9-11-2014

Imaging electronic motions in atoms by energy-resolved ultrafast electron diffraction

Hua-Chieh Shao

University of Nebraska-Lincoln, hshao@unl.edu

Anthony F. Starace

University of Nebraska-Lincoln, astarace1@unl.edu

Follow this and additional works at: <http://digitalcommons.unl.edu/physicsstarace>

Shao, Hua-Chieh and Starace, Anthony F., "Imaging electronic motions in atoms by energy-resolved ultrafast electron diffraction" (2014). *Anthony F. Starace Publications*. 208.

<http://digitalcommons.unl.edu/physicsstarace/208>

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Anthony F. Starace Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Imaging electronic motions in atoms by energy-resolved ultrafast electron diffraction

Hua-Chieh Shao and Anthony F. Starace

Department of Physics and Astronomy, The University of Nebraska, Lincoln, Nebraska 68588-0299, USA

(Received 14 July 2014; published 10 September 2014)

We propose energy-resolved ultrafast electron diffraction as a means of directly imaging target electronic motions whose space, time, and energy information can be simultaneously retrieved from time-resolved diffraction measurements. The energy-resolved diffraction images are simulated for breathing, wiggling, and hybrid modes of electronic motion in the H atom. The simulations demonstrate the capabilities of ultrafast electron diffraction to image and distinguish different kinds of electronic motion. The theoretical analysis of the scattering process identifies the requirements for time- and state-resolved imaging of electronic motion and provides interpretations of the results.

DOI: [10.1103/PhysRevA.90.032710](https://doi.org/10.1103/PhysRevA.90.032710)

PACS number(s): 03.65.Nk, 34.80.Dp

I. INTRODUCTION

Direct imaging of electron dynamics elucidates the roles played by electrons in various kinds of reactions. In the last decade ultrafast electron diffraction and microscopy have been demonstrated to be effective table-top techniques for studying reaction mechanisms with atomic-level resolution in gas-phase and condensed-matter systems [1–5]. Transient structures during the course of reactions have been reported in pump-probe schemes. However, imaging electronic motion demands even more stringent temporal and spatial resolutions and coherent electron pulses. Nevertheless, nowadays sub-100-fs electron pulses have been produced [6], and various schemes to generate attosecond electron pulses have been proposed [7–10]. Simulations have demonstrated the abilities of attosecond electron pulses to directly image electronic motions in atoms and molecules [11–15].

In our previous work [15], we investigated the possibilities of imaging electronic motion in atoms by ultrafast electron diffraction. We found that the inelastic contributions can be significant in the diffraction images for small atoms, obscuring the interpretation of electronic motion. Insensitive to the pulse durations, these inelastic transitions cannot be effectively avoided by reducing the durations. Since energy transfers to the electronic states of the target seem inevitable, measuring the kinetic energies of the scattered electrons provides a possible solution and additional information about the electronic motion. Spectral measurements have been implemented in ultrafast electron microscopy [3,4]. Recently, Yurtsever *et al.* [16] reported ultrafast spectral imaging with simultaneous nanometer, femtosecond, and millielectron volt resolutions in the study of the dielectric response of nano materials to an optical excitation. However, energy-resolved measurements are rarely carried out in gas-phase ultrafast electron-diffraction experiments.

In this paper we present a general analysis of energy-resolved ultrafast electron diffraction for imaging target electronic motion. We theoretically analyze and numerically simulate time-resolved spectra of ultrafast electrons scattered from the breathing, wiggling, and hybrid modes of electronic motion in the H atom. We consider pump-probe processes in which a laser pulse creates a coherent superposition of target states that are probed by the electron pulses (Fig. 1). Varying the pump-probe delay time, the delay-dependent

scattering intensities record the ensuing electronic motions. The kinematics of the scattered electrons is fully resolved; both the scattering angles and the kinetic energies are measured. Therefore, besides the spatial and temporal information, the energy content of the electronic motions can be retrieved from the energy-resolved diffraction patterns, which provide unequivocal interpretations of the electronic motions. Because of this, we are able to explain the counterintuitive temporal behavior of the diffraction images, which show a quite different temporal behavior and little connection to the electron densities of the wiggling motion in Ref. [15].

This paper is structured as follows. The general theory and analysis for time- and energy-resolved ultrafast electron diffraction are presented in Sec. II, followed by results of simulations in Sec. III. In Sec. IV we provide an interpretation of these simulation results. Finally, we summarize our results and present some conclusions in Sec. V.

II. THEORY

We present a time-dependent scattering theory for energy-resolved ultrafast (attosecond) electron diffraction. Rarely considered as targets in conventional scattering theory, the electronic motions we investigate are nonstationary coherent superpositions of target eigenstates. In order to explore the imaging of electron dynamics, we adopt Robicheaux's general scattering theory of coherent matter beams [17] and adapt it to ultrafast electron diffraction [14,15]. The key idea for describing the time-dependent scattering process is to use a coherent wave function consisting of the wave packets of both the projectile electron and the target. By forming these wave packets, the projectile electron and the target are localized in space and in time, so the scattering events can be defined and analyzed properly. The scattering intensities, which carry the target information, can be obtained by following the development of the wave packets. The theoretical analysis is separated into kinematical and dynamical aspects of the scattering. Our analysis identifies the preferable conditions for performing time- and state-resolved measurements. We also discuss the approximations used in our numerical simulations at the end of this section. Atomic units (a.u.) are used throughout this paper unless indicated otherwise.

FIG. 1. (Color online) Schematic illustration of the experimental setup for energy-resolved ultrafast electron diffraction. The target electronic motions are initiated by the laser pulse, whereupon these motions are imaged by ultrafast (attosecond) electron pulses with controlled pump-probe delay time. The velocity analyzer determines the kinetic energies of the scattered electrons, and the detector records the time-resolved spectra. By rotating the velocity analyzer, angle-resolved spectra can be measured. By varying the pump-probe delay time, the resulting energy- and time-resolved diffraction images exhibit the target electronic motions. The coordinate system and the scattering angles θ and φ are defined here.

A. Kinematics

Consider a reaction in which an electron collides with an atomic target A ,

$$e^-(\mathbf{k}_0) + A(\mathbf{k}_1, n) \rightarrow e^-(\mathbf{k}_a) + A(\mathbf{k}_b, m), \quad (1)$$

where $\mathbf{k}_0$ and $\mathbf{k}_1$ ($\mathbf{k}_a$ and $\mathbf{k}_b$) are the respective momenta of the projectile electron and the target before (after) the collision, and n (m) symbolically denotes the set of quantum numbers characterizing the initial (final) internal state of the target. The target has some electronic motion to be imaged by the projectile electron. Let the Hamiltonian of the scattering system be

$$H = H_0 + H_1 + V, \quad (2)$$

where H_0 and H_1 are the respective Hamiltonians of the projectile electron and the target, and V describes the interaction between the two subsystems. Impact ionization is not considered here, because this reaction, in principle, can be distinguished from the other transitions by the reaction products.

1. Coherent wave packet

At time zero, the coherent wave function is written as a wave-packet integral in which the eigenstates $\psi_i^{(+)}$ of the Hamiltonian H are coherently superposed:

$$\psi_{\text{coh}}^{(+)} = \int d\mathbf{k}_0 d\mathbf{k}_1 a_0(\mathbf{k}_0) a_1(\mathbf{k}_1) \sum_n C_n \psi_i^{(+)}, \quad (3)$$

where $a_0(\mathbf{k}_0)$ and $a_1(\mathbf{k}_1)$ are the respective momentum amplitudes of the projectile electron and the target, and C_n is the amplitude of the internal state n of the target. Coherence of a system refers to the properties of the off-diagonal elements of its density matrix. The state $\psi_i^{(+)}$, labeled by the

subscript $i \equiv \{\mathbf{k}_0, \mathbf{k}_1, n\}$, is formally represented by

$$\psi_i^{(+)} = \psi_i + \mathcal{G}^{(+)}(\varepsilon_i) V \psi_i, \quad (4)$$

where ψ_i is the eigenstate of $H_0 + H_1$, and $\mathcal{G}^{(+)}(\varepsilon_i)$ is the Green's function satisfying the outgoing-wave boundary condition. The energy eigenvalue ε_i is the sum of the kinetic energies of projectile and target and the target internal energy ω_n , i.e.,

$$\varepsilon_i = E_0 + E_1 + \omega_n. \quad (5)$$

The time-dependent wave function can be obtained by acting with the operator e^{-iHt} on $\psi_{\text{coh}}^{(+)}$ to obtain

$$\psi_{\text{coh}}^{(+)}(t) = \sum_n C_n \int d\mathbf{k}_0 d\mathbf{k}_1 a_0(\mathbf{k}_0) a_1(\mathbf{k}_1) e^{-i\varepsilon_i t} \psi_i^{(+)}, \quad (6)$$

where we have made the assumption that the wave-packet integral and the time-development operator may be interchanged.

2. Transition amplitude and probability

Let ψ_f be a final state of interest that is measured in experiments. The transition amplitude to the final state is

$$\mathcal{A}_f^{(+)}(t) = (\psi_f, \psi_{\text{coh}}^{(+)}(t)), \quad (7)$$

where $f \equiv \{\mathbf{k}_a, \mathbf{k}_b, m\}$ specifies the final state. Substituting Eq. (6), together with Eq. (4), into the transition amplitude and assuming the order of integrations may be interchanged, one obtains [18]

$$\begin{aligned} \mathcal{A}_f^{(+)}(t) &= \sum_n C_n \int d\mathbf{k}_0 d\mathbf{k}_1 a_0(\mathbf{k}_0) a_1(\mathbf{k}_1) \\ &\times \frac{e^{-i\varepsilon_i t}}{\varepsilon_i - \varepsilon_f + i\alpha} (\psi_f, \mathcal{T} \psi_i), \end{aligned} \quad (8)$$

where $\mathcal{T} = V + V \mathcal{G}^{(+)} V$ is the transition operator, and $\varepsilon_f = E_a + E_b + \omega_m$ is the final-state energy. If the scattering occurs in the absence of any external potential, the total linear momentum is conserved, and a momentum δ function can be extracted from the transition matrix element $\mathcal{T}_{fi}$. Thus, we set

$$\mathcal{T}_{fi} = \delta(\mathcal{P}_f - \mathcal{P}_i) T_{fi}, \quad (9)$$

where $\mathcal{P}_i = \mathbf{k}_0 + \mathbf{k}_1$ and $\mathcal{P}_f = \mathbf{k}_a + \mathbf{k}_b$ are the total linear momenta of the reactants and products, respectively. For typical ultrafast electron-diffraction experiments, the measurements are performed in the asymptotic region long after the completion of the scattering. Hence, the asymptotic transition probability density is the limit of the absolute square of the transition amplitude as $t \rightarrow \infty$,

$$|\mathcal{A}_f|^2 \equiv \lim_{\alpha \rightarrow 0^+} \lim_{t \rightarrow \infty} |\mathcal{A}_f^{(+)}(t)|^2. \quad (10)$$

Substituting Eq. (8), together with Eq. (9), into Eq. (10) and taking the limits (which gives energy δ functions), one obtains

$$\begin{aligned} |\mathcal{A}_f|^2 &= \sum_{n'n} C_n^* C_n \int d\mathbf{k}'_0 d\mathbf{k}'_1 d\mathbf{k}_0 d\mathbf{k}_1 a_0^*(\mathbf{k}'_0) a_0(\mathbf{k}_0) \\ &\times a_1^*(\mathbf{k}'_1) a_1(\mathbf{k}_1) (2\pi)^2 \delta(\varepsilon_f - \varepsilon_i) \delta(\varepsilon_{i'} - \varepsilon_i) \\ &\times \delta(\mathcal{P}_f - \mathcal{P}_{i'}) \delta(\mathcal{P}_f - \mathcal{P}_i) T_{fi'}^* T_{fi}. \end{aligned} \quad (11)$$

Here, $i' \equiv \{\mathbf{k}'_0, \mathbf{k}'_1, n'\}$ and $\varepsilon_{i'} = E'_0 + E'_1 + \omega_{n'}$.

The partial transition probability $\mathcal{P}_m$ to the target final state m is the probability density integrated over the final-state momenta:

$$\mathcal{P}_m = \int d\mathbf{k}_a d\mathbf{k}_b |\mathcal{A}_f|^2, \quad (12)$$

and the (total) transition probability $\mathcal{P}$ is the sum over the final states of the target:

$$\mathcal{P} = \sum_m \mathcal{P}_m. \quad (13)$$

The ranges of the final-state momentum integrals in Eq. (12) and the final-state summation in Eq. (13) are determined by the experimental configurations. Here, we assume the scattering angle $\hat{\mathbf{k}}_a$ and the kinetic energy E_a are measured, but no measurement is performed on the target. Accordingly, the target final-momentum integral and the final-state summation have to be performed in Eq. (13).

With the above considerations, we introduce the (partial) doubly differential probability $d^2\mathcal{P}_m/dE_a d\hat{\mathbf{k}}_a$ to represent the scattering intensity for a final state m in energy- and angle-resolved measurements. Using Eqs. (11) and (12), one can show that

$$\begin{aligned} \frac{d^2\mathcal{P}_m}{dE_a d\hat{\mathbf{k}}_a} &= m_a |\mathbf{k}_a| \int d\mathbf{k}_b \sum_{n'n} C_{n'}^* C_n \int d\mathbf{k}'_0 d\mathbf{k}'_1 d\mathbf{k}_0 d\mathbf{k}_1 \\ &\times a_0^*(\mathbf{k}'_0) a_0(\mathbf{k}_0) a_1^*(\mathbf{k}'_1) a_1(\mathbf{k}_1) (2\pi)^2 \delta(\varepsilon_f - \varepsilon_i) \\ &\times \delta(\varepsilon_{i'} - \varepsilon_i) \delta(\mathcal{P}_f - \mathcal{P}_{i'}) \delta(\mathcal{P}_f - \mathcal{P}_i) T_{fi'}^* T_{fi}, \end{aligned} \quad (14)$$

where m_a and $|\mathbf{k}_a|$ are the mass and the magnitude of the momentum of the scattered electron, respectively. Note that the information about the electronic motion is embedded in the amplitudes C_n of the target state and the transition matrix elements T_{fi} . The product of the momentum amplitudes $a_0(\mathbf{k}_0) a_0^*(\mathbf{k}'_0) \equiv \rho_0(\mathbf{k}_0, \mathbf{k}'_0)$ is the density matrix of the projectile electron; likewise, $a_1(\mathbf{k}_1) a_1^*(\mathbf{k}'_1) \otimes C_n C_{n'}^* \equiv \rho_1(\mathbf{k}_1, \mathbf{k}'_1; n, n')$ is the density matrix for the target. From Eq. (14) we observe that all components of the density matrices ρ_0 and ρ_1 coherently contribute to the doubly differential probability, fulfilling the conservation of energy and linear momentum. If the target internal state is a nonstationary state, these conservation laws couple the off-diagonal elements of ρ_0 and ρ_1 . Hence, the coherent properties of the projectile and target can influence the results of measurements (e.g., the spatial and temporal resolutions). In terms of the density matrices, the doubly differential probability can be concisely expressed by

$$\frac{d^2\mathcal{P}}{dE_a d\hat{\mathbf{k}}_a} = \text{Tr}(S \rho_0 \otimes \rho_1 S^\dagger \mathcal{O}), \quad (15)$$

where $S \equiv \mathbb{1} - i 2\pi \delta(\varepsilon_f - \varepsilon_i) \mathcal{T}$ is the $\mathbf{S}$ matrix, and $\mathcal{O}$ is the observable that is measured (i.e., $\mathcal{O} \equiv |\mathbf{k}_a\rangle \langle \mathbf{k}_a| \otimes \mathbb{1}_b$).

3. Target amplitude and pump-probe delay time

After its initiation by some pump procedure, the electronic motion is defined by the evolution of its amplitudes C_n . Owing to the velocity difference between the optical pump and the electron probe pulses, the pump-probe delay time

can be different for targets in a gas ensemble. Therefore, the amplitudes C_n of each target at time zero generally depend on target position. This inhomogeneity can limit the temporal resolution and complicate the expression of C_n . Nevertheless, techniques have been invented to mitigate the velocity mismatch [2,19]. Therefore, we exclude this effect in our simulations and set the amplitude to be

$$C_n = c_n e^{-i\omega_n t_d}, \quad (16)$$

where t_d is the pump-probe delay time, and c_n is the amplitude at zero delay time. Substituting Eq. (16) into Eq. (14), one can recognize that $d^2\mathcal{P}_m/dE_a d\hat{\mathbf{k}}_a$ is modulated by the beat frequencies $|\omega_{n'} - \omega_n|$ of the coherent superposition state. This modulation can be monitored by varying the delay time t_d .

4. Time- and state-resolved measurements

Despite their generality, Eqs. (14) and (15) provide little insight about the requirements for and the interpretations of time- and state-resolved measurements. To further investigate the factors involved in the measurements, we analyze the very general Eq. (14) specifically for the case of ultrafast electron diffraction. First, owing to the momentum δ functions, the $\mathbf{k}_b$ and $\mathbf{k}'_1$ integrals are performed straightforwardly:

$$\begin{aligned} \frac{d^2\mathcal{P}_m}{dE_a d\hat{\mathbf{k}}_a} &= m_a |\mathbf{k}_a| \sum_{n'n} C_{n'}^* C_n \int d\mathbf{k}'_0 d\mathbf{k}_0 d\mathbf{k}_1 \\ &\times a_0^*(\mathbf{k}'_0) a_0(\mathbf{k}_0) a_1^*(\mathbf{k}_0 + \mathbf{k}_1 - \mathbf{k}'_0) a_1(\mathbf{k}_1) \\ &\times (2\pi)^2 \delta(\varepsilon_f - \varepsilon_i) \delta(\varepsilon_{i'} - \varepsilon_i) T_{fi'}^* T_{fi}. \end{aligned} \quad (17)$$

One can show that this expression is actually a direct generalization of Fermi's "golden rule" for coherent superposition states. If the target is in a stationary state and the projectile and target are treated as plane waves instead of wave packets, Eq. (17) reduces to the familiar expression of Fermi's golden rule.

Next, in order to use the energy δ functions, we transform the coordinates of the projectile electron from the momenta, $\mathbf{k}_0$ and $\mathbf{k}'_0$, to the energies, E_0 and E'_0 , and the solid angles, $\hat{\mathbf{k}}_0$ and $\hat{\mathbf{k}}'_0$. In addition, we set

$$\delta(\varepsilon_{i'} - \varepsilon_i) = \delta(E'_0 - E_0 - \Delta\mu_{nn'}), \quad (18)$$

where $\Delta\mu_{nn'}$ (which denotes an energy difference between components of the target wave packet) equals the kinetic-energy difference of the projectile electron due to energy conservation. While the quantum numbers n and n' are used to label $\Delta\mu_{nn'}$, it depends on the other kinetic variables as well (e.g., the momenta). Applying Eq. (18) to Eq. (17) and integrating over E'_0 , one obtains

$$\begin{aligned} \frac{d^2\mathcal{P}_m}{dE_a d\hat{\mathbf{k}}_a} &= m_a |\mathbf{k}_a| \sum_{n'n} C_{n'}^* C_n \int d\hat{\mathbf{k}}'_0 dE_0 d\hat{\mathbf{k}}_0 d\mathbf{k}_1 \\ &\times J(E_0 + \Delta\mu_{nn'}) J(E_0) a_0^*(E_0 + \Delta\mu_{nn'}, \hat{\mathbf{k}}'_0) \\ &\times a_0(E_0, \hat{\mathbf{k}}_0) a_1^*(\mathbf{k}_0 + \mathbf{k}_1 - \mathbf{k}'_0) a_1(\mathbf{k}_1) (2\pi)^2 \\ &\times \delta(\varepsilon_f - \varepsilon_i) T_{fi'}^* T_{fi}, \end{aligned} \quad (19)$$

where $J \equiv |\partial(\mathbf{k}_0)/\partial(E_0, \hat{\mathbf{k}}_0)|$ is the Jacobian of the coordinate transformation. Owing to energy conservation,

$d^2 \mathcal{P}_m / dE_a d\hat{\mathbf{k}}_a$ has contributions from components of a_0 that differ by $\Delta\mu_{nn'}$. Recall that in ultrafast electron imaging the projectile electrons are usually well collimated, so the shifts of the components are essentially along the longitudinal direction of the pulses. The exact expression of $\Delta\mu_{nn'}$ can be obtained by solving the equation $\varepsilon_{i'} = \varepsilon_i$. However, a concise expression for $\Delta\mu_{nn'}$ can be obtained if we consider that for ultrafast electron diffraction the kinetic energies of the incident electrons are usually much larger than those of the target (i.e., $E_0 \gg E_1$), so E_1 and E_1' can be neglected in ε_i and $\varepsilon_{i'}$. Thus, $\Delta\mu_{nn'}$ is approximated by the energy difference of the target eigenstates, namely, the beat frequency of the coherent state:

$$\Delta\mu_{nn'} \simeq \omega_n - \omega_{n'}. \quad (20)$$

Preferable conditions for time-resolved measurements can be identified from Eqs. (19) and (20). The time dependence of the diffraction images results from the interference of T_{fi} (or the scattering amplitudes) from the constituent states of the target with different energies [i.e., terms with $\omega_{n'} \neq \omega_n$ in Eq. (14)]. If the target consists of eigenstates with a large energy difference such that the relative shift of the component is much larger than the energy bandwidth of the electron pulse (i.e., $\Delta\mu_{nn'} \gg \Delta E_0$ for $\omega_n \neq \omega_{n'}$), then the product of amplitudes $a_0^*(E_0 + \Delta\mu_{nn'}, \hat{\mathbf{k}}_0') a_0(E_0, \hat{\mathbf{k}}_0) \approx 0$ is essentially zero owing to little overlap. The double summation over n and n' then reduces to a single one:

$$\sum_{n'n} C_n^* C_n \cdots \rightarrow \sum_n |C_n|^2 \cdots. \quad (21)$$

In this limit only the diagonal elements of the density matrices survive, and the information of their relative phase (given by the off-diagonal terms) is lost. The diffraction images are the sum of the contributions from each constituent state weighted by its population. Thus, the relevant electronic motion is not resolved. Therefore, a necessary condition for time-resolved measurements is to provide enough bandwidth for the electron pulses compared with the energy scale of the electronic motion. In addition to the proper bandwidth, owing to the interference of the off-diagonal elements of the density matrices, their relative phases can be manifested in the diffraction images. An unfavorable phase distribution can decrease the temporal resolution, so an additional requirement is the coherence of the pulse (with a smooth phase distribution) over its bandwidth. Since the phase and the bandwidth determine the pulse duration, the conditions simply state that the pulse durations have to be shorter than the time scale of the electronic motion in time-resolved measurements.

Likewise, we introduce Δv_{mn} for the remaining δ function:

$$\delta(\varepsilon_f - \varepsilon_i) = \delta(E_0 - E_a - \Delta v_{mn}). \quad (22)$$

Since E_0 and E_a are the kinetic energies of the projectile electron before and after the collision, Δv_{mn} represents the amount of energy transferred between the projectile and the target. To vindicate this, one can approximate Δv_{mn} using the same assumption for approximating $\Delta\mu_{nn'}$ and further assume that the target is much heavier than the projectile electron (i.e., $m_b \gg m_a$) to obtain

$$\Delta v_{mn} \simeq \omega_m - \omega_n, \quad (23)$$

which is the transition energy of the target. Applying Eq. (22) to Eq. (19) and performing the E_0 integral, the doubly differential probability becomes

$$\begin{aligned} \frac{d^2 \mathcal{P}_m}{dE_a d\hat{\mathbf{k}}_a} &= (2\pi)^2 m_a |\mathbf{k}_a| \sum_{n'n} C_n^* C_n \int d\hat{\mathbf{k}}_0' d\hat{\mathbf{k}}_0 d\mathbf{k}_1 \\ &\times J(E_a + \Delta v_{mn} + \Delta\mu_{nn'}) J(E_a + \Delta v_{mn}) \\ &\times a_0^*(E_a + \Delta v_{mn} + \Delta\mu_{nn'}, \hat{\mathbf{k}}_0') a_0(E_a + \Delta v_{mn}, \hat{\mathbf{k}}_0) \\ &\times a_1^*(\mathbf{k}_0 + \mathbf{k}_1 - \mathbf{k}_0') a_1(\mathbf{k}_1) T_{fi'}^* T_{fi}. \end{aligned} \quad (24)$$

Equation (24) indicates that the bandwidth of the electron pulse limits the spectral resolution. Due to the finite bandwidth introduced in forming the electron wave packet, each final state m in the spectrum also has a finite width. The width is essentially determined by the bandwidth of the projectile, ΔE_0 , because in typical ultrafast electron experiments $\Delta E_1 \ll \Delta E_0$. If two final states, m' and m , have an energy-level difference that is smaller than the bandwidth ΔE_0 of the incident electron (i.e., $|\omega_{m'} - \omega_m| \lesssim \Delta E_0$), then the difference in their transition energies is also within the bandwidth, $|\Delta v_{m'n} - \Delta v_{mn}| \lesssim \Delta E_0$. Therefore, the transitions to these final states overlap and, hence, cannot be resolved in spectral measurements. Since all amplitudes in Eq. (24) are shifted by Δv_{mn} , this effect is not associated with the coherence of the pulse.

5. Factorization of the transition probability

Although Eq. (24) completely describes the time-dependent diffraction patterns produced by a coherent superposition state, its complexity poses possible difficulties in the analysis of the results. Due to the finite bandwidths, multiple components superposed in the wave packets interfere with each other, adding to the challenge of interpreting the diffraction images. To diminish this effect, the contributions from the projectile electron and the target to the doubly differential probability should be disentangled, so that $d^2 \mathcal{P} / dE_a d\hat{\mathbf{k}}_a$ directly reflects the target properties, independent of the details of the electron wave packet [20]. This factorizability can be achieved, first, if the electron pulse has good monochromaticity (i.e., $\Delta E_0 / E_0 \ll 1$), so the transition matrix element T_{fi} is insensitive to the variations of the momenta within the wave-packet integral. Accordingly, T_{fi} can be approximated by evaluating at the central momenta $\mathbf{p}_0$ and $\mathbf{p}_1$ of the projectile electron and the target. More specifically, we set

$$T_{fi} \simeq T_{mn} \quad \text{and} \quad T_{fi'} \simeq T_{mn'}, \quad (25)$$

where the evaluation of the transition matrix elements T_{mn} at the central momenta is understood, and, therefore, the transition matrix elements are labeled only by the internal state of the target.

After factoring T_{fi} from the wave-packet integral, the remaining integrand in Eq. (24) is still a function of n and n' (through $\Delta\mu_{nn'}$). Different pairs n and n' can contribute differently. In order to minimize this pair dependence, we assume that a_0 and a_1 are smooth functions and that their bandwidths satisfy the conditions

$$\Delta E_0 \gg \Delta\mu_{nn'} \quad \text{and} \quad \Delta E_1 \gg \frac{m_a |\mathbf{p}_1|}{m_b |\mathbf{p}_0|} \Delta\mu_{nn'} \quad (26)$$

so that the dynamical properties of the scattering can be factorized from the pulse parameters [e.g., $a_0(E_a + \Delta\mu_{nn'}, \hat{\mathbf{k}}_0) \simeq a_0(E_a, \hat{\mathbf{k}}_0)$]. The requirements in Eq. (26) are the same conditions needed for time-resolved measurements. The wave-packet integral is then only a proportionality constant for all pairs of n and n' in Eq. (24).

In addition to the competition between the temporal and spectral resolutions in time-resolved spectral measurements, there is another conflicting situation. On the one hand, monochromaticity (i.e., small ΔE_0) is preferred in order to extract T_{fi} from the wave-packet integral; on the other hand, a large enough bandwidth ΔE_0 provides a uniform dependence on the various pairs of n and n' . Nevertheless, when the conditions in Eqs. (25) and (26) are both satisfied, Eq. (24), combined with Eq. (16), simplifies to

$$\frac{d^2 \mathcal{P}_m}{dE_a d\hat{\mathbf{k}}_a} \propto \left| \sum_n c_n T_{mn} e^{-i\omega_n t_d} \right|^2. \quad (27)$$

Equation (27) shows the desirable characteristic of an imaging process: $d^2 \mathcal{P}_m / dE_a d\hat{\mathbf{k}}_a$ directly reflects the target electronic motions. Specifically, the doubly differential probability is proportional to the coherent sum of the transition matrix elements weighted by the corresponding amplitudes of the eigenstates at the moment of collision. Therefore, under the factorization assumption, the collision process serves as a mapping mechanism from the coherent superposition state to the target final state m .

B. Dynamics

From the above kinematic analysis we identified the conditions for time- and state-resolved measurements. However, the dynamical aspects of the scattering, which depend on the interactions and the target structures, account for the imaging of the electronic motions. Energetic projectile electrons ($E_0 \gtrsim$ tens of keV) are frequently employed in ultrafast electron imaging because of their spatial resolution and their simple and direct scattering mechanism. Accordingly, the Born approximation is valid for most targets to calculate the transition matrix element $\mathcal{T}_{fi}$ [21]. Moreover, the exchange effect of the projectile and target electrons is small [22]. Finally, energetic electrons provide better monochromaticity and, thus, factorizability. Under these approximations, the transition matrix element $\mathcal{T}_{fi}$ is approximated by

$$\mathcal{T}_{fi} \simeq (\chi_a \chi_b \phi_m, V \chi_0 \chi_1 \phi_n), \quad (28)$$

where χ_0 and χ_1 (χ_a and χ_b) are the respective plane waves of the projectile electron and the target before (after) the collision, and ϕ_n is the target internal eigenstate. Factoring out the momentum δ function from $\mathcal{T}_{fi}$ [cf. Eq. (9)], the transition matrix element T_{fi} is [15]

$$T_{mn} \simeq \frac{1}{(2\pi)^2} \frac{2}{s^2} \left(-Z\delta_{mn} + \sum_{i=1}^Z \int d\{\mathbf{y}_i\} e^{i\mathbf{s} \cdot \mathbf{y}_i} \phi_m^* \phi_n \right), \quad (29)$$

where $s \equiv \mathbf{k}_0 - \mathbf{k}_a$ is the momentum transfer, δ_{mn} is the Kronecker δ function, Z is the atomic number of the target, and $\{\mathbf{y}_i\}$ is the set of coordinates of the target electrons. In Eq. (29) we have assumed that $m_b \gg m_a$.

C. Approximations used in the simulations

We have seen that in order to arrive at Eq. (27) the factorizability of the doubly differential probability must be assumed. In order to examine this assumption and study the effects of interference of the components of the wave packets, we do not assume the factorizability and perform the wave-packet integral numerically in our simulations. However, owing to the massive target, we assume the target is localized in space, so its momentum width is much larger than that of the projectile electron. Thus, $a_1(\mathbf{k}_0 + \mathbf{k}_1 - \mathbf{k}'_0) \simeq a_1(\mathbf{k}_1)$ within the wave-packet integral [cf. Eq. (24)]. We further assume that the other quantities (e.g., $\Delta\mu_{nn'}$) are insensitive to the variation of $\mathbf{k}_1$ within the wave-packet integral because $m_b \gg m_a$, so we can approximate T_{fi} and the other quantities by evaluating them at the central momentum $\mathbf{p}_1$ of the target. Hence, the $\mathbf{k}_1$ integral can be performed analytically. In short, in our simulations we used the following equation:

$$\begin{aligned} \frac{d^2 \mathcal{P}}{dE_a d\hat{\mathbf{k}}_a} &\simeq (2\pi)^2 m_a |\mathbf{k}_a| \sum_m \sum_{n'} c_n^* C_n \int d\hat{\mathbf{k}}'_0 d\hat{\mathbf{k}}_0 \\ &\times J(E_a + \Delta v_{mn} + \Delta\mu_{nn'}) J(E_a + \Delta v_{mn}) \\ &\times a_0^*(E_a + \Delta v_{mn} + \Delta\mu_{nn'}, \hat{\mathbf{k}}'_0) \\ &\times a_0(E_a + \Delta v_{mn}, \hat{\mathbf{k}}_0) T_{f\bar{i}}^* T_{f\bar{i}}, \end{aligned} \quad (30)$$

where $\bar{i} = \{\mathbf{k}_0, \mathbf{p}_1, n\}$ and $\bar{i}' = \{\mathbf{k}'_0, \mathbf{p}_1, n'\}$.

The atomic target we study is the H atom. Its kinetic energy is assumed to be the thermal energy at room temperature ($E_1 = 25$ meV). Formulas for T_{mn} for the H atom can be found in Ref. [15]. Since no measurements are performed to determine the target final state, all allowed transitions have to be included to calculate the diffraction images. Nevertheless, the final-state summation has to be truncated in the numerical simulations. In our previous work [15] we employed an extrapolation technique to calculate the differential probability $d\mathcal{P}/d\hat{\mathbf{k}}_a$ and found that the contributions of the transitions involving principal quantum number $n_f > 9$ with orbital angular momentum $0 \leq l_f \leq 6$ are less than 4% of the contributions involving $n_f \leq 9$. Therefore, we truncated the final-state sum at $n_f = 9$ in Eq. (30) since the transitions to these Rydberg states $n_f > 9$ should not alter the features of the diffraction images.

III. IMAGING OF ELECTRONIC MOTIONS IN THE H ATOM

We consider two representative kinds of electronic motion: breathing and wiggling modes (as well as a hybrid of them) in the H atom to demonstrate the capability of ultrafast electrons to image these electronic motions. We examine their features in the diffraction patterns and investigate the effects of interference of different scattering amplitudes on the scattering intensities.

A. Breathing and wiggling electronic motions

The breathing mode superposes equal-parity $3p$ and $4p$ states. One possible means of producing such a state is to use a short linearly polarized optical pump pulse with suitable central frequency and bandwidth such that the $3p$ and

FIG. 2. (Color online) Electron densities of the breathing (left column) and the wiggling (right column) modes of electronic motion in the H atom as a function of time. The breathing mode superposes equal-parity $3p$ and $4p$ states with equal amplitude, while the wiggling mode consists of opposite-parity $3d$ and $4f$ states. Both kinds of motion share the same beat period, $T = 6.25$ fs. Owing to the periodicity, only the densities in the first half period are shown.

$4p$ states are equally populated, while the populations on the other excited states are negligibly small [13]. Hence, we set the target electronic state at time zero to be

$$\phi_{\text{coh}} = \frac{1}{\sqrt{2}}(\phi_{3p} + \phi_{4p}). \quad (31)$$

The electron density as a function of time is shown in the left column of Fig. 2. The breathing mode exhibits a motion that oscillates between localization and delocalization. At time zero the electron density has a compact distribution, localizing around the nucleus with an average radius of 14 a.u. Then the density expands as time increases, reaching the maximal radius 22 a.u. at half the beat period. The symmetry of the density is maintained throughout the oscillation, because the $3p$ and $4p$ states share the same parity.

The second type of electronic motion is the wiggling mode exhibited by an equal superposition of the opposite-parity $3d$ and $4f$ states. This coherent state has been studied by Dixit *et al.* [23], where an x-ray pulse is the probe. Owing to the different parities involved, the electron density shown in the right column of Fig. 2 oscillates back and forth from one side of the nucleus to the other. Both modes of motion share the same period of oscillation: $T = 6.25$ fs. Note that, in theory, these two kinds of motion, or any combination of them, illustrate all possible kinds of electronic motion in atoms and molecules.

B. Electron pulse profile

The ultrafast electron pulses in our simulations have a central kinetic energy of 10 keV in the laboratory frame, which is the energy of one of the examples of attosecond pulse generation given in Ref. [7]. The corresponding de Broglie

wavelength is 0.12 Å, providing an adequate spatial resolution. The momentum amplitude $a_0(\mathbf{k}_0)$ has a real Gaussian shape whose longitudinal and transverse widths are determined by the pulse duration and angular divergence, respectively. Since the bandwidth affects the temporal and spectral resolutions, three pulse durations (FWHM) are considered in our simulations: 100 as, 500 as, and 3.13 fs. The durations of the first two pulses are much shorter than the beat period ($T = 6.25$ fs) of the electronic motions, but the duration of the last pulse is already half that of the beat period. The respective bandwidths (FWHM), estimated by the energy-time uncertainty relation, are 18.2, 3.65, and 0.58 eV. Although the first two pulses are short enough to resolve the electronic motions, they have relatively different bandwidths, which can affect the spectral measurements. The beam angular divergence for all cases is fixed at $\pm 10^{-4}$ rad. (FWHM). Figure 3 shows the electron pulse profiles as functions of kinetic energy E_0 and angular divergence θ_0 in the center-of-mass frame. The electron pulses peak at 9.99 keV instead of 10 keV because of the coordinate transformation from the laboratory to the

FIG. 3. (Color online) Electron pulse profiles as functions of kinetic energy E_0 and beam angular divergence θ_0 for the pulse durations [full width at half maximum (FWHM)] (a) 100 as, (b) 500 as, and (c) 3.13 fs. The profiles peak at the central energy of 9.99 keV in the center-of-mass frame of the colliding electron and the H atom, while in the laboratory frame the central pulse energy is 10 keV. The momentum amplitude $a_0(\mathbf{k}_0)$ of each pulse is assumed to have a Gaussian shape whose longitudinal width is determined by the pulse duration. The angular divergence is $\pm 10^{-4}$ rad. The contours in the bottom plane show the full width at half maximum of each pulse profile.

center-of-mass frames. Note that even for the 100-as pulse, $\Delta E_0/E_0 \approx 0.002$, so good monochromaticity is preserved and the factorization of T_{fi} is still valid. The bandwidth of the 3.13-fs pulse almost equals the energy difference of the target coherent state (0.66 eV), so the factorizability of T_{fi} may be invalid and the temporal resolution may be affected.

C. Simulation results

1. Breathing mode: $3p + 4p$

We first present time- and energy-resolved diffraction images for the breathing mode of electronic motion. The doubly differential probabilities $d^2\mathcal{P}/dE_a d\hat{\mathbf{k}}_a$ for electron pulse scattering from the $3p + 4p$ state of the H atom are shown in Fig. 4 for three pulse durations and three pump-probe delay times, $t_d = 0T$, $T/4$, and $T/2$, as functions of the scattered electron kinetic energy E_a and the scattering angle θ . The spectra for delay times larger than $T/2$ simply repeat those shown in Fig. 4 owing to the periodicity of the problem. The azimuthal scattering angle is set to zero, $\varphi = 0^\circ$. The simulation is performed in the center-of-mass frame of the colliding system, though only small changes are introduced by transforming to the laboratory frame because of the heavy target and the energetic projectile. Comparison of the spectra for different pulse durations at the same delay time shows that as the pulse duration decreases, more spectral details are revealed. No discernible structure can be observed for the 100-as pulse because of its large

bandwidth (18.2 eV) and, hence, the overlapping of the spectra from neighboring transitions. However, two distinct groups appear in the 500-as spectra, for which the possibility of a state-resolved measurement increases as the bandwidth ΔE_0 decreases. The major group around 9.99 keV (the central energy of the incident electron) results from the transitions to the neighboring states of the $3p + 4p$ state, while the minor group at higher energy corresponds to the de-excitation to the $1s$ state. Since the ground state of the H atom is far from other (excited) states, the de-excitation process to the $1s$ state has less interference from transitions to neighboring states. Thus, the $1s$ channel can be distinguished from the major group in the spectral measurements once the bandwidth is narrow enough ($\lesssim 10$ eV). Furthermore, the width of the major group narrows as the scattering angle θ increases because inelastic transitions drop rapidly as the momentum transfer increases [22]. However, for “elastic” transitions [i.e., $m = n$ in Eq. (27)] the scattering amplitude interferes coherently with the amplitude for elastic scattering from the nucleus, which extends to a larger scattering angle [cf. Eq. (29)]. This feature is more prominent for the 3.13-fs case. Fine structures in both groups can even be observed for this longest pulse. Since the bandwidth is smaller than the energy difference of the $3p$ and $4p$ states, the transition from each constituent state can even be separated at $t_d = T/2$, revealing the constituents of the superposition state.

Although the 3.13-fs pulse provides the most detailed spectra, the temporal variation diminishes because of its

FIG. 4. (Color online) Doubly differential probabilities $d^2\mathcal{P}/dE_a d\hat{\mathbf{k}}_a$ for scattering of ultrafast electrons from the $3p + 4p$ coherent superposition state of the H atom at pump-probe delay times $t_d = 0T$, $T/4$, and $T/2$ are shown for three different pulse durations. The beat period of the electronic motion is $T = 6.25$ fs. The pulse durations (FWHM) are 100 as (left column), 500 as (middle column), and 3.13 fs (right column). The beam angular divergence is $\pm 10^{-4}$ rad. (FWHM). See Fig. 3 for the pulse profiles. The electronic state equally superposes equal-parity $3p$ and $4p$ states, showing a breathing mode of motion (cf. Fig. 2). The azimuthal scattering angle is set at $\varphi = 0^\circ$ (cf. Fig. 1).

insufficient temporal resolution. In our previous work we found that the factorizability of the differential probability $d\mathcal{P}/d\hat{\mathbf{k}}_a$ is invalid for the 3.13-fs pulse (cf. Fig. 7 of Ref. [15]). Nevertheless, the visible temporal variation in the spectra suggests that the temporal resolution can be improved by performing energy-resolved measurements. Of the three cases, the 500-as pulse fits best the requirements for time-resolved spectral imaging of our particular electronic motion. Not only does the broad bandwidth afford appropriate temporal resolution and factorization (so that the time-resolved diffraction images directly reflect the electronic motion), but also the bandwidth is still narrow enough such that a certain degree of spectral resolution is maintained, i.e., the 1s channel is well separated from the other transitions. Examining the 500-as spectra as a function of delay time, one sees that the two groups behave differently. The intensity of the minor group decreases as the pump-probe delay time increases, whereas the major group behaves in the opposite way. This is because the average radius of the charge density increases from time zero to $T/2$, so the overlap of the coherent-state wave function with the 1s state decreases. Consequently, the 1s-channel transition amplitude decreases as the delay time increases from 0T to $T/2$. The relative spatial size of the coherent state with respect to the 1s state can be read from the time-resolved spectra. Note that this energy-dependent temporal oscillation cannot be obtained without measuring the kinematic energy E_a of the scattered electron. Transitions from the coherent $3p + 4p$ state to the 1s state are small owing to the large differences in the radii of these states. If E_a is not measured and instead one integrates over all values of E_a , the 1s-channel contribution to the resulting diffraction probability $d\mathcal{P}/d\hat{\mathbf{k}}_a$ is negligible relative to the sum of contributions from all target states.

Figure 5 shows the relative variation of $d^2\mathcal{P}/dE_a d\hat{\mathbf{k}}_a$ at $t_d = T/2$. The relative variation at t_d is defined by the change of the spectrum with respect to the one at time zero:

$$\frac{\Delta \text{Prob}(t_d)}{\text{Prob}(0T)} \equiv \frac{d^2\mathcal{P}/dE_a d\hat{\mathbf{k}}_a(t_d) - d^2\mathcal{P}/dE_a d\hat{\mathbf{k}}_a(0T)}{d^2\mathcal{P}/dE_a d\hat{\mathbf{k}}_a(0T)}. \quad (32)$$

All cases show comparable relative variations. Comparison of the 100-as and the 500-as cases shows that the latter indeed has a richer structure, both in its energy E_a and angle θ dependence. The 500-as relative variation implies that its spectrum exhibits contrasting landscapes on either side of $E_a \approx 10$ keV. Above 10 keV, the spectrum decreases (when $t_d = T/2$) and has a simple θ dependence, whereas below 10 keV complicated fluctuations (depending both on E_a and θ) can be seen. This latter behavior stems from the fact that the excited states are close in energy and have more complicated nodal structures than the ground state. Although the minor group has small transition probability, the magnitude of its relative temporal variation is comparable with that of the major group. On the other hand, for the 100-as spectrum we only observe the θ modulation of the spectrum owing to the high spatial resolution, but many features found in the 500-as spectrum are averaged over the bandwidth because of the pulse's insufficient spectral resolution. In short, Figs. 4 and 5 clearly show the ability of an ultrafast electron pulse to image the breathing mode of motion and the information

FIG. 5. (Color online) Relative variation of the differential scattering probability $d^2\mathcal{P}/dE_a d\hat{\mathbf{k}}_a$ at $t_d = T/2$ with respect to $t_d = 0$ for the three pulse durations as functions of E_a and θ . See Eq. (32) for the definition of the relative variation.

which can be obtained for various bandwidths of the electron wave packet.

Note also that the available information is not restricted to only the time and energy domains. Due to the short de Broglie wavelength, the spatial motions of the target electrons can also be resolved. We have shown the diffraction images for ultrafast electron diffraction from the $3p + 4p$ state without resolving E_a in our previous work, and we found that the “inelastic” channels can contribute significantly to the diffraction images [15]. However, with certain degrees of spectral resolution, by differentiating E_a one can retrieve more information by examining the diffraction patterns from different resolved channels. Because the 1s channel is isolated from the other transitions, we present the differential probabilities $d\mathcal{P}/d\hat{\mathbf{k}}_a$ of the 500-as pulse for the 1s channel and the ones that exclude the 1s-channel as a function of pump-probe delay time in Fig. 6. These diffraction images basically correspond to the minor and the major groups, respectively, in the 500-as spectra (cf. middle column of

FIG. 6. (Color online) Differential probabilities $d\mathcal{P}/d\hat{k}_a$ of a 500-as (FWHM) electron pulse for scattering from the $3p + 4p$ coherent state of the H atom at the pump-probe delay times $t_d = 0T$, $T/4$, and $T/2$. Differential probabilities are obtained without differentiating the energy of the scattered electron. Left column shows the scattering images of the de-excitation transition to the $1s$ state, while the right column corresponds to the scattering images excluding the $1s$ transition. Owing to symmetry, only the upper scattering images are shown.

Fig. 4). Compared with the $1s$ -excluded images at the same delay time, the $1s$ -channel diffraction images show a distinct angular dependence, because there is only a single channel involved in the minor group. Furthermore, since the ground state is spherically symmetric, the diffraction images directly reflect the angular dependence of the target electronic state. A dumbbell-like angular distribution for $d\mathcal{P}_{1s}/d\hat{k}_a$ implies a p -type orbital in the initial coherent state. However, the various final states having differing angular behaviors in $d\mathcal{P}_{\rightarrow 1s}/d\hat{k}_a$ make it difficult to determine the angular behavior of the initial state. As discussed above, the temporal behaviors of the diffraction patterns are different for the two groups, which is clearly seen here. The $1s$ channel also shows a contrasting temporal variation. Both behaviors are related to the overlap of the target $3p + 4p$ state with the $1s$ and the higher energy final states as a function of time. Combined with the information from the spectral measurements, the details of the breathing electronic motion can be inferred from the diffraction images.

2. Wiggling mode: $3d + 4f$

From the $3p + 4p$ case we know that the 500-as pulse provides appropriate temporal and spectral resolutions for the transition to the $1s$ state, therefore, we concentrate on the scattering of a 500-as pulse for the case of wiggling motion. Figure 7 shows the doubly differential probabilities $d^2\mathcal{P}/dE_a d\hat{k}_a$ for scattering of the 500-as pulse at zero delay time (upper panel) and the differences ΔProb of the differential probability with respect to time zero at $t_d = T/4$ and $3T/4$ (middle and lower panels). The difference of the spectrum is

FIG. 7. (Color online) (a) Doubly differential probability of a 500-as (FWHM) electron pulse scattered from the wiggling mode of electronic motion in the H atom at delay times $t_d = 0T$. (b), (c) The differences of the doubly differential probabilities at (b) $t_d = T/4$ and (c) $3T/4$ with respect to the one at zero delay time in (a) [cf. Eq. (33)]. The wiggling electronic motion is produced by synthesizing the opposite-parity $3d$ and $4f$ states with equal amplitude (cf. Fig. 2). Right and left columns correspond to the spectra at azimuthal scattering angle $\varphi = 0^\circ$ (positive z axis) and 180° (negative z axis) (cf. Fig. 1); their comparison shows the asymmetry. The spectra of (b) and (c) above 10 keV are multiplied by a factor 5×10^5 to accentuate the variation.

defined by

$$\Delta\text{Prob}(t_d) \equiv d^2\mathcal{P}/dE_a d\hat{k}_a(t_d) - d^2\mathcal{P}/dE_a d\hat{k}_a(0T). \quad (33)$$

Due to the asymmetric electronic motion (cf. Fig. 2), the spectra for two azimuthal scattering angles $\varphi = 0^\circ$ (positive z axis) and 180° (negative z axis) are juxtaposed in the right and left columns, respectively, for comparison. The spectrum at $t_d = T/2$ is not shown because it is identical with the one at zero delay time. Like the $3p + 4p$ case, two groups can be observed in panel (a). The major group around $E_a = 9.99$ keV corresponds to the transitions from the coherent $3d + 4f$ state to its adjacent states; the minor group above 10 keV represents the de-excitation transition to the $1s$ state.

Several remarks on Fig. 7 are in order. First, the panel (a) exhibits a symmetric pattern with respect to $\varphi = 0^\circ$ and 180° . However, in panels (b) and (c) the differences, ΔProb , for each E_a for both $t_d = T/4$ and $3T/4$ clearly show that the scattering intensities for $\varphi = 0^\circ$ and 180° are asymmetric, thus reflecting the wiggling motion. Second, the portions of the difference spectra above 10 keV in panels (b) and (c) are multiplied by a factor 5×10^5 to accentuate the variations of the minor peak. The relatively small transition probability to the ground state is because, besides the disparate radii between the $1s$ and $3d + 4f$ states, the centrifugal barriers of the $3d$ and $4d$ orbitals prevent the wave function of the

coherent state $3d + 4f$ from penetrating near small radii, and, hence, reduces the transition amplitude. Third, the spectra show an energy-dependent asymmetry which changes at an energy around 9.99 keV. This asymmetry is diminished if E_a is integrated because of the averaging of two comparable but opposite ΔProb over E_a (cf. Fig. 10 of Ref. [15]). Fourth, the total transition probabilities at different delay times are constant because of the odd symmetry of ΔProb . Fifth, though the asymmetric spectra reflect the wiggling motion, the spectra show a very different temporal behavior from that of their charge densities. Two different asymmetric electron densities at $0T$ and $T/2$ (cf. Fig. 2) correspond to the same symmetric spectra shown in Fig. 7(a), whereas the identical symmetric densities at $T/4$ and $3T/4$ (cf. Fig. 2) yield two different diffraction images shown in Figs. 7(b) and 7(c). Finally, for the major group the temporal variations are limited at small scattering angles θ , while the minor group's oscillations extend out to large angles θ . (See Sec. IV for further discussion.)

In Fig. 8 we present the $1s$ -channel differential probability $d\mathcal{P}_{1s}/d\hat{\mathbf{k}}_a$ at four pump-probe delay times in the left column and their φ -angle dependence at four scattering angles θ in the right column. Although the wiggling motion superposes $3d$ and $4f$ states with equal amplitude, the diffraction patterns show that the azimuthal angular dependence is like that of the spherical harmonic function Y_{lm} with $l = 2$ and $m = 0$. In other words, the constituent states contribute unequally to the diffraction images. The magnitude of the transition

amplitude from the $4f$ state to the $1s$ state is smaller than that from the $3d$ state to the $1s$ state, so the $3d$ state angular behavior dominates the diffraction images. Even for a pulse for which factorizability is valid, the mapping mechanism can be unfaithful for inelastic transitions due to the intrinsic differences in the transition matrix elements T_{mn} . Nevertheless, the coherent state asymmetry is exhibited in the diffraction images, implying opposite parities involved in the electronic superposition state.

3. Hybrid mode: Breathing + wiggling

In the breathing and wiggling modes of electronic motion the target internal wave functions are represented by superpositions of excited states [see, e.g., Eq. (31) for the breathing mode]; however, such wave functions do not describe all electronic motions, some of which may comprise hybrid motions. In this section we consider an important class of such hybrid motions. Specifically, unless population transfer to a coherent superposition of excited states is highly efficient, a considerable fraction of the population may remain in the ground state. Moreover, due to the coherent excitation the ground-state population presumably maintains coherence with those in the excited states. Thus, the ground state must be treated as part of the coherent wave function. The resulting target states, hence, include multiple eigenstates and multiple beat frequencies. To investigate the effects of a ground-state component in the target initial state, we consider a target superposition state of the H atom in which 90% of the population is in the $1s$ state, and the remaining 10% of the population is equally shared by the $3p$ and $4p$ states. Besides the aforementioned breathing mode from the superposition of the $3p$ and $4p$ states, wiggling modes of motion are introduced from the opposite-parity combinations of $1s$ and $3p$ and of $1s$ and $4p$ states. The wiggling periods for the $1s + 3p$ and $1s + 4p$ states are 342 as and 324 as, respectively. Therefore, we have a hybrid mode of electronic motion with rapid wiggling and slow breathing.

Figure 9 compares the differential probabilities $d\mathcal{P}/d\hat{\mathbf{k}}_a$ of the 100-as and the 500-as pulse durations for the hybrid mode of motion at $\theta = 0.5^\circ$ and 1.0° in panels (a)–(d) and the asymmetry of the scattering intensities between the positive and negative z axis in panels (e) and (f) at $t_d = T/8 \approx 782$ as. The asymmetry is defined as the ratio of the difference of $d\mathcal{P}/d\hat{\mathbf{k}}_a$ between $\varphi = 0^\circ$ and 180° to their sum as a function of scattering angle θ :

$$\text{Asymmetry} \equiv \frac{d\mathcal{P}/d\hat{\mathbf{k}}_a(0^\circ) - d\mathcal{P}/d\hat{\mathbf{k}}_a(180^\circ)}{d\mathcal{P}/d\hat{\mathbf{k}}_a(0^\circ) + d\mathcal{P}/d\hat{\mathbf{k}}_a(180^\circ)}, \quad (34)$$

where the argument gives the value of the angle φ . According to the above discussion, both pulse durations are able to image the slow breathing motion, but only the 100-as pulse can resolve the rapid wiggling motion. The differential probabilities of the 100-as pulse exhibit the signatures of both the breathing and wiggling motions, and the asymmetry at $t_d = T/8$ clearly shows asymmetric diffraction along the z axis. On the other hand, for the 500-as pulse no discernible asymmetry can be observed, and only the character of the breathing motion survives in the measurement. In the 500-as case the target behaves as if the target were composed of two independent

FIG. 8. (Color online) Left column: Differential probability $d\mathcal{P}_{1s}/d\hat{\mathbf{k}}_a$ of transition to the $1s$ state for scattering of a 500-as electron pulse from the $3d + 4f$ coherent state of the H atom at pump-probe delay times $t_d = 0T, T/4, T/2$, and $3T/4$. Due to symmetry, only the upper diffraction patterns are shown. Right column: Differential probability for four scattering angles θ at three delay times as a function of azimuthal scattering angle φ .

FIG. 9. (Color online) (a)–(d) Differential scattering probabilities $d^2\mathcal{P}/d\hat{\mathbf{k}}_a$ of the 100-as (left column) and the 500-as (right column) electron pulses from a hybrid mode of electronic motion at scattering angles $\theta = 0.5^\circ$ and 1.0° at $t_d = 0T$, $T/4$, and $T/2$ as a function of azimuthal scattering angle φ . (e), (f) The asymmetry of $d^2\mathcal{P}/d\hat{\mathbf{k}}_a$ at delay time $t_d = T/8 \approx 782$ as. The hybrid mode consists of slow breathing and rapid wiggling motions, comprised of 90% population in the $1s$ state, 5% populations in the odd-parity $3p$ and $4p$ states, and zero relative phase in their amplitudes c_n at time zero. See Eq. (34) for the definition of the asymmetry.

species: 10% coherent $3p + 4p$ state and 90% ground state, and the diffraction from the stationary $1s$ state is a constant background superposed on the images of the breathing mode. Furthermore, the larger absolute asymmetry at large θ in Fig. 9(e) implies that the wiggling motion occurs at small radius. (See Sec. IV for further discussion.) In other words, ultrafast electrons can distinguish the breathing and wiggling motions that occur on different spatial scales (i.e., the wiggling motion occurs at small radii and the breathing motion at larger radii). This hybrid mode thus provides an example that demonstrates the loss of information and the possible misinterpretation of results when there is insufficient temporal resolution.

IV. DISCUSSION

The traditional perspective of ultrafast electron diffraction is that in elastic scattering the projectile electron is scattered from the effective potential produced by the charge densities of the stationary states of the target. Therefore, the diffraction images should reflect the structure of the target electron density. However, we have observed the extraordinary temporal behavior of the diffraction images from the $3d + 4f$ coherent state's wiggling motion, which gives asymmetries in the diffraction patterns that are not synchronized with the electron densities. To better interpret these phenomena, we note that since the transition matrix T_{mn} is a function of the momentum transfer s [cf. Eq. (29)], the scattering process should be formulated in momentum space.

We first assume the factorizability of $d^2\mathcal{P}_m/dE_ad\hat{\mathbf{k}}_a$, so that the target electronic state is imaged without the compli-

cations arising from the shape of the projectile electron wave packet. The doubly differential probability is then considered as a function of some representative momentum transfer by fixing the scattering angles θ and φ and the kinetic energy E_a of the scattered electron. We further assume the validity of the first-order Born approximation and neglect electron exchange effects. Therefore, combining Eqs. (27) and (29) yields

$$\frac{d^2\mathcal{P}_m}{dE_ad\hat{\mathbf{k}}_a} \propto \left| \frac{1}{s^2} \int d\mathbf{y} e^{i\mathbf{s}\cdot\mathbf{y}} \phi_m^*(\mathbf{y}) \phi_{\text{coh}}(\mathbf{y}, t_d) \right|^2, \quad (35)$$

where $\phi_{\text{coh}}(\mathbf{y}, t) \equiv \sum_n c_n \phi_n(\mathbf{y}) e^{-i\omega_n t}$ is the time-dependent target electronic state. Here we only consider a single electron target in order to simplify the discussion; for similar reasons, we also assume that the final state ϕ_m excludes any eigenstate present in $\phi_{\text{coh}}(\mathbf{y}, t)$. Equation (35) shows that under the foregoing scattering assumptions the coherent wave function $\phi_{\text{coh}}(\mathbf{y}, t)$ at delay time t_d is imaged by projecting onto the final state ϕ_m , as in ordinary stationary-state scattering theory, but the usual initial stationary state ϕ_n is replaced by the coherent state ϕ_{coh} . The time dependence of $d^2\mathcal{P}/dE_ad\hat{\mathbf{k}}_a$ only indirectly relates to the evolution of $\phi_{\text{coh}}(\mathbf{y}, t_d)$ in the spatial domain because of the complicated Fourier transform and the absolute square. Recall that the Fourier transform induces different phases for even and odd functions [24].

To formulate the scattering in momentum space, we apply the convolution theorem to Eq. (35) and obtain

$$\frac{d^2\mathcal{P}_m}{dE_ad\hat{\mathbf{k}}_a} \propto \left| \frac{1}{s^2} \int d\mathbf{k}_f \phi_m^*(\mathbf{k}_f) \phi_{\text{coh}}(\mathbf{k}_i, t_d) \right|^2, \quad (36)$$

where $\mathbf{k}_i \equiv \mathbf{k}_f - \mathbf{s}$, and $\phi_m(\mathbf{k}_f)$ and $\phi_{\text{coh}}(\mathbf{k}_i, t)$ are the respective final and initial wave functions in momentum space. (Note that we use the same notations for the states and distinguish their coordinate and momentum space representations by their arguments.) In momentum space we see that the temporal behavior of the doubly differential probability is directly associated with the time dependence of the coherent state without the complication of the Fourier transform. This expression can be understood by taking into account the following observations. First, the integrand $\frac{1}{s^2} \phi_m^*(\mathbf{k}_f) \phi_{\text{coh}}(\mathbf{k}_i, t)$ is proportional to the leading-order scattering amplitude for the transition of the target electron, given the initial and final momenta $\mathbf{k}_i$ and $\mathbf{k}_f$, from the initial amplitude $\phi_{\text{coh}}(\mathbf{k}_i, t)$ to the final amplitude $\phi_m(\mathbf{k}_f)$ with the exchange of momentum s (with the projectile electron) through a single photon [25]. Second, $\phi_{\text{coh}}(\mathbf{k}_i, t) = \phi_{\text{coh}}(\mathbf{k}_f - \mathbf{s}, t)$ is shifted in Eq. (36) by s , which is a consequence of momentum conservation. During the scattering the projectile electron transfers the momentum s to the target. Due to the massive nucleus, the target electron receives most of the momentum transfer from the incident electron pulse. After receiving this momentum, the target electron's final momentum becomes $\mathbf{k}_f = \mathbf{k}_i + \mathbf{s}$, and $\phi_{\text{coh}}(\mathbf{k}_i, t)$ is displaced by s . Last, the integration over the final momentum $\mathbf{k}_f$ of the target electron is because $\mathbf{k}_f$ is not resolved in measurements, so the total transition amplitude is the coherent sum over all allowed values of $\mathbf{k}_f$.

FIG. 10. (Color online) (a),(b) Real and imaginary parts of the modified wave function $\phi'_{\text{coh}}(\mathbf{k}, t)$ of the target coherent state along the z axis as a function of time. (c) Time-dependent momentum distribution $|\phi_{\text{coh}}(\mathbf{k}, t)|^2$ along the z axis. The opposite-parity $3d$ and $4f$ states are equally superposed in the coherent state $\phi_{\text{coh}}(\mathbf{k}, t)$. The modified wave function $\phi'_{\text{coh}}(\mathbf{k}, t)$ retains only the relative phase between the $3d$ and $4f$ states. The real parts of $\phi'_{\text{coh}}(\mathbf{k}, t)$ at $t = 0T$ (red) and $T/2$ (blue) are identical, as are the imaginary parts of $\phi'_{\text{coh}}(\mathbf{k}, t)$ at $t = T/4$ (green) and $3T/4$ (black).

Let us first consider the wiggling motion, where

$$\phi_{\text{coh}}(t) = \frac{1}{\sqrt{2}}(\phi_{3d} e^{-i\omega_{3d}t} + \phi_{4f} e^{-i\omega_{4f}t}), \quad (37)$$

from the momentum-space perspective. In Fig. 10 we present the real and imaginary parts of a modified coherent wave function $\phi'_{\text{coh}}(\mathbf{k}, t)$ in momentum space in panels (a) and (b) and the momentum distribution of $\phi_{\text{coh}}(\mathbf{k}, t)$ in panel (c) along the z axis as a function of time. The modified wave function $\phi'_{\text{coh}}(\mathbf{k}, t)$ retains only the physically meaningful relative phase $e^{-i(\omega_{4f} - \omega_{3d})t}$ between the $3d$ and $4f$ states [the overall phase of $\phi_{\text{coh}}(t)$ does not appear in $d^2\mathcal{P}_m/dE_a d\hat{\mathbf{k}}_a$ of Eq. (36).] After examining the temporal behavior of the momentum distribution in panel (c), one observes that it is not synchronized with the oscillatory motion of the electron density in the right column of Fig. 2. However, the temporal behavior of the momentum distributions agrees with that of the diffraction images: Symmetric momentum distributions correspond to symmetric diffraction images, and vice versa. This agreement clearly demonstrates the closer relation between the diffraction images and the target state in momentum space.

Furthermore, Eq. (36) helps us to elucidate the diffraction images of the $1s$ channel and their temporal behaviors in Fig. 8. First, recall that ϕ_{1s} is an isotropic function. Next, due to their symmetries, the real and imaginary parts of $\phi'_{\text{coh}}(\mathbf{k}, t)$ at $t_d = 0T$ and $T/2$ have the same convolution integral with ϕ_{1s}

in Eq. (36) (up to a sign) whether the projectile electron, for fixed scattering angle θ , is deflected to azimuthal scattering angles φ or $\pi - \varphi$ since the magnitude of the momentum transfer to the target electron is determined by the angle θ . Hence, we have symmetric diffraction images with respect to $\varphi = 90^\circ$ at $t_d = 0T$ and $T/2$ in Fig. 8. On the other hand, when $t = T/4$ the real part of $\phi'_{\text{coh}}(\mathbf{k}, t)$ is asymmetric and shifted toward the negative z axis. Therefore, $\phi'_{\text{coh}}(\mathbf{k}, T/4)$ has a larger overlap with ϕ_{1s} , which is centered at the origin, if it receives a momentum transfer with a positive z component [so that $\phi'_{\text{coh}}(\mathbf{k}, T/4)$ is displaced toward the origin] than one with a negative z component (so that ϕ'_{coh} is displaced away from the origin). Accordingly, the projectile electron has larger scattering probability $d^2\mathcal{P}_{1s}/dE_a d\hat{\mathbf{k}}_a$ if it is scattered toward the negative z direction than the positive z direction, which can be seen in Fig. 8 and also in the spectra above 10 keV in Fig. 7 (b). Similarly, when the target electron oscillates back toward the positive z direction at $t_d = 3T/4$, $\phi'_{\text{coh}}(\mathbf{k}, 3T/4)$ reverses, so the diffraction pattern changes accordingly. In short, the $1s$ -channel diffraction images indicate the direction toward which the target electron density moves.

Besides its symmetry and temporal behaviors, we have observed that, compared with the spectra to the other excited states, the $1s$ channel has scattering patterns with broad temporal variations extending to large scattering angles θ [cf. panels (b) and (c) of Fig. 7], whereas the changes of the diffraction images for the excited states are limited to small θ . This θ dependence stems from the momentum widths of the final-state wave functions. Equation (36) shows that the widths of the coherent state $\phi_{\text{coh}}(\mathbf{k}_i, t)$ and the final state $\phi_m(\mathbf{k}_f)$ determine the width of the convolution. If the momentum transfer s is larger than the widths of the coherent and the final states, their overlap is small. The excited-state wave functions are much narrower than the ground state in momentum space, according to the uncertainty relation $\Delta x \Delta k \geq 1/2$. Therefore, the product $\phi_m^*(\mathbf{k}_f) \phi_{\text{coh}}(\mathbf{k}_f - s, t)$ drops quickly for transitions to excited states.

As the principal quantum number of the final state increases, the nodal structure of ϕ_m becomes more complicated. The interpretation of the corresponding diffraction pattern is more difficult because of the interference of transition amplitudes with different $\mathbf{k}_f$. We have no simple physical interpretation for the reversal of the asymmetry around $E_a \approx 9.99$ keV in Figs. 7(b) and 7(c).

For the breathing mode the temporal behavior of the diffraction image $d\mathcal{P}_{1s}/d\hat{\mathbf{k}}_a$ is mainly due to the interference of transition amplitudes for different $\mathbf{k}_f$. We have seen that the diffraction images are always symmetric with respect to $\varphi = 90^\circ$ at all delay times and that the strength of the scattering intensity decreases as the electron density expands (cf. the left column of Fig. 6). We have argued that the temporal behavior of the diffraction images is related to the relative size of the coherent wave function with respect to the $1s$ state in the spatial domain. In momentum space, on the other hand, the momentum distribution $|\phi_{\text{coh}}(\mathbf{k}, t)|^2$ oscillates opposite to that of the electron density. The momentum distribution concentrates at small momenta as the electron density expands (and vice versa). Figure 11 shows the imaginary part of the modified momentum wave function along the z axis as a function of time together with

FIG. 11. (Color online) Imaginary parts of the modified coherent momentum wave function $\phi'_{\text{coh}}(\mathbf{k}, t)$ as a function of time and the momentum space wave function of the $1s$ state of the H atom, with both plotted vs k_z . The coherent state consists of $3p$ and $4p$ states of the H atom with equal amplitude; only the relative phase between the $3p$ and $4p$ states is kept in the modified wave function. For display purposes, the $1s$ wave function is multiplied by a factor of 10.

the $1s$ state wave function of the H atom. One observes the temporal changes of the distribution of the coherent $3p + 4p$ state as compared to the fixed momentum distribution of the $1s$ state. Compared with the coherent state, the ground state has a broad and relatively smooth wave function. Moreover, the parity of the $3p + 4p$ state is different from that of the $1s$ state. Combining the above two facts, one can see a strong destructive interference for transition to the $1s$ channel. Given $\mathbf{k}_i$ and s , every transition amplitude $\frac{1}{s^2} \phi_{1s}^*(\mathbf{k}_f) \phi_{\text{coh}}(\mathbf{k}_i, t_d)$ corresponds to a comparable but out-of-phase amplitude $\frac{1}{s^2} \phi_{1s}^*(\mathbf{k}_f) \phi_{\text{coh}}(-\mathbf{k}_i, t_d)$. Therefore, after integrating over all allowed $\mathbf{k}_f$, the amplitude for transition to the $1s$ channel is small. This destructive interference is more effective as the coherent state becomes narrower in width, so the transition amplitude decreases as the delay time increases to $T/2$.

V. SUMMARY AND CONCLUSIONS

We have presented a theoretical analysis and numerical simulations for energy-resolved ultrafast electron imaging

of key kinds of electronic motion in atoms. Time-resolved spectral imaging can circumvent the complications induced by inelastic transitions during the collision process. According to our theoretical analysis, we have identified those conditions for time- and state-resolved measurements that are optimal. Specifically, the electron pulses should have pulse durations shorter than the time scale of the target electronic motions. Since the temporal modulation of the diffraction images results from the interference of the (longitudinal) components, coherence of the electron pulse also determines the temporal resolution. Moreover, if monochromaticity of the electron pulses is achieved (i.e., their bandwidth is much less than their energy), the diffraction images directly reflect the target electronic motions, insensitive to the details of the electron pulses. The simulations we presented demonstrate the capabilities of ultrafast electrons to image and differentiate the breathing and wiggling modes of electronic motion in the H atom. Both kinds of motion have energy-dependent diffraction images, showing the importance of differentiating the kinetic energies of scattered electrons. In the breathing motion, we observed that the symmetric scattering intensity oscillates with the change of the target radius. In the wiggling motion, the asymmetric diffraction patterns reflect the asymmetric motion. We have also provided a momentum-space perspective to interpret the asymmetry and temporal variation of the scattering intensities.

Although we employed the simple H atom system to illustrate breathing, wiggling, and hybrid electronic motions, the features observed in the energy-resolved diffraction images should be applicable to multielectron targets and molecules. However, further detailed investigations are necessary to examine many-particle effects on these features. Due to its ability to obtain the spatial, temporal, and spectral content of target electronic motions, energy-resolved ultrafast electron diffraction can be a useful technique for investigating electron dynamics, and the valuable information retrieved may be worth the effort.

ACKNOWLEDGMENTS

This work has been supported in part by AFOSR Award No. FA9550-12-1-0149. Our calculations were carried out at the Holland Computing Center of the University of Nebraska.

-
- [1] J. R. Dwyer, C. T. Hebeisen, R. Ernstorfer, M. Harb, V. B. Deyirmenjian, R. E. Jordan, and R. J. D. Miller, *Philos. Trans. R. Soc. A* **364**, 741 (2006).
 - [2] G. Sciaini and R. J. D. Miller, *Rep. Prog. Phys.* **74**, 096101 (2011).
 - [3] J. M. Thomas and P. A. Midgley, *Chem. Phys.* **385**, 1 (2011).
 - [4] D. J. Flannigan and A. H. Zewail, *Acc. Chem. Res.* **45**, 1828 (2012).
 - [5] P. Baum, *Chem. Phys.* **423**, 55 (2013).
 - [6] T. van Oudheusden, P. L. E. M. Pasmans, S. B. van der Geer, M. J. de Loos, M. J. van der Wiel, and O. J. Luiten, *Phys. Rev. Lett.* **105**, 264801 (2010).
 - [7] P. Baum and A. H. Zewail, *Proc. Natl. Acad. Sci. USA* **104**, 18409 (2007).
 - [8] E. Fill, L. Veisz, A. Apolonski, and F. Krausz, *New J. Phys.* **8**, 272 (2006).
 - [9] A. Gliserin, A. Apolonski, F. Krausz, and P. Baum, *New J. Phys.* **14**, 073055 (2012).
 - [10] P. Hansen, C. Baumgarten, H. Batelaan, and M. Centurion, *Appl. Phys. Lett.* **101**, 083501 (2012).
 - [11] P. Baum and A. H. Zewail, *Chem. Phys.* **366**, 2 (2009).
 - [12] P. Baum, J. Manz, and A. Schild, *Sci. China Phys. Mech. Astron.* **53**, 987 (2010).
 - [13] H.-C. Shao and A. F. Starace, *Phys. Rev. Lett.* **105**, 263201 (2010).

- [14] H.-C. Shao and A. F. Starace, [Phys. Rev. A **87**, 050701\(R\) \(2013\)](#).
- [15] H.-C. Shao and A. F. Starace, [Phys. Rev. A **88**, 062711 \(2013\)](#).
- [16] A. Yurtsever, R. M. van der Veen, and A. H. Zewail, [Science **335**, 59 \(2012\)](#).
- [17] F. Robicheaux, [Phys. Rev. A **62**, 062706 \(2000\)](#).
- [18] M. L. Goldberger and K. M. Watson, *Collision Theory* (John Wiley & Sons, Inc., New York, 1964), p. 79.
- [19] P. Baum and A. H. Zewail, [Proc. Natl. Acad. Sci. USA **103**, 16105 \(2006\)](#).
- [20] M. Inokuti, [Rev. Mod. Phys. **43**, 297 \(1971\)](#).
- [21] H. A. Bethe and R. Jackiw, *Intermediate Quantum Mechanics*, 2nd ed. (W. A. Benjamin, Inc., New York, 1968).
- [22] R. A. Bonham and M. Fink, *High Energy Electron Scattering* (Van Nostrand Reinhold Company, New York, 1974).
- [23] G. Dixit, O. Vendrell, and R. Santra, [Proc. Natl. Acad. Sci. USA **109**, 11636 \(2012\)](#).
- [24] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in Fortran 77* (Cambridge University Press, Cambridge, England, 1992), p. 491.
- [25] M. E. Peskin and D. V. Schroeder, *An Introduction to Quantum Field Theory* (Addison-Wesley, Reading, MA, 1995), p. 125.