



Correlation energy, pair-distribution functions and static structure factors of jellium

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Abstract

We discuss and clarify a simple and accurate interpolation scheme for the spin-resolved electron static structure factor (and corresponding pair correlation function) of the 3D unpolarized homogeneous electron gas which, along with some analytic properties of the spin-resolved pair-correlation functions, we have just published (Phys. Rev. B, in press). We compare our results with the very recent spin-resolved scheme by Schmidt et al. (Phys. Rev. B 46 (1992) 12497; 56 (1997) 7018; submitted for publication) and focus our attention on the spin-resolved correlation energies and the high-density limit of the correlation functions. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The homogeneous electron gas is a model solid whose positive ionic charges are smeared throughout the whole crystal volume to yield a shapeless, uniform positive background (whence the nickname of jellium). The model, by ignoring the ionic lattice which makes real materials different from one another, allows the theorists to concentrate on key aspects of the electron–electron interaction. It thus represents an obvious limit for the inhomogeneous electron gas, and, through the density functional theory (DFT) [1], its local density approximation (LDA) and other semi-local [2,3]

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and nonlocal [4] approximations, it links to a popular and very successful description of real materials.

The pair-distribution functions $g_{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)$ describe the spatial correlations between electron pairs of prescribed spin orientations: the expected number of spin- σ_2 electrons in the volume dV at \mathbf{r}_2 , when another electron of spin σ_1 is at \mathbf{r}_1 , is equal to $dN(\mathbf{r}_2\sigma_2|\mathbf{r}_1\sigma_1) = n_{\sigma_2}(\mathbf{r}_2)g_{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) dV$, where $n_\sigma(\mathbf{r})$ is the density of spin- σ electrons. In the spin-unpolarized jellium, the electronic spin density $n_\uparrow(\mathbf{r}) = n_\downarrow(\mathbf{r}) = n/2 = (8\pi r_s^3/3)^{-1}$ is uniform in space (i.e., independent of \mathbf{r}), so $g_{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)$ only depends on the distance between the two electrons $r = |\mathbf{r}_1 - \mathbf{r}_2|$. Hartree atomic units are used throughout this work. The static structure factor $S(q)$ is an “experimental” quantity which gives a measure of the instantaneous density correlations in the system, and is directly related to the Fourier transform of the pair-correlation function. For an unpolarized homogeneous electron gas, after introducing the Fermi wavevector $q_F = (3\pi^2 n)^{1/3}$, the scaled variables $\rho = q_F r$ and $k = q/q_F$ are often convenient. With these variables the spin-resolved static structure factors are written as

$$S_{\sigma_1\sigma_2}(k; r_s) = \delta_{\sigma_1, \sigma_2} + \frac{2}{3\pi} \int_0^\infty d\rho \rho^2 [g_{\sigma_1\sigma_2}(\rho; r_s) - 1] \frac{\sin(k\rho)}{k\rho}, \quad (1)$$

the total pair-distribution function is equal to $g = \frac{1}{2}(g_{\uparrow\uparrow} + g_{\downarrow\downarrow})$, and the total static structure factor to $S = S_{\uparrow\uparrow} + S_{\downarrow\downarrow}$.

The pair-distribution functions of the uniform electron gas are a key ingredient in the construction of semi-local and nonlocal density functionals [2–4]. At the densities of interest for DFT calculations, the best estimate for the pair-correlation functions and static structure factors¹ of jellium is given by quantum Monte Carlo simulations (QMC) [5–7] which are available for a discrete set of interelectronic distances ρ (or momentum transfer k) and densities r_s . In a recent work [8] we have presented simple functional forms for the spin-resolved pair-correlation functions which depend upon ρ and r_s , are analytic and closed-form both in real and reciprocal space, fulfill most of the known properties of their exact counterparts, and contain some free parameters that have been fixed by a two-dimensional $(\rho, r_s$ and $k, r_s)$ fit to the new QMC data [7], thus yielding very accurate and reliable functions in the relevant density range $0.1 \lesssim r_s \lesssim 10$. As a byproduct, we also obtained accurate spin-resolved correlation energies which fulfill the exact high-density limit by construction [8]. In Section 2 we summarize the small- ρ (k) behavior of $g_{\sigma_1\sigma_2}$ ($S_{\sigma_1\sigma_2}$) together with the corresponding large- k (ρ) behavior of $S_{\sigma_1\sigma_2}$ ($g_{\sigma_1\sigma_2}$), and we discuss and clarify some points, especially Eq. (12) of Ref. [8]. Section 3 is devoted to a brief comparison of our results with the new spin-resolution [9] of the Perdew–Wang function [10,11], and in Section 4 the corresponding spin-resolved correlation energies are discussed.

¹ The pair-correlation functions and static structure factors are independently extracted by quantum Monte Carlo simulations [5,6].

2. Behavior of the spin-resolved correlation functions for small and large arguments

The pair-distribution function $g = g_{\text{ex}} + g_c$ (and correspondingly the static structure factor) can be divided into an exchange-only contribution $g_{\text{ex}}(\rho)$ (given by the Hartree–Fock approximation) and a Coulomb-correlation contribution $g_c(\rho; r_s)$, which, in turn, can be split into its $\uparrow\downarrow$ and $\uparrow\uparrow$ parts, $g_c = \frac{1}{2}(g_{\uparrow\downarrow}^c + g_{\uparrow\uparrow}^c)$. The leading terms of $g_{\sigma_1\sigma_2}^c$, $S_{\sigma_1\sigma_2}^c$, g_{ex} , S_{ex} and of the total functions for small and large arguments are summarized below.

	$g(\rho \rightarrow 0)$	$S(k \rightarrow \infty)$	$g(\rho \rightarrow \infty)$	$S(k \rightarrow 0)$
corr. $\uparrow\downarrow$	$a \left(1 + \frac{\rho}{q_F}\right) - 1$	$-\frac{4}{3\pi q_F} \frac{a}{k^4}$	$\frac{9}{4} \left(\frac{1}{\rho^4} + \frac{1}{\rho^6}\right)$	$-\frac{3}{8}k + \frac{k^2 q_F^2}{4\omega_p} + \frac{k^3}{32}$
corr. $\uparrow\uparrow$	$b \left(\rho^2 + \frac{\rho^2}{2q_F}\right) - \frac{\rho^2}{5}$	$\frac{8}{\pi q_F} \frac{b}{k^6}$	$\frac{9}{4} \left(\frac{1}{\rho^4} + \frac{1}{\rho^6}\right)$	$-\frac{3}{8}k + \frac{k^2 q_F^2}{4\omega_p} + \frac{k^3}{32}$
exch.	$\frac{1}{2} + \frac{1}{10}\rho^2$	1	$1 - \frac{9}{4} \left(\frac{1}{\rho^4} + \frac{1}{\rho^6}\right)$	$\frac{3}{4}k - \frac{k^3}{16}$
total	$\frac{a}{2} \left(1 + \frac{\rho}{q_F}\right)$	$1 - \frac{4}{3\pi q_F} \frac{a}{k^4}$	$1 - 3d \frac{6!}{\rho^8}$	$\frac{k^2 q_F^2}{2\omega_p} + ck^4 + dk^5$

Here $\omega_p = \sqrt{3/r_s^3}$ is the classical plasma frequency and the constants a , b , c and d are not known. The small- ρ (and corresponding large- k) behavior of the correlation functions is well known [12] from the many-body Schrödinger equation when two electrons approach each other (cusp conditions). The small- k (and corresponding large- ρ) behavior of the $\uparrow\downarrow$ and $\uparrow\uparrow$ correlation functions seems, instead, to be less known [8]. It can be determined by means of the random phase approximation (RPA) (see e.g. Ref. [13]), which is exact in the $k \rightarrow 0$ limit, as follows. The RPA only takes into account direct processes, i.e., processes that occur for both parallel- and antiparallel-spin pairs. Thus, for an unpolarized gas, the RPA $\uparrow\downarrow$ and $\uparrow\uparrow$ correlation functions are equal. This simple consideration, together with the well-known small- k behavior of the total S , $q_F^2 k^2 / 2\omega_p$, tells us that, as $k \rightarrow 0$, the linear term $3k/4$ of S_{ex} must be cancelled 50% by $S_{\uparrow\downarrow}^c$ and 50% by $S_{\uparrow\uparrow}^c$. The same argument can be applied to the $-k^3/16$ term of S_{ex} ; in fact, no term $\propto k^3$ must appear in the total S , whose long-wavelength behavior is determined by the plasmon contribution and by the single-pair and multipair quasiparticle–quasihole excitation contributions, proportional to k^5 and k^4 , respectively [13,14]. While the leading $-3k/8$ term of $S_{\sigma_1\sigma_2}^c$ (which corresponds to the large- ρ term $\frac{9}{4}\rho^{-4}$) and the plasmon contribution $\propto k^2$ must hold beyond RPA, the $k^3/32$ term (which corresponds to the large- ρ term $\frac{9}{4}\rho^{-6}$) holds for the exact $S_{\sigma_1\sigma_2}^c$ in the high-density limit, but its validity at lower densities must be verified. Note also that the k^5 term in the $k \rightarrow 0$ expansion of the total static structure factor implies that the total g behaves like ρ^{-8} when $\rho \rightarrow \infty$. The functional forms proposed in Ref. [8] exactly fulfill all of the above analytic constraints.

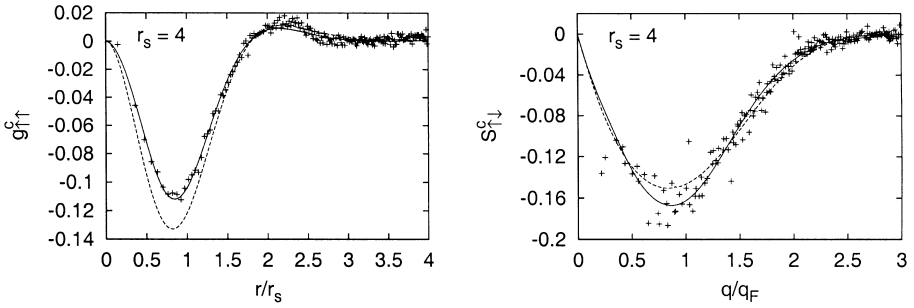


Fig. 1. Parallel-spin contribution to the pair-correlation function (left), and antiparallel-spin contribution to the static structure factor (right) for $r_s=4$. Solid line: functions from Ref. [8]; dashed line: new spin-resolved PW model [9–11]; crosses: QMC data [7].

3. Spin-resolved correlation functions

In Ref. [8] we compared our correlation functions with the widely used Perdew–Wang (PW) [10,11] model. The PW function turned out not to be accurate in its spin-resolved version, mainly because it does not fulfill the exact $k \rightarrow 0$ limit of $S_{\sigma_1\sigma_2}^c$. Based on our work, Schmidt et al. [9] have recently proposed a new spin resolution of the PW model, obtained by imposing this exact limit. Such revised PW function represents a considerable improvement over the original one, and works very well for $r_s \lesssim 2$, both in real and reciprocal space. At lower densities, however, our functions [8] provide a better interpolation of the QMC data [7], as shown, for example, by Fig. 1, where $g_{\uparrow\uparrow}^c$ and $S_{\uparrow\downarrow}^c$ for $r_s=4$ obtained from our scheme [8], the revised PW model [9] and QMC simulations [7] are reported. We have checked that, as r_s increases, the discrepancy between revised PW and QMC data becomes more pronounced. The reason of such increasing discrepancy with decreasing density can be explained as follows. The revised $\uparrow\uparrow$ PW function for the unpolarized gas is built up by rescaling the pair-correlation function of the fully polarized gas in such a way that the exact $k \rightarrow 0$ limit of $S_{\uparrow\uparrow}^c$ is fulfilled. As a result, the parallel-spin contribution to correlation tends to be overestimated (and consequently the $\uparrow\downarrow$ part is underestimated). Correlations are highly dominated by antiparallel-spin interactions, where available (see e.g. Ref. [13]), and hence simple scaling arguments which connect correlations in the fully-polarized gas (where $\uparrow\downarrow$ interactions are totally absent) and $\uparrow\uparrow$ correlations in the unpolarized gas (where $\uparrow\downarrow$ interactions are present and tend to dominate the electronic correlations) will provide less and less reliable results at lower and lower densities, as the role of Coulomb correlation with respect to exchange becomes more and more important. The same argument applies to the correlation energy, as we shall see in the next Section 4. Note that the overestimate of the PW $\uparrow\uparrow$ pair-correlation function makes the total (exchange + correlation) parallel-spin pair-distribution function be slightly negative near $r=0$ for densities $r_s \gtrsim 6$. Nonetheless, the new scaling law proposed by Schmidt et al. [9] does much better than any previous one.

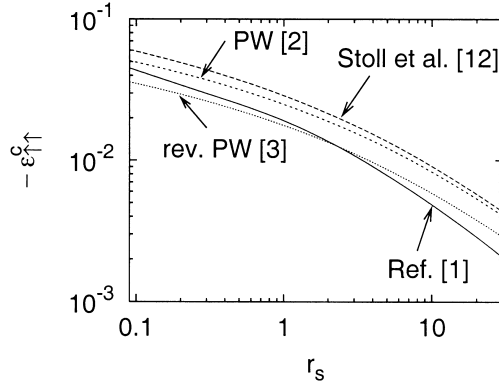


Fig. 2. Parallel-spin contribution to the correlation energy obtained from different scaling guesses compared to our interpolation scheme (solid line, Ref. [8]). Units are Hartrees per electron.

4. Spin-resolved correlation energies and the high-density limit

Correlation energy: The spin-resolved contributions to the correlation energy are defined as

$$\varepsilon_{\sigma_1\sigma_2}^c = \frac{q_F^2}{3\pi} \int_0^{r_s} dr'_s \int_0^\infty d\rho \rho g_{\sigma_1\sigma_2}^c(\rho, r'_s) \tag{2}$$

and hence $\varepsilon_c = \varepsilon_{\uparrow\downarrow}^c + \varepsilon_{\uparrow\uparrow}^c$. The corresponding exact high-density limit is recovered by applying the same argument which yielded the $k \rightarrow 0$ expansion of $S_{\sigma_1\sigma_2}^c$. In the framework of RPA (see e.g. Ref. [13]), in fact, one obtains for the unpolarized gas $\varepsilon_{\uparrow\downarrow}^c = \varepsilon_{\uparrow\uparrow}^c$ at any r_s . Since in the $r_s \rightarrow 0$ limit RPA is exact, we have

$$\lim_{r_s \rightarrow 0} \varepsilon_{\uparrow\downarrow}^c = \lim_{r_s \rightarrow 0} \varepsilon_{\uparrow\uparrow}^c = \frac{(1 - \ln 2)}{2\pi^2} \ln r_s + O(r_s^0). \tag{3}$$

Beyond RPA (beyond orders $\ln r_s$) $\varepsilon_{\uparrow\downarrow}^c$ and $\varepsilon_{\uparrow\uparrow}^c$ are not equal because of higher-order exchange terms which mainly lower the $\uparrow\uparrow$ correlation energy. The spin-resolved correlation energies presented in Ref. [8] are the best-to-date estimate of $\varepsilon_{\sigma_1\sigma_2}^c$, since they are obtained by integrating the corresponding QMC pair-correlation functions [7] interpolated by our $g_{\sigma_1\sigma_2}^c$ and $S_{\sigma_1\sigma_2}^c$ models which also incorporate the exact behavior at small and large arguments. Moreover, our $\varepsilon_{\sigma_1\sigma_2}^c$ fulfill the high-density limit of Eq. (3). Previous estimates of $\varepsilon_{\uparrow\uparrow}^c$ were obtained by scaling the correlation energy of the fully polarized gas. The most widely used scaling laws are the Stoll et al. [15,16] and the Perdew–Wang [10,11], which is now available in its revised form given by Schmidt et al. [9]. In Fig. 2 we compare our $\varepsilon_{\uparrow\uparrow}^c$ with these three schemes. It is apparent that the revised PW gives the best result, even if it does not fulfill the high-density limit of Eq. (3). As a consequence, the revised PW underestimates by $\sim 22\%$ the $\uparrow\uparrow$ correlation energy at $r_s = 0$. As expected from the corresponding $\uparrow\uparrow$ pair-correlation function (see Fig. 1), at densities $r_s \gtrsim 2$ the revised PW overestimates $\varepsilon_{\uparrow\uparrow}^c$ by an amount which increases with r_s (e.g. 3% at $r_s = 3$, 21% at $r_s = 10$). Again, we see the failure of

simple scaling laws which try to connect correlations in the fully polarized gas and $\uparrow\uparrow$ correlations in the unpolarized gas.

High-density limit of the pair-correlation functions: It is also worthwhile to discuss some points about the link between the high-density limit of the pair-correlation function and the $r_s \rightarrow 0$ limit of Eq. (3). Rassolov et al. [17] have recently computed the $r_s \rightarrow 0$ limit of g_c/r_s , which turned out to be a well-defined, r_s -independent, function. For different reasons, neither PW [9–11], nor our pair-correlation function [8] fulfill this limit. As pointed out in Ref. [8], our simple functional forms do not reconcile the known high-density limit of the pair-correlation functions at zero interelectronic distance [18,19] with Eq. (3). In this respect, the functional form used by PW [10,11] is such that when the exact $k \rightarrow 0$ limit of $S_{\sigma_1\sigma_2}^c$ is imposed to it, Eq. (3) is automatically violated. The PW spin-resolved version, thus, suffers from a different problem than ours. In summary, although major steps forward have been achieved in this area by Refs. [8,9], none of the existing models fulfills all the known properties at $r_s \rightarrow 0$, and further improvements are needed in this limit.

5. Conclusions

In this work we have clarified the behavior of the spin-resolved pair-correlation function and static structure factor of the unpolarized uniform electron gas for small and large arguments. We have then compared the two best-to-date models for these functions [8,9], pointing out their advantages and drawbacks, and we have discussed the corresponding spin-resolved correlation energies. We found that the functions in Ref. [8] provide a better fit to the QMC data [8], both in real and reciprocal space, and provide the best-to-date estimate of the spin-resolved correlation energies. At very high density, however, even the forms proposed by Refs. [8,9] are inadequate, and further work is needed. It should be also kept in mind that in this high-density limit the non-relativistic Hamiltonian, on which the whole theory is based, is no longer valid, and relativistic corrections or a fully relativistic treatment would be required [20,21].

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