

## Frequency-dependent polarizabilities, hyperpolarizabilities, and excitation energies from time-dependent density-functional theory based on the quasienergy derivative method

Fumihiko Aiga, Tsukasa Tada, and Reiko Yoshimura

Citation: *The Journal of Chemical Physics* **111**, 2878 (1999); doi: 10.1063/1.479570

View online: <http://dx.doi.org/10.1063/1.479570>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/111/7?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Excitation energies of  \$\pi\$ -conjugated oligomers within time-dependent current-density-functional theory](#)  
*J. Chem. Phys.* **121**, 10707 (2004); 10.1063/1.1810137

[Comment on "Frequency-dependent polarizabilities, hyperpolarizabilities, and excitation energies from time-dependent density-functional theory based on the quasienergy derivative method" \[\*J. Chem. Phys.\* 111, 2878 \(1999\)\]](#)  
*J. Chem. Phys.* **112**, 6938 (2000); 10.1063/1.481277

[Response to "Comment on 'Frequency-dependent polarizabilities, hyperpolarizabilities, and excitation energies from time-dependent density-functional theory based on the quasienergy derivative method'" \[\*J. Chem. Phys.\* 112, 6938 \(2000\)\]](#)  
*J. Chem. Phys.* **112**, 6939 (2000); 10.1063/1.481266

[Erratum: "Calculating frequency-dependent hyperpolarizabilities using time-dependent density functional theory" \[\*J. Chem. Phys.\* 109, 10644 \(1998\)\]](#)  
*J. Chem. Phys.* **111**, 6652 (1999); 10.1063/1.479915

[Calculating frequency-dependent hyperpolarizabilities using time-dependent density functional theory](#)  
*J. Chem. Phys.* **109**, 10644 (1998); 10.1063/1.477762

---



# Frequency-dependent polarizabilities, hyperpolarizabilities, and excitation energies from time-dependent density-functional theory based on the quasienergy derivative method

Fumihiko Aiga,<sup>a)</sup> Tsukasa Tada, and Reiko Yoshimura

Materials and Devices Research Laboratories, Toshiba Corporation, 1 Komukai Toshiba-cho, Saiwai-ku, Kawasaki 210-8582, Japan

(Received 4 December 1998; accepted 24 May 1999)

A time-dependent density-functional theory for systems in periodic external potentials in time is formulated on the assumption of the existence of the Floquet states from the quasienergy viewpoint. Coupling strength integration, which connects a noninteracting system with an interacting system, is introduced by using the time-dependent Hellmann–Feynman theorem. Coupled perturbed time-dependent Kohn–Sham equations are derived from the variational condition to the quasienergy functional with respect to parameters. Explicit expressions for frequency-dependent polarizability and first hyperpolarizability are given by the quasienergy derivative method. Excitation energies and transition moments are defined from poles and residues of frequency-dependent polarizabilities, respectively. In contrast to the previous theory, our formulation has the following three advantages: (1) The time-dependent exchange-correlation potential is defined by the functional derivative of the exchange-correlation quasienergy. (2) The formal expression for frequency-dependent polarizability, which corresponds to the exact sumover-states expression, can be obtained. (3) Explicit expressions for response properties which satisfy the  $2n+1$  rule can be automatically obtained. © 1999 American Institute of Physics. [S0021-9606(99)31031-X]

## I. INTRODUCTION

There are various reliable quantum chemical *ab initio* methods for the accurate determination of molecular properties such as excitation energies and frequency-dependent polarizabilities and hyperpolarizabilities. Singly excited configuration interaction<sup>1</sup> and random phase approximation (RPA),<sup>2</sup> which is equivalent to the time-dependent Hartree–Fock (TDHF) approximation,<sup>3</sup> are relatively crude in their theoretical level but qualitatively well describe excited state if its wave function is dominated by singly excited configurations from the ground state. Theoretical approaches based on the coupled-cluster (CC) approach such as symmetry-adapted cluster expansion configuration interaction,<sup>4</sup> equation of motion CC,<sup>5</sup> and CC linear response<sup>6,7</sup> can give quantitatively accurate excitation energies if the Hartree–Fock scheme is a good approximation for the ground state. Other theoretical approaches based on multireference theory such as multireference configuration interaction (MRCI)<sup>8,9</sup> and multireference perturbation theory (CAS-PT2,<sup>10</sup> MRMP,<sup>11</sup> MROPT1-4<sup>12</sup>) can describe not only dynamical but also non-dynamical electron correlation effects. They can be also applied to quasidegenerate states. For frequency-dependent polarizabilities and hyperpolarizabilities, TDHF<sup>13–17</sup> is known to account for precise dispersion effects in many cases in off-resonant region,<sup>18,19</sup> and various correlated methods based on MCSCF,<sup>20</sup> MRCI,<sup>21</sup> second-order Møller–Plesset perturbation theory,<sup>22–25</sup> and CC<sup>26–29</sup> have been implemented. However, since these accurate methods are compu-

tionally intensive, they are restricted to small or medium-sized molecular systems. For large molecular systems, a computationally more tractable method is required. Density-functional theory (DFT)<sup>30,31</sup> provides such a method through its time-dependent extension called time-dependent DFT (TDDFT).<sup>32–36</sup>

A formal foundation for the extension of the Hohenberg–Kohn<sup>37</sup> and Kohn–Sham<sup>38</sup> type theorems to the time-dependent case has been laid by many workers, most notably Deb and Ghosh,<sup>39</sup> Bartolotti,<sup>40</sup> and Runge and Gross.<sup>41</sup> In addition to the earlier application of TDDFT to the calculation of response properties of atoms and solids,<sup>42</sup> TDDFT has been recently applied to calculations of various response properties such as excitation energies,<sup>43–55</sup> frequency-dependent polarizabilities,<sup>47,50,55–58</sup> frequency-dependent hyperpolarizabilities,<sup>59–61</sup> Van der Waals dispersion coefficients,<sup>56,58</sup> and Raman scattering cross sections.<sup>62</sup> A time-dependent generalization of current DFT<sup>63</sup> has also been implemented to the calculation of frequency-dependent polarizabilities.<sup>64–66</sup> A time-dependent version of the optimized effective potential (OEP) method<sup>67</sup> has been applied to the calculation of excitation energies.<sup>43,44</sup>

However, time-dependent Kohn–Sham (TDKS) equation employed in the above calculations is based on the variational condition to action integral whose time interval is not rigorously defined, and time-dependent exchange-correlation potential depends on the undefined initial and final time of the action integral. The adiabatic approximation<sup>33,34,68</sup> employed in the above calculations satisfies the harmonic potential theorem.<sup>69</sup> On the other hand, frequency-dependent exchange-correlation kernel, which is

<sup>a)</sup>Electronic mail: fumihiko-aiga@mdl.rdc.toshiba.co.jp

beyond the adiabatic approximation, proposed by Gross and Kohn<sup>70</sup> is not consistent with this theorem. The explicit expression for frequency-dependent polarizability, that is the linear response function whose poles correspond to excitation energies, can be written if only the adiabatic approximation is employed. Thus, it is not clear whether frequency-dependent polarizability in TDDFT with the exact exchange-correlation potential corresponds to the exact sum-over states (SOS) expression.<sup>71</sup> A contradiction exists concerning the causality and symmetry properties of the time-dependent exchange-correlation kernel.<sup>36</sup> It is also noted<sup>72</sup> that a local gradient expansion is possible if the TDDFT is formulated in terms of the current density and that the exchange-correlation potential in the usual TDDFT is, however, an intrinsically nonlocal functional of the density which does not admit a gradient expansion.

Unless transient time-dependent processes are considered, it is sufficient to consider *periodic* external potentials in time in order to define frequency-dependent polarizabilities, hyperpolarizabilities, and excitation energies on the assumption of the existence of the Floquet states.<sup>73–78</sup> The general theory to define frequency-dependent response properties in periodic external field in time, called the quasienergy derivative method (QEDM), has been proposed by Sasagane, Itoh, and one of the authors,<sup>79</sup> and this method has been applied to the calculation of response properties at various levels of theory.<sup>7,23–25,29,79–81</sup> Although TDDFT in periodic external potentials in time was studied by Deb and Ghosh,<sup>39</sup> they did not utilize quasienergy in order to get TDKS equation and response properties. Recently, Telnov and Chu<sup>82</sup> developed the Floquet formulation of TDDFT, and they calculated ionization cross sections nonperturbatively from the imaginary part of quasienergy. In their formulation, however, response properties perturbatively defined by the real part of quasienergy, such as frequency-dependent polarizabilities, were not considered.

In this paper, we formulate TDDFT in periodic external potentials in time on the assumption of the existence of the Floquet states from the quasienergy viewpoint, and derive formal expressions for frequency-dependent polarizabilities and first hyperpolarizabilities, which satisfy the  $2n+1$  rule<sup>83</sup> by using QEDM. Excitation energies and transition moments are defined from poles and residues of frequency-dependent polarizabilities, respectively.

This paper is organized as follows. In Sec. II, the Hohenberg–Kohn theorem for the ground-Floquet state is reformulated from the quasienergy viewpoint. In Sec. III, the Kohn–Sham equation for the ground-Floquet state is verified. Coupling strength integration, which connects a noninteracting system with a real interacting system, is introduced by using the time-dependent Hellmann–Feynman theorem. Exchange-correlation potential is defined by the functional derivative of the exchange-correlation quasienergy. In Sec. IV, response equations, which are the coupled perturbed TDKS equations, are derived from the variational condition to the quasienergy functional with respect to parameters, and explicit expressions for frequency-dependent polarizability and first hyperpolarizability are given by using QEDM. Excitation energies and transition moments are defined from

poles and residues of frequency-dependent polarizabilities, respectively. In Sec. V, we make some concluding remarks.

## II. HOHENBERG–KOHN THEOREM FOR THE GROUND-FLOQUET STATE

The Hamiltonian of the system is assumed to be expressed as

$$H = H_0 + U^{(1)}, \quad (1)$$

where  $H_0$  is the nonrelativistic Born–Oppenheimer electronic Hamiltonian of the isolated molecule and expressed as

$$H_0 = K + U^{(0)} + V. \quad (2)$$

The operator  $K$  denotes the kinetic energy of electrons. The operator  $U^{(0)}$  denotes the Coulomb interaction between electrons and nucleus, and the operator  $V$  denotes the Coulomb repulsion between electrons. The operator  $U^{(1)}$  represents the interaction with the time-dependent external electric field as

$$U^{(1)} = - \sum_{i=-n}^n \sum_{\alpha=x,y,z} \epsilon_{\alpha}(\omega_i) M_{\alpha} \exp(-i\omega_i t), \quad (3)$$

where  $M_{\alpha}$  is the  $\alpha$  component of the electric dipole moment operator, and  $\epsilon_{\alpha}(\omega_i)$  is the field strength of the  $e^{-i\omega_i t}$  Fourier component. From the Hermiticity of  $U^{(1)}$ , we define

$$\omega_{-i} = -\omega_i \quad (\omega_0 = 0) \quad (4)$$

and

$$\epsilon_{\alpha}(\omega_{-i}) = \epsilon_{\alpha}^*(\omega_i) \quad [\epsilon_{\alpha}(0) = \epsilon_{\alpha}^*(0)]. \quad (5)$$

Provided that  $U^{(1)}$  is periodic in time, we can write  $\omega_i$  with the nonzero unit frequency  $\omega_u$  as follows:

$$\omega_i = N_i \omega_u, \quad (6)$$

where  $N_i$  is an integer, and the period  $T$  is defined as

$$T = \frac{2\pi}{\omega_u}. \quad (7)$$

Throughout this paper, we assume this type of periodicity which is usual in QEDM.<sup>23,24,79,80</sup> If we define  $U$  as

$$U = U^{(0)} + U^{(1)}, \quad (8)$$

we can write

$$H = K + U + V, \quad (9)$$

and the operator  $U = \sum u$  describes a local one particle potential.

The Schrödinger equation for the system is

$$i \frac{\partial}{\partial t} |\Psi\rangle = H |\Psi\rangle, \quad (10)$$

where  $|\Psi\rangle$  is assumed to be normalized as

$$\langle \Psi | \Psi \rangle = 1. \quad (11)$$

In QEDM,<sup>23,24,79,80</sup> total wave function  $|\Psi\rangle$  is expressed as

$$|\Psi\rangle = |\Phi\rangle \exp \left[ -i \int_{t_0}^t \left\langle \Phi \left| H - i \frac{\partial}{\partial t'} \right| \Phi \right\rangle dt' \right], \quad (12)$$

with

$$\langle \Phi | \Phi \rangle = 1, \quad (13)$$

where  $\Phi$  is free from the overall time-dependent phase factor of the total wave function.<sup>75</sup> Substituting Eq. (12) into Eq. (10), we can rewrite the Schrödinger equation as

$$\left( H - i \frac{\partial}{\partial t} \right) |\Phi\rangle = |\Phi\rangle W(t), \quad (14)$$

where

$$W(t) = \left\langle \Phi \left| H - i \frac{\partial}{\partial t} \right| \Phi \right\rangle \quad (15)$$

is referred to as a quasienergy.<sup>23,24,79,80</sup> In this paper, we call this quantity  $W(t)$  the time-dependent quasienergy, and time-average of  $W(t)$  over one period is called quasienergy.

Throughout this paper, we assume the existence of the Floquet states for the system of interest, and that Eq. (14) has a solution which is periodic in time. This assumption is usual in QEDM.<sup>23,24,79,80</sup> For a real system with a continuous spectrum, multiple quantum absorptions result in a decay of any state, and Floquet states generally should not exist for a real atom or molecule interacting with the classical electromagnetic field which is periodic in time.<sup>74,77</sup> Although true Floquet states are generally not expected to exist for real systems, one can develop a perturbation expression for such a state on the assumption of its existence. It should be noted that there exists only an asymptotic solution which is periodic in time by neglecting interaction with the continuum, and that the perturbation equations have solutions only up to some order. Such a truncated wave function can be a physically reasonable approximation to the true solution, and it is sufficient to explain phenomena such as the Stark effect. From the periodicity, the solution  $|\Phi\rangle$  to Eq. (14) obeys the periodic *boundary* condition in time, and it is thus unnecessary to pay attention to the *initial* condition. Therefore we can arbitrarily choose the time origin, and the domain of time is set to be one period.

Defining the density operator  $\hat{n}$ , the electron density for the system can be expressed as

$$n(\mathbf{r}, t) = \langle \Phi | \hat{n} | \Phi \rangle. \quad (16)$$

We also define the time-averaged value of an arbitrary value  $A$  over one period as

$$\{A\}_T \equiv \frac{1}{T} \int_0^T A dt. \quad (17)$$

As well as the Hohenberg–Kohn theorem for the time-independent stationary states,<sup>31,37,84</sup> we can summarize the Hohenberg–Kohn theorem for the ground-Floquet state as the following three statements on invertibility, variational access, and universality:

(1) The density  $n(\mathbf{r}, t)$  for the ground-Floquet state uniquely determines the external potential  $u = u[n]$  as well as the wave function  $\Phi[n]$ . As a consequence, the time-

averaged expectation value of any operator  $\hat{O}$  over one period is a functional of the density as  $\{\langle \Phi[n] | \hat{O} | \Phi[n] \rangle\}_T = \bar{O}[n]$ .

(2) The quasienergy functional

$$\bar{W}_u[n] = \left\{ \left\langle \Phi[n] \left| K + V + U - i \frac{\partial}{\partial t} \right| \Phi[n] \right\rangle \right\}_T \quad (18)$$

of a particular physical system characterized by the periodic external potential in time  $U$  is equal to the exact quasienergy  $\bar{W}_{\text{exact}}$  if and only if the exact ground-Floquet state density  $n_{\text{exact}}$  is inserted, and  $\bar{W}_{\text{exact}}$  and  $n_{\text{exact}}$  can be determined by solving the Euler–Lagrange equation

$$\frac{\delta}{\delta n(\mathbf{r}, t)} \bar{W}_u[n] = 0. \quad (19)$$

(3) If we express the quasienergy functional as

$$\bar{W}_u[n] = \bar{B}[n] + \left\{ \int d^3r u(\mathbf{r}, t) n(\mathbf{r}, t) \right\}_T, \quad (20)$$

where

$$\bar{B}[n] = \left\{ \left\langle \Phi[n] \left| K - i \frac{\partial}{\partial t} + V \right| \Phi[n] \right\rangle \right\}_T, \quad (21)$$

the functional  $\bar{B}[n]$  is universal in the sense that it is independent of the external potential  $U$ .

In this section, we indicate that these statements are realized in cases where a many electron system is in periodic external potentials in time on the assumption of the existence of the Floquet states.

We can define a set  $\mathbf{U}$  consisting of  $U$  in Eq. (14) with Eq. (9). Collecting the wave functions  $\Phi$  for the ground-Floquet states into the set  $\Phi$ , we can define a map

$$C: \mathbf{U} \rightarrow \Phi. \quad (22)$$

The map is surjective by construction:  $\Phi$  contains no element which is not associated with some element of  $\mathbf{U}$ . Collecting the densities calculated from Eq. (16) with the wave functions in  $\Phi$  into the set  $\mathbf{N}$ , we can also define a second map

$$D: \Phi \rightarrow \mathbf{N}. \quad (23)$$

This map is also trivially surjective. The statement 1 in the above Hohenberg–Kohn theorem can be proved by showing that maps  $C$  and  $D$  are also injective (one to one) and thus bijective (fully invertible). We can prove this by showing the next two theorems in the same way as stationary time-independent systems.

**Theorem 1.** The map  $C: \mathbf{U} \rightarrow \Phi$  is injective.

**Proof.** We show that two potentials  $U, U' \in \mathbf{U}$  satisfying

$$\left( K + V + U(t) - i \frac{\partial}{\partial t} \right) |\Phi\rangle = |\Phi\rangle W(t), \quad (24)$$

$$\left( K + V + U'(t) - i \frac{\partial}{\partial t} \right) |\Phi'\rangle = |\Phi'\rangle W'(t), \quad (25)$$

always lead to

$$|\Phi\rangle \neq |\Phi'\rangle \quad (26)$$



if the potentials differ by more than a purely time-dependent ( $\mathbf{r}$ -independent) function:

$$U(t) \neq U'(t) + c(t). \quad (27)$$

Assuming that  $|\Phi\rangle = |\Phi'\rangle$  gives

$$(U(t) - U'(t))|\Phi\rangle = |\Phi\rangle(W(t) - W'(t)) \quad (28)$$

by subtracting both sides of Eq. (25) from Eq. (24). Since  $U(t)$  and  $U'(t)$  are multiplicative operators, Eq. (28) leads to

$$U(t) - U'(t) = W(t) - W'(t) \quad (29)$$

in contradiction to Eq. (27). So Eq. (26) is satisfied, and one concludes that the map  $C$  must be injective. ■

**Theorem 2.** The map  $D: \Phi \rightarrow \mathbf{N}$  is injective.

**Proof.** We show that  $|\Phi\rangle \neq |\Phi'\rangle \Rightarrow n(\mathbf{r}, t) \neq n'(\mathbf{r}, t)$ , where

$$n'(\mathbf{r}, t) = \langle \Phi' | \hat{n} | \Phi' \rangle. \quad (30)$$

Since the Hamiltonian is periodic in time, we have<sup>75</sup>

$$\begin{aligned} \{W(t)\}_T &= \left\langle \left\langle \Phi \left| K + V + U(t) - i \frac{\partial}{\partial t} \right| \Phi \right\rangle \right\rangle_T \\ &< \left\langle \left\langle \Phi' \left| K + V + U(t) - i \frac{\partial}{\partial t} \right| \Phi' \right\rangle \right\rangle_T, \end{aligned} \quad (31)$$

and we can write

$$\begin{aligned} &\left\langle \Phi' \left| K + V + U(t) - i \frac{\partial}{\partial t} \right| \Phi' \right\rangle \\ &= W'(t) + \langle \Phi' | U(t) - U'(t) | \Phi \rangle \\ &= W'(t) + \int d^3r n'(\mathbf{r}, t)(u(\mathbf{r}, t) - u'(\mathbf{r}, t)). \end{aligned} \quad (32)$$

By using Eqs. (31) and (32), we have

$$\begin{aligned} \{W(t)\}_T &< \{W'(t)\}_T \\ &+ \left\langle \int d^3r n'(\mathbf{r}, t)(u(\mathbf{r}, t) - u'(\mathbf{r}, t)) \right\rangle_T. \end{aligned} \quad (33)$$

Starting with  $\{W'(t)\}_T$ , we have the similar relation

$$\begin{aligned} \{W'(t)\}_T &< \{W(t)\}_T \\ &+ \left\langle \int d^3r n(\mathbf{r}, t)(u'(\mathbf{r}, t) - u(\mathbf{r}, t)) \right\rangle_T. \end{aligned} \quad (34)$$

Assuming that  $n(\mathbf{r}, t) = n'(\mathbf{r}, t)$  with the inequalities (33) and (34) leads to the obvious contradiction

$$\{W(t)\}_T + \{W'(t)\}_T < \{W'(t)\}_T + \{W(t)\}_T. \quad (35)$$

So we have

$$n(\mathbf{r}, t) \neq n'(\mathbf{r}, t), \quad (36)$$

and one concludes that the map  $D$  must be injective. ■

From the above two theorems, we can define unique inversion of the map  $D$ ,

$$D^{-1}: n(\mathbf{r}, t) \rightarrow \Phi[n], \quad (37)$$

and time-averaged expectation value of any observable over one period as a unique functional of the exact ground-Floquet state density. The full inverse map

$$(CD)^{-1}: n(\mathbf{r}, t) \rightarrow u(\mathbf{r}, t) \quad (38)$$

tells us that knowledge of the ground-Floquet state density determines the external potential of the system, and consequently the entire Hamiltonian. This corresponds to statement 1 of the Hohenberg–Kohn theorem for the ground-Floquet state, which is equivalent to the one given by Deb and Ghosh.<sup>39</sup>

Statement 2 is based on the variation principle for the ground-Floquet state.<sup>75,76</sup> It is important to recognize that the variational property of the quasienergy [Eq. (19)] is appropriate for the ground state of the system only when the applied frequency is chosen to ensure that transitions into excited states cannot occur. In this paper we consider only such cases. Statement 3 tells us that constrained search formulation for the ground-Floquet state is possible in the same way as for the stationary time-independent states, and this constrained search formulation is simpler than the one for arbitrary time-dependent potentials proposed by Kohl and Dreizler.<sup>85</sup>

### III. KOHN–SHAM EQUATION FOR THE GROUND-FLOQUET STATE

#### A. Noninteracting $v$ representability

As well as the stationary time-independent Kohn–Sham scheme,<sup>31,38</sup> we assume the existence of an auxiliary time-dependent system of noninteracting particles whose density is the same as that of the real time-dependent interacting system. In other words, the interacting  $v$ -representable densities of interest are assumed to be also noninteracting  $v$  representable. So the wave function for the ground-Floquet state of the noninteracting system  $\Phi_s$  can be written as a single determinant, and density  $n(\mathbf{r}, t)$  can be expressed with one-electron functions  $\{\tilde{\phi}_i\}$  appearing in  $\Phi_s$  as

$$n(\mathbf{r}, t) = 2 \sum_{i \in \text{occ}} |\tilde{\phi}_i(\mathbf{r}, t)|^2. \quad (39)$$

In Eq. (39) and later in this paper, we concentrate on the case of closed-shell systems. The wave function  $\Phi_s$  satisfies the Schrödinger equation

$$\left( H_s - i \frac{\partial}{\partial t} \right) |\Phi_s(t)\rangle = |\Phi_s(t)\rangle W_s(t), \quad (40)$$

where

$$H_s = K + U_s, \quad (41)$$

and one-body potential  $U_s$  is unknown in detail. Eq. (40) leads to equation for one-electron function as

$$\left( -\frac{1}{2} \nabla^2 + u_s(\mathbf{r}, t) - i \frac{\partial}{\partial t} \right) |\tilde{\phi}_i(\mathbf{r}, t)\rangle = |\tilde{\phi}_i(\mathbf{r}, t)\rangle w_i(t). \quad (42)$$

The detail of one-body potential  $U_s = \sum u_s$  is clarified later in this section. We call Eqs. (40) and (42) the TDKS equations, and one-electron function  $\tilde{\phi}_i(\mathbf{r}, t)$  is called the KS orbital.

## B. Coupling strength integration

As well as the coupling constant integration for stationary time-independent systems,<sup>86,87</sup> let us imagine a continuum of partially interacting systems, having the same density as the real interacting system, in which the interelectronic Coulomb repulsion is gradually switched on by a coupling parameter  $\lambda$  which ranges from  $\lambda=0$  (noninteracting limit) to  $\lambda=1$  (fully interacting limit). The Schrödinger equation for the ground-Floquet state of this partially interacting system can be expressed as

$$\left(H_\lambda - i \frac{\partial}{\partial t}\right) |\Phi_\lambda\rangle = |\Phi_\lambda\rangle W_\lambda(t). \quad (43)$$

The Hamiltonian  $H_\lambda$  at intermediate coupling strength is given by

$$H_\lambda = K + \lambda V + U_\lambda, \quad (44)$$

where  $U_\lambda = \sum u_\lambda$  is the one-body potential that generates the same density as the real interacting system. Clearly, at the extremes  $\lambda=0$  and  $\lambda=1$  we have

$$|\Phi_{\lambda=0}\rangle = |\Phi_s\rangle, \quad (45)$$

$$|\Phi_{\lambda=1}\rangle = |\Phi\rangle,$$

$$u_{\lambda=0}(\mathbf{r}, t) = u_s(\mathbf{r}, t), \quad (46)$$

$$u_{\lambda=1}(\mathbf{r}, t) = u(\mathbf{r}, t),$$

$$W_{\lambda=0}(t) = W_s, \quad (47)$$

$$W_{\lambda=1}(t) = W(t).$$

Time-dependent Hellmann–Feynman theorem<sup>79,88</sup> for parameter  $\lambda$  can be written as

$$\begin{aligned} \frac{\partial}{\partial \lambda} \left\langle \Phi_\lambda \left| H_\lambda - i \frac{\partial}{\partial t} \right| \Phi_\lambda \right\rangle + i \frac{\partial}{\partial t} \left\langle \Phi_\lambda \left| \frac{\partial \Phi_\lambda}{\partial \lambda} \right\rangle \right. \\ \left. = \left\langle \Phi_\lambda \left| \frac{H_\lambda}{\partial \lambda} \right| \Phi_\lambda \right\rangle, \right. \end{aligned} \quad (48)$$

and the right-hand side (rhs) of Eq. (48) can be expressed as

$$\begin{aligned} \left\langle \Phi_\lambda \left| \frac{H_\lambda}{\partial \lambda} \right| \Phi_\lambda \right\rangle = \int d^3 r n(\mathbf{r}, t) \frac{\partial u_\lambda(\mathbf{r}, t)}{\partial \lambda} \\ + \frac{1}{2} \int d^3 r_1 \int d^3 r_2 \frac{n(\mathbf{r}_1, t) n(\mathbf{r}_2, t)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ + \frac{1}{2} \int d^3 r_1 \int d^3 r_2 \sum_{\sigma, \sigma'} \frac{n_\sigma(\mathbf{r}_1, t)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ \times h_\lambda^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2, t), \end{aligned} \quad (49)$$

where  $h_\lambda^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2, t)$  is the  $\lambda$ -dependent hole function as well as the stationary time-independent case. Substituting Eq. (49) for the rhs of Eq. (48), we have

$$\begin{aligned} \frac{\partial W_\lambda}{\partial \lambda} + i \frac{\partial}{\partial t} \left\langle \Phi_\lambda \left| \frac{\partial \Phi_\lambda}{\partial \lambda} \right\rangle \right. \\ = \int d^3 r n(\mathbf{r}, t) \frac{\partial u_\lambda(\mathbf{r}, t)}{\partial \lambda} \\ + \frac{1}{2} \int d^3 r_1 \int d^3 r_2 \frac{n(\mathbf{r}_1, t) n(\mathbf{r}_2, t)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ + \frac{1}{2} \int d^3 r_1 \int d^3 r_2 \sum_{\sigma, \sigma'} \frac{n_\sigma(\mathbf{r}_1, t)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ \times h_\lambda^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2, t). \end{aligned} \quad (50)$$

Multiplying both sides of Eq. (50) by  $d\lambda$  and integrating it over  $\lambda$ , we have

$$\begin{aligned} W(t) - W_s(t) = \int d^3 r n(\mathbf{r}, t) (u(\mathbf{r}, t) - u_s(\mathbf{r}, t)) \\ + \frac{1}{2} \int d^3 r_1 \int d^3 r_2 \frac{n(\mathbf{r}_1, t) n(\mathbf{r}_2, t)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ + \frac{1}{2} \int d^3 r_1 \int d^3 r_2 \sum_{\sigma, \sigma'} \frac{n_\sigma(\mathbf{r}_1, t)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ \times h_{XC}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2, t) - i \frac{\partial}{\partial t} \int_0^1 d\lambda \left\langle \Phi_\lambda \left| \frac{\partial \Phi_\lambda}{\partial \lambda} \right\rangle, \right. \end{aligned} \quad (51)$$

where  $h_{XC}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2, t)$  is the integrated exchange-correlation hole function defined by

$$h_{XC}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2, t) = \int_0^1 d\lambda h_\lambda^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2, t). \quad (52)$$

Time averaging Eq. (51) over one period, we have

$$\begin{aligned} \{W(t)\}_T - \{W_s(t)\}_T \\ = \frac{1}{T} \int_0^T dt \int d^3 r n(\mathbf{r}, t) (u(\mathbf{r}, t) - u_s(\mathbf{r}, t)) \\ + \frac{1}{T} \int_0^T dt \frac{1}{2} \int d^3 r_1 \int d^3 r_2 \frac{n(\mathbf{r}_1, t) n(\mathbf{r}_2, t)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ + \frac{1}{T} \int_0^T dt \frac{1}{2} \int d^3 r_1 \int d^3 r_2 \\ \times \sum_{\sigma, \sigma'} \frac{n_\sigma(\mathbf{r}_1, t)}{|\mathbf{r}_1 - \mathbf{r}_2|} h_{XC}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2, t), \end{aligned} \quad (53)$$

where we have used

$$\left\{ i \frac{\partial}{\partial t} \int_0^1 d\lambda \left\langle \Phi_\lambda \left| \frac{\partial \Phi_\lambda}{\partial \lambda} \right\rangle \right\}_T = 0. \quad (54)$$

Considering Eq. (40) with Eq. (41), quasienergy for the noninteracting system can be expressed as

$$\{W_s(t)\}_T = \{B_s(t)\}_T + \frac{1}{T} \int_0^T dt \int d^3 r n(\mathbf{r}, t) u_s(\mathbf{r}, t), \quad (55)$$

with

$$\{B_s(t)\}_T = \frac{1}{T} \int_0^T dt \left\langle \Phi_s(t) \left| K - i \frac{\partial}{\partial t} \right| \Phi_s(t) \right\rangle. \quad (56)$$

By using Eqs. (53) and (55), quasienergy for a real interacting system can be expressed as

$$\begin{aligned} \{W(t)\}_T = & \{B_s(t)\}_T + \frac{1}{T} \int_0^T dt \int d^3r n(\mathbf{r}, t) u(\mathbf{r}, t) \\ & + \frac{1}{2T} \int_0^T dt \int d^3r_1 \int d^3r_2 \frac{n(\mathbf{r}_1, t) n(\mathbf{r}_2, t)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ & + \frac{1}{T} \int_0^T dt W_{XC}(t), \end{aligned} \quad (57)$$

where we have defined the time-dependent exchange-correlation quasienergy as

$$W_{XC}(t) = \frac{1}{2} \int d^3r_1 \int d^3r_2 \sum_{\sigma, \sigma'} \frac{n_{\sigma}(\mathbf{r}_1, t)}{|\mathbf{r}_1 - \mathbf{r}_2|} h_{XC}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2, t). \quad (58)$$

Thanks to the periodicity of the system in time, we can consider the time-dependent exchange-correlation quasienergy  $W_{XC}(t)$  to be instantaneous, and it has no retardation effects. If we do not assume the periodicity, we cannot use Eq. (54), and the time-dependent exchange-correlation quasienergy will become more complex. Although our formulation is limited to the ground-Floquet state, it is sufficient for the calculation of frequency-dependent polarizabilities, hyperpolarizabilities, and excitation energies. It should be stressed that our formulation is simpler than time-dependent adiabatic connection for arbitrary time-dependent potentials proposed by Görling.<sup>89</sup>

### C. Exchange-correlation potential

Let us clarify the detail of one-body potential  $u_s(\mathbf{r}, t)$  in TDKS equation (42) by using a variational condition. Considering Eq. (57), the quasienergy functional for the real interacting system can be written as

$$\begin{aligned} \bar{W}[n] = & \bar{B}_s[n] + \frac{1}{T} \int_0^T dt \int d^3r n(\mathbf{r}, t) u(\mathbf{r}, t) \\ & + \frac{1}{2T} \int_0^T dt \int d^3r_1 \int d^3r_2 \frac{n(\mathbf{r}_1, t) n(\mathbf{r}_2, t)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ & + \bar{W}_{XC}[n], \end{aligned} \quad (59)$$

with

$$\bar{B}_s[n] = \frac{1}{T} \int_0^T dt \left\langle \Phi_s[n] \left| K - i \frac{\partial}{\partial t} \right| \Phi_s[n] \right\rangle. \quad (60)$$

The Hohenberg–Kohn variation principle [Eq. (19)] ensures that the quasienergy functional is stationary for small variations  $\delta n(\mathbf{r}, t)$  around the exact density  $n_{\text{exact}}(\mathbf{r}, t)$ , i.e.,

$$\begin{aligned} 0 = & \left. \frac{\delta \bar{B}_s}{\delta n(\mathbf{r}, t)} \right|_{n=n_{\text{exact}}} + u(\mathbf{r}, t) + \int d^3r' \frac{n_{\text{exact}}(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \\ & + \left. \frac{\delta \bar{W}_{XC}}{\delta n(\mathbf{r}, t)} \right|_{n=n_{\text{exact}}}. \end{aligned} \quad (61)$$

The variation  $\delta \bar{B}_s$  is given by

$$\begin{aligned} \delta \bar{B}_s = & \delta \sum_{i \in \text{occ}} \frac{1}{T} \int_0^T dt \langle \tilde{\phi}_i[n_{\text{exact}}] | \left( -\frac{1}{2} \nabla^2 - i \frac{\partial}{\partial t} \right) | \tilde{\phi}_i[n_{\text{exact}}] \rangle \\ = & \delta \left[ \sum_{i \in \text{occ}} \int_0^T dt w_i(t) - \frac{1}{T} \int_0^T dt \int d^3r \right. \\ & \left. \times u_s(\mathbf{r}, t) n_{\text{exact}}(\mathbf{r}, t) \right], \end{aligned} \quad (62)$$

where the one-particle equation (42) has been used. The variation of the time-dependent one-particle quasienergy  $w_i(t)$  can be calculated using the first-order perturbation theory<sup>84</sup> yielding

$$\delta \left[ \frac{1}{T} \int_0^T dt w_i(t) \right] = \frac{1}{T} \int_0^T dt \langle \tilde{\phi}_i | \delta u_s(\mathbf{r}, t) | \tilde{\phi}_i \rangle. \quad (63)$$

Using Eq. (63) in Eq. (62) gives

$$\delta \bar{B}_s = - \frac{1}{T} \int_0^T dt \int d^3r u_s(\mathbf{r}, t) \delta n(\mathbf{r}, t), \quad (64)$$

which, combined with Eq. (61) leads to

$$u_s(\mathbf{r}, t) = u(\mathbf{r}, t) + \int d^3r' \frac{n_{\text{exact}}(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + u_{XC}(\mathbf{r}, t), \quad (65)$$

where we have defined the exchange-correlation potential as

$$u_{XC}(\mathbf{r}, t) = \left. \frac{\delta \bar{W}_{XC}}{\delta n(\mathbf{r}, t)} \right|_{n=n_{\text{exact}}}. \quad (66)$$

Thus, we have obtained the explicit expression for the one-electron potential of the TDKS equation. In this section, it should be stressed that the exchange-correlation potential for the TDKS equation has been defined in concise form without resorting to the adiabatic approximation<sup>33,34,68</sup> by using the QEDM approach on the assumption of the existence of the Floquet states. On the other hand, most of the previous TDKS equations are based on the variational condition to action integral, whose time interval is not rigorously defined, as proposed by Runge and Gross,<sup>41</sup> and the time-dependent exchange-correlation potential depends on the undefined initial and final time of the action integral.

## IV. RESPONSE PROPERTIES FROM TDDFT BY USING QEDM

### A. Algebraic representation

We write the wave function  $\Phi_s(t)$  in the TDKS equation (40) as

$$|\Phi_s(t)\rangle = \exp(\kappa) |\text{KS}\rangle, \quad (67)$$

where  $|\text{KS}\rangle$  is the single determinant consisting of KS occupied orbitals in the absence of external electric field  $U^{(1)}$ , and

$$\kappa = \sum_{a,i} \{E_{ai} \kappa_{ai}(t) - E_{ia} \kappa_{ai}^*(t)\}, \quad (68)$$

with

$$E_{pq} = \sum_{\sigma} a_{p\sigma}^{\dagger} a_{q\sigma}. \quad (69)$$

We use the usual creation operator  $a_{p\sigma}^{\dagger}$  and annihilation operator  $a_{p\sigma}$ , where  $\sigma$  is the spin index. We use indices  $\{p, q, r, \dots\}$ ,  $\{i, j, k, \dots\}$ , and  $\{a, b, c, \dots\}$  to denote arbitrary, occupied, and virtual KS orbitals. Introducing the following notation

$$E_{\lambda} \equiv E_{ai}, \quad \kappa_{\lambda}(t) \equiv \kappa_{ai}(t) \quad (70)$$

with the negative-sign index  $-\lambda$  denoting

$$E_{-\lambda} \equiv E_{\lambda}^{\dagger}, \quad \kappa_{-\lambda}(t) \equiv -\kappa_{\lambda}^*(t), \quad (71)$$

we can rewrite Eq. (68) as

$$\kappa = \sum_{\lambda} \{E_{\lambda} \kappa_{\lambda}(t) + E_{-\lambda} \kappa_{-\lambda}(t)\} \equiv \sum_{\pm\lambda} E_{\lambda} \kappa_{\lambda}(t). \quad (72)$$

The density operator  $\hat{n}$  can be written with the KS orbitals in the absence of external electric field as

$$\hat{n} = \sum_{pq} E_{pq} \phi_p^*(\mathbf{r}) \phi_q(\mathbf{r}), \quad (73)$$

and the electron density can be expressed as

$$n(\mathbf{r}, t) = \sum_{pq} \langle \text{KS} | \exp(-\kappa) E_{pq} \exp(\kappa) | \text{KS} \rangle \phi_p^*(\mathbf{r}) \phi_q(\mathbf{r}). \quad (74)$$

We can decompose the density as

$$n(\mathbf{r}, t) = n^{(0)}(\mathbf{r}) + n'(\mathbf{r}, t), \quad (75)$$

where  $n^{(0)}(\mathbf{r})$  is independent of external electric field, and  $n'(\mathbf{r}, t)$  is expressed as

$$n'(\mathbf{r}, t) = \sum_{pq} \langle \text{KS} | \exp(-\kappa) E_{pq} \exp(\kappa) | \text{KS} \rangle \times \phi_p^*(\mathbf{r}) \phi_q(\mathbf{r}) - 2 \sum_{i \in \text{occ}} \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}). \quad (76)$$

The quasienergy functional  $\bar{W}[n]$  [Eq. (59)] can be written as

$$\begin{aligned} \bar{W}[n] = & \frac{1}{T} \int_0^T dt \left\langle \text{KS} \left| \exp(-\kappa) \left( K - i \frac{\partial}{\partial t} \right) \exp(\kappa) \right| \text{KS} \right\rangle + \frac{1}{T} \int_0^T dt \left\{ \langle \text{KS} | \exp(-\kappa) U^{(0)} \exp(\kappa) | \text{KS} \rangle \right. \\ & \left. - \sum_i \exp(-i\omega_i t) \sum_{\alpha} \epsilon_{\alpha}(\omega_i) \langle \text{KS} | \exp(-\kappa) M_{\alpha} \exp(\kappa) | \text{KS} \rangle \right\} \\ & + \frac{1}{2T} \int_0^T dt \sum_{pqrs} \langle \text{KS} | \exp(-\kappa) E_{pq} \exp(\kappa) | \text{KS} \rangle \langle \text{KS} | \exp(-\kappa) E_{rs} \exp(\kappa) | \text{KS} \rangle I_{pqrs} + \bar{W}_{XC}[n], \end{aligned} \quad (77)$$

where

$$I_{pqrs} = \int d^3r_1 \int d^3r_2 \frac{\phi_p^*(\mathbf{r}_1) \phi_q(\mathbf{r}_1) \phi_r^*(\mathbf{r}_2) \phi_s(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (78)$$

In order to express  $\bar{W}_{XC}[n]$  explicitly with  $\kappa$ , we introduce the functional Taylor expansion<sup>90</sup> of  $\bar{W}_{XC}[n]$  around  $n = n^{(0)}(\mathbf{r})$  as

$$\begin{aligned} \bar{W}_{XC}[n] = & \bar{W}_{XC}[n]|_{n^{(0)}} + \frac{1}{T} \int_0^T dt_1 \int d^3r_1 \left. \frac{\delta \bar{W}_{XC}}{\delta n(\mathbf{r}_1, t_1)} \right|_{n^{(0)}} n'(\mathbf{r}_1, t_1) \\ & + \frac{1}{2T^2} \int_0^T dt_1 \int_0^T dt_2 \int d^3r_1 \int d^3r_2 \left. \frac{\delta^2 \bar{W}_{XC}}{\delta n(\mathbf{r}_1, t_1) \delta n(\mathbf{r}_2, t_2)} \right|_{n^{(0)}} n'(\mathbf{r}_1, t_1) n'(\mathbf{r}_2, t_2) \\ & + \frac{1}{6T^3} \int_0^T dt_1 \int_0^T dt_2 \int_0^T dt_3 \int d^3r_1 \int d^3r_2 \int d^3r_3 \left. \frac{\delta^3 \bar{W}_{XC}}{\delta n(\mathbf{r}_1, t_1) \delta n(\mathbf{r}_2, t_2) \delta n(\mathbf{r}_3, t_3)} \right|_{n^{(0)}} n'(\mathbf{r}_1, t_1) n'(\mathbf{r}_2, t_2) n'(\mathbf{r}_3, t_3) \\ & + \dots \end{aligned} \quad (79)$$

Considering Eq. (58), time-dependent exchange-correlation quasienergy is instantaneous and it has no retardation effect. So we can express the exchange-correlation quasienergy functional by using the exchange-correlation energy functional for the stationary time-independent system as

$$\bar{W}_{XC}[n] = \frac{1}{T} \int_0^T dt E_{XC}[n]|_{n=n(\mathbf{r}, t)}. \quad (80)$$

This type of relation [Eq. (80)] has been employed as an approximation (the adiabatic approximation<sup>33,34,68</sup>) to formu-



late TDDFT. On the contrary, it should be noted that Eq. (80) holds *exactly* for our ground-Floquet state, and we can write

$$\bar{W}_{XC}[n]|_{n(0)} = E_{XC}[n]|_{n(0)}, \quad (81)$$

$$\left. \frac{\delta \bar{W}_{XC}}{\delta n(\mathbf{r}_1, t_1)} \right|_{n(0)} = \left. \frac{\delta E_{XC}}{\delta n(\mathbf{r}_1)} \right|_{n(0)} = u_{XC}^{(0)}(\mathbf{r}_1), \quad (82)$$

$$\left. \frac{\delta^2 \bar{W}_{XC}}{\delta n(\mathbf{r}_1, t_1) \delta n(\mathbf{r}_2, t_2)} \right|_{n(0)} = \delta_p(t_1 - t_2) \left. \frac{\delta^2 E_{XC}}{\delta n(\mathbf{r}_1) \delta n(\mathbf{r}_2)} \right|_{n(0)} \\ = \delta_p(t_1 - t_2) f_{XC}^{(0)}(\mathbf{r}_1, \mathbf{r}_2), \quad (83)$$

$$\left. \frac{\delta^3 \bar{W}_{XC}}{\delta n(\mathbf{r}_1, t_1) \delta n(\mathbf{r}_2, t_2) \delta n(\mathbf{r}_3, t_3)} \right|_{n(0)} \\ = \delta_p(t_1 - t_2) \delta_p(t_2 - t_3) \left. \frac{\delta^3 E_{XC}}{\delta n(\mathbf{r}_1) \delta n(\mathbf{r}_2) \delta n(\mathbf{r}_3)} \right|_{n(0)} \\ = \delta_p(t_1 - t_2) \delta_p(t_2 - t_3) g_{XC}^{(0)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3), \quad (84)$$

where  $\delta_p(t)$  is the periodic delta function which satisfies the following relations:

$$\frac{1}{T} \int_0^T dt \delta_p(t) = 1, \quad (85)$$

$$\frac{1}{T} \int_0^T dt \delta_p(t - t_1) f(t) = f(t_1). \quad (86)$$

The functional Taylor expansion of  $\bar{W}_{XC}[n]$  [Eq. (79)] with Eqs. (81)–(84) etc. completes formal expression with the parameters  $\{\kappa_\lambda\}$ .

## B. Response equations

In order to obtain explicit expressions for response properties perturbatively defined with respect to external electric field, we derive response equations called coupled-perturbed TDKS equations in the QEDM manner.

Let us introduce the expansion of  $\kappa$  with respect to the external field<sup>23,24,79,80</sup> as

$$\kappa = \sum_{\pm\lambda} E_\lambda \kappa_\lambda(t) \\ = \sum_i \exp(-\omega_i t) \sum_\alpha \epsilon_\alpha(\omega_i) \kappa^\alpha(\omega_i) \\ + \frac{1}{2} \sum_{i,j} \exp[-i(\omega_i + \omega_j)t] \sum_{\alpha,\beta} \epsilon_\alpha(\omega_i) \epsilon_\beta(\omega_j) \\ \times \kappa^{\alpha\beta}(\omega_i, \omega_j) + \frac{1}{6} \sum_{i,j,k} \exp[-i(\omega_i + \omega_j + \omega_k)t] \\ \times \sum_{\alpha,\beta,\gamma} \epsilon_\alpha(\omega_i) \epsilon_\beta(\omega_j) \epsilon_\gamma(\omega_k) \kappa^{\alpha\beta\gamma}(\omega_i, \omega_j, \omega_k) + \dots, \quad (87)$$

with

$$\kappa^\alpha(\omega_i) = \sum_{\pm\lambda} E_\lambda \kappa_\lambda^\alpha(\omega_i), \quad (88)$$

$$\kappa^{\alpha\beta}(\omega_i, \omega_j) = \sum_{\pm\lambda} E_\lambda \kappa_\lambda^{\alpha\beta}(\omega_i, \omega_j), \quad (89)$$

$$\kappa^{\alpha\beta\gamma}(\omega_i, \omega_j, \omega_k) = \sum_{\pm\lambda} E_\lambda \kappa_\lambda^{\alpha\beta\gamma}(\omega_i, \omega_j, \omega_k), \quad (90)$$

and

$$\kappa_{-\lambda}^\alpha(\omega_i) \equiv -\kappa_\lambda^\alpha(-\omega_i)^*, \quad (91)$$

$$\kappa_{-\lambda}^{\alpha\beta}(\omega_i, \omega_j) \equiv -\kappa_\lambda^{\alpha\beta}(-\omega_i, -\omega_j)^*, \quad (92)$$

$$\kappa_{-\lambda}^{\alpha\beta\gamma}(\omega_i, \omega_j, \omega_k) \equiv -\kappa_\lambda^{\alpha\beta\gamma}(-\omega_i, -\omega_j, -\omega_k)^*. \quad (93)$$

We write the formal expansion of  $\bar{W}$  with respect to the external field as  $\bar{W} = \bar{W}^{(0)} + \bar{W}^{(1)} + \bar{W}^{(2)} + \dots$ .

Since the quasienergy functional  $\bar{W}$  [Eq. (77)] is completely expressed with the parameters  $\{\kappa_\lambda\}$ , the Hohenberg–Kohn variation principle [Eq. (19)] can be considered as the variational condition of  $\bar{W}$  with respect to  $\{\kappa_\lambda\}$ . So considering the variational condition  $\partial \bar{W}^{(1)} / \partial \kappa_\lambda^A(0) = 0$ , we can obtain the zeroth-order response equation as

$$\langle \text{KS} | [H_s^{(0)}, E_\lambda] | \text{KS} \rangle = 0, \quad (94)$$

where  $H_s^{(0)}$  is the KS Hamiltonian in the absence of external electric field. If the KS equation in the absence of external electric field is solved, Eq. (94) is already satisfied.

Similarly, considering the variational condition  $\partial \bar{W}^{(2)} / \partial \kappa_\lambda^A(-\omega_1) = 0$ , we can obtain the first-order response equation as

$$-\langle \text{KS} | [M_B, E_\lambda] | \text{KS} \rangle + \langle \text{KS} | [H_s^{(0)}; E_\lambda, \kappa^B(\omega_1)] | \text{KS} \rangle \\ - \omega_1 \langle \text{KS} | [\kappa^B(\omega_1), E_\lambda] | \text{KS} \rangle \\ + \frac{1}{2} \sum_{pqrs} \langle \text{KS} | [E_{pq}, E_\lambda] | \text{KS} \rangle \\ \times \langle \text{KS} | [E_{rs}, \kappa^B(\omega_1)] | \text{KS} \rangle (I_{pqrs} + I_{rspq} + f_{pqrs} + f_{rspq}) \\ = 0, \quad (95)$$

and this equation can be rewritten in the matrix form as

$$\left[ \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} - \omega_1 \begin{pmatrix} \mathbf{S} & \mathbf{\Delta} \\ -\mathbf{\Delta}^* & -\mathbf{S}^* \end{pmatrix} \right] \begin{pmatrix} \mathbf{K}^B & (\omega_1) \\ -\mathbf{K}^{B*} & (-\omega_1) \end{pmatrix} \\ = \begin{pmatrix} \mathbf{m}^B \\ -\mathbf{m}^{B*} \end{pmatrix}, \quad (96)$$

where

$$A_{\nu\mu} = -\langle \text{KS} | [H_s^{(0)}; E_{-\nu}, E_\mu] | \text{KS} \rangle \\ - \frac{1}{2} \sum_{pqrs} \langle \text{KS} | [E_{pq}, E_{-\nu}] | \text{KS} \rangle \langle \text{KS} | [E_{rs}, E_\mu] | \text{KS} \rangle \\ \times (I_{pqrs} + I_{rspq} + f_{pqrs} + f_{rspq}), \quad (97)$$

$$B_{\nu\mu} = -\frac{1}{2} \sum_{pqrs} \langle \text{KS} | [E_{pq}, E_{-\nu}] | \text{KS} \rangle \langle \text{KS} | [E_{rs}, E_{-\mu}] | \text{KS} \rangle \times (I_{pqrs} + I_{rspq} + f_{pqrs} + f_{rspq}), \quad (98)$$

$$S_{\nu\mu} = \langle \text{KS} | [E_{-\nu}, E_{\mu}] | \text{KS} \rangle, \quad (99)$$

$$\Delta_{\nu\mu} = \langle \text{KS} | [E_{-\nu}, E_{-\mu}] | \text{KS} \rangle, \quad (100)$$

$$K_{\mu}^B(\omega_1) = \kappa_{\mu}^B(\omega_1), \quad (101)$$

$$m_{\mu}^B = -\langle \text{KS} | [M_B, E_{-\mu}] | \text{KS} \rangle, \quad (102)$$

$$f_{pqrs} = \int d^3r_1 \int d^3r_2 f_{XC}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) \phi_p^*(\mathbf{r}_1) \times \phi_q(\mathbf{r}_1) \phi_r^*(\mathbf{r}_2) \phi_s(\mathbf{r}_2), \quad (103)$$

and we have defined the  $n$ -tuple symmetric commutator

$$[A; B_1, B_2, \dots, B_n] = \frac{1}{n!} \mathcal{P}(1, 2, \dots, n) \times [\dots [ [A, B_1], B_2 ], \dots ], B_n], \quad (104)$$

where  $\mathcal{P}(1, 2, \dots, n)$  is a permutation operator which contains the  $n!$  permutations of indices  $1, 2, \dots, n$ .

The higher-order response equations can be obtained in the same way. However, response equations up to first order are sufficient for the calculation of first hyperpolarizability which is the third-order response property since we can apply the  $2n+1$  rule.<sup>83</sup>

### C. Response properties

By using QEDM,<sup>23,24,79,80</sup> we can write the expressions for permanent electric dipole moment, frequency-dependent polarizability, and first hyperpolarizabilities as

$$\mu_A = - \left. \frac{\partial \bar{W}}{\partial \epsilon_A(0)} \right|_{\epsilon=0} = \langle \text{KS} | M_A | \text{KS} \rangle, \quad (105)$$

$$\alpha_{AB}(-\omega_1; \omega_1) = - \left. \frac{\partial^2 \bar{W}}{\partial \epsilon_A(-\omega_1) \partial \epsilon_B(\omega_1)} \right|_{\epsilon=0} = \langle \text{KS} | [M_A, \kappa^B(\omega_1)] | \text{KS} \rangle, \quad (106)$$

$$\begin{aligned} \beta_{ABC}(-\omega_{\sigma}; \omega_1, \omega_2) &= - \left. \frac{\partial^3 \bar{W}}{\partial \epsilon_A(-\omega_{\sigma}) \partial \epsilon_B(\omega_1) \partial \epsilon_C(\omega_2)} \right|_{\epsilon=0} \\ &= \mathcal{P}[A(-\omega_1), B(\omega_1), C(\omega_2)] \left\{ \frac{1}{2} \langle \text{KS} | [M_A; \kappa^B(\omega_1), \kappa^C(\omega_2)] | \text{KS} \rangle \right. \\ &\quad - \frac{1}{4} \sum_{pqrs} \langle \text{KS} | [E_{pq}; \kappa^A(-\omega_{\sigma}), \kappa^B(\omega_1)] | \text{KS} \rangle \langle \text{KS} | [E_{rs}, \kappa^C(\omega_2)] | \text{KS} \rangle (I_{pqrs} + I_{rspq} + f_{pqrs} + f_{rspq}) \\ &\quad \left. - \frac{1}{6} \sum_{pqrst} \langle \text{KS} | [E_{pq}, \kappa^A(\omega_{\sigma})] | \text{KS} \rangle \langle \text{KS} | [E_{rs}, \kappa^B(\omega_1)] | \text{KS} \rangle \langle \text{KS} | [E_{tu}, \kappa^C(\omega_2)] | \text{KS} \rangle g_{pqrst} \right\}, \quad (107) \end{aligned}$$

where

$$g_{pqrst} = \int d^3r_1 \int d^3r_2 \int d^3r_3 g_{XC}^{(0)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \phi_p^*(\mathbf{r}_1) \phi_q(\mathbf{r}_1) \phi_r^*(\mathbf{r}_2) \phi_s(\mathbf{r}_2) \phi_t^*(\mathbf{r}_3) \phi_u(\mathbf{r}_3), \quad (108)$$

and we have used the permutation operator  $\mathcal{P}[A_1(\omega_1), A_2(\omega_2), \dots, A_n(\omega_n)]$  which contains the  $n!$  permutations of spatial indices  $A_1, A_2, \dots, A_n$  accompanied by their associated frequencies  $\omega_1, \omega_2, \dots, \omega_n$ . The expression for permanent dipole moment [Eq. (105)] is similar to the one derived by Colwell *et al.*<sup>91</sup> The expression for frequency-dependent polarizability [Eq. (106)] is similar to the one derived previously.<sup>47,56</sup> In the static limit, the expression for frequency-dependent first hyperpolarizability [Eq. (107)] is similar to the one derived by Colwell *et al.*<sup>91</sup> However, in contrast to the previous derivations, it should be noted that our expression is obtained without any approximation on the assumption of the existence of the Floquet states.

Furthermore, the spectral representation of frequency-dependent polarizability and first hyperpolarizability can be written as

$$\alpha_{AB}(-\omega_1; \omega_1) = \mathcal{P}[A(-\omega_1), B(\omega_1)] \left\{ \sum_{\pm\alpha} \text{sgn}(\alpha) \frac{\langle \text{KS} | [M_A, O_{\alpha}^{\dagger}] | \text{KS} \rangle \langle \text{KS} | [O_{\alpha}, M_B] | \text{KS} \rangle}{\omega_{\alpha} - \omega_1} \right\}, \quad (109)$$

$$\begin{aligned}
\beta_{ABC}(-\omega_\sigma; \omega_1, \omega_2) = & \mathcal{P}[A(-\omega_\sigma), B(\omega_1), C(\omega_2)] \\
& \times \left\{ \frac{1}{2} \sum_{\pm\alpha, \pm\beta} \text{sgn}(\alpha\beta) \frac{\langle \text{KS} | [M_A; O_\alpha^\dagger, O_\beta^\dagger] | \text{KS} \rangle \langle \text{KS} | [O_\alpha, M_B] | \text{KS} \rangle \langle \text{KS} | [O_\beta, M_C] | \text{KS} \rangle}{(\omega_\alpha - \omega_1)(\omega_\beta - \omega_2)} \right. \\
& - \sum_{\pm\alpha, \pm\beta, \pm\gamma} \text{sgn}(\alpha\beta\gamma) \frac{\langle \text{KS} | [O_\alpha, M_A] | \text{KS} \rangle \langle \text{KS} | [O_\beta, M_B] | \text{KS} \rangle \langle \text{KS} | [O_\gamma, M_C] | \text{KS} \rangle}{(\omega_\alpha + \omega_\sigma)(\omega_\beta - \omega_1)(\omega_\gamma - \omega_2)} \\
& \times \left( \frac{1}{4} \sum_{pqrs} \langle \text{KS} | [E_{pq}; O_\alpha^\dagger, O_\beta^\dagger] | \text{KS} \rangle \langle \text{KS} | [E_{rs}, O_\gamma^\dagger] | \text{KS} \rangle (I_{pqrs} + I_{rspq} + f_{pqrs} + f_{rspq}) \right. \\
& \left. \left. + \frac{1}{6} \sum_{pqrst} \langle \text{KS} | [E_{pq}, O_\alpha^\dagger] | \text{KS} \rangle \langle \text{KS} | [E_{rs}, O_\beta^\dagger] | \text{KS} \rangle \langle \text{KS} | [E_{tu}, O_\gamma^\dagger] | \text{KS} \rangle g_{pqrst} \right) \right\}, \quad (110)
\end{aligned}$$

where we have used the diagonalized (de)excitation operators  $\{O_\alpha^\dagger, O_\alpha\}$

$$O_\alpha^\dagger = \sum_\lambda (E_\lambda X_{\lambda\alpha} + E_{-\lambda} Y_{\lambda\alpha}) \quad (111)$$

$$O_\alpha = \sum_\lambda (E_\lambda Y_{\lambda\alpha}^* + E_{-\lambda} X_{\lambda\alpha}^*).$$

The coefficients  $\{X_{\lambda\alpha}, Y_{\lambda\alpha}\}$  are the elements of the eigenvector for the RPA-like equation

$$\left[ \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} - \omega_\alpha \begin{pmatrix} \mathbf{S} & \mathbf{\Delta} \\ -\mathbf{\Delta}^* & -\mathbf{S}^* \end{pmatrix} \right] \begin{pmatrix} \mathbf{X}_\alpha \\ \mathbf{Y}_\alpha \end{pmatrix} = \begin{pmatrix} \mathbf{0} \\ \mathbf{0} \end{pmatrix}, \quad \omega_\alpha > 0, \quad (112)$$

and we have used the following notations:

$$\omega_{-\alpha} = -\omega_\alpha, \quad O_{\pm\alpha}^\dagger = O_{\mp\alpha} \quad (113)$$

$$\text{sgn}(\alpha) = \begin{cases} 1 & (\alpha > 0) \\ -1 & (\alpha < 0) \end{cases}. \quad (114)$$

Since the spectral representation of frequency-dependent polarizability [Eq. (109)] corresponds to the exact SOS expression,<sup>71</sup> we can consider poles  $\{\omega_\alpha\}$ , calculated as the eigenvalues for RPA-like equation (112), to be the vertical excitation energies. The RPA-like equation (112) is similar to the one derived previously.<sup>34,45,47</sup> However, in contrast to the previous derivations, our derivation is obtained without any approximation on the assumption of the existence of the Floquet states. From the residue analysis, we can define transition moments between ground state  $|0\rangle$  and excited state  $|\alpha\rangle$  as

$$\langle 0 | M_A | \alpha \rangle = \langle \text{KS} | [M_A, O_\alpha^\dagger] | \text{KS} \rangle, \quad (115)$$

$$\langle \alpha | M_A | 0 \rangle = \langle \text{KS} | [O_\alpha, M_A] | \text{KS} \rangle. \quad (116)$$

We can automatically obtain the explicit expressions for response properties which satisfy the  $2n+1$  rule<sup>83</sup> by using QEDM. Since the KS state satisfies the following time-averaged time-dependent Hellmann–Feynman theorem<sup>23,88</sup> for parameter  $\epsilon_A(\omega)$  as

$$\frac{\partial \bar{W}}{\partial \epsilon_A(\omega)} = -\frac{1}{T} \int_0^T dt \exp(-i\omega t) \int d^3r n(\mathbf{r}, t) r_A, \quad (117)$$

expressions for response properties derived from quasienergy derivatives [the lhs of Eq. (117)] are equivalent to those based on the density [the rhs of Eq. (117)]. However, it should be noted that the definition based on the density does not immediately lead to expressions which satisfy the  $2n+1$  rule.

## V. CONCLUDING REMARKS

We have formulated TDDFT in periodic external potentials in time on the assumption of the existence of the Floquet states from the quasienergy viewpoint. The Hohenberg–Kohn theorem for the ground-Floquet state is reformulated in terms of quasienergy expression, and the Kohn–Sham equation for the ground-Floquet state is verified. Coupling strength integration, which connects a noninteracting system with a real interacting system, is introduced by using the time-dependent Hellmann–Feynman theorem. Exchange-correlation potential is defined by the variational condition to the quasienergy functional. Response equations, which are the coupled perturbed TDKS equations, are derived in the QEDM manner, and explicit expressions for frequency-dependent polarizability and first hyperpolarizability are given by using QEDM. Excitation energies and transition moments are defined from poles and residues of frequency-dependent polarizabilities, respectively.

In contrast to the previous TDDFT, our formulation has the following three advantages: (1) The time-dependent exchange-correlation potential is defined by the functional derivative of the exchange-correlation quasienergy. (2) The formal expression for frequency-dependent polarizability, which corresponds to the exact SOS expression, can be obtained. (3) Explicit expressions for response properties which satisfy the  $2n+1$  rule can be automatically obtained by using QEDM.

The exchange-correlation potential suitable for the calculation of response properties will be considered in the future. We would like to also consider the response theory in the time-dependent OEP method from the quasienergy viewpoint.

## ACKNOWLEDGMENT

The authors are grateful to Y. Nakasaki for his helpful comments and discussions.

- <sup>1</sup>J. B. Foresman, M. Head-Gordon, J. A. Pople, and M. J. Frisch, *J. Phys. Chem.* **96**, 135 (1992).
- <sup>2</sup>T. H. Dunning and V. McKoy, *J. Chem. Phys.* **47**, 1735 (1967).
- <sup>3</sup>P. Jørgensen, *Annu. Rev. Phys. Chem.* **26**, 359 (1975).
- <sup>4</sup>H. Nakatsuji, *Chem. Phys. Lett.* **59**, 362 (1978); **67**, 329, 334 (1979).
- <sup>5</sup>H. Sekino and R. J. Bartlett, *Int. J. Quantum Chem., Symp.* **18**, 255 (1984); J. F. Stanton and R. J. Bartlett, *J. Chem. Phys.* **98**, 7029 (1993).
- <sup>6</sup>H. Koch, H. J. Aa. Jensen, P. Jørgensen, and T. Helgaker, *J. Chem. Phys.* **93**, 3345 (1990).
- <sup>7</sup>O. Christiansen, H. Koch, A. Haliker, P. Jørgensen, T. Helgaker, and A. S. de Merás, *J. Chem. Phys.* **105**, 6921 (1996).
- <sup>8</sup>R. J. Buenker and S. D. Peyerimhoff, *Theor. Chim. Acta* **35**, 33 (1974); **39**, 217 (1975).
- <sup>9</sup>H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **89**, 5803 (1988).
- <sup>10</sup>P.-Å. Malmqvist, A. Rendell, and B. O. Roos, *J. Phys. Chem.* **94**, 5477 (1990); K. Anderson, P.-Å. Malmqvist, B. O. Roos, J. A. Sadlej, and K. Wolinski, *ibid.* **94**, 5483 (1990).
- <sup>11</sup>K. Hirao, *Chem. Phys. Lett.* **190**, 374 (1992); **201**, 59 (1993).
- <sup>12</sup>P. M. Kozłowski and E. R. Davidson, *J. Chem. Phys.* **100**, 3672 (1994).
- <sup>13</sup>E. Dalggaard, *Phys. Rev. A* **26**, 42 (1982).
- <sup>14</sup>H. Sekino and R. J. Bartlett, *J. Chem. Phys.* **85**, 976 (1986).
- <sup>15</sup>J. E. Rice, R. D. Amos, S. M. Colwell, N. C. Handy, and J. Sanz, *J. Chem. Phys.* **93**, 8828 (1990).
- <sup>16</sup>S. P. Karna and M. Dupuis, *J. Comput. Chem.* **12**, 487 (1991).
- <sup>17</sup>P. Norman, D. Jonsson, O. Vahtras, and H. Ågren, *Chem. Phys. Lett.* **242**, 7 (1995).
- <sup>18</sup>H. Sekino and R. J. Bartlett, *J. Chem. Phys.* **98**, 3022 (1993).
- <sup>19</sup>R. J. Bartlett and H. Sekino, in *Nonlinear Optical Materials: Theory and Modeling*, edited by S. P. Karna and A. T. Yeates (American Chemical Society, Washington, D.C., 1996), p. 23.
- <sup>20</sup>J. Olsen and P. Jørgensen, in *Modern Electronic Structure Theory*, edited by D. R. Yarkony (World Scientific, Singapore, 1995), p. 857.
- <sup>21</sup>D. Spelsberg and W. Meyer, *J. Chem. Phys.* **108**, 22 (1998).
- <sup>22</sup>J. E. Rice and N. C. Handy, *Int. J. Quantum Chem.* **43**, 91 (1992).
- <sup>23</sup>F. Aiga, K. Sasagane, and R. Itoh, *J. Chem. Phys.* **99**, 3779 (1993).
- <sup>24</sup>F. Aiga and R. Itoh, *Chem. Phys. Lett.* **251**, 372 (1996).
- <sup>25</sup>C. Hättig and B. A. Heß, *Chem. Phys. Lett.* **233**, 359 (1995); *J. Chem. Phys.* **105**, 9948 (1996).
- <sup>26</sup>H. Sekino and R. J. Bartlett, *Chem. Phys. Lett.* **234**, 87 (1995).
- <sup>27</sup>P. B. Rozyczko, S. A. Perera, M. Nooijen, and R. J. Bartlett, *J. Chem. Phys.* **107**, 6736 (1997).
- <sup>28</sup>T. B. Pederson and H. Koch, *J. Chem. Phys.* **106**, 8059 (1997).
- <sup>29</sup>C. Hättig and P. Jørgensen, *J. Chem. Phys.* **109**, 2762 (1998).
- <sup>30</sup>R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1989).
- <sup>31</sup>R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer, Berlin, 1990).
- <sup>32</sup>E. K. U. Gross and R. M. Dreizler, in *Density Functional Methods in Physics*, edited by R. M. Dreizler and J. da Providencia (Plenum, New York, 1985), p. 81.
- <sup>33</sup>E. K. U. Gross and W. Kohn, *Adv. Quantum Chem.* **21**, 255 (1990).
- <sup>34</sup>M. E. Casida, in *Recent Advances in Density Functional Methods*, edited by D. P. Chong (World Scientific, Singapore, 1995), Part I, p. 155.
- <sup>35</sup>M. E. Casida, in *Recent Developments and Applications of Modern Density Functional Theory*, edited by J. M. Seminario (Elsevier, Amsterdam, 1996), p. 391.
- <sup>36</sup>E. K. U. Gross, J. F. Dobson, and M. Petersilka, in *Density Functional Theory*, edited by R. F. Nalewajski, Springer Series Topics in Current Chemistry Vol. 181 (Springer, Heidelberg, 1996), p. 81.
- <sup>37</sup>P. Hohenberg and W. Kohn, *Phys. Rev. B* **136**, B864 (1964).
- <sup>38</sup>W. Kohn and L. J. Sham, *Phys. Rev. A* **140**, A1113 (1965).
- <sup>39</sup>B. M. Deb and S. K. Ghosh, *J. Chem. Phys.* **77**, 342 (1982).
- <sup>40</sup>L. J. Bartolotti, *Phys. Rev. A* **24**, 1661 (1981); **26**, 2243 (1982).
- <sup>41</sup>E. Runge and E. K. U. Gross, *Phys. Rev. Lett.* **52**, 97 (1984).
- <sup>42</sup>G. D. Mahan and K. R. Subbaswamy, *Local Density Theory of Polarizability* (Plenum, New York, 1990).
- <sup>43</sup>M. Petersilka, U. J. Gossmann, and E. K. U. Gross, *Phys. Rev. Lett.* **76**, 1212 (1996).
- <sup>44</sup>M. Petersilka and E. K. U. Gross, *Int. J. Quantum Chem., Quantum Chem. Symp.* **30**, 181 (1996).
- <sup>45</sup>R. Bauernschmitt and R. Ahlrichs, *Chem. Phys. Lett.* **256**, 454 (1996).
- <sup>46</sup>R. Bauernschmitt, M. Häser, O. Treutler, and R. Ahlrichs, *Chem. Phys. Lett.* **264**, 573 (1997).
- <sup>47</sup>C. Jamorski, M. Casida, and D. R. Salahub, *J. Chem. Phys.* **104**, 5134 (1996).
- <sup>48</sup>M. E. Casida, C. Jamorski, K. C. Casida, and D. R. Salahub, *J. Chem. Phys.* **108**, 4439 (1998).
- <sup>49</sup>M. E. Casida, K. C. Casida, and D. R. Salahub, *Int. J. Quantum Chem.* **70**, 933 (1998).
- <sup>50</sup>S. J. A. van Gisbergen, F. Kootstra, P. R. T. Schipper, O. V. Gritsenko, J. G. Snijders, and E. J. Baerends, *Phys. Rev. A* **57**, 2556 (1998).
- <sup>51</sup>R. E. Stratmann, G. E. Scuseria, and M. J. Frisch, *J. Chem. Phys.* **109**, 8218 (1998).
- <sup>52</sup>K. B. Weiberg, R. E. Stratmann, and M. J. Frisch, *Chem. Phys. Lett.* **297**, 60 (1998).
- <sup>53</sup>D. J. Tozer and N. C. Handy, *J. Chem. Phys.* **109**, 10180 (1998).
- <sup>54</sup>N. C. Handy and D. J. Tozer, *J. Comput. Chem.* **20**, 106 (1999).
- <sup>55</sup>A. Görling, H. H. Heinze, S. P. Ruzankin, M. Staufer, and N. Röscher, *J. Chem. Phys.* **110**, 2785 (1999).
- <sup>56</sup>S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends, *J. Chem. Phys.* **103**, 7401 (1995).
- <sup>57</sup>S. J. A. van Gisbergen, V. P. Osinga, O. V. Gritsenko, R. van Leeuwen, J. G. Snijders, and E. J. Baerends, *J. Chem. Phys.* **105**, 3142 (1996).
- <sup>58</sup>V. P. Osinga, S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends, *J. Chem. Phys.* **106**, 5091 (1997).
- <sup>59</sup>S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends, *Phys. Rev. Lett.* **78**, 3097 (1997).
- <sup>60</sup>S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends, *J. Chem. Phys.* **109**, 10644 (1998).
- <sup>61</sup>S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends, *J. Chem. Phys.* **109**, 10657 (1998).
- <sup>62</sup>S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends, *Chem. Phys. Lett.* **259**, 599 (1996).
- <sup>63</sup>G. Vignale, M. Rasolt, and D. J. W. Geldart, *Adv. Quantum Chem.* **21**, 235 (1990).
- <sup>64</sup>S. M. Colwell, N. C. Handy, and A. M. Lee, *Phys. Rev. A* **53**, 1316 (1996).
- <sup>65</sup>A. G. Ioannou, S. M. Colwell, and R. D. Amos, *Chem. Phys. Lett.* **278**, 278 (1997).
- <sup>66</sup>A. G. Ioannou and R. D. Amos, *Chem. Phys. Lett.* **279**, 17 (1997).
- <sup>67</sup>C. A. Ullrich, U. J. Gossmann, and E. K. U. Gross, *Phys. Rev. Lett.* **74**, 872 (1995).
- <sup>68</sup>A. Zangwill and P. Soven, *Phys. Rev.* **21**, 1561 (1980).
- <sup>69</sup>J. F. Dobson, *Phys. Rev. Lett.* **73**, 2244 (1994).
- <sup>70</sup>E. K. U. Gross and W. Kohn, *Phys. Rev. Lett.* **55**, 2850 (1985); **57**, 923 (1986).
- <sup>71</sup>B. J. Orr and J. F. Ward, *Mol. Phys.* **20**, 513 (1971).
- <sup>72</sup>G. Vignale and W. Kohn, *Phys. Rev. Lett.* **77**, 2037 (1996).
- <sup>73</sup>J. H. Shirley, *Phys. Rev.* **138**, B979 (1965).
- <sup>74</sup>R. H. Young, W. J. Deal Jr., and N. R. Kestner, *Mol. Phys.* **17**, 369 (1969).
- <sup>75</sup>P. W. Langhoff, S. T. Epstein, and M. Karplus, *Rev. Mod. Phys.* **44**, 602 (1972).
- <sup>76</sup>H. Sambe, *Phys. Rev. A* **7**, 2203 (1973).
- <sup>77</sup>J. M. Okuniewicz, *J. Math. Phys.* **15**, 1587 (1974).
- <sup>78</sup>Y. R. Dmitriev and B. O. Roos, *Int. J. Quantum Chem.* **26**, 35 (1984).
- <sup>79</sup>K. Sasagane, F. Aiga, and R. Itoh, *J. Chem. Phys.* **99**, 3738 (1993).
- <sup>80</sup>F. Aiga, K. Sasagane, and R. Itoh, *Int. J. Quantum Chem.* **51**, 87 (1994).
- <sup>81</sup>O. Christiansen, P. Jørgensen, and C. Hättig, *Int. J. Quantum Chem.* **68**, 1 (1998).
- <sup>82</sup>D. A. Telnov and S. I. Chu, *Chem. Phys. Lett.* **264**, 466 (1997); *Int. J. Quantum Chem.* **69**, 305 (1998).
- <sup>83</sup>P.-O. Löwdin, *J. Math. Phys.* **6**, 1341 (1965).
- <sup>84</sup>T. Grabo, T. Kreibich, and E. K. U. Gross, *Mol. Eng.* **7**, 27 (1997).
- <sup>85</sup>H. Kohl and R. M. Dreizler, *Phys. Rev. Lett.* **56**, 1993 (1986).
- <sup>86</sup>O. Gunnarsson and B. I. Lundqvist, *Phys. Rev. B* **13**, 4274 (1976).
- <sup>87</sup>A. D. Becke, *J. Chem. Phys.* **88**, 1053 (1987).
- <sup>88</sup>E. F. Hayes and R. G. Parr, *J. Chem. Phys.* **43**, 1831 (1965).
- <sup>89</sup>A. Görling, *Phys. Rev. A* **55**, 2630 (1997).
- <sup>90</sup>V. Volterra, *Theory of Functionals and of Integral and Integro-Differential Equations* (Dover, New York, 1959).
- <sup>91</sup>S. M. Colwell, C. W. Murray, N. C. Handy, and R. D. Amos, *Chem. Phys. Lett.* **210**, 261 (1993).