

Electron-plasmon and electron-phonon satellites in the angle-resolved photoelectron spectra of n -doped anatase TiO_2

Fabio Caruso,^{1,2} Carla Verdi,² Samuel Poncé,² and Feliciano Giustino^{2,3}

¹*Institut für Physik and IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany*

²*Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, United Kingdom*

³*Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, USA*



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We develop a first-principles approach based on many-body perturbation theory to investigate the effects of the interaction between electrons and carrier plasmons on the electronic properties of highly doped semiconductors and oxides. Through the evaluation of the electron self-energy, we account simultaneously for electron-plasmon and electron-phonon coupling in theoretical calculations of angle-resolved photoemission spectra, electron linewidths, and relaxation times. We apply this methodology to electron-doped anatase TiO_2 as an illustrative example. The simulated spectra indicate that electron-plasmon coupling in TiO_2 underpins the formation of satellites at energies comparable to those of polaronic spectral features. At variance with phonons, however, the energy of plasmons and their spectral fingerprints depends strongly on the carrier concentration, revealing a complex interplay between plasmon and phonon satellites. The electron-plasmon interaction accounts for approximately 40% of the total electron-boson interaction strength, and it is key to improve the agreement with measured quasiparticle spectra.

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I. INTRODUCTION

The excitation of collective charge-density fluctuations [1] (plasmons) is pervasive in solids and it manifests itself through distinctive signatures in spectroscopic experiments as, e.g., electron-energy loss spectroscopy (EELS) and integrated and angle-resolved photoemission spectroscopy (ARPES). The emergence of plasmon satellites [2,3], for example, has been known since the early days of photoemission spectroscopy [4–7]. More recently, the formation of plasmonic polaron bands in ARPES, dispersive spectral features that closely follow the energy-momentum dispersion of the quasiparticle bands, has been identified through first-principles calculations [8–10] and confirmed experimentally in ARPES [11].

In n -type (p -type) doped semiconductors, the extrinsic carriers injected in the conduction (valence) band through the dopant atoms may host *carrier plasmons*, that is, low-energy plasmons with characteristic energies set by the carrier concentration n via $\omega^{\text{pl}} = (4\pi n/m_b\epsilon_\infty)^{1/2}$, with m_b and ϵ_∞ being the band effective mass and the high-frequency dielectric constant, respectively. Hartree atomic units are used throughout. At variance with metals and undoped semiconductors, where the plasmon energy is of the order of 5–15 eV, for degenerate doping densities (10^{17} – 10^{19} cm^{−3}), the characteristic energy of carrier plasmons is typically smaller than 100 meV and it is thus comparable with the phonon energies of solids.

At these energy scales, plasmons influence pervasively the electronic properties of doped semiconductors, in a similar fashion to the Fröhlich interaction between electrons and longitudinal-optical (LO) phonons in polar materials [12]. First-principles calculations for highly doped silicon, for example, illustrate that the scattering with plasmons induces the relaxation of excited quasiparticle states on subpicosecond timescales, and a narrowing of the band gap by 70 meV

[13]. These processes are forbidden by energy conservation in the undoped parent compounds. The emergence of low-energy photoemission satellites due to the coupling with carrier plasmons has further been observed in the photoemission spectrum of highly doped oxides for both conduction bands [14] and core levels [15]. These phenomena are reminiscent of the Fröhlich interaction in polar materials [16,17], revealing a striking similarity that calls for an in-depth comparison of plasmonic and polaronic coupling.

Highly doped oxides constitute an optimal playground to explore the interplay between electrons, plasmons, and phonons as they simultaneously host polar LO-phonon modes and tunable carrier plasmons, which lead to a rich scenario of electron-phonon and electron-plasmon coupling phenomena. In particular, the anatase phase of n -doped titanium dioxide (TiO_2)—one of the most used materials in photocatalysis [18] and photovoltaics due to its stability, nontoxicity, and natural abundance [19]—exhibits distinctive signatures of polaronic coupling, which manifest themselves through the emergence of photoemission satellites at binding energies around 100 meV below the conduction-band bottom [20,21]. The electronic properties of this polymorph have been investigated in great detail from first-principles calculations [22–26], making TiO_2 an ideal candidate to explore the influence of the electron-plasmon interaction.

In this work, we study the combined effect of plasmons and phonons on the electronic properties of highly doped TiO_2 . We develop a many-body approach to compute the electron self-energy due to the electron-plasmon interaction from first principles. At variance with earlier developments [13], this approach circumvents the high computational cost entailed by the explicit evaluation of the dielectric function in the presence of doping. By combining state-of-the-art calculations

of the electron-phonon and electron-plasmon self-energy with the cumulant expansion approach [27], we investigate the influence of plasmons and phonons on the emergence of spectral signatures of bosonic coupling in ARPES.

Our first-principles calculations of ARPES spectra reveal that the coupling to plasmons may underpin the formation of satellites with energy and intensity comparable to those of polaronic satellites. Due to the pronounced dependence of the plasmon energy on carrier concentration, the binding energy of plasmon satellites is modulated by doping in a range between 30 and 80 meV. While at doping concentrations lower than 10^{19} cm^{-3} the signatures of plasmon satellites may be hardly distinguishable from the quasiparticle bands due to finite resolution effects, at higher carrier densities plasmons and phonons simultaneously contribute to the spectral intensity of photoemission satellites. Overall, our results indicate that the electron-plasmon interaction accounts for about 40% of the total electron-boson interaction strength, which is corroborated by the improved agreement with the experimental quasiparticle weight. Calculations of the electron linewidths further indicate that the scattering rate of excited carriers is dominated by phonons, while the contribution of electron-plasmon scattering is of the order of 10–15%.

The paper is organized as follows. In Sec. II we review the many-body theory of electron-plasmon and electron-phonon coupling and the cumulant expansion approach. Details on the numerical evaluation of the electron-plasmon self-energy are given in Sec. III. The influence of plasmons and phonons on the photoemission spectrum of TiO_2 is discussed in Sec. IV, whereas linewidths and relaxation times are addressed in Sec. V. Finally, a summary and concluding remarks are presented in Sec. VI.

II. THEORETICAL BACKGROUND

The interaction between electrons and bosonic excitations is commonly described within the formalism of many-body perturbation theory through the electron-boson coupling self-energy in the Fan-Migdal approximation [28]:

$$\Sigma_{nk}^{e-b}(\omega) = \int \frac{d\mathbf{q}}{\Omega_{\text{BZ}}} \sum_{mv} |g_{mnv}^{e-b}(\mathbf{k}, \mathbf{q})|^2 \times \left[\frac{n_{\mathbf{q}v} + f_{m\mathbf{k}+\mathbf{q}}}{\omega - \varepsilon_{m\mathbf{k}+\mathbf{q}} + \omega_{\mathbf{q}v}^b - i\eta} + \frac{n_{\mathbf{q}v} + 1 - f_{m\mathbf{k}+\mathbf{q}}}{\omega - \varepsilon_{m\mathbf{k}+\mathbf{q}} - \omega_{\mathbf{q}v}^b - i\eta} \right]. \quad (1)$$

Here, g^{e-b} denotes the electron-boson coupling matrix elements, $\omega_{\mathbf{q}v}^b$ is the boson energy, $\mathbf{k}$ and $\mathbf{q}$ are Bloch wave vectors, m and n are band indices, v is the branch index, $\varepsilon_{m\mathbf{k}+\mathbf{q}}$ is a set of single-particle eigenvalues, $n_{\mathbf{q}}$ and $f_{m\mathbf{k}+\mathbf{q}}$ are Bose-Einstein and Fermi-Dirac occupations, respectively, and η is a positive infinitesimal. The summation runs over all Bloch states, and the integral is over the Brillouin zone of volume Ω_{BZ} . Equation (1) stems from the first-order expansion of the self-energy for a coupled electron-boson system interacting through the Hamiltonian [29] $\hat{H}^{e-b} = \sum_{nmv} \sum_{\mathbf{k}, \mathbf{q}} g_{nmv}^{e-b}(\mathbf{k}, \mathbf{q}) \hat{c}_{m\mathbf{k}+\mathbf{q}}^\dagger \hat{c}_{n\mathbf{k}} (\hat{b}_{\mathbf{q}v} + \hat{b}_{-\mathbf{q}v}^\dagger)$, with $\hat{c}, \hat{c}^\dagger$ ($\hat{b}, \hat{b}^\dagger$) fermionic (bosonic) annihilation and creation operators, respectively. This Hamiltonian is commonly employed to

describe electronic coupling to bosonic modes that can approximately be represented as a set of uncoupled harmonic oscillators such as, for instance, phonons and plasmons.

The electron self-energy due to electron-phonon coupling [30] is obtained from Eq. (1) by identifying $\omega_{\mathbf{q}v}^b$ with the energy $\omega_{\mathbf{q}v}^{\text{ph}}$ of a phonon with momentum $\mathbf{q}$ and the coefficients g^{e-b} with the electron-phonon matrix elements g^{e-ph} [31]:

$$g_{mnv}^{e-ph}(\mathbf{k}, \mathbf{q}) = \langle \psi_{m\mathbf{k}+\mathbf{q}} | \Delta_{\mathbf{q}v} V_{\mathbf{K}_S} | \psi_{n\mathbf{k}} \rangle, \quad (2)$$

where $\psi_{n\mathbf{k}}$ denote Bloch single-particle states and $\Delta_{\mathbf{q}v} V_{\mathbf{K}_S}$ is the variation of the self-consistent Kohn-Sham potential [32,33] with respect to a phonon perturbation. In polar materials, such as TiO_2 , the electron-phonon coupling matrix elements exhibit a $1/|\mathbf{q}|$ singularity stemming from the induced electric field generated by the finite Born effective charges of the ions [12,34]. Such singularity is treated analytically in the following according to Refs. [16,35], whereby an efficient computational procedure has been established by devising an interpolation scheme based on maximally localized Wannier functions [36] that accounts for the long-range, singular part of the electron-phonon matrix elements.

The electron self-energy due to electron-plasmon coupling [13] can also be evaluated through Eq. (1). In this case, $\omega_{\mathbf{q}}^b$ coincides with the plasmon energy $\omega_{\mathbf{q}}^{\text{pl}}$, and the dependence on v may be dropped as we will consider systems with a single plasmon mode. The electron-plasmon coupling coefficients take the form [13]

$$g_{mn}^{e-pl}(\mathbf{k}, \mathbf{q}) = \left[\frac{\partial \epsilon(\mathbf{q}, \omega)}{\partial \omega} \Big|_{\omega_{\mathbf{q}}^{\text{pl}}} \right]^{-\frac{1}{2}} \times \left(\frac{4\pi}{\Omega_{\text{BZ}}} \right)^{\frac{1}{2}} \frac{1}{|\mathbf{q}|} \langle \psi_{m\mathbf{k}+\mathbf{q}} | e^{i\mathbf{q} \cdot \mathbf{r}} | \psi_{n\mathbf{k}} \rangle, \quad (3)$$

where ϵ is the electronic dielectric function. As revealed by Eq. (3), the electron-plasmon coupling matrix elements g^{e-pl} also exhibit an integrable $1/|\mathbf{q}|$ singularity for vanishing momentum. This behavior is analogous to the Fröhlich electron-phonon coupling matrix elements, suggesting that (i) the electron-plasmon interaction is also dominated by the coupling with long-wavelength plasmons, and (ii) phenomena that are characteristic fingerprints of the coupling to phonons (such as, e.g., lifetime effects [16], the renormalization of quasiparticle energies [37–39], and the formation of photoemission kinks [40] and satellites [17,20,41]) may result also from the interaction with plasmons, as demonstrated by recent theoretical [13] and experimental [14,42] studies on highly doped semiconductors and oxides.

The numerical evaluation of the electron-plasmon and electron-phonon self-energies via Eqs. (1)–(3) provides the starting point to investigate the combined effects of plasmons and phonons on the angle-resolved spectral properties of highly doped semiconductors and their influence on the formation of satellites. The spectral function in the diagonal approximation for the Fan-Migdal self-energy can be expressed as

$$A_{nk}(\omega) = \frac{1}{\pi} \frac{|\text{Im } \Sigma_{nk}^{\text{tot}}(\omega)|}{[\omega - \varepsilon_{nk} - \text{Re } \Sigma_{nk}^{\text{tot}}(\omega)]^2 + [\text{Im } \Sigma_{nk}^{\text{tot}}(\omega)]^2}, \quad (4)$$

where we have defined the total electron self-energy $\Sigma_{n\mathbf{k}}^{\text{tot}} = \Sigma_{n\mathbf{k}}^{\text{e-ph}} + \Sigma_{n\mathbf{k}}^{\text{e-pl}}$. The spectral function is closely related to the photoelectron current [43], and it thus provides the standard expression for relating theoretical and experimental photoemission spectra. However, this approach falls short when it comes to photoemission satellites, as it typically overestimates the satellite binding energy and its intensity [2,3]. A more accurate description of the spectroscopic signatures of the electron-boson interaction can be obtained from the cumulant expansion approach [27,44–46], whereby the spectral function may be rewritten as [17]

$$A(\mathbf{k}, \omega) = \sum_n \left[A_{n\mathbf{k}}^{\text{QP}}(\omega) + A_{n\mathbf{k}}^{\text{S1}}(\omega) * A_{n\mathbf{k}}^{\text{QP}}(\omega) + \frac{1}{2} A_{n\mathbf{k}}^{\text{S1}}(\omega) * A_{n\mathbf{k}}^{\text{S1}}(\omega) * A_{n\mathbf{k}}^{\text{QP}}(\omega) \right]. \quad (5)$$

Here, $A_{n\mathbf{k}}^{\text{QP}}(\omega)$ is obtained by replacing $\Sigma_{n\mathbf{k}}^{\text{tot}}(\omega)$ by $\Sigma_{n\mathbf{k}}^{\text{tot}}(\varepsilon_{n\mathbf{k}})$ in Eq. (4), and we defined

$$A_{n\mathbf{k}}^{\text{S1}}(\omega) = \frac{\beta_{n\mathbf{k}}(\omega) - \beta_{n\mathbf{k}}(\varepsilon_{n\mathbf{k}}) - (\omega - \varepsilon_{n\mathbf{k}}) \frac{\partial \beta_{n\mathbf{k}}}{\partial \omega} \Big|_{\varepsilon_{n\mathbf{k}}}}{(\omega - \varepsilon_{n\mathbf{k}})^2}, \quad (6)$$

with $\beta_{n\mathbf{k}}(\omega) = \pi^{-1} \text{Im} \Sigma_{n\mathbf{k}}^{\text{tot}}(\varepsilon_{n\mathbf{k}} - \omega) \theta(\omega)$. The second (third) term in Eq. (5) accounts for the spectral features arising from the simultaneous excitation of a hole and one (two) bosons, whereas A^{QP} accounts for the spectral structures corresponding to quasiparticle excitations [17].

III. THE ELECTRON-PLASMON SELF-ENERGY

While the electron-phonon self-energy for polar materials may be obtained from well-established first-principles codes [47], calculations of the electron-plasmon self-energy for doped compounds have only recently become accessible [13]. Below, we define a procedure for the evaluation of the electron-plasmon self-energy that is suitable for first-principles calculations. As the inspection of Eq. (3) reveals, the computation of the electron-plasmon matrix elements entails the evaluation of the dielectric function in the presence of doping, which requires ultrafine $\mathbf{k}$ -point sampling of the Brillouin zone. This task, due to its high computational cost, can be accomplished via direct evaluation of the Kohn-Sham states at each $\mathbf{k}$ point only for the simplest semiconductors, such as silicon, and it is thus important to define a computational procedure that circumvents this difficulty.

As a first step, we obtain a simplified expression for the dielectric function of doped semiconductors and oxides. We start by approximating the momentum-energy dispersion relations through a parabolic model for doping-induced charge carriers close to the band edges, whereas we retain the full (first-principles) dispersion for the remaining electrons. This approximation is well justified for doped semiconductors, whereby the Fermi energy typically differs by less than 0.1 eV from the band edges. The total dielectric function in the presence of doping ϵ^{D} can thus be expressed as

$$\epsilon^{\text{D}}(\mathbf{q}, \omega) = 1 - v(\mathbf{q})[\chi^{\text{I}}(\mathbf{q}, \omega) + \chi^{\text{HEG}}(\mathbf{q}, \omega)], \quad (7)$$

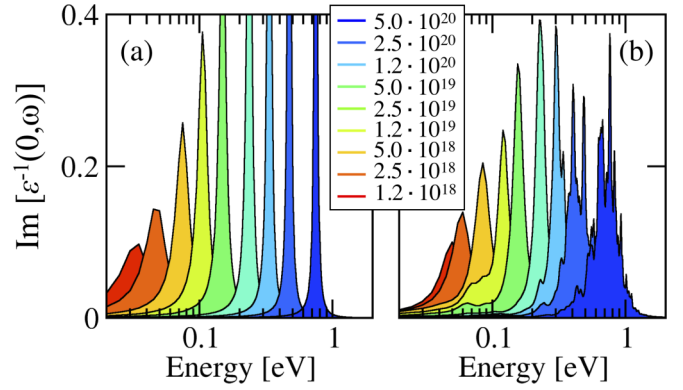


FIG. 1. (a) Loss function of doped silicon for a range of experimentally accessible carrier concentrations (in cm^{-3}) obtained from Eq. (7). (b) Same as in panel (a), obtained from the RPA.

where $v(\mathbf{q}) = 4\pi/\mathbf{q}^2$ is the Coulomb interaction. χ^{I} is the polarizability of the insulating (undoped) system evaluated within the random-phase approximation (RPA). χ^{HEG} is the RPA polarizability of a homogeneous electron gas with electron density coinciding with the concentration of extrinsic carriers and mass m_b corresponding to the isotropic effective mass of the semiconductor conduction band. χ^{HEG} can be evaluated analytically [29], and in the static limit it reduces to

$$\chi^{\text{HEG}}(\mathbf{q}, 0) = \frac{q_{\text{TF}}^2}{8\pi} \left[-1 + \frac{x^2 - 1}{2x} \ln \left| \frac{1+x}{1-x} \right| \right], \quad (8)$$

where $x = q/2k_F$, q_{TF} is the Thomas-Fermi momentum and k_F is the Fermi momentum.

We validate this approximation for the dielectric function of doped semiconductors by comparing in Fig. 1 the loss function $L(\omega) = \text{Im}[\epsilon^{\text{D}}(\mathbf{q} = \mathbf{0}, \omega)]^{-1}$ of doped silicon obtained from Eq. (7) [Fig. 1(a)] with the results of a full calculation based on the RPA [Fig. 1(b)] at $\mathbf{q} = \mathbf{0}$ for n -type doping concentrations in the range 10^{18} - 10^{21} cm^{-3} . In both panels of Fig. 1, the peaks in the loss function indicate the excitations of carrier plasmons. Electron-hole transitions (not shown) are excited only at energies larger than the direct fundamental gap of silicon ($E_g = 3.3 \text{ eV}$), and they are effectively left unchanged by the extrinsic doping at these carrier concentrations. The energy of the plasmon peaks in the RPA and its dependence on the carrier density is consistent with the plasma energy $\omega_{\text{pl}} = (4\pi n/m_b \epsilon_{\infty})^{1/2}$. As illustrated in Fig. 1, the approximate description of doping through Eq. (7) yields a loss function in excellent agreement with the RPA. The emergence of carrier plasmon peaks is reproduced well, and the plasmon energy and intensity are in good agreement with the RPA ones even though, for doping larger than 10^{20} cm^{-3} , the intensity of the plasmon peak is somewhat overestimated. Overall, the comparison reported in Fig. 1 validates the use of Eq. (7) for describing the dielectric function of doped semiconductors for a wide range of doping levels. Generally we expect this description to hold whenever the energy separation between the conduction band and other bands is much larger than the plasmon energy.

Having defined an approximate procedure to estimate ϵ^{D} , we discuss in the following how to compute the

electron-plasmon coupling matrix elements. For the sake of numerical stability, it is desirable to circumvent the explicit evaluation of the derivative term in Eq. (3). As illustrated in the supplemental material of Ref. [13], for $|\mathbf{q}| < q_c$, where $q_c = k_F[(1 + \omega_{\mathbf{q}}^{\text{pl}}/\varepsilon_F)^{1/2} - 1]$ is the critical momentum that marks the onset of Landau damping and ε_F is the Fermi energy, the derivative term in Eq. (3) can be expressed as

$$\left[\frac{\partial \epsilon}{\partial \omega} \right]_{\omega_{\mathbf{q}}^{\text{pl}}}^{-1} = -\frac{\omega_{\mathbf{q}}^{\text{pl}}}{2} [\epsilon^{\text{D}}(\mathbf{q}, 0)^{-1} - \epsilon^{\text{I}}(\mathbf{q}, 0)^{-1}], \quad (9)$$

where ϵ^{I} is the dielectric function of the undoped (insulating) system. This expression for the dielectric function relies on the assumptions that the energy of interband electron-hole transitions is much larger than the plasmon energy, and that plasmons and phonons may be treated independently, that is, possible phenomena arising from plasmon-phonon coupling, such as plasmon-phonon polaritons, are neglected. Noting that plasmons may only be excited in a narrow region of crystal momenta close to $\mathbf{q} = \mathbf{0}$, we further introduce the approximation $\langle \psi_{m\mathbf{k}+\mathbf{q}} | e^{i\mathbf{q}\cdot\mathbf{r}} | \psi_{n\mathbf{k}} \rangle = \delta_{nm}$, and we obtain an explicit expression for the electron-plasmon coupling matrix elements:

$$|g_{mn}^{\text{e-pl}}(\mathbf{k}, \mathbf{q})|^2 = \frac{2\pi \delta_{nm} \omega_{\mathbf{q}}^{\text{pl}}}{\Omega_{\text{BZ}}} \frac{[\epsilon^{\text{D}}(\mathbf{q}, 0)^{-1} - \epsilon^{\text{I}}(\mathbf{q}, 0)^{-1}]}{|\mathbf{q}|^2},$$

where ϵ^{D} is given by Eqs. (7) and (8). This expression may be further simplified by noting that, for $q < q_c$, it is a good approximation to consider $\epsilon^{\text{I}}(\mathbf{q}, 0) \simeq \epsilon_{\infty}$, where ϵ_{∞} is the high-frequency dielectric constant, which can be obtained from first-principles calculations of the RPA dielectric function in the pristine system. The final expression for the electron-plasmon matrix elements can be rewritten as

$$|g_{mn}^{\text{e-pl}}(\mathbf{k}, \mathbf{q})|^2 = \delta_{nm} \frac{v(\mathbf{q}) \omega_{\mathbf{q}}^{\text{pl}}}{2\Omega_{\text{BZ}}} \left[\frac{1}{\epsilon_{\infty} - \epsilon^{\text{HEG}}(\mathbf{q}) + 1} - \frac{1}{\epsilon_{\infty}} \right], \quad (10)$$

where $\epsilon^{\text{HEG}}(\mathbf{q}) = 1 - v(\mathbf{q})\chi^{\text{HEG}}(\mathbf{q}, 0)$ is the static Lindhard dielectric function [29]. The advantage of this procedure is that the matrix elements $g^{\text{e-pl}}$ are expressed in terms of quantities available from first-principles calculations of undoped compounds, whereas explicit calculations in the presence of doping are avoided.

We determine the electronic and lattice-dynamical properties of TiO_2 from density-functional theory (DFT) and density-functional perturbation theory (DFPT) calculations within the generalized gradient approximation [48] as implemented in the QUANTUM ESPRESSO package [49]. Only valence electrons are treated explicitly, including the semicore $3s$ and $3p$ states of Ti, whereas core electrons are accounted for through Troullier-Martins norm-conserving pseudopotentials.¹ Convergence is ensured by using a 200 Ry kinetic energy cutoff and a $6 \times 6 \times 6$ Monkhorst-Pack mesh. The DFT single-particle eigenvalues, the phonon dynamical matrices, and the electron-phonon matrix elements are first obtained on a homogeneous $4 \times 4 \times 4$

Brillouin-zone grid. To compute the electron-phonon self-energy, the electronic and phononic bands as well as the electron-phonon matrix elements are then interpolated on a dense random $\mathbf{q}$ -point mesh with 168 914 points with a denser sampling of the region close to Γ according to a Cauchy distribution of width 0.01. The interpolation is performed as in Ref. [17] using maximally localized Wannier functions within the EPW code [47] through an internal call to the WANNIER90 library [50]. The electron-plasmon self-energy has been implemented in the EPW code [47] by combining Eqs. (1) and (10) and by taking advantage of the Wannier interpolation of the electronic energies, and it has been computed using the same random grid. We describe doping within the rigid-band approximation, whereby extrinsic carriers are accounted for by means of a rigid shift of the Fermi energy. Charge neutrality is maintained through the addition of a homogeneous positively charged background.

IV. HYBRID PLASMON-PHONON SATELLITES IN PHOTOEMISSION

In the following, we employ the formalism presented in Secs. II and III to investigate the formation of plasmon and phonon satellites in anatase TiO_2 . The atomistic model for the unit cell of TiO_2 is shown in Fig. 2(a), whereas the Brillouin zone and the high-symmetry points are illustrated in Fig. 2(b).

The electron and phonon band structures calculated within DFT and DFPT are displayed in Figs. 2(c) and 2(d), respectively. The low-energy conduction bands derive from the strongly localized Ti $3d$ states. The conduction-band bottom

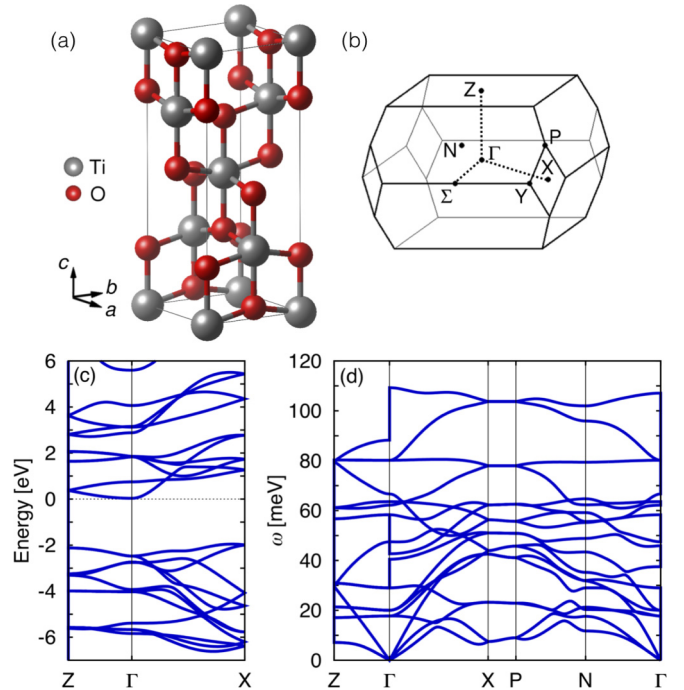


FIG. 2. (a) Atomistic model of the unit cell of anatase TiO_2 . (b) Brillouin zone and high-symmetry lines. (c) Calculated electronic band structure along the directions parallel (Γ X) and perpendicular (Γ Z) to the basal plane of the Brillouin zone. (d) Phonon dispersions computed along high-symmetry lines in the Brillouin zone.

¹ Available at <https://github.com/mmdg-oxford/papers/tree/master/Verdi-NCOMMS-2017/pseudo>

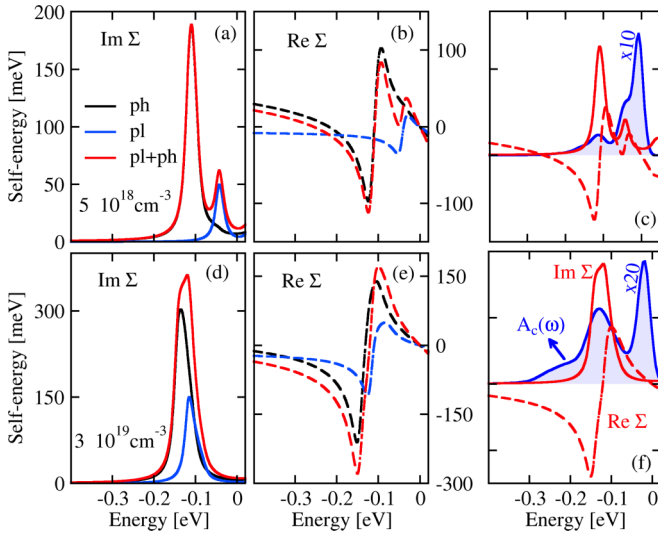


FIG. 3. (a) and (b) Imaginary (a) and real (b) part of the electron self-energy due to the electron-phonon (ph) and electron-plasmon (pl) interaction for TiO₂ at a doping concentration of $5 \times 10^{18} \text{ cm}^{-3}$. (d) and (e) Same as panels (a) and (b) for $3 \times 10^{19} \text{ cm}^{-3}$. (c), (f) Comparison between the total self-energy and the cumulant spectral function due to the combined effect of plasmons and phonons at Γ for 5×10^{18} and $3 \times 10^{19} \text{ cm}^{-3}$, respectively.

lies at the Γ point and it is formed by a single band with strongly anisotropic character in the directions perpendicular and parallel to the c axis. The phonon-dispersion relations in Fig. 2(b) show large LO-TO splittings for the three infrared-active modes. The highest-energy phonon is the E_u mode at 109 meV, which has been identified as the main source of Fröhlich-type electron-phonon coupling in anatase [17,20].

We proceed to investigate the coupling of electrons to plasmons and phonons through the calculation of the electron self-energy. The real and imaginary parts of Σ_{nk}^{tot} for the conduction band at the Γ point are illustrated in Fig. 3 for carrier concentrations of 5×10^{18} [(a) and (b)] and $3 \times 10^{19} \text{ cm}^{-3}$ [(d) and (e)], and they are compared to the real and imaginary parts of the electron-plasmon and electron-phonon self-energies. The total spectral function due to the combined effect of plasmons and phonons is obtained from the cumulant expansion through Eqs. (5) and (6) using Σ_{nk}^{tot} as a seed. In panels (c) and (f), the cumulant spectral function at Γ is reported along with the total self-energy, illustrating that the satellite features in the spectral functions occur at energies corresponding to peaks in the imaginary part of the self-energy. All energies are relative to the Fermi level. Our calculations are performed using the same carrier densities as the ARPES experiment of Ref. [20], as determined from the measured three-dimensional Fermi surfaces. The bulk sensitivity of these measurements has been proven via the inspection of the Fermi surface, which demonstrates the three-dimensional character of the band dispersion [20] as further validated by the agreement with first-principles calculation [17]. For $n = 5 \times 10^{18} \text{ cm}^{-3}$ ($3 \times 10^{19} \text{ cm}^{-3}$), the concentration of extrinsic carriers is described through a 13 meV (40 meV) shift of the Fermi level above the conduction-band bottom. Temperature effects are accounted for by considering

Fermi-Dirac and Bose-Einstein occupation factors at 20 K in Eq. (1) and by multiplying the spectral functions by the Fermi-Dirac distribution function $f(\omega, T) = (1 + e^{\omega/k_B T})^{-1}$, where k_B is the Boltzmann constant. To provide a picture of the photoemission process in closer agreement with experiment, we further account for finite resolution effects in energy and momentum through the convolution with Gaussian functions of widths 25 meV and $0.015 \text{ \AA}^{-1}$, respectively. All spectral function calculations presented in the following are based on the cumulant-expansion approach with the inclusion of finite resolution effects.

Figure 4 illustrates the calculated spectral function of TiO₂ at the conduction-band bottom for $n = 5 \times 10^{18}$ [(a)–(e)] and $3 \times 10^{19} \text{ cm}^{-3}$ [(g)–(j)], along the same line in reciprocal space as the ARPES experiment [20]. To disentangle the contribution of different mechanisms to the total spectrum, we further report cumulant spectral functions obtained separately from the electron-phonon [(a) and (f)] and electron-plasmon [(b) and (g)] self-energies. For comparison, we report in Figs. 4(d) and 4(i) ARPES measurements of the conduction-band bottom of TiO₂ from Ref. [20], and in panels (e) and (j) the cumulant spectral function at the Γ point.

All the spectra in Fig. 4 exhibit sharp spectral features at low binding energies ($\omega < 50$ meV) that follow a parabolic dispersion. These structures, which stem from the excitation of quasiparticle states at the conduction-band bottom, result from the shift of the Fermi level inside the conduction band. At binding energies between 40 and 300 meV, the spectral functions are characterized by the emergence of additional features that may not be attributed to quasiparticle excitations, revealing doping-dependent effects of electron-boson interactions. The case of electron-phonon interaction shown in Figs. 4(a) and 4(f) has been thoroughly discussed elsewhere [17]. In brief, at both doping values the spectral function exhibits well-defined satellite features separated from the bottom of the conduction band by an energy compatible with the energy of the E_u LO phonon of TiO₂, 109 meV. Additional broadened low-intensity features are observed at binding energies between 150 and 300 meV, which may be attributed to two-phonon processes.

The electron-plasmon spectral functions in Figs. 4(b) and 4(g) are also characterized by distinct satellite features that, in this case, may be ascribed to the excitation of a photohole and a plasmon. These results indicate that, at sufficiently high dopant concentrations, the strong coupling to plasmons may lead to the emergence of distinctive satellite structures in the angle-resolved spectral function of TiO₂. These features are reminiscent of the plasmonic polaron bands observed in the valence bands of (undoped) semiconductors [8,9] at binding energies of the order of 10–15 eV and in model systems [51]. In doped TiO₂, however, the satellite binding energy is comparable to the case of polaronic coupling: for $n = 5 \times 10^{18} \text{ cm}^{-3}$, the satellite is separated from the conduction band by 32 meV, whereas for $n = 3 \times 10^{19} \text{ cm}^{-3}$ we obtain an energy difference of 79 meV. The remarkable increase of satellite binding energies arises from the dependence of the plasmon energy ω^{pl} on the carrier concentration n . The phonon energy, on the other hand, can be expected to exhibit a rather weak dependence (< 5 –8 meV) on the doping concentration, which can be attributed primarily to the emergence of non-adiabatic effects beyond the Born-Oppenheimer approximation

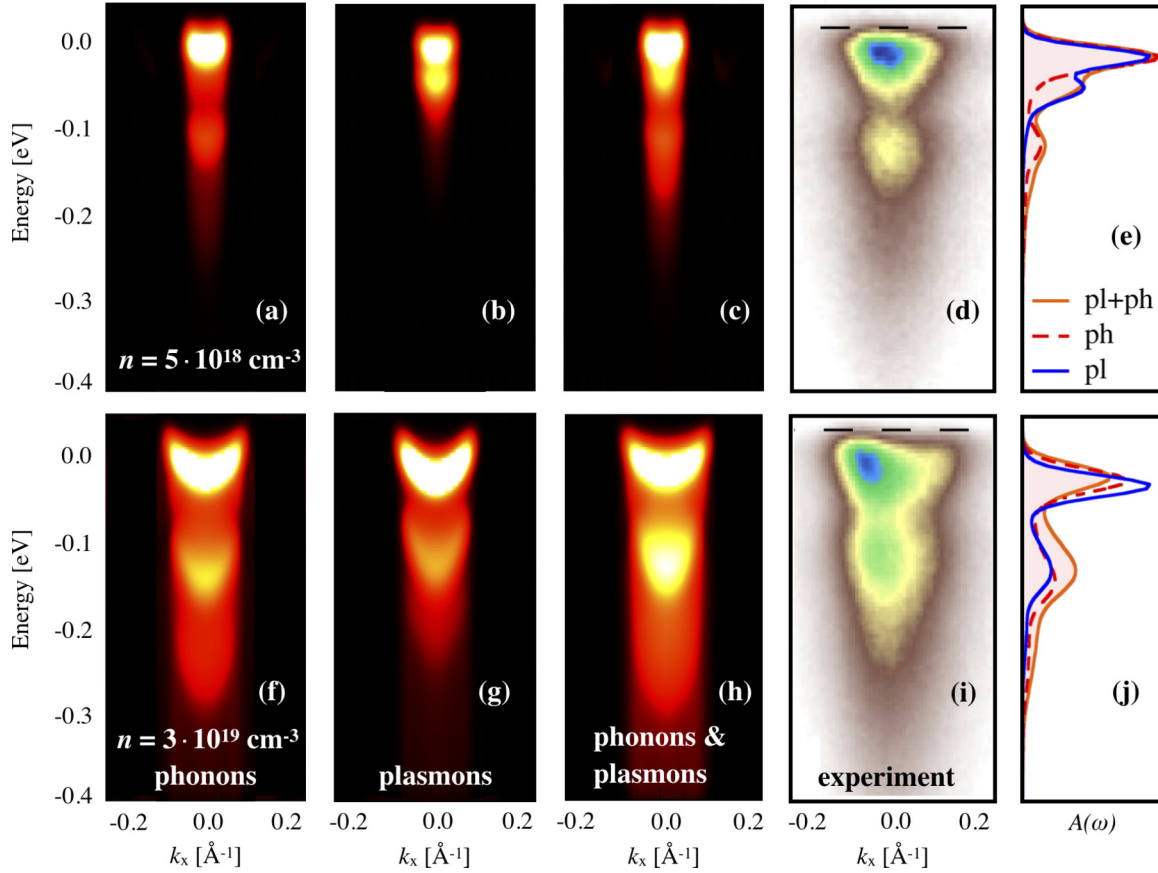


FIG. 4. (a)–(d) Spectral function of TiO_2 obtained from the cumulant expansion approach by accounting for the effects of electronic coupling to (a) phonons, (b) plasmons, and (c) both at a doping concentration of $5 \times 10^{18} \text{ cm}^{-3}$. (d) Angle-resolved photoemission spectrum of TiO_2 , adapted from Ref. [20]. (e) Spectral function at Γ due to plasmons (pl), phonons (ph), and their combined effect (pl+ph) from the cumulant expansion. (f)–(j) Same as above for $n = 3 \times 10^{19} \text{ cm}^{-3}$.

[52]. Nonadiabatic corrections to the phonon energy have been neglected here.

The total spectral function due to both plasmons and phonons is shown in Figs. 4(c) and 4(h), and its inspection reveals two different scenarios for the interplay of plasmons and phonons: (i) For $n = 5 \times 10^{18} \text{ cm}^{-3}$, the energy of the plasmon satellite $\omega^{\text{pl}} = 32 \text{ meV}$ is comparable to the experimental resolution of 25 meV and significantly smaller than the E_u LO phonon energy $\omega^{\text{ph}} = 109 \text{ meV}$. Correspondingly, the intensity of the plasmon satellite merges with the quasiparticle state, whereas the electron-phonon interaction yields an isolated polaronic satellite. (ii) For the largest carrier density, on the other hand, the plasmon energy $\omega^{\text{pl}} = 79 \text{ meV}$ differs from the phonon energy approximately by the energy resolution. The spectral signatures of plasmon and phonon satellites are thus degenerate in energy, leading to the formation of a hybrid plasmon-phonon satellite with enhanced intensity as compared with the electron-phonon spectral function of Fig. 4(f).

To quantify the contribution of plasmons to the total electron-boson interaction strength, we estimate the parameter $\lambda_{\mathbf{k}} = -\partial \Sigma_{\mathbf{k}} / \partial \omega|_{\omega=\epsilon_F}$, which is related to the enhancement of the band effective mass m^* via the relation $m^* = m_b(1 + \lambda)$, where m_b denotes the bare mass ($\Sigma = 0$) [30] and λ is the Fermi-surface average of $\lambda_{\mathbf{k}}$. We estimate $\lambda_{\mathbf{k}}$ by taking the derivative of the self-energy at the Fermi level along the ΓX direction. For the electron-phonon (electron-plasmon)

coupling, we obtain $\lambda^{\text{ph}} = 0.68, 0.66$ ($\lambda^{\text{pl}} = 0.43, 0.32$) for $n = 5 \times 10^{18}$ and $3 \times 10^{19} \text{ cm}^{-3}$. Combining the contribution of plasmons and phonons, we obtain $\lambda^{\text{pl+ph}} = 1.09, 1.00$ for the two doping levels, suggesting that the electron-plasmon interaction contributes by approximately 30–40% to the total electron-boson coupling strength. This result also suggests that the coupling of electrons to plasmons is stronger at smaller doping concentrations, provided that the doping level is high enough to sustain carrier plasmon excitations in the system, and that their characteristic energy is large enough to detect the effects of the electron-plasmon interaction within the experimental resolution.

The inspection of the quasiparticle weight $Z = 1/(1 + \lambda)$ may provide further indications of the effects of plasmons on the electronic properties of doped semiconductors and oxides. Earlier experimental studies [20] on TiO_2 have reported a quasiparticle weight $Z^{\text{exp}} = 0.36$ for a doping concentration of $3 \times 10^{19} \text{ cm}^{-3}$. If only electron-phonon interactions are accounted for, first-principles calculations yield $Z^{\text{ph}} = 0.59$, which overestimates significantly the experimental value, indicating that phonons contribute to only a fraction of the total electron-boson coupling strength. Remarkably, by combining the effects of plasmons and phonons, we obtain a quasiparticle weight $Z^{\text{pl+ph}} = 0.5$, which improves the agreement between theory and experiment. Overall, these results indicate that, while phonons provide the dominant contribution to the

formation of polaronic satellites in TiO_2 , electron-phonon coupling alone yields only a fraction of the total electron-boson coupling strength necessary to explain the small quasiparticle weight measured experimentally. Electron-plasmon coupling, as well as other mechanisms such as, e.g., scattering with electron-hole pairs and impurities, may prove important to explain the residual discrepancy between measured and calculated quasiparticle weights in highly doped semiconductors and oxides. The measured ratio between the intensity of quasiparticle and satellite peaks, and thus the quasiparticle weight, might further be influenced by the extrinsic effects. The photon energy employed to resolve polaronic features in TiO_2 ($h\nu \simeq 85$ eV) is typically smaller than that previously employed for the observation of valence satellites in undoped semiconductors ($h\nu \sim 800$ eV) [3]. Photons thus have a smaller penetration depth in the sample and, correspondingly, the photoelectrons are expected to exhibit weaker signatures of extrinsic effects. To establish quantitatively the influence of extrinsic effects on the experimental photoemission spectrum of doped TiO_2 , however, a more in-depth investigation based on quantum-mechanical simulations would be required, e.g., by following the approach presented in Ref. [53].

Recently, a combination of ARPES experiments and first-principles calculations has been employed to investigate the electronic properties of highly doped EuO samples as a function of carrier concentration [14]. In addition to quasiparticle peaks, the ARPES spectra of EuO exhibit clear signatures of polaronic satellites at low-carrier densities ($n \simeq 10^{18} \text{ cm}^{-3}$), which, in analogy to the case of TiO_2 , at higher doping concentrations are accompanied by carrier plasmon satellites. In combination with the present study, these results suggest that the emergence of carrier plasmon satellites may constitute a general feature of highly doped semiconductors and oxides.

V. HOT-CARRIER RELAXATION DUE TO PLASMONS AND PHONONS

To quantify the effects of phonons and plasmons on the dynamics of excited carriers in the conduction band of TiO_2 , illustrated in Fig. 5(a), we evaluate the low-temperature electron linewidths due to the electron-phonon and electron-plasmon interaction. The electron linewidths $\Gamma_{n\mathbf{k}}$ are obtained from the self-energy via $\Gamma_{n\mathbf{k}} = \text{Im}\Sigma_{n\mathbf{k}}(\epsilon_{n\mathbf{k}})$, and, due to their relation to the scattering time $\tau_{n\mathbf{k}} = 1/2\Gamma_{n\mathbf{k}}$, they provide direct information pertaining to the characteristic timescale of electron-boson scattering and their influence on the relaxation process for excited carriers.

In Fig. 5 we compare the electron linewidths due to electron-phonon and electron-plasmon coupling at carrier concentrations of $5 \times 10^{18} \text{ cm}^{-3}$ (b) and $3 \times 10^{19} \text{ cm}^{-3}$ (c) for crystal momenta along the X- Γ -Z high-symmetry path. In both cases, the linewidth vanishes in the vicinity of the conduction-band minimum since both plasmon and phonon emission are forbidden by energy conservation. For carrier energies smaller than 0.5 eV, we obtain electron-phonon linewidths of the order of 100 meV, corresponding to relaxation times of about 3 fs. Electron-plasmon scattering, on the other hand, yields linewidths around 10 meV (20 meV) for $n = 5 \times 10^{18}$ ($3 \times 10^{19} \text{ cm}^{-3}$), corresponding to relaxation times of 33 fs (16 fs). Overall, the electron-plasmon linewidths are signif-

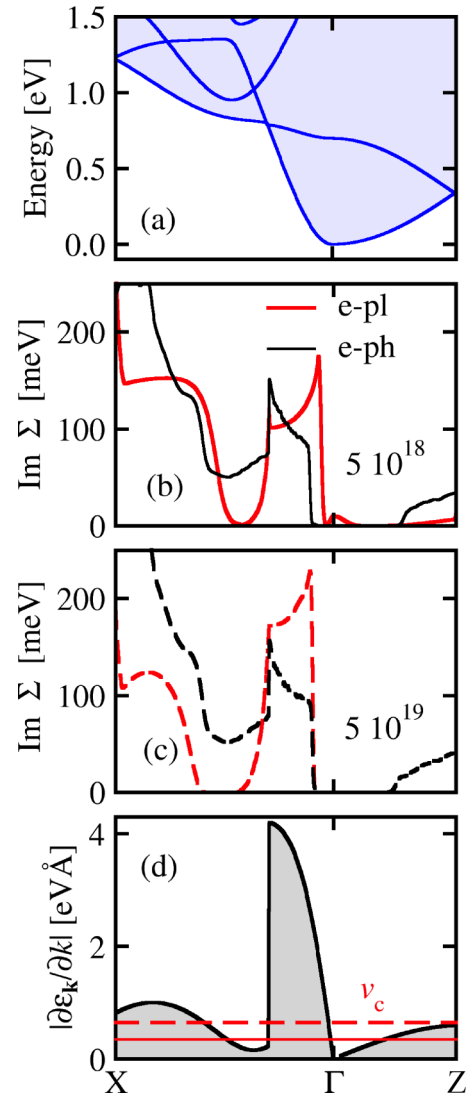


FIG. 5. (a) Lowest energy conduction bands of TiO_2 obtained from DFT. (b) and (c) Electron linewidth due to the electron-phonon and electron-plasmon interaction for a carrier concentration of (b) $5 \times 10^{18} \text{ cm}^{-3}$ and (c) $3 \times 10^{19} \text{ cm}^{-3}$. (d) Band velocity $v_{n\mathbf{k}}$ for the conduction band and critical velocity v_c for the onset of electron-plasmon scattering for $5 \times 10^{18} \text{ cm}^{-3}$ (continuous) and $3 \times 10^{19} \text{ cm}^{-3}$ (dashed).

icantly smaller than their electron-phonon counterpart, suggesting that, at these doping concentrations, carrier relaxation is dominated by electron-phonon scattering. However, at variance with the electron-phonon linewidths, which eventually decrease with the increase of doping concentration due to the screening of the electron-phonon interaction, the electron-plasmon linewidths increase with the carrier density [13], suggesting that, at higher doping values, electron-plasmon and electron-phonon scattering may contribute in a similar way to the relaxation of excited carriers.

Interestingly, the electron-plasmon linewidths vanish for several momenta in the Brillouin zone, a phenomenon that we attribute to the lack of phase space for the scattering between plasmons and excited carriers. In fact, an excited carrier with energy $\epsilon_{n\mathbf{k}}$ and crystal momentum $\mathbf{k}$ can emit a plasmon with

momentum $\mathbf{q}$ and energy $\omega_{\mathbf{q}}^{\text{pl}}$ only if there exists an empty final state with momentum $\mathbf{k} - \mathbf{q}$ and energy $\epsilon_{n\mathbf{k}-\mathbf{q}} = \epsilon_{n\mathbf{k}} - \omega_{\mathbf{q}}^{\text{pl}}$. Since plasmons can be excited only for $q < q_c$, this condition can be obeyed only if $|v_{n\mathbf{k}}| > \omega_{\mathbf{q}}^{\text{pl}}/q_c$, where $v_{n\mathbf{k}} = \partial\epsilon_{n\mathbf{k}}/\partial\mathbf{k}$ is the band velocity. In other words, an excited carrier can undergo electron-plasmon scattering only if its band velocity is larger than the critical velocity $v_c = \omega_{\mathbf{q}}^{\text{pl}}/q_c$. Based on a similar argument, one may also expect the Fröhlich coupling to LO phonons to be stronger for electronic states with a higher band velocity due to the increased phase space for electron-phonon scattering. To further validate this argument, we report in Fig. 5(d) the electron velocity along X- Γ -Z, and we indicate the critical velocity v_c by horizontal lines for both doping concentrations. The comparison with Figs. 5(b) and 5(c) confirms that the electron-plasmon linewidths vanish whenever $|v_{n\mathbf{k}}| < v_c$. Thus, the relation $|v_{n\mathbf{k}}| > v_c$ provides a new necessary condition, of general validity, for the emergence of electron-plasmon scattering. From this condition, it also follows that electrons in very dispersive bands (that is, with small effective masses) will be subject to electron-plasmon scattering to a larger extent due to the larger phase space available for these processes.

VI. CONCLUSIONS

We investigated the interplay of plasmons and phonons on the spectral properties of n -doped anatase TiO₂. To describe the coupling to carrier plasmons (resulting from the extrinsic carriers introduced via doping), we have derived and implemented a numerical approach to compute the electron self-energy due to the electron-plasmon interaction from first principles. This formalism has been applied to investigate the simultaneous influence of plasmons and phonons on (i) the formation of polaronic satellites in the ARPES spectra of highly doped TiO₂, and (ii) the characteristic relaxation timescales for excited carriers in the conduction band.

Our study reveals that electron-plasmon coupling may underpin the formation of photoemission satellites at energy scales of the order of 30–80 meV, in close analogy with the well-known scenario of polaronic coupling. At variance with phonons, however, the plasmon-satellite energy depends strongly on doping via the carrier concentration. First-principles calculations of the ARPES spectral function

indicate that at low carrier concentrations, when the plasmon energy approaches the experimental resolution, satellite and quasiparticle bands become indistinguishable, leading to the formation of a single, broad spectral feature close to the Fermi energy. At higher concentrations, the plasmon and phonon energies become comparable and their satellites merge into a more intense spectral feature. The explicit treatment of electron-plasmon interaction is important to improve the agreement with experiments for the quasiparticle weight Z , indicating that a significant fraction of the total electron-boson coupling strength can be attributed to plasmons. Finally, the computation of relaxation times suggests that, at the carrier concentrations considered here, electron-plasmon scattering occurs at a much lower rate as compared to electron-phonon scattering, indicating that phonons dominate the relaxation of excited carriers in the conduction band of TiO₂.

In conclusion, these results suggest that the interplay of electrons, plasmons, and phonons underpin a complex scenario of many-body interaction in TiO₂, whereby the simultaneous coupling to different bosonic modes depends pronouncedly on the concentration of extrinsic carriers and influences pervasively photoemission satellites, linewidths, and quasiparticle weights. These aspects emphasize the importance of explicitly accounting for the effects of both phonons and plasmons in future studies of highly doped semiconductors and oxides. Accounting for these phenomena through first-principles approaches may provide a valuable tool to unravel the fundamental quantum-mechanical processes that underpin the formation of satellites in photoemission spectroscopy and the relaxation of excited carriers.

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