Week 05

- Multidimensional integration

$$\iiint_{domain} f(x,y,z) \approx \sum_i w_i^x w_j^y w_k^z f(x_i,y_i,z_i). \qquad \text{(Cartesian)}$$

$$\iiint_{domain} f(r,\theta,\phi) \approx \sum_i w_i^\Omega w_j^r f(r_i,\theta_i,\phi_i). \qquad \textbf{(Spherical)}$$

Task 08 (Monday and Wednesday)

Objective: Evaluate the overlap integral between two functions on the form:

$$F(\mathbf{r}) = x^a y^c z^d \exp(-\alpha r^2)$$

$$O = \int_0^\infty r^2 dr \int_\Omega F_1(\mathbf{r}) F_2(\mathbf{r}) d\Omega$$

This is a multi-step project. It requires careful testing of each step.

Note: No loops allowed
Broadcasting: Operations involving numpy arrays are performed in C: faster!
Example:

```
A = B * C
```

```
for i in range(len(A)):
    A[i] = B[i] * C[i]
```

First: set up the radial and angular part of hydrogenic wave functions (for testing)

- `Rad_fun`: Returns the normalized radial hydrogenic function R_{nl} for a given r (or array of r values)

$$\psi_{n\ell m}(r,\theta,\phi) = \sqrt{\left(\frac{2}{a\,n}\right)^3 \frac{(n-\ell-1)!}{2\,n\,((n+\ell)!)^3}} \left(e^{-\frac{r}{a\,n}}\right) \left(\frac{2\,r}{a\,n}\right)^{\ell} \left(L_{n-\ell-1}^{2\ell+1}(2\,r/(a\,n))\right) Y_\ell^m(\theta,\phi)$$

angular

`scipy.special.assoc_laguerre`

Validation: ? Plot?

- `xyz2ang`: Returns θ and ϕ arrays from x, y, and z.

Validation: ?

Note: we use atomic units

- `radial_grid`: Calculate the radial quadrature weights and points for a given order n. From P. M. W. Gill, S-H. Chien, J. Comput. Chem. 24: 732 (**2003**)

$$r_i = \frac{1 + x_i}{1 - x_i} R$$

radial points

$$w_i = \frac{2\pi}{n + 1} \frac{(1 + x_i)^{5/2}}{(1 - x_i)^{7/2}} R^3$$

weights: already include the r^2 from the radial volume element

$$x_i = \cos\left(\frac{i\pi}{n + 1}\right)$$

Gauss-Chebyshev second kind quadrature points

`numpy.polynomial.chebyshev.chebgauss`

Validation: ?

- `fz`: Returns $z\exp(-\alpha r^2)$

Main:

- Load the angular grid and **check** that you can integrate the angular part correctly (normalization).
  - The quadrature data is stored in files named `Levedev.N`, where `N` is the number of angular points. The file contains on each row x, y, z coordinates on the unit sphere followed by the weight.
  - Propose a validation test.

- Generate the quadrature for the radial part and **verify** normalization. Propose a validation test.

- Perform an extra **verification** by calculating $\langle r^2 \rangle$ and comparing with the analytical result.

- Optional: Make a plot of $R_{nl}(r)$ and compare with textbooks.

- Create array with all the xyz values on the grid using the quadrature R (radial points) and θ, and ϕ (angles).
    - This should be a 1D array of length $N_{radial} \times N_{angular}$.

- Create an array with all the weight products for each grid point.
    - Verify that your integration works by checking the integration of the 1s wave function of the hydrogen atom, $\psi(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} \exp(-r)$
- Create an array with the function values on the grid points.

- Normalize the functions (you will need to integrate).

- Integrate.

Use

$F_1(\mathbf{r}) = z \exp(-\alpha_1 r^2)$ and. $F_2(\mathbf{r}) = z \exp(-\alpha_2 r^2)$

with $\alpha_1 = 0.82454724$ and $\alpha_2 = 5.447178$.

The analytical result that can be used to check is $\langle F1|F2\rangle = 0.375484$.

Additional notes:

- You may get warnings like this: `RuntimeWarning: divide by zero encountered in divide`
  What to do in this case?

- After completed, the code should print something like this:

```
integral for Y l= 2 m= 0          =          1.00000000
integral for R n= 3 l= 2          =          1.00000373
Numerical  <r**2> n= 3 l= 2       =        126.02078086
Analytical <r**2> n= 3 l= 2       =        126.00000000
Overlap numerical    <F1|F2>      =          0.37548390
Overlap analytical   <F1|F2>      =          0.37548400
```