New Variational Treatment of the Helium Like Atom Revised by James Pate Williams, Jr.

The Schrödinger wave equation for the helium like atom is given by the following:

$$-\frac{h^2}{8\pi^2 m_e}(\nabla_1^2+\nabla_2^2)\psi-\frac{e^2}{4\pi\epsilon_0}\left(\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{1}{|\vec{r}_1-\vec{r}_2|}\right)\psi=E\psi$$

This equation can be rewritten in the form [1] [2]:

$$-\frac{1}{2}(\nabla_1^2+\nabla_2^2)\psi-\frac{Z}{r_1}\psi-\frac{Z}{r_2}\psi+\frac{1}{|\vec{r}_1-\vec{r}_2|}\psi=E\psi$$

Where:

$$\nabla_i^2=\frac{\partial^2}{\partial {x_i}^2}+\frac{\partial^2}{\partial {y_i}^2}+\frac{\partial^2}{\partial {z_i}^2}$$

$$r_i=\sqrt{x_i^2+y_i^2+z_i^2}$$

$$r_{12}=|\vec{r}_1-\vec{r}_2|=\sqrt{(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2}$$

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

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

The hydrogen like Schrödinger wave function for the 1s orbital (quantum numbers n = 1, l = 0, m = 0) is given by [1] [2]:

$$\psi_{100}(r)=R_{10}(r)Y_{00}(\vartheta,\varphi)=2\zeta^{3/2}e^{-\zeta r}\frac{1}{2\sqrt{\pi}}=\frac{1}{\sqrt{\pi}}\zeta^{3/2}e^{-\zeta r}$$

Let our approximate helium wave function be expressed as follows:

$$\Psi_{100}(r_1,r_2)=\psi_{100}(r_1)\psi_{100}(r_2)=\frac{1}{\pi}{\zeta_1}^{3/2}e^{-\zeta_1 r_1}{\zeta_2}^{3/2}e^{-\zeta_2 r_2}$$

$$\nabla_1^2\psi_{100}(r_1)=\frac{d}{dr_1}\left[r_1^2\frac{d\psi_{100}(r_1)}{dr_1}\right]=\frac{d^2\psi_{100}(r_1)}{dr_1^2}+\frac{2}{r_1}\frac{d\psi_{100}(r_1)}{dr_1}$$

$$\frac{d\psi_{100}(r_1)}{dr_1}=-\frac{1}{\sqrt{\pi}}{\zeta_1}^{5/2}e^{-\zeta_1 r_1}$$

$$\frac{d^2\psi_{100}(r_1)}{dr_1^2}=\frac{1}{\sqrt{\pi}}{\zeta_1}^{7/2}e^{-\zeta_1 r_1}$$

$$-\frac{1}{2}\psi_{100}(r_1)\nabla_1^2\psi_{100}(r_1)=-\frac{1}{2\pi}{\zeta_1}^{5}e^{-2\zeta_1 r_1}+\frac{2}{\pi r_1}{\zeta_1}^{4}e^{-2\zeta_1 r_1}$$

Now we can compute the required integrals see:

Integral Calculator • With Steps! (integral-calculator.com)

We use the formulas from [1] [3] and numerical integration two dimensional function from [4]

$$\int_0^\infty\int_0^\pi\int_0^{2\pi} \psi_{100}(r_1)\nabla_1^2\psi_{100}(r_1)\, r_1^2 \sin\vartheta_1\, dr_1\, d\vartheta_1 d\varphi_1$$

$$= -2\pi\int_0^\infty \frac{1}{\pi}{\zeta_1}^5 e^{-2\zeta_1 r_1} r_1^2 dr_1 \ + 4\pi\int_0^\infty \frac{1}{\pi}{\zeta_1}^4 e^{-2\zeta_1 r_1} r_1 dr_1 = \frac{1}{2}\zeta_1^2$$

$$\int_0^\infty\int_0^\pi\int_0^{2\pi} -\psi_{100}(r_1)\frac{Z}{r_1}\psi_{100}(r_1)\, r_1^2 \sin\vartheta_1\, dr_1\, d\vartheta_1 d\varphi_1 = -Z\zeta_1$$

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

$$= 16{\zeta_1}^3{\zeta_2}^3\int_0^\infty\int_0^\infty \frac{1}{r_>}\sum_{l=0}^{\infty}\left(\frac{r_<}{r_>}\right)^l e^{-2\zeta_1 r_1} e^{-2\zeta_2 r_2} r_1^2\, r_2^2 dr_1\, dr_2 = 16{\zeta_1}^3{\zeta_2}^3 J(r_1,r_2)$$

$$J(r_1,r_2) = \int_0^\infty\int_0^\infty \frac{1}{r_>}\sum_{l=0}^{\infty}\left(\frac{r_<}{r_>}\right)^l e^{-2\zeta_1 r_1} e^{-2\zeta_2 r_2} r_1^2\, r_2^2 dr_1\, dr_2$$

$$E = \frac{1}{2}\zeta_1^2 - Z\zeta_1 + \frac{1}{2}\zeta_2^2 - Z\zeta_1 + 16\pi{\zeta_1}^3{\zeta_2}^3 J(r_1,r_2)$$

Now suppose we have a helium atom and no electron—electron repulsion then:

$$E_0 = 2 - 4 + 2 - 4 = -4$$

Converting from Hartree energy units to electron volts we have:

$$E_0 = -4 \cdot 27.211324570273 = -108.845298281092 eV$$

We calculate the actual derivatives of the total energy equation by what follows:

$$\frac{\partial E}{\partial \zeta_1} = 2\zeta_1 - 2Z\zeta_1 + 48{\zeta_1}^2{\zeta_2}^3 J(r_1,r_2) + 16{\zeta_1}^3{\zeta_2}^3\frac{\partial J(r_1,r_2)}{\partial \zeta_1}$$

We estimate the total energy derivative using the following central difference equation [5]:

$$\frac{\partial E}{\partial \zeta_1} = \frac{E(\zeta_1 + h, \zeta_2) - E(\zeta_1 - h, \zeta_2)}{2h}$$

Where h = 1.0e-12.

$$\frac{\partial J(r_1,r_2)}{\partial \zeta_1} = \frac{J(\zeta_1 + h, \zeta_2) - J(\zeta_1 - h, \zeta_2)}{2h}$$

We use a Slater determinant for helium.

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Choose an Option: 4
Generations: 2000
Population : 4
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m: 100  n: 80
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Helium atom atomic number Z = 2
Experimental ground state energy (au) = -2.90339
Experimental ground state energy (eV) = -79.0052
NUMAL's PRAXIS Results:
zeta 1 = 1.68753    zeta 2 = 1.68752
Electron-electron repulsion energy (au) = 1.0547
Electron-electron repulsion energy (eV) = 28.6999
Kinetic Energy (au) = 2.84774
Kinetic Energy (eV) = 77.4907
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 = -0.312449
Derivative 2 in atomic units = -0.31248
% Error = 1.91972
Runtime in milliseconds = 5342
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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 = 193
Evolutionary Hill-Climber One Results:
Generations: 2000
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 = 94053
Evolutionary Hill-Climber Two Results:
Generations: 2000
Population : 4
zeta 1 = 1.64568    zeta 2 = 1.52293
Electron-electron repulsion energy (au) = 0.98841
Electron-electron repulsion energy (eV) = 26.8959
Kinetic Energy (au) = 2.5138
Kinetic Energy (eV) = 68.4037
Potential energy (au) = -6.33723
Potential energy (eV) = -172.444
Total energy (au) = -2.84732
Total energy (eV) = -77.4795
Derivative 1 in atomic units = -0.35432
Derivative 2 in atomic units = -0.477065
% Error = 1.93111
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Runtime in milliseconds = 447059
Simulated Annealing Results:
zeta 1 = 1.97705    zeta 2 = 1.56664
Electron-electron repulsion energy (au) = 1.08962
Electron-electron repulsion energy (eV) = 29.6499
Kinetic Energy (au) = 3.18154
Kinetic Energy (eV) = 86.5739
Potential energy (au) = -7.08737
Potential energy (eV) = -192.857
Total energy (au) = -2.81622
Total energy (eV) = -76.633
Derivative 1 in atomic units = -0.0229499
Derivative 2 in atomic units = -0.433363
% Error = 3.00249
Runtime in milliseconds = 13679100
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References

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

[2] I. N. Levine, Quantum Chemistry 2nd Edition, Boston: Allyn and Bacon Inc, 1974.

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

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

[5] S. D. Conte and C. de Boor, Elementary Numerical Analysis An Algorithmic Approach Third Edition, New York: McGraw-Hill Book Company, 1980.