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$1/n$ expansions for two-electron Coulomb matrix elements

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Abstract. The study of $1/n$ expansions for various atomic matrix elements, where n is the principal quantum number, plays an important role in the theoretical foundations of the quantum defect method. This paper will develop an expansion in powers of $1/n^2$ for hydrogenic bound-state wavefunctions which can be used to calculate $1/n$ expansions of matrix elements. The $1/n$ expansions of the two-electron direct and exchange Coulomb integrals will be evaluated as an example.

1. Introduction

The study of $1/n$ expansions for various atomic matrix elements plays an important role in the theoretical foundations of the quantum defect method and, in particular, of the Ritz expansion for the quantum defect. If n is the principal quantum number for a Rydberg state, then the quantum defect formula for the non-relativistic ionization energy is [1]

$$T_n = R_M/[n - \delta(n)]^2 \tag{1.1}$$

where R_M is the Rydberg constant for nuclear mass M and the Ritz expansion for the quantum defect $\delta(n)$ is

$$\delta(n) = \delta_0 + \frac{\delta_2}{[n-\delta(n)]^2} + \frac{\delta_4}{[n-\delta(n)]^4} + \cdots \tag{1.2}$$

in which only the even powers of $n - \delta(n)$ appear. Recent advances in the accuracy of both theory [2] and experiment [3] for the Rydberg states of helium raise new questions concerning the limits of validity of the Ritz expansion. As discussed by Drake and Swainson [4], and by Drake [5], the Ritz expansion requires for its validity that certain equations of constraint be satisfied by the coefficients in the $1/n$ expansions of matrix elements. For example, let $\psi_n^{(0)}$ be the unperturbed two-particle wavefunction in a screened hydrogenic approximation to a Rydberg state of helium with principal quantum number n, and let V be an operator describing some correction to that model whose matrix elements have the $1/n$ expansion

$$\langle\psi_n^{(0)}|V|\psi_n^{(0)}\rangle = n^{-3}(a_0 + a_2 n^{-2} + \cdots). \tag{1.3}$$

Then the first-order correction to the energy is

$$\Delta E_n^{(1)} = \langle\psi_n^{(0)}|V|\psi_n^{(0)}\rangle \tag{1.4}$$

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and the second-order correction is

$$\Delta E_n^{(2)} = \langle \psi_n^{(1)} | V | \psi_n^{(0)} \rangle \tag{1.5}$$

where $\psi_n^{(1)}$ satisfies a first-order perturbation equation with V as the perturbation. If the $1/n$ expansion for $\Delta E_n^{(2)}$ is written in the form

$$\Delta E_n^{(2)} = n^{-3}(b_0 + b_1 n^{-1} + b_2 n^{-2} + \cdots) \tag{1.6}$$

then the validity of the Ritz expansion requires that the coefficients satisfy [4, 5]

$$b_1 = -\tfrac{3}{2} a_0^2 \tag{1.7}$$

$$b_3 = -5 a_0 a_2 \tag{1.8}$$

$$b_5 = -\tfrac{7}{2}(a_2^2 + 2a_0 a_4) \tag{1.9}$$

$$b_7 = -9(a_0 a_6 + a_2 a_4) \tag{1.10}$$

etc. Hartree's theorem [6]† that the Ritz expansion is valid for any V which is short-range, local and spherically symmetric guarantees that the above equations are also satisfied for any such case. For example, it has been explicitly demonstrated for the $-\alpha_1/r^4$ dipole polarization potential [4], and for cross terms involving polarization corrections to the direct and exchange integrals of $1/r_{12}$ [5]. The exchange part represents an extension of Hartree's theorem to non-local potentials. However, it is not known at what point, if any, the constraint equations (1.7) to (1.10) will no longer be satisfied as higher-order corrections are added, leading to a failure of the Ritz expansion. Odd powers would then also be needed in equation (1.2).

In order to answer this question, the $1/n$ expansions must be known. The purpose of this paper is to develop techniques for generating $1/n$ expansions for the two-electron direct and exchange terms that appear as corrections to the screened hydrogenic energy, and to give numerical results for cases of interest. These expansions are also of considerable value for highly excited states where direct calculations are cumbersome. In the case of unscreened hydrogenic wavefunctions, Sanders and Scherr [7] give formulae for the full direct and exchange integrals. Their tables cover the states up to $n = 20$ and $\ell = 2$.

The analysis is based on a expansion in powers of $1/n^2$ for the hydrogenic radial function

$$R_{n,\ell}(Z; r) = -Z \left(\frac{2(n-\ell-1)!}{n^3 (n+\ell)!} \right)^{1/2} r^{-1/2} \xi^{\ell+1/2} \exp(-\xi/2) L_{n-\ell-1}^{(2\ell+1)}(\xi) \tag{1.11}$$

where

$$\xi = 2Zr/n. \tag{1.12}$$

The function $L_{n-\ell-1}^{(2\ell+1)}(\xi)$ which appears in (1.11) is a generalized Laguerre polynomial as defined in the Bateman project [8] and in Magnus *et al* [9]. This definition of the Laguerre polynomial is different from the one used by Bethe and Salpeter [10]; we have chosen to use this definition, which is standard in the mathematics literature, in order to facilitate the use of other relevant results from the mathematics literature. Matrix elements can be evaluated by inserting the expansion in powers of $1/n^2$ for (1.11) and integrating term by term. We illustrate this technique by using it to compute the expansions in powers of $1/n^2$ of the direct integral J and the exchange integral K as defined by Bethe and Salpeter [10]‡. A table of the expansion coefficients for J and K for helium is provided. Convergence proofs for the expansions are given.

† Some gaps in Hartree's proof are filled by Hill and Drake, to be published. See also Langer [6].

‡ A formula for the leading term in the $1/n$ expansion of K was first obtained by Hylleraas [11].

2. Summary of results

For n large, $R_{n,\ell}(Z;r)$ has the expansion

$$R_{n,\ell}(Z;r) = -n^{-3/2}2^{1/2}Zr^{-1/2}\left[\frac{(n+\ell)!}{(n-\ell-1)!\,n^{2\ell+1}}\right]^{1/2}\sum_{k=0}^{\infty} g_k^{(\ell)}(x)n^{-2k} \tag{2.1}$$

where

$$x = \sqrt{8Zr}. \tag{2.2}$$

The expansion (2.1) converges uniformly in r for r in any bounded region of the complex r plane. However, it converges rapidly enough so that a few terms will give a good description of $R_{n,\ell}(Z;r)$ if r is smaller than the turning point $r_0 = 2n^2/Z$ and not too close to r_0. The square root in (2.1) has not been expanded in inverse powers of n because it has a branch point at $1/n = 1/\ell$ which would reduce the radius of convergence of the expansion to $1/\ell$. The coefficients $g_k^{(\ell)}(x)$ in the expansion (2.1) can be calculated recursively from equations (3.1)–(3.3) below. The first three are

$$g_0^{(\ell)}(x) = J_{2\ell+1}(x) \tag{2.3}$$

$$g_1^{(\ell)}(x) = \frac{x^3}{96(2\ell+3)}[3(\ell+1)J_{2\ell+2}(x) + \ell J_{2\ell+4}(x)] \tag{2.4}$$

$$\begin{aligned} g_2^{(\ell)}(x) = \frac{x^6}{184320(\ell+3)(2\ell+5)}&[45(\ell+1)(\ell+3)J_{2\ell+3}(x) \\ &+ 3(2\ell+5)(5\ell-1)J_{2\ell+5}(x) + \ell(5\ell-1)J_{2\ell+7}(x)]. \end{aligned} \tag{2.5}$$

The $J_\nu(x)$ which appear in (2.5) are Bessel functions of the first kind in standard notation†.

The factor $(n+\ell)!/[(n-\ell-1)!\,n^{2\ell+1}]$ whose square root appears in (2.1) has an expansion in inverse powers of n^2 of the form

$$\frac{(n+\ell)!}{(n-\ell-1)!\,n^{2\ell+1}} = \sum_{j=0}^{\ell} b_j^{(\ell)} n^{-2j}. \tag{2.6}$$

The coefficients $b_j^{(\ell)}$ in the expansion (2.6) can be calculated recursively from equations (3.4) below. The first three are

$$b_0^{(\ell)} = 1 \tag{2.7}$$

$$b_1^{(\ell)} = -\tfrac{1}{6}\ell(\ell+1)(2\ell+1) \tag{2.8}$$

$$b_2^{(\ell)} = \tfrac{1}{360}(\ell-1)\ell(\ell+1)(2\ell-1)(2\ell+1)(5\ell+6). \tag{2.9}$$

In our notation, the direct integral J and the exchange integral K are

$$J = \int_0^\infty dr_2 \int_{r_2}^\infty dr_1\, r_1 r_2 (r_2 - r_1)[R_{1,0}(Z;r_1)]^2[R_{n,\ell}(Z-1;r_2)]^2 \tag{2.10}$$

$$\begin{aligned} K = \frac{2}{2\ell+1}\int_0^\infty dr_2 \int_{r_2}^\infty dr_1\, r_1^{-\ell+1} r_2^{\ell+2} R_{1,0}(Z;r_1)R_{n,\ell}(Z-1;r_1) \\ \times R_{1,0}(Z;r_2)R_{n,\ell}(Z-1;r_2). \end{aligned} \tag{2.11}$$

† [8] p 4, equation (2); [9] p 65.

The factors $R_{1,0}(Z; r_1)$ and $R_{1,0}(Z; r_2)$ which appear in (2.10) and (2.11) are given explicitly by

$$R_{1,0}(r) = 2Z^{3/2}\exp(-Zr). \tag{2.12}$$

These factors cut off the integration fast enough so that only the values of r_1 and r_2 for which (2.1) gives a good description matter. Thus $1/n^2$ expansions of these integrals can be obtained by inserting the expansions (2.1) and (2.6) and integrating term by term. The results are

$$J = \sum_{k=0}^{\infty} c_k^{(\ell,J)}(\gamma) n^{-2k-3} \tag{2.13}$$

$$K = \sum_{k=0}^{\infty} c_k^{(\ell,K)}(\gamma) n^{-2k-3} \tag{2.14}$$

where

$$\gamma = Z/8(Z-1). \tag{2.15}$$

The expansions (2.13) and (2.14) converge for $n > (Z-1)/Z$. The coefficients $c_k^{(\ell,J)}(\gamma)$ and $c_k^{(\ell,K)}(\gamma)$ in the expansions (2.13) and (2.14) can be calculated recursively from equations (3.5)–(3.15) below. Tables 1–11 list numerical values for these coefficients for helium (i.e. for $Z = 2$, which implies $\gamma = 1/4$) for $0 \leqslant k \leqslant 15$ and $0 \leqslant \ell \leqslant 10$. The coefficients in the tables were calculated by programming the formulae of section 3 in quadruple precision arithmetic. They were checked by evaluating the integrals numerically with high-order Gaussian quadrature formulae. The two methods of evaluation agree to 30 digits. To save space, we have reported the coefficients to only 20 digits. The tables were composed directly from computer-generated output.

Table 1. Expansion coefficients for $Z = 2$ and $\ell = 0$.

k	Direct coefficient $c_k^{(0,J)}(\gamma)$	Exchange coefficient $c_k^{(0,K)}(\gamma)$
0	−0.168 417 505 735 837 221 34	0.383 369 494 490 965 857 47
1	−0.144 700 366 146 677 814 13 × 10⁻¹	0.178 916 361 865 682 700 38
2	−0.191 867 995 583 905 251 73 × 10⁻²	0.652 081 155 425 593 737 59 × 10⁻¹
3	−0.309 674 941 431 674 225 25 × 10⁻³	0.214 624 936 065 813 970 40 × 10⁻¹
4	−0.557 759 949 076 452 659 47 × 10⁻⁴	0.666 968 342 826 088 713 50 × 10⁻²
5	−0.107 594 488 431 613 456 69 × 10⁻⁴	0.199 664 997 686 120 160 06 × 10⁻²
6	−0.217 399 460 771 382 109 69 × 10⁻⁵	0.582 154 973 135 626 003 73 × 10⁻³
7	−0.454 042 507 806 025 284 98 × 10⁻⁶	0.166 430 368 987 215 891 95 × 10⁻³
8	−0.971 939 899 289 867 333 73 × 10⁻⁷	0.468 605 659 692 089 723 10 × 10⁻⁴
9	−0.212 045 076 893 944 366 99 × 10⁻⁷	0.130 347 262 852 232 455 38 × 10⁻⁴
10	−0.469 615 427 172 170 435 02 × 10⁻⁸	0.358 992 674 889 247 752 24 × 10⁻⁵
11	−0.105 277 636 090 295 390 66 × 10⁻⁸	0.980 582 529 992 159 605 81 × 10⁻⁶
12	−0.238 386 353 165 623 090 80 × 10⁻⁹	0.265 983 533 531 308 449 51 × 10⁻⁶
13	−0.544 339 498 336 490 186 65 × 10⁻¹⁰	0.717 190 423 428 257 026 54 × 10⁻⁷
14	−0.125 184 254 809 561 238 91 × 10⁻¹⁰	0.192 385 595 642 515 481 63 × 10⁻⁷
15	−0.289 656 573 209 913 526 72 × 10⁻¹¹	0.513 750 596 286 745 702 62 × 10⁻⁸

It is noteworthy that for large ℓ, the coefficients increase dramatically in size before eventually decreasing. For low ℓ, the first few figures in the leading coefficients $c_0^{(\ell,J)}$ for the direct integrals agree with those quoted by Bethe and Salpeter [10], but there are significant differences in the leading exchange coefficients $c_0^{(\ell,K)}$.

Table 2. Expansion coefficients for $Z = 2$ and $\ell = 1$.

k	Direct coefficient $c_k^{(1,J)}(\gamma)$	Exchange coefficient $c_k^{(1,K)}(\gamma)$
0	$-0.104\,458\,672\,803\,523\,112\,37 \times 10^{-1}$	$0.351\,447\,762\,543\,511\,319\,86 \times 10^{-1}$
1	$0.799\,485\,411\,653\,926\,362\,20 \times 10^{-2}$	$-0.148\,680\,197\,469\,488\,426\,78 \times 10^{-1}$
2	$0.192\,535\,977\,963\,091\,703\,46 \times 10^{-2}$	$-0.120\,391\,466\,304\,857\,768\,69 \times 10^{-1}$
3	$0.413\,102\,502\,426\,759\,028\,55 \times 10^{-3}$	$-0.534\,638\,491\,173\,086\,182\,95 \times 10^{-2}$
4	$0.881\,597\,429\,655\,884\,780\,32 \times 10^{-4}$	$-0.195\,437\,884\,082\,290\,486\,97 \times 10^{-2}$
5	$0.190\,336\,428\,122\,954\,796\,02 \times 10^{-4}$	$-0.648\,105\,065\,091\,319\,162\,43 \times 10^{-3}$
6	$0.416\,618\,056\,692\,254\,268\,11 \times 10^{-5}$	$-0.202\,741\,278\,525\,997\,157\,26 \times 10^{-3}$
7	$0.923\,567\,483\,666\,052\,330\,24 \times 10^{-6}$	$-0.610\,120\,940\,825\,144\,923\,59 \times 10^{-4}$
8	$0.207\,017\,986\,028\,941\,858\,93 \times 10^{-6}$	$-0.178\,622\,056\,711\,652\,352\,34 \times 10^{-4}$
9	$0.468\,466\,015\,577\,120\,175\,70 \times 10^{-7}$	$-0.512\,314\,773\,823\,380\,636\,91 \times 10^{-5}$
10	$0.106\,879\,028\,784\,145\,627\,49 \times 10^{-7}$	$-0.144\,623\,880\,475\,477\,957\,37 \times 10^{-5}$
11	$0.245\,562\,106\,631\,438\,415\,10 \times 10^{-8}$	$-0.403\,136\,764\,663\,568\,575\,21 \times 10^{-6}$
12	$0.567\,647\,663\,688\,288\,878\,47 \times 10^{-9}$	$-0.111\,222\,844\,509\,378\,408\,06 \times 10^{-6}$
13	$0.131\,919\,435\,026\,565\,197\,19 \times 10^{-9}$	$-0.304\,247\,259\,188\,380\,209\,76 \times 10^{-7}$
14	$0.308\,014\,581\,962\,180\,329\,63 \times 10^{-10}$	$-0.826\,293\,214\,702\,190\,051\,73 \times 10^{-8}$
15	$0.722\,157\,513\,798\,368\,395\,40 \times 10^{-11}$	$-0.223\,035\,210\,223\,881\,676\,06 \times 10^{-8}$

Table 3. Expansion coefficients for $Z = 2$ and $\ell = 2$.

k	Direct coefficient $c_k^{(2,J)}(\gamma)$	Exchange coefficient $c_k^{(2,K)}(\gamma)$
0	$-0.176\,833\,278\,750\,378\,785\,53 \times 10^{-3}$	$0.649\,742\,985\,806\,501\,172\,99 \times 10^{-3}$
1	$0.818\,063\,040\,777\,679\,445\,71 \times 10^{-3}$	$-0.279\,888\,511\,808\,944\,305\,27 \times 10^{-2}$
2	$-0.395\,581\,025\,198\,583\,430\,11 \times 10^{-3}$	$0.555\,774\,827\,792\,776\,833\,78 \times 10^{-3}$
3	$-0.175\,440\,130\,995\,196\,591\,35 \times 10^{-3}$	$0.848\,195\,404\,794\,024\,579\,23 \times 10^{-3}$
4	$-0.520\,115\,750\,129\,924\,250\,00 \times 10^{-4}$	$0.457\,749\,676\,755\,934\,497\,18 \times 10^{-3}$
5	$-0.136\,763\,182\,886\,960\,789\,42 \times 10^{-4}$	$0.187\,707\,489\,371\,786\,154\,54 \times 10^{-3}$
6	$-0.342\,047\,846\,512\,373\,446\,52 \times 10^{-5}$	$0.673\,477\,840\,246\,702\,576\,36 \times 10^{-4}$
7	$-0.835\,246\,653\,297\,285\,933\,53 \times 10^{-6}$	$0.223\,263\,625\,182\,729\,174\,61 \times 10^{-4}$
8	$-0.201\,502\,451\,852\,165\,969\,86 \times 10^{-6}$	$0.702\,599\,838\,769\,405\,325\,02 \times 10^{-5}$
9	$-0.483\,129\,319\,779\,901\,114\,24 \times 10^{-7}$	$0.213\,143\,805\,607\,571\,642\,43 \times 10^{-5}$
10	$-0.115\,492\,904\,830\,012\,862\,08 \times 10^{-7}$	$0.629\,306\,945\,004\,466\,899\,05 \times 10^{-6}$
11	$-0.275\,766\,344\,880\,760\,624\,13 \times 10^{-8}$	$0.181\,980\,250\,063\,278\,085\,02 \times 10^{-6}$
12	$-0.658\,380\,131\,207\,231\,860\,54 \times 10^{-9}$	$0.517\,683\,349\,158\,810\,940\,57 \times 10^{-7}$
13	$-0.157\,263\,868\,897\,099\,374\,97 \times 10^{-9}$	$0.145\,330\,143\,606\,255\,155\,13 \times 10^{-7}$
14	$-0.375\,970\,683\,280\,502\,447\,63 \times 10^{-10}$	$0.403\,569\,765\,944\,043\,913\,77 \times 10^{-8}$
15	$-0.899\,787\,974\,189\,558\,575\,72 \times 10^{-11}$	$0.111\,052\,805\,469\,568\,467\,37 \times 10^{-8}$

3. Formulae for computation

The functions $g_k^{(\ell)}(x)$ in the expansion (2.1) have the form

$$g_k^{(\ell)}(x) = x^{3k} \sum_{m=0}^{k} a_{k,m}^{(\ell)} J_{2\ell+2m+k+1}(x). \tag{3.1}$$

The coefficients $a_{k,m}^{(\ell)}$ are calculated recursively from

$$a_{k,m}^{(\ell)} = \frac{(2\ell+2m+k+1)}{32(2k+m)(2\ell+m+2k+1)(2\ell+2m+k-1)} \times [(2\ell+2m+k-1)a_{k-1,m}^{(\ell)} + 32(k-m+1)(2\ell+m-k)a_{k,m-1}^{(\ell)}] \tag{3.2}$$

Table 4. Expansion coefficients for $Z = 2$ and $\ell = 3$.

k	Direct coefficient $c_k^{(3,J)}(\gamma)$	Exchange coefficient $c_k^{(3,K)}(\gamma)$
0	$-0.133\,287\,966\,771\,994\,224\,76 \times 10^{-5}$	$0.506\,856\,469\,489\,406\,159\,35 \times 10^{-5}$
1	$0.179\,838\,445\,551\,812\,539\,94 \times 10^{-4}$	$-0.668\,459\,726\,736\,377\,484\,45 \times 10^{-4}$
2	$-0.560\,773\,881\,484\,851\,639\,73 \times 10^{-4}$	$0.192\,878\,772\,853\,346\,365\,20 \times 10^{-3}$
3	$0.180\,814\,635\,585\,505\,694\,89 \times 10^{-4}$	$-0.960\,271\,821\,074\,573\,597\,75 \times 10^{-5}$
4	$0.137\,256\,275\,647\,248\,805\,33 \times 10^{-4}$	$-0.565\,188\,253\,347\,535\,188\,42 \times 10^{-4}$
5	$0.530\,286\,085\,813\,680\,211\,42 \times 10^{-5}$	$-0.373\,775\,424\,381\,208\,173\,75 \times 10^{-4}$
6	$0.166\,699\,692\,951\,263\,863\,15 \times 10^{-5}$	$-0.172\,920\,507\,032\,176\,396\,77 \times 10^{-4}$
7	$0.475\,640\,912\,379\,007\,981\,05 \times 10^{-6}$	$-0.676\,132\,851\,522\,425\,496\,07 \times 10^{-5}$
8	$0.128\,624\,647\,523\,675\,243\,09 \times 10^{-6}$	$-0.239\,406\,379\,342\,029\,348\,20 \times 10^{-5}$
9	$0.336\,695\,347\,002\,933\,217\,32 \times 10^{-7}$	$-0.794\,044\,849\,438\,815\,154\,34 \times 10^{-6}$
10	$0.863\,098\,774\,146\,038\,164\,48 \times 10^{-8}$	$-0.251\,483\,973\,759\,247\,675\,88 \times 10^{-6}$
11	$0.218\,170\,151\,020\,257\,018\,59 \times 10^{-8}$	$-0.769\,726\,089\,903\,349\,177\,32 \times 10^{-7}$
12	$0.546\,174\,339\,408\,439\,881\,31 \times 10^{-9}$	$-0.229\,498\,493\,969\,371\,818\,17 \times 10^{-7}$
13	$0.135\,803\,234\,485\,766\,312\,63 \times 10^{-9}$	$-0.670\,268\,157\,372\,562\,924\,19 \times 10^{-8}$
14	$0.336\,027\,982\,008\,724\,744\,22 \times 10^{-10}$	$-0.192\,522\,518\,632\,036\,886\,57 \times 10^{-8}$
15	$0.828\,544\,831\,132\,722\,113\,71 \times 10^{-11}$	$-0.545\,472\,261\,010\,758\,653\,74 \times 10^{-9}$

Table 5. Expansion coefficients for $Z = 2$ and $\ell = 4$.

k	Direct coefficient $c_k^{(4,J)}(\gamma)$	Exchange coefficient $c_k^{(4,K)}(\gamma)$
0	$-0.560\,809\,576\,990\,186\,193\,69 \times 10^{-8}$	$0.216\,913\,339\,052\,777\,239\,33 \times 10^{-7}$
1	$0.164\,663\,005\,450\,487\,412\,58 \times 10^{-6}$	$-0.630\,502\,155\,133\,208\,557\,77 \times 10^{-6}$
2	$-0.142\,510\,016\,087\,591\,569\,32 \times 10^{-5}$	$0.532\,617\,796\,327\,846\,898\,31 \times 10^{-5}$
3	$0.366\,540\,509\,633\,952\,586\,04 \times 10^{-5}$	$-0.126\,040\,907\,437\,884\,382\,01 \times 10^{-4}$
4	$-0.685\,292\,774\,897\,320\,679\,06 \times 10^{-6}$	$-0.109\,521\,004\,881\,802\,254\,93 \times 10^{-5}$
5	$-0.978\,222\,750\,505\,411\,884\,74 \times 10^{-6}$	$0.353\,507\,026\,439\,140\,045\,75 \times 10^{-5}$
6	$-0.478\,875\,284\,112\,960\,497\,80 \times 10^{-6}$	$0.290\,537\,483\,886\,304\,075\,93 \times 10^{-5}$
7	$-0.176\,614\,327\,628\,651\,323\,10 \times 10^{-6}$	$0.151\,884\,372\,112\,395\,636\,42 \times 10^{-5}$
8	$-0.568\,566\,144\,570\,930\,405\,75 \times 10^{-7}$	$0.648\,555\,784\,545\,926\,421\,67 \times 10^{-6}$
9	$-0.169\,215\,020\,263\,560\,998\,00 \times 10^{-7}$	$0.246\,010\,120\,891\,235\,642\,01 \times 10^{-6}$
10	$-0.479\,075\,788\,444\,979\,842\,74 \times 10^{-8}$	$0.862\,998\,827\,990\,886\,071\,27 \times 10^{-7}$
11	$-0.131\,127\,545\,221\,695\,854\,11 \times 10^{-8}$	$0.286\,425\,981\,955\,249\,636\,12 \times 10^{-7}$
12	$-0.350\,443\,470\,037\,944\,793\,31 \times 10^{-9}$	$0.912\,295\,882\,885\,366\,490\,91 \times 10^{-8}$
13	$-0.920\,410\,177\,716\,464\,647\,70 \times 10^{-10}$	$0.281\,512\,755\,660\,896\,682\,23 \times 10^{-8}$
14	$-0.238\,611\,216\,093\,072\,743\,55 \times 10^{-10}$	$0.847\,187\,862\,873\,280\,459\,63 \times 10^{-9}$
15	$-0.612\,473\,017\,942\,861\,279\,78 \times 10^{-11}$	$0.249\,844\,864\,324\,619\,188\,00 \times 10^{-9}$

starting with the initial condition

$$a_{0,0}^{(\ell)} = 1. \tag{3.3}$$

Numerical values of the Bessel functions $J_\nu(x)$ which appear in (2.5) can be conveniently calculated via backwards recursion using the Miller algorithm [12]. A FORTRAN program for calculating the $J_\nu(x)$ can be obtained via e-mail from netlib†.

The coefficients $b_j^{(\ell)}$ in the expansion (2.6) are calculated recursively from

$$b_j^{(\ell)} = b_j^{(\ell-1)} - \ell^2 b_{j-1}^{(\ell-1)} \tag{3.4}$$

† For information and instructions, send the message 'send index' via e-mail to netlib@ornl.gov. The program for calculating Bessel functions $J_\nu(x)$ is rjbesl from the specfun collection.

Table 6. Expansion coefficients for $Z = 2$ and $\ell = 5$.

k	Direct coefficient $c_k^{(5,J)}(\gamma)$	Exchange coefficient $c_k^{(5,K)}(\gamma)$
0	$-0.149\,806\,722\,130\,520\,680\,69 \times 10^{-10}$	$0.585\,050\,054\,632\,936\,659\,62 \times 10^{-10}$
1	$0.812\,439\,639\,609\,019\,198\,33 \times 10^{-9}$	$-0.315\,602\,651\,868\,187\,562\,43 \times 10^{-8}$
2	$-0.146\,983\,854\,799\,573\,029\,69 \times 10^{-7}$	$0.564\,934\,442\,011\,937\,649\,10 \times 10^{-7}$
3	$0.103\,066\,450\,088\,256\,841\,58 \times 10^{-6}$	$-0.386\,227\,920\,701\,072\,246\,36 \times 10^{-6}$
4	$-0.233\,357\,099\,903\,934\,920\,46 \times 10^{-6}$	$0.799\,837\,638\,059\,471\,651\,12 \times 10^{-6}$
5	$0.133\,995\,967\,164\,953\,096\,08 \times 10^{-7}$	$0.179\,942\,703\,900\,353\,536\,99 \times 10^{-6}$
6	$0.649\,431\,679\,329\,725\,666\,31 \times 10^{-7}$	$-0.205\,750\,532\,940\,341\,477\,41 \times 10^{-6}$
7	$0.398\,413\,920\,629\,224\,034\,90 \times 10^{-7}$	$-0.216\,016\,785\,415\,572\,821\,90 \times 10^{-6}$
8	$0.170\,237\,887\,431\,122\,558\,48 \times 10^{-7}$	$-0.127\,735\,223\,590\,343\,609\,02 \times 10^{-6}$
9	$0.613\,030\,242\,314\,642\,231\,13 \times 10^{-8}$	$-0.595\,675\,022\,215\,627\,229\,65 \times 10^{-7}$
10	$0.199\,696\,617\,131\,176\,626\,11 \times 10^{-8}$	$-0.242\,220\,280\,555\,971\,900\,28 \times 10^{-7}$
11	$0.609\,462\,219\,255\,051\,096\,54 \times 10^{-9}$	$-0.899\,858\,247\,784\,059\,178\,68 \times 10^{-8}$
12	$0.177\,787\,663\,260\,348\,788\,35 \times 10^{-9}$	$-0.313\,512\,098\,046\,229\,942\,00 \times 10^{-8}$
13	$0.501\,938\,831\,493\,439\,066\,67 \times 10^{-10}$	$-0.104\,118\,624\,703\,917\,262\,36 \times 10^{-8}$
14	$0.138\,285\,723\,052\,117\,604\,01 \times 10^{-10}$	$-0.333\,215\,075\,535\,160\,353\,89 \times 10^{-9}$
15	$0.373\,902\,997\,695\,568\,790\,11 \times 10^{-11}$	$-0.103\,552\,691\,769\,312\,398\,92 \times 10^{-9}$

Table 7. Expansion coefficients for $Z = 2$ and $\ell = 6$.

k	Direct coefficient $c_k^{(6,J)}(\gamma)$	Exchange coefficient $c_k^{(6,K)}(\gamma)$
0	$-0.275\,961\,664\,087\,817\,118\,01 \times 10^{-13}$	$0.108\,422\,820\,663\,442\,555\,98 \times 10^{-12}$
1	$0.248\,653\,689\,133\,348\,928\,57 \times 10^{-11}$	$-0.973\,869\,230\,995\,670\,873\,81 \times 10^{-11}$
2	$-0.806\,357\,135\,607\,920\,789\,47 \times 10^{-10}$	$0.314\,053\,777\,708\,606\,778\,96 \times 10^{-9}$
3	$0.115\,428\,313\,583\,567\,041\,95 \times 10^{-8}$	$-0.444\,615\,130\,558\,906\,103\,61 \times 10^{-8}$
4	$-0.711\,730\,465\,479\,903\,031\,27 \times 10^{-8}$	$0.267\,035\,777\,337\,596\,463\,25 \times 10^{-7}$
5	$0.145\,927\,467\,881\,352\,063\,02 \times 10^{-7}$	$-0.497\,568\,819\,274\,034\,442\,59 \times 10^{-7}$
6	$0.107\,367\,182\,221\,858\,833\,74 \times 10^{-8}$	$-0.184\,157\,128\,875\,205\,164\,15 \times 10^{-7}$
7	$-0.404\,365\,518\,451\,742\,581\,19 \times 10^{-8}$	$0.108\,860\,283\,091\,273\,053\,49 \times 10^{-7}$
8	$-0.311\,814\,445\,243\,917\,710\,22 \times 10^{-8}$	$0.154\,260\,438\,243\,244\,683\,62 \times 10^{-7}$
9	$-0.153\,093\,262\,902\,669\,375\,91 \times 10^{-8}$	$0.103\,398\,230\,001\,249\,837\,49 \times 10^{-7}$
10	$-0.612\,514\,751\,430\,372\,284\,25 \times 10^{-9}$	$0.526\,283\,152\,770\,166\,169\,18 \times 10^{-8}$
11	$-0.217\,350\,812\,460\,702\,335\,58 \times 10^{-9}$	$0.229\,327\,287\,968\,555\,303\,74 \times 10^{-8}$
12	$-0.712\,776\,885\,126\,819\,296\,84 \times 10^{-10}$	$0.902\,367\,174\,019\,795\,628\,59 \times 10^{-9}$
13	$-0.221\,146\,266\,351\,666\,871\,76 \times 10^{-10}$	$0.330\,205\,713\,561\,593\,239\,45 \times 10^{-9}$
14	$-0.658\,753\,523\,333\,933\,439\,43 \times 10^{-11}$	$0.114\,442\,928\,216\,012\,853\,40 \times 10^{-9}$
15	$-0.190\,258\,740\,845\,922\,208\,02 \times 10^{-11}$	$0.380\,270\,661\,817\,009\,994\,52 \times 10^{-10}$

starting with the initial condition (2.7).

The coefficients $c_j^{(\ell,X)}(\gamma)$, where $X = J$ or $X = K$, in the expansions (2.13) and (2.14) are calculated recursively from

$$c_j^{(\ell,J)}(\gamma) = -\frac{Z}{16} \sum_{k=0}^{\min(j,\ell)} b_k^{(\ell)} d_{j-k}^{(\ell,J)}(\gamma) \tag{3.5}$$

$$c_j^{(\ell,K)}(\gamma) = \frac{Z\gamma^2}{(2\ell+1)} \cdot \sum_{k=0}^{\min(j,\ell)} b_k^{(\ell)} d_{j-k}^{(\ell,K)}(\gamma). \tag{3.6}$$

The coefficients $d_j^{(\ell,X)}(\gamma)$ which appear in (3.5) and (3.6) are calculated from

$$d_j^{(\ell,X)}(\gamma) = \sum_{k=0}^{j} \sum_{m=0}^{k} \sum_{m'=0}^{j-k} a_{k,m}^{(\ell)} a_{j-k,m'}^{(\ell)} e_{k,m;j-k,m'}^{(\ell,X)}(\gamma) \qquad X = J \qquad \text{or } X = K. \tag{3.7}$$

Table 8. Expansion coefficients for $Z = 2$ and $\ell = 7$.

k	Direct coefficient $c_k^{(7,J)}(\gamma)$	Exchange coefficient $c_k^{(7,K)}(\gamma)$
0	$-0.371\,299\,624\,380\,001\,919\,64 \times 10^{-16}$	$0.146\,464\,609\,148\,635\,017\,27 \times 10^{-15}$
1	$0.516\,021\,219\,696\,588\,800\,99 \times 10^{-14}$	$-0.203\,143\,269\,295\,386\,571\,43 \times 10^{-13}$
2	$-0.271\,769\,264\,186\,036\,174\,69 \times 10^{-12}$	$0.106\,636\,191\,295\,285\,646\,39 \times 10^{-11}$
3	$0.683\,463\,252\,364\,958\,537\,51 \times 10^{-11}$	$-0.266\,624\,256\,563\,966\,910\,27 \times 10^{-10}$
4	$-0.848\,064\,223\,227\,923\,349\,84 \times 10^{-10}$	$0.327\,083\,600\,394\,046\,362\,89 \times 10^{-9}$
5	$0.478\,088\,119\,325\,425\,547\,59 \times 10^{-9}$	$-0.179\,447\,002\,219\,541\,290\,66 \times 10^{-8}$
6	$-0.900\,045\,791\,679\,618\,012\,33 \times 10^{-9}$	$0.304\,812\,220\,737\,797\,714\,77 \times 10^{-8}$
7	$-0.189\,098\,786\,550\,230\,129\,32 \times 10^{-9}$	$0.160\,374\,664\,956\,050\,429\,69 \times 10^{-8}$
8	$0.235\,089\,036\,749\,917\,959\,20 \times 10^{-9}$	$-0.490\,899\,915\,784\,587\,359\,45 \times 10^{-9}$
9	$0.232\,341\,034\,625\,933\,183\,72 \times 10^{-9}$	$-0.106\,045\,280\,235\,818\,823\,72 \times 10^{-8}$
10	$0.130\,452\,143\,183\,207\,809\,01 \times 10^{-9}$	$-0.809\,253\,288\,237\,291\,897\,79 \times 10^{-9}$
11	$0.576\,849\,844\,625\,788\,775\,87 \times 10^{-10}$	$-0.449\,331\,529\,480\,891\,403\,99 \times 10^{-9}$
12	$0.222\,064\,202\,635\,872\,919\,97 \times 10^{-10}$	$-0.209\,650\,327\,340\,327\,747\,22 \times 10^{-9}$
13	$0.780\,169\,334\,711\,218\,052\,51 \times 10^{-11}$	$-0.873\,352\,606\,120\,513\,349\,67 \times 10^{-10}$
14	$0.256\,907\,908\,795\,556\,015\,06 \times 10^{-11}$	$-0.335\,641\,076\,612\,750\,551\,94 \times 10^{-10}$
15	$0.806\,315\,917\,902\,068\,358\,25 \times 10^{-12}$	$-0.121\,424\,407\,537\,134\,408\,21 \times 10^{-10}$

Table 9. Expansion coefficients for $Z = 2$ and $\ell = 8$.

k	Direct coefficient $c_k^{(8,J)}(\gamma)$	Exchange coefficient $c_k^{(8,K)}(\gamma)$
0	$-0.380\,613\,649\,172\,223\,045\,62 \times 10^{-19}$	$0.150\,558\,764\,118\,862\,655\,44 \times 10^{-18}$
1	$0.772\,075\,282\,440\,117\,232\,25 \times 10^{-17}$	$-0.304\,992\,879\,133\,343\,076\,36 \times 10^{-16}$
2	$-0.616\,144\,867\,328\,070\,569\,19 \times 10^{-15}$	$0.242\,885\,198\,001\,490\,681\,22 \times 10^{-14}$
3	$0.247\,574\,557\,190\,522\,851\,13 \times 10^{-13}$	$-0.972\,618\,573\,137\,417\,271\,97 \times 10^{-13}$
4	$-0.532\,183\,273\,670\,289\,039\,21 \times 10^{-12}$	$0.207\,828\,200\,223\,580\,061\,87 \times 10^{-11}$
5	$0.598\,639\,965\,492\,777\,436\,76 \times 10^{-11}$	$-0.231\,060\,570\,166\,703\,352\,45 \times 10^{-10}$
6	$-0.315\,301\,114\,393\,905\,369\,36 \times 10^{-10}$	$0.118\,335\,305\,871\,907\,889\,23 \times 10^{-9}$
7	$0.548\,753\,468\,362\,103\,440\,69 \times 10^{-10}$	$-0.184\,312\,277\,354\,546\,072\,69 \times 10^{-9}$
8	$0.194\,928\,967\,593\,676\,045\,66 \times 10^{-10}$	$-0.128\,406\,970\,623\,935\,524\,76 \times 10^{-9}$
9	$-0.125\,154\,176\,255\,661\,921\,40 \times 10^{-10}$	$0.146\,541\,588\,639\,116\,639\,44 \times 10^{-10}$
10	$-0.165\,984\,200\,828\,350\,094\,28 \times 10^{-10}$	$0.701\,840\,818\,809\,894\,404\,43 \times 10^{-10}$
11	$-0.106\,405\,476\,662\,366\,973\,11 \times 10^{-10}$	$0.614\,553\,386\,331\,749\,101\,19 \times 10^{-10}$
12	$-0.517\,965\,149\,624\,175\,848\,79 \times 10^{-11}$	$0.372\,200\,548\,130\,664\,042\,23 \times 10^{-10}$
13	$-0.215\,561\,348\,118\,732\,893\,18 \times 10^{-11}$	$0.185\,787\,349\,605\,183\,058\,54 \times 10^{-10}$
14	$-0.809\,128\,880\,074\,049\,156\,92 \times 10^{-12}$	$0.818\,764\,551\,269\,655\,229\,57 \times 10^{-11}$
15	$-0.282\,220\,015\,404\,740\,348\,88 \times 10^{-12}$	$0.330\,321\,029\,939\,352\,129\,31 \times 10^{-11}$

The $e_{k,m;k',m'}^{(\ell,X)}(\gamma)$ in the case $X = J$ are calculated from

$$
\begin{aligned}
e_{k,m;k',m'}^{(\ell,J)}(\gamma) = \sum_{i=0}^{i_{\max}^{(J)}} \sum_{j=-i}^{j_{\max}^{(J)}} \Bigg[& \binom{2\ell + 2k + m + 2k' + m' + 2}{i_{\max}^{(J)} - i} \binom{i + j_{\max}^{(J)}}{i + j} \\
& \times \binom{i_{\max}^{(J)}}{i} (i_{\max}^{(J)} - i)! + 2 \binom{2\ell + 2k + m + 2k' + m' + 1}{i_{\max}^{(J)} - i - 1} \\
& \times \binom{i + j_{\max}^{(J)} - 1}{i + j} \binom{i_{\max}^{(J)} - 1}{i} (i_{\max}^{(J)} - i - 1)! \Bigg] (-1)^j 8^{-k-m+m'-i-1} \\
& \times \gamma^{-2k-m-k'+m'-i-2} \exp[-1/(4\gamma)] I_{2\ell+k'+2m'+i+j+1}[1/(4\gamma)] \\
& \text{for } k + 2m \geqslant k' + 2m'
\end{aligned} \qquad (3.8)
$$

Table 10. Expansion coefficients for Z = 2 and $\ell = 9$.

k	Direct coefficient $c_k^{(9,J)}(\gamma)$	Exchange coefficient $c_k^{(9,K)}(\gamma)$
0	$-0.307\,003\,800\,613\,138\,787\,93 \times 10^{-22}$	$0.121\,687\,789\,512\,947\,939\,30 \times 10^{-21}$
1	$0.871\,042\,156\,488\,542\,352\,31 \times 10^{-20}$	$-0.344\,923\,902\,867\,215\,788\,41 \times 10^{-19}$
2	$-0.100\,031\,522\,308\,770\,646\,85 \times 10^{-17}$	$0.395\,553\,155\,264\,504\,234\,42 \times 10^{-17}$
3	$0.600\,985\,431\,580\,787\,375\,56 \times 10^{-16}$	$-0.237\,131\,269\,775\,013\,423\,10 \times 10^{-15}$
4	$-0.203\,918\,106\,540\,774\,714\,25 \times 10^{-14}$	$0.801\,783\,614\,921\,318\,549\,54 \times 10^{-14}$
5	$0.393\,408\,791\,445\,330\,037\,26 \times 10^{-13}$	$-0.153\,741\,223\,619\,724\,899\,78 \times 10^{-12}$
6	$-0.411\,581\,344\,314\,887\,931\,24 \times 10^{-12}$	$0.158\,929\,258\,641\,213\,006\,95 \times 10^{-11}$
7	$0.205\,233\,774\,892\,898\,592\,91 \times 10^{-11}$	$-0.769\,945\,508\,234\,304\,478\,43 \times 10^{-11}$
8	$-0.331\,137\,482\,121\,253\,926\,26 \times 10^{-11}$	$0.110\,132\,439\,534\,548\,139\,08 \times 10^{-10}$
9	$-0.169\,503\,378\,884\,965\,763\,83 \times 10^{-11}$	$0.975\,634\,250\,941\,950\,418\,64 \times 10^{-11}$
10	$0.578\,012\,089\,887\,358\,047\,01 \times 10^{-12}$	$0.346\,517\,319\,972\,851\,606\,63 \times 10^{-12}$
11	$0.114\,104\,871\,080\,041\,078\,20 \times 10^{-11}$	$-0.446\,021\,185\,260\,124\,238\,40 \times 10^{-11}$
12	$0.836\,604\,183\,221\,378\,016\,62 \times 10^{-12}$	$-0.454\,006\,115\,712\,750\,972\,82 \times 10^{-11}$
13	$0.447\,051\,342\,545\,857\,576\,77 \times 10^{-12}$	$-0.300\,108\,454\,977\,623\,226\,17 \times 10^{-11}$
14	$0.200\,545\,501\,994\,959\,738\,87 \times 10^{-12}$	$-0.160\,135\,700\,473\,911\,378\,95 \times 10^{-11}$
15	$0.802\,301\,136\,365\,832\,708\,80 \times 10^{-13}$	$-0.745\,966\,132\,650\,740\,854\,14 \times 10^{-12}$

Table 11. Expansion coefficients for Z = 2 and $\ell = 10$.

k	Direct coefficient $c_k^{(10,J)}(\gamma)$	Exchange coefficient $c_k^{(10,K)}(\gamma)$
0	$-0.199\,876\,717\,992\,257\,788\,27 \times 10^{-25}$	$0.793\,461\,929\,130\,680\,744\,70 \times 10^{-25}$
1	$0.766\,721\,657\,025\,002\,523\,03 \times 10^{-23}$	$-0.304\,154\,299\,334\,664\,862\,27 \times 10^{-22}$
2	$-0.121\,739\,052\,870\,150\,653\,79 \times 10^{-20}$	$0.482\,448\,172\,094\,136\,383\,88 \times 10^{-20}$
3	$0.104\,099\,948\,913\,616\,571\,52 \times 10^{-18}$	$-0.411\,940\,832\,522\,901\,409\,75 \times 10^{-18}$
4	$-0.522\,723\,176\,556\,511\,581\,29 \times 10^{-17}$	$0.206\,389\,228\,345\,634\,854\,94 \times 10^{-16}$
5	$0.157\,715\,502\,985\,684\,282\,42 \times 10^{-15}$	$-0.620\,484\,548\,605\,287\,091\,59 \times 10^{-15}$
6	$-0.280\,937\,657\,227\,901\,421\,10 \times 10^{-14}$	$0.109\,839\,317\,836\,577\,591\,87 \times 10^{-13}$
7	$0.277\,782\,463\,995\,328\,033\,94 \times 10^{-13}$	$-0.107\,287\,404\,486\,361\,494\,07 \times 10^{-12}$
8	$-0.132\,277\,173\,074\,843\,988\,96 \times 10^{-12}$	$0.495\,933\,266\,974\,520\,059\,33 \times 10^{-12}$
9	$0.197\,885\,647\,311\,680\,531\,09 \times 10^{-12}$	$-0.650\,539\,710\,239\,083\,651\,04 \times 10^{-12}$
10	$0.135\,227\,337\,827\,372\,846\,47 \times 10^{-12}$	$-0.714\,913\,977\,277\,715\,451\,68 \times 10^{-12}$
11	$-0.191\,098\,995\,999\,600\,001\,07 \times 10^{-13}$	$-0.116\,595\,743\,586\,253\,361\,25 \times 10^{-12}$
12	$-0.755\,498\,630\,181\,169\,595\,13 \times 10^{-13}$	$0.270\,365\,688\,965\,974\,596\,10 \times 10^{-12}$
13	$-0.637\,127\,535\,500\,832\,835\,36 \times 10^{-13}$	$0.326\,840\,596\,592\,785\,649\,58 \times 10^{-12}$
14	$-0.373\,093\,815\,343\,332\,387\,70 \times 10^{-13}$	$0.236\,171\,309\,058\,127\,610\,40 \times 10^{-12}$
15	$-0.179\,977\,741\,312\,436\,964\,42 \times 10^{-13}$	$0.134\,636\,077\,884\,673\,672\,25 \times 10^{-12}$

$$
\begin{aligned}
e_{k,m;k',m'}^{(\ell,J)}(\gamma) = \sum_{j=0}^{j_{\max}^{(J)}} \sum_{i=-j}^{i_{\max}^{(J)}} \Bigg[& \binom{2\ell+2k+m+2k'+m'+2}{j_{\max}^{(J)}-j} \binom{i_{\max}^{(J)}+j}{i+j} \\
& \times \binom{j_{\max}^{(J)}}{j} (j_{\max}^{(J)}-j)! + 2\binom{2\ell+2k+m+2k'+m'+1}{j_{\max}^{(J)}-j-1} \\
& \times \binom{i_{\max}^{(J)}+j-1}{i+j} \binom{j_{\max}^{(J)}-1}{j} (j_{\max}^{(J)}-j-1)! \Bigg] (-1)^i 8^{m-k'-m'-j-1} \\
& \times \gamma^{-k+m-2k'-m'-j-2} \exp[-1/(4\gamma)] I_{2\ell+k+2m+i+j+1}[1/(4\gamma)] \\
& \text{for } k+2m \leqslant k'+2m'
\end{aligned}
\tag{3.9}
$$

where

$$
i_{\max}^{(J)} = k - m + 2k' + m' + 1 \tag{3.10}
$$

$$j_{\max}^{(J)} = k' - m' + 2k + m + 1. \tag{3.11}$$

The $I_{\nu+i+j}[1/(4\gamma)]$ which appear in (3.8) and (3.9) are modified Bessel functions of the first kind† which can be calculated efficiently via backwards recursion‡. The $e_{k,m;k',m'}^{(\ell,X)}(\gamma)$ in the case $X = K$ are calculated from

$$\begin{aligned} e_{k,m;k',m'}^{(\ell,K)}(\gamma) = \sum_{i=0}^{i_{\max}^{(K)}} \sum_{j=-i}^{j_{\max}^{(K)}} \binom{2\ell + 2k + m + 2k' + m' + 4}{i_{\max}^{(K)} - i} \binom{i + j_{\max}^{(K)}}{i + j} \binom{i_{\max}^{(K)}}{i} \\ \times (i_{\max}^{(K)} - i)!(-1)^j 2^{-k-2m+k'+2m'-2i-1} \gamma^{-2k-m-k'+m'-i-4} \\ \times f(2\ell + 2k' + m' + i + j + 2, 2k + m + i + 1, 2\ell + k' + 2m' + i + j + 1; \gamma) \\ \text{for } k + 2m \geqslant k' + 2m' \end{aligned} \tag{3.12}$$

$$\begin{aligned} e_{k,m;k',m'}^{(\ell,K)}(\gamma) = \sum_{j=0}^{j_{\max}^{(K)}} \sum_{i=-j}^{i_{\max}^{(K)}} \binom{2\ell + 2k + m + 2k' + m' + 4}{j_{\max}^{(K)} - j} \binom{i_{\max}^{(K)} + j}{i + j} \binom{j_{\max}^{(K)}}{j} \\ \times (j_{\max}^{(K)} - j)!(-1)^i 2^{k+2m-k'-2m'-2j-1} \gamma^{-k+m-2k'-m'-j-4} \\ \times f(2\ell + 2k' + m' + j + 2, 2k + m + i + j + 1, 2\ell + k + 2m + i + j + 1; \gamma) \\ \text{for } k + 2m \leqslant k' + 2m' \end{aligned} \tag{3.13}$$

where

$$i_{\max}^{(K)} = k - m + 2k' + m' + 3 \tag{3.14}$$

$$j_{\max}^{(K)} = k' - m' + 2k + m + 3. \tag{3.15}$$

The $f(p, q, \nu; \gamma)$ which appear in (3.12) and (3.13) are evaluated from the power series expansion

$$f(p, q, \nu; \gamma) = \exp\left(-\frac{1}{4\gamma}\right) \sum_{j=0}^{\infty} \frac{g(p+j, q+j)}{j!\Gamma(\nu + j + 1)} \left(\frac{1}{4\gamma}\right)^{\nu+2j}. \tag{3.16}$$

Some computer time can be saved by evaluating some of the $f(p, q, \nu; \gamma)$ from

$$f(p, q, \nu; \gamma) = f(p + 1, q, \nu; \gamma) + f(p, q + 1, \nu; \gamma) \tag{3.17}$$

Because the $f(p, q, \nu; \gamma)$ are all positive, (3.17) can be safely used in the backward direction to evaluate $f(p, q, \nu; \gamma)$ from $f(p + 1, q, \nu; \gamma)$ and $f(p, q + 1, \nu; \gamma)$. However, loss of accuracy may result if (3.17) is used in the forward direction to solve for one of the terms on the right-hand side. The $g(p, q)$ which appear in (3.16) are evaluated from

$$g(p, q) = \frac{h(p, q)}{2^{p+q+2}(p + q + 1)\binom{p+q}{p}} \tag{3.18}$$

† [8] p 5, equation (12); [9] p 66.

‡ The relevant program from the specfun collection at netlib is ribesl (testdriver ritest).

after the $h(p, q)$, which are integers, have been evaluated from the recursion relation

$$h(p, q+1) = 2h(p, q) + \binom{p+q+1}{p} \tag{3.19}$$

which is started with the initial condition

$$h(p, 0) = 1. \tag{3.20}$$

Calculating the $g(p, q)$ via a recursion in integers such as (3.19)–(3.20) reduces round-off error.

The leading $c_0^{(\ell,K)}$ term in equation (2.14) can be given a simpler form than the doubly infinite summations given by Bethe and Salpeter [10]. Defining $s = j + \ell + 1$ and $u = 2(Z-1)/Z$, the result is

$$c_0^{(\ell,K)} = \frac{8Zu^{2\ell+3}\mathrm{e}^{-u}}{(2\ell+1)} \sum_{j=0}^{\infty} \frac{u^{2j}}{j!(2\ell+j+1)!}[\Phi_1(j,\ell) - u\Phi_2(j,\ell)] \tag{3.21}$$

where

$$\Phi_1(j,\ell) = 2s[2(s+1)(2s+1)g(\ell+s+1, j+1) + 3j(\ell+s)g(\ell+s, j)] \tag{3.22}$$

and

$$\Phi_2(j,\ell) = 6(s+1)(2s+1)g(\ell+s+1, j+1) + j(\ell+s)g(\ell+s, j). \tag{3.23}$$

The series is rapidly convergent.

4. Derivations

The expansion (2.1) is obtained by writing

$$\xi^{\ell+1/2}\exp(-\xi/2)L_{n-\ell-1}^{(2\ell+1)}(\xi) = \frac{(n+\ell)!}{(n-\ell-1)!\,n^{\ell+1/2}} f_n^{(\ell)}(x) \tag{4.1}$$

where

$$x = 2\sqrt{n\xi} = \sqrt{8Zr}. \tag{4.2}$$

It follows from (1.4) and (4.1) that

$$R_{n,\ell}(Z;r) = -n^{-3/2}2^{1/2}Zr^{-1/2}\left[\frac{(n+\ell)!}{(n-\ell-1)!n^{2\ell+1}}\right]^{1/2} f_n^{(\ell)}(x) \tag{4.3}$$

where $f_n^{(\ell)}(x)$ satisfies the initial condition

$$f_n^{(\ell)}(x) = \frac{(x/2)^{2\ell+1}}{(2\ell+1)!}[1 + \mathrm{O}(x^2)] \qquad \text{for } x \to 0. \tag{4.4}$$

The differential equation for $R_{n,\ell}(Z;r)$, which is

$$\left\{-\frac{\mathrm{d}^2}{\mathrm{d}r^2}-\frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}+\frac{\ell(\ell+1)}{r^2}-\frac{2Z}{r}\right\}R_{n,\ell}(Z;r)=-\frac{Z^2}{n^2}R_{n,\ell}(Z;r) \qquad (4.5)$$

can be used to show that $f_n^{(\ell)}$ is a solution of the differential equation

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}x^2}+\frac{1}{x}\frac{\mathrm{d}}{\mathrm{d}x}+1-\frac{(2\ell+1)^2}{x^2}\right]f_n^{(\ell)}(x)=\frac{x^2}{16n^2}f_n^{(\ell)}(x). \qquad (4.6)$$

We treat the right-hand side of (4.6) as a perturbation and look for a solution to (4.6) of the form

$$f_n^{(\ell)}(x)=\sum_{k=0}^{\infty}n^{-2k}g_k^{(\ell)}(x). \qquad (4.7)$$

It follows from (4.6) and (4.7) that the $f_\ell^{(k)}(x)$ can be obtained by solving the sequence of inhomogeneous differential equations

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}x^2}+\frac{1}{x}\frac{\mathrm{d}}{\mathrm{d}x}+1-\frac{(2\ell+1)^2}{x^2}\right]g_k^{(\ell)}(x)=\frac{x^2}{16}g_{k-1}^{(\ell)}(x) \qquad (4.8)$$

with the understanding that the right-hand side of (4.8) is counted as zero for $k=0$. The initial condition

$$g_k^{(\ell)}(x)=O(x^{2\ell+3}) \qquad k>0 \qquad (4.9)$$

is imposed on the higher-order terms because the $k=0$ term (given by (2.3)) satisfies the initial condition (4.4) exactly. The differential equations (4.8) can be solved by looking for a solution of the form (3.1). The recurrence and differentiation formulae† for the Bessel function $J_\nu(x)$ can be used to show that (3.1) is a solution to (4.8) if the coefficients $a_{k,m}^{(\ell)}$ are given by (3.2) and (3.3). The small x power series‡ for $J_\nu(x)$ can be used to show that the initial condition (4.9) is satisfied. A series of the form (2.1) can be obtained by rearranging an expansion given in the Bateman project§. However, the rearrangement is tedious, and for that reason we prefer the straightforward derivation recorded here.

It will now be shown that the expansion (2.1) converges uniformly in x for x in any bounded region in the complex x plane. We use the method of variation of parameters‖, which begins by writing the solution to (4.8) and its first derivative in the forms

$$g_k^{(\ell)}(x)=h_k^{(\ell,J)}(x)J_{2\ell+1}(x)+h_k^{(\ell,Y)}(x)Y_{2\ell+1}(x) \qquad (4.10)$$

$$\frac{\mathrm{d}}{\mathrm{d}x}g_k^{(\ell)}(x)=h_k^{(\ell,J)}(x)\frac{\mathrm{d}}{\mathrm{d}x}J_{2\ell+1}(x)+h_k^{(\ell,Y)}(x)\frac{\mathrm{d}}{\mathrm{d}x}Y_{2\ell+1}(x). \qquad (4.11)$$

† [8] pp 11–12, equations (54)–(56); [9] p 67.

‡ [8] p 4, equation (2); [9] p 65.

§ [8] p 199–200, equations (3), (4) and (5).

‖ The method of variation of parameters is discussed in most books on ordinary differential equations. See, for example, [13].

Equations (4.8)–(4.11) and the Wronskian relation $J_{2\ell+1}(x)Y'_{2\ell+1}(x) - Y_{2\ell+1}(x)J'_{2\ell+1}(x) = 2/(\pi x)$ are then used to show that the coefficient functions $h_k^{(\ell,J)}(x)$ and $h_k^{(\ell,Y)}(x)$ are given by

$$h_k^{(\ell,J)}(x) = -\frac{\pi}{32}\int_0^x \mathrm{d}y\, y^3 Y_{2\ell+1}(y) g_{k-1}^{(\ell)}(y) \tag{4.12}$$

$$h_k^{(\ell,Y)}(x) = \frac{\pi}{32}\int_0^x \mathrm{d}y\, y^3 J_{2\ell+1}(y) g_{k-1}^{(\ell)}(y). \tag{4.13}$$

Because $x^{-2\ell-1}J_{2\ell+1}(x)$ is an entire function and because $x^{2\ell+1}Y_{2\ell+1}(x)$ is

$$(2/\pi)x^{2\ell+1}\ln(x)J_{2\ell+1}(x)$$

plus an entire function, there exist real, positive constants $B^{(\ell,J)}(x_0)$ and $B^{(\ell,Y)}(x_0)$, independent of x but dependent on x_0, such that

$$|J_{2\ell+1}(x)| \leqslant B^{(\ell,J)}(x_0)|x|^{2\ell+1} \qquad \text{and} \qquad |Y_{2\ell+1}(x)| \leqslant B^{(\ell,Y)}(x_0)|x|^{-2\ell-1} \tag{4.14}$$

for $|x| \leqslant |x_0|$. Here x_0 can be any finite number. An explicit $B^{(\ell,J)}(x_0)$ can be obtained by replacing the terms in the power series for $x^{-2\ell-1}J_{2\ell+1}(x)$ by their absolute values to obtain $B^{(\ell,J)}(x_0) = |x_0|^{-2\ell-1}I_{2\ell+1}(|x_0|)$. An explicit $B^{(\ell,Y)}(x_0)$, which is somewhat more complicated, can be obtained by a similar computation. The bounds (4.14) are used in (2.3), (4.10), (4.12) and (4.13). Mathematical induction on k then shows that

$$|g_k^{(\ell)}(x)| \leqslant \frac{B^{(\ell,J)}(x_0)}{k!}\left(\frac{\pi B^{(\ell,J)}(x_0)B^{(\ell,Y)}(x_0)}{64}\right)^k |x|^{4k+2\ell+1} \tag{4.15}$$

for $|x| \leqslant |x_0|$. The bound (4.15) shows that the expansion (2.1) converges uniformly in x for $|x| \leqslant |x_0|$ for any finite x_0. Similar arguments show that the corresponding expansions for the derivatives converge uniformly, and that the function to which the expansion (2.1) converges is a solution of the differential equation (4.5).

The derivation of the expansions (2.13) and (2.14) for the direct integral J and the exchange integral K begins with the insertion of (1.3) and (4.3) in the definitions (1.1) and (1.2) of J and K. Change variables from r_1, r_2 to x, y via

$$r_1 = \frac{x^2}{8(Z-1)} \qquad r_2 = \frac{y^2}{8(Z-1)} \tag{4.16}$$

perform the integration over x in the integral for J, and use (2.12). The results are

$$J = -\frac{Z}{16n^3}\left[\frac{(n+\ell)!}{(n-\ell-1)!n^{2\ell+1}}\right]\int_0^\infty \mathrm{d}y\, y(y^2+\gamma^{-1})\exp(-2\gamma y^2)[f_n^{(\ell)}(y)]^2 \tag{4.17}$$

$$K = \frac{Z\gamma^2}{(2\ell+1)n^3}\left[\frac{(n+\ell)!}{(n-\ell-1)!n^{2\ell+1}}\right]\int_0^\infty \mathrm{d}y\int_y^\infty \mathrm{d}x\, x^{-2\ell+2}y^{2\ell+4} \times \exp[-\gamma(x^2+y^2)]f_n^{(\ell)}(x)f_n^{(\ell)}(y). \tag{4.18}$$

Make the definitions

$$U(\lambda, \mu, \nu; \alpha, \beta, \gamma) = \int_0^\infty J_\mu(\alpha r) J_\nu(\beta r) r^{\lambda-1} \exp(-\gamma r^2)\, \mathrm{d}r \tag{4.19}$$

$$e^{(\ell,J)}_{k,m;k',m'}(\gamma) = \int_0^\infty \mathrm{d}y\, y^{3k+3k'+1}(y^2+\gamma^{-1}) \exp(-2\gamma y^2) \times J_{2\ell+2m+k+1}(y) J_{2\ell+2m'+k'+1}(y) \tag{4.20}$$

$$e^{(\ell,K)}_{k,m;k',m'}(\gamma) = \int_0^\infty \mathrm{d}y \int_y^\infty \mathrm{d}x\, x^{-2\ell+3k+2} y^{2\ell+3k'+4} \exp[-\gamma(x^2+y^2)] J_{2\ell+2m+k+1}(x) \times J_{2\ell+2m'+k'+1}(y). \tag{4.21}$$

Formulae (3.5)–(3.7) are obtained by using (2.6), (3.1), (4.7), (4.20) and (4.21) in (4.17) and (4.18). The definition (4.19) can be used to bring (4.20) to the form

$$e^{(\ell,J)}_{k,m;k',m'}(\gamma) = U(3k+3k'+4, 2\ell+k+2m+1, 2\ell+k'+2m'+1; 1, 1, 2\gamma) + \gamma^{-1} U(3k+3k'+2, 2\ell+k+2m+1, 2\ell+k'+2m'+1; 1, 1, 2\gamma). \tag{4.22}$$

The change of variables $x = r\cos(\theta)$, $y = r\sin(\theta)$ brings (4.20) to the form

$$e^{(\ell,K)}_{k,m;k',m'}(\gamma) = \int_0^{\pi/4} \mathrm{d}\theta\, (\cos\theta)^{-2\ell+3k+2} (\sin\theta)^{2\ell+3k'+4} \times U(3k+3k'+8, 2\ell+k+2m+1, 2\ell+k'+2m'+1; \cos\theta, \sin\theta, \gamma) \tag{4.23}$$

The needed values of U are obtained from the formulae

$$U(n+2k+2, n+\nu, \nu; \alpha, \beta, \gamma) = \sum_{i=0}^{k} \sum_{j=-i}^{n+k} \binom{k}{i} \binom{n+k+i}{i+j} \binom{n+k+\nu}{k-i} (k-i)! \times (-1)^j 2^{-n-2i-1} \gamma^{-n-k-i-1} \alpha^{n+i-j} \beta^{i+j} \exp\left(-\frac{\alpha^2+\beta^2}{4\gamma}\right) I_{\nu+i+j}\left(\frac{\alpha\beta}{2\gamma}\right) \tag{4.24}$$

$$U(n+2k+2, \nu, n+\nu; \alpha, \beta, \gamma) = \sum_{j=0}^{k} \sum_{i=-j}^{n+k} \binom{k}{j} \binom{n+k+j}{i+j} \binom{n+k+\nu}{k-j} (k-j)! \times (-1)^i 2^{-n-2j-1} \gamma^{-n-k-j-1} \alpha^{i+j} \beta^{n+j-i} \exp\left(-\frac{\alpha^2+\beta^2}{4\gamma}\right) I_{\nu+i+j}\left(\frac{\alpha\beta}{2\gamma}\right) \tag{4.25}$$

which are derived below (see equations (4.30)–(4.34)). The function $I_{\nu+i+j}[(\alpha\beta)/(2\gamma)]$ which appears in (4.24) and (4.25) is a modified Bessel function of the first kind in standard notation†. Formulae (3.8)–(3.11) are an immediate consequence of (4.22), (4.24) and (4.25). Make the definition

$$f(p,q,\nu;\gamma) = \exp[-1/(4\gamma)] \int_0^{\pi/4} d\theta (\sin\theta)^{2p-\nu+1} (\cos\theta)^{2q-\nu+1} I_\nu[(\sin\theta\cos\theta)/(2\gamma)] \tag{4.26}$$

Formulae (3.12)–(3.15) are obtained by using (4.19) and (4.24)–(4.26) in (4.23). Make the definition

$$g(p,q) = \int_0^{\pi/4} d\theta (\sin\theta)^{2p+1} (\cos\theta)^{2q+1}. \tag{4.27}$$

The power series (3.16) for $f(p,q,\nu;\gamma)$ is obtained by using the small z power series† for $I_\nu(z)$ to expand the I_ν in (4.26). Term-by-term integration with the aid of (4.27), which is justified by the uniform convergence of the power series for I_ν, yields (3.16). Formula (3.17) follows immediately from (4.26) and $\sin^2\theta + \cos^2\theta = 1$. The formulae (3.18)–(3.20) for $g(p,q)$ are obtained by using the change of variables $\cos(2\theta) = t$ to bring (4.27) to the form

$$g(p,q) = (\tfrac{1}{2})^{p+q+2} \int_0^1 dt\, (1-t)^p (1+t)^q. \tag{4.28}$$

Expanding the factor $(1+t)^q$ in the integrand of (4.28) in binomial series and integrating term-by-term with the aid of the beta function [14] yields (3.18) if $h(p,q)$ is defined by the sum

$$h(p,q) = \sum_{m=0}^{q} \binom{p+q+1}{m}. \tag{4.29}$$

The recursion (3.19)–(3.20) which is used for the evaluation of $h(p,q)$ follows easily from (4.29). Equations (3.21)–(3.23) for $c_0^{(\ell,K)}$ are most easily derived by using (4.19), (4.23), (4.26) and (4.30) below to show that

$$e_{0,0;0,0}^{(\ell,K)}(\gamma) = \left(-\frac{\partial}{\partial\gamma}\right)^3 \left[\frac{1}{2\gamma} f(2\ell+2, 1, 2\ell+1; \gamma)\right]. \tag{4.30}$$

Equations (3.21)–(3.23) follow from (2.7), (3.3), (3.6), (3.7), (4.29*a*) and $u = 1/(4\gamma)$.

We turn now to the derivation of (4.24). A formula for $U(\lambda,\mu,\nu;\alpha,\beta,\gamma)$ in the special case $\lambda = 2$, $\mu = \nu$ is derived in the Bateman project‡ and recorded in Magnus *et al*§. It is

$$U(2,\nu,\nu;\alpha,\beta,\gamma) = \frac{1}{2\gamma} \exp\left(-\frac{\alpha^2+\beta^2}{4\gamma}\right) I_\nu\left(\frac{\alpha\beta}{2\gamma}\right). \tag{4.31}$$

The formula‖ $J_{\mu+1}(z) = \mu z^{-1} J_\mu(z) - J'_\mu(z)$ can be used to show that

$$U(\lambda+1,\mu+1,\nu;\alpha,\beta,\gamma) = \left(\frac{\mu}{\alpha} - \frac{\partial}{\partial\alpha}\right) U(\lambda,\mu,\nu;\alpha,\beta,\gamma) \tag{4.32}$$

† [8] p 5, equation (12); [9] p 66.

‡ [8] p 50, equation (50).

§ [9] p 93.

‖ [8] p 12, equation (55); [9] p 67.

Mathematical induction on n carried out with the aid of (4.19), (4.30), (4.31) and the formula† $I'_\mu(z) = \mu z^{-1} I_\mu(z) + I_{\mu+1}(z)$ yields

$$U(n+2, n+\nu, \nu; \alpha, \beta, \gamma) = \left(\frac{1}{2\gamma}\right)^{n+1} \exp\left(-\frac{\alpha^2+\beta^2}{4\gamma}\right) \sum_{m=0}^{n} \binom{n}{m} \times (-1)^m \alpha^{n-m} \beta^m I_{\nu+m}\left(\frac{\alpha\beta}{2\gamma}\right). \tag{4.33}$$

The formula‡ $J_{\mu+1}(z) + J_{\mu-1}(z) = 2\mu z^{-1} J_\mu(z)$ can be used to show that

$$U(n+m+4, n+\nu, \nu; \alpha, \beta, \gamma) + U(n+m+4, n+\nu+2, \nu; \alpha, \beta, \gamma) = 2\alpha^{-1}(n+\nu+1) U(n+m+3, n+\nu+1, \nu; \alpha, \beta, \gamma). \tag{4.34}$$

Mathematical induction on k carried out with the aid of (4.33) yields

$$U(n+2k+2, n+\nu, \nu; \alpha, \beta, \gamma) = \sum_{m=0}^{k} \binom{k}{m} \binom{n+k+\nu}{k-m} (k-m)! \times (-1)^m \left(\frac{2}{\alpha}\right)^{k-m} U(n+k+m+2, n+k+m+\nu, \nu; \alpha, \beta, \gamma). \tag{4.35}$$

Formula (4.24) is obtained by combining (4.32) and (4.34). Formula (4.25) can be obtained from (4.24) by interchanging α and β and using the definition (4.19) of U.

The convergence of the expansions (2.13) and (2.14) for J and K for $n > (Z-1)/Z$ follows from the following theorem, which is taken from Copson [15].

Theorem. Let the function $F(z, t)$ satisfy the following conditions: (i) it is a continuous function of both variables when z lies within a closed contour C and $a \leqslant t \leqslant T$, for every finite value of T; (ii) for each such value of t, it is an analytic function of z, regular within C; (iii) the integral $f(z) = \int_a^\infty F(z, t)\, dt$ is convergent when z lies within C and uniformly convergent when z lies in any closed region D within C. Then $f(z)$ is an analytic function of z, regular within C, whose derivatives of all orders may be found by differentiating under the sign of integration.

We apply the theorem with $z = 1/n^2$ and $f(z) = J$ or K. The differential equation (4.5) implies that the dominant part of the large r behaviour of $R_{n,\ell}(r)$ for arbitrary complex values of n comes from exponential factors $\exp[\pm(Z-1)r/n]$. The factor $R_{1,0}(r)$ contributes an exponentially decaying factor $\exp(-Zr)$. It follows that the product $R_{1,0}(r)R_{n,\ell}(r)$ decays exponentially at large r for any (real or complex) value of n for which $|n| > (Z-1)/Z$. This exponential decay is used to establish the uniform convergence required by part (iii) of the hypothesis of the theorem quoted above; verification of the other parts of the hypothesis is straightforward.

† [8] p 79, equations (23) and (24); [9] p 67.

‡ [8] p 12, equation (56); [9] p 67.

5. Discussion

This paper provides the first tabulation of the coefficients in a $1/n$ expansion for the hydrogenic two-electron direct and exchange integrals of the Coulomb interaction. Only the leading term was known from previous work [10]. The higher-order terms are essential to studies of the limits of validity of the Ritz expansion (1.2) for the quantum defect [4, 5], through the constraint equations (1.7) to (1.10). No failure of the Ritz expansion has yet been found, even when cross-terms between exchange effects and core polarization by the Rydberg electron are included [5]. Some of the same analytical techniques may be useful in extracting $1/n$ expansions for higher-order terms that may eventually set a limit on the validity of the Ritz expansion as an exact functional form for the non-relativistic energies of helium.

The extension of Hartree's theorem to cover non-local exchange effects in atoms more complicated than helium has not yet been discussed. However, the helium results suggest that for an isolated sequence of Rydberg states, the theorem applies at least in a first approximation to the pair-wise exchange interactions between a Rydberg electron and the core electrons. Multiple overlapping sequences of Rydberg states introduce further complications that can be treated by means of multi-channel quantum defect theory [16].

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