NON-LOCAL EXCHANGE CORRELATION ENERGY IN QUASI-TWO-DIMENSIONAL ELECTRON LAYERS

J. Hautman and L.M. Sander
Physics Department
University of Michigan
Ann Arbor, MI 48109

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We introduce a simple, non-local approximation for the exchange-correlation energy of an inhomogeneous electron gas. This approximation is shown to be quantitatively accurate in several important limiting cases. The method is used to calculate the non-local exchange-correlation energy for density distributions representing quasi-two-dimensional electron layers. These energies are compared to the widely used three-dimensional local-density approximation and suggest that the latter approximation may contain errors on the order of 10-30% for layer profiles typical of real systems.

In an earlier paper,[1] we outlined a simple approximation for calculating the non-local exchange-correlation energy of a very inhomogeneous electron gas. The method involved a square-well approximation for the electron-electron correlation function. The approximation was used to estimate the accuracy of the widely used local-density approximation (LDA).[2,3] In the LDA the exchange-correlation energy of an electron at a point $\vec{r}$, $\varepsilon_{xc}(\vec{r})$, is assumed to be the exchange-correlation energy per particle of a homogeneous electron gas at the density $n(\vec{r})$. This is an approximation which must become invalid for quasi-2D electron layers when the layer becomes very narrow. This follows from the observation that $\varepsilon_{xc}(\vec{r})$ in the LDA diverges from the 2D exchange-correlation energy expected in that limit. With our non-local calculations we attempted to estimate at what widths the LDA becomes invalid. The main shortcoming of the square-well approximation (SWA), is that it is not quantitatively accurate in the limit of a homogeneous system. Thus the method cannot provide a general alternative to other non-local approximations or even to the LDA, although it has some clear advantages in very inhomogeneous systems.

In this paper we propose a new approximation for the inhomogeneous correlation functions and hence for $\varepsilon_{xc}(\vec{r})$, which is correct in the homogeneous limit. This new non-local method is used to provide a more reliable test of the LDA in quasi-2D layers.

The approximate correlation functions are used to calculate $\varepsilon_{xc}(\vec{r})$, in atomic units, via the exact expression:[4]

$$\varepsilon_{xc}(\vec{r}) = \frac{1}{2} \int d\vec{r}\,' \frac{n(\vec{r}\,')h(\vec{r},\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} . \qquad (1)$$

The correlation function, $h(\vec{r},\vec{r}\,')$, is related to the usual pair correlation function $g(\vec{r},\vec{r}\,';\lambda)$, of an electron gas with coupling constant λ,

$$h(\vec{r},\vec{r}\,') = \int_0^1 d\lambda\ g(\vec{r},\vec{r}\,';\lambda) - 1. \qquad (2)$$

The function $h(\vec{r},\vec{r}\,')$ is a complicated non-local function which must, however, satisfy the following sum rule. The exchange-correlation hole, defined by $n_{xc}(\vec{r},\vec{r}\,') = n(\vec{r}\,')h(\vec{r},\vec{r}\,')$ must exclude one electron, i.e.

$$\int d\vec{r}\,'\ n(\vec{r}\,')h(\vec{r},\vec{r}\,') = -1. \qquad (3)$$

From this starting point several approximations have been studied.[5,6] In the SWA we approximated $h(\vec{r},\vec{r}\,')$ by a spherical square-well,

$$h(\vec{r},\vec{r}\,') = -h_0\theta(R(\vec{r}) - |\vec{r}-\vec{r}\,'|) \qquad (4)$$

where $R(\vec{r})$ is determined at each point by the sum rule (3) and h_0 is the magnitude of the correlation function at $\vec{r}=\vec{r}\,'$. In the case of the quasi-2D layers, this approximation illustrates the non-local nature of the exchange-correlation hole which goes from a nearly spherical 3D hole for very wide layers, to a circular 2D disc when the width goes to zero. This approximation was applied to two very inhomogeneous density distributions representative of the metal surface and of quasi-2D electron layers. The quantitative results of those calculations were much better than we had anticipated considering the crudeness

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of the approximation. The success of the method was attributed to the property that the strength of the correlations at a radius $|\vec{r}-\vec{r}'|$ are not reduced, or screened, unless some charge is present at a smaller radius. We would like to preserve this intuitively appealing property of "screened correlations" in any extensions of the theory.

The approximation we propose here is a correlation function $h(|\vec{r}-\vec{r}'|)$ which is a direct function of the screening charge inside the radius $|\vec{r}-\vec{r}'|$. The value of $h(|\vec{r}-\vec{r}'|)$ is taken to be the same as the value of a corresponding homogeneous correlation function, $h^0(R)$, at a scaled radius R which would contain the same integrated charge, i.e.

Table 1. The non-local exchange-correlation energy per electron, in atomic units, in the limit of a 2D layer of electrons. SWA is the square-well approximation of Ref. 1, SCA is the screened-correlation approximation. These are compared to the results of modified RPA calculations in 2D. (Here $\overline{r_s}$ is defined by $\overline{r_s} = (\pi N_s)^{-1/2}$, where N_s is the 2D density.)

$\overline{r_s}$	SWA	SCA	RPA[a]
0.5	-1.73	-1.13	-1.33
2	-0.43	-0.33	-0.38
4	-0.22	-0.18	-0.20
16	-0.054	-0.050	-0.057

a. References 17 and 18.

$$h(|\vec{r}-\vec{r}'|) = h^0(R;\tilde{r}_s), \qquad (5)$$

where

$$R^3 = \frac{3}{4\pi\tilde{n}} \int_0^{|\vec{r}-\vec{r}'|} d\,\tilde{r}\;\tilde{r}^2 \int d\Omega\; n(\tilde{r},\Omega). \qquad (6)$$

$h^0(R;\tilde{r}_s)$ is the correlation function of a homogeneous system at some density corresponding to $\tilde{r}_s = (3/4\pi\tilde{n})^{1/3}$. This density can be taken to be the local density, $n(\vec{r})$, or some non-local average density if the system is very inhomogeneous. In this paper we intend to look at the 2D limit and the latter approach is required. We define $\tilde{r}_s$ by a non-local generalization of the usual definition:

$$\int_0^{\tilde{r}_s} d\tilde{r}\;\tilde{r}2 \int d\Omega n(\tilde{r},\Omega) = 1\ . \qquad (7)$$

The inhomogeneous correlation function defined by (5) and (6) automatically satisfies the sum rule requirement without any variation of parameters. This remains true as long as the homogeneous correlation function, or any approximation for the homogeneous function, satisfies the sum rule in the uniform system. This can be seen by substituting (5) into the sum rule (3) and changing the integration variable to R. The large distance behavior for $\varepsilon_{xc}(\vec{r})$ that was obtained correctly with the SWA is also obtained in this approximation. The exchange-correlation hole for an electron at a distance z far from a planar metal surface correctly localizes the image charge at the surface giving $\varepsilon_{xc}(z) \to -1/4z$. Far from an atom the correct limit, $\varepsilon_{xc}(\vec{r}) \to -1/2r$ is also obtained. Most importantly this approximation retains the calculational simplicity of the square-well approximation. No iteration is needed to find the appropriate correlation functions. These functions can be constructed at each point $|\vec{r}-\vec{r}'|$ in the process of integrating the exchange-correlation energy, Eqn.(1). The correlation function responds at each point, in a physically reasonable way, to the inhomogeneous density distribution.

For the present calculations we have developed a convenient parametrization for the correlation function of the homogeneous system. The function, $h^0(r;r_s)$, includes the integration over the coupling constant λ as in Eqn.(2). We write,

$$h^0(r;r_s) = -h_0(r_s)(1 - Qr\alpha)\exp\left(-\left(\frac{\alpha r}{r_s}\right)^{c+dr_s}\right)\ , \qquad (8)$$

where $Q = (1-h_0(r_s))/h_0(r_s)$ and $h_0(r_s)$ is the magnitude of the correlation function at the origin. The parameter α is determined by the sum rule (3). Putting (8) into (1) and (3) with $n(\vec{r}) = n_0$ we obtain an expression for the homogeneous exchange-correlation energy,in atomic units,

$$\varepsilon^0_{xc}(r_s) = -\frac{1}{2r_s}\left(\frac{3h_0(r_s)}{x}\right)^{1/3}\left(\frac{\Gamma(\frac{2}{x}) - Qr_s\Gamma(\frac{3}{x})}{(\Gamma(\frac{3}{x}) - Qr_s(\frac{4}{x}))^{2/3}}\right), \qquad (9)$$

where $x = c+dr_s$. The parameters c and d are determined by fitting this expression to calculated values[7-9] for $\varepsilon^0_{xc}(\vec{r})$. In our calculations we have approximated $h_0(r_s)$ by the corresponding values calculated for the case $\lambda=1$.[8,10] We fit these values with the expression, $h_0(r_s) = 1/2 + 1/\pi\tan^{-1}(.847r_s)$.

With c = 1.6 and d = .07 the expression (9) fits the calculated values of Ceperley and Alder, for example, with at most 3% differences over the range $.1 < r_s < 20$. Motivation for these particular parametrizations will be discussed elsewhere.

Now we will use these ideas to look at the exchange-correlation energy of quasi-2D electron layers. We first note that in the extremely inhomogeneous limit of an exactly 2D layer, ($n(z) \propto \delta(z)$), the non-local calculation, referred to as the screened-correlation approximation (SCA), compares well with the expected 2D exchange-correlation energy (Recall that the LDA energy diverges in this 2D limit). Results for this limit are listed in Table 1. The analysis of the non-local effects for layers of finite thickness is the same as in Reference 1. We calculate the total non-local exchange-correlation energy E_{xc} for various widths and compare this to the energy calculcated within the LDA. In this case the LDA is calculated with accurate values of ε_{xc}^{0} given by (9). The energy is also calculated in a 2D approximation where the exchange-correlation energy per electron is taken to be the 2D limiting value of the non-local approximation. The error for both local approximations is defined as the percent deviation from the non-local calculation. Here we look at a quasi-2D layer with the Fang and Howard density profile,[11]

$$n(z) = \frac{1}{2} N_s b^3 z^2 e^{-bz} \tag{10}$$

N_s is the 2D electron density and b is a parameter which determines the layer width. This profile is expected to be a good approximation for many inversion and accumulation layers.[12,13] In Fig. 1 we plot the errors in the 2D approximation and in the LDA as a function of $w' = w/r_s^0$ where $r_s^0 = (3/4\pi n_0)^{1/3}$ is the value of r_s at the profile maximum and $w \equiv N_s/n_0 \approx 3.7/b$ is the layer width. Unlike the SWA results the errors calculated in the SCA have some weak dependence on the value of r_s^0. These results are calculated at $r_s^0 = 1$. The results of the SCA and the SWA are not very different. This indicates that inaccuracies in the SWA are largely cancelled out in comparing that non-local result to the square-well version of the LDA. The results in Fig. 1 verify that the LDA becomes questionable when the width of an electron layer becomes much less than the interparticle spacing r_s^0.

For inversion layers and accumulation layers in semiconductors we can estimate the characteristic width of a layer with the formula,[1]

$$w' \equiv \frac{w}{r_s^0 \nu^{1/3}} = \frac{1.6}{\nu^{1/3}} \left[N^* \left(\frac{\kappa}{m_z}\right)^2\right]^{1/9} \tag{11}$$

where $N^* = (N_s + 32/11\ N_{depl})$, N_{depl} is the depletion layer charge per unit area, κ is the dielectric constant, m_z is the effective mass perpendicular to the layer and ν is the valley degeneracy. Because of the extra r_s^0

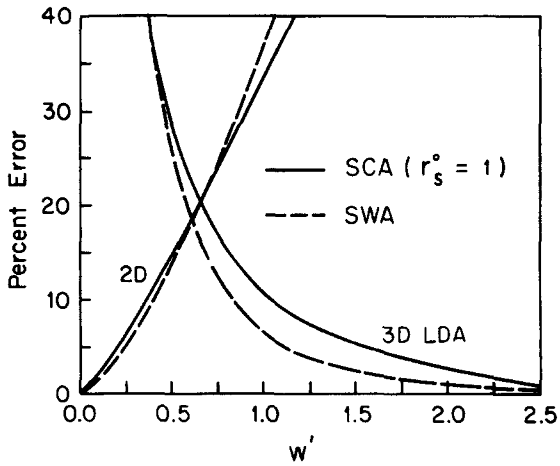

Fig. 1. The error in the LDA and in the 2D approximation when compared to the non-local exchange-correlation energy of a layer of electrons. $w' = w/r_s^0$ is the dimensionless width and r_s^0 is the value of r_s at the profile maximum. The error in the LDA is the absolute value of $(E_{xc} - E_{xc}^{LDA})/E_{xc}$ and similarly for the 2D approximation. Both the LDA and the 2D approximation overestimate E_{xc}. In the square-well approximation (SWA) both the non-local E_{xc} and E_{xc}^{LDA} are calculated with the square-well correlation function. For the screened-correlation approximation (SCA) E_{xc}^{LDA} is calculated with accurate values for the homogeneous exchange-correlation energy.

dependence in the present method the SCA results in Fig. 1 are not strictly applicable to real inversion and accumulation layers. However, we will see that this dependence is not very important, at least for the example we look at here. Let us first ignore the r_s^0 dependence and use Eqn. (11) and Fig. 1 to estimate errors for Si(100) quasi-2D layers,[3,13,14] ($m_z = 0.92$ and $\kappa = 11.8$). We find that the LDA overestimates the exchange-correlation energy by amounts ranging from 15% at $N^* = 3\text{x}10^{12}$ cm^{-2} to 26% at $N^* = 1\text{x}10^{11}$ cm^{-2}. To check this we have recalculated the errors using r_s^0 values consistent with Eqn. (11) and the definition of w. We find that these errors differ by only a few percentage points from those found with Fig. 1. The effective r_s^0 for these calculations is roughly approximated by $r_s^0\ (m_{op}/\kappa)\nu^{1/3}$ where

m_{op} = 0.19 is the optical mass for Si(100).[3] This effective r_s^0 varies from 1.1 at $N^* = 3 \times 10^{12}$ cm^{-2} to 4.9 at $N^* = 1 \times 10^{11}$ cm^{-2}. We have also used Fig. 1 to estimate the errors in the 2D approximation for these layers. In this approximation the layer is assumed to be exactly two-dimensional with density N^*. This approximation also overestimates the exchange-correlation energy calculated with the non-local theory. The errors are between 16 and 26% for densities between 1×10^{11} and 3×10^{12} cm^{-2} and are consistent with those calculated by Stern.[15]

In summary, we have proposed a simple, quantitative method for calculating non-local exchange-correlation energies in systems with an arbitrarily large degree of inhomogeneity. The method is accurate in several limits but is in need of further testing in more well understood inhomogeneous systems. Our results for quasi-2D layers provides a guide for estimating the applicability of the LDA in a given system. We suggest that there may be substantial errors in the LDA for inversion layers and accumulation layers over a wide range of 2D electron densities. As discussed in Ref. 1, this over-estimate of the exchange-correlation energy is consistent with the tendency of the LDA to overestimate subband energy level differences.[13,14,16] These non-local effects may also be important in the ongoing problem of valley degeneracy in Si layers.[13,19] We have made several approximations in applying the results contained in Fig. 1 to electron layers in real materials. In particular Eqn.(12) does not take into account the effects of a possible discontinuity in the dielectric constant. In the Si-SiO$_2$ system (κ_{Si} = 11.8 and κ_{SiO_2} = 3.9) the image potentials may play an important role[13] but in many other systems including many heterostructures the dielectric discontinuities are probably not important. In heterostructures the non-local effects discussed in this paper may be particularly important because the layer widths are more variable than in metal-oxide-semiconductor systems and can clearly be made narrow enough that the LDA must be a questionable approximation.

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