Plasmonic performance of $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ alloys from many-body perturbation theory

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Abstract

We present a detailed appraisal of the optical and plasmonic properties of ordered alloys of the form $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$, as predicted by means of first-principles many-body perturbation theory augmented by a semi-empirical Drude–Lorentz model. In benchmark simulations on elemental Au, Ag, and Cu, we find that the random-phase approximation (RPA) fails to accurately describe inter-band transitions when it is built upon semi-local approximate Kohn–Sham density-functional theory band-structures. We show that non-local electronic exchange-correlation interactions sufficient to correct this, particularly for the fully-filled, relatively narrow $d$-bands which contribute strongly throughout the low-energy spectral range (0–6 eV), may be modeled very expediently using band-stretching operators that imitate the effect of a perturbative $\text{G}_0\text{W}_0$ self-energy correction incorporating quasiparticle (QP) mass renormalization. We thereby establish a convenient work-flow for carrying out approximated $\text{G}_0\text{W}_0 + \text{RPA}$ spectroscopic calculations on alloys and, in particular here, we have considered alloy concentrations down to 12.5% in $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$, including all possible crystallographic orderings of face-centred cubic type. We develop a pragmatic procedure for calculating the Drude plasmon frequency from first principles, including self-energy effects, as well as a semi-empirical scheme for interpolating the plasmon inverse lifetimes between stoichiometries. A distinctive M-shaped profile is observed in both quantities for binary alloys, in qualitative agreement with previous experimental findings. A range of optical and plasmonic figures of merit are discussed, and plotted for ordered $\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}$ at three representative solid-state laser wavelengths. On this basis, we predict that certain compositions may offer improved performance over elemental Au for particular application types. We predict that while the loss functions for both bulk and surface plasmons are typically diminished in strength through binary alloying, certain stoichiometric ratios may exhibit higher-quality (longer-lived) localized surface-plasmons and surface-plasmon polaritons, at technologically-relevant wavelengths, than those in elemental Au.

Keywords: alloy design for plasmonics, theoretical spectroscopy, many-body perturbation theory

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(Some figures may appear in colour only in the online journal)
response in the low-energy spectral range. Hence, their alloys are naturally expected to be promising candidates for efficient opto-electronic applications. Spectroscopic measurements on alloys are mostly performed on their thin-film surfaces [10–18], which are highly dependent on the alloying technique used [19]. As a result, it is difficult to find consensus within the literature even on basic quantities such as the plasma frequency of an elemental metal.

Systematic first-principles studies of such alloys may, therefore, offer fundamental insights into the microscopic effects of alloying on optical properties, and potentially thereby even guide the tailoring of optical and plasmonic response for designated applications. This work is an exploratory investigation into the viability of such an approach using state-of-the-art theory. Specifically, in this article, we present a detailed investigation into the capabilities and limitations of contemporary theoretical spectroscopy for noble metals, and the development and testing of a set of computationally light techniques for studying the spectra of noble metals and their ordered alloys within the linear-response regime. Taking advantage of the resulting high-throughput-compatible approach, we provide various figures of merit for comparing the plasmonic performance of these alloys, from which the optimal stoichiometry for a given optical or plasmonic characteristic, at a given driving frequency, may be estimated.

2. Theoretical methodology

In the study and simulation of solid-state optical and energy-loss spectra, the macroscopic dielectric function $\varepsilon(\omega)$ is the central function due to its well-established connection to measured observables. In the low-energy spectral range, where the phenomena contributing to optical spectra are almost entirely electronic, the macroscopic dielectric function of a metallic system is constituted by two terms, explicitly by

$$\varepsilon(\omega) = \varepsilon^{\text{int}}(\omega) + \varepsilon^{\text{intr}}(\omega),$$  \hspace{1cm} (1)

where $\varepsilon^{\text{int}}(\omega)$ and $\varepsilon^{\text{intr}}(\omega)$ result from screening effects due to inter-band transitions and intra-band transitions (giving rise to the Drude plasmon), respectively.

When a solid is simulated as an infinite object, electronic transitions are envisaged as occurring simultaneously throughout the material, at a given energy of electro-magnetic (EM) radiation. Observable spectra are spatial averages of these transitions, whereas electronic transitions are microscopic events. Hence, an averaging process is required to connect microscopic quantities to macroscopic observables. Specifically, an averaging via the inverse dielectric function is the appropriate route to obtain the macroscopic dielectric function in the optical (vanishing momentum transfer) limit [20, 21], and this is given, in terms of the microscopic dielectric matrix $\varepsilon$, by

$$\varepsilon(\omega) = \lim_{\mathbf{q} \to 0} \left[ \frac{1}{\varepsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega)} \right]_{\mathbf{G}\mathbf{G}' = 0}.$$ \hspace{1cm} (2)

As the momentum $\mathbf{q}$ transferred from the incoming photon is assumed to be negligible, only vertical excitations at each point in reciprocal space are considered here. Notwithstanding, non-local screening ‘local field’ effects are explicitly incorporated by means of equation (2). Where such effects can be safely neglected, we may use the relatively simple, conveniently inversion-free formula

$$\varepsilon(\omega) \approx \lim_{\mathbf{q} \to 0} \left[ \varepsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) \right]_{\mathbf{G}\mathbf{G}' = 0}.$$ \hspace{1cm} (3)

2.1. Inter-band transitions

Inter-band transitions are electronic transitions between the valence (occupied) and conduction (unoccupied) bands. Within the linear-response regime that typically holds for photon energies in the IR-vis-UV range, the inverse microscopic dielectric function is given, in reciprocal space, by the expression

$$\varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) = \delta_{\mathbf{G}\mathbf{G}'} + v_{\mathbf{G}\mathbf{G}'}(\mathbf{q})\chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega),$$ \hspace{1cm} (4)

where the bare Coulomb interaction takes the form

$$v_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) = \frac{4\pi}{|\mathbf{q} + \mathbf{G}| |\mathbf{G}' + \mathbf{G}|}.$$ \hspace{1cm} (5)

In order to calculate $\varepsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega)$, the non-interacting random-phase approximation (RPA), also referred to as Fermi’s Golden Rule (FGR) [22] linear-response function for inter-band excitations is first calculated, in terms of independent-particle wave-functions $|\psi_{\mathbf{k}}\rangle$ with occupancies $f_{\mathbf{k}}$, as [20, 21],

$$\chi^{0}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) = 2\sum_{c, v, k} (f_{\mathbf{k}} - f_{\mathbf{-k}-\mathbf{q}})$$

$$\times \frac{|\langle \psi_{\mathbf{k}-\mathbf{q}} | \varepsilon(\mathbf{q} + \mathbf{F}) | \psi_{\mathbf{k}} \rangle|^2}{\omega - \varepsilon_{c, \mathbf{k}} + i\Gamma},$$ \hspace{1cm} (6)

where $\nu$ ($\epsilon$) indicates valence (conduction) states and $\varepsilon_{c, \mathbf{k}} - \varepsilon_{v, \mathbf{k}}$ is a difference between single-particle energy eigenvalues (using atomic units). Here, $\Gamma$ is a small, positive-valued Lorentzian broadening factor, $\mathbf{q}$ is the transferred momentum vector, which lies in the first Brillouin zone, and the factor of 2 pre-supposes and accounts for spin degeneracy. Following this, the interacting RPA [23–26] response function $\chi$ is given by [23–26]

$$\chi(\mathbf{G}\mathbf{G}'(\mathbf{q}, \omega) = \chi^{0}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega)(1 + v_{\mathbf{G}\mathbf{G}'}(\mathbf{q})\chi^{0}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega)), \hspace{1cm} (7)$$

which is a Dyson equation. Equation (7) may be rearranged into the compact form, involving matrix inversion, of

$$\chi^{-1}(\mathbf{q}, \omega) = \chi^{0}_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q}, \omega) - \nu(\mathbf{q})$$ \hspace{1cm} (8)

for the interacting response function. Alternatively, the more approximate independent-particle RPA dielectric function may be calculated as

$$\varepsilon^{0}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) = \delta_{\mathbf{G}\mathbf{G}'} - v_{\mathbf{G}\mathbf{G}'}(\mathbf{q})\chi^{0}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega).$$ \hspace{1cm} (9)

When $\varepsilon \approx \varepsilon^{0}$ is invoked it is conventional to also neglect local-field effects, by means of equation (3).

2.2. Intra-band transitions

In addition to inter-band transitions, the promotion of electrons to higher energies within the same band, at finite
temperatures, contributes very significantly to the macroscopic dielectric function of metallic solids within the low-energy regime. This is the intra-band transition effect, which gives rise to the prominent Drude plasmon divergence in the optical absorption spectrum in the static limit. This Drude plasmon can be thought of semi-classically as the collective oscillation of electrons at the Fermi level, in phase with the longitudinal part of the driving EM radiation. The Drude plasmon typically occurs at $\sim 10^{-1} eV$ in elemental late transition metals, and it can be excited, e.g. by energy loss of incident electrons with kinetic energies in the 1–20 keV range, or by using lasers tuned to the plasmon wavelength.

The direct simulation of a well-converged Drude plasmon frequency starting a set of single-particle electronic states is computationally demanding, indeed extremely so due to the requirement for dense Brillouin-zone sampling at and around the Fermi surface, for example up to $\sim 160000$ grid points in [27]. This procedure is not commonly followed, as the resulting intra-band dielectric function remains excessively sensitive to the difficult-to-estimate excitation damping (or lifetime) factor that must be imposed. The Drude plasmon lifetime is limited by a multitude of physical processes, in reality, including scattering by phonons, defects, and grain boundaries; electron–electron (including electron-plasmon and plasmon-plasmon) scattering giving rise to decay, and quantum thermodynamic effects.

More commonly, the Drude plasmon is discussed in terms of a classical model for free electrons oscillating under the influence of external electric field, namely the Drude–Lorentz model [28–31]. The Drude plasmon contribution to the macroscopic dielectric function becomes

$$\varepsilon_{\text{intra}}(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 - i\eta_p \omega},$$  \hspace{1cm} (10)

where $\omega_p$, $\eta_p$, and $\varepsilon_\infty$ are the Drude plasmon energy (not to be confused with the actual net plasma frequency of the metal—where $\text{Re} \left[ \varepsilon(\omega) \right] \approx 0$ eV), the phenomenological inverse life-time, and the electric permittivity in the infinite-frequency limit, respectively. The set $\{\omega_p, \eta_p, \varepsilon_\infty\}$ comprise the ‘Drude parameters’. Experimentally, it is standard practice to perform optical (e.g. $n$ and $k$) measurements within the infrared (IR) and the far-infrared spectral range (corresponding to $\omega \approx 0–2$ eV), and to determine these parameters by fitting to the Drude–Lorentz model [32–38].

Inspired by this, here, we start from the Drude plasmon energy in equation (10), which can be expressed as [28, 29, 39]

$$\omega_p^2 = \frac{4\pi N(E_F)}{m_{\text{eff}}},$$  \hspace{1cm} (11)

for a uniform non-interacting electron gas. In this, $N(E_F)$ is the density of states (DOS) at the Fermi level and $m_{\text{eff}}$ is the electron effective mass. In practice, for real metals, this effective mass is also evaluated at the Fermi level and, if we further assume that the metallic bands have a parabolic dispersion normal to the Fermi surface [40], we may write

$$m_{\text{eff}}^{-1} \approx \frac{1}{3} \langle v^2(E_F) \rangle = \frac{1}{3} \left( \sum_i \int S_i \, dk \, v_i^k(k) \right) \left( \sum_i \int S_i \, dk \right)^{-1},$$

$$\text{if } v_i^k(k) = \left| \frac{\partial E_k}{\partial k} \right|^2.$$  \hspace{1cm} (12)

Here, $S_i$ signifies the Fermi surface of the $i$th metallic band, and the factor of 1/3 results from the squared Fermi velocity being averaged (rather than summed) over Cartesian directions. Succinctly, the Drude plasmon energy can thus be approximated within a non-interacting, uniform-gas theory, simply and efficiently as [40]

$$\omega_p^2 = \frac{4\pi}{3} N(E_F) \langle v^2(E_F) \rangle.$$  \hspace{1cm} (13)

As previously mentioned, the routine direct calculation of experimentally-relevant Drude plasmon lifetimes is currently beyond the scope of state-of-the-art electronic structure simulation methodology. Electron–phonon and electron-impurity scattering typically dominantly contribute to the limiting DC conductivity $\sigma_0$, as compared to the more accessible electron–electron scattering processes [39]. Recent years have seen considerable progress in the successful first-principles calculation of both Drude plasmon energies and life-times for pristine elemental metals. We refer the reader to [41–44] for further details. The combination of such such approaches with the presented methodology, such as by including simplified $G_0W_0$ band-structure corrections, would be an interesting avenue for future investigation. Notwithstanding, such approaches often require well-converged first-principles phonon band-structures that, at the present time, remain challenging for high-throughput materials discovery, particularly for the larger super-cells needed for alloys. In order to circumvent this issue, we have developed a semi-empirical scheme based upon the Drude–Lorentz model, in which the scattering rate $\eta_p$ is inversely proportional to the DC conductivity and also to the effective mass of carriers, but proportional to their concentration. Noting a very plausible linear dependence between $\sigma_0$ and $\sqrt{\langle v^2(E_F) \rangle}$, we express the scattering rate (where the first equality is standard Drude–Lorentz) as

$$\eta_p = \frac{N(E_F)}{\sigma_0 m_{\text{eff}}} \approx c_p N(E_F) \langle v^2(E_F) \rangle^{1/2},$$  \hspace{1cm} (14)

where $c_p$ is our scaling coefficient to be determined.

Next, separating the real and imaginary part of $\varepsilon_{\text{intra}}(\omega)$ from equation (10), we arrive at

$$\text{Re} \left[ \varepsilon_{\text{intra}} \right] = \varepsilon_{\text{intra}}(\omega, \omega_p, \eta_p, \varepsilon_\infty) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\eta_p \omega},$$

$$\text{Im} \left[ \varepsilon_{\text{intra}} \right] = \varepsilon'_{\text{intra}}(\omega, \omega_p, \eta_p) = \frac{\eta_p \omega_p^2}{\omega^2 + \eta_p \omega^2},$$  \hspace{1cm} (15)

and note that, given the first-principles $\omega_p$, the imaginary part is parametrized only by $\eta_p$. Thus, in practice, we first determine the
2.3. Treatment of non-local many-electron effects within the quasi-particle formalism: perturbative one-shot GW: G₀W₀

In order to calculate the aforementioned response functions, e.g. in equation (6), a sufficiently complete set of well-defined single-particle electronic states is required. Density functional theory (DFT) [45] is currently the almost-universally used approach for constructing ground-state electronic structures of solids within its Kohn–Sham formalism (KS-DFT) [46]. However, the DFT is limited by the accuracy of available, computationally feasible local and semi-local approximations for exchange and correlation [46–49]. Furthermore, the energy eigenvalues (band-structures) generated by the Kohn–Sham mapping have no formal meaning in terms of electron addition or removal energies (except in certain well-documented instances), in spite of their being widely interpreted as such. The RPA, although it is a true many-body approximation, is unable to build any electron or hole QP [50–52] screening (e.g. electron-plasmon coupling) effects into an underlying Kohn–Sham eigensystem, as it treats only the screened interaction between pairs of such input particles. The fact that the absence of non-local quantum many-body effects in semi-local KS-DFT, and absent explicit long-ranged exchange in particular, often leads to inaccurate descriptions of the electronic bands in solids is well reported for various material classes, such as insulators and semi-conductors [53–57], transition-metal oxides [58–60], and metallic solids [61, 62].

In noble metals, the electronic bands that dominantly contribute to low-energy spectra are fully-filled d⁰ bands that are tightly packed in a narrow energy window close to the Fermi level. It has previously been found that these electronic bands are poorly described within approximate KS-DFT for noble metals such as bulk Au [63], and then that such errors become more pronounced in spectral simulations using the RPA [64–68]. Various corrective approaches have been developed to strengthen the connection between KS-DFT band-structures and experimental QP band-structures. Perhaps the method that is most widely used at present in high-throughput calculations is the Hubbard corrected KS-DFT, DFT+U [69–77], which is algorithmically almost cost-free. DFT+U with empirically-fitted Hubbard U parameters has previously been shown to successfully improve the match between the KS band-structures of elemental Au, Ag, and Cu with respect to experiment [78]. When experimental data is unavailable, however, such as when exploring the composition space of alloys, the Hubbard U parameters should ideally be calculated from first principles. There is little or no data available to suggest that the U parameter may be reliably interpolated in stoichiometry space. Unfortunately, the determination of the first-principles Hubbard U parameters relevant to approximate DFT has been relatively little explored to date for metals and, more generally, referring the reader to our own [79, 80], both the calculation of U and the functional form of DFT+U itself present inherent difficulties for closed-shell systems at present.

The formally correct approach to calculating band-structures from first principles is instead the QP formalism, fundamental to which is a mapping of the interacting many-body system to a weakly-interacting many-body system of virtual ones, namely the quasi-particles [81, 82]. QP wave-functions and corresponding energy levels can determined by self-consistently solving the QP equation

\[
\left[\frac{-1}{2m_{QP}} \nabla_i^2 + v_{xc}(\mathbf{r}) + v_F(\mathbf{r}) \right. \\
+ \left. \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}', \omega) \right] \psi_{QP}^i(\mathbf{r}, \omega) = \varepsilon_{QP}^{i} \psi_{QP}^i(\mathbf{r}, \omega),
\]

where \( \Sigma(\mathbf{r}, \mathbf{r}', \omega) \) is the energy-dependent, non-local, and non-Hermitian self-energy. The resulting \( \psi_{QP}^i(\mathbf{r}) \) and \( E_{QP}^i \) are the ith QP wave-function and the corresponding QP energy. In practice, QP energies are more commonly calculated using nonetheless demanding many-body perturbation theory (MBPT) [83] methods with Green’s functions instead of explicit solution of equation (16).

The GW approximation is the cornerstone of MBPT for electrons. In GW, the self-energy is calculated in one iteration formally as

\[
\Sigma = iGW,
\]

where the product here is in real space and time. The screened Coulomb interaction W consistent with the GW approximation is that which is calculated within the RPA for a given Green’s function G. Self-consistent GW is a computationally expensive approach that requires the solution of a Dyson equation multiple times, and that involves the inversion of large, complex, and near-singular matrices. Furthermore, it has been shown that it fails for systems with over half-filled 3d bands [84]. A more successful, further approximation is one-shot, non-self-consistent GW, or simply G₀W₀, which depends explicitly upon and input Green’s electronic function G₀, and stops at the first iteration of the self-energy, \( \Sigma = iG_0W_0 \).

In practice, this requires the choice of a suitable basis and, when all that is of interest are the QP energies, it is expedient to use the KS-DFT eigenbasis, on the grounds that the approximate KS-DFT density is usually reasonable, even if the KS-DFT eigenspectrum, represented in the form of G₀, is unphysical. Assuming that \( \langle \psi_i | \psi_j^{QP} \rangle \approx 1 \), the QP energies can furthermore be approximated as a first-order correction to the KS eigenvalues, as

\[
\varepsilon_{QP}^i = \varepsilon_i + Z_i \langle \psi_i | \Sigma(\varepsilon_i) \psi_i \rangle - v_{xc} |\psi_i\rangle,
\]

where

\[
Z_i = \left[ 1 - \frac{\partial \Sigma(\omega)}{\partial \omega} \right]^{-1}_{\omega = \varepsilon_i}.
\]
and $Z_i$ is called the QP re-normalization factor. This factor can be thought of as the absolute value of the charge of the QP (e.g. of the electron and its screening cloud). Here, $\tilde{v}_{xc}$ is the approximate exchange-correlation potential operator of KS-DFT. The method described by this final step is called perturbative $G_0W_0$, and it remains explicitly dependent on the choice of approximate functional in KS-DFT.

In practice, in the KS wave-function basis, the non-interacting single-particle Green function takes the form in the frequency domain, for $t' > t$ [27],

$$G_0(r, r', \omega) = 2i \sum_{i, k} \psi_i(r) \psi_i^*(r') \left( \frac{f_{ik}}{\omega - \epsilon_{ik} + i0} + \frac{1 - f_{ik}}{\omega - \epsilon_{ik} - i0} \right) \quad (19)$$

and, once $G_0$ is obtained, $W_0$ is calculated by using Dyson’s equation starting from the bare Coulomb interaction with

$$W_0 = \varepsilon^{-1}v,$$ \quad (20)

where $W^0$ is a function of $\omega$ through the inverse dielectric function $\varepsilon^{-1}$. In reciprocal space, $W_0$ is expressed by equations (5) and (9) as the direct product

$$W_{G,G'}(q, \omega) = \varepsilon^{-1}_{G,G'}(q, \omega) \frac{4\pi}{|q + G + G'|} \quad (21)$$

Computationally, the inversion of the dielectric function, which is a large matrix with frequency-dependent complex entities, is troublesome. Hence, the frequency-dependent complex entities are approximated by Lorentzian peaks within the plasmon-pole approximation (PPA) [85, 86]. The idea behind the PPA is to replace the single-particle transitions marking the various levels of theory studied against experimental spectra. The work-flow for simulations of spectra with FGR, RPA and Yambo color codes are assigned to each software with QE as orange, Yambo as pink, and in-house code as gray.

Figure 1. The work-flow followed here to calculate the optical spectra of $\text{Au}_{x}\text{Ag}_{y}\text{Cu}_{1-x-y}$ using Quantum ESPRESSO (QE) and Yambo. Color codes are assigned to each software with QE as orange, Yambo as pink, and in-house code as gray.

generated $4 \times 4 \times 4$ uniform Monkhorst–Pack Brillouin zone sampling, without imposing any crystal symmetry. For band-structure calculations, we moved down to a plane-wave cutoff energy of $E_{\text{cut}} = 25 \text{ Ha}$, which is sufficient to attain a total-energy tolerance of $\Delta E_{\text{tot}} \leq 0.001 \text{ Ha per atom}$, but up to a uniform Brillouin zone sampling of $16 \times 16 \times 16$ at the NSCF level, which was necessary to converge the expectation value of the exchange self-energy. Experimental spectra have large inter-band smearing $\Gamma$ values due to finite temperature effects and impurities in practice [31, 92, 93]. Hence, a Lorentzian smearing parameter of full-width $0.2 \text{ eV}$ was adopted for spectral simulation with the Yambo code [94]. Final simulations with a common set of parameters were performed on Au, Ag, and Cu for the purposes of benchmarking the various levels of theory studied against experimental spectra. The work-flow for simulations of spectra with FGR, RPA and $G_0W_0 + \text{RPA}$ is illustrated in figure 1.

3. Computational details

Geometry optimization, self-consistent field (SCF) and non-self-consistent field (NSCF) simulations were performed using the Quantum ESPRESSO software [87, 88]. For this, norm-conserving PBE pseudo-potentials were produced using the pseudo-potential generator OPIUM [89]. The initial crystallographic information for bulk Au, Ag, and Cu in their face-centred cubic structures were adopted from x-ray diffraction data at 1072 K [90], for consistency with choice of smearing parameter for the Marzari–Vanderbilt cold smearing [91], namely $0.1 \text{ eV}$. Full geometry relaxations were then performed with variable cell parameters at over-converted plane-wave cutoff energies ($E_{\text{cut}} = 75 \text{ Ha}$) with automatically

4. Work-flow optimization and benchmarking on pure metals: Au, Ag, and Cu

For noble metals, we have found that even a converged inaccurate semi-local KS-DFT description of the relevant QP bands requires demanding run-time parameters and accurate pseudopotentials. Therefore, when larger crystallographic unit cells are of interest such as for the alloys central to this work, even perturbative $G_0W_0$ becomes computationally impractical, and we cannot routinely go very far beyond KS-DFT.
in terms of computational overhead. Hence, here, we have pursued an intermediate, compromise approach in which non-local QP screening effects are incorporated approximately, in a scalable manner which incurs a minimum additional computational cost that is insignificant compared to the final RPA calculation for the spectrum.

In principle, $G_0W_0 +$ RPA spectra require a full QP band-structure as a starting point. To obtain the QP band-structure, we would need to evaluate QP energies for each point in the Brillouin zone, for every band. For a given band and point in the Brillouin zone $(i, k)$, such an operation consists of summing throughout the Brillouin zone and over bands to determine $G_0$, as well as $W_0$ through the inverse dynamic dielectric function for the self-energy operator in equation (18). Such a task is highly demanding both in terms of CPU hours as well as RAM. This operation needs to load all information about KS wave-functions in each processor unit, when using Yambo. Since our eventual goal here is to construct optical spectra rather than QP bands, an averaged stretching of the underlying KS band-structure via stretching operators close to the Fermi level is sufficient, as well as more feasible for the spectral range of interest. The idea of stretching operators is to approximate QP energies as linears-functions of the KS energies, and for metals in particular we simply have

$$\epsilon_{QP}^c = s_c \epsilon_c, \quad \text{and} \quad \epsilon_{QP}^v = s_v \epsilon_v,$$

(23)

where $s_v$ and $s_c$ are separate stretching factors for the valence and conduction bands, respectively. Such an approach introduces averaged corrections to the valence and conduction bands around Fermi level for the missing non-local electronic exchange-correlation effects, whilst keeping the Fermi level fixed. The stretching operators were determined by linear regression on $\epsilon_i$ versus $\epsilon_{QP}^i$. For pure metals, QP energies were calculated for six valence bands and six conduction bands at 10 points at and around Γ, and the stretching operators were determined by linear fitting as shown in figure 2 with the values listed in table 1. In figure 2, two branches are observed in the valence manifolds. These distinctive branches are due to different non-local exchange contributions to $s$ and $d$-bands, but nonetheless a single stretching factor proved to be adequate.

The stretching operators modify the KS band-structure as shown in figure 3. The Fermi–Dirac distribution for the chosen electronic temperature was used to interpolate between the distinct stretching parameters for the valence and conduction bands. KS-DFT tends to excessively flatten the fully filled $d$-bands due to a deficiency of attractive non-local exchange. In a sense, the stretching operator approximately corrects the dispersions of the bands, particularly for the occupied $d$-bands but also for the half-occupied $s$-band, which is made less dispersive. In figure 3(c) for Cu, the bands close to the Fermi level are more narrowly packed and flattened compared to those of Ag and Au cases, reflecting the fact that the error in the KS-DFT treatment, and hence $\Delta \epsilon_c$, is the largest amongst the three. The inverse behavior is seen, however, for the conduction stretching operators of pure metals, which is due to correlation effects only, as Ag has the largest stretching factor in the conduction manifold, albeit that the differences between the metals are less pronounced here.

### 4.1. Drude parameters for pure metals

Before constructing optical spectra, the Drude parameters are needed for the intra-band part of the dielectric function in equation (15). Our first step is to calculate the Drude plasmon energies using equation (13). For this purpose, the energies of bands crossing the Fermi level at each k-point were extracted from the output of NSCF calculations and interpolated on a fine grid in the Brillouin zone (601 points in each reciprocal-space direction), and the Fermi surface was located on this grid with a $\pm 0.01$ eV tolerance for each system. Then, the square of the Fermi velocities, averaged over the Fermi surface, were calculated by means of equation (12). The calculated Fermi velocities for pure Au, Ag, and Cu are listed in table 2 along with results of [95], which uses a similar procedure with an extremely dense Brillouin zone sampling as $200 \times 200 \times 200$ rather than interpolating, as we have. Furthermore, the average Fermi velocity magnitudes for QP band-structures were approximated by applying the geometric averages (more appropriate to simulate intra-band response

|       | $s_v$   | $s_c$  |
|-------|---------|--------|
| Au    | 1.419797| 0.825253|
| Ag    | 1.376302| 0.846172|
| Cu    | 1.735804| 0.809883|

Table 1. Calculated values for stretching operators used to stretch KS band-structures in order to imitate perturbative $G_0W_0$ QP band-structures for pure Au, Ag, and Cu.

Figure 2. Determination of the stretching operators for Au, Ag, and Cu by means linear fitting to KS-DFT versus QP eigen-energies using 10 points around the Γ point for six valence (blue points) and six conduction (red points) bands. The Fermi levels are shifted to 0 eV in each case. (a) Au, (b) Ag, (c) Cu.
than the arithmetic mean) of the valence and conduction stretching operators, specifically using the formula

$$v_{G0W0}(E_F) = \sqrt{s_{v_{KS}}(E_F)}.$$  

(24)

Our averaged KS-DFT Fermi velocities slightly underestimate those of [95], as shown in the third column of table 2, and the origin of this discrepancy is not evident. Considering the much smaller computational cost of our interpolation scheme, our values are very reasonable estimates of the Drude plasmon energies. Lastly, the DOS based on the KS band-structure and QP band-structure were extracted by applying a 0.1 eV Lorentzian broadening using a post-processing tool of Yambo. Using equation (13), the Drude plasmon energies were estimated for the KS band-structures and QP band-structures with their respective DOS at the Fermi level.

The next step is to approximate the inverse life-time of the Drude plasmon, as well as the electric permittivity in the infinite-frequency limit, using our semi-empirical approach illustrated in figure 4. Scaling factors for the inverse life-times $\tau_\text{p}$ in equation (14) were determined by fitting the imaginary part of the dielectric function to the experimental curves in [96], and then $\varepsilon_\infty$ values were determined by fitting the real part of the dielectric function with sets of $\{\omega_\text{p}, \tau_\text{p}\}$ to the same experimental curves for Au, Ag, and Cu. The resulting values for FGR, RPA and $G_0W_0 + \text{RPA}$ are summarized in the supporting information (SI) (stacks.iop.org/JPhysCM/31/315901/mmedia).

In experimental studies, the Drude parameters are commonly determined by least-squares fitting of the Drude–Lorentz model in equation (15) to measurements in the IR spectral range. Such measurements are highly sensitive to experimental details, and the resulting literature for the Drude parameters is not in good consensus as shown figure 5. This figure shows that, despite the relative simplicity of the approaches adopted in this work, our Drude parameters are comparable with experimental predictions (particularly those of Ordal [32]).

4.2. Optical spectra of pure metals

The spectra of our elemental metals were obtained by applying FGR and RPA to the approximate KS-DFT band-structures, and RPA upon our approximate QP band-structures. The real and imaginary part of the total dielectric function are shown for pure metals in figures 6-8, along with the experimental spectra from the detailed work by Babar and Weaver in [96]. Also, the electron energy-loss spectrum (EELS) [23–25, 97–100] is shown, as calculated using the relation [55]

$$\text{EELS}(\omega) = -\text{Im} \left[ \varepsilon^{-1}(\omega) \right].$$  

(25)

For all three systems, both FGR and RPA predict the lowest band-to-band absorptions to be at energies $\sim$0.5–1.5 eV lower than those of the experimental absorption spectra. Furthermore, for higher energies, both approaches produce strong absorption peaks that contradict experiments. On the other hand, $G_0W_0 + \text{RPA}$ locates the low-lying peaks at $\sim$4–5 eV in Au, at $\sim$4–5 eV in Ag, and at $\sim$2–3 eV in Cu more accurately, and does well for the overall curve trend, with respect to the experimental absorption spectra. All three approaches reproduce the behavior of $\varepsilon_1^{Cu}$ and $\varepsilon_1^{Au}$ successfully (we use...
subscripts 1 for the real part and 2 for the imaginary part), and particularly so for $E_{\text{Ag}}^{1}\text{Re}$. Such improvements, along with the very substantial improvement in $E_{\text{Ag}}^{2}\text{Im}$ given by $\text{G}_0\text{W}_0 + \text{RPA}$, lead us to locate the first plasmonic peaks in all systems quite accurately in EELS, where FGR and RPA miss the salient features completely (see figures 6–8). As one can observe, the improvements provided by $\text{G}_0\text{W}_0 + \text{RPA}$ become less effective at higher energies, although some improvements are still achieved with respect to FGR and RPA. This depletion of performance at higher energies is to be expected, as the QP band-structures were approximated using an averaged stretching factor determined using only bands close to the Fermi level. Hence, by construction, our streamlined approach is more effective for transitions between bands close to the Fermi level, which constitute the lower part of the spectra, which are always those relevant to practical plasmonic applications.

5. Spectra of Au$_x$Ag$_y$Cu$_{1-x-y}$ alloys

Initial geometries for selected ordered alloys with compositions in multiples of 12.5% were constructed by using supercells of pure metals and substituting the desired number of atoms of other species to achieve primitive unit cells for each stoichiometric ratio. These geometries were optimised at the DFT level. Sample crystal structures for each stoichiometric ratio are shown in the SI. Alloys with the stoichiometric ratios of \{2 : 1 : 1\} and \{6 : 1 : 1\} have 3 and 4 possible phases, respectively, and in total 39 structures were studied through the standardized workflow shown in figure 1. For systems with multiple primitive phases, we calculated our final spectra by means of a thermodynamic averaging process using the Boltzmann factor defined as

$$p_i = \exp \left( \frac{E_0 - E_i}{k_B T} \right) \left( \sum_j \exp \left( \frac{E_0 - E_j}{k_B T} \right) \right)^{-1},$$

(26)

where $j$ is the phase index, and $E_0$ and $E_i$, respectively, are the lowest ground-state energy among all phases and the ground-state energy of the $i$th phase. The final spectra of \{2 : 1 : 1\} and \{6 : 1 : 1\} are thus linear combinations of the spectra of their respective phases, with corresponding weighting constants.

5.1. Stretching operators for alloys

Stretching operators were generated using the converged geometry of each ordered alloy cell, on each of which perturbative $\text{G}_0\text{W}_0$ simulations were performed. Specifically, band
stretching operators were calculated for all valence bands and an equal number of conduction bands at 10 points at and around the $\Gamma$ point for each crystal structure of each stoichiometric ratio. The QP renormalization factors expressed in equation (18) show a steady decreasing trend with increasing Cu ratio, both in the valence and the conduction manifolds, as shown in figures 9(a) and (b). The valence stretching operator in figure 9(c) grows significantly larger for increasing Cu ratios. Pure Cu has the largest reciprocal unit cell, where the $d$-bands are spuriously flattened and narrowly packed the most by KS-DFT, as seen in figure 3(c). Hence, a larger QP stretching of the valence manifold is expected to result from an increasing Cu concentration. The conduction stretching operators show inverse trends, providing a slightly smaller stretching at the conduction manifold for increasing Cu concentrations. For simplicity, we will only discuss our approximated QP results in combination with the RPA, labelled $G_0W_0 + \text{RPA}$, from here.

5.2. Drude parameters for alloys

Using a similar procedure to that used for pure metals, the Fermi velocities and DOS at the Fermi level were computed for each alloy system. The stoichiometric dependence of the averaged QP Fermi velocities and DOS at the Fermi level are shown in figure 10. The Fermi velocities show some symmetric features, while they are lower in the case of predominantly Cu-based stoichiometric ratios. Conversely, the DOS becomes large for increasing Cu ratios as the volumes of the systems contract with increasing Cu concentrations.

Competing trends in the Fermi velocities in figure 10(a) and DOS in figure 10(b) compensate for each other, and lead to a symmetric trend in the interpolated contour-plot of the Drude plasmon energies in figure 11(a). The inverse life-times in figure 11(b) were evaluated by using equation (14), where \(\{c_\eta\}\) coefficients were produced via arithmetic averaging of the inverse-life times of pure metals with respect to the stoichiometric ratios, explicitly as

\[
c_\eta^{\text{Au}_x\text{Ag}_y\text{Cu}_{1-x-y}} = xc_\eta^{\text{Au}} + yc_\eta^{\text{Ag}} + (1 - x - y)c_\eta^{\text{Cu}}.
\]

As the inverse life-times are proportional to the Fermi velocities and the DOS at the Fermi level, they show similar symmetries to the Drude plasmon energies. The electric permittivities in the infinite-frequency limit are simply approximated by the arithmetic averaging of their values for pure metals, with respect to the stoichiometric ratios; hence, the trend is a flat plane by construction.

6. Plasmonic performance of Au$_x$Ag$_y$Cu$_{1-x-y}$ alloys

Even though plasmon generation cross-sections and plasmon lifetimes are highly dependent on the size and geometry of nano-materials, some fundamental formulae for bulk crystals can be used to assess the potential of alloy for plasmonic applications. The primary requirement for a strong plasmonic response is the presence of a high-density of free electrons such as in alkali and noble metals, where the latter in particular dominate plasmonic applications [101]. Moreover, plasmon quality is predominantly limited by loss [102, 103], which can occur through various phenomena such as radiative damping, surface scattering, thermal loss [104], and imperfections in materials such as surface roughness [105] and grain boundaries [106]. Approximate methods have been suggested in which the individual contributions of these conditions are combined, in order to determine the overall plasmon quality [104]. As we work on perfectly ordered bulk systems here, and their thermodynamic averages, our aim is to determine some universal preliminary optical and plasmonic figures of merit, independent of grain size and structural properties, in order to estimate stoichiometric plasmon qualities starting from the bulk macroscopic dielectric functions. In bulk
crystals one predominantly speak of bulk plasmons, which result from a combination of both intra-band and inter-band transitions [101]. The bulk plasmon energy $\Omega_p$ is expected to lie at a lower energy than the bare plasmon energy $\omega_p$ due to screening by inter-band transitions. In addition to bulk plasmons, there typically surface plasmons in realistic systems. EELS provides a signature for bulk plasmons, and it has been suggested that the associated loss function requires a slight modification due to the presence of $d$-bands to capture surface plasmons, in the form of [107]

$$-\Im \left[ \frac{1}{1 + \varepsilon} \right].$$

(28)

This implies the condition $\varepsilon_1 \approx -1$ and $\varepsilon_2 \approx 0$ for significant surface plasmons. Furthermore, particular quality measures (the plasmon lifetime is proportional to this, and inversely proportional to frequency) have been proposed for more intricate plasmon types, such as the localized surface-plasmon (LSP) [108, 109], and surface-plasmon polaritons (SPP) [110], which are crucial to many plasmonic applications [111] such as optical circuits [112] and switching [113, 114]. In [103], various measures have been investigated using the relation between $\varepsilon_1$ and $\varepsilon_2$ for describing LSPs and SPPs in the low-loss and electrostatic limits. $\varepsilon_1$ essentially provides a condition that checks for the presence of free electrons, while
is related to loss due to the decay of plasmons to particle-hole pairs. Blaber et al \[101\] have suggested some universal quality factors for LSP and SSP in metallic systems, of the form

\[
Q_{LSP}(\omega) = -\frac{E_1}{E_2}, \quad \text{and} \quad Q_{SPP}(\omega) = \frac{E_1^2}{E_2^2}.
\]

These quality factors can provide insights into the general capacity of metals to produce the surface plasmons relevant to different technological applications.

6.1. Plasmonic response at common solid-state laser wavelengths

Three common, representative solid-state laser wavelengths were chosen to numerically investigate our predicted plasmonic efficiencies of \(\text{Au}_{x}\text{Ag}_{y}\text{Cu}_{1-x-y}\). The first wavelength is that of common red lasers, at 650 nm (1.91 eV), which are produced using InGaAIP \[115\] and used in a wide range of applications. An interesting example of applied plasmonics at this wavelength is the imaging and sensing of biological systems using noble-metal heterostructures, taking advantage of the high sensitivity of EELS to light elements at the nanoscale \[3, 116, 117\].

In figure 12, the EELS and surface-EELS of \(\text{Au}_{x}\text{Ag}_{y}\text{Cu}_{1-x-y}\) alloys show quite weak amplitudes on the order of \(10^{-2} - 10^{-3}\) (unitless), implying inefficient plasmon generation by incident electron throughout the ternary stoichiometric ratio domain. This is because, as the wavelength 650 nm typically lies somewhere between the Drude tail and inter-band transition edges of \(E_2\), the \(E_2\) tends to be very close to 0, while \(E_1\) is very far from 0. Nonetheless, clearly the stoichiometries \(\text{Au}_{6}\text{AgCu}\) and \(\text{AuAgCu}_{6}\) seem to offer advantages over \(\text{Au}\) in this regard, and of course electron energy loss is not the only way to excite bulk and surface plasmons.

Thus good bulk and surface plasmon life-times are predicted to be available (see figures 12(c) and (d), respectively) far in excess of those of bulk \(\text{Au}\) for many stoichiometries, although here we must emphasize again that grain size and disorder effects are neglected here. However, for the most promising systems for plasmon generation, such as \(\text{Au}_{6}\text{AgCu}\) and \(\text{AuAgCu}_{6}\), which exhibit relatively larger EELS and surface-EELS, LSP and SPP qualities drop substantially. The approximate mirror symmetry of all ternary plots here about the line joining \(\text{Ag}\) to \(\text{AuCu}\) is serendipitous, breaking down as we move to shorter wavelengths.

Facile plasmon generation by incident electron and quick plasmon decay appear to both occur at 650 nm, and it seems plausible that that his may be a general trend. It is worth considering carefully, however, whether an approximate inverse relationship between loss spectrum and quality factor is strictly necessitated in theory or, on the contrary, whether the very favourable situation of readily excited but nonetheless long-lived plasmons may arise in theory. The relationship between the figures of merit for plasmon generation and decay...
can be examined through their definitions in terms of the macroscopic dielectric function $\varepsilon$. To illustrate this, we have plotted the bulk and surface EELS, $Q_{\text{LSP}}$, and $Q_{\text{SPP}}$ as functions of the $\varepsilon_1$ and $\varepsilon_2$ in figure 13. When making the connection to band-structure engineering and alloy design, we must recall that $\varepsilon_1$ and $\varepsilon_2$ inter-depend through the Kramer–Kronig relation [118, 119]. Nonetheless, $\varepsilon_1$ and $\varepsilon_2$ are presented here as independent variables for the sake of illustration.

On one hand, in figure 13(a), we see that the pre-condition that low $\varepsilon_1$ and $\varepsilon_2$ provide for the presence of free electrons with little decay, respectively, gives rise to a small region centered at origin where a very large EELS signal is predicted. The EELS signal falls off with the inverse-square of $\varepsilon_1$ but, more slowly, with the inverse of $\varepsilon_2$. The surface-EELS (figure 13(b)) shows an identical behavior, except for a simple shift by $-1$ in the $\varepsilon_1$ axis, as imposed by definition in equation (28). On the other hand, the quality factors for LSPs and SPPs, which are proportional to the lifetimes of these plasmons, diverge inversely with $\varepsilon_2$ as it approaches zero, as shown in figures 13(c) and (d), respectively, as an increasing $\varepsilon_2$ represents a larger rate of loss. Simultaneously, large values of $\varepsilon_1$ are more favourable for plasmon lifetimes. In both cases, we can say that strong EELS and long plasmon lifetimes are competing requirements, to an extent.

Turning next to the product of EELS with $Q_{\text{LSP}}$, which is a relative indicator of the LSP population for a given EELS beam intensity, presented in figure 13(e), we observe a somewhat similar trend to that of the EELS alone, insofar as that low values of both $\varepsilon_1$ and $\varepsilon_2$ are optimal. Their relative importance are reversed however, with respect to EELS, in that EELS $\times Q_{\text{LSP}}$ falls off with the inverse of $\varepsilon_1$ but, more quickly, with the inverse-square of $\varepsilon_2$. Finally, we find that the greatest tolerance for simultaneous facile generation and long lifetimes is offered by SPPs, as we plot EELS $\times Q_{\text{SPP}}$ in figure 13(f). For this quantity, we find that, interestingly, the same value is given if $\varepsilon_1$ and $\varepsilon_2$ are varied in constant proportion to each other. The regime where $\varepsilon_2/\varepsilon_1$ approaches zero is optimal, where in fact EELS $\times Q_{\text{SPP}}$ tends to unity. Our finding that EELS $\times Q_{\text{SPP}}$ remains high over a larger area in the space of $\varepsilon_1$ and $\varepsilon_2$ pairs is promising for the future computational optimization of alloy compositions for harboring SPPs at targeted wavelengths. We direct the reader’s attention to section 5 of our supporting information, where we plot of the stoichiometry dependence of EELS $\times Q_{\text{LSP}}$ and EELS $\times Q_{\text{SPP}}$. At 650 nm, in particular, we find that the SPP population indicator EELS $\times Q_{\text{SPP}}$ remains close to its theoretical maximum value of unity for almost all of the alloy compositions studied here.

The second frequency considered is that of the common laser used in Blu-ray devices, at 405 nm (3.06 eV), generally produced using InGaN [120] for efficient optical recording in conjunction with noble metal nano-clusters [121]. Here, to a greater extent than what we observed at 650 nm, we find that alloys of the stoichiometric form $X_2Y$ and $X_3YZ$ seem to have a particular propensity for plasmon generation by electron energy loss, more so than their closest elemental metals, but that this comes at the expense of shorter lifetimes. However, once again, the large EELS signal overcomes the
fast decrement in the $Q_{\text{LSP}}$ in their product, particularly for AuAg$_6$Cu (see SI). On one hand, the optimal Au to Cu ratio for SPP lifetime at all wavelengths considered is Au$_3$Cu. On the other hand, the optimal Au-heavy Au to Cu ratio for surface EELS at all wavelengths considered is instead at Au$_7$Cu, with a severe trade-off between plasmon generation rate and lifetime. Elemental Ag is predicted to exhibit a particularly long-lived LSP at 405 nm, albeit based on the bulk figure of merit.

Lastly, the deep-UV laser at 290 nm (4.28 eV) commonly produced in Ce:LiSAF/Ce:LiCAF media with Nd:YAG lasers [122] is presented in order to show what happens when we move in to the inter-band regime. Broadly, we find that all ternary plot contrast drop, indicating that plasmonic performance becomes more forgiving of deviations in stoichiometric ratio, such as possibly by partial phase-segregation in practice, in the UV regime. In figure 15, we see that the bulk and surface EELS profiles show a considerable strength in Ag, Au, Au$_6$AgCu, and Au$_5$Ag$_2$Cu, together with a newly arising strong intensity in Au$_7$Ag$_2$Cu. The addition of Cu appears to be detrimental to EELS cross section, in contrast to what we have seen at the longer wavelengths. The approximate inverse behavior of EELS cross section and plasmon lifetime, this drop in quality factor is not much compensated for by the increase in driving frequency.

The stoichiometry-dependent plasmonic responses of Au$_x$Ag$_y$Cu$_{1-x-y}$ show complex behavior, in general. This behavior clearly cannot be simply interpolated based on the stoichiometric ratios alone, despite the ostensibly rather similar electronic structures of the constituent elemental metals. Consistent first-principles simulations are thus potentially very helpful to the design of alloys for optical and plasmonic applications, and we believe that they are particularly promising with the added benefit of well-controlled approximations ensuring reasonable computational costs, as we have sought to offer here.

7. Conclusion

We have demonstrated that the RPA built upon a semi-local KS-DFT band-structure fails to acceptably locate peaks in the absorption spectra of Au, Ag, and Cu, with respect to experimental observation. RPA starting even from a very approximate genuine QP band-structure (i.e. one including electron-excitation and hole-excitation coupling, however perturbatively) performs significantly better in this regard, and sufficiently for it to be used in a predictive sense. Such approximate QP band-structures can be achieved with little additional computational cost by means of pre-calculated average stretching to the electron and hole bands separately. The necessary stretching factors can be obtained using the perturbative $G_0W_0$ approximation on a small set of grid points in the Brillouin zone, and of energies around the Fermi level.
Furthermore, we have shown how first-principles ingredients such as the Fermi density and Fermi velocity, may be used, together with a minimal set of experimentally-derived factors for elemental metals, to interpolate the Drude plasmon frequency and lifetime across stoichiometric ratios, assuming that bulk crystal like scattering conditions hold. Bulk dielectric functions may be used to determine indicative optical and plasmonic figures of merit for excitations such as LSPs and SPPs at technologically-relevant wavelengths. Indeed, we find the ability to observe how these evolve across the stoichiometric domain very evocative from a materials design and discovery perspective.

Our presented methodological work-flow may be extended in diverse ways depending on the targeted functionality and metal type, for example to include electronic and vibrational finite-temperature effects; to encode information concerning thermodynamic stability such as (temperature-dependent) order-disorder transitions; to study the effects of mechanical stress and defect concentrations on predicted optical spectra, as well as the effect of dopants that might be used to deliberately shift the Fermi level and possibly enhance plasmonic performance. We anticipate that approximated many-body approximations for the electronic problem will see increasing use within emerging high-throughput materials design and discovery frameworks over the coming years, and that both research areas can come together to find new ways to gainfully compliment experiment.

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