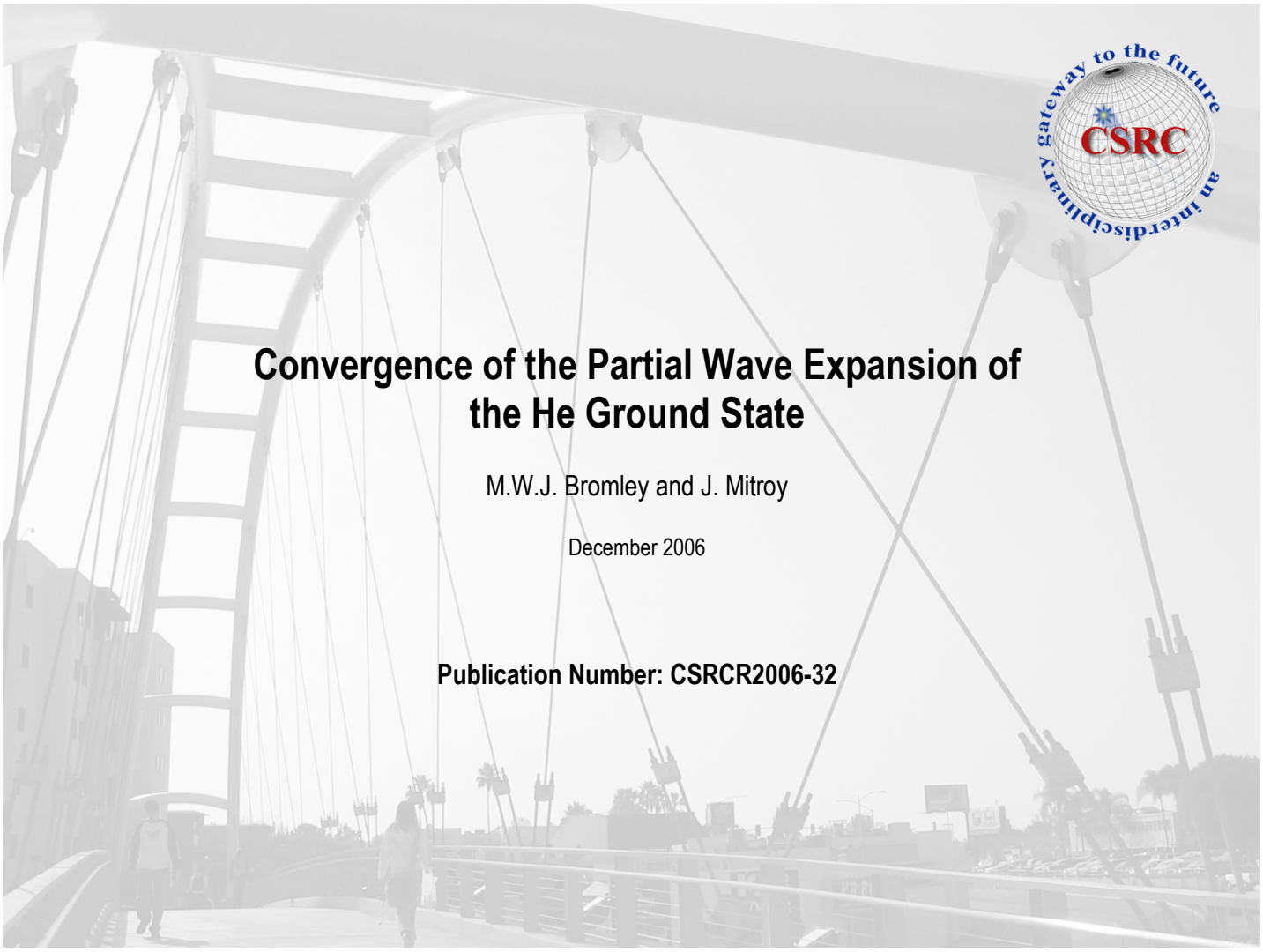

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Convergence of the partial wave expansion of the He ground state

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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 ℓ ranging from 0 to 12 resulting in basis sets in excess of 400 orbitals. The convergence of the energy and electron-electron δ-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 $\Delta X_J = A_E(J+\frac{1}{2})^{-p} + B_E(J+\frac{1}{2})^{-p-1} + \ldots$, 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 $J\rightarrow\infty$ 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 $\langle\delta\rangle$ 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 [2–8]. 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:

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

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 ℓ are smaller than the number of low ℓ. The justification for this is that the high ℓ partial waves make a smaller contribution to the energy and other expectation values of than the low ℓ 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 ℓ 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 severe manner in CI calculations of the positron-atom problem. The CI method has recently been applied to the study of positronic atoms (electronically stable states consisting of a positron bound to an atom) [11–20] and also to positron-atom scattering states [21–23]. 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, 19, 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^+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 [1], one struggles to find an adjective that could characterize the convergence properties of positronic systems!

The two most important expectation values for positronic systems are the energy, and the rate for

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electron-positron annihilation. The annihilation rate, which is proportional to the expectation of the electron-positron δ-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 [7, 15, 28]:

$$\Delta\Gamma^J = \langle\Gamma\rangle^J - \langle\Gamma\rangle^{J-1} \approx \frac{A_\Gamma}{(J+\frac{1}{2})^2} \ , \tag{2}$$

To put this in perspective, it would take a calculation with $J \approx 250$ to recover 99% of the PsH annihilation rate [10]. In addition to the slow convergence with J, the δ-function operator also exhibits very slow convergence with respect to the radial basis [10].

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 δ-function expectation value is also studied due to its relation with the electron-positron annihilation operator (which is also a δ-function). It should be noted that the δ-function operator also appears in the Breit-Pauli relativistic correction as the two-body Darwin interaction [7, 29]. 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 [30].

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,

$$|\Psi; LS\rangle = \sum_{i,j} c_{ij}\, \mathcal{A}_{ij} \quad \langle \ell_i m_i \ell_j m_j | L M_L \rangle \ \ \langle \tfrac{1}{2}\mu_i \tfrac{1}{2}\mu_j | S M_S \rangle \times \quad \phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2) \quad . \tag{3}$$

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

$$\phi(\mathbf{r}) = P(r) Y_{\ell m}(\hat{\mathbf{r}}) \ . \tag{4}$$

All observable quantities can be defined symbolically as

$$\langle X\rangle^J = \sum_{L=0}^{J} \Delta X^L \ , \tag{5}$$

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

$$\Delta X^J = \langle X\rangle^J - \langle X\rangle^{J-1} \ . \tag{6}$$

Hence, one can write formally

$$\langle X\rangle^\infty = \langle X\rangle^J + \sum_{L=J+1}^{\infty} \Delta X^L \ . \tag{7}$$

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 ℓ-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 δ-function, $\langle\delta\rangle^\infty = \langle\delta(\mathbf{r}_1 - \mathbf{r}_2)\rangle^\infty$. For helium, terms with $\ell > 2$ contribute only 0.033% of the total energy. For purely electronic systems these higher ℓ 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 [1], Hill [3] and Kutzelnigg and associates [4, 7]. Analytic work indicates that the energy increments are given by

$$\Delta E^J = \frac{A_E}{(J+\frac{1}{2})^4} + \frac{B_E}{(J+\frac{1}{2})^5} + \frac{C_E}{(J+\frac{1}{2})^6} + \ldots \tag{8}$$

where

$$A_E = -6\pi^2 \int |\Psi(r,r,0)|^2 r^5 dr = -0.074226 \tag{9}$$

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

given a two-body wave function $\Psi(r_1, r_2, (\mathbf{r}_1 - \mathbf{r}_2))$. No expressions for C_E have been presented. At large J, one expects the energy increments to be well described by eq. (1).

For the δ-function one can write

$$\Delta\delta^J = \frac{A_\delta}{(J+\frac{1}{2})^2} + \frac{B_\delta}{(J+\frac{1}{2})^3} + \frac{C_\delta}{(J+\frac{1}{2})^4} + \ldots \tag{11}$$

where A_δ is believed [7] to be

$$A_\delta = -4\pi \int |\Psi(r,r,0)|^2 r^3 dr = -0.04287 \tag{12}$$

(Ottschofski 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 $A_\delta/(J+\frac{1}{2})^2$ convergence is due to the two-electron Darwin term). It should be noted that Gribakin and Ludlow [28] have also derived an expression equivalent to eq. (12) in the context of positron annihilation. The numerical value was taken from a variational wave function of the

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 $N_{\rm orb}$ while the LTO exponent for $\ell = J$ is listed in the λ 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.

	20LTO				35LTO			
J	λ	$N_{\rm orb}$	$\langle E\rangle^J$	$\langle\delta\rangle^J$	λ	$N_{\rm orb}$	$\langle E\rangle^J$	$\langle\delta\rangle^J$
0	4.8	20	-2.879 028 507	0.155 789 346	8.6	44	-2.879 028 760	0.155 766 769
1	7.8	40	-2.900 515 873	0.128 501 540	11.6	80	-2.900 516 228	0.128 460 082
2	10.1	60	-2.902 766 378	0.120 923 186	14.4	115	-2.902 766 823	0.120 862 126
3	12.1	80	-2.903 320 527	0.117 264 315	17.2	150	-2.903 321 045	0.117 183 496
4	14.0	100	-2.903 517 973	0.115 104 494	19.2	185	-2.903 518 552	0.115 004 651
5	15.5	120	-2.903 605 022	0.113 681 991	21.2	220	-2.903 605 654	0.113 563 078
6	17.1	140	-2.903 649 142	0.112 676 622	22.8	255	-2.903 649 820	0.112 539 353
7	18.7	160	-2.903 673 821	0.111 930 245	24.8	290	-2.903 674 539	0.111 775 243
8	20.1	180	-2.903 688 677	0.111 355 981	26.5	325	-2.903 689 430	0.111 183 690
9	21.5	200	-2.903 698 142	0.110 901 652	28.0	360	-2.903 698 926	0.110 712 681
10	22.9	220	-2.903 704 451	0.110 534 160	29.5	395	-2.903 705 263	0.110 329 155
11	24.2	240	-2.903 708 815	0.110 231 642	31.0	430	-2.903 709 652	0.110 011 117
12	25.5	260	-2.903 711 927	0.109 978 870	32.5	465	-2.903 712 786	0.109 743 369
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			-2.903 724 362	0.106 527
Method 2			-2.903 723 252	0.107 178			-2.903 724 249	0.106 630
Method 3			-2.903 723 205	0.107 334			-2.903 724 240	0.106 698

He ground state with a basis of 250 explicitly correlated gaussians and an energy of -2.9037243752 Hartree.

As can be imagined there have been a number of very large CI calculations upon the helium ground state that have addressed the convergence issue [2, 4–6, 8, 32]. These calculations can be roughly divided into two classes, those that represented the radial wave function on a grid or used piecewise polynomials [2, 5, 32], and those that describe the radial wave function as a linear combination of analytic basis functions [4, 6, 8]. The first systematic calculation was the seminal investigation by Carroll, Silverstone and Metzger (CSM) [2] who used a piece-wise polynomial basis to construct a natural orbital expansion. Besides performing some very large calculations they also estimated the completeness limit of their radial basis. The largest explicit calculation by CSM will be termed the CSM calculation while the extrapolated calculation will be denoted as CSM_∞. Despite their importance, these calculations have been largely superseded by the grid-based calculation of Salomonson and Oster (SO) [32] and the B-spline calculation of Decleva, Lisini and Venuti (DLV) [5]. The SO calculation obtained energies, $\langle E\rangle^J$ accurate to about 10^{-8} Hartree by extrapolating the radial basis to the variational limit. This extreme level of accuracy has not been achievable with the three calculations that used Slater Type Orbitals (STO) to represent the radial wave function [4, 6, 8]. Linear dependence problems become severe as the basis set is expanded toward completeness. Indeed, recourse was made to very high precision (REAL*24) arithmetic in the Sims and Hagstrom (SH) calculation [8] which is the largest calculation of this type so far reported.

III. THE PRESENT CI CALCULATIONS

The present calculations use a basis set consisting of Laguerre Type Orbitals (LTOs) [15, 16, 33, 34]. The LTOs of a given ℓ 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 ℓ with the largest calculation including orbitals up to $\ell = 12$. The LTO exponents for a given ℓ were the same and the values of the exponents were optimized in a quasi-perturbative fashion. The exponents for $\ell = 0, 1$

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 $N_{\rm orb}$ while the LTO exponent for $\ell = J$ is listed in the λ 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.

			35LTO*		35LTO$^*_\infty$	
J	λ	$N_{\rm orb}$	$\langle E\rangle^J$	$\langle\delta\rangle^J$	$\langle E\rangle^J$	$\langle\delta\rangle^J$
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	-2.903 518 601	0.114 973 165
5	15.5	210	-2.903 605 568	0.113 593 010	-2.903 605 710	0.113 523 543
6	17.1	245	-2.903 649 729	0.112 573 360	-2.903 649 884	0.112 491 488
7	18.7	280	-2.903 674 443	0.111 813 216	-2.903 674 609	0.111 719 074
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	0.109 921 236
12	25.5	455	-2.903 712 675	0.109 799 333	-2.903 712 882	0.109 645 079
			$\langle E\rangle^\infty$ and $\langle\delta\rangle^\infty$ Extrapolations			
Method 1			-2.903 724 243	0.106 881	-2.903 724 476	0.106 328
Method 2			-2.903 724 123	0.106 757	-2.903 724 378	0.106 341
Method 3			-2.903 724 109	0.106 847	-2.903 724 384	0.106 334

and 2 orbitals were optimized in a CI calculation with all 60 orbitals. The exponents for $\ell > 2$ were optimized separately for each ℓ with CI calculations that also included the $\ell = 0, 1, 2$ orbitals. Once the exponents were optimized, a sequence of calculations to give the $\langle E\rangle^J$ and $\langle\delta\rangle^J$ 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 I.

The second set of calculations were much larger. Here there were 35 LTOs per ℓ with the exception of $\ell = 0$ and 1 where respectively 44 and 36 LTOs were used respectively. The orbital exponents were optimized for each ℓ 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 I.

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 ℓ 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 ℓ 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]

$$\Delta E^N = \frac{a_E}{N^{7/2}} + \frac{b_E}{N^{8/2}} + \frac{c_E}{N^{9/2}} + \ldots \qquad (13)$$

$$\Delta\delta^N = \frac{a_\delta}{N^{5/2}} + \frac{b_\delta}{N^{6/2}} + \frac{c_\delta}{N^{7/2}} + \ldots \qquad (14)$$

It is possible to estimate the $N \to \infty$ limits for the radial basis once the a_E, a_δ, b_E, ... 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* basis, while the basis including the $N \to \infty$ correction is termed the 35LTO$^*_\infty$ basis. The energies and expectation values for these two calculations are listed in Table II.

TABLE III: Comparison of different CI calculations of the He atom ground state energy $\langle E\rangle^J$ as a function of J. To aid interpretation, the ΔE^J energy differences are also tabulated. The energies of the SO_∞, CSM_∞ and $35LTO^*_\infty$ are the estimated energies in an infinite radial basis. The $35LTO^*_\infty$ $\langle E\rangle^J$ and ΔE^J are the smoothed values. The DLV energies for $J \geq 5$ are obtained by adding the ΔE^J from Table IV of Ref. [5] to their estimate of $\langle E\rangle^4$.

J	35LTO	$35LTO^*_\infty$	SH [8]	CSM_∞ [2]	SO_∞ [32]	DLV [5]
$\langle E\rangle^0$	-2.879 028 760	-2.879 028 766	-2.879 028 757	-2.879 028 765	-2.879 028 77	-2.879 028 767
$\langle E\rangle^1$	-2.900 516 228	-2.900 516 246	-2.900 516 220	-2.900 516 220	-2.900 516 25	-2.900 516 245
$\langle E\rangle^2$	-2.902 766 823	-2.902 766 853	-2.902 766 805	-2.902 766 822	-2.902 766 85	-2.902 766 849
$\langle E\rangle^3$	-2.903 321 045	-2.903 321 084	-2.903 321 016	-2.903 321 079	-2.903 321 09	-2.903 321 079
$\langle E\rangle^4$	-2.903 518 552	-2.903 518 601	-2.903 518 465	-2.903 518 598	-2.903 518 60	-2.903 518 600
$\langle E\rangle^5$	-2.903 605 654	-2.903 605 710	-2.903 605 515	-2.903 605 71	-2.903 605 72	-2.903 605 97
$\langle E\rangle^6$	-2.903 649 820	-2.903 649 884	-2.903 649 644	-2.903 649 88	-2.903 649 89	-2.903 650 24
$\langle E\rangle^7$	-2.903 674 539	-2.903 674 609	-2.903 674 328	-2.903 674 59	-2.903 674 62	-2.903 675 01
$\langle E\rangle^8$	-2.903 689 430	-2.903 689 505	-2.903 689 193	-2.903 689 47	-2.903 689 52	-2.903 689 93
$\langle E\rangle^9$	-2.903 698 926	-2.903 699 006	-2.903 698 656	-2.903 698 95	-2.903 699 02	-2.903 699 44
$\langle E\rangle^{10}$	-2.903 705 263	-2.903 705 349	-2.903 704 974	-2.903 705 27	-2.903 705 37	-2.903 705 79
$\langle E\rangle^{11}$	-2.903 709 652	-2.903 709 742	-2.903 709 325	-2.903 709 64		-2.903 710 19
$\langle E\rangle^{12}$	-2.903 712 786	-2.903 712 882	-2.903 712 433			-2.903 713 33
			ΔE^J increments			
ΔE^1	-0.021 487 468	-0.021 487 480	-0.021 487 463	-0.021 487 455	-0.021 487 48	-0.021 487 478
ΔE^2	-0.002 250 594	-0.002 250 606	-0.002 250 585	-0.002 250 662	-0.002 250 61	-0.002 250 604
ΔE^3	-0.000 554 223	-0.000 554 232	-0.000 554 211	-0.000 554 197	-0.000 554 23	-0.000 554 230
ΔE^4	-0.000 197 507	-0.000 197 516	-0.000 197 449	-0.000 197 519	-0.000 197 52	-0.000 197 521
ΔE^5	-0.000 087 102	-0.000 087 109	-0.000 087 050	-0.000 087 112	-0.000 087 11	-0.000 087 37
ΔE^6	-0.000 044 166	-0.000 044 174	-0.000 044 129	-0.000 044 17	-0.000 044 18	-0.000 044 27
ΔE^7	-0.000 024 719	-0.000 024 725	-0.000 024 683	-0.000 024 71	-0.000 024 73	-0.000 024 77
ΔE^8	-0.000 014 891	-0.000 014 896	-0.000 014 866	-0.000 014 88	-0.000 014 90	-0.000 014 92
ΔE^9	-0.000 009 496	-0.000 009 501	-0.000 009 463	-0.000 009 48	-0.000 009 50	-0.000 009 51
ΔE^{10}	-0.000 006 337	-0.000 006 342	-0.000 006 318	-0.000 006 32	-0.000 006 35	-0.000 006 35
ΔE^{11}	-0.000 004 389	-0.000 004 394	-0.000 004 351	-0.000 004 37		-0.000 004 40
ΔE^{12}	-0.000 003 134	-0.000 003 139	-0.000 003 108			-0.000 003 14

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 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 $35LTO^*_\infty$ basis sets, along with the SH, CSM_∞, SO_∞ and DLV calculations. These same sets of data are also presented as energy differences between consecutive calculations ΔE^J. The energies of the SH calculation, which used the even-tempered STO basis, are consistently the worst, and are 3×10^{-7} Hartree larger than the 35LTO calculation at $J = 12$. Even though CSM_∞ 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_∞ values of ΔE^J were smaller than those of the 35LTO calculation. The present $35LTO^*_\infty$, SO_∞ 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 $35LTO^*_\infty$ energies gives an indication of the incompleteness of the 35LTO basis and by $J = 12$ the difference is 0.96×10^{-7} Hartree.

The good agreement between the $35LTO^*_\infty$, SO_∞ and DLV energies is not present for $J \geq 5$. Although the $35LTO^*_\infty$ and SO_∞ energies generally agree at the level of 10^{-8} Hartree, it is seen the DLV ΔE^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 2×10^{-7} Hartree larger than the $35LTO^*_\infty$ and SO_∞ increments. It has also been noticed that DLV do overstate the accuracy of their calculation, they assert an accuracy of 7.8×10^{-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 [5]), and this energy is in

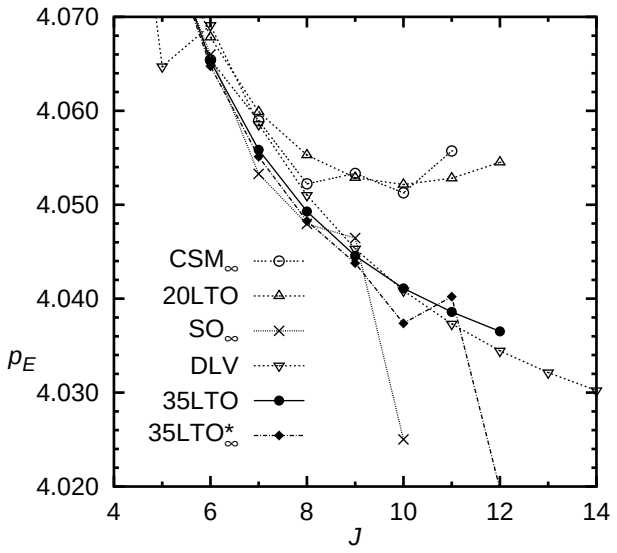

FIG. 1: The exponents p_E as a function of J for the different CI calculations of the He ground state energy as listed in Table III.

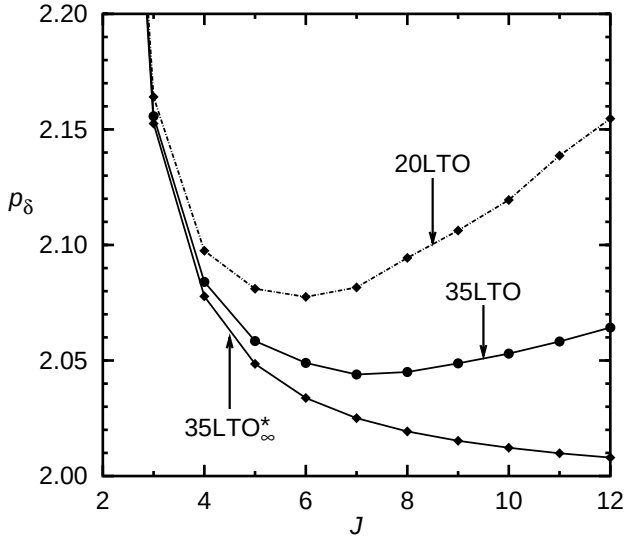

FIG. 2: The exponents p_δ as a function of J for the LTO calculations of the He ground state $\langle\delta\rangle$.

error by 1.3×10^{-6} Hartree!

A. Scrutiny of the partial wave increments

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

$$\Delta X^J \approx \frac{A_E}{(J+\frac{1}{2})^p} \ , \tag{15}$$

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

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

The exponent derived from the energy increments is p_E while the exponent derived from the δ-function increments is p_δ. One expects $p_E \to 4$ [1] and $p_\delta \to 2$ as $J \to \infty$ [7, 28], in agreement with eqs. (8) and (11).

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_∞, CSM_∞ 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_∞ and SO_∞ curves are a consequence of the number of digits at which the energies were published [2, 32]. Plots of p_E vs J were examined (but not plotted in Figure 1) for some calculations [6, 8] 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_∞ 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 ΔE^J increments are decreasing too quickly at the higher J values. The larger SO_∞, 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_∞ and $35LTO_\infty$ curves. It will be demonstrated later that the behavior of the 20LTO and CSM_∞ curves is due to slower convergence of the radial basis at high ℓ.

The tendency for p_E to approach the limiting value of 4 from above is a consequence of the fact that the A_E and B_E coefficients of eq. (8) have the same sign. The coefficients A_E and B_E are derived from second and third order perturbation theory respectively [3, 7] 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 $p_E \to 4$ from below, and this is indeed the case [10, 15–18].

The incremental exponent for the δ-function, p_δ, is shown in Figure 2 for the 20LTO, 35LTO and $35LTO^*_\infty$ basis sets. It should be noted that the values of p_δ were sensitive to the precision of the calculation. Originally, the diagonalization of the Hamiltonian was performed using the Davidson algorithm [35]. However, this method could not give δ-function expectation values to better than 8 significant figures (irrespective of the convergence

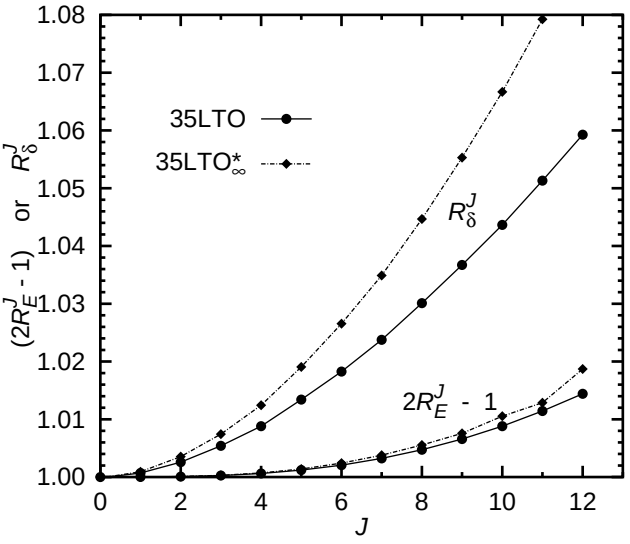

FIG. 3: The 35LTO:20LTO and $35LTO^*_\infty$:20LTO ratios of the increments to $\langle E\rangle^J$ and $\langle\delta\rangle^J$ (refer to eq. (17)) as a function of J for the calculations of the He ground state.

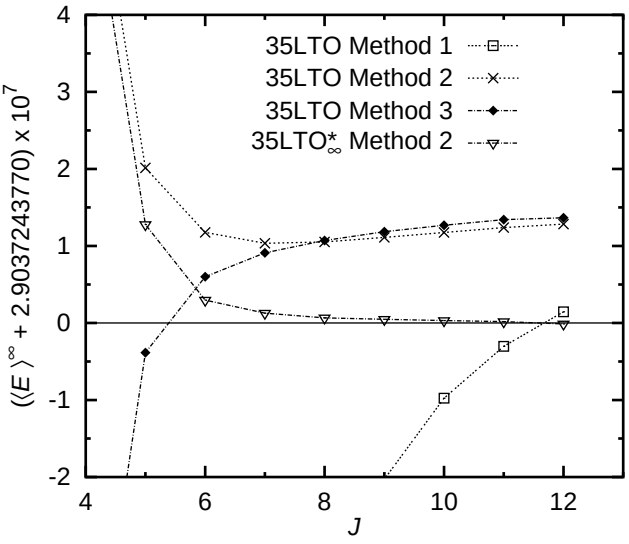

FIG. 4: The extrapolated $J \to \infty$ limit for the He ground state energy $\langle E\rangle^\infty$ using three different methods to complete the partial wave series. The input $\langle E\rangle^J$ upon which the extrapolations were based were those of the 35LTO and the smoothed $35LTO^*_\infty$ calculations.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

tolerance for the energy). This lead to noticeable fluctuations in the p_δ 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 $p_\delta \to 2$ limit as $J \to \infty$. The 20LTO curve has a p_δ 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_δ based on the $35LTO^*_\infty$ sequence does exhibit the correct qualitative behavior as J increases. The $N \to \infty$ 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_δ 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 ΔE^J increments as J increases. The ratios

$$R_E^J = \frac{(\Delta E^J)_{35}}{(\Delta E^J)_{20}} \tag{17}$$

gives a measure of the relative impact of the 20LTO, 35LTO and $35LTO^*_\infty$ basis sets to a J energy increment. One can define a similar ratio, R_δ^J, for the δ-function $\Delta\delta^J$ increments.

The behavior of these ratios versus J are depicted in Figure 3. Both R_E^J and R_δ^J increase steadily with J. The slower convergence of the energy at higher J is also evident in Table I of [7] and explicit comment about this point has been made previously [9]. The $\langle\delta\rangle^J$ expectation value is much more sensitive to the increase in the dimension of the radial basis and there was a 9.3% increase in $\Delta\delta^{12}$ between the 20LTO and $35LTO^*_\infty$ calculations. The corresponding increase in the ΔE^{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 $35LTO^*_\infty$ energies

It is apparent from Figures 1 and 3 that including the radial extrapolations has resulted in irregularities appearing in the $35LTO^*_\infty$ 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 $(R_E^J - 1) \propto J^s$. Accordingly a fit of $(R_E^J - 1) = \left(\frac{\Delta E^J_{35LTO^*_\infty}}{\Delta E^J_{20LTO}} - 1\right)$ 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 $35LTO^*_\infty$ values of $\langle E\rangle^J$ and ΔE^J given in Table III are those of the smoothed energy sequence. The largest change to any of the energies was 2×10^{-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 $\langle X\rangle^J$ 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 $\langle E\rangle^J$ to determine A_E. Three successive values of $\langle X\rangle^J$ 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 $\langle X\rangle^J$ 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 $\langle X\rangle^J$ 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:

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

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

Figures 4 and 5 show the behavior of the extrapolated E and δ-function for the three different extrapolations as a function of J. Tables I and II 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 $\langle E\rangle^\infty$ 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^*_∞ energies gave $\langle E\rangle^\infty$ = -2.903 724 378 Hartree, an energy that is in error by 10^{-9} 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_∞ calculation, their estimate of the energy in the J *to*∞ limit was -2.903 724 39 Hartree [32].

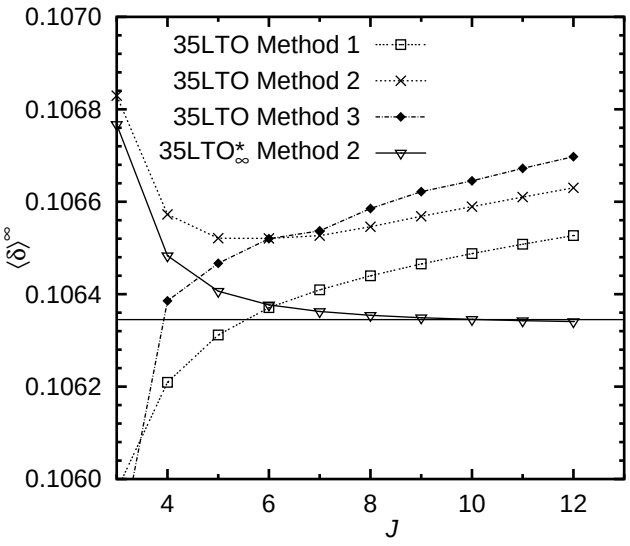

FIG. 5: The extrapolated $J \to \infty$ limit for the He ground state $\langle\delta\rangle^\infty$ using three different methods to complete the partial wave series. The horizontal line shows the value of Drake [31].

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^*_∞ sequence permitted a much more accurate extrapolation to the $J \to \infty$ limit. The 35LTO^*_∞ 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 $\langle\delta\rangle^J$ values, the relative size of the individual $\Delta\delta^J$ increments were much larger than the ΔE^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 *a-priori* from eqs. (9), (10) and (12). Estimates of these parameters are also obtained during the

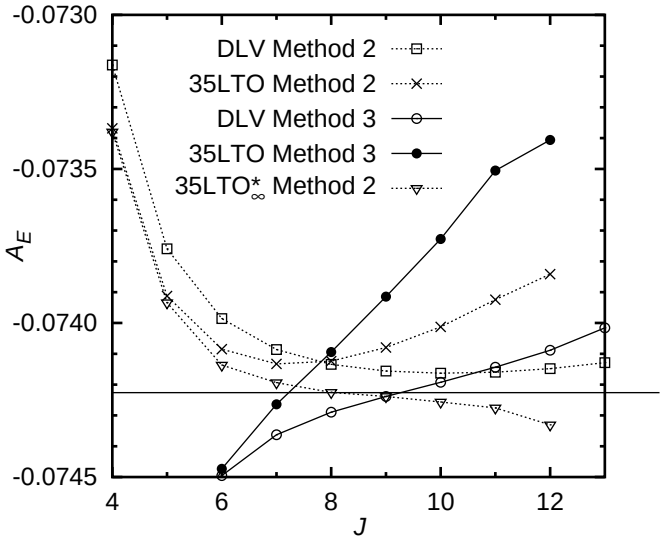

FIG. 6: The value of A_E as extracted from sequences of $\langle E\rangle^J$ data. The horizontal line shows the value of from eq. (9), namely -0.074226. Estimates of A_E from Method 2 are drawn with dashed lines while estimates of A_E from Method 3 are drawn with solid lines. The DLV data analyzed here was solely from their Table IV of Ref.[5], since this avoided the discontinuity at $J = 4$ and gave a smooth curve.

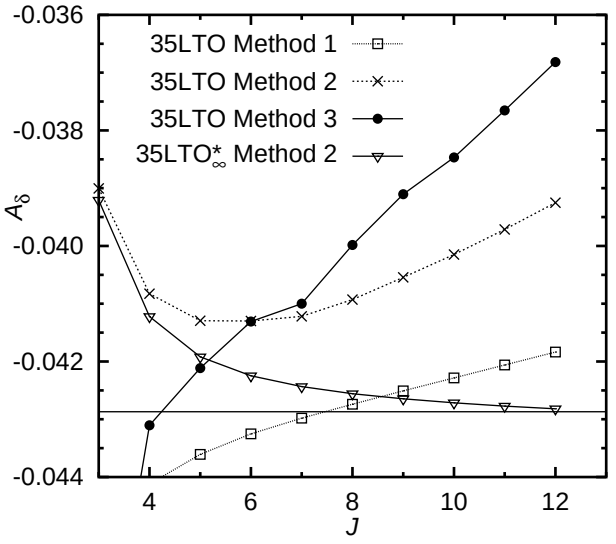

FIG. 7: The value of A_δ as extracted from sequences of $\langle\delta\rangle^J$ data. The horizontal line shows the value of eq. (12), namely $A_\delta = -0.04287$.

fit of the inverse power series to a set of $\langle E\rangle^J$ or $\langle\delta\rangle^J$. An ideal consistency check would be estimates of A_E and A_δ 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_∞ energies gave $A_E = -0.0740$ and $B_E = 0.031$ [2]. However, this value of A_E is only achieved when using $\langle E\rangle^J$ for $J \in [5, 8]$. The very large calculations of DLV reported $A_E = -0.07415$ and $B_E = 0.0317$ [5]. However, a cursory examination of Figure 6 which depicts values of A_E obtained from three successive $\langle E\rangle^J$ 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 $35\mathrm{LTO}^*_\infty$ 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 $35\mathrm{LTO}^*_\infty$ 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 since it has been demonstrated that the 35LTO ΔE^J are increasingly underestimated as J increases. It would therefore be hoped that values of A_E^J extracted from the $35\mathrm{LTO}^*_\infty$ 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_δ 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_δ vs J curve that approached the correct value as J increased. This is another manifestation of the very slow convergence of $\langle\delta\rangle^J$ with respect to the dimension of the radial basis set. There was a significant improvement when A_δ was extracted from the $35\mathrm{LTO}^*_\infty$ sequence using method 2. In this case, A_δ does appear to be converging to the expected value of -0.04287 and at $J = 12$ one obtains $A_\delta = -0.04282$

The small irregularities in the $35\mathrm{LTO}^*_\infty$ $\langle\delta\rangle^J$ sequence resulted in irregularities in A_δ 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_δ 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

calculation reported here with a minimum of 35 LTO's per ℓ gave an energy that was accurate to 1.2×10^{-5} Hartree. Including energy corrections obtained from the 2- and 3-term inverse power series in J resulted in a He ground state energy that was accurate to $\approx 1 \times 10^{-7}$ Hartree. Improved accuracy required the use of extrapolations in the radial basis set to get an estimate of the variational limit for $\langle E \rangle^J$. 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 2×10^{-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 δ-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 ℓ 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 $\langle \delta \rangle = 0.106341\ a_0^3$ 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 [30].

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 [30], it eminently conceivable that estimates of the annihilation rate at better than 0.1% accuracies will be achievable for single-center basis sets.

VI. ACKNOWLEDGMENTS

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