Two-Electron Time-Delay Interference in Atomic Double Ionization by Attosecond Pulses

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A two-color two-photon atomic double ionization experiment using subfemtosecond uv pulses can be designed such that the sequential two-color process dominates and one electron is ejected by each pulse. Nonetheless, *ab initio* calculations show that, for sufficiently short pulses, a prominent interference pattern in the joint energy distribution of the sequentially ejected electrons can be observed that is due to their indistinguishability and the exchange symmetry of the wave function.

The availability of subfemtosecond uv and x-ray pulses from either high harmonic generation [1] or new free-electron laser facilities is opening the path to probing electron dynamics in atoms and molecules on its intrinsic time scale. One consequence of these developments has been the observation of quantum interferences in ionization processes made possible by the correspondence of pulse durations or delays with the time scale of electronic motion. Double slit interferences in the time-energy domain in single ionization have been recently observed in the attosecond regime [2]. Interference patterns in the angular distribution of single ionization of atoms can be observed with a train of attosecond pulses in an experiment called an "attosecond stroboscope" [3]. Here we report *ab initio* calculations of an intrinsically two-electron interference phenomenon that differs from those previously seen in ultrafast experiments in three ways: (1) it only occurs due to the indistinguishability of the ejected electrons and reveals their spin coupling; (2) it appears in the joint distribution of electron energies in which the two electrons share the total energy of the two absorbed photons; and (3) it occurs in two-photon double photoionization under conditions where it is necessarily dominated by sequential ionization by the two pulses. The interference oscillations are visible even for very short time delays, although the associated angular distributions can show important differences from those expected from a pure sequential mechanism.

In the 1980s, the idea of two-particle interferometry was proposed theoretically [4] as an example of a general quantum phenomenon. Later, quantum interference arising from exchange symmetry was predicted [5] for electrons and observed in coincidence measurements of photoelectrons and Auger electrons [6,7]. In that case the photoelectron energy must lie within the Auger width of the energy of the Auger electron, and the only adjustable condition in the experiment is the photoelectron energy. In contrast, the variable time delay and bandwidths of two subfemtosecond uv pulses in the present case allow a significantly richer set of possible experiments.

The prototype situation we consider is one in which two short uv pulses with different central frequencies doubly ionize the helium atom as shown in Fig. 1 to produce electrons with similar energies. The subfemtosecond duration of each pulse gives it an appreciable energy bandwidth. If, for example, a pulse with central frequency corresponding to a photon energy of 35 eV precedes one with a central energy of 69 eV, electrons are ejected with energy distributions centered around 10.4 and 14.6 eV. The energy bandwidths of subfemtosecond pulses can cause those distributions to overlap, and an electron with a given energy can have been ejected by either pulse. Because the electrons are indistinguishable, and because their spins must remain coupled in the same way as in the initial state of the atom (singlet in this case), the resulting probabilities for ejecting electrons of energies E_1 and E_2, restricted to sum to the same total determined by the double ionization energy of He and the photon energies, shows interference oscillations that depend on the time delay between the pulses as well as their durations. Here we predict those photoejection probabilities based on precise *ab initio* numerical calculations, and then provide a simple theoretical model that captures the essential physics and that can be
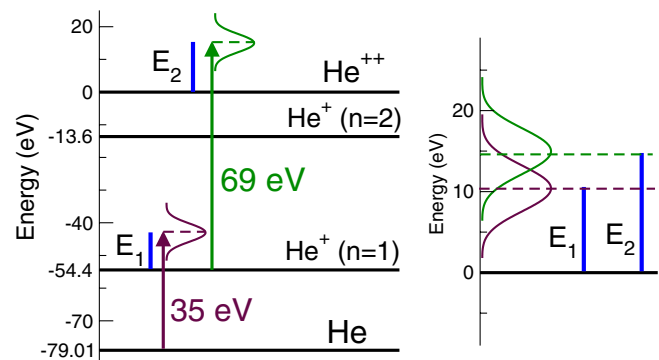

FIG. 1 (color online). Scheme for two-color two-photon double ionization process in helium, showing the expected energies for electrons ejected from each sequential process.

used to semiquantitatively describe this process in many-electron atoms.

Our study of this system is based on accurate solutions of the time-dependent Schrödinger equation. The underlying methods have been described in detail elsewhere [8], and so we describe only the essential ideas here. We solve the time-dependent Schrödinger equation from $t = 0$ to $t = T$, where the second pulse ends at time T, and where $\Psi(t = 0)$ is the ground state of the atom,

$$i\frac{\partial}{\partial t}\Psi(t) = [H_0 + V_t]\Psi(t). \tag{1}$$

The laser-atom interaction, in the dipole approximation and length gauge, is $V_t = \mathbf{E}(t) \cdot (\mathbf{r_1} + \mathbf{r_2})$, and H_0 is the atomic Hamiltonian. The electromagnetic field, $\mathbf{E}(t) = (E^{\omega_1}(t) + E^{\omega_2}(t))\boldsymbol{\epsilon}$, corresponds to two pulses with different central frequencies and possibly different durations and intensities, but with the same polarization vector $\boldsymbol{\epsilon}$ in this example. The individual pulses are specified by

$$E^{\omega_1}(t) = E_0^{(1)}f^{(1)}(t)\sin(\omega_1 t), \qquad t \in [0, T_1],$$
$$E^{\omega_2}(t) = E_0^{(2)}f^{(2)}(t - t_2)\sin(\omega_2(t - t_2)), \qquad t \in [t_2, T], \tag{2}$$

on the time intervals where they are nonzero, where $f^{(i)}(t)$ is the pulse envelope, chosen here to be $\sin^2(\pi t/T_i)$. The pulse durations are T_1 and T_2; τ is the time delay between the centers of the pulses as sketched in the top panel of Fig. 2, and $t_2 = \tau + (T_1 - T_2)/2$.

After the second pulse the electrons are still interacting and the wave function continues to evolve under H_0. Calculating the ejection amplitudes for a fixed total energy formally requires propagating for an infinite time after the second pulse and Fourier transforming the result. However, it is exactly equivalent to solve the driven equation $(E - H)\Psi_{\rm sc} = \Psi(T)$, for the function $\Psi_{\rm sc}$ at a particular total energy, E, shared by the two outgoing electrons. By solving this driven equation using exterior complex scaling (ECS) of the electronic radial coordinates [8], we automatically impose pure outgoing boundary conditions on the scattered wave function. Then from $\Psi_{\rm sc}$ we can extract the amplitude $C(\mathbf{k}_1, \mathbf{k}_2)$ for double ionization with electronic wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$, as we have done in several previous studies of double ionization [8,9]. The numerical solution of Eq. (1) was performed using products of radial basis functions (discrete variable representation) and coupled spherical harmonics, as described in Ref. [8]. Convergence was achieved using a maximum total angular momentum of $L = 2$, individual angular momenta up to $l = 14$, and radial grids extending to 170 bohr.

The probabilities we report here correspond to a sine squared envelope for the pulses, $f^{(i)}(t)$ in Eq. (2). Calculations with Gaussian envelopes show that the calculated probabilities display the same oscillations. We have also verified that the present results employ pulses with
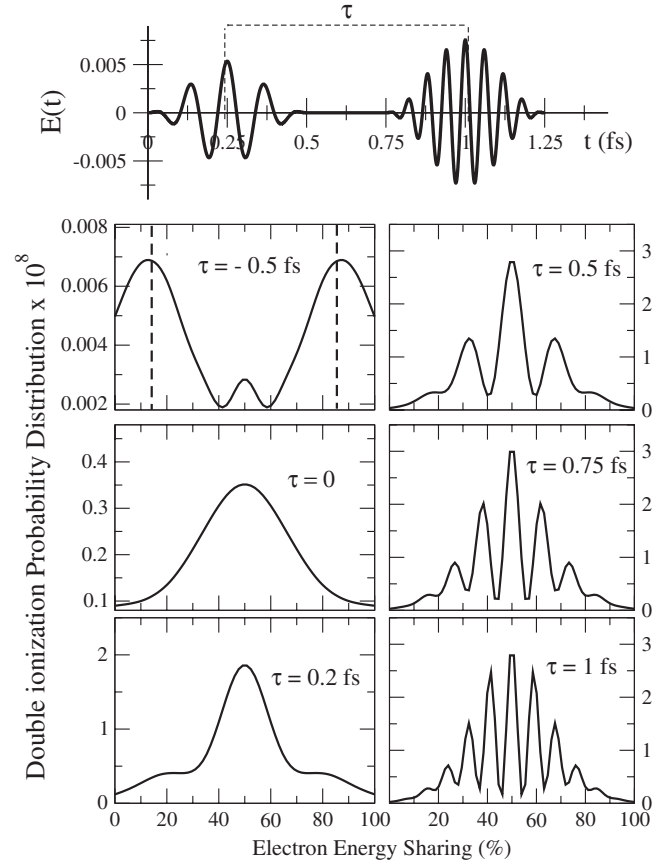

FIG. 2. Electron energy-sharing distributions at different time delays for two-color two-photon double ionization. The energy shared by the photoelectrons is 25 eV. Central frequencies: $\omega_1 = 35$ and $\omega_2 = 69$ eV. Pulse durations: $T_1 = T_2 = 500$ as. Intensities: $I_1 = 10^{12}$ W cm^{-2} and $I_2 = 2 \times 10^{12}$ W cm^{-2}.

sufficiently large numbers of oscillations to be essentially independent of the carrier phases.

As an example of the two-electron interference phenomenon, we solve the time-dependent Schrödinger equation for different time delays, using two pulses of 500 as: one with a central energy of 35 eV and intensity 10^{12} W cm^{-2}, and a second pulse of 69 eV and 2×10^{12} W cm^{-2}. In Fig. 2 we show the energy-sharing distributions, $k_1 k_2 \int d\Omega_1 \int d\Omega_2 |C(\mathbf{k}_1, \mathbf{k}_2)|^2$, resulting from the double ionization amplitudes for a total energy equal to the sum of the central energies of the pulses (104 eV) less the total binding energy of the helium atom. Positive time delays, τ correspond to the 35 eV pulse arriving first. For a negative time delay of $\tau = -0.5$ fs the two-color sequential process takes place through excitation ionization: the 69 eV pulse ionizes He leaving He$^+$ in the $2p$ state, and the 35 eV photon ionizes the excited He$^+$ atom. The vertical lines in the corresponding panel of Fig. 2 indicate the energies of electrons ejected sequentially by the excitation ionization pathway at the central frequencies of the two pulses in that case.

When both pulses reach the target simultaneously ($\tau = 0$) the maximum ionization probability is centered at 50%

energy sharing. As the time delay increases up to 1 fs in
Fig. 2, an increasing number of oscillations appear in these
electron distributions, their number being in principle un-
limited in the infinite energy resolution of the *ab initio*
theoretical calculation. The separations of the peaks as
function of the difference in the electron energies, $E_2 -
E_1$ is a measure of the time delay between the short pulses
and is approximately equal to $2\pi\hbar/\tau$ for pulses of equal
duration. If we extract the ionization amplitudes over a
range of total energies from a single wave packet following
the pulses we can see the entire interference pattern shown
in Fig. 3 as it would appear in coincident energy detection
of the electrons integrated over all angles.

The sensitivity of the oscillations to the duration of
subfemtosecond pulses is shown in the top panel of
Fig. 4 where we plot energy-sharing distributions resulting
from different combinations of pulse durations for the
same time delay of 500 as. The energy spacing of the
oscillations remains essentially the same while their rela-
tive intensities and contrast ratios change. Not shown in
that figure is the result of using pulse durations longer than
5 fs, when their energy bandwidths do not overlap for these
central energies. In that case the interference pattern is
replaced by two well-separated peaks at the sequential
energies, labeled E_1 and E_2 in Fig. 1, determined by the
central frequencies of the pulses.

There is good reason to believe these effects can be
practically observed. The integral of the double ionization
probability over $dE_1 dE_2$ in the region of the interference
pattern shown in Fig. 3 is 4×10^{-9}. With gas densities
typical in contemporary momentum imaging or coinci-
dence experiments, events with this probability are com-
monly observed. If the He^{++} nuclear recoil is observed in

coincidence with one electron, the background due to
single ionization might be avoided.

To understand the origin of these interferences, and to
produce a semiquantitative model that can be used for
other atoms, we can treat the problem using second-order
time-dependent perturbation theory. If we limit the sum
over intermediate states to the ground state of the He^+ ion,
the amplitude for populating the doubly ionized state
$\Psi^-_{\mathbf{k}_1 \mathbf{k}_2}$ with electron momenta $\mathbf{k}_1$ and $\mathbf{k}_2$ from the ground
state Φ_0 of He is

$$C(\mathbf{k}_1, \mathbf{k}_2) \approx \left(\frac{-i}{\hbar}\right)^2 \int d^3\mathbf{k}_0 \langle \Psi^-_{\mathbf{k}_1 \mathbf{k}_2} | \mu | \psi^-_{\mathbf{k}_0, 1s} \rangle \langle \psi^-_{\mathbf{k}_0, 1s} | \mu | \Phi_0 \rangle$$

$$\times \int_0^T dt' \int_0^T dt' e^{i\omega_{k_1, k_2; k_0, 1s} t} e^{\omega_{k_0, 1s; 0} t'} E(t) E(t'), \quad (3)$$

where the integral is over intermediate ionized momenta,
$\mathbf{k}_0$, and transition frequencies are $\omega_{k_1 k_2; k_0, 1s} = k_1^2/2 +
k_2^2/2 - k_0^2/2 - E_{1s(\text{He}^+)}$ and $\omega_{k_0, 1s; 0} = k_0^2/2 + E_{1s(\text{He}^+)} -
E_{\text{He}}$. To evaluate this expression approximately we appeal
to the same approximations that we used previously in a
similar model for two-photon ionization from a single
pulse [8]. The key approximations are to the amplitude
$\langle \Psi^-_{\mathbf{k}_1 \mathbf{k}_2} | \mu | \psi^-_{\mathbf{k}_0, 1s} \rangle$. We first neglect final state interaction
completely and write the doubly ionized state as the sym-
metrized product

$$\Psi^-_{\mathbf{k}_1 \mathbf{k}_2} \approx (\varphi^{(-)}_{\mathbf{k}_1}(\mathbf{r}_1) \varphi^{(-)}_{\mathbf{k}_2}(\mathbf{r}_2) + \varphi^{(-)}_{\mathbf{k}_1}(\mathbf{r}_2) \varphi^{(-)}_{\mathbf{k}_2}(\mathbf{r}_1))/\sqrt{2} \quad (4)$$

where $\varphi^{(-)}_{\mathbf{k}}$ denotes a momentum-normalized Coulomb
scattering function for charge $Z = 2$, and the $+$ sign
corresponds to singlet spin coupling. We then make the
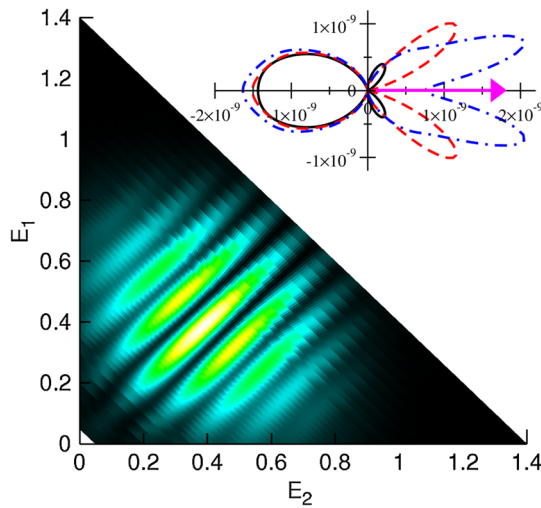seemingly radical approximation of neglecting screening

FIG. 3 (color online).   Electron energy joint distribution for
pulses of 500 as with time delay of 1 fs with other parameters
as in Fig. 2. Energies in hartrees. Inset: angular distributions for
$E_1 = E_2$ with $\tau = 0$ (solid), 0.5 fs (dashed), and 1 fs (chained)
and one electron (arrow) ejected along the polarization direction.
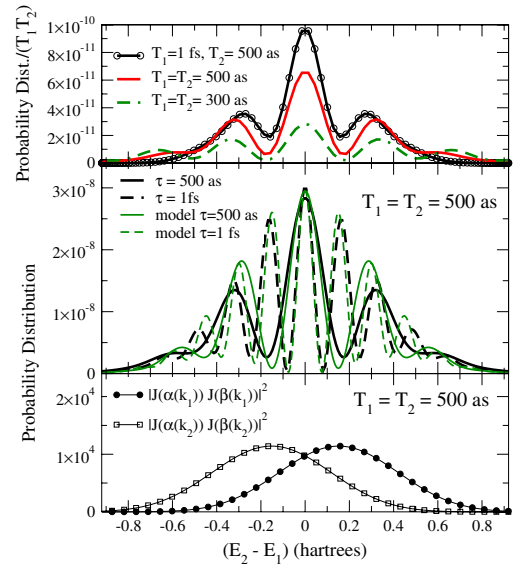

FIG. 4 (color online).   Top: Energy distributions (divided by
$T_1 \times T_2$) for different pulse durations with delay $\tau = 0.5$ fs.
Middle: Comparison of *ab initio* and model calculations.
Bottom: Moduli of separate interfering factors in sequential
model (atomic units).

and correlation entirely for the intermediate state, writing it as the product, $\psi^-_{\mathbf{k}_0,1s} \approx \varphi^{(-)}_{\mathbf{k}_0}(\mathbf{r}_1)\varphi^{\mathrm{He}^+}_{1s}(\mathbf{r}_2)$, of a Coulomb function with $Z = 2$ and the ground state of He^+. Because the dipole operator is a one-body operator, the integration over $\mathbf{k}_0$ in Eq. (3) can then be performed using the resulting momentum conserving delta functions, leaving only the time integrations.

With the electric fields in Eq. (2) substituted into Eq. (3) we get a particularly simple result in the case that the pulses do not overlap and if we neglect double ionization by either of the two pulses separately, which produces electrons at very different final energies,

$$C(\mathbf{k}_1, \mathbf{k}_2) \approx \left(\frac{-i}{\hbar}\right)^2 \frac{1}{\sqrt{2}} (\langle \varphi^{(-)}_{\mathbf{k}_2}|\mu|\varphi^{\mathrm{He}^+}_{1s}\rangle\langle\psi^-_{\mathbf{k}_1,1s}|\mu|\Phi_0\rangle$$
$$\times [e^{i(\alpha(k_1)+\omega_2)\Delta t}J_2(\alpha(k_1))J_1(\beta(k_1))]$$
$$+ \langle\varphi^{(-)}_{\mathbf{k}_1}|\mu|\varphi^{\mathrm{He}^+}_{1s}\rangle\langle\psi^-_{\mathbf{k}_2,1s}|\mu|\Phi_0\rangle$$
$$\times [e^{i(\alpha(k_2)+\omega_2)\Delta t}J_2(\alpha(k_2))J_1(\beta(k_2))]), \quad (5)$$

where $\alpha(k_i) = k_1^2/2 + k_2^2/2 - k_i^2/2 - E_{1s(\mathrm{He}^+)} - \omega_2$, $\beta(k_i) = k_i^2/2 + E_{1s(\mathrm{He}^+)} - E_{\mathrm{He}} - \omega_1$, and $\Delta t = \tau + (T_1 - T_2)/2$. The only time integrals surviving are then

$$J_i(\gamma) \equiv E_0^{(i)}\int_0^{T_i} e^{i\gamma t}f^{(i)}(t)dt. \quad (6)$$

The oscillations in the double ionization probability, $|C(\mathbf{k}_1, \mathbf{k}_2)|^2$ as a function of the energies of the electrons arise from the interference of the two terms being added in Eq. (5). If we neglect the phases of the dipole amplitudes appearing there, and approximate them in terms of the square roots of the corresponding single ionization cross sections, e.g., $\langle\psi^-_{\mathbf{k},1s}|\boldsymbol{\epsilon}\cdot\mathbf{r}|\Phi_0\rangle \approx ((d\sigma/d\Omega)/(4\pi^2\alpha k\omega))^{1/2}$ for the photoionization amplitude of the He atom (where α here is the fine structure constant), we find that in this case the dependence of $|C(\mathbf{k}_1, \mathbf{k}_2)|^2$ on the directions of ejected electrons factors off and is merely the product of two dipole distributions $\cos^2\theta_1\cos^2\theta_2$. The model and *ab initio* energy-sharing distributions in Figs. 2–4 are integrated over the angular dependences.

In Fig. 4 we show results of this simple model with corresponding exact calculations of the energy-sharing distributions. In spite of the severe approximations necessary to produce an analytical model, the results match the *ab initio* calculations well both in shape and magnitude for this case. If in Eq. (5) we ignore the energy dependences of the phases of the J_i integrals, which depend on the shapes of the pulses and their durations, then the relative phase of the two terms is $(\alpha(k_2) - \alpha(k_1))\Delta t = (E_1 - E_2)\Delta t$, which explains (approximately) the periods of the oscillations as a function of either electron's energy in the joint probability distribution for ionization. The exact spacing also reflects the phases in Eq. (5) ignored in this simplified picture.

It is important to observe that while the sequential model correctly describes the features of the energy-sharing probability distribution, it fails to describe the actual angular distributions in detail, especially for short time delays. In Fig. 3 we show calculated *ab initio* angular distributions for $\tau = 0$, 0.5, and 1 fs. With no time delay, we see a tendency to back-to-back ejection which persists in modified form to at least $\tau = 1$ fs, although apparently changing towards the simple dipole pattern of the sequential model. This behavior suggests strong interaction in the final state between sequentially ejected electrons also seen in some other situations [8,10].

If the initial state of He were a triplet, the plus sign in Eq. (5) would be a minus, and minima would appear where there are maxima in the interference patterns in Figs. 2–4. For many-electron atoms the overall spin state of the ion and ejected electrons have to be the same as that of the neutral. In that case two-electron interference patterns would provide a direct measure of the residual ion's spin state. In such a system (or for pulses with different polarizations) the angular dependence of double ionization does not necessarily factor out of Eq. (5), and the interference pattern can vary with the angles of ejection as well as energy sharing. The arguments leading to the sequential model for this process in Eq. (5) can easily be extended to many-electron atoms where this phenomenon could be used to probe the dynamics of double photoejection when multiple states of the residual ion can be created.

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