

Exciton-Enhanced Spontaneous Parametric Down-Conversion in Two-Dimensional Crystals

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We show that excitonic resonances and interexciton transitions can enhance the probability of spontaneous parametric down-conversion, a second-order optical response that generates entangled photon pairs. We benchmark our *ab initio* many-body calculations using experimental polar plots of second harmonic generation in NbOI₂, clearly demonstrating the relevance of excitons in the nonlinear response. A strong double-exciton resonance in 2D NbOCl₂ leads to giant enhancement in the second order susceptibility. Our work paves the way for the realization of efficient ultrathin quantum light sources.

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Spontaneous parametric down-conversion (SPDC) is a second-order nonlinear optical process in which a pump photon with frequency ω_p spontaneously splits into two correlated photons—a signal photon with frequency ω_s and an idler photon with frequency $\omega_i = \omega_p - \omega_s$ [1–3]. Such entangled photons are fundamental to the realization of quantum communication and quantum information applications [3]. The signal and idler frequencies can be the same (degenerate SPDC), or different (nondegenerate SPDC). Just recently, entangled photon pairs were generated through SPDC in 46-nm-thick NbOCl₂ [4]. Traditionally, bulk materials are used for the generation of entangled photon pairs, because the probability amplitude for this process scales linearly with volume. Moving to the 2D limit is, however, at the forefront of experimental research in nonlinear optics, due to inherent advantages such as reduction in losses due to optical absorption, and more facile integration with hybrid quantum photonic platforms that can enhance the incident light intensities [5–7]. Importantly, the relaxation of phase-matching conditions in two dimensions is not only helpful from a technical viewpoint, but also broadens the frequency spectrum for entangled photon pairs [8].

The theory of the general nonlinear optical response in semiconductors has been studied mostly within the independent particle approximation (IPA) [9–14]. However, in layered 2D materials, dielectric screening is reduced, and electron-hole (or excitonic) interactions dominate the linear optical response [15]. It is therefore critical to understand

the effect of excitons on the nonlinear optical response. A number of studies on nonlinear optical properties [16–19] have been performed using real-time approaches that account for excitonic effects. However, these real-time approaches do not provide clear insights into the origin of the peaks in the nonlinear susceptibilities. On the other hand, spectra for second-harmonic-generation (SHG), the inverse process of degenerate SPDC, were computed for bulk zinc-blende structures within a first principles *GW* plus Bethe-Salpeter-equation (*GW*-BSE) approach in the frequency domain [20–22], but the origin of the SHG peaks was not discussed. Some excitonic effects were observed in the SHG spectra, albeit not drastic [20–22].

In this work, we evaluate the Lehmann representation of the second-order susceptibility, using as a basis the many-body excitations obtained from *GW*-BSE. Applying the approach to monolayer NbOX₂ ($X = \text{I, Cl}$), prototypical 2D materials of significant current interest in nonlinear optics [4,23–25], we show that the probability amplitude of generating entangled photon pairs is significantly enhanced by excitonic effects. Interexciton transitions together with excitonic resonances lead to order-of-magnitude enhancements in the second-order optical response. We benchmark our approach by comparing our computed polarization-dependent SHG intensities with recent experiments [23]; good agreement is obtained and the importance of excitons is clearly illustrated. We further predict the existence of a double-exciton resonance condition for NbOCl₂, that can dramatically increase the expected yield of entangled

photon pairs compared to the nonresonant case. This work illustrates the fundamental excitonic origins of SPDC in 2D layered materials, and demonstrates the potential of exciton-enhanced SPDC in 2D crystals, thus paving the way for further advancements in the field of 2D quantum photonics.

Central to the theoretical description of SPDC is the second-order susceptibility, $\chi_{\alpha\beta\gamma}^{(2)}(\omega_3; \omega_1, \omega_2)$, arising from light-matter interaction [3,26]. The Lehmann representation of $\chi_{\alpha\beta\gamma}^{(2)}(\omega_3; \omega_1, \omega_2)$ can be expressed as (summing over spin and setting $\hbar = 1$):

$$\chi_{\alpha\beta\gamma}^{(2)}(\omega_3; \omega_1, \omega_2) = \frac{-ie^3}{m^3 \tilde{\omega}_3 \tilde{\omega}_1 \tilde{\omega}_2} \sum_{SS'} \left[\frac{\alpha_{0S} \beta_{SS'} \gamma_{S'0}}{(\tilde{\omega}_2 - \Omega_{S'}) (\tilde{\omega}_3 - \Omega_S)} + \frac{\beta_{0S} \gamma_{SS'} \alpha_{S'0}}{(\tilde{\omega}_1 + \Omega_S) (\tilde{\omega}_3 + \Omega_{S'})} - \frac{\gamma_{0S} \alpha_{SS'} \beta_{S'0}}{(\tilde{\omega}_1 - \Omega_{S'}) (\tilde{\omega}_2 + \Omega_S)} \right. \\ \left. + \frac{\alpha_{0S} \gamma_{SS'} \beta_{S'0}}{(\tilde{\omega}_1 - \Omega_{S'}) (\tilde{\omega}_3 - \Omega_S)} + \frac{\gamma_{0S} \beta_{SS'} \alpha_{S'0}}{(\tilde{\omega}_2 + \Omega_S) (\tilde{\omega}_3 + \Omega_{S'})} - \frac{\beta_{0S} \alpha_{SS'} \gamma_{S'0}}{(\tilde{\omega}_2 - \Omega_{S'}) (\tilde{\omega}_1 + \Omega_S)} \right], \quad (1)$$

where $\alpha_{SS'}$ refer to momentum matrix elements $\langle S | P^\alpha | S' \rangle$ and similarly for $\beta_{SS'}$ and $\gamma_{SS'}$. Here, $\tilde{\omega}_1 = \omega_1 + i\eta$, $\tilde{\omega}_2 = \omega_2 + i\eta$ and $\tilde{\omega}_3 = \tilde{\omega}_1 + \tilde{\omega}_2$, and \mathbf{P} is the many-body momentum operator, i.e., $\mathbf{P} = \sum_i \mathbf{p}_i$ where \mathbf{p}_i is the single-particle momentum operator acting on particle i . η is a small positive number that describes the adiabatic switching-on of the electromagnetic field, and is bounded below by the inverse of the thermal equilibration time in the material [27]. This expression is obtained through second order perturbation theory [20,28], which is valid for typical laser intensities [29].

The excitonic effect in $\chi^{(2)}$ is taken into account by defining Ω_S and $|S\rangle$ to be the many-body excitation energies and excited states obtained from GW -BSE within the Tamm-Dancoff approximation:

$$(E_{ck} - E_{vk}) A_{vc\mathbf{k}}^S + \sum_{v'c'\mathbf{k}'} K_{vc\mathbf{k},v'c'\mathbf{k}'} A_{v'c'\mathbf{k}'}^S = \Omega_S A_{vc\mathbf{k}}^S, \quad (2)$$

where $|S\rangle = \sum_{vc\mathbf{k}} A_{vc\mathbf{k}}^S \hat{a}_{c\mathbf{k}}^\dagger \hat{a}_{v\mathbf{k}} |0\rangle$ [30]. E_{nk} are quasiparticle energies obtained from a G_0W_0 calculation [31] and K is the electron-hole interaction kernel [30]. Numerical details and convergence checks for linear and nonlinear optical spectra are provided in the Supplemental Material [32].

The atomic structure of monolayer (ML) NbOX_2 ($X = \text{I}, \text{Cl}$) is shown in Fig. 1(a). Nb atoms are displaced off center along the x (polar) direction [42,43], resulting in three nonvanishing components $\chi_{xxx}^{(2)}$, $\chi_{xyy}^{(2)}$, $\chi_{yxy}^{(2)}$, which can lead to type 0, I, and II SPDC processes, respectively [3]. The band structures of ML NbOI_2 and NbOCl_2 [Figs. 1(c) and 1(e)] are computed using many-body perturbation theory within the GW approximation. The valence bands in NbOCl_2 are deeper than in NbOI_2 , reflecting the greater ionicity of the Nb-Cl bonds.

Figure 1(b) shows the computed linear optical response $\varepsilon_{2,yy}$ for NbOI_2 compared to experiment [23] (with a broadening chosen to be similar to the experiment at low energies). There is good agreement to within 0.1 eV

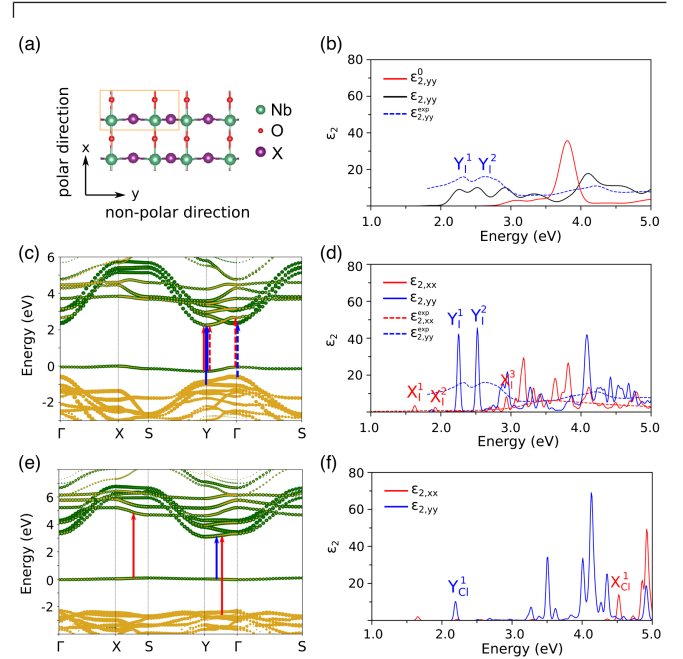


FIG. 1. (a) Atomic structure for ML NbOX_2 . (b) Optical absorption spectra for ML NbOI_2 , for light polarized in the nonpolar direction computed using the GW -BSE (black) and GW -IPA (red) approaches, compared with experiment [23] (blue dashed). The broadening value used is 0.10 eV. (c) GW band structure for ML NbOI_2 . (d) Optical absorption spectra for ML NbOI_2 computed within the GW -BSE approach, with a broadening of 0.02 eV. Red: polar direction, Blue: nonpolar direction. (e),(f) Similar to (c)–(d) but for ML NbOCl_2 . Experimental data for NbOI_2 nanosheets are also shown in (d). The green and yellow colors in the band structure denote projections onto Nb and X, respectively. Selected excitonic resonances are labeled in the absorption spectra. Note that X_1^3 refers to a group of excitons with very similar energies. Dashed blue and solid blue arrows in (c) illustrate the predominant optical transitions contributing to the excitons labeled, respectively, by Y_1^1 and Y_1^2 in (d), and solid red and dashed red arrows illustrate those for excitons X_1^1 and X_1^2 , respectively. Likewise, red and blue arrows in (e) correspond to X_{Cl}^1 and Y_{Cl}^1 in (f).

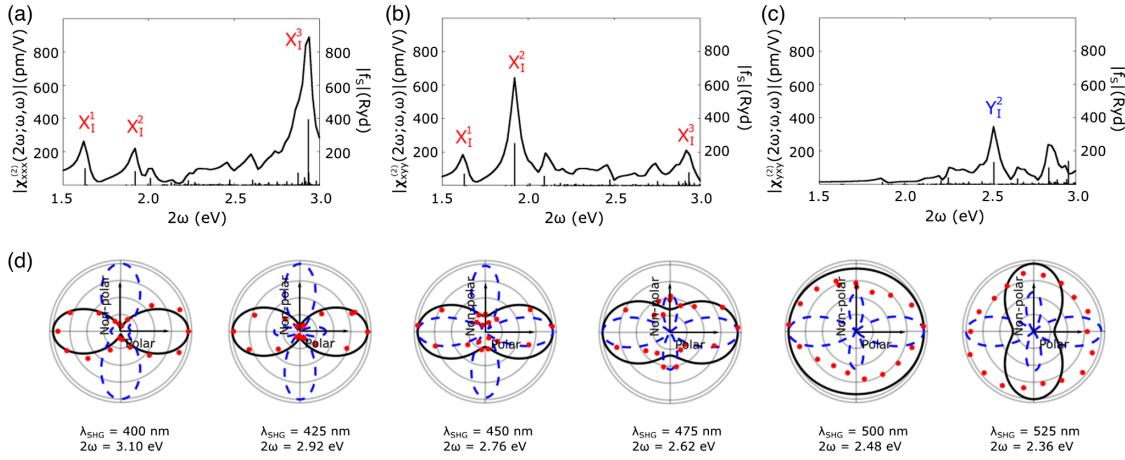


FIG. 2. Degenerate SPDC and SHG in NbOI₂. (a)–(c) Absolute value of (a) $\chi_{xxx}^{(2)}$, (b) $\chi_{xyy}^{(2)}$, (c) $\chi_{yxy}^{(2)}$ (left axis) corresponding to degenerate SPDC or SHG in ML NbOI₂. The 2ω -resonance strengths $|f_S^{2\omega}|$ (black vertical lines) are plotted against Ω_S (right axis) (see text). Selected peaks are labeled by the associated excitonic resonances. The lowest ω resonances are > 3.0 eV as the first excitation in ϵ_2^{xx} is > 1.5 eV. (d) Total SHG intensity plotted as a function of the polarization angle of the incoming light for NbOI₂. Solid black lines: GW-BSE, Dashed blue lines: GW-IPA, Red dots: Experiment [23]. The absolute values of the computed SHG intensities have been renormalized so that the shape of the polar plots can be seen clearly on the same scale.

between the GW-BSE (black) and experimental (blue) peak positions, in particular for Y_1^1 and Y_1^2 . Differences between GW-BSE and experiment at higher energies may result from energy-dependent broadening effects [44]. In contrast, in the GW-IPA result (red), the two peaks labeled by Y_1^1 and Y_1^2 are clearly absent. Instead, a large peak arises close to 4.0 eV in the IPA, due to band nesting between two relatively flat Nb bands; this band nesting effect is completely removed by destructive interference among the dipole matrix elements when electron-hole interactions are taken into account. Figures 1(d) and 1(f) present more GW-BSE results for the linear optical response, and compared to the GW-IPA results (Fig. S12 [32]), we see that there is a significant difference in spectral shape, and the BSE response has excitations at lower energies, as we expect from attractive electron-hole interactions.

Next we look at the magnitude of the calculated second order susceptibilities in Figs. 2 and 3, for NbOI₂ and NbOCl₂, respectively. Compared to the $\chi^{(2)}$ computed within the IPA (see Fig. S13 [32]), we see that excitonic effects enhance the nonlinear response by orders of magnitude and significantly alter its frequency dependence. This is in contrast to previous studies on bulk zinc-blende systems, where excitonic effects did not have such drastic effects on the SHG spectra [20–22]. To investigate whether these giant excitonic effects on $\chi^{(2)}$ can be observed experimentally, we focus on the inverse of the degenerate SPDC process—SHG. Figure 2(d) shows the frequency-dependent polar plots of the total SHG intensity against the polarization angle of the incoming light for NbOI₂ [Fig. 2(d)] [32]. The GW-BSE results (black) agree well with experiment [23] (red dots), except for the plot for $2\omega = 2.36$ eV. The GW-IPA results (dashed blue)

deviate significantly from experiment across the energy range shown. We emphasize that the better agreement between BSE and experiment is robust to small energy shifts (see Fig. S7 and discussion in the Supplemental Material [32]).

The shape of the polar plot is determined by the relative magnitudes and phases of different $\chi^{(2)}$ components (see Fig. S7a). For this energy range, the contribution from $|\chi_{yxy}^{(2)}|$ is small in comparison to those from $|\chi_{xxx}^{(2)}|$ or $|\chi_{xyy}^{(2)}|$, due to absorption of the outgoing y-polarized light [32]. For $2\omega \sim 2.7$ – 2.8 eV, $|\chi_{xyy}^{(2)}| > |\chi_{xxx}^{(2)}|$ in the IPA (Fig. S13), but $|\chi_{xxx}^{(2)}| > |\chi_{xyy}^{(2)}|$ for BSE. As we discuss below, the peaks in $\chi^{(2)}$ in Fig. 2 are attributed to excitonic resonances with $2\omega \sim \Omega_S$. We note that the IPA transitions in ~ 2.7 – 2.8 eV are the dominant transitions in the X_1^2 exciton at ~ 1.9 eV.

In both IPA and BSE, $|\chi_{xyy}^{(2)}| > |\chi_{xxx}^{(2)}|$ for the 2ω resonance corresponding to this transition; in this case, the discrepancy between IPA and experiment is due to the energy shift from the exciton binding energy. For $2\omega \sim 2.4$ – 2.5 eV, we see, interestingly, experimental evidence that the relative phases of the different $\chi^{(2)}$ components matter—in both the experiment and BSE plots, $\chi_{xyy}^{(2)}$ and $\chi_{xxx}^{(2)}$ have similar phases, in contrast to the IPA (Fig. S14 [32]). This comparison illustrates the fundamental excitonic origins of the experimentally observed SHG [23].

To provide deeper insights into the contribution of excitonic resonances to $\chi^{(2)}$, we define 2ω -resonance and ω -resonance strengths, $f_S^{2\omega}$ and f_S^ω . These quantities describe the contribution to $\chi^{(2)}$ arising from resonances of the incoming and outgoing photon energies with the many-body excitation energies. Keeping the terms in Eq. (1) which contribute the most at positive ω , we have

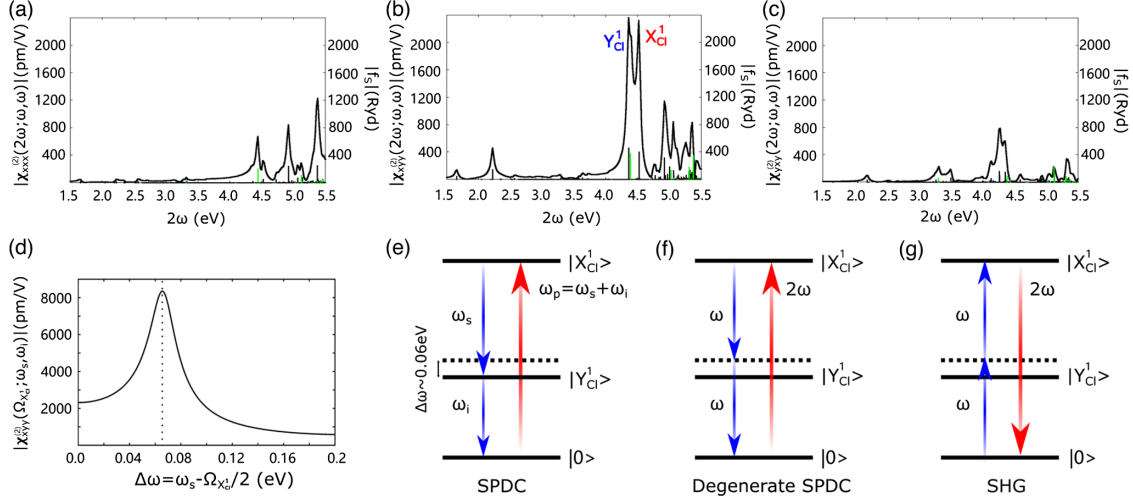


FIG. 3. SPDC and SHG in ML NbOCl₂. (a),(b),(c) Absolute value of (a) $\chi_{xxx}^{(2)}$, (b) $\chi_{xyy}^{(2)}$, (c) $\chi_{xyx}^{(2)}$ (left axis) corresponding to degenerate SPDC or SHG. The 2ω -resonance strengths $|f_S^{2\omega}|$ (black vertical lines) are plotted against Ω_S , and the ω -resonance strengths $|f_S^\omega|$ (green vertical lines) are plotted against Ω_S . Selected peaks are labeled by the associated excitonic resonances. (d) Absolute value of $\chi_{xyy}^{(2)}(\omega_p; \omega_s, \omega_i)$ with $\omega_p = \Omega_{X_{Cl}^1}$, plotted against $\Delta\omega = \omega_s - \Omega_{X_{Cl}^1}/2$, computed using GW-BSE. (e) Schematic figure for nondegenerate SPDC process with the exact double-exciton resonance condition. (f),(g) Schematic figures for the degenerate SPDC (f) and SHG (g) processes corresponding to the double-exciton resonance peak in (b).

$$\begin{aligned} \chi_{\alpha\beta\gamma}^{(2)}(2\omega; \omega, \omega) &\approx \frac{-ie^3}{m^3 \tilde{\omega}^3} \sum_{S'S'} \frac{\alpha_{0S} \{\beta_{SS'} \gamma_{S'0}\}}{(\tilde{\omega} - \Omega_{S'}) (2\tilde{\omega} - \Omega_S)} \\ &\approx \frac{e^3}{m^3} \left[\sum_S \frac{2f_S^{2\omega}}{2\tilde{\omega} - \Omega_S} + \sum_{S'} \frac{f_{S'}^\omega}{\tilde{\omega} - \Omega_{S'}} \right], \end{aligned} \quad (3)$$

where $\{\beta_{SS'} \gamma_{S'0}\} = (\beta_{SS'} \gamma_{S'0} + \gamma_{SS'} \beta_{S'0})/2$, and

$$f_S^{2\omega} = \frac{8}{\Omega_S^3} \sum_{S'} \frac{-i\alpha_{0S} \{\beta_{SS'} \gamma_{S'0}\}}{\Omega_S - 2\Omega_{S'}}, \quad (4)$$

$$f_{S'}^\omega = -\frac{1}{\Omega_{S'}^3} \sum_S \frac{-i\alpha_{0S} \{\beta_{SS'} \gamma_{S'0}\}}{\Omega_S - 2\Omega_{S'}}. \quad (5)$$

Because the energy axis for $\chi^{(2)}$ corresponds to the outgoing energy 2ω , in order to illustrate the contributions to peaks in $\chi^{(2)}$, we plot $|f_S^{2\omega}|$ against Ω_S and $|f_{S'}^\omega|$ against $2\Omega_{S'}$ (the incoming photon energy is resonant with $\Omega_{S'}$) [Figs. 2(a)–2(c) and 3(a)–3(c)]. We label selected peaks in $|\chi^{(2)}(2\omega; \omega, \omega)|$ with the excitons that predominantly contribute to the peaks through the resonance effect and large resonance strengths f . For the energy range shown here, most of the peaks in $\chi^{(2)}$ arise from 2ω resonances (black), except for a few ω resonances in NbOCl₂ (green; Fig. 3). The resonance strengths for each exciton S arise from the collective effect of interexciton transitions $\langle S|\mathbf{P}|S'\rangle$, $S' \neq S$, where S' involves both low and high energy excitations [32] (see Fig. S15). Terms involving intraexciton transitions ($\langle S|\mathbf{P}|S\rangle$) can only contribute to $\chi^{(2)}$ in systems with broken time-reversal symmetry [32]. For a fixed exciton

S (e.g., X_1^2 or X_1^3), the observed differences in $|f_S^{2\omega}|$ for $\chi_{xxx}^{(2)}$ and $\chi_{xyy}^{(2)}$ can be primarily attributed to differences in $\langle S|\mathbf{P}^x|S'\rangle$ and $\langle S|\mathbf{P}^y|S'\rangle$ across the range of excitons S' (see, e.g., Fig. S16). In particular, we also note that $|f_S|$ can be very large even when the oscillator strength for S is small, leading to large nonlinear optical responses.

The order-of-magnitude larger $|\chi^{(2)}|$ values in BSE compared to the IPA can be attributed to the correspondingly larger values of $|f_S^{2\omega}|$ and $|f_{S'}^\omega|$ (Figs. 2–3 vs Fig. S13). Exciton states are a linear combination of interband transitions at different k points. This opens up more interexciton transition channels as can be seen from the BSE and corresponding IPA expressions for $\langle S|\mathbf{P}|S'\rangle$:

$$\begin{aligned} \langle S|\mathbf{P}|S'\rangle &= \sum_{vcc'\mathbf{k}} A_{vc\mathbf{k}}^{S*} A_{v'c'\mathbf{k}}^{S'} \mathbf{p}_{cc'\mathbf{k}} - \sum_{v'vck} A_{vc\mathbf{k}}^{S*} A_{v'c\mathbf{k}}^{S'} \mathbf{p}_{v'v\mathbf{k}} \\ &\stackrel{|S\rangle=|v_1c_1\mathbf{k}_1\rangle}{\stackrel{|S'\rangle=|v_2c_2\mathbf{k}_2\rangle}{\approx}} \mathbf{p}_{c_1c_2\mathbf{k}_2} \delta_{\mathbf{k}_1\mathbf{k}_2} \delta_{v_1v_2} - \mathbf{p}_{v_2v_1\mathbf{k}_1} \delta_{\mathbf{k}_1\mathbf{k}_2} \delta_{c_1c_2}. \end{aligned} \quad (6)$$

When the exciton is reduced to a momentum-conserving interband transition between Bloch states in the IPA, many $\langle S|\mathbf{P}|S'\rangle$ elements become zero due to the collapse of the exciton wave function to a single point in reciprocal space [45]. Furthermore, in the BSE case, peaks in $\chi^{(2)}$ are observed to correspond to sharp spikes in $|f_S|$, i.e., a few excitons S have particularly large resonance strengths; this is not the case in the IPA (Fig. S13 [32]), where the variation in $|f_S|$ is smaller. We expect these excitonic effects, leading to enhanced SPDC/SHG, and stronger and

sharper resonance contributions, to be larger in 2D and quasi-2D layered materials compared to bulk 3D systems due to the reduced electronic screening in 2D materials.

Comparing NbOI₂ and NbOCl₂, we recall that in NbOCl₂, the valence bands are deeper, and consequently, there are fewer excitations in the lower energy range. We therefore show $|\chi^{(2)}|$ at a higher energy range in Fig. 3. We observe a giant double-exciton resonance feature at $2\omega \sim 4.5$ eV for $\chi_{xyy}^{(2)}$ in NbOCl₂ [Fig. 3(b)], as the energy of the Y_{Cl}¹ exciton is approximately half that of X_{Cl}¹; both ω and 2ω are nearly resonant with one of the exciton energies [Figs. 3(b), 3(f), and 3(g)]. We generalize our discussion of the double-exciton resonance feature to the case of nondegenerate SPDC, the generation of entangled photons with different frequencies, with $\omega_s = (\omega_p/2) + \Delta\omega$ and $\omega_i = (\omega_p/2) - \Delta\omega$. Figure 3(d) shows the predicted $|\chi_{xyy}^{(2)}|$ for an incoming photon resonant with X_{Cl}¹, as a function of $\Delta\omega$; it is clear that $|\chi_{xyy}^{(2)}|$ increases significantly as the exact double-exciton resonance condition (for both ω_p and ω_s) [Fig. 3(e)] is approached.

Our work provides convincing evidence of the fundamental excitonic origins of nonlinear optical responses in layered 2D materials, and calls for future experimental studies to realize potentially higher yields of entangled photons using the double-exciton resonance condition. This paves the way for 2D sources of correlated photons in next-generation quantum photonics devices.

Note added.—Recently, a paper on excitonic effects in SHG for 2D materials appeared on the arXiv [46].

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