Plasmon-enhanced technologies enabled by metal nanoparticles (NPs) provide promising avenues for, e.g., harvesting and converting sunlight to chemical energy and driving photochemical reactions. The underlying processes rely on the decay of plasmonic excitations and the subsequent generation of non-equilibrium carrier distributions. The latter are often collectively referred to as hot carriers, even though the actual distributions vary substantially with time after excitation.

Hot carriers (HCs) generated by plasmon decay can in principle be transferred to a chemically attached acceptor such as a semiconductor or a molecule, a process that is potentially useful for technologies such as photovoltaics, photo-detection, photon up-conversion, and photocatalysis and that is potentially relevant for NP growth processes.

There are, however, substantial gaps in our understanding that limit the exploitation of plasmon-generated hot carriers in applications. To resolve these questions, a purely experimental approach is limited both due to time constraints and the difficulty associated with disentangling different contributions. In the context of photocatalysis, in particular, it is paramount to discern processes at the atomic scale. Here, theoretical and computational approaches can provide highly valuable insight as they enable us to scrutinize the relevant microscopic processes on the electronic and atomic scale.

Earlier theoretical studies on plasmonic HC generation have mostly focused on flat metal surfaces or jellium NPs neglecting the underlying atomic structure. While atomic-scale effects in nanoplasmonics has been increasingly addressed in recent years, an atomic scale description of plasmonic HC generation is only emerging. In this work, we directly analyze the effect of local structure on HCs generation and demonstrate that the distribution of HCs after plasmon decay is in fact very sensitive to the atomic scale details. We quantitatively resolve the effect of surface orientation, step edges, corner sites, and ultimately NP shape and size on HC distribution. To this end, we develop a fully atomistic, parameter-free, and generally applicable description of plasmonic HC generation based on Kohn–Sham (KS)-density-functional theory (DFT) and time-dependent density-functional theory (TDDFT).

Results

Real-time dynamics of localized surface plasmons. We start with a comprehensive description of plasmon formation and subsequent dephasing. For illustration, we consider an icosahedral Ag$_{550}$ silver NP with a clear plasmon resonance (Fig. 1a). The ground-state electronic structure of the NP is with DFT calculated using the GLLB-SC exchange-correlation (XC) potential for an improved d-band description and the response is calculated with TDDFT using the random-phase approximation (RPA) or the adiabatic GLLB-SC (see Methods for details).

We consider the real-time dynamics of the electrons under a monochromatic ultrafast Gaussian light pulse $E(t + t_0) = E_0 \cos(\omega_0 t) \exp(-t^2/\tau_0^2)$, where the pulse frequency $\omega_0 = 3.6$ eV is tuned to the plasmon resonance, the pulse duration is determined by $\tau_0 = 3$ fs, and the pulse is centered at $t_0 = 10$ fs (Fig. 1b). The pulse strength is weak, $E_0 = 51 \mu$V/Å, putting the response in linear response regime. In frequency space, the pulse is wide enough to cover the whole plasmon resonance (Fig. 1a).

We use the dipole approximation, where the light pulse creates a time-dependent external potential $v_{\text{pulse}}(t) = zE(t)$ that causes the time evolution of the KS states $|\psi_n(t)\rangle$ and excitation of the localized surface plasmon resonance (LSPR). The light pulse induces a strong dipole-moment response [Fig. 1c(1–3)]. The corresponding electron density oscillations [Fig. 1d(1–3)] are composed of a surface-to-surface component associated with delocalized valence electrons near the Fermi energy and...
atom-localized contributions that correspond to screening due to virtual excitations from the d-band. As time proceeds to \( t \approx 17 \text{ fs} \), the excited electrons start to lose their collective plasmonic motion via a dephasing process commonly referred to as Landau damping, which takes places due to the presence of multiple excitation eigenstates forming the broadened plasmon peak in the photoabsorption spectrum. As the plasmon dephases, the dipole moment decays [Fig. 1c(4–5)] corresponding to vanishing surface-to-surface density oscillation [Fig. 1d(4–5)].

**Time-dependent energy contributions.** Since the pulse is tuned to the LSPR, the electronic system absorbs energy from the incident light and remains in an excited state after the pulse has vanished. To analyze the distribution of this energy, consider the total time-dependent energy of the system given by

\[
E_{\text{tot}}(t) = E_{\text{tot}}^{(0)} + \Delta E(t) + E_{\text{pulse}}(t),
\]

where \( E_{\text{tot}}^{(0)} \) is the ground-state energy, \( \Delta E(t) \) is the time-dependent energy stored in the excited state (Fig. 1e, black line), and \( E_{\text{pulse}}(t) = -\mu(t)E(t) \) is the potential energy of the system under the external electric field.

The incident light pulse pumps energy into the system, i.e., it does work on the system as \( \Delta E(t) = \delta\mu(t)\mathcal{E}(t) \), where dots indicate time derivatives and \( \delta\mu(t) = \mu(t) - \mu^{(0)} \) is the induced dipole moment. Thus, the total accumulated electronic energy can be written as

\[
\Delta E(t) = \int_0^t \delta\mu(\tau)\mathcal{E}(\tau)d\tau.
\]

The electronic energy increases through absorption in a step-wise manner following the pulse intensity (Fig. 1e, \( t \approx 5 \ldots 15 \text{ fs} \)). After the pulse has ended (\( t \gtrsim 15 \text{ fs} \)), the absorbed energy remains in the system and the total energy has attained a new constant value given by the photoabsorption cross section [Fig. 1a; Eq. (11) in Methods].

While the total energy remains constant, the electronic energy does not stay equally distributed among the electron-hole transitions \( i \rightarrow a \) excited by the light pulse. To quantify this effect, we consider a decomposition in electron-hole transitions that is based on the linear response of the KS density matrix, \( \delta\rho_{ia}(t) \), expressed in the basis of the eigenstates \( (\epsilon_i, \psi_i^{(0)}) \) of the ground-state Hamiltonian. The electron-hole decomposition of energy is (see Supplementary Note 1 for derivation)

\[
\Delta E(t) = \sum_{ia} \omega_{ia}P_{ia}(t) + E_{ia}^C(t),
\]

where the sum is restricted by ground-state occupation numbers \( f_n \) so that the indices \( i \) and \( a \) correspond to the created hole and electron states, respectively. Here, \( \omega_{ia} = \epsilon_a - \epsilon_i \) is the transition energy (the KS eigenvalue difference), \( P_{ia}(t) \) is the transition probability defined as

\[
P_{ia}(t) = \left| \frac{\delta\rho_{ia}(t)}{\sqrt{f_i - f_a}} \right|^2,
\]

and \( E_{ia}^C(t) \) is the Coulomb energy given by the Hartree–exchange-correlation kernel (defined in Supplementary Note 1).

Plasmon formation and dephasing are scrutinized by considering the energy stored in the electronic system in
FIG. 2. Electron-hole transition contributions to plasmon formation and decay. (a) Electron-hole contributions to the photoabsorption at the resonance energy visualized as a transition contribution map (TCM). Density of states (DOS) is also shown along the energy axes. (b) Electron-hole contributions to the time-dependent electronic energy visualized as TCM on a logarithmic color scale. The solid diagonal line corresponds to the transition energies matching with the pulse frequency \( \omega_0 \) and the dotted diagonal lines are drawn at \( \omega_0 \pm 2\sigma \) to indicate the pulse width \( \sigma = \sqrt{2/\tau_0} \), defining the boundaries for resonant and non-resonant transitions (Fig. 1e). (c) Occupation probabilities of hole and electron states. Solid blue and red lines denote state occupations from resonant transitions, and dashed lines denote occupations from all transitions (resonant and non-resonant). The figure columns (1–5) show panels (b) and (c) for the time instances labeled in Fig. 1. The color scale and axis limits are the same in all the columns.

After plasmon dephasing, the energy remains almost exclusively stored in the resonant transitions [Fig. 2b(5)], which constitute the plasmon-generated hot carriers. At larger time scales, the electronic system would dissipate the absorbed energy to the environment via radiation, atomic motion, or other processes, but such decay pathways are not included within the description used here, and there is no significant dynamics at time scales beyond \( t \gtrsim 30 \) fs due to the strong dephasing in Ag$_{5561}$ (Supplementary Fig. 3). However, the dynamics can be very different in small clusters with discrete excitation spectrum. For example, in Ag$_{55}$ cluster individual electron-hole transitions couple strongly to plasmon, which is often referred to as plasmon fragmentation. Consequently, the time-domain response can exhibit occasional energy transfer back from the resonant transitions to the plasmon [3,45] (Supplementary Fig. 4) due to the incomplete Landau damping enabling the re-emergence of coherence between plasmonic transitions.

Since the coupling of transitions via Coulomb interaction is recognized as an essential characteristic of plasmonic excitations, it is instructive to consider the Coulomb energy \( E_C(t) = \sum_{ia} E_C^{ia}(t) \). This energy exhibits strong oscillations (Fig. 1e, grey line) analogous to the dipole moment (Fig. 1c) as only the electron density oscillation contributes to the Coulomb energy. At the maxima of the surface-to-surface density oscillation [time instances (1) and (3) in Figs. 1d–e], the Coulomb contribution is a significant part of the plasmon energy, but at the minima in between [e.g., time instance (2)] the Coulomb energy is vanishing as the electronic energy is stored in the electron current flowing through the particle.

Temporal evolution of HC distributions. Now that we have established the real-time picture of plasmon formation and decay, we are in the position to analyze the distributions of electrons and holes during the process. The probabilities for creating a hole in the initially occupied state \( i \) or an electron in the initially unoccupied state \( a \) are given directly by the transition probability of Eq. (5) as

\[
P^{h}_i(t) = \sum_a P_{ia}(t) \quad \text{and} \quad P^{e}_a(t) = \sum_i P_{ia}(t),
\]

respectively. \( P^{h}_i \) and \( P^{e}_a \) determine exactly the diago-
nal elements of the second order response of the density matrix (Supplementary Note 1); in other words, they correspond to the increase of the occupation of the initially unoccupied state at and the decrease of the occupation of the initially occupied state at i, respectively.

The occupation probabilities given by Eq. (6) show strong oscillations during the time evolution [Fig. 2c(1–3); dashed lines]. These oscillations are explained by the oscillation of Coulomb energy. As the Coulomb energy contribution is carried only by non-resonant transitions, the occupation probabilities of the electron and hole states contributing to these non-resonant transitions oscillate analogously to the Coulomb energy. The oscillations are especially visible in the occupations of electron and hole states that form the plasmon, i.e., the states near the Fermi energy, often referred to as Drude states. These oscillations are explained by the oscillation of Coulomb energy. As the Coulomb energy contribution is carried only by non-resonant transitions, the occupation probabilities of the electron and hole states contributing to these non-resonant transitions oscillate analogously to the Coulomb energy. The oscillations are especially visible in the occupations of electron and hole states that form the plasmon, i.e., the states near the Fermi energy, often referred to as Drude states.47 The oscillatory population and depopulation of these states indicate that they would not likely be individually separable while they are a part of the plasmon as Coulomb interaction is an essential part of the excitation.48

The resonant transitions have zero Coulomb energy contribution and the occupations of the corresponding electron and hole states grow steadily as the plasmon decays [Fig. 2c; solid lines]. At the end of the dynamic evolution considered here [Fig. 2c(5)], electrons and holes are still coupled in the form of electron-hole transitions, and the distribution at t = 30 fs corresponds to the initial non-thermal HC distributions. At longer time scales (not described here) these carriers would separate and thermalize via electron–electron and electron–phonon scattering processes.5 The slight asymmetry between the hole and electron distributions is caused by a non-zero width of the pulse in frequency space (Fig. 1a).

**Energetic and spatial distributions of hot carriers: Role of structure.** We can now analyze the distribution of plasmon-generated hot carriers in space and the impact of local structure. We start by considering the series of icosahedral silver NPs Ag_{147}, Ag_{309}, and Ag_{561}, the photoabsorption properties of which we have described in detail in earlier work27,38 (see Supplementary Fig. 5 for photoabsorption spectra and densities of states). The light pulse is tuned to the plasmon resonance of the NPs and the initial HC distributions are analyzed after the plasmon has dephased, i.e., at time t = 30 fs. The HC distributions show a very pronounced dependence on NP size (Fig. 3a) and local structure (Fig. 3b–c) as discussed in the following.

As particle size increases, the HC distributions are increasingly dominated by interband d-electron transitions (hole $\sim -4$ eV $\rightarrow$ electron $\sim 0$ eV) converging toward the distributions obtained for flat surfaces.18,19 In contrast to extended systems, geometry confinement effects are significant for plasmonic HC generation in nanoscale systems.49 Due to the broken crystal symmetry in NPs, additional “intraband” transitions are available for HC generation in comparison to extended systems. This allows the population of higher-energy electron and hole states (Fig. 3a; electrons $> 0.5$ eV, holes $> -3.5$ eV). The relative contribution of these states is most pronounced in smaller NPs (Ag_{147}, Ag_{309}) but they are even non-negligible in Ag_{561}. Similar size-dependent trends are also present in silver NPs of other shapes, while the detailed relative contributions of different transitions vary (Supplementary Fig. 6).

Considering the icosahedral Ag_{561} NP, the calculated spatial probability distributions (see Methods) reveal that plasmon-generated holes and electrons are distributed spatially differently (Fig. 3b–c): Holes are localized at atomic sites throughout the particle, which is expected as the majority of holes originates from the atom-localized d-states. As a result, their energy distribution is

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**FIG. 3. HC distributions after plasmon decay.** (a) Occupation probabilities of hole and electron states in icosahedral silver NPs of 55–561 atoms. (b) Occupation probabilities at different atomic sites of Ag_{561}. All the panels use the same axis limits (normalized by the number of atoms). (c) Spatial density profiles of all induced holes and electrons and induced electrons with energy of more than 1 eV in Ag_{561}. Plots show isosurfaces corresponding to 10% and 20% of maximum value, respectively, and slices are taken through the center of the NP.
FIG. 4. **Atomic-scale distributions of hot electrons in silver NPs.** Spatial distribution of hot electrons generated on different atomic sites in icosahedral (Ih), cuboctahedral (Cub-Oh), and regularly truncated octahedral (RTO) NPs. Sites with lower coordination exhibit a higher proportion of hot electrons than core sites. A spatially uniform distribution corresponds to a normalized probability of unity. The insets show the atomic structures with the different atomic sites colored.

very similar for core and surface sites. Hot electrons, on the other hand, are more delocalized and primarily reside in the surface region. The surface contribution is even more pronounced for higher-energy hot electrons (\(>1\) eV electrons in Fig. 3c). Especially at low-coordinated edge and corner sites the probability density for hot electrons with more than 1 eV is strongly enhanced compared to sites in the core and on flat surfaces (Fig. 3b).

A more quantitative view is obtained by considering the total per-atom occupation probability of hot electrons at a particular atomic site in comparison to the total per-atom occupation probability throughout the system (Fig. 4). Hot electrons with more than 1 eV are almost three times more likely to be found in the vicinity of a corner site than on any other site in a icosahedral \(\text{Ag}_{561}\) NP on average. We emphasize that these are per-atom considerations, that is, as the 12 corner atoms constitute only around 2% of the atoms in the particle, it is expected that 6% of the electrons with more than 1 eV would be generated in the vicinity of the corner atoms. Hot electrons with more than 1 eV constitute 30 to 60% of all hot electrons depending on system (Supplementary Fig. 7). The absolute total number of HCs generated depends on the light energy that is absorbed, which is in turn determined by photoabsorption cross-section and light intensity.

Similarly to icosahedral shapes, hot electrons in the cuboctahedral and regularly truncated octahedral NPs are more likely to be generated at surface sites than in the core (Fig. 4). The preference for surface sites is even more pronounced for hot electrons with more than 1 eV. For the cuboctahedral and regularly truncated octahedral NPs the corner sites do, however, not show an as extreme proportion of hot electrons as in the icosahedral \(\text{Ag}_{561}\) particle. This further underlines the sensitivity of HC generation to atomic scale details and the exact electronic structure of the NP and site(s) in question. As a general trend, lower-coordinated sites exhibit an enhancement of hot electrons compared to higher-coordinated sites. This is observed for corner and edge sites, but one also finds that more hot electrons are generated on the lower-coordinated \{100\} surface than on the \{111\} surface. In contrast to strong spatial variation of hot electrons, plasmon-generated holes do not show strong spatial dependence (Supplementary Fig. 7).

**DISCUSSION**

For practical utilization, HCs need to be transferred to the environment. In general, HC transfer can occur indirectly, i.e. carriers are first produced in the metal and subsequently transferred to the acceptor\(^2,3,50,51\) or directly, i.e. plasmon dephasing leads directly to the injection of HCs in empty acceptor (and occupied donor) states\(^32-57\) (The direct transfer process has also been referred to as coherent charge transfer\(^53,54\) plasmon-induced interfacial charge-transfer transition when the acceptor is a semiconductor,\(^52\) and chemical interface damping in the case of adsorbed molecules\(^2,3,33,58,59\)) Both experiments\(^60-62\) and calculations\(^20,49,62,63\) indicate that HCs generated in the metal can quickly relax back to the Fermi level via electron-electron scattering, which renders the indirect pathway inefficient. The direct-transfer
process, on the other hand, can overcome the problem of fast HC relaxation and presents an opportunity to obtain more efficient plasmonic HC devices. Moreover, in principle it enables the injection of HCs in particular acceptor states, which is of special interest for applications in catalysis.

In this work, we have quantitatively analyzed the impact of local atomic structure on plasmon decay and HC generation using a predictive and material specific first-principles framework without resorting to empirical parameters. The simulations allow us to follow the real-time dynamics of localized surface plasmons during the first 50–100 fs or so after excitation, which includes plasmon formation and decay into the initial non-thermal HC distribution. The latter is immediately relevant for direct transfer processes either across interfaces and onto molecules. This HC distribution also represents the initial condition for longer-time scale dynamics, which are governed by electron-electron ($t \lesssim 100$ ps) and electron-phonon ($10$ ps $\lesssim t \lesssim 10$ ns) scattering processes and are relevant for indirect excitation transfer.

We find that in the silver NPs considered here the distribution of hot electrons is very sensitive to local structure whereas the distribution of hot holes is relatively homogeneous. These features can be traced to the electronic structure as hole and electron states exhibit localized d and delocalized s-type character, respectively. We therefore expect the present insight to be qualitatively transferable to other late transition metals, which are more likely to be present on lower coordinated sites. The details are shape dependent. For example on icosahedral NP, the proportion of hot electrons at corner and edge sites can be strongly enhanced compared to flat surface and bulk sites, whereas in cuboctahedral and regularly truncated octahedral particles, more hot electrons are generated per site on lower-coordinated {100} than on denser {111} facets.

The prevalence of hot electrons on lower-coordinated surface sites described here facilitates their utility in direct transfer processes. It is, however, crucial to also consider the hybridization of the surface electronic states with acceptor states, where the latter can originate e.g., from an adsorbed molecule or a semiconductor. To maximize the efficiency for direct excitation transfer the emitting (surface) receiving (acceptor) states should be energetically aligned and spatially overlapped. Going forward, the framework introduced here enables one to analyze and quantify these transfer processes at the atomic scale with material specificity without resorting to empirical parameters. This provides the opportunity to identify promising surface-acceptor combinations and design future experiments.

In conclusion, we have presented a comprehensive first-principles account of the real-time dynamics of plasmonic HC formation and its dephasing into incoherent HCs. In larger particles, the HC density usually decays away from the surface due to propagation of electronic modes. In smaller NPs, as demonstrated in this work, HCs are, however, well defined electronic resonances within the particle apt to assist for example in heterogeneous photocatalytic redox reactions. The present results further show that the energetic distribution of hot electrons is very sensitive to the local structure and higher energy electrons are preferentially generated at sites with low coordination. First-principles predictions of plasmonic HC generation, as presented here, can thereby open avenues for tuning and optimizing photocatalytic systems down to the atomic scale.

METHODS

Computational details. The ground-state electronic structures were calculated with KS-DFT using the GLLB-SC exchange-correlation potential. The time-domain responses were calculated with TDDFT starting from the ground state. The dynamical response was described with RPA for the data in Figs. 1–2 and in Supplementary Figs. 1–4, while all the other data was calculated with the adiabatic GLLB-SC. The two response kernels yield very similar results (Supplementary Fig. 8), but the GLLB-SC potential is not suitable for obtaining the total energies.

All the calculations are carried out with the open-source GPAW code package using localized basis sets and the real-time propagation TDDFT implementation. We used 11-electron projector augmented-wave setups for Ag, treating the remaining electrons as frozen core. We used an extended “p-valence” basis set that includes diffuse 5p functions, which are important for describing plasmon resonances. The basis set is similar to the ones used in Refs. 27 and 38.

The photoabsorption spectra were calculated using the $\delta$-kick technique yielding linear impulse response. The photoabsorption of icosahedral particles is isotropic and the electric field was aligned along the $x$ direction. The resulting HCs do not exhibit a strong variation between different sites (Fig. 3c). For the time propagation, we used a time step of 10 as and total propagation time of at least 30 fs. The spectra were broadened using Gaussian damping with $\sigma = 0.07$ eV corresponding to a full width at half-maximum of 0.16 eV. The real-time response to a pulse was calculated as a post-processing step via convolution as described below in detail. In the convolution Fourier transforms or time-domain response there is no artificial damping.

A grid spacing parameter of $h = 0.3$ Å was chosen to represent densities and potentials and the nanoparticles were surrounded by a vacuum region of at least 6 Å. The Hartree potential was evaluated with a Poisson solver using the monopole and dipole corrections for the poten-
Fermi-Dirac smearing was applied to the occupation numbers to facilitate convergence. The KS electron-hole basis included electron-hole pairs with occupation number difference $f_i - f_a \geq 10^{-3}$.

Before the response calculations, all geometries were relaxed using the BFGS optimizer in the open-source ASE package. The relaxation calculations used the Perdew-Burke-Ernzerhof (PBE) functional, double-$\zeta$ polarized (dzp) basis sets, and $h = 0.2 \, \text{Å}$.

**Pulse response from convolution.** The photoabsorption spectrum can be efficiently calculated from real-time propagation using the $\delta$-kick perturbation as in the linear-response regime all the frequencies are independent of each other. We utilize this property in the present work for calculating the linear response of the density matrix to the Gaussian pulse of Eq. (1) as a post-processing step. First, the time-propagation is carried out for perturbation $v_{\text{kick}}(t) = zK_0\delta(t)$ yielding the impulse response of the system and the corresponding time-dependent density matrix $\delta \rho_{\text{ia}}^{\text{kick}}(t)$. Then, in the linear-response regime, the response to the pulse of Eq. (1) is obtained via convolution

$$\delta \rho_{\text{ia}}(t) = \frac{1}{K_0} \int_{-\infty}^{\infty} \delta \rho_{\text{ia}}^{\text{kick}}(\tau) \mathcal{E}(t - \tau) \, d\tau,$$

which can be very efficiently calculated in frequency space via the convolution theorem and inverse Fourier transformation

$$\delta \rho_{\text{ia}}(t) = \frac{1}{2\pi K_0} \int_{-\infty}^{\infty} \delta \rho_{\text{ia}}^{\text{kick}}(\omega) \mathcal{E}(\omega) e^{-i\omega t} \, d\omega,$$

where $\delta \rho_{\text{ia}}^{\text{kick}}(\omega)$ and $\mathcal{E}(\omega)$ are Fourier transforms of the respective time-domain quantities. Here, $\delta \rho_{\text{ia}}^{\text{kick}}(\omega)$ can be efficiently calculated from the impulse response by using the computational framework developed in Ref. 38.

The time derivatives required for calculating the energy (Supplementary Note 4) are obtained similarly as

$$\delta \dot{\rho}_{\text{ia}}(t) = -i \frac{e}{2\pi K_0} \int_{-\infty}^{\infty} \omega \delta \rho_{\text{ia}}^{\text{kick}}(\omega) \mathcal{E}(\omega) e^{-i\omega t} \, d\omega,$$

$$\delta \ddot{\rho}_{\text{ia}}(t) = -\frac{1}{2\pi K_0} \int_{-\infty}^{\infty} \omega^2 \delta \rho_{\text{ia}}^{\text{kick}}(\omega) \mathcal{E}(\omega) e^{-i\omega t} \, d\omega.$$

In practice $\mathcal{E}(\omega)$ is non-vanishing only on a finite frequency interval (see, e.g., Fig. 1a), which narrows the integration limits.

It should be emphasized here that the time-dependent density matrix $\delta \rho_{\text{ia}}(t)$ is a complex quantity in time domain, so in practical calculations it is convenient to carry out Fourier transformations for the real $\text{Re}\delta \rho_{\text{ia}}(t)$ and imaginary $\text{Im}\delta \rho_{\text{ia}}(t)$ parts separately to utilize the properties of Fourier transformations of real quantities.

We also note in passing that the impulse response $\delta \rho_{\text{ia}}^{\text{kick}}(\omega)$ can be equivalently calculated from the Casida linear-response frequency-space formalism. Hence, the linear real-time response to any pulse can also be calculated from the Casida solutions via convolution of Eq. (8).

**Total absorbed energy.** By invoking Fourier transformation, the total absorbed energy after the pulse has vanished is obtained as

$$\int_{0}^{\infty} \delta \mathcal{E}(t) \, dt = \frac{1}{2} \int_{0}^{\infty} S(\omega) |\mathcal{E}(\omega)|^2 \, d\omega,$$

where $S(\omega) = \frac{2\pi}{\varepsilon} \text{Im}|\alpha(\omega)|$ is the dipole strength function, which equals the photoabsorption cross section safe for a constant multiplier.

**HC distributions.** The hot-electron energy distributions corresponding to the state occupation probabilities $P_a$ of Eq. (6) are obtained as (time-dependence is not explicitly marked)

$$P_e(\epsilon) = \sum_a P_a \delta(\epsilon - \epsilon_a) = \frac{1}{2} \sum_{ia} (q_{ia}^2 + p_{ia}^2) \delta(\epsilon - \epsilon_a),$$

where $q_{ia}$ and $p_{ia}$ correspond to scaled real and imaginary parts of $\delta \rho_{ia}$ (see Supplementary Note 2 for definitions).

For visualization purposes, Gaussian smoothing (convolution) is applied with respect to the $\epsilon$ axis.

The spatial probability density of hot electrons is obtained by using the full electron-electron part of the second-order density matrix as (see Supplementary Note 1 and note that only the real part contributes due to the hermiticity of the density matrix)

$$P_e(r) = \frac{1}{2} \sum_{iaa'} (q_{ia}q_{ia'} + p_{ia}p_{ia'}) \psi_{ia}(0)(r) \psi_{ia'}(0)(r).$$

The diagonal and degenerate states dominate the spatial density contributions, which allows us to define a spatio-energetic distribution

$$P_e(\epsilon, r) = \frac{1}{2} \sum_{iaa'} (q_{ia}q_{ia'} + p_{ia}p_{ia'}) \psi_{ia}(0)(r) \psi_{ia'}(0)(r) \delta(\epsilon - \epsilon_a),$$

which is used to calculate the spatial density of hot electrons with e.g., more than 1 eV as $P_e^{>1 \, \text{eV}}(r) = \int_{1 \, \text{eV}}^{\infty} P_e(\epsilon, r) \, d\epsilon$, and the energy distribution of hot electrons in a spatial volume $V$ as $P_e^{>1 \, \text{eV}}(r) = \int_{1 \, \text{eV}}^{\infty} P_e(\epsilon, r) \, d\epsilon$. The distribution at a specific atomic site (e.g., corner atoms) is obtained by integration over the Voronoi cell associated with the site.

The spatial and energetic distributions of hot holes are calculated analogously to the electrons.

**Software used.** The GPAW package with linear combination of atomic orbitals (LCAO) mode was used for DFT calculations. The real-time propagation LCAO-TDDFT implementation in GPAW was used for the TDDFT calculations. Density-matrix-based analysis tools in frequency space and in real time (present work) were used for analysis. The ASE library was used for...
constructing atomic structures and geometry relaxation. The NumPy and Matplotlib Python packages and the VMD software were used for processing and plotting data.

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