Advanced materials modelling in the thermodynamic limit: An analysis of the asymptotic behavior of finite size errors using coupled cluster theory

Tina N Mihm\textsuperscript{(a),(b)}, Bingdi Yang\textsuperscript{(a)}, and James J. Shepherd\textsuperscript{(a),(b)∗}

\textsuperscript{(a)} Department of Chemistry, University of Iowa
\textsuperscript{(b)} University of Iowa Informatics Initiative, University of Iowa

(Dated: July 24, 2020)

We show that the conventional power law of the inverse of the particle number ($N^{-1}$) for extrapolation of total energies into the thermodynamic limit does not reproduce the Gell-Mann and Brueckner results for the three-dimensional high density electron gas, even when system sizes of $N \sim 2000$ electrons are used. Instead, a power law of $N^{-1/3}$ fits the data beyond 1000 electrons, which has also been found by other authors. The $N^{-1/3}$ power law also appears to fit data from other densities better than $N^{-1}$. To explain this observation, we develop a novel analysis of the low-$G$ components of the wavefunction, and show they are not well-sampled enough, even at high electron numbers, to yield a straight-forward $N^{-1}$ convergence to the thermodynamic limit (TDL). We show that, for most practical calculations, the TDL correlation energy lies between the extrapolation from $N^{-1}$ and the extrapolation from $N^{-1/3}$. Furthermore, the energy extrapolation from an $N^{-1/3}$ power law tends to either increase or decrease with increasing system size, but when energies increase is an indication that $N^{-1}$ can effectively be used for extrapolation.

\textbf{Introduction:-} Coupled cluster theory, with its balance of cost and accuracy in treating electronic structure, has recently been highlighted for its ability to accurately determine defect energies \cite{1}, calculate energy differences between spin states \cite{2} and phases \cite{3}, identify plasmons \cite{4}, calculate optical gaps \cite{5}, and describe the interactions between water and graphene \cite{6}. Each of these has required a degree of detail in the wavefunction and properties need to be carefully extrapolated to the thermodynamic, or infinite-size, limit \cite{7-10}. There is, therefore, a critical need to understand the exact way in which the correlation energy approaches the thermodynamic limit, in terms of a limiting power law. As there is some significant disagreement in the modern literature about what form the power law ought to take, \cite{7-10} practitioners can be uncertain over the accuracy of extrapolated energies. This is important to resolve, as coupled cluster theory should reproduce appropriate convergence to the thermodynamic limit for a range of simple systems. The rationale for this is that the random phase approximation (RPA), an infinite-order resummation of ring diagrams, is sufficient to reproduce the long-range pair correlation function \cite{10, 11} and that coupled cluster theory contains the appropriate diagrams to do the same \cite{12-15}.

In order to make progress towards resolving this debate, we set out to find the exact asymptotic power law obeyed by the correlation energy. Our initial analysis takes advantage of the fact that the random phase approximation (RPA) is exact in the high-density limit of the uniform electron gas \cite{16, 17} and that, therefore, finite-sized coupled cluster doubles (CCD) calculations will be exact at small $N$ \cite{13, 14, 18}. We therefore performed CCD calculations of up to $N = 2042$ with twist averaging. We found that an $N^{-1/3}$, instead of a $N^{-1}$, power law reproduces the exact thermodynamic limit. This is significant, because there are a growing number of studies that have generally taken $N^{-1}$ as the correct power law for the coupled cluster correlation energy \cite{2, 6, 14, 19} (inspired by a similar extrapolation for the total energy).

Since our findings were unexpected, we turned to analytically modelling the long-range part of the wavefunction, which gives rise to finite-size effects. We found that the there is a cross-over between the effectiveness using an $N^{-1/3}$ power law extrapolation and an $N^{-1}$ power law extrapolation: the way in which the extrapolated energies from the $N^{-1/3}$ power law behave with increasing system size determines which power law is most effective. We here compare our findings with recent reports of various power laws in the approximate \textit{ab initio} calculations of solids \cite{7, 19-22} and discuss the implications of our work for practice.

\textbf{Coupled cluster doubles on the uniform electron gas:-} We follow methods and procedures outlined more thoroughly elsewhere \cite{14, 18, 23}; however, for the benefit of the reader, we will highlight some key methodological details here. Coupled cluster theory uses an exponential ansatz for the wavefunction: $\Psi = e^T \Psi_{HF}$.

This formulation yields self-consistent equations for the individual elements $t_{ijab}$ of the operator $T$, and an expression for the correlation energy $E_{\text{corr}} = E_{\text{total}} - E_{\text{HF}}$ as follows:

\begin{equation}
E_{\text{corr}} = \frac{1}{4} \sum_{ijab} t_{ijab} \bar{t}_{ijab}
\end{equation}

\textsuperscript{∗} jame-shepherd@uiowa.edu
where $\bar{u}_{ijab}$ are antisymmetrized four-index electron repulsion integrals. Here, $i$ and $j$ refer to occupied orbitals, and $a$ and $b$ refer to virtual orbitals over some finite basis set. This energy expression is related to the transition structure factor recently coined by Grüneis and coworkers, $S_G = \sum_{ijab}(2t_{ijab} - t_{ijab})$, where the prime indicates that the sum is only taken over excitations that are related by the momentum transfer $G$ [6, 19, 24].

In the electron gas, all orbitals are plane waves: $\phi_j \propto \exp(\text{i}k_j \cdot \mathbf{r})$, where $k_j$ is a vector of the momentum quantum numbers in 3D, $\mathbf{r}$ is the electron coordinate, and $\text{i} = \sqrt{-1}$. A simple cubic three-dimensional box is used with electron numbers which correspond to closed-shell configurations at the Γ-point. We use the Ewald interaction (per convention) for calculations with periodic boundary conditions. This gives rise to matrix elements $v_{ijab}$ (electron repulsion integrals) that take the familiar form $1/G^2$, where $G$ is the magnitude of the momentum transfer during the $i,j$ to $a,b$ excitation, provided the excitation is allowed by momentum conservation (i.e., $k_a - k_i = k_j - k_b = G$). We explicitly calculate and include a Madelung term, $v_M$ in our calculations [25]. For example, at a Wigner-Seitz radius $r_s = 1.0$ and $N = 14$, $v_M = 0.7303$ [26]. A finite basis set for coupled cluster calculations is defined by the $M$ orbitals that lie inside a kinetic energy cutoff $E_{\text{cut},m} = \frac{1}{2}k^2_{\text{cut}}$.

The Hartree–Fock eigenvalues for the occupied and virtual orbitals are, following our previous work [23]:

$$\epsilon_p = \begin{cases} \frac{1}{2}k^2_p - \sum_{p \in \text{occ}} v_{pj} - v_M, & p \in \text{occ} \\ \frac{1}{2}k^2_p - \sum_{p \in \text{virt}} v_{pj}, & p \in \text{virt} \end{cases}$$ (2)

In these equations $\frac{1}{2}k^2_p$ is the kinetic energy of an electron in orbital $p$, and $v_{pj}$ is the exchange energy between orbitals $p$ and $j$. We note that the occupied orbitals are each lowered in energy by $v_M$, the Madelung constant. This represents the exchange interaction of an electron with itself. In the thermodynamic limit, $v_M \to 0$.

We now detail two recent developments which allow us to undertake this study. The first improves the speed of twist averaging for CCD. This development, referred to as connectivity twist averaging, identifies a special twist angle (which depends on the electron number $N$ and the basis set size $M$) that allows for a single CCD calculation to closely approximate (within 1 mHa/el) the twist-averaged CCD energy—reducing the number of CCD calculations that need to be run by a factor of 100 [27]. The second is the ability to extrapolate to the complete basis set and thermodynamic limits independently from one another [28], which we further adapt here.

**Connectivity twist averaging:**- Twist averaging is employed to reduce the fluctuations in the energy with respect to system size on converging to the thermodynamic limit [6, 9, 19, 29–35]. In general, this amounts to offsetting the grid of momenta by applying a twist angle, $k_s$, to each orbital such that: $\phi_j \propto \exp(\text{i} (k_j - k_s) \cdot \mathbf{r})$, and then averaging the correlation energy over all twists angles such that:

$$\langle E_{\text{corr}} \rangle_{k_s} = \frac{1}{N_s} \sum_{t=1}^{N_s} E_{\text{corr}}(k_{s_t})$$ (3)

where $N_s$ is the number of twist angles used in the twist averaging. Instead of calculating this costly sum explicitly, we instead use the connectivity twist averaging scheme. This method estimates a single twist angle for each calculation that has the same energy as the twist-averaged energy, allowing us to compute the twist-averaged energy using only one calculation [27]. The connectivity twist averaging scheme reduces the computational cost by a factor of approximately $N_s$, which is vital for our work here.

**Removing basis set error:**- Running calculations in a finite basis set of $M$ orbitals incurs an error referred to as basis set incompleteness error. Previous work has shown that, for a three-dimensional solid, this error decays as $1/M$ as $M \to \infty$ [18, 28, 36, 37]. In general, to study convergence to the thermodynamic limit, we must first eliminate basis set incompleteness error for each electron number $N$; then, we must find the way that these energies asymptote as $N \to \infty$. Performing this extrapolation in both $M$ and $N$ by brute force is impractical. We instead derive a correction for basis set incompleteness error that we may apply before analyzing convergence to the thermodynamic limit. Full technical details of this procedure are given in the Supplemental Material and summarized below.

Following Shepherd and Grüneis [14, 28], we use a fixed ratio between the energy cutoff for the virtual and occupied space for the correlated calculation: $f_{\text{cut}} = E_{\text{cut},M}/E_{\text{cut},N}$. This ratio is set to be consistent across a set of calculations that share the same density, but differ in electron number $N$. Then, a correction is derived from a smaller electron number (here, $N = 186$) extrapolated to the complete basis set limit, assuming the independence of the complete basis set and thermodynamic limits.

**Numerical comparison to exact results support an $N^{-1/3}$ power law:**- Figure 1 shows the finite-size error for two different densities over a range of electron numbers. To isolate the finite-size error, the difference between the complete basis set, finite-$N$ CCD energy and the exact thermodynamic limit energy was taken. For $r_s = 0.01$ and 0.1, RPA energies [17] first derived by Gellmann and Brueckner are known to be exact [16], and CCD can be expected to reproduce these numbers. The $r_s = 0.01$ calculations required us to use a minimal basis ($f_{\text{cut}} = \sqrt{2}$) to be able to afford calculations with larger electron numbers. The remainder used a larger basis set ($f_{\text{cut}} = 4$), which afforded a better residual basis set incompleteness error after correction. Since we are trying to confirm which power law predominates in the large $N$
Figure 1. Finite size errors for \( r_s = 0.01 \) and 0.1. The electron number ranges for each data set are \( N = 114 \) to \( N = 2042 \) for \( r_s = 0.01 \) and \( N = 114 \) to \( N = 730 \) for \( r_s = 0.1 \). The dashed line represent free fit exponents (i.e., \( \alpha \) in \( N^\alpha \)) of \(-0.36(5)\) and \(-0.39(3)\) for \( r_s = 0.01 \) and \( r_s = 0.1 \), respectively.

Figure 2. A wide range of \( r_s \) values have correlation energy convergence to the thermodynamic limit (TDL) which can be fit to \( E_{corr} = E_{TDL} + F N^{-1/3} \). In the left panel, we plot \((E_{corr} - E_{TDL})/F\). The black line is \((E_{corr} - E_{TDL})/F = N^{-1/3}\). Different \( r_s \) values converge at different rates, but settle down to an \( N^{-1/3} \) trend at large values of \( N \). In the right panel, the same analysis is shown for \( N^{-1} \).

For completeness, the full thermodynamic limit data we collected can be found in the Supplemental Material, where we further compare the \( N^{-1} \) and \( N^{-1/3} \) extrapolations.

**Analysis of the transition structure factor shows a cross-over between \( N^{-1/3} \) and \( N^{-1} \):** We have now shown a significant quantity of numerical data to support an asymptotic \( N^{-1/3} \) power law in the thermodynamic limit which should reasonably extend to the total energy in other wavefunction methods; however, our findings are at odds with a considerable body of literature and analysis which support an \( N^{-1} \) power law \([2, 8–11, 14, 25, 29, 38–49]\). If this slow asymptotic convergence is true exclusively for coupled cluster theory, it represents a significant challenge for applying this method to real solids; on the other hand, if it applies for all correlation energy calculations, it is a problem for a wide range of previous calculations that use an \( N^{-1} \) extrapolation. In order to explain this seeming contradiction, we need to analyze a property of the coupled cluster wavefunction called the transition structure factor, which was recently introduced by Grünneis and coworkers \([6, 19, 24]\). The transition structure factor \( S_G \) is defined by re-writing the correlation energy expression as: \( E_{corr} = \frac{1}{4} \sum_{ijkl} t_{ijkl} v_{ijkl} = \sum_G S_G V_G \), where \( V_G \) is the electron repulsion integral; both \( S_G \) and \( V_G \) are Fourier components labelled with a momentum \( G \). In the \( S_G = 0 \) limit, \( S_G \sim G^2 \) can be shown to give rise to the \( N^{-1} \) relationship derived in the literature \([11, 48, 50]\). In our penultimate section we explain the relationship between \( S_G \) and the true ground-state wavefunction.

In order to analyze how the \( N^{-1/3} \) power law emerges and crosses over to \( N^{-1} \), we start with fitting a functional form for \( S_G \). A convenient form of the function is:

\[
S_G \propto \frac{1}{(G^2 + \lambda^2)^{1/4}} G^2. \tag{4}
\]

Our inspiration for this fit is that it comes from a screened potential, \( \tilde{v} = e^{-\lambda r} \) \([51]\), and includes a \( G^2 \) term from the sums over the occupied manifold at small \( G \) \([50]\). This functional form fits the numerically-determined structure factor for the UEG. If the smallest \( G \) present in the calculation is given by \( G' \), then \( F(G') = \int_{\theta} G'^2 S_G V_G G^2 dG \) (where the factor \( G^2 \) comes from the G-space volume element in 3D) gives the finite-size error in the correlation energy. Since \( G' = \frac{2\pi}{L} \propto N^{-1/3} \), the \( G' \) derivative of \( F(G') \) gives the slope of the convergence into the TDL if a \( N^{-1/3} \) power law is assumed. The remaining FSE after extrapolation is:

\[
F(G') - G'^{d/dG'} F(G'). \tag{5}
\]

An analogous expression can be evaluated for an extrapolation based on \( G^3 \propto N^{-1} \).

Figure 3 shows the results of this analysis, taking \( \lambda = 1 \) (and ignoring energy prefactors for simplicity, yielding
arbitrary units). Two regimes can be seen on either side of the minimum in \( S(G') \). For \( G' \) values to the right of the minimum (i.e., when the system size is small), the \( N^{-1/3} \) extrapolation falls with increasing \( N \), and reaches the thermodynamic limit more quickly than the \( N^{-1} \) extrapolation. However, as \( G' \) decreases and the system size gets larger, the \( N^{-1/3} \) extrapolation eventually overshoots the true thermodynamic limit. For \( G' \) to the left of the minimum (i.e., when the system size is large), the \( N^{-1} \) extrapolation becomes closer to the thermodynamic limit, and the \( N^{-1/3} \) extrapolation rises with increasing \( N \). Although \( N^{-1} \) is clearly the correct extrapolation, at large \( G' \), it gives larger errors than the \( N^{-1/3} \) extrapolation. The way in which the \( N^{-1/3} \) extrapolation behaves with increasing \( N \) tells us which regime we are in. If the prediction from the \( N^{-1/3} \) extrapolation decreases with increasing \( N \), we are a long way off the true \( N^{-1} \) asymptote, and \( N^{-1/3} \) extrapolation gives the best result; however, if the \( N^{-1/3} \) extrapolation increases with increasing \( N \), then the \( N^{-1} \) extrapolation gives the best result.

**Practical consequences for calculations:-** These analytical results can also be seen in our real extrapolation data, shown in Fig. 4. In both \( r_s = 0.1 \) and \( r_s = 5.0 \), the \( N^{-1/3} \) extrapolated result first falls, and then rises again. This shows remarkable visual agreement with Fig. 3.

To evaluate the transferability of this model to real calculations, we found the \( G \) (and thus the \( N \)) corresponding to the minimum in the transition structure factor (and thus the cross-over point from the \( N^{-1/3} \) regime to the \( N^{-1} \) regime) for each density. For metallic densities between \( r_s = 5.0 \) and \( r_s = 20.0 \), the minimum was found at \( N = 100 \), and the onset of the best \( N^{-1} \) behaviors required calculations using \( 150 < N < 250 \). We can use these electron number ranges to transfer these predictions to real metals. For example, with a lithium unit cell, which is an \( s \)-block metal and thus a close analog to the UEG, we would expect to need \( k \)-point meshes finer than \( 5 \times 5 \times 5 \) for an \( N^{-1} \) extrapolation. Coarser meshes, such as \( 2 \times 2 \times 2 \) to \( 3 \times 3 \times 3 \), are better extrapolated with an \( N^{-1/3} \) power law.

**Relationship to the true ground-state wavefunction:-** The coupled cluster amplitudes, \( t_{ijab} \), are related to the true wavefunction: When coupled cluster theory is exact, these are the coefficients in the intermediate-normalized full configuration interaction (FCI) wavefunction, i.e., \( t_{ijab} \to c_{ijab} \) where \( c_{ijab} = \langle \Psi | a_i^\dagger a_j^\dagger a_\alpha a_\beta | \Psi_{HF} \rangle \); \( a \) are creation and annihilation operators and \( \Psi_{HF} \) is the Hartree–Fock (HF) wavefunction. The relationship \( t_{ijab} = c_{ijab} \) is valid in the high density limit; we believe it is good enough to discuss thermodynamic limit and basis set extrapolations for all densities. Thus, the transition structure factor is a property (albeit non-observable) of the exact ground-state wavefunction that is a subset of

**Concluding remarks:-** In summary, we have performed coupled cluster calculations on the high-density uniform electron gas with the intent to derive the power law governing the convergence of energies to the TDL. This was motivated by a recent dilemma that has arisen in the literature around whether an \( N^{-1/3} \) or an \( N^{-1} \) power law matches convergence of the correlation en-
ergy to the thermodynamic limit. By developing and applying a correction for basis set incompleteness error, complete-basis-set-corrected twist-averaged correlation energies show a clear $N^{-1/3}$ trend in their convergence to the thermodynamic limit. These results and theoretical observations support recent literature that has shown that this power law is obeyed for insulators and semiconductors treated in (finite) periodic Gaussian basis sets [7] and the spin-polarized gas [8]. However, when we examined the transition structure factor for the UEG, we found that our calculations were distant from the $N^{-1}$ asymptote, even at the large system sizes we were able to reach. We showed analytically that the observation of $N^{-1/3}$ is a result of using too small an electron number to resolve the minimum in the transition structure factor (in other words, insufficiently small $G$ to show the appropriate screening in the interaction), and that the power law reverts to a $N^{-1}$ behavior at large $N$. The observation of an $N^{-1/3}$ power law behavior is related to a property derived from the ground-state wavefunction in intermediate normalization and means that this result should generalize to correlation energy calculations across a broad range of methods.

We believe this conclusively explains recent observations related to $N^{-1/3}$ power laws [7], placing them in the context of the general expectation that correlation energies, as a component of the total energy, would follow an $N^{-1}$ power law [2, 8–11, 14, 25, 29, 38–49], (although $N^{-2/3}$ can also be proposed based on the exchange energy [9, 41]). There are, of course, more sophisticated methods to make corrections or models for how the total energy approaches the thermodynamic limit beyond extrapolation [9–11, 25, 38–40, 42, 44, 45, 48]. We argue that our work is important even in the context of these approaches, as it shows that coupled cluster theory has the same power law dependence at the doubles level as these other wavefunction methods.

We also discussed that the $N^{-1/3}$ extrapolation proves to be a powerful predictive tool for whether an $N^{-1}$ extrapolation would be valid in the absence of analyzing the transition structure factor directly. This is significant, because there are a large number of people now trying to use coupled cluster theory for materials design [1, 2, 4, 6, 7, 20–22, 24, 53–59]. Finally, we believe this is the first attempt to derive such a simple power law for the energy prior to the $N^{-1}$ asymptote that also signals which extrapolation regime is being simulated, and that this general observation is useful well beyond just the coupled cluster correlation energy.

**Acknowledgements:** We gratefully acknowledge the University of Iowa for funding and computer resources through the University of Iowa Informatics Initiative. We are also grateful to Neil Drummond, Matthew Foulkes, Andreas Grüneis, and Lubos Mitas for their emails and comments on this work. We thank Ali Alavi, David Ceperley, Richard Needs, and Pablo Lopez Rios for useful conversations on related topics. Code used throughout this was a locally modified version of a github repository used in previous work [18, 23].

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