A real-time TDDFT study of femtosecond laser driven monolayer NbSe₂

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We studied femtosecond laser driven electronic response of monolayer NbSe₂ using state-of-the-art computational methods, synthesis and optical characterization. Earlier studies have found distinct signatures of charge density wave (CDW) ordered phases in the ground state (∼ 0 K) of NbSe₂ monolayer, in co-existence with superconducting phase. Driving such systems with ultra-short (femtosecond) laser pulse can provide the highly sought knowledge on how to effectively control various exotic phases (e.g. CDW) of monolayer NbSe₂ with external control parameters such as pulse intensity. This will not only provide a fundamental understanding of non-equilibrium phase-transitions in NbSe₂, but also will open path-forward to revolutionize quantum information technologies such as valleytronics. Inspired by this, we have studied higher harmonic generation (HHG) in monolayer NbSe₂ under various intensities of femtosecond laser pulse using real-time time-dependent density functional theory (RT-TDDFT). Our computation predicted distinct signatures in HHG spectra for some higher harmonic modes in the presence of CDW orders in monolayer NbSe₂. Excitation energies under strong pulse, and power-law behavior of HHG spectra are also reported.

I. INTRODUCTION

Electronic instabilities have led to novel phases such as superconductivity (SC) and charge density ordering (CDW) in several lower dimensional transition-metal dichalcogenide (TMDC) systems. Extensive experimental and theoretical studies have identified SC phases in monolayer PbTe₂ [1], 2H-TaS₂ [2], 2H-TaSe₂ [2], and 2H-NbSe₂ [3]. Interestingly, a co-existing CDW ordered phase has also been identified in 2H-NbSe₂ [4, 5] below T_{c,CDW} = 33 K and in 2H-TaSe₂ below T_{c,CDW} = 120 K. Earlier neutron scattering [8] and X-ray diffraction [9] data have revealed the periodic lattice distortion in monolayer NbSe₂, which causes the CDW ordered superlattice. However, the fundamental mechanism and the nature of CDW phase in monolayer NbSe₂ have not been fully understood and remains a matter of great discussions [7]. Although 2D Pierls type instability due to Fermi surface nesting was proposed earlier [10], more compelling experimental evidence and theoretical arguments are now developed in favor of electron-phonon mediated CDW order formation in monolayer NbSe₂ [11, 12], which remains metallic below 33 K and superconducting below 7 K. Such a unique metallic CDW phase in NbSe₂ has been supported by structural characterization [8, 9, 13], where slightly incommensurate CDW modulation in a 3 × 3 supercell of monolayer NbSe₂ was observed.

In this Article, we study the conduction electron response in CDW ordered phase of monolayer NbSe₂ under ultra-short laser pulse. Electronic excitation under strong driving field creates rich electro-optical phenomenon such as higher harmonic generation (HHG) [14, 15] causing some non-equilibrium phase-transition. The modes in higher harmonic spectra in solid materials often carry valuable spectral signatures, which helps to identify various dynamical symmetry-breaking (or ordering) of lattice-structure information. Controlling such non-equilibrium phases in monolayer NbSe₂ with femtosecond laser pulse could, in principle, provide a pathway to understand the fundamental competing mechanisms (e.g. SC, CDW), which in turn will potentially develop new insights for tuning material functionalities such as conductance and valley degrees of freedom highly relevant for quantum information technology.

To theoretically probe the CDW ordered phase of monolayer NbSe₂ under intense field, we employed real-time time-dependent density functional theory (RT-TDDFT) [18, 19] as implemented in SALMON code [20]. State-of-the-art non-perturbative TDDFT formulation, also known as velocity gauge [21, 22], is used in our theoretical approach in order to preserve the translation-symmetry in periodic solid under strong driving field. Starting with an undistorted (non-CDW) monolayer of 2H-NbSe₂, we have calculated HHG spectra for varying field intensities. Several peak features (odd and even higher harmonic modes) displayed the qualitative nature of symmetry of the system, while non-linear opto-electronic behavior was identified with increasing field amplitude. In this non-linear limit, we also studied the HHG spectra of a CDW ordered monolayer NbSe₂ by considering a commensurate 3 × 3 superlattice. Earlier theoretical work [23] has found negligible difference in the electronic structures between commensurate and nearly incommensurate superlattice structures. Our calculations show interesting differences in some particular HHG spectral modes between CDW and non-CDW ordered phases of NbSe₂ monolayer, thus providing guidance for experimental identification of structural phases, should the material go through some strong laser field. For validation of our theoretical prediction, we have also done preliminary synthesis and optical characterization.
of NbSe$_2$ and found promising qualitative agreements.

II. METHOD

The first-principles RT-TDDFT calculations are performed to understand the nonlinear response of monolayer NbSe$_2$ under intense laser field. Synthesis of single layer NbSe$_2$ is immensely challenging due to a stringent growth requirement [26].

A. Theoretical Approach

The workhorse of our calculations is RT-TDDFT, which is a non-perturbative method suitably designed for electronic excitations under strong external field. This real-time approach is developed on the foundation of conventional density functional theory [27, 28], but goes well beyond the perturbative or linear response range of time-dependent DFT (TDDFT) [29] approach. The two key features on which the RT-TDDFT method for periodic systems relies are - (i) stable and efficient real-time propagation of the time-dependent Kohn-Sham orbitals using a time dependent Hamiltonian, and (ii) ‘velocity gauge’ formulation of Hamiltonian where a time-dependent vector gauge field is used in the kinetic term instead of a time-dependent interaction term which otherwise will break the translational symmetry of periodic systems. Bertsch and Yabana [21, 22] originally proposed the velocity gauge formulation of real-time time-dependent Kohn-Sham (TDKS) equation, which has recently been implemented in a few TDDFT codes. We briefly describe the governing RT-TDDFT equations here starting with a general time-dependent Kohn-Sham Hamiltonian:

\[
i \hbar \frac{\partial}{\partial t} \psi_i(r,t) = \hat{H}_{KS} \psi_i(r,t),
\]

where

\[
\hat{H}_{KS} = \frac{p^2}{2m} + \hat{V}_{\text{ion}} + \int \frac{e^2}{|r - r'|} n(r,t) + V_{xc}[n(r,t)] + e\mathbf{E}(t) \cdot \mathbf{r}.
\]

The third term represents Hartree Coulomb interaction while the fourth term $V_{xc}$ is the exchange-correlation potential. Here electron density $n(r,t) = \sum_i |\psi_i(r,t)|^2$. One instantly recognizes that time-dependent external interaction potential term $e\mathbf{E}(t) \cdot \mathbf{r}$ breaks the translational symmetry of periodic systems. Such concerns are addressed by adopting the ‘velocity gauge’ where a vector field, defined as

\[
\mathbf{A}(t) = -c \int_t^T \mathbf{E}(t') dt',
\]

is used to gauge-transform the KS wave functions as

\[
\psi'(r,t) = \exp \left[ \frac{ie}{\hbar c} \mathbf{A}(t) \cdot \mathbf{r} \right] \psi(r,t).
\]

The velocity-gauge TDKS Hamiltonain now takes the form:

\[
\hat{H}_{KS}^{\text{RT}} = \frac{1}{2m} \left[ \mathbf{p} + \frac{e}{c} \mathbf{A}(t) \right]^2 + \hat{V}_{\text{ion}}
+ \int \frac{e^2}{|r - r'|} n(r,t) + V_{xc}[n(r,t)],
\]

The external field or interaction potential is now incorporated in the kinetic energy term, and consequently the translational symmetry of the Hamiltonian is restored. The time-dependent KS orbitals are now evolved using:

\[
i \hbar \frac{\partial}{\partial t} \psi_i(r,t) = \hat{H}_{KS}^{\text{RT}} \psi_i(r,t).
\]

Different time evolution propagators are constructed from the above equation, and their forms depend on the choice of basis set (e.g. overlap and Hamiltonian matrix elements) of the original DFT formalism. Detailed discussion on the propagators can be found elsewhere [30, 31].

Finally, the time-dependent current density

\[
\mathbf{J}(t) = -\frac{i}{2\hbar} \int_\Omega \mathbf{r} \sum_i [\psi_i^*(r,t) \nabla \psi_i(r,t) - \text{c.c.}]
\]

is obtained, whose Fourier transform gives the HHG spectra:

\[
\text{HHG}(\omega) = \omega^2 \left| \int_0^T \mathbf{J}(t) \exp(-i\omega t) dt \right|^2.
\]
FIG. 2: (Color online) HHG spectra for non-CDW phase of monolayer NbSe$_2$.

FIG. 3: (Color online) Comparing HHG spectra in CDW distorted phase vs non-CDW phase of monolayer NbSe$_2$. The applied external field is in a-direction.

B. Computational Approach

The above formalism for RT-TDDFT has been implemented in a handful of codes such as TDAP [32], RT-SIESTA [22], OCTOPUS [33], and SALMON [20] among a few others with some variations to adopt to their original DFT methods. We have used SALMON which showed efficient scalable behavior in modern HPC platform, particularly suitable for our systems of interest. Since SALMON can only consider rectangular unit cell, we have considered a rectangular cut (Fig. 3(c)) with $3 \times 6$ supercell 2H-NbSe$_2$, which has a minimal size to capture the experimentally established CDW distorted periodic superlattice. We used $2 \times 2 \times 2$ $k$-point sampling in the Brillouin Zone (BZ) of the supercell. Higher accuracy was achieved using a $28 \times 32 \times 30$ real-space grid. We have used Trouiller-Martin type LDA-FHI pseudo-potentials for Nb and Se atoms [34, 35], where 5 ($4d^45s^1$) and 6 ($4s^24p^4$) valence electrons were considered, respectively.

To be compatible with experiments, we have used a laser-pulse with crystal $a$-direction and [100] polarization (a-direction in xy plane) with pulse shape:

$$A_x(t) = -c E_o \frac{\omega_o}{\omega_o} \cos(\frac{\pi L}{\omega_o}) \ln\left(\frac{\tau}{\tau - t}\right), \quad (9)$$

where the electric field can alternatively be defined as:

$$E_x(t) = -\frac{1}{c} \frac{\partial A_x(t)}{\partial t} = \frac{E_o}{\omega_o} \frac{\partial}{\partial t} \left[ \frac{\cos(\frac{\pi t}{\omega_o}) \sin^2(\frac{\pi t}{\tau_L})}{\Theta(\tau - t)} \right], \quad (10)$$

In this calculation, we have considered the width of the pulse $\tau=30$ fs and frequency $\omega = 0.6$ eV. The intensity of the pulse is related to the amplitude by $I \approx c E_o^2/8\pi$. Such equality only holds for infinite unmodulated wave trains (not pulse), but we ignored the subtle differences and considered the above approximate relation following Bertsch and Yabana [36]. In this work, we have considered three different pulse intensities: $10^{10}$, $10^{12}$, and $10^{14}$ W/cm$^2$. The external field $E_x(t)$ pulse shapes for these intensities are presented in Fig. 1(a). Fourier transformed components (real and imaginary) of the strongest pulse ($10^{14}$ W/cm$^2$) is shown in Fig. 1(b). In this Fourier transformed plot, the dominant peak is observed around $\omega = 0.6$ eV. The electronic response is also expected to be strongest at this frequency as discussed in the ‘results’ section.

Calculations for both CDW and non-CDW structures were performed for 55 fs time-propagation using $\Delta t = 0.0019$ fs as the time step. Such small time-steps are required for the computational stability of real-time propagation algorithm. Both these values were tested to be sufficient for a converged HHG spectra. For time-propagation, we used ‘enforced time-reversal symmetry’ propagator [33].

III. RESULTS AND DISCUSSION

A. HHG Spectra in monolayer NbSe$_2$

One of our primary motivations is to identify distinct key features of the HHG spectra between CDW and non-CDW ordered phases of monolayer 2H-NbSe$_2$ under strong laser pulse. This helps establish a correlation between the external field intensity and non-linear electronic response of materials. Starting with non-CDW ordered phase and using RT-TDDFT approach, we calculated time-dependent current densities at three different laser pulse intensities: $10^{10}$, $10^{12}$, and $10^{14}$ W/cm$^2$ as shown in Fig. 1(c). The dominant peak features in $J(t)$ spectra is found up to 30 fs, which is also the width of the laser pulse. Beyond 30 fs, the tail of the spectra...
FIG. 4: (Color online) Excitation spectra and power law of HHG spectral intensity for the first mode.

shows complex modulated pattern as shown in the inset of Fig. 1(c) for pulse intensity $10^{14}$ W/cm$^2$. This is a clear signature of the non-linear response of the system as the excited electrons in metallic 2H-NbSe$_2$ relax after the pulse passes through. Under intense laser pulse, the conduction and (or) valence electrons go through both interband and intra-band transitions. The spectral feature of real-time current density take the shape of incident laser pulse, which is an indicator of strong intra-band Bloch type oscillation response in metallic monolayer NbSe$_2$. At high enough intensity, the current density has finer features (inset of Fig.1(c)) capturing the non-linear response generating due to inter- and intra-band transitions. Such features are best represented in the Fourier transformed frequency space where various higher order modes in the current density spectra are readily identified. Since our pulse frequency was set to 0.6 eV, we represented the odd- and even-modes as the odd and even integer multiples of this fundamental frequency respectively for the HHG($\omega \rightarrow \text{mode}$) spectra.

Non-linear higher harmonic response of materials is symmetry dependent, and the corresponding optical selection rules [16] prohibits any even-mode transition when the system is purely centrosymmetric with full inversion symmetry. However, the monolayer 2H-NbSe$_2$ crystal structure is slightly noncentrosymmetric, where the inversion symmetry is not fully conserved. Consequently, the HHG spectra shows some signs of weak even-mode peaks (Fig. 2). For the three laser pulse intensities considered in this work, the odd-modes are most distinct for high laser intensity $10^{14}$ W/cm$^2$ (solid black spectra in Fig. 2). Stronger higher harmonic odd-modes and weaker even-modes in the HHG spectra are indicators that the monolayer 2H-NbSe$_2$, though primarily centrosymmetric, does not have full inversion symme-

try. This brings up some of the weaker even-mode peaks. Therefore, it is expected that emergence of any ordering (e.g. CDW) in this system might enhance some even-mode peaks, and could be a signature of the corresponding phase. For verification, we considered a CDW ordered 3×6 superlattice structure (Fig. 3c) and computed the HHG spectra for laser intensity $10^{14}$ W/cm$^2$. Interestingly, some enhancement of 2nd and 6th harmonic modes are observed (Fig. 3b). These are clear signatures of the CDW ordered phase of NbSe$_2$ under intense laser pulse. We also present RT-TDDFT calculated total excitation energies of undistorted (non-CDW) and distorted (CDW) phase of monolayer NbSe$_2$ as shown in Fig. 4 (top panel). Corresponding vector gauge field is also plotted. The peak amplitudes of HHG spectra follow a power-law behavior with increasing pulse intensity. Such behavior for the first mode amplitude is shown in Fig. 4 (bottom panel).

IV. CONCLUSION

As a proof of principle, our study of higher harmonic generation in monolayer NbSe$_2$ under ultrashort laser-pulse has demonstrated significant promise in revealing the CDW ordered phases and their controlled behavior under driven condition. The characteristic features of the HHG spectral peaks show underlying symmetry properties, and how they evolve with increasing laser intensity. We have theoretically identified enhancement of some higher order even-modes (e.g. 2nd and 6th) in the HHG spectra of CDW ordered NbSe$_2$ in comparison to that of non-CDW ordered pure crystalline phase. These predictions provide guidance for future experiments by reducing the parametric search space for characterizing the non-linear electronic response of monolayer NbSe$_2$. The work presented here creates a path forward to discover new ‘tuning’ and ‘control’ principles for lower dimensional TMDC materials in general with competing quantum phases.

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