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Matrix Elements of the Coulomb Green Function Between Slater Orbitals*

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Analytic expressions are given for integrals of the Coulomb Green function with Slater type atomic orbitals. The results involve hypergeometric functions.

Key words: Perturbation theory – Coulomb Green function.

In recent years Green functions have been applied to problems in quantum chemistry to an increasing extent [1, 2]. Our own recent work [3] has required the evaluation of matrix elements of the Coulomb Green function (CGF) between Slater type orbitals. Reid [4] has given a numerical solution of this problem, but it is still desirable to obtain an analytic solution. In fact several authors have already calculated the matrix elements of the CGF between hydrogenic orbitals [5–8] and two that we know of have done it for Slater orbitals. However, the answer is generally buried as a minor result in papers which sometimes deal extensively with a broad topic. In addition either the derivation or final solution (or both) are given without much detail. Thus it seems justified to present a short paper on this problem alone in the hope of saving others from expending time in rederiving the result independently.

The CGF, $G(\boldsymbol{r}, \boldsymbol{r}', \omega)$, is the kernel of the operator which is the inverse of $\omega+\frac{1}{2}\nabla^2+(Z/r)$.

We start with the following partial wave expansion of the CGF derived by a number of authors [11–13]

$$G(\boldsymbol{r}, \boldsymbol{r}', \omega)=\sum_{l=0}^{\infty}\sum_{m=-l}^{l} G_l(r, r', \omega)\, Y_{lm}(\hat{\boldsymbol{r}})\, Y^*_{lm}(\hat{\boldsymbol{r}}') \tag{1}$$

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The $Y_{lm}(\hat{\boldsymbol{r}})$ are the usual, normalized, complex spherical harmonics. The radial Green function is, using atomic units [14]:

$$G_l(r, r', \omega) = \frac{\Gamma(l+1-i\nu)}{ikrr'} W_{i\nu,l+\frac{1}{2}}(-2ikr_>)\mathcal{M}_{i\nu,l+\frac{1}{2}}(-2ikr_<) \tag{2}$$

where

$$k = (2\omega)^{1/2}, \qquad \nu = Z/k$$

and

$$r_>(r_<)$$

is the greater (lesser) of r and r'. The Whittaker functions $W_{i\nu,l+\frac{1}{2}}$ and $\mathcal{M}_{i\nu,l+\frac{1}{2}}$ are well known [15–17].

The integral that we desire is

$$J(\xi_1, \mathrm{n}_1, \lambda_1, \mu_1; \xi_2, \mathrm{n}_2, \lambda_2, \mu_2; \omega) \equiv \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{r}' S_{\xi_1 n_1 \lambda_1 \mu_1}(\boldsymbol{r}) G(\boldsymbol{r}, \boldsymbol{r}', \omega) S_{\xi_2 n_2 \lambda_2 \mu_2}(\boldsymbol{r}') \tag{3}$$

where the Slater orbitals are

$$S_{\xi \mathrm{n} \lambda \mu}(\boldsymbol{r}) = A r^{n-1} e^{-\xi r} Y_{\lambda\mu}(\hat{\boldsymbol{r}}). \tag{4}$$

Substituting (1) and (4) into (3), we find

$$J = \delta_{\lambda_1\lambda_2}\delta_{\mu_1\mu_2} A_1 A_2 K(\xi_1, \mathrm{n}_1; \xi_2, \mathrm{n}_2; i\nu, -ik, l) \tag{5}$$

where

$$K(a, \alpha; b, \beta; \kappa, t, l) \equiv -t^{-1}\Gamma(l+1-\kappa) \times \int_0^\infty \mathrm{d}r \int_0^\infty \mathrm{d}r' r^\alpha\, \mathrm{e}^{-ar} r'^\beta \mathrm{e}^{-br'} W_{\kappa,l+\frac{1}{2}}(2tr_>)\mathcal{M}_{\kappa,\ \, l+\frac{1}{2}}^{\ \ 4}(2tr_<). \tag{6}$$

To evaluate this integral, we use an integral representation for the product of the two Whittaker functions [14, 16, 18] and find when β is an integer

$$K = (-2)\int_1^\infty \mathrm{d}\zeta \frac{(\zeta+1)^{\kappa-1/2}}{(\zeta-1)^{\kappa+1/2}} \int_0^\infty \mathrm{d}r r^{\alpha+1/2}\, \mathrm{e}^{-(a+t\zeta)r} \times (-1)^{\beta-l} \frac{\partial^{\beta-l}}{\partial b^{\beta-l}} D(b, \beta; t, \zeta, l) \tag{7}$$

where

$$D(b, \beta; t, \zeta, l) \equiv \int_0^\infty \mathrm{d}r'\, r'^{l+1/2}\, \mathrm{e}^{-br'} I_{2l+1}[2tr^{1/2}(\zeta^2-1)^{1/2} r'^{1/2}] \tag{8}$$

In Eq. [8], I_{2l+1} is a modified Bessel function [19]. From Ref. [20] and Eq. (2.9b) of Ref. [16] we find

$$D=\frac{[t^2(\zeta^2-1)]^{l+1/2}}{[b+t\zeta]^{2l+2}}\,r^{l+1/2}\,\mathrm{e}^{t^2(\zeta^2-1)/(b+t\zeta)r}. \tag{9}$$

Thus for integral (α) we obtain:

$$K=-2(-1)^{\beta-l}\frac{\partial^{\beta-l}}{\partial b^{\beta-l}}\int_1^\infty \mathrm{d}\zeta\,\frac{(\zeta+1)^{\kappa-1/2}}{(\zeta-1)^{\kappa+1/2}}\frac{[t^2(\zeta^2-1)]^{l+1/2}}{[b+t\zeta]^{2l+2}}$$
$$\times(-1)^{\alpha-l}\frac{\partial^{\alpha-l}}{\partial a^{\alpha-l}}E(a,\alpha;t,\zeta,l) \tag{10}$$

where the E integral is elementary

$$E(a,\alpha;t,\zeta,l)\equiv\int_0^\infty \mathrm{d}r\,r^{2l+1}\exp\left\{-\left[(a+t\zeta)-\frac{t^2(\zeta^2-1)}{(b+t\zeta)}\right]r\right\}$$
$$=(2l+1)!\Big/\left[(a+t\zeta)-\frac{t^2(\zeta^2-1)}{(b+t\zeta)}\right]^{2l+2}. \tag{11}$$

For K we now have

$$K=-2t^{2l+1}(2l+1)!(-1)^{\alpha+\beta}\frac{\partial^{\alpha-l}}{\partial a^{\alpha-l}}\frac{\partial^{\beta-l}}{\partial b^{\beta-l}}$$
$$\times\left\{[ab+t^2]^{-(2l+2)}\int_1^\infty \mathrm{d}\zeta\,(\zeta+1)^{\kappa+l}(\zeta-1)^{l-\kappa}\left[1+\frac{(a+b)t}{(ab+t^2)}\right]^{-(2l+2)}\right\}. \tag{12}$$

Changing to a new variable of integration $X\equiv(\zeta-1)/(\zeta+1)$ we find that the resulting integral over X is a representation of Gauss' hypergeometric function [21] and finally we obtain for K the expression

$$K=\frac{2(2t)^{2l+1}(2l+1)!}{(l+1-\kappa)}(-1)^{\alpha+\beta+1}$$
$$\times\frac{\partial^{\alpha-l}}{\partial a^{\alpha-l}}\frac{\partial^{\beta-l}}{\partial b^{\beta-l}}\frac{{}_2F_1(2l+2,l+1-\kappa;l+2-\kappa;{}^2u)}{(t+a)^{2l+2}(t+b)^{2l+2}} \tag{13}$$

where

$$u\equiv\frac{(t-a)(t-b)}{(t+a)(t+b)}.$$

Note that J and K are symmetric in (a,α), (b,β). The hypergeometric function in Eq. (13) is defined by the hypergeometric series for u within the unit circle and by analytic continuation outside [15].

We have taken a few of the lower derivatives in (13) and checked them as Reid did by considering the case where one of the Slater orbitals is a hydrogenic eigenfunction. Since the derivative of a hypergeometric function is proportional to a hypergeometric function, the first few derivatives in (13) are not excessively complicated and so they are included here.

Letting $\Delta \equiv [(ab+t^2)+(a+b)t]$, we have the following specific results:

$$K(a, l; b, l+1; \kappa, t, l) = \frac{-2(2l+1)!}{(t^2-b^2)(a+b)^{2l+2}} - \frac{2^{2l+3}(2l+1)!\,t^{2l+1}(\kappa t-(l+1)b)\,{}_2F_1}{(l+1-\kappa)(t^2-b^2)(t+a)^{2l+2}(t+b)^{2l+2}}$$

$$K(a, l; b, l+2; \kappa, t, l) = \frac{-4(2l+1)!}{(t^2-b^2)(a+b)^{2l+2}}\left\{\frac{\kappa t-(l+2)b}{(t^2-b^2)}+\left(\frac{l+1}{a+b}\right)\right\} - \frac{2^{2l+3}(2l+1)!\,t^{2l+1}\,{}_2F_1}{(l+1-\kappa)(t^2-b^2)\Delta^{2l+2}} \times\left\{l+1+\frac{[\kappa t-(l+1)b][\kappa t-(l+2)b]}{t^2-b^2}\right\}$$

$$K(a, l+1; b, l+1; \kappa, t, l) = \frac{-2(2l+1)!}{(t^2-a^2)(t^2-b^2)(a+b)^{2l+2}} \times\left\{[\kappa t-(l+1)(a+b)]+\frac{(l+1)(t^2+ab)}{a+b}\right\} - \frac{2^{2l+4}(2l+1)!\,t^{2l+1}[\kappa t-(l+1)b][\kappa t-(l+1)a]\,{}_2F_1}{(l+1-\kappa)(t^2-b^2)(t^2-a^2)\Delta^{2l+2}}.$$

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