

# Reply to “Comment on ‘Origin of symmetry-forbidden high-order harmonic generation in the time-dependent Kohn-Sham formulation’”

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In reply to the Comment by O. Neufeld *et al.* [*Phys. Rev. A* **105**, 047101 (2022)], we argue that the conclusions of *Phys. Rev. A* **103**, 043106 (2021) remain valid. We disprove the claim that the unphysical even-order harmonics originate from convergence issues related to reflections at the boundary of the simulation box. By additional calculations, we show that such reflections perturb the high-order harmonic generation spectra by oscillations with periods much smaller than the distance between the harmonics. We also demonstrate that the convergence argument of the Comment, in contrast to our multielectron excitations argument, cannot explain why there are no unphysical even-order harmonics in one-electron systems. Moreover, we show that the argument put forward in the Comment to conclude that the time-dependent Kohn-Sham equations are superior to the time-dependent natural Kohn-Sham equations is not valid.

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Let us first clarify that we do not claim in Ref. [1] (as indicated in the Comment [2]) that unphysical multielectron excitations break the inversion symmetry. The radius of the simulation box used for the H<sub>2</sub> molecule in Ref. [1] is 20 Å and not 20 bohr as claimed in Ref. [2]. Thus, the claim of Ref. [2] that the simulation box would be too small is not correct. The following results are obtained by the OCTOPUS code. We employ Troullier-Martins pseudopotentials and the local-density approximation with self-interaction correction. The dipole approximation is employed for the light-matter interaction with electric field,

$$E(t) = \begin{cases} E_0 \cos^2\left(\frac{\pi(\sigma-t)}{2\sigma}\right) \sin(\omega t) & \text{for } t \leq 2\sigma, \\ 0 & \text{for } t > 2\sigma, \end{cases} \quad (1)$$

where  $E_0$  and  $\omega$  are the strength and frequency, respectively, and  $2\sigma$  is the duration of the laser pulse.

The first point raised in Ref. [2] is that the unphysical even-order harmonics observed in Ref. [1] originate from convergence issues related to reflections at the boundary of the simulation box. We do not agree with this assertion. First, such reflections manifest in high-order harmonic generation (HHG) spectra as oscillations with periods much smaller than the distance between the harmonics. To confirm this point,

we have conducted additional simulations for the H atom and H<sub>2</sub> molecule with the absorbing potential removed, see the results in Figs. 1(a) and 1(b). Second, the even-order harmonics shown in Figs. 1(c) and 1(d) of Ref. [2], thus, are not due to reflections at the boundary of the simulation box but must have another origin. Third, we do not observe even-order harmonics in the HHG spectrum of the H atom (which is a one-electron system with lower ionization energy than the H<sub>2</sub> molecule) using the same absorbing potential as for the H<sub>2</sub> molecule. We have conducted an additional simulation that shows that the same applies to a H<sub>2</sub><sup>+</sup> molecule (which is a one-electron system with higher ionization energy than the H<sub>2</sub> molecule), see the result in Fig. 1(c). Therefore, the claim of Ref. [2] that the reflections at the boundary of the simulation box do not cause even-order harmonics in case of the H atom due to the lower ionization energy is disproved.

To further demonstrate that the unphysical even-order harmonics are not due to convergence issues, we repeat the calculations underlying Figs. 1(a) and 1(b) of Ref. [2]. We use the same parameters, except for the time step and height of the complex absorbing potential (CAP) as those are not specified in Ref. [2]. The time step is small enough and the box radius is large enough for convergence since there is no obvious difference between Figs. 2(b) and 2(c). The high-frequency oscillations in the blue box of Fig. 2(a) are due to reflections at the boundary of the simulation box. When we increase the width of the CAP, the spectrum converges in the sense that the high-frequency oscillations vanish, see Fig. 2(b). The difference between the spectrum in Fig. 2(b) and that in Fig. 1(b) of Ref. [2] is probably due to a different height of the CAP (not specified in Ref. [2]). In any case, the spectra in Fig. 1 of

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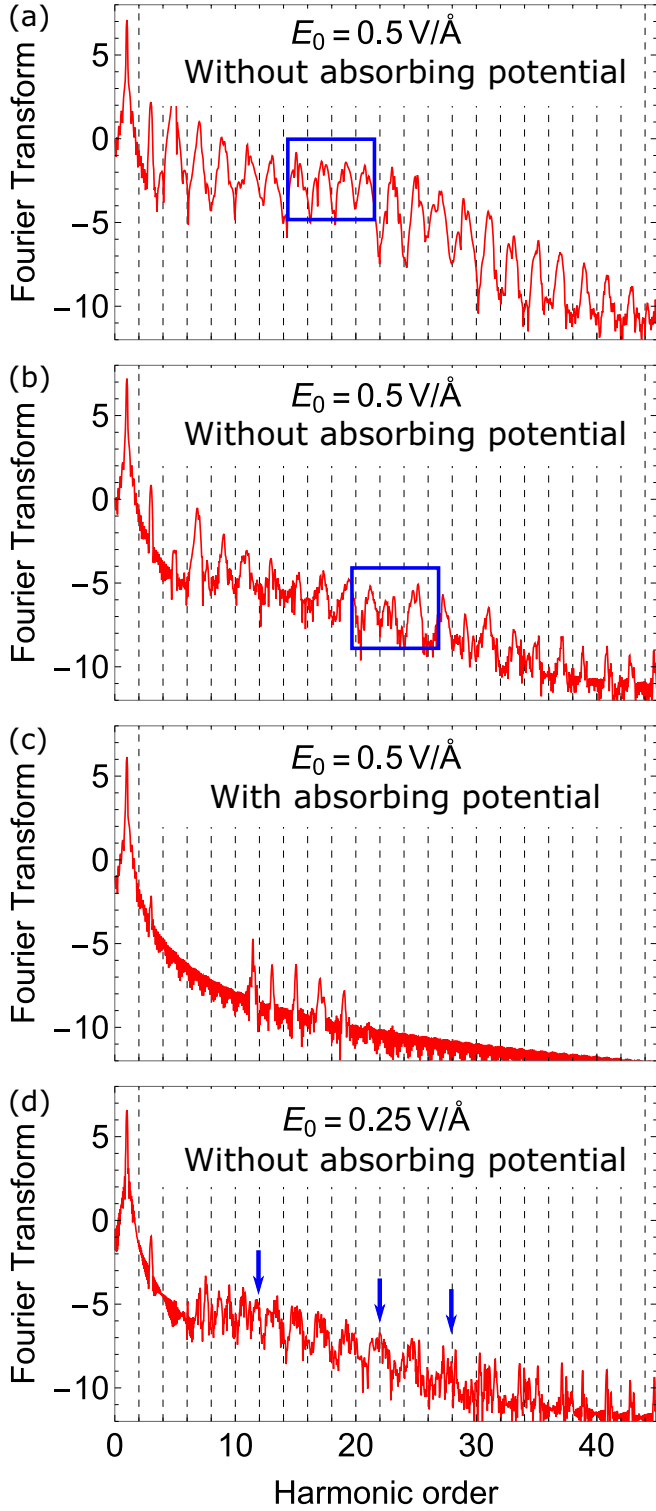


FIG. 1. Time-dependent Kohn-Sham HHG spectra of a (a) H atom, (b) and (d)  $\text{H}_2$  molecule, and (c)  $\text{H}_2^+$  molecule, using  $E_0 = 0.5 \text{ V/\AA}$  but without absorbing potential in (a), (b), and (d) and  $E_0 = 0.25 \text{ V/\AA}$  in (d). Blue squares highlight the oscillations due to reflections, and blue arrows indicate even-order harmonics. The used parameters are the same as in Fig. 1 of Ref. [1] ( $\hbar\omega = 1.55 \text{ eV}$  and  $2\sigma = 5.34 \times 10^{-14} \text{ s}$ ). The simulation box has a radius of  $20 \text{ \AA}$ . It is discretized in increments of  $0.2 \text{ \AA}$ . The time step is  $2.4 \times 10^{-19} \text{ s}$ .

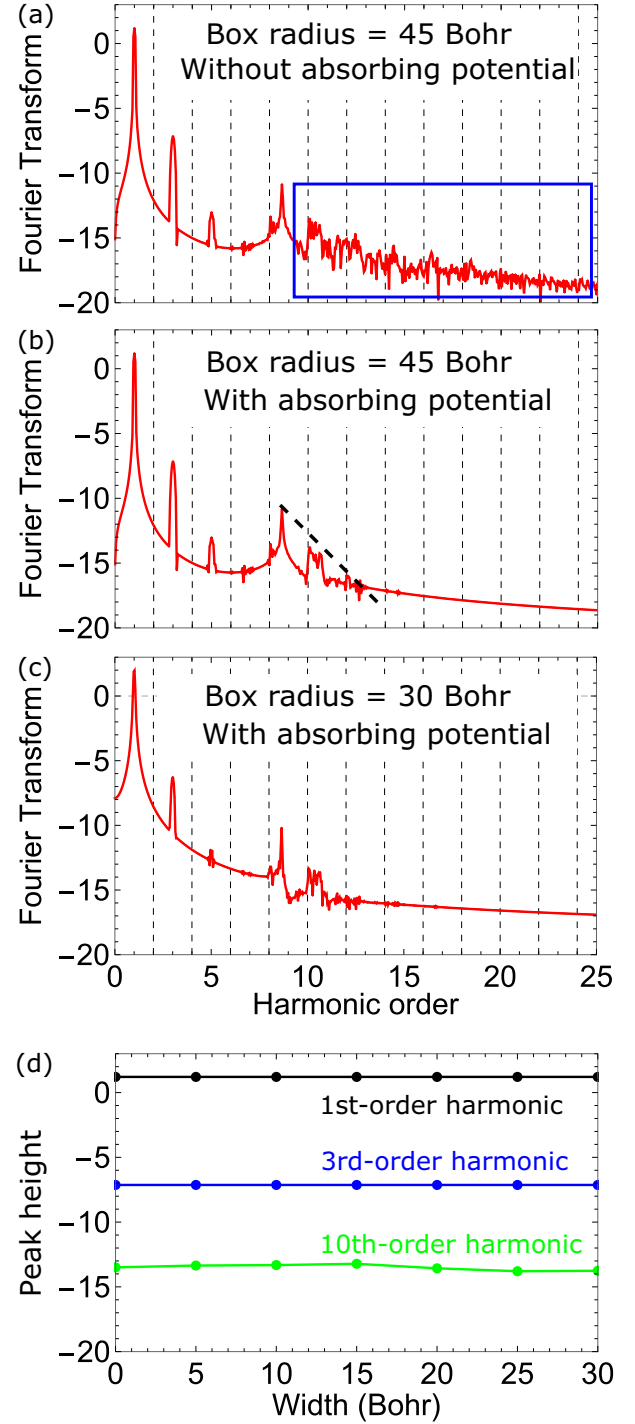


FIG. 2. Time-dependent Kohn-Sham HHG spectra of a  $\text{H}_2$  molecule (a) without absorbing potential, (b) with a CAP of 30 bohr width, and (c) with a CAP of 10 bohr width. The crossing point of the black dashed line and the spectrum in (b) defines the highest appearing harmonic. (d) Peak heights of the first-order (black), third-order (blue), and tenth-order (green) harmonics as functions of the width of the CAP. The used parameters are the same as in Fig. 1 of Ref. [2] ( $\hbar\omega = 1.55 \text{ eV}$  and  $2\sigma = 5.34 \times 10^{-14} \text{ s}$ ). The simulation box has a radius of 45 bohr for (a), (b), and (d) and of 30 bohr for (c). It is discretized in increments of  $0.4 \text{ bohr}$ . The time step is  $1.2 \times 10^{-18} \text{ s}$  for (a), (b), and (d) and  $2.4 \times 10^{-19} \text{ s}$  for (c). The height of the CAP is  $-0.35 \text{ hartree}$  (not specified in Ref. [2]).

Ref. [2] are not converged due to the high-frequency oscillations that resemble our spectrum without the absorbing potential in Fig. 2(a). Probably a much larger height of the CAP is used in Fig. 1 of Ref. [2]. The spectrum in Fig. 2(b) shows no effect of reflections. Figure 2(d) shows that neither the peak heights of the physical nor those of the unphysical harmonics change when the width of the CAP increases. All this demonstrates that the unphysical harmonics are not due to convergence issues.

Moreover, the time-dependent natural Kohn-Sham equations, which do not include unphysical multielectron excitations [3], generate merely odd-order harmonics for both one-electron and two-electron systems [1]. This suggests that neither the absorbing potential nor the reflections at the boundary of the simulation box give rise to an issue in time-dependent density functional theory. Note that there are no even-order harmonics in the HHG spectra of the H atom and  $\text{H}_2^+$  molecule calculated without the absorbing potential, compare Fig. 1(a). The HHG spectrum of the  $\text{H}_2$  molecule calculated with a weaker electric field, see Fig. 1(d), shows that the oscillations due to the reflections at the boundary of the simulation box perturb strongly the whole spectrum and ruin the harmonics from sixth to tenth order whereas for higher orders they are still clearly visible. Since there is no absorbing potential, the even-order harmonics must be due to unphysical two-electron excitations. All these points demonstrate that the unphysical even-order harmonics observed for the  $\text{H}_2$  molecule are not due to convergence issues.

The second point raised in Ref. [2] is concerned with the fitting to the Lewenstein model. We agree that usage

of the highest appearing harmonic as the cutoff introduces some inaccuracy when the cutoff region is wide, however, this does not invalidate our conclusions (see below). The Lewenstein model is suitable for evaluating HHG spectra with a steep cutoff region after a plateau as in this case the end of the plateau (as predicted by the Lewenstein model) defines the cutoff. It cannot be used for HHG spectra with a wide cutoff region for which the highest appearing harmonic should be considered as the cutoff [4,5]. Therefore, the approach put forward in Ref. [2] is not valid. The blue dashed lines in Fig. 2 of Ref. [2] indicate an exponential decrease of the peak height in the cutoff region when the harmonic order increases. Thus, the highest appearing harmonic can be defined by the crossing point between the blue dashed lines and the spectra. The argumentation in Ref. [1] is based on a comparison to the time-dependent configuration interaction HHG spectra, which shows that the highest appearing harmonic is better predicted by the time-dependent natural Kohn-Sham than the time-dependent Kohn-Sham equations. Also, note that in Fig. 2 of Ref. [2] the cutoff should be calculated as  $F(I_p/U_p)I_p + 3.17U_p$  [6]. While  $F(I_p/U_p) \sim 1$  for  $I_0 = 2 \times 10^{13} \text{ W/cm}^2$ ,  $F(I_p/U_p) \sim 1.3$  for  $I_0 = 1 \times 10^{14} \text{ W/cm}^2$  cannot be neglected.

To summarize, we have elucidated issues in the argumentation of Ref. [2] and have confirmed the conclusions of Ref. [1] by additional simulations. In particular, we have shown that the symmetry-forbidden even-order harmonics observed in time-dependent Kohn-Sham HHG spectra can be attributed to unphysical multielectron excitations. The time-dependent natural Kohn-Sham equations do not generate such unphysical even-order harmonics.

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- [1] X. Zang, C. Shang, P. Zhang, Y. Zhu, Z. Zhu, and U. Schwingenschlöggl, Origin of symmetry-forbidden high-order harmonic generation in the time-dependent Kohn-Sham formulation, *Phys. Rev. A* **103**, 043106 (2021).
  - [2] O. Neufeld, N. Tancogne-Dejean, and A. Rubio, Comment on “Origin of symmetry-forbidden high-order harmonic generation in the time-dependent Kohn-Sham formulation”, *Phys. Rev. A* **105**, 047101 (2022).
  - [3] X. Zang, U. Schwingenschlöggl, and M. T. Lusk, Identification and Resolution of Unphysical Multielectron Excitations in

- the Real-Time Time-Dependent Kohn-Sham Formulation, *Phys. Rev. Lett.* **124**, 026402 (2020).
- [4] I. P. Christov, M. M. Murnane, and H. C. Kapteyn, High-Harmonic Generation of Attosecond Pulses in the “Single-Cycle” Regime, *Phys. Rev. Lett.* **78**, 1251 (1997).
- [5] B. Shan and Z. Chang, Dramatic extension of the high-order harmonic cutoff by using a long-wavelength driving field, *Phys. Rev. A* **65**, 011804(R) (2001).
- [6] 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).