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Brief Reports

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Hohenberg-Kohn kernel $K(\mathbf{r}-\mathbf{r}')$

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In a classic paper Hohenberg and Kohn wrote the energy of an electron gas as a functional of the charge density $n(\mathbf{r})$: $E[n]=\int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}+\frac{1}{2}\int [n(\mathbf{r})n(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|]d\mathbf{r}\,d\mathbf{r}'+G[n]$. For a gas of almost constant density, $n(\mathbf{r})=n_0+\tilde{n}(\mathbf{r})$ with $\tilde{n}(\mathbf{r})/n_0 \ll 1$ they expanded $G[n]=G[n_0]+\int K(\mathbf{r}-\mathbf{r}')\tilde{n}(\mathbf{r})\tilde{n}(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'+\cdots$. The kernel $K(\mathbf{r})$ may be written as a sum of kinetic, exchange, and correlation terms, $K(\mathbf{r})=K_s(\mathbf{r})+K_x(\mathbf{r})+K_c(\mathbf{r})$. We present here graphs of $K_s(\mathbf{r})$ and $K_x(\mathbf{r})$ which are exact to within our numerical accuracy.

In a classic paper Hohenberg and Kohn[1] wrote the energy of an electron gas as a functional of the charge density

$$E[n]=\int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}+\frac{1}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}|}d\mathbf{r}\,d\mathbf{r}'+G[n] \ . \tag{1}$$

For a gas of almost constant density

$$n(\mathbf{r})=n_0+\tilde{n}(\mathbf{r}) \tag{2}$$

with

$$\tilde{n}(\mathbf{r})/n_0 \ll 1 \ , \tag{3}$$

they expanded $G[n]$:

$$G[n]=G[n_0]+\int K(\mathbf{r}-\mathbf{r}')\tilde{n}(\mathbf{r})\tilde{n}(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' \ . \tag{4}$$

Now $K(\mathbf{r})$ may be separated into its component parts,

$$K(\mathbf{r})=K_s(\mathbf{r})+K_x(\mathbf{r})+K_c(\mathbf{r}) \ , \tag{5}$$

where $K_s(\mathbf{r})$ is the kinetic energy kernel for noninteracting Kohn-Sham[2] eigenfunctions, $K_x(\mathbf{r})$ is the exchange energy kernel, and $K_c(\mathbf{r})$ is the correlation energy kernel. Although $K_s(\mathbf{k})$ and $K_x(\mathbf{k})$ have been known for a long time, no one seems to have been curious enough to Fourier transform them in order to see what they look like in real space. In this Brief Report we display graphs of $K_s(\mathbf{r})$ and $K_x(\mathbf{r})$ which are exact to within our computational accuracy.

It was shown in Ref. 1 that

$$K_s(\mathbf{k})=1/2\chi_0(\mathbf{k}) \ , \tag{6}$$

where $\chi_0(\mathbf{k})$ is the RPA susceptibility,

$$\chi_0(\kappa)=\frac{k_F}{(2\pi)^2}\left[2+\left[\frac{2}{\kappa}-\frac{\kappa}{2}\right]\ln\left|\frac{2+\kappa}{2-\kappa}\right|\right] \ . \tag{7}$$

We work with dimensionless quantities $\boldsymbol{\kappa}=\mathbf{k}/k_F$ and $\mathbf{R}=\mathbf{r}/\alpha r_s$ where $k_F=1/\alpha r_s$ and $\alpha=(4/9\pi)^{1/3}$. Noting that $\chi_0 \sim \kappa^{-2}$ for large κ we expanded $1/2\chi_0(\kappa)$ in that limit to obtain

$$K_s(\kappa\rightarrow\infty)=\frac{2\pi^2}{k_F}\left(\tfrac{3}{16}\kappa^2-\tfrac{3}{20}-\tfrac{24}{175}\kappa^{-2}\right) \ . \tag{8}$$

Noting that $d^3k/(2\pi)^3=k_F^3d^3\kappa/(2\pi)^3$ we have

$$\begin{aligned}\int K_s(\kappa\rightarrow\infty)e^{i\mathbf{k}\cdot\mathbf{r}}d^3k&=\frac{k_F^2}{4\pi}\int\left(\tfrac{3}{16}\kappa^2-\tfrac{3}{20}-\tfrac{24}{175}\kappa^{-2}\right)e^{i\kappa R\cos\theta}2\pi\sin\theta\,d\theta\,\kappa^2d\kappa\\&=\frac{k_F^2}{R}\int\left(\tfrac{3}{16}\kappa^3-\tfrac{3}{20}\kappa-\tfrac{24}{175}\kappa^{-1}\right)\sin(\kappa R)d\kappa=-\frac{12\pi}{175}\frac{k_F^2}{R}+\Delta_s \ ,\end{aligned} \tag{9}$$

where

$$\Delta_s = k_F^2 \lim_{\alpha\to 0} \left[\frac{9\alpha(\alpha^2 - R^2)}{2(\alpha^2+R^2)^4} - \frac{3\alpha}{10(\alpha^2+R^2)^2} \right] . \tag{10}$$

We have used the standard trick of including a convergence factor $e^{-\alpha\kappa}$ with $\alpha\to 0$ in the integrand. We then subtract and add $K_s(\kappa\to\infty)$ from $K_s(\kappa)$ and Fourier-transform to obtain

$$K_s(R) = \frac{k_F^2}{R}\left[\int_0^\infty \left\{ \left[2+\left[\frac{2}{\kappa}-\frac{\kappa}{2}\right]\ln\left|\frac{2+\kappa}{2-\kappa}\right|\right]^{-1} - \left(\tfrac{3}{16}\kappa^2 - \tfrac{3}{20} - \tfrac{24}{175}\kappa^{-2}\right)\right\}\kappa \sin(\kappa R)\, d\kappa - \frac{12\pi}{175}\right] + \Delta_s . \tag{11}$$

The integral was numerically integrated up to $\kappa = 10$ at which point the magnitude of the integrand is less than 0.000 03. With $\bar{K}_s$ defined as $K_s - \Delta_s$, the dimensionless quantities $(\alpha r_s)^2 \bar{K}_s(R)$ and $(\alpha r_s)^2 R\bar{K}_s(R) = \alpha r_s r K_s(R)$ are displayed in Fig. 1. Note that Δ_s vanishes except at $R=0$ where it is infinite. Therefore we rewrite Eq. (4) as follows:

$$G[n] = G[n_0] + \int \bar{K}_s(|\mathbf{r}-\mathbf{r}'|)\tilde{n}(\mathbf{r})\tilde{n}(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}' + J_s[\tilde{n}] , \tag{12}$$

where, expanding $\mathbf{r}$ and $\mathbf{r}'$ about r_+,

$$J_s = k_F^{-3} \int \Delta_s(R) \left[\tilde{n}(\mathbf{r}_+) + \frac{1}{2k_F}\mathbf{R}\cdot\nabla\tilde{n}(\mathbf{r}_+) + \tfrac{1}{2}(2k_F)^{-2}\sum_{i,j} R_i R_j \frac{\partial\partial}{\partial x_i \partial x_j}\tilde{n}(\mathbf{r}_+)\right] \times \left[\tilde{n}(\mathbf{r}_+) - \frac{1}{2k_F}\mathbf{R}\cdot\nabla\tilde{n}(\mathbf{r}_+) + \tfrac{1}{2}(2k_F)^{-2}\sum_{i,j} R_i R_j \frac{\partial\partial}{\partial x_i \partial x_j}\tilde{n}(\mathbf{r}_+)\right] d\mathbf{r}_+ d\mathbf{R} \tag{13}$$

with $\mathbf{r}_+ = \frac{1}{2}(\mathbf{r}+\mathbf{r}')$ and $\mathbf{R}/k_F = \mathbf{r}-\mathbf{r}'$. Taking advantage of the inherent symmetry we have

$$J_s = k_F^{-3} \int \Delta_s(R)\{[\tilde{n}(\mathbf{r}_+)]^2 - \tfrac{1}{3}(R/2k_F)^2[\nabla\tilde{n}(\mathbf{r}_+)]^2 + \tfrac{1}{3}(R/2k_F)^2\tilde{n}(r_+)\nabla^2\tilde{n}(\mathbf{r}_+) + O(R^4)\} 4\pi R^2 dR\, d\mathbf{r}_+ . \tag{14}$$

After some tedious integration we find, noting that terms of order R^4 and higher all integrate to zero, and integrating by parts to eliminate the $\nabla^2\tilde{n}$ term,

$$J_s = \frac{2\pi^2}{k_F}\int \left[-\tfrac{2}{20}[\tilde{n}(\mathbf{r})]^2 + \frac{3}{16k_F^2}[\nabla n(\mathbf{r})]^2 \right] d\mathbf{r} . \tag{15}$$

If $\tilde{n} = e^{i\mathbf{k}\cdot\mathbf{r}} + e^{-i\mathbf{k}\cdot\mathbf{r}}$, this yields the first two terms of Eq. (8) for $K_s(\kappa\to\infty)$ as it must. For very rapidly oscillating $n(\mathbf{r})$ the $\bar{K}_s$ integral in (12) becomes vanishing small; thus in that limit $G[n]$ assumes a form that looks exactly like a gradient expansion (with, of course, different coefficients than the long-wavelength expansion).

Jones[3] has derived a result similar to ours. The first two terms of his Eq. (3) are identical to our Eq. (15). However, his third term (which appears to be a factor of 2 too large) corresponds to replacing our $\alpha r_s r\bar{K}_s(R)$ curve by its $R=0$ limit, $-12\pi/175$. Thus our result is new, in that it is valid for any κ whereas his is meant to be valid only in the $\kappa\to\infty$ limit. Jones and Young[4] calculated the linear-response function using the $\kappa\to 0$ gradient expansion coefficient for the $\tilde{n}$ term and the $\kappa\to\infty$ limit for the ∇n term coefficient. Thus is agrees in both limits, but not for intermediate κ, with the exact Lindhard response function. Had they used the $\kappa\to\infty$ value for the $\tilde{n}$ coefficient, they would have extended the large-κ range of validity of the approximate response function at the expense of the small-κ result. Had they also included contributions from $\bar{K}_s(R)$, they would, of course, have reproduced the Lindhard function. Herring[5] performed a calculation similar to ours. His formulation was different, resulting in a different coefficient for the $\tilde{n}$ term and a different $\bar{K}_s(R)$; these differences presumably cancel in a total kinetic energy calculation.

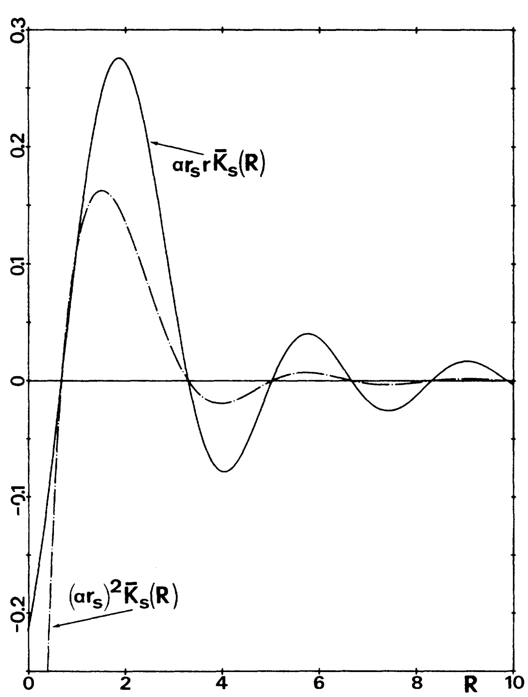

FIG. 1. Graphs of the dimensionless quantities $(\alpha r_s)^2\bar{K}_s$ and $\alpha r_s r\bar{K}_s$ as functions of the dimensionless distance R.

We have recently calculated[6,7]

$$G_x[n]=G_x[n_0]-\frac{9\pi\Omega}{4k_F^2}\sum_{\kappa}\tilde{n}(\boldsymbol{\kappa})F_x(\boldsymbol{\kappa})\tilde{n}(-\boldsymbol{\kappa})\ , \qquad (16)$$

where Ω is a normalization volume. $F_x(\kappa)$ for $0<\kappa<4$ and $(27\kappa^2/8)F_x(\kappa)$ for $4<\kappa<\infty$ are displayed in Figs. 1 and 2 of Ref. 7. This $G_x[n]$ represents the exchange energy of Kohn-Sham eigenfunctions and is exact to within the numerical accuracy with which $F_x(\kappa)$ was calculated. No exact Hartree-Fock $F_x(\kappa)$ has ever been calculated (its expansion about $\kappa=0$ is singular[8–10]), but even if it could be, it would not represent the exchange energy alone; it would, of necessity, have to contain the difference between the kinetic energy of Hartree-Fock eigenfunctions and that of Kohn-Sham eigenfunctions. Thus we believe this is the preferred definition of the exchange energy in a density-functional calculation. It is now known that an earlier, first order in e^2, Hartree-Fock calculation of $F_x(\boldsymbol{\kappa})$ by Sham,[11] is equivalent to the exact Kohn-Sham eigenfunction $F_x(\boldsymbol{\kappa})$.

We fit $K_x(\kappa)=-(9\pi/4k_F^2)F_x(\kappa)$ for large κ with

$$K_x(\kappa\to\infty)=-\frac{2\pi}{3k_f^2}\frac{\kappa^6-0.402\kappa^2+58.996}{(\kappa^2-0.728^2)^4+164.62} \qquad (17)$$

to within 0.000 05 of its calculated value[7] for all $\kappa>3.4$. Its Fourier transform, obtained by the method of residues, is

$$K_x(R)=-\frac{2}{3}\frac{k_F}{R}[0.050\,896e^{-0.675\,135R}\cos(1.875\,801R)+0.199\,104e^{-1.617\,389R}\cos(0.783\,002R)]\ . \qquad (18)$$

Subtracting (17) from $K_x(\kappa)$, numerically Fourier transforming, and adding (18) we obtained the graphs displayed in Fig. 2 for the dimensionless quantities $-\alpha r_s K_x(R)$ and $\frac{1}{2}\gamma(R)=-rK_x(R)$. Although it may not be a useful concept, one may consider the $\tilde{n}(\mathbf{r})$ contribution to the exchange energy to be an antiscreened Coulomb interaction

$$\tilde{E}_x=\frac{1}{2}\int\frac{\tilde{n}(\mathbf{r})\gamma(\mathbf{r}-\mathbf{r}')\tilde{n}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' \qquad (19)$$

with γ playing the role of the antiscreening function. In the inset of Fig. 2 we compare $\frac{1}{2}\gamma(R)$ with a phase-shifted spherical Bessel function $cj_1(\kappa R+\phi)$ where $c=0.4474$, $\kappa=1.9814$, and $\phi=0.1979\pi$. We see that $\gamma(R)$ falls off only slightly more rapidly than $j_1(\kappa R+\phi)$ and has a well-defined oscillation wavelength. We note that $K_x(\kappa)$ has a sharp peak at $\kappa=1.95$ and a very large derivative (probably logarithmically infinite) at $\kappa=2.00$; thus an oscillation with wave vector $\kappa=1.98$ is not surprising. On the other hand, $K_s(\kappa)$ has a logarithmically infinite derivative at $\kappa=2.00$ but the oscillations in $K_s(R)$ do not appear to be settling down to a fixed wavelength.[12]

The correlation kernel $K_c(R)$ remains undetermined. There appear to be two schools of thought concerning the effect of correlation on K_{xc}. One based on an approximate many-body calculation[13] for $\chi(\kappa)$ says that correlation screens exchange and smooths out all the structure in $K_x(\kappa)$. This implies that $K_{xc}(R)$ will have, at most, very weak long-range oscillations, i.e., that, for all r_s, $K_c(R)$ has oscillations of essentially equal magnitude and wavelength but opposite phase to those of $K_x(R)$. The fact that it was necessary to approximate the dynamic screening function with a static one in Ref. 13 leaves room for the second school to question these conclusions. They would claim that the fact that $G_c[n_0]$ is negligible with respect to $G_x[n_0]$ for small r_s is a strong indication that so is $K_c(R)$ with respect to $K_x(R)$. They would also say that in spite of the fact that correlation screens exchange interactions, the correlation energy is independent of and additive to the exchange energy. Thus no conclusions concerning $K_c(R)$ (other than, perhaps, its approximate magnitude) can be drawn from our knowledge of $K_x(R)$. In any event, an accurate determination of $K_c(R)$ and $K_c(\kappa)$ remains an important unsolved problem.

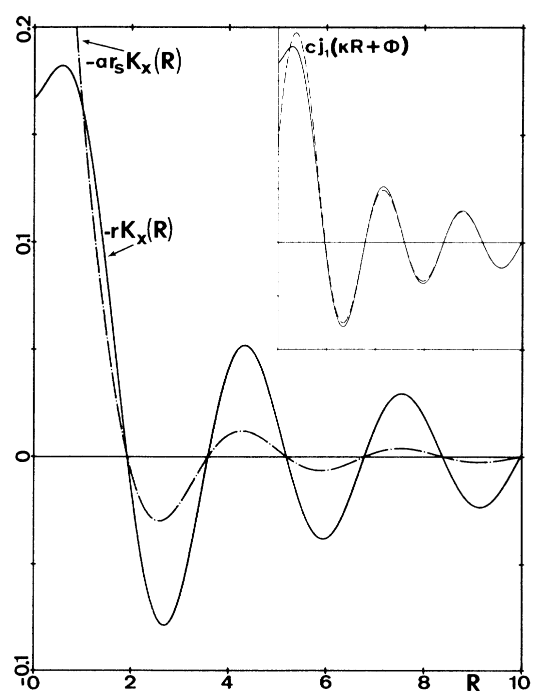

FIG. 2. Graphs of the dimensionless quantities $-\alpha r_s K_x$ and $-rK_x$ as functions of the dimensionless distance R. The inset compares $-rK_x$ with a phase-shifted spherical Bessel function.

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