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Ab initio calculations of the second dynamic hyperpolarizability of LiH by means of Floquet theory approach

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Abstract. Floquet theory is used to describe the response of a molecule to applied radiation electric field. The method of *ab initio* calculation of frequency dependent (hyper)polarizabilities based on combination of perturbation theory with the finite field method has been developed. Electron correlation is taken into account by means of the CIPSI algorithm. The total wave function expansion involves spectral, pseudo-spectral states and polynomial terms. The developed approach is applied to the calculation of the second hyperpolarizability of the lithium hydride molecule subjected to the superposition of harmonic and static electric fields. The method can be used to calculate the higher order nonlinear properties of molecules.

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1 Introduction

It has generally been accepted that second- and third-order processes are related to the most important phenomena in nonlinear optics. As these processes are governed by atomic and molecular dynamic hyperpolarizabilities the latter are of considerable interest.

Many *ab initio* calculations of these frequency-dependent properties were carried out at different levels of the theory including electron correlation effects during the last decade (see [1] and references herein). Jonsson *et al.* [2] reported the application of the multiconfiguration cubic response theory to the SHG hyperpolarizabilities of LiH and CO. Hättig *et al.* [3–5] presented the coupled cluster second and cubic response theories and reported the results of the first and second dynamic hyperpolarizabilities calculations. The coupled cluster response theory in the equation of motion (EOC-CC) formulation has been developed in Bartlett group by Rozyczko *et al.* [6,7]. The time-dependent generalization of the density functional theory (TDDFT), which can be considered as DFT extension of RPA, has been formulated by Colwell *et al.* [8]. The application of time-dependent DFT to the nonlinear properties of organic molecules has been given by van Gisbergen *et al.* [9,10].

Recently Kobayashi *et al.* [11,12] reported the implementation of the first and second frequency-dependent hyperpolarizabilities of the number of molecules, using the quasienergy derivative (QED) method at the second-order Møller-Plesset perturbation theory (MP2) level. The authors (Sasagane *et al.*) developed this approach earlier [13,14] and called it QED-MP2 response theory.

It should be noted that the term *quasienergy* was first introduced to indicate the time-independent energy-like quantity $\mathcal{E}$, appearing in the overall phase factor of the Floquet states wave function [15–18]. It has been shown [19], that in the case of time-periodic perturbation this quantity can be obtained as the time average over one period of the real time-periodic integrand $W(t)$, which determines the phase of the whole wave function. Rice and Handy [20,21] called $W(t)$ the time-dependent energy or more strictly *pseudo-energy*. However it becomes common in quantum chemistry literature that $W(t)$ is referred to as quasienergy while $\mathcal{E}$ is termed "time-independent" or "time-average" quasienergy.

The important feature of the QED method [11] and CC response theory of Hättig *et al.* [3–5], is that they are quite equivalent to the method of using the derivatives of the quasienergy $\mathcal{E}$. However the Floquet states approach has the advantages of higher universality. It can be used with slight modifications in the case when the field frequencies are close to the transition energy of the system. It also

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holds for the polychromatic fields [22] unrestricted by the frequencies commensurable condition specific to the QED and closely related approaches.

The distinctive property of the Floquet theory is that Floquet states describe a quantum system subjected to the finite electromagnetic field in the same manner as the stationary states do in the case of the time-independent Hamiltonian. As has been indicated by Dmitriev and Roos [23], this allows the finite field method to be used in calculations of molecular nonlinear dynamic properties even if all the frequencies of the field are non-zero. This statement was demonstrated in calculations of the second dynamic hyperpolarizabilities of hydrogen molecule over a wide wavelength range up to the first resonance.

It should be emphasized that feasibility of the finite field method as well as the finite-order perturbation theory, substantially depends on the basis set properties. Both of these approximations are widely employed using a finite basis set. However the radii of convergence of Floquet state quasienergy or dipole moment power-series expansions in the field strength tends towards zero as the basis size increases [25]. This means, that the basis set does not have to be too large in practice. However, to describe any actual many-electron system, which always has an infinite number of states the basis set must be sufficiently large (excluding the resonance case), or alternatively must involve the terms of special form.

In this paper we consider an example of the use of Floquet theory in combination with the "time-independent" perturbation theory for Floquet states in composed Hilbert space $R^3 \otimes \tau$ [16], with the finite field method. This approach was developed by Shtoff *et al.* [26], where a finite basis set consisting of orthogonal field free molecule spectral states was used for calculations of higher-order hyperpolarizabilities.

Our first aim is to investigate the advantages of adding to such a basis set the polynomial and quasi-spectral wave functions previously proposed by Rérat *et al.* [27–29] in the time-dependent gauge-invariant (TDGI) calculations. Since additional basis set terms are not orthogonal our second aim is to extend the theory, developed in [26], to the case of general non-orthogonal basis. The third purpose of this paper is to calculate the dispersion of the second hyperpolarizabilities for a wide range of wavelengths for different processes, revealing opportunities which are offered by this approach.

2 Theory

In the semiclassical radiation theory behavior of a many-electron system subjected to an electromagnetic field induced by light is described by the solution of the time-dependent Schrödinger equation for the system in external time-dependent electric field $\mathbf{E}(t)$:

$$\mathrm{i}\frac{\partial \Psi}{\partial t} = (H_0(\mathbf{r}) + V(\mathbf{r},t))\Psi \tag{1}$$

where the perturbation term $V(\mathbf{r},t)$ in the dipole approximation is given by $V(\mathbf{r},t) = \mathbf{E}(t)\cdot\mathbf{r}$. In equation (1) and throughout, all values are expressed in atomic units. $H_0(\mathbf{r})$ is the Hamiltonian for the unperturbed molecule and is assumed to have an orthonormal set of eigenfunctions ψ_i corresponding to spectral states of the molecule with energies ε_i. The vector $\mathbf{r}$ is used to represent the coordinates of all electrons. We are interested in the normalized particular solution of equation (1) corresponding to the state of a perturbed molecule which originally ($t \to -\infty$) was in the lowest energy spectral state. It is well-known [16,19] that if the field periodic in time has been switched on sufficiently smoothly and the energy of photon (or photons for the strong field) is far from the transition energies, the required solution takes the form of a quasiperiodic state,

$$\Psi(\mathbf{r},t) = \exp(-\mathrm{i}\mathcal{E}t)u(\mathbf{r},t) \tag{2}$$

where quasienergy $\mathcal{E}$ and time periodic steady state function $u(\mathbf{r},t)$ are solutions of "time-independent" steady state Schrödinger equation:

$$\mathcal{H}(\mathbf{r},t)u(\mathbf{r},t) = \mathcal{E}u(\mathbf{r},t). \tag{3}$$

The operator $\mathcal{H}(\mathbf{r},t) = H_0(\mathbf{r}) + V(\mathbf{r},t) - \mathrm{i}\partial/\partial t$ acts in the composite Hilbert space $R^3 \otimes \tau$ including the time variable, with the inner product:

$$\langle\langle u(\mathbf{r},t)|\nu(\mathbf{r},t)\rangle\rangle = \frac{1}{T}\int_0^T \mathrm{d}t \int \mathrm{d}\mathbf{r}\; u^*(\mathbf{r},t)\nu(\mathbf{r},t)$$

where T is the field period. The states described by the wave function (2) are referred to as Floquet or quasienergy states.

We shall assume the external field to be polychromatic and is consistent of N monochromatic linearly polarized harmonic components and a static term:

$$\mathbf{E} = \mathbf{E}_0 + 1/2\sum_{k=1}^{N}(\mathbf{E}_{\omega_k}\exp(-\omega_k t) + \mathbf{E}_{-\omega_k}\exp(\omega_k t)) \tag{4}$$

where $\mathbf{E}_{\omega_k} = \mathbf{E}_{0\omega_k}\exp(-\mathrm{i}\eta_k)$ is the complex amplitude, η_k and $\mathbf{E}_{0\omega_k}$ are the time-independent initial phase and real amplitude of the kth harmonic. Despite of the fact that the external field is not time-periodic, the solutions of equation (1) in the form of Floquet states (2) do exist. To obtain these solutions one can introduce a new Hamiltonian with the interaction operator, depending on N time variables

$$V(\mathbf{r},t_1,...,t_N) = \mathbf{r}\mathbf{E}_0 + 1/2\sum_{k=1}^{N}\mathbf{r}(\mathbf{E}_{\omega_k}\exp(-\omega_k t_k) + \mathbf{E}_{-\omega_k}\exp(\omega_k t_k)) \tag{5}$$

and solve an auxiliary time-dependent equation [22] with this new Hamiltonian

$$\mathrm{i}\sum_{k=1}^{N}\frac{\partial \Phi(\mathbf{r},t_1,...,t_N)}{\partial t_k} = H(\mathbf{r},t_1,...,t_N)\Phi(\mathbf{r},t_1,...,t_N) \tag{6}$$

where $H(\mathbf{r}, t_1, ..., t_N) = H_0(\mathbf{r}) + V(\mathbf{r}, t_1, ..., t_N)$.

The Hamiltonian of equation (6) is a time-periodic function in the N-dimensional space, and according to the Floquet theorem [30] the solution of equation (6) can be written as

$$\Phi(\mathbf{r}, t_1, ..., t_N) = \exp\left(-\mathrm{i}\sum_{k=1}^{N} \mathcal{E}_k t_k\right) v(\mathbf{r}, t_1, ..., t_N) \qquad (7)$$

where $v(\mathbf{r}, t_1, ..., t_N)$ meets the periodic conditions

$$v\left(\mathbf{r}, t_1, ..., t_k + \frac{2\pi}{\omega_k}, ..., t_N\right) = v(\mathbf{r}, t_1, ..., t_k, ..., t_N), \qquad k = 1, ..., N. \qquad (8)$$

Substituting (7) into equation (6) we find that $v(\mathbf{r}, t_1, ..., t_N)$ should satisfy the following eigenproblem equation:

$$\mathcal{H}(\mathbf{r}, t_1, ..., t_N) v(\mathbf{r}, t_1, ..., t_N) = \mathcal{E} v(\mathbf{r}, t_1, ..., t_N) \qquad (9)$$

where quasienergy $\mathcal{E} = \mathcal{E}_1 + \cdots + \mathcal{E}_N$.

"Hamiltonian"

$$\mathcal{H}(\mathbf{r}, t_1, ..., t_N) = H_0(\mathbf{r}) + V(\mathbf{r}, t_1, ..., t_N) - \mathrm{i}\sum_{k=1}^{N} \partial/\partial t_k$$

acts in the extended composed Hilbert space $R^3 \otimes \tau_1 \otimes \cdots \otimes \tau_N$ with the inner product

$$(v, w) = \frac{1}{T_1 \cdots T_N} \int_0^{T_1} \mathrm{d}t_1 \cdots \times \int_0^{T_N} \mathrm{d}t_N \langle v(\mathbf{r}, t_1, ..., t_N) | w(\mathbf{r}, t_1, ..., t_N)\rangle.$$

If we have the solution $v(\mathbf{r}, t_1, ..., t_N)$ of equation (9) which satisfies periodic conditions (8), then the function

$$\Psi(\mathbf{r}, t) = \exp(-\mathrm{i}\mathcal{E}t) v(\mathbf{r}, t, ..., t) = \exp(-\mathrm{i}\mathcal{E}t) u(\mathbf{r}, t) \qquad (10)$$

defined by Φ with coinciding time variables $t_1 = \cdots = t_N = t$ satisfies the Schrödinger equation (1) with Hamiltonian $H = H_0 + V(\mathbf{r}, t)$ that can be checked by direct substitution [22].

To find the approximate solutions of the eigenproblem (9) it is possible to employ the variational principle for quasienergy. It has been established [16] that the accurate solutions of equation (9) correspond to the stationary points of the quasienergy functional

$$\mathcal{E}[\tilde{v}(\mathbf{r}, t_1, ..., t_N)] = \frac{(\tilde{v}(\mathbf{r}, t_1, ..., t_N), \mathcal{H}\tilde{v}(\mathbf{r}, t_1, ..., t_N))}{(\tilde{v}(\mathbf{r}, t_1, ..., t_N), \tilde{v}(\mathbf{r}, t_1, ..., t_N))} \cdot \qquad (11)$$

Using the Lagrange multiplier method one can reformulate the variational problem (11) to arrive at the following equation

$$\delta(\tilde{v}(\mathbf{r}, t_1, ..., t_N), (\mathcal{H} - \mathcal{E})\tilde{v}(\mathbf{r}, t_1, ..., t_N)) = 0 \qquad (12)$$

where the Lagrange multiplier $\mathcal{E}$ refers to the quasienergy and corresponds to normalization requirement

$$(\tilde{v}, \tilde{v}) = 1. \qquad (13)$$

To solve the variational equation (12) we represent the trial function in the form of N-dimensional time-dependent Fourier series

$$\tilde{v}(\mathbf{r}, t_1, ..., t_N) = \sum_{n_1, ..., n_N} f_{n_1, ..., n_N}(\mathbf{r}) \exp[\mathrm{i}(n_1\omega_1 t_1 + ... + n_N\omega_N t_N)]$$

and expand the Fourier coefficients in terms of M orthonormal basis set functions, involving the ground and the first $M-1$ lowest-energy excited spectral states $\psi_k(\mathbf{r})$ of the field free molecule. To compensate for the limited size of the basis set thus constructed we added to this expansion the first degree polynomial terms $g(\mathbf{r})\psi_0(\mathbf{r})$ where $\psi_0(\mathbf{r})$ is the field free ground state, $g(\mathbf{r}) = \sum_\alpha b_\alpha r_\alpha$ (with $\alpha = x, y, z$), and the linear combination of M_1 quasi-spectral one-determinantal functions $\varphi_k(\mathbf{r})$ [28].

To summarize, the trial wave function is expressed as

$$\tilde{v}(\mathbf{r}, t_1, ..., t_N) = \sum_{sn_1, ..., n_N} C_{sn_1, ..., n_N} \exp[\mathrm{i}(n_1\omega_1 t_1 + ... + n_N\omega_N t_N)]\chi_s(\mathbf{r}) \qquad (14)$$

where

$$\begin{aligned}
&\chi_s(\mathbf{r}) = \psi_k(\mathbf{r}), && k = 0, ..., M-1, && s = 1, ..., M,\\
&\chi_s(\mathbf{r}) = r_\alpha\psi_0(\mathbf{r}), && \alpha = x, y, z, && s = M+1, M+2, M+3,\\
&\chi_s(\mathbf{r}) = \varphi_m(\mathbf{r}), && m = 1, ..., M_1 && s = M+4, ..., M+3+M_1.
\end{aligned}$$

Employing the trial function ansatz (14) and equation (12) we arrive at generalized matrix eigenvalue problem

$$(\boldsymbol{\mathcal{H}} - \mathcal{E}\boldsymbol{\mathcal{S}})\mathbf{C} = 0 \qquad (15)$$

where $(N+1)$-dimensional supermatrices $\boldsymbol{\mathcal{H}}$ and $\boldsymbol{\mathcal{S}}$ can be written as:

$$\begin{aligned}
\mathcal{H}_{rm_1...m_N sn_1...n_N} = {} & \left(H_{0rs} + \mathbf{E}_0 \cdot \mathbf{r}_{rs} + \sum_{k=1}^{N} (n_k\omega_k) S_{rs}\right) \delta_{m_1n_1} \cdots \delta_{m_Nn_N}\\
& + 1/2 \sum_{k=1}^{N} \mathbf{r}_{rs} \left(\mathbf{E}_{\omega_k}\delta_{m_k, n_k-1} + \mathbf{E}^*_{\omega_k}\delta_{m_k, n_k+1}\right)\\
& \times \delta_{m_1n_1} \cdots \delta_{m_{k-1}n_{k-1}} \delta_{m_{k+1}n_{k+1}} \cdots \delta_{m_Nn_N},
\end{aligned} \qquad (16)$$

$$\mathcal{S}_{rm_1...m_N sn_1...n_N} = S_{rs}\delta_{m_1n_1} \cdots \delta_{m_Nn_N} \qquad (17)$$

and symmetric matrices H_0, r and S are given by their

$$\mathsf{H}_0 = \begin{array}{c|c|c|c}
 & k=0,...,M-1 & \beta=x,y,z & m_2=1,...,M_1 \\
\hline
i=0,...,M-1 & \varepsilon_i\delta_{ik} & -\langle\psi_i|\nabla_\beta|\psi_0\rangle+\varepsilon_0\langle\psi_i|r_\beta|\psi_0\rangle & \varepsilon_i\langle\psi_i|\varphi_{m_2}\rangle \\
\hline
\alpha=x,y,z & & 1/2n_{\mathrm{el}}\delta_{\alpha\beta}+\varepsilon_0\langle\psi_0|r_\alpha r_\beta|\psi_0\rangle & \langle\psi_0|\nabla_\alpha|\varphi_{m_2}\rangle+\varepsilon_0\langle\psi_0|r_\alpha|\varphi_{m_2}\rangle \\
\hline
m_1=1,M_1 & & & \langle\varphi_{m_1}|H_0|\varphi_{m_2}\rangle
\end{array}$$

$$\mathsf{r} = \begin{array}{c|c|c|c}
 & k=0,...,M-1 & \beta=x,y,z & m_2=1,...,M_1 \\
\hline
i=0,...,M-1 & \langle\psi_i|\mathbf{r}|\psi_k\rangle & \langle\psi_i|\mathbf{r}r_\beta|\psi_0\rangle & \langle\psi_i|\mathbf{r}|\varphi_{m_2}\rangle \\
\hline
\alpha=x,y,z & & \langle\psi_0|r_\alpha\mathbf{r}r_\beta|\psi_0\rangle & \langle\psi_0|r_\alpha\mathbf{r}|\varphi_{m_2}\rangle \\
\hline
m_1=1,...,M_1 & & & \langle\varphi_{m_1}|\mathbf{r}|\varphi_{m_2}\rangle
\end{array}$$

$$\mathsf{S} = \begin{array}{c|c|c|c}
 & k=0,...,M-1 & \beta=x,y,z & m_2=1,...,M_1 \\
\hline
i=0,...,M-1 & \delta_{ik} & \langle\psi_i|r_\beta|\psi_0\rangle & \langle\psi_i|\varphi_{m_2}\rangle \\
\hline
\alpha=x,y,z & & \langle\psi_0|r_\alpha r_\beta|\psi_0\rangle & \langle\psi_0|r_\alpha|\varphi_{m_2}\rangle \\
\hline
m_1=1,M_1 & & & \delta_{m_1m_2}
\end{array}$$

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triangles:

see matrices above

where n_{el} is the total number of electrons.

Restricting our consideration to the electron contribution to the molecular dipole moment

$$\mathbf{P}(t) = -\langle\Psi(\mathbf{r},t)|\mathbf{r}|\Psi(\mathbf{r},t)\rangle \tag{18}$$

and using the steady state wave function (14) we expand the right-hand side of (18) in Fourier series

$$\mathbf{P}(t) = -1/2\sum_{\omega_\sigma}\mathbf{P}_{\omega_\sigma}\exp(-\mathrm{i}\omega_\sigma t) \tag{19}$$

where $\omega_\sigma = n_1\omega_1+\dots+n_N\omega_N$, $n_1,...,n_N$ being integers, and

$$\begin{aligned}\mathbf{P}_{\omega_\sigma} = \mathbf{P}_{n_1\cdots n_N} &= (2-\delta_{0,\omega_\sigma}) \\ &\times\sum_{rsm_1\cdots m_N} C^*_{r(m_1+n_1)\cdots(m_N+n_N)}C_{sm_1\cdots m_N}\langle\chi_r|\mathbf{r}|\chi_s\rangle.\end{aligned} \tag{20}$$

The hyperpolarizability tensor $\gamma^{(k)}_{\mu\beta_1...\beta_k}$ arises when the Cartesian components of the molecular dipole Fourier amplitudes $\mathbf{P}_{\omega_\sigma}$ are expanded in a power series of the field strength Cartesian components.

Generally when the applied field consists of several harmonics of frequencies ω_i (including the term with $\omega_i = 0$) this expansion can be written in the following form [31]:

$$(P_{\omega_\sigma})_\mu = \sum_k (P^k_{\omega_\sigma})_\mu \tag{21}$$

$$\begin{aligned}(P^k_{\omega_\sigma})_\mu = &\sum_{\beta_1\omega'_1...\beta_k\omega'_k}(k!)^{-1}N(\omega'_1,...,\omega'_k) \\ &\times\gamma^{(k)}_{\mu\beta_1...\beta_k}(-\omega_\sigma;\omega'_1,...,\omega'_k)(E_{\omega'_1})_{\beta_1}...(E_{\omega'_k})_{\beta_k}\end{aligned} \tag{22}$$

where the numerical factor $N(\omega'_1,...,\omega'_k)$ depends on the process being studied.

The frequencies ω'_j involved in (22) take on the values of the applied field frequencies $\pm\omega_i$, 0, and are subject to the condition:

$$\omega_\sigma = \omega'_1+...+\omega'_k. \tag{23}$$

As the number of monochromatic waves is usually small, the power series terms for each order, except the first one, can include several amplitudes E_{ω_i} of the same frequency ω_i (including the zero frequency). Later on for the sake of simplicity we will not use the superscripts for the frequencies involved in the power series, bearing in mind that the set of $\omega_1,...,\omega_k$ in the kth order term can include identical field frequencies (positive, negative, or zero). The actual values of the field frequencies involved in the power series terms of particular order are determined by the nonlinear process under consideration.

Comparing the general expression of the Taylor series coefficients with (22) we immediately obtain:

$$\begin{aligned}\gamma^{(k)}_{\mu\beta_1...\beta_k}(-\omega_\sigma;\omega_1,...,\omega_k) &= (N(\omega_1,...,\omega_k))^{-1} \\ &\times\left(\frac{\partial^k(P_{\omega_\sigma})_\mu}{\partial(E_{\omega_1})_{\beta_1}...\partial(E_{\omega_k})_{\beta_k}}\right)_{E_{\omega_1}=...=E_{\omega_k}=0}.\end{aligned} \tag{24}$$

Thus for theoretical prediction of the molecular hyperpolarizabilities one can calculate the derivatives of Fourier components of molecular dipole moment with respect to the field strengths amplitudes. It is obvious that in any response theory the differentiation of the dipole moment with respect to the complex field strengths $(E_{\omega_k})_{\beta_k} = (E_{0\omega_k})_{\beta_k}\exp(-\mathrm{i}\eta_k)$ is supposed to be performed with initial phase η_k held constant, that is

$$\frac{\partial}{\partial(E_{\omega_k})_{\beta_k}} = \exp(\mathrm{i}\eta_k)\frac{\partial}{\partial(E_{0\omega_k})_{\beta_k}}\,.$$

It is seen that the derivative of the power series term of any order does not contain initial phases and differentiation of the dipole moment with respect to complex field strength is reduced to differentiation of the dipole moment with respect to real field strength $(E_{0\omega_k})_{\beta_k}$ at zero initial phases. This means, that if the molecular dipole moment can be expressed in terms of a power series in the field amplitude strengths, one can set equal to zero all initial phases of the perturbation term in the Schrödinger equation while calculating the hyperpolarizabilities as the dipole moment derivatives. In this case Hermitian supermatrix $\mathcal{H}$ (16) as well as its eigenvectors will be real.

Turning back to Floquet theory one can see that two radically different strategies of calculations are possible in this theory. The first widely accepted approach is based on the time-independent perturbation theory applied to Floquet matrix eigenvalue problem (15). As a first approximation one can solve the eigenproblem for the matrix of a field-free molecule Hamiltonian H_0 and find perturbed vectors of the first lowest orders by solving the set of perturbation theory equations. Then differentiating equation (20) with respect to the field amplitudes, replacing derivatives of eigenvectors by perturbed vectors of corresponding orders and using equation (24) one obtains the required hyperpolarizability.

The second approach [23,32,33] can be called the finite field method because it is closely analogous to the finite field method in the theory of static susceptibilities. The essence of this method is to calculate Floquet matrix eigenvectors and Fourier components of the dipole moment (20) as functions of the field amplitudes by solving equation (15) at different points of the field amplitudes space. Then the required derivatives of dipole moment Fourier component are found by some numerical methods.

To extend the capabilities of both methods, an alternative two-step strategy combining both approaches has been proposed [26]. At the first step the unperturbed part $\boldsymbol{\mathcal{H}}^{(0)}$ of the Floquet matrix $\boldsymbol{\mathcal{H}}$ is extracted and the eigenvalue problem for this unperturbed matrix is solved. The choice of $\boldsymbol{\mathcal{H}}^{(0)}$ is dependent on the specific features of the problem. Next the derivatives of dipole moment Fourier components are calculated as functions of the field amplitudes involved in $\boldsymbol{\mathcal{H}}^{(0)}$ by solving perturbation theory equations at the points of this finite field. (If the field is equal to zero, this step corresponds to the first approach and the derivatives are directly proportional to the hyperpolarizabilities of corresponding order.) At the second step the calculated derivatives are differentiated numerically to obtain the hyperpolarizabilities of the higher orders.

When the whole matrix $\boldsymbol{\mathcal{H}}$ is chosen as the unperturbed one, the perturbation can be defined by small variations $\delta\mathbf{E}_{\omega_k}$ of the field amplitudes.

Let the Floquet matrix (16) be partitioned to unperturbed and perturbed parts such that

$$\boldsymbol{\mathcal{H}}=\boldsymbol{\mathcal{H}}^{(0)}+\boldsymbol{\mathcal{H}}^{(1)}. \tag{25}$$

The perturbed part $\boldsymbol{\mathcal{H}}^{(1)}$ can be expressed as

$$\boldsymbol{\mathcal{H}}^{(1)}=\sum_{k\alpha}\alpha_k\boldsymbol{\mathcal{H}}^{(1)}_{\alpha_k}. \tag{26}$$

where α_k denotes the Cartesian component of the kth monochromatic field amplitude $\mathbf{E}_{0\omega_k}$, or its small variation. When $k=0$, α_0 represents the Cartesian coordinates of the static field $\mathbf{E}_0$, or its small variation.

If $k\neq 0$, the matrix elements of $\boldsymbol{\mathcal{H}}^{(1)}_{\alpha_k}$ can be written as

$$\mathcal{H}^{(1)}_{\alpha_k r m_1\ldots m_N s n_1\ldots n_N}= \frac{1}{2}(r_\alpha)_{rs}(\delta_{m_k,n_k-1}+\delta_{m_k,n_k+1})\delta_{m_1n_1} \cdots\delta_{m_{k-1}n_{k-1}}\delta_{m_{k+1}n_{k+1}}\cdots\delta_{m_Nn_N}, \tag{27}$$

otherwise

$$\mathcal{H}^{(1)}_{\alpha_0 r m_1\ldots m_N s n_1\ldots n_N}=(r_\alpha)_{rs}\delta_{m_1n_1}\cdots\delta_{m_Nn_N}. \tag{28}$$

Suppose that the ground energy level is non-degenerate and the field frequency is far from the transition energies of the molecule. Then it means that the unperturbed quasienergy in question is also non-degenerate and one can use the non-degenerate perturbation theory to solve equation (15). Expanding $\mathbf{C}$ and $\mathcal{E}$ according to

$$\mathbf{C}=\mathbf{C}^{(0)}+\sum_{i\alpha}\alpha_i\mathbf{C}^{(1)}_{\alpha_i}+1/2\sum_{ij\alpha\beta}\alpha_i\beta_j\mathbf{C}^{(2)}_{\alpha_i\beta_j} +1/6\sum_{ijk\alpha\beta\gamma}\alpha_i\beta_j\gamma_k\mathbf{C}^{(3)}_{\alpha_i\beta_j\gamma_k}+... \tag{29}$$

$$\mathcal{E}=\mathcal{E}^{(0)}+\sum_{i\alpha}\alpha_i\mathcal{E}^{(1)}_{\alpha_i}+1/2\sum_{ij\alpha\beta}\alpha_i\beta_j\mathcal{E}^{(2)}_{\alpha_i\beta_j} +1/6\sum_{ijk\alpha\beta\gamma}\alpha_i\beta_j\gamma_k\mathcal{E}^{(3)}_{\alpha_i\beta_j\gamma_k}+..., \tag{30}$$

substituting these expansions into equation (15) and equating the coefficients of the same powers of α,β and γ, we obtain the equations

$$\left[\boldsymbol{\mathcal{H}}^{(0)}-\mathcal{E}^{(0)}\boldsymbol{\mathcal{S}}\right]\mathbf{C}^{(0)}=0 \tag{31}$$

$$\left[\boldsymbol{\mathcal{H}}^{(0)}-\mathcal{E}^{(0)}\boldsymbol{\mathcal{S}}\right]\mathbf{C}^{(1)}_{\alpha_i}=\left[\mathcal{E}^{(1)}_{\alpha_i}\boldsymbol{\mathcal{S}}-\boldsymbol{\mathcal{H}}^{(1)}_{\alpha_i}\right]\mathbf{C}^{(0)} \tag{32}$$

$$\left[\boldsymbol{\mathcal{H}}^{(0)}-\mathcal{E}^{(0)}\boldsymbol{\mathcal{S}}\right]\mathbf{C}^{(2)}_{\alpha_i\beta_j}=\mathcal{E}^{(2)}_{\alpha_i\beta_j}\boldsymbol{\mathcal{S}}\mathbf{C}^{(0)} +\left[\mathcal{E}^{(1)}_{\alpha_i}\boldsymbol{\mathcal{S}}-\boldsymbol{\mathcal{H}}^{(1)}_{\alpha_i}\right]\mathbf{C}^{(1)}_{\beta_j} +\left[\mathcal{E}^{(1)}_{\beta_j}\boldsymbol{\mathcal{S}}-\boldsymbol{\mathcal{H}}^{(1)}_{\beta_j}\right]\mathbf{C}^{(1)}_{\alpha_i} \tag{33}$$

etc. The normalization requirement (13) yields another set of equations:

$$\mathbf{C}^{(0)+}\mathbf{S}\mathbf{C}^{(0)}=1, \tag{34}$$

$$\mathbf{C}^{(0)+}\boldsymbol{\mathcal{S}}\boldsymbol{\mathcal{C}}^{(1)}_{\alpha}=0, \tag{35}$$

$$\mathbf{C}^{(0)+}\boldsymbol{\mathcal{S}}\boldsymbol{\mathcal{C}}^{(2)}_{\alpha_i\beta_j}+\mathbf{C}^{(1)+}_{\alpha_i}\boldsymbol{\mathcal{S}}\boldsymbol{\mathcal{C}}^{(1)}_{\beta_j}=0. \tag{36}$$

Multiplying equations (31–33) from the left by $\mathbf{C}^{(0)+}$ and using normalization conditions (Eqs. (34–36)) it is easy to obtain the following expressions for perturbed eigenvalues and eigenvectors:

$$\mathcal{E}^{(1)}_{\alpha_i}=\mathbf{C}^{(0)+}\boldsymbol{\mathcal{H}}^{(1)}_{\alpha_i}\mathbf{C}^{(0)} \tag{37}$$

$$\mathcal{E}^{(2)}_{\alpha_i\beta_j}=\mathbf{C}^{(0)+}\boldsymbol{\mathcal{H}}^{(1)}_{\alpha_i}\mathbf{C}^{(1)}_{\beta_j}+\mathbf{C}^{(0)+}\boldsymbol{\mathcal{H}}^{(1)}_{\beta_j}\mathbf{C}^{(1)}_{\alpha_i} \tag{38}$$

etc.

$$\mathbf{C}^{(1)}_{\alpha_i} = \left[\boldsymbol{\mathcal{H}}^{(0)} - \boldsymbol{\mathcal{S}}\mathcal{E}^{(0)}\right]^{-1} (P-1) \left(\boldsymbol{\mathcal{H}}^{(1)}_{\alpha i} - \boldsymbol{\mathcal{S}}\mathcal{E}^{(1)}_{\alpha_i}\right) \mathbf{C}^{(0)} \tag{39}$$

$$\begin{aligned} \mathbf{C}^{(2)}_{\alpha_i\beta_j} = {} & \left[\boldsymbol{\mathcal{H}}^{(0)} - \boldsymbol{\mathcal{S}}\mathcal{E}^{(0)}\right]^{-1} (P-1) \left[\left(\boldsymbol{\mathcal{H}}^{(1)}_{\alpha_i} - \boldsymbol{\mathcal{S}}\mathcal{E}^{(1)}_{\alpha_i}\right) \mathbf{C}^{(1)}_{\beta_j} \right. \\ & \left. + \left(\boldsymbol{\mathcal{H}}^{(1)}_{\beta_j} - \boldsymbol{\mathcal{S}}\mathcal{E}^{(1)}_{\beta_j}\right) \mathbf{C}^{(1)}_{\alpha_i}\right] - \left(\mathbf{C}^{(1)+}_{\alpha_i}\boldsymbol{\mathcal{S}}\mathbf{C}^{(1)}_{\beta_j}\right) \mathbf{C}^{(0)} \end{aligned} \tag{40}$$

etc. where the generalized projection operator P acts on the arbitrary vector $\mathbf{C}$ according to the following rule: $P\mathbf{C} = \boldsymbol{\mathcal{S}}\mathbf{C}^{(0)}(\mathbf{C}^{(0)+}\mathbf{C})$.

Differentiating equation (20) with respect to the field amplitudes, replacing the derivatives of the CI coefficients by perturbed coefficients of corresponding order, we obtain the derivatives of dipole moment Fourier components in terms of perturbed eigenvectors and eigenvalues of the Floquet matrix. These expressions depend on the form of the Floquet matrix separation into unperturbed and perturbed parts, that is on the problem being solved.

As an example we consider the harmonic field, which can include the static component. For this field Floquet matrix is given by the following expression:

$$\begin{aligned} \mathcal{H}_{rmsn} = {} & \left(H_{0rs} + \mathbf{E}_0\mathbf{r}_{rs} + n\omega\mathcal{S}_{rs}\right)\delta_{mn} \\ & + \frac{1}{2}\mathbf{E}_{0\omega}\mathbf{r}_{rs}\left(\delta_{m,n-1} + \delta_{m,n+1}\right). \end{aligned} \tag{41}$$

Introducing the small variations $\alpha_0 = \delta(E_0)_\alpha$ and $\alpha_1 = \delta(E_{0\omega})_\alpha$ of the field amplitudes $\mathbf{E}_0$, $\mathbf{E}_{0\omega}$, we can treat the matrix (41) as unperturbed one and define the perturbation term as

$$\boldsymbol{\mathcal{H}}^{(1)} = \sum_\alpha \left(\alpha_0\boldsymbol{\mathcal{H}}^{(1)}_{\alpha_0} + \alpha_1\boldsymbol{\mathcal{H}}^{(1)}_{\alpha_1}\right) \tag{42}$$

where

$$\begin{aligned} \mathcal{H}^{(1)}_{\alpha_0 rmsn} &= (r_\alpha)_{rs}\delta_{m,n} \\ \mathcal{H}^{(1)}_{\alpha_1 rmsn} &= \frac{1}{2}(r_\alpha)_{rs}(\delta_{m,n-1} + \delta_{m,n+1}). \end{aligned} \tag{43}$$

In this case the following expressions of the first and second field-dependent derivatives of the dipole moment components are easily obtained:

$$\frac{\partial(P_{\omega_\sigma})_\mu}{\partial(E_{0\omega_i})_\alpha} = 4\mathbf{C}^{(0)+}\boldsymbol{\mathcal{H}}^{(1)}_\mu(n\omega)\mathbf{C}^{(1)}_{\alpha_i} \tag{44}$$

$$\begin{aligned} \frac{\partial^{(2)}(P_{\omega_\sigma})_\mu}{\partial(E_{0\omega_i})_\alpha\partial(E_{0\omega_j})_\beta} = {} & 4\mathcal{P}_2\left[\mathbf{C}^{(1)+}_\mu(n\omega)\left(\boldsymbol{\mathcal{H}}^{(1)}_{\alpha_i}\right.\right. \\ & \left. -\mathcal{E}^{(1)}_{\alpha_i}\boldsymbol{\mathcal{S}}\right)\mathbf{C}^{(1)}_{\beta_j} + \mathbf{C}^{(1)+}_{\alpha_i}\left(\boldsymbol{\mathcal{H}}^{(1)}_\mu(n\omega)\right. \\ & \left.\left. -\mathcal{E}^{(1)}_\mu(n\omega)\boldsymbol{\mathcal{S}}\right)\mathbf{C}^{(1)}_{\beta_j}\right] \end{aligned} \tag{45}$$

where $\omega_\sigma = n\omega$ and n can take on values $0, 1, 2, 3$ depending on the process being studied. The indices i, j are equal to $0, 1$ for the static and harmonic field components correspondingly. The matrix $\boldsymbol{\mathcal{H}}^{(1)}_\mu(q\omega)$ in the right-hand side of equation (45) can be written as $\mathcal{H}^{(1)}_{\mu rmsn}(q\omega) = \frac{1}{2}(r_\mu)_{rs}(\delta_{m,n-q} + \delta_{m,n+q})$, and all other values depending on $q\omega$ are the solutions of the perturbation theory equations, corresponding to the perturbation $\boldsymbol{\mathcal{H}}^{(1)}_\mu(q\omega)$. The permutation operator $\mathcal{P}_2$ yields all the actually different terms with transposed indices α_i, β_j involved in the right-hand side of the equation.

The other example is evaluation of the second derivative of the dipole moment with respect to the field amplitudes for a system in the two-mode radiation field. In this case Floquet matrix takes the form:

$$\begin{aligned} \mathcal{H}_{rm_1m_2sn_1n_2} = {} & (H_{0rs} + (n_1\omega_1 + n_2\omega_2)S_{rs})\delta_{m_1n_1}\delta_{m_2n_2} \\ & + \frac{1}{2}\mathbf{E}_{0\omega_1}\mathbf{r}_{rs}(\delta_{m_1,n_1-1} + \delta_{m_1,n_1+1})\delta_{m_2n_2} \\ & + \frac{1}{2}\mathbf{E}_{0\omega_2}\mathbf{r}_{rs}\delta_{m_1n_1}(\delta_{m_2,n_2-1} + \delta_{m_2,n_2+1}) \end{aligned} \tag{46}$$

where $H_{0rs}\delta_{m_1n_1}\delta_{m_2n_2}$ is the part of the matrix, corresponding to the field-free molecule. It is appropriate here to divide Floquet matrix into an unperturbed part and a perturbation, according to the following scheme:

$$\begin{aligned} \mathcal{H}^{(0)}_{rm_1m_2sn_1n_2} = {} & \left[\left(H_{0rs} + (n_1\omega_1 + n_2\omega_2)S_{rs}\right)\delta_{m_1n_1}\right. \\ & \left. + \frac{1}{2}\mathbf{E}_{0\omega_1}\mathbf{r}_{rs}(\delta_{m_1,n_1-1} + \delta_{m_1,n_1+1})\right]\delta_{m_2n_2}, \end{aligned} \tag{47}$$

$$\mathcal{H}^{(1)}_{rm_1m_2sn_1n_2} = \frac{1}{2}\mathbf{E}_{0\omega_2}\mathbf{r}_{rs}\delta_{m_1n_1}(\delta_{m_2,n_2-1} + \delta_{m_2,n_2+1}). \tag{48}$$

In accordance with this separation, the zero-order eigenvalues $\mathcal{E}^{(0)}_J$ and eigenvectors $\mathbf{C}^{J(0)}$ of two-mode Floquet matrix can be represented through the quasienergies ε_j and eigenvectors $\mathbf{C}^j$ of one-frequency Floquet matrix for the first mode, which are supposed to be known:

$$\begin{aligned} \mathcal{E}^{(0)}_J &= \varepsilon_j + n_{2j}\omega_2, \\ C^{J(0)}_{rm_1m_2} &= C^{(j,n_{2j})}_{rm_1m_2} = C^j_{rm_1}\delta_{m_2,n_{2j}}. \end{aligned} \tag{49}$$

Here n_{2j} is the integer, which is treated as the photon quantum number for the second frequency, determining the corresponding “Brillouin zone”. This quantity can be chosen equal to zero, that is

$$\begin{aligned} \mathcal{E}^{(0)}_J &= \varepsilon_j, \\ C^{J(0)}_{rm_1m_2} &= C^j_{rm_1}\delta_{m_2,0}, \end{aligned} \tag{50}$$

The time-independent perturbation theory yields the first-order correction to the eigenvector, caused by Cartesian component of the second frequency field $\mathbf{E}_{0\omega_2\alpha}$, in the form:

$$C^{(1)}_{\alpha_2rm_1m_2} = C^{(+1)}_{\alpha_2rm_1}\delta_{m_2,1} + C^{(-1)}_{\alpha_2rm_1}\delta_{m_2,-1}. \tag{51}$$

$$\begin{aligned}\frac{\partial^2(P_{n_1\omega_1+n_2\omega_2})_\mu}{\partial(E_{0\omega_2})_\beta\partial(E_{0\omega_2})_\gamma} = 2\Big\{&\delta_{n_2,-2}\Big[\mathbf{C}_\mu^{(+1)+}(n_1\omega_1,-2\omega_2)\left(\mathbf{h}_{\beta_2}^{(1)}\mathbf{C}_{\gamma_2}^{(+1)}+\mathbf{h}_{\gamma_2}^{(1)}\mathbf{C}_{\beta_2}^{(+1)}\right)\\ &+\mathbf{C}_\mu^{(-1)+}(n_1\omega_1,2\omega_2)\left(\mathbf{h}_{\beta_2}^{(1)}\mathbf{C}_{\gamma_2}^{(-1)}+\mathbf{h}_{\gamma_2}^{(1)}\mathbf{C}_{\beta_2}^{(-1)}\right)+\mathbf{C}_{\beta_2}^{(-1)+}\mathbf{h}_\mu^{(+1)}(n_1\omega_1)\mathbf{C}_{\gamma_2}^{(+1)}+\mathbf{C}_{\beta_2}^{(+1)+}\mathbf{h}_\mu^{(-1)}(n_1\omega_1)\mathbf{C}_{\gamma_2}^{(-1)}\Big]\\ &+2\delta_{n_2,0}\Big[\mathbf{C}_\mu^{(1)+}(n_1\omega_1)\left(\mathbf{h}_{\beta_2}^{(1)}\left(\mathbf{C}_{\gamma_2}^{(+1)}+\mathbf{C}_{\gamma_2}^{(-1)}\right)+\mathbf{h}_{\gamma_2}^{(1)}\left(\mathbf{C}_{\beta_2}^{(+1)}+\mathbf{C}_{\beta_2}^{(-1)}\right)\right)+\mathbf{C}_{\beta_2}^{(+1)+}\mathbf{h}_\mu^{(1)}(n_1\omega_1)\mathbf{C}_{\gamma_2}^{(+1)}\\ &+\mathbf{C}_{\beta_2}^{(-1)+}\mathbf{h}_\mu^{(1)}(n_1\omega_1)\mathbf{C}_{\gamma_2}^{(-1)}-\left(\mathbf{C}_{\beta_2}^{(+1)+}\mathbf{S}\mathbf{C}_{\gamma_2}^{(+1)}+\mathbf{C}_{\beta_2}^{(-1)+}\mathbf{S}\mathbf{C}_{\gamma_2}^{(-1)}\right)\mathbf{C}^{j+}\mathbf{h}_\mu^{(1)}(n_1\omega_1)\mathbf{C}^j\Big]\\ &+\delta_{n_2,2}\Big[\mathbf{C}_\mu^{(+1)+}(n_1\omega_1,2\omega_2)\left(\mathbf{h}_{\beta_2}^{(1)}\mathbf{C}_{\gamma_2}^{(-1)}+\mathbf{h}_{\gamma_2}^{(1)}\mathbf{C}_{\beta_2}^{(-1)}\right)+\mathbf{C}_\mu^{(-1)+}(n_1\omega_1,-2\omega_2)\left(\mathbf{h}_{\beta_2}^{(1)}\mathbf{C}_{\gamma_2}^{(+1)}+\mathbf{h}_{\gamma_2}^{(1)}\mathbf{C}_{\beta_2}^{(+1)}\right)\\ &+\mathbf{C}_{\beta_2}^{(-1)+}\mathbf{h}_\mu^{(-1)}(n_1\omega_1)\mathbf{C}_{\gamma_2}^{(+1)}+\mathbf{C}_{\beta_2}^{(+1)+}\mathbf{h}_\mu^{(+1)}(n_1\omega_1)\mathbf{C}_{\gamma_2}^{(-1)}\Big]\Big\}. \qquad (56)\end{aligned}$$

The vectors $\mathbf{C}_{\alpha_2}^{(\pm1)}$ in equation (51) are solutions of the first order nonhomogeneous equations of perturbation theory for one-frequency field:

$$\left(\boldsymbol{\mathcal{H}}^{(\text{one})}-(\varepsilon_j\pm\omega_2)\boldsymbol{\mathcal{S}}^{(\text{one})}\right)\mathbf{C}_{\alpha_2}^{(\pm1)}=-\mathbf{h}_{\alpha_2}^{(1)}\mathbf{C}^j, \qquad (52)$$

where

$$h_{\alpha rmsn}^{(1)}=\frac{1}{2}(r_\alpha)_{rs}\delta_{mn}.$$

We can also introduce the auxiliary vectors $\mathbf{C}_\mu^{(1)}(n_1\omega_1)$ and $\mathbf{C}_\mu^{(\pm1)}(n_1\omega_1,\mp2\omega_2)$ which satisfy the auxiliary one-frequency first order perturbation theory equations:

$$\left(\boldsymbol{\mathcal{H}}^{(\text{one})}-\varepsilon_j\boldsymbol{\mathcal{S}}^{(\text{one})}\right)\mathbf{C}_\mu^{(1)}=-\mathbf{h}_\mu^{(1)}(n_1\omega_1)\mathbf{C}^j \qquad (53)$$

$$\begin{aligned}\left(\boldsymbol{\mathcal{H}}^{(\text{one})}-(\varepsilon_j\pm2\omega_2)\boldsymbol{\mathcal{S}}^{(\text{one})}\right)\mathbf{C}_\mu^{(\pm1)}(n_1\omega_1,\mp2\omega_2)&=\\ -\mathbf{h}_\mu^{(\pm1)}(n_1\omega_1)\mathbf{C}^j&, \qquad (54)\end{aligned}$$

where $\boldsymbol{\mathcal{H}}^{(\text{one})}$ and $\boldsymbol{\mathcal{S}}^{(\text{one})}$ are the one-frequency Floquet and overlap matrices for the first mode,

$$\begin{aligned}h_{\mu rmsn}^{(1)}(n_1\omega_1)&=\frac{1}{2}r_{\mu rs}(\delta_{m,n-n_1}+\delta_{m,n+n_1}),\\ h_{\mu rmsn}^{(\pm1)}(n_1\omega_1)&=\frac{1}{2}r_{\mu rs}\delta_{m,n\pm n_1}.\end{aligned}$$

The third order term in the power series of the dipole moment, is given by

$$\begin{aligned}\left(P_{\omega_\sigma}^{(3)}\right)_\mu&=\sum_{\alpha\beta\gamma}(3!)^{-1}N\left(\omega_1{}',\omega_2{}',\omega_3{}'\right)\\ &\times\gamma_{\mu\alpha_1\beta_2\gamma_2}^{(3)}\left(-\omega_\sigma;\omega_1{}',\omega_2{}',\omega_3{}'\right)E_{\omega_1{}'\alpha}E_{\omega_2{}'\beta}E_{\omega_3{}'\gamma} \qquad (55)\end{aligned}$$

where $\omega_\sigma=n_1\omega_1+n_2\omega_2$, $n_i=0,\pm1,\pm2,\pm3$.

Let us consider the most interesting alternatives $n_1=\pm1$, $n_2=0$, ±2 embracing the a.c. Kerr effect, coherent anti-Stokes Raman scattering, simulated Raman scattering, two-photon absorption and a number of connected processes [31]. In the case being considered the second hyperpolarizability is defined by the third derivative

$$\frac{\partial^3(P_{\omega_\sigma})_\mu}{\partial(E_{0\omega_1})_\alpha\partial(E_{0\omega_2})_\beta\partial(E_{0\omega_2})_\gamma}.$$

In our approach we propose to calculate the second derivative

$$\frac{\partial^2(P_{\omega_\sigma})_\mu}{\partial(E_{0\omega_2})_\beta\partial(E_{0\omega_2})_\gamma}$$

at different points of the field $\mathbf{E}_{0\omega_1}$ and then to obtain the third derivative by means of numerical differentiation with respect to the amplitudes of the second mode. Using the perturbation theory equations we express the second derivative in a form, involving only the first order eigenvector corrections assigned to the solution of the first one-frequency field problem:

see equation (56) above.

It is seen that combining the finite field method with perturbation theory makes it possible to calculate the second hyperpolarizability in the two-frequency field as well as in the monochromatic field by a relatively simple method. One needs only to solve the first order perturbation theory equations for one-frequency mode and then use numerical procedures.

The higher order hyperpolarizabilities also can be calculated combining numerical methods with perturbation theory. The minimal order of the perturbation theory equations to be solved is determined by the features of the considered process as well as by the accuracy and efficiency of the selected method of calculation.

3 Computational details and discussion of results

The first step of the calculation is to construct the wave functions of the molecule in the ground and the first singlet excited states of Σ^+ and Π symmetries, necessary for calculation of the ground state electric susceptibilities. The atomic orbitals basis set used for Li consisted of $(10s6p4d)$ Gaussian type functions developed by Sadlej *et al.* [34,35] for obtaining accurate values for the electric property. In addition a $(10s6p)$ basis set as described in [36] has been used for H. Diffuse Gaussian functions of *s*-, *p*- and *d*-type with corresponding exponents 0.003, 0.002 and 0.002 have been added on Li atom as well as functions $s(0.003)$ and $p(0.01)$ on H. The calculations have been carried out for

Table 1. Transition energies (a.u.) and oscillator strengths.

Transitions	ΔE	f_r	f_∇
$X^1\Sigma^+ \rightarrow A^1\Sigma^+$	0.1337 0.1354^a	0.2359 0.2381^a	0.2316
$X^1\Sigma^+ \rightarrow 2^1\Sigma^+$	0.2186	0.0672	0.0660
$X^1\Sigma^+ \rightarrow 3^1\Sigma^+$	0.2320	0.0077	0.0073
$X^1\Sigma^+ \rightarrow 4^1\Sigma^+$	0.2394	0.1226	0.1187
$X^1\Sigma^+ \rightarrow 5^1\Sigma^+$	0.2564	0.0173	0.0168
$X^1\Sigma^+ \rightarrow B^1\Pi$	0.1707 0.1718^a	0.6159 0.5912^a	0.5975
$X^1\Sigma^+ \rightarrow 2^1\Pi$	0.2385	0.0039	0.0040
$X^1\Sigma^+ \rightarrow 3^1\Pi$	0.2410	0.1199	0.1177
$X^1\Sigma^+ \rightarrow 4^1\Pi$	0.2635	0.0011	0.0010
$X^1\Sigma^+ \rightarrow 5^1\Pi$	0.2656	0.0467	0.0452

a: references [39,40].

the *ab initio* configuration interaction (CI) level using the experimental internuclear distance 3.015 a.u. Correlation effects have been taken into account by means of the multireference, second-order, many-body perturbation theory through the CIPSI algorithm [37,38] (configuration interaction with perturbation selected interactions).

First the wave functions are spanned over a subspace including the most significant determinants (about 400) and built up iteratively from the total set of canonical orbitals in order to obtain their lowest energy. Then the most important second-order perturbational Slater determinants ($\simeq$ 50 000) of the multireference are also added within the energetic criterion. The low-lying spectroscopic states ($M = 15$) are finally obtained by diagonalization of the zero order perturbation $H^{(0)}$ matrix. To check the accuracy of these spectroscopic states we have used the velocity and length operators in the calculation of the transition moments between these states and verify the hypervirial theorem through employing the transition energies obtained. The first 5 transition energies and corresponding oscillator strengths are displaced in Table 1 and are compared to the theoretical values obtained by Partridge and Langhoff [39,40]. This comparison shows a perfect agreement between our calculated transition energies and oscillator strengths for the first $X^1\Sigma^+ \rightarrow A^1\Sigma^+$ and $X^1\Sigma^+ \rightarrow B^1\Pi$ transitions with the corresponding values of Partridge and Langhoff. The relative difference between the oscillator strengths in f_r and f_∇ representations does not exceed 9% which points to sufficiently high accuracy for the spectral states calculations.

The quasi-spectral series ($M_l \leq 100$), corresponds to Slater determinants, belonging or not to excited spectroscopic states, which perturb significantly the ground state through the first order perturbation Hamiltonian equal to $\mathbf{r}$ or $\boldsymbol{\nabla}$ according to the gauge chosen.

Table 2 gives the total energy, dipole moment and Cartesian components of the static polarizability, the first and the second hyperpolarizabilities of LiH in the ground state. The static susceptibilities have been obtained by our method through the elimination of non-diagonal blocks from the Floquet matrix and equating the frequency in diagonal blocks to zero. These values are compared with the previously published *ab initio* calculations, accomplished by using various GTO basis sets, and considering the electron correlation at different levels. It is seen that our calculated polarizabilities are in a good agreement with other theoretical results. It should be noted that theoretical values of hyperpolarizabilities depend largely on the method of calculations used. Comparing our values of the first hyperpolarizability tensor components with those of Tunega and Noga [44], which are apparently the most accurate, we can note fair agreement of longitudinal β_{zzz} components but worse correlation of transverse ones. At the same time one should recognize the poor correlation of β_{xxz} values, obtained by other methods, in which case the disagreement between the values obtained by coupled cluster calculations carried out at different levels [43,44] is especially typical.

Our second hyperpolarizabilities are compared with full CI (FCI) [2] and CASSCF [2,42] results obtained with the Sadlej's GTO basis set [34], similar to the set used in our calculations, as well as with the data of the coupled cluster calculations [44]. As the referenced CASSCF wave function was spanned over the large CAS4 active space $(16, 7, 7, 2)$, the FCI and CASSCF results are quite similar. We note the excellent agreement between our values and the data for both the FCI and CASSCF calculations. However our results correlate less well with the result of Tunega and Noga which were calculated using the CCSD(T) method using an extremely large Gaussian basis set [44]. Agreement can be improved by taking into account the second order polynomial terms and increasing the number of the spectral and pseudo-spectral terms in the wave function expansion as well as by enlarging the Gaussian basis set.

Coming to the frequency dependent properties, we first investigated the convergence of our method with respect to the number of photon states, corresponding to Fourier harmonics, included in the wave function expansion. As can be seen in Table 3 and should be obvious from perturbation theory the convergence depends on the order of hyperpolarizability linearly. Therefore the size of Floquet matrix is enlarged moderately as the order of hyperpolarizability is increased.

Figure 1 illustrates the influence of the first order polynomial and pseudo-spectral terms. This influence is most significant for polarizabilities, where improvement of static and dynamic components is as much as 30%. At the same time one can observe, that the relative influence for higher-order susceptibilities becomes less efficient. The improvement amounts to about 8% for the first hyperpolarizability and up to 4.5% for the second one. This simply implies that inclusion of the polynomials of the second and higher degrees and increasing the number of quasi-spectral terms becomes more important for the prediction of higher-order nonlinear properties.

There is no reliable experimental data concerning dispersion of the studied properties for the different processes. Hence comparison with most accurate numerical

Table 2. Ground state properties of LiH a.u. for the experimental bond length $3.015a_0$.

Property	This work	MCSCF[a]	CASSCF CAS 4[b]	Full CI[b]	MP2[d]	CCD/BO[d]	CCSD(T) *spdf*[e]	CCSD(T) R12 *spdf*[e]
Energy	–8.06011	–8.02036	–	–			–8.06952	–8.07047
μ	2.304	2.311	–	–	2.332	2.300	2.294	2.294
α_{zz}	25.4	26.4	26.84	26.89	23.90	25.73	25.88	25.79
α_{xx}	29.5	29.8	–	–	27.06	29.52	29.63	29.57
β_{zzz}	676	686	721	729	742	635	639	630
β_{xxz}	356	364	–	–	364	593	237	234
$\gamma_{zzzz} \times 10^3$	126.7	–	124.3[c]	127.1	–	–	113.3	111.5
$\gamma_{xxzz} \times 10^3$	38.3	–	34.4[c]	–	–	–	49.9	49.3
$\gamma_{xxxx} \times 10^3$	62.4	–	64.4[c]	–	–	–	93.1	92.0

a: reference [41], *b*: reference [2], *c*: $(16, 7, 7, 2)$ active space CASSCF with Sadlej's basis reference [34] values, obtained in this work using DALTON program reference [42], *d*: reference [43], *e*: reference [44].

Table 3. Convergence of method with respect to the photon states number n at $\omega = 0.01$ a.u.

n	1	2	3	4
$\alpha_{zz}(-\omega;\omega)$	26.269	26.269	26.269	26.269
$\beta_{zzz}(-2\omega;\omega,\omega)$	290.62	779.65	779.65	779.65
$\gamma_{zzzz}(-3\omega;\omega,\omega,\omega)$	–137.3	43.81	139.4	139.4

data has to be carried out. Figure 2 compares the third harmonic generation curves for all Cartesian components with corresponding values calculated by the FCI method [2]. All longitudinal and mixed components are in excellent agreement with the FCI values. This indicates the remarkable potential of the TDGI method combined with Floquet theory for the study of nonlinear properties of molecules. The weaker correlation of transverse component γ_{xxxx} can be improved similar to the static case, by using a more accurate description of the wave function expansion.

4 Conclusions

In this work we develop a new approach to theoretical investigation of nonlinear molecular dynamic properties based on a combination of the perturbation theory approximation with the finite field method in Floquet theory. The compact expressions of dipole Fourier component derivatives are given for different nonlinear dynamic properties of molecules including the formula applicable for superposition of two monochromatic fields with incommensurable frequencies. This approach appears to be quite efficient when it is used in conjunction with CIPSI algorithm which was designed to obtain accurate values of transition moments and energies. The accuracy of the presented method is related to the ability to use flexible expansion of the wave function involving polynomial terms and pseudo-spectral states. The algorithm submitted in the paper is found to be relatively cheap. This is

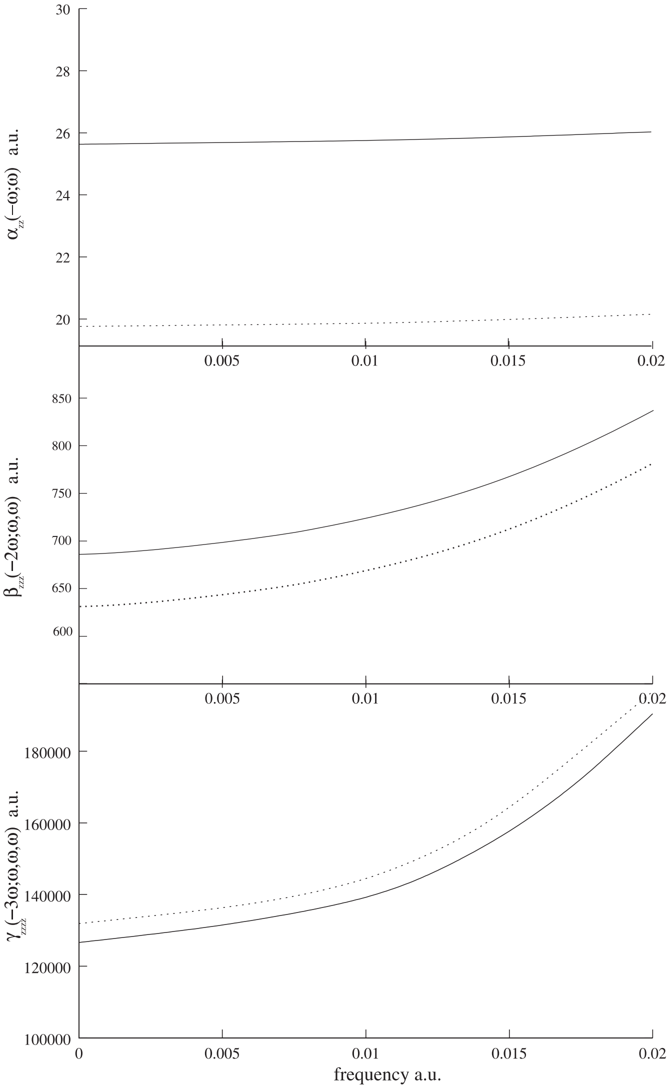

Fig. 1. Individual components of dynamic polarizabilities, first and second hyperpolarizabilities, calculated with basis sets of different levels; dotted line: only spectral states; solid line: spectral + pseudospectral states + polynomial terms.

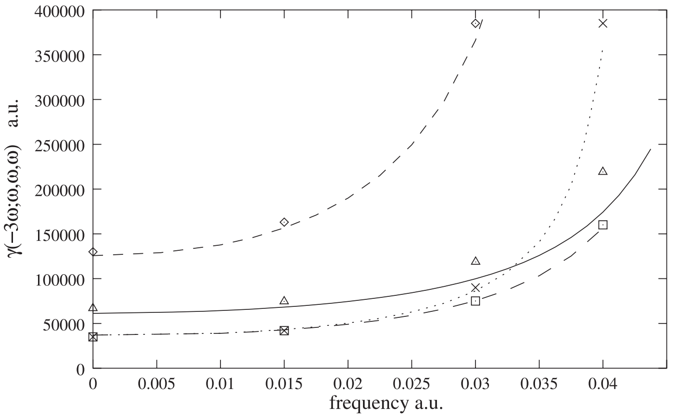

Fig. 2. THG dispersion of LiH; short dashed line: γ_{zzzz}, dotted line: γ_{zzxx}, long dashed line: γ_{xxzz}, solid line: γ_{xxxx}, (◇) γ_{zzzz} [2], (×) γ_{zzxx} [2], (□) γ_{xxzz} [2], (△) γ_{xxxx} [2].

because the most time consuming part of the simultaneous calculations of the dispersion curves of several second order nonlinear properties, namely, multireference CI calculation of a field free molecule, is carried out only once. Therefore in some cases our method may be a good alternative to other sophisticated but more expansive algorithms. There is reason to hope that with the use of the larger quasi-spectral basis sets and by taking into account the higher order polynomials, the method can be applied without any additional modifications to calculations of second order and higher order dynamic response properties and opens the way to the investigation as yet unexplored nonlinear optical processes.

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