Matrix elements

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Abstract

The article Kamta and Bandrauk, Phys. Rev. A 71, 053407 (2005) descibes how to set up the H_2^+ problem using prolate spherodal coordinates (PSC). In the appendix, the article writes the formula for general matrix elements in the overlap matrix, S, and the hamiltonian matrix, H. Some of the formulas are written out fully, and are ready to be implemented, but some are only scetches, and additional work is needed to reach an implementable formula. This note shows the additional work on eq. (A6).

1 Starting point

Equation (A6) reads

$$h^m_{\nu',\nu} = \int_1^\infty U^m_{\nu'}(\xi)\left[\frac{\partial}{\partial\xi}\left((\xi^2-1)\frac{\partial}{\partial\xi}\right) - \frac{m^2}{\xi^2-1} + 2ZR\xi\right]U^m_\nu(\xi)d\xi \tag{1}$$

The article further supplies a recurrence formula, A(10),

$$\begin{aligned} \frac{\partial}{\partial\xi}L^{2|m|}_{\nu-|m|}[2\alpha(\xi-1)] &= \\ \frac{\nu-|m|+1}{\xi-1}L^{2|m|}_{\nu-|m|+1}[2\alpha(\xi-1)] &- \\ \frac{\nu+|m|+1-2\alpha(\xi-1)}{\xi-1}L^{2|m|}_{\nu-|m|}[2\alpha(\xi-1)] \end{aligned} \tag{2}$$

with which we can remove the differentiations from (A6), so that a Gauss Laguerre quadrature rule can be applied. Thus we only need the expression for $U^m_\nu(\xi)$,

$$U^m_\nu(\xi) = N^m_\nu e^{-\alpha(\xi-1)}(\xi^2-1)^{|m|/2}L^{2|m|}_{\nu-|m|}[2\alpha(\xi-1)] \tag{3}$$

and the work can begin.

2 The Work

Let's go straight for the differentiation:

$$\frac{\partial}{\partial\xi}U_\nu^m(\xi) = N_\nu^m e^{-\alpha(\xi-1)}(\xi^2-1)^{|m|/2}\left(-\alpha L_0 + |m|\frac{\xi}{\xi^2-1}L_0 + \left[\frac{\nu-|m|+1}{\xi-1}L_1 - \frac{\nu+|m|+1-2\alpha(\xi-1)}{\xi-1}L_0\right]\right)$$
$$= N_\nu^m e^{-\alpha(\xi-1)}(\xi^2-1)^{|m|/2}\left[\left(\alpha - \frac{|m|}{\xi^2-1} - \frac{\nu+1}{\xi-1}\right)L_0 + \frac{\nu-|m|+1}{\xi-1}L_1\right] \quad (4)$$

The shorthand L_i for $L_{\nu-|m|+i}^{2|m|}[2\alpha(\xi-1)]$ is introduced to somewhat limit the monstrousness of the expression.

Moving on to the double differentiation:

$$\begin{aligned}\frac{\partial^2}{\partial\xi^2}U_\nu^m(\xi) = N_\nu^m e^{-\alpha(\xi-1)}(\xi^2-1)^{|m|/2}\times\\
\left(\left[\alpha\left(\alpha + \frac{|m|\xi}{\xi^2-1} - \frac{\nu+|m|+1}{\xi-1}\right)\right.\right.\\
-|m|\left(\frac{\alpha}{\xi^2-1} - \frac{(\nu+3)(\xi+1)+|m|-2}{(\xi^2-1)^2}\right)\\
\left.-(\nu+1)\left(\frac{\alpha}{\xi-1} + \frac{|m|-1}{(\xi-1)^2} - \frac{|m|}{(\xi^2-1)(\xi-1)} - \frac{\nu+|m|+1}{(\xi-1)^2}\right)\right]L_0\\
+\left[(\nu-|m|+1)\left(\frac{\alpha}{\xi-1} - \frac{|m|}{(\xi^2-1)(\xi-1)} - \frac{\nu+1}{(\xi-1)^2} + \frac{\alpha}{\xi-1}\right.\right.\\
\left.\left.+\frac{|m|-1}{(\xi-1)^2} - \frac{|m|}{(\xi^2-1)(\xi-1)} - \frac{\nu+|m|+2}{(\xi-1)^2}\right)\right]L_1\\
\left.+\left[\frac{(\nu-|m|+1)(\nu-|m|+2)}{(\xi-1)^2}\right]L_2\right)\end{aligned} \quad (5)$$

Some simplification is possible.

$$\begin{aligned}\frac{\partial^2}{\partial\xi^2}U_\nu^m(\xi) = N_\nu^m e^{-\alpha(\xi-1)}(\xi^2-1)^{|m|/2}\times\\
\left(\left[\alpha^2 + \frac{\alpha|m|}{\xi+1} - \frac{\alpha(2\nu+|m|+2)}{\xi-1} + \frac{|m|(|m|-2)}{(\xi^2-1)^2} + \frac{(\nu+1)(\nu+2)}{(\xi-1)^2} + \frac{2|m|(\nu+2)}{(\xi^2-1)(\xi-1)}\right]L_0\right.\\
+\left[2(\nu-|m|+1)\left(\frac{\alpha}{\xi-1} - \frac{|m|}{(\xi^2-1)(\xi-1)} - \frac{\nu+2}{(\xi-1)^2}\right)\right]L_1\\
\left.+\left[\frac{(\nu-|m|+1)(\nu-|m|+2)}{(\xi-1)^2}\right]L_2\right)\end{aligned} \quad (6)$$

This expression can fortunately be verified numerically.

In order to use the Gauss Laguerre quadrature formula, one needs to do a substitution,
$X = 2\alpha(\xi-1)$. Equation (3) will then look like this,

$$U_\nu^m(X) = N_\nu^m e^{-\frac{X}{2}}\left(\frac{X}{2\alpha}\right)^{|m|/2}\left(\frac{X}{2\alpha}+2\right)^{|m|/2}L_{\nu-|m|}^{2|m|}[X] \quad (7)$$

Equation (4) will look like this,

$$
\begin{aligned}
\frac{\partial}{\partial \xi} U_\nu^m(X) = N_\nu^m e^{-X/2} \left(\frac{X}{2\alpha}\right)^{|m|/2} \left(\frac{X}{2\alpha}+2\right)^{|m|/2} \times \\
\left[\left(\alpha - \frac{4\alpha^2|m|}{X\,(X+4\alpha)} - \frac{2\alpha(\nu+1)}{X}\right) L_0 + \frac{2\alpha(\nu-|m|+1)}{X} L_1\right]
\end{aligned} \tag{8}
$$

and eq. (6) will look like this

$$
\begin{aligned}
\frac{\partial^2}{\partial \xi^2} U_\nu^m(X) = N_\nu^m e^{-X/2} \left(\frac{X}{2\alpha}\right)^{|m|/2} \left(\frac{X}{2\alpha}+2\right)^{|m|/2} \times \\
\left(\left[\alpha^2 + \frac{2\alpha^2|m|}{X+4\alpha} - \frac{2\alpha^2(2\nu+|m|+2)}{X} + \frac{16\alpha^4|m|(|m|-2)}{X^2(X+4\alpha)^2}\right.\right. \\
\left. + \frac{4\alpha^2(\nu+1)(\nu+2)}{X^2} + \frac{16\alpha^3|m|(\nu+2)}{X^2(X+4\alpha)}\right] L_0 \\
+ \left[4\alpha(\nu-|m|+1)\left(\frac{\alpha}{X} - \frac{4\alpha^2|m|}{X^2(X+4\alpha)} - \frac{2\alpha(\nu+2)}{X^2}\right)\right] L_1 \\
\left. + \left[\frac{4\alpha^2(\nu-|m|+1)(\nu-|m|+2)}{X^2}\right] L_2 \right)
\end{aligned} \tag{9}
$$

Now all the pieces are in place. Using the substitution, eq. (1) will end up looking like this,

$$
\begin{aligned}
h_{\nu',\nu}^m = \frac{1}{2\alpha} \int_0^\infty U_{\nu'}^m \left(\frac{X}{\alpha}+2\right) \frac{\partial U_\nu^m}{\partial \xi} \\
+ U_{\nu'}^m \left(\frac{X}{2\alpha}\right)\left(\frac{X}{2\alpha}+2\right) \frac{\partial^2 U_\nu^m}{\partial \xi^2} \\
+ U_{\nu'}^m \left(2ZR\left[\frac{X}{2\alpha}+1\right] - \frac{4\alpha^2 m^2}{X(X+4\alpha)}\right) U_\nu^m \, dX
\end{aligned} \tag{10}
$$

where the $1/2\alpha$ in the start is due to the substitution. All the terms in the integrand contain the same exponential function, e^{-X}. Factoring this out fulfills the criteria for the Gauss Laguerre quadrature formula.