Density-functional theory of the nonlinear optical susceptibility: Application to cubic semiconductors

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We present a general scheme for the computation of the time-dependent (TD) quadratic susceptibility ($\chi^{(2)}$) of an extended insulator obtained by applying the "$2n+1$" theorem to the action functional as defined in TD density-functional theory. The resulting expression for $\chi^{(2)}$ includes self-consistent local-field effects, and is a simple function of the linear response of the system. We compute the static $\chi^{(2)}$ of nine III-V and five II-VI semiconductors using the local density approximation (LDA), obtaining good agreement with experiment. For GaP we also evaluate the TD $\chi^{(2)}$ for second-harmonic generation using TD-LDA. [S0163-1829(96)00319-0]

I. INTRODUCTION

Nonlinear optics is a growing field of research which has applications in many technical areas such as optoelectronics, laser science, optical signal processing, and optical computing.[1] In these fields the description of several physical phenomena, such as optical rectification, wave mixing, the Kerr effect, or multiphoton absorbtion relies on the knowledge of the nonlinear optical (NLO) susceptibilities. Moreover, nonlinear spectroscopy is a powerful tool to analyze the structural and electronic properties of extended and low-dimensional systems. In the present work we give a general scheme to compute from first principles the time-dependent (TD) quadratic susceptibility ($\chi^{(2)}$) of real materials within TD–density-functional theory (DFT). Furthermore, we show that the values of the static $\chi^{(2)}$ obtained in the local density approximation (LDA) are in good agreement with measured values for the cubic semiconductors. Our approach makes feasible the computation of $\chi^{(2)}$ in cells containing up to 100 atoms, since it requires the same numerical effort as the computation of the total energy. This allows the evaluation of $\chi^{(2)}$ for systems of technological and scientific relevance that cannot be handled by the traditional methods, such as surfaces or crystals of organic molecules.

Nowadays many first-principle calculations for the ground-state properties of materials are performed within DFT. Even in its simplest form, namely, in the LDA for the exchange and correlation energy, this scheme gives results which, in many cases, are in surprisingly good agreement with experiments. A rigorous extension of DFT to TD phenomena has been proposed in Refs. 2 and 3. Although the available approximations for the exchange and correlation energy are less accurate in the TD domain than in the static case, this scheme is sufficiently general to allow many pos-

sible improvements in the future. Therefore TD-DFT seems to be a promising framework for the study of the NLO susceptibilities.

Standard quantum-mechanical perturbation theory can be used to compute the $\chi^{(2)}$. The straightforward application of perturbation theory leads to an expression for $\chi^{(2)}$, which diverges for an infinite solid in the static limit. However, for an insulator, these divergences have been shown to be apparent.[4] This kind of approach has been applied to compute the $\chi^{(2)}$ from first principles. The non-self-consistent expression for $\chi^{(2)}$ reported in Ref. 4 has been evaluated by Huang and Ching[5] using the DFT-LDA wave functions and eigenvalues. A fully self-consistent theory of the NLO susceptibility within DFT has been proposed in a series of papers by Levine and Allan.[6] Their method is feasible but algebraically very involved due to the necessity of dealing with the second-order perturbation of the wave functions and with the apparent divergences. Their final expression is not easy to handle and its evaluation requires summations over the conduction band states, which are time consuming and difficult to converge.

In a previous paper two of us[7] have shown that it is convenient to regard the static $\chi^{(2)}$ as a third-order derivative of the total energy with respect to a uniform electric field. We pointed out that this derivative can be obtained by combining a Wannier representation of the electronic wave functions with the "$2n+1$" theorem of perturbation theory.[8,9] We also found an equivalent expression of the static $\chi^{(2)}$ in terms of Bloch wave functions.

In the present work we show that the method of Ref. 7 applies also to TD periodic perturbations and to the self-consistent TD-DFT functional. The TD $\chi^{(2)}$ can be regarded as a third-order derivative of the total action. The stationary principle for the action functional,[2,3] which replaces in the

TD case the miminum principle for the energy functional, allows the use of the "$2n+1$" theorem. As in the static case the third-order derivative depends only on the unperturbed wave functions and on their first-order change due to the TD electric field. All the self-consistent contributions are included in the formalism in a simple way. The final expression avoids perturbation sums and does not present any apparent divergency. We apply our formalism to the computation of the static $\chi^{(2)}$ of nine III-V and five II-VI cubic semiconductors within the LDA. For GaP we also evaluate the TD $\chi^{(2)}$ for second-harmonic generation (SHG) using TD-LDA.[10]

The rest of the paper is organized as follows: In Sec. II we introduce the TD-DFT. In Sec. III we derive an expression for $\chi^{(2)}$ using the "$2n+1$" theorem. In Sec. IV we use the LDA to compute $\chi^{(2)}$ for cubic semiconductors. Conclusions are given in Sec. V.

II. TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY

In the Kohn–Sham (KS) formulation of DFT the ground-state density $n^g(\mathbf{r})$ of a system of N interacting electrons in an external potential $V_{\text{ext}}(\mathbf{r})$ is written in terms of $N/2$ single-particle wave functions $\{\phi^g\}$. The set $\{\phi^g\}$ minimizes the KS energy functional $E[\{\phi\}]$ and the ground-state energy is obtained as $E^g = E[\{\phi^g\}]$. A formalism similar to that of the static case can be introduced also in the TD domain if one restricts to Hamiltonians periodic in time and to the evolution of the system that is steady and has the same periodicity of the Hamiltonian.[11] In TD-DFT the TD steady density $n^s(\mathbf{r},t)$ of a system of N interacting electrons in an external TD potential $V_{\text{ext}}(\mathbf{r},t)$, periodic in time with period T is expressed in terms of a $N/2$ TD single-particle wave function $\{\psi^s\}$.[2,3] The set $\{\psi^s\}$ make stationary the KS action functional $A[\{\psi\}]$, i.e.,

$$\delta A[\{\psi^s\}]/\delta\langle\psi_k(t)| = 0, \tag{1}$$

and the steady action is obtained as $A^s = A[\{\psi^s\}]$. The KS action functional $A[\{\psi\}]$ is defined as (atomic units are used throughout)

$$A[\{\psi\}] = \int_0^T \frac{dt}{T}\left[\sum_{i=1}^{N/2} 2\langle\psi_i(t)| -\frac{1}{2}\nabla^2 - i\frac{\partial}{\partial t}|\psi_i(t)\rangle \right.$$

$$\left. + \int d^3r\, V_{\text{ext}}(\mathbf{r},t)n(\mathbf{r},t) \right] + A_H[n] + A_{\text{xc}}[n].$$

Here $|\psi_i(t)\rangle = |\psi_i(t+T)\rangle$, $\langle\psi_i(t)|\psi_j(t)\rangle = \delta_{ij}$,

$$A_H[n] = \int_0^T \frac{dt}{T} \int d^3r\, d^3r'\, \frac{n(\mathbf{r},t)n(\mathbf{r}',t)}{2|\mathbf{r}-\mathbf{r}'|} \tag{2}$$

is the Hartree functional, $A_{\text{xc}}[n]$ is the exchange and correlation functional, and

$$n(\mathbf{r},t) = \sum_{i=1}^{N/2} 2\langle\psi_i(t)|\mathbf{r}\rangle\langle\mathbf{r}|\psi_i(t)\rangle, \tag{3}$$

where the 2 factor is for spin degeneracy. At this stage no approximation for the exchange and correlation functional is made. The stationary principle in Eq. (1) yields the TD KS equations:[13]

$$i\frac{\partial}{\partial t}|\psi_k^s(t)\rangle = [H_{\text{KS}}(t) - \epsilon_k]|\psi_k^s(t)\rangle, \tag{4}$$

here ϵ_k are the steady state eigenvalues, $H_{\text{KS}}(t) = -\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r},t) + V_{H\text{xc}}[n](\mathbf{r},t)$ is the time-dependent KS Hamiltonian, and $V_{H\text{xc}}[n](\mathbf{r},t) = T\delta(A_H[n] + A_{\text{xc}}[n])/\delta n(\mathbf{r},t)$.

III. TIME-DEPENDENT NONLINEAR SUSCEPTIBILITY FROM THE "$2n+1$" THEOREM

Now we consider a potential of the form $V_{\text{ext}}(\mathbf{r},t,\mathbf{a}) = V_{\text{ext}}^0(\mathbf{r}) + a_1\mathbf{e}_1\cdot\mathbf{r}\cos(\omega_1 t) + a_2\mathbf{e}_2\cdot\mathbf{r}\cos(\omega_2 t) + a_3\mathbf{e}_3\cdot\mathbf{r}\cos(\omega_3 t)$, where $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$ are unit vectors describing the orientation of three TD uniform electric fields, $\omega_1 + \omega_2 + \omega_3 = 0$, and $\mathbf{a} = (a_1, a_2, a_3)$ describes the strength of the fields. Then the steady state wave functions $\{\psi^s(\mathbf{a})\}$ and action $A^s(\mathbf{a})$ depend also on $\mathbf{a}$. Note that for $\mathbf{a} = \mathbf{0}$ the potential is time independent and the action coincides with the static DFT energy. By using the Hellmann-Feynman theorem we obtain the derivative of the action with respect to the parameter a_1:

$$\frac{\partial A^s(\mathbf{a})}{\partial a_1} = \int_0^T \frac{dt}{T}\cos(\omega_1 t)\int d^3r\, \mathbf{e}_1\cdot\mathbf{r} n^s(\mathbf{r},t,\mathbf{a})$$

$$= -\mathbf{e}_1\cdot\mathbf{P}^s(\omega_1,\mathbf{a})V, \tag{5}$$

where V is the volume of the system and $\mathbf{P}^s(\omega_1,\mathbf{a})$ is the macroscopic electronic polarization per unit volume, oscillating at frequency ω_1.[12] Then the quadratic susceptibility tensor, which is defined as

$$\chi^{(2)}_{\mathbf{e}_1;\mathbf{e}_2,\mathbf{e}_3}(-\omega_1;\omega_2,\omega_3) = \frac{2}{V}\frac{\partial^2\mathbf{P}^s(\omega_1,\mathbf{0})}{\partial a_2\partial a_3}, \tag{6}$$

is equal to

$$\chi^{(2)}_{\mathbf{e}_1;\mathbf{e}_2,\mathbf{e}_3}(-\omega_1;\omega_2,\omega_3) = -\frac{2}{V}\frac{\partial^3 A^s(\mathbf{0})}{\partial a_1\partial a_2\partial a_3}. \tag{7}$$

The computation of the derivatives of $A^s(\mathbf{a})$ with respect to $\mathbf{a}$ can be performed by using the "$2n+1$" theorem, which states that the derivatives up to order $2n+1$ of the steady action depend only on the change of the orbitals up to order n:

$$\frac{\partial^{2n+1}A^s(\mathbf{a})}{\partial\mathbf{a}^{2n+1}} = \mathcal{P}^{2n+1}\left(\frac{\partial\{\psi^s(\mathbf{a})\}}{\partial\mathbf{a}}, \ldots, \frac{\partial^n\{\psi^s(\mathbf{a})\}}{\partial\mathbf{a}^n} \right), \tag{8}$$

where $\mathcal{P}^{2n+1}$ is a polynomial of degree $2n+1$ in its arguments. Indeed, as shown in Refs. 7 and 8, Eq. (8) relies just on the stationary condition, Eq. (1). Therefore,

$$\chi^{(2)}_{\mathbf{e}_1;\mathbf{e}_2,\mathbf{e}_3}(-\omega_1;\omega_2,\omega_3) = -\frac{2}{V}\mathcal{P}^3\left(\frac{\partial\{\psi^s(\mathbf{a})\}}{\partial\mathbf{a}} \right). \tag{9}$$

The derivation of an explicit expression of $\mathcal{P}^3$ for an infinite periodic system requires particular care because the expecta-

tion value of the **r** operator between Bloch states is ill defined. In an insulating solid this problem can be solved following Ref. 7: first we apply the ''$2n+1$'' theorem in a Wannier representation where the **r** operator is well defined; then we recast the resulting expression in a Bloch representation.[14] The final expression is

$$
\chi^{(2)}_{\mathbf{e}_1;\mathbf{e}_2,\mathbf{e}_3}(-\omega_1;\omega_2,\omega_3)
$$

$$
= -4\sum_{m,n}^{N/2}\sum_{\sigma=\pm}\int_{\mathrm{BZ}}\frac{d^3k}{(2\pi)^3}\left[\langle u^0_{\mathbf{k},m}|\frac{\mathbf{e}_2}{2}\cdot\frac{-i\partial}{\partial\mathbf{k}}(|u^0_{\mathbf{k},n}\rangle\right.
$$

$$
\times\langle u^{a_1,-\sigma}_{\mathbf{k},n}|)|u^{a_3,\sigma}_{\mathbf{k},m}\rangle+\delta_{m,n}\langle u^{a_1,-\sigma}_{\mathbf{k},n}|V^{a_2}_{H\mathrm{xc}}|u^{a_3,\sigma}_{\mathbf{k},m}\rangle
$$

$$
\left.-\langle u^0_{\mathbf{k},m}|V^{a_2}_{H\mathrm{xc}}|u^0_{\mathbf{k},n}\rangle\langle u^{a_1,-\sigma}_{\mathbf{k},n}|u^{a_3,\sigma}_{\mathbf{k},m}\rangle\right]
$$

$$
-\frac{4}{6}\int d^3r\ d^3r'\ d^3r''K_{\mathrm{xc}}(\omega_2,\omega_3,\mathbf{r},\mathbf{r}',\mathbf{r}'')
$$

$$
\times n^{a_1}(\mathbf{r})n^{a_2}(\mathbf{r}')n^{a_3}(\mathbf{r}'')+\Pi\{1,2,3\}. \tag{10}
$$

Here $\Pi\{1,2,3\}$ indicates the sum over the five permutations of the indexes 1,2,3, and

$$
V^{a_1}_{H\mathrm{xc}}(\mathbf{r})=\int d^3r'\left[\frac{1}{|\mathbf{r}-\mathbf{r}'|}+M_{\mathrm{xc}}(\omega_1,\mathbf{r},\mathbf{r}')\right]n^{a_1}(\mathbf{r}'),
$$

$$
n^{a_1}(\mathbf{r})=2\sum_m^{N/2}\sum_{\sigma=\pm}\int_{\mathrm{BZ}}\frac{\Omega d^3k}{(2\pi)^3}\mathrm{Re}[\langle u^0_{\mathbf{k},m}|\mathbf{r}\rangle\langle \mathbf{r}|u^{a_1,\sigma}_{\mathbf{k},m}\rangle],
$$

$$
M_{\mathrm{xc}}(\omega_1,\mathbf{r},\mathbf{r}')=T\int_0^T dt\frac{\delta^2A_{\mathrm{xc}}[n^0]}{\delta n(\mathbf{r},0)\delta n(\mathbf{r}',t)}e^{i\omega_1 t},
$$

$$
K_{\mathrm{xc}}(\omega_2,\omega_3,\mathbf{r},\mathbf{r}',\mathbf{r}'')=\int_0^T dt\frac{\delta M_{\mathrm{xc}}[n^0](\omega_2,\mathbf{r},\mathbf{r}')}{\delta n(\mathbf{r}'',t)}e^{i\omega_3 t},
$$

$$
\tag{11}
$$

n^0 is the unperturbed charge density, $|u^0_{\mathbf{k},m}\rangle$ is the periodic part of the unperturbed Bloch eigenstate normalized on the unit cell Ω, with eigenvalue $\epsilon^0_{\mathbf{k},m}$, and $|u^{a_1,\pm}_{\mathbf{k},m}\rangle$ is the perturbed orbitals projected on the unperturbed conduction band subspace, i.e., the solution of the linear system:

$$
(\epsilon^0_{\mathbf{k},m}-H^0_{\mathrm{KS}}\pm\omega_1)|u^{a_1,\pm}_{\mathbf{k},m}\rangle=Q_{\mathbf{k}}\left(\frac{\mathbf{e}_1\cdot\mathbf{r}}{2}+V^{a_1}_{H\mathrm{xc}}\right)|u^0_{\mathbf{k},m}\rangle, \tag{12}
$$

with $Q_{\mathbf{k}}=\mathbf{1}-\Sigma_m^{N/2}|u^0_{\mathbf{k},m}\rangle\langle u^0_{\mathbf{k},m}|$.

Note that the evaluation of Eq. (10) requires only the knowledge of unperturbed valence wave functions $|u^0_{\mathbf{k},m}\rangle$ and of their linear variation $|u^{a_1,\pm}_{\mathbf{k},m}\rangle$. Moreover, the solution of Eq. (12) can be obtained by minimizing a suitably defined functional with a numerical effort similar to the computation of the total energy.[9,15,16] Thus our formulation makes the evaluation of $\chi^{(2)}$ in systems containing up to 100 atoms feasible.

TABLE I. LDA nonlinear susceptibilities ($\chi^{(2)}$) of III-V cubic semiconductors computed without nonlinear core corrections. We report also the theoretical lattice constant (a_0), the direct gap at the Γ point (E_Γ), and the dielectric constant (ε_∞). Experimental values are given in parentheses. All computations are performed with 28 special **k** points except for InAs and InSb for which we used 60 special **k** points.

	a_0 (a.u.)	E_Γ (eV)	ε_∞	$\chi^{(2)}$ (pm/V)
AlP	10.19 (10.33)	3.5 (3.6)	8.2 (7.5)	39 (—)
AlAs	10.56 (10.69)	2.2 (3.1)	9.3 (8.2)	64 (—)
AlSb	11.46 (11.58)	1.9 (2.3)	11.4 (11.3)	146 (98)
GaP	10.01 (10.28)	2.8 (2.9)	9.8 (9.0)	68 (74)
GaAs	10.40 (10.68)	1.3 (1.5)	11.9 (10.9)	158 (166)
GaSb	11.25 (11.49)	0.8 (0.8)	15.6 (14.4)	433 (838)
InP	10.84 (11.09)	1.5 (1.4)	9.5 (9.6)	105 (287)
InAs	11.06 (11.45)	0.7 (0.4)	11.5 (12.2)	191 (838)
InSb	11.88 (12.23)	0.6 (0.2)	14.0 (15.7)	407 (1120)

IV. APPLICATION TO CUBIC SEMICONDUCTORS

We have applied Eq. (10) to compute the static $\chi^{(2)}$ of nine III-V and five II-VI cubic semiconductors, evaluating the exchange and correlation energy within the LDA. We do not use any scissor operator to correct for the LDA band-gap error, contrary to what has been done in other *ab initio* calculations.[5,6] Indeed the static $\chi^{(2)}$ is a ground-state property, which is defined as a difference of ground-state total energies and is not related to the LDA band gap.[17] We think that improvements over LDA require a better E_{xc} functional, which could be ultranonlocal,[18] instead of an *ad hoc* correction of the LDA band gap. Furthermore, our purpose here is to give reference values for the static $\chi^{(2)}$ which are completely consistent within LDA.

We used norm-conserving pseudopotentials and a plane-wave kinetic energy cutoff of 24 Ry. The derivative with respect to **k** which appears in Eq. (10) has been computed by means of finite differences.[7] We studied the effect of d electrons of Ga and In atoms, by performing for the compounds containing these elements two calculations: with and without nonlinear core corrections (NLCC).[19] For II-VI semiconductors the effect of the cation d electrons is even more important[20] and our reported values have been computed using only the NLCC. For AlP, AlAs, GaP, and GaAs we have also verified that our results for the $\chi^{(2)}$ reproduce the LDA values obtained in Ref. 6 if the same pseudopotentials (without NLCC) and lattice constants are used.

In Table I we report the values of the $\chi^{(2)}$ of the III-V cubic semiconductors computed without the NLCC at the corresponding theoretical lattice constant (a_0), also reported in the table. In Table II we report the values of the $\chi^{(2)}$ of the Ga and In III-V compounds and for the IV-VI cubic semiconductors computed with the NLCC at the corresponding theoretical a_0. Note that in the Ga and the In compounds the use of NLCC influences the results for $\chi^{(2)}$. Thus it is necessary to use at least the NLCC to obtain the correct LDA values for $\chi^{(2)}$ in the compounds containing these elements.

In Tables I and II we also show the direct band gap at the Γ point, E_Γ, and the static dielectric constant ε_∞ computed at the theoretical a_0. Known experimental values for a_0,

TABLE II. LDA nonlinear susceptibilities ($\chi^{(2)}$) of In and Ga III-V and of II-VI cubic semiconductors computed with nonlinear core corrections. We report also the theoretical lattice constant (a_0), the direct gap at the Γ point (E_Γ), and the dielectric constant (ε_∞). Experimental values are given in parentheses. All computations are performed with 28 special **k**-points, but for InSb for which we used 60 special **k**-points.

	a_0 (a.u.)	E_Γ (eV)	ε_∞	$\chi^{(2)}$ (pm/V)
GaP	10.12 (10.28)	2.0 (2.9)	10.0 (9.0)	83 (74)
GaAs	10.50 (10.68)	1.0 (1.5)	12.5 (10.9)	205 (166)
GaSb	11.37 (11.49)	0.5 (0.8)	16.7 (14.4)	617 (838)
InP	10.94 (11.09)	1.0 (1.4)	10.2 (9.6)	145 (287)
InAs	11.34 (11.45)	-0.1 (0.4)	— (12.2)	— (838)
InSb	12.10 (12.23)	0.1 (0.2)	16.1 (15.7)	957 (1120)
ZnS	10.29 (10.22)	2.4 (3.8)	5.4 (5.1)	33 (61)
ZnSe	10.71 (10.71)	1.6 (2.8)	6.7 (6.3)	65 (156)
ZnTe	11.44 (11.51)	1.6 (2.4)	8.1 (7.3)	122 (184)
CdSe	11.49 (11.44)	0.8 (1.8)	6.9 (6.2)	118 (72)
CdTe	12.17 (12.24)	1.1 (1.6)	7.8 (7.1)	167 (118)

E_Γ, and ε_∞ are reported in parentheses. Note that E_Γ computed at the theoretical a_0 is closer to the experimental values than the ones computed at the experimental a_0. Well established experimental data for $\chi^{(2)}$ do not exist since the values reported by different authors may differ by more than a factor of 2. Moreover, in some cases only data obtained at frequencies close to the absorbtion edge are available. Therefore we refer the readers to Refs. 21 and 22 for a complete review of the experimental results. Just to give an indicative value, we show in parentheses the experimental results from Ref. 21 that correspond to measurements done at the smallest frequencies. For GaP, GaAs, and CdSe we have taken the values from Ref. 22 obtained after an appropriate rescaling of the experimental data. In the case of InAs we cannot compute $\chi^{(2)}$ and ε_∞ when we use NLCC, since within LDA the system is a metal. For all other compounds the computed $\chi^{(2)}$ obtained with NLCC are in the range of variation of the available experimental data.[21,22]

As a second application we compute the TD $\chi^{(2)}$ for SHG

TABLE III. The frequency-dependent nonlinear optical susceptibility for second-harmonic generation of GaP, $\chi^{(2)}(2\omega;\omega,\omega)$.

$\chi^{(2)}$ pm/V	$\hbar\omega = 0.117$ eV	$\hbar\omega = 0.585$ eV	$\hbar\omega = 0.94$ eV
Theor.	83	98	135
Expt.	74 ± 4	94 ± 20	98 ± 18, 112 ± 12

of GaP. For this calculation we used the TD-LDA. In the TD case the use of LDA is less justified since, in contrast to the exact TD-DFT, it does not describe correctly the position of the absorption edge.[3] We note that this is a limitation of the approximation to A_{xc} used here, and *not* of Eq. (10) itself. In Table III we report $\chi^{(2)}(2\omega;\omega,\omega)$ computed as a function of ω in the nonabsorbing regime computed with NLCC. We obtain good agreement with the experimental measurements, which are taken from Refs. 22 and 6.

V. CONCLUSION

In conclusion, we have presented a consistent theory for the computation of the static and dynamic nonlinear optical susceptibilities within DFT. To this purpose we have applied the "$2n+1$" theorem to the TD-DFT action functional. We have presented applications for 14 cubic semiconductors. Our results show that LDA reproduces the experimental static nonlinear susceptibilities in these compounds without using any scissor operator, provided that the computations are performed at the theoretical lattice constant and NLCC are included for Ga, In, Zn, and Cd atoms.

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[12] Here for simplicity we consider $\mathbf{P}^s(\omega_1,\mathbf{a})$ oscillating in phase with the field a_1. This assumption is exact only in the nonabsorbing regime. To obtain $\chi^{(2)}$ in the absorbing regime is sufficient to make the analytical continuation of Eq. (10) to complex frequencies ω_1, ω_2, and ω_3.

[13] Equation (1) is invariant under a TD unitary transformation in the occupied subspace, such as $|\widetilde{\psi}_i(t)\rangle = U_{ij}(t)|\psi_j(t)\rangle$, with $U_{ik}^*(t)U_{kj}^*(t) = \delta_{ij}$ and $U_{ij}(t) = U_{ij}(t+T)$. Thus if the set $\{\psi^s\}$ satisfies Eq. (1), so does $\{\widetilde{\psi}^s\}$.

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