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Convergence of configuration-interaction single-center calculations of positron-atom interactions

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The configuration interaction (CI) method using orbitals centered on the nucleus has recently been applied to calculate the interactions of positrons interacting with atoms. Computational investigations of the convergence properties of binding energy, phase shift, and annihilation rate with respect to the maximum angular momentum of the orbital basis for the e^+Cu and PsH bound states, and the e^+-H scattering system were completed. The annihilation rates converge very slowly with angular momentum, and moreover the convergence with radial basis dimension appears to be slower for high angular momentum. A number of methods of completing the partial wave sum are compared; an approach based on a $\Delta X_J = a\left(J+\frac{1}{2}\right)^{-n} + b\left(J+\frac{1}{2}\right)^{-(n+1)}$ form [with $n=4$ for phase shift (or energy) and $n=2$ for the annihilation rate] seems to be preferred on considerations of utility and underlying physical justification.

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I. INTRODUCTION

In the last few years there have been a number of calculations of positron binding to atoms [1–11] and positron scattering from atoms and ions [12–14] using orthodox CI type methods with large basis sets of single center orbitals. Besides the calculations on atoms, there have some attempts to calculate the properties of positrons bound to molecules with modified versions of standard quantum chemistry methods [15–18]. One of the reasons for this increased activity lies in the fact that positron bound states can have a very large influence in the dynamics of positron annihilation in gases and other media [18–23].

One feature common to all these CI-type calculations is the slow convergence of the binding energy, and the even slower convergence of the annihilation rate. 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 [2,9,24,25]. 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 [1,2,26,27]. For example, the largest CI calculations on PsH and the group II positronic atoms have typically involved single particle basis sets with eight radial functions per angular momenta, ℓ, and inclusion of angular momenta up to $\ell_{\max}=10$ [5,6,9]. Even with such large basis sets, between 5% and 60% of the binding energy and some 30%–80% of the annihilation rate were obtained by extrapolating from the $\ell_{\max}=10$ to the $\ell_{\max}=\infty$ limit.

Even though single center basis sets are not well suited to describe the physics of electron-positron correlation, they do have the advantage that at least some sort of calculation can be performed. The alternative is to use explicitly correlated basis sets with basis functions involving the electron-positron coordinate. For example, Hylleraas-type basis functions have been used to determine the structures of two to three particles systems accurately [28–30], but they cannot be used for more complex systems. And the more flexible explicitly correlated Gaussian (ECG) function [31–33] also becomes more tedious to use as the system increases in size [25]. Furthermore, there are no examples of ECGs being used in Kohn variational scattering of positron-atom scattering. Explicitly correlated basis sets have the advantage that they can generate very accurate energies and wave functions for those systems that permit their usage [25,34–36].

Since our initial CI calculations on group II and IIB atoms [5–7], advances in computer hardware mean larger dimension CI calculations are possible. In addition, program improvements have removed the chief memory bottleneck that previously constrained the size of the calculation. As a result, it is now appropriate to revisit these earlier calculations to obtain improved estimates of the positron binding energies and other expectation values. However, as the calculations are increased in size, it has become apparent that the issue of slow convergence of the physical observables with the angular momenta of the basis orbitals is the central technical issue in any calculation.

While it is desirable to minimize the amount of mechanical detail in any discussion (so as not to distract from the physics), the ability to draw reliable conclusions from any calculation depends crucially on the treatment of the higher partial waves. For example, the treatment of the higher partial waves in separate calculations by Saito [11] has already been shown to be flawed [37] while the present work exposes the defects in the methods of Gribakin and Ludlow [14]. The present work, therefore, is solely devoted to an in-depth examination of the convergence properties of mixed electron-positron calculations.

In our previous works, [5–7,12,13], a relatively simple solution to this problem was adopted. In effect, it was as-

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sumed that the successive increments to any observable scaled as an inverse power series in $\ell_{\max}$. This approach does have limitations as do the approaches adopted by other groups [10,11,14,37]. In the present article, we examine the convergence properties of positron binding calculations upon PsH and e^+Cu, and a positron scattering calculation upon the e^+-H system with respect to angular momentum and the dimension of the radial basis sets. The limitations of existing calculations are exhibited, and some improved prescriptions for estimating the variational limit are introduced and tested.

II. EXISTING METHODS OF PERFORMING THE ANGULAR MOMENTUM EXTRAPOLATION

A. The nature of the problem

The positron-atom wave function is written as a linear combination of states created by multiplying atomic states to single particle positron states with the usual Clebsch-Gordan coupling coefficients;

$$|\Psi;LS\rangle = \sum_{i,j} c_{i,j} \left\langle L_i M_i \ell_j m_j | L M_L \right\rangle \left\langle S_i M_{S_i} \tfrac{1}{2} \mu_j \middle| S M_S \right\rangle \times \Phi_i(\text{atom};L_iS_i)\phi_j(\mathbf{r}_0). \quad (1)$$

In the case of a single electron system, e.g., H, $\Phi_i(\text{atom};\ L_iS_i)$ is just a single electron wave function, i.e., an orbital. For a divalent system, $\Phi_i(\text{atom};\ L_iS_i)$ is an antisymmetric product of two single electron orbitals coupled to have good L_i and S_i quantum numbers. The function $\phi_j(\mathbf{r}_0)$ is a single positron orbital. The single particle orbitals are written as a product of a radial function and a spherical harmonic:

$$\phi(\mathbf{r}) = P(r)Y_{\ell m}(\hat{\mathbf{r}}). \quad (2)$$

The radial wave functions are a linear combination of Slater-type orbitals (STOs) [38] and Laguerre-type orbitals (LTOs). Most of the time the radial functions are LTOs, the exceptions occurring for single electron states with angular momenta equal to those of any occupied core orbitals. Since the Hartree-Fock core orbitals are written as a single combination of STOs, some of the active electron basis is written as linear combinations of STOs before the switch to a LTO basis is made. The LTO basis [5,6] has the property that the basis can be expanded toward completeness without having any linear independence problems.

The present discussion is specific to positronic systems with a total orbital angular momentum of zero. It is straightforward to generalize the discussion to states with $L>0$, but this just adds additional algebraic complexities without altering any of the general conclusions.

For a one electron system, the basis can be characterized by the index J, the maximum orbital angular momentum of any single electron or single positron orbital included in the expansion of the wave function.

For two electron systems, the $L=0$ configurations are generated by letting the two electrons and the positron populate the single particle orbitals subject to two selection rules,

$$\max(\ell_0,\ell_1,\ell_2) \leqslant J, \quad (3)$$

$$\min(\ell_1,\ell_2) \leqslant L_{\text{int}}. \quad (4)$$

In these rules ℓ_0 is the positron orbital angular momentum, while ℓ_1 and ℓ_2 are the angular momenta of the electrons. The maximum angular momentum of any electron or positron orbital included in the CI expansion is J. The other parameter, L_{int}, is used to eliminate configurations involving the simultaneous excitation of both electrons into high ℓ states. Double excitations of the two electrons into excited orbitals are important for taking electron-electron correlations into account, but the electron-electron correlations converge a lot more quickly with L_{int} than electron-positron correlations do with J. Calculations of the positronic bound states of the group II atoms and PsH [5,6] showed that the annihilation rate changed by less than 1% when L_{int} was varied from 1 to 3. The present set of calculations upon PsH was performed with $L_{\text{int}}=4$. Further details about the methods used to perform the calculations can be found elsewhere [5,6].

Various expectation values are computed to provide information about the structure of these systems. All observable quantities can be defined symbolically as

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

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.,

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

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 most expectation values, $\langle X\rangle^J$, converge relatively slowly with J and so the contribution of the second term can be significant. A sensible working strategy is to make J as large as possible while simultaneously trying to use the best possible approximation to mop up the rest of the partial wave sum.

B. Existing extrapolation techniques and their limitations

One of the first groups to confront this issue and attempt a solution was the York University group of McEachran and Stauffer. They performed a series of polarized orbital calculations of positron scattering from rare gases [39–42]. The decrease in energy when the target atom relaxed in the field of a fixed positron was used to determine the polarization potential as a function of the distance from the nucleus. The polarized orbital method implicitly includes the influence of virtual Ps formation (within an adiabatic approximation), and this means that slow convergence can be expected. McEachran and Stauffer found that the scattering observables, namely the phase shift, and the Z_{eff} annihilation pa-

rameter, converged slowly with J, the largest angular momentum of the polarized electron orbital set used to represent the adjustment of the atomic charge cloud in the field of the positron. They took this into consideration by assuming their polarization potential scaled as J^{-p} and the polarized orbital scaled as J^{-q} at large J. They found $p \approx 3.8$ and $q \approx 1.8$ for the rare gases at $J \approx 12$.

The recent CI-type calculations of Mitroy and collaborators also used an inverse power relation of J^{-p}, to complete the partial wave sum [5,6,12]. In this case, the observables, ε^J, δ^J, Γ^J, and Z_{eff}^J, were extrapolated. This contrasts with the polarized orbital calculations where the polarization potential and polarized orbital were extrapolated. The value of p was given by

$$p = \ln\left(\frac{\Delta X^{J-1}}{\Delta X^J}\right) \Bigg/ \ln\left(\frac{J-1}{J}\right), \tag{8}$$

while the constant factor is

$$A_X = \Delta X^J J^p. \tag{9}$$

The correction factor was then evaluated by doing the sum $\Sigma_{L=J+1}^{\infty} A_X / L^p$ explicitly with an upper limit in the thousands.

Gribakin and Ludlow [43] applied perturbation theory and the ideas of Schwartz [44,45] to determine the asymptotic behavior of the partial wave increments to the binding energies, phase shifts, and annihilation rates of positron-atom systems. This work is largely derived from previous work on the partial wave expansion of two electron atoms [46–49]. They determined that the binding energy E, annihilation rate Γ, phase shift δ, and collisional annihilation parameter Z_{eff} obey

$$\Delta E^J = \langle E \rangle^J - \langle E \rangle^{J-1} \sim \frac{B_E}{\left(J+\frac{1}{2}\right)^4}, \tag{10}$$

$$\Delta \Gamma^J = \langle \Gamma \rangle^J - \langle \Gamma \rangle^{J-1} \sim \frac{B_\Gamma}{\left(J+\frac{1}{2}\right)^2}, \tag{11}$$

$$\Delta \delta^J = \langle \delta \rangle^J - \langle \delta \rangle^{J-1} \sim \frac{B_\delta}{\left(J+\frac{1}{2}\right)^4}, \tag{12}$$

$$\Delta Z_{\text{eff}}^J = \langle Z_{\text{eff}} \rangle^J - \langle Z_{\text{eff}} \rangle^{J-1} \sim \frac{B_Z}{\left(J+\frac{1}{2}\right)^2}. \tag{13}$$

These expressions are merely the leading order terms of a series of the form

$$\Delta X^J = \frac{B_X}{\left(J+\frac{1}{2}\right)^n} + \frac{C_X}{\left(J+\frac{1}{2}\right)^{n+1}} + \cdots. \tag{14}$$

To perform the actual extrapolation during a calculation of positron-hydrogen scattering, Gribakin and Ludlow [14] did a fit to calculated values at $J=9$ and $J=10$ with the formulas

$$\delta = \langle \delta \rangle^\infty = \langle \delta \rangle^J + \sum_{L=J+1}^{\infty} \frac{B_\delta}{\left(L+\frac{1}{2}\right)^4} \approx \langle \delta \rangle^J + \frac{B_\delta}{3\left(J+\frac{1}{2}\right)^3}, \tag{15}$$

$$Z_{\text{eff}} = \langle Z_{\text{eff}} \rangle^\infty = \langle Z_{\text{eff}} \rangle^J + \sum_{L=J+1}^{\infty} \frac{B_Z}{\left(L+\frac{1}{2}\right)^2} \approx \langle Z_{\text{eff}} \rangle^J + \frac{B_Z}{J+\frac{1}{2}}, \tag{16}$$

and so determined Z_{eff} and δ. They used the approximate identities in Eqs. (15) and (16) rather than explicitly evaluating the infinite sum. The identities appear to have been derived as an approximation to the $\int_{J+1}^{\infty} \left(L+\frac{1}{2}\right)^{-2} dL$ integral. However, in equating the sum to the integral they implicitly assume a rectangle rule representation of the integral which is in error of 5%–10% for $J \in [7,10]$ [the net effect of this is that Gribakin and Ludlow state that the increments decrease as $B/\left(L+\frac{1}{2}\right)^n$ but actually assume a B/L^n decrease when evaluating the $J \to \infty$ correction]. A better approximation to the series is obtained by using a midpoint rule to represent the integral. Doing this leads to

$$\sum_{L=J+1}^{\infty} \frac{1}{\left(L+\frac{1}{2}\right)^n} \approx \frac{1}{(n-1)(J+1)^{n-1}}. \tag{17}$$

This approximation is accurate to 0.1% for $n=2$ and $J=7$.

It will be shown that a more serious problem with the Gribakin and Ludlow methodology is that Eqs. (15) and (16) cannot reveal whether the calculated Z_{eff}^J are deviating from the expected asymptotic form. For example, successive increments to either the phase shift or Z_{eff} have usually decreased more slowly with J (for J ranging between 10 and 18) than indicated by Eqs. (10)–(13) [5,6,12,13]. Instead of having $p=2$ or $p=4$ the successive increments often gave slightly smaller values for p. The approach adopted by Gribakin and Ludlow is insensitive to these deviations.

Saito has investigated the structure of the PsH and the Ps-halogen systems with the CI method [9,11]. A natural orbital (NO) truncation algorithm based on the energy was used to reduce the dimensionality of the secular equations, thus making calculations on the heavier halogen atoms viable. Besides using the inverse power series, Saito used the functional form

$$\Delta X^J = 10^{-\alpha(\log_{10} J)^\beta + \gamma} \tag{18}$$

to complete the partial wave sum for the annihilation rate. This function was not based on any physical principles, and its usage was justified on the grounds that the increments were decreasing faster than J^{-2}. However, it has been suggested that the annihilation rate increments were decreasing too quickly because the dimension of the radial basis used in the Ps-halogen calculations was simply too small [37]. So the rationale behind the usage of Eq. (18) is questionable.

Some mention must be made of the difficulties associated with the slower convergence of the annihilation rate. Consider the PsH system, a calculation with $J=9$ gave 72% of the total annihilation rate [5]. If one doubled the size of J, then Eq. (11) suggests that the explicit calculation would only recover 86% of the total annihilation rate. And it would take a calculation with $J \approx 250$ to recover 99% of the annihilation rate. The situation is even more sobering when one

considers that the annihilation rate converges faster for PsH (since it is the most compact) than for any other positron binding system.

III. COMPARISON OF EXISTING AND NEW APPROACHES TO THE PARTIAL WAVE EXTRAPOLATION

A. The different alternatives

In order to expose the strengths and deficiencies of existing approaches, very large calculations have been performed on three mixed electron-positron systems. These are the e^+-H scattering system for the $\ell=0$ partial wave, and the bound PsH and e^+Cu systems. It will be seen that the typical calculations on these real-world systems do not agree perfectly with the leading order asymptotic form given by Gribakin and Ludlow, i.e., Eqs. (10)–(13). Accordingly, six different extrapolation methods for determining the $J\rightarrow\infty$ correction were tested. These were the following.

Method p. The successive increments to all quantities are assumed to obey an

$$X^J = \frac{A_X}{\left(J+\frac{1}{2}\right)^p}, \tag{19}$$

law with the exponent p determined from Eq. (20). The value of p derived from three successive calculations of X^{J-2}, X^{J-1}, and X^J is given by

$$p = \ln\left(\frac{\Delta X^{J-1}}{\Delta X^J}\right) \Bigg/ \ln\left(\frac{J+\frac{1}{2}}{J-\frac{1}{2}}\right). \tag{20}$$

(Note, in previous works we have used a J^{-p} series [1,5,6,12].) The notations p_E, p_Γ, p_δ, and p_Z are used to denote the exponents derived from the partial wave expansions of the energy, annihilation rate, phase shift, and $Z_{\rm eff}$. The discrete sum over L in (7) is done explicitly up to $J=200$. The remainder of the sum is then estimated using Eq. (17).

Method p_{av}. This is based on method p. Three successive calculations for $(J-2)$, $(J-1)$, and J are once again used with Eqs. (19) and (20) to determine an initial estimate of p_0. Then, p is set to the average of p_0 and the expected value of either 2 or 4. This method makes an admittedly crude attempt to correct method p in those cases where p_δ and p_Z were significantly different from 4 and 2 [6]. Once p has been fixed, Eq. (19) can then be used to determine A_X and the discrete sum over L in (7) is done explicitly up to $J=200$. The remainder of the sum is then estimated using Eq. (17).

Method GL. The relations Eqs. (15) and (16) are assumed to be exact. The two largest values of $\langle X\rangle^J$ are used to determine $\langle Z_{\rm eff}\rangle^\infty$ and $\langle\delta\rangle^\infty$. This method mimics the procedure adopted by Gribakin and Ludlow [14].

Method I. The functional form

$$\Delta X^J = \frac{B_X}{\left(J+\frac{1}{2}\right)^n} \tag{21}$$

is assumed to apply and the ΔX^J increment is used to determine B_X. The exponent n is set to 2 for the annihilation rate and 4 for the energy or phase shift. The discrete sum over L in (7) is done explicitly up to $J=200$ and beyond that point Eq. (17) is used. This method has similarities with the GL method.

Method II. The functional form

$$\Delta X^J = \frac{B_X}{\left(J+\frac{1}{2}\right)^n} + \frac{C_X}{\left(J+\frac{1}{2}\right)^{n+1}} \tag{22}$$

is assumed to apply and the ΔX^J and ΔX^{J-1} increments are used to determine B_X and C_X. The second term in Eq. (22) comes from third-order perturbation theory [46–48]. The exponent n is set to 2 for the annihilation rate and 4 for the energy or phase shift. The discrete sum over L in (7) is done explicitly up to $J=200$ and beyond that point Eq. (17) is used.

Method III. The functional form

$$\Delta X^J = \frac{B_X}{\left(J+\frac{1}{2}\right)^n} + \frac{C_X}{\left(J+\frac{1}{2}\right)^{n+1}} + \frac{D_X}{\left(J+\frac{1}{2}\right)^{n+2}} \tag{23}$$

is assumed to apply and the ΔX^J, ΔX^{J-1}, and ΔX^{J-2} increments are used to determine B_X, C_X, and D_X. Other particulars are the same as those for methods I and II.

Method S. The functional form adopted by Saito, Eq. (18), is used. The parameters α, β, and γ are determined from ΔX^{J-2}, ΔX^{J-1}, and ΔX^J. Then the series is completed by summing to $J=2000$.

B. The e^+-H scattering system

The CI-Kohn method has already been used to generate phase shift and annihilation parameter data for the e^+-H scattering system [12]. New calculations with a radial basis set (i.e., the number of LTOs per ℓ) of increased dimensionality have been done in order to minimize the influence of the radial basis upon any conclusions that are drawn. The present investigation examines s-wave e^+-H scattering at $k=0.4\ a_0^{-1}$. There has been a measurement of the total cross section for e^+-H scattering for $E>5$ eV [50,51]. The experimental cross section is not applicable to the present calculation since it is not of high enough resolution to discriminate between the fine differences of some very large calculations.

The largest calculation for e^+-H included a minimum of 30 LTOs per ℓ with additional LTOs included at small ℓ. Special attention was given to the $\ell=1$ positron basis since this channel is responsible for the long-range polarization potential. The dimension of the LTO basis was 80 in this case. All radial integrations were taken to 729 a_0 on a composite Gaussian grid. The earlier calculations of Bromley and Mitroy [12] with a minimum of 17 LTOs per ℓ will be presented for comparison. Table I gives the e^+-H phase shift and $Z_{\rm eff}$ for s-wave scattering at $k=0.4\ a_0^{-1}$ up to $J=12$. The larger basis will be referred to as basis 2 while the older basis will be named basis 1.

First of all, the values of p_δ and p_Z derived from the earlier [12] and present CI-Kohn calculations are shown together in Fig. 1 as a function of J. This figure tests whether Eqs. (12) and (13) describe the behavior of a real-world calculation.

Neither p_δ nor p_Z are within 1% of the expected asymptotic value at $J=12$ and both are approaching the ex-

TABLE I. Results of CI-Kohn calculations for s-wave e^+-H scattering at $k=0.4\ a_0^{-1}$. The variational and close-coupling data in the last three rows are taken from calculations which have basis functions that explicitly depend on the electron-positron distance. The $J\to\infty$ limits were taken at $J=12$ using the various extrapolation methods as described in the text. The values of p were determined at $J=12$ using Eq. (20). The previous CI-Kohn estimates [12] include the $J\to\infty$ correction as determined at that time.

J	$\langle\delta\rangle^J$ (radians)	$\langle Z_{\rm eff}\rangle^J$
0	−0.199 209 766 4	0.452 953 759 7
1	−0.010 022 157 05	1.018 467 362
2	0.053 398 005 96	1.466 777 767
3	0.081 756 047 07	1.798 430 751
4	0.096 267 354 69	2.043 817 341
5	0.104 382 919 1	2.228 559 914
6	0.109 233 830 4	2.370 688 616
7	0.112 290 722 5	2.482 386 967
8	0.114 302 363 8	2.571 897 852
9	0.115 675 000 2	2.644 890 677
10	0.116 640 847 2	2.705 331 457
11	0.117 338 626 9	2.756 059 864
12	0.117 854 396 9	2.799 146 079
	$J\to\infty$ limits	
p	3.6248	1.9583
Method p	0.120 065 2	3.340 20
Method p_{av}	0.119 902 0	3.328 23
Method GL	0.119 669 1	3.294 64
Method I	0.119 759 3	3.316 75
Method II	0.119 948 4	3.327 50
Method III	0.119 945 6	3.300 92
Method S	0.119 883 4	3.219 89
	Other calculations	
CI-Kohn $J\to\infty$ [12]	0.1198	3.232
Optical potential [35,52]	0.1201	3.327
Variational[a] [14,36,53]	0.1198	3.407
Close coupling [54,55]	0.1191	3.332

[a]The variational results of van Reeth *et al.* [36,53] are only given in tabular form in [14].

pected asymptotic limit from below. The two calculations give almost exactly the same p_δ while the larger calculation tends to give smaller values of p_Z with the difference becoming greater as J increases. The increasing difference between p_Z for the two calculations suggests that a converged calculation of $\Delta Z_{\rm eff}^J$ needs an increasingly larger radial basis as J increases. This point is addressed in more detail later. In most of the calculations we have performed, the values of p derived from Eq. (20) have been slightly smaller than the expected value at $J\approx 10$ [5–7,13]. We also note that in all the calculations we have so far performed, the values of p increase steadily (once the broad features of the physical system have been achieved) as J increases. While the asymptotic increments to δ and $Z_{\rm eff}$ do not agree exactly with

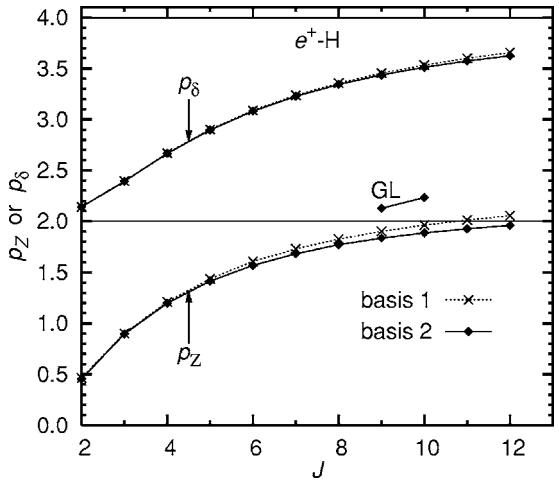

FIG. 1. The exponents p_δ and p_Z as a function of J for two different CI-Kohn calculations of s-wave e^+-H scattering at $k=0.4\ a_0^{-1}$. The short curve labeled GL was plotted using $\langle Z_{\rm eff}\rangle^J$ data of GL [14].

Eqs. (12) and (13), the observed trends do appear to be consistent with their derived limits.

Figures 2 and 3 show the behavior of the extrapolated δ and $Z_{\rm eff}$ as a function of J for some of the different extrapolations. Table I gives estimates of δ and $Z_{\rm eff}$ using the calculated values at the largest possible J value (i.e., 12) to determine the $J\to\infty$ corrections.

There is one problem in interpreting the results of Figs. 2 and 3 and Table I. The exact value of $Z_{\rm eff}$ is imprecise at the level of 2%–3%. The old calculation of Bhatia *et al.* using r_{ij} coordinates gives 3.327 [35,52], the close coupling calculation by Ryzhikh and Mitroy using the T-matrix method gives 3.332 [54,55], while the variational calculation of van Reeth *et al.* gives 3.407 [14,36,53]. There is also some scatter in the estimates of the phase shifts, but the degree of difference between the Bhatia *et al.* and van Reeth *et al.* phase shifts is

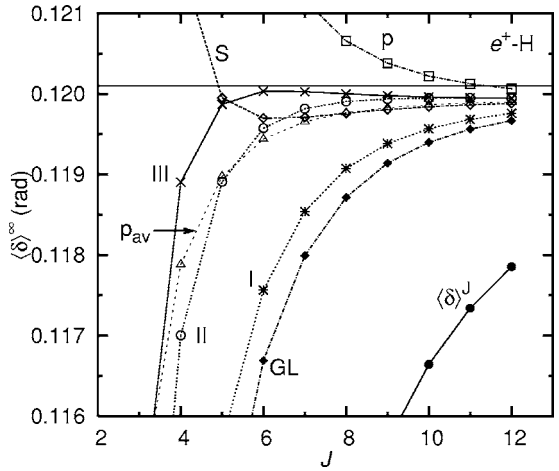

FIG. 2. The extrapolated $J\to\infty$ limit of the phase shift (in radians) δ for e^+-H scattering at $k=0.4\ a_0^{-1}$ as a function of J. The horizontal solid line shows the phase shift of Bhatia *et al.* [35]. The phase shift without any $J\to\infty$ correction is given by the curve labeled $\langle\delta\rangle^J$.

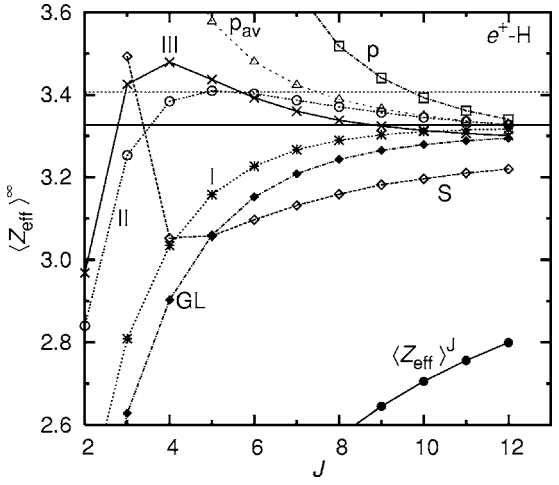

FIG. 3. The extrapolated $J\to\infty$ limit using the different methods to complete the partial wave series for the e^+-H $Z^J_{\rm eff}$ at $k=0.4\ a_0^{-1}$ as a function of J. The horizontal solid line shows the $Z_{\rm eff}$ of Bhatia *et al.* [52] while the horizontal dotted line shows the $Z_{\rm eff}$ of van Reeth *et al.* [14,36,53].

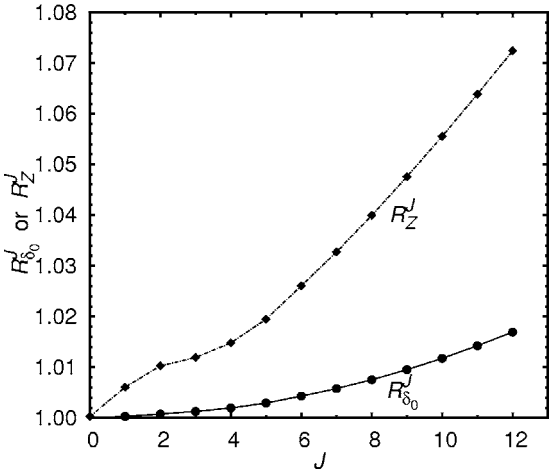

FIG. 4. The ratio of the increments to $\langle\delta\rangle^J$ and $\langle Z_{\rm eff}\rangle^J$ [refer to Eq. (24)] for e^+-H scattering at $k=0.4\ a_0^{-1}$ as a function of J for the 17 and 30 LTO calculations.

only 0.3%. (The T-matrix phase shift is only expected to have an accuracy of about 1% [54].)

Figure 2 shows that inclusion of the $J\to\infty$ correction leads to greatly improved estimates of $\langle\delta\rangle^\infty$. In terms of their impact, the methods belong to three operational classes. First, method p consistently gives the largest values of $\langle\delta\rangle^\infty$. Fixing p_δ to a set value at a finite J inevitably results in the $J\to\infty$ correction being overestimated. For example, using $p_\delta=3.343$ at $J=8$ to fix p_δ for all J results in increments to $\Delta\delta^J$ that do not decrease quickly enough. Methods I and GL, on the other hand, tend to underestimate the size of the $J\to\infty$ correction since $p_\delta=4$ is fixed prior to the sequence of $\Delta\delta^J$ increments achieving the expected $(J+\frac{1}{2})^{-4}$ form.

Those methods which attempt to allow for deviations from the leading order behavior, namely methods II, III, and p_{av}, approach the expected $J\to\infty$ limit much earlier. Indeed, their estimates of $\langle\delta\rangle^\infty$ differ by less than 0.5% at $J=6$. Table I reveals that these three methods give $\langle\delta\rangle^\infty$ estimates that differ by less than 0.1% at $J=12$. Of the three alternatives, the three-term asymptotic series, namely method III, seems to possess the best convergence properties. Method S also appears to give a reasonable estimate of $\langle\delta\rangle^\infty$ when $J\geqslant 6$.

The tabulated estimates of $\langle\delta\rangle^\infty$ at $J=12$ reflect the discussions in the above paragraph. Method p gives the largest phase shift while methods GL and I give the smallest phase shifts. The maximum difference between any of the phase shifts is only 0.3% since the net effect of the $J\to\infty$ contribution to the phase shift is only 2%.

Figure 3 for $Z_{\rm eff}$ shows some features in common with Fig. 2. Once again, application of a $J\to\infty$ correction is seen to give much improved estimates of the $\langle Z_{\rm eff}\rangle^\infty$ limit. Method p also gives the largest estimate of $Z_{\rm eff}$. Method S gives values of $\langle Z_{\rm eff}\rangle^\infty$ that are generally the smallest, and Table I reveals that it gives a value that is 0.1 smaller than any of the other approaches at $J=12$. It is not surprising that a method based on a fitting function with no physical justification performs so poorly, and its reasonable estimate of $J\to\infty$ correction to the phase shift can be regarded as a numerical coincidence. No further discussion of method S will be made although values are reported in the later tables for reasons of completeness.

A more detailed analysis and discussion of Fig. 3 cannot be made until the convergence properties of the underlying radial basis are exposed.

C. Convergence properties of the radial basis

In addition to converging very slowly with J, the annihilation rate also converges slowly with respect to the number of radial basis functions since the actual wave function has a cusp at the electron-positron coalescence point. A previous CI investigation on helium in an $\ell=0$ model indicates that the electron-electron δ-function converged as $O(N^{-5/2})$ where N is number of Laguerre orbitals [56]. It has also been demonstrated that the relative accuracy of the electron-electron δ-function increment for a given size radial basis decreased as L increased [57].

Some sample ratios can be used to illustrate these points. The ratio R^J_Z compares the two calculations of $\Delta Z^J_{\rm eff}$ for e^+-H scattering by determining the ratio for basis 1(17 LTOs) and basis 2(30 LTOs). It is defined as

$$R^J_Z=\frac{(\Delta Z^J_{\rm eff})_{30}}{(\Delta Z^J_{\rm eff})_{17}}. \tag{24}$$

A similar ratio, R^J_δ, can be defined for the increment to the phase shifts. A plot of these two ratios is given in Fig. 4, while Table II lists values of R^J_δ and R^J_Z for some selected J values. Figure 4 clearly demonstrates that $\Delta Z^J_{\rm eff}$ converges more slowly than the phase shift increments at large J. First, the annihilation rate is more sensitive to the size of the radial basis than is the phase shift. Second, the higher partial waves are more sensitive to the size of the radial basis than the lower partial waves. For example there was a 4.0% increase in $\Delta Z^8_{\rm eff}$ between the basis 1 and basis 2 calculations while

TABLE II. Ratios of the partial wave increments to the energy (or phase shift); annihilation rate (or $Z_{\rm eff}$) taken from the two different basis sets used for each system.

J	R_δ	R_Z
	e^+-H	
6	1.0043	1.0261
8	1.0075	1.0399
10	1.0117	1.0556
12	1.0169	1.0724
J	R_E	R_Γ
	e^+Cu	
8	1.0100	1.0288
12	1.0258	1.0552
16	1.0477	1.0869
	PsH	
4	1.0096	1.0478
6	1.0114	1.0825
9	1.0626	1.1357

there was a larger 7.2% increase in $\Delta Z_{\rm eff}^{12}$. However, the increase in $\Delta\delta^{12}$ was only 1.7%.

Since the lack of completeness in the radial basis has the largest impact at high J, it will obviously affect the $J\to\infty$ correction. For example, method II gives $\Delta Z_{\rm eff}^{J>12}=0.4695$ for basis 1. For basis 2, the correction of $\Delta Z_{\rm eff}^{J>12}=0.5284$ is significantly larger.

The implications of these results can be seen by consideration of the method II plot of $Z_{\rm eff}^{\infty}$ depicted in Fig. 3. This achieves a maximum value of 3.41 at $J=5$, and then decreases until it is 3.328 at $J=12$. The question to be addressed is whether the decrease from $J>6$ is due to convergence properties of the calculation with respect to J or the convergence properties of the basis with respect to N, the number of orbitals per ℓ? Although there are seven estimates of $Z_{\rm eff}$ that lie between 3.30 and 3.34 in Table I, we believe that the true value of $Z_{\rm eff}$ lies closer to 3.407 (the value of van Reeth *et al.*) than to 3.327 (the value of Bhatia *et al.*).

This interpretation is supported by a crude estimate of the variational limit deduced from Fig. 4. The assumption is made that the $\Delta Z_{\rm eff}^J$ increments converge as $O(N^{-5/2})$ [56]. Consequently, one deduces that the plotted R_Z^J ratios comprise some 57% of the necessary correction to the variational limit. The variational limit for any increment is then estimated to be $\Delta Z_{\rm eff}^J\times[1+0.43\times(R_Z^J-1)/0.57]$. Applying this correction to the data in Table I gives $\langle Z_{\rm eff}\rangle^{\infty}=3.410$ when method II is used to estimate the $J\to\infty$ limit (the actual correction of $\Delta Z_{\rm eff}^{J>12}$ of 0.578 was about 9% larger than the basis 2 value). Determination of the variational limit for the phase shift can also be done by assuming that the $\Delta\delta^J$ increments converge as $O(N^{-7/2})$ [56]. In this case, the plotted R_δ^J ratios comprise some 76% of the correction to the variational limit and thus the final estimates of the phase shift increments would be $\Delta\delta^J\times[1+0.24\times(R_\delta^J-1)/0.76]$. The method II phase shift only increased by 1.3×10^{-5} rad giving $\langle\delta\rangle^{\infty}=0.12008$ rad.

One point from Table I warrants special attention. The three-term asymptotic series, namely method III, gives a smaller $\langle Z_{\rm eff}\rangle^{\infty}$ than method I. This seems ridiculous given that $p=1.9583$ at $J=12$. The tendency for the $\Delta Z_{\rm eff}^J$ increments to be systematically underestimated results in the corruption of the B_Z, C_Z, and D_Z coefficients extracted from the three-term fit and renders method III unreliable for determination of $\langle Z_{\rm eff}\rangle^{\infty}$.

Even though data for only one system have been presented, it is possible to make some general comments about the performance of the difference methods since analysis of the e^+Cu and PsH data will confirm these conclusions (they are also compatible with the results of large basis CI calculations of He [57]).

Since the p_δ and p_Z exponents tend to be smaller than 4 and 2, respectively, at finite J, method p has an inherent tendency to overestimate the $J\to\infty$ corrections. Application of this approach in the past has not resulted in any gross errors since the problems associated with fixing p at values less than 2 and 4 tend to cancel out the errors associated with a radial basis of finite size p [7]. This method should only be applied in situations when the asymptotic form of the expectation value under investigation is unknown.

Method I generally underestimates the $J\to\infty$ correction. It gives a useful estimate of the $J\to\infty$ correction and should mainly be applied to give rough estimates for low precision calculations. Method GL can be regarded as a variety of method I that happens to give inferior $J\to\infty$ corrections.

Methods II and p_{av} were seen to give $J\to\infty$ corrections that were close to each other once the calculation reached a certain value of J. Method II should be preferred since it is founded in correct asymptotics.

Method III seems to give the earliest reliable estimate of the phase shift. However, it should not be applied to the annihilation rate unless the radial basis is substantially larger than the present basis. Method III should only be applied in situations where the underlying partial wave increments have an accuracy of better than 1% and in addition the increments should vary smoothly and not exhibit fluctuations.

D. The e^+Cu ground state

Table III gives the e^+Cu binding energy and annihilation rate as a function of J up to $J=18$ for the calculation with 25 LTOs. The table also includes values from a calculation with the fixed core stochastic variation method (FCSVM) [8,58]. The FCSVM basis includes the electron-positron coordinate explicitly and is very close to convergence. The FCSVM calculation uses a slightly different model potential so it is not expected that the CI energy and Γ should be exactly the same. Figure 5 displays p_E and p_Γ versus J for two different CI calculations of the e^+Cu ground state. One plot is derived from the earlier calculation of Bromley and Mitroy [12] which included a minimum of 15 LTOs per ℓ value (basis 1). The present calculation (basis 2) is much larger with a minimum of 25 LTOs per ℓ value (note, more than 25 LTOs were included for $\ell=0$, 1, and 2 since these make the largest contribution to the energy and annihilation rate).

The plots of p_E and p_Γ against J for e^+Cu are similar to the plots of p_δ and p_Z for e^--H scattering. Both exponents are

TABLE III. Results of CI calculations on e^+Cu vs J for the energy and annihilation rate for a series of J. The binding energy of the positron to neutral Cu is denoted ε (the energy of Cu with respect to the core was −0.283 942 27 hartree [8]). The spin-averaged 2γ annihilation rates are given for the core (Γ_c) and valence (Γ_v) electrons. The results in the row ∞ include the $J\to\infty$ correction evaluated at $J=18$ using the various methods described in the text.

J	ε (hartree)	Γ_c (10^9 s^{-1})	Γ_v (10^9 s^{-1})
0	−0.001 124 67	0.000 289	0.000 132
1	−0.000 802 92	0.001 443	0.001 692
2	−0.000 373 56	0.004 818	0.009 728
3	0.000 311 79	0.011 213	0.033 656
4	0.001 119 95	0.017 605	0.070 360
5	0.001 879 58	0.022 223	0.110 121
6	0.002 517 36	0.025 271	0.147 793
7	0.003 028 52	0.027 272	0.181 727
8	0.003 431 36	0.028 611	0.211 657
9	0.003 747 74	0.029 526	0.237 830
10	0.003 996 92	0.030 168	0.260 656
11	0.004 194 29	0.030 627	0.280 571
12	0.004 351 74	0.030 963	0.297 984
13	0.004 478 32	0.031 212	0.313 256
14	0.004 580 86	0.031 402	0.326 694
15	0.004 664 56	0.031 547	0.338 564
16	0.004 733 38	0.031 660	0.349 087
17	0.004 790 37	0.031 749	0.358 454
18	0.004 837 88	0.031 821	0.366 821
	$J\to\infty$		
p	3.2751	4.0511	2.0295
Method p	0.005 201 2	0.032 219	0.513 07
Method p_{av}	0.005 148 1		0.515 26
Method GL	0.005 099 8		0.513 25
Method I	0.005 108 0		0.517 51
Method II	0.005 158 4		0.515 29
Method III	0.005 160 3		0.493 64
Method S	0.005 139 4		0.463 98
	Earlier calculations		
FCSVM [8,58]	0.005 597	0.0339	0.544
CI, $J=18$ [8]	0.004 786	0.031 73	0.354 99
CI, $J\to\infty$ [8]	0.005 117	0.0321	0.4744

generally smaller than the expected asymptotic limits but steadily increase as J increases. The actual value of p_Γ at $J=18$, namely 2.030, was marginally larger than the expected asymptotic limit of $p_\Gamma=2$. The estimates of $\langle\varepsilon\rangle^\infty$ and $\langle\Gamma\rangle^\infty$ as a function of J are shown in Figs. 6 and 7.

Table III reveals an 8% increase in Γ when compared with the earlier CI calculation value of Γ, namely 0.474 $\times 10^9$ s^{-1} [8]. This is a consequence of the bigger radial basis used in the present work. The selected values of R_Γ^J listed in Table II reveal an 8.7% increase in $\Delta\Gamma^{16}$ for basis 2 compared to basis 1. It is expected that further increases in the radial basis would eventually lead to a p_Γ that was smaller than 2.0 at all $J=18$. Again it is noticed that R_Γ^J (and R_E^J) increase with increasing J.

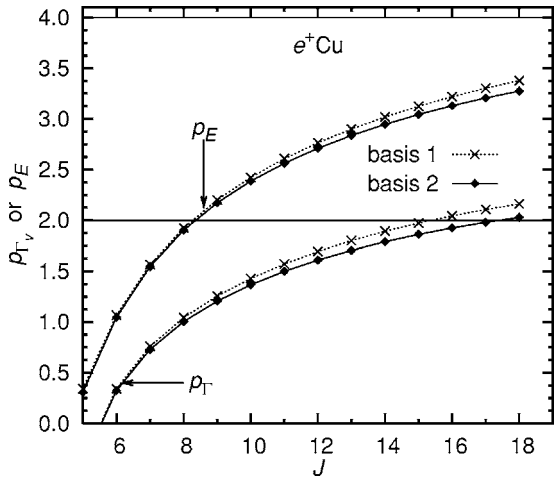

FIG. 5. The exponents (p_E and p_Γ) for two different CI calculations of e^+Cu as a function of J.

The estimates of the annihilation rate in Table III are all very close together (with the exception of method III). This occurs because $p_\Gamma=2.030$ is very close to the expected value of 2.0. The variations between the different approaches are largely concerned with taking care of the deviations from the $p_\Gamma=2$ behavior and, with a minimal deviation at $J=18$, one should expect minimal differences between the final results. Method III is the least accurate (discounting method S) since it is the most susceptible to the inaccuracies in $\Delta\Gamma^J$.

Figure 7 shows that method p systematically overestimates $\langle\Gamma\rangle^\infty$ at smaller values of J. Method I, on the other hand, generally gives the smallest estimates of the $\langle\Gamma\rangle^\infty$ and is consistently too small at lower J.

Method III obtains a reasonable estimate of $\langle\varepsilon\rangle^\infty$ the quickest. Beyond $J>12$ the method III binding energy does

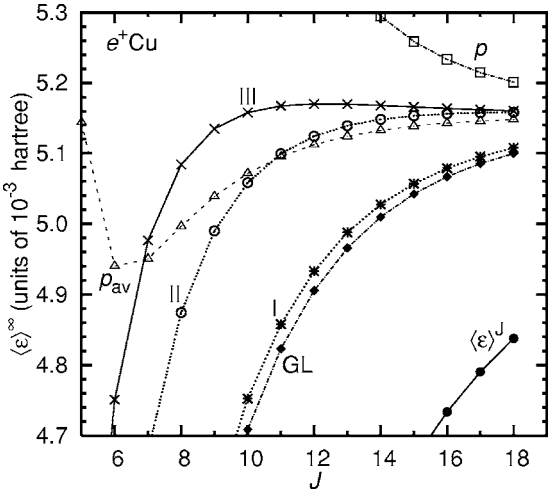

FIG. 6. The e^+Cu binding energy as a function of J. The different curves use different algorithms to estimate the $J\to\infty$ correction as discussed in the text.

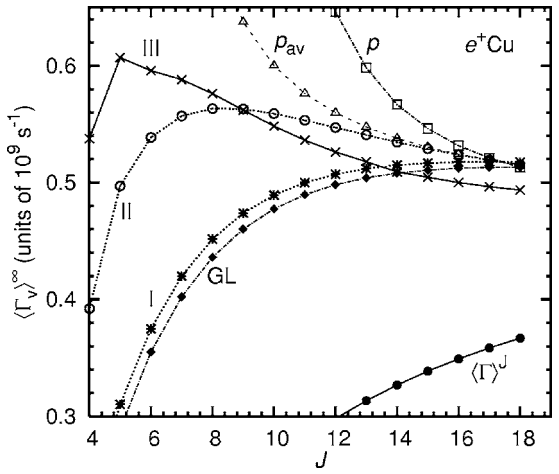

FIG. 7. The e^+Cu annihilation rate (in units of 10^9 s^{-1}) as a function of J. The different curves use different algorithms to estimate the $J\rightarrow\infty$ correction as discussed in the text.

decrease slightly. This may be due to slower convergence of the radial basis at higher J. Methods II and p_{av} give roughly equal estimates of $\langle\varepsilon\rangle^\infty$ for $J>10$, and the spread between the methods II, III, and p_{av} estimates of $\langle\varepsilon\rangle^\infty$ is only 0.2% at $J=18$.

Method p gives the largest estimate of $\langle\varepsilon\rangle^\infty$ for all J shown in Fig. 6, while methods I and GL give the smallest values (with method GL once again being worse that method I). It is worth mentioning that methods II, III, and p_{av} are all roughly constant after $J=16$ while methods I, GL, and p are still increasing or decreasing.

In summary, the totality of information in Table III and Figures 5–7 is very reminiscent of the situation for e^+-H scattering and is consistent with the conclusions derived from the analysis of e^+-H scattering.

E. The PsH ground state

The best two-electron system for validation purposes is the positronium-hydride (PsH) system since its properties are very well known as a result of previous investigations [28,59–61]. The stochastic variational method (SVM) expectation values listed in Table IV are taken from a new calculation with 1800 ECGs. The energy of this wave function, $E=-0.789\,167\,4$ hartree is the lowest variational energy for PsH$^\infty$ that has so far been reported [59]. A low precision experimental determination of the binding energy of PsH into dissociation into Ps+H does exist [62] (1.1 ± 0.2 eV) that is compatible with the theoretical estimates ($\approx$0.0389 hartree=1.06 eV).

The orbital basis used in the present calculation was about twice as large as that used in previous calculations [5,9]. The number of radial functions per ℓ was 15 with the exception of $\ell=0$ and $\ell=1$, where 17 and 16 functions, respectively, were used. The largest J was 13 while $L_{\rm int}$ was set to 4. The basis functions for each ℓ used a common exponent that had been energy optimized during some preliminary and smaller calculations. It must be emphasized that choosing a common λ for both electron and positron states was not arbitrary but was a consequence of energy optimization process. The results of the CI calculation are listed in Table IV.

TABLE IV. Results of CI calculations on PsH for orbital bases with $L_{\rm int}=4$ and for a series of J. The total number of electron and positron orbitals is denoted by $N_{\rm orb}$, the total number of configurations is given by $N_{\rm CI}$, and the LTO exponent for $\ell=J$ is listed in the λ column. The three-body energy of the PsH system in hartree is denoted by E(PsH) and the Γ is given in 10^9 s^{-1}. The $J\rightarrow\infty$ extrapolations were carried out at $J=13$.

J	λ	$N_{\rm orb}$	N_{CI}	E(PsH)	Γ
0	2.10	17	2601	−0.691 336 18	0.374 196
1	2.26	33	9265	−0.747 059 69	0.782 256
2	2.36	48	22 810	−0.766 200 31	1.080 456
3	2.46	63	44 650	−0.775 141 28	1.292 538
4	2.52	78	78 640	−0.779 952 86	1.448 216
5	2.72	93	120 265	−0.782 744 94	1.566 206
6	2.93	108	165 265	−0.784 495 97	1.658 344
7	3.13	123	213 415	−0.785 652 20	1.732 023
8	3.34	138	263 365	−0.786 445 38	1.792 061
9	3.56	153	314 890	−0.787 006 39	1.841 756
10	3.75	168	366 415	−0.787 413 30	1.883 366
11	3.95	183	417 940	−0.787 714 85	1.918 595
12	4.15	198	469 465	−0.787 942 47	1.948 689
13	4.35	213	520 990	−0.788 117 07	1.974 632
			$J\rightarrow\infty$ limits		
p				3.445 47	1.923 75
Method p				−0.788 997 4	2.3352
Method p_{av}				−0.788 899 5	2.3232
Method GL				−0.788 789 4	2.2988
Method I				−0.788 819 8	2.3121
Method II				−0.788 921 8	2.3225
Method III				−0.788 923 1	2.2915
Method S				−0.788 884 3	2.2203
			Other calculations and earlier CI calculations		
SVM [59]				−0.789 196 74	2.4712
$J=9$, $L_{\rm int}=4$ [5]		90/91	63 492	−0.786 681 8	1.7903
$J=9$, $L_{\rm int}=9$ [5]		90/91	95 324	−0.786 776 1	1.7913
$J=9$ [9]		∞	∞	−0.786 949	1.8230

The variation of p_E and p_Γ with J in Fig. 8 reflects the behavior seen in Figs. 1 and 5. The values of p are smaller than the predicted asymptotic limits and seem to be approaching the correct value. Computational constraints mean that the dimensions of the radial basis, e.g., 15 e^+ and e^- LTOs per ℓ, are smaller than those in the e^+-H and e^+Cu calculations. The PsH radial basis is further from convergence than the basis sets used for the equivalent calculations upon e^+-H and e^+Cu.

Figure 8 gives p values taken from the CI calculations of Saito [9]. Saito used natural orbital techniques to reduce the dimension of the final diagonalization while using an orbital basis with $J=9$ (this is about the same size as in [5]). Saito estimated the variational limit at each J and the curves in

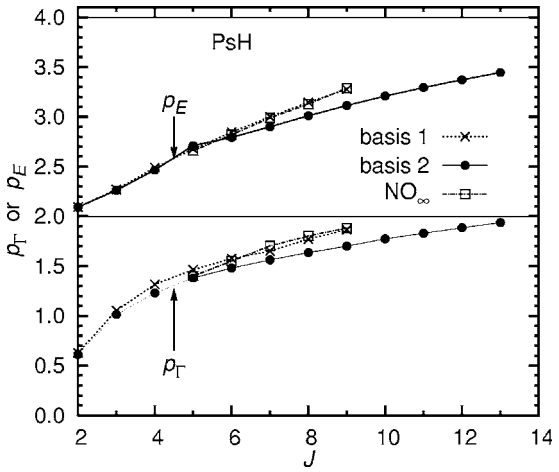

FIG. 8. The exponents p_E and p_Γ as a function of J for two different CI calculations of PsH. Both the basis 1 and basis 2 with $L_{\text{int}}=4$. The third data set was taken from the "full CI" calculations of Saito [9].

Fig. 8 were derived from this "full CI limit" calculation. Although the Saito curves have irregularities, they exhibit a p vs J variation similar to the early Bromley and Mitroy calculation [5].

Figure 9 shows the variation of $\langle\varepsilon\rangle^\infty$ vs J. Once again, the three-term series, method III achieves its asymptotic value at the smallest value of J. Methods II and p_{av} achieve their limiting values near $J=10$. Methods I and GL again tend to underestimate $\langle\varepsilon\rangle^\infty$ while method p overestimates $\langle\varepsilon\rangle^\infty$.

The best CI estimate of the PsH energy is obtained by adding an L_{int} correction of 9.5×10^{-5} hartree (the difference between the $L_{\text{int}}=4$ and $L_{\text{int}}=9$ energies [5]) to the method III ε of 0.038 923 hartree. The resulting binding energy of $\varepsilon=0.039\,018$ hartree is only 0.38% smaller than the SVM ε of 0.039 167 4 hartree.

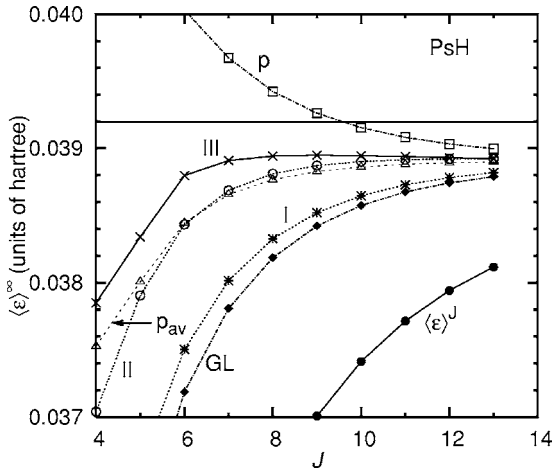

FIG. 9. The PsH binding energy (in units of hartree) with respect to the Ps+H threshold of −0.750 hartree as a function of J. The different curves use different algorithms to estimate the $J\to\infty$ correction as discussed in the text. The close to converged SVM energy [59] is shown as the horizontal line for comparison purposes.

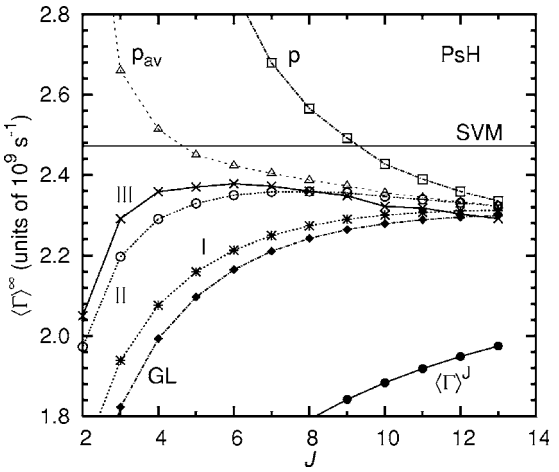

FIG. 10. The PsH annihilation rate ($\langle\Gamma\rangle^\infty$ in units of 10^9 s^{-1}) as a function of J. The close to converged SVM annihilation rate is shown as the horizontal line.

Figure 10 shows the annihilation rate versus J. The CI calculation does not converge to the SVM annihilation rate since a radial basis of 15 LTOs per ℓ is simply too small. The R_Γ^J entries in Table II reveal a 13.5% increase in $\Delta\Gamma^9$ between the basis 1 and basis 2 calculations. The conclusions that can be drawn from Table IV under such circumstances are somewhat limited. But method III is again susceptible to the accuracy of the $\Delta\Gamma^J$ increments and again gives a final $\langle\Gamma\rangle^\infty$ that is smaller than method I. Methods II and p_{av} again give final estimates of $\langle\Gamma\rangle^\infty$ that are close together. Method p gives the largest estimate of $\langle\Gamma\rangle^\infty$ while methods I and GL give the smallest.

Another problem with method III arose from the usage of the Davidson method to perform the matrix diagonalization. This only gives values of $\langle\Gamma\rangle^J$ that are stable to six to seven significant digits and this leads to the irregularities in the $\langle\Gamma\rangle^\infty$ evident in Fig. 10. The problem of decreased precision when using the Davidson algorithm had been previously noted in CI calculations of helium [57] and may be generic to iterative matrix solvers.

IV. COMMENT ON THE SCALING OF THE ANNIHILATION RATE

There is one class of system that has not been studied in the present work, namely the close to threshold scattering of positrons from atoms that can bind a positron. The behavior of the ΔZ_{eff}^J increments is complicated by a parametric dependence on the scattering length, A [8,12,63]. Once J is large enough to formally bind a positron, the magnitude of the scattering length decreases as J increases. Since $Z_{\text{eff}}\propto A^2$, the decrease in A as J increases impinges on the increase in Z_{eff}^J that would otherwise occur. Indeed, one of the reasons why calculations on e^+Cu were originally taken to $J=18$ was to minimize the disruption that the scattering length had on Z_{eff} [8,12].

It was not worthwhile to try and analyze the behavior of the partial wave expansion for the e^++Cu scattering system

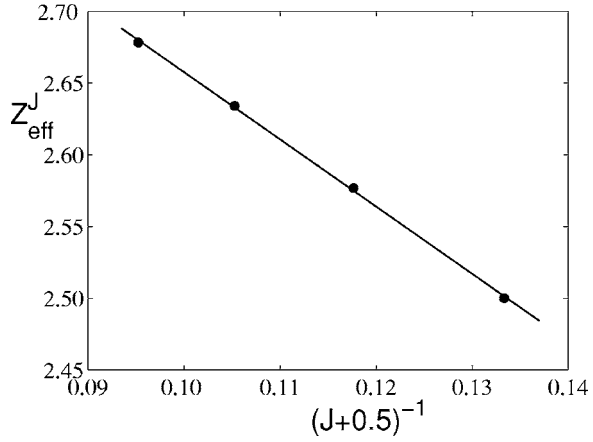

FIG. 11. Plot of $Z^J_{\rm eff}$ vs $\left(J+\frac{1}{2}\right)^{-1}$ for the synthetic data as discussed in the text. The line shows the fit to Eq. (16) while the ● give the synthetic data points with the $\Delta Z^J_{\rm eff}\sim\left(J+\frac{1}{2}\right)^{-2.6}$ dependence. This data sequence is about the same size as the present Kohn $Z^J_{\rm eff}$ data sequence for *s*-wave positron-hydrogen scattering.

with its two major complications, the effect of the radial basis set and, secondly, the effect of the A versus J variation. Such an investigation is best delayed until substantially larger basis sets can be deployed.

V. COMMENTARY ON THE EXTRAPOLATION OF GRIBAKIN AND LUDLOW

The problems caused by the slow convergence of $Z_{\rm eff}$ can be exposed by a detailed analysis of the recent Gribakin and Ludlow [14] calculation of the annihilation rate for e^+-H scattering. This calculation used a variant of many-body perturbation theory (MBPT) to generate the initial set of $\langle Z_{\rm eff}\rangle^J$ data. They then did a fit to Eq. (16) over the $J=7-10$ interval and then plotted the results of that fit under the assumption that this demonstrated that their data obeyed Eq. (16). However, this procedure as applied by GL could hardly have been better suited to concealing deviations of the sequence of $\langle Z_{\rm eff}\rangle^J$ values from the leading order $\left(J+\frac{1}{2}\right)^{-2}$ term (note, in this section the GL acronym refers to the results presented in [14]). In effect, Figs. 7 and 8 of GL are actually a demonstration of Taylor's theorem, namely that any continuous function will approximate a straight line if examined over a sufficiently small domain.

To illustrate this point, consider a sequence of synthetic $\langle Z_{\rm eff}\rangle^J$ data generated by the prescription, $\langle Z_{\rm eff}\rangle^7=2.5$ and $\Delta Z^J_{\rm eff}=20\times\left(J+\frac{1}{2}\right)^{-2.6}$ [such a data sequence could be generated exactly from a three-term expansion of Eq. (14)]. A fit to this sequence was made using Eq. (16) and the results of that fit are shown in Fig. 11. Even though the data were generated according to $p=2.6$, a visual inspection (and it should be noted that Fig. 11 is much higher resolution than Figs. 7 and 8 of GL) suggests that the data are in good agreement with a $p=2$ power law decay whereas this is certainly not the case.

The p_Z exponent derived from the recent GL calculation [14] is depicted in Fig. 1. Although GL assume $p_Z=2$ when making the extrapolation, the actual exponent extracted from their sequence of $Z_{\rm eff}$ values is $p=2.233$ at $J=10$. The present basis 2 calculation gives $p_Z=1.885$ at $J=10$. It is obvious that the GL calculation overestimates the rate at which $\Delta Z^J_{\rm eff}$ increments are decreasing. This implies that the GL estimates of $\Delta Z^J_{\rm eff}$ will be too small at higher J and this is the case. GL get $\Delta Z^{10}_{\rm eff}=0.0501$ while the CI-Kohn calculation gives $\Delta Z^{10}_{\rm eff}=0.0604$. Consequently, the GL calculation gives $\Delta Z^{J>10}_{\rm eff}=0.48$, while the basis 2 CI-Kohn calculation gives $\Delta Z^{J>10}_{\rm eff}\approx 0.62$. The assertion by GL that their calculation has converged to the region in which the $\Delta Z^J_{\rm eff}=B\left(J+\frac{1}{2}\right)^{-2}$ formula is valid is incorrect.

Besides directly leading to less reliable extrapolation corrections, a related problem with the GL procedure is that it does not have the sensitivity to flag potential problems with the radial basis. A plot of p_Z vs J that crosses the $p_Z=2$ line is a good indicator of some inadequacy in the basis. There is no indication that GL were aware that their $\Delta Z^J_{\rm eff}$ were decreasing much too quickly as J increased; their statement that "the use of a B-spline basis means that fast convergence is achieved with respect to the number of states with a particular angular momentum" is difficult to reconcile with the present analysis. However, it should be noted that they do indicate that they could improve the quality of their answers by "pushing harder the numerics."

The tendency for the GL calculation to overestimate the convergence of the annihilation rate increments probably does not arise from MBPT *per se*, rather it most likely comes from the underlying single electron basis. Besides the inherently slower convergence at higher J mentioned earlier, another possibility is due to the confinement of the basis to a box of radius 15 a_0. Confining the basis in this way will result in mean excitation energies (e.g., for predicting the multi-pole polarizabilities) that will eventually increase as $\sim\ell^2$, where ℓ is the orbital angular momentum, while for a real H atom the mean excitation energy for any ℓ is less than 1.0 hartree [64]. Thus the occupancy of the higher J orbitals, which contribute significantly to $Z_{\rm eff}$, will be inhibited, and successive $\Delta Z^J_{\rm eff}$ will decrease too rapidly with increasing J.

The relevance of these issues is best illustrated by a comparison with the exact value of $Z_{\rm eff}$ which will be taken to be 3.407 at $k=0.4\ a_0^{-1}$. This is 0.295 larger than the GL value of 3.112. The underestimation of the higher partial wave contribution in the GL calculation, estimated at $0.14=0.62-0.48$ is responsible for about 50% of the existing discrepancy.

The discrepancies of GL with the best calculations are not that severe for *s*-wave scattering since imposition of the $p=2$ condition for $J\geqslant 10$ prevents the inherent deficiencies in their B-spline basis from becoming too excessive. Also an *s*-wave e^+-H scattering system is certainly one of the easier positron annihilation calculations. However, the inadequacy of the GL methodology manifests itself more severely in other positron annihilation situations.

The CI expansion converges quicker for electron-positron annihilations that take place at small distances from the nucleus than for annihilations that take place at large distances [8,13,25]. The presence of the centrifugal barrier for $L>0$ scattering leads to the electron-positron annihilations occurring further from the nucleus. Consequently the conver-

gence problem is more serious for p- and d-wave scattering since a proportionally larger part of $Z_{\rm eff}$ comes from the $J \rightarrow \infty$ correction [12,13]. We have not repeated the earlier p-wave calculations [12] with a larger radial basis, but a comparison with the CI-Kohn data at $k=0.4\ a_0^{-1}$ indicates that the GL calculation again underestimates the impact of the high J orbitals. The CI-Kohn calculation reported in [12] gave $\Delta Z_{\rm eff}^{10}=0.0480$ while the GL calculation gave 0.0416. In addition, the CI-Kohn calculation gave $p=1.852$ for $J=10$ while the GL calculation gave $p=2.152$ (it is likely that an infinite basis CI-Kohn calculation would have $p<1.80$ at $J=10$). The GL calculation (which gave $Z_{\rm eff}=1.607$) underestimates the $L=1$ $Z_{\rm eff}$ by about 0.18 at $k=0.4\ a_0^{-1}$ (the T-matrix calculation gives 1.786 [54,55] while van Reeth *et al.* gave 1.794 [14,36,53]). It is likely that at least 0.10 of the discrepancy will arise from orbitals with $J \geqslant 10$.

One of the major results of the GL calculations was their demonstration that the enhancement factor is independent of energy. The enhancement factor can be defined as the factor that the annihilation rate, calculated as a simple product of the electron and positron densities, needs to be increased in order to agree with the exact annihilation rate [13,63,65]. They (GL) based this conclusion solely on a forensic analysis of the $Z_{\rm eff}$ annihilation rate matrix element. Figure 13 of GL reveals that the variation of the d-wave enhancement factor with energy is noticeably larger than either the s- or p-wave enhancement factor [14]. Since a larger fraction of the d-wave $Z_{\rm eff}$ comes from $J \geqslant 10$, the possibility exists that this stronger energy dependence is due to extrapolation issues as opposed to dynamical effects. Although GL seem unaware of the result, the slow variation of the enhancement factor with energy had been demonstrated in a model potential analysis [63]. Comparisons of model potential calculations with *ab initio* variational and polarized orbital calculations had shown that a model potential calculation tuned to reproduce the energy dependence of the phase shifts also gave the energy dependence of $Z_{\rm eff}$ [63]. The variation of the d-wave enhancement factor was determined by tuning a model potential to the large basis phase shifts of [66] and then normalizing to a similar calculation of $Z_{\rm eff}$ [55]. The variation in the d-wave enhancement factor over the energy range from $k=0$ to $0.5\ a_0^{-1}$ was less than 4%. Although the model potential result is not conclusive, it does appear that the variation in the d-wave $Z_{\rm eff}$ is less than that indicated by the GL calculation.

Another area where application of the GL methodology could lead to larger than anticipated errors is in the determination of the angular correlation or the γ energy spectrum [67]. These two properties depend on the relative momentum of the annihilating electron-positron pair [60,68]. It is known from investigations of momentum space wave functions that the low momentum part of the wave function largely arises from the large r part of the wave function while the high momentum properties come from the small r part of the wave function [69]. Under such circumstances, application of the GL method could easily result in errors to the $J \rightarrow \infty$ corrections that depend systematically on the γ-energy or recoil momentum.

VI. SUMMARY AND CONCLUSIONS

Single center methods represent a superficially attractive method to study mixed electron positron systems since existing computer codes can be adapted without too much effort. The penalty associated with this approach is the slow convergence of the binding energy and, more noticeably, the annihilation rate with respect to the partial wave expansion of the single particle basis. The results presented here are generally consistent with the asymptotic limits derived from second-order perturbation theory by Gribakin and Ludlow [43]. The actual calculations at finite J generally give increments to the energy (phase shift) and annihilation rate that decrease slightly slower than the GL limits, but the overall trends are compatible with the GL limits.

The tendency for the convergence with respect to the radial basis size to slow down as J increases does have implications for the design of any CI-type calculation. Some sort of extrapolation in J is necessary in order to determine the energy and more particularly the annihilation rate. But there is no point in making J bigger if this is done at the expense of the radial basis set. One simply ends up with increments to the energy or annihilation rate which are systematically too small at higher J. This problem does not seem to be restricted to the LTO basis used in the present work. Convergence problems at high J are also present for the Gribakin and Ludlow calculations which used a B-spline basis [14] and the Saito calculations which used a natural orbital basis [9,11,37]. It is amusing to note that one of the first manifestations of this problem occurred over 40 years ago [44,70].

The best methods for estimating the $J \rightarrow \infty$ corrections depends on the quality of the underlying calculation. For a low precision calculation, method I would seem to be appropriate. A low precision calculation can probably be regarded as one with p_E or p_Γ exceeding 4 or 2, respectively, when the $J \rightarrow \infty$ correction is evaluated (assuming that p approaches its limiting value from below). Method II or III would seem to be the preferred options for a high precision calculation. As a general principle, inclusion of the second term in the asymptotic series leads to improved $\langle X \rangle^\infty$ predictions when compared with asymptotic series with the single term series. Method III is more susceptible to imperfections in the radial basis and should not be applied to the calculation of the annihilation rate unless a very large radial basis set is employed. Irrespective of how the $J \rightarrow \infty$ corrections are evaluated, it is essential that the exponents p relating the changes in the expectation values be examined as a test of the quality of the radial basis.

The overall situation regarding the use of single center methods to compute positron-atom phase shifts or energies is that calculations to the sub-1% accuracy level are achievable for those systems that have a parent atom ionization potential greater than 0.250 hartree. The use of CI methods is not recommended for atomic systems such as e^+Li or e^+Na which contain a loosely bound Ps cluster [8,25]. Here, explicitly correlated basis sets remain the best option (assuming that it is actually possible to do a calculation). The $O(\left(J+\frac{1}{2}\right)^{-4})$ convergence means a J of 10 or slightly larger will generally suffice as long as the method used to perform the $J \rightarrow \infty$ correction is more sophisticated than those used

previously. However, the situation with respect to the annihilation rate is much grimmer and it is not possible to guarantee 1% accuracy for even the simple e^+-H system. Here the $O((J+\frac{1}{2})^{-2})$ convergence means the $J\to\infty$ correction is larger, and moreover the slow convergence with respect to the radial basis is further complicated by the fact that it is slower at high J than low J. In this case, it appears that "God is on the side of the big basis set" [71].

The conclusions that have been derived should be applicable for all calculation methods that use a single center basis with one possible complication. Methods that use a bounded cavity basis need further examination. The extent to which the finite cavity radius can impact on the convergence of the partial wave series is unknown and deserves investigation. It would also be worthwhile to investigate whether alternate forms of the annihilation operator that depends more on the global properties of the wave function [72,73] has a faster convergence pattern.

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