Dissecting strong-field excitation dynamics with atomic-momentum spectroscopy

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Observation of internal quantum dynamics relies on a correlation between the system being observed and the measurement apparatus. We propose using the center-of-mass (c.m.) degrees of freedom of atoms and molecules as a “built-in” monitoring device for observing their internal dynamics in non-perturbative laser fields. We illustrate the idea on the simplest model system - the hydrogen atom in an intense, tightly-focused infrared laser beam. To this end, we develop a numerically-tractable, quantum-mechanical treatment of correlations between internal and c.m. dynamics. We show that the transverse momentum records the time excited states experience the field, allowing femtosecond reconstruction of the strong-field excitation process. The ground state becomes weak-field seeking, an unambiguous and long sought-for signature of the Kramers-Henneberger regime.

In this Letter we show that adding an artificial trap-field seeking, an unambiguous and long sought-for signature of the Kramers-Henneberger regime.

The process of measurement in quantum mechanics relies on establishing a correlation between an internal quantum degree of freedom and a classical degree of freedom of a measurement apparatus. Finding a suitable classical outcome for a quantum system of interest is particularly important for achieving optimal temporal and spatial resolution. One classical degree of freedom available to every gas-phase system is the translational motion of its center of mass (c.m.), effectively attaching an individual measurement apparatus to each atom or molecule. The closely-related prescription of using the c.m. motion as a control device has been very successful in Mössbauer[1] and other Doppler spectroscopies[2].

The coupling between the internal quantum dynamics and the c.m. motion has not received much attention in strong-field atomic, molecular, and optical (AMO) science. In intense visible and infra-red fields, this coupling is a subtle effect, intimately connected to the breakdown of the dipole approximation. The fundamental importance of non-dipole effects has been recognized early on[3–5], but only recently, enabled by refined theoretical and experimental approaches, processes beyond the dipole-approximation are coming into focus. These include radiation pressure[6], momentum distribution between fragments upon ionization[7–9], chiral effects in HHG[10], and atomic acceleration[11]. These effects have been investigated for very intense (relativistic and near-relativistic) infra-red (IR) fields[12–15], as well as for shorter-wavelength fields which are becoming available in the strong-field regime[16].

Because the c.m. coupling effects in strong-field physics are small, numerical treatment of their contribution is challenging. The standard technique appears to be the treatment on full-product grids[17], which would require a 6D numerical simulation even for the simplest realistic target – the hydrogen atom.

In this Letter we show that adding an artificial trapping potential, chosen not to disturb the c.m. motion, allows the effective dimensionality of the problem to be reduced to 3D. This enables detailed computational investigation of c.m. dynamics of strong-field processes. By using the c.m. motion as the “built-in” measurement apparatus, we obtain information on the dynamics of the excited-state formation in intense IR fields. Using this technique, we provide the first unambiguous, experimentally-realizable method for confirming the atomic ground state transiently entering the Kramers-Henneberger (KH) regime in such fields.

In the KH (or acceleration) frame of reference, the laser field dominates the electronic motion. For a laser field with the peak electric field amplitude $F_0$ and carrier frequency $\omega$, linearly polarized along the direction $\hat{n}$, the lowest-order Fourier component of the interaction potential in the KH frame takes the form[18]:

$$U_{KH}(\vec{r}) = \frac{1}{2\pi} \int_0^{2\pi} U(\vec{r} + \vec{l}_0 \sin(\tau)) d\tau,$$  (1)

where $U$ is the interaction potential in the laboratory frame and the electron oscillation amplitude $\vec{l}_0 = \hat{n} F_0 \omega^{-2}$.

If higher-order corrections to Eq. (1) can be neglected for a given state, the system is said to be in the Kramers-Henneberger regime. A remarkable property of the KH states in low-frequency fields is that the effective polarizability rapidly approaches $-\omega^{-2}[19]$ with increasing $\vec{l}_0$ magnitude. As the result, a system in a KH state experiences the same ponderomotive potential as a free electron.

Kramers-Henneberger states have been postulated to explain photoelectron spectra in strong fields[20], ionization-free filamentation in gases[21], and ponderomotive acceleration of neutral excited states[11, 19, 22–25]. Rydberg states readily satisfy the KH criteria in intense IR fields, and are commonly accepted to be in the KH regime in such fields. Because the KH states exist only transiently in the presence of the intense field, their unambiguous detection remains elusive[19]. The mechanism of their formation in low-frequency fields, and for the ground state even their existence, remain
controversial[26–30], despite extensive investigation[31–39].

In the simplest case of a 1-electron, neutral atom, the laboratory-frame Hamiltonian is given by (unless noted otherwise, atomic units ($\hbar = m = |e| = 1$) are used throughout):

$$
\hat{H} = \frac{1}{2m_1} \left( \hat{p}_1 + A(\hat{r}_1, t) \right)^2 + \frac{1}{2m_2} \left( \hat{p}_2 - A(\hat{r}_2, t) \right)^2 + v(\chi) + u(\vec{R}) \tag{2}
$$

where $\hat{p}_{1,2}$ are the momentum operators of particles 1 (electron, charge $q_1 = -1$) and 2 (nucleus, $q_2 = +1$), $\vec{A}(\vec{r}, t)$ is the transverse ($\vec{\nabla} \cdot \vec{A} = 0$) laboratory-space vector-potential, $v(\chi)$ is the interaction potential between the particles, and $u(\vec{R})$ is the c.m. trapping potential (in free space, $u = 0$). Finally, $\chi = \vec{r}_1 - \vec{r}_2$ and $\vec{R} = (m_1/M)\vec{r}_1 + (m_2/M)\vec{r}_2$, where $M = m_1 + m_2$.

For systems of interest here, $m_1 \ll m_2$. Introducing $\mu = m_1 m_2 / M$ and neglecting correction terms of the order $O(\mu/M)$ in the laser interaction, Eq. (2) simplifies to[40]:

$$
\hat{H}_{\text{CoM}} = \hat{H}_\chi + \hat{H}_R \tag{3}
$$

$$
\hat{H}_\chi = \frac{1}{2\mu} \left( \hat{p}_1 + A(\vec{R} + \chi, t) \right)^2 + v(\chi) \tag{4}
$$

$$
\hat{H}_R = \frac{1}{2M} \vec{p}_R^2 + u(\vec{R}) \tag{5}
$$

We have verified that the terms omitted in Eq. (3) do not affect the results reported below[41].

The appropriate choice of the trapping potential $u(\vec{R})$ in Eq. (5) and the shape of the initial c.m. wavepacket are the key ingredients of our treatment. The extent of the c.m. wavepacket should be on the order of the thermal de Broglie wavelength of the target gas. The trapping potential should not significantly disturb the targeted observables on the time scale of the simulation. We have verified that the parabolic trapping potential used presently satisfies these requirements[41].

The general-case treatment of Eq. (3), which contains a non-separable coupling term through $A(\vec{R} + \chi, t)$, remains a formidable numerical task. For the short (sub-picosecond) and moderately-intense IR fields, the c.m. displacements remain small compared to both the characteristic electron excursion and the laser-field wavelength. We therefore seek solutions of the time-dependent Schrödinger equation (TDSE) in the close-coupling form:

$$
\Psi(\chi, \vec{R}, t) = \sum_n \phi_n(\chi, t) \zeta_n(\vec{R}) \tag{6}
$$

(From now on, we will omit arguments of $\phi_n$, $\zeta_n$ and other spatially- and time-dependent quantities, as long as their choice is unambiguous.) In Eq. (6), functions $\zeta_n$ are orthonormalized, time-independent eigenfunctions of $\hat{H}_R$ (Eq. (5)) with eigenvalues $\epsilon_n$. We assume that the potential $u(\vec{R})$ in Eq. (5) is such that the set of the discrete solutions $\{\zeta_n\}$ is complete.

Substituting the Ansatz (6) into the TDSE for the Hamiltonian (3) and projecting on each $\zeta_m$ on the left, we obtain:

$$
i \frac{\partial}{\partial t}\phi_m = \left( \hat{h} + \epsilon_m \right) \phi_m + \sum_n \hat{h}_{mn} \phi_n. \tag{7}
$$

The explicit form of the one-electron operators $\hat{h}$ and $\hat{h}_{mn}$ is given by the Eqs. (S2)–(S5)[41].

The system of coupled PDEs (7) can be propagated in time at a cost comparable to that of a standard, fixed-nuclei electronic TDSE, provided that the number of the nuclear-coordinate channels is not excessive. At the end of the pulse, the expectation of a c.m. observable $\hat{O}$, conditional on the internal degree of freedom being described by a normalized wavefunction $\phi_a(\chi)$, is given by:

$$
\langle \hat{O} \rangle_a = \sum_{mn} \langle \zeta_m | \hat{O} | \zeta_n \rangle \langle \phi_m | \phi_a \rangle \langle \phi_a | \phi_n \rangle. \tag{8}
$$

Choosing $\hat{O} = \hat{p}_R$ and $\hat{O} = \hat{\chi}$ yields the expectation of the momentum and the state population, respectively. The c.m. velocity of the atom in an internal state $\phi_a$ is then:

$$
v_a = \frac{1}{M} \langle \hat{\vec{R}} \rangle_a. \tag{9}
$$

We emphasize that the quantity $v_a$ is determined from the expectation values calculated after the field vanishes. It does not depend on field gauge choice, and defines a physical observable.

We solve Eq. (7) for a 3-dimensional hydrogen atom ($\mu = 1$, $M = 1836$), initially in the $1s$ electronic ground state, exposed to a Gaussian pulse of beam waist $w_0 = 30236 \, a_0$, central frequency $\omega = 0.057$ ($\lambda \approx 799$ nm), and full-width-half-maximum $\tau_0 = 220$ ($\approx 5.32$ fs). We choose for each Cartesian direction the following convention: $x$–beam propagation, $y$–transverse, and $z$–polarization. For further details of the numerical parameters see[41].

In a spatially non-uniform laser field, the excited atoms acquire the velocity both in the forward and in the transverse directions. The final c.m. velocity along laser polarization remains negligible, as required by symmetry. We have verified numerically that the forward velocity is insensitive to moderate spatial-intensity gradients. As a result, we discuss the two components of the velocity independently.

The forward (propagation-direction) component of velocity is a consequence of the radiation pressure. Strong-field excitation between hydrogenic levels with the principal quantum numbers $n$ and $n'$ transfers the energy of
\[ \Delta E = 0.5(n^{-2} - n'^{-2}) \] from the laser field to the atom. The corresponding momentum transfer is \( \Delta E/c \), giving the forward velocity:

\[ \Delta v_f = \frac{\Delta E}{Mc}. \tag{10} \]

Because it is determined solely by the initial and the final internal state of the atom, it contains no information on the intervening dynamics. Our numerical results (See Figs. S1, S2[41]) are consistent with these expectations.

In the transverse direction the atoms are accelerated by the spatial gradient of the ponderomotive potential. Classically, the final outward velocity of an initially-stationary particle with dipole polarizability \( \alpha \) entering the field at time \( t_b \) in the vicinity of the beam waist (\( x = 0 \), Eq. (S12)) is given by[41]:

\[ \Delta v_t = \frac{\alpha}{4M} \int_{t_b}^{\infty} \frac{\partial}{\partial r} F_0^2(r,t) \, dt \tag{11} \]

where \( F_0(r,t) \) is the envelope of the laser electric field (see Eq. (S16)). The hydrogen ground state (\( \alpha_0 = 4.5 \)) is expected to be accelerated towards stronger fields (\( \frac{\partial}{\partial r} F_0^2 < 0 \)). Conversely, high-Rydberg states, which exhibit the free-electron-like dynamical polarizabilities in low-frequency fields (\( \alpha_f \approx -\omega^{-2} \approx -308 \) at 799 nm), are expected to move towards weaker fields.

A comparison of the calculated transverse velocity (Eq. (9)) with the classical Eq. (11) for a state a known polarizability allows us to infer \( t_b \) — the time this state has entered the field[41]. The integrand in Eq. (11) is negative, so that \( t_b \) is a monotonic function of \( \Delta v_t \) and defines a clock. Because \( \alpha_f \), the low-frequency dynamical polarizability of the Rydberg states, is a cycle-averaged quantity[41], the time resolution of this clock is \( \approx 1/2 \) of the laser-cycle duration (\( \approx 1.3 \) fs at 799 nm).

The composition of the Rydberg states populated by strong-field excitation is sensitively affected by channel closings[35, 38, 39]. We therefore expect a similar effect to arise in the c.m. velocity spectroscopy. At 799 nm, channel closings occur each 26 TW cm\(^{-2} \) (\( \Delta I_{\text{channel}} = 4\omega^3 \)). For a tightly-focused beam used presently (\( w_0 = 2\lambda \)), in the vicinity of the beam half-waist a channel closing occurs each 648 \( a_0 \), or \( \approx 34 \) nm. We consider the channel-closing effects by repeating the calculations at seven, equidistant transverse points spaced by 216 \( a_0 \), placed around the beam half-waist. We average the results equally among these points. This volume averaging effectively suppresses resonance contributions, which are highly sensitive to the intensity (See [41]).

The maximum gradient of the ponderomotive potential occurs in the focal plane, \( w_0/2 \) away from the focal spot. We choose the point displaced in the \( y \) direction, perpendicular to both the propagation and polarization directions. The volume-averaged numerical results at this point are illustrated in Fig. 1. The local peak intensity of the field is \( \approx 607 \) TW cm\(^{-2} \). The ionization is in the saturation regime, with \( \approx 9 \% \) of the population surviving in the 1s ground state after the pulse. Additionally, \( \approx 2.4 \% \) of the atoms are excited to Rydberg states with \( n \leq 6 \). Although our simulation volume does not allow an accurate determination of excitation probabilities for higher Rydberg states, we estimate that at least \( 2 \% \) of the atoms are left in Rydberg states with \( n \geq 7 \). Most of the excited states possess magnetic quantum number \( m = 0 \), same as the initial state.

For all electronic states in Fig. 1c other than the ground state, the final transverse velocities are in the range of 12–20 m s\(^{-1} \). Solving Eq. (11) for \( t_b \) yields the
excitation time. The results for the volume-averaged excitation time reconstruction are presented in Fig. 2. In all cases, excited states are formed within the laser cycle immediately preceding the peak of the envelope. Although the excitation clock defined by the Eq. (11) does not offer true sub-cycle resolution, it appears that the Rydberg states with low principal quantum numbers tend to be populated later in the laser pulse. This observation is consistent with the expectations of the frustrated tunneling model[33]: formation of the more compact, low-\(n\) states requires a tunnel exit point closer to the nucleus and consequently higher electric field, reached closer to the peak of the envelope.

We present further fixed-intensity results (Figs. S1–S3), and explore the effects of the carrier-envelope phase (CEP, Figs. S4, S5), pulse duration (Figs. S6, S7), and non-paraxial effects arising in a tightly-focused beam (Figs. S8, S9) in [41]. In all cases, we can successfully assign the preferred excitation times based on the volume-averaged c.m.-velocity spectra, confirming that the technique is universally applicable and experimentally realizable. With a few exceptions, the reconstructed excitation times are before the peak of the envelope, and tend to fall within the same laser cycle. For longer pulses (See Figs. S6,S7), the preferred excitation times shift to earlier times, before the peak of the envelope. They however remain clustered within one laser cycle.

Because the ponderomotive clock is not sub-cycle accurate, we cannot associate the time of the excitation with the specific phase of the field. It may be possible to improve the time resolution of the excitation clock using multi-color techniques, which have been successful for the reconstruction of the ionization and recollision times in high-harmonic spectroscopy[42, 43]. Another possibility involves breaking the symmetry of the interaction with a static, external magnetic field. Both possibilities are currently under investigation.

One remarkable result seen in Fig. 1c, which so far has not been commented upon, is the behavior of the 1s ground state. For the laser pulse in Fig. 1a, it is weak-field seeking, reaching the final outward velocity of \(\approx 3.2 \text{ m s}^{-1}\). The low-field-seeking behavior of the 1s state persists for other field parameters as well[41]. The final 1s velocity is insensitive to channel-closing effects, indicating that it arises due to adiabatic modification of the ground state, rather than transient population of high-Rydberg states.

For the initial 1s state, \(t_b \to -\infty\), and Eq. (11) yields the effective polarizability \(\alpha_{\text{eff}}\), shown as a function of the peak intensity of the laser pulse in Fig. 3. At intensities below 50 TW cm\(^{-2}\), the numerical accuracy is insufficient to determine the final c.m. velocity (Fig. S10 [41]). The effective polarizability is negative, as opposed to \(+4.5\) expected for 1s in a weak field. It is characteristic of entering the Kramers-Henneberger regime[19]. Observation of Kramers-Henneberger regime for an atomic ground state in strong, low-frequency fields has been long sought after, with no unambiguous detection thus far[19].

To summarize, we have developed a computationally-tractable quantum mechanical approach to correlations between c.m. motion and internal electronic dynamics in strong, non-uniform laser fields. Using the technique, we demonstrate that the final c.m. velocity is sensitive to the internal excitation dynamics. In particular the transverse, ponderomotive velocity is determined by the total time the excited state spends in the field. In the absence of resonances, it yields a measurement of the preferential time of excitation. This procedure is robust to limited volume averaging, and can be applied for different CEP values, for longer pulses, and for non-paraxial beams. Finally, we demonstrate an unambiguous signature of the atomic ground state entering the Kramers-Henneberger regime in strong, low-frequency fields, which has been
long sought-for. Taken together, our results suggest that c.m.-velocity spectroscopy is a powerful, and so far overlooked tool for understanding strong-field bound-state electronic dynamics on their natural timescale.

We expect that similar ideas, using a collective, nearly-classical degrees of freedom of a quantum system as an intrinsic measurement device may become useful in other contexts as well.

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SUPPLEMENTAL MATERIAL

Choice of the trapping potential and the c.m. wavepacket

Unless noted otherwise, we apply the parabolic trapping potential \( u(R) = kR^2/2 \) with \( k = 10^{-4} \). We include four c.m. eigenstates: the initially-populated ground state and the three singly-excited harmonic vibrational modes, one along each Cartesian direction. For this choice of the force constant \( k \), the free-oscillation period in the parabolic trap is \( \approx 650 \text{ fs} \), much longer than any of the pulses considered in the simulations. For simulations discussed below and in the main text, electronic populations associated with the excited c.m. states do not exceed \( 7 \times 10^{-3} \). The populations of the higher trap modes are therefore expected to be \( < 10^{-4} < (7 \times 10^{-3})^2 \) and can be safely neglected for our purposes.

The spatial extent (the full width at the half-maximum) of the initial Gaussian wavepacket in \( \approx 2.6a_0 \). This value should be compared to the thermal de Broglie wavelength of the target gas \( \Lambda \):

\[
\Lambda = \left( \frac{2\pi}{MKT} \right)^{1/2}.
\]

For a hydrogen atom \( (M \approx 1837) \), \( \Lambda = 2.6 \) corresponds to the target gas temperature of \( \approx 160 \text{ K} \). This value is consistent with the target expectation for an effusive source.

We have repeated some of the simulations using a modified trap with \( k' = 3k = 3 \times 10^{-4} \). This choice decreases the final populations of the excited c.m. modes by a factor of \( \sqrt{k'/k} = 1/\sqrt{3} \). The final, state-resolved c.m. velocities remain numerically unchanged, confirming that the trap does not significantly influence the c.m. dynamics on the time scale of the simulation.

Explicit form of the Eq. (7)

Our working equations are given by Eq. (7) of the main text:

\[
\frac{i}{\hbar} \frac{\partial}{\partial t} \phi_m = \left( \hat{h} + \epsilon_m \right) \phi_m + \sum_n \hat{h}_{mn} \phi_n
\]

The operators \( \hat{h} \) and \( \hat{h}_{mn} \) are given by:

\[
\hat{h} = \frac{1}{2\mu} \hat{p}_x^2 + v + \frac{1}{\mu} \hat{A} \cdot \hat{p}_x + \frac{1}{2\mu} A^2
\]

\[
\hat{h}_{mn} = \eta_{mn} \cdot \hat{p}_x + \kappa_{mn}
\]

\[
\eta_{mn} = \frac{1}{\mu} \sum_{b=x,y,z} \bar{A}^{(b)} \langle \zeta_m | R_b | \zeta_n \rangle
\]

\[
\kappa_{mn} = \frac{1}{\mu} \sum_{b=x,y,z} \left( \frac{\partial}{\partial \zeta_b} A^2 \right) \langle \zeta_m | R_b | \zeta_n \rangle + \frac{1}{\mu} \sum_{b=x,y,z} \bar{A}^{(b)} \cdot \bar{A}^{(c)} \langle \zeta_m | R_b R_c | \zeta_n \rangle.
\]

In Eqs. (S2)–(S5), \( \bar{A} \) and \( \bar{A}^{(b)} \) are functions of the inter-particle distance \( \zeta \) and time \( t \). We further assume that the higher-order terms in the Taylor expansion for the c.m. coordinate:

\[
\bar{A}(\bar{R} + \chi, t) = \bar{A}(\chi, t) + \sum_{a=x,y,z} \bar{A}^{(a)}(\chi, t) R_a + \ldots
\]

can be neglected. This assumption is valid for non-relativistic IR fields and short pulse durations, where nuclear displacements remain small compared to the laser wavelength.

Treatment for the general masses and charges

The minimal-coupling non-relativistic Hamiltonian for two particles is given by:

\[
\hat{H} = \frac{1}{2m_1} \left( \hat{p}_1 - q_1 \bar{A}(\bar{r}_1, t) \right)^2 + \frac{1}{2m_2} \left( \hat{p}_2 - q_2 \bar{A}(\bar{r}_2, t) \right)^2 + v(\chi) + u(\bar{R})
\]

where \( m_i \), \( q_i \), and \( \hat{p}_i \), \( i = 1, 2 \) are respectively the mass, charge, and momentum operator for particles 1 and 2. Using the standard c.m. variable substitution (see the main text), we obtain, for the transverse field \( \bar{A} \):

\[
\hat{H} = \frac{1}{2\mu} \hat{p}_x^2 - \left( \frac{1}{m_1} \bar{A}_1 - \frac{1}{m_2} \bar{A}_2 \right) \cdot \hat{p}_x + \frac{1}{2m_1} \bar{A}_1^2 + \frac{1}{2m_2} \bar{A}_2^2 + v(\chi) + \frac{1}{2M} \hat{p}_R^2 - \frac{1}{M} \left( \bar{A}_1 + \bar{A}_2 \right) \cdot \hat{p}_R + u(\bar{R}) - \frac{1}{\mu} R_a (\bar{A}^{(a)}_1 + \bar{A}^{(a)}_2) \cdot \hat{p}_x
\]
\[-R_a \left( \frac{1}{m_2} \vec{A}_1^{(a)} - \frac{1}{m_1} \vec{A}_2^{(a)} \right) \cdot \hat{p}_R + \frac{1}{\mu} R_a \left( \vec{A}_1 \cdot \vec{A}_1^{(a)} - \vec{A}_2 \cdot \vec{A}_2^{(a)} \right) + \frac{1}{2 \mu} R_a R_b \left( \frac{M}{m_2} \vec{A}_1^{(a)} \cdot \vec{A}_1^{(b)} + \frac{M}{m_1} \vec{A}_2^{(b)} \cdot \vec{A}_2^{(a)} \right) \] (S8)

where summation over indices \(a\) and \(b\) is implied, and quantities \(\vec{A}_i\) and \(\vec{A}_i^{(a)}\) \((i = 1, 2; a = x, y, z)\) are given by:

\[
\vec{A}_1(\chi) = q_1 \vec{A}^{m_2} \left( \frac{m_2}{M} \chi \right)
\]
(S9)

\[
\vec{A}_2(\chi) = q_2 \vec{A}^{m_1} \left( -\frac{m_1}{M} \chi \right)
\] (S10)

\[
\vec{A}_i^{(a)}(\chi) = \frac{\partial}{\partial x_a} \vec{A}_i(\chi).
\] (S11)

In deriving Eq. (S8) we assumed that \(\vec{R}\) is small compared to the laser wavelength, so that the higher-order terms can be neglected in Eq. (S6).

Equation (S8) has been implemented numerically within the Ansatz of the Eq. (6), and is propagated numerically for the same grids and trap parameters as the Eq. (7) in the main text. The propagation cost is \(\approx 5\times\) that of Eq. (7). For atomic hydrogen, the results on the scale of the graphs shown in the main text and the supplementary material are indistinguishable from those of the approximate Eq. (7).

Discretization and numerical integration

The electronic wavefunction is discretized on a uniform, Cartesian-product grid extending to \(\pm 78.6 \ a_0\) in the \(X\) and \(Y\) directions, and to \(\pm 152.1 \ a_0\) along \(Z\) (the laser polarization direction). Uniform grid spacing is 0.35 \(a_0\). A transmission-free absorbing boundary[1] is applied starting 9.4 \(a_0\) from all grid edges.

Eqs. (7) are integrated using the leap-frog propagator with the time step of 0.005. Using the 4th-order Runge-Kutta propagator leads to numerically equivalent results. We analyze the results by projecting the final wavefunctions onto hydrogenic states (Eq. (8)). Our simulation volume is sufficient to resolve Rydberg states up to the principal quantum number \(n = 6\). We verified that a further increase in the simulation volume does not affect these results.

Beam profile

The laser beam propagates toward the positive \(X\) direction. We model the vector-potential of the beam by a paraxial \(\text{TEM}_{00}\) mode, including the lowest-order longitudinal correction[2]:

\[
A_Z = A_0 f \left( t - \frac{x}{c} \right) R \left[ \left( 1 - \frac{iz}{z_R} \right)^{-1} e^\Phi \right]
\] (S12)

\[
\Phi = -\frac{ikx}{v} + i\omega t + i\varphi_0 - \frac{r^2}{w_0^2} \left( 1 - \frac{iz}{z_R} \right)^{-1}
\] (S14)

where the beam waist \(w_0 = 30236 \ a_0\), Rayleigh range \(z_R = \pi w_0/\lambda\), \(\lambda = 2\pi c/\omega\) is the wavelength, \(k = 2\pi/\lambda\) is the wavevector, and \(c \approx 137\) is the speed of light. Unless noted otherwise, the slowly-varying envelope \(f(t - x/c)\) is a truncated Gaussian[3] with the FWHM of 220 \(\approx 5.32\) fs and baseline duration of 800 \(\approx 19.4\) fs. The carrier frequency \(\omega = 0.057\), corresponding to \(\lambda \approx 799\) nm. The peak vector-potential at the focal-spot center is 2.9615, corresponding to a peak field intensity of \(\approx 1\) PW cm\(^{-2}\).

In the vicinity of the beam waist \((x = 0)\), the transverse component of the vector-potential becomes:

\[
A_x \approx \frac{F_0}{\omega} \cos (\omega t - kx + \varphi_0),
\] (S15)

where

\[
F_0 = \omega A_0 f \left( t - \frac{x}{c} \right) e^{-r^2/w_0^2}.
\] (S16)

For a slowly-varying envelope \(f\), the laser electric field is given by:

\[
F_z = -\frac{\partial}{\partial t} A_z \approx F_0 \sin (\omega t - kx + \varphi_0)
\] (S17)

All numerical calculations reported in the main text and below used the full vector-potential expressions (Eqs. (S12)-(S14)). The envelope approximation of Eq. (S16) is however extremely useful for the classical interpretation of the results (See Eq. (11) in the main text and its derivation below).

Derivation of the Eq. (11)

Let us consider the motion of a classical particle with charge \(Q\), mass \(M\), and dipole polarizability \(\alpha_0\). The particle enters the field of a laser pulse at the time \(t_b\), at the position \(\bar{r}_b\), with the velocity \(\bar{v}_b\). We assume that the displacement of the particle remains small compared to the wavelength of the laser field and to the characteristic scale of spatial inhomogeneity. Under these assumptions we can treat the spatial variation of the laser field as a perturbation to the motion in the uniform field.

Newton’s equation of motion for the particle in a uniform field \(F(t)\) are given by:

\[
\ddot{\bar{r}} = \frac{Q}{M} F(t)
\] (S18)

Integrating over the time, we obtain:

\[
\bar{r} = \bar{v}_b + \frac{Q}{M} \int_{t_b}^{t} F(t') \, dt'
\]
\[
\dot{\mathbf{r}} = \mathbf{v}_b + \frac{Q}{M} \tilde{A}(t_b) - \frac{Q}{M} \int_{t_b}^{t} \mathbf{A}(t') \, dt'.
\] (S22)

The total energy \( E \) of the particle is then given by:

\[
E = E_0 - \frac{\alpha_0}{2} \mathbf{F}^2 + \frac{M \pi^2}{2} - \frac{Q^2}{2M} \tilde{A}^2 - Q \mathbf{\pi} \cdot \mathbf{\tilde{A}}.
\] (S23)

In the slowly-varying envelope approximation (cf. Eqs. (S15),(S17)),

\[
\tilde{A} \approx \frac{1}{\omega} \mathbf{F}_0(r,t) \Re \mathbf{e}^{i(\omega t - \mathbf{r} \cdot \mathbf{\phi}_0)}
\] (S24)

\[
\mathbf{F} \approx \mathbf{F}_0(r,t) \Im \mathbf{e}^{i(\omega t - \mathbf{r} \cdot \mathbf{\phi}_0)}
\] (S25)

where the envelope \( \mathbf{F}_0(r,t) \) is a slowly-varying function of both arguments (we omit \( \mathbf{F}_0 \) arguments from now on). Replacing all rapidly-oscillating quantities in Eq. (S23) by their carrier-cycle averages, we then obtain:

\[
\langle E \rangle = E_0 + \frac{M}{2} \pi^2 - \frac{\alpha_0}{4} F_0^2 + \frac{Q^2}{4M\omega^2} F_0^2,
\] (S26)

where \( E_0 \) is the energy of the particle in the absence of the field.

For a weakly-inhomogeneous field envelope \( F_0 \), the additional momentum imparted on the particle is given by the perturbation-theory expression:

\[
\Delta \mathbf{p} = -\int_{t_b}^{t} \frac{\partial}{\partial \mathbf{r}} \langle E \rangle \, dt
\]

\[
= \frac{\alpha}{4} \int_{t_b}^{t} \frac{\partial}{\partial \mathbf{r}^2} F_0^2 \, dt,
\] (S27)

where

\[
\alpha = \alpha_0 - \frac{Q^2}{M \omega^2}
\] (S28)

For states which remain bound after the end of the pulse, the drift velocity of the electron \( \dot{\mathbf{r}} \approx 0 \), and the entire momentum \( \Delta \mathbf{p} \) is transferred to the center of mass of the atom. Dividing \( \Delta \mathbf{p} \) of the Eq. (S27) by the total mass \( M \) we therefore obtain Eq. (11) of the main text.

From the cycle-average derivation above, it is clear that Eq. (11) does not provide sub-cycle resolution for \( t_b \). Rather, the clock defined by Eq. (11) corresponds to the time under the pulse envelope.

Substituting the specific envelope (S16) used in our numerical simulations into Eq. 11, and limiting the consideration to the beam-waist plane, we obtain:

\[
\Delta v_t = -\frac{\alpha}{4M} \mathbf{A}_0^2 \tau_0 r \sqrt{\frac{\pi}{\ln 2}} \mathbf{e}^{-2r^2/\mathbf{w}_0^2} \operatorname{erfc}\left(2\sqrt{\ln 2} \frac{t_b}{\tau_0}\right)
\] (S29)

where \( \tau_0 \) is the FWHM duration of the laser pulse. Eq. S29 is a monotonous function of \( t_b \). Solving it for \( t_b \) with \( \alpha = -\omega^2 \) yields the desired envelope clock.

### Additional results

We begin by briefly examining the dynamics of a hydrogen atom at the center of the focal spot (Fig. S1), where the laser field remains essentially a planewave. At the 1 PW cm\(^{-2}\) local peak intensity, ionization is in the saturation regime. Only 0.6% of the hydrogen atoms remain in the 1s ground state. Additionally, approximately 1.3% of the atoms are excited to Rydberg states with \( n \leq 6 \). We further estimate that at least 2% of the atoms are left in Rydberg states with \( n \geq 7 \). Most of the excited states possess magnetic quantum number \( m = 0 \), same as the initial state. Due to their low population, we do not consider \( m \neq 0 \) states any further. The individual excitation probabilities and final c.m. velocities are collected in Fig. S1. These results are qualitatively similar to those at the half-waist position, discussed below and in the main text.

The final populations of the \( m = 0 \) states are illustrated in Fig. S1b. The corresponding c.m. velocities in the propagation direction are shown in Fig. S1c. We find that the calculated velocities become erratic for very low final populations, which amplify the inevitable numerical noise in the solutions (see Eq. (9)). As a result, we choose to disregard the calculated c.m. velocities when the corresponding solutions diverge below \( 5 \times 10^{-5} \) (e.g. for the 6s state in Fig. S1c). The net number of photons absorbed from the laser field is zero for the 1s ground state, which consequently acquires no forward velocity. For all other states in Fig. S1c, the final forward velocity is in the range of 2.8 m s\(^{-1}\) (2s) to 4.6 m s\(^{-1}\) (6h).

These values are consistent with the momentum transfer due to the radiation pressure (Eq. (10)), and carry no information on the internal dynamics of the system.
We now turn to positions away from the center of the focal spot, where the laser field is no longer well-approximated by a plane wave. As discussed in the main text, the maximum of the spatial gradient of the ponderomotive potential is found on a ring of the radius $w_0/2$ around the focal spot, normal to the beam propagation direction. We begin by choosing the point displaced in the $y$ direction, perpendicular to both the propagation and polarization directions. The non-paraxial corrections of Eq. (S13) vanish in the vicinity of this point. The local peak intensity of the field is $\approx 607 \text{ TW cm}^{-2}$. The ionization remains in the saturation regime, with $\approx 10\%$ of the population surviving in the ground state after the pulse. The numerical results at this point are illustrated in Fig. S2. The final populations of the Rydberg states are of a similar overall magnitude to those found at the beam center, with $\approx 1.4\%$ left in Rydberg states with $n \leq 6$, and $\geq 3\%$ in states with $n \geq 7$.

The forward velocities at the half-waist position (Fig S2c) follow a trend similar to the beam center, and are consistent with the radiation-pressure effects. The forward velocity is insensitive to the small transverse velocity (Fig S2d) follows a trend similar to the beam center, and is consistent with the radiation-pressure effects. The forward velocity is insensitive to the small transverse velocity.
verse intensity gradient. Repeating the calculation with a planewave field at the 607 TW cm\(^{-2}\) peak intensity yields results visually identical to Fig. S2c.

From Eq. (11), we expect the transverse, ponderomotive acceleration to yield the maximum velocity when a Rydberg state is formed early within the laser pulse \((t_b \to -\infty)\). This sets the upper bound on the final transverse velocity a state with \(\alpha = \alpha_f \approx -308\) could reach. For the field parameters in Fig. S2, the limit is 24.6 m s\(^{-1}\), indicated by the dotted line in panel (d). This limit is exceeded by the 3p and 5d states, indicating that the magnitude of their effective polarizability exceeds the free-electron value. In the case of the 3p state, which reaches the final transverse velocity of 41 m s\(^{-1}\), we speculate that the likely reason is a 1-photon resonance with the Stark-shifted 2s state (1.9 eV away in the absence of the field). The resonance depleted the 2s state (final population of 1.9\times10^{-5}, while simultaneously increasing the effective polarizability and the acceleration of the 3p state. Because strong-field resonances are highly-sensitive to the local peak intensity, we anticipate such resonances to be washed out by the spatial averaging (see below and in the main text).

We can now invert Eq. (11) to extract the time estimate \(t_b\). We assume that the frequency-dependent polarizability of the final state is \(\alpha_f = -\omega_0^{-2} (\approx -308)\). Away from resonances, this estimation becomes progressively more accurate for higher Rydberg states. The resulting excitation-time reconstruction is shown in Fig. S3.

In the volume-averaged simulation (Fig. 1 of the main text), \(t_b\) can be consistently assigned for all final states. Because suppression of resonances appears to be important for a successful reconstruction of the excitation time, all subsequent results use volume-averaging protocol similar to that in Fig. 1 (\(\pm 648 a_0\) along the maximum intensity-gradient direction, covering \(\pm 2\) channel closings).

![Figure S3](image_url)

**FIG. S3.** (Color online) Reconstructed excitation times for the c.m. velocity spectra in Fig. S2 (see text). No excitation times can be assigned for the 3p, 5s, 5d, and 6p states, which are affected by resonances, or for the 1s ground state. The solid line is the vector-potential from Fig. S2. Note that the nominal resolution of the envelope clock (Eq. (11)) is \(\approx 1/2\) of the carrier cycle (\(\approx 1.3\) fs).

![Figure S4](image_url)

**FIG. S4.** (Color online) Same as Fig. 1, but for the vector-potential CEP of \(\pi/2\). The results are an equally-weighted average over the initial positions are within \(\pm 648 a_0\) of the beam half-waist position along \(y\). Also see captions of Figs. 1 and S2. See Fig. S5 for the detailed reconstruction of the excitation times (blue dots on the time axis, panel a).

![Figure S5](image_url)

**FIG. S5.** (Color online) Reconstructed excitation times for the data in Fig. S4. Also see Fig. 2 caption.

Up to now, we have considered a short, 2-cycle pulse with cosine CEP for the vector-potential. It is important to establish that the reconstruction is applicable to other
pulse phases, longer pulses, and for the more realistic, non-paraxial tightly-focused beam models. The results for the pulse with sine vector-potential CEP phase (all other parameters remain the same as is Fig. 1) are shown in Fig. S4. This pulse leaves \( \approx 9.5\% \) of the atoms in the 1s ground state, \( \approx 2.5\% \) in Rydberg states with \( n \leq 6 \), and at least 2.5% in higher Rydberg states. The final transverse velocity of the 1s ground state is \( \approx 3.3 \text{ m s}^{-1} \). The reconstructed excitation times are shown in Fig. S5. These results are qualitatively similar to Figs. 1, 2 of the main text: The excitation is confined to the single laser cycle, immediately preceding the peak of the laser field. The low-\( n \) states tend to be formed later within the cycle, although the apparent preference is weaker than for the zero CEP (Fig. 2).

The results for the 440 (\( \approx 10.64 \text{ fs} \)) FWHM, cosine CEP pulse (all other parameters same as in Fig. 1) are shown in Fig. S6. The longer pulse leads to a stronger depletion, with only 0.8% of the atoms surviving in the 1s ground state. The fraction of the Rydberg states remains essentially unchanged, with 1.2% of the atoms remaining in \( m = 0 \) states with \( n \leq 6 \), and at least 1.3% in higher states. Due to the longer pulse duration, the ground state now reaches the higher transverse velocity of \( \approx 5.2 \text{ m s}^{-1} \), 11% of the free electron limit (49.1 m s\(^{-1}\)). Our analysis still concentrates on the \( m = 0 \) states, which dominate the \( n \leq 6 \) population. The reconstructed excitation times are shown in Fig. S7. These values follow the same pattern as before, with the excitation preferentially occurring within a single laser cycle. In contrast to the results seen with the shorter, 2-cycle pulses, the excitation occurs earlier, approximately one cycle before the peak of the envelope is reached. The preference for the late formation of the low-\( n \) states is now essentially absent.

Our final test case uses the same pulse and beam parameters as Fig. 1, but considers an initial position displaced along the field polarization direction \( z \). For this geometry, the non-paraxial contributions to the vector-potential become significant (see Eq. S13 and red dashed line in Fig. S8a). Again, the numerical results are averaged along a \( \pm 648 a_0 \) line in the maximum intensity-gradient direction (\( z \)). The ground-state survival probability is unchanged at 9%, compared to Fig. 1. The excitation probabilities remain similar, at \( \approx 1.8\% \) for \( n \leq 6 \) and at least 1.7% for higher Rydberg states with \( m = 0 \). At the same time, the laser field now has a non-paraxial component in the propagation direction, which enables efficient excitation of \( m \neq 0 \) states. The transverse velocity of the 1s ground state remains unchanged at \( \approx 3.2 \text{ m s}^{-1} \). Finally, the reconstructed excitation times, shown in Fig. S9, follow the same pattern as before. It therefore appears that the non-paraxial effects do not play a significant role for our field parameters.
FIG. S8. (Color online) Same as Fig. 1, but for the initial position displaced along the laser polarization (z) direction (0, 0, 0). Non-paraxial effects are no longer negligible for this beam position, see Eq. (S13). (a) Vector-potential in the along the polarization (green solid line) and propagation (red dashed line) directions. Also see caption of Figs. 1 and S2, and Fig. S9 for reconstructed excitation times.

FIG. S9. (Color online) Reconstructed excitation times for the data in Fig. S8. Also see Fig. 2 caption.

FIG. S10. (Color online) Final outward transverse velocity for the hydrogen 1s ground state as a function of the peak intensity at the center of the beam. Pulse parameters and the initial conditions are given in the Fig. 3 caption.
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