Blog Entry © Monday, October 7, 2024, by James Pate Williams, Jr. Recent Voyages into the World of Quantum Chemistry

The following results involve the variational treatment of the period 1 two-electron helium atom. Using a one parameter method the best percent error is about 2%. One of the best values is found using Slater's effective atomic number of 1.7. We use six algorithms to find the best ground state energy for the helium atom:

1. Z = 2, the atomic number of the standard helium atom
2. Z = 1.7 Slater's rule for the effective atomic number for helium
3. Praxis an optimization method that does not require derivatives and is found in the book *A Numerical Library in C for Scientists and Engineers* © 1994 by H. T. Lau, PhD
4. An evolutionary hill-climber by this author
5. A second evolutionary hill-climber by this author
6. Simulated annealing using the famous Metropolis heuristic

The percent errors are 5.28%, 1.92%, 1.92%, 1.92%, 1.93%, and 1.95%.

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Helium atom atomic number Z = 2
Experimental ground state energy (au) = -2.9033858777
Experimental ground state energy (eV) = -79.005154539
First Approximation Results:
zeta 1 = 2     zeta 2 = 2
Electron-electron repulsion energy (au) = 1.2500000278
Electron-electron repulsion energy (eV) = 34.014156471
Kinetic Energy (au) = 4
Kinetic Energy (eV) = 108.84529828
Potential energy (au) = -8
Potential energy (eV) = -217.69059656
Total energy (au) = -2.7499999722
Total energy (eV) = -74.83114181
Derivative 1 in atomic units = 0
Derivative 2 in atomic units = 0
% Error = 5.2832157002
Runtime in milliseconds = 427
Using Slater's Rule:
zeta 1 = 1.7   zeta 2 = 1.7
Electron-electron repulsion energy (au) = 1.0625001512
Electron-electron repulsion energy (eV) = 28.912036472
Kinetic Energy (au) = 2.89
Kinetic Energy (eV) = 78.640728008
Potential energy (au) = -6.8
Potential energy (eV) = -185.03700708
Total energy (au) = -2.8474998488
Total energy (eV) = -77.484242598
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Derivative 1 in atomic units = 0
Derivative 2 in atomic units = 0
% Error = 1.9250793821
Runtime in milliseconds = 473
NUMAL's PRAXIS Results:
zeta 1 = 1.6875051192    zeta 2 = 1.6874761751
Electron-electron repulsion energy (au) = 1.0546818267
Electron-electron repulsion energy (eV) = 28.699289504
Kinetic Energy (au) = 2.8476246845
Kinetic Energy (eV) = 77.487639544
Potential energy (au) = -6.7499625887
Potential energy (eV) = -183.67542284
Total energy (au) = -2.8476560775
Total energy (eV) = -77.488493789
Derivative 1 in atomic units = 0
Derivative 2 in atomic units = 0
% Error = 1.9196984787
Runtime in milliseconds = 4985
Evolutionary Hill-Climber One Results:
Generations: 500
Population : 10
zeta 1 = 1.6860866115    zeta 2 = 1.684316538
Electron-electron repulsion energy (au) = 1.0532508124
Electron-electron repulsion energy (eV) = 28.660349709
Kinetic Energy (au) = 2.8399051308
Kinetic Energy (eV) = 77.277580264
Potential energy (au) = -6.740806299
Potential energy (eV) = -183.42626807
Total energy (au) = -2.8476503558
Total energy (eV) = -77.488338094
Derivative 1 in atomic units = 0
Derivative 2 in atomic units = 0
% Error = 1.9198955478
Runtime in milliseconds = 74093
Evolutionary Hill-Climber Two Results:
Generations: 500
Population : 10
zeta 1 = 1.6693624683    zeta 2 = 1.7178868984
Electron-electron repulsion energy (au) = 1.0582553532
Electron-electron repulsion energy (eV) = 28.796529893
Kinetic Energy (au) = 2.8689532232
Kinetic Energy (eV) = 78.068017333
Potential energy (au) = -6.7744987335
Potential energy (eV) = -184.34308384
Total energy (au) = -2.8472901571
Total energy (eV) = -77.478536611
Derivative 1 in atomic units = 0
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Derivative 2 in atomic units = 0
% Error = 1.932301679
Runtime in milliseconds = 13506
Simulated Annealing Results:
m: 1000000     n: 10000
zeta 1 = 1.645680105     zeta 2 = 1.7178868984
Electron-electron repulsion energy (au) = 1.0505341104
Electron-electron repulsion energy (eV) = 28.586424651
Kinetic Energy (au) = 2.8296992018
Kinetic Energy (eV) = 76.999863417
Potential energy (au) = -6.7271340068
Potential energy (eV) = -183.05422689
Total energy (au) = -2.8469006945
Total energy (eV) = -77.467938818
Derivative 1 in atomic units = 0
Derivative 2 in atomic units = 0
% Error = 1.9457157326
Runtime in milliseconds = 14593
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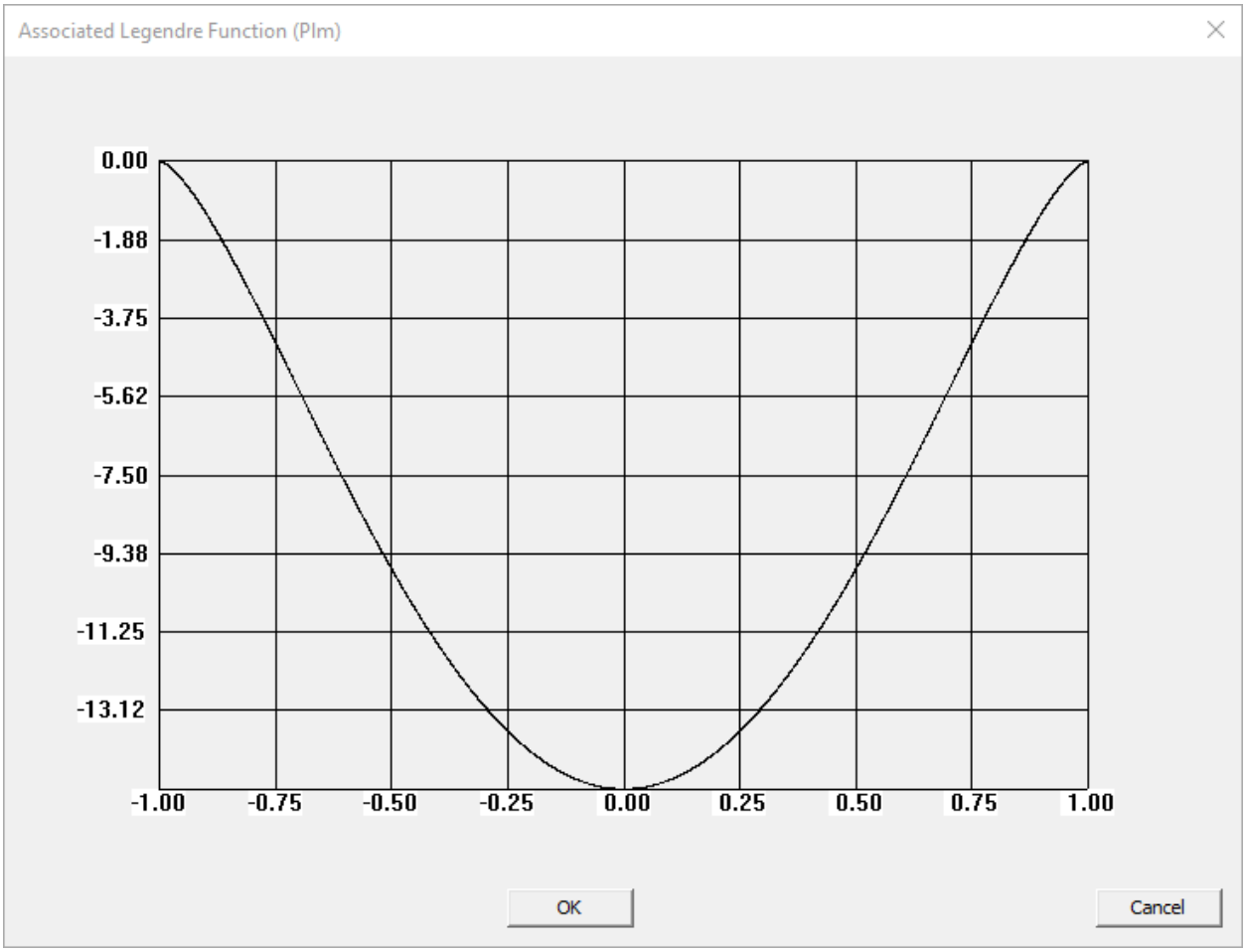
Next, we explore the universe of Slater Type Orbitals (STOs). STOs compete with Gaussian Type Orbitals (GTOs) in *ab initio* quantum chemistry. The author used some of the formulas found on the following webpage:

https://academicjournals.org/article/article1380546086_Ozdogan%20and%20Nalcaci.pdf

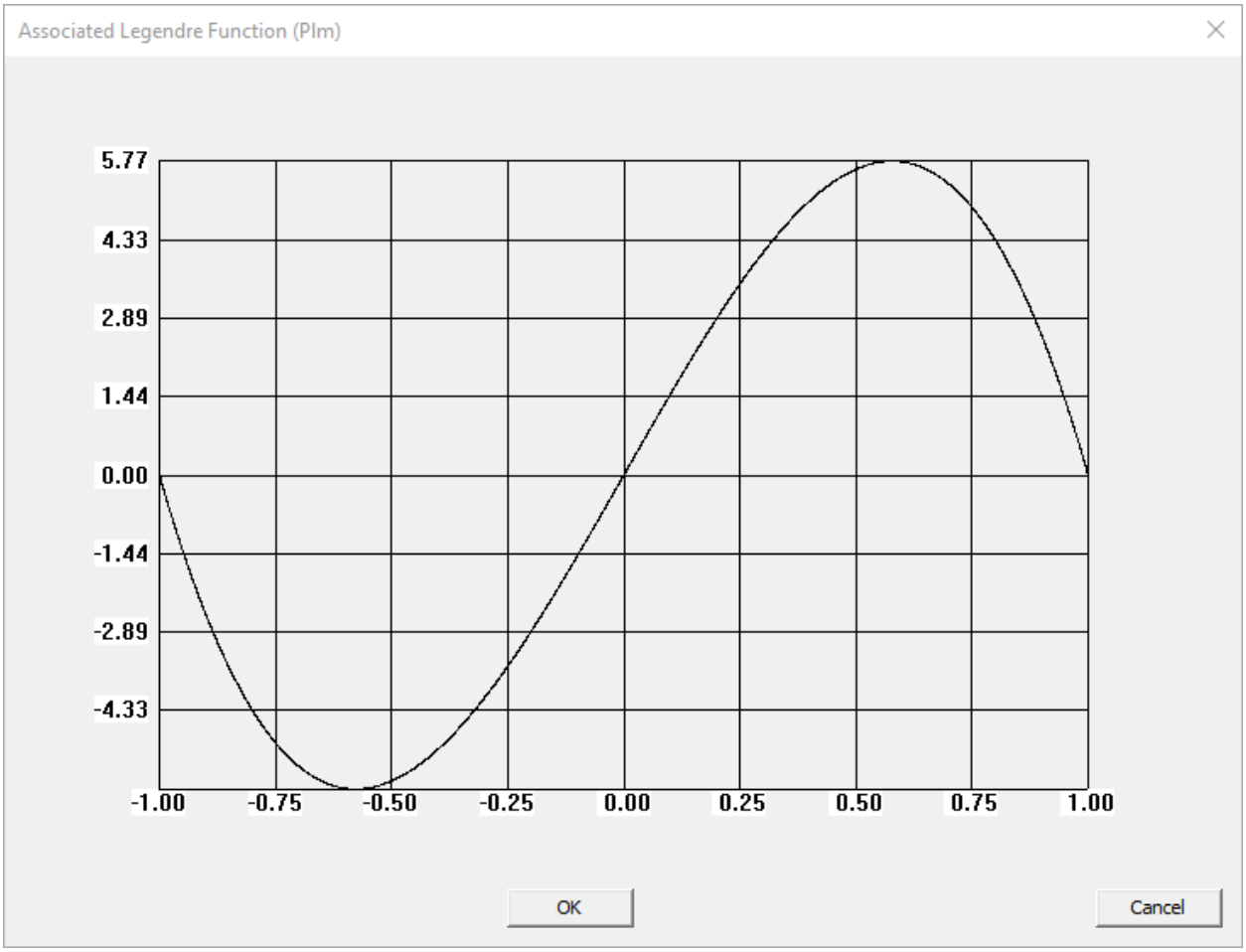
The functions that were calculated:

1. associated Legendre polynomials
2. real valued magnetic wave functions
3. Slater type orbitals

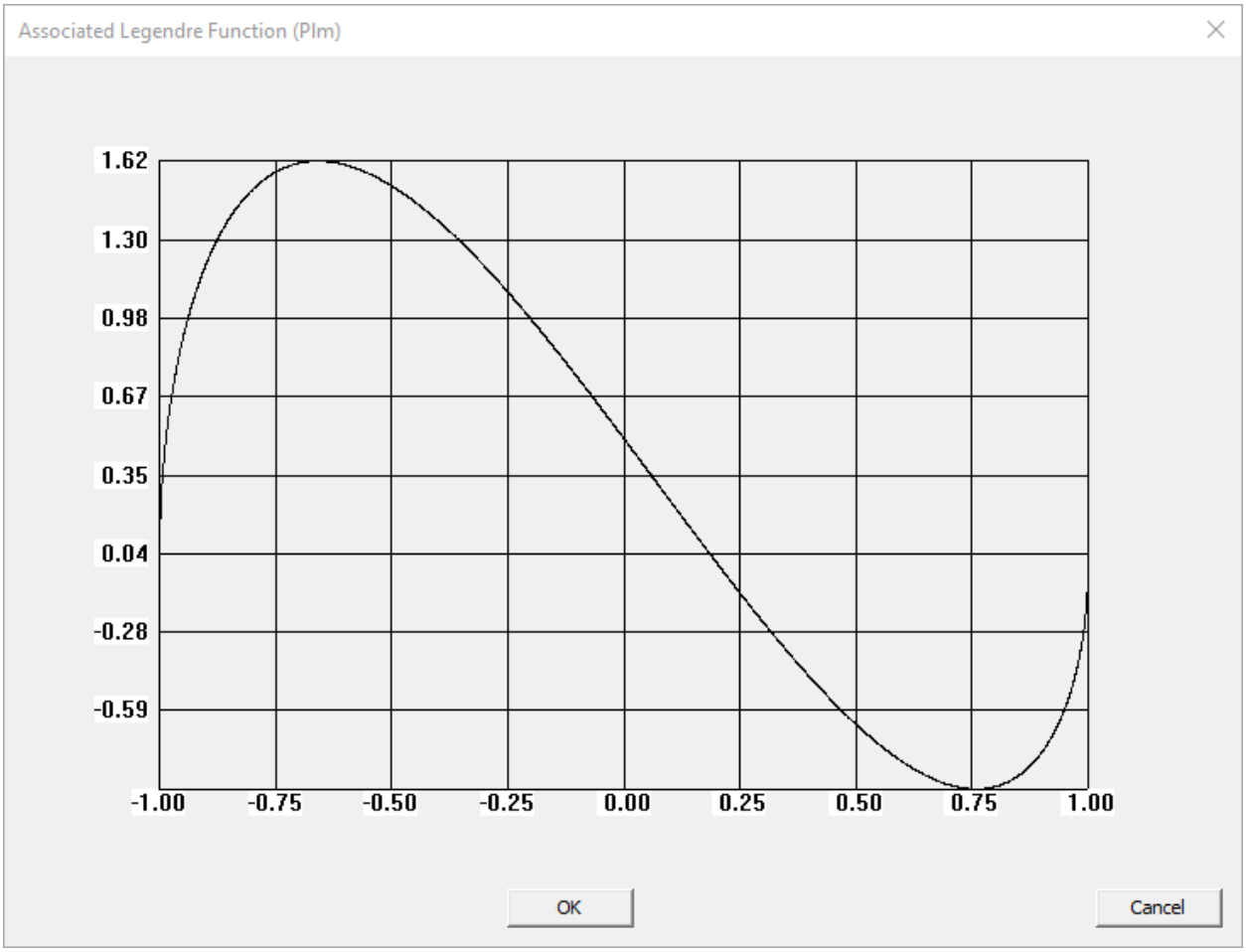
I created a C++ Win32 application to graph the three functions previously mentioned.


Associated Legendre Function (Plm)
0.00
-1.88
-3.75
-5.62
-7.50
-9.38
-11.25
-13.12
-1.00
-0.75
-0.50
-0.25
0.00
0.25
0.50
0.75
1.00
OK
Cancel

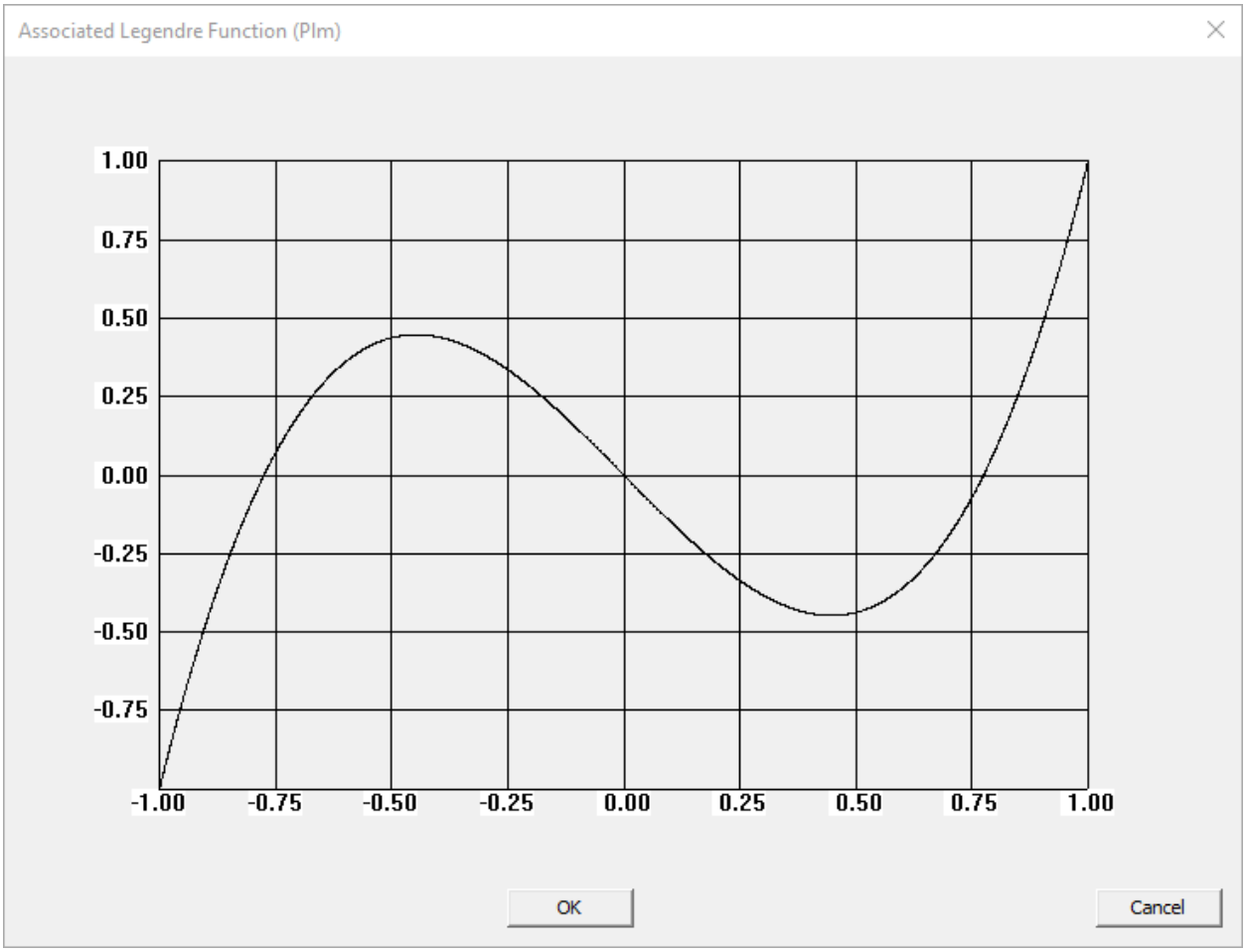
l = 3, m = 3


Associated Legendre Function (Plm)
5.77
4.33
2.89
1.44
0.00
-1.44
-2.89
-4.33
-1.00
-0.75
-0.50
-0.25
0.00
0.25
0.50
0.75
1.00
OK
Cancel

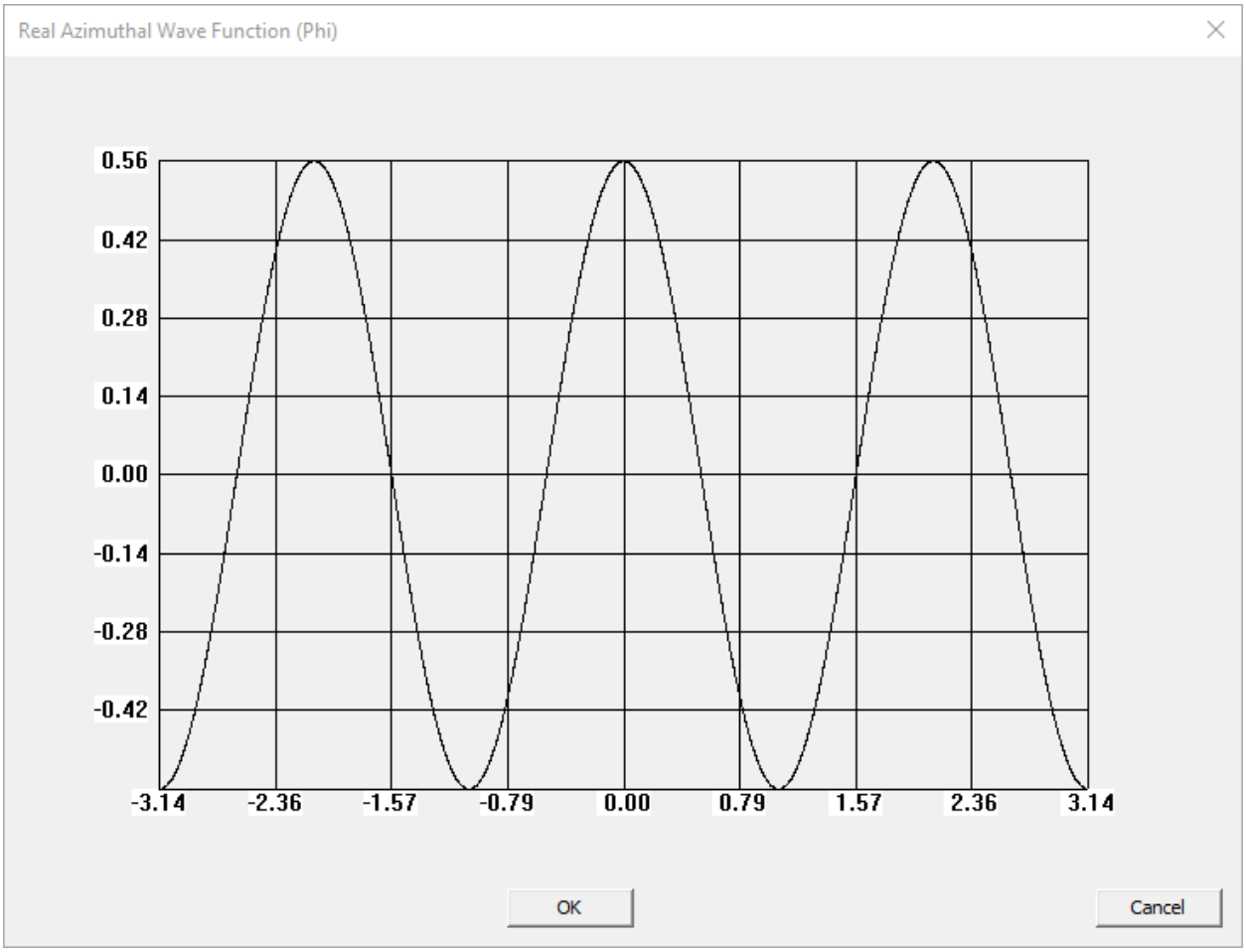
l = 3, m = 2


Associated Legendre Function (Plm)
1.62
1.30
0.98
0.67
0.35
0.04
-0.28
-0.59
-1.00
-0.75
-0.50
-0.25
0.00
0.25
0.50
0.75
1.00
OK
Cancel

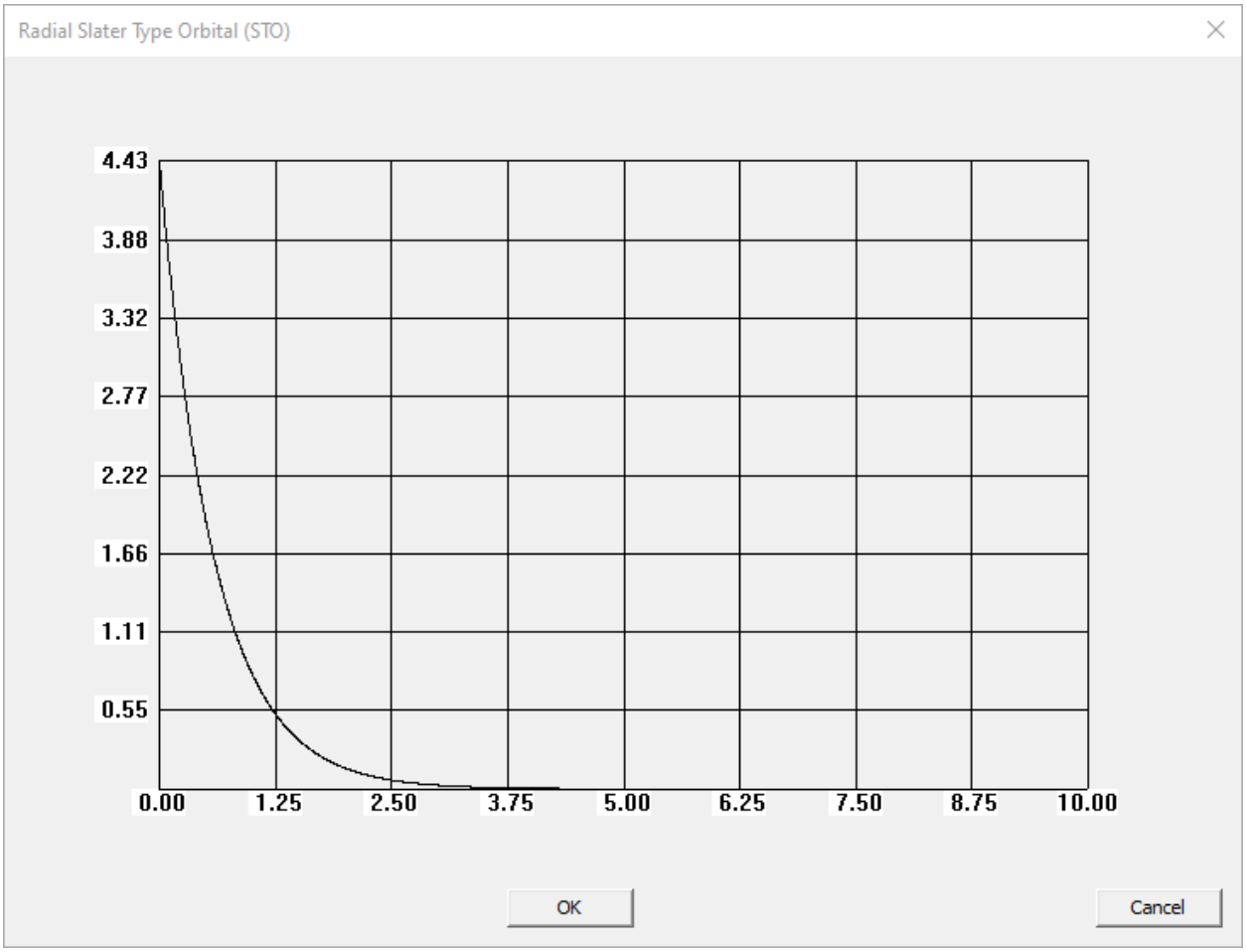
l = 3, m = 1


Associated Legendre Function (Plm)
1.00
0.75
0.50
0.25
0.00
-0.25
-0.50
-0.75
-1.00
-0.75
-0.50
-0.25
0.00
0.25
0.50
0.75
1.00
OK
Cancel

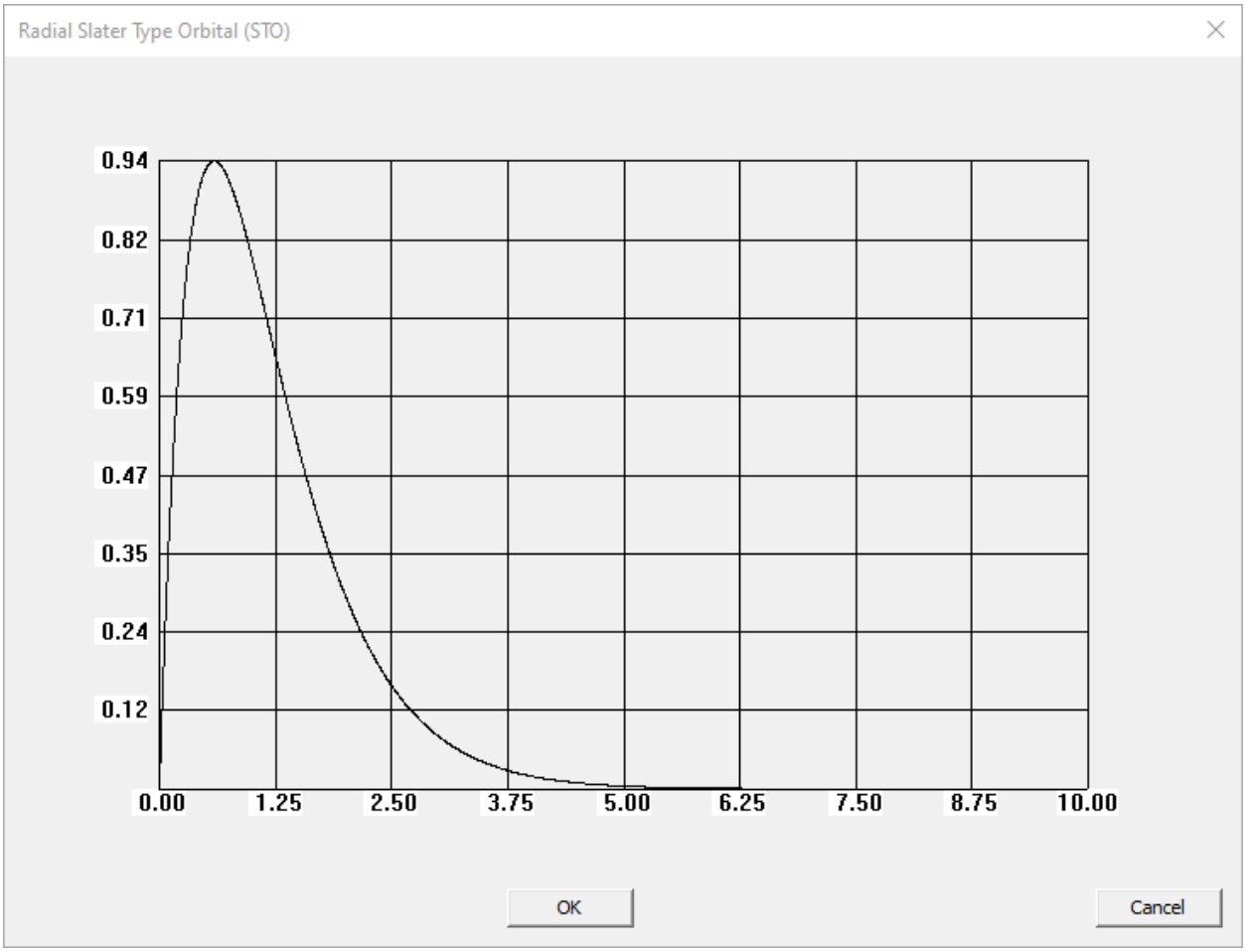
l = 3, m = 0



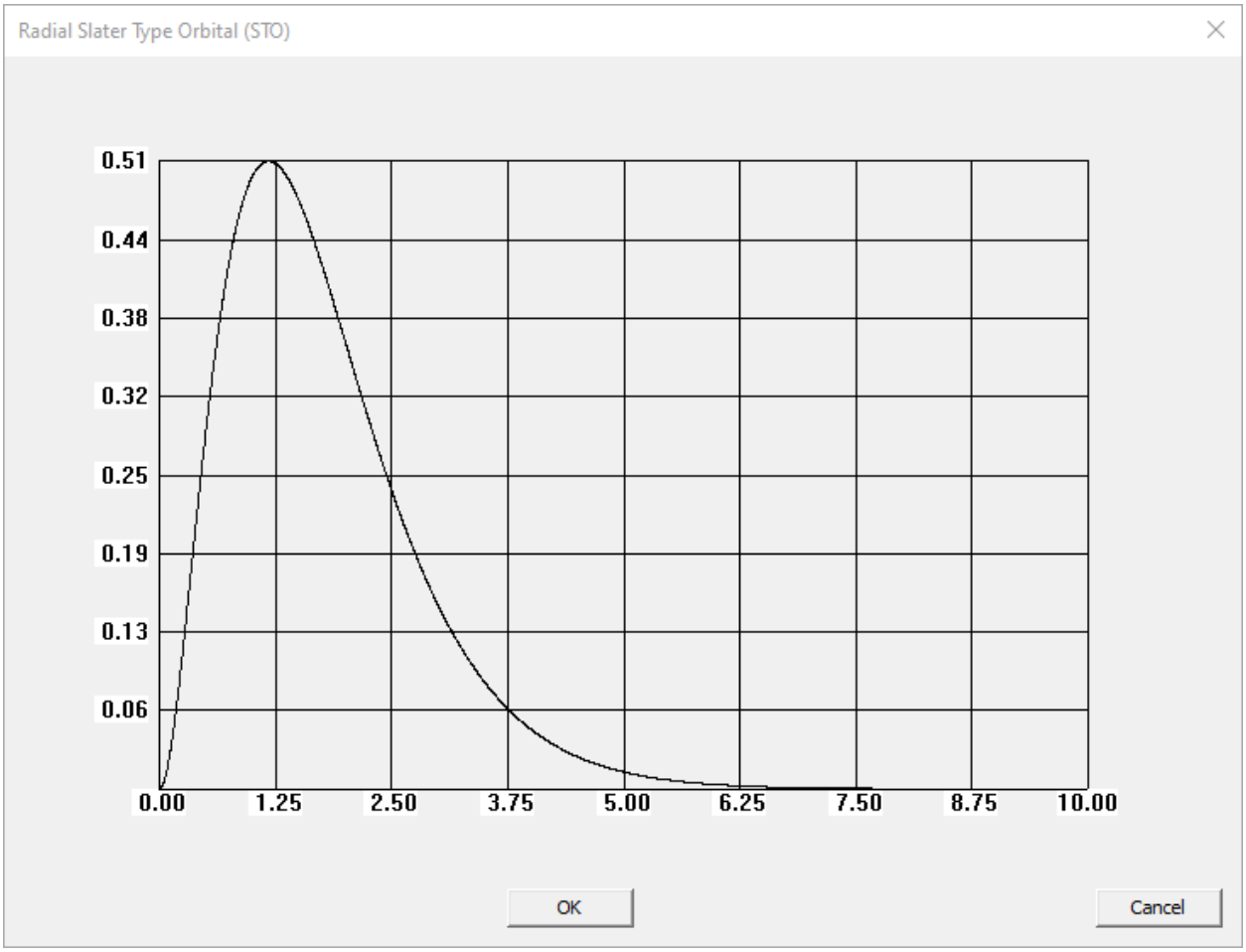
m = 3, real magnetic wave function


Radial Slater Type Orbital (STO)
4.43
3.88
3.32
2.77
2.22
1.66
1.11
0.55
0.00
1.25
2.50
3.75
5.00
6.25
7.50
8.75
10.00
OK
Cancel

zeta = 1.7, n = 1


Radial Slater Type Orbital (STO)
0.94
0.82
0.71
0.59
0.47
0.35
0.24
0.12
0.00
1.25
2.50
3.75
5.00
6.25
7.50
8.75
10.00
OK
Cancel

zeta = 1.7, n = 2


Radial Slater Type Orbital (STO)
0.51
0.44
0.38
0.32
0.25
0.19
0.13
0.06
0.00
1.25
2.50
3.75
5.00
6.25
7.50
8.75
10.00
OK
Cancel

zeta = 1.7, n = 3