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REAL-SPACE METHOD FOR NONLINEAR RESPONSES OF MOLECULES AND CLUSTERS

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Real-space method is presented to calculate dynamic hyperpolarizability of molecules and clusters. The method is based on the time-dependent density functional theory (TD-DFT). All calculations are performed on a three-dimensional uniform grid. The method works efficiently for large systems. Numerical results are shown for water molecule and fullerene. Results agree well with those by other method for water molecule, while our calculation gives much larger hyperpolarizability for fullerene than that in the conventional calculation with basis functions.

Key words: TD-DFT, real-space method, hyperpolarizability, nonlinear optics, fullerene

1. INTRODUCTION

There have been much theoretical efforts to explore materials of technological use with large nonlinear polarizabilities. The nonlinear response of atomic clusters has been investigated in this respect: For example, the hyperpolarizability of C_{60} has been calculated extensively [1]. A possible enhancement of the second harmonic generation is discussed for metallic clusters deposited on a surface [2, 3].

As a theoretical tool for the optical response, the time-dependent density functional theory (TD-DFT) has been widely used [4]. The dynamic hyperpolarizability was first studied in the TD-DFT for rare-gas atoms by Senatore and Subbaswamy [5]. The TD-DFT calculation of the hyperpolarizability has been extended to molecules [1, 6]. The calculations are usually performed with a quantum chemistry method employing basis functions and require inclusion of the diffuse basis functions to obtain convergent results. For large molecules, it is often difficult to reach convergent results.

A real-space method is now widely used in the first-principle calculations [7]. We have recently developed a real-time, real-space method to solve the time-dependent Kohn-Sham (TDKS) equation[8]. The method is quite useful to calculate the linear response properties of molecules, clusters, [8, 9] and bulk [10]. However, the applicability of the real-time method seems to be limited to the linear response. For nonlinear response, instead, we have developed a real-space method in the response function formalism where the frequency representation is used instead of solving the equation in real time [11]. In this note, we present the framework, numerical method, and applications to some molecules.

2. THEORY

The response function formalism of dynamic hyperpolarizability based on the TD-DFT was presented in Ref.[5] for third harmonic generation. We generalize the formalism for various nonlinear optical processes of molecules.

2.1 Definition of hyperpolarizability [12]

The dipole moment induced by an external electric field with moderate intensity is expressed in a power series as

$$\mathbf{p}(t) = \mathbf{p}^{(0)}(t) + \mathbf{p}^{(1)}(t) + \mathbf{p}^{(2)}(t) + \cdots, \qquad (1)$$

where $\mathbf{p}^{(1)}(t)$ is linear in the field, $\mathbf{p}^{(2)}(t)$ is quadratic $\cdots$, and so on. When we consider a superposition of monochromatic waves as an external perturbation

$$\mathbf{E}(t) = \frac{1}{2}\sum_{\omega_i \geq 0}\left\{\mathbf{E}_{\omega_i}e^{-i\omega_i t} + \mathbf{E}_{-\omega_i}e^{i\omega_i t}\right\}, \qquad (2)$$

$\mathbf{p}^{(n)}(t)$ can be written in a similar form

$$\mathbf{p}^{(n)}(t) = \frac{1}{2}\sum_{\omega_\sigma \geq 0}\left\{\mathbf{p}^{(n)}_{\omega_\sigma}e^{-i\omega_\sigma t} + \mathbf{p}^{(n)}_{-\omega_\sigma}e^{i\omega_\sigma t}\right\}, \qquad (3)$$

where the Cartesian μ-component of $\mathbf{p}^{(n)}_{\omega_\sigma}$ is given by

$$\left(\mathbf{p}^{(n)}_{\omega_\sigma}\right)_\mu = \frac{1}{n!}\sum_{\alpha_1,\cdots,\alpha_n}\sum_{\{\omega_1,\cdots,\omega_n\}} K(-\omega_\sigma;\omega_1,\cdots,\omega_n)$$
$$\times \quad \chi^{(n)}_{\mu\alpha_1\cdots\alpha_n}(-\omega_\sigma;\omega_1,\cdots,\omega_n)(\mathbf{E}_{\omega_1})_{\alpha_1}\cdots(\mathbf{E}_{\omega_n})_{\alpha_n}. \qquad (4)$$

$\chi^{(n)}_{\mu\alpha_1\cdots\alpha_n}(-\omega_\sigma;\omega_1,\cdots,\omega_n)$ is called the n-th order nonlinear polarizability tensor, or $(n-1)$-th order hyperpolarizability tensor. The sum $\sum_{\{\omega_1,\cdots,\omega_n\}}$ is taken over all distinct sets of $\{\omega_1,\cdots,\omega_n\}$.

$K(-\omega_\sigma;\omega_1,\cdots,\omega_n)$ is a numerical factor which is defined as

$$K(-\omega_\sigma;\omega_1,\cdots,\omega_n)=2^{l+m-n}p, \tag{5}$$

where p is the number of distinct permutations of $\{\omega_1,\cdots,\omega_n\}$, n is the order of nonlinearity, m is the set of n frequencies $\{\omega_1,\cdots,\omega_n\}$ are zero. $l=1$ if $\omega_\sigma\neq 0$, otherwise $l=0$.

2.2 Time-dependent density functional response theory (TD-DFRT)

The time evolution of the single-particle density under the external field (2) is described by the TDKS equation

$$i\hbar\frac{\partial}{\partial t}\psi_i(\mathbf{r},t)=\left(h[\rho](\mathbf{r},t)+v^{ext}(\mathbf{r},t)\right)\psi_i(\mathbf{r},t), \tag{6}$$

$$\begin{aligned}h[\rho](\mathbf{r},t)&=\frac{-\hbar^2}{2m}\nabla^2+V_{ion}(\mathbf{r})\\&+\ e^2\int d\mathbf{r}'\frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}+V_{xc}[\rho](\mathbf{r},t),\end{aligned} \tag{7}$$

$$\rho(\mathbf{r},t)=\sum_i^{occ.}|\psi_i(\mathbf{r},t)|^2. \tag{8}$$

We utilize the norm-conserving pseudopotential [13] for electron-ion interaction. The static exchange-correlation potential is used for the response calculation, which is known as the adiabatic approximation.

When the external perturbation is sufficiently small, we can expand the single particle density $\rho(\mathbf{r},t)$ as

$$\rho(\mathbf{r},t)=\rho^{(0)}(\mathbf{r})+\rho^{(1)}(\mathbf{r},t)+\rho^{(2)}(\mathbf{r},t)+\cdots. \tag{9}$$

$\rho^{(n)}(\mathbf{r},t)$ can be expressed as

$$\begin{aligned}&\rho^{(n)}(\mathbf{r},t)\\&=\frac{1}{2}\sum_{\omega_\sigma\geq 0}\left\{\rho^{(n)}_{\omega_\sigma}(\mathbf{r})e^{-i\omega_\sigma t}+\rho^{(n)}_{-\omega_\sigma}(\mathbf{r})e^{i\omega_\sigma t}\right\},\end{aligned} \tag{10}$$

$$\begin{aligned}\rho^{(n)}_{\omega_\sigma}(\mathbf{r})&=\frac{1}{n!}\sum_{\alpha_1,\cdots,\alpha_n}\sum_{\{\omega_1,\cdots,\omega_n\}}K(-\omega_\sigma;\omega_1,\cdots,\omega_n)\\&\times\rho^{(n)}_{\alpha_1\cdots\alpha_n}(\mathbf{r}|-\omega_\sigma;\omega_1,\cdots,\omega_n)(\mathbf{E}_{\omega_1})_{\alpha_1}\cdots(\mathbf{E}_{\omega_n})_{\alpha_n}.\end{aligned} \tag{11}$$

The $(n-1)$-th order hyperpolarizability tensor can be obtained from the n-th order transition density as

$$\begin{aligned}&\chi^{(n)}_{\mu\alpha_1\cdots\alpha_n}(-\omega_\sigma;\omega_1,\cdots,\omega_n)\\&=-e\int d\mathbf{r}r_\mu\rho^{(n)}_{\alpha_1\cdots\alpha_n}(\mathbf{r}|-\omega_\sigma;\omega_1,\cdots,\omega_n).\end{aligned} \tag{12}$$

We can show that the transition densities satisfy the following equation,

$$\begin{aligned}&\rho^{(n)}_{\alpha_1\cdots\alpha_n}(\mathbf{r}|-\omega_\sigma;\omega_1,\cdots,\omega_n)\\&=\ \int d\mathbf{r}'\chi^{(1)}(\mathbf{r},\mathbf{r}';\omega_\sigma)\\&\quad\times\int d\mathbf{r}''\left\{\frac{e^2}{|\mathbf{r}'-\mathbf{r}''|}+f_{xc}(\mathbf{r}',\mathbf{r}'';\omega_\sigma)\right\}\\&\quad\times\ \rho^{(n)}_{\alpha_1\cdots\alpha_n}(\mathbf{r}''|-\omega_\sigma;\omega_1,\cdots,\omega_n)\\&+\ b^{(n-1)}(\mathbf{r}),\end{aligned} \tag{13}$$

where f_{xc} is the so-called exchange-correlation kernel. $\chi^{(1)}$ is the independent particle response function

$$\begin{aligned}&\chi^{(1)}(\mathbf{r},\mathbf{r}';\omega_\sigma)\\&=\ \sum_i^{occ.}\left\{\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}')G^{(+)}(\mathbf{r},\mathbf{r}';\epsilon_i+\hbar\omega_\sigma)\right.\\&\quad\left.+\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}')G^{(-)}(\mathbf{r},\mathbf{r}';\epsilon_i-\hbar\omega_\sigma)\right\},\end{aligned} \tag{14}$$

where $\phi_i(\mathbf{r})$ and ϵ_i are the static Kohn-Sham orbitals and energies, respectively. Single-particle Green functions are given by

$$G^{(\pm)}(\mathbf{r},\mathbf{r}';E)=\sum_j\frac{\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')}{E-\epsilon_j\pm i\eta}, \tag{15}$$

where η is a small positive number. The term $b^{(n-1)}(\mathbf{r})$ is a collection of terms which can be written in terms of the $(n-1)$-th order quantities. For example, zero-th order is

$$b^{(0)}(\mathbf{r})=\int d\mathbf{r}'\chi^{(1)}(\mathbf{r},\mathbf{r}';\omega_\sigma)v^{ext}_{\omega_\sigma}(\mathbf{r}'). \tag{16}$$

Equation (13) is the basic equation for the n-th order transition density. It should be noted that the structure of the equation for the n-th order transition density is the same as that of the self-consistent equation in the random-phase approximation. Explicit expressions of $b^{(n)}(\mathbf{r})(n\geq 1)$ will be given elsewhere.

3. NUMERICAL PROCEDURE

The numerical procedure is described in Refs. [9] and [11]. We briefly discuss some important points in solving Eq. (13) in the real-space method.

In the finite-difference approximation, Equation (13) is a linear-algebraic equation for an unknown vector $\rho^{(n)}(i)$ $(i=1,\cdots,M)$ where M is the number of grid points. We solve this equation by an iterative method such as the conjugate-residual method. We further need to calculate integrals involving Coulomb potential and Green function. Since the number of grid points is very large, typically 10^4 to 10^5, it is not convenient or even impossible to construct the matrix explicitly and to perform integration by summing up over grid points. Instead of integrations, we convert them into equivalent differential equations and solve them by iterative methods.

For the Hartree potential, we solve the Poisson equation

$$\nabla^2 V_H^{(n)}(\mathbf{r}) = -4\pi e^2 \rho^{(n)}(\mathbf{r}), \qquad (17)$$

instead of the integral involving Coulomb potential. For the integral involving Green function,

$$\psi_i^{(+)}(\mathbf{r}) \equiv \int d\mathbf{r}' G^{(+)}(\mathbf{r},\mathbf{r}';E) V_H^{(n)}(\mathbf{r}')\phi_i(\mathbf{r}'), \qquad (18)$$

we recast it into the Schrödinger equation with source term. The method here is known as the modified Sternheimer method [15].

$$\left(E - h[\rho^{(0)}]\right) \psi_i^{(+)}(\mathbf{r}) = V_H^{(n)}(\mathbf{r})\phi_i(\mathbf{r}). \qquad (19)$$

This is again a linear algebraic equation with sparse-symmetric matrix. The equation can be solved efficiently by, for example, the conjugate-gradient method.

4. APPLICATIONS

4.1 Water molecule

We apply our method to calculate the hyperpolarizabilities of two molecules, water molecule and C_{60}. For water molecule, accurate calculations in the TD-DFT are reported in the literature. Here we simply aim to check our method by comparison.

We used a geometry specified by R(O-H)=0.957Å and θ(HOH)=104.5°. The grid points are generated by 0.2Å mesh. The points inside a spherical box of 7Å are used in the calculation. The VWN potential is utilized[16] for both the potential and the kernel of exchange-correlation.

In Table I., linear polarizabilities α, first and second hyperpolarizabilities β, γ of water molecule are presented. All theoretical values as well as the measured values are averaged over orientation.

The agreement between the results of the present real-space method and those employing basis functions [6] are quite good. Compared with the other *ab initio* calculations and measured values, we can see that the TD-DFT somewhat overestimates the hyperpolarizability. This is related with the well known deficiency of the potential in the local-density approximation: it does not have a correct assymptotic behaviour. A gradient correction method which produces correct asymptotic potential has been proposed and is known to remedy the discrepancy[6].

4.2 C_{60} molecule

We used a geometry specified by R(C-C)=1.45Å and R(C=C)=1.39Å. The VWN potential and kernel is used again. Calculations are performed with grid points inside a box of radius 10Å with 0.3 Å mesh. We confirmed that these radius and mesh-spacing are sufficient to obtain converged results within a few percent level.

In Table II., linear polarizabilities α and second hyperpolarizabilities γ of C_{60} are presented. For centro symmetric molecules, the first hyperpolarizability vanishes identically.

In contrast to the case of water molecule, our real-space calculation gives larger hyperpolarizbility than that by the basis function calculation [1] even for the static hyperpolarizability. In the conventional calculation, results are usually sensitive to the choice of the basis functions. For a molecule of this size, it would not be easy to reach convergence in the method employing basis functions [11].

It is difficult at present to make comparison between the measured and calculated hyperpolarizabilities of C_{60}. All the measurements are achieved in solutions or in thin films. In early measurements, results are reported with discrepancy as large as a few orders of magnitude [20]. As is found in Table II., all the measured values are substantially larger than the calculated results. In recent measurement, the upper limit of the hyperpolarizability is reported as $\gamma < 220 \times 10^{-36}$(esu) [20].

5. SUMMARY

We present a real-space method to calculate dynamic hyperpolarizability in the time-dependent density functional theory. The method is efficient for large molecules and clusters. In particular,

Table I. hyperpolarizabilities of water molecule (Units; α(Å^3), β(10^{-33}esu) , γ(10^{-36}esu))

	$\hbar\omega$ (eV)	TDLDA^a	TDLDA^b	TDHF^c	CCSD(T)^c	EXP.
α_{static}	0	1.56	1.56	1.27	1.45	1.45^d
β_{static}	0	-225	-222	-93.3	-156	
$\beta(0;\omega,-\omega)$	1.786	-247	-243	-97.6	-164	
$\beta(-2\omega;\omega,\omega)$	1.786	-303	-297	-109	-182	-190±8^e
γ_{static}	0	1.60	1.61	0.509	0.907	
$\gamma(-\omega;\omega,-\omega,\omega)$	1.786	1.77		0.574	1.01	
$\gamma(-2\omega;\omega,\omega,0)$	1.786	2.38	2.42	0.612	1.11	1.16±0.060^e
$\gamma(-3\omega;\omega,\omega,\omega)$	1.786	4.34		0.763	1.36	

^{a}Present Real-Space calculation, ^{b}Basis set calculation[6]

^{c}Time-dependent Hartree-Fock, Coupled-Cluster method[17]

^{d}Ref.[18], ^{e}Ref.[19]

Table II. hyperpolarizabilities of C_{60} (Units; $\alpha(\text{Å}^3)$, $\gamma(10^{-36}\text{esu})$)

	$\hbar\omega$ (eV)	TDLDA[a]	TDLDA[b]	RPA[c]	EXP.
α_{static}	0	80.2	82.5	75.3	$88.3^{c,d}$
γ_{static}	0	62.5	44.0	57.3	
$\gamma(-\omega;\omega,-\omega,\omega)$	1.165	80.1			$60 \times \gamma_{benzene}{}^{e}$
$\gamma(-2\omega;\omega,\omega,0)$	0.65	67.5			$4.50\times10^{3\,f}$
$\gamma(-3\omega;\omega,\omega,\omega)$	0.52	69.5			$171\pm25^{c,d}$

[a] Present Real-Space calculation, [b] Basis set calculation[1], [c] Random-Phase-Approximation[21]
[d] Thin film[24], [e] Benzene solution[22] (our TD-DFT value of benzene is 9.17×10^{-36}esu)
[f] Toluene solution[23]

convergence of the result as to the spatial extension can be conveniently examined by changing box size and mesh spacing. Our method thus allows us to obtain convergent results of dynamic hyperpolarizability of molecules as large as C_{60}. For small molecules, real-space method gives basically the same results as those in the conventional method employing basis functions. However, for C_{60} molecule, our convergent result is found to be larger than that in the basis function method by 30%.

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