First-principles nonequilibrium Green’s function approach to transient photoabsorption: Application to atoms

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We put forward a first-principle NonEquilibrium Green’s Function (NEGF) approach to calculate the transient photoabsorption spectrum of optically thin systems. The method can deal with pump fields of arbitrary strength, frequency and duration as well as for overlapping and nonoverlapping pump and probe pulses. The electron-electron repulsion is accounted for by the correlation self-energy, and the resulting numerical scheme deals with matrices that scale quadratically with the system size. Two recent experiments, the first on helium and the second on krypton, are addressed. For the first experiment we explain the bending of the Autler-Townes absorption peaks with increasing the pump-probe delay τ, and relate the bending to the thickness and density of the gas. For the second experiment we find that sizable spectral structures of the pump-generated admixture of Kr ions are fingerprints of dynamical correlation effects, and hence they cannot be reproduced by time-local self-energy approximations. Remarkably, the NEGF approach also captures the retardation of the absorption onset of Kr2+ with respect to Kr2 0 as a function of τ.

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I. INTRODUCTION

Transient photoabsorption (TPA) spectroscopy has today become a popular technique to investigate the ultrafast dynamics of electrons and nuclei in atoms, molecules and nanostructures.1–5 A reliable physical interpretation of the TPA spectrum is inescapably linked to a reliable calculation of the probe-induced polarization in the pump-driven system. State-of-the-art calculations are based on the Configuration Interaction (CI) expansion of the time-evolved many-electron state. The time-dependent CI coefficients are either varied with respect to the probe field6–11 or used to construct the dipole response function from the Lehmann representation,12–14 the latter approach being applicable only provided that the dressed pump and probe fields do not overlap.15 However, the size of the arrays in CI calculations scale exponentially with the number of basis functions and the time-step to achieve convergence is typically much smaller than the time-step used in statistical approaches. Due to these numerical limitations the CI approach is confined to the study of rather small systems.

One possible statistical approach to TPA spectroscopy is Time Dependent Density Functional Theory (TDDFT).16 In TDDFT are the occupied single-particle wavefunctions that are propagated in time and since they scale linearly with the number of basis functions TDDFT is suitable to study much larger systems than those accessible by CI. In the framework of the Adiabatic Local Density Approximation (ALDA) TDDFT has been recently and successfully applied to the study of TPA in small- and medium-sized molecules17 as well as to monitor the vibronic-mediated charge transfer in donor-acceptor complexes.18,19 Still, ALDA functionals have drawbacks that could compromise the description of photoabsorption spectra even in equilibrium systems. For example, ALDA misses correlation-induced spectral features like double-excitations20,21 and long-range charge-transfer excitations;22–24 it also provides a poor description of the energy-level alignment in metal/molecule interfaces25,26 and of the Coulomb blockade phenomenon.27,28 In this work we discover yet another correlation effect missed by ALDA.

An alternative statistical approach to TDDFT is the many-body diagrammatic theory. Here the building blocks of the formalism are the NonEquilibrium Green’s Functions (NEGF),29–32 and correlation effects are included by a proper selection of self-energy diagrams. Double-excitations and other properties missed by ALDA are within reach of diagrammatic theory already with basic self-energies. Recently, it has been shown that the TPA spectrum follows from the solution of a nonequilibrium Bethe-Salpeter equation (BSE) provided that the time-scale of the pump-induced electron dynamics is much longer than the life-time of the dressed probe field.33 In general, however, for pump fields of arbitrary strength, frequency and duration and/or for overlapping pump and probe pulses, the nonequilibrium BSE is inadequate and the full time-propagation of the NEGF is unavoidable. Nevertheless, as the size of the arrays in NEGF calculations scales quadratically with the number of basis functions, this formalism too allows for extending the range of CI accessible systems.

In this work we formulate a general first-principle NEGF scheme to TPA and apply it to reproduce the transient spectra of a thick helium gas13 and of a krypton gas.34 For helium we address the exponential damping of the probe-induced dipole, and relate it to the thickness and density of the gas. We then provide the explanation of the bending of the Autler-Townes absorption peaks with increasing the pump-probe delay. We
also propose a useful formula for fitting the experimental TPA spectra. The krypton gas constitutes a more severe test for NEGF due to non-trivial correlation effects. We find that for a proper description of the (pump-generated) evolving admixture of Kr ions the self-energy should have memory. Static (or adiabatic) approximations like the Hartree-Fock or the Markovian approximations perform rather poorly as only the spectrum of Kr\(^{1+}\) is visible. Instead, the TPA spectrum calculated using the (memory-dependent) second-Born self-energy approximations implemented in this work. Remarkably, we are also able to reproduce the femtosecond retardation of the absorption onset of Kr\(^{2+}\) with respect to Kr\(^{1+}\) as a function of the pump-probe delay.

The paper is organized as follows. In Section II we relate the TPA spectrum to the microscopic quantum mechanical average of the transverse, probe-induced dipole-wave propagating toward the detector. In Section III we put forward the NEGF approach to TPA and provide the explicit expression of the self-energy approximations implemented in this work. The helium gas is studied in Section IV. In Section V we extend the NEGF approach to deal with pump-induced ionization processes and then apply the extended approach to the study of the krypton gas in Section VI. Summary and conclusions are drawn in Section VII.

II. TRANSIENT PHOTOABSORPTION SPECTRUM

We consider a gas of atoms or molecules perturbed by a strong time-dependent transverse electric field \(E(r,t)\) (pump) propagating along the unit vector \(\mathbf{N}\) and a feeble time-dependent transverse electric field \(e(r,t)\) (probe) propagating along the unit vector \(\mathbf{n}\), see Fig. 1. The direction of propagation \(\mathbf{N} \neq \mathbf{n}\) and in experiments the photodetector is positioned along the probe beam-line. Let \(\mathcal{E}_p(r,t)\) be the component of the total electric field (external plus induced) propagating toward the detector and \(\mathcal{E}_p(t)\) be the value of \(\mathcal{E}_p(r,t)\) at the detector surface. Then the transmitted energy measured by the detector is

\[
E_T = S \frac{c}{2\pi} \int \frac{d\omega}{2\pi} |\mathcal{E}_p(\omega)|^2,
\]

with \(S\) the surface of the sample (assumed to be smaller than the laser beam cross section). Here and in the following we use the convention that quantities with the tilde symbol on top denote the Fourier transform of the corresponding time-dependent quantities. Replacing \(\mathcal{E}_p\) in Eq. (1) with the external probe field \(e\) we obtain the energy \(E_I\) of the incident probe beam. The absorbed energy \(E_A\) is defined according to

\[
E_A = E_I - E_T = S \frac{c}{2\pi} \int \frac{d\omega}{2\pi} \left( |\tilde{e}(\omega)|^2 - |\tilde{\mathcal{E}}_p(\omega)|^2 \right).
\]

By means of a spectrometer it is possible to measure the absorbed energy per unit frequency, i.e.,

\[
\mathcal{G}(\omega) = S \frac{c}{2\pi} \left( |\tilde{e}(\omega)|^2 - |\tilde{\mathcal{E}}_p(\omega)|^2 \right).
\]

The quantity \(\mathcal{G}(\omega)\) is the transient photoabsorption (TPA) spectrum that we are interested in.

As both \(E\) and \(e\) are transverse fields we have \(E(r,t) = E(X,t)\) with \(X = \mathbf{N} \cdot r\) and \(e(r,t) = e(x,t)\) with \(x = \mathbf{n} \cdot r\). By definition \(\mathcal{E}_p\) too depends only on \(x\), i.e., \(\mathcal{E}_p(\omega) = \mathcal{E}_p(x,t)\), since it is a transverse field propagating along \(\mathbf{n}\). Without loss of generality we choose the coordinates of the boundaries of the sample in \(x = 0\) and \(x = \ell\), \(\ell\) being the thickness of the gas, see Fig. 1. From Maxwell equations the relation between the total field and the incident probe field is

\[
\mathcal{E}_p(x,t) = e(x,t) + \frac{2\pi}{c} \frac{d}{dt} \int_0^x dx' \mathbf{d}_p(x')
\]

where \(\mathbf{d}_p(x,t)\) is the component of the \textit{probe-induced} dipole density propagating toward the detector.\(^{15}\) Notice that \(\mathbf{d}_p(x,t)\) vanishes for \(x > \ell\); hence \(\mathcal{E}_p(\ell,t)\) and \(\mathcal{E}_p(t)\) (the electric field at the detector surface) differ only by a time-shift. This time-shift is completely irrelevant for the calculation of the spectrum, so we can either use \(\mathcal{E}_p(\ell,t)\) or \(\mathcal{E}_p(\ell)\) in Eq. (3).

Equation (4) connects the experimental outcome \(\mathcal{G}(\omega)\) to a quantum-mechanical average. Let us define \(\mathbf{d}_p(x,t)\) more rigorously. We denote by \(|\Psi(\tau,t)\rangle\) the many-body state of an atom located in a volume element around \(r\) at time \(t\) when both pump and probe fields are present; similarly \(|\Psi_P(\tau,t)\rangle\) is the many-body state of the same atom when only the pump is present (probe-free state). The average of the atomic dipole operator \(\mathbf{d}(\tau)\) over these two states is \(\mathbf{d}^{(at)}(\tau) = \langle \Psi_P(t) | \mathbf{d}(\tau) | \Psi_P(t) \rangle\) and \(\mathbf{d}^{(at)}(\tau) = \langle \Psi_P(t) | \mathbf{d}(\tau) | \Psi_P(t) \rangle\) respectively. The atomic probe-induced dipole is therefore

\[
\mathbf{d}^{(at)}_p(\tau) \equiv \mathbf{d}^{(at)}(\tau - \mathbf{d}^{(at)}_p(\tau) t).
\]

For isotropic systems the probe-free \(\mathbf{d}^{(at)}_p(\tau) = \mathbf{d}^{(at)}(\tau)\) is a transverse field propagating along \(\mathbf{N}\). Instead the atomic dipole \(\mathbf{d}^{(at)}(\tau)\) is a transverse field propagating along all possible directions \(kN + KN \) with \(k\) and \(K\) real numbers. To first order in \(|e|\) the component propagating along \(N\) \((k = 0\) is exactly \(\mathbf{d}^{(at)}_p(\tau)\). It is reasonable to expect that for \(k \neq 0\) and for small \(|e|\) the dominant component of \(\mathbf{d}^{(at)}(\tau)\) is the one propagating along the same direction \(\mathbf{n}\) of the external probe. In this case the probe-induced atomic dipole \(\mathbf{d}^{(at)}_p(\tau) = \mathbf{d}^{(at)}_p(\tau)\) is a transverse field propagating along \(\mathbf{n}\) and the function \(\mathbf{d}_p\) appearing in Eq. (4) is simply

\[
\mathbf{d}_p(x,t) = \mathbf{d}^{(at)}(x',t) \big|_{x' = x}
\]

FIG. 1: (Color online) Schematic illustration of a pump-probe experiment.

The quantity \(\mathcal{G}(\omega)\) is the transient photoabsorption (TPA) spectrum that we are interested in.
$n_{(at)}^p \mathbf{d}_{(at)}$, $n_{(at)}$ being the density of the gas. We can therefore calculate $\mathbf{d}_{(at)}$ by performing a time-propagation with pump and probe, another time-propagation with only the pump and then subtracting the resulting dipoles. Below we derive the basic equations to perform these calculations.

For an atom with unperturbed Hamiltonian $\hat{H}(r)$ the evolution of the state $\ket{\Psi(r,t)}$ is governed by the Schrödinger equation

$$i \frac{d}{dt} \ket{\Psi(r,t)} = \left[ \hat{H}(r) + \mathbf{E}(r \cdot t) \cdot \mathbf{d}(r) \right] \ket{\Psi(r,t)}$$

(6)

where $\mathbf{E}$ is the total electric field. We choose the pump and probe propagation directions such that $\mathbf{N} \cdot \mathbf{n} = 1$. Then $X = r \cdot \mathbf{N} \simeq r \cdot n = x$ inside the sample and every r-dependent quantity can be approximated with an x-only dependent quantity. In particular the total field can be approximated as

$$\mathbf{E}(x,t) = \mathbf{E}(x,t) + \mathbf{e}(x,t) + \frac{2\pi}{c} n_{(at)} \frac{d}{dt} \int_0^x dx' \mathbf{d}_{(at)}(x',t).$$

(7)

For optically thin samples the dipole oscillations in two points $x_1$ and $x_2$ are time-shifted by an amount $|x_1 - x_2|/c$ which is much smaller than the inverse of the typical dipole frequencies. Therefore $\mathbf{d}_{(at)}(x',t)$ is weakly dependent on $x'$ inside the gas and we can approximate the integral in Eq. (7) with $x \mathbf{d}_{(at)}(t)$. The mathematical simplification brought about by this approximation is that every atom can be evolved separately. Consider the state $\ket{\Psi(t)} \equiv \ket{\Psi(\ell y z t)}$ of an atom at the interface in $x = \ell$ and let $\hat{H} = \hat{H}(\ell y z)$ and $\mathbf{d} = \mathbf{d}(\ell y z)$ be the atomic Hamiltonian and dipole operator. Then for $r = (\ell y z)$ Eq. (6) reads

$$i \frac{d}{dt} \ket{\Psi(t)} = \left[ \hat{H} + \mathbf{E}(\ell y z) \cdot \mathbf{d} \right] \ket{\Psi(t)},$$

(8)

with

$$\mathbf{E}(\ell y z) = \mathbf{E}(\ell y z) + \mathbf{e}(\ell y z) + \frac{2\pi \ell}{c} n_{(at)} \frac{d}{dt} \mathbf{d}_{(at)}(t)$$

(9)

and

$$\mathbf{d}_{(at)}(t) = \langle \Psi(t) | \mathbf{d} | \Psi(t) \rangle,$$

(10)

Equations (8-10) form a close system of three coupled equations. The same equations could be solved for $e = 0$ to obtain the probe-free atomic dipole $\mathbf{d}_p(\ell y z)$ and hence the probe-induced dipole $\mathbf{d}_{p(\ell y z)}$ in accordance with Eq. (5). Having $\mathbf{d}_p(\ell y z)$ we can calculate the probe-induced dipole density $\mathbf{d}_p(\ell y z) = n_{(at)} \mathbf{d}_p(\ell y z)$ and subsequently the component of the electric field propagating toward the detector from Eq. (4), i.e.,

$$\mathbf{E}_p(\ell y z) = \mathbf{e}(\ell y z) + \frac{2\pi \ell}{c} \frac{d}{dt} \mathbf{d}_p(\ell y z).$$

(11)

Fourier transforming $\mathbf{E}_p(\ell y z)$ and $\mathbf{e}(\ell y z)$ the TPA spectrum $\mathcal{S}(\omega)$ in Eq. (3) follows:

$$\mathcal{S}(\omega) = -2\text{Im} \left[ \omega \mathbf{S}^* (\ell \omega) \cdot \mathbf{d}_p(\ell \omega) \right] - \frac{2\pi \ell}{Sc} \left| \omega \mathbf{d}_p(\ell \omega) \right|^2.$$  

(12)

The numerical solution of Eqs. (8-10) is impractical for heavy atoms or moderate size molecules. In the next section we describe a statistical approach which avoids solving the Schrödinger equation for the many-electron system. This approach is based on the Nonequilibrium Green’s Functions combined with the Generalized Kadanoff-Baym Ansatz (GKBA), and it has been successfully applied to the electron gas, two-band model semiconductors and more recently bulk silicon, Hubbard chains and donor-acceptor junctions. Here we extend it to perform first-principles simulations of laser-driven quantum systems.

III. NEGF APPROACH

We work in the formalism of second quantization and denote by $\hat{c}_{\sigma} (\hat{c}_{\sigma}^\dagger)$ the annihilation (creation) operator for an electron in the orbital $\phi_{\sigma}(r)$ with spin $\sigma = +, -$. Without loss of generality, the basis $\{ \phi_{\sigma} \}$ is taken orthonormal. The unperturbed Hamiltonian reads

$$\hat{H} = \sum_{ij} \hbar \omega_{ij} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \frac{1}{2} \sum_{ijmn} v_{ijmn} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma}^\dagger \hat{c}_{m\sigma} \hat{c}_{n\sigma},$$

(13)

with $\hbar \omega_{ij} \equiv \int d\mathbf{r} \varphi_i^\dagger(\mathbf{r}) \left[ -\frac{1}{2} \nabla^2 + V_n(\mathbf{r}) \right] \varphi_j(\mathbf{r})$ the one-electron integrals with nuclear potential $V_n$ and

$$v_{ijmn} \equiv \int d\mathbf{r} d\mathbf{r'} \varphi_i^\dagger(\mathbf{r}) \varphi_j^\dagger(\mathbf{r'}) \varphi_m(\mathbf{r'}) \varphi_n(\mathbf{r})$$

(14)

the four-index Coulomb integrals. Similarly the dipole operator reads

$$\hat{\mathbf{d}} = \sum_{ij} d_{ij} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma}$$

(15)

with $d_{ij} \equiv \int d\mathbf{r} \varphi_i^\dagger(\mathbf{r}) \mathbf{r} \varphi_j(\mathbf{r})$ the matrix elements of the dipole vector. The time-dependent average of the atomic dipole, see Eq. (10), is therefore

$$\mathbf{d}_{(at)}(t) = \sum_{ij} d_{ij} \langle \Psi(t) | \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} | \Psi(t) \rangle.$$  

(16)

Let us introduce the evolution operator $\mathcal{U}(t, t_0)$ from a time $t_0$ when the system is unperturbed to an arbitrary time $t$. Then $|\Psi(t)\rangle = \mathcal{U}(t, t_0) |\Psi_{0}\rangle$ with $|\Psi_{0}\rangle$ the state of the unperturbed system. To distinguish the Heisenberg from the Schrödinger picture we insert a subscript “H” to an operator $\hat{O}(t)$ in the Schrödinger picture, $\hat{O}_H(t) \equiv \mathcal{U}(t_0, t) \hat{O}(t) \mathcal{U}(t, t_0)$. The lesser ($G^<$) and greater ($G^>$) Green’s functions are defined according to

$$G^<_{ij}(t,t') \equiv i \langle \Psi_0 | \hat{c}_{i\sigma,H}(t') \hat{c}_{j\sigma,H}(t) | \Psi_0 \rangle,$$

(17a)

$$G^>_{ij}(t,t') = -i \langle \Psi_0 | \hat{c}_{i\sigma,H}(t) \hat{c}_{j\sigma,H}(t') | \Psi_0 \rangle,$$

(17b)

and have the property

$$G^<_{ij}(t,t') = -[G^>_j(t',t)]^*,$$

(18)
implying that from $G^S$ with times $t \geq t'$ or $t \leq t'$ we can reconstruct the entire $G^S$. In this work we consider spin-compensated systems with no spin-orbit interaction; hence $G^S$ takes the same value for $\sigma = \uparrow, \downarrow$. The NEGF formalism, however, is not limited to this case and it can easily be generalized to Hamiltonians that are not diagonal in spin space. From $G^S$ at equal times we can calculate the time-dependent average of any one-body operator; in particular the atomic dipole in Eq. (16) reads $d^{(\text{atom})}(t) = -2i \sum_{ij} d_{ij} G^R_{ij}(t,t)$.

The lesser and greater Green’s functions satisfy nonlinear integro-differential equations known as the Kadanoff-Baym equations (KBE).\textsuperscript{19–32} At present the numerical solution of the KBE for inhomogeneous systems is possible only for moderate size basis sets,\textsuperscript{49–55} and still the CPU time is of the order of a few days for a propagation of $\sim 10^5$ time steps and $\sim 10^4$ basis functions. Considering that a TPA spectrum typically requires $10^4$ time steps for every delay between the pump and probe pulses, the KBE are not feasible in this context. A way to drastically reduce the computational effort consists in making the GKBA\textsuperscript{35}

\begin{align}
G^< (t,t') &= -G^R (t,t') \rho (t') + \rho (t) G^A (t,t'), \quad (19a) \\
G^> (t,t') &= G^R (t,t') \rho (t') - \rho (t) G^A (t,t'), \quad (19b)
\end{align}

In these equations $G^R (t,t') = [G^A (t',t)]^\dagger$ is the retarded Green’s function and $\rho (t) = -i G^< (t,t) = 1 - \rho (t) = 1 - i G^> (t,t)$ is the one-particle density matrix (the quantity of interest for the calculation of the atomic dipole). The GKBA is exact in the Hartree-Fock (HF) approximation and it is expected to be accurate in systems with well-defined quasiparticles, see Ref. 48 for a recent discussion. From the KBE we can easily derive, see Appendix A, the following equation of motion for $\rho$ (in matrix form)

\begin{align}
-i \frac{d}{dt} \rho (t) + [h_{\text{HF}} (t), \rho (t)] = i I (t) - \text{H.c.}, \quad (20)
\end{align}

where the HF single-particle Hamiltonian reads

\begin{align}
h_{\text{HF},ij} (t) = h_{ij} + \varepsilon (t) \cdot d_{ij} + \sum_{nm} w_{imnj} \rho_{nm} (t), \quad (21)
\end{align}

with

\begin{align}
w_{imnj} \equiv 2 t_{imnj} - v_{imjn}, \quad (22)
\end{align}

and the collision integral reads (in matrix form)

\begin{align}
I (t) = \int_{-\infty}^t dt' \left[ \Sigma^< (t,t') G^> (t',t) + \Sigma^> (t,t') G^< (t',t) \right]. \quad (23)
\end{align}

The correlation self-energy $\Sigma^S$ appearing in Eq. (23) is a functional of $G^< \text{ and } G^>$ which, in turn, are functionals of $\rho$ through the GKBA. Thus, Eq. (20) is a closed nonlinear integro-differential equation for $\rho$ once we specify the functional form of the self-energy and the retarded Green’s function.

In this work we present results obtained using the second-Born (2B) self-energy

\begin{align}
\Sigma^S_{ij} (t,t') = \sum_{nm} v_{irpn} w_{mqsj} G^S_{nm} (t,t') G^S_{ij} (t',t) G^R_{pq} (t',t) G^S_{sr} (t',t) \quad (24)
\end{align}

whose diagrammatic representation is shown in Fig. 2. For the retarded Green’s function we consider

\begin{align}
G^R (t,t') = -i \theta (t - t') T \left[ e^{-i \int_t^{t'} dt' h_{\text{HF}} (t')} \right] \quad (25)
\end{align}

where $T$ is the time-ordering operator. In Ref. 48 we discussed how to include correlation effects (beyond HF) in $G^R$ and showed their importance in quantum transport calculations. For the finite systems analyzed here, however, we found that the HF $G^R$ of Eq. (25) is accurate enough. Similar findings were recently found in strongly correlated systems as well.\textsuperscript{56,57} In addition to the simplicity of Eq. (25), the use of a HF $G^R$ within the NEGF+GKBA scheme guarantees the satisfaction of all basic conservation laws.\textsuperscript{47}

We emphasize that the equation of motion for $\rho$ is an equation with memory since the evaluation of the collision integral at time $t$ involves the density matrix at all times $t' \leq t$. Using the GKBA expression for the lesser and greater Green’s function the collision integral can be rewritten as

\begin{align}
I_{ik} (t) = \sum_{nm} \sum_{pq} v_{irpn} w_{mqsj} \int_{-\infty}^t dt' \left[ (G^R (t,t') \rho (t'))_{nm} (G^R (t,t') \rho (t'))_{pq} (\rho (t') G^A (t',t))_{sr} (\rho (t') G^A (t',t))_{jk} \\
+ (G^R (t,t') \rho (t'))_{nm} (G^R (t,t') \rho (t'))_{pq} (\rho (t') G^A (t',t))_{sr} (\rho (t') G^A (t',t))_{jk} \right]. \quad (26)
\end{align}
From Eq. (26) it is evident that the computational cost scales quadratically with the maximum propagation time. The quadratic scaling can be reduced to a linear scaling if the collision integral is evaluated in the Markov approximation. The Markov approximation consists in neglecting memory effects by replacing the pair $\rho(t')$ and $\rho'(t')$ with the pair $\rho(t)$ and $\rho(t)$, and in using the equilibrium HF retarded Green's function $G^R(t, t') = -i\delta(t - t') \exp[-iH^R_{eq}(t - t')]$, with $h^R_{eq}$ the HF single-particle Hamiltonian of the equilibrium system. In this case the integral over $t'$ can be done analytically and the collision integral becomes a quartic polynomial in $\rho(t)$. Thus the equation of motion for $\rho$ reduces to a nonlinear differential equation. In the next sections we benchmark the Markov approximation against Configuration Interaction (CI) and full NEGF+GKBA simulations.

IV. HELIUM

In this section we simulate the TPA spectrum of helium atoms recently measured in Ref. 11. Helium is among one of the most studied systems in the context of TPA, and density $n_{eff} = 2.4 \times 10^{17} \text{ cm}^{-3}$. The pump and probe pulses are given in the main text. Results obtained with CI (top-left), HF (top-right), 2B (bottom-left) and the Markovian 2B (bottom-right).

FIG. 3: (Color online) Density plot of the TPA spectrum (normalized to the maximum height) of a helium gas with $\ell_{eff} = 0.16 \text{ mm}$ and density $n_{eff} = 2.4 \times 10^{17} \text{ cm}^{-3}$. The pump and probe pulses are $2\pi \times 10^{-13} \text{ cm}$ and $40.000$ time steps in CI, and $\Delta t = 0.0012 \text{ fs}$ and $7.500$ time steps in NEGF+GKBA. In CI, we observe that the time-step to achieve convergence in CI is about an order of magnitude smaller than in NEGF+GKBA, thereby CI requires about ten-times more time steps than NEGF+GKBA to have the same frequency resolution.

In Fig. 3 we compare the TPA spectrum in the four different schemes for a gas with $\ell_{eff} = 0.16 \text{ mm}$ and density $n_{eff} = 2.4 \times 10^{17} \text{ cm}^{-3}$. The spectra are obtained by a fast Fourier transform of $d^R_{eff}(t)$ calculated using a time-step $\Delta t = 0.0012 \text{ fs}$ and $40.000$ time steps in CI, and $\Delta t = 0.006 \text{ fs}$ and $7.500$ time steps in NEGF+GKBA. In CI, the equilibrium peak of the $1s - 2p$ transition is not accurate. Nevertheless, as our interest is in the evolution of the $1s - 2p$ transition as the pump-probe delay is varied, the VB2 basis is suitable for our purposes. The overall shape of the CI TPA spectrum is well reproduced by all NEGF approximations, see, e.g., the size of the splitting and the relaxation toward the equilibrium spectrum. The only relevant difference is a uniform frequency shift.

We obtained the one- and two-electron integrals as well as the dipole matrix elements from the SMILES package using the VB2 Slater-type orbital (STO) basis, consisting of 15 basis functions. We performed CI time-propagation as well as NEGF+GKBA propagations in the HF ($\Sigma = 0$), 2B and Markovian 2B approximation. As a general comment we observe that the time-step to achieve convergence in CI is about an order of magnitude smaller than in NEGF+GKBA, thereby CI requires about ten-times more time steps than NEGF+GKBA to have the same frequency resolution.
the damping mechanism of the dipole moment is not driven by electron-electron scattering. The damping mechanism does not have its origin in the radiative decay either (in He relaxation through radiative decay is no shorter than hundreds of fs). We will explain the origin of the damping mechanism in Section IV A. Here we address a different issue, i.e., the bending of the AT absorption peaks as $\tau$ decreases and the possible formation of a subsplitting structure.

Consider a three-level He model with basis functions $1_s$, $2s$, $2p$ in the oscillating state induced by the probe. If the probe is switched off at $t = 0$ then for $t > 0$ the probe-induced dipole (along the $x$ component) is $d_p(t) = d_{0x} \sin(\omega_0 t)$, where $\omega_0$ is the energy of the $1s-2p$ transition and $d_{0x} = d_x|_{s=2p}$ is the dipole matrix element. At time $-\tau > 0$ we switch on a pump field $E(t) = E_0 e^{-\gamma_P(t+\tau)} \sin(\omega_P(t+\tau))$, of duration $\Delta_P \sim 1/\gamma_P$, which couples the $2s$ and $2p$ levels. We choose $\omega_P$ in resonance with the energy of the $2s-2p$ transition and work in the rotating wave approximation. Then for times $t > -\tau$ we find $d_p(t) = d_{0x} \sin(\omega_0 t) \cos(E_0 d_0 e^{-\gamma_P(t+\tau)})$ (we assumed for simplicity that the matrix element $d_x|_{s=2p} = d_{0x}$). Collecting these results and introducing an exponential damping $\gamma \sim 1/W$ (the origin of which is explained in Section IV A) we can write

$$\frac{d_p(t)}{d_{0x}} = e^{-\gamma t} \sin(\omega_0 t) \times \begin{cases} 1 & t < -\tau \\ \cos(E_0 d_0 e^{-\gamma_P(t+\tau)}) & \gamma_P \end{cases}$$

and $d_p(t) = 0$ for $t < 0$ (before the probe). This equation clearly illustrates the behavior previously discussed. For $t > -\tau + 1/\gamma_P$ the cosine is essentially constant. Thus, if $\gamma \ll \gamma_P$ (hence $W \gg \Delta_P$) then the pump modifies the $\sin(\omega_0 t)$ profile only in the time window $(-\tau, -\tau + 1/\gamma_P)$, too short to change the position of the peaks in $\pm \omega_0$ of the Fourier transform $\tilde{d}_p(\omega)$. Let us now consider the opposite limit $\gamma \gg \gamma_P$ (hence $W \ll \Delta_P$). For all times $t$ smaller than $1/\gamma$ (after this time the dipole is exponentially small) we can approximate the cosine with $\cos(E_0 d_0 (t+\tau))$. In this approximation the Fourier transform $\tilde{d}_p(\omega)$ has a simple analytic form and for, e.g., $\omega \simeq \omega_0 + E_0 d_0$, we find

$$-\text{Im}[\tilde{d}_p(\omega)] \simeq \frac{e^{-\gamma t} \gamma}{4} \frac{\gamma \cos(\omega t) + (\omega - E_0 d_0) \sin(\omega t)}{(\omega - E_0 d_0)^2 + \gamma^2}$$

with $\omega \equiv \omega - \omega_0$. The denominator of Eq. (28) has a minimum in $\omega = E_0 d_0$ which is independent of $\tau$. However, the maximum of $-\text{Im}[\tilde{d}_p(\omega)]$ does not coincide with the minimum of the denominator as $\tau$ decreases from zero. For small negative $\tau$ the maximum occurs at frequencies $\omega \simeq E_0 d_0 (1 + \gamma \Delta_P) / \gamma_0$. This explains the bending of the AT absorption peaks (a similar analysis can be done for frequencies $\omega \simeq \omega_0 - E_0 d_0$).

Noteworthy, the full Fourier transform of the dipole in Eq. (27) yields spectra that resemble very closely those in Figs. 3 and 4. In Fig. 5 we display the density plot of $-\omega \text{Im}[\tilde{d}_p(\omega)] \propto \tilde{S}(\omega)$ for $\omega_0 = 21.3$ eV, $E_0 d_0 = 0.5$ eV, $\gamma_P = 0.41$ eV (corresponding to a duration $\Delta_P \sim 10$ fs) and for $\gamma = 0.21$ eV (left panel, compare with Fig. 3) and $\gamma = 1.37$ eV (right panel, compare with Fig. 4). Equation (27) does therefore provide a convenient analytic parametrization of experimental TPA spectra. For longer pumps Eq. (27) pre-

FIG. 4: (Color online) Density plot of the TPA spectrum (normalized to the maximum height) of a helium gas with $\ell_{\text{eff}} = 1.6$ mm and density $n^{(\text{at})} = 2.4 \times 10^{17} \text{ cm}^{-3}$. The pump and probe pulses are given in the main text. Results obtained with CI (top-left), HF (top-right), 2B (bottom-left) and the Markovian 2B (bottom-right).
The damping of the probe-induced dipole in the helium gas has been systematically investigated both numerically and experimentally in Ref. 66. Here we provide a transparent explanation based on the analytic solution of the Schrödinger equation (8) for a simple two-level model with two-particle states $|1s^2\rangle$ and $|1s2p_x\rangle$. We take the equilibrium Hamiltonian $\hat{H}$ diagonal on this basis and let $c_1$ and $c_2$ be the corresponding eigenenergies. We denote by $d_0 = \langle 1s^2|\hat{d}_x|1s2p_x\rangle$ the $x$-component of dipole matrix element and write the dressed probe field along $x$ in accordance with Eq. (11), i.e., $\mathcal{E}_p(t) = \epsilon(t) + \alpha d(t)$, where $\alpha = 2\pi \epsilon_{\text{eff}}(\omega)/c > 0$ and $d(t) = \langle \Psi(t)|\hat{d}_x|\Psi(t)\rangle$. Expanding the time-dependent two-particle state as $|\Psi(t)\rangle = c_1(t)|1s^2\rangle + c_2(t)|1s2p_x\rangle$ we find

$$i\dot{c}_1(t) = \epsilon(c_1(t) + d_0\mathcal{E}_p(t)c_2(t)), \quad (29a)$$

$$i\dot{c}_2(t) = \epsilon(c_2(t) + d_0\mathcal{E}_p(t)c_1(t)). \quad (29b)$$

For any real $\mathcal{E}_p$ the time evolution of the coefficients $c_1$ and $c_2$ is unitary. The expression of the time-dependent dipole in terms of $c_1$ and $c_2$ reads $d(t) = 2d_0\Re[c_1(t)c_2(t)]$. We can get a differential equation for $d$ if we introduce two more real functions $g(t) = (\Im[c_1(t)c_2(t)])$ and $f(t) = |c_1(t)|^2 - |c_2(t)|^2$. It is a matter of simple algebra to show that after the probe (hence $\epsilon(t) = 0$) these three functions satisfy the

$$\dot{f}(t) = -2d_0\omega_0 g(t), \quad (30a)$$

$$\dot{g}(t) = -\frac{\omega_0}{2d_0} d(t) + \alpha d(t) f(t), \quad (30b)$$

$$\dot{d}(t) = 2d_0\omega_0 g(t). \quad (30c)$$

where we introduced $\omega_0 = \epsilon_1 - \epsilon_2$. Taking the time derivative of Eq. (30c) and using Eq. (30b) we find

$$\dot{d}(t) + \omega_0^2 d(t) - 2\alpha d_0^2\omega_0 f(t)\dot{d}(t) = 0. \quad (31)$$

With the help of Eq. (30c) we rewrite Eq. (30a) as $\dot{f}(t) = -\frac{\alpha}{\omega_0^2}\dot{d}(t)$. Therefore $f(t)$ is a monotonically decreasing function of time and, by definition, it is bounded between $-1$ and $1$. This implies that $\lim_{t\to\infty} f(t) = f_\infty \in (-1, 1)$. If $f_\infty$ were positive then the long-time solution of Eq. (31) would be an oscillatory function with an exponentially increasing amplitude, in contradiction with the fact that $d(t) \in (d_0, -d_0)$. We conclude that the limiting value $f_\infty \in (-1, 0)$ independently of the initial condition. Consequently, for large $t$ the function $d(t)$ oscillates at frequency $\omega_0$ with an amplitude decaying as $e^{-\gamma t}$, where $\gamma = 2\alpha d_0^2\omega_0 |f_\infty|$. Our analysis does explain the physical origin of the damping as well as the dependence of $\gamma$ on the thickness and density of the gas. In fact, $\gamma \propto \alpha \propto \ell_{\text{eff}}(\omega_0)$; therefore the larger the thickness and/or the density is and the faster the amplitude of the dipole oscillations decays.

V. PUMP-INDUCED IONIZATION

In this Section we extend the NEGF+GKBA formalism to deal with ionization processes induced by the pump. For this purpose it is convenient to work with the HF orbitals. Let $\rho^{\text{eq}}$ be the equilibrium density matrix and

$$h_{\text{HF},ij}^{\text{eq}} = h_{ij} + \sum_{mn} w_{ijnm}^{\text{eq}} \rho_{nm}^{\text{eq}}. \quad (32)$$
the equilibrium HF Hamiltonian in the original basis. The HF orbitals \( \varphi_\mu(r) = \sum_j a_{\mu j}^{\text{HF}} \varphi_j(r) \) diagonalize both \( h_{\text{HF}}^\text{id} \) and \( \rho_{\mu\nu}^\text{id} \), and are orthonormal. To distinguish the HF basis from the original basis we use greek letters to label the former. We have

\[
h_{\text{HF,\mu\nu}}^\text{id} = \delta_{\mu\nu} \epsilon_\mu,
\]

and \( \rho_{\mu\nu}^\text{id} = \delta_{\mu\nu} n_\nu \) where \( n_\nu = 1 \) if \( \epsilon_\nu < \epsilon_F < 0 \) and \( n_\mu = 0 \) otherwise, \( \epsilon_F \) being the Fermi energy.

In finite systems like atoms and molecules the HF orbitals with \( \epsilon_\nu > 0 \) are states in the continuum. These are the states that get occupied by the photoelectron in an ionization process. We assume that the Coulomb interaction between photoelectrons and bound electrons is negligible and set to zero the two-electron integrals \( v_{\mu\rho\alpha\beta} \) with at least one of the four indices in the continuum (this amounts to neglect Auger transitions). Then the self-energy has nonvanishing matrix elements only in the continuum (this amounts to neglect Auger transitions). We assume that the Coulomb interaction between photoelectrons and bound electrons is negligible and set to zero the two-electron integrals \( v_{\mu\rho\alpha\beta} \). Therefore, the \( \Sigma \) self-energy is replaced by the ion-electrons is not conserved) and it is calculated like in Eq. (23)

\[
\langle \varphi_j(t) \rangle = \frac{1}{\mathcal{Z}} \int \mathcal{D} \varphi \mathcal{D} \rho \mathcal{D} \delta \mathcal{D} \rho' \exp \left\{ \int dt \left[ \mathcal{L}(t) - \frac{1}{2} \mathcal{L}(t) \right] \right\},
\]

where

\[
\mathcal{L}(t) = \sum_{\mu \nu} \left[ \frac{\partial}{\partial t} \delta_{\mu\nu} \right] \varphi_\mu(t) \varphi_\nu(t) + \frac{1}{2} \left( \sum_{\rho \sigma} \delta_{\rho\sigma} \varphi_\rho^{\text{HF}}(t) \varphi_\rho^{\text{HF}}(t) - \varphi_\rho(t) \varphi_\rho(t) \right).
\]

In Appendix A we prove that the equation of motion for the density matrix with both indices in the bound sector reads

\[
-i \frac{d}{dt} \rho(t) + [h_{\text{HF}}(t), \rho(t)] = i \frac{1}{2} \left[ \mathcal{L}(t) + \frac{1}{2} \mathcal{L}(t) \right] - \text{H.c.}.
\]

In Eq. (34) every matrix has indices running over the bound states. The integral \( I_{\text{ion}} \) accounts for the pump-induced ionization (since \( \text{Tr}[\rho_{\text{ion}} + \text{H.c.}] \neq 0 \) the number of bound electrons is not conserved) and it is calculated like in Eq. (23) except that the correlation self-energy is replaced by the ion self-energy \( \Sigma_{\text{ion}} \). The latter has a vanishing lesser part and a greater part given by (see Appendix A)

\[
\Sigma_{\text{ion}}^{\geq}(t, t') = \sum_{ij} \mathcal{E}_i(t) \sigma^{ij}(t - t') \mathcal{E}_j(t').
\]

Here \( \mathcal{E}_i \) is the \( i \)-th component of the electric field \( \mathcal{E} = (\mathcal{E}_x, \mathcal{E}_y, \mathcal{E}_z) \) and the tensor

\[
\sigma^{ij}(t - t') = -i \sum_{\alpha, \beta} d_{i, \mu\alpha} e^{-i \omega_\alpha(t - t')} d_{j, \nu\beta},
\]

where \( d_i \) is the \( i \)-th component of the vector of matrices \( d = (d_x, d_y, d_z) \) and the sum over \( \alpha \) runs in the continuum. In Fourier space

\[
\tilde{\sigma}_{\mu\nu}^{ij}(\omega) = -2\pi i \sum_{\alpha, \beta} d_{i, \mu\alpha} \delta(\omega - \epsilon_\alpha) d_{j, \nu\beta}
\]

\approx 2i \sum_{\alpha, \beta} d_{i, \mu\alpha} \text{Im} \left[ \frac{1}{\omega - \epsilon_\alpha + i\eta} \right] d_{j, \nu\beta},
\]

where \( \eta \) is a positive constant of the order of the level spacing of the continuum states. Typically the ionization is caused by the action of a pump pulse with a Fourier transform peaked around some frequency \( \omega_P \) (larger than the ionization energy of the system). Therefore, \( \Sigma_{\text{ion}}^{\geq} \) is dominated by those terms in \( \sigma(t - t') \) that oscillate at frequency \( \epsilon_\alpha \approx \omega_P \). By virtue of this observation we implement a time-local approximation

\[
\tilde{\sigma}_{\mu\nu}^{ij}(\omega) \approx \tilde{\sigma}_{\mu\nu}^{ij}(\omega_P),
\]

which implies \( \sigma_{\mu\nu}^{ij}(t - t') = \tilde{\sigma}_{\mu\nu}^{ij}(\omega_P) \delta(t - t') \). Substituting this result into Eq. (35) yields

\[
\Sigma_{\text{ion}}^{\geq}(t, t') = -i \delta(t - t') \Gamma_{\mu\nu}(t),
\]

where

\[
\Gamma_{\mu\nu}(t) = i \sum_{ij} \mathcal{E}_i(t) \tilde{\sigma}_{\mu\nu}(\omega_P) \mathcal{E}_j(t)
\]

is a self-adjoint positive-definite matrix for all times \( t \).

The time-local approximation allows us to simplify the integral \( I_{\text{ion}}(t) \) appearing in Eq. (34). Taking into account that \( \Sigma_{\text{ion}}^{\geq} = 0 \) we have

\[
I_{\text{ion}}(t) = \int_{-\infty}^t dt' \Sigma_{\text{ion}}^{\geq}(t, t') G^<(t', t) = \Gamma(t) \rho(t).
\]

Inserting this result into Eq. (34) we finally obtain

\[
-i \frac{d}{dt} \rho(t) + [h_{\text{HF}}(t), \rho(t)] = i \left\{ \Gamma(t), \rho(t) \right\} = i \mathcal{L}(t) - \text{H.c.}
\]

where the curly brackets signify an anticommutator. Equation (42) constitutes the generalization of the NEGF+GKBA formalism to open systems. 48

VI. KRYPTON

We apply the formalism of the previous Section to address a retardation effect observed by Goulielmakis et al. 34 in the TPA spectrum of a krypton gas. In the experiment a strong pump is shone on the gas, electrons from the 4p shell are expelled and an admixture of Kr atoms and Kr\(^{2+}\) ions, with \( n = 1, 2, 3 \ldots \) is formed. The admixture is subsequently probed with an ultrafast pulse, thus inducing transitions from the 3d to the 4p shell. The main focus in Ref. 34 was on the coherent oscillations of the peak intensities of the Kr\(^{2+}\) ion as a function of the pump-probe delay \( \tau \). However, the experimental TPA spectrum reveals another interesting feature as a function of \( \tau \). The absorption peaks of Kr\(^{2+}\) develop with the absorption peaks of Kr\(^{+}\), implying that it is faster to expel one electron than two electrons. To reproduce this retardation effect theoretically a formalism for the TPA spectrum of an evolving admixture is needed. The NEGF+GKBA approach is in principle suitable for this purpose. As we shall see, important qualitative aspects of the admixture are intimately related to the diagrammatic structure of the self-energy.

The Kr gas is ionized by a few-cycle NIR pump \( E(t) = (E(t), 0, 0) \) with \( E(t) = E_0 \sin^2(\pi t/\Delta_p) \sin(\omega_p t) \) for \( 0 < t < \Delta_p \). The experimental pump intensity is \( I_0 = 7 \times 10^{14} \text{ W/cm}^2 \), corresponding to an electric field \( E_0 = \sqrt{2I_0/c\varepsilon_0} = 7.2 \times 10^{13} \text{ V/m} \), the duration of the pump pulse is \( \Delta_p = 7.6 \text{ fs} \) and the NIR frequency is \( \omega_p \sim 1.65 \text{ eV} \). After a time \( \tau \) the Kr admixture is probed with an extreme ultraviolet attosecond pulse \( e(t) = (e(t), 0, 0) \), with \( e(t) = e_0 \sin^2(\pi(t - \tau)/\Delta_p) \sin(\omega_p(t - \tau)) \) for \( \tau < t < \tau + \Delta_p \).
FIG. 7: (Color online) Transient ionization yield per spin (solid line) in HF and 2B (indistinguishable) and amplitude of the pump pulse (dashed line) in arbitrary units.

Here $\tau = \tilde{\tau} - (\Delta P - \Delta p)/2$ is the time-distance between the maxima of the pump and probe pulses. The probe pulse has duration $\Delta p \sim 150$ as, it is centered at frequency $\omega_p = 80$ eV and it has an intensity $i_0 \sim 10^{11}$ W/cm$^2$, which corresponds to an electric field $e_0 = 8.6 \times 10^8$ V/m. We discard the dressing of the probe field and solve the equation of motion for $\rho$ with $\mathcal{E} = e$.

The one- and two-electron integrals as well as the dipole matrix elements have been calculated with the SMILES package$^{64,65}$ using the 66 STO basis functions taken from Ref. 67. As we are not interested in the coherent oscillations of the peak intensities we do not include the spin-orbit coupling responsible for the splitting of the $4p$ and $3d$ orbitals. Thus we should expect one main absorption peak per ion, corresponding to transitions from the $4p$ to the $3d$ shell. We find eighteen HF states with energy below zero. The remaining HF states are used to construct the ionization self-energy according to Eq. (37). The simulations show that electrons are essentially removed from the $4p$ shell in agreement with the analysis of Ref. 34. In Fig. 7 we display the transient ionization yield, i.e., the expelled charge per spin, during the action of the pump. The charge is expelled in pockets at a rate of twice the frequency of the laser pulse, in agreement with the CI calculations.$^{12,34}$ Interestingly, the HF and 2B yields are indistinguishable. The situation is drastically different for the TPA spectrum, with the 2B approximation performing much better than the HF one (see below). Whether the absorption onset of Kr$^{2+}$ is earlier than the absorption onset of Kr$^{1+}$ is the central issue addressed below.

In the upper panel of Fig. 8 we report the TPA spectrum of the Kr admixture in the HF approximation. We have propagated the system for $\sim 50$ fs after the action of the probe with a time step $\Delta t = 0.0025$ fs (corresponding to 20,000 time steps) and then broadened the Fourier transform of $d_p(t)$ by 0.8 eV to account for the experimental resolution. The result is extremely disappointing. The HF TPA spectrum constitutes of one doublet (merged in Fig. 8 in one single line-shape due to the broadening) with a simultaneous raise of both peaks. The peaks correspond to transitions from the $3d$ shell to either the $4p_x$ orbital or the $4p_{y,z}$ orbitals. In fact, these transitions are nondegenerate in the HF approximation. As the pump is polarized along $x$ the $4p_x$ orbital looses more charge than the $4p_{y,z}$ orbitals, thereby breaking the degeneracy (albeit only slightly). Even more noteworthy, however, is the absence of spectral structures due absorption of multiply ionized Kr atoms. The numerical simulation has been repeated with pump fields of different frequencies and intensities but no sign of other absorption peaks has been observed. The first important conclusion of this preliminary study is that the appearance of absorption peaks in multiply ionized Kr atoms is a correlation effect.

We have then included correlation effects at the level of the Markovian 2B approximation but the outcome has not changed (not shown). The main difference between the HF
and the Markovian 2B spectra is an overall frequency shift. The so far accumulated numerical evidence leads us to conjecture that any time-local approximation (no memory) to the self-energy is doomed to fail. We mention that the equation of motion for $\rho$ with a time-local $\Sigma$ has the same mathematical structure of the Time-Dependent Density Functional Theory (TDDFT) equations at the level of the Adiabatic Local Density Approximation (ALDA). Hence, TDDFT spectra at the ALDA level would also fail in capturing the absorption peaks of multiply ionized atoms. The second important conclusion is that static correlation effects are not enough.

Dynamical correlation effects are contained in the full (non-local in time) 2B self-energy. We have solved the equations of motion for $\rho$ with the collision integral of Eq. (26). The TPA spectrum is shown in the lower panel of Fig. 8. We clearly distinguish two structures corresponding to the TPA spectrum of Kr$^{1+}$ and Kr$^{2+}$. In fact, the energy gap between the structures is consistent with the $\sim 3$ eV experimental gap of these two ions. Remarkably, the high-energy structure develops $\sim 3$ fs after the low-energy one. This is the aforementioned retardation effect which we have just proved to be within reach of the NEGF+GKBA approach. Furthermore, the obtained delay is commensurate with the 5 fs delay observed in experiments. A non-local in time self-energy is crucial for the appropriate description of the Kr (and probably of any other) evolving admixture.

Although the 2B approximation represents a noticeable improvement over time-local approximations there still remains one issue to address. The experimental TPA spectrum contains small absorption peaks attributable to transitions in the Kr$^{1+}$ ion. We have not been able to see these structure within the 2B approximation. Although we are not aware of any formal result relating the possibility of describing multiply ionized atoms to the diagrammatic structure of the self-energy we observe that the kernel $\delta \Sigma / \delta G$ contains at most one particle-hole excitation in HF and two particle-hole excitations in 2B. It is therefore tempting to argue that in order to observe the absorption peaks of Kr$^{n+}$ the kernel $\delta \Sigma / \delta G$ should contain at least $n$ particle-hole excitations, which implies that $\Sigma$ should contain diagrams of order at least $n$ in the interaction. Finding a general solution to this problem would certainly be valuable and contribute to advance the understanding of many-body diagrammatic theories.

VII. CONCLUSIONS

We have introduced a NEGF+GKBA approach to transient photoabsorption experiment suitable for pump fields of arbitrary strength, frequency and duration and for any delay between pump ad probe pulses (hence for delays in the overlapping regime too). The size of the arrays in NEGF calculations scales quadratically with the number of basis functions. The Coulomb interaction between electrons is included diagrammatically through the correlation self-energy and the possibility of ionization can be described through the ionization self-energy.

The approach has been benchmarked against the TPA spectrum of He reported in Ref. 11. Helium is a weakly correlated system and all self-energy approximations have been shown to agree with the CI results. We have provided a simple yet rigorous explanation of the bending of the AT absorption peaks and derived a useful formula for fitting the experimental TPA spectra. We have also addressed the exponential damping of the probe-induced dipole and related it to the thickness and density of the gas.

A more severe test for the NEGF+GKBA approach is the TPA spectrum of Kr reported in Ref. 34. We have shown that for a proper description of the evolving admixture of the Kr ions the self-energy should have memory. This is not the case for the HF and Markovian 2B self-energies which yield the TPA spectrum of a pure Kr$^{1+}$ ion. We argue that the situation does not change in TDDFT with ALDA exchange-correlation potentials. On the contrary, the full 2B self-energy leads to a second structure in the TPA spectrum that is assigned to Kr$^{2+}$ and that develops about 2-3 fs after the first, in fair agreement with the experiment. More theoretical and numerical work is needed to understand the relation between self-energy diagrams and the emergence of absorption peaks due to multiply ionized atoms.

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Appendix A: The embedded GKBA equation for $\rho$

The lesser and greater Green’s functions follow from the Keldysh Green’s function $G(z, z')$ with arguments $z$ and $z'$ on the Keldysh contour. In particular $G^< (G^>)$ is the Keldysh $G$ with the first (second) contour argument on the forward branch and the second (first) contour argument on the backward branch. The Keldysh $G$ satisfies the equations of motion (in matrix form)

$$\left[i \frac{d}{dz} - h_{\text{HF}}(z)\right]G(z, z') = \delta(z, z')$$

$$+ \int dz \Sigma(z, \bar{z})G(\bar{z}, z') \tag{A1}$$

$$G(z, z')[\left[-i \frac{d}{dz'} - h_{\text{HF}}(z')\right]] = \delta(z, z')$$

$$+ \int dz G(z, \bar{z})\Sigma(\bar{z}, z') \tag{A2}$$

where the integral is over the Keldysh contour. Choosing $z$ on the backward branch and $z'$ on the forward branch, and applying the Langreth rules we obtain the equations of motion
for $G^<$

$$
\left[ i \frac{d}{dt} - h_{HF}(t) \right] G^<(t, t') = \int dt' \Sigma^R(t, t') G^<(t, t') \\
+ \int dt' G^<(t, t') \Lambda^A(t, t').
$$

(A3)

Thus, the continuum states can be downfolded in an exact way into an effective equation for $G^<$. In the bound-bound sector Eq. (A1) reads

$$
\left[ i \frac{d}{dz} - h_{HF}^{cb}(z) \right] G^{cb}(z, z') = \left[ \mathcal{E}(z) \cdot \mathbf{d}^{cb} \right] G^{cb}(z, z')
$$

(A11)

whereas in the continuum-bound sector the same equation reads

$$
\left[ i \frac{d}{dz} - h_{HF}^{cb}(z) \right] G^{cb}(z, z') = \left[ \mathcal{E}(z) \cdot \mathbf{d}^{cb} \right] G^{cb}(z, z') = 0.
$$

(A12)

We can make use of the block structure of $h_{HF}$ and $\Sigma$ to simplify the equations of motion for the Keldysh $G$. In the bound-bound sector Eq. (A1) reads

$$
\left[ i \frac{d}{dz} - h_{HF}^{bb}(z) \right] G^{bb}(z, z') = \left[ \mathcal{E}(z) \cdot \mathbf{d}^{bc} \right] G^{cb}(z, z')
$$

$$
= \left[ \mathcal{E}(z) \cdot \mathbf{d}^{cb} \right] G^{cb}(z, z')
$$

(A13)

and rewrite Eq. (A12) in integral form

$$
G^{cb}(z, z') = \int dz'' G^{cc}(z, z'') \left[ \mathcal{E}(z'') \cdot \mathbf{d}^{cb} \right] G^{bb}(z'', z').
$$

(A14)

Inserting Eq. (A14) into Eq. (A11) we find

$$
\left[ i \frac{d}{dz} - h_{HF}^{bb}(z) \right] G^{bb}(z, z') = \delta(z, z')
$$

$$
+ \int dz'' \left[ \Sigma^{bb}(z, z'') + \Sigma^{cb}_{ion}(z, z'') \right] G^{bb}(z'', z'),
$$

(A15)

with the ionization self-energy defined according to

$$
\Sigma^{bb}_{ion}(z, z') = \left[ \mathcal{E}(z') \cdot \mathbf{d}^{bc} \right] g^{cc}(z, z') \left[ \mathcal{E}(z') \cdot \mathbf{d}^{cb} \right].
$$

(A16)

Thus, the continuum states can be downfolded in an exact way into an effective equation for $G^{cb}$. A similar equation can be derived starting from Eq. (A2) and reads

$$
G^{bb}(z, z') = \left[ i \frac{d}{dz} - h_{HF}^{bb}(z') \right] G^{bb}(z, z')
$$

$$
\int dz G^{bb}(z, z') \left[ \Sigma^{bb}(z, z') + \Sigma^{cb}_{ion}(z, z') \right].
$$

(A17)

Below we use Eqs. (A15, A17) to generate an equation for the density matrix in the bound-bound sector. To lighten the notation we omit the upper indices “$bb$”, so a matrix with no upper indices is a matrix in the bound-bound sector.

Comparing Eqs. (A15, A17) with Eqs. (A1, A2) we deduce that the equations of motion for $G^<$ are the same as Eqs. (A3, A4) except that the correlation self-energy is replaced by $\Sigma + \Sigma^{bb}_{ion}$. Therefore, the equation of motion for $\rho$ is the same as Eq. (20) except that the collision integral is calculated with $\Sigma^< + \Sigma^{bc}_{ion}$. From Eq. (A13) we have

$$
g^{cc,bb}_{\mu\nu}(t, t') = -i \sum_{\alpha} U^{cc}_{\mu\alpha}(t) n_{\alpha}^{<} \left[ U^{cc}(t') \right]_{\alpha\nu}^+.
$$

(A18)
where \( U^{cc}(t) = T[e^{-i \int_0^t dt' \hat{H}_{cc}(t')} ] \) is the evolution operator in the continuum sector whereas \( n_\alpha^c = n_\alpha \) and \( n_\alpha^c = 1 - n_\alpha \). For \( \alpha \) in the continuum we have \( e_\alpha > \epsilon_F \) and hence \( n_\alpha^c = 0 \) (which implies \( g^{\alpha c} = 0 \)) and \( n_\alpha^c = 1 \). The evolution operator takes a very simple form if we ignore the effect of the pump between continuum states, i.e., if we approximate \( d^{cc} \approx 0 \). In this case \( h_{IHF, \mu \nu} = \delta_{\mu \nu} \epsilon_\mu \), see Eqs. (A6, A7), and hence

\[
g_{\mu \nu}^{cc, >}(t, t') = -i d_{\mu \nu} e^{-i \epsilon_\mu (t-t')} , \tag{A19}
\]

From Eq. (A16) it follows that the greater ionization self-energy is

\[
\Sigma_{\text{ion}, \mu \nu}(t, t') = -i \sum_\alpha [ \mathcal{E}(t) \cdot d_{\mu \alpha}^{hc} e^{-i \epsilon_\alpha (t-t')} [ \mathcal{E}(t') \cdot d_{\nu \alpha}^{hc} ] ] , \tag{A20}
\]

which agrees with Eqs. (35, 36).
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