

Impact of electron correlation on photoelectron angular distributions in sequential double photoionization of Ne^+

Holly Lavery , Andrew C. Brown , and Hugo W. van der Hart 

Centre for Light-Matter Interactions, School of Mathematics and Physics, [Queen's University Belfast](#), Belfast BT7 1NN, Northern Ireland



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We present a combination of the R-matrix theory with time dependence (RMT) method with density matrix theory to model sequential ionization processes. Separate RMT calculations model the individual ionization stages, while a density matrix describes the coherences within the intermediate ion. As proof of concept, we quantify changes in the angular distribution of photoelectrons in the final stage of sequential ionization of Ne^+ to Ne^{3+} by x-ray free-electron laser radiation with photon energies of 95 eV.

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I. INTRODUCTION

When an atom interacts with an intense light field, multiple ionization processes can occur in sequence. This occurs for intense fields in both the XUV and infrared (IR) regimes, although the underlying mechanisms differ. Sequential ionization processes were first investigated at 780-nm wavelengths and intensities around 10^{18} W/cm² approximately 20 years ago [1]. At these wavelengths, ionization is dominated by the emission of the outermost electrons. Sequential ionization was also one of the first processes observed at free-electron laser (FEL) facilities. Xenon atoms were irradiated by intense (10^{16} W/cm²) FEL laser light at a photon energy of 93 eV [2], leading to the observation of Xe^{21+} ions. In this case, initial ionization is dominated by the emission of inner-shell electrons with binding energies around the photon energy. Understanding of these sequential ionization processes remains of paramount interest, as it impacts the application of x-ray free-electron laser radiation to study properties of much larger systems [3].

Insight into sequential ionization processes is provided primarily by rate equation models, originally proposed 25 years ago for intense IR fields [4]. They were subsequently extended to atoms irradiated by high-frequency light fields [5,6]. These latter models include many additional processes beyond photoemission of a single electron, as inner-shell vacancies can be filled by autoionization, and a single, high-energy photon can eject multiple electrons at once. Rate equation models continue as the dominant theoretical tool in the field, as demonstrated by recent studies on the dynamics of the ionic electron cloud (see, e.g., Refs. [7,8] and references therein).

Initial comparisons of model results and experiments provided significant scientific insight; they evidenced the presence of correlated electron dynamics in strong-field

ionization. In sequential ionization driven by strong IR fields, experimental ion yields were replicated by theoretical models employing ionization rates for electrons with magnetic quantum number $m = 0$ [1]. The ionization rates for electrons with $m = \pm 1$ could be neglected. This was explained through electron correlation [9]: A double vacancy in the $m = 0$ levels can be filled by simultaneous electron transfer from the $m = +1$ and $m = -1$ levels through electron-electron exchange interactions (and vice versa). Averaged over time, therefore, the $m = 0$ level is populated by a single electron, and sequential ionization is then dominated by the ionization rate for a single $m = 0$ electron. We note, however, that this initial demonstration of the electron correlation's role in the dynamics employed an excitation-ionization setup rather than describing sequential ionization directly [9].

Recent theoretical research has focused on the dynamics of the electron cloud during the sequential ionization of a noble gas atom by a FEL pulse [7,8,10,11]. Within rate-equation studies, it is typically assumed that the various intermediate atomic states are separable and are populated incoherently. However, electron-electron interactions, and the associated transfer of electrons between the different m levels, should not be ignored *a priori* as part of these cloud dynamics. For example, the $2p^2\ ^1S$ and 1D states with total magnetic quantum number $M = 0$ are built from the same uncoupled wave functions: the individual magnetic quantum numbers for the two electrons can be either $m_1 = 0, m_2 = 0$ or $m_1 = \pm 1, m_2 = \mp 1$. When these two $2p^2\ ^1S$ and 1D states are populated coherently, the energy difference between them changes the superposition over time. This reflects population transfer between the two components, and thus dynamics in the overall electron cloud, as the $m = 0$ wave functions are aligned along the laser polarization axis whereas the $m = \pm 1$ wave functions are aligned within the plane perpendicular to it.

In this report, we wish to quantify the importance of these correlation dynamics within sequential ionization through a pump-probe spectroscopy investigation using the R-matrix-with-time-dependence (RMT) approach [12–14]. We go beyond our previous study (Ref. [9]) by considering ionized

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states as intermediate states, whilst maintaining their quantum correlation. The RMT approach can, in principle, be extended to the treatment of double ionization processes directly [15], but this approach is (1) highly inefficient for the treatment of sequential ionization, and (2) only (currently) applicable to two-electron systems, and three-electron systems with reduced dimensionality [16]. Via analysis of the RMT output through a density matrix approach [17], however, we can combine separate calculations for different ionization stages as part of a single overall simulation.

The density matrix was originally introduced to describe statistical concepts in quantum mechanics [17]. Currently, it is an important tool that allows us to describe quantum interference effects. Density matrix approaches have already been applied extensively for the interpretation of ultrafast dynamics. For example, previous studies have used density matrix theory combined with rate equations to model sequential double ionization [18] and multiorbital tunnel ionization [19], while others have used density matrix theory to describe the time evolution of electron dynamics in attosecond transient absorption spectroscopy [20]. Most recently, an experiment has started to measure the quantum state of photoelectrons created in ultrafast photoionization via construction of their density matrix [21].

The process of applying density matrices to sequential ionization processes is well established. In these systems, the density matrix is often used to describe the coherences between residual ion states (see, e.g., Refs. [22,23]). Alternatively, the time-dependent density matrix theory has been developed, in which the density matrix evolves over time as specified by first-order differential equations. This approach has been used to describe sequential double ionization [24] and multiphoton ionization of neon [25].

To investigate the efficiency of combining RMT theory with a density-matrix approach, in this report we study sequential ionization of Ne^+ to Ne^{3+} via photoionization at 95 eV. We study the most convenient approach to analyze the RMT output data and investigate the suitability of the RMT approach for pump-probe spectroscopy. For the probe ionization stage, we investigate the influence of pump-probe time delay on the photoelectron angular distribution. We assess the influence of electron correlation on the overall electron-cloud dynamics in the intermediate Ne^{2+} ion. The changes in the angular shape of the $2p^4$ shell are quantified via the angular distribution of the photoelectrons arising from Ne^{2+} ionization. We note that spin-orbit dynamics involving a superposition of residual ion states obtained through a single RMT calculation was analyzed through a density matrix approach [26]. The present approach for sequential ionization uses a nonrelativistic description, and thus does not describe spin-orbit dynamics.

II. METHOD

A. R-matrix theory with time dependence

We employ RMT theory to model the behavior of an atomic ion during each ionization stage of a pump-probe experiment. The approach and associated computer code have been described in detail previously [13,14,27], so we limit the description here to only those parts most relevant to the

present study. In R-matrix theory, configuration space is partitioned into two regions: An inner and an outer region, with the boundary between the two set at a distance $r = a$. The region defined by $r \leq a$ is known as the inner region, within which the interactions between all electrons are considered in full detail. One electron is allowed to escape to distances $r > a$ into the outer region. In the outer region, electron-exchange interactions involving the outer electron and the electrons attached to the residual ion are neglected. We note that the residual ion is located within the sphere with boundary $r = a$, but the overall system extends beyond this sphere, as the outermost electron has $r > a$.

In the current modeling of a pump-probe experiment, each of the stages is considered separately. The physics induced by the pump and probe laser fields are investigated through separate RMT calculations. The quantum information in the residual ion created by the pump pulse needs to be carried over to the probe laser calculation. This information is fully contained within the outer region wave function at the end of the pump laser calculation. This time-dependent $(N + 1)$ -electron outer-region wave function is given by [27]

$$\psi(\mathbf{X}_{N+1}, t) = \sum_{p=1}^n \Phi_p(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}, \sigma_{N+1}) \frac{1}{r_{N+1}} f_p(r_{N+1}, t),$$

$$r \geq a, \quad (1)$$

where r_{N+1} is the radial variable of the $(N + 1)$ th electron, $\Phi_p(\mathbf{X}_N; \hat{\mathbf{r}}_{N+1}, \sigma_{N+1})$ are so-called channel functions combining the residual atom wave functions, and $\mathbf{X}_N = \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N$ are the space and spin coordinates of the N electrons in the residual ion with the angular and spin (σ_{N+1}) functions of the ejected electron. The summation variable p is a channel index, which accounts for all possible combinations of the residual-ion state and allowed angular momentum and spin quantum numbers. The radial wave function $f_p(r, t)$ describes the motion of the ejected electron in the p th channel.

This particular description of the wave function retains coupling between the residual-ion state and the outgoing electron, and is thus not immediately suitable for the transfer of quantum information, when the residual ion and outgoing electron are uncoupled. The outer-region wave function is therefore transformed onto a basis in which the residual ion and the outgoing electron are uncoupled [28]. This outgoing electron wave function is then described in spherical coordinates and transformed into radial momentum form. We rewrite the final wave function as

$$\psi(\mathbf{X}_{N+1}, t) = \sum_q \chi_q(\mathbf{X}_N) \frac{1}{k_{N+1}} g_q$$

$$\times (k_{N+1}, \theta_{N+1}, \phi_{N+1}, \sigma_{N+1}, t),$$

$$r \geq a', \quad (2)$$

where the index q specifies the complete residual ion state χ_q , including all magnetic quantum numbers. g_q represents the angular wave function of the photoelectron within the momentum representation, inclusive of electron spin. Compared to Eq. (1), χ_q does not include spin or the angular momentum functions of the outgoing electron. Outer-region-electron wave functions are thus obtained for each available residual-ion state. The transformation from the radial coordinate into

momentum is normally applied from a distance $a' \geq a$ to minimize contributions from bound Rydberg states extending into the outer region. However, within the present study, we keep $a' = a$ as the influence of Rydberg states is negligible.

B. Density matrix theory

The dynamics involving intermediate states in sequential ionization processes requires capture of the coherences between the residual ion states through the so-called density matrix, an expression of the density operator in matrix form. The density operator is defined as the outer product of a wave function with its complex conjugate [17],

$$\rho = |\psi\rangle \langle\psi|. \quad (3)$$

Here, we need the coherences of the residual ion left after ionization, in which $|\psi\rangle$ represents the residual ion state. We can then express this density operator as a matrix ρ_{mn} , where each index m, n represents a specific residual ion state. The size of the density matrix is defined by the number of combinations of values of the angular momentum L , magnetic m_l , and spin m_s quantum numbers of the residual ion states in each electron-emission channel.

Computationally, we obtain the values of each element of the density matrix via

$$\rho_{mn} = \iiint \langle \Psi(X_{N+1}, t) | \psi_m \rangle \langle \psi_n | \Psi(X_{N+1}, t) \rangle \times k_{N+1}^2 \sin \theta_{N+1} dk_{N+1} d\theta_{N+1} d\phi_{N+1} \delta_{\sigma_{N+1,m}, \sigma_{N+1,n}}. \quad (4)$$

In this expression, the brackets filter out the angular wave function of the photoelectron separately for each of the residual ion states. The integrations cover the angular coordinates and momentum for the outgoing electron. Only terms in which the outgoing electron has the same magnetic spin quantum number in both brackets contribute. The diagonal elements of the density matrix are real and give the population of each of the residual ion states. The off-diagonal elements are complex and measure the degree of quantum correlation between the residual ion states at the end of the calculation. The density matrix can be calculated by integrating over the angular wave functions in the momentum representation g_q , shown in Eq. (2).

The density matrix allows us to coherently add final states of the second RMT calculation from the superposition of final states of the first. In the absence of any external field, the residual-ion states are well-defined eigenstates, which can be propagated in time via the universal field-free time propagator $U_0(t)$,

$$U_0(\Delta t) = e^{-(i/\hbar)H_0\Delta t}, \quad (5)$$

where H_0 is the Hamiltonian in the absence of an external laser field and Δt the time delay between the end of the RMT calculation for the first ionization step and the start of the second ionization calculation. The field-free time propagation of the density matrix is then given by

$$\rho_{mn}(\Delta T) = U_0(\Delta t) \rho_{mn}(t_{\text{final}}) U_0^\dagger(\Delta t), \quad (6)$$

where t_{final} is defined as the final time of the first RMT calculation.

The influence of quantum correlation on the dynamics of the Ne^{2+} electron cloud is evaluated by investigating changes

in the angular distribution of photoelectrons obtained by Ne^{2+} photoionization. These photoelectron angular distributions are extracted by analysis of the outer-region wave function obtained from the RMT calculations for the second ionization for each intermediate state. Formally, we can write the propagation of the density matrix during the RMT calculation as

$$\rho_{mn}(\Delta t + T) = U(T) \rho_{mn}(\Delta t) U^\dagger(T), \quad (7)$$

where $U(T)$ indicates the propagation of the wave functions through the time-dependent Schrödinger equation, and T indicates the duration of the calculation. With $|\chi_q\rangle$ indicating the wave function for a specific Ne^{3+} residual-ion state as defined in Eq. (2), we can then obtain the photoelectron angular distribution associated with the residual-ion state q via

$$\frac{d\sigma_q(k_2, \theta_2, \phi_2)}{d\Omega dk} = \sum_{mn} \langle \chi_q | \rho_{mn}(\Delta t + T) | \chi_q \rangle. \quad (8)$$

In this expression, integration within the bracket is restricted to electrons within each residual-ion state. In practice, this means that RMT calculations are performed for all intermediate Ne^{2+} states and levels, and the output obtained is given by Eq. (2). All pairs of Ne^{2+} states (m, n) with associated nonzero density matrix element ρ_{mn} , as given by Eq. (4) or (6), are considered for Eq. (8), giving

$$\frac{d\sigma_q}{d\Omega dk} = \sum_{(m,n)} g_{mq}^* \rho_{mn}(\Delta T) g_{nq}, \quad (9)$$

where we use $\rho_{mn}(\Delta T)$ from Eq. (6) as Eq. (8) considers the formal density matrix at the end of the RMT calculation.

C. Running the RMT calculations

Pump-probe sequential double ionization of Ne^+ is chosen for an initial demonstration of the use of density-matrix theory within RMT studies, as the intermediate Ne^{2+} ion can show signs of quantum dynamics via superposition of the $2p^4 \ ^1S$ and $\ ^1D$ states. Both pump and probe pulses have a central photon energy of 95 eV. This photon energy is well above the ionization thresholds, which avoids population of Rydberg states, and simplifies the analysis of the outer-region wave function. Photon energies of around 95 eV have previously been used for other sequential ionization experiments [2,25,29]. The ground state of Ne^+ has $^2P^o$ symmetry, and thus calculations are carried for initial levels with total magnetic quantum number $M = 0$ and $M = \pm 1$.

RMT calculations are carried out separately for the $\text{Ne}^+ \rightarrow \text{Ne}^{2+}$ and $\text{Ne}^{2+} \rightarrow \text{Ne}^{3+}$ ionization stages. Two types of basis sets were used to describe the electronic structure of Ne^+ and Ne^{2+} . The basic description employs Hartree-Fock (HF) orbitals [30] and permits ionization from only the outer-valence ($2p$) orbital. This description includes only intermediate $2p^4$ states of Ne^{2+} : $\ ^1S$, $\ ^1D$, and $\ ^3P$. For the second (probe) calculation, individual RMT calculations are run for each of these possible Ne^{2+} states and each possible M value. At the end of the second calculation, Ne^{3+} will be left in $2s^2 2p^3$.

An extended calculation uses input wave functions generated previously for photoionization studies of Ne^+ [31] and Ne^{2+} [32]. The residual ion states in this set of calculations are obtained from a configuration-interaction (CI) calculation. These basis sets allow for excitation of both $2s$ and $2p$

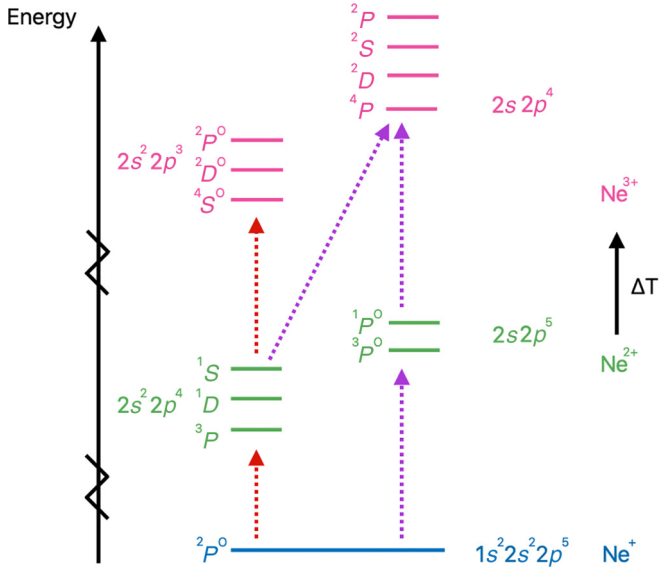


FIG. 1. The electron configurations and ionization thresholds of Ne^+ , Ne^{2+} (green), and Ne^{3+} (pink) used in our calculations. The dark blue line represents the $\text{Ne}^+ 2p^o$ ground state. The red dashed lines represent the ionization pathways available to both the Hartree-Fock and CI basis sets, while the purple dashed lines represent ionization pathways available only to the CI basis set. The vertical axis represents energy (not to scale). ΔT refers to the time delay between ionization stages.

electrons to $3s$, $3p$, and $3d$ states in the CI expansion for residual-ion states, and in the expansion for atomic states. In addition, in the analysis of ionization processes, we now account for emission of both $2p$ and $2s$ electrons through the Ne^{2+} intermediate $2s2p^5$ states: $1P^o$ and $3P^o$. Double emission of $2s$ electrons is not accounted for. The $\text{Ne}^{3+} 2p^5$ state lies at a much higher energy, so that it can only be reached from the $2s2p^5 1P^o$ threshold. Moreover, it lies among the $2s^2 2p^2 3d$ thresholds, so its description will be more sensitive to CI effects.

A full account of the states involved, as well as the electron configurations, is given in Fig. 1. This figure also indicates the dominant ionization processes involving direct emission of a single electron with no reconfiguration of the residual ion required. The CI basis set allows for all transitions, whereas the Hartree-Fock basis set allows for sequential emission of $2p$ electrons only.

The intermediate Ne^{2+} states are obtained twice in both the CI and the HF calculations: once as thresholds within a Ne^+ calculation, and once as initial states within a Ne^{2+} calculation. Energy differences and wave functions need to remain consistent between these different calculations. All threshold energies, and associated binding energies, are thus set to their experimental values [33]. The density matrix is also corrected for any phase change, arising from phase changes in the eigenfunctions during diagonalization of the Hamiltonian in the setup of the initial data.

III. RESULTS

The pump-probe laser scheme involves two laser pulses, and the observables will depend on the properties of both.

However, the quantum correlation of the intermediate Ne^{2+} system is determined by the properties of the pump pulse only. We initially keep the probe pulse parameters constant and vary the parameters of the pump pulse to assess the importance of pulse length on the final Ne^{3+} ion yields. Subsequently, we identify the signatures of intermediate state dynamics in the angular distribution of photoelectrons ejected by the probe pulse for short pump-pulse lengths.

Sequential ionization commences with an initial pump pulse to ionize Ne^+ to Ne^{2+} . Pump-probe calculations for all pulse durations are halted at the same final time of 2.42 fs from the start of the laser pulse, by which time the ionized wave packet has left the inner region, and it can be analyzed fully within the outer region.

After a further time delay, a second probe pulse ionizes Ne^{2+} to Ne^{3+} . We define the total time delay ΔT such that the time difference between the start of the pump pulse and the start of the probe pulse is given by 2.42 fs plus a variable delay time Δt . All delay times reported correspond to ΔT .

The length of the pump pulse is varied from 6 to 60 cycles, whereas the length of the probe pulse is fixed at eight cycles. Each pulse is constructed with a three-cycle, $\sin^2$ ramp on/off. The photon energy for both pulses is 95 eV, and the laser intensity is 10^{13} W/cm^2 .

Figure 2 shows the yields for the different Ne^{3+} states following Ne^{2+} ionization by the probe pulse as a function of delay time ΔT for a range of pump-pulse lengths. Yields are normalized for effective pump-pulse length to account for the different pulse lengths. Yields for each state are obtained through integration of the ejected electron momentum, obtained via Eq. (8), over the outgoing electron for each residual Ne^{3+} ion state. Each of the final states shown display dynamics in the form of oscillations in the yield as a function of pump-probe delay, with the $2s^2 2p^3 2P^o_{M=0}$ state showing the largest oscillation. An oscillation with about half this magnitude is observed in the $2P^o_{M=\pm 1}$ state. An oscillation, smaller by more than an order of magnitude, is seen for the $2D^o_{M=\pm 1,2}$ states, whereas no oscillations are seen in the yields for $2D^o_{M=0}$ and $4S^o$ states. Figure 2 furthermore shows that the amplitude of the oscillations decreases with increasing pulse lengths. Maxima in the oscillations vary with delay time. The pump-pulse calculations use the same final time, and the change in phase of the oscillation reflects the different mid-points of the pump laser pulse. The period of the oscillations in the ionization yields for each final state is 1.12 fs. This corresponds to the energy gap between the states $1S$ and $1D$ of Ne^{2+} , which is equal to 3.7 eV [33]. This energy gap enters through the field-free time propagation of the density matrix, and does not originate from the RMT calculations.

The populations of the $2P^o_{M=\pm 1}$ states oscillate in almost perfect antiphase with the population of the $2P^o_{M=0}$ state. This can be explained as the main dynamics being induced by the pump pulse is the quantum correlation between the $2p^4 1S$ and $2p^4 1D$ states, and a coherent transfer of two electrons simultaneously from $m=0$ to $m=\pm 1$ and back again.

Secondary dynamics are seen within the $M=\pm 1$ and $M=\pm 2$ levels of the $2D^o$ threshold. These dynamics cannot be understood by direct photoionization, as the $2D^o$ threshold cannot be reached directly from the $1S$ state, and quantum

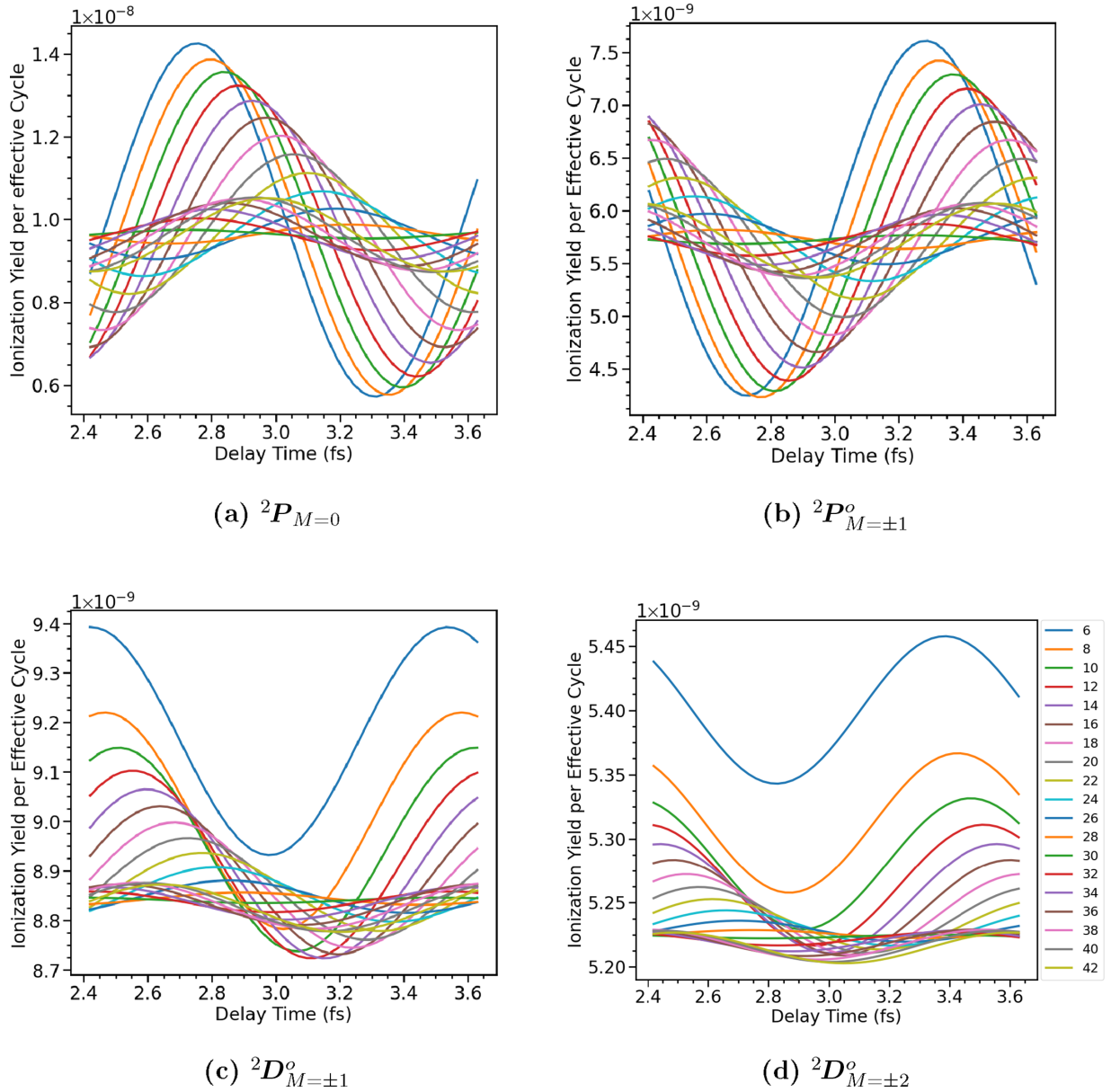


FIG. 2. The ionization yield per effective cycle for (a) ${}^2P_{M=0}$, (b) ${}^2P_{M=\pm 1}^o$, (c) ${}^2D_{M=\pm 1}^o$, and (d) ${}^2D_{M=\pm 2}^o$ $2s^22p^3$ final states of Ne^{3+} as a function of the delay time for pump pulse lengths between 6 and 42 cycles. These yields were obtained using the HF basis set. Yields for the ${}^2D_{M=0}^o$ and ${}^4S^o$ states show no dependence on time delay.

coherence dynamics requires contributions from both $2p^4\ ^1D$ and $2p^4\ ^1S$ states of Ne^{2+} . However, photoionization from 1S , with emission of an electron with $m = -1$, would leave a residual ${}^2P^o$ state with $M = 1$. Additional long-range couplings could then transfer residual-ion-state population to ${}^2D^o$ with $M = 2$. The requirement for these additional couplings notably reduces the importance of these channels for an initial 1S state, and thus also reduces the overall magnitude of the dynamics for these final Ne^{3+} states.

No dynamics are seen for the residual ${}^4S^o$ or ${}^2D^o\ M = 0$ symmetries. The ${}^4S^o$ state can only be reached from a 3P intermediate Ne^{2+} state, which implies an absence of quantum coherence. For linearly polarized light, photoionization from the 1S state leaving ${}^2D_{M=0}^o$ is symmetry forbidden. Hence, the coherence between the 1S and 1D states disappears. We

note that the approach can be extended to incorporate spin-sensitive detection of photoelectrons. Such detection methods would be required for the observation of coherence involving the 1D and 3P intermediate states.

Figure 3 compares ionization yields of the various states of Ne^{3+} for the HF and CI basis sets. The change in basis sets does not affect the overall dynamics, but the yields per cycle for the CI basis are notably smaller than those obtained using the HF basis: the difference between the HF and CI cases is 30% for the ${}^2P^o$ and ${}^2D_{M=\pm 2}^o$ final states. For the ${}^2D_{M=0,\pm 1}^o$ states, the percentage difference is in the order of 40%.

This difference can be explained by the additional atomic structure present in the CI basis set, which can lead to a more tightly bound ground state. This may reduce the overlap between the $2s^22p^{N+1}$ and $2s^22p^N$ states, and thereby reduce

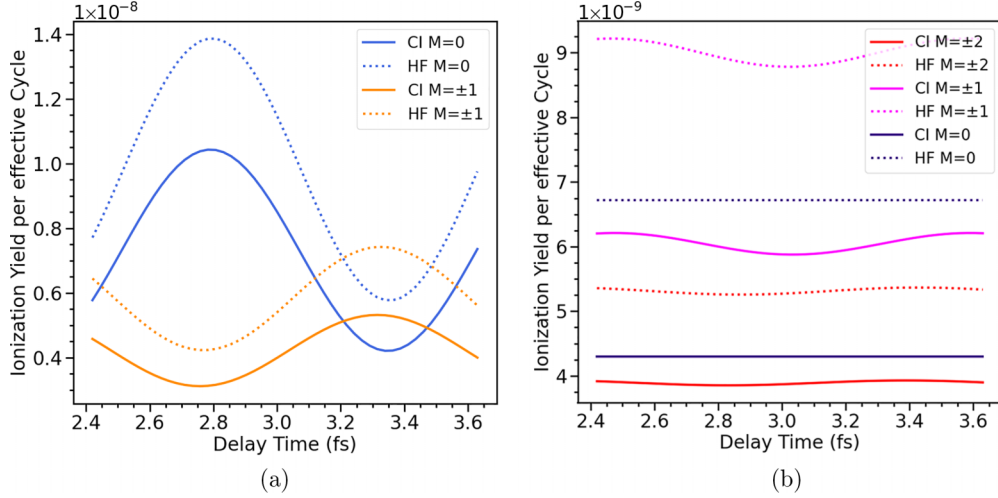


FIG. 3. The ionization yield per effective pulse cycle for (a) the $2P^\circ$ and (b) the $2D^\circ$ states of Ne^{3+} for both the HF (dotted lines) and CI (solid lines) basis sets. Yields shown are for an eight-cycle pump pulse. Overall yields are typically reduced by 25% using the CI basis compared to the HF one.

the overall ionization yield (Fig. 3). This reduced ionization yield is also found in calculations using the CI basis set for differing pulse lengths (not shown).

The importance of quantum coherence on the overall dynamics for the Ne^{3+} residual ion states can be appreciated more clearly by considering the relative range of the oscillations for both the HF and CI basis sets as a function of pulse length. The relative range is defined as the distance between the maximum and minimum value divided by the midpoint between the two values. This is shown in Fig. 4.

The largest relative range is observed in the shortest pulse lengths, with maximum values just under 90% ($2P^\circ_{M=0}$) and just under 60% ($2P^\circ_{M=\pm 1}$). With increasing pulse length the relative range shows the expected $|\sin(x)|/x$ behavior, arising

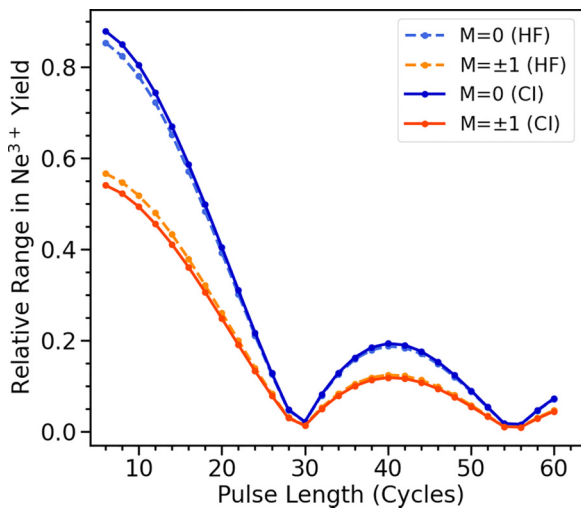


FIG. 4. The relative range of the oscillations in the $2P^\circ_{M=0}$ (blue) and $2P^\circ_{M=\pm 1}$ (orange) states of Ne^{3+} as a function of pump-pulse length. Dashed lines denote results using the HF basis and solid lines the CI basis set. The range follows $|\sin(x)|/x$ behavior with a frequency given by the energy separation between the Ne^{2+} $2s^2 2p^4$ 1S and 1D states.

from phase accumulation over the pump pulse. This behavior is present in Fig. 2 but is harder to appreciate there. At short pulse lengths, some deviations from the $|\sin(x)|/x$ behavior are seen due to the increase in importance of the ramp-on and ramp-off of the pulse.

While our RMT calculations allow for easy calculation of the ionization yields, photoelectron angular distributions (PADs) are easier to obtain in experiment. We therefore switch our attention to these distributions. The PAD for a specific residual ion state can be calculated using the wave function of that specific ion state, combined with the sum over the off-diagonal elements of the density matrix as defined in Eq. (8). Any oscillation in the M value of a residual ion threshold should be reflected in oscillations in the m values of the photoelectrons, which govern the angular distribution. The largest quantum coherence is observed for shorter pulse durations, and thus all subsequent results are obtained for an eight-cycle pump pulse. Angular distributions are calculated at delay times of 2.81 and 3.36 fs, as this corresponds to the maximum and the minimum in the $2P^\circ_{M=0}$ ionization yield [c.f. Fig. 2(a)]. As the primary mode involves the transfer between $2P^\circ_{M=0}$ and $2P^\circ_{M=\pm 1}$, these delay times should provide the most prominent signatures of dynamics. Results shown are computed using the CI basis. Results using the Hartree-Fock basis set show the same general behavior, so are omitted for brevity.

To compute the PAD we take a weighted average of the PADs arising from simulations starting in the $M=0$ and $M=1$ initial states of Ne^+ , with the weighted average taken from photoemission of a $2p$ electron from Ne. Figure 5 shows that the dynamics seen in Fig. 2 are visible as significant change in the photoelectron yield along the laser polarization axis for the $2P^\circ$ ionic state for the two pump-probe delays shown. In comparison, no noticeable dynamics can be seen in the distributions for $2D^\circ$ [Fig. 5(b)] or $4S^\circ$ [Fig. 5(c)]. However, because the largest contribution to the total yield comes from the $2P^\circ$ final states, the dynamics are visible in the total PAD, with an 8% difference in the ionization yield along the polarization axis between the two time delays. These inter-

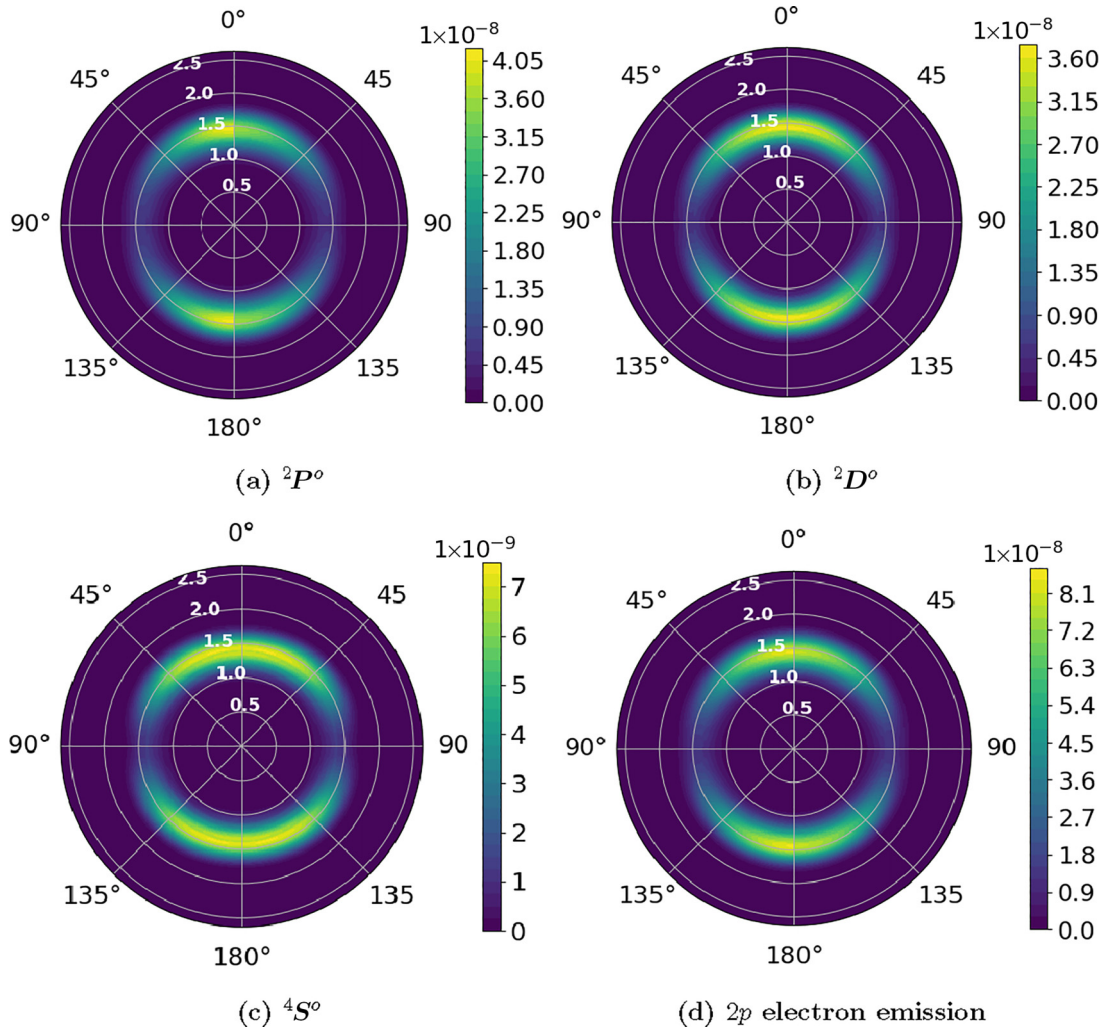


FIG. 5. PADs associated with the individual (a) $^2P^\circ$, (b) $^2D^\circ$, and (c) $^4S^\circ$ $2s^22p^3$ residual ion states of Ne^{3+} and for the overall distribution (d). These states are associated with the emission of two $2p$ electrons. The PADs are plotted with respect to momentum in a.u. The PADs shown are a weighted average of the PADs for initial $M = 0$ and $M = \pm 1$ levels of Ne^+ . The left half of each PAD corresponds to a delay time of 2.81 fs and the right side to a delay of 3.36 fs. For (a), the percentage difference in the ionization yield along the polarization axis is 16%. For the total (d), the percentage difference is 8%.

ference dynamics arise from the quantum correlation between the intermediate 1S and 1D states in Ne^{2+} , as quantified in the off-diagonal elements of the density matrix.

This behavior should thus persist for different pulse lengths: the oscillations observed in Fig. 2 occur at all pulse lengths. The only effect would be the level of difference in the yield at the two time delays, which can be quantified through Fig. 4.

For the HF basis, the angular distributions (not shown) peak at a momentum value of approximately 1.5 a.u. This momentum corresponds to the emission of a $2p$ electron from $2s^22p^4$. The angular distributions obtained for the CI basis set (Fig. 5) show additional ionization processes arising from the emission of a $2s$ electron. Because of the higher binding energy of the $2s$ electron, processes involving the $2s$ appear at lower photoelectron momenta of up to about 0.8 a.u. (corresponding to an energy of around 8 eV). Photoemission of a $2p$ electron from $2s2p^5$ spans a broader range of photoelectron momenta compared to $2p$ -electron photoemission from only $2s^22p^4$: 1.2–1.6 a.u.

The additional ionization processes available within the CI basis set are readily visible in Fig. 6, where the photoelectron angular distributions for Ne^{3+} are separated into those for the residual $2s^22p^3$ configuration and for the residual $2s2p^4$ configuration. The latter correspond to the emission of a $2s$ and $2p$ electron in either order, while the former correspond to the emission of two $2p$ electrons as allowed in the Hartree-Fock calculations. The angular distribution associated with the final $\text{Ne}^{3+} 2s^22p^3$ states remains concentrated in a band at a momentum of 1.5 a.u., while the angular distribution for $\text{Ne}^{3+} 2s2p^4$ states shows several bands covering momentum values of between 0.5 and 1.6 a.u. For this latter configuration, the angular distribution still peaks at a momentum of 1.5 a.u. The change in delay time for the probe maintains its influence in the CI calculations when Ne^{3+} is left in $2s^22p^3$, but it has no observable effect when Ne^{3+} is left in $2s2p^4$. This is not surprising: correlation in the intermediate Ne^{2+} ion is restricted to the superposition of $2s^22p^4$ 1S and 1D . The final configuration is then reached by photoemission of a $2s$ electron, but this

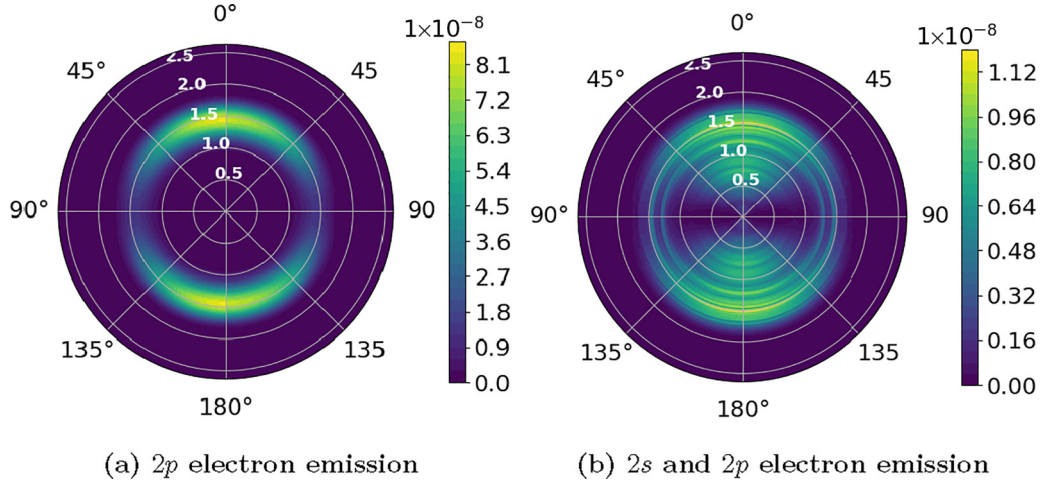


FIG. 6. The angular distribution for the outgoing electron momentum, in a.u., for Ne^{3+} in the CI basis set as a function of the angle of distribution θ ($0^\circ \leq \theta < 180^\circ$) for (a) $2s^22p^3$ final Ne^{3+} states, corresponding to the emission of two $2p$ electrons ($^2P^\circ$, $^2D^\circ$, and $^4S^\circ$), and (b) $2s2p^4$ final Ne^{3+} states, corresponding to the emission of a $2s$ and a $2p$ electron (2P , 2S , 2D , and 4P). The left half of these figures shows the angular distribution for a delay time of 2.81 fs, while the right side shows the one for a delay time of 3.36 fs. For (a), the percentage change in the ionization yield is 8%. For (b), the PAD does not change with time delay.

predominantly connects to separate final $2s2p^4$ states with 2S and 2D symmetry.

An important aspect to consider is the relative magnitude of the behavior shown in Figs. 5 and 6. Figure 7 shows the triple differential cross section of the outgoing electron from Ne^{2+} along the laser polarization direction. Differences are concentrated to momentum values between 1.3 and 1.6 a.u., with a relative difference between the peak values for delays of 2.81 and 3.36 fs of 5.8%.

Figure 8 shows the photoelectron density for both the CI and Hartree-Fock basis sets at a momentum of 1.5 a.u. as a function of emission angle. For both the Hartree-Fock and

CI basis sets, the only state affected by the change in delay time is the $^2P^\circ$ state, and the change is most notable along the polarization axis with changes of 26.2% for the Hartree-Fock basis and 16.1% for the CI basis for the $^2P^\circ$ residual-ion state specifically. This then leads to an oscillation amplitude of 8.9% for the Hartree-Fock basis set and 7.9% for the CI basis set, when all sequential $2p$ emission processes are accounted for. The change in basis sets has the most impact for $^2D^\circ$, with the $^2D^\circ$ angular distribution being 45.2% smaller in the CI angular distribution compared to the Hartree-Fock.

IV. DISCUSSION

The main driver of dynamics observed in this investigation is the coherent superposition that the intermediate Ne^{2+} ion is left in upon pump-pulse ionization. The $M = 0$ levels of the $2p^4$ 1S and 1D state are built from the same independent electron basis states, as follows:

$$\begin{aligned}
 ^1S : \frac{1}{\sqrt{3}} |1, -1_2\rangle - \frac{1}{\sqrt{3}} |0, 0_2\rangle + \frac{1}{\sqrt{6}} |-1, 1_2\rangle &= p^2 \ ^1S, \\
 M = 0, \\
 ^1D : \frac{1}{\sqrt{6}} |1, -1_2\rangle + \sqrt{\frac{2}{3}} |0, 0_2\rangle + \frac{1}{\sqrt{6}} |-1, 1_2\rangle &= p^2 \ ^1D, \\
 M = 0. \quad (10)
 \end{aligned}$$

Equation (10) expresses $p^2 \ ^1S$ and 1D in terms of uncoupled electron functions. Thus, it also describes the shape of the electron holes in the $2p^4$ states. The uncoupled electron functions form the basis for the description of an electron cloud. The shape of the electron cloud therefore depends on the phase relation between the 1S and 1D components. To account for these phase effects and their impact on the shape of the electron cloud, the phase differences between the excitation of 1S and 1D must be accounted for within the off-diagonal elements of the LS-coupled density matrix. This phase difference is not generally included in ionization rate calculations.

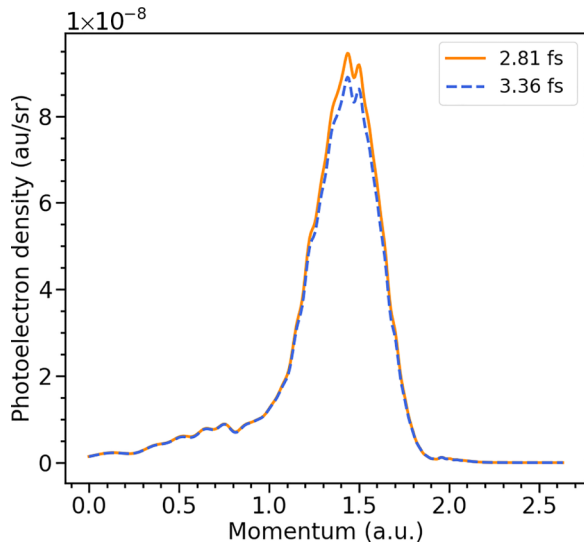


FIG. 7. The triple differential cross section of the outgoing electron from Ne^{3+} along the laser polarization axis as a function of momentum. Angular distributions are given for a delay time of 2.81 fs (dashed blue line) and a delay time of 3.36 fs (solid orange line). These results were calculated using the CI basis set, and the pump and probe length of the pulses was fixed at eight cycles. These results account for all allowed final states of Ne^{3+} .

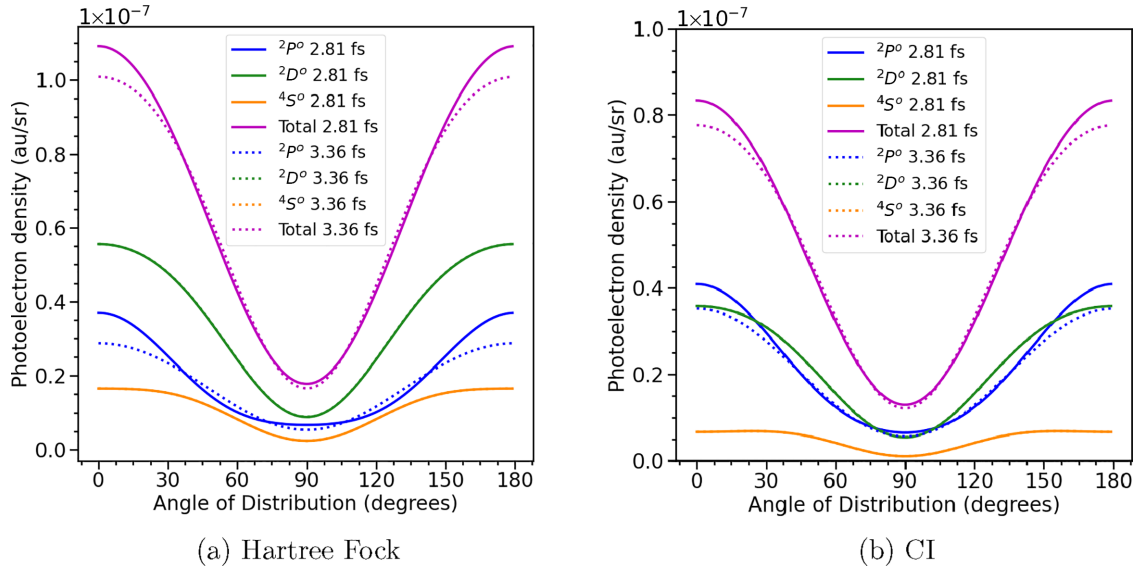


FIG. 8. The angular distribution of the outgoing electron for the states of Ne^{3+} as a function of the angle of distribution θ ($0^\circ \leq \theta \leq 180^\circ$), where the momentum is taken to be 1.47 a.u. (a) shows the angular distribution results calculated using the Hartree-Fock basis, while (b) shows these results calculated for the CI basis set. Both figures show the angular distribution for $^2P^o$ (blue lines), $^2D^o$ (green lines), $^4S^o$ (orange lines), and the sum of the distribution seen in $^2D^o$, $^2P^o$, and $^4S^o$ (magenta lines). Angular distributions are provided for both time delays of 2.81 fs (solid lines) and 3.36 fs (dotted lines).

The coherent superposition between these Ne^{2+} levels provides the time variation of these independent-electron basis states, which can be observed through the probe pulse. The main Ne^{3+} state impacted by this coherent superposition is $2s^22p^3\ ^2P^o$, as it is the only state reachable by single-photon absorption from both $2s^22p^4\ ^1S$ and 1D . It is this coherent superposition between the 1S and 1D states of Ne^{2+} , combined with the energy gap between these two states [33], that is the cause of the dynamics seen in Ne^{3+} . The overall impact of electron correlation on the physical observables is rather modest, as the $^2P^o$ final state accounts for only around 35% of the final ion yield. Furthermore, within the first ionization stage, most ionization is directed toward pure final states, with mixed states contributing a smaller fraction. Hence, the significant dynamics in the overall shape of the electron cloud within the mixed states reduces to minor fluctuations within the overall electron cloud. The outcome of a rate-equation model should be given by the timeaverage of the yields presented here. Therefore, rate-equation models are expected to give a good description of the overall dynamics of the electron cloud during high-frequency sequential-ionization processes.

This conclusion cannot be extended directly to strong-field ionization at IR wavelengths. At IR wavelengths, ionization is dominated by electrons aligned along the laser polarization axis. The ionization process exhibits greater selectivity from the different m levels of the $2p$ shell, leading to greater distortions to the electron cloud.

The best description of the system, either in terms of independent electrons or in terms of atomic states, depends on the timescale of the electron-exchange dynamics, which in the case of the $2p$ shell corresponds to the timescale for transfer of a pair of $m = 0$ electrons to $m = \pm 1$ and vice versa. This transfer timescale varies between 550, as for Ne^{2+} , to around 200, as for Ne^{4+} . For longer pulses, the atomic-structure pic-

ture will give an appropriate representation, whereas shorter processes may be better investigated theoretically by considering the ejection of individual electrons.

V. CONCLUSION

In conclusion, we have combined RMT theory with density-matrix techniques for the investigation of sequential ionization through a pump-probe study. The technique can be implemented efficiently by construction of the angular wave function associated with each residual ion state. Through investigation of sequential ionization of Ne^+ , we have demonstrated that it can be applied readily to investigate dynamics involving a fair amount of atomic structure in the intermediate states.

The application to sequential ionization of Ne^+ at high-frequency light fields demonstrated that sequential ionization on an ultrashort timescale is affected by quantum coherence in the intermediate state, although the overall impact on photoelectron angular distributions is rather modest at 5%–10%. Corrections to rate-equation models on electron-cloud dynamics should therefore be modest.

For the correct implementation of the approach, it is essential that the atomic structure of the residual-ion state is very similar between its calculation as a threshold state and its calculation as an initial state. The current application required a consistency check on the phase of the two wave functions. For more complicated atomic structure, more stringent checks on the wave-function decomposition may be necessary. In addition, the time delay between the two pulses should not be too short: the postcollision interaction in electron scattering was necessary to explain observations where the emission of secondary electrons affected the observation of the primary outcome [34,35]. This effect needs to be accounted for

whenever multiple ionization processes occur with ultrashort time separation.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [37–39]. The RMT code is part of the UK-AMOR suite, and can be found on GitLab [36]. The data used to generate the results shown can be found on Zenodo [37–39].

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