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 $N \to \infty$. We select the basis functions, represented in coordinate-space, to be of the form

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

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 $N \to \infty$. For elements of this basis, the one-electron Hydrogenic-atom Hamiltonian assumes the form

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

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

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

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

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

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

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

2 Laguerre Basis

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

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

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

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

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

$$L_0^t(x) = 1$$
$$L_1^t(x) = 1 + t - x$$
$$(n+1)L_{n+1}^t(x) = (2n+1+t-x)L_n^t(x) - (n+t)L_{n-1}^t(x) \quad \text{for} \quad n = 1, 2, \ldots.$$

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

$$\widetilde{\varphi}_{1,\ell}(r) = (2\alpha r)^{\ell+1}\exp(-\alpha r)$$
$$\widetilde{\varphi}_{2,\ell}(r) = 2(\ell+1-\alpha r)(2\alpha r)^{\ell+1}\exp(-\alpha r)$$
$$(k-1)\widetilde{\varphi}_{k,\ell}(r) = 2(k-1+\ell-\alpha r)\widetilde{\varphi}_{k-1,\ell}(r) - (k+2\ell-1)\widetilde{\varphi}_{k-2,\ell}(r) \quad \text{for} \quad k = 3, 4, \ldots,$$

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

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

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

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

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

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

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

```fortran
 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 + l) * (k + 2*l)!)
12   !                      * (2*alpha*r)^{l+1}
13   !                      * exp(-alpha*r)
14   !                      * L_{k - 1}^{2*l + 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((l + 1) * gamma(dble((2 * l) + 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 + l)) / &
47             dble((kk + l) * (kk + (2 * l))))
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(:)) ** (l + 1)) * &
56         exp(-alpha_grid(:))
57
58     if (n_basis >= 2) then
59       basis(:, 2) = 2.0d0 * (dble(l + 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 + l) - alpha_grid(:)) * basis(:, kk-1)) &
66              - dble(kk + (2 * l) - 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 ℓ and α. The first four functions have been plotted for the following cases:

- The case of $\ell = 0$, $\alpha = 1.0$ is shown in Figure 1.

3   Kinetic Energy Matrix Elements

3.1   Extension: Overlap Matrix Elements

4   Atomic Hydrogen States

4.1   Extension: He$^+$ Ion

4.2   Extension: Surface Plot in xz Plane

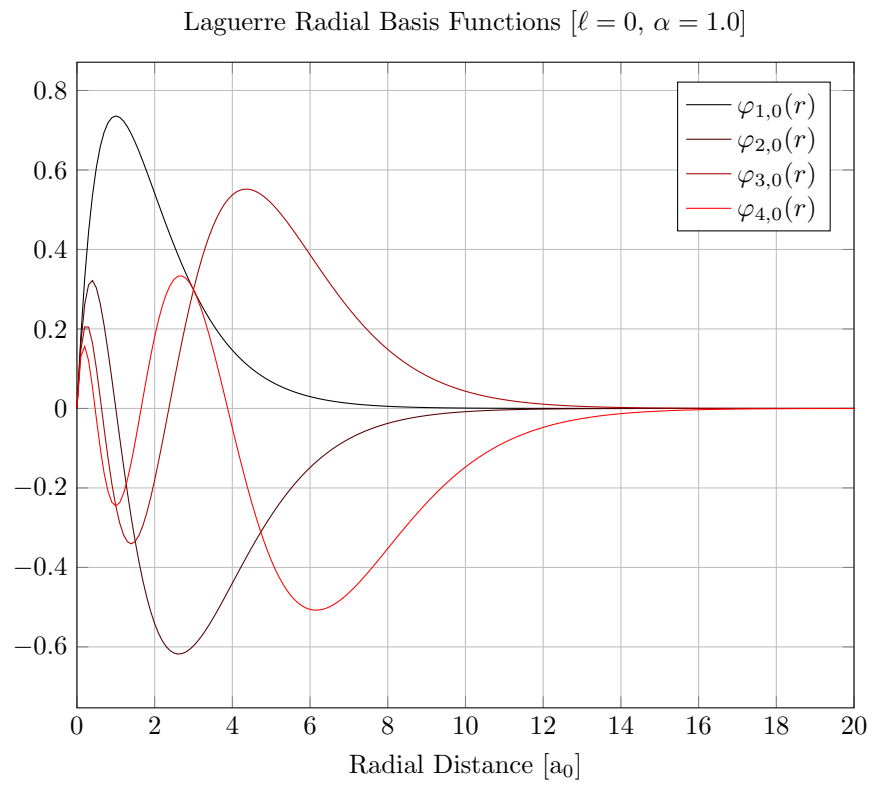## 4.3   Extension: Numerically Calculating Potential Matrix Elements

Laguerre Radial Basis Functions $[\ell = 0,\ \alpha = 1.0]$

Figure 1: ...