Does the exchange-correlation kernel f_{xc} have a very long-ranged dependence on the groundstate electron density?

John F. Dobson · János G. Ángyán ·
Tim Gould

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Abstract We consider the dispersion energy between two well-separated molecules. Provided that exchange overlap effects can be neglected, the Generalized Casimir Polder (GCP) formula gives the dispersion energy exactly to second order in the inter-system Coulomb pair potential, in terms of the density response functions of the isolated molecules. One can alternatively calculate the dispersion interaction from the density response in a supramolecular (dimer) energy TDDFT/ACFD calculation. This uses the density response from Time Dependent Density Functional Theory (TDDFT) and the Adiabatic Connection (ACFD) groundstate electronic energy formula, and treats the two systems together. Some of us recently [JCTC 13, 5829 (2017)] showed that the supramolecular TDDFT/ACFD approach can fail to reproduce the exact GCP result, when the exchange-correlation kernel f_{xc} in the TDDFT calculation is assumed to be local. Here we examine ways in which a nonlocal density dependence of f_{xc} might be able to remove this discrepancy.

Keywords ACFD · TDDFT · RPA · Size consistency

John F. Dobson
Qld Micro- and Nanotechnology Centre,
Griffith University,
Nathan, Qld 4111, Australia E-mail: john12dobson@gmail.com

János G. Ángyán (deceased)
Laboratoire de Cristallographie, Résonance Magnétique et Modélisations (CRM2, UMR
CNRS 7036),
Institut Jean Barriol, Université de Lorraine,
F-54506 Vandœuvre-lès-Nancy, France

Tim Gould
Qld Micro- and Nanotechnology Centre,
Griffith University,
Southport, Qld 4215, Australia

1 Introduction

Time-Dependent Density Functional Theory (TDDFT) is an important electronic structure tool in the analysis of the response of chemical and solid state systems to external stimuli. A major class of problems involves linear response: for example one can obtain many properties from the electron density response χ , which relates the change $\delta n(\mathbf{r}, t)$ in electron number density to the time-dependent external potential $\delta v^{\text{ext}}(\mathbf{r}, t)$ via the relation

$$\delta n(\mathbf{r}, t) = \int_{-\infty}^t \chi(\mathbf{r}, \mathbf{r}', t - t') \delta v^{\text{ext}}(\mathbf{r}', t') d\mathbf{r}' dt'.$$

The response contains information of relevance to spectroscopy, and also, as shall be the focus in this manuscript, long-range (van der Waals dispersion) forces between quantum species.

TDDFT gives an in-principle way to calculate the density response χ exactly:

$$\chi = \chi_0 + \chi_0 * (v + f_{\text{xc}}) * \chi. \quad (1)$$

(the precise meaning of the $*$ will be introduced later, but for now we need only understand that it acts like a matrix or operator multiplication) The Dyson-like “screening” equation (1) relates the exact electron density response $\chi(\mathbf{r}, \mathbf{r}', \omega)$ (including all electron-electron Coulomb interactions) to the bare or Kohn-Sham response χ_0 , which is the response of independent but Pauli-compliant electrons moving in the one-electron groundstate Kohn-Sham potential $V_s(\mathbf{r})$.

a) Direct electron-electron effects

b) Indirect functional effects

Fig. 1 Illustration of the effects discussed in this manuscript. **a)** shows the direct Coulomb interactions between species A and B. **b)** shows an example secondary effect of non-local density functional contributions from n_B , that can modify either (or both) the effective (screened) field or the density in A. The latter case is illustrated.

In (1) the bare electron-electron Coulomb interaction $v(\mathbf{r}, \mathbf{r}') = e^2/|\mathbf{r} - \mathbf{r}'|$ is supplemented by the exchange-correlation potential (kernel) $f_{\text{xc}}[n](\mathbf{r}, \mathbf{r}', \omega)$,

which depends on two space variables $\mathbf{r}, \mathbf{r}'$ and also has a functional dependence on the groundstate electron density $n(\mathbf{r}'')$ at all space points $\mathbf{r}''$. The kernel f_{xc} is not known exactly and must be approximated since it embodies a solution of the interacting many-body problem, but TDDFT shows that such a kernel exists and gives χ exactly via (1) [1]. Some examples of simple approximate xc kernels are given later. Most existing approximations are short-ranged (local or semi-local) in their dependence on the two space points $\mathbf{r}, \mathbf{r}'$. Furthermore, given the values of $\mathbf{r}$ and $\mathbf{r}'$, most functionals are also local or semilocal in their dependence on the groundstate density. That is $f_{xc}[n](\mathbf{r}, \mathbf{r}', \omega)$ only samples values of $n(\mathbf{r}'')$ for $\mathbf{r}''$ near to $\mathbf{r}$ and/or $\mathbf{r}'$. These two ideas of non-locality are illustrated in Figure 1.

Here we argue that to resolve the previously identified [2] Casimir Polder size consistency issue, one may need to consider functionals that are very long-ranged in their dependence on $n(\mathbf{r}'')$. We arrived at this conclusion in the course of our work on dispersion forces, so we next establish that scenario.

2 The GCP formula: dispersion interaction between two non-overlapping species

The Generalized Casimir Polder (GCP) formula [3,4] describes the dispersion interaction between two species (molecules, atoms, solids) A and B . It is usually approached from a zeroth-order situation where each electron can be considered to belong to one species, either A or B , and distinguishability of A and B electrons is assumed. The Coulomb interaction between A and B is then treated as a perturbation. This causes some conceptual problems given that there is inevitably some overlap between the electron clouds, so that electron indistinguishability and the Pauli principle must be considered. It is usually assumed, however, that such overlap effects decay exponentially with spatial separation R between the species A and B and so constitute a small effect. We will subscribe to this viewpoint here. The Symmetry Adapted Perturbation Theory (SAPT) [5,6] is one way to deal with this, but is not used in the Generalized Casimir Polder approach.

To derive the GCP formula we assume a knowledge of the exact many-electron eigenstates $|\Psi_{AI}\rangle, |\Psi_{BJ}\rangle$ and energies E_{AI}, E_{BJ} of each species A, B , in the complete absence of the other species. The inter-species Coulomb potential v_{AB} is then treated via quantum perturbation theory, giving the following inter-species interaction energy in the joint groundstate:

$$E_{AB}^{(2)} = - \sum_{IJ} \frac{\langle \Psi_{AI} \Psi_{BJ} | \hat{v}_{AB} | \Psi_{A0} \Psi_{B0} \rangle \langle \Psi_{A0} \Psi_{B0} | \hat{v}_{BA} | \Psi_{AI} \Psi_{BJ} \rangle}{E_{AI} - E_{A0} + E_{BJ} - E_{B0}} \quad (2)$$

Here $|\Psi_{A0}\rangle, |\Psi_{B0}\rangle$ are the groundstates of the isolated species. Under the non-overlap assumptions described above, (2) is exact to $O(v_{AB}^2)$.

Using the identity

$$\frac{1}{a+b} = \frac{2}{\pi} \int_0^\infty \frac{ab}{(a^2+u^2)(b^2+u^2)} du$$

lets us further write (2) as

$$E^{(2)} = -\hbar \int d\mathbf{r}_A d\mathbf{r}'_A d\mathbf{r}_B d\mathbf{r}'_B v_{AB}(\mathbf{R} + \mathbf{r}_A - \mathbf{r}_B) v_{AB}(\mathbf{R} + \mathbf{r}'_A - \mathbf{r}'_B) \times \\ \times \int_0^\infty \frac{du}{2\pi} \chi_A(\mathbf{r}_A, \mathbf{r}'_A, \omega = iu) \chi_B(\mathbf{r}_B, \mathbf{r}'_B, \omega = iu). \quad (3)$$

Here, $\mathbf{R}$ is a vector describing the displacement between systems A and B , $\mathbf{r}_{A/B}$ and $\mathbf{r}'_{A/B}$ are vectors within system A/B , and

$$\chi_A(\mathbf{r}_A, \mathbf{r}'_A, \omega = iu) = \\ = -2 \sum_K \frac{(E_{AK} - E_{A0}) \langle \Psi_{A0} | \delta \hat{n}(\mathbf{r}_A) | \Psi_{AK} \rangle \langle \Psi_{AK} | \delta \hat{n}(\mathbf{r}'_A) | \Psi_{A0} \rangle}{(E_{AK} - E_{A0})^2 + \hbar u^2} \quad (4)$$

is the linear density-density response of system A in its groundstate in isolation, evaluated at imaginary frequency $\omega = iu$, and $\delta \hat{n}$ is the electron number density operator minus the average number of electrons.

The GCP formula (3) is, in fact, non-divergent in R even if the two systems A and B overlap, but is only expected to be accurate for well-separated systems. In the limit of large separation $R = |\mathbf{R}|$ one can make a dipolar expansion of the Coulomb interaction v_{AB} in (3), from which one obtains to leading order

$$U^{(2)} = -\frac{C_6}{R^6}, \quad C_6 = \frac{\hbar}{2\pi} \int \sum_{\beta\gamma} \alpha_{A,\beta\gamma}(iu) \alpha_{B,\gamma\beta}(iu) du \quad (5)$$

where (for $\beta, \gamma \in \{x, y, z\}$)

$$\alpha_{A,\alpha\beta} = \int r_\beta r'_\gamma \chi(\mathbf{r}, \mathbf{r}', iu) d\mathbf{r} d\mathbf{r}' \quad (6)$$

is the dipolar polarizability tensor of system A in isolation. Higher coefficients in the dispersion energy series, falling off as higher powers of R , can be obtained by making higher multipole approximations to v_{AB} . Thus, any approximation for the isolated density responses χ_A , χ_B allows one to predict dispersion energies.

2.1 Time-Dependent Density Functional Theory and the GCP

High-level first-principle approaches have been used to predict the polarizabilities α for use in (6) and (5). Among these, TDDFT plays an important role.

The simplest TDDFT approximation is to set $f_{xc} = 0$, and then χ from (1) is termed the (direct) Random Phase Approximation (dRPA) response, here denoted χ^{dRPA} . This approximation can be very useful, but since the neglected f_{xc} tends to be negative, the dRPA tends to “over-screen” the electron-electron

interaction, making χ too small. As a consequence, the dRPA dispersion coefficient C_6^{dRPA} from (5) and (6) tends to be too small by $O(10\%)$.

Another simple approximation for f_{xc} is the frequency-independent Adiabatic Local Density Approximation (ALDA) [7]

$$f_{xc}[n](\mathbf{r}, \mathbf{r}', \omega) = \delta^3(\mathbf{r} - \mathbf{r}') \frac{d^2 n \varepsilon_{xc}^{\text{hom}}(n)}{dn^2} \Big|_{n=n(\mathbf{r})}$$

in which the input data is the exchange-correlation energy $\varepsilon_{xc}^{\text{hom}}(n)$ per electron of the homogeneous electron gas with electron number density n , a known quantity. This approximation over-estimates the (negative) f_{xc} at higher frequencies. Consequently the ALDA under-screens χ , and the resulting C_6^{ALDA} from (6) and (5) tends to be too large, by about $O(10\%)$.

Accordingly, there has been interest in finding better approximations for f_{xc} . [?, 17, 8–11, 23] Many of these are mildly nonlocal in the $\mathbf{r}, \mathbf{r}'$ variables. As a result of the considerations explained below, we believe, however, that it may be equally important to include a highly nonlocal functional dependence of f_{xc} on the groundstate electron number density $n(\mathbf{r})$.

2.2 The dimer (supramolecular) approach within TDDFT / ACFD

It is important to be able to predict dispersion interactions in situations where overlap between the interacting systems cannot be ignored, so that the GCP is not accurate. This can be done via seamless supramolecular approaches that do not artificially divide the total composite system into subsystems A and B . One approach to this problem is by looking at the electron density response. The dispersion energy between two systems A and B is part of the electronic correlation energy of the combined super-molecule.

If the density response $\chi(\mathbf{r}, \mathbf{r}', iu)$ of an arbitrary system (e.g. the combined system $A \cup B$) is known exactly, its correlation energy can be obtained exactly from the Adiabatic Connection Fluctuation Dissipation (ACFD) approach [12]:

$$E_c^{A \cup B} = -\frac{\hbar}{2\pi} \int_0^\infty du \int_0^1 d\lambda \int_0^\infty du \text{Tr} \left[v * (\chi_\lambda - \chi_0) \right]. \quad (7)$$

Here (and elsewhere) $*$ represents spatial convolution, $(a * b)(\mathbf{r}, \mathbf{r}') = \int d\mathbf{r}'' a(\mathbf{r}, \mathbf{r}'') b(\mathbf{r}'', \mathbf{r}')$, and $\text{Tr}[a * b] = \int d\mathbf{r} (a * b)(\mathbf{r}, \mathbf{r}) = \int d\mathbf{r} d\mathbf{r}' a(\mathbf{r}, \mathbf{r}') b(\mathbf{r}', \mathbf{r})$ represents a further integral over the outer space variable. Here χ_λ is the exact density response of a fictitious system in which the Coulomb potential is replaced by $\lambda e^2 |\mathbf{r} - \mathbf{r}'|$ while an external potential is applied to keep the groundstate density $n(\mathbf{r})$ constant at the true ($\lambda = 1$) value at all points $\mathbf{r}$.

3 The problem: violation of Casimir-Polder size consistency by seamless TDDFT/ACFD theories

If one uses a particular approximation for $f_{xc}[n](\mathbf{r}, \mathbf{r}', \omega = iu)$ in (1) and (7), then one has a particular seamless approximation for the dispersion energy. In a recent publication[2] we showed that simple local approximations for f_{xc} used in this way can lead to inconsistencies in the calculation of dispersion energies (violation of Casimir-Polder size consistency[13]). Specifically if the seamless supramolecular approach is applied to a pair of well-separated systems A and B , and the seamless correlation energy is expanded to second order in the intersystem Coulomb interaction v_{AB} , one may not necessarily obtain the Generalized Casimir Polder result (3) with the same kernel f_{xc} used in (1) to calculate the individual responses χ_A and χ_B .

The energy discrepancy ΔU^{AB} by which supramolecular TDDFT/ACFD (we shall henceforth use ACFD to refer to this case) fails to satisfy Casimir Polder Size Consistency was found to be

$$\Delta U^{AB} = \int_0^1 d\lambda \text{Tr} \left[\lambda^2 \chi_{\lambda, BB} v_{BA} \chi_{\lambda, AA} h_{xc, \lambda, AA} \chi_{\lambda, AA} v_{AB} \right] + A \leftrightarrow B \quad (8)$$

(see Eq (12) of [2]). Note, here we have generalized the exchange only case reported previously by setting $h_{xc, \lambda, AA} = \frac{\partial f_{xc, \lambda, AA}}{\partial \lambda}$.

We showed that this discrepancy can be relatively large for the case of a strictly local exchange-only kernel; of the same order as the errors in C_6 that are made by using either dRPA or ALDA response functions χ_A , χ_B in the CGP expression (3). Such a result is worthy of attention as it means that the same problem studied under the same apparent approximation can give appreciably different values for long-ranged interactions, depending on whether results are calculated using a dimer calculation, or by combining monomer approximations. Here, subscripts A and B indicate locality, s.t. $a_{AB} \equiv a(\mathbf{r}_A, \mathbf{r}'_B)$ and a single index (e.g. on $\chi_{0, A}$) indicates a quantity calculated in total isolation acting only in the given region of space. We now drop the $*$ between terms, for succinctness.

In order to understand this discrepancy and seek a resolution, we re-examine the working in [2] and [14]. In these works space was divided into disjoint regions, one containing system A and one containing system B . The assumptions made in [2] were that:

1. the bare response χ_0 does not couple the two systems/regions: i.e., $\chi_0(\mathbf{r}_A, \mathbf{r}_B, \omega) = 0$, where space point $\mathbf{r}_A$ lies in system A and $\mathbf{r}_B$ lies in B .
2. the exchange correlation kernel does not have an ultra-long-ranged position dependence, in the sense that $f_{xc}(\mathbf{r}_A, \mathbf{r}_B) = 0$.
3. in the Dyson-like equation (1) of TDDFT, the intra-system bare response $\chi_0(\mathbf{r}_A, \mathbf{r}'_A, \omega)$ and kernel $f_{xc}(\mathbf{r}_A, \mathbf{r}'_A, \omega)$ are to be calculated for system A in isolation, without the presence of system B , and vice versa.

With these assumptions, the bare Coulomb interaction was split as follows

$$v = \mu(v_{AA} + v_{BB}) + \gamma(v_{AB} + v_{BA})$$

and an expansion of the Dyson-like screening equation (1) was carried out through second order in the inter-system Coulomb strength γ , with substitution into (7), ultimately setting $\gamma = \mu = \lambda$ before the final λ integration.

The dimer interaction energy contribution that is of $O(\gamma^2)$ comes from two terms, $\Delta U^{\gamma^2} = \Delta U_{(d)}^{\gamma^2} + \Delta U_{(s)}^{\gamma^2}$ arising in the ACFD formula (7). Here, the “direct” (d) term is

$$\Delta U_{(d)}^{\gamma^2} = \text{Tr} \left[\gamma \Delta \chi_{AB}^{\gamma} \gamma v_{AB} + \gamma \Delta \chi_{BA}^{\gamma} \gamma v_{BA} \right] \quad (9)$$

and the “spectator” (s)[15] term is

$$\Delta U_{(s)}^{\gamma^2} = \text{Tr} \left[\gamma^2 \Delta \chi_{AA}^{\gamma^2} v_{AA} + \gamma^2 \Delta \chi_{BB}^{\gamma^2} v_{BB} \right]. \quad (10)$$

$\Delta \chi^{\gamma}$ and $\Delta \chi^{\gamma^2}$ are perturbations beyond the sum of isolated responses, respectively to leading and second orders. They can be obtained by solving a generalized Dyson-like screening equation:

$$\begin{aligned} \chi_{\mu\gamma,AA} &= \chi_{0,A} + \chi_{00,AA} [\mu v_{AA} + f_{xc\mu\gamma,AA}] \chi_{\mu\gamma,AA} \\ &\quad + \chi_{00,AA} [\gamma v_{AB} + f_{xc\mu\gamma,AB}] \chi_{\mu\gamma,BA}, \\ \chi_{\mu\gamma,AB} &= \chi_{00,AA} [\mu v_{AA} + f_{xc\mu\gamma,AA}] \chi_{\mu\gamma,AB} \\ &\quad + \chi_{00,AA} [\gamma v_{AB} + f_{xc\mu\gamma,AB}] \chi_{\mu\gamma,BB}, \end{aligned}$$

and $B \leftrightarrow A$, and expanding terms as $\chi_{\mu\gamma} \equiv \chi_{\mu 0} + \gamma \Delta \chi_{\mu}^{\gamma} + \gamma^2 \Delta \chi_{\mu}^{\gamma^2} + \dots$

The first (direct) term $\Delta U_{(d)}^{\gamma^2}$, from Eq. (9), folds the bare inter-system Coulomb potential with the first-order inter-system density response. The second term, Eq. (10), folds the bare intra-system coulomb potential with a second-order “spectator” correction to the intra-system density response. The terms $\Delta U_{(d)}$ and $\Delta U_{(s)}$ are completely accounted for in dimer dRPA/ACFD calculations, as shown explicitly in [14, 13] and implicitly in [2].

As shown in [2], however, when one adds an xc kernel f_{xc} to the Coulomb potential, thus performing a dimer ACFD calculation, the terms $\Delta U_{(s)}$ are not fully accounted for when one assumes that the intra-system kernel $f_{xc}(\mathbf{r}_A, \mathbf{r}'_A)$ is the same for the dimer situation as it is for the isolated systems: this results in the discrepancy given by (8). This constancy of $f_{xc}(\mathbf{r}_A, \mathbf{r}'_A)$ during the approach of a second system B was assumed in [2], and indeed constancy is necessarily true when one (a) assumes the monomer densities stay constant during this process (for wide separations outside the overlap regime) and (b) makes the usual doubly local approximations for f_{xc} [locality in both $\mathbf{r}, \mathbf{r}'$ and the dependence on groundstate density $n(\mathbf{r}'')$].

3.1 A long-ranged density dependence in f_{xc} ?

The discrepancy between GCP and ACFD-dimer approaches is significant, since the GCP gives the exact interaction energy to $O(\gamma^2)$ (up to some uncertainty about overlap and exchange effects) and so the supramolecular ACFD

approach must be inaccurate. One solution to this apparent contradiction could be that there is a contribution to $f_{xc}(\mathbf{r}_A, \mathbf{r}'_A)$ that is of $O(\gamma^2)$. Equivalently, there is an $O(\gamma^2)$ part of $f_{xc}(\mathbf{r}_A, \mathbf{r}'_A)$ that depends on the presence of the other system B , implying a very long-ranged dependence of f_{xc} on the groundstate electronic density. Such a possibility was neglected in [2], where f_{xc} was assumed to be the same for space arguments $\mathbf{r}_A, \mathbf{r}'_A$ inside system A , regardless of the presence of a distant system B , as is the case in many approximations to the kernel.

It seems possible that, by adding such an extra contribution to f_{xc} , one could cancel the incorrect energy term (8). There would initially seem to be two possibilities for cancelling to CP-consistency-violating term (8) in this fashion:

- (i) there could be a term in f_{xc} of $O(\gamma)$ that is highly nonlocal in the $\mathbf{r}, \mathbf{r}'$ variables. This term would then modify the “direct” energy contribution (9). This would have to be in the exchange part of f_{xc} , as the correlation part f_c is known [16] to be of second order and higher in the Coulomb interaction, and would then produce an $O(\gamma^3)$ term in (9). Thus one is left with a long-ranged part of the pure exchange kernel f_x , which seems implausible given how reliant exchange is on overlap of orbitals.
- (ii) there could be an $O(\gamma^2)$ contribution to f_{xc} that does not couple space points in different systems A and B , and so is (relatively) short-ranged in space. Instead its values $f_{xc}[n](\mathbf{r}_A, \mathbf{r}'_A, iu)$ inside system A would depend on the groundstate density $n(\mathbf{r}_B)$ inside system B - representing a highly nonlocal dependence on the groundstate electron density $n(\mathbf{r})$. An example of this case is illustrated in Figure 1b.

The arguments presented in (i) suggest that (ii) is the correct assumption, and we will proceed on this basis. Moreover, such an effect has a precedent in the highly non-local “step”-like terms in the exact exchange kernel, which has been studied in previous works. [17–23]

4 A solution? Postulated extra contribution to within-species f_{xc} that only appears when a second species is present

The above discussion suggests that there is an extra contribution to $f_{xc,AA}$ that is of second order in γ :

$$\Delta f_{xc\mu\gamma,AA}^{\text{extra}} \equiv \gamma^2 s_{xc\mu}[n_A, n_B](\mathbf{r}_A, \mathbf{r}'_A). \quad (11)$$

Although acting only on system A , this expression has an explicit functional dependence on both n_A and n_B , i.e. it can (and as we shall show must) depend on the density of species A and B . Such a term is also suggested by diagrammatic theory, an approach that we will discuss elsewhere.

This $\Delta f_{xc,AA}$ will cause a change $\Delta\chi_{AA}$ in the “naive” response

$$\chi_{\mu\gamma,AA} = \chi_{00,A} \{1 - \chi_{00,A}[\mu v_{AA} + f_{xc\mu\gamma,AA}]\}^{-1}.$$

that is obtained from a purely local theory on one side. The correction is given by:

$$\begin{aligned}\chi_{\mu\gamma,AA} + \Delta\chi_{\mu\gamma,AA} &= \chi_{00,A} \{1 - \chi_{00,A} [\mu v_{AA} + f_{xc\mu\gamma,AA} + \Delta f_{xc\mu\gamma,AA}^{\text{extra}}]\}^{-1}, \\ &\equiv \chi_{\mu\gamma,AA} \{1 - \chi_{\mu\gamma,AA} \Delta f_{xc\mu\gamma,AA}^{\text{extra}}\}^{-1}.\end{aligned}\quad (12)$$

Here $\mu\gamma$ indicates the strength coefficients μ and γ multiplying interactions within and between systems, respectively. We used $c_1 = [1 - c_0 f_1]^{-1} c_0 \rightarrow c_0^{-1} = c_1^{-1} + f_1$ and $c_2 = [1 - c_0(f_1 + f_2)]^{-1} c_0 \rightarrow c_0^{-1} = c_2^{-1} + f_1 + f_2$, from which it follows that $c_1^{-1} = c_2^{-1} + f_2$ and $c_2 = [1 - c_1 f_2]^{-1} c_1$. Truncating a series expansion in Δf_{xc} to leading $O(\gamma^2)$, and setting $\mu = \gamma = \lambda$ then transforms (12) into

$$\Delta\chi_{\lambda,AA}^{\text{extra}} \approx \chi_{\lambda 0,AA} \Delta f_{xc\lambda AA}^{\text{extra}} \chi_{\lambda 0,AA} \equiv \lambda^2 \chi_{\lambda 0,AA} s_{xc\lambda,AA} \chi_{\lambda 0,AA}.$$

The extra term in the energy from $\Delta f_{xc}^{\text{extra}}$ is part of the “spectator” energy from (10):

$$\Delta U_{\text{spectator}}^{\gamma^2} = \bar{\text{Tr}} \left[v_{AA} \Delta\chi_{AA}^{\text{extra}} \right] + (A \leftrightarrow B) \quad (13)$$

$$= \bar{\text{Tr}} \left[\lambda^2 v_{AA} \chi_{\lambda 0,AA} s_{xc\lambda,AA} \chi_{\lambda 0,AA} \right] + (A \leftrightarrow B) \quad (14)$$

where $\bar{\text{Tr}} \equiv \frac{1}{2\pi} \int_0^\infty d\omega \int_0^1 d\lambda \text{Tr}$. This is to be compared with the violation energy by which ACFD fails to satisfy Casimir Polder Consistency with an AB -local f_{xc} , from (8), which we repeat here for comparison: $\Delta U^{AB} = \int_0^1 d\lambda \text{Tr} [\lambda^2 \chi_{\lambda 0,BB} v_{BA} \chi_{\lambda 0,AA} h_{xc,AA} \chi_{\lambda 0,AA} v_{AB}] + A \leftrightarrow B$

Eq. (8) explicitly contains the isolated responses $\chi_{\lambda 0,AA}$, $\chi_{\lambda 0,BB}$, of both systems A and B , whereas in (14) only one of these one-sided responses appears explicitly. Therefore, if (14) is to cancel the spurious energy (8), $\Delta f_{xc\lambda,AA}$ must carry a hidden dependence on $\chi_{\lambda 0,BB}$, and $\Delta f_{xc\lambda,BB}$ must carry a dependence on $\chi_{\lambda 0,AA}$. Since the arguments of $\chi_{\lambda 0,AA}$ lie inside system A , this amounts to a very long-ranged dependence of $f_{xc,AA}$ on the presence of system B . Since f_{xc} is in general regarded as a functional of the groundstate density $n(\mathbf{r})$, it must be a long-ranged functional of the density in order to sample the presence of system B . *This is one of the primary results of the present work.*

Let us briefly consider this point mathematically. The energy can be cancelled when (14) removes (8), i.e.,

$$\text{Tr} [\chi_{\lambda 0,AA} s_{xc\lambda,AA} \chi_{\lambda 0,AA} v_{AA}] = - \text{Tr} [\chi_{\lambda 0,AA} v_{AB} \chi_{\lambda 0,BB} v_{BA} \chi_{\lambda 0,AA} h_{xc,AA}].$$

A sufficient, but not necessary, way to do this is to ensure that the terms inside the trace cancel point by point, as written or under permutation of terms inside the trace. Using appropriate functional inverses, and ensuring

appropriate symmetry under exchange of $\mathbf{r}$ and $\mathbf{r}'$, we get

$$s_{\text{xc}\lambda,AA}^{\text{trial}} = -\frac{1}{2} \left\{ v_{AB}\chi_{\lambda 0,BB}v_{BA}\chi_{\lambda 0,AA}h_{\text{xc},AA}[\chi_{\lambda 0,AA}v_{AA}]^{-1} \right. \\ \left. + [v_{AA}\chi_{\lambda 0,AA}]^{-1}h_{\text{xc},AA}\chi_{\lambda 0,AA}v_{AB}\chi_{\lambda 0,BB}v_{BA} \right\}. \quad (15)$$

Note, this highly speculative trial choice is only one possibility to ensure Casimir-Polder size consistency is maintained at second order in the inter-species interactions. Nonetheless, (15) is sufficient to illustrate the strong non-locality that is required of the spectator term, via $v_{AB}\chi_{\lambda 0,BB}v_{BA}$.

5 An alternative solution? A spectator term in the groundstate density $n(\mathbf{r}_A)$ coming from the presence of $n(\mathbf{r}_B)$

Another possibility is as follows. It is known that the groundstate electronic density $n(\mathbf{r}_A)$ inside system A is affected by the presence of system B , even if orbital overlap is neglected. Specifically from work investigating the Feynman approach to dispersion forces [24] (and other works) it is known there is a term of form $\gamma^2 \Delta n^{\gamma^2}(\mathbf{r}_A)$ modifying the density of system A because of the presence of system B . Such a change was not discussed in [2] and would represent a special type of density-driven error [25].

A question then arises whether, with the assumption that f_{xc} depends only in a short-ranged fashion on the groundstate electron density $n(\mathbf{r})$, the necessary correction term cancelling (8) might arise through a short-ranged dependence of f_{xc} on $n(\mathbf{r})$. If this is the case, perhaps the correct dispersion interaction can be obtained from dimer ACFD calculations provided that the groundstate density is calculated self-consistently at each value of the spatial separation between the systems A and B . At present this is only a conjecture, however.

Such a result would have interesting implications for the dRPA. In that case, there is no functional dependence on the kernel, as it is simply the Coulomb potential. There is, however, a functional dependence of χ_0 on n_A . This raises fundamental questions about how the change to χ_0 might be accommodated when considering the known Casimir-Polder size consistency of the dRPA, and what density is appropriate to use in ACFD calculations.

6 Summary

We have discussed two ways (Generalized Casimir Polder and supramolecular TDDFT/ACFD) of predicting the dispersion energy between two non-overlapping systems A and B . We re-examined a discrepancy between these approaches (violation of Casimir-Polder size consistency by the supramolecular TDDFT/ACFD) that was pointed out by Gould *et al* [2]. From these considerations we have here deduced that

- (a) the exchange-correlation kernel $f_{xc}[n(\mathbf{r}'')](\mathbf{r}, \mathbf{r}', \omega)$ of TDDFT may contain a very long-ranged dependence on the groundstate electron density $n(\mathbf{r}'')$, giving rise to a term (14). Such a kernel may, formally, be obtained using (15) or via alternative means: and/or
- (b) it may be necessary, in supramolecular TDDFT/ACFD, to calculate the groundstate density self-consistently at each spacing between the interacting species A and B . In this case it is possible that a local dependence of f_{xc} on $n(\mathbf{r})$ may be able to resolve the discrepancy noted above. We gave no specific way in which this could occur, in contrast to case (a) above.

There is also some support for scenario (a) from diagrammatic perturbation theory of the beyond-dRPA spectator terms, not discussed here. We are currently attempting to generate a specific nonlocal functional via diagrammatic means.

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References

1. E. Runge, E.K.U. Gross, Density-functional theory for time-dependent systems, *Phys. Rev. Lett.* **52**, 997 (1984)
2. T. Gould, J. Toulouse, J.G. Ángyán, J.F. Dobson, Casimir–polder size consistency: A constraint violated by some dispersion theories, *J. Chem. Theory Comput.* **13**(12), 5829 (2017). DOI 10.1021/acs.jctc.7b00996. PMID: 29111709
3. H.B.G. Casimir, D. Polder, The influence of retardation on the london-van der waals forces, *Phys. Rev.* **73**, 360 (1948). DOI 10.1103/PhysRev.73.360
4. R. Kevorkyants, H. Eshuis, M. Pavanello, Fde-vdw: A van der waals inclusive subsystem density-functional theory, *J. Chem. Phys.* **141**(4), 044127 (2014)
5. B. Jeziorski, R. Moszynski, K. Szalewicz, Perturbation theory approach to intermolecular potential energy surfaces of van der waals complexes, *Chemical Reviews* **94**(7), 1887 (1994). DOI 10.1021/cr00031a008. URL <https://doi.org/10.1021/cr00031a008>
6. K. Szalewicz, Symmetryadapted perturbation theory of intermolecular forces, *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2**(2), 254 (2011). DOI 10.1002/wcms.86. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/wcms.86>
7. A. Zangwill, P. Soven, Resonant photoemission in barium and cerium, *Phys. Rev. Lett.* **45**, 204 (1980). DOI 10.1103/PhysRevLett.45.204
8. S. Sharma, J.K. Dewhurst, A. Sanna, E.K.U. Gross, Bootstrap approximation for the exchange-correlation kernel of time-dependent density-functional theory, *Phys. Rev. Lett.* **107**, 186401 (2011). DOI 10.1103/PhysRevLett.107.186401
9. A. Ruzsinszky, J.P. Perdew, G.I. Csonka, A simple but fully nonlocal correction to the random phase approximation, *The Journal of Chemical Physics* **134**(11), 114110 (2011)
10. T. Gould, Communication: Beyond the random phase approximation on the cheap: Improved correlation energies with the efficient “radial exchange hole” kernel, *J. Chem. Phys.* **137**(11), 111101 (2012). DOI 10.1063/1.4755286. URL <http://link.aip.org/link/?JCP/137/111101/1>
11. T. Olsen, K.S. Thygesen, Beyond the random phase approximation: Improved description of short-range correlation by a renormalized adiabatic local density approximation, *Phys. Rev. B* **88**, 115131 (2013). DOI 10.1103/PhysRevB.88.115131

12. O. Gunnarsson, B.I. Lundqvist, Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formalism, *Phys. Rev. B* **13**, 4274 (1976). DOI 10.1103/PhysRevB.13.4274
13. J.F. Dobson, in *Fundamentals of Time Dependent Density Functional Theory*, vol. 837, ed. by M.A. Marques, N.T. Maitra, F.M. Nogueira, E.K. Gross, A. Rubio (Springer Science & Business Media, 2012)
14. J.F. Dobson, in *Topics in Condensed Matter Physics*, ed. by M.P. Das (Nova Science Publisher, 1994), pp. 121–142. Available as arXiv preprint cond-mat/0311371
15. D.C. Langreth, M. Dion, H. Rydberg, E. Schröder, P. Hyldgaard, B.I. Lundqvist, Van der waals density functional theory with applications, *Int. J. Quantum Chem.* **101**(5), 599 (2005). DOI 10.1002/qua.20315
16. A. Görling, M. Levy, Correlation-energy functional and its high-density limit obtained from a coupling-constant perturbation expansion, *Phys. Rev. B* **47**(20), 13105 (1993)
17. A. Görling, Exact exchange kernel for time-dependent density-functional theory, *Int. J. Quantum Chem.* **69**(3), 265 (1998). DOI 10.1002/(SICI)1097-461X(1998)69:3<265::AID-QUA6;3.0.CO;2-T. URL [http://dx.doi.org/10.1002/\(SICI\)1097-461X\(1998\)69:3<265::AID-QUA6;3.0.CO;2-T](http://dx.doi.org/10.1002/(SICI)1097-461X(1998)69:3<265::AID-QUA6;3.0.CO;2-T)
18. M. Hellgren, U. von Barth, Linear density response function within the time-dependent exact-exchange approximation, *Phys. Rev. B* **78**, 115107 (2008). DOI 10.1103/PhysRevB.78.115107
19. A. Heßelmann, A. Görling, Random phase approximation correlation energies with exact kohn–sham exchange, *Mol. Phys.* **108**(3-4), 359 (2010). DOI 10.1080/00268970903476662
20. M. Hellgren, U. von Barth, Correlation energy functional and potential from time-dependent exact-exchange theory, *J. Chem. Phys.* **132**(4), 044101 (2010). DOI 10.1063/1.3290947. URL <http://link.aip.org/link/?JCP/132/044101/1>
21. M. Hellgren, E.K.U. Gross, Discontinuities of the exchange-correlation kernel and charge-transfer excitations in time-dependent density-functional theory, *Phys. Rev. A* **85**, 022514 (2012). DOI 10.1103/PhysRevA.85.022514
22. P. Bleiziffer, A. Heßelmann, A. Görling, Resolution of identity approach for the kohn-sham correlation energy within the exact-exchange random-phase approximation, *J. Chem. Phys.* **136**(13), 134102 (2012). DOI 10.1063/1.3697845. URL <http://link.aip.org/link/?JCP/136/134102/1>
23. M. Hellgren, E.K.U. Gross, Discontinuous functional for linear-response time-dependent density-functional theory: The exact-exchange kernel and approximate forms, *Phys. Rev. A* **88**, 052507 (2013). DOI 10.1103/PhysRevA.88.052507
24. K. Hunt, Dispersion dipoles and dispersion forces: Proof of feynmans conjecture and generalization to interacting molecules of arbitrary symmetry, *The Journal of chemical physics* **92**(2), 1180 (1990)
25. M.C. Kim, E. Sim, K. Burke, Understanding and reducing errors in density functional calculations, *Phys. Rev. Lett.* **111**, 073003 (2013). DOI 10.1103/PhysRevLett.111.073003. URL <https://link.aps.org/doi/10.1103/PhysRevLett.111.073003>