Ultrafast quantum dynamics driven by the strong space charge field of a relativistic electron beam

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Abstract: In this article, we illustrate how the Coulomb field of a highly relativistic electron beam can be shaped into a broadband pulse suitable for driving ultrafast and strong-field physics. In contrast to a solid-state laser, the Coulomb field creates a pulse which can be intrinsically synchronized with an x-ray free electron laser (XFEL), can have a cutoff frequency which is broadly tunable from THz to EUV, and which acts on target systems as a “half-cycle” impulse. Explicit examples are presented to emphasize how the unique features of this excitation can be a tool for novel science at XFEL facilities like the LCLS.

Introduction

Over the last decade, x-ray free electron lasers (XFELs) have been a transformative tool for the physical sciences by delivering intense bursts of x-rays which can probe electronic structure with site-specificity and ultrafast temporal resolution [1]. The high intensity of the XFEL allows the pump-probe framework to be applied to traditional x-ray imaging and spectroscopy, where the pump is most often either a secondary x-ray pulse [2–4] or a solid-state laser that has been synchronized to the x-ray probe [5–7]. More recently, novel electron-beam shaping techniques have extended XFEL temporal resolution to the attosecond regime and made it possible to chart coherent charge dynamics in molecular systems [8,9].

In this article, we propose to extend the reach of ultrafast science at XFELs by directly pumping quantum systems with the same relativistic electron beam used to generate x-rays (Fig. 1a). The beam interacts with valence electrons primarily through the optical cross-section (rather than the comparatively small collisional cross-section [10]), such that we can think of its Coulomb field as a strong, “half-cycle”, radially-polarized laser. Pioneering experiments at the Sub-Picosecond Pulse Source (SPPS) [11] and FACET [12] facilities demonstrate that this beam field can be used to drive magnetic switching [13,14] and ultrafast changes in conductivity [15].

More generally, the field of the beam is an ultra-broadband impulse which drives processes ranging from “DC”-like Stark shifts up to ultraviolet ionization of valence electrons. The resulting dynamics are a complex superposition of excited states most similar to those created by single-cycle THz sources (Fig. 1b); however, we identify four main distinctions: Firstly, the pulse length can be much shorter than that of conventional lasers; indeed, by using techniques developed to produce attosecond x-rays [16,17], we can create half-cycle fields with intensity profiles as short as 250 as, corresponding to 12 eV bandwidth; Secondly, the field is truly a “unipolar” impulse, such that the direct momentum transfer \(A = -\int E dt\) is nonzero. Thirdly, we can create strong fields up to tens of V/Å by focusing the electron beam to sub-wavelength spot sizes. And, lastly, the field is intrinsically synchronized to the x-ray pulses generated by the bunch.

The importance of the last point should not be underestimated: state-of-the-art timing jitter between an optical laser and an XFEL pulse is between 20 and 100 fs [18], such that time-stamping techniques must be used to re-sort data on a shot-by-shot basis [19]—a feat which will become increasingly difficult as the next generation of high-rate superconducting FELs come online. Intrinsic synchronization bypasses this issue and directly enables attosecond pump-probe experiments.

In this paper, we will discuss how to generate, characterize, and ultimately use ultrafast space-charge and x-ray pulses...
for photon-electron pumpprobe experiments (PEPPEx). Our discussion is grounded by start-to-end simulations at the LCLS-II CuS beamline [20], although the same concepts are adaptable to other FEL beamlines. We show how the electron beam’s phase space can be manipulated with a laser heater to produce two spikes suitable for a pump-probe experiment. We calculate the x-ray and space-charge fields from this beam, and we show how photo-electron streaking can be used to reconstruct those same fields. Then we discuss the interaction of the space-charge field with three distinct quantum systems.

1. Pulse synthesis

To prepare an ultrafast pump-probe experiment we first shape the electron beam to have two short current spikes: the later (‘tail’) spike is used to generate x-rays, while the earlier (‘head’) spike will be used for its Coulomb field. A small magnetic chicane can then be used to delay the electron beam relative to the x-rays and precisely set the overlap between the Coulomb field and the x-ray pulse. To optimize this arrangement, it is necessary to control the chirp of the two current spikes separately, since the Coulomb spike should be fully compressed while the lasing spike should be strongly chirped (the addition of an x-ray delay line would create additional flexibility, but we do not use one here).

One method to create such a bunch is based on laser heater shaping, as described in detail in ref [55]. In short, the process plays out as illustrated in Fig. 2, which is based on start-to-end simulations of the LCLS-II CuS beamline [20] (using IMPACT-T for the injector and Elegant for the transport from the injector to the undulators [56–58]). First, a stack of Gaussian laser heater pulses creates time-dependent slice-energy spread. Then, after the first bunch compressor, the energy spread is converted into current modulations which seed the microbunching instability and are amplified during transport. Finally, anomalous dispersion in the magnetic dogleg compresses the space-charge induced chirp into two large current spikes. The compression ratio of the two spikes can be controlled separately by changing the delay between successive heater pulses (relative both to each other and to the beam center) in order to optimize the microbunching gain for each spike separately.

This procedure leaves us with a strongly chirped tail spike which we use to generate the x-ray probe by matching
Fig. 2. (A) Cartoon of the LCLS-II cuS beamline. (C-G) Snapshots of the electron beam longitudinal phase space. A coherent energy modulation is applied by a stack of 0.7 ps long laser-heater pulses. This modulation evolves into two large spikes separated by approximately 50 fs. The undulator (450 eV) is chirp-taper matched to the tail (left) spike so that the (ensemble averaged) peak power (B) from the tail grows fastest and dominates the total x-ray radiation.

The undulator taper to the beam chirp \[8,16\]. Genesis [59] simulations based on the LCLS-II soft x-ray line [20] show that, with a matched taper, the tail spike can produce 450 eV soft x-rays with an average power over 120 GW, compared to \(<10\) GW from the head spike. The inset to Fig. 1(B) shows many individual simulations of the tail spike, each with a unique random seed leading to unique FEL dynamics. Most often the individual pulses have a 0.6 fs full-width-at-half-maximum (FWHM) pulse length, but varying amounts of post-saturation slippage broaden the ensemble-averaged intensity to 0.8 fs FWHM. This 0.2 fs difference is expected to be the dominant component of the pump-probe jitter between the x-rays and the electron beam.

After lasing, a 40 fs chicane delay overlaps the x-ray pulse with the current spike at the head of the bunch, as shown in Fig. 1(B). At the same time, this chicane fully compresses the head spike into a 13.5 kA peak with a FWHM width of only 250 as and an energy spread of 25 MeV. Small changes in dispersion from the chicane can be used to control the pump-probe delay within an effective Rayleigh length of \(35\) fs (outside of which the current spike begins to de-compress). Note also that the head spike loses a small, but variable, amount of energy while lasing, and this leads to negligible jitter (compared to rf induced jitter) in the compressed spike-width—the current profile in Fig. 1(B) shows a typical case.

Meanwhile, the electrons in our beam collectively form a strong electromagnetic impulse which closely approximates a “half-cycle” laser pulse. For a transversely Gaussian charge density we can estimate the electric field as:

\[
\rho_\perp = \frac{I(t)}{2\pi \sigma_\perp^2} e^{-\frac{1}{2}\left(\frac{\sigma_\perp}{r}\right)^2}
\]

with an associated azimuthal magnetic field given by \(B = (\beta c \times E)\). This model for the field produced by the beam is valid provided that: (a) we only consider frequencies commensurate with the bunch length \(f \leq 1/\sigma_t\), such that the field of the individual electrons add coherently and we can neglect stochastic effects \[10,60\]; (b) we consider only cases in which the beam can be approximated by a long cylinder in its rest frame: \(\sigma_r < \gamma c \sigma_t\); and finally (c) that the beam density is a 1D Gaussian cylinder. Of these conditions, only (c) is regularly violated in practice. In particular, while an individual slice of the electron beam may resemble a Gaussian cross section, the centroid is often a strong function of \(t\) thanks to coherent synchrotron radiation (CSR) induced energy loss in the bunch compressor. Thus, to get an accurate space-charge field, we use the numerical Poisson solver from the tracking code GPT [61]. It is this field, evaluated a single point in space, that is plotted as the blue curve in Fig. 1(B).

2. Pulse Characterization

The “gold standard” for the metrology of sub-femtosecond XUV and X-ray pulses is photoemission streaking with long wavelength fields. In this technique, an ultrashort laser pulse is overlapped with a longer wavelength dressing laser field. The combined field is incident on a gas-sample and the momentum distribution of electrons ionized by the ultrashort
field are displaced ("streaked") by the long-wavelength dressing field \(62–64\). This two-color ionization process encodes the information of the short-wavelength pulse into the measured photoelectron momentum distribution. The pulse profiles can be retrieved from the resultant spectrogram (recorded by scanning the relative delay between the x-ray pulse and IR field) via a number of proposed algorithms \(65–68\). To date, streaking at x-ray free electron laser (XFEL) facilities relies on an external laser pulse which must be temporarily overlapped with the XFEL pulse inside a gas phase sample. The shot-to-shot jitter of the relative laser/x-ray arrival time precludes measurements which are not single-shot, and thus the dressing field has always been either long wavelength \(69\) or circularly polarized \(8,70,71\). But, by using a naturally synchronized, unipolar streaking field we have the possibility to average together many independent shots and thus greatly increase measurement sensitivity.

Streaked photo-electron spectra are conventionally calculated within the strong field approximation to the Schrödinger equation for a single active electron, which ignores the effect of the Coulomb potential on the emitted electron. In this approximation, the probability for observing an electron with momentum \(\mathbf{k}\) is given by:

\[
W(\mathbf{k} - \tau) = \left| \int_{-\infty}^{\infty} dt \ e^{iQ(t)} D(\mathbf{k} + A(t)) E_x(t - \tau) \right|^2
\]

where \(D(\mathbf{k})\) is the photoionization dipole moment (here approximated with the value for hydrogen atoms \(D(\mathbf{k}) = \frac{\mathbf{k}}{(k^2 + 2IP)}\)), \(IP\) is the ionization potential, \(E_x(t')\) is the electric field of the ionizing x-ray pulse, and \(A(t) = -\int dt E(t)\) is vector potential of the streaking (space-charge) field with \(A(\infty) = 0\). \(Q(t)\) is the so-called Volkov phase. In anticipation of averaging over many shots, we will re-write this in terms of the first-order correlation function \(\Gamma(t_1, t_2) = \langle E(t_1) E^*(t_2) \rangle\) which allows us to account for the SASE jitter:

\[
W(\mathbf{k} - \tau) = \left| \int_{-\infty}^{\infty} dt_1 dt_2 e^{i(Q(t_1) - Q(t_2))} D(\mathbf{k} + A(t_1)) D^*(\mathbf{k} + A(t_2)) \Gamma(t_1 - \tau, t_2 - \tau) \right|^2
\]

Within the quasi-classical model we imagine that an ionizing x-ray pulse creates photo-electrons at time \(t_i\) with probability \(I(t)\) (the intensity of the incident x-ray pulse) and energy \(k_f^2/2\) with probability \(I(w)\) (possibly with some \(t - \omega\) correlation due to chirp). If the streaking field is strong, then the Coulomb potential can be neglected and the now-free electrons are accelerated to a final momentum of \(k_f = k_i - A\).

In Fig. 3, we simulate a spectrogram \(W(\mathbf{k}, \tau)\) based on the fields from the previous section (for photo-electrons emitted from a single point in space and collected parallel to the x-ray polarization). For each time delay, we average the spectrum from equation 2 calculated using many independent random seeds for the SASE radiation (but neglecting any changes in \(A\) due to machine jitter). The quasi-classical model allows a straightforward interpretation: we see...
two distinct populations separated by $2k_i = 2\sqrt{2(h\omega - IP)}$ for an ionization potential IP, corresponding to electrons emitted in directions parallel and anti-parallel to the streaking field. Each group of electrons then follows the vector $A(t)$ as the pump-probe delay is changed. Where the streaking field is large, the spectral width of the photo-electron peak is proportional to its pulse duration, and where the streaking field is weak it is proportional to the x-ray spectrum. In-between, as we can see in the inset to Fig. 3, the width of the parallel and anti-parallel populations are different, due to the the average chirp of the x-ray beam (originating from the chirp-taper FEL configuration [8]).

After averaging over many shots to produce a spectrogram, we are no longer sensitive to the pulse length of individual shots. Instead, we measure the first order correlation function $\Gamma(t_1, t_2)$, as indicated by Eq. 4. An example $\Gamma(t_1, t_2)$ calculated directly from the FEL simulations is shown in Fig. 3(b): the main diagonal ($t_1 = t_2$) yields the average FEL power, while the off-diagonals ($t_1 = -t_2$) are related to the coherence length. Because the FEL is not a stationary process, the coherence length is not constant, but in fact increases towards the head (upper right) of the pulse, where the slippage has built up coherent power.

In order to fully reconstruct $\Gamma(t_1, t_2)$ and the streaking field $A(t)$, we adopt an procedure similar to [72] and [68], in which we first estimate the streaking field based on the average spectrum $A(t) \approx \langle W(\tau) \rangle_k$ and then iteratively solve the least squares problem for $\Gamma(t_1, t_2)$ (i.e. Eq. 4). This avoids the approximations used in the common FROG-CRAB algorithms, which are not applicable to our case. To speed-up convergence, we represent the underlying $\Gamma$ in a compact basis, an extension of the Von Neumann basis used in [72]. We can then refine our guess for $A(t)$ because we know that, within the quasi-classical approximation, the average spectrum is the convolution of the streaking field and the average x-ray power: $\langle W(\tau) \rangle_k = A(\tau) \ast \Gamma(\tau, \tau)$. We demonstrate this technique in Fig. 3(b-d), where we have calculated $\Gamma$ once, using only the portion of the spectrum between 25 and 15 fs, where our assumption of slowly changing $A$ is well-justified. Finally, we improve our guess of $A$ by the de-convolution with $\Gamma(\tau, \tau)$.

The reconstruction of $\Gamma(\tau, \tau)$ quickly converges to the correct average power. It also captures the increasing coherence length towards the head of the pulse. However, the simulated $\Gamma(\tau, \tau)$ shows small coherent satellites near the tail (corresponding to pulse splitting), which are not recovered in this reconstruction. In order to capture these weak features, one could create a streaking field with higher power in $k$ and a larger range of streaking fields, but in practice resolving such weak features will be difficult. Further iteration including non-linear optimization of $A$ (as in [68]) can improve the reconstruction of the sharp current spike near $t = 0$, but at the cost of significant computational resources.

Once the streaking amplitude is well-calibrated from an average spectrogram, it is possible to estimate single-shot FEL pulse lengths from streaked spectra. To do so accurately, one should set the pump-probe delay such that the streaking field is large and the x-ray spectrum is negligible. Where this is not possible, one can still make an estimate of single-shot parameters, especially if both the parallel and anti-parallel bunches can be gathered and the x-ray spectrum measured downstream (since a comparison of the two gives direct information about the x-ray chirp).

3. Beam driven quantum dynamics

The relativistic electron beam is a uniquely broadband pump pulse that is both faster and stronger than comparable “single-cycle” pulses (see Figure 1). It can excite electronic transitions, shift electronic energy levels, and drive large-scale nuclear motion. The pulses are fast enough that they can act impulsively [73], and yet strong enough to manipulate wavepacket dynamics.

The wide range of quantum dynamics triggered by the electron beam pump can be tuned by altering the space-charge field’s cut-off frequency and field-strength. We consider two cases (Fig. 1b): a 250 as 12 kA current spike, and a 250 fs 1 kA flat-top electron beam. The current spike contains 4 µJ within its FWHM profile and extends out to 12 eV at 3.5 V/Å; while the flat-top beam contains 11 µJ within its FWHM profile and extends out to 1 THz at 0.15 V/Å. Both beams are focused to 20 µm (rms) spot-size as a compromise between pumped-volume and field strength. If an ion-microscope is used to spatially resolve the pumped volume [74], then the beams could be designed with a tighter focus in order to further increase the field strength. Indeed, at FACET-II a tighter focus and stronger compression are expected to push beam driven fields into the regime of relativistic optics and QED [75].

The resulting physics can be directly probed by the intrinsically synchronized XFEL pulse. In the attosecond modality discussed in the previous sections, which builds on previous work at LCLS [8, 9], we imagine using soft-x ray absorption spectroscopy to make a chemically-resolved diagnostic of ultra-fast motion. But it is also possible to measure structural changes directly from x-ray diffraction. In either case, the x-ray probe provides mechanistic insight into the ultrafast dynamics that can’t easily be obtained from an optical probe.

Here we discuss three pump-probe scenarios which highlight the flexibility of the electron beam pump source. Firstly, we consider photo-chemical reactions pumped by the EUV spectral component of an attosecond current spike. Secondly, we consider electronic transitions in a large band-gap dielectric where an attosecond current spike causes...
Fig. 4. (a) Wigner-Ville distribution of the Coulomb field. (b) Spectrum of the Coulomb field with and without the current spike. With the current spike, the spectrum extends out well into the EUV where it can directly excite many valence transitions. Without the current spike, the spectrum does not extend beyond the THz frequencies. The compression of the beam can be tuned to control the cutoff frequency.

direct ionization to the conduction band and then a long THz-like pedestal accelerates the free-carriers. Finally, we discuss using a long flattop electron beam in order to drive large-amplitude ion motion in the model battery solid electrolyte Na\(\beta/\beta'\)\(\alpha\)-alumina. For this case, we estimate how soft-x-ray absorption can be used to track large excursions in the mobile Na ion density and thus create a pathway towards a mechanistic understanding of ionic conductivity and its vibrational origins.

3.1. Ultrafast photochemistry

Ultrafast photochemistry provides opportunities for improving our understanding in synthetic chemistry and energy storage by delivering energy directly to a target molecule in an otherwise cold system. The current spike simulated in this article can drive the electronic excitation significantly faster than conventional ultraviolet (UV) lasers, which allows us to selectively probe ultrafast reaction pathways. It is difficult, however, to predict the photochemical reactivity based on the reactant structure through structure-reactivity relationships (in all but the simplest cases). Beyond this, non-adiabatic dynamics near conical intersections (CIs) in excited electronic states involve an interplay of electronic and nuclear degrees of freedom, which cannot be described within the Born-Oppenheimer approximation, and are responsible for much of the excited state behavior in photochemistry. By shaping the current profile of our electron beam, we may be able to exert control over the conical interaction and alter the non-adiabatic dynamics [76–79].

The role of a short current spike in driving photo-chemical reactions can be thought of as arising from the EUV-field associated with electromagnetic field of the beam. We visualize this effect in Fig. 4 for the 250 as spike, shown in Fig. 2 by calculating the time-frequency Wigner-Ville distribution of the electric field. The short spike in the beam leads to a 250 as window with spectral content out to 12 eV. The pedestal accompanying that short spike can cause strong-field ionization if the beam is focused too tightly, but in the perturbative regime it simply causes a Stark-shift of the energy levels. In this case, the ultrafast spike can transition valence electrons into excited states on an impulsive time-scale.

3.2. Electronic dynamics in a model dielectric

Studies of light-matter interaction at the ultrafast time-scale can give unique insight into the optoelectronic properties and device physics of emerging materials. Specifically, the charge-carrier dynamics following light excitation have direct implications for optoelectronic device performance in terms of charge-carrier generations, recombination, and charge-transfer processes. High intensity fields can be used to drive electrons far from their equilibrium, leading to Bloch oscillations within each sub-band of a solid and processes like high harmonic generation [80]. The space-charge field opens a new regime for controlling electron dynamics in solids by providing a strong field which can rapidly excite free carriers and drive them to high energies before scattering. Here, as a proof-of-concept, we have performed simulations on the space-charge field interaction within a dielectric. The dielectric is simplified in our simulations with a one-dimensional periodic lattice potential that has a band gap of 9 eV, close to the band gap of crystalline quartz (see Fig. 5a)). We solved the time-dependent Schrödinger equation in the basis of accelerated Bloch states, as described in [81]. In this model, all electrons initially occupy valence states in a periodic potential, the parameters of which were identical to those in [82]. The broad spectrum of the space-charge field allows for single-photon transitions across the 9-eV band gap, which are largely confined to the central spike. The spike itself is too short to significantly accelerate the
Fig. 5. The interaction of the space-charge field (grey dashed curve) with a one-dimensional periodic lattice potential that has a band gap of 9 eV (equivalent to the band gap of crystalline quartz). (a) From the time evolution of the conduction-band population (blue curve), we see that transitions from valence to conduction bands mainly happen during the main spike of the electric field. The inset shows the band structure within the first Brillouin zone \( k_{BZB} = 0.628 \) Å \(^{-1}\). (b) Photo-injected electrons are rapidly accelerated by the space-charge field, crossing multiple Brillouin-zone boundaries (BZB), which promotes them to high conduction bands. While panel (a) shows the occupation averaged over crystal momenta, this pseudocolor diagram represents the motion of the electron wave packet in reciprocal space, where the bands are unfolded into the extended-zone scheme, and the colors in this diagram represent the occupations of Bloch states in the first five conduction bands.

charge carriers that it creates, but the electric field that follows the spike makes electrons acquire kinetic energies on the order of tens of electronvolts. Electrons gain energy by making transitions to higher conduction bands as they cross the Brillouin-zone borders. While Fig. 5a) shows the occupation averaged over crystal momenta, Fig. 5b) represents the motion of the electron wave packet in reciprocal space. The simulations show that probing the unfolding changes in charge motion upon excitation by the space-charge field with attosecond time resolution and atomic specificity would open up exciting perspectives in attosecond material science, including the development of petahertz optoelectronic switches.

3.3. Nuclear motion in ionic conductors

For frequencies up to several THz, the spectral intensities and peak fields of the space-charge field can be more than 10\(^x\) those of single-cycle tabletop sources [83]. This makes it an attractive strong-field source for triggering lattice dynamics that couple to exotic non-equilibrium phases [84, 85] or large-amplitude ionic motions that couple to ionic conduction [86, 87]. Soft x-ray radiation from the same electron beam can then provide chemical resolution to selectively target shifts in the active ions and to probe the time-resolved ion trajectory and associated intermediate states. This would enable a new view of the microscopic processes that underlie how ion motion occurs in rechargeable batteries and other electrochemical systems. [86].

Applications include pure ionic conductors such as Na\(\beta\)/\(\beta\)'-aluminas [87, 88], mixed ion-electron conductors such as the layered-oxide cathodes Li(Ni,Mn,Co)O\(_2\) [89, 90] or Na\(_2\)Mn\(_5\)O\(_7\) [91], quantum paraelectrics such as SrTiO\(_3\) [84], and many others. Here, we simulate the pumping of the vibrations of conducting mobile Na\(^+\) ions in Na\(\beta\)-alumina (Figure 6a). The strongly anharmonic vibrations couple to translations called "hops" and ultimately to long-range ionic conduction, but this coupling remains challenging to both trigger and probe due to fluctuating potential-energy landscapes and the rarity of the hopping events [87]. The ionic response to a strong-field pump simulated with large-scale molecular dynamics [87, 88, 92, 93] shows a substantially perturbed radial distribution function (RDF) around the...
mobile Na ions (Figure 6bc) due to their rapid displacements driven by the pump. The x-ray absorption spectrum of a representative ion computed in FEFF [94] (see appendix) based on the molecular-dynamics trajectory also shows strong changes relative to the same ion in an unperturbed material (Figure 6d), both in the near-edge and EXAFS regions.

This simplified model suggests that core-level absorption spectroscopy can be used to track the ultrafast ionic motion driven by the strong field of the beam. Furthermore, since the timescales of lattice dynamics and especially metastable states accessed by strong-field excitations can extend much longer than the temporal length of the FEL pulses themselves, additional probes can be subsequently employed for multi-modal characterization of the dynamics triggered by the Coulomb pump.

4. Conclusions

In this article we have discussed how to produce and characterize ultra-fast pump-probe fields at an FEL facility. By deliberately seeding coherent microbunches in an electron beam, we can create pairs of ultrashort current spikes. The tail spike generates sub-fs x-ray pulses which then slip ahead to overlap with the head spike resulting in an intrinsically synchronized pump-probe scheme between x-rays and the space-charge field of the beam.

We show that, compared to a conventional laser, the relativistic Coulomb field has unique properties which lend it to novel studies of ultrafast and strong-field dynamics. It can be compressed to attosecond pulse lengths and focused to atomic field strengths, all while supporting frequency content from 0 to 12 eV. Within this novel parameter space, we find that the beam can be used to explore ultrafast reaction pathways in photo-chemistry, to study opto-electronic proprieties of materials, and to drive large amplitude nuclear motion. The combination of short pulses and large momentum transfer will allow the space charge field to test the limits of material proprieties and improve our understanding of energy transfer on ultrafast time scales.

We support our assertion that an electron beam can be shaped to create both attosecond soft x-ray pulses and a powerful space-charge field by showing start-to-end simulations of the LCLS-II facility. The specificity of our example belies the flexibility of our technique. Indeed, a programmable laser heater can be used to etch complicated shapes into...
the electron beam current profile [55]. By synthesizing electric field transients with sub-femtosecond features we can control the potential landscape and thus the dynamics of the resulting excitation [76–79]. And with the addition of a dedicated post-lasing compressor we will be able to create high-contrast current spikes capable of cleanly driving the impulsive excitation of valence electrons—a powerful method for wave-packet control which has previously been available only to Rydberg electrons [73]. The opportunity to not only generate excited states, but also to control them and then probe them with soft x-rays would open a new regime of attosecond physics only possible at state-of-the-art x-ray free electron lasers.

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X-ray Absorption Near Edge Spectra (XANES) at the Na K-edge were simulated for selected structural motifs of Na $\beta$/$\beta''$-alumina derived from classical molecular dynamics simulations of the electric field driven ion hopping process. The ab initio real-space multiple scattering method as implemented in the FEFF10 [94] code was employed for this purpose. Accordingly, cluster models of Na $\beta$/$\beta''$-alumina with ion configurations representative of both the un-perturbed and electric field perturbed systems were considered. In each case the clusters (10×10×10 supercells)
consisting of approximately 12000 atoms were constructed centered on the XANES target Na ion of interest. Full multiple scattering (FMS) and self-consistent field (SCF) radii were both set to 9 Å around the reference Na site to ensure convergence in real-space and to satisfy the convergence of spectra less than $10^{-3}$ arb. u. at each point.