

Reduced density matrix description of high-harmonic generation in multielectron atoms: Exploring subcycle correlation effects

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High-harmonic generation (HHG) is one of the fundamental processes at the heart of attosecond physics. Traditionally viewed as an effective single-particle effect, recent advances have focused on contributions to the harmonic spectrum beyond this single-particle picture, as well as on probing electron correlations through HHG in atoms, molecules, and solids. In this paper, we introduce a reduced density matrix description to explore and to quantify correlation effects on a subcycle timescale and apply this approach to prototypical multielectron atoms. By comparing noble gas atoms (He, Ne) with alkaline-earth atoms (Be, Mg) exposed to driving fields with similar Keldysh parameters, we show that the subcycle variation of correlation parameters differs markedly for noble gases and alkaline-earth atoms. We provide an intuitive explanation of these surprising effects based on the dynamics of natural orbitals and discuss the effect of this ultrafast correlation dynamics on the HHG spectrum.

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I. INTRODUCTION

One of the most striking signatures of the nonlinear responses of matter to driving with strong fields is the generation of high harmonics. First observed in atomic vapors irradiated by strong infrared (IR) fields [1,2], high-harmonic generation (HHG) has developed into a powerful tool for generating attosecond pulse trains [3–7], isolated attosecond pulses [8–12], and tunable tabletop sources of extreme ultraviolet and X-ray radiation [13–16], giving rise to the new field of attosecond physics [17,18]. The appearance of the HHG spectrum extending into the XUV regime was readily identified as a clear signature of the breakdown of multiphoton perturbation theory and explained by the so-called three-step model [19–21]. It provides an intuitive (semiclassical) picture of HHG in terms of a sequence of three subsequent one-electron processes: tunneling (or over-the-barrier) ionization near the peak of the strong IR field lowering the potential barrier, followed by acceleration of the ionized electron along a trajectory that will eventually steer the electron back to the ion with high

kinetic energy, and finally the radiative recombination with the parent ion converting the acquired kinetic energy into high-energy radiation. This single-active electron (SAE) picture is at the core of several variants of the so-called strong-field approximation as well as of many numerical simulations, capturing in many cases the essential properties of the HHG spectrum.

More recently, several features have been observed that cannot be explained within the single-electron framework because of the crucial role of multielectron effects. One prominent example is the giant dipole resonance in Xe [22,23], where the interplay between the $5p$ and $4d$ shells upon recombination leads to a dramatic enhancement in the yield near 100 eV [22,23]. Enhancements typically spectrally limited to one or a few harmonics have been observed (see, e.g., Refs. [24–27]) and theoretically analyzed in other multielectron atoms and ions (see, e.g., Refs. [28,29]). Another prominent example, where multielectron correlations have dramatic effects on the yield in HHG, is the secondary plateau that extends far beyond the energy cutoff expected for the most weakly bound electron. The emergence of secondary plateaus has been observed numerically, e.g., in He [30] and has been traced back to the correlated electron dynamics. The mechanism identified for He [31] corresponds to the correlated backaction of one electron on the other during tunnel ionization, which leaves the ion in an excited state such that the electron returning to the ion sees a larger ionization potential. In turn, in Be ionized by strong laser fields, the appearance of the

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extended plateau was attributed to a recollision-induced decrease in the two-electron ionization probability such that recombination occurs into the Be^{2+} ion [32]. A similar mechanism was later found to lead to extended plateaus also in Li and Na [33]. A systematic numerical study of noble gas atoms within time-dependent density functional theory (TDDFT) showed that correlations strongly influence the harmonic yield as a function of the ellipticity of the driving field [34].

By applying HHG spectroscopy to extended systems and solids [35–39], it was numerically demonstrated that strong driving can lead to the ultrafast formation of correlated pair states called doublons for the strongly correlated Fermi-Hubbard system whose dynamics leaves marked fingerprints on the HHG spectrum [40]. This observation suggests HHG as a potential spectroscopic tool to investigate the ultrafast dynamics of strongly correlated materials. For example, theoretical investigations of HHG in strongly correlated materials have pointed to dynamical modifications of effective interaction parameters [41]. Such a dynamical renormalization of the Coulomb repulsion has been, indeed, subsequently measured in a strongly correlated cuprate material upon strong-field driving [42].

In this paper, we describe and quantify the role of electronic correlations by introducing a reduced density matrix (RDM) description for HHG that allows to express the radiation amplitude according to the Larmor formula in terms of a superposition of independent radiating oscillators for any correlated many-electron system. This description extends the very first theoretical approach to HHG by Kuchiev [19] in terms of “atomic antennas” to correlated systems. We show that these antennas can be fully characterized by the natural orbitals and their occupation numbers of the many-electron system. Employing correlation and entanglement measures from quantum information theory, ultrafast variations of electron correlations on subcycle timescales can be extracted from the time-dependent occupation numbers of these natural orbitals. We apply this approach to prototypical multielectron noble gas (He, Ne) and alkaline-earth (Be, Mg) atoms based on fully converged multiconfiguration time-dependent Hartree-Fock (MCTDHF) [43–48] calculations. We show that strongly driven noble gas and alkaline-earth atoms feature markedly different subcycle dynamics of the time-dependent correlations referred to in the following as dynamic correlations and discuss their implications for the resulting HHG spectra.

The paper is structured as follows. In Sec. II, we derive within the framework of the Larmor formula of classical radiation theory an explicit expression for the amplitude of HHG radiation in terms of the one-particle reduced density matrix (1RDM) for an arbitrary N -electron system. The equations of motion for the 1RDM under strong-field driving by the laser field will be analyzed in Sec. III. Measures for time-dependent correlations to quantify the correlation dynamics will be introduced in Sec. IV. Numerical applications to noble gas and alkaline-earth atoms will be presented in Sec. V. Conclusions and an outlook to future extensions of this work will be given in Sec. VI. Unless stated otherwise, we use atomic units throughout the paper, i.e., $\hbar = m_e = e = 1$.

II. REDUCED DENSITY MATRIX REPRESENTATION OF HHG

We consider in the following an interacting system of N identical particles driven by a strong laser field and governed by the time-dependent Schrödinger equation

$$i\partial_t|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle. \quad (1)$$

The general form of the Hamiltonian $\hat{H}(t)$ is given by

$$\hat{H}(t) = \sum_{n=1}^N \hat{h}_n + \hat{V}_n(t) + \frac{1}{2} \sum_{n \neq m}^N \hat{W}_{nm}, \quad (2)$$

where $\hat{h}_n$ stands for the single-particle operators of the unperturbed system, which in our application to atoms will include the kinetic energy operator and the nuclear Coulomb potential. The coupling to the strong laser field is given by the single-particle operator $\hat{V}_n(t)$, which takes the form $\hat{V}_n^{(L)}(t) = \hat{z}_n F(t)$ in the length gauge and $\hat{V}_n^{(V)}(t) = \hat{p}_{z_n} A(t)/c$ in the velocity gauge with $A(t)$ the vector potential associated with the strong electric field $F(t)$ oriented in the following along the z axis. For atomic systems, the electron-electron Coulomb interaction will play the role of the interparticle interaction $\hat{W}_{nm}$ and the identical particles are fermions, i.e., electrons. It should be noted that Eq. (2) and the following description is general and applies also to systems featuring short-ranged interactions and to extended systems as well.

Within the classical description of the emitted radiation field underlying the Larmor formula, the high-harmonic yield is given by

$$I^{\text{HHG}} = \frac{2}{3c} |\tilde{a}(\omega)|^2, \quad (3)$$

with $\tilde{a}(\omega)$ being the Fourier transform of the dipole acceleration

$$\begin{aligned} \mathbf{a}(t) &= -\frac{d^2}{dt^2} \sum_{n=1}^N \langle \Psi(t) | \hat{\mathbf{r}}_n | \Psi(t) \rangle \\ &= \frac{d}{dt} \sum_{n=1}^N \langle \Psi(t) | \hat{\mathbf{p}}_n | \Psi(t) \rangle \\ &= i \sum_{n=1}^N \langle \Psi(t) | [\hat{h}_n + \hat{V}_n(t), \hat{\mathbf{p}}_n] | \Psi(t) \rangle \\ &= \sum_{n=1}^N \langle \Psi(t) | \hat{\mathbf{a}}_n | \Psi(t) \rangle. \end{aligned} \quad (4)$$

The operator of the dipole acceleration $\hat{\mathbf{a}}_n = i[\hat{h}_n + \hat{V}_n(t), \hat{\mathbf{p}}_n]$ is governed by the spatial gradient of the one-particle potential terms in Eq. (2), i.e., the nuclear Coulomb potential, and, depending on the gauge, by the laser field. The contributions from electron-electron interactions cancel each other out because the electrons do not exert any net force on themselves. With the use of Eq. (3), we restrict ourselves to a regime of driving fields that is frequently referred to as the “dipole oasis” [49]. Accordingly, relativistic and nondipole field effects are not accounted for. Moreover, quantum effects of the photonic field are neglected from the outset, while electronic

correlation effects are fully included on the level of quantum many-body theory.

Since the physical observable of interest, the acceleration $\hat{a} = \sum_{n=1}^N \hat{a}_n$, is a one-body operator, its expectation value [Eq. (4)] evaluated for the exact time-dependent many-electron state $|\Psi(t)\rangle$ [Eq. (1)] can be equivalently expressed by the 1RDM D_1 without invoking any approximation in the electronic degrees of freedom. The 1RDM is obtained from the many-body wavefunction $|\Psi(t)\rangle$ by tracing out all but one particle:

$$D_1(t) = N \text{Tr}_{2 \dots N} |\Psi(t)\rangle \langle \Psi(t)|. \quad (5)$$

We label here and in the following all one-particle operators by the subscript 1. In terms of D_1 [Eq. (5)], Eq. (4) reduces to

$$a(t) = \text{Tr}[\hat{a}_1(t) D_1(t)]. \quad (6)$$

At any instant of time, the 1RDM can be diagonalized in terms of the time-dependent natural orbitals $\{|\eta_j(t)\rangle\}$ and their eigenvalues $\eta_j(t)$, the occupation numbers of these orbitals $|\eta_j(t)\rangle$,

$$D_1(t) = \sum_j \eta_j(t) |\eta_j(t)\rangle \langle \eta_j(t)|, \quad (7)$$

with j being a combined index of a spatial orbital and the spin ($j = q_j, \sigma_j$), $|\eta_j\rangle = |v_{q_j}\rangle \otimes |\sigma_j\rangle$. They play a key role in the present analysis of dynamic correlations. In line with its usage in the fields of atomic and photonic collisions (see, e.g., Ref. [50]), the term dynamic correlations refers to time-dependent electron-electron correlations in the non-stationary, in particular, explicitly time-dependent externally driven, many-electron system. Their importance is derived from the fact that they leave their mark on the asymptotic ($t \rightarrow \infty$) final state of the wave packet or, more generally, on the elements of the S -matrix of the light-atom scattering process. This term is to be distinguished from the notion of static or dynamical correlations frequently employed in quantum chemistry [51], which is used to characterize different distributions of natural orbital occupation numbers η_j in stationary states, in particular, in ground states of many-electron systems. While the present formulation includes the time dependence of the latter, it goes beyond this concept: As will be shown below, the correlation-induced temporal changes of the natural orbitals $|\eta_j(t)\rangle$ themselves play a decisive role in determining the asymptotic final state, in the present case, the resulting HHG spectrum, as well.

Within any mean-field approach such as the time-dependent Hartree-Fock approximation (TDHF) [52], the TDDFT [53], or any SAE approximation, Eq. (7) reduces to

$$D_1(t) \approx \sum_{j=1}^{N_{\text{occ}}} |\eta_j(t)\rangle \langle \eta_j(t)|, \quad (8)$$

i.e., the occupation numbers of such mean-field (spin) orbitals are

$$\eta_j(t) = \begin{cases} 1, & j \leq N_{\text{occ}}, \\ 0, & j > N_{\text{occ}}, \end{cases} \quad (9)$$

where N_{occ} is the number of occupied orbitals. One crucial difference that distinguishes the fully correlated N -electron dynamics [Eq. (7)] from the mean-field description [Eq. (8)]

is that, in general, a larger number of fractionally occupied natural orbitals contribute, the number of which is decoupled from the number of electrons N in the system. The occupation numbers are only constrained by

$$\sum_j \eta_j(t) = N. \quad (10)$$

Consequently, the expression for the dipole acceleration [Eq. (4)] reads

$$a(t) = \sum_j \eta_j(t) \langle \eta_j(t) | \hat{a}_1 | \eta_j(t) \rangle. \quad (11)$$

Thus, the amplitude of the emitted high-harmonic radiation is given by the superposition of the fields generated by an ensemble of strongly driven charge oscillators or, in the terminology of Kuchiev's pioneering early work on HHG [19], by an ensemble of "atomic antennas". The effective oscillator strength of these antennas is controlled by both the time-dependent dipole acceleration expectation values $\langle \eta_j(t) | \hat{a}_1 | \eta_j(t) \rangle$ and the occupation numbers, $\eta_j(t)$. The strength of these oscillations introduced in Eqs. (10) and (11) should not be confused with the conventional oscillator strength for atomic dipole transitions in the perturbative limit. The number of such "atomic antennas" ($\geq N$) that effectively contribute is controlled by the initial state and the dynamic correlations present in the driven system.

We note that Eq. (11) is general and equally applicable to atoms, molecules, and solids, and is independent of the strength of correlations. Apart from neglecting effects of the quantized radiation field by way of using the Larmor formula for dipole radiation, Eq. (11) is exact as far as the electronic degrees of freedom are concerned. Moreover, Eq. (11) can be generalized to other physical observables that can be written as sums of expectation values of one-body operators. In the specific case of HHG in multielectron atoms, the expectation value of the dipole acceleration initially vanishes prior to the action of the symmetry-breaking driving field, but will become nonzero as a function of the time when the laser field starts to polarize the state, creating a state of mixed parity, i.e., containing angular momentum contributions of both even and odd l . Furthermore, Eq. (11) suggests that the intuitive picture of the three-step model for HHG should be mirrored in and can be mapped onto the time evolution of individual "antennas", even when the independent-particle model fails and electron correlations significantly contribute.

III. TIME EVOLUTION OF NATURAL ORBITALS

The time dependence of the dipole acceleration [Eq. (11)], which governs the resulting HHG spectrum [Eq. (3)] is completely determined by the time dependence of the natural orbitals $|\eta_j(t)\rangle$ and of their eigenvalues $\eta_j(t)$. It is therefore of considerable conceptual interest to explicitly determine the equations of motion for $|\eta_j(t)\rangle$ and $\eta_j(t)$ for strongly driven N -electron systems.

Starting point is the equation of motion of the 1RDM, which is the lowest-order member of the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy [54] and takes the form of a Liouville-von Neumann equation including a collision term that couples the 1RDM to the two-particle reduced density

matrix (2RDM) D_{12} ,

$$i\partial_t D_1 = [\hat{h}_1 + \hat{V}_1(t), D_1] + \text{Tr}_2[\hat{W}_{12}, D_{12}]. \quad (12)$$

The 2RDM is given by

$$D_{12}(t) = N(N-1)\text{Tr}_{3\dots N}|\Psi(t)\rangle\langle\Psi(t)|. \quad (13)$$

The collision term [second term on the right-hand side of Eq. (12)] represents the interaction of particle 1 with all other particles surrounding it. This term includes both mean-field contributions and electron-electron (or, more generally, pair) correlations. In order to separate these two contributions from each other, we employ the decomposition of the 2RDM into an uncorrelated (or Hartree-Fock) term and the two-particle correlation term as

$$D_{12}(t) = \hat{A}D_1(t)D_2(t) + \Delta_{12}(t). \quad (14)$$

In Eq. (14), $\hat{A}$ denotes the antisymmetrization operator acting on the product of the two 1RDMs. It antisymmetrizes all terms resulting from pairwise particle exchange in the product of D_1D_2 , e.g., $\hat{A}(\langle i|D_1|j\rangle\langle k|D_2|l\rangle) = \langle i|D_1|j\rangle\langle k|D_2|l\rangle - \langle i|D_1|l\rangle\langle k|D_2|j\rangle$. Δ_{12} denotes the two-particle correlator, frequently also referred to as the two-particle cumulant [55,56]. Projecting onto the basis of natural orbitals, i.e., the eigenstates of the 1RDM, at each instant of time, the matrix representation of Eq. (12) becomes [for reasons of brevity, we omit the explicit time dependence of $\eta_j(t)$ and $|\eta_j(t)\rangle$ in the notation of Eqs. (15)–(17)]

$$\begin{aligned} \langle\eta_i|i\partial_t D_1|\eta_j\rangle &= \langle\eta_i|[\hat{h}_1 + \hat{V}_1(t), D_1] + \text{Tr}_2[\hat{W}_{12}, D_{12}]|\eta_j\rangle \\ &= (\eta_j - \eta_i)\langle\eta_i|\hat{h}_1 + \hat{V}_1(t)|\eta_j\rangle \\ &\quad + \langle\eta_i|\text{Tr}_2[\hat{W}_{12}, D_{12}]|\eta_j\rangle. \end{aligned} \quad (15)$$

On the other hand, in the representation of the 1RDM in the natural-orbital basis [Eq. (7)], the equation of motion can be equivalently written as

$$\langle\eta_i|i\partial_t D_1|\eta_j\rangle = i\dot{\eta}_i\langle\eta_i|\eta_j\rangle + i\eta_j\langle\eta_i|\dot{\eta}_j\rangle + i\eta_i\langle\dot{\eta}_i|\eta_j\rangle. \quad (16)$$

Using $\langle\eta_i|\eta_j\rangle = \delta_{ij}$ and

$$\frac{d}{dt}\langle\eta_i|\eta_j\rangle = \langle\eta_i|\dot{\eta}_j\rangle + \langle\dot{\eta}_i|\eta_j\rangle = 0, \quad (17)$$

equating Eqs. (15) and (16), and inserting Eq. (14) yields for the diagonal elements $i = j$ the equation of motion for the natural orbital occupation numbers:

$$\begin{aligned} \partial_t \eta_j(t) &= -i\langle\eta_j(t)|\text{Tr}_2[\hat{W}_{12}, \Delta_{12}(t)]|\eta_j(t)\rangle \\ &= -i\langle\eta_j(t)|\hat{C}_1(t)|\eta_j(t)\rangle \\ &= \text{Im}\langle\eta_j(t)|\hat{C}_1(t)|\eta_j(t)\rangle. \end{aligned} \quad (18)$$

In Eq. (18), we have introduced the reduced collision operator $\hat{C}_1$ whose spatial and spin representation reads

$$\begin{aligned} C_1(\mathbf{r}_1, \sigma_1, \mathbf{r}'_1, \sigma'_1; t) &= \sum_{\sigma_2} \int d^3 r_2 [W_{12}(\mathbf{r}_1 - \mathbf{r}_2) - W_{12}(\mathbf{r}'_1 - \mathbf{r}_2)] \\ &\quad \times \Delta_{12}(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \mathbf{r}'_1, \sigma'_1, \mathbf{r}_2, \sigma_2; t). \end{aligned} \quad (19)$$

This collision operator is nonlocal and describes the coupling and transfer of electrons between $(\mathbf{r}_1, \sigma_1)$ and $(\mathbf{r}'_1, \sigma'_1)$ due to

correlations with surrounding electrons. As with all the terms on the right-hand side of a Liouville von Neumann-type equation [Eq. (12)], the collision operator is also anti-Hermitian and its diagonal elements are purely imaginary. Since $\hat{C}_1$ represents the coupling of the one-particle system to its environment (i.e., the other particles), the imaginary part of its diagonal elements can effect changes of the natural orbital occupation numbers.

The equations of motion of the natural orbitals $|\eta_j(t)\rangle$ follow from the off-diagonal ($i \neq j$) elements of Eqs. (15) and (16) as

$$\begin{aligned} i\partial_t |\eta_j(t)\rangle &= \hat{h}_1 |\eta_j(t)\rangle + \hat{V}_1(t) |\eta_j(t)\rangle \\ &\quad + \sum_{i \neq j} (\hat{W}_i^i(t) \eta_i |\eta_j\rangle - \hat{W}_j^i(t) \eta_i |\eta_i\rangle) \\ &\quad + \sum_{i \neq j} |\eta_i(t)\rangle \frac{\langle\eta_i(t)|\text{Tr}_2[\hat{W}_{12}, \Delta_{12}(t)]|\eta_j(t)\rangle}{\eta_j(t) - \eta_i(t)}. \end{aligned} \quad (20)$$

In the present case of strong-field driving of atoms, the first line on the right-hand side of Eq. (20) includes the kinetic energy, the nuclear Coulomb potential, and the interaction with the laser field. The second line represents the direct and exchange mean-field contributions in which the conventional two-electron Coulomb matrix elements

$$\begin{aligned} W_{jl}^{ik}(t) &= \langle\eta_i(t)\eta_k(t)|\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}|\eta_j(t)\eta_l(t)\rangle \\ &= \delta_{\sigma_j}^{\sigma_i} \delta_{\sigma_l}^{\sigma_k} \int d^3 r_1 d^3 r_2 v_{q_i}^*(\mathbf{r}_1; t) v_{q_k}^*(\mathbf{r}_2; t) \\ &\quad \times \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} v_{q_j}(\mathbf{r}_1; t) v_{q_l}(\mathbf{r}_2; t) \end{aligned} \quad (21)$$

appear as effective one-electron operators whose spatial and spin representation reads

$$W_j^i(\mathbf{r}_1; t) = \delta_{\sigma_j}^{\sigma_i} \int d^3 r_2 v_{q_i}^*(\mathbf{r}_2; t) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} v_{q_j}(\mathbf{r}_2; t). \quad (22)$$

The third line of Eq. (20) contains the contributions from the collision operator [Eq. (18)] unambiguously signifying correlation effects on the propagation of natural orbitals. [We note that terms in Eq. (20) where the denominator vanishes do not effectively contribute.] Comparison between Eqs. (18) and (20) shows that temporal variations of the occupation numbers are exclusively due to the collision operator, i.e., due to correlation effects ($\propto \Delta_{12}$) and obviously absent in any mean-field description, while the time evolution of the natural orbitals is governed by a combination of both one-particle and two-particle interactions. The time dependence of the occupation numbers is therefore a particularly sensitive probe of time-dependent electron-electron correlations during strong-field driving. We note that $\hat{C}_1$ bears some resemblance to the so-called time-dependent transition density matrix (TDM) employed in TDDFT, mostly in the perturbative regime [57,58]. However, while the TDM depends on all nonlocal couplings encoded in the 1RDM, including those due to mean-field effects, $\hat{C}_1$ selects exclusively those couplings and transitions that are caused by two-particle correlations.

IV. MEASURES OF CORRELATIONS

Within the context of quantum information theory, the 1RDM has been extensively used to quantify entanglement in many-body quantum systems [59]. Frequently employed measures include the purity $P = \text{Tr} D_1^2$, often also referred to as the linear entropy [60], and the von Neumann entropy (or entanglement entropy) [59]

$$S_1(t) = -\text{Tr}[D_1(t) \ln D_1(t)]. \quad (23)$$

From the spectral representation of D_1 [Eq. (7)], it is obvious that both the linear entropy and the von Neumann entropy are completely characterized by the eigenvalues of D_1 ,

$$P(t) = \sum_j \eta_j(t)^2, \quad (24)$$

$$S_1(t) = -\sum_j \eta_j(t) \ln \eta_j(t). \quad (25)$$

In turn, as the temporal evolution of occupation numbers is exclusively determined by correlation effects beyond mean field [see Eq. (18)], these measures are equally well suited to quantify the temporal variation of correlations. In fact, entanglement and correlations have become the focus of recent studies of photoionization [61–67] and portions of D_1 have been directly measured for photoelectrons in a RABBITT-like setting [68,69].

Focusing in the following on the von Neumann entropy [Eq. (23)], S_1 is well suited to characterize the statistical distribution of occupation numbers. For an uncorrelated state of indistinguishable fermions, i.e., a Slater determinant, the eigenvalues of the 1RDM are restricted to $\eta_j = 1$ or 0 and S_1 vanishes ($S_1 = 0$). In particular, mean-field approximations such as TDHF or TDDFT will give $S_1 = 0$ for all times. In contrast, for correlated states $S_1 > 0$. Accordingly, time-dependent correlations due to strong driving by the laser field can be quantified by the time-dependent variation of the von Neumann entropy $\delta S_1(t) = S_1(t) - S_1(0)$, where $S_1(0)$ quantifies the initial correlations of the many-electron (ground) state prior to the onset of the laser field.

Alternatively to S_1 , the time-dependent two-particle cumulant $\Delta_{12}(t)$ itself [see Eqs. (14) and (18)] can be employed as a measure of correlations as it explicitly represents two-particle correlations. We therefore introduce as an alternative measure the magnitude of Δ_{12} determined by the Hilbert-Schmidt norm (or Schatten 2-norm) $||\Delta_{12}||$. In our applications to multielectron atoms, we will compare the temporal variation of S_1 with that of $||\Delta_{12}||$. We find that these two measures yield qualitatively remarkably similar results. We note that the subcycle variations of the energies of the natural orbitals and of the spatial energy densities have been previously suggested as an alternative tool to distinguish dynamic correlations from mean-field effects in molecules [70].

V. CORRELATIONS AND HHG IN MULTIELECTRON ATOMS

A. Simulation methods

In this section, we present first applications of the quantitative description of correlation dynamics to strong-field driving

TABLE I. Parameters used in the simulation of strong-field driving of He, Ne, Be, and Mg by a two-cycle laser pulse chosen to yield comparable Keldysh parameters. I_p : ionization potential [71], λ : wavelength, I_0 : intensity of the driving field, γ : Keldysh parameter [Eq. (30)], E_{cutoff} : HHG cutoff energy calculated with the classical formula (29), and P_I : ionization probability at the conclusion of the pulse.

	He	Ne	Be	Mg
I_p (eV)	24.6	21.6	9.32	7.65
λ (nm)	800	800	2000	3200
I_0 (W/cm ²)	1.15×10^{15}	1×10^{15}	5×10^{13}	1.6×10^{13}
γ	0.425	0.426	0.501	0.502
E_{cutoff} (eV)	242	211	68.5	56.1
P_I	0.03	0.07	0.10	0.03

and HHG in multielectron systems. As prototypical examples, we consider the noble gas atoms He and Ne and the alkaline-earth atoms Be and Mg (see Table I). As the driving field, we use a two-cycle laser pulse given by

$$A_z(t) = -c \int_{-\infty}^t F(t') dt', \quad (26)$$

$$F(t) = \begin{cases} 0, & t \leq 0, \\ F_0 \cos(\omega t) \sin^2\left(\frac{\omega t}{4}\right), & 0 < t \leq 2T, \\ 0, & t > 2T, \end{cases} \quad (27)$$

linearly polarized in the z direction with intensities $I = cF_0^2/8\pi$ (Table I). The choice of this two-cycle laser field [see Fig. 1(a)] is motivated by the fact that for this field we can identify and analyze two different ionization scenarios triggered by the same pulse. One sequence starts with the ionization by a still (relatively) weak field near the first extremum [a minimum in Fig. 1(a)], followed by acceleration of the liberated electron by a stronger field near the second extremum [a maximum in Fig. 1(a)]. The other sequence starts with the ionization burst triggered by the strong field near this maximum, followed by acceleration by the already weaker field near the third extremum. Contributions from these two

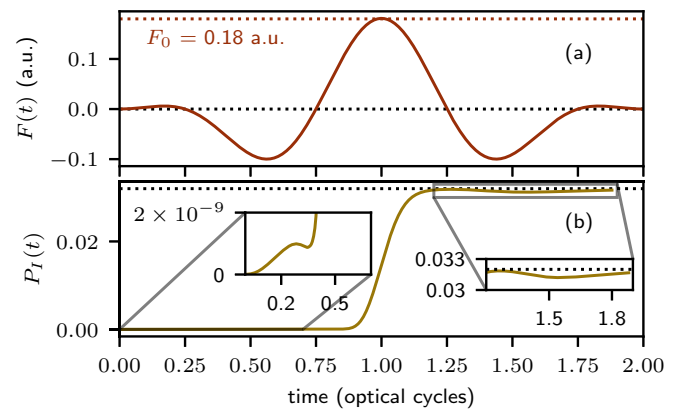


FIG. 1. (a) Two-cycle pulse $F(t)$ oriented along the z axis with peak field strength $F_0 = 0.18$ for He. (b) The single-ionization probability $P_I(t)$ [Eq. (31)] for He as a function of time for $R_I = 20$ on a linear scale; small deviations from the monotonic increase are shown on an expanded linear scale in the subframes.

processes can be well distinguished from each other in the resulting HHG spectrum as their respective yields are, as suggested by the three-step model, governed by the product of the ionization rate $\dot{N}_{\text{ion}}$ at the ionization time t_{ion} and the recombination probability P_{rec} at the time t_{rec} :

$$I^{\text{HHG}} \propto \dot{N}_{\text{ion}}(t_{\text{ion}})P_{\text{rec}}(t_{\text{rec}}). \quad (28)$$

The first sequence can reach the cutoff energy

$$E_{\text{cutoff}} = 3.17U_p + I_p, \quad (29)$$

corresponding to the ponderomotive energy $U_p = \frac{F_0^2}{4\omega^2}$ of the peak field and I_p the ionization energy. However, it has a lower yield than the second sequence since the tunnel ionization rate $\dot{N}_{\text{ion}}$ is still relatively small near the first field extremum. In turn, the second sequence can only reach a much lower energy since the electron is accelerated by an already diminished field. The present choice of the field parameters (F_0 and ω) is furthermore optimized such that significant one-electron ionization takes place while two-electron ionization remains negligible. With this choice, specific correlation effects that can be attributed to double ionization (see, e.g., Ref. [33]) are largely suppressed.

In order to realize comparable scenarios for the different atomic species, we have chosen the laser parameters such that the corresponding Keldysh parameter

$$\gamma = \sqrt{\frac{I_p}{2U_p}} \quad (30)$$

is similar ($\gamma \approx 0.5$) for all four cases despite the large differences in the ionization potentials I_p (Table I).

The one-electron ionization probability is calculated from

$$P_I(t) = \int_{|r| > R_I} d^3r \rho(\mathbf{r}, t) \quad (31)$$

with the electron density given by the diagonal elements of the 1RDM in spatial representation $\rho(\mathbf{r}, t) = \sum_{\sigma} D_1(\mathbf{r}, \sigma, \mathbf{r}, \sigma; t)$. (For numerical values of R_I see Appendix A.) Since the double ionization probability remains negligible in the present simulations, the ionization rate in Eq. (28) can be obtained from

$$\dot{N}_{\text{ion}}(t) = \frac{d}{dt} P_I(t). \quad (32)$$

While Eq. (31) can serve as a reliable measure for the ionization probability only for sufficiently large R_I and after the conclusion of the pulse, the time-dependent ionization rate $\dot{N}_{\text{ion}}(t)$ can be used to approximately characterize the ionization burst during tunneling or over-the-barrier ionization also in the presence of the laser field.

For the present numerical results, we determine the “exact” (i.e., converged) time-dependent N -electron wavefunction $|\Psi(t)\rangle$ from the solution of the Schrödinger equation [Eq. (1)] using the MCTDHF method [43–48]. Briefly, the ansatz for the wavefunction is given by

$$|\Psi(t)\rangle = \sum_J C_J(t) |\Phi_J(t)\rangle, \quad (33)$$

with the time-dependent configuration-interaction coefficients $C_J(t)$, and $|\Phi_J(t)\rangle$ the corresponding Slater-determinant ba-

sis built from $2M$ time-dependent spin orbitals $\{|\xi_i(t)\rangle\}$ with $|\xi_i\rangle = |\varphi_{q_i}\rangle \otimes |\sigma_i\rangle$ and $i = (q_i, \sigma_i) = (nl_{m_i}, \uparrow)$ for $i < M$ and $(nl_{m_i}, \downarrow)$ for $i > M$ (where we use the standard spectroscopy labeling for the orbitals according to their zero-field designation). The sum in Eq. (33) runs over all possible Slater determinants built from the $2M$ spin orbitals. The fact that within the MCTDHF method the orbitals can self-consistently adapt to external driving is crucial for simulations of the multielectron dynamics in strong fields. Any stationary basis would require a prohibitively large number of configurations in Eq. (33). For the orbitals entering the Slater-determinant basis, a partial-wave expansion

$$\varphi_{k,m}(r, \theta, \phi, t) = \sum_{l=0}^{l_{\text{max}}} R_{k,m}^l(r, t) Y_{lm}(\theta, \phi) \quad (34)$$

with l_{max} depending on the atom varying from 47 to 95 (for details see Appendix A) is employed accounting for the l mixing by the driving field. For linear polarization along the z axis [see Eq. (27)], the magnetic quantum number m is preserved.

From the propagated wavefunction $|\Psi(t)\rangle$, the reduced density matrix [Eq. (5)], the corresponding measures of correlations [Eqs. (23) and (14)], and the HHG spectra [Eq. (3)] are deduced.

B. Dynamics of correlations

The time-dependent variation of the ionization probability $P_I(t)$ [Eq. (31)] driven by the pulse displayed in Fig. 1(a) is shown for He in Fig. 1(b). $P_I(t)$ is an almost monotonically increasing function during the central half cycle with the half-way point at the center of the pulse, $P_I(1.0T) = P_I(\infty)/2$ with $P_I = P_I(\infty) = 0.03$. Small modulations due to the first ionization burst near $t = 0.3T$ and during rescattering or recombination near $t = 1.5T$ become visible only on an expanded scale [Fig. 1(b)]. Structurally identical results (not shown) are found for Ne with $P_I = 0.07$, Be with $P_I = 0.10$, and Mg with $P_I = 0.03$.

Changes in the occupation numbers of the natural orbitals under the influence of strong-field driving [Eq. (18)] are displayed for He in Fig. 2(a), where we compare the initial (ground)-state occupation numbers at $t = 0$ with those at $t = 1.05T$ (i.e., close to the peak of the field at $t = T$). At this particular instant of time, the maximum in the correlation measures is reached as shown in Fig. 4(a). Note that for convenience the labeling of the natural orbital occupation numbers in Fig. 2 and the following figures refers to their initial ground-state designation. In the presence of the driving field, the radial shapes of the natural orbitals as well as their l characteristics are strongly perturbed. Since the initial state includes ground-state correlations, the “Fermi edge” in the occupation numbers is not a perfect step function at $t = 0$ [compare with Eq. (8)] but (slightly) smoothed. Under the influence of the strong-field driving, the Fermi edge gets further smoothed as the population is shifted to additional higher orbitals. While the latter appears to be, at first glance, intuitively obvious, it represents, in fact, a nontrivial dynamical correlation effect as changes in the occupation of the natural orbitals are exclusively driven by the two-particle

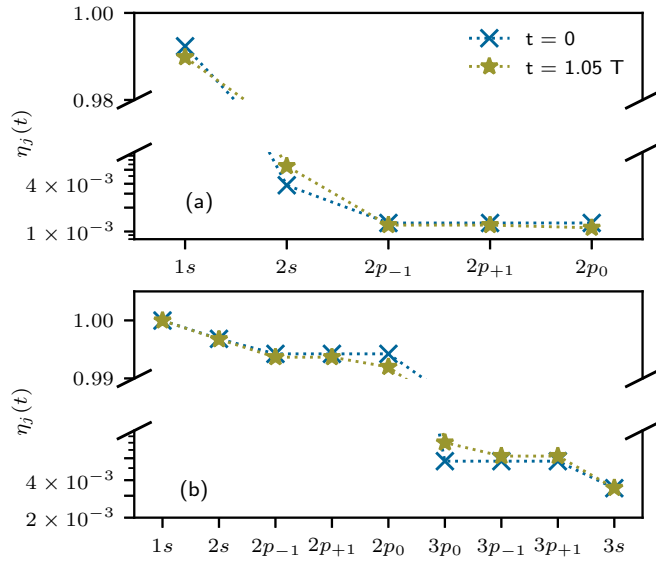


FIG. 2. Snapshots of occupation numbers for natural orbitals with spin-up of noble gas atoms He [panel (a)] and Ne [panel (b)] prior to the pulse ($t = 0$) and near the peak of the pulse strength ($t = 1.05 T$) (field parameters as described in the text). The natural orbitals are labeled according to their zero-field designation, and spin-up and spin-down occupation numbers are identical. Note the change in scale to display small occupation numbers above the Fermi edge.

correlator [Eq. (18)], while strong-field and mean-field effects are, to leading order, already included in the (occupied) natural orbitals themselves [Eq. (20)]. A qualitatively very similar pattern emerges for Ne [Fig. 2(b)]. In contrast, for the alkaline-earth atoms Be [Fig. 3(a)] and Mg [Fig. 3(b)], a markedly and surprisingly different time evolution of the

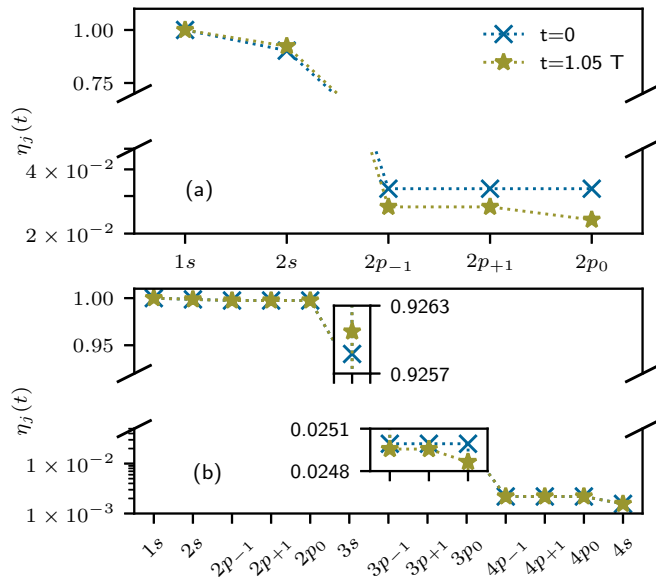


FIG. 3. Same as Fig. 2 but for the alkaline-earth atoms Be [panel (a)] and Mg [panel (b)], where the subframes show zoomed in images of the HONO and LUNO orbitals to enhance the visibility of small changes.

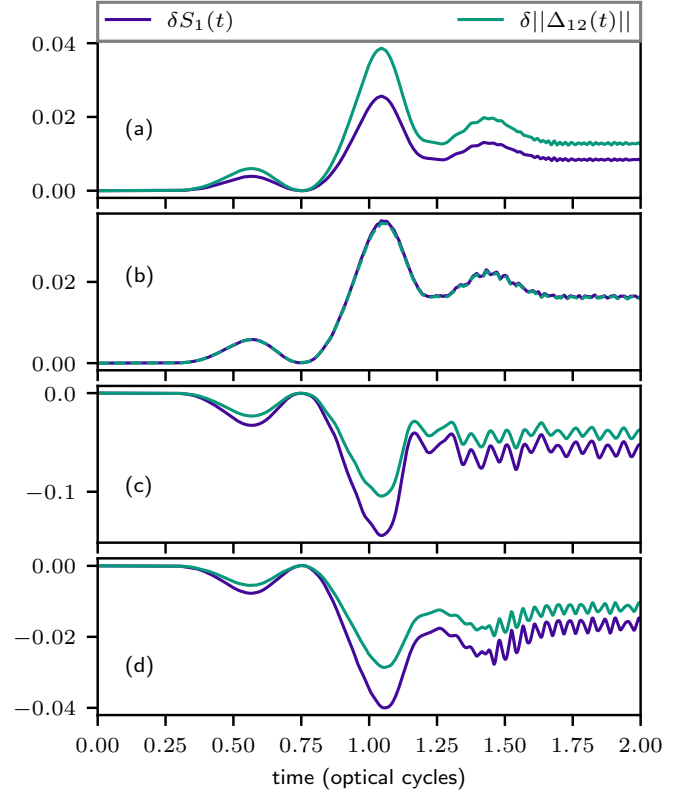


FIG. 4. Measures for dynamical correlations. Variation of the von Neumann entropy $\delta S_1(t) = S_1(t) - S_1(0)$ and of the norm of the two-particle cumulant $\delta ||\Delta_{12}(t)|| = ||\Delta_{12}(t)|| - ||\Delta_{12}(0)||$ for (a) He, (b) Ne, (c) Be, and (d) Mg. Note the sign change between panels (a), (b) and (c), (d).

natural orbital occupation is observed. The Fermi edge of the occupation numbers gets sharper in the presence of the strong field rather than smoother.

These trends observed by the snapshots at $t = 1.05 T$ are confirmed by the time dependence of the correlation measures, the field-induced temporal variation of entropy S_1 , $\delta S_1(t) = S_1(t) - S_1(0)$, and of the variation of the norm of the cumulant $\delta ||\Delta_{12}(t)|| = ||\Delta_{12}(t)|| - ||\Delta_{12}(0)||$ (Fig. 4). While the von Neumann entropy and the norm of the two-particle correlator both increase—even though nonmonotonically—during the strong-field driving of He and Ne, they decrease for Be and Mg. For all systems investigated, the time evolution of these two complementary measures of correlations closely agrees with each other, supporting the notion of the close correspondence between entanglement and correlations for strongly driven fermionic systems. The local extrema of the correlation measures are approximately (but not exactly) synchronized with the extrema of the field amplitude. For the noble gases, the dynamic correlation has local maxima near the field extrema, while for alkaline-earth atoms these correspond to local minima.

A simple qualitative explanation of the different correlation dynamics for noble-gas and alkaline-earth atoms refers to the electronic structure of the initial ground state: For noble gas atoms, the strong-field excitation and ionization opens their initial closed-shell electronic structure, thereby naturally

increasing correlation effects. By contrast, for alkaline-earth atoms with two relatively weakly bound electrons outside the noble-gas closed-shell configuration featuring (relatively) strong correlations in their initial ground state prior to the interaction with the laser field, strong-field ionization of one of these electrons results in an increased phase-space (i.e., position and momentum) separation between this electron pair, thereby reducing electron correlations.

A more detailed quantitative analysis requires the investigation of the properties of the collision operator [Eq. (18)] governing the influence of two-particle correlations on the natural orbitals and their occupation [Eq. (12)]. Taking into account that during the time evolution in the laser field both $\hat{C}_1(t)$ and the natural orbitals $|\eta_j(t)\rangle$ acquire complex phases, the time differential change in the occupation number [Eq. (18)] is governed by the matrix element of the collision operator

$$\begin{aligned} \text{Im}\langle\eta_j|\hat{C}_1|\eta_j\rangle &= \sum_{\sigma_1} \int d^3r_1 d^3r'_1 C_1^I(\mathbf{r}_1, \sigma_1, \mathbf{r}'_1, \sigma_1) \\ &\quad \times [v_{q_j}^R(\mathbf{r}_1)v_{q_j}^R(\mathbf{r}'_1) + v_{q_j}^I(\mathbf{r}_1)v_{q_j}^I(\mathbf{r}'_1)] \\ &\quad + \sum_{\sigma_1} \int d^3r_1 d^3r'_1 C_1^R(\mathbf{r}_1, \sigma_1, \mathbf{r}'_1, \sigma_1) \\ &\quad \times [v_{q_j}^R(\mathbf{r}_1)v_{q_j}^I(\mathbf{r}'_1) - v_{q_j}^I(\mathbf{r}_1)v_{q_j}^R(\mathbf{r}'_1)], \quad (35) \end{aligned}$$

with $v_{q_j}^R(\mathbf{r}_1) = \text{Re } v_{q_j}(\mathbf{r}_1)$, $v_{q_j}^I(\mathbf{r}_1) = \text{Im } v_{q_j}(\mathbf{r}_1)$, $C_1^R = \text{Re } C_1$, and $C_1^I = \text{Im } C_1$. To explore the local behavior of the collision operator along the field direction (z), we rewrite this matrix elements as

$$\text{Im}\langle\eta_j|\hat{C}_1|\eta_j\rangle = \int dz_1 \int dz'_1 \text{Im}(\eta_j|\hat{C}_1(z_1, z'_1)|\eta_j), \quad (36)$$

where the parentheses stand for the integration over the transverse coordinates (x_1, y_1, x'_1, y'_1) only. We study the spatially resolved time variation of $\text{Im}(\eta_j|\hat{C}_1(z_1, z'_1)|\eta_j)$. The physical interpretation of the diagonal elements of the collision operator $\text{Im}(\eta_j|\hat{C}_1(z_1, z'_1)|\eta_j)$ is that of a local one-particle transition rate per unit time and unit area for a projected population of the natural orbital j when one (projected) coordinate of the natural orbital along the direction of the driving field is at z_1 and the other at z'_1 . We focus on the matrix elements for the two orbitals closest to the Fermi edge set at $\eta_j = 0.5$, with the highest (i.e., strongly) occupied natural orbital (HONO), $\eta_j > 0.5$, and the lowest unoccupied (more precisely, weakly occupied) natural orbital (LUNO), $\eta_j < 0.5$. We take snapshots of their distributions in the $z_1 - z'_1$ plane at the instants of time when the population transfer between them ($\sim |d\eta_j/dt|$) has local maxima (e.g., $0.45T$, $0.95T$, $1.15T$, and $1.50T$ for He).

Figure 5 shows $\text{Im}(\eta_j|\hat{C}_1(z_1, z'_1)|\eta_j)$ for He for which the first two natural orbitals are the HONO ($q_1 = 1s$) and the LUNO ($q_2 = 2s$). For simplicity, we label them by their ground-state designation in the absence of the laser field, even though their angular and radial nodal structures are distorted

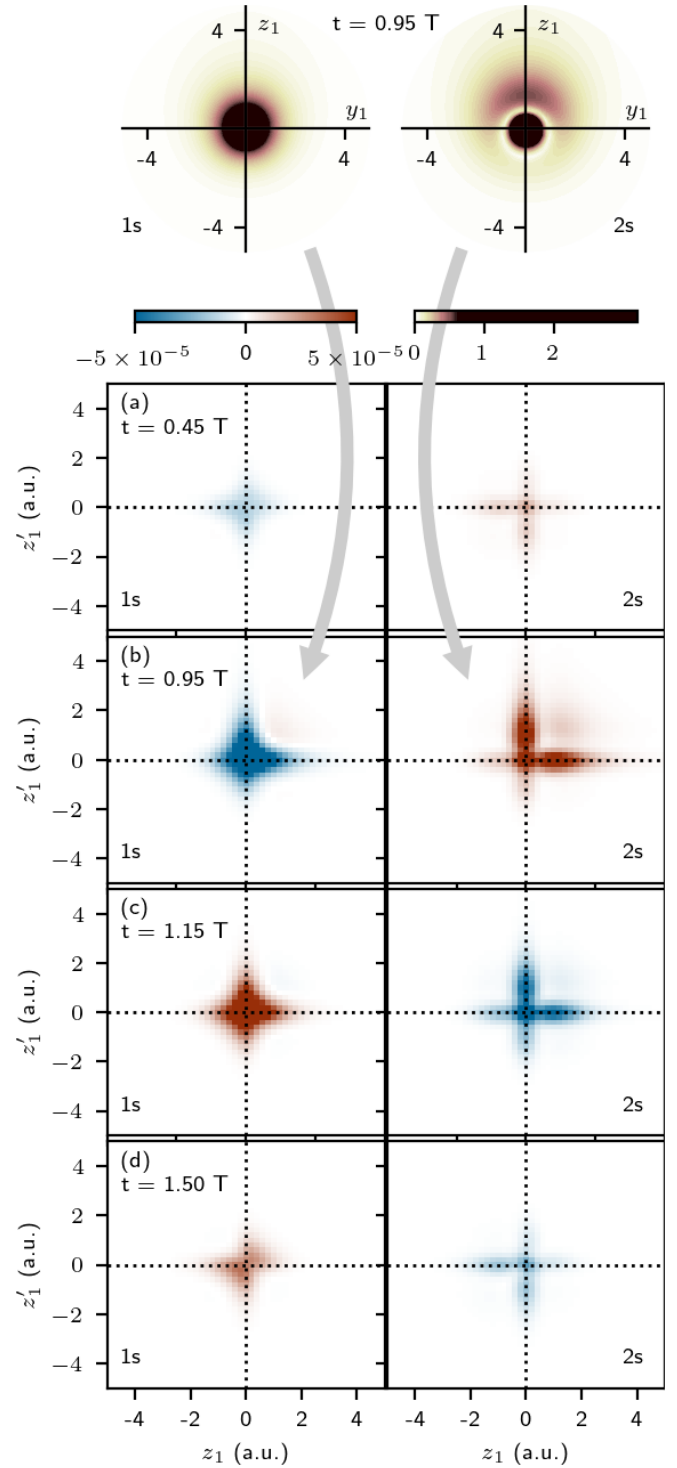


FIG. 5. Spatial distribution of $\text{Im}(\eta_j|\hat{C}_1(z_1, z'_1)|\eta_j)$ in the $z_1 - z'_1$ plane for the HONO (left) and the LUNO (right) of He at (a) $t = 0.45T$, (b) $t = 0.95T$, (c) $t = 1.15T$, and (d) $t = 1.50T$. Source regions with positive values of $\text{Im}(\eta_j|\hat{C}_1(z_1, z'_1)|\eta_j)$ in red, sinks in blue. The two top frames display the magnitude of the spatial HONO and LUNO orbitals in the $x_1 = 0$ plane $|v_{q_j}(x_1 = 0, y_1, z_1; t)|$ at time $t = 0.95T$.

by the driving field. On the rising flank of the pulse envelope (at $t = 0.45T$ and $t = 0.95T$), the population flux is directed from the HONO ($1s$) to the LUNO ($2s$) as expected from the smoothing of the Fermi edge [Fig. 2(a)]. This correlation-

induced flux originates predominantly from the region in the $z_1 - z'_1$ plane where both coordinates are on the same side of the atom near the tunneling barrier, i.e., in the third quadrant at $t = 0.45T$ and in the first quadrant at $t = 0.95T$ (Fig. 5). Tunneling (or over-barrier) excitation and ionization dynamics thus enhances the correlation-induced transfer at closely spaced coordinate pairs in He. On the falling flank of the envelope (at $t = 1.15T$ and $t = 1.50T$), the population flux originates again preferentially from regions on the same side of the atom near the barrier (first quadrant at $t = 1.15T$, third quadrant at $t = 1.50T$), but the direction of the flux is now reversed, i.e., from the LUNO to the HONO. The latter signifies the field-driven return to the ionic core of the ionized wave packet, where a small portion of it will recombine. A qualitatively similar pattern emerges for Ne (Fig. 6). In this case, the $z_1 - z'_1$ distribution of $\text{Im}(\eta_j|\hat{C}_1|\eta_j)$ displays a more complex nodal structure with nodal planes $z_1 = 0$ and $z'_1 = 0$ of the $2p_0$ and $3p_0$ orbitals visible. In addition, also remnants of the radial node of the $3p_0$ orbital are recognizable, similar to those of the $2s$ orbitals for He (Fig. 5). Overall, the temporal evolution of the matrix element of the collision operator for the HONO and LUNO closely matches that of He, underscoring the structurally similar response of noble gas atoms to strong driving. Both the direction of flux between HONO and LUNO and the preferred region of its origin in the $z_1 - z'_1$ plane, on the same side and near the lowered tunneling barrier, agree.

Drastically different $z_1 - z'_1$ distributions of the matrix elements of the collision operator are found for the alkaline-earth atoms Be (Fig. 7) and Mg (Fig. 8). The direction of flux between HONO and LUNO in the alkaline-earth atoms is opposed to that in the noble gas atoms. As strong-field ionization increases on the rising flank of the pulse, the flux is directed from the LUNO to the HONO, while on the falling flank the flux is heading back toward the LUNO. As in Figs. 5 and 6 for He and Ne, Figs. 7 and 8 show the instances of time when the time derivative of the HONO occupation has local extrema. These are now minima on the rising flank and maxima on the falling flank of the field. Interestingly, these instances of time are also slightly different compared to those for He and Ne. This is most likely due to the involvement of the $2p_{\pm 1}$ orbitals in Be and $3p_{\pm 1}$ orbitals in Mg. Even more surprising and important is the fact that the spatial distributions of the collision operator are entirely different for the earth-alkaline atoms compared to the noble gas atoms: Sinks and sources of the flux are predominantly localized on opposite sides of the atom (i.e., in the second and fourth quadrants) with only one coordinate near the tunneling barrier and larger distances between z_1 and z'_1 . This is a consequence of the fact that the initial state of the two electrons outside the closed shell is both more strongly correlated and more delocalized. Furthermore, the positions of the peaks of the sinks and sources are only slightly affected by the strong field, displaying only slight shifts along the direction of the field ionization, i.e., along the diagonal coordinate $z_1 + z'_1$.

Unlike for noble gases, the LUNO for alkaline-earth atoms features in addition to the dominant flux contribution from the second and fourth quadrants also a weak but clearly visible contribution of flux in the opposite direction stem-

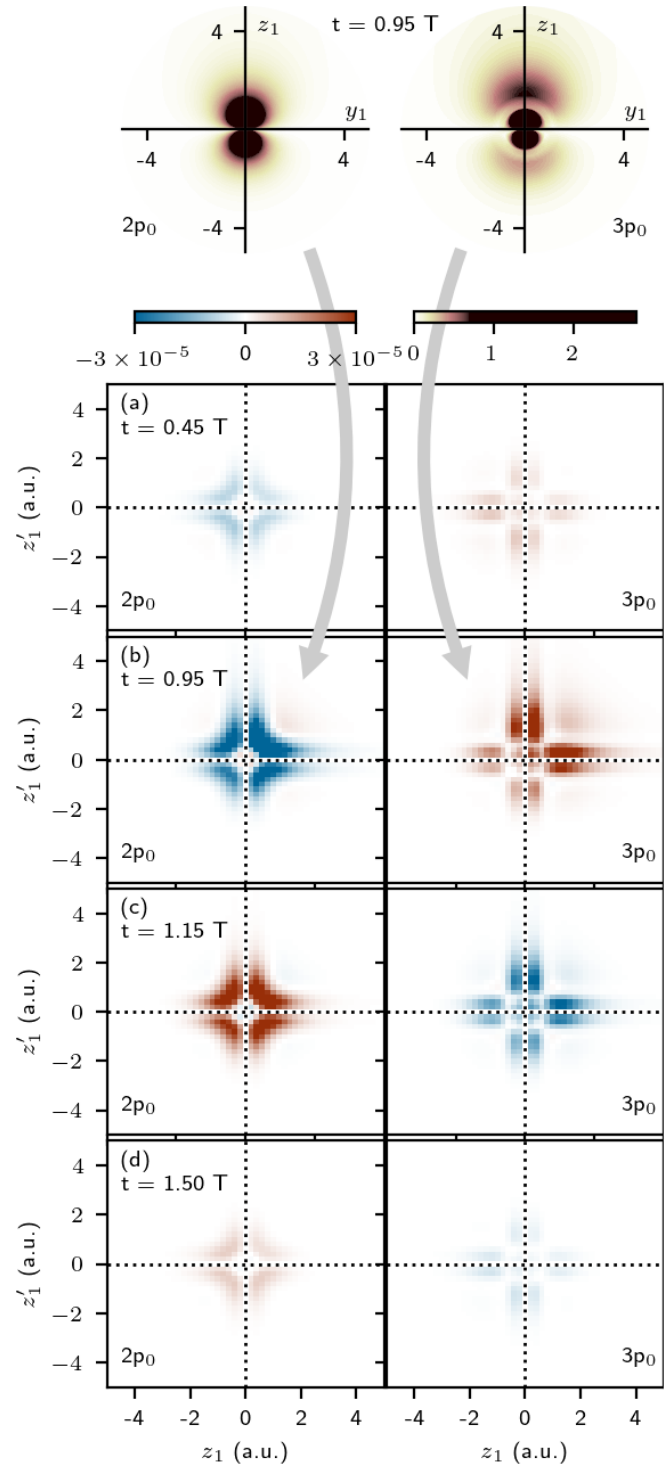


FIG. 6. As Fig. 5, but for Ne.

ming from the first and third quadrants (Figs. 7 and 8). This pattern originates most likely from the change of parity under the reflection symmetry R_z ($z \rightarrow -z$) when transitioning between the R_z -even HONO ($2s$ in Be, $3s$ in Mg) and the R_z -odd LUNO ($2p_0$ in Be, $3p_0$ in Mg). The influence of the nodal plane ($z_1 = 0$) remains also clearly visible in the $x_1 = 0$ cut of the magnitude of the spatial orbitals $|\nu_{q_j}(x_1 = 0, y_1, z_1; t)|$ of the HONO and LUNO displayed in the top

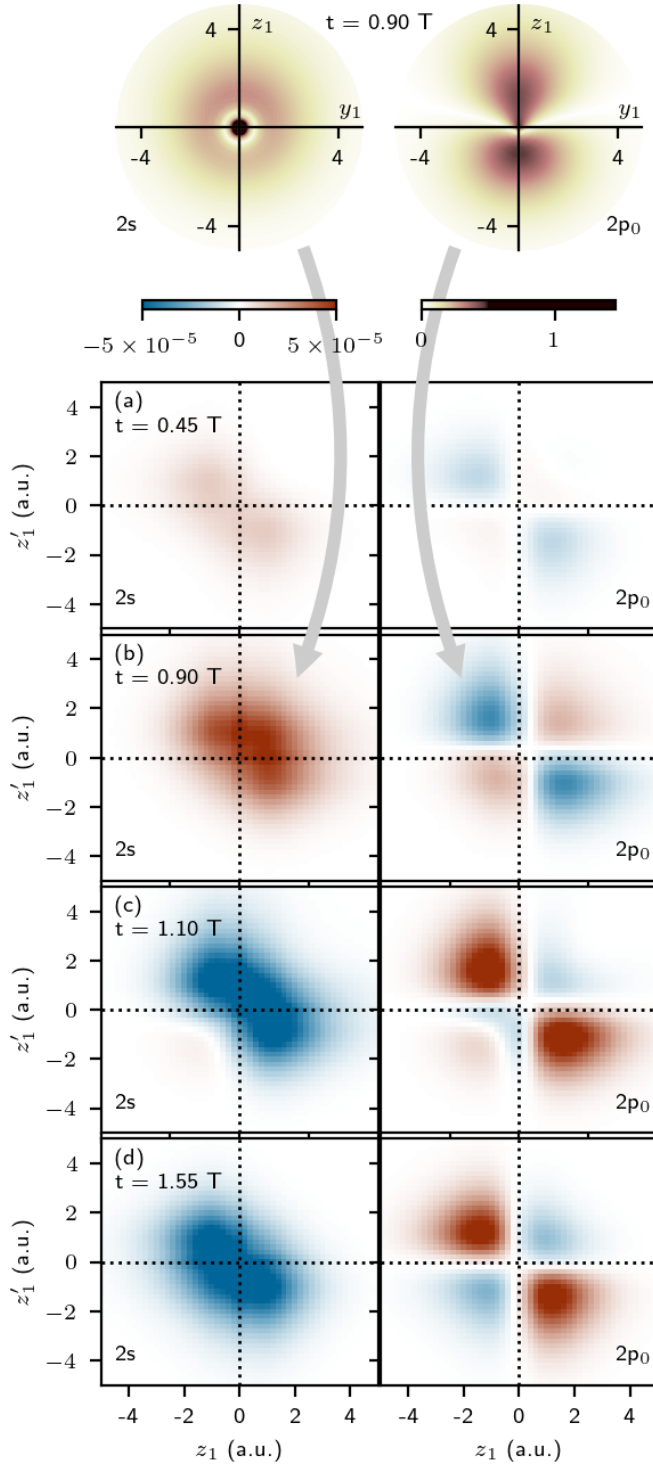


FIG. 7. As Fig. 5, but for Be and at (a) $t = 0.45T$, (b) $t = 0.90T$, (c) $t = 1.10T$, and (d) $t = 1.55T$.

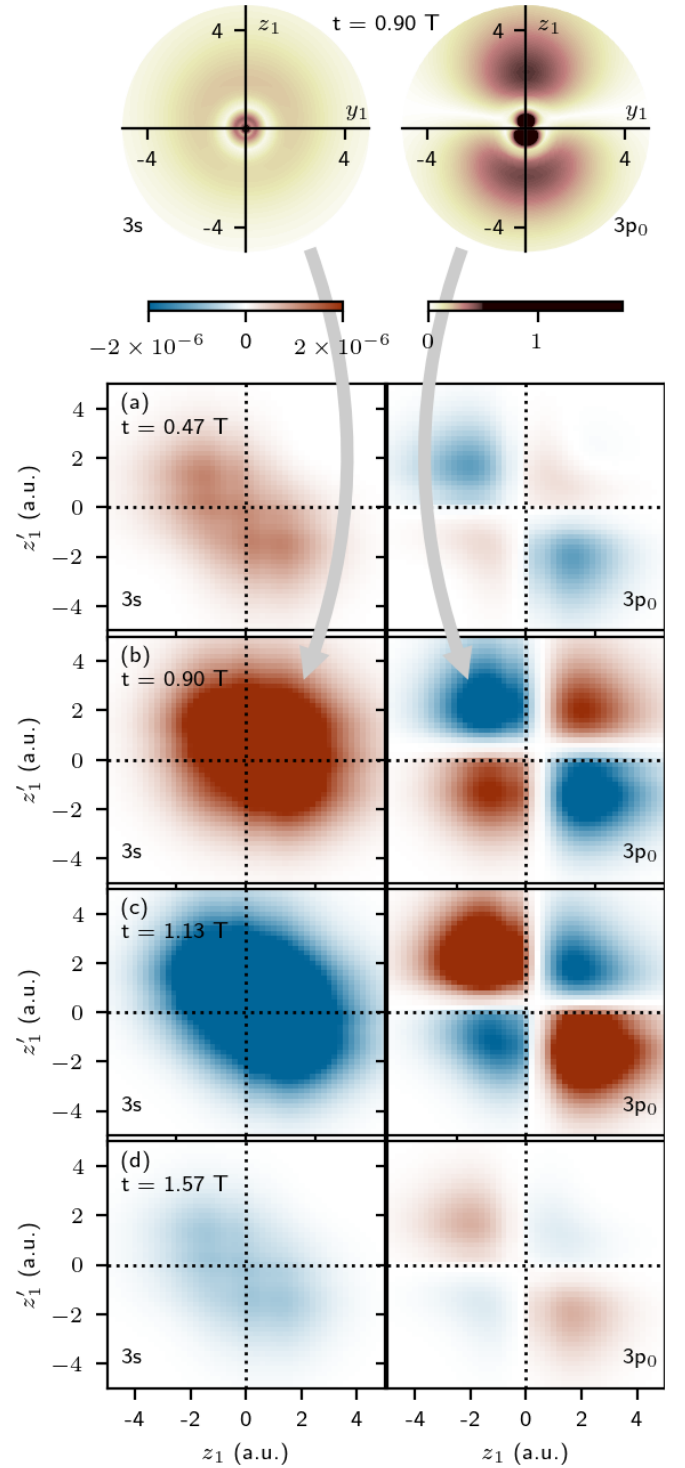


FIG. 8. As Fig. 5, but for Mg and at (a) $t = 0.47T$, (b) $t = 0.90T$, (c) $t = 1.13T$, and (d) $t = 1.57T$.

C. HHG spectra

frames of Figs. 5–8. For noble gases, the nodal plane (or its absence) is preserved in the transition between HONO and LUNO, while for alkaline-earth atoms the nodal plane appears (or disappears) when switching between the HONO and the LUNO.

We turn now to the impact of the time-dependent dynamic electron correlations on HHG. Unambiguously separating correlation effects from mean-field effects in a strong-field scenario has remained a challenge, which we attempt to address in the following. We emphasize that we focus here on the single-atom response omitting from the results propagation

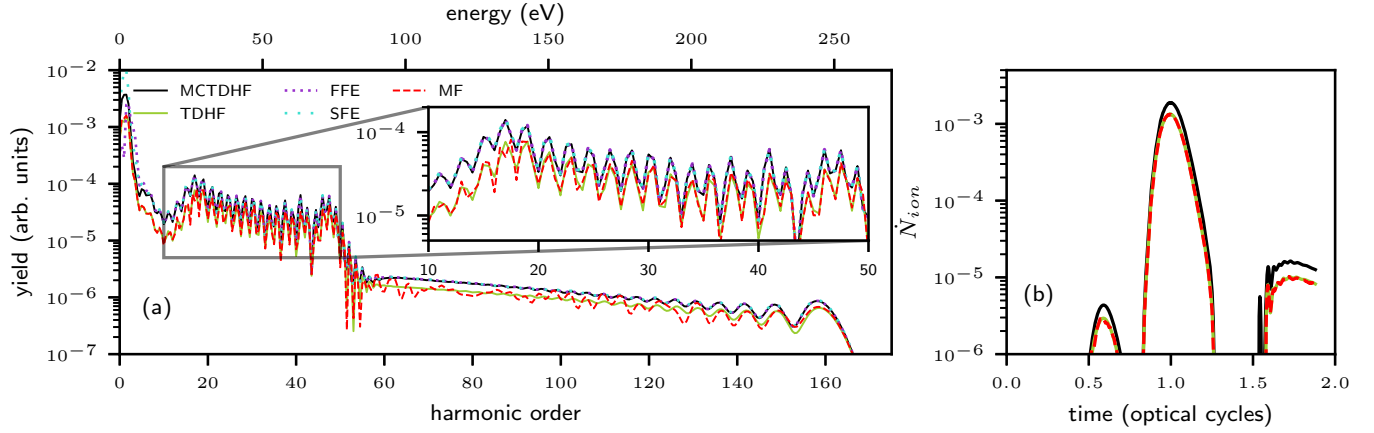


FIG. 9. He driven by a strong two-cycle laser field with parameters according to Table I. (a) HHG spectrum obtained by MCTDHF (black), TDHF (green), MF (red), FFE (purple), and SFE (blue). Note that FFE and SFE nearly coincide with MCTDHF. Inset: Magnification of the harmonics in the region of the first plateau. (b) Ionization rate $\dot{N}_{\text{ion}}$ as a function of time [Eq. (32)]; same color code as in panel (a).

effects and ensemble averages, which would need to be included when simulating HHG spectra of a realistic gas target.

The most straightforward approach is the direct comparison between the HHG spectra from a calculation that fully includes correlations taken to be in the following from the MCTDHF method and those from well-established mean-field methods such as TDHF, which excludes correlations [see Figs. 9–12(a)], or TDDFT [see Fig. 12(a) and Appendix B], which includes correlations only indirectly via an effective one-particle exchange-and-correlation potential. An example of such a comparison is shown in Fig. 12 for Mg (additional data for other atoms is shown in Appendix B, Fig. 13). All spectra display the expected two-plateau structure. For Mg (Fig. 12), the higher-intensity plateau extending to about the 60th harmonic originates from the strongest ionization burst near the center of the pulse ($t \approx T$) [peak in $\dot{N}_{\text{ion}}$ see Fig. 12(b)] where the electrons are accelerated by and driven back to the ion by the laser pulse with the amplitude already diminished. The low-intensity plateau extends all the way to about the 160th harmonic stemming from the first ionization burst generated by the still relatively weak field at $t \approx 0.5T$

[Fig. 12(b)], followed by the acceleration by the stronger field around $t \approx T$. The relative height of the plateaus [Fig. 12(a)] is controlled by the strength of the respective ionization bursts [Fig. 12(b)]. For example, the difference in strength between the first and second ionization bursts is much larger in MCTDHF than in TDDFT. This translates into a pronounced height difference between the first and second plateaus of the HHG spectrum predicted by MCTDHF, as compared to TDDFT.

The significant discrepancies between the HHG spectra predicted by the fully correlated MCTDHF and the mean-field calculations (TDDFT or TDHF) cannot be immediately attributed to the effect of dynamic correlations, as already differences in the initial ground state, in particular, differences in the respective ionization potentials as well as differences in the mean-field dynamics, can contribute to such discrepancies. To unambiguously pinpoint the role of the dynamical change in the correlations (increase for noble gas atoms and decrease for alkaline-earth atoms), the present formulation in terms of RDMs allows to selectively switch on or off two-particle correlations during strong-field driving. We use for this purpose the collision operator $\hat{C}_1$ in the equations of motion for the

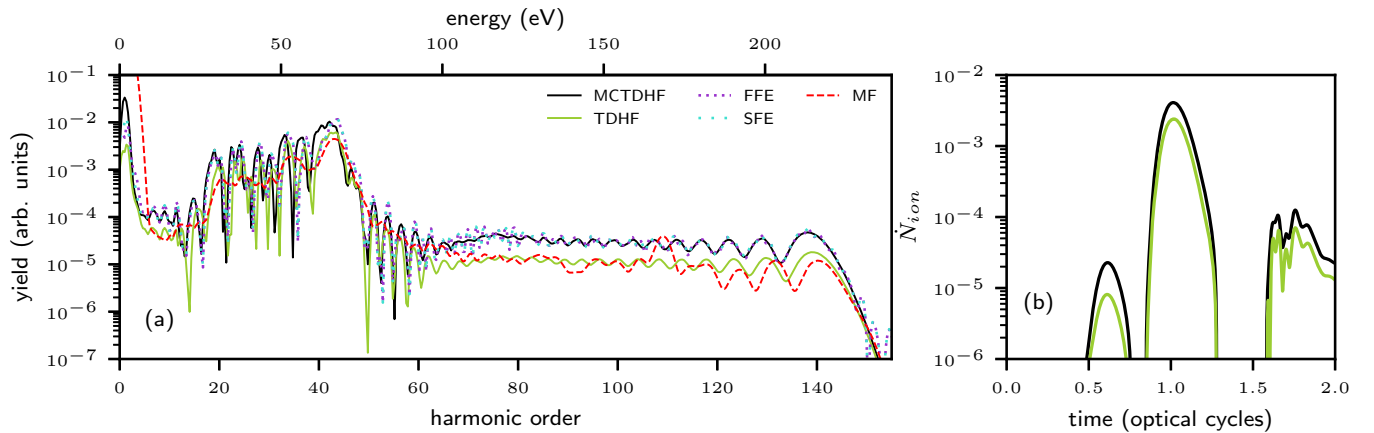


FIG. 10. Ne driven by a strong two-cycle laser field with parameters according to Table I. (a) HHG spectrum obtained by MCTDHF (black), TDHF (green), MF (red), FFE (purple), and SFE (blue). Note that FFE and SFE nearly coincide with MCTDHF. (b) Ionization rate $\dot{N}_{\text{ion}}$ [Eq. (32)]; same color code as in panel (a).

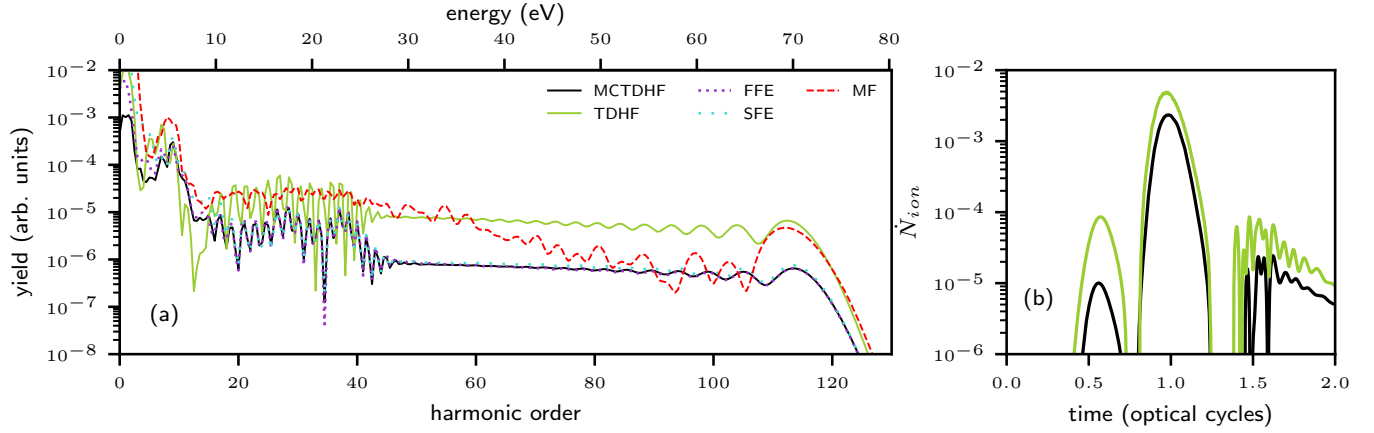


FIG. 11. Be driven by a strong two-cycle laser field with parameters according to Table I. (a) HHG spectrum obtained by MCTDHF (black), TDHF (green), MF (red), FFE (purple), and SFE (blue). Note that FFE and SFE nearly coincide with MCTDHF. (b) Ionization rate $\dot{N}_{\text{ion}}$ [Eq. (32)]; same color code as in panel (a).

natural orbital occupation numbers [Eq. (18)] and the natural orbitals [Eq. (20)].

Probing time-dependent dynamical correlation effects can proceed on different levels of approximation. Starting point is the same correlated initial state given by the natural orbitals $\{|\eta_j(0)\rangle\}_j$ and eigenvalues of the 1RDM, $\{\eta_j(0)\}_j$, derived from the MCTDHF calculations. Initial ground-state correlations, unlike time-dependent variations of correlations, are, thus, fully included. Orbitals and/or occupation numbers are, then, propagated without including the collision operator. Setting $\hat{C}_1 = 0$ (or $\Delta_{12} = 0$) in both Eqs. (18) and (20), the orbitals propagate only under the influence of the mean-field (MF) operator [first two lines on the right-hand side of Eq. (20)], $|\eta_j^{\text{MF}}(t)\rangle$, with the initial state taken to be the exact ground-state natural orbital $|\eta_j^{\text{MF}}(0)\rangle = |\eta_j(0)\rangle$ with occupation numbers $\eta_j(0)$. The latter remain constant when $\hat{C}_1 = 0$ [see Eq. (18)]. Within this approximation, the change of correlations over time in both the occupation numbers and the orbitals is neglected and the dipole acceleration describing the emitted radiation of the atomic “antennas” [compare with

Eq. (11)] is given by

$$\mathbf{a}_{\text{MF}}(t) = \sum_j \eta_j(0) \langle \eta_j^{\text{MF}}(t) | \hat{\mathbf{a}}_1 | \eta_j^{\text{MF}}(t) \rangle. \quad (37)$$

It should be noted that with this choice the initial states are not eigenstates of the MF propagator. This results in additional high-frequency oscillations (“beats”) unrelated to strong driving, which should be removed when analyzing the spectrum.

A less drastic approximation consists of neglecting only the changes in the natural orbital occupation numbers driven by the time-varying correlations, i.e., setting the collision operator $\hat{C}_1 = 0$ only in Eq. (18) but not in Eq. (20). This amounts to a frozen Fermi edge (FFE) of the initial state by neglecting its time-dependent variation while including the full evolution of the natural orbitals themselves. In this approximation, the dipole acceleration is given by

$$\mathbf{a}_{\text{FFE}}(t) = \sum_j \eta_j(0) \langle \eta_j(t) | \hat{\mathbf{a}}_1 | \eta_j(t) \rangle. \quad (38)$$

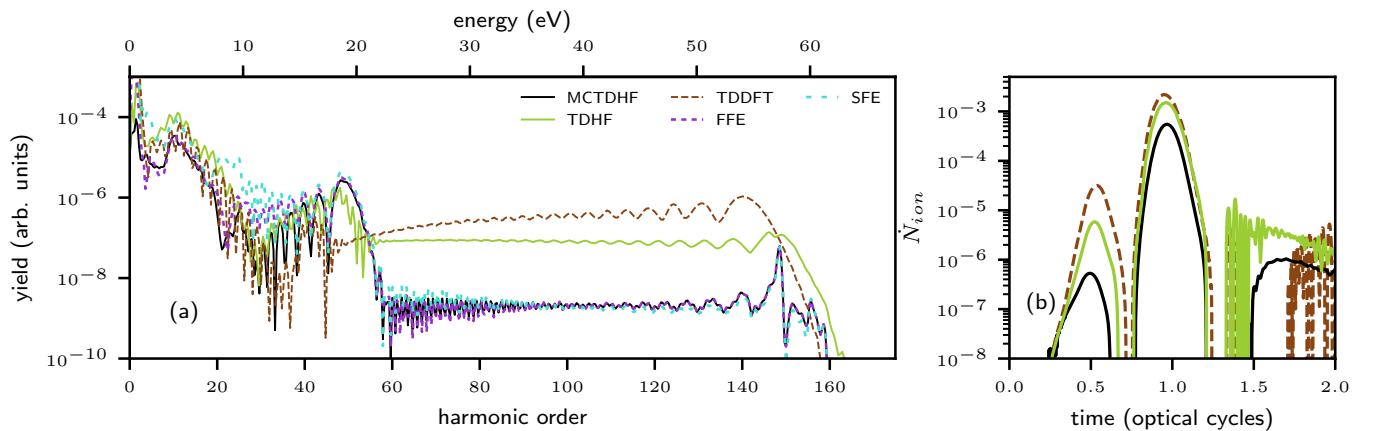


FIG. 12. Mg driven by a strong two-cycle laser field with parameters according to Table I. (a) HHG spectrum obtained by MCTDHF (black), TDHF (green), TDDFT (brown), FFE (purple), and SFE (blue). (b) Ionization rate $\dot{N}_{\text{ion}}$ [Eq. (32)]; same color code as in panel (a).

Furthermore, in the limiting case where the shape of the initial Fermi edge is entirely neglected and the occupation numbers are set to those of the Hartree-Fock approximation, which features a sharp Fermi edge (SFE) [Eq. (9)], but the correlated orbital propagation is still fully included, Eq. (38) reduces to

$$a_{\text{SFE}}(t) = \sum_{j=1}^{N_{\text{occ}}} \langle \eta_j(t) | \hat{a}_1 | \eta_j(t) \rangle. \quad (39)$$

Comparing the HHG spectra predicted by Eqs. (37)–(39) with those resulting from fully correlated dynamics allows us to assess in detail the influence of different contributions to time-dependent dynamic correlations. Examples are presented for helium [Fig. 9(a)], Ne [Fig. 10(a)], Be [Fig. 11(a)], and Mg [Fig. 12(a)]. Results for the MF model [Eq. (37)] are only shown for the cases where numerical convergence could be achieved [Figs. 9, 10(a), and 11(a)]. Consistent with the relatively small correlation-induced changes of the occupation numbers relative to the sharp Fermi edge (Figs. 2 and 3), the FFE and SFE models [Eqs. (38) and (39)], which involve only approximations to the occupation numbers $\eta_j(t)$ while fully accounting for correlation dynamics of the natural orbitals $|\eta_j(t)\rangle$, yield HHG spectra in close agreement with the full MCTDHF calculation in most cases. A remarkable exception are the lower harmonics for the alkaline-earth atoms [Figs. 11(a) and 12(a)]. In contrast, when neglecting two-particle correlations in the orbital propagation by using the MF propagation [Eq. (37)], i.e., setting $\hat{C}_1 = 0$ in the equations of motion, the resulting smoothed HHG spectra resemble those of the Hartree-Fock approximation. The drastic change in magnitude of the HHG spectrum by about one half to one order of magnitude in the second plateau region above the 50th harmonic between the TDHF and the MCTDHF can thus unambiguously be assigned to the direct influence of the collision operator representing two-particle correlation effects beyond the mean field on the dynamics of the natural orbitals. Furthermore, this influence on the spectra can be traced back to a considerable extent to its influence on the subcycle ionization bursts $\dot{N}_{\text{ion}}(t)$ [see Fig. 9(b)]. Electron-electron correlations enhance the (mostly tunneling) ionization rate in the noble gases (Fig. 9 for He and Fig. 10 for Ne), while $\dot{N}_{\text{ion}}(t)$ is reduced by correlations in the alkaline-earth atoms (Fig. 11 for Be and Fig. 12 for Mg). This opposing trend is consistent with the opposing direction of the probability flux in the collision operator $\text{Im}(\eta_j | \hat{C}_1(z_1, z'_1) | \eta_j)$ between HONO and LUNO (Figs. 6 and 7). While for noble gases the flux on the rising flank of the pulse that dominantly contributes to the high-energy plateau is directed from the HONO to the LUNO, for alkaline-earth atoms the direction is reversed. For magnesium, we also show TDDFT results (Fig. 12) that resemble those of TDHF but significantly differ from fully correlated MCTDHF results. In Appendix B, we show that these discrepancies persist irrespective of the choice of the exchange-correlation functional. The adiabatic TDDFT thus yields large, systematic deviations from the exact MCTDHF. Given the large size of the changes in the yields of the high harmonics due to dynamic correlations (see Fig. 12), we believe that such enhancement should be experimentally accessible. While a direct measurement of the *absolute* yield, e.g., of the high-energy harmonics of the second plateau,

would be challenging in view of the uncertainties due to propagation effects, focal point averaging, target gas density, and phase matching conditions, the *relative* change under variation of the mixing fraction of a gas mixture should allow to unambiguously identify correlation-induced variation of the HHG yield. For example, measuring the yields from a mixture of He and Ne at known and adjustable fractions should reveal that the yield from Ne is more than an order of magnitude larger than the yield from He, contrary to the prediction within mean-field methods, which predict almost the same yield.

VI. CONCLUSIONS AND OUTLOOK

We have investigated the role of dynamical electron correlations in multielectron atoms on ultrafast timescales. We have developed a 1RDM description within which the exact N -electron strong-field response entering the Larmor formula can be described by an ensemble of atomic oscillators, each of which is given by an eigenstate and eigenvalue of the 1RDM. This formulation can be viewed as the extension of Kuchiev's one-electron atomic antenna model [19] to an exact many-body description. For monitoring and following the dynamic correlations, we employ measures from quantum information theory.

Applications to noble gases (He, Ne) and alkaline-earth atoms (Be, Mg) reveal striking differences. While the correlation measures in the noble gas atoms develop local maxima at each extremum of the driving laser field, surprisingly, in the alkaline-earth atoms correlations feature local minima. By analyzing the matrix elements of the collision operator, we can attribute these dynamical changes in electronic correlations to the shape of the natural orbitals involved. At the present laser intensities, the natural orbitals approximately retain their original s - or p -wave character when they are distorted along the laser field. While in He and Ne the HONO and the LUNO have the same parity, in Be and Mg the HONO has an (approximate) s -wave character while the LUNO has an (approximate) p -wave character.

To pinpoint the influence of correlations on HHG, we decompose the exact evolution of the 1RDM in terms of the natural orbitals and their occupation numbers. While the time variation of the occupation numbers is exclusively due to two-particle correlations represented by the collision operator, the evolution of the natural orbitals is governed by a combination of the strong-field driving, mean-field effects, and two-particle correlations. We have shown that the HHG spectra, in particular, the high-energy plateau, are strongly and unambiguously influenced by two-particle correlations and their effect on the evolution of the natural orbitals, whereas the correlation-driven variation of the occupation numbers has only a minor impact on HHG. The time dependence of two-particle correlations itself can be conveniently monitored by the occupation numbers and functions thereof such as the entropy. Their impact on the HHG mostly manifests itself through their influence on the natural orbitals.

The RDM framework presented in this work is, in principle, exact in the electronic degrees of freedom and is applicable to systems of arbitrary degrees of electronic correlations and of arbitrary strength (within the dipole oasis) and polarization of the driving field. It provides the foundation

for our future investigations of correlation effects in larger and more complex atoms such as Xe as well as extended systems. In Xe, the interplay between the outermost p - and d -shells leads to dramatic enhancements of the HHG yield in the spectral region of the giant dipole resonance (GDR). Understanding the correlation dynamics near the GDR under strong-field driving is still an open problem [22,23,72]. Even larger atoms may show similar effects and have the potential to dramatically increase the yield in the ultraviolet or extreme ultraviolet region promising technological applications. Systems with the number of electrons of Xe ($N = 54$) or larger currently cannot be described within MCTDHF or even extensions thereof such as time-dependent complete active space self-consistent field methods [48,73] due to the prohibitive exponential increase of the configuration space. Therefore, we plan to employ the polynomially scaling time-dependent two-particle reduced density matrix method [74–77], which is capable of accurately describing two-particle correlations, for studies of larger systems.

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DATA AVAILABILITY

The data that support the findings of this article 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. The data are available from the authors upon reasonable request.

APPENDIX A: NUMERICAL PARAMETERS FOR THE SIMULATIONS

For He ($N = Z = 2$), we used $M = 5$ orbitals with $l_{\max} = 71$ expanded on a radial grid with $r_{\max} = 200$ on 100 elements within a finite element discrete variable representation (FEDVR) [78] with 20 grid points in each element. An absorbing boundary of the shape $\cos^4$ is applied, starting at 80% of $r_{\max}$. The ground state, obtained by imaginary time propagation, is propagated in velocity gauge using an exponential Runge-Kutta [79] method with 20 000 time steps per optical cycle. Convergence of the results for these parameters has been verified.

TABLE II. Comparison of the total binding energy of He in eV obtained via imaginary-time propagation by MCTDHF, TDHF, and TDDFT with PBE, VWN, and LB94 exchange-correlation functionals and measurement [71].

Binding energy (eV)	
MCTDHF	78.53
TDHF	77.55
TDDFT PBE	77.73
TDDFT VWN	76.82
TDDFT LB94	73.81
Measured [71]	79.01

For Ne ($N = Z = 10$) with $M = 9$ orbitals, all parameters are kept as above but convergence is already reached for $l_{\max} = 47$ and 50 FEDVR elements with 20 grid points in each element.

For Be ($N = Z = 4$) with $M = 5$, the radial grid was expanded to $r_{\max} = 300$ with 75 elements to reach convergence. All other parameters are the same as for He.

For Mg ($N = Z = 12$) with $M = 13$, the radial grid was expanded to $r_{\max} = 280$ with 70 elements and $l_{\max} = 71$. For convergence, 30 000 time steps per optical cycle are used. For the l expansion of the electron-electron interaction (see Ref. [48]), the same $l_{\max}$ as for the expansion of the orbitals is used.

All TDHF and TDDFT calculations use the same parameters as the MCTDHF calculations for the same atom.

For the calculation of the ionization probability [Eq. (31)], the ionization radius is set to $R_I = 20$ for all simulations. The time-dependent ionization probabilities are shifted in time to account for the time it takes the electron to propagate to $r = 20$, similar to the shift described in Ref. [48]. Including this shift, the maximum in P_I coincides with the maximum field amplitude.

APPENDIX B: TDDFT RESULTS FOR HHG

In this Appendix, we present additional details on the TDDFT predictions for the HHG yields and their dependence on the choice of exchange-correlation functionals. Figure 13 shows the HHG spectra for He, Ne, Be, and Mg obtained by MCTDHF, TDHF (same as in Figs. 9–12), and TDDFT calculations using adiabatic local correlation functionals PBE [80] and VWN [81] and the Slater exchange functional [82], as well as the general gradient approximation exchange-correlation functional LB94 [83]. The exchange and correlation functionals are taken from the LibXC [84] library. All these functionals assume the validity of the adiabatic approximation [85].

TDDFT appears to overestimate the yield, in particular, in the region of the second plateau (above the ~ 60 th harmonic) for all investigated atoms. Since for this spectral region the probability for ionization and rescattering is governed by tunnel ionization in a still relatively weak driving field, this deviation is in part due to the errors in the initial ground state, i.e., in their DFT description. In Table II, we compare the full binding energy of He in the ground state obtained from exper-

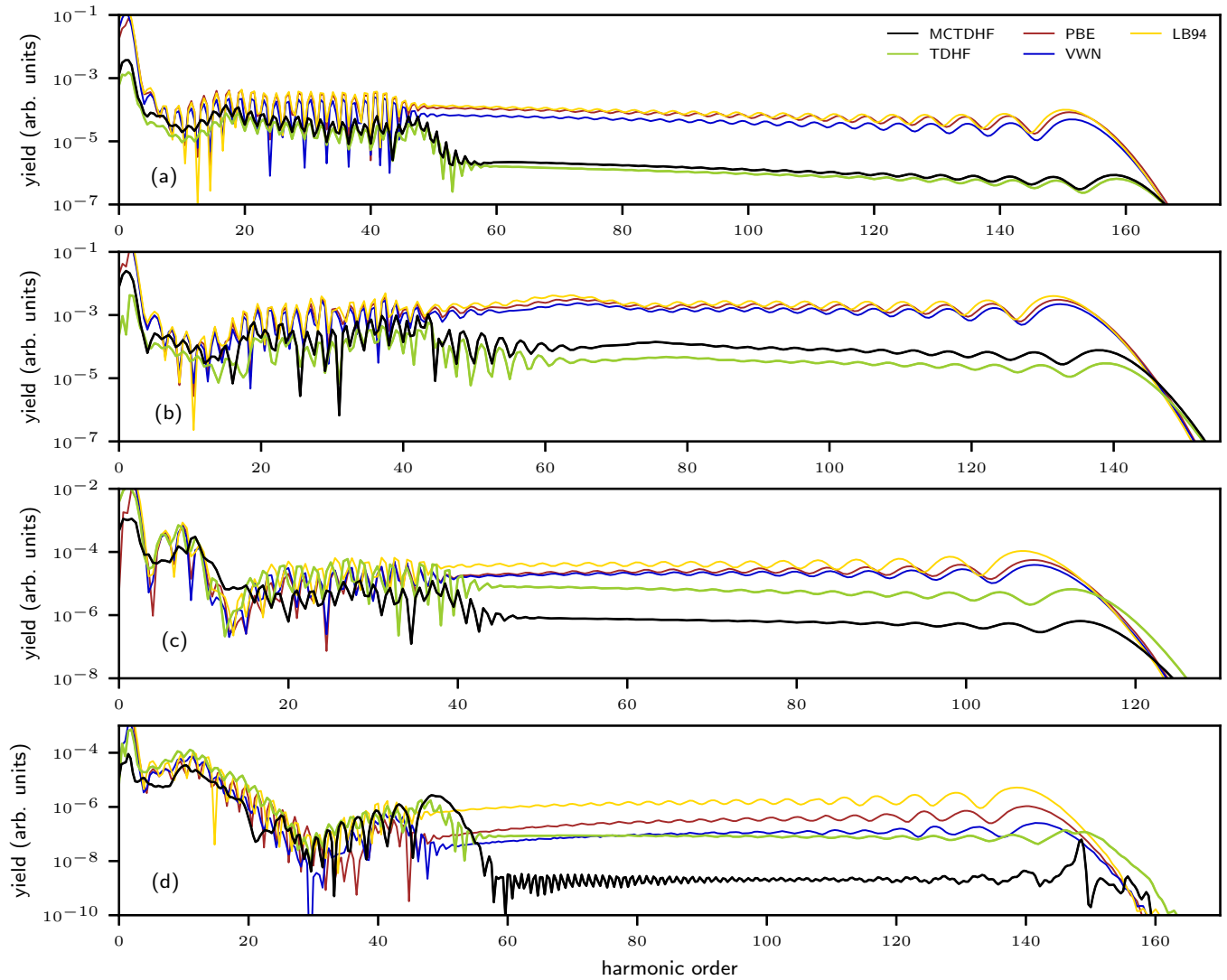


FIG. 13. He [panel (a)], Ne [panel (b)], Be [panel (c)], and Mg [panel (d)] driven by a strong two-cycle laser field with parameters according to Table I. HHG spectra obtained by MCTDHF (black), TDHF (green), TDDFT PBE (brown), TDDFT VWN (blue), and TDDFT LB94 (yellow).

iment [71] with the calculated ground-state binding energies obtained via imaginary-time propagation using MCTDHF, TDHF, and TDDFT with all three exchange-correlation functionals. All exchange-correlation potentials underestimate the total binding energy by up to 5 eV and therefore tend to overestimate tunneling ionization. Note, however, that the binding energies predicted by PBE and HF are very similar while the HHG yields differ by orders of magnitude in the high-energy region [see Fig. 13(a)]. This underscores another limita-

tion of adiabatic TDDFT exchange-correlation functionals: They fail to accurately capture the time-dependent exchange and correlation effects in strong-field driving. Improvements in including dynamic correlations by incorporation self-interaction corrections (SIC) within an optimized effective potential approach have been suggested [86]. The results presented in this paper illustrate that the HHG yield is a sensitive measure for the accurate inclusion of dynamic electron correlations.

- [1] A. McPherson, G. Gibson, H. Jara, U. Johann, T. S. Luk, I. A. McIntyre, K. Boyer, and C. K. Rhodes, Studies of multiphoton production of vacuum-ultraviolet radiation in the rare gases, *J. Opt. Soc. Am. B* **4**, 595 (1987).
- [2] M. Ferray, A. L'Huillier, X. F. Li, L. A. Lompre, G. Mainfray, and C. Manus, Multiple-harmonic conversion of 1064 nm ra-

diation in rare gases, *J. Phys. B: At., Mol. Opt. Phys.* **21**, L31 (1988).

- [3] J. M. Schins, P. Breger, P. Agostini, R. C. Constantinescu, H. G. Muller, G. Grillon, A. Antonetti, and A. Mysyrowicz, Observation of laser-assisted Auger decay in argon, *Phys. Rev. Lett.* **73**, 2180 (1994).

- [4] V. Vénier, R. Taïeb, and A. Maquet, Phase dependence of $(N+1)$ -color ($N > 1$) IR-UV photoionization of atoms with higher harmonics, *Phys. Rev. A* **54**, 721 (1996).
- [5] P. M. Paul, E. S. Toma, P. Breger, G. Mullot, F. Augé, P. Balcou, H. G. Muller, and P. Agostini, Observation of a train of attosecond pulses from high harmonic generation, *Science* **292**, 1689 (2001).
- [6] S. A. Aseyev, Y. Ni, L. J. Frasinski, H. G. Muller, and M. J. J. Vrakking, Attosecond angle-resolved photoelectron spectroscopy, *Phys. Rev. Lett.* **91**, 223902 (2003).
- [7] R. López-Martens, K. Varjú, P. Johnsson, J. Mauritsson, Y. Mairesse, P. Salières, M. B. Gaarde, K. J. Schafer, A. Persson, S. Svanberg, C.-G. Wahlström, and A. L'Huillier, Amplitude and phase control of attosecond light pulses, *Phys. Rev. Lett.* **94**, 033001 (2005).
- [8] M. Nisoli, S. De Silvestri, O. Svelto, R. Szipöcs, K. Ferencz, C. Spielmann, S. Sartania, and F. Krausz, Compression of high-energy laser pulses below 5 fs, *Opt. Lett.* **22**, 522 (1997).
- [9] M. Drescher, M. Hentschel, R. Kienberger, M. Uiberacker, V. Yakovlev, A. Scrinzi, T. Westerwalbesloh, U. Kleineberg, U. Heinzmann, and F. Krausz, Time-resolved atomic inner-shell spectroscopy, *Nature (London)* **419**, 803 (2002).
- [10] R. Kienberger, E. Goulielmakis, M. Uiberacker, A. Baltuska, V. Yakovlev, F. Bammer, A. Scrinzi, T. Westerwalbesloh, U. Kleineberg, U. Heinzmann, M. Drescher, and F. Krausz, Atomic transient recorder, *Nature (London)* **427**, 817 (2004).
- [11] R. Santra, V. S. Yakovlev, T. Pfeifer, and Z.-H. Loh, Theory of attosecond transient absorption spectroscopy of strong-field-generated ions, *Phys. Rev. A* **83**, 033405 (2011).
- [12] S. Chen, M. J. Bell, A. R. Beck, H. Mashiko, M. Wu, A. N. Pfeiffer, M. B. Gaarde, D. M. Neumark, S. R. Leone, and K. J. Schafer, Light-induced states in attosecond transient absorption spectra of laser-dressed helium, *Phys. Rev. A* **86**, 063408 (2012).
- [13] 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).
- [14] T. Popmintchev, M.-C. Chen, D. Popmintchev, P. Arpin, S. Brown, S. Ališauskas, G. Andriukaitis, T. Balčiūnas, O. D. Mücke, A. Pugzlys, A. Baltuška, B. Shim, S. E. Schrauth, A. Gaeta, C. Hernández-García, L. Plaja, A. Becker, A. Jaron-Becker, M. M. Murnane, and H. C. Kapteyn, Bright coherent ultrahigh harmonics in the keV X-ray regime from mid-infrared femtosecond lasers, *Science* **336**, 1287 (2012).
- [15] 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).
- [16] O. A. Naranjo-Montoya, M. Bridger, R. Bhar, L. Kalkhoff, M. Schleberger, H. Wende, A. Tarasevitch, and U. Bovensiepen, Table-top source for X-ray absorption spectroscopy with photon energies up to 350 eV, *Rev. Sci. Instrum.* **95**, 103001 (2024).
- [17] T. Brabec and F. Krausz, Intense few-cycle laser fields: Frontiers of nonlinear optics, *Rev. Mod. Phys.* **72**, 545 (2000).
- [18] F. Krausz and M. Ivanov, Attosecond physics, *Rev. Mod. Phys.* **81**, 163 (2009).
- [19] M. Y. Kuchiev, Atomic antenna, *JETP Lett.* **45**, 404 (1987).
- [20] P. B. Corkum, Plasma perspective on strong field multiphoton ionization, *Phys. Rev. Lett.* **71**, 1994 (1993).
- [21] M. Lewenstein, P. Balcou, M. Y. Ivanov, A. L'Huillier, and P. B. Corkum, Theory of high-harmonic generation by low-frequency laser fields, *Phys. Rev. A* **49**, 2117 (1994).
- [22] A. D. Shiner, B. E. Schmidt, C. Trallero-Herrero, H. J. Wörner, S. Patchkovskii, P. B. Corkum, J.-C. Kieffer, F. Légaré, and D. M. Villeneuve, Probing collective multi-electron dynamics in xenon with high-harmonic spectroscopy, *Nat. Phys.* **7**, 464 (2011).
- [23] S. Pabst and R. Santra, Strong-field many-body physics and the giant enhancement in the high-harmonic spectrum of xenon, *Phys. Rev. Lett.* **111**, 233005 (2013).
- [24] R. A. Ganeev, M. Suzuki, M. Baba, H. Kuroda, and T. Ozaki, Strong resonance enhancement of a single harmonic generated in the extreme ultraviolet range, *Opt. Lett.* **31**, 1699 (2006).
- [25] R. A. Ganeev, P. A. Naik, H. Singhal, J. A. Chakera, and P. D. Gupta, Strong enhancement and extinction of single harmonic intensity in the mid- and end-plateau regions of the high harmonics generated in weakly excited laser plasmas, *Opt. Lett.* **32**, 65 (2007).
- [26] R. A. Ganeev, V. V. Strelkov, C. Hutchison, A. Zaïr, D. Kilbane, M. A. Khokhlova, and J. P. Marangos, Experimental and theoretical studies of two-color-pump resonance-induced enhancement of odd and even harmonics from a tin plasma, *Phys. Rev. A* **85**, 023832 (2012).
- [27] S. Haessler, V. Strelkov, L. B. Elouga Bom, M. Khokhlova, O. Gobert, J.-F. Hergott, F. Lepetit, M. Perdrix, T. Ozaki, and P. Salières, Phase distortions of attosecond pulses produced by resonance-enhanced high harmonic generation, *New J. Phys.* **15**, 013051 (2013).
- [28] 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).
- [29] 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).
- [30] A. N. Artemyev, L. S. Cederbaum, and P. V. Demekhin, Impact of two-electron dynamics and correlations on high-order-harmonic generation in He, *Phys. Rev. A* **95**, 033402 (2017).
- [31] A. De Las Heras, C. Hernández-García, and L. Plaja, Spectral signature of back reaction in correlated electron dynamics in intense electromagnetic fields, *Phys. Rev. Res.* **2**, 033047 (2020).
- [32] I. Tikhomirov, T. Sato, and K. L. Ishikawa, High-harmonic generation enhanced by dynamical electron correlation, *Phys. Rev. Lett.* **118**, 203202 (2017).
- [33] Y. Li, T. Sato, and K. L. Ishikawa, High-order harmonic generation enhanced by laser-induced electron recollision, *Phys. Rev. A* **99**, 043401 (2019).
- [34] O. Neufeld and O. Cohen, Probing ultrafast electron correlations in high harmonic generation, *Phys. Rev. Res.* **2**, 033037 (2020).
- [35] S. Ghimire, A. D. DiChiara, E. Sistrunk, P. Agostini, L. F. DiMauro, and D. A. Reis, Observation of high-order harmonic generation in a bulk crystal, *Nat. Phys.* **7**, 138 (2011).
- [36] S. Ghimire, G. Ndabashimiye, A. D. DiChiara, E. Sistrunk, M. I. Stockman, P. Agostini, L. F. DiMauro, and D. A. Reis, Strong-field and attosecond physics in solids, *J. Phys. B: At., Mol. Opt. Phys.* **47**, 204030 (2014).

- [37] T. T. Luu, M. Garg, S. Y. Kruchinin, A. Moulet, M. T. Hassan, and E. Goulielmakis, Extreme ultraviolet high-harmonic spectroscopy of solids, *Nature (London)* **521**, 498 (2015).
- [38] G. Vampa, T. J. Hammond, N. Thiré, B. E. Schmidt, F. Légaré, C. R. McDonald, T. Brabec, D. D. Klug, and P. B. Corkum, All-optical reconstruction of crystal band structure, *Phys. Rev. Lett.* **115**, 193603 (2015).
- [39] I. Floss, C. Lemell, G. Wachter, V. Smejkal, S. A. Sato, X.-M. Tong, K. Yabana, and J. Burgdörfer, *Ab initio* multiscale simulation of high-order harmonic generation in solids, *Phys. Rev. A* **97**, 011401 (2018).
- [40] R. E. F. Silva, I. V. Blinov, A. N. Rubtsov, O. Smirnova, and M. Ivanov, High-harmonic spectroscopy of ultrafast many-body dynamics in strongly correlated systems, *Nat. Photon.* **12**, 266 (2018).
- [41] N. Tancogne-Dejean, M. A. Sentef, and A. Rubio, Ultrafast modification of Hubbard U in a strongly correlated material: *Ab initio* high-harmonic generation in NiO, *Phys. Rev. Lett.* **121**, 097402 (2018).
- [42] D. R. Baykusheva, H. Jang, A. A. Husain, S. Lee, S. F. TenHuisen, P. Zhou, S. Park, H. Kim, J.-K. Kim, H.-D. Kim, M. Kim, S.-Y. Park, P. Abbamonte, B. Kim, G. Gu, Y. Wang, and M. Mitrano, Ultrafast renormalization of the on-site Coulomb repulsion in a cuprate superconductor, *Phys. Rev. X* **12**, 011013 (2022).
- [43] J. Caillat, J. Zanghellini, M. Kitzler, O. Koch, W. Kreuzer, and A. Scrinzi, Correlated multielectron systems in strong laser fields: A multiconfiguration time-dependent Hartree-Fock approach, *Phys. Rev. A* **71**, 012712 (2005).
- [44] T. Kato and H. Kono, Time-dependent multiconfiguration theory for electronic dynamics of molecules in an intense laser field, *Chem. Phys. Lett.* **392**, 533 (2004).
- [45] M. Nest, T. Klamroth, and P. Saalfrank, The multiconfiguration time-dependent Hartree-Fock method for quantum chemical calculations, *J. Chem. Phys.* **122**, 124102 (2005).
- [46] D. J. Haxton, K. V. Lawler, and C. W. McCurdy, Multiconfiguration time-dependent Hartree-Fock treatment of electronic and nuclear dynamics in diatomic molecules, *Phys. Rev. A* **83**, 063416 (2011).
- [47] A. Karabanov, I. Kuprov, G. T. P. Charnock, A. van der Drift, L. J. Edwards, and W. Köckenberger, On the accuracy of the state space restriction approximation for spin dynamics simulations, *J. Chem. Phys.* **135**, 084106 (2011).
- [48] T. Sato, K. L. Ishikawa, I. Březinová, F. Lackner, S. Nagele, and J. Burgdörfer, Time-dependent complete-active-space self-consistent-field method for atoms: Application to high-order harmonic generation, *Phys. Rev. A* **94**, 023405 (2016).
- [49] H. R. Reiss, The tunnelling model of laser-induced ionization and its failure at low frequencies, *J. Phys. B: At., Mol. Opt. Phys.* **47**, 204006 (2014).
- [50] J. H. McGuire, *Electron Correlation Dynamics in Atomic Collisions*, *Cambridge Monographs on Atomic, Molecular and Chemical Physics No. 8* (Cambridge University Press, Cambridge, 1997).
- [51] P. G. Szalay, T. Müller, G. Gidofalvi, H. Lischka, and R. Shepard, Multiconfiguration self-consistent field and multireference configuration interaction methods and applications, *Chem. Rev.* **112**, 108 (2012).
- [52] K. Kulander, K. Schafer, and J. Krause, *Time-Dependent Studies of Multiphoton Processes* (Academic Press Inc., New York, 1992), pp. 247–300.
- [53] E. Runge and E. K. U. Gross, Density-functional theory for time-dependent systems, *Phys. Rev. Lett.* **52**, 997 (1984).
- [54] N. N. Bogoljubov, *Lectures on Quantum Statistics: Quantum Statistics* (Gordon and Breach, New York, 1985), Vol. 1.
- [55] D. A. Mazziotti, Approximate solution for electron correlation through the use of Schwinger probes, *Chem. Phys. Lett.* **289**, 419 (1998).
- [56] W. Kutzelnigg and D. Mukherjee, Cumulant expansion of the reduced density matrices, *J. Chem. Phys.* **110**, 2800 (1999).
- [57] F. Furche, On the density matrix based approach to time-dependent density functional response theory, *J. Chem. Phys.* **114**, 5982 (2001).
- [58] Y. Li and C. Ullrich, Time-dependent transition density matrix, *Chem. Phys.* **391**, 157 (2011).
- [59] M. A. Nielsen and I. L. Chuang, *Quantum Computation and Quantum Information*, 10th ed. (Cambridge University Press, Cambridge, 2010).
- [60] S. Bose and V. Vedral, Mixedness and teleportation, *Phys. Rev. A* **61**, 040101 (2000).
- [61] C. Bourassin-Bouchet, L. Barreau, V. Gruson, J.-F. Hergott, F. Quéré, P. Salieres, and T. Ruchon, Quantifying decoherence in attosecond metrology, *Phys. Rev. X* **10**, 031048 (2020).
- [62] M. J. Vrakking, Control of attosecond entanglement and coherence, *Phys. Rev. Lett.* **126**, 113203 (2021).
- [63] L.-M. Koll, L. Maikowski, L. Drescher, T. Witting, and M. J. Vrakking, Experimental control of quantum-mechanical entanglement in an attosecond pump-probe experiment, *Phys. Rev. Lett.* **128**, 043201 (2022).
- [64] S. Nandi *et al.*, Generation of entanglement using a short-wavelength seeded free-electron laser, *Sci. Adv.* **10**, eado0668 (2024).
- [65] W.-C. Jiang, M.-C. Zhong, Y.-K. Fang, S. Donsa, I. Březinová, L.-Y. Peng, and J. Burgdörfer, Time delays as attosecond probe of interelectronic coherence and entanglement, *Phys. Rev. Lett.* **133**, 163201 (2024).
- [66] K. L. Ishikawa, K. C. Prince, and K. Ueda, Control of ion-photoelectron entanglement and coherence via Rabi oscillations, *J. Phys. Chem. A* **127**, 10638 (2023).
- [67] B.-R. Shen, Y.-J. Mao, Z.-H. Zhang, Y. Li, T. Sato, K. L. Ishikawa, and F. He, Coherent control of ion-photoelectron dynamics through Rabi oscillations: An *ab initio* study, *Phys. Rev. A* **111**, 063113 (2025).
- [68] H. Laurell, D. Finkelstein-Shapiro, C. Dittel, C. Guo, R. Demjaha, M. Ammitzböll, R. Weissenbilder, L. Neoričić, S. Luo, M. Gisselbrecht, C. L. Arnold, A. Buchleitner, T. Pullerits, A. L'Huillier, and D. Busto, Continuous-variable quantum state tomography of photoelectrons, *Phys. Rev. Res.* **4**, 033220 (2022).
- [69] H. Laurell, S. Luo, R. Weissenbilder, M. Ammitzböll, S. Ahmed, H. Söderberg, C. L. M. Petersson, V. Poulain, C. Guo, C. Dittel, D. Finkelstein-Shapiro, R. J. Squibb, R. Feifel, M. Gisselbrecht, C. L. Arnold, A. Buchleitner, E. Lindroth, A. F. Kockum, A. L'Huillier, and D. Busto, Measuring the quantum state of photoelectrons *Nat. Photon.* **19**, 352 (2025).
- [70] T. Kato and H. Kono, Time-dependent multiconfiguration theory for ultrafast electronic dynamics of molecules in an intense

- laser field: Electron correlation and energy redistribution among natural orbitals, *Chem. Phys. Attosecond Mol. Dyn.* **366**, 46 (2009).
- [71] A. Kramida, Yu. Ralchenko, J. Reader, and NIST ASD Team, NIST Atomic Spectra Database (version 5.12) [Online] (National Institute of Standards and Technology, Gaithersburg, MD, 2024), <https://physics.nist.gov/asd> (23 December 2024).
- [72] 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).
- [73] T. Sato and K. L. Ishikawa, Time-dependent complete-active-space self-consistent-field method for multielectron dynamics in intense laser fields, *Phys. Rev. A* **88**, 023402 (2013).
- [74] F. Lackner, I. Brezinová, T. Sato, K. L. Ishikawa, and J. Burgdörfer, Propagating two-particle reduced density matrices without wavefunctions, *Phys. Rev. A* **91**, 023412 (2015).
- [75] F. Lackner, I. Brezinová, T. Sato, K. L. Ishikawa, and J. Burgdörfer, High-harmonic spectra from time-dependent two-particle reduced-density-matrix theory, *Phys. Rev. A* **95**, 033414 (2017).
- [76] S. Donsa, F. Lackner, J. Burgdörfer, M. Bonitz, B. Kloss, A. Rubio, and I. Brezinová, Nonequilibrium correlation dynamics in the one-dimensional Fermi-Hubbard model: A testbed for the two-particle reduced density matrix theory, *Phys. Rev. Res.* **5**, 033022 (2023).
- [77] E. Pescoller, M. Eder, and I. Brezinová, Projective purification of correlated reduced density matrices, *Phys. Rev. Res.* **7**, 013211 (2025).
- [78] T. N. Rescigno and C. W. McCurdy, Numerical grid methods for quantum-mechanical scattering problems, *Phys. Rev. A* **62**, 032706 (2000).
- [79] W. Auzinger, I. Brezinová, A. Grosz, H. Hofstätter, O. Koch, and T. Sato, Efficient adaptive exponential time integrators for nonlinear Schrödinger equations with nonlocal potential, *J. Comput. Math. Data Sci.* **1**, 100014 (2021).
- [80] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [81] S. H. Vosko, L. Wilk, and M. Nusair, Accurate spin-dependent electron liquid correlation energies for local spin density calculations: A critical analysis, *Can. J. Phys.* **58**, 1200 (1980).
- [82] P. A. M. Dirac, Note on exchange phenomena in the Thomas atom, *Math. Proc. Cambridge Philos. Soc.* **26**, 376 (1930).
- [83] A. P. Gaiduk and V. N. Staroverov, Construction of integrable model Kohn-Sham potentials by analysis of the structure of functional derivatives, *Phys. Rev. A* **83**, 012509 (2011).
- [84] S. Lehtola, C. Steigemann, M. J. Oliveira, and M. A. Marques, Recent developments in LIBXC—A comprehensive library of functionals for density functional theory, *SoftwareX* **7**, 1 (2018).
- [85] C. A. Ullrich, *Time-Dependent Density-Functional Theory: Concepts and Applications* (Oxford University Press, Oxford, 2013).
- [86] X.-M. Tong and S.-I. Chu, Time-dependent density-functional theory for strong-field multiphoton processes: Application to the study of the role of dynamical electron correlation in multiple high-order harmonic generation, *Phys. Rev. A* **57**, 452 (1998).