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Assessing different forms of the strong-field approximation for harmonic generation in molecules

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We analyze three different formulations of the strong-field approximation for high-harmonic generation in diatomic molecules, based on length, velocity, and acceleration form for the recombination amplitude. We compare the predictions for the two-centre interference with those from the time-dependent Schrödinger equation. We find that the velocity form gives the closest agreement with the exact results while being the simplest from a computational point of view.

Keywords: Harmonic generation; Interference effects; Ehrenfest theorem; Strong-field approximation

1 Introduction

Harmonic generation (HG) is the underlying process of interesting applications such as attosecond-pulse generation [1], molecular tomography [2], or attosecond probing of proton dynamics [3]: atoms and molecules irradiated by intense laser pulses emit high harmonics, i.e. coherent radiation in the extreme ultraviolet regime. A qualitative picture of the HG process is provided by the three-step model [4], which comprises the steps (i) ionization, (ii) electron acceleration by the laser field, and (iii) recombination under emission of a high-frequency photon. This paper addresses an important issue in the theoretical description of HG, namely the question whether the emission spectrum should be calculated from the time-dependent dipole, dipole momentum, or dipole acceleration. It is well known that the harmonic spectrum $S(\omega)$ is proportional to the modulus squared of the Fourier transformed dipole acceleration in the laser-driven system [5–8],

$$S(\omega) \propto |\tilde{\mathbf{a}}(\omega)|^2 = \left| \int \mathbf{a}(t)\, e^{i\omega t} dt \right|^2 . \tag{1}$$

If the time integration in eq. (1) is from minus infinity to infinity, we can ignore the contribution from asymptotic times, and using the Ehrenfest theorem it is straightforward to show that $|\tilde{\mathbf{a}}(\omega)|$ can be replaced by $|\omega^2 \tilde{\mathbf{d}}(\omega)|$, where $\tilde{\mathbf{d}}(\omega)$ is the Fourier-transformed time-dependent dipole moment ("length form"). Alternatively, $|\tilde{\mathbf{a}}(\omega)|$ may be replaced by $|\omega \tilde{\mathbf{v}}(\omega)|$, where $\tilde{\mathbf{v}}(\omega)$ is the Fourier-transformed dipole velocity ("velocity form"). This simple replacement is no longer correct when the time integration is over a finite interval (which is the usual theoretical procedure in short-pulse harmonic generation), and it has been shown that the acceleration form is preferable to the length form [7]. In calculations where the time-dependent Schrödinger equation (TDSE) is solved numerically, another reason to choose the acceleration form is that the acceleration expectation value $\mathbf{a}(t)$, when calculated directly without using the time-dependent dipole $\mathbf{d}(t)$, i.e.,

$$\mathbf{a}(t) = \langle \Psi(t) | \nabla V + \mathbf{E}(t) | \Psi(t) \rangle, \tag{2}$$

is sensitive only to the parts of the wave function near the core region. The length and velocity formulations are sensitive to the full wave function, so they are disturbed significantly by absorbing boundary conditions. In practice, the difference between the different formulations concerns mainly the noise level in the spectra as long as the Schrödinger equation is solved numerically. In this case the formulations are "approximately" equivalent.

On the other hand, within the strong-field approximation (SFA) [9, 10] the situation is dramatically different. The electronic wave functions are approximated, namely the continuum states are usually replaced by plane waves. The different formulations of the HG amplitude (length, velocity or acceleration) appear as different forms of the recombination matrix element between plane wave and ground state. As it was pointed out recently [11], the choice of operator in the matrix element has huge impact on the accuracy of the results.

The recombination matrix element is the same as the one that determines the inverse process, namely single-photon ionization, and in fact the different formulations have been compared much earlier in the context of photoionization. In [12] it was shown that the velocity and acceleration forms within the plane-wave approximation for the continuum electron have the correct asymptotic limit at high electron energies. In contrast, the plane-wave length form *has not* the correct limit *unless* the plane wave describing the continuum electron is corrected to first order in the binding potential. Moreover, the discussion in [12] assumed that exact bound states are used. When not, as it is often the case (e.g. when using the linear combination of atomic orbitals (LCAO) for the ground states of molecules), the same reference [12] states that 'the velocity and the acceleration forms may differ, one being proportional to the derivative and the other to the value of the wave function at the origin'.

We notice that in the context of HG, calculations have almost exclusively been based on either the dipole or on the acceleration, whereas the velocity form has received little attention. In the present work, we demonstrate that the velocity form of the SFA gives the most reliable results, albeit similar to the acceleration-based SFA, while being much easier and faster to evaluate than the acceleration form.

Molecules provide a better ground than atoms for comparing the different formulations, because the spectra can be investigated as a function of internuclear distance and/or molecular orientation. It is known that the two-centre interference pattern in molecular HG [13, 14] is mainly determined by the recombination matrix element. Therefore the two-centre interference is a good indicator of how well each formulation of the matrix element performs.

Regarding the ability of the SFA to predict the interference minimum of the HG spectra in molecules, the authors of [14] conclude that the length form gives poorer results than the acceleration form. Actually, due to some approximations made in the evaluation of the acceleration matrix element, their final expression, eq. (13) of [14] corresponds to the momentum matrix element, i.e. to the velocity form. Very similar conclusions are reached in [11], where the acceleration form is found in good agreement with the results obtained from the numerical integration of the Schrödinger equation.

2 Theory

The strong-field approximation [9] approximates the wave function of the electron in the continuum as a Volkov wave function, which is a plane wave driven by the electric field of the laser pulse. Therefore, the SFA does not exactly reproduce the two-centre interference minimum [13, 14], which occurs when the energy of the recollision electron matches the condition for destructive interference between the two atoms in a diatomic molecule. A possible way to achieve a better prediction of the interference minimum is to use a more accurate wave function that takes into account the presence of the two Coulombic centres. Such an approach was used successfully to describe one-photon ionisation in the hydrogen molecular ion [15]. For HG, this is analysed in detail in [16].

In this work, we look at the predictions within the plane-wave approximation, for all the three formulations that emerge from the Ehrenfest theorem. We consider an H_2^+ molecule in the yz plane and the laser polarised along the z axis. We investigate the harmonics polarised along the z axis, i.e. the relevant momentum of the continuum electron is taken to be along the polarisation direction. The angle between the molecular axis and the polarisation axis is denoted by θ, and the positions of the two protons are $-\mathbf{R}/2$ and $\mathbf{R}/2$. For this work, R = 2 a.u. for which the ionization potential of H_2^+ is $I_\mathrm{p} = 1.1$ a.u. The LCAO approximation is assumed for the ground state of H_2^+,

$$\psi_0(\mathbf{r},\mathbf{R}) = \frac{1}{\sqrt{2[1+s(R)]}}\left[\psi_h(\mathbf{r}+\mathbf{R}/2)+\psi_h(\mathbf{r}-\mathbf{R}/2)\right], \tag{3}$$

where $\psi_h(\mathbf{r}) \equiv \exp(-r)/\sqrt{\pi}$ is the ground state of hydrogen and $s(R) = \exp(-R)(1+R+R^2/3)$ is the overlap integral between the two atomic orbitals. The length form of the transition matrix element reads

$$\begin{aligned}\mathbf{d}_{\mathrm{rec}}(\mathbf{k},\mathbf{R}) &= \langle \mathbf{k}|\mathbf{r}|\psi_0(\mathbf{R})\rangle = \\ &= \sqrt{\frac{2}{1+s(R)}}\left[-\frac{\mathbf{R}}{2}\sin\left(\frac{\mathbf{k}\cdot\mathbf{R}}{2}\right)\tilde{\psi}_h(\mathbf{k})\right. \\ &\left. +\cos\left(\frac{\mathbf{k}\cdot\mathbf{R}}{2}\right)\frac{\partial\tilde{\psi}_h(\mathbf{k})}{\partial\mathbf{k}}\right],\end{aligned} \tag{4}$$

where $|\mathbf{k}\rangle$ is a plane wave normalized in the momentum scale and $\tilde{\psi}_h(\mathbf{k})$ is the Fourier transform of the hydrogen ground-state wave function, $\tilde{\psi}_h(\mathbf{k}) = (\pi\sqrt{2})^{-1}(\mathbf{k}^2/2+1/2)^{-2}$. We omit the electron's charge, $-|e|$, in this and the following matrix elements. The velocity and the acceleration forms are calculated to be, respectively,

$$\begin{aligned}\mathbf{v}_{\mathrm{rec}}(\mathbf{k},\mathbf{R}) &= \langle \mathbf{k}|-i\boldsymbol{\nabla}|\psi_0(\mathbf{R})\rangle = \\ &= \mathbf{k}\sqrt{\frac{2}{1+s(R)}}\cos(\mathbf{k}\cdot\mathbf{R}/2)\tilde{\psi}_h(\mathbf{k}),\end{aligned} \tag{5}$$

and

$$\begin{aligned}\mathbf{a}_{\mathrm{rec}}(\mathbf{k},\mathbf{R}) &= \langle \mathbf{k}|-\boldsymbol{\nabla}V(\mathbf{r})|\psi_0(\mathbf{R})\rangle = \\ &= \sqrt{\frac{2}{1+s(R)}}\left\{\cos(\mathbf{k}\cdot\mathbf{R}/2)\mathbf{I}_{1\mathrm{C}}(\mathbf{k})+\right. \\ &\left. +\,i\,\mathrm{Im}\left[\mathrm{e}^{i\mathbf{k}\cdot\mathbf{R}/2}\mathbf{I}_{2\mathrm{C}}(\mathbf{k},\mathbf{R})\right]\right\},\end{aligned} \tag{6}$$

where the interaction of the electron with the two protons is $V(\mathbf{r}) = -(1/|\mathbf{r}-\mathbf{R}/2| + 1/|\mathbf{r}+\mathbf{R}/2|)$. Here, the electric field $\mathbf{E}(t)$ that appears in eq. (2) has been dropped since it affects only the very low-energetic harmonics. The expression $\mathbf{I}_{1\mathrm{C}}$ is the one-centre integral

$$\mathbf{I}_{1\mathrm{C}}(\mathbf{k}) \equiv \int d^3r\,\frac{e^{-i\mathbf{k}\cdot\mathbf{r}-Zr}}{2^{3/2}\pi^2}\boldsymbol{\nabla}\frac{1}{r}, \tag{7}$$

while $\mathbf{I}_{2C}$ is the one-electron two-centre integral

$$\mathbf{I}_{2C}(\mathbf{k},\mathbf{R}) \equiv \int d^3r \frac{e^{-i\mathbf{k}\cdot\mathbf{r}-Zr}}{2^{3/2}\pi^2} \boldsymbol{\nabla} \frac{1}{|\mathbf{r}-\mathbf{R}|}. \tag{8}$$

The nuclear-charge parameter is taken $Z = 1$ in our case. Both integrals are given in the Appendix together with some computational details.

3 Numerical results and conclusions

For a range of fixed electron wavelengths $\lambda = 2\pi/k$, we calculated the orientation angle of the molecule at which the matrix elements (4),(5), and (6) attain their minimum. Figure 1 shows the results for all the three approaches: the length, velocity, and acceleration form, compared to the results from the numerical integration of the Schrödinger equation (from table II in [14]). As mentioned before, the largest overall deviation is found for the length form. In contrast, the velocity and acceleration form are closer to the TDSE result. Moreover, the two latter forms become asymptotically identical at high electron energies (i.e. in the small wavelength region), in agreement with [12]. Nevertheless, at low electron-energies, there is an increasing discrepancy with respect to the TDSE results, showing the need to take better into account the two-centre nature of the binding potential in describing the continuum electron (see [16]).

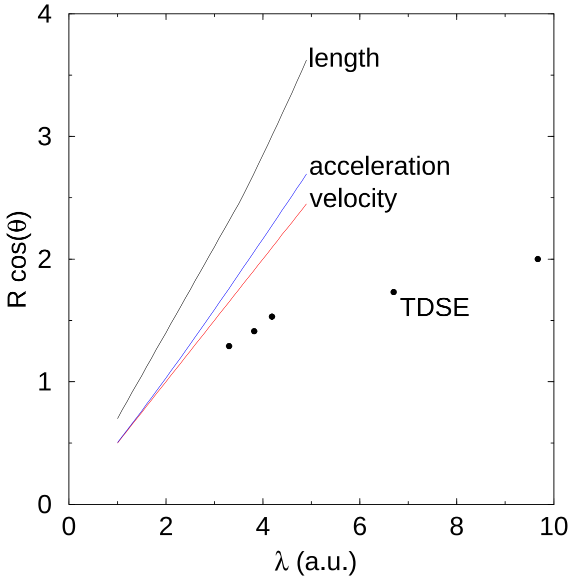

Figure 1. Projected internuclear separation for the molecular orientation where the modulus of the recombination amplitudes is minimal. The time-dependent results are taken from table II in [14], defining $\lambda = 2\pi/\sqrt{2(\Omega_\mathrm{m} - I_\mathrm{p})}$, with Ω_m being the harmonic energy where the interference minimum occurs in the TDSE spectra for a given orientation.

Figure 2 shows the full length-gauge SFA spectra[1] for harmonic emission polarised along the laser polarisation axis, in the case $\theta = 40°$. The calculation has been carried out for all the three Ehrenfest formulations, and the vertical lines show the predicted interference minimum, as given by fig. 1, together with the TDSE result from [14]. A trapezoidal shape is assumed for the vector potential $\mathbf{A}(t)$, with three optical cycle linear turn-on and -off and four optical cycles of constant amplitude. The position of the minima agree well with the estimates of figure 1, which were made based solely on the analysis of the recombination matrix elements [see eqns. (4), (5), and (6)]. The velocity formulation, apart from the computational simplicity, predicts an interference minimum closest to the TDSE result. Similarly, the acceleration formulation is in good agreement with TDSE, but it is computationally more demanding than the velocity form. For high harmonic orders, i.e. at high recollision-electron energies, the acceleration-form spectrum is almost the same as in the velocity form, which can be also inferred from fig. 1. The length form is seen to differ significantly from TDSE.

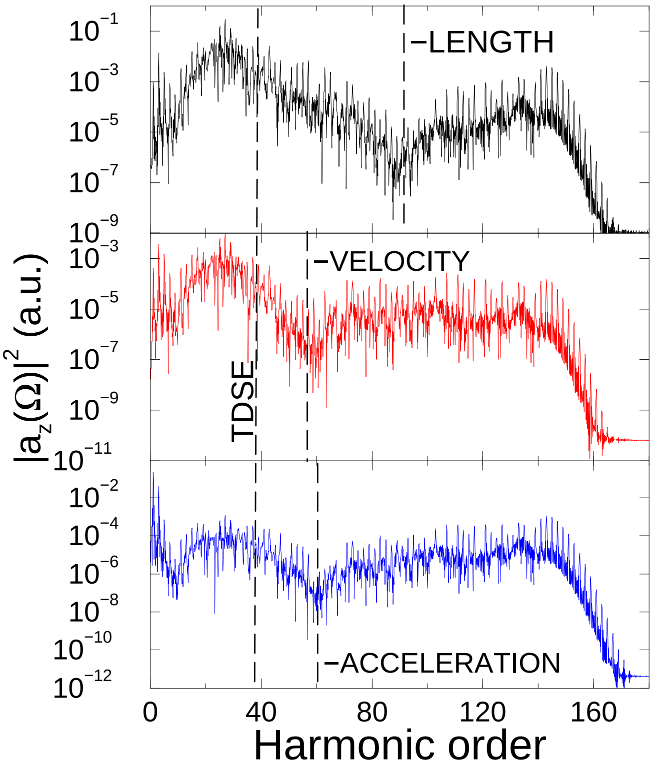

Figure 2. Harmonic spectra for radiation polarised along the laser polarisation direction, calculated for all the three formulations. The laser intensity is 1×10^{15} W/cm^2 and the carrier wavelength is 800 nm. The molecular axis makes an angle of 40 degrees with the electric field of the laser. The vertical lines indicate the minimum positions expected on the basis of figure 1.

The agreement between all the three forms and the TDSE being not quite satisfactory, we conclude that an improved description for the continuum electron in the presence of two attractive centres,

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[1] The length-gauge refers here to the form of the Hamiltonian, and not to the form of the recombination matrix element.

instead of a plane wave, is desirable, at least for slow returning electrons [16]. Nevertheless, among the different versions of the plane-wave SFA, the velocity form yields acceptable results and is superior to the acceleration form. Moreover, the velocity form is simpler to evaluate than the acceleration from.

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Appendix

The one-centre integral is readily calculated

$$\mathbf{I}_{1\mathrm{C}}(\mathbf{k}) = \hat{\mathbf{k}}\frac{i\sqrt{2}}{\pi k}\left[1 - \frac{\arctan(k/Z)}{k/Z}\right]. \tag{9}$$

For the two-centre integral, we employ the technique described in detail in [17]. It uses a combination of the Fourier transform of the binding potential and the Feynman identities. The final result reduces to a one-dimensional integration

$$\begin{aligned}\mathbf{I}_{2\mathrm{C}}(\mathbf{k},\mathbf{R}) = \frac{iZ}{\pi\sqrt{2}}\int_0^1 dx\ \frac{xe^{-R\sqrt{A}-ix\mathbf{k}\cdot\mathbf{R}}}{\sqrt{A}}\Bigg[& -i\mathbf{R} + \\ & + \mathbf{k}\frac{x}{\sqrt{A}}\left(R + \frac{1}{\sqrt{A}}\right)\Bigg],\end{aligned} \tag{10}$$

with $A \equiv x[Z^2 + (1-x)k^2]$.

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