Curve Fitting 1s Gaussian Type Orbitals (GTOs) to a Hydrogen 1s Wavefunction

The hydrogen 1s orbital's wave function is:

$$\phi_{1s}^{H}(r,\zeta) = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r}$$

A Gaussian Type Orbital 1s orbital is as follows:

$$\phi_{1s}^{GTO}(r,\zeta) = \left(\frac{2\zeta}{\pi}\right)^{3/4} e^{-\zeta r^2}$$

A set of GTOs is defined by the equation:

$$\phi_{1s}^{CGTO}(r, c_1, \ldots, c_n, \zeta_1, \ldots, \zeta_n) = N \sum_{i=1}^{n} N_i e^{-\zeta_i r^2}$$

$$N_i = \left(\frac{2\zeta_i}{\pi}\right)^{3/4}$$

The overall normalization constant can be calculated from the integral below:

$$\iiint \phi_{1s}^{CGTO} \phi_{1s}^{CGTO} d\tau$$

$$= N^2 \sum_{i=1}^{n} \sum_{j=1}^{n} N_i N_j c_i c_j \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} e^{-\zeta_i r^2} e^{-\zeta_j r^2} r^2 \sin\vartheta dr d\vartheta d\varphi$$

$$= 4\pi N^2 \sum_{i=1}^{n} \sum_{j=1}^{n} N_i N_j c_i c_j \int_0^{\infty} e^{-\zeta_i r^2} e^{-\zeta_j r^2} r^2 dr = \pi^{3/2} N^2 \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{N_i N_j c_i c_j}{\left(\zeta_i + \zeta_j\right)^{3/2}} = 1$$

$$N = \left[\pi^{3/2} \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{N_i N_j c_i c_j}{\left(\zeta_i + \zeta_j\right)^{3/2}}\right]^{-1/2}$$

We are going to minimize the mean square error (MSE) between the hydrogen 1s orbital and the set of GTOs aka CGTO. We will need the first partial derivatives of the coefficients (the cs) and the exponents (the zetas) in the N equation. Back in May 2015 when I implemented this effort in the C# language, I probably had some minor calculational errors. I think I will numerically compute the Jacobian of N. But on second thought there is no need to compute the Jacobian of N. I use an evolutionary hill-climber to determine the coefficients and effective atomic number (Greek letter zeta) which is sometimes approximated using Slater's Screening Constant Rules. However, I will calculate the partial derivatives to check my hill-climber.

$$\frac{\partial N}{\partial c_k} = -\frac{1}{2}\pi^{3/2}\left[\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{N_i N_j \delta_{ik} c_j}{\left(\zeta_i+\zeta_j\right)^{3/2}} + \sum_{i=1}^{n}\sum_{j=1}^{n}\frac{N_i N_j c_i \delta_{jk}}{\left(\zeta_i+\zeta_j\right)^{3/2}}\right]\left[\pi^{3/2}\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{N_i N_j c_i c_j}{\left(\zeta_i+\zeta_j\right)^{3/2}}\right]^{-3/2}$$

$$= -\frac{1}{2}\pi^{3/2}\left[\sum_{j=1}^{n}\frac{N_k N_j c_j}{\left(\zeta_k+\zeta_j\right)^{3/2}} + \sum_{i=1}^{n}\frac{N_i N_k c_i}{(\zeta_i+\zeta_k)^{3/2}}\right]N^{-3/2}$$

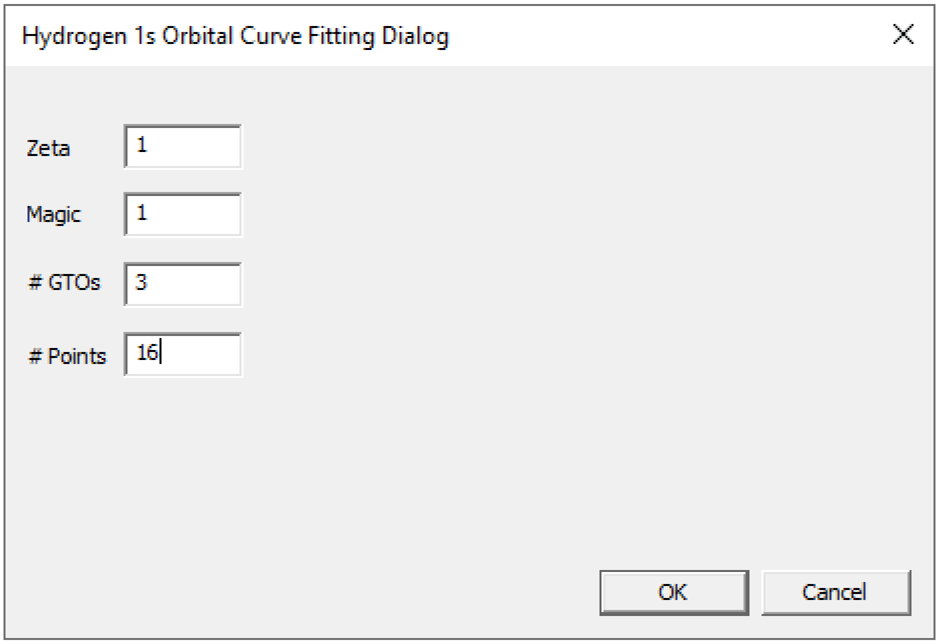
$$= -\pi^{3/2}\left[\sum_{i=1}^{n}\frac{N_i N_k c_i}{(\zeta_i+\zeta_k)^{3/2}}\right]N^{-3/2} = 0$$

$$\sum_{i=1}^{n}\frac{N_i N_k c_i}{(\zeta_i+\zeta_k)^{3/2}} = 0$$

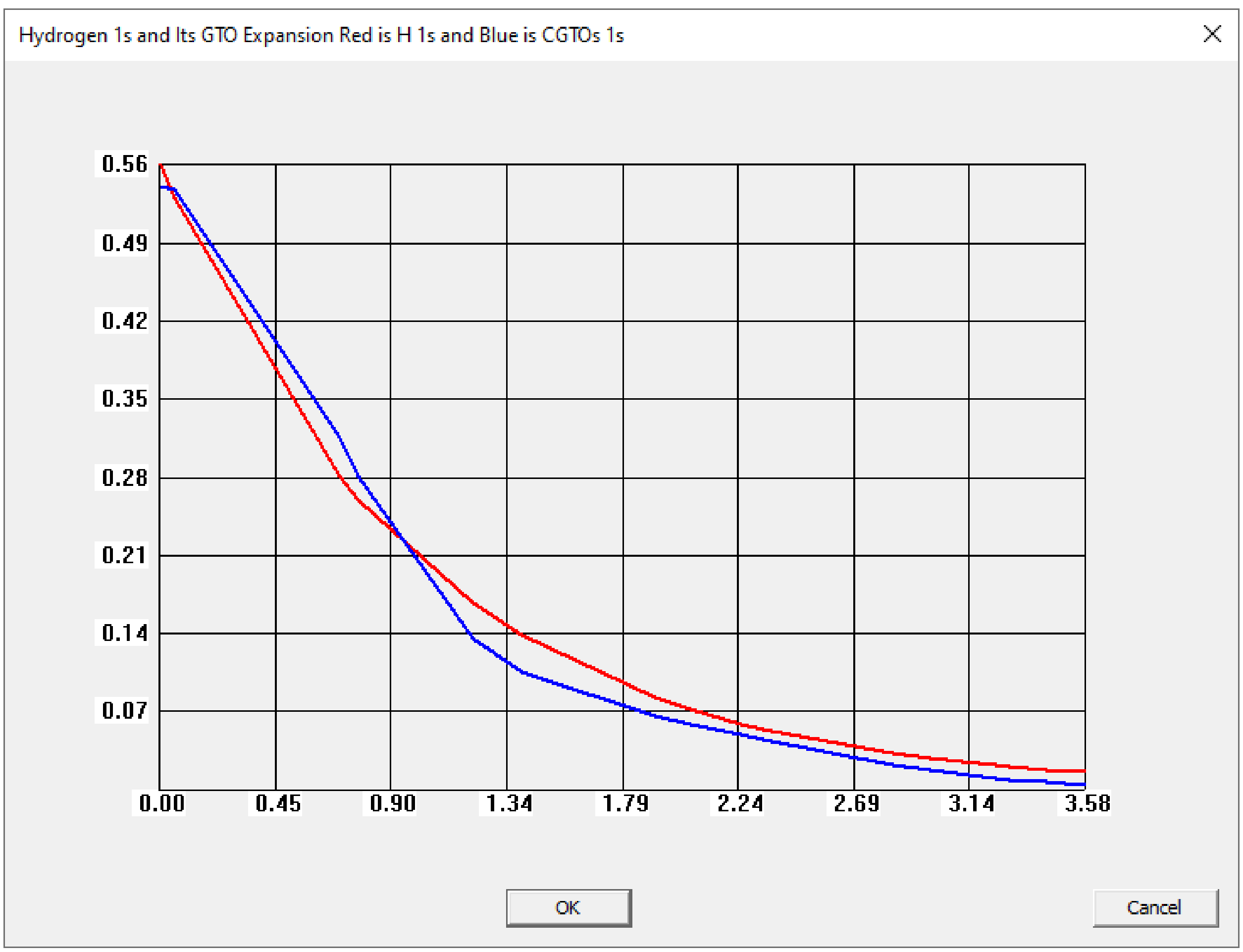
$$N = \left[\pi^{3/2}\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{c_i c_j}{\left(\zeta_i+\zeta_j\right)^{3/2}}\left(\frac{2\zeta_i}{\pi}\right)^{3/4}\left(\frac{2\zeta_j}{\pi}\right)^{3/4}\right]^{-1/2}$$

$$\begin{aligned}\frac{\partial N}{\partial \zeta_k} = -\frac{1}{2}\pi^{3/2}\Bigg[&\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{c_i c_j}{\left(\zeta_i+\zeta_j\right)^{3/2}}\frac{2\delta_{ik}}{\pi}\left(\frac{2\zeta_i}{\pi}\right)^{-1/4}\left(\frac{2\zeta_j}{\pi}\right)^{3/4} \\ &+ \sum_{i=1}^{n}\sum_{j=1}^{n}\frac{\delta_{jk} c_i c_j}{\left(\zeta_i+\zeta_j\right)^{3/2}}\left(\frac{2\zeta_i}{\pi}\right)^{3/4}\frac{2\delta_{jk}}{\pi}\left(\frac{2\zeta_j}{\pi}\right)^{-1/4} \\ &- \frac{3}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{\delta_{ik} c_i c_j}{\left(\zeta_i+\zeta_j\right)^{5/2}}\left(\frac{2\zeta_i}{\pi}\right)^{3/4}\left(\frac{2\zeta_j}{\pi}\right)^{3/4} \\ &- \frac{3}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{\delta_{jk} c_i c_j}{\left(\zeta_i+\zeta_j\right)^{5/2}}\left(\frac{2\zeta_i}{\pi}\right)^{3/4}\left(\frac{2\zeta_j}{\pi}\right)^{3/4}\Bigg]N^{-3/2} = 0\end{aligned}$$

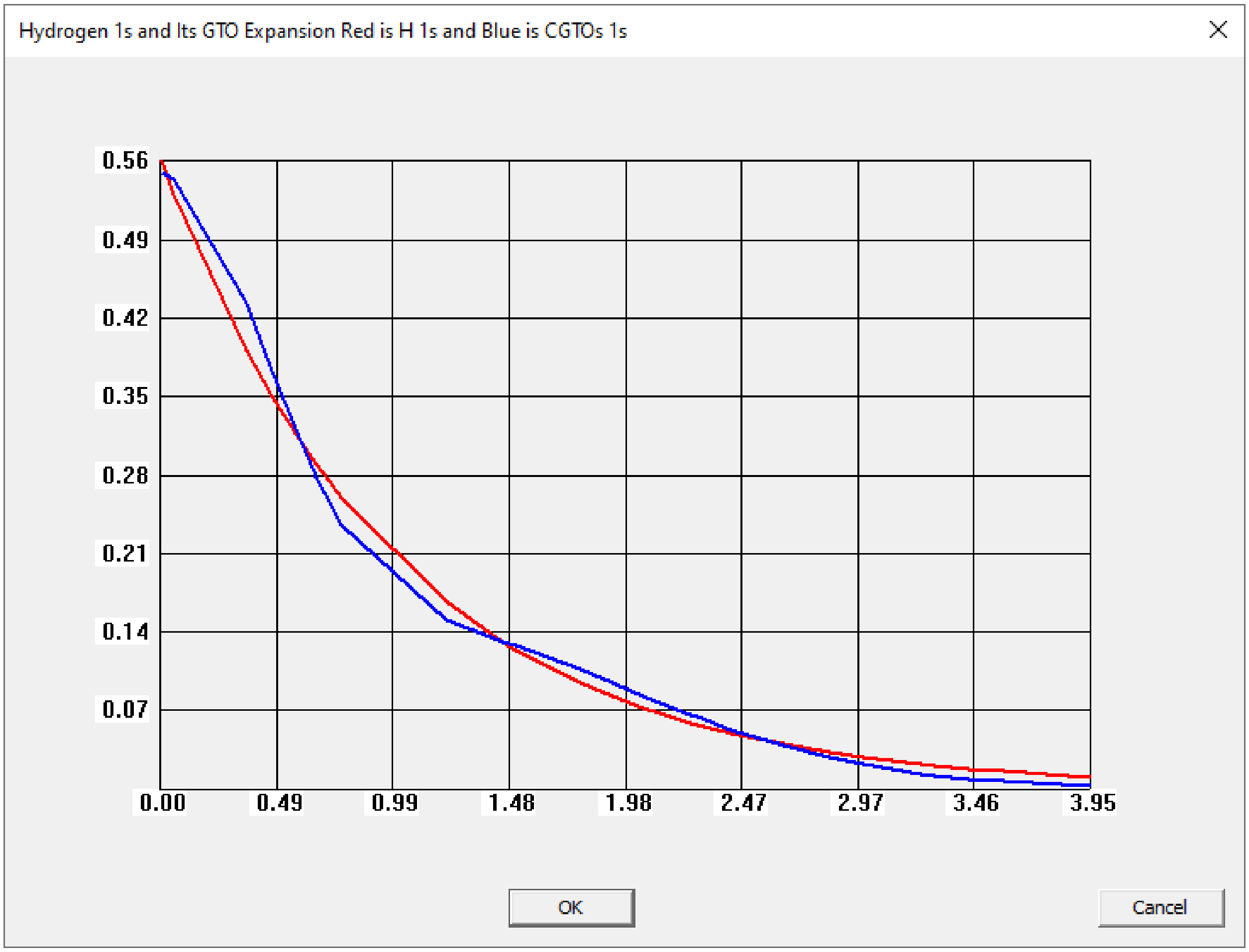
$$\begin{aligned}&\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{c_i c_j}{\left(\zeta_i+\zeta_j\right)^{3/2}}\frac{2\delta_{ik}}{\pi}\left(\frac{2\zeta_i}{\pi}\right)^{-1/4}\left(\frac{2\zeta_j}{\pi}\right)^{3/4} + \sum_{i=1}^{n}\sum_{j=1}^{n}\frac{\delta_{jk} c_i c_j}{\left(\zeta_i+\zeta_j\right)^{3/2}}\left(\frac{2\zeta_i}{\pi}\right)^{3/4}\frac{2\delta_{jk}}{\pi}\left(\frac{2\zeta_j}{\pi}\right)^{-1/4} \\ &\quad - \frac{3}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{\delta_{ik} c_i c_j}{\left(\zeta_i+\zeta_j\right)^{5/2}}\left(\frac{2\zeta_i}{\pi}\right)^{3/4}\left(\frac{2\zeta_j}{\pi}\right)^{3/4} \\ &\quad - \frac{3}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{\delta_{jk} c_i c_j}{\left(\zeta_i+\zeta_j\right)^{5/2}}\left(\frac{2\zeta_i}{\pi}\right)^{3/4}\left(\frac{2\zeta_j}{\pi}\right)^{3/4} = 0\end{aligned}$$



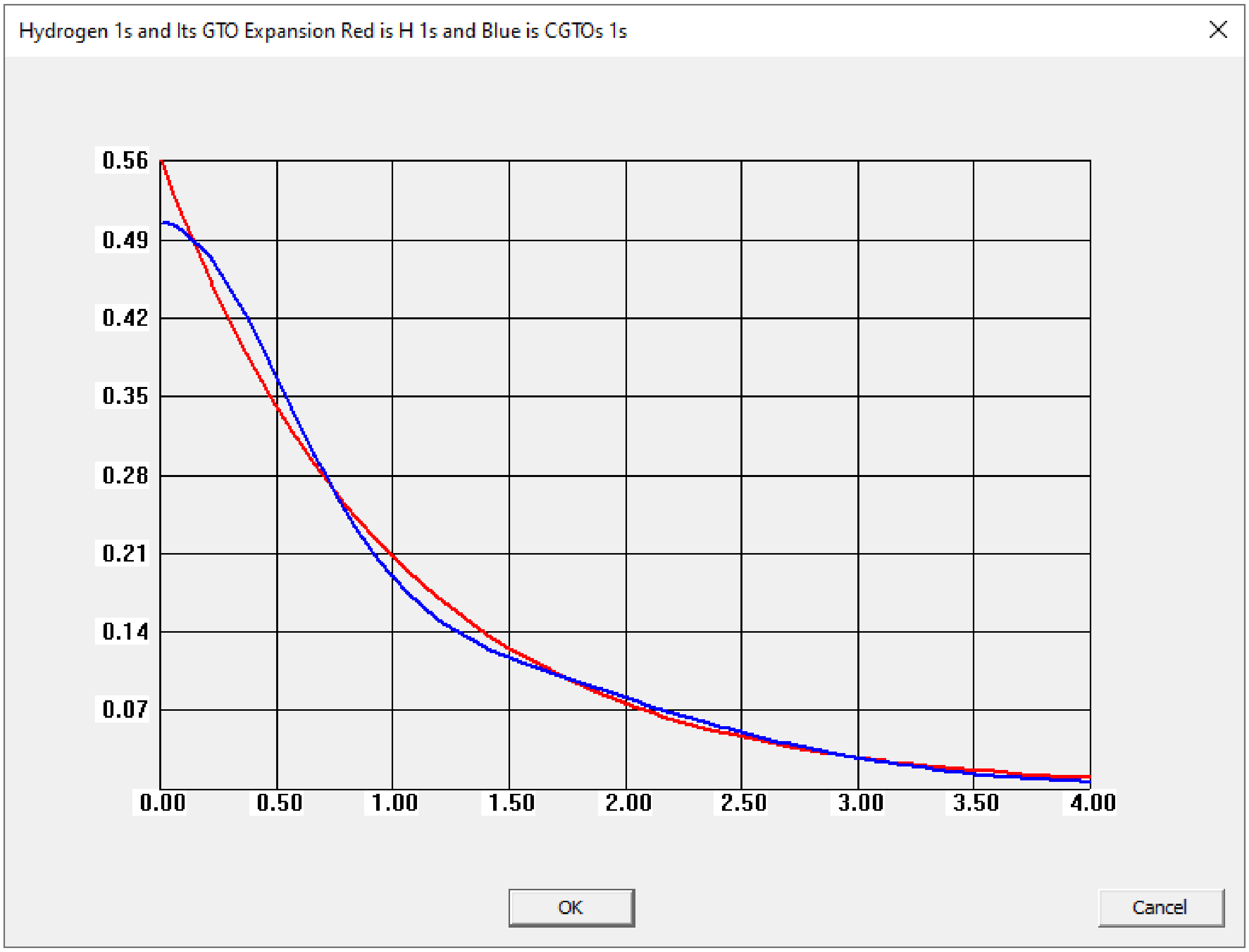
Hydrogen 1s Orbital Curve Fitting Dialog
Zeta
1
Magic
1
GTOs
3
Points
16
OK
Cancel



Hydrogen 1s and Its GTO Expansion Red is H 1s and Blue is CGTOs 1s
0.56
0.49
0.42
0.35
0.28
0.21
0.14
0.07
0.00
0.45
0.90
1.34
1.79
2.24
2.69
3.14
3.58
OK
Cancel



Hydrogen 1s and Its GTO Expansion Red is H 1s and Blue is CGTOs 1s
0.56
0.49
0.42
0.35
0.28
0.21
0.14
0.07
0.00
0.49
0.99
1.48
1.98
2.47
2.97
3.46
3.95
OK
Cancel


Hydrogen 1s and Its GTO Expansion Red is H 1s and Blue is CGTOs 1s
0.56
0.49
0.42
0.35
0.28
0.21
0.14
0.07
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
OK
Cancel