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Correlation holes in a spin-polarized dense electron gas

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Double perturbation theory is used to calculate the form of the correlation hole in polarized and unpolarized dense electron gas. The analytical dependence on the polarization of the correlation hole at the origin is obtained. The normalized hole depth at the origin is minimal for the unpolarized gas. The correlation hole is always negative. It can be adequately described at the short range by the product of a spin-independent and density-dependent function on the uncorrelated pair-distribution function. [S0163-1829(99)05324-2]

I. INTRODUCTION

The development of density functional theory (DFT) and its successful applications to many atomic and molecular systems has focused renewed attention on the description of correlation effects in a uniform electron gas. Adequate description of the electron pair distribution is important in building exchange-correlation functionals in the framework of the local spin density (LSD) approximation.[1,2] For molecular environments, it is particularly important to know pair-distribution functions $g(R)$ of a polarized electron gas for relatively short electron separation distances R. The pair-distribution function is defined as the probability to find an electron at a given distance R from another electron. Depending on the relative spins of these two electrons, the pair-distribution function can be subdivided into $\alpha\alpha$, $\alpha\beta$, and $\beta\beta$ parts. The correlation hole for a given spin pair is defined as the difference between the exact pair-distribution function for these spins and the corresponding pair distribution in the uncorrelated system. Knowledge of the correlation holes would permit separation of the correlation energy into short- and long-range parts and may help in building LSD density functionals suited for molecular environments.

The pair distribution in the uncorrelated electron gas can be obtained through the Hartree-Fock calculation. For the pair of electrons of opposite spins this function is constant. The pair-distribution function for the uncorrelated electrons of the same spin is defined as the exchange hole and was obtained by Dirac.[3] The current knowledge about the correlation holes comes either from Monte Carlo calculations[4] or through interpolation of data from $g(0)$ for a dense unpolarized gas, coupled with the cusp condition,[5,6] the value of the $\alpha\beta$ correlation hole at the origin for the unpolarized dense electron gas,[7] and knowledge of the exchange-only hole of the polarized gas.[8,9] There is no information on the polarization dependence of the correlation hole near the origin, apart from numerical Monte Carlo simulations. Such simulations, while very useful in the investigation of existing models, are difficult to use for the construction of new models.

The aim of the present work is to study further the correlation hole near the origin in a dense polarized electron gas. Double perturbation theory[10] is well suited for this purpose, giving the exchange-only hole at the lowest order of perturbation, and describing perturbation of the electron distribution through electron correlation at higher orders. It is exact for a sufficiently dense electron gas, assuming the expansion series to be convergent at least partially. The exact polarization data for a dense gas may help to improve the existing density functionals based on the electron gas model.[11]

II. METHOD

We use double perturbation theory[10] to explore the pair correlation function. The noninteracting electron gas is simultaneously perturbed by the Coulombic electron repulsion $P_C=e^2/r_{12}$ and by the δ function probe $P_{\delta(R)}=\lambda\delta(R-r_{12})$. The energy of such a system can be written as a Taylor expansion

$$\begin{aligned} E&=\sum_{i,j} E_{ij},\\ E_{1,0}&=\langle\Psi_0|P_C|\Psi_0\rangle,\\ E_{0,1}&=\langle\Psi_0|P_{\delta(R)}|\Psi_0\rangle,\\ E_{1,1}&=2\sum_k \frac{\langle\Psi_0|P_{\delta(R)}|\Psi_k\rangle\langle\Psi_k|P_C|\Psi_0\rangle}{E_k-E_0}\\ &\vdots \end{aligned} \tag{1}$$

The pair-distribution function $g(R)$ at electron separation R can be found through such expansion by considering the term corresponding to the first derivative of the total energy with respect to the perturbation parameter λ. This derivative is proportional to the pair-distribution function at the point where the probing δ function is not zero.

$$g(R)=\lim_{\lambda\to 0}\left(\frac{\partial E}{\partial\lambda}\right)=\sum_i g_i(R), \tag{2}$$

$$g_i(R)=\frac{E_{i,1}}{\lambda}. \tag{3}$$

This expression gives the pair-distribution function as a series with respect to the strength of the electron-electron interaction. It is convenient to replace the effective coupling constant e^2 with the dimensionless Wigner-Seitz radius $r_s=(me^2/\hbar^2)/[9\pi/2(\alpha^3+\beta^3)]^{1/3}$, where α and β are Fermi momenta for alpha and beta electrons, respectively. This corresponds to the radius of a sphere containing a single electron, in atomic units. For a dense electron gas, r_s is small, so the leading terms of Eq. 2 are the most important. The first term $g_0(R)$ gives the pair-distribution function for a noninteracting electron gas, or the exchange-only pair-distribution function. The correlation part of the pair-distribution function is defined as $g(R)-g_0(R)$, $g_1(R)$ being the leading term for small r_s.

The computation of terms beyond $g_1(R)$ suffers from divergence of the integrals, similar to divergence of integrals involved in calculation of correlation energy for the dense electron gas.[12] Fortunately, the important $g_1(R)$ term is free from this problem and can be calculated in relatively straightforward fashion, although large values of interelectron distance R require careful handling, as numerical stability deteriorates for the limit $R\to\infty$. Since the pair-distribution function is well described at long range through its Fourier transform,[8] this study primarily focuses on the short-range part of the pair-distribution function.

It is convenient to analyze the pair-distribution function in terms of distributions of electrons of particular spin combinations $g^{\alpha\alpha}(R)$, $g^{\alpha\beta}(R)$, and $g^{\beta\beta}(R)$.

A significant amount of information about the pair-distribution function can be obtained from its value at the origin. Combining this information with proper cusp behavior allows construction of relatively accurate correlation holes for short separation distances.[9] Because of antisymmetry requirements $g^{\alpha\alpha}(0)=g^{\beta\beta}(0)=0$. The value of $g_1^{\alpha\beta}(0)$ was computed by Geldart[7] for the unpolarized electron gas. The present approach enables us to derive an analytic expression for $g_1^{\alpha\beta}(0)$ for a dense electron gas of arbitrary polarization.

III. COMPUTATION

We will use atomic units through the rest of the manuscript. The pair-distribution function of a dense electron gas is

$$g_1(R)=\sum_{i,j\to a,b}\frac{2}{\lambda}\frac{\langle\Psi_0|P_C|\Psi_{i,j}^{a,b}\rangle\langle\Psi_{i,j}^{a,b}|P_{\delta(R)}|\Psi_0\rangle}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b},\tag{4}$$

where Ψ_0 is the wave function for a noninteracting electron gas. The excited state $\Psi_{i,j}^{a,b}$ describes double electron excitation from occupied states i and j with momenta $\mathbf{p}_1$ and $\mathbf{p}_2$ and energies $\epsilon_i=p_1^2/2$ and $\epsilon_j=p_2^2/2$ into states a and b with momenta $\mathbf{p}_1+\mathbf{q}$ and $\mathbf{p}_2+\mathbf{q}'$ and orbital energies $\epsilon_a=(\mathbf{p}_1+\mathbf{q})^2/2$ and $\epsilon_b=(\mathbf{p}_2+\mathbf{q}')^2/2$, respectively. The conservation of momentum requires that $\mathbf{q}=-\mathbf{q}'$. The $g_1^{\alpha\alpha}(R)$ and $g_1^{\beta\beta}(R)$ contain both direct $i\to a$, $j\to b$ and cross-terms of type $i\to b$, $j\to a$ with respect to both perturbations, while the $g_1^{\alpha\beta}(R)$ term contains only direct terms. This makes $E_{11}^{\alpha\beta}$ significantly simpler to compute.

A. Pair-distribution function of electrons of opposite spins

Integrating plane waves over coordinate space, one easily finds that, for the excitation with momentum exchange q, the Coulombic repulsion operator $1/r_{12}$ transforms to $4\pi/q^2$ in momentum space. The $P_{\delta(R-r_{12})}/\lambda$ perturbation transforms in momentum space to $\sin(qR)/(qR)$. Taking care of proper normalization factors, we get

$$\begin{aligned}g_1^{\alpha\beta}(R)=&-\frac{16\pi}{(2\pi)^9}\int_0^\infty q^2dq\int_{p_1\langle\alpha,|\mathbf{p}_1+\mathbf{q}|\rangle\alpha}d^3\mathbf{p}_1\\&\times\int_{p_2\langle\beta,|\mathbf{p}_2-\mathbf{q}|\rangle\beta}d^3\mathbf{p}_2\frac{4\pi\sin(qR)}{q^2qR}\\&\times\frac{1}{(\mathbf{p}_1+\mathbf{q})^2-p_1^2+(\mathbf{p}_2-\mathbf{q})^2-p_2^2}\\=&\frac{-1}{16\pi^7}\int_0^\infty dq\frac{\sin(qR)}{q^2R}\int_{p_1\langle\alpha,|\mathbf{p}_1+\mathbf{q}|\rangle\alpha}dp_1d\cos\theta_1\\&\times\int_{p_2\langle\beta,|\mathbf{p}_2-\mathbf{q}|\rangle\beta}dp_2d\cos\theta_2\\&\times\frac{1}{q+p_1\cos\theta_1-p_2\cos\theta_2},\end{aligned}\tag{5}$$

where α is the Fermi momentum for electron 1, β is the Fermi momentum for electron 2, and θ_1, θ_2 are angles between the momentum transfer $\mathbf{q}$ and initial momenta of electrons 1 and 2, respectively.

It is convenient to introduce an inverse Laplace transform to separate variables of two electrons,

$$\frac{1}{q+p_1\cos\theta_1-p_2\cos\theta_2}=\int_0^\infty ds\,e^{-sq-sp_1\cos\theta_1+sp_2\cos\theta_2}.\tag{6}$$

Now we can integrate electrons 1 and 2 out to get

$$g_1^{\alpha\beta}(R)=\frac{-1}{4\pi^5}\int_0^\infty dq\frac{\sin(qR)}{q^2R}\int_0^\infty ds\,e^{-sq}J_\alpha(s,q)J_\beta(s,q),\tag{7}$$

where auxiliary functions J are

$$J_x(s,q)=\begin{cases}\frac{1}{s^3}[(sx+1)(e^{-sx}-e^{-s(x-q)})+sqe^{sq/2}] & \text{if } q\leqslant 2x\\[1ex]\frac{1}{s^3}[(sx-1)e^{sx}+(sx+1)e^{-sx}] & \text{if } q\geqslant 2x.\end{cases}\tag{8}$$

This equation can be further reduced to expressions which involve integration of a single variable q by analytically integrating over variable s. The final integration of q was performed numerically for moderate values of q, and analytically for large q. Details can be found in the Appendix. The plots of the pair-distribution function are given in Fig. 1.

It can be easily shown that the interelectron cusp condition[5,13] yields $\partial g/\partial R|_{R=0}=1$. Pair-distribution functions in Fig. 1 satisfy this with 0.1% accuracy.

An important feature of $g_1^{\alpha\beta}(R)$ is that it is negative for any finite R. Therefore, it does not satisfy the normalization

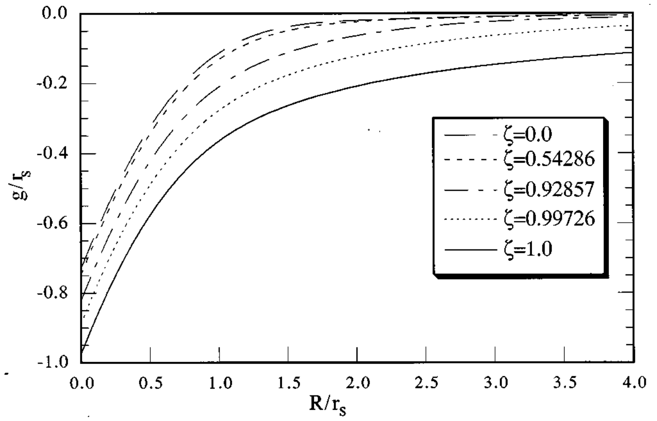

FIG. 1. Correlation hole in the dense electron gas for electrons of opposite spins. Both distribution function and separation distance are normalized per Wigner-Seitz radius r_s. Distribution function is given per electron pair of opposite spins. Values of polarization are given for different curves.

condition $\int g_1^{\alpha\beta}(r) r^2 dr = 0$ which is required for any finite system. Effectively, part of the electronic cloud is pushed to infinity. Since the correlation energy can be expressed as the integral of the pair-distribution function with Coulomb operator over the whole space, the all-negative pair-distribution function may lead to the overestimation of the correlation energy, as compared to that in the finite system.

The correlation hole of the fully polarized gas is significantly deeper than for the unpolarized one. This shows the weakness of the original Perdew-Wang (PW) model[9] which adopts the exchange-only spin dependence of the correlation hole. The exchange-only dependence is essentially a normalization factor, making the PW correlation hole normalized per number of α-β pairs polarization independent. Deepening of the α-β correlation hole with the polarization increase is expected as the average α-β electron pair becomes less constrained with the polarization increase.

Pair-distribution function at the origin

Due to the presence of the Fermi hole in the pair-distribution function for electrons of parallel spin, the only contribution to $g(0)$ comes from excitations of electrons of opposite spins. Setting the electron separation distance $R=0$, we get from Eq. (7)

$$g_1(0) = \frac{-1}{4\pi^5}\int_0^\infty \frac{dq}{q}\int_0^\infty ds\, e^{-sq} J_\alpha(s,q) J_\beta(s,q), \tag{9}$$

where auxiliary functions J are defined in Eq. (8).

Now we transform with respect to parameters α and β and integrate the transformed expression

$$\left(\frac{[g_1(0)]''_{\alpha\beta}}{\alpha\beta}\right)''_{\alpha\beta} = \frac{-1}{4\pi^5}\int_0^\infty \frac{dq}{q}\int_0^\infty ds\, e^{-sq}\tilde{J}_\alpha(s,q)\tilde{J}_\beta(s,q)$$

$$= \frac{-1}{4\pi^5}\,\frac{2}{\alpha+\beta}\ln\left(\frac{\alpha+\beta}{\alpha-\beta}\right). \tag{10}$$

We assume $\alpha \geqslant \beta$. The auxiliary functions $\tilde{J}$ are

$$\tilde{J}_x(s,q) \equiv \left(\frac{[J_x(s,q)]'_x}{x}\right)'_x = \begin{cases} e^{-sx}(1-e^{sq}) & \text{if } q \leqslant 2x \\ e^{sx}+e^{-sx} & \text{if } q \geqslant 2x. \end{cases} \tag{11}$$

Since we have to integrate Eq. (10) with respect to parameters α and β it is convenient to represent it as series

$$\left(\frac{[g_1(0)]''_{\alpha\beta}}{\alpha\beta}\right)''_{\alpha\beta} = \frac{1}{\pi^5}\sum_{i=1}^{\infty}(-1)^i \frac{\beta^i}{\alpha^{i+1}}\sum_{j=0}^{[(i-1)/2]}\frac{1}{2j+1}, \tag{12}$$

where $[(i-1)/2]$ implies the integer part of $(i-1)/2$.

The biggest problem now is to recover the integration constants when we transform Eq. (12) back to obtain $g_1(0)$. This is easier to do in steps, first recovering constants lost in the final differentiation in Eq. (10). It is also helpful to remember that from the dimensional arguments E_{11} is proportional to the fifth power of momentum, i.e., $E_{11} \sim \alpha^y \beta^{5-y}$.

$$\frac{[g_1(0)]''_{\alpha\beta}}{\alpha\beta} = \frac{-1}{4\pi^5}\left(\beta\frac{\pi^2}{2} + O(\beta^2)\right) \tag{13}$$

so

$$[g_1(0)]''_{\alpha\beta} = \frac{-1}{4\pi^5}\Bigg(\alpha\beta^2\frac{\pi^2}{2} - 2\beta^3$$

$$+4\sum_{i=2}^{\infty}\frac{(-1)^i\beta^{i+2}\alpha^{1-i}}{i(i+1)}\sum_{j=0}^{[(i-1)/2]}\frac{1}{2j+1}\Bigg). \tag{14}$$

The remaining two constants of integration of Eq. (14) are of the order β^5 and α^5. From physical meaning we know that $\lim_{\beta\to 0}[g_1(0)] = 0$, so the only remaining constant to recover is the one on the order of β^5. We cannot study the limit $\alpha \to 0$ of Eq. (7) directly since we used the condition $\alpha \geqslant \beta$, so we investigate the asymptotic behavior of

$$\left(\frac{[g_1(0)]'_\beta}{\beta}\right)'''_{\beta\beta\beta} = \frac{-1}{4\pi^5}\left[4\ln\left(\frac{\alpha}{\beta}\right) - \frac{\pi^2}{2}\right] + O(\beta), \tag{15}$$

which, together with Eq. (14), leads to

$$g_1(0) = \frac{-1}{4\pi^5}\Bigg\{\frac{\pi^2\alpha^2\beta^3}{12} - \frac{\alpha\beta^4}{2} + \left[\frac{61}{225} - \frac{\pi^2}{60} + \frac{2}{15}\ln\left(\frac{\alpha}{\beta}\right)\right]\beta^5$$

$$-4\sum_{i=3}^{\infty}\frac{(-1)^i\beta^{i+3}\alpha^{2-i}}{(i-2)i(i+1)(i+3)}\sum_{j=0}^{[(i-1)/2]}\frac{1}{2j+1}\Bigg\}. \tag{16}$$

After normalizing per density of $\alpha\beta$ electron pairs

$$\rho_\alpha\rho_\beta = \frac{1}{(2\pi)^6}\left(\frac{4}{3}\pi\right)^2\alpha^3\beta^3 \tag{17}$$

and expressing Fermi momenta α and β through more conventional Wigner-Seitz radius r_s and polarization $\zeta = (\alpha^3 - \beta^3)/(\alpha^3+\beta^3)$, we get for the density of electrons at the coalescence point

$$
\begin{aligned}
g_1(0)={}&-r_s\left(\frac{324}{\pi^4(1+\zeta)}\right)^{1/3}\left\{\frac{\pi^2}{12}-\frac{1}{2}\left(\frac{1-\zeta}{1+\zeta}\right)^{1/3}\right.\\
&+\left(\frac{1-\zeta}{1+\zeta}\right)^{2/3}\left[\frac{61}{225}-\frac{\pi^2}{60}+\frac{2}{45}\ln\left(\frac{1+\zeta}{1-\zeta}\right)\right]\\
&+4\frac{1-\zeta}{1+\zeta}\sum_{i=0}^{\infty}\left(\frac{1-\zeta}{1+\zeta}\right)^{i/3}\\
&\left.\times\frac{(-1)^i}{(i+1)(i+3)(i+4)(i+6)}\sum_{j=0}^{[i/2+1]}\frac{1}{2j+1}\right\}\\
&+O(r_s^2).
\end{aligned}
\tag{18}
$$

For the special case of unpolarized electron gas $\zeta=0$, and we get

$$
\begin{aligned}
g(0)^{\zeta=0}={}&-r_s\left(\frac{324}{\pi^4}\right)^{1/3}\left(\frac{\pi^2}{15}-\frac{103}{450}\right.\\
&\left.+4\sum_{i=0}^{\infty}\frac{(-1)^i}{(i+1)(i+3)(i+4)(i+6)}\sum_{j=0}^{[i/2+1]}\frac{1}{2j+1}\right)\\
\simeq{}&-0.731\,670r_s\,.
\end{aligned}
\tag{19}
$$

This is in agreement with $-0.7317r_s$ calculated by Geldart.[7]

For a fully polarized electron gas $\zeta=1$ and the density of α electrons on top of a single β electron looks especially simple,

$$
g(0)^{\zeta=1}=-r_s\left(\frac{3\pi^2}{32}\right)^{1/3}\simeq-0.974\,444r_s\,. \tag{20}
$$

Both fully polarized and unpolarized correlation holes at the origin, as well as its ζ dependence have been recently calculated by Burke, Perdew, and Ernzerhof.[14] Our expression looks somewhat simpler, especially for the fully polarized gas. It is interesting to note that the correlation hole in the polarized gas is deeper than that of the unpolarized one. Of course, the contribution of this hole to total correlation energy in the latter case will be less significant, since the number of opposite-spin electron pairs will be lower.

B. Pair-distribution function of electrons of same spins

The value of $g_1^{\alpha\alpha}(R)$, normalized per number of α-α electron pairs, does not depend on the amount of β electrons in the system, and vice versa. This is not true for higher orders in g_i, but at the level of our analysis this allows us to construct pair-distribution functions for electrons of parallel spins that are independent of polarization. Let us then assume for simplicity that we are considering a fully polarized gas with $\beta=0$.

Now we have contributions from both direct and cross-terms with respect to both Coulomb and δ function probe operators. For direct contributions the momentum representation of both operators is identical to that for the $g_1^{\alpha\beta}$ case, being $4\pi/q^2$ for the Coulomb operator and $\sin(qR)/(qR)$ for the δ function probe. For cross-terms these operators are $4\pi/(\mathbf{q}+\mathbf{p}_1-\mathbf{p}_2)^2$ and $\sin(|\mathbf{q}+\mathbf{p}_1-\mathbf{p}_2|R)/(|\mathbf{q}+\mathbf{p}_1-\mathbf{p}_2|R)$. Assuming $\alpha=1$ we get

$$
\begin{aligned}
g_1^{\alpha\alpha}(R)={}&\frac{-1}{8\pi^7}\int_0^{\infty}q^2dq\int_{p_1\langle 1,|\mathbf{p}_1+\mathbf{q}|\rangle 1}d^3\mathbf{p}_1\\
&\times\int_{p_2\langle 1,|\mathbf{p}_2-\mathbf{q}|\rangle 1}d^3\mathbf{p}_2\left(\frac{1}{q^2}-\frac{1}{(\mathbf{q}+\mathbf{p}_1-\mathbf{p}_2)^2}\right)\\
&\times\left(\frac{\sin(qR)}{(qR)}-\frac{\sin(|\mathbf{q}+\mathbf{p}_1-\mathbf{p}_2|R)}{(|\mathbf{q}+\mathbf{p}_1-\mathbf{p}_2|R)}\right)\\
&\times\frac{1}{2\mathbf{q}(\mathbf{q}+\mathbf{p}_1-\mathbf{p}_2)}.
\end{aligned}
\tag{21}
$$

The integrand of this equation does not depend on $\mathbf{p}_1+\mathbf{p}_2$, although such dependence is implicit in the limits of integration. We can change variables as

$$
\begin{aligned}
\mathbf{x}&=\frac{\mathbf{p}_1+\mathbf{p}_2}{2},\\
\mathbf{y}&=\mathbf{p}_1-\mathbf{p}_2\,.
\end{aligned}
\tag{22}
$$

This gives

$$
\begin{aligned}
g_1^{\alpha\alpha}(R)={}&\frac{-1}{4\pi^6}\int_0^{\infty}qdq\int_0^2dy\int_0^{\pi}\sin\theta d\theta\\
&\times\left(\frac{1}{q^2}-\frac{1}{q^2+y^2+2qy\cos\theta}\right)\\
&\times\left(\frac{\sin(qR)}{qR}-\frac{\sin(\sqrt{q^2+y^2+2qy\cos\theta}R)}{\sqrt{q^2+y^2+2qy\cos\theta}R}\right)\\
&\times\frac{1}{q+y\cos\theta}V(q,y,\theta)\\
={}&\frac{-1}{2\pi^6}\int_0^{\infty}qdq\int_0^2\frac{dy}{y}\int_{|q-y|}^{q+y}sds\left(\frac{1}{q^2}-\frac{1}{s^2}\right)\\
&\times\left(\frac{\sin(qR)}{qR}-\frac{\sin(sR)}{sR}\right)\frac{V(q,y,s)}{q^2-y^2+s^2},
\end{aligned}
\tag{23}
$$

$$
s=\sqrt{q^2+y^2+2qy\cos\theta},
$$

where θ is the angle between $\mathbf{q}$ and $\mathbf{y}$, and $V(q,y,\theta)$, or $V(q,y,s)$ is a result of integration of variable x and is equal to the volume of a figure shown in Fig. 2. The origin is marked with 0. Placement of vector $\mathbf{x}$ within the sphere $\mathbf{p}_1$, which is the unit sphere shifted from the origin by $-\mathbf{y}/2$, ensures that momentum $p_1<1$. In addition to that, the requirement $|\mathbf{p}_1+\mathbf{q}|>1$ constrains $\mathbf{x}$ to be outside the sphere created by displacing sphere p_1 by $-\mathbf{q}$. Similar requirements with respect to the momentum of the second electron keep $\mathbf{x}$ within the crescent of sphere p_2. Therefore, the volume of integration of x is represented by the intersection of two crescents, or

$$
\begin{aligned}
V(q,y,\theta)={}&v(p_1,p_2)-v(p_1,p_2,p_1+q)-v(p_1,p_2,p_2-q)\\
&+v(p_1,p_2,p_1+q,p_2-q),
\end{aligned}
\tag{24}
$$

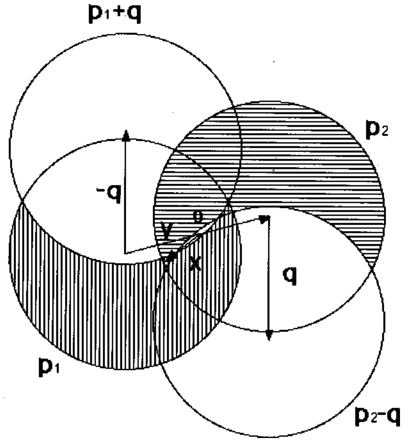

FIG. 2. Volume of integration in momentum space with respect to average momentum of two electrons, labeled by the overlapping vertical and horizontal grids. The center of symmetry is marked with ‘‘0.’’

where $v(a,b,\ldots)$ is volume of intersection of spheres $a,b,\ldots$. The volume of intersection of three spheres of unit radii was calculated by Powell.[15] The volume of intersection of four spheres can be reduced to those for two and three spheres due to the symmetry of the problem (the whole picture has center of symmetry at the origin). For $q \geqslant 1$ this volume is reduced to $v(p_1,p_2)$.

Due to the complexity of $V(q,y,s)$ Eq. (23) has to be calculated numerically. The numerical integration is complicated by large derivatives in $V(q,y,s)$, especially near the critical region of small s when $q \simeq y$. Unfortunately, analytical representation of V is very complicated even as a Taylor series for small s, so we had to resort to a very dense integration grid in this region. The calculated $g_1^{\alpha\alpha}(R)$ is shown in Fig. 3, along with maxima of $g_0^{\alpha\alpha}(R)$. Unfortunately, limited numerical accuracy prevents checking the cusp condition,[6] since it requires numerical computation of the third derivative.

The exchange-only pair-distribution function for the uniform fully polarized electron gas is

$$g_0=1-9\left(\frac{\sin x - x\cos x}{x^3}\right)^2, \quad x=\left(\frac{9\pi}{4}\right)^{1/3}\frac{R}{r_s}. \tag{25}$$

The first term describes the classical distribution of the electrons, and the second term is due to the exchange interaction. It is nonpositive everywhere, and breaks the whole space into shells. On the surface of each shell the exchange term is equal to zero. The physical effect of the exchange interaction on the distribution function is to remove parts of the electron distribution from between the shells, and leave it constant on their surfaces.

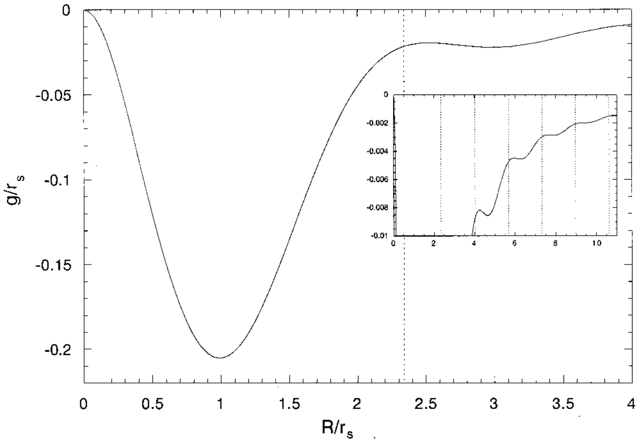

FIG. 3. Correlation hole in the dense electron gas for electrons of same spins. Both distribution function and separation distance are normalized per r_s. Distribution function is given per electron pair of same spins. The tail of the distribution function is given in the inset.

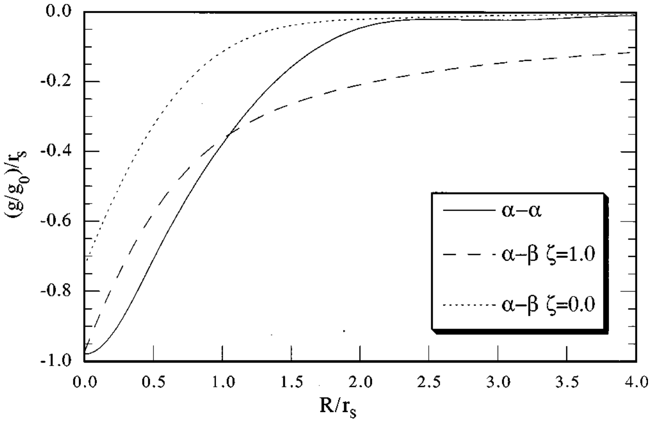

FIG. 4. Correlation holes in dense electron gas normalized per r_s and divided by the uncorrelated distribution functions g_0. Both same- and opposite-spin correlation holes are given for comparison.

To the leading order, the correlation effects are more pronounced between shells, further reducing the exchange-depleted electron distribution. Unlike the exchange interaction, the distribution on the shell surfaces is also reduced. The electrons are pushed towards infinity, since the $g_1(R)$ is nonpositive everywhere. This effect is due to the infiniteness of the electron gas, and, like the correlation distribution for $\alpha\beta$ electrons, may lead to the overestimation of the correlation energy in the finite systems.

C. Comparison of the pair-distribution functions

The absolute values of the α-α and α-β correlation holes are very different. This difference is, however, much less pronounced for the correlation pair distribution relative to the uncorrelated pair distribution. The relative distribution functions, defined as $g_1(R)/g_0(R)$ are given in Fig. 4. The values of the relative α-α correlation hole very close to the origin ($R/r_s<0.1$) may be unreliable as they involve the division of two small numbers.

The relative α-β distribution is equivalent to the absolute one, since the exchange-only distribution function for the α-β pairs is a constant. The relative α-α correlation hole, however, reveals its similarity with the α-β hole. Its short-range ($R/r_s \leqslant 1$) part is similar to the fully polarized α-β hole, while its tail ($R/r_s \geqslant 2$) is quite close to the unpolarized α-β correlation hole. This suggests that the density functionals based on the Hartree-Fock-Kohn-Sham method[2] can be spin independent.

The correlation hole computed via perturbation theory is exact for a dense electron gas. To find the range of the smallness parameter r_s for which the leading term is expected to

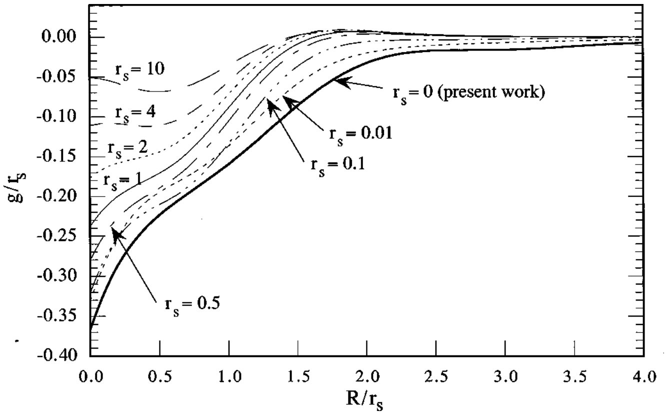

FIG. 5. Spin-integrated correlation hole of unpolarized dense electron gas normalized per r_s and compared with the Perdew-Wang model for different values of r_s.

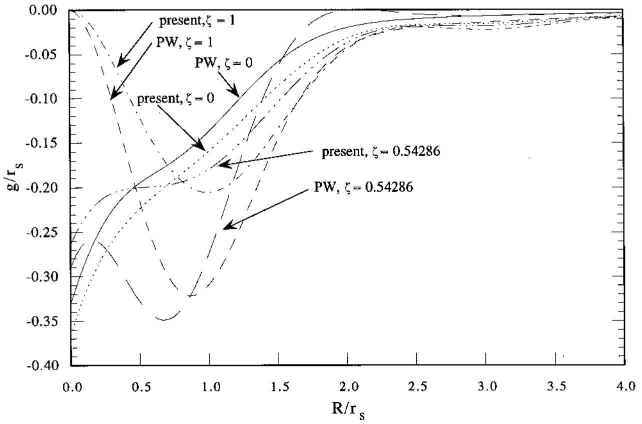

FIG. 6. Comparison of the Perdew-Wang ($r_s = 0.01$) and the exact correlation holes in dense electron gas for different values of the polarization parameter ζ.

dominate the shape of correlation hole, we plot in Fig. 5 the spin-integrated PW correlation hole of an unpolarized electron gas for different values of r_s. For small values of r_s in the range between 0.1 and 0.01 the PW correlation hole divided by r_s is nearly constant and is slightly different from the exact correlation hole (the PW hole divided by r_s starts to diverge for r_s below 0.01). This difference is probably due to the use of Padé approximation for the correlation hole shape in the PW model.[8] Taking this discrepancy as an acceptable margin of error, the dense electron gas correlation hole is satisfactory for $r_s < 1$.

Comparison of the PW model for polarized electron gas with present calculations shows some shortcomings of the PW model. Figure 6 compares the PW model for very small value of $r_s = 0.01$ with the exact result. In the absence of polarization the agreement is very good. In a fully polarized gas the PW model has a qualitatively correct shape, but is deeper near the origin. The discrepancy with the exact result starts very near the origin and is probably due to the absence of the interelectron cusp constraint[6] for the parallel-spin electrons.[9] The largest discrepancy is for the partially polarized gas. The PW correlation hole for $\zeta \approx 0.542\,86$ (corresponding to Fermi momentum of β electrons 2/3 of that for α ones) is qualitatively different from the exact result. As Fig. 4 shows, a more accurate approximation of the correlation hole would model it as a universal and possibly spin-independent function multiplied on the uncorrelated pair-distribution function.

III. CONCLUSIONS

We used double perturbation theory to study the correlation hole in the polarized electron gas. This enabled us to derive analytically the depth of the correlation hole at the origin. For the special case of the unpolarized gas our formula yields the value obtained by Geldart[7] and it agrees with Burke, Perdew, and Ernzerhof for the fully polarized case.[14] When normalized per opposite-spin electron pairs, this depth is smallest in the unpolarized case and grows by almost a third in the fully polarized gas. This contradicts the Perdew-Wang model[9] which assumes the polarization-independent correlation hole.

Our study of the correlation hole away from the origin shows that in the dense electron gas limit both same- and opposite-spin components of the correlation hole are nonpositive everywhere in space. Therefore, the correlation effectively removes some electrons from the interaction region. This effect leads to the ''overcorrelation,'' as compared to the correlation energy in the finite system.

From comparison with the PW model, the dense electron gas correlation hole is satisfactory for $r_s < 1$. The polarized gas hole in the PW model reproduces that of dense electron gas near the origin for the unpolarized case, is qualitatively correct but 50% deeper in the fully polarized case, and is incorrect for intermediate polarizations. At the same time, the ratio of the correlation to the exchange holes is similar for the same- and the opposite-spin electron pairs. This suggests modeling the correlation hole as a spin-independent and density-dependent function multiplied on the pair distribution of the uncorrelated system.

The present study of the correlation hole in the polarized electron gas near the origin is very appropriate for the modeling of correlation potentials for molecular environments due to the importance of relatively short-range correlation effects there. The correlation effects in the electron gas are energetically important at the longer length scale on the order $\sqrt{r_s}$,[9] which is not described at the level of perturbation used here.

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APPENDIX

Integration with respect to s transforms Eq. (7) into

$$g_1(0) = \frac{-1}{4\pi^5}\int_0^\infty dq \frac{\sin(qR)}{q^2 R} F(\alpha,\beta,q), \tag{A1}$$

where

$$F(\alpha,\beta,q)=\begin{cases}
\frac{(\alpha+\beta)q^2}{480}(44\alpha^2+28\alpha\beta+44\beta^2-3q^2)-\frac{\alpha^3q^2}{3}\ln\left(\frac{\alpha+\beta}{\alpha}\right)-\frac{\beta^3q^2}{3}\ln\left(\frac{\alpha+\beta}{\beta}\right)\\
-\ln\left(\frac{\alpha+\beta+q}{\alpha+\beta}\right)*(\alpha+\beta+q)^3\left(-\frac{\alpha\beta}{6}+\frac{(\alpha+\beta+q)(\alpha+\beta)}{24}-\frac{(\alpha+\beta+q)^2}{120}\right)\\
-\ln\left(\frac{\alpha+\beta-q}{\alpha+\beta}\right)(\alpha+\beta-q)^3\left(-\frac{\alpha\beta}{6}+\frac{(\alpha+\beta-q)(\alpha+\beta)}{24}-\frac{(\alpha+\beta-q)^2}{120}\right)\\
-\frac{\beta^4q}{24}\left[\left(1+\frac{q}{2\beta}\right)^3\left(-3+\frac{q}{2\beta}\right)\ln\left(1+\frac{q}{2\beta}\right)-\left(1-\frac{q}{2\beta}\right)^3\left(-3-\frac{q}{2\beta}\right)\ln\left(1-\frac{q}{2\beta}\right)\right]\\
-\frac{\alpha^4q}{24}\left[\left(1+\frac{q}{2\alpha}\right)^3\left(-3+\frac{q}{2\alpha}\right)\ln\left(1+\frac{q}{2\alpha}\right)-\left(1-\frac{q}{2\alpha}\right)^3\left(-3-\frac{q}{2\alpha}\right)\ln\left(1-\frac{q}{2\alpha}\right)\right] & \text{if } q\leqslant 2\beta\\
\frac{\beta q(2\alpha+q)}{480}(44\alpha^2+14\alpha q+44\beta^2-3q^2)-\ln(\alpha-\beta+q)(\alpha-\beta+q)^3\\
\left(-\frac{\alpha\beta}{6}+\frac{(\alpha-\beta+q)(\beta-\alpha)}{24}+\frac{(\alpha-\beta+q)^2}{120}\right)\\
-\ln(\alpha+\beta+q)(\alpha+\beta+q)^3\left(-\frac{\alpha\beta}{6}+\frac{(\alpha+\beta+q)(\beta+\alpha)}{24}-\frac{(\alpha+\beta+q)^2}{120}\right)\\
-\ln(\alpha-\beta)(\alpha-\beta)^3\left(\frac{\alpha\beta}{6}+\frac{(\alpha-\beta)^2}{30}\right)\\
-\ln(\alpha+\beta)(\alpha+\beta)^3\left(\frac{\alpha\beta}{6}-\frac{(\alpha+\beta)^2}{30}\right)\\
+\ln\left(\frac{q}{2}-\beta\right)\frac{q}{6}\left(\frac{q}{2}-\beta\right)^3\left(\frac{3b}{4}+\frac{q}{8}\right)+\ln\left(\frac{q}{2}+\beta\right)\frac{q}{6}\left(\frac{q}{2}+\beta\right)^3\left(\frac{3b}{4}-\frac{q}{8}\right) & \text{if } 2\beta<q\leqslant 2\alpha\\
\frac{\alpha\beta q}{30}(11\alpha^2+11\beta^2+q^2)+\ln\left(1-\frac{\alpha+\beta}{q}\right)\frac{(q-\alpha-\beta)^3}{6}\left(\alpha\beta+\frac{(q-\alpha-\beta)(\alpha+\beta)}{4}+\frac{(q-\alpha-\beta)^2}{20}\right)\\
+\ln\left(1+\frac{\alpha+\beta}{q}\right)\frac{(q+\alpha+\beta)^3}{6}\left(\alpha\beta-\frac{(q+\alpha+\beta)(\alpha+\beta)}{4}+\frac{(q+\alpha+\beta)^2}{20}\right)\\
+\ln\left(1-\frac{\alpha-\beta}{q}\right)\frac{(q-\alpha+\beta)^3}{6}\left(\alpha\beta-\frac{(q-\alpha+\beta)(\alpha-\beta)}{4}-\frac{(q-\alpha+\beta)^2}{20}\right)\\
+\ln\left(1+\frac{\alpha-\beta}{q}\right)\frac{(q+\alpha-\beta)^3}{6}\left(\alpha\beta+\frac{(q+\alpha-\beta)(\alpha-\beta)}{4}-\frac{(q+\alpha-\beta)^2}{20}\right) & \text{if } 2\alpha<q.
\end{cases} \tag{A2}$$

For $q>30\alpha$ the function $F(\alpha,\beta,q)$ was approximated by

$$F(\alpha,\beta,q)\simeq\frac{4}{9}(\alpha\beta)^3\left[\frac{1}{q}+\frac{\alpha^2+\beta^2}{5q^3}+\frac{15\alpha^4+42\alpha^2\beta^2+15\beta^4}{175q^5}+\frac{5\alpha^6+27\alpha^2\beta^2(\alpha^2+\beta^2)+5\beta^6}{105q^7}\right]. \tag{A3}$$

This expansion was computed with the MATHEMATICA package for symbolic computation.[16]

Numerical integration of Eq. (A1) was performed up to $q>100$ or $q>100*R$ (whatever is greater). The rest of the range of q was integrated analytically over the power expansion from the above equation.

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