7 Intermolecular Forces and Generalized Response Functions in Liouville Space

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7.1 Introduction

Consider two interacting sub-systems with nonoverlapping charge distributions. How can the properties of the combined system be expressed in terms of properties of the individual sub-systems alone? This general problem appears in a wide variety of physical, chemical, and biological systems [Joester 2003, Stone 1996, Moore 2001]. In this chapter we provide a prescription for addressing this issue by the computation of (i) response functions and (ii) correlation functions of spontaneous fluctuations of relevant degrees of freedom in the individual sub-systems.

The computation of response and correlation functions is greatly simplified by using the density matrix in Liouville space [Mukamel 1995]. Hilbert and Liouville spaces 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 only the ket, moving it both 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 [Haug 1996] are connected with the wavefunction. The density matrix which uses the real laboratory time 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 directly calculates physical observables. Moreover, dephasing processes (damping of off-diagonal elements of the density matrix caused by phase fluctuations) which are naturally included into the Liouville space formulation may not be described in terms of the wavefunction. The "causality paradox" of TDDFT [Gross 1996] can be clearly resolved in Liouville space [Mukamel 2005].

In this chapter we present a method for expressing the joint response of two interacting sub-systems in terms of their correlation and response functions. This factorization appears quite naturally in Liouville space. The p^{th} order response of the individual systems is a linear combination of 2^p distinct $(p+1)$-point correlation functions known as *Liouville space pathways* [Mukamel 1995], which differ by whether the interaction at each time

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is with the bra or the ket. The p^{th} 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) [Cohen 2003, Cohen 2003b, Cohen 2005, Chernyak 1995]. One of the GRFs is the ordinary (causal) response function. The other GRFs represent spontaneous fluctuations, and the response of such 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 [Hult 1999, Lein 1999, Kohn 1998]. 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 [Dobson 1994b, Misquitta 2003].

7.2 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 [Mukamel 2003]. 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 then becomes a matrix of dimension $N^2 \times N^2$, and is called a *superoperator*. Two special superoperators, $\breve{A}_L$ and $\breve{A}_R$, are associated with every Hilbert space operator, $\hat{A}$, and implement "left" and "right" multiplication on another operator $\hat{X}$: $\breve{A}_L\hat{X} \Leftrightarrow \hat{A}\hat{X}$, $\breve{A}_R\hat{X} \Leftrightarrow \hat{X}\hat{A}$. These relations are not written as equalities because $\hat{X}$ is a vector in Liouville space and a matrix in Hilbert space.

It will be useful to define the symmetric $\breve{A}^+ \equiv \frac{1}{2}(\breve{A}_L + \breve{A}_R)$ and antisymmetric $\breve{A}^- \equiv \breve{A}_L - \breve{A}_R$ combinations. Hereafter we shall use Greek indices to denote superoperators $\breve{A}^\nu$ with $\nu = +, -$. Using ordinary Hilbert space operators we get

$$\breve{A}^+\hat{X} \Leftrightarrow \frac{1}{2}(\hat{A}\hat{X} + \hat{X}\hat{A}), \quad \breve{A}^-\hat{X} \Leftrightarrow \hat{A}\hat{X} - \hat{X}\hat{A}\,. \tag{7.1}$$

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

$$(\breve{AB})^- = \breve{A}^+\breve{B}^- + \breve{A}^-\breve{B}^+, \quad (\breve{AB})^+ = \breve{A}^+\breve{B}^+ + \frac{1}{4}\breve{A}^-\breve{B}^-\,. \tag{7.2}$$

We now consider products of superoperators that depend parametrically on time. We introduce a *time ordering operator* $\hat{\mathcal{T}}$ in Liouville space, which orders all superoperators to its right such that time decreases from left to right. This natural time-ordering follows chronologically the various interactions with the density matrix. We can freely commute operators following a $\hat{\mathcal{T}}$ operation without worrying about commutations because in the end the order will be determined by $\hat{\mathcal{T}}$.

The expectation value of any superoperator, $\breve{A}_\nu$, is defined as,

$$\langle \breve{A}^\nu(t) \rangle = \mathrm{Tr}\{\breve{A}^\nu(t)\hat{\rho}_{\mathrm{eq}}\} \ , \tag{7.3}$$

where $\hat{\rho}_{\mathrm{eq}}$ is the equilibrium density matrix. For any two operators $\hat{A}$ and $\hat{B}$, we have

$$\langle \hat{\mathcal{T}} \breve{A}^+(t)\breve{B}^-(t') \rangle = 0 \quad \text{if} \quad t' > t \ . \tag{7.4}$$

$\langle \hat{\mathcal{T}} \breve{A}^+(t)\breve{B}^-(t') \rangle$ is thus a retarded (i.e., causal) function. Equation (7.4) follows from the definitions (7.1): A "$-$" superoperator corresponds to a commutator in Hilbert space, so for $t < t'$, $\langle \hat{\mathcal{T}} \breve{A}^+(t)\breve{B}^-(t') \rangle$ becomes a trace of a commutator which vanishes. Similarly, the trace of two "$-$" operators vanishes:

$$\langle \hat{\mathcal{T}} \breve{A}^-(t)\breve{B}^-(t') \rangle = 0 \quad \text{for all } t \text{ and } t' \ . \tag{7.5}$$

We next introduce the interaction picture for superoperators. To that end, we partition the Hamiltonian, $\hat{H} = \hat{H}_0 + \hat{H}_1$, into a reference part, $\hat{H}_0$, which can be diagonalized, and the remainder, interaction part, $\hat{H}_1$. We define the corresponding superoperators, $\breve{\mathcal{H}}^-$, as $\breve{\mathcal{H}}^- = \breve{\mathcal{H}}_0^- + \breve{\mathcal{H}}_1^-$. The time evolution of the density matrix is given by the Liouville equation:

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{\mathrm{i}}{\hbar}\breve{\mathcal{H}}^- \hat{\rho} \ . \tag{7.6}$$

The formal Green function solution of (7.6) is $\hat{\rho}(t) = \breve{\mathcal{U}}(t,t_0)\hat{\rho}(t_0)$. Note that the time evolution operator, $\breve{\mathcal{U}}$, acts only from the left, implying forward evolution of the density matrix. The total time evolution operator

$$\breve{\mathcal{U}}(t,t_0) = \hat{\mathcal{T}} \exp\left\{-\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t} \mathrm{d}\tau \, \breve{\mathcal{H}}^-(\tau)\right\} \ , \tag{7.7}$$

can be partitioned as:

$$\breve{\mathcal{U}}(t,t_0) = \breve{\mathcal{U}}_0(t,t_0)\breve{\mathcal{U}}_1(t,t_0) \tag{7.8}$$

where $\breve{\mathcal{U}}_0$ describes the time evolution due to $\hat{H}_0$

$$\breve{\mathcal{U}}_0(t,t_0) = \theta(t-t_0)\exp\left\{-\frac{\mathrm{i}}{\hbar}\breve{\mathcal{H}}_0^-(t-t_0)\right\} \ , \tag{7.9}$$

and $\breve{\mathcal{U}}_1$ is the time evolution operator in the *interaction picture*

$$\breve{\mathcal{U}}_1(t,t_0) = \hat{\mathcal{T}} \exp\left\{-\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t} \mathrm{d}\tau \, \breve{\mathcal{H}}_1^{I-}(\tau)\right\} \ . \tag{7.10}$$

The time dependent superoperator $\breve{A}(t)$ in the interaction picture, denoted by a $\breve{A}^I$, is defined as

$$\breve{A}^{I\nu}(t) \equiv \breve{\mathcal{U}}_0^{\dagger}(t,t_0)\breve{A}^{\nu}(t_0)\breve{\mathcal{U}}_0(t,t_0)\ . \tag{7.11}$$

The equilibrium density matrix of the interacting system can be generated from the noninteracting density matrix $\hat{\rho}_0$ by adiabatically switching the interaction H_1, starting at time $t = -\infty$: $\hat{\rho}^I_{\mathrm{eq}} = \breve{\mathcal{U}}_I(0,-\infty)\hat{\rho}_0$. 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 [Negele 1988]; this unphysical phase never shows up in Liouville space.

For a set of operators $\{\hat{A}_i\}$, the p^{th} order *generalized response functions* (GRF) are defined as

$$R^{\nu_{p+1}\dots\nu_1}_{i_{p+1}\dots i_1}(t_{p+1}\dots t_1) = \left(\frac{-\mathrm{i}}{\hbar}\right)^{p'} \left\langle \hat{\mathcal{T}}\breve{A}^{\nu_{p+1}}_{i_{p+1}}(t_{p+1})\dots\breve{A}_{i_1\nu_1}(t_1)\right\rangle_0\ , \tag{7.12}$$

where $\langle\dots\rangle_0$ represents a trace with respect to $\hat{\rho}_0$, and the indices $\nu_n = +$ or $-$, and p' denote 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 p^{th} order GRF represents to a different physical process. For example, there are two first order GRFs,

$$R^{++}_{i_2i_1}(t_2,t_1) = \langle\hat{\mathcal{T}}\breve{A}^{+}_{i_2}(t_2)\breve{A}^{+}_{i_1}(t_1)\rangle_0 \tag{7.13a}$$

$$R^{+-}_{i_2i_1}(t_2,t_1) = \frac{-\mathrm{i}}{\hbar}\langle\hat{\mathcal{T}}\breve{A}^{+}_{i_2}(t_2)\breve{A}^{-}_{i_1}(t_1)\rangle_0\ . \tag{7.13b}$$

Recasting them in Hilbert space we have

$$\begin{aligned} R^{+-}_{i_2i_1}(t_2,t_1) &= \frac{-\mathrm{i}}{\hbar}\theta(t_2-t_1)\left[\mathrm{Tr}\{\hat{A}_{i_2}(t_2)\hat{A}_{i_1}(t_1)\hat{\rho}_0\} - \mathrm{Tr}\{\hat{A}_{i_2}(t_2)\hat{A}_{i_1}(t_1)\hat{\rho}_0\}\right] \\ &= \hbar^{-1}\theta(t_2-t_1)\mathrm{Im}J(t_2,t_1) \qquad (7.14\mathrm{a}) \\ R^{++}_{i_2i_1}(t_2,t_1) &= \mathrm{Tr}\{\hat{A}_{i_1}(t_1)\hat{A}_{i_2}(t_2)\hat{\rho}_0\} + \mathrm{Tr}\{\hat{A}_{i_2}(t_2)\hat{A}_{i_1}(t_1)\hat{\rho}_0\} \\ &= \mathrm{Re}J(t_2,t_1)\ , \qquad (7.14\mathrm{b}) \end{aligned}$$

where $J(t_2,t_1) = \mathrm{Tr}\{\hat{A}_{i_2}(t_2)\hat{A}_{i_1}(t_1)\hat{\rho}_0\}$. With the factor $\hbar^{-1}$, the GRF R^{+-} has a well defined classical limit [Mukamel 2003]. R^{+-} is causal [see (7.5)] 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.

7.3 TDDFT Equations of Motion for the GRFs

Time dependent density functional theory is based on the effective one-body Kohn-Sham (KS) Hamiltonian [Gross 1996],

$$\hat{H}_{\mathrm{KS}}[n] = -\frac{\hbar^2\nabla^2}{2m} + v_{\mathrm{ext}}(\boldsymbol{r}_1) + v_{\mathrm{H}}[n](\boldsymbol{r}_1,t) + v_{\mathrm{xc}}[n](\boldsymbol{r}_1,t) \ , \tag{7.15}$$

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 $\hat{\rho}$ [Tretiak 2002, Chernyak 1996, Ring 1980, Blaizot 1986, Berman 2003, Coleman 2000] 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, $\rho(\boldsymbol{r}_1,\boldsymbol{r}_2)$ with $\boldsymbol{r}_1 \neq \boldsymbol{r}_2$, represent electronic coherences. We further denote the ground state density matrix by $\hat{\rho}^{\mathrm{GS}}$.

The GRF corresponding to the charge density may be calculated by solving the time dependent generalized KS equation of motion for $\hat{\rho}$ [Mukamel 2005, Harbola 2004],

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\delta\hat{\rho} = [\hat{H}_{\mathrm{KS}},\hat{\rho}(t)] + v_{\mathrm{ket}}(t)\hat{\rho}(t) - \hat{\rho}(t)v_{\mathrm{bra}}(t) \ , \tag{7.16}$$

where $\delta\rho(\boldsymbol{r}_1,\boldsymbol{r}_2,t) \equiv \rho(\boldsymbol{r}_1,\boldsymbol{r}_2,t) - \rho^{\mathrm{GS}}(\boldsymbol{r}_1,\boldsymbol{r}_2)$ is the change in the density matrix induced by the external potentials v_{ket} and v_{bra}. Equation (7.16) differs from the standard TDDFT equations in that the system is coupled to two external potentials, a "left" one v_{ket} acting on the ket and a "right" one v_{bra} acting on the bra.

We next define the new variables,

$$v_-(\boldsymbol{r},t) \equiv \frac{1}{2}\left[v_{\mathrm{ket}}(\boldsymbol{r},t) + v_{\mathrm{bra}}(\boldsymbol{r},t)\right] \tag{7.17a}$$

$$v_+(\boldsymbol{r},t) \equiv \frac{1}{2}\left[v_{\mathrm{bra}}(\boldsymbol{r},t) - v_{\mathrm{ket}}(\boldsymbol{r},t)\right] \ , \tag{7.17b}$$

and the diagonal matrices

$$v_-(\boldsymbol{r}_1,\boldsymbol{r}_2) = v_-(\boldsymbol{r}_1)\delta(\boldsymbol{r}_1-\boldsymbol{r}_2) \quad , \quad v_+(\boldsymbol{r}_1,\boldsymbol{r}_2) = v_+(\boldsymbol{r}_1)\delta(\boldsymbol{r}_1-\boldsymbol{r}_2) \ . \tag{7.18}$$

We further introduce two matrices (operators) in real space $\hat{V}_-$ and $\hat{V}_+$ with elements $v_-(\boldsymbol{r}_1,\boldsymbol{r}_2)$ and $v_+(\boldsymbol{r}_1,\boldsymbol{r}_2)$, respectively. $\delta\hat{\rho}$ serves as a *generating function* for GRFs, which are obtained by a perturbative solution of (7.16) in $v_-(\boldsymbol{r},t)$ and $v_+(\boldsymbol{r},t)$ using $\hat{H}^{(0)} = \hat{H}_{\mathrm{KS}}$ as a reference, as we shall shortly see. The reason for assigning the + and the − subscripts to v in (7.17a) and (7.17b) is to keep track of the perturbative terms that arise from the external potential that couples to the density matrix through commutators and anticommutators.

Equation (7.16) can be recast in terms of superoperators,

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\delta\hat{\rho} = \breve{\mathcal{H}}^{-}_{\mathrm{KS}}\hat{\rho}(t) + \breve{\mathcal{V}}^{-}(t)\hat{\rho}(t) - \breve{\mathcal{V}}^{+}(t)\hat{\rho}(t)\,, \tag{7.19}$$

where

$$\breve{\mathcal{V}}^{-}\hat{\rho} \equiv [\hat{V}_{-},\hat{\rho}], \quad \breve{\mathcal{V}}^{+}\hat{\rho} \equiv [\hat{V}_{+},\hat{\rho}]_{+}, \quad \breve{\mathcal{H}}^{-}_{\mathrm{KS}}\hat{\rho} \equiv [\hat{H}_{\mathrm{KS}},\hat{\rho}]\,. \tag{7.20}$$

The p^{th} order GRFs $\chi^{\nu_{p+1}\cdots\nu_1}$, 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, v_+ and v_-. Adopting the abbreviated space-time notation $\boldsymbol{x}_n \equiv (\boldsymbol{r}_n, t_n)$, we get

$$\begin{aligned}\langle\delta n^{+}(\boldsymbol{x}_{p+1})\rangle^{(p)} \equiv \int \mathrm{d}^3 r_p \int \mathrm{d}t_p \ldots \int \mathrm{d}^3 r_1 \int \mathrm{d}t_1 \\ \chi^{\nu_{p+1}\nu_p\ldots\nu_1}(\boldsymbol{x}_{p+1},\boldsymbol{x}_p,\ldots,\boldsymbol{x}_1)\, v_{\nu_p}(\boldsymbol{x}_p) v_{\nu_{p-1}}(\boldsymbol{x}_{p-1})\ldots v_{\nu_1}(\boldsymbol{x}_1)\,.\end{aligned} \tag{7.21}$$

It follows from (7.16) and (7.21) that

$$\chi^{\nu_{p+1}\ldots\nu_1}(\boldsymbol{x}_{p+1}\ldots\boldsymbol{x}_1) = \left(\frac{-\mathrm{i}}{\hbar}\right)^{p'} \left\langle \hat{\mathcal{T}}\,\delta n^{\nu_{p+1}}(\boldsymbol{x}_{p+1})\ldots\delta n^{\nu_1}(\boldsymbol{x}_1)\right\rangle \tag{7.22}$$

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

$$\begin{aligned}\chi^{++}(\boldsymbol{x}_1,\boldsymbol{x}_2) &= \langle\hat{\mathcal{T}}\delta n^{+}(\boldsymbol{x}_1)\delta n^{+}(\boldsymbol{x}_2)\rangle & (7.23\mathrm{a})\\ &= \theta(t_1-t_2)\langle\delta n^{+}(\boldsymbol{x}_1)\delta n^{+}(\boldsymbol{x}_2)\rangle + \theta(t_2-t_1)\langle\delta n^{+}(\boldsymbol{x}_2)\delta n^{+}(\boldsymbol{x}_1)\rangle \\ \chi^{+-}(\boldsymbol{x}_1,\boldsymbol{x}_2) &= \frac{-\mathrm{i}}{\hbar}\langle\hat{\mathcal{T}}\delta n^{+}(\boldsymbol{x}_1)\delta n^{-}(\boldsymbol{x}_2)\rangle & (7.23\mathrm{b})\\ &= \frac{-\mathrm{i}}{\hbar}\theta(t_1-t_2)\langle\delta n^{+}(\boldsymbol{x}_1)\delta n^{-}(\boldsymbol{x}_2)\rangle\,.\end{aligned}$$

The standard TDDFT equations which only yield ordinary response functions are obtained by setting $v_{\mathrm{ket}} = v_{\mathrm{bra}}$ so that $\breve{\mathcal{V}}^{+} = 0$ in (7.19). By allowing v_{ket} to be different from v_{bra} we can generate the complete set of GRF. The ordinary response function χ^{+-} represents the response of the density to an applied potential v_- [Mukamel 1995]. Similarly, χ^{++} can be formally obtained as the response to the artificial external potential, v_+, that couples to the charge density through an anticommutator. χ^{++} represents equilibrium charge fluctuations and is therefore non-retarded.

7.4 Collective Electronic Oscillator 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, $\hat{K}(\hat{\xi})$ [Chernyak 1996, Thouless 1961].

$$\delta\hat{\rho}(t) = \hat{\xi}(t) + \hat{K}(\hat{\xi}(t)) \; . \qquad (7.24)$$

Note that $\hat{\rho}(t)$ is the KS density matrix which corresponds to a noninteracting system. It follows from the idempotent property, $\hat{\rho}^2 = \hat{\rho}$, that $\hat{K}$ (and $\delta\hat{\rho}$) is uniquely determined by the interband part $\hat{\xi}$ [Ring 1980, Chernyak 1996].

$$\hat{K}(\hat{\xi}) = \frac{1}{2}(2\hat{\rho}^{\mathrm{GS}} - \hat{I})\left(\hat{I} - \sqrt{\hat{I} - 4\hat{\xi}\hat{\xi}}\right) \; . \qquad (7.25)$$

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

We next expand H_{KS} in powers of $\delta n(\boldsymbol{r}, t)$:

$$\begin{aligned}
\hat{H}_{\mathrm{KS}} &= \hat{H}^{(0)}_{\mathrm{KS}} + \hat{H}^{(1)}_{\mathrm{KS}} + \hat{H}^{(2)}_{\mathrm{KS}} + \ldots && (7.26a)\\
\hat{H}^{(0)}_{\mathrm{KS}}[\bar{n}] &= -\frac{\hbar^2}{2m}\nabla^2 + v_{\mathrm{ext}}(\boldsymbol{r}_1) + v_{\mathrm{H}}[\bar{n}](\boldsymbol{r}_1, t) + v_{\mathrm{xc}}[\bar{n}](\boldsymbol{r}_1, t) && (7.26b)\\
\hat{H}^{(1)}_{\mathrm{KS}}[\delta n] &= \int \mathrm{d}^3 r_2 \left\{ \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} + f_{\mathrm{xc}}(\boldsymbol{r}_1, \boldsymbol{r}_2) \right\} \delta n(\boldsymbol{r}_2, t) \; , && (7.26c)
\end{aligned}$$

with f_{xc} the first order exchange correlation kernel in the adiabatic approximation where it is assumed to be frequency independent (see Chap. 1)

$$f_{\mathrm{xc}}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \left. \frac{\delta v_{\mathrm{xc}}[n](\boldsymbol{r}_1)}{\delta n(\boldsymbol{r}_2)} \right|_{\bar{n}} \; . \qquad (7.27$$

The second order term in density fluctuations is,

$$\hat{H}^{(2)}_{\mathrm{KS}}[\delta n] = \int \mathrm{d}^3 r_2 \int \mathrm{d}^3 r_3 \, g_{\mathrm{xc}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) \delta n(\boldsymbol{r}_2, t) \delta n(\boldsymbol{r}_3, t) \; , \qquad (7.28$$

with the kernel (in the adiabatic approximation),

$$g_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) = \left. \frac{\delta^2 v_{\mathrm{xc}}[n](\boldsymbol{r}_1)}{\delta n(\boldsymbol{r}_2) \delta n(\boldsymbol{r}_3)} \right|_{\bar{n}} \; . \qquad (7.29$$

A quasiparticle algebra can be developed for $\hat{\xi}$ by expanding it in th basis set of *collective electronic oscillator* (CEO) modes, $\hat{\xi}_\alpha$, which are th eigenvectors of the linearized TDDFT eigenvalue equation with eigenvalue Ω_α [Chernyak 1996, Tretiak 2002].

$$\check{L}\hat{\xi}_\alpha = \Omega_\alpha \hat{\xi}_\alpha \; , \qquad (7.30$$

The linearized Liouville space operator, $\check{L}$ is obtained by substituting (7.26) into (7.16),

$$\check{L}\hat{\xi}_\alpha = [\hat{H}^{(0)}_{\mathrm{KS}}[\bar{n}], \hat{\xi}_\alpha] + [\hat{H}^{(1)}_{\mathrm{KS}}[\xi_\alpha], \hat{\rho}^{\mathrm{GS}}] \,. \tag{7.31}$$

$\hat{H}^{(0)}_{\mathrm{KS}}$ and $\hat{H}^{(1)}_{\mathrm{KS}}$ are diagonal matrices with matrix elements

$$H^{(0)}_{\mathrm{KS}}[\bar{n}](\boldsymbol{r}_1, \boldsymbol{r}_2) \;= \delta(\boldsymbol{r}_1 - \boldsymbol{r}_2) H^{(0)}_{\mathrm{KS}}[\bar{n}](\boldsymbol{r}_1) \tag{7.32a}$$

$$\begin{aligned} H^{(1)}_{\mathrm{KS}}[\xi_\alpha](\boldsymbol{r}_1, \boldsymbol{r}_2) &= \delta(\boldsymbol{r}_1 - \boldsymbol{r}_2) \\ &\times \int \mathrm{d}^3 r_3 \left\{ \frac{e^2}{|\boldsymbol{r}_2 - \boldsymbol{r}_3|} + f_{\mathrm{xc}}(\boldsymbol{r}_2, \boldsymbol{r}_3) \right\} \xi_\alpha(\boldsymbol{r}_3, \boldsymbol{r}_3) \end{aligned} \tag{7.32b}$$

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 $\hat{\xi}_{-\alpha} = \hat{\xi}^\dagger_\alpha$. Each pair of modes represents a 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 (7.25) and (7.24), we obtain the following expansion for the density matrix

$$\delta\rho(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = \sum_\alpha \mu_\alpha(\boldsymbol{r}_1, \boldsymbol{r}_2)\bar{z}_\alpha(t) + \frac{1}{2}\sum_{\alpha,\beta} \mu_{\alpha,\beta}(\boldsymbol{r}_1, \boldsymbol{r}_2)\bar{z}_\alpha(t)\bar{z}_\beta(t) + \ldots \tag{7.33}$$

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

Upon the substitution of (7.24) and (7.25) into (7.16) 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, v_{ν_1}. To second order we get

$$\mathrm{i}\hbar\frac{\mathrm{d}\bar{z}_\alpha(t)}{\mathrm{d}t} = \Omega_\alpha \bar{z}_\alpha(t) + K_{-\alpha}(t) + \sum_\beta K_{-\alpha\beta}(t)\bar{z}_\beta(t) \,, \tag{7.34}$$

with the coefficients,

$$K_{-\alpha}(t) \;= \sum_\nu \int \mathrm{d}^3 r_1 \, v_\nu(\boldsymbol{r}_1, t)\mu^\nu_{-\alpha}(\boldsymbol{r}_1) \tag{7.35a}$$

$$K_{-\alpha\beta}(t) = \sum_\nu \int \mathrm{d}^3 r_1 \, v_\nu(\boldsymbol{r}_1, t)\mu^\nu_{-\alpha\beta}(\boldsymbol{r}_1) \,. \tag{7.35b}$$

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

We further expand $\bar{z}_\alpha = z^{\nu_1}_\alpha + z^{\nu_1\nu_2}_\alpha + \ldots$, in powers of the external potentials, where $z^{\nu_1\nu_2\ldots\nu_p}$ denotes the n^{th} order term in the potentials, $v_{\nu_1}v_{\nu_2}\ldots v_{\nu_p}$. By comparing the terms in both sides, we obtain equations of motion for $z_\alpha^{\nu_1 \dots \nu_p}$ for each order in the external potential. This gives to first order,

$$
\mathrm{i}\hbar \frac{\mathrm{d}z_\alpha^{\nu_1}(t)}{\mathrm{d}t} = \Omega_\alpha z_\alpha^{\nu_1}(t) + K_{-\alpha}(t) \,. \tag{7.36}
$$

The solution of (7.36) gives the generalized linear response functions

$$
\begin{aligned}
\chi^{++}(\boldsymbol{r}_1 t_1, \boldsymbol{r}_2 t_2) &= \theta(t_1 - t_2) \sum_\alpha \mu_\alpha(\boldsymbol{r}_1) \bar{\mu}_{-\alpha}(\boldsymbol{r}_2) \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\Omega_\alpha (t_1 - t_2)} \\
&\quad + \theta(t_2 - t_1) \sum_\alpha \mu_\alpha(\boldsymbol{r}_2) \bar{\mu}_{-\alpha}(\boldsymbol{r}_1) \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\Omega_\alpha (t_1 - t_2)} && \text{(7.37a)} \\
\chi^{+-}(\boldsymbol{r}_1 t_1, \boldsymbol{r}_2 t_2) &= -\frac{\mathrm{i}}{\hbar} \theta(t_1 - t_2) \sum_\alpha s_\alpha \mu_\alpha(\boldsymbol{r}_1) \mu_{-\alpha}(\boldsymbol{r}_2) \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\Omega_\alpha (t_1 - t_2)} \,, && \text{(7.37b)}
\end{aligned}
$$

with $s_\alpha = \mathrm{sign}(\alpha)$. Higher order GRF can be obtained by repeating this procedure [Harbola 2004].

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

$$
\begin{aligned}
\langle \delta n^+(\boldsymbol{r}_{p+1}, \omega_{p+1}) \rangle^{(p)} &= \int \mathrm{d}^3 r_p \int_{-\infty}^{\infty} \mathrm{d}\omega_p \dots \int \mathrm{d}^3 r_1 \int_{-\infty}^{\infty} \mathrm{d}\omega_1 \\
&\quad v_{\nu_p}(\boldsymbol{r}_p, \omega_p) \dots v_{\nu_1}(\boldsymbol{r}_1, \omega_1) \chi^{\nu_{p+1} \dots \nu_1}(\boldsymbol{r}_{p+1}\omega_{p+1}, \boldsymbol{r}_p \omega_p, \dots, \boldsymbol{r}_1 \omega_1) \,, && \text{(7.38)}
\end{aligned}
$$

where the frequency transform is defined as

$$
\chi^{\nu_1 \nu_2}(\boldsymbol{r}_1 \omega_1, \boldsymbol{r}_2 \omega_2) = \int_{-\infty}^{\infty} \mathrm{d}t_1 \int_{-\infty}^{\infty} \mathrm{d}t_2 \, \mathrm{e}^{\mathrm{i}(\omega_1 t_1 + \omega_2 t_2)} \chi^{\nu_1 \nu_2}(\boldsymbol{x}_1, \boldsymbol{x}_2) \,. \tag{7.39}
$$

Equation (7.39) together with (7.37) gives

$$
\chi^{++}(\boldsymbol{r}_1 \omega_1, \boldsymbol{r}_2 \omega_2) = \mathrm{i}\hbar \delta(\omega_1 + \omega_2) \sum_\alpha \left[\frac{\mu_\alpha(\boldsymbol{r}_1) \bar{\mu}_{-\alpha}(\boldsymbol{r}_2)}{\omega_2 - \Omega_\alpha + \mathrm{i}\eta} - \frac{\mu_\alpha(\boldsymbol{r}_2) \bar{\mu}_{-\alpha}(\boldsymbol{r}_1)}{\omega_2 + \Omega_\alpha - \mathrm{i}\eta} \right] \tag{7.40a}
$$

$$
\chi^{+-}(\boldsymbol{r}_1 \omega_1, \boldsymbol{r}_2 \omega_2) = \delta(\omega_1 + \omega_2) \sum_\alpha \frac{s_\alpha \mu_\alpha(\boldsymbol{r}_1) \mu_{-\alpha}(\boldsymbol{r}_2)}{\omega_2 + \Omega_\alpha - \mathrm{i}\eta} \,. \tag{7.40b}
$$

The CEO representations of the ordinary response functions to third order were given in [Tretiak 2002] and the GRF to second order were given in [Harbola 2004].

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

$$
\chi^{++}(\boldsymbol{r}_1 \omega; \boldsymbol{r}_2 - \omega) = \coth\left(\frac{\beta\hbar\omega}{2}\right) \chi^{+-}(\boldsymbol{r}_1 \omega, \boldsymbol{r}_2 - \omega) \,. \tag{7.41}
$$

To linear order, the ordinary response function χ^{+-} provides the complete information. However such fluctuation-dissipation relations are not that obvious for the higher order response functions [Wang 2002] and the complete set of GRF are required to describe all possible fluctuations and response functions of the charge density.

7.5 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. Wavefunction based theories for intermolecular forces (polarization theory, symmetry-adapted perturbation theory and many-body symmetry-adapted theory) are well developed [Jeziorski 1994]. The response function based formulation presented here can be applied to study non-equilibrium effects (e.g., when the two sub-systems are at different temperaturs) as well as coupling to nuclear degrees of freedom [Cohen 2003]. At time $t = -\infty$ we take the density matrix to be a direct-product of the density matrices of the individual molecules (sub-systems), $\hat{\rho}_0^a$ and $\hat{\rho}_0^b$, $\hat{\rho}_0^{\mathrm{GS}} = \hat{\rho}_0^a \hat{\rho}_0^b$. 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 $\hat{H}_\lambda = \hat{H}_a + \hat{H}_b + \lambda \hat{H}_{ab}$, where H_a and H_b represent the Hamiltonians for the individual molecules and their coupling $\hat{H}_{ab}$ is multiplied by the control parameter λ, $0 \leq \lambda \leq 1$, where $\lambda = 1$ corresponds to the physical Hamiltonian. Primed and unprimed indices will 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. $\hat{H}_{ab}$ is the Coulomb interaction

$$\hat{H}_{ab} = -\int \mathrm{d}^3 r \int \mathrm{d}^3 r' \, v_{\mathrm{ee}}(\boldsymbol{r} - \boldsymbol{r}') n_a(\boldsymbol{r}) n_b(\boldsymbol{r}') - \sum_{k,k'} v_{\mathrm{ee}}(\boldsymbol{R}_k - \boldsymbol{R}_{k'}) Z_k Z_{k'} + \sum_{P,k} \int \mathrm{d}^3 r' \, v_{\mathrm{ee}}(\boldsymbol{R}_k - \boldsymbol{r}') Z_k n_b(\boldsymbol{r}') \,, \tag{7.42}$$

where $v_{\mathrm{ee}}(\boldsymbol{r} - \boldsymbol{r}') \equiv 1/|\boldsymbol{r} - \boldsymbol{r}'|$ and $\boldsymbol{R}_k$ ($\boldsymbol{R}_{k'}$) represents the position of kth (k'th) nucleus in molecule a (b) with charge Z_k ($Z_{k'}$). The symbol $\sum_P$ 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 [Kohn 1998]

$$E_{ab} = \int_0^1 \mathrm{d}\lambda \, \langle \hat{H}_{ab} \rangle_\lambda \,. \tag{7.43}$$

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, $E_{ab} = E_{ab}^{(0)} + E_{ab}^{(I)} + E_{ab}^{(II)}$, where

$$E_{ab}^{(0)} = -\int \mathrm{d}^3r \int \mathrm{d}^3r'\, v_{\mathrm{ee}}(\boldsymbol{r}-\boldsymbol{r}')\bar{n}_a(\boldsymbol{r})\bar{n}_b(\boldsymbol{r}') - \sum_{k,k'} v_{\mathrm{ee}}(\boldsymbol{R}_k - \boldsymbol{R}_{k'}) Z_k Z_{k'} + \sum_{P,k} \int \mathrm{d}^3r'\, v_{\mathrm{ee}}(\boldsymbol{R}_k - \boldsymbol{r}') Z_k \bar{n}_b(\boldsymbol{r}') \,, \tag{7.44}$$

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

$$E_{ab}^{(I)} = -\int_0^1 \mathrm{d}\lambda \int \mathrm{d}^3r \int \mathrm{d}^3r'\, v_{\mathrm{ee}}(\boldsymbol{r}-\boldsymbol{r}')\left[\bar{n}_a(\boldsymbol{r})\langle\delta\hat{n}_b(\boldsymbol{r}')\rangle_\lambda + \bar{n}_b(\boldsymbol{r}')\langle\delta\hat{n}_a(\boldsymbol{r})\rangle_\lambda\right] + \sum_{P,k}\int \mathrm{d}^3r'\, v_{\mathrm{ee}}(\boldsymbol{R}_k - \boldsymbol{r}') Z_k(\boldsymbol{R}_k)\langle\delta\hat{n}_b(\boldsymbol{r}')\rangle_\lambda \tag{7.45a}$$

$$E_{ab}^{(II)} = -\int_0^1 \mathrm{d}\lambda \int \mathrm{d}^3r \int \mathrm{d}^3r'\, v_{\mathrm{ee}}(\boldsymbol{r}-\boldsymbol{r}')\langle\delta\hat{n}_a(\boldsymbol{r})\delta\hat{n}_b(\boldsymbol{r}')\rangle_\lambda \,. \tag{7.45b}$$

The expectation values $\langle\delta\hat{n}_a(\boldsymbol{r}_1)\rangle_\lambda$ and $\langle\delta\hat{n}_a(\boldsymbol{r}_1)\delta\hat{n}_b(\boldsymbol{r}'_2)\rangle_\lambda$ can be computed perturbatively in $\lambda\hat{H}_{ab}$ in the interaction picture. The interaction $\lambda\hat{H}_{ab}$ is switched on adiabatically to generate the interacting ground state density matrix in terms of the non-interacting one. Substituting for $\hat{H}_{ab}$ from (7.42), and expanding in powers of λ yields a perturbation series in terms of the p^{th} order joint response function, using $\boldsymbol{x}'_n = (\boldsymbol{r}'_n, t_n)$,

$$R_a^{(p)}(\boldsymbol{x}, \boldsymbol{x}_p, \boldsymbol{x}'_p \dots \boldsymbol{x}_1, \boldsymbol{x}'_1) = \langle \hat{T}\delta\hat{n}_a^{I\,+}(\boldsymbol{x})[\hat{n}_a^I(\boldsymbol{x}_p)\hat{n}_b^I(\boldsymbol{x}'_p)]^- \dots [\hat{n}_a^I(\boldsymbol{x}_1)\hat{n}_b^I(\boldsymbol{x}'_1)]^-\rangle_0 \,. \tag{7.46}$$

Making use of (7.2) 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:

$$\begin{aligned} R_a^{(1)}(\boldsymbol{x}, \boldsymbol{x}_1, \boldsymbol{x}'_1) &= \left\langle \hat{T}\delta\hat{n}_a^{I\,+}(\boldsymbol{x})[\hat{n}_a^I(\boldsymbol{x}_1)\hat{n}_b^I(\boldsymbol{x}'_1)]^- \right\rangle_0 \\ &= \mathrm{Tr}\left\{\hat{T}\delta\hat{n}_a^{I\,+}(\boldsymbol{x})[\hat{n}_a^I(\boldsymbol{x}_1)\hat{n}_b^I(\boldsymbol{x}'_1)]^- \hat{\rho}_a^0\hat{\rho}_b^0\right\} \,. \end{aligned} \tag{7.47}$$

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

$$R_a^{(1)}(\boldsymbol{x}, \boldsymbol{x}_1, \boldsymbol{x}'_1) = \mathrm{i}\bar{n}_b(\boldsymbol{r}'_1)\chi_a^{+-}(\boldsymbol{x}, \boldsymbol{x}_1) \,, \tag{7.48}$$

where χ_a^{+-} represents the linear order GRF for molecule a [see (7.22)]. 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 interactions with nuclei in (7.42). The quantities $\langle\delta\hat{n}_a(\boldsymbol{r}_1)\rangle_\lambda$ and $\langle\delta\hat{n}_a(\boldsymbol{r}_1)\delta\hat{n}_b(\boldsymbol{r}'_1)\rangle_\lambda$

and consequently the interaction energies $E_{ab}^{(I)}$ and $E_{ab}^{(II)}$ can be expanded perturbatively in terms of the GRFs of the individual molecules [Harbola 2004]. We shall collect terms in $E_{ab}^{(I)}$ and $E_{ab}^{(II)}$ by their order with respect to charge fluctuations. The total energy is then, $E_{ab} = \sum_j E_{ab}^{(j)}$, where $E_{ab}^{(j)}$ represents contribution from jth order charge fluctuation. $W^{(0)}$ was given in (7.44) and $E_{ab}^{(1)} = 0$. $E_{ab}^{(j)}$ to sixth order are given in [Harbola 2004].

$$E_{ab}^{(2)} = -\frac{1}{2}\sum_P \int_{-\infty}^{t_1} \mathrm{d}t_2 \int \mathrm{d}^3\underline{r}_1 \int \mathrm{d}^3\underline{r}_2\, \bar{n}_b(\boldsymbol{r}'_1)\bar{n}_b(\boldsymbol{r}'_2)\chi_a^{+-}(\boldsymbol{x}_1,\boldsymbol{x}_2)v_{\mathrm{ee}}(\boldsymbol{s}_1)v_{\mathrm{ee}}(\boldsymbol{s}_2) \tag{7.49a}$$

$$\begin{aligned} E_{ab}^{(3)} &= \frac{1}{6}\sum_P \int_{-\infty}^{t_1} \mathrm{d}t_2 \int_{-\infty}^{t_1} \mathrm{d}t_3 \int \mathrm{d}^3\underline{r}_1 \int \mathrm{d}^3\underline{r}_2 \int \mathrm{d}^3\underline{r}_3\, v_{\mathrm{ee}}(\boldsymbol{s}_1)v_{\mathrm{ee}}(\boldsymbol{s}_2)v_{\mathrm{ee}}(\boldsymbol{s}_3) \\ &\quad \times \bar{n}_b(\boldsymbol{r}'_1)\chi_a^{+--}(\boldsymbol{x}_1,\boldsymbol{x}_2,\boldsymbol{x}_3)\bar{n}_b(\boldsymbol{r}'_2)\bar{n}_b(\boldsymbol{r}'_{)}3 \end{aligned} \tag{7.49b}$$

$$\begin{aligned} E_{ab}^{(4)} &= \frac{1}{6}\sum_P \int_{-\infty}^{t_1} \mathrm{d}t_2 \int_{-\infty}^{t_1} \mathrm{d}t_3 \int \mathrm{d}^3\underline{r}_1 \int \mathrm{d}^3\underline{r}_2 \int \mathrm{d}^3\underline{r}_3\, v_{\mathrm{ee}}(\boldsymbol{s}_1)v_{\mathrm{ee}}(\boldsymbol{s}_2)v_{\mathrm{ee}}(\boldsymbol{s}_3) \\ &\quad \times \left[\bar{n}_a(\boldsymbol{r}_2)\bar{n}_b(\boldsymbol{r}'_3)\chi_a^{+-}(\boldsymbol{x}_1,\boldsymbol{x}_3)\chi_b^{+-}(\boldsymbol{x}'_1,\boldsymbol{x}'_2)\right. \\ &\quad \left. + \bar{n}_b(\boldsymbol{r}'_1)\bar{n}_a(\boldsymbol{r}_3)\chi_a^{+-}(\boldsymbol{x}_1,\boldsymbol{x}_2)\chi_b^{+-}(\boldsymbol{x}'_2,\boldsymbol{x}'_3)\right] \\ &\quad - \frac{1}{2}\sum_P \int_{-\infty}^{t_1} \mathrm{d}t_2 \int \mathrm{d}^3\underline{r}_1 \int \mathrm{d}^3\underline{r}_2\, v_{\mathrm{ee}}(\boldsymbol{s}_1)v_{\mathrm{ee}}(\boldsymbol{s}_2)\chi_a^{++}(\boldsymbol{x}_1,\boldsymbol{x}_2)\chi_b^{+-}(\boldsymbol{x}'_1,\boldsymbol{x}'_2) \end{aligned} \tag{7.49c}$$

$$\begin{aligned} E_{ab}^{(5)} &= \frac{1}{6}\sum_P \int_{-\infty}^{t_1} \mathrm{d}t_2 \int_{-\infty}^{t_1} \mathrm{d}t_3 \int \mathrm{d}^3\underline{r}_1 \int \mathrm{d}^3\underline{r}_2 \int \mathrm{d}^3\underline{r}_3\, v_{\mathrm{ee}}(\boldsymbol{s}_1)v_{\mathrm{ee}}(\boldsymbol{s}_2)v_{\mathrm{ee}}(\boldsymbol{s}_3) \\ &\quad \times \Big\{\chi_b^{+--}(\boldsymbol{x}'_1,\boldsymbol{x}'_2,\boldsymbol{x}'_3)\left[\bar{n}_a(\boldsymbol{r}_1)\chi_a^{++}(\boldsymbol{x}_2,\boldsymbol{x}_3) + \bar{n}_a(\boldsymbol{r}_2)\chi_a^{++}(\boldsymbol{x}_1,\boldsymbol{x}_3)\right. \\ &\qquad \left. + \bar{n}_a(\boldsymbol{r}_3)\chi_a^{++}(\boldsymbol{x}_1,\boldsymbol{x}_2) + \bar{n}_a(\boldsymbol{r}_1)\chi_a^{+-}(\boldsymbol{x}_1,\boldsymbol{x}_3)\right] \\ &\quad + \chi_b^{++-}(\boldsymbol{x}'_1,\boldsymbol{x}'_2,\boldsymbol{x}'_3)[\bar{n}_a(\boldsymbol{r}_2)\chi_a^{+-}(\boldsymbol{x}_1,\boldsymbol{x}_3) + \bar{n}_b(\boldsymbol{r}'_3)\chi_b^{+-}(\boldsymbol{x}'_1,\boldsymbol{x}'_2)]\Big\} \end{aligned} \tag{7.49d}$$

$$\begin{aligned} E_{ab}^{(6)} &= \frac{1}{6}\sum_P \int_{-\infty}^{t_1} \mathrm{d}t_2 \int_{-\infty}^{t_1} \mathrm{d}t_3 \int \mathrm{d}^3\underline{r}_1 \int \mathrm{d}^3\underline{r}_2 \int \mathrm{d}^3\underline{r}_3\, v_{\mathrm{ee}}(\boldsymbol{s}_1)v_{\mathrm{ee}}(\boldsymbol{s}_2)v_{\mathrm{ee}}(\boldsymbol{s}_3) \\ &\quad \times \Big[\,\chi_a^{+++}(\boldsymbol{x}_1,\boldsymbol{x}_2,\boldsymbol{x}_3)\chi_b^{+--}(\boldsymbol{x}'_1,\boldsymbol{x}'_2,\boldsymbol{x}'_3) \\ &\quad + \chi_a^{++-}(\boldsymbol{x}_1,\boldsymbol{x}_2,\boldsymbol{x}_3)\chi_b^{++-}(\boldsymbol{x}'_1,\boldsymbol{x}'_2,\boldsymbol{x}'_3)\Big]\ , \end{aligned} \tag{7.49e}$$

where for brevity we have used the notations, $\int \mathrm{d}^3\underline{r}_n = \int \mathrm{d}^3 r_n \int \mathrm{d}^3 r'_n$ and $v_{\mathrm{ee}}(\boldsymbol{s}_n) = v_{\mathrm{ee}}(\boldsymbol{r}_n - \boldsymbol{r}'_n)$.

We have now at hand all the ingredients necessary for computing the intermolecular energies using the GRF of the individual molecules calculated at the TDDFT level.

The second term in (7.49c) reproduces McLachlan's expression for the van der Waals intermolecular energy [Misquitta 2003, McLachlan 1963a, McLachlan 1963b]. 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^{+-}.

$$E_{\mathrm{vdW}}^{(4)} = -\frac{1}{2\hbar}\int_{-\infty}^{\infty}\mathrm{d}\omega \int \mathrm{d}^3\underline{r}_1 \int \mathrm{d}^3\underline{r}_2\, v_{\mathrm{ee}}(\boldsymbol{s}_1) v_{\mathrm{ee}}(\boldsymbol{s}_2) \coth\left(\frac{\beta\hbar\omega}{2}\right) \alpha_a^{+-}(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega)\alpha_b^{+-}(\boldsymbol{r}_1',\boldsymbol{r}_2',\omega)\,, \quad (7.50)$$

where $\chi^{\nu_2\nu_1}(\boldsymbol{r}_2\omega_2,\boldsymbol{r}_1\omega_1) = (\hbar^{-1})^{p'}\alpha_a^{\nu_2\nu_1}(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega_1)\delta(\omega_1+\omega_2)$. Equation (7.50) gives

$$E_{\mathrm{vdW}}^{(4)} = -k_{\mathrm{B}}T\sum_{n=0}^{\infty}\int \mathrm{d}^3 \int \mathrm{d}^3\underline{r}_1\, \underline{r}_2 v_{\mathrm{ee}}(\boldsymbol{s}_1)v_{\mathrm{ee}}(\boldsymbol{s}_2)\alpha_a^{+-}(\boldsymbol{r}_1,\boldsymbol{r}_2,\mathrm{i}\omega_n)\alpha_b^{+-}(\boldsymbol{r}_1',\boldsymbol{r}_2',\mathrm{i}\omega_n)\,, \quad (7.51)$$

where $\omega_n = (2\pi n k_{\mathrm{B}}T/\hbar)$ are the Matsubara frequencies. However, life is not as simple for the higher order responses. The $(p+1)$, p^{th} order generalized response functions, $\chi^{\nu_{p+1}\nu_p\cdots\nu_1}$, 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 (7.49a)–(7.49e) 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 (7.37) in (7.49c), the fourth order term is obtained in terms of CEO modes as

$$\begin{aligned} E_{ab}^{(4)} = &-\frac{1}{2\hbar}\sum_P \int \mathrm{d}^3\underline{r}_1 \int \mathrm{d}^3\underline{r}_2 \frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_1'||\boldsymbol{r}_2-\boldsymbol{r}_2'|} \\ &\times \sum_{\alpha\alpha'} \frac{s_{\alpha'}\bar{\mu}_{-\alpha}(\boldsymbol{r}_1)\mu_\alpha(\boldsymbol{r}_2)\mu_{-\alpha'}(\boldsymbol{r}_1')\mu_{\alpha'}(\boldsymbol{r}_2')}{(\Omega_\alpha+\Omega_{\alpha'})} \\ &-\frac{1}{6\hbar^2}\sum_P \int \mathrm{d}\underline{r}_1 \int \mathrm{d}\underline{r}_2 \int \mathrm{d}^3\underline{r}_3 \frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_1'||\boldsymbol{r}_2-\boldsymbol{r}_2'||\boldsymbol{r}_3-\boldsymbol{r}_3'|}\bar{n}_b(\boldsymbol{r}_3') \\ &\times \sum_{\alpha\alpha'} \frac{s_\alpha s_{\alpha'}\mu_\alpha(\boldsymbol{r}_3)\mu_{\alpha'}(\boldsymbol{r}_1')\mu_{-\alpha'}(\boldsymbol{r}_2')}{\Omega_\alpha\Omega_{\alpha'}}\left[\bar{n}_a(\boldsymbol{r}_1)\mu_\alpha(\boldsymbol{r}_2)+\bar{n}_a(\boldsymbol{r}_2)\mu_\alpha(\boldsymbol{r}_1)\right]\,. \end{aligned} \quad (7.52)$$

Expansions of higher order terms in CEO modes are given in [Harbola 2004]. 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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