Signatures of collective electron dynamics in the angular distributions of electrons ejected during ultrashort laser pulse interactions with C⁺

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Abstract. We use the time-dependent R-matrix approach to investigate an ultrashort pump–probe scheme to observe collective electron dynamics in C⁺ driven by the repulsion of two equivalent p electrons. By studying the two-dimensional momentum distributions of the ejected electron as a function of the time-delay between an ultrashort pump pulse and an ionizing ultrashort probe pulse it is possible to track the collective dynamics inside the C⁺ ion in the time domain.

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1. Introduction

The recent generation of light pulses with durations in the attosecond range (1 as = $10^{-18}$ s) [1] represents an exciting new era for ultrafast science. Since the time structure of these light pulses is comparable to the timescale of atomic inner-shell processes, these pulses have opened up the possibility for the measurement of time-resolved electron dynamics inside atoms and molecules. The ultrafast techniques that have been demonstrated so far include attosecond streaking spectroscopy [2], which is an extension of streaking to positive-energy electrons and attosecond tunnelling spectroscopy [3], where electrons shaken up to the valence band are released from bound states by tunnel ionization. Such methods have led to the first real-time observations of the decay of an inner-shell vacancy [2] and of interference effects in the double ionization of Ne due to shake-up processes [3]. Attosecond streaking spectroscopy has also recently been extended to solid surfaces [4], promising time-resolved observations of electronic processes in condensed matter systems.

In all of these schemes, the attosecond pulses are formed from high harmonic radiation, which is typically generated from a laser-driven atomic gas. This high-harmonic generation process currently has a low conversion efficiency resulting in attosecond pulses with weak field strengths. As a consequence, ultrafast pump–probe experiments have so far only employed attosecond pulses as a pumping tool to initiate the ultrafast electron dynamics, with a second time-delayed few-cycle infrared light field used as a probe to sample the process under study. However, the recent demonstration of new harmonic radiation sources [5, 6] that are based on dense plasmas instead of atomic or molecular gases could enable the generation of attosecond pulses with higher field strengths, paving the way to implementing the so-called attosecond absorption spectroscopy [7]. In this scheme, the attosecond pulse is used as the probing tool with the future prospect of seeded free-electron laser (FEL)-based extreme ultra violet (XUV) sources used as the pump pulse to initiate the ultrafast dynamics. It is anticipated that such kinds of spectroscopy may answer one of the outstanding questions regarding atomic physics on the ultrashort timescale: how does electron–electron correlation affect the electron dynamics of atomic systems and can such collective dynamics be observed on the ultrashort timescale?

On the theoretical front, the most sophisticated methods available to describe ultrafast electron dynamics are methods devoted to two-active-electron systems [8, 9]. However, very few methods currently exist for treating general multielectron atoms irradiated by intense ultrashort light fields, and those that do typically employ the single-active-electron (SAE) approximation [10]. Within the SAE approximation, only one electron is assumed to be active. As a consequence, ultrafast electron–electron interactions inside atoms have so far been investigated only to a limited extent. Most investigations have primarily focused on the influence of dielectronic interactions on two-photon double ionization of He [11]–[13]. Dielectronic repulsion can be studied in more detail in excited states. For example, a recent theoretical investigation [14] proposed using an attosecond light pulse to doubly ionize a superposition of low-lying doubly excited states in He. By measuring the momentum vectors of the two ejected electrons in coincidence, it would be possible to observe the time-varying collective behaviour of the two electrons.

In a more recent theoretical study [15], a genuine multielectron ultrafast pump–probe experiment was proposed in which collective dynamics driven by the dielectronic repulsion within a configuration could be extracted from the ionization yield. The proposed experiment considered a C$^+$ ion in its 1s$^2$2s$^2$2p $^2$P$^o$ ground state with total magnetic quantum number $M = 0$. 

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Using an ultrashort XUV pulse, the C\(^+\) ion was excited into a superposition of the 2s2p\(^2\) 2\(^S\)\(_e\) and 2\(^D\)\(_e\) excited states. By varying the time-delay between the pump pulse and a second ultrashort ionizing probe pulse, it was found that the ionization probability of the coherent superposition of the 2s2p\(^2\) 2\(^D\) and 2\(^S\) states showed rapid modulation due to collective dynamics of the two equivalent 2p electrons. The results indicated that an uncoupled-electron basis provided a clearer interpretation of the ionization probability than the traditional LS-coupling scheme. Using the uncoupled-electron basis, the rapid oscillations in the ionization probability were ascribed to a breathing motion between two different angular distributions, explaining the modulation of the ionization yield as a function of time-delay between the pump and probe pulse. The investigation was carried out using the recently developed three dimensional (3D) time-dependent R-matrix (TDRM) theory [16, 17]. This non-perturbative theory enables the interaction of ultrashort light fields with multielectron atoms and atomic ions to be determined from first principles, and has also been employed to investigate ultrafast laser-driven excitation dynamics in Ne [16].

In this paper, we investigate collective dynamics in greater detail, by studying the 2D momentum distribution of the electron ejected due to the probe pulse in a similar experimental scheme as described in [15]. In recent years, with the introduction of cold target recoil-ion momentum spectroscopy detectors, 2D momentum spectra of photoelectrons have been widely reported [18, 19]. These measurements reveal considerable structure not only in the energy distributions but also in the angular distributions of the ejected electron. The final properties of the electron can, in turn, often yield information about the structure and processes occurring inside the system from which the electron was released [19]. Here, we investigate how the 2D momentum distribution of the ejected electron behaves as a function of the time delay between the pump and the probe pulse. While the previous scheme provided insight into the collective dynamics by studying the ionization probability as a function of time delay between the two pulses, it will be shown here that the angular distributions of the ejected electron provide an even more explicit measure of the collective dynamics taking place inside the C\(^+\) ion.

2. TDRM theory

Our investigations of the ejected electron momentum distributions are carried out using the recently developed TDRM method. Both a spatially limited R-matrix inner-region version of the TDRM method and the TDRM method itself have already been used to obtain 2D momentum distributions for electrons ejected from Ne irradiated by a sequence of attosecond pulses [17, 20]. In [20], momentum distributions were obtained for both the emission of a 2p electron and an inner 2s electron from Ne. In both of these studies, it was emphasized that the key advantage of a dedicated multielectron approach such as the TDRM method is the ability to describe electrons with different \(m\) values in a single calculation, as opposed to SAE-based approaches where separate calculations are required.

In this paper, we give a brief description of the TDRM theory. A more detailed description of the theory can be found in [17] and we therefore give only an overview here. The TDRM theory starts from the non-relativistic time-dependent Schrödinger equation (TDSE) describing the interaction of the light field with a general \((N+1)\)-electron atom or ion. Throughout our analysis we assume that the light field is linearly polarized and spatially homogeneous. Using the unitary Cayley form of the time evolution operator \(\exp(-i t H(t))\) and neglecting terms of \(O(\Delta t^3)\), the solution of the TDSE (in atomic units) at time \(t = t_{q+1}\) can then be expressed in
terms of the solution at $t = t_q$ using the Crank–Nicholson method as follows:

$$(H(t_q + (1/2)) - E)\Psi(X_{N+1}, t_{q+1}) = \Theta(X_{N+1}, t_q),$$

(1)

where

$$\Theta(X_{N+1}, t_q) = -(H(t_q + (1/2)) + E)\Psi(X_{N+1}, t_q).$$

(2)

In equations (1) and (2), $X_{N+1} \equiv x_1, x_2, \ldots, x_{N+1}$, where $x_i \equiv r_i \sigma_i$ are the space and spin coordinates of the $i$th electron, $H(t_q + (1/2))$ is the time-dependent Hamiltonian at the midpoint of times $t_q$ and $t_{q+1}$, and it is described in the length gauge throughout. In this formalism, the imaginary energy defines the time step and is given by $E \equiv 2i \Delta t^{-1}$.

The solution of equation (1) is accomplished by partitioning configuration space into an internal and external region as in the standard $R$-matrix method [21] with the boundary at radius $r = a_0$ as seen in figure 1. In the internal region, electron exchange and electron–electron correlation effects between the ejected electron and the remaining $N$ electrons are important, while in the external region such effects are negligible. Hence, in the external region the ejected electron moves in the local long-range multipole potential of the residual $N$-electron atom or atomic ion together with the laser potential.

Since the Hamiltonian $H(t_q + (1/2))$ in equation (1) is not Hermitian in the internal region $r \leq a_0$ due to the kinetic energy term in $H(t_q + (1/2))$, we introduce the Bloch operator $\mathcal{L}$ following standard $R$-matrix theory [21] such that $H_{N+1} + \mathcal{L}$ is Hermitian in the internal region. We thus rewrite equation (1) in the internal region as

$$\Psi = \left(\frac{1}{H + \mathcal{L} - E}\right)\mathcal{L} \Psi + \left(\frac{1}{H + \mathcal{L} - E}\right)\Theta,$$

(3)

where for notational simplicity we have omitted the arguments in $H$, $\Psi$ and $\Theta$. The first term on the right-hand side of equation (3) resembles the form of the well-known time-independent wavefunction in the $R$-matrix theory for electron scattering (see equation (6) in [21]). The second term on the right-hand side of equation (3) accounts for the time-propagation of the wavefunction. It would be the only term present if the $R$-matrix boundary would not exist. The presence of the boundary modifies the time propagation in the second term. This
modification is then corrected by the first term, which can thus be seen as a correction to the time-dependent wavefunction due to the presence of the \(R\)-matrix boundary. In the internal region, an \(R\)-matrix basis expansion of the wavefunction \(\Psi\) is adopted and we use a recently developed \(R\)-matrix inner region approach [22] to set up the linear equations given by equation (3). Using a linear solver at each time step enables the \(R\)-matrix, \(R\) as defined in [17], to be calculated on the boundary, \(r = a_0\) of this region and also enables the calculation of an inhomogeneous T-vector, \(T\) also as defined in [17].

To link the internal region with the external region, we first need to know the form of the wavefunction in the external region. In this region, we expand the wavefunction \(\Phi_1\) in terms of reduced radial functions \(\bar{F}_p(r)\) which represent the motion of the outer electron in the \(p\)th channel as follows:

\[
\Psi(X_{N+1}, t_{q+1}) = \sum_{p=1}^{n} \bar{\Phi}_p'(X_N; \hat{r}_{N+1} \sigma_{N+1}) r_{N+1}^{-1} F_p(r_{N+1}),
\]

where \(\bar{\Phi}_p'\) are the channel functions, which are formed by coupling the residual atom or ion states \(\Phi_i\) with angular and spin functions of the ejected electron [21]. The subscript \(p\) represents the channel quantum numbers \(L\) and \(i\) and \(\gamma = \alpha S M_L M_S \pi\).

To connect the internal region and external region wavefunctions, we thus project equation (3) onto the channel functions \(\bar{\Phi}_i'\) and evaluate on the boundary of the internal region to obtain

\[
F_p(a_0) = \sum_{p'=1}^{n} R_{p'p}(a_0) \bar{\Phi}_p'(a_0) + T_p(a_0), \quad p = 1, \ldots, n,
\]

where the reduced radial wavefunctions \(\bar{F}_p(a_0)\) are defined by

\[
\bar{F}_p(a_0) = \langle \bar{\Phi}_p' r_{N+1}^{-1} | \Psi \rangle_{r_{N+1}=a_0}
\]

and the modified derivative functions \(\bar{F}_p'(a_0)\) are defined by

\[
\bar{F}_p'(a_0) = \left. \frac{d\bar{F}_p}{dr} \right|_{r=a_0}.
\]

The prime on the matrix elements means that the integral is carried out over space and spin coordinates of all \(N+1\) electrons except the radial coordinate \(r_{N+1}\) of the ejected electron. The only unknown in equation (5) is \(\bar{F}_p'(a_0)\), which can be determined from the results of the external region. Hence, the wavefunction \(\Psi(X_{N+1}, t_{q+1})\), which provides the starting point for the calculation in the next time step can be determined from equation (5).

In the external region, the coupled second-order differential equations satisfied by the reduced radial wavefunctions \(\bar{F}_p(r)\) can be obtained by substituting equation (4) into equation (1) and projecting onto the channel functions \(\bar{\Phi}_i'\). These inhomogeneous equations can be written in matrix form as

\[
(H - EI)F(r) = \theta(r),
\]

where the Hamiltonian matrix \(H\) is now defined by

\[
H = -\frac{1}{2} \left( 1 \frac{d^2}{dr^2} + V(r) - 2W(r) + k^2 \right),
\]

where \(I\) is the unit matrix and \(V(r)\) represents the combined nuclear and centrifugal potential matrix and \(k^2\) can be expressed in terms of the diagonal energy eigenvalue matrix \(E_n\) of the
residual $N$-electron atom or ion, by the equation $k^2 = -2E_n$. $W(r)$ is the long-range potential matrix coupling the channels as described in [17]. Finally, the inhomogeneous term $\theta(r)$ in equation (8) is defined for a single channel by

$$\theta_p(r) = \langle \hat{\Phi}^c_p(X_N;\hat{r}_{N+1}\sigma_{N+1})r_{N+1}^{-1}\rangle \langle \Theta \rangle,$$

where $\Theta$ has already been defined in equation (2) and where we have omitted the time variable in $\theta_p(r)$ and in the potential terms $W(r)$ in equation (9) for notational convenience. The complex energy $E$ in equations (8) and (9) is measured from the lowest threshold of the residual atom or ion.

In order to solve equation (8), we sub-divide the external region into $n_s$ sub-regions and propagate the $R$-matrix and $T$-vector calculated at $r = a_0$ for a given time step across the sub-regions to yield the $R$-matrix and $T$-vector at $r = a_p$, which can then be used to propagate the wavefunction backwards across the $n_s$ sub-regions, as indicated in figure 1, commencing with the boundary condition $F(a_p) = 0$. In the $s$th sub-region, we introduce a Bloch operator $L_s$ defined in [17], which is such that $H + L_s$ is Hermitian over the $s$th sub-region $a_{s-1} \leq r \leq a_s$. We can then write the formal solution of equation (8) in the $s$th sub-region with $a_{s-1} \leq r \leq a_s$ as

$$F(r) = 2 \int_{a_{s-1}}^{a_s} G_s(r, r')L_s F(r')dr' + J(r), \quad (11)$$

where

$$J(r) = 2 \int_{a_{s-1}}^{a_s} G_s(r, r')r(r')dr' \quad (12)$$

and $G_s(r, r') = (H + L_s - E \hat{I})^{-1}$. We use a spectral representation of Green’s function in equations (11) and (12) [26], where we use a basis of B-splines and solve a system of linear equations in each sub-region. Evaluating equation (11) at $r = a_{s-1}$ and $r = a_s$ then yields the following outward propagation equations for $R_s$ and $T(a_s)$:

$$a_s R_s = G_s(a_s, a_s) - G(a_s, a_{s-1}) \left[ G_s(a_{s-1}, a_{s-1}) + a_s^{-1}R_{s-1} \right]^{-1} G_s(a_{s-1}, a_s) \quad (13)$$

and

$$T(a_s) = J(a_s) + G_s(a_s, a_{s-1}) \left[ G_s(a_{s-1}, a_{s-1}) + a_s^{-1}R_{s-1} \right]^{-1} (T(a_{s-1}) - J(a_{s-1})). \quad (14)$$

The $R$-matrix and $T$-vector on the boundary $r = a$ of the internal region are obtained from solving equation (3) in the internal region. Finally, we obtain the following inward propagation equation for the wavefunction

$$F(a_{s-1}) = a_{s-1}R_{s-1} \left[ G_s(a_{s-1}, a_{s-1}) + a_s^{-1}R_{s-1} \right]^{-1} \left[ G_s(a_{s-1}, a_s)a_s^{-1}R_{s-1}^{-1}(F(a_s) - T(a_s)) \right. \left. + G_s(a_{s-1}, a_{s-1})a_s^{-1}R_{s-1}^{-1}T(a_{s-1}) + J(a_{s-1}) \right]. \quad (15)$$

The wavefunction for all values of $r$ is then obtained from equation (11) and hence the inhomogeneous terms in equations (2) and (14) can be calculated for the next time integration step. In this way equation (1) can be stepped forward in time for all positive $t_q$ given the wavefunction at time $t = 0$. 

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3. The pump–probe scheme

The ultrafast pump–probe scheme that we propose here has a close similarity to the scheme used in the previous investigation of the collective dynamics in C⁺ [15]. The basic features of the proposed experiment are explained in the schematic diagram in figure 2. As in the previous study, we consider a C⁺ ion in its 1s²2s²2p² 1S₀ ground state with total magnetic quantum number M = 0. This ion is excited by the first XUV pulse, linearly polarized in the z-direction, into a superposition of the 2s2p² 2Sₐ and 2Dₐ excited states. The energy separation between the 2s2p² 2Sₐ and 2Dₐ states, caused by the Coulomb repulsion between the two equivalent 2p electrons, results in a temporal interference between the two states with a characteristic frequency determined by the energy separation. In a naive single-configuration picture, the responsible dielectronic repulsion integral is the F₂(2p, 2p) integral [25]. Hence, this repulsion governs the dynamical behaviour of the electron wavepacket (EWP), which continues to evolve after the end of the pump pulse. Subsequent irradiation of the C⁺ ion with the time delayed XUV ultrashort pulse will ionize the C⁺ ion.

The structure of C⁺ is described in the R-matrix internal region using the R-matrix basis developed for electron impact studies of C²⁺ [27], although we extend the inner region to a radius of 20 au, while the set of continuum orbitals contains 90 continuum functions for each available angular momentum of the continuum electron. The present calculations have been performed including the 1s²2s² 1S₀ ground state and the 1s²2s2p³ 3P₀ and 1P₀ excited states of C²⁺ as target states. The description of C⁺ includes all 1s²2s²2l and 1s²2s2p2l’ channels up to L_max = 5. In the external region, we propagate the R-matrix and T-vector outwards to a radial distance of typically 2000 au in order to prevent any reflections of the wavefunction from the
external region boundary. Each external region sector is typically 3 au wide and contains 35 B-splines per channel with order $k = 9$.

In the proposed experiment shown in figure 2, the pump laser pulse has a central photon energy $\omega_1 = 10.9$ eV in order to be near-resonant with the $2s2p^2 \ ^2S_e$ and $^2D_e$ states. It is defined by a three-cycle $\sin^2$ ramp-on of the electric field followed by a three-cycle $\sin^2$ ramp-off giving a pulse duration of 2.28 fs and has an energy bandwidth of 3.6 eV (FWHM). The XUV ultrashort light pulse has a central photon energy $\omega_2 = 21.8$ eV and is also described by a three-cycle $\sin^2$ ramp-on followed by a three-cycle $\sin^2$ ramp-off of the electric field giving a pulse duration of 1.14 fs. Both pulses have a maximum intensity of $5 \times 10^{12}$ W cm$^{-2}$. The fundamental difference between the experiment proposed here and the experiment described in [15] is the central photon energy of the XUV probe pulse. In the previous study, a central photon energy of 17 eV was used, which provided enough energy to transfer population from the $2s2p^2 \ ^2S_e$ and $^2D_e$ excited states to continuum channels coupled to the $C_{2+}^2s_2^22s^2 \ ^1S_e$ ground state. Since the laser light was polarized in the z-direction, total magnetic quantum number $M$ was conserved, $\Delta M = 0$, and so, in this scheme, the outgoing electron was only allowed to have $m = 0$. In our current study, we use a probe pulse with a central photon energy $\omega_2 = 21.8$ eV, which provides enough energy to transfer the population from the $2s2p^2 \ ^2S_e$ and $^2D_e$ excited states to continuum channels coupled to the $2s2p \ ^3P_o$ first excited state of $C_{2+}^2$. This means that the outgoing electron is no longer restricted to having $m = 0$, but now has the possibility of having $m = -1, 0, or 1$. This allows us to investigate the collective dynamics by observing the angular distribution of the ejected electron, as shall be seen below.

After letting the pumped $C^+$ ion freely evolve for $\sim 1$ fs, we start to probe the bound state population from $\sim 3.8$ fs onwards by irradiating $C^+$ at different time delays with the XUV probe pulse. We then allow the system to relax freely for $\sim 30$ fs to enable the emitted electron to reach a distance beyond 200 au. This relaxation time also accounts for some decay of autoionizing states, but these could have lifetimes that are too long to fully take autoionization into account in a time-dependent calculation.

The outer region channel functions that are obtained at the end of the time-dependent calculation contain all angular and spin information, including the coupling between spin and angular momentum of the final $C_{2+}^2$ states and those of the continuum electron. To obtain the wavefunction of just the continuum electron, we need to decouple its spin and angular momentum. This decoupling can be performed using Clebsch–Gordan coefficients. However, following the decoupling, we need to treat each $m$ value of the outgoing electron separately, since different $m$ values correspond to different angular distributions. Wavepackets with different $m$ do not interfere, so their associated probability amplitudes must be added incoherently. Once we have obtained the wavefunction for the ejected electron, we transform it, for $r > 400$ au, into momentum representation under the assumption that the long-range Coulomb potential is negligible.

4. Results

Figure 3 shows the 2D momentum spectra of the ejected electron in the $k_x, k_z$ plane for increasing time delays between the pump pulse and probe pulse. The momentum spectra are obtained by transforming the continuum wavefunctions coupled to the $1s^22s2p \ ^3P_o$ excited state of $C_{2+}^2$ shown in figure 2 at the end of the calculation into the momentum representation. The reason for only including channels with a coupling to this residual ion state in the analysis is due to the fact

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that the ejected electron in these channels can have \( m = -1, 0 \) or 1. This is not the case for the dominant channels coupled to the ground state of C\(^{2+}\) which can only have an outgoing electron with \( m = 0 \) and hence the omission of these dominant channels from the analysis makes the collective dynamics inside C\(^{+}\) easier to observe through the study of the angular distribution of the ejected electron.

The most striking feature of figure 3 is the oscillation between two different angular distributions of the ejected electron as a function of the time delay between the two pulses with the period of oscillation given by \( \sim 1.5 \) fs. It is evident in figure 3(b) that at a delay of \( \Delta \tau = 4.16 \) fs the angular distribution is aligned predominantly along the laser polarization axis indicating the ejection of an electron with \( m = 0 \). The momentum distribution shown in figure 3(f) shows that at a time delay of 4.70 fs the angular distribution of the ejected electron is no longer aligned along the \( z \)-axis, but now exhibits the behaviour of an electron with \( |m| = 1 \). At a longer time...
Figure 4. Population of the excited bound states as a function of time. Top: the $2s2p^2 \, ^2\text{S}$ population is shown in blue and the $2s2p^2 \, ^2\text{D}$ population is shown as red dashes. The bound state populations are shown here without the presence of the ultrashort pulse to show how the system freely evolves in time. Bottom: both the $|2p_0, 2p_0\rangle$ population (blue solid line) and the $|2p_1, 2p_{-1}\rangle_\text{S}$ population (red dashes). The black circles indicate the times at which the peak of the probe pulse interacts with the C$^+$ system resulting in the corresponding momentum distributions shown in figure 3.

delay of 5.43 fs, the distribution shown in figure 3(i) indicates that the angular distribution has returned once again to behaviour that suggests the emission of an electron with $m = 0$. Finally, the momentum distribution in figure 3(k) shows that at a time delay of 6.15 fs the emission of an electron with $|m| = 1$ dominates once again. At the intermediate time delays shown in figures 3(c), (d), (g), (h) and (j), it is less clear whether the distributions are dominated by either $m = 0$ or $|m| = 1$ electron emission, which suggests that the outgoing electron is in a superposition of $m = 0$ and $|m| = 1$ states. We also note that the distributions are complicated by the presence of a series of autoionization resonances at the higher momentum end of the distributions. These resonances will be discussed in more detail later.

As a first step to understanding this oscillation between the angular distributions dominated by either an $m = 0$ electron or an $|m| = 1$ electron, we start by investigating the populations of the ‘probed’ $2s2p^2 \, ^2\text{S}$ and $^2\text{D}$ excited states inside the C$^+$ ion as a function of time. The top half of figure 4 shows the population of the $2s2p^2 \, ^2\text{S}$ and $^2\text{D}$ excited states as a function of time, where $t = 0$ is the start time of the pump pulse. It can be seen that the populations of the two states steadily increase during the pump pulse and evolve to a steady-state after the end of the pump pulse. However, it is also clear that the behaviour of the population of the bound
states shows no indication of any interference effects which could give rise to the oscillatory behaviour of the angular distributions of the outgoing electron.

To elucidate the dynamics, we transform, similar to [15], from the LS coupled basis to the uncoupled basis $|2p_m, 2p_{-m}\rangle$, in which the role of magnetic substates becomes more transparent. Since we consider light polarized in the $z$-direction, total magnetic number $M$ is conserved, $M = 0$. The $2s$ electron can be considered as a spectator electron, so that the LS coupled $2p^2$ $^1S$ and $^1D$ configurations can be decomposed as follows:

$$
|2p_0, 2p_0\rangle = -\sqrt{\frac{1}{3}}|2p^2 \; ^1S\rangle + \sqrt{\frac{2}{3}}|2p^2 \; ^1D\rangle, \quad (16a)
$$

$$
|2p_1, 2p_{-1}\rangle_s = \sqrt{\frac{2}{3}}|2p^2 \; ^1S\rangle + \sqrt{\frac{1}{3}}|2p^2 \; ^1D\rangle, \quad (16b)
$$

where the subscript $S$ indicates singlet spin coupling between the $m = 1$ and $m = -1$ electrons. These two electrons can also couple to form a triplet $^3P_e$ state, but this state is not included due to the fact that the initial ground state of $C^+$ has $M = 0$ and we use linearly polarized light to pump the system, so that $\Delta L = 0$ transitions are not allowed. The decomposition given in equation (16) immediately suggests that angular dynamics in the $2s2p^2$ configuration involves collective dynamics of the two electrons: if the $m$ value of one electron changes, the other electron must also experience a change.

The bottom half of figure 4 shows the population of the $|2p_m, 2p_{-m}\rangle$ functions in the uncoupled basis as a function of time. The most striking feature in this figure is the periodic oscillation in the population of $|2p_0, 2p_0\rangle$ and $|2p_1, 2p_{-1}\rangle_s$. The period of these oscillations ($\sim 1.5$ fs) closely matches the period of the observed oscillation in the angular distributions of the ejected electron. Hence, the uncoupled basis provides a much clearer interpretation of the ultrafast dynamics of $C^+$ explored in the present investigation. This transformation into the uncoupled basis allows an assessment of the reasons why the angular distribution of the ejected electron oscillates with the time delay between the pump pulse and the probe pulse. After the $C^+$ system has been excited by the pump pulse, the excited multielectron wavepacket is in a breathing motion between two different angular distributions. When the population of $|2p_0, 2p_0\rangle$ has reached its maximum, the probe pulse interacts with a wavepacket dominated by $m = 0$ electrons, and hence the angular distribution of the ejected electron will be aligned predominantly along the laser-polarization axis as seen in figures 3(b) and (i). Alternatively, when the population of $|2p_1, 2p_{-1}\rangle_s$ has reached a maximum, the probe pulse interacts with an EWP dominated by $|m| = 1$ electrons resulting in the angular distribution of the outgoing electron directed at an angle of $45^\circ$ to the laser polarization axis as seen in figures 3(f) and (k). The present pump–probe scheme thus allows the observation of collective breathing motions in superpositions of low-lying atomic states, while the frequency of these motions is a measure of the magnitude of electron–electron repulsion.

The analysis of the angular distributions of the ejected electron, as opposed to the ionization probability, as has been previously investigated [15], provides a more sensitive means of investigating the correlation in the $2s2p^2$ configuration. As has been mentioned, the momentum distributions in figure 3 are complicated by the presence of a series of autoionization resonances at the higher momentum end of the spectrum. These resonances are populated due to the broadband nature of the ultrashort probe pulse and their full inclusion in any theoretical approach is essential for an accurate description of ultrashort light pulses interacting with
multielectron systems. In the present study, they are due to transitions from the pumped 2s2p$^2$ $^2S^e$ and $^2D^e$ excited states to series of 2s2p($^1P$)nd and 2s2p($^1P$)ns autoionizing states converging to the 2s2p $^1P$ threshold. The 2s2p($^1P$)nd resonances can be excited from both the $|2p_0, 2p_0\rangle$ and the $|2p_1, 2p_{-1}\rangle$ states. Hence, these resonances are present in all of the distributions seen in figure 3. Since they decay by autoionization, which leads to an additional (variable) time delay, the effect of a given time delay of the probe pulse will be washed out. Hence for all time delays, we see emission of $m = 0$ and $|m| = 1$ electrons. The 2s2p($^1P$)ns resonances can, however, only be excited from the $|2p_0, 2p_0\rangle$ state. Hence, these resonances are suppressed at delays of 4.89 and 6.15 fs. This is most clearly seen for the 2s2p($^1P$)4s resonance, visible at the low momentum end of the distribution ($k_z \approx 0.3$ au). Indeed, this 2s2p($^1P$)4s resonance is visible only at time delays at which the probe pulse is interacting with the EWP when the EWP is dominated by $m = 0$ electrons.

One of the main advantages of the TDRM approach is its ability to describe the entire atom or ion, including resonance effects. Another example of the importance of describing the system in its entirety is revealed in the behaviour of the ionization probability as a function of time delay between the two pulses [15]. The ionization probability shows a modulation due to the energy difference between the 2s2p$^2$ $^2S^e$ and $^2D^e$ excited states. However, the ionization process is complicated by the fact that there are interferences between the initial C$^+$ ground state and the pumped 2s2p$^2$ $^2S^e$ and $^2D^e$ excited states which result in higher frequency oscillations superimposed on the dominant oscillatory behaviour of the ionization probability. Since any EWP will have to be prepared by a finite bandwidth pulse, some population will remain in the initial state of the system. This population will interfere with the excited states and therefore the influence of the initial state needs to be included in any realistic calculation.

Although the present theoretical investigation offers insight into such collective dynamics, the use of C$^+$ as a target system in a real experiment may not be the ideal choice. Since we start off with the ground state of C$^+$ with $M = 0$, the dominant ionization process for the case of linear polarization of the laser field will result in the residual C$^{2+}$ ions being left in the 1s$^2$2s$^2$ $^1S^e$ ground state with $M = 0$ so that total magnetic quantum number is conserved. This means that the ionization process will be dominated by the ejection of $m = 0$ electrons making it difficult to experimentally observe the interference effects in the angular distributions of the ejected electron coupled to the C$^{2+}$ 2s2p $^3P^o$ excited state as shown in this study. A possible choice for avoiding this effect may be the ionization of the O$^{2+}$ ion, since the 2s$^2$2p$^2$ $^3P^o$ ground state of O$^{3+}$ consists of both $m = 0$ and $|m| = 1$ sublevels. However, the investigation of O$^{2+}$ would require the description of an $M = 1$ system. This requires some extensions to the present code due to the additional photoexcitation and photoionization pathways.

Although C$^+$ may not be the most suitable system to study for the reasons just stated, the use of ionic systems rather than neutral systems does offer an important advantage. The fact that configurations in an ion are more separated in energy than in a neutral system provides the opportunity to investigate electron–electron dynamics within a single configuration. This is not the case for neutral systems where configurations lie close in energy with the consequence that inter-configuration interactions will lead to more complicated dielectronic repulsion dynamics [14]. With regard to the excitation mechanism of the 2s2p$^2$ configuration, it may be possible to form and probe such a coherent superposition using longer chirped pulses [28].
5. Conclusion

We have used the TDRM approach to propose an ultra-fast pump–probe scheme in which the dynamics of configuration interaction inside C$^+$ can be investigated. By varying the time delay between the pump pulse and probe pulse, the angular distribution of the ejected electron oscillates between a distribution dominated by an $m = 0$ electron and one which is dominated by an $|m| = 1$ electron. By using an uncoupled electron basis instead of the traditional LS coupling scheme, we are able to ascribe the behaviour of the angular distributions of the ejected electron to a collective EWP inside C$^+$ breathing between two different angular distributions. The analysis of the angular distributions of the ejected electron, as opposed to the ionization probability, as has been previously investigated, provides an even more direct means of tracking the collective dynamics inside the ion. The frequency of the oscillation between the two angular distributions is, in a naive picture related to a particular electron–electron repulsion integral, $F^2(2p,2p)$. This breathing motion between angular distributions could be a general feature of the multielectron response to strong laser fields, and could have a significant effect on multiple ionization processes and the generation of high-harmonic radiation from open-shell systems.

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References

[1] Sansone G et al 2006 Science 314 443
[2] Drescher M et al 2002 Nature 419 803
[3] Uiberacker M et al 2007 Nature 446 627
[4] Cavalieri A L et al 2007 Nature 449 1029
[5] Dromey B et al 2007 Phys. Rev. Lett. 99 085001
[6] Nomura Y et al 2009 Nat. Phys. 5 124
[7] Krausz F and Ivanov M 2009 Rev. Mod. Phys. 81 163
[8] Hu S X and Collins L A 2006 Phys. Rev. Lett. 96 073004
[9] Parker J S, Doherty B J, Taylor K T, Schultz K D, Blaga C I and DiMauro L F 2006 Phys. Rev. Lett. 96 133001
[10] Abu-samha M and Madsen L B 2008 J. Phys. B: At. Mol. Opt. Phys. 41 151001
[11] Laulan S and Bachau H 2003 Phys. Rev. A 68 013409
[12] Barna I F, Wang J and Burgdörfer 2006 Phys. Rev. A 73 023402
[13] Fournou E, Antoine P, Bachau H and Piraux B 2008 New J. Phys. 10 025017
[14] Morishita T, Watanabe S and Lin C D 2007 Phys. Rev. Lett. 98 083003
[15] Lysaght M A, Burke P G and van der Hart H W 2009 Phys. Rev. Lett. 102 193001
[16] Lysaght M A, Burke P G and van der Hart H W 2008 Phys. Rev. Lett. 101 253001
[17] Lysaght M A, van der Hart H W and Burke P G 2009 Phys. Rev. A 79 053411
[18] Kling M F et al 2008 New. J. Phys. 10 025024
[19] Remetter T et al 2006 Nat. Phys. 2 323
[20] van der Hart H W, Lysaght M A and Burke P G 2008 Phys. Rev. A 77 065401
[21] Burke P G and Berrington K A 1993 Atomic and Molecular Processes: An R-matrix Approach (Bristol: Institute of Physics Publishing)

[22] van der Hart H W, Lysaght M A and Burke P G 2007 Phys. Rev. A 76 043405

[23] Burke P G and Burke V M 1997 J. Phys. B: At. Mol. Opt. Phys. 30 L383

[24] Guan X, Noble C J, Zatsarinny O, Bartschat K and Schneider B I 2008 Phys. Rev. A 78 053402

[25] Froese Fischer C, Brage T and Jönsson P J 1997 Computational Atomic Structure: An MCHF Approach (Bristol: Institute of Physics Publishing) chapter 2.2.2

[26] Baluja K L, Burke P G and Morgan L A 1982 Comput. Phys. Commun. 27 299

[27] Berrington K A, Burke V M, Burke P G and Sciulla S 1989 J. Phys. B: At. Mol. Opt. Phys. 22 665

[28] Yudin G L, Bandrauk A D and Corkum P B 2006 Phys. Rev. Lett. 96 063002