

Correlation-induced phase shifts and time delays in resonance-enhanced high-harmonic generation

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We investigate resonance-enhanced high-harmonic generation (rHHG) in Cr^+ by comparing a one-dimensional (1D) shape-resonant model, time-dependent density functional theory (TDDFT), and independent particle approximation (IPA) simulations. Previous studies linked rHHG to the $3p \rightarrow 3d$ giant resonance, suggesting a modified four-step model where recolliding electrons are first captured in the autoionization state before recombining into the ground state, potentially leading to an emission delay associated with the resonance lifetime. While both the 1D model and TDDFT reproduce experimental spectra, TDDFT reveals that rHHG counterintuitively originates from spin-down $3p$ states, while spin-up $3d$ electrons negligibly contribute. The IPA fails to reproduce rHHG, highlighting the significance of electron correlations. Furthermore, TDDFT revealed a correlation-induced ~ 480 as time delay, accompanied by a strong phase shift across the resonance, potentially explaining earlier reconstruction of attosecond beating by interference of two-photon transitions measurements. Our work sheds light on long-standing open questions in rHHG and should advance ultrafast spectroscopies of electron correlations and resonances.

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I. INTRODUCTION

High-harmonic generation (HHG) is a fundamental process in strong-field physics, enabling generation of coherent extreme ultraviolet and soft x-ray radiation [1–5]. It presents a powerful tool for probing ultrafast electron dynamics and structural properties of matter across phases [6–21]. In gases, HHG is well described by the three-step model [22,23] whereby an electron (1) tunnel ionizes, (2) is accelerated by the laser, and (3) recombines with the parent ion, emitting a photon. The coherence of the electronic wave function throughout this process is key toward utilizing HHG for ultrafast spectroscopy, as has been demonstrated for charge migration [16,24], molecular symmetry and orientation [25–33], and more.

One known gas-phase system that deviates from this three-step model picture is transition-metal ions. Experimentally, HHG from laser-ablated plasma is known to lead to a significant resonant enhancement of a single harmonic order [34–36]. Resonant HHG (rHHG) has been established to originate at the single-atom level, with macroscopic effects playing a negligible role [36]. The energy of the enhanced harmonic photon aligns with a transition to an autoioniza-

tion state (AIS) in the cation, related to the $3p \rightarrow 3d$ giant resonance. Briefly, this autoionization transition involves the excitation of a $3p$ core electron to an unoccupied $3d$ subshell [37–39], after which the resulting highly excited state (e.g., $3p^5 3d^{n+1}$) is unstable and decays via autoionization, typically filling the $3p$ hole and emitting an outer electron (e.g., $3p^6 3d^{n-1} + \epsilon l$). Resonances in photoionization spectra and resonant photoionization have been the subject of extensive study [40]. For Cr^+ , the ground-state configuration is $3p^6 3d^5(^6S)$ in LS coupling notation, corresponding to a half-filled $3d$ subshell with five spin-up electrons. This configuration breaks symmetry between spin-up/down electrons due to an exchange interaction. The dominant excitation is still the $3p \rightarrow 3d$ transition, i.e., $\text{Cr}^+ 3p^6 3d^5(^6S) + \gamma \rightarrow \text{Cr}^+ 3p^5(^2P)3d^6(^5D)(^6P)$ followed by autoionization into $\text{Cr}^{2+} 3p^6 3d^4(^5D) + \epsilon l$ with $l = 3$ being the dominant channel [37–39].

To account for enhancement in rHHG in the presence of multiphoton transitions, an extended semiclassical single-active electron (SAE) four-step model was suggested [41]. It replaces the recombination step of the three-step model with electron capture in the AIS, followed by a transition to the ground state and photon emission.

Alternatively, one can describe rHHG numerically with methods falling into two categories: (1) SAE models where the AIS is approximated by a resonance in a barrier-well potential, forming a metastable state (MS) [41–44]. These models qualitatively reproduce the measured enhancement, but do so by synthetically fitting the transition energies. It remains unclear to what extent the SAE approximation captures the full dynamics of rHHG and if any time delay or phase shift is inflicted on the resonant photon. Approach (2) is to perform

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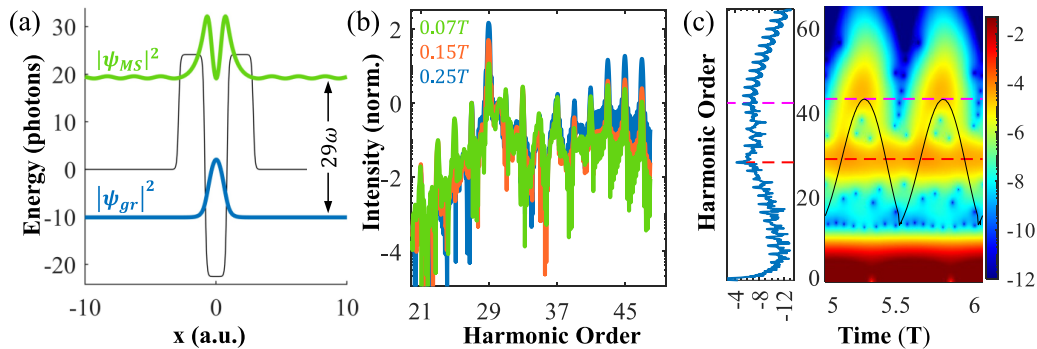


FIG. 1. rHHG from the 1D model. (a) Potential supporting a shape resonance (MS, black). The ground state (blue) and MS (green) densities are plotted in their respective eigenenergies. The vertical axis (energy) is normalized to the driving photon energy. (b) HHG spectra for different barrier widths/MS lifetimes. Curves are normalized to the 27th harmonic. The enhancement coefficient increases with the MS lifetime. (c) (Right) Gabor transform of HHG emission for an MS lifetime of $0.17T$ (T is the period of the driving laser). Red, purple, and black curves indicate the resonant harmonic energy, the semiclassical cutoff energy, and semiclassical emission times (trajectories), respectively. (Left) Corresponding spectrum. The enhancement of the resonant harmonic H29 is evident in both the spectrum and the Gabor transform. The harmonic emission times are in strong agreement with the semiclassical model.

ab initio simulations of rHHG using either time-dependent density functional theory (TDDFT) [45,46] or multiconfiguration time-dependent approaches [47,48]. These schemes lead to spectra in agreement with experiments without the need of external parameters, but are more difficult to analyze and extract the physical mechanism. Still, with *ab initio* schemes it was established that in some systems correlations play a dominant role in enabling resonant emission [45], and that deeper orbitals often play a crucial role in dynamics [47]. What remains unclear is how these effects transpire, and how they depend on the electronic spin in magnetic ions such as Cr^+ . In particular, the phase and time delay of rHHG have not yet been explored with multielectron theories (only with model semianalytic approaches [42]).

We perform here an extensive theoretical analysis of rHHG from magnetic Cr^+ employing three complementary levels of theory: (1) a shape-resonant SAE model; (2) *ab initio* spin-TDDFT simulations; and (3) simulations on par with the spin-TDDFT but where electron correlations are artificially frozen, denoted as the independent particle approximation (IPA). This comparison allows pinpointing the mechanism of rHHG—A low-lying $3d$ electron is tunnel ionized and gains high kinetic energy in the laser field. When it recollides with the parent ion, it promotes a deep-level $3p$ electron via electron-electron interactions into empty d bands, forming the autoionization state, from which an enhanced rHHG photon is emitted. We show that this transition, which does not occur in uncorrelated theories, inflicts a time delay and phase shift onto the rHHG emission, suggesting correlated corrections to the four-step model. Importantly, this transition is only facilitated by spin-down electrons that can pass through the empty d bands. Our results shed light onto fundamental rHHG physics and could lead to HHG spectroscopy of attosecond correlated multielectron systems.

II. METHODS

Let us briefly describe our numerical approach and examined setup. First, we explore HHG and corresponding

time-frequency plots from a one-dimensional (1D) SAE model that includes a shape resonance matching the experimental resonant transition (all numerical details are delegated to the Appendix). The results in Fig. 1 show a good agreement with experimental rHHG spectra from Cr^+ [36,49]. We examine the behavior of resonant H29 for different resonance lifetimes [Fig. 1(b)], especially quantifying its enhancement factor, defined as $\frac{I_{29}}{I_{27}}$. In doing so, we hope to resolve whether a recollision picture is valid in rHHG in the SAE case. While the overall harmonic yield decreases with increasing lifetime (see Supplemental Material [50]), the enhancement factor increases. This is consistent with a recollision-based picture, since the increase in lifetime is achieved by widening the barrier, thereby decreasing the tunneling rate. To further investigate this interpretation, we gradually extended the complex absorbing potential (CAP) inward from the box boundary toward its center. As the CAP approached the semiclassical long trajectories, these progressively disappeared from the time-frequency plots (Fig. S2 of Supplemental Material [50]), while short trajectories were unaffected. By extending the CAP inward, the harmonic yields reduce, including H29, further supporting the recollision mechanism for rHHG.

III. RESULTS

Time-frequency analysis for an exemplary case is shown in Fig. 1(c). The semiclassical trajectories match the quantum SAE simulations with high accuracy—there is no distinguishable time delay for the resonant H29. We note that according to the four-step model, H29 is emitted after the electron is captured in the AIS; therefore, some delay is anticipated, though we could not resolve it in our conditions.

Next, we employ an *ab initio* TDDFT scheme (for details, see the Appendix). Figure 2 shows HHG spectra and time-frequency analysis under similar conditions to Fig. 1 separated to spin-up/down channels [Figs. 2(c) and 2(d)], and the total spin-summed response [Fig. 2(b)]. While both channels contribute to the resonance emission, the spin-down channel response is about an order of magnitude larger than the spin-

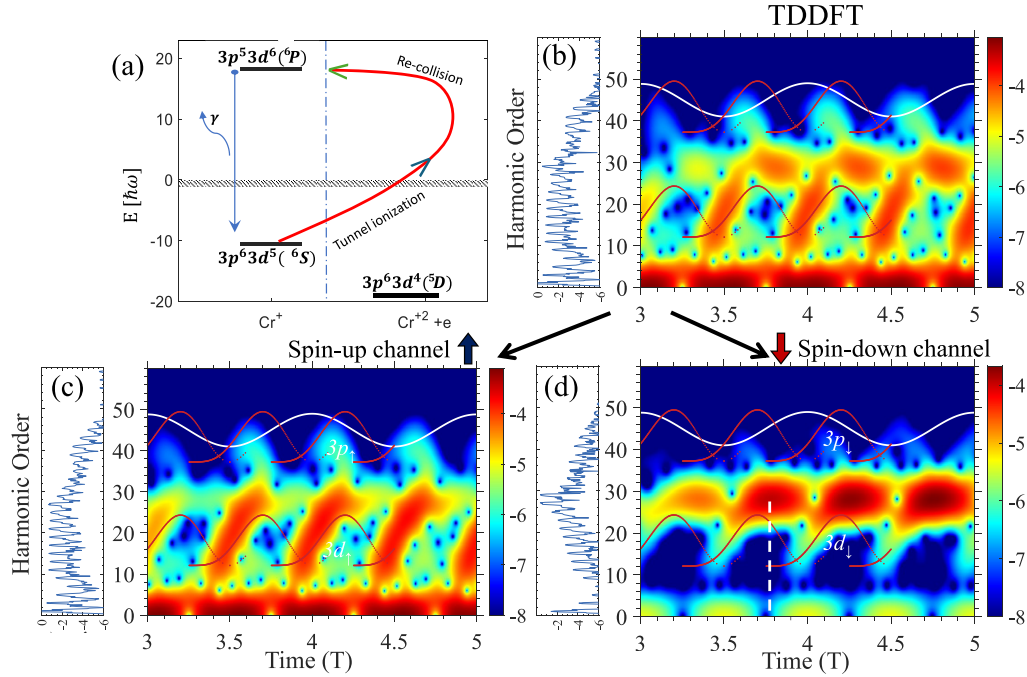


FIG. 2. rHHG with TDDFT. (a) Energy level configuration in Cr^+ . (b) (Right) Gabor transform of total calculated HHG emission. (Left) Corresponding HHG spectrum. Top and bottom red curves denote the emission time and energy according to the classical trajectories of the three-step model (low-energy curves are associated with $3d$ electrons and high-energy curves are associated with $3p$ electrons). White lines illustrate the driving field. (c) Same as panel (a) but for spin-up response, roughly following the semiclassical model for $3d$ electrons. (d) Same as panel (c) but for spin-down response, where $3p$ spin-down states dominate rHHG [see color scales in panels (c) and (d)], which is delayed by ~ 480 as relative to spin-up response.

up, dominating rHHG. This is counterintuitive if considering the typical physical mechanism of atomic HHG and the energy level diagram in Fig. 2(b)—The spin-up channel includes initially occupied $3d$ states that have a much lower ionization potential compared to the $3p$ levels. *A priori*, this should make their tunnel ionization and recombination exponentially more efficient. However, the fact that $3p$ spin-down states dominate the resonant response indicates that they become intrinsically linked to the AIS through interaction with the laser. In these calculations, the long trajectories are slightly suppressed compared to the 1D case, as is common in *ab initio* theory [51] due to the three-dimensional (3D) nature of the simulation.

Another surprising feature can be seen in the time-frequency plots in Fig. 2. First, we notice that the HHG emission time in the spin-up channel largely follows the semiclassical trajectories with ionization potential matching the $3d$ levels. This is expected since the $3d$ spin-up subshell is initially occupied and its ionization energy is much lower than the ionization energy of the $3p$ electrons. The most striking feature is that the HHG emission from the spin-down channel also largely follows the classical trajectories initiated from $3d$ electrons, even though the $3d$ states are not initially occupied by spin-down electrons. This is a direct indication that rHHG induces a $3p \rightarrow 3d$ transition, while this channel is blocked for the $3p$ spin-up electrons as the $3d$ spin-up bands are fully occupied.

Another prominent feature of the *ab initio* spectra is that the timing of the resonance emission is shifted from the expected long/short trajectories. From Fig. 2(c), the resonant emission time in the spin-up channel follows roughly the

typical long/short HHG semiclassical trajectories (as in the 1D model). However, in the more dominant spin-down channel, the resonance emission is delayed by $\sim 0.18T \approx 480$ as. This result contradicts that from our 1D SAE model, suggesting an electronic interaction and spin-selective mechanism by which AIS resonances enhance HHG. Interestingly, the resonant emission yield builds up as the simulation progresses, while this buildup is absent in the nonresonant harmonics and in the spin-up channel, suggesting that population of the AIS is playing a key role. A possible mechanism for this is given by the four-step model in which a $3d$ electron first tunnels out ($\text{Cr}^+ 3p^6 3d^5(^6S) \rightarrow \text{Cr}^{2+} 3p^6 3d^4(^5D) + e$), gains kinetic energy in the laser field, and recollides with Cr^{+2} to excite a partial $3p$ spin-down electronic wave packet into the $\text{Cr}^+ 3p^5(^2P) 3d^6(^5D)(^6P)$ AIS, forming a superposition of AIS and ground state. This superposition has a time-dependent dipole moment that oscillates at the frequency of H29.

To further explore this conjecture, we invoke the IPA, freezing electronic interactions altogether. The results are shown in Fig. 3 for both spin channels and the total emission, and reflect a prominent effect: upon freezing correlations, the resonance enhancement is completely suppressed. Similar results were recently shown in another system [45]. Here however, the spin-up channel HHG response remains largely similar with/without the IPA, while the spin-down HHG response is substantially suppressed and is the source of the disappearance of rHHG. Notably, the emission from the spin-down electrons no longer follows the semiclassical trajectories of the $3d$ electrons, proving that the spin-down $3p \rightarrow 3d$ transition is facilitated by dynamical electron

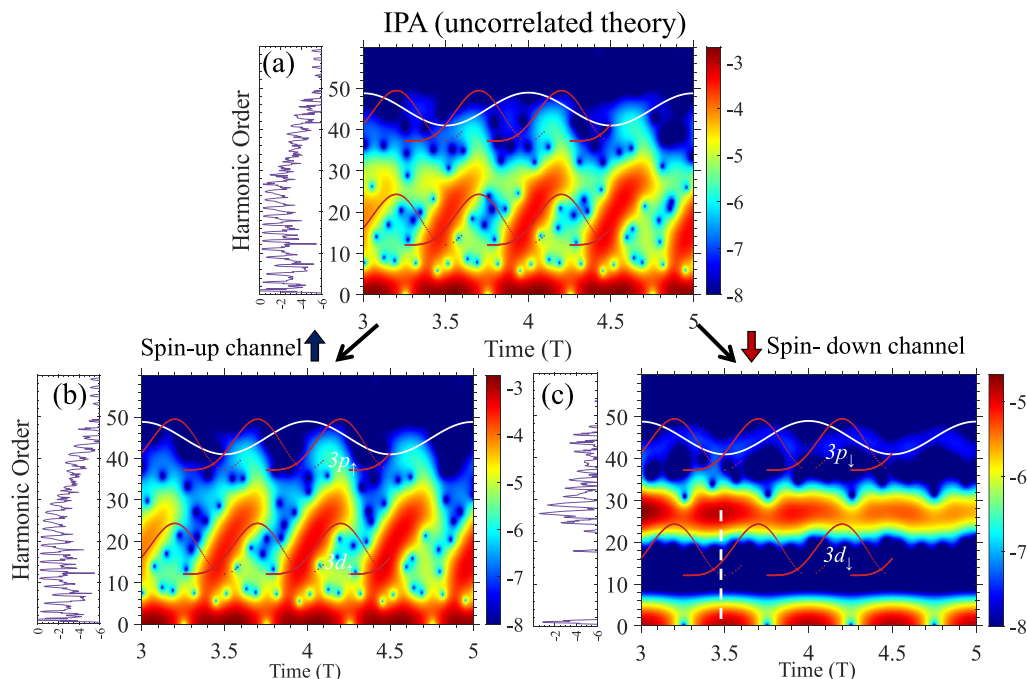


FIG. 3. rHHG within the IPA. (a)–(c) Same as panels (b)–(d) in Fig. 2. Note the spin-down response on resonance is in-phase with the maxima/minima of the driving field and strongly suppressed, unlike in Fig. 2 (indicated by dashed white lines in both figures).

correlations even in the tunneling regime. Further, while the resonance emission line still exists in the IPA spin-down channel, it is orders of magnitude weaker, has phase shifted, and is now aligned with the maximum of the electric field, similar to the perturbative low-order harmonics. In that respect, even though the atomic system still supports a resonant state in the absence of correlations, it does not contribute to rHHG since emission from typical HHG channels is more prominent, and the resonance emission mechanism differs from that of the correlated system.

The spin-down emission spectra in both the IPA and correlated models closely resemble the 1D model, exhibiting a dip at lower harmonics followed by a peak at resonance. In the 1D case, this has been attributed to the returning electron's reduced ability to penetrate the potential barrier [43].

Overall, we conclude that in the IPA, the $3p$ down states do not transition into $3d$ states, and the resonance is emitted by pure multiphoton transitions rather than excitation through the continuum. In contrast, spin-down $3p$ electrons require electronic correlations in order to resonantly emit HHG in Cr^+ in experimental settings, following their transition into $3d$ levels, also incurring a time delay. These results are further corroborated by *ab initio* simulations for the single-photon absorption and ionization cross sections (see Supplemental Material [50]), supporting our conclusions that the down spin channel is the main contributor to absorption at the resonance.

Finally, we explore the phase of the harmonics at all levels of theory with a RABBIT-like simulation. We extract the harmonic phase across orders, as well as the RABBIT sideband (SB) visibility per order (see Supplemental Material [50] for details). The results presented in Fig. 4(a) show a sharp negative phase jump across the resonance that arises only in the correlated theory. This shift is up to 2.3π through the resonance, accompanied by a reduction in SB

visibility. A vertically shifted IPA curve that aligns with the start and end of the correlated curve shows excellent agreement between the models, except near the resonance. We have found that differences in the 1D and IPA simulations can be corrected for with group velocity delay corrections [blue line in Fig. 4(a); see Supplemental Material [50] for details], rendering both theories analogous. The phase jump in rHHG can potentially explain previous measurements of reduced SB visibility [52], since it suggests a sharp phase jump even within the resonant harmonic itself (the 2.3π shift occurs abruptly over three harmonic orders).

To further test this, Fig. 4(b) presents the actual numerically observed RABBIT SB visibility and the expected visibility due to two-source interference with unequal intensities. The normalized visibility is shown in Fig. 4(c). For both SB28 and SB30 (adjacent to the resonance), across all models, the expected visibility is larger than the observed, with the exception of SB30 IPA spin-down where they are roughly equal. For both SBs the normalized correlated visibility is drastically lower than the normalized IPA visibility (SB28: 15.1% vs 27.1%; SB30: 5.6% vs 35%). The spin-resolved components show similar behavior, most noticeably the spin-down component in SB30 (4% vs 103.5%). An outlier is the spin-up component of SB30 (48.5% vs 4.5%), which we attribute to the extremely low harmonic signal in this channel. Interestingly, the 1D SAE model yields a normalized visibility similar to that of the spin-down component in the correlated model. This contrasts with the harmonic phase, which more closely resembles that of the IPA model. While this may seem unexpected, it is important to note that the 1D and IPA models are not equivalent. The 1D model employs a synthetic potential supporting a sharp shape resonance, which may differ from the IPA simulations, where this resonance could be less pronounced. Crucially, only the fully correlated theory

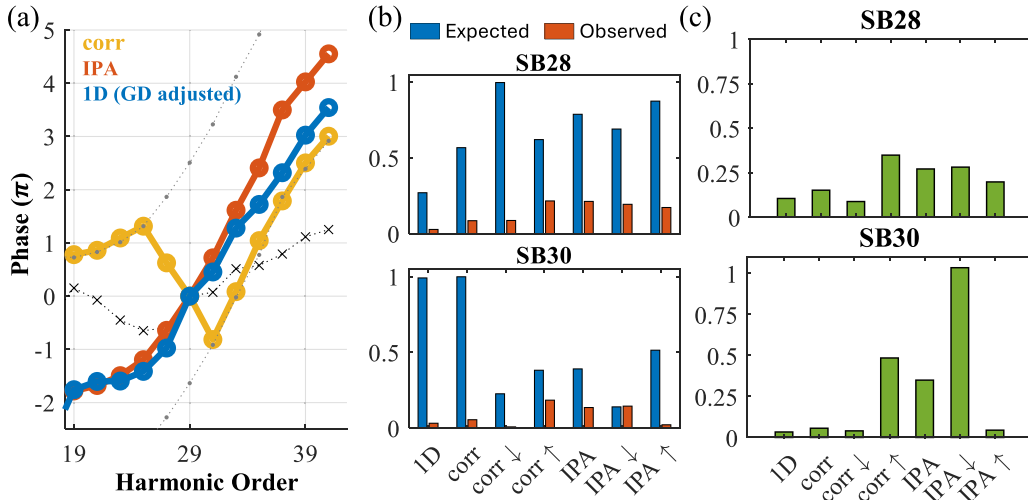


FIG. 4. rHHG phase and RABBIT analysis. (a) Harmonic phase comparison with varying levels of theory. Yellow and orange curves denote the fully correlated and IPA simulations, respectively. The blue line denotes the group-delay-corrected 1D simulation. Gray dotted lines with dot markers indicate the vertically shifted IPA, while the gray dotted line with $\times$ markers corresponds to the unadjusted 1D result. (b) Observed and expected SB visibility (for SB28 and SB30) for various levels of theory and spin channels. (c) Normalized visibility for both sidebands and various levels of theory. The correlated theory shows strongly reduced normalized visibility, corresponding to the strong phase jump in panel (a).

accurately reproduces the correct harmonic phase near resonance, also strongly reducing SB visibility in correspondence with measurements [52].

IV. CONCLUSION

In summary, we theoretically explored resonance-enhanced high-harmonic generation in Cr^+ by employing three complementary approaches: (1) a 1D SAE model where the resonance is modeled by a shape resonance, (2) *ab initio* spin-time-dependent density functional theory; and (3) spin-TDDFT within the independent particle approximation with electronic interactions artificially removed.

The 1D model successfully reproduces experimental rHHG spectra, where we showed that the mechanism for rHHG in this case is tunnel ionization followed by recollision (without associated time delays). TDDFT also reproduces experimental spectra, but offers a more comprehensive view into rHHG physics. We uncovered that the primary contribution to enhancement originates from spin-down $3p$ states rather than spin-up $3d$ electrons (that intuitively should dominate due to their lower ionization potential). Strikingly, the more dominant spin-down emission is delayed by ~ 480 as compared to the spin-up $3d$ emission. These effects contrast with the 1D model and IPA simulations and point to a mechanism involving electron interaction and spin selectivity, also aligning with the four-step picture: A $3d$ spin-up electron tunnel ionizes and accelerates in the continuum, recollides with the parent ion, exciting a $3p$ spin-down electron (only possible through correlations), exciting an autoionization state. This proceeds to coherently decay to the ground state, emitting a resonantly enhanced photon. Finally, we explored RABBIT simulations that investigate the harmonic phases and sideband visibility. These simulations showed a sharp phase jump ($\sim 2.3\pi$) across the resonance, only in the correlated theory. Correspondingly,

normalized sideband visibility near the resonance was drastically lower in the correlated theory compared to the IPA (especially for the dominant spin-down component), which might explain earlier measurements [52].

Overall, our work establishes that the resonance enhancement mechanism is physically different in the absence of correlations, and thus suggests that SAE and semiclassical models must be phase and time-delay corrected due to electronic interactions. Our work resolves several open questions in the field and should pave the way to ultrafast spectroscopies of electron correlations and resonances.

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DATA AVAILABILITY

All raw data are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. All raw data pertaining to this manuscript are not publicly available. The data are available from the authors upon reasonable request.

APPENDIX

Computational methods

We employed three theoretical descriptions of rHHG from Cr^+ . First, we implemented a 1D scheme with a potential supporting a shape resonance (metastable state). We used a square barrier-well system, smoothing the domain edges using a hyperbolic function $\tanh(\alpha x)$, with $\alpha = \frac{1}{8 \text{ a.u.}}$ (see Supplemental Material [50]): $V(x) = V_w$ if $|x| \leq l_w$; $-V_b$ if $l_w < |x| \leq l_w + l_b$; 0 otherwise, where l_w and l_b are the widths of the potential well and barrier, respectively, $V_w < 0$ is depth of the potential well, and $V_b > 0$ is the barrier height. The values of the ionization potential I_p and the MS energy E_{MS} approximately match those of Cr^+ (model $I_p \sim 15.8 \text{ eV}$, experimental $I_p \sim 16.4 \text{ eV}$ [53]). The energy levels, including I_p and E_{MS} , are computed using complex scaling [54]. Tuning the model parameters allows to systematically control the lifetime of the MS state, e.g., by increasing the barrier width (reducing the tunneling rate), thereby increasing the lifetime, while altering the ground-state energy and wave function only negligibly. Following Ref. [55], the lifetime is calculated as $\tau = -\frac{\hbar}{2\text{Im}[E_{\text{res}}]}$. The time-dependent Schrödinger equation (TDSE) is represented on a real-space grid where the initial state is an s -like (symmetric) ground state and the shape resonance residing in a p -like level. The driving field is of the form $E(t) = f(t) \cos(\omega t)$, where $f(t)$ is an envelope function given by a super-sine function [56], remains constant, and then decays. The driving frequency ω is set such that H29 is in resonance with the ground-MS transition $29\omega = I_p + E_{\text{MS}}$. For the main simulation, corresponding to an MS lifetime of $0.17T$, this results in $\omega = 0.0621 \text{ [a.u.]}$, or 734 nm . We solved the TDSE in the dipole approximation and length gauge, given in atomic units by

$$\left[i \frac{\partial}{\partial t} + \frac{1}{2} \frac{\partial^2}{\partial x^2} - V(x) - xE(t) \right] \psi(x) = 0, \quad (\text{A1})$$

and implement CAP in the form of perfectly matched layers [57].

From the propagated state, $\psi(x, t)$, we obtain the dipole acceleration through Ehrenfest's theorem [58] as $a(t) = \frac{1}{i} \langle [\hat{P}, \hat{H}] \rangle$, and calculate the HHG spectrum by taking the Fourier transform: $I(\Omega) = |\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} a(t) e^{-i\Omega t} dt|^2$. Time domain information is obtained with a Gabor analysis (see Supplemental Material [50]).

In the second approach, we employed state-of-the-art time-dependent spin density functional theory [59] using Octopus code [60]. The ground state of Cr^+ is calculated first with

DFT (utilizing the local spin density approximation with an added self-interaction correction [61], which performs well for HHG [51]). In the ground state, the system is magnetic with half-filled $3d$ orbitals, while all deeper levels are fully occupied [see Fig. 2(a)]. Semicore $3p$ levels are included in the calculation, while deeper states are treated by norm-conserving pseudopotentials [62]. After obtaining the ground state, the system's response to an 800 nm laser pulse with similar shape and intensity as in the 1D case is calculated by solving the time-dependent Kohn-Sham (KS) equations

$$i\partial_t \psi_n^{\text{KS}}(\mathbf{r}, t) = \left[-\frac{1}{2} \nabla^2 + v_{\text{KS}}(\mathbf{r}) - \mathbf{E}(t) \cdot \mathbf{r} \right] \psi_n^{\text{KS}}(\mathbf{r}, t), \quad (\text{A2})$$

where n is the orbital index, $\mathbf{r}$ is the electronic coordinate, $\psi_n^{\text{KS}}(\mathbf{r}, t)$ are the time-dependent KS orbitals, and v_{KS} is the KS potential:

$$v_{\text{KS}}(\mathbf{r}, t) = v_{e\text{-ion}} + \int d^3r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{XC}}[\rho(\mathbf{r}, t)], \quad (\text{A3})$$

where the first term in Eq. (A3) describes electron-ion interactions (including also interactions with the frozen core states through the pseudopotentials, as well as a self-interaction correction), the second term is the electrostatic Hartree repulsive interaction between electrons, and the last term is the exchange-correlation potential taken in the adiabatic and local spin density approximation with $\rho(\mathbf{r}, t)$ the spin density matrix [from which the electron density $n(\mathbf{r}, t)$ can be obtained]. In this notation, the orbital index n also refers to spin sublevels, since up/down spin channels are no longer energy degenerate (e.g., as a result of spin exchange interactions), though deviations are small.

The TDDFT equations for all initially occupied levels are propagated in real time (see Supplemental Material [50] for further details), from which we obtain the HHG spectra and time-frequency analysis in a similar manner to the 1D model, but with separation into spin channels [by separating up/down channel contribution to $n(\mathbf{r}, t)$]. Time-dependent simulations include a CAP.

We employ a third technique where the KS equations are solved by applying the independent particle approximation, i.e., fixing the KS potential to its form at $t = 0$ with $v_{\text{KS}}[\rho(\mathbf{r}, t)] = v_{\text{KS}}[\rho(\mathbf{r}, t = 0)]$. The different orbitals decouple and no longer interact through mean-field terms, only through the effective potential of the ground-state system, removing dynamic e-e interactions. The IPA is usually a very good approximation in strong-field physics; however, it has already been shown to be inadequate in resonance HHG from Ga ions [45], and is not expected to hold also in Cr^+ [47,63].

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- [1] S. Hädrich, M. Krebs, A. Hoffmann, A. Klenke, J. Rothhardt, J. Limpert, and A. Tünnermann, Exploring new avenues in high repetition rate table-top coherent extreme ultraviolet sources, *Light Sci. Appl.* **4**, e320 (2015).
 [2] Z. Chang, A. Rundquist, H. Wang, M. M. Murnane, and H. C. Kapteyn, Generation of coherent soft x rays at

2.7 nm using high harmonics, *Phys. Rev. Lett.* **79**, 2967 (1997).

- [3] C. Spielmann, N. H. Burnett, S. Sartania, R. Koppitsch, M. Schnürer, C. Kan, M. Lenzner, P. Wobrauschek, and F. Krausz, Generation of coherent x-rays in the water window using 5-femtosecond laser pulses, *Science* **278**, 661 (1997).

- [4] J. Li *et al.*, Attosecond science based on high harmonic generation from gases and solids, *Nat. Commun.* **11**, 2748 (2020).
- [5] G. Marcus *et al.*, Subfemtosecond *K*-shell excitation with a few-cycle infrared laser field, *Phys. Rev. Lett.* **108**, 023201 (2012).
- [6] D. Shafir *et al.*, Resolving the time when an electron exits a tunneling barrier, *Nature (London)* **485**, 343 (2012).
- [7] O. Smirnova *et al.*, High harmonic interferometry of multi-electron dynamics in molecules, *Nature (London)* **460**, 972 (2009).
- [8] L. Veisz *et al.*, Generation and applications of sub-5-fs multi-10-TW light pulses, in *Conference on Lasers and Electro-Optics/Pacific Rim* (Optical Society of America, Washington, DC, U.S., 2013), paper TuD2_3.
- [9] B. Bergues *et al.*, Tabletop nonlinear optics in the 100-eV spectral region, *Optica* **5**, 237 (2018).
- [10] E. Sobolev *et al.*, Terawatt-level three-stage pulse compression for all-attosecond pump-probe spectroscopy, *Opt. Express* **32**, 46251 (2024).
- [11] A. Mondal *et al.*, High-harmonic spectroscopy of low-energy electron-scattering dynamics in liquids, *Nat. Phys.* **19**, 1813 (2023).
- [12] Y. Deng *et al.*, Laser-induced inner-shell excitations through direct electron re-collision versus indirect collision, *Opt. Express* **28**, 23251 (2020).
- [13] J. Alcalá *et al.*, High-harmonic spectroscopy of quantum phase transitions in a high- T_c superconductor, *Proc. Natl. Acad. Sci. USA* **119**, e2207766119 (2022).
- [14] O. Neufeld and O. Cohen, Probing ultrafast electron correlations in high harmonic generation, *Phys. Rev. Res.* **2**, 033037 (2020).
- [15] O. Neufeld, D. Ayuso, P. Decleva, M. Y. Ivanov, O. Smirnova, and O. Cohen, Ultrasensitive chiral spectroscopy by dynamical symmetry breaking in high harmonic generation, *Phys. Rev. X* **9**, 031002 (2019).
- [16] K. A. Hamer, F. Mauger, A. S. Folorunso, K. Lopata, R. R. Jones, L. F. DiMauro, K. J. Schafer, and M. B. Gaarde, Characterizing particle-like chargemigration dynamics with high-order harmonic sideband spectroscopy, *Phys. Rev. A* **106**, 013103 (2022).
- [17] J. Freudenstein *et al.*, Attosecond clocking of correlations between Bloch electrons, *Nature (London)* **610**, 290 (2022).
- [18] O. Neufeld, J. Zhang, U. D. Giovannini, H. Hübener, and A. Rubio, Probing phonon dynamics with multidimensional high harmonic carrier-envelope-phase spectroscopy, *Proc. Natl. Acad. Sci. USA* **119**, e2204219119 (2022).
- [19] C. Heide *et al.*, Probing topological phase transitions using high-harmonic generation, *Nat. Photonics* **16**, 620 (2022).
- [20] C. P. Schmid *et al.*, Tunable non-integer high-harmonic generation in a topological insulator, *Nature (London)* **593**, 385 (2021).
- [21] J. Zhang, Z. Wang, F. Lengers, D. Wigger, D. E. Reiter, T. Kuhn, H. J. Wörner, T. T. Luu, High-harmonic spectroscopy probes lattice dynamics, *Nat. Photonics* **18**, 792 (2024).
- [22] J. L. Krause, K. J. Schafer, and K. C. Kulander, High-order harmonic generation from atoms and ions in the high intensity regime, *Phys. Rev. Lett.* **68**, 3535 (1992).
- [23] P. B. Corkum, Plasma perspective on strong field multiphoton ionization, *Phys. Rev. Lett.* **71**, 1994 (1993).
- [24] L. He *et al.*, Filming movies of attosecond charge migration in single molecules with high harmonic spectroscopy, *Nat. Commun.* **13**, 4595 (2022).
- [25] D. Baykusheva, M. S. Ahsan, N. Lin, and H. J. Wörner, Bicircular high-harmonic spectroscopy reveals dynamical symmetries of atoms and molecules, *Phys. Rev. Lett.* **116**, 123001 (2016).
- [26] E. Frumker, C. T. Hebeisen, N. Kajumba, J. B. Bertrand, H. J. Wörner, M. Spanner, D. M. Villeneuve, A. Naumov, and P. B. Corkum, Oriented rotational wave-packet dynamics studies via high harmonic generation, *Phys. Rev. Lett.* **109**, 113901 (2012).
- [27] O. Neufeld, O. Wengrowicz, O. Peleg, A. Rubio, and O. Cohen, Detecting multiple chiral centers in chiral molecules with high harmonic generation, *Opt. Express* **30**, 3729 (2022).
- [28] N. Saito, P. Xia, F. Lu, T. Kanai, J. Itatani, and N. Ishii, Observation of selection rules for circularly polarized fields in high-harmonic generation from a crystalline solid, *Optica* **4**, 1333 (2017).
- [29] O. Neufeld, D. Podolsky, and O. Cohen, Floquet group theory and its application to selection rules in harmonic generation, *Nat. Commun.* **10**, 405 (2019).
- [30] K.-J. Yuan and A. D. Bandrauk, Symmetry in circularly polarized molecular high-order harmonic generation with intense bicircular laser pulses, *Phys. Rev. A* **97**, 023408 (2018).
- [31] R. de Nalda, E. Heesel, M. Lein, N. Hay, R. Velotta, E. Springate, M. Castillejo, and J. P. Marangos, Role of orbital symmetry in high-order harmonic generation from aligned molecules, *Phys. Rev. A* **69**, 031804 (2004).
- [32] R. Torres *et al.*, Probing orbital structure of polyatomic molecules by high-order harmonic generation, *Phys. Rev. Lett.* **98**, 203007 (2007).
- [33] C. B. Madsen and L. B. Madsen, Theoretical studies of high-order harmonic generation: Effects of symmetry, degeneracy, and orientation, *Phys. Rev. A* **76**, 043419 (2007).
- [34] M. Suzuki, M. Baba, R. Ganeev, H. Kuroda, and T. Ozaki, Anomalous enhancement of a single high-order harmonic by using a laser-ablation tin plume at 47 nm, *Opt. Lett.* **31**, 3306 (2006).
- [35] R. A. Ganeev, Generation of high-order harmonics of high-power lasers in plasmas produced under irradiation of solid target surfaces by a prepulse, *Phys. Usp.* **52**, 55 (2009).
- [36] N. Rosenthal and G. Marcus, Discriminating between the role of phase matching and that of the single-atom response in resonance plasma-plume high-order harmonic generation, *Phys. Rev. Lett.* **115**, 133901 (2015).
- [37] J. T. Costello, E. T. Kennedy, B. F. Sonntag, and C. W. Clark, $3p$ photoabsorption of free and bound Cr, Cr^+ , Mn, and Mn^+ , *Phys. Rev. A* **43**, 1441 (1991).
- [38] T. Osawa *et al.*, Photoion-yield study of the $3p$ - $3d$ giant resonance excitation region of isolated Cr, Mn and Fe atoms, *J. Phys. B* **45**, 225204 (2012).
- [39] M. V. Frolov, N. L. Manakov, and A. F. Starace, Potential barrier effects in high-order harmonic generation by transition-metal ions, *Phys. Rev. A* **82**, 023424 (2010).
- [40] A. S. Kheifets, Resonant photoionization and time delay, *J. Phys. B* **58**, 072001 (2025).
- [41] V. Strelkov, Role of autoionizing state in resonant high-order harmonic generation and attosecond pulse production, *Phys. Rev. Lett.* **104**, 123901 (2010).

- [42] V. V. Strelkov, M. A. Khokhlova, and N. Y. Shubin, High-order harmonic generation and Fano resonances, *Phys. Rev. A* **89**, 053833 (2014).
- [43] M. Tudorovskaya and M. Lein, High-order harmonic generation in the presence of a resonance, *Phys. Rev. A* **84**, 013430 (2011).
- [44] R. A. Ganeev *et al.*, Isolated sub-fs XUV pulse generation in Mn plasma ablation, *Opt. Express* **20**, 25239 (2012).
- [45] A. A. Romanov, V. V. Strelkov, and A. A. Silaev, Simulation of resonance-enhanced high-order harmonic generation and autoionization decay in Ga^+ based on time-dependent density-functional theory, *Phys. Rev. A* **110**, 063109 (2024).
- [46] A. A. Romanov, A. A. Silaev, T. S. Sarantseva, M. V. Frolov, and N. V. Vvedenskii, Study of high-order harmonic generation in xenon based on time-dependent density-functional theory, *New J. Phys.* **23**, 043014 (2021).
- [47] I. S. Wahyutama, T. Sato, and K. L. Ishikawa, Time-dependent multiconfiguration self-consistent-field study on resonantly enhanced high-order harmonic generation from transition-metal elements, *Phys. Rev. A* **99**, 063420 (2019).
- [48] I. Tikhomirov, T. Sato, and K. L. Ishikawa, High-harmonic generation enhanced by dynamical electron correlation, *Phys. Rev. Lett.* **118**, 203202 (2017).
- [49] R. A. Ganeev and H. Kuroda, Resonance-affected high-order harmonic emission from atomic and molecular chromium laser-induced plasmas, *OSA Continuum* **4**, 1545 (2021).
- [50] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/rwtl-3b3g> for detailed description of the 1D Time-Dependent Schrodinger Equation numerical methods, and an overview of the Time-Dependent Density Functional Theory including the Independent Particle Approximation.
- [51] O. Neufeld, N. Tancogne-Dejean, and A. Rubio, Benchmarking functionals for strong-field light-matter interactions in adiabatic time-dependent density functional theory, *J. Phys. Chem. Lett.* **15**, 7254 (2024).
- [52] S. Haessler *et al.*, Phase distortions of attosecond pulses produced by resonance-enhanced high harmonic generation, *New J. Phys.* **15**, 013051 (2013).
- [53] C. J. Sansonetti and G. Nave, Extended analysis of the spectrum of singly ionized chromium (Cr II), *Astrophys. J. Suppl. Ser.* **213**, 28 (2014).
- [54] N. Moiseyev, Quantum theory of resonances: Calculating energies, widths and cross-sections by complex scaling, *Phys. Rep.* **302**, 212 (1998).
- [55] N. Moiseyev, *Non-Hermitian Quantum Mechanics* (Cambridge University Press, Cambridge, 2011).
- [56] O. Neufeld and O. Cohen, Background-free measurement of ring currents by symmetry-breaking high-harmonic spectroscopy, *Phys. Rev. Lett.* **123**, 103202 (2019).
- [57] S. G. Johnson, Notes on perfectly matched layers (PMLs), [arXiv:2108.05348](https://arxiv.org/abs/2108.05348).
- [58] M. R. Miller, *Time Resolving Electron Dynamics in Atomic and Molecular Systems Using High-Harmonic Spectroscopy* (University of Colorado, Boulder, 2016).
- [59] M. A. L. Marques and E. K. U. Gross, Time-dependent density functional theory, *Annu. Rev. Phys. Chem.* **55**, 427 (2004).
- [60] N. Tancogne-Dejean *et al.*, Octopus, a computational framework for exploring light-driven phenomena and quantum dynamics in extended and finite systems, *J. Chem. Phys.* **152**, 124119 (2020).
- [61] C. Legrand, E. Suraud, and P.-G. Reinhard, Comparison of self-interaction-corrections for metal clusters, *J. Phys. B* **35**, 1115 (2002).
- [62] C. Hartwigsen, S. Goedecker, and J. Hutter, Relativistic separable dual-space Gaussian pseudopotentials from H to Rn, *Phys. Rev. B* **58**, 3641 (1998).
- [63] A. W. Bray, D. Freeman, F. Naseem, V. K. Dolmatov, and A. S. Kheifets, Correlation-enhanced high-order-harmonic-generation spectra of Mn and Mn^+ , *Phys. Rev. A* **101**, 053415 (2020).