Ultrafast quantum interference in the charge migration of Tryptophan

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Abstract

Extreme-ultraviolet-induced charge migration in bio-relevant molecules is a fundamental step in the complex path leading to photo-damage. In this work we propose a simple interpretation of the charge migration recently observed in an attosecond pump-probe experiment on the amino acid Tryptophan. We find that the decay of the prominent low-frequency spectral structure with increasing pump-probe delay is due to a quantum beating between two geometrically distinct, almost degenerate charge

oscillations. Quantum beating is ubiquitous in these systems and, at least on the few-to-tens femtosecond timescales, it may dominate over decoherence the line intensities of time-resolved spectra. We also address the experimentally observed phase shift in the charge oscillations of two different amino acids, Tryptophan and Phenylalanine. Our results indicate that a beyond mean-field treatment of the electron dynamics is necessary to reproduce the correct behavior.

The progress in attosecond science offers nowadays invaluable tools to study electrons moving at their natural timescale with unprecedented temporal resolution.¹⁻³ Typically, the electronic motion in a molecule is initiated by an external laser field through excitation or ionization, thus the subsequent charge rearrangement, or *charge migration*,⁴⁻⁸ occurs through coherent oscillations that may precede nuclear motion.⁹⁻¹¹

The first time-resolved observation of ultrafast charge migration (UCM) in a biochemically relevant molecule has been reported for the amino acid Phenylalanine (Phe),¹² opening new avenues for the study of coherent electronic processes in biological systems. From the theoretical point of view, the UCM in relatively large molecules is a highly complex phenomenon since the ionizing pulse leaves the system in a superposition of several cationic eigenstates^{2,12,13} whose energies, wavefunctions and coefficients are, in general, difficult to determine. A method which does not rely on knowledge of the time-dependent wavefunction is the first-principles implementation of the non-equilibrium Green's functions (NEGF) theory.¹⁴ The NEGF approach has been successfully applied to the study of UCM in Phe,¹⁵ Glycine¹⁶ and Adenine,¹⁷ thus proving to be a feasible numerical tool to address the ultrafast dynamics of simple organic molecules.

In this work we use the first-principles NEGF approach to investigate UCM in the Tryptophan (Trp) amino acid and address the results of a recent time-resolved photofragmentation experiment.^{18,19} In that experiment the time-dependent yield of the immonium dication showed a low-frequency oscillation lasting for about 15 fs. Furthermore, this oscillation was phase shifted with respect to the one at almost the same frequency measured in Phe in the

Figure 1: Molecular structure of the most abundant conformer of Trp amino acid. Black spheres represent carbon atoms; gray spheres, hydrogen atoms; blue sphere, nitrogen atoms; and red spheres, oxygen atoms.

same experimental conditions.¹⁹ We disentangle the large manifold of cationic transitions and propose a simple interpretation of the raise-up followed by an equally fast decay of the Trp low-frequency oscillation. We demonstrate that this behavior is mainly due to a quantum beating between two geometrically distinct charge modes, one involving the amino-carboxyl groups and the other the amino-indole groups. The existence of these two modes is also confirmed experimentally after averaging the outcomes of three independent measures. Finally, we address the observed phase shift¹⁹ by comparing the time-dependent simulations of Trp with recent simulations on Phe,¹⁵ and find that correlation (beyond mean-field) effects are crucial to reproduce the correct behavior.

Trp is an α -amino acid containing an amino group (NH_2), a carboxylic group (COOH) and a side chain indole ($\text{C}_8\text{H}_7\text{N}$) as radical group. Hence, Trp has 78 valence electrons in the charge neutral state. There exist 57 Trp conformers²⁰ and at the experimental temperature of 450 K¹⁸ the probability abundance of the lowest-energy conformer is $\sim 50\%$. Among the higher-energy conformers two have probability $\sim 15\%$, three have probability $\sim 5\%$ and all remaining others have less than 1% probability of being found. Therefore in the simulations we have considered only the most abundant conformer whose structure is shown in Fig. 1.

Ultrafast charge dynamics in Trp was experimentally investigated by means of two-color

pump-probe measurements, using attosecond pump pulses and 4-fs visible/near-infrared (VIS/NIR) probe pulses, in combination with mass spectroscopy.^{18,19} A clean plume of gas-phase Trp molecules was generated by evaporation of the amino acid from a thin metallic foil heated by a continuous-wave laser.⁵ The parent and fragment ions produced by the interaction of the molecules with the pump and probe pulses were then collected by a linear time-of-flight spectrometer for mass analysis and the temporal evolution of their production yield was measured as a function of pump-probe delay, τ . As already observed in Phe,¹² the production yield of immonium dication (i.e., the doubly charged fragment resulting from the loss of the carboxyl group, $(\text{Trp-COOH})^{+2}$) is expected to be strongly sensitive to the charge density on the amino group. The temporal evolution of the immonium dication yield as a function of pump-probe delay, $Y(\tau)$, shows a sharp increase at zero time delay followed by a decay with a time constant of ~ 30 fs. The most interesting experimental result was the observation of a periodic modulation of $Y(\tau)$, with a period of ~ 4 fs, for pump-probe delays in the range between ~ 3 fs and ~ 20 fs. The temporal characteristics of this modulation can be analyzed by calculating the sliding-window Fourier transform of $Y(\tau)$, assuming a sliding window Gaussian function $g(\tau, t_d) = \exp[-(\tau - t_d)^2/t_0^2]$ with $t_0 = 10$ fs:

$$\tilde{Y}(\omega, t_d) = \int d\tau e^{-i\omega\tau} g(\tau, t_d) Y(\tau), \quad (1)$$

The result is reported in Fig. 2(a), which shows frequency and time information on the same plot. A single and broad peak around 0.25 PHz [corresponding to the oscillation period of ~ 4 fs observed in the pump-probe evolution of $Y(\tau)$] forms in ~ 3 fs (onset time) and vanishes after ~ 20 fs (end time). Numerical simulations have been performed in Ref.¹⁸ using Time-Dependent Density Functional Theory (TDDFT) with an adiabatic exchange-correlation potential. Although TDDFT captures the broad peak around 0.25 PHz both the onset and end times of the signal were overestimated by ~ 5 fs. Furthermore, the physical explanation of the signal decay has so far remained elusive.

Figure 2: Color plot of the spectrogram of the experimentally measured abundance of immo-nium dications $\tilde{Y}(\omega, t_d)$ [panel (a)] and of the spectrograms of the calculated charge around the amino group $\tilde{N}_{\text{amine}}(\omega, t_d)$ using the 2B [panel (b)] and HF [panel (c)] approximations. On the vertical axis the delay t_d (in fs) and on the horizontal axis the frequency ω (in PHz = 1/fs). The spectrograms are obtained by a sliding-window Fourier transform, see Eq. (1), with a gaussian of width 10 fs centered at different times t_d in the range (0, 25) fs.

To achieve a physical interpretation of the experimental results we have performed numerical simulations using NEGF. We drive Trp out of equilibrium by a linearly polarized, 400-as XUV electric field of temporal profile $\mathcal{E}(t)$, displayed in Fig. 3 (a), and peak intensity 3×10^{10} W/cm², see Fig. 3 (b) for the power spectrum. The XUV pulse is the same as the one used in the experiment of Ref.¹⁸ Time-dependent local quantities are calculated from the interacting one-particle density matrix $\rho_{\mu\nu}(t) = \langle \Phi(t) | \hat{c}_\nu^\dagger \hat{c}_\mu | \Phi(t) \rangle$, where $\Phi(t)$ is the interacting many-body state at time t and $\hat{c}_\mu$ ($\hat{c}_\nu^\dagger$) annihilates (creates) an electron in the μ -th (ν -th) Hartree-Fock (HF) valence orbital, $\mu, \nu = 1, \dots, 39$. In particular the density of electrons is obtained from

$$n(\mathbf{r}, t) = \sum_{\mu\nu} \varphi_\mu(\mathbf{r}) \rho_{\mu\nu}(t) \varphi_\nu(\mathbf{r}), \quad (2)$$

where the sum runs over all couples of valence HF orbitals φ_μ and φ_ν , see Section 1. In the present work $\rho(t)$ is evolved in time using the `CHEERS@YAMBO` code^{21,22} which solves the NEGF equations of motion in the Generalized Kadanoff-Baym ansatz.²³ Theoretical and implementation details can be found in Section 1. We present results in the HF approximation as well as in the second-Born (2B) approximation which has been shown to be accurate in finite and not too strongly correlated systems.^{24–32} The 2B approximation is the next-to-leading order self-consistent approximation in the Coulomb interaction (the leading order being HF) and it amounts to include a single direct and exchange electron-electron scattering in the two-particle propagator. Due to the large size of the Trp molecule and the quadratic scaling (in time) of the NEGF approach we had to arrest the time evolution after 26 fs.

In panels (c), (d) and (e) of Fig. 3 we plot the hole occupations of the 39 HF orbitals during XUV illumination for three orthogonal polarization directions, see Fig. 1 for axis definition. The ionization rate is highly anisotropic and it is not monotonous in the HF orbital energy ϵ_μ (orbitals are ordered in energy, i.e., $\epsilon_\mu > \epsilon_\nu$ if $\mu > \nu$). The molecule is left in a superposition of several cationic states and, at least during the first few femtoseconds, it is expected to evolve coherently. Indeed, the experiment indicates that at low frequencies coherence is preserved even up to 20 fs,¹⁸ as shown in Fig. 2(a).

Figure 3: Temporal profile of the XUV pulse $\mathcal{E}(t)$ used in the simulations [panel (a)] and its power spectrum $|\mathcal{E}(\omega)|^2$ [panel (b)]. Hole occupation for the lowest 39 HF orbitals (multiplied by a factor 10^5) calculated in the 2B approximation during the action of the ionizing XUV pulse, for polarization along x [panel (a)], y [panel (b)], z [panel (c)]. Thick dashed lines highlight the ionization curves of the HF orbitals $\mu = 19, 22, 23, 27$.

Following previous works^{12,15,33} we assign the experimentally observed modulation of $Y(\tau)$ to the pump-induced oscillations of the charge in the amino group of the molecule. Accordingly, we calculate

$$N_{\text{amine}}(t) = \int_{\text{box}} d\mathbf{r} n(\mathbf{r}, t) \quad (3)$$

where the integral is over a box centered on the amino group. The box is also chosen to yield the correct number of valence electrons in equilibrium, that is, $N_{\text{amine}}(0) = 7$. Other partition schemes for defining the amine charge do not change the general conclusions, see below. The density is obtained by averaging the results of three different simulations, one for each polarization direction of the XUV pulse, to account for the random orientation of the molecules in the experimental setup. We have then performed the sliding Fourier transform with a gaussian window of width 10 fs centered at different times t_d as in Eq. (1) and extracted $\tilde{N}_{\text{amine}}(\omega, t_d)$. The theoretical spectrograms calculated using both the 2B and HF approximations at clamped nuclei are displayed in Figs. 2 (b,c). The NEGF approach captures correctly the two main experimental features, i.e., the single prominent structure at frequency $\Omega = 0.25$ PHz and the signal amplitude between 0 and 20 femtoseconds. The agreement between the experimental and theoretical spectrograms is reasonably good, confirming that nuclear-induced decoherence does not have a major impact on the low-frequency and short-time behavior of $Y(\tau)$.¹⁸ We also observe that the HF and 2B approximations give similar results, suggesting that Trp is less correlated than other amino acids like Phe¹⁵ and Glycine,¹⁶ where correlations are responsible for shifting the oscillation frequencies, redistributing the spectral weights and giving rise to new spectral structures.

To shed light on the delay-dependent behavior of the spectral structure at frequency $\Omega = 0.25$ PHz we search for those pairs of orbitals $\{\mu, \nu\}$ with a sizable amplitude on the amino group and for which the matrix elements $\rho_{\mu\nu}(t)$ oscillate at frequency Ω . From Eq. (2) we indeed expect that these pairs give the most relevant contribution at low frequency. In Fig. 4 we plot the Fourier transform $\tilde{\rho}_{\mu\nu}(\omega)$, with $\{\mu, \nu\} = \{19, 22\}, \{23, 27\}$, for each polarization. These are the only pairs giving rise to nontrivial structures in the spectral region

Figure 4: Fourier transform of $\rho_{19,22}(t)$ (green curve) and $\rho_{23,27}(t)$ (orange curve) for the three different polarizations of the XUV pulse. Vertical lines indicate the frequencies $\Omega_A = 0.27$ PHz (green) and $\Omega_B = 0.23$ PHz (orange). All quantities are calculated in the 2B approximation.

around Ω . The matrix element $\tilde{\rho}_{19,22}$ exhibits a dominant peak at frequency $\Omega_A = 0.27$ PHz induced by the XUV pulse polarized along y whereas $\tilde{\rho}_{23,27}$ exhibits a dominant peak at frequency $\Omega_B = 0.23$ PHz induced by the XUV pulse polarized along x . Interestingly, the orbitals 19, 22, 23, 27 are also among those that ionize the most during the XUV illumination, see the thick dashed lines in Fig. 3 (a,b,c). The existence of two low-frequencies emerges also from the Fourier transform $\tilde{Y}(\omega)$ of the full time-dependent immonium abundance.¹⁸ Actually, the frequencies Ω_A and Ω_B are in excellent agreement with the peak positions in $\Omega_A^{\text{exp}} = 0.28$ PHz and $\Omega_B^{\text{exp}} = 0.23$ PHz of $\tilde{Y}(\omega)$. The spectrogram in Fig. 2 (a) makes these frequencies visible only for $t_d > 14$ fs while it blends them in a broad structure at $(\Omega_A^{\text{exp}} + \Omega_B^{\text{exp}})/2 = \Omega = 0.25$ PHz for $t_d < 14$ fs.

We can assign a well defined geometrical interpretation to the charge modes at Ω_A and Ω_B . In Fig. 5 we plot the spatial shape of the four involved orbitals $|\varphi_\mu(\mathbf{r})|^2$ as well as the overlap functions $\varphi_\mu(\mathbf{r})\varphi_\nu(\mathbf{r})$. The function $\varphi_{19}(\mathbf{r})\varphi_{22}(\mathbf{r})$ has a large amplitude around the amino group and an opposite amplitude on the carboxylic group; the function $\varphi_{23}(\mathbf{r})\varphi_{27}(\mathbf{r})$, instead, has a large amplitude around the indole group and an opposite amplitude on the amino group. These overlaps play a crucial role in characterizing the time-dependent behavior since the occupations of the HF orbitals (i.e., the diagonal elements of the density matrix $\rho_{\mu\mu}$) vary

Figure 5: Square modulus $|\varphi_\mu(\mathbf{r})|^2$ of the HF orbitals $\mu = 19, 22, 23, 27$ and overlap functions $\varphi_{19}(\mathbf{r})\varphi_{22}(\mathbf{r})$ and $\varphi_{23}(\mathbf{r})\varphi_{27}(\mathbf{r})$.

very little in time after the XUV pulse. Therefore, in accordance with Eq. (2), the change of $N_{\text{amine}}(t)$ is mainly dictated by the off-diagonal elements $\rho_{\mu\nu}(t)$. We then define the following two contributions to the total charge of the amino group

$$\begin{aligned} n_A(t) &= 2 \int_{\text{box}} d\mathbf{r} \varphi_{19}(\mathbf{r})\varphi_{22}(\mathbf{r}) \times \text{Re}[\rho_{19,22}(t)] \\ &\approx 0.48 \times \text{Re}[\rho_{19,22}(t)] \end{aligned} \quad (4)$$

and

$$\begin{aligned} n_B(t) &= 2 \int_{\text{box}} d\mathbf{r} \varphi_{23}(\mathbf{r})\varphi_{27}(\mathbf{r}) \times \text{Re}[\rho_{23,27}(t)] \\ &\approx -0.30 \times \text{Re}[\rho_{23,27}(t)]. \end{aligned} \quad (5)$$

In panels (a) and (b) of Fig. 6 we show the time evolution of $n_A(t)$ and $n_B(t)$ in the 2B approximation. According to our previous analysis $n_A(t)$ is associated to the charge mode of frequency $\Omega_A = 0.27$ PHz (period 3.7 fs) between the carboxylic group and the amino group, while $n_B(t)$ is associated to the charge mode of frequency $\Omega_B = 0.23$ PHz (period 4.3 fs)

Figure 6: Time evolution of the function $n_A(t)$ defined in Eq. (4) [panel (a), left] and $n_B(t)$ defined in Eq. (5) [panel (b), left] together with their corresponding geometrical interpretation [panels (a,b), right]. Panel (c): Beating function $n_A(t) + n_B(t)$ (left) and relative spectrogram $\tilde{n}_A + \tilde{n}_B$ (right). The functions $n_A(t)$ and $n_B(t)$ are evaluated in the 2B approximation and in the plots are scaled up by a factor 10^5 .

between the amino group and the indole group. By comparing the spectrogram of $\tilde{N}_{\text{amine}}$ in Fig. 2 (b) with the spectrogram of $\tilde{n}_A + \tilde{n}_B$ in Fig. 6 (c) we infer that the low-frequency behavior of $N_{\text{amine}}(t)$ is well approximated by the sum of its dominant contributions, i.e.

$$N_{\text{amine}}(t) \approx n_A(t) + n_B(t). \quad (6)$$

The two contributions n_A and n_B interfere in the coherent dynamics of the Trp cation and the charge of the amino group experiences a quantum beating, see left panel of Fig. 6 (c). As the amplitudes of the two contributions are similar, this interference is characterized by a central frequency $\Omega_+ \approx (\Omega_A + \Omega_B)/2 = 0.25$ PHz and an “envelope” frequency $\Omega_- \approx (\Omega_A - \Omega_B)/2 = 0.04$ PHz. The central frequency Ω_+ coincides with the frequency Ω observed in the experimental spectrogram, while the envelope frequency Ω_- (dictating the beating period) is fairly consistent with the measured time of the experimental signal, that is $1/2\Omega_- \approx 12$ fs. The experimental curve $Y(\tau)$ can therefore be fitted by a beating function involving two similar frequencies (possibly multiplied by an exponential damping function to account for nuclear-induced decoherence at longer times). We emphasize that our analysis is fairly independent of the partition scheme used to define the amine charge. Indeed only the pairs $\{\mu, \nu\} = \{19, 22\}$ and $\{23, 27\}$ of HF orbitals have both a sizable weight on the amine cell and a $\tilde{\rho}_{\mu\nu}(\omega)$ with a peak around 0.25 PHz. Therefore, a different partition can change the amplitudes $n_A^{(0)} \equiv 0.48$ and $n_B^{(0)} \equiv -0.30$ in Eqs. (4) and (5) but Eq. (6) would still hold. We have verified that varying the ratio $n_B^{(0)}/n_A^{(0)}$ in the range $(-0.5, -2)$ the level of agreement with the experimental spectrogram remains unaltered. Interestingly, if the amplitude of the two modes is comparable, i.e., $n_B^{(0)}/n_A^{(0)} \simeq -1$, then a bifurcation (similar to the one visible in the experimental spectrogram for $t_d > 14$ fs) develops around the time of maximum constructive interference. Viceversa, the occurrence of a bifurcation is a peculiar fingerprint of the quantum beating between charged modes. For our box the amplitude of n_B is about 0.6 times smaller than the amplitude of n_A and only a weak bifurcation is visible in Fig. 6 (c).

Figure 7: Comparison between the experimental yield of immonium dications $Y(\tau)$ versus the pump-probe delay τ for Trp and Phe.

The prominent slow oscillation in the time-resolved yield of the immonium dication of Trp¹⁸ was observed also in the same experiment on Phe.¹² Although the associated frequencies are very close, namely $\Omega_{\text{Trp}} = \Omega = 0.25$ PHz for Trp and $\Omega_{\text{Phe}} = 0.24$ PHz for Phe (for positive delays larger than 10 fs), the physical origins are different. In Trp the frequency Ω_{Trp} emerges from the interference between two geometrically distinct charged modes while in Phe the frequency Ω_{Phe} is due to a single charge mode where electrons oscillate between the amino group and the carboxylic group. In Fig. 7 we compare the experimental oscillations of the immonium dication for the two molecules (after subtracting the slow envelope dynamics^{18,19}) as a function of the attosecond-XUV-pump few-fs-visible probe delay. The experimental data (grey circles) are fitted with sinusoidal functions (solid black lines). Purple-green bars (crest and trough regions) are used to guide the eye through the time window in which the oscillations at Ω_{Trp} in Trp and Ω_{Phe} in Phe coexist. The synchronisation of the time axis for the two molecules was obtained with a precision of 0.5 fs, following the method explained in Ref.¹⁹ In the overlapping region the two yields are almost out of phase. We now show that the NEGF approach captures also this phase difference.¹⁹

We begin by observing that according to our calculated spectrograms for Trp and Phe¹⁵ the frequencies are almost the same in both the HF and 2B approximations. In particular,

Figure 8: Comparison between the calculated charge $N_{\text{amine}}(t)$ on the amino group in the HF approximation for Trp and Phe. Grey cyrcles denote the numerical outcome of the NEGF simulations. For a better visualization oscillations with frequencies larger than 0.4 PHz and smaller than 0.15 PHz have been filtered out. The curves have been scaled up by a factor 10^6 . Solid black lines are used to fit the numerical data with a beating function for Trp [see Eq.(6)] and a sinusoidal function with frequency $\Omega_{\text{Phe}}^{\text{HF}}$ for Phe.

Figure 9: Same analysis as in Fig. 8 performed in the 2B approximation

$\Omega_{\text{Trp}}^{\text{HF}} \approx \Omega_{\text{Trp}}^{2\text{B}} = 0.25$ PHz for Trp, see Fig. 2, and $\Omega_{\text{Phe}}^{\text{HF}} = 0.26$ PHz and $\Omega_{\text{Phe}}^{2\text{B}} = 0.25$ PHz for Phe,¹⁵ again for positive delays larger than 10 fs. In Fig. 8 we compare $N_{\text{amine}}(t)$ for the two molecules in the HF approximation and draw purple-green bars using the same criterion as in Fig. 7. The overlapping region is wider than the experimental one and, most importantly, the Phe and Trp oscillations are essentially in phase. The scenario is different in the (correlated) 2B approximation, see Fig. 9. Here the two oscillations are correctly out-of phase and the overlapping region is much closer to the experimental one. As anticipated, electronic correlations (beyond HF) are crucial for phase-shifting the HF results toward the correct value.

In conclusion, we have studied the charge migration dynamics in the amino acid Tryptophan induced by a weak attosecond XUV pulse using a first-principles NEGF approach which treats electronic correlations beyond the mean field HF approximation and keeps the nuclei clamped in their equilibrium position. The fixed nuclei approximation is supported by theoretical calculations on the same system using time-dependent density functional theory in combination with Ehrenfest molecular dynamics.¹⁸ Although we cannot utterly exclude that nuclear-induced decoherence may have a role, our results indicate that the quantum beating is certainly a competing process to account for in the interpretation of the experimental outcome.

The numerical analysis shows that the quantum beating occurs between two geometrically distinct and almost degenerate coherent oscillations which survive up to 20 femtoseconds. Despite the complexity of the Trp molecule these are the only two modes responsible for the low-frequency (below 0.5 PHz) dynamics. They are associated to charge motion along the amino-carboxyl and amino-indole backbones; noteworthy, they are activated by laser pulses polarized along orthogonal directions. The interference between the two modes explains the rapid raise-up followed by an equally fast decay of the line intensity at frequency $\Omega = 0.25$ PHz of the time-resolved spectrum. Our results also suggest that the same pump-probe experiment on non-random oriented molecules may be used to selectively activate and

Figure 10: Valence KS spectrum (left panel) and valence HF spectrum (right panel) of the Trp molecule.

monitor different dynamical processes.

Comparing the correlated 2B dynamics of Tryptophan and of another amino acid Phenylalanine we have also found that the charges on the amino group are out of phase in the time-window of pump-probe delays where the slow dynamics of both molecules is dominated by a coherent oscillation of frequency around 0.25 PHz. This phase difference as well as the length of the time-interval (about 4 fs) agree with the experimental finding, pointing to the importance of using beyond mean-field approximations (for which no agreement is found) in the time-dependent simulations.

1 Theoretical Methods

The one-particle basis used to construct the many-body Hamiltonian in second quantization of Trp is generated with Density Functional Theory (DFT). We place the isolated Trp in a cubic cell of linear dimension $24 \text{ \AA}$ and solve the self-consistent Kohn-Sham (KS) problem using the **QuantumEspresso** package³⁴ with PBE exchange-correlation potential and an energy cutoff of 50 Ry. Core electrons are treated with norm-conserving Troullier-Martins

Figure 11: Square modulus of the 39 occupied KS orbitals.

pseudopotentials.³⁵ The resulting KS one-particle spectrum consists of 50 bound states. The charge neutral molecule has the lowest 39 states doubly occupied with the KS-HOMO located 5.22 eV below the onset of the continuum which we set at zero, see Fig. 10 (left panel). The square modulus of the valence orbitals is illustrated in Fig. 11. The remaining 11 bound states above the KS-HOMO (not shown) have a binding energy lesser than 3.5 eV. All other KS states are delocalized and have positive energy (continuum states). We checked the convergence of the KS calculation by increasing the box size and the energy cutoff.

We have chosen the 50 bound KS states as the basis to solve the Hartree-Fock (HF) problem, a preliminary step to add correlations in the NEGF framework. The **Yambo** package³⁶ has been used to extract the KS matrix elements of the DFT exchange-correlation potential as well as the four-index Coulomb integrals, necessary to build the HF potential. We have recently shown that this procedure provides accurate HF valence orbitals $\varphi_\mu(\mathbf{r})$ and energies ϵ_μ .¹⁶ The valence HF spectrum is illustrated in Fig. 10 (right panel). As the system is weakly correlated the ground state is approximated by the Slater determinant of the first 39 HF states. The remaining (highest) 11 HF states turn out to have positive energies and

together with the continuum KS states are treated as noninteracting photoelectron states. Hence all Green's functions and self-energies in our NEGF simulations are 39×39 matrices.²¹ The light-matter interaction is treated in the dipole approximation and the dipole matrix elements are evaluated with the **Yambo** code.³⁶

The one-particle density matrix $\rho(t)$ is the main output of the NEGF simulation. We are particularly interested in the electron density

$$n(\mathbf{r}, t) \equiv \langle \Phi(t) | \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}(\mathbf{r}) | \Phi(t) \rangle, \quad (7)$$

where $\Phi(t)$ is the interacting many-body state at time t and $\hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}(\mathbf{r}) = \hat{n}(\mathbf{r})$ is the density operator written in terms of the second-quantization creation and annihilation operators for an electron in $\mathbf{r}$. Expanding these operators in the HF basis $\hat{\psi}(\mathbf{r}) = \sum_\mu \varphi_\mu(\mathbf{r}) \hat{c}_\mu$ we get Eq. (2).

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