Selection Rules for the High Harmonic Generation Spectra

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For three-dimensional many-electron time periodic Hamiltonians which are invariant under dynamical symmetry of order N we prove that only the $(nN \pm 1)$th, $n = 1, 2, \ldots$, harmonics are generated. We discuss the application of the dynamical symmetry based selection rules to the generation of high harmonics by thin crystals. The derived selection rules are demonstrated numerically for a one-dimensional model, showing that the dynamically symmetric systems can be used not only as "filters" of the very high harmonics but also as their "amplifiers." [S0031-9007(98)05899-2]

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Numerous experimental and theoretical investigations of harmonic generation spectra (HGS) of noble gases in intense linearly polarized laser fields were stimulated by the interest in short-wavelength sources [1]. For example, by using ultrahigh powerful lasers Sarukura *et al.* [2] found the relative intensities of 9th to 23rd harmonics of He, and more recently Preston *et al.* [3] published new experimental data with HGS extending up to the 35th harmonic. Most recently Moiseyev and Weinhold have shown that the HGS in He can be treated as a *single* Floquet state phenomenon [4]. Calculations show that even for nonperiodic Hamiltonians the HGS can be obtained from the Fourier analysis of the time dependent dipole moment for a *single Floquet state*, provided the duration of the pulse is sufficiently long (see, for example, Fig. 7 of Ref. [5]). We, therefore, study the HGS employing Floquet formalism. Using the extended Hilbert space formalism of Sambe and Howland [6] the probability to get the nth harmonic from a system found in a Floquet state, $\Psi_\varepsilon = \exp(-i\varepsilon t/\hbar)\Phi_\varepsilon$, is given by

$$\sigma_\varepsilon^{(n)} \propto n^4 |\langle\langle \Phi_\varepsilon | \hat{\mu} e^{-in\omega t} | \Phi_\varepsilon \rangle\rangle|^2, \tag{1}$$

where the double bra-ket notation, $\langle\langle \cdots \rangle\rangle$, stands for the integration over spatial variables and over time, $\hat{\mu}$ for the dipole moment operator, and ω for the laser frequency.

It is well known that the HGS of atoms in linearly polarized fields are composed only of odd harmonics [7]. A nonperturbative proof valid for quasienergy eigenstates was given by Ben-Tal, Beswick, and Moiseyev [8].

The proof can be reformulated in the following way: Suppose that no Floquet states are degenerate (accidental degeneracies of these states may occur at specific values of the field parameters [9], but generically the Floquet states of the systems of interest in this work are nondegenerate). Then $|\Phi_\varepsilon\rangle\rangle$ are simultaneous eigenfunctions of the second order dynamical symmetry (DS) operator, $\hat{P}_2 = (x \to -x, t \to t + \pi/\omega)$, with eigenvalues ± 1 and of the Floquet Hamiltonian (here we assume that the field is polarized in $\hat{x}$ direction). The nth harmonic is emitted if and only if $\langle\langle \Phi_\varepsilon | \hat{f}^{(n)} | \Phi_\varepsilon \rangle\rangle = \langle\langle \hat{P}_2 \Phi_\varepsilon | \hat{P}_2 \hat{f}^{(n)} \hat{P}_2^{-1} | \hat{P}_2 \Phi_\varepsilon \rangle\rangle \neq 0$, where $\hat{f}^{(n)} = \hat{\mu}(x) e^{-in\omega t}$. Since in our case $\hat{P}_2 \Phi_\varepsilon = \pm \Phi_\varepsilon$, it implies that $\hat{P}_2 \hat{f}^{(n)} \hat{P}_2^{-1} = \hat{f}^{(n)}$, i.e., $\hat{f}^{(n)}$ belongs to the trivial representation of the DS group generated by $\hat{P}_2$. Consequently, the nonzero values of $\sigma_\varepsilon^{(n)}$ are obtained if and only if $\hat{\mu}(x) e^{-in\omega t} = \hat{\mu}(-x) e^{-in\omega(t+\pi/\omega)}$, that is, for odd n's. This result holds for HGS of any many-electron three-dimensional (3D) system of the second order DS. It will be extended below to the case of a DS of an arbitrary order N.

The question we address here is how one can use such selection rules for the HGS to choose systems and the proper field polarization in order to filter out all high harmonics up to the nth one. The next question we shall answer is how stable are the results to perturbations which break the DS. Of course, it is interesting to know whether the selected system acts not only as a "filter" but also as an "amplifier" of the high harmonics.

For the sake of clarity and without loss of generality (with regard to many dimensions and many-electron systems), let us consider first the following effectively one-dimensional Hamiltonian which describes an electron's motion in a circle under the influence of a time independent potential, $V(\varphi)$, and the circularly polarized time dependent electric field:

$$\hat{H}(\varphi, t) = \frac{\hat{P}_\varphi^2}{2m\rho_0^2} + V(\varphi) + eE_0\rho_0 \cos(\varphi - \omega t). \tag{2}$$

The circle plane is assumed to be perpendicular to the field propagation direction. Suppose that $V(\varphi)$ possesses an N-fold symmetry axis. In such a case, the Hamiltonian of Eq. (2) is invariant under the following DS operator (written *symbolically* and not explicitly),

$$\hat{P}_N = \left(\varphi \to \varphi + \frac{2\pi}{N}, t \to t + \frac{2\pi}{N\omega}\right). \tag{3}$$

Thus, the eigenfunctions of the Floquet Hamiltonian, $\hat{\mathcal{H}}_f(\varphi, t) = -i\hbar\frac{\partial}{\partial t} + \hat{H}(\varphi, t)$, are eigenfunctions of $\hat{P}_N$ as well,

$$\hat{\mathcal{H}}_f(\varphi, t)\Phi_\varepsilon(\varphi, t) = \varepsilon\Phi_\varepsilon(\varphi, t),$$

$$\hat{P}_N \Phi_\varepsilon(\varphi, t) = \sqrt[N]{1}\, \Phi_\varepsilon(\varphi, t),$$

where, *a priori,* each one of the N roots is possible: $\sqrt[N]{1} \equiv e(-2\pi i^p/N)$, $p = 0, 1, \ldots, N-1$ (here we again disregard the possibility of an accidental degeneracy of a pair of Floquet states and treat the generic case). The HG functional takes the form,

$$\sigma_{\varepsilon}^{(n)} \propto n^4 |\langle\langle \Phi_{\varepsilon}| \hat{f}^{(n)} |\Phi_{\varepsilon}\rangle\rangle|^2 , \tag{4}$$

where $\hat{\mu}$ of Eq. (1) is equal to $\rho_0 \exp(i\varphi)$ [or $\rho_0 \exp(-i\varphi)$] for the components of the emitted radiation circularly polarized in the anticlockwise (clockwise) direction. $\hat{f}^{(n)}$ is, therefore, given by $\hat{f}_{\pm}^{(n)}(\varphi, t) \equiv \rho_0 \exp(\pm i\varphi) \exp(-in\omega t)$. The Nth order *cyclic* DS group generated by the operator $\hat{P}_N$ acting in the extended Hilbert space is $\mathcal{G}_N \equiv \{\hat{P}_N, \hat{P}_N^2, \ldots, \hat{P}_N^{N-1}, \hat{P}_N^N = \mathbf{I}\}$. The nth harmonic is emitted if and only if $\hat{f}_{\pm}^{(n)}$ belongs to the trivial representation of $\mathcal{G}_N$, i.e., $\hat{P}_N \hat{f}_{\pm}^{(n)}(\varphi, t) \hat{P}_N^{-1} = f_{\pm}^{(n)}(\varphi, t)$, or

$$e^{\pm i(\varphi + \frac{2\pi}{N})} e^{-in\omega(t + \frac{2\pi}{N\omega})} = e^{\pm i\varphi} e^{-in\omega t} \Rightarrow e^{-i\frac{2\pi(n \mp 1)}{N}} = 1 .$$

It leads immediately to the conclusion that $\sigma_{\varepsilon}^{(n)}$ is nonzero if and only if $n = 1$, $lN \pm 1$, $l \in \mathcal{N}$. Moreover, for $N \geq 3$ the $(lN + 1)$th harmonics are circularly polarized in the anticlockwise direction (as the incident light is), while the $(lN - 1)$th harmonics are circularly polarized in the clockwise direction. The polarization of high harmonics in $\mathcal{G}_2$ DS systems has been a subject of recent studies [10].

The extension of the proof given above to a 3D single electron system is straightforward. Let us formulate the problem in cylindrical coordinates. Then $\hat{P}_N$ of Eq. (3) is an exact DS operation at any specific value of ρ and z, provided that the 3D potential, $V(\rho, \varphi, z)$, is of C_N symmetry. Therefore, the selection rules for $\varphi_{\varepsilon}^{(n)}$'s hold in a 3D case. The integration in Eq. (4) is performed now over ρ and z in addition to the integration over φ and t. In the 3D case $\hat{f}_{\pm}^{(n)}$ are equal to $\rho \exp(\pm i\varphi) \exp(-in\omega t)$.

The proof given above can be easily extended to the case of 3D many-electron systems. The Hamiltonian for M electrons moving in a potential of C_N symmetry and interacting with circularly polarized light reads

$$\hat{H}_M(\vec{\rho}, \vec{\varphi}, \vec{z}, t) = \sum_{i=1}^{M} \hat{H}(\rho_i, \varphi_i, z_i, t) + e^2 \sum_{i<j}^{M} [\rho_i^2 + \rho_j^2 - 2\rho_i \rho_j \cos(\varphi_i - \varphi_j) + (z_i - z_j)^2]^{-1/2}, \tag{5}$$

where $\hat{H}(\rho_i, \varphi_i, z_i, t)$ is the 3D single electron Hamiltonian invariant under $\mathcal{G}_N$. The Hamiltonian [Eq. (5)] is invariant under two mutually disjoint groups: the Nth order cyclic DS group, $\mathcal{G}_{N,M}$, and the M electron permutation group, S_M. The former is generated by the simultaneous rotation of all the electrons $[\vec{\varphi} \equiv (\varphi_1, \ldots, \varphi_M)]$ and the appropriate translation in time:

$$\hat{P}_{N,M} = \left(\vec{\varphi} \to \vec{\varphi} + \frac{2\pi}{N}, t \to t + \frac{2\pi}{N\omega}\right). \tag{6}$$

The HG functional in the M electron case takes the form

$$\varphi_{\varepsilon,M}^{(n)} \propto n^4 |\langle\langle \Phi_{\varepsilon,M}| \hat{f}_M^{(n)} |\Phi_{\varepsilon,M}\rangle\rangle|^2, \tag{7}$$

where $\hat{f}_{\pm,M}^{(n)}(\vec{\rho}, \vec{\varphi}, t) = \sum_{i=1}^{M} \hat{f}_{\pm}^{(n)}(\rho_i, \varphi_i, t)$.

As one can see, $\hat{f}_{\pm,M}^{(n)}$ belongs to the trivial irreducible representation of the permutation group S_M. $|\Phi_{\varepsilon,M}|^2$ belongs to this representation as well. Thus, the permutational symmetry and the existence of the pairwise interaction do not affect the selection rules for the HGS. Indeed, the analysis of the HG functional [Eq. (7)] with respect to the DS [Eq. (6)] results in the selection rules *identical* to the ones obtained in the single electron case with the DS of the same order.

Next, let us apply the DS considerations to the problem of HG by electrons moving in a periodic potential [11]. More specifically, we would like to discuss the problem of an interaction of a thin crystal with laser light propagating perpendicularly to the crystal plane [12,13]. Let us consider the case of a thin crystal processing C_N symmetry axes and circularly polarized incident light. The selection rules derived above for a general multielectron system certainly hold in this case as well. However, we would like to show that the same selection rules are obtained within the framework of the independent electron approximation (see, e.g., Ref. [13]), which simplifies the theoretical treatment of HGS of thin crystals.

Without loss of generality, we treat the problem as essentially two dimensional. In this case the probability to obtain the component of the nth harmonic circularly polarized in the anticlockwise (clockwise) direction is associated with the expectation value of $v_x \pm iv_y$, $v_{x,y}$ being an electron's velocity components. The expectation value should be calculated with Floquet-Bloch states [13,14],

$$\Psi_{\varepsilon(\vec{k}),\vec{k}}(\vec{r}, t) = \exp\left(i\frac{\vec{k} \cdot \vec{r}}{\hbar}\right) \exp\left(-i\frac{\varepsilon(\vec{k})t}{\hbar}\right) \Phi_{\varepsilon(\vec{k}),\vec{k}}(\vec{r}, t) ,$$

where $\vec{k}$ is the quasimomentum vector, and $\vec{r}$ is the position vector. Calculating the harmonic emission probability, one has to take the integral over spatial variables within the unit cell, over time, and over all the values of quasimomentum up to the Fermi surface. Therefore, the relevant DS operator should commute with the Floquet-Bloch Hamiltonian, $\hat{\mathcal{H}}_{\vec{k}}^{\mathrm{FB}}(\vec{r}, t) \equiv \exp(-i\vec{k} \cdot \vec{r}/\hbar) \hat{\mathcal{H}}_f(\vec{r}, t) \exp(i\vec{k} \cdot \vec{r}/\hbar)$ rather than with the Floquet Hamiltonian. The expression for the nth harmonic emission probability takes the following form:

$$\sigma^{(n)} \propto n^2 |\langle\langle\langle \Phi_{\varepsilon(\vec{k}),\vec{k}}| \hat{f}^{(n)} |\Phi_{\varepsilon(\vec{k}),\vec{k}}\rangle\rangle\rangle|^2, \tag{8}$$

where the triple bra-ket notation, $\langle\langle\langle \cdots \rangle\rangle\rangle$, stands for the integration over the extended Hilbert space and over all values of the quasimomentum, $\vec{k}$, up to the Fermi surface, and

$$\hat{f}_{\pm}^{(n)} = \exp(-in\omega t)\exp\left(-i\frac{\vec{k}\cdot\vec{r}}{\hbar}\right)\left[\left(\hat{p}_x - \frac{e}{c}A_x(t)\right) \pm i\left(\hat{p}_y - \frac{e}{c}A_y(t)\right)\right]\exp\left(i\frac{\vec{k}\cdot\vec{r}}{\hbar}\right)$$
$$= \exp(-in\omega t)\exp\left(-i\frac{kr\cos(\varphi_k - \varphi)}{\hbar}\right)\left[\hbar e^{\pm i\varphi}\left(-i\frac{\partial}{\partial r} - \frac{1}{r}\frac{\partial}{\partial\varphi}\right) + \frac{eE_0}{\omega}e^{\pm i\omega t}\right]\exp\left(i\frac{kr\cos(\varphi_k - \varphi)}{\hbar}\right),$$

where $k \equiv |\vec{k}|$, $\varphi_k \equiv \arctan(k_y/k_x)$. The new DS operator acting in $(\vec{r}, \vec{k}, t)$ space is composed of the rotation of the coordinate and quasimomentum vectors by the same angle and the appropriate translation in time:

$$\hat{P}_N^{\mathrm{FB}} = \left(\varphi \to \varphi + \frac{2\pi}{N}, \varphi_k \to \varphi_k + \frac{2\pi}{N}, t \to t + \frac{2\pi}{N\omega}\right). \quad (9)$$

The analysis of the HG functional [Eq. (8)] with respect to the DS [Eq. (9)] results in the selection rules *identical* to the ones obtained in the general case with the DS of the order N. However, the possible thin crystal symmetries restrict the values of N to 1, 2, 3, 4, or 6. Note that the use of the current density instead of electron's velocity as an HG source (as in Ref. [13]) does not alter the selection rules.

The selection rules derived above hold, of course, for a general ionizing or dissociating system. Nevertheless, we choose to illustrate them numerically using a simple bound model described by the Hamiltonian of Eq. (2) with $V(\varphi) = -(V_0/2)[\cos(N\phi) + 1]$. It can serve as a naive model of electronic motion in a cluster of N atoms arranging in a ring. The corresponding Floquet states were found by diagonalization of the time evolution operator. The latter was calculated using the (t, t') method [4,15].

Most of the HG experiments are performed on the rare gases and employ the laser frequencies much smaller than the first ionization energy of the atom. Accordingly, we have chosen our model potential parameters to be within the range of values characteristic of the rare gas atoms: $V_0 = 0.6272$ a.u.; $\rho_0 = N(4.3357/2\pi)$ a.u. The field parameters were chosen to be $E_0 = 2.2358 \times 10^{-2}$ a.u. and $\omega = 0.02$ a.u. ≈ 0.54 eV. The chosen field strength corresponds to the relatively moderate field intensity of about 1.8×10^{13} W/cm^2. The HGS for $N = 100$ is given in Fig. 1. As expected on the basis of the selection rules, the harmonics produced are the 99th, 101st, 199th, 201st, ... ones.

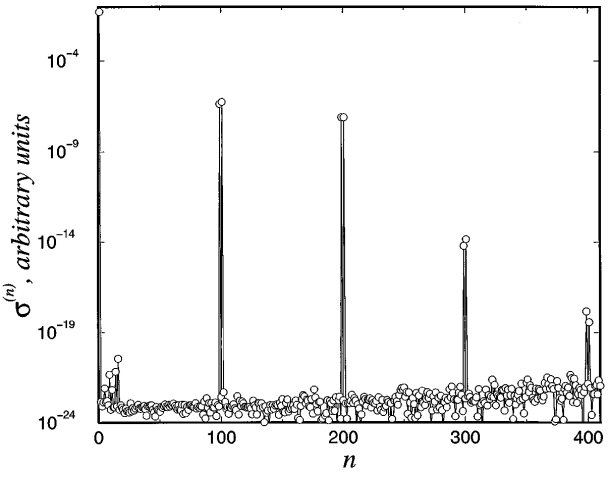

FIG. 1. HGS for a model of $N = 100$ atoms, which are placed equidistantly on a circle exposed to circularly polarized field of the intensity 1.8×10^{13} W/cm^2. The first high harmonic has the frequency of $99\omega \approx 2$ a.u.

In order to study the stability of the spectrum to weak DS-breaking perturbations we choose to replace the circularly polarized field in the Hamiltonian [Eq. (2)] by an elliptically polarized field, $\vec{E} = E_0\cos(\omega t)\hat{x} + E_0\sin(\omega t + \theta)\hat{y}$. A similar deformation can account, for example, for an imperfect orientation of a cluster with respect to the laser light propagation direction. The results presented in Fig. 2 demonstrate that the $(lN \pm 1)$th harmonics are by several orders of magnitude more dominant than the rest within a finite range of θ. The dependence of the emission probabilities of the harmonics, which are forbidden at circular polarization, on θ in the small θ limit can be predicted by perturbation theory. To the first order in θ, the DS-breaking part of the perturbation is given by $(1/2)E_0\rho_0 e\theta\sin(\varphi + \omega t)$. The analysis of this term with respect to its DS properties shows that only the $(lN \pm 3)$th harmonics are allowed in the first order in θ. Consequently, the $(lN \pm 3)$th harmonic strengths vary as θ^2, while the others are

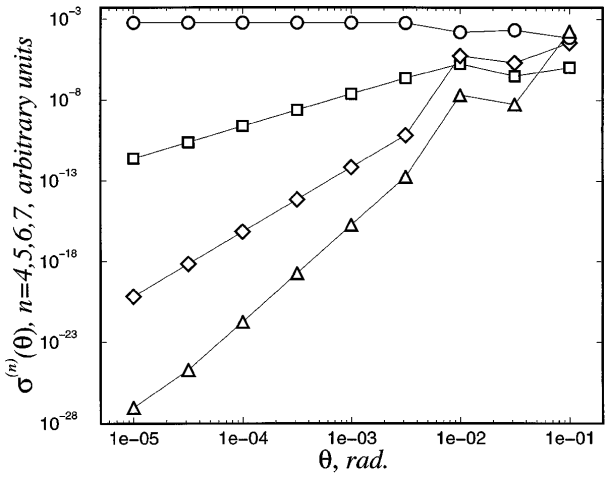

FIG. 2. Stability plot of the probability to generate the symmetry-allowed 6th harmonic and the 4th, 5th, and 7th (symmetry-forbidden) harmonics. Note that (a) $\sigma^{(6)}$ (circles) is more dominant by several orders of magnitude than that of the symmetry-forbidden harmonics for $\theta < 0.1$ rad; (b) $\sigma^{(4)}$ (squares) varies initially as θ^2; (c) $\sigma^{(5)}$ (diamonds) varies initially as θ^4; (d) $\sigma^{(7)}$ (triangles) varies initially as θ^6.

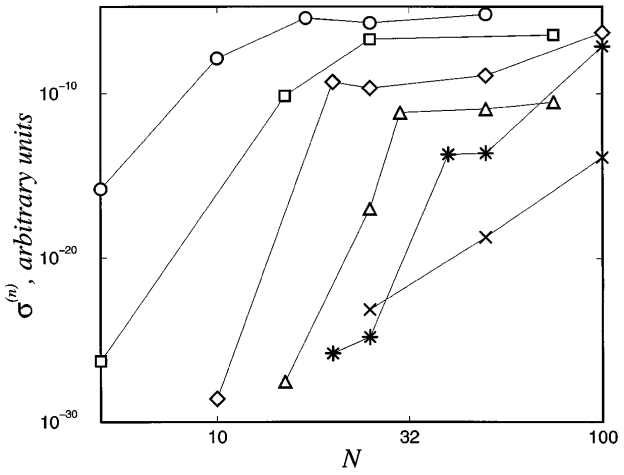

FIG. 3. The probability to get the nth harmonic as a function of the number N of the atoms which are placed equidistantly on a circle (a log-log plot). Circles: the 51st harmonic (the 50th for $N = 17$); squares: the 76th harmonic; diamonds: the 101st harmonic; triangles: the 151st harmonic; stars: the 201st harmonic; $\times$'s: the 301st harmonic. As N increases the higher harmonics are amplified.

expected to grow at least as θ^4. Actually, the analysis of the second order correction shows that starting with $N = 7$ some harmonics, e.g., the (lN)th, grow even slower, at least as θ^6. Our numerical results are found to be in complete agreement with these predictions. It should be noted that for even N's only odd harmonics appear in the HGS at an arbitrary polarization due to $\mathcal{G}_2$ DS.

The results presented in Figs. 1 and 2 show that the DS based selection rules enable one to design a system (a target and a time dependent electric field) which filters out the selected high harmonics only.

The fact that the system which possesses the DS [Eq. (3)] acts not only as a filter but also as an amplifier is illustrated in Fig. 3. Our results show that the probability to generate the high harmonics increases as the number of the "atoms" in the cluster is increased.

The selection rules for HGS derived in the present Letter can be demonstrated in a wide variety of experiments. One possibility is to study the HGS of molecules possessing the Nth order symmetry axis in a circularly polarized field. In such a case, the target molecule must be oriented in the plane perpendicular to the light propagation direction. Choosing a molecule possessing a dipole moment along the symmetry axis, such as C_5H_5Tl (C_{5v}), would allow one to orient it properly by a dc electric field without breaking the DS. Another possibility is to study the HGS of molecules of high symmetry, e.g., C_{60}. A promising possibility which avoids the orientation problem is that of thin crystals possessing C_N axes. The $N \leq 6$ restriction of plane groups can be overcome, if one goes beyond the dipole approximation validity regime. For example, one can direct a *linearly* polarized incident light in the plane of a thin crystal. Tuning the laser wavelength to be a multiple of the lattice constant along the propagation direction, $\lambda = Na$, would result, in principle, in a formation of a system with an arbitrarily high DS. Considering the selection rules for harmonic emission due to the time dependent dipole moment in the incident beam *propagation* direction, one finds [16] that only very high energy photons, if any, will be emitted perpendicularly to the thin crystal plane.

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