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Article

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Massive and massless plasmons in germanene nanosheets

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Atomic thin crystals may exhibit peculiar dispersive electronic states equivalent to free charged particles of ultralight to ultraheavy masses. A rare coexistence of linear and parabolic dispersions yields correlated charge density modes exploitable for nanometric light confinement. Here, we use a time-dependent density-functional approach, under several levels of increasing accuracy, from the random-phase approximation to the Bethe-Salpeter equation formalism, to assess the role of different synthesized germanene samples as platforms for these plasmon excitations. In particular, we establish that both freestanding and some supported germanene monolayers can sustain infrared massless modes, resolved into an out-of-phase (optical) and an in-phase (acoustic) component. We further indicate precise experimental geometries that naturally host infrared massive modes, involving two different families of parabolic charge carriers. We thus show that the interplay of the massless and massive plasmons can be finetuned by applied extrinsic conditions or geometry deformations, which constitutes the core mechanism of germanene-based optoelectronic and plasmonic applications.

Keywords: Light-matter modes, germanene, Dirac cone materials, dielectric screening, plasmon resonances, time-dependent density-functional theory, GW approximation, Bethe Salpeter Equation.

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I. INTRODUCTION

The understanding of collective electron phenomena at the nanoscale is a main theme in the research on novel artificial heterostructures and related device architectures. In this exploration, a number of superior qualities are offered by two-dimensional (2D) crystals with linear electronic bands, or Dirac cones, crossing around the Fermi energy $E_F$.

Such 2D Dirac cone materials (2DDMs) host massless charge carriers of large group velocities, which strongly couple to light via excited charge density waves quantized as plasmons. The Dirac cones with vertices at $E_F$ are commonly characterized at the corners (K points) of the first Brillouin zone (1st BZ) in graphene, the first isolated 2DDM composed of carbon atoms in a honeycomb lattice.

However, in spite of the hundreds of 2D materials discovered so far, experimental observations of 2DDMs other than graphene are rather few. In particular, a number of single and multiple low-buckled hexagonal phases of germanium were characterized on gold, aluminum, and silver. A few other realizations of this kind, grown on large to moderate gapped substrates, such as AlN and MoS$_2$, showed clear hallmarks Dirac cones near $E_F$. The corresponding overlayers, here referred to as quasi-freestanding germanene (QFGe) sheets, additionally exhibited another bunch of parabolically dispersing electronic states approaching or even crossing $E_F$.

These achievements, while confirming the massless nature of the charge carriers, derived from the linear bands, also indicate coexistence of massive charge carriers, originating from the parabolic bands, which further boosts the interest in germanene-based 2DDMs. Similar features were observed in metal quantum well structures grown on graphene, while a more extreme correlation of linear and flat bands was recognized in twisted sandwiched graphene.

Given these premises, a major issue is on the dielectric response and related plasmon modes of the QFGe sheets, with particular reference to their role in extreme light trapping.

Here we provide such a study, starting from a time-dependent density-functional theory (TDDFT) approach, in the random phase approximation (RPA), with a local kernel designed for 2D systems. Accordingly, we compute the optical absorption and energy loss function of the FGe and QFGe monolayers that allow us to explore their leading single-particle excitations (SPEs) processes and charge density modes, over the infrared (IR) to below the ultraviolet (UV) range.

Next, we consider the explicit inclusion of quasiparticle GW corrections, in an RPA+GW approach. Finally, we compare our results with optical macroscopic permittivity calculations, performed within the Bethe-Salpeter equation (BSE) and BSE+GW frameworks.
II. RESULTS

A. Band dispersions and density of states

We carried out the electronic structure calculations using the plane-wave (PW) approach\textsuperscript{57,58} to Kohn-Sham (KS) density-functional-theory (DFT), within the local density approximation\textsuperscript{59,60} (LDA) supported by an efficient norm-conserving pseudopotential\textsuperscript{61}.

Figure 1 reports the energy bands, along the high-symmetry ΓKMG path of the 1\textsuperscript{st}BZ, and the density of states (DOS) of the two above outlined QFGe sheets, in comparison with freestanding germanene (FGe). The key electronic states implicated in optical processes belong to the two highest bands below and the two lowest bands above the Dirac cone vertex, at energy $E_C$. The energy-wave-vector dispersion of these bands are highly affected by the equilibrium geometry of the corresponding lattices, which also determine the peak positions and widths of the associated DOS profiles. Nonetheless, some typical trends of group IV monolayers with honeycomb lattice can be identified.

\[ E_C = \frac{\hbar^2}{2m_e} \left( \frac{\pi}{a} \right)^2 \]

In particular, the Dirac cones emerge at the K point, being characterized by two bands of dominant $\pi$ and $\pi^*$ character, apparent in the projected band structures (see Supplementary Information, Sec. I). The cone shape is practically untouched by geometry effects, with a slope (or Fermi velocity) of 0.24, in units of the Bohr velocity, being about 63\% of the Fermi velocity of freestanding graphene, as calculated within the LDA\textsuperscript{13}. The $\pi$-like and $\pi^*$-like...
bands approach the M point with flat dispersions, associated to the first van Hove singularity (VHS) pair in the DOS profiles. The second highest band, below $E_C$, exhibits two non-degenerate minima with $\sigma$-like character towards the middle of the $\Gamma K$ and $M\Gamma$ lines, where the first lowest band, above $E_C$, presents two non-degenerate maxima with $\pi^*$-like character.

An unparalleled feature is the highest occupied and lowest unoccupied states around $\Gamma$, which respectively form two $\sigma$-like bands, approaching the degenerate energy $E^\Gamma_\sigma$, and one $\sigma^*$-like or $\pi^*$-like band, depending on the system's geometry. Unlike graphene and silicene\cite{24}, the energies of the $\sigma$-like states are sufficiently close to $E_F$ that substrate-induced lattice deformations gradually turn the nature of the germanene overlayer from zero gap semimetal (FGe and QFGe on AlN) to metal (QFGe on MoS$_2$).

Specifically, the AlN-induced compression (2.1\% \cite{37}) shifts up the $\sigma$-like and $\sigma^*$-like bands of the QFGe overlayer, leaving untouched the $\pi$-like and $\pi^*$-like bands, with inclusion of the Dirac cone at vertex $E_C=E_F$ and the VHSs’ structure [Fig. 1(b)]. This QFGe system is still a semimetal, along with FGe, though the degenerate top level of the $\sigma$-like bands is increased by 0.30 eV towards $E_F$, which corresponds to a higher onset of the decreasing behavior of the occupied DOS, vanishing at the Dirac cone.

The MoS$_2$-induced compression (7.4\%) produces a more significant upshift of the $\sigma$-like bands that cross the Fermi level at $\Gamma$, with $E^\Gamma_\sigma$ lying at $\sim 0.11$ eV above $E_F$, which yields a small spike in the associated DOS [Fig. 1(c)]. As a result, this other QFGe system is a metal with the Dirac cone downshifted to $E_C=0.29$ eV below $E_F$, corresponding to a non-vanishing DOS point, and a hole pocket left at $\Gamma$ with two different dispersions. The latter are equivalent to two families of positive charge carriers of effective masses $0.45 m_e$ and $0.07 m_e$, with $m_e$ denoting the electron rest mass.

Further tuning of $E_F$ in synthesized germanene overlayers can be achieved by proper combination of chemical doping or electrostatic gating and mechanical stress or strain\cite{46-60}.

B. Dielectric Properties

The above outlined electronic structures are primarily involved in the macroscopic permittivity response $\varepsilon^M$ of the FGe and QFGe monolayers. The other key element is the interaction generated by light-induced changes in charge density that we approximated to a truncated Coulomb potential, specific for 2D materials\cite{40-44}, see Sec.II D-Sec.II E. We used the same potential, in conjunction with a plasmon pole model\cite{37}, to correct the band energies of Fig. 1 at the level of the GW approximation\cite{48-50}, as reported in Sec. II F. We further considered other two-particle, excitonic effects were treated within the BSE approximation\cite{52-54}, see also Sec. II F.

In the following, we present the behavior of $\text{Im}(\varepsilon^M)$ and $-\text{Im}(1/\varepsilon^M)$ vs the probing energy $\omega$ and transferred momentum $\mathbf{q}$. These two quantities, being respectively proportional to the absorption cross-section and the so-called energy-loss function, provide complementary spectral representations of plasmon propagation and damping. The peak structures of $-\text{Im}(1/\varepsilon^M)$ are blueshifted relative to $\text{Im}(\varepsilon^M)$, with the plasmon resonances following the absorption peaks and lying just below the loss peaks, at the closest-to-zero permittivity point\cite{37}. Undamped plasmons are more markedly spotted in the double sign change of $\text{Re}(\varepsilon^M)$, in particular, at the largest zero of $\text{Re}(\varepsilon^M)$, which matches the negligibly small value of $\text{Im}(\varepsilon^M)$ relative to its peak (see Supplementary Information, Sec. III).

C. Charge Carrier Concentration

Our main concern is on doping- or gating- induced shifting of $E_F$ at fixed (room) temperature. This amounts to inject or eject small electron concentrations $n_e$ or $n_h$ that cause positive or negative shifts $\Delta E_F$, while leaving unaltered the underlying electronic structure of the intrinsic systems.

Figure 2 shows the $n_{e/h}$ profiles against $\Delta E_F$, within the range where the highest occupied valence band, and the lowest unoccupied conduction band, have linear ($\pi$-like or $\pi^*$-like), parabolic ($\sigma$-like), and flat ($\sigma^*$-like) dispersions around $K$, $\Gamma$, and $M$, respectively.

In FGe, the filling or emptying of the Dirac cone states is the main mechanism for doping or gating, which activates a 2D optical plasmon (2DP) similarly to graphene and silicene\cite{37,38}.

In QFGe on AlN, a moderate shift $\Delta E_F<0.3$ eV, i.e., an ejected electron density $n_e\gtrsim 3\times 10^{13}$ cm$^{-2}$, is sufficient to empty part of the $\sigma$-like bands and leave a hole pocket at $\Gamma$, which produces another $\sigma$-like plasmon ($\sigma P$) interacting with the 2DP.

In QFGe on MoS$_2$, a consistent hole pocket is already present in the intrinsic system (set by $\Delta E_F=0$ or $n_{e/h}=0$), along with strongly overlapping 2DP and $\sigma P$ modes. Significant variations of $n_{e/h}$, around $10^{11}$ cm$^{-2}$, may be locally induced by point defects in MoS$_2$\cite{25}. Nonetheless, much larger injected electron densities, $n_e\gtrsim 5.5\times 10^{13}$ cm$^{-2}$, are required
to shift $E_F$ above the $\sigma$-like bands and deactivate the $\sigma$P. Conversely, an ejected electron density $n_h=9.8\times10^{13}$ cm$^{-2}$ can restore $E_F$ at the Dirac cone vertex.

In all cases, the unoccupied VHS states act as a barrier to Fermi level shifting [Fig. 1(b), (c)], making it hard to achieve values of $\Delta E_F$ larger than 0.4 eV in FGe or QFGe on AlN, and 0.25 eV in QFGe on MoS$_2$.

D. Absorption Spectra

We begin by analyzing the absorption properties of the germanene monolayers in their intrinsic state, at the the level of TDDFT in our RPA approach. Accordingly, we focus on the energy dependence of the macroscopic imaginary permittivity $\text{im}(\varepsilon^\omega)$ in the optical momentum limit, i.e., at a fixed momentum transfer of $2.5-2.6\times10^{-3}$ Å$^{-1}$, which corresponds to the typical momentum of a photon in the few-eV energy range.

Three main peak structures are distinguished in the far-infrared (FIR) to mid-infrared (MIR), near-infrared (NIR) to visible (VIS), and VIS to mid-ultraviolet (MUV) regimes, as attested by the absorption lineshapes of Fig. 3.
1st BZ, thus involving thermally excited π-like and π*-like charge carriers at the Dirac cone, which is a consequence of the quasimetal nature of the monolayers. A higher peak intensity, of about a factor of eight, is recorded in QFGe on MoS$_2$, because of the Fermi level shifting above the Dirac cone, and the corresponding metal nature of the system. By inspecting the differences in the charge-carrier concentration profiles of Fig. 2, we have estimated a population of $n_{h\pi} = 2.4 \times 10^{13}$ cm$^{-2}$ electrons in the π*-like part of the Dirac cone, between $E_C$ and $E_F$. We have further estimated a population of $n_{e\pi} = 2.8 \times 10^{13}$ cm$^{-2}$ holes in the σ-like bands, between $E_F$ and $E_G^\pi$. Accordingly, the FIR-MIR peak in QFGe on MoS$_2$ is determined by intraband SPEs around K and Γ.

A shoulder appears in QFGe on MoS$_2$ at MIR to NIR wavelengths, i.e., in the energy range between 0.4 and 0.8 eV. This is a signature of interband SPEs between the occupied and empty σ-like states at the crossing point with $E_F$, as confirmed by a joint DOS analysis (see Supplementary Information, Sec. II). These σ-σ excitations originate from parabolic-like bands and contribute with a broader and much less intense peak, being partly superimposed with the MIR tail of the FIR-MIR peak.

The NIR to VIS peak structure extends from 1.2 eV in FGe, 1.4 eV in QFGe on AlN, and 1.5 eV in QFGe on MoS$_2$, to 1.8 eV, being mostly determined by interband SPEs around Γ and M (see Supplementary Information, Sec. II).

In FGe and QFGe on AlN the onset energy, on the NIR range, coincides with the gap between the σ-like and σ*-like bands at Γ, thus involving σ-σ* SPEs between the corresponding band maxima and minima.

In QFGe on MoS$_2$, the initial NIR structure has a smoother trend, originating from transitions from the occupied σ-like states to the unoccupied σ*-like states at Γ. Accordingly, the σ-σ* SPEs lead to a broad maximum around 1.6 eV, due to transitions to the σ* band minimum.

In all monolayers the VIS peak at 1.8 eV arises from transitions from the π-like to π*-like bands, at the corresponding VHS points. The latter appears as a weak feature in QFGe on MoS$_2$, being superimposed to the spectrum of σ-σ* SPEs, away from Γ.

The VIS to MUV peak structure, covering the 2.6-4.6 eV range, involves SPEs between the highest (or second-highest) valence band and the second-lowest (or lowest) conduction band, with dominant transitions from π-like (or σ-like) to σ*-like (or π*-like) states, around the corresponding DOS peaks (see Supplementary Information, Sec. II).

In FGe and QFGe on AlN, the 3.1 and 3.4-3.4 eV peaks mainly originate from σ-π* SPEs, with a maximum intensity due to transitions towards Γ, and around the mid points the ΓK and MG segments. The weak 3.7-3.9 eV peak is mostly due to π-σ* SPEs around the mid points of the KM and MG lines. The 4.1-4.2 eV peak has a main contribution from σ-σ* SPEs along the ΓK and MG lines, close to Γ.

In QFGe on MoS$_2$, all the 2.6, 3.2, 3.5, and 4.1 eV peaks mainly originate from σ-π* SPEs around the mid points of the ΓK and MG segments. Other contributions at 3.4 eV and 3.5 eV are respectively due to π-σ* SPEs around M and σ-σ* SPEs along ΓK, close to Γ.

The different peak positions and intensities of the VIS to MUV feature in QFGe on MoS$_2$, as compared to FGe and QFGe on AlN, are a consequence of the different positions of the DOS peaks around the π-like (or σ-like) band minima and the σ*-like (or π*-like) band maxima.

E. Loss Spectra

We now move to the energy loss properties of the three monolayers, within the TDDFT-RPA framework. As a preliminary analysis, we focus on the behavior of $-\text{Im}(1/e^{i\omega})$ at small momentum transfers along ΓM, say, $q<5.4 \times 10^{-2}$ Å$^{-1}$ down to the optical limit, displayed in Fig. 4. We notice the existence of distinct dispersive peak structures, which at the lowest sampled momentum correspond to the FIR-MIR, MIR-NIR, NIR-VIS and VIS-MUV absorption features of Fig. 3.

In particular, FGe and QFGe on AlN exhibit a 2DP mode of low intensity at 0.01-0.04 eV, due to charge density oscillations of the fraction of thermally excited Dirac cone electrons and holes at room temperature, with the 2DP peaks in Fig. 4(a), (b) representing the loss counterpart of the FIR-MIR absorption peaks in Fig. 3(a), (b).

In QFGe on MoS$_2$, on the other hand, we detect an intriguing scenario where the 0.29 eV shifting of $E_P$ above $E_C$ induces a strong 2DP at 0.04-0.3 eV, involving the above-calculated $n_{h\pi}$ concentration of massless Dirac cone electrons. This oscillation coexists with the intraband modes (σP) of the above-calculated $n_{e\pi}$ concentration of massive parabolic holes, associated with the two σ-like bands, which cross the Fermi energy close to Γ. The massless and massive modes are superimposed to each other, and cannot be disentangled in intrinsic conditions, yielding the 2DP+σP peak in Fig. 4(b), which corresponds to the FIR-MIR absorption peak of Fig. 3(c). The peak to peak ratio of the 2DP, in FGe and QFGe on AlN, and the 2DP+σP, in QFGe on MoS$_2$, at the lowest sampled momentum, parallels the difference in the corresponding absorption peak intensities respectively displayed Fig. 3(a), (b) and 3(c).

Looking at the real macroscopic permittivity, in Fig. 4(d)-(f), we can further observe that the 2DP propagates undamped in the Landau sense over a different momentum transfer range, $q<0.8 \times 10^{-2}$ Å$^{-1}$, in FGe and
QFGe on AlN, and $q<3.2 \times 10^{-2} \text{Å}^{-1}$, in QFGe on MoS$_2$, where $\text{re}(\epsilon''(q))$ presents a well-defined pair of zeros. On the other hand, the $\sigma P$ modes of QFGe on MoS$_2$ are largely damped, being not related to a clear change of sign in $\text{re}(\epsilon''(q))$, though they leave a signature in $\text{re}(\epsilon''(q))$ below the 2DP zeros.

Another peculiar collective motion of the $\sigma$-like charge carriers in QFGe on MoS$_2$ is related to the 0.4-1.3 eV dispersive feature in Fig. 4(c), whose lowest momentum peak at $\sim 0.6$ eV corresponds to the MIR shoulder in the absorption spectrum of Fig. 3(c). The sequence of peak positions, ranging from 0.6 to 0.9 eV with increasing $q$, suggests that this feature is a manifestation of the interband plasmon ($\sigma\pi$) assisted by SPEs between the occupied and empty metal states at $\Gamma$.

The other two peak structures, at 1.4-2.2 eV and 2.6-5.0 eV, are the optical counterparts of the so-called $\pi$-like plasmon ($\pi\pi$) and $\pi\sigma$-like plasmon ($\pi\sigma\pi$), which are commonly characterized in group IV honeycomb sheets and heterostructures. These appear as largely damped charge density oscillations, being respectively superimposed to the $\pi\pi^*$ SPE spectrum and the $\sigma\pi^*$, $\sigma\sigma^*$, $\sigma\pi^*$ SPE spectra.

An even more informative representation is provided by the density maps of the FIR to VIS modes, given in Fig. 5 for a broad range of momentum transfers $q<0.15 \text{Å}^{-1}$ along $\Gamma M$. FGe [Fig. 5(a)] and QFGe on AlN [Fig. 5(b)] present very similar loss spectra, sharing an identical weak 2DP mode with monotonically increasing dispersive trend. An appreciable difference is detectable in the onset of the $\pi\pi$ structure, based on the positions of the top ($\sigma$-like) and bottom ($\sigma\pi$-like) band levels at $\Gamma$, as discussed above with reference to Figs. 1(a), (b) and 2(a), (b).

Again, the most interesting feature is due to the 2DP+$\sigma\pi$ and $\sigma\pi\pi$ modes in QFGe on MoS$_2$ [Fig. 5(c)], which follow an interfering pathway due to the different massless and massive plasmons involved. Also visible in Fig. 5(a)-(c) is that the $\pi\pi$ peak position increases monotonically with increasing $q$, though the actual dispersion, width and onset of the associated spectral structures in FGe and QFGe on AlN vs QFGe on MoS$_2$ are significantly different, as a consequence of the quasimetal vs metal nature of the monolayers.

Additional insights come from the zoom on the 2DP+$\sigma\pi$ and $\sigma\pi\pi$ structures, shown in Fig. 6(a), for $q<0.08 \text{Å}^{-1}$.
along ΓK, where we see that the highest peak propagates in the region where Dirac cone SPEs at the K point of the 1st BZ are absent, being mostly determined by the massless 2DP. Such a condition is confirmed by the energy position of the same mode in FGe with similar Fermi level shift relative to $E_C$. Complementary, the lowest peak occurs in the region where Γ-point excitations are absent, being entirely determined by the massive $\sigma^P$.

A way to isolate the $\sigma^P$ mode is to drive the Fermi level of QFGe on MoS$_2$ at the Dirac cone vertex, which reduces the massless plasmon to the tiny structure recorded in intrinsic FGe [Fig. 5(a)] and QFGe on AlN [Fig. 5(b)]. This particular extrinsic condition is shown in the loss function of Fig. 6(b), where the highest peak must be ascribed to the intraband massive plasmon, because it lies $\sim$0.2 eV above the expected massless 2DP energy (see Supplementary Information, Sec. III and Sec.IV).

As the Fermi level is lowered down from the Dirac cone vertex, the 2DP mode comes into play and interferes with the $\sigma^P$ mode, which is shown in Fig. 6(c), where an intermediate extrinsic condition is considered, between the intrinsic and half-filled Dirac cone cases.

Another important situation pops up when $E_F$ is driven around $E_F^\pi$, as displayed in Fig. 7(a), where a different form of 2DP-$\sigma$ correlation emerges, with the $\sigma^P$ being shifted in momentum space and assuming a V-shaped feature for $q>0.1 \text{ Å}^{-1}$. This peculiar massless-massive plasmon interaction can be controlled by finetuning of $E_F$ and geometry driven band distortion. Indeed, a similar scenario appears in QFGe on AlN, as detailed in Fig. 7(b), where the different QFGe geometry offers a similar Fermi level positioning relative to the $\sigma^*$-like bands, with respect to QFGe on MoS$_2$. 

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**FIG. 5.** Intrinsic loss functions (in arb. units) of (a) FGe, (b) QFGe on AlN and (c) QFGe on MoS$_2$, displayed as density maps vs $\omega<1.4$ eV and $q<0.08$ Å$^{-1}$ with $q||\Gamma K$. The color scale is normalized to the maximum intensity of the $\omega<0.4$ eV mode, with the red dots labeling the undamped plasmon resonances. The dominant intraband (2DP, $\sigma^P$) and interband ($\sigma^P$, $\pi^P$) modes are highlighted as in Fig. 3.

**FIG. 6.** Loss functions (in arb. units) of QFGe on MoS$_2$, displayed as density maps vs $\omega<1.4$ eV and $q<0.08$ Å$^{-1}$, with $q||\Gamma K$, for different doping or gating conditions, with the Fermi level driven from the intrinsic state (a) to the Dirac cone vertex (b), passing from an intermediate position (c). The color scale is normalized to the maximum intensity of the $\omega<0.4$ eV mode, with the red lines delimit the undamped plasmon resonances, and the dominant plasmon modes marked as in Fig. 5. The dashed lines delimit the regions where one-electron excitations, involving the $\pi$ and $\pi^*$ bands, occur around the K point (SPE$\pi$), and one-electron excitations, involving the $\sigma$ and $\sigma^*$ bands, occur around the Γ point (SPE$\sigma$).
Additionally, the $\sigma_P$ becomes competitive with the 2DP when the $\sigma^*$-like band comes into play, as in the case of FGe stretched by 4.4 % relative to its LDA geometry\textsuperscript{58,69}, where the extrinsic condition $\Delta E_F = 0.4 \text{eV}$ leads to the strongly correlated 2DP-$V\sigma_P$ feature given in Fig. 7(c).

![Fig. 7. Loss function (in arb. units) of (a) QFGe on MoS\textsubscript{2}, (b) QFGe on AlN, and (c) stretched FGe (4.4 % wider than the LDA geometry of Fig. 1(a), defined by $\alpha = 4.06 \text{Å}$ and $\Delta = 0.69 \text{Å}$) for applied momentum transfers along $\Gamma K$. The Fermi level is driven to the top of the $\sigma$-like bands in (a), (b), and to the bottom of the $\sigma^*$-like band in (c). The color scale is normalized to the highest FIR-MIR peak, with the undamped plasmon resonances, the 2DP mode, and the SPE region delimiters marked as in in Fig. 6. AP denotes a weak acoustic modes of the Dirac cone charge-carriers activated by the specific direction of the incident momentum ($q||\Gamma K$). $V\sigma P$ in (c) labels novel massive mode disjoint from the massless 2DP and AP.](image)

Finally, when $E_F$ is kept within the $\sigma$-$\sigma^*$ band gap at $\Gamma$, the massive plasmon is excluded, which opens up the typical scenario of group IV 2D honeycomb lattices, where the 2DP propagates out-of-phase with square-root-like dispersion, in parallel with a smaller in-phase acoustic plasmon (AP) triggered by momentum transfers along selected directions, e.g., $q||\Gamma K$\textsuperscript{37,38}. The 2DP and AP modes are shown in Fig. 8, with the loss functions of the FGe and QFGe monolayers computed at the same Fermi level shift relative to the Dirac cone vertex. The massless plasmons are also exclusively implicated in the FIR-NIR dielectric response of FGe and QFGe, within a broad range of extrinsic conditions (see Supplementary Information, Sec. III and Sec.IV).

On the other hand, in both the stretched FGe and QFGe geometries, the AP mode can be detected along with the 2DP and massive modes for momentum transfers along $\Gamma K$, see Fig. 7. The AP disappears for momentum transfers along $\Gamma M$, as already observed in graphene and silicene\textsuperscript{37,38} (see also Supplementary Information, Sec. IV).

![Fig. 8. Loss function (in arb. units) of (a) QFGe on MoS\textsubscript{2}, (b) QFGe on AlN, and (c) FGe for applied momentum transfers along $\Gamma K$. The Fermi level is driven well above the top of the $\sigma$-like bands, at 0.49 eV with respect to the Dirac cone vertex, in such a way that only the massless 2DP and AP modes are present. The color scale is normalized to the highest FIR-MIR peak, with the undamped plasmon resonances and the SPE$\pi$ region delimiters marked as in in Figs. 6-7.](image)
F. Many-body quasiparticle and excitonic effects

To improve the reliability of the above presented analysis, we first estimated the role of GW quasiparticle corrections to the LDA band energies. We focused in particular on FGe and QFGe on MoS$_2$ as complementary examples of purely massless and massless-massive plasmonic substrates, under specific extrinsic regimes. Then, we applied the TDDFT-RPA machinery and calculated the dielectric properties of both overlayers by replacing the LDA band energies with the GW corrected band energies, while leaving unaltered the systems’ wave functions.

The GW bands of FGe, shown in Fig. 9(a), exhibit a significant narrowing of the Dirac cone relative to the LDA bands, equivalent to an increased slope of 0.30, in units of the Bohr velocity. A similar though lower increase rate has been reported for the Fermi velocity in graphene. Additionally, the GW energy of the top $\sigma$-like states are downshifted by $\sim$0.04 eV with respect to the LDA value. All other energies, related with the two highest occupied and lowest unoccupied bands, are reported to differ by a maximum value of 0.4 eV.

Fig. 9(b) and Fig. 9(c) display the loss function of extrinsic FGe, respectively obtained within the RPA and the RPA+GW frameworks. The considered Fermi level shifting, $\Delta E_F = 0.4$ eV, activates highly resolved 2DP and AP modes, excluding the massive modes. Indeed, the latter would be present under extreme doping or gating conditions, being such that $-0.55 \leq \Delta E_F \leq 0.58$ eV with the LDA energies, and $-0.60 \leq \Delta E_F \leq 0.95$ eV including the GW quasiparticle corrections. By comparing Fig. 9(b) with Fig. 9(c), we see that the RPA and RPA+GW loss spectra exhibit qualitatively similar propagation and damping trends, though the change in Fermi velocity results in smaller amounts of charge carriers and narrower SPE regions.

On the other hand, as reported in Fig. 9(d), both the Dirac cone vertex and the highest $\sigma$-like states of QFGe on MoS$_2$ experience very small changes, below 0.04 eV. Additionally, the GW Dirac cone slope is increased by 6%, while the
GW mass of the \(\sigma\)-like charge carriers are practically identical to the corresponding LDA values. All other energies, within the two highest occupied and lowest unoccupied bands, differ by a maximum value of 0.3 eV.

Nonetheless, the peculiar RPA plasmon structures of Figs. 6(a) and 7(a) correspond to the RPA+GW scenarios depicted in Figs. 9(e) and 9(f), after \(\Delta E_F\) is adjusted to compensate the differences in the GW and LDA values of the Dirac cone energy and Fermi velocity. In particular, the extrinsic condition \(\Delta E_F = -0.10\) eV in Fig. 9(e) drives the intrinsic Fermi level at the same position, relative to the Dirac cone vertex, as Fig. 6(a), yielding almost identical concentrations of massless and massive charge carriers. Furthermore, the extrinsic condition \(\Delta E_F = -0.32\) eV in Fig. 9(f) drives the intrinsic Fermi level at the Dirac cone vertex, as in Fig. 7(a). Thus, the expected tunability of the 2DP, AP, and \(\sigma P\) modes can be improved by correcting the LDA band energies of the germanene monolayers with more accurate predictions coming from many-body correlations or experimental data.

As a final scrutiny, we estimated the role of excitonic effects on the dielectric properties of FGe and QFGe on MoS\(_2\), using the BSE framework\(^{52-54}\), which we implemented with the bare, three-dimensional (3D) Coulomb potential. In this, we considered a minimum applied momentum of \(2\) eV\(\cdot\)Å\(^{-1}\), with respect to our RPA and RPA+GW calculations. To suppress the increased noise within the RPA or RPA+GW treatments, are an artifact of the reduced resolution in BSE computations. On the other hand, that the sub-peaks in (b), (c), (e), (f), superimposed to the main intraband and interband absorption peaks, already identified within the RPA or RPA+GW treatments, are an artifact of the reduced resolution in BSE computations. On the other hand, the RPA and RPA+GW computations presented here have a much more accurate resolution on the 1st BZ, thus giving a more reliable prediction of the FIR-NIR feature.

Fig. 10 reports the BSE and BSE+GW macroscopic permittivity of FGe and QFGe on MoS\(_2\) against their RPA, RPA\(^*\), and RPA+GW counterparts. To ease the comparison, an overall renormalization factor is applied to the RPA and RPA+GW results, to compensate for the use of the 3D Coulomb interaction without our 2D truncation in the
RPA*, BSE and BSE+GW calculations.

Apart from the different broadening in the real and imaginary permittivity parts, we find that the plasmon resonances, of the 2DP, πP, and σπP modes, and the intraband and interband peak positions are well defined in both approaches, being in close agreement with each other, within a maximum difference below 0.02 eV. We also notice that the overall VIS-NUV features of the RPA and BSE permittivities, or the RPA+GW and BSE+GW permittivities, have very similar trends.

At a closer look, the comparison of the BSE and the control RPA* calculations suggests that excitonic effects may play a non-negligible role at lower and higher ends of the optical band. More importantly, the MIR-NIR absorption peaks in the BSE and BSE+GW approximation suffer from the low resolution on the 1st BZ sampling.

Additionally, the intraband and interband absorption peaks, plus related plasmon modes of the metal states in QFGe on MoS2, are confirmed to exist with both the RPA and BSE approaches, with the interband σ-σ* feature being correctly described with the RPA+GW and BSE+GW formalisms. We can thus safely conclude that the inclusion of excitonic effects confirms the existence of a competitive interplay of massive and massless plasmon in germanene sheets with selected geometries.

III. DISCUSSION

The key role of optical plasmons in light coupling has been long identified in a wide variety of nano-objects and fully elucidated in simple 2D honeycomb materials.

In the present study, we have singled out the additional versatility of germanene monolayers and related interfaces, whose multiple light-matter modes are strongly dependent on both geometry and charge carrier concentration. We remark that the latter is a novel feature, which marginally involve other 2DDMs, and as such it requires an improved analysis, in line with what has been reported here, for a correct tuning of the input parameters of possible germanene-based devices.

Our investigation has provided a complete picture of the massless and differently massive charge density waves in currently synthesized germanene sheets, outlining a unique playground of collective states in 2D quantum matter that can be manipulated for on-demand optoelectronic or plasmonic purposes.

This may serve to embed germanene-based building blocks in novel van der Waals heterostructures, or implement 2D platforms for extreme light confinement, compatible with standard semiconductor technology.

IV. METHODS

The TDDFT and GW calculations were carried out using a package of Open-MP/MPI Fortran codes, developed by M.P. and A.S., which were interfaced with the DFT output from Abinit, and implemented in one of the high-performance computing facilities provided by the CINECA consortium (Italy).

A. Density Functional Calculations

As a routinely established framework, our TDDFT-RPA calculations required a preliminary DFT step to access the ground state of FGe, QFGe on AlN, and QFGe on MoS2, which we reconstructed by the PW pseudopotential approach. This involves the basis set of space functions indexed by the wave vectors of the 1st BZ and the reciprocal lattice vectors, in the normalization volume. Specifically, we expressed the outer electron properties of the three germanene phases, artificially replicated in three-dimensions, in terms of KS energy levels associated to single-particle states, accordingly expanded in the PW basis, where denotes the band number. We adopted an LDA scheme, based on the Teter-Pade exchange-correlation functional combined with a norm conserving Troullier-Martins pseudopotential. In all cases, we chose a periodic out-of-plane separation of 20 Å between the replicated germanene planes, which resulted in numerically negligible KS wave functions at distances larger than ~6 Å from each replica (within an error of 10−6 %). As for the in-plane geometry, our PW-LDA optimizations provided the two defining parameters of the FGe lattice, namely, the hexagonal lattice constant a=3.970 Å and the buckling distance ∆=0.640 Å, between the two germanium atoms of the crystal basis, which turned out to be consistent with the literature. Within the same PW-LDA scheme, we simulated the two QFGe geometries, using the experimentally derived values a = 3.928 Å, ∆ = 0.705 Å for AlN-distorted germanene, and a = 3.820 Å, ∆ = 0.860 Å for MoS2-distorted germanene, which respectively correspond to a 2.1 % and 7.4 % lattice compression, relative to FGe in the LDA geometry. In the self-consistent runs, first we limited the number of PWs in |νk| to ~104, by the energy cutoff |k + G|2/2 < 25 Ha. Then, we sampled the 1st BZ [Fig. 1(e)] with
Figs. 4 were found to 33 Sup-
mission of the self-energy Σ
leaving unaltered the experimentally derived parameters of the QGe structures23,24. We recorded minor differences between the LDA and GGA electronic structures, in an energy window of ∼2.5 eV around the Fermi level (see Supplementary Information, Sec. V), which covers electronic transitions and collective excitations in the FIR to VIS range, being the core interest of our study.

B. Time-Dependent Density Functional Approach

As a second step of the TDDFT machinery, we refined the KS eigensystem \{\varepsilon_{\nu k}, \ket{\nu k}\} in non-self-consistent runs on an MP grid of 720×720×1 k points. We further included more than 10 unoccupied bands to encompass all possible SPEs below ∼5 eV. Then, we plugged this information into the Adler-Wiser formula31,32

$$\chi^0_{GG} = \frac{2}{\Omega} \sum_{\nu k, \nu k'} \frac{(f_{\nu k} - f_{\nu k+q}) \rho_{\nu \nu'}(G) \rho_{\nu' \nu}(G')^*}{\omega + \varepsilon_{\nu k} - \varepsilon_{\nu' k+q} + i\eta},$$

To obtain the non-interacting density-density response function of the KS electrons. Here, \(\chi^0_{GG}\) is triggered by an optical photon of in-plane momentum \(q\) and energy \(\omega\). \(f_{\nu k}\) and \(f_{\nu' k+q}\) respectively denote the Fermi-Dirac occupations of the energy levels \(\varepsilon_{\nu k}\) and \(\varepsilon_{\nu' k+q}\), with the factor of 2 arising from electron spin degeneracy. \(\rho_{\nu \nu'}(G) = (\nu k | e^{-i(q+G)\cdot r} | \nu k + q)\) and \(\rho_{\nu' \nu}(G')^*\) are oscillator (or screened) matrix elements. Retarded propagation or damping is governed by the positive infinitesimal broadening \(\eta\), replaced by \(\eta = 0.01\) eV for numerical convenience.

Subsequently, we calculated the interacting density-density response function by the fundamental equation of TDDFT, namely, \(\chi_{GG} = \chi^0_{GG} + \{\chi^0(v + f_\nu)\chi^0_{GG}\}. In the procedure, we neglected the exchange-correlation part \(f_\nu\) of the interaction kernel \(v + f_\nu\). Additionally, we replaced the \(v\)-operator with the RPA local kernel

$$v_{GG} = 2\pi^2 \int_{-L/2}^{L/2} dz \int_{-L/2}^{L/2} dz' e^{i(G_z z - G'_z z') - |q + g||z + z'|},$$

Based on the 2D Coulomb potential \(v_{GG} = 2\pi \delta_{gG}/|q + g|\), with \(g, g', G, G'\) respectively labeling the in-plane and out-of-plane components of \(G\) and \(G'\). The advantage of \(v_{GG}\) is the deletion of redundant density-density interactions among the replicated monolayer slabs35-44, which provides far more accuracy to the low-momentum dielectric response of 2D materials with respect to the usual Coulomb potential \(v_{GG} = \lim_{L \to \infty} v_{GG} = 4\pi \delta_{gG}/|q + G|^2\).

Next, we treated the fundamental equation of TDDFT at the RPA level in the small \(v\)-limit, to obtain

$$\chi_{GG} = [\chi^0(1 + v \chi^0)^{-1}]_{GG},$$

Finally, we determined the inverse dielectric matrix \(\varepsilon_{GG}^{-1} = \delta_{GG} + (v \chi_{GG})^\dagger\), which gives access to the macroscopic permittivity \(\varepsilon^\parallel = 1/\varepsilon_{GG}\). In doing so, we efficiently included crystal-local field effects, associated with the off-diagonal elements of \(\chi^0_{GG}\), \(\chi_{GG}\) and \(\varepsilon_{GG}^{-1}\), by restricting the calculation to the smallest \(\sim 100\) G-vectors of the form \((0, 0, G_z)\).

The TDDFT-RPA framework just outlined can be tuned by adjusting the occupation factors in \(\chi^0_{GG}\) to account for changes in both Fermi level and temperature. Working at room temperature, we simulated the intrinsic and extrinsic dielectric responses of the germanane sheets by replacing \(E_F\) with \(E_F + \Delta E_F\) in \(f_{\nu k}\) and \(f_{\nu k+q}\), while leaving unaltered the KS energies, \(\varepsilon_{\nu k}\) and \(\varepsilon_{\nu k+q}\), and oscillator matrix elements, \(\rho_{\nu \nu'}(G)\) and \(\rho_{\nu' \nu}(G')^*\).

The main outputs from such calculations are given in Figs. 3-8. In particular, the optical absorption features were computed at the smallest sampled momenta allowed by the chosen MP-grid, namely, \(q_0^{M} = \pi/(180\sqrt{3}\alpha)\), along ΓM, and \(q_0^{K} = \pi/(180\alpha)\), along ΓK, with \(\alpha\) the lattice constant. The \(q||ΓM\) absorption spectra of Fig. 3 were found to be identical to the \(q||ΓK\) absorption spectra, within the numerical errors. The energy loss spectra of Figs. 4-8 were computed over a broad range of sampled momenta \(q = q_0^{M} - 100 q_0^{M}\), along ΓM, and \(q = q_0^{K} - 60 q_0^{K}\), along ΓK.

C. GW calculations

We probed the accuracy of our TDDFT-LDA-RPA framework by implementing the simplest first-order GW expansion of the self-energy \(\Sigma_{\nu k}\), around the LDA xc potential \(v_{ioa}^{lda}\). Specifically, we computed the quasiparticle energy
corrections

\[ \varepsilon_{\nu k}^{\text{GW}} = \varepsilon_{\nu k} + \frac{\Sigma_{\nu k}(\omega) - \nu_{\nu k}^{\text{LDA}}}{1 - \partial \Sigma_{\nu k}(\omega)/\partial \omega}_{\omega=\varepsilon_{\nu k}}, \]

to the unperturbed LDA energies \( \{\varepsilon_{\nu k}\} \) of FGe and QFGe. Accordingly, we evaluated the static, exchange part of the total self-energy

\[ \Sigma_{\nu k}^e(\omega) = -\frac{1}{\Omega} \sum_{\rho\rho'} \sum_{G,G'} \rho_{\rho\nu}(G) \rho_{\nu\rho'}(G')^* \upsilon_{GG'}(q), \]

with cutoffs of 5 Ha on the unperturbed KS wave functions and 10 Ha on the \( G \) vectors. As for the dynamic, correlated self-energy

\[ \Sigma_{\nu k}^c(\omega) = \frac{i}{2\pi\Omega} \sum_{\nu\nu'} \sum_{G,G'} \rho_{\nu\nu}(G) \rho_{\nu\nu'}(G')^* \upsilon_{GG'}(q) J_{\nu\nu'}^G G_{-q}(q,\omega) \]

we reduced the \( G \)-vector cutoff to 5 Ha, and replaced the \( J \) kernel with a plasmon pole model. We found well converged results using a 72x72x1 MP grid to represent the unperturbed PW-LDA eigensystem \( \{\varepsilon_{\nu k}, |\nu k\rangle\} \), over a total of 50 occupied and unoccupied bands. We further adopted the 2D-truncated local kernel of our TDDFT-RPA approach for the \( \upsilon_{GG'} \) matrix elements. The GW bands from FGe and QFGe on MoS\(_2\) are respectively reported in Fig. 9(a) and 9(d), in comparison with the LDA bands of Fig. 1(a) and Fig. 1(c).

As a final exploration, we implemented a modified TDDFT machinery, by replacing the LDA energies, sampled over the 720x720x1 MP-grid, with the GW energies of Fig. 9(a), (d), interpolated over the 720x720x1 MP-grid. In this way, we obtained the RPA+GW loss spectra of Fig. 9(c), (e), (f).

D. BSE calculations

We further compared our RPA and RPA+GW permittivity calculations with the macroscopic dielectric function

\[ \varepsilon_{\text{BSE}}^M = 1 - \nu_{00}^{3D} \sum_{\nu\nu'k} \sum_{i,j} \rho_{\nu\nu}(0) \rho_{\nu\nu'}(0)^* \sum_{\lambda} \frac{a_{\nu\nu'k}\lambda_{\nu\nu'}^{\lambda} a_{\nu\nu'k}\lambda_{\nu\nu'}}{\omega - \varepsilon_{\nu} + \imath \eta}, \]

obtained from the BSE and BSE+GW approximations, as implemented in the YAMBO code, which relies on the bare 3D Coulomb potential elements \( \nu_{00}^{3D} = 4\pi/|q|^2 \). Accordingly, we refined the DFT-LDA electronic structures of the monolayers on an MP grid of 72x72x1, thus adopting a reduced resolution on the transferred momenta by one tenth, relative to our TDDFT-RPA computations. To compensate for the lack in resolution, and reduce the noise in the behavior of \( \varepsilon_{\text{BSE}}^M \) vs \( \omega \), we adopted a broadening parameter \( \eta \) of 0.05 eV, that is five times larger than our TDDFT+RPA computations. We then considered the lowest sampled momentum \( q_{\text{BSE}}^M \) along \( \Gamma M \), in the above mentioned coarse grid, with \( q_{\text{BSE}}^M = \pi/(18\sqrt{3}a) \). Such a value is ten times larger than the optical momentum \( q_{\text{BSE}}^M \), used to derive the absorption spectra in our TDDFT-RPA approach. Next, we computed the eigenvalues \( \varepsilon_{\nu} \) and eigenvectors \( a_{\nu\nu'k}^{\lambda} \) of the two-particle hamiltonian

\[ h_{\nu\nu'k} = (\varepsilon_{\nu k} - \varepsilon_{\nu' k}) \delta_{\nu\nu'} \delta_{\nu'\nu} \delta_{kk'} + (f_{\nu k} - f_{\nu' k})(2u_{\nu\nu'k} - w_{\nu\nu'k}), \]

on a limited number of states, allowing the \( \nu, \nu', \nu' \), and \( \nu' \) indexes to run over the three highest occupied and lowest unoccupied bands. Finally, we computed the electron-hole exchange interaction matrix elements

\[ u_{\nu\nu'k}^{\nu'\nu k} = \frac{1}{\Omega} \sum_{G \neq 0} \nu_{GG}^{3D} \rho_{\nu\nu}(0) \rho_{\nu'\nu'}(0)^* \]

with \( \sim 10^4 \) reciprocal lattice vectors, and the electron-hole attraction matrix elements

\[ w_{\nu\nu'k}^{\nu'\nu k} = \frac{1}{\Omega} \sum_{G,G'} \nu_{GG'}^{3D} \varepsilon_{GG'}^{1/2} \rho_{\nu\nu}(G) \rho_{\nu'\nu'}(G)^* \delta_{kk+q} \]

with \( \sim 10^2 \) reciprocal lattice vectors, to obtain the BSE permittivity of Fig. 10(a), (b), (d), (e). We further corrected the LDA band energies with suitable renormalization factors on the first conduction and first valence bandwidths, derived from our GW calculations. In this way we obtained the BSE+GW permittivity of Fig. 10(c), (f).
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Contributions

A.S. and M.P. directed the research, implemented the TDDFT code, provided the main interpretation of the results and wrote the paper, in close consultation with C.V.G. M.P. ran the TDFT-RPA calculations in close consultation with A.S. and C.V.G. A.S. ran the TDFT-RPA+GW and BSE calculations in close consultation with M.P. and C.V.G.

V. ETHICS DECLARATIONS

Competing Interests

The Authors declare no Competing Financial or Non-Financial Interests.

DATA AVAILABILITY

The authors declare that the data supporting the findings of this study are available within the paper (and its Supplementary Information files). Further data, concerning the outputs and codes from DFT and TDDFT calculations, are also available from the corresponding author upon reasonable request.

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