

The entire code repository used to calculate the data for this report, and including the `.tex` file used to produce this pdf, can be found at <https://github.com/dgsaf/acqm-workshop-1>.

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

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

We solve the system by the method of basis expansion, which is to say that we expand the pseudostates, $\{|\Phi_i\rangle\}_{i=1}^N$ of \hat{H} in terms of the basis \mathcal{B} , as

$$|\Phi_i\rangle = \sum_{j=1}^N C_{i,j} |\phi_j\rangle$$

which, in the limit as $N \rightarrow \infty$, satisfy, for $k = 1, \dots, N$,

$$\hat{H} |\Phi_k\rangle = E_k |\Phi_k\rangle.$$

Whence, for $k = 1, \dots, N$, we have that

$$\begin{aligned} \langle \phi_i | \hat{H} | \Phi_k \rangle &= E_k \langle \phi_i | \Phi_k \rangle \\ \sum_{j=1}^N C_{k,j} \langle \phi_i | \hat{H} | \phi_j \rangle &= E_k \sum_{j=1}^N C_{k,j} \langle \phi_i | \phi_k \rangle \\ \sum_{j=1}^N C_{k,j} (\langle \phi_i | \hat{H} | \phi_j \rangle - E_k \langle \phi_i | \phi_k \rangle) &= 0 \\ \sum_{j=1}^N C_{k,j} (H_{i,j} - E_k B_{i,j}) &= 0 \end{aligned}$$

yielding a set of generalised eigenvalue problems. Lastly, due to the Hamiltonian being reducible for given ℓ, m , we introduce the notation that

$$|\Phi_{k,\ell,m}\rangle = \sum_{i=1}^N C_{k,i}^{(\ell,m)} |\phi_{i,\ell,m}\rangle$$

as well as the radial functions of the pseudostates

$$|\bar{\Phi}_{k,\ell,m}\rangle = \sum_{i=1}^N C_{k,i}^{(\ell,m)} |\varphi_{i,\ell,m}\rangle.$$

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 in [Listing 1](#).

```

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](#).

It can be seen from [Figure 1](#) that as ℓ increases, the Laguerre radial functions are somewhat shifted further from the origin; that is, they are suppressed at the origin, peak at a further distance away from the origin, and extend further away from the origin before exponentially decaying to 0. They also have wider and less pronounced peaks.

It can also be seen from [Figure 1](#) that as α_ℓ decreases, the Laguerre radial basis functions extend much further away from the origin before exponentially decaying to 0, and have wider and less pronounced peaks.

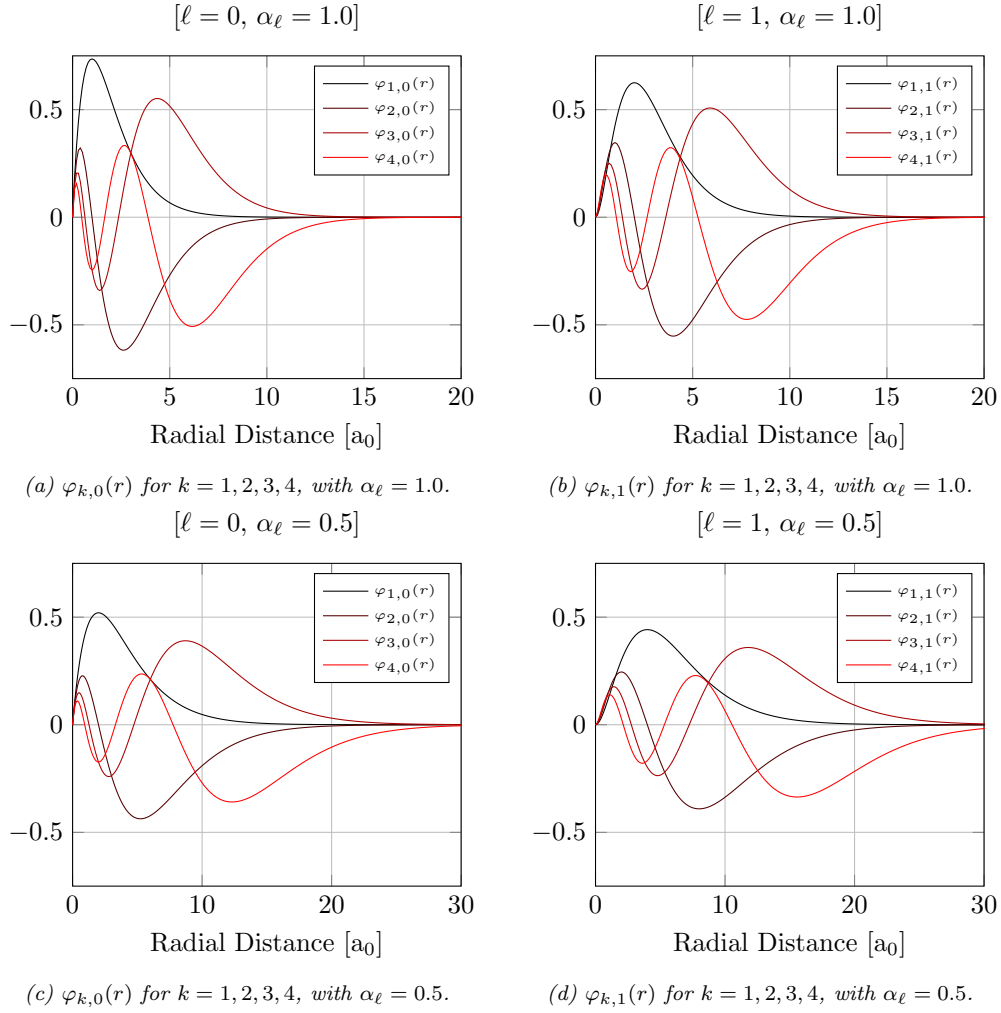


Figure 1: The first four Laguerre radial basis functions are plotted for various cases of ℓ and α_ℓ . Note that every figure has the same y-axis bounds $[-0.75, 0.75]$, whereas the x-axis bounds are $[0, 20]$ for the $\alpha_\ell = 1.0$ cases, and $\{0, 30\}$ for the $\alpha_\ell = 0.5$ cases. Observe 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.

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

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

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

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

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

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

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

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

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

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

3.1 Extension: Overlap Matrix Elements

4 Atomic Hydrogen States

4.1 Hydrogenic Atom Code

4.1.1 Overlap Matrix Elements

FORTRAN code for calculating the overlap matrix elements for a Laguerre radial basis of a given dimension can be found in `src/laguerre.f90`: `subroutine overlap_matrix()`, and is shown in Listing 2.

```

77  ! overlap_matrix
78  !
79  ! < phi_{k'}, l, m | phi_{k, l, m} >
80  !
81  ! Overlap matrix elements for given l, m.
82  ! We can restrict our attention to considering fixed l and m, since the matrix
83  ! elements are zero when l' /= l or where m' /= m.
84  ! Furthermore, the exponential decay variable, alpha, has no influence on
85  ! these matrix elements, nor does the magnetic quantum number, m.
86  !
87  ! Also returns an error code <ierr> where:
88  ! - 0 indicates successful execution,
89  ! - 1 indicates invalid arguments.
90  pure subroutine overlap_matrix(l, n_basis, B, ierr)
91      integer , intent(in) :: l, n_basis
92      double precision , intent(out) :: B(n_basis, n_basis)
93      integer , intent(out) :: ierr
94      integer :: kk
95
96      ! check if arguments are valid
97      ierr = 0
98
99      if ((l < 0) .or. (n_basis < 1)) then
100          ierr = 1
101          return
102      end if
103
104      ! initialise overlap matrix to zero
105      B(:, :) = 0.0d0
106
107      ! determine tri-diagonal overlap matrix elements
108      do kk = 1, n_basis-1
109          B(kk, kk) = 1.0d0
110
111          B(kk, kk+1) = - 0.5d0 * sqrt(1 - &
112              (dble(l * (l + 1)) / dble((kk + 1) * (kk + 1 + 1))))
113
114          B(kk+1, kk) = B(kk, kk+1)
115      end do
116
117      ! last term (not covered by loop)
118      B(n_basis, n_basis) = 1.0d0
119
120  end subroutine overlap_matrix

```

Listing 2: Calculation of overlap matrix elements for a Laguerre radial basis of a given dimension.

4.1.2 Kinetic Energy Matrix Elements

FORTTRAN code for calculating the kinetic energy matrix elements for a Laguerre radial basis of a given dimension can be found in `src/laguerre.f90`: `subroutine kinetic_matrix()`, and is shown in Listing 3.

```

122 ! kinetic_matrix
123 !
124 ! < phi_{k', l, m} | K | phi_{k, l, m} >
125 !
126 ! Kinetic matrix elements for given l, m, alpha.
127 ! We can restrict our attention to considering fixed l and m, since the matrix
128 ! elements are zero when l' /= l or where m' /= m.
129 ! Furthermore, the magnetic quantum number, m, has no influence on these
130 ! matrix elements.
131 !
132 ! Also returns an error code <ierr> where:
133 ! - 0 indicates successful execution,
134 ! - 1 indicates invalid arguments.
135 pure subroutine kinetic_matrix(l, alpha, n_basis, K, ierr)
136   integer , intent(in) :: l, n_basis
137   double precision , intent(in) :: alpha
138   double precision , intent(out) :: K(n_basis, n_basis)
139   integer , intent(out) :: ierr
140   integer :: kk
141
142   ! check if arguments are valid
143   ierr = 0
144
145   if ((l < 0) .or. (n_basis < 1)) then
146     ierr = 1
147     return
148   end if
149
150   ! initialise kinetic matrix to zero
151   K(:, :) = 0.0d0
152
153   ! determine tri-diagonal kinetic matrix elements
154   do kk = 1, n_basis-1
155     K(kk, kk) = 0.5d0 * (alpha ** 2)
156
157     K(kk, kk+1) = (alpha ** 2) * 0.25d0 * sqrt(1 - &
158       (dble(1 * (1 + 1)) / dble((kk + 1) * (kk + 1 + 1))))
159
160     K(kk+1, kk) = K(kk, kk+1)
161   end do
162
163   ! last term (not covered by loop)
164   K(n_basis, n_basis) = 0.5d0 * (alpha ** 2)
165
166 end subroutine kinetic_matrix

```

Listing 3: Calculation of kinetic energy matrix elements for a Laguerre radial basis of a given dimension.

4.1.3 Coulomb Potential Matrix Elements

FORTTRAN code for calculating the Coulomb potential matrix elements for a Laguerre radial basis of a given dimension can be found in `src/laguerre.f90: subroutine coulomb_matrix()`, and is shown in Listing 4.

```

168 ! coulomb_matrix
169 !
170 ! < phi_{k', l, m} | 1/r | phi_{k, l, m} >
171 !
172 ! Coulomb matrix elements for given l, m, alpha.
173 ! We can restrict our attention to considering fixed l and m, since the matrix
174 ! elements are zero when l' /= l or where m' /= m.
175 ! Furthermore, the magnetic quantum number, m, has no influence on these
176 ! matrix elements.
177 !
178 ! Also returns an error code <ierr> where:
179 ! - 0 indicates successful execution,
180 ! - 1 indicates invalid arguments.
181 pure subroutine coulomb_matrix(l, alpha, n_basis, V, ierr)
182   integer , intent(in) :: l, n_basis
183   double precision , intent(in) :: alpha
184   double precision , intent(out) :: V(n_basis, n_basis)
185   integer , intent(out) :: ierr
186   integer :: kk
187
188   ! check if arguments are valid
189   ierr = 0
190
191   if ((l < 0) .or. (n_basis < 1)) then
192     ierr = 1
193     return
194   end if
195
196   ! initialise coulomb matrix to zero
197   V(:, :) = 0.0d0
198
199   ! determine diagonal coulomb matrix elements
200   do kk = 1, n_basis
201     V(kk, kk) = alpha / dble(kk + 1)
202   end do
203
204   end subroutine coulomb_matrix

```

Listing 4: Calculation of Coulomb potential matrix elements for a Laguerre radial basis of a given dimension.

4.1.4 Hamiltonian Matrix Elements

FORTTRAN code for calculating the overlap, kinetic energy, potential energy, and Hamiltonian matrix elements for a Laguerre radial basis of a given dimension can be found in `src/laguerre.f90: subroutine hydrogenic_matrices()`, and is shown in Listing 5.

```

206 ! hydrogenic_matrices
207 !
208 ! Yields overlap, kinetic, potential and Hamiltonian matrices for given l, m,
209 ! alpha, atomic_charge; that is: B, K, V, H.

```

```

210 ! We can restrict our attention to considering fixed l and m, since the matrix
211 ! elements are zero when l' /= l or where m' /= m.
212 ! Furthermore, the magnetic quantum number, m, has no influence on these
213 ! matrix elements.
214 !
215 ! Also returns an error code <ierr> where:
216 ! - 0 indicates successful execution,
217 ! - 1 indicates invalid arguments.
218 pure subroutine hydrogenic_matrices(l, alpha, atomic_charge, n_basis, B, &
219     K, V, H, ierr)
220     integer , intent(in) :: l, atomic_charge, n_basis
221     double precision , intent(in) :: alpha
222     double precision , intent(out) :: B(n_basis, n_basis), K(n_basis, n_basis), &
223         V(n_basis, n_basis), H(n_basis, n_basis)
224     integer , intent(out) :: ierr
225
226     ! check if arguments are valid
227     ierr = 0
228
229     if ((l < 0) .or. (n_basis < 1)) then
230         ierr = 1
231         return
232     end if
233
234     ! calculate matrices
235     call overlap_matrix(l, n_basis, B, ierr)
236
237     call kinetic_matrix(l, alpha, n_basis, K, ierr)
238
239     call coulomb_matrix(l, alpha, n_basis, V, ierr)
240     V(:, :) = - dble(atomic_charge) * V(:, :)
241
242     H(:, :) = K(:, :) + V(:, :)
243
244 end subroutine hydrogenic_matrices

```

Listing 5: Calculation of overlap, kinetic energy, potential energy, and Hamiltonian matrix elements for a Laguerre radial basis of a given dimension.

4.1.5 Hydrogenic Atom Program

A FORTRAN program which calculates the pseudo-energies and pseudo-states of a one-electron Hydrogenic-atom Hamiltonian by the method of basis expansion, using the Laguerre radial basis, for given $(\ell, m, \alpha_\ell, Z, n_{\text{basis}}, d_r, r_{\text{max}})$, can be found in [src/hydrogenic_atom.f90](#) and is shown in Listing 6.

```

1 !>
2 program hydrogenic_atom
3
4     use laguerre
5     use io
6
7     implicit none
8
9     ! global flags
10    logical , parameter :: debugging = .true.

```

```

11  logical , parameter :: display_bases = .false.
12  logical , parameter :: display_matrices = .true.
13
14  ! angular quantum number variables
15  integer :: l, m
16  double precision :: alpha
17
18  ! atomic variables
19  integer :: atomic_charge
20
21  ! radial grid variables
22  integer :: n_r
23  double precision :: d_r, r_max
24  double precision , allocatable :: r_grid(:)
25
26  ! basis variables
27  integer :: n_basis
28  double precision , allocatable :: basis(:, :)
29  double precision , allocatable :: eigen_basis(:, :)
30
31  ! matrices
32  double precision , allocatable :: B(:, :), K(:, :), V(:, :), H(:, :)
33  double precision , allocatable :: eigen_values(:), eigen_vectors(:, :)
34
35  ! local variables
36  integer :: ierr
37  integer :: ii
38
39  ! read parameters from command line arguments
40  call read_input(l, m, alpha, atomic_charge, n_basis, d_r, r_max)
41
42  ! check if parameters are valid
43  if ((l < 0) .or. (abs(m) > l) &
44      .or. (alpha < 0.0d0) &
45      .or. (n_basis < 1) &
46      .or. (d_r < 0.0d0) .or. (r_max < 0.0d0)) then
47      ierr = 1
48      write (*, *) "parameters are invalid, failing with <ierr>: ", ierr
49      call exit(ierr)
50  end if
51
52  ! set n_r
53  n_r = ceiling(r_max / d_r) + 1
54
55  ! allocate arrays
56  allocate(r_grid(n_r))
57
58  allocate(basis(n_r, n_basis))
59  allocate(eigen_basis(n_r, n_basis))
60
61  allocate(B(n_basis, n_basis))
62  allocate(K(n_basis, n_basis))
63  allocate(V(n_basis, n_basis))
64  allocate(H(n_basis, n_basis))
65
66  allocate(eigen_values(n_basis))
67  allocate(eigen_vectors(n_basis, n_basis))
68

```

```

69  ! initialise radial grid
70  do ii = 1, n_r
71    r_grid(ii) = d_r * (ii - 1)
72  end do
73
74  ! calculate radial basis functions
75  call radial_basis(1, alpha, n_r, r_grid, n_basis, basis, ierr)
76
77  if (ierr /= 0) then
78    write (*, *) "radial_basis() failed with <ierr>: ", ierr
79    call exit(ierr)
80  end if
81
82  if (display_bases) then
83    write (*, *) "basis(n_r, n_basis)"
84    call display_basis(n_r, r_grid, n_basis, basis)
85  end if
86
87  ! calculate matrix elements
88  call hydrogenic_matrices(1, alpha, atomic_charge, n_basis, B, K, V, H, ierr)
89
90  if (ierr /= 0) then
91    write (*, *) "hydrogenic_matrices() failed with <ierr>: ", ierr
92    call exit(ierr)
93  end if
94
95  if (display_matrices) then
96    write (*, *) "B(n_basis, n_basis)"
97    call display_matrix(n_basis, n_basis, B)
98
99    write (*, *) "K(n_basis, n_basis)"
100    call display_matrix(n_basis, n_basis, K)
101
102    write (*, *) "V(n_basis, n_basis)"
103    call display_matrix(n_basis, n_basis, V)
104
105    write (*, *) "H(n_basis, n_basis)"
106    call display_matrix(n_basis, n_basis, H)
107  end if
108
109  ! diagonalise
110  call diagonalise(n_r, n_basis, basis, B, H, eigen_values, eigen_vectors, &
111    eigen_basis)
112
113  if (display_matrices) then
114    write (*, *) "eigen_values(n_basis)"
115    call display_vector(n_basis, eigen_values)
116
117    write (*, *) "eigen_vectors(n_basis, n_basis)"
118    call display_matrix(n_basis, n_basis, eigen_vectors)
119  end if
120
121  if (display_bases) then
122    write (*, *) "eigen_basis(n_r, n_basis)"
123    call display_basis(n_r, r_grid, n_basis, eigen_basis)
124  end if
125
126  ! write output to file

```

```

127  call write_output(l, m, alpha, atomic_charge, n_r, r_grid, n_basis, basis, &
128      B, K, V, H, eigen_values, eigen_vectors, eigen_basis)
129
130  ! deallocate arrays
131  deallocate(r_grid)
132
133  deallocate(basis)
134  deallocate(eigen_basis)
135
136  deallocate(B)
137  deallocate(K)
138  deallocate(V)
139  deallocate(H)
140
141  deallocate(eigen_values)
142  deallocate(eigen_vectors)
143
144  contains
145
146  ! diagonalise
147  ! Note that since the call to rsg modifies the matrices it is given, we send
148  ! it copies of B, H.
149  subroutine diagonalise (n_r, n_basis, basis, B, H, eigen_values, &
150      eigen_vectors, eigen_basis)
151      integer , intent(in) :: n_r, n_basis
152      double precision , intent(in) :: basis(n_r, n_basis)
153      double precision , intent(in) :: B(n_basis, n_basis), H(n_basis, n_basis)
154      double precision , intent(out) :: eigen_values(n_basis)
155      double precision , intent(out) :: eigen_vectors(n_basis, n_basis)
156      double precision , intent(out) :: eigen_basis(n_r, n_basis)
157      double precision :: B_copy(n_basis, n_basis), H_copy(n_basis, n_basis)
158      integer :: ii, jj, kk
159      integer :: ierr
160      double precision :: temp_sum
161
162      ! create copies of B, H matrices to use in call to rsg subroutine
163      B_copy(:, :) = B(:, :)
164      H_copy(:, :) = H(:, :)
165
166      ! solve eigenvalue matrix equation
167      eigen_values(:) = 0.0d0
168      eigen_vectors(:, :) = 0.0d0
169
170      call rsg(n_basis, n_basis, H_copy, B_copy, eigen_values, 1, eigen_vectors, &
171          ierr)
172
173      if (ierr /= 0) then
174          write (*, *) "rsg() failed with <ierr>: ", ierr
175          call exit(ierr)
176      end if
177
178      ! calculate eigen-basis
179      eigen_basis(:, :) = 0.0d0
180
181      do jj = 1, n_basis
182          do ii = 1, n_r
183              temp_sum = 0.0d0

```



```
185         do kk = 1, n_basis
186             temp_sum = temp_sum + (eigen_vectors(kk, jj) * basis(ii, kk))
187         end do
188
189         eigen_basis(ii, jj) = temp_sum
190     end do
191 end do
192
193 end subroutine diagonalise
194
195 end program hydrogenic_atom
```

Listing 6: Calculation of pseudo-energies and pseudo-states of a one-electron Hydrogenic-atom Hamiltonian by the method of basis expansion, using the Laguerre radial basis.

4.2.2 Behaviour of Bound Energy Spectrum with Varying α_ℓ

The bound energy spectrum of a one-electron Hydrogen atom, calculated for $l = 0$, $n_{\text{basis}} = 64$, and for varying $\alpha_\ell = 0.50, 0.75, \dots, 1.50$, is shown in Figure 3. It is compared with the analytical energies, which are known to be

$$E_n = -\frac{1}{2n^2} \quad \text{for } n = 1, 2, \dots$$

in atomic units. Note that all pseudo-energies greater than 0, obtained by diagonalising the Hamiltonian matrix, are not presented in Figure 3. Note also that the basis size is identical for each calculation, but the number of bound pseudo-energies is not necessarily identical.

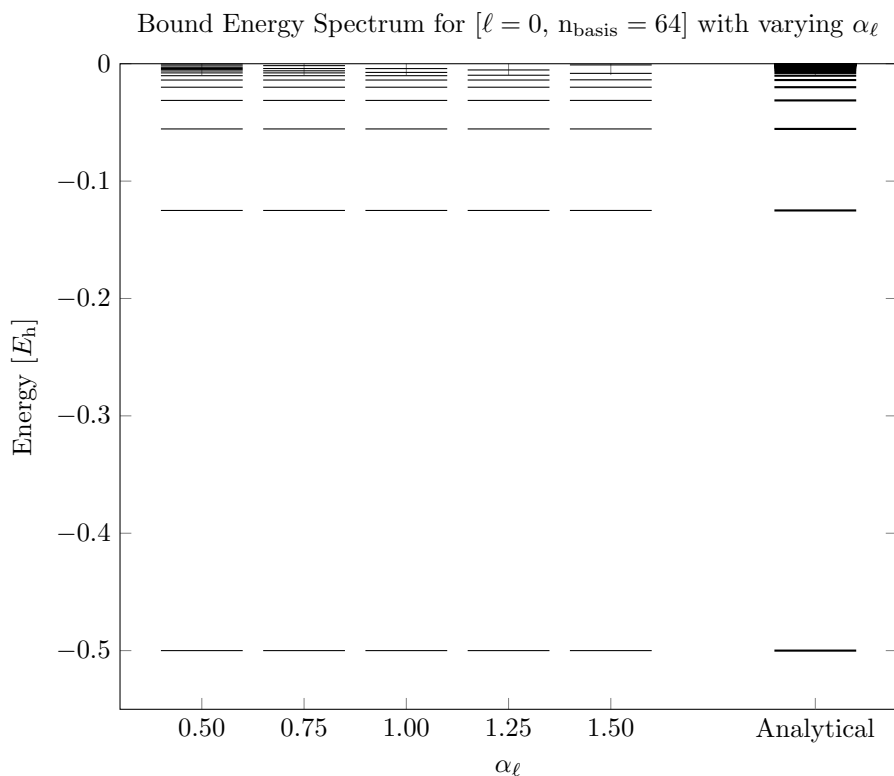


Figure 3: Bound energy spectrums, in units of E_h , for a one-electron Hydrogen atom, where $\ell = 0$, $n_{\text{basis}} = 64$, and where $\alpha = 0.50, 0.75, \dots, 1.50$. It is compared with the analytical energies, represented at the label $n_{\text{basis}} = \infty$.

It can be seen that as α_ℓ decreases, the bound energy spectrum becomes increasingly dense, and thus, it can be inferred that the continuum energy spectrum becomes increasingly sparse (since the total number of psuedo-states, across bound and continuum states, is identical for each calculation). Conversely, as α_ℓ increases, the bound energy spectrum becomes increasingly sparse, while the continuum energy spectrum becomes increasingly dense.

An implication of this observation is that for scattering calculations, if a radial basis with a small value of α_ℓ is utilised for the target states, then the discretisation of the continuum energy spectrum might be insufficient to model long-range interactions between the target electron and the projectile. That is, over-emphasising short-range or long-range structure, by using either a small or large value for α_ℓ may lead to inaccurate scattering calculations.

4.2.3 Comparison of Calculated and Analytical Radial Functions

We observe that for $n_{\text{basis}} = 128$, the calculation is sufficiently convergent to analytical solutions of the one-electron Hydrogen atom. We present, for $\alpha_\ell = 1.0$ and $n_{\text{basis}} = 128$, the first three bound-state calculated radial functions, for the cases of $\ell = 0, 1$, in [Figure 4](#), and compare them with the analytical solutions for the one-electron Hydrogen atom, which are of the form

$$\bar{\Phi}_{k,\ell}(r) = \sqrt{\left(\frac{2}{k+\ell}\right)^3 \frac{(k-1)!}{2(k+\ell)(k+2\ell)!}} r \left(\frac{2r}{k+\ell}\right)^\ell \exp\left(-\frac{r}{k+\ell}\right) L_{k-1}^{2\ell+1}\left(\frac{r}{k+\ell}\right)$$

for $k = 1, 2, \dots$, for any given $\ell \in \{0, 1, \dots\}$.

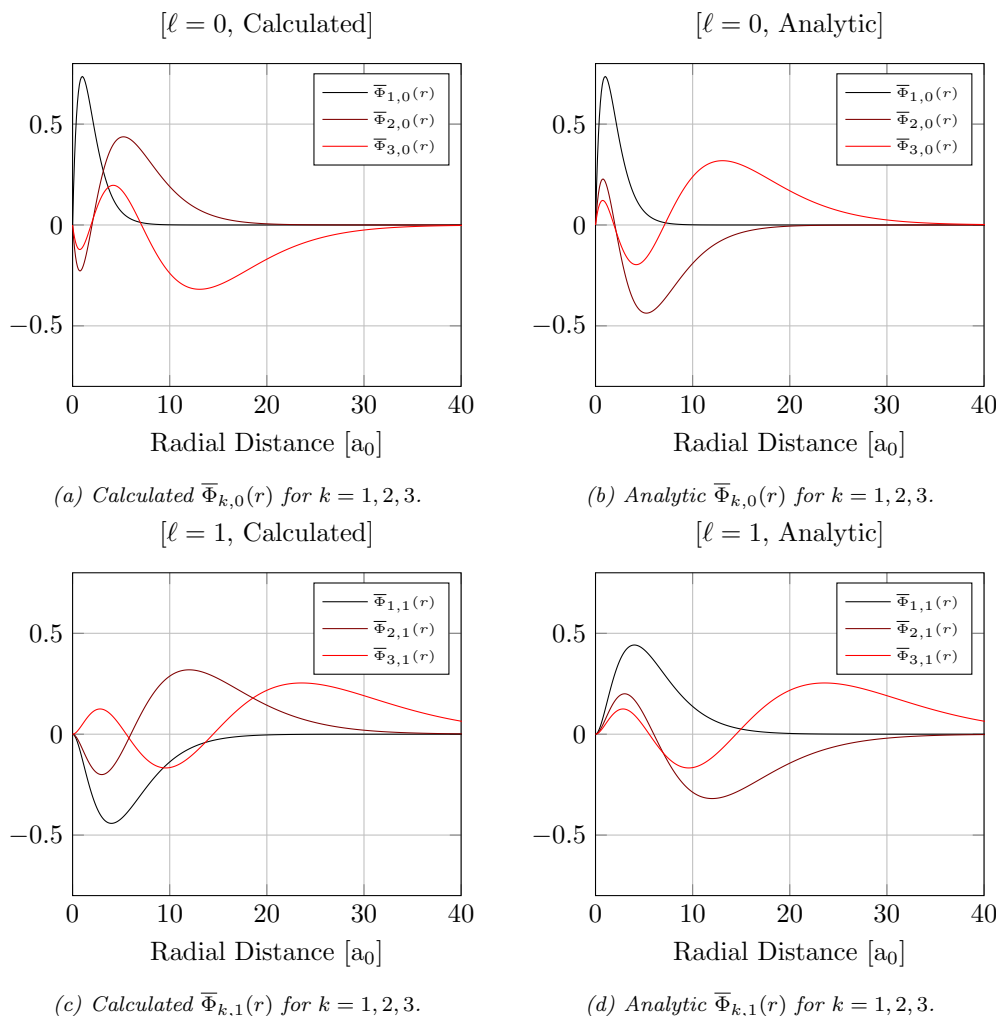


Figure 4: The radial functions of the first three bound pseudostates of the one-electron Hydrogen atom, $\bar{\Phi}_{k,\ell,0}(r)$ for $k = 1, 2, 3$, for the cases of $\ell = 0, 1$ are plotted and compared with the analytic solutions. Note that both sets of calculated radial functions were calculated with $\alpha_\ell = 1.0$ and $n_{\text{basis}} = 128$. Note that these are the radial functions $|\bar{\Phi}_{k,\ell,m}\rangle = \sum_i C_{k,i} |\varphi_{i,\ell,m}\rangle$, and so do not include the $\frac{1}{r}$ term. Observe that some of the analytic radial functions are phase-shifted from the calculated radial functions by a factor of $e^{i\pi} = -1$. However, the analytic and calculated radial functions represent the same state, as states are considered to be equivalent under a phase-shift transformation.

4.3 Extension: He^+ Ion

4.4 Extension: Surface Plot in xz Plane

4.5 Extension: Numerically Calculating Potential Matrix Elements