\ell_{qm}+\mathcal{C}^\ell_{nq}v^{\rm LDA,a}_{qm}\right) \\
(\mathcal{V}^{\rm LDA,a}_{nm})_{;k^{\rm b}} &= \frac{1}{2}\sum_q\left(v^{\rm LDA,a}_{nq}\mathcal{C}^\ell_{qm}+\mathcal{C}^\ell_{nq}p^{\rm LDA,a}_{qm}\right)_{;k^{\rm b}} \\
&= \frac{1}{2}\sum_q\left((v^{\rm LDA,a}_{nq})_{;k^{\rm b}}\mathcal{C}^\ell_{qm}+v^{\rm LDA,a}_{nq}(\mathcal{C}^\ell_{qm})_{;k^{\rm b}}+(\mathcal{C}^\ell_{nq})_{;k^{\rm b}}v^{\rm LDA,a}_{qm}+\mathcal{C}^\ell_{nq}(v^{\rm LDA,a}_{qm})_{;k^{\rm b}}\right),
\end{aligned}
\tag{C2}
$$

where we omitted $\mathbf{k}$ in all quantities. From Eq. (B8) we know that $\mathbf{v}^{\rm nl}_{nm}(\mathbf{k})$ can be readily calculated, and from Appendix H, both v^a_{nm} and $\mathcal{C}^\ell_{nm}$ are also known quantities, and thus the $\mathbf{v}^{\rm LDA}_{nm}(\mathbf{k})$

are known, which in turns means that $\mathcal{V}^{\mathrm{LDA,a},\ell}_{nm}$ are also known. For the generalized derivative $(\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k}))_{;\mathbf{k}}$ we use Eq. (21) to write

$$\begin{aligned}
(v^{\mathrm{LDA,a}}_{nm})_{;k^{\mathrm{b}}} &= im_e(\omega^{\mathrm{LDA}}_{nm} r^{\mathrm{a}}_{nm})_{;k^{\mathrm{b}}} \\
&= im_e(\omega^{\mathrm{LDA}}_{nm})_{;k^{\mathrm{b}}} r^{\mathrm{a}}_{nm} + im_e\omega^{\mathrm{LDA}}_{nm}(r^{\mathrm{a}}_{nm})_{;k^{\mathrm{b}}} \\
&= im_e\Delta^b_{nm} r^{\mathrm{a}}_{nm} + im_e\omega^{\mathrm{LDA}}_{nm}(r^{\mathrm{a}}_{nm})_{;k^{\mathrm{b}}} \quad \text{for} \quad n \neq m,
\end{aligned} \tag{C3}$$

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

Likewise,

$$\mathcal{V}^{S,\mathrm{a},\ell}_{nm} = \frac{1}{2}\sum_q \left((v^{S,\mathrm{a}}_{nq})_{;k^{\mathrm{b}}} \mathcal{C}^\ell_{qm} + v^{S,\mathrm{a}}_{nq}(\mathcal{C}^\ell_{qm})_{;k^{\mathrm{b}}} + (\mathcal{C}^\ell_{nq})_{;k^{\mathrm{b}}} v^{S,\mathrm{a}}_{qm} + \mathcal{C}^\ell_{nq}(v^{S,\mathrm{a}}_{qm})_{;k^{\mathrm{b}}} \right), \tag{C4}$$

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

$$(v^{S,\mathrm{a}}_{nm})_{;k^{\mathrm{b}}} = i\Delta f_{mn}(r^{\mathrm{a}}_{nm})_{;k^{\mathrm{b}}}. \tag{C5}$$

To evaluate $(\mathcal{C}^\ell_{nm})_{;k^{\mathrm{a}}}$, 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,

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

The interband part reduces to,

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

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

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

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then from Eq. (C6)

$$\left((\mathcal{C}^\ell_{nm})_{;\mathbf{k}} - i\sum_q \left(\xi^{\rm a}_{nq}\mathcal{C}^\ell_{qm} - \mathcal{C}^\ell_{nq}\xi^{\rm a}_{qm}\right) - i\mathcal{C}^\ell_{nm}(\xi^{\rm a}_{mm} - \xi^{\rm a}_{nn})\right) i\delta(\mathbf{k}-\mathbf{k}') = 0$$

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

since in every $\xi^{\rm a}_{nm}$, $n \neq m$, thus we replace it by $r^{\rm a}_{nm}$.

For the general case of

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

above result would lead to a more general expression,

$$(\mathcal{G}_{nm}(\mathbf{k}))_{;k^{\rm a}} \;=\; \mathcal{U}_{nm}(\mathbf{k}) + i\sum_{q\neq(nm)} \left(r^{\rm a}_{nq}(\mathbf{k})\mathcal{G}_{qm}(\mathbf{k}) - \mathcal{G}_{nq}(\mathbf{k})r^{\rm a}_{qm}(\mathbf{k})\right) + ir^{\rm a}_{nm}(\mathbf{k})(\mathcal{G}_{mm}(\mathbf{k}) - \mathcal{G}_{nn}(\mathbf{k})), \qquad \text{(C11)}$$

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

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

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

$$\langle n\mathbf{k}|\hat{H}^S_0|m\mathbf{k}'\rangle = \delta_{nm}\delta(\mathbf{k}-\mathbf{k}')\hbar\omega^S_m(\mathbf{k}), \qquad \text{(D1)}$$ a_conH0

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

$$\begin{aligned}
(H^S_{0,nn})_{;\mathbf{k}} &= \nabla_{\mathbf{k}} H^S_{0,nn}(\mathbf{k}) - iH^S_{0,nn}(\mathbf{k})\left(\boldsymbol{\xi}_{nn}(\mathbf{k}) - \boldsymbol{\xi}_{nn}(\mathbf{k})\right) \\
&= \hbar\nabla_{\mathbf{k}}\omega^S_m(\mathbf{k}), \qquad \text{(D2)}
\end{aligned}$$

where from Eq. (A18),

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

then

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

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From Eq. (11)

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

a_hr

therefore, substituting above into

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

a_hrt

we get

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

a_hrt2

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)

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

a_gradw2

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 χ^s_{abc} in terms of $\mathcal{V}_{mn}^{\Sigma,\mathbf{a},\ell}$

appv

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. Interband Contributions

For the int$E$rband term, Eq. (75) we get

$$\begin{aligned}
E &= A\left[-\frac{1}{2\omega_{lm}^S(2\omega_{lm}^S - \omega_{nm}^S)}\frac{1}{\omega_{lm}^S - \omega} + \frac{2}{\omega_{nm}^S(2\omega_{lm}^S - \omega_{nm}^S)}\frac{1}{\omega_{nm}^S - 2\omega} + \frac{1}{2\omega_{lm}^S\omega_{nm}^S}\frac{1}{\omega}\right] \\
&- B\left[-\frac{1}{2\omega_{nl}^S(2\omega_{nl}^S - \omega_{nm}^S)}\frac{1}{\omega_{nl}^S - \omega} + \frac{2}{\omega_{nm}^S(2\omega_{nl}^S - \omega_{nm}^S)}\frac{1}{\omega_{nm}^S - 2\omega} + \frac{1}{2\omega_{nl}^S\omega_{nm}^S}\frac{1}{\omega}\right],
\end{aligned} \tag{E1}$$

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

??Needs to be completed??

2. Intraband Contributions

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

$$
\begin{aligned}
I \;=\; & C\left[-\frac{1}{2(\omega^S_{nm})^2}\frac{1}{\omega^S_{nm}-\omega}+\frac{2}{(\omega^S_{nm})^2}\frac{1}{\omega^S_{nm}-2\omega}+\frac{1}{2(\omega^S_{nm})^2}\frac{1}{\omega}\right] \\
- \; & D\left[-\frac{3}{2(\omega^S_{nm})^3}\frac{1}{\omega^S_{nm}-\omega}+\frac{4}{(\omega^S_{nm})^3}\frac{1}{\omega^S_{nm}-2\omega}+\frac{1}{2(\omega^S_{nm})^3}\frac{1}{\omega}-\frac{1}{2(\omega^S_{nm})^2}\frac{1}{(\omega^S_{nm}-\omega)^2}\right], \qquad \text{(E2)}
\end{aligned}
$$

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

Time-reversal symmetry leads to the following relationships:

$$
\begin{aligned}
\mathbf{r}_{mn}(\mathbf{k})|_{-\mathbf{k}} &= \mathbf{r}_{nm}(\mathbf{k})|_{\mathbf{k}}, \\
(\mathbf{r}_{mn})_{;\mathbf{k}}(\mathbf{k})|_{-\mathbf{k}} &= (-\mathbf{r}_{nm})_{;\mathbf{k}}(\mathbf{k})|_{\mathbf{k}}, \\
\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}(\mathbf{k})|_{-\mathbf{k}} &= -\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm}(\mathbf{k})|_{\mathbf{k}}, \\
(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn})_{;\mathbf{k}}(\mathbf{k})|_{-\mathbf{k}} &= (\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm})_{;\mathbf{k}}(\mathbf{k})|_{\mathbf{k}}, \qquad \text{(E3)} \\
\omega^S_{mn}(\mathbf{k})|_{-\mathbf{k}} &= \omega^S_{mn}(\mathbf{k})|_{\mathbf{k}}, \\
\Delta^a_{nm}(\mathbf{k})|_{-\mathbf{k}} &= -\Delta^a_{nm}(\mathbf{k})|_{\mathbf{k}}.
\end{aligned}
$$

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 (E2) 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

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

and likewise,

$$
\begin{aligned}
D \to f_{mn}\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}\Delta^{\mathrm{c}}_{nm}|_{\mathbf{k}} + f_{mn}\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}\Delta^{\mathrm{c}}_{nm}|_{-\mathbf{k}}& \\
&= f_{mn}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}\Delta^{\mathrm{c}}_{nm}|_{\mathbf{k}} + \left(-\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm}\right) r^{\mathrm{LDA,b}}_{mn}\left(-\Delta^{\mathrm{c}}_{nm}\right)|_{\mathbf{k}}\right] \\
&= f_{mn}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm} + \mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm} r^{\mathrm{LDA,b}}_{mn}\right]\Delta^{\mathrm{c}}_{nm} \\
&= f_{mn}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm} + \left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}\right)^*\right]\Delta^{\mathrm{c}}_{nm} \\
&= 2f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}\right]\Delta^{\mathrm{c}}_{nm}.
\end{aligned} \tag{E5}
$$

The last term in the second line of Eq. (E2) is dealt with as follows.

$$
\begin{aligned}
\frac{D}{2(\omega^S_{nm})^2}\frac{1}{(\omega^S_{nm}-\omega)^2} &= \frac{f_{mn}}{2}\frac{\mathcal{V}^{\Sigma,\mathrm{a}}_{mn} r^{\mathrm{b}}_{nm}}{(\omega^S_{nm})^2}\frac{\Delta^{\mathrm{c}}_{nm}}{(\omega^S_{nm}-\omega)^2} = -\frac{f_{mn}}{2}\frac{\mathcal{V}^{\Sigma,\mathrm{a}}_{mn} r^{\mathrm{b}}_{nm}}{(\omega^S_{nm})^2}\left(\frac{1}{\omega^S_{nm}-\omega}\right)_{;k^{\mathrm{c}}} \\
&= \frac{f_{mn}}{2}\left(\frac{\mathcal{V}^{\Sigma,\mathrm{a}}_{mn} r^{\mathrm{b}}_{nm}}{(\omega^S_{nm})^2}\right)_{;k^{\mathrm{c}}}\frac{1}{\omega^S_{nm}-\omega},
\end{aligned} \tag{E6}
$$

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

$$
\left(\frac{\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}}{(\omega^S_{nm})^2}\right)_{;k^{\mathrm{c}}} = \frac{r^{\mathrm{LDA,b}}_{nm}}{(\omega^S_{nm})^2}\left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\right)_{;k^{\mathrm{c}}} + \frac{\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}}{(\omega^S_{nm})^2}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}} - \frac{2\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}}{(\omega^S_{nm})^3}\left(\omega^S_{nm}\right)_{;k^{\mathrm{c}}}, \tag{E7}
$$

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

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

the second term is reduced to

$$
\begin{aligned}
\frac{\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}}{(\omega^S_{nm})^2}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}|_{\mathbf{k}} + \frac{\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}}{(\omega^S_{nm})^2}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}|_{-\mathbf{k}} &= \frac{\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}}{(\omega^S_{nm})^2}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}|_{\mathbf{k}} + \frac{\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm}}{(\omega^S_{nm})^2}\left(r^{\mathrm{LDA,b}}_{mn}\right)_{;k^{\mathrm{c}}}|_{\mathbf{k}} \\
&= \frac{1}{(\omega^S_{nm})^2}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}} + \left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right)^*\right] \\
&= \frac{2}{(\omega^S_{nm})^2}\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right],
\end{aligned} \tag{E9}
$$

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

$$
\begin{aligned}
\frac{2\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}}{(\omega^S_{nm})^3} \left(\omega^S_{nm}\right)_{;k^{\mathrm{c}}} |_{\mathbf{k}} + \frac{2\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}}{(\omega^S_{nm})^3} \left(\omega^S_{nm}\right)_{;k^{\mathrm{c}}} |_{-\mathbf{k}} &= \frac{2\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}}{(\omega^S_{nm})^3} \Delta^{\mathrm{c}}_{nm}|_{\mathbf{k}} + \frac{2\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}}{(\omega^S_{nm})^3} \Delta^{\mathrm{c}}_{nm}|_{-\mathbf{k}} \\
&= \frac{2\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm} r^{\mathrm{LDA,b}}_{mn}}{(\omega^S_{nm})^3} \Delta^{\mathrm{c}}_{nm}|_{\mathbf{k}} + \frac{2\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}}{(\omega^S_{nm})^3} \Delta^{\mathrm{c}}_{nm}|_{\mathbf{k}} \\
&= \frac{2}{(\omega^S_{nm})^3} \left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm} r^{\mathrm{LDA,b}}_{mn} + \left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm} r^{\mathrm{LDA,b}}_{mn}\right)^*\right] \Delta^{\mathrm{c}}_{nm} \\
&= \frac{4}{(\omega^S_{nm})^3} \mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm} r^{\mathrm{LDA,b}}_{mn}\right] \Delta^{\mathrm{c}}_{nm}. \qquad \text{(E10)}
\end{aligned}
$$

Combining the results from (E8), (E9), and (E10) into (E7),

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

$$
\left(2\,\mathrm{Re}\left[r^{\mathrm{LDA,b}}_{nm}\left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\right)_{;k^{\mathrm{c}}}\right] + 2\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right] - \frac{4}{\omega^S_{nm}}\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm} r^{\mathrm{LDA,b}}_{mn}\right] \Delta^{\mathrm{c}}_{nm}\right) \frac{f_{mn}}{2(\omega^S_{nm})^2} \frac{1}{\omega^S_{nm} - \omega}. \tag{E11}
$$

We substitute (E4), (E5), and (E11) in (E2),

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

If we simplify,

$$
\begin{aligned}
I = &-\frac{2f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right]}{2(\omega^S_{nm})^2} \frac{1}{\omega^S_{nm} - \omega} + \frac{4f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right]}{(\omega^S_{nm})^2} \frac{1}{\omega^S_{nm} - 2\omega} \\
&+ \frac{6f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}\right] \Delta^{\mathrm{c}}_{nm}}{2(\omega^S_{nm})^3} \frac{1}{\omega^S_{nm} - \omega} - \frac{8f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}\right] \Delta^{\mathrm{c}}_{nm}}{(\omega^S_{nm})^3} \frac{1}{\omega^S_{nm} - 2\omega} \\
&+ \frac{2f_{mn}\,\mathrm{Re}\left[r^{\mathrm{LDA,b}}_{nm}\left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\right)_{;k^{\mathrm{c}}}\right]}{2(\omega^S_{nm})^2} \frac{1}{\omega^S_{nm} - \omega} \\
&+ \frac{2f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right]}{2(\omega^S_{nm})^2} \frac{1}{\omega^S_{nm} - \omega} \\
&- \frac{4f_{mn}\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm} r^{\mathrm{LDA,b}}_{mn}\right] \Delta^{\mathrm{c}}_{nm}}{2(\omega^S_{nm})^3} \frac{1}{\omega^S_{nm} - \omega},
\end{aligned}
\tag{E12}
$$

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

$$\begin{aligned} I_{2\omega} &= -\frac{e^3}{\hbar^2}\sum_{mn\mathbf{k}}\left[\frac{4f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right]}{(\omega^S_{nm})^2} - \frac{8f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}\right]\Delta^{\mathrm{c}}_{nm}}{(\omega^S_{nm})^3}\right]\frac{1}{\omega^S_{nm}-2\omega} \\ &= -\frac{e^3}{\hbar^2}\sum_{mn\mathbf{k}}\frac{4f_{mn}}{(\omega^S_{nm})^2}\left[\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right] - \frac{2\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}\right]\Delta^{\mathrm{c}}_{nm}}{\omega^S_{nm}}\right]\frac{1}{\omega^S_{nm}-2\omega}. \end{aligned} \tag{E13}$$
2wchii

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,

$$\lim_{\eta\to 0}\frac{1}{x\pm i\eta} = P\frac{1}{x} \mp i\pi\delta(x), \tag{E14}$$
limit_eta

and can finally rewrite (2wchii E13) in the desired form,

$$\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{a},\ell\mathrm{bc},2\omega}] = -\frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\frac{4}{(\omega^S_{cv})^2}\left(\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc}\left(r^{\mathrm{LDA,b}}_{cv}\right)_{;k^{\mathrm{c}}}\right] - \frac{2\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc} r^{\mathrm{LDA,b}}_{cv}\right]\Delta^{\mathrm{c}}_{cv}}{\omega^S_{cv}}\right)\delta(\omega^S_{cv}-2\omega). \tag{E15}$$
imchi2w

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

We do the same for the ω terms in (simplified_i E12) to obtain

$$\begin{aligned} I_{\omega} = -\frac{e^3}{2\hbar^2}\sum_{nm\mathbf{k}}\Bigg[&-\frac{2f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right]}{(\omega^S_{nm})^2} + \frac{6f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}\right]\Delta^{\mathrm{c}}_{nm}}{(\omega^S_{nm})^3} \\ &+\frac{2f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\left(r^{\mathrm{LDA,b}}_{nm}\right)_{;k^{\mathrm{c}}}\right]}{(\omega^S_{nm})^2} - \frac{4f_{mn}\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{nm} r^{\mathrm{LDA,b}}_{mn}\right]\Delta^{\mathrm{c}}_{nm}}{(\omega^S_{nm})^3} \\ &+\frac{2f_{mn}\,\mathrm{Re}\left[r^{\mathrm{LDA,b}}_{nm}\left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\right)_{;k^{\mathrm{c}}}\right]}{(\omega^S_{nm})^2}\Bigg]\frac{1}{\omega^S_{nm}-\omega}. \end{aligned} \tag{E16}$$
wchii

We reduce in the same way as (2wchii E13),

$$I_{\omega} = -\frac{e^3}{2\hbar^2}\sum_{nm\mathbf{k}}\frac{f_{mn}}{(\omega^S_{nm})^2}\left[2\,\mathrm{Re}\left[r^{\mathrm{LDA,b}}_{nm}\left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn}\right)_{;k^{\mathrm{c}}}\right] + \frac{2\,\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{mn} r^{\mathrm{LDA,b}}_{nm}\right]\Delta^{\mathrm{c}}_{nm}}{\omega^S_{nm}}\right]\frac{1}{\omega^S_{nm}-\omega}, \tag{E17}$$
wchii_simpli

and using (limit_eta E14) we obtain our final form,

$$\mathrm{Im}[\chi^{s,\ell}_{i,\mathrm{a},\ell\mathrm{bc},\omega}] = -\frac{\pi|e|^3}{2\hbar^2}\sum_{cv\mathbf{k}}\frac{1}{(\omega^S_{cv})^2}\left(\mathrm{Re}\left[r^{\mathrm{LDA,b}}_{cv}\left(\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc}\right)_{;k^{\mathrm{c}}}\right] + \frac{\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a},\ell}_{vc} r^{\mathrm{LDA,b}}_{cv}\right]\Delta^{\mathrm{c}}_{cv}}{\omega^S_{cv}}\right)\delta(\omega^S_{cv}-\omega), \tag{E18}$$

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

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

gdernl

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. (conhr I7))

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

na_hrdab

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

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

na_hrdab2

so

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

na_hrdab3

From Eq. (conmri3 A18) and (gendev A19)

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

na_rip

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

na_ripn

and

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

Using Eqs. (na_rip F4) and (na_rep F6) into Eq. (na_hrdab3 F3) gives

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

then

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

and from Eq. (F5),

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

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

Case $n=m$

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

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 $n\neq m$

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

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

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

where the $-i\mathcal{T}_{nm}$ term, generalizes the usual expresion of $\mathbf{r}_{nm;\mathbf{k}}$ for local Hamiltonians,[13,29,32,33] aversaPRB95,nastosPRB05,cab to the case of a nonlocal potential in the Hamiltonian.

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

calt

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

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

for which we need the following triple commutator

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

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

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

Then,

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

We use the following identity

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

to write

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

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 $[\hat{V}^{\rm nl}(\hat{\mathbf{r}},\hat{\mathbf{r}}'),\hat{r}^{\rm b}]$,[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)

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

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

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

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 (Chon:de tu libreta copia el algebra que nos lleva a esta ecuación)

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

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 Eq. (H2) we recover the well known result

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

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

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