Correlation energy of the paramagnetic electron gas at the thermodynamic limit

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The variational and diffusion quantum Monte Carlo methods are used to calculate the correlation energy of the paramagnetic three-dimensional homogeneous electron gas at intermediate to high density. Ground state energies in finite cells are determined using Slater-Jastrow-backflow trial wave functions, and finite-size effects are removed using twist-averaged boundary conditions and extrapolation of the energy per particle to the thermodynamic limit of infinite system size. Our correlation energies in the thermodynamic limit are lower (i.e., more negative, and therefore more accurate according to the variational principle) than previous results, and can be used for the parameterization of density functionals to be applied to high-density systems.

I. INTRODUCTION

The pairwise Coulomb repulsion between electrons results in many-body correlations in electronic systems such as the homogeneous electron gas (HEG)1 2. The so-called correlation energy is a negative correction to the mean-field Hartree-Fock energy. Although the correlation energy is usually only a small percentage of the total energy of an electronic system, it is crucial for an accurate description of chemical and electronic properties 3,4. Unfortunately it is also the most complicated part of the energy to calculate accurately.

The three-dimensional (3D) HEG plays a crucial role in our understanding of the nature of electronic correlation in real materials 5–8. Moreover, the HEG is one of the most important models for our understanding of bulk systems under extreme conditions, such as warm dense matter, which is an exotic, highly compressed state of matter that exists between solid and plasma phases at high temperatures 9–11. The correlation energy of the 3D HEG as a function of density 12–14 is a fundamental element in the description of the electronic properties of real systems by density functional theory (DFT)15,16. However, calculating the correlation energy accurately requires many-body wave function-based methods 17 such as quantum Monte Carlo (QMC) techniques 18–25. The variational (VMC) and diffusion quantum Monte Carlo (DMC) methods 18,26 are stochastic approaches for obtaining expectation values of quantum operators. These techniques are especially efficient for calculating the ground state energies of interacting fermions. The main object is an approximate trial wave function, whose accuracy governs the final energy and intrinsic statistical fluctuations in the simulations.

The DMC simulations of Ceperley and Alder 18 presented important data connecting the high- and low-density regimes of the correlation energy of the 3D HEG. Their data have been used in parameterizations of the correlation energy over a wide density range and are frequently used in DFT calculations. Well-known parameterizations that make use of Ceperley and Alder’s results were provided by Perdew and Zunger (PZ81) 27, Vosko, Wilk, and Nusair (VWN80) 28, and Perdew and Wang (PW92) 29, among others. The PW92 functional includes five parameters, two determined from analytic high-density constraints and three by fitting to the QMC data. A density parameter interpolation (DPI) 12, which was constructed by imposing four high-density and three low-density constraints on a seven-parameter functional form, provided a check based purely on the satisfaction of the exact constraints. Spink et al. 23 performed QMC calculations for spin-unpolarized and spin-polarized 3D HEGs over the high- and intermediate-density ranges, which can be regarded as the most accurate QMC data reported so far. In the present work, we provide new QMC data for the correlation energy of the paramagnetic (i.e., spin unpolarized) 3D HEG, which are lower than previously reported results. We use long-range backflow correlations to make fixed-node errors more consistent between different cell sizes. Instead of using the analytic finite-size corrections, we extrapolate our results to infinite system size which provides more accurate results at the thermodynamic limit 11. QMC energies in finite simulation cells obey the variational principle and it is reasonable to assume that the QMC energy per particle extrapolated to infinite system size is also an upper bound on the true energy per particle. Hence the fact that our energies are lower than previous works strongly suggests that our results are more accurate.

We have used the VMC and DMC methods to obtain 3D HEG correlation energies at different densities. In the VMC method, parameters in a trial wave function are optimized according to the variational principle, with energy expectation values calculated by Monte Carlo in-
integration in the $3N$-dimensional space of electron position vectors. In the DMC method, the imaginary-time Schrödinger equation is used to evolve a statistical ensemble of electronic configurations towards the ground state. Fermionic antisymmetry is maintained by the fixed-phase approximation, in which the complex phase of the wave function is constrained to equal that of an approximate trial wave function optimized within VMC.

The simplest fermionic wave function is a Slater determinant, which describes exchange effects but not correlation. Multideterminant wave functions and pairing (geminal) wave functions [31] can also be used. The most efficient method of going beyond the Slater wave function is to multiply it by a Jastrow factor $\exp(J)$, resulting in a Slater-Jastrow wave function [20, 21]. The Jastrow factor usually depends explicitly on the distances between particles, introducing correlation into the wave function. The Jastrow factor is positive everywhere and symmetric with respect to electron exchange, taking the form

$$J = U + P + H = \sum_{i<j} u(r_{ij}) + \sum_{i<j<k} p(r_{ijk}) + \sum_{i<j} h(r_{jk}, r_{ik}, r_{ij}),$$

where

$$u(r) = \sum_{l=0}^{N_e} \alpha_l r^l (r - L_a)^C \Theta(L_a - r),$$

where $r$ is the minimum-image distance between two electrons, the cutoff length $L_a$ is less than or equal to the radius of the largest sphere that can be inscribed in the Wigner-Seitz cell of the simulation cell, $C = 3$ specifies how smooth the function is at the cutoff length, $\Theta$ is the Heaviside step function, and $\{\alpha_l\}$ are optimizable parameters, which differ for parallel- and antiparallel-spin electrons. To satisfy the Kato cusp conditions [33, 34], we fix $\alpha_1 = \Gamma / (-L_a)^C + \alpha_0 C / L_a$, where $\Gamma = 1/2$ for opposite-spin electrons and $\Gamma = 1/4$ for same-spin electrons. We chose $N_a = 8$. The $p$ term has the symmetry of the simulation-cell Bravais lattice and allows a description of correlation in the “corners” of the simulation cell. Its form is

$$p(r) = \sum_A a_A \sum_{G \in A^+} \cos(G \cdot r),$$

where $A$ represents a star of symmetry-equivalent, nonzero, simulation-cell reciprocal-lattice vectors $G$, and $A^+$ is a subset of $A$ that consists of one out of each $\pm G$ pair. The $\{a_A\}$ are optimizable parameters. We used 46 stars of $G$ vectors in $p$. The Jastrow also includes symmetric three-electron terms [35, 36]

$$h(r, r', r'') = \sum_{l=0}^{N_h} \sum_{m=0}^{N_h} \sum_{n=0}^{N_h} c_{lmn} r^l (r')^m (r'')^n \times (r - L_h)^c (r' - L_h)^c (r'' - L_h)^c \Theta(L_h - r) \Theta(L_h - r') \Theta(L_h - r''),$$

where $L_h$ is a cutoff length and $c_{lmn}$ are linear parameters. Constraints were placed on the linear parameters to ensure that $h$ is cuspless. We chose $N_h = 4$. Different $h$ terms, meaning different $\{c_{lmn}\}$, may be used for electron triplets involving different combinations of spins. However, in this work, the parameters in the three-electron Jastrow factors were constrained to be independent of spin.

Including a backflow transformation in the trial wave function, the Slater part of the wave function $S$ is evaluated at transformed “quasiparticle” coordinates $X(R) = R + \xi(R)$, where

$$\xi_i(R) = \sum_{j \neq i} \eta(r_{ij}) r_{ij} + \sum_{j \neq i} \pi(r_{ij})$$

is the backflow displacement of electron $i$. $\eta$ is a cuspless, smoothly truncated, isotropic polynomial function of minimum-image electron-electron distance $r_{ij}$. The polynomial coefficients are optimizable parameters, and are different for parallel- and antiparallel-spin electrons [32]. The form of $\eta(r)$ is mathematically equivalent to that of the Jastrow $u(r)$ term [Eq. (2)], with $\Gamma = 0$ for same-spin electrons and optimizable for opposite-spin electrons. Typically we used $N_\eta = 8$ in the polynomial expansions. The $\pi$ term has the form of the gradient of a Jastrow $p$ term [Eq. (3)]:

$$\pi(r) = -\sum_A c_A \sum_{G \in A^+} \sin(G \cdot r) G,$$
The wave functions were optimized by variance minimization followed by energy minimization. The CASINO package was used for all our QMC calculations.

III. FINITE-SIZE EFFECTS

Monte Carlo-sampled canonical ensemble twist-averaged (TA) boundary conditions were used to reduce quasirandom single-particle finite-size errors in total energies due to momentum quantization effects. The Hartree-Fock kinetic and exchange energies were used as control variates to improve the precision of the twist-averaged energy. Systematic finite-size errors due to the use of the Ewald interaction rather than \(1/r\) to evaluate the interaction between each electron and its exchange-correlation hole and the incomplete description of long-range two-body correlations were removed by fitting \(E(N) = E(\infty) + b/N\) to the TA DMC energy per particle at different system sizes. Unlike the previous work of Spink et al., we do not rely on analytic finite-size correction formulas, but instead use the analytic results to provide the exponents used in finite-size extrapolation formulas. All our calculations were performed using face-centered cubic simulation cells, maximizing the distance between each particle and its closest periodic image.

At very high density \(r_s \ll 1\), systematic finite-size effects are more challenging. In this regime, the QMC energy is close to the Hartree-Fock energy, and hence the QMC energy per particle initially shows the Hartree-Fock \(O(N^{-2/3})\) scaling with system size, before eventually crossing over to the asymptotic \(O(N^{-1})\) scaling when the finite-size error becomes small compared with the correlation energy.

IV. CORRELATION ENERGIES

We studied the paramagnetic 3D HEG at density parameters \(r_s = 0.5, 0.75, 1, 2, 3, 4, 5, 7, 10, 20\). For each density, QMC calculations were performed for simulation cells with \(N = 130, 226\), and 338 electrons. Our DMC energies were extrapolated linearly to zero time step, with the target walker population being varied in inverse proportion to the time step. The difference between the twist-averaged DMC energy at small \(r_s\) (i.e., \(r_s \leq 1.0\)) obtained with time step \(\tau = 0.02r_s^2\) and the energy at zero time step is not statistically significant. The same behavior was observed at large \(r_s\) with \(\tau = 0.01r_s^2\). The energies and variances calculated using SJB wave functions for different system sizes are reported in the Supplemental Material.

The correlation energy is defined as the difference between the Hartree-Fock energy per electron [which is \(E_{HF} = 3(9\pi/4)^{2/3}/(10r_s^2) - 3(9\pi/4)^{1/3}/(4\pi r_s)\) for the paramagnetic HEG] and the exact ground-state energy per electron, where the latter is approximated by our SJB-DMC results extrapolated to the limit of infinite system size.

Table I summarizes the contribution of each term of the trial wave function to the correlation energy per particle in a simulation cell containing \(N = 54\) electrons. We considered two systems with \(r_s = 0.5\) and \(r_s = 20\). Figure 1 shows the improvements in the VMC and DMC correlation energies resulting from the inclusion of different terms in the Jastrow and backflow functions.

According to Spink et al., the TA VMC energy of the spin-unpolarized 3D HEG at \(r_s = 0.5\) at a system size of \(N = 118\) is 3.41378(2) Ha/elec. Our TA VMC simulation for the same system size yields the energy as...
3.412460(4) Ha/elec., which is ~36 meV/elec. lower, because of the inclusion of the \( \pi \) term in our work.

### TABLE I. TA VMC and DMC correlation energies for \( N = 54 \) system size obtained using different terms in the Jastrow exponent and using both SJB and SJ wave functions. Where Jastrow terms are not specified, \( U, P, \) and \( H \) terms were used; where the backflow terms are not specified, \( \eta \) and \( \pi \) terms were used.

| Wave function | Correlation energy (eV/elec.) | \( r_s = 0.5 \) | \( r_s = 20 \) |
|---------------|-------------------------------|----------------|----------------|
|               | VMC | DMC | VMC | DMC |
| SJ(\(U\))     | -2.5112(3) | -2.5684(4) | -0.311717(2) | -0.317465(4) |
| SJ(\(U + H\)) | -2.5161(3) | -2.5680(5) | -0.313798(3) | -0.317469(5) |
| SJ            | -2.5381(3) | -2.5685(4) | -0.314464(3) | -0.317492(5) |
| SJ(\(\eta\))  | -2.6056(5) | -2.6166(5) | -0.319082(3) | -0.320579(5) |
| SJB           | -2.6331(3) | -2.6366(4) | -0.319346(2) | -0.320756(4) |

Our VMC and DMC energies extrapolated to the limit of infinite system size are listed in Table II. To obtain the best linear fit and reduce the noise in the energies as a function of the number of particles \( N \), a larger number of twists was used for higher densities and smaller system sizes. The smallest and largest number of twists were 120 and \( 10^4 \), respectively. Comparing our infinite-system VMC and DMC results with the DMC results of Spink et al. [23] demonstrates not only the improvement of the trial wave function due to the inclusion of long-range \( \pi \) backflow terms, but also the importance of removing finite-size effects by extrapolation rather than relying on analytic correction formulas.

### TABLE II. TA VMC and DMC energies of the 3D HEG extrapolated to the thermodynamic limit from different system sizes \( (N = 130, 226, \) and \( 338) \), compared with the DMC results of Spink et al. [23], and Ceperley and Alder [18]. Our DMC energies have been extrapolated to zero time step.

| \( r_s \) | VMC Pres. wk. | DMC Pres. wk. | Spink et al. Pres. wk. | Ceperley & Alder Pres. wk. |
|----------|---------------|---------------|------------------------|---------------------------|
| 0.5      | 3.4255(1)     | 3.4254(1)     | 3.4301(1)              | ...                       |
| 0.75     | 1.28625(5)    | 1.28620(5)    | ...                    | ...                      |
| 1.0      | 0.5864(3)     | 0.5864(2)     | 0.5870(1)              | 0.5870(5)                 |
| 2.0      | 0.00195(2)    | 0.001917(9)   | 0.002380(5)            | 0.002050(2)              |
| 3.0      | -0.06728(1)   | -0.067309(9)  | -0.067075(4)           | ...                      |
| 4.0      | -0.07767(1)   | -0.07771(1)   | ...                    | ...                      |
| 5.0      | -0.07594(1)   | -0.07597(1)   | -0.075881(1)           | -0.07560(5)              |
| 7.0      | -0.06630(5)   | -0.066348(2)  | ...                    | ...                      |
| 10.0     | -0.053503(2)  | -0.053527(5)  | -0.0535116(5)          | -0.0533750(2)            |
| 20.0     | -0.031720(6)  | -0.031755(3)  | -0.0317868(5)          | -0.0316450(1)            |

Following Ceperley [21], we fit

\[ E_c(r_s) = \frac{\gamma}{1 + \beta_1 \sqrt{r_s} + \beta_2 r_s} \]

(7)
to our SJ-B DMC correlation energies (Fig. 2). The fitting parameters \( \gamma, \beta_1, \) and \( \beta_2 \) are \(-0.151(5)\) Ha \(1.18(7)\), and \(0.338(5)\), respectively. The \( \chi^2 \) value of the fit is 307.48 per degree of freedom. Equation (7) is accurate for large \( r_s \), as we have shown in our recent work on the low-density phase diagram of the HEG, where our DMC correlation energies for \( 30 \leq r_s \leq 100 \) were fitted to Eq. (7) giving a \( \chi^2 \) per degree of freedom of 0.521 [1]. We found that the \( \chi^2 \) per degree of freedom becomes 0.686 by fitting DMC correlation energies for \( 20 \leq r_s \leq 100 \) to Eq. (7) and we found the fitting parameters \( \gamma, \beta_1, \) and \( \beta_2 \) to be \(-0.1278(55)\) Ha/elec., \(0.897(53)\), and \(0.299(12)\), respectively.

According to the all-orders perturbation theory of Gell-Mann and Brueckner [17] the correlation energy at high density is given by \( E_c(r_s) = A \ln(r_s) + C + O(\ln(r_s)) \), where \( A = \frac{1}{2} \left[ 1 - \ln(2) \right] \approx 0.0311 \) Ha and \( C \approx -0.0465 \) Ha. The appearance of powers of \( \ln(r_s) \) in this formula shows that the correlation energy is a nonanalytic function of \( r_s \) for \( r_s \to 0 \) and describes the failure of the naive perturbation approach. The constant term \( C \) is the sum of the second order Onsager's exchange integral and a numerical constant caused by the sum over divergent contributions [33]. In practice, this asymptotic formula is accurate only for very small \( r_s \ll 1 \). We fitted our VMC and DMC correlation energies for \( r_s = 0.5, 0.75, \) and 1 to the Gell-Mann-Brueckner expression (Fig. 2). The fitting parameters are \( A_{\text{VMC}} = 0.0250(5) \) Ha, \( C_{\text{VMC}} = -0.06030(2) \) Ha, \( A_{\text{DMC}} = 0.0250(5) \) Ha, and \( C_{\text{DMC}} = -0.06040(1) \) Ha. The difference between the VMC and DMC fitting parameters is small because the random errors due to twist averaging at high density dominate. Figure 2 shows that at \( r_s \leq 0.1 \) the correlation energy predicted by the Gell-Mann-Brueckner formula becomes smaller than VMC and DMC.

One can include an additional term in the Gell-Mann-Brueckner expansion and write the high-density expansion of the correlation energy per electron as

\[ E_c(r_s) = A \ln(r_s) + C + Br_s \ln(r_s) + O(r_s), \]

(8)
where the exact value of the coefficient of \( r_s \ln(r_s) \) is 
\[
B = 0.00922921 \quad [13].
\]
We fitted our DMC correlation energies for \( r_s = 0.5, 0.75, 1.0, \) and 2.0 to the extended expansion, and we found that the fitting parameters \( A, C, \) and \( B \) are 0.0275(4), -0.06001(7), and -0.0031(2) Ha/elec., respectively, with a \( \chi^2 \) value of 3.52579.

We fitted all our DMC correlation energies for \( 0.5 \leq r_s \leq 100 \), which are reported in this work and in our recently published paper [1], to Eq. (7) plus Eq. (8) and we found the \( \chi^2 \) per degree of freedom to be 54.3. We searched for the best fit with the smallest \( \chi^2 \) value and discovered that by adding a \( r_s^{-3/4} \) term to the sum of Eqs. (7) and (8) the \( \chi^2 \) value is reduced to 1.26. Hence,
The fitting parameters are listed in Table IV. which covers the high-, middle-, and low-density regimes.

\[
E_c(r_s) = A \ln(r_s) + C + Br_s \ln(r_s) + \frac{D}{r_s^{3/4}} + \frac{\gamma}{1 + \beta_1 \sqrt{r_s} + \beta_2 r_s},
\]

(9)
can describe the correlation energy of the 3D paramagnetic HEG within the density range 0.5 ≤ r_s ≤ 100, which covers the high-, middle-, and low-density regimes. The fitting parameters are listed in Table IV.

V. CONCLUSION

In conclusion, we have performed VMC and DMC simulations using SJB trial wave functions to calculate the correlation energy of the paramagnetic 3D HEG at high and intermediate densities. We corrected finite-size errors by twist averaging and extrapolation to the thermodynamic limit. Our correlation energies, which are lower than previously reported results, can be used to parameterize the correlation energy of the 3D HEG for use in DFT calculations.

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TABLE III. Correlation energies for the spin-unpolarized 3D HEG from the PZ81 [27], VWN80 [28], PW92 [29], and DPI [12] parameters, DMC (Spink et al. [23]), and this work (VMC and DMC).

| r_s  | PZ81   | VWN80  | PW92   | DPI   | DMC (Spink et al.) | VMC   | DMC   |
|------|--------|--------|--------|-------|-------------------|-------|-------|
| 0.5  | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 |
| 0.75 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 |
| 1.0  | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 |
| 2.0  | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 |
| 3.0  | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 |
| 4.0  | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 |
| 5.0  | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 |
| 7.0  | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 |
| 10.0 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 |
| 20.0 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 |

TABLE IV. Fitting parameters of Eq. (9) in Hartree.

| Fitting parameter | Value | Asymptotic std. err. |
|-------------------|-------|---------------------|
| A (Ha/elec.)      | 0.000435098 | 0.00001665 |
| C (Ha/elec.)      | -0.00221852 | 0.0008169 |
| B (Ha/elec.)      | -3.02312 × 10⁻⁷ | 1.493 × 10⁻⁷ |
| D (Ha/elec.)      | -0.0134875 | 0.005071 |
| γ (Ha/elec.)      | -0.077337 | 0.004517 |
| β₁                | 0.470881 | 0.05071 |
| β₂                | 0.262613 | 0.004956 |

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FIG. 2. Correlation energy of the spin-unpolarized 3D HEG as a function of $r_s$. (Top panel) The VMC and DMC correlation energies are fitted to Eq. (7) and are compared with the PZ81 [27] parameterization. (Middle panel) VMC and DMC correlation energies at high density ($r_s = 0.5, 0.75,$ and 1) are fitted to Gell-Mann and Brueckner’s asymptotic formula. The fitting parameters are presented in the main text. (Bottom panel) Difference between our DMC correlation energy (Pres. wk−DMC) and the PZ81 [27], VWN80 [25], PW92 [29], and DPI [12] DFT functionals.

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