Convergence of the partial wave expansion of the He ground state

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The Configuration Interaction (CI) method using a very large Laguerre orbital basis is applied to the calculation of the He ground state. The largest calculations included a minimum of 35 radial orbitals for each \( \ell \) ranging from 0 to 12 resulting in basis sets in excess of 400 orbitals. The convergence of the energy and electron-electron \( \delta \)-function with respect to \( J \) (the maximum angular momenta of the orbitals included in the CI expansion) were investigated in detail. Extrapolations to the limit of infinite in angular momentum using expansions of the type \( \Delta X_J = A_X (J + \frac{1}{2})^{-p} + B_X (J + \frac{1}{2})^{-p-1} + \ldots \), gave an energy accurate to \( 10^{-7} \) Hartree and a value of \( \langle \delta \rangle \) accurate to about 0.5%. Improved estimates of \( \langle E \rangle \) and \( \langle \delta \rangle \), accurate to \( 10^{-8} \) Hartree and 0.01% respectively, were obtained when extrapolations to an infinite radial basis were done prior to the determination of the \( J \to \infty \) limit. Round-off errors were the main impediment to achieving even higher precision since determination of the radial and angular limits required the manipulation of very small energy and \( \delta \) differences.

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I. INTRODUCTION

Large configuration interaction (CI) calculations of the helium ground state are performed here in order to more precisely elucidate the convergence properties of the CI expansion for this atom. The general properties of the CI expansion have been known since the seminal work of Schwartz [1], which provided the underlying foundation for the later analytic and computational investigations [2, 3, 4, 5, 6, 7, 8]. The CI expansion using single center orbitals is slowly convergent 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 expected to behave at high \( J \) as:

\[
\Delta E^J = \langle E \rangle^J - \langle E \rangle^{J-1} \approx \frac{A_E}{(J + \frac{1}{2})^4}.
\]

Although there have been a number of very large CI calculations performed on helium, all of the earlier calculations using analytic basis sets treat the higher \( J \) contributions to the energy with less precision than the low \( J \) contributions. Typically, the number of radial orbitals for the high \( \ell \) are smaller than the number of low \( \ell \). The justification for this is that the high \( \ell \) partial waves make a smaller contribution to the energy and other expectation values of than the low \( \ell \) orbitals. At first sight this approach would seem reasonable for obtaining estimates of the total energy. However, this approach does lead to problems when studying the convergence properties of CI expansion itself. Here it is necessary to ensure that the successive contributions to the energy are obtained with the same relative accuracy and this can hardly be guaranteed with a radial basis that decreases in size as \( \ell \) increases. Indeed, the evidence suggests that the dimension of the radial basis should be increased as \( J \) increases if the relative accuracy of the energy is to be maintained [9, 10].

The convergence problems present in CI calculations of atomic and molecular structure are also present in a much more severe manner in CI calculations of the positron-atom problem. The CI method has recently been applied to the study of positronium atoms (electronically stable states consisting of a positron bound to an atom) [11, 12, 13, 14, 15, 16, 17, 18, 19, 20] and also to positron-atom scattering states [21, 22, 23]. The attractive electron-positron interaction leads to the formation of a Ps cluster (i.e. something akin to a positronium atom) in the outer valence region of the atom [12, 14, 24, 25].

The accurate representation of a Ps cluster using only single particle orbitals centered on the nucleus requires the inclusion of orbitals with much higher angular momenta than a roughly equivalent electron-only calculation [11, 12, 26, 27]. In the most extreme case so far considered, namely \( e^+ + \text{Li} \), a calculation with \( J = 30 \) was required before the energy had decreased enough to establish binding. Given that helium is described as slowly convergent [11], one struggles to find an adjective that could characterize the convergence properties of...
positional and positronic systems!

The two most important expectation values for positional systems are the energy, and the rate for electron-positron annihilation. The annihilation rate, which is proportional to the expectation of the electron-positron $\delta$-function, has the inconvenient property that it is even more slowly convergent than the energy with respect to orbital angular momentum. One has successive increments decreasing at high $J$ according to $\delta$:

\[ \Delta \Gamma^J = (\Gamma)^J - (\Gamma)^{J-1} \approx \frac{A_J}{(J + \frac{1}{2})^2}, \quad (2) \]

To put this in perspective, it would take a calculation with $J \approx 250$ to recover 99% of the PsH annihilation rate $\delta$. In addition to the slow convergence with $J$, the $\delta$-function operator also exhibits very slow convergence with respect to the radial basis $\delta$.

In the present work, large basis CI calculations of the He ground state are performed in order to more exactly understand the convergence of the CI expansion. Since the properties of the He ground state are known to high precision it is a very useful laboratory system with which to test methods of extrapolating the radial and partial wave expansions to completion. The insights obtained from helium should then be applicable to positronic systems and also possibly give additional guidance about how to approach purely electronic systems. Besides looking at the energy, the convergence of the CI expansion of the electron-electron $\delta$-function expectation value is also studied due to its relation with the electron-positron annihilation operator (which is also a $\delta$-function). It should be noted that the $\delta$-function operator also appears in the Breit-Pauli relativistic correction as the two-body Darwin interaction $\delta$. The present work builds on an earlier investigation that studied the convergence of the radial basis in a simplified model of the helium atom which only included $l = 0$ orbitals $\delta$.

II. THE CI METHOD AND CONVERGENCE PROPERTIES

The CI wave function in a single-center basis is a linear combination of anti-symmetrised two-electron states with the usual Clebsch-Gordan coupling coefficients,

\[ | \Psi ; LS \rangle = \sum_{i,j} c_{ij} A_{ij} \langle \ell_i m_i \ell_j m_j | L M_L \rangle \langle \frac{1}{2} \mu_i \frac{1}{2} | \ell_j | \frac{1}{2} \mu_j | S M_S \rangle \times \phi_i(r_1) \phi_j(r_2). \quad (3) \]

The functions $\phi(r)$ are single electron orbitals written as a product of a radial function and a spherical harmonic:

\[ \phi(r) = P(r) Y_{\ell m}(\hat{r}). \quad (4) \]

All observable quantities can be defined symbolically as

\[ \langle X \rangle^J = \sum_{L=0}^{J} \Delta X^L, \quad (5) \]

where $\Delta X^J$ is the increment to the observable that occurs when the maximum orbital angular momentum is increased from $J - 1$ to $J$, e.g.

\[ \Delta X^J = \langle X \rangle^J - \langle X \rangle^{J-1}. \quad (6) \]

Hence, one can write formally

\[ \langle X \rangle^\infty = \langle X \rangle^J + \sum_{L=J+1}^{\infty} \Delta X^L. \quad (7) \]

The first term on the right hand side will be determined by explicit computation while the second term must be estimated. The problem confronting all single center calculations is that part of $\langle X \rangle^\infty$ arises from terms with $\ell$-values that are not included in the largest explicit calculation. The two expectation values that were investigated were that of the energy $\langle E \rangle^\infty$ and the electron-electron $\delta$-function, $\langle \delta \rangle^\infty = \langle \delta(r_1 - r_2) \rangle^\infty$. For helium, terms with $\ell > 2$ contribute only 0.033% of the total energy. For purely electronic systems these higher $\ell$ terms make a small (but slowly convergent) correction to the total energy and other expectation values.

The extrapolation schemes used later in this paper have their basis in the work of Schwartz $\delta$, Hill $\delta$ and Kutzelnigg and associates $\delta$. Analytic work indicates that the energy increments are given by

\[ \Delta E^J = \frac{A_E}{(J + \frac{1}{2})^2} + \frac{B_E}{(J + \frac{1}{2})^6} + \frac{C_E}{(J + \frac{1}{2})^{10}} + \ldots \quad (8) \]

where

\[ A_E = -6\pi^2 \int |\Psi(r, r, 0)|^2 r^5 dr = -0.074226 \quad (9) \]

\[ B_E = -\frac{48\pi}{5} \int |\Psi(r, r, 0)|^2 r^6 dr = -0.030989 \quad (10) \]

given a two-body wave function $\Psi(r_1, r_2, (r_1 - r_2))$. No expressions for $C_E$ have been presented. At large $J$, one expects the energy increments to be well described by eq. $\delta$.

For the $\delta$-function one can write

\[ \Delta \delta^J = \frac{A_\delta}{(J + \frac{1}{2})^2} + \frac{B_\delta}{(J + \frac{1}{2})^6} + \frac{C_\delta}{(J + \frac{1}{2})^{10}} + \ldots \quad (11) \]

where $A_\delta$ is believed $\delta$ to be

\[ A_\delta = -4\pi \int |\Psi(r, r, 0)|^2 r^3 dr = -0.04287 \quad (12) \]

(Ottochofski and Kutzelnigg give a formula similar to this for the leading relativistic contribution to the energy of two-electron atoms. We have assumed the slow
III. THE PRESENT CI CALCULATIONS

The present calculations use a basis set consisting of Laguerre Type Orbitals (LTOs) \[12, 15, 28, 32\]. The LTOs of a given \(\ell\) are chosen to have a common exponential parameter which means they are automatically orthogonal. Hence, the basis can be expanded toward completeness without causing any linear dependence problems. The CI basis can be characterized by the index \(J\), the maximum orbital angular momentum of any single electron orbital included in the expansion of the wave function. It should be noted that all matrix elements were evaluated using gaussian quadrature even though the basis functions have an analytical form \[15\].

Three sets of calculations have been performed for the He ground state. In the first set, there were 20 LTOs per \(\ell\) with the largest calculation including orbitals up to \(\ell = 12\). The LTO exponents for a given \(\ell\) were the same and the values of the exponents were optimized in a quasi-perturbative fashion. The exponents for \(\ell = 0, 1\) and 2 orbitals were optimized in a CI calculation with all 60 orbitals. The exponents for \(\ell > 2\) were optimized separately for each \(\ell\) with CI calculations that also included the \(\ell = 0, 1, 2\) orbitals. Once the exponents were optimized, a sequence of calculations to give the \(\langle E\rangle_J^J\) and \(\langle \delta \rangle_J^J\) for successive \(J\) were carried out. The basis is denoted the 20LTO basis and the results of the calculations with this basis are reported in Table II.

The second set of calculations were much larger. Here there were 35 LTOs per \(\ell\) with the exception of \(\ell = 0\) and 1 where respectively 44 and 36 LTOs were used respectively. The orbital exponents were optimized for each \(\ell\) in a manner similar to that described above and the calculations were taken to \(J = 12\). A total of 465 single electron orbitals were included in the largest calculation, which required the diagonalization of a hamiltonian matrix of dimension 8586. This calculation was an example of a very large explicit calculation. The basis is denoted the 35LTO basis and the results of the calculations with this basis are reported in Table III.

The idea behind the third calculation was to exploit extrapolation techniques to estimate the variational limit for each partial wave. A sequence of calculations with 32, 33, 34 and 35 LTOs per \(\ell\) was done for a basis that was defined with the same exponential parameters as the 20LTO calculation. The number of basis functions were varied so that all partial waves had the same basis dimension. Optimizing the LTO basis for the largest radial basis has been shown to result in distortions in the convergence pattern with respect to the number of radial basis functions. This can be avoided if the basis is optimized in a basis that has at least 10 fewer LTOs per \(\ell\) than the active calculation \[30\]. The variational limit for the radial basis can be estimated by fitting the increments to \(\langle E\rangle\) and \(\langle \delta \rangle\) to the inverse series \[30\].

\[
\Delta E^N = \frac{a_1}{N^{5/2}} + \frac{b_1}{N^{5/2}} + \frac{c_1}{N^{9/2}} + \ldots \tag{13}
\]

\[
\Delta \delta^N = \frac{a_2}{N^{5/2}} + \frac{b_2}{N^{5/2}} + \frac{c_2}{N^{9/2}} + \ldots \tag{14}
\]

It is possible to estimate the \(N \to \infty\) limits for the radial basis once the \(a_1, b_1, c_1, \ldots\) coefficients have been determined. A two-term series was used for both eqs. \[13\] and \[14\]. It would have been preferable to use three-term series but the impact of round-off error rendered this impractical. The basis for this set of calculations is denoted the 35LTO\(^\ast\) basis, while the basis including the \(N \to \infty\) correction is termed the 35LTO\(^\ast\)\(\infty\) basis. The energies and expectation values for these two calculations are listed in Table III.

IV. INVESTIGATION OF THE PARTIAL WAVE SEQUENCE

The validity of these results can be tested by examination of the energy increments of large CI calculations.
TABLE I: Results of the present set of 20LTO and 35LTO CI calculations of He giving the energy \( \langle E \rangle^J \) and delta-function \( \langle \delta \rangle^J \) expectation values as a function of \( J \) (all energies are given in Hartree, while \( \langle \delta \rangle^J \) is in \( a_0^{-3} \)). The total number of electron orbitals is \( N_{\text{orb}} \) while the LTO exponent for \( \ell = J \) is listed in the \( \lambda \) column. The results in the three \( \langle E \rangle^\infty \) rows use inverse power series of different length to estimate the \( J \to \infty \) extrapolation.

| \( J \) | \( \lambda \) | \( N_{\text{orb}} \) | \( \langle E \rangle^J \) | \( \langle \delta \rangle^J \) | \( \langle E \rangle^J \) | \( \langle \delta \rangle^J \) |
|---|---|---|---|---|---|---|
| 0 | 4.8 | 20 | -2.879 028 507 | 0.155 789 346 | 8.6 | 44 |
| 1 | 7.8 | 40 | -2.900 515 873 | 0.128 501 540 | 11.6 | 80 |
| 2 | 10.1 | 60 | -2.902 766 378 | 0.120 923 186 | 14.4 | 115 |
| 3 | 12.1 | 80 | -2.903 512 527 | 0.117 264 315 | 17.2 | 150 |
| 4 | 14.0 | 100 | -2.903 517 973 | 0.115 104 494 | 19.2 | 185 |
| 5 | 15.5 | 120 | -2.903 605 022 | 0.113 681 991 | 21.2 | 220 |
| 6 | 17.1 | 140 | -2.903 649 142 | 0.112 676 622 | 22.8 | 255 |
| 7 | 18.7 | 160 | -2.903 673 821 | 0.111 930 245 | 24.8 | 290 |
| 8 | 20.1 | 180 | -2.903 688 677 | 0.111 355 981 | 26.5 | 325 |
| 9 | 21.5 | 200 | -2.903 698 142 | 0.110 901 652 | 28.0 | 360 |
| 10 | 22.9 | 220 | -2.903 704 451 | 0.110 534 186 | 29.5 | 395 |
| 11 | 24.2 | 240 | -2.903 708 815 | 0.110 231 642 | 31.0 | 430 |
| 12 | 25.5 | 260 | -2.903 711 927 | 0.109 978 870 | 32.5 | 465 |

Exact \[31\] -2.903 724 377 034 | 0.106 345 371

\( \langle E \rangle^\infty \) and \( \langle \delta \rangle^\infty \) extrapolations

Method 1 -2.903 723 421 | 0.106 943
Method 2 -2.903 723 252 | 0.107 178
Method 3 -2.903 723 205 | 0.107 334

FIG. 1: The exponents \( p_E \) as a function of \( J \) for the different CI calculations of the He ground state energy as listed in Table III.

of helium. Besides the present calculations, data from a number of previous CI calculations have been used.

Table III gives the energies of the present 35LTO and 35LTO\(^*\) basis sets, along with the SH, CSM\(_{\omega}^\infty\), SO\(_{\infty}^\infty\) and DLV calculations. These same sets of data are also presented as energy differences between consecutive calculations \( \Delta E^J \). The energies of the SH calculation, which used the even-tempered STO basis, are consistently the worst, and are \( 3 \times 10^{-7} \) Hartree larger than the 35LTO calculation at \( J = 12 \). Even though CSM\(_{\omega}^\infty\) does attempt to achieve the variational limit for each \( J \), in reality it is only about as good as the 35LTO calculation. Indeed for \( J > 7 \), the CSM\(_{\omega}^\infty\) values of \( \Delta E^J \) were smaller than those of the 35LTO calculation. The present 35LTO\(^*\), SO\(_{\infty}^\infty\) and DLV calculations are in agreement to \( 10^{-8} \) Hartree (or better) for \( J \leq 4 \). This is expected, since all three calculations are large and use extrapolation techniques to achieve the variational limit. The energy difference between the 35LTO and 35LTO\(^*\) energies gives an indication of the incompleteness of the 35LTO basis and by \( J = 12 \) the difference is \( 0.96 \times 10^{-7} \) Hartree.

The good agreement between the 35LTO\(^*\), SO\(_{\infty}^\infty\) and DLV energies is not present for \( J \geq 5 \). Although the 35LTO\(^*\) and SO\(_{\infty}^\infty\) energies generally agree at the level of \( 10^{-8} \) Hartree, it is seen the DLV \( \Delta E^J \) increments are larger than these two other calculations. For example, DLV give \( \Delta E^5 = 8.737 \times 10^{-5} \) Hartree which is about \( 2 \times 10^{-7} \) Hartree larger than the 35LTO\(^*\) and SO\(_{\infty}^\infty\) increments. It has also been noticed that DLV do overstate the accuracy of their calculation, they assert an accuracy...
assume a power law decay of the form

$$\langle E \rangle^J_j \approx \frac{A_E}{(J + \frac{1}{2})^p}$$ \hspace{2cm} (15)

and determine the value of $p$ for a succession of three $\langle X \rangle^J$ values using

$$p = \ln \left( \frac{\Delta X^{J-1}}{\Delta X^J} \right) / \ln \left( \frac{J + \frac{1}{2}}{J - \frac{1}{2}} \right)$$ \hspace{2cm} (16)

The exponent derived from the energy increments is $p_E$ while the exponent derived from the $\delta$-function increments is $p_\delta$. One expects $p_E \to 4$ and $p_\delta \to 2$ as $J \to \infty$, in agreement with eqs. (13) and (14).

A useful way to scrutinize the partial wave series is to assume a power law decay of the form

$$\langle E \rangle \approx e^{-J \delta}$$

while the exponent derived from the energy increments is $p_E$, and this energy is in error by $1.3 \times 10^{-6}$ Hartree! The values of $p_E$ for the He energies presented in Table III are plotted in Figure 1 as a function of $J$. One of the noticeable features of Figure 1 are the irregularities in some of the calculations, e.g. the SO$_\infty$, CSM$_\infty$ and 35LTO$_\infty$ calculations. The fluctuations in the present 35LTO$_\infty$ curve are due to the impact of round-off error on the radial extrapolations. The determination of the coefficients in eq. (13) involves the subtraction of the energies for calculations that differ by a single LTO. The resulting energy differences are very small and therefore are susceptible to the essentially random errors resulting from round-off that gradually accumulate during the course of the computations. The irregularities in the CSM$_\infty$ and SO$_\infty$ curves are a consequence of the number of digits at which the energies were published [2, 12]. Plots of $p_E$ vs $J$ were examined (but not plotted in Figure 1) for some calculations that used an STO basis set. These plots of $p_E$ showed much larger fluctuations than any of the calculations depicted in Figure 1.

The smaller 20LTO and CSM$_\infty$ calculations had plots of $p_E$ vs $J$ that tended to level out at $p_E \approx 4.05$. Indeed, the tendency for 20LTO trajectory to curve up indicates that the successive $\Delta E^J$ increments are decreasing too quickly at the higher $J$ values. The larger SO$_\infty$, DLV, 35LTO and 35LTO$_\infty$ calculations have $p_E$ versus $J$ trajectories that steadily decrease with increasing $J$ and appear to be approaching the expected limit of $p_E \approx 4.05$ although this is obscured somewhat for the SO$_\infty$ and 35LTO$_\infty$ curves. It will be demonstrated later that the behavior of the 20LTO and CSM$_\infty$ curves is due to slower convergence of the radial basis at high $J$.

The tendency for $p_E$ to approach the limiting value of 4 from above is a consequence of the fact that the $A_E$ of $7.8 \times 10^{-8}$ Hartree. However, this accuracy is based on a calculation which gives $\langle E \rangle^3 = -2.903319811$ Hartree (2nd column of Table IV of [3]), and this energy is in error by $1.3 \times 10^{-6}$ Hartree!

### Table II: Results of the 35LTO$^*$ and 35LTO$^*_\infty$ CI calculations of He for the $\langle E \rangle^J$ and $\langle \delta \rangle^J$ expectation values as a function of $J$ (all energies are given in Hartree, while $\langle \delta \rangle^J$ is in $a_0^3$). The total number of electron orbitals is $N_{\text{orb}}$ while the LTO exponent for $\ell = J$ is listed in the $\lambda$ column. The results in the three $\langle E \rangle^\infty$ rows use inverse power series of different lengths to estimate the $J \to \infty$ extrapolation.

| $J$ | $\lambda$ | $N_{\text{orb}}$ | $\langle E \rangle^J$ | $\langle \delta \rangle^J$ | $\langle E \rangle^\infty$ | $\langle \delta \rangle^\infty$ |
|-----|-----|-----|-----|-----|-----|-----|
| 0  | 4.8 | 35  | -2.879 028 716 | 0.155 774 273 | -2.879 028 766 | 0.155 763 804 |
| 1  | 7.8 | 70  | -2.900 516 172 | 0.128 472 171 | -2.900 516 246 | 0.128 451 020 |
| 2  | 10.1| 105 | -2.902 766 757 | 0.120 878 722 | -2.902 766 852 | 0.120 845 876 |
| 3  | 12.1| 140 | -2.903 320 971 | 0.117 204 759 | -2.903 321 084 | 0.117 159 843 |
| 4  | 14.0| 175 | -2.903 518 472 | 0.115 030 202 | -2.903 518 016 | 0.115 070 165 |
| 5  | 15.5| 210 | -2.903 605 568 | 0.113 593 010 | -2.903 605 016 | 0.113 523 543 |
| 6  | 17.1| 245 | -2.903 649 729 | 0.112 573 360 | -2.903 649 882 | 0.112 534 534 |
| 7  | 18.7| 280 | -2.903 674 443 | 0.111 813 216 | -2.903 674 609 | 0.111 719 047 |
| 8  | 20.1| 315 | -2.903 689 330 | 0.111 225 558 | -2.903 689 506 | 0.111 119 165 |
| 9  | 21.5| 350 | -2.903 698 823 | 0.110 758 273 | -2.903 699 007 | 0.110 639 719 |
| 10 | 22.9| 385 | -2.903 705 157 | 0.110 378 300 | -2.903 705 349 | 0.110 247 727 |
| 11 | 24.2| 420 | -2.903 709 543 | 0.110 063 722 | -2.903 709 741 | 0.110 921 236 |
| 12 | 25.5| 455 | -2.903 712 675 | 0.109 799 333 | -2.903 712 882 | 0.109 645 079 |

| Method | $\langle E \rangle^\infty$ and $\langle \delta \rangle^\infty$ Extrapolations |
|--------|--------------------------------------------------|
| Method 1| -2.903 724 243 | 0.106 881 |
|        | -2.903 724 123 | 0.106 757 |
|        | -2.903 724 243 | 0.106 881 |

The smaller 20LTO and CSM$_\infty$ calculations had plots of $p_E$ vs $J$ that tended to level out at $p_E \approx 4.05$. Indeed, the tendency for 20LTO trajectory to curve up indicates that the successive $\Delta E^J$ increments are decreasing too quickly at the higher $J$ values. The larger SO$_\infty$, DLV, 35LTO and 35LTO$_\infty$ calculations have $p_E$ versus $J$ trajectories that steadily decrease with increasing $J$ and appear to be approaching the expected limit of $p_E = 4$. Although this is obscured somewhat for the SO$_\infty$ and 35LTO$_\infty$ curves. It will be demonstrated later that the behavior of the 20LTO and CSM$_\infty$ curves is due to slower convergence of the radial basis at high $J$.

The tendency for $p_E$ to approach the limiting value of 4 from above is a consequence of the fact that the $A_E$ of $7.8 \times 10^{-8}$ Hartree. However, this accuracy is based on a calculation which gives $\langle E \rangle^3 = -2.903319811$ Hartree (2nd column of Table IV of [3]), and this energy is in error by $1.3 \times 10^{-6}$ Hartree!
and $B_E$ coefficients of eq. (3) have the same sign. The coefficients $A_E$ and $B_E$ are derived from second and third order perturbation theory respectively (3) and have the same sign due to repulsive nature of the electron-electron interaction. One surmises that a mixed electron-positron system, with its attractive electron-positron interaction should have $p_{E} \rightarrow 4$ from below, and this is indeed the case (10, 11). 

The incremental exponent for the $\delta$-function, $p_{\delta}$, is shown in Figure 2 for the 20LTO, 35LTO and 35LTO$_{\infty}$ basis sets. It should be noted that the values of $p_{\delta}$ were sensitive to the precision of the calculation. Originally, the diagonalization of the Hamiltonian was performed using the Davidson algorithm (33). However, this method could not give $\delta$-function expectation values to better than 8 significant figures (irrespective of the convergence tolerance for the energy). This led to noticeable fluctuations in the $p_{\delta}$ versus $J$ plot. The diagonalization was subsequently performed using the EISPACK libraries, reducing the size of the fluctuations. The trajectories of the 20LTO and 35LTO calculations do not appear to be approaching the $p_{\delta} \rightarrow 2$ limit as $J \rightarrow \infty$. The 20LTO curve has a $p_{\delta}$ trajectory that diverges from 2 for $J > 6$ while the 35LTO curve diverges from 2 for $J > 7$. The 20LTO basis gives $p_{\delta} = 2.155$ at $J = 12$ while the 35LTO basis gives $p_{\delta} = 2.064$ at this $J$ value.

However, the plot of $p_{\delta}$ based on the 35LTO$_{\infty}$ sequence does exhibit the correct qualitative behavior as $J$ increases. The $N \rightarrow \infty$ corrections have a larger impact on $\langle \delta \rangle^J$ than on $\langle E \rangle^J$ since the former converges as $O(N^{-5/2})$ while the latter converges as $O(N^{-7/2})$. The $J = 12$ value of $p_{\delta}$ was 2.008.

The behavior exhibited in Figures 1 and 2 can be attributed to the convergence of the radial basis. A larger radial basis is required to predict successive $\Delta E^J$ increments as $J$ increases. The ratios

$$R_E^J = \frac{(\Delta E^J)_{35}}{(\Delta E^J)_{20}}$$  (17)
FIG. 2: The exponents \( p_\delta \) as a function of \( J \) for the LTO calculations of the He ground state \( \langle \delta \rangle \).

FIG. 3: The 35LTO:20LTO and 35LTO\( ^* \):20LTO ratios of the increments to \( \langle E \rangle \) and \( \langle \delta \rangle \) as a function of \( J \) for the calculations of the He ground state.

FIG. 4: The extrapolated \( J \to \infty \) limit for the He ground state energy \( \langle E \rangle^\infty \) using three different methods to complete the partial wave series. The input \( \langle E \rangle^J \) upon which the extrapolations were based were those of the 35LTO and the smoothed 35LTO\( ^* \) calculations. The horizontal line shows the exact helium energy [31].

increase in \( \Delta \delta^{12} \) between the 20LTO and 35LTO\( ^* \) calculations. The corresponding increase in \( \Delta E^{12} \) was only 0.8%. This extra sensitivity of \( \langle \delta \rangle^J \) is something we have noticed in calculations of positron annihilation rates in positron-atom systems [16, 17, 21, 22], even though explicit mention of this point has not been made.

B. Smoothing of the 35LTO\( ^* \) energies

It is apparent from Figures 1 and 4 that including the radial extrapolations has resulted in irregularities appearing in the 35LTO\( ^* \) energy sequence. These irregularities are of order \( 10^{-9} \) Hartree at \( J = 12 \) and should be removed before the \( J \to \infty \) corrections are determined.

Examination of Figure 3 suggested that \( (R_E^J - 1) \propto J^s \) as a function of \( J \). Accordingly a fit of \( (R_E^J - 1) = \left( \frac{\Delta E^{20LTO}}{\Delta E^{35LTO}} - 1 \right) \) to a \( G + H \times J^s \) functional form was performed over the \( J \in [5, 12] \) interval. An adjustment to the \( \langle E \rangle^J \) energy sequence was made once \( G \), \( H \) and \( s \) were fixed. The values of \( s \) was approximately \( s \approx 2.85 \).

The 35LTO\( ^* \) values of \( \langle E \rangle \) and \( \Delta E \) given in Table III are those of the smoothed energy sequence. The largest change to any of the energies was \( 2 \times 10^{-9} \) Hartree.

C. Extrapolation of the partial wave series

One of the major aims of this paper was to determine whether it is possible to extract the \( J \to \infty \) limit from a
finite sequence of calculations. To this end, fits of inverse power series of different lengths are made to sequences of \((X)^j\) data, and then those inverse power series are summed to infinity.

Equations 8 and 11 are the working equations. Fits are performed retaining just the leading order term (Method 1), the first two terms (Method 2), and the first three terms (Method 3) of these series. The fits of these equations use the minimum information necessary. So, method 1, which only retains the first \(A_E\) term of eq. 8, only requires two successive values of \((E)^j\) to determine \(A_E\). Three successive values of \((X)^j\) are used to determine \(A_X\) and \(B_X\) when the two leading terms of eq. 8 or eq. 11 are used. Four successive values of \((X)^j\) are used to determine \(A_X\), \(B_X\) and \(C_X\) when the three leading terms of eq. 8 or eq. 11 are used. The fits to determine \(A_X\) and/or \(B_X\) and/or \(C_X\) can be done to different sequences of \(J\) values as a self-consistency to check that the two-term fits to the \(J = 8, 9, 10\) or \(J = 10, 11, 12\) sets of \((X)^j\) give answers that are numerically close.

Once the coefficients of the inverse power series have been determined, the \(J \to \infty\) contribution is determined by a two-step procedure. Firstly, the series 8 and 11 are summed explicitly up to \(J + 200\). The remainder from \(\geq J + 201\) is determined using the approximate result:

\[
\sum_{L=J+1}^{\infty} \frac{1}{(L+\frac{1}{2})^p} \approx \frac{1}{(p-1)(J+1)^{p-1}}. \tag{18}
\]

Eq. 18 can be regarded as an approximation to the \(\int_{J+1}^{\infty} \frac{1}{(L+\frac{1}{2})^p} dL\) integral using the mid-point rule. This approximation is accurate to 0.1% for \(p = 2\) and \(J = 7\).

Figures 3 and 4 show the behavior of the extrapolated \(\langle E \rangle\) and \(\langle \delta \rangle\) as a function of \(J\). Tables II and III gives estimates of \(\langle E \rangle^\infty\) and \(\langle \delta \rangle^\infty\) using the calculated values at the largest possible \(J\) values to determine the \(J \to \infty\) corrections.

Figure 4 shows that the quality of the 35LTO energy extrapolation using method 1 is inferior to methods 2 and 3 which give \(\langle E \rangle^\infty\) energies in agreement which each other at the \(10^{-9}\) Hartree level for \(J \geq 8\). However, using the 35LTO energies in conjunction with methods 2 and 3 gives \(\langle E \rangle\) values that are too large by about \(10^{-7}\) Hartree. This is a consequence of using a large but not quite complete radial basis. The use of the 35LTO energies results in an energy limit that is an order of magnitude more precise than those of the 35LTO basis. Using method 2 for the \(J = 10, 11, 12\) 35LTO\(\infty\) energies gave \(\langle E \rangle^\infty = -2.903 724 378\) Hartree. An energy that is in error by \(10^{-7}\) Hartree. The \(J \to \infty\) corrections were only made using method 2 since the more sophisticated method 3 is more sensitive to the imperfections of the smoothed data sets.

The smoothed energy sequence is probably not a perfect reproduction of the actual sequence and there is a tendency for the \(\langle E \rangle^\infty\) limit to be more negative than the exact energy. The method 3 estimate of \(\langle E \rangle^\infty\), at \(J = 12\), namely -2.903 724 384 Hartree, is about \(10^{-8}\) more negative than the exact energy. A similar level of accuracy was achieved in the earlier SO\(\infty\) calculation, their estimate of the energy in the \(J \to \infty\) limit was -2.903 724 39 Hartree.

The difficulties in obtaining sub 0.1% accuracy in \(\langle \delta \rangle^\infty\) for the 35LTO sequence are readily apparent from Figure 5. As one increases \(J\), the estimates of \(\langle \delta \rangle^\infty\) also increase and the discrepancy with the accurate value of Drake 31 gets larger. The ultimate accuracy achievable for the 35LTO basis is between 0.1 and 0.5%. The apparent superiority of method 1 for the 35LTO basis arises because errors resulting from a finite dimension radial basis act to partially cancel errors that arise from this least sophisticated \(J \to \infty\) extrapolation.

However, usage of the 35LTO\(\infty\) sequence permitted a much more accurate extrapolation to the \(J \to \infty\) limit. The 35LTO\(\infty\) basis gives estimates of \(\langle \delta \rangle^\infty\) that are two orders of magnitude more precise. The method 2 extrapolation was only \(6 \times 10^{-6} a_0^3\) larger than the exact value 31. While the radial extrapolations did introduce fluctuations into the \(\langle \delta \rangle^\infty\) values, the relative size of the individual \(\Delta \delta^j\) increments were much larger than the \(\Delta E^j\) increments and thus did not lead to fluctuations in \(\langle \delta \rangle^\infty\) as long as method 2 was used for the angular extrapolations. However, the use of method 3 did result in fluctuations of order \(10^{-5} a_0^3\) in \(\langle \delta \rangle^\infty\) so is not depicted in Figure 5.

D. The coefficients of the inverse power series

The coefficients of the asymptotic forms, 8 and 11, are known \textit{a-priori} from eqs. 9, 10 and 12. Estimates of these parameters are also obtained during the
FIG. 6: The value of $A_E$ as extracted from sequences of $(E)^J$ data. The horizontal line shows the value of from eq. 9, namely -0.074226. Estimates of $A_E$ from Method 2 are drawn with dashed lines while estimates of $A_E$ from Method 3 are drawn with solid lines. The DLV data analyzed here was solely from their Table IV of Ref. 5, since this avoided the discontinuity at $J = 4$ and gave a smooth curve.

FIG. 7: The value of $A_4$ as extracted from sequences of $(\delta)^J$ data. The horizontal line shows the value of eq. 10, namely $A_4 = -0.04287$.

since it has been demonstrated that the 35LTO $\Delta E^J$ are increasingly underestimated as $J$ increases. It would therefore be hoped that values of $A^J_E$ extracted from the 35LTO* would show better convergence to the expected limit as $J$ increases. This expectation has only been partly realized, there are indications that $A_E$ may be converging to the correct value, but the application of smoothing has probably introduced a systematic bias that resulted in a tendency to overestimate the magnitude of $A_E$.

Figure 7 shows the values $A_4$ as obtained from the 35LTO basis using Methods 1, 2 and 3 as a function of $J$. None of the calculations using the 35LTO basis resulted in an $A_4$ vs $J$ curve that approached the correct value as $J$ increased. This is another manifestation of the very slow convergence of $(\delta)^J$ with respect to the dimension of the radial basis set. There was a significant improvement when $A_4$ was extracted from the 35LTO* sequence using method 2. In this case, $A_4$ does appear to be converging to the expected value of $-0.04287$ and at $J = 12$ one obtains $A_4 = -0.04282$.

The small irregularities in the 35LTO* $(\delta)^J$ sequence resulted in irregularities in $A_4$ when using the more sophisticated and sensitive method 3 fit; so this was not depicted in Figure 7. It is also worth noting that $A_3$ was also subject to irregularities of $\pm 2\%$ when the Davidson method was used to diagonalize the Hamiltonian and generate the ground state wave function.

V. SUMMARY AND CONCLUSIONS

Results of a set of very large CI calculations of the He ground state have been presented. The largest explicit CI fit of the inverse power series to a set of $(E)^J$ or $(\delta)^J$. An ideal consistency check would be estimates of $A_E$ and $A_\delta$ that steadily approached -0.074226 and -0.04287 as $J$ increased and as the number of terms included in eqs. 8 and 11 increased. Unfortunately, this has not yet been achieved. The least squares analysis of the CSM$_\infty$ energies gave $A_E = -0.0740$ and $B_E = 0.0317$ 2. However, this value of $A_E$ is only achieved when using $(E)^J$ for $J \in [5, 8]$. The very large calculations of DLV reported $A_E = -0.07415$ and $B_E = 0.0317$ 2. However, a cursory examination of Figure 6 which depicts values of $A_E$ obtained from three successive $(E)^J$ energies demonstrates that their value of $A_E$ is not converging to -0.074226 with increasing $J$. Applying the more sophisticated 3-term inverse power series to the DLV energies leads to an $A_E$ that exhibits a 4% variation between $J = 6$ and $J = 13$.

Figure 6 also shows the variation in $A_E$ when fitting the 35LTO and 35LTO* energy sequences to eq. 8. Fits were performed with both methods 2 and 3 for the 35LTO energy sets, and only with method 2 (for reasons discussed earlier) to the 35LTO* sequence. The $A_E$ coefficients for a given method are computed using the minimum range of $J$ values that permitted the unique determination of the coefficients.

Application of method 2 to the 35LTO data reveals that $A_E$ achieves a minimum value of $A_E = -0.07413$ at $J = 7$ before increasing at larger $J$. Application of method 3 results in values of $A_E$ that are clearly not approaching the correct value. This should be expected...
These fluctuations are magnified by an order of magnitude in the radial extrapolation were about 2 \times 10^{-9} Hartree. Improved accuracy required the use of extrapolations in the radial basis set to get an estimate of the variational limit for \( (E) \). This permitted the He ground state energy to be predicted to better than 10^{-8} Hartree, an improvement of a factor of 1000 over the largest explicit calculation. The main impediments to more refined predictions of the He ground state are those due to round-off errors. Estimating the coefficients of the inverse power series involves manipulating very small energy differences which will be sensitive to round-off errors. The fluctuations in the radial extrapolation were about 2 \times 10^{-9} Hartree at \( J = 12 \). While this in itself is not that bad, these fluctuations are magnified by an order of magnitude when the angular momentum extrapolation is then done. The impact of the fluctuations was somewhat mitigated by the introduction of a smoothing procedure, at the cost of introducing a small systematic error.

The prediction of the electron-electron \( \delta \)-function was considerably more difficult due to the \( O(L + \frac{1}{2})^2 \) convergence. In this case, the explicit calculation was accurate to 3% at \( J = 12 \). Application of the inverse power series (Method 2) to include higher \( J \) contributions improved the accuracy to 0.3%. The main reason for the low accuracy was the slow convergence with respect to the number of radial basis functions. The relative accuracy of successive \( \Delta \delta J \) increments decreases as \( J \) increases if the number of radial basis functions per \( \ell \) is kept the same. Once again, extrapolating the radial basis to the variational limit lead to an improved prediction of \( \langle \delta \rangle \). The best CI estimate of \( \langle \delta \rangle = 0.106341 a_0^2 \) was within 0.01% of the close to exact variational estimate [31]. The extrapolations of \( \langle \delta \rangle \) were less susceptible to round-off error simply because the \( \Delta \delta J \) increments were larger.

While the use of extrapolations did improve the quality of the calculation, the full potential of the method has not been realized due to round-off error. The radial matrix elements are evaluated with gaussian quadratures and the achievable precision for the larger calculations is about 10^{-12} Hartree. This accuracy could be improved by the either the development of a convenient analytic form for the electron-electron matrix elements or the usage of quadruple precision arithmetic. This would then permit the use of inverse power series with more terms leading to improved radial and angular extrapolations. For example, an accuracy of 10^{-14} Hartree was achievable for a CI calculation restricted to \( \ell = 0 \) orbitals [31].

These results have implications for the prediction of the annihilation rate of positronic atoms from single-center CI type calculations [10]. Some sort of extrapolation in \( J \) is needed to determine the energy and more particularly the annihilation rate. One way to minimize the impact of the extrapolation in \( J \) is to run the calculation to the highest possible angular momentum. However, the high \( J \) parts of the annihilation rate will tend to be increasingly underestimated as \( J \) increases unless accurate estimates of the radial variational limit can be made. Since this can now be achieved for a Laguerre basis [31], it eminently conceivable that estimates of the annihilation rate at better than 0.1% accuracies will be achievable for single-center basis sets.

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11

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