Method to deal with random phases generated in \textit{ab-initio} algorithms

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Transition dipole moments between energy bands of solids deserve special attention nowadays as non-adiabatic transition can be easily achieved by strong laser. Driven by strong laser with long wavelength, the excited electron wavepacket can even go across the first Brillouin zone. It requires continuous and periodic transition dipole moments if people want to deal with the interaction of strong laser with crystal in a finite space. While, it is hard to get such kind of transition dipole moments from the \textit{ab-initio} algorithms because random phases will be introduced into the eigenfunction for each $k$ point. In this paper, we show how to get the continuous and periodic $k$-dependent dipole moments in “smooth-periodic” gauge. Based on the accurate transition dipole moments, high-order harmonic generations from MgO with inversion symmetry and ZnO with broken symmetry are revisited. The symmetry properties of transition dipole moments with respect to $k$ ensure the absence of even-order harmonics in system with inversion symmetry, even though multiband excitation exists in the laser-driven transition. The harmonic spectrum from ZnO is also improved with accurate transition dipole moments compared to the previous simulation.

I. INTRODUCTION

In the past, band theory has been successfully applied to explain many phenomena in solids. Many physical concepts are built based on it. In the past decade, strong laser technology paved the way to investigate many high-order nonlinear and ultrafast phenomena in solids, such as high-order harmonic generation (HHG)\cite{15}, laser-induced charge transfer\cite{6,2}, Bloch oscillation\cite{10,12}, laser-controlled dielectrics\cite{13,14} and ultrafast renormalization\cite{15,17}. There are too many works that we can’t cite all of them here. Equations of motion based on band theory and crystal-momentum representation, for example semiconductor Bloch equations (SBEs)\cite{18,20} and other extended forms\cite{21,22}, have already been used to explain these ultrafast phenomenons. As more and more experimental data we got, it is found that $k$-dependent transition dipole moments (TDMs) between energy bands should be treated in a more accurate way. In the interaction of strong laser with solids, non-adiabatic transitions of electrons between bands sometimes become remarkable. And, the excited electron wavepacket can even go across the first Brillouin zone driven by strong laser with long wavelength. As we know, when the carrier is moving along a path, the wavepacket will acquire a dynamical phase and a geometry phase\cite{23}. Previously, people thought only when the path is closed the geometry phase can be ensured gauge-invariant. Now, it is clear that when the dipole phase is included in the SBEs, the combination of geometry phase and dipole phase is well defined\cite{27}, no matter the path is closed or open. Both of these two phases will be encoded in the macroscopic polarization, and thus the photonic signal\cite{26}.

In order to describe the interaction of strong laser with solids in a finite $k$ space and include the phase obtained by moving wavepacket, it requires that: 1) the TDMs should be calculated accurately for the whole first Brillouin zone; 2) the TDMs with $k$-dependent phase should be continuous and periodic with respect to $k$. Chao et al.\cite{24} obtained improved HHG spectra by calculating the absolute values of TDMs using ab-initio software. While, it is not easy to ensure the continuity of TDMs if the phases are kept, because the \textit{ab-initio} algorithms will introduce random phases into the eigenfunction for each $k$. Jiang et al.\cite{28} reproduced the orientation-dependent feature of the experimental HHG spectra from ZnO using analytic dipole phase obtained from tight-binding model. While this is not a very general method because it is quite hard to get accurate analytic solutions of eigenvectors for these systems that many atomic orbitals contribute to the states involved by the laser.

The problem of random phase has been studied for a long time\cite{29,32}. While, as pointed by Yakovlev\cite{32}, they either do not ensure the periodicity with respect to $k$ or require the evaluation of so-called covariant derivatives. Recently, the “smooth procedure” provided in Ref.\cite{32}, which will be shown in detail later, is widely used in strong field\cite{27,34,35}. In the present work, we will show that this “smooth procedure” is not robust. It is proved that this method will introduce Zak’s phase\cite{32} into the eigenfunction which will break the periodicity of the TDMs. We provide different ways for systems with and without inversion symmetry to take off the non-periodic part of the additional phase in order to ensure the periodicity of TDMs. We call the final gauge
“smooth-periodic” gauge to distinguish it from the “periodic gauge”. In this gauge, we conclude the symmetry properties of k-dependent eigenfunctions and TDMs for system with inversion symmetry. This kind of symmetry properties can ensure the absence of even-order harmonics in system with inversion symmetry driven by long pulses, even though multi-band excitation exists in the excitation process. HHG from ZnO in the direction with broken symmetry is also revisited using the improved TDMs. The HHG spectrum is improved greatly compared with previous simulation.

II. COMMONLY USED “Smooth Procedure”

The commonly used “smooth procedure” was described by M. Hjelm[32] in detail and widely used in many other works. It is necessary to show this method briefly here. The Bloch wavefunction is expressed as \( \Phi_m(k, r) = e^{ikr}u_m(k, r) \) where \( u_m(k, r) \) is periodic \( u_m(k, r) = u_m(k, r + \hat{R}) \) in most of the ab-initio softwares, the periodic part k is expanded by plane waves \( u_m(k, r) = \sum_n a(k + G_n)e^{iG_n r} \). In principle, the Bloch functions are periodic in k space \( \Phi_m(k, r) = \Phi_m(k + G, r) \). Here, G is the reciprocal lattice vector. While, the eigenfunctions are obtained separately for different k points which leads to random phases \( \varphi_m(k) \), \( u'_m(k, r) = u_m(k, r)e^{i\varphi_m(k)} \). Please note that \( \varphi_m(k) \) is randomly generated and is discrete with respect to k. In the “smooth procedure”, a complex number \( z_m(k) \) is defined as

\[
z_m(k) = |z_m(k)|e^{i\alpha_m(k)} = (u'_m(k, r)|u''_m(k + \Delta k, r))
\]

(1)

A new wavefunction is constructed by

\[
u'_m(k + \Delta k, r) = u'_m(k + \Delta k, r)e^{-i\alpha_m(k)}
\]

(2)

By renaming the function \( u''_m(k + \Delta k, r) \) according to

\[
u''_m(k + \Delta k, r) = u''_m(k + \Delta k, r)
\]

the same procedure can be repeated to the next point

\[
u''_m(k + 2\Delta k, r)
\]

When this procedure goes over the first Brillouin zone, the phase-modified wavefunction become continuous with respect to k. We rename the final wavefunction after the “smooth procedure” as \( u''_m(k, r) \) to distinguish it from the original one generated by ab-initio software.

While, the validity of this method is still worth discussing. As \( \Delta k \) is small enough,

\[
e^{i\Delta k(u_m(k, r)|\nabla_k u_m(k, r)) + i(\varphi_m(k + \Delta k) - \varphi_m(k))}
\]

(4)

which leads that

\[
u''_m(k + \Delta k, r) = u_m(k + \Delta k, r)e^{-\Delta k(u_m(k, r)|\nabla_k u_m(k, r)) + i\varphi_m(k)}
\]

(5)

As the procedure of Eq. (1-3) goes over the path \( k_0 \rightarrow k_0 + k \), the phase-modified wavefunction becomes

\[
u'_m(k, r) = u_m(k, r)e^{i\int_{k_0}^k dsD_{mm}(k)e^{i\varphi_m(k)}}
\]

(6)

where \( D_{mm}(k) = i\langle u_m(k, r)|\nabla_k u_m(k, r) \rangle \) is the Berry connection. To conclude this method, it forces the wavefunction to be continuous with respect to k, and the new Berry connection \( D_{mm}(k) = i\langle u''_m(k, r)|\nabla_k u''_m(k, r) \rangle = 0 \). While, at the same time it introduces a phase of \( \Theta_m(k) = \int_{k_0}^k dsD_{mm}(k) + \varphi_m(k) \) to the eigenfunction. The additional phase \( \Theta_m(k) \) will break the periodicity of the eigenfunction. Because \( u''_m(k, r) \) can be derived by gauge transformation from \( u''_m(k, r) \) somehow, e.g. \( u''_m(k, r) = u''_m(k, r)e^{i\beta(k)} \). Here, \( u''_m(k, r) \) satisfies the k-p equation, which means

\[
u''_m(-k, r) = \sum_m u''_m(k, r)e^{i\beta(k)}
\]

(7)

In order to ensure \( D_{mm}(k) = 0 \), \( \beta(k) = \Delta(k) + \text{const.} \) where \( \Delta(k) \) is an odd function with respect to k. Further, if the system has inversion symmetry,

\[
u''_m(k, r) = \pm u''_m(k, -r), u''_m(-k, r) = \pm u''_m(k, -r)
\]

(8)

and \( \beta(k) = \text{const.} \). In the followed two sections, we will provide different methods to deal with the non-periodicity for systems with and without inversion symmetry.

III. SYSTEM WITH INVERSION SYMMETRY

Please keep in mind that, the eigenfunction \( u_m(k, r) \) is defined in “periodic gauge”[37]. As shown by Zak[36], in 1989, the Zak’s phase \( \gamma = \int_{k_0}^{k_0 + G} dsD_{mm}(k) \) equals to 0 or \( \pi \) in “periodic gauge”. Thus, the situation becomes clear for system with inversion symmetry. The most easy way is to extend the “smooth procedure” to the second Brillouin zone. In this way, phase difference between the starting point \( k_0 \) and \( k_0 + 2G \) is 0 or \( 2\pi \), which means the periodicity of eigenfunction in k space is \( 2G \).

In this section, rock-salt MgO with inversion symmetry is taken as example to explain our method. Fig. 1 (b) shows the band structure of MgO along \((-1,0,0)\rightarrow(0,0,0)\rightarrow(1,0,0)\). Fig. 1 (c)-(e) are the corresponding TDMs calculated by the above method between different pairs of bands. The eigenfunctions are calculated by DFT package in VASP[38] using the Perdew-Burke-Ernzeroff GGA functional. The cutoff energy of plane wave is 500 eV. K-point grid of 20\times20\times20 with none-zero weight in the first Brillouin zone and 400 points with zero weight along \((-1,0,0)\rightarrow(0,0,0)\rightarrow(1,0,0)\) is set. Since the DFT simulation underestimates the band gap, the conduction bands are shifted to get better agreement with the experimental gap 7.8 eV. As expected, both the energy bands and TDMs are periodic with \( 2G \). In Fig.
2, we also present the HHG spectra calculated by semi-conductor Bloch equations (SBEs) with one valence band (band 2) and two conduction bands (band 3 and band 4) included. The right part of the dashed line is from the recombination of electron-hole pair from the second conduction band (band 4) to the valence band (band 2) [26]. The green arrow is similar to the cooper minimum which comes from the minimum of the absolute value of dipole moments between band 2 and band 3. This minimum can be also seen in the TD-DFT simulation in Ref. [39]. So, it is promising to observe this minimum in the experiment, if the range of the detected photon energy can be increased [26, 40, 41]. This kind of minimum will be discussed in detail in another paper [42].

Because the difference of the dipole phases for positive and negative Brillouin zone is 0 or 2π, it is not needed to consider the dipole phase when considering the interference between two adjacent XUV bursts (see Eq. (2) in [26]).

There is no doubt that even-order harmonics are absent if the driven laser is long pulse because of the inversion symmetry of MgO. In the work of R. Huber et al. [5], they used multiband excitation (ME) to explain the generation of even harmonics in GaSe. Why the ME can’t generate even harmonics in system with inversion symmetry even though more than two bands are involved?

![Figure 1](image)

**TABLE I.** properties of TDMs for different “parities” of eigenfunctions

| $u_m(k, r)$ | $u_m^e(k, r)$ | $D_m^e(k)$ |
|-------------|---------------|-----------|
| $u_m(-k, r)$ | $u_m(-k, r)$ | $D_m^e(-k)$ |
| $u_m^e(-k, r)$ | $u_m^e(-k, r)$ | $D_m^e(-k)$ |
| $u_m(k, r)$ | $u_m^e(k, r)$ | $D_m^e(k)$ |
| $u_m(-k, r)$ | $u_m(-k, r)$ | $D_m^e(-k)$ |

**IV. SYSTEM WITH BROKEN SYMMETRY**

For system with broken symmetry, the Zak’s phase can be any value. Thus the method above for system with
FIG. 2. HHG spectra from MgO calculated by three-band SBEs. The equations are solved in the extended Brillouin zone and all the elements used in the SBEs model are from Fig. 1. Laser parameter: 50 fs/1300nm/1×10^{13} W/cm^2

FIG. 3. Illustration of transition path of electrons for gas phase and solid phase with inversion symmetry. For gas phase, a triangle system will never be formed because the transition between states with same parity is forbidden. While, for solid case where the energy levels are extended into bands, transition between bands at these k points away from Γ are not strictly forbidden. The symmetry properties of the TDMs will ensure the absence of even order optical signal.

inversion symmetry is not valid anymore. Please keep in mind that in the periodic gauge the Berry connection is periodic \( D_{mm}(k) = D_{mm}(k + G) \), which means it can be expanded as

\[
D_{mm}(k) = g_m(k) + \sigma_m
\]

where \( g_m(k) = \sum_{n=1}^{\infty} f_1(n) \cos(nLk) + f_2(n) \sin(nLk) \) is the AC component and \( \sigma_m \) is a constant which can be regarded as DC component. The AC component will lead to divergence of the introduced additional phase \( \Theta_m(k) = \int_{k_0}^{k} d\kappa D_{mm}(\kappa) + \varphi_m(k_0) \). We don't need to care about the AC part, because this component won't influence the periodicity, continuity and the final observable physical quantity \[27\]. If the “smooth procedure” is carried out for the first Brillouin zone, the DC-induced non-periodic phase of the TDMs between band \( m \) and \( n \) is \( (\sigma_n - \sigma_m)k \).

FIG. 4. Red line is the k-dependent dipole phase generated by “smooth procedure”. This kind of phase is not periodic because of the DC part in the additionally introduced phase. The black line is the k-dependent dipole phase after the DC component is taken away by our method.

Here we take the direction \( \Gamma - A \) of wurtzite ZnO as an example. In Fig. 4, the red line is the k-dependent dipole phase for the first Brillouin zone obtained from VASP using “smooth procedure”. As stated above, the dipole phase can not be ensured to be periodic, because of the DC component. While, it is easy to get the slope by \( (\sigma_n - \sigma_m) = (\alpha_{mn}(\pi/L) - \alpha_{mn}(-\pi/L))/G \). Here, \( \alpha_{mn} \) are the phase of TDMs which are read from the data generated by “smooth procedure” shown by the red line in Fig. 4. Then, we can get the periodic dipole phase by taking off the DC part, \( D_{p_{mn}}(k) = D_{p_{mn}}(k)e^{i(\sigma_m - \sigma_n)k} \) which is shown by the black line in Fig. 4 for ZnO. At the same time, the Berry connection is changed from zero to \( D_{p_{mn}}^\pi(k) - D_{p_{mn}}^\xi(k) = \sigma_m - \sigma_n \). Now, all the elements in the SBEs model are periodic and continuous with respect to k. That is to say the equation of motion for carriers can be solved in a finite k space validly at this very moment. In Fig. 5, the calculated HHG spectrum (blue line) by solving two-band SBEs model using TDMs obtained by our “smooth-periodic” procedure is compared with the experimental data (green line). We also present the spectrum (red line) by solving two-band SBEs including only dipole phase obtained from tight-binding model. Even though tight-binding model can approximatively reproduce the orientation-dependent feature of HHG spectra, usually it is too rough to produce the relative strength between odd and even order harmonics. Using accurate TDMs obtained from ab-initio software with the help of our “smooth-periodic” procedure, the harmonic spectrum has been improved greatly.
to deal with non-adiabatic dynamics, especially when the external field is strong laser. We show that the commonly used “smooth procedure” can not ensure the periodicity of the wavefunction. In this paper, we provide two different methods to overcome this defect for system with and without inversion symmetry. Because our approaches ensure the continuity and periodicity of all the elements used in the equations of motion, the gauge resulting by the transformation of our methods can be referred to as “smooth-periodic” gauge to distinguish it from Resta’s periodic gauge. Based on this gauge, the HHG from solids with and without inversion symmetry is revisited. It is emphasized that the symmetry properties are the key factors to ensure the absence of even order harmonics for system with inversion symmetry. With the accurate TMDs with dipole phase and Berry connection, the HHG spectrum from ZnO with broken symmetry is also improved greatly. Our work is a foundation to the application of optical signal from solids, such as laser waveform control, band/dipole reconstruction and detecting dynamic information.

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[1] S. Ghimire, A. D. DiChiara, E. Sistrunk, P. Agostini, L. F. DiMauro, and D. A. Reis, Nat. Phys. 7, 130 (2011).
[2] S. Gholam-Mirzaei, J. Beeta, and M. Chini, Appl. Phys. Lett. 110, 061101 (2017).
[3] G. Vampa, et al., Nature (London) 522, 462 (2015).
[4] T. T. Luu, et al., Nature 523, 490 (2015).
[5] M. Hohenleutner, et al., Nature (London) 523, 572 (2015).
[6] A. Schiffrin, et al., Nature 493, 70 (2013).
[7] S. Yu. Kruchinin, M. Frohman, V. S. Yakovlev, Phys. Rev. B 87, 112201 (2015).
[8] T. Paasch-Colberg et al., Nat. Photon. 8, 214 (2014).
[9] G. Wachter, et al., Phys. Rev. Lett. 113, 087401 (2014).
[10] O. Schubert et al., Nat. Photonics 8, 119 (2014).
[11] L. Li, P. Lan, X. Liu, L. He, X. Zhu, O. D. Mücke, P. Lu, Optics Express 26, 23844 (2018).
[12] L. Liu, J. Zhao, J. M. Yuan, Z. X. Zhao, Chin. Phys. B 28, 114205 (2019).
[13] M. Schultze et al., Nature 493, 75 (2013).
[14] M. Schultze, et al., Science 346, 1348 (2014).
[15] A. Chernikov, C. Ruppert, H. M. Hill, A. F. Rigosi, T. F. Heinz, Nature Photonics 9, 466 (2015).
[16] L. Meckbach, T. Stroucken, and S. W. Koch, Appl. Phys. Lett. 112, 061104 (2018).
[17] L. Meckbach, et al., Ultrafast band-gap renormalization and build-up of optical gain in monolayer MoTe₂. arXiv preprint arXiv:1903.08553 (2019).
[18] D. Golde, et al., Phys. Rev. B 77, 075330 (2008).
[19] T. T. Luu, H. J. Wörner, Phys. Rev. B 94, 115164 (2016).
[20] H. Haug, S. W. Koch, Quantum Theory of the Optical and Electronic Properties of Semiconductors: Fifth Edition. World Scientific Publishing Company, 2009.
[21] G. Vampa, et al., Phys. Rev. B 91, 064302 (2015).
[22] Z. Wang, et al., Nat. Commun. 8, 1686 (2017).
[23] L. Meckbach, T. Stroucken, and S. W. Koch, Phys. Rev. B 97, 0354425 (2018).
[24] C. Yu, et al., Phys. Rev. A 94, 013846 (2016).
[25] M. V. Berry, Proc. R. Soc. London, Ser. A 392, 45 (1984).
[26] Y. S. You, et al., Opt. Lett. 42, 1816 (2017).
[27] J. Li, et al., Phys. Rev. A 100, 043404 (2019).
[28] S. C. Jiang, et al., Phys. Rev. Lett. 120, 253201 (2018).
[29] K. S. Virk, J. E. Sipe, Phys. Rev. B 76, 035213 (2007).
[30] R. W. Nunes, X. Gonze, Phys. Rev. B 63, 155107 (2001).
[31] I. Souza, et al., Phys. Rev. B 69, 085106 (2004).
[32] U. Lindefelt, H. E. Nilsson, and M. Hjelm, Semicond. Sci. Technol. 19, 1061 (2004).
[33] V. S. Yakovlev, M. S. Wismer, Comput. Phys. Commun. 217, 82-88 (2017).
[34] M. X. Wu, et al., Phys. Rev. A 91, 043839 (2015).
[35] M. Du, C. Liu, Y. Zheng, Z. Zeng, R. Li, Phys. Rev. A 100, 043840 (2019).
[36] J. Zak, Phys. Rev. Lett. 62, 2747 (1989).
[37] R. Resta, J. Phys: Condens. Mat. 12, R107 (2000).
[38] G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).
[39] Tancogne-Dejean, et al., Nature communications 8, 745 (2017).

[40] Y. S. You, D. A. Reis, and S. Ghimire, Nature physics, 13, 345 (2017).
[41] Y. S. You, et al., Opt. Lett. 44, 530 (2019).
[42] Y. Zhao, et al., arXiv:1911.12092.