Long- and Medium-Ranged Nonlocal Correlations in Density Functional Theory

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A scheme within Density Functional Theory is proposed that provides a basis for systematic improvements beyond the local (LDA) and semilocal density approximations (GGA), to incorporate medium- and long-ranged correlations, including the van der Waals forces. The exchange-correlation energy is exactly decomposed into a "regular" part, simply expressed in terms of a generalized polarization operator, known in the uniform limit, and a remaining nonlocal correlation part, expressed in the same generalized polarization operator. The resulting power series is proven to converge very rapidly under certain useful conditions. An explicit nonlocal density functional utilizing this decomposition is developed, and tested on several prior studies.

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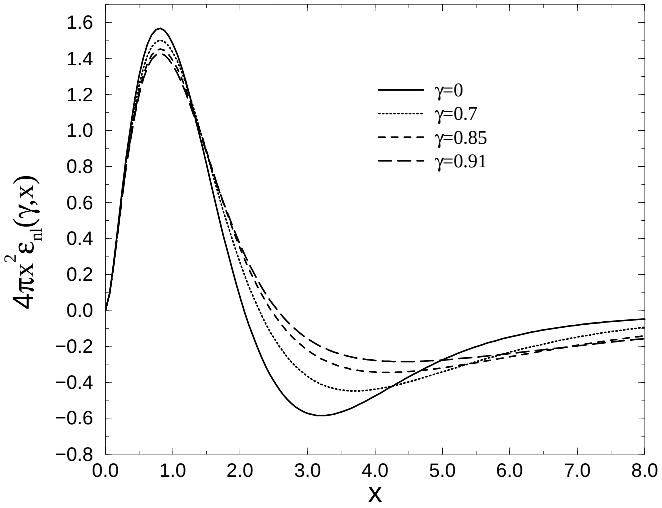

FIG. 1. Universal nonlocal correlation-interaction function $\varepsilon_{\rm nl}(\gamma, x)$, obtained using a simple model of the generalized polarization operator, derived in this report. The figure shows the spherical average of the interaction function between points $\mathbf{r}$ and $\mathbf{r}'$, as a function of scaled distance $x = q_{\rm eff}\,|\mathbf{r}-\mathbf{r}'|$, and inhomogeneity measure γ. Both $q_{\rm eff}$ and γ are functions of the density, and defined in Sec. V.

I. INTRODUCTION

Densely-packed materials are today described very well with regard to properties like cohesion, bonds and structures.[1−4] This success story of the Density Functional Theory (DFT)[5,6,1] is performed worldwide with approximate *local* and *semilocal* density functionals for the exchange-correlation (XC) functional $E_{xc}[n]$.[6] The driving force behind this impressive development is the desire to treat first largely homogeneous systems like simple metals and semiconductors, where LDA[6,7] is appropriate, and secondly inhomogeneous systems like compounds, surfaces, and interfaces, where members of the GGA family[8−10] give improved descriptions. Soft, sparsely-packed materials are at least as abundant. In such systems there are interparticle separations, where *nonlocal* interactions such as van der Waals (vdW) forces are influential.

The DFT[5,6,1] expresses the ground-state energy of an interacting system in an external potential $v(\mathbf{r})$ as a functional $E[n]$ of the particle density $n(\mathbf{r})$, and this energy has its minimum at the true ground-state density.[5] The intricate interactions among the electrons are exactly accounted for in terms of the XC potential $v_{\rm xc}[n](\mathbf{r}) = \delta E_{\rm xc}[n]/\delta n(\mathbf{r})$.[6] The $v_{\rm xc}[n]$ acts locally on each electron,

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and thus propagates the interactions only through its dependence on the density. To treat sparsely packed systems, where long-ranged forces originating in the quantum correlations between electrons are important, it is nescessary to also account for the *nonlocal* effects in $E_{\rm xc}$.

There are several approximate functionals proposed to account for these effects,[11–15] approaching the problem from different directions, and with different virtues. Apart from the obvious requirements that the functional should be general and sufficiently well understood to allow physical insight, the practical requirement on such a functional is that it must be simple enough to allow efficient computations. None of the so-far-proposed functionals encompasses all these requirements.

In order to address the nonlocal XC energy, it is expedient to decompose $E_{\rm xc}$ into two parts; one regular part representing the present knowledge of the functional, and one containing the nonlocal properties. The word "regular" is here used in the sense "major", "simple", "predictable", "local" or "semi-local", and emphasizes that the regular portion of the XC energy is large and well known within the framework of the LDA and GGA.[6–10] A decomposition of this kind has already been suggested,[15] and is given formally by

$$E_{\rm xc}[n] = E^0_{\rm xc}[n] + E^{\rm nl}_c[n]. \tag{1}$$

The regular part, $E^0_{\rm xc}$, should be calculated using established knowledge and serve as a foundation for the construction of the nonlocal part, $E^{\rm nl}_c$, which in a sense is treated as a perturbation. In the uniform limit, $E^0_{\rm xc}$ is equal to LDA, and in general, it contains all exchange effects plus a regular piece of the correlation, further discussed in Sec. V.

A key property of a general XC functional is robustness; as a functional of the density, it should work for all systems, in particular inhomogeneous ones. Prior studies[12,16,17] have given the asymptotic behavior of $E^{\rm nl}_c$, and a first step towards more medium-ranged interactions in $E^{\rm nl}_c$,[15] which are important for soft matter. To date, these long- and medium-range investigations have been completely separated from more close-ranged[18,19] or general[13,14] (but intractable) ditto. It goes without saying that the close-range energetics of the regular energy gives poor guidance to the asymptotic properties, but in the intermediate regime that is no longer so.[15] As the regimes are merged, the information from both ends becomes equally important. This is fortunate, because it means that $E^0_{\rm xc}$ may serve as a powerful tool for the approximate construction of $E^{\rm nl}_c$. To that end, it is desirable to express both $E^0_{\rm xc}$ and $E^{\rm nl}_c$ in the same quantity, so that maximum use can be made of established knowledge, and to devise a robust approximation to the nonlocal part $E^{\rm nl}_c$.

The present approach to $E^{\rm nl}_c$ has the following guiding principles: (i) Express $E^0_{\rm xc}$ and $E^{\rm nl}_c$ in the *same* quantity, hereafter called $s_{\rm xc}$; (ii) Make a simple parameterization of $s_{\rm xc}$, based on previous studies of nonlocal functionals;[12,16,17,15] (iii) Adjust the parameterization to both regular and nonlocal key properties, utilizing previous studies of the XC hole.[7,8,20,18,19]

Step (i) is made in Sec. II, step (ii) in Sec. IV, and step (iii) in Sec. V. In Sec. VI the resulting functional, Eq. (63), shown in Fig. 1, is tested against several prior studies, and Sec. VII, finally, gives some concluding remarks.

II. GENERALIZED POLARIZATION OPERATOR $S_{\rm xc}$

In order to arrive at a robust approximation to $E_{\rm xc}$ for inhomogeneous systems, $E^0_{\rm xc}$ and $E^{\rm nl}_c$ should be expressed in terms of their common denominator, $s_{\rm xc}$. In Ref. 15, the regular energy $E^0_{\rm xc}$ is defined in an RPA-like approximation as[21]

$$E^0_{\rm xc}[n] = \int_0^\infty \frac{du}{2\pi}\,{\rm Tr}\left[\ln(\epsilon)\right] - E_{\rm self}, \tag{2}$$

where $\epsilon[n](iu, \mathbf{r}, \mathbf{r}')$ is the isotropic dielectric function, and $E_{\rm self}$ is a trivial self energy.[15] Eq. (2) becomes the only contribution in the uniform limit, and can readily be put on the same general, simple form as LDA and GGA, making it a suitable starting point. Within the RPA, $\epsilon = \frac{1}{3}\sum_i \epsilon^{\rm KS}_{i,i}$, the isotropic dielectric function of the non-interacting (Kohn-Sham) system, but Eq. (2) is not limited to isotropic RPA, an issue discussed in Appendix A. However, a definite advantage of RPA compared with a more general treatment is that $\epsilon^{\rm KS}$ is constructed from the one-electron KS orbitals, which in turn implicitly depend on the density only. In that sense $\epsilon^{\rm KS}$ is regular, although it may contain long-ranged tails due to delocalized electrons, like in metals. For bounded systems, like atoms and molecules, it is even localized.

In the same treatment, the nonlocal energy, $E^{\rm nl}_c$, is expressed as[15]

$$E^{\rm nl}_c[n] = \int_0^\infty \frac{du}{2\pi}\,{\rm Tr}\left[\ln(1+\Delta)\right], \tag{3}$$

with Δ given by

$$\Delta = \epsilon^{-1}\left[\boldsymbol{\nabla}, \epsilon\right]\cdot\boldsymbol{\nabla}{\rm G}. \tag{4}$$

Here, ${\rm G} = -1/4\pi\,|\mathbf{r}-\mathbf{r}'|$ is the Coulomb Green's function such that $\nabla^2{\rm G} = 1$. Although both Eq. (2) and Eq. (3) are expressed in terms of ϵ, it enters in such a way that a direct approximation becomes unwieldy. It suffices to think of getting $\ln(\epsilon)$ or ϵ^{-1} from the knowledge of ϵ only.

From Eq. (2), it is suggestive to make a trivial definition of $s_{\rm xc}$ as the logarithmic expression

$$s_{\rm xc}[n] = \ln(\epsilon[n]), \tag{5}$$

which renders $E^0_{\rm xc}$ linear in $s_{\rm xc}$; the problem of evaluating $\ln(\epsilon)$ is avoided completely if $s_{\rm xc}$ is parameterized directly in terms of the density.

With Eq. (5), Eq. (2) is simply expressed in terms of $s_{\rm xc}$, and it turns out that also Eq. (3) is expressed quite conveniently in terms of $s_{\rm xc}$, via the series

$$\Delta = \sum_{n=1}^{\infty} \frac{1}{n!} \mathbf{d}_n \cdot \mathbf{d}_0 \mathrm{G} \equiv \sum_{n=1}^{\infty} \Delta_n, \tag{6}$$

where

$$\mathbf{d}_{n+1} = [s_{\rm xc}, \mathbf{d}_n], \tag{7}$$

and the starting criterion, $\mathbf{d}_0 = \boldsymbol{\nabla}$. In a uniform, translationally invariant system, Eq. (7) and consequently Eq. (6) vanishes identically, so that a rapid convergence of Eq. (6) in a slowly varying system is immediately apparent. As shown in Appendix B 1, this holds true also for slightly more general conditions.

A. Evaluation of $E_c^{\rm nl}$

From Eq. (4), it is evident that Δ is independent of a simple scaling of ϵ, and hence depend only on the nonuniform character of ϵ. One could further expect that the eigenvalues of Δ in general are small, so that the second-order expansion of the logarithm in Eq. (3) becomes of interest,

$$\mathrm{Tr}\left[\ln(1+\Delta)\right] = \mathrm{Tr}\left[\Delta\right] - \frac{1}{2}\mathrm{Tr}\left[\Delta^2\right] + \mathcal{O}(\delta^3), \tag{8}$$

where δ is a small measure, discussed in Appendix B 2. A consistent second-order expansion in δ may be formed by keeping the terms Δ_1 and Δ_2 for the first order term, and Δ_1 for the second-order term. Evaluating the expressions one obtains

$$\mathrm{Tr}\left[\Delta_1\right] = 0, \tag{9}$$

$$\mathrm{Tr}\left[\Delta_2\right] = \mathrm{Tr}\left[s_{\rm xc}^2 - s_{\rm xc}\mathbf{d}_0 \cdot s_{\rm xc}\mathbf{d}_0\mathrm{G}\right], \tag{10}$$

$$\mathrm{Tr}\left[\Delta_1^2\right] = 2\mathrm{Tr}\left[\Delta_2\right] + \mathrm{Tr}\left[(\mathbf{d}_0 \cdot s_{\rm xc}\mathbf{d}_0\mathrm{G})^2 - s_{\rm xc}^2\right]. \tag{11}$$

Equation (10) is contained also in Eq. (11), simplifying matters considerably. The final expression for the nonlocal energy becomes

$$E_c^{\rm nl} = \int_0^{\infty} \frac{du}{4\pi}\, \mathrm{Tr}\left[s_{\rm xc}^2 - (s_{\rm xc}\mathbf{T})^2\right] + \mathcal{O}(\delta^3), \tag{12}$$

where $\mathbf{T} \equiv \boldsymbol{\nabla}\mathrm{G}\boldsymbol{\nabla}$ is the 3x3 dyadic operator such that $\mathbf{T}^2 = \mathbf{T}$ and the trace over the 3x3 matrix yields 1.

Several points can be made about Eq. (12): (i) It is positive for all $s_{\rm xc}$ (Sec. IV) and hence the non-local contributions (to second order) are always positive; (ii) It contains no term linear in $s_{\rm xc}$, and is therefore a pure correlation energy; (iii) For a uniform system, it vanishes identically, since $s_{\rm xc}$ then commutes with $\mathbf{T}$; (iv) It is equivalent to the second-order expansion of the particular approximation used in Ref. 15. Hence, Eq. (12) is a three-dimensional generalization of that functional, with the addition of allowing more realistic polarizability models.

In addition, Eq. (12) can be viewed as a direct generalization of the traditional dipole expansion which is applicable at long range.

The remainder of this paper is devoted to the evaluation of Eq. (12), in terms of an explicit formula for the nonlocal energy $E_c^{\rm nl}$. The scheme to achieve that goal, in general, can be stated as: (i) Make a simple, but physically sound, parameterization of $s_{\rm xc}$, based on previous studies of nonlocal functionals;[12,16,17,15] (ii) Adjust the parameterization to both regular and nonlocal key properties, utilizing previous studies of the XC hole.[7,8,20,18,19]

III. CONSTRAINTS ON $S_{\rm xc}$

The constraints on $s_{\rm xc}$ are numerous. This is fortunate, however, since it increases the prospects of parameterizations of $s_{\rm xc}$ to have meaning. What is not so fortunate, is that the number of parameters must be kept very low in order to get something practical, something that can be readily calculated. In any respect, the constraints tell us more about the nature of $s_{\rm xc}$, and gives a better insight in how to treat the nonlocal corrections, so to start with, those constraints will here be listed, one by one. Since what is sought is an understanding of the nonuniform system, the constraints will also be investigated under small deviations from uniformity, expressed in the reduced density gradient[22]

$$s(\mathbf{r}) = \frac{|\boldsymbol{\nabla} n(\mathbf{r})|}{2k_F n(\mathbf{r})}. \tag{13}$$

This s should not be confused with the polarizability operator $s_{\rm xc}$. The prescriptions later on will be for general densities, but in order to accurately define various components, it is important that the slowly varying limit is described appropriately.

A. Regular constraints on $s_{\rm xc}$

The regular energy is expressed in terms of the diagonal of $s_{\rm xc}$, $s_{\rm xc}(iu, \mathbf{r}, \mathbf{r})$, on which there are ample requirements via the known approximations to the exchange-correlation hole ($n_{\rm xc}$).[8,20,18,19] The basic sum rule is that the total XC hole must integrate to negative unity. This is by construction respected by $s_{\rm xc}$ (charge-conservation).[15] Another important constraint is given by the regular exchange-correlation energy. Other, more elaborate constraints concern the general shape of the exchange-correlation hole ($n_{\rm xc}$)[7] both in the uniform limit[8,20,18] and in a gradient environment.[19]

In the weakly perturbed limit, the exchange energy per particle is given by

$$\varepsilon_x[n] = -\frac{3}{4\pi}k_F(1+\mu_x s^2). \tag{14}$$

The gradient coefficient is known to be $\mu_x = 10/81$,[23] which is different from the earlier estimates,[24,25] but it is believed that the numbers presented here are the correct ones.[22] The coefficient for exchange-correlation is known in the high-density limit, $\mu_{\rm xc} = -0.1331$, yielding a positive contribution to the energy.[26] As devised in Ref. 26, the correlation coefficient should be $\mu_c = \mu_{\rm xc} - \mu_x = -0.2566$. It is enlightning to also write down the enhancement factor $F_{\rm xc}$,[18]

$$F_{\rm xc} = F_{\rm xc}^{\rm uni} + \mu_{\rm xc}s^2. \tag{15}$$

Equation (15) states that $F_{\rm xc}$ should decrease for a small perturbation, but the prevailing approximation to $F_{\rm xc}$, the GGA,[19] always increase with s, for delicate reasons.[27] The basic argument is that the term proportional to s^2 is improper for the long-ranged contributions to $E_{\rm xc}$. Another way to state this is: local or semilocal approximations, like LDA and GGA, *cannot by definition* account for the global change due to an applied perturbation, and therefore the exact global results does not apply, unless they are really local in nature.

This delicate state of affairs should be possible to improve upon, by investigating how the nonlocal energy Eq. (3) behaves under small perturbations; it is shown in Sec. IV that it is always positive. Following the introduction, it is expedient to decompose the enhancement factor into the two parts

$$F_{\rm xc} = F_{\rm xc}^0 + F_c^{\rm nl}, \tag{16}$$

with gradient coefficients μ_0 and $\mu_{\rm nl}$, respectively. The exchange is all contained in $F_{\rm xc}^0$, and since $E_c^{\rm nl}$ vanishes for a uniform system, one obtains in the slowly varying limit

$$F_{\rm xc}^0 = F_{\rm xc}^{\rm uni} + \mu_x s^2 + (\mu_c - \mu_{\rm nl})s^2, \tag{17}$$

and

$$F_c^{\rm nl} = \mu_{\rm nl}s^2. \tag{18}$$

From Eq. (17) and Eq. (18) it is clear that if $\mu_{\rm nl} \sim \mu_c$, the effective gradient coefficient for $F_{\rm xc}^0$ would behave similarly to the way $F_{\rm xc}$ is effectively implemented in the GGA (although $F_{\rm xc}^0$ is not by any means equal to the GGA). Apparently, the more regular changes in the energy should behave as the GGA, and together with Eq. (3), a full account for the global change should become within reach.

B. Nonlocal constraints on $s_{\rm xc}$

In the $u \to 0$, $q \to 0$ limit, corresponding to the integrated $s_{\rm xc}$, the polarizability and the known small-q behavior[28] puts additional constraints on $s_{\rm xc}$. The basic quantities are the polarizabilities and the van der Waals coefficients, together with more special ones, like the nonlocal surface energies.

A simple model of the polarization $\mathbf{P} = \alpha_{\rm ext}\mathbf{E}_{\rm ext}$ in response to an applied field $\mathbf{E}_{\rm ext}$ is

$$\alpha_{\rm ext} = \frac{\alpha}{1+4\pi\alpha/D}, \tag{19}$$

where α is the polarization response to the total field, $\mathbf{P} = \alpha\mathbf{E}$. The dimensionality factor D may vary between different objects. Equation 19 with $D = 2$ is exact for a planar step surface, and with $D = 3$, for hard spheres. Integrated over space, Eq. (19) is the static polarizability, α_0, which is restricted to an approximate interval, corresponding to the range of physical values of D.

In the case of perfect conduction, $\alpha \to \infty$, and Eq. (19) reduces to $\alpha_{\rm ext} \to D/4\pi$. Although true for a uniform, translationally invariant system, $\alpha \to \infty$ does *not* hold in a bounded, finite system.

A principal system, in which gradients plays a negligible role, is the system of two semi-infinite, planar surfaces, a distance d apart. The van der Waals attraction between the two surfaces has been studied,[29,15] yielding an energy on the form $-C_2/d^2$, and specifically, the effects beyond second-order expansions, the so-called multiple reflections, are small enough to justify a simple interaction picture. Since Eq. (3) is a second-order expansion in eigenvalues, it does not suffer, in principle, from the multiple reflection problem. To further simplify matters, the two surfaces will be taken to be steps, and of the same kind, so the asymptotic limit of this system may be evaluated and compared to the devised van der Waals coefficients, C_2. These have been obtained from the Lifshitz formula, using a simple model dielectric function,[29]

$$C_2^{\rm lifshitz} = \frac{0.006764}{r_s^{3/2}}, \tag{20}$$

where $r_s = (3/4\pi n)^{1/3}$ is the usual electron-gas parameter.

At this stage, it is necessary to discuss the applicability of the Lifshitz result to bounded systems. In Ref. 15, the C_2 coefficients obtained were substantially smaller than Eq. (20). It is of course possible that this discrepancy is due to some general non-account for long-ranged behavior in the dielectric function used,[15] but the more plausible explanation is that the true van der Waals forces actually are damped due to a broadening of the exchange-hole at the surface edge, an effect not accounted for in Eq. (20). To what extent this broadening affects the scaling with r_s is not known.

The reason for the discussion is that the resulting functional obtained in this paper exhibits a scaling drastically different from Eq. (20) in the high-density limit. Although the derived result should not be taken as fact, and there is reason to believe it is in turn underestimating the response at high density, it points to the possibility of a large discrepancy. It should be safe to state the following. E_c^{nl} does not, in general, contain all the correlation energy, although it should contain all truly nonlocal interactions, when treated in the RPA. What is often overlooked is that there are two distinctly different physical origins for long ranged correlations. One is due to an overlap of electrons, which occurs in regions of large densities, even if the density is varying. The other origin is the Coulombic interaction between points in space separated by regions of low density. Clearly, the first type will not survive across regions of small density, and the latter type should only be a fraction of the former in size. In the analysis that follows, it should be born in mind that although this question has been addressed, it has not been resolved.

IV. MODEL OF S_{xc}

In order to give a density functional account for the nonlocal energy, and arrive at an explicit form of $\varepsilon_{\mathrm{nl}}$, a specific model for s_{xc} shall now be adopted, and the corresponding $\varepsilon_{\mathrm{nl}}$ be derived.

The polarization operator s_{xc} is defined in terms of an isotropic dielectric function ϵ as

$$s_{\mathrm{xc}} = \ln(\epsilon). \tag{21}$$

In RPA, $\epsilon = \epsilon^{\mathrm{KS}}$, the isotropic non-interacting (Kohn-Sham) dielectric function.[30] In the uniform limit, a useful approximation is[31,15]

$$\hat{\epsilon}(iu, q) = 1 + \frac{\omega_p^2}{u^2 + \tilde{\omega}_q^2}, \tag{22}$$

where $\omega_p^2 = 4\pi n$, and $\tilde{\omega}_q$ is an appropriate dispersion model. The use of Eq. (22) in Eq. (21) gives a logarithmic form. However, the major objective here is to find a sufficiently simple, yet physically sound, approximation to s_{xc}, such that a useful formula for the nonlocal energy Eq. (3) can be found. To that end, it is more suitable to "undo" the integral over the coupling constant λ, to obtain

$$\hat{s}_{\mathrm{xc}}^{\mathrm{uni}}(iu, q) = \int_0^1 d\lambda \, \frac{\omega_p^2}{u^2 + \tilde{\omega}_q^2 + \lambda\omega_p^2}. \tag{23}$$

By the mean value theorem, Eq. (23) may also be written

$$\hat{s}_{\mathrm{xc}}^{\mathrm{uni}}(iu, q) = \frac{\omega_p^2}{u^2 + \tilde{\omega}_q^2 + \tilde{\lambda}(iu, q)\omega_p^2}. \tag{24}$$

In this way, the λ-dependence is absorbed into the dispersion, such that one may write

$$\hat{s}_{\mathrm{xc}}^{\mathrm{uni}}(iu, q) = \frac{\omega_p^2}{u^2 + \omega_q^2(iu)}. \tag{25}$$

To further simplify the resulting expressions, the frequency-dependence of ω_q will be neglected, thus resulting in an approximation for s_{xc} on the same form as the simple Eq. (22), although the appropriate dispersion model in Eq. (25) of course differs from the former.

Crude as this treatment may seem, it is still physical, for the following reasons: (i) The high-q and high-u limits are correctly accounted for. (ii) The low-u and low-q limits can not in general be accounted for separately but collectively. (iii) In many specific cases, the ratio ω_p/ω_q is actually small enough so that $s_{\mathrm{xc}} \approx 4\pi\alpha$ is a valid approximation. (vi) As a *direct*, beyond-RPA approximation to the *true* s_{xc}, Eq. (25) is on equal footing with Eq. (22). (v) Neither Eq. (25) nor Eq. (22) is *a priori* a good model for the nonuniform system, and hence can in either case only serve as a hint for the uniform limit; what is really needed is a reliable approximation for the *nonuniform* case.

A. Nonuniform Construction

To find a suitable approximation for the nonuniform s_{xc}, it is important that it obeys certain basic constraints. From Eq. (21), it is seen that s_{xc} must be hermitean, since ϵ is hermitean, *i.e.,* the reciprocity condition

$$s_{\mathrm{xc}}^*(iu, \mathbf{r}', \mathbf{r}) = s_{\mathrm{xc}}(iu, \mathbf{r}, \mathbf{r}') \tag{26}$$

must hold. Moreover, s_{xc} should be positive (semi) definite, since the eigenvalues of ϵ are real and greater or equal to unity. In the uniform limit, it should reduce to Eq. (25). An expression obeying these constraints is $s_{\mathrm{xc}} = aa^\dagger$, or explicitly,

$$s_{\mathrm{xc}}(iu, \mathbf{r}, \mathbf{r}') = \int d^3\bar{r} \, a(iu, \mathbf{r}, \bar{\mathbf{r}}) a^*(iu, \mathbf{r}', \bar{\mathbf{r}}), \tag{27}$$

where a is not subject to any particular symmetry constraints, and yet to be specified.

As it stands, Eq. (3) involves integrations over four space variables, which is computationally forbidding. To make a sufficient simplification, the form of a must be constrained, in such a way that four reduces to two. To that end, $a(iu, \mathbf{r}, \bar{\mathbf{r}})$ is first decomposed into Fourier components,

$$a(iu, \mathbf{r}, \bar{\mathbf{r}}) = \sum_q \hat{a}(iu, \bar{\mathbf{r}}, \mathbf{q}) e^{i\mathbf{q}\cdot(\mathbf{r}-\bar{\mathbf{r}})}, \tag{28}$$

where the summation sign denotes a properly normalized Fourier integral, $\sum_q = \int \frac{d^3q}{(2\pi)^3}$. Secondly, $\hat{a}(iu, \mathbf{q}, \bar{\mathbf{r}})$ is approximated by

$$\hat{a}(iu, \bar{\mathbf{r}}, \mathbf{q}) = \frac{\omega_p(\bar{\mathbf{r}})}{iu + \omega_q(\bar{\mathbf{r}})}. \tag{29}$$

An important detail of Eq. (29) is the spatial dependence, allowed to vary only in the $\bar{\mathbf{r}}$ space coordinate. In this way, when Eq. (27) is multiplied by a translationally invariant operator from either side, only the q-dependence will change, and the rest will stay intact, reducing the number of space integrations in Eq. (3) to two. From Eq. (29) it is easily seen that Eq. (27) reduces to Eq. (25) in the uniform limit.

B. Regular energy; E^0_{xc}

The particular form (27,28,29) for s_{xc} yields a particular approximation to E^0_{xc}, as follows. The regular energy is given by Eq. (2), involving the diagonal $s_{\mathrm{xc}}(iu,\mathbf{r},\mathbf{r})$. After integrating over u, one obtains

$$\sum_u s_{\mathrm{xc}}(iu,\mathbf{r},\mathbf{r}) = \int d^3\bar{r} \sum_{q,q'} \frac{\omega_p^2(\bar{\mathbf{r}}) e^{i(\mathbf{q}-\mathbf{q}')\cdot(\mathbf{r}-\bar{\mathbf{r}})}}{\omega_q(\bar{\mathbf{r}})+\omega_{q'}(\bar{\mathbf{r}})}. \quad (30)$$

The dependence on $\mathbf{r}$ is simple, and the integral can be performed to yield

$$\int d^3r \sum_u s_{\mathrm{xc}}(iu,\mathbf{r},\mathbf{r}) = \int d^3r \sum_q \frac{\omega_p^2(\mathbf{r})}{2\omega_q(\mathbf{r})}. \quad (31)$$

Equation (31) displays an energy precisely on the usual regular form. The self-interaction E_{self} may be decomposed in the same way, with ω_q replaced by

$$\omega_q^{\mathrm{self}} = q^2/2, \quad (32)$$

which is just the free-particle dispersion.[15] Dividing Eq. (31) by two, inserting $\omega_p^2 = 4\pi n$ and subtracting the decomposed E_{self} yields the regular energy

$$E^0_{\mathrm{xc}} = \int d^3r\, n(\mathbf{r})\varepsilon^0_{\mathrm{xc}}[n](\mathbf{r}), \quad (33)$$

where $\varepsilon^0_{\mathrm{xc}}[n](\mathbf{r})$ is the energy per particle,

$$\varepsilon^0_{\mathrm{xc}}[n](\mathbf{r}) \equiv \sum_q (\frac{\pi}{\omega_q[n](\mathbf{r})} - \frac{\pi}{\omega_q^{\mathrm{self}}}). \quad (34)$$

It must be born in mind that although Eq. (34) has a local appearance, it should still, in principle, contain all the "regular" nonlocal dependence on the density; it all depends on the dispersion model $\omega_q[n]$, which may in principle, and arguably should, be nonlocal.

As a comment, Eq. (34) is of course not intended to replace the LDA, but to serve as a ground point for the nonlocal energy, which would otherwise risk to become unphysical. The reasoning is that a model for s_{xc} must give a reasonable value for E^0_{xc} as well as E^{nl}_c, and the deviations should indicate the relative accuracy of the functional. A certain percental error in E^0_{xc} may be totally unacceptable, but the same error in the much smaller E^{nl}_c might be more than sufficient.

C. Asymptotic Limit; $\alpha(iu)$ and C_2

In the second order approximation, Eq. (3), it is easily shown that the asymptotic interaction between two well-separated objects a distance R apart is given by

$$E_{\mathrm{vdW}} = -\frac{1}{R^6}\frac{3}{\pi}\int_0^\infty du\, \alpha(iu)\alpha'(iu), \quad (35)$$

where the *prime* denotes different species, and the polarizabilities $\alpha(iu)$ are given by

$$\alpha(iu) = \frac{1}{4\pi}\int d^3r d^3r' s_{\mathrm{xc}}(iu,\mathbf{r},\mathbf{r}'), \quad (36)$$

which after insertion of Eq. (27) becomes

$$\alpha(iu) = \frac{1}{4\pi}\int d^3r\, \frac{\omega_p^2(\mathbf{r})}{u^2+\omega^2_{q=0}(\mathbf{r})}. \quad (37)$$

Equation (37) is reminiscent to the standard form,[32–34,11] although different in that here ω_q does not correspond exactly to the physical dispersion. Nevertheless, Eq. (37) should come out right in general, and specifically the static limit, $\alpha(0)$, should be compared with the model Eq. (19).

In the special case of two flat, parallel, semi-infinite surfaces, Eq. (35) may be further simplified. The integration of $1/R^6$ over the two surfaces yield $\pi/12d^2$ per surface area. The interaction between the two surfaces becomes $E_{\mathrm{vdW}} = -C_2/d^2$, with the C_2 coefficient

$$C_2 = \frac{n_0^2}{4}\int_0^\infty du\, \frac{1}{(u^2+\omega_0^2)(u^2+{\omega'_0}^2)}, \quad (38)$$

where ω_0 is the bulk value, independent of gradients. The frequency integral can be performed to yield

$$C_2 = \frac{\pi n_0^2}{8}\frac{1}{\omega_0\omega'_0(\omega_0+\omega'_0)}, \quad (39)$$

which should be compared with Eq. (20), given a particular model of ω_q.

An issue is whether a local approximation to s_{xc} can account for Eq. (37) in general, or whether gradient corrections to s_{xc} are needed. Also, there is an issue regarding the polarizability of a uniform system, which crucially depends on the macroscopic polarization.[35,36] The first issue will be discussed in Sec. V, whereas the second is left unanswered in this report.

D. Slowly varying limit; Z_{nl}

In the slowly varying, high-density limit, the nonlocal contribution E^{nl}_c may be found exactly. In that limit, Eq. (3) becomes, in principle, the exact deviation to E^{nl}_c, given the exact s_{xc}. The nonlocal response kernel $K_{\mathrm{nl}}(q)$ is defined via

$$\delta E^{\mathrm{nl}}_c[n] = \frac{1}{2}\sum_q K_{\mathrm{nl}}(q)\,|\delta n_q|^2\,. \quad (40)$$

$K_{\mathrm{nl}}(q)$ expressed in terms of s_{xc} is easiest found directly from Eq. (3). Consider a small perturbation from uniformity, $s_1 = s_0 + \delta s_0$, inserted into the trace of Eq. (3). Because $[s_0,\mathbf{T}] = 0$, $\mathbf{T}^2 = \mathbf{T}$ and $\mathrm{Tr}\,[A\mathbf{T}] = \mathrm{Tr}\,[A]$, for any scalar operator A, one obtains

$$\mathrm{Tr}\left[s_1^2 - (s_1\mathbf{T})^2\right] = \mathrm{Tr}\left[(\delta s_0)^2 - (\delta s_0\mathbf{T})^2\right], \qquad (41)$$

which means it is sufficient to go to first order in δs_0 to obtain the second order change in E_c^{nl}. Equation (3) becomes easier to analyze in "double Fourier" space,

$$E_c^{\mathrm{nl}}[n] = \frac{1}{4}\sum_{u,k,k'}(1-(\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}')^2)\left|\tilde{s}_{\mathrm{xc}}(iu,\mathbf{k},\mathbf{k}')\right|^2, \qquad (42)$$

with further details given in Appendix C. Equation (42) proves that $E_c^{\mathrm{nl}} \geq 0$ holds for all systems, and specifically that $K_{\mathrm{nl}}(q) \geq 0$.

To ease the comparison with existing calculations,[26] the gradient coefficient Z_{nl} is defined as

$$Z_{\mathrm{nl}} = \frac{4k_F^4}{3\pi}\nabla_q^2 K_{\mathrm{nl}}(q)|_{q=0}, \qquad (43)$$

which puts Z_{nl} on the same scale as Z_0.[26] After some algebra (Appendix C), one obtains

$$\nabla_q^2 K_{\mathrm{nl}}(q)|_{q=0} = \sum_{u,q}\frac{2}{q^2}\left|\frac{\delta\hat{s}_{\mathrm{xc}}^{\mathrm{uni}}(iu,q)}{\delta n}\right|^2. \qquad (44)$$

With the definition Eq. (43), the coefficient μ_{nl} of Sec. III becomes $\mu_{\mathrm{nl}} = -Z_{\mathrm{nl}}/9$.

E. Evaluation of E_c^{nl}

Consider the trace in Eq. (3) after insertion of Eq. (27). The cyclic property yields

$$\mathrm{Tr}\left[aa^\dagger\mathbf{T}aa^\dagger\mathbf{T}\right] = \mathrm{Tr}\left[a^\dagger\mathbf{T}aa^\dagger\mathbf{T}a\right]. \qquad (45)$$

Because of the particular form of a, $a^\dagger\mathbf{T}a$ may be evaluated directly,

$$a^\dagger\mathbf{T}a = \sum_q \frac{\omega_p(\mathbf{r})\omega_p(\mathbf{r}')\mathbf{T}(\mathbf{q})e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}}{(-iu+\omega_q(\mathbf{r}))(iu+\omega_q(\mathbf{r}'))}. \qquad (46)$$

After insertion into Eq. (3), and some algebra given in Appendix D, E_c^{nl} takes on the form of an effective electron-electron interaction energy,

$$E_c^{\mathrm{nl}} = \frac{1}{2}\int d^3r d^3r'\, n(\mathbf{r})\varepsilon_{\mathrm{nl}}(\mathbf{r},\mathbf{r}')n(\mathbf{r}'), \qquad (47)$$

which is the desired quantity. For a particular and sufficiently simple dispersion model, $\varepsilon_{\mathrm{nl}}[n](\mathbf{r},\mathbf{r}')$ may be readily evaluated and tabulated, hence yielding an explicit form for the interaction.

In the limit of large separations, $\varepsilon_{\mathrm{nl}}(\mathbf{r},\mathbf{r}')$ tends to

$$\varepsilon_{\mathrm{nl}}(\mathbf{r},\mathbf{r}') \to \frac{(-3/2)}{\omega_0(\mathbf{r})\omega_0(\mathbf{r}')(\omega_0(\mathbf{r})+\omega_0(\mathbf{r}'))\left|\mathbf{r}-\mathbf{r}'\right|^6}, \qquad (48)$$

with details given in Appendix D. Eq. (48) is in agreement with Eq. (35) and Eq. (39), and in form, although as discussed not in detail, to prior results.[34]

V. DISPERSION MODEL

Given the construction in Sec. IV, the next step is to pick a particular form of the dispersion $\omega_q(\mathbf{r})$, and fit to most or all of the constraints outlined in Sec. III. Before commencing, the essential features of ω_q should be discussed.

In the long-ranged van der Waals limit, it is utterly important that the polarizability is finite for all densities. This is stressed, because naively applying a typical bulk dielectric function, such as the Drude formula, leads to a gross overestimate of the response at low densities.[37] To remedy this, the use of some kind of cutoff[34] has been nescessary.[11,12,17,15] In this work, the cutoff is built directly into the dispersion model in a *smooth* fashion, as opposed to the prior sharp ones, making the model applicable also in the intermediate range.

The second essential limit is the large-q, or Coulomb scattering, limit. In order to cancel the singularity in E_{self}, and to produce finite regular energies, $\omega_q \to \omega_q^{\mathrm{self}}$, must hold as $q \to \infty$, *i.e.*, the free-electron model. With those basic features settled, the goal is to find a reasonable interpolation between the two extremes, so as to account for the constraints as accurately as possible.

In order to keep the parameterization of s_{xc} tractable, ω_q should ultimately only depend on one spatial parameter, $q_0(\mathbf{r})$. The generic dispersion model that will be investigated here is given the form

$$\omega_q(\mathbf{r}) = q^2/2h(q/q_0(\mathbf{r})), \qquad (49)$$

where $h(y)$ is a scaling function. This is of course a severe restriction, but is done out of necessity; the benefits from having a tractable model for the nonlocal energy are sufficiently many so as to justify this rather crude treatment.

From Eq. (37), it is clear that $\omega_{q\to 0}(\mathbf{r})$ must be finite in order to produce finite static ($u=0$) polarizabilities, so $h(y) \to y^2$ as $y \to 0$. For large y, $h(y) \to 1$, to recover the free-electron limit.

In the uniform limit, the scaling function $h(q)$ is exactly related to the wave-vector decomposition of the coupling-constant averaged exchange-correlation hole[20] $\bar{n}_{\mathrm{xc}}(q)$ as

$$h(y) = 1 + \bar{n}_{\mathrm{xc}}(q_0 y), \qquad (50)$$

which follows after some manipulations of Eq. (A1).

The quantities of Sec. IV may be simply expressed in terms of $h(y)$. The regular energy, Eq. (34), becomes

$$\varepsilon_{\mathrm{xc}}^0(\mathbf{r}) = \frac{q_0(\mathbf{r})}{\pi}\int_0^\infty dy\,(h(y)-1), \qquad (51)$$

where the integral is just a number, depending only on the scaling function $h(y)$. The polarizability Eq. (37) becomes

$$\alpha(iu) = \int d^3r\,\frac{n(\mathbf{r})}{u^2 + (q_0^2(\mathbf{r})/h_0'')^2}, \qquad (52)$$

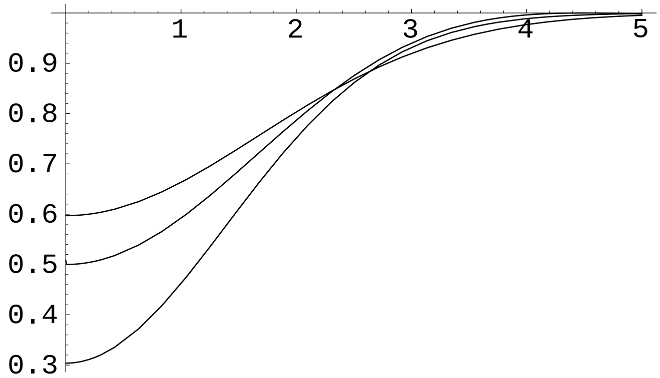

FIG. 2. The pair distribution function $g(x = k_F r)$, obtained from the Gaussian model, Eq. (55), compared to the uniform exchange hole (middle). The figure shows $g(x)$ for two values of f, Eq. (65). *Upper curve:* $f = 1$. *Lower curve:* $f = 1.2$.

where h''_0 is the second derivative with respect to y at the origin. The C_2 coefficient, Eq. (39), becomes

$$C_2 = \frac{\pi n^2}{16(q_0^2/h''_0)^3} = \frac{k_F^6}{144\pi^3(q_0^2/h''_0)^3}, \tag{53}$$

containing only bulk properties. The gradient coefficient $Z_{\rm nl}$ depends more intricately on the scaling function $h(y)$, and will be treated separately.

Clearly, the value of h''_0 is very important, and should ultimately be a function of the density. However, this immediately imposes some problems, since a single-parameter model is sought, for computational reasons. Also, it is not clear how much h''_0 affects Eq. (51), for instance, so even with a more general prescription, a great deal of additional knowledge would need to be added, knowledge that goes beyond local and semilocal treatments. As an example of this, consider the value of h''_0 in the uniform RPA, obtained from inserting the small-q expansion of Ref. 20 into Eq. (50),

$$h_0''^{\rm uni-RPA} = 3.070 q_0^2/k_F^{3/2}. \tag{54}$$

Inserted into Eq. (53) yields $C_2 = 0.01723/r_s^{3/2}$, a factor 2.5 times larger than the Lifshitz result, Eq. (20). This suggests that long-ranged behavior may have poor transferability from the uniform limit to the nonuniform case – even if the error is due to the approximations made. In that respect, integrated quantities like energies should be much more reliable.

Notably, q_0 and h''_0 enter both Eq. (52) and Eq. (53) as q_0^2/h''_0, so a consistent treatment of those two quantities is possible. Equation (51) presumably scales differently with h''_0 in general. Judging from the argument of the previous paragraph, it might be better to use in fixing the scaling of $h(y)$ than the former ones. The most important property is the gradient coefficient, $Z_{\rm nl}$, however, since it should both be readily transferable to the nonuniform case *and* important to the size of the nonlocal energy, so the main concern is to choose $h(y)$ such that $Z_{\rm nl}$ becomes reasonable.

A. Scaling function $h(y)$

A reasonable scaling function $h(y)$ is the simple Gaussian,

$$h^{\rm gauss}(y) = 1 - e^{-\eta y^2/2}, \tag{55}$$

with $h''_0 = \eta$. With Eq. (55), Eq. (51) also scales with $q_0/\sqrt{h''_0}$, so η may be chosen arbitrarily. A suitable choice is $\eta = 8\pi/9$, for which Eq. (51) becomes

$$\varepsilon_{\rm xc}^{0\ \rm gauss}[n] = -\frac{3}{4\pi} q_0[n] \equiv -\frac{3}{4\pi} k_F f[n], \tag{56}$$

which has the same appearance as Eq. (14). A comparison of the pair distribution corresponding to Eq. (55), and that of the uniform exchange hole is shown in Fig. 2. The on-top hole becomes negative for $f > 1.35$, a documented flaw of RPA approximations.[20]

Inserting Eq. (55) into Eq. (44), an explicit expression for the gradient coefficient, $Z_{\rm nl}$, in terms of the parameter $q_0[n]$, may be obtained. After differentiation of Eq. (25) and a considerable amount of algebra (not repeated here) one finds

$$Z_{\rm nl}^{\rm gauss} = \frac{r_s(1.893 + 0.3687 p(r_s) + 10.20 p^2(r_s))}{f^5(r_s)}, \tag{57}$$

where p is the logarithmic derivative $p = r_s f'(r_s)/f(r_s)$.

B. Evaluation of $E_c^{\rm nl}$

With Eq. (49), Eq. (47) may be further specified. Let

$$q_{\rm eff} = \sqrt{(q_0^2 + {q'_0}^2)/2}, \tag{58}$$

$$\gamma = (q_0^2 - {q'_0}^2)/(q_0^2 + {q'_0}^2). \tag{59}$$

Then $q_0 = \sqrt{1+\gamma}\, q_{\rm eff}$ and $q'_0 = \sqrt{1-\gamma}\, q_{\rm eff}$. Further let $x = q_{\rm eff}\,|\mathbf{r} - \mathbf{r}'|$, and define

$$\nu_y = y^2/2h(y/\sqrt{1+\gamma}x), \tag{60}$$

$$\nu'_y = y^2/2h(y/\sqrt{1-\gamma}x). \tag{61}$$

Using the result of Appendix D, the nonlocal interaction $\varepsilon_{\rm nl}(\mathbf{r}, \mathbf{r}')$ can then be expressed in terms of a simple function $\varepsilon_{\rm nl}(\gamma, x)$,

$$\varepsilon_{\rm nl}(\mathbf{r}, \mathbf{r}') = \varepsilon_{\rm nl}(\gamma, q_{\rm eff}\,|\mathbf{r} - \mathbf{r}'|), \tag{62}$$

where

$$\varepsilon_{\rm nl}(\gamma, x) = \frac{(4\pi)^2}{2} \sum_{y_1, y_2} \frac{v(y_1, y_2)}{y_1^3 y_2^3} \times \frac{1}{(\nu_{y_1} + \nu'_{y_1})(\nu_{y_2} + \nu'_{y_2})} \left(\frac{1}{\nu_{y_1} + \nu_{y_2}} + \frac{1}{\nu'_{y_1} + \nu'_{y_2}}\right). \tag{63}$$

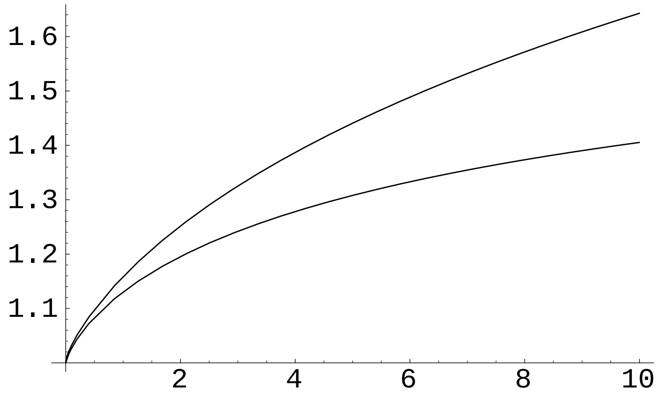

FIG. 3. The enhancement factor ${F_{\rm xc}}^{10}$, versus r_s. *Upper curve:* LDA in the RPA, Eq. (66). *Lower curve:* LDA, obtained from Ref. 22.

The function $v(y_1, y_2)$ is given in Eq. (D7). Equation (63) is a two-valued function, which can be readily tabulated as a function of γ and x. Figure 1 shows $\varepsilon_{\rm nl}(\gamma, x)$ for different values of γ. Notably, is is almost independent of γ at short range, whereas the effect becomes large at intermediate and long range. The long-range limit becomes

$$\varepsilon_{\rm nl}(\gamma, x) \to -\frac{3}{2}\frac{1}{\nu_0\nu_0'(\nu_0+\nu_0')} = -\frac{3\eta^3}{4(1-\gamma^2)x^6}, \qquad (64)$$

which of course is equivalent to Eq. (48).

C. Uniform scaling; $F_{\rm xc}$

Dividing Eq. (56) by the exchange energy one obtains an expression for $f[n]$ in terms of the regular enhancement factor, Eq. (17),

$$f[n] = F_{\rm xc}^0[n]. \qquad (65)$$

In the uniform limit, Eq. (56) is the only contribution to $E_{\rm xc}$, $F_{\rm xc}^0 = F_{\rm xc}^{\rm uni}$, and since the nonlocal energies are small, $f[n]$ should in general scale as $F_{\rm xc}[n]$, although for nonuniform systems not exactly.

In the high density limit, $F_{\rm xc} \to 1$, and the XC hole tends to the exchange hole, suggesting that f should approach unity. From Eq. (57), it is seen that if f tends to unity, $Z_{\rm nl}$ must tend to zero. For comparison, the total correlation gradient coefficient, Z_c, approaches a constant as $r_s \to 0$.[26,38] More severely, C_2 approaches a constant, in sharp contrast to the assumed scaling Eq. (20). On the one hand, a complete independence of r_s at high densities does not seem quite right, but on the other hand, Eq. (20) is based on the dielectric function in the Drude form, and no effect of the broadening of the exchange-hole has been taken into account, an effect that is also supported by intermediate-range studies of the same system.[15] Although it would be sufficient for f to slowly approach zero as r_s approaches zero, in order for C_2 to scale like Eq. (20), that seems severely inappropriate, since it would mean that the regular energy approaches zero, which is clearly not the case. With this and the comment on Eq. (54) in mind, it is judged more important to assure a reasonable scaling of the regular energy, and so at present, $f \to 1$, as $r_s \to 0$, is adopted.

In the low density limit, the polarizability density should increase slowly or reach some finite value. C_2 should naturally decrease. Moreover, $F_{\rm xc}^0$ should increase, preferably approaching an upper limit so as to satisfy the Lieb-Oxford bound.[39] However, since the electron gas undergoes a transition to the nonuniform Wigner lattice, there are now *two* energies. This means that the limit on $F_{\rm xc}^0$ can be relaxed somewhat, as long as the nonlocal energy increases at the same rate as the regular energy decreases. Eq. (53) suggests that $f[n] \to r_s^{1/4}$, as $r_s \to \infty$, roughly in line also with the increase of Eq. (52), the decrease of $Z_{\rm nl}$, and the increase of $F_{\rm xc}$.

At all densities, as stated, the scaling of $f[n]$ should follow $F_{\rm xc}$, which is possible if $F_{\rm xc}$ scales as described above. The scaling of $F_{\rm xc}$ depends on the actual approximation used for the energy of the uniform electron gas. In the RPA, a simple parameterization may be found,

$$F_{\rm xc}^{\rm RPA}[n] = (1 + 0.2534 r_s^{1/2} + 0.5484 r_s)^{1/4}, \qquad (66)$$

which is accurate enough for the present purpose. It reproduces the known low-density limit of RPA,[20] and does scale as desired. A comparison between Eq. (66) and the LDA[22] is shown in Fig. 3.

As a further consistency check, the C_2 coefficient as a function of r_s, obtained using Eqs. (55) and (66), is shown in Fig. 4, compared to Eq. (20). At $r_s = 2$, the C_2 coefficient is well in line with the findings of Ref. 15.

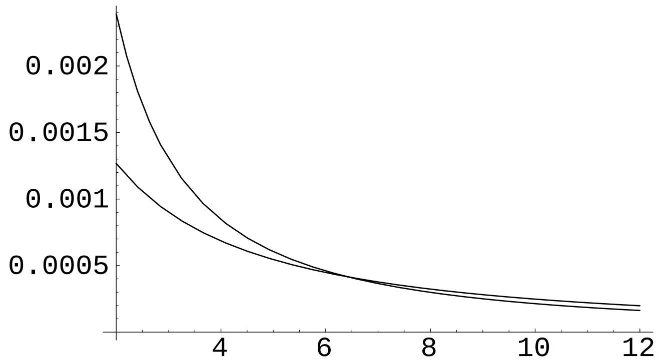

FIG. 4. *Lower curve:* The $C_2[n]$ coefficient of Eq. (53) versus r_s, using $f[n] = F_{\rm xc}^{\rm RPA}[n]$. *Upper curve:* Eq. (20).

D. Nonuniform scaling

The r_s-dependence of the gradient coefficient $Z_{\rm nl}(r_s)$ is shown in Fig. 5. The somewhat unexpected behavior at small r_s is an open question, not resolved in this report.

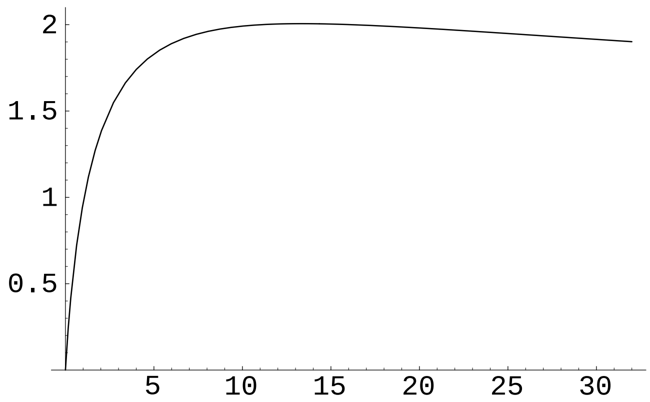

FIG. 5. The Z_{nl} coefficient of Eq. (57), versus r_s.

According to Eq. (17), and using $F_{\mathrm{xc}}^{\mathrm{RPA}}$, $f[n]$ is in the slowly varying limit given by

$$f[n] = F_{\mathrm{xc}}^{\mathrm{uni}}[n] + \mu_0[n]s^2. \tag{67}$$

As Eq. (67) correctly suggests, it is inappropriate to implement a response cutoff solely in a local approximation; the detailed behavior of the static polarizability density requires a generalization of $f[n]$ to also depend on the gradient. For large s, it may seem natural to simply extend Eq. (66) according to the GGA enhancement factor.[10] However, both the LDA and GGA F_{xc} respects the Lieb-Oxford bound locally, approaching a constant as $r_s \to \infty$, quite different from $F_{\mathrm{xc}}^{\mathrm{RPA}}$. Moreover, Eq. (67) would not cut off the response completely if s were saturated, as in the GGA. Equation (67) should be used as is.

In order to evaluate Eq. (67), the coefficient μ_0 needs to be determined. A complete discussion will not be performed here, but rather a simple straight-forward choice will be devised and tested. The cutoff becomes important in the low-density tails at the boundary of a body. In the low-density region, it is seen from Fig. 5 that $Z_{\mathrm{nl}}(r_s) \approx 2$, the value of the correlation coefficient in the Langreth-Mehl functional.[40] The decrease of Z_{nl} for large r_s is also consistent with the known behavior, as calculated by Rasolt and Geldart.[38] Adding these two observations, one may conclude that $\mu_{\mathrm{nl}} \approx \mu_c$ in that region. Further, adopting the argument of Ref. 10, that in order to retain the linear response properties of LDA, $\mu_{\mathrm{xc}} = 0$ must hold (for small s), it implies that $\mu_x = -\mu_{\mathrm{nl}}$, which for $Z_{\mathrm{nl}} = 2$ becomes very close to the effective exchange gradient coefficient, $\mu_{\mathrm{eff}} = 0.2195$, used in the GGA.[10]

VI. RESULTS

TABLE I. Nonlocal jellium surface correlation energies γ_{nl}, obtained by evaluating Eq. (47) using Eq. (63) and Eq. (68).

r_s	γ_{nl} [a]	γ_{nl} [b]
2.00	366	472
2.07	366	432
2.30	281	329
2.66	200	223
3.00	154	160
3.28	114	127
4.00	73	72
5.00	40	37

[a]This work. [b]Reference 41.

TABLE II. Atomic polarizabilities and van der Waals coefficients, obtained from Eqs. (52) and (68). Roothan-Hartree-Fock densities were used.

Atom	α_0 [a]	α_0 [b]	C_6 [c]	C_6 [d]
H	2.42	4.5	2.53	6.5
He	0.71	1.38	0.51	1.46
Li	48.5	164	246	1390
Be	18.4	37.5	78.5	212
Ne	1.26	2.67	2.07	6.9
Mg	32.3	70	186	620
Ar	5.15	11.1	20.1	67
Kr	7.74	16.7	38.4	133
Xe	12.7	27.3	85.9	299
C_{60}	386	570	67k	125k

[a] This work. [b] Ref. [c] This work. [d] Ref.

Using the universal function Eq. (63), and the following expression for $f[n]$,

$$f[n] = F_{\mathrm{xc}}^{\mathrm{RPA}}[n] + \mu_{\mathrm{eff}}s^2, \tag{68}$$

where $\mu_{\mathrm{eff}} = 0.2195$, Eq. (3) may be calculated for explicit physical systems. The following paragraphs show some illustrative comparisons to prior results, showing an overall good agreement.

Table I shows the result for the nonlocal correction to the surface energy of jellium, compared to other data.[42,43,41] The dependence of $f[n]$ on gradients has a negligible effect in this case. The discrepancies at smaller r_s are due to the neglect of the change in the regular correlation, reflected in the fact that $Z_{\mathrm{nl}}(r_s) \neq Z_c$, and an additional regular correlation energy should be added to retain the full nonlocal correlation energy. The corrections from also taking gradients into account in Eq. (67), however, are very small.

Table II shows the static polarizability and van der Waals coefficients C_6, calculated from the asymptotic formula, Eq. (52), and using Eq. (68). The coefficients are much too small, pointing at the difficulty to find a parameterization, with which the asymptotic behavior *and* the intermediate-range behavior are reproduced simultaneously. The severe underestimation is in line with what was previously reported for surfaces and slabs.[15] Even if much of the discrepancy may be remedied by more elaborate cutoff functions, Eq. (67), this remains an unsolved problem.

In Fig. 6, the interaction energy between two slabs of jellium $r_s = 2.07$ is shown, calculated from Eq. (67) with

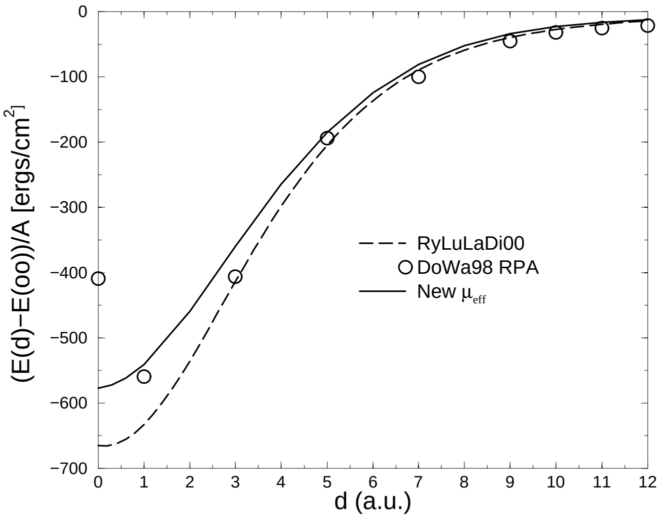

FIG. 6. The nonlocal correlation energy between two slabs of jellium. *Circles:* Ref. 14. *Solid line:* Result using μ_{eff}. *Dashed line:* Result using μ_0.

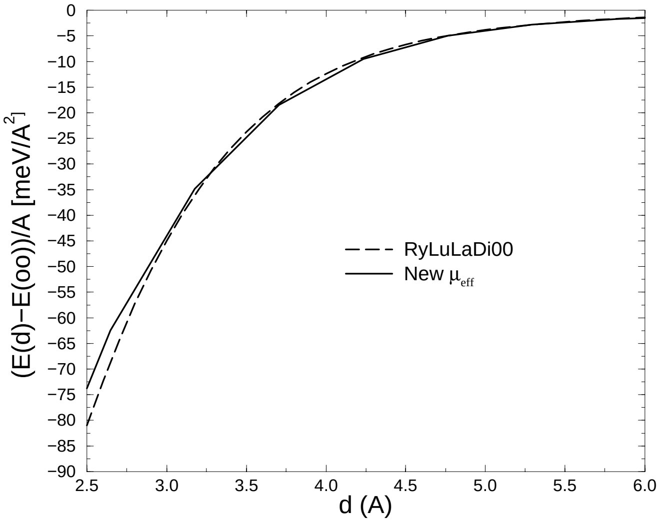

FIG. 7. The nonlocal correlation energy between two graphene slabs. *Solid Line:* Ref. 15. *Circles:* Result using μ_{eff}. *Diamonds:* Result using μ_0.

$\mu = \mu_{\mathrm{eff}}$ added. The comparison with benchmark data[14] can be seen to be generally good.

In Fig. 7, the interaction energy between two laterally averaged sheets of graphite, graphene, is shown. The calculation is in close agreement with Ref. 44, which has an additional parameter, fixed to a DFT calculation, as input. This indicates that it is possible to find functional forms with parameters built in in a physical way.

VII. CONCLUSIONS

In conclusion, A DFT scheme is proposed that provides a basis for systematic improvements beyond the local (LDA) and semilocal density approximations (GGA), to incorporate medium- and long-ranged correlations. The exchange-correlation energy is decomposed into two parts, expressed in terms of a generalized polarization operator, s_{xc}. A parameterization is devised, and fitted to the regular XC energy in the RPA. The relation between the essential cutoff and the regular enhancement factor is shown. An explicit nonlocal density functional is developed, and tested on several prior studies. The parameterization does not reproduce the long-ranged behavior well but yield results for the intermediate-range energies in close agreement with prior studies.

Although caution is needed, and many issues have been unanswered in this report, the simplistic nature of the functional and the excellent results for the intermediate-ranged regime bring great promise.

APPENDIX A: DETAILS ON THE EXISTENCE OF ϵ

To render the treatment of Ref. 15 and Sec. II exact, ϵ should satisfy the equation

$$\boldsymbol{\nabla} \cdot \epsilon \boldsymbol{\nabla} \mathrm{G} = e^{-\int_0^1 d\lambda\, \chi_\lambda V}, \tag{A1}$$

where χ_λ is the exact many-body response function at coupling-strength λ and $V = -4\pi\mathrm{G}$. The issue is whether $\epsilon(\mathbf{r}, \mathbf{r}')$ exist, *i.e.,* whether ϵ can be taken to be isotropic without loss of generality. It suffices to prove that there exist a ϕ such that

$$\boldsymbol{\nabla}_r \cdot \boldsymbol{\nabla}_{r'} \phi(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}, \mathbf{r}'), \tag{A2}$$

for an arbitrary bounded, charge-conserving function $\rho(\mathbf{r}, \mathbf{r}')$, *i.e.,* that satisfy

$$\int d^3r\, \rho(\mathbf{r}, \mathbf{r}') = \int d^3r'\, \rho(\mathbf{r}, \mathbf{r}') = 0, \tag{A3}$$

and which vanishes outside some region Ω. In Fourier space, Eq. (A2) transforms to

$$(-i\mathbf{q} \cdot \boldsymbol{\nabla}_r + q^2)\hat{\phi}(\mathbf{r}, \mathbf{q}) = \hat{\rho}(\mathbf{r}, \mathbf{q}), \tag{A4}$$

where $\hat{\phi}(\mathbf{r},\mathbf{q})$ (and analogously $\hat{\rho}(\mathbf{r},\mathbf{q})$) is defined via

$$\phi(\mathbf{r},\mathbf{r}') = \int \frac{d^3q}{(2\pi)^3}\hat{\phi}(\mathbf{r},\mathbf{q})e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}. \tag{A5}$$

One solution to Eq. (A4) is

$$\hat{\phi}(\mathbf{r},\mathbf{q}) = \frac{1}{2iq}\int_{-\infty}^{\infty} dt\, \mathrm{sgn}\,(t)\, e^{iqt}\hat{\rho}(\mathbf{r}+t\hat{\mathbf{q}},\mathbf{q}), \tag{A6}$$

which is proved by inserting Eq. (A6) into Eq. (A4). Moreover, if ρ is real, ϕ is also real, since

$$\begin{aligned}\hat{\phi}^*(\mathbf{r},-\mathbf{q}) &= -\frac{1}{2iq}\int_{-\infty}^{\infty} dt\, \mathrm{sgn}\,(t)\, e^{-iqt}\hat{\rho}^*(\mathbf{r}-t\hat{\mathbf{q}},-\mathbf{q}) \\ &= -\frac{1}{2iq}\int_{-\infty}^{\infty} dt\, \mathrm{sgn}\,(t)\, e^{-iqt}\hat{\rho}(\mathbf{r}-t\hat{\mathbf{q}},\mathbf{q}) \\ &= \frac{1}{2iq}\int_{-\infty}^{\infty} dt\, \mathrm{sgn}\,(t)\, e^{iqt}\hat{\rho}(\mathbf{r}+t\hat{\mathbf{q}},\mathbf{q}) = \hat{\phi}(\mathbf{r},\mathbf{q}). \end{aligned} \tag{A7}$$

In the case of translational invariance, $\hat{\rho}$ becomes independent of $\mathbf{r}$, and the t integral of Eq. (A6) may be done, yielding $\hat{\phi}(\mathbf{q}) = \hat{\rho}(\mathbf{q})/q^2$, in accordance with Eq. (A4).

To conclude this appendix: there exist at least one isotropic ϵ that satisfies Eq. (A1). What was prior[15] assumed to be an approximative treatment turns out to be completely general.

APPENDIX B: DETAILS ON THE CONVERGENCE OF THE Δ SERIES

1. Convergence of Δ_n

In order for the series Eq. (6) to be interesting it has to converge rapidly, which is the case at least in the limit of small variations. To prove this, the use of the energy norm $||A||^2 = \mathrm{Tr}\left[A^\dagger A\right]$ turns out useful. First, write s_{xc} in its diagonal basis,

$$s_{\mathrm{xc}}(iu,\mathbf{r},\mathbf{r}') = \sum_k s_k(iu)\psi_k(iu,\mathbf{r})\psi_k^\dagger(iu,\mathbf{r}'). \tag{B1}$$

In what follows, the frequency dependence is suppressed for notational clarity. Next, express the energy norm in the ψ_k basis,

$$||\mathbf{d}_n||^2 = \sum_{u,i,j} |d|^2_{i,j}\,(s_i - s_j)^{2n}, \tag{B2}$$

where

$$\mathbf{d}_{i,j} = \int d^3r\, \psi_i^\dagger(\mathbf{r})\boldsymbol{\nabla}\psi_j(\mathbf{r}). \tag{B3}$$

From Eq. (B2), it is clear that the following inequality holds,

$$||\mathbf{d}_{n+1}|| \le \kappa||\mathbf{d}_n||, \tag{B4}$$

where κ is the difference between the largest and the smallest eigenvalue of s_{xc}, which is equivalent to the logarithm of the condition number of ϵ, $\kappa = \ln(\epsilon_{\max}/\epsilon_{\min})$. For sufficiently small variations, not necessarily slow, $\kappa < 1$, and the convergence of the sequence $\mathbf{d}_n$ is exponential. Due to the factorial constant in Eq. (6), together with Eq. (B4), the series converges extremely fast: only the first few terms need to be considered. For example, provided $\kappa < 1/2$, the series may be truncated at $n = 2$, with less than 5% relative error.

Although for the level of approximation aimed at here, the above argument is sufficient, Eq. (B4) is not limited to small variations. For instance, consider a localized basis ψ_i on the form Eq. (B1), where each basis function is localized around a point $\mathbf{r}_i$. In such a case, the points $\mathbf{r}_i$ form a spatial distribution in space, and both s_i and $d_{i,j}$ follow the same topology. One could then define a smooth function $s(\mathbf{r})$, which interpolates between all the points $\mathbf{r}_i$. In the vicinity of each point, then, the variations in $s(\mathbf{r})$ are bounded by a Leibnitz criterion

$$|s(\mathbf{r}) - s(\mathbf{r}_i)| \le |\mathbf{r}-\mathbf{r}_i|\,/l_d, \tag{B5}$$

where l_d denotes the minimum length scale on which $s(\mathbf{r})$ varies. In the same manner, $d_{i,j}$ can be expressed as an interpolating function $d(\mathbf{r},\mathbf{r}')$. Since $\boldsymbol{\nabla}$ has compact support, the decay of $d(\mathbf{r},\mathbf{r}')$ is governed by the decay of the basis functions ψ_i. Provided the basis functions are sufficiently localized, it makes sense to define a length-scale l_s such that $d(\mathbf{r}_i,\mathbf{r})$ is negligible outside the radius $|\mathbf{r}-\mathbf{r}_i| < l_s$. Equation (B5) then never exceeds l_s/l_d, and inserting into Eq. (B2) yields the inequality

$$||\mathbf{d}_{n+1}|| \le \frac{l_s}{l_d}\,||\mathbf{d}_n||. \tag{B6}$$

Hence the series Eq. (6) converges rapidly whenever the "screening length" l_s is smaller than l_d, the scale of the variations in s_{xc}. This criterion is for example obeyed by the particular approximation to ϵ used in Ref. 15.

There are more properties of $\mathbf{d}_n$ worth noting. The odd orders of $\mathbf{d}_{2k+1}$ are hermitian, whereas the even orders $\mathbf{d}_{2k}$ are anti-hermitian, which follows directly from the definition Eq. (7). Hence, it makes little sense physically to consider more than the two first terms, from the symmetry argument alone.

To conclude so far: Equation (B4) is the key point, with $\kappa \ll 1$ at least in the case of sufficiently small variations, with an argument suggesting that it holds true also in other, more general cases. A value smaller than $\kappa < 1/2$ leads to such a fast convergence of the series Eq. (6) that only the first two terms $\mathbf{d}_1$ and $\mathbf{d}_2$ need to be considered.

2. Convergence of $\ln(1+\Delta)$

In order for Eq. (8) to have meaning, the error needs to be small. An exact upper bound may be found using the energy norm introduced in Appendix B 1. Let $\delta = ||\Delta||$. By virtue of the Cauchy-Schwarz inequality, each power of Δ is bounded by δ,

$$\left|\mathrm{Tr}\left[\Delta^k\right]\right| \le ||\Delta||^k \equiv \delta^k. \tag{B7}$$

Expanding the trace of $\ln(1+\Delta)-\Delta(1+\Delta/2)$ in a Taylor series, one obtains

$$\left|\sum_{k=3}^{\infty}\frac{(-1)^k}{k}\mathrm{Tr}\left[\Delta^k\right]\right| \le \sum_{k=3}^{\infty}\frac{1}{k}\left|\mathrm{Tr}\left[\Delta^k\right]\right| \le \sum_{k=3}^{\infty}\frac{1}{k}\delta^k$$
$$= \ln(1/(1-\delta)) - \delta(1+\delta/2) = \mathcal{O}(\delta^3). \tag{B8}$$

Eq. (B8) gives a relative error in Eq. (8) smaller than 1% whenever $\delta < 0.2$, roughly. To put δ in context, the relation to the convergence ratio κ shall now be derived. Using the triangle inequality and Eq. (6),

$$\delta = ||\Delta|| \le \sum_{n=1}^{\infty}||\Delta_n||. \tag{B9}$$

From Eq. (B2), it is clear that $\mathbf{d}_n$ scales with κ^n for $n > 1$, with the addition that s_{xc} is bounded also for $n = 1$. Since $\mathbf{d}_n$ scales with κ^n, and Δ_n is bounded, there must exist a constant C, independent of κ and n, such that

$$||\Delta_n|| = \frac{1}{n!}||\mathbf{d}_n \cdot \mathbf{d}_0\mathrm{G}|| \le C\frac{\kappa^n}{n!}. \tag{B10}$$

Inserting Eq. (B10) into Eq. (B9) one obtains the simple inequality

$$\delta \le C(e^{\kappa}-1). \tag{B11}$$

The constant C is system-dependent and cannot be known *a priori*, but will here be assumed to be small enough for Eq. (8) to be valid. For sufficiently small κ, $\delta \approx C\kappa$, and only terms to second order in κ need to be kept in Eq. (8). By Eq. (B7), this means keeping Δ_1 and Δ_2 for the first order term, but only Δ_1 for the second term. Also, at small κ, $\delta \approx ||\Delta_1||$, which may be expressed explicitly in fourier space as

$$\delta^2 \approx ||\Delta_1||^2 = \int\frac{d^3q d^3r}{(2\pi)^3 q^2}\left|\hat{\mathbf{q}}\cdot\boldsymbol{\nabla}_r\hat{s}_{\mathrm{xc}}(iu,\mathbf{r},\mathbf{q})\right|^2, \tag{B12}$$

where $\hat{s}_{\mathrm{xc}}(iu,\mathbf{r},\mathbf{q})$ is defined as in Eq. (A5). From Eq. (B12), it is evident that δ is small for a slowly varying system. Moreover, because of the $1/q^2$ term, variations in s_{xc} at small q will be noticeable, whereas variations at large q may be forgiven. Since small q measures structure on a large length scale, the spatial variations are expected to be smaller, and although here only proven in the limit of small or slow perturbations, one could suspect that Eq. (B12) is small for a larger class of density variations.

APPENDIX C: DETAILS ON THE EVALUATION OF Z_{nl}

The "double fourier" transform of $\tilde{s}_{\mathrm{xc}}(iu,\mathbf{k},\mathbf{k}')$ is defined as

$$\tilde{s}_{\mathrm{xc}}(iu,\mathbf{k},\mathbf{k}') = \int d^3r d^3r'\, e^{-i\mathbf{k}\cdot\mathbf{r}} s_{\mathrm{xc}}(iu,\mathbf{r},\mathbf{r}') e^{i\mathbf{k}'\cdot\mathbf{r}'}. \tag{C1}$$

Inserting Eq. (27) into Eq. (C1) one obtains

$$\tilde{s}_{\mathrm{xc}}(iu,\mathbf{k},\mathbf{k}') = \int d^3\bar{r}\,\frac{\omega_p^2(\bar{\mathbf{r}})e^{i(\mathbf{k}'-\mathbf{k})\cdot\bar{\mathbf{r}}}}{(iu+\omega_k(\bar{\mathbf{r}}))(-iu+\omega_{k'}(\bar{\mathbf{r}}))}. \tag{C2}$$

The first-order change of $\omega_k[n]$ on $\delta n(\mathbf{r})$, when starting from the uniform limit, must be a translationally invariant function, so according to Eq. (C2), the change $\delta\tilde{s}_0(iu,\mathbf{k},\mathbf{k}')$ must take the form

$$\delta\tilde{s}_0 = \int d^3\bar{r} d^3r e^{i(\mathbf{k}'-\mathbf{k})\cdot\bar{\mathbf{r}}} w_{iu,k,k'}(\bar{\mathbf{r}}-\mathbf{r})\delta n(\mathbf{r}), \tag{C3}$$

where

$$w_{iu,k,k'}(\bar{\mathbf{r}}-\mathbf{r}) = \frac{\delta}{\delta n(\mathbf{r})}\frac{\omega_p^2(\bar{\mathbf{r}})}{(iu+\omega_k(\bar{\mathbf{r}}))(-iu+\omega_{k'}(\bar{\mathbf{r}}))}. \tag{C4}$$

Substituting $\bar{\mathbf{r}} \to \bar{\mathbf{r}} + \mathbf{r}$ and doing the integrals yields

$$\delta\tilde{s}_0(iu,\mathbf{k},\mathbf{k}') = \hat{w}_{iu,k,k'}(\mathbf{k}'-\mathbf{k})\delta\hat{n}(\mathbf{k}'-\mathbf{k}), \tag{C5}$$

where $\hat{n}(\mathbf{q})$ and $\hat{w}_{iu,k,k'}(\mathbf{q})$ are the fourier components of $n(\mathbf{r})$ and $w_{iu,k,k'}(\mathbf{r})$, respectively. Inserting Eq. (C5) into Eq. (41) and comparing to Eq. (40) finally yield

$$K_{\mathrm{nl}}(q) = \frac{1}{2}\sum_{u,k}(1-(\hat{\mathbf{k}}\cdot\widehat{(\mathbf{k}+\mathbf{q})})^2)\left|\hat{w}_{iu,\mathbf{k},\mathbf{k}+\mathbf{q}}(\mathbf{q})\right|^2. \tag{C6}$$

To obtain the curvature of $K_{\mathrm{nl}}(q)$ at the origin, it is most convenient to differentiate Eq. (C6) with respect to q. Since

$$(1-(\hat{\mathbf{k}}\cdot\widehat{(\mathbf{k}+\mathbf{q})})^2)|_{q=0} = 0, \tag{C7}$$

and

$$\boldsymbol{\nabla}_q(1-(\hat{\mathbf{k}}\cdot\widehat{(\mathbf{k}+\mathbf{q})})^2)|_{q=0} = \mathbf{0}, \tag{C8}$$

and

$$\nabla_q^2(1-(\hat{\mathbf{k}}\cdot\widehat{(\mathbf{k}+\mathbf{q})})^2)|_{q=0} = \frac{4}{k^2}, \tag{C9}$$

the gradients of $\hat{w}_{iu,\mathbf{k},\mathbf{k}+\mathbf{q}}(\mathbf{q})$ with respect to $\mathbf{q}$ need not be evaluated. Moreover, from Eq. (C4) it is seen that $\hat{w}_{iu,\mathbf{k},\mathbf{k}}(0) = \delta\hat{s}_{\mathrm{xc}}^{\mathrm{uni}}(iu,k)/\delta n$, as defined in Eq. (25). After a last change of variables one finally obtains

$$\nabla_q^2 K_{\mathrm{nl}}(q)|_{q=0} = \sum_{u,q}\frac{2}{q^2}\left|\frac{\delta\hat{s}_{\mathrm{xc}}^{\mathrm{uni}}(iu,q)}{\delta n}\right|^2. \tag{C10}$$

APPENDIX D: DETAILS ON THE EVALUATION OF $E_C^{\rm nl}$

The trace over the $3x3$ matrices simply becomes

$$\mathrm{Tr}\,[\mathbf{T}(\mathbf{q})\mathbf{T}(\mathbf{q}')] = (\hat{\mathbf{q}}\cdot\hat{\mathbf{q}'})^2. \tag{D1}$$

Inserting Eqs. (46) and (D1) into Eq. (3), the result may be expressed as

$$E_c^{\rm nl} = \frac{1}{4}\int d^3r d^3r'\, \omega_p^2(\mathbf{r})A(\mathbf{r},\mathbf{r}')\omega_p^2(\mathbf{r}'), \tag{D2}$$

where A is given by ($\mathbf{R} = \mathbf{r}-\mathbf{r}'$)

$$A = \sum_{u,q,q'} \frac{(1-(\hat{\mathbf{q}}\cdot\hat{\mathbf{q}'})^2)e^{i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{R}}}{(-iu+\omega_q)(iu+\omega_q')(-iu+\omega_{q'}')(iu+\omega_{q'})}$$

$$= \sum_{q,q'} \frac{(1-(\hat{\mathbf{q}}\cdot\hat{\mathbf{q}'})^2)e^{i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{R}}}{(\omega_q+\omega_q')(\omega_{q'}+\omega_{q'}')}\left(\frac{1}{\omega_q+\omega_{q'}}+\frac{1}{\omega_q'+\omega_{q'}'}\right). \tag{D3}$$

The dispersion model ω_q shall now be assumed to only depend on the magnitude of q. It is done here due to the actual approximation made (Eq. (49)), and does not present a fundamental restriction. Expressing the coordinates as

$$\hat{\mathbf{q}} = (\sqrt{1-t_1^2}, 0, t_1)$$

$$\hat{\mathbf{q}'} = (\sqrt{1-t_2^2}cos(\phi), \sqrt{1-t_2^2}sin(\phi), t_2) \tag{D4}$$

the integrals over angles may be performed. Doing the average over ϕ yields

$$\left\langle 1-(\hat{\mathbf{q}}\cdot\hat{\mathbf{q}'})^2\right\rangle = \frac{1}{2}(1+t_1^2+t_2^2-3t_1^2t_2^2). \tag{D5}$$

Averaging the two t integrals and making the substitution $q = y_1/R$ and $q' = y_2/R$ yield

$$A = \sum_{y_1,y_2} \frac{v(y_1,y_2)}{y_1^3y_2^3R^6}\frac{1}{(\omega_{y_1/R}+\omega_{y_1/R}')(\omega_{y_2/R}+\omega_{y_2/R}')}$$

$$\times\left(\frac{1}{\omega_{y_1/R}+\omega_{y_2/R}}+\frac{1}{\omega_{y_1/R}'+\omega_{y_2/R}'}\right), \tag{D6}$$

where

$$v(y_1,y_2) = 2\sin(y_1)((3-y_1^2)y_2\cos(y_2)+(y_1^2+y_2^2-3)\sin(y_2)) - 2y_1\cos(y_1)(3y_2\cos(y_2)+(y_2^2-3)\sin(y_2)). \tag{D7}$$

With $\omega_p^2 = 4\pi n$, and $\varepsilon_{\rm nl} = (4\pi)^2A/2$, Eq. (3) takes on the form of the effective electron-electron interaction Eq. (47). For large R values, the integrals over y_1 and y_2 become independent of ω_q, which can then be integrated analytically, yielding the factor $-3/8\pi^2$. In the limit of large R then, $\varepsilon_{\rm nl}(R)$ tends to

$$\varepsilon_{\rm nl}(R) \to -\frac{3}{2}\frac{1}{R^6}\frac{1}{\omega_0\omega_0'(\omega_0+\omega_0')}. \tag{D8}$$

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