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Frequency-dependent hyperpolarizabilities in the Møller–Plesset perturbation theory

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A formulation for calculating frequency-dependent hyperpolarizabilities in the Møller–Plesset perturbation theory is presented as the correlation correction to the TDHF approximation. Our quasienergy derivative (QED) method is applied, and the difference between the QED method and the pseudoenergy derivative (PED) method by Rice and Handy is discussed. The Lagrangian technique is utilized to obtain simple and practical expressions for response properties in which the TDHF orbital rotation parameters satisfy the $2n+1$ rule and the Lagrange multipliers satisfy the $2n+2$ rule. Explicit expressions for response properties up to third order $[\mu,\ \alpha(-\omega_1;\omega_1),\ \beta(-\omega_\sigma;\omega_1,\omega_2)]$ are derived in the second-order Møller-Plesset perturbation theory.

I. INTRODUCTION

Both experimentalists and theoreticians are interested in the determination of molecular hyperpolarizabilities.[1] For theoreticians, the explicit inclusion of the frequency dependence is necessary in order to make a direct comparison with the experiment. The simplest but justfiable approximation is the time-dependent Hartree–Fock (TDHF) method,[2–9] which is known to represent the precise dispersion effects in most cases.[10–14] Several authors[15–18] have proposed the methods in which the frequency dependence and the electron correlation for hyperpolatrizabilities are evaluated simultaneously. We have studied frequency-dependent first hyperpolarizabilities of the FH for various frequencies in the TDHF quadratic response function formalism.[19] In our previous paper,[20] hereafter referred to as paper I, we have presented a response theory based on the quasienergy derivative (QED) method, and explicit expressions for response properties up to fifth order [$\delta(-\omega_\sigma;\omega_1,\omega_2,\omega_3,\omega_4)$] are derived for the single exponential-transformation (SET) ansatz which covers the full CI response and the TDHF approximation, and ones up to fourth order $[\gamma(-\omega_\sigma;\omega_1,\omega_2,\omega_3)]$ are derived for the double exponential-transformation (DET) ansatz which covers the TDMCSCF approximation and the limited-CI response.

In this paper, we present a formulation of calculating frequency-dependent polarizabilities and hyperpolarizabilities in the Møller–Plesset perturbation theory (MPPT). For the first- and second-order properties, perturbative correlation correction theory has been studied not only for the static case[21–23] but also for the dynamic case,[24–26] and a lot of static calculations have been performed in the finite-field method. In the propagator formalism, the second-order polarization propagator approximation (SOPPA)[27,28] has been presented. For the dynamic hyperpolarizabilities, on the other hand, we know only one work by Rice and Handy.[18] We apply the QED method to derive the response properties up to third order $[\beta(-\omega_\sigma;\omega_1,\omega_2)]$ in the second-order Møller–Plesset (MP2) perturbation theory starting with the TDHF approximation. The way of partitioning the Hamiltonian is the same as the one by Rice and Handy, but their pseudoenergy derivative (PED) method is quite different in the choice of the "vanishing" condition from our QED method. In the QED method, derivatives are always symmetric with respect to the permutations of spacial indices accompanied by their frequencies. In the PED method, on the other hand, derivatives are not always symmetric. In order to obtain the practical expression for the QEDs, we take advantage of the Lagrangian technique[29,30] which has been developed for the geometrical energy derivatives in the case of the nonvariational wave functions. It is ensured that the TDHF orbital rotation responses to order n determine the QEDs to order $2n+1$, if only the Lagrange multipliers, which satisfy the $2n+2$ rule, are determined.

The outline of this paper is as follows: In Sec. II the QED method is briefly reviewed. In Sec. III we discuss the general scheme of the MPPT correction starting with the TDHF approximation. "The TDHF orbital energy matrix" is defined in the second quantization language, and we consider the TDHF response equations based on the orbital energy matrix in comparison with the generalized Ehrenfest theorem. The MP2 quasienergy Lagrangian is introduced. In Sec. IV we discuss the MP2 response equations for each parameter, required for calculating the MP2 QEDs to third order. In Sec. V the explicit expressions for the response properties in the QED form are given. In Sec. VI we give some concluding remarks.

II. GENERAL THEORY

Let us briefly review the general theory, focusing on the QED method. A more complete description is given in paper I. The Hamiltonian of the system is assumed to be expressed as

$$H=H_0+H_1 \tag{1}$$

$$H_1=-\sum_{i=-n}^{n}\sum_{\alpha=x,y,z}\epsilon_\alpha(\omega_i)M_\alpha\exp(-i\omega_i t), \tag{2}$$

where H_0 is the nonrelativistic Born–Oppenheimer electronic Hamiltonian of the isolated molecule, and H_1 is the operator which represents the interaction with the time-

dependent external electric field. M_α is the α 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 H_1, we define

$$\omega_{-i}=-\omega_i \quad (\omega_0=0) \tag{3}$$

and

$$\epsilon_\alpha(\omega_{-i})=\epsilon_\alpha^*(\omega_i) \quad [\epsilon_\alpha(0)=\epsilon_\alpha^*(0)]. \tag{4}$$

Provided that H_1 is periodic in time, we can write ω_i with the nonzero unit frequency ω as follows:

$$\omega_i=N_i\omega, \tag{5}$$

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

$$T=\frac{2\pi}{\omega}. \tag{6}$$

Throughout this paper, we assume this type of periodicity which is known as the many-mode Floquet theory.[31] This assumption does not cause loss of generality in practice. We also assume that the summation over i in Eq. (2) can contain "indirect" oscillating fields which do not appear in the real input light. The strengths of such indirect fields are considered to be zero. The Schrödinger equation of the system is

$$i\frac{\partial}{\partial t}|\Psi\rangle=H|\Psi\rangle, \tag{7}$$

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

$$\langle\Psi|\Psi\rangle=1. \tag{8}$$

The total wave function $|\Psi\rangle$ may be expressed as[2]

$$|\Psi\rangle=|\Phi\rangle\exp\left[-i\int_{t_0}^{t}\langle\Phi|H-i\frac{\partial}{\partial t'}|\Phi\rangle dt'\right], \tag{9}$$

with

$$\langle\Phi|\Phi\rangle=1. \tag{10}$$

Substituting Eq. (9) into Eq. (7), we can rewrite the Schrödinger equation as

$$\left(H-i\frac{\partial}{\partial t}\right)|\Phi\rangle=|\Phi\rangle W(t), \tag{11}$$

where

$$W(t)=\langle\Phi|H-i\frac{\partial}{\partial t}|\Phi\rangle \tag{12}$$

is referred to as a quasienergy, which is a real value since $|\Phi\rangle$ is normalized.[2,32]

The time-dependent Hellmann–Feynman theorem[33] for the parameter $\epsilon_A(\omega)$ in the phase-isolated form may be written as

$$-\langle\Phi|M_A|\Phi\rangle\exp(-i\omega t)=\frac{\partial W(t)}{\partial\epsilon_A(\omega)}+i\frac{\partial}{\partial t}\left\langle\Phi\left|\frac{\partial\Phi}{\partial\epsilon_A(\omega)}\right\rangle\right. . \tag{13}$$

This theorem is satisfied for the exact wave function and the variational wave functions which obey the time-dependent variational principle (TDVP)[2,34]

$$\delta W(t)+i\frac{\partial}{\partial t}\langle\Phi|\delta\Phi\rangle=0. \tag{14}$$

According to the rhs of Eq. (13), the time-dependent electric dipole moment (the A component) $\mu_A(t)$ is defined as

$$\mu_A(t)=-\left[\frac{\partial W(t)}{\partial\epsilon_A(\omega)}+i\frac{\partial}{\partial t}\left\langle\Phi\left|\frac{\partial\Phi}{\partial\epsilon_A(\omega)}\right\rangle\right.\right]\exp(i\omega t), \tag{15}$$

where $\epsilon_A(\omega)$ is the A-direction field strength of an *arbitrary* [$\exp(-i\omega t)$] Fourier component. If the time-dependent Hellmann–Feynman theorem is satisfied, $\mu_A(t)$ is equivalent to the expectation value of the dipole moment operator. For nonvariational wave functions, $\mu_A(t)$ is not equivalent to the expectation value of the dipole moment operator. However, in this case, Eq. (15) is preferable to the form of the expectation value since this definition satisfies the requirement that the response properties should be identical with ones in the finite-field method in the static limit.

The essense of the QED method is as follows: If $\omega+\omega_1+\omega_2+\cdots+\omega_n=0$, we have

$$i\frac{\partial^{n+1}}{\partial\epsilon_D(\omega_n)\cdots\partial\epsilon_C(\omega_2)\partial\epsilon_B(\omega_1)\partial t}\left\langle\Phi\left|\frac{\partial\Phi}{\partial\epsilon_A(\omega)}\right\rangle\right.\Big|_0=0. \tag{16}$$

This is a condition that the second term of the rhs of Eq. (15) vanishes. This condition leads to the following definition of the response properties:

$$\mu_A=-\frac{\partial W(t)}{\partial\epsilon_A(0)}\Big|_0, \tag{17}$$

$$\alpha_{AB}(-\omega_1;\omega_1)=-\frac{\partial^2 W(t)}{\partial\epsilon_A(-\omega_1)\epsilon_B(\omega_1)}\Big|_0, \tag{18}$$

$$\beta_{ABC}(-\omega_\sigma;\omega_1,\omega_2)=-\frac{\partial^3 W(t)}{\partial\epsilon_A(-\omega_\sigma)\partial\epsilon_B(\omega_1)\partial\epsilon_C(\omega_2)}\Big|_0. \tag{19}$$

These equations can be also obtained if we rewrite $\mu(t)$ in the form based on the time average of the time-dependent Hellmann–Feynman relation [Eq. (13)] over one period T. Defining the time average of an arbitrary operator A as

$$\{A\}_T\equiv\frac{1}{T}\int_0^T A\,dt, \tag{20}$$

we can write the time average of Eq. (13) as[2,35]

$$-\{\langle\Phi|M_A|\Phi\rangle\exp(-i\omega t)\}_T=\frac{\partial\{W(t)\}_T}{\partial\epsilon_A(\omega)}. \tag{21}$$

According to the rhs of Eq. (21), we define the following time average $\{\mu_A(t)\exp(-i\omega t)\}_T$ instead of $\mu_A(t)$:

$$\{\mu_A(t)\exp(-i\omega t)\}_T=-\frac{\partial\{W(t)\}_T}{\partial\epsilon_A(\omega)}. \tag{22}$$

Equations (17)–(19) are obtained through searching for the special frequencies ω which does not make Eq. (22) zero.

At the end of this section, we also introduce the time-averaged form of the TDVP Eq. (14) as[2,35]

$$\delta\{W(t)\}_T=0, \tag{23}$$

which will be used in Sec. IV.

III. THE MPPT CORRECTION STARTING WITH TDHF

In this section we discuss the general scheme of the MPPT correlation correction method starting with the TDHF approximation, and the MP2 quasienergy Lagrangian is constructed. We concentrate ourselves on the case of the closed-shell system.

A. TDHF response equations

We use indices $\{p,q,r,...\}$, $\{i,j,k,...\}$, and $\{a,b,c,...\}$ to denote arbitrary, occupied, and virtual orbitals, respectively. We also use the usual creation operator $a^\dagger_{p\sigma}$ and the annihilation operator $a_{p\sigma}$, where σ is the spin index. In the TDHF method the wave function $|\Phi\rangle$ is approximated as a single determinant[5]

$$|\Phi_{\mathrm{TDHF}}\rangle=|\Phi_0\rangle=\exp(\kappa)|\mathrm{HF}\rangle, \tag{24}$$

where

$$\kappa=\sum_{a,i}\{E_{ai}\kappa_{ai}(t)-E_{ia}\kappa^*_{ai}(t)\} \tag{25}$$

with

$$E_{pq}=\sum_\sigma a^\dagger_{p\sigma}a_{q\sigma}. \tag{26}$$

Introducing the following notation

$$E_\lambda\equiv E_{ai},\quad \kappa_\lambda(t)\equiv\kappa_{ai}(t) \tag{27}$$

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

$$E_{-\lambda}\equiv E^\dagger_\lambda,\quad \kappa_{-\lambda}(t)\equiv-\kappa^*_\lambda(t), \tag{28}$$

we can rewrite Eq. (25) as

$$\kappa=\sum_\lambda\{E_\lambda\kappa_\lambda(t)+E_{-\lambda}\kappa_{-\lambda}(t)\}\equiv\sum_{\pm\lambda}E_\lambda\kappa_\lambda(t). \tag{29}$$

The set of parameters $\kappa_\lambda(t)$ is usually determined by the TDVP, or the generalized Ehrenfest theorem.[5,15,36,37] Let us now define the TDHF orbital energy matrix in the second quantized form

$$\theta_{pq}=\frac{1}{2}\sum_\sigma\langle\mathrm{HF}|\left[a^\dagger_{q\sigma},\left[a_{p\sigma},\exp(-\kappa)\times\left(H-i\frac{\partial}{\partial t}\right)\exp(\kappa)\right]\right]_+|\mathrm{HF}\rangle. \tag{30}$$

This expression is obtained from the first quantized form of the TDHF equation [38]

$$\left(f-i\frac{\partial}{\partial t}\right)|\phi_r\rangle=\sum_s|\phi_s\rangle\theta_{sr}, \tag{31}$$

where f is the Fock operator and $|\phi\rangle$ is the orbital function. In terms of Eq. (30), the set of parameters $\kappa_\lambda(t)$ may be determined by the Brillouin condition

$$\theta_{ai}=\theta_{ia}=0. \tag{32}$$

We will now show that the condition Eq. (32) is exactly equivalent to imposing the generalized Ehrenfest theorem. Equation (32) is written as

$$\langle\mathrm{HF}|\left[E_{\pm\lambda},\exp(-\kappa)\left(H-i\frac{\partial}{\partial t}\right)\exp(\kappa)\right]|\mathrm{HF}\rangle=0, \tag{33}$$

more explicitly

$$\begin{aligned}&\langle\mathrm{HF}|E_{\pm\lambda}\exp(-\kappa)H\exp(\kappa)|\mathrm{HF}\rangle\\&-\langle\mathrm{HF}|\exp(-\kappa)H\exp(\kappa)E_{\pm\lambda}|\mathrm{HF}\rangle\\&-i\langle\mathrm{HF}|E_{\pm\lambda}\exp(-\kappa)\frac{\partial\exp(\kappa)}{\partial t}|\mathrm{HF}\rangle\\&+i\langle\mathrm{HF}|\exp(-\kappa)\frac{\partial\exp(\kappa)}{\partial t}E_{\pm\lambda}|\mathrm{HF}\rangle=0.\end{aligned} \tag{34}$$

The generalized Ehrenfest theorem for an arbitrary operator Y is expressed as

$$\langle\Phi|[Y,H]|\Phi\rangle-i\left\langle\Phi\left|Y\right|\frac{\partial\Phi}{\partial t}\right\rangle-i\left\langle\frac{\partial\Phi}{\partial t}\right|Y\left|\Phi\right\rangle=0. \tag{35}$$

Considering Φ as the TDHF wave function [Eq. (24)], and Y as $\exp(\kappa)E_{\pm\lambda}\exp(-\kappa)$, we obtain

$$\begin{aligned}&\langle\mathrm{HF}|E_{\pm\lambda}\exp(-\kappa)H\exp(\kappa)|\mathrm{HF}\rangle\\&-\langle\mathrm{HF}|\exp(-\kappa)H\exp(\kappa)E_{\pm\lambda}|\mathrm{HF}\rangle\\&-i\langle\mathrm{HF}|E_{\pm\lambda}\exp(-\kappa)\frac{\partial\exp(\kappa)}{\partial t}|\mathrm{HF}\rangle\\&-i\langle\mathrm{HF}|\frac{\partial\exp(-\kappa)}{\partial t}\exp(\kappa)E_{\pm\lambda}|\mathrm{HF}\rangle=0.\end{aligned} \tag{36}$$

Comparing Eq. (34) with Eq. (36), they are equivalent to each other if

$$\frac{\partial\exp(-\kappa)}{\partial t}\exp(\kappa)=-\exp(-\kappa)\frac{\partial\exp(\kappa)}{\partial t}, \tag{37}$$

which is easily shown by differentiating the identity $\exp(-\kappa)\exp(\kappa)=1$ with respect to t. Thus, it is proved that the condition Eq. (32) leads to the standard TDHF equation.

Introducing the expansion of κ with respect to the external field as

$$\kappa=\sum_{\pm\lambda} E_\lambda\kappa_\lambda(t)=\sum_i \exp(-\omega_i t)\sum_\alpha \epsilon_\alpha(\omega_i)\kappa^\alpha(\omega_i)$$
$$+\frac{1}{2}\sum_{i,j}\exp[-i(\omega_i+\omega_j)t]\sum_{\alpha,\beta}\epsilon_\alpha(\omega_i)\epsilon_\beta(\omega_j)\kappa^{\alpha\beta}(\omega_i,\omega_j)$$
$$+\frac{1}{6}\sum_{i,j,k}\exp[-i(\omega_i+\omega_j+\omega_k)t]\sum_{\alpha,\beta,\gamma}\epsilon_\alpha(\omega_i)\epsilon_\beta(\omega_j)\epsilon_\gamma(\omega_k)\kappa^{\alpha\beta\gamma}(\omega_i,\omega_j,\omega_k)+\cdots, \tag{38}$$

with

$$\kappa^\alpha(\omega_i)=\sum_{\pm\lambda} E_\lambda\kappa_\lambda^\alpha(\omega_i), \tag{39}$$

$$\kappa^{\alpha\beta}(\omega_i,\omega_j)=\sum_{\pm\lambda} E_\lambda\kappa_\lambda^{\alpha\beta}(\omega_i,\omega_j), \tag{40}$$

$$\kappa^{\alpha\beta\gamma}(\omega_i,\omega_j,\omega_k)=\sum_{\pm\lambda} E_\lambda\kappa_\lambda^{\alpha\beta\gamma}(\omega_i,\omega_j,\omega_k), \tag{41}$$

and

$$\kappa^\alpha_{-\lambda}(\omega_i)\equiv-\kappa^\alpha_\lambda(-\omega_i)^*,$$
$$\kappa^{\alpha\beta}_{-\lambda}(\omega_i,\omega_j)\equiv-\kappa^{\alpha\beta}_\lambda(-\omega_i,-\omega_j)^*\cdots, \tag{42}$$

the explicit response equations for each order are obtained. The details up to third order are given in paper I.

At the perturbed state the orbital energy matrix can be diagonalized by considering occupied–occupied and virtual–virtual parts of the orbital mixing, but we do not insist on the canonical representation since the denominators as $(\theta_i-\theta_j-\omega)$ may cause numerical instabilities. Since the MPPT energy is invariant to the orbital rotation among the occupied orbitals or among the virtual orbitals with no frozen core or virtual orbitals, we have to consider only the occupied–virtual and virtual–occupied parts of the orbital rotation in the QED method. In the PED method, on the other hand, the occupied–occupied and virtual–virtual parts of the orbital mixing have to be considered to fulfill the vanishing condition[18,25]

$$\left\langle\Phi\left|\frac{\partial\Phi}{\partial\epsilon(0)}\right\rangle\right.=0. \tag{43}$$

B. The general scheme of MPPT

The Møller–Plesset partitioning of the Hamiltonian is expressed as[25]

$$H-i\frac{\partial}{\partial t}=F-i\frac{\partial}{\partial t}+V \tag{44}$$

with

$$V=H-F, \tag{45}$$

where the operator $(F-i\partial/\partial t)$ is written in the second quantized form as

$$F-i\frac{\partial}{\partial t}\leftrightarrow\sum_{pq}\theta_{pq}\tilde{E}_{pq} \tag{46}$$

with

$$\tilde{E}_{pq}=\exp(\kappa)E_{pq}\exp(-\kappa). \tag{47}$$

Since the TDHF wave function $|\Phi_0\rangle$ [Eq. (24)] is an eigenfunction of the operator defined in Eq. (46), we can write

$$\left(F-i\frac{\partial}{\partial t}\right)|\Phi_0\rangle=|\Phi_0\rangle W_0, \tag{48}$$

where

$$W_0=\langle\Phi_0|F-i\frac{\partial}{\partial t}|\Phi_0\rangle=2\sum_i^{occ}\theta_{ii}. \tag{49}$$

The quasienergy in the TDHF approximation is expressed as

$$W_{\mathrm{TDHF}}=\langle\Phi_0|H-i\frac{\partial}{\partial t}|\Phi_0\rangle$$
$$=\langle\Phi_0|F-i\frac{\partial}{\partial t}+V|\Phi_0\rangle$$
$$=W_0+\langle\Phi_0|V|\Phi_0\rangle, \tag{50}$$

which means that the correlation correction to the TDHF approximation begins with the second-order for V as the usual MPPT of the unperturbed system.

Let us introduce the formal expansion of W and $|\Phi\rangle$ with respect to V

$$W(t)=\sum_{k=0}^{\infty}W_k=W_{\mathrm{TDHF}}+\sum_{k=2}^{\infty}W_k, \tag{51}$$

$$|\Phi\rangle=\sum_{k=0}^{\infty}|\Phi_k\rangle=|\Phi_{\mathrm{TDHF}}\rangle+\sum_{k=1}^{\infty}|\Phi_k\rangle. \tag{52}$$

Substituting Eqs. (51) and (52) into Eq. (11), the nth order $(n\geqslant 1)$ equation for $|\Phi\rangle$ may be written as

$$\tilde{G}|\Phi_n\rangle=-V|\Phi_{n-1}\rangle+\sum_{m=0}^{n-1}|\Phi_m\rangle W_{n-m}, \tag{53}$$

where we define $\tilde{G}$ as

$$\tilde{G}=F-i\frac{\partial}{\partial t}-W_0=\sum_{pq}\theta_{pq}\tilde{E}_{pq}-W_0. \tag{54}$$

Multiplying Eq. (53) on the left by $\langle\Phi_0|$, we have

$$W_n=\langle\Phi_0|V|\Phi_{n-1}\rangle-\sum_{m=1}^{n-1}\langle\Phi_0|\Phi_m\rangle W_{n-m}, \tag{55}$$

where we use $\tilde{G}|\Phi_0\rangle=0$. We have to notice that we can not use the intermediate normalization $\langle\Phi_0|\Phi\rangle=1$ since $|\Phi\rangle$ must be normalized as Eq. (10). So generally the value $\langle\Phi_0|\Phi_m\rangle$ in Eq. (55) is not zero, except for $\langle\Phi_0|\Phi_1\rangle=0$, which is used afterward. However, $|\Phi\rangle$ does not necessarily have to be normalized in the QED method. If $|\Phi\rangle$ is not normalized, the quasienergy $W(t)$ has to be defined as a complex value[2,32] and we can write $W(t)=\mathrm{Re}\,W(t)+i\,\mathrm{Im}\,W(t)$. Remembering

$$\mathrm{Im}\,W(t)=\frac{\partial}{\partial t}\left[-\frac{1}{2}\ln\langle\Phi|\Phi\rangle\right], \tag{56}$$

we can see

$$\{\mathrm{Im}\,W(t)\}_T=0. \tag{57}$$

So QEDs are always real whether $|\Phi\rangle$ is normalized or not. This feature is important when the QED method is applied to the higher-order MPPT and the coupled cluster model. In the PED method, on the other hand, response properties will be complex if $|\Phi\rangle$ is not normalized. It will not be easy to divide the complex response properties into the real and imaginary parts.

C. The MP2 quasienergy Lagrangian

Equation (53) with $n=1$ gives

$$\tilde{G}|\Phi_1\rangle=-V|\Phi_0\rangle+|\Phi_0\rangle W_1. \tag{58}$$

We can write $|\Phi_1\rangle$ as

$$|\Phi_1\rangle=\sum_K \exp(\kappa)|K\rangle t_K, \tag{59}$$

where $\{|K\rangle\}$ is the set of all doubly excited states. Substituting Eq. (24) and Eq. (59) into Eq. (58), we have

$$\sum_K \tilde{G}\exp(\kappa)|K\rangle t_K=-V\exp(\kappa)|\mathrm{HF}\rangle + \exp(\kappa)|\mathrm{HF}\rangle W_1. \tag{60}$$

Multiplying Eq. (60) on the left by $\langle L|\exp(-\kappa)$, we have

$$\sum_K \langle L|G|K\rangle t_K=-\langle L|\exp(-\kappa)V\exp(\kappa)|\mathrm{HF}\rangle, \tag{61}$$

where

$$G=\exp(-\kappa)\tilde{G}\exp(\kappa)=\sum_{pq}\theta_{pq}E_{pq}-W_0. \tag{62}$$

The amplitudes t_K are determined from Eq. (61). Substituting Eqs. (24) and (59) into Eq. (55) with $n=2$, we have the MP2 correlation correction of the quasienergy

$$W_2=\langle\Phi_0|V|\Phi_1\rangle = \sum_K \langle\mathrm{HF}|\exp(-\kappa)V\exp(\kappa)|K\rangle t_K. \tag{63}$$

In analogy to the Lagrangian in the geometrical energy derivatives,[30] we introduce the quasienergy Lagrangian at the MP2 level

$$L(\epsilon;\zeta,\bar{t},\kappa,t)=W_{\mathrm{TDHF}}(\epsilon;\kappa)+\sum_K\langle\mathrm{HF}|\exp(-\kappa)V\exp(\kappa)|K\rangle t_K + \sum_L \bar{t}_L\left[\sum_K G_{LK}t_K+\langle L|\exp(-\kappa)V\exp(\kappa)|\mathrm{HF}\rangle\right]+\sum_{\pm\lambda}\zeta_\lambda\langle\mathrm{HF}|\left[E_\lambda,\exp(-\kappa)\left(H-i\frac{\partial}{\partial t}\right)\exp(\kappa)\right]|\mathrm{HF}\rangle, \tag{64}$$

where $\bar{t}_L$ and ζ_λ are Lagrange multipliers for the first order MP amplitudes and TDHF orbital rotations, respectively, and $G_{LK}=\langle L|G|K\rangle$. The Lagrangian L is considered to be variational for κ, t, $\bar{t}$, and ζ. Now we can write the response properties at the MP2 level of theory as the following derivatives of the Lagrangian

$$\mu_A=-\left.\frac{\partial L}{\partial\epsilon_A(0)}\right|_0, \tag{65}$$

$$\alpha_{AB}(-\omega_1;\omega_1)=-\left.\frac{\partial^2 L}{\partial\epsilon_A(-\omega_1)\epsilon_B(\omega_1)}\right|_0, \tag{66}$$

$$\beta_{ABC}(-\omega_\sigma;\omega_1,\omega_2)=-\left.\frac{\partial^3 L}{\partial\epsilon_A(-\omega_\sigma)\partial\epsilon_B(\omega_1)\partial\epsilon_C(\omega_2)}\right|_0. \tag{67}$$

IV. MP2 RESPONSE EQUATIONS

In this section we derive the zeroth- and first-order MP2 response equations. Though the electron correlation operator V is expanded with respect to the external field as $V=V^{(0)}+V^{(1)}+\cdots$, we have to consider only the zeroth-order $V^{(0)}$ at the MP2 level since $V^{(n)}$ is the one electron operator for $n\geqslant 1$.

A. Response equations for t

The amplitudes t_K are expanded with respect to the external field as

$$t_K = t_K^{(0)} + \sum_i \exp(-\omega_i t) \sum_\alpha \epsilon_\alpha(\omega_i) t_K^\alpha(\omega_i)$$
$$+\frac{1}{2}\sum_{i,j} \exp[-i(\omega_i+\omega_j)t] \sum_{\alpha,\beta} \epsilon_\alpha(\omega_i)\epsilon_\beta(\omega_j) t_K^{\alpha\beta}(\omega_i,\omega_j)$$
$$+\frac{1}{6}\sum_{i,j,k} \exp[-i(\omega_i+\omega_j+\omega_k)t] \sum_{\alpha,\beta,\gamma} \epsilon_\alpha(\omega_i)\epsilon_\beta(\omega_j)\epsilon_\gamma(\omega_k) t_K^{\alpha\beta\gamma}(\omega_i,\omega_j,\omega_k) + \cdots . \tag{68}$$

Introducing the following notation

$$G_{LK}\{A\} \equiv \frac{1}{2}\sum_{pq}\sum_\sigma \langle \mathrm{HF}|[a_{q\sigma}^\dagger,[a_{p\sigma},A]]_+|\mathrm{HF}\rangle \langle L|E_{pq}|K\rangle - \sum_i \sum_\sigma \langle \mathrm{HF}|[a_{i\sigma}^\dagger,[a_{i\sigma},A]]_+|\mathrm{HF}\rangle \delta_{LK}, \tag{69}$$

the matrix elements G_{LK} are expanded with respect to the external field as

$$G_{LK} = G_{LK}^{(0)} + \sum_i \exp(-\omega_i t) \sum_\alpha \epsilon_\alpha(\omega_i) G_{LK}^\alpha(\omega_i)$$
$$+\frac{1}{2}\sum_{i,j} \exp[-i(\omega_i+\omega_j)t] \sum_{\alpha,\beta} \epsilon_\alpha(\omega_i)\epsilon_\beta(\omega_j) G_{LK}^{\alpha\beta}(\omega_i,\omega_j)$$
$$+\frac{1}{6}\sum_{i,j,k} \exp[-i(\omega_i+\omega_j+\omega_k)t] \sum_{\alpha,\beta,\gamma} \epsilon_\alpha(\omega_i)\epsilon_\beta(\omega_j)\epsilon_\gamma(\omega_k) G_{LK}^{\alpha\beta\gamma}(\omega_i,\omega_j,\omega_k) + \cdots , \tag{70}$$

where

$$G_{LK}^{(0)} = G_{LK}\{H_0\}, \tag{71}$$

$$G_{LK}^\alpha(\omega_i) = G_{LK}\{-M_\alpha + [H_0,\kappa^\alpha(\omega_i)] - \omega_i \kappa^\alpha(\omega_i)\} \tag{72}$$

$$G_{LK}^{\alpha\beta}(\omega_i,\omega_j) = \mathscr{P}[\alpha(\omega_i),\beta(\omega_j)]\left(\tfrac{1}{2}G_{LK}\{[H_0,\kappa^{\alpha\beta}(\omega_i,\omega_j)]\} - \tfrac{1}{2}G_{LK}\{(\omega_i+\omega_j)\kappa^{\alpha\beta}(\omega_i,\omega_j)\} - G_{LK}\{[M_\alpha,\kappa^\beta(\omega_j)]\}\right.$$
$$\left. + \tfrac{1}{2}G_{LK}\{[H_0;\kappa^\alpha(\omega_i),\kappa^\beta(\omega_j)]\} - \tfrac{1}{2}G_{LK}\{\omega_i[\kappa^\alpha(\omega_i),\kappa^\beta(\omega_j)]\}\right), \tag{73}$$

$$G_{LK}^{\alpha\beta\gamma}(\omega_i,\omega_j,\omega_k) = \mathscr{P}[\alpha(\omega_i),\beta(\omega_j),\gamma(\omega_k)]\left(\tfrac{1}{6}G_{LK}\{[H_0,\kappa^{\alpha\beta\gamma}(\omega_i,\omega_j,\omega_k)]\}\right.$$
$$-\tfrac{1}{6}G_{LK}\{(\omega_i+\omega_j+\omega_k)\kappa^{\alpha\beta\gamma}(\omega_i,\omega_j,\omega_k)\} - \tfrac{1}{2}G_{LK}\{[M_\alpha,\kappa^{\beta\gamma}(\omega_j,\omega_k)]\}$$
$$-\tfrac{1}{4}G_{LK}\{(\omega_i-\omega_j-\omega_k)[\kappa^\alpha(\omega_i),\kappa^{\beta\gamma}(\omega_j,\omega_k)]\} + \tfrac{1}{2}G_{LK}\{[H_0;\kappa^\alpha(\omega_i),\kappa^{\beta\gamma}(\omega_j,\omega_k)]\}$$
$$-\tfrac{1}{2}G_{LK}\{[M_\alpha;\kappa^\beta(\omega_j),\kappa^\gamma(\omega_k)]\} + \tfrac{1}{6}G_{LK}\{[H_0;\kappa^\alpha(\omega_i),\kappa^\beta(\omega_j),\kappa^\gamma(\omega_k)]\}$$
$$\left. -\tfrac{1}{6}G_{LK}\{\omega_i[\kappa^\alpha(\omega_i);\kappa^\beta(\omega_j),\kappa^\gamma(\omega_k)]\}\right). \tag{74}$$

We have used the n-tuple symmetric commutator

$$[A;B_1,B_2,\ldots,B_n] = \frac{1}{n!}\mathscr{P}(1,2,\ldots,n) \times [[\cdots[[A,B_1],B_2],\cdots],B_n], \tag{75}$$

where $\mathscr{P}(1,2,\ldots,n)$ is a permutation operator which contains the $n!$ permutations of indices $1,2,\ldots,n$. We have also used the permutation operator $\mathscr{P}[A_1(\omega_1),A_2(\omega_2),\cdots,A_n(\omega_n)]$ which contains the $n!$ permutations of spatial indices $A_1,A_2,\ldots,A_n$ accompanied by their associated frequencies $\omega_1,\omega_2,\ldots,\omega_n$. Substituting Eqs. (68) and (70) into Eq. (61), we have

$$\sum_K G_{LK}^{(0)} t_K^{(0)} = -\langle L|V^{(0)}|\mathrm{HF}\rangle \tag{76}$$

as the zeroth-order equations. Since $G_{LK}^{(0)}$ is diagonal, the set of Eq. (76) is immediately solved as

$$t_L^{(0)} = -\frac{\langle L|V^{(0)}|\mathrm{HF}\rangle}{G_{LL}^{(0)}}. \tag{77}$$

Similarly, the first-order equations

$$\sum_K G_{LK}^{(0)} t_K^A(\omega_1) + \sum_K G_{LK}^A(\omega_1) t_K^{(0)} = -\langle L|[V^{(0)},\kappa^A(\omega_1)]|\mathrm{HF}\rangle \tag{78}$$

are solved as

$$t_L^A(\omega_1)=-\frac{\langle L|[V^{(0)},\kappa^A(\omega_1)]|\mathrm{HF}\rangle}{G_{LL}^{(0)}}-\sum_K\frac{G_{LK}^A(\omega_1)t_K^{(0)}}{G_{LL}^{(0)}}$$

$$=-\frac{\langle L|[V^{(0)},\kappa^A(\omega_1)]|\mathrm{HF}\rangle}{G_{LL}^{(0)}}$$

$$+\sum_K\frac{G_{LK}^A(\omega_1)\langle K|V^{(0)}|\mathrm{HF}\rangle}{G_{LL}^{(0)}G_{KK}^{(0)}}. \tag{79}$$

B. Response equations for $\bar{t}$

In order to determine the multipliers $\bar{t}$, we use the condition that the variation of L with respect to t should fulfill the TDVP Eq. (23). We define the expansion of $\bar{t}$ with respect to the external field as well as Eq. (68) and the expansion of L as $L=L^{(0)}+L^{(1)}+L^{(2)}+\ldots$. Considering the condition $\partial\{L^{(1)}\}_T/\partial t_K^A(0)=0$, the zeroth-order equations are obtained as

$$\langle\mathrm{HF}|V^{(0)}|K\rangle+\sum_L\bar{t}_L^{(0)}G_{LK}^{(0)}=0, \tag{80}$$

which are solved as

$$\bar{t}_K^{(0)}=-\frac{\langle\mathrm{HF}|V^{(0)}|K\rangle}{G_{KK}^{(0)}}. \tag{81}$$

Equation (81) has the form of the complex conjugate of Eq. (77), which is reasonable since we can write the MP2 correction of the quasienergy

$$W_2=\sum_K\bar{t}_K\langle K|\exp(-\kappa)V\exp(\kappa)|\mathrm{HF}\rangle \tag{82}$$

instead of Eq. (63). Considering the condition $\partial\{L^{(2)}\}_T/\partial t_K^A(-\omega_1)=0$, the first-order equations

$$\langle\mathrm{HF}|[V^{(0)},\kappa^B(\omega_1)]|K\rangle$$

$$+\sum_L\bar{t}_L^{(0)}G_{LK}^B(\omega_1)+\sum_L\bar{t}_L^B(\omega_1)G_{LK}^{(0)}=0 \tag{83}$$

are also solved as

$$\bar{t}_K^B(\omega_1)=-\frac{\langle\mathrm{HF}|[V^{(0)},\kappa^B(\omega_1)]|K\rangle}{G_{KK}^{(0)}}-\sum_L\frac{\bar{t}_L^{(0)}G_{LK}^B(\omega_1)}{G_{KK}^{(0)}}$$

$$=-\frac{\langle\mathrm{HF}|[V^{(0)},\kappa^B(\omega_1)]|K\rangle}{G_{KK}^{(0)}}$$

$$+\sum_L\frac{\langle\mathrm{HF}|V^{(0)}|L\rangle G_{LK}^B(\omega_1)}{G_{LL}^{(0)}G_{KK}^{(0)}}, \tag{84}$$

which correspond to Eq. (79) for t.

C. Response equations for ζ

In order to determine the multipliers ζ, we use the condition that the variation of L with respect to κ should fulfill the TDVP Eq. (23). The expansion of ζ with respect to the external field is written as

$$\zeta_\lambda=\zeta_\lambda^{(0)}+\sum_i\exp(-\omega_i t)\sum_\alpha\epsilon_\alpha(\omega_i)\zeta_\lambda^\alpha(\omega_i)$$

$$+\frac{1}{2}\sum_{i,j}\exp[-i(\omega_i+\omega_j)t]\sum_{\alpha,\beta}\epsilon_\alpha(\omega_i)\epsilon_\beta(\omega_j)\zeta_\lambda^{\alpha\beta}(\omega_i,\omega_j)$$

$$+\frac{1}{6}\sum_{i,j,k}\exp[-i(\omega_i+\omega_j+\omega_k)t]\sum_{\alpha,\beta,\gamma}\epsilon_\alpha(\omega_i)\epsilon_\beta(\omega_j)\epsilon_\gamma(\omega_k)\zeta_\lambda^{\alpha\beta\gamma}(\omega_i,\omega_j,\omega_k)+\cdots. \tag{85}$$

Considering the condition $\partial\{L^{(1)}\}_T/\partial\kappa_\mu^A(0)=0$, the zeroth-order equations may be written as

$$\sum_{\pm\lambda}\zeta_\lambda^{(0)}A_{\lambda\mu}^{(0)}=-\gamma_\mu{}^{(0)}, \tag{86}$$

where

$$A_{\lambda\mu}^{(0)}=\langle\mathrm{HF}|[E_\lambda,[H_0,E_\mu]]|\mathrm{HF}\rangle \tag{87}$$

$$\gamma_\mu^{(0)}=\sum_K\langle\mathrm{HF}|[V^{(0)},E_\mu]|K\rangle t_K^{(0)}+\sum_L\bar{t}_L^{(0)}\Big[\sum_K G_{LK}\{[H_0,E_\mu]\}t_K^{(0)}+\langle L|[V^{(0)},E_\mu]|\mathrm{HF}\rangle\Big]. \tag{88}$$

The multipliers $\zeta_\lambda^{(0)}$ are determined from the coupled set of Eq. (86).

Considering the condition $\partial\{L^{(2)}\}_T/\partial\kappa_\mu^A(-\omega_1)=0$, the first-order equations are obtained as

$$\sum_{\pm\lambda}\zeta_\lambda^B(\omega_1)(A_{\lambda\mu}^{(0)}+\omega_1 S_{\lambda\mu}^{(0)})=-\gamma_\mu^B(\omega_1), \tag{89}$$

where

$$S_{\lambda\mu}^{(0)}=\langle\mathrm{HF}|[E_\lambda,E_\mu]|\mathrm{HF}\rangle \tag{90}$$

$$\gamma_\mu^B(\omega_1)=\sum_K[\langle \mathrm{HF}|[V^{(0)};E_\mu,\kappa^B(\omega_1)]|K\rangle t_K^{(0)}+\langle \mathrm{HF}|[V^{(0)},E_\mu]|K\rangle t_K^B(\omega_1)]$$
$$+\sum_L \bar{t}_L^{(0)}\Big[\sum_K G_{LK}\{-[M_B,E_\mu]+[H_0;E_\mu,\kappa^B(\omega_1)]+\omega_1[E_\mu,\kappa^B(\omega_1)]\}t_K^{(0)}$$
$$+\sum_K G_{LK}\{[H_0,E_\mu]+\omega_1 E_\mu\}t_K^B(\omega_1)+\langle L|[V^{(0)};E_\mu,\kappa^B(\omega_1)]|\mathrm{HF}\rangle\Big]$$
$$+\sum_L \bar{t}_L^B(\omega_1)\Big[\sum_K G_{LK}\{[H_0,E_\mu]+\omega_1 E_\mu\}t_K^{(0)}+\langle L|[V^{(0)},E_\mu]|\mathrm{HF}\rangle\Big]$$
$$+\sum_{\pm\lambda}\xi_\lambda^{(0)}[-\langle \mathrm{HF}|[E_\lambda,[M_B,E_\mu]]|\mathrm{HF}\rangle+\langle \mathrm{HF}|[E_\lambda,[H_0;E_\mu,\kappa^B(\omega_1)]]|\mathrm{HF}\rangle$$
$$+\omega_1\langle \mathrm{HF}|[E_\lambda,[E_\mu,\kappa^B(\omega_1)]]|\mathrm{HF}\rangle]. \tag{91}$$

The multipliers $\xi_\lambda^B(\omega_1)$ are determined from the coupled set of Eq. (89).

V. MP2 RESPONSE PROPERTIES

Employing the response equations, the response properties at the MP2 level of theory in the QED form Eqs. (65) – (67) can be written as follows:

$$\mu_A=\langle \mathrm{HF}|M_A|\mathrm{HF}\rangle+\sum_L \bar{t}_L^{(0)}G_{LK}\{M_A\}t_K^{(0)}+\sum_{\pm\lambda}\xi_\lambda{}^{(0)}\langle \mathrm{HF}|[E_\lambda,M_A]|\mathrm{HF}\rangle \tag{92}$$

$$\alpha_{AB}(-\omega_1;\omega_1)=\mathscr{P}[A(-\omega_1),B(\omega_1)]\Big\{-\langle \mathrm{HF}|J^{AB}(-\omega_1;\omega_1)|\mathrm{HF}\rangle-\frac{1}{2}\sum_K\langle \mathrm{HF}|[V^{(0)};\kappa^A(-\omega_1),\kappa^B(\omega_1)]|K\rangle t_K^{(0)}$$
$$-\frac{1}{2}\sum_L \bar{t}_L^{(0)}\langle L|[V^{(0)};\kappa^A(-\omega_1),\kappa^B(\omega_1)]|\mathrm{HF}\rangle-\sum_{L,K}\bar{t}_L^{(0)}G_{LK}\{J^{AB}(-\omega_1;\omega_1)\}t_K^{(0)}$$
$$+\sum_L \bar{t}_L^A(-\omega_1)G_{LL}^{(0)}t_L^B(\omega_1)-\sum_{\pm\lambda}\xi_\lambda^{(0)}\langle \mathrm{HF}|[E_\lambda,J^{AB}(-\omega_1;\omega_1)]|\mathrm{HF}\rangle\Big\} \tag{93}$$

$$\beta_{ABC}(-\omega_\sigma;\omega_1,\omega_2)=\mathscr{P}[A(-\omega_\sigma),B(\omega_1),C(\omega_2)]\Big\{-\langle \mathrm{HF}|J^{ABC}(-\omega_\sigma;\omega_1,\omega_2)]|\mathrm{HF}\rangle$$
$$-\frac{1}{6}\sum_K\langle \mathrm{HF}|[V^{(0)};\kappa^A(-\omega_\sigma),\kappa^B(\omega_1),\kappa^C(\omega_2)]|K\rangle t_K^{(0)}$$
$$-\frac{1}{6}\sum_L \bar{t}_L^{(0)}\langle L|[V^{(0)};\kappa^A(-\omega_\sigma),\kappa^B(\omega_1),\kappa^C(\omega_2)]|\mathrm{HF}\rangle$$
$$-\frac{1}{2}\sum_K\langle \mathrm{HF}|[V^{(0)};\kappa^A(-\omega_\sigma),\kappa^B(\omega_1)]|K\rangle t_K^C(\omega_2)$$
$$-\frac{1}{2}\sum_L \bar{t}_L^C(\omega_2)\langle L|[V^{(0)};\kappa^A(-\omega_\sigma),\kappa^B(\omega_1)]|\mathrm{HF}\rangle-\sum_{LK}\bar{t}_L^{(0)}G_{LK}\{J^{ABC}(-\omega_\sigma;\omega_1,\omega_2)\}t_K^{(0)}$$
$$-\sum_{LK}\bar{t}_L^{(0)}G_{LK}\{J^{AB}(-\omega_\sigma;\omega_1)\}t_K^C(\omega_2)-\sum_{LK}\bar{t}_L^C(\omega_2)G_{LK}\{J^{AB}(-\omega_\sigma;\omega_1)\}t_K^{(0)}$$
$$-\sum_{LK}\bar{t}_L^C(\omega_2)G_{LK}^A(-\omega_\sigma)t_K^B(\omega_1)-\sum_{\pm\lambda}\xi_\lambda^{(0)}\langle \mathrm{HF}|[E_\lambda,J^{ABC}(-\omega_\sigma;\omega_1,\omega_2)]|\mathrm{HF}\rangle$$
$$-\sum_{\pm\lambda}\xi_\lambda^C(\omega_2)\langle \mathrm{HF}|[E_\lambda,J^{AB}(-\omega_\sigma;\omega_1)]|\mathrm{HF}\rangle\Big\}, \tag{94}$$

where

$$J^{AB}(\omega_1;\omega_2)=-[M_A,\kappa^B(\omega_2)]+\tfrac{1}{2}[H_0;\kappa^A(\omega_1),\kappa^B(\omega_2)]-\tfrac{1}{2}\omega_1[\kappa^A(\omega_1),\kappa^B(\omega_2)] \tag{95}$$

$$J^{ABC}(\omega_1;\omega_2,\omega_3)=-\tfrac{1}{2}[M_A;\kappa^B(\omega_2),\kappa^C(\omega_3)]+\tfrac{1}{6}[H_0;\kappa^A(\omega_1),\kappa^B(\omega_2),\kappa^C(\omega_3)]-\tfrac{1}{6}\omega_1[\kappa^A(\omega_1);\kappa^B(\omega_2),\kappa^C(\omega_3)]. \tag{96}$$

We discuss some general features of the expressions. Equations (92)–(94) contain the Hartree–Fock contributions as the first term. For Eqs. (93) and (94), the Hartree–Fock terms may be written in the more practical form as follows:

$$-\mathscr{P}[A(-\omega_1),B(\omega_1)]\langle \mathrm{HF}|J^{AB}(-\omega_1;\omega_1)|\mathrm{HF}\rangle = \langle \mathrm{HF}|[M_A,\kappa^B(\omega_1)]|\mathrm{HF}\rangle$$
$$= \langle \mathrm{HF}|[M_B,\kappa^A(-\omega_1)]|\mathrm{HF}\rangle, \tag{97}$$

$$-\mathscr{P}[A(-\omega_\sigma),B(\omega_1),C(\omega_2)]\langle \mathrm{HF}|J^{ABC}(-\omega_\sigma;\omega_1,\omega_2)]|\mathrm{HF}\rangle$$
$$= \mathscr{P}[A(-\omega_\sigma),B(\omega_1),C(\omega_2)]\{\tfrac{1}{2}\langle \mathrm{HF}|[M_A;\kappa^B(\omega_1),\kappa^C(\omega_2)]|\mathrm{HF}\rangle$$
$$-\tfrac{1}{6}\langle \mathrm{HF}|[H_0;\kappa^A(-\omega_\sigma),\kappa^B(\omega_1),\kappa^C(\omega_2)]|\mathrm{HF}\rangle\}. \tag{98}$$

In Eq. (93) the multipliers $\bar{t}_L^A(-\omega_1)$ appear. They can easily be eliminated according to the $2n+2$ rule, but this does not lead to computational simplifications.[30]

We can compare Eq. (93) with the analytical expression of $\alpha_{AB}(-\omega_1;\omega_1)$ in the PED method.[25] We can directly define $\alpha_{AB}(-\omega_1;\omega_1)$ from the QED [Eq. (18) or (66)]. In the PED method, on the other hand, $\alpha_{AB}(-\omega_1;\omega_1)$ must be defined as $\frac{1}{2}[(\partial^2 W/\partial\epsilon_A(0)\partial\epsilon_B(\omega_1))+(\partial^2 W/\partial\epsilon_A(\omega_1)\partial\epsilon_B(0))]$. The QED form Eq. (93) only contains the orbital rotation parameters $\kappa(\pm\omega_1)$, but the PED form contains the parameters $U(0)$ in addition to $U(\pm\omega_1)$ which correspond to $\kappa(\pm\omega_1)$.

Since the MP2 wave function is nonvariational, it does not satisfy the time-dependent Hellmann–Feynman theorem and we cannot regard Eqs. (93) and (94) as the linear and quadratic response functions. In order to see this, we give the spectral representation of Eq. (93) as

$$\alpha_{AB}(-\omega_1;\omega_1)=\mathscr{P}[A(-\omega_1),B(\omega_1)]\Bigg\{\frac{1}{2}\sum_{\pm p}\mathrm{sgn}(p)\frac{\langle \mathrm{HF}|[M_A,O_p^\dagger]|\mathrm{HF}\rangle\langle \mathrm{HF}|[O_p,M_B]|\mathrm{HF}\rangle}{\omega_p-\omega_1}$$
$$-\frac{1}{2}\sum_{\pm p,\pm q}\mathrm{sgn}(pq)(\langle \mathrm{HF}|[V^{(0)};O_p^\dagger,O_q^\dagger]|t^{(0)}\rangle+\langle \bar{t}^{(0)}|[V^{(0)};O_p^\dagger,O_q^\dagger]|\mathrm{HF}\rangle)$$
$$\times\frac{\langle \mathrm{HF}|[O_p,M_A]|\mathrm{HF}\rangle\langle \mathrm{HF}|[O_q,M_B]|\mathrm{HF}\rangle}{(\omega_p+\omega_1)(\omega_q-\omega_1)}$$
$$+\sum_{\pm p}\mathrm{sgn}(p)\frac{\langle \bar{t}^{(0)}|G\{[M_A,O_p^\dagger]\}|t^{(0)}\rangle\langle \mathrm{HF}|[O_p,M_B]|\mathrm{HF}\rangle}{\omega_p-\omega_1}$$
$$-\frac{1}{2}\sum_{\pm p,\pm q}\mathrm{sgn}(pq)\langle \bar{t}^{(0)}|G\{[H_0;O_p^\dagger,O_q^\dagger]\}+G\{\omega_1[O_p^\dagger,O_q^\dagger]\}|t^{(0)}\rangle$$
$$\times\frac{\langle \mathrm{HF}|[O_p,M_A]|\mathrm{HF}\rangle\langle \mathrm{HF}|[O_q,M_B]|\mathrm{HF}\rangle}{(\omega_p+\omega_1)(\omega_q-\omega_1)}$$
$$+\sum_K\Bigg(\sum_{\pm p}\mathrm{sgn}(p)\frac{\langle \mathrm{HF}|[V^{(0)},O_p^\dagger]|K\rangle-\langle \bar{t}^{(0)}|G\{[H_0,O_p^\dagger]+\omega_1 O_p^\dagger\}|K\rangle}{\omega_p+\omega_1}$$
$$\times\langle \mathrm{HF}|[O_p,M_A]|\mathrm{HF}\rangle+\langle \bar{t}^{(0)}|G\{M_A\}|K\rangle\Bigg)\times\Bigg(\frac{\langle K|G\{M_B\}|t^{(0)}\rangle}{G_{KK}^{(0)}}$$
$$+\sum_{\pm q}\mathrm{sgn}(q)\frac{(\langle K|[V^{(0)},O_q^\dagger]|\mathrm{HF}\rangle-\langle K|G\{[H_0,O_q^\dagger]-\omega_1 O_q^\dagger\}|t^{(0)}\rangle)\langle \mathrm{HF}|[O_q,M_B]|\mathrm{HF}\rangle}{G_{KK}^{(0)}(\omega_q-\omega_1)}\Bigg)$$
$$+\sum_{\pm p}\mathrm{sgn}(p)\frac{\langle \mathrm{HF}|[\zeta^{(0)},[M_A,O_p^\dagger]]|\mathrm{HF}\rangle\langle \mathrm{HF}|[O_p,M_B]|\mathrm{HF}\rangle}{\omega_p-\omega_1}$$
$$-\frac{1}{2}\sum_{\pm p,\pm q}\mathrm{sgn}(pq)\langle \mathrm{HF}|[\zeta^{(0)},[H_0;O_p^\dagger,O_q^\dagger]+\omega_1[O_p^\dagger,O_q^\dagger]]|\mathrm{HF}\rangle$$
$$\times\frac{\langle \mathrm{HF}|[O_p,M_A]|\mathrm{HF}\rangle\langle \mathrm{HF}|[O_q,M_B]|\mathrm{HF}\rangle}{(\omega_p+\omega_1)(\omega_q-\omega_1)}\Bigg\}, \tag{99}$$

where

$$\langle \bar{t}^{(0)}| = \sum_K \bar{t}_K^{(0)} \langle K|\ , |t^{(0)}\rangle = \sum_K |K\rangle t_K^{(0)}, \tag{100}$$

$$\xi^{(0)} = \sum_{\pm\lambda} E_\lambda \xi_\lambda^{(0)}, \tag{101}$$

and the "diagonalized" (de)excitation operators $\{O_p^\dagger, O_p\}$ are written as

$$\begin{aligned} O_p^\dagger &= \sum_\lambda (E_\lambda X_{\lambda p} + E_{-\lambda} Y_{\lambda p}) \\ O_p &= \sum_\lambda (E_\lambda Y_{\lambda p}^* + E_{-\lambda} X_{\lambda p}^*) \end{aligned} \tag{102}$$

The coefficients $\{X_{\lambda p}, Y_{\lambda p}\}$ compose the eigenvector of the free-oscillation equation (the RPA equation)

$$\left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} - \omega_p \begin{pmatrix} \mathbf{S} & \mathbf{\Delta} \\ -\mathbf{\Delta}^* & -\mathbf{S}^* \end{pmatrix}\right]\begin{pmatrix} \mathbf{X}_p \\ \mathbf{Y}_p \end{pmatrix} = \begin{pmatrix} \mathbf{0} \\ \mathbf{0} \end{pmatrix}, \quad \omega_p > 0, \tag{103}$$

where the eigenvalues $\{\omega_p\}$ are the excitation energies in the TDHF approximation. We have used the following notations:

$$\omega_{-p} = -\omega_p, \quad O_{\pm p}^\dagger = O_{\mp p} \tag{104}$$

$$\mathrm{sgn}(p) = \begin{cases} 1 & (p>0) \\ -1 & (p<0) \end{cases}, \quad \text{so } \mathrm{sgn}(p)\mathrm{sgn}(q) = \mathrm{sgn}(pq). \tag{105}$$

The detailed derivation of the spectral representations is also given in paper I. It is observed that Eq. (99) has the poles when $|\omega|$ is equal to one of the TDHF excitation energies. However, Eq. (99) has the second-order poles in addition to the first-order poles. So the pole structures of Eqs. (93) and (94) are not compatible with ones of the exact response functions. SOPPA[27,28] is the perturbative correlation correction approach in which the form of the exact response functions is kept. But its extension to the nonlinear response has not appeared to our knowledge.

VI. DISCUSSION

We have derived the response properties up to third order $[\beta(-\omega_\sigma;\omega_1,\omega_2)]$ at the MP2 level of theory in the quasienergy derivative (QED) method. The MP2 quasienergy Lagrangian has been constructed, and the TDHF orbital rotation responses through order n determine the QEDs through order $2n+1$. The Lagrange multipliers satisfy the $2n+2$ rule. The QEDs can always be written in the symmetric form with the permutation operator $\mathscr{P}[A_1(\omega_1), A_2(\omega_2), \cdots, A_n(\omega_n)]$. The response properties derived in the QED method satisfy the requirement that the properties should be identical with ones in the finite-field method in the static limit.

In the PED method the vanishing condition $\langle \Phi | \partial\Phi/\partial\epsilon(0)\rangle = 0$ has to be considered. Since this condition gives the different constraints to the parameters when a different approximation model is empolyed, the constraints derived by Rice and Handy for MP2 cannot be used straightforwardly when the higher-order MPPT or the coupled cluster (CC) model is employed. In these approximation models, it seems rather difficult to consider the condition. In the QED method we do not have to think about such a condition.

The applications of the QED method to the full CI response, the TDHF approximation, the TDMCSCF approximation, and the limitted CI response have been presented in paper I. We discuss the possibility of the application to other approximation models below. It is possible to extend the QED method to the higher-order MPPT, if we consider the expanded electron correlation operator $V^{(n)}$ with respect to the external field. It is also possible to extend our method to the CC model. Since the CC wave function is not normalized, the quasienergy will have to be defined as a complex value[2,32] in general. But the QEDs are always real as discussed in Sec. III. The details will be reported elsewhere.[39]

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