

# Intermolecular forces and nonbonded interactions: Superoperator nonlinear time-dependent density-functional-theory response approach

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Electrostatic and dispersive interactions of polarizable molecules are expressed in terms of generalized (nonretarded) charge-density response functions of the isolated molecules, which in turn are expanded using the collective electronic oscillator (CEO) eigenmodes of linearized time-dependent density-functional theory. Closed expressions for the intermolecular energy are derived to sixth order in charge fluctuation amplitudes.

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## I. INTRODUCTION

Weak nonbonded interactions originating from correlated charge density fluctuations [1–6] control many important chemical and biological dynamical processes. They determine the structure of molecular aggregates, supramolecular assemblies [7,8], and biological complexes ( $\pi$  stacking in DNA and RNA) [9,10] and are vital for molecular recognition and enzymatic activity which depend on protein-protein and protein-ligand binding [7,9,11–15]. Numerous applications ranging from catalysis and packing of nanostructures to the rational drug design depend on accurate predictions of intermolecular forces. The most widely studied and best understood interactions are the dispersive van der Waals (vdW) forces between neutral species or macroscopic objects (Casimir forces) calculated to second order in intermolecular coupling (i.e., fourth order in charge fluctuations). Both electrodynamic (retarded) [5,6,16,17] and electrostatic [1,2] approaches have been used in their calculation, treating the molecules as point dipoles or higher multipoles. Recent advances have been made in the application of *ab initio* techniques [9,18]. These yield very accurate results but at high computational cost.

McLachlan had shown that vdW forces may be computed using the nonlocal linear polarizabilities or charge response functions of the individual molecules [19]. This type of formulation is particularly appealing since it provides a clear real-space physical picture for the origin of the interactions. It therefore allows to pinpoint precisely which functional groups contribute to the response and could be used for qualitative predictions and analysis. Remarkable progress in density functional techniques [20–28] have made it possible to compute nonlocal response functions at an affordable cost.

The direct DFT simulation of vdW complexes by treating them as supermolecules turned out to be a complicated task [29–31] since it requires nonlocal energy functionals. The response approach makes good use of the perturbative nature of these couplings and recasts the energies in terms of properties of individual molecules which, in turn, may be calculated using local functionals thus circumventing the problem of constructing nonlocal functionals [32–34].

In this paper we combine the Liouville space superoperator formulation of nonlinear response [35–38] with time-

dependent density-functional theory (TDDFT) [21,39–43] to develop a systematic real space approach to nonbonded interactions in terms of nonlinear molecular polarizabilities. McLachlan's expressions are recovered to fourth order in charge density fluctuations, but the complete expansion is recast in terms of higher order generalized nonlinear response functions as well as electrostatic contributions.

It is tempting to assume that a complete knowledge of higher order ordinary polarizabilities should be sufficient for computing intermolecular forces to any order in charge fluctuations. However, using nonlinear response theory, Cohen and Mukamel [38,44] have shown that such a naive generalization of the celebrated McLachlan expression is not possible. The building blocks of the  $p$ th order response are  $2^p$ ,  $(p+1)$ -point correlation functions which differ by permutations of their time arguments. Each correlation function represents a *Liouville Space pathway* [36]. A complete description of intermolecular forces requires a set of  $p+1$  combinations of these pathways denoted as *generalized response functions* (GRF) [38]. The  $p$ th order polarizability is only one member of that family. Ordinary response functions represent the response to an external potential and are therefore causal (retarded). The GRFs on the other hand are non causal since they also describe correlated spontaneous charge fluctuations where both partners should be treated along the same footing with no obvious cause and effect. The dynamics of such fluctuations is the key for intermolecular forces.

We extend the treatment of Cohen and Mukamel [38] which was restricted to the dipole approximation and show how intermolecular forces may be recast in terms of generalized nonlocal response functions of the charge density to an external potential. The latter are then computed using TD-DFT quasiparticles, and closed expressions are derived to six order in the magnitude of charge fluctuations.

In Sec. II, we introduce the Liouville space GRFs of individual molecules. Formal expressions for the intermolecular interaction energy in terms of GRF are given in Appendix A (time domain) and in Appendix B (frequency domain). The GRFs are recast in terms of collective electronic oscillator (CEO) TDDFT modes in Sec. III. The second order GRFs are given in Appendix C (time domain) and in Appendix D (frequency domain). In Sec. IV we combine the results of Secs. II and III and derive closed expressions for intermo-

molecular energies in terms of CEO modes to fourth order in charge fluctuations. Fifth and Sixth order expressions are given in Appendices E and F.

## II. INTERMOLECULAR ENERGIES AND GENERALIZED MOLECULAR RESPONSE FUNCTIONS

We consider two coupled molecules (or nonbonded segments of the same molecule)  $a$  and  $b$  with nonoverlapping charge distributions described by the Hamiltonian,

$$H_\lambda = H_a + H_b + \lambda H_{ab}, \quad (1)$$

where  $H_a$  and  $H_b$  represent the individual molecules and their coupling  $H_{ab}$  is multiplied by the control parameter  $\lambda$ ,  $0 \leq \lambda \leq 1$ , where  $\lambda=1$  corresponds to the physical Hamiltonian. We shall denote the charge density of molecule  $a$  at point  $\mathbf{r}$  by  $n_a(\mathbf{r})$  and of molecule  $b$  at  $\mathbf{r}'$  by  $n_b(\mathbf{r}')$ . The intermolecular Coulomb interaction is then given by

$$H_{ab} = - \int \int d\mathbf{r} d\mathbf{r}' J(\mathbf{r} - \mathbf{r}') n_a(\mathbf{r}) n_b(\mathbf{r}'), \quad (2)$$

where  $J(\mathbf{r} - \mathbf{r}') \equiv e^2/|\mathbf{r} - \mathbf{r}'|$ .

Using the Hellmann-Feynman theorem,  $dE(\lambda)/d\lambda = \langle \Psi_\lambda | \partial H_\lambda / \partial \lambda | \Psi_\lambda \rangle$ , the total energy of the system is obtained by switching the parameter  $\lambda$  from 0 to 1 [31,32,45],

$$W \equiv E(\lambda = 1) - E(\lambda = 0) = \int_0^1 d\lambda \langle H_{ab} \rangle_\lambda. \quad (3)$$

Here  $\langle A \rangle_\lambda \equiv \text{Tr}\{A \hat{\rho}_\lambda\}$  denotes the expectation value with respect to the  $\lambda$ -dependent ground state many-electron density matrix of the system,  $\hat{\rho}_\lambda$ . The charge density of molecule  $a$  at point  $\mathbf{r}$  will be partitioned as  $n_a(\mathbf{r}) = \bar{n}_a(\mathbf{r}) + \delta n_a(\mathbf{r})$ , where  $\bar{n}_a(\mathbf{r})$  is the average charge density of the isolated molecule and  $\delta n_a(\mathbf{r})$  represents a charge fluctuation. Substituting this partitioning for  $n_a(\mathbf{r})$  and  $n_b(\mathbf{r}')$  in Eq. (3) gives  $W = W^{(0)} + W^{(n)} + W^{(m)}$ , where

$$W^{(0)} = - \int \int d\mathbf{r} d\mathbf{r}' J(\mathbf{r} - \mathbf{r}') \bar{n}_a(\mathbf{r}) \bar{n}_b(\mathbf{r}'), \quad (4)$$

is the average electrostatic energy, and the remaining two terms represent the effects of correlated fluctuations

$$W^{(n)} = - \int_0^1 d\lambda \int \int d\mathbf{r} d\mathbf{r}' J(\mathbf{r} - \mathbf{r}') \times [\bar{n}_a(\mathbf{r}) \langle \delta n_b(\mathbf{r}') \rangle_\lambda + \bar{n}_b(\mathbf{r}') \langle \delta n_a(\mathbf{r}) \rangle_\lambda], \quad (5)$$

$$W^{(m)} = - \int_0^1 d\lambda \int \int d\mathbf{r} d\mathbf{r}' J(\mathbf{r} - \mathbf{r}') \langle \delta n_a(\mathbf{r}) \delta n_b(\mathbf{r}') \rangle_\lambda.$$

The bookkeeping of the various interactions and their time ordering is greatly simplified by introducing superoperator Liouville space algebra. With each ordinary operator  $A$  we associate two superoperators  $\mathcal{A}^+$  and  $\mathcal{A}^-$  defined by their action on any ordinary Hilbert space operator  $X$  [37,40,46–49],

$$\begin{aligned} \mathcal{A}^+ X &\equiv \frac{1}{2}(AX + XA), \\ \mathcal{A}^- X &\equiv AX - XA. \end{aligned} \quad (6)$$

A “+” superoperator is an anticommutator while a “−” denotes a commutator.

We start at time  $t \rightarrow -\infty$  with the density matrix,  $\hat{\rho}_g^0 \equiv \hat{\rho}_a^0 \hat{\rho}_b^0$ , of the noninteracting system (setting  $\lambda=0$ ). Upon switching on the interaction adiabatically, we can expand all quantities perturbatively in  $H_{ab}$  and recast them in terms of the expectation values with respect to  $\hat{\rho}_g^0$ , i.e.,  $\langle A \rangle = \text{Tr}\{A \hat{\rho}_g^0\}$ . We shall represent the set of space-time coordinates  $(\mathbf{r}_i, t_i)$ ,  $i=1, 2, \dots$ , by  $\mathbf{x}_i$ .

The  $p$ th order generalized response functions of molecule  $a$  are defined by

$$\begin{aligned} \chi_a^{\nu_{p+1} \nu_p \dots \nu_1}(\mathbf{x}_{p+1}, \mathbf{x}_p, \dots, \mathbf{x}_1) \\ = (-i)^{p'} \langle \mathcal{T} \delta n_a^{\nu_{p+1}}(\mathbf{x}_{p+1}) \delta n_a^{\nu_p}(\mathbf{x}_p) \dots \delta n_a^{\nu_1}(\mathbf{x}_1) \rangle, \end{aligned} \quad (7)$$

where  $\delta n_a^\nu(\mathbf{x}_i)$ , ( $\nu = +, -$ ), is the charge density superoperator and  $p'$  is the number of “−” indices in the set  $\nu_1 \dots \nu_{p+1}$ . In Eq. (7) the time evolution of superoperators is defined with respect to  $H_a$ :

$$\delta n_a^\nu(\mathbf{x}_p) \equiv \delta n_a^\nu(\mathbf{r}_p, t_p) = \exp(iH_a^- t_p) \delta n_a^\nu(\mathbf{r}_n) \exp(-iH_a^- t_p). \quad (8)$$

Analogous expressions corresponding to molecule  $b$  are obtained by simply replacing  $a, \mathbf{x}_p \rightarrow b, \mathbf{x}'_p$  where  $\mathbf{x}'_p \equiv (\mathbf{r}'_p, t_p)$ .  $\mathcal{T}$  is the Liouville space time ordering operator: when acting on a product of superoperators, it rearranges them so that time increases from right to left.

Equation (7) defines a family of GRF obtained by making all possible choices of  $\nu_{p+1} \dots \nu_1 = “+”$  or “−”. By definition, each GRF is symmetric with respect to any permutation of its indices  $(\nu_p, \mathbf{x}_p)$ . We further note that the last  $\nu$  on the left of a time ordered product must be a “plus” otherwise the GRF becomes a trace of a commutator and vanishes. There are therefore  $p+1$   $p$ th order GRF which differ by the number of “minus” indices  $0, 1, \dots, p$ . The ordinary  $p$ th order response functions,  $\chi^{+-}, \chi^{++}, \dots$ , etc., have  $p$   $\delta n^-$  terms representing the coupling to an external potential [see Eq. (16)] and the last  $\delta n^+$  term represents the final expectation value of  $\delta n$ . For example, there are two linear GRF:

$$\begin{aligned} \chi_a^{++}(\mathbf{x}_1, \mathbf{x}_2) &= \langle \mathcal{T} \delta n_a^+(\mathbf{x}_1) \delta n_a^+(\mathbf{x}_2) \rangle \\ &= \theta(t_1 - t_2) \langle \delta n_a^+(\mathbf{x}_1) \delta n_a^+(\mathbf{x}_2) \rangle \\ &\quad + \theta(t_2 - t_1) \langle \delta n_a^+(\mathbf{x}_2) \delta n_a^+(\mathbf{x}_1) \rangle, \\ \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_2) &= -i \langle \mathcal{T} \delta n_a^+(\mathbf{x}_1) \delta n_a^-(\mathbf{x}_2) \rangle \\ &= -i \theta(t_1 - t_2) \langle \delta n_a^+(\mathbf{x}_1) \delta n_a^-(\mathbf{x}_2) \rangle, \end{aligned} \quad (9)$$

where

$$\langle \delta n_a^+(\mathbf{x}_1) \delta n_a^+(\mathbf{x}_2) \rangle = \frac{1}{2} [\langle \delta n_a(\mathbf{x}_1) \delta n_a(\mathbf{x}_2) \rangle + \langle \delta n_a(\mathbf{x}_2) \delta n_a(\mathbf{x}_1) \rangle],$$

$$\langle \delta n_a^+(\mathbf{x}_1) \delta n_a^-(\mathbf{x}_2) \rangle = \langle \delta n_a(\mathbf{x}_1) \delta n_a(\mathbf{x}_2) \rangle - \langle \delta n_a(\mathbf{x}_2) \delta n_a(\mathbf{x}_1) \rangle. \quad (10)$$

Similarly, there are three second order GRF,  $\chi_a^{+++}$ ,  $\chi_a^{+-}$ , and  $\chi_a^{++}$ . Classical mode coupling theories are formulated in terms of linear response and correlation functions [50–54]  $\chi^{+-}$  and  $\chi^{++}$ , respectively. the GRF extend these to higher order.

In Appendix A we expand the expectation values,  $\langle \delta n_a(\mathbf{r}_1) \rangle_\lambda$  and  $\langle \delta n_a(\mathbf{r}_1) \delta n_b(\mathbf{r}'_1) \rangle_\lambda$  which appear in Eq. (4) for the interacting system perturbatively in  $H_{ab}$  and show how, order by order, they can be factorized and expressed in terms of time domain GRFs of the individual molecules. This factorization is made possible by the adiabatic switching of interactions whereby the initial ( $t \rightarrow -\infty$ ) density matrix of the combined system is taken to be a direct product of the density matrices of the two molecules. Corresponding frequency domain expressions are given in Appendix B. In the next section we extend the collective electronic oscillator (CEO) scheme [55] originally developed for calculating ordinary response functions [39,42] towards computing the GRF. These results will be combined in Sec. IV to yield closed expressions for intermolecular energies.

### III. TDDFT EQUATIONS OF MOTION FOR THE GENERALIZED RESPONSE FUNCTIONS

The present calculation is applicable to an arbitrary many-electron system (molecule  $a$  or  $b$ ). For brevity we shall drop the indices  $a$  and  $b$  in this section. Time dependent density functional theory is based on the Kohn Sham (KS) Hamiltonian [21],

$$H^{KS}(n(\mathbf{r}_1, t)) = -\frac{\nabla^2}{2m} + U(\mathbf{r}_1) + e^2 \int d\mathbf{r}_2 \frac{n(\mathbf{r}_2, t)}{|\mathbf{r}_1 - \mathbf{r}_2|} + U_{xc}(n(\mathbf{r}_1, t)), \quad (11)$$

where the four terms represent the kinetic energy, the nuclear potential, the Hartree, and the exchange correlation potential, respectively.

We now introduce the reduced single electron density matrix  $\hat{\rho}$  [39,40,42,56,57] whose diagonal elements give the charge distribution,  $n(\mathbf{r}_1, t) = \rho(\mathbf{r}_1, \mathbf{r}_1, t)$  and the off-diagonal elements,  $\rho(\mathbf{r}_1, \mathbf{r}_2)$ , represent electronic coherences. We shall denote a matrix in real space such as  $\hat{\rho}$  by a caret. We further denote the ground state density matrix by  $\hat{\rho}^g$ .

We start with the time dependent generalized KS equations of motion for  $\hat{\rho}$ ,

$$i \frac{\partial}{\partial t} \delta \rho(\mathbf{r}_1, \mathbf{r}_2, t) = [H^{KS}(n), \rho(\mathbf{r}_1, \mathbf{r}_2, t)] + U_L(\mathbf{r}_1, t) \rho(\mathbf{r}_1, \mathbf{r}_2, t) - U_R(\mathbf{r}_2, t) \rho(\mathbf{r}_1, \mathbf{r}_2, t), \quad (12)$$

where  $\delta \rho(\mathbf{r}_1, \mathbf{r}_2, t) \equiv \rho(\mathbf{r}_1, \mathbf{r}_2, t) - \rho^g(\mathbf{r}_1, \mathbf{r}_2)$  is the change in the density matrix induced by the external potentials. Equation (12) differs from the standard KS equation in that the system is coupled to two external potentials, a “left” field  $U_L$  acting on the ket and a “right” field  $U_R$  acting on the bra. The actual density matrix is obtained by setting  $U_L = U_R$ . How-

ever, this  $\delta \rho$  serves as a *generating function* for GRF, as we shall shortly see.

We next define

$$U_-(\mathbf{r}, t) \equiv \frac{1}{2}(U_L(\mathbf{r}, t) + U_R(\mathbf{r}, t)), \quad (13)$$

$$U_+(\mathbf{r}, t) \equiv U_L(\mathbf{r}, t) - U_R(\mathbf{r}, t),$$

and the diagonal matrices  $\hat{U}_-(\mathbf{r}_1, \mathbf{r}_2) = U_-(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2)$ ,  $\hat{U}_+(\mathbf{r}_1, \mathbf{r}_2) = U_+(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2)$ . Note that  $U_-$  is given by a sum and  $U_+$  by a difference. The reason for this somewhat confusing notation is that  $U_-(U_+)$  will enter in a commutator (anticommutator) in Eq. (14), where we further introduce the superoperators

$$\mathcal{U} \hat{\rho} \equiv [\hat{U}_-, \hat{\rho}],$$

$$\mathcal{U}^+ \hat{\rho} \equiv [\hat{U}_+, \hat{\rho}]_+, \quad (14)$$

$$\mathcal{H}_{KS}^- \hat{\rho} \equiv [\hat{H}^{KS}, \hat{\rho}].$$

Equation (12) can then be recast in terms of superoperators,

$$i \frac{\partial}{\partial t} \rho(\mathbf{r}_1, \mathbf{r}_2, t) = \mathcal{H}_{KS}^- \rho(\mathbf{r}_1, \mathbf{r}_2, t) - \mathcal{U}(\mathbf{r}_1, \mathbf{r}_2, t) \rho(\mathbf{r}_1, \mathbf{r}_2, t) - \mathcal{U}^+(\mathbf{r}_1, \mathbf{r}_2, t) \rho(\mathbf{r}_1, \mathbf{r}_2, t). \quad (15)$$

The GRFs, Eq. (7), are defined as the kernels in a perturbative expansion of the charge density fluctuation,  $\delta n(\mathbf{r}_1, t) = \delta \rho(\mathbf{r}_1, \mathbf{r}_1, t)$ , in the applied potentials,  $U_+$  and  $U_-$ ,

$$\langle \delta n^+(\mathbf{x}_{p+1}) \rangle^{(p)} \equiv \int d\mathbf{r}_p dt_p \dots$$

$$\times \int d\mathbf{r}_1 dt_1 \chi^{p_{p+1} p_p \dots p_1}(\mathbf{x}_{p+1}, \mathbf{x}_p, \dots, \mathbf{x}_1)$$

$$\times U_{v_p}(\mathbf{x}_p) U_{v_{p-1}}(\mathbf{x}_{p-1}) \dots U_{v_1}(\mathbf{x}_1). \quad (16)$$

The standard TDDFT equations which only generate ordinary response functions are obtained by setting  $U_L = U_R$  so that  $\mathcal{U}^+ = 0$  in Eq. (15). By allowing  $U_L$  and  $U_R$  to be different we can obtain the complete set of GRF. Similar to the ordinary response function  $\chi^{+-}$ , which represents the density response of the system to an applied potential  $U_-$  [36],  $\chi^{++}$  can be formally obtained as the response to the artificial external potential,  $U_+$ , that couples to the charge density through an anticommutator.  $\chi^{++}$  represents equilibrium charge fluctuations and is therefore nonretarded. The same arguments hold for higher order response functions.

Since the TDDFT density matrix,  $\hat{\rho}(t)$ , corresponds to a many-electron wave function given by a single Slater determinant at all times, it can be separated into its electron-hole (interband) part  $\hat{\xi}$  and the electron-electron and hole-hole (intra-band) components,  $T(\hat{\xi})$ .

$$\delta\hat{\rho}(t) = \hat{\xi}(t) + \hat{T}(\hat{\xi})(t). \quad (17)$$

It follows from the idempotent property,  $\hat{\rho}^2 = \hat{\rho}$ , that  $\hat{T}$  is uniquely determined by  $\hat{\xi}$  so that  $\delta\hat{\rho}$  can be expressed solely in terms of  $\hat{\xi}$  [39,56]

$$\hat{T}(\hat{\xi}) = \frac{1}{2}(2\hat{\rho}^s - \hat{I})\left\{\hat{I} - \sqrt{\hat{I} - 4\hat{\xi}\hat{\xi}}\right\}. \quad (18)$$

The elements of  $\hat{\xi}$  (but not of  $\delta\hat{\rho}$ ) can thus be considered as independent coordinates for describing the electronic structure.

We next expand  $H^{KS}$  in powers of  $\delta n(\mathbf{r}, t)$ ,

$$H^{KS} = H_0^{KS} + H_1^{KS} + H_2^{KS} + \dots,$$

$$H_0^{KS}(\bar{n})(\mathbf{r}_1) = -\frac{\nabla_{\mathbf{r}_1}^2}{2m} + e^2 \int d\mathbf{r}_2 \frac{\bar{n}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} + U_{xc}(\bar{n}(\mathbf{r}_1)) + U(\mathbf{r}_1), \quad (19)$$

$$H_1^{KS}(\delta n)(\mathbf{r}_1) = \int d\mathbf{r}_2 \left( \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{xc}(\mathbf{r}_1, \mathbf{r}_2) \right) \delta n(\mathbf{r}_2, t),$$

with the first order adiabatic exchange correlation kernel,

$$f_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \left. \frac{\delta U_{xc}(n(\mathbf{r}_1))}{\delta n(\mathbf{r}_2, t_2)} \right|_{\bar{n}}. \quad (20)$$

The second order term in density fluctuations is

$$H_2^{KS}(\delta n, \delta n)(\mathbf{r}_1) = \int \int d\mathbf{r}_2 d\mathbf{r}_3 g_{xc}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \delta n(\mathbf{r}_2, t) \delta n(\mathbf{r}_3, t) \quad (21)$$

with the kernel

$$g_{xc}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \left. \frac{\delta^2 U_{xc}(n(\mathbf{r}_1))}{\delta n(\mathbf{r}_2, t_2) \delta n(\mathbf{r}_3, t_3)} \right|_{\bar{n}}. \quad (22)$$

A quasiparticle algebra can then be developed for  $\hat{\xi}$  by expanding it in the basis set of CEO modes,  $\hat{\xi}_\alpha$ , which are the eigenvectors of the linearized TDDFT eigenvalue equation with eigenvalues  $\Omega_\alpha$  [39,40],

$$\hat{L}\hat{\xi}_\alpha = \Omega_\alpha \hat{\xi}_\alpha. \quad (23)$$

The linearized Liouville space operator,  $\hat{L}$  is obtained by substituting Eqs. (19) into Eq. (12),

$$\hat{L}\hat{\xi}_\alpha = [\hat{H}_0^{KS}(\bar{n}), \hat{\xi}_\alpha] + [\hat{H}_1^{KS}(\hat{\xi}_\alpha), \hat{\rho}^s]. \quad (24)$$

$\hat{H}_0^{KS}$  and  $\hat{H}_1^{KS}$  are diagonal matrices with matrix elements

$$H_0^{KS}(\bar{n})(\mathbf{r}_1, \mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_2) H_0^{KS}(\bar{n})(\mathbf{r}_1), \quad (25)$$

$$H_1^{KS}(\hat{\xi}_\alpha)(\mathbf{r}_1, \mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_2) \int d\mathbf{r}_3 \times \left( \frac{e^2}{|\mathbf{r}_2 - \mathbf{r}_3|} + f_{xc}(\mathbf{r}_2, \mathbf{r}_3) \right) \hat{\xi}_\alpha(\mathbf{r}_3, \mathbf{r}_3).$$

The eigenmodes  $\hat{\xi}_\alpha$  come in pairs corresponding to positive

and negative values of  $\alpha$ , and we adopt the notation,  $\Omega_{-\alpha} = -\Omega_\alpha$  and  $\hat{\xi}_{-\alpha} = \hat{\xi}_\alpha^\dagger$ . Each pair of modes represents a collective electronic oscillator, and the complete set of modes  $\hat{\xi}_\alpha$  may be used to describe all response and spontaneous charge fluctuation properties of the system.

We next expand  $\hat{\xi}$  in the CEO eigenmodes,

$$\hat{\xi} = \sum_\alpha \bar{z}_\alpha(t) \hat{\xi}_\alpha, \quad (26)$$

where  $\alpha$  runs over all modes (positive and negative) and  $\bar{z}_\alpha$  are numerical coefficients.

Substituting Eq. (26) in Eqs. (18) and (17) yields the following expansion for the density matrix

$$\delta\rho(\mathbf{r}_1, \mathbf{r}_2, t) = \sum_\alpha \mu_\alpha(\mathbf{r}_1, \mathbf{r}_2) \bar{z}_\alpha(t) + \frac{1}{2} \sum_{\alpha, \beta} \mu_{\alpha, \beta}(\mathbf{r}_1, \mathbf{r}_2) \bar{z}_\alpha(t) \bar{z}_\beta(t) + \dots, \quad (27)$$

where we have introduced the auxiliary quantities,

$$\hat{\mu}_\alpha = \hat{\xi}_\alpha,$$

$$\hat{\mu}_{\alpha\beta} = (2\hat{\rho}^s - \hat{I})(\hat{\xi}_\alpha \hat{\xi}_\beta + \hat{\xi}_\beta \hat{\xi}_\alpha). \quad (28)$$

By substituting Eqs. (17), (18), and (26) in Eq. (12) we obtain equations of motion for the CEO amplitudes  $\bar{z}_\alpha$  which can then be solved successively order by order in the external potentials,  $U_{v_i}$ . To second order, we get

$$i \frac{d\bar{z}_\alpha(t)}{dt} = \Omega_\alpha \bar{z}_\alpha(t) + K_{-\alpha}(t) + \sum_\beta K_{-\alpha\beta}(t) \bar{z}_\beta(t), \quad (29)$$

with the coefficients,

$$K_{-\alpha}(t) = \sum_\nu \int d\mathbf{r}_1 U_\nu(\mathbf{r}_1, t) \mu_{-\alpha}^\nu(\mathbf{r}_1), \quad (30)$$

$$K_{-\alpha\beta}(t) = \sum_\nu \int d\mathbf{r}_1 U_\nu(\mathbf{r}_1, t) \mu_{-\alpha\beta}^\nu(\mathbf{r}_1).$$

Here  $\mu_\alpha^-(\mathbf{r}_1) \equiv \mu_\alpha(\mathbf{r}_1, \mathbf{r}_1)$ ,  $\mu_{\alpha\beta}^-(\mathbf{r}_1) \equiv \hat{\mu}_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_1)$ ,  $\mu_\alpha^+(\mathbf{r}_1) \equiv \tilde{\mu}_{-\alpha}(\mathbf{r}_1, \mathbf{r}_1) = \frac{1}{2}(2\hat{\rho}^s - \hat{I})\hat{\xi}_\alpha(\mathbf{r}_1, \mathbf{r}_1)$  and  $\mu_{\alpha\beta}^+(\mathbf{r}_1) \equiv \tilde{\mu}_{\alpha\beta}(\mathbf{r}_1) = \frac{1}{2}(2\hat{\rho}^s - \hat{I})(\hat{\xi}_\alpha \hat{\xi}_\beta - \hat{\xi}_\beta \hat{\xi}_\alpha)(\mathbf{r}_1, \mathbf{r}_1)$ .

We further expand  $\bar{z}_\alpha = z_\alpha^{v_1} + z_\alpha^{v_1 v_2} + \dots$ , in powers of the external potentials, where  $z_\alpha^{v_1 v_2 \dots v_p}$  denotes the  $n$ th order term in the potentials,  $U_{v_1} U_{v_2} \dots U_{v_p}$ . By comparing the terms in both sides, we obtain the equations of motion for  $z_\alpha^{v_1 \dots v_p}$  to each order in the external potential. To first order, we get

$$i \frac{\partial z_\alpha^{v_1}(t)}{\partial t} = \Omega_\alpha z_\alpha^{v_1}(t) + K_{-\alpha}(t). \quad (31)$$

The solution of Eq. (31) can be readily obtained as

$$z_\alpha^+(t_1) = i \int_{-\infty}^{\infty} dt_2 \int d\mathbf{r}_1 U_+(\mathbf{r}_1, t_2) \tilde{\mu}_{-\alpha}(\mathbf{r}_1) G_\alpha(t_1 - t_2), \quad (32)$$

$$z_{\alpha}^{-}(t_1) = i s_{\alpha} \int_{-\infty}^{\infty} dt_2 \int d\mathbf{r}_1 U_{-}(\mathbf{r}_1, t_2) \mu_{-\alpha}(\mathbf{r}_1) G_{\alpha}(t_1 - t_2),$$

with  $s_{\alpha} = \text{sgn}(\alpha)$  and the Green function,

$$G_{\alpha}(t_1 - t_2) = \theta(t_1 - t_2) e^{-i\Omega_{\alpha}(t_1 - t_2)}. \quad (33)$$

Substituting Eq. (32) in Eq. (27) and taking the diagonal element, we obtain to lowest order in  $U_{\nu}$ ,

$$\delta n(\mathbf{x}_1) = \int_{-\infty}^{\infty} dt_2 \int \int d\mathbf{r}_2 \tilde{\chi}^{\nu\nu_1}(\mathbf{x}_1, \mathbf{x}_2) U_{\nu_1}(\mathbf{x}_2), \quad (34)$$

where  $\tilde{\chi}^{\nu_1\nu_2} = i \langle \delta n^{\nu_1}(\mathbf{x}_1) \delta n^{\nu_2}(\mathbf{x}_2) \rangle$ .

Recalling that the leftmost index,  $\nu$ , must be a “+,” we only have two second order Liouville space correlation functions,

$$\langle \delta n^{+}(\mathbf{x}_1) \delta n^{-}(\mathbf{x}_2) \rangle = \sum_{\alpha} s_{\alpha} \mu_{\alpha}(\mathbf{r}_1) \mu_{-\alpha}(\mathbf{r}_2) G_{\alpha}(t_1 - t_2), \quad (35)$$

$$\langle \delta n^{+}(\mathbf{x}_1) \delta n^{+}(\mathbf{x}_2) \rangle = \sum_{\alpha} \mu_{\alpha}(\mathbf{r}_1) \tilde{\mu}_{-\alpha}(\mathbf{r}_2) G_{\alpha}(t_1 - t_2).$$

The generalized linear response functions are finally obtained by substituting Eq. (35) in Eq. (9),

$$\begin{aligned} \chi^{++}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) &= \theta(t_1 - t_2) \sum_{\alpha} \mu_{\alpha}(\mathbf{r}_1) \tilde{\mu}_{-\alpha}(\mathbf{r}_2) e^{-i\Omega_{\alpha}(t_1 - t_2)} \\ &\quad + \theta(t_2 - t_1) \sum_{\alpha} \mu_{\alpha}(\mathbf{r}_2) \tilde{\mu}_{-\alpha}(\mathbf{r}_1) e^{i\Omega_{\alpha}(t_1 - t_2)}, \\ \chi^{+-}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) &= -i \theta(t_1 - t_2) \sum_{\alpha} s_{\alpha} \mu_{\alpha}(\mathbf{r}_1) \mu_{-\alpha}(\mathbf{r}_2) e^{-i\Omega_{\alpha}(t_1 - t_2)}. \end{aligned} \quad (36)$$

By repeating this procedure we obtain the second order GRF given in Appendix C.

We further consider generalized susceptibilities defined by the Fourier transform of the response functions to the frequency domain,

$$\begin{aligned} \langle \delta n^{+}(\mathbf{r}_{p+1} \omega_{p+1}) \rangle^{(p)} &= \int_{-\infty}^{\infty} d\mathbf{r}_p d\omega_p \dots \\ &\quad \times \int_{-\infty}^{\infty} d\mathbf{r}_1 d\omega_1 U_{\nu_p}(\mathbf{r}_p \omega_p) \dots U_{\nu_1}(\mathbf{r}_1 \omega_1) \\ &\quad \times \chi^{\nu_{p+1} \dots \nu_1}(\mathbf{r}_{p+1} \omega_{p+1}, \mathbf{r}_p \omega_p, \dots, \mathbf{r}_1, \omega_1), \end{aligned} \quad (37)$$

where

$$\begin{aligned} \chi^{\nu_1 \nu_2}(\mathbf{r}_1 \omega_1, \mathbf{r}_2 \omega_2) &= \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \\ &\quad \times \exp\{i(\omega_1 t_1 + \omega_2 t_2)\} \chi^{\nu_1 \nu_2}(\mathbf{x}_1, \mathbf{x}_2) \end{aligned} \quad (38)$$

and

$$\begin{aligned} \chi^{\nu_1 \nu_2 \nu_3}(\mathbf{r}_1 \omega_1, \mathbf{r}_2 \omega_2, \mathbf{r}_3 \omega_3) &= \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{\infty} dt_3 \\ &\quad \times \exp\{i(\omega_1 t_1 + \omega_2 t_2 + \omega_3 t_3)\} \\ &\quad \times \chi^{\nu_1, \nu_2, \nu_3}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3). \end{aligned} \quad (39)$$

Equation (38) together with Eq. (36) give

$$\begin{aligned} \chi^{++}(\mathbf{r}_1 \omega_1, \mathbf{r}_2 \omega_2) &= i \delta(\omega_1 + \omega_2) \sum_{\alpha} \left[ \frac{\mu_{\alpha}(\mathbf{r}_1) \tilde{\mu}_{-\alpha}(\mathbf{r}_2)}{\omega_2 - \Omega_{\alpha} + i\epsilon} \right. \\ &\quad \left. - \frac{\mu_{\alpha}(\mathbf{r}_2) \tilde{\mu}_{-\alpha}(\mathbf{r}_1)}{\omega_2 + \Omega_{\alpha} - i\epsilon} \right], \end{aligned} \quad (40)$$

$$\chi^{+-}(\mathbf{r}_1 \omega_1, \mathbf{r}_2 \omega_2) = \delta(\omega_1 + \omega_2) \sum_{\alpha} \frac{s_{\alpha} \mu_{\alpha}(\mathbf{r}_1) \mu_{-\alpha}(\mathbf{r}_2)}{\omega_2 + \Omega_{\alpha} - i\epsilon}.$$

We further define

$$\chi^{\nu_1 \nu_2}(\mathbf{r}_1 \omega_1, \mathbf{r}_2 \omega_2) = \alpha^{\nu_1 \nu_2}(\mathbf{r}_1, \mathbf{r}_2, \omega) \delta(\omega_1 + \omega_2). \quad (41)$$

The linear GRFs,  $\chi^{++}$  and  $\chi^{+-}$ , are connected by the fluctuation dissipation relation,

$$\chi^{+-}(\mathbf{r}_1, \mathbf{r}_2, t) = \frac{i}{\pi} \int_{-\infty}^{\infty} \alpha^{+-}(\mathbf{r}_1, \mathbf{r}_2, \omega) e^{-i\omega t} d\omega, \quad (42)$$

$$\chi^{++}(\mathbf{r}_1, \mathbf{r}_2, t) = \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} \alpha^{++}(\mathbf{r}_1, \mathbf{r}_2, \omega) e^{-i\omega t} d\omega,$$

where

$$\alpha^{++}(\mathbf{r}_1, \mathbf{r}_2, \omega) = \coth\left(\frac{\beta \hbar \omega}{2}\right) \alpha^{+-}(\mathbf{r}_1, \mathbf{r}_2, \omega). \quad (43)$$

In the classical, high temperature, limit  $\coth(\beta \hbar \omega / 2) \sim 2k_B T / (\hbar \omega)$ , and the two GRFs are then related through the classical fluctuation-dissipation (FD) relation,

$$\chi^{+-}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_1 + t) = -\frac{1}{k_B T} \theta(t) \frac{d}{dt} \chi^{++}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_1 + t). \quad (44)$$

However such FD relations are not that simple for the higher order response functions [58]. The second order generalized response functions in the frequency domain are given in Appendix D.

#### IV. INTERMOLECULAR INTERACTION ENERGIES

At this point we have derived all the ingredients necessary for computing the intermolecular energies. We shall start with the time domain expressions given in Eqs. (A5)–(A9). The contributions to the intermolecular energy will be classified by their order in density fluctuations. We write  $W = \sum_{j=0}^{\infty} W^{(j)}$ . The lowest (zeroth order) contribution  $W^{(0)}$  is given by Eq. (4) in terms of the ground state densities of the two molecules. The first order term,  $W^{(1)}$ , vanishes. The second order contribution, Eq. (A5), comes from the first term in the expansion of  $W_I$  [see Eq. (5)]. Substituting  $\chi^{+-}$  from Eq. (36) in Eq. (A5), we get

$$W^{(2)} = -\frac{1}{2\hbar} \sum_P \int \int \int \int \frac{d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}'_1 d\mathbf{r}'_2}{|\mathbf{r}_1 - \mathbf{r}'_1| |\mathbf{r}_2 - \mathbf{r}'_2|} \bar{n}_a(\mathbf{r}_1) \bar{n}_a(\mathbf{r}_2) \sum_{\alpha'} \frac{s_{\alpha'} \mu_{-\alpha'}(\mathbf{r}'_1) \mu_{\alpha'}(\mathbf{r}'_2)}{\Omega_{\alpha'}}. \quad (45)$$

The third order contribution is obtained by substituting the second order GRF [Eq. (C8)] in Eq. (A6),

$$W^{(3)} = -\frac{1}{6\hbar^2} \sum_P \int \int \int \int \int \int \frac{d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}'_1 d\mathbf{r}'_2 d\mathbf{r}'_3}{|\mathbf{r}_1 - \mathbf{r}'_1| |\mathbf{r}_2 - \mathbf{r}'_2| |\mathbf{r}_3 - \mathbf{r}'_3|} \bar{n}_a(\mathbf{r}_1) \bar{n}_a(\mathbf{r}_2) \bar{n}_a(\mathbf{r}_3) s_{\alpha'} s_{\beta'} \\ \times \left[ \sum_{\alpha' \beta' \gamma'} \frac{s_{\gamma'} \mu_{\alpha'}(\mathbf{r}'_1) \mu_{-\beta'}(\mathbf{r}'_2) \mu_{\gamma'}(\mathbf{r}'_3) V_{-\alpha', \beta', \gamma'}}{\Omega_{\alpha'} \Omega_{\beta'} \Omega_{\gamma'}} - \sum_{\alpha' \beta'} \left( \frac{\mu_{-\alpha' \beta'}(\mathbf{r}'_1) \mu_{\alpha'}(\mathbf{r}'_2) \mu_{\beta'}(\mathbf{r}'_3)}{\Omega_{\alpha'} \Omega_{\beta'}} \right. \right. \\ \left. \left. + \frac{\mu_{\alpha' \beta'}(\mathbf{r}'_1) \mu_{-\alpha'}(\mathbf{r}'_2) \mu_{-\beta'}(\mathbf{r}'_3)}{2\Omega_{\alpha'} \Omega_{\beta'}} \right) \right] \quad (46)$$

and to fourth order, we substitute Eqs. (36) in Eq. (A7),

$$W^{(4)} = -\frac{1}{2\hbar} \sum_P \int \int \int \int \frac{d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}'_1 d\mathbf{r}'_2}{|\mathbf{r}_1 - \mathbf{r}'_1| |\mathbf{r}_2 - \mathbf{r}'_2|} \sum_{\alpha \alpha'} \frac{s_{\alpha'} \bar{\mu}_{-\alpha}(\mathbf{r}_1) \mu_{\alpha}(\mathbf{r}_2) \mu_{-\alpha'}(\mathbf{r}'_1) \mu_{\alpha'}(\mathbf{r}'_2)}{(\Omega_{\alpha} + \Omega_{\alpha'})} \\ - \frac{1}{6\hbar^2} \sum_P \int \int \int \int \int \int \frac{d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}'_1 d\mathbf{r}'_2 d\mathbf{r}'_3}{|\mathbf{r}_1 - \mathbf{r}'_1| |\mathbf{r}_2 - \mathbf{r}'_2| |\mathbf{r}_3 - \mathbf{r}'_3|} \bar{n}_b(\mathbf{r}'_3) \sum_{\alpha \alpha'} \frac{s_{\alpha} s_{\alpha'} \mu_{\alpha}(\mathbf{r}_3) \mu_{\alpha'}(\mathbf{r}'_1) \mu_{-\alpha'}(\mathbf{r}'_2)}{\Omega_{\alpha} \Omega_{\alpha'}} [\bar{n}_a(\mathbf{r}_1) \mu_{\alpha}(\mathbf{r}_2) \\ + \bar{n}_a(\mathbf{r}_2) \mu_{\alpha}(\mathbf{r}_1)]. \quad (47)$$

Here  $\sum_P$  represents the sum over the single permutation of all primed and unprimed quantities and of the indices  $a$  and  $b$ . Higher (fifth and sixth) order contributions are given in Appendices E and F.

The first term in Eq. (47) [see also Eq. (B1)] reproduces McLachlan's expression for the van der Waals intermolecular energy [19,33]. There are two generalized linear response functions:  $\chi^{+-}$  represents the ordinary response to an external potential whereas  $\chi^{++}$  represents equilibrium charge fluctuations. Since the two are related by the fluctuation-dissipation theorem, the McLachlan expression may be recast solely in terms of the ordinary response of both molecules,  $\chi_a^{+-}$  and  $\chi_b^{+-}$ :

$$W_{vdW}^{(4)} = -\frac{1}{2\hbar} \int_{-\infty}^{\infty} d\omega \int d\mathbf{r}_1 \int d\mathbf{r}'_1 \int d\mathbf{r}_2 \int d\mathbf{r}'_2 \alpha_a^{+-} \\ \times (\mathbf{r}_1, \mathbf{r}_2, \omega) \alpha_b^{+-}(\mathbf{r}'_1, \mathbf{r}'_2, \omega) \\ \times \coth\left(\frac{\beta\hbar\omega}{2}\right) J(\mathbf{r}_1 - \mathbf{r}'_1) J(\mathbf{r}_2 - \mathbf{r}'_2), \quad (48)$$

which gives

$$W_{vdW}^{(4)} = -k_B T \sum_{n=0}^{\infty} \int \int \int \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}'_1 d\mathbf{r}'_2 \alpha_a^{+-} \\ \times (\mathbf{r}_1, \mathbf{r}_2, i\omega_n) \alpha_b^{+-}(\mathbf{r}'_1, \mathbf{r}'_2, i\omega_n) \\ \times J(\mathbf{r}_1 - \mathbf{r}'_1) J(\mathbf{r}_2 - \mathbf{r}'_2), \quad (49)$$

where  $\omega_n = (2\pi n k_B T / \hbar)$  are the Matsubara frequencies. However, life is not as simple for the higher order responses [58].

The  $(p+1)$ ,  $p$ th order generalized response functions,  $\chi^{p+1 p \dots p_1}$ , may not be simply related to the fully retarded ordinary response,  $\chi^{+ \dots}$ . The complete set of generalized response functions is thus required to represent intermolecular forces.

Polarizable force fields widely used in MD simulations are based on approximate treatments of charge fluctuations underlying intermolecular forces [59–64]. These force fields use parametrized electronegativity and hardness matrices to represent the nonlocal polarizabilities<sup>60,63,64</sup>. The choice of the number and type of polarization variables is based on chemical intuition. The present formulation of intermolecular forces suggests a new strategy for constructing polarizable force fields by using the oscillators to represent the density matrix (rather than the charge density). The CEO modes offer an alternative, unbiased and systematic choice of these variables, fully derivable from TDDFT.

Finally, the GRF provide new insight into the ‘‘causality paradox’’ of TDDFT which is connected with the retarded nature of the ordinary response functions. As a consequence it is in principle not possible to obtain the necessary functions as derivatives of a functional. This paradox was pointed out by Gross [20] and was recently addressed by Van Leuween [65] by introducing Keldysh [66] time variables. The general connection between the Keldysh variable and Liouville space was discussed in Ref. [67]. The GRF provide a more physically transparent resolution of this problem: GRF are not generally causal and there is no difficulty to derive the entire family of GRF as functional derivatives, thus providing a unified approach to response and spontaneous fluctuations.

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## APPENDIX A: TIME DOMAIN EXPRESSIONS FOR INTERMOLECULAR ENERGIES

The expectation values  $\langle \delta n_a(\mathbf{r}_1) \rangle_\lambda$  and  $\langle \delta n_a(\mathbf{r}_1) \delta n_b(\mathbf{r}'_2) \rangle_\lambda$  can be computed perturbatively in the GRFs of the individual molecules. To that end we treat  $\lambda H_{ab}$  in Eq. (1) as a perturbation and assume that at  $t \rightarrow -\infty$  the density matrix is a direct product of the density matrices of the two molecules. We then switch on the coupling  $\lambda H_{ab}$  adiabatically and the expectation value of any operator is then given by the interaction picture expression [37,38],

$$\langle A(t_1) \rangle_\lambda = \left\langle \mathcal{T} \tilde{A}^+(t_1) \exp \left\{ -\frac{i\lambda}{\hbar} \int_{-\infty}^{t_1} d\tau \tilde{H}_{ab}^-(\tau) \right\} \right\rangle, \quad (\text{A1})$$

where a  $(\tilde{\phantom{A}})$  represents quantities in the interaction picture.

Taking  $A \equiv \delta n_a$  and expanding in powers of  $\lambda$  yields a perturbation series in terms of the  $p$ th order response function,

$$R_a^{(p)}(t_1, t_2 \dots t_{p+1}) = \langle \mathcal{T} \delta n_a^+(t_1) H_{ab}^-(t_2) \dots H_{ab}^-(t_{p+1}) \rangle. \quad (\text{A2})$$

Substituting Eq. (2) and recalling that the initial density matrix is a direct product of the density matrices of the individual molecules,  $R^{(p)}$  is factorized in terms of the GRFs corresponding to the individual molecules defined in Eq. (7). The final expressions for  $\langle \delta n_a(\mathbf{r}_1) \rangle_\lambda$  and  $\langle \delta n_a(\mathbf{r}_1) \delta n_b(\mathbf{r}'_1) \rangle_\lambda$  in terms of GRF for individual molecules are obtained as

$$\begin{aligned} \langle \delta n_a(\mathbf{r}_1) \rangle_\lambda &\equiv \langle \delta n_a^+(\mathbf{r}_1) \rangle_\lambda = \frac{\lambda}{\hbar} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \int \int d\mathbf{r}_2 d\mathbf{r}'_2 \bar{n}_b(\mathbf{r}'_2) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_2) J(\mathbf{r}_2 - \mathbf{r}'_2) \\ &\quad - \frac{1}{2} \left( \frac{\lambda}{\hbar} \right)^2 \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 \int \int \int d\mathbf{r}_2 d\mathbf{r}'_2 d\mathbf{r}_3 d\mathbf{r}'_3 J(\mathbf{r}_2 - \mathbf{r}'_2) J(\mathbf{r}_3 - \mathbf{r}'_3) [\chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \chi_b^{++}(\mathbf{x}'_2, \mathbf{x}'_3) \\ &\quad + \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \chi_b^{+-}(\mathbf{x}'_2, \mathbf{x}'_3) + \bar{n}_b(\mathbf{r}'_2) \bar{n}_b(\mathbf{r}'_3) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) + \bar{n}_a(\mathbf{r}_3) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_2) \chi_b^{+-}(\mathbf{x}'_2, \mathbf{x}'_3)] + \dots, \end{aligned} \quad (\text{A3})$$

$$\begin{aligned} \langle \delta n_a(\mathbf{r}_1) \delta n_b(\mathbf{r}'_1) \rangle_\lambda &\equiv \langle \delta n_a^+(\mathbf{r}_1) \delta n_b^+(\mathbf{r}'_1) \rangle_\lambda = \frac{\lambda}{\hbar} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \int \int d\mathbf{r}_2 d\mathbf{r}'_2 J(\mathbf{r}_2 - \mathbf{r}'_2) [\chi_a^{++}(\mathbf{x}_1, \mathbf{x}_2) \chi_b^{+-}(\mathbf{x}'_1, \mathbf{x}'_2) \\ &\quad + \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_2) \chi_b^{++}(\mathbf{x}'_1, \mathbf{x}'_2)] - \frac{1}{2} \left( \frac{\lambda}{\hbar} \right)^2 \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 \int \int \int d\mathbf{r}_2 d\mathbf{r}'_2 d\mathbf{r}_3 d\mathbf{r}'_3 J(\mathbf{r}_2 - \mathbf{r}'_2) J(\mathbf{r}_3 - \mathbf{r}'_3) \\ &\quad \times \{ \bar{n}(\mathbf{r}_2) \bar{n}_b(\mathbf{r}'_3) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_3) \chi_b^{+-}(\mathbf{x}'_1, \mathbf{x}'_2) + \chi_b^{+-}(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}'_3) [\bar{n}(\mathbf{r}_2) \chi_a^{++}(\mathbf{x}_1, \mathbf{x}_3) + \bar{n}_a(\mathbf{r}_3) \chi_a^{++}(\mathbf{x}_1, \mathbf{x}_2)] \\ &\quad + \bar{n}_a(\mathbf{r}_2) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_3) \chi_b^{++}(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}'_3) + \bar{n}_b(\mathbf{r}'_3) \chi_b^{+-}(\mathbf{x}'_1, \mathbf{x}'_2) \chi_a^{++}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \\ &\quad + \chi_a^{++}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \chi_b^{+-}(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}'_3) + \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \chi_b^{++}(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}'_3) + \chi_b^{++}(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}'_3) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \\ &\quad + \chi_b^{+-}(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}'_3) \chi_a^{++}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) + \bar{n}_b(\mathbf{r}'_2) \bar{n}_a(\mathbf{r}_3) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_2) \chi_b^{+-}(\mathbf{x}'_1, \mathbf{x}'_3) \\ &\quad + \bar{n}_b(\mathbf{r}'_2) \chi_a^{++}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \chi_b^{+-}(\mathbf{x}'_1, \mathbf{x}'_3) + \bar{n}(\mathbf{r}'_2) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \chi_b^{++}(\mathbf{x}'_1, \mathbf{x}'_3) \\ &\quad + \bar{n}_a(\mathbf{r}_3) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_2) \chi_b^{++}(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}'_3) + \bar{n}_b(\mathbf{r}'_3) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \chi_b^{++}(\mathbf{x}'_1, \mathbf{x}'_2) \} + \dots. \end{aligned} \quad (\text{A4})$$

By substituting Eqs. (A3) and (A4) in Eq. (4) and collecting terms by their order with respect to charge fluctuations we obtain the total energy,  $W = \sum_{j=0}^6 W^{(j)}$ .  $W^{(0)}$  was given in Eq. (4),  $W^{(1)}=0$  and the higher terms are

$$W^{(2)} = -\frac{1}{2\hbar} \sum_p \int_{-\infty}^{t_1} dt_2 \int \int \int d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2 \bar{n}_b(\mathbf{r}'_1) \bar{n}_b(\mathbf{r}'_2) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_2) J(\mathbf{r}_1 - \mathbf{r}'_1) J(\mathbf{r}_2 - \mathbf{r}'_2), \quad (\text{A5})$$

$$\begin{aligned} W^{(3)} &= \frac{1}{6\hbar^2} \sum_p \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 \int \int \int \int d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2 d\mathbf{r}_3 d\mathbf{r}'_3 J(\mathbf{r}_1 - \mathbf{r}'_1) J(\mathbf{r}_2 - \mathbf{r}'_2) J(\mathbf{r}_3 - \mathbf{r}'_3) \\ &\quad \times \bar{n}_b(\mathbf{r}'_1) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \bar{n}_b(\mathbf{r}'_2) \bar{n}_b(\mathbf{r}'_3), \end{aligned} \quad (\text{A6})$$

$$\begin{aligned}
W^{(4)} = & -\frac{1}{2\hbar} \sum_P \int_{-\infty}^{t_1} dt_2 \int \int \int \int d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2 J(\mathbf{r}_1 - \mathbf{r}'_1) J(\mathbf{r}_2 - \mathbf{r}'_2) \chi_a^{++}(\mathbf{x}_1, \mathbf{x}_2) \chi_b^{+-}(\mathbf{x}'_1, \mathbf{x}'_2) \\
& + \frac{1}{6\hbar^2} \sum_P \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_1} dt_3 \int \int \int \int \int d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2 d\mathbf{r}_3 d\mathbf{r}'_3 J(\mathbf{r}_1 - \mathbf{r}'_1) J(\mathbf{r}_2 - \mathbf{r}'_2) J(\mathbf{r}_3 - \mathbf{r}'_3) \\
& \times [\bar{n}_a(\mathbf{r}_2) \bar{n}_b(\mathbf{r}'_3) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_3) \chi_b^{+-}(\mathbf{x}'_1, \mathbf{x}'_2) + \bar{n}_b(\mathbf{r}'_1) \bar{n}_a(\mathbf{r}_3) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_2) \chi_b^{+-}(\mathbf{x}'_2, \mathbf{x}'_3)], \tag{A7}
\end{aligned}$$

$$\begin{aligned}
W^{(5)} = & \frac{1}{6\hbar^2} \sum_P \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_1} dt_3 \int \int \int \int \int d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2 d\mathbf{r}_3 d\mathbf{r}'_3 J(\mathbf{r}_1 - \mathbf{r}'_1) J(\mathbf{r}_2 - \mathbf{r}'_2) J(\mathbf{r}_3 - \mathbf{r}'_3) \{ \chi_b^{+-}(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}'_3) \\
& \times [\bar{n}_a(\mathbf{r}_1) \chi_a^{++}(\mathbf{x}_2, \mathbf{x}_3) + \bar{n}_a(\mathbf{r}_2) \chi_a^{++}(\mathbf{x}_1, \mathbf{x}_3) + \bar{n}_a(\mathbf{r}_3) \chi_a^{++}(\mathbf{x}_1, \mathbf{x}_2) + \bar{n}_a(\mathbf{r}_1) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_3)] + \chi_b^{+-}(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}'_3) [\bar{n}_a(\mathbf{r}_2) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_3) \\
& + \bar{n}_b(\mathbf{r}'_3) \chi_b^{+-}(\mathbf{x}'_1, \mathbf{x}'_2)] \}, \tag{A8}
\end{aligned}$$

$$\begin{aligned}
W^{(6)} = & \frac{1}{6\hbar^2} \sum_P \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_1} dt_3 \int \int \int \int \int d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2 d\mathbf{r}_3 d\mathbf{r}'_3 [ \chi_a^{+++}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \chi_b^{+-}(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}'_3) \\
& + \chi_a^{+++}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \chi_b^{+-}(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}'_3) ], \tag{A9}
\end{aligned}$$

where  $\sum_P$  represents the sum over the single permutation of all primed and unprimed quantities and of the indices  $a$  and  $b$ .

## APPENDIX B: EXPANSION OF INTERMOLECULAR ENERGIES IN FREQUENCY DOMAIN GRF

The interaction energy is related to the zero-frequency component of the joint response functions of the two molecules  $a$  and  $b$  [38]. By transforming Eqs. (A5)–(A9) to the frequency domain we obtain

$$W^{(2)} = -\frac{1}{2\hbar} \sum_P \int \int \int \int d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2 \bar{n}_b(\mathbf{r}'_1) \bar{n}_b(\mathbf{r}'_2) \chi_a^{+-}(\mathbf{r}_1, \omega_1 = 0; \mathbf{r}_2, \omega_2 = 0) J(\mathbf{r}_1 - \mathbf{r}'_1) J(\mathbf{r}_2 - \mathbf{r}'_2), \tag{B1}$$

$$\begin{aligned}
W^{(3)} = & \frac{1}{6\hbar^2} \sum_P \int \int \int \int \int \int d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2 d\mathbf{r}_3 d\mathbf{r}'_3 J(\mathbf{r}_1 - \mathbf{r}'_1) J(\mathbf{r}_2 - \mathbf{r}'_2) J(\mathbf{r}_3 - \mathbf{r}'_3) \bar{n}_b(\mathbf{r}'_1) \bar{n}_b(\mathbf{r}'_2) \bar{n}_b(\mathbf{r}'_3) \chi_a^{+-} \\
& \times (\mathbf{r}_1, \omega_1 = 0; \mathbf{r}_2, \omega_2 = 0; \mathbf{r}_3, \omega_3 = 0), \tag{B2}
\end{aligned}$$

$$\begin{aligned}
W^{(4)} = & -\frac{1}{2\hbar} \sum_P \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \int \int \int \int d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2 J(\mathbf{r}_1 - \mathbf{r}'_1) J(\mathbf{r}_2 - \mathbf{r}'_2) \chi_a^{++}(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2) \chi_b^{+-}(\mathbf{r}'_1, -\omega_1; \mathbf{r}'_2, -\omega_2) \\
& + \frac{1}{6\hbar^2} \sum_P \int_{-\infty}^{\infty} d\omega_1 \int \int \int \int \int \int d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2 d\mathbf{r}_3 d\mathbf{r}'_3 J(\mathbf{r}_1 - \mathbf{r}'_1) J(\mathbf{r}_2 - \mathbf{r}'_2) J(\mathbf{r}_3 - \mathbf{r}'_3) [\bar{n}_a(\mathbf{r}_2) \bar{n}_b(\mathbf{r}'_3) \chi_a^{+-} \\
& \times (\mathbf{r}_1, \omega_1; \mathbf{r}_3, \omega_3 = 0) \chi_b^{+-}(\mathbf{r}'_1, -\omega_1; \mathbf{r}'_2, \omega_2 = 0) + \bar{n}(\mathbf{r}'_1) \bar{n}_a(\mathbf{r}_3) \chi_a^{+-}(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2 = 0) \chi_b^{+-}(\mathbf{r}'_2, -\omega_1; \mathbf{r}'_3, \omega_3 = 0)], \tag{B3}
\end{aligned}$$

$$\begin{aligned}
W^{(5)} = & \frac{1}{6\hbar^2} \sum_P \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_3 \int \int \int \int \int \int d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2 d\mathbf{r}_3 d\mathbf{r}'_3 \{ \chi_b^{+-}(\mathbf{x}'_1, \omega_1; \mathbf{x}'_2, \omega_2; \mathbf{x}'_3, \omega_3) [\bar{n}_a(\mathbf{r}_1) \chi_a^{++}(\mathbf{r}_2, \\
& -\omega_2; \mathbf{r}_3, -\omega_3) \delta(\omega_1) + \bar{n}(\mathbf{r}_2) \chi_a^{++}(\mathbf{r}_1, -\omega_1; \mathbf{r}_3, -\omega_3) \delta(\omega_2) + \bar{n}_a(\mathbf{r}_3) \chi_a^{++}(\mathbf{r}_1, -\omega_1; \mathbf{r}_2, -\omega_2) \delta(\omega_3) + \bar{n}_a(\mathbf{r}_1) \chi_a^{+-}(\mathbf{r}_1, -\omega_1; \mathbf{r}_3, \\
& -\omega_3) \delta(\omega_2)] + \chi_b^{+-}(\mathbf{r}'_1, \omega_1; \mathbf{r}'_2, \omega_2; \mathbf{r}'_3, \omega_3) [\bar{n}_a(\mathbf{r}_2) \chi_a^{+-}(\mathbf{r}_1, -\omega_1; \mathbf{r}_3, -\omega_3) \delta(\omega_2) + \bar{n}_a(\mathbf{r}_3) \chi_a^{+-}(\mathbf{r}_1, -\omega_1; \mathbf{r}_2, \omega_2) \delta(\omega_2)] \} \\
& \times J(\mathbf{r}_1 - \mathbf{r}'_1) J(\mathbf{r}_2 - \mathbf{r}'_2) J(\mathbf{r}_3 - \mathbf{r}'_3), \tag{B4}
\end{aligned}$$

$$\begin{aligned}
W^{(6)} = & \frac{1}{6\hbar^2} \sum_P \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_3 \int \int \int \int \int \int d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2 d\mathbf{r}_3 d\mathbf{r}'_3 [ \chi_a^{+++}(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2; \mathbf{r}_3, \omega_3) \chi_b^{+-} \\
& \times (\mathbf{r}'_1, -\omega_1; \mathbf{r}'_2, -\omega_2; \mathbf{r}'_3, -\omega_3) + \chi_a^{+++}(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2; \mathbf{r}_3, \omega_3) \chi_b^{+-}(\mathbf{r}'_1, -\omega_1; \mathbf{r}'_2, -\omega_2; \mathbf{r}'_3, -\omega_3) ]. \tag{B5}
\end{aligned}$$

Here  $\sum_P$  represents the sum over the single permutation of all primed and unprimed quantities and of the indices  $a$  and  $b$ .



**APPENDIX C: TIME-DOMAIN EXPRESSIONS FOR SECOND ORDER GENERALIZED  
RESPONSE FUNCTIONS**

To express  $\chi^{\nu_3, \nu_2, \nu_1}$  in terms of CEO modes, we start with Eq. (29). Expanding  $\bar{z}_\alpha$  in the external potentials and considering terms only up to second order in  $U_\nu$ , we obtain

$$i \frac{dz_\alpha^{\nu_1 \nu_2}(t)}{dt} = \Omega_\alpha z_\alpha^{\nu_1 \nu_2}(t) + \sum_{\alpha\beta} V_{-\alpha, \beta\gamma} z_\beta^{\nu_1}(t) z_\gamma^{\nu_2}(t) + \sum_{\beta} z_\beta^{\nu_1}(t) \int d\mathbf{r}_1 U_{\nu_2}(\mathbf{r}_1, t) \mu_{\alpha\beta}^{\nu_2}(\mathbf{r}_1), \quad (C1)$$

where  $\mu_{\alpha\beta}^+(\mathbf{r}_1) = \tilde{\mu}_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_1)$  and  $\mu_{\alpha\beta}^-(\mathbf{r}_1) = \mu_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_1)$ . Here

$$V_{\alpha\beta\gamma} = \frac{1}{2} \text{Tr}\{(\hat{I} - 2\hat{\rho}^g)[(\hat{\xi}_\alpha \hat{\xi}_\beta + \hat{\xi}_\beta \hat{\xi}_\alpha) \bar{V}(\xi_\gamma) + (\hat{\xi}_\beta \hat{\xi}_\gamma + \hat{\xi}_\gamma \hat{\xi}_\beta) \bar{V}(\xi_\alpha) + (\hat{\xi}_\alpha \hat{\xi}_\gamma + \hat{\xi}_\gamma \hat{\xi}_\alpha) \bar{V}(\xi_\beta)]\} \quad (C2)$$

and  $\bar{V}(\xi_\alpha)(\mathbf{r}_1) \hat{\xi}_\beta = H_1^{KS}(\xi_\alpha)(\mathbf{r}_1) \hat{\xi}_\beta + H_2^{KS}(\xi_\alpha \xi_\beta)(\mathbf{r}_1) \hat{\rho}^g$ , where

$$H_2^{KS}(\xi_\alpha, \xi_\beta)(\mathbf{r}_1) = \int \int d\mathbf{r}_2 d\mathbf{r}_3 g_{xc}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \xi_\alpha(\mathbf{r}_2, \mathbf{r}_2) \xi_\beta(\mathbf{r}_3, \mathbf{r}_3). \quad (C3)$$

Equation (C1) is derived in an analogous manner to Eq. (31). Its solution is

$$\begin{aligned} z_\alpha^--(t) &= is_\alpha \int_{-\infty}^{\infty} d\tau \int \int d\mathbf{r}_1 d\mathbf{r}_2 G_\alpha(t-\tau) \Gamma_\alpha^--(\tau, \mathbf{r}_1, \mathbf{r}_2), \\ z_\alpha^{++}(t) &= i \int_{-\infty}^{\infty} d\tau \int \int d\mathbf{r}_1 d\mathbf{r}_2 G_\alpha(t-\tau) \Gamma_\alpha^{++}(\tau, \mathbf{r}_1, \mathbf{r}_2), \\ z_\alpha^{+-}(t) &= is_\alpha \int_{-\infty}^{\infty} d\tau \int \int d\mathbf{r}_1 d\mathbf{r}_2 G_\alpha(t-\tau) \Gamma_\alpha^{+-}(\tau, \mathbf{r}_1, \mathbf{r}_2), \end{aligned} \quad (C4)$$

where

$$\begin{aligned} \Gamma_\alpha^--(\mathbf{r}_1, \mathbf{r}_2, t) &= \sum_{\beta\gamma} V_{-\alpha, \beta\gamma} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 U_-(\mathbf{r}_1, t_1) U_-(\mathbf{r}_2, t_2) \mu_{-\beta}(\mathbf{r}_1) \mu_{-\gamma}(\mathbf{r}_2) G_\beta(t-t_1) G_\gamma(t-t_2) \\ &+ i \sum_{\beta} s_\beta \int_{-\infty}^{\infty} dt_1 U_-(\mathbf{r}_2, t_1) U_-(\mathbf{r}_1, t) \mu_{\alpha\beta}(\mathbf{r}_1) \mu_{-\beta}(\mathbf{r}_2) G_\beta(t-t_1), \end{aligned} \quad (C5)$$

$$\begin{aligned} \Gamma_\alpha^{++}(\mathbf{r}_1, \mathbf{r}_2, t) &= \sum_{\beta\gamma} V_{-\alpha, \beta\gamma} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 U_+(\mathbf{r}_1, t_1) U_+(\mathbf{r}_2, t_2) \tilde{\mu}_{-\beta}(\mathbf{r}_1) \tilde{\mu}_{-\gamma}(\mathbf{r}_2) G_\beta(t-t_1) G_\gamma(t-t_2) \\ &+ i \sum_{\beta} s_\beta \int_{-\infty}^{\infty} dt_1 U_+(\mathbf{r}_2, t_1) U_+(\mathbf{r}_1, t) \mu_{\alpha\beta}(\mathbf{r}_1) \tilde{\mu}_{-\beta}(\mathbf{r}_2) G_\beta(t-t_1), \end{aligned} \quad (C6)$$

$$\begin{aligned} \Gamma_\alpha^{+-}(\mathbf{r}_1, \mathbf{r}_2, t) &= i \sum_{\beta} \int_{-\infty}^{\infty} dt_1 U_+(\mathbf{r}_2, t_1) U_-(\mathbf{r}_1, t) \mu_{-\alpha\beta}(\mathbf{r}_1) \tilde{\mu}_{-\beta}(\mathbf{r}_2) G_\beta(t-t_1) \\ &+ i \sum_{\beta} \int_{-\infty}^{\infty} dt_1 U_+(\mathbf{r}_1, t) U_-(\mathbf{r}_2, t_1) s_\beta \tilde{\mu}_{-\alpha\beta}(\mathbf{r}_2) \mu_{-\beta}(\mathbf{r}_1) G_\beta(t-t_1) + 2 \sum_{\beta\gamma} V_{-\alpha, \beta\gamma} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 U_+(\mathbf{r}_1, t_1) U_-(\mathbf{r}_2, t_2) \\ &\times \tilde{\mu}_{-\beta}(\mathbf{r}_1) s_\gamma \mu_\gamma(\mathbf{r}_2) G_\beta(t-t_1) G_\gamma(t-t_2). \end{aligned} \quad (C7)$$

The generalized second order responses are obtained by substituting Eqs. (32) and (C4) in Eq. (27) and collecting terms to second order in the fields. This finally gives

$$\begin{aligned} \chi^{+-}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2, \mathbf{r}_3 t_3) &= - \sum_{\alpha\beta} s_\alpha s_\beta \mu_{-\alpha\beta}(\mathbf{r}_1) \mu_\alpha(\mathbf{r}_2) \mu_{-\beta}(\mathbf{r}_3) G_\alpha(t_1-t_2) G_\beta(t_2-t_3) - \frac{1}{2} \sum_{\alpha, \beta} s_\alpha s_\beta \mu_{\alpha\beta}(\mathbf{r}_1) \mu_{-\alpha}(\mathbf{r}_2) \mu_{-\beta}(\mathbf{r}_3) G_\alpha(t_1-t_2) \\ &\times G_\beta(t_1-t_3) + i \sum_{\alpha\beta\gamma} s_\alpha s_\beta s_\gamma \mu_\alpha(\mathbf{r}_1) \mu_{-\beta}(\mathbf{r}_2) \mu_{-\gamma}(\mathbf{r}_3) V_{\alpha, \beta\gamma} \int_{-\infty}^{\infty} d\tau G_\alpha(t_1-\tau) G_\beta(\tau-t_2) G_\gamma(\tau-t_3), \end{aligned} \quad (C8)$$

$$\begin{aligned} \chi^{+++}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2, \mathbf{r}_3 t_3) = & - \sum_{\alpha, \beta} \tilde{\mu}_{-\alpha\beta}(\mathbf{r}_2) \mu_{\alpha}(\mathbf{r}_1) \tilde{\mu}_{-\beta}(\mathbf{r}_3) G_{\alpha}(t_1 - t_2) G_{\beta}(t_2 - t_3) - \frac{1}{2} \sum_{\alpha, \beta} \mu_{\alpha\beta}(\mathbf{r}_1) \tilde{\mu}_{-\alpha}(\mathbf{r}_2) \tilde{\mu}_{-\beta}(\mathbf{r}_3) G_{\alpha}(t_1 - t_2) G_{\beta}(t_1 - t_3) \\ & + i \sum_{\{1,2\}} \sum_{\{1,3\}} \sum_{\alpha\beta\gamma} \mu_{\alpha}(\mathbf{r}_1) \tilde{\mu}_{-\beta}(\mathbf{r}_2) \tilde{\mu}_{-\gamma}(\mathbf{r}_3) V_{-\alpha,\beta,\gamma} \int_{-\infty}^{\infty} d\tau G_{\alpha}(t_1 - \tau) G_{\beta}(\tau - t_2) G_{\gamma}(\tau - t_3), \end{aligned} \quad (\text{C9})$$

$$\begin{aligned} \chi^{+++}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = & - \sum_{\alpha, \beta} s_{\alpha} s_{\beta} \tilde{\mu}_{-\alpha\beta}(\mathbf{r}_2) \mu_{\alpha}(\mathbf{r}_1) \mu_{-\beta}(\mathbf{r}_3) G_{\alpha}(t_1 - t_2) G_{\beta}(t_2 - t_3) - \frac{1}{2} \sum_{\alpha, \beta} s_{\beta} \mu_{\alpha\beta}(\mathbf{r}_1) \tilde{\mu}_{-\alpha}(\mathbf{r}_2) \mu_{-\beta}(\mathbf{r}_3) G_{\alpha}(t_1 - t_2) G_{\beta}(t_1 - t_3) \\ & + 2i \sum_{\{\mathbf{x}_1, \mathbf{x}_2\}} \sum_{\alpha\beta\gamma} s_{\alpha} s_{\gamma} \mu_{\alpha}(\mathbf{r}_1) \tilde{\mu}_{-\beta}(\mathbf{r}_2) \mu_{-\gamma}(\mathbf{r}_3) V_{-\alpha,\beta,\gamma} \int_{-\infty}^{\infty} d\tau G_{\alpha}(t_1 - \tau) G_{\beta}(\tau - t_2) G_{\gamma}(\tau - t_3). \end{aligned} \quad (\text{C10})$$

$\sum_{\{j,k\}}$  represents sum over permutation of  $\mathbf{r}_j t_j$  and  $\mathbf{r}_k t_k$ . Note that  $\chi^{---}$  vanishes by definition [Eq. (6)].

#### APPENDIX D: FREQUENCY-DOMAIN EXPRESSIONS FOR SECOND ORDER GENERALIZED RESPONSE FUNCTIONS

The second order generalized susceptibilities are given by the Fourier transform of Eqs. (C8)–(C10). Here molecular labels  $a$  and  $b$  are not used because these expressions are equally valid for both molecules:

$$\begin{aligned} \chi^{+++}(\mathbf{r}_1 \omega_1, \mathbf{r}_2 \omega_2, \mathbf{r}_3, \omega_3) = & \sum_{\alpha\beta\gamma} \frac{s_{\beta} s_{\gamma} V_{-\alpha\beta\gamma} \mu_{\alpha}(\mathbf{r}_1) \mu_{-\beta}(\mathbf{r}_2) \mu_{-\gamma}(\mathbf{r}_3) \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 + \omega_3 + \Omega_{\alpha} - i\epsilon)(\omega_2 + \Omega_{\beta} - i\epsilon)(\omega_3 + \Omega_{\gamma} - i\epsilon)} \\ & + \frac{1}{2} \sum_{\alpha\beta} \frac{s_{\alpha} s_{\beta} \mu_{\alpha}(\mathbf{r}_1) \mu_{-\alpha\beta}(\mathbf{r}_2) \mu_{-\beta}(\mathbf{r}_3) \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 + \omega_3 + \Omega_{\alpha} - i\epsilon)(\omega_3 + \Omega_{\beta} - i\epsilon)} \\ & + \frac{1}{2} \sum_{\alpha\beta} \frac{s_{\alpha} s_{\beta} \mu_{\alpha}(\mathbf{r}_1) \mu_{-\alpha\beta}(\mathbf{r}_3) \mu_{-\beta}(\mathbf{r}_2) \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 + \omega_3 + \Omega_{\alpha} - i\epsilon)(\omega_2 + \Omega_{\beta} - i\epsilon)} \\ & - \frac{1}{2} \sum_{\alpha\beta} \frac{s_{\alpha} s_{\beta} \mu_{\alpha\beta}(\mathbf{r}_1) \mu_{-\alpha}(\mathbf{r}_2) \mu_{-\beta}(\mathbf{r}_3) s_{\beta} s_{\alpha} \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 + \Omega_{\alpha} - i\epsilon)(\omega_3 + \Omega_{\beta} - i\epsilon)}, \end{aligned} \quad (\text{D1})$$

$$\begin{aligned} \chi^{+++}(\mathbf{r}_1 \omega_1, \mathbf{r}_2 \omega_2, \mathbf{r}_3, \omega_3) = & \sum_{\alpha\beta\gamma} \frac{V_{-\alpha\beta\gamma} \mu_{\alpha}(\mathbf{r}_1) \tilde{\mu}_{-\beta}(\mathbf{r}_2) \tilde{\mu}_{-\gamma}(\mathbf{r}_3) \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 + \omega_3 + \Omega_{\alpha} - i\epsilon)(\omega_2 + \Omega_{\beta} - i\epsilon)(\omega_3 + \Omega_{\gamma} - i\epsilon)} \\ & + \sum_{\alpha\beta\gamma} \frac{V_{-\alpha\beta\gamma} \mu_{\alpha}(\mathbf{r}_2) \tilde{\mu}_{-\beta}(\mathbf{r}_1) \tilde{\mu}_{-\gamma}(\mathbf{r}_3) \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 - \Omega_{\alpha} + i\epsilon)(\omega_2 + \omega_3 - \Omega_{\beta} + i\epsilon)(\omega_3 + \Omega_{\gamma} - i\epsilon)} \\ & + \sum_{\alpha\beta\gamma} \frac{V_{-\alpha\beta\gamma} \mu_{\alpha}(\mathbf{r}_3) \tilde{\mu}_{-\beta}(\mathbf{r}_1) \tilde{\mu}_{-\gamma}(\mathbf{r}_2) \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 + \omega_3 - \Omega_{\gamma} + i\epsilon)(\omega_2 + \Omega_{\beta} - i\epsilon)(\omega_3 - \Omega_{\gamma} + i\epsilon)} + \frac{1}{2} \sum_{\alpha\beta} \frac{\mu_{\alpha}(\mathbf{r}_1) \tilde{\mu}_{-\alpha\beta}(\mathbf{r}_2) \tilde{\mu}_{-\beta}(\mathbf{r}_3) \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 + \omega_3 + \Omega_{\alpha} - i\epsilon)(\omega_3 + \Omega_{\beta} - i\epsilon)} \\ & + \frac{1}{2} \sum_{\alpha\beta} \frac{\mu_{\alpha}(\mathbf{r}_2) \tilde{\mu}_{-\alpha\beta}(\mathbf{r}_1) \tilde{\mu}_{-\beta}(\mathbf{r}_3) \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 - \Omega_{\alpha} + i\epsilon)(\omega_3 + \Omega_{\beta} - i\epsilon)} + \frac{1}{2} \sum_{\alpha\beta} \frac{\mu_{\alpha}(\mathbf{r}_1) \tilde{\mu}_{-\alpha\beta}(\mathbf{r}_3) \tilde{\mu}_{-\beta}(\mathbf{r}_2) \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 + \omega_3 + \Omega_{\alpha} - i\epsilon)(\omega_2 + \Omega_{\beta} - i\epsilon)} \\ & + \frac{1}{2} \sum_{\alpha\beta} \frac{\mu_{\alpha}(\mathbf{r}_2) \tilde{\mu}_{-\alpha\beta}(\mathbf{r}_3) \tilde{\mu}_{-\beta}(\mathbf{r}_1) \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 - \Omega_{\alpha} + i\epsilon)(\omega_2 + \omega_3 - \Omega_{\beta} + i\epsilon)} + \frac{1}{2} \sum_{\alpha\beta} \frac{\mu_{\alpha}(\mathbf{r}_3) \tilde{\mu}_{-\alpha\beta}(\mathbf{r}_1) \tilde{\mu}_{-\beta}(\mathbf{r}_2) \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_3 - \Omega_{\alpha} + i\epsilon)(\omega_2 + \Omega_{\beta} - i\epsilon)} \\ & + \frac{1}{2} \sum_{\alpha\beta} \frac{\mu_{\alpha}(\mathbf{r}_3) \tilde{\mu}_{-\alpha\beta}(\mathbf{r}_2) \tilde{\mu}_{-\beta}(\mathbf{r}_1) \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_3 - \Omega_{\alpha} + i\epsilon)(\omega_2 + \omega_3 - \Omega_{\beta} + i\epsilon)} - \frac{1}{2} \sum_{\alpha\beta} \frac{\mu_{\alpha\beta}(\mathbf{r}_1) \tilde{\mu}_{-\alpha}(\mathbf{r}_2) \tilde{\mu}_{-\beta}(\mathbf{r}_3) \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 + \Omega_{\alpha} - i\epsilon)(\omega_3 + \Omega_{\beta} - i\epsilon)} \\ & - \frac{1}{2} \sum_{\alpha\beta} \frac{\mu_{\alpha\beta}(\mathbf{r}_2) \tilde{\mu}_{-\alpha}(\mathbf{r}_1) \tilde{\mu}_{-\beta}(\mathbf{r}_3) \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 + \omega_3 - \Omega_{\alpha} + i\epsilon)(\omega_3 + \Omega_{\beta} - i\epsilon)} - \frac{1}{2} \sum_{\alpha\beta} \frac{\mu_{\alpha\beta}(\mathbf{r}_3) \tilde{\mu}_{-\alpha}(\mathbf{r}_2) \tilde{\mu}_{-\beta}(\mathbf{r}_1) \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 + \omega_3 - \Omega_{\alpha} + i\epsilon)(\omega_2 + \Omega_{\beta} - i\epsilon)}, \end{aligned} \quad (\text{D2})$$

and

$$\begin{aligned}
\chi^{+++}(\mathbf{r}_1\omega_1, \mathbf{r}_2\omega_2, \mathbf{r}_3, \omega_3) = & 2 \sum_{\alpha\beta\gamma} \frac{s_\gamma V_{-\alpha\beta\gamma} \mu_\alpha(\mathbf{r}_1) \tilde{\mu}_{-\beta}(\mathbf{r}_2) \mu_{-\gamma}(\mathbf{r}_3) \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 + \omega_3 + \Omega_\alpha - i\epsilon)(\omega_2 + \Omega_\beta - i\epsilon)(\omega_3 + \Omega_\gamma - i\epsilon)} \\
& + \sum_{\alpha\beta\gamma} \frac{s_\gamma V_{-\alpha\beta\gamma} \mu_\alpha(\mathbf{r}_2) \tilde{\mu}_{-\beta}(\mathbf{r}_1) \mu_{-\gamma}(\mathbf{r}_3) \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 - \Omega_\alpha + i\epsilon)(\omega_2 + \omega_3 - \Omega_\beta + i\epsilon)(\omega_3 + \Omega_\gamma - i\epsilon)} \\
& - \sum_{\alpha\beta} \frac{s_\alpha \mu_\alpha(\mathbf{r}_1) [\mu_{-\alpha\beta}(\mathbf{r}_2) \tilde{\mu}_{-\beta}(\mathbf{r}_3) - s_\beta \tilde{\mu}_{-\alpha\beta}(\mathbf{r}_2) \mu_{-\beta}(\mathbf{r}_3)] \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 + \omega_3 + \Omega_\beta - i\epsilon)(\omega_2 + \Omega_\alpha - i\epsilon)} \\
& - \sum_{\alpha\beta} \frac{s_\alpha \mu_\alpha(\mathbf{r}_1) [\mu_{-\alpha\beta}(\mathbf{r}_3) \tilde{\mu}_{-\beta}(\mathbf{r}_2) - s_\beta \tilde{\mu}_{-\alpha\beta}(\mathbf{r}_3) \mu_{-\beta}(\mathbf{r}_2)] \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 + \omega_3 + \Omega_\alpha - i\epsilon)(\omega_2 + \Omega_\beta - i\epsilon)} \\
& - \sum_{\alpha\beta} \frac{s_\alpha \mu_\alpha(\mathbf{r}_2) [\mu_{-\alpha\beta}(\mathbf{r}_1) \tilde{\mu}_{-\beta}(\mathbf{r}_3) - s_\beta \tilde{\mu}_{-\alpha\beta}(\mathbf{r}_1) \mu_{-\beta}(\mathbf{r}_3)] \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_3 + \Omega_\beta - i\epsilon)(\omega_2 - \Omega_\alpha + i\epsilon)} \\
& - \sum_{\alpha\beta} \frac{s_\alpha \mu_\alpha(\mathbf{r}_2) [\mu_{-\alpha\beta}(\mathbf{r}_3) \tilde{\mu}_{-\beta}(\mathbf{r}_1) - s_\beta \tilde{\mu}_{-\alpha\beta}(\mathbf{r}_3) \mu_{-\beta}(\mathbf{r}_1)] \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 + \omega_3 - \Omega_\beta + i\epsilon)(\omega_2 - \Omega_\alpha + i\epsilon)} \\
& - \sum_{\alpha\beta} \frac{s_\beta \mu_{\alpha\beta}(\mathbf{r}_2) \tilde{\mu}_{-\alpha}(\mathbf{r}_1) \mu_{-\beta}(\mathbf{r}_3) \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 + \Omega_\alpha - i\epsilon)(\omega_3 + \Omega_\beta - i\epsilon)} - \sum_{\alpha\beta} \frac{s_\beta \mu_{\alpha\beta}(\mathbf{r}_1) \tilde{\mu}_{-\alpha}(\mathbf{r}_2) \mu_{-\beta}(\mathbf{r}_3) \delta(\omega_1 + \omega_2 + \omega_3)}{(\omega_2 + \omega_3 - \Omega_\alpha + i\epsilon)(\omega_3 + \Omega_\beta - i\epsilon)}.
\end{aligned} \tag{D3}$$

#### APPENDIX E: FIFTH ORDER CONTRIBUTION TO THE ENERGY

The contributions to the interaction energy to fifth order in charge fluctuations are obtained by substituting GRF from Eqs. (36) and (C8) in Eq. (A8). This is written as the sum,  $W^{(5)} = \sum_{j=1}^4 W_j^{(5)}$ , where

$$\begin{aligned}
W_1^{(5)} = & \frac{1}{6\hbar^2} \sum_P \int \int \int \int \int \int \frac{d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}'_1 d\mathbf{r}'_2 d\mathbf{r}'_3}{|\mathbf{r}_1 - \mathbf{r}'_1| |\mathbf{r}_2 - \mathbf{r}'_2| |\mathbf{r}_3 - \mathbf{r}'_3|} \bar{n}_a(\mathbf{r}_1) \sum_{\alpha\alpha'\beta'\gamma'} s_{\alpha'} s_{\beta'} \mu_\alpha(\mathbf{r}_2) \tilde{\mu}_{-\alpha}(\mathbf{r}_3) \\
& \times \left[ \frac{\mu_{-\alpha'}, \beta'(\mathbf{r}'_1) \mu_{\alpha'}(\mathbf{r}'_2) \mu_{-\beta'}(\mathbf{r}'_3) (2\Omega_\alpha + \Omega_{\beta'})}{\Omega_{\beta'} (\Omega_\alpha + \Omega_{\alpha'}) (\Omega_\alpha + \Omega_{\beta'})} + \frac{\mu_{\alpha'}, \beta'(\mathbf{r}'_1) \mu_{-\alpha'}(\mathbf{r}'_2) \mu_{-\beta'}(\mathbf{r}'_3) (3\Omega_{\beta'} + \Omega_\alpha)}{\Omega_{\beta'} (\Omega_\alpha + \Omega_{\alpha'} + \Omega_{\beta'}) (\Omega_\alpha + \Omega_{\beta'})} \right. \\
& \left. - \frac{s_{\gamma'} \mu_{\alpha'}(\mathbf{r}'_1) \mu_{-\beta'}(\mathbf{r}'_2) \mu_{-\gamma'}(\mathbf{r}'_3) V_{-\alpha', \beta' \gamma'}}{\Omega_{\alpha'} (\Omega_{\alpha'} + \Omega_\beta) (\Omega_\alpha + \Omega_{\alpha'})} \right],
\end{aligned} \tag{E1}$$

$$\begin{aligned}
W_2^{(5)} = & \frac{1}{6\hbar^2} \sum_P \int \int \int \int \int \int \frac{d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}'_1 d\mathbf{r}'_2 d\mathbf{r}'_3}{|\mathbf{r}_1 - \mathbf{r}'_1| |\mathbf{r}_2 - \mathbf{r}'_2| |\mathbf{r}_3 - \mathbf{r}'_3|} \bar{n}_a(\mathbf{r}_1) \sum_{\alpha\alpha'\beta'\gamma'} s_\alpha \mu_\alpha(\mathbf{r}_2) \mu_{-\alpha}(\mathbf{r}_3) \left[ \frac{\tilde{\mu}_{-\alpha'}, \beta'(\mathbf{r}'_1) \mu_{\alpha'}(\mathbf{r}'_2) \mu_{-\beta'}(\mathbf{r}'_3) s_{\beta'}}{\Omega_{\beta'} (\Omega_\alpha + \Omega_{\beta'})} \right. \\
& \left. + \frac{\mu_{\alpha'}, \beta'(\mathbf{r}'_1) \tilde{\mu}_{-\alpha'}(\mathbf{r}'_2) \mu_{-\beta'}(\mathbf{r}'_3) (3\Omega_{\beta'} + \Omega_\alpha)}{\Omega_{\beta'} (\Omega_\alpha + \Omega_{\alpha'} + \Omega_{\beta'})} - \frac{2s_{\alpha'} s_{\gamma'} \mu_{\alpha'}(\mathbf{r}'_1) \tilde{\mu}_{-\beta'}(\mathbf{r}'_2) \mu_{-\gamma'}(\mathbf{r}'_3) V_{-\alpha', \beta' \gamma'}}{\Omega_{\alpha'} (\Omega_{\alpha'} + \Omega_\alpha) (\Omega_\alpha + \Omega_{\beta'} + \Omega_{\gamma'})} \right],
\end{aligned} \tag{E2}$$

$$\begin{aligned}
W_3^{(5)} = & -\frac{1}{3\hbar^2} \sum_P \int \int \int \int \int \int \frac{d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}'_1 d\mathbf{r}'_2 d\mathbf{r}'_3}{|\mathbf{r}_1 - \mathbf{r}'_1| |\mathbf{r}_2 - \mathbf{r}'_2| |\mathbf{r}_3 - \mathbf{r}'_3|} \bar{n}_b(\mathbf{r}'_3) \sum_{\alpha\beta\gamma\alpha'} s_\alpha s_\beta \mu_{\alpha'}(\mathbf{r}'_1) \tilde{\mu}_{\alpha'}(\mathbf{r}'_2) \\
& \times \left\{ \frac{s_\gamma V_{-\alpha\beta\gamma} \mu_\alpha(\mathbf{r}_1) \mu_{-\beta}(\mathbf{r}_3) \mu_{-\gamma}(\mathbf{r}_2) \left( \frac{1}{\Omega_\alpha + \Omega_{\alpha'}} + \frac{1}{\Omega_\alpha + \Omega_{\beta'}} + \frac{1}{\Omega_\alpha + \Omega_{\gamma'}} \right)}{(\Omega_\alpha + \Omega_{\alpha'}) (\Omega_{\alpha'} + \Omega_{\beta'} + \Omega_{\gamma'})} - \frac{\mu_\alpha(\mathbf{r}_1) \mu_{-\alpha\beta}(\mathbf{r}_2) \mu_{-\beta}(\mathbf{r}_3)}{\Omega_{\beta'} (\Omega_\alpha + \Omega_{\alpha'})} - \frac{\mu_{\alpha\beta}(\mathbf{r}_1) \mu_{-\alpha}(\mathbf{r}_2) \mu_{-\beta}(\mathbf{r}_3)}{2\Omega_{\beta'} (\Omega_\alpha + \Omega_{\beta'} + \Omega_{\alpha'})} \right. \\
& \left. - \frac{\mu_\alpha(\mathbf{r}_1) \mu_{-\alpha\beta}(\mathbf{r}_3) \mu_{-\beta}(\mathbf{r}_2)}{(\Omega_{\alpha'} + \Omega_\beta) (\Omega_\alpha + \Omega_{\alpha'})} - \frac{\mu_{-\alpha}(\mathbf{r}_3) \mu_{\alpha\beta}(\mathbf{r}_1) \mu_{-\beta}(\mathbf{r}_2)}{(\Omega_{\alpha'} + \Omega_\beta) (\Omega_\alpha + \Omega_{\beta'} + \Omega_{\alpha'})} \right\},
\end{aligned} \tag{E3}$$

$$\begin{aligned}
W_4^{(5)} = & -\frac{1}{3\hbar^2} \sum_P \int \int \int \int \int \int \int \frac{d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}'_1 d\mathbf{r}'_2 d\mathbf{r}'_3}{|\mathbf{r}_1 - \mathbf{r}'_1| |\mathbf{r}_2 - \mathbf{r}'_2| |\mathbf{r}_3 - \mathbf{r}'_3|} \bar{n}_b(\mathbf{r}'_3) \sum_{\alpha\beta\gamma\alpha'} s_{\alpha'} \mu_{\alpha'}(\mathbf{r}'_1) \mu_{\alpha'}(\mathbf{r}'_2) \\
& \times \left\{ \frac{s_{\alpha} s_{\gamma} V_{-\alpha\beta\gamma} \mu_{\alpha}(\mathbf{r}_1) \tilde{\mu}_{-\beta}(\mathbf{r}_2) \mu_{-\gamma}(\mathbf{r}_3)}{(\Omega_{\alpha} + \Omega_{\alpha'}) (\Omega_{\alpha'} + \Omega_{\beta} + \Omega_{\gamma})} \left( \frac{1}{\Omega_{\alpha'} + \Omega_{\beta}} + \frac{1}{\Omega_{\alpha'}} \right) - \frac{s_{\beta} \mu_{\alpha}(\mathbf{r}_1) \tilde{\mu}_{-\alpha\beta}(\mathbf{r}_2) \mu_{-\beta}(\mathbf{r}_3)}{\Omega_{\beta} (\Omega_{\alpha} + \Omega_{\alpha'})} - \frac{s_{\beta} \mu_{\alpha\beta}(\mathbf{r}_1) \tilde{\mu}_{-\alpha}(\mathbf{r}_2) \mu_{-\beta}(\mathbf{r}_3)}{\Omega_{\beta} (\Omega_{\alpha} + \Omega_{\beta} + \Omega_{\alpha'})} \right. \\
& \left. - \frac{s_{\beta} \mu_{\alpha}(\mathbf{r}_1) \tilde{\mu}_{-\alpha\beta}(\mathbf{r}_3) \mu_{-\beta}(\mathbf{r}_2)}{(\Omega_{\alpha'} + \Omega_{\beta}) (\Omega_{\alpha} + \Omega_{\alpha'})} - \frac{s_{\beta} \tilde{\mu}_{-\alpha}(\mathbf{r}_3) \mu_{\alpha\beta}(\mathbf{r}_1) \mu_{-\beta}(\mathbf{r}_2)}{(\Omega_{\alpha'} + \Omega_{\beta}) (\Omega_{\alpha} + \Omega_{\beta} + \Omega_{\alpha'})} \right\}. \tag{E4}
\end{aligned}$$

$\Sigma_P$  represents the sum over the single permutation of all primed and unprimed quantities and of the indices  $a$  and  $b$ .

#### APPENDIX F: SIXTH ORDER CONTRIBUTION TO THE ENERGY

The contributions to the interaction energy to sixth order in charge fluctuations are obtained by substituting Eqs. (C8)–(C10) in Eq. (A9). This is written as the sum,  $W^{(6)} = \sum_{j=1}^7 W_j^{(6)}$ , where

$$\begin{aligned}
W_1^{(6)} = & \frac{1}{6\hbar^2} \sum_P \int \int \int \int \int \int \int \frac{d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}'_1 d\mathbf{r}'_2 d\mathbf{r}'_3}{|\mathbf{r}_1 - \mathbf{r}'_1| |\mathbf{r}_2 - \mathbf{r}'_2| |\mathbf{r}_3 - \mathbf{r}'_3|} \sum_{\alpha\beta\gamma} \sum_{\alpha'\beta'\gamma'} s_{\alpha} \mu_{\alpha}(\mathbf{r}_1) \tilde{\mu}_{-\beta}(\mathbf{r}_2) \tilde{\mu}_{-\gamma}(\mathbf{r}_3) \mu_{-\beta'}(\mathbf{r}'_1) V_{-\alpha,\beta\gamma} \\
& \times \left\{ \mu_{\alpha'}(\mathbf{r}'_1) \mu_{\gamma'}(\mathbf{r}'_3) V_{-\alpha',\beta'\gamma'} \left[ \frac{2\Omega_{\alpha}}{(\Omega_{\gamma} + \Omega_{\gamma'}) (\Omega_{\beta} + \Omega_{\gamma} + \Omega_{\alpha'}) (\Omega_{\beta} + \Omega_{\gamma} + \Omega_{\beta'} + \Omega_{\gamma'}) (\Omega_{\alpha}^2 - (\Omega_{\beta} + \Omega_{\gamma})^2)} \right. \right. \\
& - \frac{1}{(\Omega_{\alpha} + \Omega_{\alpha'}) (\Omega_{\alpha} - \Omega_{\beta} + \Omega_{\gamma'}) (\Omega_{\alpha} - \Omega_{\beta} - \Omega_{\gamma}) (\Omega_{\alpha} - \Omega_{\beta'} + \Omega_{\gamma'})} \\
& \left. \left. + \frac{1}{(\Omega_{\alpha} + \Omega_{\alpha'}) (\Omega_{\alpha} + \Omega_{\beta} + \Omega_{\gamma'}) (\Omega_{\alpha} + \Omega_{\beta} + \Omega_{\gamma}) (\Omega_{\alpha} + \Omega_{\beta'} + \Omega_{\gamma'})} \right] - \mu_{\alpha'}(\mathbf{r}'_2) \mu_{-\alpha',\beta'}(\mathbf{r}'_3) \right. \\
& \times \left[ \frac{1}{(\Omega_{\alpha} + \Omega_{\alpha'}) (\Omega_{\alpha} - \Omega_{\beta} + \Omega_{\beta'}) (\Omega_{\alpha} - \Omega_{\beta} - \Omega_{\gamma})} - \frac{1}{(\Omega_{\alpha} + \Omega_{\alpha'}) (\Omega_{\alpha} - \Omega_{\beta} - \Omega_{\beta'}) (\Omega_{\alpha} - \Omega_{\beta} - \Omega_{\gamma})} \right. \\
& \left. - \frac{2\Omega_{\alpha}}{(\Omega_{\gamma} + \Omega_{\beta'}) (\Omega_{\alpha'} + \Omega_{\beta} + \Omega_{\gamma}) (\Omega_{\alpha}^2 - (\Omega_{\beta} + \Omega_{\gamma})^2)} \right] - \frac{1}{2} \mu_{\alpha'\beta'}(\mathbf{r}'_2) \mu_{\alpha'}(\mathbf{r}'_3) \\
& \times \left[ \frac{2\Omega_{\alpha}}{(\Omega_{\gamma} + \Omega_{\beta'}) (\Omega_{\beta} + \Omega_{\gamma} + \Omega_{\alpha'} + \Omega_{\beta'}) (\Omega_{\alpha}^2 - (\Omega_{\beta} + \Omega_{\gamma})^2)} - \frac{1}{(\Omega_{\alpha} - \Omega_{\beta} + \Omega_{\beta'}) (\Omega_{\alpha} - \Omega_{\beta} - \Omega_{\gamma}) (\Omega_{\alpha} + \Omega_{\alpha'} + \Omega_{\beta'})} \right. \\
& \left. \left. + \frac{1}{(\Omega_{\alpha} + \Omega_{\beta} + \Omega_{\beta'}) (\Omega_{\alpha} + \Omega_{\beta} + \Omega_{\gamma}) (\Omega_{\alpha} + \Omega_{\alpha'} + \Omega_{\beta'})} \right] \right\}, \tag{F1}
\end{aligned}$$

$$\begin{aligned}
W_2^{(6)} = & -\frac{1}{12\hbar^2} \sum_P \int \int \int \int \int \int \int \frac{d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}'_1 d\mathbf{r}'_2 d\mathbf{r}'_3}{|\mathbf{r}_1 - \mathbf{r}'_1| |\mathbf{r}_2 - \mathbf{r}'_2| |\mathbf{r}_3 - \mathbf{r}'_3|} \sum_{\alpha\beta\gamma} \sum_{\alpha'\beta'\gamma'} s_{\alpha} s_{\alpha'} s_{\beta'} \tilde{\mu}_{-\alpha,\beta}(\mathbf{r}_1) \mu_{\alpha}(\mathbf{r}_2) \tilde{\mu}_{-\beta}(\mathbf{r}_3) \\
& \times \left\{ s_{\gamma'} \mu_{\alpha'}(\mathbf{r}'_1) V_{-\alpha',\beta'\gamma'} \mu_{-\beta'}(\mathbf{r}'_2) \mu_{-\gamma'}(\mathbf{r}'_3) \frac{(\Omega_{\alpha'} - \Omega_{\beta'} - \Omega_{\gamma'})}{(\Omega_{\beta} + \Omega_{\gamma'}) (\Omega_{\alpha} - \Omega_{\beta} - \Omega_{\gamma}) (\Omega_{\alpha} + \Omega_{\alpha'}) (\Omega_{\alpha} + \Omega_{\beta'} + \Omega_{\gamma'})} \right. \\
& \left. + \frac{\mu_{\alpha'\beta'}(\mathbf{r}'_1) \mu_{-\alpha'}(\mathbf{r}'_2) \mu_{-\beta'}(\mathbf{r}'_3) (\Omega_{\alpha'} + \Omega_{\beta'})}{(\omega_{\beta} + \Omega_{\beta'}) ((\Omega_{\alpha'} + \Omega_{\beta'})^2 - \Omega_{\alpha}^2)} + \frac{\mu_{\alpha',\beta'}(\mathbf{r}'_1) \mu_{\alpha'}(\mathbf{r}'_2) \mu_{-\beta'}(\mathbf{r}'_3)}{(\Omega_{\beta} + \Omega_{\beta'}) (\Omega_{\alpha} + \Omega_{\alpha'})} \right\}, \tag{F2}
\end{aligned}$$

$$\begin{aligned}
W_3^{(6)} = & -\frac{1}{6\hbar^2} \sum_P \int \int \int \int \int \int \int \frac{d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}'_1 d\mathbf{r}'_2 d\mathbf{r}'_3}{|\mathbf{r}_1 - \mathbf{r}'_1| |\mathbf{r}_2 - \mathbf{r}'_2| |\mathbf{r}_3 - \mathbf{r}'_3|} s_{\alpha'} s_{\beta'} \mu_{\alpha\beta}(\mathbf{r}_1) \tilde{\mu}_{-\alpha}(\mathbf{r}_2) \tilde{\mu}_{-\beta}(\mathbf{r}_3) \mu_{\beta'}(\mathbf{r}'_1) \\
& \times \left\{ \frac{\mu_{\alpha'}(\mathbf{r}'_2) \mu_{-\gamma'}(\mathbf{r}'_3) V_{-\alpha',\beta'\gamma'} s_{\gamma'}}{(\Omega_{\beta'} + \Omega_{\gamma'}) (\Omega_{\alpha} + \Omega_{\beta} + \Omega_{\alpha'}) (\Omega_{\alpha} + \Omega_{\beta} + \Omega_{\beta'} + \Omega_{\gamma'})} + \frac{\mu_{-\alpha',\beta'}(\mathbf{r}'_2) \mu_{\alpha'}(\mathbf{r}'_3)}{(\Omega_{\beta'} - \Omega_{\beta}) (\Omega_{\alpha} + \Omega_{\alpha'} - \Omega_{\beta})} \right. \\
& \left. + \frac{\mu_{\alpha',\beta'}(\mathbf{r}'_2) \mu_{-\alpha'}(\mathbf{r}'_3)}{(\Omega_{\beta'} + \Omega_{\beta}) (\Omega_{\alpha} + \Omega_{\beta} + \Omega_{\alpha'} + \Omega_{\beta'})} \right\}, \tag{F3}
\end{aligned}$$

$$W_4^{(6)} = \frac{1}{12\hbar^2} \sum_P \int \int \int \int \int \int \frac{d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}'_1 d\mathbf{r}'_2 d\mathbf{r}'_3}{|\mathbf{r}_1 - \mathbf{r}'_1| |\mathbf{r}_2 - \mathbf{r}'_2| |\mathbf{r}_3 - \mathbf{r}'_3|} \sum_{\alpha\beta} \sum_{\alpha'\beta'} s_{\alpha'} s_{\beta'} \frac{\mu_{\alpha\beta}(\mathbf{r}_1) \mu_{\alpha'\beta'}(\mathbf{r}'_1) \tilde{\mu}_{-\alpha}(\mathbf{r}_2) \mu_{-\alpha'}(\mathbf{r}'_2) \mu_{-\beta}(\mathbf{r}_3) \tilde{\mu}_{-\beta'}(\mathbf{r}'_3)}{(\Omega_{\beta} + \Omega_{\beta'}) (\Omega_{\alpha} + \Omega_{\beta} + \Omega_{\alpha'} + \Omega_{\beta'})}, \quad (\text{F4})$$

$$\begin{aligned} W_5^{(6)} = & -\frac{1}{6\hbar^2} \sum_P \int \int \int \int \int \int \frac{d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}'_1 d\mathbf{r}'_2 d\mathbf{r}'_3}{|\mathbf{r}_1 - \mathbf{r}'_1| |\mathbf{r}_2 - \mathbf{r}'_2| |\mathbf{r}_3 - \mathbf{r}'_3|} \sum_{\alpha\beta\gamma} \sum_{\alpha'\beta'\gamma'} s_{\alpha'} s_{\gamma} s_{\alpha'} \\ & \times \tilde{\mu}_{-\beta}(\mathbf{r}_1) \mu_{\alpha}(\mathbf{r}_2) \mu_{-\gamma}(\mathbf{r}_3) V_{-\alpha\beta\gamma} \left\{ s_{\gamma'} s_{\beta'} V_{-\alpha',\beta'\gamma'} \mu_{\alpha'}(\mathbf{r}'_1) \mu_{-\beta'}(\mathbf{r}'_2) \right. \\ & \times \left[ \frac{2}{(\Omega_{\gamma} + \Omega_{\gamma'}) (\Omega_{\beta} + \Omega_{\gamma} + \Omega_{\beta'} + \Omega_{\gamma'}) (\Omega_{\alpha} - \Omega_{\beta} - \Omega_{\gamma}) (\Omega_{\beta} + \Omega_{\gamma} + \Omega_{\gamma'})} \right. \\ & - \frac{2\Omega_{\beta}}{(\Omega_{\alpha} + \Omega_{\alpha'}) (\Omega_{\alpha} + \Omega_{\beta} + \Omega_{\gamma'}) (\Omega_{\gamma} + \Omega_{\beta'} + \Omega_{\gamma'}) ((\Omega_{\alpha} - \Omega_{\gamma})^2 - \Omega_{\beta}^2)} \\ & - \left. \frac{1}{(\Omega_{\gamma} + \Omega_{\gamma'}) (\Omega_{\alpha} + \Omega_{\beta} - \Omega_{\gamma}) (\Omega_{\alpha} + \Omega_{\beta} + \Omega_{\gamma'}) (\Omega_{\gamma} + \Omega_{\beta'} + \Omega_{\gamma'})} \right] - \mu_{-\alpha'\beta'}(\mathbf{r}'_1) \tilde{\mu}_{-\beta'}(\mathbf{r}'_2) \mu_{\alpha'}(\mathbf{r}'_3) \\ & \times \left[ \frac{1}{(\Omega_{\gamma} + \Omega_{\beta'}) (\Omega_{\alpha} - \Omega_{\beta} - \Omega_{\gamma}) (\Omega_{\beta} + \Omega_{\gamma} + \Omega_{\alpha'})} - \frac{2\Omega_{\beta}}{(\Omega_{\alpha} + \Omega_{\beta} + \Omega_{\beta'}) (\Omega_{\alpha} + \Omega_{\alpha'}) ((\Omega_{\alpha} - \Omega_{\gamma})^2 - \Omega_{\beta}^2)} \right. \\ & - \left. \frac{1}{(\Omega_{\alpha} + \Omega_{\beta} - \Omega_{\gamma}) (\Omega_{\alpha} + \Omega_{\beta} + \Omega_{\beta'}) (\Omega_{\gamma} + \Omega_{\gamma'})} \right] - \mu_{\alpha'\beta'}(\mathbf{r}'_1) \mu_{-\alpha'}(\mathbf{r}'_2) \tilde{\mu}_{-\beta'}(\mathbf{r}'_3) \\ & \times \left\{ \left[ \frac{1}{2(\Omega_{\beta} + \Omega_{\gamma} + \Omega_{\alpha'} + \Omega_{\beta'}) (\Omega_{\alpha} - \Omega_{\beta} - \Omega_{\gamma}) (\Omega_{\gamma} + \Omega_{\gamma'})} + \frac{1}{2(\Omega_{\alpha} - \Omega_{\beta} - \Omega_{\gamma}) (\Omega_{\gamma} + \Omega_{\alpha'} + \Omega_{\beta'}) (\Omega_{\alpha} + \Omega_{\beta} + \Omega_{\alpha'} + \Omega_{\beta'})} \right. \right. \\ & \left. \left. - \frac{\Omega_{\beta}}{(\Omega_{\alpha} + \Omega_{\alpha'} + \Omega_{\beta'}) (\Omega_{\alpha} + \Omega_{\beta} + \Omega_{\beta'}) ((\Omega_{\alpha} - \Omega_{\gamma})^2 - \Omega_{\beta}^2)} \right] \right\}, \quad (\text{F5}) \end{aligned}$$

$$\begin{aligned} W_6^{(6)} = & \frac{1}{6\hbar^2} \sum_P \int \int \int \int \int \int \frac{d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}'_1 d\mathbf{r}'_2 d\mathbf{r}'_3}{|\mathbf{r}_1 - \mathbf{r}'_1| |\mathbf{r}_2 - \mathbf{r}'_2| |\mathbf{r}_3 - \mathbf{r}'_3|} \sum_{\alpha\beta} \sum_{\alpha'\beta'\gamma'} s_{\alpha} s_{\beta} s_{\alpha'} \tilde{\mu}_{-\alpha\beta}(\mathbf{r}_1) \mu_{\alpha}(\mathbf{r}_2) \mu_{-\beta}(\mathbf{r}_3) \\ & \times \left\{ \frac{s_{\beta'} V_{-\alpha'\beta'\gamma'} \mu_{\alpha'}(\mathbf{r}'_1) \mu_{-\beta'}(\mathbf{r}'_2) \tilde{\mu}_{-\gamma'}(\mathbf{r}'_3)}{(\Omega_{\alpha} + \Omega_{\alpha'}) (\Omega_{\beta} + \Omega_{\gamma'}) (\Omega_{\alpha} + \Omega_{\beta'} + \Omega_{\gamma'})} - \frac{\mu_{-\alpha'\beta'}(\mathbf{r}'_1) \tilde{\mu}_{-\beta'}(\mathbf{r}'_2) \mu_{\alpha'}(\mathbf{r}'_3)}{(\Omega_{\alpha} + \Omega_{\alpha'}) (\Omega_{\beta} + \Omega_{\beta'})} - \frac{\mu_{\alpha'\beta'}(\mathbf{r}'_1) \mu_{-\alpha'}(\mathbf{r}'_2) \tilde{\mu}_{-\beta'}(\mathbf{r}'_3)}{(\Omega_{\beta} + \Omega_{\beta'}) (\Omega_{\alpha} + \Omega_{\alpha'} + \Omega_{\beta'})} \right\}, \quad (\text{F6}) \end{aligned}$$

$$\begin{aligned} W_7^{(6)} = & -\frac{1}{12\hbar^2} \sum_P \int \int \int \int \int \int \frac{d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}'_1 d\mathbf{r}'_2 d\mathbf{r}'_3}{|\mathbf{r}_1 - \mathbf{r}'_1| |\mathbf{r}_2 - \mathbf{r}'_2| |\mathbf{r}_3 - \mathbf{r}'_3|} \sum_{\alpha\beta} \sum_{\alpha'\beta'\gamma'} s_{\beta} s_{\alpha'} \mu_{-\alpha\beta}(\mathbf{r}_1) \tilde{\mu}_{-\alpha}(\mathbf{r}_2) \mu_{-\beta}(\mathbf{r}_3) \\ & \times \left\{ \frac{s_{\alpha'} s_{\beta'} V_{-\alpha'\beta'\gamma'} \mu_{-\alpha'}(\mathbf{r}'_1) \mu_{-\beta'}(\mathbf{r}'_2) \tilde{\mu}_{-\gamma'}(\mathbf{r}'_3)}{(\Omega_{\alpha} + \Omega_{\beta} + \Omega_{\alpha'}) (\Omega_{\beta} + \Omega_{\gamma'}) (\Omega_{\alpha} + \Omega_{\beta} + \Omega_{\beta'} + \Omega_{\gamma'})} - \frac{\mu_{-\alpha'\beta'}(\mathbf{r}'_1) \tilde{\mu}_{-\beta'}(\mathbf{r}'_2) \mu_{\alpha'}(\mathbf{r}'_3)}{(\Omega_{\alpha} + \Omega_{\beta} + \Omega_{\alpha'}) (\Omega_{\beta} + \Omega_{\beta'})} \right\}. \quad (\text{F7}) \end{aligned}$$

Here  $\sum_P$  represents the sum over the single permutation of all primed and unprimed quantities and of the indices  $a$  and  $b$ .

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