Influence of Coulomb correlations on high harmonic generation in monolayer TMDCs

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ABSTRACT

We use microscopic many-body models based on first principle density functional theory to investigate the high harmonic generation (HHG) in monolayer transition metal dichalcogenides (ML-TMDCs) at the example of MoS_2. A two-dimensional bandstructure model is utilized that allows for the realistic inclusion of Coulomb correlations. It is shown that for off-resonant mid-IR excitation Coulomb correlations lead to a dramatic enhancement of HHG intensity by up to two orders of magnitude. For resonant excitation near the fundamental excitonic resonance the Coulomb interaction leads to dressed harmonics. These have a sub-floor of broad spectral contributions. The amplitude of these contributions is about four to six orders of magnitude below the peak. The width scales linearly with the exciting field and can reach hundreds of meV.

Keywords: transition-metal dichalcogenides, monolayer, 2D materials, high harmonic generation, semiconductor Bloch equations, Coulomb, exciton, dressed harmonics

1. INTRODUCTION

Monolayer transition metal dichalcogenides (ML-TMDC) are known to exhibit exceptionally strong optical nonlinearities. This, combined with the low volume of the two-dimensional material makes ML-TMDCs very promising candidates for applications like micro-sources for high harmonic generation (HHG). It has been pointed out that intrinsic symmetry breaking in ML-TMDCs introduces a rich variety of directional-, spin-, and valley-selective HHG emission characteristics.[1–3]

ML-TMDCs are also known for their particularly strong Coulomb interactions. The reduced screening of the Coulomb interaction outside the plane of the monolayer leads to exciton binding energies on the order of hundreds of meV, about two orders of magnitude stronger than in typical III-V materials. Even for fields in the extreme nonlinear regime of HHG, these binding energies and underlying Coulomb effects are of the same order as the optical coupling as measured by the Rabi-energy. While excitons are completely ionized in III-V semiconductors in this regime, Coulomb correlations remain important in ML-TMDCs.

Under typical HHG conditions, the strong optical excitations on a hundred femtosecond timescale create significant coherent polarizations and distributions that screen the Coulomb interaction and lead to dynamic renormalizations of transition energies and field coupling strengths. For pulses that are shorter than the decoherence time, one should expect ultrafast signatures of Coulomb correlations in the HHG signal.

Here we use results of first principle density functional theory (DFT) as input to the semiconductor Bloch equations (SBE) to investigate the influence of Coulomb correlations on HHG in monolayer TMDCs. The SBE are solved in the length gauge including the phase dependencies of the dipoles as described in Refs.[4–7]. The model is based on a two-dimensional bandstructure that allows to realistically include all relevant Coulomb effects. The lowest two conduction bands and six valence bands that show the largest dipole coupling in the region of interest are taken into account. These bands are shown along the assumed polarization direction of

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the light, Γ-K and zero momentum perpendicular to it in the inset to Fig.1 (a). Unlike simpler one-dimensional models, the two-dimensional model yields realistic densities of states and energy- and momentum-dependent Coulomb effects. More details about the theoretical model can be found in Ref.[8].

2. RESULTS

The following results are for a monolayer of MoS_2 that is suspended in air. We assume excitation with a Gaussian pulse,

$$E(t) = E_0\, e^{i\omega_0 t}\, e^{-2\,ln(2)\,t^2\,/\,\tau^2}, \tag{1}$$

with a width $\tau = 100\,\text{fs}$. The field is polarized along the Γ-K direction and the HHG emission is measured parallel to the excitation. All results are for a lattice temperature of 300 K. We assume a decoherence time for the dephasing of the polarizations of $T_2 = 10$ fs.

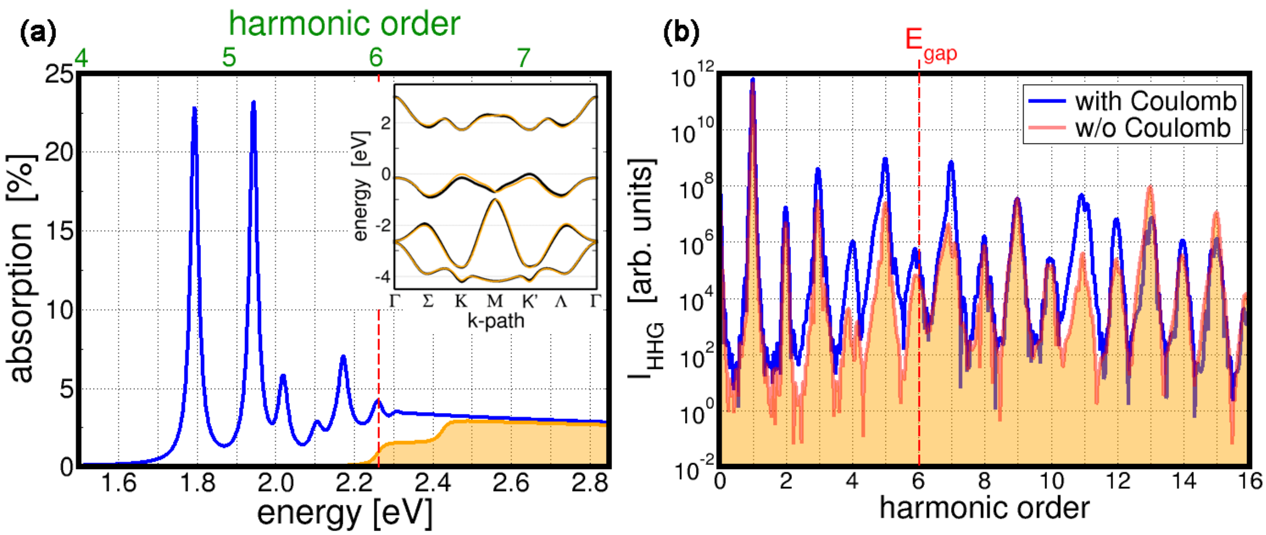

Figure 1. (a) Linear absorption of a monolayer of MoS_2. The top axis gives the energy in multiples of the excitation energy used for the HHG spectrum shown in picture (b). Inset: Bandstructure along the field direction. Black/orange: spin-up/down bands. (b) HHG for the ML of MoS_2 for an excitation wavelength $\lambda_0 = 3.3\ \mu$m and a field $E_0 = 10.24$ MV/cm. Blue (orange): calculated with (without) Coulomb interaction. The vertical dashed red line marks the bandgap.

Fig.1 (a) shows the linear absorption of the monolayer of MoS_2 calculated as described in Ref.[9]. Spectra calculated including Coulomb effects show pronounced excitonic resonances associated with transitions between the spin-up ('A') and spin-down ('B') bands closest to the gap are located about 470 meV below the onset of the single particle gap and and associated absorption.

In the linear regime of weak excitation the energetic region between the fundamental excitonic resonances and the free particle bandgap is obviously the most affected by the Coulomb effects. In the strong field regime of HHG the field distorts the Coulomb potential and partially ionizes excitons. Thus, the Coulomb effects should be expected to be spectrally more delocalized in this regime.

Fig.1 (b) shows HHG spectra for excitation at $\lambda_0 = 3.3\mu$m with a field strength E_0 of 10.24 MV/cm calculated with and without taking into account Coulomb effects. Here, the Coulomb correlations lead to a strong enhancement of the HHG intensity. The enhancement is strongest in the spectral region near the exciton resonances and bandgap where it reaches about two orders of magnitude. Significant enhancement also occurs outside this energy region, well below and above the bandgap.

The ratio of intensities at the peak of harmonics with and without Coulomb correlations is shown in Fig.2 for $E_0 = 10.24$ MV/cm and various excitation wavelengths. As can be seen, for excitation energies up to about the exciton binding energy ($\lambda_0 \gtrsim 2.5\ \mu$) the Coulomb effects lead to an enhancement of up to about two orders

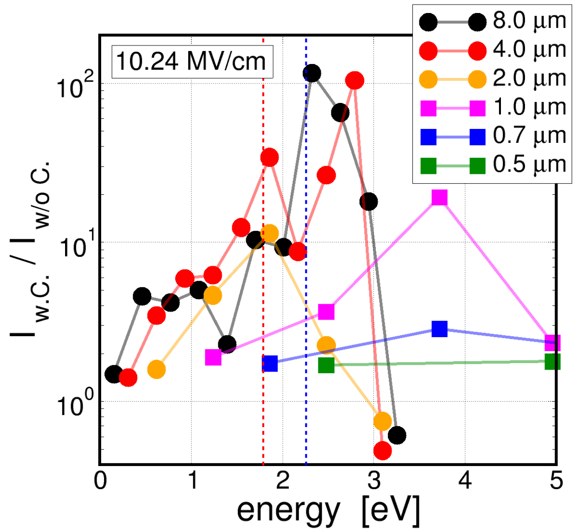

Figure 2. Ratio between HHG intensity with and without Coulomb interaction for a field E_0 of 10.24 MV/cm and excitation wavelengths λ_0 of 8.0, 4.0, 2.0, 1.0, 0.7 and 0.5 μm. Symbols mark the ratio at the peak of harmonics. Lines are guides to the eye. For $\lambda_0 = 8.0\,\mu$m ratios are only given at odd harmonics since even harmonics are not clearly identifiable for this case where the spectral width of the harmonics exceeds the separation between. The vertical red and blue lines mark the energy of the A-exciton and the bandgap, respectively.

of magnitude. For longer wavelengths the coupling to various excitonic states becomes less effective and the enhancement is limited to only about one order of magnitude.

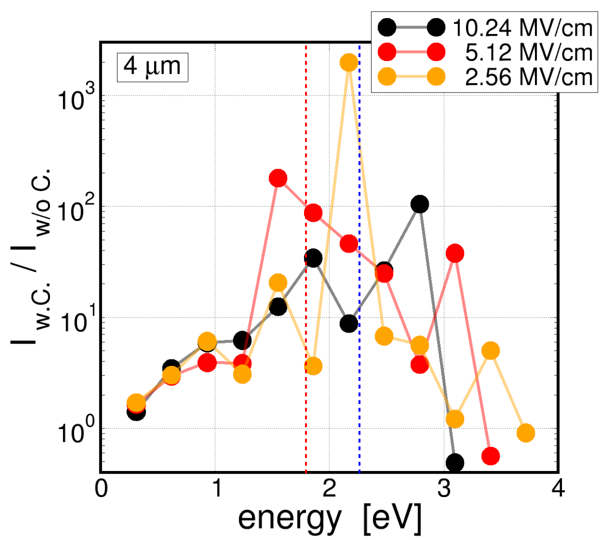

Figure 3. As Fig. 2, here for $\omega_0 = 4.0\,\mu$m and fields E_0 of 2.56, 5.12 and 10.24 MV/cm.

Fig.3 shows the ratio between harmonic peak intensities calculated with and without Coulomb effects for a wavelength of 4 μm and peak field strengths E_0 of 2.56, 5.12 and 10.24 MV/cm. The enhancement follows the same trend for all field strengths with maximum enhancements of at least two orders of magnitude in the energetic range near the excitons and bandgap. For lower fields where excitons remain strongly bound the coupling between well pronounced resonances allows for the strongest enhancement, exceeding more than three orders of magnitude for the weakest field shown here.

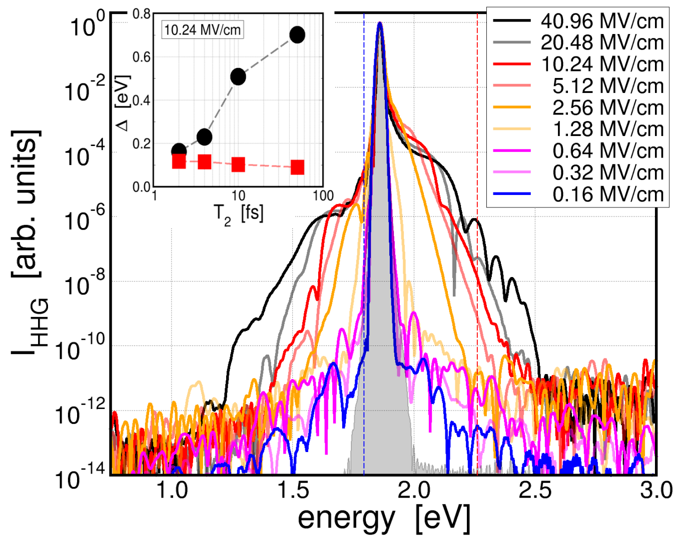

Figure 4. Normalized intensity of the fundamental harmonic for a dephasing time T_2 of 10 fs, excitation at 1.86 eV ($\omega_0 = 0.666\ \mu$m) and fields E_0 from 0.16 to 40.96 MV/cm. Lines: with Coulomb. Grey area: without Coulomb and $E_0 = 10.24$ MV/cm. Inset: Width, Δ, of the harmonic at six orders of magnitude below the peak for $E_0 = 10.24\ MV/cm$ and various dephasing times. Black/Red: with/without Coulomb.

For excitation near the fundamental exciton ($\lambda_0 \approx 0.7\ \mu$m) Coulomb correlations create a strongly broadened base of the harmonics. Fig.4 shows this for a wavelength λ_0 =0.666 μm and various field strengths. Shown there is the fundamental harmonic. Similar broadening occurs at higher harmonics.

The broadening increases about linearly with the field. For the dephasing time $T_2 = 10$ fs assumed here, the width of the broadening six orders of magnitude below the peak of the harmonic is comparable to the Rabi energy and reaches close to one eV for the highest fields shown here of $E_0 = 40.96$ MV/cm.

Since the Coulomb correlations are mediated by interband polarizations their impact depends on the lifetime of the polarizations. As shown in the inset to Fig.4, for dephasing times in the single femtosecond range the broadening for a given field is significantly diminished. At $T_2 = 2$ fs the broadening is almost absent and the linewidth approaches the one for the Coulomb-free case. For such a short dephasing time no clear excitonic resonances remain visible in the linear spectrum since the line broadening is similar to the exciton binding energy.

It should be noted that the enhancement of the peaks of the harmonics does not show such a dependence on the polarization dephasing time. For all decoherence times shown in the inset of Fig.4 we find a similar enhancement of about two orders of magnitude for off-resonant excitation.

3. SUMMARY

We use a microscopic many-body model based on a two-dimensional bandstructure to study the influence of Coulomb correlations high harmonic generation in monolayer TMDCs at the example of MoS_2. The extraordinarily strong Coulomb interaction in the TMDCs is shown to lead to a dramatic enhancement of the harmonics of up to about two orders of magnitude for off-resonant excitation at energies near or below the exciton binding energy (≈ 0.5 eV, wavelengths larger than about 2.5 μm). For resonant excitation near the fundamental excitonic resonances and bandgap ($\approx$ 2eV) the enhancement is reduced to factors of about 2 to 10. For the latter excitation energies the Coulomb interaction creates a spectrally broad sub-floor of the harmonics. The amplitude of these contributions is about four to six orders weaker than the peak of the harmonic. The spectral width scales about linearly with the strength of the exciting field, whereas the exact values depend on the dephasing time of the polarizations. For a dephasing time of ten femtoseconds the broadening reaches one eV for fields of about 40 MV/cm.

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