

1 Introduction

We consider the one-electron Hydrogenic-atom Hamiltonian, which is of the form

$$\hat{H} |\psi\rangle = E |\psi\rangle$$

where $\hat{H} = \hat{K} + \hat{V}$, with

$$\hat{K} |\psi\rangle = \left[-\frac{1}{2r} \frac{\partial^2}{\partial r^2} (r \cdot) + \frac{1}{2r^2} \hat{L}^2 \right] |\psi\rangle \quad \text{and} \quad \hat{V} |\psi\rangle = -\frac{Z}{r} |\psi\rangle$$

and where $\hat{L} = \hat{L}_x + \hat{L}_y + \hat{L}_z$ is the angular momentum operator, which has eigenstates $|Y_\ell^m\rangle$ which satisfy

$$\hat{L}^2 |Y_\ell^m\rangle = \ell(\ell+1) |Y_\ell^m\rangle \quad \text{and} \quad \hat{L}_z |Y_\ell^m\rangle = m |Y_\ell^m\rangle.$$

We solve this system by the method of basis expansion, where we utilise a basis of the form, $\mathcal{B} = \{|\phi_i\rangle\}_{i=1}^N$ which we suppose to be complete in the limit as $N \rightarrow \infty$. We select the basis functions, represented in coordinate-space, to be of the form

$$\phi_i(r, \Omega) = \frac{1}{r} \varphi_{k_i, \ell_i}(r) Y_{\ell_i}^{m_i}(\Omega) \quad \text{for} \quad i = 1, \dots, N$$

where the radial functions, $\mathcal{R} = \{|\varphi_{k_i, \ell_i}\rangle\}_{i=1}^N$ form a complete basis for the radial function space, in the limit as $N \rightarrow \infty$. For elements of this basis, the one-electron Hydrogenic-atom Hamiltonian assumes the form

$$\begin{aligned} \hat{H} |\phi_i\rangle &= \left[-\frac{1}{2r} \frac{\partial^2}{\partial r^2} (r \cdot) + \frac{1}{2r^2} \hat{L}^2 - \frac{Z}{r} \right] |\phi_i\rangle \\ &= \left[-\frac{1}{2r} \frac{\partial^2}{\partial r^2} (r \cdot) + \frac{\ell_i(\ell_i+1)}{2r^2} - \frac{Z}{r} \right] |\phi_i\rangle \\ &= \left[-\frac{1}{2r} \frac{\partial^2}{\partial r^2} (r \cdot) + \frac{\ell_i(\ell_i+1)}{2r^2} - \frac{Z}{r} \right] \left| \frac{1}{r} \varphi_{k_i, \ell_i}, Y_{\ell_i}^{m_i} \right\rangle \end{aligned}$$

thus reducing to operator which acts purely to radial terms, indexed by ℓ_i . Lastly, we note that the inner product is of the form

$$\langle \phi_i | \hat{A} | \phi_j \rangle = \int_0^\infty dr r^2 \int_\Omega d\Omega \overline{\phi_i(r, \Omega)} \hat{A} [\phi_j(r, \Omega)]$$

where \hat{A} is an arbitrary linear operator, and whence, in the case where \hat{A} can be reduced to an operator which acts only on radial terms, indexed by ℓ , we have that

$$\begin{aligned} \langle \phi_i | \hat{A} | \phi_j \rangle &= \int_0^\infty dr r^2 \overline{\frac{1}{r} \varphi_{k_i, \ell_i}(r)} \hat{A}_{\ell_j} \left[\frac{1}{r} \varphi_{k_j, \ell_j}(r) \right] \int_\Omega d\Omega \overline{Y_{\ell_i}^{m_i}(\Omega)} Y_{\ell_j}^{m_j}(\Omega) \\ &= \int_0^\infty dr r^2 \overline{\frac{1}{r} \varphi_{k_i, \ell_i}(r)} \hat{A}_{\ell_j} \left[\frac{1}{r} \varphi_{k_j, \ell_j}(r) \right] \delta_{\ell_i, \ell_j} \delta_{m_i, m_j} \\ &= \left\langle \frac{1}{r} \varphi_{k_i, \ell_i} \left| \hat{A}_{\ell_j} \right| \frac{1}{r} \varphi_{k_j, \ell_j} \right\rangle \delta_{\ell_i, \ell_j} \delta_{m_i, m_j} \end{aligned}$$

where we have defined the radial inner product to be of the form

$$\left\langle \frac{1}{r} \varphi_{k_i, \ell_i} \left| \hat{A}_{\ell_j} \right| \frac{1}{r} \varphi_{k_j, \ell_j} \right\rangle = \int_0^\infty dr r^2 \overline{\frac{1}{r} \varphi_{k_i, \ell_i}(r)} \hat{A}_{\ell_j} \left[\frac{1}{r} \varphi_{k_j, \ell_j}(r) \right].$$

2 Laguerre Basis

We utilise a Laguerre basis for the set of radial functions which, for $k = 1, 2, \dots$ and where $\ell \in \{0, 1, \dots\}$, are of the following form in coordinate-space

$$\varphi_{k,\ell}(r) = N_{k,\ell} (2\alpha_\ell r)^{\ell+1} \exp(-\alpha_\ell r) L_{k-1}^{2\ell+1}(2\alpha_\ell r)$$

where $\alpha_\ell \in (0, \infty)$ is an arbitrarily chosen constant, where $N_{k,\ell}$ are the normalisation constants, given by

$$N_{k,\ell} = \sqrt{\frac{\alpha_\ell (k-1)!}{(k+\ell)(k+2\ell)!}}$$

and where $L_{k-1}^{2\ell+1}$ are the generalised Laguerre polynomials.

2.1 Recurrence Relation

We construct the Laguerre basis by means of the following recurrence relation of the Laguerre polynomials

$$\begin{aligned} L_0^t(x) &= 1 \\ L_1^t(x) &= 1 + t - x \\ (n+1)L_{n+1}^t(x) &= (2n+1+t-x)L_n^t(x) - (n+t)L_{n-1}^t(x) \quad \text{for } n = 1, 2, \dots \end{aligned}$$

Firstly, we write $\varphi_{k,\ell}(r) = N_{k,\ell} \tilde{\varphi}_{k,\ell}(r)$, whence we note that

$$\begin{aligned} \tilde{\varphi}_{1,\ell}(r) &= (2\alpha_\ell r)^{\ell+1} \exp(-\alpha_\ell r) \\ \tilde{\varphi}_{2,\ell}(r) &= 2(\ell+1-\alpha_\ell r)(2\alpha_\ell r)^{\ell+1} \exp(-\alpha_\ell r) \\ (k-1)\tilde{\varphi}_{k,\ell}(r) &= 2(k-1+\ell-\alpha_\ell r)\tilde{\varphi}_{k-1,\ell}(r) - (k+2\ell-1)\tilde{\varphi}_{k-2,\ell}(r) \quad \text{for } k = 3, 4, \dots, \end{aligned}$$

from which can trivially recover the functions $\varphi_{k,\ell}(r)$.

2.2 Normalisation Constant Recurrence Relation

To circumvent overflow errors when calculating the normalisation constant, $N_{k,\ell}$, we construct these constants using a recurrence relations. We note that

$$\begin{aligned} N_{k,\ell} &= \sqrt{\frac{\alpha_\ell (k-1)!}{(k+\ell)(k+2\ell)!}} \\ &= \sqrt{\frac{(k-1)(k-1+\ell)}{(k+\ell)(k+2\ell)} \frac{\alpha_\ell (k-2)!}{(k-1+\ell)(k+2\ell-1)!}} \\ &= \sqrt{\frac{(k-1)(k-1+\ell)}{(k+\ell)(k+2\ell)}} N_{k-1,\ell} \end{aligned}$$

for $k = 2, 3, \dots$ and where $\ell \in \{0, 1, \dots\}$, and that

$$N_{1,\ell} = \sqrt{\frac{\alpha_\ell}{(\ell+1)(2\ell+1)!}}$$

yielding a numerically-stable recurrence relation for the normalisation constants as required.

2.3 Laguerre Radial Basis Code

FORTRAN code for calculating the Laguerre basis functions for a given radial grid can be found in [src/laguerre.f90](#): `subroutine radial_basis()`, and is shown below

```

7  ! radial_basis
8  !
9  ! phi_{k, l, m}(r, theta, phi) = (varphi_{k, l}(r) / r) * Y_{l, m}(theta, phi)
10 ! where
11 ! varphi_{k, l}(r) = sqrt(alpha * (k - 1)! / (k + 1) * (k + 2*1)!)
12 !                   * (2*alpha*r)^{l+1}
13 !                   * exp(-alpha*r)
14 !                   * L_{k - 1}^{2*1 + 1}(2*alpha*r)
15 ! where L_{i}^{j} are the generalised Laguerre polynomials.
16 !
17 ! For given l, alpha, and r_grid, yields the functions varphi_{k, l}(r) for
18 ! k = 1, ..., n_basis, on the radial values specified in the grid.
19 !
20 ! Also returns an error code <ierr> where:
21 ! - 0 indicates successful execution,
22 ! - 1 indicates invalid arguments.
23 pure subroutine radial_basis (l, alpha, n_r, r_grid, n_basis, basis, ierr)
24   integer , intent(in) :: l, n_r, n_basis
25   double precision , intent(in) :: alpha
26   double precision , intent(in) :: r_grid(n_r)
27   double precision , intent(out) :: basis(n_r, n_basis)
28   integer , intent(out) :: ierr
29   double precision :: norm(n_basis)
30   double precision :: alpha_grid(n_r)
31   integer :: kk
32
33   ! check if arguments are valid
34   ierr = 0
35
36   if ((l < 0) .or. (n_basis < 1) .or. (n_r < 1)) then
37     ierr = 1
38     return
39   end if
40
41   ! recurrence relation for basis normalisation constants
42   norm(1) = sqrt(alpha / dble((1 + 1) * gamma(dble((2 * 1) + 2))))
43
44   if (n_basis >= 2) then
45     do kk = 2, n_basis
46       norm(kk) = norm(kk-1) * sqrt(dble((kk - 1) * (kk - 1 + 1)) / &
47         dble((kk + 1) * (kk + (2 * 1))))
48     end do
49   end if
50
51   ! in-lined array since r_grid(:) on its own is never used
52   alpha_grid(:) = alpha * r_grid(:)
53
54   ! recurrence relation for basis functions
55   basis(:, 1) = ((2.0d0 * alpha_grid(:)) ** (1 + 1)) * &
56     exp(-alpha_grid(:))
57
58   if (n_basis >= 2) then
59     basis(:, 2) = 2.0d0 * (dble(1 + 1) - alpha_grid(:)) * basis(:, 1)

```

```

60     end if
61
62     if (n_basis >= 3) then
63         do kk = 3, n_basis
64             basis(:, kk) = &
65                 ((2.0d0 * (dble(kk - 1 + 1) - alpha_grid(:)) * basis(:, kk-1)) &
66                 - dble(kk + (2 * 1) - 1) * basis(:, kk-2)) / dble(kk - 1)
67         end do
68     end if
69
70     ! scaling basis functions by normalisation constants
71     do kk = 1, n_basis
72         basis(:, kk) = basis(:, kk) * norm(kk)
73     end do
74
75 end subroutine radial_basis

```

Listing 1: Calculation of Laguerre radial basis functions for a given radial grid.

2.4 Laguerre Radial Basis Figures

A radial grid has been constructed, for given d_r and r_{\max} , of the form

$$\{r_i = d_r \cdot (i - 1)\}_{i=1}^{n_r}$$

where n_r is the smallest integer such that

$$d_r \cdot (n_r - 1) \geq r_{\max}.$$

The Laguerre basis functions have been calculated on this radial grid, for various values of ℓ and α_ℓ . The plots of the first 4 basis functions for these values of ℓ and α_ℓ are shown in [Figure 1](#).

3 Kinetic Energy Matrix Elements

Here, we shall derive an analytic expression for the kinetic energy matrix elements, with regard to the Laguerre radial basis. Firstly, we note that the kinetic energy matrix elements are defined by

$$K_{i,j} = \langle \phi_i | \hat{K} | \phi_j \rangle = \langle \phi_i | \left[-\frac{1}{2r} \frac{\partial^2}{\partial r^2} (r \cdot) + \frac{1}{2r^2} \hat{L}^2 \right] | \phi_j \rangle$$

whence we note that

$$\begin{aligned}
 K_{i,j} &= \left\langle \frac{1}{r} \varphi_{k_i, \ell_i}, Y_{\ell_i}^{m_i} \right| \left[-\frac{1}{2r} \frac{\partial^2}{\partial r^2} (r \cdot) + \frac{1}{2r^2} \hat{L}^2 \right] \left| \frac{1}{r} \varphi_{k_j, \ell_j}, Y_{\ell_j}^{m_j} \right\rangle \\
 &= \left\langle \frac{1}{r} \varphi_{k_i, \ell_i} \right| \left[-\frac{1}{2r} \frac{d^2}{dr^2} (r \cdot) + \frac{\ell_j(\ell_j + 1)}{2r^2} \right] \left| \frac{1}{r} \varphi_{k_j, \ell_j} \right\rangle \langle Y_{\ell_i}^{m_i} | Y_{\ell_j}^{m_j} \rangle \\
 &= \left\langle \frac{1}{r} \varphi_{k_i, \ell_i} \right| \hat{K}_{\ell_j} \left| \frac{1}{r} \varphi_{k_j, \ell_j} \right\rangle \delta_{\ell_i, \ell_j} \delta_{m_i, m_j}.
 \end{aligned}$$

We note that since the matrix element is necessarily zero, where $\ell_i \neq \ell_j$, we restrict our attention to the case where $\ell_i = \ell_j = \ell$. It follows that the radial terms can be written in the form

$$\begin{aligned} \langle \frac{1}{r} \varphi_{k_i, \ell} | \hat{K}_\ell | \frac{1}{r} \varphi_{k_j, \ell} \rangle &= \langle \frac{1}{r} \varphi_{k_i, \ell} | \left[-\frac{1}{2r} \frac{d^2}{dr^2}(r \cdot) + \frac{\ell(\ell+1)}{2r^2} \right] | \frac{1}{r} \varphi_{k_j, \ell} \rangle \\ &= \int_0^\infty dr r^2 \overline{\frac{1}{r} \varphi_{k_i, \ell}(r)} \left[-\frac{1}{2r} \frac{d^2}{dr^2}(r \cdot) + \frac{\ell(\ell+1)}{2r^2} \right] (\frac{1}{r} \varphi_{k_j, \ell}(r)) \\ &= \int_0^\infty dr \varphi_{k_i, \ell}(r) \left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2} \right] \varphi_{k_j, \ell}(r) \end{aligned}$$

where we have dropped the conjugacy due to the Laguerre radial basis functions being entirely real-valued. Expanding this fully, we have that

$$\begin{aligned} \langle \frac{1}{r} \varphi_{k_i, \ell} | \hat{K}_\ell | \frac{1}{r} \varphi_{k_j, \ell} \rangle &= \int_0^\infty dr (N_{k_i, \ell}(2\alpha r)^{\ell+1} \exp(-\alpha r) L_{k_i-1}^{2\ell+1}(2\alpha r)) \\ &\quad \times \left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2} \right] (N_{k_j, \ell}(2\alpha r)^{\ell+1} \exp(-\alpha r) L_{k_j-1}^{2\ell+1}(2\alpha r)) \end{aligned}$$

whence we introduce the variable transformation $x = 2\alpha r$, to yield an equivalent integral of the form

$$\begin{aligned} \langle \frac{1}{r} \varphi_{k_i, \ell} | \hat{K}_\ell | \frac{1}{r} \varphi_{k_j, \ell} \rangle &= (2\alpha) N_{k_i, \ell} N_{k_j, \ell} \int_0^\infty dx x^{\ell+1} \exp(-\frac{x}{2}) L_{k_i-1}^{2\ell+1}(x) \\ &\quad \times \left[-\frac{1}{2} \frac{d^2}{dx^2} + \frac{\ell(\ell+1)}{2x^2} \right] (x^{\ell+1} \exp(-\frac{x}{2}) L_{k_j-1}^{2\ell+1}(x)). \end{aligned}$$

At this point, we note that

$$\begin{aligned} \frac{d^2}{dx^2} (x^{\ell+1} \exp(-\frac{x}{2}) L_{k_j-1}^{2\ell+1}(x)) &= x^{\ell+1} \exp(-\frac{x}{2}) \\ &\quad \times \left(\left(\frac{\ell(\ell+1)}{x^2} - \frac{\ell+1}{x} + \frac{1}{4} \right) L_{k_j-1}^{2\ell+1}(x) + \left(\frac{2(\ell+1)}{x} - 1 \right) \frac{d}{dx} (L_{k_j-1}^{2\ell+1}(x)) + \frac{d^2}{dx^2} (L_{k_j-1}^{2\ell+1}(x)) \right) \end{aligned}$$

whence

$$\begin{aligned} \left[-\frac{1}{2} \frac{d^2}{dx^2} + \frac{\ell(\ell+1)}{2x^2} \right] (x^{\ell+1} \exp(-\frac{x}{2}) L_{k_j-1}^{2\ell+1}(x)) &= -\frac{1}{2} x^{\ell+1} \exp(-\frac{x}{2}) \\ &\quad \times \left(\left(-\frac{\ell+1}{x} + \frac{1}{4} \right) L_{k_j-1}^{2\ell+1}(x) + \left(\frac{2(\ell+1)}{x} - 1 \right) \frac{d}{dx} (L_{k_j-1}^{2\ell+1}(x)) + \frac{d^2}{dx^2} (L_{k_j-1}^{2\ell+1}(x)) \right). \end{aligned}$$

We utilise the following recurrence relation of the generalised Laguerre polynomials,

$$\frac{t+1-x}{x} \frac{d}{dx} (L_n^t(x)) + \frac{d^2}{dx^2} (L_n^t(x)) = -\frac{n}{x} L_n^t(x)$$

to further simplify the above term to the form

$$\left[-\frac{1}{2} \frac{d^2}{dx^2} + \frac{\ell(\ell+1)}{2x^2} \right] (x^{\ell+1} \exp(-\frac{x}{2}) L_{k_j-1}^{2\ell+1}(x)) = \frac{1}{2} \left(\frac{k_j + \ell}{x} - \frac{1}{4} \right) x^{\ell+1} \exp(-\frac{x}{2}) L_{k_j-1}^{2\ell+1}(x)$$

whence the integral becomes

$$\langle \frac{1}{r} \varphi_{k_i, \ell} | \hat{K}_\ell | \frac{1}{r} \varphi_{k_j, \ell} \rangle = \alpha N_{k_i, \ell} N_{k_j, \ell} \int_0^\infty dx \left(k_j + \ell - \frac{x}{4} \right) x^{2\ell+1} \exp(-x) L_{k_i-1}^{2\ell+1}(x) L_{k_j-1}^{2\ell+1}(x)$$

We note that

$$\langle \frac{1}{r} \varphi_{k_i, \ell} | \frac{1}{r} \varphi_{k_j, \ell} \rangle = \frac{N_{k_i, \ell} N_{k_j, \ell}}{2\alpha} \int_0^\infty dx x^{2\ell+2} \exp(-x) L_{k_i-1}^{2\ell+1}(x) L_{k_j-1}^{2\ell+1}(x)$$

whence the previous integral can be separated as

$$\begin{aligned} \langle \frac{1}{r} \varphi_{k_i, \ell} | \hat{K}_\ell | \frac{1}{r} \varphi_{k_j, \ell} \rangle &= \alpha N_{k_i, \ell} N_{k_j, \ell} (k_j + \ell) \int_0^\infty dx x^{2\ell+1} \exp(-x) L_{k_i-1}^{2\ell+1}(x) L_{k_j-1}^{2\ell+1}(x) \\ &\quad - \frac{\alpha}{4} N_{k_i, \ell} N_{k_j, \ell} \int_0^\infty dx x^{2\ell+2} \exp(-x) L_{k_i-1}^{2\ell+1}(x) L_{k_j-1}^{2\ell+1}(x) \\ &= \alpha N_{k_i, \ell} N_{k_j, \ell} (k_j + \ell) \int_0^\infty dx x^{2\ell+1} \exp(-x) L_{k_i-1}^{2\ell+1}(x) L_{k_j-1}^{2\ell+1}(x) \\ &\quad - \frac{\alpha^2}{2} \langle \frac{1}{r} \varphi_{k_i, \ell} | \frac{1}{r} \varphi_{k_j, \ell} \rangle. \end{aligned}$$

At this point we note the following property of the generalised Laguerre polynomials,

$$\int_0^\infty dx x^t \exp(-x) L_n^t(x) L_m^t(x) = \frac{(n+t)!}{n!} \delta_{m,n}$$

whence the radial term of the kinetic energy matrix elements is shown to be given analytically by the expression

$$\begin{aligned} \langle \frac{1}{r} \varphi_{k_i, \ell} | \hat{K}_\ell | \frac{1}{r} \varphi_{k_j, \ell} \rangle &= \alpha N_{k_i, \ell}^2 (k_j + \ell) \frac{(k_j + 2\ell)!}{(k_j - 1)!} \delta_{k_i, k_j} - \frac{\alpha^2}{2} \langle \frac{1}{r} \varphi_{k_i, \ell} | \frac{1}{r} \varphi_{k_j, \ell} \rangle \\ &= \alpha^2 \delta_{k_i, k_j} - \frac{\alpha^2}{2} \langle \frac{1}{r} \varphi_{k_i, \ell} | \frac{1}{r} \varphi_{k_j, \ell} \rangle. \end{aligned}$$

It follows that the kinetic energy matrix elements are thus of the form

$$K_{i,j} = \left(\alpha^2 \delta_{k_i, k_j} - \frac{\alpha^2}{2} \langle \frac{1}{r} \varphi_{k_i, \ell} | \frac{1}{r} \varphi_{k_j, \ell} \rangle \right) \delta_{\ell_i, \ell_j} \delta_{m_i, m_j}.$$

3.1 Extension: Overlap Matrix Elements

4 Atomic Hydrogen States

4.1 Extension: He⁺ Ion

4.2 Extension: Surface Plot in xz Plane

4.3 Extension: Numerically Calculating Potential Matrix Elements

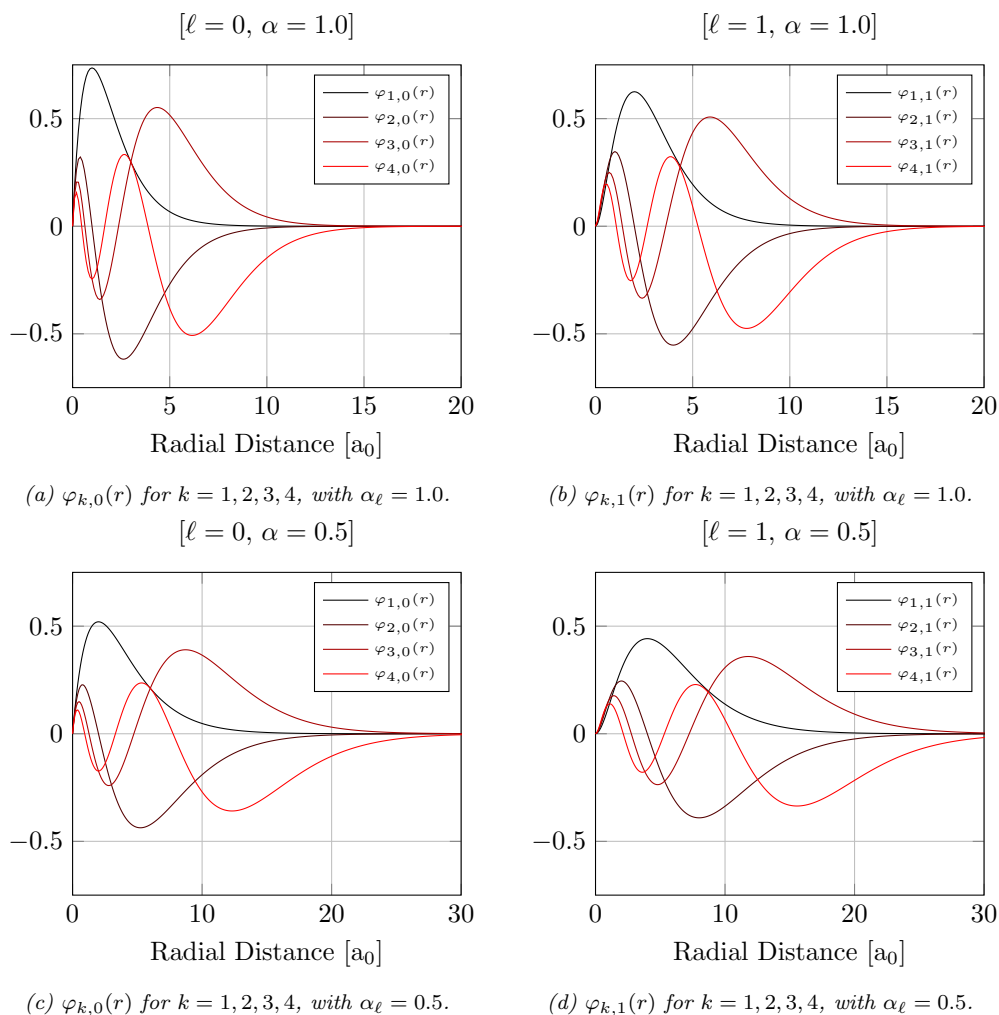


Figure 1: The first four Laguerre radial basis functions are plotted for various cases of ℓ and α_ℓ . Note that every figure has the same y-axis bounds $[-0.75, 0.75]$, whereas the x-axis bounds are $[0, 20]$ for the $\alpha_\ell = 1.0$ cases, and $\{0, 30\}$ for the $\alpha_\ell = 0.5$ cases. Observe that $\varphi_{k,\ell}(r)$ has k extremal points, with each extrema being larger (in magnitude) than the preceding extrema, before eventually exhibiting exponential decay to 0, after the last extremal point.