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Longitudinal Gauge Theory of Surface Second Harmonic Generation

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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.

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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] downer01 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.[1–8] downer01,mendoza01a,lim00,gav00,mendoza99,mendoza98a,mendoza96,guyot90

In a previous article,[9] mendoza01b 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.[10] arzate00 The approach consisted in the separation of the different contributions to the nonlinear susceptibility according to 1ω and 2ω transitions and to the 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

longi

To calculate the optical properties of a given system within the longitudinal gauge, we follow the article by Aversa and Sipe.[11] aversa95 A more recent derivation can also be found in Ref. 12 sipe00 and 13 lambrecht00. Assuming the long-wavelength approximation, which implies a position independent electric field, the hamiltonian in the so called length gauge approximation is given by

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

where $H_0 = p^2/2m + V(\mathbf{r}) + V^{\mathrm{nl}}(\mathbf{r}, \mathbf{p})$, where $V(\mathbf{r}) = V(\mathbf{r}+\mathbf{R})$ is the periodic crystal potential, with $\mathbf{R}$ the real-space lattice vector, and $\hat{V}^{\mathrm{nl}}$ a nonlocal potential. The electric field $\mathbf{E} = -\dot{\mathbf{A}}/c$, with $\mathbf{A}$ the vector potential. H_0 has eigenvalues $\hbar\omega_n(\mathbf{k})$ and eigenvectors $|n\mathbf{k}\rangle$ (Bloch states) labeled by a band index n and crystal momentum $\mathbf{k}$. The r representation of the Bloch states is given by

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r}|n\mathbf{k}\rangle = \sqrt{\frac{\Omega}{8\pi^3}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \tag{2}$$ bloch

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

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

$$\langle n\mathbf{k}|m\mathbf{k}'\rangle = \delta_{nm}\delta(\mathbf{k}-\mathbf{k}'), \tag{4}$$ nbraket

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

$$\frac{\partial}{\partial \mathbf{k}} \langle n\mathbf{k}|m\mathbf{k}'\rangle = \delta_{nm} \frac{\partial}{\partial \mathbf{k}} \delta(\mathbf{k}-\mathbf{k}'), \tag{5}$$ ddk1

on the other,

$$\begin{aligned} \frac{\partial}{\partial \mathbf{k}} \langle n\mathbf{k}|m\mathbf{k}'\rangle &= \frac{\partial}{\partial \mathbf{k}} \int d\mathbf{r} \langle n\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|m\mathbf{k}'\rangle \\ &= \int d\mathbf{r} \left(\frac{\partial}{\partial \mathbf{k}} \psi^*_{n\mathbf{k}}(\mathbf{r}) \right) \psi_{m\mathbf{k}'}(\mathbf{r}), \end{aligned} \tag{6}$$

the derivative of the wavefunction is simply given by

$$\frac{\partial}{\partial \mathbf{k}} \psi^*_{n\mathbf{k}}(\mathbf{r}) = \sqrt{\frac{\Omega}{8\pi^3}} \left(\frac{\partial}{\partial \mathbf{k}} u^*_{n\mathbf{k}}(\mathbf{r}) \right) e^{-i\mathbf{k}\cdot\mathbf{r}} - i\mathbf{r}\psi^*_{n\mathbf{k}}(\mathbf{r}). \tag{7}$$ dpsi

dkbraket

We take this back into Eq. (6), to obtain

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

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

$$\int d^3r\, e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}} f(\mathbf{r}) = \frac{8\pi^3}{\Omega}\delta(\mathbf{q}-\mathbf{k})\int_\Omega d^3r\, f(\mathbf{r}), \tag{9}$$

to finally write,[14]

$$\begin{aligned}\frac{\partial}{\partial\mathbf{k}}\langle n\mathbf{k}|m\mathbf{k}'\rangle &= \delta(\mathbf{k}-\mathbf{k}')\int_\Omega d\mathbf{r}\left(\frac{\partial}{\partial\mathbf{k}}u^*_{n\mathbf{k}}(\mathbf{r})\right)u_{m\mathbf{k}}(\mathbf{r}) \\ &\quad -i\langle n\mathbf{k}|\hat{\mathbf{r}}|m\mathbf{k}'\rangle. \end{aligned}\tag{10}$$

where Ω is the volume of the unit cell. From

$$\int_\Omega u_{m\mathbf{k}}u^*_{n\mathbf{k}}d\mathbf{r} = \delta_{nm}, \tag{11}$$

we easily find that

$$\int_\Omega d\mathbf{r}\left(\frac{\partial}{\partial\mathbf{k}}u_{m\mathbf{k}}(\mathbf{r})\right)u^*_{n\mathbf{k}}(\mathbf{r}) = -\int_\Omega d\mathbf{r}\, u_{m\mathbf{k}}(\mathbf{r})\left(\frac{\partial}{\partial\mathbf{k}}u^*_{n\mathbf{k}}(\mathbf{r})\right). \tag{12}$$

Therefore, we define

$$\boldsymbol{\xi}_{nm}(\mathbf{k}) \equiv i\int_\Omega d\mathbf{r}\, u^*_{n\mathbf{k}}(\mathbf{r})\nabla_\mathbf{k}u_{m\mathbf{k}}(\mathbf{r}), \tag{13}$$

with $\partial/\partial\mathbf{k} = \nabla_\mathbf{k}$. Now, from Eqs. (5), (8), and (13), we have that the matrix elements of the position operator of the electron are given by

$$\langle n\mathbf{k}|\hat{\mathbf{r}}|m\mathbf{k}'\rangle = \delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nm}(\mathbf{k}) + i\delta_{nm}\nabla_\mathbf{k}\delta(\mathbf{k}-\mathbf{k}'), \tag{14}$$

Then, from Eq. (14), 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

$$\langle n\mathbf{k}|\hat{\mathbf{r}}_i|m\mathbf{k}'\rangle = \delta_{nm}\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nn}(\mathbf{k}) + i\nabla_\mathbf{k}\delta(\mathbf{k}-\mathbf{k}')\right], \tag{15}$$

$$\langle n\mathbf{k}|\hat{\mathbf{r}}_e|m\mathbf{k}'\rangle = (1-\delta_{nm})\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nm}(\mathbf{k}). \tag{16}$$

To proceed, we relate Eq. (16) to the matrix elements of the momentum operator as follows. We start from the basic relation,

$$\hat{\mathbf{v}} = \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{H}_0], \tag{17}$$

with $\hat{\mathbf{v}}$ the velocity operator, and H_0 could contain a nonlocal potential, then

$$\hat{\mathbf{v}}^S = \frac{\hat{\mathbf{p}}}{m_e} + \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{V}^{\mathrm{nl}}] = \mathbf{v}^{\mathrm{LDA}} + \mathbf{v}^{\mathrm{nl}} \tag{18}$$

with $\hat{\mathbf{p}} = -i\hbar\boldsymbol{\nabla}$ the momentum operator, with m_e the mass of the electron. Considering that $\hat{V}^{\rm nl} \to \hat{S}$ where $\hat{S}$ is the scissors operator,

$$S(\mathbf{r},\mathbf{p}) = \hbar\Delta \sum_n \int d^3k'(1-f_n)|n\mathbf{k}'\rangle\langle n\mathbf{k}'|, \tag{19}$$ chon.0

we have that

$$H_0|n\mathbf{k}\rangle = \hbar\omega_n^S(\mathbf{k})|n\mathbf{k}\rangle, \tag{20}$$ chon.1

with $\omega_n^S(\mathbf{k}) = \omega_n^{\rm LDA}(\mathbf{k}) + \Delta(1-f_n)$ is the scissored energy, and $\Delta = E_g - E_g^{\rm LDA}$, where E_g could be the experimental or GW gap. From Eq. (conhr 18), we obtain that

$$\mathbf{v}^{\rm nl}_{nm} = i\Delta f_{mn}\mathbf{r}_{nm} = \frac{\Delta f_{mn}}{\omega^{\rm LDA}_{nm}}\mathbf{v}^{\rm LDA}_{nm} \tag{21}$$ chon.2

On the other hand,

$$\langle n\mathbf{k}|[\hat{\mathbf{r}},\hat{H}_0]|m\mathbf{k}\rangle = \langle n\mathbf{k}|\hat{\mathbf{r}}\hat{H}_0 - \hat{H}_0\hat{\mathbf{r}}|m\mathbf{k}\rangle = (\hbar\omega_m^S(\mathbf{k}) - \hbar\omega_n^S(\mathbf{k}))\langle n\mathbf{k}|\hat{\mathbf{r}}|m\mathbf{k}\rangle, \tag{22}$$ conhrnm

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

$$\begin{aligned}
\mathbf{r}_{nm}(\mathbf{k}) &= \frac{\mathbf{v}^S_{nm}(\mathbf{k})}{i\omega^S_{nm}(\mathbf{k})} = \frac{\mathbf{v}^{\rm LDA}_{nm} + \frac{\Delta f_{mn}}{\omega^{\rm LDA}_{nm}}\mathbf{v}^{\rm LDA}_{nm}}{i\omega^S_{nm}(\mathbf{k})} \\
&= \frac{\mathbf{v}^{\rm LDA}}{i\omega^{\rm LDA}_{nm}}\frac{\omega^{\rm LDA}_{nm} + \Delta f_{mn}}{\omega^S_{nm}} \\
&= \frac{\mathbf{v}^{\rm LDA}}{i\omega^{\rm LDA}_{nm}} \qquad n \neq m,
\end{aligned} \tag{23}$$

since $\omega^{\rm LDA}_{nm} + \Delta f_{mn} = \omega^S_{nm}$. Therefore, the matrix elements of $\mathbf{r}_{nm}$ are the same wether we use the LDA or the scissored Hamiltonian.

Comparing above result with Eq. (rnme 16), we can identify

$$(1-\delta_{nm})\boldsymbol{\xi}_{nm} \equiv \mathbf{r}_{nm}, \tag{24}$$ xir

and the we can write

$$\langle n\mathbf{k}|\hat{\mathbf{r}}_e|m\mathbf{k}\rangle = \mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{p}_{nm}(\mathbf{k})}{im_e\omega_{nm}(\mathbf{k})} \qquad n \neq m, \tag{25}$$ rnmenm

which gives the interband matrix elements of the position operator in terms of the matrix elements of the well defined momentum operator.

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

$$\begin{aligned}
\langle n\mathbf{k}|[\hat{\mathbf{r}}_i,\hat{\mathcal{O}}]|m\mathbf{k}'\rangle &= \sum_{\ell,\mathbf{k}''}\Big(\langle n\mathbf{k}|\hat{\mathbf{r}}_i|\ell\mathbf{k}''\rangle\langle\ell\mathbf{k}''|\hat{\mathcal{O}}|m\mathbf{k}'\rangle \\
&\quad -\langle n\mathbf{k}|\hat{\mathcal{O}}|\ell\mathbf{k}''\rangle\langle\ell\mathbf{k}''|\hat{\mathbf{r}}_i|m\mathbf{k}'\rangle\Big) \\
&= \sum_{\ell}\big(\langle n\mathbf{k}|\hat{\mathbf{r}}_i|\ell\mathbf{k}'\rangle\mathcal{O}_{\ell m}(\mathbf{k}') \\
&\quad -\mathcal{O}_{n\ell}(\mathbf{k})|\ell\mathbf{k}\rangle\langle\ell\mathbf{k}|\hat{\mathbf{r}}_i|m\mathbf{k}'\rangle\big)\,,
\end{aligned} \tag{26}$$

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. (15), to obtain

$$\begin{aligned}
\sum_{\ell} & \Big(\delta_{n\ell}\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nn}(\mathbf{k})+i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right]\mathcal{O}_{\ell m}(\mathbf{k}') \\
& -\mathcal{O}_{n\ell}(\mathbf{k})\delta_{\ell m}\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{mm}(\mathbf{k})+i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right]\Big) \\
=& \Big(\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{nn}(\mathbf{k})+i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right]\mathcal{O}_{nm}(\mathbf{k}') \\
& -\mathcal{O}_{nm}(\mathbf{k})\left[\delta(\mathbf{k}-\mathbf{k}')\boldsymbol{\xi}_{mm}(\mathbf{k})+i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right]\Big) \\
=& \delta(\mathbf{k}-\mathbf{k}')\mathcal{O}_{nm}(\mathbf{k})\left(\boldsymbol{\xi}_{nn}(\mathbf{k})-\boldsymbol{\xi}_{mm}(\mathbf{k})\right)+i\mathcal{O}_{nm}(\mathbf{k}')\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}') \\
& +i\delta(\mathbf{k}-\mathbf{k}')\nabla_{\mathbf{k}}\mathcal{O}_{nm}(\mathbf{k})-i\mathcal{O}_{nm}(\mathbf{k}')\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}') \\
=& i\delta(\mathbf{k}-\mathbf{k}')\Big(\nabla_{\mathbf{k}}\mathcal{O}_{nm}(\mathbf{k})-i\mathcal{O}_{nm}(\mathbf{k})\left(\boldsymbol{\xi}_{nn}(\mathbf{k})-\boldsymbol{\xi}_{mm}(\mathbf{k})\right)\Big) \\
\equiv& i\delta(\mathbf{k}-\mathbf{k}')(\mathcal{O}_{nm})_{;\mathbf{k}}.
\end{aligned} \tag{27}$$

Then,

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}_i,\hat{\mathcal{O}}]|m\mathbf{k}'\rangle = i\delta(\mathbf{k}-\mathbf{k}')(\mathcal{O}_{nm})_{;\mathbf{k}}, \tag{28}$$

conmri3

with

$$(\mathcal{O}_{nm})_{;\mathbf{k}} = \nabla_{\mathbf{k}}\mathcal{O}_{nm}(\mathbf{k})-i\mathcal{O}_{nm}(\mathbf{k})\left(\boldsymbol{\xi}_{nn}(\mathbf{k})-\boldsymbol{\xi}_{mm}(\mathbf{k})\right), \tag{29}$$

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. (27), thus giving a well defined commutator of the intraband position operator with an arbitrary operator $\hat{\mathcal{O}}$. We use Eq. (25) and (28) in the next section.

III. TIME-DEPENDENT PERTURBATION THEORY

tdpt

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

$$\mathcal{O} = \mathrm{Tr}(\hat{\mathcal{O}}\hat{\rho}) = \mathrm{Tr}(\hat{\rho}\hat{\mathcal{O}}), \tag{30}$$

traza

where Tr is the trace, that is invariant under cyclic permutations. The dynamical equation of motion for ρ is given by

$$i\hbar \frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}], \qquad (31) \quad \boxed{\texttt{eqrho}}$$

where it is more convenient to work in the interaction picture, for which we transform all the operators according to

$$\hat{\mathcal{O}}_I = \hat{U}\hat{\mathcal{O}}\hat{U}^\dagger, \qquad (32) \quad \boxed{\texttt{ip}}$$

where

$$\hat{U} = e^{i\hat{H}_0 t/\hbar}, \qquad (33) \quad \boxed{\texttt{ou}}$$

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. (eqrho 31) into

$$i\hbar \frac{d\hat{\rho}_I(t)}{dt} = [-e\hat{\mathbf{r}}_I(t) \cdot \mathbf{E}(t), \hat{\rho}_I(t)], \qquad (34) \quad \boxed{\texttt{intrho}}$$

that leads to

$$\hat{\rho}_I(t) = \hat{\rho}_I(t = -\infty) + \frac{ie}{\hbar} \int_{-\infty}^{t} dt' [\hat{\mathbf{r}}_I(t') \cdot \mathbf{E}(t'), \hat{\rho}_I(t')]. \qquad (35) \quad \boxed{\texttt{intrho2}}$$

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

$$\mathbf{E}(t) = \mathbf{E} e^{-i\omega t} e^{\eta t}, \qquad (36) \quad \boxed{\texttt{efield}}$$

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 $\eta \to 0$. Instead of Eq. (efield 36) we use

$$\mathbf{E}(t) = \mathbf{E} e^{-i\tilde{\omega} t}, \qquad (37) \quad \boxed{\texttt{efield2}}$$

with

$$\tilde{\omega} = \omega + i\eta. \qquad (38) \quad \boxed{\texttt{got}}$$

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

$$\langle n\mathbf{k}|\hat{\rho}_0|m\mathbf{k}'\rangle = f_n(\hbar\omega_n(\mathbf{k}))\delta_{nm}\delta(\mathbf{k} - \mathbf{k}'), \qquad (39) \quad \boxed{\texttt{nrhon}}$$

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

We solve Eq. (35) using the standard iterative solution, for which we write

$$\hat{\rho}_I = \hat{\rho}_I^{(0)} + \hat{\rho}_I^{(1)} + \hat{\rho}_I^{(2)} + \cdots, \tag{40}$$

rhop

where $\hat{\rho}_I^{(N)}$ is the density operator to order N in $\mathbf{E}(t)$. Then, Eq. (35) reads

$$\hat{\rho}_I^{(0)} + \hat{\rho}_I^{(1)} + \hat{\rho}_I^{(2)} + \cdots = \hat{\rho}_0 + \frac{ie}{\hbar}\int_{-\infty}^{t} dt' [\hat{\mathbf{r}}_I(t')\cdot\mathbf{E}(t'), \hat{\rho}_I^{(0)} + \hat{\rho}_I^{(1)} + \hat{\rho}_I^{(2)} + \cdots], \tag{41}$$

intrho3

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

$$\hat{\rho}_I^{(0)} \equiv \hat{\rho}_0, \tag{42}$$

rho0

and

$$\hat{\rho}_I^{(N)}(t) = \frac{ie}{\hbar}\int_{-\infty}^{t} dt' [\hat{\mathbf{r}}_I(t')\cdot\mathbf{E}(t'), \hat{\rho}_I^{(N-1)}(t')]. \tag{43}$$

rhoN

It is simple to show that matrix elements of Eq. (43) 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

$$\rho_{I,nm}^{(N+1)}(\mathbf{k};t) = \frac{ie}{\hbar}\int_{-\infty}^{t} dt' \langle n\mathbf{k}|[\hat{\mathbf{r}}_I(t'), \hat{\rho}_I^{(N)}(t')]|m\mathbf{k}\rangle \cdot \mathbf{E}(t'). \tag{44}$$

rtilde

Now we work out the commutator of Eq. (44). Then,

$$\begin{aligned}
\langle n\mathbf{k}|[\hat{\mathbf{r}}_I(t), \hat{\rho}_I^{(N)}(t)]|m\mathbf{k}\rangle &= \langle n\mathbf{k}|[\hat{U}\hat{\mathbf{r}}\hat{U}^\dagger, \hat{U}\hat{\rho}^{(N)}(t)\hat{U}^\dagger]|m\mathbf{k}\rangle \\
&= \langle n\mathbf{k}|\hat{U}[\hat{\mathbf{r}}, \hat{\rho}^{(N)}(t)]\hat{U}^\dagger|m\mathbf{k}\rangle \\
&= e^{i\omega_{nm\mathbf{k}}t}\left(\langle n\mathbf{k}|[\hat{\mathbf{r}}_e, \hat{\rho}^{(N)}(t)] + [\hat{\mathbf{r}}_i, \hat{\rho}^{(N)}(t)]|m\mathbf{k}\rangle\right).
\end{aligned} \tag{45}$$

We calculate the interband term first, so using Eq. (25) we obtain

$$\begin{aligned}
\langle n\mathbf{k}|[\hat{\mathbf{r}}_e, \hat{\rho}^{(N)}(t)]|m\mathbf{k}\rangle &= \sum_{\ell}\Big(\langle n\mathbf{k}|\hat{\mathbf{r}}_e|\ell\mathbf{k}\rangle\langle\ell\mathbf{k}|\hat{\rho}^{(N)}(t)|m\mathbf{k}\rangle \\
&\quad -\langle n\mathbf{k}|\hat{\rho}^{(N)}(t)|\ell\mathbf{k}\rangle\langle\ell\mathbf{k}|\hat{\mathbf{r}}_e|m\mathbf{k}\rangle\Big) \\
&= \sum_{\ell\neq n,m}\left(\mathbf{r}_{n\ell}(\mathbf{k})\rho_{\ell m}^{(N)}(\mathbf{k};t) - \rho_{n\ell}^{(N)}(\mathbf{k};t)\mathbf{r}_{\ell m}(\mathbf{k})\right) \\
&\equiv \mathbf{R}_e^{(N)}(\mathbf{k};t).
\end{aligned} \tag{46}$$

Now, from Eq. (28) we simply obtain,

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}_i, \hat{\rho}^{(N)}(t)]|m\mathbf{k}'\rangle = i(\rho_{nm}^{(N)}(t))_{;\mathbf{k}} \equiv \mathbf{R}_i^{(N)}(\mathbf{k};t). \tag{47}$$

conmri4

Then Eq. (rtilde 44) becomes,

$$\rho^{(N+1)}_{I,nm}(\mathbf{k};t) = \frac{ie}{\hbar}\int_{-\infty}^{t} dt' e^{i(\omega_{nm\mathbf{k}}-\tilde{\omega})t'}\left[R_e^{\mathrm{b}(N)}(\mathbf{k};t') + R_i^{\mathrm{b}(N)}(\mathbf{k};t')\right]E^{\mathrm{b}}, \tag{48}$$ rtilde2

where, the roman superindices $\mathrm{a}, \mathrm{b}, \mathrm{c}$ denote Cartesian components that are summed over if repeated. We start with the linear response, then from Eq. (nrhon 39) and (conmu2 46),

$$\begin{aligned} R_e^{\mathrm{b}(0)}(\mathbf{k};t) &= \sum_\ell \left(r^{\mathrm{b}}_{n\ell}(\mathbf{k})\rho^{(0)}_{\ell m}(\mathbf{k}) - \rho^{(0)}_{n\ell}(\mathbf{k}) r^{\mathrm{b}}_{\ell m}(\mathbf{k})\right) \\ &= \sum_\ell \left(r^{\mathrm{b}}_{n\ell}(\mathbf{k})\delta_{\ell m} f_m(\hbar\omega_m(\mathbf{k})) - \delta_{n\ell} f_n(\hbar\omega_n(\mathbf{k})) r^{\mathrm{b}}_{\ell m}(\mathbf{k})\right) \\ &= f_{mn\mathbf{k}} r^{\mathrm{b}}_{nm}(\mathbf{k}), \end{aligned} \tag{49}$$

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. (conmri4 47) and Eq. (gendev 29)

$$R_i^{\mathrm{b}(0)}(\mathbf{k}) = i(\rho^{(0)}_{nm})_{;k^{\mathrm{b}}} = i\delta_{nm}(f_{n\mathbf{k}})_{;k^{\mathrm{b}}} = i\delta_{nm}\nabla_{k^{\mathrm{b}}} f_{n\mathbf{k}}. \tag{50}$$ 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 $\mathbf{R}_i^{(0)} = 0$. Therefore the linear response has no contribution from intraband transitions. Then,

$$\begin{aligned} \rho^{(1)}_{I,nm}(\mathbf{k};t) &= \frac{ie}{\hbar} f_{mn\mathbf{k}} r^{\mathrm{b}}_{nm}(\mathbf{k}) E^{\mathrm{b}} \int_{-\infty}^{t} dt' e^{i(\omega_{nm\mathbf{k}}-\tilde{\omega})t'} \\ &= \frac{e}{\hbar} f_{mn\mathbf{k}} r^{\mathrm{b}}_{nm}(\mathbf{k}) E^{\mathrm{b}} \frac{e^{i(\omega_{nm\mathbf{k}}-\tilde{\omega})t}}{\omega_{nm\mathbf{k}}-\tilde{\omega}} \\ &= e^{i\omega_{nm\mathbf{k}}t} B^{\mathrm{b}}_{mn}(\mathbf{k}) E^{\mathrm{b}}(t) \\ &= e^{i\omega_{nm\mathbf{k}}t}\rho^{(1)}_{nm}(\mathbf{k};t). \end{aligned} \tag{51}$$

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

$$\rho^{(1)}_{nm}(\mathbf{k};t) = B^{\mathrm{b}}_{mn}(\mathbf{k},\omega_\alpha) E^{\mathrm{b}}_{\omega_\alpha} e^{-i\tilde{\omega}_\alpha t}, \tag{52}$$ rhonoi1

with

$$B^{\mathrm{b}}_{nm}(\mathbf{k},\omega_\alpha) = \frac{e}{\hbar}\frac{f_{mn\mathbf{k}} r^{\mathrm{b}}_{nm}(\mathbf{k})}{\omega_{nm\mathbf{k}}-\tilde{\omega}_\alpha}, \tag{53}$$ rho1

that for the scissored hamiltonian would be

$$B^{\mathrm{b}}_{nm}(\mathbf{k},\omega_\alpha) = \frac{e}{\hbar}\frac{f_{mn\mathbf{k}} r^{\mathrm{b}}_{nm}(\mathbf{k})}{\omega^S_{nm\mathbf{k}}-\tilde{\omega}_\alpha}, \tag{54}$$ rho1

since as we saw, the $\mathbf{r}_{nm}$ are the same as in LDA, and thus they do not need to be scissored.

Now, we calculate the second-order response. Then, from Eq. (conmu2 46)

$$
\begin{aligned}
R_e^{\mathrm{b}(1)}(\mathbf{k};t) &= \sum_\ell \left(r^{\mathrm{b}}_{n\ell}(\mathbf{k})\rho^{(1)}_{\ell m}(\mathbf{k};t) - \rho^{(1)}_{n\ell}(\mathbf{k};t) r^{\mathrm{b}}_{\ell m}(\mathbf{k})\right) \\
&= \sum_\ell \left(r^{\mathrm{b}}_{n\ell}(\mathbf{k}) B^{\mathrm{c}}_{\ell m}(\mathbf{k},\omega_\beta) - B^{\mathrm{c}}_{n\ell}(\mathbf{k},\omega_\beta) r^{\mathrm{b}}_{\ell m}(\mathbf{k})\right) E^{\mathrm{c}}_{\omega_\beta}(t), \qquad (55)
\end{aligned}
$$

and from Eq. (conmri4 47)

$$
R_i^{\mathrm{b}(1)}(\mathbf{k};t) = i(\rho^{(1)}_{nm}(t))_{;k^{\mathrm{b}}} = i E^{\mathrm{c}}_{\omega_\beta}(t)(B^{\mathrm{c}}_{nm}(\mathbf{k},\omega_\beta))_{;k^{\mathrm{b}}}. \tag{56}
$$

R1i

Using Eqs. (R1e 55) and (R1i 56) in Eq. (rtilde2 48), and generalizing to two different perturbing fields, we obtain

$$
\begin{aligned}
\rho^{(2)}_{I,nm}(\mathbf{k};t) &= \frac{ie}{\hbar}\Bigg[\sum_\ell \left(r^{\mathrm{b}}_{n\ell}(\mathbf{k}) B^{\mathrm{c}}_{\ell m}(\mathbf{k},\omega_\beta) - B^{\mathrm{c}}_{n\ell}(\mathbf{k},\omega_\beta) r^{\mathrm{b}}_{\ell m}(\mathbf{k})\right) \\
&\quad + i(B^{\mathrm{c}}_{nm}(\mathbf{k},\omega_\beta))_{;k^{\mathrm{b}}}\Bigg] E^{\mathrm{b}}_{\omega_\alpha} E^{\mathrm{c}}_{\omega_\beta} \int_{-\infty}^{t} dt' e^{i(\omega_{nm\mathbf{k}} - \tilde\omega_\alpha - \tilde\omega_\beta)t'} \\
&= \frac{e}{\hbar}\Bigg[\sum_\ell \left(r^{\mathrm{b}}_{n\ell}(\mathbf{k}) B^{\mathrm{c}}_{\ell m}(\mathbf{k},\omega_\beta) - B^{\mathrm{c}}_{n\ell}(\mathbf{k},\omega_\beta) r^{\mathrm{b}}_{\ell m}(\mathbf{k})\right) \\
&\quad + i(B^{\mathrm{c}}_{nm}(\mathbf{k},\omega_\beta))_{;k^{\mathrm{b}}}\Bigg] E^{\mathrm{b}}_{\omega_\alpha} E^{\mathrm{c}}_{\omega_\beta} \frac{e^{i(\omega_{nm\mathbf{k}} - \tilde\omega_3)t}}{\omega_{nm\mathbf{k}} - \tilde\omega_3} \\
&= e^{i\omega_{nm\mathbf{k}}t} \rho^{(2)}_{nm}(\mathbf{k};t). \qquad (57)
\end{aligned}
$$

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

$$
\begin{aligned}
\rho^{(2)}_{nm}(\mathbf{k};\omega_3) &= \frac{e}{i\hbar}\frac{1}{\omega_{nm\mathbf{k}} - \tilde\omega_3}\Bigg[-(B^{\mathrm{c}}_{nm}(\mathbf{k},\omega_\beta)_{;k^{\mathrm{b}}} \\
&\quad + i\sum_\ell \left(r^{\mathrm{b}}_{n\ell} B^{\mathrm{c}}_{\ell m}(\mathbf{k},\omega_\beta) - B^{\mathrm{c}}_{n\ell}(\mathbf{k},\omega_\beta) r^{\mathrm{b}}_{\ell m}\right)\Bigg] E^{\mathrm{b}}_{\omega_\alpha} E^{\mathrm{c}}_{\omega_\beta} \qquad (58)
\end{aligned}
$$

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 $i = \alpha, \beta$. We use Eq. (rho2 58) in section nonchi V. For the scissored hamiltonian,

$$
\begin{aligned}
\rho^{(2)}_{nm}(\mathbf{k};\omega_3) &= \frac{e}{i\hbar}\frac{1}{\omega^s_{nm\mathbf{k}} - \tilde\omega_3}\Bigg[-(B^{\mathrm{c}}_{nm}(\mathbf{k},\omega_\beta)_{;k^{\mathrm{b}}} \\
&\quad + i\sum_\ell \left(r^{\mathrm{b}}_{n\ell} B^{\mathrm{c}}_{\ell m}(\mathbf{k},\omega_\beta) - B^{\mathrm{c}}_{n\ell}(\mathbf{k},\omega_\beta) r^{\mathrm{b}}_{\ell m}\right)\Bigg] E^{\mathrm{b}}_{\omega_\alpha} E^{\mathrm{c}}_{\omega_\beta}, \qquad (59)
\end{aligned}
$$

where we now determine how to write $(B^{\mathrm{c}}_{nm}(\mathbf{k},\omega_\beta)_{;k^{\mathrm{b}}}$ within the scissored hamiltonian.

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 $\chi^{slab}_{abc} = 0$, 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 $\chi^{slab}_{abc} \neq 0$, 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 χ^{slab}_{abc}.

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

$$S_\ell(z) = \Theta(z - z_\ell + \Delta^{\mathrm{b}}_\ell)\Theta(z_\ell - z + \Delta^{f}_\ell), \tag{60}$$

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

Now, we show how this "cut function" $S_\ell(z)$ is introduced in the calculation of χ_{ijl}. The

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

microscopic current density is given by

$$\mathbf{j}(\mathbf{r},t) = \mathrm{Tr}(\hat{\mathbf{j}}(\mathbf{r})\hat{\rho}(t)), \tag{61}$$ $\boxed{\texttt{jmic}}$

where the operator for the electron's current is

$$\hat{\mathbf{j}}(\mathbf{r}) = \frac{e}{2}\left(\hat{\mathbf{v}}|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}\right), \tag{62}$$ $\boxed{\texttt{hatjmic}}$

where $\hat{\mathbf{v}}$ 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

$$\begin{aligned}
\mathrm{Tr}(\hat{\mathbf{j}}(\mathbf{r})\hat{\rho}(t) &= \mathrm{Tr}(\hat{\rho}(t)\hat{\mathbf{j}}(\mathbf{r})) = \frac{e}{2}\left(\mathrm{Tr}(\hat{\rho}\hat{\mathbf{v}}\hat{\mu}) + \mathrm{Tr}(\hat{\rho}\hat{\mu}\hat{\mathbf{v}})\right) \\
&= \frac{e}{2}\sum_{n\mathbf{k}}\left(\langle n\mathbf{k}|\hat{\rho}\hat{\mathbf{v}}\hat{\mu}|n\mathbf{k}\rangle + \langle n\mathbf{k}|\hat{\rho}\hat{\mu}\hat{\mathbf{v}}|n\mathbf{k}\rangle\right) \\
&= \frac{e}{2}\sum_{nm\mathbf{k}}\langle n\mathbf{k}|\hat{\rho}|m\mathbf{k}\rangle\left(\langle m\mathbf{k}|\hat{\mathbf{v}}|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle + \langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}|n\mathbf{k}\rangle\right) \\
\mathbf{j}(\mathbf{r},t) &= \sum_{nm\mathbf{k}}\rho_{nm}(\mathbf{k};t)\mathbf{j}_{mn}(\mathbf{k};\mathbf{r}), \qquad (63)
\end{aligned}$$

where

$$\mathbf{j}_{mn}(\mathbf{k};\mathbf{r}) = \frac{e}{2}\left(\langle m\mathbf{k}|\hat{\mathbf{v}}|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle + \langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}|n\mathbf{k}\rangle\right), \tag{64}$$ $\boxed{\texttt{jmic3}}$

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

$$\frac{1}{\Omega}\int d^3r\, S_\ell(z)\,\mathbf{j}(\mathbf{r},t) \equiv \mathbf{J}^{(\ell)}(t), \tag{65}$$ $\boxed{\texttt{jsz}}$

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

$$e\boldsymbol{\mathcal{V}}^{(\ell)}_{mn}(\mathbf{k}) \equiv \int d^3r\, S_\ell(z)\,\mathbf{j}_{mn}(\mathbf{k};\mathbf{r}), \tag{66}$$ $\boxed{\texttt{vcal}}$

to write

$$J^{(N,\ell)}_a(t) = \frac{e}{\Omega}\sum_{mn\mathbf{k}}\mathcal{V}^{a(\ell)}_{mn}(\mathbf{k})\rho^{(N)}_{nm}(\mathbf{k};t), \tag{67}$$ $\boxed{\texttt{jmac}}$

as the induced macroscopic current, to order N-th in the external perturbation, of the ℓ-th layer. The matrix elements of the density operator for $N = 1, 2$ are given by Eqs. (rho1 54) and (rho2 58), respectively.

We proceed to give an explicit expression for $\mathcal{V}^{a(\ell)}_{mn}(\mathbf{k})$, for which we should work with the velocity operator, that is given by

$$\begin{aligned} i\hbar\hat{\mathbf{v}} &= [\hat{\mathbf{r}}, \hat{H}_0] \\ &= [\hat{\mathbf{r}}, \frac{\hat{\mathbf{p}}^2}{2m} + \hat{V}(\mathbf{r}) + \hat{v}(\mathbf{r},\hat{\mathbf{p}})] \approx [\hat{\mathbf{r}}, \frac{\hat{\mathbf{p}}^2}{2m}] = i\hbar\frac{\hat{\mathbf{p}}}{m}, \end{aligned} \tag{68}$$

where the possible contribution of the non-local pseudopotential $\hat{v}(\mathbf{r},\hat{\mathbf{p}})$ is neglected. Now, from above equation,

$$m\hat{\mathbf{v}} \approx \hat{\mathbf{p}} = -i\hbar\boldsymbol{\nabla}, \tag{69}$$ velo

is the explicit functional form of the velocity or momentum operator. From Eq. (64), we need

$$\langle\mathbf{r}|\hat{\mathbf{v}}|n\mathbf{k}\rangle = \int d^3r'\langle\mathbf{r}|\hat{\mathbf{v}}|\mathbf{r}'\rangle\langle\mathbf{r}'|n\mathbf{k}\rangle \approx \frac{1}{m}\hat{\mathbf{p}}\psi_{n\mathbf{k}}(\mathbf{r}), \tag{70}$$ vnm

where we used

$$\langle\mathbf{r}|\hat{v^x}|\mathbf{r}'\rangle \approx \frac{1}{m}\langle\mathbf{r}|\hat{p^x}|\mathbf{r}'\rangle = \delta(y-y')\delta(z-z')\left(-i\hbar\frac{\partial}{\partial x}\delta(x-x')\right), \tag{71}$$ rvnk

with similar results for the y and z Cartesian directions. Now, from Eqs. (66) and (64) we obtain

$$\boldsymbol{\mathcal{V}}^{(\ell)}_{mn}(\mathbf{k}) = \frac{1}{2}\int \mathrm{d}^3r\, S_\ell(z)\Big[\langle m\mathbf{k}|\mathbf{v}|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle + \langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\mathbf{v}|n\mathbf{k}\rangle\Big], \tag{72}$$ intj

and using Eq. (70), we can write, for any function $S(z)$ used to identify the response from a region of the slab, that

$$\begin{aligned} \boldsymbol{\mathcal{V}}_{mn}(\mathbf{k}) &\approx \frac{1}{2m}\int d^3r S(z)\Big[\psi_{n\mathbf{k}}(\mathbf{r})\hat{\mathbf{p}}^*\psi^*_{m\mathbf{k}}(\mathbf{r}) + \psi^*_{m\mathbf{k}}(\mathbf{r})\hat{\mathbf{p}}\psi_{n\mathbf{k}}(\mathbf{r})\Big], &(73)\\ &= \frac{1}{m}\int d^3r\psi^*_{m\mathbf{k}}(\mathbf{r})\left[\frac{S(z)\mathbf{p}+\mathbf{p}S(z)}{2}\right]\psi_{n\mathbf{k}}(\mathbf{r}), &(74)\\ &= \frac{1}{m}\int d^3r\psi^*_{m\mathbf{k}}(\mathbf{r})\hat{\boldsymbol{\mathcal{P}}}\psi_{n\mathbf{k}}(\mathbf{r}) \equiv \frac{1}{m}\boldsymbol{\mathcal{P}}_{mn}(\mathbf{k}). &(75) \end{aligned}$$

Here an integration by parts is performed on the first term of the right hand side of Eq. (73); since the $\langle\mathbf{r}|n\mathbf{k}\rangle = e^{-i\mathbf{k}\cdot\mathbf{r}}\psi_{n\mathbf{k}}(\mathbf{r})$ are periodic over the unit cell, the surface term vanishes. From Eqs. (73) we see that the replacement

$$\hat{\mathbf{p}} \to \hat{\boldsymbol{\mathcal{P}}} = \left[\frac{S(z)\hat{\mathbf{p}}+\hat{\mathbf{p}}S(z)}{2}\right], \tag{76}$$ pcali

is what it takes to change the momentum operator of the electron, $\hat{\mathbf{p}}$, to the new momentum operator $\hat{\boldsymbol{\mathcal{P}}}$ that implicitly takes into account the contribution of the region of the slab given by $S(z)$. Note that $\hat{\boldsymbol{\mathcal{P}}}$ is properly symmetrized.

Finally, the Fourier component of macroscopic current of Eq. (67) is given by

$$J_{\rm a}^{(N,\ell)}(\omega_3) = \frac{e}{m\Omega}\sum_{mn\mathbf{k}} \mathcal{P}_{mn}^{\rm a(\ell)}(\mathbf{k})\rho_{nm}^{(N)}(\mathbf{k};\omega_3), \tag{77}$$

where the non-local contribution of H_0 is neglected, and from Eq. (74)

$$\mathcal{P}_{mn}^{\rm a(\ell)} = \int d^3r\psi^*_{m\mathbf{k}}(\mathbf{r})\left[\frac{S_\ell(z)p^{\rm a} + p^{\rm a}S_\ell(z)}{2}\right]\psi_{n\mathbf{k}}(\mathbf{r}). \tag{78}$$

Actually, to limit the response to one surface, the Eq. (76) was proposed in Ref. 15, and latter used in Refs. 16 and 17 in the context of SHG. Then, the layer-by-layer analysis of Refs. 18 and 19 actually used Eq. (60) 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. 20 for the linear optical response, and here for the non-linear optical response of semiconductors.

From the following well known result, $im_e\omega_{nm}\mathbf{r}_{nm} = \mathbf{p}_{nm}$ $(n \neq m)$, we can write

$$\mathcal{R}^{\rm a}_{nm} = \frac{\mathcal{P}^{\rm a}_{nm}}{im_e\omega_{nm}} \quad (n \neq m), \tag{79}$$

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

$$\begin{aligned} P_{\rm a}(\omega_3) \;=\; & \chi_{\rm abc}(-\omega_3;\omega_1,\omega_2)E_{\rm b}(\omega_1)E_{\rm c}(\omega_2) \\ & +\chi_{\rm abcl}(-\omega_3;\omega_1,\omega_2)E_{\rm b}(\omega_1)\nabla_{\rm c}E_{\rm l}(\omega_2) + \cdots, \end{aligned} \tag{80}$$

where $\chi_{\rm abc}$ and $\chi_{\rm abcl}$, 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

$$P_{\rm a}(\mathbf{r}) = \chi_{\rm abc}E_{\rm b}(\mathbf{r})E_{\rm c}(\mathbf{r}) + \chi_{\rm abcl}E_{\rm b}(\mathbf{r})\frac{\partial}{\partial \mathbf{r}_{\rm c}}E_{\rm l}(\mathbf{r}) + \cdots, \tag{81}$$

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

$$\begin{aligned} P_{\rm a}(-\mathbf{r}) \;=\; & \chi_{\rm abc}E_{\rm b}(-\mathbf{r})E_{\rm c}(-\mathbf{r}) \\ & +\chi_{\rm abcl}E_{\rm b}(-\mathbf{r})\frac{\partial}{\partial(-\mathbf{r}_{\rm c})}E_{\rm l}(-\mathbf{r}) + \cdots, \end{aligned} \tag{82}$$

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. fsystem

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,[21] we have that Eq. (82) reduces to

$$
\begin{aligned}
-P_{\rm a}(\mathbf{r}) &= \chi_{\rm abc}(-E_{\rm b}(\mathbf{r}))(-E_{\rm c}(\mathbf{r})) - \chi_{\rm abcl}(-E_{\rm b}(\mathbf{r}))(-\frac{\partial}{\partial \mathbf{r}_{\rm c}})(-E_{\rm l}(\mathbf{r})) + \cdots , \\
P_{\rm a}(\mathbf{r}) &= -\chi_{\rm abc}E_{\rm b}(\mathbf{r})E_{\rm c}(\mathbf{r}) + \chi_{\rm abcl}E_{\rm b}(\mathbf{r})\frac{\partial}{\partial \mathbf{r}_{\rm c}}E_{\rm l}(\mathbf{r}) + \cdots ,
\end{aligned} \tag{83}
$$

that when compared with Eq. (81) leads to the conclusion that

$$
\chi_{\rm abc} = 0 \qquad \text{for a centrosymmetric bulk.} \tag{84}
$$
sshg

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

$$
\begin{aligned}
\int d\mathbf{R} \int dz P_{\rm a}(\mathbf{R}, z) &\approx \mathcal{S} d P_{\rm a} \\
&= \mathcal{S} P^s_{\rm a} \\
&= \chi_{\rm abc} E_{\rm b} E_{\rm c},
\end{aligned} \tag{85}
$$

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

$$
P^s_{\rm a} = \frac{1}{\mathcal{S}}\chi_{\rm abc}E_{\rm b}E_{\rm c} = \chi^s_{\rm abc}E_{\rm b}E_{\rm c}, \tag{86}
$$

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

$$
P^b_{\rm a}(\mathbf{r}) = \chi_{\rm abcl}E_{\rm b}(\mathbf{r})\nabla_{\rm c}E_{\rm l}(\mathbf{r}), \tag{87}
$$
sshgp3

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. $\chi_{\rm abc}$, and 4 for the bulk, i.e. $\chi_{\rm abcl}$. 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 $\chi^s_{\rm abc}$, we start from the basic relation, $\mathbf{J} = d\mathbf{P}/dt$ with $\mathbf{J}$ the current calculated in Sec. IV, and from Eq. (77) we obtain

$$J^{(2,\ell)}_{\rm a}(\omega_3) = -i\omega_3 P_{\rm a}(\omega_3) = \frac{e}{m_e\Omega}\sum_{mn\mathbf{k}} \mathcal{P}^{{\rm a}(\ell)}_{mn}(\mathbf{k})\rho^{(2)}_{nm}(\mathbf{k};\omega_3), \tag{88}$$

which upon using Eqs. (58) and (86) leads to

$$\begin{aligned}\chi^{s(\ell)}_{\rm abc}(-\omega_3;\omega_1,\omega_2) &= \frac{ie}{m_e\Omega E^{\rm b}_1 E^{\rm c}_2 \mathcal{S}\omega_3}\sum_{mn\mathbf{k}} \mathcal{P}^{{\rm a}(\ell)}_{mn}(\mathbf{k})\rho^{(2)}_{nm}(\mathbf{k};\omega_3)\\ &= \frac{e^2}{\mathcal{S}m_e\Omega\hbar\omega_3}\sum_{mn\mathbf{k}}\frac{\mathcal{P}^{{\rm a}(\ell)}_{mn}(\mathbf{k})}{\omega_{nm\mathbf{k}}-\tilde{\omega}_3}\Big[-\left(B^{\rm c}_{nm}(\mathbf{k},\omega_\beta)\right)_{;k^{\rm b}}\\ &\quad + i\sum_\ell\left(r^{\rm b}_{n\ell}B^{\rm c}_{\ell m}(\mathbf{k},\omega_\beta) - B^{\rm c}_{n\ell}(\mathbf{k},\omega_\beta)r^{\rm b}_{\ell m}\right)\Big],\end{aligned} \tag{89}$$

which gives the surface susceptibility of layer ℓ-th. As can be seen from Eq. (58), $\chi^{s(\ell)}_{\rm abc}$ can be split into two terms, one coming from the first term and the other from the second term of Eq . (58). Then we have, after substituting Eq. (54), that

$$\chi^{s(\ell)}_{i,{\rm abc}} = -\frac{e^3}{m_e\Omega\hbar^2\omega_3}\sum_{mn\mathbf{k}}\frac{\mathcal{P}^{{\rm a}(\ell)}_{mn}}{\omega_{nm}-\omega_3}\left(\frac{f_{mn}r^{\rm b}_{nm}}{\omega_{nm}-\omega_\beta}\right)_{;k^{\rm c}}, \tag{90}$$

and

$$\chi^{s(\ell)}_{e,{\rm abc}} = \frac{ie^3}{m_e\Omega\hbar^2\omega_3}\sum_{\ell mn\mathbf{k}}\frac{\mathcal{P}^{{\rm a}(\ell)}_{mn}}{\omega_{nm}-\omega_3}\left(\frac{r^{\rm c}_{n\ell}r^{\rm b}_{\ell m}f_{m\ell}}{\omega_{\ell m}-\omega_\beta} - \frac{r^{\rm b}_{n\ell}r^{\rm c}_{\ell m}f_{\ell n}}{\omega_{n\ell}-\omega_\beta}\right), \tag{91}$$

where $\boldsymbol{\chi}^{s(\ell)}_i$ is related to intraband transitions and $\boldsymbol{\chi}^{s(\ell)}_e$ to interband transitions. We mention that Eq. (90) and Eq. (91) need to be symmetrized for intrinsic permutation symmetry, i.e. $\chi^{\rm abc}(-\omega_3;\omega_1,\omega_2) = \chi^{\rm acb}(-\omega_3;\omega_2,\omega_1)$,[22] (for SHG $\omega_1=\omega_2=\omega$ and $\omega_3 = 2\omega$). We mention that above equations diverge as $\omega_3\to 0$. This apparent divergence is removed in the following section.

The generalized derivative in Eq. (90) is obtained from the chain rule as

$$\left(\frac{f_{mn}r^{\rm b}_{nm}}{\omega_{nm}-\omega_2}\right)_{;k^{\rm c}} = \frac{f_{mn}}{\omega_{nm}-\omega}\left(r^{\rm b}_{nm}\right)_{;k^{\rm c}} - \frac{f_{mn}r^{\rm b}_{nm}}{(\omega_{nm}-\omega)^2}\left(\omega_{nm}\right)_{;k^{\rm c}}, \tag{92}$$

here $(\omega_{nm})_{;k^a} = (\omega_n)_{;k^a} - (\omega_m)_{;k^a}$. In the appendices we show that

$$(\omega_{nm})_{;k^{\mathrm{c}}} = \frac{p^{\mathrm{c}}_{nn} - p^{\mathrm{c}}_{mm}}{m_e} \equiv \Delta^{\mathrm{c}}_{nm}, \tag{93}$$

and that

$$(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}} = \frac{r^{\mathrm{c}}_{nm}\Delta^{\mathrm{b}}_{mn} + r^{\mathrm{b}}_{nm}\Delta^{\mathrm{c}}_{mn}}{\omega_{nm}} + \frac{i}{\omega_{nm}}\sum_{\ell}\left(\omega_{\ell m} r^{\mathrm{c}}_{n\ell} r^{\mathrm{b}}_{\ell m} - \omega_{n\ell} r^{\mathrm{b}}_{n\ell} r^{\mathrm{c}}_{\ell m}\right). \tag{94}$$

Above formulas give a complete set of relationships in order to calculate the nonlinear susceptibility of any given layer ℓ as $\boldsymbol{\chi}^{s(\ell)} = \boldsymbol{\chi}^{s(\ell)}_e + \boldsymbol{\chi}^{s(\ell)}_i$. Then, we can calculate the surface susceptibility as

$$\chi^{s}_{\mathrm{abc}}(2\omega) \equiv \sum_{\ell_0}^{\ell_d} \chi^{(\ell)}_{\mathrm{abc}}(2\omega), \tag{95}$$

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. (95) for either the front or the back surface. Likewise

$$\chi^{(\ell_f)}_{\mathrm{abc}}(2\omega) \equiv \sum_{\ell_d}^{\ell_f} \chi^{(\ell)}_{\mathrm{abc}}(2\omega), \tag{96}$$

is a dipolar bulk susceptibility, with the property that,

$$\chi^{(\ell_f)}_{\mathrm{abc}}(2\omega) \stackrel{\ell_f \to \ell_b}{=} 0, \tag{97}$$

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. (84). We remark that ℓ_d is not universal, and ℓ_b should be found according to Eq. (97).

VI. DIVERGENCE-FREE χ^s

To obtain divergence free expressions for SHG that are manageable for programing, we take Eqs. (90) and (91) and perform a partial fraction expansion in ω to get the following terms for the *intErband* term

$$\begin{aligned} E &= A\left[-\frac{1}{2\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega} + \frac{2}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega} + \frac{1}{2\omega_{lm}\omega_{nm}}\frac{1}{\omega}\right] \\ &- B\left[-\frac{1}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nl}-\omega} + \frac{2}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega} + \frac{1}{2\omega_{nl}\omega_{nm}}\frac{1}{\omega}\right], \end{aligned} \tag{98}$$

where $A = f_{ml}\mathcal{P}^{\mathrm{a}}_{mn} r^{\mathrm{c}}_{nl} r^{\mathrm{b}}_{lm}$ and $B = f_{ln}\mathcal{P}^{\mathrm{a}}_{mn} r^{\mathrm{b}}_{nl} r^{\mathrm{c}}_{lm}$, and the following terms for the *Intraband* terms (using Eq. (92))

$$\begin{aligned} I &= C\left[-\frac{1}{2\omega^2_{nm}}\frac{1}{\omega_{nm}-\omega} + \frac{2}{\omega^2_{nm}}\frac{1}{\omega_{nm}-2\omega} + \frac{1}{2\omega^2_{nm}}\frac{1}{\omega}\right] \\ &- D\left[-\frac{3}{2\omega^3_{nm}}\frac{1}{\omega_{nm}-\omega} + \frac{4}{\omega^3_{nm}}\frac{1}{\omega_{nm}-2\omega} + \frac{1}{2\omega^3_{nm}}\frac{1}{\omega} - \frac{1}{2\omega^2_{nm}}\frac{1}{(\omega_{nm}-\omega)^2}\right], \end{aligned} \tag{99}$$

where $C = f_{mn}\mathcal{P}^{\rm a}_{mn}(r^{\rm b}_{nm})_{;k^{\rm c}}$, and $D = f_{mn}\mathcal{P}^{\rm a}_{mn}r^{\rm b}_{nm}\Delta^{\rm c}_{nm}$. Time-reversal symmetry allow us to write, $\mathbf{r}_{mn}(\mathbf{k}) = \mathbf{r}_{nm}(-\mathbf{k})$, $\mathbf{r}_{mn;\mathbf{k}}(\mathbf{k}) = -\mathbf{r}_{nm;\mathbf{k}}(-\mathbf{k})$, $\mathcal{P}^{\rm a}_{mn}(-\mathbf{k}) = -\mathcal{P}^{\rm a}_{nm}(\mathbf{k})$, $\omega^S_{mn}(-\mathbf{k}) = \omega^S_{mn}(\mathbf{k})$, and $\Delta^a_{nm}(-\mathbf{k}) = -\Delta^a_{nm}(\mathbf{k})$. Also, 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 $f_{nm} = -f_{mn}$. Then adding the $\mathbf{k}$ and $-\mathbf{k}$ terms, we can easily show that the $1/\omega$ terms in both Eq. (98) and Eq. (99) cancel each other. The last term in the second line of Eq. (99) is dealt with as follows.

$$
\begin{aligned}
\frac{D}{2\omega^2_{nm}}\frac{1}{(\omega_{nm}-\omega)^2} = \frac{f_{mn}\mathcal{P}^{\rm a}_{mn}r^{\rm b}_{nm}\Delta^{\rm c}_{nm}}{2\omega^2_{nm}}\frac{1}{(\omega_{nm}-\omega)^2} &= -\frac{im_ef_{mn}}{2}\frac{\mathcal{R}^{\rm a}_{mn}r^{\rm b}_{nm}}{\omega_{nm}}\frac{\Delta^{\rm c}_{nm}}{(\omega_{nm}-\omega)^2} \\
&= \frac{im_ef_{mn}}{2}\frac{\mathcal{R}^{\rm a}_{mn}r^{\rm b}_{nm}}{\omega_{nm}}\left(\frac{1}{\omega_{nm}-\omega}\right)_{;k^{\rm c}} \\
&= -\frac{im_ef_{mn}}{2}\left(\frac{\mathcal{R}^{\rm a}_{mn}r^{\rm b}_{nm}}{\omega_{nm}}\right)_{;k^{\rm c}}\frac{1}{\omega_{nm}-\omega},
\end{aligned} \tag{100}
$$

where we used Eqs. (93) and (79), and for the last line, we performed an integration by parts over the Brillouin zone, where the contribution from the edges vanishes.[26] Using the chain rule, we obtain

$$
\left(\frac{\mathcal{R}^{\rm a}_{mn}r^{\rm b}_{nm}}{\omega_{nm}}\right)_{;k^{\rm c}} = \frac{r^{\rm b}_{nm}}{\omega_{nm}}\left(\mathcal{R}^{\rm a}_{mn}\right)_{;k^{\rm c}} + \frac{\mathcal{R}^{\rm a}_{mn}}{\omega_{nm}}\left(r^{\rm b}_{nm}\right)_{;k^{\rm c}} - \frac{\mathcal{R}^{\rm a}_{mn}r^{\rm b}_{nm}}{\omega^2_{nm}}\left(\omega_{nm}\right)_{;k^{\rm c}}, \tag{101}
$$

where in the appendix F we show that (we take c $\to$ b)

$$
(\mathcal{R}^{\rm a}_{nm})_{;k^{\rm b}} = \frac{\mathcal{R}^{\rm a}_{nm}\Delta^{\rm b}_{mn} + r^{\rm b}_{nm}\Delta^{\rm a(\ell)}_{mn}}{\omega_{nm}} + \frac{i}{\omega_{nm}}\sum_{\ell\neq m,n}\left(\omega_{\ell m}r^{\rm b}_{n\ell}\mathcal{R}^{\rm a}_{\ell m} - \omega_{n\ell}\mathcal{R}^{\rm a}_{n\ell}r^{\rm b}_{\ell m}\right), \tag{102}
$$

with

$$
\Delta^{\rm a(\ell)}_{mn} = \mathcal{V}^{\rm a(\ell)}_{mm} - \mathcal{V}^{\rm a(\ell)}_{nn} = \frac{\mathcal{P}^{\rm a(\ell)}_{mm} - \mathcal{P}^{\rm a(\ell)}_{nn}}{m_e}. \tag{103}
$$

Therefore, all the remaining non-zero terms in expressions (98) and (99) are simple ω and 2ω resonant denominators well behaved at zero frequency.

Using time-reversal invariance and simple index manipulation, we show in the appendix that

$$
\mathrm{Im}[\chi^{s(\ell)}_{e,\mathrm{abc},\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\sum_{l\neq(v,c)}\left[\frac{\omega^S_{lc}\mathrm{Re}[\mathcal{R}^{\rm a(\ell)}_{lc}\{r^{\rm b}_{cv}r^{\rm c}_{vl}\}]}{\omega^S_{cv}(2\omega^S_{cv}-\omega^S_{cl})} - \frac{\omega^S_{vl}\mathrm{Re}[\mathcal{R}^{\rm a(\ell)}_{vl}\{r^{\rm c}_{lc}r^{\rm b}_{cv}\}]}{\omega^S_{cv}(2\omega^S_{cv}-\omega^S_{lv})}\right]\delta(\omega^S_{cv}-\omega), \tag{104}
$$

$$
\mathrm{Im}[\chi^{s(\ell)}_{e,\mathrm{abc},2\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}4\left[\sum_{v'\neq v}\frac{\mathrm{Re}[\mathcal{R}^{\rm a(\ell)}_{vc}\{r^{\rm b}_{cv'}r^{\rm c}_{v'v}\}]}{2\omega^S_{cv'}-\omega^S_{cv}} - \sum_{c'\neq c}\frac{\mathrm{Re}[\mathcal{R}^{\rm a(\ell)}_{vc}\{r^{\rm c}_{cc'}r^{\rm b}_{c'v}\}]}{2\omega^S_{c'v}-\omega^S_{cv}}\right]\delta(\omega^S_{cv}-2\omega), \tag{105}
$$

$$
\mathrm{Im}[\chi^{s(\ell)}_{i,\mathrm{abc},\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{cv\mathbf{k}}\frac{1}{\omega^S_{cv}}\left[\mathrm{Im}[\{r^{\rm b}_{cv}\left(\mathcal{R}^{\rm a(\ell)}_{vc}\right)_{;k^{\rm c}}\}] + \frac{2\mathrm{Im}[\mathcal{R}^{\rm a(\ell)}_{vc}\{r^{\rm b}_{cv}\Delta^{\rm c}_{cv}\}]}{\omega^S_{cv}}\right]\delta(\omega^S_{cv}-\omega), \tag{106}
$$

and

$$\mathrm{Im}[\chi^{s(\ell)}_{i,\mathrm{abc},2\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\frac{4}{\omega^S_{cv}}\left[\mathrm{Im}[\mathcal{R}^{\mathrm{a}(\ell)}_{vc}\{\left(r^{\mathrm{b}}_{cv}\right)_{;k^{\mathrm{c}}}\}] - \frac{2\mathrm{Im}[\mathcal{R}^{\mathrm{a}(\ell)}_{vc}\{r^{\mathrm{b}}_{cv}\Delta^{\mathrm{c}}_{cv}\}]}{\omega^S_{cv}}\right]\delta(\omega^S_{cv}-2\omega), \tag{107}$$ imchi2wn

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, and then $\chi^{s(\ell)}_{\mathrm{abc}} = \chi^{s(\ell)}_{e,\mathrm{abc},\omega}+\chi^{s(\ell)}_{e,\mathrm{abc},2\omega}+\chi^{s(\ell)}_{i,\mathrm{abc},\omega}+\chi^{s(\ell)}_{i,\mathrm{abc},2\omega}$. Also, 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 the continuous limit of $\mathbf{k}$ $(1/\Omega)\sum_{\mathbf{k}} \to \int d^3\mathbf{k}/(8\pi^3)$, and with the help of Eq. (93), (94), (102) and (103), Eqs. (104)-(107) could be readily evaluated.

Also, since we are working in the length-gauge, it is trivial to incorporate the scissors operator in above expressions for $\boldsymbol{\chi}^{s(\ell)}$ by simple taking $\omega_n \to \omega^S_n$, where $\omega^S_n = \omega_n + (1-f_n)\Delta$ with Δ the rigid scissor correction.[27,28]

VII. CONTRIBUTION OF A NON-LOCAL POTENTIAL

We go back to Eq. (68) and keep the contribution coming form the non-local potential, i.e.

$$\begin{aligned}\hat{\mathbf{v}} &= \frac{\hat{\mathbf{p}}}{m} + \hat{\mathbf{v}}^{\mathrm{nl}}\\ \hat{\mathbf{v}}^{\mathrm{nl}} &= \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{v}(\mathbf{r},\hat{\mathbf{p}})].\end{aligned} \tag{108}$$

We get that

$$\langle\mathbf{r}|\hat{\mathbf{v}}^{\mathrm{nl}}|n\mathbf{k}\rangle = \int d^3r'\langle\mathbf{r}|\hat{\mathbf{v}}^{\mathrm{nl}}|\mathbf{r}'\rangle\langle\mathbf{r}'|n\mathbf{k}\rangle = \hat{\mathbf{v}}^{\mathrm{nl}}\int d^3r'\langle\mathbf{r}|\mathbf{r}'\rangle\langle\mathbf{r}'|n\mathbf{k}\rangle = \hat{\mathbf{v}}^{\mathrm{nl}}\psi_{n\mathbf{k}}(\mathbf{r}), \tag{109}$$ nl.2

and Eq. (72) is now

$$
\begin{aligned}
\boldsymbol{\mathcal{V}}^{(\ell)}_{mn}(\mathbf{k}) \;&=\; \frac{1}{2}\int \mathrm{d}^3r\, S_\ell(z)\Big[\langle m\mathbf{k}|\frac{\mathbf{p}}{m_e}+\mathbf{v}^{\mathrm{nl}}|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle+\langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\frac{\mathbf{p}}{m_e}+\mathbf{v}^{\mathrm{nl}}|n\mathbf{k}\rangle\Big],\\
&=\; \frac{1}{2}\int \mathrm{d}^3r\, S_\ell(z)\Big[\langle m\mathbf{k}|\frac{\mathbf{p}}{m_e}|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle+\langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\frac{\mathbf{p}}{m_e}|n\mathbf{k}\rangle\Big],\\
&+\; \frac{1}{2}\int \mathrm{d}^3r\, S_\ell(z)\Big[\langle m\mathbf{k}|\mathbf{v}^{\mathrm{nl}}|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle+\langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\mathbf{v}^{\mathrm{nl}}|n\mathbf{k}\rangle\Big],\\
&=\; \frac{1}{2m_e}\int \mathrm{d}^3r\, S(z)\Big[\psi_{n\mathbf{k}}(\mathbf{r})\hat{\mathbf{p}}^*\psi^*_{m\mathbf{k}}(\mathbf{r})+\psi^*_{m\mathbf{k}}(\mathbf{r})\hat{\mathbf{p}}\psi_{n\mathbf{k}}(\mathbf{r})\Big]\\
&+\; \frac{1}{2}\int \mathrm{d}^3r\, S_\ell(z)\Big[\psi_{n\mathbf{k}}(\mathbf{r})\hat{\mathbf{v}}^{\mathrm{nl}*}\psi^*_{m\mathbf{k}}(\mathbf{r})+\psi^*_{m\mathbf{k}}(\mathbf{r})\hat{\mathbf{v}}^{\mathrm{nl}}\psi_{n\mathbf{k}}(\mathbf{r})\Big]\\
&=\; \frac{1}{m_e}\int \mathrm{d}^3r\, \psi^*_{m\mathbf{k}}(\mathbf{r})\left[\frac{S(z)\mathbf{p}+\mathbf{p}S(z)}{2}\right]\psi_{n\mathbf{k}}(\mathbf{r})\\
&+\; \int \mathrm{d}^3r\, \psi^*_{m\mathbf{k}}(\mathbf{r})\left[\frac{S(z)\mathbf{v}^{\mathrm{nl}}+\mathbf{v}^{\mathrm{nl}}S(z)}{2}\right]\psi_{n\mathbf{k}}(\mathbf{r})\\
&=\; \frac{1}{m_e}\int \mathrm{d}^3r\, \psi^*_{m\mathbf{k}}(\mathbf{r})\boldsymbol{\mathcal{P}}^{(\ell)}\psi_{n\mathbf{k}}(\mathbf{r})+\int \mathrm{d}^3r\, \psi^*_{m\mathbf{k}}(\mathbf{r})\boldsymbol{\mathcal{V}}^{\mathrm{nl}(\ell)}\psi_{n\mathbf{k}}(\mathbf{r})\\
&=\; \frac{1}{m_e}\boldsymbol{\mathcal{P}}^{(\ell)}_{mn}(\mathbf{k})+\boldsymbol{\mathcal{V}}^{\mathrm{nl}(\ell)}_{mn}(\mathbf{k}),
\end{aligned} \tag{110}
$$

where we used the hermitian property of $\mathbf{p}$ and $\mathbf{v}^{\mathrm{nl}}$ and defined

$$
\boldsymbol{\mathcal{V}}^{\mathrm{nl}(\ell)} = \frac{S(z)\mathbf{v}^{\mathrm{nl}}+\mathbf{v}^{\mathrm{nl}}S(z)}{2}, \tag{111}
$$

and the superscript ℓ is inherited from $S(z)$. We would obtain, instead of Eq. (90) and (91)

$$
\chi^{s(\ell)}_{i,\mathrm{abc}} = -\frac{e^3}{m_e\Omega\hbar^2\omega_3}\sum_{mn\mathbf{k}}\frac{m_e\mathcal{V}^{\mathrm{a}(\ell)}_{mn}}{\omega_{nm}-\omega_3}\left(\frac{f_{mn}r^{\mathrm{b}}_{nm}}{\omega_{nm}-\omega_\beta}\right)_{;k^{\mathrm{c}}}, \tag{112}
$$

chiinl

and

$$
\chi^{s(\ell)}_{e,\mathrm{abc}} = \frac{ie^3}{m_e\Omega\hbar^2\omega_3}\sum_{\ell mn\mathbf{k}}\frac{m_e\mathcal{V}^{\mathrm{a}(\ell)}_{mn}}{\omega_{nm}-\omega_3}\left(\frac{r^{\mathrm{c}}_{n\ell}r^{\mathrm{b}}_{\ell m}f_{m\ell}}{\omega_{\ell m}-\omega_\beta}-\frac{r^{\mathrm{b}}_{n\ell}r^{\mathrm{c}}_{\ell m}f_{\ell n}}{\omega_{n\ell}-\omega_\beta}\right), \tag{113}
$$

chienl

where

$$
m_e\mathcal{V}^{\mathrm{a}(\ell)}_{mn}(\mathbf{k}) = \mathcal{P}^{\mathrm{a}(\ell)}_{mn}(\mathbf{k}) + m_e\mathcal{V}^{\mathrm{nl,a}(\ell)}_{mn}(\mathbf{k}), \tag{114}
$$

VIII. CONCLUSIONS

con

We have presented a complete derivation of the required elements to calculate the surface SHG susceptibility tensor $\boldsymbol{\chi}^s(2\omega)$ 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: Divergence Free Expressions for $\chi^s_{\rm abc}$

We add the $\mathbf{k}$ and $-\mathbf{k}$ terms of expressions (98) and (99) to obtain:

$$
\begin{aligned}
A\left[-\frac{1}{2\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}\right] &= -\frac{f_{ml}}{2}\left[\frac{\mathcal{P}^{\rm a}_{mn}r^{\rm c}_{nl}r^{\rm b}_{lm}}{\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}|_{\mathbf{k}}\right.\\
\left.+\frac{\mathcal{P}^{\rm a}_{mn}r^{\rm c}_{nl}r^{\rm b}_{lm}}{\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}|_{-\mathbf{k}}\right] &= -\frac{f_{ml}}{2}\left[\frac{\mathcal{P}^{\rm a}_{mn}r^{\rm c}_{nl}r^{\rm b}_{lm}}{\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}|_{\mathbf{k}}\right.\\
\left.-\frac{\mathcal{P}^{\rm a}_{nm}r^{\rm c}_{ln}r^{\rm b}_{ml}}{\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}|_{\mathbf{k}}\right] &= -\frac{f_{ml}}{2}\frac{1}{\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}\\
&\quad\times\left[\mathcal{P}^{\rm a}_{mn}r^{\rm c}_{nl}r^{\rm b}_{lm}-\mathcal{P}^{\rm a}_{nm}r^{\rm c}_{ln}r^{\rm b}_{ml}\right] \qquad \text{(A1)}\\
=-\frac{f_{ml}}{2}\frac{1}{\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}\left[\mathcal{P}^{\rm a}_{mn}r^{\rm c}_{nl}r^{\rm b}_{lm}-(\mathcal{P}^{\rm a}_{mn}r^{\rm c}_{nl}r^{\rm b}_{lm})^*\right] &= -\frac{f_{ml}}{2}\frac{2i{\rm Im}[\mathcal{P}^{\rm a}_{mn}r^{\rm c}_{nl}r^{\rm b}_{lm}]}{\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega},
\end{aligned}
$$

where we used the Hermiticity of the momentum and position operators. Likewise we get that

$$
A\left[\frac{2}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\right] = f_{ml}\frac{4i{\rm Im}[\mathcal{P}^{\rm a}_{mn}r^{\rm c}_{nl}r^{\rm b}_{lm}]}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}. \qquad \text{(A2)}
$$

Also,

$$
\begin{aligned}
&- f_{ln}\mathcal{P}^{\rm a}_{mn}r^{\rm b}_{nl}r^{\rm c}_{lm}\left[-\frac{1}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nl}-\omega}+\frac{2}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\right]\\
&= -2if_{ln}{\rm Im}[\mathcal{P}^{\rm a}_{mn}r^{\rm b}_{nl}r^{\rm c}_{lm}]\left[-\frac{1}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nl}-\omega}+\frac{2}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\right], \quad \text{(A3)}
\end{aligned}
$$

and therefore

$$
\begin{aligned}
E &= 2if_{ml}{\rm Im}[\mathcal{P}^{\rm a}_{mn}r^{\rm c}_{nl}r^{\rm b}_{lm}]\left[-\frac{1}{2\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}+\frac{2}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\right]\\
&- 2if_{ln}{\rm Im}[\mathcal{P}^{\rm a}_{mn}r^{\rm b}_{nl}r^{\rm c}_{lm}]\left[-\frac{1}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nl}-\omega}+\frac{2}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\right]. \quad \text{(A4)}
\end{aligned}
$$

Using above results into Eq. (91) implies

$$
\begin{aligned}
\chi^{s(\ell)}_{e,{\rm abc}} &= -\frac{2e^3}{m_e\hbar^2}\sum_{\ell mn\mathbf{k}}\left[f_{ml}{\rm Im}[\mathcal{P}^{\rm a}_{mn}r^{\rm c}_{nl}r^{\rm b}_{lm}]\left[-\frac{1}{2\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}+\frac{2}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\right]\right.\\
&\left.- f_{ln}{\rm Im}[\mathcal{P}^{\rm a}_{mn}r^{\rm b}_{nl}r^{\rm c}_{lm}]\left[-\frac{1}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nl}-\omega}+\frac{2}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\right]\right]\\
&= -\frac{2e^3}{m_e\hbar^2}\sum_{\ell mn\mathbf{k}}\left[f_{ml}{\rm Im}[\mathcal{P}^{\rm a}_{mn}\{r^{\rm c}_{nl}r^{\rm b}_{lm}\}]\left[-\frac{1}{2\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}+\frac{2}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\right]\right.\\
&\left.- f_{ln}{\rm Im}[\mathcal{P}^{\rm a}_{mn}\{r^{\rm b}_{nl}r^{\rm c}_{lm}\}]\left[-\frac{1}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nl}-\omega}+\frac{2}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\right]\right], \qquad \text{(A5)}
\end{aligned}
$$

where $\{\}$ is the symmetrization of the Cartesian indices bc, i.e. $\{u^{\mathrm{b}}s^{\mathrm{c}}\} = (u^{\mathrm{b}}s^{\mathrm{c}} + u^{\mathrm{c}}s^{\mathrm{b}})/2$. Then, we see that $\chi^{s(\ell)}_{e,\mathrm{abc}} = \chi^{s(\ell)}_{e,acb}$. We further simplify the last equation as follows:

$$
\begin{aligned}
\chi^{s(\ell)}_{e,\mathrm{abc}} &= -\frac{2e^3}{2m_e\hbar^2}\sum_{\ell mn\mathbf{k}}\left[\left[-\frac{f_{ml}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}\}]}{2\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega} + \frac{2f_{ml}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}\}]}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\right]\right. \\
&+ \left.\left[\frac{f_{ln}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}\}]}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nl}-\omega} - \frac{2f_{ln}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}\}]}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nm}-2\omega}\right]\right] \\
&= -\frac{2e^3}{m_e\hbar^2}\sum_{\ell mn\mathbf{k}}\left[\left[\frac{2f_{ml}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}\}]}{\omega_{nm}(2\omega_{lm}-\omega_{nm})} - \frac{2f_{ln}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}\}]}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\right]\frac{1}{\omega_{nm}-2\omega}\right. \\
&+ \left.\left[\frac{f_{ln}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}\}]}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nl}-\omega} - \frac{f_{ml}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}\}]}{2\omega_{lm}(2\omega_{lm}-\omega_{nm})}\frac{1}{\omega_{lm}-\omega}|_{\ell\leftrightarrow m}\right]\right] \\
&= -\frac{e^3}{m_e\hbar^2}\sum_{\ell mn\mathbf{k}}\left[\left[\frac{2f_{ml}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}\}]}{\omega_{nm}(2\omega_{lm}-\omega_{nm})} - \frac{2f_{ln}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}\}]}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\right]\frac{1}{\omega_{nm}-2\omega}\right. \\
&+ \left.\left[\frac{f_{ln}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}\}]}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nl}-\omega} - \frac{f_{lm}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{ln}\{r^{\mathrm{c}}_{nm}r^{\mathrm{b}}_{ml}\}]}{2\omega_{ml}(2\omega_{ml}-\omega_{nl})}\frac{1}{\omega_{ml}-\omega}|_{n\leftrightarrow m}\right]\right] \\
&= -\frac{e^3}{m_e\hbar^2}\sum_{\ell mn\mathbf{k}}\left[\left[\frac{2f_{ml}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}\}]}{\omega_{nm}(2\omega_{lm}-\omega_{nm})} - \frac{2f_{ln}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}\}]}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\right]\frac{1}{\omega_{nm}-2\omega}\right. \\
&+ \left.\left[\frac{f_{ln}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}\}]}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\frac{1}{\omega_{nl}-\omega} - \frac{f_{ln}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{lm}\{r^{\mathrm{c}}_{mn}r^{\mathrm{b}}_{nl}\}]}{2\omega_{nl}(2\omega_{nl}-\omega_{ml})}\frac{1}{\omega_{nl}-\omega}\right]\right] \\
&= -\frac{e^3}{m_e\hbar^2}\sum_{\ell mn\mathbf{k}}\left[\left[\frac{2f_{ml}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}\}]}{\omega_{nm}(2\omega_{lm}-\omega_{nm})} - \frac{2f_{ln}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}\}]}{\omega_{nm}(2\omega_{nl}-\omega_{nm})}\right]\frac{1}{\omega_{nm}-2\omega}\right. \\
&+ \left. f_{ln}\left[\frac{\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}\}]}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})} - \frac{f_{ln}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{lm}\{r^{\mathrm{c}}_{mn}r^{\mathrm{b}}_{nl}\}]}{2\omega_{nl}(2\omega_{nl}-\omega_{ml})}\right]\frac{1}{\omega_{nl}-\omega}\right],
\end{aligned} \tag{A6}
$$

where the 2 in the denominator of the prefactor after the first equal sign comes from the $\mathbf{k}$ and $-\mathbf{k}$ addition, i.e. $\chi \to \sum_{\mathbf{k}>0}[\chi(\mathbf{k}) + \chi(-\mathbf{k})]/2$. Taking $\omega \to \omega + i\eta$ and use $\lim_{\eta\to 0} 1/(x - i\eta) = P(1/x) + i\pi\delta(x)$, to get

$$
\begin{aligned}
\mathrm{Im}[\chi^{s(\ell)}_{e,\mathrm{abc}}] &= \frac{2\pi e^3}{m_e\hbar^2}\sum_{\ell mn\mathbf{k}}\left[\left[\frac{2f_{ln}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}\}]}{\omega_{nm}(2\omega_{nl}-\omega_{nm})} - \frac{2f_{ml}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}\}]}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}\right]\delta(\omega_{nm}-2\omega)\right. \\
&+ \left. f_{ln}\left[\frac{\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{lm}\{r^{\mathrm{c}}_{mn}r^{\mathrm{b}}_{nl}\}]}{2\omega_{nl}(2\omega_{nl}-\omega_{ml})} - \frac{\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}\}]}{2\omega_{nl}(2\omega_{nl}-\omega_{nm})}\right]\delta(\omega_{nl}-\omega)\right].
\end{aligned} \tag{A7}
$$

We change $l \leftrightarrow m$ in the last term, to write

$$
\begin{aligned}
\mathrm{Im}[\chi^{s(\ell)}_{e,\mathrm{abc}}] &= \frac{\pi e^3}{m_e\hbar^2}\sum_{\ell mn\mathbf{k}}\left[\left[\frac{2f_{ln}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{b}}_{nl}r^{\mathrm{c}}_{lm}\}]}{\omega_{nm}(2\omega_{nl}-\omega_{nm})} - \frac{2f_{ml}\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{mn}\{r^{\mathrm{c}}_{nl}r^{\mathrm{b}}_{lm}\}]}{\omega_{nm}(2\omega_{lm}-\omega_{nm})}\right]\delta(\omega_{nm}-2\omega)\right. \\
&+ \left. f_{mn}\left[\frac{\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{ml}\{r^{\mathrm{c}}_{ln}r^{\mathrm{b}}_{nm}\}]}{2\omega_{nm}(2\omega_{nm}-\omega_{lm})} - \frac{\mathrm{Im}[\mathcal{P}^{\mathrm{a}}_{ln}\{r^{\mathrm{b}}_{nm}r^{\mathrm{c}}_{ml}\}]}{2\omega_{nm}(2\omega_{nm}-\omega_{nl})}\right]\delta(\omega_{nm}-\omega)\right].
\end{aligned} \tag{A8}
$$

From the delta functions it follows that $n = c$ and $m = v$, then $f_{ln} = 1$ with $l = v'$, $f_{ml} = 1$ with $l = c'$, and $f_{mn} = 1$ with $l = c'$ or v', and

$$\begin{aligned}
\mathrm{Im}[\chi^{s(\ell)}_{e,\mathrm{abc}}] &= \frac{\pi e^3}{m_e\hbar^2}\sum_{vc\mathbf{k}}\Bigg[\Bigg[\sum_{v'\neq v}\frac{2\mathrm{Im}[\mathcal{P}^{\mathrm{a}(\ell)}_{vc}\{r^{\mathrm{b}}_{cv'}r^{\mathrm{c}}_{v'v}\}]}{\omega_{cv}(2\omega_{cv'}-\omega_{cv})} - \sum_{c'\neq c}\frac{2\mathrm{Im}[\mathcal{P}^{\mathrm{a}(\ell)}_{vc}\{r^{\mathrm{c}}_{cc'}r^{\mathrm{b}}_{c'v}\}]}{\omega_{cv}(2\omega_{c'v}-\omega_{cv})}\Bigg]\delta(\omega_{cv}-2\omega) \\
&+ \sum_{l\neq(v,c)}\Bigg[\frac{\mathrm{Im}[\mathcal{P}^{\mathrm{a}(\ell)}_{vl}\{r^{\mathrm{c}}_{lc}r^{\mathrm{b}}_{cv}\}]}{2\omega_{cv}(2\omega_{cv}-\omega_{lv})} - \frac{\mathrm{Im}[\mathcal{P}^{\mathrm{a}(\ell)}_{lc}\{r^{\mathrm{b}}_{cv}r^{\mathrm{c}}_{vl}\}]}{2\omega_{cv}(2\omega_{cv}-\omega_{cl})}\Bigg]\delta(\omega_{cv}-\omega)\Bigg], \qquad \text{(A9)}
\end{aligned}$$

where we put the layer ℓ dependence in $\mathcal{P}$. Using Eq. (79), we can obtain the following result

$$\begin{aligned}
2i\mathrm{Im}[\mathcal{P}^{\mathrm{a}(\ell)}_{nm}\{r^{\mathrm{b}}_{ml}r^{\mathrm{c}}_{ln}\}] &= \mathcal{P}^{\mathrm{a}(\ell)}_{nm}\{r^{\mathrm{b}}_{ml}r^{\mathrm{c}}_{ln}\} - (\mathcal{P}^{\mathrm{a}(\ell)}_{nm}\{r^{\mathrm{b}}_{ml}r^{\mathrm{c}}_{ln}\})^* \\
&= im_e\omega_{nm}\mathcal{R}^{\mathrm{a}(\ell)}_{nm}\{r^{\mathrm{b}}_{ml}r^{\mathrm{c}}_{ln}\} - (im_e\omega_{nm}\mathcal{R}^{\mathrm{a}(\ell)}_{nm}\{r^{\mathrm{b}}_{ml}r^{\mathrm{c}}_{ln}\})^* \\
&= im_e\omega_{nm}\left(\mathcal{R}^{\mathrm{a}(\ell)}_{nm}\{r^{\mathrm{b}}_{ml}r^{\mathrm{c}}_{ln}\} + (\mathcal{R}^{\mathrm{a}(\ell)}_{nm}\{r^{\mathrm{b}}_{ml}r^{\mathrm{c}}_{ln}\})^*\right) \\
&= 2im_e\omega_{nm}\mathrm{Re}[\mathcal{R}^{\mathrm{a}(\ell)}_{nm}\{r^{\mathrm{b}}_{ml}r^{\mathrm{c}}_{ln}\}], \qquad \text{(A10)}
\end{aligned}$$

then, using $\omega_{vc} = -\omega_{vc}$ we obtain

$$\begin{aligned}
\mathrm{Im}[\chi^{s(\ell)}_{e,\mathrm{abc}}] &= \frac{\pi e^3}{\hbar^2}\sum_{vc\mathbf{k}}\Bigg[\Bigg[-\sum_{v'\neq v}\frac{2\mathrm{Re}[\mathcal{R}^{\mathrm{a}(\ell)}_{vc}\{r^{\mathrm{b}}_{cv'}r^{\mathrm{c}}_{v'v}\}]}{2\omega_{cv'}-\omega_{cv}} + \sum_{c'\neq c}\frac{2\mathrm{Re}[\mathcal{R}^{\mathrm{a}(\ell)}_{vc}\{r^{\mathrm{c}}_{cc'}r^{\mathrm{b}}_{c'v}\}]}{2\omega_{c'v}-\omega_{cv}}\Bigg]\delta(\omega_{cv}-2\omega) \\
&+ \sum_{l\neq(v,c)}\Bigg[\frac{\omega_{vl}\mathrm{Re}[\mathcal{R}^{\mathrm{a}(\ell)}_{vl}\{r^{\mathrm{c}}_{lc}r^{\mathrm{b}}_{cv}\}]}{2\omega_{cv}(2\omega_{cv}-\omega_{lv})} - \frac{\omega_{lc}\mathrm{Re}[\mathcal{R}^{\mathrm{a}(\ell)}_{lc}\{r^{\mathrm{b}}_{cv}r^{\mathrm{c}}_{vl}\}]}{2\omega_{cv}(2\omega_{cv}-\omega_{cl})}\Bigg]\delta(\omega_{cv}-\omega)\Bigg]. \qquad \text{(A11)}
\end{aligned}$$

Finally, following Ref. 27,28 we simply change $\omega_{nm} \to \omega^S_{nm}$ to obtain the scissored expresion of

$$\begin{aligned}
\mathrm{Im}[\chi^{s(\ell)}_{e,\mathrm{abc}}] &= \frac{\pi e^3}{2\hbar^2}\sum_{vc\mathbf{k}}\Bigg[4\Bigg[-\sum_{v'\neq v}\frac{\mathrm{Re}[\mathcal{R}^{\mathrm{a}(\ell)}_{vc}\{r^{\mathrm{b}}_{cv'}r^{\mathrm{c}}_{v'v}\}]}{2\omega^S_{cv'}-\omega^S_{cv}} + \sum_{c'\neq c}\frac{\mathrm{Re}[\mathcal{R}^{\mathrm{a}(\ell)}_{vc}\{r^{\mathrm{c}}_{cc'}r^{\mathrm{b}}_{c'v}\}]}{2\omega^S_{c'v}-\omega^S_{cv}}\Bigg]\delta(\omega^S_{cv}-2\omega) \\
&+ \sum_{l\neq(v,c)}\Bigg[\frac{\omega^S_{vl}\mathrm{Re}[\mathcal{R}^{\mathrm{a}(\ell)}_{vl}\{r^{\mathrm{c}}_{lc}r^{\mathrm{b}}_{cv}\}]}{\omega^S_{cv}(2\omega^S_{cv}-\omega^S_{lv})} - \frac{\omega^S_{lc}\mathrm{Re}[\mathcal{R}^{\mathrm{a}(\ell)}_{lc}\{r^{\mathrm{b}}_{cv}r^{\mathrm{c}}_{vl}\}]}{\omega^S_{cv}(2\omega^S_{cv}-\omega^S_{cl})}\Bigg]\delta(\omega^S_{cv}-\omega)\Bigg], \qquad \text{(A12)}
\end{aligned}$$

where we have "pulled" a factor of 1/2, so the prefactor is the same as that of the velocity gauge formalism.[28] For the I term of Eq. (99), we notice that the energy denominators are invariant under $\mathbf{k} \to -\mathbf{k}$, and then we only look at the numerators, then

$$\begin{aligned}
C \to f_{mn}\mathcal{P}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}}|_{\mathbf{k}} + f_{mn}\mathcal{P}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}}|_{-\mathbf{k}} &= f_{mn}\left[\mathcal{P}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}}|_{\mathbf{k}} + (-\mathcal{P}^{\mathrm{a}}_{nm})(-(r^{\mathrm{b}}_{mn})_{;k^{\mathrm{c}}})|_{\mathbf{k}}\right] \\
&= f_{mn}\left[\mathcal{P}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}} + \mathcal{P}^{\mathrm{a}}_{nm}(r^{\mathrm{b}}_{mn})_{;k^{\mathrm{c}}}\right] \\
&= f_{mn}\left[\mathcal{P}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}} + (\mathcal{P}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}})^*\right] \\
&= m_e f_{mn}\omega_{mn}\left[i\mathcal{R}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}} + (i\mathcal{R}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}})^*\right] \\
&= im_e f_{mn}\omega_{mn}\left[\mathcal{R}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}} - (\mathcal{R}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}})^*\right] \\
&= -2m_e f_{mn}\omega_{mn}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}}], \qquad \text{(A13)}
\end{aligned}$$

with similar results for $D = -2f_{mn}\omega_{mn}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}$. Now, from Eq. (101), we obtain that the first term reduces to

$$
\begin{aligned}
\frac{r^{\mathrm{b}}_{nm}}{\omega_{nm}}\left(\mathcal{R}^{\mathrm{a}}_{mn}\right)_{;k^{\mathrm{c}}}|_{\mathbf{k}} + \frac{r^{\mathrm{b}}_{nm}}{\omega_{nm}}\left(\mathcal{R}^{\mathrm{a}}_{mn}\right)_{;k^{\mathrm{c}}}|_{-\mathbf{k}} &= \frac{r^{\mathrm{b}}_{nm}}{\omega_{nm}}\left(\mathcal{R}^{\mathrm{a}}_{mn}\right)_{;k^{\mathrm{c}}}|_{\mathbf{k}} - \frac{r^{\mathrm{b}}_{mn}}{\omega_{nm}}\left(\mathcal{R}^{\mathrm{a}}_{nm}\right)_{;k^{\mathrm{c}}}|_{\mathbf{k}} \\
&= \frac{1}{\omega_{nm}}\left[r^{\mathrm{b}}_{nm}\left(\mathcal{R}^{\mathrm{a}}_{mn}\right)_{;k^{\mathrm{c}}} - \left(r^{\mathrm{b}}_{nm}\left(\mathcal{R}^{\mathrm{a}}_{mn}\right)_{;k^{\mathrm{c}}}\right)^*\right] \\
&= \frac{2i}{\omega_{nm}}\mathrm{Im}[r^{\mathrm{b}}_{nm}\left(\mathcal{R}^{\mathrm{a}}_{mn}\right)_{;k^{\mathrm{c}}}], \qquad \text{(A14)}
\end{aligned}
$$

with similar results for the other two terms. First, we collect the 2ω terms form Eq. (99) that contribute to Eq. (90)

$$
\begin{aligned}
I_{2\omega} &= -\frac{e^3}{2\hbar^2}\sum_{mn\mathbf{k}}\left[\frac{-4f_{mn}\omega_{mn}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}\left(r^{\mathrm{b}}_{nm}\right)_{;k^{\mathrm{c}}}]}{\omega^2_{nm}} - \frac{-8f_{mn}\omega_{mn}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}}{\omega^3_{nm}}\right]\frac{1}{\omega_{nm}-2\omega} \\
&= \frac{e^3}{2\hbar^2}\sum_{mn\mathbf{k}}\left[\frac{4f_{mn}\omega_{mn}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}\left(r^{\mathrm{b}}_{nm}\right)_{;k^{\mathrm{c}}}]}{\omega^2_{nm}} - \frac{8f_{mn}\omega_{mn}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}}{\omega^3_{nm}}\right]\frac{1}{\omega_{nm}-2\omega} \\
&= \frac{e^3}{2\hbar^2}\sum_{mn\mathbf{k}}\left[\frac{-4f_{mn}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}\left(r^{\mathrm{b}}_{nm}\right)_{;k^{\mathrm{c}}}]}{\omega_{nm}} + \frac{8f_{mn}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}}{\omega^2_{nm}}\right]\frac{1}{\omega_{nm}-2\omega}, \qquad \text{(A15)}
\end{aligned}
$$

where the 2 in the denominator of the prefactor comes from the $\mathbf{k}$ and $-\mathbf{k}$ addition, as previously noted. Taking $\eta \to 0$ we get that

$$
\begin{aligned}
\mathrm{Im}[\chi^{s(\ell)}_{i,\mathrm{abc},2\omega}] &= \frac{\pi|e|^3}{2\hbar^2}\sum_{mn\mathbf{k}}\frac{4f_{mn}}{\omega_{nm}}\left[\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}\left(r^{\mathrm{b}}_{nm}\right)_{;k^{\mathrm{c}}}] - \frac{2\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}}{\omega_{nm}}\right]\delta(\omega_{nm}-2\omega) \\
&= \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\frac{4}{\omega^S_{cv}}\left[\mathrm{Im}[\mathcal{R}^{\mathrm{a}(\ell)}_{vc}\{\left(r^{\mathrm{b}}_{cv}\right)_{;k^{\mathrm{c}}}\}] - \frac{2\mathrm{Im}[\mathcal{R}^{\mathrm{a}(\ell)}_{vc}\{r^{\mathrm{b}}_{cv}]\Delta^{\mathrm{c}}_{cv}\}}{\omega^S_{cv}}\right]\delta(\omega^S_{cv}-2\omega), \text{(A16)}
\end{aligned}
$$

where from the delta term we must have $n = c$ and $m = v$. The expression is symmetric in the last two indices and is properly scissor shifted as well.

The ω terms are

$$
\begin{aligned}
I_\omega &= -\frac{e^3}{m_e 2\hbar^2}\sum_{nm\mathbf{k}}\left[\left[-\frac{C}{2\omega_{nm}^2}+\frac{3D}{2\omega_{nm}^3}\right]\frac{1}{\omega_{nm}-\omega}+\frac{D}{2\omega_{nm}^2}\frac{1}{(\omega_{nm}-\omega)^2}\right]\\
&= -\frac{e^3}{m_e 2\hbar^2}\sum_{nm\mathbf{k}}\left[\left[-\frac{-2m_e f_{mn}\omega_{mn}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}}]}{2\omega_{nm}^2}+\frac{3(-2m_e f_{mn}\omega_{mn}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm})}{2\omega_{nm}^3}\right]\frac{1}{\omega_{nm}-\omega}\right.\\
&+ \left.\frac{-im_e f_{mn}}{2}\left(\frac{\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}}{\omega_{nm}}\right)_{;k^{\mathrm{c}}}\frac{1}{\omega_{nm}-\omega}\right]\\
&= \frac{|e|^3}{2\hbar^2}\sum_{nm\mathbf{k}}f_{mn}\left[-\frac{\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}}]}{\omega_{nm}}+\frac{3\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}}{\omega_{nm}^2}-\frac{i}{2}\left(\frac{\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}}{\omega_{nm}}\right)_{;k^{\mathrm{c}}}\right]\frac{1}{\omega_{nm}-\omega}\\
&= \frac{|e|^3}{2\hbar^2}\sum_{nm\mathbf{k}}f_{mn}\left[-\frac{\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}}]}{\omega_{nm}}+\frac{3\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}}{\omega_{nm}^2}-\frac{i}{2}\left[\frac{r^{\mathrm{b}}_{nm}}{\omega_{nm}}\left(\mathcal{R}^{\mathrm{a}}_{mn}\right)_{;k^{\mathrm{c}}}\right.\right.\\
&+ \left.\left.\frac{\mathcal{R}^{\mathrm{a}}_{mn}}{\omega_{nm}}\left(r^{\mathrm{b}}_{nm}\right)_{;k^{\mathrm{c}}}-\frac{\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}}{\omega_{nm}^2}\left(\omega_{nm}\right)_{;k^{\mathrm{c}}}\right]\right]\frac{1}{\omega_{nm}-\omega}\\
&= \frac{|e|^3}{2\hbar^2}\sum_{nm\mathbf{k}}f_{mn}\left[-\frac{\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}}]}{\omega_{nm}}+\frac{3\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}}{\omega_{nm}^2}-\frac{i}{2}\left[\frac{2i}{\omega_{nm}}\mathrm{Im}[r^{\mathrm{b}}_{nm}\left(\mathcal{R}^{\mathrm{a}}_{mn}\right)_{;k^{\mathrm{c}}}]\right.\right.\\
&+ \left.\left.\frac{2i}{\omega_{nm}}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}\left(r^{\mathrm{b}}_{nm}\right)_{;k^{\mathrm{c}}}]-\frac{2i}{\omega_{nm}^2}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}\right]\right]\frac{1}{\omega_{nm}-\omega}\\
&= \frac{|e|^3}{2\hbar^2}\sum_{nm\mathbf{k}}f_{mn}\left[-\frac{\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}}]}{\omega_{nm}}+\frac{3\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}}{\omega_{nm}^2}+\frac{1}{\omega_{nm}}\mathrm{Im}[r^{\mathrm{b}}_{nm}\left(\mathcal{R}^{\mathrm{a}}_{mn}\right)_{;k^{\mathrm{c}}}]\right.\\
&+ \left.\frac{1}{\omega_{nm}}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}\left(r^{\mathrm{b}}_{nm}\right)_{;k^{\mathrm{c}}}]-\frac{1}{\omega_{nm}^2}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}\right]\frac{1}{\omega_{nm}-\omega},
\end{aligned}
\tag{A17}
$$

or

$$
\begin{aligned}
I_\omega &= \frac{|e|^3}{2\hbar^2}\sum_{nm\mathbf{k}}\frac{f_{mn}}{\omega_{nm}}\left[-\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}(r^{\mathrm{b}}_{nm})_{;k^{\mathrm{c}}}]+\frac{3\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}}{\omega_{nm}}+\mathrm{Im}[r^{\mathrm{b}}_{nm}\left(\mathcal{R}^{\mathrm{a}}_{mn}\right)_{;k^{\mathrm{c}}}]\right.\\
&+ \left.\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}\left(r^{\mathrm{b}}_{nm}\right)_{;k^{\mathrm{c}}}]-\frac{1}{\omega_{nm}}\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}\right]\frac{1}{\omega_{nm}-\omega}\\
&= \frac{|e|^3}{2\hbar^2}\sum_{nm\mathbf{k}}\frac{f_{mn}}{\omega_{nm}}\left[\frac{2\mathrm{Im}[\mathcal{R}^{\mathrm{a}}_{mn}r^{\mathrm{b}}_{nm}]\Delta^{\mathrm{c}}_{nm}}{\omega_{nm}}+\mathrm{Im}[r^{\mathrm{b}}_{nm}\left(\mathcal{R}^{\mathrm{a}}_{mn}\right)_{;k^{\mathrm{c}}}]\right]\frac{1}{\omega_{nm}-\omega}.
\end{aligned}
\tag{A18}
$$

Taking $\eta\to 0$ we get that

$$
\mathrm{Im}[\chi^{s(\ell)}_{i,\mathrm{abc},\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{cv\mathbf{k}}\frac{1}{\omega^S_{cv}}\left[\mathrm{Im}[\{r^{\mathrm{b}}_{cv}\left(\mathcal{R}^{\mathrm{a}(\ell)}_{vc}\right)_{;k^{\mathrm{c}}}\}]+\frac{2\mathrm{Im}[\mathcal{R}^{\mathrm{a}(\ell)}_{vc}\{r^{\mathrm{b}}_{cv}\}\Delta^{\mathrm{c}}_{cv}\}}{\omega^S_{cv}}\right]\delta(\omega^S_{cv}-\omega), \tag{A19}
$$

where from the delta term we must have $n=c$ and $m=v$. The expression is symmetric in the last two indices and is properly scissor shifted as well. Eq. (A12), (A16) and (A19) are the main results of this appendix, from which we have that $\chi^{s(\ell)}_{\mathrm{abc}}=\chi^{s(\ell)}_{e,\mathrm{abc}}+\chi^{s(\ell)}_{i,\mathrm{abc}}$ where $\chi^{s(\ell)}_{i,\mathrm{abc}}=\chi^{s(\ell)}_{i,\mathrm{abc},\omega}+\chi^{s(\ell)}_{i,\mathrm{abc},2\omega}$. In the continuous limit of $\mathbf{k}$ $(1/\Omega)\sum_{\mathbf{k}}\to\int d^3\mathbf{k}/(8\pi^3)$ and the real part is obtained with a Kramers-Kronig transformation. We have checked that these results are equivalent to Eqs. 40 and 41 of Cabellos et. al., Ref. 28, for a bulk system for which we simply take $\mathcal{R}^{\mathrm{a}(\ell)}_{nm}\to r^{\mathrm{a}}_{nm}$.

In summary we have

$$\mathrm{Im}[\chi^{s(\ell)}_{e,\mathrm{abc},\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\sum_{l\neq(v,c)}\left[\frac{\omega^S_{lc}\mathrm{Re}[\mathcal{R}^{\mathrm{a}(\ell)}_{lc}\{r^{\mathrm{b}}_{cv}r^{\mathrm{c}}_{vl}\}]}{\omega^S_{cv}(2\omega^S_{cv}-\omega^S_{cl})} - \frac{\omega^S_{vl}\mathrm{Re}[\mathcal{R}^{\mathrm{a}(\ell)}_{vl}\{r^{\mathrm{c}}_{lc}r^{\mathrm{b}}_{cv}\}]}{\omega^S_{cv}(2\omega^S_{cv}-\omega^S_{lv})}\right]\delta(\omega^S_{cv}-\omega), \tag{A20}$$

$$\mathrm{Im}[\chi^{s(\ell)}_{e,\mathrm{abc},2\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}4\left[\sum_{v'\neq v}\frac{\mathrm{Re}[\mathcal{R}^{\mathrm{a}(\ell)}_{vc}\{r^{\mathrm{b}}_{cv'}r^{\mathrm{c}}_{v'v}\}]}{2\omega^S_{cv'}-\omega^S_{cv}} - \sum_{c'\neq c}\frac{\mathrm{Re}[\mathcal{R}^{\mathrm{a}(\ell)}_{vc}\{r^{\mathrm{c}}_{cc'}r^{\mathrm{b}}_{c'v}\}]}{2\omega^S_{c'v}-\omega^S_{cv}}\right]\delta(\omega^S_{cv}-2\omega), \tag{A21}$$

$$\mathrm{Im}[\chi^{s(\ell)}_{i,\mathrm{abc},\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{cv\mathbf{k}}\frac{1}{\omega^S_{cv}}\left[\mathrm{Im}[\{r^{\mathrm{b}}_{cv}\left(\mathcal{R}^{\mathrm{a}(\ell)}_{vc}\right)_{;k^{\mathrm{c}}}\}] + \frac{2\mathrm{Im}[\mathcal{R}^{\mathrm{a}(\ell)}_{vc}\{r^{\mathrm{b}}_{cv}\Delta^{\mathrm{c}}_{cv}\}]}{\omega^S_{cv}}\right]\delta(\omega^S_{cv}-\omega), \tag{A22}$$

and

$$\mathrm{Im}[\chi^{s(\ell)}_{i,\mathrm{abc},2\omega}] = \frac{\pi|e|^3}{2\hbar^2}\sum_{vc\mathbf{k}}\frac{4}{\omega^S_{cv}}\left[\mathrm{Im}[\mathcal{R}^{\mathrm{a}(\ell)}_{vc}\{\left(r^{\mathrm{b}}_{cv}\right)_{;k^{\mathrm{c}}}\}] - \frac{2\mathrm{Im}[\mathcal{R}^{\mathrm{a}(\ell)}_{vc}\{r^{\mathrm{b}}_{cv}\Delta^{\mathrm{c}}_{cv}\}]}{\omega^S_{cv}}\right]\delta(\omega^S_{cv}-2\omega), \tag{A23}$$

where $e^3=-|e|^3$. With the help of Eq. (93), (94), (102) and (103) could be readily evaluated.

Appendix B: Some results of Dirac's notation

ap_dirac

We derive a series of results that follow from Dirac's notation and that are useful in the various derivations.

Let's start with the Fourier transform of the wave function written in the Schrödinger representation, i.e.

$$\psi(\mathbf{r}) = \frac{1}{(2\pi\hbar)^{3/2}}\int d\mathbf{p}\,\psi(\mathbf{p})e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}, \tag{B1}$$

ap_ft

and inversely

$$\psi(\mathbf{p}) = \frac{1}{(2\pi\hbar)^{3/2}}\int d\mathbf{r}\,\psi(\mathbf{r})e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}. \tag{B2}$$

ap_tf

Now,

$$\langle\mathbf{r}|\psi\rangle = \psi(\mathbf{r}) = \int d\mathbf{p}\langle\mathbf{r}|\mathbf{p}\rangle\langle\mathbf{p}|\psi\rangle = \int d\mathbf{p}\langle\mathbf{r}|\mathbf{p}\rangle\psi(\mathbf{p}), \tag{B3}$$

rpsi

that when compared with Eq. (B1) allow us to identify,

$$\langle\mathbf{r}|\mathbf{p}\rangle = \frac{1}{(2\pi\hbar)^{3/2}}e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}. \tag{B4}$$

rp2

By the same token,

$$\langle\mathbf{p}|\psi\rangle = \psi(\mathbf{p}) = \int d\mathbf{r}\langle\mathbf{p}|\mathbf{r}\rangle\langle\mathbf{r}|\psi\rangle = \int d\mathbf{r}\langle\mathbf{p}|\mathbf{r}\rangle\psi(\mathbf{r}), \tag{B5}$$

rpsi2

that when compared with Eq. (B2) allow us to identify,

$$\langle \mathbf{p}|\mathbf{r}\rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}, \tag{B6}$$

rp

where

$$\langle \mathbf{r}|\mathbf{p}\rangle = (\langle \mathbf{p}|\mathbf{r}\rangle)^*, \tag{B7}$$

ap_good

is succinctly verified.

We calculate the matrix elements of $\mathbf{p}$ in the $\mathbf{r}$ representation,

$$\begin{aligned} \langle \mathbf{r}|\hat{p}_x|\mathbf{r}'\rangle &= \int d\mathbf{p} \langle \mathbf{r}|\hat{p}_x|\mathbf{p}\rangle\langle \mathbf{p}|\mathbf{r}'\rangle \\ &= \int d\mathbf{p} p_x \langle \mathbf{r}|\mathbf{p}\rangle\langle \mathbf{p}|\mathbf{r}'\rangle \\ &= \frac{1}{(2\pi\hbar)^3}\int d\mathbf{p} p_x e^{i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')/\hbar} \\ &= \frac{1}{(2\pi\hbar)^3}\int dp_x p_x e^{ip_x(x-x')/\hbar}\int dp_y e^{ip_y(y-y')/\hbar}\int dp_z e^{ip_z(z-z')/\hbar} \\ &= \frac{1}{2\pi\hbar}\int dp_x p_x e^{ip_x(x-x')/\hbar}\delta(y-y')\delta(z-z'), \end{aligned} \tag{B8}$$

where we used the fact that

$$\hat{\mathbf{p}}|\mathbf{p}\rangle = \mathbf{p}|\mathbf{p}\rangle, \tag{B9}$$

ap_otra

and that

$$\delta(q-q') = \frac{1}{2\pi\hbar}\int dp e^{ip(q-q')/\hbar}. \tag{B10}$$

ap_delta

Now,

$$\frac{1}{2\pi\hbar}\int dp_x p_x e^{ip_x(x-x')/\hbar} = -i\hbar\frac{\partial}{\partial x}\int \frac{dp_x}{2\pi\hbar} e^{ip_x(x-x')/\hbar} = -i\hbar\frac{\partial}{\partial x}\delta(x-x'), \tag{B11}$$

ap_mas

from where we finally get

$$\langle \mathbf{r}|\hat{p}_x|\mathbf{r}'\rangle = (-i\hbar\frac{\partial}{\partial x}\delta(x-x'))\delta(y-y')\delta(z-z'), \tag{B12}$$

ap_fin

with similar results for $\hat{p}_y$ and $\hat{p}_z$. Now we can calculate

$$\begin{aligned} \langle \mathbf{r}|\hat{p}_x|\psi\rangle &= \int d\mathbf{r}' \langle \mathbf{r}|\hat{p}_x|\mathbf{r}'\rangle\langle \mathbf{r}'|\psi\rangle \\ &= \int dx'(-i\hbar\frac{\partial}{\partial x}\delta(x-x'))\int dy'\delta(y-y')\int dz'\delta(z-z')\psi(x',y',z') \\ &= -i\hbar\int dx'(\frac{\partial}{\partial x}\delta(x-x'))\psi(x',y,z) = -i\hbar\frac{\partial}{\partial x}\int dx'\delta(x-x')\psi(x',y,z) \\ &= -i\hbar\frac{\partial}{\partial x}\psi(x,y,z), \end{aligned} \tag{B13}$$

which confirms that in the $\mathbf{r}$ representation, the $\hat{\mathbf{p}}$ operator is replaced with the differential operator $-i\hbar\boldsymbol{\nabla}$.

Appendix C: Basic relationships

ap_basic

We present some basic results needed in the derivation of the main results. The normalization of the states $\psi_{n\mathbf{q}}(\mathbf{r})$ are chosen such that

$$\psi_{m\mathbf{q}}(\mathbf{r}) = \left(\frac{\Omega}{8\pi^3}\right)^{\frac{1}{2}} u_{m\mathbf{q}}(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}}, \tag{C1}$$ a_uno

and

$$\int_\Omega d^3r\, u^*_{n\mathbf{k}}(\mathbf{r}) u_{m\mathbf{q}}(\mathbf{r}) = \delta_{nm}\delta_{\mathbf{k},\mathbf{q}}, \tag{C2}$$ a_dos

where Ω is the volume is the unit cell and $\delta_{a,b}$ is the Kronecker delta that gives one if $a = b$ and zero otherwise. For box normalization, where we have N unit cells in some volume $V = N\Omega$, this gives

$$\int_V d^3r\, \psi^*_{n\mathbf{k}}(\mathbf{r})\psi_{m\mathbf{q}}(\mathbf{r}) = \frac{V}{8\pi^3}\delta_{nm}\delta_{\mathbf{k},\mathbf{q}}, \tag{C3}$$ a_tres

which lets us have in the limit of $N \to \infty$

$$\int d^3r\, \psi^*_{n\mathbf{k}}(\mathbf{r})\psi_{m\mathbf{q}}(\mathbf{r}) = \delta_{nm}\delta(\mathbf{k}-\mathbf{q}), \tag{C4}$$ a_4

for which the Kornecker-δ is replaced by

$$\delta_{\mathbf{k},\mathbf{q}} \to \frac{8\pi^3}{V}\delta(\mathbf{k}-\mathbf{q}), \tag{C5}$$ a_5

and we recall that $\delta(x) = \delta(-x)$. Now, for any periodic function $f(\mathbf{r}) = f(\mathbf{r}+\mathbf{R})$ we have

$$\begin{aligned}
\int d^3r\, e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}} f(\mathbf{r}) &= \sum_j^{\text{unit cells}} \int_\Omega d^3r\, e^{i(\mathbf{q}-\mathbf{k})\cdot(\mathbf{r}+\mathbf{R}_j)} f(\mathbf{r}+\mathbf{R}_j), \\
&= \sum_j^{\text{unit cells}} \int_\Omega d^3r\, e^{i(\mathbf{q}-\mathbf{k})\cdot(\mathbf{r}+\mathbf{R}_j)} f(\mathbf{r}), \\
&= \int_\Omega d^3r\, e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}} f(\mathbf{r}) \sum_j^{\text{unit cells}} e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{R}_j}, \\
&= \int_\Omega d^3r\, e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}} f(\mathbf{r}) N \sum_{\mathbf{K}} \delta_{\mathbf{K},\mathbf{q}-\mathbf{k}}, \\
&= N \int_\Omega d^3r\, e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}} f(\mathbf{r}) \delta_{\mathbf{0},\mathbf{q}-\mathbf{k}}, \\
&= N\delta_{\mathbf{q},\mathbf{k}} \int_\Omega d^3r\, f(\mathbf{r}), \\
&= \frac{8\pi^3}{\Omega}\delta(\mathbf{q}-\mathbf{k}) \int_\Omega d^3r\, f(\mathbf{r}),
\end{aligned} \tag{C6}$$

where we have assumed that $\mathbf{k}$ and $\mathbf{q}$ are restricted to the first Brillouin zone, and thus the reciprocal lattice vector $\mathbf{K} = 0$.

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

gendevomega

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

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

a_conH0

then Eq. (29) gives

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

where from Eq. (28),

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

then

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

a_wgendev

Now, from Eq. (22)

$$\langle n\mathbf{k}|[\hat{\mathbf{r}}_e,\hat{H}_0]|m\mathbf{k}\rangle = i\hbar\frac{\mathbf{p}_{nm}(\mathbf{k})}{m} \qquad n\neq m, \tag{D5}$$

a_hre

and from Eq. (18)

$$\langle n\mathbf{k}|[\hat{\mathbf{r}},\hat{H}_0]|m\mathbf{k}\rangle = i\hbar\frac{\mathbf{p}_{nm}(\mathbf{k})}{m}, \tag{D6}$$

a_hr

therefore, substituting above into

$$\langle n\mathbf{k}|[\hat{\mathbf{r}},\hat{H}_0]|m\mathbf{k}\rangle = \langle n\mathbf{k}|[\hat{\mathbf{r}}_i,\hat{H}_0]|m\mathbf{k}\rangle + \langle n\mathbf{k}|[\hat{\mathbf{r}}_e,\hat{H}_0]|m\mathbf{k}\rangle, \tag{D7}$$

a_hrt

we get

$$i\hbar\frac{\mathbf{p}_{nm}(\mathbf{k})}{m} = i\delta_{nm}\hbar\nabla_{\mathbf{k}}\omega_m(\mathbf{k}) + i\hbar(1-\delta_{nm})\frac{\mathbf{p}_{nm}(\mathbf{k})}{m}, \tag{D8}$$

a_hrt2

from where

$$\frac{\mathbf{p}_{nn}(\mathbf{k})}{m} = \nabla_{\mathbf{k}}\omega_n(\mathbf{k}), \tag{D9}$$

a_gradw

so from Eq. (D4)

$$(\omega_n(\mathbf{k}))_{;k^{\mathrm{a}}} = \frac{p^{\mathrm{a}}_{nn}(\mathbf{k})}{m}. \tag{D10}$$

a_gradw2

Appendix E: Generalized derivative $(\mathbf{r}_{nm}(\mathbf{k}))_{;\mathbf{k}}$

ap_genderr

We obtain the generalized derivative $(\mathbf{r}_{nm}(\mathbf{k}))_{;\mathbf{k}}$. We start with the basic result

$$[r^{\mathrm{a}}, p^{\mathrm{b}}] = i\hbar\delta_{ab}, \tag{E1}$$

a_hrdab

then

$$\langle n\mathbf{k}|[r^{\mathrm{a}}, p^{\mathrm{b}}]|m\mathbf{k}'\rangle = i\hbar\delta_{ab}\delta_{nm}\delta(\mathbf{k}-\mathbf{k}'), \tag{E2}$$

a_hrdab2

so

$$\langle n\mathbf{k}|[r_i^{\mathrm{a}}, p^{\mathrm{b}}]|m\mathbf{k}'\rangle + \langle n\mathbf{k}|[r_e^{\mathrm{a}}, p^{\mathrm{b}}]|m\mathbf{k}'\rangle = i\hbar\delta_{ab}\delta_{nm}\delta(\mathbf{k}-\mathbf{k}'). \tag{E3}$$

a_hrdab3

From Eq. (conmri3 28) and (gendev 29)

$$\langle n\mathbf{k}|[r_i^{\mathrm{a}}, p^{\mathrm{b}}]|m\mathbf{k}'\rangle = i\delta(\mathbf{k}-\mathbf{k}')(p^{\mathrm{b}}_{nm})_{;k^{\mathrm{a}}} \tag{E4}$$

a_rip

$$(p^{\mathrm{b}}_{nm})_{;k^{\mathrm{a}}} = \nabla_{k^{\mathrm{a}}} p^{\mathrm{b}}_{nm}(\mathbf{k}) - ip^{\mathrm{b}}_{nm}(\mathbf{k})\left(\xi^{\mathrm{a}}_{nn}(\mathbf{k}) - \xi^{\mathrm{a}}_{mm}(\mathbf{k})\right), \tag{E5}$$

a_ripn

and

$$\begin{aligned}
\langle n\mathbf{k}|[r_e^{\mathrm{a}}, p^{\mathrm{b}}]|m\mathbf{k}'\rangle &= \sum_{\ell\mathbf{k}''}\Bigg(\langle n\mathbf{k}|r_e^{\mathrm{a}}|\ell\mathbf{k}''\rangle\langle \ell\mathbf{k}''|p^{\mathrm{b}}|m\mathbf{k}'\rangle \\
&\quad -\langle n\mathbf{k}|p^{\mathrm{b}}|\ell\mathbf{k}''\rangle\langle \ell\mathbf{k}''|r_e^{\mathrm{a}}|m\mathbf{k}'\rangle\Bigg) \\
&= \sum_{\ell\mathbf{k}''}\Bigg((1-\delta_{n\ell})\delta(\mathbf{k}-\mathbf{k}'')\xi^{\mathrm{a}}_{n\ell}\delta(\mathbf{k}''-\mathbf{k}')p^{\mathrm{b}}_{\ell m} \\
&\quad -\delta(\mathbf{k}-\mathbf{k}'')p^{\mathrm{b}}_{n\ell}(1-\delta_{\ell m})\delta(\mathbf{k}''-\mathbf{k}')\xi^{\mathrm{a}}_{\ell m}\Bigg) \\
&= \delta(\mathbf{k}-\mathbf{k}')\sum_{\ell}\Bigg((1-\delta_{n\ell})\xi^{\mathrm{a}}_{n\ell}p^{\mathrm{b}}_{\ell m} \\
&\quad -(1-\delta_{\ell m})p^{\mathrm{b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m}\Bigg) \\
&= \delta(\mathbf{k}-\mathbf{k}')\Bigg(\sum_{\ell}\left(\xi^{\mathrm{a}}_{n\ell}p^{\mathrm{b}}_{\ell m} - p^{\mathrm{b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m}\right) \\
&\quad +p^{\mathrm{b}}_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn})\Bigg).
\end{aligned} \tag{E6}$$

Using Eqs. (a_rip E4) and (a_rep E6) into Eq. (a_hrdab3 E3) gives

$$\begin{aligned}
i\delta(\mathbf{k}-\mathbf{k}')\Bigg((p^{\mathrm{b}}_{nm})_{;k^{\mathrm{a}}} \quad &-i\sum_{\ell}\left(\xi^{\mathrm{a}}_{n\ell}p^{\mathrm{b}}_{\ell m} - p^{\mathrm{b}}_{n\ell}\xi^{\mathrm{a}}_{\ell m}\right) \\
&-ip^{\mathrm{b}}_{nm}(\xi^{\mathrm{a}}_{mm} - \xi^{\mathrm{a}}_{nn})\Bigg) = i\hbar\delta_{ab}\delta_{nm}\delta(\mathbf{k}-\mathbf{k}'),
\end{aligned} \tag{E7}$$

then

$$(p^{\rm b}_{nm})_{;k^{\rm a}} \;=\; \hbar\delta_{ab}\delta_{nm} + i\sum_{\ell}\Big(\xi^{\rm a}_{n\ell}p^{\rm b}_{\ell m} - p^{\rm b}_{n\ell}\xi^{\rm a}_{\ell m}\Big) + ip^{\rm b}_{nm}(\xi^{\rm a}_{mm} - \xi^{\rm a}_{nn}), \tag{E8}$$

and from Eq. (E5),

$$\nabla_{k^{\rm a}}p^{\rm b}_{nm} = \hbar\delta_{ab}\delta_{nm} + i\sum_{\ell}\Big(\xi^{\rm a}_{n\ell}p^{\rm b}_{\ell m} - p^{\rm b}_{n\ell}\xi^{\rm a}_{\ell m}\Big). \tag{E9}$$

Now, there are two cases. We use Eqs. (24) and (25).

Case $n = m$

$$\frac{1}{\hbar}\nabla_{k^{\rm a}}p^{\rm b}_{nn} = \delta_{ab} - \frac{m_e}{\hbar}\sum_{\ell}\omega_{\ell n}\Big(r^{\rm a}_{n\ell}r^{\rm b}_{\ell n} + r^{\rm b}_{n\ell}r^{\rm a}_{\ell n}\Big), \tag{E10}$$

that gives the familiar expansion for the inverse effective mass tensor $(m_n^{-1})_{ab}$.[26]

Case $n \neq m$

$$\begin{aligned}
(p^{\rm b}_{nm})_{;k^{\rm a}} \;&=\; \hbar\delta_{ab}\delta_{nm} + i\sum_{\ell\neq m\neq n}\Big(\xi^{\rm a}_{n\ell}p^{\rm b}_{\ell m} - p^{\rm b}_{n\ell}\xi^{\rm a}_{\ell m}\Big)\\
&\quad + i\Big(\xi^{\rm a}_{nm}p^{\rm b}_{mm} - p^{\rm b}_{nm}\xi^{\rm a}_{mm}\Big)\\
&\quad + i\Big(\xi^{\rm a}_{nn}p^{\rm b}_{nm} - p^{\rm b}_{nn}\xi^{\rm a}_{nm}\Big) + ip^{\rm b}_{nm}(\xi^{\rm a}_{mm} - \xi^{\rm a}_{nn})\\
&=\; -m_e\sum_{\ell}\Big(\omega_{\ell m}r^{\rm a}_{n\ell}r^{\rm b}_{\ell m} - \omega_{n\ell}r^{\rm b}_{n\ell}r^{\rm a}_{\ell m}\Big) + i\xi^{\rm a}_{nm}(p^{\rm b}_{mm} - p^{\rm b}_{nn})\\
&=\; -m_e\sum_{\ell}\Big(\omega_{\ell m}r^{\rm a}_{n\ell}r^{\rm b}_{\ell m} - \omega_{n\ell}r^{\rm b}_{n\ell}r^{\rm a}_{\ell m}\Big) + im_e r^{\rm a}_{nm}\Delta^{\rm b}_{mn},
\end{aligned} \tag{E11}$$

where

$$\Delta^{\rm b}_{mn} = \frac{p^{\rm b}_{mm} - p^{\rm b}_{nn}}{m_e}. \tag{E12}$$

Now, for $n \neq m$, Eqs. (25), (D10) and (E11) and the chain rule, give

$$
\begin{aligned}
(r^{\rm b}_{nm})_{;k^{\rm a}} &= \left(\frac{p^{\rm b}_{nm}}{im_e\omega_{nm}}\right)_{;k^{\rm a}} = \frac{1}{im_e\omega_{nm}}\left(p^{\rm b}_{nm}\right)_{;k^{\rm a}} - \frac{p^{\rm b}_{nm}}{im_e\omega^2_{nm}}\left(\omega_{nm}\right)_{;k^{\rm a}} \\
&= \frac{i}{\omega_{nm}}\sum_\ell\left(\omega_{\ell m}r^{\rm a}_{n\ell}r^{\rm b}_{\ell m} - \omega_{n\ell}r^{\rm b}_{n\ell}r^{\rm a}_{\ell m}\right) + \frac{r^{\rm a}_{nm}\Delta^{\rm b}_{mn}}{\omega_{nm}} \\
&\quad - \frac{r^{\rm b}_{nm}}{\omega_{nm}}\left(\omega_{nm}\right)_{;k^{\rm a}} \\
&= \frac{i}{\omega_{nm}}\sum_\ell\left(\omega_{\ell m}r^{\rm a}_{n\ell}r^{\rm b}_{\ell m} - \omega_{n\ell}r^{\rm b}_{n\ell}r^{\rm a}_{\ell m}\right) + \frac{r^{\rm a}_{nm}\Delta^{\rm b}_{mn}}{\omega_{nm}} \\
&\quad - \frac{r^{\rm b}_{nm}}{\omega_{nm}}\frac{p^{\rm a}_{nn} - p^{\rm a}_{mm}}{m_e} \\
&= \frac{r^{\rm a}_{nm}\Delta^{\rm b}_{mn} + r^{\rm b}_{nm}\Delta^{\rm a}_{mn}}{\omega_{nm}} \\
&\quad + \frac{i}{\omega_{nm}}\sum_\ell\left(\omega_{\ell m}r^{\rm a}_{n\ell}r^{\rm b}_{\ell m} - \omega_{n\ell}r^{\rm b}_{n\ell}r^{\rm a}_{\ell m}\right)
\end{aligned}
\tag{E13}
$$

Appendix F: $\left(\mathcal{R}^{\rm a}_{nm}\right)_{;k^{\rm b}}$

calr

We rewrite Eq. (E11) and (25) as

$$
(p^{\rm a}_{nm})_{;k^{\rm b}} = ir^{\rm b}_{nm}(p^{\rm a}_{mm} - p^{\rm a}_{nn}) + i\sum_{\ell\neq m,n}\left(p^{\rm a}_{\ell m}r^{\rm b}_{n\ell} - p^{\rm a}_{n\ell}r^{\rm b}_{\ell m}\right),
\tag{F1}
$$

which is valid for any operator $\hat{\mathbf{p}}$, thus $p^{\rm a} \to \mathcal{P}^{\rm a}$, then

$$
\begin{aligned}
(\mathcal{P}^{\rm a}_{nm})_{;k^{\rm b}} &= ir^{\rm b}_{nm}(\mathcal{P}^{\rm a}_{mm} - \mathcal{P}^{\rm a}_{nn}) + i\sum_{\ell\neq m,n}\left(\mathcal{P}^{\rm a}_{\ell m}r^{\rm b}_{n\ell} - \mathcal{P}^{\rm a}_{n\ell}r^{\rm b}_{\ell m}\right) \\
&= im_e r^{\rm b}_{nm}\Delta^{{\rm a}(\ell)}_{mn} + i\sum_{\ell\neq m,n}\left(\mathcal{P}^{\rm a}_{\ell m}r^{\rm b}_{n\ell} - \mathcal{P}^{\rm a}_{n\ell}r^{\rm b}_{\ell m}\right),
\end{aligned}
\tag{F2}
$$

where

$$
\Delta^{{\rm a}(\ell)} = \frac{\mathcal{P}^{\rm a}_{mm} - \mathcal{P}^{\rm a}_{nn}}{m_e},
\tag{F3}
$$ l12

where we omitted the ℓ-layer label from $\mathcal{P}$. Eq. (25) trivially gives

$$
\mathcal{R}^{\rm a}_{nm} = \frac{\mathcal{P}^{\rm a}_{nm}}{im_e\omega_{nm}} \qquad n \neq m,
\tag{F4}
$$ rnmenm69

then, using Eq. (F2)

$$
\begin{aligned}
(\mathcal{R}^{\rm a}_{nm})_{;k^{\rm b}} &= \left(\frac{\mathcal{P}^{\rm a}_{nm}}{im_e\omega_{nm}}\right)_{;k^{\rm b}} = \frac{1}{im_e\omega_{nm}}\left(\mathcal{P}^{\rm a}_{nm}\right)_{;k^{\rm b}} - \frac{\mathcal{P}^{\rm a}_{nm}}{im_e\omega^2_{nm}}\left(\omega_{nm}\right)_{;k^{\rm b}} \\
&= \frac{r^{\rm b}_{nm}\Delta^{{\rm a}(\ell)}_{mn}}{\omega_{nm}} + \frac{i}{\omega_{nm}}\sum_\ell\left(\omega_{\ell m} r^{\rm b}_{n\ell}\mathcal{R}^{\rm a}_{\ell m} - \omega_{n\ell}\mathcal{R}^{\rm a}_{n\ell} r^{\rm b}_{\ell m}\right) \\
&\quad -\frac{\mathcal{R}^{\rm a}_{nm}}{\omega_{nm}}\left(\omega_{nm}\right)_{;k^{\rm b}} \\
&= \frac{r^{\rm b}_{nm}\Delta^{{\rm a}(\ell)}_{mn}}{\omega_{nm}} + \frac{i}{\omega_{nm}}\sum_\ell\left(\omega_{\ell m} r^{\rm b}_{n\ell}\mathcal{R}^{\rm a}_{\ell m} - \omega_{n\ell}\mathcal{R}^{\rm a}_{n\ell} r^{\rm b}_{\ell m}\right) \\
&\quad -\frac{\mathcal{R}^{\rm a}_{nm}}{\omega_{nm}}\frac{p^{\rm b}_{nn} - p^{\rm b}_{mm}}{m_e} \\
&= \frac{r^{\rm b}_{nm}\Delta^{{\rm a}(\ell)}_{mn}}{\omega_{nm}} + \frac{i}{\omega_{nm}}\sum_\ell\left(\omega_{\ell m} r^{\rm b}_{n\ell}\mathcal{R}^{\rm a}_{\ell m} - \omega_{n\ell}\mathcal{R}^{\rm a}_{n\ell} r^{\rm b}_{\ell m}\right) \\
&\quad +\frac{\mathcal{R}^{\rm a}_{nm}\Delta^{\rm b}_{mn}}{\omega_{nm}} \\
&= \frac{r^{\rm b}_{nm}\Delta^{{\rm a}(\ell)}_{mn} + \mathcal{R}^{\rm a}_{nm}\Delta^{\rm b}_{mn}}{\omega_{nm}} + \frac{i}{\omega_{nm}}\sum_\ell\left(\omega_{\ell m} r^{\rm b}_{n\ell}\mathcal{R}^{\rm a}_{\ell m} - \omega_{n\ell}\mathcal{R}^{\rm a}_{n\ell} r^{\rm b}_{\ell m}\right) \qquad \text{(F5)}
\end{aligned}
$$

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