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Variational solution of the Dirac–Coulomb equation using explicitly correlated wavefunctions. Matrix elements and radial integrals

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Abstract. An algorithm for the evaluation of two-electron integrals appearing in an implementation of the Hylleraas-CI method for solving the Dirac–Coulomb eigenvalue problem is presented. All integrals have been expressed analytically, though in some cases as infinite series.

1. Introduction

A variational solution of the Dirac–Coulomb eigenvalue problem for a two-electron atom using an explicitly correlated trial function was not attempted until very recently [1, 2]. Therefore the matrix elements and the elementary integrals which are relevant for solving this problem are not available in the literature. In this paper integrals which arose when solving the Dirac–Coulomb equation by means of either the Hylleraas-CI (Hy-CI) [3, 4] or the superposition of correlated configurations (SCC) [5] method are evaluated using an approach originally formulated by Sack [6]. Some of the integrals discussed in this paper have also been evaluated, using another method, by Kołakowska [2].

The method of Sack [6] is based on the following generalization of the well known Laplace expansion of r_{12}^{-1}

$$f(r_{12}) = \sum_{l=0}^{\infty} f_l(r_>, r_<) P_l(\cos\theta_{12}) \tag{1}$$

where $f(r_{12})$ is a function which can be represented as a finite or infinite sum of powers of r_{12}, not necessarily integer; $r_> \stackrel{\text{def}}{=} \max\{r_1, r_2\}$, $r_< \stackrel{\text{def}}{=} \min\{r_1, r_2\}$, and

$$P_l(\cos\theta_{12}) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y^*_{l,m}(1) Y_{l,m}(2) \tag{2}$$

is a Legendre polynomial. Due to Sack's expansion (1) an arbitrary matrix element of $f(r_{12})$ between either scalar or spinor bras ($\langle B|$) and kets ($|K\rangle$) may be expressed as

$$\langle B|f(r_{12})\breve{o}|K\rangle = \sum_{l=0}^{\infty} \langle R_B(r_1, r_2)|f_l(r_>, r_<)|R_K(r_1, r_2)\rangle_R \langle \Psi_{J_B}|P_l(\cos\theta_{12})\breve{o}|\Psi_{J_K}\rangle_\Omega \tag{3}$$

where $\breve{o}$ is an operator acting on the angular variables, R_B/R_K are the radial parts (assumed to be scalar) and Ψ_{J_B}/Ψ_{J_K} are the angular and spinor parts of $\langle B|/|K\rangle$. It is important to

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note that, due to the triangle inequality, only a finite number of terms in equation (3) do not vanish. Let us note that equation (3) is a generalization of the analogous Slater formula of non-relativistic theory of atoms [7].

2. Reduction of two-electron matrix elements

Let B and K denote non-correlated configurations corresponding, respectively, to the bra and ket wavefunctions. Each of them may be represented as a product of a radial function $R_{B/K}(r_1, r_2)$ and an angular function

$$\Psi_{J,M,j_1,j_2,\pi_1,\pi_2}(1,2) = \sum_{m_1,m_2} (-1)^{j_1-j_2+M}\sqrt{2J+1}\begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M \end{pmatrix}\varphi^{\pi_1}_{j_1,m_1}(1)\otimes\varphi^{\pi_2}_{j_2,m_2}(2) \tag{4}$$

with $\pi_i = \pm 1$ defined so that $j_i = l_i + \frac{\pi_i}{2}$ and $\varphi^{\pi_i}_{j_i,m_i}$, $i = 1, 2$, are one-electron spin-angular functions formed by the combination of the Pauli spinor with the spherical harmonics. The angular functions are eigenfunctions of the angular momentum defined by a complete set of the quantum numbers J, M, j_1, j_2, π_1 and π_2. Let $g_{B/K}(r_{12})$ denote the following correlation factors r^q_{12}, $(T_i r^q_{12})$ and $(T_i T_j r^q_{12})$, where $T_i \stackrel{\text{def}}{=} \boldsymbol{\sigma}_i \boldsymbol{p}_i$ and q is an arbitrary real number. Let Tg denote the operator defined as

$$Tg = (Tg) + gT$$

where (Tg) is the result of action of T on g. As one can see T_i is Hermitian. The matrices

$$(T_1 r_{12}) = -\mathrm{i}\boldsymbol{\sigma}_1\hat{r}_{12} \qquad (T_2 r_{12}) = -\mathrm{i}\boldsymbol{\sigma}_2\hat{r}_{21}$$

where $\hat{r}_{ij} = \frac{r_{ij}}{r_{12}}$ and i is the imaginary unit, are unitary. Indeed,

$$(T_i r_{12})^\dagger (T_i r_{12}) = (\boldsymbol{\sigma}_i \hat{r}_{12})^2 = \hat{r}^2_{12} = I$$

where I is a 2×2 unit matrix. In general $\hat{r}$ stands hereafter for $\boldsymbol{r}/r$, where $\boldsymbol{r}$ is a vector and $r = |\boldsymbol{r}|$. Similarly, the matrix $(T_1 f(r_{12})) = -\mathrm{i}(\boldsymbol{\sigma}_1 \mathrm{grad}_1 f(r_{12}))$ is anti-Hermitian since it is a product of $\mathrm{i}\boldsymbol{\sigma}_1$ by a real scalar function. Obviously, also $(T_2 f(r_{12}))$ is anti-Hermitian. All two-electron matrix elements appearing in a two-electron Hy-CI Dirac–Coulomb problem may be expressed in terms of:

$$C_{BK}(\hat{o}) = \langle g_B(r_{12})B|\hat{o}|g_K(r_{12})K\rangle \tag{5}$$

where $\hat{o}$ stands for one of the following operators: 1, $1/r_{12}$ and T_i. We assume hereafter that the basis functions are constructed in such a way that all matrix elements $C_{BK}(\hat{o})$ are real.

The operators

$$T_i = -\mathrm{i}\boldsymbol{\sigma}_i \boldsymbol{\nabla}_i \tag{6}$$

play a crucial role in the further considerations. Therefore it is useful to list their properties:

$$r^p_{12}(T_i r^q_{12}) = \begin{cases} \dfrac{q}{p+q}\left(T_i r^{p+q}_{12}\right) & \text{if } p+q \neq 0 \\ q(T_i \ln r_{12}) & \text{if } p+q = 0 \end{cases} \tag{7}$$

$$(T_i^2 r^p_{12}) = -p(p+1)r^{p-2}_{12} \tag{8}$$

$$\langle B|(T_i f(r_{12}))|K\rangle = \langle T_i B|f(r_{12})|K\rangle - \langle B|f(r_{12})|T_i K\rangle \tag{9}$$

$$(T_1 r^p_{12})(T_2 r^q_{12}) = \frac{pq}{(p+q)(p+q-2)}(T_1 T_2 r^{(p+q)}_{12}) + \frac{pq}{p+q-2} r^{(p+q-2)}_{12}\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2 \tag{10}$$

$$(T_i r_{12}) = \frac{\mathrm{i}}{r_{12}} \boldsymbol{\sigma}_i (\boldsymbol{r}_j - \boldsymbol{r}_i) \tag{11}$$

$$(T_j \boldsymbol{\sigma}_i \boldsymbol{r}_j) = -\mathrm{i} \boldsymbol{\sigma}_i \boldsymbol{\sigma}_j . \tag{12}$$

Let us note that equation (10) is not applicable when $p + q = 0, 2$, in that case one has to use equations (11) and (12). In the spherical coordinates it may be expressed as

$$T_i = -\mathrm{i}(\boldsymbol{\sigma}_i \hat{r}_i) \left(\frac{\partial}{\partial r_i} - \frac{\boldsymbol{\sigma}_i \boldsymbol{L}_i}{r_i} \right) \tag{13}$$

where $\boldsymbol{\sigma}_i \boldsymbol{L}_i$ acts on the spherical variables only. The eigenfunctions of $\boldsymbol{\sigma}_i \boldsymbol{L}_i$ are (4) and the eigenvalues are equal to $\lambda_i = \pi_i (j_i + \frac{1}{2}) - 1$. Therefore, T_i when it acts on either B or K may be reduced to

$$T_i = -\mathrm{i}(\boldsymbol{\sigma}_i \hat{r}_i) \left(\frac{\partial}{\partial r_i} - \frac{\lambda_i}{r_i} \right) \tag{14}$$

acting on the radial part of the respective function (B or K). Using the properties of T_i and equations (7)–(12) one may express matrix elements $C_{BK}(\hat{o})$ in terms of

$$D_{BK}(f(r_{12})\breve{o}) = \langle B | f(r_{12}) \breve{o} | K \rangle \tag{15}$$

where $f(r_{12})$ stands for either r_{12}^s or $\ln r_{12}$ and $\breve{o}$ denotes one of the following operators: 1, $(\boldsymbol{\sigma}_1 \boldsymbol{\sigma}_2)$, $(\boldsymbol{\sigma}_i \hat{r}_j)$, $(\boldsymbol{\sigma}_i \hat{r}_i)$, or $[(\boldsymbol{\sigma}_1 \hat{r}_1)(\boldsymbol{\sigma}_2 \hat{r}_2)]$.

3. Radial integrals

In the following sections three kinds of radial integrals corresponding to three different forms of $f(r_{12})$ in equation (3):

- $f(r_{12}) = r_{12}^s$, where $s \in \mathbb{R}$,
- $f(r_{12}) = r_{12}^k$, where $k = -1, 0, 1, 2, \ldots$,
- $f(r_{12}) = \ln(r_{12})$,

are considered. The form of the radial functions $R_B(r_1, r_2)$ and $R_K(r_1, r_2)$ has been restricted to

$$R_A(r_1, r_2) = r_1^{\gamma_1^A} r_2^{\gamma_2^A} \exp(-\alpha_1^A r_1 - \alpha_2^A r_2)$$

where $\alpha_j^A > 0$ for $A = B, K$ and $j = 1, 2$. We define

$$R(r_1, r_2) \equiv R_B(r_1, r_2) R_K(r_1, r_2) r_1^2 r_2^2 \equiv r_1^{\gamma_1} r_2^{\gamma_2} \exp(-\alpha_1 r_1 - \alpha_2 r_2) \tag{16}$$

with $\gamma_j = \gamma_j^B + \gamma_j^K + 2$ and $\alpha_j = \alpha_j^B + \alpha_j^K$, $j = 1, 2$. The parameters in these radial functions may be chosen to allow for their correct asymptotic behaviour both at the origin and infinity. The correlation factors are usually chosen as polynomials in r_{12}. However, the Dirac–Coulomb cusp condition Kutzelnigg [8] requires real powers of r_{12}. Using integer powers of r_{12} is motivated by the simplicity of the resulting formalism. However, as it is shown in the next section, the formalism in which the correlation factors contain real powers of r_{12} is only slightly more complicated than its counterpart with integer powers only (using integer powers only implies that the logarithmic terms must be included).

The most complicated are the formulae for the integrals containing logarithmic terms. Therefore, for this case both analytical and numerical algorithm have been presented. The analytical method is the most efficient for $\alpha_1 = \alpha_2$. With increasing difference between α_1 and α_2 its convergence gradually deteriorates and, in some cases, the numerical approach may be more efficient.

3.1. Real powers of r_{12}

If ($s \in \mathbb{R}$) then, according to Sack [6],

$$f_l(r_>, r_<) \equiv f_{l,s} = \frac{(-\frac{1}{2}s)_l}{(\frac{1}{2})_l} r_>^s \left(\frac{r_<}{r_>}\right)^l {}_2\mathrm{F}_1\left(l - \frac{s}{2}, -\frac{1}{2} - \frac{s}{2}; l + \frac{3}{2}; \frac{r_<^2}{r_>^2}\right). \tag{17}$$

By expanding the hypergeometric function into a power series one obtains

$$f_{l,s} = \sum_{t=0}^{\infty} (2l+1) C_{slt} r_<^{l+2t} r_>^{s-(l+2t)} \tag{18}$$

where

$$C_{slt} = \frac{2^l(-\frac{1}{2}s)_l}{(2l+1)!!} \frac{(l - \frac{1}{2}s)_t(-\frac{1}{2} - \frac{1}{2}s)_t}{(l + \frac{3}{2})_t t!} \tag{19}$$

and $(\alpha)_t$ is the Pochhammer's symbol. If we define

$$\Theta_l \stackrel{\text{def}}{=} 4\pi \left\langle \Psi_{J_B} \middle| \left(\sum_{m=-l}^{l} Y_{l,m}^*(1) Y_{l,m}(2) \right) \breve{o} \middle| \Psi_{J_K} \right\rangle_\Omega \tag{20}$$

and note that $\Theta_l = 0$ unless $l = l_{\min}, l_{\min}+2, l_{\min}+4, \ldots, l_{\max}$, then the angular integration gives

$$\langle \Psi_{J_B} | r_{12}^s \breve{o} | \Psi_{J_K} \rangle_\Omega = \sum_{\substack{q=l_{\min} \\ (\text{step2})}}^{\infty} r_<^q r_>^{s-q} \sum_{\substack{l=l_{\min} \\ (\text{step2})}}^{\min(q, l_{\max})} C_{slt} \Theta_l \tag{21}$$

where $t = \frac{q-l}{2}$. The radial integrals are given by

$$\begin{aligned} \Upsilon_q(s) &\equiv \langle R_B(r_1, r_2) | r_<^q r_>^{s-q} | R_K(r_1, r_2) \rangle_R \\ &= V(\alpha_1, \alpha_2; \gamma_1 + q, \gamma_2 + s - q) + V(\alpha_2, \alpha_1; \gamma_2 + q, \gamma_1 + s - q) \end{aligned} \tag{22}$$

where the standard notation [9, 10]:

$$V(\alpha_1, \alpha_2; \gamma_1, \gamma_2) \stackrel{\text{def}}{=} \int_0^\infty \mathrm{d}r_1 \int_{r_1}^\infty \mathrm{d}r_2 \, r_1^{\gamma_1} r_2^{\gamma_2} \mathrm{e}^{-\alpha_1 r_1 - \alpha_2 r_2} \tag{23}$$

$$= \frac{\Gamma(\gamma_1 + \gamma_2 + 2)}{(\gamma_1 + 1)(\alpha_1 + \alpha_2)^{\gamma_1 + \gamma_2 + 2}} {}_2\mathrm{F}_1\left(1, \gamma_1 + \gamma_2 + 2; \gamma_1 + 2; \frac{\alpha_1}{\alpha_1 + \alpha_2}\right) \tag{24}$$

for the integrals corresponding to $\gamma_1 \geqslant 0 \wedge \gamma_1 + \gamma_2 \geqslant -1$ has been introduced. Finally,

$$\langle B | r_{12}^s \breve{o} | K \rangle = \sum_{\substack{q=l_{\min} \\ (\text{step2})}}^{\infty} \Upsilon_q(s) \sum_{\substack{l=l_{\min} \\ (\text{step2})}}^{\min(q, l_{\max})} C_{slt} \Theta_l. \tag{25}$$

As one can see by inspection of equations (24) and (25), $\langle B | r_{12}^s \breve{o} | K \rangle$ is expressed as a double series. Therefore a direct application of equation (25) is rather cumbersome. A considerable simplification results from using recurrent relations for the integrals:

$$V(\alpha_1, \alpha_2; \gamma_1, \gamma_2) = \frac{1}{\alpha_2(\gamma_1 + 1)} \left[\alpha_1 \gamma_2 V(\alpha_1, \alpha_2; \gamma_1 + 1, \gamma_2 - 1) + \frac{\Gamma(\gamma_1 + \gamma_2 + 2)}{(\alpha_1 + \alpha_2)^{\gamma_1 + \gamma_2 + 1}} \right] \tag{26}$$

$\gamma_1 \geqslant 0, \gamma_1 + \gamma_2 \geqslant -1$.

As one can see, the radial integrals which appear in the series (25) asymptotically behave as follows

$$V(\alpha_1, \alpha_2; \gamma_1 + n, \gamma_2 - n) \leqslant \frac{C}{\delta + n} \underset{n \to \infty}{\longrightarrow} 0$$

where C and δ are real constants. Moreover, using the Gauss criterion, it is easy to check, that the series (25) is convergent for $s > -3$.

3.2. Integer powers of r_{12}

In the case of integer powers of r_{12}, expansion (1) reduces to the Perkins formula [11]:

$$r_{12}^k = 4\pi \sum_{l=0}^{L_1^k} \left(\sum_{m=-l}^{l} Y_{lm}^*(1) Y_{lm}(2) \right) \left(\sum_{t=0}^{L_2^{k,l}} C_{klt} r_<^{l+2t} r_>^{k-(l+2t)} \right) \qquad (27)$$
$$k = -1, 0, 1, 2, \ldots$$

where $L_1^k = k/2$ and $L_2^{k,l} = k/2 - l$ if k is even while $L_1^k = \infty$ and $L_2^{k,l} = (k+1)/2$ if k is odd. The coefficient C_{klt} are given as

$$C_{klt} = \frac{1}{k+2} \binom{k+2}{2t+1} \prod_{\alpha=0}^{\min[l-1,(k+1)/2]} \frac{2t-k+2\alpha}{2t+1+2l-2\alpha} \qquad \text{if } l > 0$$
$$C_{k0t} = \frac{1}{k+2} \binom{k+2}{2t+1}.$$

As one can see, in this case all sums are finite.

If k is even, then

$$\langle \Psi_{J_B} | r_{12}^k | \Psi_{J_K} \rangle_\Omega = \sum_{\substack{q=l_{\min} \\ (\text{step2})}}^{k-l_{\min}} r_1^q r_2^{k-q} \sum_{\substack{l=l_{\min} \\ (\text{step2})}}^{\min(q,k-q,l_{\max})} C_{klt} \Theta_l \qquad (28)$$

where $t = \frac{q-l}{2}$. The result of integration may be expressed, in this case, in terms of r_1 and r_2 rather than $r_<$ and $r_>$. This is because the RHS of equation (27) is a symmetric function of $r_<$ and $r_>$. After using equations (16) and (28) one obtains

$$\langle B | r_{12}^k \breve{o} | K \rangle = \sum_{\substack{q=l_{\min} \\ (\text{step2})}}^{k-l_{\min}} \frac{\Gamma(\gamma_1+q+1)}{\alpha_1^{\gamma_1+q+1}} \frac{\Gamma(\gamma_2+k-q+1)}{\alpha_2^{\gamma_2+k-q+1}} \sum_{\substack{l=l_{\min} \\ (\text{step2})}}^{\min(q,k-q,l_{\max})} C_{klt} \Theta_l. \qquad (29)$$

In this case a substantial simplification of the final result is due to the explicit separation of the radial variables r_1 and r_2.

If k is odd, then

$$\langle \Psi_{J_B} | r_{12}^k | \Psi_{J_K} \rangle_\Omega = \sum_{\substack{q=l_{\min} \\ (\text{step2})}}^{l_{\max}+k+1} r_<^q r_>^{k-q} \sum_{\substack{l=\max(q-k-1,l_{\min}) \\ (\text{step2})}}^{\min(q,l_{\max})} C_{klt} \Theta_l \qquad (30)$$

where $t = \frac{q-l}{2}$. The final result is, in this case, analogous to that for the real powers of r_{12} (equation (25)):

$$\langle B | r_{12}^k \breve{o} | K \rangle = \sum_{\substack{q=l_{\min} \\ (\text{step2})}}^{l_{\max}+k+1} \Upsilon_q(k) \sum_{\substack{l=\max(q-k-1,l_{\min}) \\ (\text{step2})}}^{\min(q,l_{\max})} C_{klt} \Theta_l. \qquad (31)$$

However, the sums in the last equation are finite.

3.3. Logarithmic terms

In this case the radial functions in the expansion of Sack [6] for $l > 0$ are given by

$$f_l(r_>, r_<) \equiv f_l^{\ln}(r_>, r_<) = -\frac{(l-1)!}{(\frac{3}{2})_{l-1}} \left(\frac{r_<}{r_>}\right)^l {}_2\mathrm{F}_1\left(l, -\frac{1}{2}; l+\frac{3}{2}; \frac{r_<^2}{r_>^2}\right). \tag{32}$$

For $l = 0$ the radial function reads:

$$f_0^{\ln}(r_>, r_<) = \ln(r_>) + \sum_{t=1}^{\infty} \frac{(r_</r_>)^{2t}}{2t(4t^2-1)}. \tag{33}$$

The expansion (1) of $f(r_{12})$ becomes

$$\ln(r_{12}) = \ln(r_>) + \sum_{t=1}^{\infty} C_{0,t}^{\ln} r_<^{2t} r_>^{-2t} + 4\pi \sum_{l=1}^{\infty} \left(\sum_{m=-l}^{l} Y_{lm}^*(1) Y_{lm}(2) \right) \left(\sum_{t=0}^{\infty} C_{lt}^{\ln} r_<^{l+2t} r_>^{-(l+2t)} \right) \tag{34}$$

where

$$C_{lt}^{\ln} = 2^{l-1} \frac{(l+t-1)!(2t+1)!!}{(4t^2-1)t!(2l+2t+1)!!}. \tag{35}$$

Let us note that $C_{lt}^{\ln}$ is undefined for $l = 0 \wedge t = 0$. By defining

$$C_{0,0}^{\ln} \stackrel{\text{def}}{=} 0 \tag{36}$$

one may rewrite equation (34) in a compact form:

$$\ln(r_{12}) = \ln(r_>) + 4\pi \sum_{l=0}^{\infty} \left(\sum_{m=-l}^{l} Y_{lm}^*(1) Y_{lm}(2) \right) \left(\sum_{t=0}^{\infty} C_{lt}^{\ln} r_<^{l+2t} r_>^{-(l+2t)} \right). \tag{37}$$

The angular integration gives

$$\langle \Psi_{J_B} | \ln(r_{12}) \check{o} | \Psi_{J_K} \rangle_\Omega = \ln(r_>)\Theta_0 + \sum_{\substack{q=l_{\min} \\ (\text{step2})}}^{\infty} r_<^q r_>^{-q} \sum_{\substack{l=l_{\min} \\ (\text{step2})}}^{\min(q, l_{\max})} C_{lt}^{\ln} \Theta_l \tag{38}$$

where $t = \frac{q-l}{2}$. The radial integrals are equal to

$$\langle B | \ln(r_{12}) \check{o} | K \rangle = \int_0^\infty \int_0^\infty \ln(r_>) r_1^{\gamma_1} r_2^{\gamma_2} \mathrm{e}^{-\alpha_1 r_1 - \alpha_2 r_2} \, \mathrm{d}r_1 \, \mathrm{d}r_2 \, \Theta_0 + \sum_{\substack{q=l_{\min} \\ (\text{step2})}}^{\infty} \Upsilon_q(0) \sum_{\substack{l=l_{\min} \\ (\text{step2})}}^{\min(q, l_{\max})} C_{lt}^{\ln} \Theta_l. \tag{39}$$

The second term on the RHS of equation (39) is similar to the one in equation (25) and may be evaluated using the same method. It is easy to see that the corresponding series behaves asymptotically, for $q \to \infty$, as $1/q^3$. The first term (containing $\ln(r_>)$) is more difficult to calculate. It may be expressed as

$$\int_0^\infty \int_0^\infty \ln(r_>) r_1^{\gamma_1} r_2^{\gamma_2} \mathrm{e}^{-\alpha_1 r_1 - \alpha_2 r_2} \, \mathrm{d}r_1 \, \mathrm{d}r_2 = \boldsymbol{L}_1 + \boldsymbol{L}_2 \tag{40}$$

where

$$\boldsymbol{L}_1 \equiv \int_0^\infty \mathrm{d}r_1 \int_{r_1}^\infty \mathrm{d}r_2 \, \ln(r_2) r_1^{\gamma_1} r_2^{\gamma_2} \mathrm{e}^{-\alpha_1 r_1 - \alpha_2 r_2}$$

and

$$\boldsymbol{L}_2 \equiv \int_0^\infty \mathrm{d}r_2 \int_{r_2}^\infty \mathrm{d}r_1\ \ln(r_1) r_1^{\gamma_1} r_2^{\gamma_2} \mathrm{e}^{-\alpha_1 r_1 - \alpha_2 r_2}.$$

The integrals may be evaluated as follows. A multiple integration by parts gives

$$\boldsymbol{L}_1 = \sum_{k=1}^{n} \frac{\alpha_1^{k-1}}{(\gamma_1+1)_k} \frac{\Gamma(\gamma_1+\gamma_2+k+1)}{(\alpha_1+\alpha_2)^{\gamma_1+\gamma_2+k+1}} [\Psi(\gamma_1+\gamma_2+k+1) - \ln(\alpha_1+\alpha_2)] + R_n^{\ln}$$

where Ψ stands for digamma function, and $R_n^{\ln}$ is the remainder

$$R_n^{\ln} = \frac{\alpha_1^n}{(\gamma_1+1)_n} \int_0^\infty \mathrm{d}r_1\, r_1^{\gamma_1+n} \mathrm{e}^{-\alpha_1 r_1} \int_{r_1}^\infty \mathrm{d}r_2\, r_2^{\gamma_2} \ln(r_2) \mathrm{e}^{-\alpha_2 r_2} \tag{41}$$

and it is easy to prove that it tends to 0 when $n \to \infty$. As one can check, asymptotically for $n \to \infty$,

$$|R_n^{\ln}| \leqslant C(n+\delta)^\delta \left(\frac{\alpha_1}{\alpha_1+\alpha_2}\right)^n$$

where δ and C are real constants. After some rearrangement one finds

$$\boldsymbol{L}_1 = \frac{\Gamma(\gamma_1+\gamma_2+2)}{(\alpha_1+\alpha_2)^{\gamma_1+\gamma_2+2}} \frac{1}{(\gamma_1+1)} \sum_{k=0}^{n-1} \left(\frac{\alpha_1}{\alpha_1+\alpha_2}\right)^k \frac{(\gamma_1+\gamma_2+2)_k}{(\gamma_1+2)_k}$$
$$\times \left[\sum_{l=0}^{k} \frac{1}{\gamma_1+\gamma_2+1+l} + \Psi(\gamma_1+\gamma_2+1) - \ln(\alpha_1+\alpha_2) \right] + R_n^{\ln}.$$

Finally, the exact expression for $\boldsymbol{L}_1$ may be written as

$$\boldsymbol{L}_1 = \frac{\Gamma(\gamma_1+\gamma_2+2)}{(\alpha_1+\alpha_2)^{\gamma_1+\gamma_2+2}} \frac{1}{(\gamma_1+1)} \left\{ {}_2\mathrm{F}_1\left(1, \gamma_1+\gamma_2+2; \gamma_1+2; \frac{\alpha_1}{\alpha_1+\alpha_2}\right) \right.$$
$$\times [\Psi(\gamma_1+\gamma_2+1) - \ln(\alpha_1+\alpha_2)]$$
$$\left. + \sum_{k=0}^{\infty} \left(\frac{\alpha_1}{\alpha_1+\alpha_2}\right)^k \frac{(\gamma_1+\gamma_2+2)_k}{(\gamma_1+2)_k} \sum_{l=0}^{k} \frac{1}{\gamma_1+\gamma_2+1+l} \right\}. \tag{42}$$

A similar analysis may be performed for $\boldsymbol{L}_2$.

Alternatively, the integrals containing the logarithmic terms may be evaluated numerically [12, 13]. The numerical method proved to be very stable and accurate (only two significant figures are lost relative to the double precision accuracy). The numerical approach has been derived using the following consideration. Let us introduce functions $\bar{f}_l(r_1, r_2)$ defined in the following way

$$\bar{f}_l(r_1, r_2) \stackrel{\text{def}}{=} f_l(r_>(r_1, r_2), r_<(r_1, r_2)).$$

As one can show (Sack [6]),

$$\bar{f}_0^{\ln} = \ln|r_1 - r_2| + \frac{(r_1+r_2)^2}{4r_1 r_2} \ln\left|\frac{r_1+r_2}{r_1-r_2}\right| - \frac{1}{2} \tag{43}$$

$$\bar{f}_1^{\ln} = \frac{3}{16}\left(\frac{r_1^2-r_2^2}{r_1 r_2}\right)^2 \ln\left|\frac{r_1+r_2}{r_1-r_2}\right| - \frac{3}{8}\left(\frac{r_1^2+r_2^2}{r_1 r_2}\right) \tag{44}$$

and for $l \geqslant 1$ the recurrent relation:

$$\frac{r_1^2+r_2^2}{r_1 r_2} \bar{f}_l^{\ln} - \frac{2l+4}{2l+3} \bar{f}_{l+1}^{\ln} - \frac{2l-2}{2l-1} \bar{f}_{l-1}^{\ln} + \delta_{l,1} = 0. \tag{45}$$

As in the case of equation (40) one may conveniently split the integration area into two parts:

$$\langle R_B(r_1, r_2)|\bar{f}_l^{\ln}(r_1, r_2)|R_K(r_1, r_2)\rangle_R = \boldsymbol{P}_1 + \boldsymbol{P}_2 \tag{46}$$

where

$$\boldsymbol{P}_1 \equiv \int_0^\infty \mathrm{d}r_1 \int_{r_1}^\infty \mathrm{d}r_2\, \bar{f}_l^{\ln} r_1^{\gamma_1} r_2^{\gamma_2} \mathrm{e}^{-\alpha_1 r_1 - \alpha_2 r_2}$$

and

$$\boldsymbol{P}_2 \equiv \int_0^\infty \mathrm{d}r_2 \int_{r_2}^\infty \mathrm{d}r_1\, \bar{f}_l^{\ln} r_1^{\gamma_1} r_2^{\gamma_2} \mathrm{e}^{-\alpha_1 r_1 - \alpha_2 r_2}.$$

By introducing new variables $s = r_2$ and $t = r_1/r_2$, equations (43) and (44) may be expressed as

$$\bar{f}_0^{\ln} = \ln(s) + \frac{(1+t)^2}{4t}\ln(1+t) - \frac{(1-t)^2}{4t}\ln|1-t| - \frac{1}{2} \tag{47}$$

$$\bar{f}_1^{\ln} = \frac{3}{16}\left(\frac{1-t^2}{t}\right)^2 \ln\left|\frac{1+t}{1-t}\right| - \frac{3}{8}\left(\frac{1+t^2}{t}\right). \tag{48}$$

Then, $\bar{f}_0^{\ln}$ and $\bar{f}_1^{\ln}$ may be expressed as $\bar{f}_l^{\ln} = \delta_{0,l}\ln s + \tilde{f}_l(t)$, where $l = 0, 1$ and, consequently, $\boldsymbol{P}_1$ may be expressed as a sum of $\boldsymbol{N}_1$ and $\boldsymbol{N}_2$, where

$$\boldsymbol{N}_1 \equiv \int_0^\infty \mathrm{d}r_1 \int_{r_1}^\infty \mathrm{d}r_2\, \delta_{0,l} \ln(r_2) r_1^{\gamma_1} r_2^{\gamma_2} \mathrm{e}^{-\alpha_1 r_1 - \alpha_2 r_2}$$

may be evaluated analytically using equation (42) and

$$\boldsymbol{N}_2 \equiv \int_0^\infty \mathrm{d}r_1 \int_{r_1}^\infty \mathrm{d}r_2\, \tilde{f}_l(r_1/r_2) r_1^{\gamma_1} r_2^{\gamma_2} \mathrm{e}^{-\alpha_1 r_1 - \alpha_2 r_2}$$

may be transformed as follows

$$\begin{aligned}\boldsymbol{N}_2 &= \int_0^\infty \mathrm{d}r_2 \int_0^{r_2} \mathrm{d}r_1\, \tilde{f}_l(r_1/r_2) r_1^{\gamma_1} r_2^{\gamma_2} \mathrm{e}^{-\alpha_1 r_1 - \alpha_2 r_2} \\ &= \int_0^\infty s\,\mathrm{d}s \int_0^1 \mathrm{d}t\, \tilde{f}_l(t) s^{\gamma_1+\gamma_2} t^{\gamma_1} \mathrm{e}^{-s(\alpha_2 + t\alpha_1)} \\ &= \Gamma(\gamma_1+\gamma_2+2) \int_0^1 \tilde{f}_l(t) \frac{t^{\gamma_1}}{(\alpha_2 + t\alpha_1)^{\gamma_1+\gamma_2+2}}\,\mathrm{d}t. \end{aligned} \tag{49}$$

Then $\boldsymbol{N}_2$ is expressed by an integral in which the integrand has endpoint singularities of algebraico-logarithmic type:

$$\int_0^1 g(t) t^\alpha (1-t)^\beta \ln(1-t)\,\mathrm{d}t.$$

If $g(t)$ is regular for $t \in [0, 1]$ and $\alpha, \beta > -1$ (as it is in the case under consideration), a numerical evaluation of this integral may be performed using a standard package of numerical integration procedures. A similar procedure may be performed for $\boldsymbol{P}_2$.

The integrals with $l > 1$ may be determined using the recurrent relation (45):

$$\begin{aligned}&\int_0^\infty \int_0^\infty f_{l+1}^{\ln}(r_1, r_2) r_1^{\gamma_1} r_2^{\gamma_2} \mathrm{e}^{-\alpha_1 r_1 - \alpha_2 r_2}\,\mathrm{d}r_1\,\mathrm{d}r_2 \\ &\qquad = \frac{2l+3}{2l+4}\left[\int_0^\infty \int_0^\infty \left(\frac{r_1}{r_2} + \frac{r_2}{r_1}\right) f_l^{\ln}(r_1, r_2) r_1^{\gamma_1} r_2^{\gamma_2} \mathrm{e}^{-\alpha_1 r_1 - \alpha_2 r_2}\,\mathrm{d}r_1\,\mathrm{d}r_2\right.\end{aligned}$$

$$-\frac{2l-2}{2l-1}\int_0^\infty\int_0^\infty f_l^{\ln}(r_1,r_2)r_1^{\gamma_1}r_2^{\gamma_2}\mathrm{e}^{-\alpha_1 r_1-\alpha_2 r_2}\,\mathrm{d}r_1\,\mathrm{d}r_2$$
$$+\delta_{l,1}\int_0^\infty\int_0^\infty r_1^{\gamma_1}r_2^{\gamma_2}\mathrm{e}^{-\alpha_1 r_1-\alpha_2 r_2}\,\mathrm{d}r_1\,\mathrm{d}r_2\Bigg]. \tag{50}$$

Unfortunately, only the integrals for which $\gamma_1, \gamma_2 \geqslant l$ may be evaluated using equation (50).

4. Conclusions

This work gives a new method for evaluation of matrix elements appearing when the variational approach is applied to solving the Dirac–Coulomb equation using explicitly correlated trial functions. Within this method all matrix elements may be expressed as linear combinations of products of several primitive angular and radial integrals. The method is applicable also in the case when the relativistic two-electron terms (Gaunt or Breit corrections) are taken into account. The algorithm is numerically stable—its accuracy is limited only by the accuracy of the representations of the numbers in the computer. Although the evaluation of the integrals constitutes a small fraction of the total CPU time needed for solving the Dirac–Coulomb problem, looking for more efficient and simpler algorithms is still a challenge.

The method has been implemented in a FORTRAN 77 program designed to solve variationally the Dirac–Coulomb equation for helium-like ions. The results are being prepared for publication [14].

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