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From Nano- to Picocavities: The Role of Atomistic Features

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ABSTRACT

Understanding how atomistic structural features reshape plasmonic properties is essential for the rational design of nanostructures for enhancing light-matter interactions at the nanoscale. Here, we investigate the optical response of realistic Ag and Au nanocavities by means of the fully atomistic frequency-dependent fluctuating charges and fluctuating dipoles (ω FQF μ) approach, which enables the description of realistic systems while also accounting for quantum tunneling effects. We compare nanocavities formed by smooth tip-substrate junctions with picocavities generated by atomistically defined needles. We further push the analysis to the ultimate atomistic limit by considering a picocavity formed by a single adatom. By combining absorption spectra, induced charge densities, electric field maps, and effective localization areas, we show that atomistic details strongly affect plasmon modes, field confinement, and enhancement. Remarkably, Ag and Au nanostructures display similar but distinct plasmonic behaviors, reflecting the different intrinsic electronic responses of the two metals. These results establish a direct structure-property relation between atomic-scale morphology and plasmon localization, providing physical insight for the design of plasmonic cavities with tailored near-field properties.

1 | Introduction

Recent advances in nanoscience and nanofabrication have enabled the experimental realization of metal nanostructures with atomically defined features, including sharp protrusions, adatoms, and subnanometric junctions [1–5]. In plasmonic architectures, such structural details can generate extremely confined optical *hot spots*, enabling single-molecule detection and even submolecular spatial resolution in surface-enhanced spectroscopies [6–17]. Among the most emblematic examples are nanocavities and picocavities, where light can be confined to subnanometer and even atomic length scales [11, 18–23]. In particular, picocavities have recently attracted considerable attention because of their exceptional capability to localize electromagnetic fields within atomic-scale volumes [11, 18–23]. They are often associated with single-atom defects, commonly referred to

as adatoms, formed on noble surfaces [18]. Experimentally, these structures are frequently realized within nanocavities obtained in nanoparticle-on-mirror (NPoM) configurations [24–27], where a metallic nanoparticle is separated from a metallic film by a molecular spacer that defines the gap width. Similar atomic-scale cavities also emerge in less controlled plasmonic environments, such as granular silver nanoparticle films or electrochemically roughened noble-metal surfaces [28] and in tip-enhanced Raman scattering (TERS) platforms for particularly shrunk tips [14–17, 29]. In all these cases, the resulting *hot spots* can sustain nanometric effective mode volumes, which can potentially be exploited in molecular electronics and photocatalysis [11, 12, 23, 30–33].

Despite the remarkable experimental progress, a detailed understanding of the plasmonic response of these systems remains challenging. At subnanometric scales, the optical response is governed

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by a subtle interplay between morphology, atomic-scale structure, and quantum effects such as charge transfer and tunneling [21, 34–42]. Classical electrodynamics methods, including Mie theory, the discrete dipole approximation (DDA), finite-difference time-domain approaches (FDTD), and the boundary element method (BEM) [43–47], can efficiently describe realistic system sizes, but they generally struggle to account for atomically defined surfaces and nonclassical effects in small junctions [20, 28, 38, 48–52]. On the other hand, *ab initio* approaches, based on quantum mechanics, can properly describe quantum effects, but their computational cost limits their applicability to systems much smaller than those typically investigated experimentally [53–55]. These limitations thus hamper a physically grounded description of the electric field morphology in nano- and picocavities, which is essential to elucidate the structure-property relations governing plasmon localization at the atomic scale.

Here, we investigate how atomistic protrusions and single-atom defects reshape the induced charge distribution, the near-field confinement, and the associated enhancement, and whether these effects follow the same trends in different noble metals. We tackle this challenge by means of the fully atomistic frequency-dependent fluctuating charges and fluctuating dipoles (ω FQF μ) approach, specifically developed to describe the plasmonic response of metal nanostructures [56, 57]. ω FQF μ provides an accuracy comparable to state-of-the-art time-dependent density functional theory even for structures below the quantum size limit [57] while also allowing the effective inclusion of quantum tunneling effects [56, 58]. At the same time, being based on a classical atomistic framework, it can be applied to nanostructures of realistic size that remain inaccessible to fully *ab initio* treatments [59].

We consider Ag and Au nanojunctions inspired by scanning tunneling microscopy geometries [12], in which a metallic tip is placed above a metallic substrate, and the gap distance is varied from the nanometric to the subnanometric regime. Two related morphologies are investigated: a nanocavity, obtained from a smooth tip–substrate junction and a picocavity, generated by introducing an atomistically defined protrusion at the tip apex. We then push this picture to the ultimate atomistic limit by considering a picocavity formed by a single adatom. By combining absorption spectra, induced charge densities, electric field maps, and effective localization areas, we show how atomistic structural features control plasmon modes, field confinement, and enhancement in experimentally relevant silver and gold nanojunctions. In particular, we highlight that the impact of atomistic details is strongly metal-dependent, thereby providing a physical rationale for the different behavior of Ag and Au nano- and picocavities.

2 | Methods

To physically model the optical properties of nanocavities characterized by atomistic features, we adopt the classical, fully atomistic frequency-dependent fluctuating charges and fluctuating dipoles ω FQF μ approach. In ω FQF μ , the electron density is projected into atomic charges and dipoles that respond to the external monochromatic electric field [57]. Charges and dipoles are not point-like but have a quantum-like distribution, which is obtained

by endowing them with a Gaussian smearing [57, 60]. In particular, the charge exchange between atoms is governed by the Drude mechanism, modulated by quantum tunneling effects, guaranteeing the correct plasmonic behavior when nanoparticle gaps are subnanometric. While charge models intraband effects, interband transitions are taken into account by the atomic dipole moments, which act as additional polarization sources defined in terms of interband polarizabilities. The method is remarkably able to correctly model the plasmonic properties derived from the presence of *d*-states in noble metals because it properly describes *d*-electrons as polarizable shells placed at the atomic sites [61]. In the frequency domain, the equation of motion for charges reads [56]

$$-i\omega q_i(\omega) = \frac{2n_0\tau}{1-i\omega\tau} \sum_j [1-f(l_{ij})] \frac{\mathcal{A}_i}{l_{ij}} (\phi_j^{\text{el}} - \phi_i^{\text{el}}) \quad (1)$$

where the complex-valued $q_i(\omega)$ is the Fourier component at the frequency ω of the oscillating atomic charge on atom *i*. τ is the scattering time, n_0 the metal electronic density, l_{ij} is the distance between *i*-th *j*-th atoms, and $\mathcal{A}_i$ represents the area of the conduction channel through which the charge is exchanged between neighboring atoms. In ω FQF μ , it is approximated as the square of the atomic radius, parametrized as $\sim 1.64 \text{ \AA}$ for both Ag and Au. ϕ_i^{el} is the electrochemical potential acting on the *i*-th metal atom, which takes into account the Coulomb interactions with the charges (V_i^q) and dipoles (V_i^μ) placed on different atoms and the interaction with the external electric field (V_i^{ext})

$$\phi_i^{\text{el}}(\omega) = V_i^{\text{ext}}(\omega) + V_i^q(\omega) + V_i^\mu(\omega)$$

In Equation (1), $f(l_{ij})$ is a Fermi-like function that mimics quantum tunneling effect [56]

$$f(l_{ij}) = \frac{1}{1 + \exp\left[-d\left(\frac{l_{ij}}{s \cdot l_{ij}^0} - 1\right)\right]} \quad (2)$$

where l_{ij}^0 is the equilibrium distance between nearest neighbors. The dimensionless parameters d and s determine the sharpness and the center of the step function, respectively [56]. The $1/l_{ij}$ factor in Equation (1) arises from the finite-difference approximation of the electric field projection along the interatomic bond, $\langle \mathbf{E}(\omega) \rangle \cdot \hat{l}_{ji} \approx (\mu_j^{\text{el}} - \mu_i^{\text{el}})/l_{ij}$ (see also ref. [56]).

The induced atomic dipole moments μ_i are obtained by solving the following set of linear equations [57]

$$\mu_i(\omega) = \alpha_i^\omega (\mathbf{E}_i^{\text{ext}}(\omega) + \mathbf{E}_i^\mu(\omega) + \mathbf{E}_i^q(\omega)) \quad (3)$$

where $\mathbf{E}_i^{\text{ext}}$, $\mathbf{E}_i^\mu$, and $\mathbf{E}_i^q$ are the external electric field, the field generated by the other dipole moments, and the charges, respectively, acting on atom *i*. The interband transition can effectively be modeled by defining the atomic complex polarizability, α_i^ω , obtained by extracting the interband contribution to the permittivity function [57]. In order to couple both the intraband (Drude) and the interband transitions and account for their coupling effects, Equations (1) and (3) are solved simultaneously. Due to its atomistic nature, ω FQF μ can describe atomically defined surfaces, potentially allowing for the treatment of any geometrical

arrangements [57, 62–65]. Also, its classical nature allows for the description of real-size, experimentally relevant, nanostructures, whose typical dimensions are tens of nm and are generally composed of more than 100k atoms.

3 | Results and Discussion

We start our analysis by considering a nanocavity inspired by a scanning tunneling microscopy (STM) junction, which has been recently studied by Yang et al. [12] and is constituted by a tip with an atomistically protuberant feature at its end, placed above a silver bulk substrate (see Figure 1a). In our modeling, the tip is constructed by endowing a paraboloid of radius $r \approx 8$ nm and height $h \approx 11.5$ nm with a needle of height $d \approx 1$ nm. The substrate is a disk of diameter $l \approx 19$ nm (see Figure 1a,b). The structures are composed of about 140,000 atoms, thus demonstrating the potential of our approach to describe realistic-size systems while maintaining atomistic detail, which is essential to properly describe the local field properties close to atomistic defects. We remark, indeed, that in ω FQF μ all atoms are explicitly included in the calculation. To quantitatively analyze the effect of the atomistic protuberance, similar structures without the needle were also considered (see Figure 1b). The two morphologies are referred to as pico- and nanocavities, respectively. We consider both silver- and gold-based nanostructures (see Figure 1). To analyze the dependence of the plasmonic properties on the tip-substrate distance D , we vary D from 3 to 20 Å for both geometrical arrangements. We exploit ω FQF μ to compute the absorption cross section (σ^{abs}) and the electric-field enhancement factor arising in the cavities ($|E|/|E_0|$, where E_0 is the intensity of the incident electric field) as implemented in the open-source plasmonX code [66]. We note that our finite tip-substrate model is also representative of a nanoparticle on-mirror (NPoM) junction [18, 26]. We remark that ω FQF μ is defined within the quasi-static regime; thus, our analysis focuses on the near-field response within the gap (induced densities, field confinement, and localization), which is mainly governed by the local junction geometry.

We first discuss the results obtained for Ag nanostructures. For Ag picocavities (see Figure 2a, left), the absorption at large gaps

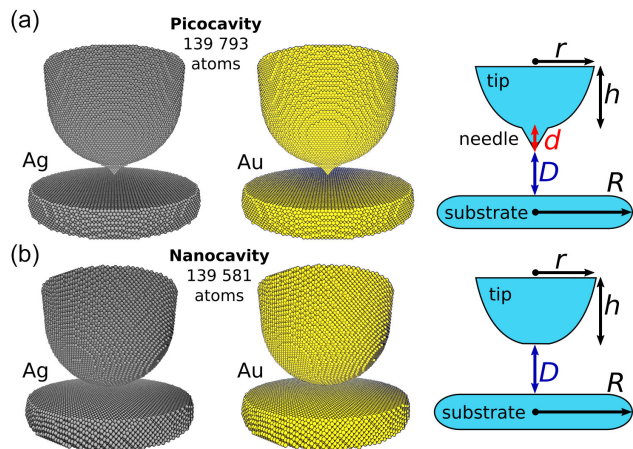


FIGURE 1 | Graphical depiction of Ag and Au pico (a) and nanocavities (b). Geometrical parameters are also given on the right panel.

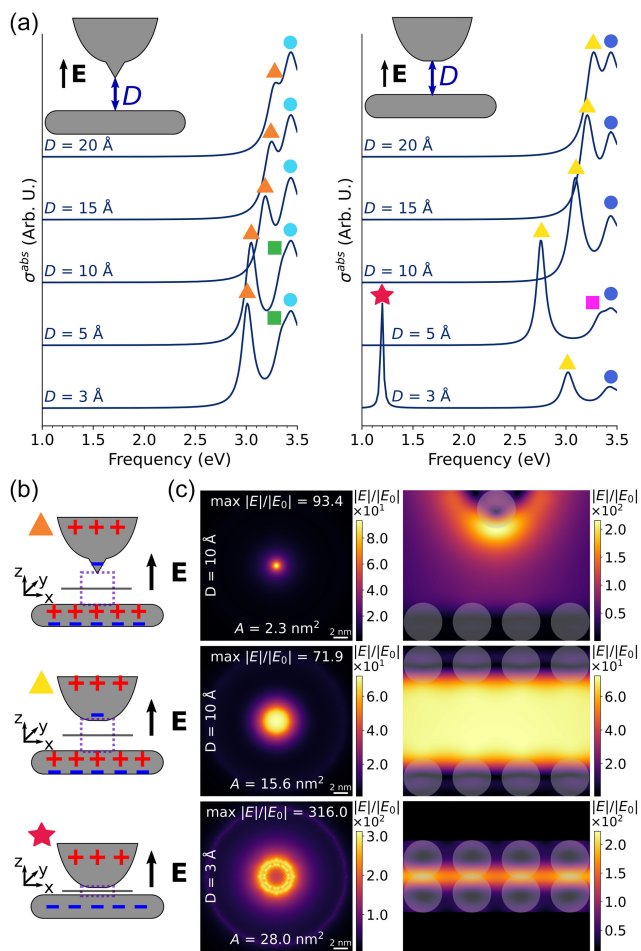


FIGURE 2 | (a) Absorption cross section σ^{abs} of Ag pico (left) and nanocavities (right) as a function of the gap's width D . (b) Schematic representation of induced densities and (c) field enhancement maps in xy (left) and xz (right) planes of Ag pico and nanocavities calculated at the main PRFs at $D=10$ Å and $D=3$ Å. The effective localization area and maximum electric field enhancement within the considered planes are also reported. Note that the color scale varies across geometries.

(≥ 10 Å) is characterized by two main peaks. The band at about 3.44 eV (azure dots), which remains unaltered upon varying D , and a second peak, at lower energy (orange triangles), which instead redshifts from 3.3 to 3.0 eV as D is reduced from 20 to 3.0 Å. The charge densities arising across the whole structure at the lowest plasmon resonance frequencies (PRFs) of the σ_{abs} peaks (highlighted in Figure 2a) are schematically reported in Figure 2b (see Figures S1–S5 in the Supporting Information for the charge densities induced at all PRFs). The peak at about 3.44 eV is characterized by two octupolar-dominated modes on both the tip and the substrate, thus resulting in a boundary octupolar plasmon (BOP) (see Figure S3 in the Supporting Information for $D=10$ Å). The lower-energy peak (2.9–3.3 eV, orange triangle) is instead associated with a boundary dipolar plasmon (BDP) mode (see Figures 2b top and S3). We remark that the finite size of the studied structures inherently limits the absolute field enhancement values. However, physical insights can be gained from the detailed comparison among the various configurations, gap distances, and metals. The BDP mode is responsible for the maximum field enhancement for all gaps. Indeed, at $D=10$ Å, the maximum field enhancement in the xy plane at the mid-gap (see

Figure 2b for a graphical representation of the considered plane) is $|E|/|E_0| \approx 93$ (see also Table 1), about 11 times higher than the enhancement corresponding to the peak at 3.44 eV, for which $|E|/|E_0| \approx 8$ (see Figures 2c and S3 in the Supporting Information). Such a finding is consistently reported for all gap distances considered. To appreciate the induced field morphology, we also plot the field enhancement in a reduced portion of the xz plane (see Figure 2b, purple region). Figure 2c shows that the maximum enhancement is found close to the Ag atom terminating the needle, in agreement with the so-called tip effect [67]. The near-field response is governed by the apex geometry of the needle rather than by its precise registry with the underlying substrate lattice. Remarkably, the electric field is overall enhanced within the gap.

At short gaps ($D < 10 \text{ \AA}$), a third peak arises as a shoulder of the peak located at 3.44 eV (green squares). This is characterized by a charge distribution similar to that of the peak at 3.44 eV and, consistently, does not show a significant dependence on the gap distance. Although the peak features present a plasmon distribution similar to that corresponding to the peak at about 3.44 eV (i.e., BOP), the enhancement factor corresponding to such a PRF, for a gap width $D = 5 \text{ \AA}$, reaches a value of $|E|/|E_0| \approx 107$ (see Figure S2), which is about 5 times higher than the value obtained at 3.44 eV (i.e., $|E|/|E_0| \approx 20$).

To further analyze the electric field morphology, we introduce a quantification of the induced electric field localization in terms of the effective localization area previously introduced in ref. [42]. Here, we calculate it in the xy plane at the middle of the gap as

$$A = \int_S \frac{|E(x, y)|^2}{|E_{\max}|^2} dS \quad (4)$$

TABLE 1 | Maximum electric field enhancement $|E|/|E_0|$ and effective localization area A for the BDP mode of Ag and Au nano- and picocavities as a function of the gap width (D).

$D, \text{ \AA}$	Ag			
	Picocavity		Nanocavity	
	$\max E / E_0 $	$A, \text{ nm}^2$	$\max E / E_0 $	$A, \text{ nm}^2$
3	568.1	0.3	132.4	13.3
5	405.1	0.5	306.3	8.5
10	93.4	2.3	71.9	15.6
15	40.2	5.4	32.7	22.2
20	22.0	9.7	19.3	29.0

$D, \text{ \AA}$	Au			
	Picocavity		Nanocavity	
	$\max E / E_0 $	$A, \text{ nm}^2$	$\max E / E_0 $	$A, \text{ nm}^2$
3	62.5	0.5	20.1	17.1
5	49.0	1.0	76.8	9.2
10	13.1	8.2	12.7	24.1
15	7.2	21.6	6.7	41.2
20	4.9	37.8	5.1	53.5

where E and $E_{\max}$ are the induced field and its maximum value, calculated within a reduced surface S , which, for symmetry reasons, is defined as a circle centered at the middle of the xy plane and with radius 8 nm. This corresponds to the radius of the paraboloid (see Figures S1–S5 in the Supporting Information for a graphical depiction of S within the xy plane). The smallest localization area is reported for the BDP for all structures, with values ranging from about $0.3\text{--}0.5 \text{ nm}^2$ ($D = 3\text{--}5 \text{ \AA}$) to about 10 nm^2 ($D = 20 \text{ \AA}$). Overall, the localization area assumes very small values, confirming that the presence of the needle within the picocavity results in a substantial confinement of the induced electric field.

To directly connect the structural features of the needle with the electric field morphology and the associated enhancement inside the cavity, we move to the analysis of the nanocavity (see Figure 2a, right). As before, the absorption spectrum features two main peaks at large gaps D ($D \geq 10 \text{ \AA}$). Similarly to the picocavity, the peak at about 3.45 eV is independent of the gap distance (blue circle) and splits into two bands for narrower junctions (azure square). The peak at lower energies (yellow triangle) redshifts upon decreasing the gap, moving from about 3.25 eV ($D = 20 \text{ \AA}$) to 2.8 eV ($D = 5 \text{ \AA}$). These two peaks maintain the same charge density distribution as in the picocavity (see Figures 2b, middle and S6–S10 in the Supporting Information). Indeed, the peak that redshifts in energy upon decreasing the gap width corresponds to a BDP mode and is still responsible for the maximum enhancement factor. For $D = 10 \text{ \AA}$, the maximum electric field enhancement in the xy mid-gap plane $|E|/|E_0|$ (see Figure 2c and Table 1) reaches about 72, which is close to, but lower than that predicted for the picocavity. The band at a higher energy (3.45 eV) instead shows a BOP mode and is associated with an enhancement factor of 7.5 (blue circle).

The predicted absorption spectrum for a gap distance of $3 \text{ \AA}$ drastically differs from that of all others. In fact, a new peak appears in the absorption spectrum at about 1.1 eV (see Figure 2a right, red star), corresponding to a charge-transfer plasmon (CTP) mode (see the charge distribution reported in Figure 2b, bottom). Remarkably, the charge transfer across the cavity is responsible for the crowding of charges at the main surfaces of the whole structure, increasing the enhancement factor by almost an order of magnitude in the middle of the nanojunction and displaying a clear circular symmetry, which is markedly different from BDP, which reflects the overall symmetry of the system. Note, however, that a gap of $3 \text{ \AA}$ is very narrow and cannot accommodate a molecule, perhaps chemisorbed atoms at most. The prediction of such a plasmon is indeed not trivial and is due to the inclusion in $\omega\text{FQF}\mu$ of a phenomenological treatment of quantum tunneling by means of Equation (2). The described spectral evolution can be rationalized within an equivalent-circuit picture, in which the junction behaves as a nanoscale capacitor: as the gap D narrows, the gap capacitance increases and the capacitive coupling across the junction strengthens, producing the observed red shift of the BDP. Within the same picture, the small contact area of the needle contributes only marginally to the total gap capacitance, so that in the picocavity, the needle mainly acts to localize the near field rather than to reshape the overall spectral response, as instead observed in the nanocavity. Notably, no CTP emerges in the picocavity at the same gap because the single-atom apex contact does not provide sufficient tunneling conductance to sustain a charge–transfer oscillation across the junction.

The contribution of the needle to field localization and, in turn, to the enhancement factor value and distribution can be understood by comparing the color maps of the induced electric field at the gap center for the structure with and without the needle (see Figure 2c). In particular, the field distribution of the nanocavity resembles the shape of the tip, creating a radial but large *hot spot*. As a consequence, for the same gap distances, the effective localization area increases by about an order of magnitude (reaching values of the order of tens of nm², see Table 1). For the nanocavity, the induced field in the *xz* plane within the cavity is almost constant, resembling, as expected, the constant field of a parallel-plate capacitor (see Figure 2c, right). On the other hand, when the metallic tip is endowed with a needle, creating a picocavity, the effective localization area drops, also promoting a further increase in the field enhancement by a factor of about 1.3. We can estimate the enhancement factor potentially measured by SERS spectroscopy by considering the fourth power of the induced field. Remarkably, the picocavity can be associated with enhancement factors of the order of 10⁷ at $D=10\text{ \AA}$, which is almost three times the value estimated for the nanocavity, highlighting the potential role of atomistic protuberances in molecular surface-enhanced spectroscopy [10, 55].

We now move to the results for Au nano- and picocavities, as reported in Figure 3. The absorption cross sections (Figure 3a) show trends similar to those discussed above for Ag; however, clear differences related to the specific electronic properties of gold emerge. In fact, independently of D , the picocavity σ^{abs} (left) is dominated by a single peak associated with a BDP mode (see Figures 3b and S11 in the Supporting Information for a graphical depiction of the induced densities), which only slightly redshifts as a function of D (orange triangle). This behavior originates from the fact that Au NPs exhibit interband transitions around 2.4–2.5 eV, which mask the additional bands observed in Ag. On the other hand, in the nanocavity arrangement, the BDP peak (yellow triangle, see Figure 3b) undergoes a much more pronounced redshift when moving from $D=20\text{ \AA}$ to $D=5\text{ \AA}$ and then blue shifts for $D=3\text{ \AA}$. Similarly to Ag, at $D=3\text{ \AA}$ an additional low-energy peak, associated with a CTP mode, emerges due to quantum tunneling effects (see also Figure S12). A direct comparison between the nano- and picocavity σ^{abs} shows that the presence of the needle only marginally affects the plasmonic response at large distances because of its relatively small size compared with the overall structure. By contrast, the presence/absence of the needle dominates the response for $D \leq 10\text{ \AA}$.

To better quantify the differences between the two geometric arrangements, we analyze the electric field enhancements and the effective localization area of the plasmon modes that govern the optical response at $D=10\text{ \AA}$. The corresponding color maps of the induced electric field computed at the middle of the gap are shown in Figure 3c for the *xy* and *xz* planes. First, as in Ag, we note that the induced field is more localized in the picocavity than in the nanocavity, as expected from the tip effect introduced by the picocavity geometry. However, in this case, the difference between the two structures is only about a factor of 3, with the effective area predicted for the picocavity remaining relatively large (about 8 nm²). This is related to the diverse electronic properties of gold, which result in a different optical response [57]. In the case of Au nanocavities, we find a smaller but very close enhancement than in picocavities. This translates into estimated SERS enhancement

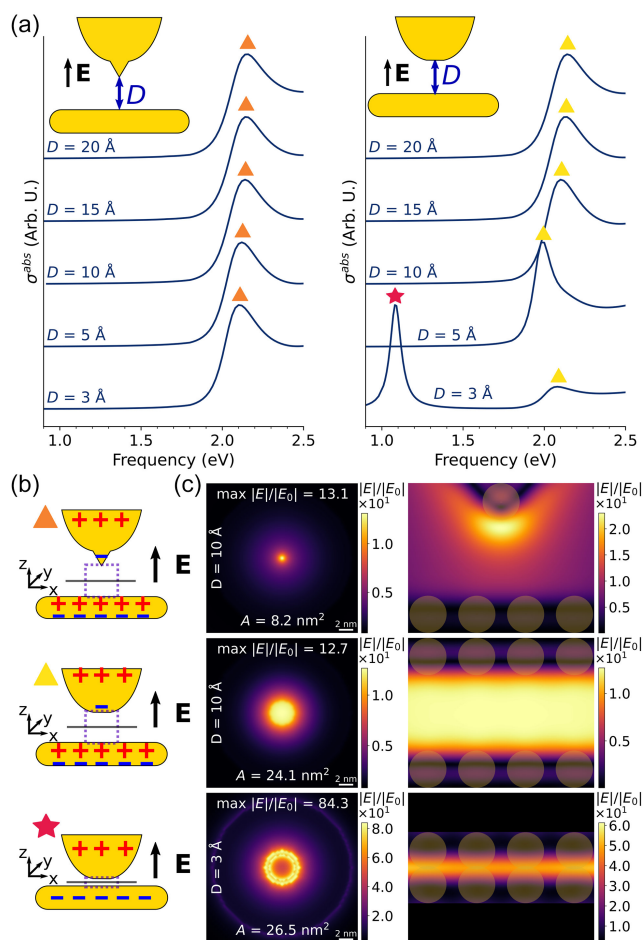


FIGURE 3 | (a) Absorption cross section σ^{abs} of Au pico (left) and nanocavities (right) as a function of the gap's width D . (b) Schematic representation of induced densities and (c) field enhancement maps in *xy* (left) and *xz* (right) planes of Ag pico and nanocavities calculated at the main PRFs at $D=10\text{ \AA}$ and $D=3\text{ \AA}$. The effective localization area and maximum electric field enhancement within the considered planes are also reported. Note that the color scale varies across geometries.

factors that are very similar ($\sim 3 \cdot 10^4$). The enhanced field in the *xz* plane further shows that, in the picocavity, the field is strongly localized near the needle tip and is overall larger than that in the nanocavity, where it remains approximately constant throughout the gap region. Finally, also for gold nanoparticles, the maximum enhancement is found for the CTP mode at $D=3\text{ \AA}$, where the same circular symmetry predicted for Ag is recovered, however, with the same caveat on the gap narrowness.

To further explore the possible deviations induced by atomistic details in these structures, we push to the extreme the concept of picocavity modeled so far as a pyramidal needle and introduce a model picocavity consisting of a single atomic defect (adatom) located on one of the two approaching faces of the nanocavity. This is consistent with experimental evidence [11, 18]. In this case, the adatom is placed at the center of the paraboloid, in the adjacent atomic shell ($2.04\text{ \AA}$) for both Ag and Au (they have very similar lattice parameters). The resulting structures are shown in Figure 4a (Ag) and e (Au), where the insets display a zoom of the gap region. In all cases, we focus on a gap distance of 1 nm ($10\text{ \AA}$), as this is the value typically imposed experimentally

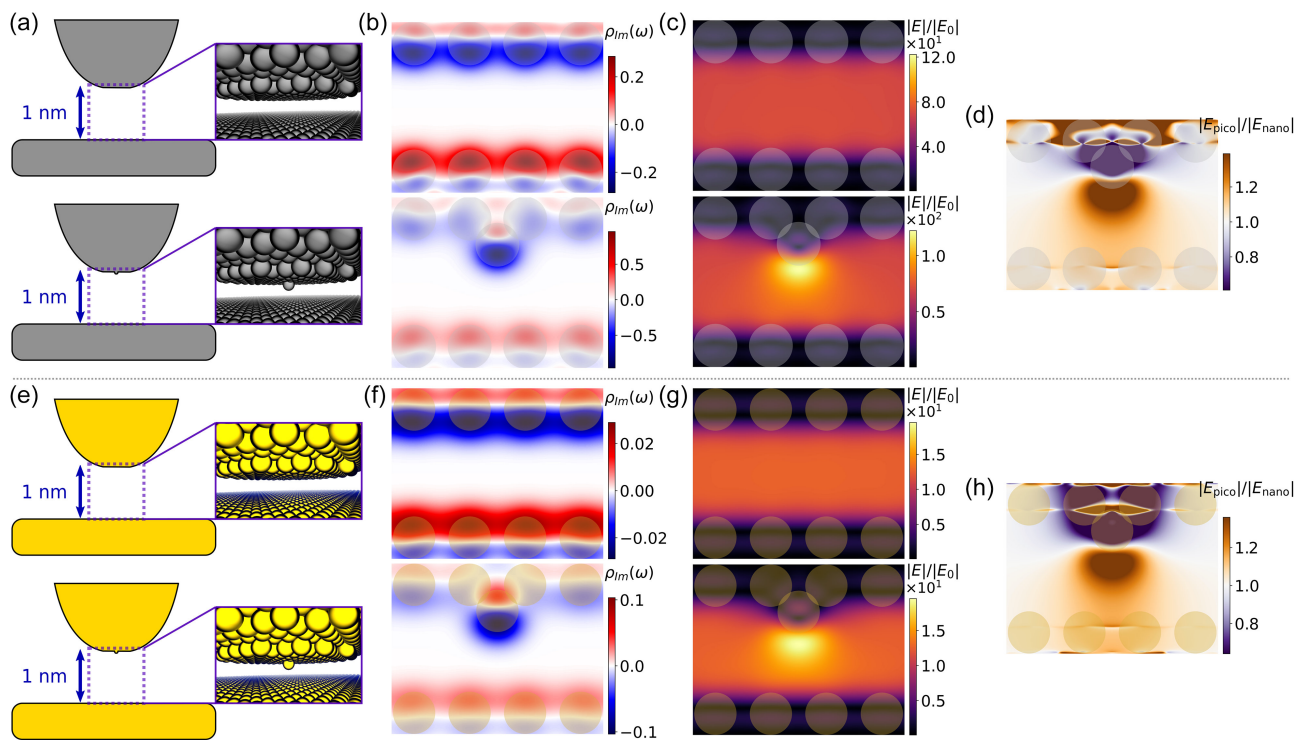


FIGURE 4 | Ag (a–d) and Au (e–h) nano (top) and single adatom picocavities (bottom). Ag and Au Induced densities (b,f,imaginary part), electric field enhancement maps (c,g) computed at the PRF within the xz field highlighted in purple in panels (a) and (e). (d,h) Electric field maps of the ratio between pico and nanocavities induced fields. Ag and Au atoms are represented as silver and gold spheres using their van der Waals radius.

in the so-called nanoparticle-on-mirror (NPoM) configurations by means of molecular spacers [18], in which the formation of single-atom defects has been reported. The response properties of both the nano- and picocavity are evaluated at the PRF corresponding to the BDP of the nanocavity since the presence of a single atom does not modify the optical response of this system [60]. The induced density in the gap region (purple areas in panels a and e) is graphically shown in Figure 4b (Ag) and f (Au). As expected, in the nanocavity, we observe opposite negative and positive regions on the two facing surfaces, whereas in the picocavity, the induced density becomes inhomogeneous and is characterized by the presence of an induced dipole on the adatom, with a marked asymmetry, particularly evident in the Ag case. In both systems, however, the induced density is found to be strongly concentrated on the adatom (see the color scale), showing how even a single atomic defect can substantially affect the induced electronic distribution.

In panels c and g of Figure 4, we report the enhanced induced field $|E|/|E_0|$ maps. In both nanocavities, the induced field is essentially constant inside the gap, as expected and as discussed above, consistently with the field of a parallel-plate capacitor, with the enhancement factor being strongly dependent on the nature of the metal. Also, the enhanced field in the picocavities depends on the nature of the metal. In particular, for Ag, the induced field displays a maximum close to the adatom, remaining overall enhanced throughout the entire region considered, with the exception of the equatorial region close to the adatom. A similar induced field is predicted within the Au picocavity, which is, however, characterized by a larger depletion zone, together with a broader enhancement region that further extends above the adatom. To better highlight the difference between the two

metals, in Figure 4d,h we show the ratio between the induced field in the pico- and nanocavity, where the depletion regions in both systems become particularly evident. The origin of this depletion zone can be traced back to the fact that, within $\omega FQF\mu$, the electronic quantities are physically associated with entities possessing their own spatial distribution (Gaussian), exactly as expected for quantum objects [57]. The smaller depletion region in Ag is due to the fact that the induced distribution is much more localized on the adatom (compare the bottom panels of Figure 4b,f), thus approaching the limit of a nearly point-like distribution for which an overall enhancement can be found analytically [60]. These findings are directly connected to both the structure and the electronic nature of the metals, further demonstrating the physical consistency of our results. We note that the discussed Ag/Au differences may also reflect the proximity in energy of the BDP to the Au interband transitions for the specific tip geometry analyzed in this paper, which, however, do not affect the qualitative role of the atomistic features, such as field localization, CTP emergence, and adatom-induced charge redistribution.

4 | Summary and Conclusions

In summary, we have investigated the plasmonic response of realistic Ag and Au nanojunctions by means of the fully atomistic $\omega FQF\mu$ approach, which enables the description of the plasmonic properties of experimentally relevant structures while accounting for nonlocal and quantum tunneling effects. By comparing smooth nanocavities, picocavities generated by atomistic protrusions, and the ultimate atomistic limit of a single-adatom defect, we have established a direct connection between the atomic-scale morphology and optical response. In

both metals, atomistic details strongly reshape induced charges, electric field morphology, and localization areas, while subnanometric gaps promote the emergence of charge–transfer plasmons. At the same time, the effect of atomistic features is found to be metal-dependent: in both metals, the atomistic features enhance field confinement and overall increase the near-field enhancement, but in Au, the more spatially extended electronic response of the metal results in a larger depletion zone.

In conclusion, our results show that the transition from nano- to picocavities cannot be interpreted as a purely geometrical sharpening effect, as highlighted by the induced charge redistribution and, in the subnanometric regime, by the quantum tunneling-driven emergence of charge–transfer plasmons, which are nongeometrical in nature and independent of the overall size of the structure. This picture explains the qualitatively different behavior observed for Ag and Au and rationalizes the field morphology arising even in the presence of a single atomic defect. However, we remark, in line with the discussion above, that the qualitative Ag/Au difference may also be related to the specific tip geometry, without, however, affecting the qualitative role of the atomistic features. Furthermore, we highlight that $\omega\text{FQF}\mu$ can be coupled to a quantum-mechanical description of an adsorbed molecule within a fully atomistic QM/classical embedding scheme, allowing for the simulation of surface-enhanced spectroscopies, such as SERS [68–70]. Taken together, our findings establish a clear structure-property relation linking atomistic features to plasmon localization in realistic metal nano- and picocavities, providing a physically grounded framework for the interpretation and design of plasmonic cavities with tailored near-field properties.

Author Contributions

T.G., L.B., and L.N. performed $\omega\text{FQF}\mu$ calculations. All the authors analyzed and discussed the results. T.G., S.C., and C.C. supervised the work. All authors contributed to the writing of the manuscript.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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