Supplemental Material - "Accurate Homogeneous Electron Gas Exchange-Correlation Free Energy for Local Spin-Density Calculations"

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Implausible behavior outside the RPIMC data domain

Strictly speaking a fitted functional is supposed to be valid only in the range of the fitted data and in those regions where the correct limiting conditions were enforced. The form given in Eq. (9) incorporates correct zero-T, small-r_s, and high-T limits. Physically plausible behavior in the intermediate regions between those limits and the range of RPIMC data relies on the smoothness of the fitting function. A relevant question is the range of system density. The highest value of r_s in the RPIMC data corresponds to a very low density in Hydrogen, $\rho_H(r_s = 40) = 0.000042$ g/cm^3. But the lowest value in the RPIMC data set, $r_s = 1$, corresponds to a H density $\rho_H(r_s = 1) = 2.7$ g/cm^3. This is not high enough for many applications, including those in the WDM regime. For example, recently the EOS of Deuterium in the WDM regime was calculated [1] up to $r_s = 0.15$, which corresponds to an H material density of $\rho_H(r_s = 0.15) = 798$ g/cm^3. Moreover, because AIMD simulations of WDM can involve such high densities, the simulations may have regions in which the ionic configurations correspond to very small electronic r_s.

Thus we compare the Brown *et al.* [2] fit ("BDHC"; as before this is the corrected version) and fit A against the ε_{xc} data in Figs. S1 and S2 as a function of r_s for a considerable range of t. Note particularly the implausible behavior of the BDHC fit in regions of small electronic r_s. The Perrot-Dharma-wardana function [3] exhibits somewhat similar implausible behavior.

Another test for r_s values below the fitting range ($r_s < 1$) is to pay attention to the region of intermediate temperatures where the functional behavior is not entirely guaranteed by the fitting procedure. In that sense the PDW00 functional [3], which fits data obtained by the classical-map hypernetted-chain (CHNC) method for $1 \leq r_s \leq 10$, exhibits completely irregular behavior for $r_s < 1$, hence cannot serve as a reference. The PDW84 functional [4] provides data of random phase approximation (RPA) quality in the range $0.1 < r_s < 6$ where it was fitted, hence should be useful at least as a guide.

Figure S3 compares XC *free* and XC *internal* energies for $r_s = 0.25$ calculated with the fit A, PDW84, and BDHC functionals. The results for $\zeta = 0$ from fit A and PDW84 are in good agreement. The BDHC XC free energy, calculated by numerical integration of Eq. (5), differs significantly from the PDW84 fit in the small r_s regime. Note also that the BDHC fit for $\zeta = 1$ exhibits anomalous behavior in the range $0.01 < t < 100$.

Thermodynamic consistency studies

As summarized in the text, after use of different RPIMC data in the fitting by means of Eqs. (5), (7), or (8) (fits A, B, D respectively) or by (7) and (8) together (fit C), thermodynamic consistency was tested against all the RPIMC data subsets. We note two aspects of that consistency testing.

First, the reported precision of the RPIMC kinetic energy data τ is poorer than for the potential energy u_{ee}, with MAREs of 0.2% and 0.04% respectively. Nonetheless, those errors are substantially smaller than the MAREs of the fits, which in most cases are between 0.5% and 2% (see Table II in the paper). Thus, both RPIMC data sets are precise enough to be used in the fitting.

Second, as there is no control on absolute maximum relative error (AMRE) in our fitting procedures, a straight-forward criterion for assessing the merit of a particular fit is its AMRE. Because the focus is on f_{xc}, the ε_{xc} RPIMC data set is most directly relevant. Examination of Table II in the main text with these two standards in mind immediately leads to elimination of fit D. Its MARE and AMRE values for both polarizations are large compared to the other fits. Though fit B delivers reasonable MARE and AMRE on its own data set u_{ee}, it does worse than A or C for MARE on the other two data sets for $\zeta = 0$ and much worse on AMRE for τ at $\zeta = 1$. This leaves fits A and C; we chose A on grounds of best MARE and AMRE for ε_{xc}.

Numerical values of ε_{xc}, f_x, f_c, f_{xc}, and $v_{xc} = \partial(nf_{xc})/\partial n$ calculated using fit A for all RPIMC data points are given in Table S1 for $\zeta = 0$ and 1 correspondingly. The f_x values differ slightly from those of Ref. 1 Supp. Mat. (denoted there as $E_{x,HF}$) because we used the Perrot-Dharma-wardana analytical fit [4] whereas Ref. 1 calculated the Fermi integral. For simulations the fit is much faster. Table S1 also gives $\phi(r_s, t, \zeta)$ values for $\zeta = 0.34$.

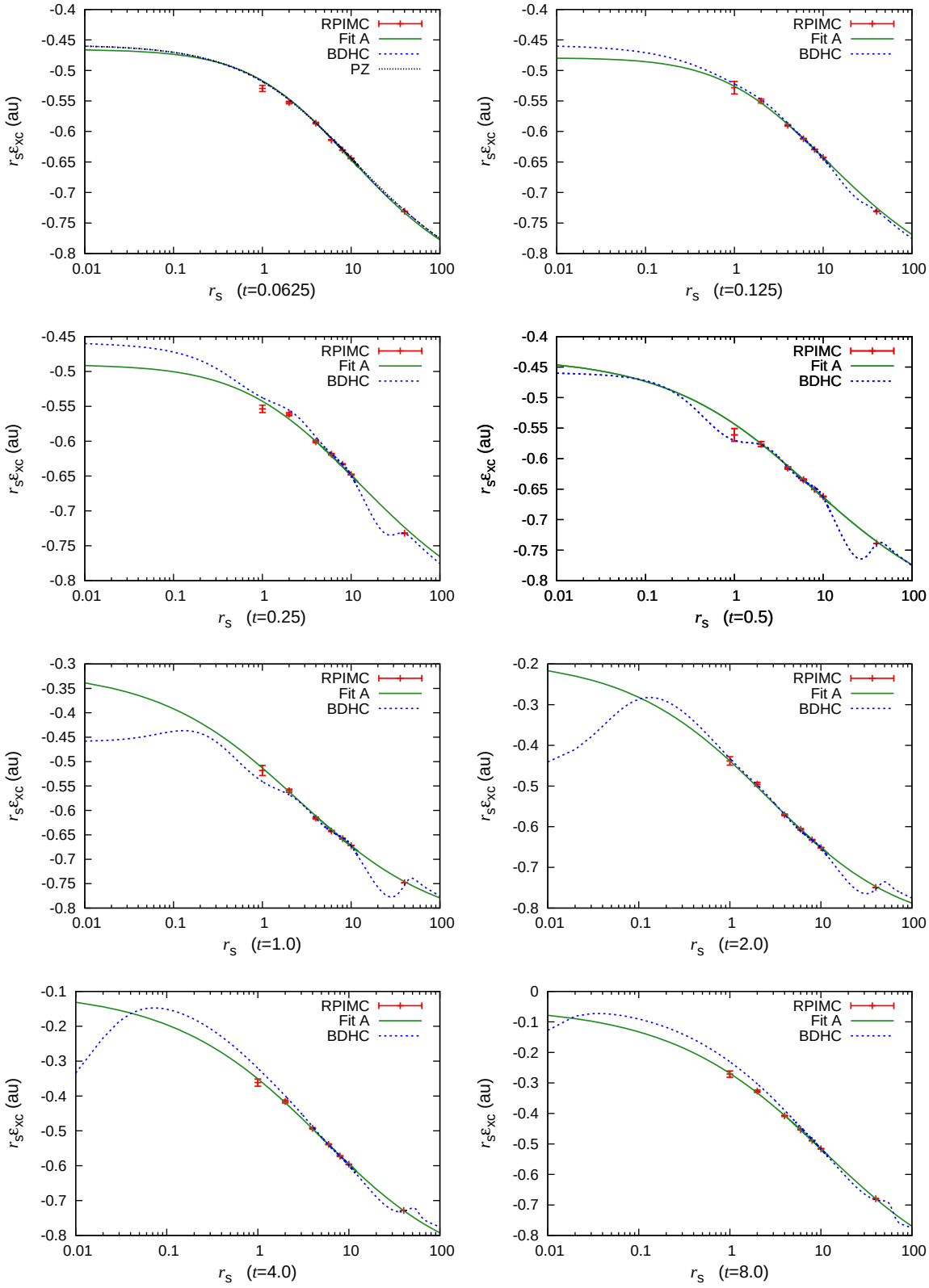

FIG. S1: $r_s\varepsilon_{xc}$ from fit A and BDHC compared to the RPIMC data; all for $\zeta = 0$.

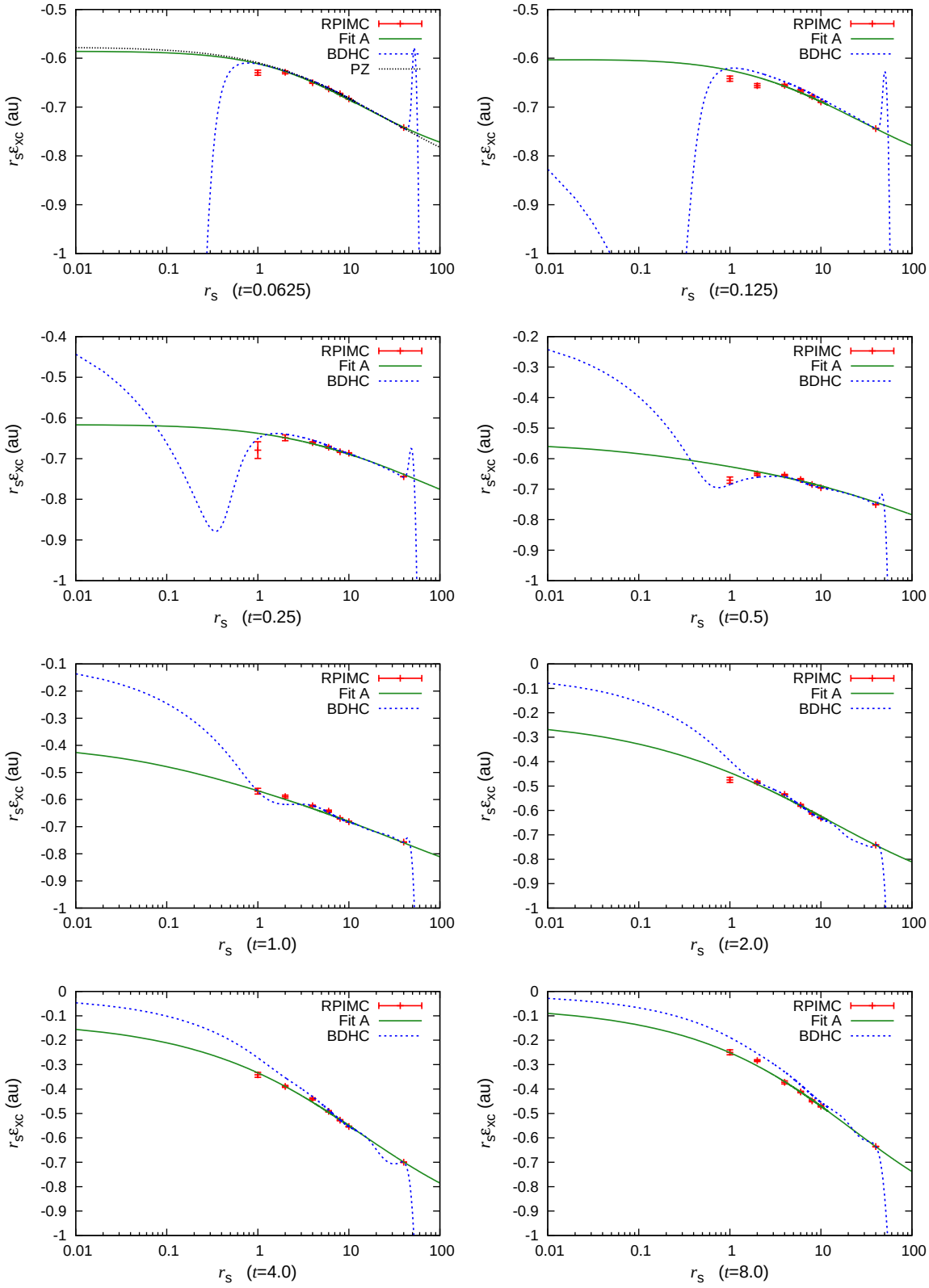

FIG. S2: As in Fig. S1 for $\zeta = 1$.

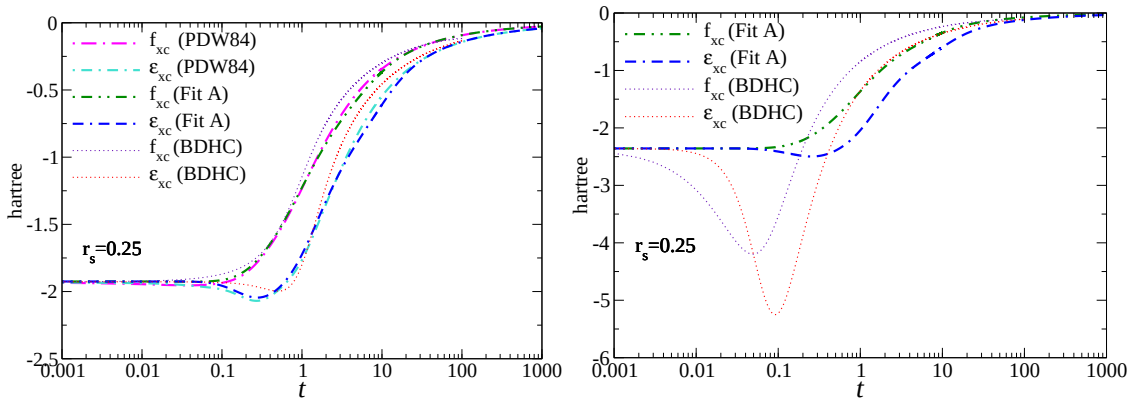

FIG. S3: Comparison between $\varepsilon_{\rm xc}$ and $f_{\rm xc}$ from calculations with different functionals for $\zeta = 0$ (left) and $\zeta = 1$ (right) for $r_{\rm s} = 0.25$.

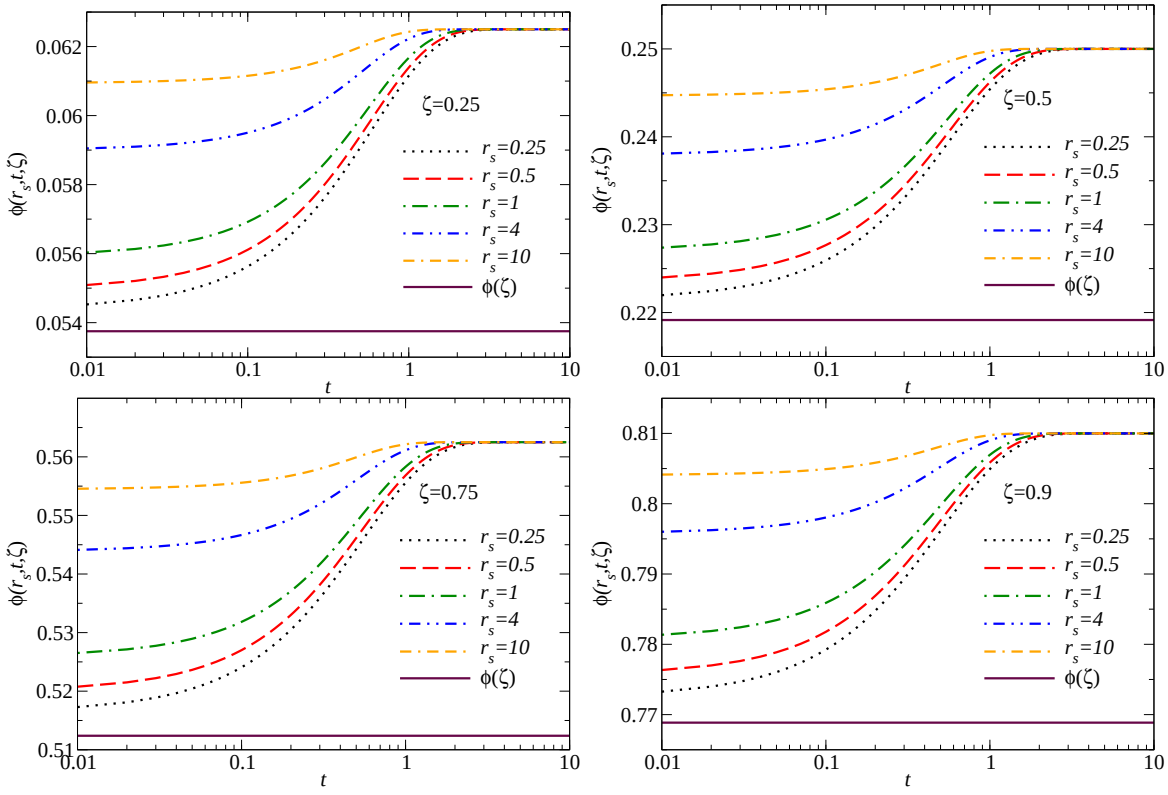

FIG. S4: Polarization function $\phi(r_{\rm s}, t, \zeta)$, Eqs. (18)-(19), as a function of t for selected $r_{\rm s}$ values at $\zeta = 0.25$, 0.5, 0.75, and 0.9. The zero-T polarization function, Eq. (18), is shown for comparison.

TABLE S1: Values of $\varepsilon_{\rm xc}$, $f_{\rm x}$, $f_{\rm c}$, $f_{\rm xc}$, and $v_{\rm xc} = \partial(nf_{\rm xc})/\partial n$ calculated using fit A for each value of $r_{\rm s}$ and t (hartree au) for the unpolarized case ($\zeta = 0$) and for the fully polarized case ($\zeta = 1$). Additionally, values of $\phi(r_{\rm s}, t, \zeta = 0.34)$ are shown in the last column.

		$\zeta = 0$					$\zeta = 1$					$\zeta = 0.34$
$r_{\rm s}$	t	$\varepsilon_{\rm xc}$	$f_{\rm x}$	$f_{\rm c}$	$f_{\rm xc}$	$v_{\rm xc}$	$\varepsilon_{\rm xc}$	$f_{\rm x}$	$f_{\rm c}$	$f_{\rm xc}$	$v_{\rm xc}$	ϕ
1.0	0.0625	-0.5169	-0.4508	-0.0691	-0.5199	-0.6784	-0.6112	-0.5679	-0.0413	-0.6093	-0.8067	0.1050
2.0	0.0625	-0.2734	-0.2254	-0.0499	-0.2753	-0.3575	-0.3136	-0.2840	-0.0290	-0.3129	-0.4132	0.1072
4.0	0.0625	-0.1464	-0.1127	-0.0344	-0.1471	-0.1908	-0.1622	-0.1420	-0.0198	-0.1618	-0.2132	0.1099
6.0	0.0625	-0.1019	-0.0751	-0.0270	-0.1021	-0.1326	-0.1106	-0.0947	-0.0156	-0.1103	-0.1452	0.1114
8.0	0.0625	-0.0788	-0.0563	-0.0225	-0.0789	-0.1025	-0.0844	-0.0710	-0.0131	-0.0841	-0.1107	0.1124
10.0	0.0625	-0.0646	-0.0451	-0.0194	-0.0645	-0.0839	-0.0684	-0.0568	-0.0114	-0.0681	-0.0897	0.1131
40.0	0.0625	-0.0183	-0.0113	-0.0069	-0.0182	-0.0239	-0.0185	-0.0142	-0.0043	-0.0185	-0.0243	0.1155
1.0	0.125	-0.5259	-0.4309	-0.0891	-0.5200	-0.6833	-0.6247	-0.5429	-0.0591	-0.6019	-0.8101	0.1061
2.0	0.125	-0.2766	-0.2154	-0.0607	-0.2761	-0.3600	-0.3194	-0.2714	-0.0384	-0.3099	-0.4147	0.1081
4.0	0.125	-0.1471	-0.1077	-0.0399	-0.1476	-0.1916	-0.1644	-0.1357	-0.0246	-0.1603	-0.2136	0.1105
6.0	0.125	-0.1020	-0.0718	-0.0306	-0.1024	-0.1329	-0.1118	-0.0905	-0.0188	-0.1093	-0.1453	0.1119
8.0	0.125	-0.0786	-0.0539	-0.0251	-0.0790	-0.1025	-0.0851	-0.0679	-0.0155	-0.0834	-0.1106	0.1127
10.0	0.125	-0.0643	-0.0431	-0.0215	-0.0646	-0.0839	-0.0689	-0.0543	-0.0133	-0.0676	-0.0896	0.1133
40.0	0.125	-0.0181	-0.0108	-0.0074	-0.0181	-0.0237	-0.0186	-0.0136	-0.0049	-0.0184	-0.0243	0.1155
1.0	0.25	-0.5427	-0.3749	-0.1315	-0.5064	-0.6823	-0.6377	-0.4724	-0.1001	-0.5725	-0.7965	0.1080
2.0	0.25	-0.2841	-0.1875	-0.0850	-0.2724	-0.3612	-0.3244	-0.2362	-0.0616	-0.2978	-0.4088	0.1096
4.0	0.25	-0.1500	-0.0937	-0.0532	-0.1469	-0.1926	-0.1659	-0.1181	-0.0374	-0.1555	-0.2109	0.1116
6.0	0.25	-0.1035	-0.0625	-0.0398	-0.1023	-0.1336	-0.1123	-0.0787	-0.0278	-0.1066	-0.1435	0.1127
8.0	0.25	-0.0796	-0.0469	-0.0322	-0.0791	-0.1031	-0.0853	-0.0590	-0.0225	-0.0815	-0.1093	0.1134
10.0	0.25	-0.0649	-0.0375	-0.0272	-0.0647	-0.0843	-0.0689	-0.0472	-0.0190	-0.0663	-0.0885	0.1138
40.0	0.25	-0.0181	-0.0094	-0.0088	-0.0182	-0.0238	-0.0185	-0.0118	-0.0065	-0.0183	-0.0241	0.1155
1.0	0.5	-0.5433	-0.2784	-0.1895	-0.4678	-0.6517	-0.6264	-0.3507	-0.1587	-0.5094	-0.7418	0.1110
2.0	0.5	-0.2879	-0.1392	-0.1193	-0.2585	-0.3519	-0.3214	-0.1754	-0.0962	-0.2716	-0.3867	0.1121
4.0	0.5	-0.1531	-0.0696	-0.0728	-0.1424	-0.1906	-0.1653	-0.0877	-0.0575	-0.1452	-0.2022	0.1134
6.0	0.5	-0.1058	-0.0464	-0.0537	-0.1001	-0.1331	-0.1122	-0.0585	-0.0423	-0.1008	-0.1386	0.1140
8.0	0.5	-0.0814	-0.0348	-0.0430	-0.0778	-0.1030	-0.0853	-0.0438	-0.0339	-0.0778	-0.1061	0.1144
10.0	0.5	-0.0664	-0.0278	-0.0360	-0.0639	-0.0844	-0.0690	-0.0351	-0.0286	-0.0636	-0.0863	0.1147
40.0	0.5	-0.0184	-0.0070	-0.0112	-0.0182	-0.0239	-0.0186	-0.0088	-0.0094	-0.0182	-0.0240	0.1156
1.0	1.0	-0.5131	-0.1744	-0.2280	-0.4023	-0.5832	-0.5675	-0.2197	-0.1934	-0.4131	-0.6336	0.1141
2.0	1.0	-0.2808	-0.0872	-0.1437	-0.2308	-0.3262	-0.2997	-0.1098	-0.1192	-0.2291	-0.3409	0.1147
4.0	1.0	-0.1528	-0.0436	-0.0877	-0.1313	-0.1817	-0.1583	-0.0549	-0.0724	-0.1273	-0.1839	0.1151
6.0	1.0	-0.1066	-0.0291	-0.0647	-0.0937	-0.1285	-0.1090	-0.0366	-0.0536	-0.0903	-0.1283	0.1153
8.0	1.0	-0.0823	-0.0218	-0.0517	-0.0735	-0.1002	-0.0837	-0.0275	-0.0432	-0.0707	-0.0994	0.1154
10.0	1.0	-0.0673	-0.0174	-0.0434	-0.0608	-0.0825	-0.0681	-0.0220	-0.0365	-0.0584	-0.0815	0.1155
40.0	1.0	-0.0186	-0.0044	-0.0135	-0.0179	-0.0238	-0.0190	-0.0055	-0.0121	-0.0176	-0.0237	0.1156
1.0	2.0	-0.4382	-0.0960	-0.2256	-0.3216	-0.4786	-0.4450	-0.1209	-0.1886	-0.3095	-0.4809	0.1155
2.0	2.0	-0.2513	-0.0480	-0.1440	-0.1920	-0.2796	-0.2466	-0.0605	-0.1195	-0.1800	-0.2712	0.1156
4.0	2.0	-0.1422	-0.0240	-0.0894	-0.1134	-0.1618	-0.1367	-0.0302	-0.0746	-0.1048	-0.1534	0.1156
6.0	2.0	-0.1011	-0.0160	-0.0666	-0.0826	-0.1167	-0.0967	-0.0202	-0.0561	-0.0762	-0.1099	0.1156
8.0	2.0	-0.0790	-0.0120	-0.0538	-0.0658	-0.0922	-0.0756	-0.0151	-0.0456	-0.0607	-0.0867	0.1156
10.0	2.0	-0.0651	-0.0096	-0.0454	-0.0550	-0.0766	-0.0624	-0.0121	-0.0388	-0.0509	-0.0721	0.1156
40.0	2.0	-0.0187	-0.0024	-0.0147	-0.0171	-0.0231	-0.0186	-0.0030	-0.0133	-0.0163	-0.0224	0.1156
1.0	4.0	-0.3509	-0.0498	-0.1946	-0.2443	-0.3715	-0.3337	-0.0627	-0.1646	-0.2273	-0.3530	0.1156
2.0	4.0	-0.2096	-0.0249	-0.1262	-0.1511	-0.2253	-0.1948	-0.0313	-0.1066	-0.1379	-0.2089	0.1156
4.0	4.0	-0.1236	-0.0124	-0.0800	-0.0925	-0.1354	-0.1136	-0.0157	-0.0680	-0.0836	-0.1238	0.1156
6.0	4.0	-0.0899	-0.0083	-0.0606	-0.0689	-0.0998	-0.0826	-0.0104	-0.0518	-0.0622	-0.0910	0.1156
8.0	4.0	-0.0714	-0.0062	-0.0494	-0.0556	-0.0800	-0.0658	-0.0078	-0.0425	-0.0504	-0.0730	0.1156
10.0	4.0	-0.0596	-0.0050	-0.0421	-0.0470	-0.0673	-0.0550	-0.0063	-0.0364	-0.0427	-0.0615	0.1156
40.0	4.0	-0.0182	-0.0012	-0.0144	-0.0157	-0.0217	-0.0175	-0.0016	-0.0130	-0.0146	-0.0204	0.1156
1.0	8.0	-0.2688	-0.0252	-0.1485	-0.1738	-0.2742	-0.2510	-0.0318	-0.1259	-0.1576	-0.2549	0.1156
2.0	8.0	-0.1664	-0.0126	-0.0987	-0.1113	-0.1720	-0.1526	-0.0159	-0.0836	-0.0995	-0.1569	0.1156
4.0	8.0	-0.1017	-0.0063	-0.0643	-0.0706	-0.1070	-0.0925	-0.0079	-0.0548	-0.0627	-0.0966	0.1156
6.0	8.0	-0.0757	-0.0042	-0.0496	-0.0538	-0.0806	-0.0687	-0.0053	-0.0424	-0.0477	-0.0725	0.1156
8.0	8.0	-0.0611	-0.0032	-0.0410	-0.0442	-0.0656	-0.0556	-0.0040	-0.0352	-0.0392	-0.0591	0.1156
10.0	8.0	-0.0516	-0.0025	-0.0353	-0.0378	-0.0558	-0.0470	-0.0032	-0.0304	-0.0336	-0.0503	0.1156
40.0	8.0	-0.0170	-0.0006	-0.0130	-0.0136	-0.0194	-0.0159	-0.0008	-0.0115	-0.0123	-0.0178	0.1156

TABLE S2: MARE and AMRE (in %) of interpolation with use of the function of Eqs. (18) and (19) with respect to QMC data [7] at two intermediate polarizations ($\zeta = 0.34,\ 0.66$). Errors are calculated for both correlation only and for XC as the relative difference between interpolated and exact values for intermediate polarizations. Also shown are the interpolation errors for the finite-T CHNC data given in Table IV of Ref. 3.

Function	$\varepsilon_c^{\rm QMC}$	$\varepsilon_{xc}^{\rm QMC}$	$f_{xc}^{\rm CHNC}$
PDW00[a]	0.7/3.1	0.07/0.2	0.02/0.07
PDW00(repar.)[b]	0.6/3.7	0.04/0.2	0.02/0.07

[a] Eqs. (18), (19) with original PDW00 parameters [3].
[b] Eqs. (18), (19) reparametrized to the zero-T QMC and finite-T CHNC data.

Exact spin scaling in finite-T exchange

Oliver and Perdew [5] have shown how a spin-unpolarized functional can be extended to the spin-polarized case for those energy contributions which are defined in terms of one-electron orbitals, *i.e.*, for the kinetic and exchange energy functionals. Exactly the same arguments can be applied to the finite-T exchange, so the appropriate spin-density generalization for the X free energy of the HEG at density $n = N/V$ takes the form

$$\begin{aligned}\mathcal{F}_{\rm x}(n_\uparrow, n_\downarrow, T) &= \frac{1}{2}\Big[\mathcal{F}_{\rm x}(2n_\uparrow, T) + \mathcal{F}_{\rm x}(2n_\downarrow, T)\Big] \\ &\equiv \frac{V}{2}\Big[(2n_\uparrow) f_{\rm x}^0(2n_\uparrow, t(2n_\uparrow, T)) \\ &+ (2n_\downarrow) f_{\rm x}^0(2n_\downarrow, t(2n_\downarrow, T))\Big], \qquad \text{(S1)}\end{aligned}$$

where $f_{\rm x}^0$ is the spin-unpolarized finite-T exchange free energy per particle.

Using spin polarization, ζ, and the total electron density, n, instead of $n_\uparrow$ and $n_\downarrow$, Eq. (S1) can be simplified to the following form (compare Eq. (2.14) of Ref. 5)

$$\begin{aligned}f_{\rm x}(n, T, \zeta) &\equiv \mathcal{F}_{\rm x}(n_\uparrow, n_\downarrow, T)/N \\ &= \tfrac{1}{2}\Big[(1+\zeta)^{4/3} f_{\rm x}^0(n, t_\uparrow) + (1-\zeta)^{4/3} f_{\rm x}^0(n, t_\downarrow)\Big], \qquad \text{(S2)}\end{aligned}$$

where $t_{\uparrow/\downarrow} \equiv t(2n_{\uparrow/\downarrow}, T) = 2k_B T/[3\pi^2(2n_{\uparrow/\downarrow})]^{2/3}$, and $n_{\uparrow/\downarrow} = (1 \pm \zeta)n/2$.

Polarization interpolation

Table S2 provides a comparison of the original and reparametrized Perrot-Dharma-wardana interpolation functions. Figure S4 shows $\phi(r_s, t, \zeta)$ (with parameters given in Table II) as a function of reduced temperature for $r_s = 0.25$, 0.5, 1, 4, and 10 and $\zeta = 0.25$, 0.5, 0.75, and 0.9. At low-t ($t < 1$), the polarization function shows small dispersion with respect to r_s. Similarly, $\phi(r_s, t, \zeta)$ as a function of t at fixed r_s and ζ exhibits only weafitting chebyshev polinomialsk temperature dependence.

Zero-T correlation energy comparison

Given the importance of the existing and widely used $T = 0$ K LDA polarization interpolation, Fig. S5 shows the comparison between the zero-T correlation energy of fit A calculated with Eq. (22), with Perdew-Zunger (PZ) LSDA, and the QMC simulation data. The correlation energy as a function of ζ is shown for (from bottom-to-top) $r_s = 0.25$, 0.5, 1, 2, 3, 5, 10, and 20. Fit A agrees quite well with PZ and with the QMC results. The maximum relative difference between fit A and PZ correlation energies occurs at $r_s = 0.25$ and 0.5 and is about 4%.

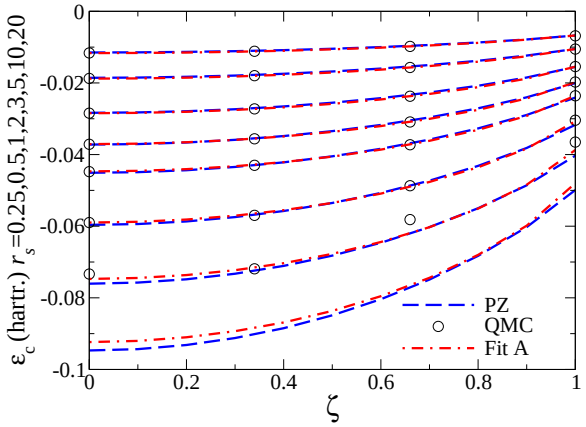

FIG. S5: Zero-T correlation energies calculated by the Perdew-Zunger LSDA functional [6] and by the zero-T limit of fit A, Eq. (22), compared to QMC [7] data.

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