$$\left(-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{\hbar^2\ell(\ell+1)}{2\mu r^2}-\frac{Ze^2}{4\pi\epsilon_0 r}\right)P_{n\ell}(r)=EP_{n\ell}(r). \tag{1}$$

Numerical solution

The following dimensionless variables were defined:

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

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 (1) can be written

$$\hat{H}u = -\beta^2\left(\frac{\mathrm{d}^2}{\mathrm{d}\xi^2}-\frac{\ell(\ell+1)}{\xi^2}+\frac{2}{\beta\xi}\right)u = E'u \tag{3}$$

where $\beta = m_e/(Z\mu\alpha)$. The numerical solution to (3) is written as a linear combination of n B-splines of degree k:

$$\hat{u}(\xi)=\sum_{j=0}^{n-1}c_jB_{j,k}(\xi). \tag{4}$$

The boundary conditions $u(0) = u(1) = 0$ are satisfied by placing multiple knot points at $\xi = 0$ and $\xi = 1$. 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 $\xi = 1$. Since the wavefunction is vanishing for ξ closer to one, it becomes more efficient to place distribute the knot points unevenly over $[0,1]$ such that there are more of them closer to zero than closer to one. The knots were thus placed according to the function $2^{x^2}-1$ where $x \in (0,1)$.

so that closer to zero than closer to oneThe boundary conditions are thus satisfied by setting $c_0 = c_{n-1} = 0$. Inserting this into equation (3), multiplying by $B_{i,k}(x)$ and integrating over $(0,1)$ yields:

$$\sum_{j=1}^{n-2}c_j\int_0^1 B_{i,k}\hat{H}B_{j,k} = E'\sum_{j=1}^{n-2}c_j\int_0^1 B_{i,k}B_{j,k} \tag{5}$$

which is a generalized eigenvalue problem of the form $A\mathbf{c} = E'B\mathbf{c}$. This is solved with a 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.

Results

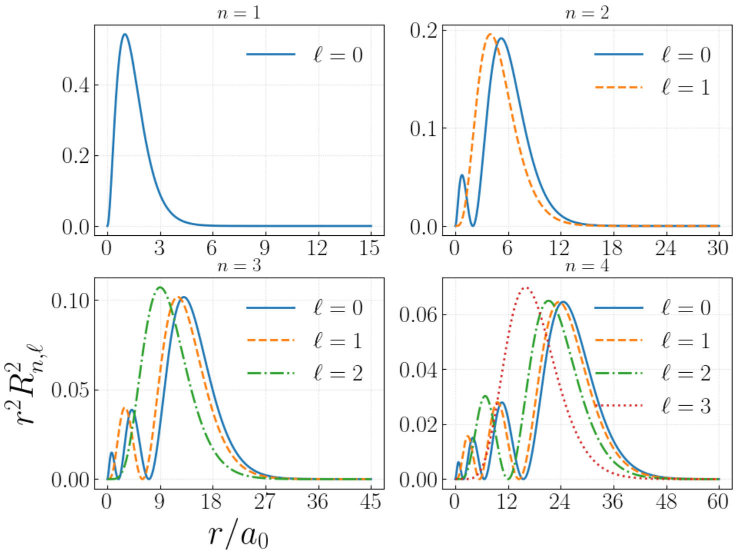

Figure 1

n	ℓ	$\lvert E'-1/n^2\rvert$
1	0	$1.7\cdot10^{-3}$
2	0	$4.2\cdot10^{-4}$
2	1	$1.1\cdot10^{-9}$
3	0	$1.8\cdot10^{-4}$
3	1	$1.2\cdot10^{-7}$
3	2	$3.5\cdot10^{-8}$
4	0	$1.0\cdot10^{-4}$
4	1	$2.6\cdot10^{-6}$
4	2	$1.2\cdot10^{-6}$
4	3	$2.7\cdot10^{-7}$

Table 1