Calculation of HHG spectra in complex atoms.

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Abstract. We propose a procedure for calculating the high harmonics yield from complex atoms. The procedure relies on the description of an atomic system by means of the Hartree-Fock potential including the exchange interaction to describe the motion of the single active electron.

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1. Introduction

High harmonic generation (HHG) is a nonlinear atomic phenomenon which can be described qualitatively as a 3-step process. At the first step, the atomic electron undergoes a tunneling ionization. If this event occurs at the right moment of time such that the classical trajectory of the electron in the electromagnetic (EM) field will eventually return to the nucleus, the electron can recombine and emit a photon. This essentially classical model proposed by Corkum (1993) explains many characteristic features of HHG such as the existence of the plateau in the spectrum (Krause *et al* 1992, L'Huillier and Balcou 1993). A typical pattern of the HHG spectrum consists of the first few generally quickly decreasing harmonics followed by a plateau. The plateau ends with a sharp cut-off located at the photon energy of approximately $I_\mathrm{p} + 3.17U_\mathrm{p}$, where I_p and U_p are the ionization potential of the atom and the ponderomotive energy of electronic motion in the EM field. These general features of HHG follow also from semiclassical (Becker *et al* 1994, Kuchiev and Ostrovsky 1999, Kuchiev and Ostrovsky 2001) or quantum (Usachenko and Pazderezsky 2002) approaches to the description of HHG. From the quantum mechanical point of view, HHG can still be regarded as release and quantum evolution of the atomic electron followed by emission of the HHG photon.

For a quantitative description of HHG, one has to develop a procedure allowing to describe these steps for a real atomic or molecular system of certain complexity. A complete, *ab initio* solution of this problem is hardly possible for systems with more than one electron. One has to adopt various approximations to make the problem tractable. This can be, for example, the so-called strong field approximation (SFA) (Usachenko and Pazderezsky 2002, Milošević 2006, Milošević 2007) which neglects the influence of the atomic potential on the motion of the released electron during the second stage of the HHG process. The electron motion is described by a propagator constructed from the Volkov states (Milošević 2006, Milošević 2007) which simplifies the problem considerably. Modification of this approach which takes into account the atomic structure is possible in principle (Ivanov and Kheifets 2008*a*, Ivanov and Kheifets 2008*b*). Such a modification helps to understand the known effect of the atomic structure

on the HHG spectra (Ganeev *et al* 2006a, 2006b, 2007a, 2007b) . However, this method can hardly be used as a computational tool for studying HHG in complex atoms or molecules.

The method which is commonly employed to describe qualitatively HHG and a closely related process of the above threshold ionization (ATI) in complex systems is the single active electron (SAE) approximation (Krause *et al* 1992, Takahashi *et al* 2007, Peng and Starace 2006, Shon *et al* 2000). In SAE, the atomic structure is replaced by an effective potential so chosen as to represent accurately the energies of the ground and first few excited states. Solution of the time-dependent Schrödinger equation (TDSE) for the active electron in such a potential is possible in three dimensions without further approximations and can be used to compute HHG or ATI spectra.

This method allowed to solve successfully many otherwise almost untractable problems such as the ATI spectra in argon which were reproduced in good agreement with experiment Nandor *et al* (1999). Calculations of HHG using the SAE approximation revealed such features of the HHG process as spectral cutoff, the phase structure and formation of the attosecond pulses.

The choice often made for the effective potential in the SAE approximation is the Hartree-Slater potential (Shon *et al* 2000). Below, we describe a procedure which goes one step further. We employ the Hartree-Fock potential which includes the exchange interaction to describe the motion of the active electron in SAE approximation. This gives us a better description of the atomic core and more accurate energies of the ground and excited states.

It should be realized, of course, that SAE has its inherent limitations. A limited description of electron correlations used in SAE implies that such effects as resonances due to excited states or core excitations cannot be treated properly. It is known, for example (Gordon *et al* 2006), that SAE predicts similar emission rates in all noble gases contradicting the experiment, which shows that heavier noble gases have much stronger harmonics yield. It is known also (Kitzler *et al* 2004) that SAE cannot describe properly extended, highly polarizable systems, such as large molecules. More elaborate methods

are needed in these cases, such as multi-configurational time-dependent Hartree-Fock method (Kitzler *et al* 2004), three-dimensional time-dependent Hartree-Fock approach (Nikolopoulos *et al* 2007), or time-dependent density functional theory (Tong and Chu 1998). Application of such methods poses a difficult computational task, often necessitating the use of other approximations such as reducing dimensionality of the TDSE. On the other hand, the SAE approximation, effectively reducing the problem to a single-electron one, allows to solve the three-dimensional TDSE with moderate computational efforts. The latter property is especially important if we are interested in description of generation of the harmonics of high orders when retaining terms with high angular momenta in the wave function is important.

Below, we describe the procedure based on the description of an atomic system by means of the Hartree-Fock potential including exchange interaction, and apply it to the calculation of HHG spectra in Li, K, and Rb atoms.

2. Theory.

We are looking for a weak solution of the TDSE for the atom in the external EM field:

$$\langle \Phi | \left(i\frac{\partial}{\partial t} - \hat{H}_{\rm atom} - \hat{H}_{\rm int}(t) \right) \Psi \rangle = 0, \tag{1}$$

where $|\Phi\rangle$ is any vector from certain subspace $\mathcal{V}$ of the Hilbert space $\mathcal{H}$ which we will specify below.

In Equation (1) $\hat{H}_{\rm atom}$ is the Hamiltonian of the field-free atom. We describe the field-free atom in the ground state by solving a set of self-consistent Hartree-Fock equations (Chernysheva *et al* 1976). We adopt the single active electron approach and describe the one-electron excitations from the valence shell in the frozen-core Hartree-Fock (FCHF) approximation. This part of the atomic Hamiltonian is thus a non-local integro-differential operator. To account for the polarization effects, the polarization potential $V(r) = -\frac{\alpha}{2(r^2+r_0^2)^2}$, is added to the Hamiltonian to provide a limited description of the core polarization (Bray and Stelbovics 1995). Here α is atomic polarizability, the parameter r_0 is chosen such that the energy of the first excited atomic state is reproduced accurately.

To describe interaction of the atom and the external electromagnetic field we use the length gauge. The EM field is chosen to be linearly polarized along the z-axis. The operator $\hat{H}_{\rm int}(t)$ in Equation (1) reads in atomic units:

$$\hat{H}_{\rm int}(t) = f(t) z F \cos \Omega t \tag{2}$$

Here $f(t)$ is a switching function which is smoothly growing from 0 to 1 on a switching interval $0 < t < T_1$, and is constant for $t > T_1$. The switching time is $T_1 = 5T$ where T is a cycle of the laser field. The whole interval of time on which the time-evolution was computed was 30 cycles of EM field.

To approximate a weak solution of TDSE (1), the subspace $\mathcal{V}$ has to span as large portion of the entire Hilbert space $\mathcal{H}$ as possible. This can be achieved using for $\mathcal{V}$ a subspace spanned by the set of the so-called pseudostates. This set can be obtained by diagonalizing the field-free Hamiltonian in a square integrable basis (Bray 1994):

$$\langle f^N_{nl} | \hat{H}_{\rm atom} | f^N_{n'l'} \rangle = E_{nl} \delta_{nn'} \delta_{ll'} \ . \tag{3}$$

Here E_{nl} is the energy of a pseudostate and N is the size of the basis. It can be shown (Bray 1994, Bray and Stelbovics 1995) that for a sufficiently large basis size N, pseudostates span a large portion of the Hilbert space. In particular, they can be efficiently used to represent atomic states belonging to continuum. Experience shows that a good convergence with respect to the basis size can be achieved for $N \approx 50$ for each value of l. We used this value in the calculations presented below. After diagonalization (3) is achieved, we do not need to use the complicated non-local operator $\hat{H}_{\rm atom}$, all information about the Hamiltonian of the field-free atom is encapsulated in the set of the pseudostates.

To construct the set of pseudostates satisfying Equation (3) we use either the Laguerre basis, or set of the B-splines. Both sets of functions are defined in a box of sufficiently large size $R_{\rm max}$ ($R_{\rm max} = 200$ a.u. in the present calculation). The set of B-splines is much more convenient to handle numerically for large angular momenta ($l > 10$) which we have to consider if our goal is to study harmonics of high orders. We used a set of B-splines of the order $k = 7$ with the knots located at the sequence of points lying in $[0, R_{\rm max}]$. All the knots t_i were simple ones except for the knots located at the

origin and the outer boundary $R = R_{\max}$ of the box. These knots had multiplicity $k = 7$. The simple knots were distributed in $(0, R_{\max})$ according to the rule $t_{i+1} = \alpha t_i + \beta$. The parameter α was close to 1, so that the resulting distribution of the knots was almost equidistant. For each value of the angular momentum l the first $l+1$ B-splines and the last B-spline resulting from this sequence of knots were discarded. This ensures, that any B-spline in the set decreases as r^{l+1} (or faster) at the origin, and assumes zero value at the outer boundary.

For systems with non-empty core, the FCHF atomic Hamiltonian $\hat{H}_{\rm atom}$ has low lying eigenstates corresponding to the core states which must be excluded from consideration. We supplement, therefore, Equation (1) with the orthogonality requirements $\langle \Phi_i | \Psi \rangle = 0$, where $|\Phi_i\rangle$ is any core state.

The subspace $\mathcal{V}$ in which the solution of Equation (1) is sought, is thus a span of all pseudostates, defined in Equation (3), which do not belong to the atomic core:

$$\Psi(\boldsymbol{r}, t) = \sum_{j \notin \text{core}} a_j(t) f_j(\boldsymbol{r}). \tag{4}$$

In the calculations we present below, the pseudostates with angular momenta $l < 60$ were included in Equation (4). This implies that for a modestly strong electric fields of the order of 0.01 a.u. corresponding to 3.5×10^{12} W/cm^2 intensity we may hope to describe accurately formation of harmonics of the order of 60.

As noted above, the pseudostates (3) are computed within a box of the finite size. Possible reflections of the wavepackets from the boundaries of the box may lead to the appearance of the spurious harmonics in the spectrum. This effect may be present even if, as in the results given below, excursion radius of electronic motion in the EM field is small comparing to the size of the box (Krause *et al* 1992). To exclude this possibility, we add to the Hamiltonian the complex absorbing potential $-iW(\boldsymbol{r})$ which is chosen as a smooth function, zero for $r \leq 180$ a.u. and continuously growing to a constant $-iW_0$ with $W_0 = 2$ a.u. outside this region.

With thus defined total Hamiltonian, equations (1) and (4) lead to a system of differential equations for the coefficients $a_j(t)$, which, in the matrix form, can be written

as:

$$i\dot{\boldsymbol{a}} = \left(\hat{\boldsymbol{H}}_{\mathbf{atom}} + F\boldsymbol{D}f(t)\cos\Omega t - i\boldsymbol{W}\right)\cdot\boldsymbol{a}, \tag{5}$$

where $\hat{\boldsymbol{H}}_{\mathbf{atom}}$, $\boldsymbol{D}$ and $\boldsymbol{W}$ are correspondingly matrices of FCHF atomic Hamiltonian, dipole operator, and absorbing potential computed in the basis introduced in Equation (4). We find solution of this system of equations for the time interval $(0, T_1)$, $T_1 = 30T$ using the Crank-Nicholson method.

The harmonics spectrum is calculated as prescribed by Krause *et al* (1992):

$$|d(\omega)|^2 = \left|\frac{1}{t_2 - t_1}\int_{t_1}^{t_2} e^{-i\omega t} d(t)\ dt\right|^2 . \tag{6}$$

Here $d(t) = \langle\Psi(t)|z|\Psi(t)\rangle$ is expectation value of the dipole momentum, t_1, t_2 are chosen to be large enough to minimize the transient effects (we use typically last 10 cycles of the pulse duration, i.e., $t_1 = 20T$, $t_2 = 30T$).

3. Results.

In all cases we consider below, the atom is prepared initially in the ground state. In Figure 1 we present a harmonics spectrum obtained from the Rb atom subjected to the EM field with parameters indicated in the figure caption. Here the harmonics intensity is plotted versus the harmonics number $N = \omega/\Omega$, where Ω is the frequency of the driving EM field.

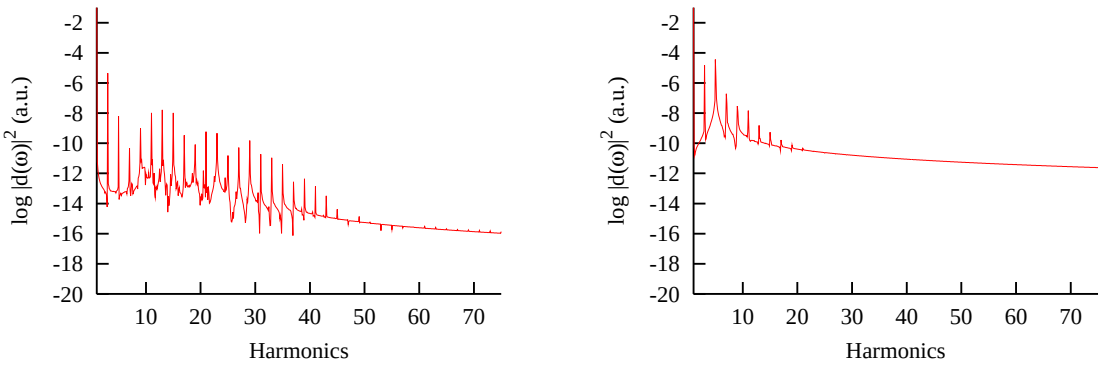

Figure 1. Harmonics spectrum of Rb, peak strength of the EM field $F = 0.0027$ a.u., $\Omega = 0.162$ eV, $N_{\text{cutoff}} \approx 50$ (left panel); $F = 0.0027$ a.u, $\Omega = 0.3$ eV, $N_{\text{cutoff}} \approx 20$ (right panel)

In Figure 1, we see clearly the harmonics cutoffs at $N_{\text{cutoff}} \approx 50$ and $N_{\text{cutoff}} \approx 20$ for the field parameters corresponding to the left and right panels, respectively. Harmonics spectra show little sensitivity to the interval of time which we use for calculating the integral in Equation (6). If, instead of using the integration limits $t_1 = 20T, t_2 = 30T$ we chose $t_1 = 25T, t_2 = 30T$, we would obtain a very similar spectrum shown on the right panel of Figure 2. The harmonic intensities are well converged, especially for the harmonics of the orders up to $N = 30$.

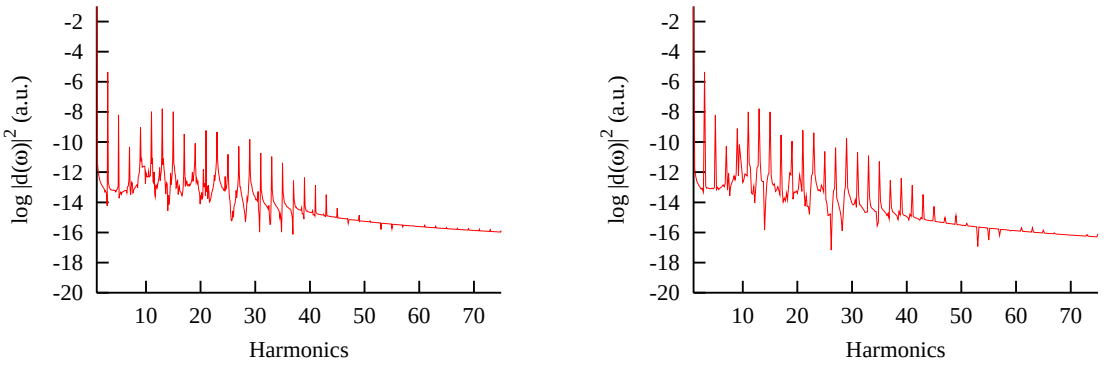

Figure 2. Harmonics spectrum of Rb, peak strength of the EM field $F = 0.0027$ a.u., $\Omega = 0.162$ eV; $t_1 = 20T, t_2 = 30T$ (left panel), $t_1 = 25T, t_2 = 30T$ (right panel)

Analogous calculations were performed for K and Li atoms. Results for various field strengths and frequencies of the EM field are presented in Figure 3 and Figure 4. These results show a typical behavior of the HHG spectra exhibiting the cutoffs at the orders prescribed by the $I_{\text{p}} + 3.17U_{\text{p}}$ rule.

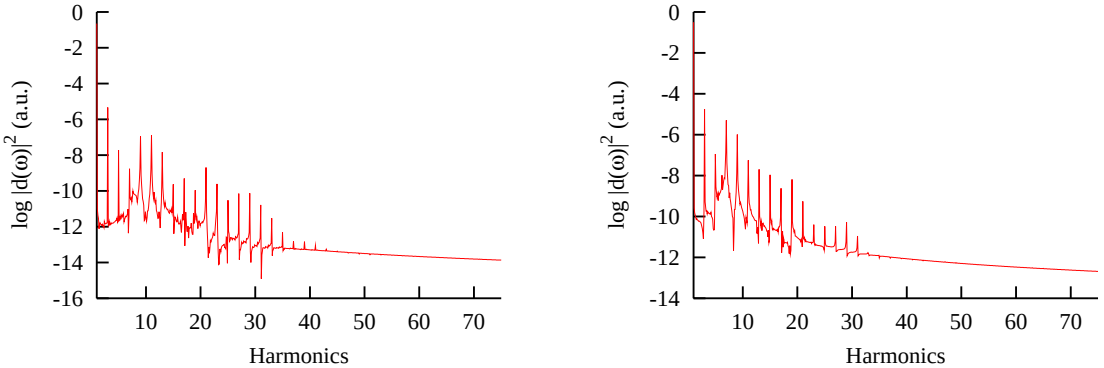

Figure 3. Harmonics spectrum of K, peak strength of the EM field $F = 0.003$ a.u., $\Omega = 0.2$ eV, $N_{\text{cutoff}} \approx 40$ (left panel); $F = 0.0035$ a.u, $\Omega = 0.25$ eV, $N_{\text{cutoff}} \approx 30$ (right panel)

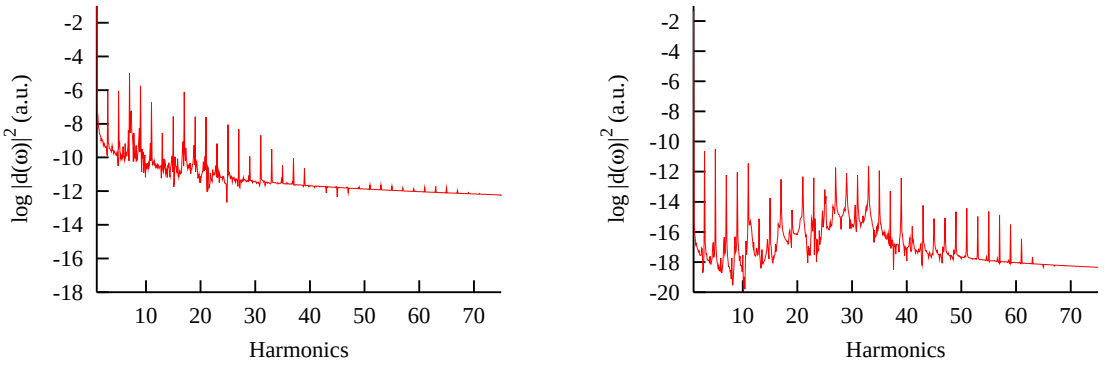

Figure 4. Harmonics spectrum of Li, peak strength of the EM field $F = 0.005$ a.u., $\Omega = 0.25$ eV, $N_{\rm cutoff} \approx 45$ (left panel); $F = 0.0025$ a.u, $\Omega = 0.16$ eV, $N_{\rm cutoff} \approx 60$ (right panel).

Using as an example the calculation for K with the field parameters from the left panel of Figure 3, we shall discuss the role played by the Hamiltonian chosen for the description of the atomic system. The prime motivation to use for this purpose the Hatree-Fock Hamiltonian (including the polarization potential) is to represent accurately a large number of excited atomic states. As can bee seen from Table 1, the Hatree-Fock description gives considerably more accurate energy eigenvalues of the first lowest excited levels as compared with the description without polarization potential or the description relying on the Hatree-Slater potential.

Level	NIST	HF	$V_{\rm pol} = 0$	Hartree-Slater potential
$4p$	1.61	1.62	1.41	1.34
$5s$	2.61	2.61	2.35	2.07
$3d$	2.67	2.62	2.43	2.05
$5p$	3.06	3.07	2.77	2.49
$4d$	3.40	3.37	3.12	2.74
$6s$	3.40	3.45	3.15	2.83
$4f$	3.49	3.49	3.16	2.77

Table 1. The lowest excited states of potassium. The excitation energies (in eV) are from the NIST data base (Sansonetti *et al* 2005). The calculated values are from the Hartree-Fock method (third column), the Hartree-Fock without the polarization potential (fourth column) and the local Hartree-Slater potential (fifth column).

This difference with which excited levels are represented in different models is

translated into different HHG spectra. These spectra, for the calculations using the HF description without polarization potential and the Hartree-Slater local potential are shown in Figure 5. These spectra are to be compared with the spectrum shown on the left panel of Figure 3 which was obtained using the Hartree-Fock Hamiltonian including the polarization interaction.

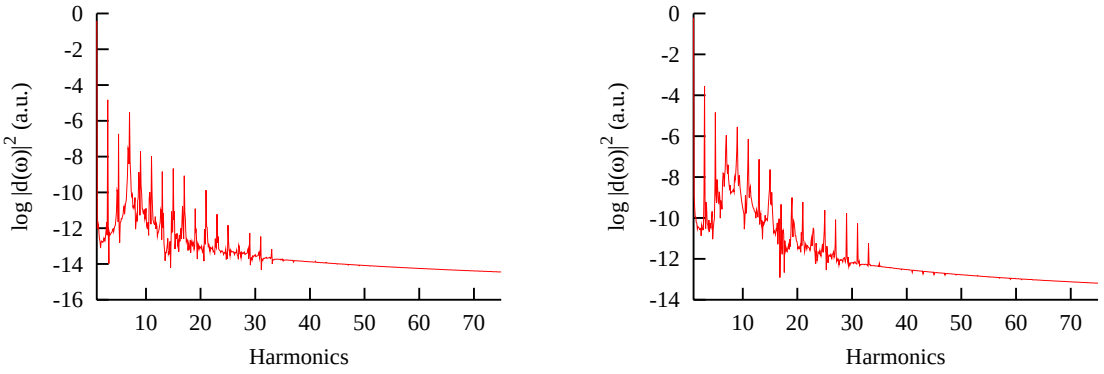

Figure 5. Harmonics spectrum of K, peak strength of the EM field $F = 0.003$ a.u., $\Omega = 0.2$ eV; calculation without polarization potential (left panel); calculation using Hartree-Slater potential (right panel).

One can see that account or neglect of the polarization potential produces a relatively small change in the HHG spectrum, both for harmonics and background intensities. Replacing the Hartree-Fock Hamiltonian by the Hartree-Slater one leads to far more substantial changes in the HHG spectra. Harmonics in the latter case are typically one or two orders of magnitude more intense. The reason of this difference in the HHG spectra might be due to the considerable difference of the spectra of the Hartree-Fock and Hartree-Slater Hamiltonians as seen from the data shown in Table 1).

Finally, to make sure that the presently employed box size $R_{\max} = 200$ a.u. is chosen adequately and no spurious effects due to the reflections of the wavepacket from the box boundary are present, we show in Figure 6 the evolution of the spatial electronic density with time for the EM field parameters corresponding to the left panel of Figure 4. Profiles of the spatial densities indicate absence of the wavepackets traveling back to the nucleus.

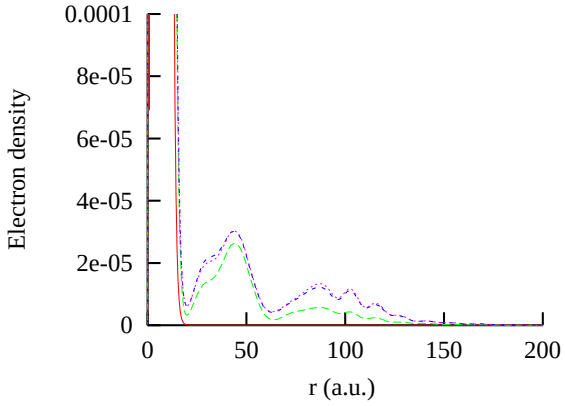

Figure 6. Evolution of spatial electron density for the Li atom in EM field with $F = 0.005$ a.u., $\Omega = 0.25$ eV at the initial moment of time (red) solid line, $t = 10T$ (green) long dash, $t = 20T$ (green) long dash, $t = 30T$ (magenta) dots.

4. Conclusion.

As we noted in the Introduction, SAE is a well-established procedure allowing to treat interaction of complex atoms or molecules with EM radiation, in particular, to describe the HHG process in these systems. The usual requirement to the effective potential, which mimics the effect of the atomic core, is realistic representation of the ground and several excited states of the system under consideration. The Hartree-Slater potential which is often used for this purpose neglects the exchange effects.

We described a computational procedure which relies on the Hartree-Fock potential, including the non-local exchange interaction, This choice gives us a more detailed description of the atomic system of interest. All the information about the potential is contained in the set of the pseudostates defined according to Equation (3). Once this set is constructed, we can solve the three-dimensional TDSE with moderate computational effort. This circumstance is very useful if our goal is description of the generation of the harmonics of high orders. In this case, the terms with high angular momenta are to be retained in Equation (4).

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