Atomic systems with one and two active electrons in electromagnetic fields: ionization and high harmonics generation

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Abstract. We describe a theoretical procedure for solving the time-dependent Schrödinger equation (TDSE) for atomic systems with one or two valence electrons. Motion of the valence electrons is described by means of the Hartree-Fock potential including the exchange interaction. We apply the procedure to various physical phenomena occurring in atoms exposed to strong electromagnetic fields. As an illustration, we consider below the processes of high harmonics generation and attosecond pulses production.

1. Introduction
Nonlinear optical phenomena, such as above-threshold ionization (ATI) [1] or high harmonics generation (HHG) [2], occur when atomic systems are exposed to an intense electromagnetic (EM) field. Qualitatively, many features of these phenomena can be understood using simple pictures of classical physics, which makes their study particularly interesting. For the HHG process such a picture is provided by the well-known 3-step model [3]. In the framework of this model, atomic electron emerges into the continuum with zero velocity at a particular moment of time $t_0$ within the optical cycle. For some selected values of $t_0$ classical electron trajectory returns to the nucleus, where the electron can recombine and emit a photon. The frequency of the emitted photon is determined by the amount of energy acquired by the electron, and the atomic ionization potential $I_p$, assuming that the electron recombines to the ground state. A simple analysis of the classical trajectories shows, that the electron kinetic energy cannot exceed the value of $3.17U_p$, where $U_p$ is the ponderomotive potential. This leads to the well-known $I_p + 3.17U_p$ cut-off rule for the maximum energy of a photon emitted in the recombination process. A classical picture of the ATI process differs in the respect that the released electron rescatters instead of recombining, thereby acquiring additional energy of up to $10U_p$ [4].

A quantum mechanical description [5] explains the reason of the success of the classical approach. Instead of the classical electron trajectories in the EM field, this approach uses the quantum-mechanical description of the motion of the released electron. Such a description is greatly simplified if the so-called strong-field approximation (SFA) is used. SFA neglects the influence of the atomic potential on the motion of the released electron during the second stage of the HHG process. In the framework of this approximation the well-known Volkov states can be employed for the quantum mechanical description of the electronic motion in presence of the EM
field, and the problem becomes analytically tractable. Calculation of the transition amplitudes in this approach can be performed with the help of the saddle-point method, and the classical trajectories naturally emerge as extrema in the saddle-point analysis of the quantum-mechanical amplitudes computed within the SFA.

The quantum mechanical description based on the SFA takes into account only the influence of the EM field on the electron and neglects the atomic potential. Yet, it is known that the atomic structure may considerably modify the observed spectra. In the HHG process, for instance, resonant enhancement of harmonics in the spectrum may take place if a multiphoton resonance occurs between the ground and an excited level [6]. Such phenomena can, in principle, be described by employing the exact propagator [7] instead of the Volkov propagator used in the SFA theory. However, this approach is very difficult to implement in practical calculations. Below, we present an alternative procedure describing the atom–EM field interaction, which is based on solving the TDSE for an atomic system described by means of the Hartree-Fock and polarization potentials.

For illustration purposes, we shall consider below only the systems with one valence electron. All formulas presented below can easily be modified for the case of two valence electrons. We illustrate the proposed computational procedure by applying it to the HHG process in the lithium atom.

2. Theory

Our goal is to find a weak solution of the TDSE for the atom in the external EM field:

\[
\langle \Phi \mid \left(i\frac{\partial}{\partial t} - \hat{H}_{\text{atom}} - \hat{H}_{\text{int}}(t)\right) \Psi \rangle = 0,
\]

where \(\Phi\) is any vector from a subspace \(V\) of the Hilbert space \(\mathcal{H}\). The subspace \(V\) is constructed using the set of pseudostates, obtained by diagonalizing the field-free atomic Hamiltonian in a square integrable basis [8]:

\[
\langle f_j^N \mid \hat{H}_{\text{atom}} \mid f_j'^N \rangle = E_{jj'} \delta_{jj'}.
\]

In Eq.(2), \(\hat{H}_{\text{atom}}\) is the Hamiltonian of the field-free atom. We describe the field-free atom in the ground state by solving the set of self-consistent Hartree-Fock equations [9], which enables us to define direct and exchange potentials for the valence electrons. The core polarization effects are included by means of the polarization potential.

For systems with a non-empty core, field-free atomic Hamiltonian \(\hat{H}_{\text{atom}}\) has low-lying eigenstates corresponding to the core states, which must be excluded from consideration. The subspace \(V\) in which the solution of Eq.(1) is sought, is thus a span of all pseudostates defined in Eq.(2), which do not belong to the atomic core:

\[
\Psi(r, t) = \sum_{j \notin \text{core}} b_j(t) f_j(r).
\]

To describe the interaction of the atom and the external EM field we employ either velocity or length gauges.

To construct the set of pseudostates satisfying Eq. (2), we use the Laguerre basis, or (for large angular momenta) a set of B-splines, confined to a box of the size \(R_{\text{max}} = 200\) a.u. The B-splines of the order \(k = 7\) with the knots located at the (approximately equidistant) sequence of points lying in \([0, R_{\text{max}}]\) are used in the calculation presented below.

The fact that the system is confined to a box of a finite size, may lead to spurious effects, such as appearance of extra harmonics in the HHG spectrum due to reflection of the wavepackets from the boundaries of the box [2]. One can minimize this effect by using a mask function or an
absorbing potential. We use the absorbing potential \(-iW(r)\), which is 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.

In the calculations relying on the length gauge to describe atom–EM field interaction, the pseudostates with angular momenta \(l < 120\) were included in Eq. (3). This implies, that for EM field strength of the order of 0.01 a.u., corresponding to \(3.5 \times 10^{12} \text{ W/cm}^2\) field intensity, we may describe accurately formation of harmonics of the order of a hundred. Considerably smaller number of the angular momentum states is needed if the velocity gauge is used [10].

With the total Hamiltonian thus defined, equations (1) and (3) lead to a system of differential equations for the coefficients \(b_j(t)\). We find solution of this system for the time interval \((0, 30T)\), where \(T\) is the period of the field oscillation, by using the Crank-Nicholson method [11]. With the solution of the TDSE thus obtained, the harmonics spectrum can be calculated as Fourier image of the time-dependent dipole operator [2].

3. Results

3.1. Optimization of the high harmonics generation.

In this section, we study the effect of the form of the driving laser pulse on the cut-off of the HHG process. We consider a special class of the waveforms, which can be represented as a superposition of a number of the harmonics of a base frequency \(\Omega = 2\pi/T\), corresponding to a given period \(T\), and which do not contain the DC component:

\[
F(t) = 2\text{Re} \sum_{k=1}^{K} a_k e^{i k \Omega t}
\]  

(4)

Remarkable success of the classical model of the HHG process in predicting the cut-off values of the harmonics generation suggests the following strategy. We first consider a problem of classical mechanics of finding a set of coefficients \(a_k\) in Eq. (4) such, that the maximum classical kinetic energy of the recombining electron is achieved. To show, that the increase of the HHG cut-off value obtained classically is not an artifact of a simplified treatment, we supplement the classical trajectory analysis by a quantum mechanical TDSE calculation.

Thus, we begin with a purely classical study of the returning trajectories of an electron moving in a periodic EM field given by Eq. (4). Our task is to find the set of coefficients \(a_k\) in Eq. (4), for which electron returning to the nucleus possesses the highest possible kinetic energy. To make the problem well-defined, we impose some restrictions on the possible choice of this set. A natural requirement is that only the fields \(F(t)\) with the fixed fluency are to be considered.

This implies that \(4 \sum_{k=1}^{K} |a_k|^2 = F_0^2\), where the field strength \(F_0\) is related to the intensity via \(W = 3.5 \times 10^{16} F_0^2\). Here the field intensity \(W\) is measured in \(\text{W/cm}^2\) and the field strength is expressed in the atomic units. Another restriction is that we consider pulses with only low order harmonic terms \(k \leq 5\) in Eq. (4), which is motivated primarily by practical feasibility of the pulse creation.

Following the procedure adopted in the classical 3-step model theory of HHG, we neglect the influence of the atomic core on the electron motion. Classical equations of motion of an electron in the EM field given by Eq. (4) are solved with the initial conditions \(x(t_0) = 0, \dot{x}(t_0) = 0\), where \(t_0\) is a moment of time at which atomic ionization event occurs. Among these trajectories we are interested only in the returning trajectories, for which we compute electron kinetic energy \(E\) at the moment of return to the nucleus.

We use the following field parameters: \(F_0 = 0.0053\) a.u. (corresponding to the intensity of \(10^{12} \text{ W/cm}^2\)), \(\Omega = 0.185\) eV. For this set of the field parameters, the value of the Keldysh parameter \(\gamma = \sqrt{I/2U_p} = 0.8\), where \(I = 0.196\) a.u. is the ionization potential of the Li atom.
Table 1. Coefficients (multiplied by \(10^3\)) for cosine wave and the optimized pulse.

| \(k\) | Cosine wave | Optimized pulse |
|-------|-------------|-----------------|
| 1     | 2.665       | 2.123 \(-1.033i\) |
| 2     | 0           | 0.403 + 0.754i  |
| 3     | 0           | \(-0.558 + 0.271i\) |
| 4     | 0           | \(-0.302 - 0.358i\) |
| 5     | 0           | 0.224 \(-0.248i\) |

For the pure cosine form of the EM field, the classical procedure described above gives the well-known curve of the dependence of the kinetic energy \(E\) at the moment of return on the time of release, shown in Figure 1 by the solid (red) line. To find the set of parameters in Eq. (4) for which recollision energy is maximized (with the constraints of a fixed fluency and \(K = 5\) in Eq. (4)), we look for a maximum of the quantity \((E + I)/\Omega\), considered as a function of the coefficients \(a_k\) in the Eq. (4), imposing the two constraints which we mentioned above. This strategy gives us the pulse composition summarized in Table 1, and dependence of the kinetic energy on the time of release, shown in Figure 1 by the dashed (green) line.

In Figure 2 we show results of the TDSE calculations of the HHG yield for both pulses formed with the coefficients from Table 1. Harmonics spectrum is computed as Fourier image \(d(\omega)\) of the time-dependent dipole operator in the length and velocity gauges. Results of the quantum calculation show, in agreement with the classical picture of Figure 1, that optimization of the pulse given by Eq. (4) with \(K = 5\) allows to increase the cut-off position by about 20%.

On the right panel of Figure 2 we show the results obtained for the pure cosine waveform of a driving pulse for various forms of the Hamiltonian representing atom-field interaction, and various forms of the dipole operator. As we noted above, we can employ either length or velocity gauges to represent atom-field interaction when solving the TDSE. We may also use either length or velocity forms of the dipole operator when computing the harmonics spectrum. In Figure 2 we refer to these calculations, using combinations of letters L and V. For example, the LV calculation uses the length gauge to solve the TDSE, and the velocity form of the dipole operator, the VL calculation uses the velocity gauge for the solution of the TDSE, and the length form of the dipole operator to compute the harmonics spectrum. Comparing the results of the calculations using different gauges to solve the TDSE, and different dipole operator forms, gives us a reliable indicator of the accuracy with which the TDSE has been solved.

There are waveforms which allow to achieve more substantial increase in the HHG cutoff position. Such are the ideal waveform proposed in [12], for which we should allow the term...
with \( k = 0 \) in the sum in Eq. (4)), or the field configurations containing subharmonic fields with frequencies \( \Omega/2 \) [13, 14]. Such waveforms cannot be described by Eq. (4). Our result presents an upper limit for the increase of the HHG cutoff achieved for the class of the waveforms given by Eq. (4), i.e. for the waveforms which are periodic with a given period \( T \) and do not contain the DC components.

3.2. Generation of short pulses of EM radiation.
In this section, we consider application of the so-called polarization gate technique [15, 16] for generation of very short bursts of EM radiation. This technique employs a field configuration consisting of two pulses of left and right circular polarizations, separated by a time delay. For such a configuration, the polarization of the total EM field is close to linear only for the time interval on which both pulses significantly overlap. The reason why this field configuration turns out to be so efficient for the generation of the short pulses is clear, if one takes into account the role played by the classical returning trajectories in the process of HHG. Such trajectories exist only for linearly polarized EM field. Thus, the field configuration used in the polarization gating method, reduces the time interval during which the return to the nucleus is possible to the interval of overlap of both pulses. Quantum-mechanical simulations relying on the SFA approach, performed in works [15, 16], confirmed that this field configuration could be used to produce single attosecond pulses.

Below we study the harmonics formation for this field configuration by means of the TDSE approach, which takes into account the atomic structure. As a target, we again choose the lithium atom. For the present setup, when the atom interacts with two pulses of right and left circular polarizations, arriving with the time-delay \( \Delta \), the interaction Hamiltonian in the length gauge can be written as:

\[
\hat{H}_{\text{int}}(t) = E_0 \left[ x f_1(t) \cos \omega t + y f_2(t) \sin \omega t \right],
\]

where \( f_1(t) = f(t) + f(t-\Delta) \), \( f_2(t) = f(t) - f(t-\Delta) \), and \( f(t) \) is the function describing envelope of the pulse. The envelope function \( f(\tau) \) is constant for \( \tau \in (T, 4T) \), where \( T = 2\pi/\omega \) is a cycle duration corresponding to the carrier frequency in Eq. (5). The fields are ramped on and off smoothly, so that the field strength, and its first time-derivative remain continuous. The total duration of the left- and right-polarized pulses of EM radiation is therefore \( T_1 = 6T \). The atom thus interacts with the combined pulse during the interval of time \((0, T_2)\), where \( T_2 = 6T + \Delta \). In this interval the left and right polarized pulses overlap within the time interval \((\Delta, 6T)\). On
the interval \((\Delta + T, 5T)\) of duration \(4T - \Delta\) both overlapping pulses are completely ramped on, the resulting EM field is therefore polarized linearly along the \(x\)-axis. Field parameters in Eq. (5) are \(E_0 = 0.0035\) a.u. and \(\omega = 0.16\) eV.

We analyze the solution of TDSE by means of the wavelet transform – the time-frequency technique, which allows us to track the process of harmonics formation in time, and which combines both the frequency and temporal resolution of the signal [17, 18, 19].

![Wavelet time-frequency spectrum of Li for \(\Delta = 0, 2T, 3T\).](image)

In Figure 3 we show results of such analysis of the induced dipole momentum for the lithium atom and the field configuration described above. One can observe that, in agreement with the classical model of the process, with increasing \(\Delta\) harmonics formation is confined to ever decreasing time interval in which the light polarization is linear.

4. Conclusion

We presented a procedure describing interaction of atoms with strong EM fields. The field-free atom is described within the Hartree-Fock approximation, including the non-local exchange interaction. This choice gives us more detailed account of the atomic system of interest, allowing to describe phenomena in which atomic structure plays important role, such as resonant enhancement of harmonics in the HHG spectrum.

As an illustration, we presented results of the optimization of the HHG cut-off value for the waveforms satisfying Eq. (4), and considered application of the polarization gating technique to the lithium atom.

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