Mechanisms of ultrahigh-order harmonic generation

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We analyze mechanisms of high-order harmonic generation from two-center molecules at large internuclear separations in linearly polarized laser fields. Since laser-driven electrons acquire instantaneous kinetic energies of up to 8 times the ponderomotive potential U_p, recombination at an appropriately placed nucleus leads to ultrahigh-order harmonic emission [P. Moreno, L. Plaja, and L. Roso, Phys. Rev. A **55**, R1593 (1997)]. By solving the time-dependent Schrödinger equation for model systems, we show that this mechanism is only efficient if the single-particle orbital of the electron is coherently delocalized over the two potential wells. This is realized in the ground state of a one-electron molecular ion. In a neutral molecule or in a molecular ion created by ionization of a neutral molecule at large internuclear distance, the coherence is destroyed by electron-electron correlation.

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The generation of coherent light in the extreme ultraviolet range has been achieved, reaching wavelengths down to a few nanometers [1,2]. This type of radiation is produced by high-order harmonic generation (HHG) [3], i.e., the process where many incoming laser photons are converted into a single high-energy photon. During the last decade, there has been a great effort to push HHG to higher photon energies and better conversion efficiencies.

From a classical model [4] it follows that atoms driven by a laser with field strength E_0 and frequency ω emit photon energies up to $3.17U_p+I_p$ where $U_p=E_0^2/(4\omega^2)$ is the ponderomotive potential and I_p is the ionization potential. Thus, in principle, the cutoff can be increased by increasing the field strength. However, if the laser becomes too intense, HHG will be accompanied by strong ionization. This leads to an increasing phase mismatch in the propagation of fundamental and harmonic beams, and thus limits the conversion efficiency. Although this problem may be overcome using sophisticated quasi-phase-matching techniques [8], it seems desirable to find mechanisms that can generate very high harmonics without introducing too much ionization.

The recollision model [4] describes HHG as a sequence of strong-field ionization, acceleration of the electron in the field, and recombination with the core. The standard cutoff law follows from the maximum return energy of the laser-driven electron, $3.17U_p$. Scenarios in which the electron trajectories are modified in order to obtain higher return energies, for example by applying an additional confining potential [5] or via backscattering from a nearby ion [6], have been proposed, but their experimental implementation and control appears difficult. Perturber atoms or ions placed at random positions around the laser-driven atom are not sufficient to extend the harmonic plateau since the random variation of the harmonic phase destroys the coherence of emission [7].

Eight years ago, a new mechanism of HHG was predicted to occur in stretched molecules [9–11]: the electron may recombine not at the atomic site where it originated from, but at the neighboring site. Assuming that the electrons start with zero velocity, the maximum cutoff is found to be $8U_p+I_p$ for appropriate internuclear distances. The transfer mechanism, as we shall refer to it in the following, has not been confirmed experimentally up to now. On one hand, this may be due to the fact that the required internuclear distances are much larger than typical equilibrium distances. On the other hand, we will show below that the mechanism exists only in the special case where the active electron can be considered to be in a single-particle orbital that is delocalized over the two atomic sites. This is realized, e.g., in the H_2^+ electronic ground state at any internuclear separation. In a neutral molecule with large internuclear distance, however, electron correlation prohibits such a description. Rather, the electrons are localized on individual sites. In this case, ultrahigh-order harmonics are suppressed. Such a reduction has been suspected in earlier theoretical work on atomic clusters [12], but nevertheless harmonics beyond the atomic cutoff were clearly visible in the calculated harmonic spectra. The purpose of the present work is to study HHG for a set of well-defined situations in two-center systems in order to clarify the role of delocalization and electron correlation.

The cutoff for the transfer mechanism [9] in a linearly polarized monochromatic laser field $\mathbf{E}(t)=\mathbf{E}_0 \sin \omega t$ is easily derived from the electron's classical equation of motion (atomic units are used throughout),

$$\ddot{\mathbf{r}} = -\mathbf{E}_0 \sin \omega t. \tag{1}$$

Assuming that the electron is ejected with zero initial velocity from an atom at $\mathbf{r}=0$ at time t_0, we have

$$\dot{\mathbf{r}}(t) = \frac{\mathbf{E}_0}{\omega}(\cos \omega t - \cos \omega t_0) \tag{2}$$

and

$$\mathbf{r}(t) = \boldsymbol{\alpha}[\sin \omega t - \sin \omega t_0 - \omega(t-t_0)\cos \omega t_0], \tag{3}$$

with the quivering amplitude $\boldsymbol{\alpha}=\mathbf{E}_0/\omega^2$. From Eq. (2) it is obvious that the largest possible electron velocity, $v_{max}=2E_0/\omega$, corresponding to a kinetic energy of $8U_p$, is reached at times t_1 when $|\cos \omega t_1 - \cos \omega t_0|=2$. This maximum value can thus only be reached when the electron starts

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at a time of zero electric field. In order to enable HHG from recombination at a neighboring site located at $\mathbf{R}$, we require $\mathbf{r}(t_1)=\mathbf{R}$. This leads to

$$\mathbf{R} = \pm(2n+1)\pi\boldsymbol{\alpha}, \quad n=0,1,\ldots. \tag{4}$$

At the internuclear separations given by Eq. (4) the maximum harmonic cutoff $8U_p+I_p$ is obtained. We note in passing that even higher cutoffs are possible when, instead of recombination at $\mathbf{r}=\mathbf{R}$, the electron is elastically backscattered and recombines with its parent ion at $\mathbf{r}=0$ [6]. In this case, a maximum cutoff of $32U_p+I_p$ is realized for internuclear separations satisfying

$$\mathbf{R} = \pm 3(2m+1)\pi\boldsymbol{\alpha}, \quad m=0,1,\ldots. \tag{5}$$

In the following, we check the existence of the two mechanisms in quantum mechanical simulations of HHG. We study two different one-dimensional model systems with fixed nuclei, one modeling an H_2 molecule with two active interacting electrons and another one modeling an H_2^+ molecular ion. In both cases, we employ a two-center soft-core binding potential of the form

$$V(x) = -\frac{1}{\sqrt{(x+R/2)^2+\epsilon}} - \frac{1}{\sqrt{(x-R/2)^2+\epsilon}}, \tag{6}$$

where we choose a softening parameter of $\epsilon=2$ to reproduce the ionization potential of isolated H atoms in the limit $R\to\infty$. For the model H_2^+ molecular ion in a laser field $E(t)$, the velocity-gauge Hamiltonian is then given by

$$H = \frac{p^2}{2} + pA(t) + V(x), \tag{7}$$

where $A(t)=-\int^t E(t')dt'$.

For H_2, we introduce an electron-electron interaction of the form

$$W(x_1,x_2) = \frac{1}{\sqrt{(x_1-x_2)^2+\eta}} \tag{8}$$

so that the Hamiltonian reads

$$H = \sum_{k=1,2}\left[\frac{p_k^2}{2} + p_kA(t) + V(x_k)\right] + W(x_1,x_2). \tag{9}$$

The softening parameter η is set to 1.621. With this choice, the H^- ground-state energy -0.5278 a.u. is reproduced by the ground state of the two-electron model system when one of the two potential wells is switched off so that both electrons are bound to the same site. In this way, electron-atom collisions as well as electron-ion collisions occurring in the course of the interaction with the laser are described energetically correctly.

For both systems, we solve the time-dependent Schrödinger equation numerically by means of the split-operator method [13], starting from the field-free ground state, which is obtained by propagation in imaginary time. The harmonic spectra are calculated by Fourier transforming the time-dependent dipole acceleration expectation value [14]. A Welch window is applied to the dipole acceleration to obtain cleaner spectra [15].

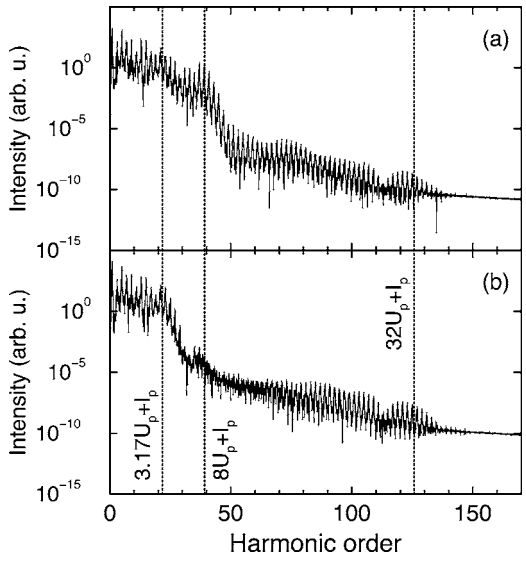

FIG. 1. Harmonic spectra calculated for (a) one-dimensional H_2^+ and (b) one-dimensional H_2 at the internuclear distance $R=3\pi\alpha=150$ a.u. The vertical lines indicate the cutoffs expected from the classical model. A laser pulse with wavelength 800 nm and intensity 9.35×10^{13} W/cm^2 is used.

In Fig. 1 we show the results for an internuclear distance of $R=3\pi\alpha=150$ a.u. in a laser field with 800 nm wavelength and 9.35×10^{13} W/cm^2 intensity. Trapezoidal 10-cycle laser pulses with a two-cycle turn-on and a two-cycle turn-off are used. The dotted lines indicate the three cutoffs that we expect from the classical model. Both spectra clearly display the atomic cutoff at $3.17U_p+I_p$ and the reflection cutoff at $32U_p+I_p$. However, the spectra show a striking difference as far as the transfer mechanism is concerned. In H_2^+, the respective harmonics (near $8U_p+I_p$) are clearly visible, with intensities only about an order of magnitude lower than the harmonics in the atomic cutoff. In H_2, the transfer harmonics are hardly visible. At first sight, a reasonable explanation appears to be that in the neutral molecule the electron cannot recombine at the neighboring site since that site is already occupied by the other electron. Although this is true in the sense that the electron can hardly be captured, the full explanation is somewhat deeper. To that end, we inspect the dipole acceleration expectation value,

$$\left\langle \sum_{k=1}^{N_e} a_k(t) \right\rangle = \left\langle \Psi(t) \middle| \sum_{k=1}^{N_e} [\partial V(x_k) + E(t)] \middle| \Psi(t) \right\rangle, \tag{10}$$

for the two different cases with N_e being the number of electrons. In the case of the one-electron system, the ground-state wave function $\Psi_0(x)$ is coherently delocalized over the two centers,

$$\Psi_0(x) = [\phi_A(x) + \phi_B(x)]/\sqrt{2}, \tag{11}$$

where $\phi_{A,B}$ are functions localized on either of the two potential wells which we refer to as site A and site B. In Eq. (11), we have assumed that the internuclear distance is large enough to neglect the overlap between ϕ_A and ϕ_B. Under the

influence of the laser, the state evolves into a superposition of the ground state and excited states. We are particularly interested in the population of continuum states which are able to support the motion of an electron wave packet from site A to site B. At certain times t_1, such a wave packet overlaps with site B. Ignoring electrons emitted from site B, the wave function can then be written as

$$\Psi(x,t_1) = \beta_1\phi_A(x) + \beta_2\phi_{A\to B}(x) + \beta_3\phi_B(x), \qquad (12)$$

where $\phi_{A\to B}(x)$ is a wave packet that was emitted from site A and overlaps with $\phi_B(x)$ at time t_1. The numbers β_1, β_2, and β_3 are complex coefficients. Radiative recombination at site B is obviously possible since the dipole acceleration Eq. (10), when evaluated using the wave function in Eq. (12), contains a term proportional to

$$\beta_2^*\beta_3\langle\phi_{A\to B}|a(t_1)|\phi_B\rangle, \qquad (13)$$

where $a(t)=\partial V(x)+E(t)$ is the acceleration operator.

In the two-electron system, the ground-state wave function has the form

$$\Psi_0(x_1,x_2) = [\phi_A(x_1)\phi_B(x_2) + \phi_A(x_2)\phi_B(x_1)]/\sqrt{2} \qquad (14)$$

if the two potential wells are sufficiently separated. Equation (14) arises because the electron-electron repulsion forbids the presence of both electrons at the same site. When the laser drives an electron from site A to site B, we have the equivalent of Eq. (12),

$$\Psi(x_1,x_2,t_1) = [\gamma_1\phi_A(x_1) + \gamma_2\phi_{A\to B}(x_1)]\phi_B(x_2) + (x_1 \leftrightarrow x_2), \qquad (15)$$

where $(x_1 \leftrightarrow x_2)$ denotes the interchange of electron coordinates. The term describing the radiative recombination at site B reads now

$$\gamma_2^*\langle\phi_{A\to B}|a_1(t_1)|\phi_B\rangle(\gamma_1\langle\phi_B|\phi_A\rangle + \gamma_2\langle\phi_B|\phi_{A\to B}\rangle). \qquad (16)$$

For large internuclear distances, there is essentially no overlap between ϕ_B and ϕ_A. Furthermore, $\phi_{A\to B}$ is a superposition of continuum states and thus orthogonal to ϕ_B. Consequently, Eq. (16) vanishes, i.e., the process does not yield any coherent radiation. The physical reason is that the initial state of the system is correlated in the sense that an individual electron cannot be described by a single-particle orbital extending over the two centers. For efficient HHG, the electron must be able to interfere with itself.

It is conceivable that the electron wave packet is partially captured when it collides with the neighboring site so that a wave function coherently delocalized over both sites is formed. Electron wave packets arriving afterwards can then interfere and generate high harmonics. Yet, this double transfer process appears to be inefficient in H_2 since there is almost no sign of it in Fig. 1(b). This is not a surprise since the electron-electron repulsion suppresses electron capture. To avoid confusion, we stress that capture alone does not involve harmonic emission but rather feeds the electron energy back into the fundamental laser field.

To further support the above line of arguments, we show in Fig. 2 the spectra for the case of H_2^+ when the initial state is not the delocalized ground state but describes an electron

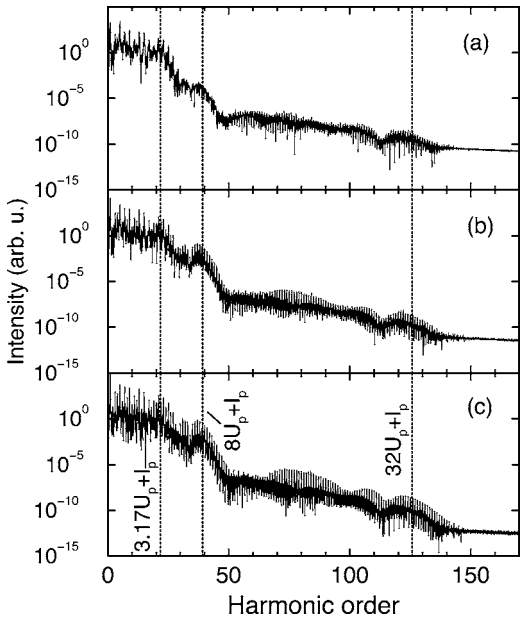

FIG. 2. Harmonic spectra calculated for H_2^+ at $R=3\pi\alpha=150$ a.u. with the electron initially localized at the left potential well. (a) (2-6-2) pulse, (b) (2-12-2) laser pulse, (c) (2-24-2) pulse. Laser wavelength and intensity as in Fig. 1.

localized in the left potential well. As before, trapezoidal laser pulses are used. Pulses with different durations of the constant-intensity part (6, 12, and 24 optical cycles) but identical turn-on and turn-off times (two cycles each) are compared. Two main observations can be made in these results. First, the harmonics from the transfer mechanism (near $8U_p+I_p$) are substantially reduced as compared to the delocalized initial state [Fig. 1(a)]. This confirms that coherent delocalization is required. Second, the intensity of the transfer harmonics increases with increasing pulse duration. This indicates that a double transfer mechanism is at work as described above; i.e., with some probability the electron is first captured in the right potential well so that harmonic emission becomes possible for electron wave packets arriving afterwards. This process becomes more likely with increasing pulse length since time is needed for capturing the electron. In contrast to H_2, the capture probability is significant since the electron impinges on an unoccupied site. The harmonics in the atomic plateau and in the reflection plateau extending up to $32U_p+I_p$ exhibit much less enhancement as the pulse length is increased.

An important question concerns the behavior of H_2^+ ions generated by ionization of H_2. In the following, we distinguish two cases. (i) The molecule is ionized at an internuclear distance small enough to guarantee significant overlap between the two atomic wave functions. We then create H_2^+ in a well-defined electronic state. Dissociation of this intermediate complex provides a coherent superposition of two distant electron wave packets. Along the lines of pump-probe experiments on H_2/D_2 [16,17], this state may serve as initial state for an appropriately timed second pulse. (ii) The molecule is ionized at internuclear distances so large that the electronic ground state is of the form of Eq. (14). In this case, the state after single ionization has the following structure:

$$\Psi^+(x_1,x_2) \sim [\phi_A(x_1)\phi_B^{\rm ion}(x_2) + \phi_A^{\rm ion}(x_2)\phi_B(x_1)] + (x_1 \leftrightarrow x_2), \tag{17}$$

where $\phi_{A/B}$ are the bound orbitals as before and $\phi_{A/B}^{\rm ion}$ denote the wave functions corresponding to electrons ejected from site A or B, respectively. Proceeding as above, we obtain that the contribution from the transfer mechanism to the dipole acceleration is proportional to

$$\langle \phi_{A\to B}|a_1(t_1)|\phi_B\rangle\langle\phi_B^{\rm ion}|\phi_A^{\rm ion}\rangle. \tag{18}$$

This term essentially vanishes since the wave functions $\phi_A^{\rm ion}$ and $\phi_B^{\rm ion}$ are practically orthogonal to each other. We conclude that the transfer mechanism is inefficient if the ion is prepared by ionizing a neutral molecule with well-separated atoms. Therefore one may ask whether this mechanism can be responsible for the extension of HHG beyond the atomic cutoff in atomic clusters that was observed theoretically [12] and, to a lesser degree, experimentally [18]. The extension could also be due to a classical electron heating mechanisms [19] followed by electron recombination with the parent ion.

To summarize, we have shown by quantum-mechanical calculations that HHG by transfer of an electron between distant atomic sites in a molecule is only efficient when the initial state of the electron is coherently delocalized over both sites. If the electron is initially localized at one site, the transfer mechanism becomes possible only after an electron wave packet has been captured at the other site. In a neutral molecule, electron correlation both prohibits the initial coherent delocalization and suppresses the laser-induced capture. The realization of the transfer mechanism with ultrahigh harmonic energies up to $8U_{\rm p}+I_{\rm p}$ may be realized by using a pump-probe scheme where a moderate-intensity preparation pulse dissociates H_2^+ before an intense pulse generates high harmonics at the appropriate internuclear separation. We have not addressed the question of whether the coherence of the harmonic-generation process could be partially destroyed by the nuclear motion, but it may be anticipated that such problems can be solved by choosing heavier molecules. A detailed analysis of this point is out of the scope of the present work since it requires quantum-mechanical treatment of the nuclear motion.

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[1] Z. H. Chang, A. Rundquist, H. W. Wang, M. M. Murnane, and H. C. Kapteyn, Phys. Rev. Lett. **79**, 2967 (1997).
[2] C. Spielmann *et al.*, Science **278**, 661 (1997).
[3] A. McPherson *et al.*, J. Opt. Soc. Am. B **4**, 595 (1987).
[4] P. B. Corkum, Phys. Rev. Lett. **71**, 1994 (1993).
[5] C. Figueira de Morisson Faria and J. M. Rost, Phys. Rev. A **62**, 051402(R) (2000).
[6] M. Lein and J. M. Rost, Phys. Rev. Lett. **91**, 243901 (2003).
[7] V. V. Strelkov, V. T. Platonenko, and A. Becker, Phys. Rev. A **71**, 053808 (2005).
[8] A. Paul *et al.*, Nature **421**, 48 (2003).
[9] P. Moreno, L. Plaja, and L. Roso, Phys. Rev. A **55**, R1593 (1997).
[10] A. D. Bandrauk, S. Chelkowski, H. Yu, and E. Constant, Phys. Rev. A **56**, R2537 (1997).
[11] R. Kopold, W. Becker, and M. Kleber, Phys. Rev. A **58**, 4022 (1998).
[12] V. Véniard, R. Taïeb, and A. Maquet, Phys. Rev. A **65**, 013202 (2001).
[13] M. D. Feit, J. A. Fleck, Jr., and A. Steiger, J. Comput. Phys. **47**, 412 (1982).
[14] K. Burnett, V. C. Reed, J. Cooper, and P. L. Knight, Phys. Rev. A **45**, 3347 (1992).
[15] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes* (Cambridge University Press, Cambridge, 1992).
[16] C. Trump, H. Rottke, and W. Sandner, Phys. Rev. A **59**, 2858 (1999).
[17] T. Ergler, A. Rudenko, B. Feuerstein, K. Zrost, C. D. Schröter, R. Moshammer, and J. Ullrich, Phys. Rev. Lett. **95**, 093001 (2005).
[18] T. D. Donnelly, T. Ditmire, K. Neuman, M. D. Perry, and R. W. Falcone, Phys. Rev. Lett. **76**, 2472 (1996).
[19] R. Numico, D. Giulietti, A. Giulietti, L. A. Gizzi, and L. Roso, J. Phys. B **33**, 2605 (2000).