The Hartree-Fock Results for Lithium

The ground electronic configuration of Lithium is $1s^2 2s^1$ and the atom is in a ^2S state. To solve the restricted open shell Hartree-Fock equations for this atom one must first specify the gaussian expansion basis. S. Huzinaga studied this and we will present his results. Since the atomic orbitals are s orbitals one only uses s gaussians in the expansion of the 1s and 2s orbitals. Two questions must be addressed:

1. How many gaussians will be used in the expansion?
2. What are their exponents?

Huzinaga first fixed the number of gaussians (say at 6) and then determined the exponents, which minimized the Hartree-Fock energy. The variation principle insures that the resulting energy is greater than or equal to the true Hartree-Fock energy. He then increased the number of gaussians in the expansion (to say 7) and repeated the process. The resulting approximate Hartree-Fock energy decreases as the number of basis functions increases and with further increases in the number of gaussians eventually converges to the true Hartree-Fock energy. The following table summarizes his results for Lithium.

Convergence of Li Hartree-Fock energy
as a function of expansion basis length

Basis	ε_{1s} (au)	ε_{2s} (au)	Energy(au)	ΔEnergy(mh)
6s	-2.47625	-0.19500	-7.42786	0.0
7s	-2.47802	-0.19495	-7.43032	2.46
8s	-2.47840	-0.19492	-7.43100	0.68
9s	-2.47759	-0.19630	-7.43229	1.29
10s	-2.47763	-0.19630	-7.43251	0.22
11s	-2.47769	-0.19632	-7.43263	0.12
∞ s			-7.43273	0.10