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How Accurate are the Parametrized Correlation Energies of the Uniform Electron Gas?

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Density functional approximations to the exchange-correlation energy are designed to be exact for an electron gas of uniform density parameter r_s and relative spin polarization ζ, requiring a parametrization of the correlation energy per electron, $\epsilon_c(r_s, \zeta)$. We consider three widely-used parametrizations (Perdew-Zunger or PZ 1981, Vosko-Wilk-Nusair or VWN 1980, Perdew-Wang or PW 1992) that interpolate the Quantum Monte Carlo (QMC) correlation energies of Ceperley-Alder 1980, while extrapolating them to known high-($r_s \to 0$) and low- ($r_s \to \infty$) density limits. For the physically important range $0.5 \leq r_s \leq 20$, they agree closely with one another, with differences of 0.01 eV (0.5%) or less between the latter two. The density parameter interpolation (DPI), designed to predict these energies by interpolation between the known high- and low-density limits, with almost no other input (and none for $\zeta = 0$), is also reasonably close, both in its original version and with corrections for $\zeta \neq 0$. Moreover, the DPI and PW92 at $r_s = 0.5$ are very close to the high-density expansion. The larger discrepancies with the QMC of Spink *et al.* 2013, of order 0.1 eV (5%) at $r_s = 0.5$, are thus surprising, suggesting that the constraint-based PW92 and VWN80 parametrizations are more accurate than the QMC for $r_s < 2$. For $r_s > 2$, however, the QMC of Spink *et al.* confirms the dependence upon relative spin polarization predicted by the parametrizations.

I. Introduction

The correlation energy of a many-electron system arises from the effects of mutual Coulomb repulsion among the electrons. In wavefunction theory, it is the correction to the Hartree-Fock energy, while in modern density functional theory (DFT),[1,2] it is the correction to the Kohn-Sham exchange-only energy. It reduces the Coulomb repulsion due to electronic mutual avoidance, and is necessarily negative. While it can be a small part of the total energy of an atom, molecule, or solid, it plays a crucial role to strengthen the bonding of one atom to another. It is also the most complicated and challenging part of the total energy.

The electron gas of uniform spin density provided an early and useful way to understand and approximate the correlation energy. While the random phase approximation (RPA)[3] and corrections to it[4] provided estimates of the correlation energy per electron and its dependence upon the spin densities, the Quantum Monte Carlo (QMC) results of Ceperley and Alder[5] provided perhaps the first reliable reference values. Parametrizations that interpolated between discrete QMC values, with extrapolations to known high- and low-density limits, were provided by Perdew and Zunger (PZ81)[6], Vosko, Wilk and Nusair (VWN80)[7], Perdew and Wang (PW92)[8], and others[9,10]. A density parameter interpolation (DPI)[11] provided a check based primarily on the satisfaction of known exact constraints. PZ81 used a form suggested by Ceperley and Alder[5] for $r_s > 1$, and a different form motivated by the high-density limit for $r_s < 1$. Unlike the simpler PZ81, the other parametrizations and the DPI employ a single analytic form for the whole range $0 \leq r_s \leq \infty$, although this form varies from one to another. For a review of the uniform electron gas see Ref. 12.

Approximations to the density functional[1,2] for the exchange-correlation energy of a many-electron system are often used to predict the ground-state energies and electron spin densities of real molecules and materials. Typically these approximations need a parametrization of the correlation energy per electron for an electron gas of uniform spin densities, since they are designed to be exact in the limit of slow spatial variation. The PW92[8] parametrization was chosen as an input to the Perdew-Burke-Ernzerhof (PBE)[13] generalized gradient approximation (GGA) and to the strongly constrained and appropriately normed (SCAN)[14] meta-GGA. PW92 incorporated the sophisticated spin interpolation of VWN80[7] (also known as VWN5), while adding a more correct high-density limit as well as a fitting adapted to the uncertainties of the QMC calculation. The 2010 density parameter interpolation (DPI)[11] was not intended to be more accurate than PW92. Instead it was designed to show that the satisfaction of exact constraints, which had been used to progress from the local spin density approximation[2,3] to PBE (and later to SCAN), could also be used to estimate the uniform gas correlation energy input, with no QMC input in the spin-unpolarized limit and very little more generally.

The recent QMC calculation of Spink *et al.*[15] confirmed the accuracy of the QMC of Ceperley and Alder[5] for the fully unpolarized and fully polarized limits, over the density range of the latter, but extended them to intermediate relative spin polarizations and to higher densities. A comparison with PZ81 was also made in Ref. 15, which called for an improved parametrization at the higher densities. The results of Ref. 15 have been employed in Ref. 10 and Ref. 16 for the zero-temperature limit of a parametrized finite-temperature exchange-correlation free energy per electron. The parametrization of Ref. 10 for the exchange-correlation energy is compared with the fermionic configuration path integral Monte Carlo (CPIMC) results at low temperature in Ref. 17.

At the highest density ($r_s = 0.5$), the Spink *et al.* correlation energy is less negative than PW92 by about 0.1 eV (5%) or more, possibly reflecting a variational overestimate of the total energy. This difference may not be of practical importance, for two reasons: (1) This density is considerably higher than typical valence electron densities. (2) At this and higher densities for the spin-unpolarized uniform electron gas, the magnitudes of the exchange energy (treated exactly in all parametrizations) and of the kinetic energy are respectively more than about 12 and more than 58 times the magnitude of the correlation energy.

Although the more expensive QMC is normally more accurate than constraint-satisfying density functional approximations, the jellium surface energy[18] was, until recently[19], a notable exception. We suggest here that the uniform gas correlation energy at $r_s = 0.5$ may be another exception. For $r_s > 2$ (lower densities), however, the QMC of Spink *et al.* confirms the dependence upon relative spin polarization ζ of the standard parametrizations.

II. Limits

The Seitz radius or density parameter r_s and relative spin polarizations ζ are defined as,

$$r_s = \left[\frac{3}{4\pi(n_\uparrow + n_\downarrow)}\right]^{\frac{1}{3}} \tag{1}$$

$$\zeta = \frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow} \tag{2}$$

The high-density limit (HDL) for the uniform gas correlation energy per electron $\epsilon_c(r_s, \zeta)$ can be found from the expansion given by Gell-Mann and Brueckner for $r_s \to 0$[11,20]

$$\epsilon_c(r_s, \zeta) = \sum_{n=0}^{\infty}[a_n(\zeta) ln(r_s) + b_n(\zeta)] r_s^n \tag{3}$$

The low-density limit (LDL) can be found from the expansion

$$\begin{aligned}\epsilon_c(r_s, \zeta) = \frac{f_0 - c_x(\zeta)}{r_s} + \frac{f_1}{r_s^{\frac{3}{2}}} + \frac{f_2 - c_s(\zeta)}{r_s^2} \\ + \sum_{n=3}^{\infty} \frac{f_n}{r_s^{1+\frac{n}{2}}} + e_{exp}(r_s, \zeta)\end{aligned} \tag{4}$$

for $r_s \to \infty$[7,8,11,21,22], where the f_n are constant coefficients.

Here, $e_{exp}(r_s, \zeta) \sim exp[-g(\zeta) r_s^{\frac{1}{2}}]$ and the three parameters f_0, f_1 and f_2 have values of -0.9,1.5 and 0 respectively constrained to exact or near exact values as provided in the work of Sun, Perdew and Seidl[11]. Expressions for $c_x(\zeta)$ and $c_s(\zeta)$[8] are given as-

$$c_s(\zeta) = \frac{3}{10}(\frac{9\pi}{4})^{\frac{2}{3}} \frac{1}{2}[(1+\zeta)^{\frac{5}{3}} + (1-\zeta)^{\frac{5}{3}}] \tag{5}$$

$$c_x(\zeta) = -\frac{3}{4\pi}(\frac{9\pi}{4})^{\frac{1}{3}} \frac{1}{2}[(1+\zeta)^{\frac{4}{3}} + (1-\zeta)^{\frac{4}{3}}] \tag{6}$$

Unless otherwise stated, all our equations are in atomic units (hartrees and bohrs).

III. Comparison & Discussion

In Table I we compare correlation energies per electron from the PZ81, VWN80, and PW92 parametrizations, in the ranges $0.5 \leq r_s \leq 20$ and $0 \leq \zeta \leq 1$. The maximum absolute deviation of PZ81 from PW92 is 0.07 eV (4%) for $r_s = 0.5$ and $\zeta = 0.66$. The corresponding maximum absolute deviation of VWN80 from PW92 is much smaller: 0.01 eV (0.6%) at $r_s = 0.5$ and $\zeta = 0.34$.

In Table I we also present the twist-averaged diffusion Quantum Monte Carlo results from Spink *et al.* They show a maximum absolute deviation from PW92 of 0.18 eV (11%) at $r_s = 0.5$ and $\zeta = 0.66$.

Table I also presents the correlation energies of the density parameter interpolation (DPI) in its original form from Sun *et al.*[11] and as corrected here. The DPI interpolates between available derived high- and low-density limits. One of the high-density coefficients in Eq. 3 is $a_1(\zeta)$, and the Carr-Maradudin[23] integral for it is given in our Eq. A1. However, the parameter $a_1(\zeta = 1)$ used by Sun *et al.* (0.003125) was in error due to an order-of-limits problem identified recently by Loos and Gill[12,24]. We have obtained a value (0.004799) that differs negligibly from the exact Loos-Gill value (0.004792) by evaluating the DuBois integral[25] (Appendix A) for values approaching 1. Although $a_1(\zeta)$ is known analytically[24], it is represented here by an accurate fit since the exact analytic expression takes a long time to calculate. Our careful fit is an expansion in even functions of zeta that have zero derivative at $\zeta = 0$ and infinite derivative at $\zeta = 1$:

$$\begin{aligned} a_1(\zeta) = 0.00922921 - 0.00159532 \arcsin(\zeta^2) \\ -0.00559489 \arcsin(\zeta^4) + 0.0264127 \arcsin(\zeta^6) \\ -0.0597952 \arcsin(\zeta^8) + 0.060373 \arcsin(\zeta^{10}) \\ -0.0226208 \arcsin(\zeta^{12}) \end{aligned} \tag{7}$$

Fig. 1 shows that the approximate $a_1(\zeta)$ fits perfectly with the exact one.

Appendix A presents the analytic integration and analytic expression for the DuBois[25] integral $R^{(1)}(iu, \zeta)$.

TABLE I: Correlation energies per electron (in eV) for the uniform electron gas from PZ81, VWN80, and PW92, QMC of Spink *et al.*, the original density parameter interpolation (DPI), and the corrected DPI. The differences are most noticeable at $r_s = 0.5$. Note that 1 hartree = 27.2114 eV.

	r_s	$\zeta = 0$	$\zeta = 0.34$	$\zeta = 0.66$	$\zeta = 1$
PZ81	0.5	-2.069	-1.972	-1.690	-1.097
	1	-1.623	-1.547	-1.326	-0.863
	2	-1.227	-1.170	-1.004	-0.656
	3	-1.013	-0.966	-0.830	-0.546
	5	-0.771	-0.736	-0.635	-0.422
	10	-0.505	-0.483	-0.420	-0.286
	20	-0.313	-0.300	-0.263	-0.184
VWN80	0.5	-2.097	-2.017	-1.771	-1.092
	1	-1.633	-1.570	-1.376	-0.858
	2	-1.219	-1.171	-1.025	-0.649
	3	-1.004	-0.964	-0.844	-0.541
	5	-0.766	-0.735	-0.644	-0.420
	10	-0.505	-0.485	-0.426	-0.286
	20	-0.314	-0.302	-0.267	-0.185
PW92	0.5	-2.085	-2.005	-1.759	-1.094
	1	-1.627	-1.562	-1.367	-0.860
	2	-1.218	-1.168	-1.020	-0.651
	3	-1.005	-0.964	-0.840	-0.542
	5	-0.768	-0.736	-0.641	-0.420
	10	-0.505	-0.484	-0.423	-0.285
	20	-0.314	-0.301	-0.265	-0.184
Spink et al.	0.5	-1.996	-1.957	-1.583	-0.994
	1	-1.605	-1.550	-1.325	-0.827
	2	-1.218	-1.170	-1.014	-0.642
	3	-1.010	-0.969	-0.841	-0.537
	5	-0.774	-0.741	-0.645	-0.420
	10	-0.510	-0.489	-0.427	-0.287
	20	-0.316	-0.303	-0.267	-0.186
Original DPI	0.5	-2.108	-2.032	-1.787	-1.103
	1	-1.637	-1.576	-1.381	-0.862
	2	-1.215	-1.166	-1.016	-0.645
	3	-0.996	-0.955	-0.830	-0.534
	5	-0.755	-0.724	-0.629	-0.412
	10	-0.495	-0.474	-0.413	-0.279
	20	-0.308	-0.295	-0.259	-0.181
Corrected DPI	0.5	-2.108	-2.031	-1.787	-1.113
	1	-1.637	-1.576	-1.382	-0.870
	2	-1.215	-1.166	-1.016	-0.650
	3	-0.996	-0.955	-0.831	-0.537
	5	-0.755	-0.724	-0.629	-0.413
	10	-0.495	-0.474	-0.413	-0.279
	20	-0.308	-0.295	-0.259	-0.181

This integral was evaluated correctly (for $\zeta \neq 1$) in Refs. 8 (Eq. B3)), 11 (Eq. A3), and 24 (Eq. 15), but those references did not display the derivation and presented a recurring transcription error : $arctan(u)$ must be replaced by $arctan(\frac{1}{u})$ to obtain the correct expression Eq. A14.

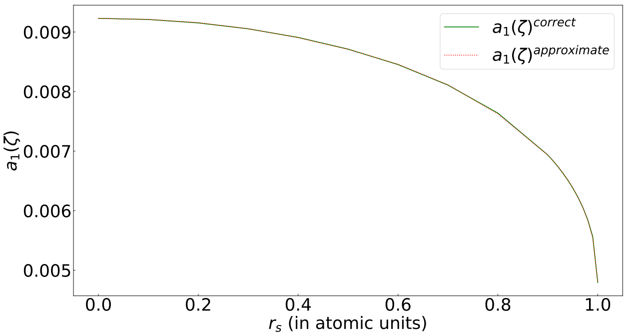

FIG. 1: Comparison of fitted $a_1(\zeta)$ from Eq. 7 with the exact integral of Eq. A1

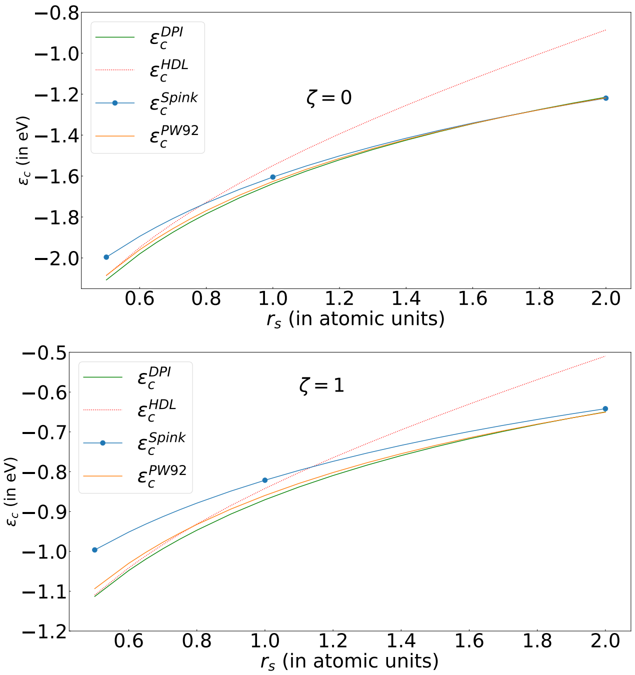

FIG. 2: Corrected density parameter interpolation (DPI) and high-density limit (HDL) of the correlation energy per electron of the a) spin-unpolarized b) spin-polarized uniform electron gas, for $0.5 \leq r_s \leq 2$. Here the HDL is the sum of the n=0 and n=1 terms of Eq. 3. This shows that the DPI and PW92 for $r_s \sim 0.5$ are very close to the high density limit in both cases. In contrast, the correlation energy from Spink *et al.* deviates strongly from the HDL. For the Spink *et al.* curves, we have used Eq. 3 and Table V of Ref. 15.

The corrected $a_1(\zeta = 1)$ necessitates a change in the coefficient $b_1(\zeta)$ (known exactly only for $\zeta = 0$) in the DPI model. Following the procedure of Ref. 11 , we find $b_1(\zeta = 1) = -0.005205$ instead of -0.006746. Thus we obtain a correction, but a small one (as also pointed out in Ref. 24). Our corrected DPI values in Table I agree to within 0.001 eV with those presented in Ref. 24.

Fig. 2 shows that, at r_s near 0.5, the DPI and

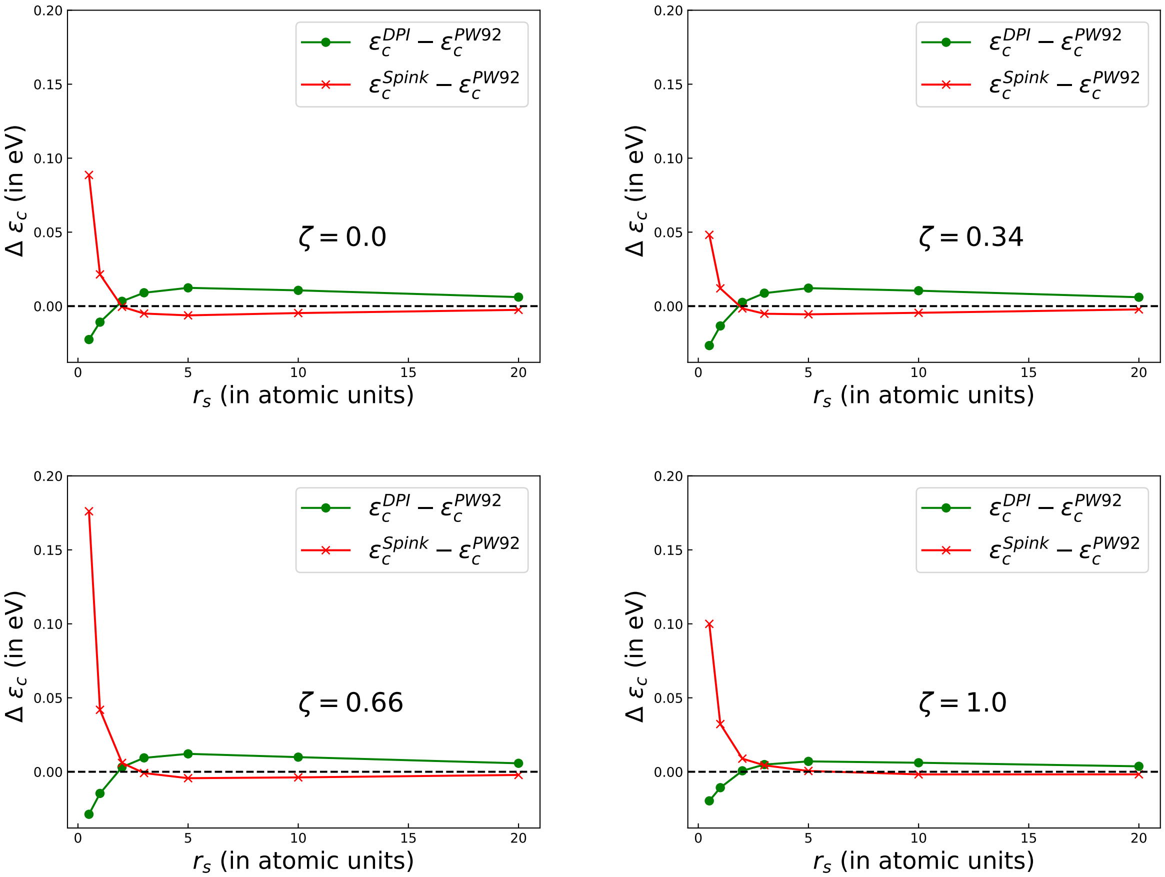

FIG. 3: Deviation from PW92 of the corrected density parameter interpolation (DPI) and the QMC of Spink *et al.* correlation energies per electron for the uniform electron gas, as functions of the density parameter, for four values of the relative spin polarization. Note the close agreeement between PW92 and Spink *et al.* for all $r_s > 2$ and all ζ.

PW92 are extremely close to the high-density expansion for both polarized and unpolarized states. On the other hand, the Spink *et al.* QMC results for the correlation energy are far from the HDL near $r_s = 0.5$. Fig. 10 of Ref. 15 omits the $b_1(\zeta)r_s$ term of the high-density expansion that we include with the value of -0.07 eV for $r_s = 0.5$ and $\zeta = 1$, but more significantly that figure does not show what our Fig. 2 shows: that the QMC correlation energy of Spink *et al.* diverges away from the high-density expansion as r_s tends toward 0, for both $\zeta = 0$ and $\zeta = 1$.

Fig. 3 also shows that the Spink *et al.* DMC correlation energy per electron is remarkably close to PW92 for $r_s \geq 2$ and for all ζ . The differences grow rapidly as r_s decreases to 1 and then to 0.5. Fig. 3 also shows the difference between DPI and PW92.

IV. Conclusions

We have compared three parametrizations (PZ81, VWN80, and PW92) of the correlation energy per electron of the uniform electron gas from the QMC of Ceperley and Alder, finding little difference among them, especially between the latter two. We have also compared these to the original and the slightly-corrected density parameter interpolation (DPI), which is almost independent of QMC input, and with the recent QMC of Spink *et al.*, which extends the Ceperley-Alder results to fractional spin polarization and to higher densities or smaller r_s. While the latter QMC confirms the spin-dependence of the parametrizations at the lower densities, it is less negative by about 0.1 eV at $r_s = 0.5$. The high consistency among the three parametrizations and the DPI, and their closeness to the high-density limit at $r_s = 0.5$, suggest the possibility that the parametrizations (especially the sophisticated PW92) are correct at all r_s.

Further support for this conclusion will be found in Fig. 1 of Ref. 26. This figure shows that an RPA-like calculation with a sophisticated constraint-based frequency-dependent exchange-correlation kernel[27] produces correlation energies per electron for the spin-unpolarized case in close agreement with those of PW92 over the whole range of r_s from 0 to 15. The maximum absolute deviation is about 0.02 eV. We suggest that the PW92 and VWN80 constraint-satisfying approximations may be more accurate for $r_s < 2$ than the QMC of Spink *et al.*[15] or the more recent parametrizations[10,16] based on that QMC and not on the high-density expansion. The difference is in any case irrelevant to density functional calculations for real materials. It is important to note that all the parametrizations in Table I (not including the QMC of Spink *et al.*) have the correct n=0 term in their high-density expansions of Eq. 3. The n=1 term is much less important, and varies considerably from one parametrization to another (Table 1 of Ref. 11). Even a simple one-parameter fit[28] based on the correct $n = 0$ term of the high-density expansion agrees more closely with PW92 than with the QMC of Spink *et al.* at $r_s = 0.5$.

A referee has pointed that the fixed node error in a QMC calculation grows as $|lnr_s|$ when $r_s \to 0$.

Acknowledgments

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Appendix A Evaluation of Integrals for the High-Density Limit

The coefficient $a_1(\zeta)$[11,23] is

$$a_1(\zeta) = -\frac{3\alpha}{4\pi^5}\int_{-\infty}^{\infty}[4R(u,\zeta)^2 R_1(u,\zeta) - \pi R(u,\zeta)R^{(1)}(iu,\zeta)] \tag{A1}$$

where

$$\alpha = \left(\frac{4}{9\pi}\right)^{\frac{1}{3}} \tag{A2}$$

$$R(u,\zeta) = \frac{1}{2}\left[\frac{R(x_1u)}{x_1} + \frac{R(x_2u)}{x_2}\right] \tag{A3}$$

$$R_1(u,\zeta) = \frac{1}{2}[x_1R_1(x_1u) + x_2R_1(x_2u)] \tag{A4}$$

$$x_1 = (1-\zeta)^{-\frac{1}{3}}, x_2 = (1+\zeta)^{-\frac{1}{3}} \tag{A5}$$

$$R(u) = 1 - u\arctan\left(\frac{1}{u}\right) \tag{A6}$$

$$R_1(u) = -\frac{\pi}{3(1+u^2)^2} \tag{A7}$$

$$R^{(1)}(iu,\zeta) = \frac{1}{2}[R^{(1)}(ix_1u) + R^{(1)}(ix_2u)]. \tag{A8}$$

Expression A5 of Dubois[25] is

$$\begin{aligned} R^{(1)}\left(\frac{\omega}{q}\right) = \int_{-1}^{1} x_1dx_1\int_{-1}^{1} x_2dx_2\frac{(x_1-x_2)}{|x_1-x_2|} \\ \frac{1}{(x_1-\frac{\omega}{q})^2}\frac{1}{x_2-\frac{\omega}{q}} \end{aligned} \tag{A9}$$

The integral over x_2 gives $2x_1 - \frac{\omega}{q}ln[-1-\frac{\omega}{q}] - \frac{\omega}{q}ln[1-\frac{\omega}{q}] + 2\frac{\omega}{q}ln[-\frac{\omega}{q} + x_1]$. Assuming that $\frac{\omega}{q}$ is not real, Mathematica[30] gives for the integral over x_1

$$\begin{aligned} R^{(1)}\left(\frac{\omega}{q}\right) = \frac{1}{-1+\left(\frac{w}{q}\right)^2}\Bigg[-4+12\left(\frac{w}{q}\right)^2 - 2\left(\frac{w}{q}\right) \\ \left(-2+3\left(\frac{w}{q}\right)^2\right)\left(ln\{-1-\left(\frac{w}{q}\right)\} - ln\{1-\left(\frac{w}{q}\right)\}\right)\Bigg]. \end{aligned} \tag{A10}$$

Changing $(\frac{w}{q})$ to iu gives

$$\begin{aligned} R^{(1)}(iu) = \frac{1}{1+u^2}\Big[4+12u^2 - 2iu(2+3u^2) \\ \Big(ln\{-1-iu\} - ln\{1-iu\}\Big)\Big] \end{aligned} \tag{A11}$$

and using the relations

$$\begin{aligned} arctan(u) &= \frac{-i}{2}ln\left[\frac{-1-iu}{1-iu}\right] + \frac{\pi}{2} \\ arctan\left(\frac{1}{u}\right) &= \frac{\pi}{2} - arctan(u) \\ u &> 0 \end{aligned} \tag{A12}$$

$$\begin{aligned} arctan(u) &= \frac{-i}{2}ln\left[\frac{-1-iu}{1-iu}\right] - \frac{\pi}{2} \\ arctan\left(\frac{1}{u}\right) &= -\frac{\pi}{2} - arctan(u) \\ u &< 0 \end{aligned} \tag{A13}$$

we get

$$\begin{aligned} R^{(1)}(iu) = \frac{4}{1+u^2}[(1+3u^2) - u(2+3u^2) \\ arctan\left(\frac{1}{u}\right)]. \end{aligned} \tag{A14}$$

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