PHYSICAL REVIEW A **74**, 052505 (2006)

Ab initio calculation of harmonic generation spectra of helium using a time-dependent non-Hermitian formalism

Ido Gilary,[1] Petra R. Kaprálová-Žd'ánská,[2] and Nimrod Moiseyev[1]
[1]*Department of Chemistry and Minerva Center for Nonlinear Physics of Complex Systems, Technion-Israel Institute of Technology, Haifa 32000, Israel*
[2]*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo 2, 166 10 Prague 6, Czech Republic*

(Received 22 August 2006; published 20 November 2006)

The high harmonic spectra of helium atoms which are exposed to external monochromatic linearly polarized laser fields are calculated by solving the time-dependent non-Hermitian Schrödinger equation. The entire electronic correlation effects with and without the presence of the field are included in our calculations. The full high-harmonic generation spectra (HGS) were calculated (and not only the intensities of the integer harmonics frequencies as calculated before by non-Hermitian quantum mechanics). The HGS were calculated when the helium atoms are initially in their ground state, or in the $1s2p$ excited state or in a superposition of the two field free states. In the first two cases only odd-order harmonics are obtained. However, in the latter, in addition to the odd-order harmonics also pronounced even-order harmonics are obtained. The even order peaks are much broader than the peaks of the odd-order high harmonics. The association of the widths of the peaks in the HGS with the lifetime of the photoinduced resonances which control the dynamics is discussed.

DOI: 10.1103/PhysRevA.74.052505 PACS number(s): 31.15.Ar, 02.70.−c

I. INTRODUCTION

In the past decades numerous experimental works as well as theoretical studies have shown that rare gas atoms exposed to high intensity lasers emit odd multiples of the incident radiation frequency [1]. This phenomenon termed high harmonic generation (HHG) has been tagged as a possible future source of coherent x-ray radiation [2] as well as a method to facilitate the generation of short attosecond laser pulses [3]. The selection rules allowing the generation of only odd multiples of the incident radiation have been explained theoretically [4] as well as the anticipated selection rules for molecular systems with different symmetries [5]. As we will elaborate later these selection rules are due to the dynamical symmetry properties of the Floquet Hamiltonian. It has been demonstrated that these selection rules can be altered by breaking or changing the dynamical symmetry of the system, for example, by radiating with two different laser frequencies [6] or by using very short laser pulses for which the Floquet picture is not applicable [7].

The selection rules for harmonic generation spectra (HGS) were derived under the assumption that the duration of the laser pulse is sufficiently long and supports many optical cycles. Only then the Floquet theory is applicable. Moreover the dynamical symmetry analysis for the HGS is based on the assumption that a single Floquet quasienergy state controls the photoinduced dynamical process. Within Hermitian quantum mechanics (QM) this can never happen in strong laser fields where photoinduced ionization occurs and competes with the process of generation of high order harmonics. In Hermitian QM a single eigenstate is a stationary solution which by definition cannot describe the ionization phenomenon. Therefore, the photoinduced dynamics is described by a wave packet consisting of linear combination of many eigenstates of the Hermitian Floquet operator. This, however, is not the case in non-Hermitian (NH) QM, where the photoinduced dynamics (even in the presence of strong laser fields) can be described by a single resonance Floquet state.

A long time ago Reinhardt and Chu [8] were the first to calculate the field induced rate of decay by calculating the resonance complex quasienergies of the complex scaled Floquet operator. The problem they solved represented a driven one particle model Hamiltonian. Years later Moiseyev and Cederbaum [9] calculated the resonance quasienergies for a driven helium atom where the dynamical electronic correlation in the presence of the strong laser fields was taken into consideration. They showed that there is a similarity in the functional dependence of the decay rate of the doubly excited helium on the field intensity and the functional dependence of the resonance decay rate of doubly excited hydrogen molecule on the intranuclear distance. Moiseyev and Weinhold used the resonance Floquet eigenstate of helium in strong laser field (which has more than 90% overlap with the field free helium ground state) to calculate the HGS [10]. Their results showed remarkable agreement with the experimental HGS. However two open questions remain: (1) how can one calculate, using the NHQM formalism the entire HGS and not only a "stick diagram" (i.e., only the values at even and odd harmonics) and (2) how can the HGS be calculated by the time-dependent (TD) NHQM formalism when the field free initial state populates several quasienergy (QE) eigenstates of the complex scaled (CS) Floquet operator?

The answer to the second question requires the solution of a key open problem in NHQM which is known as the time asymmetry problem [11]. The time asymmetry problem is associated with the fact that the propagation of a given wave packet (WP) in NHQM from time $t=0$ to $t=-\infty$ diverges exponentially. Without solving this problem one cannot calculate the time-dependent expectation values within the framework of NHQM. Most recently Moiseyev and Lein suggested to calculate the propagation of a given WP back in

©2006 The American Physical Society

time not by solving the time-dependent Schrödinger equation (TDSE) but from the eigenstates of the CS Floquet type Hamiltonian [12]. The time asymmetry problem in NHQM can be resolved by redefining the inner product which has been termed by Moiseyev and Lein as the *F* product (finite range). The analysis of the analytical expression they derived for the HGS on the basis of their formalism explains the appearance of only odd-order harmonics even when short laser pulses are used (see a detailed explanation of this phenomenon in Ref. [13]). Based on that analysis it is expected that the population of two resonance QE states which have about the same lifetime and are non degenerate eigenfunctions of the dynamical symmetry operator will result in the generation of even as well as odd order high harmonics. The HGS calculated from propagation calculations using the conventional (Hermitian) QM formalism supports the conclusions obtained from the analysis of these expressions [12]. A more direct support for the TD-NHQM formalism (using the *F* product) was given most recently by comparing the survival probabilities which were obtained for the same situation by carrying out Hermitian time-dependent propagation calculations for a one-dimensional time independent potential and by carrying out NHQM WP propagation calculations [14]. The agreement between the Hermitian and non-Hermitian results is remarkable.

The purpose of this work is to use the TD-NHQM formalism for calculating the full HGS (and not only the stick diagram spectra as obtained before) for helium and its dependence on different initially prepared WP. Since Gaussian basis sets have proven to be most efficient and commonly used in *ab initio* calculations of many atomic and molecular properties [15] we use this basis set in accurate calculations of the resonance QE eigenstates of the CS Floquet operator. Using the resonance QE states, the time-dependent WP propagation calculations in TD-NHQM were carried out and provided the HGS of helium for different initially prepared WP's.

The paper is structured as follows. First we provide a brief review of the formalism that enables the WP propagation in TD-NHQM and its application for calculating the HGS. Then, we describe the numerical application of the TD-NHQM formalism to helium in strong laser fields and the calculations of the HGS of helium for different types of initial states. In the last section we conclude.

II. A BRIEF REVIEW OF THE HGS WITHIN THE TIME-DEPENDENT NON-HERMITIAN QUANTUM MECHANICAL FORMALISM

For the sake of clarity and coherence of the representation of the numerical approach and the results of our calculations we give here a brief review of the TD-NHQM formalism and its use for deriving the expressions for the HGS. When an atom or molecule interacts with a laser field all of its bound states become metastable due to the coupling to the continuum through the electromagnetic radiation. When the laser pulse supports a sufficient number of oscillations the interaction can be described by the Floquet formalism [16]. That is, the time period of the time-dependent Hamiltonian is given by $T=2\pi/\omega$, where ω is the fundamental frequency of the laser. Within the Floquet theory it is possible to define quasistationary solutions $\Psi_k(\vec{r},t)$ of the TDSE given by

$$\Psi_k(\vec{r},t) = \exp\left(\frac{-\imath E_k t}{\hbar}\right)\Phi_k(\vec{r},t),$$

$$\Phi_k(\vec{r},t) = \Phi_k(\vec{r},t+T). \tag{1}$$

The time periodic part of the Floquet solution $\Phi_k(\vec{r},t)$ satisfies the following eigenvalue problem for the Floquet Hamiltonian $\mathcal{H}_F$:

$$\hat{\mathcal{H}}_F\Phi_k(\vec{r},t) = E_k\Phi_k(\vec{r},t),$$

$$\hat{\mathcal{H}}_F = \hat{H} - \imath\hbar\frac{\partial}{\partial t}. \tag{2}$$

The eigenvalues E_k are usually referred to as quasienergies (QE's), and are defined up to modulo $\hbar\omega$, such that $E_k + n\hbar\omega$ is also a solution of Eq. (2). The Floquet solutions form a complete set and therefore a general wavefunction, Ψ, can be represented as a linear combination of these Floquet states

$$\Psi(\vec{r},t) = \sum_k c_k\Psi_k(\vec{r},t). \tag{3}$$

In conventional QM, a system which was in its ground state prior to the application of the laser pulse, populates many QE states densely distributed around the corresponding resonance energy, making it very difficult to perform *ab-initio* calculations. In principle, infinite number of Floquet states is populated by the initial WP. Due to the truncation of the size of the basis set, only a finite number of Floquet QE states is populated, but as the basis set is increased, the number of such populated states is increased as well. The numerical effort increases when dealing with many electron atoms especially when electronic correlation effects are taken into account. Yet, it is possible to overcome these numerical difficulties and carry out WP propagation for atoms in strong laser fields which include the electronic correlation within the framework of the conventional (Hermitian) QM formalism in various methods (see, for example, Ref. [17]).

However, it is not possible to use conventional QM methods for calculations of time-dependent expectation values within the framework of TD-NHQM, without resolving the time asymmetry problem. Therefore below, we present a formalism which overcomes the time asymmetry problem in TD-NHQM and allows us to calculate the HGS by using the numerical approaches which were originally developed for bound states.

The Hamiltonian can become NH due to the use of different types of analytical continuation transformations. One such method is complex scaling (CS) where $\hat{H}(\mathbf{r}) \to \hat{H}(\mathbf{r}e^{\imath\theta})$ [18–21]. Another common method is the introduction of complex absorbing local energy independent potentials (CAPs), also known as optical potentials, into the Hamiltonian [22] such that $\hat{H} \to \hat{H} + \hat{V}_{\text{CAP}}$. The QE's in the NH-QM formalism obtain complex values given by

$$E_k = \varepsilon_k - \imath\Gamma_k/2, \tag{4}$$

where the real part $\varepsilon_k = \mathrm{Re}(E_k)$ is associated with the energy while the complex part is related to the decay rate $\Gamma_k/\hbar$ of the resonance state by $\Gamma_k = -2\,\mathrm{Im}(E_k)$ such that the lifetime of the resonance state is given by $\hbar/\Gamma_k$. The NH property of the transformed Hamiltonian requires a modification of the inner product used in conventional QM. Since the Hamiltonian is NH, it yields different functions when operating from the right or from the left, therefore the eigenvectors are not mutually orthogonal via the conventional inner product $\langle\langle\Phi_k|\Phi_{k'}\rangle\rangle = \delta_{k,k'}$ (here the integration is over all space and over one period of the field) but a different relation which is commonly termed the *c* product [21,23]

$$(\Phi_k|\Phi_{k'}) = \frac{1}{T}\int_0^T dt \int_{\text{all space}} d\vec{r}\,\Phi^L_{k'}(\vec{r},t)\Phi^R_k(\vec{r},t) = \delta_{k',k}, \tag{5}$$

where $\Phi^{R,L}_{k'}$ are the right and left quasienergy (QE) eigenfunctions of the NH Floquet operator $\mathcal{H}_F$, respectively. The right QE eigenfunction is given by Eq. (2), where we add the superscript "*R*." The corresponding left QE eigenfunction represents the (right) eigenfunction of the transposed Floquet Hamiltonian $\mathcal{H}_F^{\dagger *}$. Consequently,

$$\Phi^R_k(\vec{r},t) = \sum_{n=-\infty}^{+\infty} \exp(i\omega n t)\,\varphi^R_{n,k}(\vec{r}) \tag{6}$$

and

$$\Phi^L_{k'}(\vec{r},t) = \sum_{n'=-\infty}^{+\infty} \exp(-i\omega n' t)\,\varphi^L_{n',k'}(\vec{r}). \tag{7}$$

The functions $\varphi^R_{n,k}(\vec{r});n=-\infty,\ldots,0,\ldots,+\infty$ define components of a vector $\vec{\varphi}^R_k$, where $\vec{\varphi}^R_k$ is an eigenvector of the Floquet matrix $\mathcal{H}_F$ given by

$$[\mathcal{H}_F]_{n',n} = \frac{1}{T}\int_0^T dt\,\exp(-i\omega n' t)\hat{\mathcal{H}}_F\exp(+i\omega n t). \tag{8}$$

That is,

$$\mathcal{H}_F\vec{\varphi}^R_k = (\varepsilon_k - \imath\Gamma_k/2)\vec{\varphi}^R_k. \tag{9}$$

Similarly, the functions $\varphi^L_{n,k}(\vec{r});n=-\infty,\ldots,0,\ldots,+\infty$ define components of an eigenvector of the transposed matrix $\mathcal{H}_F{}^t$. That is,

$$\mathcal{H}_F{}^t\vec{\varphi}^L_k = (\varepsilon_k - \imath\Gamma_k/2)\vec{\varphi}^L_k. \tag{10}$$

When $\mathcal{H}_F$ is a complex and symmetric matrix (note that *any* matrix which supports a complete spectrum can be transformed to a symmetric form [24]) then

$$\vec{\varphi}^L_k = \vec{\varphi}^R_k \tag{11}$$

and we can omit the "*L*/*R*" labels.

The HGS can be obtained from the spectral decomposition of the dipole acceleration

$$\sigma(\Omega) = \int_0^\infty dt\,\exp(-\imath\Omega t)\frac{d^2}{dt^2}\big(\chi^L(t)|\hat{D}|\chi^R(t)\big), \tag{12}$$

where $\hat{D}$ is the dipole operator,

$$\hat{D} = E_0\hat{\mu}, \tag{13}$$

where E_0 is the maximum field amplitude. For linearly polarized light where z is an axis perpendicular to the light propagation axis, $\hat{\mu}$ is defined as (in atomic units)

$$\hat{\mu} = \vec{r}\cdot\vec{e}_z = z, \tag{14}$$

where z stands here for the sum over all z components of the electronic vector positions. How should the time-dependent expectation values be calculated by overcoming the pitfall of the time asymmetry problem in NHQM? Let us denote the $\chi^R(t)$ and $\chi^L(t)$ as the general right and left WP's describing the evolution of the atom in time which can be expanded in the basis of the QE solutions

$$\chi^R(t) = \sum_k C^R_k \exp(-\imath E_k t/\hbar)\Phi^R_k(\vec{r},t), \tag{15}$$

where

$$C^R_k = \big(\Phi^L_k(t=0)|\chi^R(t=0)\big). \tag{16}$$

However, the left time-dependent WP will be defined according to the *F*-product formalism as

$$\chi^L(t) = \sum_k C^L_k \exp\big(+\imath(E_k)^* t/\hbar\big)\Phi^L_k(\vec{r},t), \tag{17}$$

where

$$C^L_k = \big(\Phi^R_k(t=0)|\chi^L(t=0)\big). \tag{18}$$

Equation (17) plays a key role in the solution of the time asymmetry problem in TD-NHQM. See the detailed discussions in Refs. [12,14]. Now the HGS of a superposition of QE states as given in Eqs. (15) and (17) will be

$$\sigma(\Omega) = \left|\sum_{k,k'} C^L_{k'}C^R_k \sum_{n,n'=-\infty}^{\infty} \frac{[(n-n')\omega + E^*_{k'} - E_k]^2}{\Omega - [(n-n')\omega + E^*_{k'} - E_k]} \times(\varphi_{k',n'}|\hat{\mu}|\varphi_{k,n})\right|^2. \tag{19}$$

In the case where only one resonance Φ_k dominates the dynamics this expression is reduced to

$$\sigma_k(\Omega) = \left|\sum_{n,n'=-\infty}^{\infty} \frac{[(\imath\Gamma_k/\hbar\ + (n-n')\omega]^2}{\Omega - [\imath\Gamma_k/\hbar + (n-n')\omega]}(\varphi_{n',k}|\hat{\mu}|\varphi_{n,k})\right|^2. \tag{20}$$

We note that using the *c*-product formalism only the harmonic frequency peaks are attainable whereas using the *F*-product formalism [see Eqs. (19) and (20)] we obtain the full spectrum. The intensities of harmonic peaks for the case where many QE states are populated are given by

$$\sigma(\Omega = N\omega) = \left| \sum_k C_k^L C_k^R \frac{(N\omega + \imath\Gamma_k/\hbar)^2}{\Gamma_k/\hbar} \sum_{n=-\infty}^{\infty} (\varphi_{n-N,k}|\hat{\mu}|\varphi_{n,k}) \right|^2 \tag{21}$$

while for the one resonance case the following expression is obtained:

$$\sigma_k(\Omega = N\omega) = \left| \frac{(N\omega + \imath\Gamma_k/\hbar)^2}{\Gamma_k/\hbar} \sum_{n=-\infty}^{\infty} (\varphi_{n-N,k}|\hat{\mu}|\varphi_{n,k}) \right|^2 . \tag{22}$$

The selection rules allowing only odd harmonics when a single QE states controls the dynamics are readily derived from Eq. (22) [25], since when the electromagnetic field is linearly polarized the Floquet Hamiltonian is symmetrical under the transformation: $\vec{r} \to -\vec{r}$, $t \to t + T/2$. In other words the eigenfunctions of the Floquet Hamiltonian are also eigenfunctions of a second order dynamical symmetry (DS) operator $\hat{P}_2$ such that $\hat{P}_2\Phi_k = \pm\Phi_k$. This means that $\Phi_k(-\vec{r}, t + T/2) = \pm\Phi_k(\vec{r}, t)$ and therefore the Fourier components $\varphi_{n,k}$ have a distinct parity $\varphi_{n,k}(\vec{r}) = \pm(-1)^n\varphi_{n,k}(-\vec{r})$. Now the integrals $(\varphi_{n-N,k}|\hat{\mu}|\varphi_{n,k})$ will vanish when $\varphi_{n-N,k}$ and $\varphi_{n,k}$ have the same parity which will be the case when N is even. Thus only odd harmonics are obtained.

An important feature of the HGS of a superposition of QE states is the appearance of sidebands (often called hyper-Raman lines). These peaks occur at frequencies corresponding to the energy difference between QE's plus integer multiples of the incident laser frequency:

$$\sigma\left(\Omega = \frac{\varepsilon_k - \varepsilon_{k'}}{\hbar} + N\omega\right) = \left| C_{k'}^L C_k^R \frac{[\Omega + \imath(\Gamma_k + \Gamma_{k'})/(2\hbar)]^2}{(\Gamma_k + \Gamma_{k'})/(2\hbar)} \sum_{n=-\infty}^{\infty} (\varphi_{n-N,k'}|\hat{\mu}|\varphi_{n,k}) \right|^2 . \tag{23}$$

Note that it is now possible to obtain even multiples of the incident radiation shifted by the corresponding QE energy difference due to the interference between two QE states k, k' belonging to different symmetries of the DS operator $\hat{P}_2$. Now the integrals $(\varphi_{n-N,k'}|\hat{\mu}|\varphi_{n,k})$ will not vanish for an even integer N due to the different parity of $\varphi_{n-N,k'}$ and $\varphi_{n,k}$.

III. APPLICATION OF THE TD-NHQM FORMALISM TO HELIUM IN STRONG LASER FIELDS

In order to apply Eq. (19) to helium we first calculate the bound, resonance, and continuum states of the complex scaled field free hamiltonian and use them as a basis set. Since to the best of our knowledge the ability of calculating the complex rotated continuum by using Gaussian basis set has not been studied before we carry out CI calculations to check this point.

A. Spectra of the complex scaled field free helium Hamiltonian by a Gaussian basis set

Complex scaled NH spectrum of the field free helium atom is calculated for a later use as a basis set for the driven helium atom, where a limited number of the field free states of helium, which include the bound states, resonances, and non-Hermitian continuum, is used. Two quantities are needed in order to construct the complex scaled Floquet Hamiltonian: the complex field free eigenenergies and the corresponding transition moments. These quantities are calculated here for a set of values of the CS parameter θ.

The NH complex scaled spectrum of helium is obtained in two steps: First, one-electron orbitals for the complex scaled Hartree-Fock operator are found [26,27]. The primitive basis set consists of even tempered Gaussians ($30s15p10d$), where the Gaussian exponents range from 10^{-7} to 100 for the s-type, from 2.66×10^{-4} to 30 for the p-type, and from 2.66×10^{-4} to 15.85 for the d-type Gaussians. Second, the complex scaled full CI calculations based on the complex atomic orbitals are performed [26]. The prior Hartree-Fock calculations allow us to easily determine occupations of atomic orbitals in the full correlated NH states. The helium states are further classified according to their symmetry which includes the rotational quantum numbers $L(M)$, the parity P, and the spin quantum numbers $S(M_S)$. The symmetry puts restrictions to the coupling of states via transition moments, which are non-zero only for cases given by $\langle S, M_S, L, M, P|\hat{\mu}|S, M_S, L \pm 1, M, -P\rangle$.

A large Gaussian basis set allows us to obtain a well converged NH spectrum of field free helium: The complex scaled energies of bound states and resonances are very stable with respect to the CS parameter varied in the interval $0 \leqslant \theta \leqslant 0.4$, where the positions and widths are varied only by about 1×10^{-4} a.u. (Table I). The rotated NH continuum is clearly displayed in the complex scaled spectrum for this range of the CS parameter (Fig. 1): Up to four ionization thresholds are obtained, given by the ground and excited states of He$^+$ [$E_n = (-2 \text{ a.u.})/n^2$, where $n = 1, 2, \ldots$]. These factors indicate a good convergence with respect to the number of primitive Gaussians per each included symmetry (s, p, d). However, a comparison with exact energies of bound states and resonances shows that the present values most often include an error about 1×10^{-3} a.u. [28,29]. These errors would improve by including a larger rotational basis set (in exact calculations, rotational expansion up to $l = 10$ and $l = 11$ have been used [28]).

B. Calculations of the photoinduced resonance quasienergy states for helium in a strong laser field

The field induced resonance QE states of helium are solved by the (t, t') method [30] using the field free CS eigenstates as basis functions. The Floquet Hamiltonian is given in the length gauge by

$$\hat{\mathcal{H}}_F = \hat{H}_0 + eE_0(z_1 + z_2)\cos(\omega t) - \imath\hbar\frac{\partial}{\partial t}, \tag{24}$$

where $\hat{H}_0$ is the field free Hamiltonian of the helium atom and the oscillating field is linearly polarized along the z axis.

TABLE I. Mean energies $\bar{E}$ and widths $\bar{\Gamma}$ and standard errors σ_E, σ_Γ (in brackets) for field free helium states for the complex scaling parameter varied in the interval $0 \leqslant \theta \leqslant 0.4$. The present results are compared with highly accurate results.

		Present for $0 \leqslant \theta \leqslant 0.4$		Exact	
		$\bar{E}$ (σ_E) (a.u.)	$\bar{\Gamma}$ (σ_Γ) (a.u.)	E (a.u.)	Γ (a.u.)
		low lying bound states			
$1\,^1S^e$	$1s^2$	$-2.9021(2\times10^{-4})$		-2.90372[a]	
$2\,^3S^e$	$1s2s$	$-2.1748(1\times10^{-4})$		-2.17523[a]	
$2\,^1S^e$	$1s2s$	$-2.1455(1\times10^{-4})$		-2.14597[a]	
$2\,^3P^o$	$1s2p$	$-2.1320(1\times10^{-4})$		-2.13316[a]	
$2\,^1P^o$	$1s2p$	$-2.1222(1\times10^{-4})$		-2.12384[a]	
		doubly excited states ($\theta > 0.1$ for resonances)			
$^1S^e$	$2s^2$	$-0.7779(2\times10^{-4})$	$0.00439(8\times10^{-5})$	-0.777868	0.004541[b]
$^3P^o$	$2s2p$	$-0.75541(1\times10^{-5})$	$0.00028(7\times10^{-5})$	-0.760492	0.000299[b]
$^1P^e$	$2p^2$	$-0.71015(5\times10^{-5})$		-0.710500[b]	
$^1P^o$	$2s2p$	$-0.66317(1\times10^{-5})$	0.001424	-0.693135	0.001373[b]
$^1S^e$	$2p^2$	$-0.6199(5\times10^{-4})$	$0.00003(2\times10^{-4})$	-0.621926	0.000216[b]

[a] Accad *et al.*, Ref. [28].

[b] Lindroth, Ref. [27].

The Floquet matrix constructed in this basis consists of blocks of the different Floquet channels which are given by Eq. (8). The diagonal block $[\mathcal{H}_F]_{n,n}$ is composed of diagonal matrices of the field free eigenvalues plus or minus a given number photons energy $n\hbar\omega$ corresponding to each channel. The off diagonal blocks $[\mathcal{H}_F]_{n',n}$, which are nonzero for $|n-n'|=1$ are given by the transition dipole matrix. In order to get the field induced QE states, the full Floquet matrix needs to be diagonalized in principle. This is a rather difficult numerical task since when high intensity fields are involved, many Floquet channels are coupled and huge matrices are required in order to achieve converged results. However using the (t,t') approach, one does not need to diagonalize the full Floquet matrix. Instead, only a one period time evolution operator is diagonalized, yielding the eigenvalues $\lambda_k = \exp(-\imath E_k T/\hbar)$ which are directly associated with the QE's, E_k [30]. While the size of the Floquet matrix is as large as $(NM)\times(NM)$, where N represents the number of the field free states and M is the number of Floquet channels, the one period evolution operator is given by only $N \times N$ matrix. Therefore, the diagonalization of the one period evolution operator is a much less demanding task.

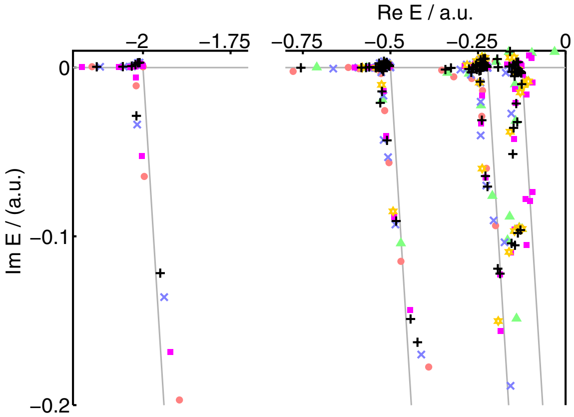

FIG. 1. (Color online) Complex scaled spectrum of field free helium obtained via electronic structure calculations (full CI method). He states fall in six symmetry groups, denoted by different markers as follows: ●: $^1S^e$, △: $^1P^e$, ×: $^1P^o$, ■: $^3S^e$, ★: $^3P^e$, +: $^3P^o$. The value of the complex scaling parameter is given by $\theta = 0.32$; the full lines show an ideal rotated non-Hermitian continuum for the four lowest ionization thresholds.

C. The HGS of helium by the TD-NHQM formalism

Different HGSs of helium are calculated using Eq. (19), where the QE resonance widths and positions as well as the Fourier components of their eigenfunctions $\varphi_{n,k}$ are obtained by the (t,t') formalism as described in Sec. III B. The field parameters are chosen in correspondence with customary laboratory setup such that the laser frequency is 5 eV with intensity of 2.8×10^{16} W/cm^2. Under these conditions, only one QE state has a significant overlap (99.9%) with the ground state of the field free helium atom ($^1S^e$) which is mostly $1s1s$. Another QE state overlaps the $^1P^o$ helium field free state which is mostly $1s2p$ with a 97% overlap. Therefore we consider only contributions from these two QE states when regarding the generation of high harmonics from either the $1s1s$ ($^1S^e$) ground state or the $1s2p$ ($^1P^o$) excited state of helium.

The HGS for helium in its ground state interacting with a cw laser with intensity of 0.08 a.u. and frequency $\omega = 5$ eV (0.057 a.u.) is presented in Fig. 2. The selection rule allowing only odd harmonics in the spectrum is evident. The peaks are very narrow due to the small width (about 1×10^{-6} a.u.) of the QE resonance state. Similarly, if we choose the QE

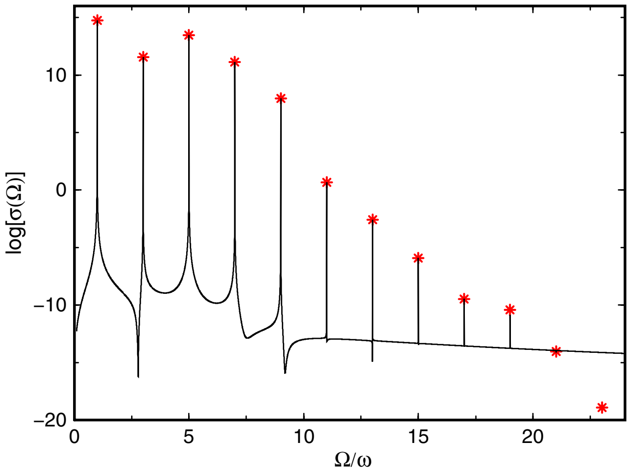

FIG. 2. (Color online) HGS of helium in the ground state (1s1s) configuration. ω=5 eV, E_0=0.08 a.u. The full line is a result of full calculation using the F product formalism as given in Eq. (20), the stars are the estimations for the harmonic frequencies peaks as given in Eq. (22).

resonance with the highest overlap to the excited 1s2p state as an initial state, we obtain the spectrum in Fig. 3. Here the same selection rules apply and only odd harmonics are produced but the peaks are much wider due to the larger width of the excited resonance state (about 1.5×10^{-2} a.u.). The intensity of the emitted high harmonics is much smaller for the same reason.

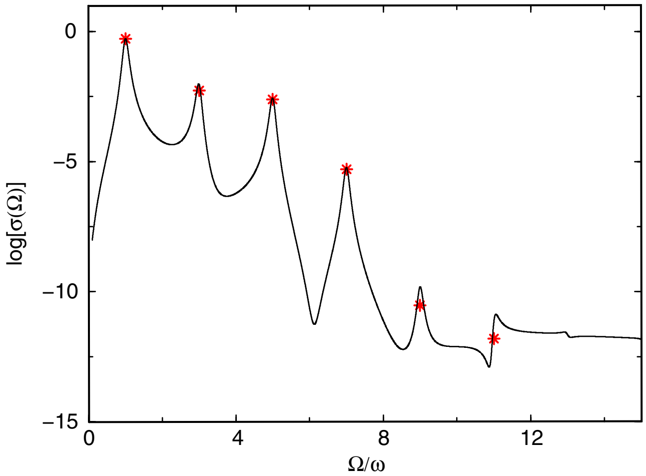

FIG. 3. (Color online) HGS of helium in the first excited P configuration (1s2p). ω=5 eV, E_0=0.08 a.u. The full line is a result of full calculation using the F-product formalism as given in Eq. (20), the stars are the estimations for the harmonic frequencies peaks as given in Eq. (22).

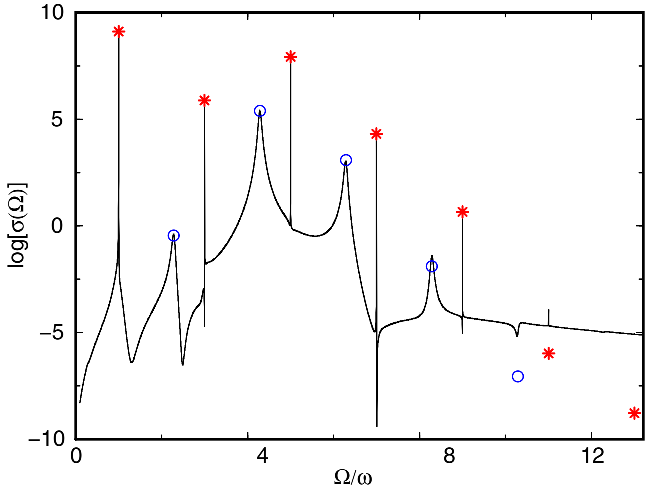

FIG. 4. (Color online) HGS of helium in a linear combination of the ground state (1s1s) configuration and the first excited P configuration (1s2p). ω=5 eV, E_0=0.08 a.u. The full line is a result of full calculation using the F-product formalism as given in Eq. (19), the red stars are the estimations for the harmonic frequencies peaks as given in Eq. (21) and the blue circles are the estimations for the sidebands as given in Eq. (23).

It is clear that in order to observe also the even harmonics, one needs to break the dynamical symmetry of the system. This can be done by populating more than one QE state. When two QE states with different symmetry are populated, the interference term between them accounts for the generation of even high harmonics. The even harmonics are shifted by the energy difference between the respective QE states, according to Eq. (23). It has been shown in Ref. [12] that the lifetimes of the two involved QE states must be of similar orders of magnitude in order to observe the hyper-Raman lines. This, however, was found here to be a requirement which is too strong. As can be seen in Fig. 4, where the initial state is an equal weight superposition of the two QE states overlapping the field free 1s1s and 1s2p states, the even harmonics can be as intense as the odd ones even due to interference between a narrow and a wide resonance states. Since these two states belong to different dynamical symmetries of the Floquet operator, their Fourier components have different parity and their interference term in Eq. (19) gives rise to shifted even harmonics. As can be seen in Fig. 4, the intensity of these side bands can be estimated very accurately using Eq. (23) as depicted by the circles in Fig. 4.

It is also evident in Fig. 4 that the peaks of the even harmonics are much broader than those of the odd harmonics. This can be easily understood by examining the different contribution to the odd harmonic peaks in Eq. (21) and to the sidebands in Eq. (23). The odd harmonic peaks are narrow since the contribution of the narrow 1s1s resonance to the sum in Eq. (21) which goes as $1/\Gamma_k$ dominates over that of the much wider 1s2p resonance. In contrast, the wider 1s2p resonance determines the shape of the sidebands peaks. This is due to the fact that the sidebands are created by the interference of two resonances and, according to Eq. (23), the width of the peak is determined by the sum of the widths of the interfering resonances.

From these results we can infer that if the helium atom (or any other noble gas) is prepared in the lab in a suitable superposition of ground and excited states also the even harmonics will be observed in experiment. An important point though is that the laser pulse interacting with the gas must support enough oscillations validating the Floquet treatment of the system.

IV. CONCLUDING REMARKS

The F-product formalism allows us to calculate the time-dependent expectation value of the dipole moment within the framework of NHQM, when the helium atom is exposed to external monochromatic linearly polarized laser field. The Fourier transform of the complex time-dependent expectation value of the acceleration (second time derivative of the dipole) provides the HGS. The electronic correlation is fully accounted for in our calculations. Unlike the previous NHQM calculations of the HGS where only the intensities of the integer harmonics frequencies were attainable, here for the first time the full HGS are calculated by the NHQM formalism. Our calculations show that when helium atoms are initially in their ground state the HGS is characterized by sharp narrow peaks at the odd harmonic frequencies. Similarly when helium atoms are initially prepared in their $1s2p$ excited state only the odd harmonics peaks are obtained. However, the peaks in the HGS are much broader, as long as the resonance state associated with the excited state has a much shorter lifetime than the resonance state associated with the field free ground electronic state of helium. The fact that the peaks in the HGS have about the same widths reflects the contribution of a single QE resonance state to the HGS. A most interesting result is obtained where the initial state is given by a superposition of the ground (1^1S^e) and excited (2^1P^o) states of the field free helium. Theoretical analysis of the expression for the HGS derived in the NHQM formalism suggests the appearance of even harmonic peaks due to the contribution to the photoinduced dynamics of two resonances of similar lifetimes (but with different symmetry) [12]. Our results clearly show that even though the lifetimes of the two resonances which are associated with the ground and the excited electronic states of helium are different by several order of magnitudes (this fact is reflected by the differences in the widths of the peaks in the HGS, see Figs. 1 and 2), pronounced peaks of even high harmonics appear in HGS when the initial state is given by a superposition of the ground and electronic states of helium (see Fig. 3). We hope that our theoretical results will encourage experimentalists to carry out HGS measurements of rare gas atoms in initially prepared superposition of ground and excited electronic states.

ACKNOWLEDGMENTS

This work was supported in part by the by the Israel Science Foundation (Grant No. 1152/04), by the Fund of promotion of research at the Technion, by the Grant Agency of the Academy of Sciences of the Czech Republic Grant No. KJB100550501 (P.K.), and the Ministry of Education of the Czech Republic Grant No. LC512 (P.K.).

---

[1] P. Salières, A. L'Huillier, P. Antoine, and M. Lewenstein, Adv. At., Mol., Opt. Phys. **41**, 83 (1999); T. Brabec and F. Krausz, Rev. Mod. Phys. **72**(2), 745 (2000).

[2] H. C. Kapteyn, M. M. Murnane, and I. P. Christov, Phys. Today **58**, 39 (2005); C. Spielmann, X-Ray Spectrom. **33**, 49 (2004); J. G. Eden, Prog. Quantum Electron. **28**, 197 (2004); O. E. Alon, V. Averbukh, and N. Moiseyev, Adv. Quantum Chem. **47**, 393 (2004).

[3] P. B. Corkum, N. H. Burnett, and M. Y. Ivanov, Springer Ser. Chem. Phys. **60**, 29 (1994); P. Antoine, A. L'Huillier, and M. Lewenstein, Phys. Rev. Lett. **77**, 1234 (1996); D. B. Dejan, A. L'Huillier, M. B. Gaarde, P. Salieres, and M. Lewenstein, Phys. Rev. A **56**, 4960 (1997); I. P. Christov, M. M. Murnane, and H. C. Kapteyn, *ibid.* **57**, R2285 (1998); P. M. Paul, E. S. Toma, P. Berger, G. Mullot, F. Aug, Ph. Balcou, H. G. Muller, and P. Agostini, Science **292**, 1689 (2001); J. G. Eden, Prog. Quantum Electron. **28**, 197 (2004); Z. Chang, Phys. Rev. A **70**, 043802 (2004); V. V. Strelkov, V. T. Platonenko, and A. Becker, Laser Phys. **15**, 799 (2005).

[4] N. Ben-Tal, J. A. Beswick, and N. Moiseyev, J. Phys. B **26**, 3017 (1993).

[5] O. E. Alon, V. Averbukh, and N. Moiseyev, Phys. Rev. Lett. **80**, 3743 (1998).

[6] M. D. Perry and J. K. Crane, Phys. Rev. A **48**, R4051 (1993); H. Eichmann, A. Egbert, S. Nolte, C. Momma, B. Wellegehausen, W. Becker, S. Long, and J. K. McIver, *ibid.* **51**, R3414 (1995); S. Long, W. Becker, and J. K. McIver, *ibid.* **52**, 2262 (1995); I. J. Kim, C. M. Kim, H. T. Kim, G. H. Lee, Y. S. Lee, J. J. Park, K. H. Hong, and C. H. Nam, Appl. Phys. B **78**, 859 (2004); C. M. Kim, I. J. Kim, and C. H. Nam, Phys. Rev. A **72**, 033817 (2005); A. Fleischer, A. K. Gupta, and N. Moiseyev, Int. J. Quantum Chem. **103**, 824 (2005).

[7] For theoretical works see for example S. X. Hu and Z. Z. Xu, Phys. Rev. A **56**, 3916 (1997); S. Dionissopoulou, T. Mercouris, and C. A. Nicolaides, *ibid.* **61**, 063402 (2000); A. Di Piazza and E. Fiordilino, *ibid.* **64**, 013802 (2001); V. Véniard, R. Taïeb, and A. Maquet, *ibid.* **65**, 013202 (2001). For experimental works see for example T. Millack and A. Maquet, *ibid.* **40**, 2161 (1993); N. Hay, R. de Nalda, T. Halfmann, K. J. Mendham, M. B. Mason, M. Castillejo, and J. P. Marangos, Eur. Phys. J. D **14**, 231 (2001).

[8] S. I. Chu and W. P. Reinhardt, Phys. Rev. Lett. **39**, 1195 (1977).

[9] N. Moiseyev and L. S. Cederbaum, J. Phys. B **32**, L279 (1999).

[10] N. Moiseyev and F. Weinhold, Phys. Rev. Lett. **78**, 2100 (1997).

[11] A. Bohm, Phys. Rev. A **60**, 861 (1999); A. Bohm and N. L. Harshman, Lect. Notes Phys. **504**, 181 (1998); A. Bohm, Adv. Chem. Phys. **122**, 301 (2002); A. Bohm *et al.*, Fortschr. Phys. **51**, 551 (2003); I. Prigogine, Int. J. Quantum Chem. **53**, 105 (1995); C. A. Nicolaides, Lect. Notes Phys. **622**, 357 (2003); C. A. Nicolaides and D. R. Beck, Int. J. Quantum Chem. **14**, 457 (1978); C. A. Nicolaides, *ibid.* **89**, 94 (2002).

[12] N. Moiseyev and M. Lein, J. Phys. Chem. **107**, 7181 (2003).

[13] A. Fleischer and N. Moiseyev, Phys. Rev. A **72**, 032103 (2005).

[14] I. Gilary, A. Fleischer, and N. Moiseyev, Phys. Rev. A **72**,

012117 (2005).

[15] I. Shavitt, Isr. J. Chem. **33**, 357 (1994); S. Wilson and D. Moncrieff, Adv. Quantum Chem. **28**, 47 (1997).

[16] G. Floquet, Ann. Sci. Ec. Normale Super. **12**, 47 (1883); J. Howland, Math. Ann. **207**, 315 (1974).

[17] S. Dionissopoulou, Th. Mercouris, and C. A. Nicolaides, Phys. Rev. A **61**, 063402 (2000); X. Guan, X.-M. Tong, and Shih-I. Chu, *ibid.* **73**, 023403 (2006); x.-M. Tong and Shih-I. Chu, *ibid.* **57**, 452 (1998); P. G. Burke, P. Francken, and C. J. Joachain, *ibid.* **24**, 761 (1991).

[18] B. R. Junker, Adv. At. Mol. Phys. **18**, 207 (1982).

[19] W. P. Reinhardt, Annu. Rev. Phys. Chem. **33**, 223 (1982).

[20] Y. K. Ho, Phys. Rep. **99**, 1 (1983).

[21] N. Moiseyev, Phys. Rep. **302**, 211 (1998).

[22] J. G. Muga, J. P. Palao, B. Navarro, and I. L. Equsquiza, Phys. Rep. **395**, 357 (2004); R. Santra and L. S. Cederbaum, *ibid.* **368**, 1 (2002).

[23] N. Moiseyev, P. R. Certain, and F. Weinhold, Mol. Phys. **36**, 1617 (1978).

[24] J. H. Wilkinson, *The Algebraic Eigenvalue Problem* (Clarendon Press, Oxford, 1965).

[25] N. Ben-Tal, N. Moiseyev, C. Leforestier, and R. Kosloff, J. Chem. Phys. **94**, 1636 (1991).

[26] P. Ždánská and N. Moiseyev, J. Chem. Phys. **123**, 194105 (2005).

[27] M. Mishra, Y. Ohrn, and P. Froelich, Phys. Lett. **84A**, 4 (1981).

[28] E. Lindroth, Phys. Rev. A **49**, 4473 (1994).

[29] Y. Accad, C. L. Pekeris, and B. Schiff, Phys. Rev. A **4**, 516 (1971).

[30] U. Peskin and N. Moiseyev, J. Chem. Phys. **99**, 4590 (1993).