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## An alternative proof of some relations between hydrogenic matrix elements

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**Abstract.** A relationship between certain integrals of the product of two Laguerre polynomials is obtained. It is shown how this relationship, together with two known Hankel transforms, allows for an alternative derivation of some relations between matrix elements of  $r^k$  for hydrogenic ions. A further relation, involving matrix elements of logarithmic functions, is obtained in a similar manner.

### 1. Introduction

Some years ago Blanchard [1] discovered a recurrence relation between matrix elements of hydrogenic radial wavefunctions from which he was able to deduce that, for  $|l-l'| \leq k \leq l+l'$

$$\langle nl|r^{-k-2}|nl\rangle = (-1)^{l-l'}(2/an)^{2k+1}(l+l'-k)!k!^2 \times \langle n'l|r^{k-1}|nl\rangle / [(l+l'+1+k)!(k+l-l)!(k+l'-l)!], \quad (1.1)$$

The matrix elements are defined such that, given any function  $h(r)$ ,

$$\langle n'l|h(r)|nl\rangle = \int_0^\infty R_{n'l}(r)h(r)R_{nl}(r)r^2 dr \quad (1.2)$$

where the radial functions are [2]

$$R_{nl}(r) = N_{nl}r^l e^{-r/an} L_{n-l-1}^{2l+1}(2r/an) \quad (1.3)$$

$$N_{nl} = (2/n^2 a^{3/2})[(n-l-1)!/(n+l)!]^{1/2}(2/an)^l \quad (1.4)$$

and  $a = a_0/Z$  is the scaled Bohr radius.  $L_n^\alpha(x)$  is a generalised Laguerre polynomial [3].

The identity (1.1) generalised two earlier results by Pasternak [4] and Pasternak and Sternheimer [5]. Pasternak [4] showed that, for  $k = 0, 1, \dots, 2l$

$$\langle nl|r^{-k-2}|nl\rangle = (2/an)^{2k+1}(2l-k)!/(2l+1+k)!\langle nl|r^{k-1}|nl\rangle \quad (1.5)$$

while Pasternak and Sternheimer [5] showed that, for  $l \neq l'$  and  $k = 0, 1, \dots, |l-l'|-1$

$$\langle n'l|r^{-k-2}|nl\rangle = 0 \quad (1.6)$$

The significance of these identities is that they relate the radial matrix elements of positive and negative powers of  $r$  (although the matrix element of  $r^{-1}$  is not covered).

The relation (1.1) was rediscovered (though not proven) by More [6], and a further proof, relying on various properties of generalised hypergeometric functions of unit

argument, was found by Ojha and Crothers [7]. Several group-theoretical investigations of hydrogenic matrix elements have been published, notably that by Armstrong [8], wherein the properties of a particular physical realisation of the  $SO(2, 1)$  Lie algebra are shown to lead to the Pasternak-Sternheimer identity (1.6).

The analysis of hydrogenic radial matrix elements continues to attract the attention of workers in various branches of atomic physics. The Schrödinger radial ladder operator [9] has been found to lead to recurrence relations between such matrix elements, including some which are special cases of (1.1). In the context of many-electron theory hydrogenic radial integrals have been found to be useful for calculations employing the screened hydrogenic model [10]. And the long-standing problem of deriving tight closed-form expressions for the radial matrix elements remains essentially unsolved (see though [11] and [12] for special cases).

A further proof of (1.1), though of interest in and of itself, is useful in view of the light it may shed on the underlying principles behind that and similar results. We have found a curious relationship (2.9) between certain integrals of products of two Laguerre polynomials which, together with well established Hankel transformations, leads us to a proof of (1.1) entirely within the framework of classical special function theory. This work will be presented in section 2. We have been unable to find any previous reference to the relationship given in (2.9). Our work is in some ways complementary to that of Ojha and Crothers [7] in that we have dissected their direct proof into several distinct steps which highlight the few specific properties of Laguerre polynomials which lead to (1.1). Nonetheless, our proof, which was found independently, is somewhat more general. All three relations, (1.1), (1.5) and (1.6) follow from our analysis.

Blanchard [1] also discovered a relationship between matrix elements of  $\log r$  and powers of  $r$ . In section 3 we extend our work to include logarithmic factors in the integrands and show how, in much the same manner, we can derive Blanchard's additional formulae. Such an extension to the logarithmic case, though relatively straightforward in the work presented here, was not attempted in [7].

## 2. Matrix elements of $r^k$

The following generating function for Laguerre polynomials [13],

$$\sum_{i=0}^{\infty} t^i L_i^{\alpha-i}(x) = (1+t)^{\alpha} e^{-tx} \quad (2.1)$$

implies that

$$\begin{aligned} \sum_{p,q} t^p s^q \int_0^{\infty} e^{-x} x^{\gamma} L_p^{\beta-p+m}(x) L_q^{\alpha-q+n}(x) dx \\ = \Gamma(\gamma+1)(1+t)^{\beta+m}(1+s)^{\alpha+n}/(1+t+s)^{\gamma+1} \end{aligned} \quad (2.2)$$

from which we can deduce that

$$\begin{aligned} \int_0^{\infty} e^{-x} x^{\gamma} L_n^{\beta-n+m}(x) L_m^{\alpha-m+n}(x) dx \\ = \frac{\Gamma(\gamma+1)}{m!n!} \frac{\partial^n}{\partial t^n} \frac{\partial^m}{\partial s^m} \left[ (1+t)^{\beta+m}(1+s)^{\alpha+n}/(1+t+s)^{\gamma+1} \right]_{t=s=0}. \end{aligned} \quad (2.3)$$

Since

$$[(1+t)(1+s)/(1+t+s)]^{\gamma+1} = \sum_{i=0}^{\infty} (\gamma+1)_i / i! [ts/(1+t)(1+s)]^i \tag{2.4}$$

and

$$\left. \frac{d^p}{dx^p} x^i (1+x)^{-\sigma-i} \right|_{x=0} = (-1)^p (-p)_i (\sigma)_p / (\sigma)_i \tag{2.5}$$

it follows that

$$\begin{aligned} & \int_0^{\infty} e^{-x} x^{\gamma} L_n^{\beta-n+m}(x) L_m^{\alpha-m+n}(x) dx \\ &= {}_3F_2 \left[ \begin{matrix} -n, -m, \gamma+1; 1 \\ \gamma+1-m-\beta, \gamma+1-n-\alpha \end{matrix} \right] (-1)^{n+m} \Gamma(\gamma+1) \\ & \quad \times (\gamma+1-m-\beta)_n (\gamma+1-n-\alpha)_m / (n!m!). \end{aligned} \tag{2.6}$$

where the generalised hypergeometric function of unit argument is defined in the usual way [13] and  $(\sigma)_i = \Gamma(\sigma+i)/\Gamma(\sigma)$ .

Letting  $\alpha \rightarrow \beta - n + m$  and  $\beta \rightarrow \alpha - m + n$  leads immediately to

$$\begin{aligned} & \int_0^{\infty} e^{-x} x^{\gamma} L_n^{\alpha}(x) L_m^{\beta}(x) dx \\ &= {}_3F_2 \left[ \begin{matrix} -n, -m, \gamma+1; 1 \\ \gamma-\alpha-n+1, \gamma-\beta-m+1 \end{matrix} \right] (-1)^{m+n} \Gamma(\gamma+1) \\ & \quad \times (\gamma+1-\alpha-n)_n (\gamma+1-\beta-m)_m / (n!m!). \end{aligned} \tag{2.7}$$

It is not difficult to see that if  $\gamma - \alpha = \gamma - \beta = k$ , a non-negative integer less than  $|m - n|$ , then the integral vanishes:

$$\int_0^{\infty} e^{-x} x^{\gamma} L_n^{\gamma-k}(x) L_m^{\gamma-k}(x) dx = 0 \quad k = 0, 1, \dots, |m - n| - 1. \tag{2.8}$$

Finally, since  $(\sigma - n)_m / (\sigma - m)_n = (\sigma)_{m-n}$ , (2.6) and (2.7) together imply that

$$\begin{aligned} & \int_0^{\infty} e^{-x} x^{\gamma} L_n^{\alpha}(x) L_m^{\beta}(x) dx \\ &= \int_0^{\infty} e^{-x} x^{\gamma} L_n^{\beta-n+m}(x) L_m^{\alpha-m+n}(x) dx \\ & \quad \times [(\gamma - \alpha + 1)_{m-n} (\gamma - \beta + 1)_{n-m}]^{-1}. \end{aligned} \tag{2.9}$$

The formulae given in (2.8) and (2.9) constitute the main result of this paper.

Specific choices of the parameters in (2.8) and (2.9) give rise to several interesting results. We make mention of only one, since it constitutes a sort of generalised orthogonality property of Laguerre polynomials. Put  $\alpha = \gamma - k$  in (2.8); then

$$\int_0^{\infty} e^{-x} x^{\alpha+k} L_n^{\alpha}(x) L_m^{\alpha}(x) dx = 0 \quad k = 0, 1, \dots, |m - n| - 1 \tag{2.10}$$

which, when  $k = 0$  and  $n \neq m$ , reduces to the usual orthogonality condition [3].

Another specific choice of the parameters leads to a proof of (1.1). Erdelyi [14] has shown that

$$e^{-x}x^\sigma L_p^{\sigma+q-p}(x)L_q^{\sigma+p-q}(x) = (-1)^{p+q} \int_0^\infty e^{-y}y^\sigma L_p^\sigma(y)L_q^\sigma(y)J_{2\sigma}(2\sqrt{xy}) dy \tag{2.11}$$

where  $J_\nu$  is a Bessel function of order  $\nu$ , and since [13]

$$\int_0^\infty x^{-\kappa-1}J_{2\sigma}(2\sqrt{xy}) dx = y^\kappa \Gamma(\sigma - \kappa) / \Gamma(\sigma + \kappa + 1) \quad (0 < \kappa < \sigma) \tag{2.12}$$

we can deduce that

$$\begin{aligned} \int_0^\infty e^{-x}x^{\sigma-\kappa-1}L_p^{\sigma+q-p}(x)L_q^{\sigma+p-q}(x) dx \\ &= (-1)^{p+q} \int_0^\infty x^{-\kappa-1} \int_0^\infty e^{-y}y^\sigma L_p^\sigma(y)L_q^\sigma(y)J_{2\sigma}(2\sqrt{xy}) dy dx \\ &= (-1)^{p+q} \int_0^\infty e^{-y}y^\sigma L_p^\sigma(y)L_q^\sigma(y) \int_0^\infty x^{-\kappa-1}J_{2\sigma}(2\sqrt{xy}) dx dy \\ &= (-1)^{p+q} \Gamma(\sigma - \kappa) / \Gamma(\sigma + \kappa + 1) \int_0^\infty e^{-y}y^{\sigma+\kappa}L_p^\sigma(y)L_q^\sigma(y) dy. \end{aligned} \tag{2.13}$$

Finally, employing our integral formulae (2.8) and (2.9), we have

$$\begin{aligned} \int_0^\infty e^{-x}x^{\sigma-\kappa-1}L_p^{\sigma+q-p}(x)L_q^{\sigma+p-q}(x) dx \\ &= (-1)^{p+q} \Gamma(\sigma - \kappa) / [\Gamma(\sigma + \kappa + 1)(\kappa + 1)_{p-q}(\kappa + 1)_{q-p}] \\ &\quad \times \int_0^\infty e^{-y}y^{\sigma+\kappa}L_p^{\sigma+q-p}(y)L_q^{\sigma+p-q}(y) dy \end{aligned} \tag{2.14}$$

for  $0 < \kappa < \sigma$  with the integral vanishing for  $\kappa$  a positive integer less than  $|p - q|$ .

We now have everything necessary to prove the three identities given in the introduction. Letting  $p = n - l - 1$ ,  $q = n - l' - 1$ , and  $\sigma = l + l' + 1$  and noting the definition of the radial hydrogenic wavefunctions (1.3) we see that (2.14) implies

$$\langle nl' | r^{-\kappa-2} | nl \rangle = 0 \tag{2.15}$$

for  $\kappa$  a non-negative integer less than  $|l - l'|$ , and

$$\begin{aligned} \langle nl' | r^{-\kappa-2} | nl \rangle &= (-1)^{l+l'} \frac{\Gamma(l+l'-\kappa+1)\Gamma(\kappa+1)^2}{\Gamma(l+l'+\kappa+2)\Gamma(\kappa+l-l'+1)\Gamma(\kappa+l'-l+1)} \\ &\quad \times (2/an)^{2\kappa+1} \langle nl' | r^{\kappa-1} | nl \rangle \end{aligned} \tag{2.16}$$

for all other  $\kappa$  such that  $0 \leq \kappa \leq l + l'$ .

### 3. Matrix elements of $r^k \log r$

The matrix elements of  $\log r$  can be treated in a manner entirely similar to those of  $r$ . To achieve this we first derive an analogue of our integral formula (2.9). Noting that

$$x^\gamma \log x = d/d\gamma(x^\gamma) \tag{3.1}$$

and [3]

$$d/d\sigma\Gamma(\sigma) = \Gamma(\sigma)\psi(\sigma) \tag{3.2}$$

on differentiating (2.9) with respect to  $\gamma$  we find

$$\begin{aligned} \int_0^\infty e^{-x}x^\gamma[\log x - \psi(\gamma+1-\alpha) - \psi(\gamma+1-\beta)]L_n^\alpha(x)L_m^\beta(x) dx \\ = \int_0^\infty e^{-x}x^\gamma[\log x - \psi(\gamma+1-\alpha+m-n) - \psi(\gamma+1-\beta+n-m)] \\ \times L_n^{\beta-n+m}(x)L_m^{\alpha-m+n}(x) dx / (\gamma-\alpha+1)_{m-n}(\gamma-\beta+1)_{n-m}. \end{aligned} \tag{3.3}$$

Now, proceeding exactly as before, taking account of (2.11) and the further Hankel transform given by [13]

$$\begin{aligned} \int_0^\infty x^{-\kappa-1} \log x J_{2\sigma}(2\sqrt{xy}) dx \\ = y^\kappa\Gamma(\sigma-\kappa)/\Gamma(\sigma+\kappa+1)[\psi(\sigma-\kappa) + \psi(\sigma+\kappa+1) - \log y] \\ (0 \leq \kappa \leq \sigma) \end{aligned} \tag{3.4}$$

we deduce that

$$\begin{aligned} \int_0^\infty e^{-x}x^{\sigma-\kappa-1} \log x L_p^{\sigma+q-p}(x)L_q^{\sigma+p-q}(x) dx \\ = (-1)^{p+q}\Gamma(\sigma-\kappa)/[\Gamma(\sigma+\kappa+1)(\kappa+1)_{p-q}(\kappa+1)_{q-p}] \\ \times \left( [\psi(\sigma-\kappa) + \psi(\sigma+\kappa+1) - 2\psi(\kappa+1) \right. \\ \left. + \psi(\kappa+1+p-q) + \psi(\kappa+1+q-p)] \right. \\ \left. \times \int_0^\infty e^{-x}x^{\sigma+\kappa}L_p^{\sigma+q-p}(x)L_q^{\sigma+p-q}(x) dx \right. \\ \left. - \int_0^\infty e^{-x}x^{\sigma+\kappa} \log x L_p^{\sigma+q-p}(x)L_q^{\sigma+p-q}(x) dx \right) \end{aligned} \tag{3.5}$$

for  $0 \leq \kappa \leq \sigma$ . When  $\kappa$  is a non-negative integer less than  $|p-q|$ ,  $1/(\kappa+1)_{-|p-q|}$  is zero, but then so is  $1/\psi(\kappa+1-|p-q|)$ . Thus in this latter case only one term on the RHS of (3.5) is non-zero; in fact

$$\begin{aligned} \int_0^\infty e^{-x}x^{\sigma-\kappa-1} \log x L_p^{\sigma+q-p}(x)L_q^{\sigma+p-q}(x) dx \\ = (-1)^{p+q}\Gamma(\sigma-\kappa)/[\Gamma(\sigma+\kappa+1)(\kappa+1)_{|p-q|}] \\ \times \int_0^\infty e^{-x}x^{\sigma+\kappa}L_p^{\sigma+q-p}(x)L_q^{\sigma+p-q}(x) dx. \end{aligned} \tag{3.6}$$

It is now a simple matter to deduce the formulae relating matrix elements of  $r^k$  and  $r^k \log r$  presented by Blanchard [1]. We find, for  $k=0, 1, \dots, |l-l'|-1$

$$\begin{aligned} \langle nl'|r^{-k-2} \log 2r/an|nl\rangle \\ = (-1)^k(2/an)^k \frac{(l+l'-k)! (|l-l'-k-1)! k!^2}{(l+l'+k+1)!(k+|l-l'|)!} \langle nl'|r^{k-1}|nl\rangle \end{aligned} \tag{3.7}$$

and for  $0 \leq \kappa \leq l+l'$

$$\begin{aligned}
& \langle nl' | r^{-\kappa-2} \log 2r/an | nl \rangle \\
&= (-1)^{l+l'} (2/an)^{2\kappa+1} \frac{\Gamma(l+l'+1-\kappa)\Gamma(\kappa+1)^2}{\Gamma(l+l'+\kappa+2)\Gamma(\kappa+l-l'+1)\Gamma(\kappa+l'-l+1)} \\
&\quad \times \{ [\psi(l+l'+1-\kappa) + \psi(l+l'+\kappa+2) - 2\psi(\kappa+1) + \psi(\kappa+l-l'+1) \\
&\quad + \psi(\kappa+l'-l+1)] \langle nl' | r^{\kappa-1} | nl \rangle - \langle nl' | r^{\kappa-1} \log 2r/an | nl \rangle \} \quad (3.8)
\end{aligned}$$

which are the results established by Blanchard [1].

In summary, the derivation presented here reveals that equations (2.8) and (2.9) are the fundamental integral properties of the Laguerre polynomials which, together with Erdelyi's relation (2.11), leads to the identity (1.1) for the radial matrix elements. In the case of integrals involving  $\log x$ , the corresponding integral property is equation (3.3).

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### References

- [1] Blanchard P 1974 *J. Phys. B: At. Mol. Phys.* **7** 993
- [2] Bethe H A and Salpeter E E 1957 *Quantum Mechanics of One- and Two-Electron Atoms* (New York: Academic)
- [3] Lebedev N N 1972 *Special Functions and their Applications* (New York: Dover)
- [4] Pasternak S 1937 *Proc. Natl. Acad. Sci.* **23** 91
- [5] Pasternak S and Sternheimer R M 1962 *J. Math. Phys.* **3** 1280
- [6] More R M 1983 *J. Phys. B: At. Mol. Phys.* **16** 3859
- [7] Ojha P C and Crothers D S F 1984 *J. Phys. B: At. Mol. Phys.* **17** 4797
- [8] Armstrong L L 1970 *J. Physique* **31** C4 17
- [9] Ding Y B 1987 *J. Phys. A: Math. Gen.* **20** 6293
- [10] Khandelwal G S, Pritchard W M, Grubb G, Khan F 1989 *Phys. Rev. A* **39** 3960
- [11] Bockasten K 1974 *Phys. Rev. A* **9** 1087
- [12] Badawi M, Bessis N, Bessis G, Hadinger G 1973 *Phys. Rev. A* **8** 727
- [13] Gradshteyn I S and Ryzhik I M 1980 *Table of Integrals, Series and Products* (New York: Academic)
- [14] Erdelyi A 1938 *J. London Math. Soc.* **13** 146