Blog Entry © Sunday, August 10, 2025, First-Order Perturbation Treatment of the Helium Atom by James Pate Williams, Jr.

The spherical harmonics are defined as follows [1]:

$$Y_{lm}(\vartheta,\varphi)=\epsilon\left[\frac{2l+1}{4\pi}\frac{(l-|m|!)}{(l+|m|!)}\right]^{1/2}P_l^m(\cos\vartheta)e^{im\varphi}$$

$$\epsilon=\begin{matrix}(-1)^m\forall m>0\\ 1\forall m\leq 0\end{matrix}$$

The associated Legendre functions are specified as shown below [2]:

$$P_l^m(w)=(1-w^2)^{|m|/2}\frac{d^{|m|}}{dw^{|m|}}P_l(w)$$

$$(l+1)P_{l+1}(w)=(2l+1)wP_l(w)-lP_{l-1}(w)$$

The associated Laguerre functions are defined by the equation [3]:

$$L_{n+l}^{2l+1}(\rho)=\sum_{k=0}^{n-l-1}(-1)^{k+2l+1}\frac{[(n+l)!]^2\rho^k}{(n-l-1-k)!\,(2l+1+k)!\,k!}$$

The radial wave function for the hydrogen-like atom is given by the following equation [3]:

$$R_{nl}(r)=-\left\{\left(\frac{2Z}{na_0}\right)^3\frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{1/2}e^{-\rho/2}\rho^l L_{n+l}^{2l+1}(\rho)$$

$$a_0=\frac{h^2}{4\pi^2\mu e^2}$$

$$\rho=\frac{2Z}{na_0}r$$

The inter-electron reciprocal distance can be expanded by spherical harmonics [5]:

$$\frac{1}{r_{12}}=\frac{1}{r_1}\sum_{l=0}^{\infty}\left(\frac{r_2}{r_1}\right)^l P_l(\cos\vartheta)\forall r_1>r_2$$

$$\frac{1}{r_{12}}=\frac{1}{r_2}\sum_{l=0}^{\infty}\left(\frac{r_1}{r_2}\right)^l P_l(\cos\vartheta)\forall r_1<r_2$$

$$P_l(\cos\vartheta)=P_l(\cos\vartheta_1)P_l(\cos\vartheta_2)+2\sum_{m=1}^{l}\frac{(l-m)!}{(l+m)!}P_l^m(\cos\vartheta_1)P_l^m(\cos\vartheta_2)\cos m(\varphi_1-\varphi_2)$$

The exact electron interaction energy for the ground state of the helium atom in atomic units is given in the previously cited reference:

$$\left\langle \psi_1 \middle| \frac{1}{r_{12}} \middle| \psi_1 \right\rangle = \frac{5Z}{8} = \frac{10}{8} = 1.25$$

The approximate ground state energy of the helium atom is as follows using first-order perturbation theory:

$$E = -\frac{Z_1^2}{2n_1^2} - \frac{Z_2^2}{2n_2^2} + \left\langle \psi_1 \middle| \frac{1}{r_{12}} \middle| \psi_1 \right\rangle \cong -\frac{4}{2} - \frac{4}{2} + 1.247356 = -4 + 1.247356 = -2.752644$$

```
Lmax = 10
Nmax = 50000
Rmax = 10
zeta1 = 2
zeta2 = 2
n1 = 1
n2 = 1
l1 = 0
l2 = 0
m1 = 0
m2 = 0
real integral = +1.247356
imag integral = +0.000000

D:\CoulombIntegral\x64\Release\CoulombIntegral.exe (process
15156) exited with code 0 (0x0).
Press any key to close this window . . .
```

The exact ground state energy of the helium atom is: -2.903392458 atomic units. The percentage error between the approximate and exact values is 5.192149%.

References

[1] L. I. Schiff, "Spherical Harmonics," in *Quantum Mechanics Third Edition*, New York, McGraw-Hill, Inc, 1968, pp. 79-81.

[2] L. I. Schiff, "Legendre Polynomials," in *Quantum Mechanics Third Edition*, New York, McGraw-Hill, Inc, 1968, pp. 78-79.

[3] L. I. Schiff, "Laguerre Polynomials," in *Quantum Mechanics Third Edition*, New York, McGraw-Hill, Inc, 1968, pp. 92-93.

[4] L. I. Schiff, "Hydrogen-Atom Wave Functions," in *Quantum Mechanics Third Edition*, New York, McGraw-Hill, Inc, 1968, pp. 93-94.

[5] L. I. Schiff, "Electron Interaction Energy," in *Quantum Mechanics Third Edition*, New York, McGraw-Hill, Inc, 1968, pp. 258-259.