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

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

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

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

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

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

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

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

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

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

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

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

for $k = 2, 3, \ldots$, 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 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 + 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.

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