

# Longitudinal Gauge Theory of Surface Second Harmonic Generation

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## Abstract

A theoretical review of surface second harmonic generation from semiconductor surfaces based on the longitudinal gauge is presented. The so called, layer-by-layer analysis is carefully presented in order to show how a surface calculation of second harmonic generation (SHG) can readily be carried out. The nonlinear susceptibility tensor  $\chi$  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.<sup>1</sup> 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.<sup>1-8</sup>

In a previous article,<sup>9</sup> 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.<sup>10</sup> The approach consisted in the separation of the different contributions to the nonlinear susceptibility according to  $1\omega$  and  $2\omega$  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 possible 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.<sup>11</sup> A more recent derivation can also be found in Ref. 12 and 13. Assuming the long-wavelength approximation, which implies a position independent electric field,  $\mathbf{E}(t)$ , the hamiltonian in the so called length gauge approximation is given by

$$\hat{H} = \hat{H}_0^S - e\hat{\mathbf{r}} \cdot \mathbf{E}, \quad (1) \quad \{\text{ache}\}$$

with

$$\hat{H}_0^S = \hat{H}_0^{\text{LDA}} + \hat{S}(\mathbf{r}, \mathbf{p}), \quad (2) \quad \{\text{ache.1}\}$$

and

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

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

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

with  $\psi_{n\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r} | n\mathbf{k} \rangle$ , the real space representation of the Bloch state  $|n\mathbf{k}\rangle$  labeled by its band index  $n$  and crystal momentum  $\mathbf{k}$ . Here,  $m_e$  is the bare mass of the electron.

The nonlocal scissors operator is given by

$$S(\mathbf{r}, \mathbf{p}) = \hbar\Delta \sum_n \int d^3k' (1 - f_n) |n\mathbf{k}'\rangle \langle n\mathbf{k}'|,\tag{5} \quad \{\text{chon.0}\}$$

with  $f_n$  the Fermi-Dirac factor. We have that

$$\begin{aligned}H_0^{\text{LDA}}|n\mathbf{k}\rangle &= \hbar\omega_n^{\text{LDA}}(\mathbf{k})|n\mathbf{k}\rangle \\ H_0^S|n\mathbf{k}\rangle &= \hbar\omega_n^S(\mathbf{k})|n\mathbf{k}\rangle,\end{aligned}\tag{6} \quad \{\text{chon.1}\}$$

where

$$\hbar\omega_n^S(\mathbf{k}) = \hbar\omega_n^{\text{LDA}}(\mathbf{k}) + \Delta(1 - f_n),\tag{7} \quad \{\text{chon.78}\}$$

is the  $\mathbf{k}$ -independent scissored energy, with  $\Delta = E_g - E_g^{\text{LDA}}$ , where  $E_g$  could be the experimental or GW band gap. In above we used the fact that  $|n\mathbf{k}\rangle^{\text{LDA}} \approx |n\mathbf{k}\rangle^S$ , and thus there is no need to label the Bloch states with LDA or S, superscripts.

To properly obtain the contribution of the nonlocal part of the pseudopotential and of the scissors operator, in the calculation, we obtain the velocity operator matrix elements starting from

$$\begin{aligned}\hat{\mathbf{v}}^\Sigma &= \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{H}_0^S] = \frac{\hat{\mathbf{p}}}{m_e} + \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{V}^{\text{nl}}(\mathbf{r}, \mathbf{r}')] + \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{S}(\mathbf{r}, \mathbf{p})] \\ &\equiv \mathbf{v} + \mathbf{v}^{\text{nl}} + \mathbf{v}^S = \mathbf{v}^{\text{LDA}} + \mathbf{v}^S,\end{aligned}\tag{8} \quad \{\text{vop}\}$$

where we have defined

$$\begin{aligned}\mathbf{v} &= \frac{\hat{\mathbf{p}}}{m_e} \\ \mathbf{v}^{\text{nl}} &= \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{V}^{\text{nl}}(\mathbf{r}, \mathbf{r}')] \\ \mathbf{v}^S &= \frac{1}{i\hbar}[\hat{\mathbf{r}}, \hat{S}(\mathbf{r}, \mathbf{p})] \\ \mathbf{v}^{\text{LDA}} &= \mathbf{v} + \mathbf{v}^{\text{nl}}\end{aligned}\tag{9} \quad \{\text{conhr}\}$$

with  $\hat{\mathbf{p}} = -i\hbar\nabla$  the momentum operator Using Eq. (5) into above equation, we obtain that

$$\mathbf{v}_{nm}^S = i\Delta f_{mn}\mathbf{r}_{nm}, \quad (10) \quad \{\text{chon.2}\}$$

with  $f_{nm} = f_n - f_m$ , where we see that  $\mathbf{v}_{nn}^S = 0$ . On the other hand,

$$\langle n\mathbf{k} | [\hat{\mathbf{r}}, \hat{H}_0^S] | m\mathbf{k} \rangle = \langle n\mathbf{k} | \hat{\mathbf{r}}\hat{H}_0^S - \hat{H}_0^S\hat{\mathbf{r}} | m\mathbf{k} \rangle = (\hbar\omega_m^S(\mathbf{k}) - \hbar\omega_n^S(\mathbf{k}))\langle n\mathbf{k} | \hat{\mathbf{r}} | m\mathbf{k} \rangle, \quad (11) \quad \{\text{conhrnm}\}$$

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

$$\mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}_{nm}^\Sigma(\mathbf{k})}{i\omega_{nm}^S(\mathbf{k})} \quad n \neq m, \quad (12) \quad \{\text{pmnrnm}\}$$

where

$$\begin{aligned} \mathbf{v}_{nm}^\Sigma &= \mathbf{v}_{nm}^{\text{LDA}} + i\Delta f_{mn}\mathbf{r}_{nm} \\ &= \mathbf{v}_{nm}^{\text{LDA}} + i\Delta f_{mn} \frac{\mathbf{v}_{nm}^\Sigma(\mathbf{k})}{i\omega_{nm}^S(\mathbf{k})} \\ \mathbf{v}_{nm}^\Sigma \frac{\omega_{nm}^S - \Delta f_{mn}}{\omega_{nm}^S} &= \mathbf{v}_{nm}^{\text{LDA}} \\ \mathbf{v}_{nm}^\Sigma \frac{\omega_{nm}^{\text{LDA}}}{\omega_{nm}^S} &= \mathbf{v}_{nm}^{\text{LDA}} \\ \frac{\mathbf{v}_{nm}^\Sigma}{\omega_{nm}^S} &= \frac{\mathbf{v}_{nm}^{\text{LDA}}}{\omega_{nm}^{\text{LDA}}}, \end{aligned} \quad (13) \quad \{\text{chon.8}\}$$

since  $\omega_{nm}^S - \Delta f_{mn} = \omega_{nm}^{\text{LDA}}$ . Therefore, Eq. (12) gives

$$\mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}_{nm}^\Sigma(\mathbf{k})}{i\omega_{nm}^S(\mathbf{k})} = \frac{\mathbf{v}_{nm}^{\text{LDA}}(\mathbf{k})}{i\omega_{nm}^{\text{LDA}}(\mathbf{k})} \quad n \neq m, \quad (14) \quad \{\text{chon.10}\}$$

thus, the matrix elements of  $\mathbf{r}$  are the same wether we use the LDA or the scissored Hamiltonian.

Comparing above result with Eq. (J15), we can identify

$$(1 - \delta_{nm})\boldsymbol{\xi}_{nm} \equiv \mathbf{r}_{nm}, \quad (15) \quad \{\text{xir}\}$$

and the we can write

$$\langle n\mathbf{k} | \hat{\mathbf{r}}_e | m\mathbf{k} \rangle = \mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}_{nm}^{\text{LDA}}(\mathbf{k})}{i\omega_{nm}^{\text{LDA}}(\mathbf{k})} \quad n \neq m, \quad (16) \quad \{\text{chon.98}\}$$

which gives the interband matrix elements of the position operator in terms of the matrix elements of  $\mathbf{v}^{\text{LDA}}$ . For fully separable pseudopotentials in the Kleinman-Bylander form,<sup>?, ?</sup> the matrix elements  $\mathbf{v}_{nm}^{\text{nl}}(\mathbf{k})$  can be readily calculated.<sup>?</sup>

### 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

$$\mathcal{O} = \text{Tr}(\hat{\mathcal{O}}\hat{\rho}) = \text{Tr}(\hat{\rho}\hat{\mathcal{O}}), \quad (17) \quad \{\text{traza}\}$$

where  $\text{Tr}$  is the trace, that is invariant under cyclic permutations. The dynamical equation of motion for  $\rho$  is given by

$$i\hbar \frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}], \quad (18) \quad \{\text{eqrho}\}$$

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

$$\hat{\mathcal{O}}_I = \hat{U}\hat{\mathcal{O}}\hat{U}^\dagger, \quad (19) \quad \{\text{ip}\}$$

where

$$\hat{U} = e^{i\hat{H}_0 t/\hbar}, \quad (20) \quad \{\text{ou}\}$$

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. (18) into

$$i\hbar \frac{d\hat{\rho}_I(t)}{dt} = [-e\hat{\mathbf{r}}_I(t) \cdot \mathbf{E}(t), \hat{\rho}_I(t)], \quad (21) \quad \{\text{intrho}\}$$

that leads to

$$\hat{\rho}_I(t) = \hat{\rho}_I(t = -\infty) + \frac{ie}{\hbar} \int_{-\infty}^t dt' [\hat{\mathbf{r}}_I(t') \cdot \mathbf{E}(t'), \hat{\rho}_I(t')]. \quad (22) \quad \{\text{intrho2}\}$$

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

$$\mathbf{E}(t) = \mathbf{E}e^{-i\omega t}e^{\eta t}, \quad (23) \quad \{\text{efield}\}$$

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  $\eta \rightarrow 0$ . Instead of Eq. (23) we use

$$\mathbf{E}(t) = \mathbf{E}e^{-i\tilde{\omega} t}, \quad (24) \quad \{\text{efield2}\}$$

with

$$\tilde{\omega} = \omega + i\eta. \quad (25) \quad \{\text{got}\}$$

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

$$\langle n\mathbf{k} | \hat{\rho}_0 | m\mathbf{k}' \rangle = f_n(\hbar\omega_n(\mathbf{k}))\delta_{nm}\delta(\mathbf{k} - \mathbf{k}'), \quad (26) \quad \{\text{nrhon}\}$$

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

We solve Eq. (22) using the standard iterative solution, for which we write

$$\hat{\rho}_I = \hat{\rho}_I^{(0)} + \hat{\rho}_I^{(1)} + \hat{\rho}_I^{(2)} + \dots, \quad (27) \quad \{\text{rhop}\}$$

where  $\hat{\rho}_I^{(N)}$  is the density operator to order  $N$  in  $\mathbf{E}(t)$ . Then, Eq. (22) reads

$$\hat{\rho}_I^{(0)} + \hat{\rho}_I^{(1)} + \hat{\rho}_I^{(2)} + \dots = \hat{\rho}_0 + \frac{ie}{\hbar} \int_{-\infty}^t dt' [\hat{\mathbf{r}}_I(t') \cdot \mathbf{E}(t'), \hat{\rho}_I^{(0)} + \hat{\rho}_I^{(1)} + \hat{\rho}_I^{(2)} + \dots], \quad (28) \quad \{\text{intrho3}\}$$

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

$$\hat{\rho}_I^{(0)} \equiv \hat{\rho}_0, \quad (29) \quad \{\text{rho0}\}$$

and

$$\hat{\rho}_I^{(N)}(t) = \frac{ie}{\hbar} \int_{-\infty}^t dt' [\hat{\mathbf{r}}_I(t') \cdot \mathbf{E}(t'), \hat{\rho}_I^{(N-1)}(t')]. \quad (30) \quad \{\text{rhoN}\}$$

It is simple to show that matrix elements of Eq. (30) 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

$$\rho_{I,nm}^{(N+1)}(\mathbf{k}; t) = \frac{ie}{\hbar} \int_{-\infty}^t dt' \langle n\mathbf{k} | [\hat{\mathbf{r}}_I(t'), \hat{\rho}_I^{(N)}(t')] | m\mathbf{k} \rangle \cdot \mathbf{E}(t'). \quad (31) \quad \{\text{rtilde}\}$$

Now we work out the commutator of Eq. (31). Then,

$$\begin{aligned} \langle n\mathbf{k} | [\hat{\mathbf{r}}_I(t), \hat{\rho}_I^{(N)}(t)] | m\mathbf{k} \rangle &= \langle n\mathbf{k} | [\hat{U} \hat{\mathbf{r}} \hat{U}^\dagger, \hat{U} \hat{\rho}^{(N)}(t) \hat{U}^\dagger] | m\mathbf{k} \rangle \\ &= \langle n\mathbf{k} | \hat{U} [\hat{\mathbf{r}}, \hat{\rho}^{(N)}(t)] \hat{U}^\dagger | m\mathbf{k} \rangle \\ &= e^{i\omega_{nm}t} \left( \langle n\mathbf{k} | [\hat{\mathbf{r}}_e, \hat{\rho}^{(N)}(t)] + [\hat{\mathbf{r}}_i, \hat{\rho}^{(N)}(t)] | m\mathbf{k} \rangle \right). \end{aligned} \quad (32) \quad \{\text{conmu1}\}$$

We calculate the interband term first, so using Eq. (16) we obtain

$$\begin{aligned} \langle n\mathbf{k} | [\hat{\mathbf{r}}_e, \hat{\rho}^{(N)}(t)] | m\mathbf{k} \rangle &= \sum_{\ell} \left( \langle n\mathbf{k} | \hat{\mathbf{r}}_e | \ell\mathbf{k} \rangle \langle \ell\mathbf{k} | \hat{\rho}^{(N)}(t) | m\mathbf{k} \rangle \right. \\ &\quad \left. - \langle n\mathbf{k} | \hat{\rho}^{(N)}(t) | \ell\mathbf{k} \rangle \langle \ell\mathbf{k} | \hat{\mathbf{r}}_e | m\mathbf{k} \rangle \right) \\ &= \sum_{\ell \neq n, m} \left( \mathbf{r}_{n\ell}(\mathbf{k}) \rho_{\ell m}^{(N)}(\mathbf{k}; t) - \rho_{n\ell}^{(N)}(\mathbf{k}; t) \mathbf{r}_{\ell m}(\mathbf{k}) \right) \\ &\equiv \mathbf{R}_e^{(N)}(\mathbf{k}; t). \end{aligned} \quad (33) \quad \{\text{conmu2}\}$$

Now, from Eq. (J18) we simply obtain,

$$\langle n\mathbf{k} | [\hat{\mathbf{r}}_i, \hat{\rho}^{(N)}(t)] | m\mathbf{k}' \rangle = i(\rho_{nm}^{(N)}(t))_{;\mathbf{k}} \equiv \mathbf{R}_i^{(N)}(\mathbf{k}; t). \quad (34) \quad \{\text{conmri4}\}$$

Then Eq. (31) becomes,

$$\rho_{I,nm}^{(N+1)}(\mathbf{k}; t) = \frac{ie}{\hbar} \int_{-\infty}^t dt' e^{i(\omega_{nm\mathbf{k}} - \tilde{\omega})t'} \left[ R_e^{b(N)}(\mathbf{k}; t') + R_i^{b(N)}(\mathbf{k}; t') \right] E^b, \quad (35) \quad \{\text{rtilde2}\}$$

where, the roman superindices a, b, c denote Cartesian components that are summed over if repeated. We start with the linear response, then from Eq. (26) and (33),

$$\begin{aligned} R_e^{b(0)}(\mathbf{k}; t) &= \sum_{\ell} \left( r_{n\ell}^b(\mathbf{k}) \rho_{\ell m}^{(0)}(\mathbf{k}) - \rho_{n\ell}^{(0)}(\mathbf{k}) r_{\ell m}^b(\mathbf{k}) \right) \\ &= \sum_{\ell} \left( r_{n\ell}^b(\mathbf{k}) \delta_{\ell m} f_m(\hbar\omega_m(\mathbf{k})) - \delta_{n\ell} f_n(\hbar\omega_n(\mathbf{k})) r_{\ell m}^b(\mathbf{k}) \right) \\ &= f_{mn\mathbf{k}} r_{nm}^b(\mathbf{k}), \end{aligned} \quad (36) \quad \{\text{R0e}\}$$

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. (34) and Eq. (J19)

$$R_i^{b(0)}(\mathbf{k}) = i(\rho_{nm}^{(0)})_{;\mathbf{k}^b} = i\delta_{nm}(f_{n\mathbf{k}})_{;\mathbf{k}^b} = i\delta_{nm} \nabla_{\mathbf{k}^b} f_{n\mathbf{k}}. \quad (37) \quad \{\text{R0i}\}$$

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,

$$\begin{aligned} \rho_{I,nm}^{(1)}(\mathbf{k}; t) &= \frac{ie}{\hbar} f_{mn\mathbf{k}} r_{nm}^b(\mathbf{k}) E^b \int_{-\infty}^t dt' e^{i(\omega_{nm\mathbf{k}} - \tilde{\omega})t'} \\ &= \frac{e}{\hbar} f_{mn\mathbf{k}} r_{nm}^b(\mathbf{k}) E^b \frac{e^{i(\omega_{nm\mathbf{k}} - \tilde{\omega})t}}{\omega_{nm\mathbf{k}} - \tilde{\omega}} \\ &= e^{i\omega_{nm\mathbf{k}}t} B_{mn}^b(\mathbf{k}) E^b(t) \\ &= e^{i\omega_{nm\mathbf{k}}t} \rho_{nm}^{(1)}(\mathbf{k}; t). \end{aligned} \quad (38) \quad \{\text{rtilde2n}\}$$

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

$$\rho_{nm}^{(1)}(\mathbf{k}; t) = B_{mn}^b(\mathbf{k}, \omega_{\alpha}) E_{\omega_{\alpha}}^b e^{-i\tilde{\omega}_{\alpha}t}, \quad (39) \quad \{\text{rhono1}\}$$

with

$$B_{nm}^b(\mathbf{k}, \omega_{\alpha}) = \frac{e}{\hbar} \frac{f_{mn\mathbf{k}} r_{nm}^b(\mathbf{k})}{\omega_{nm\mathbf{k}} - \tilde{\omega}_{\alpha}}, \quad (40) \quad \{\text{rho1}\}$$



that for the scissored hamiltonian would be

$$B_{nm}^b(\mathbf{k}, \omega_\alpha) = \frac{e}{\hbar} \frac{f_{mn\mathbf{k}} r_{nm}^b(\mathbf{k})}{\omega_{nm\mathbf{k}}^S - \tilde{\omega}_\alpha}, \quad (41) \quad \{\text{rho1n}\}$$

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. (33)

$$\begin{aligned} R_e^{b(1)}(\mathbf{k}; t) &= \sum_{\ell} \left( r_{n\ell}^b(\mathbf{k}) \rho_{\ell m}^{(1)}(\mathbf{k}; t) - \rho_{n\ell}^{(1)}(\mathbf{k}; t) r_{\ell m}^b(\mathbf{k}) \right) \\ &= \sum_{\ell} \left( r_{n\ell}^b(\mathbf{k}) B_{\ell m}^c(\mathbf{k}, \omega_\beta) - B_{n\ell}^c(\mathbf{k}, \omega_\beta) r_{\ell m}^b(\mathbf{k}) \right) E_{\omega_\beta}^c(t), \end{aligned} \quad (42) \quad \{\text{R1e}\}$$

and from Eq. (34)

$$R_i^{b(1)}(\mathbf{k}; t) = i(\rho_{nm}^{(1)}(t))_{;k^b} = iE_{\omega_\beta}^c(t)(B_{nm}^c(\mathbf{k}, \omega_\beta))_{;k^b}. \quad (43) \quad \{\text{R1i}\}$$

Using Eqs. (42) and (43) in Eq. (35), and generalizing to two different perturbing fields, we obtain

$$\begin{aligned} \rho_{I,nm}^{(2)}(\mathbf{k}; t) &= \frac{ie}{\hbar} \left[ \sum_{\ell} \left( r_{n\ell}^b(\mathbf{k}) B_{\ell m}^c(\mathbf{k}, \omega_\beta) - B_{n\ell}^c(\mathbf{k}, \omega_\beta) r_{\ell m}^b(\mathbf{k}) \right) \right. \\ &\quad \left. + i(B_{nm}^c(\mathbf{k}, \omega_\beta))_{;k^b} \right] E_{\omega_\alpha}^b E_{\omega_\beta}^c \int_{-\infty}^t dt' e^{i(\omega_{nm\mathbf{k}} - \tilde{\omega}_\alpha - \tilde{\omega}_\beta)t'} \\ &= \frac{e}{\hbar} \left[ \sum_{\ell} \left( r_{n\ell}^b(\mathbf{k}) B_{\ell m}^c(\mathbf{k}, \omega_\beta) - B_{n\ell}^c(\mathbf{k}, \omega_\beta) r_{\ell m}^b(\mathbf{k}) \right) \right. \\ &\quad \left. + i(B_{nm}^c(\mathbf{k}, \omega_\beta))_{;k^b} \right] E_{\omega_\alpha}^b E_{\omega_\beta}^c \frac{e^{i(\omega_{nm\mathbf{k}} - \tilde{\omega}_3)t}}{\omega_{nm\mathbf{k}} - \tilde{\omega}_3} \\ &= e^{i\omega_{nm\mathbf{k}}t} \rho_{nm}^{(2)}(\mathbf{k}; t). \end{aligned} \quad (44) \quad \{\text{rtilde33}\}$$

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

$$\begin{aligned} \rho_{nm}^{(2)}(\mathbf{k}; \omega_3) &= \frac{e}{i\hbar} \frac{1}{\omega_{nm\mathbf{k}} - \tilde{\omega}_3} \left[ - (B_{nm}^c(\mathbf{k}, \omega_\beta))_{;k^b} \right. \\ &\quad \left. + i \sum_{\ell} \left( r_{n\ell}^b B_{\ell m}^c(\mathbf{k}, \omega_\beta) - B_{n\ell}^c(\mathbf{k}, \omega_\beta) r_{\ell m}^b \right) \right] E_{\omega_\alpha}^b E_{\omega_\beta}^c \end{aligned} \quad (45) \quad \{\text{rho2}\}$$

where  $\tilde{\omega}_3 = \tilde{\omega}_\alpha + \tilde{\omega}_\beta$  and  $\mathbf{E}_{\omega_i}$  is the amplitude of the perturbing field with  $\omega_i$  for  $i = \alpha, \beta$ . We use Eq. (45) in section V. For the scissored hamiltonian,

$$\begin{aligned} \rho_{nm}^{(2)}(\mathbf{k}; \omega_3) &= \frac{e}{i\hbar} \frac{1}{\omega_{nm\mathbf{k}}^S - \tilde{\omega}_3} \left[ - (B_{nm}^c(\mathbf{k}, \omega_\beta))_{;k^b} \right. \\ &\quad \left. + i \sum_{\ell} \left( r_{n\ell}^b B_{\ell m}^c(\mathbf{k}, \omega_\beta) - B_{n\ell}^c(\mathbf{k}, \omega_\beta) r_{\ell m}^b \right) \right] E_{\omega_\alpha}^b E_{\omega_\beta}^c, \end{aligned} \quad (46) \quad \{\text{rho2n}\}$$

where we take  $B_{nm}^c(\mathbf{k}, \omega_\beta)$  from Eq. (41), i.e. within the scissored hamiltonian.

#### IV. LAYERED CURRENT DENSITY

{cd}

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  $\chi_{abc}^{slab} = 0$ , and thus we must devise a way in which this artifact of a centrosymmetric slab is bypassed in order to have a finite  $\chi_{abc}^s$  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  $\chi_{abc}^{slab} \neq 0$ , we need a procedure to extract the front surface  $\chi_{abc}^f$  and the back surface  $\chi_{abc}^b$  from the slab non-linear susceptibility  $\chi_{abc}^{slab}$ .

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

$$\mathcal{F}_\ell(z) = \Theta(z - z_\ell + \Delta_\ell^b)\Theta(z_\ell - z + \Delta_\ell^f), \quad (47) \quad \{\mathbf{sz}\}$$

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

Now, we show how this “cut function”  $\mathcal{F}_\ell(z)$  is introduced in the calculation of  $\chi_{ijl}$ . The microscopic current density is given by

$$\mathbf{j}(\mathbf{r}, t) = \text{Tr}(\hat{\mathbf{j}}(\mathbf{r})\hat{\rho}(t)), \quad (48) \quad \{\mathbf{jmic}\}$$

where the operator for the electron’s current is

$$\hat{\mathbf{j}}(\mathbf{r}) = \frac{e}{2} (\hat{\mathbf{v}}|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}), \quad (49) \quad \{\text{hatjmic}\}$$

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

$$\begin{aligned}
\text{Tr}(\hat{\mathbf{j}}(\mathbf{r})\hat{\rho}(t)) &= \text{Tr}(\hat{\rho}(t)\hat{\mathbf{j}}(\mathbf{r})) = \frac{e}{2} (\text{Tr}(\hat{\rho}\hat{\mathbf{v}}\hat{\mu}) + \text{Tr}(\hat{\rho}\hat{\mu}\hat{\mathbf{v}})) \\
&= \frac{e}{2} \sum_{n\mathbf{k}} (\langle n\mathbf{k}|\hat{\rho}\hat{\mathbf{v}}\hat{\mu}|n\mathbf{k}\rangle + \langle n\mathbf{k}|\hat{\rho}\hat{\mu}\hat{\mathbf{v}}|n\mathbf{k}\rangle) \\
&= \frac{e}{2} \sum_{nm\mathbf{k}} \langle n\mathbf{k}|\hat{\rho}|m\mathbf{k}\rangle (\langle m\mathbf{k}|\hat{\mathbf{v}}|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle + \langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}|n\mathbf{k}\rangle) \\
\mathbf{j}(\mathbf{r}, t) &= \sum_{nm\mathbf{k}} \rho_{nm}(\mathbf{k}; t) \mathbf{j}_{mn}(\mathbf{k}; \mathbf{r}),
\end{aligned} \tag{50} \quad \{\text{jmic2}\}$$

where

$$\mathbf{j}_{mn}(\mathbf{k}; \mathbf{r}) = \frac{e}{2} (\langle m\mathbf{k}|\hat{\mathbf{v}}|\mathbf{r}\rangle\langle\mathbf{r}|n\mathbf{k}\rangle + \langle m\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\hat{\mathbf{v}}|n\mathbf{k}\rangle), \tag{51} \quad \{\text{jmic3}\}$$

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  $\ell$ -th layer of the slab is given by

$$\frac{1}{\Omega} \int d^3r \mathcal{F}_\ell(z) \mathbf{j}(\mathbf{r}, t) \equiv \mathbf{J}^\ell(t), \tag{52} \quad \{\text{jsz}\}$$

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

$$e\mathcal{V}_{mn}^\ell(\mathbf{k}) \equiv \int d^3r \mathcal{F}_\ell(z) \mathbf{j}_{mn}(\mathbf{k}; \mathbf{r}), \tag{53} \quad \{\text{vcal}\}$$

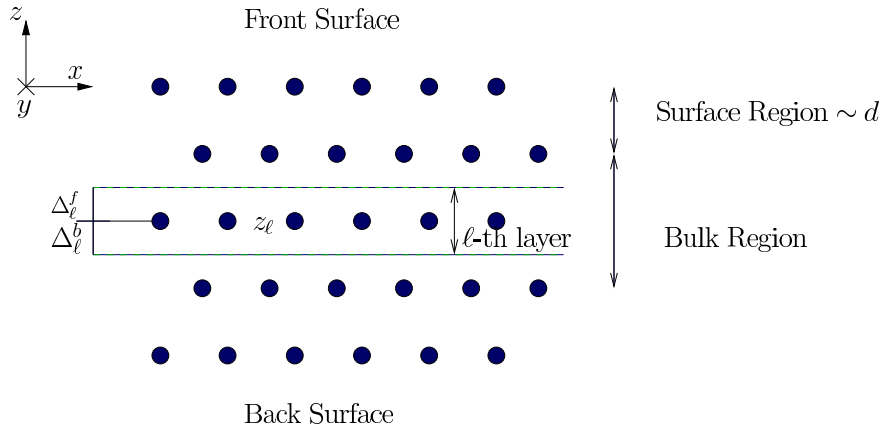


FIG. 1: We show a sketch of the slab, where the small circles represent the atoms. See the text for the details.

$\{\text{fslab}\}$

to write

$$J_a^{(N,\ell)}(t) = \frac{e}{\Omega} \sum_{mn\mathbf{k}} \mathcal{V}_{mn}^{a,\ell}(\mathbf{k}) \rho_{nm}^{(N)}(\mathbf{k}; t), \quad (54) \quad \{\text{jmac}\}$$

as the induced macroscopic current, to order  $N$ -th in the external perturbation, of the  $\ell$ -th layer. The matrix elements of the density operator for  $N = 1, 2$  are given by Eqs. (41) and (46), respectively. The Fourier component of macroscopic current of Eq. (54) is given by

$$J_a^{(N,\ell)}(\omega_3) = \frac{e}{\Omega} \sum_{mn\mathbf{k}} \mathcal{V}_{mn}^{a,\ell}(\mathbf{k}) \rho_{nm}^{(N)}(\mathbf{k}; \omega_3). \quad (55) \quad \{\text{jmac2}\}$$

We proceed to give an explicit expression of  $\mathcal{V}_{mn}^\ell(\mathbf{k})$ . From Eqs. (53) and (51) we obtain

$$\mathcal{V}_{mn}^\ell(\mathbf{k}) = \frac{1}{2} \int d^3r \mathcal{F}_\ell(z) \left[ \langle m\mathbf{k} | \mathbf{v} | \mathbf{r} \rangle \langle \mathbf{r} | n\mathbf{k} \rangle + \langle m\mathbf{k} | \mathbf{r} \rangle \langle \mathbf{r} | \mathbf{v} | n\mathbf{k} \rangle \right], \quad (56) \quad \{\text{intj}\}$$

for which we use  $\mathbf{v} \rightarrow \mathbf{v}^\Sigma$  to include the scissors correction, and the following property

$$\langle \mathbf{r} | \hat{\mathbf{v}}^\Sigma(\mathbf{r}, \mathbf{r}') | n\mathbf{k} \rangle = \int d^3r'' \langle \mathbf{r} | \hat{\mathbf{v}}^\Sigma(\mathbf{r}, \mathbf{r}') | \mathbf{r}'' \rangle \langle \mathbf{r}'' | n\mathbf{k} \rangle = \hat{\mathbf{v}}^\Sigma(\mathbf{r}, \mathbf{r}'') \int d^3r'' \langle \mathbf{r} | \mathbf{r}'' \rangle \langle \mathbf{r}'' | n\mathbf{k} \rangle = \hat{\mathbf{v}}^\Sigma(\mathbf{r}, \mathbf{r}') \psi_{n\mathbf{k}}(\mathbf{r}), \quad (57) \quad \{\text{n1.2}\}$$

due to the fact that the operator  $\mathbf{v}^\Sigma(\mathbf{r}, \mathbf{r}')$  does not act on  $\mathbf{r}''$ . Then,

$$\begin{aligned} \mathcal{V}_{mn}^{\Sigma,\ell}(\mathbf{k}) &= \frac{1}{2} \int d^3r \mathcal{F}_\ell(z) \left[ \psi_{n\mathbf{k}}(\mathbf{r}) \hat{\mathbf{v}}^{\Sigma*} \psi_{m\mathbf{k}}^*(\mathbf{r}) + \psi_{m\mathbf{k}}^*(\mathbf{r}) \hat{\mathbf{v}}^\Sigma \psi_{n\mathbf{k}}(\mathbf{r}) \right] \\ &= \int d^3r \psi_{m\mathbf{k}}^*(\mathbf{r}) \left[ \frac{\mathcal{F}_\ell(z) \mathbf{v}^\Sigma + \mathbf{v}^\Sigma \mathcal{F}_\ell(z)}{2} \right] \psi_{n\mathbf{k}}(\mathbf{r}) \\ &= \int d^3r \psi_{m\mathbf{k}}^*(\mathbf{r}) \mathcal{V}^{\Sigma,\ell} \psi_{n\mathbf{k}}(\mathbf{r}) \end{aligned} \quad (58) \quad \{\text{n1.3}\}$$

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

$$\mathcal{V}^{\Sigma,\ell} = \frac{\mathcal{F}_\ell(z) \mathbf{v}^\Sigma + \mathbf{v}^\Sigma \mathcal{F}_\ell(z)}{2}, \quad (59) \quad \{\text{n1.4}\}$$

and the superscript  $\ell$  is inherited from  $\mathcal{F}_\ell(z)$ . Then, we see that the replacement

$$\hat{\mathbf{v}}^\Sigma \rightarrow \hat{\mathcal{V}}^{\Sigma,\ell} = \left[ \frac{\mathcal{F}_\ell(z) \hat{\mathbf{v}}^\Sigma + \hat{\mathbf{v}}^\Sigma \mathcal{F}_\ell(z)}{2} \right], \quad (60) \quad \{\text{vcali}\}$$

is what it takes to change the velocity operator of the electron,  $\hat{\mathbf{v}}^\Sigma$ , to the new velocity operator,  $\mathcal{V}^{\Sigma,\ell}$  that implicitly takes into account the contribution of the region of the slab given by  $\mathcal{F}_\ell(z)$ .

From Eq. (8),

$$\mathcal{V}^{\Sigma,\ell} = \mathcal{V}^\ell + \mathcal{V}^{\text{nl},\ell} + \mathcal{V}^{S,\ell}, \quad (61) \quad \{\text{vopii}\}$$

and the expressions for the matrix elements of above operators are given in App. F.

Actually, to limit the response to one surface, the equivalent of Eq. (59) for  $\mathcal{V}^\ell$  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. (47) 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.

## V. NON-LINEAR SURFACE SUSCEPTIBILITY

{nonchi}

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

$$\begin{aligned} P_a(\omega_3) = & \chi_{abc}(-\omega_3; \omega_1, \omega_2) E_b(\omega_1) E_c(\omega_2) \\ & + \chi_{abcl}(-\omega_3; \omega_1, \omega_2) E_b(\omega_1) \nabla_c E_l(\omega_2) + \dots, \end{aligned} \quad (62) \quad \{\text{mshg}\}$$

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

$$P_a(\mathbf{r}) = \chi_{abc} E_b(\mathbf{r}) E_c(\mathbf{r}) + \chi_{abcl} E_b(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}_c} E_l(\mathbf{r}) + \dots, \quad (63) \quad \{\text{mshg2}\}$$

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

$$\begin{aligned} P_a(-\mathbf{r}) = & \chi_{abc} E_b(-\mathbf{r}) E_c(-\mathbf{r}) \\ & + \chi_{abcl} E_b(-\mathbf{r}) \frac{\partial}{\partial (-\mathbf{r}_c)} E_l(-\mathbf{r}) + \dots, \end{aligned} \quad (64) \quad \{\text{mshg3}\}$$

as the polarization in the coordinate system where inversion is taken, i.e.  $\mathbf{r} \rightarrow -\mathbf{r}$ . Note that we have kept the same susceptibility tensors, since as the system is centrosymmetric, they must be invariant under  $\mathbf{r} \rightarrow -\mathbf{r}$ . Recalling that  $\mathbf{P}(\mathbf{r})$  and  $\mathbf{E}(\mathbf{r})$ , are polar vectors,<sup>21</sup> we have that Eq. (64) reduces to

$$\begin{aligned} -P_a(\mathbf{r}) = & \chi_{abc}(-E_b(\mathbf{r}))(-E_c(\mathbf{r})) - \chi_{abcl}(-E_b(\mathbf{r}))(-\frac{\partial}{\partial \mathbf{r}_c})(-E_l(\mathbf{r})) + \dots, \\ P_a(\mathbf{r}) = & -\chi_{abc} E_b(\mathbf{r}) E_c(\mathbf{r}) + \chi_{abcl} E_b(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}_c} E_l(\mathbf{r}) + \dots, \end{aligned} \quad (65) \quad \{\text{mshg4}\}$$

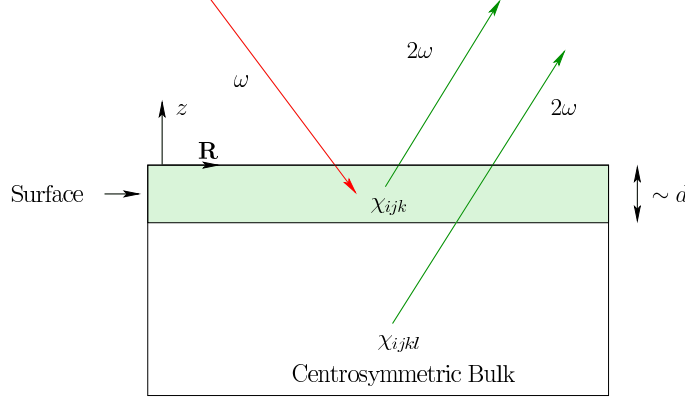


FIG. 2: (color online) We show a sketch of the semi-infinite system with a centrosymmetric bulk. The surface region is of width  $\sim d$ . The incoming photon of frequency  $\omega$  is represented by a downward red arrow, whereas both the surface and bulk created second harmonic photons of frequency  $2\omega$  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,  $\chi_{abc}$ , and quadrupolar,  $\chi_{abcl}$ , 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}

that when compared with Eq. (63) leads to the conclusion that

$$\chi_{abc} = 0 \quad \text{for a centrosymmetric bulk.} \quad (66) \quad \{\text{sshg}\}$$

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  $\chi_{abc}$ . Thus, we conclude that the leading term of the polarization in a surface region is given by

$$\begin{aligned} \int d\mathbf{R} \int dz P_a(\mathbf{R}, z) &\approx \mathcal{S} d P_a \\ &= \mathcal{S} P_a^s \\ &= \chi_{abc} E_b E_c, \end{aligned} \quad (67) \quad \{\text{sshgp1}\}$$

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

$$P_a^s = \frac{1}{\mathcal{S}} \chi_{abc} E_b E_c = \chi_{abc}^s E_b E_c, \quad (68) \quad \{\text{sshgp2}\}$$

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

$$P_a^b(\mathbf{r}) = \chi_{abcl} E_b(\mathbf{r}) \nabla_c E_l(\mathbf{r}), \quad (69) \quad \{\text{sshgp3}\}$$

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.  $\chi_{abc}$ , and 4 for the bulk, i.e.  $\chi_{abcd}$ . 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 than the dipolar surface response, SH is readily used as a very useful and powerful optical surface probe.<sup>1</sup>

To calculate  $\chi_{abc}^s$ , we start from the basic relation,  $\mathbf{J} = d\mathbf{P}/dt$  with  $\mathbf{J}$  the current calculated in Sec. IV, and from Eq. (55) we obtain

$$J_a^{(2,\ell)}(\omega_3) = -i\omega_3 P_a(\omega_3) = \frac{e}{\Omega} \sum_{mn\mathbf{k}} \mathcal{V}_{mn}^{\Sigma,a,\ell}(\mathbf{k}) \rho_{nm}^{(2)}(\mathbf{k}; \omega_3), \quad (70) \quad \{\text{Pj i k n}\}$$

which upon using Eqs. (46) and (68) leads to

$$\begin{aligned} \chi_{abc}^{s,\ell}(-\omega_3; \omega_1, \omega_2) &= \frac{ie}{\Omega E_1^b E_2^c \mathcal{S} \omega_3} \sum_{mn\mathbf{k}} \mathcal{V}_{mn}^{\Sigma,a,\ell}(\mathbf{k}) \rho_{nm}^{(2)}(\mathbf{k}; \omega_3) \\ &= \frac{e^2}{\mathcal{S} \Omega \hbar \omega_3} \sum_{mn\mathbf{k}} \frac{\mathcal{V}_{mn}^{\Sigma,a,\ell}(\mathbf{k})}{\omega_{nm}^S - \omega_3} \left[ - (B_{nm}^c(\mathbf{k}, \omega_\beta))_{;k^b} \right. \\ &\quad \left. + i \sum_{\ell} \left( r_{n\ell}^b B_{\ell m}^c(\mathbf{k}, \omega_\beta) - B_{n\ell}^c(\mathbf{k}, \omega_\beta) r_{\ell m}^b \right) \right], \end{aligned} \quad (71) \quad \{\text{Pj i k n 2}\}$$

which gives the surface susceptibility of layer  $\ell$ -th, where  $\mathcal{V}^\Sigma$  is given in Eq. (??). Using Eq. (41), we split above equation into two, one coming from the first term and the other from the second term on the r.h.s.,

$$\chi_{i,abc}^{s,\ell} = -\frac{e^3}{\Omega \hbar^2 \omega_3} \sum_{mn\mathbf{k}} \frac{\mathcal{V}_{mn}^{\Sigma,a,\ell}}{\omega_{nm}^S - \omega_3} \left( \frac{f_{mn} r_{nm}^b}{\omega_{nm}^S - \omega_\beta} \right)_{;k^c}, \quad (72) \quad \{\text{ch i i}\}$$

and

$$\chi_{e,abc}^{s,\ell} = \frac{ie^3}{\Omega \hbar^2 \omega_3} \sum_{\ell mn\mathbf{k}} \frac{\mathcal{V}_{mn}^{\Sigma,a,\ell}}{\omega_{nm}^S - \omega_3} \left( \frac{r_{n\ell}^c r_{\ell m}^b f_{m\ell}}{\omega_{\ell m}^S - \omega_\beta} - \frac{r_{n\ell}^b r_{\ell m}^c f_{\ell n}}{\omega_{n\ell}^S - \omega_\beta} \right), \quad (73) \quad \{\text{ch i e}\}$$

where  $\chi_i^{s,\ell}$  is related to intraband transitions and  $\chi_e^{s,\ell}$  to interband transitions. We warn the reader not to be confused by the already confusing notation, lower case  $s$  refers to the surface, whereas the capital case  $S$  refers to the Scissors correction. We mention that Eq. (72) and Eq. (73) need to be symmetrized for intrinsic permutation symmetry, i.e.  $\chi^{abc}(-\omega_3; \omega_1, \omega_2) = \chi^{acb}(-\omega_3; \omega_2, \omega_1)$ ,<sup>22</sup> (for SHG  $\omega_1 = \omega_2 = \omega$  and  $\omega_3 = 2\omega$ ). We mention that above equations diverge as  $\omega_3 \rightarrow 0$ . This apparent divergence is removed in the following section.

The generalized derivative in Eq. (72) is obtained from the chain rule as

$$\left( \frac{f_{mn} r_{nm}^b}{\omega_{nm}^S - \omega_2} \right)_{;k^c} = \frac{f_{mn}}{\omega_{nm}^S - \omega} (r_{nm}^b)_{;k^c} - \frac{f_{mn} r_{nm}^b}{(\omega_{nm}^S - \omega)^2} (\omega_{nm}^S)_{;k^c}, \quad (74) \quad \{\text{gene}\}$$

here  $(\omega_{nm}^S)_{;k^a} = (\omega_n^S)_{;k^a} - (\omega_m^S)_{;k^a}$ , and from Appendix D we show that  $(\omega_m^S)_{;k^a} = (\omega_m^{\text{LDA}})_{;k^a}$ , thus

$$(\omega_{nm}^S)_{;k^c} = (\omega_{nm}^{\text{LDA}})_{;k^c} = \frac{p_{nn}^c - p_{mm}^c}{m_e} \equiv \Delta_{nm}^c, \quad (75) \quad \{\text{wk}\}$$

and that,<sup>27</sup>

$$\begin{aligned} (r_{nm}^{S,b})_{;k^c} &= (r_{nm}^{\text{LDA},b})_{;k^c} = \frac{r_{nm}^c \Delta_{mn}^b + r_{nm}^b \Delta_{mn}^c}{\omega_{nm}^{\text{LDA}}} + \frac{1}{m_e \omega_{nm}^{\text{LDA}}} \sum_{\ell} \left( r_{n\ell}^c p_{\ell m}^b - p_{n\ell}^b r_{\ell m}^c \right). \\ &= \frac{r_{nm}^c \Delta_{mn}^b + r_{nm}^b \Delta_{mn}^c}{\omega_{nm}^{\text{LDA}}} + \frac{i}{\omega_{nm}^{\text{LDA}}} \sum_{\ell} \left( \omega_{\ell m}^{\text{LDA}} r_{n\ell}^c r_{\ell m}^b - \omega_{n\ell}^{\text{LDA}} r_{n\ell}^b r_{\ell m}^c \right), \end{aligned} \quad (76) \quad \{\text{rgk}\}$$

where we used Eq. (16). Therefore,

$$\left( \frac{f_{mn} r_{nm}^b}{\omega_{nm}^S - \omega_2} \right)_{;k^c} = \frac{f_{mn}}{\omega_{nm}^S - \omega} (r_{nm}^{\text{LDA},b})_{;k^c} - \frac{f_{mn} r_{nm}^b \Delta_{nm}^c}{(\omega_{nm}^S - \omega)^2}, \quad (77) \quad \{\text{gene2}\}$$

where LDA and scissored energies combine.

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

$$\chi_{\text{abc}}^s(2\omega) \equiv \sum_{\ell_0}^{\ell_d} \chi_{\text{abc}}^{\ell}(2\omega), \quad (78) \quad \{\text{chiijsur}\}$$

where  $\ell_0$  represents the first layer right at the surface, and  $\ell_d$  the layer at a distance  $\sim d$  from the surface (see Fig. 2). Of course we can use Eq. (78) for either the front or the back surface. Likewise

$$\chi_{\text{abc}}^{(\ell_f)}(2\omega) \equiv \sum_{\ell_d}^{\ell_f} \chi_{\text{abc}}^{\ell}(2\omega), \quad (79) \quad \{\text{chiijklf}\}$$

is a dipolar bulk susceptibility, with the property that,

$$\chi_{\text{abc}}^{(\ell_f)}(2\omega) \stackrel{\ell_f \rightarrow \ell_b}{=} 0, \quad (80) \quad \{\text{chiijkbul}\}$$

where  $\ell_b$  is a bulk layer such that the bulk centrosymmetry is fully established and the dipolar non-linear susceptibility is identically zero, in accordance with Eq. (66). We remark that  $\ell_d$  is not universal, and  $\ell_b$  should be found according to Eq. (80).



## VI. DIVERGENCE-FREE $\chi^s$

To obtain divergence free expressions for SHG that are manageable for programing, we take Eqs. (72) and (73) and perform a partial fraction expansion in  $\omega$  to get the following terms for the interband term (bellow, any energy is scissored, we have to change them!!)

$$E = A \left[ -\frac{1}{2\omega_{lm}(2\omega_{lm} - \omega_{nm})} \frac{1}{\omega_{lm} - \omega} + \frac{2}{\omega_{nm}(2\omega_{lm} - \omega_{nm})} \frac{1}{\omega_{nm} - 2\omega} + \frac{1}{2\omega_{lm}\omega_{nm}} \frac{1}{\omega} \right] \\ - B \left[ -\frac{1}{2\omega_{nl}(2\omega_{nl} - \omega_{nm})} \frac{1}{\omega_{nl} - \omega} + \frac{2}{\omega_{nm}(2\omega_{nl} - \omega_{nm})} \frac{1}{\omega_{nm} - 2\omega} + \frac{1}{2\omega_{nl}\omega_{nm}} \frac{1}{\omega} \right], \quad (81) \quad \{\text{pfe}\}$$

where  $A = f_{ml} \mathcal{V}_{mn}^{\Sigma,a} r_{nl}^c r_{lm}^b$  and  $B = f_{ln} \mathcal{V}_{mn}^{\Sigma,a} r_{nl}^b r_{lm}^c$ , and the following terms for the intraband terms (using Eq. (77))

$$I = C \left[ -\frac{1}{2\omega_{nm}^2} \frac{1}{\omega_{nm} - \omega} + \frac{2}{\omega_{nm}^2} \frac{1}{\omega_{nm} - 2\omega} + \frac{1}{2\omega_{nm}^2} \frac{1}{\omega} \right] \\ - D \left[ -\frac{3}{2\omega_{nm}^3} \frac{1}{\omega_{nm} - \omega} + \frac{4}{\omega_{nm}^3} \frac{1}{\omega_{nm} - 2\omega} + \frac{1}{2\omega_{nm}^3} \frac{1}{\omega} - \frac{1}{2\omega_{nm}^2} \frac{1}{(\omega_{nm} - \omega)^2} \right], \quad (82) \quad \{\text{pfi}\}$$

where  $C = f_{mn} \mathcal{V}_{mn}^{\Sigma,a} (r_{nm}^{\text{LDA},b})_{;kc}$ , and  $D = f_{mn} \mathcal{V}_{mn}^{\Sigma,a} r_{nm}^b \Delta_{nm}^c$ . Time-reversal symmetry allow us to write,  $\mathbf{r}_{mn}(\mathbf{k}) = \mathbf{r}_{nm}(-\mathbf{k})$ ,  $\mathbf{r}_{mn;\mathbf{k}}(\mathbf{k}) = -\mathbf{r}_{nm;\mathbf{k}}(-\mathbf{k})$ ,  $\mathcal{V}_{mn}^{\Sigma,a}(-\mathbf{k}) = -\mathcal{V}_{nm}^{\Sigma,a}(\mathbf{k})$ ,  $\omega_{mn}^S(-\mathbf{k}) = \omega_{nm}^S(\mathbf{k})$ , and  $\Delta_{nm}^a(-\mathbf{k}) = -\Delta_{nm}^a(\mathbf{k})$ . 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. (81) and Eq. (82) cancel each other. The last term in the second line of Eq. (82) is dealt with as follows.

$$\frac{D}{2(\omega_{nm}^S)^2} \frac{1}{(\omega_{nm}^S - \omega)^2} = \frac{f_{mn}}{2} \frac{\mathcal{V}_{mn}^{\Sigma,a} r_{nm}^b}{(\omega_{nm}^S)^2} \frac{\Delta_{nm}^c}{(\omega_{nm}^S - \omega)^2} = \frac{f_{mn}}{2} \frac{\mathcal{V}_{mn}^{\Sigma,a} r_{nm}^b}{(\omega_{nm}^S)^2} \left( \frac{1}{\omega_{nm}^S - \omega} \right)_{;kc} \\ = -\frac{f_{mn}}{2} \left( \frac{\mathcal{V}_{mn}^{\Sigma,a} r_{nm}^b}{(\omega_{nm}^S)^2} \right)_{;kc} \frac{1}{\omega_{nm}^S - \omega}, \quad (83) \quad \{\text{dresn}\}$$

where we used Eqs. (75) and (I13), and for the last line, we performed an integration by parts over the Brillouin zone, where the contribution from the edges vanishes.<sup>26</sup> Using the chain rule, we obtain

$$\left( \frac{\mathcal{V}_{mn}^{\Sigma,a} r_{nm}^b}{(\omega_{nm}^S)^2} \right)_{;kc} = \frac{r_{nm}^b}{(\omega_{nm}^S)^2} (\mathcal{V}_{mn}^{\Sigma,a})_{;kc} + \frac{\mathcal{V}_{mn}^{\Sigma,a}}{(\omega_{nm}^S)^2} (r_{nm}^b)_{;kc} - \frac{\mathcal{V}_{mn}^{\Sigma,a} r_{nm}^b}{2(\omega_{nm}^S)^3} (\omega_{nm}^S)_{;kc}, \quad (84) \quad \{\text{chnr}\}$$

where in the appendix F we show how to calculate  $(\mathcal{V}_{nm}^{\Sigma,a})_{;kb}$ . Therefore, all the remaining non-zero terms in expressions (81) and (82) are simple  $\omega$  and  $2\omega$  resonant denominators well behaved at zero frequency.

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

Still needs to be worked out!!

$$\text{Im}[\chi_{e,abc,\omega}^{s,\ell}] = \frac{\pi|e|^3}{2\hbar^2} \sum_{v\mathbf{c}\mathbf{k}} \sum_{l \neq (v,c)} \left[ \frac{\omega_{lc}^S \text{Re}[\mathcal{R}_{lc}^{a,\ell} \{r_{cv}^b r_{vl}^c\}]}{\omega_{cv}^S (2\omega_{cv}^S - \omega_{cl}^S)} - \frac{\omega_{vl}^S \text{Re}[\mathcal{R}_{vl}^{a,\ell} \{r_{lc}^c r_{cv}^b\}]}{\omega_{cv}^S (2\omega_{cv}^S - \omega_{lv}^S)} \right] \delta(\omega_{cv}^S - \omega), \quad (85) \quad \{\text{imchiwn}\}$$

$$\text{Im}[\chi_{e,abc,2\omega}^{s,\ell}] = \frac{\pi|e|^3}{2\hbar^2} \sum_{v\mathbf{c}\mathbf{k}} 4 \left[ \sum_{v' \neq v} \frac{\text{Re}[\mathcal{R}_{vc}^{a,\ell} \{r_{cv'}^b r_{v'v}^c\}]}{2\omega_{cv'}^S - \omega_{cv}^S} - \sum_{c' \neq c} \frac{\text{Re}[\mathcal{R}_{vc}^{a,\ell} \{r_{cc'}^c r_{c'v}^b\}]}{2\omega_{c'v}^S - \omega_{cv}^S} \right] \delta(\omega_{cv}^S - 2\omega), \quad (86) \quad \{\text{imchie2wn}\}$$

$$\text{Im}[\chi_{i,abc,\omega}^{s,\ell}] = \frac{\pi|e|^3}{2\hbar^2} \sum_{cv\mathbf{k}} \frac{1}{\omega_{cv}^S} \left[ \text{Im}[\{r_{cv}^b (\mathcal{R}_{vc}^{a,\ell})_{;k^c}\}] + \frac{2\text{Im}[\mathcal{R}_{vc}^{a,\ell} \{r_{cv}^b \Delta_{cv}^c\}]}{\omega_{cv}^S} \right] \delta(\omega_{cv}^S - \omega), \quad (87) \quad \{\text{imchiwn}\}$$

and

$$\text{Im}[\chi_{i,abc,2\omega}^{s,\ell}] = \frac{\pi|e|^3}{2\hbar^2} \sum_{cv\mathbf{k}} \frac{4}{\omega_{cv}^S} \left[ \text{Im}[\mathcal{R}_{vc}^{a,\ell} \{r_{cv}^b\}_{;k^c}] - \frac{2\text{Im}[\mathcal{R}_{vc}^{a,\ell} \{r_{cv}^b \Delta_{cv}^c\}]}{\omega_{cv}^S} \right] \delta(\omega_{cv}^S - 2\omega), \quad (88) \quad \{\text{imchi2wn}\}$$

where we have split the interband and intraband  $1\omega$  and  $2\omega$  contributions. The real part of each contribution can be obtained through a Kramers-Kronig transformation, and then  $\chi_{abc}^{s,\ell} = \chi_{e,abc,\omega}^{s,\ell} + \chi_{e,abc,2\omega}^{s,\ell} + \chi_{i,abc,\omega}^{s,\ell} + \chi_{i,abc,2\omega}^{s,\ell}$ . Also, the  $\{\}$  notation symmetrizes the Cartesian indices bc, i.e.  $\{u^b s^c\} = (u^b s^c + u^c s^b)/2$ , from where we obtain that  $\chi_{abc}^{s,\ell} = \chi_{acb}^{s,\ell}$ . In the continuous limit of  $\mathbf{k}$   $(1/\Omega) \sum_{\mathbf{k}} \rightarrow \int d^3\mathbf{k}/(8\pi^3)$ , and with the help of Eq. (75), (76), (??) and (??), Eqs. (85)-(88) 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  $\chi^{s,\ell}$  by simple taking  $\omega_n \rightarrow \omega_n^S$ , where  $\omega_n^S = \omega_n + (1 - f_n)\Delta$  with  $\Delta$  the rigid scissor correction.<sup>27,28</sup>

## VII. CONCLUSIONS

{con}

We have presented a complete derivation of the required elements to calculate the surface SHG susceptibility tensor  $\chi^s(2\omega)$  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 $\chi_{\text{abc}}^s$

We add the  $\mathbf{k}$  and  $-\mathbf{k}$  terms of expressions (81) and (82) to obtain:

$$\begin{aligned}
& A \left[ -\frac{1}{2\omega_{lm}(2\omega_{lm} - \omega_{nm})} \frac{1}{\omega_{lm} - \omega} \right] = -\frac{f_{ml}}{2} \left[ \frac{\mathcal{P}_{mn}^a r_{nl}^c r_{lm}^b}{\omega_{lm}(2\omega_{lm} - \omega_{nm})} \frac{1}{\omega_{lm} - \omega} \right]_{\mathbf{k}} \\
& + \frac{\mathcal{P}_{mn}^a r_{nl}^c r_{lm}^b}{\omega_{lm}(2\omega_{lm} - \omega_{nm})} \frac{1}{\omega_{lm} - \omega} \Big|_{-\mathbf{k}} = -\frac{f_{ml}}{2} \left[ \frac{\mathcal{P}_{mn}^a r_{nl}^c r_{lm}^b}{\omega_{lm}(2\omega_{lm} - \omega_{nm})} \frac{1}{\omega_{lm} - \omega} \right]_{\mathbf{k}} \\
& - \frac{\mathcal{P}_{nm}^a r_{ln}^c r_{ml}^b}{\omega_{lm}(2\omega_{lm} - \omega_{nm})} \frac{1}{\omega_{lm} - \omega} \Big|_{\mathbf{k}} = -\frac{f_{ml}}{2} \frac{1}{\omega_{lm}(2\omega_{lm} - \omega_{nm})} \frac{1}{\omega_{lm} - \omega} \\
& \times \left[ \mathcal{P}_{mn}^a r_{nl}^c r_{lm}^b - \mathcal{P}_{nm}^a r_{ln}^c r_{ml}^b \right] \quad (\text{A1}) \quad \{\text{chi1}\} \\
& = -\frac{f_{ml}}{2} \frac{1}{\omega_{lm}(2\omega_{lm} - \omega_{nm})} \frac{1}{\omega_{lm} - \omega} \left[ \mathcal{P}_{mn}^a r_{nl}^c r_{lm}^b - (\mathcal{P}_{mn}^a r_{nl}^c r_{lm}^b)^* \right] = -\frac{f_{ml}}{2} \frac{2i\text{Im}[\mathcal{P}_{mn}^a r_{nl}^c r_{lm}^b]}{\omega_{lm}(2\omega_{lm} - \omega_{nm})} \frac{1}{\omega_{lm} - \omega},
\end{aligned}$$

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

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

Also,

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

and therefore

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

Using above results into Eq. (73) implies

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

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

$$\begin{aligned}
\chi_{e,abc}^{s,\ell} &= -\frac{2e^3}{2m_e\hbar^2} \sum_{\ell mn\mathbf{k}} \left[ \left[ -\frac{f_{ml}\text{Im}[\mathcal{P}_{mn}^a\{r_{nl}^c r_{lm}^b\}]}{2\omega_{lm}(2\omega_{lm} - \omega_{nm})} \frac{1}{\omega_{lm} - \omega} + \frac{2f_{ml}\text{Im}[\mathcal{P}_{mn}^a\{r_{nl}^c r_{lm}^b\}]}{\omega_{nm}(2\omega_{lm} - \omega_{nm})} \frac{1}{\omega_{nm} - 2\omega} \right] \right. \\
&\quad \left. + \left[ \frac{f_{ln}\text{Im}[\mathcal{P}_{mn}^a\{r_{nl}^b r_{lm}^c\}]}{2\omega_{nl}(2\omega_{nl} - \omega_{nm})} \frac{1}{\omega_{nl} - \omega} - \frac{2f_{ln}\text{Im}[\mathcal{P}_{mn}^a\{r_{nl}^b r_{lm}^c\}]}{\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}\text{Im}[\mathcal{P}_{mn}^a\{r_{nl}^c r_{lm}^b\}]}{\omega_{nm}(2\omega_{lm} - \omega_{nm})} - \frac{2f_{ln}\text{Im}[\mathcal{P}_{mn}^a\{r_{nl}^b r_{lm}^c\}]}{\omega_{nm}(2\omega_{nl} - \omega_{nm})} \right] \frac{1}{\omega_{nm} - 2\omega} \right. \\
&\quad \left. + \left[ \frac{f_{ln}\text{Im}[\mathcal{P}_{mn}^a\{r_{nl}^b r_{lm}^c\}]}{2\omega_{nl}(2\omega_{nl} - \omega_{nm})} \frac{1}{\omega_{nl} - \omega} - \frac{f_{ml}\text{Im}[\mathcal{P}_{mn}^a\{r_{nl}^c r_{lm}^b\}]}{2\omega_{lm}(2\omega_{lm} - \omega_{nm})} \frac{1}{\omega_{lm} - \omega} \right]_{\ell \leftrightarrow m} \right] \\
&= -\frac{e^3}{m_e\hbar^2} \sum_{\ell mn\mathbf{k}} \left[ \left[ \frac{2f_{ml}\text{Im}[\mathcal{P}_{mn}^a\{r_{nl}^c r_{lm}^b\}]}{\omega_{nm}(2\omega_{lm} - \omega_{nm})} - \frac{2f_{ln}\text{Im}[\mathcal{P}_{mn}^a\{r_{nl}^b r_{lm}^c\}]}{\omega_{nm}(2\omega_{nl} - \omega_{nm})} \right] \frac{1}{\omega_{nm} - 2\omega} \right. \\
&\quad \left. + \left[ \frac{f_{ln}\text{Im}[\mathcal{P}_{mn}^a\{r_{nl}^b r_{lm}^c\}]}{2\omega_{nl}(2\omega_{nl} - \omega_{nm})} \frac{1}{\omega_{nl} - \omega} - \frac{f_{lm}\text{Im}[\mathcal{P}_{ln}^a\{r_{nm}^c r_{ml}^b\}]}{2\omega_{ml}(2\omega_{ml} - \omega_{nl})} \frac{1}{\omega_{ml} - \omega} \right]_{n \leftrightarrow m} \right] \\
&= -\frac{e^3}{m_e\hbar^2} \sum_{\ell mn\mathbf{k}} \left[ \left[ \frac{2f_{ml}\text{Im}[\mathcal{P}_{mn}^a\{r_{nl}^c r_{lm}^b\}]}{\omega_{nm}(2\omega_{lm} - \omega_{nm})} - \frac{2f_{ln}\text{Im}[\mathcal{P}_{mn}^a\{r_{nl}^b r_{lm}^c\}]}{\omega_{nm}(2\omega_{nl} - \omega_{nm})} \right] \frac{1}{\omega_{nm} - 2\omega} \right. \\
&\quad \left. + \left[ \frac{f_{ln}\text{Im}[\mathcal{P}_{mn}^a\{r_{nl}^b r_{lm}^c\}]}{2\omega_{nl}(2\omega_{nl} - \omega_{nm})} \frac{1}{\omega_{nl} - \omega} - \frac{f_{ln}\text{Im}[\mathcal{P}_{lm}^a\{r_{mn}^c r_{nl}^b\}]}{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}\text{Im}[\mathcal{P}_{mn}^a\{r_{nl}^c r_{lm}^b\}]}{\omega_{nm}(2\omega_{lm} - \omega_{nm})} - \frac{2f_{ln}\text{Im}[\mathcal{P}_{mn}^a\{r_{nl}^b r_{lm}^c\}]}{\omega_{nm}(2\omega_{nl} - \omega_{nm})} \right] \frac{1}{\omega_{nm} - 2\omega} \right. \\
&\quad \left. + f_{ln} \left[ \frac{\text{Im}[\mathcal{P}_{mn}^a\{r_{nl}^b r_{lm}^c\}]}{2\omega_{nl}(2\omega_{nl} - \omega_{nm})} - \frac{f_{ln}\text{Im}[\mathcal{P}_{lm}^a\{r_{mn}^c r_{nl}^b\}]}{2\omega_{nl}(2\omega_{nl} - \omega_{ml})} \right] \frac{1}{\omega_{nl} - \omega} \right], \tag{A6} \quad \{\text{pfen2}\}
\end{aligned}$$

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.  $\chi \rightarrow \sum_{\mathbf{k}>0} [\chi(\mathbf{k}) + \chi(-\mathbf{k})]/2$ . Taking  $\omega \rightarrow \omega + i\eta$  and use  $\lim_{\eta \rightarrow 0} 1/(x - i\eta) = P(1/x) + i\pi\delta(x)$ , to get

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

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

$$\begin{aligned}
\text{Im}[\chi_{e,abc}^{s,\ell}] &= \frac{\pi e^3}{m_e\hbar^2} \sum_{\ell mn\mathbf{k}} \left[ \left[ \frac{2f_{ln}\text{Im}[\mathcal{P}_{mn}^a\{r_{nl}^b r_{lm}^c\}]}{\omega_{nm}(2\omega_{nl} - \omega_{nm})} - \frac{2f_{ml}\text{Im}[\mathcal{P}_{mn}^a\{r_{nl}^c r_{lm}^b\}]}{\omega_{nm}(2\omega_{lm} - \omega_{nm})} \right] \delta(\omega_{nm} - 2\omega) \right. \\
&\quad \left. + f_{mn} \left[ \frac{\text{Im}[\mathcal{P}_{ml}^a\{r_{ln}^c r_{nm}^b\}]}{2\omega_{nm}(2\omega_{nm} - \omega_{lm})} - \frac{\text{Im}[\mathcal{P}_{ln}^a\{r_{nm}^b r_{ml}^c\}]}{2\omega_{nm}(2\omega_{nm} - \omega_{nl})} \right] \delta(\omega_{nm} - \omega) \right]. \tag{A8} \quad \{\text{imchie2}\}
\end{aligned}$$

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

$$\begin{aligned} \text{Im}[\chi_{e,\text{abc}}^{s,\ell}] &= \frac{\pi e^3}{m_e \hbar^2} \sum_{v\mathbf{ck}} \left[ \left[ \sum_{v' \neq v} \frac{2\text{Im}[\mathcal{P}_{vc}^{a,\ell} \{r_{cv'}^b r_{v'v}^c\}]}{\omega_{cv}(2\omega_{cv'} - \omega_{cv})} - \sum_{c' \neq c} \frac{2\text{Im}[\mathcal{P}_{vc}^{a,\ell} \{r_{cc'}^c r_{c'v}^b\}]}{\omega_{cv}(2\omega_{c'v} - \omega_{cv})} \right] \delta(\omega_{cv} - 2\omega) \right. \\ &\quad \left. + \sum_{l \neq (v,c)} \left[ \frac{\text{Im}[\mathcal{P}_{vl}^{a,\ell} \{r_{lc}^c r_{cv}^b\}]}{2\omega_{cv}(2\omega_{cv} - \omega_{lv})} - \frac{\text{Im}[\mathcal{P}_{lc}^{a,\ell} \{r_{cv}^b r_{vl}^c\}]}{2\omega_{cv}(2\omega_{cv} - \omega_{cl})} \right] \delta(\omega_{cv} - \omega) \right], \end{aligned} \quad (\text{A9}) \quad \{\text{imchie3}\}$$

where we put the layer  $\ell$  dependence in  $\mathcal{P}$ . Using Eq. (I13), we can obtain the following result

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

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

$$\begin{aligned} \text{Im}[\chi_{e,\text{abc}}^{s,\ell}] &= \frac{\pi e^3}{\hbar^2} \sum_{v\mathbf{ck}} \left[ \left[ - \sum_{v' \neq v} \frac{2\text{Re}[\mathcal{R}_{vc}^{a,\ell} \{r_{cv'}^b r_{v'v}^c\}]}{2\omega_{cv'} - \omega_{cv}} + \sum_{c' \neq c} \frac{2\text{Re}[\mathcal{R}_{vc}^{a,\ell} \{r_{cc'}^c r_{c'v}^b\}]}{2\omega_{c'v} - \omega_{cv}} \right] \delta(\omega_{cv} - 2\omega) \right. \\ &\quad \left. + \sum_{l \neq (v,c)} \left[ \frac{\omega_{vl} \text{Re}[\mathcal{R}_{vl}^{a,\ell} \{r_{lc}^c r_{cv}^b\}]}{2\omega_{cv}(2\omega_{cv} - \omega_{lv})} - \frac{\omega_{lc} \text{Re}[\mathcal{R}_{lc}^{a,\ell} \{r_{cv}^b r_{vl}^c\}]}{2\omega_{cv}(2\omega_{cv} - \omega_{cl})} \right] \delta(\omega_{cv} - \omega) \right]. \end{aligned} \quad (\text{A11}) \quad \{\text{imchie3n}\}$$

Finally, following Ref. 27,28 we simply change  $\omega_{nm} \rightarrow \omega_{nm}^S$  to obtain the scissored expression of

$$\begin{aligned} \text{Im}[\chi_{e,\text{abc}}^{s,\ell}] &= \frac{\pi e^3}{2\hbar^2} \sum_{v\mathbf{ck}} \left[ 4 \left[ - \sum_{v' \neq v} \frac{\text{Re}[\mathcal{R}_{vc}^{a,\ell} \{r_{cv'}^b r_{v'v}^c\}]}{2\omega_{cv'}^S - \omega_{cv}^S} + \sum_{c' \neq c} \frac{\text{Re}[\mathcal{R}_{vc}^{a,\ell} \{r_{cc'}^c r_{c'v}^b\}]}{2\omega_{c'v}^S - \omega_{cv}^S} \right] \delta(\omega_{cv}^S - 2\omega) \right. \\ &\quad \left. + \sum_{l \neq (v,c)} \left[ \frac{\omega_{vl}^S \text{Re}[\mathcal{R}_{vl}^{a,\ell} \{r_{lc}^c r_{cv}^b\}]}{\omega_{cv}^S(2\omega_{cv}^S - \omega_{lv}^S)} - \frac{\omega_{lc}^S \text{Re}[\mathcal{R}_{lc}^{a,\ell} \{r_{cv}^b r_{vl}^c\}]}{\omega_{cv}^S(2\omega_{cv}^S - \omega_{cl}^S)} \right] \delta(\omega_{cv}^S - \omega) \right], \end{aligned} \quad (\text{A12}) \quad \{\text{imchies}\}$$

where we have “pulled” a factor of 1/2, so the prefactor is the same as that of the velocity gauge formalism.<sup>28</sup> For the  $I$  term of Eq. (82), we notice that the energy denominators are invariant under  $\mathbf{k} \rightarrow -\mathbf{k}$ , and then we only look at the numerators, then

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

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

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

with similar results for the other two terms. First, we collect the  $2\omega$  terms from Eq. (82) that contribute to Eq. (72)

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

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

$$\begin{aligned} \text{Im}[\chi_{i,\text{abc},2\omega}^{s,\ell}] &= \frac{\pi|e|^3}{2\hbar^2} \sum_{mn\mathbf{k}} \frac{4f_{mn}}{\omega_{nm}} \left[ \text{Im}[\mathcal{R}_{mn}^a (r_{nm}^b)_{;k^c}] - \frac{2\text{Im}[\mathcal{R}_{mn}^a r_{nm}^b]\Delta_{nm}^c}{\omega_{nm}} \right] \delta(\omega_{nm} - 2\omega) \\ &= \frac{\pi|e|^3}{2\hbar^2} \sum_{v\mathbf{k}} \frac{4}{\omega_{cv}^S} \left[ \text{Im}[\mathcal{R}_{vc}^{a,\ell} \{ (r_{cv}^b)_{;k^c} \}] - \frac{2\text{Im}[\mathcal{R}_{vc}^{a,\ell} \{ r_{cv}^b \}]\Delta_{cv}^c}{\omega_{cv}^S} \right] \delta(\omega_{cv}^S - 2\omega), \end{aligned} \quad (\text{A16}) \quad \{\text{imchi2w}\}$$

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  $\omega$  terms are

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

$$\begin{aligned}
& + \frac{\mathcal{R}_{mn}^a}{\omega_{nm}} \left( r_{nm}^b \right)_{;k^c} - \frac{\mathcal{R}_{mn}^a r_{nm}^b}{\omega_{nm}^2} (\omega_{nm})_{;k^c} \Big] \frac{1}{\omega_{nm} - \omega} \\
& = \frac{|e|^3}{2\hbar^2} \sum_{nm\mathbf{k}} f_{mn} \left[ -\frac{\text{Im}[\mathcal{R}_{mn}^a (r_{nm}^b)_{;k^c}]}{\omega_{nm}} + \frac{3\text{Im}[\mathcal{R}_{mn}^a r_{nm}^b] \Delta_{nm}^c}{\omega_{nm}^2} - \frac{i}{2} \left[ \frac{2i}{\omega_{nm}} \text{Im}[r_{nm}^b (\mathcal{R}_{mn}^a)_{;k^c}] \right. \right. \\
& + \left. \left. \frac{2i}{\omega_{nm}} \text{Im}[\mathcal{R}_{mn}^a (r_{nm}^b)_{;k^c}] - \frac{2i}{\omega_{nm}^2} \text{Im}[\mathcal{R}_{mn}^a r_{nm}^b] \Delta_{nm}^c \right] \right] \frac{1}{\omega_{nm} - \omega} \\
& = \frac{|e|^3}{2\hbar^2} \sum_{nm\mathbf{k}} f_{mn} \left[ -\frac{\text{Im}[\mathcal{R}_{mn}^a (r_{nm}^b)_{;k^c}]}{\omega_{nm}} + \frac{3\text{Im}[\mathcal{R}_{mn}^a r_{nm}^b] \Delta_{nm}^c}{\omega_{nm}^2} + \frac{1}{\omega_{nm}} \text{Im}[r_{nm}^b (\mathcal{R}_{mn}^a)_{;k^c}] \right. \\
& + \left. \frac{1}{\omega_{nm}} \text{Im}[\mathcal{R}_{mn}^a (r_{nm}^b)_{;k^c}] - \frac{1}{\omega_{nm}^2} \text{Im}[\mathcal{R}_{mn}^a r_{nm}^b] \Delta_{nm}^c \right] \frac{1}{\omega_{nm} - \omega}, \tag{A17} \quad \{\text{pfia}\}
\end{aligned}$$

or

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

Taking  $\eta \rightarrow 0$  we get that

$$\text{Im}[\chi_{i,\text{abc},\omega}^{s,\ell}] = \frac{\pi|e|^3}{2\hbar^2} \sum_{cv\mathbf{k}} \frac{1}{\omega_{cv}^S} \left[ \text{Im}[\{r_{cv}^b (\mathcal{R}_{vc}^{a,\ell})_{;k^c}\}] + \frac{2\text{Im}[\mathcal{R}_{vc}^{a,\ell} \{r_{cv}^b\} \Delta_{cv}^c]}{\omega_{cv}^S} \right] \delta(\omega_{cv}^S - \omega), \tag{A19} \quad \{\text{imchiw}\}$$

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  $\chi_{\text{abc}}^{s,\ell} = \chi_{e,\text{abc}}^{s,\ell} + \chi_{i,\text{abc}}^{s,\ell}$  where  $\chi_{i,\text{abc}}^{s,\ell} = \chi_{i,\text{abc},\omega}^{s,\ell} + \chi_{i,\text{abc},2\omega}^{s,\ell}$ . In the continuous limit of  $\mathbf{k}$   $(1/\Omega) \sum_{\mathbf{k}} \rightarrow \int d^3\mathbf{k}/(8\pi^3)$  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  $\mathcal{R}_{nm}^{a,\ell} \rightarrow r_{nm}^a$ .

In summary we have

$$\text{Im}[\chi_{e,\text{abc},\omega}^{s,\ell}] = \frac{\pi|e|^3}{2\hbar^2} \sum_{v\mathbf{c}\mathbf{k}} \sum_{l \neq (v,c)} \left[ \frac{\omega_{lc}^S \text{Re}[\mathcal{R}_{lc}^{a,\ell} \{r_{cv}^b r_{vl}^c\}]}{\omega_{cv}^S (2\omega_{cv}^S - \omega_{cl}^S)} - \frac{\omega_{vl}^S \text{Re}[\mathcal{R}_{vl}^{a,\ell} \{r_{lc}^c r_{cv}^b\}]}{\omega_{cv}^S (2\omega_{cv}^S - \omega_{lv}^S)} \right] \delta(\omega_{cv}^S - \omega), \tag{A20} \quad \{\text{imchiew}\}$$

$$\text{Im}[\chi_{e,\text{abc},2\omega}^{s,\ell}] = \frac{\pi|e|^3}{2\hbar^2} \sum_{v\mathbf{c}\mathbf{k}} 4 \left[ \sum_{v' \neq v} \frac{\text{Re}[\mathcal{R}_{vc}^{a,\ell} \{r_{cv'}^b r_{v'v}^c\}]}{2\omega_{cv'}^S - \omega_{cv}^S} - \sum_{c' \neq c} \frac{\text{Re}[\mathcal{R}_{vc}^{a,\ell} \{r_{cc'}^c r_{c'v}^b\}]}{2\omega_{c'v}^S - \omega_{cv}^S} \right] \delta(\omega_{cv}^S - 2\omega), \tag{A21} \quad \{\text{imchie2w}\}$$

$$\text{Im}[\chi_{i,\text{abc},\omega}^{s,\ell}] = \frac{\pi|e|^3}{2\hbar^2} \sum_{cv\mathbf{k}} \frac{1}{\omega_{cv}^S} \left[ \text{Im}[\{r_{cv}^b (\mathcal{R}_{vc}^{a,\ell})_{;k^c}\}] + \frac{2\text{Im}[\mathcal{R}_{vc}^{a,\ell} \{r_{cv}^b\} \Delta_{cv}^c]}{\omega_{cv}^S} \right] \delta(\omega_{cv}^S - \omega), \tag{A22} \quad \{\text{imchiwf}\}$$

and

$$\text{Im}[\chi_{i,\text{abc},2\omega}^{s,\ell}] = \frac{\pi|e|^3}{2\hbar^2} \sum_{v\mathbf{c}\mathbf{k}} \frac{4}{\omega_{cv}^S} \left[ \text{Im}[\mathcal{R}_{vc}^{a,\ell} \{ (r_{cv}^b)_{,k^c} \}] - \frac{2\text{Im}[\mathcal{R}_{vc}^{a,\ell} \{ r_{cv}^b \Delta_{cv}^c \}]}{\omega_{cv}^S} \right] \delta(\omega_{cv}^S - 2\omega), \quad (\text{A23}) \quad \{\text{imchi2wf}\}$$

where  $e^3 = -|e|^3$ . With the help of Eq. (75), (76), (??) and (??) 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.

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

and inversely

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

Now,

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

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

$$\langle \mathbf{r} | \mathbf{p} \rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}. \quad (\text{B4}) \quad \{\text{rp2}\}$$

By the same token,

$$\langle \mathbf{p} | \psi \rangle = \psi(\mathbf{p}) = \int d\mathbf{r} \langle \mathbf{p} | \mathbf{r} \rangle \langle \mathbf{r} | \psi \rangle = \int d\mathbf{r} \langle \mathbf{p} | \mathbf{r} \rangle \psi(\mathbf{r}), \quad (\text{B5}) \quad \{\text{rpsi2}\}$$

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

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

where

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

is succinctly verified.



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

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

where we used the fact that

$$\hat{\mathbf{p}}|\mathbf{p}\rangle = \mathbf{p}|\mathbf{p}\rangle, \tag{B9} \quad \{\text{ap\_otra}\}$$

and that

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

Now,

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

from where we finally get

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

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

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

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

### 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

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

and

$$\int_{\Omega} d^3r u_{n\mathbf{k}}^*(\mathbf{r}) u_{m\mathbf{q}}(\mathbf{r}) = \delta_{nm} \delta_{\mathbf{k},\mathbf{q}}, \quad (\text{C2}) \quad \{\mathbf{a\_dos}\}$$

where  $\Omega$  is the volume of 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

$$\int_V d^3r \psi_{n\mathbf{k}}^*(\mathbf{r}) \psi_{m\mathbf{q}}(\mathbf{r}) = \frac{V}{8\pi^3} \delta_{nm} \delta_{\mathbf{k},\mathbf{q}}, \quad (\text{C3}) \quad \{\mathbf{a\_tres}\}$$

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

$$\int d^3r \psi_{n\mathbf{k}}^*(\mathbf{r}) \psi_{m\mathbf{q}}(\mathbf{r}) = \delta_{nm} \delta(\mathbf{k} - \mathbf{q}), \quad (\text{C4}) \quad \{\mathbf{a\_4}\}$$

for which the Kronecker- $\delta$  is replaced by

$$\delta_{\mathbf{k},\mathbf{q}} \rightarrow \frac{8\pi^3}{V} \delta(\mathbf{k} - \mathbf{q}), \quad (\text{C5}) \quad \{\mathbf{a\_5}\}$$

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

$$\begin{aligned} \int d^3r e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}} f(\mathbf{r}) &= \sum_j^{\text{unit cells}} \int_{\Omega} d^3r e^{i(\mathbf{q}-\mathbf{k})\cdot(\mathbf{r}+\mathbf{R}_j)} f(\mathbf{r} + \mathbf{R}_j), \\ &= \sum_j^{\text{unit cells}} \int_{\Omega} d^3r e^{i(\mathbf{q}-\mathbf{k})\cdot(\mathbf{r}+\mathbf{R}_j)} f(\mathbf{r}), \\ &= \int_{\Omega} d^3r e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}} f(\mathbf{r}) \sum_j^{\text{unit cells}} e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{R}_j}, \\ &= \int_{\Omega} d^3r e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}} f(\mathbf{r}) N \sum_{\mathbf{K}} \delta_{\mathbf{K},\mathbf{q}-\mathbf{k}}, \\ &= N \int_{\Omega} d^3r e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}} f(\mathbf{r}) \delta_{\mathbf{0},\mathbf{q}-\mathbf{k}}, \\ &= N \delta_{\mathbf{q},\mathbf{k}} \int_{\Omega} d^3r f(\mathbf{r}), \\ &= \frac{8\pi^3}{\Omega} \delta(\mathbf{q} - \mathbf{k}) \int_{\Omega} d^3r f(\mathbf{r}), \end{aligned} \quad (\text{C6}) \quad \{\mathbf{a\_6}\}$$

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 $(\omega_n(\mathbf{k}))_{;\mathbf{k}}$

{gwk}

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

$$\langle n\mathbf{k}|\hat{H}_0^S|m\mathbf{k}'\rangle = \delta_{nm}\delta(\mathbf{k}-\mathbf{k}')\hbar\omega_m^S(\mathbf{k}), \quad (\text{D1}) \quad \{\text{a\_conH0}\}$$

then Eq. (J19) gives

$$\begin{aligned} (H_{0,nm}^S)_{;\mathbf{k}} &= \nabla_{\mathbf{k}}H_{0,nm}^S(\mathbf{k}) - iH_{0,nm}^S(\mathbf{k}) (\xi_{nn}(\mathbf{k}) - \xi_{mm}(\mathbf{k})) \\ &= \delta_{nm}\hbar\nabla_{\mathbf{k}}\omega_m^S(\mathbf{k}), \end{aligned} \quad (\text{D2}) \quad \{\text{a\_genderH0}\}$$

where from Eq. (J18),

$$\langle n\mathbf{k}|\hat{\mathbf{r}}_i, \hat{H}_0|m\mathbf{k}\rangle = i\delta_{nm}\hbar(\omega_m^S(\mathbf{k}))_{;\mathbf{k}} = i\delta_{nm}\hbar\nabla_{\mathbf{k}}\omega_m^S(\mathbf{k}), \quad (\text{D3}) \quad \{\text{a\_rih0}\}$$

then

$$(\omega_n^S(\mathbf{k}))_{;\mathbf{k}} = \nabla_{\mathbf{k}}\omega_n^S(\mathbf{k}). \quad (\text{D4}) \quad \{\text{a\_wgendev}\}$$

From Eq. (8)

$$\langle n\mathbf{k}|\hat{\mathbf{r}}, \hat{H}_0|m\mathbf{k}\rangle = i\hbar\mathbf{v}_{nm}^\Sigma, \quad (\text{D5}) \quad \{\text{a\_hr}\}$$

therefore, substituting above into

$$\langle n\mathbf{k}|\hat{\mathbf{r}}, \hat{H}_0|m\mathbf{k}\rangle = \langle n\mathbf{k}|\hat{\mathbf{r}}_i, \hat{H}_0|m\mathbf{k}\rangle + \langle n\mathbf{k}|\hat{\mathbf{r}}_e, \hat{H}_0|m\mathbf{k}\rangle, \quad (\text{D6}) \quad \{\text{a\_hrt}\}$$

we get

$$i\hbar\mathbf{v}_{nm}^\Sigma = i\delta_{nm}\hbar\nabla_{\mathbf{k}}\omega_m^S(\mathbf{k}) + \omega_{mn}^S\mathbf{r}_{e,nm}, \quad (\text{D7}) \quad \{\text{a\_hrt2}\}$$

from where

$$\begin{aligned} \nabla_{\mathbf{k}}\omega_n^S(\mathbf{k}) &= \mathbf{v}_{nn}^\Sigma \\ \nabla_{\mathbf{k}}\omega_n^{\text{LDA}}(\mathbf{k}) &= \frac{\mathbf{p}_{nn}}{m_e}. \end{aligned} \quad (\text{D8}) \quad \{\text{a\_gradw}\}$$

where we used  $\mathbf{v}_{nn}^\Sigma = \mathbf{p}_{nn}/m_e$  (see Eq. (10)), and Eq. (7). Thus, from Eq. (D4)

$$(\omega_n^S(\mathbf{k}))_{;k^a} = (\omega_n^{\text{LDA}}(\mathbf{k}))_{;k^a} = \frac{p_{nn}^a(\mathbf{k})}{m_e}, \quad (\text{D9}) \quad \{\text{a\_gradw2}\}$$

the same for the LDA and scissored Hamiltonians.

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

{gder}

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

$$[r^a, p^b] = i\hbar\delta_{ab}, \quad (\text{E1}) \quad \{\mathbf{a\_hrdab}\}$$

then

$$\langle n\mathbf{k} | [r_i^a, p^b] | m\mathbf{k}' \rangle = i\hbar\delta_{ab}\delta_{nm}\delta(\mathbf{k} - \mathbf{k}'), \quad (\text{E2}) \quad \{\mathbf{a\_hrdab2}\}$$

so

$$\langle n\mathbf{k} | [r_i^a, p^b] | m\mathbf{k}' \rangle + \langle n\mathbf{k} | [r_e^a, p^b] | m\mathbf{k}' \rangle = i\hbar\delta_{ab}\delta_{nm}\delta(\mathbf{k} - \mathbf{k}'). \quad (\text{E3}) \quad \{\mathbf{a\_hrdab3}\}$$

From Eq. (J18) and (J19)

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

$$(p_{nm}^b)_{;k^a} = \nabla_{k^a} p_{nm}^b(\mathbf{k}) - ip_{nm}^b(\mathbf{k}) (\xi_{nn}^a(\mathbf{k}) - \xi_{mm}^a(\mathbf{k})), \quad (\text{E5}) \quad \{\mathbf{a\_ripn}\}$$

and

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

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

$$\begin{aligned} i\delta(\mathbf{k} - \mathbf{k}') \left( (p_{nm}^b)_{;k^a} - i \sum_{\ell} \left( \xi_{n\ell}^a p_{\ell m}^b - p_{n\ell}^b \xi_{\ell m}^a \right) \right. \\ \left. - ip_{nm}^b (\xi_{mm}^a - \xi_{nn}^a) \right) = i\hbar\delta_{ab}\delta_{nm}\delta(\mathbf{k} - \mathbf{k}'), \quad (\text{E7}) \quad \{\mathbf{a\_rapb}\} \end{aligned}$$

then

$$(p_{nm}^b)_{;k^a} = \hbar\delta_{ab}\delta_{nm} + i \sum_{\ell} \left( \xi_{n\ell}^a p_{\ell m}^b - p_{n\ell}^b \xi_{\ell m}^a \right) + i p_{nm}^b (\xi_{mm}^a - \xi_{nn}^a), \quad (\text{E8}) \quad \{\text{a\_rapb2}\}$$

and from Eq. (E5),

$$\nabla_{k^a} p_{nm}^b = \hbar\delta_{ab}\delta_{nm} + i \sum_{\ell} \left( \xi_{n\ell}^a p_{\ell m}^b - p_{n\ell}^b \xi_{\ell m}^a \right). \quad (\text{E9}) \quad \{\text{cogno}\}$$

Now, there are two cases. We use Eqs. (15) and (16).

*Case  $n = m$*

$$\frac{1}{\hbar} \nabla_{k^a} p_{nn}^b = \delta_{ab} - \frac{m_e}{\hbar} \sum_{\ell} \omega_{\ell n} \left( r_{n\ell}^a r_{\ell n}^b + r_{n\ell}^b r_{\ell n}^a \right), \quad (\text{E10}) \quad \{\text{tita}\}$$

that gives the familiar expansion for the inverse effective mass tensor  $(m_n^{-1})_{ab}$ .<sup>26</sup>

*Case  $n \neq m$*

$$\begin{aligned} (p_{nm}^b)_{;k^a} &= \hbar\delta_{ab}\delta_{nm} + i \sum_{\ell \neq m \neq n} \left( \xi_{n\ell}^a p_{\ell m}^b - p_{n\ell}^b \xi_{\ell m}^a \right) \\ &\quad + i \left( \xi_{nm}^a p_{mm}^b - p_{nm}^b \xi_{mm}^a \right) \\ &\quad + i \left( \xi_{nn}^a p_{nm}^b - p_{nn}^b \xi_{nm}^a \right) + i p_{nm}^b (\xi_{mm}^a - \xi_{nn}^a) \\ &= -m_e \sum_{\ell} \left( \omega_{\ell m} r_{n\ell}^a r_{\ell m}^b - \omega_{n\ell} r_{n\ell}^b r_{\ell m}^a \right) + i \xi_{nm}^a (p_{mm}^b - p_{nn}^b) \\ &= -m_e \sum_{\ell} \left( \omega_{\ell m} r_{n\ell}^a r_{\ell m}^b - \omega_{n\ell} r_{n\ell}^b r_{\ell m}^a \right) + i m_e r_{nm}^a \Delta_{mn}^b, \end{aligned} \quad (\text{E11}) \quad \{\text{mes}\}$$

where

$$\Delta_{mn}^b = \frac{p_{mm}^b - p_{nn}^b}{m_e}. \quad (\text{E12}) \quad \{\text{a\_delta}\}$$

Now, for  $n \neq m$ , Eqs. (16), (D9) and (E11) and the chain rule, give

$$\begin{aligned} (r_{nm}^b)_{;k^a} &= \left( \frac{p_{nm}^b}{i m_e \omega_{nm}} \right)_{;k^a} = \frac{1}{i m_e \omega_{nm}} (p_{nm}^b)_{;k^a} - \frac{p_{nm}^b}{i m_e \omega_{nm}^2} (\omega_{nm})_{;k^a} \\ &= \frac{i}{\omega_{nm}} \sum_{\ell} \left( \omega_{\ell m} r_{n\ell}^a r_{\ell m}^b - \omega_{n\ell} r_{n\ell}^b r_{\ell m}^a \right) + \frac{r_{nm}^a \Delta_{mn}^b}{\omega_{nm}} \\ &\quad - \frac{r_{nm}^b}{\omega_{nm}} (\omega_{nm})_{;k^a} \\ &= \frac{i}{\omega_{nm}} \sum_{\ell} \left( \omega_{\ell m} r_{n\ell}^a r_{\ell m}^b - \omega_{n\ell} r_{n\ell}^b r_{\ell m}^a \right) + \frac{r_{nm}^a \Delta_{mn}^b}{\omega_{nm}} \end{aligned}$$

$$\begin{aligned}
& -\frac{r_{nm}^b}{\omega_{nm}} \frac{p_{nn}^a - p_{mm}^a}{m_e} \\
& = \frac{r_{nm}^a \Delta_{mn}^b + r_{nm}^b \Delta_{mn}^a}{\omega_{nm}} + \frac{i}{\omega_{nm}} \sum_{\ell} \left( \omega_{\ell m} r_{n\ell}^a r_{\ell m}^b - \omega_{n\ell} r_{n\ell}^b r_{\ell m}^a \right)
\end{aligned} \tag{E13} \quad \{\text{a\_rgendevn}\}$$

**Appendix F:**  $(\mathcal{V}_{nm}^{\Sigma, \text{a}, \ell})_{;k^b}$

{calvs}

$$(\mathcal{V}_{nm}^{\Sigma, \text{a}, \ell})_{;k^b} = \frac{1}{m_e} (\mathcal{P}_{nm}^{\text{a}, \ell})_{;k^b} + (\mathcal{V}_{nm}^{\text{nl}, \text{a}, \ell})_{;k^b} + (\mathcal{V}_{nm}^{S, \text{a}, \ell})_{;k^b}. \tag{F1} \quad \{\text{a.1}\}$$

For the canonical momentum  $\mathbf{p} = -i\hbar \nabla$ , we have

$$\begin{aligned}
\mathcal{P}_{nm}^{\text{a}, \ell} &= \frac{1}{2} (p^{\text{a}} \mathcal{F}^{\ell} + \mathcal{F}^{\ell} p^{\text{a}})_{nm} \\
&= \frac{1}{2} \sum_q (p_{nq}^{\text{a}} \mathcal{F}_{qm}^{\ell} + \mathcal{F}_{nq}^{\ell} p_{qm}^{\text{a}}) \\
(\mathcal{P}_{nm}^{\text{a}})_{;k^b} &= \frac{1}{2} \sum_q (p_{nq}^{\text{a}} \mathcal{F}_{qm}^{\ell} + \mathcal{F}_{nq}^{\ell} p_{qm}^{\text{a}})_{;k^b} \\
&= \frac{1}{2} \sum_q \left( (p_{nq}^{\text{a}})_{;k^b} \mathcal{F}_{qm}^{\ell} + p_{nq}^{\text{a}} (\mathcal{F}_{qm}^{\ell})_{;k^b} + (\mathcal{F}_{nq}^{\ell})_{;k^b} p_{qm}^{\text{a}} + \mathcal{F}_{nq}^{\ell} (p_{qm}^{\text{a}})_{;k^b} \right),
\end{aligned} \tag{F2} \quad \{\text{a.2}\}$$

where we omitted  $\mathbf{k}$  in all quantities. At this stage we have to neglect the contribution coming from  $V^{\text{nl}}(\mathbf{r}, \mathbf{r}')$ , since the sum rules that are used in order to get the generalized derivative  $(\mathbf{r}_{nm}(\mathbf{k}))_{;\mathbf{k}}$  are only valid for  $V^l(\mathbf{r})$  (Eq. (3)), i.e. local potentials.<sup>27</sup> Then, we neglect  $\mathbf{v}^{\text{nl}}$ , with which  $\mathbf{v}^{\text{LDA}} \rightarrow \mathbf{p}/m_e$  (Eq. (9)). Now, for  $(p_{nm}^{\text{a}})_{;k^b}$  we can use Eq. (16) to write

$$\begin{aligned}
(p_{nm}^{\text{a}})_{;k^b} &= im_e (\omega_{nm}^{\text{LDA}} r_{nm}^{\text{a}})_{;k^b} \\
&= im_e (\omega_{nm}^{\text{LDA}})_{;k^b} r_{nm}^{\text{a}} + im_e \omega_{nm}^{\text{LDA}} (r_{nm}^{\text{a}})_{;k^b},
\end{aligned} \tag{F3} \quad \{\text{a.3}\}$$

and use Eqs. (D9) and (E13) (with  $\omega_n \rightarrow \omega_n^{\text{LDA}}$ ). Likewise,

$$\mathcal{V}_{nm}^{S, \text{a}, \ell} = \frac{1}{2} \sum_q ((v_{nq}^{S, \text{a}})_{;k^b} \mathcal{F}_{qm}^{\ell} + v_{nq}^{S, \text{a}} (\mathcal{F}_{qm}^{\ell})_{;k^b} + (\mathcal{F}_{nq}^{\ell})_{;k^b} v_{qm}^{S, \text{a}} + \mathcal{F}_{nq}^{\ell} (v_{qm}^{S, \text{a}})_{;k^b}), \tag{F4} \quad \{\text{a.3}\}$$

where  $(v_{nm}^{S, \text{a}})_{;k^b}$  is given in A(6) of Ref. 28,

$$(v_{nm}^{S, \text{a}})_{;k^b} = i\Delta f_{mn} (r_{nm}^{\text{a}})_{;k^b}. \tag{F5} \quad \{\text{choni.1}\}$$

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

$$\langle n\mathbf{k} | [r^{\text{a}}, \mathcal{F}(z)] | m\mathbf{k}' \rangle = \langle n\mathbf{k} | [r_e^{\text{a}}, \mathcal{F}(z)] | m\mathbf{k}' \rangle + \langle n\mathbf{k} | [r_i^{\text{a}}, \mathcal{F}(z)] | m\mathbf{k}' \rangle = 0. \tag{F6} \quad \{\text{a.4}\}$$

The interband part reduces to,

$$\begin{aligned}
[r_e^a, \mathcal{F}(z)]_{nm} &= \sum_{q\mathbf{k}''} (\langle n\mathbf{k} | r_e^a | q\mathbf{k}'' \rangle \langle q\mathbf{k}'' | \mathcal{F}(z) | m\mathbf{k}' \rangle - \langle n\mathbf{k} | \mathcal{F}(z) | q\mathbf{k}'' \rangle \langle q\mathbf{k}'' | r_e^a | m\mathbf{k}' \rangle) \\
&= \sum_{q\mathbf{k}''} \delta(\mathbf{k} - \mathbf{k}'') \delta(\mathbf{k}' - \mathbf{k}'') ((1 - \delta_{qn}) \xi_{nq}^a \mathcal{F}_{qm} - (1 - \delta_{qm}) \mathcal{F}_{nq} \xi_{qm}^a) \\
&= \delta(\mathbf{k} - \mathbf{k}') \left( \sum_q (\xi_{nq}^a \mathcal{F}_{qm} - \mathcal{F}_{nq} \xi_{qm}^a) + \mathcal{F}_{nm} (\xi_{mm}^a - \xi_{nn}^a) \right), \tag{F7} \quad \{\text{a.5}\}
\end{aligned}$$

where we used Eq. (J15), and the  $\mathbf{k}$  and  $z$  is implicitly understood. From Eq. (J18) the intraband part is,

$$\langle n\mathbf{k} | [\hat{\mathbf{r}}_i, \mathcal{F}(z)] | m\mathbf{k}' \rangle = i\delta(\mathbf{k} - \mathbf{k}') (\mathcal{F}_{nm})_{;\mathbf{k}}, \tag{F8} \quad \{\text{a.6}\}$$

then from Eq. (F6)

$$\begin{aligned}
&\left( (\mathcal{F}_{nm})_{;\mathbf{k}} - i \sum_q (\xi_{nq}^a \mathcal{F}_{qm} - \mathcal{F}_{nq} \xi_{qm}^a) - i \mathcal{F}_{nm} (\xi_{mm}^a - \xi_{nn}^a) \right) i\delta(\mathbf{k} - \mathbf{k}') = 0 \\
\frac{1}{i} (\mathcal{F}_{nm})_{;\mathbf{k}} &= \sum_q (\xi_{nq}^a \mathcal{F}_{qm} - \mathcal{F}_{nq} \xi_{qm}^a) + \mathcal{F}_{nm} (\xi_{mm}^a - \xi_{nn}^a) \\
&= \sum_{q \neq n, m} (\xi_{nq}^a \mathcal{F}_{qm} - \mathcal{F}_{nq} \xi_{qm}^a) + (\xi_{nn}^a \mathcal{F}_{nm} - \mathcal{F}_{nn} \xi_{nm}^a)_{q=n} + (\xi_{nm}^a \mathcal{F}_{mm} - \mathcal{F}_{nm} \xi_{mm}^a)_{q=m} \\
&\quad + \mathcal{F}_{nm} (\xi_{mm}^a - \xi_{nn}^a) \\
(\mathcal{F}_{nm})_{;\mathbf{k}} &= i \sum_{q \neq n, m} (\xi_{nq}^a \mathcal{F}_{qm} - \mathcal{F}_{nq} \xi_{qm}^a) + i \xi_{nm}^a (\mathcal{F}_{mm} - \mathcal{F}_{nn}) \\
&= i \sum_{q \neq n, m} (r_{nq}^a \mathcal{F}_{qm} - \mathcal{F}_{nq} r_{qm}^a) + i r_{nm}^a (\mathcal{F}_{mm} - \mathcal{F}_{nn}), \tag{F9} \quad \{\text{a.7}\}
\end{aligned}$$

since in every  $\xi_{nm}^a$ ,  $n \neq m$ .

For the general case of

$$\langle n\mathbf{k} | [\hat{r}^a, \hat{\mathcal{G}}(\mathbf{r}, \mathbf{p})] | m\mathbf{k}' \rangle = \mathcal{C}_{nm}(\mathbf{k}), \tag{F10} \quad \{\text{a.8}\}$$

above result would lead to a more general expression,

$$(\mathcal{G}_{nm}(\mathbf{k}))_{;\mathbf{k}^a} = \mathcal{C}_{nm}(\mathbf{k}) + i \sum_{q \neq (nm)} (r_{nq}^a(\mathbf{k}) \mathcal{G}_{qm}(\mathbf{k}) - \mathcal{G}_{nq}(\mathbf{k}) r_{qm}^a(\mathbf{k})) + i r_{nm}^a(\mathbf{k}) (\mathcal{G}_{mm}(\mathbf{k}) - \mathcal{G}_{nn}(\mathbf{k})), \tag{F11} \quad \{\text{a.9}\}$$

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

## Appendix G: $(\mathcal{R}_{nm}^a)_{;k^b}$

We rewrite Eq. (E11) and (16) as

$$(p_{nm}^a)_{;k^b} = ir_{nm}^b(p_{mm}^a - p_{nn}^a) + i \sum_{\ell \neq m, n} \left( p_{\ell m}^a r_{n\ell}^b - p_{n\ell}^a r_{\ell m}^b \right), \quad (\text{G1}) \quad \{\text{calr}\} \quad \{\text{mesnn}\}$$

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

$$\begin{aligned} (\mathcal{P}_{nm}^a)_{;k^b} &= ir_{nm}^b(\mathcal{P}_{mm}^a - \mathcal{P}_{nn}^a) + i \sum_{\ell \neq m, n} \left( \mathcal{P}_{\ell m}^a r_{n\ell}^b - \mathcal{P}_{n\ell}^a r_{\ell m}^b \right) \\ &= im_e r_{nm}^b \Delta_{mn}^{a,\ell} + i \sum_{\ell \neq m, n} \left( \mathcal{P}_{\ell m}^a r_{n\ell}^b - \mathcal{P}_{n\ell}^a r_{\ell m}^b \right), \end{aligned} \quad (\text{G2}) \quad \{\text{mesnn2}\}$$

where

$$\Delta^{a,\ell} = \frac{\mathcal{P}_{mm}^a - \mathcal{P}_{nn}^a}{m_e}, \quad (\text{G3}) \quad \{112\}$$

where we omitted the  $\ell$ -layer label from  $\mathcal{P}$ . Eq. (16) trivially gives

$$\mathcal{R}_{nm}^a = \frac{\mathcal{P}_{nm}^a}{im_e \omega_{nm}} \quad n \neq m, \quad (\text{G4}) \quad \{\text{rnmnm69}\}$$

then, using Eq. (G2)

$$\begin{aligned} (\mathcal{R}_{nm}^a)_{;k^b} &= \left( \frac{\mathcal{P}_{nm}^a}{im_e \omega_{nm}} \right)_{;k^b} = \frac{1}{im_e \omega_{nm}} (\mathcal{P}_{nm}^a)_{;k^b} - \frac{\mathcal{P}_{nm}^a}{im_e \omega_{nm}^2} (\omega_{nm})_{;k^b} \\ &= \frac{r_{nm}^b \Delta_{mn}^{a,\ell}}{\omega_{nm}} + \frac{i}{\omega_{nm}} \sum_{\ell} \left( \omega_{\ell m} r_{n\ell}^b \mathcal{R}_{\ell m}^a - \omega_{n\ell} \mathcal{R}_{n\ell}^a r_{\ell m}^b \right) \\ &\quad - \frac{\mathcal{R}_{nm}^a}{\omega_{nm}} (\omega_{nm})_{;k^b} \\ &= \frac{r_{nm}^b \Delta_{mn}^{a,\ell}}{\omega_{nm}} + \frac{i}{\omega_{nm}} \sum_{\ell} \left( \omega_{\ell m} r_{n\ell}^b \mathcal{R}_{\ell m}^a - \omega_{n\ell} \mathcal{R}_{n\ell}^a r_{\ell m}^b \right) \\ &\quad - \frac{\mathcal{R}_{nm}^a}{\omega_{nm}} \frac{p_{nn}^b - p_{mm}^b}{m_e} \\ &= \frac{r_{nm}^b \Delta_{mn}^{a,\ell}}{\omega_{nm}} + \frac{i}{\omega_{nm}} \sum_{\ell} \left( \omega_{\ell m} r_{n\ell}^b \mathcal{R}_{\ell m}^a - \omega_{n\ell} \mathcal{R}_{n\ell}^a r_{\ell m}^b \right) \\ &\quad + \frac{\mathcal{R}_{nm}^a \Delta_{mn}^b}{\omega_{nm}} \\ &= \frac{r_{nm}^b \Delta_{mn}^{a,\ell} + \mathcal{R}_{nm}^a \Delta_{mn}^b}{\omega_{nm}} + \frac{i}{\omega_{nm}} \sum_{\ell} \left( \omega_{\ell m} r_{n\ell}^b \mathcal{R}_{\ell m}^a - \omega_{n\ell} \mathcal{R}_{n\ell}^a r_{\ell m}^b \right) \end{aligned} \quad (\text{G5}) \quad \{\text{a_rgendevnn}\}$$



## Appendix H: Explicit expressions for $\mathcal{P}^{a,\ell}$ and $\mathcal{V}^{a,\ell}$

{pw}

## Appendix I: Odds and Ends

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

$$\begin{aligned} i\hbar\hat{\mathbf{v}} &= [\hat{\mathbf{r}}, \hat{H}_0] \\ &= [\hat{\mathbf{r}}, \frac{\hat{\mathbf{p}}^2}{2m} + \hat{V}(\mathbf{r}) + \hat{v}(\mathbf{r}, \hat{\mathbf{p}})] \approx [\hat{\mathbf{r}}, \frac{\hat{\mathbf{p}}^2}{2m}] = i\hbar \frac{\hat{\mathbf{p}}}{m}, \end{aligned} \quad (\text{I1}) \quad \{\text{vop2}\}$$

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

$$m\hat{\mathbf{v}} \approx \hat{\mathbf{p}} = -i\hbar\nabla, \quad (\text{I2}) \quad \{\text{velo}\}$$

is the explicit functional form of the velocity or momentum operator. From Eq. (51), we need

$$\langle \mathbf{r} | \hat{\mathbf{v}} | n\mathbf{k} \rangle = \int d^3r' \langle \mathbf{r} | \hat{\mathbf{v}} | \mathbf{r}' \rangle \langle \mathbf{r}' | n\mathbf{k} \rangle \approx \frac{1}{m} \hat{\mathbf{p}} \psi_{n\mathbf{k}}(\mathbf{r}), \quad (\text{I3}) \quad \{\text{vnm}\}$$

where we used

$$\langle \mathbf{r} | \hat{v}^x | \mathbf{r}' \rangle \approx \frac{1}{m} \langle \mathbf{r} | \hat{p}^x | \mathbf{r}' \rangle = \delta(y - y') \delta(z - z') \left( -i\hbar \frac{\partial}{\partial x} \delta(x - x') \right), \quad (\text{I4}) \quad \{\text{rvnk}\}$$

with similar results for the  $y$  and  $z$  Cartesian directions. Now, from Eqs. (53) and (51) we obtain

$$\mathcal{V}_{mn}^\ell(\mathbf{k}) = \frac{1}{2} \int d^3r \mathcal{F}_\ell(z) \left[ \langle m\mathbf{k} | \mathbf{v} | \mathbf{r} \rangle \langle \mathbf{r} | n\mathbf{k} \rangle + \langle m\mathbf{k} | \mathbf{r} \rangle \langle \mathbf{r} | \mathbf{v} | n\mathbf{k} \rangle \right], \quad (\text{I5}) \quad \{\text{intj}\}$$

and using Eq. (I3), we can write, for any function  $\mathcal{F}_\ell(z)$  used to identify the response from a region of the slab, that

$$\mathcal{V}_{mn}(\mathbf{k}) \approx \frac{1}{2m} \int d^3r \mathcal{F}_\ell(z) \left[ \psi_{n\mathbf{k}}(\mathbf{r}) \hat{\mathbf{p}}^* \psi_{m\mathbf{k}}^*(\mathbf{r}) + \psi_{m\mathbf{k}}^*(\mathbf{r}) \hat{\mathbf{p}} \psi_{n\mathbf{k}}(\mathbf{r}) \right], \quad (\text{I6}) \quad \{\text{pofs1}\}$$

$$= \frac{1}{m} \int d^3r \psi_{m\mathbf{k}}^*(\mathbf{r}) \left[ \frac{\mathcal{F}_\ell(z) \mathbf{p} + \mathbf{p} \mathcal{F}_\ell(z)}{2} \right] \psi_{n\mathbf{k}}(\mathbf{r}), \quad (\text{I7}) \quad \{\text{pofs2}\}$$

$$= \frac{1}{m} \int d^3r \psi_{m\mathbf{k}}^*(\mathbf{r}) \hat{\mathcal{P}} \psi_{n\mathbf{k}}(\mathbf{r}) \equiv \frac{1}{m} \mathcal{P}_{mn}(\mathbf{k}). \quad (\text{I8})$$

Here an integration by parts is performed on the first term of the right hand side of Eq. (I6); 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.

\*\*\*\*\*

We would obtain, instead of Eq. (72) and (73)

$$\chi_{i,\text{abc}}^{s,\ell} = -\frac{e^3}{m_e \Omega \hbar^2 \omega_3} \sum_{mn\mathbf{k}} \frac{m_e \mathcal{V}_{mn}^{a,\ell}}{\omega_{nm} - \omega_3} \left( \frac{f_{mn} r_{nm}^b}{\omega_{nm} - \omega_\beta} \right)_{;k^c}, \quad (\text{I9}) \quad \{\text{chiinl}\}$$

and

$$\chi_{e,abc}^{s,\ell} = \frac{ie^3}{m_e \Omega \hbar^2 \omega_3} \sum_{\ell m n \mathbf{k}} \frac{m_e \mathcal{V}_{mn}^{a,\ell}}{\omega_{nm} - \omega_3} \left( \frac{r_{n\ell}^c r_{\ell m}^b f_{m\ell}}{\omega_{\ell m} - \omega_\beta} - \frac{r_{n\ell}^b r_{\ell m}^c f_{\ell n}}{\omega_{n\ell} - \omega_\beta} \right), \quad (\text{I10}) \quad \{\text{chien1}\}$$

where

$$m_e \mathcal{V}_{mn}^{a,\ell}(\mathbf{k}) = \mathcal{P}_{mn}^{a,\ell}(\mathbf{k}) + m_e \mathcal{V}_{mn}^{S,a,\ell}(\mathbf{k}), \quad (\text{I11}) \quad \{\text{n1.5}\}$$

where the non-local contribution of  $H_0$  is neglected, and from Eq. (I7)

$$\mathcal{P}_{mn}^{a,\ell} = \int d^3 r \psi_{m\mathbf{k}}^*(\mathbf{r}) \left[ \frac{\mathcal{F}_\ell(z) p^a + p^a \mathcal{F}_\ell(z)}{2} \right] \psi_{n\mathbf{k}}(\mathbf{r}). \quad (\text{I12}) \quad \{\text{calpmn}\}$$

\*\*\*\*\*

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

$$\mathcal{R}_{nm}^a = \frac{\mathcal{P}_{nm}^a}{im_e \omega_{nm}} \quad (n \neq m), \quad (\text{I13}) \quad \{\text{rcal}\}$$

## Appendix J: $\mathbf{r}_e$ and $\mathbf{r}_i$

\*\*\*\*\*

The  $r$  representation of the Bloch states is given by

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r} | n\mathbf{k} \rangle = \sqrt{\frac{\Omega}{8\pi^3}} e^{i\mathbf{k} \cdot \mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \quad (\text{J1}) \quad \{\text{bloch}\}$$

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

$$\int_{\Omega} d^3 r u_{n\mathbf{k}}^*(\mathbf{r}) u_{m\mathbf{k}'}(\mathbf{r}) = \delta_{nm} \delta_{\mathbf{k},\mathbf{k}'}, \quad (\text{J2}) \quad \{\text{normal}\}$$

with  $\Omega$  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

$$\langle n\mathbf{k} | m\mathbf{k}' \rangle = \delta_{nm} \delta(\mathbf{k} - \mathbf{k}'), \quad (\text{J3}) \quad \{\text{nbraket}\}$$

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

$$\frac{\partial}{\partial \mathbf{k}} \langle n\mathbf{k} | m\mathbf{k}' \rangle = \delta_{nm} \frac{\partial}{\partial \mathbf{k}} \delta(\mathbf{k} - \mathbf{k}'), \quad (\text{J4}) \quad \{\text{ddk1}\}$$

on the other,

$$\begin{aligned} \frac{\partial}{\partial \mathbf{k}} \langle n\mathbf{k} | m\mathbf{k}' \rangle &= \frac{\partial}{\partial \mathbf{k}} \int d\mathbf{r} \langle n\mathbf{k} | \mathbf{r} \rangle \langle \mathbf{r} | m\mathbf{k}' \rangle \\ &= \int d\mathbf{r} \left( \frac{\partial}{\partial \mathbf{k}} \psi_{n\mathbf{k}}^*(\mathbf{r}) \right) \psi_{m\mathbf{k}'}(\mathbf{r}), \end{aligned} \quad (\text{J5}) \quad \{\text{dkbraket}\}$$

the derivative of the wavefunction is simply given by

$$\frac{\partial}{\partial \mathbf{k}} \psi_{n\mathbf{k}}^*(\mathbf{r}) = \sqrt{\frac{\Omega}{8\pi^3}} \left( \frac{\partial}{\partial \mathbf{k}} u_{n\mathbf{k}}^*(\mathbf{r}) \right) e^{-i\mathbf{k}\cdot\mathbf{r}} - i\mathbf{r} \psi_{n\mathbf{k}}^*(\mathbf{r}). \quad (\text{J6}) \quad \{\text{dpsi}\}$$

We take this back into Eq. (J5), to obtain

$$\begin{aligned} \frac{\partial}{\partial \mathbf{k}} \langle n\mathbf{k} | m\mathbf{k}' \rangle &= \sqrt{\frac{\Omega}{8\pi^3}} \int d\mathbf{r} \left( \frac{\partial}{\partial \mathbf{k}} u_{n\mathbf{k}}^*(\mathbf{r}) \right) e^{-i\mathbf{k}\cdot\mathbf{r}} \psi_{m\mathbf{k}'}(\mathbf{r}) \\ &\quad - i \int d\mathbf{r} \psi_{n\mathbf{k}}^*(\mathbf{r}) \mathbf{r} \psi_{m\mathbf{k}'}(\mathbf{r}) \\ &= \frac{\Omega}{8\pi^3} \int d\mathbf{r} e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} \left( \frac{\partial}{\partial \mathbf{k}} u_{n\mathbf{k}}^*(\mathbf{r}) \right) u_{m\mathbf{k}'}(\mathbf{r}) \\ &\quad - i \langle n\mathbf{k} | \hat{\mathbf{r}} | m\mathbf{k}' \rangle. \end{aligned} \quad (\text{J7}) \quad \{\text{dkbraket2}\}$$

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

$$\int d^3r e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}} f(\mathbf{r}) = \frac{8\pi^3}{\Omega} \delta(\mathbf{q} - \mathbf{k}) \int_{\Omega} d^3r f(\mathbf{r}), \quad (\text{J8}) \quad \{\text{periodic}\}$$

to finally write,<sup>14</sup>

$$\begin{aligned} \frac{\partial}{\partial \mathbf{k}} \langle n\mathbf{k} | m\mathbf{k}' \rangle &= \delta(\mathbf{k} - \mathbf{k}') \int_{\Omega} d\mathbf{r} \left( \frac{\partial}{\partial \mathbf{k}} u_{n\mathbf{k}}^*(\mathbf{r}) \right) u_{m\mathbf{k}}(\mathbf{r}) \\ &\quad - i \langle n\mathbf{k} | \hat{\mathbf{r}} | m\mathbf{k}' \rangle. \end{aligned} \quad (\text{J9}) \quad \{\text{dkbraket3}\}$$

where  $\Omega$  is the volume of the unit cell. From

$$\int_{\Omega} u_{m\mathbf{k}} u_{n\mathbf{k}}^* d\mathbf{r} = \delta_{nm}, \quad (\text{J10}) \quad \{\text{dnm1}\}$$

we easily find that

$$\int_{\Omega} d\mathbf{r} \left( \frac{\partial}{\partial \mathbf{k}} u_{m\mathbf{k}}(\mathbf{r}) \right) u_{n\mathbf{k}}^*(\mathbf{r}) = - \int_{\Omega} d\mathbf{r} u_{m\mathbf{k}}(\mathbf{r}) \left( \frac{\partial}{\partial \mathbf{k}} u_{n\mathbf{k}}^*(\mathbf{r}) \right). \quad (\text{J11}) \quad \{\text{dnm2}\}$$

Therefore, we define

$$\xi_{nm}(\mathbf{k}) \equiv i \int_{\Omega} d\mathbf{r} u_{n\mathbf{k}}^*(\mathbf{r}) \nabla_{\mathbf{k}} u_{m\mathbf{k}}(\mathbf{r}), \quad (\text{J12}) \quad \{\text{zeta}\}$$

with  $\partial/\partial \mathbf{k} = \nabla_{\mathbf{k}}$ . Now, from Eqs. (J4), (J7), and (J12), we have that the matrix elements of the position operator of the electron are given by

$$\langle n\mathbf{k} | \hat{\mathbf{r}} | m\mathbf{k}' \rangle = \delta(\mathbf{k} - \mathbf{k}') \xi_{nm}(\mathbf{k}) + i \delta_{nm} \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}'), \quad (\text{J13}) \quad \{\text{erre}\}$$

Then, from Eq. (J13), 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

$$\langle n\mathbf{k} | \hat{\mathbf{r}}_i | m\mathbf{k}' \rangle = \delta_{nm} [\delta(\mathbf{k} - \mathbf{k}') \xi_{nm}(\mathbf{k}) + i \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}')], \quad (\text{J14}) \quad \{\text{rnmi}\}$$

$$\langle n\mathbf{k} | \hat{\mathbf{r}}_e | m\mathbf{k}' \rangle = (1 - \delta_{nm}) \delta(\mathbf{k} - \mathbf{k}') \xi_{nm}(\mathbf{k}). \quad (\text{J15}) \quad \{\text{rnme}\}$$

To proceed, we relate Eq. (J15) to the matrix elements of the momentum operator as follows.

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

$$\begin{aligned}
\langle n\mathbf{k} | [\hat{\mathbf{r}}_i, \hat{\mathcal{O}}] | m\mathbf{k}' \rangle &= \sum_{\ell, \mathbf{k}''} \left( \langle n\mathbf{k} | \hat{\mathbf{r}}_i | \ell\mathbf{k}'' \rangle \langle \ell\mathbf{k}'' | \hat{\mathcal{O}} | m\mathbf{k}' \rangle \right. \\
&\quad \left. - \langle n\mathbf{k} | \hat{\mathcal{O}} | \ell\mathbf{k}'' \rangle \langle \ell\mathbf{k}'' | \hat{\mathbf{r}}_i | m\mathbf{k}' \rangle \right) \\
&= \sum_{\ell} \left( \langle n\mathbf{k} | \hat{\mathbf{r}}_i | \ell\mathbf{k}' \rangle \mathcal{O}_{\ell m}(\mathbf{k}') \right. \\
&\quad \left. - \mathcal{O}_{n\ell}(\mathbf{k}) | \ell\mathbf{k} \rangle \langle \ell\mathbf{k} | \hat{\mathbf{r}}_i | m\mathbf{k}' \rangle \right), \tag{J16} \quad \{\text{conmri}\}
\end{aligned}$$

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. (J14), to obtain

$$\begin{aligned}
&\sum_{\ell} \left( \delta(\mathbf{k} - \mathbf{k}') [\delta(\mathbf{k} - \mathbf{k}') \xi_{nn}(\mathbf{k}) + i \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}')] \mathcal{O}_{\ell m}(\mathbf{k}') \right. \\
&\quad \left. - \mathcal{O}_{n\ell}(\mathbf{k}) \delta_{\ell m} [\delta(\mathbf{k} - \mathbf{k}') \xi_{mm}(\mathbf{k}) + i \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}')] \right) \\
&= \left( [\delta(\mathbf{k} - \mathbf{k}') \xi_{nn}(\mathbf{k}) + i \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}')] \mathcal{O}_{nm}(\mathbf{k}') \right. \\
&\quad \left. - \mathcal{O}_{nm}(\mathbf{k}) [\delta(\mathbf{k} - \mathbf{k}') \xi_{mm}(\mathbf{k}) + i \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}')] \right) \\
&= \delta(\mathbf{k} - \mathbf{k}') \mathcal{O}_{nm}(\mathbf{k}) (\xi_{nn}(\mathbf{k}) - \xi_{mm}(\mathbf{k})) + i \mathcal{O}_{nm}(\mathbf{k}') \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}') \\
&\quad + i \delta(\mathbf{k} - \mathbf{k}') \nabla_{\mathbf{k}} \mathcal{O}_{nm}(\mathbf{k}) - i \mathcal{O}_{nm}(\mathbf{k}') \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}') \\
&= i \delta(\mathbf{k} - \mathbf{k}') \left( \nabla_{\mathbf{k}} \mathcal{O}_{nm}(\mathbf{k}) - i \mathcal{O}_{nm}(\mathbf{k}) (\xi_{nn}(\mathbf{k}) - \xi_{mm}(\mathbf{k})) \right) \\
&\equiv i \delta(\mathbf{k} - \mathbf{k}') (\mathcal{O}_{nm})_{;\mathbf{k}}. \tag{J17} \quad \{\text{conmri2}\}
\end{aligned}$$

Then,

$$\langle n\mathbf{k} | [\hat{\mathbf{r}}_i, \hat{\mathcal{O}}] | m\mathbf{k}' \rangle = i \delta(\mathbf{k} - \mathbf{k}') (\mathcal{O}_{nm})_{;\mathbf{k}}, \tag{J18} \quad \{\text{conmri3}\}$$

with

$$(\mathcal{O}_{nm})_{;\mathbf{k}} = \nabla_{\mathbf{k}} \mathcal{O}_{nm}(\mathbf{k}) - i \mathcal{O}_{nm}(\mathbf{k}) (\xi_{nn}(\mathbf{k}) - \xi_{mm}(\mathbf{k})), \tag{J19} \quad \{\text{gendev}\}$$

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. (J17), thus giving a well defined commutator of the intraband position operator with an arbitrary operator  $\hat{\mathcal{O}}$ . We use Eq. (16) and (J18) in the next section.

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