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LETTER TO THE EDITOR

Expansion theorem involving a negative exponential

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Abstract. Expansion theorems for $(r')^{m-1}\exp(-\alpha r')$ are extended to the case $m=-1$.

The expansion theorem for the function $|\boldsymbol{r}_1-\boldsymbol{r}_2|^{-1}\exp(-\alpha|\boldsymbol{r}_1-\boldsymbol{r}_2|)$ for the standard case of $\boldsymbol{r}_2=r_2\hat{\boldsymbol{k}}$ directed along the z axis is well known from the Green function for the modified Helmholtz equation (Arfken 1970):

$$|\boldsymbol{r}_3-r_2\hat{\boldsymbol{k}}|^{-1}\exp(-\alpha|\boldsymbol{r}_1-r_2\hat{\boldsymbol{k}}|)=\alpha\sum_{l=0}^{\infty}(2l+1)\mathrm{P}_l(\cos\theta)\mathrm{i}_l(\alpha r)\mathrm{k}_l(\alpha R) \qquad (1)$$

where P_l are the legendre polynomials, i_l and k_l are the spherical modified Bessel functions of the first and second kind respectively, and r, R are respectively the smaller and greater of r_1, r_2; the polar angle of $\boldsymbol{r}'$ is θ.

Expansion theorems for $(r')^{m-1}\exp(-\alpha r')$, where $\boldsymbol{r}'=\boldsymbol{r}_1-r_2\hat{\boldsymbol{k}}$, for $m=1,2,\ldots$, may be obtained from (1) by m-fold differentiation with respect to the parameter α. Appropriate recursion formulae, based on the properties of spherical Bessel functions, have been developed by Barnett and Coulson (1951). Such expansions are needed, for instance, to re-express Slater or hydrogenic orbitals with respect to a displaced origin to facilitate the evaluation of two-centre integrals (Slater 1963†).

There remains one more case of interest (bearing in mind the factor $r^2\,\mathrm{d}r$ in any volume integration), namely when $m=-1$. This could arise when an operator as well as a wavefunction has to be expressed with respect to a different centre.

The purpose of this letter is to discuss the evaluation of the coefficients in the expansion

$$(r')^{-2}\exp(-\alpha r')=\sum_{l=0}^{\infty}(2l+1)\mathrm{P}_l(\cos\theta)\mathscr{I}_l(\alpha;r_1,r_2). \qquad (2)$$

Integration of (1) gives

$$\mathscr{I}_l=\int_{\alpha}^{\infty}\beta\,\mathrm{i}_l(\beta r)\mathrm{k}_l(\beta R)\,\mathrm{d}\beta. \qquad (3)$$

For $l=0$, explicit integration gives

$$\mathscr{I}_0=(2rR)^{-1}[E_1(\alpha(R-r))-E_1(\alpha(R+r))] \qquad (4)$$

† Equation (A15-4) of this book is in error: the first symbol inside the square bracket should be n.

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where E_1 is the exponential integral (Abramowitz and Stegun 1972)

$$E_1(x) = \int_x^\infty t^{-1} \exp(-t)\, \mathrm{d}t. \tag{5}$$

We now derive a recursion relation which allows the calculation of all $\mathscr{I}_l$, $l > 0$. Differentiation through the integral of $\mathscr{I}_l$ with respect to r gives an integrand

$$\beta^2[\mathrm{i}_{l+1}(\beta r) + l(\beta r)^{-1}\mathrm{i}_l(\beta r)]\mathrm{k}_l(\beta R) \tag{6}$$

where we have used a standard recursion relation (Arfken 1970) to re-express i_l'. The first product is then rewritten using a recursion relation for k_l, yielding for the integrand

$$-(l+2)R^{-1}\beta \mathrm{i}_{l+1}(\beta r)\mathrm{k}_{l+1}(\beta R) - R^{-1}\beta^2 \mathrm{i}_{l+1}(\beta r)(\partial/\partial\beta)(\mathrm{k}_{l+1}(\beta R)) + l\beta r^{-1}\mathrm{i}_l(\beta r)\mathrm{k}_l(\beta R). \tag{7}$$

A corresponding expression may be written down for the integrand upon differentiation of $\mathscr{I}_l$ with respect to R. Then

$$R\frac{\partial}{\partial r}\mathscr{I}_l + r\frac{\partial}{\partial R}\mathscr{I}_l = -2(l+2)\mathscr{I}_{l+1} - \int_\alpha^\infty \beta^2 \frac{\partial}{\partial\beta}(\mathrm{i}_{l+1}(\beta r)\mathrm{k}_{l+1}(\beta R))\, \mathrm{d}\beta + l(r^2+R^2)(rR)^{-1}\mathscr{I}_l. \tag{8}$$

Integration by parts enables the remaining integral to be expressed in a convenient form, giving finally

$$2(l+1)\mathscr{I}_{l+1} = \alpha^2 \mathrm{i}_{l+1}(\alpha r)\mathrm{k}_{l+1}(\alpha R) + l(r^2+R^2)(rR)^{-1}\mathscr{I}_l - [R(\partial/\partial r)\mathscr{I}_l + r(\partial/\partial R)\mathscr{I}_l]. \tag{9}$$

For example, setting $l = 0$ yields

$$\mathscr{I}_1 = (2Rr)^{-2}[\![(r^2+R^2)[E_1(\alpha(R-r)) - E_1(\alpha(R+r))] - \alpha^{-2}\{[1+\alpha(R-r)]\exp[-\alpha(R-r)] - [1+\alpha(R+r)]\exp[-\alpha(R+r)]\}]\!] \tag{10}$$

as may also be confirmed by direct integration in (3).

Any higher-order expansion coefficient $\mathscr{I}_l$ in (2) may now be obtained from (4) by repeated application of the recursion formula (9).

References

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