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Journal
Canadian Journal of Physics, 58(8)

ISSN
0008-4204 1208-6045

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Publication Date
1980-08-01

DOI
10.1139/p80-159

Peer reviewed

Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis[1]

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Received March 19, 1980

We assess various approximate forms for the correlation energy per particle of the spin-polarized homogeneous electron gas that have frequently been used in applications of the local spin density approximation to the exchange-correlation energy functional. By accurately recalculating the RPA correlation energy as a function of electron density and spin polarization we demonstrate the inadequacies of the usual approximation for interpolating between the para- and ferro-magnetic states and present an accurate new interpolation formula. A Padé approximant technique is used to accurately interpolate the recent Monte Carlo results (para and ferro) of Ceperley and Alder into the important range of densities for atoms, molecules, and metals. These results can be combined with the RPA spin-dependence so as to produce a correlation energy for a spin-polarized homogeneous electron gas with an estimated maximum error of 1 mRy and thus should reliably determine the magnitude of non-local corrections to the local spin density approximation in real systems.

Nous évaluons différentes formes de l'énergie de corrélation par particule dans un gaz homogène d'électrons avec polarisation du spin qui ont été utilisées dans des applications de l'approximation densité locale de spin à la fonctionnelle de l'énergie de corrélation et d'échange. En recalculant de façon précise l'énergie de corrélation RPA en fonction de la densité électronique et de la polarisation du spin nous montrons les insuffisances de l'approximation usuelle pour l'interpolation entre les états para- et ferromagnétiques et nous présentons une nouvelle formule précise d'interpolation. Une technique d'appoximants de Padé est utilisée pour faire une interpolation précise des résultats Monte Carlo récents (para- et-ferro-) de Ceperley et Alder dans l'intervalle important de densités pour les atomes, les molécules et les métaux. Ces résultats peuvent être combinés avec la dépendance de spin RPA de façon à donner une énergie de corrélation pour un gaz homogène d'électrons avec polarisation du spin dont l'erreur maximum estimée est de 1 mRy, déterminant ainsi de façon plus sûre la grandeur des corrections non locales à l'approximation de densité locale de spin dans les systèmes réels.

[Traduit par le journal]

Can. J. Phys., **58**, 1200 (1980)

1. Introduction

The importance of the correlation energy for many-electron systems has long been appreciated and a great deal of effort has been directed towards its study. In particular, the homogeneous electron gas has received much attention for nearly 50 years (see Pines (1) for a review of pre-1955 work) primarily as an idealized model of a metal. More recently the development and success of the Hohenberg, Kohn, and Sham spin density functional (SDF) formalism (for recent reviews see Lang (2), Rajagopal (3), and Mackintosh and Andersen (4)) and especially the local spin density approximation (LSDA) to the exchange-correlation (XC) energy functional has given the correlation energy of the homogeneous electron gas added significance for the study of real many-electron systems. Specifically, the correlation energy per particle of the homogeneous electron gas, $\varepsilon_c(r_s, \zeta)$, where r_s and ζ are the usual density and spin polarization parameters, respectively (see Sect. 2), is an essential ingredient of the LSDA and if known accurately would hopefully improve agreement between theory and experiment, and if not, enable one to assess unambiguously the importance of non-local corrections to the LSDA in atoms, molecules, and metals.

The past several years have seen a very large computational effort (4, 5) based on various approximate forms for the fundamental quantity $\varepsilon_c(r_s, \zeta)$. In our view, sufficient attention has not been given to the accuracy of this quantity used in calculations,

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0008-4204/80/081200-12$01.00/0

especially with regard to its spin dependence. Since various authors use different forms for $\varepsilon_c(r_s, \zeta)$ in complicated self-consistent calculations, it is difficult to appreciate the meaning and significance of similarities and differences in their results. Although there have been many approximate determinations of the correlation energy (i.e., beyond the so-called random phase approximation, hereinafter referred to as the RPA) for the paramagnetic state, $\varepsilon_c(r_s, 0)$, it was not until very recently (6, 7) that highly accurate results were available for both the para- and ferro-magnetic electron liquid states, albeit for a limited number of electron densities.

In the present work we will compare and assess the adequacy of the various approximate forms for $\varepsilon_c(r_s, \zeta)$ that have been frequently used in applications of the LSDA. Since the spin dependence of these approximate forms is based on a suggestion of von Barth and Hedin (8) (to be referred to as vBH) derived from their RPA calculation, we have carefully re-examined the spin dependence of the RPA in Sect. 3 and found the vBH form inaccurate for densities corresponding to $r_s \leq 6$. A new parametrization of the RPA is introduced which is accurate to better than 1% for all r_s and ζ. These new RPA results are combined with Ceperley and Alder's calculations by means of a two-point Padé approximant interpolation formula to produce a new $\varepsilon_c(r_s, \zeta)$ that is accurate for the important densities in atoms, molecules, and solids, and thus should provide a reliable means for judging the validity of the LSDA.

2. General Comments and Criteria for Assessing Correlation Energy

The essential ingredients for applying the SDF formalism to calculating the ground state properties of any system is the exchange-correlation functional $E_{xc}[n_\uparrow, n_\downarrow]$, where $n_{\uparrow/\downarrow}$ is the density for spin up/down electrons, respectively. The LSDA assumes $E_{xc}[n_\uparrow, n_\downarrow]$ is

$$[2.1] \quad E_{xc}^{L}[n_\uparrow, n_\downarrow] = \int d\mathbf{r}\, n(\mathbf{r}) \varepsilon_{xc}(n_\uparrow, n_\downarrow)$$

where $\varepsilon_{xc}(n_\uparrow, n_\downarrow)$ is the XC energy (per particle) of a homogeneous electron gas with spin densities $n_{\uparrow/\downarrow}$ and $n = n_\uparrow + n_\downarrow$. For discussing ε_{xc} it is more convenient to use the standard variables r_s and ζ for density and spin polarization, respectively ($\zeta = (n_\uparrow - n_\downarrow)/n$). It is well known (e.g., refs. 8 and 9) that the exchange energy can be written in the form

$$[2.2] \quad \varepsilon_x(r_s, \zeta) = \varepsilon_x^{P}(r_s) + [\varepsilon_x^{F}(r_s) - \varepsilon_x^{P}(r_s)] f(\zeta) \equiv \varepsilon_x^{P}(r_s) + \Delta\varepsilon_x(r_s, \zeta)$$

where P/F stand for para/ferro-magnetic states, respectively, with

$$\varepsilon_x^{P}(r_s) = -3/2\pi\alpha r_s = \varepsilon_x^{F}(r_s)/2^{1/3}$$
$$\alpha = (4/9\pi)^{1/3}$$

and

$$[2.3] \quad f(\zeta) = \frac{[(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2]}{2(2^{1/3} - 1)}$$

Unfortunately there is no analogous simple closed form for the correlation energy $\varepsilon_c(r_s, \zeta)$. Nonetheless $\varepsilon_c(r_s, \zeta)$ can always be written as

$$[2.4] \quad \varepsilon_c(r_s, \zeta) \equiv \varepsilon_c^{P}(r_s) + \Delta\varepsilon_c(r_s, \zeta)$$

where $\varepsilon_c^{P}(r_s) = \varepsilon_c(r_s, 0)$, thus defining $\Delta\varepsilon_c(r_s, \zeta)$ which should not be confused with the von Barth and Hedin suggestion for approximating it (see Sect. 3). We will begin with a review of recent calculations of the correlation energy and present some simple criteria for judging their accuracy. These results will provide a standard for our new estimates in Sect. 4. Our main emphasis will be on its spin dependence and the importance of calculating it in a consistent manner. The reason for this is that $\varepsilon_c^{P}(r_s)$ and $\varepsilon_x^{P}(r_s)$ are of the same sign (both being negative) and $|\varepsilon_x^{P}| > |\varepsilon_c^{P}|$ for important densities. On the other hand $\Delta\varepsilon_c(r_s, \zeta)$ is positive while $\Delta\varepsilon_x(r_s, \zeta)$ is negative (this is just the well-known fact that correlation inhibits ferromagnetism (10)) and although $|\Delta\varepsilon_c(r_s, \zeta)|$ is smaller than $|\Delta\varepsilon_x(r_s, \zeta)|$, it is of much more similar magnitude especially in the range $r_s \gtrsim 3$, so that any error in $\Delta\varepsilon_c(r_s, \zeta)$ is magnified in $\Delta\varepsilon_{xc}(r_s, \zeta)$.

There have been numerous studies of $\varepsilon_c^{P}(r_s)$ and recently Ceperly and Alder (7) have also studied $\varepsilon_c^{F}(r_s) = \varepsilon_c(r_s, 1)$ for several values of r_s, but the ζ-dependence over the whole range has been calculated only in the RPA by von Barth and Hedin (8) for metallic densities and more recently Dunaevskii (11) has attempted to use the method of Singwi *et al.* (12) to study $\Delta\varepsilon_c(r_s, \zeta)$. We do not believe that his results are correct since his $\Delta\varepsilon_c(r_s, 1)$ conflicts with the known high density behaviour (see below and Fig. 2). The factorization of the correlation energy in [2.4] has more significance than might appear at first glance. Firstly, it emphasizes the independence of the spin polarization part from the paramagnetic 'background' and accentuates that $\varepsilon_c^{P}(r_s)$ and $\Delta\varepsilon_c(r_s, \zeta)$ can be taken from different sources, with the condition that $\Delta\varepsilon_c(r_s, 0) = 0$, to obtain a more accurate $\varepsilon_c(r_s, \zeta)$ than from, say, an RPA calculation. Secondly, [2.4] stresses that when calculating $\Delta\varepsilon_c(r_s, \zeta)$ it is essential to use the same approximation for the $\varepsilon_c^{P}(r_s)$ and the $\varepsilon_c(r_s, \zeta)$ parts, i.e., include the same Feynman graphs. In fact there are strong reasons for believing that $\Delta\varepsilon_c(r_s, \zeta)$ converges more

TABLE 1. Recent calculations of $-\varepsilon_c^P(r_s)$ in mRy. Quantities in parentheses were obtained by interpolation from values at different r_s's. 'Av' denotes the average value of $-\varepsilon_c^P(r_s)$ not including RPA, H-67, KW, and MRT

	$-\varepsilon_c^P(r_s)$ (mRy)					
	$r_s = 1$	$r_s = 2$	$r_s = 3$	$r_s = 4$	$r_s = 5$	$r_s = 6$
RPA	157.6	123.6	105.5	93.6	85.0	78.2
H-67 (23)		92	75	64		
STLS (24)	125	97	80	70	63	57
SSTL (12)	124	92	75	64	56	50
KW (25)	76.3	70.6	60.3	52.3	46.0	40.7
VS (21)	130	98	81	70	62	56
LB (26)	125	91.9	74.2	62.5	54.4	
CW (27)	(117)	91.3	(76.5)	67.9	(61.0)	(56.5)
F (16)	118	88.4	73.3	63.6	56.7	51.5
MRT (28)	137	103	85	74	65	59
C-78 (6)	122	87.4	72.2	62.4	55.0	(49.8)
Av	123	92.3	76.0	65.8	58.3	53.5

rapidly than $\varepsilon_c^P(r_s)$. For example, the leading correction to the RPA correlation energy $\varepsilon_{RPA}(r_s, \zeta)$ at high density is the second-order exchange $\varepsilon_b^{(2)} = 48.36$ mRy (13, 14) and is the same order of magnitude as $\varepsilon_{RPA}(r_s, \zeta)$ (see Table 1). However, it is simple to show that $\varepsilon_b^{(2)}$ is independent of ζ as well as r_s (15) so that the two leading terms of $\Delta\varepsilon_c(r_s, \zeta)$ are given exactly by the RPA in the high density limit. Recall that $\varepsilon_b^{(2)}$ contains two bare coulomb interactions, thus graphs of this structure will become ζ-dependent when screening is included. Freeman (16) has calculated the effect of replacing one bare coulomb line in the second-order exchange graph by a dynamically screened line for $\zeta = 0$ and finds a weak r_s dependence (he denotes this contribution by ΔE_{cx}^R). However, it should be pointed out that Freeman does not include all the graphs which give corrections of the order $r_s \ln r_s$ and r_s to $\varepsilon_b^{(2)}$ which must be grouped together (17) to obtain the correct coefficients of these terms. Generalizing DuBois (17) to allow for spin polarization, we will denote the combination of these terms as $\varepsilon_{1x}(r_s, \zeta)$. In the high density limit

$$[2.5] \quad \varepsilon_{1x}(r_s, 0) = \varepsilon_b^{(2)} + r_s(A_{1x} \ln r_s + C_{1x}) + O(r_s^2)$$

The constants A_{1x} and C_{1x} have been evaluated by Carr and Maradudin (18) to be 13 and -21 mRy, respectively. For graphs of this structure Misawa (19) has pointed out a scaling relation between $\zeta = 0$ and 1, namely $\varepsilon_{1x}(r_s, 1) = \varepsilon_{1x}(r_s/2^{4/3}, 0)$. (This relation is consistent with $\varepsilon_b^{(2)}$ being constant.) It should be contrasted with RPA scaling (10, 19), i.e., $\varepsilon_{RPA}(r_s, 1) = \frac{1}{2}\varepsilon_{RPA}(r_s/2^{4/3}, 0)$. The ζ-dependence of higher order graphs has not been investigated; however, there is good evidence (Ceperley and Alder (7), see Sect. 4) that $\Delta\varepsilon_c(r_s, 1)$ differs from $\Delta\varepsilon_{RPA}(r_s, 1)$ by at most 11% while $\varepsilon_c^P(r_s)$ differs from the RPA value by 25 to 30% for metallic densities.

Janak, Moruzzi, and Williams' (20) (hereinafter JMW) effort to improve on the RPA is in the spirit of [2.4]. They took $\varepsilon_c^P(r_s)$ from the calculation of Vashishta and Singwi (21); however, their procedure for estimating $\Delta\varepsilon_c(r_s, \zeta)$ suffers in two aspects (which in fact do compensate for some values of r_s and ζ, see Sect. 5): (*i*) $\varepsilon_c^F(r_s)$ was determined from $\varepsilon_c^P(r_s)$ by RPA scaling which clearly does not satisfy the above criterion for consistency and (*ii*) the von Barth and Hedin suggestion for expressing $\Delta\varepsilon_c(r_s, \zeta)$ as $[\varepsilon_c^F(r_s) - \varepsilon_c^P(r_s)]f(\zeta)$ is inaccurate (see Sect. 3).

Table 1 contains a summary of recent calculations of $\varepsilon_c^P(r_s)$. Hubbard's classic 1957 work (22) has been omitted since it has been superceded by his 1967 work (23). Also, Ceperley and Alder (7) (hereinafter to be referred to as CA) have improved Ceperley's (6) calculations for a few values of r_s (2, 5, 10, 20, 50, and 100). Since only two values are in the range considered in Table 1 we delay discussion of their work until Sect. 4. It is very difficult to judge the accuracy of any one of these calculations, especially in the range $2 \leq r_s \leq 6$. In particular, even at as high a density as $r_s = 1$ the maximum disagreement is 50 mRy (i.e., -11 to $+40$% of the average) while at $r_s = 6$ the extreme values differ from the average by approximately 20%. It is not difficult to establish criteria for assessing the validity of these calculations, at least in the high density limit. Recall that the correlation energy can be written as a sum of Feynman graphs, the dominant contribution being the RPA which contains the $\ln r_s$ singularity. Thus it is useful to write

$$[2.6] \quad \varepsilon_c(r_s, \zeta) = \varepsilon_{RPA}(r_s, \zeta) + \varepsilon_b^{(2)} + \delta\varepsilon_c(r_s, \zeta)$$

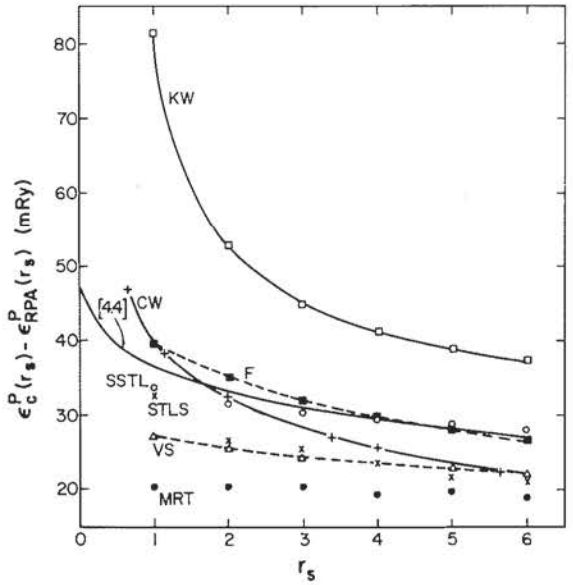

FIG. 1. A comparison of results for $\varepsilon_c^P(r_s) - \varepsilon_{RPA}^P(r_s)$ (see Table 1 for notation). Equation [4.4] refers to our Padé fit to Ceperley and Alder (7) as described in the text (see Table 5).

where $\delta\varepsilon_c(r_s, \zeta)$ is smaller than the other two terms for the range of r_s of interest and is a smooth function of r_s. In the high density limit, according to [2.5], it is

$$[2.7] \quad \delta\varepsilon_c(r_s, 0) = r_s(A_{1x} \ln r_s + C_{1x}) + Dr_s + O(r_s^2)$$

The constant D has not been evaluated (17, 18). Thus if one considers

$$[2.8] \quad \delta_1\varepsilon_c(r_s, \zeta) = \varepsilon_c(r_s, \zeta) - \varepsilon_{RPA}(r_s, \zeta)$$

it should tend smoothly to $\varepsilon_b^{(2)}$ as $r_s \to 0$. A more refined criterion for $\varepsilon_c^P(r_s)$ is provided by the quantity

$$[2.9] \quad \delta_2\varepsilon_c(r_s, 0) = \delta_1\varepsilon_c(r_s, 0) - \varepsilon_b^{(2)} - r_s(A_{1x} \ln r_s + C_{1x})$$

which should approach zero linearly as $r_s \to 0$. Either of these criteria immediately throws doubt on the validity of the Keiser and Wu (KW) (25) and Mandal, Rao, and Tripathy (MRT) (28) results (see Fig. 1). Also, a smooth extrapolation of the Chakravarty and Woo (CW) (27) results for $r_s = 0.565$ and 1.13 does not appear to be approaching the correct limit. Furthermore, a similar plot of criterion [2.9] suggests that the Vashishta and Singwi (21) calculations are inaccurate for r_s near 1. In an effort to present an unbiased view we have used all the results in Table 1 except RPA, KW, MRT, and H-67 to arrive at the average presented there. We expect that its maximum error is a few millirydbergs. Thus combining the average value of $\varepsilon_c^P(r_s)$ given in Table 1 with accurate RPA calculations for $\Delta\varepsilon_c(r_s, \zeta)$ will result in an $\varepsilon_c(r_s, \zeta)$ which has a maximum error of 10% for metallic densities and for the important transition metals where $r_s \leq 2$ the error will be even less.

Since there have been very few calculations of $\varepsilon_c^F(r_s)$ it is even more important to have criteria for assessing $\Delta\varepsilon_c(r_s, 1)$. Using the fact that $\varepsilon_b^{(2)}$ is independent of r_s and ζ, the analogue of [2.8] is that

$$[2.10] \quad \delta_1\Delta\varepsilon_c(r_s, 1) \equiv \Delta\varepsilon_c(r_s, 1) - \Delta\varepsilon_{RPA}(r_s, 1)$$

must go to zero as $r_s \to 0$ with a positive value having an infinite slope at $r_s = 0$ (see [2.11]). By using the scaling relation for $\varepsilon_{1x}(r_s, \zeta)$ given above to obtain the analogues of A_{1x} and C_{1x} for $\zeta = 1$ we note that

$$[2.11] \quad \delta_2\Delta\varepsilon_c(r_s, 1) = \delta_1\Delta\varepsilon_c(r_s, 1) - r_s\{\Delta A_{1x} \ln r_s + \Delta C_{1x}\}$$

where

$$\Delta A_{1x} = \left(\frac{1}{2^{4/3}} - 1\right) A_{1x}$$

and

$$\Delta C_{1x} = \left(\frac{1}{2^{4/3}} - 1\right) C_{1x} - (\tfrac{4}{3} A_{1x} \ln 2)/2^{4/3}$$

must tend to zero linearly with r_s. For the level of accuracy presently available for $\Delta\varepsilon_c(r_s, 1)$ criterion [2.10] is most useful. Figure 2 contains plots of $\delta_1\Delta\varepsilon_c(r_s, 1)$ for the calculations of Dunaevskii (11), the parametrized forms of Gunnarsson and Lundqvist (9) (hereinafter GL) and JMW used in LSDA calculations, the result from Freeman's (16) calculation using the scaling relation for $\varepsilon_{1x}(r_s, \zeta)$, Perdew's parametrization of Ceperley's old calculation (6), and our result obtained by interpolating CA's (see Sect. 4) most recent calculations. Clearly the results from Dunaevskii, GL, and JMW have the wrong behaviour for $r_s \to 0$. (Recall that $\delta_1\Delta\varepsilon_c(r_s, 1)$ must be positive in the vicinity of $r_s = 0$.) The values derived from Freeman's and CA's calculations agree with this rigorous result. For $r_s > 1$ we favour our result (as derived from CA in Sect. 4) for two reasons: (*i*) Freeman's calculation is not really consistent in retaining all graphs of a given order in r_s (see above) and (*ii*) even if the errors estimated by CA are off by a factor of 2 or 3, $\delta_1\Delta\varepsilon_c(r_s, 1)$ would remain positive and not change significantly. Thus we must conclude that the GL and JMW values of $\Delta\varepsilon_c(r_s, 1)$ are in error by approximately 10 mRy in the metallic density range. It should be emphasized that this will not necessarily give an error of 10 mRy per spin since ζ is usually less than one.

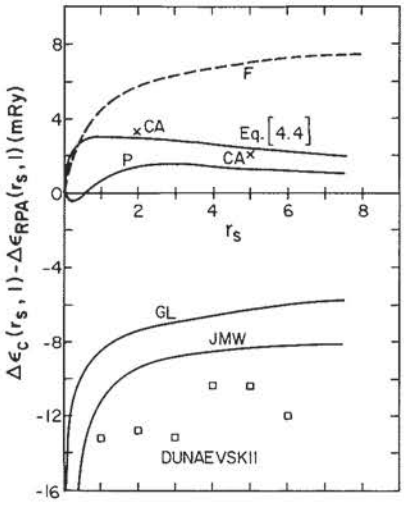

FIG. 2. Results for $\Delta\varepsilon_c(r_s, 1) - \Delta\varepsilon_{RPA}(r_s, 1)$ from various approximations for $\varepsilon_c^P(r_s)$ and $\varepsilon_c^F(r_s)$. GL, Gunnarsson and Lundqvist (9); JMW, Janak, Moruzzi, and Williams (20); Dunaevskii (11); P, Perdew (private communication), CA, numerical values from Ceperley and Alder (7); F, as derived from Freeman (16) by use of scaling; and eq. [4.4] refers to values obtained from our Padé fits to Ceperley and Alder (7).

It was pointed out by Vosko and Perdew (29) that the spin susceptibility of paramagnets in the LSDA is determined by the sum of the exchange and correlation contributions to the spin stiffness $\alpha_{xc}(r_s) = (\partial^2\varepsilon_{xc}(r_s, \zeta)/\partial\zeta^2)_0$ (the subscript denotes $\zeta = 0$). However, it has not always been appreciated that for metallic ferromagnets $|\zeta| \leq 0.15$ and for ζ's in this range $\Delta\varepsilon_{xc}(r_s, \zeta)$ can be accurately approximated by the first non-vanishing term in the Taylor series:

$$[2.12] \quad \Delta\varepsilon_{xc}(r_s, \zeta) \simeq \tfrac{1}{2}\alpha_{xc}(r_s)\zeta^2$$

To illustrate the validity of this approximation for $\Delta\varepsilon_x(r_s, \zeta)$ we have tabulated $f(\zeta)$ and $\frac{1}{2}f''(0)\zeta^2$ in Table 2. Even for $\zeta = 0.2$ the error is less than 0.4%. Noting that the XC contribution to the spin stiffness is related to the non-interacting and interacting spin susceptibilities, $\chi_0(r_s)$ and $\chi_h(r_s)$, respectively, of a homogeneous electron gas (10, 29) by

$$[2.13] \quad \alpha_{xc}(r_s) = \frac{3\alpha\pi}{2r_s^2}\left\{\frac{\chi_0(r_s)}{\chi_h(r_s)} - 1\right\}$$

a calculation of $\chi_h(r_s)$ determines $\Delta\varepsilon_{xc}(r_s, \zeta)$ for ζ's of interest in solids.

There have been many calculations of the correlation contribution to $\chi_h(r_s)$. A complete list of references is given in Kushida *et al.* (ref. 30, see Fig. 6). Because of the agreement between a number of methods (31–33) which appeared to be different, these results took on a degree of credibility. However, Shastry (34) has recently shown that they are all equivalent to an RPA calculation of $\varepsilon_c(r_s, \zeta)$ and then using α_c to obtain $\chi_h(r_s)$. Keiser and Wu (25) have also calculated $\chi_h(r_s)$ by their method and although when used in LSDA calculations for the spin susceptibility of Li, Na, and K (35) it gave excellent agreement with experiment we now have reason to doubt the validity of their results. First, as pointed out above their calculation of $\varepsilon_c^P(r_s)$ appears to be incorrect. Also, one can apply a criterion analogous to [2.8], namely

$$[2.14] \quad \delta_1\alpha_c(r_s) = \alpha_c(r_s) - \alpha_{RPA}(r_s)$$

should tend smoothly to zero as $r_s \to 0$. The reason for this is that $\varepsilon_b^{(2)}$ is independent of ζ so that the high density corrections to $\alpha_c(r_s)$ are $O(r_s \ln r_s, r_s)$. Their results do not satisfy this criterion (see Table 6). For these reasons we cannot accept their values in the range $3 \leq r_s \leq 6$. In our view there is no calculation presently available which gives reliable corrections to the RPA.

TABLE 2. Comparison of $f(\zeta)$ and $\frac{1}{2}f''(0)\zeta^2$ where $f(\zeta)$ is defined in [2.3]

ζ	$f(\zeta)$	$\frac{1}{2}f''(0)\zeta^2$
0.1	0.008550	0.008550
0.2	0.034327	0.034198
0.4	0.138935	0.136794
0.8	0.589705	0.547175
1.0	1.000	0.855

3. The Spin-dependence of the Random Phase Approximation Correlation Energy

The analysis of $\Delta\varepsilon_c(r_s, \zeta)$ in Sect. 2 is limited to $|\zeta| \leq 0.2$ and ζ near 1. To apply the SDF formalism to general systems the whole range of ζ is needed. Based on an analysis of their RPA calculation of $\varepsilon_c(r_s, \zeta)$, von Barth and Hedin (8) suggested that the form

$$[3.1] \quad \Delta\varepsilon_{RPA}(r_s, \zeta) = \Delta\varepsilon_{RPA}(r_s, 1)f(\zeta)$$

gives an adequate representation of the ζ-dependence, where $f(\zeta)$ is defined in [2.3]. This form, with different choices for $\varepsilon_c^P(r_s)$ and $\varepsilon_c^F(r_s)$ (9, 20) has been adopted by most researchers doing SDF calculations. In fact it is a rather poor representation in that the error it introduces for the important density range $r_s \leq 6$ and $|\zeta| \leq 0.2$ is likely larger than the error in the RPA itself to $\Delta\varepsilon_c(r_s, \zeta)$. This is illustrated in Table 3 where the vBH values of $\varepsilon_c^P(r_s)$ and $\Delta\varepsilon_c(r_s, \zeta)$ are reproduced and the latter are compared with [3.1]. For example, if we consider $r_s = 0.5$ and 1.0, densities which are particularly important for transition metals and where the RPA should be most accurate, the $\zeta = 0.2$ values of $\Delta\varepsilon_c(r_s, \zeta)$ given by [3.1] are in error by 20%.

TABLE 3. The RPA correlation energy in mRy (present) compared with the results obtained by von Barth and Hedin (vBH (8)) and interpolation formulas [3.1] and [3.2]

			$\Delta\varepsilon_{RPA}(r_s, \zeta)$				
r_s		$\varepsilon_{RPA}{}^{P}(r_s)$	$\zeta = 0.2$	$\zeta = 0.4$	$\zeta = 0.6$	$\zeta = 0.8$	$\zeta = 1.0$
0.5	Present	−194.628	1.974	8.057	19.087	36.509	70.977
	Eq. [3.1]		2.436	9.861	22.678	41.856	70.977
	Eq. [3.2]		1.968	8.009	18.874	37.093	70.977
1.0	vBH	−157.30	1.5	6.2	14.8	28.3	53.3
	Eq. [3.1]		1.8	7.4	17.0	31.4	53.3
	Present	−157.599	1.553	6.324	14.958	28.410	53.849
	Eq. [3.1]		1.848	7.481	17.205	31.755	53.849
	Eq. [3.2]		1.548	6.296	14.769	28.705	53.849
2.0	vBH	−123.40	1.2	4.7	11.0	20.9	38.4
	Eq. [3.1]		1.3	5.3	12.3	22.6	38.4
	Present	−123.621	1.163	4.725	11.152	21.000	38.797
	Eq. [3.1]		1.332	5.390	12.396	22.879	38.797
	Eq. [3.2]		1.162	4.719	11.016	21.152	38.797
3.0	vBH	−105.30	0.9	3.8	9.0	17.0	30.7
	Eq. [3.1]		1.1	4.3	9.8	18.1	30.7
	Present	−105.532	0.956	3.878	9.140	17.118	31.170
	Eq. [3.1]		1.070	4.331	9.959	18.381	31.169
	Eq. [3.2]		0.956	3.881	9.036	17.225	31.169
4.0	vBH	−93.50	0.9	3.4	7.8	14.6	26.1
	Eq. [3.1]		0.9	3.6	8.3	15.4	26.1
	Present	−93.621	0.821	3.327	7.831	14.611	26.345
	Eq. [3.1]		0.904	3.660	8.418	15.536	26.346
	Eq. [3.2]		0.822	3.334	7.747	14.696	26.346
5.0	vBH	−84.80	0.7	2.9	6.8	12.8	22.8
	Eq. [3.1]		0.8	3.2	7.3	13.4	22.8
	Present	−84.946	0.724	2.930	6.891	12.819	22.952
	Eq. [3.1]		0.788	3.189	7.333	13.535	22.952
	Eq. [3.2]		0.725	2.939	6.820	12.892	22.952
6.0	vBH	−78.10	0.7	2.7	6.1	11.4	20.2
	Eq. [3.1]		0.7	2.8	6.5	11.9	20.2
	Present	−78.239	0.650	2.627	6.173	11.460	20.408
	Eq. [3.1]		0.701	2.835	6.520	12.034	20.408
	Eq. [3.2]		0.650	2.637	6.112	11.524	20.408
7.5	Present	−70.505	0.565	2.283	5.361	9.927	17.570
	Eq. [3.1]		0.603	2.441	5.614	10.361	17.570
	Eq. [3.2]		0.566	2.294	5.311	9.982	17.570
10.0	Present	−61.317	0.467	1.885	4.422	8.164	14.348
	Eq. [3.1]		0.493	1.993	4.584	8.461	14.348
	Eq. [3.2]		0.468	1.895	4.383	8.209	14.348
15.0	Present	−49.859	0.350	1.411	3.305	6.080	10.598
	Eq. [3.1]		0.364	1.472	3.386	6.250	10.598
	Eq. [3.2]		0.350	1.419	3.277	6.113	10.598
20.0	Present	−42.762	0.281	1.133	2.652	4.870	8.449
	Eq. [3.1]		0.290	1.174	2.699	4.982	8.449
	Eq. [3.2]		0.281	1.140	2.630	4.895	8.449
30.0	Present	−34.136	0.203	0.818	1.913	3.505	6.048
	Eq. [3.1]		0.208	0.840	1.933	3.567	6.049
	Eq. [3.2]		0.203	0.823	1.897	3.522	6.048
50.0	Present	−25.360	0.131	0.529	1.237	2.263	3.887
	Eq. [3.1]		0.133	0.540	1.242	2.292	3.887
	Eq. [3.2]		0.131	0.532	1.226	2.272	3.887
75.0	Present	−19.845	0.092	0.371	0.853	1.579	2.700
	Eq. [3.1]		0.093	0.375	0.863	1.592	2.700
	Eq. [3.2]		0.092	0.371	0.854	1.581	2.700
100.0	Present	−16.602	0.070	0.285	0.656	1.214	2.072
	Eq. [3.1]		0.071	0.288	0.662	1.222	2.072
	Eq. [3.2]		0.070	0.285	0.657	1.215	2.072

TABLE 4. The RPA spin stiffness constant $\alpha_{RPA}(r_s)$ (mRy) defined by [3.2] and the fitting parameter $\beta_{RPA}(r_s)$ of [3.3]

r_s	$\alpha_{RPA}(r_s)$	$\beta_{RPA}(r_s)$
0.5	97.98	0.2387
1	77.10	0.1943
2	57.86	0.1466
3	47.62	0.1192
4	40.92	0.1008
5	36.09	0.0875
6	32.39	0.0774
7.5	28.18	0.0661
10	23.29	0.0533
15	17.45	0.0386

To clarify the situation for the whole range of densities of interest in atoms, molecules, surfaces, etc., we have recalculated $\varepsilon_{RPA}(r_s, \zeta)$ for $r_s = 0.5$ to 100 and have presented the values in Table 3. Greater care has been taken in performing the necessary two-dimensional integrals so that the results are accurate to the number of digits quoted. It is clear from Table 3 that the raw results of vBH are generally accurate to the number of digits they quoted and the inadequacy of [3.1] for $\zeta \leq 0.4$ persists to at least $r_s = 10$. To summarize our results and put them in a form that is useful for SDF calculations we have introduced a new formula for interpolating over ζ. To ensure that the formula is accurate for $\zeta \leq 0.2$ we have made a direct calculation of the RPA contribution to the spin stiffness, $\alpha_{RPA}(r_s)$, using the RPA result for $\varepsilon_c(r_s, \zeta)$ (see Shastry (34)) and written

$$[3.2] \quad \Delta\varepsilon_{RPA}(r_s, \zeta) = \alpha_{RPA}(r_s)[f(\zeta)/f''(0)] \times [1 + \beta_{RPA}(r_s)\zeta^4]$$

where

$$[3.3] \quad \beta_{RPA}(r_s) = \frac{f''(0)\Delta\varepsilon_{RPA}(r_s, 1)}{\alpha_{RPA}(r_s)} - 1$$

which has been chosen so that $\Delta\varepsilon_{RPA}(r_s, 1)$ is also given exactly. The value of $\beta_{RPA}(r_s)$ is a measure of the inadequacy of [3.1]. Equation [3.2] is slightly more complicated than the vBH form; however, it fits the data in Table 3 to better than 1%. The values of $\alpha_{RPA}(r_s)$ and $\beta_{RPA}(r_s)$ are given in Table 4.

4. New Estimates of Correlation Energies by Padé Approximant Interpolation

New values of $\varepsilon_c^P(r_s)$ and $\varepsilon_c^F(r_s)$ have recently become available from the work of Ceperley and Alder (7). These results are based on an 'exact' calculation of the total energy for a finite number of electrons in liquid para- and ferro-magnetic states. The correlation energy is obtained by subtracting out the corresponding kinetic and exchange energies. Their new results are significantly more accurate than Ceperley's (6) previous combined variational-Monte Carlo calculation but for a more limited range of r_s. Because $\varepsilon_c^P(r_s)$ and $\varepsilon_c^F(r_s)$ have very small error estimates, especially for $r_s \geq 10$ (see Table 5), and have been evaluated by the same procedure we expect that $\Delta\varepsilon_c(r_s, 1)$ is likely quite accurate. However, the values of r_s available are inadequate for use in LSDA calculations. To extend the r_s range we have developed an interpolation formula which yields the leading two terms for $\varepsilon_c(r_s)$ when $r_s \to 0$ and can be fit to the CA values. The interpolation formula, based on a two-point Padé approximant, is similar to the work of Isihara and Montroll (36) except that we are concerned with $\varepsilon_c(r_s)$ only, while they considered the total energy.

Recall from Sect. 2 that for $r_s \ll 1$,

$$[4.1] \quad \varepsilon_c^i(r_s) = A^i \ln r_s + C^i + r_s[A_1^i \ln r_s + C_1^i] + \ldots$$

where i = P/F, while for $r_s \gg 1$, $\varepsilon_c^i(r_s)$ can be written (37) as

$$[4.2] \quad \varepsilon_c^i(r_s) = \frac{g_0^i}{r_s} + \frac{g_1^i}{r_s^{3/2}} + \frac{g_2^i}{r_s^2} + \ldots$$

We shall be concerned with reproducing the terms containing A^i and C^i of [4.1] exactly and a series of the form in [4.2] for $r_s \gg 1$. (The superscript i will now be dropped except when necessary.) A function with these characteristics can be constructed by making a [1, 3] two-point Padé approximant for $r_s\, d\varepsilon_c/dr_s$ as follows:

$$[4.3] \quad r_s \frac{d\varepsilon_c}{dr_s} = A \frac{1 + b_1 x}{1 + b_1 x + b_2 x^2 + b_3 x^3}$$

where $x = r_s^{1/2}$. In a true application of the Padé method (36) the quantities b_1, b_2, and b_3 would be determined by g_0, g_1, and g_2. However, these latter quantities are not known for an electron liquid. Moreover, although such a procedure would give the $A \ln r_s$ term there is no guarantee that the constant C in [4.1] would be reproduced. Since we are primarily interested in the $r_s < 6$ range we prefer to reproduce C as well as $A \ln r_s$ so that criterion [2.8] is satisfied. This is accomplished by regarding the quantities b_1, b_2, and b_3 as parameters and making a least-squares fit to the CA data (see below) and the constant C. Since the denominator in [4.3] is a cubic it must have at least one real root (x_0) which we will insist is negative so that $d\varepsilon_c/dr_s$ is finite for all $r_s > 0$, and we will assume that the other roots are complex (this is consistent with the best estimates (38) of the g's in [4.2]). Equation [4.3] can be integrated with the

TABLE 5. Ceperley and Alder's (7) correlation energies (mRy) are given in the second and third columns (the quantity in parentheses is their estimated error in the last significant figure due to statistical and systematic errors). The third and fourth columns were obtained by fitting their $r_s = 10$ to 100 results using formula [4.4] as described in the text. The last two columns compare the present results with the RPA. $\delta = \Delta\varepsilon_c(r_s, 1) - \Delta\varepsilon_{RPA}(r_s, 1)$. The corresponding values of x_0, b, and c for P and F are -0.10498, 3.72744, 12.9352, and -0.32500, 7.06042, 18.0578, respectively

r_s	$-\varepsilon_c^P$[CA]	$-\varepsilon_c^F$[CA]	$-\varepsilon_c^P$	$-\varepsilon_c^F$	$\Delta\varepsilon_c(r_s, 1)$	δ	$\frac{\Delta\varepsilon_c(r_s, 1)}{\Delta\varepsilon_{RPA}(r_s, 1)}$
0.5			154.13	80.24	73.89	2.92	1.04
1			120.04	63.06	56.98	3.14	1.06
2	90.2(4)	48.0(6)	89.57	47.71	41.85	3.05	1.08
3			73.77	39.74	34.02	2.85	1.09
4			63.57	34.58	28.99	2.64	1.10
5	56.3(1)	31.2(2)	56.27	30.87	25.40	2.45	1.11
6			50.71	28.03	22.68	2.27	1.11
7.5			44.40	24.79	19.61	2.04	1.12
10	37.22(5)	21.0(1)	37.09	21.00	16.09	1.74	1.12
15			28.30	16.38	11.92	1.33	1.13
20	23.00(3)	13.55(3)	23.10	13.59	9.51	1.06	1.12
50	11.40(1)	7.09(2)	11.41	7.10	4.31	0.42	1.11
100	6.379(5)	4.146(5)	6.37	4.13	2.24	0.17	1.08

condition that $\varepsilon_c(r_s) \to 0$ as $r_s \to \infty$. The result is most usefully written as

$$[4.4] \quad \varepsilon_c(r_s) = A\left\{\ln\frac{x^2}{X(x)} + \frac{2b}{Q}\tan^{-1}\frac{Q}{2x+b} - \frac{bx_0}{X(x_0)}\left[\ln\frac{(x-x_0)^2}{X(x)} + \frac{2(b+2x_0)}{Q}\tan^{-1}\frac{Q}{2x+b}\right]\right\}$$

where x_0, b, c replace the parameters b_1, b_2, b_3, with $X(x) = x^2 + bx + c$, $Q = (4c - b^2)^{1/2}$. Expression [4.4] satisfies criterion [2.8] by construction.

To test the adequacy of formula [4.4] to interpolate over the important range of r_s based on the values at $r_s = 10$, 20, 50, and 100 we used it on $\varepsilon_{RPA}(r_s, \zeta)$ given in Table 3 with the appropriate values of A^i and $C_{RPA}{}^i$ ($A^P = 2A^F = 0.0621814$, $C_{RPA}{}^P = -0.1416455$, $C_{RPA}{}^F = -0.0995567$). The best fitting parameters x_0, b, c were found to be -0.409286, 13.0720, and 42.7198 for the paramagnetic case, and -0.743294, 20.1231, and 101.578 for the ferromagnetic case, respectively. For $r_s \leq 15$ the values given by formula [4.4] differed from the RPA values by less than 1.5%. We have deliberately omitted from the fitting procedure the other values of r_s available (2 and 5) for two reasons: (*i*) the CA results are more accurate for low densities, especially for the ferromagnetic state and (*ii*) the $r_s = 2$ and 5 values can be used as an independent test of the adequacy of the method for the important range of densities in metals and atoms. The parameters obtained from fitting the CA values are given in Table 5 with the resulting values of $\varepsilon_c^P(r_s)$ and $\varepsilon_c^F(r_s)$ for the important r_s values.

From Table 5 we see that formula [4.4] is not only capable of reproducing the CA input values at $r_s = 10$, 20, 50, and 100 but also 'predicts' their results for $r_s = 2$ and 5 to within 0.3 mRy. A comparison of ε_c^P(Av) from Table 1 with the corresponding result in Table 5 derived from the fitting procedure shows that they agree to within 2 mRy. We note that this is not due to the fitting procedure since it also occurs with the CA results for $r_s = 2$ and 5. This gives us confidence that we are able to obtain $\varepsilon_c^P(r_s)$ and $\Delta\varepsilon_c(r_s, 1)$ to within $\sim\frac{1}{2}$ mRy by use of [4.4] with the parameters listed in Table 5. It is important to note that the maximum difference between $\Delta\varepsilon_c(r_s, 1)$ and $\Delta\varepsilon_{RPA}(r_s, 1)$ is 13%, occurring at $r_s = 15$. For metallic densities the difference is smaller than 11%.

As pointed out in Sect. 3, knowledge of $\Delta\varepsilon_c(r_s, 1)$ is inadequate to give accurate values of $\Delta\varepsilon_c(r_s, \zeta)$ for the intermediate range of ζ. According to [3.3] and [3.4], the minimum additional information necessary is $\alpha_c(r_s)$. Unfortunately, values of $\alpha_c(r_s)$ at the level of accuracy for $\varepsilon_c^P(r_s)$ and $\varepsilon_c^F(r_s)$ recently calculated by CA are unavailable. Until more accurate calculations of $\Delta\varepsilon_c(r_s, \zeta)$ for $0 < \zeta < 1$ become available there are a number of possibilities for incorporating our new more accurate value of $\Delta\varepsilon_c(r_s, 1)$ into an approximation for $\Delta\varepsilon_c(r_s, \zeta)$, always keeping in mind that the correction to $\Delta\varepsilon_{RPA}(r_s, \zeta) \lesssim 13\%$.

The crudest approximation would be to follow the suggestion of vBH given in [3.1] and write

$$[4.5] \quad \Delta\varepsilon_c(r_s, \zeta)_1 = \Delta\varepsilon_c(r_s, 1)f(\zeta)$$

TABLE 6. Values of the spin stiffness in mRy: X refers to the exchange contribution; the others correspond to various authors', as referenced, estimates of the correlation contribution; 'Fit' refers to the Padé fit as described at the end of Sect. 4

	Spin stiffness (mRy)						
	$r_s = 0.5$	$r_s = 1$	$r_s = 2$	$r_s = 3$	$r_s = 4$	$r_s = 5$	$r_s = 6$
X	−814.5	−407.3	−203.6	−135.8	−101.8	−81.5	−67.9
RPA	98.0	77.1	57.9	47.6	40.9	36.1	32.4
Rice (39)		92.3	74.3	59.1	51.8		
KW (25)		127.3	63.1	53.4	48.1	44.4	40.9
vBH (8)	122.7	94.7	68.2	53.7	44.2	37.3	32.0
GL (9)	105.1	78.0	53.7	41.5	33.8	28.5	24.6
JMW (20)	97.6	72.9	50.1	38.0	30.3	24.8	20.6
P[a]	121.1	93.3	68.9	56.0	47.5	41.5	37.0
Eq. [4.6]	103.0	82.5	63.1	52.5	45.4	40.3	36.3
Eq. [4.7]	102.0	81.6	62.4	52.0	45.0	39.9	36.0
Fit	100.1	79.4	60.1	49.8	43.0	38.0	34.2

[a]J. P. Perdew, private communication (1979).

where $\Delta\varepsilon_c(r_s, 1)$ is our new value. However, as can be seen by comparing Tables 3 and 5 the corrections to $\Delta\varepsilon_{RPA}(r_s, 1)$ for $r_s \leq 2$ are smaller than the errors introduced by this formula. Unless there are some very fortuitous cancellations of errors (which we do not expect) we cannot recommend using this approximation.

A better choice than [4.5] is to approximate $\Delta\varepsilon_c(r_s, \zeta)$ by

$$[4.6] \quad \Delta\varepsilon_c(r_s, \zeta)_{II} = \Delta\varepsilon_{RPA}(r_s, \zeta) + [\Delta\varepsilon_c(r_s, 1) - \Delta\varepsilon_{RPA}(r_s, 1)]f(\zeta)$$

which becomes exact for $\zeta \to 1$. Since the correction to $\Delta\varepsilon_{RPA}(r_s, 1) \leq 13\%$ and the exact ζ-dependence of this correction is unknown but is likely to be similar to $f(\zeta)$, this form is unlikely to produce any large errors for small ζ, i.e., [4.6] should be within a few percent of the exact $\Delta\varepsilon_c(r_s, \zeta)$.

If one assumes that the ζ-dependence of $\Delta\varepsilon_c(r_s, \zeta)$ is the same as $\Delta\varepsilon_{RPA}(r_s, \zeta)$ for fixed r_s, then it is natural to write

$$[4.7] \quad \Delta\varepsilon_c(r_s, \zeta)_{III} = \frac{\Delta\varepsilon_c(r_s, 1)}{\Delta\varepsilon_{RPA}(r_s, 1)} \Delta\varepsilon_{RPA}(r_s, \zeta)$$

We have no a priori criterion for choosing between the forms [4.6] and [4.7]. Direct calculation shows that they differ by at most 0.2 mRy which is smaller than the accuracy of the fitting procedure for $\Delta\varepsilon_c(r_s, 1)$.

The obvious criticism that could be made of the forms [4.6] and [4.7] is that the $\alpha_c(r_s)$ derived from them do not have the correct high density behaviour, i.e., they violate criterion [2.14]. This difficulty can be overcome in a number of ways. The simplest method is to use the form [3.2] with $\beta_{RPA}(r_s)$ replaced by

$$[4.8] \quad \beta_1(r_s) = \frac{f''(0)\Delta\varepsilon_c(r_s, 1)}{\alpha_{RPA}(r_s)} - 1$$

This choice, referred to as $\Delta\varepsilon_c(r_s, \zeta)_{IV}$, will not differ from the RPA for small ζ, but will approach the new value as $\zeta \to 1$. Using $\beta_1(r_s)$ in [3.2] produces a $\Delta\varepsilon_c(r_s, \zeta)_{IV}$ which differs from the 'II' and 'III' by at most 1 mRy for intermediate ζ's.

As emphasized in Sect. 2, for metals $|\zeta| \lesssim 0.15$ so that only $\alpha_c(r_s)$ is needed. Most attempts (see Kushida *et al.* (30)) to improve on the RPA give an $\alpha_c(r_s)$ which is larger than $\alpha_{RPA}(r_s)$. The corresponding α_c's for a number of works are given in Table 6. The work of Rice (39) is often quoted. However, it is based on Hubbard's 1957 work (22) which has been superceded by his 1967 method (23) and thus cannot be considered reliable. We have also presented the $\alpha_c(r_s)$ corresponding to the approximations [4.6] and [4.7]. It should be noted that they follow the trend of being larger than $\alpha_{RPA}(r_s)$.

With a view to the future we wish to point out that the Padé interpolation procedure developed above for $\varepsilon_c(r_s)$ can also be used for $\alpha_c(r_s)$. This can be done because $\alpha_c(r_s)$ has the same r_s dependence as $\varepsilon_c(r_s)$. Brueckner and Sawada (15) (as corrected by Shastry (34)) have shown that for $r_s \ll 1$

$$[4.9] \quad \alpha_c(r_s) = A_\alpha \ln r_s + C_\alpha$$

where $A_\alpha = -1/3\pi^2$ Ry and

$$[4.10] \quad C_\alpha = \frac{\ln(16\pi/\alpha) - 3 + \langle \ln R \rangle_{AV}}{3\pi^2} \text{ Ry}$$

Brueckner and Sawada evaluated $\langle \ln R \rangle_{AV}$ to be 0.534. We have recalculated this integral and found it to be 0.531504. Due to cancellation in [4.10] this

TABLE 7. Values of $-\varepsilon_c^P(r_s)$ (see Table 6 for notation). X denotes values of $-\varepsilon_x^P(r_s)$ (eq. [2.2])

	$-\varepsilon_c^P(r_s)$							
	$r_s = 0.5$	$r_s = 1$	$r_s = 2$	$r_s = 3$	$r_s = 4$	$r_s = 5$	$r_s = 6$	$r_s = 10$
X	1832.7	916.3	458.2	305.4	229.1	183.3	152.7	91.6
RPA	194.6	157.6	123.6	105.5	93.6	85.0	78.2	61.3
Wigner (1)[a]	106.0	100.0	89.8	81.5	74.6	68.8	63.8	49.4
GL (9)	190.3	148.0	109.0	88.3	74.9	65.4	58.1	40.6
JMW (20)	154.8	125.1	96.7	81.1	70.7	63.0	57.0	41.9
P[b]	150.8	117.6	88.4	72.8	62.7	55.4	49.8	36.3
Present	154.1	120.0	89.6	73.8	63.6	56.3	50.7	37.1

[a]E. P. Wigner, as corrected by Pines (ref. 1, p. 375).
[b]J. P. Perdew, private communication (1979).

difference produces a significant change in C_α ($=70.949$ mRy). We have tested formula [4.4] on $\alpha_{RPA}(r_s)$ with A and C replaced by A_α and C_α, respectively, using $r_s = 10$, 20, 50, and 100 as fitting points. With the fitting parameters $x_0 = -0.228344$, $b = 1.06835$, and $c = 11.4813$ the maximum error for $r_s \leq 100$ is 0.2%! Thus, if accurate values of $\alpha_c(r_s)$ can be obtained for low densities (the method of Ceperley and Alder appears to have this potential) it should be possible to interpolate them accurately into the metallic range by this procedure.

It was noted in Sect. 3 that for $r_s \geq 10$, $\Delta\varepsilon_{RPA}(r_s, \zeta) \approx \Delta\varepsilon_{RPA}(r_s, 1)f(\zeta)$ (maximum error $\leq 5\%$). Thus, it is not unreasonable to expect that this behaviour is approximately universal and [4.7] is more accurate in this range. With this assumption we have used the $r_s = 10$, 20, 50, and 100 values for $\alpha_c(r_s)_{III}$ (i.e., from [4.7]) as fitting values for the Padé formula. The results are labelled as 'fit' in Table 6 and correspond to the fitting parameters $x_0 = -0.00475840$, $b = 1.13107$, and $c = 13.0045$. We found that to within a few percent, the values of $\alpha_c(r_s)$ generated for metallic densities are insensitive to 5–10% changes in the input values and are less than $\alpha_c(r_s)_{III}$. Thus, we expect that α_c 'fit' is very near the true value and that $\alpha_{RPA}(r_s) < \alpha_c(r_s) < \alpha_c(r_s)_{III}$ for $r_s \leq 6$. This α_c-fit can be used to obtain yet another $\Delta\varepsilon_c(r_s, \zeta)$ of the form [3.2] by using it in place of $\alpha_{RPA}(r_s)$ in [3.2] and [4.8]. By construction this $\Delta\varepsilon_c(r_s, \zeta)_V$ will satisfy the criteria [2.10] and [2.14]. Its maximum deviation from the forms "II", "III", and "IV" is 0.8 mRy and

$$\Delta\varepsilon_c(r_s, \zeta)_{II} > \Delta\varepsilon_c(r_s, \zeta)_{III} > \Delta\varepsilon_c(r_s, \zeta)_V > \Delta\varepsilon_c(r_s, \zeta)_{IV}$$

Since $\Delta\varepsilon_c(r_s, \zeta)_V$ is easiest to implement in LSDA calculations we recommend its use.

5. Discussion and Conclusions

Most applications of the SDF formalism to the ground state properties of atoms, molecules, and solids have written $\varepsilon_c(r_s, \zeta)$ in the form [2.4] with the vBH suggestion [3.1] for $\Delta\varepsilon_c(r_s, \zeta)$. However, there have been a number of choices for the $\varepsilon_c^P(r_s)$ and $\varepsilon_c^F(r_s)$ components (recall that $\Delta\varepsilon_c(r_s, 1) = \varepsilon_c^F(r_s) - \varepsilon_c^P(r_s)$. The most frequently used are those of vBH, GL, and JMW (refer to Tables 6 and 7 for notation). To assess the significance of these calculations (for recent reviews to the literature see Moruzzi *et al.* (6), Rajagopal (3), and Mackintosh and Andersen (4)) we will compare the corresponding values of $\varepsilon_c^P(r_s)$, $\alpha_c(r_s)$, and $\Delta\varepsilon_c(r_s, 1)$ with the RPA, Perdew's parametrization, and the present results. To appreciate the relative importance of correlation and exchange we also include the latter in Tables 6 and 7.

For numerical convenience vBH, GL, and JMW parametrized $\varepsilon_c(r_s)$ using the form introduced by Hedin and Lundqvist (41):

$$[5.1] \quad \varepsilon_c^i(r_s) = -C_i\left\{(1 + x_i)^3 \ln\left(1 + \frac{1}{x_i}\right) + \frac{x_i}{2} - x_i^2 - \frac{1}{3}\right\} \text{Ry}$$

where i = P/F, $x_i = r_s/r_i$, and the parameters c_i and r_i were chosen to fit some estimates of $\varepsilon_c^P(r_s)$ and $\varepsilon_c^F(r_s)$. This parametrization introduces a further approximation. However, since it is what has been used in the applications it is the appropriate quantity to compare.

Table 7 makes explicit the point made earlier, namely $|\varepsilon_x^P(r_s)| > |\varepsilon_c^P(r_s)|$, both being of the same sign. Note also that the differences in the various $\varepsilon_c^P(r_s)$'s relative to $\varepsilon_x^P(r_s)$ are not large. However, it is well known that $\varepsilon_c^P(r_s)$ makes an important contribution to the cohesive energy, bulk modulus, surface energy, work function, etc. For example, Perdew (40) has shown that using his parametrization of Ceperley's (6) data produces a significant change in the surface energy and work function of

the jellium model from that obtained using Wigner's classic result (as corrected by Pines (ref. 1, p. 375)). We note that our new result is within 1 mRy of Perdew's for $r_s \geq 2$.

Because of the sign difference in $\alpha_x(r_s)$ and $\alpha_c(r_s)$ Table 6 must be examined carefully. For $r_s > 3$ $\alpha_c(r_s)$ and $\alpha_x(r_s)$ are of the same order of magnitude, so that errors in $\alpha_c(r_s)$ produce large percentage errors in $\alpha_{xc}(r_s)$. It is interesting to note that even though vBH was derived from an RPA calculation the corresponding $\alpha_c(r_s)$ is considerably different, being larger for small r_s and smaller for large r_s. This is due to a combination of the errors produced by the parametrization [5.1] of $\varepsilon_c^{\,i}(r_s)$ and the form [3.1]. Thus, metallic magnetic properties obtained from vBH cannot be called true RPA. The values of $\varepsilon_c^{\,P}(r_s)$ and $\varepsilon_c^{\,F}(r_s)$ calculated by GL were obtained by a plasmon pole approximation to the RPA. Their results took on more significance because the $\varepsilon_c^{\,P}(r_s)$ produced is in closer agreement than the RPA with calculations of higher quality (see Tables 1 and 7) especially for $r_s > 4$. However, we see from Table 6 that the $\alpha_c(r_s)$ is particularly poor for $r_s > 2$. Although the JMW $\alpha_c(r_s)$ is even worse in this region it is very similar to $\alpha_{RPA}(r_s)$ for $r_s < 1$. This may be the reason for the similarity between their results and those of Callaway and Wang (42) for Fe and Ni. The low value of JMW's $\alpha_c(r_s)$ explains their larger value of 'I' for the alkali metals obtained by Wilk *et al.* (35). Although Perdew's parametrization produces a $\Delta\varepsilon_c(r_s, 1)$ that is very similar to ours (see Fig. 2), the resulting $\alpha_c(r_s)$ is much larger than ours for $r_s < 2$. This is due to his use of [3.1] to describe the ζ-dependence.

We should note that the values of $\alpha_c(r_s)$ obtained by Keiser and Wu are considerably larger than our best estimates. Thus the good agreement between the experimental spin susceptibility and the LSDA calculations by Wilk *et al.* using the Keiser and Wu $\alpha_c(r_s)$ must now be reconsidered. However, all of our new estimates of $\alpha_c(r_s)$ are larger than the RPA in the direction of most efforts to improve upon the RPA and needed to improve the RPA–LSDA calculations of the spin susceptibility.

We conclude by noting that our results for $\varepsilon_c^{\,P}(r_s)$, $\varepsilon_c^{\,F}(r_s)$, and α_c-fit using the Padé interpolation formulas and form [3.2] to generate $\Delta\varepsilon_c(r_s, \zeta)_V$ should be sufficiently accurate for all r_s and ζ so as to truly test the ability of the LSDA for exchange and correlation to describe the ground state properties of many electron systems. This will make it possible to judge the importance of non-local corrections to the exchange-correlation energy functional.

Acknowledgments

One of the authors (S.H.V.) wishes to thank Dr. David Ceperley for providing the recent results before publication and several informative conversations, and Dr. James F. Janak for a number of helpful and stimulating discussions.

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