

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

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

For elements of this basis, the one-electron Hydrogenic-atom Hamiltonian assumes the form

$$\begin{aligned} \hat{H} |\phi_i\rangle &= \left[-\frac{1}{2r} \frac{\partial^2}{\partial r^2} (r \cdot) + \frac{1}{2r^2} \hat{L}^2 - \frac{Z}{r} \right] |\phi_i\rangle \\ &= \left[-\frac{1}{2r} \frac{\partial^2}{\partial r^2} (r \cdot) + \frac{\ell_i(\ell_i+1)}{2r^2} - \frac{Z}{r} \right] |\phi_i\rangle \\ &= \left[-\frac{1}{2r} \frac{\partial^2}{\partial r^2} + \frac{\ell_i(\ell_i+1)}{2r^3} - \frac{Z}{r^2} \right] |\varphi_{k_i, \ell_i}\rangle \otimes |Y_{\ell_i}^{m_i}\rangle \end{aligned}$$

thus reducing to operator which acts purely to radial terms.

2 Laguerre Basis

We utilise a Laguerre basis for the set of radial functions which, in coordinate-space, are of the form

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

3 Kinetic Energy Matrix Elements

3.1 Extension: Overlap Matrix Elements

4 Atomic Hydrogen States

4.1 He⁺ Ion

4.2 Surface Plot in xz Plane

4.3 Numerically Calculating Potential Matrix Elements