

Atomistic Multiscale Modeling of Colloidal Plasmonic Nanoparticles

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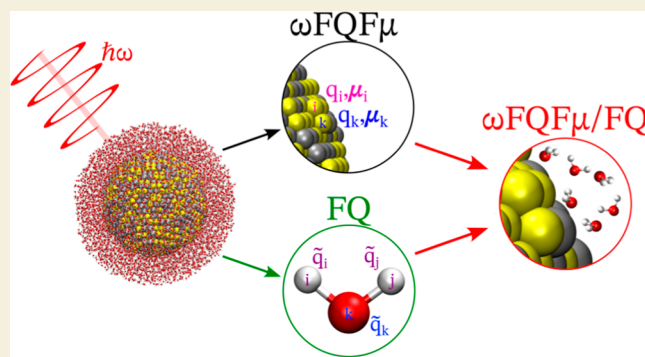
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ABSTRACT: A novel fully atomistic multiscale classical approach to model the optical response of solvated real-size plasmonic nanoparticles (NPs) is presented. The model is based on the coupling of the Frequency Dependent Fluctuating Charges and Fluctuating Dipoles (ω FQF μ), specifically designed to describe plasmonic substrates, and the polarizable Fluctuating Charges (FQ) classical force field to model the solvating environment. The resulting ω FQF μ /FQ approach accounts for the interactions between the radiation and the NP, as well as with the surrounding solvent molecules, by incorporating mutual interactions between the plasmonic substrate and solvent. ω FQF μ /FQ is validated against reference TD-DFTB/FQ calculations, demonstrating remarkable accuracy, particularly in reproducing plasmon resonance frequency shifts for structures below the quantum-size limit. The flexibility and reliability of the approach are also demonstrated by simulating the optical response of homogeneous and bimetallic NPs dissolved in pure solvents and solvent mixtures.

KEYWORDS: atomistic, solvent effects, silver, gold, alloys, colloids, plasmonics



1. INTRODUCTION

In the past decades, colloidal nanoparticles (NPs), i.e. NPs dissolved in solution, have gained significant interest due to their applications in many technological contexts, such as sensing,¹ biomedical applications,² optoelectronics,³ and energy conversion.⁴ By choosing different precursors, reducing agents, solvents, and capping agents, nanostructured materials can be synthesized with a fine control of shape and size.⁵ Size, shape, chemical composition, and the solvent can indeed affect the plasmon resonance frequency (PRF), i.e. the maximum of the NP absorption spectrum.⁶ Such a feature is the basis of a particular class of sensors, which exploit the shift of the PRF upon change of the local refractive index (RI) of the solvent in which the plasmonic NPs are dissolved. Such devices have been widely employed in biosensing,^{7,8} where maximizing the induced PRF shift as a function of RI is crucial to enhance sensitivity.^{1,9}

Rationalizing solvent effects on the PRF of colloidal NPs is particularly challenging from a theoretical point of view. In fact, the optical properties of colloidal NPs result from the interplay of complex phenomena originating under the action of the external electric field, such as the appearance of a localized surface plasmon (LSP) excitation and the polarization of the solvent electron cloud. Solvent effects on PRFs result from a delicate balance between NP-solvent electrostatic (and polarization) interactions, charge-transfer effects, and the possible alteration of the plasmon decaying channels.¹⁰

In principle, a proper description of all possible NP-solvent effects would require an ab initio treatment of the whole system. However, first principle approaches become rapidly unfeasible due to their unfavorable scaling as a function of the system's size, thus hindering the simulation of realistic systems. For these reasons, commonly exploited theoretical approaches to simulate plasmonic colloidal NPs are rooted in classical physics,^{11–15} generally making use of the classical Mie theory,¹¹ the Boundary Element Method (BEM),¹² the Discrete Dipole Approximation (DDA),^{13,16} and the Finite Difference Time Domain (FDTD).¹⁴ However, all these approaches are based on approximated descriptions of both the NP and the solvent, which is generally modeled as a continuum dielectric characterized by its specific permittivity ϵ . In addition, such approaches do not retain the atomistic nature of the system.

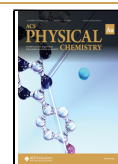
In this paper, we propose a novel multiscale method where both the plasmonic NP and the solvent are treated at full atomistic level. In particular, we employ the fully atomistic electromagnetic model called Frequency Dependent Fluctuating Charges Fluctuating Dipoles (ω FQF μ)¹⁷ to describe the

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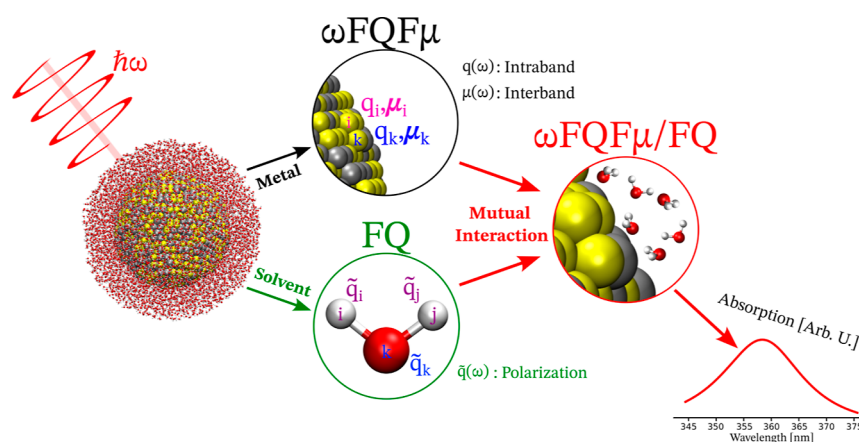


Figure 1. Pictorial view of the multiscale scheme employed to develop $\omega\text{FQF}\mu/\text{FQ}$.

optical response of plasmonic NPs. Such a model is remarkably versatile and can be applied to NPs of any shape¹⁷ and chemical composition,¹⁸ even at the quantum size limit (<5 nm).¹⁷ The solvent is modeled employing the polarizable Fluctuating Charges (FQ) force field,^{19–21} which is specifically designed to model the polarization of the electron cloud of molecular systems. For this reason, it has been widely exploited in the context of computational spectroscopy of solvated systems.^{22–25}

The two approaches, $\omega\text{FQF}\mu$ and FQ, are coupled in a multiscale fashion so that the resulting $\omega\text{FQF}\mu/\text{FQ}$ model accounts for the mutual electrostatic interaction between the solvent and the plasmonic NP, allowing for the modeling of the optical properties of generic colloidal plasmonic NPs. $\omega\text{FQF}\mu/\text{FQ}$ is also coupled to classical molecular dynamics (MD) simulations, which are exploited to sample the NP-solvent phase space. Therefore, differently from previous methods,^{11–14} the dynamical aspects of the solvation phenomenon, which are crucial to properly model solvent effects on spectroscopy, are taken into account.^{22,24,26}

Note that, if solvent molecules are not adsorbed on the surface of the NP, the main solvent effect on plasmonic properties is the local RI variation of the medium surrounding the nanomaterial. This leads to a modification of the local optical field, generally causing a PRF redshift.^{10,27} Such effect is harnessed in many colorimetric sensors for the detection of specific biomolecular analytes.^{7,8,11,28–35} In this work, we model the physical processes that lead to plasmon shift upon change of the local RI of the embedding medium.

The paper is organized as follows: first, the novel $\omega\text{FQF}\mu/\text{FQ}$ approach is presented after the theoretical foundations of $\omega\text{FQF}\mu$ and FQ methods are recalled. Then, the computational protocol is presented and $\omega\text{FQF}\mu/\text{FQ}$ is validated in comparison with reference Time-Dependent Density Functional Tight Binding/Fluctuating Charges (TD-DFTB/FQ³⁶) results. The versatility and robustness of the approach are demonstrated by studying real-size homogeneous and bimetallic NPs dissolved in pure solvent or solvent mixtures. A summary and the main conclusions of the work end the manuscript.

2. METHODS

2.1. Theoretical Model

In this section, $\omega\text{FQF}\mu$ and FQ are briefly recalled and the $\omega\text{FQF}\mu/\text{FQ}$ approach for modeling the optical properties of colloidal plasmonic NPs is presented (see Figure 1).

2.1.1. Plasmonic Nanoparticle: the Atomistic-Electromagnetic $\omega\text{FQF}\mu$ Model. $\omega\text{FQF}\mu$ models the plasmonic NP atomistically. Each atom is endowed with a set of complex frequency-dependent atom-centered charges $q(\omega)$ (ωFQs), and dipoles $\mu(\omega)$ ($\omega\text{F}\mu\text{s}$) (see Figure 1), accounting for intraband and interband mechanisms, respectively. Charges are obtained by solving the following equation of motion, obtained by modulating a Drude-like conduction mechanics with quantum tunneling^{37,38}

$$-i\omega q_i(\omega) = \sum_j \left(\frac{A_j n_j (1 - f_{ji}(l_{ij}))}{1/\tau_j - i\omega} + \frac{A_i n_i (1 - f_{ij}(l_{ij}))}{1/\tau_i - i\omega} \right) \frac{\phi_i(\omega) - \phi_j(\omega)}{l_{ij}} \quad (1)$$

In eq 1 A_j , n_j , and τ_j are the atomic effective area, the electron density, and the relaxation time associated with the intraband scattering events of the i -th atom, respectively. Quantum tunneling effects are expressed in terms of a Fermi-like damping function $f_{ij}(l_{ij})$, which exponentially damps the charge exchange between the atoms (l_{ij} is the distance between i -th and j -th atoms). $\phi_i(\omega)$ is the chemical potential of i -th atom, which reads

$$\phi_i(\omega) = V_i^q(\omega) + V_i^\mu(\omega) + V_i^{\text{ext}}(\omega) \quad (2)$$

where V_i^{ext} is the electric potential associated with the optical radiation, whereas V_i^q and V_i^μ are the electric potentials induced by charges and dipoles on the i -th atomic site (see ref 17 for more details).

The plasmonic properties of alkali metals and graphene in the Pauli-blocking regime are correctly described by ωFQs which properly models intraband mechanisms.^{37–40} However, when the interband absorption energy threshold is comparable to the plasmon resonance frequency (PRF), such as in noble metal nanoparticles, interband transitions become relevant to the decaying mechanism.⁴¹ To model this process, an additional complex frequency-dependent dipole $\mu(\omega)$ is assigned to each atom

$$\mu_i(\omega) = \alpha_i^{\text{IB}}(\omega) \mathbf{E}_i^{\text{tot}}(\omega) \quad (3)$$

$$\mu_i(\omega) = \alpha_i^{\text{IB}}(\omega) [\mathbf{E}_i^q(\omega) + \mathbf{E}_i^\mu(\omega) + \mathbf{E}_i^{\text{ext}}(\omega)] \quad (4)$$

where $\alpha_i^{\text{IB}}(\omega)$ is the interband frequency-dependent polarizability of the i -th atom, and $\mathbf{E}_i^{\text{tot}}(\omega)$ is the total electric field acting on the i -th dipole, accounting for charge–dipole (\mathbf{E}^q), dipole–dipole (\mathbf{E}^μ), and

dipole-field (\mathbf{E}^{ext}) interactions (see ref 17 for more details). For homogeneous materials, $\alpha_i^{\text{IB}}(\omega)$ is determined from the frequency-dependent bulk-permittivity, whereas in the case of multimetallic systems, the interband polarizability of the i -th atom is expressed as a function of the local composition of the system.^{17,18}

The ω FQF μ charge–dipole coupled equations can be recast in the following set of complex linear equations

$$\begin{pmatrix} \mathbf{A}(\omega)\mathbf{T}^{\text{q}q} - \mathbf{Z}(\omega) & \mathbf{A}(\omega)\mathbf{T}^{\text{q}\mu} \\ \mathbf{T}^{\mu\text{q}} & \mathbf{T}^{\mu\mu} - \mathbf{Z}^{\text{IB}}(\omega) \end{pmatrix} \begin{pmatrix} \mathbf{q} \\ \boldsymbol{\mu} \end{pmatrix} = \begin{pmatrix} -\mathbf{A}(\omega)\mathbf{V}^{\text{ext}} \\ -\mathbf{E}^{\text{ext}} \end{pmatrix} \quad (5)$$

where $\mathbf{A}(\omega)$ is a frequency-dependent matrix containing NP chemical and geometrical parameters, while $\mathbf{Z}(\omega)$, and $\mathbf{Z}^{\text{IB}}(\omega)$ are diagonal matrices. $\mathbf{T}^{\text{q}q}$, $\mathbf{T}^{\text{q}\mu}$, $\mathbf{T}^{\mu\text{q}}$ and $\mathbf{T}^{\mu\mu}$ are charge–charge, charge–dipole, dipole–charge, and dipole–dipole interaction kernels, respectively (see ref 42 for more details).

When the linear system in eq 5 is solved, charges and dipoles modeling the optical intra- and interband response of the plasmonic NP are obtained. From such variables, the NP complex polarizability and the absorption cross-section $\sigma^{\text{abs}}(\omega)$ can be computed (see refs 17 and 18 for further details about the ω FQF μ model).

2.1.2. Solvent: the Fluctuating Charges Model (FQ). The physics governing the optical response of solvent systems is utterly different from that of plasmonic materials. When external electric fields are applied, solvent molecules might experience several phenomena ranging from electronic transitions to molecular rovibrations depending on the external field frequency. In the following, we focus only on solvents that are transparent in the spectral region where the plasmonic nanostructure absorbs light. Note that this is generally the case for noble metal nanoparticles, whose PRF falls within the visible range (400–700 nm).^{43,44} In this way, the external fields exciting the plasmons have energies lower than those of the electronic transitions of the solvent molecules but sufficiently high to quench rovibrational effects completely. Thus, the interaction with the external field only yields the polarization of the solvent's electron cloud. This is modeled by using the Fluctuating Charges (FQ) force field,^{19–21} which has been extensively used in computational quantum chemistry for the modeling of molecules in solution.^{22,24,45} Within FQ, each solvent atom is endowed with a charge \tilde{q} whose value is not fixed but can vary as a response to the external electric potential (see Figure 1). Such charge fluctuation is governed by the electronegativity equalization principle (EEP),^{46,47} which states that at equilibrium, each atom has the same electronegativity, i.e. the negative of the chemical potential, as reported by Parr.⁴⁸ The FQ energy, i.e. the energy required to create a partial charge on each atom is generally written as a second-order Taylor expansion in the charges. For a polyatomic system, this can be written as¹⁹

$$U(\tilde{\mathbf{q}}) = \sum_{\alpha,i} \left(\chi_{\alpha i} \tilde{q}_{\alpha i} + \frac{1}{2} \eta_{\alpha i} \tilde{q}_{\alpha i}^2 + \tilde{V}_{\alpha i}^{\text{tot}} \tilde{q}_{\alpha i} \right) + \sum_{\beta,k < \alpha,i} \tilde{q}_{\beta k} T_{\beta k, \alpha i}^{\text{q}\tilde{q}} \tilde{q}_{\alpha i} \quad (6)$$

where Greek and Roman indices run over molecules and atoms, respectively. $\chi_{\alpha i}$ is the electronegativity of the i -th atom of the α -th molecule, and $T^{\text{q}\tilde{q}}$ is the charge–charge interaction kernel⁴² of which the diagonal elements $\eta_{\alpha i}$ are chemical hardnesses, representing self-interaction polarization term. Both electronegativity and chemical hardness are well rooted in Conceptual Density Functional Theory⁴⁹ and are the only free parameters defining the model. Moreover, $\tilde{\mathbf{V}}^{\text{tot}}$ is the total external electric potential on each atomic site, which in the FQ case is the potential associated with the external optical field ($\tilde{\mathbf{V}}^{\text{tot}} = \tilde{\mathbf{V}}^{\text{ext}}$). To constrain the charge of each molecule Q_{α}^{tot} to a constant, a set of Lagrange multipliers λ_{α} is exploited. The energy functional in eq 6 thus becomes

$$F(\tilde{\mathbf{q}}, \boldsymbol{\lambda}) = U(\tilde{\mathbf{q}}) + \sum_{\alpha} \lambda_{\alpha} \left(\sum_i \tilde{q}_{\alpha i} - Q_{\alpha}^{\text{tot}} \right) \quad (7)$$

From the minimization of eq 7 with respect to the variables ($\tilde{\mathbf{q}}$ and $\boldsymbol{\lambda}$), the FQ polarization equations are obtained, implying that the

electronic degrees of freedom of the solvent instantaneously rearrange without energy dissipation.¹⁹ Such an approximation is also valid for optical fields in the visible range and for transparent solvents.^{22,23,50} When the total electric field is monochromatic at frequency ω , the FQ polarization equations in the frequency domain read as follows (see Section S1.1 in the Supporting Information, for further details)

$$\begin{pmatrix} \mathbf{T}^{\text{q}\tilde{q}} & \mathbf{1} \\ \mathbf{1}^{\text{T}} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \tilde{\mathbf{q}}(\omega) \\ \boldsymbol{\lambda}(\omega) \end{pmatrix} = \begin{pmatrix} -\tilde{\mathbf{V}}^{\text{ext}}(\omega) \\ 0 \end{pmatrix} \quad (8)$$

where $\mathbf{1}$ is a rectangular matrix containing the blocks associated with the Lagrange multipliers. By solving eq 8, the atom-centered FQ charges, modeling the instantaneous polarization of the electronic cloud of the solvent under the application of an external monochromatic field, are obtained.

2.1.3. Optical Response of a Plasmonic Nanoparticle in Solution: The ω FQF μ /FQ Model. ω FQF μ for describing the nanostructure's response and FQ for modeling solvent polarization are coupled in a multiscale fashion. In the resulting ω FQF μ /FQ approach, mutual polarization effects between the solvent and the metal NP are introduced (see Figure 1). To this end, we include the solvent-induced electric potential $\mathbf{V}^{\tilde{q}}(\omega)$ and electric field $\mathbf{E}^{\tilde{q}}(\omega)$ acting on the NP's charges $\mathbf{q}(\omega)$ and dipoles $\boldsymbol{\mu}(\omega)$ respectively. Thus, the total chemical potential and field (eq 2 and eq 4, respectively) acting on each atomic site now read

$$\phi_i(\omega) = V_i^q(\omega) + V_i^{\mu}(\omega) + V_i^{\tilde{q}}(\omega) + V_i^{\text{ext}}(\omega) \quad (9)$$

$$\mathbf{E}_i^{\text{tot}}(\omega) = \mathbf{E}_i^q(\omega) + \mathbf{E}_i^{\mu}(\omega) + \mathbf{E}_i^{\tilde{q}}(\omega) + \mathbf{E}_i^{\text{ext}}(\omega) \quad (10)$$

The electric potential and field induced by the FQ solvent charges $\tilde{\mathbf{q}}(\omega)$ on the NP's atomic sites read

$$V_i^{\tilde{q}}(\omega) = \sum_{\alpha,k} T_{i, \alpha k}^{\text{q}\tilde{q}} \tilde{q}_{\alpha k}(\omega) \quad (11)$$

$$\mathbf{E}_i^{\tilde{q}}(\omega) = \sum_{\alpha,k} \mathbf{T}_{i, \alpha k}^{\mu\tilde{q}} \tilde{q}_{\alpha k}(\omega) \quad (12)$$

$\mathbf{T}^{\text{q}\tilde{q}}$ and $\mathbf{T}^{\mu\tilde{q}}$ are the Coulomb interaction kernels between the FQ solvent charges and ω FQF μ plasmonic charges and dipoles respectively, i.e.

$$T_{ij}^{\text{q}\tilde{q}} = \frac{1}{|\mathbf{r}_{ij}|} \quad (13)$$

$$\mathbf{T}_{ij}^{\mu\tilde{q}} = \nabla_i T_{ij}^{\text{q}\tilde{q}} \quad (14)$$

where \mathbf{r}_{ij} is the distance between atoms i and j .

To account for mutual polarization effects, the total potential $\tilde{\mathbf{V}}^{\text{tot}}$ acting on the solvent atomic sites includes the potential generated by the NP's charges $\tilde{\mathbf{V}}^q(\omega)$ and dipoles $\tilde{\mathbf{V}}^{\mu}(\omega)$

$$\tilde{V}_{\alpha i}^{\text{tot}}(\omega) = \tilde{V}_{\alpha i}^q(\omega) + \tilde{V}_{\alpha i}^{\mu}(\omega) \quad (15)$$

where the electric potential and field induced by the ω FQF μ charges and dipoles on the i -th solvent atom of the α -th molecule read

$$\tilde{V}_{\alpha i}^q(\omega) = \sum_k T_{\alpha i, k}^{\text{q}q} q_k(\omega) \quad (16)$$

$$\tilde{V}_{\alpha i}^{\mu}(\omega) = \sum_k \mathbf{T}_{\alpha i, k}^{\mu\mu} \boldsymbol{\mu}_k(\omega) \quad (17)$$

Note that in eq 15 we neglect local field effects (i.e., $\tilde{V}_{\alpha i}^{\text{ext}}(\omega) = 0$).

The coupled ω FQF μ and FQ equations can thus be recast in a linear system defining the ω FQF μ /FQ master equations

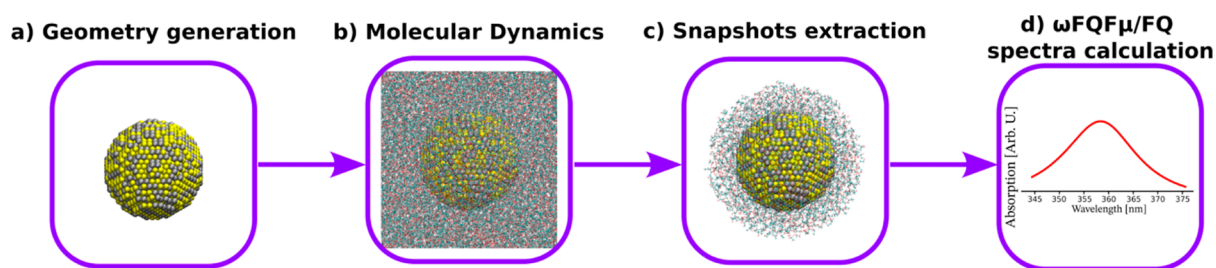


Figure 2. Graphical scheme of the computational protocol employed to compute $\omega\text{FQF}\mu/\text{FQ}$ absorption spectra of colloidal plasmonic NPs (see also Sections S2.1, S2.2, S2.4, and S2.3 in the Supporting Information).

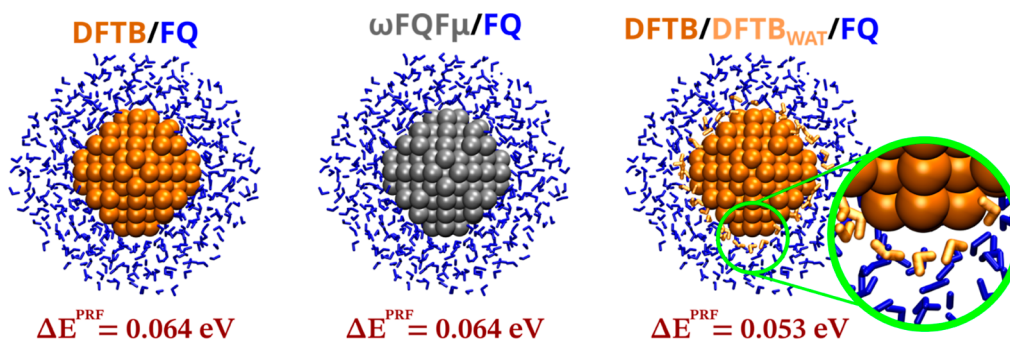


Figure 3. Vacuo-to-water PRF shifts (in eV) computed by using DFTB/FQ, $\omega\text{FQF}\mu/\text{FQ}$, and DFT/DFTB_{WAT}/FQ levels of theory. A graphical depiction of the structure used for each calculation is presented and the elements are colored according to the level of theory used (orange-DFTB, gray- $\omega\text{FQF}\mu$, blue-FQ). In the green inset a zoom of the DFTB/DFTB_{WAT}/FQ structure is reported to highlight the presence of water molecules treated at the DFTB level of theory (orange).

$$\begin{pmatrix} \mathbf{A}(\omega)\mathbf{T}^{\text{qq}} - \mathbf{Z}(\omega) & \mathbf{A}(\omega)\mathbf{T}^{\text{q}\mu} & \mathbf{A}(\omega)\mathbf{T}^{\text{q}\bar{\text{q}}} & \mathbf{0} \\ \mathbf{T}^{\mu\text{q}} & \mathbf{T}^{\mu\mu} - \mathbf{Z}^{\text{B}}(\omega) & \mathbf{T}^{\mu\bar{\text{q}}} & \mathbf{0} \\ \mathbf{T}^{\bar{\text{q}}\text{q}} & \mathbf{T}^{\bar{\text{q}}\mu} & \mathbf{T}^{\bar{\text{q}}\bar{\text{q}}} & \mathbf{1} \\ \mathbf{0} & \mathbf{0} & \mathbf{i}^t & \mathbf{0} \end{pmatrix} \begin{pmatrix} \mathbf{q} \\ \boldsymbol{\mu} \\ \bar{\mathbf{q}} \\ \boldsymbol{\lambda} \end{pmatrix} = \begin{pmatrix} -\mathbf{A}(\omega)\mathbf{V}^{\text{ext}}(\omega) \\ -\mathbf{E}^{\text{ext}}(\omega) \\ \mathbf{0} \\ \mathbf{0} \end{pmatrix} \quad (18)$$

By solving eq 18, the charges and dipoles defining the response of the nanostructure as modified by the presence of the solvent are obtained. This allows the simulation of the optical response of plasmonic substrates with arbitrary shape and chemical composition embedded in a generic solvent or solvent mixture (see Section S1.2 in the Supporting Information).

2.2. Computational Protocol

In this work, we apply $\omega\text{FQF}\mu/\text{FQ}$ to the calculation of the absorption cross-section of plasmonic nanoparticles in solution. To reproduce the experimental PRF shift induced by solvent effects, the dynamic nature of the solvation phenomena needs to be properly described. To this end, we adapt the protocol designed for molecular systems in solution²² to the specific case of colloidal plasmonic NPs.

The protocol can be divided into four main steps (see Figure 2).

2.2.1. Geometry Generation. The geometry of isolated plasmonic NPs is generated by using an in-house code that employs the Atomic Simulation Environment (ASE) Python module v. 3.17⁵¹ (see Figure 2a and Section S2.1 in the Supporting Information).

2.2.2. Molecular Dynamics. The nanostructure is solvated. To sample the NP-solvent phase-space, we perform a classical Molecular Dynamics (MD) simulation of the solvated colloidal system by using the GROMACS software package (version 2020.4) and a suitable force-field⁵² (see Figure 2b and Section S2.2 in the Supporting Information).

2.2.3. Extraction of Structures. From the MD trajectory, we extract 25 uncorrelated representative structures of the whole system. The number of structures ensures convergence of the spectral signal (see Section S2.4.2 in the Supporting Information). For each structure, we retain all solvent molecules that are at most 15 Å from the NP surface, resulting in a spherical droplet (see Figure 2c and Section S2.4.1 in the Supporting Information).

2.2.4. $\omega\text{FQF}\mu/\text{FQ}$ Spectral Calculations. For each spherical droplet, absorption cross sections are computed at the $\omega\text{FQF}\mu/\text{FQ}$ level. The overall spectroscopic response is then recovered as the average over all structures (see Figure 2d and Section S2.3 in the Supporting Information). All $\omega\text{FQF}\mu/\text{FQ}$ calculations are performed by employing a stand-alone Fortran 95 package.

3. RESULTS AND DISCUSSION

In this section, $\omega\text{FQF}\mu/\text{FQ}$ is applied to compute the absorption properties of noble metal NPs in solution. First, the model is validated by reproducing reference data. Then, it is employed to study solvent effects on realistic homogeneous and bimetallic NPs dissolved in a pure solvent or a solvent mixture, showcasing the potential and flexibility of the approach.

3.1. Model Validation

The $\omega\text{FQF}\mu/\text{FQ}$ approach is validated against vacuo-to-water PRF shifts of a small silver spherical-like cluster composed of 164 atoms (Ag_{164}). $\omega\text{FQF}\mu/\text{FQ}$ values are compared to polarizable Time-Dependent Density Functional Tight Binding/Fluctuating Charges (TD-DFTB/FQ) calculations.³⁶ The advantageous computational scaling of TD-DFTB/FQ, which is reached through the approximation of two-electron interactions, makes it capable of handling larger systems than Time-Dependent Density Functional Theory-based methods (TD-DFT) while preserving accuracy.³⁶ The initial geometry of Ag_{164} is taken from ref 53: from that structure, MD

simulations in aqueous solution are run, a single random snapshot is extracted and cut in a spherical droplet containing water (WAT) molecules within 10 Å from the surface of the NP, resulting in a total number of 807 water molecules. Such distance is chosen to account for the most relevant NP-water interactions (see Section S2.4.1 in the Supporting Information). The absorption spectrum of Ag₁₆₄ in vacuo (i.e., by removing all water molecules from the snapshot) and in aqueous solution (Ag₁₆₄/WAT₈₀₇) are computed by using ω FQF μ and DFTB, and ω FQF μ /FQ and DFTB/FQ, respectively (see Section S2.5 in the Supporting Information for more details on the DFTB/FQ calculations). To evaluate quantum effects at the NP-solvent interface, we also performed DFTB/DFTB_{WAT}/FQ calculations, where the first solvation shell is treated at the DFTB level of theory (109 water molecules), whereas the remaining 698 WAT molecules are described at the FQ level. ω FQF μ parameters are recovered from ref 17. The FQ WAT molecules are modeled by using the parameters reported in ref 19 (WAT₁, see Table S1 in Section S2.3 in the Supporting Information). Note that additional calculations were performed by using the FQ parameters reported in refs 54–56 (see Section S3 in the Supporting Information).

In Figure 3, we report the PRF shifts ($\Delta E^{\text{PRF}} = E^{\text{VAC}} - E^{\text{WAT}}$) in eV calculated at the DFTB/FQ level (panel A), ω FQF μ /FQ (panel B), and DFTB/DFTB_{WAT}/FQ (panel C).

All methods predict a very similar vacuo-to-water PRF redshift. The sign of the shift is expected due to the increase of the refractive index of the NP surrounding medium, as also supported by experimental observations.^{57,58} Notably, the hybrid DFTB/FQ and the fully classical ω FQF μ /FQ approaches predict the same solvatochromic shift (64 meV). This is particularly remarkable because the dimension of the studied NP falls within the quantum size region, where quantum effects are expected to play a major role. Our results highlight the accuracy of ω FQF μ in describing such structures.⁵⁹ When the first solvation shell of water molecules is described at the DFTB level (DFTB/DFTB_{WAT}/FQ), the predicted solvatochromic shift decreases by ~ 10 meV (53 meV). Such reduction can be attributed to the inclusion of purely quantum NP-solvent interactions, mainly related to Pauli repulsion effects,^{36,60,61} which are not taken into account by both DFTB/FQ and ω FQF μ /FQ. Remarkably, the computational cost associated with ω FQF μ /FQ is negligible as compared to DFTB-based methods (see Table S4 in the Supporting Information). Indeed, the favorable computational scaling of ω FQF μ /FQ provides a substantial 99.4% speed-up of the calculation with respect to DFTB/FQ, thus representing an effective, reliable, and cost-effective alternative to state-of-the-art ab initio methods.

3.2. Homogeneous Colloidal NPs

The favorable computational scaling of ω FQF μ /FQ opens up to computing the plasmonic response of large NPs in solution. We first consider homogeneous silver and gold spherical NPs (diameter = 5 nm, 3851 atoms) in aqueous solution, as modeled by using the WAT₁ parametrization.¹⁹ The average number of WAT molecules in the FQ region is 6464 (19,392 atoms). Computed absorption cross sections both in vacuo (VAC) and in water (WAT) are plotted in Figure 4A,B, respectively, together with the corresponding vacuo-to-water PRF shifts ($\Delta\lambda$, in nm). The spectra of both systems are characterized by a main plasmonic band centered at about 360

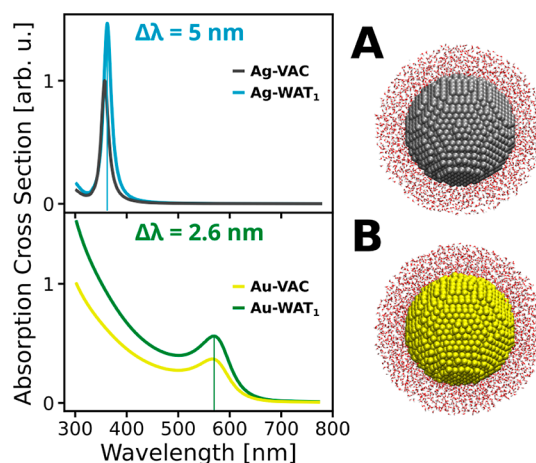


Figure 4. ω FQF μ /FQ absorption spectra of (A) Ag₃₈₅₁ and (B) Au₃₈₅₁ in vacuo (VAC) and water (WAT₁). $\Delta\lambda$ is the vacuo-to-water solvatochromic shift in nm. All spectra are normalized to the corresponding maximum in vacuo.

nm (Ag NPs) and 570 nm (Au NPs). Au peaks are broader than Ag bands, in agreement with previous observations.^{62,63} In the studied region (300–800 nm), the spectra of Au systems are also characterized by the presence of a broad and intense band associated with interband absorption.¹⁷ When dissolved in solution, the main spectral features are maintained. However, we note that the plasmonic peak increases in intensity and slightly redshifts, in line with experimental data.^{9,57,58,64} For Ag, ω FQF μ /FQ predicts a red-shift of the plasmonic peak larger than Au NPs, again in agreement with experiments.^{9,57,58,64} Such shift is due to the refractive index sensitivity (RIS) of the LSP, a quantity that is commonly exploited in plasmonic colorimetric sensors.^{30,31,65,66} RIS is generally expressed as $\Delta\lambda$ (in nm) over refractive index unit— $\Delta\lambda(\text{nm})/\text{RIU}$.

The computed ω FQF μ /FQ RIS values are 15.0 nm/RIU for Ag and 7.9 nm/RIU for Au, while the experimentally measured RIS are 120–160 nm/RIU (Ag) and 70 nm/RIU (Au).^{30,31,65,66} Therefore, ω FQF μ /FQ absolute RIS values are systematically lower than experimental ones for Ag and Au NPs, however ω FQF μ /FQ can nicely reproduce the experimental Ag/Au ratio (~ 2). The discrepancy can be related to the FQ parameters employed for modeling water, which have not been specifically tuned to describe solvated NPs.¹⁹ Nevertheless, although experimental absolute RIS values are underestimated by a factor of 10, the capability of ω FQF μ /FQ to match the Ag/Au sensitivity ratio is a remarkable feature of the model, which can be used to rationalize the optical behavior of plasmonic nanostructures with high RIS, with potential applications in sensor design.

3.3. Au@Ag core-shell Colloidal NPs

By taking advantage of the favorable computational scaling of ω FQF μ /FQ, its atomistic nature, and its capability of correctly reproducing Ag/Au RI sensitivity ratio, the model is challenged to optimize the sensitivity of Au@Ag core-shell spherical NPs. In fact, colorimetric sensors exploiting the PRF shift of noble metals upon change of the local refractive index (RI) are widely used in biosensing.^{7,8,11,28–35} Among the various substrates used for this technology, gold-silver core-shell (Au@Ag) NPs are the most employed^{67–72} due to their high RIS.^{11,72} By studying such structures, we aim to showcase the

potentialities of ω FQF μ /FQ, open up to colorimetric LSP sensor design.

We first consider spherical Au@Ag core–shell NPs (diameter = 5 nm, 3851 atoms) characterized by an Au core of increasing size ($d_{\text{Au}} = 2, 3,$ and 4 nm—see Figure 5A–C), in

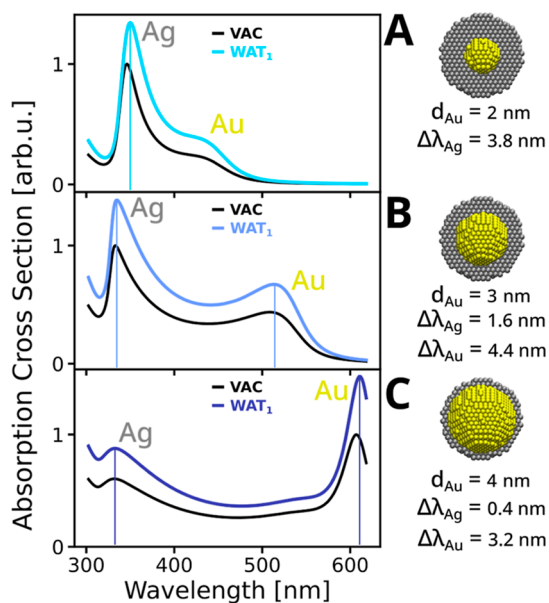


Figure 5. ω FQF μ /FQ absorption spectra of core–shell Au@Ag spherical NPs in vacuo (VAC) and in aqueous solution (WAT₁) as a function of the diameter of the Au core (d_{Au} : (A) 2.0 nm, (B) 3.0 nm and (C) 4.0 nm). The solvatochromic shifts of “Ag” ($\Delta\lambda_{\text{Ag}}$) and “Au” ($\Delta\lambda_{\text{Au}}$) peaks are reported in nm. All spectra are normalized to the maximum in vacuo.

aqueous solution. To sample the NP–solvent phase space, we perform a classical MD simulation of a single Ag NP in the aqueous solution. We then construct the Ag@Au core–shell bimetallic NP by properly substituting the metal atoms after the MD snapshot’s extraction, which is a physically consistent procedure due to the almost equal lattice constants of the two metals.⁷³ On average, 6464 water molecules are considered in the FQ region and modeled employing the WAT₁ parametrization.¹⁹

In Figure 5, ω FQF μ /FQ absorption spectra of Au@Ag core–shell NPs in vacuo (black) and water (blue) are reported. For all structures, absorption spectra in vacuo and solution feature two main bands at short (~ 350 nm) and long wavelengths (>400 nm), in agreement with previous theoretical and experimental observations.^{11,12,74,75} Such peaks are located in the spectral region of the plasmon bands of pure Ag and Au spheres (see Figure 4A,B). For this reason, we call them “Ag” and “Au” peaks, respectively. Their position and intensity strongly depend on the diameter of the Au core both in the gas phase and solution. In particular, by first focusing on vacuo results, for Au-core thickness of 1 nm (Figure 5A), the “Ag” peak, located around 346 nm, dominates the computed spectrum, while the “Au” band appears as a shoulder. By increasing the Au-core size, the “Ag” peak slightly blueshifts of about 10 nm while decreasing in intensity. On the contrary, the “Au” peak largely redshifts of about 150 nm, and significantly increases in intensity, becoming dominant for Au-core diameters of 4 nm (1 nm Ag-shell thickness). Including the solvent redshifts both “Ag” and “Au” peaks and increases

their intensity. The shift differs for each peak and each Au-core diameter. In particular, all “Ag” peaks show lower solvatochromic shifts as compared to pure Ag spheres ($\Delta\lambda = 5.0$ nm see Figure 4A), and increasing the Au-core size reduces the redshift of the “Ag” peak from $\Delta\lambda_{\text{Ag}} = 3.8$ nm ($d_{\text{Au}} = 2$ nm) to $\Delta\lambda_{\text{Ag}} = 0.4$ nm ($d_{\text{Au}} = 4$ nm). The shift of the “Au” peak is generally larger (e.g., $\Delta\lambda_{\text{Au}} = 4.4$ nm for $d_{\text{Au}} = 2$ nm) than that of a pure Au sphere ($\Delta\lambda = 2.6$ nm, see Figure 4B). This suggests that for small NPs ($d \sim 5$ nm), the “Au” peak RIS can be increased by coating the NP with an Ag layer. Remarkably, our findings align with previous theoretical and experimental observations.^{11,69,72}

To showcase more potentialities of ω FQF μ /FQ, we now move to study the effect of alloying the Ag shell on the refractive index sensitivity, for which an atomistic picture is essential.¹⁸ Note that, to the best of our knowledge, the use of atomistic modeling in this field has received only a little attention.^{11,12,76}

We consider a substantially more complex system composed of a spherical Au@Ag core–shell bimetallic NP (see Figure 6)

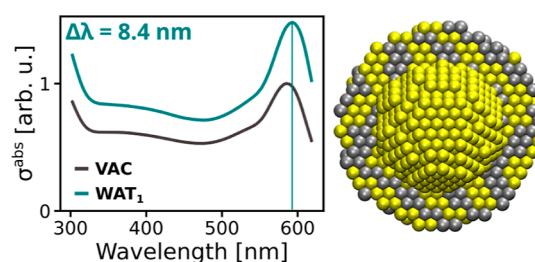


Figure 6. ω FQF μ /FQ absorption cross section (σ^{abs}) of core–shell Au@Ag spherical NP with an Au core diameter of 3 nm and featuring an alloyed (50% Au/Ag) external layer of 1 nm (see right panel) in vacuo (VAC) and aqueous solution (WAT₁). $\Delta\lambda$ indicates the solvatochromic shift (in nm). All spectra are normalized to the maximum in vacuo.

of 5 nm of diameter (3851 atoms) with an Au core of diameter (d_{Au}) of 3 nm, and featuring a 50% Ag 50%Au random bimetallic layer of 1 nm. Such NP is solvated in aqueous solution, exploiting the same procedure discussed above. Figure 6, shows computed ω FQF μ /FQ absorption cross-section (σ^{abs}) both in vacuo and water. The computed spectrum substantially deviates from the corresponding perfect core–shell system (Figure 5B). In fact, the “Au” peak is shifted at higher wavelengths (~ 600 nm) and dominates the spectrum, while the “Ag” peak disappears in a dim spectral feature between 350 and 500 nm. Remarkably, the computed PRF shift of the gold peak ($\Delta\lambda_{\text{Au}}$) is 8.4 nm, almost double the original Au@Ag core–shell structure ($\Delta\lambda_{\text{Au}} = 4.4$ nm, see Figure 5B), and more than three times than a pure Au sphere of the same dimensions ($\Delta\lambda = 2.6$ nm, see Figure 4). Remarkably, the same trend is also obtained for the computed ω FQF μ /FQ RIS sensitivity, which reaches 25.5 nm/RIU. The obtained results thus suggest that the alloying of the Ag shell of an Au@Ag core–shell can potentially improve the refractive index sensitivity of the system by almost a factor of 2.

To finally showcase the flexibility of ω FQF μ /FQ, we solvate the NP in a 1:1 water–ethanol mixture (WAT-ETH). The even more complex chemical nature of this system enforces the need for a fully atomistic model to simulate its optical properties. To the best of our knowledge, ω FQF μ /FQ is the first fully atomistic model capable of calculating the response of

a generic multimetallic plasmonic NP embedded in a multicomponent solvent.

To sample the NP-solvent phase space, we perform a classical MD simulation of a single Ag NP in the WAT-ETH mixture. We then construct the Ag@Au core-shell bimetallic NP by properly substituting the metal atoms after the MD snapshot extraction. The FQ parametrization employed for the water molecules is WAT₁, while for ethanol we exploit the parameters proposed in ref 56 (see Table S1 in the Supporting Information). On average 1800 ETH and 1218 WAT molecules are included in the spherically shaped snapshot (i.e., 19,854 atoms in total).

In Figure 7, the absorption spectrum of the complex bimetallic Au/Ag NP both in vacuo (VAC) and solvated in the

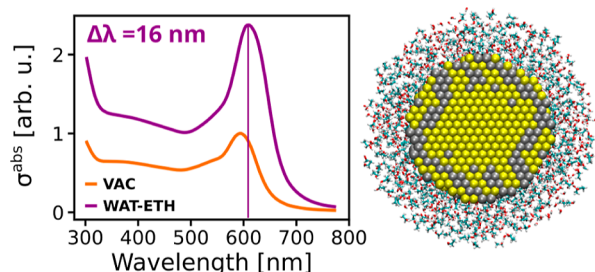


Figure 7. ω FQF μ /FQ absorption cross section (σ^{abs}) of core-shell Au@Ag spherical NP with an Au core diameter of 3 nm and featuring an alloyed (50% Au/Ag) external layer of 1 nm (see right panel) in vacuo (VAC) and a 1:1 water-ethanol mixture (WAT-ETH). The vacuo-to-mixture solvatochromic shift is given in nm. All spectra are normalized to the maximum in vacuo.

1:1 water-ethanol mixture (WAT-ETH) is graphically depicted, together with the corresponding computed PRF shift ($\Delta\lambda$ in nm). Notably, absorption spectra both in vacuo and in solution present a sharp peak around 600 nm which can be assigned to the Au plasmonic dipolar band, and a shoulder at about 350–400 nm associated with the Ag plasmonic absorption. Solvent effects provided by the WAT-ETH mixture lead to a huge enhancement of the peak absorption (almost twice that in vacuo), which is also red-shifted by 16 nm. Considering a refractive index for the WAT-ETH mixture of 1.36,⁷⁷ a computed RIS of about 44.0 nm/RIU is obtained. Such a value is almost twice that obtained in pure water, highlighting a nontrivial RIS dependence on the solvent composition.

4. SUMMARY AND CONCLUSIONS

We have presented a novel fully atomistic multiscale classical model, named ω FQF μ /FQ, which is capable of simulating the optical properties of real-size plasmonic colloidal nanoparticles (NPs) of a generic chemical nature. ω FQF μ /FQ is a multiscale model based on the mutual electrostatic interaction between the solvent and the NP. More specifically, the interaction of the plasmonic substrate with the external optical field is modeled employing ω FQF μ ,^{17,18} where each atom is endowed with a frequency-dependent charge and dipole, modeling intraband and interband plasmon decaying mechanisms, respectively. The solvent environment is considered transparent to the optical radiation and its instantaneous polarization is modeled through the polarizable FQ force field.^{19–21}

ω FQF μ /FQ has been challenged to reproduce reference TD-DFTB/FQ values, showing an almost perfect match with

the TD-DFTB/FQ vacuo-to-water plasmon resonance frequency (PRF) shift of a small silver cluster (Ag₁₆₄), with a substantial 99.4% speed-up of the calculation. Then, we have showcased the capabilities of ω FQF μ /FQ by simulating the optical properties of real-size homogeneous Ag and Au spherical NPs (~5 nm of diameter, 3851 metal atoms with 6464 water molecules), highlighting how the computed ratio between the refractive index sensitivities of Au and Ag NPs matches the experiments. Remarkably, ω FQF μ /FQ can also be used to study the sensitivity of colorimetric LSP sensors, as demonstrated by the chemical substitution of Au atoms in Au@Ag core-shell NPs, which can potentially enhance the sensitivity by a factor 2–3. Finally, the flexibility of ω FQF μ /FQ is validated by simulating the absorption spectrum of a bimetallic Ag/Au NP solvated in a 1:1 water-ethanol mixture. Remarkably, the model can be applied to any solvent or solvent mixtures, including green solvents,⁷⁸ pending a reliable parametrization of the FQ force field.⁵⁶ Our results are particularly promising; however, it is important to mention that ω FQF μ /FQ have been validated on a small data set, due to the limited computational studies dealing with colloidal plasmonic nanostructures.

It is worth noting that, in ω FQF μ /FQ, the nanostructure-solvent interactions are limited to electrostatics and polarization. Thus, purely quantum effects, such as Chemical Interface Damping (CID)^{10,79,80} or Pauli repulsion effects, are neglected. However, for noncovalently bonded molecules, as in the case of solvents, CID effect on plasmonic response is generally negligible.^{79,81} The extension of ω FQF μ /FQ to consider CID effects will be the topic of future communications.

In conclusion, ω FQF μ /FQ is the first fully atomistic classical model capable of providing a platform for the calculation of LSP shifts of plasmonic NPs with the accuracy of ab initio methodologies for systems in the quantum confinement size region, but with a computational cost that consents its application to realistic-sized colloidal NPs. Such a development can potentially pave the way for future in-silico rational design of colorimetric sensors.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsphyschemau.4c00052>.

Details on ω FQF μ /FQ, computational details, convergence of ω FQF μ /FQ spectra as a function of the radius of the solvent droplet and number of snapshots, MD analysis for spherical NPs (diameter = 5 nm) in solution (PDF)

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CRedit: **Luca Nicoli** data curation, formal analysis, investigation, methodology, software, validation, visualization, writing - original draft; **Sveva Sodomaco** data curation, formal analysis, investigation, methodology, validation, visualization, writing - original draft; **Piero Lafiosca** data curation, formal analysis, investigation, methodology, software, validation, writing - original draft; **Tommaso Giovannini** conceptualization, formal analysis, methodology, project administration, software, supervision, writing - review & editing; **Chiara Cappelli** conceptualization, formal analysis, funding acquisition, methodology, project administration, resources, supervision, writing - review & editing.

Notes

The authors declare no competing financial interest.

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