Large exciton-driven linear and nonlinear optical processes and band nesting in monolayers of nitrogen arsenide and nitrogen antimonide

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Abstract

We demonstrate that atomically thin nitrogen-based binary group-V wide band-gap indirect semiconductors (NX (X=As, Sb)) can show strong linear and nonlinear optical activities. Contrary to NAs, we find that the fundamental optical absorption in NSb is infact quite resilient towards the temperature variations between 0-450 K. Exciton in NSb is however found to be less strongly bound (1.40 eV) compared to the more tight case in NAs (1.63 eV), leading to a more delocalised Mott-Wannier type texture. The inhomogenous excitonic linewidths for both monolayers within these temperatures are found to be in the range of 100-400 meV. The largest nonlinear second harmonic optical coefficient (2ω resonances) in NAs and NSb monolayers are obtained to be ~270 and 636 pm/V at 2.6 eV (477 nm) and 3.2 eV (387 nm) respectively. We also provided a detailed analysis of in-plane biaxial strain on these structures. We found that a tensile strain is energetically more favorable and does not influence the exciton binding energy in NAs. The nonlinear coefficient also significantly improves at the two most important 810 and 1560 nm wavelengths compared to the cases offered by the monolayer transitional metal dichalcogenides. Our analysis is based on a fully *ab-initio* G_0W_0 +Bethe-Salpeter excited state theory. The temperature-dependent linear absorption spectra are evaluated by including the electron-phonon self-energies, whereas the nonlinear spectra are treated using the modern theory of polarization within the same perturbative approach.

Introduction

Excitons are the basic ingredients responsible for optical excitation in materials. Fundamentally pictured as a quasi-particle in the framework of many body interactions, an exciton is an electron-hole pair bounded together by a Coulombic force of attraction. Out of many possibilities, this pair can be generated when the electron is kicked out by, for example, photons from the ground-state orbital. How long this pair will hold together depends on the duo's binding energy. This interaction picture, once the pair is formed, resembles much like a one-electron atomic system (Hydrogen), and therefore likewise distinct optical spectra are expected. Similar to the hydrogen electronic energy quantization, the exciton Coulombic energy lowers width of the direct band-gap of the material. One electron picture obtained from the standard generalized gradient approximation (GGA) density functional theory (DFT) in principle does not account for such interactions. Instead, excitons are two-body dynamically correlated phenomena and thus to understand their energy and lifetime, many-body methods must be used; such as the Bethe-Salpeter equation (BSE) over the single-shot GW corrections (applied on top of the ground-state energies). The former gives a direct access to the optical absorption and binding energies; and hence the fundamental optical gap, while the later fixes the missing energy eigenvalues that the DFT constantly struggles for. These methods nowadays have become a standard routine task to unravel and understand the excitonic driven optical properties.

There is, however, a basic part missing which is also needed to be addressed. The BSE so developed was, however, accounted only for the frozen atom condition, i.e., atoms were

assumed to be fixed in space or in other words, in the absence of lattice vibrations. As a result, the pole of the dielectric function (imaginary part) is required to be manually fixed such that the spectra correlate with the experimental broadening. The role of this broadening carries significant importance here since it directly adheres to the Heisenberg's uncertainty principle. The absence of the broadening would simply mean that the exciton lives forever in that state and thus the spectra take the shape of a Dirac delta function. In principle, this thermal broadening should enter as an exciton-phonon coupling matrix in the BSE. However, the current theoretical strategy addresses this formidable challenge by adopting the entry of this broadening as an electron-phonon coupling matrix into the BSE Hamiltonian. This approach, however, also quintessentially removes the manual selection of the broadening in the dielectric function. This first-cut approximation is in fact quite successful to justify the temperature-dependent excitonic binding energies, lifetimes, and spectra in both semiconductor bulk and monolayers (MLs) within limited errors. Nevertheless, the temperature dependency on optical properties are therefore more accurate and challenging to compute, which makes the process flow more complicated and expensive and thus rare to find in literature.

When the intensity of the light becomes very high, the semiconductor optical properties enter into the nonlinear regime. In such a case, one can observe frequency overtones like second, third, and other higher harmonics. For example, if the crystal structure is such that both the inversion and time-reversal symmetries are broken, one can then show that the induced time-varying electric dipoles do not cancel out, instead leading to a minimum detected second harmonic signal as a nonlinear one. If the intensity is gradually decreased, this nonlinear behavior converges to the above discussed linear optical properties. Nevertheless, in order to capture these nonlinear dynamics, a time-dependent DFT (TDDFT) is therefore needed. This was initially developed by Runge and Gross who numerically integrated the timedependent Kohn-Sham equation directly in the real-time domain. However, the accuracy of the results depends on the approximation used in the exchange-correlation kernel in the timedependent Hamiltonian. The hierarchy in this Jacob's ladder starts from the independent particle approximation (only the Kohn-Sham eigenvalues) to time-dependent Hartree (arising due to local field effects resulting in system inhomogeneities) to adiabatic local density approximation (quasi-statically space and time-varying density) to finally time-dependent screen exchange (electron-hole correlation is screen exchanged). The last one therefore also involves excitonic dynamics and is also known as time-dependent BSE (TDBSE) or the dynamical BSE. Modern theory of polarization developed by Kingsmith and Vanderbilt prescribes a method to obtain the coupling between the time-varying electric field and the Bloch electrons in an extended system. The Berry's phase change around the complete Brillouin zone (BZ) leads to the macroscopic time-varying polarization and therefore the TD Kohnsham equation of motion can be solved. The nonlinear coefficients can then be obtained by imposing a suitable cut-off in the polarization Fourier series.

Two quantities are greatly required in order to observe strong exciton-driven optical properties in semiconductors: a weak dielectric screening and crystalline noncentrosymmetry (i.e., lack of inversion symmetry). Whether or not spin-orbit coupling (SoC) will originate depends if an additional time-reversal symmetry is present or not. The later leads to the coupling between spin and momentum in the valleys and defines the momentum forbidden dark and bright states. For example, the monolayer transitional metal dichalcogenide (TMDC) WSe₂ posses a time-reversal symmetry and thus has a large spin-orbit splitting in its valence band at **K** point. The bright exciton is thus formed when an intravalley (intervalley) electron pairs with a hole having a parallel(antiparallel) spin.¹ In the past, there have been many benchmark strategic experiments to push the binding energies and nonlinear coefficients to their extremes (for example, see Table S1 in the supplemental information). Excitons in twodimensional semiconductors rather possess larger binding energies and oscillator strengths due to an in-plane quantum confinement compared to their bulk counterparts. In the later case, the electric field is properly screened out by the surrounding charges, while in monolayers it is not because of which an intense Coulombic interaction develops leading to a very strongly bounded pair. There is, however, another justification to why such an atomic layer should absorb a large amount of light. Castro Neto et. al.² showed that strong peaks in the optical conductivity can be justified from the ground state electronic band structure. The peak corresponds to those points in the BZ where the transition bands run parallel to each other. This is known as band-nesting. It was recently demonstrated that this band-nesting can also justify the nonlinear second harmonic generation (SHG) signals in uniaxially tensile strained TMDCs.³

Shifting the focus from the traditional planer monolayers, Taheri et. al.⁴ demonstrated that group-V monolayers based on nitrogen (NX, where X=P, As, and Sb) in their β -phase exhibits thermodynamically stable buckled structures. Using a purely *ab-initio* technique at the level of temperature dependent BSE, it was recently shown by the authors⁵ that β phase nitrogen phosphide (NP) monolayer can exhibit very high excitonic binding energy and strong absorbance spectra in the visible region. The nonlinear coefficients SHG along with the third harmonic generation (THG) were also found very high compared to the traditional TMDCs and monolayer transitional metal monochalcogenides (TMMCs). In this work, we extend the road-map of optical activity in monolayers of β -phase nitrogen arsenide NAs and nitrogen antimony NSb. We ask the followings: (1) How an electron taking part in the formation of an exciton relaxes from the conduction band in the presence of lattice vibrations, (2) how temperature controls the excitonic non-radiative line widths via excitonphonon coupling, (3) can band-nesting in these cases justify the strong absorption, (4) are the excitons Mottt-Wannier or Frenkel type, (5) what are the SHG coefficients, and (6) can an in-plane biaxial strain improve the binding energies and SHG coefficients. We response to these questions in a purely *ab-initio* way. We use many-body perturbation theory at the level of BSE to justify the excitonic-driven linear spectra. All temperature corrections are computed using density functional perturbation theory on the top of the ground state DFT eigenvalues. The nonlinear SHG coefficient is computed by solving TDBSE in real-time domain. Berry's phase polarization is used to compute the couplings between Bloch electrons and time-dependent electric-field. All strain-dependent calculations follow the same methodology as discussed above. Our results on the optical properties of β -phase NAs and NSb are summarized in Tables 1, 2, and 3. An extensive comparison with other monolayers and bulks are provided in Tables S1, S2, and S3 of the supplemental information. In addition, we also put there all the required theoretical background and convergence results. What follows, in the methodology section, we present a lucid picture of our computational details for ground state, excited state, and nonlinear analysis. In the results and discussion section, we justify our results together with summarizing our outcomes.

Methodologies

Ground state calculations

 β -phase NAs and NSb monolayers are thermodynamically stable in their non co-planer structures. A unit cell composed of two atoms was thus made, leading to a C_{3v} 3m point group three-fold symmetry. To cut-down the Coulombic interactions due to periodic images along the out-of-plane direction, a vacuum-slab-vacuum structure was created with a vacuum separation extending to 20 Å on either side. The figure below demonstrate the schematic view of such a monolayer. The optimized in-plane and out-of plane lattice constants were found to be (2.79, 1.00)Å for NAs and (3.00, 1.13)Å for NSb respectively. These optimization were done by using the open source Quantum Espresso DFT package.⁶ Fully relativistic norm-conserving pseudopotentials were first generated⁷ which also included nonlinear core-corrections in N (core states: [He], valence states 2s and 2p), As (core states [Ar], valence states 3d, 4s and 4p) and Sb (core states [Kr], valence states 4d, 5s and 5p). A Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional was used rather than a local density approximation (LDA) since the later is known to underestimate the electronphonon couplings by 30%.⁸ A kinetic cut-off energy of 80 Ry for all the atomic species was found to be sufficient to achieve energy convergences on a Γ -centred 12×12×1 MonkhorstPack grid. A plane-wave basis set was then used and the cell was finally allowed to undergo energy minimization constraining all forces and energy cut-offs below 10^{-5} Ry/bohr and 10^{-5} Ry respectively. The self-consistent charge densities and states were computed using the two-spinor wavefunction and switching on the noncollinear spin-orbit interactions.

Electron-phonon coupling calculations

The lattice vibration computations were calculated using the extended PHonon package within the same DFT code. For both the structures, a regular dense phonon \mathbf{q} -grid $18 \times 18 \times 1$ was chosen at a rigid self-consistent energy threshold 10^{-16} Ry and single iteration mixing factor of 0.7 Ry. In order to compute the electron-phonon couplings, the entire irreducible BZ was first randomly sampled to a fine 200 phonon \mathbf{q} -grids. The dynamical matrices, using the same energy threshold, and the perturbed potentials on these grids were then computed by mapping the self-consistent charge densities on the regular grids. A non-self consistent calculation was then carried out on these random grids which leads to the electron-phonon corrected electronic states along the BZ. Using this last step, the electron-phonon matrix elements were finally evaluated after constructing the initial states.

Linear spectra G_0W_0 +BSE calculations

The excited state corrections were computed using the MBPT open source code package Yambo.⁹ The G_0W_0 corrections were applied on to the 5 electronic bands on the either side of the valence band maximum which we also find to be most crucial in order to capture the optical transitions. A total of 200 bands (lowest 20 occupied bands and highest 180 unoccupied bands) were used to sum up the irreducible polarization response function. Local field effects were introduced in this linear response sum by switching on the random-phase approximation kernel. An energy cut-off of 10 Ry was found sufficient to converge this sum describing the system inhomogeneity. The microscopic dielectric function function is then

constructed by convoluting the polarization function with the bare Coulomb potential. The dynamic screening is then computed by convoluting the inverse of the microspopic function again with the bare Coulomb potential. A final convolution between this Coulombic screening and the non-interacting Green's function (G_0) leads to the full frequency G_0W_0 self-energy. We note here that most of the open source code splits this self-energy into a pure exchange term and a correlational term for computational convenience. The former is static while the later is a dynamic in frequency and is thus a complex quantity. The inverse microscopic dielectric function inside the dynamic screening term demands some comments. This inverse function is plagued with numerous poles located near the real axis which makes the screening convolution integral very expensive to compute. To implement this practically, a plasmon-pole model is often used which mimics the inverse dielectric function by approximating it at the most prominent pole, which is the plasmonic frequency. The plasmon-pole model by Godby and Needs¹⁰ is used in the package which uses one pole at zero frequency while the other at the plasmon frequency. The later is to be chosen such that the dielectric function converges. This correlational self-energy is then updated for each energy starting from the non-interacting Kohn-Sham eigenvalue and put back again into the nonlinear quasiparticle equation. However such an iteration would create a redundancy in computing the self-energy. Thus, the nonlinear equation is linearized using the Taylor's series up to the first order under the assumption that the renormalized energies are not far from the Kohn-Sham mean fields. This leads to the quasi-particle energies. In case if the non-interacting Green's function and the dynamic screening is also updated at each iteration process, then the computation scheme becomes GW. If the dynamic screening is updated only once, then it is a G_0W_0 process. Coulombic divergences occurring in all self-energies are fixed by integrating them over the irreducible BZ space by assuming first that the density matrices are the smooth function of momenta. The diverging quantities are then numerically integrated by using a Montecarlo technique that creates numerous randomly small BZs about each momenta vector. We therefore used 10^7 random points distributed all over the irreducible BZ with a cut-off of about 3 Ry to converge the integrals. In addition to these, a Coulomb truncation (similar to the DFT case) is applied to cut down the periodic interactions between the repeated monolayer images.

The absorption spectra is obtained by solving the time independent BSE. The same cut-offs are used to build up the exchange electron-hole attractive and repulsive kernels in the BSE matrix. An important note is that electronic transition are very sensitive to BZ samplings. A dense sampling would then be more meaningful to capture optical transitions properly along the high symmetry routes. For this purpose, we fine sample the entire BZ into $48 \times 48 \times 1$ on a shifted grid. First, on these grids we obtain the kernels for the independent-particle cases. Next, we obtain the interacting BSE kernels on the unshifted $12 \times 12 \times 1$ course grids. The BSE kernels on the fine grids are now interpolated using a Wannier interpolator which maps the fine and the course grids. This methodology¹¹ makes the expensive fine-grid BSE computation relatively quick without losing accuracy. We go beyond the standard Tamm-Dancoff approximation¹² by including both the resonant and antiresonant electronhole matrix elements in the BSE hamiltonian. A manual broadening of 0.1 eV is applied to construct a Lorentizan shape spectra together with an in-plane perturbing electric field. The quasi-particle energy corrections and the static screening are then added from the previous G_0W_0 calculation. In the presence of lattice vibrations, instead the corrections corresponding to the electron-phonon interactions on the energy bands are implemented. The G_0W_0 gaps are now opened up using a scissor operator that provides a rigid shift to the bands. No external broadening is required as the exciton line-widths are now computed using the electron-phonon matrix elements. The BSE matrix is then diagonalized and solved to obtain the poles which corresponds to the transition energies.

Nonlinear SHG calculations

The presence of an external electric field breaks down the crystal symmetry. Thus, we removed the symmetry of the crystal (the initial $12 \times 12 \times 1$ grid) in order to compute the

nonlinear coefficient first. The symmetry was removed by choosing an in-plane electric field. We map to this to a dense symmetry removed $48 \times 48 \times 1$ shifted grid in the presence of the same electric field. The time-dependent BSE was then solved at these dense $48 \times 48 \times 1$ sampling grids. The linear coefficient was extracted by applying a delta-like pulse where as a monochromatic sinusoidal wave is used to obtain the nonlinear SHG coefficient. The time-dependent polarization was obtained from the Berry's curvature. This TDBSE was finally solved using the Crank-Nicholson algorithm¹³ at a time step of 0.01 fs. The sudden switching on of the electric filed results in spurious noise at the initial level of the polarization signal. Thus, we increase the simulation time to 55 sec in order to get a clean signal. Additionally, to mimic effects from thermal broadening, defects, etc. a damping coefficient of about 0.17 eV was found suitable. All the linear and nollinear coefficients are obtained from the clean polarization signal.

Table 1: Electronic *ab-initio* energy comparisons in β -NX (X=As, Sb). *a* and *z* are the in-plane lattice parameter and buckling heights, respectively. The direct-gap is along Γ -M while the indirect-gaps are in the direction Γ -K-M.

Material	a	z	Indirect-gap	Direct-gap
(ML)	(Å)	(Å)	(eV)	(eV)
NAs	2.79	1.00	2.36 (PBE, $\mathbf{M}^{\frown}\mathbf{\Gamma} \leftrightarrow \mathbf{K}$)	$3.06 \text{ (PBE, } \mathbf{M}^{\frown} \mathbf{\Gamma})$
			4.51 ($G_0W_0, \mathbf{M}^\frown \mathbf{\Gamma} \leftrightarrow \mathbf{K}$)	5.00 (G ₀ W ₀ , $\mathbf{M}^{\frown}\mathbf{\Gamma}$)
NSb	3.00	1.13	2.06 (PBE, $\mathbf{M}^{\frown}\mathbf{\Gamma} \leftrightarrow \mathbf{K}$)	$2.52 (PBE, \mathbf{K})$
			3.70 (G ₀ W ₀ , $\Gamma^{\frown}K$)	$4.80 \; (G_0 W_0, \mathbf{K})$
				$3.58~(\mathrm{PBE},~\Gamma)$
				4.45 (G ₀ W ₀ , Γ)
				2.88 (PBE, $\mathbf{M}^{\frown}\mathbf{\Gamma}$)
				4.77 ($G_0W_0, \mathbf{M}^{\frown}\mathbf{\Gamma}$)

Table 2: Lattice vibrational *ab-initio* energy comparisons in β -NX (X=As, Sb). $\omega_{\rm LO}$ and $\omega_{\rm TO}$ are the zone-centre longitudinal and transverse optical in-plane frequencies while $\omega_{\rm ZO}$ is the optical out-of plane frequency. ZPM denotes quasi-harmonic zero-point motion and $\frac{dE_g^i}{dT}$ shows the temperature dependent indirect band gap.

Material (ML)	$\begin{array}{c} \omega_{\rm LO} - \omega_{\rm TO} \big _{\Gamma} \\ (\rm cm^{-1}) \end{array}$	$\begin{array}{c} \omega_{\mathrm{ZO}} _{\Gamma} \ (\mathrm{cm}^{-1}) \end{array}$	$\begin{array}{c} { m ZPM} \\ { m (meV)} \end{array}$	$(\text{meVK}^{\frac{dE_g^i}{dT}})$
NAs NSb	$\frac{566}{523}$	$672 \\ 596$	105 80	-0.18 -0.47

Table 3: Quasi-particle direct band-gap between Γ and \mathbf{M} of the BZ, fundamental exciton binding energy (BE), linewidth (LW) and nonlinear coefficients (at excitation wavelength in nm) in NAs and NSb monolayers. Notations: rt = room temperature (300 K).

Material	Substrate	rt Band-gap	rt BE	rt LW	$\chi^{(2)}$ (λ nm)
		(eV)	(eV)	(meV)	(pm/V)
NAs	isolated	3.27 (PBE, $\mathbf{M}^{\frown}\mathbf{\Gamma}$)	1.83	278	636 (387)
		5.38 (G_0W_0 , $\mathbf{M}^{\frown}\Gamma$)			52(810)
					14(1560)
NSb	isolated	3.58 (PBE, Γ)		258	275(477)
		4.45 (G ₀ W ₀ , Γ)	1.79		31 (810)
		4.77 (G ₀ W ₀ , $\mathbf{M}^{\frown}\mathbf{\Gamma}$)			21(1560)

The respective $G_0 \overline{W_0}$ corrections are added to the temperature dependent PBE gaps.

Results and discussion



Figure 1: Bare electronic dispersion of NAs monolayer showing the partial density of states projected on the former. Plots (a) nitrogen $3P_{j=\frac{1}{2}}$, $m_s=-\frac{1}{2}$ and (b) arsenic $4P_{j=\frac{3}{2}}$, $m_s=+\frac{1}{2}$ shows the spin orbital occupancy in valence and conduction bands respectively. The arrows in (b) demonstrate how the electron that takes part in optical transition gets scattered due to the thermal broadening of the energy bands.



Figure 2: Bare electronic dispersion of NSb monolayer showing the partial density of states projected on the former. Plots (a) nitrogen $3P_{j=\frac{1}{2}}$, $m_s=-\frac{1}{2}$ and (b) antimony $4P_{j=\frac{3}{2}}$, $m_s=+\frac{1}{2}$ shows the spin orbital occupancy in valence and conduction bands respectively. The arrows in (b) demonstrate how the electron that takes part in optical transition gets scattered due to the thermal broadening of the energy bands.

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Figure 3: $|\nabla_k (E_C - E_V)|$ and $E_C - E_V$ in (a) NAs and (b) NSb monolayer along the BZ route. E_C and E_V represents the lowest conduction and highest valence band respectively.

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Figure 4: Latice vibration spectra, phonon density of states and electron-phonon Eliashberg function of (a)-(c) NAs and (d)-(f) NSb monolayers respectively. The individual Eliashberg functions at the ground state conduction maxima and valence minima for both the NAs and NSb are calculated, justifying why the indirect gap should decrease with increasing temperature.

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Figure 5: Temperature dependence of the DFT gaps in the presence of electron-phonon couplings in (a) NAs and (b) NSb monolayers. The direct-gap in (a) corresponds to transition between \mathbf{M} - Γ , while the indirect-gap is between \mathbf{M} and Γ - \mathbf{K} of the BZ. Similarly, the direct-gaps in (b) corresponds to "I" (between \mathbf{M} and Γ - \mathbf{K} , see Fig. 2(b)) and at \mathbf{K} , while he indirect-gap is between \mathbf{M} and Γ - \mathbf{K} , see Fig. 2(b)) and at \mathbf{K} , while he indirect-gap is between \mathbf{M} and Γ - \mathbf{K} of the BZ. The slopes are measured at 300 K. Dots are the ab-initio data. The decreasing trends of the broken lines are the fit to the Varshney's equation.

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Figure 6: Spectral functions dependencies on temperature in NAs and NSb monolayer. (a)-(b) represents the spectral function NAs monolayer at the direct valence and conduction state (see Fig. 1(b)), whereas (c)-(d) represents the same at the indirect valence and conduction state respectively. The spectra in (e)-(l) depicts the cases for NSb monolayer (see Fig. 2(b) for high-symmetry points). The vertical dash lines represents the band edges in the absence of electron-phonon couplings.

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Figure 7: Ground state (grey) and G_0W_0 (black) electronic band structure in (a) NAs and (b) NSb monolayers. The horizontal dashed lines are with respect to the DFT top and G_0W_0 bottom of the valence and conduction bands respectively. All the vertical arrows represent direct quasi-particle gaps with most of the electronic transition weights.



Figure 8: Fundamental exciton formation in (a) NAs and (b) NSb monolayers. The electronic transitions representing exciton weights are projected onto the ground state electronic dispersion in both the cases are shown by the yellow shade. The inset exhibits the corresponding excitonic weights in the BZ of the two cases.



Figure 9: Excitonic wave functions for first excitons, a) NAs, b) NSb.



Figure 10: (a) NAs and (b) NSb excitonic oscillator strengths as a function of temperature for all exciton with strengths more than 10 %.



Figure 11: Absorption spectra and joint density of states in (a) NAs and (b) NSb monolayers. solid line corresponds to the G_0W_0 +BSE calculations in absence of lattice vibration. The effect of lattice vibrations on the spectra changes the widths and positions, and are shown for temperatures 0 K (dashed curve) upto 450 K at a step of 50 K. The vertical dashed lines are the direct quasi-particle gaps. The dots are the guide to eye showing the shifts of the peak positions.



Figure 12: (a) Inhomogeneous linewidth of fundamental exciton in NAs monolayer. The symbols are the *ab-initio* data while the dashed line is the phenomenological excitonic width equation. (b) Exciton phonon coupling function variation with phonon frequency showing the most prominent mode that build this fundamental exciton.



Figure 13: (a) Inhomogeneous linewidth of fundamental exciton in NSb monolayer. The symbols are the *ab-initio* data while the dashed line is the phenomenological excitonic width equation. (b) Exciton phonon coupling function variation with phonon frequency showing the most prominent mode that build this fundamental exciton.



Figure 14: (a) Convergence demonstration of the absorption spectra using the approach of nonlinear real-time BSE and static BSE for NAs monolayer. The shaded region (yellow) demonstrates that in the presence of a delta-like field with low intensity (500 KWcm⁻² in this case), the linear response (black) can be obtained from the solution of the time-dependent BSE. A scissor is added in the exciton Hamiltonian to mimic the G_0W_0 gap in both the cases. The time-dependent induced polarization along the crystalline *a*-axis are also shown due to (b) delta-like field and (c) a quasi-monochromatic field along the *b*-axis respectively.



Figure 15: (a) Convergence demonstration of the absorption spectra using the approach of nonlinear real-time BSE and static BSE for NSb monolayer. The shaded region (yellow) demonstrates that in the presence of a delta-like field with low intensity (500 KWcm⁻² in this case), the linear response (black) can be obtained from the solution of the time-dependent BSE. A scissor is added in the exciton Hamiltonian to mimic the G_0W_0 gap in both the cases. The time-dependent induced polarization along the crystalline *a*-axis are also shown due to (b) delta-like field and (c) a quasi-monochromatic field along the *b*-axis respectively.



Figure 16: Phase-delay between the induced polarization and the applied field in monolayers of (a) NAs and (b) NSb respectively. The real and imaginary parts of the linear spectra is obtained from the real-time approach. All the analyses are obtained within the TD-BSE level of theory. Note the convergence of the delay to π at low frequencies.



Figure 17: (a) Absolute SHG coefficient in NAs monolayer within the time-dependent (TD) BSE (TD-BSE) level of theory exhibiting the peaks A_1 , and A'_1 due to the bound and resonant excitons B_1 and R'_1 respectively. The *x* axis is the laser frequency. (b) The absorption spectra at ω and $\omega/2$ under the same TD-BSE level of theory. The vertical dashed line exhibits the $\omega/2$ gap. One can see that the $\Im \chi^{(2)}_{aab}$ goes to zero below half of the gap. (c)-(d) are all respective cases in NSb monolayer.



Figure 18: Quasi-particle G_0W_0 gaps in biaxially strained (a) NAs and (b) NSb monolayers.



Figure 19: (a) Excitonic energies and (b) binding energies in biaxially strained NAs and NSb monolayers.



Figure 20: Absorption spectra and joint density of states of monolayer NAs under biaxial (a)-(e) tensile and (f)-(j) compressive strains respectively. TThe vertical dotted lines are the most important electronic transitions with maximum relative exitonic intensity, while the dashed lines are the direct quasiparticle gaps.



Figure 21: Absorption spectra and joint density of states of monolayer NSb under biaxial (a)-(e) tensile and (f)-(j) compressive strains respectively. The vertical dotted lines are the most important electronic transitions with maximum relative exitonic intensity, while the dashed lines are the direct quasiparticle gaps.



Figure 22: Improvements in second harmonic coefficients in monolayer NAs under biaxial (a) tensile and (b) compressive strains respectively. The dotted and dashed lines are the two important wavelengths 1560 nm and 810 nm respectively.



Figure 23: Improvements in second harmonic coefficients in monolayer NSb under biaxial (a) tensile and (b) compressive strains respectively. The dotted and dashed lines are the two important wavelengths 1560 nm and 810 nm respectively.