Convergence of an $s$-Wave Calculation of the He Ground State

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ABSTRACT: The configuration interaction (CI) method using a large Laguerre basis restricted to $\ell = 0$ orbitals is applied to the calculation of the He ground state. The maximum number of orbitals included was 60. The numerical evidence suggests that the energy converges as $\Delta E_N \sim A/N^{7/2} + B/N^{8/2} + \cdots$, where $N$ is the number of Laguerre basis functions. The electron–electron $\delta$-function expectation converges as $\delta N \sim A/N^{8/2} + B/N^{9/2} + \cdots$, and the variational limit for the $\ell = 0$ basis is estimated as $0.1557637174(2) \ a_0^3$. It was seen that extrapolation of the energy to the variational limit is dependent on the basis dimension at which the exponent in the Laguerre basis was optimized. In effect, it may be best to choose a nonoptimal exponent if one wishes to extrapolate to the variational limit. An investigation of the natural orbital asymptotics revealed the energy converged as $\Delta E_N \sim A/N^4 + B/N^5 + \cdots$, while the electron–electron $\delta$-function expectation converged as $\delta N \sim A/N^4 + B/N^5 + \cdots$. The asymptotics of expectation values other than the energy showed fluctuations that depended on whether $N$ was even or odd. © 2006 Wiley Periodicals, Inc. Int J Quantum Chem 107: 907–920, 2007

Key words: helium; ground state; configuration interaction; Laguerre-type orbitals; basis set convergence

Introduction

There have been a number of studies of the convergence of the configuration interaction (CI) expansion of the helium ground state [1–8] following the pioneering work of Schwartz [9].

These studies have investigated the convergence of the energy with respect to the number of partial waves included in the wave function, and also with respect to the dimension of the radial basis.

It has been known since 1962 [9] that the energy converges slowly with respect to $J$, the maximum angular momentum of any orbital included in the CI expansion. In particular, the leading term to the energy increment is known to behave as
\[ \Delta E^j = \langle E \rangle^j - \langle E \rangle^{j-1} \sim \frac{A_E}{(j + \frac{1}{2})^4} \]  
\[ \Delta E^j = \frac{A_E}{(j + \frac{1}{2})^4} + \frac{B_E}{(j + \frac{3}{2})^6} + \frac{C_E}{(j + \frac{5}{2})^8} + \cdots, \]  
\[ \Delta E^N = \langle E \rangle^N - \langle E \rangle^{N-1} \sim \frac{A_E'}{N^4} + \frac{B_E'}{N^{10}} + \frac{C_E'}{N^{16}} + \cdots. \]

No expressions for \(C_E\) exist. The numerical values in Eqs. (3) and (4) are obtained from close to exact wave functions [2].

However, the convergence with respect to \(j\) represents only one aspect of the convergence problem. Just as important is the convergence with respect to the dimension of the radial basis \(N\), for a given \(j\). How do the increments to \(E\) with increasing \(N\) behave? In effect, what are the values of \(p\) and \(t\)? This aspect of the CI expansion is not as well understood as the convergence with \(J\), and there have been no studies equivalent in sophistication to those of Schwartz [9], Hill [2], and Kutzelnigg and collaborators [3, 6]. Some attention has been given to the radial convergence of the hydrogen atom in Gaussian basis sets [10]. The seminal investigation of Carroll and collaborators concluded that \(p \approx 6\) for a natural orbital (NO) basis [1, 11]. This result has been quite influential, and can be regarded as ultimately motivating the use of principal quantum number expansions to extrapolate energies to the infinite basis limit from correlation consistent basis sets [12]. More recently, Goldman [13] performed a regression analysis to give \(p \approx 5.7\) for a NO basis and \(p \approx 3.8\) for a Slater basis with a common exponent.

The radial basis sets used for the configuration interaction or many body perturbation theory treatments of atomic structure can be broadly divided into two classes. In the first class, one defines a box and a piecewise polynomial (e.g., a spline) is used to define the radial dependence of the wave function in the interior of the box. The properties of the radial basis are determined by the size of the box, the number of knot points, and where they are located. The other approach typically expands the wave function in terms of a basis of functions with a convenient analytic form, examples would be an evenly tempered set of Slater type orbitals (STOs) [3, 7] (this type of basis set is often optimized with respect to a couple of parameters used to defined a sequence of exponents) or a set of Laguerre-type orbitals (LTOs) [14–16].

The two most recent examples of these two approaches are the calculations by Decleva et al. [4] (B-splines) and Sims and Hagstrom [7] (Slater basis), which are the biggest calculations of their respective type. The B-spline calculation has given estimates of the \(\Delta E^j\) increments that are believed to be accurate to within \(10^{-8}\) hartree or better. One of the reasons this accuracy is possible is that \(\Delta E^j\) varies smoothly as the number of knot points is adjusted. This made it possible to obtain reasonable estimates of the infinite basis limit. Their estimate of the \(s\)-wave limit was accurate to better than \(10^{-9}\) hartree. Achieving this extreme level of accuracy was not possible when using the Slater basis [7], since linear dependence issues made it problematic to expand their radial basis to completeness. Indeed, resorting to REAL*24 arithmetic still resulted in an error of \(4 \times 10^{-6}\) hartree.

In some investigations of the convergence properties of the CI expansion for the helium atom [8] and mixed electron–positron systems [17], it became apparent that a better understanding of the issues that influence the convergence of the radial basis was desirable. For example, it was apparent that the dimension of the radial basis should be increased as \(J\) increases, to ensure the successive \(\Delta E^j\) increments are computed to the same relative accuracy [8, 17, 18]. In addition, it was readily apparent that extrapolation of the radial LTO basis to the \(N \to \infty\) limit was not straightforward.

In this work, we investigate the radial convergence of the CI expansion for a more manageable model of the helium atom with the orbitals restricted to the \(\ell = 0\) partial wave. The linear depen-
Table I

<table>
<thead>
<tr>
<th>(M)</th>
<th>(\lambda_M)</th>
<th>(\langle E \rangle^M)</th>
<th>(\langle E \rangle^{60})</th>
<th>(\langle \delta \rangle^M)</th>
<th>(\langle \delta \rangle^{60})</th>
</tr>
</thead>
<tbody>
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<td>10</td>
<td>3.07</td>
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<td>-2.879 028 727 964</td>
<td>-2.879 028 766 767</td>
<td>0.155 922 600 334</td>
</tr>
<tr>
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<td>-2.879 025 844 899</td>
<td>-2.879 028 767 761</td>
<td>0.155 789 354 524</td>
</tr>
<tr>
<td>30</td>
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<td>-2.879 028 766 601</td>
<td>-2.879 028 761 447</td>
<td>-2.879 028 767 762</td>
<td>0.155 772 304 341</td>
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<tr>
<td>40</td>
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<td>-2.879 028 766 467</td>
<td>-2.879 028 763 935</td>
<td>-2.879 028 767 763</td>
<td>0.155 767 637 040</td>
</tr>
<tr>
<td>50</td>
<td>9.57</td>
<td>-2.879 028 764 441</td>
<td>-2.879 028 765 118</td>
<td>-2.879 028 767 760</td>
<td>0.155 765 847 239</td>
</tr>
<tr>
<td>60</td>
<td>11.10</td>
<td>-2.879 028 765 650</td>
<td>-2.879 028 766 650</td>
<td>-2.879 028 766 761</td>
<td>0.155 765 002 122</td>
</tr>
</tbody>
</table>


The expectation value of the electron-electron \(\delta\) function (in \(a_0^2\)) is denoted as \(\langle \delta \rangle\). The data in the \(\langle E \rangle^M\) and \(\langle E \rangle^{60}\) columns are the energies (in hartree) with \(N = M\) and \(N = 60\) basis sets, respectively. The data in the \(\langle \delta \rangle^M\) and \(\langle \delta \rangle^{60}\) columns are obtained by doing an explicit calculation with \(N = 60\) and then adding in the \(60 \rightarrow \infty\) correction, assuming an \(A/N^\delta\) asymptotic form.

Convergence issues that are such a problem for a Slater basis are eliminated by choosing the radial basis to consist of LTOs [15, 19] (formally, the LTO basis spans the same space as the common exponent Slater basis, i.e., \(r^n \exp(-\lambda r)\)). We note in passing the previous work of Holøein [16], who also investigated the convergence of a (small) LTO basis for an \(s\)-wave model of helium. Initially, we examine the merits of using an LTO basis with the exponent optimized to the basis dimension. The nature of the asymptotic expansion for the energy increments is then deduced. Finally, the density matrix for our best wave function is diagonalized, and the convergence properties of the NO expansion are also determined. As part of this analysis, attention is also given to the convergence of the electron-electron coalescence matrix element, since it arises in calculations of the two-electron relativistic Darwin correction [20] and electron-positron annihilation [21].

**s-Wave Energy for Helium**

The nonrelativistic Hamiltonian for the \(1S^e\) ground state of helium

\[
H = -\sum_{i=1}^{N_e} \left( \frac{1}{2} \nabla_i^2 + 2 \frac{1}{r_i} + \frac{1}{r_{12}} \right),
\]

is diagonalized in a basis consisting of anti-symmetric products of single electron orbitals

\[
|\Psi; S = 0\rangle = \sum_{i,j} c_{ij} A_{12} \left| \begin{array}{c} 1 \mu \ 1 \mu \\ 2 \mu \end{array} \right| \langle 00 \rangle \phi_i(x_1) \phi_j(x_2).
\]
Calculations with \( N \) ranging from 1 to 60 have been performed for the six values of \( \lambda_M \) listed in Table I. The dimension of the Hamiltonian for the largest calculation was 1830. The quantities listed in the tables and the text are given in atomic units (a.u.). The most precise energy for the helium \( s \)-wave model is that of Goldman [13, 24], who used a basis written in terms of \( r_x, r_y \) coordinates to obtain an energy of \( E = -2.879028767319214 \) hartree.

### USE OF QUADRUPLE PRECISION ARITHMETIC

All the present calculations were performed with quadruple precision arithmetic. It was possible to get energies precise to only 13 significant digits for the largest calculations when double precision arithmetic was used. This was caused by round-off error gradually accumulating during the course of the rather extensive calculations, and the 13 digits appear to be the limit that can be achieved for double precision arithmetic (some experimentation revealed that the last 2 digits of the 15 double precision digits were sensitive to different Fortran compilers, and even the optimization options of those compilers). The analysis requires investigation of the energy differences of Eq. (5), and these energy differences can be rather small (e.g., \( E_{60} = 1.5 \times 10^{-10} \) hartree for the \( \lambda_{60} \) basis). The fluctuations caused by roundoff did have a noticeable impact on the parameters derived from these energy differences at large \( N \). These fluctuations were removed once quadruple precision arithmetic was adopted.

#### Simple Power Law Decay

All observable quantities can be defined symbolically as

\[
\langle X \rangle^N = \sum_{n=1}^{N} \Delta X^n,
\]

where \( \Delta X^n \) is the increment to the observable that occurs when the basis dimension is increased from \( n-1 \) to \( n \), e.g.,

\[
\Delta X^n = \langle X \rangle^n - \langle X \rangle^{n-1}.
\]

Hence, one can express the limiting value formally as

\[
\langle X \rangle \approx \frac{\sum_{n=1}^{N} \Delta X^n}{N^p},
\]

and then determine the value of \( p \) from two successive values of \( \Delta X \) using

\[
p = \frac{\ln(\Delta X^{N-1})}{\ln(N-1)}.
\]

Figure 1 plots the exponent derived from the energy increments for six different values of \( \lambda_M \).
The succession of curves show that $p_E$ tends to peak at values larger than 10 at an intermediate $N$ and then shows a tendency to decrease. The value at $N = 60$ was $p_E \approx 3.7$ for the most of the curves shown in Figure 1.

The salient point to be extracted from Figure 1 is that the value of $p_E$ for a given $\lambda_M$ at $N = M$ is quite different from the asymptotic value; e.g., the value of $p_E$ for the $\lambda_{20}$ curve is much larger at $N = 20$ than it is at $N = 60$. This is quite an annoying result. Ideally, one would like to perform the largest calculation with the exponent optimized for that dimension basis. Then the specific form of the power law decay would be estimated by analyzing the energies obtained from a series of slightly smaller calculations. This information would subsequently be used to estimate the energy or other expectation value in the variational limit. However, this is not possible, since the energy increments will not have achieved their asymptotic form.

Although there are problems in using an optimized exponent, it may still be possible to analyze a sequence of energies from a calculation with a nonoptimized exponent and thereby estimate the variational limit. Assuming that the increments obey Eq. (13), one can write

$$AX = N^p \Delta X^N,$$

and thus the $n > N$ remainder term

$$\sum_{n > N+1} \frac{A_X}{N^n} \approx \frac{A_X}{(p - 1)
\left(N + \frac{1}{2}\right)^{p-1}}$$

(16)

can be derived from $\langle X \rangle^{N-2}$, $\langle X \rangle^{N-1}$ and $\langle X \rangle^N$ [8, 17]. When this remainder was evaluated in this work, the first 10,000 terms of the sum over $n$ were computed explicitly. Then the approximate relation Eq. (16) was used.

Figure 2 shows the estimated variational limit as a function of $N$ for the $\lambda_1$ listed in Table I. An explicit calculation including $N$ LTOs was initially performed to determine $\langle E \rangle^N$. Then Eq. (16) was used to estimate the remainder and hence deduce the variational limit. The variational limits in Table I were extracted from the calculations with $N = 60$. The exact variational limit can be predicted to the 9th digit after the decimal point. The most inaccurate estimate of the variational limit is that from the $\lambda_{60}$ calculation. So the calculation that is explicitly optimized at $N = 60$ (i.e., with $\lambda_{60}$), and gives the best energy at $N = 60$, gives the worst estimate of the variational limit!

A CI calculation of the Li$^+$ ground state restricted to the $\ell = 0$ partial wave was also performed to check whether the conclusions above were peculiar to He. Once again, the exponent $p_E$ was approximately 3.7 at $N = 60$, and the convergence pattern for $N < M$ was distorted by optimizing of the exponent.

## $\delta$-Function Expectation Value

Part of the motivation for the present study is to gain a better understanding of how to perform CI calculations for mixed electron–positron systems. Apart from the energy, the next most important expectation value for a positronic system is the electron–positron annihilation rate [21]. The annihilation rate is proportional to the expectation of the electron–positron delta function, and has the inconvenient property that it is even more slowly convergent than the energy [15, 26]. Accordingly, the convergence of the electron–electron $\delta$-function is investigated using the methodology previously used for the energy. The only independent investigation of this quantity for an $s$-wave model of helium was by Halkier et al. [20], who obtained 0.155786 $\alpha_0^3$.

![Energy extrapolation](image-url)

**FIGURE 2.** Extrapolated $N \rightarrow \infty$ limit for the He ground-state energy for different values of $\lambda_M$. Exact $s$-wave energy is taken from the $J = 0$ calculation of Goldman [13].
Figure 3 tracks the behavior of the exponent $p_{\delta}$ derived from Eq. (14). It can be seen that $p_{\delta}$ achieves values exceeding 10 before it decreases to its asymptotic values. The present calculations give $p_{\delta} \approx 2.6$ at $N = 60$, although $p_{\delta}$ is still exhibiting a slow but steady decrease.

Although distortions in the convergence pattern are still present, they are less severe than the energy, since the successive $\Delta \delta^N$ increments are larger. As a rule, $p_{\delta}$ was at least 10% larger than 2.6 at $N = M$. A choice of $N \equiv (M + 10)$ would generally lead to $p_{\delta}$ in the asymptotic region.

Figure 4 shows the estimated variational limit of $\langle \delta \rangle^\infty$ as a function of $N$ for the six different values of $\lambda_M$ listed in Table I. An explicit calculation including $N$ LTOs was initially performed; Eq. (16) was then used to estimate the variational limit. A variational limit of $\langle \delta \rangle = 0.1557637174(2) \ a_0^3$ (see later discussion) was assumed for plotting purposes. The notable feature is that the $\lambda_{60}$ estimate of the limit at $N = 60$ is one of the least accurate.

**Closer Look at the Asymptotic Power Laws**

Figures 5 and 6 show the behavior of the $p_E$ and $p_{\delta}$ versus $1/\sqrt{N}$ for values of $N$ greater than 16. Curves are not shown for all the $\lambda_M$ exponents. In some cases, the values of $p_{\delta}$ did not fall within the plotting window.

The notable feature to be gleaned from both set of curves is the essentially linear behavior $p_{\delta}$ with respect to $1/\sqrt{N}$ for values of $N$ greater than 16 and...
a visual inspection suggests that the limiting exponents is $p_\delta = 2.5$. The purely visual evidence that the lowest-order term of $p_\delta$ is $O(N^{-1/2})$ is not as compelling as that for $p_\delta$, but, by analogy, this form has been assumed and subjected to extensive testing.

More substantial evidence is provided by a fit of the $p$ vs $N$ data to an inverse power series of the form

$$p = p_0 + \sum_{i=1}^{N_p} \frac{p_i}{\sqrt{N}}. \quad (17)$$

What we have done is fit $(N_p + 1)$ successive $p_\delta$ or $p_\delta$ values to Eq. (17) for the $\lambda_{10}$ data sequence. The results of those fits are given in Table II.

Using a 4- or 5-term fit (and 6-term fit in the case of $p_\delta$) results in limiting exponents very close to either 3.5 (for $p_\delta$) or 2.5 (for $p_\delta$). These estimates were also reasonably stable. For example, the value of $p_\delta$ for a 5-term fit for a data sequence terminating at $N = 50$ (as opposed to $N = 60$ in Table II) was 3.4970.

The validity of the series, Eq. (17) immediately suggests that the asymptotic forms for $\Delta E_N$ are

$$\Delta E_N = \frac{A_k}{N^{5/2}} + \frac{B_k}{N^{4/2}} + \frac{C_k}{N^{3/2}} + \cdots \quad (18)$$

(In Appendix A, it is demonstrated that an exponent variation of $p = p_\delta + B/\sqrt{N}$ arises from an inverse power series in $\Delta X_N$, with a leading term of $B/N^{\alpha}$, and with the power increasing by $\sqrt{N}$ for successive terms.) Although Eqs. (18) and (19) are best described as conjecture, the numerical evidence in support of the conjecture will be seen to be strong.

### TABLE II

<table>
<thead>
<tr>
<th>$N_p$</th>
<th>$p_0$</th>
<th>$p_1$</th>
<th>$A_{\delta}$</th>
<th>$\langle X \rangle^\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(E)</td>
<td>(\delta)</td>
</tr>
<tr>
<td>LTO data sequence: $\lambda_{10}$ basis</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3.4310</td>
<td>2.0481</td>
<td>$-0.00182$</td>
<td>$-2.8790287670519$</td>
</tr>
<tr>
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<td>$-0.00225$</td>
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<tr>
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<td>3.4978</td>
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<td>$-2.8790287673154$</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>(E)</td>
<td>(\delta)</td>
</tr>
<tr>
<td>NO data sequence</td>
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</tr>
<tr>
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<td>2.4975</td>
<td>0.6872</td>
<td>$-0.00562$</td>
<td>0.1557637156</td>
</tr>
<tr>
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<td>2.4989</td>
<td>0.6810</td>
<td>$-0.00559$</td>
<td>0.1557637174</td>
</tr>
</tbody>
</table>

* The results for the LTO data sequences were taken from the largest calculations for the $\lambda_{10}$ exponents. The results for the NO data sequences were extracted at $N = 20$, while those for the energy-optimized LTO sequence were determined at $N = 30$.

* Data obtained using a weighted average (as described in the text) due to fluctuations, depending on whether the $N$ was even or odd.
The applicability and utility of Eqs. (18) and (19) was tested by fitting these equations to \( \langle E \rangle_\lambda \) and \( \langle \delta \rangle_\lambda \) values and then using Eq. (16) to determine the \( N \to \infty \) limits for the individual terms. Asymptotic series with up to 5 term (i.e., \( N_p = 4 \)) were also investigated.

Figure 7 shows \( \langle E \rangle_\lambda \) for the \( \lambda_{10} \) basis, using the asymptotic series of different lengths to estimate the \( N \to \infty \) correction. It is notable that all the representations in Eq. (18) exhibit better convergence properties than Eq. (13), and the 6-term representation has the best convergence characteristics for \( N > 30 \). (It should be noted that the 3-, 4-, 5-, and 6-term extrapolations to \( \langle E \rangle_\lambda \) exhibited fluctuations of order \( 10^{-5} \) to \( 10^{-9} \) hartree when the calculation was performed in double precision arithmetic.) The increasingly better convergence characteristics as \( N_p \) increases is consistent with Eq. (18) as the asymptotic form describing the energy convergence with respect to a LTO basis. The estimated \( \langle E \rangle_\lambda \) limits at \( N = 60 \) for the various asymptotic expressions are given in Table II. The 6-term estimate was \( \langle E \rangle_\lambda = -2.87902876731920 \) hartree, which agrees with the value achieved by Goldman, i.e., \( E = -2.87902876731921 \) to \( 1 \times 10^{-14} \) hartree. The precision of the extrapolated value exceeds the precision of the raw \( \langle E \rangle_\lambda \) energy by a factor of 1,000,000! This improvement is best put into perspective by noting that the \( \lambda_{10} \) calculation would have to be extended to \( N \approx 10^6 \) to achieve the same level of precision.

This extreme accuracy is not reproduced if one uses other forms for the asymptotic series. For example, making the choice \( \Delta \beta_\lambda = A_\lambda / N^\delta_\lambda \) results in much poorer estimates of \( \langle E \rangle_\lambda \). Using a 4-term series for the \( \lambda_{10} \) basis set for this asymptotic series gave \( \langle E \rangle_\lambda = -2.879028802777 \) hartree, which is in error by \( 3.5 \times 10^{-7} \) hartree.

The ability to predict \( \langle E \rangle_\lambda \) accurately using Eq. (18) has been tested for other values of \( \lambda \). Making the choice \( \lambda = \lambda_{20} \) gave \( \langle E \rangle_\lambda = -2.87902876731919 \) hartree when the 6-term series was used to make the extrapolation. In summary, there is strong numerical evidence that Eq. (18) correctly describes the convergence of the energy with \( N \).

The slower convergence of the electron–electron \( \delta \)-function as \( \Delta \delta_\lambda = A / N^{5/2} \) means that the ability to extrapolate to the \( N \to \infty \) limit is even more important in obtaining accurate expectation values. Figure 8 shows the \( \langle \delta \rangle_\lambda \) estimates for the \( \lambda_{10} \) basis while using Eqs. (13) and (19) to describe the large \( N \) limiting behavior. It is noticed that the convergence improved as \( N_p \) increased as long as \( N \) was sufficiently large. Choosing \( N > (M + 10) \) would appear sufficient for 2-term or 3-term fits to Eq. (19). The specific numerical estimates of \( \langle \delta \rangle_\lambda \) for various extrapolations at \( N = 60 \) are given in Table II. The 5-term fit gave \( \langle \delta \rangle_\lambda = 0.1557637174 \) \( a_0 \). Given that...
The improvement in precision from the 5-term expansion is usually ordered in terms of decreasing ground-state occupancy. In its NO form, the wave function for a \(^1S^0\) state is written

\[
|\Psi\rangle = \sum_i d_i A_i \left( \frac{1}{2} \mu_i \nu_i \right) |00\rangle \phi_i(\mathbf{r}_1) \phi_i(\mathbf{r}_2). \tag{20}
\]

The NO expansion is usually ordered in terms of decreasing \(d_i\).

Table III gives \(\langle E\rangle\) and \(\langle \delta \rangle\) for the sequence of increasingly larger NO expansions. For these calculations, the generated NOs were added successively and \(\langle E\rangle^N\) and \(\langle \delta \rangle^N\) computed once the Hamiltonian was diagonalized. The calculations were taken up to a maximum NO expansion length of 20. The LTO basis of dimension 70 was not large enough to give a precise representation of the NOs beyond that point. The energies in the table are expected to be accurate estimates of the “exact” NO energy for all digits, with the possible exception of the last two. The energies in Table III are slightly lower than the previous tabulations of the s-wave NO energies by Carroll et al. [1] and Goldman [13]. We treat the NOs merely as a particularly optimal set of orbitals to input into a CI calculation. So, unlike Carroll et al. and Goldman, the configuration space is not restricted to include only \(\phi_i(\mathbf{r}_1) \phi_i(\mathbf{r}_2)\)-type configurations. It should be noted that we have also done some calculations using the pure NO configuration space and, when this is done, the energies agree with those of Carroll et al. and Goldman to all digits. The \(\langle \delta \rangle^N\) values in Table III are expected to approximate those of the “exact” basis to about 10 digits.

Figure 9 shows the variation of \(p_E\) and \(p_\delta\) versus \(1/N\) for a sequence of increasingly larger NO calculations up to \(N = 20\). The visual inspection of the \(p_E\) vs \(1/N\) curve immediately suggests that \(p_E = 6 + A/N + \cdots\) and \(p_\delta = 4 + A/N + \cdots\). The supposition has been confirmed by doing fits to the asymptotic form

\[
p = p_0 + \sum_{i=1}^{N_p} \frac{p_i}{N_i}, \tag{21}
\]

for increasingly larger values of \(N_p\). The results for \(p_0\) and \(p_1\) are given in Table II. The present calculations give \(p_0\) values of 5.992, 5.997, and 5.996 (the 5-term series, which gave \(p_0 = 5.967\), is likely to be more susceptible to small imperfections in the NOs). A least-squares fit to the function \(p_E = p_0 + \)

### Table III

<table>
<thead>
<tr>
<th>(N)</th>
<th>(\langle E\rangle^N)</th>
<th>(\langle \delta \rangle^N)</th>
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was obtained by weighted average, e.g.,

The oscil-

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varies by more than 10% between

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is the principal quantum number of the NO. The

are defined and the convergence pattern was quite irreg-

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oscillated between 3.94 and 4.06, depending on whether

was even or odd (the oscillations in

were more marked). The oscillations became larger for the 4-term fit; here, it was found that the

typically flipped between 3.4 and 4.6. The actual values given in Table II were obtained by weighted average, e.g.,

were

not the “exact” NO energies, but merely very good estimates of these energies. Also, use of the NO basis inevitably means a more complicated calculation, and so it is more likely to be affected by round-off errors and discretization errors in the numerical quadratures.
The coefficient of the leading order term for

was

This dependence is consistent with earlier work of Halkier et al. [20], who found that the variation of

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principal quantum number of the NO. When analyzing this set of data, it was discovered that there were regular fluctuations in the derived parameters as a function of

, as the analysis was made more sophisticated. When the 3-term approximation to

was used, the value of

was overestimated by more than 10% between

and

This level of agreement is acceptable given the fact that Carroll et al. actually use a slightly different

functional form (and do not allow for higher-order terms) and extract the value of

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for a single-term asymptotic formula). The precision of the Carroll et al. calculation is also less than that of the present calculation (they obtained

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strongly oscillating plot of $p_r$ vs $1/N$ observed in Figure 9. The oscillations disappear if $(r)^N$ for only even $N$ (or only odd $N$) are used in a slightly modified version of Eq. (14), and one finds the leading order term in $\Delta r^N$ is $O(N^{-6})$. It should be noted that similar even–odd fluctuations have also been observed in high-precision calculations using correlated basis sets [12, 28, 29].

The asymptotic behavior of the NO configuration coefficients was also determined. The coefficients are the $d_i$ in Eq. (20). Assuming that the $d_i$ scale as an inverse power series, $d_i = A_i^2/\tilde{r}_{\text{NO}}$ gives

$$p_{\text{NO}} = \ln \left( \frac{d_i^N}{d_{i-1}} \right) / \ln \left( \frac{i}{i-1} \right).$$

(24)

A fit of $p$ to $i$ using the formula

$$p_{\text{NO}} = p_0 + \frac{p_1}{i} + \frac{p_2}{i^2},$$

(25)

gave values of $p_0$ that ranged from 3.998 to 4.003 for successive fits to the three previous values for $i$-values between 12 and 20 for the $\lambda_{60}$ basis. It was found that

$$d_i = \frac{0.362}{i^4} + \frac{0.589}{i^3} + \frac{1.492}{i^2},$$

(26)

at $i = 20$. Carroll et al. [1] obtained the result $d_i \approx [0.271/(i - 1/2)]^{0.5}$. 

### Convergence of an Optimized Basis

In this section, the convergence properties of the LTO basis, which is energy optimized at each $N$, are studied. Developing the sequence of exponents $\lambda_M$ that gave the lowest energy for a LTO basis of dimension $M$ was tedious. Defining $s(\delta)$ as the differences in $\langle E \rangle$ and $\delta(s)$ arising from an imprecisely known $\lambda_M$, one has the relations

$$\delta(E) = A(\delta \lambda)^2$$

(27)

$$\delta(s) = B(\delta \lambda).$$

(28)

The quadratic dependence of $\delta(E)$ with respect to $\delta \lambda$ does make it easier to generate the sequence of $\langle E \rangle^N$ values. But this quadratic dependence on $\delta \lambda$ does make it harder to determine $\lambda_M$, since the energy only depends weakly on $\lambda$ in the vicinity of the minimum. Since $\delta(\delta)$ depends linearly on $\delta \lambda$, any imprecision in $\lambda_M$ impacts the precision of the $\delta(\delta)^N$ sequence more severely.

Some specific data can be used to put this in perspective. The $\lambda_M$ for $M = 1, \ldots, 30$ have been determined to a precision for $10^{-6}$ for the calculations reported in this section. These gave an energy that was accurate to $10^{-18}$ hartree for the $M = 15$ calculation, but $\delta(\delta)$ was only known to a precision of $10^{-11}$ $\delta \lambda$. Determination of $\langle E \rangle$ to a precision of $10^{-15}$ $\delta \lambda$ would require fixing $\lambda_M$ with an accuracy of $10^{-10}$, which would necessitate an energy given to a accuracy of $10^{-26}$ hartree.

The behavior of $p_E$ and $p_\delta$ vs $N$ was sufficiently complicated that an initial least-squares fit to the equation $p = p_0 + p_1/N^r$ was performed for $N \in [18, 30]$. The results of the fit gave

$$p_E = 5.6562 + \frac{15.69}{N^{2.7236}}$$

(29)

$$p_\delta = 3.8093 - \frac{0.3832}{N^{0.5018}}.$$  

(30)

The distinctive aspect about the fit is the difference in the leading terms of the inverse power series for $p_E$ and $p_\delta$. Figure 10 shows that variation of $p_E$ for the optimized LTO basis as a function of $1/N^{2.7236}$ up to $N = 30$. The plot of $p_\delta$ is tending to curl up for
the smallest values of $1/N^{2.7326}$ because it is not linear in $1/N^{2.7326}$.

Another notable feature of Figure 10 were the oscillations in $p_E$ and $p_\delta$ for even and odd values of $N$. Oscillations in $p_\delta$ were previously seen for the NO sequence, but the $p_\delta$ oscillations in Figure 10 are more pronounced than those in Figure 9. Some of the values in Table II were given using the 3-point averaging used previously for the NO sequence.

The asymptotic analysis to determine the variational limits were performed with the following series

$$\Delta E^N = \frac{A_E}{N^{5.6562}} + \frac{B_E}{N^{8.3888}} \quad (31)$$

$$\Delta \delta^N = \frac{A_\delta}{N^{3.8093}} + \frac{B_\delta}{N^{4.3531}}. \quad (32)$$

The results of the analysis are given in Table II. The energy is predicted with an accuracy of $10^{-10}$ hartree, while $(\delta)^N$ is given to an accuracy of $10^{-8}$ a.u. Equations (31) and (32) were not worth extending to include more terms. The power of the next term in Eq. (31) is not obvious (refer to Appendix A), and the oscillations in $p_\delta$ to a certain extent negate the value of extending Eq. (32) to include additional terms (even if we knew what those terms were!).

### Summary and Conclusions

The results of a sequence of CI calculations of the He ground state with an $\ell = 0$ basis have been presented. This can be regarded as the simplest model of a real atom that has a correlation cusp. The energy dependence of the LTO basis was $\Delta E \approx O(N^{-7/2})$. This rather slow convergence rate can be improved by fitting a succession of $(E)^N$ values to the inverse power series $A^f = A_E/N^{-7/2} + B_E/N^{-8/2} + \cdots$ and estimating the $N \to \infty$ limit. It ultimately proved possible, after adopting quadruple precision arithmetic, to reproduce the known energy in this model to an accuracy of $1 \times 10^{-14}$ hartree. The specific choice of the asymptotic series should be regarded as conjecture supported by numerical evidence. More definite proof would require the calculations to be extended to $N > 100$. The common exponent of the LTO basis should not be chosen to optimize the energy for the largest calculation, since this results in a distorted convergence pattern. In effect, optimizing the LTO exponent for N LTOs, and then using the $(N - 3), (N - 2), (N - 1)$, and $N$ energies to determine the coefficients of a 3-term expansion to Eq. (18) will give an inaccurate estimate of the energy correction needed to achieve the variational limit. Any extrapolation would seem to require that $N$ (the number of LTOs) should exceed $M$ (the basis dimension at which $\lambda$ was optimized) by about 10 or more. This conclusion holds for both the energy and electron–electron $\delta$-function. The very slow $O(1/N^{5/2})$ convergence of $(\delta)$ was also circumvented by the use of the $N \to \infty$ corrections.

The examinations of the convergence rate for an NO basis set revealed a faster convergence. The NO basis converged as $O(N^{-5.6562})$ with the next term being $O(N^{-7})$. The present determinations of the convergence rates are more rigorous than those of Carroll et al. [1]. One surprising result was the slight even–odd oscillation in the convergence of the interelectronic $\delta$-function. Examination of the $(r)$ revealed noticeable even–odd oscillations in $p_\delta$. The presence of these ripples could complicate determination of the variational limit of expectation values other than the energy. It was possible to extrapolate the energy of a 20-orbital NO basis to the variational limit with an accuracy of $\sim 10^{-12}$ hartree.

The convergence rate of the optimized LTO basis was $O(N^{-5.6562})$ with the next term being $O(N^{-8.3888})$. The degree of uncertainty in both of these exponents is much larger than for the fixed $\lambda$ LTO sequence or the NO sequence. The extremely tedious nature of the $\lambda$ optimization, combined with the lack of knowledge about the nature of the asymptotic series beyond the first two terms, make this extrapolation a less attractive proposition. The noticeable even–odd oscillation in $p_\delta$ and even $p_E$ further render the method even more unattractive. The implications of this behavior are not confined to the present work. For example, it is likely that correlated exponential basis sets composed of functions with

$$\xi(r_1, r_2, r_{12}) = r_1^{\mu} r_2^{\nu} \exp(-\lambda r_1) \exp(-\lambda r_2) \quad (33)$$

could also exhibit complicated convergence patterns, since $\lambda$ is often energy optimized as the basis dimension is increased in size [30]. Consequently, it would not be surprising for estimates of the $N \to \infty$ energy correction for variational calculations on systems using a Hylleraas basis to be unreliable. For example, Yan and Ho [31] have estimated the variational limit in a high-precision calculation of PsH,
using a Hylleraas-type basis. Their estimated energy correction for the PsH ground-state energy (only $9.6 \times 10^{-8}$ hartree) was too small by at least a factor of 3 [32].

One of the main motivations for the present study was to gain insight into solving the problems associated with the very slow convergence of CI calculations for mixed electron–positron systems [15, 17, 23, 33]. In effect, the problem is to determine the complete basis set limit [12, 34, 35] for these exotic systems. The slow $O(N^{-7/2})$ convergence of the energy for an LTO basis set is greatly improved by the adoption of extrapolation schemes. Using the $N = 10$ energy for the $\lambda_{10}$ basis and the best extrapolation of the $N = 60$ calculation in Table II as two reference points, one deduces an effective convergence rate of $O(N^{-10})$. The penalty associated with the use of the extrapolation formulae is the necessity to use quadruple precision arithmetic if 3 or more terms are retained in the inverse power series (note that a 3-term series for $\Delta E_N$ was numerically stable in double precision arithmetic). The need to use the quadruple precision arithmetic is caused by the very small size of the $\Delta E_N$ increments and the impact of round-off error on the fit to the inverse power series. One somewhat ironic feature is that it is necessary to use a basis that is not energy optimized so that the extrapolation to the variational limit can be done reliably.

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References


Appendix A: Analysis of the $p$-Dependence

Let us demonstrate that an asymptotic series

$$\Delta X^N = \frac{A}{N^p} + \frac{B}{N^{p+1}} \ldots = \frac{A}{N^p} \left( 1 + \frac{C}{N} \right) \ldots \quad (A1)$$

(with $C = B/A$) leads to $p = q + F/N^l$ when $p$ is defined from successive $\Delta X^N$ increments by

$$p = \ln \left( \frac{\Delta X^{N-1}}{\Delta X^N} \right) / \ln \left( \frac{N}{N-1} \right). \quad (A2)$$
Substituting $\Delta X^N$ and $\Delta X^{N-1}$ from Eq. (A1) gives

$$p = \ln \left( \frac{A}{(N-1)^2} \left[ 1 + \frac{B}{(N-1)} \right] \right) / \ln \left( \frac{N}{N-1} \right). \quad (A3)$$

The logarithm in the numerator can be split into two terms:

$$\ln \left( \frac{\Delta X^{N-1}}{\Delta X^{N}} \right) = q \ln \left( \frac{N}{N-1} \right) + \ln \left[ 1 + \frac{C}{(N-1)^2} \right] \left( 1 - \frac{C}{N^2 + C^2} \right). \quad (A4)$$

The first term conveniently cancels with the denominator to give $q$. The argument of the second term can be expanded

$$1 + \frac{C}{(N-1)^2} = \left( 1 + \frac{C}{N^2} + \frac{tC}{N^{t+1}} \right) \left( 1 - \frac{C}{N^2 + C^2} \right)$$

$$= 1 + \frac{tC}{N^{t+1}} + \cdots. \quad (A5)$$

Using $\ln(1 + x) \approx x$ leads to

$$\ln \left( 1 + \frac{C}{(N-1)^2} \right) \approx \frac{tC}{N^{t+1}}. \quad (A6)$$

The denominator is simplified using $\ln(N/(N-1)) = \ln(1 + 1/(N-1)) \approx 1/N$, to finally give

$$p = q + \frac{tC}{N^t} + \cdots. \quad (A7)$$

as required. If Eq. (A1) has successive terms where the power increments by $t = 1$ or $t = 1/2$ indefinitely, this leads to a corresponding series, Eq. (A7), that also have powers that respectively increment by 1 or 1/2 indefinitely. This is not necessarily true for arbitrary $t$ in Eq. (A1).

### Appendix B: Scaling of the 2-Electron Integrals

The most time-consuming part of the calculation was the generation of the electron–electron and annihilation matrix elements. However, the expense of this was greatly reduced by generating an initial set of integrals for a given $\lambda$, and then using a scaling factor to generate the integral lists for other values of $\lambda$.

The basic integral that has to be done is

$$R(n_a, n_b, n_c, n_d, \lambda) = \int \int dx_1 dx_2 N_d(\lambda) N_b(\lambda)$$

$$\times N_c(\lambda) N_d(\lambda) f_a(x_1) f_b(x_2)$$

$$\times V(x_1, x_2) f_c(x_1) f_d(x_2). \quad (B1)$$

All integrals can be defined in terms of $R(n_a, n_b, n_c, n_d, \lambda = 1)$. Consider the integral (B1), and make the transformation $\lambda r = u$. Therefore, $r_1 = u_1/\lambda$ and $r_2 = u_2/\lambda$. Similarly, $dr_1 = du_1/\lambda$ and $dr_2 = du_2/\lambda$ and therefore

$$R(n_a, n_b, n_c, n_d, \lambda) = \frac{1}{\lambda^2} \int \int du_1 du_2 N_a(\lambda) N_b(\lambda)$$

$$\times N_c(\lambda) N_d(\lambda) f_a(u_1) f_b(u_2)$$

$$\times V(r_1, r_2) f_c(u_1) f_d(u_2). \quad (B2)$$

From Eq. (9), $N_d(\lambda) = \lambda^{1/2} N_d(\lambda = 1)$, so

$$R(n_a, n_b, n_c, n_d, \lambda) = \int \int du_1 du_2 N_a(1) N_b(1)$$

$$\times N_c(1) N_d(1) f_a(u_1) f_b(u_2)$$

$$\times V(r_1, r_2) f_c(u_1) f_d(u_2). \quad (B3)$$

The scaling for the electron–electron repulsion integral is $|r_1 - r_2|^{-1} = \lambda |u_1 - u_2|^{-1}$. Hence,

$$R(n_a, n_b, n_c, n_d, \lambda) = \lambda R(n_a, n_b, n_c, n_d, 1), \quad (B4)$$

for the electron–electron integral. When the operator is the $\delta$-function, one uses the result $\delta(r_1 - r_2) = \lambda \delta(u_1 - u_2)$ to give

$$R(n_a, n_b, n_c, n_d, \lambda) = \lambda R(n_a, n_b, n_c, n_d, 1). \quad (B5)$$