Gaussian Basis Sets

Gaussian Primitives (use because integrals with r^n are well known closed form functions)

$$g_S(\alpha,r) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2} \qquad g_X(\alpha,r) = \left(\frac{128\alpha^5}{\pi^3}\right)^{1/4} x\ e^{-\alpha r^2}$$

Atomic Orbitals (linear combination of Gaussian Primitives)

$$\phi_\mu = \sum_{i=1}^{n} d_{\mu i}\, g_i(\alpha,r)$$

3-21G basis set: core 1s orbital is sum of 3 gaussians
valence shell 2s and 2p orbitals are split into two parts:
inner part is sum of 2 gaussians
outer part is 1 gaussian

Lithium 3-21G basis set as listed in Gaussian94.

	α_i	d_{si}	d_{xi}
S	3 1.00		
	0.3683820000D+02	0.6966860000D-01	
	0.5481720000D+01	0.3813460000D+00	
	0.1113270000D+01	0.6817020000D+00	
SP	2 1.00		
	0.5402050000D+00	-0.2631270000D+00	0.1615460000D+00
	0.1022550000D+00	0.1143390000D+01	0.9156630000D+00
SP	1 1.00		
	0.2856450000D-01	0.1000000000D+01	0.1000000000D+01

Ψ_{1s}

$= 0.0697\, g_S(36.8,r) + 0.381\, g_S(5.48,r) + 0.682\, g_S(1.11,r)$

$$= 0.0697\left(\frac{2\cdot 36.8}{\pi}\right)^{3/4} e^{-36.8r^2} + 0.381\left(\frac{2\cdot 5.48}{\pi}\right)^{3/4} e^{-5.48r^2} + 0.682\left(\frac{2\cdot 1.11}{\pi}\right)^{3/4} e^{-1.11r^2}$$

$\Psi_{2s}(\text{inner}) = -0.263\, g_S(0.540,r) + 1.14\, g_S(0.102,r)$

$\Psi_{2s}(\text{outer}) = 1.00\, g_S(0.0286,r)$ $\qquad \Psi_{2s} = a\Psi_{2s}(\text{inner}) + b\Psi_{2s}(\text{outer})$

$\Psi_{2px}(\text{inner}) = 0.162\, g_X(0.540,r) + 0.916\, g_X(0.102,r)$

$\Psi_{2px}(\text{outer}) = 1.00\, g_X(0.0286,r)$

E(Li,3-21G)=-200.78 eV $\qquad$ E(exp.)=$-IP_1 - IP_2 - IP_3$ = -202.42eV

6-311G basis set: core 1s orbital is sum of 6 gaussians
valence shell 2s and 2p orbitals are split into three parts:
contracted part is sum of 3 gaussians
more diffuse part is 1 gaussian
most diffuse part is 1 gaussian

Lithium 6-311G basis set as listed in Gaussian94.

	α_i	d_{si}	d_{xi}
S	6 1.00		
	0.9004600000D+03	0.2287040000D-02	
	0.1344330000D+03	0.1763500000D-01	
	0.3043650000D+02	0.8734340000D-01	
	0.8626390000D+01	0.2809770000D+00	
	0.2483320000D+01	0.6587410000D+00	
	0.3031790000D+00	0.1187120000D+00	
SP	3 1.00		
	0.4868900000D+01	0.9332930000D-01	0.3276610000D-01
	0.8569240000D+00	0.9430450000D+00	0.1597920000D+00
	0.2432270000D+00	-0.2798270000D-02	0.8856670000D+00
SP	1 1.00		
	0.6350700000D-01	0.1000000000D+01	0.1000000000D+01
SP	1 1.00		
	0.2436830000D-01	0.1000000000D+01	0.1000000000D+01

E(Li,6-311G)=–202.15eV E(exp.)=-IP_1 - IP_2 - IP_3 = -202.42eV

Carbon 3-21G basis set as listed in Gaussian94.

	α_i	d_{si}	d_{xi}
C			
S	3 1.00		
	0.1722560000D+03	0.6176690000D-01	
	0.2591090000D+02	0.3587940000D+00	
	0.5533350000D+01	0.7007130000D+00	
SP	2 1.00		
	0.3664980000D+01	-0.3958970000D+00	0.2364600000D+00
	0.7705450000D+00	0.1215840000D+01	0.8606190000D+00
SP	1 1.00		
	0.1958570000D+00	0.1000000000D+01	0.1000000000D+01