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Time-resolved photoabsorption in finite systems: A first-principles NEGF approach

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Abstract. We describe a first-principles NonEquilibrium Green's Function (NEGF) approach to time-resolved photoabsortion spectroscopy in atomic and nanoscale systems. The method is used to highlight a recently discovered dynamical correlation effect in the spectrum of a Krypton gas subject to a strong ionizing pump pulse. We propose a minimal model that captures the effect, and study the performance of time-local approximations versus time-nonlocal ones. In particular we implement the time-local Hartree-Fock and Markovian second Born (2B) approximation as well as the exact adiabatic approximation within the Time-Dependent Density Functional Theory framework. For the time-nonlocal approximation we instead use the 2B one. We provide enough convincing evidence for the fact that a proper description of the spectrum of an evolving admixture of ionizing atoms requires the simultaneous occurrence of *correlation* and *memory* effects.

1. Introduction

Time-resolved photoabsorption spectroscopy is a cutting edge experimental technique to probe quantum systems in nonstationary states [1–5]. The sample is driven out of equilibrium by a strong pump pulse (whose intensity can exceed 10^{15} W/cm^2) and subsequently probed with a weak ultrashort (down to hundreds of as) pulse. By measuring the energy per unit frequency carried by the transmitted probe as a function of the delay between the pump and probe pulses one obtains the time-dependent photoabsorption spectrum. From this spectrum it is possible to read out information like, e.g., charge/exciton dynamics [6–19], dynamical screening effects [20–23] and several other nonequilibrium properties [24–33].

For optically thin samples (atoms, molecules and more generally nanostructures) the transmitted probe pulse can be expressed in terms of the time-dependent *probe-induced* change of the dipole moment [34–41]. The latter is defined as the difference between the time-dependent dipole moment originating from the pump+probe fields and the time-dependent dipole moment originating from the pump only. Both quantities can be calculated from the time-dependent

quantum average of the dipole operator over the many-electron state of the system evolving according to the Schrödinger equation with the appropriate electric field. Due to electron correlations these averages are difficult to compute using the Configuration Interaction (CI) method since the number of configurations scales exponentially with the number of electrons. CI is often implemented in the so called Single Active Electron (SAE) approximation [42, 43] which, by construction, neglects double or higher excitations. An alternative approach, statistical in nature, to tackle the problem is provided by Time-Dependent Density Functional Theory (TDDFT) [44]. In TDDFT the interacting many-body system is mapped onto a fictitious noninteracting system having the same density, and hence the same dipole moment, as the interacting one [45, 46]. Therefore, TDDFT is ideal to study much larger systems than those accessible by CI. However, most TDDFT calculations are performed using the Adiabatic Local Density Approximation (ALDA) for the potential of the fictitious system but, unfortunately, the ALDA potential suffers from the same drawbacks of the SAE approximation in CI [47, 48]. Other critical drawbacks of the ALDA potential in the context of photoabsorption are that (i) the renormalization of the molecular levels due to the nearby presence of a highly polarizable structure or medium is poorly described [49–54] and (ii) single-particle excitation with a long-range charge-transfer character are missed [55–57].

In Ref. [41] we investigated the possibility of using a statistical approach based on NonEquilibrium Green's Functions (NEGF) [58–62]. The NEGF approach is computationally more expensive than TDDFT but still more convenient than CI. From the theoretical point of view the advantage of NEGF over TDDFT is that the relevant electron-electron scattering processes can be incorporated through a proper selection of Feynman diagrams for the self-energy Σ from which the Green's function $G = G_0 + G_0\Sigma G$ can be self-consistently calculated, G_0 being the noninteracting Green's function. The aforementioned drawbacks of the ALDA potential in TDDFT are absent in NEGF already with rather simple self-energies. It is also worth observing that the self-energy $\Sigma[G]$ is a functional of the Green's function and hence the NEGF approach is a *nonperturbative* approach as it amounts to sum a subset of Feynman diagrams to infinite order in the interaction strength.

Actually, the most convenient method to calculate the nonequilibrium G is not through the Dyson equation $G = G_0+G_0\Sigma G$ but through the so called Kadanoff-Baym Equations (KBE) [58–62]. The KBE are nonlinear integro-differential equations for the lesser and greater components of G, $G^<$ and $G^>$ respectively. For a given self-energy the computational cost for the solution of the KBE scales like N_t^3 [63–71], where N_t is the number of time steps. This poses severe limitations to the maximum propagation time, essentially preventing the use of NEGF for an acceptable frequency resolution of the time-resolved photoabsorption spectra. The scaling of the computational cost can be reduced from N_t^3 to N_t^2 using the Generalized Kadanoff-Baym Ansatz (GKBA) [72]. The GKBA is an ansatz for $G^{\lessgtr}(t,t')$ in terms of the one-particle density matrix $\rho(t) = -iG^<(t,t)$, and allows for collapsing the KBE into a single nonlinear integro-differential equation for the one-time quantity $\rho(t)$. The ansatz is exact for the Hartree-Fock (HF) self-energy and an approximation for correlated self-energies (beyond HF). Nevertheless, this approximation turns out to be extremely accurate in systems with well-defined quasiparticles (like atoms and molecules) and more generally whenever the collision time is much smaller than the quasiparticle lifetime [72]. We wish to emphasize here that within the GKBA the NEGF formalism is converted into a theory for the one-particle density matrix which could provide useful hints for the development of TDDFT functionals beyond the ALDA.

In this work we briefly describe the NEGF+GKBA approach to time-resolved photoabsorption spectroscopy and apply it to model Hamiltonians with few bound states and a continuum of states. Our purpose is to shed light on a recently discovered dynamical correlation effect in a gas of Krypton atoms [28, 41]. In the experiment the gas is perturbed by a strong near infrared pump pulse responsible for the ionization of some of the atoms. During the action of the pump the

neutral gas evolves into an admixture of Kr atoms and Kr^{n+} ions with $n = 1, 2, 3, \ldots$. By probing the admixture with a weak, extreme ultraviolet attosecond pulse having a delay τ with respect to the pump pulse one can monitor the evolution of the photoabsorption spectrum as a function of τ. The development of absorption peaks in different spectral regions are fingerprints of the presence of Kr ions with different charge. Our calculations have shown that the HF self-energy as well as other time-local self-energies, e.g., the Markovian second-Born (M2B), capture at most the absorption of Kr^{1+} [41]. Thus, time-local approximations to the self-energy do not describe the absorption of multiply ionized Kr atoms. Instead the full (nonlocal in time) second-Born (2B) approximation correctly captures the absorption of Kr^{1+} and Kr^{2+} as well as the retardation in the onset of the absorption peak of Kr^{2+} with respect to the onset of the absorption peak of Kr^{1+}. In this work we introduce a simple model Hamiltonian to clarify the role of time-nonlocal correlations in the formation of an admixture of multiply ionized atoms. The simplicity of the model also allows for obtaining an analytic expression of the exact exchange-correlation potential of static DFT, and hence to perform exact adiabatic TDDFT simulations. We show that similarly to the HF and the M2B approximations also the exact adiabatic approximation of TDDFT fails in reproducing the absorption peaks of multiply ionized atoms. This provides a conclusive evidence for the fact that a proper description of the time-resolved spectrum of an evolving admixture of ions requires the simultaneous inclusion of *correlations* and *memory* effects.

2. Time-resolved photoabsorption spectrum

We consider a finite system like an atom or a molecule driven out of equilibrium by a pump pulse. Choosing the pump frequency appropriately electrons can be expelled from the system, thus changing its absorption properties. Our goal is to study the photoabsorption spectrum of the system during the ionization process. For this purpose we assign a single-particle basis consisting of a certain number of orthonormal bound wavefunctions $\{\varphi_i(\mathbf{r})\}$ and of a continuum of extended wavefunctions $\{\varphi_k(\mathbf{r})\}$. Let $\hat{c}_{\alpha\sigma}$ ($\hat{c}^\dagger_{\alpha\sigma}$) be the annihilation (creation) operator for an electron with spin $\sigma =\uparrow,\downarrow$ in $\varphi_\alpha(\mathbf{r})$, where α can be either a bound index or a continuum index. For ionization processes from the valence shells Auger recombination are unlikely to occur. Furthermore, as we are not interested in the energy of the photoelectrons, we ignore the Coulomb repulsion between bound and extended electrons. The equilibrium Hamiltonian then reads

$$\hat{H}_{\rm eq} = \sum_{k,\sigma} \epsilon_k \hat{c}^\dagger_{k\sigma}\hat{c}_{k\sigma} + \sum_{ij,\sigma} h_{ij}\hat{c}^\dagger_{i\sigma}\hat{c}_{j\sigma} + \frac{1}{2}\sum_{\substack{ijmn\\ \sigma\sigma'}} v_{ijmn}\hat{c}^\dagger_{i\sigma}\hat{c}^\dagger_{j\sigma'}\hat{c}_{m\sigma'}\hat{c}_{n\sigma}. \tag{1}$$

Without any loss of generality we have chosen the set $\{\varphi_k(\mathbf{r})\}$ to be the set of continuum eigenstates with energy ϵ_k of the single particle Hamiltonian $h(\mathbf{r}) = -\frac{\nabla^2}{2} + V_{\rm n}(\mathbf{r})$, $V_{\rm n}(\mathbf{r})$ being the nuclear potential. The one- and two-electron integrals appearing in Eq. (1) are defined according to $h_{ij} \equiv \int d\mathbf{r}\, \varphi^*_i(\mathbf{r}) h(\mathbf{r}) \varphi_j(\mathbf{r})$ and $v_{ijmn} \equiv \int d\mathbf{r}\, d\mathbf{r'}\, \varphi^*_i(\mathbf{r})\varphi^*_j(\mathbf{r'})\varphi_m(\mathbf{r'})\varphi_n(\mathbf{r})/|\mathbf{r}-\mathbf{r'}|$. The interaction between light and matter is treated in the dipole approximation. Let $\boldsymbol{\mathcal{E}}(t)$ be the electric field and $\mathbf{d}_{\alpha\beta} \equiv \int d\mathbf{r}\, \varphi^*_\alpha(\mathbf{r})\mathbf{r}\varphi_\beta(\mathbf{r})$ the matrix elements of the dipole vector. The Hamiltonian of the light-matter interaction reads

$$\hat{H}_{\rm LM}(t) = \sum_{\alpha\beta,\sigma} \left[\boldsymbol{\mathcal{E}}(t)\cdot\mathbf{d}_{\alpha\beta}\right] \hat{c}^\dagger_{\alpha\sigma}\hat{c}_{\beta\sigma} \tag{2}$$

where the sum runs over all bound and continuum states. The time-evolution of any many-body state $|\Psi(t)\rangle$ is therefore governed by the Schrödinger equation $i\frac{d}{dt}|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle$ where

$$\hat{H}(t) = \hat{H}_{\rm eq} + \hat{H}_{\rm LM}(t) \tag{3}$$

is the total Hamiltonian.

Let $\mathbf{E}(t)$ be the pump field and $\mathbf{e}(t)$ the probe field. The pump field is typically a few-cycle pulse with frequency centered around the transition from a valence state to a low-energy continuum state. Thus for $\boldsymbol{\mathcal{E}} = \mathbf{E}$ we can ignore the terms in the sum of Eq. (2) where both indices α, β are continuum indices. On the contrary the main effect of the probe field is to promote transitions in the bound sector. Therefore we can restrict the sum in Eq. (2) to bound indices $\alpha, \beta = i, j$ for $\boldsymbol{\mathcal{E}} = \mathbf{e}$. It follows that for $\boldsymbol{\mathcal{E}} = \mathbf{E}$ we have

$$\hat{H}_{\rm LM}(t) = \hat{H}_P(t) \equiv \sum_{ij,\sigma} \left[\mathbf{E}(t)\cdot\mathbf{d}_{ij}\right] \hat{c}^\dagger_{i\sigma}\hat{c}_{j\sigma} + \sum_{ik,\sigma} \Big(\left[\mathbf{E}(t)\cdot\mathbf{d}_{ik}\right] \hat{c}^\dagger_{i\sigma}\hat{c}_{k\sigma} + \text{H.c.} \Big), \tag{4}$$

whereas for $\boldsymbol{\mathcal{E}} = \mathbf{E} + \mathbf{e}$ we have

$$\hat{H}_{\rm LM}(t) = \hat{H}_{P\&p}(t) \equiv \hat{H}_{\rm P}(t) + \sum_{ij,\sigma} \left[\mathbf{e}(t)\cdot\mathbf{d}_{ij}\right] \hat{c}^\dagger_{i\sigma}\hat{c}_{j\sigma}. \tag{5}$$

These approximations are based on physical considerations and simplify the presentation. However, they are not necessary for the theory developed in the next section.

We are interested in calculating the time-resolved photoabsorption spectrum $\mathfrak{S}(\omega)$ for frequencies corresponding to transitions between bound many-particle states. Using the convention that quantities with a tilde denote the Fourier transform of the corresponding time-dependent quantities, the spectrum for the frequencies of interest is given by

$$\mathfrak{S}(\omega) = -2\text{Im}\left[\omega\, \tilde{\mathbf{e}}^*(\omega)\cdot\tilde{\mathbf{d}}_p(\omega)\right] \tag{6}$$

where $\mathbf{d}_p$ is the *probe-induced* change of the time-dependent average of the dipole operator $\hat{\mathbf{d}} = \sum_{ij,\sigma} \mathbf{d}_{ij}\hat{c}^\dagger_{i\sigma}\hat{c}_{j\sigma}$. In order to calculate $\mathbf{d}_p$ one has to calculate the time-dependent average $\mathbf{d}_{P\&p}(t)$ of the dipole operator with $\hat{H}_{\rm LM} = \hat{H}_{P\&p}$, the time-dependent average $\mathbf{d}_P(t)$ of the dipole operator with $\hat{H}_{\rm LM} = \hat{H}_P$ and then subtract the two

$$\mathbf{d}_p(t) \equiv \mathbf{d}_{P\&p}(t) - \mathbf{d}_P(t). \tag{7}$$

We observe that $\tilde{\mathbf{d}}_p(\omega)$ is *not* proportional to $\tilde{\mathbf{e}}(\omega)$ since the system is out of equilibrium. The spectrum $\mathfrak{S}(\omega)$ depends on the entire function $\mathbf{e}(t)$ and not only on its frequency component $\tilde{\mathbf{e}}(\omega)$. In particular $\mathfrak{S}(\omega)$ depends on the delay between the pump and probe pulses.

3. NEGF+GKBA approach

In this section we describe the NEGF+GKBA approach to calculate $\mathbf{d}_{P\&p}$. The same approach can be used for $\mathbf{d}_P$ by setting $\mathbf{e} = 0$. The average $\mathbf{d}_{P\&p}(t) = -2i\sum_{ij}\mathbf{d}_{ij}G^<_{ji}(t,t)$ where $G^<(t,t)$ is the equal-time lesser component of the Green's function $G(z,z')$ with arguments on the Keldysh contour. The latter is a matrix function with indices in both the bound and extended sector and it satisfies the equation of motion

$$\left[i\frac{d}{dz} - h_{\rm HF}(z)\right] G(z,z') = \delta(z,z') + \int d\bar{z}\, \Sigma(z,\bar{z})G(\bar{z},z'). \tag{8}$$

In accordance with the considerations of the previous section the HF hamiltonian in Eq. (8) reads

$$h_{{\rm HF},\alpha\beta}(z) = \begin{cases} \delta_{kk'}\epsilon_k & (\alpha,\beta) = (k,k') \\ \mathbf{E}(z)\cdot\mathbf{d}_{ik} & (\alpha,\beta) = (i,k) \\ \mathbf{E}(z)\cdot\mathbf{d}_{ki} & (\alpha,\beta) = (k,i) \\ h_{ij} + [\mathbf{E}(z)+\mathbf{e}(z)]\cdot\mathbf{d}_{ij} + \sum_{mn} w_{imnj}\rho_{nm}(z) & (\alpha,\beta) = (i,j) \end{cases} \tag{9}$$

with $w_{imnj} \equiv 2v_{imnj} - v_{imjn}$ and $\rho_{nm}(z) = -iG_{nm}(z, z^+) = -iG^<_{nm}(t, t)$ independently of the branch of the contour where z lies. The correlation self-energy Σ is a functional of G and has nonvanishing matrix elements only in the bound sector. As for the calculation of $\mathbf{d}_{P\&p}$ we only need G with bound indices we project Eq. (8) onto the bound sector and find

$$\sum_m \big[i\frac{d}{dz}\delta_{im} - h_{\mathrm{HF},im}(z)\big]G_{mj}(z,z') \; - \; \sum_k \big[\mathbf{E}(z)\cdot\mathbf{d}_{ik}\big]G_{kj}(z,z') \\ = \delta(z,z')\delta_{ij} + \sum_m \int d\bar{z}\, \Sigma_{im}(z,\bar{z})G_{mj}(\bar{z},z'). \tag{10}$$

Similarly we can obtain an equation for G_{kj}. Taking into account Eq. (9) we find

$$\big[i\frac{d}{dz} - \epsilon_k\big]G_{kj}(z,z') - \sum_m \big[\mathbf{E}(z)\cdot\mathbf{d}_{km}\big]G_{mj}(z,z') = \delta(z,z'). \tag{11}$$

Next we define the noninteracting Green's function g_k as the solution of

$$\big[i\frac{d}{dz} - \epsilon_k\big]g_k(z,z') = \delta(z,z') \tag{12}$$

with Kubo-Martin-Schwinger boundary conditions, and rewrite Eq. (11) in integral form

$$G_{kj}(z,z') = \int d\bar{z}\, g_k(z,\bar{z}) \sum_m \big[\mathbf{E}(\bar{z})\cdot\mathbf{d}_{km}\big]G_{mj}(\bar{z},z'). \tag{13}$$

Substitution of this result into Eq. (10) leads to

$$\sum_m \big[i\frac{d}{dz}\delta_{im} - h_{\mathrm{HF},im}(z)\big]G_{mj}(z,z') = \delta(z,z')\delta_{ij} + \sum_m \int d\bar{z}\, \big[\Sigma_{\mathrm{ion}}(z,\bar{z}) + \Sigma(z,\bar{z})\big]_{im} G_{mj}(\bar{z},z'), \tag{14}$$

where we defined the ionization self-energy according to

$$\Sigma_{\mathrm{ion},ij}(z,z') = \sum_k \big[\mathbf{E}(z)\cdot\mathbf{d}_{ik}\big]g_k(z,z')\big[\mathbf{E}(z')\cdot\mathbf{d}_{kj}\big]. \tag{15}$$

Although the ionization self-energy resembles the embedding self-energy in quantum transport [73–75] its physical origin is different, see below.

Equation (14) is a closed equation for the Green's function in the bound sector. Subtracting from it the adjoint of Eq. (14) and setting $z = z^+$ we obtain an equation for the one-particle density matrix $\rho_{ij}(t)$ with indices in the bound sector

$$-i\frac{d}{dt}\rho(t) + [h_{\mathrm{HF}}(t), \rho(t)] = i\,[I(t) + I_{\mathrm{ion}}(t)] - \mathrm{H.c.}. \tag{16}$$

where the collision integral $I(t)$ reads

$$I(t) = \int_{-\infty}^{t} dt' \big[\Sigma^<(t,t')G^>(t',t) + \Sigma^>(t,t')G^<(t',t)\big], \tag{17}$$

and the ionization integral $I_{\mathrm{ion}}(t)$ is defined as $I(t)$ with Σ_{ion} in place of Σ. Due to the presence of the off-diagonal in time $G^{\lessgtr}$ in the collision and ionization integrals Eq. (16) is not a closed equation for ρ. The GKBA is an approximation that relates $G^{\lessgtr}(t,t')$ to $\rho(t)$ and $\rho(t')$ [72],

thereby transforming Eq. (16) into a closed integro-differential equation for ρ. According to the GKBA

$$G^<(t,t') = -G^{\rm R}(t,t')\rho(t') + \rho(t)G^{\rm A}(t,t'), \tag{18a}$$
$$G^>(t,t') = +G^{\rm R}(t,t')\bar\rho(t') - \bar\rho(t)G^{\rm A}(t,t'), \tag{18b}$$

with $\bar\rho_{ij} = \delta_{ij} - \rho_{ij}$. It is worth noting that the GKBA results are extremely sensitive to the choice of the quasiparticle propagator $G^{\rm R}(t,t') = [G^{\rm A}(t',t)]^\dagger$. For $\Sigma = 0$ (no correlations) the Green's functions $G^\lessgtr$ that solve the equation of motion (10) can be written as in Eqs. (18) provided that

$$G^{\rm R}(t,t') = -i\theta(t-t')\,T\left[e^{-i\int_{t'}^t d\bar t\, h_{\rm HF}(\bar t)}\right] \tag{19}$$

is the HF propagator. The numerical simulations presented in Ref. [41] show that for atomic systems the HF propagator yields accurate results in the correlated case too. Similar accuracies were recently reported for Hubbard clusters [76] and for the two-dimensional Anderson–Hubbard model [77]. A nice property of the HF propagator is that it guarantees the satisfaction of all basic conservation laws provided that the self-energies is conserving [78]. The results presented in this work have been obtained using Eq. (19). Nevertheless, it should be emphasized that the performance of the HF propagator is not always this good for all systems. In open systems, e.g., in molecular junctions attached to metallic electrodes, it is pivotal to include relaxation effects due to electron collisions and to the presence of the electrodes (electronic bath) [79].

Before closing this section let us discuss and simplify the ionization self-energy. From Eq. (12) we have

$$g_k^\lessgtr(t,t') = -if^\lessgtr(\epsilon_k)e^{-i\epsilon_k(t-t')} \tag{20}$$

with $f^<(\epsilon_k)$ the Fermi function and $f^> = 1 - f^<$. As the energy of the extended states is larger than the chemical potential we have $f^<(\epsilon_k) = 0$ and $f^>(\epsilon_k) = 1$. This implies that the lesser ionization self-energy vanishes. On the other hand the greater component reads

$$\begin{aligned}\Sigma^>_{{\rm ion},ij}(t,t') &= -i\sum_k \big[\mathbf{E}(t)\cdot\mathbf{d}_{ik}\big]e^{-i\epsilon_k(t-t')}\big[\mathbf{E}(t')\cdot\mathbf{d}_{kj}\big] \\ &= \mathbf{E}(t)\overleftrightarrow{\sigma}_{ij}(t-t')\mathbf{E}(t'),\end{aligned} \tag{21}$$

where in the last equality we defined the dyad $\overleftrightarrow{\sigma}_{ij}(t) = -i\sum_k \mathbf{d}_{ik}e^{-i\epsilon_k t}\mathbf{d}_{kj}$. In Fourier space

$$\overleftrightarrow{\sigma}_{ij}(\omega) = -2\pi i\sum_k \mathbf{d}_{ik}\,\delta(\omega-\epsilon_k)\,\mathbf{d}_{kj} \approx 2i\sum_k \mathbf{d}_{ik}\,{\rm Im}\left[\frac{1}{\omega-\epsilon_k+i\eta}\right]\mathbf{d}_{kj}, \tag{22}$$

where η is a positive constant of the order of the level spacing of the continuum states. We already mentioned that the pump pulse is a few cycles pulse centered around some ionization frequency ω_P. Therefore, $\Sigma^>_{\rm ion}$ is dominated by those terms in $\overleftrightarrow{\sigma}(t-t')$ that oscillate at frequency $\epsilon_k \simeq \omega_P$. Then, for simplicity, we implement a time-local approximation $\overleftrightarrow{\sigma}_{ij}(\omega) \approx \overleftrightarrow{\sigma}_{ij}(\omega_P)$ which implies $\overleftrightarrow{\sigma}_{ij}(t-t') = \overleftrightarrow{\sigma}_{ij}(\omega_P)\delta(t-t')$. Substituting this result into Eq. (21) yields

$$\Sigma^>_{\rm ion}(t,t') = -i\delta(t-t')\Gamma(t), \tag{23}$$

where

$$\Gamma_{ij}(t) = i\mathbf{E}(t)\overleftrightarrow{\sigma}_{ij}(\omega_P)\mathbf{E}(t) \tag{24}$$

is a self-adjoint positive-definite matrix for all times t. Inserting this result into the ionization integral the equation of motion (16) for ρ becomes

$$-i\frac{d}{dt}\rho(t) + [h_{\rm HF}(t),\rho(t)] - i\,\{\Gamma(t),\rho(t)\} = iI(t) - {\rm H.c.} \tag{25}$$

where the curly brackets signify an anticommutator. From Eq. (25) we clearly see that the ionization self-energy is responsible for taking away particles from the system. We also see that the draining of particles is effective only during the pump since $\Gamma(t)$ vanishes for $\mathbf{E}(t) = 0$. This corresponds to the intuitive picture that no ionization occurs after the pump pulse has passed through the system.

4. Numerical Results

In this Section we present numerical results on a simple model system in order to illustrate the performance of various approximations in describing the strong-field multiple ionization and the subsequent formation of a mixture of different ions. The model consists of two levels, one describing a $3d$ orbital (level 1) and the other describing a $4p$ orbital (level 2) of a Kr atom. The pump couples level 1 and 2 via the dipole matrix $\mathbf{d}_{ij} = \hat{\boldsymbol{x}} d_0(1-\delta_{ij})$, and at the same time couples level 2 to the continuum states, thus generating a ionization dyad $\overleftrightarrow{\sigma}_{ij}(\omega_P) = -i\sigma_0\delta_{i2}\delta_{j2}$. The remaining quantities of the model are $h_{ij} = \varepsilon_i\delta_{ij}$ and $v_{imnj} = U_{im}\delta_{ij}\delta_{mn}$, with $i,j = 1,2$. The numerical values of the model parameters have been chosen to closely reproduce energy- and time-scales of the first-principle simulations of Ref. [41]. These values are all reported in the caption of Fig. 1.

Equation (25) has been solved within two different approximations, namely HF and 2B. In the first case the collision integral $I(t)$ is identically zero, while within 2B we have [61]

$$I^{(2\mathrm{B})}_{ik}(t) = \sum_{\substack{nm\\pq\\sr}}\sum_{j} v_{irpn}w_{mqsj}\int_{-\infty}^{t} dt' \Big[G^{<}_{nm}(t,t')G^{<}_{pq}(t,t')G^{>}_{sr}(t',t)G^{>}_{jk}(t',t) + G^{>}_{nm}(t,t')G^{>}_{pq}(t,t')G^{<}_{sr}(t',t)G^{<}_{jk}(t',t)\Big]. \quad (26)$$

The real-time propagation has been performed with a time step $\Delta = 0.1$ a.u. and the spectra have been obtained by a discrete Fourier transform of the probe-induced dipole with $N_t = 10^4$ time-steps.

The atom, initially in its ground state with both levels filled, is ionized by a few-cycle pump $\mathbf{E}(t) = \boldsymbol{\eta}_P E(t)$ where $E(t) = E_0 \sin^2(\pi t/\Delta_P)\sin(\omega_P t)$. The expelled charge as a function of time is diplayed in Fig. 1. During the ionization process the occupation of level 1 remains roughly constant, meaning that the atom is loosing charge mainly from level 2. We also notice that the time-evolution of the expelled charge calculated within HF and 2B is essentially the same. This fact could suggest that the system is weakly correlated and that HF well captures the physics of the problem. However, the expelled charge is just one possible observable. Below we show that the HF and 2B photoabsorption spectra exhibit qualitative different features (although the local density in these two approximations agrees with high accuracy).

After a time τ the system is probed with an ultrashort pulse $\mathbf{e}(t) = \boldsymbol{\eta}_p e(t)$, with $e(t) = e_0 \sin^2(\pi(t-\tilde{\tau})/\Delta_p)\sin(\omega_p(t-\tilde{\tau}))$ for $\tilde{\tau} < t < \tilde{\tau} + \Delta_p$. Here $\tau = \tilde{\tau} - (\Delta_P - \Delta_p)/2$ is the time distance between the maxima of the pump and probe pulses. The frequency ω_p of the probe is chosen to promote the intra-atomic excitation between the levels 1 and 2.

The transient absorption spectrum within the HF approximation is displayed in the top-left panel of Fig. 2. Only one absorption peak appears, corresponding to the absorption of a singly ionized atom. We verified that the only effect of increasing the intensity of the pump is a shift in the position of the peak. We also varied the frequency and duration of the pump but we found no sign of absorption peaks due multiply ionized atoms. A single-peak absorption spectrum is also observed within the M2B approximation [41] (not shown), thus suggesting that the solution of Eq. (25) without the inclusion of memory effects in the self-energy cannot describe multiple ionization. However, the occurrence of multiple ionization (and subsequent absorption) for a strong enough pump is physically expected [28].

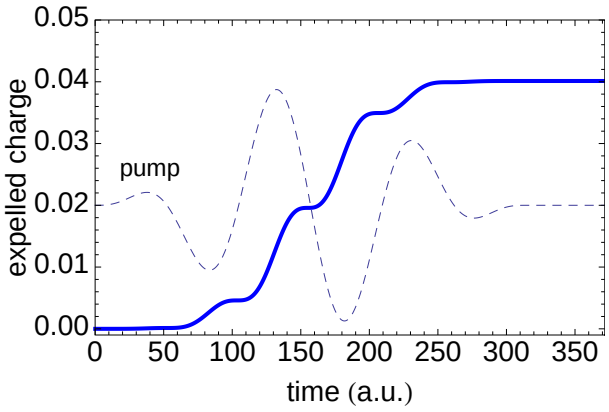

Figure 1: Total expelled charge (solid line) as a function of time. The pump profile $E(t)$ (in arbitrary units) is displayed as a dashed line. The model parameters (in atomic units) are: $\varepsilon_1 = -6.82$, $\varepsilon_2 = -2.25$, $U_{11} = 1.8$, $U_{22} = 0.5$, $U_{12} = U_{21} = 0.6$, $d_0 = 0.1$, $\sigma_0 = 1.8$, $E_0 = 0.14$, $\omega_P = 0.061$, $\Delta_P = 314$, $\boldsymbol{\eta}_P = \hat{\boldsymbol{x}}$. The expelled charge does not vary appreciably within the different approximations used in this work, see main text.

We then performed a full 2B simulation, by including time-nonlocal correlation effects according to Eq. (26), and calculated the time-resolved spectrum, see the top-right panel of Fig. 2. We clearly see the development of a second peak at higher energy, corresponding to the absorption of a doubly ionized atom. Furthermore the onset of the high-energy peak as function of τ is *retarded* with respect to the onset of the absorption peak at lower energy. This is consistent with the fact that expelling two electron requires more time than expelling one electron, and is also in qualitative agreement with both the experimental data [28] and our previous analysis [41].

We argue that the difference between time-local approximations, like HF and M2B, and the 2B approximation in describing the double ionization process is due to the absence of multiple excitations in the formers. Multiple excitation are a direct consequence of the simultaneous presence of *correlation* and *memory* effects in the self-energy. We therefore conjecture that correlations alone are not sufficient to describe the absorption of multiply ionized atoms as obtained from a real-time propagation. To reinforce this conjecture we have performed a TDDFT calculation using the exact-adiabatic (EX-ADIA) exchange-correlation potential of the model system. The EX-ADIA approximation produces the exact level densities in equilibrium. However, being it an adiabatic approximation, the EX-ADIA ignores memory effects entirely. Within this approximation the time propagation is performed by setting the collision integral $I(t) = 0$ and by replacing in Eq. (25) the HF Hamiltonian $h_{\rm HF}(t)$ with the Kohn-Sham Hamiltonian $h_{\rm KS}(t)$. The matrix element of the Kohn-Sham Hamiltonian are $h_{{\rm KS},ij}(t) = h_{ij} + [\mathbf{E}(t) + \mathbf{e}(t)] \cdot \mathbf{d}_{ij} + \delta_{ij} v_{\rm Hxc}[n_1, n_2]$, with $n_i = \rho_{ii}$ the density at level i. Since the occupation numbers commute with the equilibrium Hamiltonian, the exact Hartree+exchange-correlation potential $v_{\rm Hxc}$ of the model is a step-wise function of the total density $n_1 + n_2$ [80, 81], and is explicitly displayed in the bottom-left panel Fig. 2. In the bottom-right panel of Fig. 2 we show the corresponding EX-ADIA absorption spectrum. Notice that during and after the action of the pump the total number of electrons $n_1 + n_2$ remains close to four and hence the $v_{\rm Hxc}$ value stays on the highest energy plateau. This implies that $v_{\rm Hxc}$ is essentially a constant energy shift and consequently the spectrum is similar to the noninteracting spectrum. In particular the position of the peak is very close to the single-particle energy difference $\varepsilon_2 - \varepsilon_1 = 4.57$ a.u.. Even more important for our analysis is that in this case too only a single peak develops, no matter of the strenght of the pump, thus confirming our conjecture that time-local approximations do

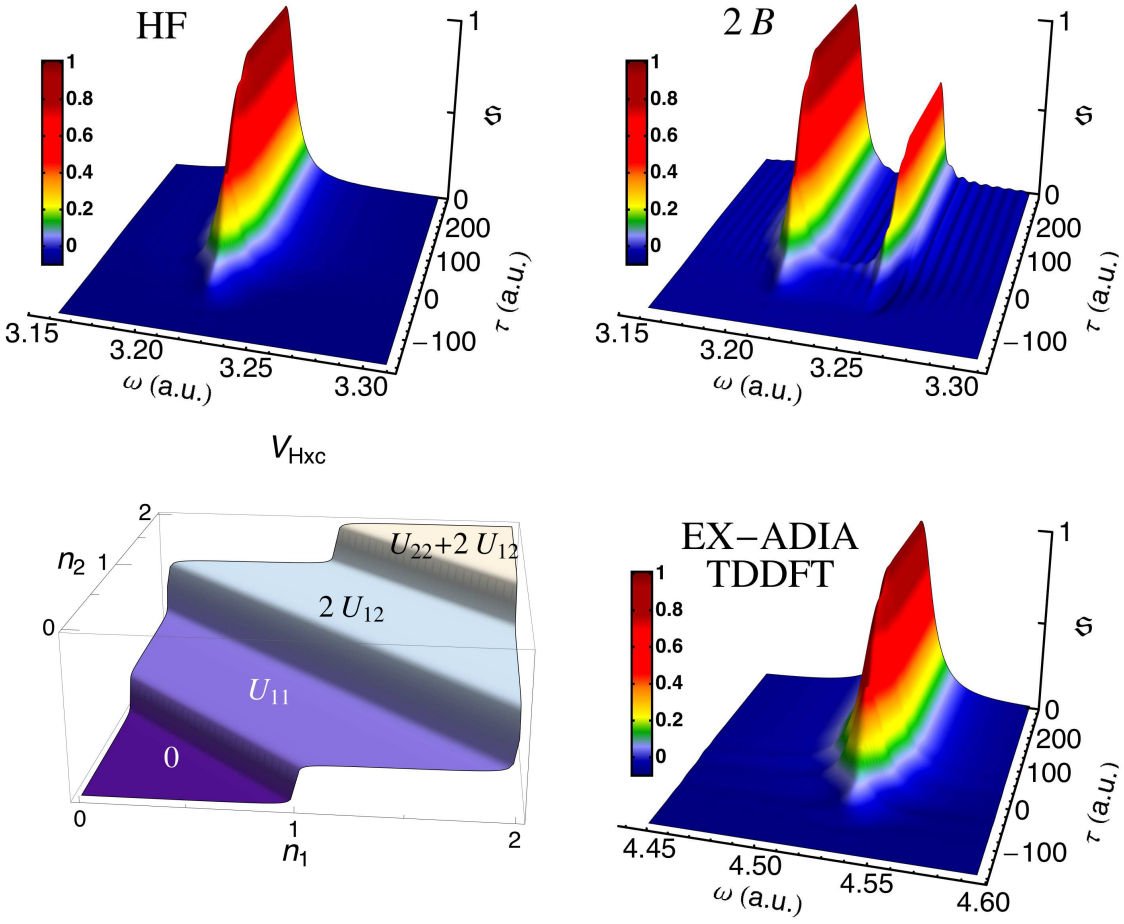

Figure 2: TPA spectrum (normalized to the maximum height) within HF (top-left), 2B (top-right) and EX-ADIA TDDFT (bottom-right). The probe parameters are (in atomic units) $e_0 = 1.7 \times 10^{-3}$, $\omega_p = 2.94$, $\Delta_p = 6.19$, $\boldsymbol{\eta}_p = \hat{\boldsymbol{x}}$. A broadening of 0.03 a.u. has been introduced in order to smoothen the finite-time Fourier transform of $\mathbf{d}_p(t)$. In the bottom-left panel we show the exact Hartree+exchange-correlation potential $v_{\rm Hxc}$ of the model as a function of the densities n_i of the two levels. The value of $v_{\rm Hxc}$ in the different plateaus is reported explicitly as a function of the repulsion parameters U_{ij}. The exact sharp discontinuities occurring at integer values of the total density $n_1 + n_2$ have been artificially broadened for graphical reasons.

not describe the absorption of multiply ionized atoms.

5. Conclusions

We discussed the recently proposed NEGF-based approach to calculate the time-resolved photoabsorption spectrum of finite systems [41]. The approach relies on the GKBA and amounts to solving an approximate equation of motion for the one-particle density matrix of the system. The external driving fields are treated to all orders, while correlation effects are included systematically by means of non-equilbrium many-body perturbation theory. Strong-field ionization can be accurately described via an appropriate ionization self-energy $\Sigma_{\rm ion}$, that accounts for the coupling to a continuum of extended states. The inclusion of $\Sigma_{\rm ion}$ renders the

real-time evolution not unitary and it is responsible for the loss of electrons during the ionization process.

We studied a two-level model coupled to a continuum to illustrate how different approximations perform in describing the time-resolved photoabsorption spectrum of finite systems under the action of a strong ionizing pump. The model stems from our analysis [41] of a recent experiment on Krypton [28] where the pump causes multiple ionization, as one can infer from the presence of different absorption peaks attributable to Kr^+, Kr^{2+} and Kr^{3+}. The proper description of the produced admixture of ions constitutes the central issue of the present work. We computed the spectrum using the time-local approximations HF and M2B for the collision integral as well as using the EX-ADIA approximation in TDDFT. In all cases we only observed the absorption from a single ion. Our numerical results show unambiguosly that 2B is the only scheme able to provide more than a single absorption peak. We conclude that the inclusion of time-nonlocal correlations is crucial for a correct description of the absorption spectra of an evolving admixture of ionizing atoms.

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