3. Kohn-Sham equation

Goal: solve

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{2}{r} + V_H(r) + V_x(r) + V_c(r)\right]u = \varepsilon u$$

$$u(0) = u(r_{max}) = 0$$

Test: solve hydrogen:

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\right]u = Eu$$

Apply finite difference:

$$u(r) \longmapsto u(r_i) = u_i$$

$$\frac{d^2u}{dr^2} \longmapsto \frac{u_{i+1} - 2u_i + u_{i+1}}{h^2}$$

Operators as matrices:

$$D^2 = \frac{1}{h^2}\begin{pmatrix} 2 & -1 & & & 0 \\ -1 & 2 & -1 & & \\ & -1 & \ddots & \ddots & \\ 0 & & \ddots & \ddots & -1 \\ & & & -1 & 2 \end{pmatrix}$$

$$r = \begin{pmatrix} r_0 & & & 0 \\ & r_1 & & \\ & & \ddots & \\ 0 & & & r_n \end{pmatrix}$$

Potentials given element wise:

$$V(r) = \begin{pmatrix} V(r_0) & & 0 \\ & \ddots & \\ 0 & & V(r_n) \end{pmatrix}$$

$$r^{-1} = \begin{pmatrix} 1/r_0 & & 0 \\ & \ddots & \\ 0 & & 1/r_n \end{pmatrix}$$

Solve eigenvalue problem

$$\left(-\frac{1}{2}D^2 - 2r^{-1}\right)\vec{u} = E\vec{u}$$

e.g. using numpy (np.eig)

Analytical solution:

$$\psi_{100}(r) = \frac{1}{\sqrt{\pi}} e^{-r} \qquad E_0 = -\frac{1}{2}$$