Practical work 2: Calculation of atomic orbitals

1 Introduction.

In this practical work we shall solve numerically the Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2 + V(r)\right]\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}) \tag{1}$$

For a central potential $V(r)$, this equation leads to the corresponding radial equation:

$$\frac{\mathrm{d}^2 y_n}{\mathrm{d}r^2} = \left[-2E_n + 2V + \frac{l(l+1)}{r^2}\right] y_n \tag{2}$$

To solve this equation we apply the Numerov's method.

2 The Numerov's method.

The Numerov's method is employed to solve numerically second order differential equations. In particular, the one dimensional Schrödinger equation (2) can be written as

$$y''(r) = 2(W - E)y \tag{3}$$

To obtain the Numerov's algorithm we express the fourth derivative using central differences in the form:

$$y_i^{(4)} = \frac{y''_{i+1} - 2y''_i + y''_{i-1}}{s^2} + O(s^4) \tag{4}$$

We add the Taylor expansions for y_i and y_{i+1}:

$$\begin{aligned} y_{i+1} &= y_i + sy'_i + \frac{s^2}{2}y''_i + ... \\ y_{i-1} &= y_i - sy'_i + \frac{s^2}{2}y''_i + ... \end{aligned} \tag{5}$$

which, using (4), yields

$$y_{i+1} + y_{i-1} = 2y_i + \frac{s^2}{12}(y''_{i+1} + 10y''_i + y''_{i-1}) + O(s^6) \tag{6}$$

and substituting the Schrödinger equation (3) leads to:

$$y_{i+1} = \frac{[2 + \frac{5s^2}{6}(W_i - E)]y_i - [1 - \frac{s^2}{12}(W_{i-1} - E)]y_{i-1}}{1 - \frac{s^2}{12}(W_{i+1} - E)} \tag{7}$$

3 Application.

As a first example we consider the simple Coulomb potential $V(r) = -Z/r$. We have the following MATLAB routines:

- solvcoul.m: Obtain the radial functions and radial densities for a one-electron atom. It calls the subroutine numerov. The input of this program are: energy E, angular momentum quantum number, l, and nuclear charge, Z. The integration starts at $r = 0$, where the wavefunctions have the form $r^{(l+1)}$. The integration stops at 30 a.u., which can be changed by editing the program.
- numerov.m: solves the differential equation. It calls the subroutine Coulomb.
- Coulomb.m: Calculates the effective potential W(r).

To run the program write:

[x,y,densi]=solvcoul(-0.125,0,1);
plot(x,y)
plot(x,densi)

Repeat the calculation with E=-0.130, -1/18, and discuss the results. Try other values of l.

The second example involves the use of the model potential

$$V(r) = -\frac{Z - N_c}{r} - \frac{Nc}{r}(1 + \alpha r)\exp(-2\alpha r) \tag{8}$$

to obtain atomic orbitals for a many-electron atom. The required matlab m-files are **solvpotmod.m,** which calls **numerov.m** and **potmod.m** where the potential is programmed.

We shall employ this model potential to obtain the 2p atomic orbital radial function of the Ne atom. The appropriate parameters are: E=-0.7925a.u., Z=8, N_c=7, l=1, α=1.3996.

[xx,y,densi]=solvpotmod(-0.7925,1,8,7,1.3996);
plot(x,y)
plot(x,densi)

Repeat the calculation for $\alpha = 1.30$.