Attosecond Light Pulses for Probing Two-Electron Dynamics of Helium in the Time Domain

Toru Morishita,[1] Shinichi Watanabe,[1] and C. D. Lin[2]
[1]*Department of Applied Physics and Chemistry, University of Electro-Communications, 1-5-1 Chofu-ga-oka, Chofu-she, Tokyo 182-8585, Japan*
[2]*Department of Physics, Kansas State University, Manhattan, Kansas 66506, USA*

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Using attosecond light pulses to doubly ionize a two-electron wave packet of helium, we showed that the time-resolved correlated motion of the two electrons can be probed by measuring their six-dimensional momentum distributions. For simple wave packets, we showed that the measured momenta, when analyzed in appropriate coordinates, can reveal the stretching, the rotational, and the bending vibrational modes of their joint motion in momentum space, in spite of the Coulomb distortion in the final states.

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Following the recent developments in laser technology, ultrashort xuv (extreme ultraviolet) light pulses with duration of several hundred attoseconds have been reported [1–4]. Such pulse durations are comparable to the time scale of the electronic motion in atoms and molecules, thus opening up a route to the time-resolved study of electron dynamics in matter, akin to the time-resolved tracking of the atomic motion in a molecule enabled by the advent of femtosecond laser pulses [5]. Ideally one would like to use such pulses to probe the truly many-body nature of electrons in atoms and molecules, i.e., to address the so-called electron correlation effect in the time domain. Existing time-domain probing techniques of the electronic motion in two-electron atoms have not been directed to this issue, either experimentally [6] or theoretically [7]. How to observe such responses experimentally turns out to be difficult, even conceptually. This difficulty is rooted in the overwhelming success of the shell model, which led us to rely on the mean-field approximation for describing electrons in atoms where each electron "sees" only the average potential from the other electrons plus the nucleus, while we wish to probe a departure from the average.

To observe time-domain phenomena, one has to create a wave packet. We begin with a simple example. Assume that at $t = 0$, a wave packet given by $1s^2\,{}^1S^e + 1s2s\,{}^1S^e$ is created. The energy difference between the two stationary states is 20.6 eV, (see left part of Fig. 1) so this wave packet has to be created by an attosecond pulse, using its broadband spectrum. If left alone, this wave packet is expected to execute the usual two-state oscillation with a period of $T =$ 200 asec. To observe this oscillation, it has to be probed by another attosecond pulse. An "easy" experiment would be to measure the total double ionization probability, for example, by a 95.2 eV, 100 asec (FWHM) pulse, at different time delays. Indeed, the calculated double ionization probability from such a wave packet does confirm this oscillation, as shown in Fig. 2(b). However, these "experimental" data tell nothing about two-electron dynamics. For this simple wave packet, it is clear that one of the electrons stays in the $1s$ orbital, while the second one moves in and out radially. Since the two electrons are indistinguishable, it is better to express this relative in-out oscillation in terms of a density expressed in a "democratic" coordinate R, defined by $R = \sqrt{r_1^2 + r_2^2}$, where r_1 and r_2 are the radial distances of the two electrons from the nucleus. In Fig. 2(a) we show the two-electron density vs R, at $t = 0$, $T/4$, and $T/2$, after being integrated over all the other coordinates. By comparing the two frames in Fig. 2, we only learned that the double ionization probability is large when both electrons are close to the nucleus. The theoretical two-electron dynamics shown in Fig. 2(a) is not seen in the experimental data of Fig. 2(b). In this Letter, we show that to probe electron correlation dynamics in the time domain, one has to doubly ionize the two-electron wave packet, quantify the momenta of both electrons in coincidence, and then analyze the multidimensional momentum spectra in suitable coordinates.

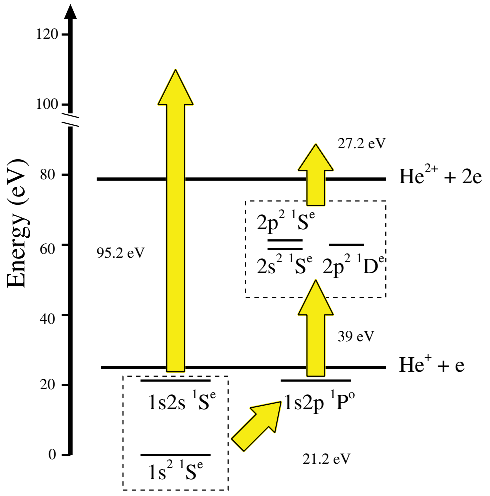

FIG. 1 (color online). Schematic energy level diagram and possible pump-probe schemes for probing electron dynamics of He.

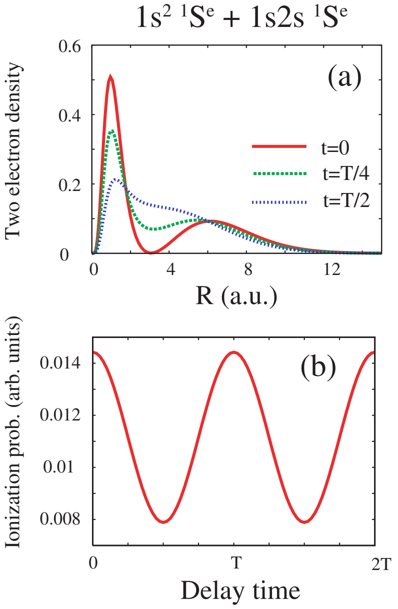

FIG. 2 (color online). (a) Time-dependent two-electron density of the coherent state made of $1s^2 + 1s2s\,{}^1S^e$ as a function of $R = \sqrt{r_1^2 + r_2^2}$, averaged over all other degrees of freedom. (b) Double ionization probability by a 100 asec, 95.2 eV pulse. The oscillation period, $T = 200$ asec. Note that peak ionization occurs when the two electrons are near the origin.

To explore true two-electron correlation dynamics, we consider wave packets made of doubly excited states, where correlation is known to be predominant. For these states, energy domain studies done over the last three decades have shown that they are most adequately described by drawing an analogy with the rotation and vibration of a floppy triatomic molecule [8–14]. For a quantitative description, it is convenient to use hyperspherical coordinates. We replace the independent electron coordinates, $\mathbf{r}_1$ and $\mathbf{r}_2$, by defining a hyperradius, $R = \sqrt{r_1^2 + r_2^2}$, two hyperangles, $\Omega_v = \{\alpha = \tan^{-1} r_2/r_1, \theta_{12} = \cos^{-1} \hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2\}$, and three Euler angles, $\Omega_r = (\alpha', \beta', \gamma')$. In this coordinate system, R stands for the size of the atom, α and θ_{12} measure the stretching and the bending vibrational motions, respectively, and the Euler angles are used to describe the rotation of the atom with respect to a fixed laboratory axis. Since the full wave function is six-dimensional besides the spins, visualizing the full wave function or density is not possible. Thus one has to resort to averages that have apparent classical analogy, such as vibrational and rotational density distributions,

$$\rho_j^{\mathrm{vib}}(\Omega_v) = \int |\varphi_j|^2 d\Omega_r dR, \tag{1}$$

$$\rho_j^{\mathrm{rot}}(\Omega_r) = \int |\varphi_j|^2 d\Omega_v dR, \tag{2}$$

defined for each state φ_j. In presenting ρ^{rot}, we choose $\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2$ and $\hat{\mathbf{r}}_1 \times \hat{\mathbf{r}}_2$ to be parallel to the z' and y' axes of the body-fixed frame, respectively.

We next consider wave packets made of doubly excited states. Based on their energy levels and various theoretical analysis (see Ref. [11] and references therein), doubly excited states are known to form rotational and vibrational supermultiplets [9]. For example, among the three doubly excited states shown on the right half of Fig. 1, the $2s^2\,{}^1S^e$ state is the ground state of the rovibrational motion, the $2p^2\,{}^1D^e$ state is the first rotational excited state, and $2p^2\,{}^1S^e$ is the first excited vibrational state. They lie 21.2, 19.1, and 16.9 eV below the double ionization threshold, respectively. These states exhibit large configuration mixing so that they are more adequately characterized using the $(K,T)^A$ quantum numbers as described in Ref. [11]. For the present purpose, we will nonetheless use the more familiar conventional designation.

In Fig. 3 the vibrational and rotational densities of these three states are given for the $M = 0$ component of the total angular momentum, together with a classical sketch of the motion of the two electrons. Note that we plot the rotational density as a function of α' and β', since it does not depend on γ' for $M = 0$. For $2s^2\,{}^1S^e$, ρ^{vib} has a maximum at $\theta_{12} = \pi$ and ρ^{rot} is isotropic. For $2p^2\,{}^1D^e$, ρ^{vib} is similar to $2s^2\,{}^1S^e$, but ρ^{rot} has nodes in β', which is similar to $|Y_{20}(\beta', \alpha')|^2$ due to total angular momentum $L = 2$; i.e., this state is rotationally excited. For $2p^2\,{}^1S^e$, ρ^{rot} is isotropic, but there is a nodal line in ρ^{vib} at about $\theta_{12} = \pi/2$, so this state is vibrationally excited.

First, consider a coherent state made of $2s^2\,{}^1S^e + 2p^2\,{}^1S^e$ at $t = 0$. This is a bending vibrational wave packet, with an oscillation period of $T = 980$ asec. The momentum density of this two-electron wave packet with respect to $\theta_{p12} = \cos^{-1} \hat{\mathbf{p}}_1 \cdot \hat{\mathbf{p}}_2$ is shown in Fig. 4(a). To probe this wave packet we use a linearly polarized Gaussian pulse to doubly ionize it and the momentum vectors of both electrons are measured. The mean energy of the attosecond probe pulse is $E_{\mathrm{ph}} = 27.2$ eV (see right part of Fig. 1),

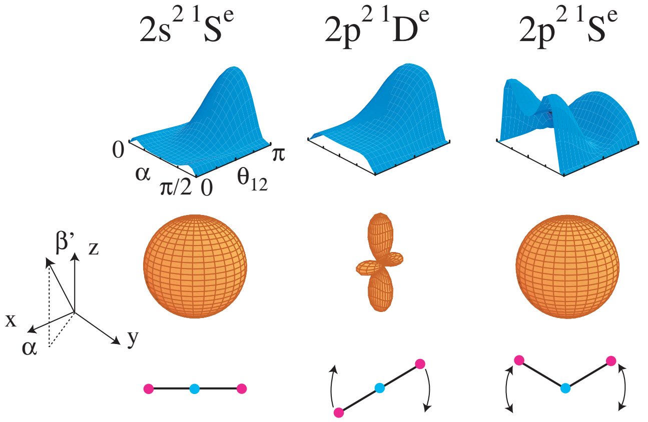

FIG. 3 (color online). Density plots of doubly excited states. The top row presents the relief plots of $\rho^{\mathrm{vib}}(\alpha, \theta_{12})$, and the middle row shows $\rho^{\mathrm{rot}}(\alpha', \beta')$. The bottom row sketches the corresponding classical rotational and bending vibrational modes of the two correlated electrons.

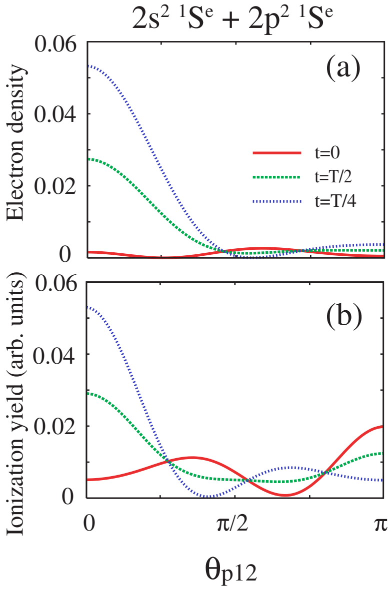

FIG. 4 (color online). (a) Time dependence of the momentum space two-electron density of a coherent state made of $2s^2\,{}^1S^e$ and $2p^2\,{}^1S^e$, shown for its θ_{p12} dependence for $E = p_1^2/2 + p_2^2/2 = 8.2$ eV. (b) The double ionization yields from this state by a 200 asec, 27.2 eV attosecond probe pulse, averaged over the total electron energy. Shown are the angular distributions for $\theta_{p1} = -\theta_{p2}$, where the angles are measured from the laser polarization direction. $T = 980$ asec.

duration $\tau = 200$ asec (FWHM, energy width 9 eV) which is close to what has been achieved recently[4]. The double ionization probability $P(\mathbf{p}_1, \mathbf{p}_2, t)$ is a function of the six-dimensional momenta of the two electrons, $(\mathbf{p}_1, \mathbf{p}_2)$ and time delay t. In Fig. 4(b) we plot the double ionization yield $s(\mathbf{p}_1, \mathbf{p}_2, t) \propto P(\mathbf{p}_1, \mathbf{p}_2, t)/[\hat{\epsilon} \cdot (\mathbf{p}_1 + \mathbf{p}_2)]^2$ as a function of θ_{p12} with the polarization axis $\hat{\epsilon}$ bisecting the two momentum vectors $\mathbf{p}_1$ and $\mathbf{p}_2$, averaged over the total energy. Clearly the time dependence between the two figures resembles each other reasonably well, illustrating that the bending vibrational motion of this simple wave packet can be nicely revealed by such an attosecond probe pulse.

As a technical note, for the weak pulse employed here, we calculated the double ionization yield at each time delay by the first order perturbation theory. The initial wave functions of the wave packet were calculated using the configuration interaction method. The final two-electron continuum wave functions were represented by the properly symmetrized product of Coulomb functions, each with effective charge $Z = 1$, and the dipole matrix elements were calculated in the velocity gauge. We checked that our results do not depend strongly on the effective charge used.

The similarity of the two frames in Fig. 4 is encouraging. Note that it is often incorrectly assumed that one can make a "movie" of the wave packet by probing it. A nearly verbatim reproduction of the density of the initial state in momentum space is possible only if the final states can be represented by plane waves. Figure 4 shows that the Coulomb distortion from the final state interaction is still tolerable such that the experimental signal does follow reasonably the time dependence of the initial wave packet. We comment that in the calculation the autoionization of the two states (lifetimes of 5.3 and 110 fs, respectively) has not been included. The inclusion would introduce a gradual damping of the total ionization yield. Additionally the spectra in Fig. 4(b) are also affected by the pulse duration. For longer pulses the oscillation of the ionization yield vs time delay will be washed out. In general, pulse duration longer than one half of the shortest oscillation period would smooth out the modulation of that particular mode in the time domain.

Figure 4 shows only a very small slice of the theoretical and experimental two-electron wave packet in the momentum space. One can analyze the double ionization yield on the (θ_{p12}, α_p) plane in the momentum space, where $\alpha_p = \tan^{-1} p_2/p_1$. Figure 5(b) shows the results extracted from

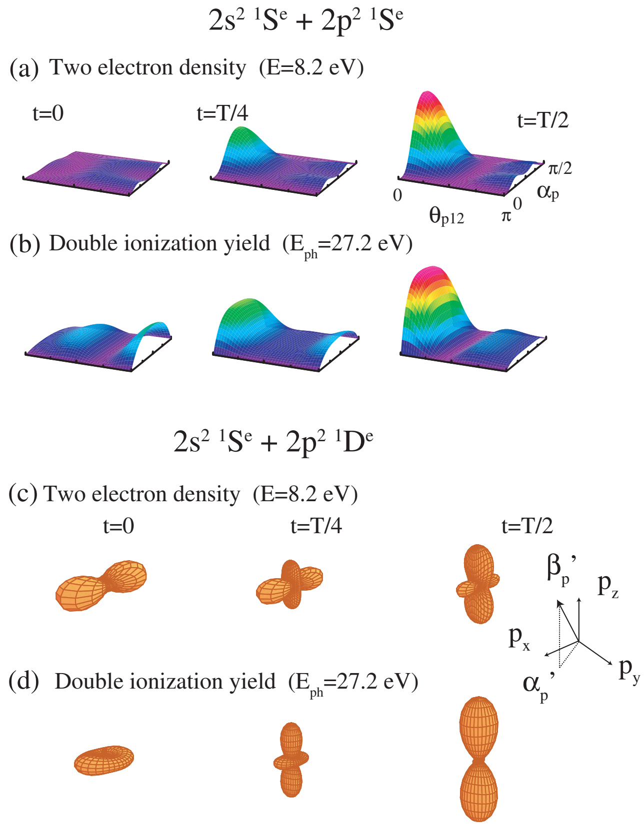

FIG. 5 (color online). (a) Time-dependent vibrational density of a coherent state made of $2s^2\,{}^1S^e + 2p^2\,{}^1S^e$ in momentum space as a function of (α_p, θ_{p12}) at the fixed total energy $E = 8.2$ eV, averaged over the rotational degrees of freedom. $T = 980$ as. (b) Double ionization yield of the vibrational wave packet by a 200 asec, 27.2 eV pulse, averaged over the total electron energy. (c) Polar plot of the time-dependent rotational density of a coherent state made of $2s^2\,{}^1S^e + 2p^2\,{}^1D^e$ in momentum space, averaged over the vibrational degrees of freedom. $T = 2.0$ fs. (d) Polar plot of double ionization yield by a 200 asec, 27.2 eV pulse, averaged over the total electron energy.

the 6D momentum space double ionization yield at the three different delay times indicated. The corresponding electron density of the wave packet in the momentum space with a fixed total energy of 8.2 eV are shown in Fig. 5(a). This example shows the close resemblance of the double ionization yield with the density distribution of the two-electron wave packet in the momentum space. For this special wave packet, the six-dimensional electron momentum spectra indeed allow us to "watch" the bending vibrational motion of the two electrons, albeit with some distortions. This is a true feature of electron correlation in the time domain, showing the two electrons executing bending vibrational motion at the attosecond time scale. We also emphasize that such vibrational motion cannot be clearly visualized unless the measured 6D momentum spectra are displayed on the (θ_{p12}, α_p) plane.

In another example, we consider a wave packet made of $2s^2\,{}^1S^e + 2p^2\,{}^1D^e$ at $t = 0$. Note that this is a rotational wave packet, with an oscillation period of $T = 2.0$ fs. The rotational density distribution of the wave packet is shown in Fig. 5(c) at the indicated three time steps. Assuming the same laser pulse setup, we extract the corresponding probability density on the (β'_p, α'_p) plane in Fig. 5(d). The experiment indeed reveals the rotational motion of the two electrons, but we do notice some distortions of the ionization signal reflecting the effect of the final state interaction from the Coulomb force by the ionized electrons.

So far we have considered "designer's" two-electron wave packets where the stretching, vibrational, and rotational motions of the two electrons can be watched by doubly ionizing the helium using an attosecond pulse. Experimentally, the generation of the wave packet and its measurement are to be carried out in a pump-probe setup. We next consider how a simple two-electron wave packet can be generated with a pump pulse. A wave packet made of $2s^2\,{}^1S^e$, $2p^2\,{}^1S^e$, and $2p^2\,{}^1D^e$ states can be created by two-photon absorption from the ground state, or by single photon absorption from the excited $1s2p\,{}^1P$ state with an xuv attosecond pulse (see right part of Fig. 1). The latter can be generated by nanosecond lasers; see Ref. [15]. Alternatively, one can focus an attosecond xuv pulse onto a few-cycle ir laser, say of duration of about 5 fs. In this case many doubly excited states can be coherently populated and thus a two-electron wave packet will be generated [16]. To analyze such a wave packet, averages like the rotational density, vibrational density, and the functional dependence on R, can all be used to display the time evolution of this two-electron wave packet. The dynamic evolution of a two-electron wave packet cannot be viewed "fully" at a given time, it can only be visualized from a certain projection, and a few such projections will be needed to reveal the time-varying electron-electron interaction dynamics. By measuring the momenta of the two electrons in coincidence, the data can be viewed in different cuts. This is the standard procedure for data taken with, for example, COLTRIMS detectors. In this Letter we suggested how such cuts be made in order to follow the time-varying electron correlation of a two-electron wave packet.

In summary, we have shown that by using an attosecond light pulse to doubly ionize a two-electron wave packet, the time-varying correlated motion of the two electrons can be revealed only by measuring their momentum vectors in coincidence. For simple wave packets the stretching, the rotational, and the bending vibrational motion of the two electrons can be extracted from the measured momentum spectra when they are analyzed in special coordinates. The Coulomb interaction in the final state does not distort the electron momentum spectra significantly such that the probe pulse indeed can be used to "peek" the time-varying two-electron wave packet. While attosecond pump-probe experiments are not realized yet, we believe that experimental progress would make such measurements feasible in the near future. To fulfill the promise of using attosecond pulses for probing electron dynamics in the time domain, we believe the analysis suggested in this Letter is essential. Finally, we comment that the present analysis can be used to probe the correlated motion of any doubly excited states of an atom. Depending on the mean energy of the attosecond pulses available, specific atoms can be chosen such that optimal contrast in the ionization yields can be observed.

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