The plasmonic character of monolayer silicene is investigated by time-dependent density functional theory in the random phase approximation. Both the intrinsic (undoped) and several extrinsic (carrier doped or gated) conditions are explored by simulating injection of a probe particle (i.e., an electron or a photon) of energy below 20 eV and in-plane momentum smaller than 1.1 Å. The energy-loss function of the system is analyzed, with particular reference to its induced charge-density fluctuations, i.e., plasmon resonances and corresponding dispersions, occurring in the investigated energy-momentum region. At energies larger than 1.5 eV, two intrinsic interband modes are detected and characterized. The first one is a hybridized π-like plasmon, which is assisted by competing one-electron processes involving sp and sp states, and depends on the slightest changes in specific geometric parameters, such as nearest-neighbor atomic distance and buckling constant. The second one is a more conventional π-σ plasmon, which is more intense than the π-like plasmon and more affected by one-electron processes involving the σ bands with respect to the analogous collective oscillation in monolayer graphene. At energies below 1 eV, two extrinsic intraband modes are predicted to occur, which are generated by distinct types of Dirac electrons (associated with different Fermi velocities at the so-called Dirac points). The most intense of them is a two-dimensional plasmon, having an energy-momentum dispersion that resembles that of a two-dimensional electron gas. The other is an acoustic plasmon that occurs for specific momentum directions and competes with the two-dimensional plasmon at mid-infrared energies. The strong anisotropic character of this mode cannot be explained in terms of the widely used Dirac-cone approximation. As in mono-, bi-, and few-layer graphene, the extrinsic oscillations of silicene are highly sensitive to the concentration of injected or ejected charge carriers. More importantly, the two-dimensional and acoustic plasmons appear to be a signature of the honeycomb lattice, independently of the chemistry of the group-IV elements and the details of the unit-cell geometry.

I. INTRODUCTION

Atomically thin materials, organized in hexagonal honeycomb-like geometry, have been through intense scrutiny due to their exceptional electronic properties, the most intriguing of which is, perhaps, the strong coupling between their quantized charge-density fluctuations, i.e., plasmon modes, and light or other charged particles [1–5]. Control and manipulation of the plasmon properties of these two-dimensional systems, including graphene and beyond, are expected to guide the design of next-generation nanophotonic and nanoelectronic devices, with the enhanced capability to operate from terahertz (THz) to infrared (IR) frequencies. Indeed, plasmon-like modes appear as the “true” low-energy excitations of low-dimensional systems [6, 7], while charged and spinful modes are realized as coherent states, with their own peculiar dynamics [8, 9], both in normal, and in superconducting phases [10–13]. Fundamental research and technological applications have been historically focused on monolayer graphene (MG) [14, 15], whose extrinsic plasmons exhibit much stronger confinement, larger tunability and lower losses compared to gold and silver nanoparticles [16]. Recent studies have thoroughly characterized the plasmon dispersions in MG [17–22] and some other graphene-related materials, such as bilayer graphene (BLG) [23, 24] and graphene nanoribbons (GNRs) arranged in regular planar arrays which, unlike MG, offer geometrically controllable band gaps [25–27]. Further advances are expected from the analysis of nanocarbon-metal interfaces together with associated application developments in biological sensing, optical signal processing and quantum information technology [3, 28–32].

Nonetheless, the incompatibility of carbon-based materials with current silicon-based electronics makes the former unsuitable for immediate use, for which reason, other candidates among the group-IV elements, e.g., Silicon and Germanium in honeycomb lattice, have been explored [33–40] that, similarly to MG, have, in their free-standing forms, linear dispersing valence (π) and conduction (π′) bands, crossing at the inequivalent K (and K′) points [41, 42], where charge-carryes behave as massless Dirac fermions.

In particular, silicene has been recognized to have four principal advantages with respect to MG: (i) compatibility with current electronics; (ii) large spin-orbit induced band gap of 1-10 meV [42, 43], with respect to the 10^{-3} meV value predicted for MG [44], which has been confirmed by an experimental realization of the quantum spin Hall effect [45]; (iii) tunable band gap in the presence of a perpendicular electric field [35, 46–49], with band gap values of several meV that increase with increasing the field strength, or by hydrogenation [50–
and fluorination [53]; and (iv) synthesis on various substrates with different electronic properties [39]. This and other beyond-graphene systems are expected to be good competitors with graphene-related materials, sharing with the latter many of the superior features of MG, plus enhanced controllable electronic properties for specific applications. A further support in this direction has been the fabrication of a silicene-based field-effect transistor [54].

From the structural point of view, atomic resolved scanning tunneling microscopy (STM) experiments, combined with density-functional calculations [34, 52, 55, 56], have demonstrated that silicene is characterized by a buckled honeycomb lattice where the sp² hybridized orbitals get slightly dehybridized into sp³ like orbitals causing a weakening of the π bonds. This mixed sp²-sp³ hybridization yields a nearest-neighbor Si-Si distance of 2.2-2.3 Å and a low buckling of 0.45-0.55 Å.

On the practical side, silicene has been successfully grown on transition metals, such as Ag(001), Ag(110), Ag(111) [36, 39, 40], Ir(111) [57], metal dichalcogenides, like MoS₂ [58, 59], and ceramic materials, e.g., ZrB₂(0001) [60]. Combined experimental and theoretical studies have demonstrated that the Dirac cone disappears in silicene grown on Ag substrates, due to strong hybridization between Si and Ag orbitals [61-64]. Further theoretical scrutiny has also predicted silicene to be energetically stable (with unperturbed Dirac cones) on h-BN, H-passivated C-SiC(0001), Si-SiC(0001), Cl-passivated Si(111), CaF₂, AlAs(111), AlP(111), GaAs(111), GaP(111), ZnSe(111), and ZnS(111) [40, 62, 65-68]. Semiconducting substrates with large band gaps like h-BN turn out to be excellent candidates to adsorb pristine silicene, simply because no substrate states appear close to the Fermi level and, accordingly, the interaction silicene-substrate cannot perturb the Dirac-cone structure.

Although the structural properties of pristine silicene are well established, a comprehensive approach and description of its plasmon properties at low and high energies, from the IR to ultraviolet (UV) range, has not been presented so far. A few theoretical studies [69-72], based on the analysis of the electron energy-loss function and absorption spectrum, have reported the existence of two interband plasmons in intrinsic silicene, occurring at energies larger than 1.5 eV for vanishingly small momentum transfers. These are counterparts to the well-known π and π-σ plasmons found in MG, BLG and graphite [73]. Otherwise, MG, silicene and germanene have been proved to have the same IR frequency absorbance [74], which is a universal feature of the two-dimensional honeycomb lattice and does not depend on the chemistry of the group-IV element, buckling parameter or hybridization state. Furthermore, some noteworthy approaches have investigated the effect of an external, perpendicular electric field [47, 48], plus an additional exchange field [49], probing the spin-orbit band-structure of silicene, below some tenths of eV around the K and K' points. In these studies, the use of an effective two-spinor Hamiltonian, with an emergent Dirac-cone structure perturbed by spin-orbit [73] and external/field terms, has revealed presence and interplay of extrinsic plasmons, at meV energies and far-IR wave lengths, displaying features of different regimes, including those of a topological insulator and a valley-spin polarized metal. In the same energy-momentum region, of key-interest for nanodevice applications, it has been demonstrated that the electron-phonon interaction plays a critical role [76, 77], leading the in-plane phonon modes to hybridize with the extrinsic plasmons.

Here, we present a full ab initio approach, based on time-dependent (TD) density functional theory (DFT) within the random phase approximation (RPA), to scrutinize the plasmon properties of pristine and doped silicene in absence of external fields and spin-orbit effects, which makes an excellent approximation for applications in the mid-IR to UV range, with the plasmon-phonon coupling reduced to a minor extent. First, we focus on the intrinsic IR and UV plasmons, whose long-wavelength behavior is in agreement with the absorbance predictions of Refs. 71 and 72. In particular, we describe the role played by sp² and sp³ hybridization in the Landau damping mechanism, which affects the silicene counterpart of the MG π plasmon. Next, we discuss the mid-IR to near-IR extrinsic plasmons, highlighting the occurrence of two distinct tunable modes, which may be seen as a universal feature of the gapless band-structure of group IV elements in honeycomb lattice.

Our arguments are organized as follows. In section II, we briefly outline the key concepts of our TDDFT+RPA scheme, suitable for two-dimensional periodic systems. In section III, we analyze the energy-loss spectrum of silicene at high energies (larger than ~ 1.5 eV), with reference to the coupling of the intrinsic plasmons and single-particle (SP) processes, involving sp² and sp³ hybridized states. In section IV, we investigate the low-energy end of the energy-loss spectrum (below ~ 1 eV) in the presence of carrier doping, and show the interrelation between two extrinsic intraband modes: one of them is a two-dimensional plasmon, already observed in a variety of graphene-based materials; the other is an acoustical plasmon, direct consequence of the anisotropic band structure of the system around the Dirac points, i.e., the failure of the Dirac-cone approximation. In section V, we draw our conclusions.

II. METHODS

In this section, we first provide the input parameters of our ground-state density functional calculations of monolayer silicene (Sec. II A). Then, we highlight the main features of our TDDFT approach, yielding the complex permittivity and loss function of the system under both intrinsic and extrinsic conditions (Sec. II B). Hartree atomic units are used throughout, unless oth-
A. DFT calculation

The equilibrium electronic properties of silicene were determined by DFT in the local density approximation (LDA) [79], with the Kohn-Sham (KS) electron wave functions expanded in the plane-wave (PW) basis [80]. The latter is represented by the space functions

$$\text{PW}_{k+G}(r) = \Omega_0^{-1/2} e^{i(k+G) \cdot r},$$

where \(k\) is a wave vector in the first Brillouin zone (BZ), \(G\) a reciprocal-lattice vector, and \(\Omega_0\) the unit-cell volume associated to the real-space lattice [Fig. 1(a) and 1(b)]. The number of PWs was limited by the energy cut off \(|k + G|/2 \leq 25\) Hartrees. Norm conserving pseudopotentials of the Troullier-Martins type were adopted to eliminate the core electrons [81]. The three-dimensional periodicity inherent in our PW-DFT approach was generated by replicating the silicene planes with a minimum separation \(L\) of 20 Å.

Geometry optimization and ground state calculations were carried out on the irreducible part of the first BZ [\(TKM\) triangle in Fig. 1(b)], using a \(\Gamma\)-centered and unshifted Monkhorst-Pack (MP) grid of \(N = 180 \times 180 \times 1\) \(k\) points [82]. The optimized lattice constant \(a\) and buckling parameter \(\Delta\) were found to be \(a = 3.82\ Å\) and \(\Delta = 0.45\ Å\), respectively [Fig. 1(a)]. Slightly larger lattice-constant values available from the literature [42, 52, 66, 83] were also tested, while keeping the buckling parameter fixed to its optimized value (see Appendix A).

As for the LDA electronic structure, the KS energies \(\varepsilon_{\nu k}\) and wave functions

$$\langle r | \nu k \rangle = N^{-1/2} \sum_G C_{k-G} \text{PW}_{k+G}(r),$$

were computed for \(\nu \leq 50\) bands, with the \(G\) sum being limited by the energy cut off condition set forth above to include \(\sim 5000\) coefficients \(c_{\nu k+G}\) per wave function.

A simple visual perspective of the band energies [Fig. 1(c)] shows that silicene presents a Dirac-cone structure at the \(K\) points, within \(\sim 0.8\) eV around the Fermi energy \(E_F\). Looking at the density of states (DOS) as function of the band energies [Fig. 1(d)], we notice that the two peaks closest to \(E_F\) correspond to \(\pi\) and \(\pi^*\) flat band dispersions at the \(M\) point [Fig. 1(c)]. Other two peculiar DOS-peak structures, appearing at \(\sim 3\)-4 eV above and below \(E_F\), are direct consequence of the mixed \(sp^2-sp^3\) hybridization and buckled conformation of silicene. A more-detailed insight into these hybridization mechanisms is offered by the orbital projected band structure and DOS of Fig. 1(e) and 1(f), respectively, where we have separated the contribution of \(s\) and \(p_\parallel\) states, forming \(sp^2\) like bonds, from \(p_\perp\) states, involved in \(\pi\) bonds, and \(d\) states of the unit-cell Si atoms. The valence bands have well-defined \(\sigma\) and \(\pi\) characters, with sharp avoided-crossings features in correspondence of the DOS peaks at \(2.5-3.5\) eV below \(E_F\). The conduction states above the Dirac point are also of the \(\pi\) form, yielding an antibonding \(\pi^*\) band responsible for the DOS peak at \(2.7\) eV above \(E_F\) [41]. Another conduction band denoted \(\sigma_g^*\) lies close to the \(\pi^*\) band and produces a DOS peak at \(3\) eV above \(E_F\). It has a dominant \(\sigma\)-character contaminated by \(d\) states. Other conduction bands are strongly influenced by \(d, f\), and higher principal quantum numbers, as it can be deduced by comparing the full DOS and its projected \(sp, p_\perp\) and \(d\) components at
energies larger than $\sim 3$ eV above $E_F$. These characteristics (not found in MG [84]) play an important role in the plasmonic properties of silicene at probing energies larger than 1.5 eV, as we will see in Sec. III.

As for the Dirac point features of the $\pi$-$\pi^*$ electrons, an average Fermi-velocity value $v_F = 0.54 \times 10^6$ m/s can be extracted from the band data, which is roughly 65% of that derived from local density calculations in MG, and reflects a relatively reduced mobility of the massless Dirac fermions of Silicene. A more detailed analysis is made possible by inspection of the partial DOS as function of the $\pi$-$\pi^*$ energies and group velocities parallel to $\Gamma K$ [Figs. 2(a) and 2(b)] and $\Gamma M$ [Figs. 2(c) and 2(d)]. Along $\Gamma K$, the DOS is peaked at two distinct Fermi-velocity values, corresponding to the $B_1$ and $B_2$ branches above $E_F$ in Fig. 2(a). On the other hand, along $\Gamma M$, the DOS is peaked around one single Fermi-velocity value, associated to the $B'_1$ branch below $E_F$ and $B_1$ branch above $E_F$ in Fig. 2(c).

Like in MG [18, 22], this anisotropic behavior is outside the Dirac-cone approximation, and yields markedly different extrinsic plasmon responses at probing energies smaller than 1.0 eV.

B. TDDFT+RPA approach

Plasmons in solid state materials are typically triggered by electron-beam radiation or photo-currents below a few eV, and charged ions with incident kinetic energy of the order of 0.1-1 keV [85–92]. In the present context, we consider introducing an electron or a photon, with incident momentum $q$ and frequency $\omega$, which weakly perturbs the KS electrons of silicene. The unperturbed density-density response function of the system to the test particle is provided by the Adler-Wiser formula [93–95]. The latter is generally represented in the reciprocal space as follows

$$
\chi_{GG'}^{0} = \frac{2}{NH_0} \sum_{k,\nu,\nu'} \langle f_{\nu k} - f_{\nu' k+\mathbf{q}} \rangle \rho_{\nu\nu'}^{k\mathbf{q}}(G) \rho_{\nu'\nu}^{k\mathbf{q}}(G')^* \frac{1}{\omega + \varepsilon_{\nu k} - \varepsilon_{\nu' k+\mathbf{q}} + i \eta}.
$$

Here, the factor of 2 accounts for the spin degeneracy, $f_{\nu k}$ labels the Fermi-Dirac distribution,

$$
\rho_{\nu\nu'}^{k\mathbf{q}}(G) = \int_\Omega d^3r \langle \nu k | r | \nu' \mathbf{k+q} \rangle e^{-i(q+G) \cdot r} \langle \nu' k | r \rangle v_{\mathbf{k+q}}
$$

are density-density correlation matrix elements, and $\eta$ yields a positive broadening (chosen to the value of 0.02 eV).

The interacting density-density response function stems from the central equation of TDDFT [96, 97]

$$
\chi_{GG'} = \chi_{GG'}^0 + (\chi^0 v^0)_{GG'},
$$

where $v_{GG'}$ represent the Fourier coefficients of an effective electron-electron interaction. In the RPA, these terms are approximated to the bare Coulomb potential:

$$
v_{GG'} \approx 4\pi \delta_{GG'}/|q + G|^2,
$$

where a purely 3D periodic system is taken into account. The drawback of this approach is the non-negligible interaction between the periodic replicas, no matter how large their relative distance is. To cancel out this unphysical phenomenon, basically due to the long-range character of the effective electron-electron interaction. In the RPA, these terms are approximated to the bare Coulomb potential:

$$
v_{GG'} \approx 4\pi \delta_{GG'}/|q + G|^2,
Once the interacting matrix elements in Eq. (5) have been set by Eq. (7), the inverse dielectric matrix is obtained as
\[
\left(\varepsilon^{-1}\right)_{GG} = \delta_{GG} + (i\chi)_{GG}.
\]
Collective excitations (plasmons) are established by the zeros in the real part of the macroscopic dielectric function (permittivity) \(\varepsilon^\text{M} = 1/(\varepsilon^{-1})_{00}\), whose imaginary part gives the optical absorption spectrum.

The plasmon structure is provided by the energy-loss function, being proportional to the imaginary part of the inverse permittivity:
\[
E_{\text{LOSS}} = -\text{Im}[\varepsilon^{-1}(00)].
\]

Nonlocal field effects are included in Eq. (9) through the off-diagonal elements of \(\chi_{GG}\). As in MG and BLG, we verified that 51 G vectors of the form \((0,0, G_z)\), sorted in length order from smallest to largest, lead to well-converged results.

In what follows we discuss the dielectric and energy-loss properties of silicene, as obtained from the outlined TDDFT+RPA scheme at room temperature and under several intrinsic or extrinsic conditions.

### III. INTRINSIC SILICENE

The ground-state electron density for the optimized lattice constant \(a = 3.82\ \text{Å}\) and buckling parameter \(\Delta = 0.45\ \text{Å}\) (Sec. II A) was used in a non self-consistent run to improve the resolution on the KS eigensystem \(\{\psi_\mathbf{k}, \varepsilon_\mathbf{k}\}\). The latter was recalculated on an MP mesh of \(N = 360 \times 360 \times 1\) k points, including up to 60 bands. This result was plugged in the TDDFT+RPA machinery, summarized by Eqs. (3)-(9), to have an accurate representation of the electronic excitations and energy loss properties up to 20 eV. Similar calculations were run for the lattice-constant values \(a = 3.86\) and \(3.89\ \text{Å}\), as reported in Appendix A.

The energy-loss spectrum of undoped (intrinsinc) silicene, with the LDA optimized geometry, is reported in Fig. 3 for a broad range of frequencies, ranging from the lower THz to the UV, and incident momenta along \(\Gamma K\) and \(\Gamma M\). Two plasmon structures can be clearly distinguished, i.e., a \(\pi\) like plasmon and a \(\pi\)-\(\sigma\) plasmon that are peaked respectively at \(\omega \sim 1.7\ \text{eV}\) and \(\omega \sim 4\ \text{eV}\), in correspondence with the lowest sampled \(q\) values, being smaller than \(10^{-2}\ \text{Å}^{-1}\). The outlined interband modes are counterparts to the well-known \(\pi\) and \(\pi\)-\(\sigma\) plasmons of MG, BLG, fewlayer graphene (i.e., five to ten stacked MG sheets) and graphite [18, 22, 24, 73, 98, 99], sharing with the former a square-root behavior of the energy-momentum dispersions in the optical region. Nevertheless, the reduced width of the \(\pi\) (\(\pi^*\)) and \(\sigma\) (\(\sigma_d^*\)) bands [Fig. 1(b)] and the peculiar DOS features [Fig. 1(c)], which characterize silicene with respect to MG, cause a red-shift and a different relative weight of the intrinsic plasmon peaks.

Indeed the \(\pi\) and \(\pi\)-\(\sigma\) structures of MG have similar peak intensities [73], whereas the \(\pi\)-\(\sigma\) peak of silicene is generally larger (by a factor of 3 at \(q > 0.1\ \text{Å}^{-1}\)) than the \(\pi\) like peak. This fact can be ascribed to the weakening of the \(\pi\) bonds in silicene due to the mixed \(sp^2\)-\(sp^3\) hybridization discussed in Sec. II A. Another distinctive aspect of the intrinsic response of silicene is the double (quasilinear) dispersion of the \(\pi\) like plasmon in the energy-momentum region \(\omega \gtrsim 2.5\ \text{eV}\) and \(q \gtrsim 0.3\ \text{Å}^{-1}\), along \(\Gamma M\) [Fig. 3(c) and 3(d)]. In this region, the collective oscillation is associated to SP excitations between high DOS points connecting the \(\pi\) and \(\sigma_d^*\) or \(\pi^*\) bands [Fig. 1(c)].

A more detailed view on the \(\pi\) like plasmon is offered by Fig. 4, where we see how the very close (or overlapping) energy levels in the \(\pi^*\) and \(\sigma_d^*\) bands [Fig. 1(c)] generate distinct plasmon features at high-DOS points [Fig. 1(d)]. For small incident momenta around the \(M\) point (\(q < 0.1\ \text{Å}^{-1}\)) and energies below 2.5 eV, the large \(\pi\) DOS peak hides the \(\sigma_d^*\) contribution [Fig. 1(d) and 1(f)], and a single plasmon character dominates along both \(\Gamma K\) and \(\Gamma M\). As \(q\) increases above \(\sim 0.3\ \text{Å}^{-1}\) and \(\omega\) gets larger than 3 eV, the \(\sigma_d^*\) component increases becoming of the same order as the \(\pi^*\) component [Fig. 1(d) and 1(f)]. This increase is associated to a larger splitting between the antibonding bands, which leads to a well-resolved

![FIG. 3. Energy-loss function of undoped silicene at \(T = 300\ \text{K}\) vs \(\omega\leq20\ \text{eV}\) and \(q\) along the full \(\Gamma K\) [(a),(b)] and \(\Gamma M\) [(c),(d)] paths of Fig. 1. In (b) and (d), the intensity scale is cut at 70% of the peak maximum, due to the \(\pi\)-\(\sigma\) plasmon (as also shown in Fig. 12).](image-url)
two-peak structure in the energy-loss spectra. The latter presents markedly distinct features along ΓK and ΓM, being a signature of the deeply anisotropic character of the dielectric response of the system. In either cases, the π like plasmon is indeed a hybridized plasmon where the role of π-π* and π-σ* components, i.e., the relative spectral weight of the associated SP processes, is modulated by the excited electronic structure. In addition, slight changes in the lattice constant cause some distortions of the π like plasmon peaks without altering the peak ratio of the π-π* and π-σ* parts (Appendix A).

E_{loss} at 300K

![Graph](image)

**FIG. 4.** $E_{loss}$ of undoped silicene vs ω < 5 eV and momentum $q < 0.7 \text{ Å}^{-1}$ along ΓK [(a),(c),(e)] and ΓM [(b),(d),(f)]. The intensity scale in (c), (d) is cut at 24% of the peak maximum, occurring at low $q$ and low ω [shown in (a), (b)]

Besides the π like and π-σ plasmons, Fig. 4 also shows a nonnegligible intraband plasmon, peaked at energies below 1 eV, which is generated by a conduction electron concentration $n^*$ of $2.9\times10^{11}$ cm$^{-2}$ at room temperature. This value is larger than the one found in MG, because of the smaller Fermi-velocity values that characterize silicene, in spite of its larger unit-cell area, which correspond to a lower slope in the vanishing DOS at the K points (Figs. 1 and 2). The intraband feature is barely visible in Figs. 3 and 4, where it is hidden by the onset of the π like structure. However, it can be detected at the lowest $q$’s in Figs. 5 and Figs. 12 (of Appendix A), where an extra peak below 1 eV is clearly spotted in both $E_{loss}$ and Im($\epsilon^M$). Hence, intraband plasmons are also possible in the intrinsic limit when finite temperature is considered.

From a closer analysis of $\epsilon^M$, we realize that only the π-
σ peak is a well-defined plasmon in a specific region of the energy-momentum domain, with \( q \sim 0.1 - 0.2 \, \text{Å}^{-1} \) and \( \omega \sim 5 - 7 \, \text{eV} \), where it corresponds to a zero in \( \text{Re}(\epsilon^M) \) at a frequency where \( \text{Im}(\epsilon^M) \) is small. All other \( \pi \) like and \( \pi-\sigma \) structures can still be treated as collective excitations, superimposed to SP processes between high-DOS points, whose average lifetime broadening \( (\eta = 0.02 \, \text{eV} \) in Eq. (3)) induces a large Landau damping.

A parallel situation has been reported in MG \cite{18, 24, 99, 100}. Indeed, as we let the lifetime broadening parameter tend artificially to zero, the condition for occurrence of a collective oscillation becomes more and more likely to be satisfied. In support of this argument, Figs. 5(g)-5(i) display \( \text{Re}(\epsilon^M) \) for \( \eta = 0.02, 0.005 \) and \( \eta = 0.001 \, \text{eV} \). The intraband and \( \pi \)-like plasmon structures are evidently related to quasi-zeros in \( \text{Re}(\epsilon^M) \). Interestingly enough, the complex permittivity and energy-loss function display a nearly isotropic behavior for small values of the transferred momentum, below \( 0.15 \, \text{Å}^{-1} \), while as \( q \) gets larger than \( 0.15 \, \text{Å}^{-1} \) the dielectric response of the system acquires a tensor character. Similar trends have been reported for MG \cite{18, 101} and BLG \cite{24}. As for the absorption spectrum, \( \text{Im}(\epsilon^M) \) reflects the main features of the dielectric response of the system corresponding to quasi-zeros in \( \text{Re}(\epsilon^M) \).

TABLE I. Fermi-level shifts \( \Delta E_F \) induced by adding (+) or removing(-) \( \bar{n}_0 \) electrons per unit cell, with positive or negative charge-carrier concentrations \( n^* \), which correspond to charge-carrier concentrations \( n^* \) at \( T = 300 \, \text{K} \).

| \( n^* \) (el per uc) | \( \bar{n}_0 \) (10\(^7\) × \text{cm}^{-2}) | \( \Delta E_F \) (eV) |
|--------------------------|--------------------------|--------------------------|
| -0.4                     | -0.0510                  | -4.039                   |
| -0.2                     | -0.0126                  | -1.000                   |
| 0.0                      | -                        | -0.029                   |
| 0.2                      | 0.0135                   | 1.071                    |
| 0.4                      | 0.0597                   | 4.727                    |

\( \Delta E_F = \pm 0.4 \, \text{eV} \) and \( \Delta E_F = \pm 0.2 \, \text{eV} \) are shown as density plots in Figs. 6 and 7, respectively. The most striking feature here is the appearance of two distinct plasmon resonances, which are nearly absent in intrinsic silicene at room temperature [Fig. 4(a) and 4(c)].

The energy-loss spectra for \( \Delta E_F = \pm 0.4 \, \text{eV} \) and \( \Delta E_F = \pm 0.2 \, \text{eV} \) are nearly absent in intrinsic silicene at room temperature [Fig. 4(a) and 4(c)].

The mass transfer of acoustic nature, denoted AP, is clearly visible for momentum transfers along \( \Gamma K \), being generated by the two type of Dirac electrons responsible for the conventional plasmon of a two-dimensional electron gas. This mode has been predicted and analyzed in a number of theoretical studies on extrinsic MG, ranging from two-band models in the Dirac cone approximation \cite{102} to TDDFT approaches \cite{18, 22, 99}, and it is at the heart of technological applications in graphene plasmonics \cite{2, 3, 5}.

Despite the difference in intensity, a second plasmon of acoustic nature, denoted AP, is clearly visible for momentum transfers along \( \Gamma K \), being generated by the two type of Dirac electrons responsible for the conventional plasmon of a two-dimensional electron gas. This mode has been predicted and analyzed in a number of theoretical studies on extrinsic MG, ranging from two-band models in the Dirac cone approximation \cite{102} to TDDFT approaches \cite{18, 22, 99}, and it is at the heart of technological applications in graphene plasmonics \cite{2, 3, 5}.

A signature of the asymmetric dielectric response of the material is provided by the observation that the 2DP mode is present along both \( \Gamma K \) and \( \Gamma M \), whereas the AP mode is present only along \( \Gamma K \). This means that the widely used Dirac cone approximation is capable of reproducing only the 2DP features. By comparing Figs. 6 and 7, we see that the 2DP and the AP are strongly sensitive to the extrinsic conditions, including the doping sign, being associated to different charge-carrier densities (Table I). More importantly, there is a region in the energy-momentum domain, corresponding to \( q \sim 0.1 - 0.2 \, \text{Å}^{-1} \), \( \omega \sim 0.2 - 0.6 \, \text{eV} \), where the AP mode is competitive with the 2DP. Although many recent calculations have reported the existence of two extrinsic plasmons in graphene-related materials \cite{24, 103}, the peculiarity of the AP mode in silicene and MG \cite{18, 22} is that it occurs in a single, virtually gapless band. Our study suggests that the occurrence of such a mode is another universal characteristic of the honeycomb lattice (in

IV. EXTRINSIC SILICENE

We now move to the loss properties of extrinsic silicene with LDA-optimized geometry. In Appendix A, we will discuss how the effect of stretching the lattice constant (from \( a = 3.82 \) to \( a = 3.86 \) and 3.89 Å) does not alter the extrinsic plasmon features. In what follows, we specifically consider four different charge-carrier concentrations, inducing negative and positive Fermi energy shifts \( \Delta E_F \), in the range of \(-0.4 \) to \( 0.4 \, \text{eV} \), relative to the Dirac-point energy. To achieve these extrinsic conditions, we adjusted the occupation factors \( f_{\bar{k}} \) and \( f_{\bar{k}+\bar{q}} \) in Eq. (3) by shifting the Fermi-energy values by \( \Delta E_F = \pm 0.2 \) and \( \pm 0.4 \, \text{eV} \), respectively. A summary of the sampled doping levels–and corresponding conduction-electron or valence-hole densities–is given in Table I. The \( \pi \) like and \( \pi-\sigma \) plasmons of the previous section were found to be rather insensitive to the simulated extrinsic conditions, as already indicated by several studies on graphene-related systems \cite{18, 24, 26, 27}.

Then, we present a zoomed view of the energy-momentum region \( \omega \leq 2.5 \, \text{eV} \), \( q < 0.35 \, \text{Å}^{-1} \), which was computed with the TDDFT+RPA method illustrated in Sec. II B, using an equilibrium electronic structure represented on an MP grid of \( N = 720 \times 720 \times 1 \, \text{k points and 12 bands.} \)
addition to the above mentioned infrared absorbance. It is worth mentioning that the 2DP and the π-like structure tend to get closer to each other, as the doping decreases. This is why at room temperature and zero doping the onset of π-like mode mostly hides the 2DP contribution [as already pointed out in Sec. III, with reference to Figs. 4 and 5].

Also interesting to notice is the opening of a gap in the SP excitation spectrum for low q and ω, along both ΓK and ΓM. Such a gap is in close agreement with the triangular region predicted by two-band models in the Dirac cone approximation [102]. The latter is delimited by dashed green lines in Figs. 6 and 7, which correspond to ω = vF q and ω = 2ΔEF − vF q (with vF being the average Fermi-velocity introduced in Sec. II A).

The 2DP falls onto the no-SP excitation region at the lowest q’s, where it appears as a sharp peak not affected by Landau damping, as displayed in Figs. 6(e)-6(h), 7(e)-7(h), 8(a) and 8(b). Accordingly, the real permittivity has well defined zeros in this region [reported as black dots in Figs. 6(a)-6(d) and 7(a)-7(d)]. For (ω, q) points outside the no-SP excitation region, the 2DP gets more and more damped, with the Re(eM) = 0 condition being
FIG. 8. \( \text{Re}(\epsilon M) \) and \( E_{\text{loss}} \)—normalized to their maximum values—for extrinsic silicene at \( \Delta E_F = 0.4 \) eV [(a), (c)] and \( \Delta E_F = 0.2 \) eV [(b), (d)] for some fixed \( q \) points along \( \Gamma K \).

violated at large \( q \) values, as shown in Fig. 8(c) and 8(d), where the competition mechanism between the 2DP and AP modes is emphasized. This explains why the intrinsic response of Silicene does not offer well-defined plasmon excitations, with the area of the no-SP-excitation region being virtually zero. As a further evidence in support of this argument, in Fig. 9 we show a complete analysis of the macroscopic dielectric function and the two-plasmon structure for \( \Delta E_F = 0.4 \) eV. Indeed, Figs. 9(c), 9(d) prove that the 2DP is a genuine collective oscillation in the no-SP-excitation region. On the other hand the AP mode lies outside this region, and the corresponding plasmon oscillation is always damped in the Landau sense.

V. CONCLUSIONS

We have presented a full TDDFT+RPA analysis of the dielectric properties and plasmon dispersion of intrinsic and extrinsic silicene in freestanding form, in absence of external fields and spin-orbit coupling, suitable for energies above 0.1 eV and incident momenta larger than \( 10^{-4} \) Å\(^{-1}\). The energy-loss spectra of intrinsic silicene have singled out two interband plasmon structures, lying at energies above 1.5 eV, which resembles the \( \pi \) and \( \pi-\sigma \) modes of MG. The low-\( q \) features of the plasmon peaks have been found in agreement with previous absorbance calculations [74]. A more careful analysis has revealed that the \( \pi \) like plasmon of silicene is assisted by SP processes between hybridized \( sp^2 \) and \( sp^3 \) states, connecting the \( \pi \) band to the \( \pi^* \) and \( \sigma^* \) like bands, which generates a double energy-momentum dispersion, best resolved for momentum transfers along \( \Gamma M \). Similar characteristics are expected to occur also in other buckled two-dimensional materials in honeycomb geometry, such as germanene.

At lower energies (below \( \sim 1 \) eV), the energy-loss spectra of extrinsic silicene show two distinct oscillations; whose relative strength can be modulated by the doping concentration of injected or ejected electrons. Similarly to MG, silicene presents a two-dimensional plasmon, whose relative strength can be modulated by the doping concentration of injected or ejected electrons, plus an acoustic mode, being observable only along specific directions of the incident momentum. Unlike the spin-polarized valley modes found at meV energies and far-IR momentum transfers [47–49], being related to the opening of a
band gap, these two modes are generated in a gapless band-structure by two different types of charge carriers, i.e., Dirac electrons moving with distinct Fermi velocities.

Our findings suggest that the 2DP and AP modes exist in other two-dimensional materials in honeycomb lattice, such as germanene, making this features independent on the chemistry of the group-IV element, buckling parameter, or hybridization state. More importantly, they support the argument that silicene-based nanomaterials are excellent options for the design of next-generation nanodevices, in competition with graphene-based nanomaterials.

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Appendix A: Influence of the unit-cell extension on the plasmon structure

In this first Appendix, we report on how the loss properties of silicene are affected by geometry, specifically focusing on the intrinsic $\pi$ like and extrinsic plasmon features, analyzed in Sec. III and IV, respectively. To this end, we applied the TDDFT+RPA scheme on three different Si-Si bond lengths (yielding the lattice constant values $a = 3.82$, 3.86, 3.89 Å) that have been quoted in the literature [83]. The buckling parameter has been fixed to its LDA-optimized value in all cases ($\Delta = 0.45$ Å).

The calculated loss function is shown in Fig. 10 for intrinsic silicene and Fig. 11 for extrinsic silicene. The only sensible effect is a red-shift of the $\pi$ like plasmon peaks with the increase of $a$. In particular, at long wavelengths, peak variations of 3.8% (along $\Gamma K$ for $q = 0.04$ Å$^{-1}$) and 1.3% (along $\Gamma M$ for $q = 0.02$ Å$^{-1}$) are recorded in response to a change in lattice constant of 1.8%. The same change yields a peak variation of 4% at small wavelengths along both $\Gamma K$ and $\Gamma M$ for $q = 0.4-0.45$ Å$^{-1}$. The extrinsic plasmon structure appears to be independent on lattice-constant variations considered here.

Appendix B: Role of the two-dimensional cut off on the Coulomb interaction

To complete our study, we focus on the long wavelength limit ($q < 10^3$Å$^{-1}$) and mid infrared to near ultraviolet frequency range ($\omega < 5$ eV) of the plasmon spectra of undoped silicene, and consider some previous theoretical results in comparison with the findings presented in the main text.

Mohan and coworkers [69] have reported two-plasmon features, with the $\pi$-plasmon lying at 2.16 eV and the $\pi$-$\sigma$-plasmon being peaked at 7 eV. The same peaks have been predicted to be around 2 eV and 9 eV, respectively, by Das et al [70]. To verify these results, we have solved the Dysonlike equation for the full susceptibility (Eq. (5)) with the bare Coulomb potential coefficients (Eq. (6)). The resulting loss function presents a narrow $\pi$-plasmon peak at 2 eV and a broad $\pi$-$\sigma$-plasmon peak at 7 eV along both $\Gamma K$ (a,b) and $\Gamma M$ (c,d). Slightly different lattice constant values ($a=3.82$, 3.86, 3.89 Å) have been tested.
FIG. 11. Energy-loss function of undoped silicene vs $\omega \leq 3$ eV for specific small and large $q$ values (in $\text{Å}^{-1}$) along $\Gamma K$. Slightly different lattice constant values ($a = 3.82, 3.86, 3.89 \text{ Å}$) have been tested.

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FIG. 12. Energy-loss function obtained with the TDDFT+RPA method illustrated in Sec. II B, using the cut-off potential of Eq. (9) [(a),(c)] and the bare Coulomb potential of Eq. (6) [(b),(d)]. The loss curves (shifted vertically for clarity) are plotted vs \( \omega < 20 \text{ eV} \) for sampled \( q \) values (in \( \text{Å}^{-1} \)) along \( \Gamma K \) [(a),(b)] and \( \Gamma M \) [(c),(d)]. The different behavior of the two methods is better illustrated in (e) and (f), where the energy-loss curves are plotted for the lowest two \( q \) values along \( \Gamma K \) (e) and \( \Gamma M \) (f).

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