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Computation of Bethe Logarithms and Other Matrix Elements of Analytic Functions of Operators

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A general method is given for the calculation of a matrix element $\langle\varphi|\, f(A)\, |\psi\rangle$ of an analytic function f of an operator A. The method begins by writing $\langle\varphi|\, f(A)\, |\psi\rangle$ as a contour integral of the corresponding matrix element $\langle\varphi|\, (\zeta - A)^{-1}\, |\psi\rangle$ of the resolvent $(\zeta - A)^{-1}$, where the contour surrounds the spectrum of A. The contour is then deformed to obtain $\langle\varphi|\, f(A)\, |\psi\rangle$ as a sum of contributions from branch points and poles of f. The numerical evaluation of the Bethe logarithm, which is the dominant contribution to the Lamb shift, is used as an example. The difficulties which arise when the resolvent matrix element $\langle\varphi|\, (\zeta - A)^{-1}\, |\psi\rangle$ must be evaluated by approximate methods are discussed.

1. INTRODUCTION

A matrix element $\langle\varphi| f(A)\, |\psi\rangle$ of a function f of an operator A can be quite difficult to compute when the function is anything more complicated than a low order polynomial. The obvious approach of diagonalizing the operator to obtain the matrix element as a sum over states of the form

$$\langle\varphi| f(A)\, |\psi\rangle = \sum_i f(a_i)\langle\varphi \mid e_i\rangle\langle e_i \mid \psi\rangle, \tag{1.1}$$

where the a_i and $|e_i\rangle$ are the eigenvalues and eigenfunctions of A, can be ineffective if the sum over i converges too slowly or contains continuum contributions which

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are hard to handle. It fails completely if A cannot be diagonalized. The present paper will present an alternative method which works when the function f is analytic in a neighborhood of the spectrum of A if the matrix element $\langle\varphi|\,(\zeta - A)^{-1}\,|\psi\rangle$ of the resolvent of A can be calculated at the singularities of f.

This alternative method begins by writing the desired matrix element as a Cauchy integral in the complex ζ plane:

$$\langle\varphi| f(A)\,|\psi\rangle = \frac{1}{2\pi i} \oint_C d\zeta \left[f(\zeta)\langle\varphi|\,\frac{1}{\zeta - A}\,|\psi\rangle - g(\zeta) \right]. \tag{1.2}$$

Here the contour C surrounds the spectrum of A. $f(\zeta)$ and $g(\zeta)$ are assumed to be analytic within and on C. The only singularities inside the contour C are then the singularities of the resolvent at the points of the spectrum of A. The function $g(\zeta)$ contributes nothing when the right-hand side of (1.2) is evaluated as a sum of contributions from the singularities inside C, but may be needed to permit deforming the contour C into a new contour C' which surrounds the singularities of f and g. If such contour deformation can be carried out, a formula for the matrix element $\langle\varphi| f(A)\,|\psi\rangle$ as a sum of contributions from these singularities is obtained, just as in the familiar evaluation of definite integrals via the calculus of residues.

The Cauchy integral formula for a function f of a linear operator A, where f is analytic in a neighborhood of the spectrum of A, was first introduced by Dunford [1]. Such Cauchy integrals have been a useful tool in the rigorous mathematical analysis of Schrodinger operators; applications to perturbation theory are discussed by Kato [2], by Reed and Simon [3, Chap. XII], and by Hunziker [4]. However, they have not, to the best of the authors' knowledge, been used as a tool in a numerical computation.

The need for accurate values of Bethe logarithms provided the initial motivation for the use of the Cauchy integral formula (1.2) in a numerical method. For this reason, the present paper will describe the numerical use of (1.2) primarily as a way of evaluating Bethe logarithms. A preliminary account of this method appeared in [5, pp. 123–145]. The method has been used by Jonathan D. Baker in Ph.D. research under the direction of John D. Morgan III to calculate Bethe logarithms for the ground state and first excited S state of helium; the values obtained by Baker improve the agreement between theory and experiment for these energy levels by two orders of magnitude. However, the method is much more widely applicable; this paper should serve as a useful guide to the use of (1.2) for other problems for which (1.1) is ineffective. The evaluation of logarithmic mean excitation energies other than the Bethe logarithm via the methods of this paper should be particularly straightforward. The various logarithmic mean excitation energies, and the physical context in which they arise, have been discussed in [6], where they are evaluated for hydrogen and helium. See also [7].

The accuracy of the calculated Bethe logarithms can be known only if a careful error analysis has been performed. In order to facilitate this error analysis, asymptotic error estimates and rigorous error bounds are provided for the numerical integration which is the last step in the computational method. The convergence rate for the variational principle used to evaluate resolvent matrix elements is examined. Methods of accelerating this convergence are provided. An error formula for this variational principle is given; its use is illustrated by calculations on hydrogen in a Laguerre polynomial basis.

The paper is organized as follows. Section 2 outlines the main features of the calculation of a Bethe logarithm with the aid of (1.2), with the hydrogen ground state Bethe logarithm as an example, and obtains a value for this Bethe logarithm whose accuracy is limited only by the precision of the arithmetic used; this value is given in (2.29) below. We are indebted to S. P. Goldman for informing us that he has used the algebraic matrix method of Huff [8] to obtain comparable accuracy; Goldman's result agrees with ours to all but the last digit shown (Goldman was unable to confirm our last digit because the Cyber 2000 which he used has a smaller mantissa than the IBM 3090 on which we performed our calculations). Section 3 works out the large $|\zeta|$ asymptotic behavior of the matrix element of the resolvent needed in the Bethe logarithm problem. Section 4 discusses a variational principle which can be used for the approximate calculation of this matrix element of the resolvent. Section 5 analyzes the convergence rate for this variational principle when using a Laguerre polynomial basis, and shows how to accelerate this convergence for large $|\zeta|$. The connection of the present method of calculating Bethe logarithms with the technique introduced by C. Schwartz [9] is outlined in Appendix A.

2. The Bethe Logarithm

The Bethe logarithm [10, pp. 94–99, 103–104, 358–359] is a fundamental term in the theory of QED corrections in atoms and molecules. If H is the Hamiltonian, the Bethe logarithm $\ln K$ for a state $|\psi_n\rangle$ of energy E_n is

$$\ln K = \beta / \langle \psi_n | \mathbf{P} \cdot (H - E_n) \mathbf{P} | \psi_n \rangle, \tag{2.1}$$

where

$$\beta = \langle \psi_n | \mathbf{P} \cdot (H - E_n) \ln |H - E_n| \mathbf{P} | \psi_n \rangle. \tag{2.2}$$

Here $\mathbf{P}$ is the total electron momentum operator:

$$\mathbf{P} = \sum_{j=1}^{N} \mathbf{p}_j = -i \sum_{j=1}^{N} \nabla_j, \tag{2.3}$$

with $\mathbf{p}_j = -i\nabla_j$ the momentum of the jth electron. The Hamiltonian H will be assumed to have the form

$$H = T + V \tag{2.4}$$

with

$$T = -\frac{1}{2} \sum_{j=1}^{N} \nabla_j^2 \tag{2.5}$$

and

$$V = \sum_{j=1}^{N} \sum_{k=1}^{K} \frac{-Z_k}{|\mathbf{r}_j - \mathbf{R}_k|} + \sum_{j=1}^{N} \sum_{k=1}^{j-1} \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|}. \tag{2.6}$$

This H describes a molecule in Born–Oppenheimer approximation having K nuclei of charge Z_k at the points $\mathbf{R}_k$, and N electrons moving nonrelativistically with Coulomb interactions only. The denominator of (2.1) is easily evaluated for this Hamiltonian: one uses $(H - E_n)|\psi_n\rangle = 0$ and $\nabla_j^2 |\mathbf{r}_j - \mathbf{R}_k|^{-1} = -4\pi\, \delta(\mathbf{r}_j - \mathbf{R}_k)$ to write

$$\begin{aligned}
&\langle\psi_n|\, \mathbf{P} \cdot (H - E_n)\, \mathbf{P}\, |\psi_n\rangle \\
&\quad = \tfrac{1}{2} \langle\psi_n|\, \{\mathbf{P} \cdot [(H - E_n), \mathbf{P}] - [(H - E_n), \mathbf{P}] \cdot \mathbf{P}\}\, |\psi_n\rangle \\
&\quad = 2\pi \sum_{j=1}^{N} \sum_{k=1}^{K} Z_k \langle\psi_n|\, \delta(\mathbf{r}_j - \mathbf{R}_k)\, |\psi_n\rangle.
\end{aligned} \tag{2.7}$$

Thus the denominator in (2.1) depends only on the values of the wave function when one electron is at a nucleus. The modifications needed when this denominator is zero because the wave function vanishes at the nucleus are discussed in Bethe and Salpeter [10, p. 103]. Bethe logarithm calculations for the $l \neq 0$ excited states of hydrogen, where this difficulty arises, have been reported by Klarsfeld and Maquet [11] and by Drake and Swainson [12].

It is the numerator β in (2.1) which has been difficult to calculate. The formal application of the Cauchy integral (1.2) to (2.2), with $f(\zeta) = \zeta \ln(\zeta)$, $g(\zeta) = \ln(\zeta) \langle\psi_n|\, \mathbf{P} \cdot [1 + \zeta^{-1}(H - E_n)]\, \mathbf{P}\, |\psi_n\rangle$, $|\varphi\rangle = |\psi\rangle = P_j |\psi_n\rangle$ (where P_j is the jth Cartesian component of $\mathbf{P}$), and $A = H - E_n$ yields

$$\beta = \frac{1}{2\pi i} \oint_C d\zeta\, \zeta \ln(\zeta) \langle\psi_n|\, \mathbf{P} \cdot \left[\frac{1}{\zeta - H + E_n} - \frac{1}{\zeta} - \frac{1}{\zeta^2}(H - E_n)\right] \mathbf{P}\, |\psi_n\rangle. \tag{2.8}$$

As will be shown later in Section III, the matrix element $\langle\psi_n|\, \mathbf{P} \cdot (\zeta - H + E_n)^{-1}\, \mathbf{P}\, |\psi_n\rangle$ of the resolvent behaves like $g(\zeta)/f(\zeta) + O(\zeta^{-5/2})$ for large ζ. Thus the $g(\zeta)$ term in (2.8) subtracts out the leading terms of the matrix element of the resolvent, leaving an integrand in (2.8) which behaves like $\zeta^{-3/2} \ln(\zeta)$ for large ζ.

We will now look for a suitable contour C. The function $f(\zeta) = \zeta \ln(\zeta)$ has a branch cut which runs from $-\infty$ to 0 along the negative real axis. The operator $A = H - E_n$ has point spectrum at $E_m - E_n$ for $m = 0, 1, 2, \ldots$, and continuous spectrum beginning at $E_\infty - E_n$, where E_∞ is the lowest dissociation threshold for the Hamiltonian H. If the eigenvalues E_n of H are ordered such that $m<n$ implies $E_m \leqslant E_n$, then the point spectrum at $E_m - E_n$ for $m=0, 1, 2, ..., n$ overlaps the branch cut of f on the negative real axis, violating the assumption that f is analytic on the spectrum of A. This difficulty can be overcome by noting that, since $|\psi_m\rangle$ is the eigenvector belonging to the eigenvalue E_m, the resolvent matrix element $\langle\psi_n| \mathbf{P}\cdot(\zeta - H + E_n)^{-1} \mathbf{P} |\psi_n\rangle$ has first-order poles with residue $\langle\psi_n| \mathbf{P} |\psi_m\rangle \cdot \langle\psi_m| \mathbf{P} |\psi_n\rangle$ at $\zeta = E_m - E_n$. Thus we are led to introduce the projection operators $Q^{(n)}$ and $Q_\perp^{(n)}$ via

$$Q^{(n)} = \sum_{m=0}^{n-1} |\psi_m\rangle\langle\psi_m| \tag{2.9}$$

$$Q_\perp^{(n)} = I - Q^{(n)} \tag{2.10}$$

(where I is the identity operator) and replace (2.8) by

$$\beta = \frac{1}{2\pi i} \oint_C d\zeta\, \zeta \ln(\zeta) \langle\psi_n| \mathbf{P}\cdot Q_\perp^{(n)} \left[\frac{1}{\zeta - H + E_n} - \frac{1}{\zeta} - \frac{1}{\zeta^2}(H - E_n)\right] \times Q_\perp^{(n)} \mathbf{P} |\psi_n\rangle + \sum_{m=0}^{n-1} |\langle\psi_m| \mathbf{P} |\psi_n\rangle|^2 (E_m - E_n) \ln |E_m - E_n|. \tag{2.11}$$

In (2.9), it is understood that $\sum_{m=0}^{n-1}$ is empty, and hence is counted as zero, for $n=0$. Thus $Q_\perp^{(n)} = I$, and (2.11) reduces to (2.8), for $n=0$. We note that the pole of the resolvent matrix element at $\zeta = 0$, which comes from the bound state of energy E_n, need not be subtracted out because the ζ^{-1} pole term is cancelled by the ζ in $f(\zeta) = \zeta \ln(\zeta)$. The contour C in (2.11) can now be taken to surround the singularities of the integrand on the positive real axis as shown in Fig. 1. These singularities include poles at $E_m - E_n$ for $m = n+1, n+2, n+3, ...,$ and a branch cut which runs from $E_\infty - E_n$ to $+\infty$.

Because the integrand in (2.11) behaves like $\zeta^{-3/2} \ln(\zeta)$ for large ζ, the contour C can be deformed into a new contour C' which runs clockwise around the origin and the logarithmic branch cut on the negative real axis as shown in Fig. 1. By

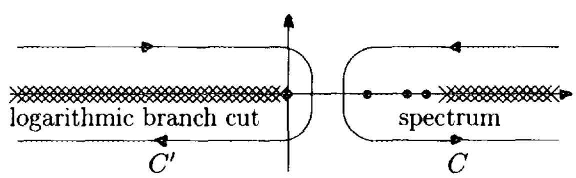

FIG. 1. The contour C surrounding the spectrum of $H - E_n$, and the contour C' surrounding the logarithmic branch cut. Dots denote point spectrum. The branch cuts from the continuous spectrum and the logarithm are denoted by cross hatching.

using the fact that the discontinuity of $\ln(\zeta)$ across the negative real axis is $2\pi i$, it can be shown that

$$\beta = \beta_1 + \beta_2 + \sum_{m=0}^{n-1} |\langle \psi_m | \mathbf{P} | \psi_n \rangle|^2 (E_m - E_n) \ln |E_m - E_n| \tag{2.12}$$

where

$$\beta_1 = \int_0^1 f_1(W^{(1)})\, dW^{(1)} \tag{2.13}$$

and

$$\beta_2 = \int_1^\infty f_2(W^{(2)})\, dW^{(2)} \tag{2.14}$$

with

$$f_1(W) = \langle \psi_n | \mathbf{P} \cdot Q_\perp^{(n)} \left[\frac{W}{H - E_n + W} - 1 \right] Q_\perp^{(n)} \mathbf{P} | \psi_n \rangle \tag{2.15}$$

and

$$f_2(W) = f_1(W) + W^{-1} \langle \psi_n | \mathbf{P} \cdot Q_\perp^{(n)} (H - E_n)\, Q_\perp^{(n)} \mathbf{P} | \psi_n \rangle. \tag{2.16}$$

The integrand $f_1(W)$ differs from the integrand $f_2(W)$ because the integral of $\zeta^{-1} \ln(\zeta)$ along the piece of the contour C' which runs from $-1 + i\varepsilon$ around the origin to $-1 - i\varepsilon$ is zero. This formulation of the problem is closely related to that given by Schwartz [9], as is spelled out in detail in Appendix A.

Numerical integration is used to evaluate (2.13) and (2.14). The analyticity properties of the integrands in (2.13) and (2.14) imply that a numerical integration scheme introduced by Stenger [13, Subsection 3.2; Examples 4.1–4.4] will be rapidly convergent. Appendix B derives the modified version of Stenger's method which we use and obtains error estimates.

This numerical integration scheme is

$$\begin{aligned} \beta_1 = \sum_{k=-N_-^{(1)}}^{N_+^{(1)}} & \frac{h \exp(kh)}{[1 + \exp(kh)]^2} \\ & \times f_1(W_k^{(1)}) + \varepsilon_I^{(1)}(h) + \varepsilon_{T,-}^{(1)}(N_-^{(1)}, h) + \varepsilon_{T,+}^{(1)}(N_+^{(1)}, h), \end{aligned} \tag{2.17}$$

$$\beta_2 = \sum_{k=-N_-^{(2)}}^{N_+^{(2)}} h \exp(kh) f_2(W_k^{(2)}) + \varepsilon_I^{(2)}(h) + \varepsilon_{T,-}^{(2)}(N_-^{(2)}, h) + \varepsilon_{T,+}^{(2)}(N_+^{(2)}, h), \tag{2.18}$$

where the nodes $W_k^{(j)}$ are

$$W_k^{(1)} = \exp(kh)/[1 + \exp(kh)], \qquad W_k^{(2)} = 1 + \exp(kh). \tag{2.19}$$

The interpolation errors $\varepsilon_I^{(j)}(h)$ are bounded by

$$|\varepsilon_I^{(j)}(h)| \leqslant \frac{\pi}{\sinh^2(\pi^2 h^{-1})} \langle \psi_n | \mathbf{P} \cdot Q_\perp^{(n)}(H - E_n) Q_\perp^{(n)} \mathbf{P} | \psi_n \rangle$$
$$\sim 4\pi \exp(-2\pi^2 h^{-1}) \langle \psi_n | \mathbf{P} \cdot Q_\perp^{(n)}(H - E_n) Q_\perp^{(n)} \mathbf{P} | \psi_n \rangle. \tag{2.20}$$

The truncation errors $\varepsilon_{T,\pm}^{(1)}(N, h)$ and $\varepsilon_{T,-}^{(2)}(N, h)$ are bounded by

$$0 \leqslant -f_1(W_{-N-1}^{(1)}) S^{(1)}(N) \leqslant -\varepsilon_{T,-}^{(1)}(N, h) \leqslant -f_1(0) S^{(1)}(N)$$
$$\leqslant \exp(-Nh) \langle \psi_n | \mathbf{P} \cdot Q_\perp^{(n)} \mathbf{P} | \psi_n \rangle, \tag{2.21}$$
$$0 \leqslant -f_1(1) S^{(1)}(N) \leqslant -\varepsilon_{T,+}^{(1)}(N, h) \leqslant -f_1(W_{N+1}^{(1)}) S^{(1)}(N)$$
$$\leqslant \exp(-Nh) \langle \psi_n | \mathbf{P} \cdot Q_\perp^{(n)} \mathbf{P} | \psi_n \rangle, \tag{2.22}$$
$$0 \leqslant f_2(W_{-N-1}^{(2)}) S^{(2)}(N) \leqslant \varepsilon_{T,-}^{(2)}(N, h) \leqslant f_2(1) S^{(2)}(N)$$
$$\leqslant \exp(-Nh) \langle \psi_n | \mathbf{P} \cdot Q_\perp^{(n)}(H - E_n) Q_\perp^{(n)} \mathbf{P} | \psi_n \rangle, \tag{2.23}$$

where

$$S^{(1)}(N) = \sum_{k=N+1}^{\infty} \frac{h \exp(kh)}{[1 + \exp(kh)]^2} = \sum_{k=1}^{\infty} (-1)^{k+1} \frac{kh \exp(-Nkh)}{\exp(kh) - 1}, \tag{2.24}$$

$$S^{(2)}(N) = \sum_{k=N+1}^{\infty} h \exp(-kh) = h \exp(-Nh)/[\exp(h) - 1]. \tag{2.25}$$

The truncation error $\varepsilon_{T,+}^{(2)}(N_+^{(2)}, h)$ can be estimated by using the asymptotic expansion

$$\varepsilon_{T,+}^{(2)}(N, h) = \frac{C_1 h \exp(-\frac{1}{2} Nh)}{\exp(\frac{1}{2} h) - 1}$$
$$+ \left\{ \frac{C_2 N h^2}{\exp(h) - 1} + \frac{C_2 h^2 \exp(h)}{[\exp(h) - 1]^2} + \frac{C_3 h}{\exp(h) - 1} \right\} \exp(-Nh)$$
$$+ \frac{(C_4 - \frac{3}{2} C_1) h \exp(-\frac{3}{2} Nh)}{\exp(\frac{3}{2} h) - 1} + O[Nh \exp(-2Nh)]. \tag{2.26}$$

The constants C_1, C_2, C_3, and C_4 which appear in (2.26) are given in (3.2)–(3.5) below. The integration rules (2.17) and (2.18) are applied by first choosing h small enough to make the interpolation error bound (2.20) sufficiently small. With h fixed, the truncation errors $\varepsilon_{T,\pm}^{(1)}(N_\pm^{(1)}, h)$ and $\varepsilon_{T,-}^{(2)}(N_-^{(2)}, h)$ can be evaluated by choosing $N_\pm^{(1)}$ and $N_-^{(2)}$ large enough so that the upper and lower bounds in (2.21)–(2.23) agree to the number of digits to which these truncation errors must be evaluated. The truncation error $\varepsilon_{T,+}^{(2)}(N_+^{(2)}, h)$ can be evaluated by choosing $N_+^{(2)}$ large enough to make the error term in the asymptotic formula (2.26) small.

Alternatively, we can choose $N_{\pm}^{(1)}$ and $N_{\pm}^{(2)}$ large enough to make the truncation errors so small that they need not be evaluated. We could, for example, make the interpolation error and truncation error bounds comparable by choosing $N_{-}^{(1)}=N_{+}^{(1)}=N_{-}^{(2)}=\frac{1}{2}N_{+}^{(2)}=N=2\pi^2h^{-2}$ (the factor of $\frac{1}{2}$ in front of $N_{+}^{(2)}$ arises because the leading term in (2.26) falls off like $\exp(-\frac{1}{2}Nh)$, while the other truncation errors fall off like $\exp(-Nh)$). This leads to an error which decreases like $\exp(-\pi\sqrt{2N})$, which is much faster than the N^{-k} power law decrease of the error for more familiar numerical integration rules based on polynomial interpolation on the real axis. The number of function evaluations needed is then $2N+1$ for the evaluation of β_1, and $3N+1$ for the evaluation of β_2.

The numerical results in Table I exhibit this rapid $\exp(-\pi\sqrt{2N})$ convergence for the evaluation of the hydrogen ground state Bethe logarithm. $\delta\beta_1$, $\delta\beta_2$, and $\delta\beta$ are the differences between β_1, β_2, and β and their exact values, for which we have used our best values, which are

$$\beta_1 = -0.64608\ 11931\ 49311\ 80288\ 26059\ 89438, \tag{2.27}$$

$$\beta_2 = 5.22804\ 39435\ 60416\ 40556\ 76959\ 2655, \tag{2.28}$$

$$\beta = 2.29098\ 13752\ 05552\ 30134\ 25449\ 6855. \tag{2.29}$$

These values are believed to be accurate to the number of digits shown. The quantities ρ_1, ρ_2, and ρ, which can be seen to vary slowly with N, are the errors $\delta\beta_1$, $\delta\beta_2$, and $\delta\beta$ divided by the factor $\exp(-\pi\sqrt{2N})$ which gives the dominant behavior of these errors.

TABLE I

The Dependence of the Numerical Integration Errors on N

N	$\delta\beta_1$	ρ_1	$\delta\beta_2$	ρ_2	$\delta\beta$	ρ
1	-1.1×10^{-1}	-9.0	4.4×10^{-2}	3.8	-3.1×10^{-2}	-2.6
4	-1.2×10^{-3}	-8.4	-4.2×10^{-4}	-3.0	-7.9×10^{-4}	-5.7
9	-8.6×10^{-6}	-5.3	-1.1×10^{-5}	-6.5	-9.6×10^{-6}	-5.9
16	-1.1×10^{-7}	-5.8	-1.7×10^{-7}	-8.7	-1.4×10^{-7}	-7.3
25	-1.3×10^{-9}	-5.8	-2.3×10^{-9}	-10.2	-1.8×10^{-9}	-8.0
36	-1.1×10^{-11}	-4.1	-3.0×10^{-11}	-11.2	-2.0×10^{-11}	-7.7
49	-1.4×10^{-13}	-4.4	-3.7×10^{-13}	-11.9	-2.5×10^{-13}	-8.1
64	-1.8×10^{-15}	-4.9	-4.5×10^{-15}	-12.2	-3.1×10^{-15}	-8.6
81	-1.5×10^{-17}	-3.6	-5.3×10^{-17}	-12.3	-3.4×10^{-17}	-7.9
100	-1.7×10^{-19}	-3.4	-6.2×10^{-19}	-12.2	-4.0×10^{-19}	-7.8
121	-2.6×10^{-21}	-4.4	-7.2×10^{-21}	-12.0	-4.9×10^{-21}	-8.2
144	-2.4×10^{-23}	-3.4	-8.3×10^{-23}	-11.8	-5.3×10^{-23}	-7.6
169	-2.1×10^{-25}	-2.6	-9.5×10^{-25}	-11.5	-5.8×10^{-25}	-7.0
196	-3.6×10^{-27}	-3.7	-1.1×10^{-26}	-11.2	-7.3×10^{-27}	-7.5
225	-4.1×10^{-29}	-3.6	-1.3×10^{-28}	-11.2	-8.4×10^{-29}	-7.4

The hydrogen ground state Bethe logarithm was chosen for the initial test of the method because closed form expressions for f_1 and f_2 can be obtained. For hydrogen, with

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r}, \tag{2.30}$$

$$E_0 = -\frac{1}{2}, \tag{2.31}$$

and

$$\psi_0(\mathbf{r}) = \pi^{-1/2}\exp(-r), \tag{2.32}$$

it can be shown that

$$\langle \psi_0 | \, p^2 \, | \psi_0 \rangle = 1, \tag{2.33}$$

$$\langle \psi_0 | \, \mathbf{p} \cdot (H - E_0) \, \mathbf{p} \, | \psi_0 \rangle = 2, \tag{2.34}$$

and

$$\langle \psi_0 | \, \mathbf{p} \cdot \frac{W}{H - E_0 + W} \mathbf{p} \, | \psi_0 \rangle = \frac{192 v^3 (1-v)}{(2-v)(1+v)^7} \, {}_2F_1\left(4, 2-v; 3-v; \frac{(1-v)^2}{(1+v)^2}\right), \tag{2.35}$$

where

$$v = (1 + 2W)^{-1/2}. \tag{2.36}$$

In (2.35), ${}_2F_1$ is the hypergeometric function in standard notation [14, p. 56; 15, p. 37]. The derivation of (2.33) and (2.34) is straightforward; (2.35) can be obtained from the formula for the Laplace transform of the Coulomb Green's function given by Huxtable and Hill [16], or from equivalent formulas of other authors [17]. Replacing the nuclear charge Z by one in Eq. (1.6) and (2.1)–(2.3) of Huxtable and Hill yields

$$I_l(\lambda, \lambda'; E) = \int d^3\mathbf{r} \, d^3\mathbf{r}' \exp(-\lambda r - \lambda' r')(rr')^{l-1} \, \overline{Y_{l,m}(\theta, \phi)} \times G(\mathbf{r}, \mathbf{r}'; E) \, Y_{l,m}(\theta', \phi'), \tag{2.37}$$

$$I_l(\lambda, \lambda'; E) = -\frac{2(2l+1)!}{l-v+1}\left[\frac{v}{2}\right]^{2l+3}\left[\frac{4}{(v\lambda+1)(v\lambda'+1)}\right]^{2l+2} \times {}_2F_1(2l+2, l-v+1; l-v+2; 1-\zeta), \tag{2.38}$$

$$v = (-2E)^{-1/2}, \tag{2.39}$$

$$\zeta = \frac{2v(\lambda+\lambda')}{(v\lambda+1)(v\lambda'+1)}. \tag{2.40}$$

Here $G(\mathbf{r}, \mathbf{r}'; E)$ is the coordinate space representative $\langle \mathbf{r}|\, (E-H)^{-1}\, |\mathbf{r}'\rangle$. Equation (2.35) is obtained by using (2.37)–(2.40) with $l=1$ and $E=E_0-W=-\frac{1}{2}-W$.

The numerical evaluation of $f_2(W)$ for large W must be handled with care to avoid the excessive roundoff error which arises when floating point arithmetic is used to combine terms which are almost equal in magnitude and opposite in sign. For hydrogen, these terms can be combined analytically if the expansion

$$
\begin{aligned}
{}_2F_1(4, 2-\nu; 3-\nu; z)
&= \frac{(2-\nu)}{3}(1-z)^{-3} + \frac{(2-\nu)(1+\nu)}{6}(1-z)^{-2} \\
&\quad + \frac{\nu(2-\nu)(1+\nu)}{6}(1-z)^{-1} + \frac{\nu(2-\nu)(1-\nu^2)}{6} \\
&\quad \times \left\{ z^{\nu-2}\log(1-z) + \sum_{n=0}^{\infty} \frac{(2-\nu)_n}{n!}\left[\Psi(n+2-\nu) - \Psi(n+1)\right](1-z)^n \right\}, \qquad (2.41)
\end{aligned}
$$

which can be found in the Bateman project [14, p. 110, Eqs. (14) and (15)] and in Magnus, Oberhettinger, and Soni [15, p. 44], is used to evaluate the hypergeometric function in (2.35) for values of W greater than $\frac{3}{2}$, for which the argument $(1-\nu)^2/(1+\nu)^2$ is greater than $\frac{1}{2}$. The expansion of ${}_2F_1(4, 2-\nu; 3-\nu; z)$ in powers of z about $z=0$ is used when $W \leqslant \frac{3}{2}$. It should be noted that there is a sign error in the last term of Eq. (15) on page 110 of [14].

Almost all of the computer time spent on the numerical integration of $f_1(W)$ and $f_2(W)$ to obtain the values of β_1 and β_2 is used for function evaluation. Because the amount of computer time needed for one function evaluation depends on W, the numerical integration should be done in a way which minimizes the number of nodes which occur for values of W for which the function evaluation is expensive. Table II lists the nodes for the evaluation of β_1 with $N=16$. As can be seen from

TABLE II

Nodes for Integrating from 0 to 1 to Obtain β_1

K	Node	K	Node	K	Node
−16	0.0000000191	−5	0.0038585274	6	0.9987260070
−15	0.0000000581	−4	0.0116252446	7	0.9995800879
−14	0.0000001765	−3	0.0344841672	8	0.9998616750
−13	0.0000005359	−2	0.0978414942	9	0.9999544424
−12	0.0000016272	−1	0.2477365458	10	0.9999849964
−11	0.0000049410	0	0.5000000000	11	0.9999950590
−10	0.0000150036	1	0.7522634542	12	0.9999983728
−9	0.0000455576	2	0.9021585058	13	0.9999994641
−8	0.0001383250	3	0.9655158328	14	0.9999998235
−7	0.0004199121	4	0.9883747554	15	0.9999999419
−6	0.0012739930	5	0.9961414726	16	0.9999999809

the table, these nodes tend to cluster near the endpoints of the integration interval; this happens because the endpoints are a step-function singularity. A similar clustering near the endpoints occurs for β_2. The most expensive function evaluations are those for which W is large enough to introduce a second length scale, proportional to $W^{-1/2}$, but not large enough for a few terms of the large W asymptotic expansion to give sufficient accuracy (this second length scale is discussed in Section 5, following). Fortunately the endpoints $W=0$, $W=1$, and $W=\infty$ at which the nodes cluster are not in this region where function evaluation is expensive.

3. Asymptotic Behavior of the Matrix Elements of the Resolvent

In this section we will derive the first few terms in the large W asymptotic expansion of $f_2(W)$. The result is

$$\begin{aligned} f_2(W) = {} & C_1 W^{-3/2} + C_2 W^{-2}\ln(W) + C_3 W^{-2} \\ & + C_4 W^{-5/2} + O[W^{-3}\ln(W)], \end{aligned} \tag{3.1}$$

where the coefficients are given by

$$C_1 = 4\pi\sqrt{2}\sum_{j=1}^{N}\sum_{k=1}^{K} Z_k^2 \langle\psi_n|\,\delta(\mathbf{r}_j-\mathbf{R}_k)\,|\psi_n\rangle, \tag{3.2}$$

$$C_2 = -4\pi\sum_{j=1}^{N}\sum_{k=1}^{K} Z_k^3 \langle\psi_n|\,\delta(\mathbf{r}_j-\mathbf{R}_k)\,|\psi_n\rangle, \tag{3.3}$$

$$\begin{aligned} C_3 = {} & \sum_{j=1}^{N}\sum_{k=1}^{K}\sum_{j'=1}^{N}\sum_{k'=1}^{K} Z_k Z_{k'}(1-\delta_{j,j'}\delta_{k,k'})\,\langle\psi_n|\,\frac{(\mathbf{r}_j-\mathbf{R}_k)\cdot(\mathbf{r}_{j'}-\mathbf{R}_{k'})}{|\mathbf{r}_j-\mathbf{R}_k|^3\,|\mathbf{r}_{j'}-\mathbf{R}_{k'}|^3}\,|\psi_n\rangle \\ & + \sum_{j=1}^{N}\sum_{k=1}^{K} Z_k^2\left\{\int\frac{d^3\mathbf{r}}{r^4}\,[\langle\psi_n|\,\delta(\mathbf{r}_j-\mathbf{R}_k-\mathbf{r})\,|\psi_n\rangle-(1-2Z_k r)\,\Theta(1-r)\right. \\ & \times\langle\psi_n|\,\delta(\mathbf{r}_j-\mathbf{R}_k)\,|\psi_n\rangle]+4\pi[(1+\ln 2-2\gamma)\,Z_k-1] \\ & \left.\times\langle\psi_n|\,\delta(\mathbf{r}_j-\mathbf{R}_k)\,|\psi_n\rangle\right\}-\sum_{m=0}^{n-1}|\langle\psi_m|\,\mathbf{P}\,|\psi_n\rangle|^2\,(E_m-E_n)^2, \end{aligned} \tag{3.4}$$

$$\begin{aligned} C_4 = {} & 2\pi\sqrt{2}\sum_{j=1}^{N}\sum_{k=1}^{K} Z_k^2\left\{\left[E_n+\left(1-\frac{\pi^2}{3}\right)Z_k^2\right]\langle\psi_n|\,\delta(\mathbf{r}_j-\mathbf{R}_k)\,|\psi_n\rangle\right. \\ & -\langle\psi_n|\,\delta(\mathbf{r}_j-\mathbf{R}_k)\left(V+\frac{Z_k}{|\mathbf{r}_j-\mathbf{R}_k|}+T-\frac{1}{2}p_j^2\right)|\psi_n\rangle \\ & \left.-\frac{1}{4\pi}\left[\frac{\partial^2\rho^{(j,k,k)}_{0,0;0,0;n}(r,r)}{\partial r^2}\right]_{r=0}-\frac{3}{4\pi}\sum_{m=-1}^{1}\rho^{(j,k,k)}_{1,m;1,m;n}(0,0)\right\}. \end{aligned} \tag{3.5}$$

The $\Theta(1-r)$ in (3.4) is a Heaviside unit step function with the values one for $r<1$ and zero for $r>1$. The factor containing the Heaviside function tames the r^{-4} singularity enough to make the result finite. The function $\rho^{(j,k,k')}_{l,m;l',m';n}(r,r')$ which appears in C_4 is defined in (3.29) and (3.30) below. The fact that the leading term in (3.1) is of order $W^{-3/2}$ can be understood by observing that a naive expansion in powers of W^{-1} produces a leading term of order W^{-2} whose coefficient is an integral which diverges like $\int r^{-2}\,dr$ at small r. A more careful treatment introduces a cutoff of order $W^{-1/2}$ and obtains $W^{-2}\int_{W^{-1/2}}^{\infty} r^{-2}\,dr = W^{-3/2}$. The $W^{-2}\ln(W)$ term can be understood in the same way. The formulas (3.2)–(3.4) for C_1, C_2, and C_3 agree with Schwartz ([9] and Appendix A). Verifying the agreement for C_3 requires the integration by parts formula $\int_0^\infty \ln(r)\,\bar{\rho}_i''(r)\,dr = \bar{\rho}_i(0)+\bar{\rho}_i'(0) - \int_0^1 r^{-2}[\bar{\rho}_i(r) - \bar{\rho}_i(0) - r\bar{\rho}_i'(0)]\,dr - \int_1^\infty r^{-2}\bar{\rho}_i(r)\,dr$ and the cusp condition $\bar{\rho}_i'(0) = -2Z\bar{\rho}_i(0)$. The expression (3.5) for C_4, which is new, agrees with Schwartz for hydrogen.

The derivation begins by rewriting $f_2(W)$ in a convenient form. The next step expands $(H-E_n+W)^{-1} = (T+V-E_n+W)^{-1}$ in powers of $(T-E_n+W)^{-1/2}\times V(T-E_n+W)^{-1/2}$. The last step of the calculation exploits the fact that the coordinate space representative of $(T-E_n+W)^{-1}$ is sharply peaked when W is large.

The convenient form for $f_2(W)$ is

$$f_2(W) = f_3(W) - W^{-1}\sum_{m=0}^{n-1} |\langle\psi_m|\,\mathbf{P}\,|\psi_n\rangle|^2\,(E_m-E_n)^2\,(E_m-E_n+W)^{-1}, \tag{3.6}$$

where

$$f_3(W) = W^{-1}\langle\psi_n|\,\mathbf{P}(H-E_n)\cdot\frac{1}{(H-E_n+W)}(H-E_n)\,\mathbf{P}\,|\psi_n\rangle. \tag{3.7}$$

The large W expansion of the second term in (3.6) is obtained immediately by expanding $(E_m-E_n+W)^{-1}$ in a series in powers of $(E_n-E_m)/W$. The large W expansion of $f_3(W)$ is more difficult. By computing the commutator of $(H-E_n)$ with $\mathbf{P}$ from the definitions (2.3)–(2.6) and using $(H-E_n)\,|\psi_n\rangle = 0$, Eq. (3.7) can be brought to the form

$$\begin{aligned} f_3(W) = W^{-1}\sum_{m=-1}^{1} &\langle\Psi_{n,m}|\,(T-E_n+W)^{1/2} \\ &\times(H-E_n+W)^{-1}\,(T-E_n+W)^{1/2}\,|\Psi_{n,m}\rangle, \end{aligned} \tag{3.8}$$

where

$$|\Psi_{n,m}\rangle = (T-E_n+W)^{-1/2}\sum_{j=1}^{N}\sum_{k=1}^{K} Z_k\left(\frac{r_{j,m}-R_{k,m}}{|\mathbf{r}_j-\mathbf{R}_k|^3}\right)|\psi_n\rangle. \tag{3.9}$$

$(T-E_n+W)^{\pm 1/2}$ in (3.8) and (3.9) is the unique positive square root of $(T-E_n+W)^{\pm 1}$. The $r_{j,m}-R_{k,m}$ in (3.9) are the spherical components [18, p. 69] of $\mathbf{r}_j-\mathbf{R}_k$.

The series expansion in powers of $(T-E_n+W)^{-1/2}\,V(T-E_n+W)^{-1/2}$ is

$$\begin{aligned}\langle \Psi_{n,m}|\,(T-E_n+W)^{1/2}\,(H-E_n+W)^{-1}\,(T-E_n+W)^{1/2}\,|\Psi_{n,m}\rangle\\ =\sum_{j=0}^{J}(-1)^j\langle\Psi_{n,m}|\,[(T-E_n+W)^{-1/2}\\ \times V(T-E_n+W)^{-1/2}]^j\,|\Psi_{n,m}\rangle+R_V(J),\end{aligned} \tag{3.10}$$

where $R_V(J)$ is the remainder. It is shown in Appendix C that $(T-E_n+W)^{-1/2}\times V(T-E_n+W)^{-1/2}$ is an operator from $L^2[R^{3N}]$ to $L^2[R^{3N}]$ whose 2-norm has the bound

$$\|(T-E_n+W)^{-1/2}\,V(T-E_n+W)^{-1/2}\|_2\leqslant B(W-E_n)^{-1/2}, \tag{3.11}$$

where

$$B=N\left[\frac{N-1}{4}+\frac{1}{\sqrt{2}}\sum_{k=1}^{K}Z_k\right]. \tag{3.12}$$

The bound (3.11) implies that the series (3.10) converges for $(W-E_n)^{1/2}>B$ and that the remainder $R_V(J)$ has the bounds

$$\begin{aligned}|R_V(J)|&\leqslant\frac{B\,\langle\Psi_{n,m}|\,[(T-E_n+W)^{-1/2}\,V(T-E_n+W)^{-1/2}]^J\,|\Psi_{n,m}\rangle}{(W-E_n)^{1/2}-B}\\ &\leqslant\frac{\langle\Psi_{n,m}\,|\,\Psi_{n,m}\rangle\,B^{J+1}}{(W-E_n)^{J/2}\,[(W-E_n)^{1/2}-B]}.\end{aligned} \tag{3.13}$$

Thus the series (3.10) is an expansion in powers of $(W-E_n)^{-1/2}$ with bounded coefficients which depend on W.

We now turn to the evaluation of the first few terms of the series (3.10) for large W. The coordinate space representative of $(T-E_n+W)^{-1}$ is

$$\begin{aligned}\langle \mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N|\,(T-E_n+W)^{-1}\,|\mathbf{r}'_1,\mathbf{r}'_2,...,\mathbf{r}'_N\rangle\\ =2(2\pi)^{-3N/2}\,(\nu R)^{(-3N+2)/2}\,K_{(3N-2)/2}(\nu^{-1}R),\end{aligned} \tag{3.14}$$

where $K_\mu(z)$ is a modified Bessel function of the third kind in standard notation [15, p. 66; 19, p. 5], $\nu=[2(W-E_n)]^{-1/2}$, and

$$R=\sqrt{(\mathbf{r}_1-\mathbf{r}'_1)^2+(\mathbf{r}_2-\mathbf{r}'_2)^2+\cdots+(\mathbf{r}_N-\mathbf{r}'_N)^2}. \tag{3.15}$$

The large z asymptotic approximation $K_\mu(z)=[\pi/(2z)]^{1/2}\exp(-z)[1+O(z^{-1})]$ shows that (3.14) peaks sharply about $R=0$. A standard method for the asymptotic evaluation of an integral with a sharply peaked integrand like this uses repeated integration by parts, integrating the sharply peaked function and differentiating everything else. This is equivalent to formally expanding $(T - E_n + W)^{-1}$ in powers of $T/(W - E_n)$; it works if the "everything else" which is differentiated is nonsingular with non-singular derivatives. Unfortunately the "everything else" in our case has singular factors like the $(r_{j,m} - R_{k,m})\,|\mathbf{r}_j - \mathbf{R}_k|^{-3}$ which appear in the expression (3.9) for $|\Psi_{n,m}\rangle$. Furthermore, derivatives of the wave function $\langle \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N \mid \psi_n\rangle$ have singularities (cusps) at the points where the Coulomb potentials in the Hamiltonian are singular. Thus the standard integration by parts method described above must be modified to include the singular factors in the part which is integrated. For a term which contains the factor $(r_{j,m} - R_{k,m})\,|\mathbf{r}_j - \mathbf{R}_k|^{-3}$, this modification can be carried out by introducing the spherical coordinates $|\mathbf{r}_j - \mathbf{R}_k|$, $\theta_{j,k}$, $\phi_{j,k}$ of $\mathbf{r}_j$ about the point $\mathbf{R}_k$, and expanding the $\mathbf{r}_j$-dependence of $\langle \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N \mid \psi_n\rangle$ in a partial wave expansion about this point. The lth partial wave in such an expansion behaves like $|\mathbf{r}_j - \mathbf{R}_k|^l$ for $|\mathbf{r}_j - \mathbf{R}_k|$ small (a general theorem which includes this behavior as a special case has been recently announced in [20]). Hence only a few partial waves will be sufficiently singular to require special treatment. We define the projection operator $P^{(j,k)}_{l,m}$ by specifying its action on an arbitrary vector $|\chi\rangle$:

$$\begin{aligned}
&\langle \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N|\, P^{(j,k)}_{l,m}\, |\chi\rangle \\
&\quad = Y_{l,m}(\theta_{j,k}, \phi_{j,k}) \Big[\int \overline{Y_{l,m}(\theta'_{j,k}, \phi'_{j,k})} \\
&\qquad \times \langle \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{j-1}, \mathbf{r}'_j, \mathbf{r}_{j+1}, ..., \mathbf{r}_N \mid \chi\rangle \, d\Omega'_{k,j} \Big]_{|r'_j - R_k| = |r_j - R_k|}.
\end{aligned} \tag{3.16}$$

The projection operator $P^{(j,k)}_l$ is then defined by

$$P^{(j,k)}_l = \sum_{m=-l}^{l} P^{(j,k)}_{l,m}. \tag{3.17}$$

This projection operator is used to define the vector

$$|\psi^{(j,k)}_{l;m,n}\rangle = (T - E_n + W)^{-1/2}\,(r_{j,m} - R_{k,m})\,|\mathbf{r}_j - \mathbf{R}_k|^{-3}\, P^{(j,k)}_l\, |\psi_n\rangle. \tag{3.18}$$

It follows that

$$\begin{aligned}
\sum_{m=-1}^{1} \langle \Psi_{n,m} \mid \Psi_{n,m}\rangle &= \sum_{j=1}^{N} \sum_{k=1}^{K} \sum_{j'=1}^{N} \sum_{k'=1}^{K} Z_k Z_{k'} \\
&\quad \times \sum_{l=0}^{\infty} \sum_{l'=0}^{\infty} \sum_{m=-1}^{1} \langle \psi^{(j,k)}_{l;m,n} \mid \psi^{(j',k')}_{l';m,n}\rangle.
\end{aligned} \tag{3.19}$$

If $\langle \psi^{(j,k)}_{l;m,n} | T - E_n | \psi^{(j',k')}_{l';m,n} \rangle$ exists, the identity $(T - E_n + W)^{-1} = W^{-1} - W^{-1}(T - E_n + W)^{-1/2}(T - E_n)(T - E_n + W)^{-1/2}$ can be used to show that

$$\sum_{m=-1}^{1} \langle \psi^{(j,k)}_{l;m,n} | \psi^{(j',k')}_{l';m,n} \rangle$$
$$= W^{-1} \langle \psi_n | P^{(j,k)}_l \frac{(\mathbf{r}_j - \mathbf{R}_k) \cdot (\mathbf{r}_{j'} - \mathbf{R}_{k'})}{|\mathbf{r}_j - \mathbf{R}_k|^3 \, |\mathbf{r}_{j'} - \mathbf{R}_{k'}|^3} P^{(j',k')}_{l'} | \psi_n \rangle + O(W^{-2}). \quad (3.20)$$

Values of l and l' for which (3.20) is valid can be determined by noting that the lth partial wave in the partial wave expansion of the $\mathbf{r}_j$-dependence of $\langle \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N | \psi_n \rangle$ about the point $\mathbf{R}_k$ behaves like $|\mathbf{r}_j - \mathbf{R}_k|^l$ for $|\mathbf{r}_j - \mathbf{R}_k|$ small. The operator p_j^2 can at worst introduce two additional negative powers of $|\mathbf{r}_j - \mathbf{R}_k|$. Counting powers of $|\mathbf{r}_j - \mathbf{R}_k|$ and $|\mathbf{r}_{j'} - \mathbf{R}_{k'}|$ then shows that $\langle \psi^{(j,k)}_{l;m,n} | T - E_n | \psi^{(j',k')}_{l';m,n} \rangle$ exists and that (3.20) is valid for $l \geqslant 2$ and $l' \geqslant 2$. Establishing (3.20) for the other values of l and l' for which it holds requires the more sophisticated analysis of Appendix C. Similar power counting shows that $\langle \psi^{(j,k)}_{l;m,n} | T - \frac{1}{2} p_j^2 - E_n | \psi^{(j',k')}_{l';m,n} \rangle$ exists for all l and l' when $j = j'$, and that $\langle \psi^{(j,k)}_{l;m,n} | T - \frac{1}{2} p_j^2 - \frac{1}{2} p_{j'}^2 - E_n | \psi^{(j',k')}_{l';m,n} \rangle$ exists for all l and l' when $j \neq j'$. A modified version of the analysis which led to (3.20) then yields

$$\begin{aligned} \langle \psi^{(j,k)}_{l;m,n} | \psi^{(j,k')}_{l';m,n} \rangle &= \langle \psi_n | P^{(j,k)}_l \overline{(r_{j,m} - R_{k,m})} \, |\mathbf{r}_j - \mathbf{R}_k|^{-3} \\ &\quad \times (\tfrac{1}{2} p_j^2 - E_n + W)^{-1} (r_{j,m} - R_{k',m}) \\ &\quad \times |\mathbf{r}_j - \mathbf{R}_{k'}|^{-3} P^{(j,k')}_{l'} | \psi_n \rangle + O(W^{-2}), \end{aligned} \quad (3.21)$$

$$\begin{aligned} \langle \psi^{(j,k)}_{l;m,n} | \psi^{(j',k')}_{l';m,n} \rangle &= \langle \psi_n | P^{(j,k)}_l \overline{(r_{j,m} - R_{k,m})} \, |\mathbf{r}_j - \mathbf{R}_k|^{-3} \\ &\quad \times (\tfrac{1}{2} p_j^2 + \tfrac{1}{2} p_{j'}^2 - E_n + W)^{-1} (r_{j',m} - R_{k',m}) \\ &\quad \times |\mathbf{r}_{j'} - \mathbf{R}_{k'}|^{-3} P^{(j',k')}_{l'} | \psi_n \rangle + O(W^{-2}). \end{aligned} \quad (3.22)$$

The next step is the evaluation of the first term on the right-hand side of (3.21) and (3.22). The case $j = j'$, $k = k'$ will be worked out first. We use the partial wave expansion

$$\begin{aligned} &\langle \mathbf{r}_j | (\tfrac{1}{2} p_j^2 - E_n + W)^{-1} | \mathbf{r}'_j \rangle \\ &\quad = \frac{\exp(-v^{-1} |\mathbf{r}_j - \mathbf{r}'_j|)}{2\pi |\mathbf{r}_j - \mathbf{r}'_j|} \\ &\quad = \frac{1}{v} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y_{l,m}(\theta_{j,k}, \phi_{j,k}) \overline{Y_{l,m}(\theta'_{j,k}, \phi'_{j,k})} \, g_l(v^{-1} r, v^{-1} r'), \end{aligned} \quad (3.23)$$

where the radial coordinates are $r = |\mathbf{r}_j - \mathbf{R}_k|$ and $r' = |\mathbf{r}'_j - \mathbf{R}_k|$. The function g_l is defined by the integral representation

$$g_l(z_1, z_2) = \int_{-\infty}^{\infty} \frac{t^2 \, dt}{1 + t^2} \frac{J_{l+1/2}(t z_1)}{(t z_1)^{1/2}} \frac{J_{l+1/2}(t z_2)}{(t z_2)^{1/2}} \quad (3.24)$$

where $J_{l+1/2}$ is a Bessel function of the first kind in standard notation [15, pp. 65 and 72; 19, p. 4]. Contour integration can be used to show that

$$g_l(z_1, z_2) = 2\,\frac{I_{l+1/2}(z_<)}{\sqrt{z_<}}\,\frac{K_{l+1/2}(z_>)}{\sqrt{z_>}}, \tag{3.25}$$

where $I_{l+1/2}$ and $K_{l+1/2}$ are modified Bessel functions of the first and third kinds in standard notation, and $z_<$ is the smaller and $z_>$ is the larger of the coordinates z_1, z_2.

The angular integrations over $\theta_{j,k}$, $\phi_{j,k}$, $\theta'_{j,k}$, and $\phi'_{j,k}$ are performed by inserting

$$r_{j,m} - R_{k,m} = (4\pi/3)^{1/2}\,|\mathbf{r}_j - \mathbf{R}_k|\; Y_{1,m}(\theta_{j,k}, \phi_{j,k}) \tag{3.26}$$

for the spherical components and using the formula for the integral of a product of three spherical harmonics [18, p. 63, Eq. (4.6.3); Appendix C, Eq. (C.7)]. The sum over m is performed with the aid of the orthogonality relation for the Wigner 3-j symbol [18, p. 47, Eq. (3.7.8)]. The result is

$$\begin{aligned}\sum_{m=-1}^{1} &\langle \psi^{(j,k)}_{l;m,n} \mid \psi^{(j,k)}_{l';m,n}\rangle \\ &= \sum_{m=-l}^{l} \frac{l M^{(j,k)}_{l-1,m;n;0} + (l+1)\, M^{(j,k)}_{l+1,m;n;1}}{(2l+1)}\,\delta_{l,l'} + O(v^4)\end{aligned} \tag{3.27}$$

where

$$\begin{aligned}M^{(j,k)}_{l,m;n;p} = v^{-1} \int_0^\infty dr \int_0^\infty dr' (rr')^{l-2p+1}\, g_l(v^{-1}r, v^{-1}r') \\ \times \rho^{(j,k,k)}_{l-2p+1,m;\,l-2p+1,m;\,n}(r, r')\end{aligned} \tag{3.28}$$

with

$$\begin{aligned}\rho^{(j,k,k')}_{l,m;l',m';n}(r, r') = r^{-l}(r')^{-l'} \int d^3\mathbf{r}_1\, d^3\mathbf{r}_2, ..., d^3\mathbf{r}_{j-1}\, d^3\mathbf{r}_{j+1}, ..., d^3\mathbf{r}_N \\ \times \overline{f^{(j,k)}_{l,m,n}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{j-1}, \mathbf{r}_{j+1}, ..., \mathbf{r}_N; r)} \\ \times f^{(j,k')}_{l',m',n}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{j-1}, \mathbf{r}_{j+1}, ..., \mathbf{r}_N; r'),\end{aligned} \tag{3.29}$$

where

$$\begin{aligned}f^{(j,k)}_{l,m,n}&(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{j-1}, \mathbf{r}_{j+1}, ..., \mathbf{r}_N; |\mathbf{r}_j - \mathbf{R}_k|) \\ &= \int d\Omega_{k,j}\, \overline{Y_{l,m}(\theta_{j,k}, \phi_{j,k})}\, \langle \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{j-1}, \mathbf{r}_j, \mathbf{r}_{j+1}, ..., \mathbf{r}_N \mid \psi_n\rangle.\end{aligned} \tag{3.30}$$

For v small, most of the contribution to the integral (3.28) comes from the neighborhood of a sharp peak at $r=r'$. We exploit this observation via an integration by parts which differentiates $\rho^{(j,k,k)}_{l-2p+1,m;l-2p+1,m;n}(r,r')$ and integrates everything else, with the indefinite integrals chosen to vanish at zero and infinity. The integrated part is then the contribution which would be obtained by treating $\rho^{(j,k,k)}_{l,m;l,m;n}(r,r')$ as a constant in the neighborhood of $r=r'$. We begin with the definitions

$$J_{l,p}(z)=-\sum_{m=0}^{l-p}\frac{2^m(l-p)!}{(l-p-m)!}z^{l-m-2p+1/2}J_{l-m-1/2}(z), \tag{3.31}$$

$$I_{l,p}(z)=\sum_{m=0}^{l-p}\frac{(-2)^m(l-p)!}{(l-p-m)!}z^{l-m-2p+1/2}I_{l-m-1/2}(z), \tag{3.32}$$

$$K_{l,p}(z)=-\sum_{m=0}^{l-p}\frac{2^m(l-p)!}{(l-p-m)!}z^{l-m-2p+1/2}K_{l-m-1/2}(z), \tag{3.33}$$

$$G_{l,p}(z_1,z_2)=\int_{-\infty}^{\infty}\frac{dt}{1+t^2}t^{4p-2l-2}[J_{l,p}(tz_<)-J_{l,p}(0)]\,J_{l,p}(tz_>). \tag{3.34}$$

In (3.31)–(3.34), p is restricted to $p=0$ and $p=1$, with the additional restriction $l\geqslant 1$ when $p=1$.

We have defined the functions $g_l(z_1,z_2)$ and $G_{l,p}(z_1,z_2)$ via (3.24) and (3.34) because integral representations are a convenient starting point for establishing the continuity needed for integration by parts and for deriving series expansions. This is particularly important in the more difficult $j\neq j'$ and/or $k\neq k'$ cases analyzed in Appendix C, where the needed functions do not always have representations like (3.25) and (3.39) in terms of known, well studied functions. It is straightforward to show that

$$\frac{d}{dz}J_{l,p}(z)=z^{l-2p+1/2}J_{l+1/2}(z), \tag{3.35}$$

$$\frac{d}{dz}I_{l,p}(z)=z^{l-2p+1/2}I_{l+1/2}(z), \tag{3.36}$$

$$\frac{d}{dz}K_{l,p}(z)=z^{l-2p+1/2}K_{l+1/2}(z), \tag{3.37}$$

$$\frac{\partial^2}{\partial z_1\,\partial z_2}G_{l,p}(z_1,z_2)=(z_1z_2)^{l-2p+1}g_l(z_1,z_2), \qquad z_1\neq z_2. \tag{3.38}$$

$G_{l,p}(z_1,z_2)$ is the indefinite integral which is needed for integration by parts on the radial integrals. Contour integration can be used to show that

$$G_{l,p}(z_1,z_2)=2[I_{l,p}(z_<)-I_{l,p}(0)]\,K_{l,p}(z_>). \tag{3.39}$$

It is obvious from (3.39) that $G_{l,p} \to 0$ as $z_< \to 0$ or $z_> \to \infty$. The function $G_{l,p}(z_1, z_2)$ is symmetric under interchange of z_1 and z_2 and continuous at $z_1 = z_2$, but its first partial derivatives are discontinuous at $z_1 = z_2$. The discontinuity, which is defined by

$$D_{l,p}(z) = \lim_{\varepsilon \to 0+} \left\{ \left[\frac{\partial}{\partial z_1} G_{l,p}(z_1, z) \right]_{z_1 = z + \varepsilon} - \left[\frac{\partial}{\partial z_1} G_{l,p}(z_1, z) \right]_{z_1 = z - \varepsilon} \right\}, \tag{3.40}$$

is easily calculated from (3.36) via contour integration. It can be written in either of the two forms

$$\begin{aligned} D_{l,p}(z) = {} & (-1)^l \pi I_{l,p}(0) \left[z^{l-2p+1/2} I_{l+1/2}(z) \right. \\ & \left. - \sum_{n=l-p+1}^{\infty} \frac{2^{l-2n+1/2}}{n!\, \Gamma(n-l+1/2)} z^{2n-2p} \right] \end{aligned} \tag{3.41}$$

$$\begin{aligned} = {} & 2I_{l,p}(0) \left[-z^{l-2p+1/2} K_{l+1/2}(z) \right. \\ & \left. + (-1)^l \pi \sum_{n=0}^{l-p} \frac{2^{l-2n-1/2}}{n!\, \Gamma(n-l+1/2)} z^{2n-2p} \right]. \end{aligned} \tag{3.42}$$

The first form (3.41) shows that $D_{l,p}(z)$ is $O(z^{2l-2p+1}) + O(z^{2l-4p+2})$ for $z \to 0$. The second form (3.42) shows that $D_{l,p}(z)$ is $O(z^{2l-4p})$ for $z \to \infty$. For later use, we note that the second form (3.42) can be written as

$$D_{l,p}(z) = S_{l,p}(z) + P_{l,p}^{(a)}(z^2) + P_{l,p}^{(b)}(z) \exp(-z), \tag{3.43}$$

where $P_{l,p}^{(a)}(z^2)$ is a polynomial of degree $l-2p$ in z^2, $P_{l,p}^{(b)}(z)$ is a polynomial of degree $l-2p$ in z, and

$$S_{l,0}(z) = 0, \tag{3.44}$$

$$S_{l,1}(z) = \frac{2^{2l}\pi(l-1)!}{\Gamma(1/2)\,\Gamma(-l+1/2)} \frac{d}{dz} \left[\frac{1-\exp(-z)}{z} \right]. \tag{3.45}$$

The result of integrating (3.28) by parts, once with respect to r and once with respect to r', is

$$M_{l,m;n;p}^{(j,k)} = M_{l,m;n;p}^{(j,k;a)} + M_{l,m;n;p}^{(j,k;b)}, \tag{3.46}$$

where

$$M_{l,m;n;p}^{(j,k;a)} = v^{2l-4p+2} \int_0^\infty dr\, D_{l,p}(v^{-1}r)\, \rho_{l-2p+1,m;l-2p+1,m;n}^{(j,k,k)}(r, r), \tag{3.47}$$

$$\begin{aligned} M_{l,m;n;p}^{(j,k;b)} = {} & v^{2l-4p+3} \int_0^\infty dr \int_0^\infty dr' G_{l,p}(v^{-1}r, v^{-1}r') \\ & \times \frac{\partial^2}{\partial r\, \partial r'} \rho_{l-2p+1,m;l-2p+1,m;n}^{(j,k,k)}(r, r'). \end{aligned} \tag{3.48}$$

By adding and subtracting

$$\rho^{(j,k,k)}_{l-2p+1,m;l-2p+1,m;n}(0,0)+r\left[\frac{\partial}{\partial r}\rho^{(j,k,k)}_{l-2p+1,m;l-2p+1,m;n}(r,r)\right]_{r=0}, \tag{3.49}$$

using the cusp condition

$$\left[\frac{\partial}{\partial r}\rho^{(j,k,k)}_{l,m;l,m;n}(r,r')\right]_{r=0}=-\frac{Z_k}{l+1}\rho^{(j,k,k)}_{l,m;l,m;n}(0,r'), \tag{3.50}$$

and integrating by parts, it can be shown that

$$\begin{aligned}
&v^{2l-2}\int_0^\infty dr\,S_{l,1}(v^{-1}r)\,\rho^{(j,k,k)}_{l-1,m;l-1,m;n}(r,r)\\
&=-\frac{2^{2l}\pi(l-1)!}{\Gamma(1/2)\,\Gamma(-l+1/2)}v^{2l-1}\bigg(\{1-v+2Z_kl^{-1}v[\ln(v)+1-\gamma]\}\,\rho(0,0)\\
&\quad+v\left\{\int_1^\infty\frac{\rho(r,r)}{r^2}\,dr+\int_0^1\frac{\rho(r,r)-[1-2l^{-1}Z_kr]\,\rho(0,0)}{r^2}\,dr\right\}\\
&\quad-v\int_0^\infty\frac{2l^{-1}Z_k\rho(0,0)+\partial\rho(r,r)/\partial r}{r}\exp(-v^{-1}r)\,dr\bigg),\qquad l\geqslant 1.
\end{aligned} \tag{3.51}$$

The abbreviated notation $\rho(r,r')=\rho^{(j,k,k)}_{l-2p+1,m;l-2p+1,m;n}(r,r')$ has been used when writing (3.51). γ is Euler's constant: $\gamma=\int_0^1 t^{-1}[1-\exp(-t)]\,dt-\int_1^\infty t^{-1}\times\exp(-t)\,dt=0.5772156649\ldots$ The rapid decay of the exponential factor $\exp(-v^{-1}r)$ in the last term in (3.51) justifies making the small v approximation of replacing $2l^{-1}Z_k\rho(0,0)+\partial\rho(r,r)/\partial r$ by $r[\partial^2\rho(r,r)/\partial r^2]_{r=0}$ in this term; the integration over r can then be performed. It can also be shown that, in the same abbreviated notation,

$$\begin{aligned}
&v^{2l+2-4p}\int_0^\infty\rho(r,r)\,P^{(a)}_{l,p}(v^{-2}r^2)\,dr\\
&=2v^2\int_0^\infty\rho(r,r)r^{2l-4p}\,dr+O(v^4),\qquad l-2p\geqslant 0,
\end{aligned} \tag{3.52}$$

$$\begin{aligned}
&v^{2l+2-4p}\int_0^\infty\rho(r,r)\,P^{(b)}_{l,p}(v^{-1}r)\exp(-v^{-1}r)\,dr\\
&=(4\delta_{l,2}\delta_{p,1}-2\delta_{l,0}\delta_{p,0})\,v^3\rho^{(j,k,k)}_{1,m;1,m;n}(0,0)+O(v^4).
\end{aligned} \tag{3.53}$$

The asymptotic evaluation of $M^{(j,k;b)}_{l,m;n;p}$ in (3.48) for v small can be handled by methods similar to those outlined above. Again the integrand peaks sharply at $r=r'$. The leading term for $l-2p\geqslant 0$ can be obtained by evaluating $\partial^2\rho(r,r')/\partial r\,\partial r'$ at $r'=r$ and integrating over r'; this leading term is found to be $O(v^4)$. The only case for which this estimate fails is $l=1$, $p=1$. In this latter case, the leading term can be obtained by evaluating $\partial^2\rho(r, r')/\partial r\,\partial r'$ at $r=r'=0$ and integrating over r and r' with the aid of the integration formula

$$\int_0^\infty dx\,\frac{\sinh(x)}{x}\int_x^\infty dy\,\frac{\exp(-y)}{y}=\frac{\pi^2}{8}. \tag{3.54}$$

The result, after using the cusp condition (3.50) twice (once for r and once for r'), is

$$M^{(j,k;b)}_{1,m;n;1}=-\tfrac{1}{2}(\pi^2-8)\,Z_k^2 v^3\rho^{(j,k,k)}_{0,0;0,0;n}(0,0)+O(v^4). \tag{3.55}$$

The integration formula (3.54) can be established by making the change of variables $x=r\cos(\theta)$, $y=r[\cos(\theta)+\sin(\theta)]$. The integration over r (from 0 to ∞) is performed first; the remaining integral over θ (from 0 to $\pi/2$) can then be evaluated by using the change of variables $t=[1+\tan(\theta)]^{-1}$ to obtain integrals which can be evaluated in terms of the dilogarithm function [21, pp. 244, 266].

Putting all of the pieces together and adding in the first correction to the approximation (3.21) yields

$$\begin{aligned}
\sum_{l=0}^{1}\sum_{m=-1}^{1}&\langle\psi^{(j,k)}_{l;m,n}\mid\psi^{(j,k)}_{l;m,n}\rangle\\
&=2\{v+2Z_k v^2\ln(v)+[2Z_k(1-\gamma)-1]\,v^2\}\\
&\quad\times\rho^{(j,k,k)}_{0,0;0,0;n}(0,0)+2v^2\Bigg[\sum_{m=-1}^{1}\int_0^\infty\rho^{(j,k,k)}_{1,m;1,m;n}(r,r)\,dr\\
&\quad+\int_0^1\frac{\rho^{(j,k,k)}_{0,0;0,0;n}(r,r)-(1-2Z_k r)\,\rho^{(j,k,k)}_{0,0;0,0;n}(0,0)}{r^2}\,dr\\
&\quad+\int_1^\infty\frac{\rho^{(j,k,k)}_{0,0;0,0;n}(r,r)}{r^2}\,dr\Bigg]-v^3\Bigg\{\frac{1}{2}(\pi^2-8)\,Z_k^2\rho^{(j,k,k)}_{0,0;0,0;n}(0,0)\\
&\quad+2\left[\frac{\partial^2\rho^{(j,k,k)}_{0,0;0,0;n}(r,r)}{\partial r^2}\right]_{r=0}+6\sum_{m=-1}^{1}\rho^{(j,k,k)}_{1,m;1,m;n}(0,0)\\
&\quad+8\pi\,\langle\psi_n\mid\delta(\mathbf{r}_j-\mathbf{R}_k)(T-\tfrac{1}{2}p_j^2)\mid\psi_n\rangle\Bigg\}+O[v^4\ln(v)].
\end{aligned} \tag{3.56}$$

This contribution can be written in the form in which it appears in the result (3.1)–(3.5) by using

$$\sum_{l=0}^{\infty}\sum_{m=-l}^{l}r^{2l}\rho^{(j,k,k)}_{l,m;l,m;n}(r,r)=\int\langle\psi_n\mid\delta(\mathbf{r}_j-\mathbf{R}_k-r)\mid\psi_n\rangle\,d\Omega_{k,j}, \tag{3.57}$$

$$\rho^{(j,k,k)}_{0,0;0,0;n}(0,0)=4\pi\,\langle\psi_n\mid\delta(\mathbf{r}_j-\mathbf{R}_k)\mid\psi_n\rangle. \tag{3.58}$$

The cases $j \neq j'$ and/or $k \neq k'$ are treated via similar methods in Appendix C; the conclusion is that (3.20) is valid in these cases for all l and l'. The $j=1$ and $j=2$ terms in the expansion (3.10) can also be analyzed via these methods; the results are

$$\sum_{m=-1}^{1} \langle \Psi_{n,m}| (T-E_n+W)^{-1/2} V(T-E_n+W)^{-1/2} |\Psi_{n,m}\rangle$$
$$= 8\pi v^2 \sum_{j=1}^{N} \sum_{k=1}^{K} Z_k^2 \Big\{ [(1-2\ln 2) Z_k + 2vZ_k^2] \langle \psi_n| \delta(\mathbf{r}_j - \mathbf{R}_k) |\psi_n\rangle$$
$$+ v \langle \psi_n| \delta(\mathbf{r}_j - \mathbf{R}_k) \left(V + \frac{Z_k}{|\mathbf{r}_j - \mathbf{R}_k|} \right) |\psi_n\rangle \Big\} + O[v^4 \ln(v)], \tag{3.59}$$

$$\sum_{m=-1}^{1} \langle \Psi_{n,m}| [(T-E_n+W)^{-1/2} V(T-E_n+W)^{-1/2}]^2 |\Psi_{n,m}\rangle$$
$$= 8\pi v^3 \left(1 - \frac{\pi^2}{12}\right) \sum_{j=1}^{N} \sum_{k=1}^{K} Z_k^4 \langle \psi_n| \delta(\mathbf{r}_j - \mathbf{R}_k) |\psi_n\rangle + O[v^4 \ln(v)]. \tag{3.60}$$

A few of the details of the derivation of (3.59) and (3.60) are sketched in Appendix C. The coefficients C_1, C_2, C_3, and C_4 can now be assembled. Additional terms in the large W expansion (3.1) should be obtainable via the methods outlined here, but we have not tried to derive them.

4. A Variational Principle for the Matrix Elements of the Resolvent

For most problems, needed values of the matrix element $\langle \varphi| (\zeta - A)^{-1} |\psi\rangle$ of the resolvent will not be calculable in closed form in terms of known, well-studied functions, and approximate methods must be used. An appropriate tool is the Schwinger–Levine variational principle, which will be discussed here only for the special case in which A is a non-negative Hermitian operator, $\zeta = -W$ with W real and positive, and $|\varphi\rangle = |\psi\rangle = |\Psi\rangle$. This special case is all that is needed for the computation of Bethe logarithms; more general versions of the principle can be found in Stakgold [22, pp. 311, 340, 357]. In this special case the Schwinger–Levine principle is a maximum principle which takes the form

$$\lambda = \max_{|\tilde{\chi}\rangle} \tilde{\lambda}, \tag{4.1}$$

where

$$\tilde{\lambda} = \frac{|\langle \Psi | \tilde{\chi}\rangle|^2}{\langle \tilde{\chi}| (A+W) |\tilde{\chi}\rangle}. \tag{4.2}$$

The maximum, which is

$$\lambda = \langle \Psi | \frac{1}{A+W} | \Psi \rangle, \tag{4.3}$$

is achieved for $|\tilde{\chi}\rangle = |\chi\rangle$, where

$$|\chi\rangle = \frac{c}{A+W} |\Psi\rangle \tag{4.4}$$

with c an arbitrary constant. For the Bethe logarithm problem, $|\Psi\rangle$ will be either $P_m |\psi_n\rangle$ (where P_m is the mth spherical component [18, p. 69] of $\mathbf{P}$) or $AP_m |\psi_n\rangle$ and A will be $Q_\perp^{(n)}(H - E_n) Q_\perp^{(n)}$.

The use of (4.1)–(4.2) for approximate calculation is similar to the use of the familiar Rayleigh–Ritz variational principle. One chooses a basis set $\{|\xi_n\rangle\}_{n=0}^N$ and looks for an approximation $|\tilde{\chi}\rangle$ to $|\chi\rangle$ of the form

$$|\tilde{\chi}\rangle = \sum_{n=0}^{N} c_n^{(N)} |\xi_n\rangle, \tag{4.5}$$

where the $c_n^{(N)}$ are variational parameters, dependent on N as well as n, which are chosen to maximize the quotient $\tilde{\lambda}$ defined by (4.2) in the subspace spanned by the finite basis set $\{|\xi_n\rangle\}_{n=0}^N$. Let P_N be the projector onto this subspace. The best approximation with this basis can be written in the form

$$|\tilde{\chi}\rangle = \tilde{c}[P_N(A+W)P_N]^{-1} |\Psi\rangle, \tag{4.6}$$

$$\tilde{\lambda} = \langle \Psi | [P_N(A+W)P_N]^{-1} |\Psi\rangle, \tag{4.7}$$

where $[P_N(A+W)P_N]^{-1}$ is the generalized inverse (inverse on the subspace spanned by the $\{|\xi_n\rangle\}_{n=0}^N$) which satisfies

$$\begin{aligned}&[P_N(A+W)P_N]^{-1}[P_N(A+W)P_N]\\ &\quad = [P_N(A+W)P_N][P_N(A+W)P_N]^{-1} = P_N,\end{aligned} \tag{4.8}$$

and

$$\begin{aligned}&[P_N(A+W)P_N]^{-1} P_N = P_N[P_N(A+W)P_N]^{-1}\\ &\qquad = [P_N(A+W)P_N]^{-1}.\end{aligned} \tag{4.9}$$

Here $\tilde{c}$ is a constant which can be chosen arbitrarily.

Formulas which are convenient for computation in the general case of a basis which may not be orthogonal can be obtained by introducing a second basis set

$\{|\eta_n^{(N)}\rangle\}_{n=0}^N$ which spans the same $(N+1)$-dimensional space as the $|\xi_n\rangle$. The $|\eta_n^{(N)}\rangle$, which are determined uniquely by the orthogonality conditions

$$\langle \xi_m \mid \eta_n^{(N)} \rangle = \delta_{m,n}, \tag{4.10}$$

are given explicitly by

$$|\eta_m^{(N)}\rangle = \sum_{n=0}^{N} g_{n,m}^{(N)} |\xi_n\rangle, \tag{4.11}$$

where the matrix $g_{n,m}^{(N)}$ is the inverse of the Gram matrix $\langle \xi_n \mid \xi_m \rangle$. The superscript (N) is used to emphasize the fact that the $|\eta_m^{(N)}\rangle$ and the elements of the matrix $g_{n,m}^{(N)}$ will depend on N even if the $|\xi_n\rangle$ do not. The $|\eta_n^{(N)}\rangle$ can be used to write the projector P_N in the forms

$$P_N = \sum_{n=0}^{N} |\xi_n\rangle\langle \eta_n^{(N)}| = \sum_{n=0}^{N} |\eta_n^{(N)}\rangle\langle \xi_n|. \tag{4.12}$$

The representations (4.12) of P_N can be used to show that

$$[P_N(A+W)\,P_N]^{-1} = \sum_{m=0}^{N} \sum_{n=0}^{N} B_{m,n}^{(N)} |\xi_m\rangle\langle \xi_n|, \tag{4.13}$$

where the matrix $B_{m,n}^{(N)}$ is the inverse of the matrix $\langle \xi_m | \, (A+W) \, | \xi_n \rangle$. A formula for practical calculation can now be obtained by inserting (4.13) in (4.7) to obtain

$$\tilde{\lambda} = \sum_{m=0}^{N} \sum_{n=0}^{N} B_{m,n}^{(N)} \langle \Psi \mid \xi_m \rangle\langle \xi_n \mid \Psi \rangle. \tag{4.14}$$

Equation (4.14) shows that the use of a basis set $\{|\xi_n\rangle\}_{n=0}^N$ which is not orthonormal does not increase the computational effort; the auxiliary basis vectors $|\eta_m^{(N)}\rangle$ need never be calculated.

The variational method outlined above will be effective if the convergence rate is sufficiently fast; this will happen if the basis set $\{|\xi_n\rangle\}_{n=0}^N$ is chosen appropriately. Rates of convergence for variational methods are determined by the way the basis set handles the singularities of the function being approximated [23]. Thus an understanding of the singularities of $|\chi\rangle$ is needed if a good basis set is to be designed. Some of these singularities come from the driving term Ψ; others come from the operator A. In addition, large values of W will introduce a second length scale, proportional to $W^{-1/2}$, which must be handled properly by the basis set.

A first step in the discussion of convergence rates for the Schwinger–Levine variational principle is the derivation of an error formula. The choice $c = \tilde{c} = 1$ for the arbitrary constants in (4.4) and (4.6) implies that $\lambda = \langle \Psi \mid \chi \rangle$ and $\tilde{\lambda} = \langle \Psi \mid \tilde{\chi} \rangle$. Because $|\tilde{\chi}\rangle$ is in the range of the projector P_N, $\langle \tilde{\chi}| = \langle \tilde{\chi}| \, P_N$. Using these together with $\langle \Psi| = \langle \chi| (A+W)$, $|\Psi\rangle = (A+W)|\chi\rangle$, and $P_N|\Psi\rangle = P_N(A+W)P_N|\tilde{\chi}\rangle$ yields

$$\begin{aligned}\lambda - \tilde{\lambda} &= \langle \Psi | \chi\rangle - \langle \Psi | \tilde{\chi}\rangle - \langle \tilde{\chi} | \Psi\rangle + \langle \tilde{\chi}| P_N |\Psi\rangle \\ &= (\langle \chi| - \langle \tilde{\chi}|)(A+W)(|\chi\rangle - |\tilde{\chi}\rangle).\end{aligned} \tag{4.15}$$

Equation (4.15) shows that the appropriate notion of convergence for the Schwinger–Levine principle applied to the Bethe logarithm problem is convergence in the first Sobolev space, restricted to vectors $|\chi\rangle$ for which $\langle \psi_m | \chi\rangle = 0$, $0 \leqslant m \leqslant n-1$. The error formula (4.15) can be brought to a form convenient for computation by introducing the Cholesky decomposition

$$\langle \xi_m| (A+W) |\xi_n\rangle = \sum_{l=0}^{\min(m,n)} \overline{U_{l,m}}\, U_{l,n}, \tag{4.16}$$

where $U_{l,n}$ is an upper triangular matrix (i.e., $U_{l,n} = 0$ for $l > n$). $U_{l,n}$ can be systematically calculated from the formulas

$$U_{n,n} = \left[\langle \xi_n| (A+W) |\xi_n\rangle - \sum_{l=0}^{n-1} U_{l,n}^2 \right]^{1/2}, \tag{4.17}$$

$$U_{m,n} = \left[\langle \xi_m| (A+W) |\xi_n\rangle - \sum_{l=0}^{m-1} U_{l,m} U_{l,n} \right] \Big/ U_{m,m}, \qquad m < n. \tag{4.18}$$

Introduce new basis functions $|\zeta_n\rangle$ which are related to the $|\xi_n\rangle$ via

$$|\xi_n\rangle = \sum_{l=0}^{n} U_{l,n} |\zeta_l\rangle, \qquad |\zeta_n\rangle = \sum_{l=0}^{n} (U^{-1})_{l,n} |\xi_l\rangle. \tag{4.19}$$

It is easy to show that the matrix $(U^{-1})_{m,n}$ inverse to $U_{m,n}$ is also an upper triangular matrix. The elements $(U^{-1})_{m,n}$, and therefore also the $|\zeta_n\rangle$, do not depend on the dimension of the space in which the inverse is computed. The new basis functions $|\zeta_n\rangle$ obey the orthonormality relation

$$\langle \zeta_m| (A+W) |\zeta_n\rangle = \delta_{m,n}. \tag{4.20}$$

The expansions of the exact and approximate solutions $|\chi\rangle$ and $|\tilde{\chi}\rangle$ in this basis are

$$|\chi\rangle = \sum_{n=0}^{\infty} c'_n |\zeta_n\rangle, \qquad |\tilde{\chi}\rangle = \sum_{n=0}^{N} c'_n |\zeta_n\rangle, \tag{4.21}$$

where the coefficients c'_n, which do not depend on N, are given by

$$c'_n = \langle \zeta_n | \Psi\rangle. \tag{4.22}$$

It follows from (4.15), (4.20), and (4.21) that

$$\lambda - \tilde{\lambda} = \sum_{n=N+1}^{\infty} |c'_n|^2. \tag{4.23}$$

It is straightforward to show that the coefficients c'_n are related to the coefficients c_n in the expansion

$$|\chi\rangle = \sum_{n=0}^{\infty} c_n |\xi_n\rangle \tag{4.24}$$

of $|\chi\rangle$ in the original $|\xi_n\rangle$ basis by

$$c'_n = \sum_{l=n}^{\infty} U_{n,l} c_l. \tag{4.25}$$

Equations (4.23) and (4.25) can be used to compute a large N asymptotic expansion of the error $\lambda - \tilde{\lambda}$ from asymptotic expansions of $U_{n,l}$ and c_l which are valid for n and l large. The next section contains such a calculation.

5. A Basis Set for Variational Approximations to the Resolvent

Rapid convergence of variational approximations to the resolvent for hydrogen and helium for small to moderate values of W can be obtained with a Laguerre polynomial basis set. For helium, one uses Laguerre polynomials in perimetric coordinates (perimetric coordinates for helium were first introduced by James and Coolidge [24] and were used extensively by Pekeris [25]). Such a basis set is often called a Sturmian basis set in the physics and chemistry literature. It has the advantage that it builds in all of the two particle cusps, which are the most important singularities for atomic and molecular systems. It also has good numerical stability properties. For large values of W, this basis set must be supplemented with auxiliary basis functions which are designed to handle the second (short) length scale which is proportional to $W^{-1/2}$. This section begins by showing how to analyze the convergence rate for a Laguerre polynomial expansion of an arbitrary function. This analysis is then used to derive auxiliary basis functions which can be used to accelerate the convergence of such expansions. The Bethe logarithm for the hydrogen ground state is used as a concrete example; the convergence rate for the variational principle for this example is obtained from the error formula (4.23) Numerical comparisons with exact results are given.

We begin with the Laguerre polynomial expansion of an arbitrary function $f(x)$. Make the definition

$$u_n^{(\alpha',\alpha)}(x) = [n!/\Gamma(n+\alpha+1)]^{1/2} \exp(-x/2)\, x^{\alpha'} L_n^{(\alpha)}(x), \tag{5.1}$$

where $L_n^{(\alpha)}(x)$ is a Laguerre polynomial in standard notation [15, pp. 239–249; 19, pp. 188–192]. For a function $f(x)$ which involves a single length scale $1/a$, the appropriate Laguerre polynomial expansion is

$$f(x) = \sum_{n=0}^{\infty} c_n^{(\alpha',\alpha)} \xi_n^{(\alpha',\alpha)}(a; x), \tag{5.2}$$

where

$$\xi_n^{(\alpha',\alpha)}(a; x) = a^{1/2} u_n^{(\alpha',\alpha)}(ax). \tag{5.3}$$

The parameter α' should be chosen to make the small-x behavior of the basis functions the same as the small-x behavior of $f(x)$. The functions $\xi_n^{(\alpha',\alpha)}(a; x)$ are orthonormal with respect to the inner product $\langle f \mid g \rangle = \int_0^\infty \overline{f(x)}\, g(x)\, dx$ if $\alpha = 2\alpha'$; the flexibility afforded by the possibility of choosing $\alpha \neq 2\alpha'$ can be exploited to simplify matrix element evaluation and/or to make the needed matrices sparse, as will be seen below. The expansion coefficients $c_n^{(\alpha',\alpha)}$ in (5.2) are given by

$$c_n^{(\alpha',\alpha)} = a^{(2\alpha - 2\alpha' + 1)/2} [n!/\Gamma(n+\alpha+1)]^{1/2}\, I_n^{(\alpha',\alpha)}, \tag{5.4}$$

where

$$I_n^{(\alpha',\alpha)} = \int_0^\infty f(x) \exp\left(-\frac{ax}{2}\right) x^{\alpha-\alpha'} L_n^{(\alpha)}(ax)\, dx. \tag{5.5}$$

The integrals $I_n^{(\alpha',\alpha)}$ can be obtained by using the generating function

$$(1-z)^{-\alpha-1} \exp[-xz/(1-z)] = \sum_{n=0}^{\infty} L_n^{(\alpha)}(x)\, z^n \tag{5.6}$$

for the Laguerre polynomials. The $I_n^{(\alpha',\alpha)}$ are found to be the coefficients in the small-z series

$$g^{(\alpha',\alpha)}(z) = \sum_{n=0}^{\infty} I_n^{(\alpha',\alpha)} z^n \tag{5.7}$$

for the function $g^{(\alpha',\alpha)}(z)$, given by

$$g^{(\alpha',\alpha)}(z) = (1-z)^{-\alpha-1}\, F(s), \tag{5.8}$$

where

$$F(s) = \int_0^\infty x^{\alpha-\alpha'} f(x) \exp(-sx)\, dx \tag{5.9}$$

is the Laplace transform of $x^{\alpha-\alpha'} f(x)$ and s is given by

$$s = \frac{a(1+z)}{2(1-z)}. \tag{5.10}$$

The large-n behavior of $c_n^{(\alpha', \alpha)}$ is determined by the large-n behavior of $I_n^{(\alpha', \alpha)}$, which is in turn determined by the nature and location of the singularity of $g^{(\alpha', \alpha)}(z)$ which is closest to $z=0$. If there are no other singularities near this closest singularity, the detailed description of this large-n behavior can be obtained via the method of Darboux [26, pp. 532–535; 27, pp. 116–122, 145–146; 28, pp. 309–315, 321], which is best explained by an example. Suppose that

$$g^{(\alpha', \alpha)}(z) = \sum_{k=0}^{\infty} A_k (z_0 - z)^{\sigma + k} + g_1(z) \tag{5.11}$$

for z near z_0, where σ and the A_k are constants, with σ not a positive integer, that z_0 is the singularity of $g^{(\alpha', \alpha)}(z)$ closest to zero, that $g_1(z)$ is an analytic function of z, and that z_1 is the singularity of $g_1(z)$ closest to zero. The binomial expansion of $(z_0 - z)^{\sigma + k}$ is

$$(z_0 - z)^{\sigma + k} = \sum_{n=0}^{\infty} \binom{\sigma + k}{n} (-1)^n z_0^{\sigma + k - n} z^n. \tag{5.12}$$

Then the asymptotic behavior of $I_n^{(\alpha', \alpha)}$ in (5.7) is given by

$$I_n^{(\alpha', \alpha)} = \sum_{k=0}^{\infty} A_k \binom{\sigma + k}{n} (-1)^n z_0^{\sigma + k - n} + O(|z_1|^{-n+\varepsilon}). \tag{5.13}$$

The ε in the error estimate $O(z_1^{-n+\varepsilon})$ in (5.13) is an infinitesimal positive number which is needed because the nature of the singularity of $g_1(z)$ nearest the origin has not been specified. The Stirling approximation to the gamma function [14, p. 47, Eq. (2); 15, p. 12] can be used to show that

$$\binom{\sigma + k}{n} (-1)^n = \frac{1}{\Gamma(-\sigma - k)} n^{-\sigma - k - 1} [1 + O(n^{-1})] \tag{5.14}$$

for n large. Thus the $k=0$ term in (5.13) is the most important. It follows that

$$I_n^{(\alpha', \alpha)} = \frac{A_0 z_0^{\sigma}}{\Gamma(-\sigma)} z_0^{-n} n^{-\sigma - 1} [1 + O(n^{-1})]. \tag{5.15}$$

The z_0^{-n} factor in (5.15) gives the well-known exponential behavior (growth if $|z_0| < 1$, decay if $|z_0| > 1$) of power series coefficients which comes from the location of the nearest singularity. The $n^{-\sigma-1}$ power law factor is a correction which arises from the nature of the singularity. If there are several nearest singularities lying on a circle of radius $|z_0|$ and if these nearest singularities are well separated, the asymptotic behavior of $I_n^{(\alpha', \alpha)}$ is given by a sum of contributions like the right-hand side of (5.15), one for each singularity. Because the A_k in (5.11) behave like $|z_0 - z_1|^{-k}$ as k becomes large, where z_1 is the singularity closest to z_0, the method of Darboux breaks down as $|z_0 - z_1|$ becomes small.

In order to apply the method of Darboux to our problem, we must first locate the singularities of $g^{(\alpha',\alpha)}(z)$. The factor $(1-z)^{-\alpha-1}$ in (5.8) will introduce a singularity at $z=1$ unless $F(s)$ has a compensating factor. Equation (5.10) shows that $z=1$ corresponds to $s=\infty$. Since $F(s)$ is a Laplace transform, the behavior of $F(s)$ for large s can be extracted by applying Watson's lemma, which relates the large-s behavior of $F(s)$ to the small-x behavior of $x^{\alpha-\alpha'}f(x)$. Specifically, if the integral (5.9) converges, and if $f(x)$ has an asymptotic expansion for $x\to 0$ of the form

$$f(x)\sim\sum_{n=0}^{\infty} b_n x^{\mu+n}, \tag{5.16}$$

a large-s asymptotic expansion of $F(s)$ can be obtained by inserting (5.16) in (5.9) and integrating term by term to obtain

$$F(s)\sim\sum_{n=0}^{\infty} b_n \Gamma(\alpha-\alpha'+\mu+n+1)\, s^{-\alpha+\alpha'-\mu-n-1}. \tag{5.17}$$

Remark. The theorem in asymptotic analysis which is known as Watson's lemma is usually attributed to G. N. Watson [29]. However, Wyman and Wong [30] have pointed out that Watson's lemma can be regarded as a special case of an earlier theorem of Barnes [31]. See also [27, 28, 32]. Equations (5.8), (5.10), and (5.17) show that $g^{(\alpha',\alpha)}(z)$ will not have a singularity at $z=1$ if $\alpha'=\mu$; this is the origin of the statement above that α' should be chosen to make the small-x behavior of the basis functions the same as the small-x behavior of $f(x)$ (the choices $\alpha'=\mu-1$, $\mu-2$, $\mu-3$, ..., could also be used, but only if they did not make the basis functions too singular or too far from orthogonality). We now look at the singularities of $g^{(\alpha',\alpha)}(z)$ which correspond to singularities of $F(s)$. Equations (5.8) and (5.10) imply that

$$z=\frac{2s-a}{2s+a}. \tag{5.18}$$

Thus, if $F(s)$ has a singularity at s_k, $g^{(\alpha',\alpha)}(z)$ has a singularity at

$$z_k=\frac{2s_k-a}{2s_k+a}. \tag{5.19}$$

Since s_k does not depend on a, the location of the singularity of $g^{(\alpha',\alpha)}(z)$ (the value of z_k) can be changed by changing a. The most rapid convergence possible with an expansion of the form (5.2) is achieved by eliminating the singularity at $z=1$ by setting $\alpha'=\mu$, and by choosing a value of a which puts the nearest singularity of $g^{(\alpha',\alpha)}(z)$ as far from the origin as possible. Obviously a change in the value of a which moves one singularity of $g^{(\alpha',\alpha)}(z)$ further away may well move some other singularity closer, so that the other singularity becomes the nearest singularity. If this happens, the optimum choice of a is the one which makes the two singularities equidistant from the origin. Thus there will normally be a limit to the improvement in the rate of convergence which can be achieved via a good choice of a; further improvement in the convergence rate requires something else.

The "something else" is the use of additional basis functions whose expansion in the basis functions (5.3) involves expansion coefficients with the same asymptotic behavior as the $c_n^{(\alpha',\alpha)}$. Suppose that the asymptotic behavior of $I_n^{(\alpha',\alpha)}$ is given by (5.15), so that $c_n^{(\alpha',\alpha)}$, which is related to $I_n^{(\alpha',\alpha)}$ via (5.4), has the asymptotic behavior

$$c_n^{(\alpha',\alpha)} = \frac{A_0 z_0^\sigma a^{(2\alpha-2\alpha'+1)/2}}{\Gamma(-\sigma)} z_0^{-n} n^{-(\alpha/2)-\sigma-1}[1+O(n^{-1})]. \tag{5.20}$$

We want to add a function to the basis set whose expansion coefficient behaves like $c_n^{(\alpha',\alpha)}$ for large n. Call this function $h(\sigma, z_0, \alpha', \alpha, a; x)$. Then we want the coefficients $d_n(\sigma, z_0, \alpha', \alpha, a)$ in the expansion

$$h(\sigma, z_0, \alpha', \alpha, a; x) = \sum_{n=0}^{\infty} d_n(\sigma, z_0, \alpha', \alpha, a)\, \xi_n^{(\alpha',\alpha)}(a; x) \tag{5.21}$$

to have the same large-n behavior as $c_n^{(\alpha',\alpha)}/A_0$, so that we can write

$$f(x) = A_0 h(\sigma, z_0, \alpha', \alpha, a; x) + \sum_{n=0}^{\infty} c_n^{(\alpha',\alpha,1)} \xi_n^{(\alpha',\alpha)}(a; x), \tag{5.22}$$

with $c_n^{(\alpha',\alpha,1)} = c_n^{(\alpha',\alpha)} - A_0\, d_n(\sigma, z_0, \alpha', \alpha, a)$ decreasing faster for large n than $c_n^{(\alpha',\alpha)}$. The function h is found by inverting the analysis which led to the asymptotic formula for $c_n^{(\alpha',\alpha)}$. Let

$$(z_0 - z)^\sigma = (1-z)^{-\alpha-1} H\left[\frac{a(1+z)}{2(1-z)}\right], \tag{5.23}$$

where

$$H(s) = \int_0^\infty x^{\alpha-\alpha'} h(\sigma, z_0, \alpha', \alpha, a; x) \exp(-sx)\, dx. \tag{5.24}$$

The usual inversion formula for the Laplace transform yields

$$h(\sigma, z_0, \alpha', \alpha, a; x) = \frac{a^{\alpha+1}(z_0-1)^\sigma}{\Gamma(\alpha+1)} x^{\alpha'} \times \exp(-ax/2)\, {}_1F_1\left(-\sigma; \alpha+1; \frac{ax}{1-z_0}\right) \tag{5.25}$$

with ${}_1F_1$ a confluent hypergeometric function in standard notation [14, p. 262; 15, Chap. VI]. This convergence acceleration process can be repeated, leading to the expansion

$$f(x) = \sum_{k=0}^{K-1} A_k h(\sigma + k, z_0, \alpha', \alpha, a; x) + \sum_{n=0}^{\infty} c_n^{(\alpha', \alpha, K)} \xi_n^{(\alpha', \alpha)}(a; x), \tag{5.26}$$

and the asymptotic estimate

$$c_n^{(\alpha', \alpha, K)} = A_K \frac{a^{(2\alpha - 2\alpha' + 1)/2} z_0^{\sigma + K}}{\Gamma(-\sigma - K)} n^{-(\alpha/2) - \sigma - K - 1} z_0^{-n} [1 + O(n^{-1})],$$

$$K + \sigma \text{ not a positive integer or zero,} \tag{5.27}$$

which shows that each additional function $h(\sigma + k, z_0, \alpha', \alpha, a; x)$ used in (5.26) improves the convergence rate of the infinite series in (5.26) by an additional factor of $1/n$. If σ is a negative integer, so that the singularity is a pole, the improvement stops at $K = -\sigma - 1$. The analysis given above for branch points of the form (5.11) can be extended to include logarithmic branch points by taking a derivative with respect to σ to bring down a logarithm.

In order to apply this rate-of-convergence theory, it is necessary to know the location of the singularities of $F(s)$ and the form of the expansion about these singularities, at least for the singularity (or singularities) which give rise to the singularity (or singularities) of $g^{(\alpha', \alpha)}(z)$ closest to the origin in the complex z plane. In some cases this information can be obtained from known properties of $x^{\alpha - \alpha'} f(x)$ by invoking theorems on the Laplace transform. In particular, $F(s)$ is an analytic function of s in the interior of the domain in which its defining integral (5.9) converges; analytic continuation can be carried out by deforming the path of integration in (5.9). In other cases, it may be possible to Laplace transform the equation for $x^{\alpha - \alpha'} f(x)$ to obtain an equation for $F(s)$ from which the location and nature of its singularities can be deduced. Alternatively, values of s_0 and σ can be deduced by numerical fitting to empirical convergence patterns, or s_0 and σ can be treated as additional (nonlinear) variational parameters.

We will now apply the theory to the hydrogen ground state Bethe logarithm, where comparisons with exact results can be made. Introduce the spherical components p_m [18, p. 69] of the momentum $\mathbf{p}$ via

$$p_{\pm 1} = \mp \frac{1}{\sqrt{2}} (p_x \pm i p_y); \qquad p_0 = p_z. \tag{5.28}$$

Then the spherical components of $\mathbf{p} \, |\psi_0\rangle$ have the coordinate space representatives

$$\langle \mathbf{r} | \, p_m \, |\psi_0\rangle = \frac{2i}{\sqrt{3}} Y_{1,m}(\theta, \phi) \exp(-r). \tag{5.29}$$

The exact solution $|\chi\rangle$ of the variational problem (4.1), (4.2) has the coordinate space representative

$$\langle \mathbf{r} \mid \chi \rangle = \langle \mathbf{r} | \, (H - E_0 + W)^{-1} \, p_m \, |\psi_0\rangle = i Y_{1,m}(\theta, \phi) \, r^{-1} f(r), \tag{5.30}$$

which implies that $f(r)$, which is the function to be expanded in a Laguerre polynomial basis, has the representation

$$f(r) = -ir \int \overline{Y_{1,m}(\theta, \phi)} \, \langle \mathbf{r} | \, (H - E_0 + W)^{-1} \, p_m \, |\psi_0\rangle \, d\Omega, \tag{5.31}$$

where the integration is over θ and ϕ with $d\Omega = \sin(\theta)\, d\theta\, d\phi$. Since $f(r)$ behaves like r^2 for small r, we choose $\alpha' = 2$ in the Laguerre polynomial expansion. Equations (2.37), (5.9), and (5.31) then imply that the Laplace transform $F(s)$ which appears in the generating function $g^{(2,\alpha)}(z)$ for the expansion coefficients is given by

$$\begin{aligned} F(s) &= \int_0^{\infty} r^{\alpha-2} f(r) \exp(-sr)\, dr \\ &= -\frac{2}{\sqrt{3}} \left(-\frac{\partial}{\partial s} \right)^{\alpha-3} I_1\left(s, 1, -W - \frac{1}{2} \right), \qquad \alpha \geqslant 3. \end{aligned} \tag{5.32}$$

We choose $\alpha = 2\alpha' = 4$ to obtain a basis orthonormal with respect to the inner product $\langle f \mid g \rangle = \int_0^{\infty} \overline{f(r)}\, g(r)\, dr$. The right-hand side of (5.32) can be evaluated with the aid of (2.38)–(2.40); the exact expansion coefficients then follow from (5.4) and (5.7)–(5.9).

The singular points of $F(s)$ occur at $s = -1$ and at $s = -v^{-1}$, as can be shown either by using (2.38)–(2.40), (5.32), and the fact that the hypergeometric function has singularities at one and at infinity, or by Laplace transforming the differential equation satisfied by $r^2 f(r)$ to obtain a differential equation for $F(s)$. For an example, see [16, Eqs. (3.8)–(3.11)]. It follows from (5.19) that the singular points of the generating function $g^{(2,\alpha)}(z)$ are at the points

$$z_0^{(1)} = \frac{2+a}{2-a}, \qquad z_0^{(2)} = \frac{2+av}{2-av}. \tag{5.33}$$

The asymptotic approximation to $c_n^{(2,\alpha)}$ can be obtained by working out the expansion (5.11) about each of the two singularities. In order to facilitate the discussion, we introduce the contour integrals

$$g_k^{(2,\alpha)}(z) = \frac{1}{2\pi i} \oint_{C_k} (\zeta - z)^{-1} \, g^{(2,\alpha)}(\zeta)\, d\zeta, \qquad k = 1, 2, \tag{5.34}$$

$$I_{n,k}^{(2,\alpha)} = \frac{1}{2\pi i} \oint_{C_k} \zeta^{-n-1} g^{(2,\alpha)}(\zeta)\, d\zeta, \qquad k = 1, 2, \tag{5.35}$$

where the contour C_k runs clockwise around the branch cut associated with $z_0^{(k)}$, which runs from $z_0^{(k)}$ to infinity. These contour integrals are obtained by writing ordinary Cauchy integrals for $g^{(2,\alpha)}(z)$ and $I_n^{(2,\alpha)}$ in which the contour is a small circle around the origin which is large enough to contain z. This small circle is then deformed to a new contour which is the sum of C_1 and C_2, plus pieces at infinity which do not contribute. This kind of contour deformation is used in the derivation of the method of Darboux given on pages 116–122 of [27]. Then $g^{(2,\alpha)}(z)=g_1^{(2,\alpha)}(z)+g_2^{(2,\alpha)}(z)$. $I_{n,k}^{(2,\alpha)}$ is the contribution of the singularity $z_0^{(k)}$ to the asymptotic behavior of $I_n^{(2,\alpha)}$ in exact form. The expansion coefficient $c_n^{(2,\alpha)}$ is given by

$$c_n^{(2,\alpha)}=a^{(2\alpha-3)/2}[n!/\Gamma(n+\alpha+1)]^{1/2}\,[I_{n,1}^{(2,\alpha)}+I_{n,2}^{(2,\alpha)}]. \tag{5.36}$$

The asymptotic expansion of $I_{n,1}^{(2,\alpha)}$ can be obtained by using (2.41) to work out the non-analytic terms in the expansion of $I_1(s,1,-W-\frac{1}{2})$ about $s=-1$. These terms are

$$\begin{aligned} I_1\left(s,1,-W-\frac{1}{2}\right)&=\frac{-4v^2}{(1-v^2)(1+s)^3}+\frac{4v^4}{(1-v^2)^2\,(1+s)} \\ &\quad-\frac{16v^6\log(1+s)}{(1+v)^{1+v}\,(1-v)^{1-v}\,(1+vs)^{2+v}\,(1-vs)^{2-v}} \\ &\quad+\text{analytic function.} \end{aligned} \tag{5.37}$$

It follows that the first three terms of the large n expansion for $I_{n,1}^{(2,\alpha)}$ for $\alpha=4$ are

$$\begin{aligned} I_{n,1}^{(2,4)}&=\frac{-32v^2(2-a)}{\sqrt{3}\,(1-v^2)\,a(2+a)^4}\left(\frac{2-a}{2+a}\right)^n\frac{(n+3)!}{n!} \\ &\quad\times\left\{1+\left[\frac{3(2+a)}{2a}\right]\frac{1}{(n+3)}+\left[\frac{3(2+a)^2}{2a^2}\right]\right. \\ &\quad\left.\times\left[1-\frac{v^2(2-a)^2}{12(1-v^2)}\right]\frac{1}{(n+2)(n+3)}+O(n^{-3})\right\}. \end{aligned} \tag{5.38}$$

The asymptotic expansion of $I_{n,2}^{(\alpha',\alpha)}$, can be worked out by using

$$\begin{aligned} {}_2F_1(4,2-v;3-v;z)&=-\left(\frac{2-v}{2+v}\right)z^{-4}{}_2F_1(4,2+v;3+v;z^{-1}) \\ &\quad+\frac{1}{6}\Gamma(3-v)\,\Gamma(2+v)(-z)^{v-2} \end{aligned} \tag{5.39}$$

to obtain

$$g^{(2,4)}(z) = \frac{4096\pi v^8(1+a)}{\sqrt{3}\,(1-v^2)\sin(\pi v)(4-a^2v^2)^3}\left[\frac{(1-v)(2+av)}{(1+v)(2-av)}\right]^v$$
$$\times\left[z-\left(\frac{1-a}{1+a}\right)\right]\left[z-\frac{1}{z_0^{(2)}}\right]^{-3+v}[z_0^{(2)}-z]^{-3-v}$$
$$+\text{analytic function.} \tag{5.40}$$

It follows that the first three terms of the large n expansion for $I_{n,2}^{(2,\alpha)}$ for $\alpha=4$ are

$$I_{n,2}^{(2,4)} = C^{(2,4)}(v)\left(\frac{2-av}{2+av}\right)^n \frac{\Gamma(3+v+n)}{n!}$$
$$\times\left\{1+\frac{(2-v)(2+av)[6+(2+a)\,v+av^2]}{8av(n+2+v)}\right.$$
$$\left.+\frac{(1+v)(2-v)(3-v)(2+av)^3\,(8+2v+av^2)}{128a^2v^2(n+1+v)(n+2+v)}+O(n^{-3})\right\}, \tag{5.41}$$

where

$$C^{(2,4)}(v) = \frac{16\pi v^5(2-av)^2}{\sqrt{3}\,a^2(1-v^2)\sin(\pi v)\,\Gamma(2+v)(2+av)^3}$$
$$\times\left[\frac{8av(1-v)}{(1+v)(4-a^2v^2)}\right]^v. \tag{5.42}$$

The large n asymptotic expansion of $c_n^{(2,4)}$ is then obtained by inserting (5.38) and (5.41) in (5.36). This asymptotic result is compared with the exact coefficients in Table III for $v=0.01$ and $a=10$, which implies that $z_0^{(1)}=-1.5$ and $z_0^{(2)}=1.105...$. With these choices of v and a, the contribution $I_{n,1}^{(2,4)}$ from $z_0^{(1)}$ dominates for small n, and the contribution $I_{n,2}^{(2,4)}$ from $z_0^{(2)}$ dominates for large n, with a crossover at $n=25$. The relative errors listed in the last column of the table are the exact values minus the asymptotic approximations $I_{n,1}^{(2,4)}+I_{n,2}^{(2,4)}$ divided by the exact values. The anomalously large relative error at $n=25$ arises because a partial cancellation between $I_{n,1}^{(2,4)}$ and $I_{n,2}^{(2,4)}$ makes the exact value anomalously small.

It can be seen that the product vn, and not just n, must be large if (5.41) is to be a good approximation. This happens because $g^{(2,\alpha)}(z)$ has a singularity at $z=1/z_0^{(2)}$ which approaches the singularity at $z=z_0^{(2)}$ as $v\to 0$. This additional singularity is not on the top sheet of the Riemann surface for $g^{(2,\alpha)}(z)$ and therefore does not contribute to the asymptotic behavior of $I_n^{(2,\alpha)}$ when v is not small, but it does limit the radius of convergence of the expansion (5.11), giving rise to a $|z_0^{(2)}-1/z_0^{(2)}|^{-k}\propto v^{-k}$ growth of the A_k as k increases and a consequent breakdown of the method of Darboux when v is small. We can circumvent this breakdown and

TABLE III

Asymptotic Approximations to Expansion Coefficients

n	$I_{n,1}^{(2,4)}$	$I_{n,2}^{(2,4)}$	$I_{n,1}^{(2,4)}+I_{n,2}^{(2,4)}$	Relative error
		One-term asymptotic approximations		
5	-3.154×10^{-6}	9.168×10^{-9}	-3.145×10^{-6}	1.9×10^{-1}
10	2.121×10^{-6}	1.756×10^{-8}	2.139×10^{-6}	1.6×10^{-1}
15	-7.970×10^{-7}	2.201×10^{-8}	-7.750×10^{-7}	2.0×10^{-2}
20	2.278×10^{-7}	2.272×10^{-8}	2.505×10^{-7}	2.2×10^{-1}
25	-5.549×10^{-8}	2.097×10^{-8}	-3.451×10^{-8}	-1.1×10
30	1.217×10^{-8}	1.800×10^{-8}	3.017×10^{-8}	4.5×10^{-1}
35	-2.478×10^{-9}	1.467×10^{-8}	1.220×10^{-8}	5.7×10^{-1}
40	4.774×10^{-10}	1.152×10^{-8}	1.199×10^{-8}	4.8×10^{-1}
45	-8.810×10^{-11}	8.776×10^{-9}	8.687×10^{-9}	4.6×10^{-1}
50	1.571×10^{-11}	6.533×10^{-9}	6.549×10^{-9}	4.3×10^{-1}
		Two-term asymptotic approximations		
5	-3.864×10^{-6}	5.099×10^{-8}	-3.813×10^{-6}	1.5×10^{-2}
10	2.415×10^{-6}	6.431×10^{-8}	2.479×10^{-6}	3.0×10^{-2}
15	-8.767×10^{-7}	6.338×10^{-8}	-8.133×10^{-7}	-2.8×10^{-2}
20	2.456×10^{-7}	5.573×10^{-8}	3.014×10^{-7}	5.7×10^{-2}
25	-5.906×10^{-8}	4.580×10^{-8}	-1.325×10^{-8}	-3.5
30	1.283×10^{-8}	3.598×10^{-8}	4.881×10^{-8}	1.2×10^{-1}
35	-2.595×10^{-9}	2.735×10^{-8}	2.476×10^{-8}	1.3×10^{-1}
40	4.973×10^{-10}	2.028×10^{-8}	2.078×10^{-8}	1.0×10^{-1}
45	-9.141×10^{-11}	1.474×10^{-8}	1.465×10^{-8}	8.8×10^{-2}
50	1.625×10^{-11}	1.055×10^{-8}	1.057×10^{-8}	7.5×10^{-2}
		Three-term asymptotic approximations		
5	-3.985×10^{-6}	1.269×10^{-7}	-3.859×10^{-6}	3.0×10^{-3}
10	2.444×10^{-6}	1.106×10^{-7}	2.555×10^{-6}	7.3×10^{-4}
15	-8.823×10^{-7}	9.157×10^{-8}	-7.908×10^{-7}	1.2×10^{-4}
20	2.466×10^{-7}	7.287×10^{-8}	3.195×10^{-7}	2.7×10^{-4}
25	-5.922×10^{-8}	5.622×10^{-8}	-2.998×10^{-9}	-8.7×10^{-3}
30	1.286×10^{-8}	4.230×10^{-8}	5.516×10^{-8}	2.9×10^{-4}
35	-2.599×10^{-9}	3.119×10^{-8}	2.859×10^{-8}	2.9×10^{-4}
40	4.979×10^{-10}	2.261×10^{-8}	2.311×10^{-8}	1.9×10^{-4}
45	-9.149×10^{-11}	1.616×10^{-8}	1.607×10^{-8}	1.5×10^{-4}
50	1.626×10^{-11}	1.141×10^{-8}	1.142×10^{-8}	1.1×10^{-4}

obtain a large n asymptotic expansion for $I_{n,2}^{(2,4)}$ which remains valid as $v \to 0$, by inserting (5.40) in the Cauchy integral formula (5.35). The "analytic function" part of $g^{(2,4)}(z)$ does not contribute; the remaining part can be evaluated for n large by making the change of variables $z = z_0^{(2)} \exp(t)$ and using the expansions

$$\left[z-\left(\frac{1-a}{1+a}\right)\right]=\frac{2a(2+v)}{(1+a)(2-av)}+\left(\frac{2+av}{2-av}\right)\left[t+\frac{1}{2}t^2+O(t^3)\right], \tag{5.43}$$

$$\left[z-\frac{1}{z_0^{(2)}}\right]^{-3+\nu}=\left(\frac{2-a\nu}{2+a\nu}\right)^{3-\nu}(\tau+t)^{-3+\nu}\left\{1-\frac{1}{2}(3-\nu)\right.$$
$$\times t^2(\tau+t)^{-1}+\frac{1}{8}(3-\nu)(4-\nu)\,t^4(\tau+t)^{-2}$$
$$\left.-\frac{1}{6}(3-\nu)\,t^3(\tau+t)^{-1}+O(t^3)\right\}, \tag{5.44}$$

$$[z_0^{(2)}-z]^{-3-\nu}=\left(\frac{2-a\nu}{2+a\nu}\right)^{3+\nu}(-t)^{-3-\nu}$$
$$\times\left[1-\frac{1}{2}(3+\nu)\,t+\frac{1}{24}(3+\nu)(8+3\nu)\,t^2+O(t^3)\right], \tag{5.45}$$

where

$$\tau=1-[z_0^{(2)}]^{-2}=8a\nu(2+a\nu)^{-2}. \tag{5.46}$$

The expansion (5.44) is obtained by expanding $\{1+[\exp(t)-1-t](\tau+t)^{-1}\}^{-3+\nu}$ in powers of $[\exp(t)-1-t](\tau+t)^{-1}$, and then expanding the $\exp(t)$ in the result in powers of t. When the expansions (5.43)–(5.45) are multiplied, only the first three orders are kept; all terms which are of order t^3 or higher compared to the leading term are discarded. The integration over t is performed with the aid of the formula

$$\frac{1}{2\pi i}\oint\exp(-nt)(\tau+t)^{-l+\nu}(-t)^{-m-\nu}\,dt$$
$$=\frac{\tau^{-l-m+1}}{\Gamma(m+\nu)}\,U(-m-\nu+1,\,-l-m+2,\,n\tau). \tag{5.47}$$

The function $U(\alpha,\gamma,\zeta)$ in (5.47) is the irregular solution of the confluent hypergeometric equation, which can be defined by [14, pp. 255, 273; 15, pp. 277–278]

$$U(\alpha,\gamma,\zeta)=\frac{1}{\Gamma(\alpha)}\int_0^\infty\exp(-\zeta t)\,t^{\alpha-1}(1+t)^{\gamma-\alpha-1}\,dt$$
$$=\frac{\Gamma(1-\alpha)}{2\pi i}\oint\exp(-\zeta t)(-t)^{\alpha-1}\,(1+t)^{\gamma-\alpha-1}\,dt. \tag{5.48}$$

Reference [14] uses the symbol $\Phi(\alpha,\gamma,\zeta)$ for this function. The first integral representation in (5.48) is valid only if $\operatorname{Re}\alpha>0$; the second (contour) integral, in which the contour is a loop in the clockwise direction around the branch cut which runs from zero to $+\infty$ along the positive real axis, provides the analytic continuation in α and removes this restriction, but fails for α a positive integer. The philosophy behind the computation is that the factor $\exp(-nt)$ in the integrand cuts off so quickly for large n that only small t matters. The expansions (5.43)–(5.45) provide an adequate approximation in this small t region. A rigorous justification for this procedure, which embodies the same philosophy as Watson's lemma, can be supplied by generalizing the proof of Watson's lemma. The resulting uniform approximation, which remains valid as $\nu \to 0$, is

$$I_{n,2}^{(2,4)} = C^{(2,4)}(\nu)\left(\frac{2-a\nu}{2+a\nu}\right)^n n^{2+\nu}[b_0^{(2,4)}(\nu;n\tau)$$
$$+ n^{-1}b_1^{(2,4)}(\nu;n\tau) + n^{-2}b_2^{(2,4)}(\nu;n\tau) + O(n^{-3})], \tag{5.49}$$

where

$$b_0^{(2,4)}(\nu;n\tau) = (n\tau)^{-2-\nu}\, U(-2-\nu,\ -4,\ n\tau), \tag{5.50}$$

$$b_1^{(2,4)}(\nu;n\tau) = -(n\tau)^{-1-\nu}\left\{\frac{2-4a+(a-4)\,a\nu - a\nu^2}{2a}\right.$$
$$\times U(-1-\nu,\ -3,\ n\tau)$$
$$\left. + \frac{1}{2}(3-\nu)(1+\nu)(2+\nu)\, U(-\nu,\ -3,\ n\tau)\right\}, \tag{5.51}$$

$$b_2^{(2,4)}(\nu;n\tau) = (n\tau)^{-\nu}(1+\nu)$$
$$\times \left\{\frac{(2+\nu)[12(a-1)-(6a-11)\,a\nu + 3a\nu^2]}{24a}\right.$$
$$\times U(-\nu,\ -2,\ n\tau)$$
$$+ \frac{\nu(3-\nu)[2(3-4a)+(3a-10)\,a\nu - 3a\nu^2]}{12a}$$
$$\times U(1-\nu,\ -2,\ n\tau) - \frac{1}{8}\nu(3-\nu)(4-\nu)$$
$$\left. \times (2+\nu)(1-\nu)\, U(2-\nu,\ -2,\ n\tau)\right\}. \tag{5.52}$$

The functions $b_k^{(2,4)}(\nu;n\tau)$ are bounded for $0 \leqslant \nu \leqslant 1$ and $0 \leqslant n\tau \leqslant \infty$, and vary slowly with n for ν, and therefore also τ, small. The large z asymptotic expansion of $U(a, c, z)$ can be used to show that (5.49) agrees with (5.41) in the limit $n \to \infty$ with ν fixed at a finite positive value. The asymptotic results obtained using (5.49) and (5.41) are compared in Table IV for $\nu = 0.01$ and $a = 10$, which are the same values used for Table III. The relative errors, which are again the exact values minus the asymptotic approximations divided by the exact values, show that the uniform approximations are significantly better except for small n.

TABLE IV

Ordinary and Uniform Asymptotic Approximations Compared

n	$I^{(2,4)}_{n,1}+I^{(2,4)}_{n,2}$ (ordinary)	$I^{(2,4)}_{n,1}+I^{(2,4)}_{n,2}$ (uniform)	Relative error (ordinary)	Relative error (uniform)
		One-term asymptotic approximations		
5	-3.145×10^{-6}	-3.032×10^{-6}	1.9×10^{-1}	2.2×10^{-1}
10	2.139×10^{-6}	2.228×10^{-6}	1.6×10^{-1}	1.3×10^{-1}
15	-7.750×10^{-7}	-7.088×10^{-7}	2.0×10^{-2}	1.0×10^{-1}
20	2.505×10^{-7}	2.981×10^{-7}	2.2×10^{-1}	6.7×10^{-2}
25	-3.451×10^{-8}	-1.094×10^{-9}	-1.1×10	6.3×10^{-1}
30	3.017×10^{-8}	5.320×10^{-8}	4.5×10^{-1}	3.6×10^{-2}
35	1.220×10^{-8}	2.783×10^{-8}	5.7×10^{-1}	2.7×10^{-2}
40	1.199×10^{-8}	2.249×10^{-8}	4.8×10^{-1}	2.7×10^{-2}
45	8.687×10^{-9}	1.567×10^{-8}	4.6×10^{-1}	2.5×10^{-2}
50	6.549×10^{-9}	1.116×10^{-8}	4.3×10^{-1}	2.3×10^{-2}
		Two-term asymptotic approximations		
5	-3.813×10^{-6}	-3.736×10^{-6}	1.5×10^{-2}	3.5×10^{-2}
10	2.479×10^{-6}	2.526×10^{-6}	3.0×10^{-2}	1.2×10^{-2}
15	-8.133×10^{-7}	-7.851×10^{-7}	-2.8×10^{-2}	7.3×10^{-3}
20	3.014×10^{-7}	3.185×10^{-7}	5.7×10^{-2}	3.3×10^{-3}
25	-1.325×10^{-8}	-2.836×10^{-9}	-3.5	4.6×10^{-2}
30	4.881×10^{-8}	5.514×10^{-8}	1.2×10^{-1}	7.5×10^{-4}
35	2.476×10^{-8}	2.860×10^{-8}	1.3×10^{-1}	2.0×10^{-4}
40	2.078×10^{-8}	2.311×10^{-8}	1.0×10^{-1}	2.8×10^{-4}
45	1.465×10^{-8}	1.607×10^{-8}	8.8×10^{-2}	2.1×10^{-4}
50	1.057×10^{-8}	1.142×10^{-8}	7.5×10^{-2}	1.8×10^{-4}
		Three-term asymptotic approximations		
5	-3.859×10^{-6}	-3.858×10^{-6}	3.0×10^{-3}	3.1×10^{-3}
10	2.555×10^{-6}	2.555×10^{-6}	7.3×10^{-4}	6.3×10^{-4}
15	-7.908×10^{-7}	-7.907×10^{-7}	1.2×10^{-4}	2.7×10^{-4}
20	3.195×10^{-7}	3.195×10^{-7}	2.7×10^{-4}	8.7×10^{-5}
25	-2.998×10^{-9}	-2.968×10^{-9}	-8.7×10^{-3}	1.2×10^{-3}
30	5.516×10^{-8}	5.518×10^{-8}	2.9×10^{-4}	8.7×10^{-6}
35	2.859×10^{-8}	2.860×10^{-8}	2.9×10^{-4}	-2.3×10^{-6}
40	2.311×10^{-8}	2.311×10^{-8}	1.9×10^{-4}	-2.2×10^{-7}
45	1.607×10^{-8}	1.607×10^{-8}	1.5×10^{-4}	-2.2×10^{-6}
50	1.142×10^{-8}	1.143×10^{-8}	1.1×10^{-4}	-6.4×10^{-6}

The convergence is most rapid when $|z_0^{(1)}|=|z_0^{(2)}|$; this occurs for $a=2\nu^{-1/2}$, which implies that $z_0^{(1)}=-z_0^{(2)}=(1+\nu^{1/2})/(1-\nu^{1/2})$. As $W\to+\infty$, $\nu\to0$, and $|z_0^{(1)}|=|z_0^{(2)}|\to1$, the exponential decay of the $c_n^{(2,\alpha)}$ is lost, and convergence becomes slow. The emergence of a second length scale, proportional to $W^{-1/2}$, which is much shorter than the length scale of order one which comes from $|\psi_0\rangle$, is responsible for this deterioration of the convergence rate as W becomes large; the basis functions $\xi_n^{(\alpha',\alpha)}(a;x)$ introduced in (5.3), which involve only the single length scale $1/a$, cannot cope with two widely disparate length scales. The cure is the introduction of auxiliary basis functions, such as the $h(\sigma, z_0, \alpha', \alpha, a; x)$ introduced in (5.25), to handle the second length scale.

The analysis of the convergence rate given above shows how to choose the parameters σ and z_0 which appear in h (the parameters a, α', and α should have the same values in h as they do in the $\xi_n^{(\alpha',\alpha)}(a; x)$). We choose $\alpha' = 2$ as before; α will be chosen later. Equations (5.32) and (5.37) imply that the functions h which accelerate the convergence associated with the singularity of $g^{(2,\alpha)}(z)$ at $z_0^{(1)}$ have $\sigma = -\alpha$ if $\alpha \geqslant 3$; Eq. (5.32) and (5.39) imply that the functions which accelerate the convergence associated with the singularity of $g^{(2,\alpha)}(z)$ at $z_0^{(2)}$ have $\sigma = 1 - \alpha - \nu$ for $\alpha \geqslant 3$. A key consideration in the choice of basis functions is the ease with which the relevant matrix element integrals can be evaluated. Appendix D discusses these integrals in detail and shows that $\alpha \leqslant 2l + 1$ leads to considerable simplification in their evaluation for the lth partial wave in hydrogen. Since $l = 1$ here, this condition and the condition above can be satisfied only for $\alpha = 3$, which is the choice we make. With the choices $\alpha' = 2$ and $\alpha = 3$, the basis functions $\xi_n^{(\alpha',\alpha)}(a; x)$ are not orthonormal with respect to the inner product $\langle f \mid g \rangle = \int_0^\infty \overline{f(r)}\, g(r)\, dr$, but the Gram matrix and the matrix of the Hamiltonian with respect to the $\xi_n^{(\alpha',\alpha)}$ are band matrices in which only the elements on the main diagonal and adjacent to the main

TABLE V

Improving the Convergence Rate

N	$M=0$	$M=1$	$M=2$	$M=3$
		Errors when $W+\frac{1}{2}=10$, $\nu\approx 0.22$, $z_0^{(2)}\approx 1.576$		
5	1.0×10^{-3}	2.1×10^{-6}	1.2×10^{-10}	8.0×10^{-14}
10	1.1×10^{-5}	3.8×10^{-9}	5.2×10^{-14}	1.3×10^{-17}
		Errors when $W+\frac{1}{2}=10^2$, $\nu\approx 0.071$, $z_0^{(2)}\approx 1.152$		
5	8.1×10^{-3}	1.8×10^{-4}	7.9×10^{-9}	4.2×10^{-11}
10	1.0×10^{-3}	7.0×10^{-6}	1.1×10^{-10}	2.3×10^{-13}
15	1.9×10^{-4}	5.1×10^{-7}	3.8×10^{-12}	3.9×10^{-15}
		Errors when $W+\frac{1}{2}=10^3$, $\nu\approx 0.022$, $z_0^{(2)}\approx 1.046$		
5	1.1×10^{-2}	9.9×10^{-4}	1.6×10^{-8}	2.8×10^{-10}
10	2.4×10^{-3}	1.1×10^{-4}	9.2×10^{-10}	8.7×10^{-12}
15	8.0×10^{-4}	2.2×10^{-5}	1.1×10^{-10}	6.7×10^{-13}
20	3.3×10^{-4}	5.8×10^{-6}	2.0×10^{-11}	8.1×10^{-14}
		Errors when $W+\frac{1}{2}=10^4$, $\nu\approx 0.0071$, $z_0^{(2)}\approx 1.014$		
5	1.2×10^{-2}	2.0×10^{-3}	6.6×10^{-9}	2.3×10^{-10}
10	2.7×10^{-3}	3.3×10^{-4}	7.4×10^{-10}	1.8×10^{-11}
15	1.0×10^{-3}	9.5×10^{-5}	1.6×10^{-10}	2.8×10^{-12}
20	4.7×10^{-4}	3.5×10^{-5}	4.6×10^{-11}	6.6×10^{-13}

diagonal are non-zero (see (5.57)–(5.60) below). Appendix D also gives a brief discussion of matrix element integrals for helium, where similar simplifications can be achieved by an appropriate choice of α.

Table V shows the dramatic improvement in the convergence rate which can be achieved when the functions $h[-2-\nu+k, (2+a\nu)/(2-a\nu), 2, 3, a; x]$ (with k a non-negative integer) are added to the basis to handle the second (short) length scale which emerges in the Bethe logarithm problem when W becomes large. N is the number of Laguerre basis functions which are used, and M is the number of auxiliary basis functions h; a has the value 1.9991, which implies that $z_0^{(1)} \approx 4 \times 10^4$; the location of $z_0^{(2)}$ then determines the convergence rate. The errors are relative errors. The deterioration in the convergence rate as W increases and $z_0^{(2)}$ moves closer to one is readily apparent. Because these basis functions were derived by inverting the method of Darboux, which breaks down as $\nu \to 0$, the numerical performance of these auxiliary basis functions is better than expected. This can be understood by comparing the asymptotic expansion (5.41), which was obtained via the method of Darboux, with its uniform replacement (5.49). The principle difference (other than the use of the Stirling approximation for $\Gamma(3+\nu+n)/n!$) is the replacement of the constant coefficients in (5.41) by the slowly varying coefficients $b_k^{(2,4)}(\nu; n\tau)$ in (5.49); it is the slow variation of these coefficients, which becomes slower as ν gets smaller, which is responsible for the success of the auxiliary basis functions h.

We have looked at the auxiliary basis function which is obtained by inverting the analysis which leads to uniform approximations like (5.49). In the case $\alpha = 3$, which is somewhat simpler, the result is

$$x^2 \exp(-ax/2) \sum_{n=0}^{\infty} \frac{(-1)^n}{\Gamma(n-\nu+3)} \times {}_2F_1\left[2-\nu, n+4; n-\nu+3; -\left(\frac{2-a\nu}{2+a\nu}\right)\right]\left(\frac{2-a\nu}{2\nu}\right)^n x^n. \tag{5.53}$$

Matrix element evaluation with this function is considerably more difficult than matrix element evaluation with the functions h; this—together with the impressive numerical performance shown in Table V—leads us to believe that the functions h are a better choice.

Although it is not customary to discuss methods which do not work, we believe that a brief analysis of the obvious two-length-scale variational trial function

$$\chi_{M,N}(a, b; x) = \sum_{m=0}^{M} c_m^{(\alpha',\alpha)} \xi_m^{(\alpha',\alpha)}(a; x) + \sum_{n=0}^{N} d_n^{(\alpha',\alpha)} \xi_n^{(\alpha',\alpha)}(b; x) \tag{5.54}$$

would be useful. Numerical tests show that a trial function like $\chi_{M,N}(a, b; x)$ is not effective in handling the second length scale which emerges at large W. The reason (5.54) does not work can be understood by applying the rate of convergence analysis developed above. The functions $\xi_m^{(\alpha',\alpha)}(b;x)$ used in (5.54) can be expanded in the $\xi_n^{(\alpha',\alpha)}(a;x)$:

$$\xi_m^{(\alpha',\alpha)}(b;x)=\sum_{n=0}^{\infty} e_n^{(\alpha',\alpha)}\xi_n^{(\alpha',\alpha)}(a;x). \tag{5.55}$$

The analysis above applied with $f(x)=\xi_m^{(\alpha',\alpha)}(b;x)$ shows that $\sigma=-m-\alpha-1$ and $z_0=(b+a)/(b-a)$ for the expansion (5.55), so that the coefficients e_n have the asymptotic behavior

$$e_n^{(\alpha',\alpha)}=D(m)\,n^{(\alpha/2)+m}[(b+a)/(b-a)]^{-n}\,[1+O(n^{-1})], \tag{5.56}$$

where the $D(m)$ are (computable) constants which are independent of n. When the length scales $1/a$ and $1/b$ are very different, the exponential factor $[(b+a)/(b-a)]^{-n}$ approaches either $(+1)^{-n}$ or $(-1)^{-n}$, and the power law factor $n^{(\alpha/2)+m}$ becomes dominant. As m increases, the behavior of this power law factor goes in the wrong direction—what is wanted is power law factors which match the power law behavior of the $c_n^{(\alpha',\alpha)}$ in (5.2), and for which the power of n *decreases* as the number of functions added to accelerate the convergence increases. The functions $h(\sigma, z_0, \alpha', \alpha, a; x)$ defined in (5.25) have this desired behavior; the functions $\xi_m^{(\alpha',\alpha)}(b;x)$ do not.

We will now show how asymptotic formulas for expansion coefficients obtained via the above rate of convergence analysis can be used to obtain an asymptotic formula for the error $\lambda-\tilde{\lambda}$ in the expectation value of the resolvent calculated from the Schwinger–Levine variational principle for the hydrogen ground state. The first step is the asymptotic Cholesky decomposition of $\langle\xi_k|\,(A+W)\,|\xi_{k'}\rangle$, which is most easily done if $\langle\xi_k|\,(A+W)\,|\xi_{k'}\rangle$ is a band matrix. Thus we use the basis functions $\xi_k^{(2,3)}(a;r)$, for which

$$\begin{aligned}\langle\xi_k|\,(A+W)\,|\xi_{k'}\rangle&=(H-E_n+W)_{k,k'}\\&=T_{k,k'}+V_{k,k'}+(-E_n+W)G_{k,k'},\end{aligned} \tag{5.57}$$

where

$$\begin{aligned}T_{k,k'}&=\frac{1}{2}\int_0^\infty\left[\frac{\partial\xi_k^{(2,3)}(a;r)}{\partial r}\,\frac{\partial\xi_{k'}^{(2,3)}(a;r)}{\partial r}+\frac{2}{r^2}\,\xi_k^{(2,3)}(a;r)\,\xi_{k'}^{(2,3)}(a;r)\right]dr\\&=\frac{a^2}{8}\,[\sqrt{(k+1)(k+4)}\,\delta_{k+1,k'}+2(k+2)\,\delta_{k,k'}+\sqrt{k(k+3)}\,\delta_{k-1,k'}],\end{aligned} \tag{5.58}$$

$$V_{k,k'}=\frac{1}{2}\int_0^\infty\xi_k^{(2,3)}(a;r)\left(\frac{-1}{r}\right)\xi_{k'}^{(2,3)}(a;r)\,dr=-a\delta_{k,k'}, \tag{5.59}$$

$$\begin{aligned}G_{k,k'}&=\frac{1}{2}\int_0^\infty\xi_k^{(2,3)}(a;r)\,\xi_{k'}^{(2,3)}(a;r)\,dr\\&=-\sqrt{(k+1)(k+4)}\,\delta_{k+1,k'}+2(k+2)\,\delta_{k,k'}-\sqrt{k(k+3)}\,\delta_{k-1,k'}.\end{aligned} \tag{5.60}$$

Because $\langle \xi_k | (A+W) | \xi_{k'} \rangle$ is tridiagonal, the Cholesky decomposition formulas (4.17) and (4.18) simplify to

$$U_{k-1,k} = (H - E_n + W)_{k-1,k} / U_{k-1,k-1}, \tag{5.61}$$

$$U_{k,k} = \{(H - E_n + W)_{k,k} - [(H - E_n + W)_{k-1,k} / U_{k-1,k-1}]^2\}^{1/2}. \tag{5.62}$$

A large k asymptotic expansion of $U_{k,k}$ can be obtained by looking for a series solution to (5.62) of the form

$$U_{k,k} \sim k^{1/2} \sum_{l=0}^{\infty} u_k k^{-l}. \tag{5.63}$$

The lowest order equation which determines u_0 is a quartic equation with the four roots $\pm 2^{-3/2} a \pm (W + \frac{1}{2})^{1/2}$; the correct root can be selected by comparison of the asymptotic results with numerical Cholesky decomposition. The asymptotic expansion of $U_{k-1,k}$ can be obtained by inserting the asymptotic expansion of $U_{k,k}$ in (5.61). The results are

$$U_{k,k} = \sqrt{\frac{k}{2}} \left(\frac{a}{2} + \frac{1}{v} \right) \left[1 + \left(1 - \frac{v}{2} \right) k^{-1} + O(k^{-2}) \right], \tag{5.64}$$

$$U_{k-1,k} = \sqrt{\frac{k}{2}} \left(\frac{a}{2} - \frac{1}{v} \right) \left[1 + \left(1 + \frac{v}{2} \right) k^{-1} + O(k^{-2}) \right], \tag{5.65}$$

where v is defined in (2.36). The asymptotic expansion of the coefficient c_l needed to calculate the asymptotic expansion of c_n' from (4.25) can be obtained by repeating the calculations above which led to (5.38), (5.41), (5.42), and (5.49) for the case $\alpha = 3$. The analogues of (5.38), (5.41), and (5.42) are

$$\begin{aligned} I_{n,1}^{(2,3)} = &-\frac{16 v^2 (2-a)}{\sqrt{3}\, a(1-v^2)(2+a)^3} \left(\frac{2-a}{2+a} \right)^n \left\{ 1 + \frac{2+a}{a(n+2)} \right. \\ &\left. + \left[1 - \frac{v^2 a^3 (2-a)^2}{4(1-v^2)} \right] \frac{(2+a)^2}{2a^2(n+1)(n+2)} + O(n^{-3} \log(n)) \right\}, \end{aligned} \tag{5.66}$$

$$\begin{aligned} I_{n,2}^{(2,3)} = &\, C^{(2,3)}(v) \left(\frac{2-av}{2+av} \right)^n \frac{\Gamma(n+2+v)}{n!} \left[1 + \frac{(1+v)(2-v)(2+av)^2}{8av(n+1+v)} \right. \\ &\left. + \frac{v(1+v)(2-v)(3-v)(2+av)^4}{128 a^2 v^2 (n+1+v)(n+v)} + O(n^{-3}) \right], \end{aligned} \tag{5.67}$$

and

$$C^{(2,3)}(v) = \frac{8\pi v^4 (2-av)^2}{\sqrt{3}\, a^2 (1-v^2) \sin(\pi v)\, \Gamma(2+v)(2+av)^2} \left[\frac{8av(1-v)}{(1+v)(4-a^2v^2)} \right]^v. \tag{5.68}$$

Approximate methods are normally used on exactly solvable problems in order to prepare the ground for their use on more difficult problems which cannot be solved exactly. Since this is our objective here, we consider only the case in which the large n behavior of $c_n^{(2,3)}$ is dominated by the contribution from $I_{n,2}^{(2,3)}$. If v is large enough so that the expansion (5.67), rather than an analogue of the uniform expansion (5.49), can be used, c_n' has the asymptotic expansion

$$c_n' = \frac{2^{3/2}a^{5/2}}{2+av}\, C^{(2,3)}(v) \left(\frac{2-av}{2+av}\right)^n$$
$$\times n^v \left\{1 + \left[\frac{5}{2}v + \frac{(2-v-v^2)(4+a^2v^2)}{8av}\right] n^{-1} + O(n^{-2})\right\}. \qquad (5.69)$$

The result (5.69) is used in (4.23) to obtain the error $\lambda - \tilde{\lambda}$ for N large. The sum over n in (4.23) can vary too rapidly to permit use of the Euler–MacLauren sum formula (replacement of the sum by an integral plus corrections). Therefore we introduce the finite difference operator Δ_n, defined by $\Delta_n f(n) = f(n+1) - f(n)$, and apply the summation by parts formula

$$\sum_{n=N+1}^{\infty} f(n)\,\Delta_n g(n) = -f(N+1)\,g(N+1) - \sum_{n=N+1}^{\infty} g(n+1)\,\Delta_n f(n) \qquad (5.70)$$

twice, first with $f(n) = n^\gamma$ and $g(n) = z^{2n}/(z^2-1)$, and then with $f(n) = n^\gamma - (n+1)^\gamma$ and $g(n) = z^{2n+2}/(z^2-1)^2$, to obtain

$$\sum_{n=N+1}^{\infty} n^\gamma z^{2n} = \frac{z^{2N+2}}{1-z^2} N^\gamma \left[1 + \frac{\gamma}{1-z^2} N^{-1} + O(N^{-2})\right]. \qquad (5.71)$$

Evaluation of the sum over n in (4.23) with the aid of (5.71) yields

$$\lambda - \tilde{\lambda} = \frac{a^4(2-av)^2}{v(2+av)^2} \left[C^{(2,3)}(v)\right]^2 \left(\frac{2-av}{2+av}\right)^{2N} N^{2v}$$
$$\times \left\{1 + \left[6v + \frac{(2-v^2)(4+a^2v^2)}{4av}\right] N^{-1} + O(N^{-2})\right\}. \qquad (5.72)$$

The exact value of $\lambda - \tilde{\lambda}$ is compared with the right-hand side of (5.72) in Table VI. It can be seen that (5.72) works well for moderate W, but breaks down for W large (and v close to zero). This breakdown occurs because (5.67) must be replaced by the analogue of the uniform expansion (5.49) if the product Nv is not large. The summation formula (5.71) must also be replaced by a more complicated formula in this case, because v close to zero implies that $z = (2-av)/(2+av)$ is close to one.

TABLE VI

Asymptotic Estimates of $\lambda - \tilde{\lambda}$

N	$\lambda - \tilde{\lambda}$	Eq (5.72)	Relative error
	$W + \frac{1}{2} = 10,\ \nu \approx 0.22,\ z_0^{(2)} \approx 1.576$		
5	3.187×10^{-5}	3.095×10^{-5}	2.9×10^{-2}
10	3.299×10^{-7}	3.261×10^{-7}	1.2×10^{-2}
15	3.653×10^{-9}	3.631×10^{-9}	6.2×10^{-3}
20	4.084×10^{-11}	4.068×10^{-11}	3.9×10^{-3}
25	4.561×10^{-13}	4.549×10^{-13}	2.6×10^{-3}
30	5.079×10^{-15}	5.065×10^{-15}	2.7×10^{-3}
	$W + \frac{1}{2} = 10^2,\ \nu \approx 0.071,\ z_0^{(2)} \approx 1.152$		
5	2.658×10^{-5}	1.525×10^{-5}	4.3×10^{-1}
10	3.452×10^{-6}	2.561×10^{-6}	2.6×10^{-1}
15	6.288×10^{-7}	5.280×10^{-7}	1.6×10^{-1}
20	1.308×10^{-7}	1.170×10^{-7}	1.1×10^{-1}
25	2.897×10^{-8}	2.684×10^{-8}	7.3×10^{-2}
30	6.630×10^{-9}	6.273×10^{-9}	5.4×10^{-2}
	$W + \frac{1}{2} = 10^3,\ \nu \approx 0.022,\ z_0^{(2)} \approx 1.046$		
5	3.769×10^{-6}	5.510×10^{-7}	8.5×10^{-1}
10	7.982×10^{-7}	2.000×10^{-7}	7.5×10^{-1}
15	2.670×10^{-7}	9.471×10^{-8}	6.5×10^{-1}
20	1.110×10^{-7}	4.986×10^{-8}	5.5×10^{-1}
25	5.221×10^{-8}	2.775×10^{-8}	4.7×10^{-1}
30	2.657×10^{-8}	1.597×10^{-8}	4.0×10^{-1}
	$W + \frac{1}{2} = 10^4,\ \nu \approx 0.0071,\ z_0^{(2)} \approx 1.014$		
5	3.950×10^{-7}	8.524×10^{-9}	9.8×10^{-1}
10	9.021×10^{-8}	3.864×10^{-9}	9.6×10^{-1}
15	3.338×10^{-8}	2.324×10^{-9}	9.3×10^{-1}
20	1.568×10^{-8}	1.568×10^{-9}	9.0×10^{-1}
25	8.484×10^{-9}	1.126×10^{-9}	8.7×10^{-1}
30	5.044×10^{-9}	8.413×10^{-10}	8.3×10^{-1}

The methods outlined above can be used to construct the uniform analogue of (5.72) which remains valid when N is large with $N\nu$ not large, and to extend the asymptotic approximations to $\lambda - \tilde{\lambda}$ to higher order. They can also be used to include the contribution $I_{n,1}^{(2,3)}$ from the singularity at $z_0^{(1)}$; this latter extension contains an oscillating interference term between the two singularities when $z_0^{(1)}$ and $z_0^{(2)}$ have opposite sign, as is the case when the convergence rate is optimized by choosing a to have the value for which $|z_0^{(1)}| = |z_0^{(2)}|$. However, since it is our intent to be illustrative rather than exhaustive, we have elected to stop at this point and leave these further extensions as an exercise for the reader.

We now discuss auxiliary basis functions which can be used to handle the second (short) length scale at large W for atoms and molecules other than hydrogen. If

$f_3(W)$ defined in (3.7) is to be calculated via the Schwinger–Levine principle (4.1)–(4.2), the exact $|\chi\rangle$ for which the maximum is achieved is given by

$$|\chi_M\rangle = \sum_{j=1}^{N} \sum_{k=1}^{K} Z_k \frac{1}{(H - E_n + W)} \left(\frac{r_{j,M} - R_{k,M}}{|\mathbf{r}_j - \mathbf{R}_k|^3} \right) |\psi_n\rangle. \tag{5.73}$$

The derivation of the large W asymptotic expansion in Section 3 shows that the crude approximation $(H - E_n + W)^{-1} \approx W^{-1}$ is adequate except for the first few partial waves in the partial wave expansion of the $\mathbf{r}_j$-dependence of $\langle \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N \mid \psi_n \rangle$ about $\mathbf{R}_k$. Even for these first few partial waves, this crude approximation is adequate except for $|\mathbf{r}_j - \mathbf{R}_k|$ small, where more elaborate approximations, such as $(H - E_n + W)^{-1} \approx (\frac{1}{2} p_j^2 - E_n + W)^{-1}$, are needed. We exploit these observations and consider a class of approximations $|\chi_M\rangle \approx |\tilde{\chi}_M^{(s)}\rangle$, where

$$|\tilde{\chi}_M^{(s)}\rangle = \sum_{j=1}^{N} \sum_{k=1}^{K} Z_k \left[|\chi_M^{(j,k;s)}\rangle + \frac{1}{W} \left(\frac{r_{j,M} - R_{k,M}}{|\mathbf{r}_j - \mathbf{R}_k|^3} \right) (|\psi_n\rangle - |\tilde{\psi}_n^{(j,k)}\rangle) \right]. \tag{5.74}$$

The superscript s indexes the different approximations. The vector $|\tilde{\psi}_n^{(j,k)}\rangle$ is an approximation to $|\psi_n\rangle$ which gets the small $|\mathbf{r}_j - \mathbf{R}_k|$ behavior right in the first few partial waves. We will consider approximations of the form

$$\langle \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N \mid \tilde{\psi}_n^{(j,k)} \rangle = \sum_{l=0}^{1} \sum_{m=-l}^{l} Y_{l,m}(\theta_{j,k}, \phi_{j,k})\, R_l^{(k)}(|\mathbf{r}_j - \mathbf{R}_k|)$$
$$\times [r^{-l} f_{l,m,n}^{(j,k)}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{j-1}, \mathbf{r}_{j+1}, ..., \mathbf{r}_N; r)]_{r=0}, \tag{5.75}$$

where $f_{l,m,n}^{(j,k)}$ is defined in (3.30). It should be noted that the $r^{-l} f_{l,m,n}^{(j,k)}$ in the square bracket in (5.75) remains finite as $r \to 0$, because $f_{l,m,n}^{(j,k)}$ behaves like r^l for $r \to 0$ [20]. We have included only the $l = 0$ and $l = 1$ partial waves in $|\tilde{\psi}_n^{(j,k)}\rangle$ because this is enough to keep the second term in (5.74) finite when $|\mathbf{r}_j - \mathbf{R}_k| \to 0$. The function $R_l^{(k)}$ is a function which decays exponentially at large distances and which has the correct cusp behavior $R_l^{(k)}(r) = r^l[1 - Z_k r/(l+1) + O(r^2)]$ for small r. The simplest exponentially decaying function which has this cusp behavior is the lowest energy hydrogenic function in the lth partial wave, which is

$$R_l^{(k)}(r) = r^l \exp[-Z_k r/(l+1)]. \tag{5.76}$$

The vector $|\chi_M^{(j,k;s)}\rangle$ is an approximation which is chosen to get the small $|\mathbf{r}_j - \mathbf{R}_k|$ behavior right; we will consider

$$|\chi_M^{(j,k;1)}\rangle = \frac{1}{(\frac{1}{2} p_j^2 - Z_k |\mathbf{r}_j - \mathbf{R}_k|^{-1} - E_n + W)} \left(\frac{r_{j,M} - R_{k,M}}{|\mathbf{r}_j - \mathbf{R}_k|^3} \right) |\tilde{\psi}_n^{(j,k)}\rangle, \tag{5.77}$$

$$|\chi_M^{(j,k;2)}\rangle = \frac{1}{(\frac{1}{2} p_j^2 - E_n + W)} \left(\frac{r_{j,M} - R_{k,M}}{|\mathbf{r}_j - \mathbf{R}_k|^3} \right) |\tilde{\psi}_n^{(j,k)}\rangle, \tag{5.78}$$

and a third approximation to be specified later. We now analyze $|\chi_M^{(j,k;2)}\rangle$. The partial wave expansion (3.23) can be used to show that

$$\int d^3\mathbf{r}_j' \langle \mathbf{r}_j | \left(\frac{1}{2}p_j^2 - E_n + W\right)^{-1} |\mathbf{r}_j'\rangle \left(\frac{r_{j,M}' - R_{k,M}}{|\mathbf{r}_j' - \mathbf{R}_k|^3}\right) Y_{l,m}(\theta_{j,k}', \phi_{j,k}')$$
$$\times R_l^{(k)}(|\mathbf{r}_j' - \mathbf{R}_k|) = \sum_{l'=l\pm 1} (4\pi/3)^{1/2} \langle l', m+M|\, 1, M\, |l, m\rangle$$
$$\times Y_{l',m+M}(\theta_{j,k}, \phi_{j,k})\, M_{l';n;(l'-l+1)/2}^{(j,k)}(|\mathbf{r}_j - \mathbf{R}_k|), \tag{5.79}$$

where $\langle l', m+M|\, 1, M\, |l, m\rangle$ is the Gaunt coefficient (see (C.7)) and

$$M_{l;n;p}^{(j,k)}(r) = \nu^{-1} \int_0^\infty dr' g_l(\nu^{-1}r, \nu^{-1}r')\, R_{l-2p+1}^{(k)}(r'). \tag{5.80}$$

The function $M_{l;n;p}^{(j,k)}(r)$ defined in (5.80) can be handled via an integration by parts similar to the one used to evaluate (3.28). Integrating $(r')^{l-2p+1} g_l(\nu^{-1}r, \nu^{-1}r')$ and differentiating $(r')^{-l+2p-1} R_{l-2p+1}^{(k)}(r')$ yields

$$M_{l;n;p}^{(j,k)}(r) = \tilde{M}_{l;n;p}^{(j,k)}(r) + \frac{Z_k \nu^{2l-4p+3}}{l-2p+2} \int_0^\infty dr'(rr')^{-l+2p-1}$$
$$\times R_{l-2p+1}^{(k)}(r')\, \partial G_{l,p}(\nu^{-1}r, \nu^{-1}r')/\partial r, \tag{5.81}$$

where

$$\tilde{M}_{l;n;p}^{(j,k)}(r) = (\nu^{-1}r)^{-2l+4p-2} D_{l,p}(\nu^{-1}r)\, R_{l-2p+1}^{(k)}(r). \tag{5.82}$$

The factor $\partial G_{l,p}(\nu^{-1}r, \nu^{-1}r')/\partial r$ in the second term of (5.81) peaks sharply at $r = r'$. Because the peak looks like the derivative of a delta function rather than a delta function, the contribution from this term is down by a factor of ν^2 relative to the first term. Thus we are led to approximate $M_{l;n;p}^{(j,k)}(r)$ by $\tilde{M}_{l;n;p}^{(j,k)}(r)$, and define the third approximation $|\chi_M^{(j,k;3)}\rangle$, which was to be specified later, by

$$\langle \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N \,|\, \chi_M^{(j,k;3)}\rangle$$
$$= \sum_{l=0}^{1} \sum_{m=-l}^{l} \sum_{l'=l\pm 1} (4\pi/3)^{1/2} \langle l', m+M|\, 1, M\, |l, m\rangle$$
$$\times Y_{l',m+M}(\theta_{j,k}, \phi_{j,k})\, \tilde{M}_{l';n;(l'-l+1)/2}^{(j,k)}(|\mathbf{r}_j - \mathbf{R}_k|)$$
$$\times [r^{-l} f_{l,m,n}^{(j,k)}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{j-1}, \mathbf{r}_{j+1}, ..., \mathbf{r}_N; r)]_{r=0}. \tag{5.83}$$

For z large, $D_{l,p}(z) \approx 2z^{2l-4p}$. Thus $\tilde{M}_{l;n;p}^{(j,k)}(r) \approx W^{-1} r^{-2} R_{l-2p+1}^{(k)}(r)$ for $\nu^{-1}r$ large, which is the result of the crude approximation $(H - E_n + W)^{-1} \approx W^{-1}$. Integration by parts can be combined with the basic result

$$-\frac{1}{2}\left[\frac{d^2}{dz^2}+\frac{2}{z}\frac{d}{dz}-\frac{l(l+1)}{z^2}-1\right]z^{-l+2p-1}D_{l,p}(z)=z^{l-2p-1} \tag{5.84}$$

to show that

$$\begin{aligned}
&\int_0^\infty r^2\,dr\,\tilde{M}^{(j,k)}_{l;n;p}(r)\left\{-\frac{1}{2}\left[\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{l(l+1)}{r^2}\right]-E_n+W\right\}\tilde{M}^{(j,k)}_{l;n;p}(r)\\
&\quad=\int_0^\infty dr\,\tilde{M}^{(j,k)}_{l;n;p}(r)\,R^{(k)}_{l-2p+1}(r)+v^{2l-4p+2}\int_0^\infty r^2\,dr\\
&\qquad\times[(v^{-1}r)^{-l+2p-1}\,D_{l,p}(v^{-1}r)]^2\left[\frac{d}{dr}r^{-l+2p-1}R^{(k)}_{l-2p+1}(r)\right]^2\\
&\quad=\int_0^\infty dr\,\tilde{M}^{(j,k)}_{l;n;p}(r)\,R^{(k)}_{l-2p+1}(r)+Z_k^2v^3\,\delta_{l-2p+1,0}+O(v^4).
\end{aligned} \tag{5.85}$$

The approximations $\tilde{\lambda}^{(s)}_M$ obtained by using the $|\tilde{\chi}^{(s)}_M\rangle$ in the Schwinger–Levine principle (4.1)–(4.2) all have large W expansions which agree with the exact expansion (3.1) through the first three terms. The results are summarized by

$$\begin{aligned}
\sum_{M=-1}^{1}\tilde{\lambda}^{(s)}_M&=\sum_{M=-1}^{1}\frac{|\langle\tilde{\chi}^{(s)}_M|\sum_{j=1}^N\sum_{k=1}^K Z_k(r_{j,M}-R_{k,M})\,|\mathbf{r}_j-\mathbf{R}_k|^{-3}\,|\psi_n\rangle|^2}{\langle\tilde{\chi}^{(s)}_M|\,H-E_n+W\,|\tilde{\chi}^{(s)}_M\rangle}\\
&=C_1W^{-1/2}+C_2W^{-1}\ln(W)+C_3'W^{-1}\\
&\quad+C_4^{(s)}W^{-3/2}+O[W^{-2}\ln(W)],
\end{aligned} \tag{5.86}$$

where

$$C_3'=C_3+\sum_{m=0}^{n-1}|\langle\psi_m|\,\mathbf{P}\,|\psi_n\rangle|^2\,(E_m-E_n)^2. \tag{5.87}$$

The $C_4^{(s)}$ for the various choices of $|\tilde{\chi}^{(s)}_M\rangle$ can be worked out with the aid of (3.43), (3.51)–(3.55), and (5.84)–(5.85). They have the form

$$C_4^{(s)}=C_4+\pi\sqrt{2}\sum_{j=1}^{N}\sum_{k=1}^{K}Z_k^4\,\delta^{(s)}\,\langle\psi_n|\,\delta(\mathbf{r}_j-\mathbf{R}_k)\,|\psi_n\rangle, \tag{5.88}$$

where

$$\delta^{(1)}=0, \tag{5.89}$$

$$\delta^{(2)}=\tfrac{1}{6}\pi^2+8\ln^2(2)-8\ln(2)=-0.056619\ldots, \tag{5.90}$$

$$\delta^{(3)}=\tfrac{2}{3}\pi^2+8\ln^2(2)-8\ln(2)-5=-0.121817\ldots. \tag{5.91}$$

The neglect of the coulomb potential $-Z_k\,|\mathbf{r}_j-\mathbf{R}_k|^{-1}$ is responsible for the difference between $C_4^{(2)}$ and C_4 given by (5.88) and (5.90). The use of $\tilde{M}^{(j,k)}_{l;n;p}(r)$ instead of $M^{(j,k)}_{l;n;p}(r)$, and the neglect of the coulomb potential, both contribute to the difference between $C_4^{(3)}$ and C_4 given by (5.88) and (5.91). These results are independent of the exact form of the function $R_l^{(k)}$; any exponentially decaying function which has the right cusp behavior will do.

The basis function introduced by Schwartz to handle the second length scale at large W has the form

$$|\tilde{\chi}^{(S)}_M\rangle=\sum_{j=1}^{N}\sum_{k=1}^{K} Z_k\left(\frac{r_{j,M}-R_{k,M}}{|\mathbf{r}_j-\mathbf{R}_k|}\right)D_{1,1}(|\mathbf{r}_j-\mathbf{R}_k|\sqrt{2W})\,|\psi_n\rangle \tag{5.92}$$

in our notation. The approximation $\tilde{\lambda}^{(S)}_M$ obtained by using Schwartz's function $|\tilde{\chi}^{(S)}_M\rangle$ in the Schwinger–Levine principle (4.1)–(4.2) also has a large W expansion which agrees with the exact expansion (3.1) through the first three terms. This expansion again has the form (5.86)–(5.87), but $C_4^{(s)}$ is replaced by

$$\begin{aligned}C_4^{(S)}=C_4+\pi\sqrt{2}\sum_{j=1}^{N}\sum_{k=1}^{K}Z_k^2\bigg[&(Z_k^2\,\delta^{(3)}-4E_n)\\&\times\langle\psi_n|\,\delta(\mathbf{r}_j-\mathbf{R}_k)\,|\psi_n\rangle-\frac{1}{4\pi}\sum_{m=-1}^{1}\rho^{(j,k,k)}_{1,m;1,m;n}(0,0)\bigg].\end{aligned} \tag{5.93}$$

$C_4^{(S)}$ differs from C_4 because Schwartz's approximation neglects the coulomb potential, approximates $M^{(j,k)}_{l;n;p}(r)$ by $\tilde{M}^{(j,k)}_{l;n;p}(r)$, uses $\sqrt{2W}$ instead of $v^{-1}=\sqrt{2(W-E_n)}$ in the argument of $D_{1,1}(|\mathbf{r}_j-\mathbf{R}_k|\sqrt{2W})$, and gets the small-$|\mathbf{r}_j-\mathbf{R}_k|$ behavior wrong in the higher partial waves.

Matrix element integral evaluation tends to be easiest with the function $|\tilde{\chi}^{(3)}_M\rangle$. The use of functions such as $|\tilde{\chi}^{(1)}_M\rangle$, $|\tilde{\chi}^{(2)}_M\rangle$, and $|\tilde{\chi}^{(S)}_M\rangle$, which lead to more difficult matrix element integrals, can be justified only if they get additional terms in the large W expansion right. This criterion implies that $|\tilde{\chi}^{(1)}_M\rangle$ and $|\tilde{\chi}^{(3)}_M\rangle$ are the preferred choices. Another attractive possibility is a modified version of $|\tilde{\chi}^{(3)}_M\rangle$ in which $\tilde{M}^{(j,k)}_{l;n;p}(r)$ is replaced by a linear combination of the functions h introduced in (5.25). This replacement puts in the coulomb potential from $|\tilde{\chi}^{(1)}_M\rangle$ approximately and corrects the error in $|\tilde{\chi}^{(3)}_M\rangle$ which came from the approximation $M^{(j,k)}_{l;n;p}(r)\approx\tilde{M}^{(j,k)}_{l;n;p}(r)$.

APPENDIX A: The Method of C. Schwartz

By writing $\int_1^\infty f_2(W)\,dW$ as $\lim_{K\to\infty}\int_1^K f_2(k)\,dk$ and using $\int_0^K dk=K$ and $\int_1^K k^{-1}\,dk=\ln(K)$, it can be shown that (2.12)–(2.16) imply that

$$\begin{aligned}\beta &= \sum_{m=0}^{n-1} |\langle\psi_m| \mathbf{P} |\psi_n\rangle|^2 (E_m - E_n) \ln |E_m - E_n| \\ &\quad + \lim_{K\to\infty} \left\{ \int_0^K k\, dk\, \langle\psi_n| \mathbf{P} \cdot \left[\frac{1}{(H - E_n + k)} - \sum_{m=0}^{n-1} \frac{|\psi_m\rangle\langle\psi_m|}{(E_m - E_n + k)} \right] \mathbf{P} |\psi_n\rangle \right. \\ &\quad - \langle\psi_n| \mathbf{P} \cdot \left[1 - \sum_{m=0}^{n-1} |\psi_m\rangle\langle\psi_m| \right] \mathbf{P} |\psi_n\rangle K + \langle\psi_n| \mathbf{P} \cdot [(H - E_n) \\ &\quad \left. - \sum_{m=0}^{n-1} (E_m - E_n) |\psi_m\rangle\langle\psi_m| \right] \mathbf{P} |\psi_n\rangle \ln(K) \Big\} \\ &= \lim_{K\to\infty} \left[\mathscr{P} \int_0^K k\, dk\, \langle\psi_n| \mathbf{P} \cdot (H - E_n + k)^{-1} \mathbf{P} |\psi_n\rangle \right. \\ &\quad \left. - \langle\psi_n| \mathbf{P} \cdot \mathbf{P} |\psi_n\rangle K + \langle\psi_n| \mathbf{P} \cdot (H - E_n) \mathbf{P} |\psi_n\rangle \ln(K) \right]. \end{aligned} \tag{A.1}$$

Here $\mathscr{P}\int$ means that the singularities of the integrand at $k = E_n - E_m$, $m = 0, 1, 2, \ldots, n-1$, are to be handled via the principal value prescription. The final expression in (A.1) is Eq. (7) in Schwartz's paper: $\langle\psi_n| \mathbf{P} \cdot \mathbf{P} |\psi_n\rangle$ is the negative of Schwartz's $\langle\nabla^2\rangle$, $\langle\psi_n| \mathbf{P} \cdot (H - E_n) \mathbf{P} |\psi_n\rangle$ is Schwartz's $2\pi Z \psi_0^2(0)$ (see (2.7) above), and $\langle\psi_n| \mathbf{P} \cdot (H - E_n + k)^{-1} \mathbf{P} |\psi_n\rangle$ is Schwartz's $J(k)$. The comparison of our large W asymptotic expansion (3.1)–(3.5) with Schwartz's equations (17)–(19) is facilitated by noting that our $f_2(k)$ is Schwartz's $k\tilde{w}(k)$, and our $4\pi \langle\psi_n| \delta(\mathbf{r}_j - \mathbf{R}_k) |\psi_n\rangle$ is Schwartz's $\bar{\rho}_j(0)$.

The present paper improves on Schwartz's pioneering work in several respects: (1) Our method works for all of the logarithmic mean excitation energies of physical interest. It also works for other analytic functions of operators. (2) It works for excited states. (3) A very rapidly convergent numerical integration scheme, complete with error formulas, has been provided. (4) Schwartz's asymptotic formula for the resolvent matrix element at large negative energies has been carried to one more term and extended to molecules via a systematic method which shows where the various contributions come from. (5) The convergence rate for the variational approximation to the resolvent has been analyzed and an error formula given.

APPENDIX B: The Numerical Integration Method

Because it is as easy to derive the needed parts of Stenger's numerical integration method as to describe them, this appendix begins with a brief derivation. These needed parts are then used to obtain useful, easily computable error bounds for the numerical integration. The derivation begins with the formula

$$\oint_C \frac{\cos[(\pi z)/h]}{2i \sin[(\pi z)/h]} f(z)\, dz = h \sum_{n=-\infty}^{\infty} f(nh), \tag{B.1}$$

where the contour C consists of two pieces parallel to the real axis, one running left to right from $-\infty - \text{id}$ to $\infty - \text{id}$ in the lower half plane, the other running right to left from $\infty + \text{id}$ to $-\infty + \text{id}$ in the upper half plane. It is assumed that d is real and positive, that $f(z)$ is analytic on C and in the strip between these two pieces of C, and that $f(z)$ decreases fast enough as $|z| \to \infty$ within and on C to guarantee convergence of the sum and the integral in (B.1). Equation (B.1) can be established by evaluating the contour integral on the left-hand side as a sum of contributions from the poles of the integrand at the zeros of $\sin[(\pi z)/h]$. It is easy to show that

$$\frac{\cos[(\pi z)/h]}{2i\sin[(\pi z)/h]} = -\frac{1}{2} - \frac{\exp[(2\pi iz)/h]}{1-\exp[(2\pi iz)/h]} = \frac{1}{2} + \frac{\exp[-(2\pi iz)/h]}{1-\exp[-(2\pi iz)/h]}. \tag{B.2}$$

By using the first form on the piece of the contour C which is in the upper half plane, the second form on the piece in the lower half plane, and exploiting the analyticity of $f(z)$ to move the integration contour to the real axis for the $\pm\frac{1}{2}f(z)$ pieces, (B.1) can be brought to the form

$$\int_{-\infty}^{\infty} f(x)\,dx = h\sum_{k=-N_-}^{N_+} f(kh) + \varepsilon_I(h) + \varepsilon_{T,-}(N_-, h) + \varepsilon_{T,+}(N_+, h) \tag{B.3}$$

where

$$\begin{aligned}\varepsilon_I(h) = &-\int_{-\infty}^{\infty} \frac{\exp[-2\pi(d+ix)/h]\,f(x-id)}{1-\exp[-2\pi(d+ix)/h]}\,dx \\ &-\int_{-\infty}^{\infty} \frac{\exp[-2\pi(d-ix)/h]\,f(x+id)}{1-\exp[-2\pi(d-ix)/h]}\,dx\end{aligned} \tag{B.4}$$

is the interpolation error (we call this the interpolation error because it arises from interpolation via the Whittaker Cardinal function in Stenger's derivation) and

$$\varepsilon_{T,-}(N, h) = h\sum_{k=-\infty}^{-N-1} f(kh), \tag{B.5}$$

$$\varepsilon_{T,+}(N, h) = h\sum_{k=N+1}^{\infty} f(kh), \tag{B.6}$$

are the truncation errors. Equations (B.3)–(B.6) are essentially equivalent to Stenger's (3.12)–(3.14); in particular, the interpolation error $\varepsilon_I(h)$ is Stenger's $\eta(f, h)$, and the sum $\varepsilon_I(h) + \varepsilon_{T,-}(N_-, h) + \varepsilon_{T,+}(N_+, h)$ of the errors is Stenger's $\eta_N(f, h)$ if $N_- = N_+ = N$. Stenger's (3.14) contains a misprint: the $\sin[(\pi/h)(t-id)]$ in the denominator of the first term of the integrand should be $\sin[(\pi/h)(t+id)]$.

The numerical integration rules (2.17) and (2.18) follow from (B.3) via the changes of variables

$$W^{(1)} = \exp(z)/[1+\exp(z)]; \qquad z = \log[W^{(1)}/(1-W^{(1)})]. \tag{B.7}$$

$$W^{(2)} = 1+\exp(z); \qquad z = \log(W^{(2)}-1). \tag{B.8}$$

Error bounds for the numerical integration can be obtained by using the spectral theorem for self-adjoint operators [33, Chaps. VII, VIII] to express $f_1(W^{(1)})$ and $f_2(W^{(2)})$ in the form [33, p. 263, Eq. VIII.4]

$$f_j(W^{(j)}) = \int_0^\infty F_j(E, W^{(j)}) \langle \psi_n | \mathbf{P} \cdot |E\rangle\langle E| \mathbf{P} |\psi_n\rangle \, dE, \qquad j=1, 2. \tag{B.9}$$

Equation (B.9) has been written in Dirac notation, rather than the notation of Reed and Simon, so that the analysis will be easier for a physicist to follow. Here $|E\rangle\langle E|\, dE$ is the projection valued measure in terms of which the spectral theorem takes the form [33, p. 263, Theorem VIII.6]

$$Q_\perp^{(n)}(H-E_n)\, Q_\perp^{(n)} = \int_0^\infty E\, |E\rangle\langle E|\, dE. \tag{B.10}$$

The functions $F_j(E, W^{(j)})$ are

$$F_1(E, W^{(1)}) = \frac{W^{(1)}}{E+W^{(1)}} - 1, \qquad F_2(E, W^{(2)}) = \frac{W^{(2)}}{E+W^{(2)}} - 1 + \frac{E}{W^{(2)}}. \tag{B.11}$$

A bound on the interpolation error $\varepsilon_I(h)$ will now be calculated. The changes of variables (B.7), (B.8) yield

$$F_1[E, W^{(1)}(z)]\frac{dW^{(1)}}{dz} = \left[\frac{\exp(z)}{E+(E+1)\exp(z)} - 1\right]\frac{\exp(z)}{[1+\exp(z)]^2}, \tag{B.12}$$

$$F_2[E, W^{(2)}(z)]\frac{dW^{(2)}}{dz} = \frac{\exp(z)[1+\exp(z)]}{E+1+\exp(z)} - \exp(z) + E\,\frac{\exp(z)}{1+\exp(z)}. \tag{B.13}$$

The right-hand side of (B.12) has first order poles at $z=(2k+1)\,i\pi$ with residue E, and first-order poles at $z=-\log(1+E^{-1})+(2k+1)\,i\pi$ with residue $-E$, for every integer k. The right-hand side of (B.13) has first-order poles at $z=(2k+1)\,i\pi$ with residue E, and first order poles at $z=\log(1+E)+(2k+1)\,i\pi$ with residue $-E$, for every integer k. The interpolation error $\varepsilon_I^{(1)}(E, h)$ which is obtained when (B.4) is evaluated via the calculus of residues with $f(z)=F_1[E, W^{(1)}(z)]\, dW^{(1)}/dz$ is

$$\begin{aligned}\varepsilon_I^{(1)}(E, h) = 2\pi i E \sum_{k=0}^{\infty} \Bigg\{ &\frac{\exp[-2\pi^2 h^{-1}(2k+1) - 2\pi i h^{-1}\log(1+E^{-1})]}{1-\exp[-2\pi^2 h^{-1}(2k+1) - 2\pi i h^{-1}\log(1+E^{-1})]} \\ &- \frac{\exp[-2\pi^2 h^{-1}(2k+1) + 2\pi i h^{-1}\log(1+E^{-1})]}{1-\exp[-2\pi^2 h^{-1}(2k+1) + 2\pi i h^{-1}\log(1+E^{-1})]}\Bigg\}.\end{aligned} \tag{B.14}$$

The interpolation error $\varepsilon_I^{(2)}(E, h)$ which is obtained when (B.4) is evaluated via the calculus of residues with $f(z) = F_2[E, W^{(2)}(z)]\, dW^{(2)}/dz$ can be obtained from (B.14) by replacing $\log(1 + E^{-1})$ by $-\log(1 + E)$. It is straightforward to show that these interpolation errors have the bound

$$|\varepsilon_I^{(j)}(E, h)| \leqslant 4\pi E \sum_{k=0}^{\infty} \frac{\exp[-2\pi^2 h^{-1}(2k+1)]}{1 - \exp[-2\pi^2 h^{-1}(2k+1)]}$$
$$\leqslant \frac{\pi E}{\sinh^2(\pi^2 h^{-1})}, \qquad j = 1, 2. \tag{B.15}$$

The interpolation errors $\varepsilon_I^{(j)}(h)$ which are obtained when (B.4) is evaluated with $f(z) = f_j[W^{(j)}(z)]\, dW^{(j)}/dz$ are

$$\varepsilon_I^{(j)}(h) = \int_0^{\infty} \varepsilon_I^{(j)}(E, h)\, \langle \psi_n | \mathbf{P} \cdot |E\rangle \langle E| \mathbf{P} |\psi_n\rangle\, dE, \qquad j = 1, 2. \tag{B.16}$$

If the bound (B.15) is used in (B.16), the integration over E can be performed to obtain the interpolation error bound (2.20).

Truncation error bounds can be obtained by employing the inequalities $0 \leqslant -F_1(E, W_a^{(1)}) \leqslant -F_1(E, W_b^{(1)}) \leqslant 1$ for $W_a^{(1)} \geqslant W_b^{(1)} \geqslant 0$, $E \geqslant 0$, and $0 \leqslant F_2(E, W_a^{(2)}) \leqslant F_2(E, W_b^{(2)}) \leqslant E$ for $W_a^{(2)} \geqslant W_b^{(2)} \geqslant 1$, $E \geqslant 0$, in (B.9) to obtain

$$0 \leqslant -f_1(W_a^{(1)}) \leqslant -f_1(W_b^{(1)})$$
$$\leqslant \langle \psi_n | \mathbf{P} \cdot Q_\perp^{(n)} \mathbf{P} |\psi_n\rangle, \qquad W_a^{(1)} \geqslant W_b^{(1)} \geqslant 0, \tag{B.17}$$

$$0 \leqslant f_2(W_a^{(2)}) \leqslant f_2(W_b^{(2)})$$
$$\leqslant \langle \psi_n | \mathbf{P} \cdot Q_\perp^{(n)}(H - E_n)\, Q_\perp^{(n)} \mathbf{P} |\psi_n\rangle, \qquad W_a^{(1)} \geqslant W_b^{(2)} \geqslant 1. \tag{B.18}$$

The truncation error bounds (2.21)–(2.23) follow by using (B.17) and (B.18) in the definitions (B.5) and (B.6). The second form for $S^{(1)}(N)$ in (2.24) is obtained by rewriting the summand in the first form as $h \exp(-kh) \times [1 + \exp(-kh)]^{-2}$ and expanding the factor $[1 + \exp(-kh)]^{-2}$ in powers of $\exp(-kh)$ to obtain a double series. The (original) sum over k is then performed with the aid of the formula for the sum of a geometric series. The asymptotic formula (2.26) for the truncation error $\varepsilon_{T,+}^{(2)}(N_+^{(2)}, h)$ is obtained by using the asymptotic formula (3.1) for $f_2(W^{(2)})$ in the definition (B.6) and summing term by term.

APPENDIX C: Details for Section 3

This appendix records certain details which have been omitted from the presentation in Section 3. The bound (3.11) will be derived first. We begin with the explicit momentum space representative

$$\begin{aligned}&\langle \mathbf{p}_1, \mathbf{p}_2, ..., \mathbf{p}_N | (T-E_n+W)^{-1/2} r_1^{-1} (T-E_n+W)^{-1/2} | \mathbf{p}'_1, \mathbf{p}'_2, ..., \mathbf{p}'_N \rangle \\ &= \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{\Phi_{k,l}(p_1)\, Y_{l,m}(\theta_1, \phi_1)\, \overline{\Phi_{k,l}(p'_1)\, Y_{l,m}(\theta'_1, \phi'_1)}}{(k+l+1)\, q} \\ &\times \prod_{j=2}^{N} \delta(\mathbf{p}_j - \mathbf{p}'_j),\end{aligned} \tag{C.1}$$

where

$$\begin{aligned}\Phi_{k,l}(p_1) &= 2^{2l+2} q^{(2l+3)/2} l! \\ &\times \sqrt{\frac{k!\,(k+l+1)}{\pi(k+2l+1)!}}\, p_1^l (p_1^2+q^2)^{-(2l+3)/2}\, C_k^{l+1}\left(\frac{p_1^2-q^2}{p_1^2+q^2}\right),\end{aligned} \tag{C.2}$$

with C_k^{l+1} a Gegenbauer polynomial in standard notation and

$$q = \sqrt{2(W-E_n) + \sum_{j=2}^{N} |\mathbf{p}_j|^2}. \tag{C.3}$$

Formulas (C.1)–(C.3) are obtained from the bound state solutions to the hydrogen atom in momentum space [34; 10, pp. 36–40] by fixing the energy at a negative value and letting the coupling constant in front of the Coulomb potential be the eigenvalue (note that this requires rescaling the momentum in the hydrogen atom bound state wave functions by a factor of $(k+l+1)\,q$). The functions $\Phi_{k,l}(p_1)\, Y_{l,m}(\theta_1, \phi_1)$ are a complete orthonormal set in $L^2[R^3]$. It follows from (C.1) that $(T-E_n+W)^{-1/2} r_1^{-1} (T-E_n+W)^{-1/2}$ is a bounded operator from the space $L^2[R^{3N}]$ of square-integrable functions in $3N$ dimensions to $L^2[R^{3N}]$ with 2-norm

$$\|(T-E_n+W)^{-1/2} r_1^{-1} (T-E_n+W)^{-1/2}\|_2 = [2(W-E_n)]^{-1/2}. \tag{C.4}$$

A similar calculation shows that $(T-E_n+W)^{-1/2} |\mathbf{r}_1 - \mathbf{r}_2|^{-1} (T-E_n+W)^{-1/2}$ is an operator from $L^2[R^{3N}]$ to $L^2[R^{3N}]$ with 2-norm

$$\|(T-E_n+W)^{-1/2} |\mathbf{r}_1 - \mathbf{r}_2|^{-1} (T-E_n+W)^{-1/2}\|_2 = [4(W-E_n)]^{-1/2}. \tag{C.5}$$

r_1 in (C.4), and $|\mathbf{r}_1 - \mathbf{r}_2|$ in (C.5) can, of course, be replaced by $|\mathbf{r}_j - \mathbf{R}_k|$ and $|\mathbf{r}_j - \mathbf{r}_k|$ without altering the conclusions. The result (3.11)–(3.12) follows.

We now consider the evaluation of $\sum_{m=-1}^{1} \langle \psi_{l;m,n}^{(j,k)} | \psi_{l';m,n}^{(j',k')} \rangle$ for the case $j=j'$, $k \neq k'$. The "two-center" partial wave expansion

$$\begin{aligned}&\frac{\exp(-v^{-1}|\mathbf{r}_1+\mathbf{r}_2+\mathbf{r}_3|)}{2\pi |\mathbf{r}_1+\mathbf{r}_2+\mathbf{r}_3|} \\ &= \frac{4\pi}{v} \sum_{l_1=0}^{\infty} \sum_{m_1=-l_1}^{l_1} \sum_{l_2=0}^{\infty} \sum_{m_2=-l_2}^{l_2} \sum_{l_3=0}^{\infty} \sum_{m_3=-l_3}^{l_3} (-1)^{m_1} \\ &\times \langle l_1, -m_1 | l_2, m_2 | l_3, m_3 \rangle\, Y_{l_1,m_1}(\theta_1, \phi_1)\, Y_{l_2,m_2}(\theta_2, \phi_2) \\ &\times Y_{l_3,m_3}(\theta_3, \phi_3)\, g_{l_1,l_2,l_3}(v^{-1}r_1, v^{-1}r_2, v^{-1}r_3)\end{aligned} \tag{C.6}$$

will be used instead of the expansion (3.23). Here $\langle l_1, -m_1 | l_2, m_2 | l_3, m_3 \rangle$ is the Gaunt coefficient, which can be expressed in terms of Wigner 3-J symbols via

$$(-1)^{m_1} \langle l_1, -m_1 | l_2, m_2 | l_3, m_3 \rangle$$
$$= \int Y_{l_1, m_1}(\theta, \phi)\, Y_{l_2, m_2}(\theta, \phi)\, Y_{l_3, m_3}(\theta, \phi)\, d\Omega$$
$$= \left[\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}\right]^{1/2} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}. \tag{C.7}$$

The Gaunt coefficient is zero unless $l_1 + l_2 + l_3$ is an even integer and l_1, l_2, and l_3 satisfy triangle conditions. The "radial" function g_{l_1, l_2, l_3} is given by the integral representation

$$g_{l_1, l_2, l_3}(z_1, z_2, z_3) = \left(\frac{\pi}{2}\right)^{1/2} (-i)^{l_1 + l_2 + l_3} \int_{-\infty}^{\infty} \frac{t^2\, dt}{1+t^2} \prod_{j=1}^{3} \frac{J_{l_j + 1/2}(tz_j)}{(tz_j)^{1/2}}. \tag{C.8}$$

The expansion (C.6) can be obtained from the Fourier integral representation

$$\frac{\exp(-\nu^{-1} |\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3|)}{2\pi |\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3|} = \frac{1}{4\pi^3} \int \frac{d^3\mathbf{k}}{k^2 + \nu^{-2}} \exp[-i\mathbf{k} \cdot (\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3)]. \tag{C.9}$$

The exponential factor $\exp[-i\mathbf{k} \cdot (\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3)]$ is expanded by using

$$\exp(-i\mathbf{k} \cdot \mathbf{r}_j) = (2\pi)^{3/2} \sum_{l=0}^{\infty} (-i)^l \frac{J_{l+1/2}(kr_j)}{(kr_j)^{1/2}}$$
$$\times \sum_{m=-l}^{l} \overline{Y_{l,m}(\theta_k, \phi_k)}\, Y_{l,m}(\theta_j, \phi_j) \tag{C.10}$$

for $j=1$, for $j=2$, and for $j=3$. In (C.10), k, θ_k, and ϕ_k are the spherical coordinates of $\mathbf{k}$, and r_j, θ_j, and ϕ_j are the spherical coordinates of $\mathbf{r}_j$. The angular integrations over θ_k and ϕ_k are performed with the aid of (C.7). Contour integration can be used to show that

$$g_{l_1, l_2, l_3}(z_1, z_2, z_3) = (2\pi)^{1/2} (-1)^{l_1} \frac{K_{l_1+1/2}(z_1)}{z_1^{1/2}} \frac{I_{l_2+1/2}(z_2)}{z_2^{1/2}} \frac{I_{l_3+1/2}(z_3)}{z_3^{1/2}} \tag{C.11}$$

for $z_1 \geqslant 0$, $z_2 \geqslant 0$, $z_3 \geqslant 0$, and $z_1 \geqslant z_2 + z_3$. Formulas for the cases $z_2 \geqslant z_3 + z_1$ and $z_3 \geqslant z_1 + z_2$ can be obtained from (C.11) by cyclic permutation of the indices 1, 2, and 3. Contour integration can also be used to show that

$$
\begin{aligned}
&g_{l_1,l_2,l_3}(z_1,z_2,z_3)\\
&=\Bigg[\hat{g}_{l_1,l_2,l_3}(z_1,z_2,z_3)-\left(\frac{2}{\pi}\right)^{1/2}(-1)^{l_1}\frac{I_{l_1+1/2}(z_1)}{z_1^{1/2}}\\
&\quad\times\frac{K_{l_2+1/2}(z_2)}{z_2^{1/2}}\frac{K_{l_3+1/2}(z_3)}{z_3^{1/2}}-\left(\frac{2}{\pi}\right)^{1/2}(-1)^{l_2}\frac{K_{l_1+1/2}(z_1)}{z_1^{1/2}}\frac{I_{l_2+1/2}(z_2)}{z_2^{1/2}}\\
&\quad\times\frac{K_{l_3+1/2}(z_3)}{z_3^{1/2}}-\left(\frac{2}{\pi}\right)^{1/2}(-1)^{l_3}\frac{K_{l_1+1/2}(z_1)}{z_1^{1/2}}\frac{K_{l_2+1/2}(z_2)}{z_2^{1/2}}\frac{I_{l_3+1/2}(z_3)}{z_3^{1/2}}\\
&\quad-\left(\frac{2}{\pi}\right)^{3/2}\frac{K_{l_1+1/2}(z_1)}{z_1^{1/2}}\frac{K_{l_2+1/2}(z_2)}{z_2^{1/2}}\frac{K_{l_3+1/2}(z_3)}{z_3^{1/2}}\Bigg]
\end{aligned}
\tag{C.12}
$$

for $0\leqslant z_1\leqslant z_2+z_3$, $0\leqslant z_2\leqslant z_3+z_1$, $0\leqslant z_3\leqslant z_1+z_2$, where

$$
\begin{aligned}
\hat{g}_{l_1,l_2,l_3}(z_1,z_2,z_3)=\frac{\pi^{3/2}}{8}\sum_{n_1,n_2,n_3}&\frac{(z_1/2)^{2n_1-l_1-1}}{n_1!\,\Gamma(n_1-l_1+1/2)}\\
&\times\frac{(z_2/2)^{2n_2-l_2-1}}{n_2!\,\Gamma(n_2-l_2+1/2)}\frac{(z_3/2)^{2n_3-l_3-1}}{n_3!\,\Gamma(n_3-l_3+1/2)}.
\end{aligned}
\tag{C.13}
$$

The sum over n_1, n_2, and n_3 in (C.13) is subject to the restrictions $n_1\geqslant 0$, $n_2\geqslant 0$, $n_3\geqslant 0$, and $n_1+n_2+n_3\leqslant(l_1+l_2+l_3)/2$. The expansion (C.6) is used with $\mathbf{r}_1=\mathbf{r}_j-\mathbf{R}_k$, $\mathbf{r}_2=-\mathbf{r}_j'+\mathbf{R}_{k'}$, and $\mathbf{r}_3=\mathbf{R}_k-\mathbf{R}_{k'}$. Performing the angular integrations with the aid of (C.7) yields

$$
\begin{aligned}
&\langle\psi_n|\,P^{(j,k)}_{l_a,m_a}\left(\frac{\mathbf{r}_j-\mathbf{R}_k}{|\mathbf{r}_j-\mathbf{R}_k|^3}\right)\cdot\left(\tfrac{1}{2}p_j^2-E_n+W\right)^{-1}\left(\frac{\mathbf{r}_j-\mathbf{R}_{k'}}{|\mathbf{r}_j-\mathbf{R}_{k'}|^3}\right)P^{(j,k)}_{l_b,m_b}|\psi_n\rangle\\
&=\frac{4\pi}{v}\sum_{l_1=0}^{\infty}\sum_{l_2=0}^{\infty}\sum_{l_3=0}^{\infty}M^{(j,k,k')}_{l_1,l_2,l_3,m_a,m_b;n;(l_1-l_a+1)/2,(l_2-l_b+1)/2}\\
&\quad\times A(l_1,l_2,l_3,l_a,l_b;m_a,m_b)\,Y_{l_3,m_b-m_a}(\theta_{k,k'},\phi_{k,k'}),
\end{aligned}
\tag{C.14}
$$

where the angles $\theta_{k,k'}$, $\phi_{k,k'}$ specify the direction of $\mathbf{R}_k-\mathbf{R}_{k'}$. A and M are defined by

$$
\begin{aligned}
&A(l_1,l_2,l_3,l_a,l_b;m_a,m_b)\\
&=\left[\frac{(2l_a+1)(2l_b+1)(2l_3+1)}{4\pi}\right]^{1/2}(2l_1+1)(2l_2+1)(-1)^{l_2+m_a}\\
&\quad\times\begin{pmatrix}l_1&l_2&l_3\\0&0&0\end{pmatrix}\begin{pmatrix}l_a&1&l_1\\0&0&0\end{pmatrix}\begin{pmatrix}l_b&1&l_2\\0&0&0\end{pmatrix}\\
&\quad\times\sum_{m=-1}^{1}(-1)^m\begin{pmatrix}l_1&l_2&l_3\\m+m_a&-m-m_b&m_b-m_a\end{pmatrix}\\
&\quad\times\begin{pmatrix}l_a&1&l_1\\-m_a&-m&m+m_a\end{pmatrix}\begin{pmatrix}l_b&1&l_2\\m_b&m&-m-m_b\end{pmatrix},
\end{aligned}
\tag{C.15}
$$

$$M^{(j,k,k')}_{l_1,l_2,l_3,m_a,m_b;n;p_1,p_2}$$
$$= \int_0^\infty dr \int_0^\infty dr'\, r^{l_1-2p_1+1}(r')^{l_2-2p_2+1}\, g_{l_1,l_2,l_3}(v^{-1}r, v^{-1}r', v^{-1}\,|\mathbf{R}_k - \mathbf{R}_{k'}|)$$
$$\times \rho^{(j,k,k')}_{l_1-2p_1+1,m_a;l_2-2p_2+1,m_b;n}(r,r'). \tag{C.16}$$

The sums over l_1, l_2, and l_3 in (C.14) are actually finite, because the factor A in the summand is non-zero only for $l_1 = l_a \pm 1$, $l_2 = l_b \pm 1$, and $|l_1 - l_2| \leqslant l_3 \leqslant l_1 + l_2$.

The integration over r and r' in (C.16) is similar to the integration over r and r' in (3.28) and is handled in the same way. We begin with the definitions

$$G^{(1)}_{l_1,l_2,l_3;p_1,p_2}(z_1,z_2,z_3)$$
$$= \left(\frac{\pi}{2}\right)^{1/2} (-i)^{l_1+l_2+l_3} \int_{-\infty}^{\infty} \frac{dt}{1+t^2}\, t^{2p_1+2p_2-l_1-l_2-2}$$
$$\times J_{l_1,p_1}(tz_1)[J_{l_2,p_2}(tz_2) - J_{l_2,p_2}(0)]\, \frac{J_{l_3+1/2}(tz_3)}{(tz_3)^{1/2}}, \tag{C.17}$$

$$G^{(2)}_{l_1,l_2,l_3;p_1,p_2}(z_1,z_2,z_3)$$
$$= \left(\frac{\pi}{2}\right)^{1/2} (-i)^{l_1+l_2+l_3} \int_{-\infty}^{\infty} \frac{dt}{1+t^2}\, t^{2p_1+2p_2-l_1-l_2-2}$$
$$\times [J_{l_1,p_1}(tz_1) - J_{l_1,p_1}(0)]\, J_{l_2,p_2}(tz_2)\, \frac{J_{l_3+1/2}(tz_3)}{(tz_3)^{1/2}}, \tag{C.18}$$

$$G^{(3)}_{l_1,l_2,l_3;p_1,p_2}(z_1,z_2,z_3)$$
$$= \left(\frac{\pi}{2}\right)^{1/2} (-i)^{l_1+l_2+l_3} \int_{-\infty}^{\infty} \frac{dt}{1+t^2}\, t^{2p_1+2p_2-l_1-l_2-2}$$
$$\times [J_{l_1,p_1}(tz_1) - J_{l_1,p_1}(0)][J_{l_2,p_2}(tz_2) - J_{l_2,p_2}(0)]\, \frac{J_{l_3+1/2}(tz_3)}{(tz_3)^{1/2}}, \tag{C.19}$$

$$G^{(4)}_{l_1,l_2,l_3;p_1,p_2}(z_1,z_2,z_3)$$
$$= \left(\frac{\pi}{2}\right)^{1/2} (-i)^{l_1+l_2+l_3} \int_{-\infty}^{\infty} \frac{dt}{1+t^2}\, t^{2p_1+2p_2-l_1-l_2-2}$$
$$\times [J_{l_1,p_1}(tz_1)\, J_{l_2,p_2}(tz_2) - J_{l_1,p_1}(0)\, J_{l_2,p_2}(0)]\, \frac{J_{l_3+1/2}(tz_3)}{(tz_3)^{1/2}}, \tag{C.20}$$

$$G_{l_1,l_2,l_3;p_1,p_2}(z_1,z_2,z_3) = \begin{cases} G^{(1)}_{l_1,l_2,l_3;p_1,p_2}(z_1,z_2,z_3), & z_1 > z_2 + z_3, \\ G^{(2)}_{l_1,l_2,l_3;p_1,p_2}(z_1,z_2,z_3), & z_2 > z_3 + z_1, \\ G^{(3)}_{l_1,l_2,l_3;p_1,p_2}(z_1,z_2,z_3), & z_3 > z_1 + z_2, \\ G^{(4)}_{l_1,l_2,l_3;p_1,p_2}(z_1,z_2,z_3), & z_1 < z_2 + z_3, \\ \qquad z_2 < z_3 + z_1, & z_3 < z_1 + z_2. \end{cases} \tag{C.21}$$

The G defined by (C.21) is the indefinite integral needed to evaluate the radial integrals via partial integration. It is straightforward to show that

$$z_1^{l_1-2p_1+1} z_2^{l_2-2p_2+1} g_{l_1,l_2,l_3}(z_1,z_2,z_3)$$
$$= \frac{\partial^2}{\partial z_1\,\partial z_2} G_{l_1,l_2,l_3;p_1,p_2}(z_1,z_2,z_3),\quad z_1 \neq z_2+z_3, z_2 \neq z_3+z_1, z_3 \neq z_1+z_2. \tag{C.22}$$

It can be shown by differentiating through the integral sign in (C.17)–(C.20) that the $G^{(i)}$ are continuous with continuous first and second partial derivatives with respect to z_1 and z_2. Thus the discontinuities in G and its first and second derivatives across the boundaries $z_1 = z_2 + z_3$, $z_2 = z_3 + z_1$, and $z_3 = z_1 + z_2$ can be computed by evaluating the appropriate differences of the $G^{(i)}$ and their derivatives across these boundaries. We make the additional definitions

$$D^{(1)}_{l_1,l_2,l_3;p_1,p_2}(z_1,z_3) = G^{(4)}_{l_1,l_2,l_3;p_1,p_2}(z_1,z_2,z_3) - G^{(1)}_{l_1,l_2,l_3;p_1,p_2}(z_1,z_2,z_3), \tag{C.23}$$

$$D^{(2)}_{l_1,l_2,l_3;p_1,p_2}(z_2,z_3) = G^{(4)}_{l_1,l_2,l_3;p_1,p_2}(z_1,z_2,z_3) - G^{(2)}_{l_1,l_2,l_3;p_1,p_2}(z_1,z_2,z_3). \tag{C.24}$$

$D^{(1)}$ is the discontinuity of G across the line $z_1 = z_2 + z_3$, $D^{(2)}$ is the discontinuity of G across the line $z_2 = z_3 + z_1$, and $D^{(1)} + D^{(2)}$ is the discontinuity of G across the line $z_3 = z_1 + z_2$. It is easy to see that

$$D^{(2)}_{l_1,l_2,l_3;p_1,p_2}(z_1,z_3) = D^{(1)}_{l_2,l_1,l_3;p_2,p_1}(z_2,z_3). \tag{C.25}$$

Contour integration can be used to show that

$$G_{l_1,l_2,l_3;p_1,p_2}(z_1,z_2,z_3)$$
$$= (2\pi)^{1/2}(-1)^{l_1} K_{l_1,p_1}(z_1)$$
$$\times [I_{l_2,p_2}(z_2) - I_{l_2,p_2}(0)]\,\frac{I_{l_3+1/2}(z_3)}{z_3^{1/2}},\qquad z_1 > z_2 + z_3, \tag{C.26}$$

$$G_{l_1,l_2,l_3;p_1,p_2}(z_1,z_2,z_3)$$
$$= (2\pi)^{1/2}(-1)^{l_2}[I_{l_1,p_1}(z_1) - I_{l_1,p_1}(0)]$$
$$\times K_{l_2,p_2}(z_2)\,\frac{I_{l_3+1/2}(z_3)}{z_3^{1/2}},\qquad z_2 > z_3 + z_1, \tag{C.27}$$

$$G_{l_1,l_2,l_3;p_1,p_2}(z_1,z_2,z_3)$$
$$= (2\pi)^{1/2}(-1)^{l_3}[I_{l_1,p_1}(z_1) - I_{l_1,p_1}(0)]$$
$$\times [I_{l_2,p_2}(z_2) - I_{l_2,p_2}(0)]\,\frac{K_{l_3+1/2}(z_3)}{z_3^{1/2}},\qquad z_3 > z_1 + z_2, \tag{C.28}$$

$$G_{l_1, l_2, l_3; p_1, p_2}(z_1, z_2, z_3)$$
$$= \sum_{j=1}^{6} \hat{G}^{(j)}_{l_1, l_2, l_3; p_1, p_2}(z_1, z_2, z_3) - \left(\frac{2}{\pi}\right)^{1/2} (-1)^{l_1}$$
$$\times I_{l_1, p_1}(z_1)\, K_{l_2, p_2}(z_2)\, \frac{K_{l_3+1/2}(z_3)}{z_3^{1/2}} - \left(\frac{2}{\pi}\right)^{1/2} (-1)^{l_2}\, K_{l_1, p_1}(z_1)\, I_{l_2, p_2}(z_2)$$
$$\times \frac{K_{l_3+1/2}(z_3)}{z_3^{1/2}} - \left(\frac{2}{\pi}\right)^{1/2} (-1)^{l_3}\, K_{l_1, p_1}(z_1)\, K_{l_2, p_2}(z_2)\, \frac{I_{l_3+1/2}(z_3)}{z_3^{1/2}}$$
$$- \left(\frac{2}{\pi}\right)^{3/2} K_{l_1, p_1}(z_1)\, K_{l_2, p_2}(z_2)\, \frac{K_{l_3+1/2}(z_3)}{z_3^{1/2}} - 2\left(\frac{\pi}{2}\right)^{1/2} (-1)^{l_3}\, I_{l_1, p_1}(0)$$
$$\times I_{l_2, p_2}(0)\, \frac{K_{l_3+1/2}(z_3)}{z_3^{1/2}}, \qquad z_1 < z_2 + z_3,\ z_2 < z_3 + z_1,\ z_3 < z_1 + z_2, \tag{C.29}$$

$$D^{(1)}_{l_1, l_2, l_3; p_1, p_2}(z_1, z_3)$$
$$= 2\left(\frac{\pi}{2}\right)^{1/2} (-1)^{l_1}\, I_{l_2, p_2}(0)\, K_{l_1, p_1}(z_1)\, \frac{I_{l_3+1/2}(z_3)}{z_3^{1/2}}$$
$$- 2\left(\frac{\pi}{2}\right)^{1/2} (-1)^{l_3}\, I_{l_1, p_1}(0)\, I_{l_2, p_2}(0)\, \frac{K_{l_3+1/2}(z_3)}{z_3^{1/2}}$$
$$+ 2[\hat{G}^{(4)}_{l_1, l_2, l_3; p_1, p_2}(z_1, z_2, z_3) + \hat{G}^{(6)}_{l_1, l_2, l_3; p_1, p_2}(z_1, z_2, z_3)], \quad z_1 > z_3, \tag{C.30}$$

$$D^{(1)}_{l_1, l_2, l_3; p_1, p_2}(z_1, z_3)$$
$$= 2\left(\frac{\pi}{2}\right)^{1/2} (-1)^{l_3}\, I_{l_2, p_2}(0)[I_{l_1, p_1}(z_1) - I_{l_1, p_1}(0)]$$
$$\times \frac{K_{l_3+1/2}(z_3)}{z_3^{1/2}} + 2\hat{G}^{(5)}_{l_1, l_2, l_3; p_1, p_2}(z_1, z_2, z_3), \qquad z_1 < z_3, \tag{C.31}$$

where

$$\hat{G}^{(1)}_{l_1, l_2, l_3; p_1, p_2}(z_1, z_2, z_3)$$
$$= \sum_{n_1, n_2, n_3} \frac{\pi^{3/2}\, 2^{l_1 - 2p_1 + l_2 - 2p_2 + 1}}{n_1!\, n_2!\, n_3!\, (2n_1 - 2p_1 + 1)}$$
$$\times \frac{(z_1/2)^{2n_1 - 2p_1 + 1}\, (z_2/2)^{2n_2 - 2p_2 + 1}\, (z_3/2)^{2n_3 - l_3 - 1}}{(2n_2 - 2p_2 + 1)\, \Gamma(n_1 - l_1 + 1/2)\, \Gamma(n_2 - l_2 + 1/2)\, \Gamma(n_3 - l_3 + 1/2)}, \tag{C.32}$$

$$\hat{G}^{(2)}_{l_1, l_2, l_3; p_1, p_2}(z_1, z_2, z_3)$$
$$= -\left(\frac{\pi}{2}\right)^{3/2} I_{l_1, p_1}(0) \sum_{n_2, n_3} \frac{2^{l_2 - 2p_2 + 1}}{n_2!\, n_3!\, (2n_2 - 2p_2 + 1)}$$
$$\times \frac{(z_2/2)^{2n_2 - 2p_2 + 1}\, (z_3/2)^{2n_3 + l_3}}{\Gamma(n_2 - l_2 + 1/2)\, \Gamma(n_3 + l_3 + 3/2)}, \tag{C.33}$$

$$\hat{G}^{(3)}_{l_1, l_2, l_3; p_1, p_2}(z_1, z_2, z_3)$$
$$= -\left(\frac{\pi}{2}\right)^{3/2} I_{l_1, p_1}(0) \sum_{n_2, n_3} \frac{2^{l_2 - 2p_2}}{n_2!\, n_3!\, (n_2 + l_2 - p_2 + 1)}$$
$$\times \frac{(z_2/2)^{2(n_2 + l_2 - p_2 + 1)}\, (z_3/2)^{2n_3 - l_3 - 1}}{\Gamma(n_2 + l_2 + 3/2)\, \Gamma(n_3 - l_3 + 1/2)}, \tag{C.34}$$

$$\hat{G}^{(4)}_{l_1, l_2, l_3; p_1, p_2}(z_1, z_2, z_3)$$
$$= \hat{G}^{(2)}_{l_2, l_1, l_3; p_2, p_1}(z_2, z_1, z_3), \tag{C.35}$$

$$\hat{G}^{(5)}_{l_1, l_2, l_3; p_1, p_2}(z_1, z_2, z_3)$$
$$= \hat{G}^{(3)}_{l_2, l_1, l_3; p_2, p_1}(z_2, z_1, z_3), \tag{C.36}$$

$$\hat{G}^{(6)}_{l_1, l_2, l_3; p_1, p_2}(z_1, z_2, z_3)$$
$$= \frac{1}{4} \pi^{3/2} I_{l_1, p_1}(0)\, I_{l_2, p_2}(0) \sum_{n_3} \frac{(z_3/2)^{2n_3 - l_3 - 1}}{n_3!\, \Gamma(n_3 - l_3 + 1/2)}. \tag{C.37}$$

The summation limits in (C.32) are $n_1 \geqslant 0$, $n_2 \geqslant 0$, $n_3 \geqslant 0$, and $n_1 + n_2 + n_3 \leqslant \frac{1}{2}(l_1 + l_2 + l_3)$. The summation limits in (C.33) are $n_2 \geqslant 0$, $n_3 \geqslant 0$, and $n_2 + n_3 \leqslant \frac{1}{2}(l_1 + l_2 - l_3) - p_1$. The summation limits in (C.34) are $n_2 \geqslant 0$, $n_3 \geqslant 0$, and $n_2 + n_3 \leqslant \frac{1}{2}(l_1 - l_2 + l_3) - p_1$. The summation limits in (C.37) are $n_3 \geqslant 0$ and $n_3 \leqslant \frac{1}{2}(l_1 + l_2 + l_3) - p_1 - p_2 + 1$. Analogues of (C.30) and (C.31) for $D^{(2)}$ can be obtained from (C.30) and (C.31) with the aid of (C.25). Equations (C.26)–(C.37) show that $G_{l_1, l_2, l_3; p_1, p_2}(z_1, z_2, z_3)$ is zero at $z_1 = 0$ and $z_2 = 0$ and decays exponentially as $z_1 \to \infty$ in $z_1 > z_2 + z_3$ and as $z_2 \to \infty$ in $z_2 > z_3 + z_1$. These equations also show that $D^{(1)}_{l_1, l_2, l_3; p_1, p_2}(z_1, z_3)$ is independent of z_2, as indicated by the notation, and zero at $z_1 = 0$.

The result of integrating (C.16) by parts with the aid of the preceding formulas is

$$M^{(j,k,k')}_{l_1, l_2, l_3, m_a, m_b; n; p_1, p_2} = v^{l_1 - 2p_1 + l_2 - 2p_2 + 4}\big[M^{(j,k,k';a)}_{l_1, l_2, l_3, m_a, m_b; n; p_1, p_2}$$
$$+ M^{(j,k,k';b)}_{l_1, l_2, l_3, m_a, m_b; n; p_1, p_2} + M^{(j,k,k';c)}_{l_1, l_2, l_3, m_a, m_b; n; p_1, p_2}\big], \tag{C.38}$$

where

$$M^{(j,k,k';a)}_{l_1,l_2,l_3,m_a,m_b;n;p_1,p_2}$$
$$= \int_0^\infty dr\, D^{(1)}_{l_1,l_2,l_3;p_1,p_2}(v^{-1}r, v^{-1}|\mathbf{R}_k - \mathbf{R}_{k'}|)$$
$$\times \left[\frac{\partial}{\partial r}\rho^{(j,k,k')}_{l_1-2p_1+1,m_a;l_2-2p_2+1,m_b;n}(r,r')\right]_{r'=|(|\mathbf{R}_k-\mathbf{R}_{k'}|)-r|}, \tag{C.39}$$

$$M^{(j,k,k';b)}_{l_1,l_2,l_3,m_a,m_b;n;p_1,p_2}$$
$$= \int_0^\infty dr'\, D^{(2)}_{l_1,l_2,l_3;p_1,p_2}(v^{-1}r', v^{-1}|\mathbf{R}_k - \mathbf{R}_{k'}|)$$
$$\times \left[\frac{\partial}{\partial r'}\rho^{(j,k,k')}_{l_1-2p_1+1,m_a;l_2-2p_2+1,m_b;n}(r,r')\right]_{r=|(|\mathbf{R}_k-\mathbf{R}_{k'}|)-r'|}, \tag{C.40}$$

$$M^{(j,k,k';c)}_{l_1,l_2,l_3,m_a,m_b;n;p_1,p_2}$$
$$= \int_0^\infty dr \int_0^\infty dr'\, G_{l_1,l_2,l_3;p_1,p_2}(v^{-1}r, v^{-1}r', v^{-1}|\mathbf{R}_k - \mathbf{R}_{k'}|)$$
$$\times \frac{\partial^2}{\partial r\,\partial r'}\rho^{(j,k,k')}_{l_1-2p_1+1,m_a;l_2-2p_2+1,m_b;n}(r,r'). \tag{C.41}$$

The analysis of (C.39)–(C.41) shows that, if $|\mathbf{R}_k - \mathbf{R}_{k'}|$ is $O(1)$ so that $v^{-1}|\mathbf{R}_k - \mathbf{R}_{k'}|$ is large, the only contributions to $M^{(j,k,k')}_{l_1,l_2,l_3,m_a,m_b;n;p_1,p_2}$ at order v^3 come from the pieces of the $\hat{G}^{(j)}_{l_1,l_2,l_3;p_1,p_2}$ terms in which the sum of the summation indices takes on its maximum value – e.g., from the piece of $\hat{G}^{(1)}_{l_1,l_2,l_3;p_1,p_2}$ for which $n_1+n_2+n_3 = \frac{1}{2}(l_1+l_2+l_3)$. These pieces are the ones which would come from the evaluation of the residue at $t=0$ if the $(1+t^2)^{-1}$ in (C.8) and (C.17)–(C.20) were replaced by 1; this replacement is equivalent to making the approximation

$$\frac{\exp(-v^{-1}|\mathbf{r}_1+\mathbf{r}_2+\mathbf{r}_3|)}{2\pi\,|\mathbf{r}_1+\mathbf{r}_2+\mathbf{r}_3|} \approx 2v^2\,\delta(\mathbf{r}_1+\mathbf{r}_2+\mathbf{r}_3) \tag{C.42}$$

for the partial wave expansion (C.6), i.e., to approximating $(T-E_n+W)^{-1}$ by $(-E_n+W)^{-1}$. All other contributions to $M^{(j,k,k')}_{l_1,l_2,l_3,m_a,m_b;n;p_1,p_2}$ can be seen to be of order v^5 or higher. It follows that (3.20) is valid for $j=j'$ and $k \neq k'$ for all l and l'. It should be noted that the assumption $|\mathbf{R}_k - \mathbf{R}_{k'}| = O(1)$ precludes letting $\mathbf{R}_k \to \mathbf{R}_{k'}$ to obtain the $k=k'$ result.

Finally, we consider the evaluation of $\sum_{m=-1}^{1}\langle\psi^{(j,k)}_{l;m,n}\,|\,\psi^{(j',k')}_{l';m,n}\rangle$ for the case $j \neq j'$. There is no need to distinguish between $k=k'$ and $k \neq k'$, because we can expand $\mathbf{r}_j$ and $\mathbf{r}'_j$ about $\mathbf{R}_k$, and $\mathbf{r}_{j'}$ and $\mathbf{r}'_{j'}$ about $\mathbf{R}_{k'}$. The partial wave expansion needed for this case is

$$\langle \mathbf{r}_a, \mathbf{r}_b | \left(\tfrac{1}{2} p_a^2 + \tfrac{1}{2} p_b^2 - E_n + W\right)^{-1} | \mathbf{r}'_a, \mathbf{r}'_b \rangle$$
$$= \frac{1}{4\pi^3 v^2 R^2} K_2(v^{-1} R)$$
$$= v^{-4} \sum_{l_a=0}^{\infty} \sum_{m_a=-l_a}^{l_a} \sum_{l_b=0}^{\infty} \sum_{m_b=-l_b}^{l_b} Y_{l_a, m_a}(\theta_a, \phi_a)\, Y_{l_b, m_b}(\theta_b, \phi_b)\, \overline{Y_{l_a, m_a}(\theta'_a, \phi'_a)}$$
$$\times \overline{Y_{l_b, m_b}(\theta'_b, \phi'_b)}\, g_{l_a, l_b}(v^{-1} r_a, v^{-1} r_b; v^{-1} r'_a, v^{-1} r'_b), \tag{C.43}$$

where $R = \sqrt{(\mathbf{r}_a - \mathbf{r}'_a)^2 + (\mathbf{r}_b - \mathbf{r}'_b)^2}$ and

$$g_{l_a, l_b}(z_a, z_b; z'_a, z'_b) = \frac{1}{2} \int_{-\infty}^{\infty} dt_a \int_{-\infty}^{\infty} dt_b\, \frac{t_a^2 t_b^2}{1 + t_a^2 + t_b^2}\, \frac{J_{l_a+1/2}(t_a z_a)}{(t_a z_a)^{1/2}}$$
$$\times \frac{J_{l_a+1/2}(t_a z'_a)}{(t_a z'_a)^{1/2}}\, \frac{J_{l_b+1/2}(t_b z_b)}{(t_b z_b)^{1/2}}\, \frac{J_{l_b+1/2}(t_b z'_b)}{(t_b z'_b)^{1/2}}. \tag{C.44}$$

Using the expansion (C.43) with $\mathbf{r}_a$, $\mathbf{r}_b$, $\mathbf{r}'_a$, and $\mathbf{r}'_b$ replaced by $\mathbf{r}_j - \mathbf{R}_k$, $\mathbf{r}_{j'} - \mathbf{R}_{k'}$, $\mathbf{r}'_j - \mathbf{R}_k$, and $\mathbf{r}'_{j'} - \mathbf{R}_{k'}$, respectively, in (3.22) and performing the angular integrations yields

$$\sum_{m=-1}^{1} \langle \psi^{(j,k)}_{l;m,n} | \psi^{(j',k')}_{l';m,n} \rangle$$
$$= \sum_{l_{j'}=0}^{\infty} \sum_{l'_j=0}^{\infty} \sum_{m_j=-l}^{l} \sum_{m_{j'}=-l_{j'}}^{l_{j'}} \sum_{m'_j=-l'_j}^{l'_j} \sum_{m'_{j'}=-l'}^{l'} A(l, l_{j'}, l'_j, l'; m_j, m_{j'}, m'_j, m'_{j'})$$
$$\times M^{(j,j',k,k')}_{l_{j'}, l'_j; m_j, m_{j'}, m'_j, m'_{j'}; (l_{j'}-l'+1)/2, (l'_j-l+1)/2} + O(v^4), \qquad j \neq j', \tag{C.45}$$

where A and M are defined by

$$A(l_j, l_{j'}, l'_j, l'_{j'}; m_j, m_{j'}, m'_j, m'_{j'})$$
$$= \delta_{m_j+m_{j'}, m'_j+m'_{j'}} (-1)^{m_j+m'_{j'}} [(2l_j+1)(2l_{j'}+1)(2l'_j+1)(2l'_{j'}+1)]^{1/2}$$
$$\times \begin{pmatrix} l_j & 1 & l'_j \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_{j'} & 1 & l'_{j'} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_j & 1 & l'_j \\ m_j & m'_j - m_j & -m'_j \end{pmatrix} \begin{pmatrix} l_{j'} & 1 & l'_{j'} \\ m_{j'} & m'_{j'} - m_{j'} & -m'_{j'} \end{pmatrix} \tag{C.46}$$

$$M^{(j,j',k,k')}_{l_{j'}, l'_j; m_j, m_{j'}, m'_j, m'_{j'}; p_{j'}, p'_j}$$
$$= v^{-4} \int_0^{\infty} dr_a \int_0^{\infty} dr_b \int_0^{\infty} dr'_a \int_0^{\infty} dr'_b\, r_a^{l'_j - 2p'_j + 1} r_b^{l_{j'}+2}$$
$$\times (r'_a)^{l'_j+2} (r'_b)^{l_{j'} - 2p_{j'} + 1} g_{l'_j, l_{j'}}(v^{-1} r_a, v^{-1} r_b; v^{-1} r'_a, v^{-1} r'_b)$$
$$\times \rho^{(j,j',k,k')}_{l'_j - 2p'_j + 1, m_j; l_{j'}, m_{j'}; l'_j, m'_j; l_{j'} - 2p_{j'} + 1, m'_{j'}; n}(r_a, r_b; r'_a, r'_b), \tag{C.47}$$

with

$$\rho^{(j,j',k,k')}_{l_j,m_j;l_{j'},m_{j'};l'_j,m'_j;l'_{j'},m'_{j'};n}(r_a,r_b;r'_a,r'_b)$$
$$=r_a^{-l_j}r_b^{-l_{j'}}(r'_a)^{-l'_j}(r'_b)^{-l'_{j'}}$$
$$\times\int d^3\mathbf{r}_1\,d^3\mathbf{r}_2,...,d^3\mathbf{r}_{j-1}\,d^3\mathbf{r}_{j+1},...,d^3\mathbf{r}_{j'-1}\,d^3\mathbf{r}_{j'+1},...,d^3\mathbf{r}_N$$
$$\times\overline{f^{(j,j',k,k')}_{l_j,m_j;l_{j'},m_{j'};n}(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_{j-1},\mathbf{r}_{j+1},...,\mathbf{r}_{j'-1},\mathbf{r}_{j'+1},...,\mathbf{r}_N;r_a,r_b)}$$
$$\times f^{(j,j',k,k')}_{l'_j,m'_j;l'_{j'},m'_{j'};n}(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_{j-1},\mathbf{r}_{j+1},...,\mathbf{r}_{j'-1},\mathbf{r}_{j'+1},...,\mathbf{r}_N;r'_a,r'_b),\qquad\text{(C.48)}$$

where

$$f^{(j,j',k,k')}_{l_j,m_j;l_{j'},m_{j'};n}(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_{j-1},\mathbf{r}_{j+1},...,\mathbf{r}_{j'-1},\mathbf{r}_{j'+1},...,\mathbf{r}_N;r_a,r_b)$$
$$=\int d\Omega_{k,j}\,d\Omega_{k',j'}\,\overline{Y_{l_j,m_j}(\theta_{j,k},\phi_{j,k})\,Y_{l_{j'},m_{j'}}(\theta_{j',k'},\phi_{j',k'})}$$
$$\times\langle\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_{j-1},\mathbf{r}_j,\mathbf{r}_{j+1},...,\mathbf{r}_{j'-1},\mathbf{r}_{j'},\mathbf{r}_{j'+1},...,\mathbf{r}_N\,|\psi_n\rangle\qquad\text{(C.49)}$$

with $r_a=|\mathbf{r}_j-\mathbf{R}_k|$ and $r_b=|\mathbf{r}_{j'}-\mathbf{R}_{k'}|$. The sums in (C.45) are actually finite, since A is non-zero only for $l_{j'}=l'\pm 1$ and $l'_j=l\pm 1$.

The integration over r_a, r_b, r'_a, and r'_b in (C.47) is similar to the previous radial integrations and is handled in the same way. We begin with the definition

$$G_{l_a,l_b}(z_a,z_b;z'_a,z'_b)$$
$$=\frac{1}{2}(z'_a)^{l_a+2}\,z_b^{l_b+2}\int_{-\infty}^{\infty}dt_a\int_{-\infty}^{\infty}dt_b\,\frac{t_at_b}{1+t_a^2+t_b^2}$$
$$\times\frac{J_{l_a+1/2}(t_az_a)}{(t_az_a)^{1/2}}\,\frac{J_{l_a+3/2}(t_az'_a)}{(t_az'_a)^{1/2}}\,\frac{J_{l_b+3/2}(t_bz_b)}{(t_bz_b)^{1/2}}\,\frac{J_{l_b+1/2}(t_bz'_b)}{(t_bz'_b)^{1/2}}.\qquad\text{(C.50)}$$

It can be shown that $G_{l_a,l_b}(z_a,z_b;z'_a,z'_b)$, $\partial G_{l_a,l_b}(z_a,z_b;z'_a,z'_b)/\partial z'_a$, and $\partial G_{l_a,l_b}(z_a,z_b;z'_a,z'_b)/\partial z_b$ are continuous and zero when either $z'_a=0$ or $z_b=0$. It can also be shown that

$$\frac{\partial^2}{\partial z_b\,\partial z'_a}G_{l_a,l_b}(z_a,z_b;z'_a,z'_b)=(z'_a)^{l_a+2}\,z_b^{l_b+2}g_{l_a,l_b}(z_a,z_b;z'_a,z'_b),\qquad\text{(C.51)}$$

$$G_{l_a,l_b}(z_a,z_b;z'_a,z'_b)=\begin{cases}G_{l_a,l_a+1,l_b+1,l_b}(z_a,z'_a;z_b,z'_b)+\hat G^{(1)}_{l_a,l_b}(z_a,z_b;z'_a,z'_b),\\ \qquad z_a<z'_a,\ z_b<z'_b,\\ G_{l_a+1,l_a,l_b+1,l_b}(z'_a,z_a;z_b,z'_b),\\ \qquad z_a>z'_a,\ z_b<z'_b,\\ G_{l_a,l_a+1,l_b,l_b+1}(z_a,z'_a;z'_b,z_b)+\hat G^{(2)}_{l_a,l_b}(z_a,z_b;z'_a,z'_b),\\ \qquad z_a<z'_a,\ z_b>z'_b,\\ G_{l_a+1,l_a,l_b,l_b+1}(z'_a,z_a;z'_b,z_b)+\hat G^{(3)}_{l_a,l_b}(z_a,z_b;z'_a,z'_b),\\ \qquad z_a>z'_a,\ z_b>z'_b,\end{cases}\qquad\text{(C.52)}$$

where

$$
\begin{aligned}
G_{l_{a,<},l_{a,>},l_{b,<},l_{b,>}}&(z_{a,<}, z_{a,>}; z_{b,<}, z_{b,>}) \\
&= \frac{2}{\pi} \operatorname{Sgn}(l_{a,<} - l_{a,>}) \operatorname{Sgn}(l_{b,<} - l_{b,>}) (z'_a)^{l_a+2} z_b^{l_b+1} \\
&\quad \times \int_{-\infty}^{\infty} d\xi \, s_a s_b \frac{I_{l_{a,<}+1/2}(s_a z_{a,<})}{(s_a z_{a,<})^{1/2}} \frac{K_{l_{a,>}+1/2}(s_a z_{a,>})}{(s_a z_{a,>})^{1/2}} \\
&\quad \times \frac{I_{l_{b,<}+1/2}(s_b z_{b,<})}{(s_b z_{b,<})^{1/2}} \frac{K_{l_{b,>}+1/2}(s_b z_{b,>})}{(s_b z_{b,>})^{1/2}} &\text{(C.53)} \\
&= \sqrt{8/\pi z_{a,b}} \operatorname{Sgn}(l_{a,<} - l_{a,>}) \operatorname{Sgn}(l_{b,<} - l_{b,>}) (z'_a)^{l_a+2} z_b^{l_b+2} s_{a,0} s_{b,0} \\
&\quad \times \frac{I_{l_{a,<}+1/2}(s_{a,0} z_{a,<})}{(s_{a,0} z_{a,<})^{1/2}} \frac{K_{l_{a,>}+1/2}(s_{a,0} z_{a,>})}{(s_{a,0} z_{a,>})^{1/2}} \frac{I_{l_{b,<}+1/2}(s_{b,0} z_{b,<})}{(s_{b,0} z_{b,<})^{1/2}} \\
&\quad \times \frac{K_{l_{b,>}+1/2}(s_{b,0} z_{b,>})}{(s_{b,0} z_{b,>})^{1/2}} [1 + O(z_{a,b}^{-1})], \qquad s_{a,0} \geqslant s_0 > 0 \qquad \text{for} \\
&\qquad l_{a,>} = l_{a,<} + 1, \; s_{b,0} \geqslant s_0 > 0 \qquad \text{for} \quad l_{b,>} = l_{b,<} + 1, &\text{(C.54)}
\end{aligned}
$$

$$\hat{G}^{(1)}_{l_a,l_b}(z_a, z_b; z'_a, z'_b) = 2 z_a^{l_a} z_b^{l_b+2} \frac{I_{l_b+3/2}(z_b)}{z_b^{1/2}} \frac{K_{l_b+1/2}(z'_b)}{(z'_b)^{1/2}}, \tag{C.55}$$

$$
\begin{aligned}
\hat{G}^{(2)}_{l_a,l_b}(z_a, z_b; z'_a, z'_b) = 2 \bigg[& z_a^{l_a} (z'_b)^{l_b} - (z'_a)^{l_a+2} \\
& \times \frac{I_{l_a+1/2}(z_a)}{z_a^{1/2}} \frac{K_{l_a+3/2}(z'_a)}{(z'_a)^{1/2}} (z'_b)^{l_b} \\
& - z_a^{l_a} z_b^{l_b+2} \frac{K_{l_b+3/2}(z_b)}{z_b^{1/2}} \frac{I_{l_b+1/2}(z'_b)}{(z'_b)^{1/2}} \bigg],
\end{aligned}
\tag{C.56}
$$

$$\hat{G}^{(3)}_{l_a,l_b}(z_a, z_b; z'_a, z'_b) = 2 \frac{K_{l_a+1/2}(z_a)}{z_a^{1/2}} (z'_a)^{l_a+2} \frac{I_{l_a+3/2}(z'_a)}{(z'_a)^{1/2}} (z'_b)^{l_b}, \tag{C.57}$$

$$z_{a,b} = [(z_{a,>} - z_{a,<})^2 + (z_{b,>} - z_{b,<})^2]^{1/2}, \tag{C.58}$$

$$s_a = z_{a,b}^{-1}[(z_{a,>} - z_{a,<}) \cosh(\xi) + i(z_{b,>} - z_{b,<}) \sinh(\xi)], \tag{C.59}$$

$$s_b = z_{a,b}^{-1}[(z_{b,>} - z_{b,<}) \cosh(\xi) - i(z_{a,>} - z_{a,<}) \sinh(\xi)], \tag{C.60}$$

$$s_{a,0} = z_{a,b}^{-1}(z_{a,>} - z_{a,<}), \tag{C.61}$$

$$s_{b,0} = z_{a,b}^{-1}(z_{b,>} - z_{b,<}). \tag{C.62}$$

The explicit expression (C.52) is obtained from (C.50) via the standard contour integration method for the evaluation of Fourier transforms. The decomposition $J_\nu(tz) = \frac{1}{2}[H_\nu^{(1)}(tz) + H_\nu^{(2)}(tz)]$ is used for $J_{l_a+3/2}(t_a z'_a)$ when $z_a < z'_a$, and for $J_{l_a+1/2}(t_a z_a)$ when $z_a > z'_a$. The integration path for the part of the integrand containing $H_\nu^{(1)}$ is deformed into the upper half plane; the integration path for the part containing $H_\nu^{(2)}$ is deformed into the lower half plane. When $z_a < z'_a$ and $\nu = l_a + 3/2$, this decomposition leaves a pole at $t_a = 0$ in the individual integrands which was not present in (C.50). This pole is handled by deforming the contour to run below the point $t_a = 0$ before taking the integral apart; the piece containing $H_\nu^{(1)}$ will then contain a contribution from the pole, which must be evaluated in order to deform the integration path for this piece into the upper half plane. The integration over t_b is handled similarly. The $\hat{G}$ terms in (C.52) come from the poles at $t_a = 0$ and $t_b = 0$. The remaining contributions, which come from the contours in the upper and lower half planes, can be brought to the form (C.53) by computing the residues at $t_a = \pm i(1 + t_b^2)^{1/2}$ and making the changes of variable $t_b = \pm i s_b$ in the integrals over t_b which remain. The asymptotic formula (C.54) is obtained from (C.53) via the saddle point method (the saddle point is at $\xi = 0$); the restrictions $s_{a,0} \geqslant s_0 > 0$ for $l_{a,>} = l_{a,<} + 1$ and $s_{b,0} \geqslant s_0 > 0$ for $l_{b,>} = l_{b,<} + 1$ are imposed because the saddle point method breaks down due to a nearby pole when they are violated. The cure for this breakdown is described in Wong [27, pp. 356–360] and in Bleistein and Handelsman [32, pp. 380–387]. We omit the details of this cure because (C.54) has been written only to obtain the qualitative behavior of $G_{l_{a,<}, l_{a,>}, l_{b,<}, l_{b,>}}$ for $z_{a,b}$ large, which is dominated by an $\exp(-z_{a,b})$ fall-off. This exponential fall-off, which comes from the exponential factors in the explicit expressions for the modified Bessel functions of half-integral order, persists in the more complicated asymptotic formula which cures the breakdown.

The result of integrating (C.47) by parts with the aid of the preceding formulas is

$$\begin{aligned}
M^{(j,j',k,k')}_{l_{j'}, l'_j; m_j, m_{j'}, m'_j, m'_{j'}; p_{j'}, p'_j}
&= \nu^{l'_j + l_{j'} + 2} \int_0^\infty dr_a \int_0^\infty dr_b \int_0^\infty dr'_a \int_0^\infty dr'_b\, r_a^{l'_j - 2p'_j + 1} \\
&\quad \times (r'_b)^{l_{j'} - 2p_{j'} + 1}\, G_{l'_j, l_{j'}}(\nu^{-1} r_a, \nu^{-1} r_b; \nu^{-1} r'_a, \nu^{-1} r'_b) \\
&\quad \times \partial^2 \rho^{(j,j',k,k')}_{l'_j - 2p'_j + 1, m_j; l_{j'}, m_{j'}; l'_j, m'_j; l_{j'} - 2p_{j'} + 1, m'_{j'}; n}(r_a, r_b; r'_a, r'_b)/\partial r_b\, \partial r'_a.
\end{aligned} \tag{C.63}$$

It will now be shown that the only contribution of order ν^2 to (C.63) comes from the $z_a^{l_a}(z'_b)^{l_b}$ term in $\hat{G}^{(2)}_{l_a, l_b}$. The modified Bessel function terms in $\hat{G}^{(1)}_{l_a, l_b}$, $\hat{G}^{(2)}_{l_a, l_b}$, and $\hat{G}^{(3)}_{l_a, l_b}$ peak sharply at either $r_a = r'_a$ or $r_b = r'_b$; the contribution of these terms can be estimated by evaluating $\partial^2 \rho / \partial r_b\, \partial r'_a$ at the peak and integrating over the peak with the aid of the formula

$$\begin{aligned}
&\int_0^z d\zeta\, \zeta^{l+2} \frac{I_{l+3/2}(\zeta)}{\zeta^{1/2}} \frac{K_{l+1/2}(z)}{z^{1/2}} - \int_z^\infty d\zeta\, \zeta^{l+2} \frac{K_{l+3/2}(\zeta)}{\zeta^{1/2}} \frac{I_{l+1/2}(z)}{z^{1/2}} \\
&\quad = -(l+1)\, z^{-l-1} D_{l,0}(z).
\end{aligned} \tag{C.64}$$

The function $D_{l,0}$ in (C.64) is defined (and described) in (3.40)—(3.43). Because the sharply peaked terms from $\hat{G}^{(1)}_{l_a, l_b}$ and $\hat{G}^{(3)}_{l_a, l_b}$ enter with a sign opposite to the sign of the sharply peaked terms in $\hat{G}^{(2)}_{l_a, l_b}$, there is a cancellation, with the result that the contribution of these sharply peaked terms is of order v^4 instead of the v^3 which would be expected from estimating them by multiplying their value at the peak, which is of order v^2, by the width of the peak, which is of order v. The $\exp(-z_{a,b})$ exponential fall-off of $G_{l_{a,<}, l_{a,>}, l_{b,<}, l_{b,>}}$ which was deduced from (C.54) shows that this term peaks sharply at $(r_a - r'_a)^2 + (r_b - r'_b)^2 = 0$; estimating this term as the value at the peak times the area of the peak shows that it makes a contribution of order v^4 or higher. It follows that

$$
\begin{aligned}
M^{(j,j',k,k')}_{l_{j'}, l'_j; m_j, m_{j'}, m'_j, m'_{j'}; p_{j'}, p'_j}
&= 2v^2 \int_0^\infty dr_a \int_0^\infty dr'_b \, r_a^{2l'_j - 2p'_j + 1} (r'_b)^{2l_{j'} - 2p_{j'} + 1} \\
&\quad \times \rho^{(j,j',k,k')}_{l'_j - 2p'_j + 1, m_j; l_{j'}, m_{j'}; l'_j, m'_j; l_{j'} - 2p_{j'} + 1, m'_{j'}; n}(r_a, r'_b; r_a, r'_b) + O(v^4). \qquad \text{(C.65)}
\end{aligned}
$$

All but the $O(v^4)$ error estimate in (C.65) could be obtained by making the approximation

$$
g_{l_a, l_b}(z_a, z_b; z'_a, z'_b) \approx 2 \, \frac{\delta(z_a - z'_a)}{z_a z'_a} \, \frac{\delta(z_b - z'_b)}{z_b z'_b} \qquad \text{(C.66)}
$$

in (C.47), i.e., by approximating $(T - E_n + W)^{-1}$ by $(-E_n + W)^{-1}$. It follows that (3.20) is valid for $j \neq j'$ for all l and l'.

The derivation of (3.59) and (3.60) is similar. Only the $j = j'$, $k = k'$ terms contribute. Carrying out the angular integrations over $\theta_{j,k}$, $\phi_{j,k}$, $\theta'_{j,k}$, and $\phi'_{j,k}$, and the sum from -1 to 1 over m, yields the form (3.27), but with different radial integrals $M^{(j,k)}_{l,m;n;p}$. Only the $l = 1$, $p = 1$ term, which contains $\rho^{(j,k,k)}_{0,0;0,0;n}(r, r')$ and an analogue of $\rho^{(j,k,k)}_{0,0;0,0;n}(r, r')$ in which $(V + Z_k |\mathbf{r}_j - \mathbf{R}_k|^{-1})$ appears, is needed. The approximation $\rho^{(j,k,k)}_{0,0;0,0;n}(r, r') \approx \rho^{(j,k,k)}_{0,0;0,0;n}(0, 0)[1 - Z_k(r + r')]$ is used for (3.59); the cruder approximation $\rho^{(j,k,k)}_{0,0;0,0;n}(r, r') \approx \rho^{(j,k,k)}_{0,0;0,0;n}(0, 0)$ and its analogue are used for (3.60) and for the $(V + Z_k |\mathbf{r}_j - \mathbf{R}_k|^{-1})$ term in (3.59). The radial integrations are then performed with the aid of the integration formulas

$$
\int_0^\infty dz_1 \int_0^\infty dz_2 \int_0^\infty dz_3 \, g_1(z_1, z_2) \, z_2 g_1(z_2, z_3) = 4\ln(2) - 2, \qquad \text{(C.67)}
$$

$$
\int_0^\infty dz_1 \int_0^\infty dz_2 \int_0^\infty dz_3 \, g_1(z_1, z_2) \, z_2^2 g_1(z_2, z_3) = 2, \qquad \text{(C.68)}
$$

$$
\int_0^\infty dz_1 \int_0^\infty dz_2 \int_0^\infty dz_3 \, z_1 g_1(z_1, z_2) \, z_2 g_1(z_2, z_3) = 2, \qquad \text{(C.69)}
$$

$$
\int_0^\infty dz_1 \int_0^\infty dz_2 \int_0^\infty dz_3 \int_0^\infty dz_4 \, g_1(z_1, z_2) z_2 g_1(z_2, z_3) z_3 g_1(z_3, z_4) = 2 - \frac{\pi^2}{6}. \qquad \text{(C.70)}
$$

The changes of variables described following (3.55) in the text are helpful in the derivation of some of these integration formulas.

APPENDIX D: MATRIX ELEMENT INTEGRALS

We begin by listing, in a very explicit notation, three very general matrix element integral formulas:

$$
\begin{aligned}
&\langle \sigma, z_0, \alpha', \alpha, a |\, x^\lambda \,| \sigma', z_0', \alpha', \alpha, a \rangle \\
&\quad = \int_0^\infty h(\sigma, z_0, \alpha', \alpha, a; x)\, x^\lambda h(\sigma', z_0', \alpha', \alpha, a; x)\, dx \\
&\quad = \frac{a^{2\alpha - 2\alpha' - \lambda + 1}(z_0 - 1)^\sigma (z_0' - 1)^{\sigma'} \Gamma(\lambda + 2\alpha' + 1)}{\Gamma^2(\alpha + 1)} \\
&\qquad \times F_2\left(\lambda + 2\alpha' + 1, -\sigma, -\sigma', \alpha + 1, \alpha + 1; \frac{1}{1 - z_0}, \frac{1}{1 - z_0'}\right),
\end{aligned} \tag{D.1}
$$

$$
\begin{aligned}
&\langle \sigma, z_0, \alpha', \alpha, a |\, x^\lambda \frac{\partial}{\partial x} \,| \sigma', z_0', \alpha', \alpha, a \rangle \\
&\quad = \int_0^\infty h(\sigma, z_0, \alpha', \alpha, a; x)\, x^\lambda \left[\frac{\partial}{\partial x} h(\sigma', z_0', \alpha', \alpha, a; x)\right] dx \\
&\quad = \frac{a^{2\alpha - 2\alpha' - \lambda + 2}(z_0 - 1)^\sigma (z_0' - 1)^{\sigma'} \Gamma(\lambda + 2\alpha')}{\Gamma^2(\alpha + 1)} \left\{\left[\left(\alpha' + y \frac{\partial}{\partial y}\right)\right.\right. \\
&\qquad \times \left.F_2\left(\lambda + 2\alpha', -\sigma, -\sigma', \alpha + 1, \alpha + 1; \frac{1}{1 - z_0}, y\right)\right]_{y = 1/(1 - z_0')} - \left(\frac{1}{2}\lambda + \alpha'\right) \\
&\qquad \times \left. F_2\left(\lambda + 2\alpha' + 1, -\sigma, -\sigma', \alpha + 1, \alpha + 1; \frac{1}{1 - z_0}, \frac{1}{1 - z_0'}\right)\right\},
\end{aligned} \tag{D.2}
$$

$$
\begin{aligned}
&\langle \sigma, z_0, \alpha', \alpha, a |\, \frac{\partial}{\partial x} x^\lambda \frac{\partial}{\partial x} \,| \sigma', z_0', \alpha', \alpha, a \rangle \\
&\quad = -\int_0^\infty \left[\frac{\partial}{\partial x} h(\sigma, z_0, \alpha', \alpha, a; x)\right] x^\lambda \left[\frac{\partial}{\partial x} h(\sigma', z_0', \alpha', \alpha, a; x)\right] dx \\
&\quad = \frac{a^{2\alpha - 2\alpha' - \lambda + 3}(z_0 - 1)^\sigma (z_0' - 1)^{\sigma'} \Gamma(\lambda + 2\alpha' - 1)}{\Gamma^2(\alpha + 1)} \left\{\alpha'(\lambda + \alpha' - 1)\right. \\
&\qquad \times F_2\left(\lambda + 2\alpha' - 1, -\sigma, -\sigma', \alpha + 1, \alpha + 1; \frac{1}{1 - z_0}, \frac{1}{1 - z_0'}\right) \\
&\qquad + (\lambda + 2\alpha')(\lambda + 2\alpha' - 1)
\end{aligned}
$$

$$\times\left[\frac{1}{4}F_2\left(\lambda+2\alpha'+1,\ -\sigma,\ -\sigma',\ \alpha+1,\ \alpha+1;\ \frac{1}{1-z_0},\ \frac{1}{1-z_0'}\right)\right.$$
$$-\frac{1}{2}F_2\left(\lambda+2\alpha',\ -\sigma,\ -\sigma',\ \alpha+1,\ \alpha+1;\ \frac{1}{1-z_0},\ \frac{1}{1-z_0'}\right)$$
$$\left.\left.-\frac{\sigma\sigma' F_2(\lambda+2\alpha'+1, -\sigma+1, -\sigma'+1, \alpha+1, \alpha+1; 1/(1-z_0), 1/(1-z_0'))}{(1-z_0)(1-z_0')(\alpha+1)^2}\right]\right\}. \tag{D.3}$$

Here F_2 is one of the hypergeometric functions of two variables introduced by Appell, which can be defined either by the integral representation [14, p. 230, Eq. (2)]

$$F_2(\alpha, \beta, \beta', \gamma, \gamma'; x, y) = \frac{\Gamma(\gamma)\,\Gamma(\gamma')}{\Gamma(\beta)\,\Gamma(\beta')\,\Gamma(\gamma-\beta)\,\Gamma(\gamma'-\beta')} \times \int_0^1 du \int_0^1 dv\, u^{\beta-1} v^{\beta'-1} (1-u)^{\gamma-\beta-1} \times (1-v)^{\gamma'-\beta'-1}\,(1-ux-vy)^{-\alpha}, \tag{D.4}$$

or by the series expansion [14, p. 224, Eq. (7)]

$$F_2(\alpha, \beta, \beta', \gamma, \gamma'; x, y) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{(\alpha)_{m+n}\,(\beta)_m\,(\beta')_n}{(\gamma)_m\,(\gamma')_n\, m!\, n!} x^m y^n, \tag{D.5}$$

which converges for $|x| + |y| < 1$.

The formulas (D.1)–(D.3) are obtained by inserting the integral representation

$${}_1F_1(a; c; z) = \frac{\Gamma(c)}{\Gamma(a)\,\Gamma(c-a)} \int_0^1 \exp(zt)\, t^{a-1} (1-t)^{c-a-1}\, dt, \tag{D.6}$$

for the confluent hypergeometric function ${}_1F_1[-\sigma; \alpha+1; ax/(1-z_0)]$ which appears in the definition (5.25) of the basis functions $h(\sigma, z_0, \alpha', \alpha, a; x)$. The integral representation (D.6) is subject to the condition $\mathrm{Re}(c) > \mathrm{Re}(a) > 0$, but this restriction can normally be removed by analytic continuation after formulas for the matrix element integrals have been obtained.

Numerical evaluation of the Appell function F_2 which appears in (D.1)–(D.3) is inconvenient except in special cases where it can be expressed in terms of ordinary hypergeometric functions ${}_2F_1$ [14, Chap. II; 15, Chap. II], which are easy to calculate, or in terms of elementary functions. The key is the formula [14, p. 238, Eq. (3)]

$$F_2(\alpha, \beta, \beta', \alpha, \alpha; x, y) = (1-x)^{-\beta}(1-y)^{-\beta'}\, {}_2F_1\left[\beta, \beta'; \alpha; \frac{xy}{(1-x)(1-y)}\right], \tag{D.7}$$

which shows that we want to obtain Appell functions F_2 in which the first, fourth, and fifth parameters are equal. This can be achieved by exploiting the freedom to choose α, and by using the following differentiation and "step-down" formulas to obtain Appell functions F_2 for which the reduction (D.7) can be used:

$$
\begin{aligned}
y \frac{\partial}{\partial y} & F_2(\alpha, \beta, \beta', \alpha, \alpha; x, y) \\
&= \beta' y F_2(\alpha, \beta, \beta'+1, \alpha, \alpha; x, y) \\
&\quad + \alpha^{-1} \beta\beta' xy F_2(\alpha+1, \beta+1, \beta'+1, \alpha+1, \alpha+1; x, y), \qquad \text{(D.8)} \\
F_2(\alpha & +2, \beta, \beta', \alpha+1, \alpha+1; x, y) \\
&= (\alpha+1)^{-1} \beta' y F_2(\alpha+1, \beta, \beta'+1, \alpha+1, \alpha+1; x, y) \\
&\quad + [F_2(\alpha+1, \beta, \beta', \alpha+1, \alpha+1; x, y) \\
&\quad + 2(\alpha+1)^{-2} \beta\beta' xy F_2(\alpha+2, \beta+1, \beta'+1, \alpha+2, \alpha+2; x, y)] \\
&\quad + (\alpha+1)^{-1} \beta x F_2(\alpha+1, \beta+1, \beta', \alpha+1, \alpha+1; x, y). \qquad \text{(D.9)}
\end{aligned}
$$

The "step-down" formula (D.9) can be used repeatedly to reduce the first parameter in F_2 by more than one unit. "Step-down" formulas for the derivative can be obtained by differentiating (D.9) and using (D.8) in the result. The hypergeometric function ${}_2F_1(a, b; c; z)$ can be efficiently evaluated for all real z by using the transformation theory for the hypergeometric function to reduce the problem to the problem of evaluating ${}_2F_1(a', b'; c'; w)$ for $|w| \leqslant \frac{1}{2}$, which can be done via rapidly convergent series in powers of w. The transformations are: $w = 1/(1-z)$ for $z < -1$, $w = z/(z-1)$ for $-1 \leqslant z < -\frac{1}{2}$, $w = 1 - z$ for $\frac{1}{2} < z \leqslant 1$, $w = 1 - z^{-1}$ for $1 < z \leqslant 2$, and $w = 1/z$ for $z > 2$.

Matrix element formulas in which either or both of the functions h are replaced by a basis function $\xi_k^{(\alpha', \alpha)}(a; x)$ can be obtained by recognizing that the functions $\xi_k^{(\alpha', \alpha)}(a; x)$ are special cases of the functions h:

$$
h(k, 0, \alpha', \alpha, a; x) = \frac{(-1)^k \, k! \, a^{\alpha+1}}{\Gamma(k+\alpha+1)} \, \xi_k^{(\alpha', \alpha)}(a; x). \qquad \text{(D.10)}
$$

For example, matrix elements in which $h(\sigma, z_0, \alpha', \alpha, a; x)$ is replaced by $\xi_k^{(\alpha', \alpha)}(a; x)$ are obtained from (D.1)–(D.3) by first continuing analytically in σ to $\sigma = k$ to obtain an Appell function F_2 in which the sum over m is finite because the Pochhammer symbol $(-k)_m$ is 0 for $m > k$, and then letting $z_0 \to 0$.

The use of these matrix element formulas can be understood by considering the hydrogenic states of angular momentum l. For such states, the choice $\alpha' = l + 1$ gets the small r behavior right (a factor of r^l comes from the wave function, and a factor of r from the $r^2 \, dr$ part of the volume element). The Gram matrix elements are obtained from (D.1) with $\lambda = 0$, in which case the first parameter of the Appell function F_2 is $\lambda + 2\alpha' + 1 = 2l + 3$, which imposes the restriction $\alpha \leqslant 2l + 2$ if a reduction of the F_2 to a ${}_2F_1$ via (D.7) and (D.9) is to be achieved. The matrix elements of the Coulomb potential are obtained from (D.1) with $\lambda = -1$, with the condition $\alpha \leqslant 2l+1$ for reduction of the F_2 to a ${}_2F_1$. The kinetic energy matrix elements are obtained from (D.1) with $\lambda = -2$ and (D.3) with $\lambda = 0$, which would appear to give the condition $\alpha \leqslant 2l$. However, the contribution from (D.1) cancels against the first term on the right hand-side of (D.3) when $\alpha' = l+1$, leading again to the condition $\alpha \leqslant 2l+1$ for reduction of the F_2 to a ${}_2F_1$. The condition $\alpha \leqslant 2l+1$ can be understood by recognizing that it is also the condition for the Gram matrix, the matrix of the Coulomb potential, and the kinetic energy matrix to be band matrices when the basis $\xi_k^{(\alpha', \alpha)}(a; x)$ is used. When these matrices are band matrices, the matrix elements with respect to the functions h can be calculated by expanding the functions h in the $\xi_k^{(\alpha', \alpha)}(a; x)$ basis. Matrix elements between an h function and a basis function $\xi_k^{(\alpha', \alpha)}(a; x)$ then consist of a finite number of terms, and matrix elements between two h functions are singly infinite sums which can be evaluated by recognizing that they are the linear combinations of hypergeometric functions which are obtained by using (D.1)–(D.3) and (D.7)–(D.9).

The use of these functions h for helium is similar. One uses the functions

$$\begin{aligned}\Xi_{k_1, k_2, k_{12}}&(a_1, a_2, a_{12}; q_1, q_2, q_{12}) \\ &= \xi_{k_1}^{(0,0)}(a_1; q_1)\, \xi_{k_2}^{(0,0)}(a_2; q_2)\, \xi_{k_{12}}^{(0,0)}(a_{12}; q_{12}),\end{aligned} \tag{D.11}$$

as the fundamental basis, where q_1, q_2, and q_{12} are the perimetric coordinates

$$q_1 = -r_1 + r_2 + r_{12}, \tag{D.12}$$

$$q_2 = r_1 - r_2 + r_{12}, \tag{D.13}$$

$$q_{12} = r_1 + r_2 - r_{12}. \tag{D.14}$$

Auxiliary basis functions

$$\begin{aligned}H(\sigma, z_0, \alpha', \alpha, a; r_1, r_2) &= h(\sigma, z_0, \alpha', \alpha, a; r_1)\, \psi(0, r_2, r_2) \\ &\quad \pm \psi(r_1, 0, r_1)\, h(\sigma, z_0, \alpha', \alpha, a; r_2),\end{aligned} \tag{D.15}$$

where $\psi(r_1, r_2, r_{12})$ is a helium S-state wave function, can be used to handle the second short length scale which arises at large W without encountering anything worse than a ${}_2F_1$ in the matrix element evaluations if $\psi(r_1, r_2, r_{12})$ is approximated by a finite linear combination of the fundamental basis functions $\Xi_{k_1, k_2, k_{12}}(a_1, a_2, a_{12}; q_1, q_2, q_{12})$. This is still true if auxiliary basis functions

$$\begin{aligned}H'(\sigma', z_0', \alpha''', \alpha'', a; r_1, r_2) &= h(\sigma', z_0', \alpha''', \alpha'', a; r_1)\, \xi_k^{(0,0)}(a'; r_2) \\ &\quad \pm \xi_k^{(0,0)}(a'; r_1)\, h(\sigma, z_0, \alpha''', \alpha'', a; r_2)\end{aligned} \tag{D.16}$$

are included in the linear combination which approximates $\psi(r_1, r_2, r_{12})$ to handle the long length scale associated with loosely bound outer electrons in excited states.

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