Solving the radial wavefunction using B-splines

In this report, a description will be given on how the radial function for hydrogen-like atoms,

$$-\frac{\hbar^2}{2\mu}\left(\frac{1}{r^2}\left(r^2\frac{\partial R_{n\ell}}{\partial r}\right)-\frac{\ell(\ell+1)}{r^2}R_{n\ell}\right) + V(r)R_{n\ell} = ER_{n\ell}, \tag{1}$$

is solved using B-splines. Here $R_{n\ell}(r)$ is the radial function, μ is the reduced mass, n is the principal quantum number and ℓ is the azimuthal quantum number. This equation can be simplified by introducing the reduced radial wavefunction $P_{n\ell}(r) = rR_{n\ell}(r)$:

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2P_{n\ell}}{\mathrm{d}r^2}+\frac{\hbar^2\ell(\ell+1)}{2\mu r^2}P_{n\ell} + V(r)P_{n\ell} = EP_{n\ell}. \tag{2}$$

The boundary conditions of $P_{n\ell}$ are $P_{n\ell}(0) = 0$ and $P_{n\ell}(r\to\infty) = 0$. The potentials which were used were the Coulomb potential:

$$V_C = -\frac{Ze^2}{4\pi\epsilon_0 r} \tag{3}$$

and the potential from a uniformily charged shell of radius R_0:

$$V_S(r) = \begin{cases} -Ze^2(3-(r/R_0)^2)/(8\pi\epsilon_0R_0), & r < R_0, \\ -Ze^2/(4\pi\epsilon_0 r), & r \geq R_0. \end{cases} \tag{4}$$

Numerical set-up and method

The following dimensionless variables were defined:

$$\begin{aligned} \xi &= r/Da_0, \\ E' &= E/\left(Z^2\mu\hbar^2/(2m_e^2a_0^2)\right). \end{aligned} \tag{5}$$

In principle, E' should take the values $-1, -1/4, -1/9, \ldots$ for bound states. The variable ξ is on the interval $[0,1]$ and D is chosen so that the wavefunction is negliably small in the vicinity of $\xi = 1$. Using these variables, equation (2) can be written

$$\hat{H}u = -\beta^2\left(\frac{\mathrm{d}^2}{\mathrm{d}\xi^2}-\frac{\ell(\ell+1)}{\xi^2}+\frac{2}{\beta\xi}\right)u = E'u \tag{6}$$

where $\beta = m_e/(Z\mu D)$. The numerical solution to (6) is written as a linear combination of n B-splines of degree k:

$$u(\xi) = \sum_{j=0}^{n-1} c_j B_{j,k}(\xi). \tag{7}$$

The boundary conditions $u(0) = u(1) = 0$ are satisfied by placing $k+1$ knot points at $\xi = 0$ and another $k+1$ knot points at $\xi = 1$. This makes $B_{0,k}$ the only non-zero B-splines at $\xi = 0$ and $B_{n-1,k}$ the only non-zero B-spline at $\xi = 1$. The boundary conditions were thus satisfied by setting $c_0 = c_{n-1} = 0$. Since the wavefunction is vanishing for ξ closer to one, the inner knot points were distributed non-uniformily on the interval so that more knot points were closer to $\xi = 0$ than $\xi = 1$. A distribution which worked quite well was $2^{\xi^2} - 1$.

Inserting (7) into (6), multiplying by $B_{i,k}(x)$ and integrating over $(0,1)$ yields:

$$\sum_{j=1}^{n-2} c_j \int_0^1 B_{i,k}\hat{H}B_{j,k} = E'\sum_{j=1}^{n-2} c_j \int_0^1 B_{i,k}B_{j,k} \tag{8}$$

which is a generalized eigenvalue problem of the form $A\mathbf{c} = E'B\mathbf{c}$. This was solved with an inverse power method, $(A - E^*B)\mathbf{c}_{j+1} = B\mathbf{c}_j$ where E^* is a guess at an eigenvalue and $\mathbf{c}_j$ is normalized in each iteration. The iteration was carried out until the error $|A\mathbf{c} - E^*B\mathbf{c}|_{\max}$ was sufficiently small ($< 10^{-6}$). The elements of the matrices A and B were obtained by integrating with gaussian quadrature of order d,

$$\int_{-1}^{1} f(x)dx \approx \sum_{j=0}^{d-1} c_j f(x_j), \tag{9}$$

where x_k are the Legendre roots and c_k are the corresponding weights, which depend on the degree used. Since $B_{i,k}$ is non-overlapping with $B_{j,k}$ if $|j-i| > k$, it was only necessary to integrate over segments of $(0,1)$. Each such segment was divided into 20 subsegments over which the integrals were transformed to an integral over $(-1,1)$ and calculated with the gaussian quadrature formula given above.

Testing of method

The method was tested on the function P_{30} for the Coulomb potential with $Z = \mu/m_e = 1$. The result for just a few inner knot points ($N = 5$) can be seen in figure 1. The eigenvalue from the inverse power method yielded $E' = -0.1104$ which is comparable to the exact energy $-1/9 = 0.111...$. The error at $r = 13a_0$ (approximately where P_{30} is maximum)

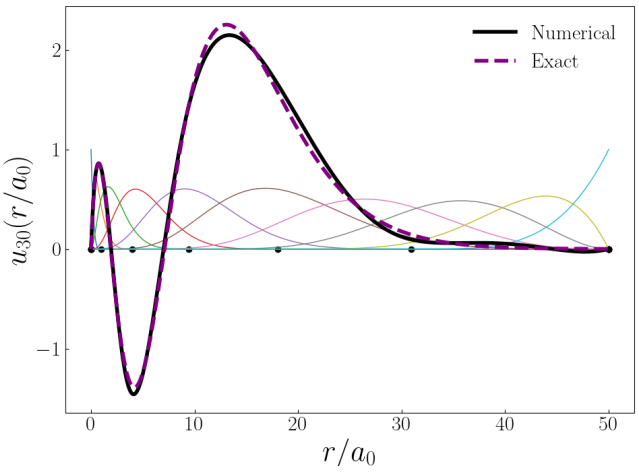

Figure 1: Numerical solution to the function P_{30} using B-splines. The number of splines is $M = 10$ and the number of inner knot points (black points) is $N = 5$.

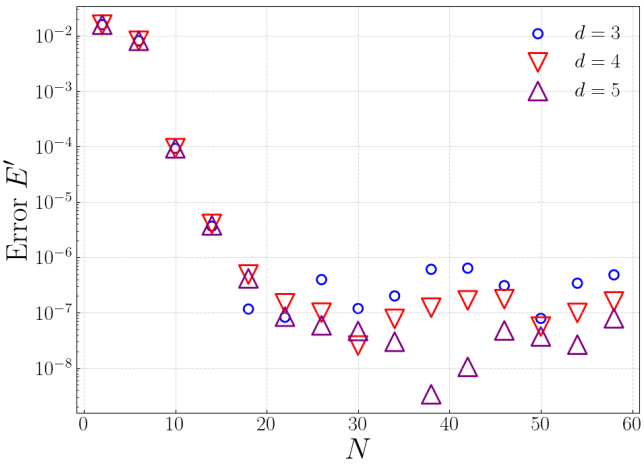

Figure 2: The error of the numerical approximation of the energy E' for the $(n, \ell) = (2, 0)$ state for different numbers of inner knot points N and order of gaussian quadrature d. The exact energy (in reduced units) is $-1/9$.

was $|u_{30}(13a_0) - P_{30}(13a_0)| = 0.10$. The order of the gaussian quadrature used to find the matrix elements was $d = 4$. The error in the energy $|E' + 1/9|$ and the error of the function at $r = 13a_0$ were investigated for different numbers of inner knot points N and order of gaussian quadrature d (see figures 2 and 3). As expected, the error decreases as N increases but then seems to level off in the vicinity of $N = 20$. Increasing the length parameter D didn't have a noticing effect on the error.

Results

The first couple of $u^2_{n\ell}$ for the Coulomb potential with $Z = \mu/m_e = 1$ can be seen in figure 4. These were obtained by using $N = 30$ inner points and

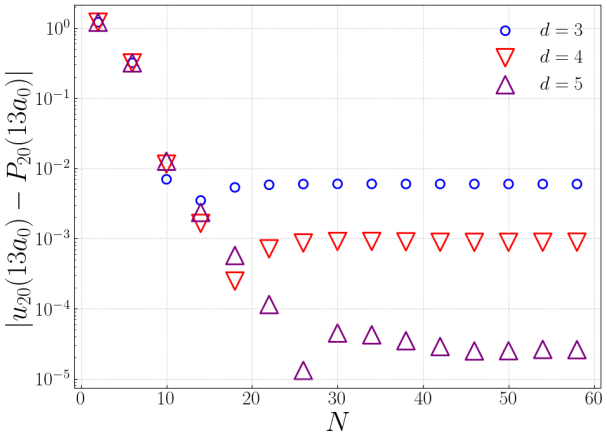

Figure 3: The error of the numerical solution to P_{20} in the point $r = 13a_0$ for different number of inner knot points N and order of gaussian quadrature d.

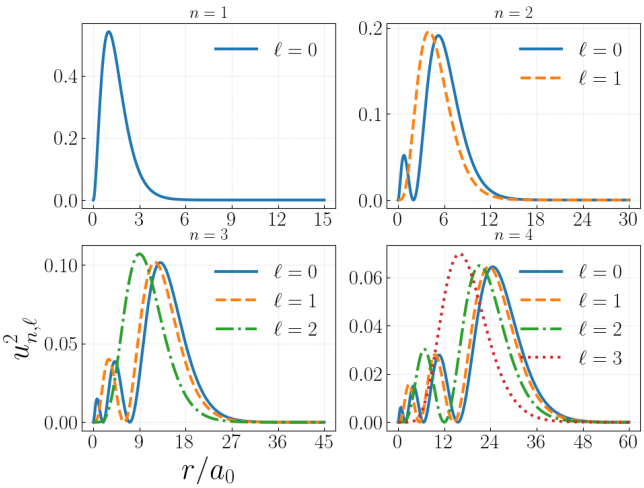

Figure 4: The first couple of squared reduced radial wavefunction for the Coulomb potential obtained with B-splines using 30 inner points.

gaussian quadrature of order $d = 5$. The error in the energy and in $u_{n\ell}$ at the point where $P_{n\ell}$ is maximum can be seen in table 1.

n	ℓ	$\lvert E' + 1/n^2 \rvert$	$\lvert u_{n\ell} - P_{n\ell} \rvert_{r=r_{\max}}$
1	0	$8.2 \cdot 10^{-9}$	$6.0 \cdot 10^{-7}$
2	0	$8.8 \cdot 10^{-8}$	$2.6 \cdot 10^{-6}$
2	1	$2.9 \cdot 10^{-8}$	$4.2 \cdot 10^{-7}$
3	0	$2.3 \cdot 10^{-7}$	$3.7 \cdot 10^{-5}$
3	1	$1.3 \cdot 10^{-7}$	$1.6 \cdot 10^{-5}$
3	2	$5.2 \cdot 10^{-8}$	$6.9 \cdot 10^{-6}$
4	0	$3.7 \cdot 10^{-6}$	$7.7 \cdot 10^{-4}$
4	1	$2.6 \cdot 10^{-6}$	$5.4 \cdot 10^{-4}$
4	2	$1.9 \cdot 10^{-6}$	$2.7 \cdot 10^{-4}$
4	3	$2.8 \cdot 10^{-7}$	$7.2 \cdot 10^{-5}$

Table 1: Error in energy and value of reduced radial wavefunction at the point where it is maximum from B-spline approximation. The number of innier points was $N = 30$ and the order of gaussian quadrature was $d = 5$.

The method was also used for a potential of a uniformily charged with radius $R_0 = 1.5a_0$ with $Z = 1$ and $\mu/m_e = 1$. The first couple of states for $\ell = 0$ and $\ell = 1$ can be seen in figure 5. A major difference compared to the Coulomb potential is that the degeneracy in ℓ is lifted. The ground state is also higher, $E' = -0.67$. For the $\ell = 0$ states, the particle seems to be further out than in the state for the Coulomb potential. For $\ell > 0$ though, the states look more the states for the Coulomb potential. This can be seen for the $\ell = 1$ states and in the energy spectrum (see figure 6).

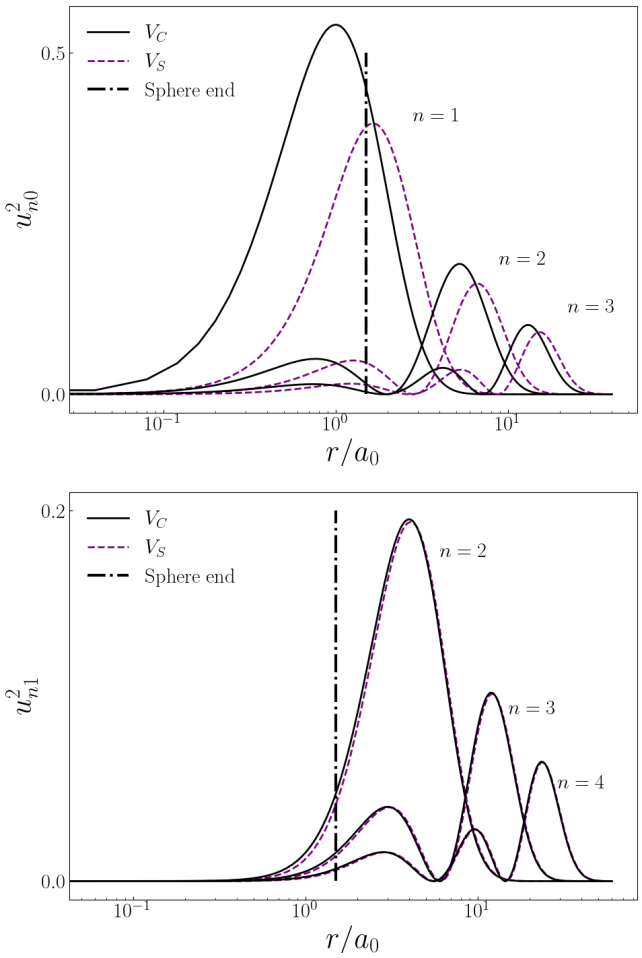

Figure 5: The square of the reduced radial function for quantum number $\ell = 0$ (top) and $\ell = 0$ (bottom) with the potential from a uniformily charged sphere with radius $R_0 = 1.5a_0$. These were obtained using B-splines with $N = 30$ inner points.

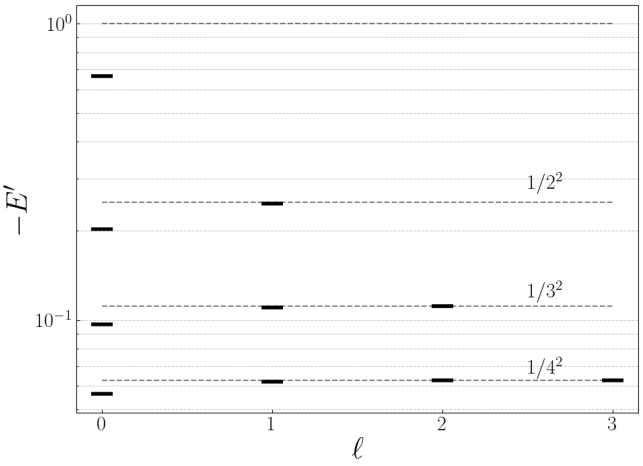

Figure 6: The energies E' (units of 13.6 eV) and quantum numbers ℓ for the potential from a uniformily charged sphere of radius $R_0 = 1.5a_0$.