Intermolecular Forces and Generalized TDDFT Response Functions in Liouville Space [*]

1 Introduction

Consider two interacting systems with nonoverlapping charge distributions. How can the properties of the combined system be expressed in terms of properties of the individual systems alone? This general problem appears in a wide variety of physical, chemical and biological contexts [1–3]. In this chapter we will provide a prescription for resolving this issue by the computation of i) response functions and ii) correlation functions of spontaneous fluctuations, of relevant degrees of freedom in the individual systems.

The computation of response and correlations is greatly simplified by using the density matrix in Liouville space[4]. Hilbert and Liouville space offer very different languages for the description of nonlinear response. Computing dynamical observables in terms of the wavefunction in Hilbert space requires both forward and backward propagations in time. In contrast, the density matrix, calculated in Liouville space should only be propagated forward. The choice is between following the ket only, moving it forward and backward, or following the joint forward dynamics of the ket and the bra. Artificial time variables (Keldysh loops) commonly used in many-body theory [5] are connected with the wavefunction. The density matrix which uses the real laboratory timescale throughout the calculation offers a more intuitive picture. Wavefunction-based theories calculate transition amplitudes, which by themselves are not observable. The density matrix on the other hand calculates physical observables. Moreover, dephasing processes (damping of off-diagonal elements of density operator resulting from phase fluctuations) can only be described in Liouville space.

In this chapter we present a method for expressing the joint response of two interacting systems in terms of the correlations and response functions of the individual systems. This factorization appears quite naturally in Liouville space. The pth order response of the individual systems is a linear combination of 2^p distinct $(p + 1)$-point correlation functions known as *Liouville space*

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pathway [4], which differ by whether the interaction at each time is with the bra or the ket. The pth order contribution to the intermolecular interaction requires a different linear combination of these same Liouville space pathways of both molecules. The 2^p Liouville space pathways are conveniently combined into $p+1$ *generalized response functions* (GRFs)[6,7]. One of the GRFs is the ordinary (causal) response function. The other GRFs represent spontaneous fluctuations, and the response of these fluctuations to a perturbation, and are therefore non-causal. The complete set of GRFs is calculated using generalized TDDFT equations in Liouville space.

A direct DFT simulation of molecular complexes by treating them as supermolecules is complicated because it requires nonlocal energy functionals[8–10]. The response approach makes good use of the perturbative nature of the coupling and recasts the energies in terms of properties of individual molecules which, in turn, may be calculated using local functionals[11,12].

2 Quantum Dynamics in Liouville Space; Superoperators

In this section we introduce the notion of Liouville space superoperators and review some of their useful properties. A detailed discussion of superoperators is given in [14]. The elements of an $N \times N$ density matrix in Hilbert space are arranged as a vector of length N^2 in Liouville space. An operator in Liouville space is then a matrix of dimension $N^2 \times N^2$, and is called a *superoperator*. Two special superoperators, A_L and A_R, are associated with every Hilbert space operator, A, and implement "left" and "right" multiplication on another operator X: $A_L X \Leftrightarrow AX$, $A_R X \Leftrightarrow XA$. These relations are not written as equalities because X is a vector in Liouville space and a matrix in Hilbert space.

It will be useful to define the symmetric $A_+ \equiv \frac{1}{2}(A_L + A_R)$ and antisymmetric $A_- \equiv A_L - A_R$ combinations. Hereafter we shall use Greek indices to denote superoperators A_ν with $\nu = L, R$ or $\nu = +, -$. Recasting these definitions in Hilbert space using ordinary operators we get

$$A_+ X \Leftrightarrow \frac{1}{2}(AX + XA); \quad A_- X \Leftrightarrow AX - XA. \tag{1}$$

A product of $\pm$ superoperators constitutes a series of nested commutators and anticommutators in Hilbert space. It is easy to verify that

$$(AB)_- = A_+ B_- + A_- B_+, \qquad (AB)_+ = A_+ B_+ + \frac{1}{4} A_- B_- . \tag{2}$$

We now consider products of superoperators that depend parametrically on time. We introduce a *time ordering operator* $\mathcal{T}$ in Liouville space, which orders all superoperators to its right such that time decreases from left to right. This is the natural time-ordering which follows chronologically the

various interactions with the density matrix [13]. We can freely commute operators following a $\mathcal{T}$ without worrying about commutations because in the end the order will be fixed by $\mathcal{T}$.

The expectation value of any superoperator, A_ν, is defined as,

$$\langle A_\nu(t)\rangle = \text{Tr}\{A_\nu(t)\rho_{eq}\}, \tag{3}$$

where ρ_{eq} is the equilibrium density matrix. It is easy to see that for any two operators A and B,

$$\langle \mathcal{T} A_+(t)B_-(t')\rangle = 0 \quad \text{if } t' > t. \tag{4}$$

$\langle \mathcal{T} A_+(t)B_-(t')\rangle$ is thus a retarded (i.e. causal) function. Equation (4) follows from the definitions (1): A '$-$' superoperator corresponds to a commutator in Hilbert space, so for $t < t'$, $\langle \mathcal{T} A_+(t)B_-(t')\rangle$ becomes a trace of a commutator which vanishes. Similarly, the trace of two '$-$' operators vanishes:

$$\langle \mathcal{T} A_-(t)B_-(t')\rangle = 0 \quad \text{for all } t \text{ and } t' . \tag{5}$$

We next introduce the interaction picture for superoperators. We partition the Hamiltonian, $H = H_0 + H_I$, into a reference part, H_0, which can be diagonalized, and the remainder, interaction part, H_I. We define a corresponding superoperator, $\mathcal{H}_-$, as $\mathcal{H}_- = \mathcal{H}_{0-} + \mathcal{H}_{I-}$. The time evolution of the density matrix is given by the Liouville equation:

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}\mathcal{H}_-\rho . \tag{6}$$

Equation (6) has the formal Green function solution, $\rho(t) = \mathcal{G}(t,t_0)\rho(t_0)$. Note that the time evolution operator, $\mathcal{G}$, acts only from the left, implying forward evolution of the density matrix. The total time evolution operator

$$\mathcal{G}(t,t_0) = \mathcal{T} \exp\left\{-\frac{i}{\hbar}\int_{t_0}^t d\tau \mathcal{H}_-(\tau)\right\}, \tag{7}$$

can be partitioned as:

$$\mathcal{G}(t,t_0) = \mathcal{G}_0(t,t_0)\mathcal{G}_I(t,t_0) \tag{8}$$

where $\mathcal{G}_0$ describes the time evolution with respect to H_0

$$\mathcal{G}_0(t,t_0) = \theta(t - t_0) \exp\left\{-\frac{i}{\hbar}\mathcal{H}_{0-}(t - t_0)\right\}, \tag{9}$$

and $\mathcal{G}_I$ is the time evolution operator in the *interaction picture*

$$\mathcal{G}_I(t,t_0) = \mathcal{T} \exp\left\{-\frac{i}{\hbar}\int_{t_0}^t d\tau \tilde{\mathcal{H}}_{I-}(\tau)\right\} . \tag{10}$$

The time dependence of a superoperator in the interaction picture, denoted by a ($\tilde{}$) is defined as

$$\tilde{A}_\nu(t) = \mathcal{G}_0^\dagger(t, t_0) A_\nu(t_0) \mathcal{G}_0(t, t_0) . \tag{11}$$

The equilibrium density matrix of the interacting system can be generated from the density matrix of the noninteracting system (ρ_0) by an adiabatic switching of the interaction H_I, starting at time $t = -\infty$: $\rho_{eq} = \mathcal{G}_I(0, -\infty)\rho_0$. In the wavefunction (Gell-Mann-Low) formulation of adiabatic switching, the wavefunction acquires a singular phase which must be cancelled by a denominator given by the closed loop S matrix[25]; this unphysical phase never shows up in Liouville space.

For a set of operators $\{A_i\}$, the pth order *generalized response functions* (GRF) are defined as

$$R_{i_{p+1}\dots i_1}^{\nu_{p+1}\dots\nu_1}(t_{p+1}\dots t_1) = \left(\frac{-i}{\hbar}\right)^{p'} \langle \mathcal{T} A_{i_{p+1}\nu_{p+1}}(t_{\nu_{p+1}})\dots A_{i_1\nu_1}(t_1)\rangle_0, \tag{12}$$

where $\langle\dots\rangle_0$ represents a trace with respect to ρ_0, the indices $\nu_n = +$ or $-$, and p' denotes the number of '$-$' indices in the set $\{\nu_{p+1}\dots\nu_1\}$. There are $p+1$, p^{th} order GRFs, having different number of '$-$' indices. Each member of the pth order GRF represents to a different physical process. For example, there are two first order GRFs,

$$R_{i_2 i_1}^{++}(t_2, t_1) = \langle \mathcal{T} A_{i_2+}(t_2) A_{i_1+}(t_1)\rangle_0$$

$$R_{i_2 i_1}^{+-}(t_2, t_1) = \frac{-i}{\hbar}\langle \mathcal{T} A_{i_2+}(t_2) A_{i_1-}(t_1)\rangle_0. \tag{13}$$

Recasting them in Hilbert space we have

$$R_{i_2 i_1}^{+-}(t_2, t_1) = \frac{-i}{\hbar}\theta(t_2 - t_1)\left[\text{Tr}\{A_{i_2}(t_2) A_{i_1}(t_1)\rho_0\} - \text{Tr}\{A_{i_2}(t_2) A_{i_1}(t_1)\rho_0\}\right]$$

$$= \hbar^{-1}\theta(t_2 - t_1)\text{Im}J(t_2, t_1)$$

$$R_{i_2 i_1}^{++}(t_2, t_1) = \text{Tr}\{A_{i_1}(t_1) A_{i_2}(t_2)\rho_0\} + \text{Tr}\{A_{i_2}(t_2) A_{i_1}(t_1)\rho_0\}$$

$$= \text{Re}J(t_2, t_1) \tag{14}$$

where $J(t_2, t_1) = \text{Tr}\{A_{i_2}(t_2) A_{i_1}(t_1)\rho_0\}$. With the factor $\hbar^{-1}$ the GRF R^{+-} has a well defined classical limit [14]. R^{+-} is causal [see (5)] and represents the response of the system at time t_2 to an external perturbation acting at an earlier time t_1. On the other hand, R^{++} is non-causal and denotes the correlation of A at two times. Each '$-$' index corresponds to the interaction with an external perturbation while a '$+$' index denotes an observation. In general, time-ordered Liouville space correlation functions with one '$+$' and several '$-$' indices, R^{+-}, R^{+--}, R^{+---}, etc. give response functions; all '$+$' correlation functions of the form R^{++}, R^{+++}, R^{++++}, etc. give ground state fluctuations, wheras R^{++-}, R^{++--}, R^{+++-}, etc. represent changes in the fluctuations caused by an external perturbation.

3   TDDFT Equations of Motion for the GRFs

Time dependent density functional theory is based on the effective one-body Kohn-Sham (KS) Hamiltonian [15],

$$H^{KS}(n(\boldsymbol{r}_1, t)) = -\frac{\hbar^2 \nabla^2}{2m} + U(\boldsymbol{r}_1) + e^2 \int d\boldsymbol{r}_2 \frac{n(\boldsymbol{r}_2, t)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} + U_{xc}(n(\boldsymbol{r}_1, t)),\ (15)$$

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 $\hat{\rho}$ [16–20] whose diagonal elements give the charge distribution, $n(\boldsymbol{r}_1, t) = \rho(\boldsymbol{r}_1, \boldsymbol{r}_1, t)$ and the off-diagonal elements, $\rho(\boldsymbol{r}_1, \boldsymbol{r}_2)$, represent electronic coherences. Hereafter we shall denote matrices in real space such as $\hat{\rho}$ by a caret. We further denote the ground state density matrix by $\hat{\rho}^g$.

The GRF corresponding to the charge density may be calculated by solving the time dependent generalized KS equation of motion for $\hat{\rho}$[27,22],

$$i\hbar \frac{\partial}{\partial t} \delta\hat{\rho} = [\hat{H}^{KS}(n), \hat{\rho}(t)] + \hat{U}_{ket}(t)\hat{\rho}(t) - \hat{\rho}(t)\hat{U}_{bra}(t), \qquad (16)$$

where $\delta\rho(\boldsymbol{r}_1, \boldsymbol{r}_2, t) \equiv \rho(\boldsymbol{r}_1, \boldsymbol{r}_2, t) - \rho^g(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is the change in the density matrix induced by the external potentials U_{ket} and U_{bra}. Equation (16) differs from the standard TDDFT equations in that the system is coupled to two external potentials, a "left" one U_{ket} acting on the ket and a "right" one U_{bra} acting on the bra.

We next define linear combinations,

$$U_-(\boldsymbol{r}, t) \equiv \frac{1}{2}(U_{ket}(\boldsymbol{r}, t) + U_{bra}(\boldsymbol{r}, t))$$

$$U_+(\boldsymbol{r}, t) \equiv \frac{1}{2}(U_{bra}(\boldsymbol{r}, t) - U_{ket}(\boldsymbol{r}, t)), \qquad (17)$$

and the diagonal matrices $U_-(\boldsymbol{r}_1, \boldsymbol{r}_2) = U_-(\boldsymbol{r}_1)\delta(\boldsymbol{r}_1 - \boldsymbol{r}_2)$, $U_+(\boldsymbol{r}_1, \boldsymbol{r}_2) = U_+(\boldsymbol{r}_1)\delta(\boldsymbol{r}_1 - \boldsymbol{r}_2)$. Note that $\hat{U}_-$ is given by a sum and $\hat{U}_+$ by a difference. The reason for this somewhat confusing notation is that $\hat{U}_-(\hat{U}_+)$ will enter in a commutator (anticommutator) in equation of motion for $\hat{\rho}(t)$. $\delta\hat{\rho}$ serves as a *generating function* for GRFs, which are obtained by a perturbative solution of (16) in $U_-(\boldsymbol{r}, t)$ and $U_+(\boldsymbol{r}, t)$ using $H_0 = H^{KS}$, as we shall shortly see.

Equation (16) can be recast in terms of superoperators,

$$i\hbar \frac{\partial}{\partial t} \delta\hat{\rho} = \mathcal{H}_-^{KS}\hat{\rho}(t) + \mathcal{U}^-(t)\hat{\rho}(t) - \mathcal{U}^+(t)\hat{\rho}(t) \qquad (18)$$

where

$$\mathcal{U}^-\hat{\rho} \equiv [\hat{U}_-, \hat{\rho}], \ \ \mathcal{U}^+\hat{\rho} \equiv [\hat{U}_+, \hat{\rho}]_+, \ \ \mathcal{H}_-^{KS}\hat{\rho} \equiv [\hat{H}^{KS}, \hat{\rho}] . \qquad (19)$$

The pth order GRFs $\chi^{\nu_{p+1}\dots\nu_1}$, are computed as the kernels in a perturbative expansion of the charge density fluctuation, $\delta n(\boldsymbol{r}_1,t)=\delta\rho(\boldsymbol{r}_1,\boldsymbol{r}_1,t)$, in the applied potentials, U_+ and U_-. Adopting the abbreviated space-time notation $\boldsymbol{x}_n \equiv (\boldsymbol{r}_n, t_n)$, we get

$$\langle\delta n^+(\boldsymbol{x}_{p+1})\rangle^{(p)} \equiv \int d\boldsymbol{r}_p dt_p \dots \int d\boldsymbol{r}_1 dt_1 \chi^{\nu_{p+1}\nu_p\dots\nu_1}(\boldsymbol{x}_{p+1}, \boldsymbol{x}_p, \dots, \boldsymbol{x}_1)$$
$$\times\, U_{\nu_p}(\boldsymbol{x}_p) U_{\nu_{p-1}}(\boldsymbol{x}_{p-1}) \dots U_{\nu_1}(\boldsymbol{x}_1)\,. \tag{20}$$

It follows from (16) and (20) that

$$\chi^{\nu_{p+1}\dots\nu_1}(\boldsymbol{x}_{p+1}\dots\boldsymbol{x}_1) = \left(\frac{-i}{\hbar}\right)^{p'} \langle\mathcal{T}\delta n^{\nu_{p+1}}(\boldsymbol{x}_{p+1})\dots\delta n^{\nu_1}(\boldsymbol{x}_1)\rangle \tag{21}$$

where p' denotes the number of "minus" indices in the set $\{\nu_{p+1}\dots\nu_1\}$. To first order ($p=1$), we have

$$\chi^{++}(\boldsymbol{x}_1,\boldsymbol{x}_2) = \langle\mathcal{T}\delta n^+(\boldsymbol{x}_1)\delta n^+(\boldsymbol{x}_2)\rangle$$
$$= \theta(t_1-t_2)\langle\delta n^+(\boldsymbol{x}_1)\delta n^+(\boldsymbol{x}_2)\rangle + \theta(t_2-t_1)\langle\delta n^+(\boldsymbol{x}_2)\delta n^+(\boldsymbol{x}_1)\rangle$$
$$\chi^{+-}(\boldsymbol{x}_1,\boldsymbol{x}_2) = \frac{-i}{\hbar}\langle\mathcal{T}\delta n^+(\boldsymbol{x}_1)\delta n^-(\boldsymbol{x}_2)\rangle$$
$$= \frac{-i}{\hbar}\theta(t_1-t_2)\langle\delta n^+(\boldsymbol{x}_1)\delta n^-(\boldsymbol{x}_2)\rangle. \tag{22}$$

The standard TDDFT equations which only yield ordinary response functions are obtained by setting $\mathcal{U}_{ket} = \mathcal{U}_{bra}$ so that $\mathcal{U}^+ = 0$ in (18). By allowing $\mathcal{U}_{ket}$ and $\mathcal{U}_{bra}$ to be different we can generate the complete set of GRF. The ordinary response function χ^{+-} characterizes the response of the density to an applied potential U_-[4]. Similarly, χ^{++} can be formally obtained as the response to the artificial external potential, U_+, that couples to the charge density through an anticommutator. χ^{++} represents equilibrium charge fluctuations and is therefore non-retarded. van Leeuwen's resolution of the "causality paradox" of TDDFT [15] has been recently formulated [27] in Liouville space.

4 Collective Electronic Oscillator (CEO) Representation of the GRF

Since the TDDFT density matrix, $\hat{\rho}(t)$, corresponds to a many-electron wavefunction 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 (intraband) components, $T(\hat{\xi})$[17,21].

$$\delta\hat{\rho}(t) = \hat{\xi}(t) + \hat{T}(\hat{\xi}(t))\,. \tag{23}$$

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 $\hat{\xi}$: [18,17]

$$\hat{T}(\hat{\xi}) = \frac{1}{2}(2\hat{\rho}^g - \hat{I})\left\{\hat{I} - \sqrt{\hat{I} - 4\hat{\xi}\hat{\xi}}\right\}. \tag{24}$$

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 $\delta n(\boldsymbol{r}, t)$:

$$H^{KS} = H_0^{KS} + H_1^{KS} + H_2^{KS} + ...$$

$$H_0^{KS}(\bar{n}(\boldsymbol{r}_1)) = -\frac{\hbar^2 \nabla^2}{2m} + U(\boldsymbol{r}_1) + e^2 \int d\boldsymbol{r}_2 \frac{\bar{n}(\boldsymbol{r}_2, t)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} + U_{xc}(\bar{n}(\boldsymbol{r}_1, t))$$

$$H_1^{KS}(\delta n(\boldsymbol{r}_1)) = \int d\boldsymbol{r}_2 \left(\frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} + f_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2)\right) \delta n(\boldsymbol{r}_2, t), \tag{25}$$

with f_{xc} the first order exchange correlation kernel in the adiabatic approximation where it is assumed to be frequency independent,

$$f_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \left|\frac{\delta U_{xc}[n(\boldsymbol{r}_1)]}{\delta n(\boldsymbol{r}_2)}\right|_{\bar{n}}. \tag{26}$$

The second order term in density fluctuations is,

$$H_2^{KS}(\delta n(\boldsymbol{r}_1)) = \int\int d\boldsymbol{r}_2 d\boldsymbol{r}_3 g_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)\delta n(\boldsymbol{r}_2, t)\delta n(\boldsymbol{r}_3, t) \tag{27}$$

with the kernel(in adiabatic approximation),

$$g_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) = \left|\frac{\delta^2 U_{xc}[n(\boldsymbol{r}_1)]}{\delta n(\boldsymbol{r}_2)\delta n(\boldsymbol{r}_3)}\right|_{\bar{n}}. \tag{28}$$

A quasiparticle algebra can 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 Ω_α [17,16].

$$\hat{L}\hat{\xi}_\alpha = \Omega_\alpha \hat{\xi}_\alpha, \tag{29}$$

The linearized Liouville space operator, $\hat{L}$ is obtained by substituting (25) into (16),

$$\hat{L}\hat{\xi}_\alpha = [\hat{H}_0^{KS}(\bar{n}), \hat{\xi}_\alpha] + [\hat{H}_1^{KS}(\xi_\alpha), \hat{\rho}^g]. \tag{30}$$

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

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

$$H_1^{KS}(\xi_\alpha)(\boldsymbol{r}_1, \boldsymbol{r}_2) = \delta(\boldsymbol{r}_1 - \boldsymbol{r}_2)\int d\boldsymbol{r}_3\left(\frac{e^2}{|\boldsymbol{r}_2 - \boldsymbol{r}_3|} + f_{xc}(\boldsymbol{r}_2, \boldsymbol{r}_3)\right)\xi_\alpha(\boldsymbol{r}_3, \boldsymbol{r}_3) \tag{31}$$

The eigenmodes $\hat{\xi}_\alpha$ come in pairs represented by positive and negative values of α, 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* (CEO) and the complete set of modes $\hat{\xi}_\alpha$ may be used to describe all response and spontaneous charge fluctuation properties of the system.

By expanding $\hat{\xi}(t)$ of the externally driven system in the CEO eigenmodes, $\hat{\xi}(t) = \sum_\alpha \bar{z}_\alpha(t)\hat{\xi}_\alpha$, where α runs over all modes (positive and negative) and $\bar{z}_\alpha$ are numerical coefficients, and substituting in (24) and (23), we obtain the following expansion for the density matrix

$$\delta\rho(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = \sum_\alpha \mu_\alpha(\boldsymbol{r}_1, \boldsymbol{r}_2)\bar{z}_\alpha(t) + \frac{1}{2}\sum_{\alpha,\beta}\mu_{\alpha,\beta}(\boldsymbol{r}_1, \boldsymbol{r}_2)\bar{z}_\alpha(t)\bar{z}_\beta(t) + \ldots, \quad (32)$$

where we have introduced the auxiliary quantities, $\hat{\mu}_\alpha = \hat{\xi}_\alpha$ and $\hat{\mu}_{\alpha\beta} = (2\hat{\rho}^g - I)(\hat{\xi}_\alpha\hat{\xi}_\beta + \hat{\xi}_\beta\hat{\xi}_\alpha)$.

By substituting (23) and (24) in (16) we can derive equations of motion for the CEO amplitudes $\bar{z}_\alpha$ which can then be solved successively order by order in the external potentials, U_{ν_1}. To second order we get,

$$i\hbar\frac{d\bar{z}_\alpha(t)}{dt} = \Omega_\alpha\bar{z}_\alpha(t) + K_{-\alpha}(t) + \sum_\beta K_{-\alpha\beta}(t)\bar{z}_\beta(t), \quad (33)$$

with the coefficients,

$$K_{-\alpha}(t) = \sum_\nu \int d\boldsymbol{r}_1 U_\nu(\boldsymbol{r}_1, t)\mu^\nu_{-\alpha}(\boldsymbol{r}_1)$$

$$K_{-\alpha\beta}(t) = \sum_\nu \int d\boldsymbol{r}_1 U_\nu(\boldsymbol{r}_1, t)\mu^\nu_{-\alpha\beta}(\boldsymbol{r}_1) . \quad (34)$$

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

We further expand $\bar{z}_\alpha = z_\alpha^{\nu_1} + z_\alpha^{\nu_1\nu_2} + ..$, in powers of the external potentials, where $z^{\nu_1\nu_2...\nu_p}$ denotes the nth order term in the potentials, $U_{\nu_1}U_{\nu_2}...U_{\nu_p}$. By comparing the terms in both sides, we obtain equations of motion for $z_\alpha^{\nu_1...\nu_p}$ for each order in external potential. To first order we get,

$$i\hbar\frac{dz_\alpha^{\nu_1}(t)}{dt} = \Omega_\alpha z_\alpha^{\nu_1}(t) + K_{-\alpha}(t) \quad (35)$$

The solution of (35) gives the generalized linear response functions

$$\chi^{++}(\boldsymbol{r}_1 t_1, \boldsymbol{r}_2 t_2) = \theta(t_1 - t_2)\sum_\alpha \mu_\alpha(\boldsymbol{r}_1)\tilde{\mu}_{-\alpha}(\boldsymbol{r}_2)e^{-\frac{i}{\hbar}\Omega_\alpha(t_1-t_2)}$$

$$+ \theta(t_2 - t_1)\sum_\alpha \mu_\alpha(\boldsymbol{r}_2)\tilde{\mu}_{-\alpha}(\boldsymbol{r}_1)e^{\frac{i}{\hbar}\Omega_\alpha(t_1-t_2)}$$

$$\chi^{+-}(\boldsymbol{r}_1 t_1, \boldsymbol{r}_2 t_2) = -\frac{i}{\hbar}\theta(t_1 - t_2)\sum_\alpha s_\alpha\mu_\alpha(\boldsymbol{r}_1)\mu_{-\alpha}(\boldsymbol{r}_2)e^{-\frac{i}{\hbar}\Omega_\alpha(t_1-t_2)} \quad (36)$$

with $s_\alpha = sign(\alpha)$. Higher order GRF can be obtained by repeating this procedure [22].

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

$$\langle \delta n^+(\boldsymbol{r}_{p+1}\omega_{p+1})\rangle^{(p)} = \int_{-\infty}^{\infty} d\boldsymbol{r}_p d\omega_p ... \int_{-\infty}^{\infty} d\boldsymbol{r}_1 d\omega_1 U_{\nu_p}(\boldsymbol{r}_p\omega_p)...U_{\nu_1}(\boldsymbol{r}_1\omega_1)$$
$$\times \chi^{\nu_{p+1}...\nu_1}(\boldsymbol{r}_{p+1}\omega_{p+1}, \boldsymbol{r}_p\omega_p, ..., \boldsymbol{r}_1, \omega_1) \qquad (37)$$

where the frequency transform is defined as,

$$\chi^{\nu_1\nu_2}(\boldsymbol{r}_1\omega_1, \boldsymbol{r}_2\omega_2) = \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \exp\{i(\omega_1 t_1 + \omega_2 t_2)\}\chi^{\nu_1\nu_2}(\boldsymbol{x}_1, \boldsymbol{x}_2) .$$
$$(38)$$

Equation (38) together with (36) gives,

$$\chi^{++}(\boldsymbol{r}_1\omega_1, \boldsymbol{r}_2\omega_2) = i\hbar\delta(\omega_1 + \omega_2)\sum_\alpha \left[\frac{\mu_\alpha(\boldsymbol{r}_1)\tilde{\mu}_{-\alpha}(\boldsymbol{r}_2)}{\omega_2 - \Omega_\alpha + i\epsilon} - \frac{\mu_\alpha(\boldsymbol{r}_2)\tilde{\mu}_{-\alpha}(\boldsymbol{r}_1)}{\omega_2 + \Omega_\alpha - i\epsilon} \right]$$

$$\chi^{+-}(\boldsymbol{r}_1\omega_1, \boldsymbol{r}_2\omega_2) = \delta(\omega_1 + \omega_2)\sum_\alpha \frac{s_\alpha\mu_\alpha(\boldsymbol{r}_1)\mu_{-\alpha}(\boldsymbol{r}_2)}{\omega_2 + \Omega_\alpha - i\epsilon} . \qquad (39)$$

The CEO representations of the ordinary response functions to third order were given in [16] and the GRF to second order were given in [22].

The linear GRFs, χ^{++} and χ^{+-}, are connected by the *fluctuation dissipation* relation,

$$\chi^{++}(\boldsymbol{r}_1, \omega; \boldsymbol{r}_2, -\omega) = \coth\left(\frac{\beta\hbar\omega}{2}\right) \chi^{+-}(\boldsymbol{r}_1, \omega; \boldsymbol{r}_2, -\omega) . \qquad (40)$$

To linear order, the ordinary response function provides the complete information and GRF are not needed. However such fluctuation dissipation relations are not that simple for the higher order response functions[23] and the complete set of GRF are required to describe the complete dynamics.

5   GRF Expressions for Intermolecular Interaction Energies

We now show how the GRF may be used to compute the energy of two interacting systems a and b with nonoverlapping charge distributions. At time $t = -\infty$ we take the density matrix to be a direct-product of the density matrices of the individual molecules. Thus initial density matrix at time $t \to -\infty$, $\hat{\rho}_0^g$, is given by, $\hat{\rho}_0^g = \hat{\rho}_0^a\hat{\rho}_0^b$, where $\hat{\rho}_0^a$ and $\hat{\rho}_0^b$ represent the density matrices of the two molecules at $t \to -\infty$. The Liouville space time-evolution operator transforms this initial state into a correlated state. The GRF allow us to

factorize the time-evolution operator into a sum of terms that individually preserve the purity of the direct-product form.

We start with the total hamiltonian of two interacting molecules $H_\lambda = H_a$ $+H_b +\lambda H_{ab}$, where H_a and H_b represent the Hamiltonians for 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 follow the convention that primed and unprimed indices correspond to molecules a and b, respectively. The charge densities of molecules a and b at space points $\boldsymbol{r}$ and $\boldsymbol{r}'$ will be denoted by $n_a(\boldsymbol{r})$ and $n_b(\boldsymbol{r}')$, respectively. H_{ab} is the Coulomb interaction

$$H_{ab} = - \int \int d\boldsymbol{r} d\boldsymbol{r}' J(\boldsymbol{r} - \boldsymbol{r}') n_a(\boldsymbol{r}) n_b(\boldsymbol{r}') - \sum_{k,k'} J(\boldsymbol{R}_k - \boldsymbol{R}_{k'}) Z_k(\boldsymbol{R}_k) Z_{k'}(\boldsymbol{R}'_k)$$

$$+ \sum_{P,k} \int d\boldsymbol{r}' J(\boldsymbol{R}_k - \boldsymbol{r}') Z_k(\boldsymbol{R}_k) n_b(\boldsymbol{r}') \tag{41}$$

where $J(\boldsymbol{r} - \boldsymbol{r}') \equiv 1/|\boldsymbol{r} - \boldsymbol{r}'|$ and $\boldsymbol{R}_k(\boldsymbol{R}'_{k'})$ represents the position of kth (k'th) nucleus in molecule $a(b)$ with charge $Z_k(Z_{k'})$. $\sum_P$ represents the sum over single permutation of primed and unprimed quantities together with indices a and b. The interaction energy of the coupled system is obtained by switching the parameter λ from 0 to 1 [10]

$$W = \int_0^1 d\lambda \langle H_{ab} \rangle_\lambda. \tag{42}$$

Here $\langle \ldots \rangle_\lambda$ denotes the expectation value with respect to the λ-dependent ground state many-electron density matrix of the system, $\hat{\rho}_\lambda$. We next partition the charge densities of both molecules as, $n_a(\boldsymbol{r}) = \bar{n}_a(\boldsymbol{r}) + \delta n_a(\boldsymbol{r})$, $n_b(\boldsymbol{r}') = \bar{n}_b(\boldsymbol{r}') + \delta n_b(\boldsymbol{r}')$, where $\bar{n}$ is the average density, $\bar{n}_a(\boldsymbol{r}) = \rho_a^0(\boldsymbol{r}, \boldsymbol{r})$, and $\bar{n}_b(\boldsymbol{r}') = \rho_b^0(\boldsymbol{r}', \boldsymbol{r}')$. Thus the total interaction energy can be written as, $W = W^{(0)} + W^{(I)} + W^{(II)}$, where,

$$W^{(0)} = - \int \int d\boldsymbol{r} d\boldsymbol{r}' J(\boldsymbol{r} - \boldsymbol{r}') \bar{n}_a(\boldsymbol{r}) \bar{n}_b(\boldsymbol{r}') - \sum_{k,k'} J(\boldsymbol{R}_k - \boldsymbol{R}_{k'}) Z_k(\boldsymbol{R}_k) Z_{k'}(\boldsymbol{R}'_k)$$

$$+ \sum_{P,k} \int d\boldsymbol{r}' J(\boldsymbol{R}_k - \boldsymbol{r}') Z_k(\boldsymbol{R}_k) \bar{n}_b(\boldsymbol{r}'), \tag{43}$$

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

$$W^{(I)} = - \int_0^1 d\lambda \int \int d\boldsymbol{r} d\boldsymbol{r}' J(\boldsymbol{r} - \boldsymbol{r}') \left[\bar{n}_a(\boldsymbol{r}) \langle \delta n_b(\boldsymbol{r}') \rangle_\lambda + \bar{n}_b(\boldsymbol{r}') \langle \delta n_a(\boldsymbol{r}) \rangle_\lambda \right],$$

$$+ \sum_{P,k} \int d\boldsymbol{r}' J(\boldsymbol{R}_k - \boldsymbol{r}') Z_k(\boldsymbol{R}_k) \langle \delta n_b(\boldsymbol{r}') \rangle_\lambda$$

$$W^{(II)} = - \int_0^1 d\lambda \int \int d\boldsymbol{r} d\boldsymbol{r}' J(\boldsymbol{r} - \boldsymbol{r}') \langle \delta n_a(\boldsymbol{r}) \delta n_b(\boldsymbol{r}') \rangle_\lambda. \tag{44}$$

The expectation values $\langle \delta n_a(\boldsymbol{r}_1) \rangle_\lambda$ and $\langle \delta n_a(\boldsymbol{r}_1) \delta n_b(\boldsymbol{r}'_2) \rangle_\lambda$ can be computed perturbatively in λH_{ab} in the interaction picture. λH_{ab} is switched on adiabatically giving the interacting ground state density matrix in terms of the non-interacting one. Substituting for H_{ab} from (41), and expanding in powers of λ yields a perturbation series in terms of the pth order joint response function, using $\boldsymbol{x}'_n = (\boldsymbol{r}'_n, t_n)$,

$$R_a^{(p)}(\boldsymbol{x}, \boldsymbol{x}_p, \boldsymbol{x}'_p \ldots \boldsymbol{x}_1, \boldsymbol{x}'_1) = \left\langle \mathcal{T} \delta \tilde{n}_a^+(\boldsymbol{x}) [\tilde{n}_a(\boldsymbol{x}_p) \tilde{n}_b(\boldsymbol{x}'_p)]^- ... [\tilde{n}_a(\boldsymbol{x}_1) \tilde{n}_b(\boldsymbol{x}'_1)]^- \right\rangle_0.$$
(45)

Making use of (2) and the fact that the initial density matrix is a direct product of the density matrices of the individual molecules, $R^{(p)}$ can be factorized in terms of GRFs of the individual molecules. For example, the first order joint response function is:

$$\begin{aligned} R_a^{(1)}(\boldsymbol{x}, \boldsymbol{x}_1, \boldsymbol{x}'_1) &= \left\langle \mathcal{T} \delta \tilde{n}_a^+(\boldsymbol{x}) [\tilde{n}_a(\boldsymbol{x}_1) \tilde{n}_b(\boldsymbol{x}'_1)]^- \right\rangle_0 \\ &= \mathrm{Tr} \left\{ \mathcal{T} \delta \tilde{n}_a^+(\boldsymbol{x}) [\tilde{n}_a(\boldsymbol{x}_1 \tilde{n}_b(\boldsymbol{x}'_1)]^- \hat{\rho}_a^0 \hat{\rho}_b^0 \right\}. \end{aligned}$$
(46)

Substituting $\tilde{n}_a^\nu(\boldsymbol{x}) = \bar{n}_a^\nu(\boldsymbol{x}) + \delta \tilde{n}_a^\nu(\boldsymbol{x})$, $\tilde{n}_b^\nu(\boldsymbol{x}') = \bar{n}_b^\nu(\boldsymbol{x}') + \delta \tilde{n}_b^\nu(\boldsymbol{x}')$, and using the identities, $\langle \delta \tilde{n}_a^\nu(\boldsymbol{x}) \rangle_{0a} = 0$ and $\langle \bar{n}_a^+(\boldsymbol{x}) \rangle_{0a} = \bar{n}_a(\boldsymbol{x})$, we obtain

$$R_a^{(1)}(\boldsymbol{x}, \boldsymbol{x}_1, \boldsymbol{x}'_1) = i \bar{n}_b(\boldsymbol{r}'_1) \chi_a^{+-}(\boldsymbol{x}, \boldsymbol{x}_1),$$
(47)

where χ_a^{+-} represents the linear order GRF for molecule a (see (21)). Similarly, second and higher order joint response functions can be expressed in terms of the GRFs of the individuals molecules.

In the present work we have ignored the contributions due to the nuclear interactions in (41). $\langle \delta n_a(\boldsymbol{r}_1) \rangle_\lambda$ and $\langle \delta n_a(\boldsymbol{r}_1) \delta n_b(\boldsymbol{r}'_1) \rangle_\lambda$, and consequently the interaction energies $W^{(I)}$ and $W^{(II)}$ can thus be expanded perturbatively in terms of the GRFs of the individual molecules [22]. We shall collect terms in $W^{(I)}$ and $W^{(II)}$ by their order with respect to charge fluctuations. The total energy is then, $W = \sum_j W^{(j)}$, where $W^{(j)}$ represents contribution from jth order charge fluctuation. $W^{(0)}$ was given in (43) and $W^{(1)} = 0$. $W^{(j)}$ to sixth order are given in [22].

$$W^{(2)} = -\frac{1}{2} \sum_P \int_{-\infty}^{t_1} dt_2 \int \int d\boldsymbol{R}_1 d\boldsymbol{R}_2 \bar{n}_b(\boldsymbol{r}'_1) \bar{n}_b(\boldsymbol{r}'_2) \chi_a^{+-}(\boldsymbol{x}_1, \boldsymbol{x}_2) J(\boldsymbol{s}_1) J(\boldsymbol{s}_2)$$
(48)

$$\begin{aligned} W^{(3)} = \frac{1}{6} \sum_P \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_1} dt_3 \int \int \int d\boldsymbol{R}_1 d\boldsymbol{R}_2 d\boldsymbol{R}_3 J(\boldsymbol{s}_1) J(\boldsymbol{s}_2) J(\boldsymbol{s}_3) \\ \times \bar{n}_b(\boldsymbol{r}'_1) \chi_a^{+--}(\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{x}_3) \bar{n}_b(\boldsymbol{r}'_2) \bar{n}_b(\boldsymbol{r}'_3) \end{aligned}$$
(49)

$$W^{(4)} = \frac{1}{6} \sum_P \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_1} dt_3 \int \int \int d\mathbf{R}_1 d\mathbf{R}_2 d\mathbf{R}_3 J(\mathbf{s}_1) J(\mathbf{s}_2) J(\mathbf{s}_3)$$

$$\times \left[\bar{n}_a(\mathbf{r}_2) \bar{n}_b(\mathbf{r'}_3) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_3) \chi_b^{+-}(\mathbf{x'}_1, \mathbf{x'}_2) \right.$$

$$\left. + \ \bar{n}_b(\mathbf{r'}_1) \bar{n}_a(\mathbf{r}_3) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_2) \chi_b^{+-}(\mathbf{x'}_2, \mathbf{x'}_3) \right]$$

$$- \frac{1}{2} \sum_P \int_{-\infty}^{t_1} dt_2 \int \int d\mathbf{R}_1 d\mathbf{R}_2 J(\mathbf{s}_1) J(\mathbf{s}_2) \chi_a^{++}(\mathbf{x}_1, \mathbf{x}_2) \chi_b^{+-}(\mathbf{x'}_1, \mathbf{x'}_2) \quad (50)$$

$$W^{(5)} = \frac{1}{6} \sum_P \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_1} dt_3 \int \int \int d\mathbf{R}_1 d\mathbf{R}_2 d\mathbf{R}_3 J(\mathbf{s}_1) J(\mathbf{s}_2) J(\mathbf{s}_3)$$

$$\times \left\{ \chi_b^{+--}(\mathbf{x'}_1, \mathbf{x'}_2, \mathbf{x'}_3) \left[\bar{n}_a(\mathbf{r}_1) \chi_a^{++}(\mathbf{x}_2, \mathbf{x}_3) + \bar{n}_a(\mathbf{r}_2) \chi_a^{++}(\mathbf{x}_1, \mathbf{x}_3) \right. \right.$$

$$\left. + \ \bar{n}_a(\mathbf{r}_3) \chi_a^{++}(\mathbf{x}_1, \mathbf{x}_2) + \bar{n}_a(\mathbf{r}_1) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_3) \right]$$

$$\left. + \chi_b^{++-}(\mathbf{x'}_1, \mathbf{x'}_2, \mathbf{x'}_3) [\bar{n}_a(\mathbf{r}_2) \chi_a^{+-}(\mathbf{x}_1, \mathbf{x}_3) + \bar{n}_b(\mathbf{r'}_3) \chi_b^{+-}(\mathbf{x'}_1, \mathbf{x'}_2)] \right\} \quad (51)$$

$$W^{(6)} = \frac{1}{6} \sum_P \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_1} dt_3 \int \int \int d\mathbf{R}_1 d\mathbf{R}_2 d\mathbf{R}_3 J(\mathbf{s}_1) J(\mathbf{s}_2) J(\mathbf{s}_3)$$

$$\times \left[\chi_a^{+++}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \chi_b^{+--}(\mathbf{x'}_1, \mathbf{x'}_2, \mathbf{x'}_3) \right.$$

$$\left. + \ \chi_a^{++-}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \chi_b^{++-}(\mathbf{x'}_1, \mathbf{x'}_2, \mathbf{x'}_3) \right], \quad (52)$$

where for brevity we have used the notations, $\int d\mathbf{R}_n = \int \int d\mathbf{r}_n d\mathbf{r'}_n$ and $J(\mathbf{s}_n) = J(\mathbf{r}_n - \mathbf{r'}_n)$.

We have now at hand all the ingredients necessary for computing the intermolecular energies. The TDDFT results for the GRF of individual molecules can be used to compute intermolecular interaction energy.

The second term in (50) reproduces McLachlan's expression for the van der Waals intermolecular energy [12,24]. Since χ^{+-} and χ^{++} are related by the fluctuation-dissipation theorem, the McLachlan expression may be recast solely in terms of the ordinary response of two molecules, χ_a^{+-} and χ_b^{+-}.

$$W_{vdW}^{(4)} = -\frac{1}{2\hbar} \int_{-\infty}^{\infty} d\omega \int \int d\mathbf{R}_1 d\mathbf{R}_2 J(\mathbf{s}_1) J(\mathbf{s}_2)$$

$$\coth\left(\frac{\beta\hbar\omega}{2}\right) \alpha_a^{+-}(\mathbf{r}_1, \mathbf{r}_2, \omega) \alpha_b^{+-}(\mathbf{r'}_1, \mathbf{r'}_2, \omega) \quad (53)$$

where $\chi^{\nu_2\nu_1}(\mathbf{r}_2\omega_2, \mathbf{r}_1\omega_1) = (\hbar^{-1})^{p'} \alpha_a^{\nu_2\nu_1}(\mathbf{r}_1, \mathbf{r}_2, \omega_1) \delta(\omega_1 + \omega_2)$. Equation (53) gives

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

$$(54)$$

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. The $(p+1)$, p^{th} order generalized response functions, $\chi^{\nu_{p+1}\nu_p..\nu_1}$, cannot all be related to the fully retarded ordinary response, $\chi^{+-\cdots-}$. The complete set of generalized response functions is thus required to represent the intermolecular forces.

By combining (48)-(52) with the CEO expansion, we can finally express the intermolecular energies in terms of CEO modes of the separate molecules. For example, substituting for χ^{+-} and χ^{++} from (36) in (50), the fourth order term is obtained in terms of CEO modes as

$$
\begin{aligned}
W^{(4)} = &-\frac{1}{2\hbar}\sum_P \int\int \frac{d\boldsymbol{R}_1 d\boldsymbol{R}_2}{|\boldsymbol{r}_1 - \boldsymbol{r'}_1||\boldsymbol{r}_2 - \boldsymbol{r'}_2|}\sum_{\alpha\alpha'}\frac{s_{\alpha'}\tilde{\mu}_{-\alpha}(\boldsymbol{r}_1)\mu_\alpha(\boldsymbol{r}_2)\mu_{-\alpha'}(\boldsymbol{r'}_1)\mu_{\alpha'}(\boldsymbol{r'}_2)}{(\Omega_\alpha + \Omega_{\alpha'})} \\
&-\frac{1}{6\hbar^2}\sum_P \int\int\int \frac{d\boldsymbol{R}_1 d\boldsymbol{R}_2 d\boldsymbol{R}_3}{|\boldsymbol{r}_1 - \boldsymbol{r'}_1||\boldsymbol{r}_2 - \boldsymbol{r'}_2||\boldsymbol{r}_3 - \boldsymbol{r'}_3|}\bar{n}_b(\boldsymbol{r'}_3) \\
&\times \sum_{\alpha\alpha'}\frac{s_\alpha s_{\alpha'}\mu_\alpha(\boldsymbol{r}_3)\mu_{\alpha'}(\boldsymbol{r'}_1)\mu_{-\alpha'}(\boldsymbol{r'}_2)}{\Omega_\alpha\Omega_{\alpha'}}\left[\bar{n}_a(\boldsymbol{r}_1)\mu_\alpha(\boldsymbol{r}_2) + \bar{n}_a(\boldsymbol{r}_2)\mu_\alpha(\boldsymbol{r}_1)\right]. \quad (55)
\end{aligned}
$$

Expansion of higher order terms in CEO modes are given in [22]. The GRF therefore provide a compact and complete description of intermolecular interactions. Both response and correlation functions can be described in terms of Liouville space pathways and can thus be treated along the same footing.

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