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Alternative form of the linear-response contribution to the exchange-correlation energy functional

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The linear-response contribution to the exchange-correlation energy functional $E_{\rm xc}[n]$ of density-functional theory is reconsidered. An alternative form for this functional is suggested that resolves the convergence problems for finite systems inherent in the original form introduced by Hohenberg and Kohn [Phys. Rev. **136B**, 864 (1964)]. Within the exchange-only approximation in which the linear response kernel is known exactly and the optimized-potential model serves as a rigorous comparative standard, the present functional is applied to spherical atoms and jellium spheres. Self-consistent results for these systems indicate that this functional might be worth a more detailed examination.

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I. INTRODUCTION

During recent years a major effort within density-functional theory (DFT) has been directed towards the construction of nonlocal corrections to the local-density approximation (LDA) for the exchange-correlation energy functional $E_{\rm xc}[n]$. Systematic schemes for the construction of nonlocal corrections have already been introduced in the seminal papers on DFT [1,2]. There, basically two routes have been suggested, differing in their degree of nonlocality. On one hand, the gradient expansion [1] (GE) has been put forward that is based on the smallness of the gradients of the density, i.e., of $\nabla n(\boldsymbol{r})/[2k_F(\boldsymbol{r})n(\boldsymbol{r})]$ [where $k_F = (3\pi^2 n)^{1/3}$], and the corresponding higher gradients. On the other hand, as a more nonlocal alternative to the GE the linear-response correction $E_{\rm xc}^{\rm LR}[n]$ to the LDA has been introduced [1–3]. This approximation allows for arbitrary variation of the induced inhomogeneity $\delta n(\boldsymbol{r})$ as long as $\delta n(\boldsymbol{r})$ is sufficiently small compared to the unperturbed density n_0. It is thus complementary to the GE as here the size of the gradients of the total density $n(\boldsymbol{r}) = n_0 + \delta n(\boldsymbol{r})$ does not restrict the applicability. Consequently the linear-response (LR) correction seems particularly suited for the description of extended systems.

Its actual application, however, suffers from technical difficulties such that few investigations have been reported in the literature [4–6]. Many of these difficulties originate from the elimination of the initial variables of $E_{\rm xc}^{\rm LR}$, i.e., $\delta n(\boldsymbol{r})$ and n_0, in favor of the complete $n(\boldsymbol{r})$. In particular, it has been shown [7] that one of the most plausible choices for the elimination of n_0 from the exchange-correlation kernel, i.e., $n_0 = n[(\boldsymbol{r}+\boldsymbol{r}')/2]$, leads to divergent exchange energies for atoms and surfaces. Moreover, even for other local substitutions of n_0 the application of the original form of $E_{\rm xc}^{\rm LR}[n]$ (at least to finite systems) suffers from the very slow convergence of some integrals involved.

Here an alternative form of $E_x^{\rm LR}[n]$ is suggested that resolves this major problem with the original form: The present form gives finite E_x's for all local substitutions of n_0 and considerably improves the convergence properties of $E_x^{\rm LR}[n]$. As a consequence the present functional is technically much easier to handle than the original one, which is demonstrated by an application to spherical atoms and jellium spheres [8–10] within the exchange-only approximation [11–13]. In the present context the restriction to the exchange-only limit offers two advantages: On one hand, the exchange-only linear-response kernel is known exactly [14–16], and, on the other hand, the optimized potential model (OPM) [17,18] provides the exact exchange-only results both for E_x as well as the exchange potential $v_x(\boldsymbol{r})$ allowing for an unambigous analysis [19].

As the present $E_x^{\rm LR}[n]$ allows for an even larger class of local substitutions of n_0, the task of finding the most adequate one is even more involved. Here two simple substitutions for n_0, i.e., $n_0 = [n(\boldsymbol{r}) + n(\boldsymbol{r}')]/2$ and $n_0 = n(\boldsymbol{r})^{\frac{1}{2}} n(\boldsymbol{r}')^{\frac{1}{2}}$, are examined in order to demonstrate the feasibility of the latter (which cannot be used in the original LR functional for finite systems and surfaces) and to check the importance of this input.

The paper is organized as follows. In Sec. II the present $E_x^{\rm LR}[n]$ is introduced and its properties are discussed in comparison to the original functional. Results for atoms and jellium spheres are presented in Sec. III. Some technical details are compiled in the Appendix. Atomic units are used throughout this paper.

II. THEORY

For a weakly inhomogeneous electron gas, $n(\boldsymbol{r}) = n_0 + \delta n(\boldsymbol{r})$, one finds, as the linear-response correction to the exchange-only energy [1],

$$E_x^{\rm LR} = \frac{1}{2}\int \frac{d^3q}{(2\pi)^3}\delta n(\boldsymbol{q})\delta n(-\boldsymbol{q}) \times [K(\boldsymbol{q},k_F) - K(\boldsymbol{0},k_F)] \,, \tag{2.1}$$

$$K(\boldsymbol{q},k_F)=\frac{\Pi^1(\boldsymbol{q},k_F)}{\left[\Pi^0(\boldsymbol{q},k_F)\right]^2}\quad, \tag{2.2}$$

where $\Pi^{0,1}(\boldsymbol{q},k_F)$ represent the static zeroth- and first-order contributions to the irreducible density-density response function of the homogeneous electron gas. In order to rewrite $E_x^{\rm LR}$ as a density functional both $\delta n(\boldsymbol{r})$ and n_0 have to be eliminated in favor of $n(\boldsymbol{r})$, which is achieved in two steps. First, Fourier transformation allows one to eliminate δn, which leads to the standard form of the linear-response functional [1–3],

$$E_x^{\rm LR}[n]=-\frac{1}{4}\int d^3r\int d^3r'[n(\boldsymbol{r})-n(\boldsymbol{r}')]^2K(|\boldsymbol{r}-\boldsymbol{r}'|,k_F)\,, \tag{2.3}$$

where

$$K(r,k_F)=\int\frac{d^3q}{(2\pi)^3}\,e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\,K(\boldsymbol{q},k_F)\,. \tag{2.4}$$

In the second step k_F inside $K(|\boldsymbol{r}-\boldsymbol{r}'|,k_F)$ has to be replaced by some appropriate functional of the inhomogeneous density $n(\boldsymbol{r})$.

While a number of choices for this replacement have been discussed in the literature [2–7,20], none of them has been tested extensively up to now. Moreover, Gunnarsson, Jonson, and Lundqvist [7] have shown that one of the most simple and physically plausible possibilities [2], i.e., $n_0\to n[(\boldsymbol{r}+\boldsymbol{r}')/2]$, leads to divergent exchange energies for atoms and surfaces. The problem originates from the $\boldsymbol{r}'$ integration in the term

$$\int d^3r\int d^3r'\;[n(\boldsymbol{r})]^2\;K(|\boldsymbol{r}-\boldsymbol{r}'|,k_F)\quad, \tag{2.5}$$

which for $k_F=\{3\pi^2n[(\boldsymbol{r}+\boldsymbol{r}')/2]\}^{\frac{1}{3}}$ does not converge for large $|\boldsymbol{r}'|$ (and arbitrary but finite $\boldsymbol{r}$). In fact, as for atoms $n[(\boldsymbol{r}+\boldsymbol{r}')/2]$ vanishes exponentially for large $|\boldsymbol{r}'|$ one finds (compare Appendix A of [7])

$$\lim_{r'\to\infty}\int d\Omega'\;K(|\boldsymbol{r}-\boldsymbol{r}'|,k_F[(\boldsymbol{r}+\boldsymbol{r}')/2])=-\frac{4\pi}{3r'}\quad,$$

such that the remaining r' integration diverges. This divergence is directly related to the violation of the identity

$$\int d^3r\;K(|\boldsymbol{r}-\boldsymbol{r}'|,k_F)=K(\boldsymbol{q}=\boldsymbol{0},k_F) \tag{2.6}$$

[which has been used to obtain (2.3)] after the local substitution of k_F.

Gunnarsson, Jonson, and Lundqvist [7] also analyzed the replacement $n_0\to[n(\boldsymbol{r})+n(\boldsymbol{r}')]/2$ and showed that it leads to finite E_x's. However, the asymptotic form of K on which they based this examination did not take into account the correct behavior of Π^1 at $q=2k_F$ (see Ref. [16]). In the following it will be shown that, while their basic conclusion about the existence of (2.3) is not affected by the different asymptotic form of K, (2.5) turns out to converge extremely slowly. For this analysis it is most appropriate to define the basic Fourier transform

$$G(x)=\int_0^\infty\frac{dQ}{\pi}\;\cos(Qx)\;\frac{k_F^2}{\pi}\;\frac{\Pi^1(\boldsymbol{q},k_F)}{[\Pi^0(\boldsymbol{q},k_F)]^2}\quad, \tag{2.7}$$

where one has used the fact that $k_F^2\Pi^1/[\Pi^0]^2$ only depends on the ratio $Q=|\boldsymbol{q}|/(2k_F)$ rather than on $\boldsymbol{q}$ and k_F separately $((k_F^2/\pi)\Pi^1(0,k_F)/[\Pi^0(0,k_F)]^2=-1)$. $G(x)$ allows one to factorize $K(r,k_F)$ into a Coulomb interaction and a screening function

$$K(r,k_F)=-\frac{2}{r}G'(2k_Fr)\quad, \tag{2.8}$$

where $G'(x)$ denotes the derivative of $G(x)$ with respect to x. As for the replacement $n_0\to[n(\boldsymbol{r})+n(\boldsymbol{r}')]/2$ the argument k_F in $K(|\boldsymbol{r}-\boldsymbol{r}'|,k_F)$ approaches the $\boldsymbol{r}'$-independent value $[3\pi^2n(\boldsymbol{r})/2]^{\frac{1}{3}}$ in the limit of large $|\boldsymbol{r}'|$, the angular integration can again be performed

$$\lim_{r'\to\infty}\int d\Omega'\;K(|\boldsymbol{r}-\boldsymbol{r}'|,k_F\{[n(\boldsymbol{r})+n(\boldsymbol{r}')]/2\})$$
$$=-\frac{2\pi}{rr'k_F}[G(2k_F|r+r'|)-G(2k_F|r-r'|)]\,. \tag{2.9}$$

From the asymptotic behavior of $G(x)$ (completely given in the Appendix),

$$G(x)\xrightarrow[x\gg1]{}-\frac{\sin(x)}{x^2}\Big(\ln|x|\Big)^2\quad,$$

it is thus obvious that the r' integration converges extremely slowly and seems rather difficult to evaluate numerically in actual applications.

These difficulties with the functional (2.3) indicate that this expression might not represent the optimum form for $E_x^{\rm LR}[n]$. In particular, it seems advantageous to eliminate $\delta n(\boldsymbol{r})$ without explicit use of Eq. (2.6). This can be achieved by rewriting Eq. (2.1) as

$$E_x^{LR}[n]=\frac{1}{2}\int d^3r\int d^3r'\;\Big[\boldsymbol{\nabla}n(\boldsymbol{r})\cdot\boldsymbol{\nabla}'n(\boldsymbol{r}')\Big]\times L(|\boldsymbol{r}-\boldsymbol{r}'|,k_F)\quad, \tag{2.10}$$

where

$$L(r,k_F)=\int\frac{d^3q}{(2\pi)^3}\;e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\;\frac{K(\boldsymbol{q},k_F)-K(\boldsymbol{0},k_F)}{q^2} \tag{2.11}$$

and $\boldsymbol{\nabla}\delta n(\boldsymbol{r})=\boldsymbol{\nabla}n(\boldsymbol{r})$ has been used. It should be emphasized that this gradient form of the linear-response correction is not restricted to the exchange-only approximation, but could also be used in the more general case of $E_{\rm xc}[n]$.

One can directly verify that for (2.10) the replacement $k_F\to\{3\pi^2n[(\boldsymbol{r}+\boldsymbol{r}')/2]\}^{1/3}$ gives convergent E_x's for finite systems. One first notes that for vanishing k_F the new kernel L becomes particularly simple,

$$\lim_{k_F\to0}L(|\boldsymbol{r}-\boldsymbol{r}'|,k_F)=\frac{1}{4k_F^2|\boldsymbol{r}-\boldsymbol{r}'|}\quad.$$

Using this limit of L the angular integrations for $\boldsymbol{r}'$ are easily carried through for spherical systems such that for brevity the following explicit evaluation is restricted to this situation:

$$\lim_{r'\to\infty}\int d\Omega'\ \nabla n(\boldsymbol{r})\cdot\nabla' n(\boldsymbol{r}')\ L(|\boldsymbol{r}-\boldsymbol{r}'|,k_F[(\boldsymbol{r}+\boldsymbol{r}')/2])$$

$$= 2\pi \lim_{r'\to\infty}\frac{n'(r)\,n'(r')}{4k_F(r'/2)^2}\int_{-1}^{1}dx\ \frac{x}{[r^2+r'^2-2rr'x]^{\frac{1}{2}}}$$

$$= \frac{\pi}{3}\frac{r\ n'(r)\ n'(r')}{r'^2\ k_F(r'/2)^2}\ .$$

The $n'(r')$ in the numerator ensures convergence of the subsequent r' integration in spite of the $k_F(r'/2)^2$ in the denominator by which the asymptotic form of L differs from that of K. Thus in contrast to (2.3), the form (2.10) allows for $n_0 \to n[(\boldsymbol{r}+\boldsymbol{r}')/2]$.

For further analysis of (2.10) it is again advantageous to introduce a dimensionless Fourier transform $H(x)$,

$$H(x)=\int_0^\infty \frac{dQ}{\pi}\,\frac{\cos(Qx)}{Q^2}\left[\frac{k_F^2}{\pi}\,\frac{\Pi^1(q,k_F)}{[\Pi^0(q,k_F)]^2}+1\right],\qquad(2.12)$$

which allows one to factorize $L(r,k_F)$ in the form

$$L(r,k_F)=-\frac{2}{(2k_F)^2 r}H'(2k_F r)\ .\qquad(2.13)$$

The kernels $H'(x)$ and $G'(x)$, which essentially characterize the screening of the Coulomb interaction in $L(r,k_F)$ and $K(r,k_F)$, respectively, are plotted in Figs. 1 and 2 [compare the evaluation of $G'(x)$ for small x in Ref. [21] and the corresponding kernels including correlation effects in Ref. [5]]. It is obvious from these figures that $H'(x)$ is more short ranged than $G'(x)$, which is a further reason for the improved convergence properties of (2.10). For completeness also the asymptotic forms of $G'(x)$ and $H'(x)$ (analytically given in the Appendix) are shown in Figs. 1 and 2, indicating their accuracy for smaller x values.

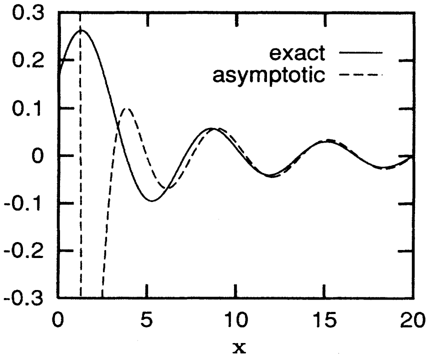

FIG. 1. Exchange-only kernel $G'(x)$, Eq. (2.8), and its asymptotic form [the derivative of (A1) with respect to x].

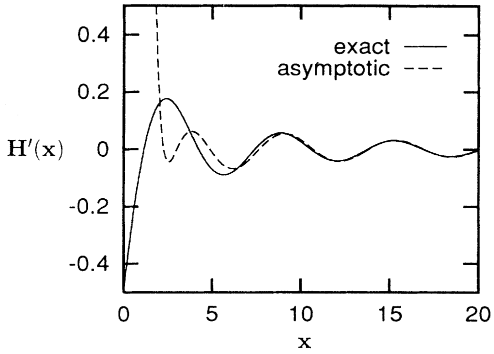

FIG. 2. Exchange-only kernel $H'(x)$, Eq. (2.13), and its asymptotic form [the derivative of (A2) with respect to x].

The exchange potential resulting from (2.10) reads

$$\begin{aligned}v_x^{\rm LR}(\boldsymbol{r}) = &-\int d^3r'\ \nabla' n(\boldsymbol{r}')\cdot\nabla L(|\boldsymbol{r}-\boldsymbol{r}'|,k_F)\\ &+\frac{1}{2}\int d^3r'\int d^3r''\ \nabla' n(\boldsymbol{r}')\cdot\nabla'' n(\boldsymbol{r}'')\\ &\times\frac{\delta k_F([n],\boldsymbol{r}',\boldsymbol{r}'')}{\delta n(\boldsymbol{r})}\,\frac{d}{dk_F}L(|\boldsymbol{r}'-\boldsymbol{r}''|,k_F)\ ,\end{aligned}\qquad(2.14)$$

where $k_F([n],\boldsymbol{r}',\boldsymbol{r}'')$ at this point could be any functional of n which reduces to $(3\pi^2 n_0)^{1/3}$ for a homogeneous system. However, a restriction of the density dependence of $k_F([n],\boldsymbol{r}',\boldsymbol{r}'')$ seems unavoidable in order to allow for the efficient application of the potential (2.14) in selfconsistent calculations. In fact, all $k_F([n],\boldsymbol{r}',\boldsymbol{r}'')$ suggested in the literature until now are simple functions either of $n[(\boldsymbol{r}'+\boldsymbol{r}'')/2]$ or of $n(\boldsymbol{r}')$ and $n(\boldsymbol{r}'')$ separately such that the functional derivative in (2.14) can be easily performed. Restricting oneself to the latter case (the former situation can be treated analogously) and assuming k_F to be symmetric with respect to $n(\boldsymbol{r}')$ and $n(\boldsymbol{r}'')$ one can rewrite $v_x^{\rm LR}(\boldsymbol{r})$ as

$$\begin{aligned}v_x^{\rm LR}(\boldsymbol{r}) = 2&\int d^3r'\ \frac{(\boldsymbol{r}-\boldsymbol{r}')\cdot\nabla' n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\\ &\times\left[\frac{H''(2k_F|\boldsymbol{r}-\boldsymbol{r}'|)}{2k_F|\boldsymbol{r}-\boldsymbol{r}'|}-\frac{H'(2k_F|\boldsymbol{r}-\boldsymbol{r}'|)}{(2k_F|\boldsymbol{r}-\boldsymbol{r}'|)^2}\right]\ .\end{aligned}\qquad(2.15)$$

$v_x^{\rm LR}(\boldsymbol{r})$ becomes particularly simple for spherical systems,

$$\begin{aligned}v_x^{\rm LR}(r) = &\frac{\pi}{2r}\int_0^\infty dr'\ \frac{n'(r')}{k_F^3}\Big[H(x_+)-H(x_-)\Big]\\ &-\frac{\pi}{r}\int_0^r r'dr'\ \frac{n'(r')}{k_F^2}\Big[H'(x_+)+H'(x_-)\Big]\\ &-\frac{\pi}{r}\int_r^\infty r'dr'\ \frac{n'(r')}{k_F^2}\Big[H'(x_+)-H'(x_-)\Big]\ ,\end{aligned}\qquad(2.16)$$

where $x_\pm = 2k_F|r\pm r'|$. On the basis of (2.16) one can directly analyze the asymptotic behavior of $v_x^{\rm LR}(r)$ for finite systems. In particular, one finds by an expansion of $H(x_\pm)$ in powers of $x_\pm$ that

$$v_x^{\mathrm{LR}}(r) \underset{r\to\infty}{\longrightarrow} -\frac{N}{3r} \tag{2.17}$$

if $k_F(n(\boldsymbol{r}),n(\boldsymbol{r}'))$ vanishes exponentially for large r. While this asymptotic form of $v_x^{\mathrm{LR}}(r)$ does not agree with the exact $-1/r$ behavior [18,13], it is nevertheless interesting that a proportionality to $1/r$ can be obtained from the functional (2.10).

Finally, it is worth pointing out that the functional (2.10) satisfies the virial relation for the exchange-only $E_x[n]$ [22],

$$E_x[n] = \int d^3r\ v_x(\boldsymbol{r})\Big[3n(\boldsymbol{r}) + \boldsymbol{r}\cdot\nabla n(\boldsymbol{r})\Big]\ , \tag{2.18}$$

as is also obvious from all numerical results. The accuracy to which the E_x's obtained directly via (2.10) agree with the values calculated from the right-hand side of Eq. (2.18) is even higher than that found in OPM calculations [23].

III. RESULTS

While one should not expect a functional based on linear response to give particularly accurate results for atoms, an application of $E_x^{\mathrm{LR}}[n]$ to atoms is nevertheless interesting as a first check on its properties. In fact, due to their very inhomogeneous density, atoms are among the most critical systems a linear-response correction can be tested for. In particular, one would expect atomic results to be rather sensitive to the local substitution of k_F inside the response kernel such that one would hope to obtain some information concerning this choice. Without aiming at a complete answer to this question, the functional (2.10) is here applied to spherical atoms using two different simple $k_F([n],\boldsymbol{r},\boldsymbol{r}')$,

$$k_F = \left[3\pi^2\frac{n(r)+n(r')}{2}\right]^{\frac{1}{3}} \qquad (\mathrm{LR1})\ , \tag{3.1}$$

$$k_F = [3\pi^2 n(r)]^{\frac{1}{6}}\ [3\pi^2 n(r')]^{\frac{1}{6}} \qquad (\mathrm{LR2})\quad . \tag{3.2}$$

While these $k_F([n],\boldsymbol{r},\boldsymbol{r}')$ both belong to the class $k_F([n],\boldsymbol{r},\boldsymbol{r}') = k_F(n(\boldsymbol{r}),n(\boldsymbol{r}'))$ for which the exchange potential has been given in Sec. II, their comparison nevertheless provides an idea of the variation of the LR results with different $k_F([n],\boldsymbol{r},\boldsymbol{r}')$. Moreover, in several studies [6,7,20] of the original linear-response functional (2.3) the replacement (3.1) has been found to represent the optimum substitution among the simple forms of $k_F([n],\boldsymbol{r},\boldsymbol{r}')$. The choice (3.2), on the other hand, belongs to the class of substitutions that cannot be used in the functional (2.3) for finite systems.

In Table I the E_x's for spherical unpolarized atoms obtained by insertion of exact OPM densities into (2.10) using (3.1) and (3.2) are compared to the exact E_x's from the OPM [23] and the results of the LDA and the second-order gradient expansion (GE2). As is obvious from the percentage errors Δ_i, neither LR1 nor LR2 improves atomic E_x's over the GE2, with LR2 being slightly superior to LR1. The most pronounced differences are found for the smallest atoms, while the errors of the GE2 and LR1,2 for the more characteristic large atoms are rather similar. This can be understood from the fact that the relevant gradients of the density, i.e., $\nabla n(\boldsymbol{r})/[2k_F(\boldsymbol{r})n(\boldsymbol{r})]$ and $\nabla^2 n(\boldsymbol{r})/[4k_F(\boldsymbol{r})^2 n(\boldsymbol{r})]$, are smaller or of the order of 0.5 over the most important range of r for medium size and in particular large atoms (compare Refs. [23,24]), while they become of the order of 1 or even larger for the smallest atoms. However, the GE2 represents a rather accurate approximation to LR for gradients smaller than 0.5, as is obvious from a comparison of the complete exchange kernel (2.2) with its second-order expansion in powers of $\boldsymbol{q}$.

However, as has become clear recently [24], the accuracy of total E_x's partially results from fortuitous cancellation of local errors (even in the case of the LDA).

TABLE I. Total exchange energies of spherical unpolarized atoms from the OPM, LDA, GE2, LR1, and LR2 obtained by insertion of OPM densities (in hartrees) and the corresponding percentage errors Δ_i.

Atom	OPM	LDA	Δ_{LDA} (%)	GE2	Δ_{GE2} (%)	LR1	Δ_{LR1} (%)	LR2	Δ_{LR2} (%)
He	1.026	0.884	-13.82	1.007	-1.86	0.982	-4.27	1.043	1.70
Be	2.666	2.312	-13.26	2.581	-3.19	2.582	-3.14	2.723	2.13
Ne	12.105	11.033	-8.85	11.775	-2.73	11.814	-2.40	12.059	-0.38
Mg	15.988	14.612	-8.61	15.510	-2.99	15.581	-2.55	15.767	-1.38
Ar	30.175	27.863	-7.66	29.293	-2.92	29.275	-2.98	29.388	-2.61
Ca	35.199	32.591	-7.41	34.183	-2.89	34.176	-2.91	34.202	-2.83
Zn	69.619	65.645	-5.71	68.109	-2.17	68.328	-1.85	68.521	-1.58
Kr	93.833	88.624	-5.55	91.651	-2.33	91.953	-2.00	92.354	-1.58
Sr	101.926	96.362	-5.46	99.560	-2.32	99.932	-1.96	100.340	-1.56
Pd	139.114	132.169	-4.99	136.145	-2.13	136.747	-1.70	137.434	-1.21
Cd	148.880	141.543	-4.93	145.702	-2.13	146.354	-1.70	147.088	-1.20
Xe	179.064	170.566	-4.75	175.304	-2.10	176.026	-1.70	176.881	-1.22
Ba	189.067	180.241	-4.67	185.156	-2.07	185.931	-1.66	186.756	-1.22
Yb	276.147	265.563	-3.83	271.806	-1.57	272.572	-1.29	272.989	-1.14
Pt	331.339	318.712	-3.81	325.752	-1.69	326.536	-1.45	326.916	-1.33
Hg	345.246	332.143	-3.80	339.372	-1.70	340.162	-1.47	340.533	-1.37
Rn	387.453	372.981	-3.74	380.811	-1.71	381.591	-1.51	381.927	-1.43

More characteristic of the quality of some approximate $E_x[n]$ than these total E_x's are the exchange potentials obtained by self-consistent calculations as these determine, e.g., the band structure and spin densities and thus the magnetic phases of solids. Figures 3 and 4 show the self-consistent $v_x(r)$'s from the LR1,2 in comparison to the exact $v_x^{\rm OPM}(r)$ for Pd and Rn (being characteristic for all atoms examined). In order to extract the interesting nonlocal part of $v_x(r)$ the self-consistent LDA potential has been subtracted from all potentials. Moreover, as the LDA and LR1,2 do not reproduce the asymptotic $-1/r$ tail of the exact $v_x^{\rm OPM}(r)$ [18,13,25], the potentials in Figs. 3 and 4 have been shifted by the differences between the highest occupied (HO) eigenvalues from OPM and LR1,2 calculations and the corresponding LDA eigenvalues (i.e., OPM in Figs. 3 and 4 represents the potential $v_x^{\rm OPM}(r) - \epsilon_{\rm HO}^{\rm OPM} + \epsilon_{\rm HO}^{LDA}$ and LR1,2 correspond to $v_x^{\rm LR1,2}(r) - \epsilon_{\rm HO}^{LR1,2} + \epsilon_{\rm HO}^{\rm LDA}$). In fact, the highest occupied eigenvalues from the LR calculations are rather close to the LDA eigenvalues (see Table II) even for the case of LR2, whose $v_x(r)$ eventually approaches $-N/(3r)$. However, this asymptotic limit does not affect $v_x^{\rm LR2}(r)$ in the physically relevant part of the asymptotic regime (1$-$4 a.u.) such that the correction $-\epsilon_{\rm HO}^{\rm LR1,2} + \epsilon_{\rm HO}^{\rm LDA}$ is negligible. The constant shift between $v_x^{\rm OPM}(r)$ and $v_x^{\rm LDA}(r)$ induced by their asymptotic behavior, on the other hand, does not affect the structure and size of the oscillations in the nonlocal part of $v_x(r)$, which are the main objective of the present analysis [compare corresponding plots without the modification of $v_x^{\rm OPM}(r)$ in Ref. [24]]. The accuracy to which these oscillations are reproduced by LR1,2, however, is more easily seen in comparison to the shifted OPM potential.

Analyzing Figs. 3 and 4 one finds that, while the LR1 improves $v_x(r)$ for small r, i.e., the innermost shells, it is not capable of following $v_x^{\rm OPM}(r)$ for intermediate and large r. In accordance with this observation only the innermost eigenvalues are improved, as can be seen from Table II. Comparing LR1 with LR2, the latter seems to be somewhat superior for intermediate and large r, while also not being really close to the exact result. However, in view of the differences between LR1 and LR2 it seems quite likely that more refined local substitutions for k_F could lead to much better results.

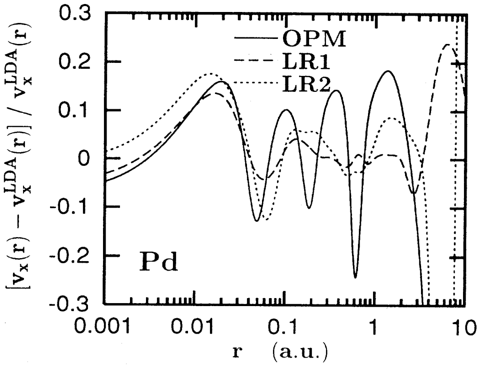

FIG. 3. Nonlocal contributions to the exchange potential of Pd obtained by self-consistent LR calculations in comparison to the exact OPM result: LR1, Eq. (3.1); LR2, Eq. (3.2). Note that the potentials have been shifted by the difference between the highest occupied eigenvalues obtained by the OPM-LR calculations and the corresponding LDA eigenvalue.

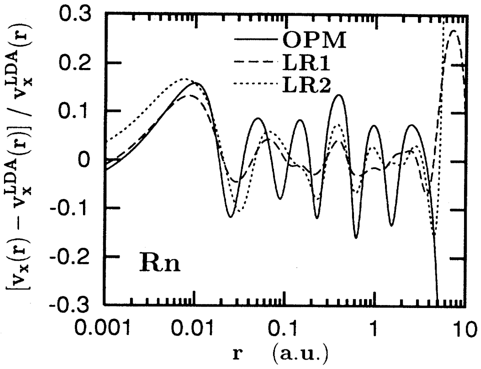

FIG. 4. Same as Fig. 3 for Rn.

In any case, it must be emphasized at this point that other approximate $E_x[n]$ also have substantial difficulties reproducing $v_x^{\rm OPM}(r)$ [for gradient-based functionals such as the GE2 or generalized-gradient approximations (GGAs) see, e.g., Refs. [23,24]]. The net effect of the error introduced by some approximate $E_x[n]$ is most clearly visible in the ground-state densities $n(r)$ resulting from self-consistent calculations. In Figs. 5 and 6 the difference between self-consistent LR2 and LDA densities is compared to the exact nonlocal density contribution $n^{\rm OPM}(r) - n^{\rm LDA}(r)$ and the result from a GGA (PW91 [26]) for Pd and Rn. Again the nonlocal shell oscillations are only partially reproduced by the LR functional. Nevertheless, LR2 turns out to be superior to the GGA. We just remark that consistent with the results for atomic $v_x(r)$'s, the densities from LR1 are less accurate than those from LR2 such that this comparison seems to indicate that the latter choice is preferable (at least for atoms). As to be expected, local quantities such as $v_x(r)$

TABLE II. Eigenvalues $-\epsilon_{nl}$ for Rn obtained from OPM, LDA, and LR1,2 by self-consistent calculations (in hartrees).

nl	OPM	LDA	LR1	LR2
1*s*	3207.2164	3204.6466	3207.0061	3207.6437
2*s*	547.0778	546.4904	546.9339	547.0804
2*p*	527.7905	527.4434	527.5872	527.4829
3*s*	133.6096	133.2938	133.2765	133.1997
3*p*	124.3429	124.0968	124.0118	123.9123
3*d*	107.0813	106.8677	106.8517	106.8648
4*s*	31.5925	31.1628	31.2270	31.2651
4*p*	27.4265	27.0410	27.0867	27.1149
4*d*	19.7113	19.3822	19.4369	19.4711
4*f*	9.1529	8.8861	8.9026	8.8944
5*s*	6.0334	5.8321	5.8217	5.8341
5*p*	4.5480	4.3518	4.3391	4.3507
5*d*	2.0447	1.8565	1.8494	1.8610
6*s*	0.7517	0.5808	0.5853	0.5765
6*p*	0.4271	0.2501	0.2537	0.2462

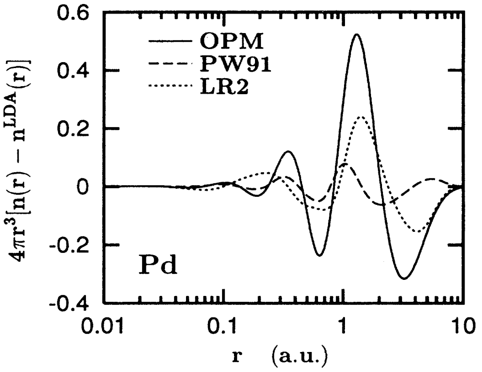

FIG. 5. Nonlocal contribution to the density of Pd obtained by self-consistent LR calculations [using LR2, Eq. (3.2)] in comparison to the exact OPM result and a GGA (PW91).

or $n(r)$ distinguish much more clearly between the various choices for k_F than total E_x's.

While these results for atoms illustrate the limitations of the functional (2.10) [at least for the choices (3.1) and 3.2)], an application to jellium spheres emphasizes its potential power for systems that satisfy the linear-response criterion $\delta n(r) \ll n_0$ (as jellium spheres in their interior — compare Ref. [8]). Self-consistent LR potentials and densities for jellium spheres are much closer to the exact OPM results than those from GGAs, as is obvious from Figs. 7-10, where the LR1 is compared to the OPM and PW91. In particular, the much more nonlocal character of (2.10) as compared to functionals based on the GE allows one to reproduce the pronounced peak at the origin in both $v_x(r)$ and $n(r)$. Unfortunately, due to numerical problems with the asymptotic regime, we are not yet able to report LR2 results for larger jellium spheres, so no comparison to LR2 is given. However, it is particularly gratifying to observe that already the most simple choice LR1 gives rather accurate results. In any case one would expect jellium sphere results to be less sensitive to this ingredient of (2.10) than those for atoms.

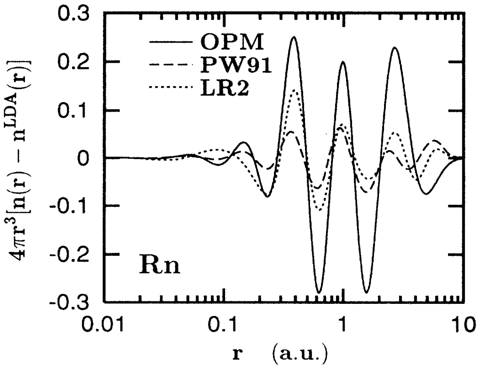

FIG. 6. Same as Fig. 5 for Rn.

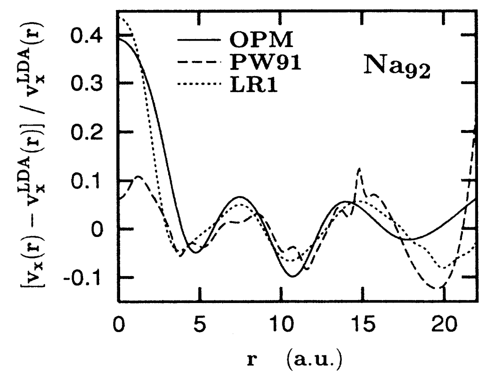

FIG. 7. Nonlocal contribution to the exchange potential of Na_{92} obtained by self-consistent LR calculations [using LR1, Eq. (3.1)] in comparison to the exact OPM result and a GGA (PW91). Note that the potentials have been shifted by the difference between the highest occupied eigenvalues obtained by the OPM-LR-GGA calculations and the corresponding LDA eigenvalue.

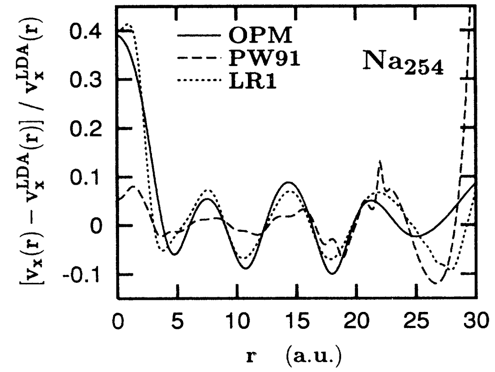

FIG. 8. Same as Fig. 7 for Na_{254}.

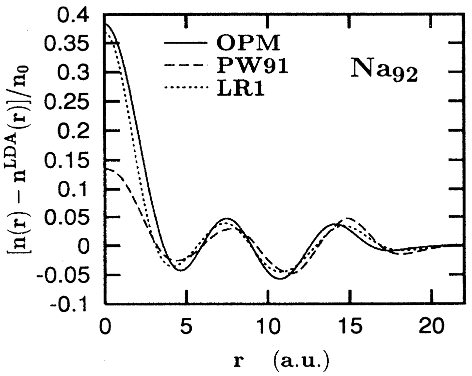

FIG. 9. Nonlocal contribution to the density of Na_{92} obtained by self-consistent LR calculations [using LR1, Eq. (3.1)] in comparison to the exact OPM result and a GGA (PW91).

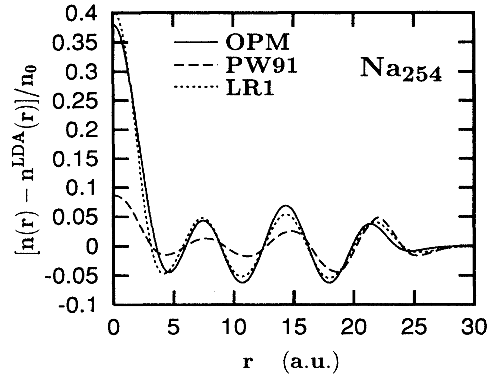

FIG. 10. Same as Fig. 9 for Na_{254}.

IV. CONCLUDING REMARKS

In this work an alternative form for the linear-response contribution to the exchange-correlation energy functional is put forward. While the general expression (2.10) is applicable to both exchange and correlation [with a suitable kernel $L(r, k_F)$], all explicit results presented here have been obtained within the exchange-only approximation. It has been shown that the present form resolves the divergence problem [7] of the original linear-response functional [1,2] for certain local substitutions of n_0 inside the response kernel. Quite generally, the present form leads to faster convergence of all integrations involved, allowing for much easier application of this functional. It seems worth mentioning that the exchange potential resulting from this $E_x^{\mathrm{LR}}[n]$ is finite both at nuclear sites and in the asymptotic regime of finite systems.

As far as the optimum local substitution for n_0 is concerned, two simple forms have been examined, leaving a more detailed investigation of this question for the future. In particular, the original suggestion [1,2] $n_0 = n[(\boldsymbol{r} + \boldsymbol{r}')/2]$, which the present $E_x^{\mathrm{LR}}[n]$ allows one to use, has not been studied yet. The comparison of the two substitutions for n_0 considered, however, indicates that at least for inhomogeneous systems such as atoms, the results of self-consistent calculations depend rather sensitively on this input. It seems that some room for improvement is left in this respect.

The present functional has been applied to both atoms and jellium spheres. While the former provide an idea of the limitations of this functional, the latter impressively demonstrate its power for those systems for which the underlying linear-response approximation is satisfied at least to a limited extent. Nevertheless, even the self-consistent ground-state densities obtained in the atomic case suggest that this functional is worth a more detailed examination.

ACKNOWLEDGMENTS

I would like to thank Professor S. H. Vosko who independently had recognized that the form (2.10) represents an alternative to (2.3) for many valuable discussions and U. R. Schmitt for his help. Financial support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

APPENDIX: ASYMPTOTIC FORM OF EXCHANGE KERNELS

In this appendix the leading two orders of the expansions of $G(x)$, Eq. (2.7), and $H(x)$, Eq. (2.12), for large x are given to facilitate use of E_x^{LR}. Their evaluation proceeds as discussed in Sec. III of Ref. [16] such that we only list the final result here (for $x = |\boldsymbol{x}|$),

$$
\begin{aligned}
G(x) \underset{x\gg 1}{=} & -\frac{\sin(x)}{x^2}\left\{\left(1 - C - \ln|2x|\right)^2 - \frac{\pi^2}{12} - 1\right\} + \frac{\cos(x)}{x^3}\left\{\frac{16}{3}\left(\frac{3}{2} - C - \ln|2x|\right)^3 + 3\left(\frac{3}{2} - C - \ln|2x|\right)^2\right. \\
& \left. + \left(\frac{2}{3}\pi^2 - 16\right)\left(\frac{3}{2} - C - \ln|2x|\right) - \frac{32}{3}\zeta(3) - \frac{\pi^2}{4} + \frac{29}{4} + \frac{4}{3}J\right\} \qquad \text{(A1)}
\end{aligned}
$$

where $C = 0.577\ldots$ represents the Euler-Mascheroni constant, $\zeta(3) = 1.202\,056\,903\ldots$ and $J = 3.606\,170\,709\ldots$. Note that the actual expansion parameter for large x is $\ln|2x|/x$ rather than just $1/x$ as one might have expected. As a consequence the accuracy of (A1) is only slowly improving with increasing x (compare Fig. 1), the percentage error being about 2% at $x = 10^2$, 0.08% at $x = 10^3$, and 0.002% at $x = 10^4$.

The asymptotic form of $H(x)$ differs from (A1) only in its first-order contribution as the dominant singularities of $[\mathcal{K}(Q) + 1]/Q^2$ and $\mathcal{K}(Q)$ at $Q = 1$ are identical,

$$
\begin{aligned}
H(x) & \underset{x\gg 1}{=} G(x) + \delta H(x) , \qquad \text{(A2)} \\
\delta H(x) & = \frac{\cos(x)}{x^3}\left\{4\left(\frac{3}{2} - C - \ln|2x|\right)^2 - \frac{\pi^2}{3} - 5\right\} .
\end{aligned}
$$

The accuracy of (A2) is very similar to that of (A1) (see also Fig. 2).

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136B**, 864 (1964).

[2] W. Kohn and L. J. Sham, Phys. Rev. **140A**, 1133 (1965).

[3] J. C. Stoddart, A. M. Beattie, and N. H. March, Int. J. Quantum Chem. **4**, 35 (1971); A. M. Beattie, J. C. Stoddart, and N. H. March, Proc. R. Soc. London Ser. A **326**, 97 (1971).

[4] L. J. Sham, Phys. Rev. B **7**, 4357 (1973).

[5] K. L. Liu, A. H. MacDonald, and S. H. Vosko, Can. J. Phys. **55**, 1991 (1977).

[6] A. H. MacDonald, K. L. Liu, S. H. Vosko, and L. Wilk, Can. J. Phys. **59**, 500 (1981).

[7] O. Gunnarsson, M. Jonson, and B. I. Lundqvist, Phys. Rev. B **20**, 3136 (1979).

[8] W. Ekardt, Phys. Rev. B **29**, 1558 (1984).

[9] D. E. Beck, Solid State Commun. **49**, 381 (1984).

[10] M. Y. Chou, A. Cleland, and M. L. Cohen, Solid State Commun. **52**, 645 (1984).

[11] V. Sahni, J. Gruenebaum, and J. P. Perdew, Phys. Rev. B **26**, 4371 (1982).

[12] D. C. Langreth and M. J. Mehl, Phys. Rev. B **28**, 1809 (1983).

[13] L. J. Sham, Phys. Rev. B **32**, 3876 (1985).

[14] D. J. W. Geldart and R. Taylor, Can. J. Phys. **48**, 155 (1970); **48**, 167 (1970).

[15] J. A. Chevary and S. H. Vosko, Bull. Am. Phys. Soc. **33**, 238 (1988); Phys. Rev. B **42**, 5320 (1990).

[16] E. Engel and S. H. Vosko, Phys. Rev. B **42**, 4940 (1990); **44**, 1446(E) (1991).

[17] R. T. Sharp and G. K. Horton, Phys. Rev. **90**, 317 (1953).

[18] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).

[19] As a consequence, both atoms and jellium spheres should be understood as model systems in the present context.

[20] M. L. Plumer and D. J. W. Geldart, J. Phys. C **16**, 677 (1983).

[21] D. M. Bylander and L. Kleinman, Phys. Rev. B **36**, 1775 (1987).

[22] M. Levy and J. P. Perdew, Phys. Rev. A **32**, 2010 (1985).

[23] E. Engel and S. H. Vosko, Phys. Rev. A **47**, 2800 (1993).

[24] E. Engel and S. H. Vosko, Phys. Rev. B **47**, 13164 (1993).

[25] E. Engel, J. A. Chevary, L. D. Macdonald, and S. H. Vosko, Z. Phys. D **23**, 7 (1992).

[26] J. P. Perdew, in *Electronic Structure of Solids 1991*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991), Vol. 11.