Enhanced high-order harmonic generation in donor-doped band-gap materials

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We find that a donor-doped band-gap material can enhance the overall high-order harmonic generation (HHG) efficiency by several orders of magnitude, compared with undoped and acceptor-doped materials. This significant enhancement, predicted by time-dependent density functional theory simulations, originates from the highest-occupied impurity state which has an isolated energy located within the band gap. The impurity-state HHG is rationalized by a three-step model, taking into account that the impurity-state electron tunnels into the conduction band and then moves according to its band structure until recombination. In addition to the improvement of the HHG efficiency, the donor-type doping results in a harmonic cutoff different from that in the undoped and acceptor-doped cases, explained by semiclassical analysis for the impurity-state HHG.

High-order harmonic generation (HHG) in gases is not only one of the fundamental strong-field phenomena in laser-matter interactions. It is also a powerful technique to produce sub-femtosecond laser pulses, providing the opportunity to explore ultrafast dynamics in matter on femto- and attosecond timescales. Recently, HHG in solids was demonstrated with potential applications for novel VUV/XUV light sources and for probing ultrafast dynamics in condensed-matter systems. Compared with gas-phase systems, solids can possibly produce HHG more efficiently due to their periodic structure and high density. Also, laser-induced processes in bulk and nanostructured materials attract theoretical interests in this new research area where strong-field laser physics meets condensed matter. It has been demonstrated that some strong-field concepts, such as the three-step model for HHG, can be generalized to describe laser-solid interactions when the band structure is taken into account. Although the understanding of HHG in solids is rapidly expanding, there are many open questions remaining to be explored.

For applications of HHG in solids as a coherent VUV/XUV source, a key question is how to control the harmonic yield. A recent experiment has demonstrated enhanced HHG emission in tailored semiconductors. Theoretical studies have proposed possibilities to enhance HHG in solids by quantum confinement, inhomogeneous fields, or substitutional doping. Indeed, impurities typically influence the physical properties of a solid, allowing one to control processes in the target material for various applications (see, e.g., the recent works). Doping-induced impurities are therefore expected to have impact on HHG in solids. The specific influence of doping-induced impurities, however, still requires further exploration, even in the case of substitutional doping. Here, to elucidate effects of substitutional doping on HHG in solids, we consider a model of undoped and doped band-gap materials interacting with a mid-infrared laser pulse, use time-dependent density functional theory (TDDFT) to perform self-consistent calculations, and provide a semiclassical analysis for the impurity-state HHG cutoff.

Our model employs a finite system so large that it behaves like a solid. We consider a linear chain of $N$ nuclei with a separation $a$ and located at $x_j = (j-(N+1)/2)a$, ($j = 1, \ldots, N$). The ionic potential reads $v_{\text{ion}}(x) = -\sum_{j=1}^N Z_j [ (x-x_j)^2 + \epsilon ]^{-1/2}$, where $Z_j$ is the nuclear charge of the $j$-th ion and $\epsilon$ is a softening parameter which smoothens the Coulomb singularity. We set $\epsilon = 2.25$ and $a = 7$ throughout, and use $Z_j = 4$ ($j = 1, \ldots, N$) to model an undoped band-gap material. For a convenient description of substitutional doping, we choose an odd number of nuclei ($N = 2M - 1$) in this work and introduce an impurity in the center by choosing a different nuclear charge of the $M$-th ion. As we will see below, such a doping rate of $\sim 1\%$ does not change the band structures significantly, but introduces new states that are energetically isolated. Also, our discussion of doping effects is insensitive to the model size; see the Supplemental Material. In our simulations, two doping cases are considered: $Z_M = 2$ (double-acceptor) and $Z_M = 6$ (double-donor). All the considered systems are charge and spin neutral. Thus the number of electrons with opposite spin is $N_\uparrow = N_\downarrow = 2N$ for the undoped case, and $N_\uparrow = N_\downarrow = 2N \pm 1$ for the systems with a doped center ($Z_M = 4 \pm 2$). We treat the field-free electronic states for these systems with density functional theory (DFT). In the Kohn-Sham (KS) scheme, we find a set of KS orbitals determined by

$$\left\{ -\frac{1}{2} \frac{\partial^2}{\partial x^2} + v_{\text{KS}}[(n_\sigma)](x) \right\} \varphi_j,\sigma(x) = \epsilon_j,\sigma \varphi_j,\sigma(x),$$

with the static KS potential $v_{\text{KS}}[(n_\sigma)](x) = v_{\text{ion}}(x) + v_{\text{H}}[n](x) + v_{\text{XC}}[(n_\sigma)](x)$. The Hartree potential reads $v_{\text{H}}[n](x) = \int dx' n(x') [(x-x')^2 + \epsilon]^{-1/2}$, and the exchange-correlation potential is treated in a local spin-density approximation $v_{\text{XC}}[n_{\sigma}](x) = -[6n_{\sigma}(x)/\pi]^{1/3}$. The spin densities are $n_{\sigma}(x) = \sum_{j=1}^N |\varphi_{j,\sigma}(x)|^2$ for spin $\sigma = \downarrow, \uparrow$, and the total density is $n(x) = \sum_{\sigma=\downarrow,\uparrow} n_{\sigma}(x)$.

For the driving laser pulse linearly polarized along
the $x$-axis, we use the vector potential $A(t) = A_0 \sin^2(\omega_0 t/(2N_\text{c})) \sin(\omega_0 t)$ for $0 \leq t \leq 2\pi N_\text{c}/\omega_0$, with $\omega_0$ the angular frequency (photon energy) and $N_\text{c}$ the number of cycles. The laser-driven many-electron system is governed by the time-dependent KS equations

$$i \frac{\partial}{\partial t} \psi_{j,\sigma}(x, t) = \left\{ -\frac{1}{2} \frac{\partial^2}{\partial x^2} - iA(t) \frac{\partial}{\partial x} + \tilde{v}_{\text{KS}}(\{|n_\sigma\}|)(x, t) \right\} \psi_{j,\sigma}(x, t),$$

where the KS potential $\tilde{v}_{\text{KS}}(\{|n_\sigma\}|)(x, t) = v_{\text{ion}}(x) + v_{\text{H}}[\bar{n}](x, t) + v_{\text{xc}}(\{|n_\sigma\}|)(x, t)$ is time-dependent due to the time dependence of $n(x, t)$ and $n_\sigma(x, t)$. We propagate the time-dependent KS orbitals using the Crank-Nicolson approach with a predictor-corrector step for updating the KS potential [44]. The initial conditions for TDDFT calculations, i.e., the field-free ground-state KS orbitals are found via imaginary time propagation with orthogonalization in each time step [44]. The simulation parameters are given in the Supplemental Material [43].

We first take a view on the doping-induced change of the field-free properties in the DFT language. The undoped model was studied in Refs. [28, 29]. Here we first emphasize the differences between the doped and undoped systems. (b) The negative-valued orbital energies in ascending order, including two valence bands (VB1 and VB2) and part of a conduction band (CB1). The considered doping scenarios do not cause any significant change of the band structures [43]; instead, they generate energetically isolated orbitals that do not belong to any band. As an illustration, we present in Fig. 1(b) the negative-valued orbital energies in ascending order. The energies include two valence bands (VB1 and VB2) and part of a conduction band (CB1), and the “in-band” energies remain almost unchanged by doping. The visible band gap (BG) allows us to indentify the doping-induced impurity orbitals with isolated energies; see also the Supplemental Material [43]. In addition to their isolated energies, the impurity orbitals are spatially localized around the impurity ion [43].

The impact of the impurity is restricted in real space to a small region around its position, the center of the system in this case, as shown in Fig. 1(a). Compared with the undoped system, the acceptor- and donor-type doping results in a shallower and deeper effective potential around the impurity ion, respectively [43].

FIG. 1. Comparisons of undoped and doped systems in the KS scheme. (a) The KS potentials around the impurity for the undoped and doped systems. (b) The negative-valued KS orbital energies in ascending order, including two valence bands (VB1 and VB2) and part of a conduction band (CB1). The BG regime for the undoped system. The HHG spectrum |$\omega_0 = 0.0114$ corresponding to a wavelength of $\sim 4000$ nm. We compute the time-dependent current

$$J(t) = \sum_{j,\sigma} \int dx \ \text{Im} \left[ \psi_{j,\sigma}^*(x, t) \frac{\partial}{\partial x} \psi_{j,\sigma}(x, t) \right],$$

and evaluate the HHG spectral intensity as the modulus square of the Fourier-transformed current, i.e., $S(\omega) \propto |\int dt J(t) \exp(-i\omega t)|^2$. Here we do not account for macroscopic propagation effects, which may modify the HHG spectra via absorption and phase mismatch. Such propagation effects, however, can be mitigated by controlling the thickness of target materials [43] or using nanowires [53]. Therefore we expect our conclusions to hold for a thin target material.

Figure 2(a) shows HHG spectra for the undoped and doped systems obtained from TDDFT calculations, for an intensity of $\sim 2.2 \times 10^{11}$ W/cm$^2$. The BG between CB1 and VB2 is $0.235 \sim 6.4$ eV typical for a dielectric, implying that harmonics up to order 20 are in the sub-BG regime for the undoped system. The HHG spectrum for the acceptor-doped system is very similar to that for
To understand the doping effects on HHG, we link our calculations with the KS potential frozen to its field-free ground-state form. The laser parameters correspond to a wavelength of $\sim 4000$ nm and a peak intensity of $\sim 2.2 \times 10^{11}$ W/cm$^2$ (see text). The vertical dashed lines indicate the first cutoffs: a cutoff of order 45 is observed for the undoped and acceptor-doped systems while a cutoff of order 25 is observed for the donor-doped system (see semiclassical analysis below).

The spectra obtained from these calculations are at low intensities well below the damage threshold of solids [28]. The considerable enhancement of HHG in the donor-type doping case and the similarity of the undoped and acceptor-doped cases are also found with this approach. As will be shown below, the frozen-KS-potential approach offers the possibility to identify the contribution from a single impurity orbital, which provides insights into the observed enhancement of HHG in the donor-type doping case. In addition, a different cutoff for the donor-doped system is found in Fig. 2, which will be analyzed below.

To understand the doping effects on HHG, we link our findings in Fig. 2 to the doping-induced changes of the field-free properties displayed in Fig. 1. Let us first revisit the intra- and interband contributions of HHG in undoped solids [12, 13]. Intraband HHG stems from the laser-driven electron motion in bands due to the anharmonicity of the band structure. Interband HHG is described by the generalized three-step model for band-gap materials: first an electron tunnels into the conduction band, leaving a hole in the valence band; then the electron and hole move in their respective bands and may recombine at a later time, emitting a photon with energy above the BG. Thus the BG energy plays a similar role as the ionization potential in atomic HHG. If the energy of the highest-occupied orbital is close to the lowest conduction-band energy, the electron has a high probability to tunnel into the conduction band, since the tunneling rate is exponentially sensitive to the energy gap [51]. As shown in Fig. 1(b), the considered doping causes no obvious change to the band structures, except for introducing the impurity orbitals. The similarity of HHG spectra for the acceptor-doped and undoped systems can then be understood by noting that the highest-occupied orbital in both cases is at the top of VB2 [see Fig. 1(b)]. For the donor-doped system, we expect that the highest-occupied impurity orbital within the BG is responsible for the enhancement of HHG observed in Fig. 2.

The role of the highest-occupied impurity orbital in the donor-doped system can be highlighted within the frozen-KS-potential approach. To this end, we calculate the current from the highest-occupied orbital by restricting the sum in Eq. (4) to that orbital, and compare the resulting HHG spectrum with the total one in Fig. 3. One can see that for a wide range of harmonic orders, from $\sim 10$ to $\sim 160$, the contribution from the single impurity orbital agrees with the total spectrum. Therefore we attribute the enhancement of HHG in the donor-doped system to the highest-occupied impurity orbital that has an isolated energy within the BG. We note that impurity-state HHG was modeled in a recent work [52] taking only the impurity-state contribution into account when evaluating the HHG spectrum. Based on the self-consistent many-electron calculations, our present work evidences that the impurity-state HHG signal may agree with the total signal for a wide range of harmonic orders in a donor-doped band-gap material.

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**FIG. 2.** HHG spectra for undoped and doped systems obtained from (a) TDDFT calculations with the KS potential dynamically updated according to the time-dependent densities, and (b) calculations with the KS potential frozen to its field-free ground-state form. The vertical dashed lines indicate the first cutoffs: a cutoff of order 45 is observed for the undoped and acceptor-doped systems while a cutoff of order 25 is observed for the donor-doped system (see semiclassical analysis below).

**FIG. 3.** HHG spectra for the donor-doped system obtained from calculations with the frozen KS potential [the thick grey curve, which is the same as the upper red curve in Fig. 2(b)]. The purple and green curves are obtained by Fourier transforming the partial current calculated with only the highest-occupied KS orbital and without this orbital, respectively.
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