

Length Gauge Theory of Surface Second Harmonic Generation

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Abstract

We present a theoretical review of surface second harmonic generation (SHG) from semiconductor surfaces based on the longitudinal gauge. This layer-by-layer analysis is carefully presented in order to show how a surface SHG calculation can be readily evaluated. The nonlinear susceptibility tensor for a surface, $\chi^S(-2\omega; \omega, \omega)$ is split into two terms relating to inter-band and intra-band one-electron transitions.

I. THEORY

{theory}

In this section we present the scheme used to calculate the surface second-order nonlinear response. Our derivation includes new terms not included before in the length gauge formalism for the surface nonlinear response.

A. Perturbation approach

We use the independent particle approximation and neglect local field and excitonic effects and treat the electromagnetic field classically, while the matter is described quantum-mechanically. We can describe the system using the one electron density operator ρ , with which we can calculate the expectation value of a single-particle observable \mathcal{O} as $\langle \mathcal{O} \rangle = \text{Tr}(\rho \mathcal{O})$, with \mathcal{O} the associated quantum mechanical operator and Tr the trace. The density operator satisfies $i\hbar(d\rho/dt) = [H(t), \rho]$, with $H(t)$ as the total single electron Hamiltonian, written as

$$H(t) = H_0 + H_I(t),$$

where H_0 is the unperturbed time-independent Hamiltonian, and $H_I(t)$ is the time-dependent potential energy due to the interaction of the electron with the electromagnetic field. To proceed with the solution of ρ it is convenient to use the interaction picture, where a unitary operator $U = \exp(iH_0 t/\hbar)$ transforms any operator \mathcal{O} into $\tilde{\mathcal{O}} = U\mathcal{O}U^\dagger$. Even if \mathcal{O} does not depend on t , $\tilde{\mathcal{O}}$ does through the explicit time dependence of U . The dynamical equation for $\tilde{\rho}$ is given by

$$i\hbar \frac{d\tilde{\rho}}{dt} = [\tilde{H}_I(t), \tilde{\rho}],$$

with solution

$$i\hbar \tilde{\rho}(t) = i\hbar \tilde{\rho}_0 + \int_{-\infty}^t dt' [\tilde{H}_I(t'), \tilde{\rho}(t')], \quad (1) \quad \{\text{trans}\}$$

where $\tilde{\rho}_0 = \tilde{\rho}(t = -\infty)$ is the unperturbed density matrix. We look for the standard perturbation series solution, $\tilde{\rho}(t) = \tilde{\rho}^{(0)} + \tilde{\rho}^{(1)} + \tilde{\rho}^{(2)} + \dots$, where the superscript denotes the order (power) with which each term depends on the perturbation $H_I(t)$. From Eq. (1) the N -th order term is

$$\tilde{\rho}^{(N)}(t) = \frac{1}{i\hbar} \int_{-\infty}^t dt' [\tilde{H}_I(t'), \tilde{\rho}^{(N-1)}(t')]. \quad (2) \quad \{\text{rhop}\}$$

The series is generated by the unperturbed density operator $\tilde{\rho}^{(0)} \equiv \tilde{\rho}_0$, assumed to be the diagonal Fermi-Dirac distribution, $\langle n\mathbf{k} | \tilde{\rho}_0 | n\mathbf{k} \rangle = f(\hbar\omega_n(\mathbf{k})) \equiv f_n$. For a clean, cold semiconductor $f_n = 1$

for n a valence (v) or occupied band and zero for n a conduction (c) or empty band. This we assume throughout. We remark that the expectation values satisfy $\langle \mathcal{O} \rangle = \text{Tr}(\rho \mathcal{O}) = \text{Tr}(\tilde{\rho} \tilde{\mathcal{O}})$.

We will look for the expectation value of the macroscopic current density, \mathbf{J} , given by

$$\mathbf{J} = \langle \mathbf{J} \rangle = \frac{e}{\Omega} \text{Tr}(\rho \dot{\mathbf{r}}), \quad (3) \quad \{\text{pe}\}$$

where $\dot{\mathbf{r}}$ is the time derivative of the position operator of the electron of charge e ,

$$\mathbf{v} \equiv \dot{\mathbf{r}} = \frac{1}{i\hbar} [\mathbf{r}, H_0], \quad (4) \quad \{\text{mv}\}$$

with \mathbf{v} the velocity operator of the electron, and Ω the normalization volume. We calculate the macroscopic polarization density \mathbf{P} , related to \mathbf{J} by $\mathbf{J} = d\mathbf{P}/dt$. For a perturbing (Maxwell macroscopic) electromagnetic field, $\mathbf{E}(t) = \mathbf{E}(\omega)e^{-i\tilde{\omega}t} + c.c.$, where $\tilde{\omega} = \omega + i\eta$, and $\eta > 0$ is used to adiabatically turn on the interaction, we write the second order nonlinear polarization as,

$$P^a(2\omega) = \chi^{abc}(-2\omega; \omega, \omega) E^b(\omega) E^c(\omega), \quad (5) \quad \{\text{pshg}\}$$

where $\chi^{abc}(-2\omega; \omega, \omega)$ is the nonlinear susceptibility responsible of surface second harmonic generation (SSHG). The superscripts in Eq. (5) denote Cartesian components, and if repeated are to be summed over. Without loss of generality we can always define $\chi^{abc}(-2\omega; \omega, \omega)$ to satisfy intrinsic permutation symmetry, $\chi^{abc}(-2\omega; \omega, \omega) = \chi^{acb}(-2\omega; \omega, \omega)$.

The unperturbed Hamiltonian is used to solve the Kohn-Sham equations¹ of Density Functional Theory (DFT), for convenience usually within the Local Density Approximation (LDA). Thus, we labeled the hamiltonian with the superscript LDA for convenience, although we could use any other approximation, like GGA, and our derivation would remain the same. Then,

$$H_0^{\text{LDA}} = \frac{p^2}{2m_e} + V \quad (6) \quad \{\text{h0}\}$$

with m_e the mass of the electron, \mathbf{p} its canonical momentum, and V the periodic crystal potential, where we neglect spin-orbit terms. To be more general in our derivation of $\chi^{abc}(-2\omega; \omega, \omega)$, we assume that the crystal potential could have a spatially non-local contribution, as is customary for most pseudopotentials, and then we replace V with

$$V^{\text{ps}} = V(\mathbf{r}) + V^{\text{nl}}, \quad (7) \quad \{\text{ps}\}$$

where $V(\mathbf{r})$ and V^{nl} are the local and non-local contributions to the pseudopotential V^{ps} , respectively. Now, the Schrödinger equation reads

$$\left(\frac{-\hbar^2}{2m_e} \nabla^2 + V(\mathbf{r}) \right) \psi_{n\mathbf{k}}(\mathbf{r}) + \int d\mathbf{r}' V^{\text{nl}}(\mathbf{r}, \mathbf{r}') \psi_{n\mathbf{k}}(\mathbf{r}') = \hbar\omega_i \psi_{n\mathbf{k}}(\mathbf{r}), \quad (8) \quad \{\text{ache.4}\}$$

where $V^{\text{nl}}(\mathbf{r}, \mathbf{r}') = \langle \mathbf{r} | V^{\text{nl}} | \mathbf{r}' \rangle$, and $\psi_{n\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r} | n\mathbf{k} \rangle = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$, are the real space representations of the Bloch states $|n\mathbf{k}\rangle$ labelled by the band index n and the crystal momentum \mathbf{k} , and $u_{n\mathbf{k}}(\mathbf{r})$ is cell periodic. In case of a local potential, i.e. $V = V(\mathbf{r})$, like that of all-electron schemes, we simply omit the contribution coming from the non-local part of the pseudopotential, V^{nl} , in the results that we will derive.

As is well known, the use of the solutions of Eq. (8) as single particle states leads to an underestimation of the band gap. A standard procedure to correct for this is to use the so-called “scissors approximation”, by which one rigidly shifts the conduction bands in energy so that the band gap corresponds to the accepted experimental band gap; this is often in fairly good agreement with the GW band gap based on a more sophisticated calculation.² Concurrently, one uses the LDA wave functions, since they produce band structures with dispersion relations similar to those predicted by the GW approximation. Mathematically, one adds the scissors (non-local) term S , to the unperturbed or unscissored Hamiltonian H_0^{LDA} , i.e.

$$H_0^\sigma = H_0^{\text{LDA}} + S$$

where

$$S = \hbar\sigma \sum_n \int d^3k (1 - f_n) |n\mathbf{k}\rangle \langle n\mathbf{k}|, \quad (9) \quad \{\text{hats}\}$$

with $\hbar\sigma$ the rigid (\mathbf{k} -independent) energy correction to be applied. The unscissored and scissored Hamiltonians satisfy

$$\begin{aligned} H_0^{\text{LDA}} \psi_{n\mathbf{k}}(\mathbf{r}) &= \hbar\omega_n^{\text{LDA}}(\mathbf{k}) \psi_{n\mathbf{k}}(\mathbf{r}), \\ H_0^\sigma \psi_{n\mathbf{k}}(\mathbf{r}) &= \hbar\omega_n^\sigma(\mathbf{k}) \psi_{n\mathbf{k}}(\mathbf{r}), \end{aligned}$$

where the scissor-shifted energies, $\omega_n^\sigma(\mathbf{k})$, are given by

$$\omega_n^\sigma(\mathbf{k}) = \omega_n^{\text{LDA}}(\mathbf{k}) + (1 - f_n)\sigma. \quad (10) \quad \{\text{wese}\}$$

We emphasize that the scissored Hamiltonian has the same eigenfunctions as the unscissored Hamiltonian.

B. Length Gauge Formalism

To calculate the optical response within the Length Gauge Formalism, the interaction Hamiltonian is given by

$$H_I(t) = -e\mathbf{r} \cdot \mathbf{E}(t). \quad (11) \quad \{\text{rde}\}$$

The treatment of the position operator \mathbf{r} for extended Bloch states, $\langle \mathbf{r} | n\mathbf{k} \rangle$, has been described,^{3,4} and in particular in Ref. 5 the correct treatment of \mathbf{r} for the calculation of the non-linear optical response is developed. Indeed, \mathbf{r} is split into the *intraband* (\mathbf{r}_i) and *interband* (\mathbf{r}_e) parts, where $\mathbf{r} = \mathbf{r}_i + \mathbf{r}_e$. For \mathbf{r}_e one uses

$$\langle n\mathbf{k} | \mathbf{r}_e | m\mathbf{k}' \rangle = (1 - \delta_{nm}) \delta(\mathbf{k} - \mathbf{k}') \boldsymbol{\xi}_{nm}(\mathbf{k}), \quad (12) \quad \{\text{rnminn}\}$$

such that $\mathbf{r}_{e,nm} = 0$ for $n = m$, and thus from Eq. (4), with $H_0 \rightarrow H_0^\sigma$, we obtain

$$\mathbf{r}_{e,nm}(\mathbf{k}) = \boldsymbol{\xi}_{nm}(\mathbf{k}) \equiv \mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}_{nm}^\sigma(\mathbf{k})}{i\omega_{nm}^\sigma(\mathbf{k})} \quad n \notin D_m, \quad (13) \quad \{\text{pmnrnm}\}$$

where we defined $\omega_{nm}^\sigma(\mathbf{k}) \equiv \omega_n^\sigma(\mathbf{k}) - \omega_m^\sigma(\mathbf{k})$, and D_m are all the possible degenerate m -states. For the intraband part, it turns out that \mathbf{r}_i only appears in commutators, as one does the derivation of the optical response, then one uses,⁵

$$\langle n\mathbf{k} | [\mathbf{r}_i, \mathcal{O}] | m\mathbf{k}' \rangle = i\delta(\mathbf{k} - \mathbf{k}') (\mathcal{O}_{nm})_{;\mathbf{k}}, \quad (14) \quad \{\text{conmri3n}\}$$

where

$$(\mathcal{O}_{nm})_{;\mathbf{k}} = \nabla_{\mathbf{k}} \mathcal{O}_{nm}(\mathbf{k}) - i\mathcal{O}_{nm}(\mathbf{k}) (\boldsymbol{\xi}_{nn}(\mathbf{k}) - \boldsymbol{\xi}_{mm}(\mathbf{k})), \quad (15) \quad \{\text{gendevnn}\}$$

is the generalized derivative of the operator \mathcal{O} . The vectors $\boldsymbol{\xi}_{nm}(\mathbf{k})$ are defined in Ref. 5, however they do not need to be calculated explicitly in what follows.

Before continue, we derive a key result for the length gauge formulation. Using again H_0^σ in Eq. (4) we obtain

$$\mathbf{v}^\sigma = \mathbf{v} + \mathbf{v}^{\text{nl}} + \mathbf{v}^S = \mathbf{v}^{\text{LDA}} + \mathbf{v}^S, \quad (16) \quad \{\text{vop2}\}$$

where we have defined

$$\mathbf{v} = \frac{\mathbf{p}}{m_e}, \quad (17a) \quad \{\text{ve}\}$$

$$\mathbf{v}^{\text{nl}} = \frac{1}{i\hbar} [\mathbf{r}, V^{\text{nl}}], \quad (17b) \quad \{\text{vn1}\}$$

$$\mathbf{v}^S = \frac{1}{i\hbar} [\mathbf{r}, S], \quad (17c) \quad \{\text{vs}\}$$

$$\mathbf{v}^{\text{LDA}} = \mathbf{v} + \mathbf{v}^{\text{nl}}, \quad (17d) \quad \{\text{vllda}\}$$

with $\mathbf{p} = -i\hbar\nabla$ the canonical momentum operator and used $[r^a, p^b] = i\hbar\delta_{ab}$, with δ_{ab} Kronecker's delta. Using Eq. (9) we obtain

$$\mathbf{v}_{nm}^S = i\sigma f_{mn} \mathbf{r}_{nm}, \quad (18) \quad \{\text{chon.2}\}$$

with $f_{nm} \equiv f_n - f_m$, where we see that $\mathbf{v}_{nn}^S = 0$. Then, it follows that

$$\mathbf{v}_{nm}^\sigma(\mathbf{k}) = \frac{\omega_{nm}^\sigma(\mathbf{k})}{\omega_{nm}^{\text{LDA}}(\mathbf{k})} \mathbf{v}_{nm}^{\text{LDA}}(\mathbf{k}), \quad (19) \quad \{\text{chon.9}\}$$

and

$$\frac{\mathbf{v}_{nm}^\sigma(\mathbf{k})}{\omega_{nm}^\sigma(\mathbf{k})} = \frac{\mathbf{v}_{nm}^{\text{LDA}}(\mathbf{k})}{\omega_{nm}^{\text{LDA}}(\mathbf{k})}, \quad (20) \quad \{\text{chon.8}\}$$

thus from Eq. (13)

$$\mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}_{nm}^\sigma(\mathbf{k})}{i\omega_{nm}^\sigma(\mathbf{k})} = \frac{\mathbf{v}_{nm}^{\text{LDA}}(\mathbf{k})}{i\omega_{nm}^{\text{LDA}}(\mathbf{k})} \quad n \notin D_m. \quad (21) \quad \{\text{chon.10}\}$$

The matrix elements of $\mathbf{r}_{nm}(\mathbf{k})$ are the same whether we use the LDA or the scissored Hamiltonian and thus there is no need to label them. Of course, is more convenient to calculate them through $\mathbf{v}_{nm}^{\text{LDA}}(\mathbf{k})$, that include the contribution of the non-local part of the pseudopotentials through $\mathbf{v}_{nm}^{\text{nl}}(\mathbf{k})$. These in turn, can be readily calculated for fully separable nonlocal pseudopotentials in the Kleinman-Bylander form,⁶⁻⁹ see Appendix A 3. Thus, the advantage of the length gauge formalism for linear and non-linear calculations of optical responses resides in the ease with which one can introduce the scissors operator into the calculations as it is also discussed in Nastos et al.¹⁰ Indeed, the length-gauge formalism for the scissored Hamiltonian can be easily worked out by simply using the unscissored LDA Hamiltonian, H_0^{LDA} , for the unperturbed system with $-\mathbf{e}\mathbf{r} \cdot \mathbf{E}(t)$ as the interaction, and then at the end of the calculation we only need to replace ω_n^{LDA} with ω_n^σ to obtain the scissored results for any susceptibility expression, whether linear or nonlinear.

Therefore, taking the matrix elements of Eq. (2) with the $H_I(t)$ of Eq. (11), we obtain $(\tilde{\rho}^{(1)}(t))_{nm} = B_{nm}^b E^b(\omega) e^{i(\omega_{nm}^\sigma - \tilde{\omega})t}$, with

$$B_{nm}^b = \frac{e}{\hbar} \frac{f_{mn} r_{nm}^b}{\omega_{nm}^\sigma - \tilde{\omega}}, \quad (22) \quad \{\text{j.1}\}$$

and

$$(\tilde{\rho}^{(2)}(t))_{nm} = \frac{e}{i\hbar} \frac{1}{\omega_{nm}^\sigma - 2\tilde{\omega}} \left[i \sum_{\ell} \left(r_{n\ell}^b B_{\ell m}^c - B_{n\ell}^c r_{\ell m}^b \right) - (B_{nm}^c)_{;k^b} \right] E^b(\omega) E^c(\omega) e^{i(\omega_{nm}^\sigma - 2\tilde{\omega})t}. \quad (23) \quad \{\text{j.2}\}$$

We have used the fact that for a cold semiconductor $\partial f_n / \partial \mathbf{k} = 0$ and thus the intraband contribution to the linear term vanishes identically. Notice that in Eq. (23) all the indices are different from each other since due to the f_{nm} factor in Eq. (22), $B_{nn}^a = 0$. The dependence of \mathbf{k} of all quantities is implicitly understood from here on. Above expression will be used in the next subsection.

C. Layered Current Density

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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 super slab that consist of a finite slab of atomic layers and a vacuum region (see Fig. 1). This super slab, which constitutes the unit cell, is repeated to form a full three dimensional crystalline structure. The slab itself consists of a front and back surface and sub-surface regions, and in between these a region that is equivalent to bulk of the system. In general the surface of a crystal reconstructs or relaxes as the atoms move to find equilibrium positions. This is due to the fact that the otherwise balanced forces are disrupted when the surface atoms do not find their partner atoms that are now absent at the surface of the slab. To take the reconstruction or relaxation into account, we take “surface” to mean the true surface of the first layer of atoms, and some of the atomic sub-layers adjacent to it. Since the front and the back surfaces of the slab are usually identical the total slab is centrosymmetric. This would imply that $\chi_{\text{abc}}^{\text{slab}} = 0$, and thus we must find a scheme in order to have a finite χ_{abc} representative of the surface. Even if the front and back surfaces of the slab are different, breaking the centrosymmetry and therefore giving an overall $\chi_{\text{abc}}^{\text{slab}} \neq 0$, we still need a procedure to extract the front surface χ_{abc}^f and the back surface χ_{abc}^b from the slab susceptibility $\chi_{\text{abc}}^{\text{slab}} = \chi_{\text{abc}}^f - \chi_{\text{abc}}^b$. We have omitted the frequency arguments of χ_{abc} for notation convenience.

A convenient way to accomplish the separation of the SH signal of either surface is to introduce a “cut function”, $\mathcal{C}(z)$, which is usually taken to be unity over one half of the slab and zero over the other half.¹¹ In this case $\mathcal{C}(z)$ will give the contribution of the side of the slab for which $\mathcal{C}(z) = 1$. As was done for the linear response,¹² we can generalize this simple choice for $\mathcal{C}(z)$ by a top-hat cut function $\mathcal{C}^\ell(z)$ that selects a given layer,

$$\mathcal{C}^\ell(z) = \Theta(z - z_\ell + \Delta_\ell^b)\Theta(z_\ell - z + \Delta_\ell^f), \quad (24) \quad \{\text{sz}\}$$

where Θ is the Heaviside function. Here, $\Delta_\ell^{f/b}$ is the distance that the ℓ -th layer extends towards the front (f) or back (b) from its z_ℓ position. We take z_ℓ at the center of an atom that belongs to layer ℓ , and thus above equation would give the ℓ -th atomic-layer contribution to the non-linear optical response. $\Delta_\ell^f + \Delta_\ell^b$ is the thickness of layer ℓ (see Fig. 1).

To introduce the cut function $\mathcal{C}^\ell(z)$ in the calculation of χ_{abc} , we start from the operator for the electron current, $\mathbf{j}(\mathbf{r}) = \frac{e}{2} (\mathbf{v}^\sigma |\mathbf{r}\rangle \langle \mathbf{r}| + |\mathbf{r}\rangle \langle \mathbf{r}| \mathbf{v}^\sigma)$, that leads to

$$\mathbf{j}^{(N)}(\mathbf{r}, t) = \text{Tr}(\mathbf{j}(\mathbf{r})\rho^{(N)}(t)) = \int \frac{dk^3}{8\pi^3} \sum_{nm} \rho_{nm}^{(N)}(\mathbf{k}; t) \mathbf{j}_{mn}(\mathbf{k}; \mathbf{r}), \quad (25) \quad \{\text{jmic}\}$$

where

$$\mathbf{j}_{mn}(\mathbf{k}; \mathbf{r}) = \frac{e}{2} (\langle m\mathbf{k} | \mathbf{v}^\sigma | \mathbf{r} \rangle \langle \mathbf{r} | n\mathbf{k} \rangle + \langle m\mathbf{k} | \mathbf{r} \rangle \langle \mathbf{r} | \mathbf{v}^\sigma | n\mathbf{k} \rangle), \quad (26) \quad \{\text{jmic3}\}$$

are the matrix elements of the microscopic current operator. Integrating the microscopic current $\mathbf{j}(\mathbf{r}, t)$ over the entire slab gives the averaged macroscopic current density, $\mathbf{J}(t)$. 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. Then, the contribution to the current density from the ℓ -th layer of the slab is given by

$$\frac{1}{\Omega} \int d^3r \mathcal{C}^\ell(z) \mathbf{j}^{(N)}(\mathbf{r}, t) \equiv \mathbf{J}^{(N),\ell}(t), \quad (27) \quad \{\text{jsz}\}$$

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

$$e\mathcal{V}_{mn}^{\sigma,\ell}(\mathbf{k}) \equiv \int d^3r \mathcal{C}^\ell(z) \mathbf{j}_{mn}(\mathbf{k}; \mathbf{r}), \quad (28) \quad \{\text{vcal}\}$$

to write the Fourier transform of Eq. (25) as

$$\mathbf{J}^{(N),\ell}(2\omega) = \frac{e}{\Omega} \int \frac{dk^3}{8\pi^3} \sum_{mn} \mathcal{V}_{mn}^{\sigma,\ell}(\mathbf{k}) \rho_{nm}^{(N)}(\mathbf{k}; 2\omega), \quad (29) \quad \{\text{jmac2}\}$$

that gives the induced microscopic current of the ℓ -th layer, to order N in the external perturbation.

From Eqs. (28) and (26) we obtain

$$\begin{aligned} \mathcal{V}_{mn}^{\sigma,\ell}(\mathbf{k}) &= \frac{1}{2} \int d^3r \mathcal{C}^\ell(z) \left[\langle m\mathbf{k} | \mathbf{v}^\sigma | \mathbf{r} \rangle \langle \mathbf{r} | n\mathbf{k} \rangle + \langle m\mathbf{k} | \mathbf{r} \rangle \langle \mathbf{r} | \mathbf{v}^\sigma | n\mathbf{k} \rangle \right] \\ &= \frac{1}{2} \int d^3r \mathcal{C}^\ell(z) \left[\psi_{n\mathbf{k}}(\mathbf{r}) \mathbf{v}^{\sigma*} \psi_{m\mathbf{k}}^*(\mathbf{r}) + \psi_{m\mathbf{k}}^*(\mathbf{r}) \mathbf{v}^\sigma \psi_{n\mathbf{k}}(\mathbf{r}) \right] \\ &= \int d^3r \psi_{m\mathbf{k}}^*(\mathbf{r}) \left[\frac{\mathcal{C}^\ell(z) \mathbf{v}^\sigma + \mathbf{v}^\sigma \mathcal{C}^\ell(z)}{2} \right] \psi_{n\mathbf{k}}(\mathbf{r}) \\ &= \int d^3r \psi_{m\mathbf{k}}^*(\mathbf{r}) \mathcal{V}^{\sigma,\ell} \psi_{n\mathbf{k}}(\mathbf{r}), \end{aligned} \quad (30) \quad \{\text{intj}\}$$

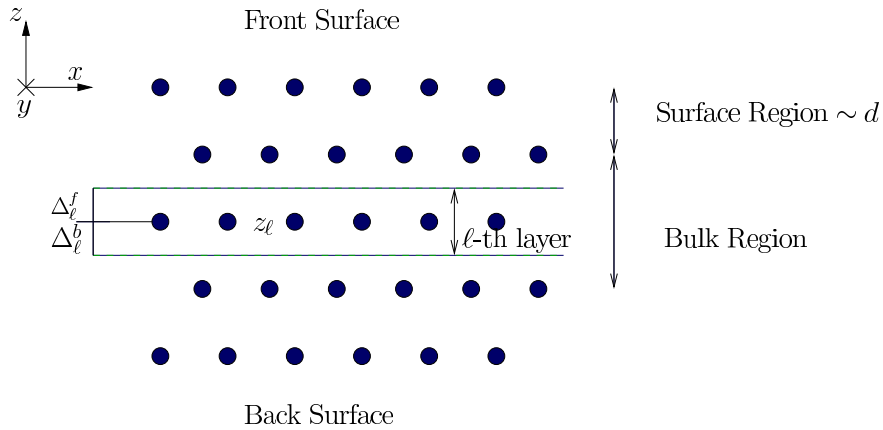


FIG. 1: A sketch of a slab where the circles represent atoms. ^{fslab}

where, we used the hermitian property of \mathbf{v}^σ and defined

$$\mathbf{v}^{\sigma,\ell} = \frac{\mathcal{C}^\ell(z)\mathbf{v}^\sigma + \mathbf{v}^\sigma\mathcal{C}^\ell(z)}{2}, \quad (31) \quad \{\text{nl.4}\}$$

where the superscript ℓ is inherited from $\mathcal{C}^\ell(z)$. We see that the replacement

$$\mathbf{V} \rightarrow \mathbf{v}^\ell = \frac{\mathcal{C}^\ell(z)\mathbf{V} + \mathbf{V}\mathcal{C}^\ell(z)}{2}, \quad (32) \quad \{\text{vcali}\}$$

is all that is needed to change any of the velocity operators of the electron \mathbf{V} to the new velocity operator \mathbf{v}^ℓ that implicitly takes into account the contribution of the region of the slab given by $\mathcal{C}^\ell(z)$. The operator \mathbf{V} could be any of those given by Eq. (16), thus

$$\begin{aligned} \mathbf{v}^{\sigma,\ell} &= \mathbf{v}^{\text{LDA},\ell} + \mathbf{v}^{S,\ell} \\ \mathbf{v}^{\text{LDA},\ell} &= \mathbf{v}^\ell + \mathbf{v}^{\text{nl},\ell} = \frac{1}{m_e}\mathcal{P}^\ell + \mathbf{v}^{\text{nl},\ell}. \end{aligned} \quad (33) \quad \{\text{vopii}\}$$

We remark that the simple renormalization that gives $\mathbf{v}_{nm}^\sigma(\mathbf{k})$ in terms of $\mathbf{v}_{nm}^{\text{LDA}}(\mathbf{k})$, given in Eq. (19), does not hold between $\mathbf{v}_{nm}^{\sigma,\ell}(\mathbf{k})$ and $\mathbf{v}_{nm}^{\text{LDA},\ell}(\mathbf{k})$, i.e. $\mathbf{v}_{nm}^{\sigma,\ell}(\mathbf{k}) \neq (\omega_{nm}^\sigma/\omega_{nm}^{\text{LDA}})\mathbf{v}_{nm}^{\text{LDA},\ell}(\mathbf{k})$, and thus, to calculate $\mathbf{v}_{nm}^{\sigma,\ell}(\mathbf{k})$ we must calculate the matrix elements of $\mathbf{v}^{\text{LDA},\ell}$ and $\mathbf{v}^{S,\ell}$ (separately) according to the expressions of Appendices A 1, A 3 and A 4.

To limit the SHG response to one surface, the equivalent of Eq. (31) for $\mathbf{v}^\ell = \mathcal{P}^\ell/m_e$ was proposed in Ref. 11 and later used in Refs. 13, 14, 15, and 16. The layer-by-layer analysis of Refs. 7,17,18 used the equivalent Eq. (24), to obtain the anisotropic linear optical response of semiconductor surfaces. However, the first formal derivation of this scheme for the linear response is presented in Ref. 12, and here in this article, for the second harmonic optical response of semiconductors.

Using $\mathbf{J} = d\mathbf{P}/dt$ and Eq. (29) we obtain the SH polarization of the ℓ -th layer as

$$\mathbf{P}^{(2),\ell}(2\omega) = \frac{ie}{2\Omega\tilde{\omega}} \int \frac{dk^3}{8\pi^3} \sum_{mn} \mathbf{v}_{mn}^{\sigma,\ell}(\mathbf{k}) \rho_{nm}^{(2)}(\mathbf{k}; 2\omega), \quad (34) \quad \{\text{Pjkn}\}$$

and using Eqs. (5) and (23) leads to

$$\begin{aligned} \chi^{\ell,\text{abc}}(-2\omega; \omega, \omega) &= \frac{e^2}{2A\hbar\tilde{\omega}} \int \frac{dk^3}{8\pi^3} \sum_{mn} \frac{\mathcal{V}_{mn}^{\sigma,\text{a},\ell}(\mathbf{k})}{\omega_{nm\mathbf{k}}^\sigma - 2\tilde{\omega}} \left[- (B_{nm}^c(\mathbf{k}, \omega))_{;k^b} \right. \\ &\quad \left. + i \sum_{\ell} \left(r_{n\ell}^b B_{\ell m}^c(\mathbf{k}, \omega) - B_{n\ell}^c(\mathbf{k}, \omega) r_{\ell m}^b \right) \right], \end{aligned} \quad (35) \quad \{\text{Pjkn2}\}$$

which gives the susceptibility $\chi_{\text{abc}}^\ell(-2\omega; \omega, \omega)$ of the ℓ -th layer of the slab, where $A = \Omega/d$ is the area of the unit cell that characterizes the surface of the system, and d is the surface region, from which the non-linear susceptibility is different from zero. We mention that the units of $\chi^{\ell,\text{abc}}(-2\omega; \omega, \omega)$

are m^2/V , as they should for a surface SH susceptibility. Using Eq. (22) we split this equation into two contributions from the first and second terms on the right hand side of Eq. (35), then,

$$\chi_i^{\ell,abc}(-2\omega; \omega, \omega) = -\frac{e^3}{A\hbar^2 2\tilde{\omega}} \int \frac{dk^3}{8\pi^3} \sum_{mn} \frac{\mathcal{V}_{mn}^{\sigma,a,\ell}}{\omega_{nm}^\sigma - 2\tilde{\omega}} \left(\frac{f_{mn} r_{nm}^b}{\omega_{nm}^\sigma - \tilde{\omega}} \right)_{;k^c}, \quad (36) \quad \{\text{chii}\}$$

that is related to intraband transitions, and

$$\chi_e^{\ell,abc}(-2\omega; \omega, \omega) = \frac{ie^3}{A\hbar^2 2\tilde{\omega}} \int \frac{dk^3}{8\pi^3} \sum_{lmn} \frac{\mathcal{V}_{mn}^{\sigma,a,\ell}}{\omega_{nm}^\sigma - 2\tilde{\omega}} \left(\frac{r_{nl}^c r_{lm}^b f_{ml}}{\omega_{lm}^\sigma - \tilde{\omega}} - \frac{r_{nl}^b r_{lm}^c f_{ln}}{\omega_{nl}^\sigma - \tilde{\omega}} \right), \quad (37) \quad \{\text{chie}\}$$

that is related to interband transitions. The generalized derivative in Eq. (36) is dealt with by using the chain rule

$$\left(\frac{f_{mn} r_{nm}^b}{\omega_{nm}^\sigma - \tilde{\omega}} \right)_{;k^c} = \frac{f_{mn}}{\omega_{nm}^\sigma - \tilde{\omega}} \left(r_{nm}^b \right)_{;k^c} - \frac{f_{mn} r_{nm}^b \Delta_{nm}^c}{(\omega_{nm}^\sigma - \tilde{\omega})^2}, \quad (38) \quad \{\text{gene2}\}$$

where by using H_0^σ into Eq. (14) and then Eq. (19) one can readily show that

$$(\omega_{nm}^\sigma)_{;k^a} = (\omega_{nm}^{\text{LDA}})_{;k^a} = v_{nn}^{\text{LDA},a} - v_{mm}^{\text{LDA},a} \equiv \Delta_{nm}^a. \quad (39) \quad \{\text{eli.13}\}$$

The apparent divergence as $\tilde{\omega} \rightarrow 0$ in Eqs. (36) and (37), is removed by a partial fraction expansion over $\tilde{\omega}$. Using time-reversal invariance, an integration by parts to remove the square in the denominator of the second term in Eq. (38), and taking the limit of $\eta \rightarrow 0$, we obtain the following expressions for the imaginary parts of Eqs. (36) and (37),

$$\text{Im}[\chi_{e,\omega}^{\ell,abc}] = \frac{\pi|e|^3}{2\hbar^2} \int \frac{dk^3}{8\pi^3} \sum_{vc} \sum_{l \neq (v,c)} \frac{1}{\omega_{cv}^\sigma} \left[\frac{\text{Im}[\mathcal{V}_{lc}^{\sigma,a,\ell} \{r_{cv}^b r_{vl}^c\}]}{(2\omega_{cv}^\sigma - \omega_{cl}^\sigma)} - \frac{\text{Im}[\mathcal{V}_{vl}^{\sigma,a,\ell} \{r_{lc}^c r_{cv}^b\}]}{(2\omega_{cv}^\sigma - \omega_{lv}^\sigma)} \right] \delta(\omega_{cv}^\sigma - \omega), \quad (40) \quad \{\text{calvimchiew}\}$$

$$\text{Im}[\chi_{i,\omega}^{\ell,abc}] = \frac{\pi|e|^3}{2\hbar^2} \int \frac{dk^3}{8\pi^3} \sum_{cv} \frac{1}{(\omega_{cv}^\sigma)^2} \left[\text{Re} \left[\left\{ r_{cv}^b \left(\mathcal{V}_{vc}^{\sigma,a,\ell} \right)_{;k^c} \right\} \right] + \frac{\text{Re} \left[\mathcal{V}_{vc}^{\sigma,a,\ell} \{r_{cv}^b \Delta_{cv}^c\} \right]}{\omega_{cv}^\sigma} \right] \delta(\omega_{cv}^\sigma - \omega), \quad (41) \quad \{\text{calvimchiwn}\}$$

$$\text{Im}[\chi_{e,2\omega}^{\ell,abc}] = -\frac{\pi|e|^3}{2\hbar^2} \int \frac{dk^3}{8\pi^3} \sum_{vc} \frac{4}{\omega_{cv}^\sigma} \left[\sum_{v' \neq v} \frac{\text{Im}[\mathcal{V}_{vc}^{\sigma,a,\ell} \{r_{cv'}^b r_{v'v}^c\}]}{2\omega_{cv'}^\sigma - \omega_{cv}^\sigma} - \sum_{c' \neq c} \frac{\text{Im}[\mathcal{V}_{vc}^{\sigma,a,\ell} \{r_{cc'}^c r_{c'v}^b\}]}{2\omega_{c'v}^\sigma - \omega_{cv}^\sigma} \right] \delta(\omega_{cv}^\sigma - 2\omega), \quad (42) \quad \{\text{calvimchie2}\}$$

and

$$\text{Im}[\chi_{i,2\omega}^{\ell,abc}] = \frac{\pi|e|^3}{2\hbar^2} \int \frac{dk^3}{8\pi^3} \sum_{vc} \frac{4}{(\omega_{cv}^\sigma)^2} \left[\text{Re} \left[\mathcal{V}_{vc}^{\sigma,a,\ell} \left\{ \left(r_{cv}^b \right)_{;k^c} \right\} \right] - \frac{2\text{Re} \left[\mathcal{V}_{vc}^{\sigma,a,\ell} \{r_{cv}^b \Delta_{cv}^c\} \right]}{\omega_{cv}^\sigma} \right] \delta(\omega_{cv}^\sigma - 2\omega), \quad (43) \quad \{\text{calvimchi2w}\}$$

where we have split the interband and intraband 1ω and 2ω contributions and suppress the ω arguments for space sake. The real part of each contribution can be obtained through a Kramers-Kronig transformation,¹⁹ and then $\chi^{\ell,abc} = \chi_{e,\omega}^{\ell,abc} + \chi_{e,2\omega}^{\ell,abc} + \chi_{i,\omega}^{\ell,abc} + \chi_{i,2\omega}^{\ell,abc}$. To fulfill the required intrinsic permutation symmetry, the $\{\}$ notation symmetrizes the bc Cartesian indices, i.e. $\{u^b s^c\} = (u^b s^c + u^c s^b)/2$, and thus $\chi^{\ell,abc} = \chi^{\ell,acb}$. We calculate the nonlinear surface susceptibility as

$$\chi(-2\omega; \omega, \omega) = \sum_{\{\ell\}} \chi^{\ell}(-2\omega; \omega, \omega), \quad (44) \quad \{\text{chiijsur}\}$$

where $\{\ell\}$ is meant to be set of layers that one chooses. For instance, one goes from a layer that encompasses half of the slab or each atomic layer till the middle of the slab. In the first case, there is one single summand in Eq. (44), in the second case a sum from $\ell = 1$ which denotes the first layer right at the surface, till $\ell = N$ that corresponds to the layer at the middle of the slab, which ought to be a bulk-like layer. We remark that the value of N is not universal, and the slab needs to have enough atomic layers for in order to give converged results for $\chi(-2\omega; \omega, \omega)$. We can use Eq. (44) for either the front or the back surface. **Talk about the correct value of d**

II. RESULTS

Appendix A

We give explicit expressions for the quantities used in the evaluation of Eq. (40)-(43); when appropriate, some intermediate steps are given for their derivation.

1. Expressions for $\mathcal{V}_{nm}^{a,\ell}(\mathbf{k})$, $\mathcal{C}_{nm}^{\ell}(\mathbf{k})$ and $(\mathcal{C}_{nm}^{\ell}(\mathbf{k}))_{;\mathbf{k}}$

{calpcalc}

Expanding the wave function in plane waves we obtain

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} A_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \quad (A1) \quad \{\text{eni.1}\}$$

where $\{\mathbf{G}\}$ are the reciprocal basis vectors satisfying $e^{\mathbf{R}\cdot\mathbf{G}} = 1$, with $\{\mathbf{R}\}$ the translation vectors in real space, and $A_{n\mathbf{k}}(\mathbf{G})$ are the expansion coefficients. Using $m_e \mathbf{v} = -i\hbar \nabla$ into the equivalent of Eq. (30) we obtain,¹²

$$\mathcal{V}_{nm}^{\ell}(\mathbf{k}) = \frac{\hbar}{2m_e} \sum_{\mathbf{G}, \mathbf{G}'} A_{n\mathbf{k}}^*(\mathbf{G}') A_{m\mathbf{k}}(\mathbf{G}) (2\mathbf{k} + \mathbf{G} + \mathbf{G}') \delta_{\mathbf{G}_{\parallel} \mathbf{G}'_{\parallel}} f^{\ell}(G_{\perp} - G'_{\perp}), \quad (A2) \quad \{\text{eni.2}\}$$

where

$$f^\ell(g) = \frac{1}{L} \int_{z_\ell - \Delta_\ell^b}^{z_\ell + \Delta_\ell^f} e^{igz} dz, \quad (\text{A3}) \quad \{\text{vn1.9}\}$$

with $f^{\ell*}(g) = f^\ell(-g)$. the reciprocal lattice vectors \mathbf{G} are decomposed into components parallel to the surface \mathbf{G}_\parallel , and perpendicular to the surface $G_\perp \hat{z}$, so that $\mathbf{G} = \mathbf{G}_\parallel + G_\perp \hat{z}$. The double summation over the \mathbf{G} vectors can be efficiently done by creating a pointer array to identify all the plane-wave coefficients associated with the same G_\parallel . Likewise we obtain that

$$\mathcal{C}_{nm}^\ell(\mathbf{k}) = \sum_{\mathbf{G}, \mathbf{G}'} A_{n\mathbf{k}}^*(\mathbf{G}') A_{m\mathbf{k}}(\mathbf{G}) \delta_{\mathbf{G}_\parallel \mathbf{G}'_\parallel} f_\ell(G_\perp - G'_\perp). \quad (\text{A4}) \quad \{\text{eni.4}\}$$

If $\mathcal{C}^\ell(z) = 1$, $f_\ell(g) = \delta_{g0}$, and from Eqs. (A2) and (A4) we obtain the full-slab or bulk values $\mathbf{v}_{nm}(\mathbf{k})$ and $\mathcal{C}_{nm}^\ell(\mathbf{k}) = \delta_{nm}$.

Since for any function $F(\mathbf{r})$, $[\mathbf{r}, F(\mathbf{r})] = 0$, using Eqs. (12), (14), and (15), we obtain

$$(\mathcal{C}_{nm}^\ell)_{;\mathbf{k}} = i \sum_q \left(\mathbf{r}_{nq} \mathcal{C}_{qm}^\ell - \mathcal{C}_{nq}^\ell \mathbf{r}_{qm} \right) + i \mathbf{r}_{nm} (\mathcal{C}_{mm}^\ell - \mathcal{C}_{nn}^\ell), \quad (\text{A5})$$

where we remind the reader that \mathbf{r}_{nm} are calculated through Eq. (21) for LDA.

2. Expressions for $(\mathcal{V}_{nm}^{\ell, \text{LDA}, a})_{;k^b}$ and $(r_{nm}^a)_{;k^b}$ for non-local potentials

{appvn1}

Using Eqs. (12), (14), (15) and defining $\mathcal{T}^{\text{ab}} \equiv [r^{\text{b}}, \mathcal{V}^{\text{LDA}, \text{a}}] \equiv [r^{\text{b}}, \mathcal{V}^{\text{a}}]$ one can show that

$$(\mathcal{V}_{nm}^{\text{LDA}, \text{a}, \ell})_{;k^b} = \mathcal{T}_{nm}^{\ell, \text{ab}} + i \sum_q \left(r_{nq}^{\text{b}} \mathcal{V}_{qm}^{\text{LDA}, \text{a}, \ell} - \mathcal{V}_{nq}^{\text{LDA}, \text{a}, \ell} r_{qm}^{\text{b}} \right) + i r_{nm}^{\text{b}} \Delta_{mn}^{\text{a}, \ell}, \quad (\text{A6}) \quad \{\text{nmesn}\}$$

where

$$\Delta_{mn}^{\text{a}, \ell} = \mathcal{V}_{nn}^{\text{LDA}, \text{a}, \ell} - \mathcal{V}_{mm}^{\text{LDA}, \text{a}, \ell}, \quad (\text{A7}) \quad \{\text{tdel}\}$$

and

$$\mathcal{T}_{nm}^{\ell, \text{ab}} = \frac{\hbar}{m_e} \delta_{\text{ab}} \mathcal{C}_{nm}^\ell - i \sum_q [r^{\text{b}}, v^{\text{nl}, \text{a}}]_{nq} \mathcal{C}_{qm}^\ell. \quad (\text{A8}) \quad \{\text{tau.1}\}$$

The matrix elements $[r^{\text{b}}, v^{\text{nl}, \text{a}}]_{nm}$ are calculated in Appendix A3.

To obtain $(r_{nm}^a)_{;k^b}$ we use Eq. (21) to write $(r_{nm}^a)_{;k^b} = (v_{nm}^{\text{LDA}, \text{a}} / i\omega_{nm}^{\text{LDA}})_{;k^b}$, and apply the chain rule. Then, $(v_{nm}^{\text{LDA}, \text{a}})_{;k^b}$ is obtained from Eq. (A6) by taking $\mathcal{C}^\ell(z) = 1$ or $\mathcal{C}_{nm}^\ell = \delta_{nm}$. Thus,

$$(r_{nm}^a)_{;k^b} = \tau_{nm}^{\text{ab}} + \frac{r_{nm}^{\text{b}} \Delta_{mn}^{\text{a}} + r_{nm}^{\text{a}} \Delta_{mn}^{\text{b}}}{\omega_{nm}^{\text{LDA}}} + \frac{i}{\omega_{nm}^{\text{LDA}}} \sum_\ell \left(\omega_{\ell m}^{\text{LDA}} r_{n\ell}^{\text{b}} r_{\ell m}^{\text{a}} - \omega_{n\ell}^{\text{LDA}} r_{n\ell}^{\text{a}} r_{\ell m}^{\text{b}} \right), \quad (\text{A9}) \quad \{\text{na_rgendevn}\}$$

where

$$\Delta_{mn}^a = v_{nn}^{\text{LDA},a} - v_{mm}^{\text{LDA},a}, \quad (\text{A10}) \quad \{\text{del}\}$$

and

$$t_{nm}^{\text{ab}} = \frac{\hbar}{m_e} \delta_{ab} \delta_{nm} + -i[r^b, v^{\text{nl},a}]_{nm}. \quad (\text{A11}) \quad \{\text{tau.1}\}$$

generalizes the usual expresion of $(r_{nm}^a)_{;k^b}$ for local Hamiltonians,^{5,10,21,22} to the case of a nonlocal Hamiltonian. Note that the layered term $\mathcal{T}_{nm}^{\ell,\text{ab}}$ reduces to τ_{nm}^{ab} , for the full-slab or bulk case.

3. Matrix elements of $\mathcal{V}^{\text{nl},\ell}$, \mathbf{v}^{nl} and $[\mathbf{r}, \mathbf{v}^{\text{nl}}]$

We take Eq. (32) and use $\sum_{\mathbf{G}} |\mathbf{k} + \mathbf{G}\rangle \langle \mathbf{k} + \mathbf{G}| = 1$, with $\langle \mathbf{r} | \mathbf{k} + \mathbf{G} \rangle = (1/\sqrt{\Omega}) \exp(i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r})$, to obtain,⁷

$$\begin{aligned} \mathcal{V}_{nm}^{\text{nl},\ell}(\mathbf{k}) &= \frac{1}{2} \sum_{\mathbf{G}} \left(\langle n\mathbf{k} | C^\ell(z) | \mathbf{k} + \mathbf{G} \rangle \langle \mathbf{k} + \mathbf{G} | \mathbf{v}^{\text{nl}} | m\mathbf{k} \rangle + \langle n\mathbf{k} | \mathbf{v}^{\text{nl}} | \mathbf{k} + \mathbf{G} \rangle \langle \mathbf{k} + \mathbf{G} | C^\ell(z) | m\mathbf{k} \rangle \right) \\ &= \frac{1}{2\hbar} \sum_{\mathbf{G}} \left(\mathcal{F}_{n\mathbf{k}}^{\ell*}(\mathbf{G}) \mathcal{H}_{m\mathbf{k}}(\mathbf{G}) + \mathcal{H}_{n\mathbf{k}}^*(\mathbf{G}) \mathcal{F}_{m\mathbf{k}}^\ell(\mathbf{G}) \right), \end{aligned} \quad (\text{A12}) \quad \{\text{vesnl}\}$$

where we have defined

$$\mathcal{F}_{n\mathbf{k}}^\ell(\mathbf{G}) = \sum_{\mathbf{G}'} A_{n\mathbf{k}}(\mathbf{G}') \delta_{\mathbf{G}_{\parallel} \mathbf{G}'_{\parallel}} f^\ell(\mathbf{G}'_{\perp} - \mathbf{G}_{\perp}), \quad (\text{A13}) \quad \{\text{vn1.10}\}$$

$$\mathcal{H}_{n\mathbf{k}}(\mathbf{G}) = \sum_{\mathbf{G}'} A_{n\mathbf{k}}(\mathbf{G}') (\nabla_{\mathbf{K}} + \nabla_{\mathbf{K}'}) V^{\text{nl}}(\mathbf{K}, \mathbf{K}'), \quad (\text{A14}) \quad \{\text{vn1.11}\}$$

and $\mathbf{K} = \mathbf{k} + \mathbf{G}$, $\mathbf{K}' = \mathbf{k} + \mathbf{G}'$. For fully separable pseudopotentials in the Kleinman-Bylander (KB) form,⁷⁻⁹ the matrix elements $\langle \mathbf{K} | V^{\text{nl}} | \mathbf{K}' \rangle = V^{\text{nl}}(\mathbf{K}, \mathbf{K}')$, along with their \mathbf{K} and \mathbf{K}' gradient can be readily calculated.^{7,9,23,24} We have implemented the calculation of $\mathcal{V}_{nm}^{\text{nl},\ell}(\mathbf{k})$ with the help pf the DPTM code.⁶ Taking $C^\ell(z) = 1$, which implies $f^\ell(g) = \delta_{g0}$, form above three expressions we obtain $\mathbf{v}_{nm}^{\text{nl}}(\mathbf{k})$. \{\text{calt}\}

Using Eq. (17b) we define

$$\mathcal{L}_{nm}^{\text{ab}}(\mathbf{k}) \equiv \frac{1}{i\hbar} \langle n\mathbf{k} | [\hat{r}^a, \hat{v}^{\text{nl},b}] | m\mathbf{k} \rangle = \frac{1}{\hbar^2} \langle n\mathbf{k} | [\hat{r}^a, [\hat{V}^{\text{nl}}(\hat{\mathbf{r}}, \hat{\mathbf{r}}'), \hat{r}^b]] | m\mathbf{k} \rangle, \quad (\text{A15}) \quad \{3.1\}$$

that uppon expanding the triple commutator, leads to

$$\begin{aligned} \mathcal{L}_{nm}^{\text{ab}}(\mathbf{k}) &= \frac{1}{\hbar^2 \Omega} \sum_{\mathbf{G}, \mathbf{G}'} A_{n\mathbf{k}}^*(\mathbf{K}) A_{m\mathbf{k}}(\mathbf{K}') \int d\mathbf{r} d\mathbf{r}' e^{-i\mathbf{K} \cdot \mathbf{r}} \left(r^a V^{\text{nl}}(\mathbf{r}, \mathbf{r}') r'^b - V^{\text{nl}}(\mathbf{r}, \mathbf{r}') r'^a r^b \right. \\ &\quad \left. - r^b r^a V^{\text{nl}}(\mathbf{r}, \mathbf{r}') + r^b V^{\text{nl}}(\mathbf{r}, \mathbf{r}') r'^a \right) e^{i\mathbf{K}' \cdot \mathbf{r}'}. \end{aligned} \quad (\text{A16}) \quad \{3.5\}$$

We use the following identity

$$\begin{aligned} & \left(\frac{\partial^2}{\partial K^a \partial K'^b} + \frac{\partial^2}{\partial K'^a \partial K'^b} + \frac{\partial^2}{\partial K^a \partial K^b} + \frac{\partial^2}{\partial K^b \partial K'^a} \right) \int d\mathbf{r} d\mathbf{r}' e^{-i\mathbf{K} \cdot \mathbf{r}} V^{\text{nl}}(\mathbf{r}, \mathbf{r}') e^{i\mathbf{K}' \cdot \mathbf{r}'} \\ &= \int d\mathbf{r} d\mathbf{r}' e^{-i\mathbf{K} \cdot \mathbf{r}} \left(r^a V^{\text{nl}}(\mathbf{r}, \mathbf{r}') r'^b - V^{\text{nl}}(\mathbf{r}, \mathbf{r}') r'^a r'^b - r^b r^a V^{\text{nl}}(\mathbf{r}, \mathbf{r}') + r^b V^{\text{nl}}(\mathbf{r}, \mathbf{r}') r'^a \right) e^{i\mathbf{K}' \cdot \mathbf{r}'}, \end{aligned} \quad (\text{A17}) \quad \{3.4\}$$

to write

$$\mathcal{L}_{nm}^{\text{ab}}(\mathbf{k}) = \frac{1}{\hbar^2 \Omega} \sum_{\mathbf{G}, \mathbf{G}'} A_{n\mathbf{k}}^*(\mathbf{K}) A_{m\mathbf{k}}(\mathbf{K}') \left(\frac{\partial^2}{\partial K^a \partial K'^b} + \frac{\partial^2}{\partial K'^a \partial K'^b} + \frac{\partial^2}{\partial K^a \partial K^b} + \frac{\partial^2}{\partial K^b \partial K'^a} \right) \langle \mathbf{K} | V^{\text{nl}} | \mathbf{K}' \rangle \quad (\text{A18}) \quad \{3.7\}$$

where

$$\langle \mathbf{K} | V^{\text{nl}} | \mathbf{K}' \rangle = \int d\mathbf{r} d\mathbf{r}' e^{-i\mathbf{K} \cdot \mathbf{r}} V^{\text{nl}}(\mathbf{r}, \mathbf{r}') e^{i\mathbf{K}' \cdot \mathbf{r}'}, \quad (\text{A19}) \quad \{\text{vkk}\}$$

The double derivatives with respect to \mathbf{K} and \mathbf{K}' can be worked out explicitly.²⁰

4. Expressions for $\mathbf{v}_{nm}^{\ell, S}$ and $(\mathbf{v}_{nm}^{\ell, S})_{;\mathbf{k}}$

From Eq. (32)

$$\mathbf{v}_{nm}^{\ell, S} = \frac{1}{2} \sum_q \left(\mathbf{v}_{nq}^S \mathcal{C}_{qm}^\ell + \mathcal{C}_{nq}^\ell \mathbf{v}_{qm}^S \right), \quad (\text{A20}) \quad \{\text{a.3b}\}$$

where $\sum_q |q\mathbf{k}\rangle \langle q\mathbf{k}| = 1$ was used, and \mathbf{v}_{nm}^S are given in Eq. (18). Taking the generalized derivative of Eq. (A21), and applying the chain rule, we obtain

$$(\mathbf{v}_{nm}^S)_{;\mathbf{k}} = \frac{1}{2} \sum_q \left((\mathbf{v}_{nq}^S)_{;\mathbf{k}} \mathcal{C}_{qm}^\ell + \mathbf{v}_{nq}^S (\mathcal{C}_{qm}^\ell)_{;\mathbf{k}} + (\mathcal{C}_{nq}^\ell)_{;\mathbf{k}} \mathbf{v}_{qm}^S + \mathcal{C}_{nq}^\ell (\mathbf{v}_{qm}^S)_{;\mathbf{k}} \right), \quad (\text{A21}) \quad \{\text{a.3b}\}$$

where from Eq. (18),

$$(\mathbf{v}_{nm}^S)_{;\mathbf{k}} = i\sigma f_{mn}(\mathbf{r}_{nm})_{;\mathbf{k}}, \quad (\text{A22}) \quad \{\text{choni.1}\}$$

in agreement with Eq. A(6) of Ref. 21.

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