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Resonant enhancement of generation of harmonics

I. A. Ivanov[*] and A. S. Kheifets
Research School of Physical Sciences and Engineering, The Australian National University, Canberra ACT 0200, Australia

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We develop a Floquet based formalism which describes a process of the generation harmonics of in an atom driven by a laser field. Using this formalism, we show that several harmonics are strongly enhanced in the spectrum when the laser frequency is such that a multiphoton resonance occurs between the initial state and a quasienergy state. We illustrate these findings by a numerical calculation of the harmonics generation in the potassium and rubidium atoms driven by a laser in the near-infrared energy range. The present formalism is also applicable when the initial state is a coherent superposition of several field-free atomic states.

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I. INTRODUCTION

High-order harmonics generation (HHG) is a nonlinear atomic process which can be qualitatively understood using classical notions. The so-called three-step model [1] describes this process as a tunneling ionization of an atomic electron followed by a (classical) motion of the electron in the electromagnetic (EM) field and eventual recombination with emission of a photon. Classical analysis of the electronic motion in the EM field (with atomic potential neglected) shows that not all the possible electronic trajectories return eventually to the nucleus. Only the electrons leaving the atom at some particular instances of time can return and emit a photon. This model describes correctly the main features of HHG such as existence of the plateau [2,3] and gives the well-known $I_\mathrm{p}+3.17U_\mathrm{p}$ cutoff rule for the extent of this plateau. Here I_p and U_p are, respectively, the ionization potential of the atom and the ponderomotive energy of electronic motion in the EM field.

Nonclassical modifications of the three-step model exist in the literature. A semiclassical treatment of the HHG process was proposed in works [4–6]. A fully quantum description was also developed [7]. A device often used in the quantum formulation of HHG is the strong field approximation (SFA) [7,8], which neglects the influence of the atomic potential on the motion of the released electron during the second stage of the HHG process. For the description of the electron motion a propagator constructed from the Volkov states [8] can then be employed, and the problem can be treated analytically.

In the case when the atom is initially in the ground state and is driven by a single colour EM field, the typical pattern of the resulting harmonics spectrum consists of the first few generally quickly decreasing harmonics followed by the plateau ending with a relatively sharp cutoff. All the harmonics are odd multipliers of the frequency of the driving EM field.

The case of the initial atomic state being a coherent superposition of several field-free atomic states was studied in Refs. [8–10]. A considerable modification of the HHG spectrum was demonstrated leading to an additional plateau [9]. It was also shown [8] that for such initial conditions the harmonics can be produced in two ways. For the harmonics with frequencies smaller than the energy difference between the lowest and excited levels, the conventional mechanism of the single-state harmonic generation produces odd multiples of the laser frequency. For harmonics with frequencies in the vicinity of the excitation energy, the resonance mechanism produces harmonics with the shifted frequencies, the shifts being equal to the separation energies of the excited states in the initial superposition. To produce such harmonics, the electron is ionized from the excited state and recombines later into the lowest lying state.

Another effect of the electronic structure of the target atom on HHG was demonstrated by Paul *et al.* [11] who observed an increase of several orders of magnitude in harmonics yield, in particular for the seventh and ninth harmonics, in the rubidium atom driven by a mid-infrared laser. Experimental conditions were such that few atomic states $(5s,5p,4d)$ were populated. The observed enhancement of the harmonics yield was attributed to the mutual interaction of these states.

The SFA description of the second stage of the HHG process takes into account only the influence of the EM field on the electron and neglects the atomic potential. This potential and, consequently, the electronic structure of the target atom can modify significantly the HHG spectrum.

Since the work by Toma *et al.* [12], it was established that the atomic structure can manifest itself in the resonance enhancement of a single harmonic in the HHG spectrum if the laser frequency is in a multiphoton resonance with an atomic transition. An analogous effect of the multiphoton resonance on the above-threshold-ionization spectra (which is a process closely related to the HHG) has been found in [13].

There is a large body of experimental facts showing such a resonant enhancement for various targets [14–17]. A review of recent developments in the field can be found in a paper by Ganeev [18]. Theoretical treatment of the resonant enhancement of a single harmonic which is in a multiphoton resonance with an atomic transition was recently given by Milosevic [19].

A systematic study of the role of the multiphoton atomic resonances in the formation of the HHG spectra was performed by Taïeb *et al.* [20]. Numerical simulations performed by the authors for a number of model potentials demonstrated that the multiphoton resonance between the ground and an excited level may lead not only to the resonance

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[*] Corresponding author. Igor.Ivanov@.anu.edu.au

enhancement of a single harmonic, but to the enhancement of several harmonics on the HHG plateau. This fact was explained by using a picture of the recolliding trajectories, one of the main ingredients of the three-step model of HHG. The effect of the resonant enhancement of several harmonics was also found in numerical calculations of HHG in the Ar [21], K [22], and Li [23] atoms.

In the present work, we give a formal systematic treatment of the effect of the atomic structure on the harmonics spectra based on the representation of the exact atomic propagator in presence of the EM field by means of the Floquet states. A sketch of this theory was given in our earlier work [23] where we applied it to explain a considerable increase of intensity of several harmonics on the HHG plateau in the case of the Li atom initially in the excited $2p$ state. In the present work, we give a more formal and complete treatment. We also consider the case of an atom initially in a coherent superposition of several atomic states. This approach shows that intensity of several harmonics may be enhanced at once for the frequencies of the driving EM field corresponding to the multiphoton resonances between initial state and a Floquet eigenstate. We illustrate the theory developed below by numerical calculations of the harmonics spectra from the potassium and rubidium atoms. These results show that, in agreement with predictions of the Floquet theory, a multiphoton resonance between the ground and an excited level may lead to the increase of intensity of several harmonics. In the case of an initial atomic state being a coherent superposition of several atomic states, the Floquet based description agrees with the results for the HHG spectra obtained earlier in Refs. [8,19].

II. THEORY

We follow the Floquet formalism as outlined by Chu and Telnov [24]. Let the target atom be described by the field-free Hamiltonian $\hat{H}_{\text{atom}}$ acting in the Hilbert space $\mathcal{H}$. Mathematically, the Floquet description of the EM field-atom interaction can be obtained if we consider evolution of an enlarged system, the Hilbert space of which is a direct product $\otimes_n \mathcal{H}_n$ of infinitely many copies of the atomic Hilbert space. Here the index n assumes all integer values. The vectors of this enlarged space can be represented as collections of vectors f_n from the atomic Hilbert space $\mathcal{H}_n$. We shall use the notation (f_n) for such collections. We shall also employ below bold capital letters to designate vectors of the enlarged space (Greek letters) and operators acting in this space (Latin letters). Thus $\boldsymbol{\Psi} \equiv (f_n)$.

Let the Floquet Hamiltonian of this enlarged system be $\hat{\boldsymbol{H}} = \hat{\boldsymbol{H}}_{\text{atom}} + \hat{\boldsymbol{H}}_{\text{F}} + \hat{\boldsymbol{V}}_{\text{I}}$. The action of the separate terms of the Hamiltonian on the vectors of the enlarged space (f_n) is defined as follows: $\hat{\boldsymbol{H}}_{\text{atom}}(f_n) = (\hat{H}_{\text{atom}} f_n)$, $\hat{\boldsymbol{H}}_{\text{F}}(f_n) = (n\omega f_n)$, $\hat{\boldsymbol{V}}_{\text{I}}(f_n) = (\frac{1}{2}\hat{V} f_{n-1} + \frac{1}{2}\hat{V} f_{n+1})$.

Let us consider a mapping of the Hilbert space of the enlarged system $\otimes_n \mathcal{H}_n$ onto the atomic Hilbert space defined as

$$\Psi(t) = \sum_{n=-\infty}^{\infty} f_n e^{in\omega t}. \tag{1}$$

It is easy to see that if the wave function $\boldsymbol{\Psi} = (f_n)$ satisfies the Schrödinger equation $i\partial\boldsymbol{\Psi}/\partial t = \hat{\boldsymbol{H}}\boldsymbol{\Psi}$ with the Floquet Hamiltonian $\hat{\boldsymbol{H}}$ introduced above, then the wave function $\Psi(t)$ on the left-hand side of Eq. (1) will satisfy the equation $i\partial\Psi/\partial t = (\hat{H}_{\text{atom}} + \hat{V}\cos\omega t)\Psi(t)$.

Thus instead of solving the time-dependent Schrödinger equation (TDSE) for the atomic system in the external EM field we can solve this equation for the enlarged system and use the mapping of Eq. (1). This may prove simpler than solving the atomic TDSE. If, for example, the operator $\hat{V}$ in the atomic TDSE is time independent, i.e., we consider the EM field with a constant envelope, the operator $\hat{\boldsymbol{V}}_{\text{I}}$ in the Floquet Hamiltonian will not depend on time. In the following, we concentrate on this particular case.

By using the complete set of eigenfunctions of the time-independent Floquet Hamiltonian, we can easily write a simple expression for the exact propagator describing the time evolution of the enlarged system. Such a set of eigenstates is, however, not very convenient for practical use since the spectrum of the eigenvalues of the Floquet Hamiltonian is generally continuous. More convenient representation for the exact propagator can be obtained if we use a combination of the Floquet states formalism and the complex rotation method (CRM) [25–27].

The complex rotation procedure can be formally described as a complex change of radial variables $r \to re^{i\theta}$, where θ is the rotation angle. The set of the eigenstates of the transformed Hamiltonian can be used to represent the resolvent operator and the exact propagator for the original, untransformed Hamiltonian [28]. For the original untransformed Floquet Hamiltonian, the expression for the exact propagator for $t > t'$ (it is zero otherwise) can be written as [28]

$$\boldsymbol{G}(t;t') = -i\sum_i R(-\theta)|\boldsymbol{\Phi}_i(\theta)\rangle\langle\bar{\boldsymbol{\Phi}}_i(\theta)|R(\theta)e^{-iE_i(\theta)(t-t')}, \tag{2}$$

where

$$R(\theta) = \exp\left(-\theta\frac{\boldsymbol{rp}+\boldsymbol{pr}}{2}\right) \tag{3}$$

is the so-called complex rotation operator and $\langle\bar{\boldsymbol{\Phi}}|$ denotes the transposed value of $|\boldsymbol{\Phi}\rangle$, not the Hermitian conjugate [28]. Summation in Eq. (2) includes only discrete terms, which is the reason why the CRM was employed. The eigenvalues and eigenvectors appearing in the spectral expansion (2) are those of the complex rotated Floquet Hamiltonian. The eigenvalues $E_i(\theta) = \text{Re}E_i - \Gamma_i/2$ are generally complex and depend on the frequency and strength of the EM field. The block structure of the Floquet Hamiltonian implies that distribution of the eigenvalues E_i and eigenvectors $|\boldsymbol{\Phi}_i(\theta)\rangle$ exhibits a certain pattern [24]. All the eigenvectors can be divided into two groups. For the eigenvectors of the first group, the components $u_{i,n}$ with even n have even spatial parities, while $u_{i,n}$ with odd n have odd parities. In the limit of the vanishing strength of the EM field, some eigenvalues E_i of this group reduce to either $\epsilon^e_a+2k\omega$ or $\epsilon^o_b+(2k+1)\omega$, where ϵ^e_a is the energy of some field-free atomic state of even parity and ϵ^o_b is the energy of some field-free atomic level of odd parity. Analogously, for the eigenvectors of the second group, the components $u_{i,n}$ with even n have odd parities, while $u_{i,n}$ with odd n have even parities. Correspondingly, in the limit of vanishingly small strength of the EM field, some eigenvalues E_i of this group reduce to either $\epsilon^e_a+(2k+1)\omega$ or $\epsilon^o_b+2k\omega$.

Using expression (2) for the exact propagator, we can write the following expression for the solution of the TDSE for the enlarged system. For the evolution starting at $t=0$ from the state $\mathbf{\Psi}_0$, we have

$$\mathbf{\Psi}(t) = \mathbf{\Psi}_0(t) + \int_0^{\infty} \boldsymbol{G}(t,t')\hat{V}_{\mathrm{I}}\mathbf{\Psi}_0(t')dt', \qquad (4)$$

where $\mathbf{\Psi}_0(t)$ satisfies the field free TDSE: $i\partial\mathbf{\Psi}_0/\partial t=(\hat{\boldsymbol{H}}_{\mathrm{atom}}+\hat{\boldsymbol{H}}_{\mathrm{F}})\mathbf{\Psi}_0(t)$.

Consider first the case when the atom is initially in an eigenstate ϕ_a of the field-free atomic Hamiltonian $\hat{H}_{\mathrm{atom}}$, having energy ϵ_a. By choosing the initial Floquet state $\mathbf{\Psi}_0$ as a set f_i, such that $f_0=\phi_a$, $f_i=0$ for $i\neq 0$ and by using the expression for the propagator (4) and the mapping (1), the solution of the atomic TDSE can be written as

$$\Psi(t) = \phi_a e^{-iE_a t} - i\frac{F_0}{2}\sum_{i,n}\int_0^{\infty} R(-\theta)u_{i,n} \times(\theta)e^{inwt-iE_a t'}c_i e^{-iE_i(\theta)(t-t')}dt', \qquad (5)$$

where $c_i=\langle\bar{u}_{i,-1}|R(\theta)D_z|a\rangle+\langle\bar{u}_{i,1}|R(\theta)D_z|a\rangle$, F_0 is the strength of the EM field, D_z is the z component of the dipole momentum. Here we adopt the length form for the EM field-atom interaction, the EM field vector being directed along the z axis. The functions $u_{i,n}$ are components of the Floquet eigenstates $\mathbf{\Phi}_i(\theta)=(u_{i,n})$. From the expression for c_i and the above discussion of the parity of the functions $u_{i,n}$, it is clear that for the initial state $|a\rangle$ of a given parity only the eigenstates with $u_{i,0}$ of the same parity contribute to the sum in Eq. (5).

It is tempting to compute the expectation value of the dipole momentum using Eq. (5) directly. This, however, cannot be done directly. As explained by Buchleitner *et al.* [28], certain care should be exercised when handling expressions containing matrix elements of the dilatation operator $R(\theta)$. Matrix elements $\langle\bar{u}_{i,n}|R(\theta)D_z|a\rangle$, appearing in the expression for the coefficients c_i above, are well-defined. The expression $R(-\theta)u_{i,n}(\theta)$, however, has only formal meaning since under the action of the dilatation operator $R(-\theta)$ the function $u_{i,n}$ may become divergent. If we needed only the matrix elements of the type $\langle b|D_zR(-\theta)|u_{i,n}\rangle$, with a state $|b\rangle$ such that $R(\theta)|b\rangle$ is well defined, this circumstance would not pose a problem, since these matrix elements can be interpreted as $\langle\bar{u}_{i,n}|R(\theta)D_z|\bar{b}\rangle$ [28]. This interpretation is not possible in our case. Indeed, if we wished to compute the expectation value of the dipole momentum operator using Eq. (5), we would have to compute matrix elements of the type $\langle u_{j,m}|R(\theta)|D_zR(-\theta)\,|u_{i,n}\rangle$ for which the above recipe cannot be applied. To compute these matrix elements we should either use some procedure of analytic continuation or to make an approximation. We shall compute the expectation value of the dipole momentum neglecting these terms. This approximation is analogous to the one made by Milošević [8] who used the Volkov propagator to describe the electron motion in the EM field. This approximation could be interpreted as neglect of the free-free transitions. Such an interpretation is not so straightforward in the case of the exact Floquet propagator taking into account the atomic potential. We can still maintain, however, that such an approximation is justified as long as we consider not very large intensities of the EM field.

Neglecting the ill-defined terms in Eq. (5), we obtain the following expression for the expectation value of the dipole momentum:

$$d(t) = -\frac{F_0}{2}\sum_{i,n} b_{i,-n}c_i e^{i(E_a-n\omega-E_i)t}\frac{e^{iE_it-iE_at}-1}{E_i-E_a} + \text{c.c.}, \qquad (6)$$

where $b_{i,m}=\langle a|D_zR(-\theta)|u_{i,n}\rangle$, E_i is the quasienergy. The expression for $b_{i,n}$ implies that the functions $|a\rangle$ and $u_{i,n}$ must have opposite parities which, in turn, means that only the terms with odd n contribute to the sum in Eq. (6). From the expression (6) we see that the harmonics intensity

$$d(\omega) = \lim_{T\to\infty}\frac{1}{T}\int_0^T d(t)e^{i\Omega t}dt$$

is nonzero only if $\Omega=N\omega$ with odd N, which is the condition of odd harmonics generation. The spectral intensity of the Nth harmonic is given by the following expression:

$$d(N\omega) = -\frac{F_0}{2}\sum_i\left(\frac{b_{i,-N}c_i}{E_i-E_a}+\frac{b^*_{i,N}c^*_i}{E^*_i-E_a}\right). \qquad (7)$$

This expression shows that harmonic intensity can be enhanced if for some eigenstate in Eq. (7) the denominator E_i-E_a is close to zero. For harmonics of different orders N only coefficients $b_{i,N}$ in Eq. (7) will differ. Energy denominators E_i-E_a in Eq. (7) are the same for all harmonics. This means that if there is a small denominator, it may lead to the simultaneous enhancement of many harmonics. Experimentally, this enhancement can be revealed if we tune the laser frequency ω such that one of the eigenvalues E_i (these depend on ω) becomes close to E_a. For the frequency such that $\mathrm{Re}E_i=E_a$, the resonance term in Eq. (7) reduces to $-iF_0(b_{i,-N}c_i-b^*_{i,N}c^*_i)/\Gamma_i$, where Γ_i is the width of the quasienergy state. If Γ_i is small enough, this term leads to enhancement of all harmonics for which the harmonic-dependent coefficients $b_{i,N}$ are not too small. Floquet equations couple the components $u_{i,n}$, $u_{i,n-1}$, and $u_{i,n+1}$ of the Floquet eigenvector. From the definition of the coefficients $b_{i,n}$ one would expect therefore that coefficients $b_{i,n}$ with adjacent n have comparable magnitudes. Thus we may expect enhancement for several harmonics simultaneously. This observation helps to explain the findings reported by Taïeb *et al.* [20]. Below, we give other examples of such simultaneous enhancement of several harmonics. We should also make the following comment concerning the position of the resonance frequencies.

As discussed above, Eq. (7) was obtained in the weak field approximation which justifies the use of the field-free energy E_a of the initial state. For stronger fields, it is more prudent to treat the initial state as a quasienergy state with the corresponding quasienergy $E_a = \mathrm{Re}E_a - i\Gamma_a/2$. The width of the ground state is typically much smaller than that of an excited state and its account, therefore we will only introduce a small correction for the resonance width.

Treating the initial state as a quasienergy state modifies the condition of the resonance into $\mathrm{Re}E_a = \mathrm{Re}E_i$. Here $\mathrm{Re}E_a = E_a^0 + \Delta E_a$, where ΔE_a is the ac Stark shift of the initial state, E_a^0 is its field-free energy. Analogously, we can write $\mathrm{Re}E_i = \epsilon_i - n\omega + \Delta E_i$, where ϵ_i is the energy of the field-free atomic level, ΔE_i is the ac shift, n is an integer.

Below, we shall consider examples of the K and Rb atoms for the EM field of the peak strength of $F_0 = 0.005$ a.u. and frequencies in the range of 0.5–0.7 eV. Using the values of the dynamic polarizability for the ground state of rubidium $\alpha(\omega) \approx 400$ a.u. [29] and potassium $\alpha(\omega) \approx 300$ a.u. [30] at $\omega = 0.6$ eV, we obtain an estimate of the ac shift of the ground states for these systems $\Delta E_a = -\alpha(\omega)F_0^2/4 \approx -0.1$ eV. Below, we shall consider examples of the resonances occurring due to the eigenvalues E_i which, in the weak field limit, reduce to the energies of the low-lying states of the field-free atom. For such states, we may expect the ac shifts to have the same order of magnitude of 0.1 eV thus leading to the estimate of 0.2 eV for the combined effect of the ac shifts $\Delta E_i - \Delta E_a$.

To determine the exact value of the laser frequency at which the resonance due to the eigenvalue $E_i = \epsilon_i - n\omega + \Delta E_i - i\Gamma/2$ occurs, let us represent the laser frequency as $\omega = \omega_0 + \Delta\omega$, where ω_0 is chosen such that

$$\epsilon_i - n\omega_0 + \Delta E_i - E_a^0 - \Delta E_a = 0. \tag{8}$$

Here ϵ_i is the energy of an atomic field-free state, E_a^0 is the energy of the initial state, ΔE_i, ΔE_a are the ac shifts of these states. As we discussed above, the integer n can be odd or even, depending on the relative parities of the initial state and the field-free atomic state to which the eigenstate with energy E_i reduces in the weak field limit. We shall consider below examples of three-, four-, and five-photon resonances in K and Rb. Using the estimates we gave above for the ac shifts, we can expect from Eq. (8) that in the examples below the shift of the resonance frequency w_0 from the field-free value $\frac{\epsilon_i - E_a^0}{n}$ is of the order of $0.2/n \approx 0.05$ eV.

Equation (7) can be rewritten as

$$d(N\omega) = \frac{F_0}{2}\left(\frac{b_{i,-N}^0 c_i^0}{n\Delta\omega + i\Gamma/2} + \frac{b_{i,N}^{0*} c_i^{0*}}{n\Delta\omega - i\Gamma/2} + f_{\mathrm{nres}}(\Delta\omega)\right), \tag{9}$$

where we isolated the resonant term and used the notation $f_{\mathrm{nres}}(\Delta\omega)$ for the sum of all nonresonant terms, which is an analytic and slowly varying function of $\Delta\omega$. In Eq. (9) notation $b_{i,-N}^0$ and c_i^0 are used to emphasize that $b_{i,-N}$ and c_i (which are functions of the laser frequency) are computed at the point $\omega = \omega_0$.

It is easy to see that ω_0, as defined in Eq. (8), does not depend on the harmonic number N. The frequency dependence of $f_{\mathrm{nres}}(\Delta\omega)$ introduces a slight complication in this simple picture. If the width Γ is small, the root of the equation $\partial|d(N\omega)|^2/\partial\omega = 0$, defining the position of the intensity maximum, can be represented as a series in powers of Γ. It is not difficult to see that the first two terms of this series can be written as

$$\omega = \omega_0 + \alpha\Gamma^4 f'_{\mathrm{nres}}(0), \tag{10}$$

where α is some constant. From the definition of $f_{\mathrm{nres}}(\Delta\omega)$ in Eq. (9) it can be seen that the second term on the right-hand side of Eq. (10) depends on the harmonic order N. This term thus introduces a correction to the resonance frequency, which depends on the harmonic order. However, this correction is expected to be small as long as we consider long-leaving resonances and not too strong EM fields, so that width Γ is small.

Thus we arrive at the following qualitative picture of the harmonics enhancement. Harmonics with various order N exhibit resonance enhancement at frequencies near the frequency ω_0 defined in Eq. (8). This frequency is determined by the field-free atomic energies and the ac Stark shifts, which are the same for all harmonics. The locations of the resonance positions for harmonics with different orders N may differ slightly due to frequency dependence of the nonresonant term in Eq. (9).

To conclude this discussion, we should note that the resonances can be densely spaced in the regions of laser frequencies, where many field-free atomic states may satisfy Eq. (8) for various n.

Coherent superposition as initial state

In this section we consider briefly the case of the initial state prepared as a superposition of several atomic field-free states. The purpose of this section is mainly illustrative, we shall rederive the already known results [8,9,19] for the harmonics frequencies in this case, thus demonstrating the overall consistency of the approach. We shall also obtain generalization of the resonance condition for the case of the initial superposition of the field-free atomic states.

Let us consider first the initial state, which is a superposition of two states of the same parity $\alpha|a\rangle + \beta|b\rangle$. Then, instead of Eq. (5), we have the following wave function:

$$\begin{aligned}\Psi(t) &= \alpha\phi_a e^{-iE_a t} + \beta\phi_b e^{-iE_b t}\\ &\quad + \frac{F_0}{2}\sum_{i,n} e^{-iE_i(\theta)t} R(-\theta) u_{i,n}(\theta) e^{inwt}\\ &\quad \times\left(\alpha c_i^a \frac{e^{iE_i t - iE_a t} - 1}{E_i - E_a} + \beta c_i^b \frac{e^{iE_i t - iE_b t} - 1}{E_i - E_b}\right),\end{aligned} \tag{11}$$

where $c_i^f = \langle \bar{u}_{i,-1}|R(\theta)D_z|f\rangle + \langle \bar{u}_{i,1}|R(\theta)D_z|f\rangle$.

From this expression it follows that c_i^f is nonzero only for those eigenstates for which $u_{i,0}$ have the same parity as the states of the initial superposition. Using reasoning based on the properties of the functions $u_{i,n}$ similar to the one presented above, it is easy to see that for the calculation of the dipole momentum only the terms with odd n in the sum of Eq. (11) are needed.

Making the same weak field approximation as above for the expectation value of the dipole momentum, we shall obtain a sum of four terms containing the products $\alpha^*\alpha$, $\beta^*\beta$, $\alpha^*\beta$, and $\beta^*\alpha$ of the coefficients of the initial superposition of the atomic states. It is easy to see that for the $\alpha^*\alpha$ and $\beta^*\beta$ terms the harmonic intensity will be nonzero if $\Omega = N\omega$, where N is odd. For the $\alpha^*\beta$ and $\beta^*\alpha$ terms the harmonic intensity will be nonzero if $\Omega = E_b - E_a + (2k+1)\omega$, in agreement with Milošević [8].

Equation (11) is also valid for the initial state taken as a superposition of two states of different parities. From the expression for c_i^f it can be seen that c_i^a will have nonzero values only for the eigenstates for which $u_{i,0}$ have the same parity as the state $|a\rangle$. Similarly, c_i^b will be nonzero only for the eigenstates for which $u_{i,0}$ have the same parity as the state $|b\rangle$.

For the expectation value of the dipole momentum we shall obtain again a sum of terms, containing $\alpha^*\alpha$, $\beta^*\beta$, $\alpha^*\beta$, and $\beta^*\alpha$ products. It is easy to see that for the $\alpha^*\alpha$ and $\beta^*\beta$ terms to have nonzero values the integer n should be odd. For the $\alpha^*\alpha$ terms, for example, $u_{i,0}$ have the same parity as the state $|a\rangle$, consequently, the dipole matrix element between $u_{i,0}$ and the state $|a\rangle$ is nonzero only for odd n. Thus these terms give rise to an ordinary harmonics spectrum with harmonics at $\Omega = N\omega$ with odd N. The same arguments based on the parity properties of the functions involved show that for the $\alpha^*\beta$ and $\beta^*\alpha$ terms to have nonzero values, n should be even. These terms therefore give rise to the harmonics at $\Omega = E_b - E_a + 2k\omega$. As in the case of the initial state being an eigenstates of the field-free Hamiltonian, Eq. (11) shows that harmonic intensity can be enhanced if for some eigenstate either $E_i - E_a$ or $E_i - E_b$ is close to zero.

Before application of these results to concrete atomic systems, we shall recap briefly the approximations which were made in deriving the above expressions and discuss the extent to which these approximations may restrict description of HHG in a real atom.

As we discussed above, direct calculation of the expectation value of the dipole matrix elements using the wave function Eq. (5) may lead to divergent expressions due to possible divergences in the matrix elements $\langle u_{j,m}|R(\theta)|D_z R(-\theta)|u_{i,n}\rangle$. These matrix elements were neglected, which is justified as long as we consider weak EM fields.

Also, strictly speaking, the CRM method, which we used to represent the propagator in Eq. (2), is only applicable to the systems which are dilatation analytic. This, by itself, is not a severe limitation as this class includes the systems with the Coulomb interaction. De facto, however, the coefficients in Eq. (7) can be computed only for a few simplest systems such as the hydrogen or helium atoms. For more complicated atoms we can consider Eq. (7) as a phenomenological expression describing behavior of the induced dipole momentum as a function of the laser frequency. In the following, we shall adopt this latter point of view.

The theory presented above considered a long EM pulse with the flat envelope. If, as in the examples we present below, we consider a more realistic case of the EM field-atom interaction which is slowly switched on so that the pulse envelope function grows steadily from 0 to 1 in the switching interval $(0,T_1)$, we can use the above formulas to describe the evolution for $t > T_1$. The initial state for this evolution would generally be a superposition of various atomic states, with amplitudes in this superposition depending on the exact form of the switching function on the interval $(0,T_1)$. We can thus apply the previous formulas for the case of the initial superposition of the atomic states. In this case, the resonance enhancement also occurs and is determined by the multiphoton resonances between the states of the initial superposition and Floquet quasienergy states.

III. HARMONICS GENERATION IN POTASSIUM AND RUBIDIUM

For illustration purposes, we consider below a few examples of harmonics generation in the potassium and rubidium atoms. In this section, we follow the approach we applied before for the numerical calculation of the harmonics generation from the ground and excited states of atomic Li [23] and for the numerical solution of TDSE for two-electron systems [31,32].

The ground state of the field-free K and Rb atoms is treated in the Hartree-Fock approximation. To describe the one-electron excitations from the valence shells we use the frozen-core approximation.

The TDSE describing the valence electron can be written as

$$i\partial\Psi/\partial t = \hat{H}\Psi, \tag{12}$$

with the Hamiltonian

$$\hat{H} = \hat{H}_{\text{atom}} + \hat{H}_{\text{int}}(t), \tag{13}$$

where $\hat{H}_{\text{atom}}$ is the Hamiltonian of the field-free atom and

$$\hat{H}_{\text{int}}(t) = f(t) zF \cos \omega t. \tag{14}$$

Here $f(t)$ is a switching function: $f(t) = 3t^2T_1^{-2} - 2t^3T_1^{-3}$ for $0 < t < T_1$, $f(t) = 1$ 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.

The solution of the TDSE is represented as

$$\Psi(\boldsymbol{r},t) = \sum_j a_j(t) f_j(\boldsymbol{r}). \tag{15}$$

Here the basis states $f_j(\boldsymbol{r})$ are pseudostates obtained by diagonalizing the field-free atomic Hamiltonian in the square integrable basis of Laguerre functions [33]:

$$\langle f_{nl}^N|\hat{H}_{\text{atom}}|f_{n'l'}^N\rangle = \epsilon_{nl}\delta_{nn'}\delta_{ll'}. \tag{16}$$

Here ϵ_{nl} is the energy of a pseudostate and N is the size of the basis. In the calculations for the K and Rb atoms presented below we retained in Eq. (15) pseudostates with $l = 0-15$. The total number of pseudostates for each l was 40.

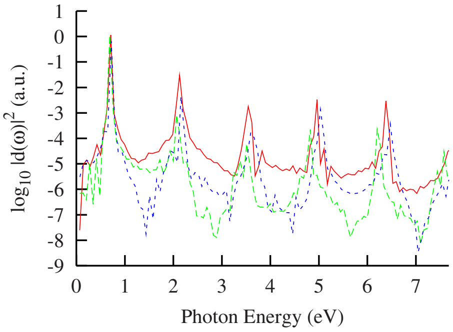

FIG. 1. (Color online) Harmonics spectra of potassium from the ground $4s$ state for laser frequencies ω=0.709 eV [(red) solid line], ω=0.689 eV [(green) dashed line], and ω=0.719 eV [(blue) short dashed line]. Peak strength of the EM field F_0=0.005 a.u.

The pseudostates defined in Eq. (16) were computed within a box (the box size of 200 a.u. was used in this work). To ensure that reflections of the wave packets from the boundaries of the box did not influence our results, we added absorbing potential $-iW(\boldsymbol{r})$ to the TDSE describing electron dynamics. This potential was chosen as a smooth function, zero for $r \leqslant 120$ a.u., and continuously growing to a constant $-iW_0$ with W_0=40 a.u. outside this region.

Substitution of Eq. (15) into TDSE gave us a system of differential equations for the functions $a_j(t)$. This system was numerically solved for the time interval $(0,30T)$. The harmonics spectrum was then calculated as [2]

$$|d(\omega)|^2 = \left| \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} e^{-i\omega t} d(t) dt \right|^2 . \qquad (17)$$

Here $d(t)=\langle \Psi(t)|z|\Psi(t)\rangle$ is expectation value of the dipole momentum integrated over the last ten cycles of the EM pulse with $t_1=20T$, $t_2=30T$.

A. Harmonics generation from the ground state of potassium

In this section, we consider the harmonics generation from the potassium atom prepared initially in the ground state. The energy dependence of the harmonics yield is investigated in the interval of the driving laser frequencies from 0.65 to 0.80 eV.

The harmonics spectra for the driving laser frequencies ω=0.689 eV, ω=0.709 eV, and ω=0.719 eV (first nine harmonics in each case) are shown in Fig. 1. The laser frequencies are slightly different in the three cases. The peaks on the figure, which are the odd multipliers of these frequencies, are slightly shifted therefore. It can be seen from the figure that harmonic intensities are highest for the frequency ω=0.709 eV. As is seen from Table I, the first frequency corresponds to the five-photon transition from the ground $4s$ state to the excited $4f$ state. The resonance behavior exhibited by the harmonics intensities can be seen more clearly in Fig. 2. In this figure we present the intensities of the third, fifth, seventh, and ninth harmonics as functions of the driving laser frequency. Clearly, the intensities of all harmonics have local maxima at $\omega \approx 0.71$ eV, close to the five-photon $4s$-$4f$ transition.

TABLE I. The lowest excited states of potassium and rubidium. The excitation energies (in eV) are from the NIST database [34].

Potassium		
nl	Term	Energy
$4s$	$^2S_{1/2}$	0.00
$4p$	$^2P_{1/2}$	1.61
$4p$	$^2P_{3/2}$	1.62
$5s$	$^2S_{1/2}$	2.61
$3d$	$^2D_{3/2,5/2}$	2.67
$5p$	$^2P_{1/2,3/2}$	3.06
$4d$	$^2D_{3/2,5/2}$	3.40
$6s$	$^2S_{1/2}$	3.40
$4f$	$^2D_{7/2,5/2}$	3.49
Rubidium		
nl	Term	Energy
$5s$	$^2S_{1/2}$	0.00
$5p$	$^2P_{1/2}$	1.56
$5p$	$^2P_{3/2}$	1.59
$4d$	$^2D_{3/2,5/2}$	2.40
$6s$	$^2S_{1/2}$	2.50
$6p$	$^2P_{1/2}$	2.94
$6p$	$^2P_{3/2}$	2.95
$5d$	$^2D_{3/2,5/2}$	3.19
$7s$	$^2S_{1/2}$	3.26

As we vary the laser frequency, many resonances due to various field-free atomic states and various photon numbers n in Eq. (8) may occur. To illustrate this fact, we present in Fig. 3 a broader region of laser frequencies from ω=0.65 eV to ω=0.8 eV for third, fifth, seventh, and ninth harmonics. We separated the figure in two panels to make the data more clearly visible.

One can distinguish two large local maxima in Fig. 3, where all harmonics intensities exhibit resonance increase of intensity. The identification of the excited field-free levels of

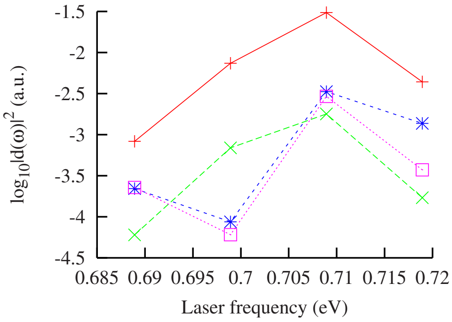

FIG. 2. (Color online) Intensities of the third [(red) solid line], fifth [(green) dashed line], seventh [(blue) short dashed line], and ninth [(magenta) dotted line] harmonics for potassium as functions of the driving laser frequency. Peak strength of the EM field F_0=0.005 a.u.

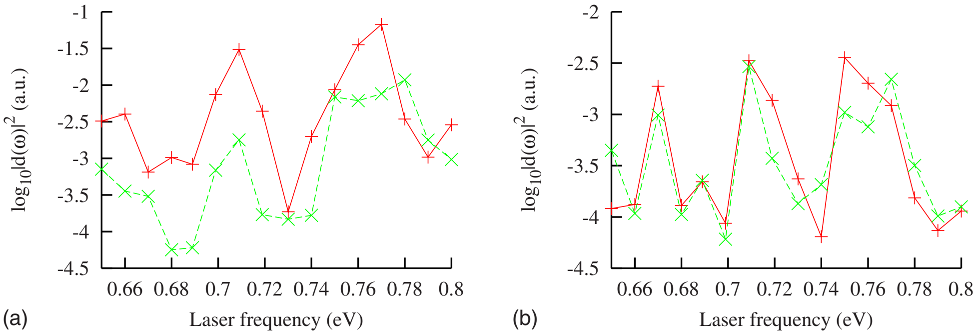

FIG. 3. (Color online) Left panel: intensities of the third [(red) solid line)] and fifth [(green) dashed line] harmonics for potassium as functions of the driving laser frequency. Peak strength of the EM field F_0=0.005 a.u. Right panel: the same for seventh [(red) solid line] and ninth [(green) dashed line] harmonics.

potassium which are responsible for the maxima is, to a certain extent, tentative. The maxima are rather closely spaced and the ac shifts estimated above are comparable in magnitude to the distances between the field-free atomic levels. The maximum at $\omega \approx 0.71$ eV, could, as we surmised above, be attributed to the five-photon resonance with the $4f$ state. The maximum at $\omega \approx 0.75$ eV could be attributed to the four-photon resonance with the $4d$ state.

There are also two local maxima, where only seventh and ninth harmonics exhibit a noticeable increase of intensity. The maximum at $\omega \approx 0.67$ eV could be attributed to four-photon resonance with the $5s$ state. A closely lying maximum at $\omega \approx 0.69$ is possibly due to a four-photon resonance with the $3d$ state.

As noted above, this identification is of a tentative character. We may observe, however, that as a rule, several harmonics simultaneously exhibit resonances at the same frequencies in agreement with the theory presented above and Eq. (7).

Which particular harmonics will be enhanced stronger at the resonance frequency depends upon the distribution of the absolute values of the coefficients $b_{i,N}$ in Eq. (7). As we mentioned above, actual calculation of these coefficients is possible only for simple one- or two-electron systems, such as the hydrogen or helium atoms. To compute the coefficients $b_{i,N}$ from the first principles, we should be able to calculate eigenvectors of the complex rotated Floquet Hamiltonian. In solving this problem we cannot rely on approximate descriptions. For example, we could not use the description of K or Rb atoms by means of the frozen core Hartree-Fock Hamiltonian (approximation which we used to solve the TDSE in this work). Hartree-Fock Hamiltonian is not dilatation analytic, hence use of the CRM would not be possible. To compute the coefficients $b_{i,N}$ for these atoms, we have to use truly *ab initio* Hamiltonians, which would present a formidable computational task.

It should be emphasized, however, that practical computational difficulties in no way undermine the validity of Eq. (7). Truly *ab initio* atomic Hamiltonians are dilatation analytic, hence this equation is valid for any atomic system, though actual calculation of the coefficients $b_{i,N}$ may be an extremely difficult problem. We may note also that results presented in the paper are actually based on the pole structure of Eq. (7), and not on the particular values of the coefficients in this equation.

B. Harmonics generation from the ground state of rubidium

In this section, we present results of similar calculations of harmonic generation for the rubidium atom initially in the ground $5s$ state. We consider the energy dependence of the harmonic intensities in the vicinity of the photon energy ω =0.6 eV which, according to Table I, corresponds to the four-photon transition from the ground $5s$ state to the excited $4d$ state. The harmonics spectra for the driving laser frequencies ω=0.614 eV, ω=0.624 eV, and ω=0.634 eV (first nine harmonics in each case) are shown in Fig. 4.

All harmonic intensities are higher for the frequency ω =0.624 eV. In Fig. 5 we present harmonic intensities of the third, fifth, and seventh harmonics as functions of the driving laser frequency. Clearly, intensities of all harmonics have local maximum at $\omega \approx 0.625$ eV, close to the four-photon $5s$-$4d$ transition. The magnitude of the shift of the maximum from the value of 0.6 eV (corresponding to the four-photon transition between field-free $5s$ and $4d$ states) is in agreement with our estimate of the ac shift for rubidium.

The harmonics intensities as functions of the driving laser frequency follow a similar pattern in agreement with Eq. (7), which states that this pattern is determined by the distribution of the poles of the resolvent of the complex rotated Floquet Hamiltonian.

IV. CONCLUSION

We presented a Floquet based theory of the harmonics generation process. We considered the cases when the atom

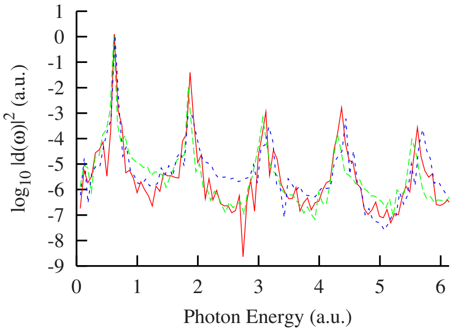

FIG. 4. (Color online) Harmonics spectra of Rb from the ground $5s$ state for laser frequencies ω=0.624 eV [(red) solid line], ω =0.614 eV [(green) dashed line], and ω=0.634 eV [(blue) short dashed line]. Peak strength of the EM field F_0=0.005 a.u.

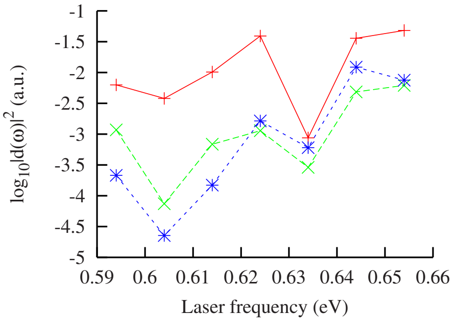

FIG. 5. (Color online) Intensities of the third [(red) solid line], fifth [(green) dashed line], and seventh [(blue) short dashed line] harmonics of rubidium as functions of laser frequency. Peak strength of the EM field $F_0=0.005$ a.u.

is initially in a field-free atomic state or in a coherent superposition of several such states. In this formalism, the harmonics intensity can be represented as a sum of contributions arising from different simple poles, associated with the eigenvalues of the complex rotated Floquet Hamiltonian. This representation shows that the harmonics yield is resonantly enhanced when the driving laser frequency is such that a multiphoton resonance occurs between the initial state and a quasienergy state. Generally, the harmonics enhancement should be expected to occur for several harmonics simultaneously. Such a behavior was previously found in the numerical simulations of the HHG process for various potentials [20]. Our approach gives a natural explanation of this fact.

For illustration purposes, we performed numerical calculations of the harmonics spectra of the potassium and rubidium atoms driven by the laser in the near-infrared energy range. We saw that the intensities of several harmonics can be simultaneously enhanced (an order of magnitude of more) if the driving laser frequency was such that a multiphoton resonance occurs between the initial state and a quasienergy state. This fact is in agreement with the previous numerical results [20] and the theory developed in the present work. Due to computational constraints on the angular momenta in the pseudostate basis, we considered numerical examples with the plateau cutoff parameters of the order of 10. The description of the potassium and rubidium atoms we adopt is based on the frozen-core Hartree-Fock approximation, which has some difficulties in reproducing states with high angular momenta ($l>10$). To describe accurately the process of absorption of N photons from the laser field, followed by the emission of the harmonic photon with frequency $N\omega$, the wave function given by Eq. (15) must contain terms with angular momenta at least as large as N.

This explanation of the role that large angular momentum states play in the formation of the harmonics of high orders uses the quantum picture of the harmonics generation process. Similar conclusions can be obtained if we rely on the classical picture of the three-step model. To describe HHG using the language of this model, we have to be able to describe accurately electron trajectories returning to the nucleus. In the conditions of the HHG proper this electron can travel quite far. For example, for the harmonics generation in the Rb atom, which we considered above, we used $\omega\approx 0.6$ eV and $F_0=0.005$ a.u. For these values of ω and F_0 we obtain excursion radius of the electron in the EM field of the order of 10 a.u., and the "plateau" containing several harmonics (the term plateau is hardly applicable here; of course, the conditions are far from the true HHG regime). In the conditions corresponding to the HHG regime, the electron excursion radius can be much larger. If, for example, we considered for Rb atom the frequency of 0.15 eV, we would have obtained cutoff energy $3.17U_\mathrm{p}+I_\mathrm{p}\approx 140\omega$ and electron excursion radius of 160 a.u. Proper description of such a motion in the framework of the atom-centered basis we use would require a vary large basis size and a large number of angular momentum states, which would constitute a major computational problem.

These computational constraints allow us therefore to consider only harmonics with orders not exceeding $N=9$. Thus we did not consider the cases of really high order harmonics. However, the mechanism of the harmonics enhancement encapsulated in Eq. (7) remains the same for harmonics of all orders. Equation (7), following from Eqs. (2) and (4), remains valid for harmonics of any order, describing resonance enhancement of a group of harmonics in the case of a multiphoton resonance.

As to the applicability of the approach based on Eqs. (2) and (4) for practical calculations of the harmonics spectra, and in particular of the HHG proper, one must realize, of course, that such a calculation would be very computationally demanding. First, as we already mentioned, actual calculation of the coefficients in Eq. (7) is possible only for simple one- or two-electron systems, such as the hydrogen or helium atoms even for harmonics of low order. If we are interested in the HHG proper, then we shall have to include high angular momentum states when building up the propagator according to Eq. (2). The necessity to include such states follows from the arguments similar to those, which we presented above, when we discussed the angular momenta constraints in our TDSE calculation. From the computational point of view this would make the problem extremely difficult.

To summarize the above, the presented theory explains harmonics enhancement at the frequencies for which initial states (or states of the initial superposition) are in a multiphoton resonance with a quasienergy level. Our numerical calculations demonstrated this enhancement for the harmonics of low order. The theory is equally applicable for the high order harmonics, though its numerical confirmation in this case constitutes a much more difficult problem.

The physical interpretation of the role that the multiphoton resonances can play in the enhancement of the harmonic intensities has already been given [20]. This interpretation relies on the following picture. If the initial atomic state is in a multiphoton resonance with an excited atomic level, this level can be resonantly populated. There is then a certain amount of electrons, which are ionized from this level, and unlike electrons ionized from the ground state, they emerge into continuum having nonzero initial velocities. Analysis of classical motion of these electrons in the EM field shows that a certain fraction of these electrons return to the nucleus. Of particular importance are the electron trajectories revisiting the nucleus twice per the period of the laser field. At the moment of return these electrons have nonzero kinetic energies. If they recombine, photons are emitted with frequencies in the range depending on the electron energies at the moment of recollision. This leads to the enhancement of the harmonics with photon energies in this range. This model generalizes the three-step model which, of course, neglects all information about the atomic structure. In the picture proposed in [20] the atomic structure manifests itself through the existence of the electron trajectories with nonzero initial velocities, which may appear in the case if in the system there is a resonantly populated level. Our approach gives more formal and fully quantum mechanical description of this process.

In the case when the initial state is a coherent superposition of several field-free atomic states, this approach reproduces the results for the HHG spectra obtained previously by Milošević [8,19].

In our earlier work [23] we considered the case of the harmonics generation from atomic lithium, when the initial state was an excited $2p$ state. As a laser source the Ti:sapphire laser with the main frequency of 1.56 eV was used. We found that the harmonics yield from this state was considerably enhanced, which we attributed to the presence of the multiphoton resonance between the $2p$ and $4s$ states. Mathematically, the resonance enhancement for the excited initial state or for the initial superposition of several atomic states is described in essentially the same way, as the appearance of resonance terms in the expression for the wave function of the system. In the case of the initial state being a superposition of two atomic states with energies E_a and E_b, this wave function is given by Eq. (11). As we discussed above, in this case the harmonics intensities can be enhanced if for some eigenstate E_i in Eq. (11) either $E_i - E_a$ or $E_i - E_b$ is close to zero. If the state with energy E_b is an excited state, then it generally lies in a denser part of the spectrum, so the resonances due to small $E_i - E_b$ should be very close to each other. The resonance structures in this case must be more densely spaced than in the case of the initial ground state. To resolve these densely spaced resonances in a numerical calculation similar to the one we presented above for the ground state, we shall have to use a very small increment of the photon energy, which makes the calculation considerably more time consuming. We plan to consider this case in the future.

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