Comment on "Origin of symmetry-forbidden high-order harmonic generation in the time-dependent Kohn-Sham formulation"

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In their recent paper [Phys. Rev. A **103**, 043106 (2021)], Zang *et al.* theoretically investigated high harmonic generation (HHG) in benchmark two-electron systems that are inversion symmetric with time-dependent density functional theory (TDDFT) in the Kohn-Sham formulation. They found that the theory wrongly predicted the emission of symmetry-forbidden even harmonics and concluded that this error originates from an inherent problem of TDDFT that unphysically populates one- and two-electron excited states. They further claimed that this effect results in an incorrect HHG cutoff energy. We reproduced their main results, but found that the unphysical even harmonics that they observed originated from numerical errors introduced by the boundary conditions. We show that contrary to their claims, the HHG cutoff energy calculated within TDDFT agrees perfectly with the standard and well-established models of HHG.

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In their recent work [1], Zang *et al.* performed HHG calculations for inversion-symmetric two-electron systems (H_2 and He) with various levels of theory, including time-dependent configuration interaction (TCI), time-dependent density functional theory (TDDFT) in the Kohn-Sham (KS) formulation, and their recently developed time-dependent natural Kohn-Sham formulation (TDNKS) [2]. Their numerical results for HHG using standard TDDFT (with either the local density approximation (LDA) or Perdew-Burke-Ernzerhof (PBE) [3] approximation for the exchange-correlation (XC) functional) showed the presence of symmetry-forbidden even harmonics that should not have been observed in these conditions due to a dynamical inversion symmetry [4], and which are standardly not observed with other levels of theory nor experimentally. They concluded that the error in H_2 and He is due to an inherent flaw in multielectron TDDFT in the KS formulation. Specifically, they argued that the occupation of excited states in TDDFT is wrong and spuriously allows for this symmetry breaking to occur. Lastly, they claimed that the HHG cutoff energy was wrongly reproduced within TDDFT due to similar considerations.

Here we repeat the calculations in Ref. [1] and argue that the observation of symmetry-forbidden harmonics in fact originated from convergence issues. We demonstrate that contrary to the claims in Ref. [1], TDDFT (even within the LDA) correctly reproduces the HHG cutoff energy in agreement with well-established models for HHG [5–8]. Lastly, we highlight that any errors in excited state occupation in TDDFT (i) cannot break any inversion (or other) inherent symmetry of the system, and (ii) are conceptually fixable by using better approximations for the XC functional (and are absent in formally exact TDDFT).

We begin by reproducing the main result of Ref. [1]—Fig. 1(a) shows our calculated HHG spectra from H_2 using TDDFT within the LDA with an added self-interaction correction (SIC) [9]. The laser parameters are chosen identical to those in Figs. 1–3 in Ref. [1], where the laser electric field is polarized along the H_2 main axis with power $I_0 = 3.36 \times 10^{12}\,\mathrm{W/cm^2}$ and wavelength $\lambda = 800\,\mathrm{nm}$ (the resulting Keldysh parameter is $\sim$6.2). Clearly, unphysical even harmonics are emitted in accordance with the results in Ref. [1] [see highlighted harmonic orders 8, 10, and 12 in Fig. 1(a)]. We also note that a similar result is obtained for a laser field transverse to the H_2 main axis, but the even harmonics in that case were much less pronounced (therefore this case is not presented or considered from this point on).

Numerically, the result in Fig. 1(a) was obtained with a Cartesian grid with the real-space TDDFT code, OCTOPUS [10–12], where the box was a sphere of radius 45 bohr and grid spacing of 0.4 bohr. The results in Ref. [1] were obtained with a similar approach but with a much smaller box size of radius 20 bohr that may initially seem too small. However, for these laser conditions the quiver length of the electron motion is 3 bohr; thus *a priori* both box sizes should suffice for obtaining converged spectra. It is important to note that counterintuitively, it can be much more difficult to numerically converge calculations for weak laser driving and high Keldysh parameters than for stronger field powers. This is because the resulting harmonic yield is often numerically close to the noise level of the calculation. Also, for low laser

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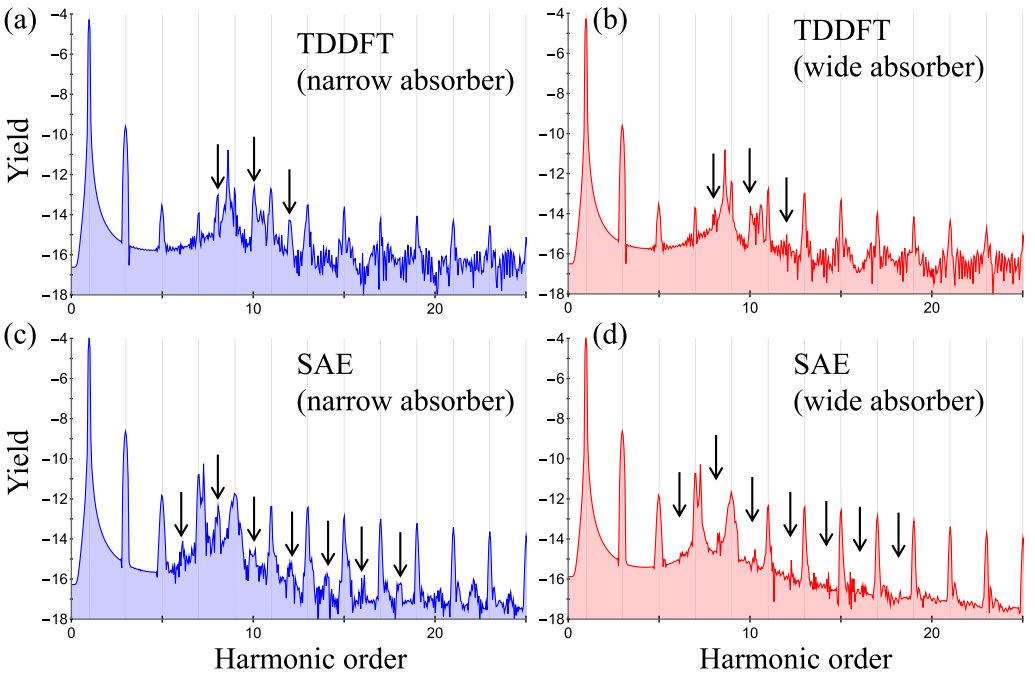

FIG. 1. Origin of spurious even harmonics in HHG calculations from H_2. (a) HHG spectra from H_2 calculated with KS-TDDFT with a 15 bohr wide CAP. (b) Same as (a) but with a 30 bohr wide CAP. (c) Same as (a) but for a SAE model from the TDSE. (d) Same as (b) but for a SAE model from the TDSE. Arrows highlight positions of unphysical even harmonics for the narrow absorber, and their absence in the wide absorber case. HHG yield is presented in logarithmic scale (with basis 10).

powers low-energy electrons are ionized that are difficult to absorb in the boundaries [13]; these can also lead to spurious reflections or numerical instability (especially for very long laser pulses as those used in Ref. [1] and Fig. 1(a) (20 optical cycles long)). Figure 1(a) was calculated with a 15 bohr wide complex absorbing potential (CAP), which is usually sufficient to obtain well-converged HHG spectra. In contrast, Fig. 1(b) shows HHG spectra in the exact same conditions as those in Fig. 1(a), but with a CAP that is 30 bohr wide. It clearly shows that the spurious even harmonic emission is almost fully suppressed. This suggests that the unphysical even harmonics are a result of convergence issues.

To further show that the unphysical emission in Fig. 1(a) is not a fundamental consequence of TDDFT or its approximations, we repeat a similar calculation for a single-active-electron (SAE) model of H_2 (such models are commonly employed in the HHG community [14–17]). For this model we use the following potential that has the correct asymptotic form and mimics some local screening effects (given in atomic units):

$$V(r) = -\frac{0.5 + 0.5 \times e^{-(r-R_0)^2}}{\sqrt{(r-R_0)^2 + a}} - \frac{0.5 + 0.5 \times e^{-(r+R_0)^2}}{\sqrt{(r+R_0)^2 + a}}, \tag{1}$$

where $R_0 = 0.6692$ bohr is half the equilibrium H-H spacing for the H_2 molecule, r is the SAE radial coordinate, and a is a free parameter set to $a = 0.102$ such that the model correctly reproduces the first ionization potential of H_2, $I_p = 15.4$ eV. Figures 1(c) and 1(d) show results of calculations using this model potential in the exact same conditions as those in Figs. 1(a) and 1(b), respectively. Clearly Fig. 1(c) shows spurious even harmonics just as in the TDDFT case. Importantly though, Fig. 1(c) corresponds to a time-dependent Schrödinger equation (TDSE) calculation for a SAE which is formally exact, and which cannot be accused of leading to spurious even harmonics. Figure 1(d) shows that with the wider CAP these errors again vanish. The fact that this error is reproduced with a SAE model directly shows that it does not originate from any inherent problem in KS-TDDFT for multielectron systems. Notably, in Ref. [1] the authors performed calculations for atomic hydrogen which is a one-electron system, but did not show such errors. We believe that this might be a result of the lower I_p of atomic hydrogen (e.g., even worse errors came up in Ref. [1] for He which has an even higher I_p). Similarly, the errors go away for higher laser powers (also seen in Ref. [1]) because the Keldysh parameter is reduced and an apparent convergence is obtained (since the harmonic spectrum is dominated by faster electrons for which the reflection error is smaller).

We also point out that in one-dimensional (1D) systems one can perform numerically exact calculations with large spatial box sizes without resorting to absorbing boundaries (because the grid is sufficiently large to avoid reflections). We have performed such TDDFT calculations for a 1D model of H_2 in conditions similar to those in Fig. 1, and have similarly seen only odd harmonics being emitted (not presented). Overall, we see no evidence that KS-TDDFT is breaking any inherent symmetry of the system.

Another point worth discussing is that symmetry-breaking harmonics can also appear in HHG in standard conditions due to symmetry-breaking elements in the laser-matter system itself (e.g., the laser pulse envelope and its final duration, and the system occupying more than one Floquet state) [4,18–20].

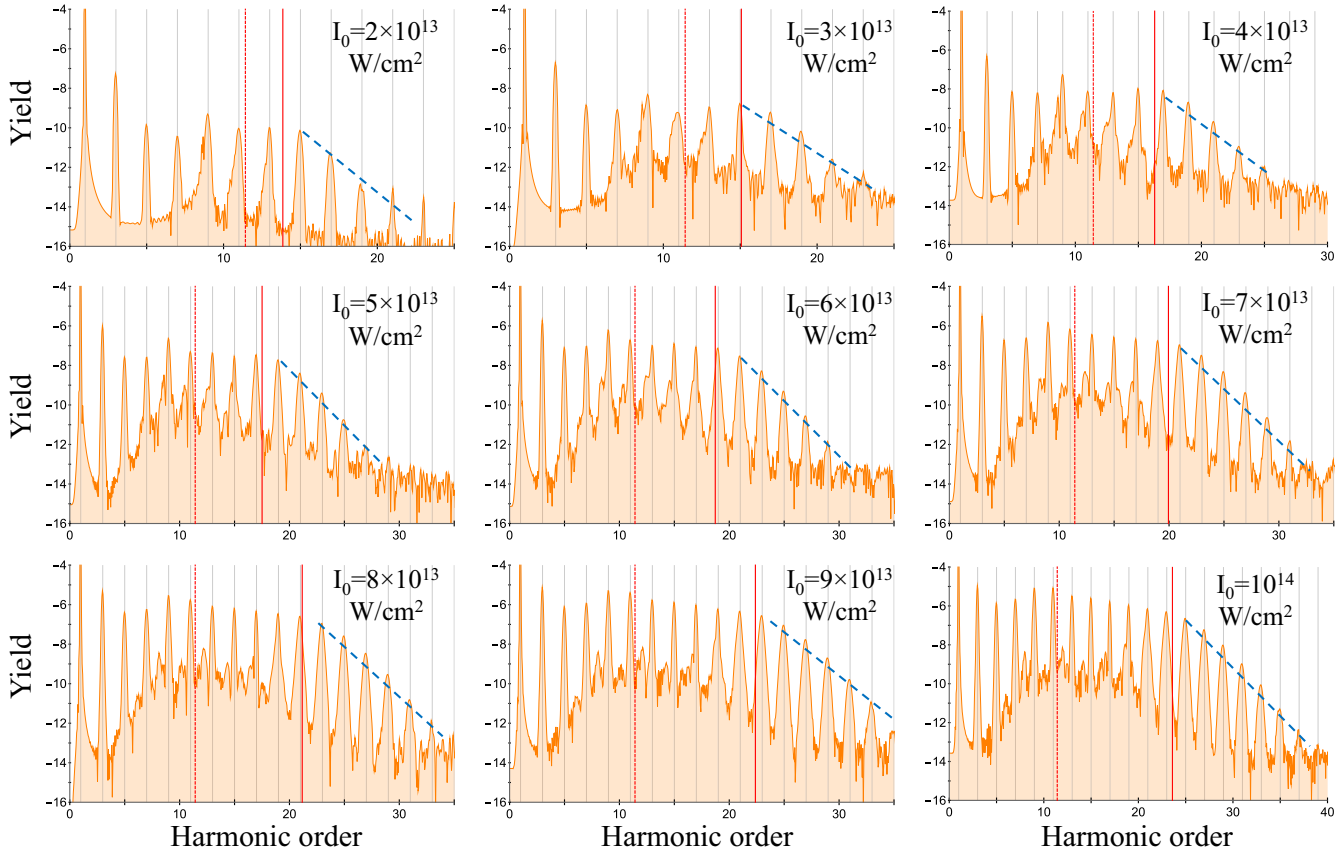

FIG. 2. HHG cutoff energy scaling with respect to laser power in TDDFT. Plots show HHG spectra from H_2 calculated with TDDFT in the same approach as in Fig. 1(b), but for various laser powers. Red dashed lines denote the I_p, red solid lines denote the Lewenstein model cutoff prediction, and dashed blue lines signify the numerical cutoff. Odd harmonics are highlighted by gray lines. HHG yield is presented in logarithmic scale (with basis 10).

Moreover, TDDFT describes nonlinear equations of motion (because the XC potential depends on the time-dependent density); thus, harmonic selection rules might also be broken by imperfections in the approximations for the XC functional [21]. Nonetheless, in this particular case we find that these issues are not the source of the symmetry-breaking harmonics.

Lastly, we address the claims in Ref. [1] that TDDFT leads to an incorrect cutoff energy as compared to the Lewenstein model of HHG [6]. Figure 2 presents calculations in H_2 with the same approach as in Fig. 1(b), but for laser powers ranging from 10^{13} to 10^{14} W/cm^2. In each subplot the I_p is highlighted in dashed red, the cutoff harmonic is highlighted in blue, and the cutoff prediction from the Lewenstein model ($I_p + 3.17U_p$ where U_p is the laser ponderomotive energy) is highlighted in red. The results agree extremely well, always within one harmonic order, as expected for long-duration laser driving pulses. Some deviations are expected due to approximations in the Lewenstein model (e.g., Coulomb focusing effects and electron-electron interactions that are neglected), but these should be small. We therefore conclude that the incorrect scaling discussed in Ref. [1] was a result of several errors: (i) Zang *et al.* incorrectly defined the cutoff as the last harmonic order above noise level. This definition is sometimes used experimentally, but is inappropriate when comparing theory to the Lewenstein model where the cutoff energy is defined as the start of an exponential drop in yield. This cutoff definition originates from analytical considerations arising from the saddle-point method applied in the Lewenstein model itself—energy conservation can only be obtained above the cutoff for imaginary times, leading to an exponentially decaying harmonic yield [6–8]. In that sense, it is conceptually not reasonable to compare cutoff energies defined as the last observable harmonic above noise level to the analytical formula from the Lewenstein model. We highlight that with the correct definition, results in Ref. [1] make much more sense for TDDFT, while the TDNKS formulation seems to incorrectly describe the HHG cutoff and plateau (the response seems largely perturbative). (ii) The box size used in Ref. [1] was too small, causing an artificial saturation of the cutoff for higher laser powers. (iii) The fitting procedure used in Ref. [1] was possibly incorrect (as Eq.(5) in Ref. [1] has a redundant 1.3 factor in front of the I_p that should be negligible in these conditions).

In summary, we could not find any evidence for an intrinsic error introduced by TDDFT that breaks inherent symmetries of the light-matter Hamiltonian (and such evidence cannot be obtained from unconverged numerical results). Additionally, if such hypothetical errors were indeed present and non-negligible, they may be suppressed by employing better approximations for the XC functional (beyond PBE) and would not appear in formally exact TDDFT. We also showed that the HHG cutoff energy agrees perfectly with standard

well-established models for HHG, and the errors discussed in Ref. [1] result from an incorrect analysis. Thus, in our opinion TDDFT remains one of the best affordable approaches for describing strong-field physics from first principles.

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