# Gauge invariant coupled cluster response theory

Thomas Bondo Pedersen and Henrik Koch
*Department of Chemistry, Odense University, DK-5230 Odense M, Denmark*

Christof Hättig
*Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark*

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We introduce a time-dependent coupled cluster based Lagrangian that includes orbital rotation. This Lagrangian is shown to give gauge invariant response properties for one-electron operators in the limit of a complete one-electron basis. The pole structure of the linear response function is compatible with that of the exact response function and the notorious problem of unphysical second-order poles in the Brueckner coupled cluster response theory is not present in this model. The total energy of the model is identical to the coupled cluster model using optimized orbitals recently revived by Sherrill *et al.* [J. Chem. Phys. **109**, 4171 (1998)]. The model provides a straightforward approach for calculating magnetic response properties in a gauge invariant manner using coupled cluster type wave functions. © *1999 American Institute of Physics.*
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## I. INTRODUCTION

In the last two decades response theory based on coupled cluster wave functions have been developed and implemented in computer programs by several research groups.[1–10] State of the art calculations on large molecules are carried out routinely using integral direct implementations and these methods have proven powerful in calculating properties like excitation energies, transition moments, electric polarizabilities, and hyperpolarizabilities. Due to this success, we find it highly desirable to evaluate magnetic response properties using the coupled cluster response methods (CCLR).[4,11]

Severe difficulties are encountered in this process, as CCLR and the related equation of motion coupled cluster methods (EOM-CC)[6] all suffer from lack of gauge invariance.[11] This has the implication that some magnetic properties, such as length gauge rotational strengths, Verdet constants, and many others, cannot be straightforwardly calculated in a gauge origin invariant manner. Even in the limit of a complete one-electron basis set, the gauge origin dependence of these properties will remain present. Only in the limit where CCLR is equivalent to full configuration interaction (FCI) it will be possible to obtain gauge origin invariant properties. Therefore a practice has evolved where calculations are carried out for molecules that fulfill gauge origin invariance due to a particular point group symmetry.[12,13] From a theoretical point of view this situation is unsatisfactory, as an inclusion of the nuclear motion in the description might again introduce a dependence on the gauge origin. In our opinion, the only satisfactory solution will be to change the basic CCLR model.

The situation is different for static magnetic properties derivable from derivatives of the total energy. In this case, gauge origin invariant properties, e.g., magnetic shielding tensors and magnetizabilities, can be calculated straightforwardly using London's gauge invariant orbitals. Such implementations are available for many *ab initio* models and are today considered standard tools in quantum chemistry, see, e.g., Ref. 14 for a review and further references. The requirements needed in order to obtain gauge origin invariance of static and dynamic magnetic properties are clearly different. Gauge origin invariance of the total energy does not imply the same for dynamic properties. In general, gauge origin invariance of dynamic magnetic properties will require gauge invariance for one-electron operators in the limit of a complete basis. This is equivalent to requiring Ehrenfest's theorem satisfied for one-electron operators, such that if $A$ is a one-electron operator then the following identity

$$\frac{d}{dt}\langle A\rangle = i\langle [H,A]\rangle + \left\langle \frac{\partial A}{\partial t}\right\rangle, \tag{1}$$

must hold for the time-dependent average value within the model. It is well known that for the random phase approximation (RPA)[15] and the multiconfigurational random phase approximation (MCRPA)[16] these relations hold and thus gauge invariance is fulfilled. In the CCLR model this is not the case[11,17,18] and the subject of this paper is to ameliorate the model in a way that gauge invariance is obtained.

The CCLR model is based on a nonlinear configuration interaction (CI) parametrization and only includes excitation operators with respect to the reference state; thus the orbital de-excitation part of Eq. (1) is only satisfied to the extent that the CI part spans these de-excitations. In general this can only be fulfilled in the FCI limit and explicit treatment of the de-excitations is needed for an incomplete wave function. The most obvious choice is to consider the so-called Brueckner-type wave functions. These wave functions are parametrized in terms of a unitary orbital rotation part and a coupled cluster part. To be more explicit, we write the phase isolated wave function as

$$|\Psi\rangle = \exp(\kappa)\exp(T)|R\rangle, \tag{2}$$

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where $\kappa$ is the anti-Hermitian orbital rotation generator, $T$ is the cluster operator including doubles and higher-order excitations, and $|R\rangle$ is a reference state. The question is then how these parameters should be determined, as a complete variational determination is out of the question. The most widely used approach is the projection approach by Chiles and Dykstra[19] and Handy *et al.*,[20] where all parameters are determined by projection of the Schrödinger equation. This procedure is normally denoted Brueckner coupled cluster doubles (BCCD) or Brueckner doubles (BD) if only double excitations are included in the cluster operator. In another approach, suggested by Purvis and Bartlett[21] and later investigated further by Scuseria and Schaefer,[22] the orbital part of the wave function is determined variationally and the coupled cluster part is determined by projection. If the coupled cluster operator is truncated after double excitations the model is denoted optimized doubles (OD)[23] or as we prefer optimized coupled cluster doubles (OCCD). Recently, Sherrill *et al.*[23] showed that BCCD and OCCD give very similar equilibrium structures and harmonic vibrational frequencies. Based on these observations the authors concluded that the main advantages in using the optimized orbital procedure are due to the computational simplifications that arise in the calculation of analytical derivatives and the treatment of inactive orbitals. These aspects are discussed in detail by Sherrill *et al.*[23] and we refer to this paper for details and references.

Considering dynamic response properties, the difference between the two models becomes much more pronounced and severe. The Brueckner coupled cluster model (BCC) has been shown by Koch *et al.*[24] and Aiga *et al.*[25] to give unphysical second-order poles in the linear response function. Such a pole structure implies an incorrect description of dispersion and makes it impossible to define transition moments. For these reasons the BCC response function was never implemented and the question of gauge invariance was not analyzed. However, the optimized coupled cluster (OCC) response function does not suffer from these artifacts. The time-dependent Lagrangian, defined in this paper, is shown to give the correct pole structure in the linear response function. Furthermore, analogously to the RPA and MCRPA approaches, the OCC model is gauge invariant for one-electron operators in the limit of a complete basis set.

This paper has been organized as follows. In Sec. II we define the time-dependent model Lagrangian and show gauge invariance of the model, and in Sec. III we explicitly treat time-independent theory. Then, in Sec. IV, follows the perturbation theoretical derivation of the linear response function including an analysis of the eigenvalue problem that determines the poles (excitation energies) of the linear response function. Our final remarks and conclusions are given in Sec. V.

## II. THE MODEL LAGRANGIAN

As reviewed in a recent publication,[26] the time-dependent variational principle[27–29] can be formulated analogously to Hamilton's principle of stationary action[30] by replacing the classical Lagrangian with a quantum mechanical functional. Expressing the quantum mechanical Lagrangian[29] $L(\boldsymbol{\lambda})$ in terms of a set of complex time-dependent variables $\boldsymbol{\lambda}(t)$, the fundamental equations for determining these parameters become the Euler–Lagrange equations,[30]

$$\frac{\partial L}{\partial \lambda_\mu} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\lambda}_\mu}\right) = 0, \tag{3}$$

where the dot denotes the time-derivative, $\dot{\boldsymbol{\lambda}} = d\boldsymbol{\lambda}/dt$. We shall here write the quantum mechanical model Lagrangian as

$$L(\mathbf{t}, \mathbf{t}^*, \overline{\mathbf{t}}, \overline{\mathbf{t}}^*, \boldsymbol{\kappa}, \boldsymbol{\kappa}^*) = \tfrac{1}{2}(Q(\mathbf{t}, \overline{\mathbf{t}}, \boldsymbol{\kappa}, \boldsymbol{\kappa}^*) + Q(\mathbf{t}, \overline{\mathbf{t}}, \boldsymbol{\kappa}, \boldsymbol{\kappa}^*)^*), \tag{4}$$

where

$$Q = \langle R|(1+\overline{\Omega})\Omega^{-1}\left(H - i\frac{d}{dt}\right)\Omega|R\rangle. \tag{5}$$

The quantum mechanical operator $H$ is the time-dependent Hamiltonian and $|R\rangle$ is the time- and parameter-independent normalized closed-shell reference determinant. The nonunitary wave operator $\Omega$ is composed of a unitary operator generating orbital rotations parametrized by $\boldsymbol{\kappa}, \boldsymbol{\kappa}^*$ and a nonunitary coupled cluster operator parametrized by $\mathbf{t}$. Thus the wave operator may be written as

$$\Omega = \exp(\kappa)\exp(T), \tag{6}$$

where the orbital rotation and cluster operators are given by

$$\kappa = -\kappa^\dagger = \sum_{\mu_1} (\kappa_{\mu_1}\tau_{\mu_1} - \kappa^*_{\mu_1}\tau^\dagger_{\mu_1}), \tag{7}$$

$$T = \sum_{\mu} t_\mu \tau_\mu, \quad \mu > \mu_1. \tag{8}$$

The set $\{\tau_{\mu_1}\}$ contains single excitation operators with respect to the reference state, and $\{\tau_\mu\}$ is composed of double excitations, triple excitations, and so forth. The operator $\overline{\Omega}$ reads

$$\overline{\Omega} = \sum_{\mu} \overline{t}_\mu \tau^\dagger_\mu, \tag{9}$$

where $\overline{t}_\mu$ is the Lagrangian multiplier corresponding to the $\mu$th excitation. Introducing the notation $|\mu_1\rangle = \tau_{\mu_1}|R\rangle$ and $|\mu\rangle = \tau_\mu|R\rangle$, we shall assume the following biorthonormality relations

$$\langle \mu_1|\nu_1\rangle = \delta_{\mu_1\nu_1}, \quad \langle \mu|\nu\rangle = \delta_{\mu\nu}, \tag{10}$$

$$\langle \mu_1|\nu\rangle = 0, \quad \langle \mu_1|R\rangle = 0, \quad \langle \mu|R\rangle = 0, \tag{11}$$

such that the normalization is

$$\langle \Phi|\Psi\rangle = 1, \tag{12}$$

where we have used the short-hand notation

$$|\Psi\rangle = \Omega|R\rangle, \tag{13}$$

$$\langle \Phi| = \langle R|(1+\overline{\Omega})\Omega^{-1}. \tag{14}$$

We note that for an untruncated cluster operator $T$, the state $|\Psi\rangle$ is merely a reparametrization of the FCI wave function. Furthermore, while the parametrization of $|\Psi\rangle$ is identical to the one used in Refs. 24 and 25 in a formulation of BCC

response theory, the Lagrangian of the present work and these references differ as we do *not* introduce multipliers corresponding to the single excitations and de-excitations but rather determine the orbitals by optimization through the Euler–Lagrange equations. The average value of a general non-Hermitian operator $A$ is then given by[26]

$$\langle A\rangle = \tfrac{1}{2}(\langle\Phi|A|\Psi\rangle + \langle\Phi|A^{\dagger}|\Psi\rangle^{*}). \tag{15}$$

Turning now to the Euler–Lagrange equations for the parameters of the model, we introduce the notation

$$\tilde{q}_{\mu_1} = \frac{\partial\Omega}{\partial\kappa_{\mu_1}}\Omega^{-1} = \frac{\partial\exp(\boldsymbol{\kappa})}{\partial\kappa_{\mu_1}}\exp(-\boldsymbol{\kappa}), \tag{16}$$

$$\tilde{q}_{\mu} = \frac{\partial\Omega}{\partial t_{\mu}}\Omega^{-1} = \exp(\boldsymbol{\kappa})\tau_{\mu}\exp(-\boldsymbol{\kappa}), \tag{17}$$

where we have used that excitation operators commute among themselves. Using the operator identity

$$\frac{\partial(\Omega^{-1}\dot{\Omega})}{\partial\lambda} = \Omega^{-1}\left[\frac{d}{dt}\left(\frac{\partial\Omega}{\partial\lambda}\Omega^{-1}\right)\right]\Omega, \tag{18}$$

where $\lambda$ is an element in one of the three parameter sets upon which the wave operator depends (i.e., $\mathbf{t}$, $\boldsymbol{\kappa}$, and $\boldsymbol{\kappa}^{*}$), we obtain

$$\langle\mu|\Omega^{-1}\left(H - i\frac{d}{dt}\right)|\Psi\rangle = 0, \tag{19}$$

$$\frac{d}{dt}\langle\Phi|\tilde{q}_{\mu}|\Psi\rangle = i\langle\Phi|[H,\tilde{q}_{\mu}]|\Psi\rangle + \langle\Phi|\dot{\tilde{q}}_{\mu}|\Psi\rangle, \tag{20}$$

$$\frac{d}{dt}\langle\tilde{q}_{\mu_1}\rangle = i\langle[H,\tilde{q}_{\mu_1}]\rangle + \langle\dot{\tilde{q}}_{\mu_1}\rangle, \tag{21}$$

from the Euler–Lagrange equations for $\bar{\mathbf{t}}$, $\mathbf{t}$, and $\boldsymbol{\kappa}$, respectively. The equations for the complex conjugated parameters ($\bar{\mathbf{t}}^{*}$, $\mathbf{t}^{*}$, and $\boldsymbol{\kappa}^{*}$) are obtained by complex conjugation of Eqs. (19), (20), and (21) as the Lagrangian is real. Equation (19) is recognized as a projected Schrödinger equation for $|\Psi\rangle$, and is equivalent to the standard equation obtained in CCLR. Equation (20) is an Ehrenfest-type equation for the operators defined in Eq. (17), although not with respect to the average value defined in Eq. (15). This is contrary to Eq. (21) where the complex conjugated equation is obtained by replacing the operator by the adjoint operator, i.e.,

$$\frac{d}{dt}\langle\tilde{q}^{\dagger}_{\mu_1}\rangle = i\langle[H,\tilde{q}^{\dagger}_{\mu_1}]\rangle + \langle\dot{\tilde{q}}^{\dagger}_{\mu_1}\rangle, \tag{22}$$

and this is due to the form of the average value in Eq. (15) satisfying $\langle A\rangle^{*} = \langle A^{\dagger}\rangle$. Equation (22) is indeed the equation obtained for $\kappa^{*}_{\mu_1}$ as may be verified on noting the relation

$$\tilde{q}^{\dagger}_{\mu_1} = -\frac{\partial\Omega}{\partial\kappa^{*}_{\mu_1}}\Omega^{-1} = -\frac{\partial\exp(\boldsymbol{\kappa})}{\partial\kappa^{*}_{\mu_1}}\exp(-\boldsymbol{\kappa}). \tag{23}$$

The special form displayed by Eq. (19) is due to $L$ being linear in $\bar{\mathbf{t}}$ and independent of $\dot{\bar{\mathbf{t}}}$. While in ordinary time-dependent coupled cluster theory[26] the projected Schrödinger equations may be solved for the cluster amplitudes $\mathbf{t}$ followed by a determination of the multipliers $\bar{\mathbf{t}}$ from the Ehrenfest-type Eq. (20) for $\{\tilde{q}_{\mu}\}$, the present model requires that all three (six) sets of equations are solved simultaneously for $\mathbf{t}$, $\bar{\mathbf{t}}$, and $\boldsymbol{\kappa}$ (and their complex conjugated). Interestingly, we note that Eq. (19) may in fact be obtained from Eq. (20) if we replace the operator $\tilde{q}_{\mu}$ by the de-excitation type operator of the form

$$\tilde{p}^{\dagger}_{\mu} = |\Psi\rangle\langle\mu|\Omega^{-1}. \tag{24}$$

Thus all parameters in the model are determined from Ehrenfest-type equations and when the operator manifold become complete, as in the FCI case, the Schrödinger equation is reproduced.

So far we have implicitly assumed that the only nonredundant orbital rotations are those between occupied and virtual orbitals. In order to verify this assumption, we now include the redundant occupied–occupied and virtual–virtual orbital rotations written in terms of the anti-Hermitian operator $\boldsymbol{\kappa}^{R}$. The redundant and nonredundant parts of the orbital rotations may be factorized as[31] $\exp(\boldsymbol{\kappa})\exp(\boldsymbol{\kappa}^{R})$, and the ''redundant'' wave operator can therefore be written in the form

$$\Omega^{R} = \exp(\boldsymbol{\kappa})\exp(\boldsymbol{\kappa}^{R})\exp(T) = \exp(\boldsymbol{\kappa})\exp(T')\exp(\boldsymbol{\kappa}^{R}), \tag{25}$$

where $T' = \exp(\boldsymbol{\kappa}^{R})T\exp(-\boldsymbol{\kappa}^{R})$. Introducing also $\bar{\Omega}' = \exp(\boldsymbol{\kappa}^{R})\bar{\Omega}\exp(-\boldsymbol{\kappa}^{R})$, we find

$$\begin{aligned}\langle R|(1+\bar{\Omega})\exp(-T)\exp(-\boldsymbol{\kappa}^{R})\exp(-\boldsymbol{\kappa}) \\ = \langle R|\exp(-\boldsymbol{\kappa}^{R})(1+\bar{\Omega}')\exp(-T')\exp(-\boldsymbol{\kappa}),\end{aligned} \tag{26}$$

and as the reference state is invariant with respect to the redundant rotations it follows that the occupied–occupied and virtual–virtual orbital rotations are indeed redundant as $T'$ and $\bar{\Omega}'$ are excitations and de-excitations, $\tau_{\mu}$ and $\tau^{\dagger}_{\mu}$, respectively. It must be stressed that these considerations are independent of the truncation level of the cluster operator. Also, it should be stressed that if orbitals are frozen such that the set of occupied orbitals is split into inactive occupied and active occupied orbitals, then rotations between the inactive and active blocks are nonredundant and must be explicitly included. Of course, this must also be done if a set of virtual orbitals are frozen.

Let us next consider the time-dependent average value of a Hermitian one-electron operator $A$. According to Eq. (15) we have

$$\langle A\rangle = \mathrm{Re}\langle\Phi|A|\Psi\rangle. \tag{27}$$

Since $A$ can be written in terms of the excitation and de-excitation operators $\{\tau_{\mu_1}\}$ and $\{\tau^{\dagger}_{\mu_1}\}$, and the generators of occupied–occupied and virtual–virtual orbital rotations that are spanned by $T$ and $\bar{\Omega}$, it immediately follows from Eqs. (21) and (22) that $\langle A\rangle$ satisfies Eq. (1). Thus, we may conclude that the model Lagrangian of Eq. (4) yields gauge invariant one-electron properties in analogy with the RPA and MCRPA approaches.

## III. THE STATIC LIMIT

We briefly discuss the static Lagrangian as this clearly illustrates the computational requirements needed in determining the zeroth-order wave function. Suppose that the Hamiltonian is time-independent, $H=H_0$. The Lagrangian, Eq. (4), still has the same form but the $Q$-functional now reduces to

$$Q_0=\langle R|\exp(-\kappa)H_0\exp(\kappa)\exp(T)|R\rangle + \sum_\mu \bar{t}_\mu\langle\mu|\exp(-T)\exp(-\kappa)H_0\exp(\kappa)\exp(T)|R\rangle, \tag{28}$$

where the parameters are time-independent, and where $\langle R|\exp(-T)=\langle R|$ has been used. In the static limit the Euler–Lagrange equations become standard stationarity conditions for $L_0$ with respect to the parameters $\mathbf{t}$, $\mathbf{t}^*$, $\bar{\mathbf{t}}$, $\bar{\mathbf{t}}^*$, $\boldsymbol{\kappa}$, and $\boldsymbol{\kappa}^*$. We shall find it convenient to express the optimized conditions at the point in parameter space where $\boldsymbol{\kappa}=\boldsymbol{\kappa}^*=\mathbf{0}$, $\mathbf{t}=\mathbf{t}^{(0)}$, $\mathbf{t}^*=\mathbf{t}^{(0)*}$, $\bar{\mathbf{t}}=\bar{\mathbf{t}}^{(0)}$, and $\bar{\mathbf{t}}^*=\bar{\mathbf{t}}^{(0)*}$, i.e., we assume that all operators and integrals refer to the optimized orbital basis. By straightforward differentiation we then obtain the equations

$$\frac{\partial L_0}{\partial \bar{t}_\mu}=\tfrac{1}{2}\langle\mu|\exp(-T^{(0)})H_0|\Psi^{(0)}\rangle=0, \tag{29}$$

$$\frac{\partial L_0}{\partial t_\mu}=\tfrac{1}{2}\langle\Phi^{(0)}|[H_0,\tau_\mu]|\Psi^{(0)}\rangle=0, \tag{30}$$

$$\frac{\partial L_0}{\partial \kappa_{\mu_1}}=\langle[H_0,\tau_{\mu_1}]\rangle_0=0, \tag{31}$$

where $|\Psi^{(0)}\rangle=\exp(T^{(0)})|R\rangle$ and $\langle\Phi^{(0)}|=\langle R|+\Sigma_\mu \bar{t}_\mu^{(0)}\times\langle\mu|\exp(-T^{(0)})$, and where the average value $\langle\cdot\rangle_0$ is simply the static limit of Eq. (15),

$$\langle A\rangle_0=\tfrac{1}{2}(\langle\Phi^{(0)}|A|\Psi^{(0)}\rangle+\langle\Phi^{(0)}|A^\dagger|\Psi^{(0)}\rangle^*). \tag{32}$$

As the Lagrangian is real, the equations for the complex conjugated parameters are obtained from Eqs. (29)–(31) by complex conjugation. Equations (29)–(31) are merely the static limits of Eqs. (19)–(21), and we observe that Eq. (31) and its complex conjugated are generalized Brillouin conditions for the orbital rotation operators (excitations as well as de-excitations). As usual, we note that if $H_0$ is a real operator we may consider only real orbital rotations and Eq. (31) can be combined with its complex conjugate to yield the stationarity condition

$$\langle[H_0,\tau_{\mu_1}-\tau_{\mu_1}^\dagger]\rangle_0=0. \tag{33}$$

This equation corresponds to writing the orbital rotation operator as $\kappa=\Sigma_{\mu_1}\kappa_{\mu_1}(\tau_{\mu_1}-\tau_{\mu_1}^\dagger)$ with all $\kappa_{\mu_1}$ real.

Once the variables have been determined, the energy can be calculated as

$$E=\mathrm{Re}\langle R|H_0\exp(T^{(0)})|R\rangle, \tag{34}$$

whereas the appropriate expression away from convergence reads

$$E=\tfrac{1}{2}(Q_0+Q_0^*). \tag{35}$$

Thus the parameters $\mathbf{t}$, $\mathbf{t}^*$, $\bar{\mathbf{t}}$, $\bar{\mathbf{t}}^*$, $\boldsymbol{\kappa}$, and $\boldsymbol{\kappa}^*$ should be determined simultaneously although the final energy is independent of the multipliers $\bar{\mathbf{t}}$. In principle, one might be able to determine the energy without solving for the multipliers, but as pointed out by Sherrill *et al.*[23] the convergence is then rather slow and simultaneous solution of the equations is recommended. Due to the variational nature of the Lagrangian, the time-independent Hellmann–Feynman theorem takes the form

$$\frac{\partial L_0}{\partial \boldsymbol{\epsilon}}=\mathrm{Re}\langle\Phi^{(0)}|\frac{\partial H_0}{\partial \boldsymbol{\epsilon}}|\Psi^{(0)}\rangle, \tag{36}$$

and standard variational perturbation techniques (see for example Ref. 32) may now be employed to calculate static properties from higher-order derivatives of the Lagrangian.

Before moving on to the derivation of the dynamic linear response function, we briefly return to the discussion of redundant orbital rotations in Sec. II and explicitly verify that occupied–occupied and virtual–virtual orbital rotations are indeed redundant. In order to prove invariance with respect to orbital rotations among occupied orbitals, we consider Eq. (31) (or, equivalently, its complex conjugate) with the excitation (de-excitation) operator replaced by $E_{ij}=a_{i\alpha}^\dagger a_{j\alpha}+a_{i\beta}^\dagger a_{j\beta}$, where $i$ and $j$ refer to occupied orbitals and $\alpha$ and $\beta$ are the spin projections. Using the identity

$$E_{ij}=\exp(T^{(0)})\exp(-T^{(0)})E_{ij}\exp(T^{(0)})\exp(-T^{(0)}) =\exp(T^{(0)})E_{ij}\exp(-T^{(0)})+[E_{ij},T^{(0)}], \tag{37}$$

we readily obtain

$$\langle\Phi^{(0)}|[H_0,E_{ij}]|\Psi^{(0)}\rangle =\langle\Phi^{(0)}|[H_0,[E_{ij},T^{(0)}]]|\Psi^{(0)}\rangle - \sum_\mu \bar{t}_\mu^{(0)}\langle\mu|E_{ij}\exp(-T^{(0)})H_0\exp(T^{(0)})|R\rangle=0, \tag{38}$$

implying $\langle[H_0,E_{ij}]\rangle_0=0$. This follows from the fact that $[E_{ij},T^{(0)}]$ can be expressed in terms of the set $\{\tau_\mu\}$ and $\langle\mu|E_{ij}$ can be expressed in terms of the set $\{\langle\nu|\}$, and from the cluster amplitude and multiplier Eqs. (29) and (30). Thus, the total energy is stationary under occupied–occupied orbital rotations. Similar arguments can be invoked to verify stationarity of the energy under virtual–virtual orbital rotations.

## IV. TIME-DEPENDENT PERTURBATION THEORY

Consider the case where the Hamiltonian is explicitly time-dependent, i.e.,

$$H=H_0+\alpha V(t), \tag{39}$$

where the time-independent strength parameter $\alpha$ is real, and the static limit outlined in the previous section is implicitly included as the special case $\alpha=0$. This strength parameter will be used for a time-dependent perturbation expansion of

the Euler–Lagrange equations. The explicitly time-dependent Hermitian perturbation operator is represented as the Fourier transform

$$V(t)=\int_{-\infty}^{\infty} V(\omega)\exp(-i\omega t)d\omega, \tag{40}$$

where $V(\omega)^{\dagger}=V(-\omega)$, and where the convergence factors have been suppressed. It follows from Eqs. (4) and (5) that the Lagrangian may be written in the form

$$L=\mathcal{H}-i\mathcal{F}, \tag{41}$$

where

$$\mathcal{H}=\mathcal{H}(\boldsymbol{\lambda},t)=\tfrac{1}{2}(\langle\Phi|H|\Psi\rangle+\langle\Phi|H|\Psi\rangle^{*}), \tag{42}$$

$$\mathcal{F}=\mathcal{F}(\boldsymbol{\lambda},\dot{\boldsymbol{\lambda}})=\frac{1}{2}\left(\langle\Phi|\frac{d}{dt}|\Psi\rangle-\langle\Phi|\frac{d}{dt}|\Psi\rangle^{*}\right). \tag{43}$$

Here $\boldsymbol{\lambda}$ compactly denotes the six independent parameters sets $\{\mathbf{t},\mathbf{t}^{*},\overline{\mathbf{t}},\overline{\mathbf{t}}^{*},\boldsymbol{\kappa},\boldsymbol{\kappa}^{*}\}$, and we note that explicit time-dependence only occurs through the Hamiltonian in $\mathcal{H}$. We also note that $\mathcal{F}$ is linear in $\dot{\boldsymbol{\lambda}}$. The Euler–Lagrange equations can now be written as

$$\frac{\partial\mathcal{H}}{\partial\lambda_{\mu}}-i\frac{\partial\mathcal{F}}{\partial\lambda_{\mu}}+i\sum_{\nu}\frac{\partial^{2}\mathcal{F}}{\partial\dot{\lambda}_{\mu}\partial\lambda_{\nu}}\dot{\lambda}_{\nu}=0, \tag{44}$$

where $\lambda_{\mu}$ is used to denote a component in any of the six sets of parameters; the notation should not be confused with that used for the cluster amplitudes and multipliers.

We now solve this system of equations perturbationally in the external perturbation parameter $\alpha$, and Taylor expansion of Eq. (44) in $\alpha$ about $\alpha=0$ (the static limit) gives, through first-order, the following equations:

$$\frac{\partial\mathcal{H}}{\partial\lambda_{\nu}}=0, \tag{45}$$

$$\sum_{\nu}\frac{\partial^{2}\mathcal{H}}{\partial\lambda_{\mu}\partial\lambda_{\nu}}\lambda_{\nu}^{(1)}-i\sum_{\nu}\left(\frac{\partial^{2}\mathcal{F}}{\partial\lambda_{\mu}\partial\dot{\lambda}_{\nu}}-\frac{\partial^{2}\mathcal{F}}{\partial\dot{\lambda}_{\mu}\partial\lambda_{\nu}}\right)\dot{\lambda}_{\nu}^{(1)}=-\frac{\partial^{2}\mathcal{H}}{\partial\lambda_{\mu}\partial\alpha}, \tag{46}$$

where it has been used that the parameters are all time-independent in the static limit, and

$$\lambda_{\mu}^{(1)}=\frac{\partial\lambda_{\nu}}{\partial\alpha}. \tag{47}$$

All derivatives must be evaluated at the expansion point $\alpha=0$. Equation (45) is identical to the static Eqs. (29)–(31) rewritten in a compact notation, and Eq. (46) determines the parameter response through first-order in the time-dependent perturbation. Introducing Fourier transforms similar to Eq. (40) for the time-dependent parameters in Eq. (46), we obtain a $6\times6$ block matrix equation for the Fourier components of the parameters. However, it will prove itself convenient later to include the equations for the first-order orbital rotation parameters twice such that the matrix equation takes an $8\times8$ block form. This can easily be done if we compensate by multiplying every entry in the matrices and in the perturbation vector (the right-hand side) not referring to $\kappa_{\mu_1}$ or $\kappa_{\mu_1}^{*}$ by 2. The resulting set of first-order response equations then appears as

$$\left[\begin{pmatrix}\mathbf{A}&\mathbf{C}&\mathbf{G}^{*}&\mathbf{D}^{\dagger}\\ \mathbf{B}&\mathbf{A}^{\dagger}&\mathbf{D}^{*}&\mathbf{F}^{*}\\ \mathbf{F}&\mathbf{D}&\mathbf{A}^{T}&\mathbf{B}^{T}\\ \mathbf{D}^{T}&\mathbf{G}&\mathbf{C}^{T}&\mathbf{A}^{*}\end{pmatrix}-\omega\begin{pmatrix}\boldsymbol{\Sigma}&\mathbf{0}&\boldsymbol{\Theta}&\boldsymbol{\Gamma}\\ \boldsymbol{\Delta}&\boldsymbol{\Sigma}^{\dagger}&-\boldsymbol{\Gamma}^{T}&\mathbf{0}\\ \mathbf{0}&\boldsymbol{\Gamma}^{\dagger}&-\boldsymbol{\Sigma}^{T}&-\boldsymbol{\Delta}^{T}\\ -\boldsymbol{\Gamma}^{*}&-\boldsymbol{\Theta}^{*}&\mathbf{0}&-\boldsymbol{\Sigma}^{*}\end{pmatrix}\right]\begin{pmatrix}\tilde{\boldsymbol{\lambda}}^{(1)}(\omega)\\ \overline{\boldsymbol{\lambda}}^{(1)}(-\omega)^{*}\\ \overline{\boldsymbol{\lambda}}^{(1)}(\omega)\\ \tilde{\boldsymbol{\lambda}}^{(1)}(-\omega)^{*}\end{pmatrix}=-\begin{pmatrix}\overline{\mathbf{V}}(\omega)\\ \tilde{\mathbf{V}}(-\omega)^{*}\\ \tilde{\mathbf{V}}(\omega)\\ \overline{\mathbf{V}}(-\omega)^{*}\end{pmatrix}, \tag{48}$$

where a superscript $T$ denotes transposition. As the submatrices are written in a $2\times2$ block form (see below), this matrix equation is on the requested $8\times8$ block form. It must be stressed that this matrix equation contains the exact same equations as the original $6\times6$ block problem. Calculation of the second derivatives of $\mathcal{H}$ at $\alpha=0$ shows that the block matrices of the nonsymmetric OCC Jacobian are given by

$$\mathbf{A}=\begin{pmatrix}\langle\mu|\exp(-T^{(0)})[H_0,\tau_{\nu}]|\Psi^{(0)}\rangle & \tfrac{1}{2}\langle\mu|\exp(-T^{(0)})[H_0,\tau_{\nu_1}]|\Psi^{(0)}\rangle\\ -\tfrac{1}{2}\langle\Phi^{(0)}|[[H_0,\tau_{\mu_1}^{\dagger}],\tau_{\nu}]|\Psi^{(0)}\rangle & -\langle[[H_0,\tau_{\mu_1}^{\dagger}],\tau_{\nu_1}]\rangle_0\end{pmatrix}, \tag{49}$$

$$\mathbf{B}=\begin{pmatrix}0 & -\tfrac{1}{2}\langle\Phi^{(0)}|[[H_0,\tau_{\nu_1}^{\dagger}],\tau_{\mu}]|\Psi^{(0)}\rangle^{*}\\ -\tfrac{1}{2}\langle\Phi^{(0)}|[[H_0,\tau_{\mu_1}^{\dagger}],\tau_{\nu}]|\Psi^{(0)}\rangle & 0\end{pmatrix}, \tag{50}$$

$$\mathbf{C}=\begin{pmatrix}0 & \tfrac{1}{2}\langle\mu|\exp(-T^{(0)})[H_0,\tau_{\nu_1}]|\Psi^{(0)}\rangle\\ \tfrac{1}{2}\langle\nu|\exp(-T^{(0)})[H_0,\tau_{\mu_1}]|\Psi^{(0)}\rangle^{*} & 0\end{pmatrix}, \tag{51}$$

$$\mathbf{D}=\begin{pmatrix} 0 & \frac{1}{2}\langle\Phi^{(0)}|[[H_0,\tau_\mu],\tau_{\nu_1}]|\Psi^{(0)}\rangle \\ -\frac{1}{2}\langle\nu|\exp(-T^{(0)})[H_0,\tau^\dagger_{\mu_1}]|\Psi^{(0)}\rangle^* & 0 \end{pmatrix}, \tag{52}$$

$$\mathbf{F}=\begin{pmatrix} \langle\Phi^{(0)}|[[H_0,\tau_\mu],\tau_\nu]|\Psi^{(0)}\rangle & \frac{1}{2}\langle\Phi^{(0)}|[[H_0,\tau_\mu],\tau_{\nu_1}]|\Psi^{(0)}\rangle \\ \frac{1}{2}\langle\Phi^{(0)}|[[H_0,\tau_{\mu_1}],\tau_\nu]|\Psi^{(0)}\rangle & \langle[[H_0,\tau_{\mu_1}],\tau_{\nu_1}]\rangle_0 \end{pmatrix}, \tag{53}$$

$$\mathbf{G}=\begin{pmatrix} 0 & -\frac{1}{2}\langle\mu|\exp(-T^{(0)})[H_0,\tau^\dagger_{\nu_1}]|\Psi^{(0)}\rangle^* \\ -\frac{1}{2}\langle\nu|\exp(-T^{(0)})[H_0,\tau^\dagger_{\mu_1}]|\Psi^{(0)}\rangle^* & \langle[[H_0,\tau_{\mu_1}],\tau_{\nu_1}]\rangle_0 \end{pmatrix}. \tag{54}$$

Note the symmetries $\mathbf{B}^\dagger=\mathbf{B}$, $\mathbf{C}^\dagger=\mathbf{C}$, $\mathbf{F}^T=\mathbf{F}$, and $\mathbf{G}^T=\mathbf{G}$. Similarly, calculation of the second derivatives of the $\mathcal{F}$-functional leads to the definition of the blocks of the OCC metric as

$$\mathbf{\Sigma}=\begin{pmatrix} \delta_{\mu\nu} & 0 \\ \frac{1}{2}\langle\Phi^{(0)}|[\tau^\dagger_{\mu_1},\tau_\nu]|\Psi^{(0)}\rangle & \langle[\tau^\dagger_{\mu_1},\tau_{\nu_1}]\rangle_0 \end{pmatrix}, \tag{55}$$

$$\mathbf{\Delta}=\begin{pmatrix} 0 & \frac{1}{2}\langle\Phi^{(0)}|[\tau^\dagger_{\nu_1},\tau_\mu]|\Psi^{(0)}\rangle^* \\ \frac{1}{2}\langle\Phi^{(0)}|[\tau^\dagger_{\mu_1},\tau_\nu]|\Psi^{(0)}\rangle & 0 \end{pmatrix}, \tag{56}$$

$$\mathbf{\Gamma}=\begin{pmatrix} 0 & -\frac{1}{2}\langle\mu|\exp(-T^{(0)})\tau^\dagger_{\nu_1}|\Psi^{(0)}\rangle \\ 0 & 0 \end{pmatrix}, \tag{57}$$

$$\mathbf{\Theta}=\begin{pmatrix} 0 & -\frac{1}{2}\langle\mu|\exp(-T^{(0)})\tau^\dagger_{\nu_1}|\Psi^{(0)}\rangle \\ \frac{1}{2}\langle\nu|\exp(-T^{(0)})\tau^\dagger_{\mu_1}|\Psi^{(0)}\rangle & 0 \end{pmatrix}, \tag{58}$$

where $\mathbf{\Delta}^\dagger=\mathbf{\Delta}$ and $\mathbf{\Theta}^T=-\mathbf{\Theta}$. In these definitions the subscripts $\mu$ (and $\mu_1$) and $\nu$ (and $\nu_1$) are used to indicate the row and column indices, respectively. This ordering of the Jacobian and metric matrices implies that the components of the response and perturbation vectors are defined as

$$\tilde{\boldsymbol{\lambda}}^{(1)}(\omega)=\begin{pmatrix} t^{(1)}_\nu(\omega) \\ \kappa^{(1)}_{\nu_1}(\omega) \end{pmatrix}, \tag{59}$$

$$\overline{\boldsymbol{\lambda}}^{(1)}(\omega)=\begin{pmatrix} \overline{t}^{(1)}_\nu(\omega) \\ \kappa^{(1)}_{\nu_1}(-\omega)^* \end{pmatrix}, \tag{60}$$

$$\overline{\mathbf{V}}(\omega)=\begin{pmatrix} 2\dfrac{\partial\langle V(\omega)\rangle}{\partial\overline{t}_\mu} \\ \left(\dfrac{\partial\langle V(-\omega)\rangle}{\partial\kappa_{\mu_1}}\right)^* \end{pmatrix}, \tag{61}$$

$$\tilde{\mathbf{V}}(\omega)=\begin{pmatrix} 2\dfrac{\partial\langle V(\omega)\rangle}{\partial t_\mu} \\ \dfrac{\partial\langle V(\omega)\rangle}{\partial\kappa_{\mu_1}} \end{pmatrix}, \tag{62}$$

where, as discussed above, entries in the perturbation vector not referring to orbital rotation parameters are multiplied by two, and where the derivatives are evaluated at $\alpha=0$.

If the matrix $\mathbf{J}-\omega\mathbf{S}$, where $\mathbf{J}$ is the Jacobian and $\mathbf{S}$ the metric, is nonsingular then the coupled response Eqs. (48) can easily be formally solved. Assuming that this solution has been obtained, we may straightforwardly derive an expression for the dynamic linear response function[33,34] within the OCC model. Suppose that, in addition to the time-dependent perturbation, the Hamiltonian contains a static perturbation related to the real time-independent strength parameter $\epsilon$, i.e.,

$$H=H_0+\alpha V(t)+\epsilon W, \tag{63}$$

where $W=W^\dagger$ is time-independent. As the Euler–Lagrange equations are satisfied for $L$, the average value of $W$ can be calculated according to[26]

$$\langle W\rangle(t)=\frac{\partial L}{\partial\epsilon}=\frac{\partial\mathcal{H}}{\partial\epsilon}, \tag{64}$$

evaluated at $\epsilon=0$. Taylor expansion of $\partial L/\partial\epsilon$ about $\alpha=0$ gives

$$\frac{\partial L}{\partial\epsilon}=\frac{\partial\mathcal{H}}{\partial\epsilon}+\frac{\alpha}{2}\int_{-\infty}^{\infty}(\tilde{\mathbf{W}}^T\overline{\mathbf{W}}^\dagger\overline{\mathbf{W}}^T\tilde{\mathbf{W}}^\dagger)\begin{pmatrix} \tilde{\boldsymbol{\lambda}}^{(1)}(\omega) \\ \overline{\boldsymbol{\lambda}}^{(1)}(-\omega)^* \\ \overline{\boldsymbol{\lambda}}^{(1)}(\omega) \\ \tilde{\boldsymbol{\lambda}}^{(1)}(-\omega)^* \end{pmatrix} \times\exp(-i\omega t)d\omega+\cdots, \tag{65}$$

where we have introduced the Fourier transforms of the parameters and used a form suitable for the $8\times8$ block Eq. (48). The derivatives of the right-hand side are evaluated at

$\epsilon=\alpha=0$. The vectors $\overline{\mathbf{W}}$ and $\tilde{\mathbf{W}}$ are defined in Eqs. (61) and (62), respectively, with $\omega=0$. Using the formal expansion,

$$\langle W\rangle(t)=\langle W\rangle_0+\alpha\int_{-\infty}^{\infty}\langle\langle W,V(\omega)\rangle\rangle_\omega\exp(-i\omega t)dt+\cdots, \tag{66}$$

we identify $\langle W\rangle_0=\partial\mathcal{H}/\partial\epsilon|_{\epsilon=\alpha=0}$ as the time-independent average value of $W$ also given in Eq. (36), and the linear response function is identified as

$$\langle\langle W,V(\omega)\rangle\rangle_\omega=\tfrac{1}{2}(\tilde{\mathbf{W}}^T\overline{\mathbf{W}}^\dagger\overline{\mathbf{W}}^T\tilde{\mathbf{W}}^T)\begin{pmatrix}\tilde{\boldsymbol{\lambda}}^{(1)}(\omega)\\ \overline{\boldsymbol{\lambda}}^{(1)}(-\omega)^*\\ \overline{\boldsymbol{\lambda}}^{(1)}(\omega)\\ \tilde{\boldsymbol{\lambda}}^{(1)}(-\omega)^*\end{pmatrix}. \tag{67}$$

It is immediately clear from this expression and Eq. (48) that the poles of the linear response function occur at the eigenvalues of the Jacobian over the metric provided, of course, they exist. Furthermore, if these eigenvalues are real, they may be interpreted as the excitation energies of the system. We therefore proceed to the formal analysis of the OCC eigenvalue problem.

### A. The OCC eigenvalue problem

Let $\mathbf{X}_R$, $\overline{\mathbf{X}}_R$, $\mathbf{Y}_R$, and $\overline{\mathbf{Y}}_R$ denote the submatrices of the matrix having as columns the right eigenvectors of the Jacobian (assuming they exist) over the metric. That is,

$$\begin{aligned}&\begin{pmatrix}\mathbf{A}&\mathbf{C}&\mathbf{G}^*&\mathbf{D}^\dagger\\ \mathbf{B}&\mathbf{A}^\dagger&\mathbf{D}^*&\mathbf{F}^*\\ \mathbf{F}&\mathbf{D}&\mathbf{A}^T&\mathbf{B}^T\\ \mathbf{D}^T&\mathbf{G}&\mathbf{C}^T&\mathbf{A}^*\end{pmatrix}\begin{pmatrix}\mathbf{X}_R\\ \overline{\mathbf{X}}_R\\ \mathbf{Y}_R\\ \overline{\mathbf{Y}}_R\end{pmatrix}_n\\ &=\begin{pmatrix}\boldsymbol{\Sigma}&\mathbf{0}&\boldsymbol{\Theta}&\boldsymbol{\Gamma}\\ \boldsymbol{\Delta}&\boldsymbol{\Sigma}^\dagger&-\boldsymbol{\Gamma}^T&\mathbf{0}\\ \mathbf{0}&\boldsymbol{\Gamma}^\dagger&-\boldsymbol{\Sigma}^T&-\boldsymbol{\Delta}^T\\ -\boldsymbol{\Gamma}^*&-\boldsymbol{\Theta}^*&\mathbf{0}&-\boldsymbol{\Sigma}^*\end{pmatrix}\begin{pmatrix}\mathbf{X}_R\\ \overline{\mathbf{X}}_R\\ \mathbf{Y}_R\\ \overline{\mathbf{Y}}_R\end{pmatrix}_n\omega_n,\end{aligned} \tag{68}$$

where $\omega_n$ denotes the eigenvalue corresponding to the $n$th column. We shall assume that all eigenvalues are real. Likewise, the corresponding left eigenvalue equation reads

$$\begin{aligned}&\begin{pmatrix}\mathbf{X}_L\\ \overline{\mathbf{X}}_L\\ \mathbf{Y}_L\\ \overline{\mathbf{Y}}_L\end{pmatrix}_n^T\begin{pmatrix}\mathbf{A}&\mathbf{C}&\mathbf{G}^*&\mathbf{D}^\dagger\\ \mathbf{B}&\mathbf{A}^\dagger&\mathbf{D}^*&\mathbf{F}^*\\ \mathbf{F}&\mathbf{D}&\mathbf{A}^T&\mathbf{B}^T\\ \mathbf{D}^T&\mathbf{G}&\mathbf{C}^T&\mathbf{A}^*\end{pmatrix}\\ &=\omega_n\begin{pmatrix}\mathbf{X}_L\\ \overline{\mathbf{X}}_L\\ \mathbf{Y}_L\\ \overline{\mathbf{Y}}_L\end{pmatrix}_n^T\begin{pmatrix}\boldsymbol{\Sigma}&\mathbf{0}&\boldsymbol{\Theta}&\boldsymbol{\Gamma}\\ \boldsymbol{\Delta}&\boldsymbol{\Sigma}^\dagger&-\boldsymbol{\Gamma}^T&\mathbf{0}\\ \mathbf{0}&\boldsymbol{\Gamma}^\dagger&-\boldsymbol{\Sigma}^T&-\boldsymbol{\Delta}^T\\ -\boldsymbol{\Gamma}^*&-\boldsymbol{\Theta}^*&\mathbf{0}&-\boldsymbol{\Sigma}^*\end{pmatrix},\end{aligned} \tag{69}$$

such that the left and right eigenvectors constitute an orthonormal system over the metric, i.e.,

$$\begin{aligned}&(\mathbf{X}_L^T\overline{\mathbf{X}}_L^T\mathbf{Y}_L^T\overline{\mathbf{Y}}_L^T)_m\begin{pmatrix}\boldsymbol{\Sigma}&\mathbf{0}&\boldsymbol{\Theta}&\boldsymbol{\Gamma}\\ \boldsymbol{\Delta}&\boldsymbol{\Sigma}^\dagger&-\boldsymbol{\Gamma}^T&\mathbf{0}\\ \mathbf{0}&\boldsymbol{\Gamma}^\dagger&-\boldsymbol{\Sigma}^T&-\boldsymbol{\Delta}^T\\ -\boldsymbol{\Gamma}^*&-\boldsymbol{\Theta}^*&\mathbf{0}&-\boldsymbol{\Sigma}^*\end{pmatrix}\\ &\times\begin{pmatrix}\mathbf{X}_R\\ \overline{\mathbf{X}}_R\\ \mathbf{Y}_R\\ \overline{\mathbf{Y}}_R\end{pmatrix}_n=\delta_{mn}.\end{aligned} \tag{70}$$

In analogy with RPA[33,35] and MCRPA,[35] it is now readily verified that the right and left eigenvalue equations both display a paired structure, and collecting the eigenvalues in the diagonal matrix $\boldsymbol{\Lambda}$ we can write the following equations:

$$\begin{aligned}&\begin{pmatrix}\mathbf{A}&\mathbf{C}&\mathbf{G}^*&\mathbf{D}^\dagger\\ \mathbf{B}&\mathbf{A}^\dagger&\mathbf{D}^*&\mathbf{F}^*\\ \mathbf{F}&\mathbf{D}&\mathbf{A}^T&\mathbf{B}^T\\ \mathbf{D}^T&\mathbf{G}&\mathbf{C}^T&\mathbf{A}^*\end{pmatrix}\begin{pmatrix}\mathbf{X}_R&\overline{\mathbf{Y}}_R^*&\overline{\mathbf{X}}_L^*&\mathbf{Y}_L\\ \overline{\mathbf{X}}_R&\mathbf{Y}_R^*&\mathbf{X}_L^*&\overline{\mathbf{Y}}_L\\ \mathbf{Y}_R&\overline{\mathbf{X}}_R^*&\overline{\mathbf{Y}}_L^*&\mathbf{X}_L\\ \overline{\mathbf{Y}}_R&\mathbf{X}_R^*&\mathbf{Y}_L^*&\overline{\mathbf{X}}_L\end{pmatrix}\\ &=\begin{pmatrix}\boldsymbol{\Sigma}&\mathbf{0}&\boldsymbol{\Theta}&\boldsymbol{\Gamma}\\ \boldsymbol{\Delta}&\boldsymbol{\Sigma}^\dagger&-\boldsymbol{\Gamma}^T&\mathbf{0}\\ \mathbf{0}&\boldsymbol{\Gamma}^\dagger&-\boldsymbol{\Sigma}^T&-\boldsymbol{\Delta}^T\\ -\boldsymbol{\Gamma}^*&-\boldsymbol{\Theta}^*&\mathbf{0}&-\boldsymbol{\Sigma}^*\end{pmatrix}\\ &\times\begin{pmatrix}\mathbf{X}_R&\overline{\mathbf{Y}}_R^*&\overline{\mathbf{X}}_L^*&\mathbf{Y}_L\\ \overline{\mathbf{X}}_R&\mathbf{Y}_R^*&\mathbf{X}_L^*&\overline{\mathbf{Y}}_L\\ \mathbf{Y}_R&\overline{\mathbf{X}}_R^*&\overline{\mathbf{Y}}_L^*&\mathbf{X}_L\\ \overline{\mathbf{Y}}_R&\mathbf{X}_R^*&\mathbf{Y}_L^*&\overline{\mathbf{X}}_L\end{pmatrix}\\ &\times\begin{pmatrix}\boldsymbol{\Lambda}&\mathbf{0}&\mathbf{0}&\mathbf{0}\\ \mathbf{0}&-\boldsymbol{\Lambda}&\mathbf{0}&\mathbf{0}\\ \mathbf{0}&\mathbf{0}&\boldsymbol{\Lambda}&\mathbf{0}\\ \mathbf{0}&\mathbf{0}&\mathbf{0}&-\boldsymbol{\Lambda}\end{pmatrix},\end{aligned} \tag{71}$$

$$\begin{aligned}&\begin{pmatrix}\mathbf{X}_L^T&\overline{\mathbf{X}}_L^T&\mathbf{Y}_L^T&\overline{\mathbf{Y}}_L^T\\ \overline{\mathbf{Y}}_L^\dagger&\mathbf{Y}_L^\dagger&\overline{\mathbf{X}}_L^\dagger&\mathbf{X}_L^\dagger\\ \overline{\mathbf{X}}_R^\dagger&\mathbf{X}_R^\dagger&\overline{\mathbf{Y}}_R^\dagger&\mathbf{Y}_R^\dagger\\ \mathbf{Y}_R^T&\overline{\mathbf{Y}}_R^T&\mathbf{X}_R^T&\overline{\mathbf{X}}_R^T\end{pmatrix}\begin{pmatrix}\mathbf{A}&\mathbf{C}&\mathbf{G}^*&\mathbf{D}^\dagger\\ \mathbf{B}&\mathbf{A}^\dagger&\mathbf{D}^*&\mathbf{F}^*\\ \mathbf{F}&\mathbf{D}&\mathbf{A}^T&\mathbf{B}^T\\ \mathbf{D}^T&\mathbf{G}&\mathbf{C}^T&\mathbf{A}^*\end{pmatrix}\\ &=\begin{pmatrix}\boldsymbol{\Lambda}&\mathbf{0}&\mathbf{0}&\mathbf{0}\\ \mathbf{0}&-\boldsymbol{\Lambda}&\mathbf{0}&\mathbf{0}\\ \mathbf{0}&\mathbf{0}&\boldsymbol{\Lambda}&\mathbf{0}\\ \mathbf{0}&\mathbf{0}&\mathbf{0}&-\boldsymbol{\Lambda}\end{pmatrix}\begin{pmatrix}\mathbf{X}_L^T&\overline{\mathbf{X}}_L^T&\mathbf{Y}_L^T&\overline{\mathbf{Y}}_L^T\\ \overline{\mathbf{Y}}_L^\dagger&\mathbf{Y}_L^\dagger&\overline{\mathbf{X}}_L^\dagger&\mathbf{X}_L^\dagger\\ \overline{\mathbf{X}}_R^\dagger&\mathbf{X}_R^\dagger&\overline{\mathbf{Y}}_R^\dagger&\mathbf{Y}_R^\dagger\\ \mathbf{Y}_R^T&\overline{\mathbf{Y}}_R^T&\mathbf{X}_R^T&\overline{\mathbf{X}}_R^T\end{pmatrix}\\ &\times\begin{pmatrix}\boldsymbol{\Sigma}&\mathbf{0}&\boldsymbol{\Theta}&\boldsymbol{\Gamma}\\ \boldsymbol{\Delta}&\boldsymbol{\Sigma}^\dagger&-\boldsymbol{\Gamma}^T&\mathbf{0}\\ \mathbf{0}&\boldsymbol{\Gamma}^\dagger&-\boldsymbol{\Sigma}^T&-\boldsymbol{\Delta}^T\\ -\boldsymbol{\Gamma}^*&-\boldsymbol{\Theta}^*&\mathbf{0}&-\boldsymbol{\Sigma}^*\end{pmatrix},\end{aligned} \tag{72}$$

such that the OCC normalization condition

$$\begin{pmatrix} \mathbf{X}_L^T & \overline{\mathbf{X}}_L^T & \mathbf{Y}_L^T & \overline{\mathbf{Y}}_L^T \\ \overline{\mathbf{Y}}_L^\dagger & \mathbf{Y}_L^\dagger & \overline{\mathbf{X}}_L^\dagger & \mathbf{X}_L^\dagger \\ \overline{\mathbf{X}}_R^\dagger & \mathbf{X}_R^\dagger & \overline{\mathbf{Y}}_R^\dagger & \mathbf{Y}_R^\dagger \\ \mathbf{Y}_R^T & \overline{\mathbf{Y}}_R^T & \mathbf{X}_R^T & \overline{\mathbf{X}}_R^T \end{pmatrix} \begin{pmatrix} \boldsymbol{\Sigma} & \mathbf{0} & \boldsymbol{\Theta} & \boldsymbol{\Gamma} \\ \boldsymbol{\Delta} & \boldsymbol{\Sigma}^\dagger & -\boldsymbol{\Gamma}^T & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\Gamma}^\dagger & -\boldsymbol{\Sigma}^T & -\boldsymbol{\Delta}^T \\ -\boldsymbol{\Gamma}^* & -\boldsymbol{\Theta}^* & \mathbf{0} & -\boldsymbol{\Sigma}^* \end{pmatrix} \times \begin{pmatrix} \mathbf{X}_R & \overline{\mathbf{Y}}_R^* & \overline{\mathbf{X}}_L^* & \mathbf{Y}_L \\ \overline{\mathbf{X}}_R & \mathbf{Y}_R^* & \mathbf{X}_L^* & \overline{\mathbf{Y}}_L \\ \mathbf{Y}_R & \overline{\mathbf{X}}_R^* & \overline{\mathbf{Y}}_L^* & \mathbf{X}_L \\ \overline{\mathbf{Y}}_R & \mathbf{X}_R^* & \mathbf{Y}_L^* & \overline{\mathbf{X}}_L \end{pmatrix} = \begin{pmatrix} \mathbf{1} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & -\mathbf{1} \end{pmatrix}, \quad (73)$$

is satisfied. Here **1** is the unit matrix. Equations (71)–(73) can be verified using only Eqs. (68)–(70) along with the symmetries of the sub-blocks of the Jacobian and metric matrices.

We thus observe that positive and negative eigenvalues occur twice and that the four corresponding eigenvectors are related in a simple way. It can therefore be concluded that the OCC eigenvalue equation yields the correct number of poles in the linear response function, also in the FCI limit (untruncated cluster operator). This conclusion may of course also be reached from the $6\times 6$ block eigenvalue problem but the ''doubly'' paired structure is most easily realized in the $8\times 8$ block form above. Although the assumption of real eigenvalues cannot be rigorously justified, we expect that it is fulfilled in most practical cases. In the following section we apply the eigenvectors and eigenvalues just obtained to derive the spectral representation of the OCC linear response function.

### B. Spectral representation of the linear response function

In order to obtain an expression for $(\mathbf{J}-\omega\mathbf{S})^{-1}$, we now subtract $\omega\mathbf{S}$ times the right eigenvector-matrix from both sides of Eq. (71). Multiplying them from left with the left eigenvector-matrix, and assuming that both right and left eigenvector-matrices are nonsingular, we readily obtain the expression

$$(\mathbf{J}-\omega\mathbf{S})^{-1} = \begin{pmatrix} \mathbf{X}_R & \overline{\mathbf{Y}}_R^* & \overline{\mathbf{X}}_L^* & \mathbf{Y}_L \\ \overline{\mathbf{X}}_R & \mathbf{Y}_R^* & \mathbf{X}_L^* & \overline{\mathbf{Y}}_L \\ \mathbf{Y}_R & \overline{\mathbf{X}}_R^* & \overline{\mathbf{Y}}_L^* & \mathbf{X}_L \\ \overline{\mathbf{Y}}_R & \mathbf{X}_R^* & \mathbf{Y}_L^* & \overline{\mathbf{X}}_L \end{pmatrix} \times \begin{pmatrix} \boldsymbol{\Lambda}-\omega\mathbf{1} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\Lambda}+\omega\mathbf{1} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \boldsymbol{\Lambda}-\omega\mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \boldsymbol{\Lambda}+\omega\mathbf{1} \end{pmatrix}^{-1} \times \begin{pmatrix} \mathbf{X}_L^T & \overline{\mathbf{X}}_L^T & \mathbf{Y}_L^T & \overline{\mathbf{Y}}_L^T \\ \overline{\mathbf{Y}}_L^\dagger & \mathbf{Y}_L^\dagger & \overline{\mathbf{X}}_L^\dagger & \mathbf{X}_L^\dagger \\ \overline{\mathbf{X}}_R^\dagger & \mathbf{X}_R^\dagger & \overline{\mathbf{Y}}_R^\dagger & \mathbf{Y}_R^\dagger \\ \mathbf{Y}_R^T & \overline{\mathbf{Y}}_R^T & \mathbf{X}_R^T & \overline{\mathbf{X}}_R^T \end{pmatrix}. \quad (74)$$

Using this expression to formally solve Eq. (48) for the first-order parameter response and inserting this result into Eq. (67), we obtain the spectral representation of the OCC linear response function as

$$\langle\langle W,V(\omega)\rangle\rangle_\omega = \frac{1}{2}\sum_n \left( \frac{\mathcal{W}_R^n \mathcal{V}_L^n(\omega) + \mathcal{V}_R^n(-\omega)^* \mathcal{W}_L^{n*}}{\omega-\omega_n} - \frac{\mathcal{W}_R^{n*} \mathcal{V}_L^n(-\omega)^* + \mathcal{V}_R^n(\omega)\mathcal{W}_L^n}{\omega+\omega_n} \right), \quad (75)$$

where

$$\mathcal{V}_R^n(\omega) = \tilde{\mathbf{V}}(\omega)^T \mathbf{X}_R^n + \overline{\mathbf{V}}(-\omega)^\dagger \overline{\mathbf{X}}_R^n + \overline{\mathbf{V}}(\omega)^T \mathbf{Y}_R^n + \tilde{\mathbf{V}}(-\omega)^\dagger \overline{\mathbf{Y}}_R^n, \quad (76)$$

$$\mathcal{V}_L^n(\omega) = \tilde{\mathbf{V}}(\omega)^T \mathbf{Y}_L^n + \overline{\mathbf{V}}(-\omega)^\dagger \overline{\mathbf{Y}}_L^n + \overline{\mathbf{V}}(\omega)^T \mathbf{X}_L^n + \tilde{\mathbf{V}}(-\omega)^\dagger \overline{\mathbf{X}}_L^n, \quad (77)$$

and $\mathcal{W}_{R,L}^n$ is defined analogously (with $\omega=0$). The superscript $n$ in the right-hand sides of Eqs. (76) and (77) denotes the $n$th column of the matrix. It is now trivial to verify the conjugation property $\langle\langle W,V(\omega)\rangle\rangle_\omega^* = \langle\langle W,V(-\omega)\rangle\rangle_{-\omega}$ for the linear response function of Eq. (75). Evidently, the linear response contains simple poles only and the residues at these poles are given by

$$\begin{aligned} &\lim_{\omega\to\omega_n} (\omega-\omega_n)\langle\langle W,V(\omega)\rangle\rangle_\omega \\ &\quad = \tfrac{1}{2}(\mathcal{W}_R^n \mathcal{V}_L^n(\omega_n) + \mathcal{V}_R^n(-\omega_n)^* \mathcal{W}_L^{n*}) \\ &\quad \equiv \langle 0|W|n\rangle\langle n|V(\omega_n)|0\rangle, \end{aligned} \quad (78)$$

and

$$\lim_{\omega\to-\omega_n} (\omega+\omega_n)\langle\langle W,V(\omega)\rangle\rangle_\omega = -[\langle 0|W|n\rangle\langle n|V(\omega_n)|0\rangle]^*. \quad (79)$$

Here we have identified the residue in Eq. (78) as a transition strength.

If $W$ is a one-electron operator, we may expand the Ehrenfest theorem of Eq. (1) to first-order in the perturbation to obtain the following equation of motion satisfied by the linear response function

$$\omega\langle\langle W,V(\omega)\rangle\rangle_\omega = \langle\langle [W,H_0],V(\omega)\rangle\rangle_\omega + \langle [W,V(\omega)]\rangle. \quad (80)$$

Taking residues on both sides of this equation, we obtain the off-diagonal hypervirial relation[36] in the form

$$\omega_n \langle 0|W|n\rangle\langle n|V(\omega_n)|0\rangle = \langle 0|[W,H_0]|n\rangle\langle n|V(\omega_n)|0\rangle, \quad (81)$$

where the transition strengths are defined in Eq. (78). This relation is satisfied within the RPA[15] as well as the MCRPA,[16] but not in the CCLR,[11] and it is satisfied within the OCC response theory due to the ''variationally'' determined orbital rotation. In this sense the OCC response theory can be regarded as gauge invariant.

## V. CONCLUDING REMARKS

A novel gauge invariant coupled cluster based response theory is formulated in this paper. The fundamental model Lagrangian explicitly includes orbital rotations; however Lagrangian multipliers are not introduced for the orbital rotations and thus the orbitals are determined from an optimization type condition (i.e., equivalent to a variational condition on the Lagrangian in the time-independent limit). The actual form of the wave function is of course essential, but of equal importance is the way the parameters are determined. This is evident from the fact that Brueckner coupled cluster response functions have a pole structure that is incompatible with the exact response function. The equations of motion for the parameters are determined using the Euler–Lagrange equations and these in turn lead to Ehrenfest-type equations for the parameters. This result is shown to assure gauge invariance for one-electron operators in the limit of a complete basis set; an essential condition needed in order to ensure gauge origin invariance of magnetic response properties. For gauge origin invariance of dynamic magnetic response properties, the requirement of complete basis set may be removed[37] through introduction of London atomic orbitals (LAOs).[38] In conjunction with LAOs, the OCC (and RPA and MCRPA) approach is thus gauge origin invariant regardless of truncation level in the cluster operator and of one-electron basis set quality.

As an example, consider the frequency-dependent optical rotatory power $\phi$ given in terms of the linear response function as[33]

$$\phi = C\sum_{\alpha} \left(\langle\langle r_\alpha, L_\alpha\rangle\rangle_\omega - \langle\langle L_\alpha, r_\alpha\rangle\rangle_\omega\right), \tag{82}$$

where $\mathbf{r}$ and $\mathbf{L}$ are the electronic position and orbital angular momentum operators, respectively, the sum is over Cartesian directions, and $C$ is a constant (see Ref. 33). Using LAOs, Bak *et al.*[37] defined a second quantized approximate angular momentum operator that possesses two particularly important properties; (1) it becomes identical to the exact angular momentum operator in the limit of a complete basis set,[37] and (2) under an origin transformation $\mathbf{r}\rightarrow\mathbf{r}-\mathbf{a}$, it transforms as[37]

$$\mathbf{L}\rightarrow\mathbf{L}+i\,\mathbf{a}\times[\mathbf{r},H_0], \tag{83}$$

where $H_0$ is the field-free (unperturbed) electronic Hamiltonian. Using this LAO based orbital angular momentum operator, the translational terms of the optical rotatory power vanish,

$$\begin{aligned}\sum_{\alpha} &\langle\langle r_\alpha, (\mathbf{a}\times[\mathbf{r},H_0])_\alpha\rangle\rangle_\omega \\ &= \sum_{\alpha\beta\gamma} \epsilon_{\alpha\beta\gamma} a_\beta \langle\langle r_\alpha, [r_\gamma, H_0]\rangle\rangle_\omega \\ &= -\omega\sum_{\alpha\beta\gamma} \epsilon_{\alpha\beta\gamma} a_\beta \langle\langle r_\alpha, r_\gamma\rangle\rangle_\omega = 0,\end{aligned} \tag{84}$$

where $\epsilon_{\alpha\beta\gamma}$ is the Levi–Civita alternating tensor. In the course of the derivation we have used the equation-of-motion of the linear response function in Eq. (80), and the conjugation relation[11]

$$\langle\langle A,B\rangle\rangle_\omega^* = \langle\langle A^\dagger, B^\dagger\rangle\rangle_{-\omega} = \langle\langle B^\dagger, A^\dagger\rangle\rangle_\omega . \tag{85}$$

While Eq. (85) is an elementary property of the linear response function, Eq. (80) requires the Ehrenfest theorem satisfied. As the position operator is a one-electron operator, the LAO formulation of the optical rotatory power is therefore inherently origin invariant in RPA, MCRPA, and truncated or untruncated OCC theory, but not in truncated CC theory.

An explicit expression for the OCC linear response function is derived and the associated nonsymmetric eigenvalue problem is shown to exhibit the same paired structure that is well known from RPA and MCRPA. This structure assures that only first-order poles are present in the response function. Transition strengths are now well defined and may be determined from an expression that only requires the solution of the non-symmetric eigenvalue problem and additional equations need not be solved as in the standard implementation of the CCLR model.[8] Of particular interest is to note two limiting cases of the OCC response model. If the cluster amplitudes are excluded then we obtain the standard RPA model, if we on the other hand exclude the orbital rotations we obtain a model like CCLR, but where single excitations need to be included in the cluster operator explicitly. This is also the case in BBC response theory and just comes to show that a correct description of limiting cases is not sufficient in obtaining the desired result.

An integral-direct[39] implementation of the OCCD wave function and the linear response function will be reported elsewhere.

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