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Imaging Electronic Motions by Ultrafast Electron Diffraction

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ABSTRACT

Recently ultrafast electron diffraction and microscopy have reached unprecedented temporal resolution, and transient structures with atomic precision have been observed in various reactions. It is anticipated that these extraordinary advances will soon allow direct observation of electronic motions during chemical reactions. We therefore performed a series of theoretical investigations and simulations to investigate the imaging of electronic motions in atoms and molecules by ultrafast electron diffraction. Three prototypical electronic motions were considered for hydrogen atoms. For the case of a breathing mode, the electron density expands and contracts periodically, and we show that the time-resolved scattering intensities reflect such changes of the charge radius. For the case of a wiggling mode, the electron oscillates from one side of the nucleus to the other, and we show that the diffraction images exhibit asymmetric angular distributions. The last case is a hybrid mode that involves both breathing and wiggling motions. Owing to the demonstrated ability of ultrafast electrons to image these motions, we have proposed to image a coherent population transfer in lithium atoms using currently available femtosecond electron pulses. A frequency-swept laser pulse adiabatically drives the valence electron of a lithium atom from the $2s$ to $2p$ orbitals, and a time-delayed electron pulse maps such motion. Our simulations show that the diffraction images reflect this motion both in the scattering intensities and the angular distributions.

Keywords: Ultrafast electron diffraction, Adiabatic passage, Imaging electronic motion

1. INTRODUCTION

Understanding gas-phase reactions relies on knowledge of both the molecular geometries of the reactants and the structural transformations of the molecules along the reaction paths. Therefore, direct observation of the structural changes during chemical reactions helps to elucidate the reaction mechanisms and, in turn, to control the reactions. Owing to their (sub-)ångström wavelengths, x rays and ultrafast electrons can image three-dimensional molecular structures with atomic spatial resolution. Moreover, due to advances in techniques to improve temporal resolutions, there has recently been growing interest in using x rays and electrons in time-resolved measurements to investigate structural dynamics in various reactions.^{1–5} Ultrafast electron diffraction, in particular, has made tremendous progress in recent decades.^{6–11} Electron pulses with ultrashort durations from picoseconds to femtoseconds (fs) have been generated and used to study various kinds of photo-induced reactions in both gas phase^{12–14} and in condensed materials.^{15–19} In addition, various schemes have been proposed to further compress electron pulses to the attosecond (as) regime, which is the typical time scale of electronic motions.^{20–22}

Owing to the steady development of ultrafast techniques, direct observation of electronic motion in reaction processes is anticipated. Deeper insight into particular reaction mechanisms will be achieved if these new techniques are used to image directly the electronic structural changes in reactions. With this in mind, we have performed a series of studies on the capabilities of ultrafast electrons to image and differentiate various types of electronic motions in atoms and molecules through diffraction^{23–26} or impact ionization²⁷ processes. In this article, we summarize our recent works on the use of ultrafast electron diffraction to image electronic motions in atoms. We first present an overview of the theory and then discuss our time-resolved diffraction image results from various coherent electronic motions in hydrogen atoms. The main purpose of this study is to characterize the features in time-resolved diffraction images due to various types of electronic motions in atoms and molecules. A virtue of atomic systems is that they provide simple electronic structures with well-defined symmetries. We therefore able to consider three prototypical electronic motions in hydrogen atoms categorized by the symmetry properties of their electronic motions. The first type of motion, termed *breathing motion*, originates from a

Figure 1. Schematic setup for ultrafast electron diffraction to image electronic motions in atoms and molecules. The electronic motion in a target is initiated by a pump laser pulse, and such motion is probed by an ultrafast electron pulse with controlled time delay. For future reference, the coordinate system is given here.

coherent superposition of equal-parity eigenstates. The electron density exhibits a symmetric periodic oscillation of its radial size. The second type of motion, termed *wiggling motion*, originates from a coherent superposition of opposite-parity eigenstates. The electron density moves asymmetrically from one side of nucleus to the other. The third type of motion, which is the most general one, is a *hybrid motion* that involves both breathing and wiggling motions. After understanding how these prototypical electronic motions are reflected in the corresponding diffraction images, we apply this knowledge to interpret the results of a laser-driven electronic motion in lithium atoms, which we present in the second part of this article.

A typical time-resolved ultrafast electron diffraction setup for imaging electronic motion in a pump-probe scheme is illustrated in Fig. 1.²⁶ The electronic motion in a target (*e.g.*, a lithium atom) is initiated by a pump laser pulse. At a certain time delay, an ultrafast electron pulse impinges on the target, and the detector records the diffraction pattern of the scattered electrons. By varying the time delay between the optical pump and the electron probe pulses, the time-varying diffraction images reflect the electronic motion. The particular kind of electronic motion can be inferred by analyzing the scattering intensities and the symmetries of the diffraction patterns.

2. IMAGING COHERENT ELECTRONIC MOTIONS IN HYDROGEN ATOMS

2.1 Theoretical Model for Time-resolved Ultrafast Electron Diffraction

In the following we briefly describe the key ideas for modeling time-dependent scattering of ultrafast electrons in order to image electronic motions in hydrogen atoms; the details of the theory can be found in Ref. [24]. The electronic motions in the hydrogen atom are assumed to be created by some pump procedures, so the electronic wave functions $\psi(t)$ can be described by coherent superposition states:

$$\psi(t) = \sum_n c_n \phi_n e^{-i\omega_n t}, \quad (1)$$

where ϕ_n is an eigenstate of the hydrogen atom with the energy ω_n , c_n is the amplitude of the eigenstate, and n denotes the quantum numbers characterizing the eigenstate. When an ultrafast electron is scattered from such a state at a delay time t_d , information on the electronic motion is carried by the scattering amplitude from which the diffraction pattern can be calculated. In order to properly describe the time-dependent scattering, the incident electron and the target are modeled as wave packets that are localized in space. The wave packets are then propagated in time, and the scattering amplitude corresponding to a transition to some eigenstate ϕ_m of the hydrogen atom can be calculated. The scattering amplitude is a coherent sum of all transitions from the components ϕ_n of $\psi(t)$ to ϕ_m weighted by their amplitudes c_n and phases $e^{-i\omega_n t}$ and convoluted with the momentum amplitude of the incident electron. The probability for the electron to be scattered at some angle is obtained by taking the absolute square of the scattering amplitude and integrating over all unresolved channels.

Since in conventional ultrafast electron diffraction experiments only the scattering angles of the electrons are measured (as shown in Fig. 1), the final states of the targets and the energies of the scattered electrons need to be summed to simulate the measured scattering probabilities. We therefore define the *differential probability*, $dP/d\Omega$, which is the probability for a projectile electron to be scattered into a unit solid angle, to represent the experimental diffraction images. In this article the terms “differential probability,” “diffraction image,” and “scattering intensity” are used interchangeably.

Owing to the entanglement of the electron and target wave packets by the collision, the final expression for the differential probability is complicated. However, under the appropriate conditions discussed below, the expression can be simplified and illustrates concisely how the diffraction image relates to the electronic motion. The first condition concerns the temporal resolution. In order to resolve the target electronic motion, the duration of the electron pulse has to be shorter than the characteristic time scale of the motion. Therefore, the electronic motion can be considered as frozen during the collision, namely, $\psi(t)$ can be approximated by the wave function $\psi(t_d)$ at the moment of collision. The second condition concerns the scattering mechanism. For high-energy collisions and light atomic targets, the first-order Born approximation (*i.e.*, a single collision) is valid, which greatly simplifies the calculation of the transition amplitudes.²⁸ Likewise, exchange effects between the projectile and the target electrons can be neglected.²⁹ Therefore, the scattering amplitudes are usually insensitive to the details of the electron pulses (*e.g.*, the energies and bandwidths of the incident electrons), thus making the physical interpretation of the results simple. The third condition concerns the monochromaticity of the pulses.³⁰ If the kinetic energy of an electron pulse is much larger than its bandwidth, the pulse can be characterized by a single momentum. Therefore, together with the above considerations, the scattering amplitude can be factorized into a kinematic part depending on the kinematics of the collision and a structural part associated with the target structure.³¹ Under the above conditions, the differential probability simplifies to

$$\frac{dP}{d\Omega} \propto \sum_m \left| \sum_n c_n T_{mn} e^{-i\omega_n t_d} \right|^2, \quad (2)$$

where T_{mn} is the usual transition amplitude of the target from an initial state ϕ_n to a final state ϕ_m .³² Comparing Eqs. (2) and (1), one sees that the quantity inside the absolute square is the wave function $\psi(t_d)$ in which ϕ_n is replaced by the transition amplitude T_{mn} . That is, ultrafast electron diffraction provides a mechanism to map the initial coherent superposition state $\psi(t)$ at delay time t_d to a final state ϕ_m of the target. Finally, the (total) differential probability sums over unresolved channels incoherently.

2.2 Breathing Motion in Hydrogen Atoms

An example of the breathing motion is the superposition of the equal-parity $3p$ and $4p$ eigenstates of the hydrogen atom. This state can be generated by a linearly-polarized laser pulse whose central frequency and bandwidth are chosen such that both eigenstates are equally populated, while the populations in the other excited states are negligible.²³ Hence, the excited wave function is approximated by

$$\psi(t) \simeq \frac{1}{\sqrt{2}} (\phi_{3p} e^{-i\omega_{3p}t} + \phi_{4p} e^{-i\omega_{4p}t}). \quad (3)$$

The left column of Fig. 2 shows the time-dependent electron density of the breathing motion in the y - z plane at times $t = 0, \Gamma/4$, and $\Gamma/2$, where $\Gamma = 6.25$ fs is the $3p$ - $4p$ beat period. The z axis is defined by the polarization of the laser. The breathing motion shows an oscillation in the average radius of the electron density. At time zero the electron density has a compact distribution localized near the nucleus. As time elapses, the density spreads and reaches the maximum average radius at the half period $t = \Gamma/2$. In the second half of the motion the density retraces back to its original size. Since the wave function has well-defined parity, the electron density maintains its inversion symmetry throughout the entire period of motion.

In order to resolve the breathing motion temporally and spatially, the electron pulses are assumed to have a full width at half maximum (FWHM) of 100 as and a kinetic energy of 10 keV. The corresponding de Broglie wavelength is about 0.12 Å. A small beam angular spread of $\pm 10^{-4}$ rad. is chosen to achieve adequate angular resolution. The longitudinal and transverse widths of the momentum distribution of the electron wave packet are set by the pulse duration and beam angular divergence, respectively. The pulses are assumed to be transform

Figure 2. Time-dependent electron densities of hydrogen atoms for the breathing (*left column*) and the wiggling (*right column*) motions at times $t = 0T$, $T/4$, and $T/2$ in the y - z plane.²⁴ In the case of breathing motion, the equal-parity $3p$ and $4p$ eigenstates are superposed equally [see Eq. (3)], whereas in the case of the wiggling motion the opposite-parity $3d$ and $4f$ states are superposed equally. The beat periods of each of the two electronic motions is $T = 6.25$ fs. See Fig. 1 for the definition of the coordinate system. Note that the scale of the color bar for the breathing motion at $t = T/2$ differs from the others.

Figure 3. Inelastic (*left column*) and restricted (*right column*) diffraction images of the breathing motion in hydrogen atoms produced by 100-as (FWHM) electron pulses at four time delays: $t_d = 0T$, $T/4$, and $T/2$.²⁴ The kinetic energies of the incident electrons are centered at 10 keV. The inelastic diffraction images include all transitions to final states having principal quantum numbers less than 9 and orbital angular momenta less than 6, while the restricted diffraction images include only transitions to the $3p$ and $4p$ states (see text for details). See Fig. 1 for the definition of the scattering angles θ and φ . Owing to symmetry, only the upper half planes of the diffraction images are shown.

limited. The time-resolved diffraction images from the breathing motion at delays $t_d = 0T$, $T/4$, and $T/2$ are presented in Fig. 3. The left column of Fig. 3 shows the *inelastic* diffraction images in which the final-state sum [*i.e.*, the m -summation of Eq. (2)] includes eigenstates whose principal quantum numbers satisfy $n_f \leq 9$ and the Rydberg states ($n_f > 9$) whose orbital angular momentum quantum numbers satisfy $l_f \leq 6$. We omit impact ionization processes. Note that although we call these diffraction images inelastic (because of the ambiguity in defining elastic scattering for coherent superposition states), they include *all* major transitions of the coherent target states. One observes that the scattering intensities increase with time delay, which reflects the increase

Figure 4. Inelastic (*left column*) and restricted (*right column*) diffraction images of the wiggling motion in hydrogen atoms produced by 100-as (FWHM) electron pulses at four time delays: $t_d = 0\text{ T}$, $\text{T}/4$, $\text{T}/2$, and $3\text{T}/4$.²⁴ The wiggling motion is produced by superposing the opposite-parity $3d$ and $4f$ states of hydrogen. The inelastic diffraction images contain all major transitions from the initial coherent superposition state, while the restricted ones include only the $3d$ and $4f$ final states.

in size of the electron density. The elongated diffraction patterns along the z axis (*i.e.*, $\varphi = 0^\circ$ and 180°) reflect the p -orbitals involved in the motion. The diffraction images also show strong forward scattering for $\theta \lesssim 0.1^\circ$, owing to inelastic transitions that usually peak in the forward direction.²⁹

In order to evaluate the significance of inelastic transitions to states besides the $3p$ and $4p$ states, we show the *restricted* diffraction images in the right column of Fig. 3 at the same delays as for the inelastic ones. The final-state sum of the restricted diffraction images is restricted to the states participating in the electronic motion (*i.e.*, the $3p$ and $4p$ states in the breathing motion). Compared with the inelastic counterparts, the restricted diffraction images show similar temporal behavior but sharper angular distributions and more pronounced temporal variations. Moreover, these inelastic transitions to the final states besides the $3p$ and $4p$ contribute predominantly in the forward direction.

2.3 Wiggling Motion in Hydrogen Atoms

The wiggling motion, in contrast to the breathing motion, occurs for coherently superposed states with opposite parities, so the electron density lacks inversion symmetry. One example is an equal superposition of the $3d$ and $4f$ eigenstates of the hydrogen atom, which has been studied in time-resolved x-ray diffraction.³³ The right column of Fig. 2 shows the wiggling of the electron density in the y - z plane as a function of time. At time zero the electron density is asymmetric and located on the right side of the nucleus. Then it moves to the left. At $t = \text{T}/4$ the electron density shows a symmetric distribution, and it proceeds to move leftward until it reaches the other side at $t = \text{T}/2$. The $3d$ - $4f$ wiggling motion has the same beat period ($\text{T} = 6.25$ fs) as the $3p$ - $4p$ breathing motion. Note that while the center of mass of the electron density vibrates from one side of the nucleus to the other, the average radius of the electron density is a constant of the motion.

Figure 4 shows the inelastic and restricted diffraction images for the wiggling motion at time delays $t_d = 0\text{ T}$, $\text{T}/4$, $\text{T}/2$, and $3\text{T}/4$. The parameters for the electron pulses are the same as those for the breathing motion. Although the changes in the inelastic diffraction patterns are difficult to discern in these two-dimensional density plots, the restricted ones do manifest the dependence on the pump-probe time delay. In particular, unlike the case of the breathing motion in which the scattering intensities change with time delay, the restricted diffraction images show asymmetric distributions with respect to $\varphi = 90^\circ$ at $t_d = \text{T}/4$ and $3\text{T}/4$ and a delay-independent total scattering probability. The changes in the inelastic diffraction images are difficult to discern because the

asymmetry (as observed in the restricted diffraction images) depends on the energies of scattered electrons, according to an energy-resolved analysis.²⁵ Therefore, if the energies of the scattered electrons are not resolved, the contrast in the asymmetry is reduced by an averaging effect.

Although the diffraction patterns indeed reflect the asymmetric electronic motion, the asymmetry of the images is asynchronous with that of the electron densities. The electron density is symmetric at $t = T/4$ (the middle panel of the right column of Fig. 2), yet the corresponding diffraction image in Fig. 4 shows an asymmetric distribution. On the other hand, the *two* different asymmetric densities at $t = 0T$ and $T/2$ correspond to the *same* symmetric diffraction image. This asynchrony can be understood from the viewpoint of momentum transfer.²⁵ In the Born approximation, the scattering can be considered as a process of momentum transfer in which the projectile electron imparts momentum to the target from which it scatters. Therefore, the probability of an electron scattered at given scattering angles depends on both the target momentum distribution as well as the projectile electron momentum transfer. Since the target electron moves leftward during the first half of the wiggling motion, its momentum density is asymmetric and shifted toward the negative z direction. Therefore, at $t_d = T/4$ the probability of an electron scattered toward the left (*i.e.*, $\varphi = 180^\circ$) is larger than that toward the right, even though the electron density is symmetric. On the other hand, whereas the electron densities are different at $t = 0T$ and $T/2$, their momentum distributions are actually identical and centrosymmetric. Hence, they share the same symmetric diffraction image. When the target electron reverses its direction of motion in the second half period of the motion, the momentum distribution shifts toward the positive z direction and, accordingly, the asymmetry of the diffraction image reverses at $t_d = 3T/4$.

2.4 Hybrid Motion in Hydrogen Atoms

The last type of electronic motion is the (general) hybrid motion that combines both breathing and wiggling motions. In Sec. 2.2 we have seen that the superposition of the $3p$ and $4p$ states yields a breathing motion. However, since only a fraction of the initial $1s$ population is excited to both states, the majority of the population remains in the ground state. Therefore, the electronic motion is actually a hybrid motion that, in addition to the slow $3p$ - $4p$ breathing, involves also the beat motions between the $1s$ and $3p$ or $4p$ states, which are rapid wiggling motions. Here we consider that 10% of the initial population of the hydrogen atom is excited and shared equally by the $3p$ and $4p$ states. The time-resolved diffraction images from such a hybrid state at fixed scattering angles $\theta = 0.5^\circ$ and 1.0° are presented in Figs. 5(a-d) as a function of the azimuthal scattering angle φ . Since the rapid beat periods between the $1s$ and $3p$ or $4p$ are about 342.0 and 324.2 as, pulse durations (FWHM) of 100 and 500 as are chosen. The 100-as pulse is short enough to resolve such rapid wiggling, while the 500-as pulse can only image the slow $3p$ - $4p$ breathing.

Comparison of the 100-as and 500-as diffraction images at small scattering angle $\theta = 0.5^\circ$ [Figs. 5(a-b)] shows that both scattering probabilities increase with delay and peak at $\varphi = 0^\circ$ and 180° , as seen in the breathing motion of the $3p$ and $4p$ states (see Fig. 3). However, in addition to the overall increase of the scattering intensities, the 100-as case exhibits an asymmetric scattering probability with respect to $\varphi = 90^\circ$ at $t_d = T/4$ (green dashed line), whereas the 500-as case has symmetric patterns for all delays. This asymmetry reflects the rapid wiggling between the $1s$ and $3p$ or $4p$ states. At large scattering angle $\theta = 1.0^\circ$ [Figs. 5(c-d)], the overall increase in the scattering probabilities is less significant than for the case of $\theta = 0.5^\circ$. However, the 100-as case still shows a clear asymmetry. Owing to its insufficient temporal resolution, the 500-as case provides an example that violates the condition on the pulse duration discussed in Sec. 2.1, so the differential probability loses the simple proportionality to the initial coherent superposition state shown in Eq. (2). However, since the pulse duration is longer than the wiggling periods, the rapidly oscillating asymmetry is essentially averaged to zero. Therefore, the differential probability is approximately an incoherent sum of the transitions from the $1s$ state but a coherent sum of the transitions from the $3p$ and $4p$ states:

$$\frac{dP}{d\Omega} \propto \sum_m \left[|c_{1s}|^2 |T_{m \leftarrow 1s}|^2 + |c_{3p} T_{m \leftarrow 3p} e^{-i\omega_{3p} t_d} + c_{4p} T_{m \leftarrow 4p} e^{-i\omega_{4p} t_d}|^2 \right]. \quad (4)$$

In order to quantify the asymmetry observed in the diffraction pattern, we define the *asymmetry* as

$$\text{Asymmetry}(\theta) \equiv \frac{dP(\theta, \varphi = 0^\circ) - dP(\theta, \varphi = 180^\circ)}{dP(\theta, \varphi = 0^\circ) + dP(\theta, \varphi = 180^\circ)}, \quad (5)$$

Figure 5. (a-d) Differential probabilities, $dP/d\Omega$, of the hybrid motion in hydrogen atoms for 100-as (*left column*) and 500-as (*right column*) electron pulses at scattering angles $\theta = 0.5^\circ$ (*first row*) and $\theta = 1.0^\circ$ (*second row*) as a function of azimuthal scattering angle φ .²⁵ Different lines correspond to the different time delays indicated by the legends in panels (a-b). The hybrid motion corresponds to the case in which 90% of the population is in the $1s$ state and 10% of the population is shared equally by the $3p$ and $4p$ states. (e-f) Asymmetry of the diffraction image as a function of scattering angle θ for the time delay $t_d = T/8$. See Eq. (5) for the definition of the asymmetry.

where dP stands for the differential probability $dP/d\Omega$. The asymmetry takes values between -1 and $+1$, with positive asymmetry corresponding to more electrons being scattered toward $\varphi = 0^\circ$. The asymmetries of the 100-as and 500-as pulses at $t_d = T/8$ are presented in Figs. 5(e-f). The 100-as case clearly shows a nonzero asymmetry for all scattering angles θ , but the asymmetry of the 500-as case is essentially zero. Furthermore, larger (absolute) asymmetries can be seen at larger scattering angles θ for the 100-as pulses. In the classical picture of Coulomb scattering, the scattering angle θ has a one-to-one correspondence with the impact parameter, and a large scattering angle corresponds to a small impact parameter. Therefore, electrons scattered at large angle probe the target electronic structure close to the nucleus. Since the $1s$ orbital has a smaller radius than those of the $3p$ and $4p$ states, the wiggling motion is localized around the nucleus, whereas the breathing motion extends to larger radii. Therefore, the asymmetry of the 100-as pulses is larger at large θ , and the overall increase of the scattering intensities at $\theta = 0.5^\circ$ is larger than that for $\theta = 1.0^\circ$.

3. IMAGING POPULATION TRANSFER IN LITHIUM ATOMS

In the previous sections we have seen how the diffraction images relate to different types of electronic motion. Since these electronic motions result from coherent superpositions of eigenstates [see Eq. (1)], the time scale of these electronic motions are set by the beat periods. Therefore, once the electronic motions are initiated, there is no possibility to control the motions. Moreover, due to the typical energy differences in electronic states, the time scale of such motions is on the order of several fs or less. However, the temporal resolution in current experiments is still insufficient to resolve such fast motions. In order to overcome these difficulties, we have proposed to image a picosecond (ps) scale electronic motion in lithium atoms driven by a tailored laser pulse.²⁶ In this scheme, the population of the lithium atoms is transferred adiabatically from the ground state to the first excited state by a chirped laser pulse, and the time scale of such motion can be controlled by the laser parameters, *i.e.*, the laser pulse duration and intensity.^{34,35}

Since the scattering process in this scheme takes place in the presence of an external laser field, the energy of the system is not conserved and the target electronic wave function is no longer a coherent superposition state [as described by Eq. (1)]. Applying the time-dependent distorted wave approximation, we generalized our theory for ultrafast electron diffraction to the case of a time-dependent Hamiltonian. The wave function for the

Figure 6. Laser-driven population transfer in the lithium atom.²⁶ (a) Time-dependence of the electric field envelope [solid (red) line] and instantaneous laser frequency [dashed (green) line]. (b) Populations of the $2s$, $2p$, and $3d$ states of lithium as a function of time. The insets show the averaged valence electron density in the y - z plane at times $t = 1.0$, 3.0 , 4.0 , and 6.0 ps. See text for discussion.

electrons of the lithium atom is

$$\psi(t) = \sum_n c_n(t) \phi_n e^{-i\omega_n t}, \quad (6)$$

where the time-dependent amplitude $c_n(t)$ reflects the time-varying population in the eigenstate ϕ_n .

3.1 Population Transfer Induced by a Chirped Laser Pulse

Figure 6(a) shows the time-dependence of the electric field profile and instantaneous frequency of the laser pulse that induces the $2s \rightarrow 2p$ population transfer in the lithium atom. The pulse profile is assumed to have a Gaussian envelope and a duration (FWHM) of 2.0 ps. The instantaneous frequency increases linearly with time and passes through the $2s$ - $2p$ resonant frequency at 3.5 ps. The peak intensity of the laser is 1.93×10^7 W/cm², and the electric field is linearly polarized along the z axis.

Using this laser pulse profile, the amplitudes $c_n(t)$ can be calculated by solving the time-dependent Schrödinger equation. Since the population transfer is essentially a one-electron process for a weak laser pulse, the eigenstates of the lithium atom are labeled by the orbitals of the valence electron. The populations of the states participating in the population transfer (*i.e.*, the $2s$ and $2p$ states) and the next excited state (*i.e.*, the $3d$ state) are presented as a function of time in Fig. 6(b). The population of the $2s$ state monotonically decreases, while the $2p$ population grows. At the end of pump pulse, almost 100% of the population is transferred to the $2p$ state, and the populations in other excited states are negligible throughout the process. The insets illustrate the averaged electron densities of the valence electron in the y - z plane at times $t = 1.0$, 3.0 , 4.0 , and 6.0 ps. They are calculated from the electron densities of the $2s$ and $2p$ orbitals weighted by their populations at the corresponding times. One can observe that at 1.0 ps, since the majority of the population is still in the $2s$ state, the density shows an isotropic distribution with a nodal circle, which reflects the character of the $2s$ orbital. As the population is transferred to the $2p$ state, the valence electron density gradually transforms to a dumbbell shape with a nodal line along the y axis.

3.2 Time-resolved Diffraction Images of the Population Transfer

The diffraction images of the $2s \rightarrow 2p$ population transfer in lithium atoms produced by 100-fs (FWHM) electron pulses at four time delays ($t_d = 1.0$, 3.7 , and 6.0 ps) are shown in the left column of Fig. 7. Because the time scale of the population transfer is about 3 ps, electron pulses of 100 fs duration are sufficient to resolve the electronic motion. The final-state sum includes all eigenstates whose principal quantum numbers satisfy $n_f \leq 9$. One can

Figure 7. Ultrafast electron diffraction of 10 keV electron pulses from lithium atoms undergoing adiabatic $2s \rightarrow 2p$ population transfer for three electron pulse durations. (a) Time-resolved diffraction images produced by 100-fs (FWHM) electron pulses from lithium atoms undergoing laser-driven population transfer for three time delays: $t_d = 1.0, 3.7$, and 6.0 ps.²⁶ (b-d) Differential probabilities (DPs) for 1-fs, 100-fs, and 2-ps electron pulses as a function of scattering angle θ for fixed azimuthal scattering angle $\varphi = 0^\circ$. The different lines correspond to different time delays, as indicated by the legends in panel (b). Both the diffraction images and the DPs are averaged over a uniform ensemble of lithium atoms having a density of 10^{10} cm^{-3} .

see the strong increase of the scattering intensities in the forward direction as the $2p$ population grows. In order to compare the effects of pulse duration on the diffraction image, we plot the differential probabilities along the $\varphi = 0^\circ$ direction for three pulse durations (FWHM of 1 fs, 100 fs, and 2 ps) in Figs. 7(b-d). Whereas the increases of the scattering intensities with delay are observed for all three pulses, the 2-ps pulses show different angular and temporal behaviors from the other two pulses. The 2-ps pulses already exhibit a strong forward peak at $t_d = 1$ ps [dash-dot-dot (green) line]. Moreover, comparing the scattering intensities for $\theta > 0.3^\circ$ for the three pulse durations, the 2-ps pulses show more uniform growth of the scattering intensities with delay, which fails to reflect the fact that most of the population is transferred between 3 and 4 ps. The similarity between the 1-fs and 100-fs pulses shows that, as discussed in Sec. 2.1, once the electron pulses have enough temporal resolution, the scattering patterns are insensitive to the details of the pulses.

The diffraction patterns not only reflect the growth of the $2p$ population, but also differentiate the symmetries of the target state. In order to see this, we plot the DPs for the diffraction images of the 1-fs, 100-fs, and 2-ps pulses at three scattering angles $\theta = 0.3^\circ, 0.9^\circ$, and 1.5° as a function of the azimuthal angle φ in Fig. 8. For any scattering angle θ , the scattering intensities for the three pulses show identical angular distributions at $t_d = 1.0$ and 6.0 ps, but differences in the scattering intensities appear between $t_d = 1.0$ and 6.0 ps. At $t_d = 1.0$ ps the scattering intensities of all pulses show isotropic distributions, and at $t_d = 6.0$ ps the scattering intensities peak at $\varphi = 0^\circ$ and 180° . This change of the angular distribution reflects the $2s \rightarrow 2p$ population transfer. Moreover, since the period of the $2s$ - $2p$ beat motion is $T = 2.13$ fs, the 1-fs pulses are short enough to resolve such motion. Therefore, the middle three delays for the 1-fs pulses are chosen to differ by half of the beat period. Note that since the $2s$ and $2p$ states have opposite parities, they give rise to a wiggling motion. Thus, one can see the asymmetry of the scattering intensities with respect to $\varphi = 90^\circ$, and this asymmetry oscillates with the period of the $2s$ - $2p$ beat motion.

4. SUMMARY

In summary, we have developed a theoretical model to describe and simulate ultrafast electron diffraction from time-varying electronic motions in the hydrogen and lithium atoms. The simulations demonstrate that ultrafast electrons can provide adequate spatial and temporal resolutions to image the electronic motions. In the case of coherent superposition states in hydrogen atoms, diffraction images from three different types of electronic motions have been presented. The scattering intensities basically reflect the size of the target, and the asymmetries

Figure 8. Comparison of the differential probabilities (DPs) of the 1-fs, 100-fs, and 2-ps pulses at scattering angles $\theta = 0.3^\circ$, 0.9° , and 1.5° as a function of azimuthal angle φ .²⁶ Each column shows the differential probabilities for the electron pulse duration listed at the top, and each row shows results for different scattering angles θ (indicated in the last column). Different lines represent the differential probabilities for different time delays given in the legends. In order to show the asymmetry of the differential probability for the 1-fs pulses, the delays of the 1-fs pulse differ from those of the 100-fs and 2-ps pulses. Note that the $2s$ - $2p$ beat period is $T = 2.13$ fs.

of the angular distributions reflect the direction of electronic motion. In the case of the $2s \rightarrow 2p$ population transfer in the lithium atom, the electronic motion is controlled by a chirped laser pulse. The time-dependent diffraction images show the $2s \rightarrow 2p$ population transfer in both the scattering intensities and the angular distributions.

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