Supporting Information

High-Order Harmonic Generation in Solids: The Role of Intraband Transitions in Extreme Nonlinear Optics

Hideki Hirori[1,], Shunsuke A. Sato[2,3,*], and Yoshihiko Kanemitsu[1,*]*

[1]Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

[2]Center for Computational Sciences, University of Tsukuba, Tsukuba 305-8577, Japan

[3]Max Planck Institute for the Structure and Dynamics of Matter, Luruper Chaussee 149, 22761 Hamburg, Germany

*Corresponding Authors: hirori@scl.kyoto-u.ac.jp (Hideki Hirori), ssato@ccs.tsukuba.ac.jp (Shunsuke A. Sato), kanemitu@scl.kyoto-u.ac.jp (Yoshihiko Kanemitsu)

1. Microscopic theory of HHG in solids

The mechanism of high-order harmonic generation (HHG) in solids is different from that in atoms and molecules. Since there exists a continuum of states in each electronic energy band of a solid, two types of transitions can play an important role in HHG in solids: those of the first type are transitions within a band (intraband transitions), and those of the second type are transitions between different bands (interband transitions). In this section, we identify the contributions of intraband and interband transitions in HHG in solids on the basis of a simple independent-particle model. Here, the dynamics are described by the time-dependent Schrödinger equation of a Bloch orbital for a single electron:

$$i\hbar\frac{\partial}{\partial t}u_{b\boldsymbol{k}}(\boldsymbol{r},t)=\left[\frac{1}{2}\left(\boldsymbol{p}+\hbar\boldsymbol{k}+e\boldsymbol{A}(t)\right)^2+v(\boldsymbol{r})\right]u_{b\boldsymbol{k}}(\boldsymbol{r},t), \quad (1)$$

where b is the band index, $\boldsymbol{k}$ is the Bloch wavevector, $u_{b\boldsymbol{k}}(\boldsymbol{r},t)$ is the time-dependent Bloch orbital, $v(\boldsymbol{r})$ is the one-body potential, and $\boldsymbol{A}(t)$ is a spatially uniform vector potential that is related to the external electric field $\boldsymbol{E}(t)$ according to $\boldsymbol{A}(t)=-\int^t dt'\,\boldsymbol{E}(t')$. The one-body potential $v(\boldsymbol{r})$ and the Bloch orbital $u_{b\boldsymbol{k}}(\boldsymbol{r},t)$ are periodic functions with respect to the lattice vector. To simplify the notation, we define the one-body Hamiltonian as

$$h_{\boldsymbol{k}+e\boldsymbol{A}(t)/\hbar} = \left[\frac{1}{2}\left(\boldsymbol{p} + \hbar\boldsymbol{k} + e\boldsymbol{A}(t)\right)^2 + v(\boldsymbol{r})\right]. \tag{2}$$

The eigenstates of the Hamiltonian are described by

$$h_{\boldsymbol{k}} u^S_{b\boldsymbol{k}}(\boldsymbol{r}) = \epsilon_{b\boldsymbol{k}} u^S_{b\boldsymbol{k}}(\boldsymbol{r}), \tag{3}$$

where $u^S_{b\boldsymbol{k}}(\boldsymbol{r})$ are the eigenstates, and $\epsilon_{b\boldsymbol{k}}$ are the eigenvalues. To analyze HHG in solids, we solve Eq. (1) with the initial condition $u_{b\boldsymbol{k}}(\boldsymbol{r}, 0) = u^S_{b\boldsymbol{k}}(\boldsymbol{r})$. Furthermore, the induced electric current density, $\boldsymbol{J}(t)$, can be evaluated with

$$\boldsymbol{J}(t) = \frac{1}{(2\pi)^3}\sum_v \int_{\mathrm{BZ}} d\boldsymbol{k} \int_\Omega d\boldsymbol{r} u^*_{b\boldsymbol{k}}(\boldsymbol{r}, t)\hat{\boldsymbol{J}}_{\boldsymbol{k}}(t) u_{b\boldsymbol{k}}(\boldsymbol{r}, t)\,, \tag{4}$$

where BZ indicates integration over the first Brillouin zone (with respect to the wavevector), and Ω is the volume of the Brillouin zone in real space. The current operator, $\hat{J}_{\boldsymbol{k}}(t)$, is defined as

$$\hat{\boldsymbol{J}}_{\boldsymbol{k}}(t) = -\frac{e}{m\hbar}\frac{\partial}{\partial \boldsymbol{k}} h_{\boldsymbol{k}+e\boldsymbol{A}(t)/\hbar}. \tag{5}$$

The power spectrum of the emitted harmonics can then be evaluated by taking the Fourier transform of the current density:

$$I_{\mathrm{HHG}}(\omega) \sim |\,\omega \int_{-\infty}^{\infty} dt\, e^{i\omega t}\boldsymbol{J}(t)\Big|^2. \tag{6}$$

Using this microscopic theory of HHG in solids, we can introduce intraband and interband transitions based on the instantaneous eigenstates. Firstly, let us consider the following expansion of the single-particle orbital in terms of Houston states[1,2]:

$$u_{v\boldsymbol{k}}(\boldsymbol{r}, t) = \sum_b c_{vb\boldsymbol{k}}(t) \exp\left[-\frac{i}{\hbar}\int_0^t dt'\, \epsilon_{b,\boldsymbol{k}+e\boldsymbol{A}(t')/\hbar}\right] \exp\left[i\phi_{bv,\boldsymbol{k}}(t)\right] u^S_{b,\boldsymbol{k}+e\boldsymbol{A}(t)/\hbar}(\boldsymbol{r})\,. \tag{7}$$

Here, $c_{vb\boldsymbol{k}}(t)$ are the expansion coefficients, and $\phi_{bv,\boldsymbol{k}}(t)$ is the geometric phase. By substituting Eq. (7) into Eq. (1), we obtain the following equation of motion:

$$i\hbar\frac{d}{dt}c_{vb\boldsymbol{k}}(t) = \sum_{b'\neq b} e^{i\left(\Delta\phi^D_{bb'\boldsymbol{k}}(t) + \Delta\phi^G_{bb'\boldsymbol{k}}(t)\right)} \boldsymbol{E}(t)\cdot\tilde{\boldsymbol{d}}_{bb'\boldsymbol{k}}(t) c_{b'v\boldsymbol{k}}(t), \tag{8}$$

where $\Delta\phi^D_{bb'\boldsymbol{k}}(t)$, $\Delta\phi^G_{bb'\boldsymbol{k}}(t)$, and $\tilde{\boldsymbol{d}}_{bb'\boldsymbol{k}}(t)$ are defined as

$$\Delta\phi^D_{bb'\boldsymbol{k}}(t) = \int_0^t dt' \left[\epsilon_{b,\boldsymbol{k}+e\boldsymbol{A}(t')/\hbar} - \epsilon_{b',\boldsymbol{k}+e\boldsymbol{A}(t')/\hbar}\right], \tag{9}$$

$$\Delta\phi^G_{bb'\boldsymbol{k}}(t) = -\left(\phi_{bv,\boldsymbol{k}}(t) - \phi_{b'v,\boldsymbol{k}}(t)\right), \tag{10}$$

$$\tilde{\boldsymbol{d}}_{bb'\boldsymbol{k}}(t) = \frac{i}{\hbar}\int_\Omega d\boldsymbol{r}\, u^{S,*}_{b,\boldsymbol{k}+e\boldsymbol{A}(t)/\hbar}\frac{\partial}{\partial\boldsymbol{k}} u^S_{b',\boldsymbol{k}+e\boldsymbol{A}(t)/\hbar}. \tag{11}$$

Here, $\Delta\phi^{D}_{bb'\boldsymbol{k}}(t)$ is the difference between the dynamical phase factors of different bands, $\Delta\phi^{G}_{bb'\boldsymbol{k}}(t)$ is the difference between the geometric phases, and $\tilde{\boldsymbol{d}}_{bb'\boldsymbol{k}}(t)$ is the dipole matrix element. The geometric phase is defined as

$$\begin{aligned}\phi_{bv,\boldsymbol{k}}(t) &= -\frac{i}{\hbar}\int_{\Omega} d\boldsymbol{r}\, u^{S,*}_{b,\boldsymbol{k}+e\boldsymbol{A}(t)/\hbar}\frac{\partial}{\partial \boldsymbol{k}} u^{S}_{b\,,\boldsymbol{k}+e\boldsymbol{A}(t)/\hbar} \\ &= \int_{C(\boldsymbol{A}(t))} d\boldsymbol{A}\ \boldsymbol{A}^{B}_{b}(\boldsymbol{k}+e\boldsymbol{A}/\hbar),\end{aligned} \tag{12}$$

where the contour C is determined by the time-dependent vector potential $\boldsymbol{A}(t)$, and $\boldsymbol{A}^{B}_{b}(\boldsymbol{k})$ is the Berry connection.

Secondly, let us consider the adiabatic limit, i.e., the time evolution of the electronic system from $t=0$ to $t=T$ [governed by Eq. (8)] under a slowly varying vector potential. By integrating Eq. (8), we obtain

$$c_{bv,\boldsymbol{k}}(T) - c_{bv,\boldsymbol{k}}(0) = -\frac{i}{\hbar}\int_{0}^{T} dt \sum_{b'\neq b} e^{i\left(\Delta\phi^{D}_{bb'\boldsymbol{k}}(t)+\Delta\phi^{G}_{bb'\boldsymbol{k}}(t)\right)}\boldsymbol{E}(t)\cdot\tilde{\boldsymbol{d}}_{bb'\boldsymbol{k}}(t)c_{b'v\boldsymbol{k}}(t). \tag{13}$$

As long as there are no degeneracies of the instantaneous eigenstates of the Hamiltonian, the right-hand side of Eq. (13) is equal to zero. Hence, the expansion coefficients $c_{bv,\boldsymbol{k}}(t)$ are constant. This implies that the basis functions used in the expansion in Eq. (7) are the solutions to the time-dependent Schrödinger equation in the adiabatic limit. For later convenience, we define the adiabatic solution as

$$u^{AD}_{b\boldsymbol{k}}(\boldsymbol{r},t) = \exp\left[-\frac{i}{\hbar}\int_{0}^{t} dt'\,\epsilon_{b,\boldsymbol{k}+e\boldsymbol{A}(t')/\hbar}\right]\exp\left[i\phi_{bv,\boldsymbol{k}}(t)\right]u^{S}_{b,\boldsymbol{k}+e\boldsymbol{A}(t)/\hbar}(\boldsymbol{r})\,. \tag{14}$$

Under the adiabatic condition, the time-dependent Bloch states are described by static Bloch states with a Bloch wavevector shift ($\boldsymbol{k}\rightarrow\boldsymbol{k}+e\boldsymbol{A}(t)/\hbar$) and the dynamical- and geometric-phase factors. The time evolution described by Eq. (14) is a transition within the same band, i.e., an intraband transition. On the other hand, we need to consider transitions among different adiabatic solutions via Eq. (8) to describe the general dynamics. These are the interband transitions.

Finally, we rewrite the time-dependent Bloch state and the corresponding equation of motion as follows:

$$u_{v\boldsymbol{k}}(\boldsymbol{r},t) = \sum_{b} c_{bv,\boldsymbol{k}}(t)\exp\left[-\frac{i}{\hbar}\int_{0}^{t} dt'\epsilon_{b,\boldsymbol{k}+e\boldsymbol{A}(t')/\hbar}\right]\exp\left[i\int_{C(\boldsymbol{A}(t))} d\boldsymbol{A}\cdot\boldsymbol{A}^{B}_{b}(\boldsymbol{k}+e\boldsymbol{A}/\hbar)\right]u^{S}_{b,\boldsymbol{k}+e\boldsymbol{A}(t)/\hbar}(\boldsymbol{r}), \tag{15}$$

$$\begin{aligned}i\hbar\frac{d}{dt}c_{b,v\boldsymbol{k}}(t) &= \sum_{b\neq b'}\exp\left[-\frac{i}{\hbar}\int_{0}^{t} dt'\epsilon_{b',\boldsymbol{k}+e\boldsymbol{A}(t')/\hbar}-\epsilon_{b,\boldsymbol{k}+e\boldsymbol{A}(t')/\hbar}\right] \\ &\times\exp\left[i\int_{C(\boldsymbol{A}(t))} d\boldsymbol{A}\cdot\left(\boldsymbol{A}^{B}_{b}(\boldsymbol{k}+e\boldsymbol{A}/\hbar)-\boldsymbol{A}^{B}_{b'}(\boldsymbol{k}+e\boldsymbol{A}/\hbar)\right)\right] \\ &\times\boldsymbol{E}(t)\cdot\left(\frac{i}{\hbar}\int_{\Omega} d\boldsymbol{r}\, u^{S,*}_{b,\boldsymbol{k}+e\boldsymbol{A}(t)/\hbar}\frac{\partial}{\partial\boldsymbol{k}}u^{S}_{b',\boldsymbol{k}+e\boldsymbol{A}(t)/\hbar}\right)c_{b'v\boldsymbol{k}}(t).\end{aligned} \tag{16}$$

Although we have $\boldsymbol{A}(t) = -\int_{0}^{t} dt'\boldsymbol{E}(t')$ in physical systems, we shall treat $\boldsymbol{A}(t)$ and $\boldsymbol{E}(t)$ as independent variables for the following mathematical analysis: If $\boldsymbol{E}(t)$ is set to zero, the right-hand side of Eq. (16) becomes zero, and the expansion coefficients become constant. In this case, the dynamics of the time-dependent Bloch states in Eq. (15) are only due to the wavevector shift $\boldsymbol{k}\rightarrow\boldsymbol{k}+e\boldsymbol{A}(t)/\hbar$. Instead, if $\boldsymbol{A}(t)$ is set to zero, the wavevector shift has no effect in Eqs. (15) and (16). Accordingly, the intraband

transitions can be defined as transitions induced by $\boldsymbol{A}(t)$, while the interband transitions can be defined as transitions induced by $\boldsymbol{E}(t)$.

References

(1) Houston, W. V. Acceleration of electrons in a crystal lattice. *Phys. Rev.* **1940**, 57, 184–186. DOI: 10.1103/PhysRev.57.184

(2) Krieger, J. B.; Iafrate, G. J. Time evolution of Bloch electrons in a homogeneous electric field. *Phys. Rev.* B **1986**, 33, 5494–5500. DOI: 10.1103/PhysRevB.33.5494