Approximate Solution of the Schrodinger Equation for the Helium Atom by James Pate Williams, Jr.

The Schrodinger equation for the helium atom is:

$$-\frac{h^2}{8\pi^2 m}(\nabla_1^2\psi + \nabla_2^2\psi) - \frac{Ze^2}{4\pi\epsilon_0}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\psi + \frac{e^2}{4\pi\epsilon_0 r_{12}}\psi = E\psi$$

Rewriting the equation in atomic units we obtain [1]:

$$-\frac{1}{2}(\nabla_1^2\psi + \nabla_2^2\psi) - Z\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\psi + \frac{1}{r_{12}}\psi = E\psi$$

$$\psi = \phi_1(r_1)\phi_2(r_2)$$

$$\phi_i(r_i) = R_{10}(r_i)Y_{00}(\vartheta_i,\varphi_i) = 2b_i^{3/2}e^{-b_i r_i}\frac{1}{2\sqrt{\pi}} = \frac{1}{\sqrt{\pi}}b_i^{3/2}e^{-b_i r_i}$$

$$r_1 = [x_1^2 + y_1^2 + z_1^2]^{1/2}$$

The radial part of the Laplacian operator is as illustrated below:

$$\nabla_1^2 = \frac{1}{r_1^2}\frac{d}{dr_1}\left[r_1^2\frac{d}{dr_1}\right]$$

We use the following formulas to compute the kinetic and potential energies:

$$KE = \frac{1}{2}(\zeta_1^2 + \zeta_2^2)$$

$$PE = -Z(\zeta_1 + \zeta_2)$$

Plugging in the following values:

$$Z = 2, \zeta_1 = 2, \zeta_2 = 2$$

Yields a kinetic energy, KE, equal 4 and a potential energy, PE, equal -8. Therefore, the total energy neglecting the Coulomb integral is -4 Hartree in atomic units.

The electron-electron repulsion (Coulomb) integral is calculated using the following equations [2] and the two-dimensional integral evaluating function, TRICUB, which is found in [3]:

$$\frac{1}{r_{12}} = \frac{1}{r_>}\sum_{l=0}^{\infty}\left(\frac{r_<}{r_>}\right)^l$$

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

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

$$\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi}\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \phi_1(r_1)\phi_2(r_2)\frac{1}{r_{12}}\phi_1(r_1)\phi_2(r_2)r_1^2 r_2^2 \sin\vartheta_1 \sin\vartheta_2 \, dr_1 dr_2 d\vartheta_1 d\vartheta_2 d\varphi_1 d\varphi_2 = J(b_1, b_2)$$

$$J(b_1, b_2) = 16\pi^2 \int_0^{\infty}\int_0^{\infty} \frac{1}{r_>} \sum_{l=0}^{\infty} \left(\frac{r_<}{r_>}\right)^l \phi_1(r_1)\phi_2(r_2)\phi_1(r_1)\phi_2(r_2) r_1^2 r_2^2 dr_1 dr_2$$

We compute the zeta derivatives using central differences [4]:

$$\frac{df(\zeta, r)}{d\zeta} = \frac{f(\zeta + h, r) - f(\zeta - h, r)}{2h}$$

$$\frac{d^2 f(\zeta, r)}{d\zeta^2} = \frac{f(\zeta - h, r) - 2f(\zeta, r) + f(\zeta + h, r)}{2h}$$

We use three different methods to minimize the energy:

1. Evolutionary hill-climber one
2. Evolutionary hill-climber two
3. Simulated annealing

The user interface of our computer program is illustrated as follows:

```
Menu
1 First Rough Approximation
2 NUMAL's Praxis Function
3 Evolutionary Hill-Climber One
4 Evolutionary Hill-Climber Two
5 Simulated Annealing
6 Exit
Choose an Option: 1
Choose an Option: 2
Choose an Option: 3
Generations: 5000
Population : 4
Choose an Option: 4
Generations: 5000
Population : 4
Choose an Option: 5
m: 100
n: 20
m: 100  n: 20
Choose an Option: 6
```

The menu item 1 result was:

```
Helium atom atomic number Z = 2
Experimental ground state energy (au) = -2.90339
Experimental ground state energy (eV) = -79.0052

First Approximation Results:
zeta 1 = 2     zeta 2 = 2
Electron-electron repulsion energy (au) = 1.24999
Electron-electron repulsion energy (eV) = 34.014
Kinetic Energy (au) = 4
Kinetic Energy (eV) = 108.845
Potential energy (au) = -8
Potential energy (eV) = -217.691
Total energy (au) = -2.75001
Total energy (eV) = -74.8313
Derivative 1 in atomic units = 0
Derivative 2 in atomic units = 0
% Error = 5.28302
Runtime in milliseconds = 54
```

The PRAXIS function found in [3] computation was:

```
NUMAL's Praxis Results:
zeta 1 = 1.68752    zeta 2 = 1.68753
Electron-electron repulsion energy (au) = 1.0547
Electron-electron repulsion energy (eV) = 28.6999
Kinetic Energy (au) = 2.84774
Kinetic Energy (eV) = 77.4908
Potential energy (au) = -6.7501
Potential energy (eV) = -183.679
Total energy (au) = -2.84766
Total energy (eV) = -77.4885
Derivative 1 in atomic units = -0.312473
Derivative 2 in atomic units = -0.312461
% Error = 1.91972
Runtime in milliseconds = 3069
```

The first evolutionary hill-climber calculation was:

```
Evolutionary Hill-Climber One Results:
Generations: 5000
Population : 4
zeta 1 = 1.68609    zeta 2 = 1.68432
Electron-electron repulsion energy (au) = 1.05325
Electron-electron repulsion energy (eV) = 28.6604
Kinetic Energy (au) = 2.83991
Kinetic Energy (eV) = 77.2776
Potential energy (au) = -6.74081
Potential energy (eV) = -183.426
Total energy (au) = -2.84765
Total energy (eV) = -77.4883
Derivative 1 in atomic units = -0.313913
Derivative 2 in atomic units = -0.315683
% Error = 1.91992
Runtime in milliseconds = 72868
```

The second evolutionary hill-climber found the results shown below:

```
Evolutionary Hill-Climber Two Results:
Generations: 5000
Population : 4
zeta 1 = 1.70135    zeta 2 = 1.71789
Electron-electron repulsion energy (au) = 1.06848
Electron-electron repulsion energy (eV) = 29.0748
Kinetic Energy (au) = 2.92286
Kinetic Energy (eV) = 79.5348
Potential energy (au) = -6.83847
Potential energy (eV) = -186.084
Total energy (au) = -2.84732
Total energy (eV) = -77.4795
Derivative 1 in atomic units = -0.298654
Derivative 2 in atomic units = -0.282113
% Error = 1.93111
Runtime in milliseconds = 333291
```

Finally, the simulated annealing algorithm discovered the energy values:

```
Simulated Annealing Results:
zeta 1 = 1.9118     zeta 2 = 1.85144
Electron-electron repulsion energy (au) = 1.17564
Electron-electron repulsion energy (eV) = 31.9908
Kinetic Energy (au) = 3.5414
Kinetic Energy (eV) = 96.3662
Potential energy (au) = -7.52647
Potential energy (eV) = -204.805
Total energy (au) = -2.80943
Total energy (eV) = -76.4483
Derivative 1 in atomic units = -0.0881985
Derivative 2 in atomic units = -0.148564
% Error = 3.23627
Runtime in milliseconds = 129881
```

References

[1] L. I. Schiff, Quantum Mechanics Third Edition, New York: McGraw-Hill Book Company, 1968.

[2] J. D. Jackson, Classical Electrodynamics Second Edition, New York: John Wiley and Sons, 1975.

[3] H. T. Lau, A Numerical Library in C for Scientists and Engineers, CRC Press: Boca Raton, 1995.

[4] S. D. d. B. C. Conte, Elementary Numerical Analysis Third Edition, New York: McGraw-Hill Book Company, 1980.