22.2.5: v. Exercise Solution

1. Two Slater type orbitals, i and j, centered on the same point results in the following overlap integrals:

$$S_{ij} = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\left(\frac{2\xi_i}{a_0}\right)^{n_i+\frac{1}{2}}\sqrt{\frac{1}{(2n_i)!}}r^{(n_i-1)}e^{\left(\frac{-\xi_i r}{a_0}\right)}Y_{l_i,m_i}(\theta,\phi)\left(\frac{2\xi_j}{a_0}\right)^{n_j+\frac{1}{2}}\sqrt{\frac{1}{(2n_j)!}}r^{(n_j-1)}e^{\left(\frac{-\xi_j r}{a_0}\right)}Y_{l_j,m_j}(\theta,\phi)r^2 sin\theta dr d\theta d\phi.$$

For these s orbitals l = m = 0 and $Y_{0,0}(\theta,\phi) = \frac{1}{\sqrt{4\pi}}$. Performing the integrations over θ and ϕ yields 4π which then cancels with these Y terms. The integral then recuces to:

$$S_{ij} = \left(\frac{2\xi_i}{a_0}\right)^{n_i+\frac{1}{2}}\sqrt{\frac{1}{(2n_i)!}}\left(\frac{2\xi_j}{a_0}\right)^{n_j+\frac{1}{2}}\sqrt{\frac{1}{(2n_j)!}}\int_0^{\infty} r^{(n_i-1+n_j-1)}e^{\left(\frac{-(\xi_i+\xi_j)r}{a_0}\right)}r^2 dr$$

$$= \left(\frac{2\xi_i}{a_0}\right)^{n_i+\frac{1}{2}}\sqrt{\frac{1}{(2n_i)!}}\left(\frac{2\xi_j}{a_0}\right)^{n_j+\frac{1}{2}}\sqrt{\frac{1}{(2n_j)!}}\int_0^{\infty} r^{(n_i-1+n_j-1)}e^{\left(\frac{-(\xi_i+\xi_j)r}{a_0}\right)}r^2 dr$$

Using integral equation (4) the integral then reduces to:

$$S_{ij} = \left(\frac{2\xi_i}{a_0}\right)^{n_i+\frac{1}{2}}\sqrt{\frac{1}{(2n_i)!}}()^{n_j+\frac{1}{2}}\sqrt{\frac{1}{(2n_j)!}}(n_i+n_j)!\left(\frac{a_0}{\xi_i+\xi_j}\right)^{n_i+n_j+1}.$$

We then substitute in the values for each of these constants:

$$\text{for i=1; n=1, l=m=0, and } \xi = 2.6906$$

$$\text{for i=2; n=2, l=m=0, and } \xi = 0.6396$$

$$\text{for i=3; n=3, l=m=0, and } \xi = 0.1503.$$

Evaluating each of these matrix elements we obtain:

$$S_{11} = (12.482992)(0.707107)(12.482992)(0.707107)(2.00)(0.006417) = 1.000000$$

$$S_{21} = S_{12} = (1.850743)(0.204124)(12.482992)(0.707107)(6.00)(0.008131) = 0.162673$$

$$S_{22} = (1.850743)(0.204124)(1.850743)(0.204124)(24.00)(0.291950) = 1.00$$

$$S_{31} = S_{13} = (0.0144892)(0.037268)(12.482992)(0.707107)(24.00)(0.005404) = 0.000635$$

$$S_{32} = S_{23} = (0.014892)(0.037268)(1.850743)(0.204124)(120.00)(4.116872) = 0.103582$$

$$S_{33} = (0.014892)(0.037268)(0.014892)(0.037268)(720.00)(4508.968136) = 1.00$$

$$S = \begin{bmatrix} 1.000000 & & \\ 0.162673 & 1.000000 & \\ 0.000635 & 0.103582 & 1.000000 \end{bmatrix}$$

We now solve the matrix eigenvalue problem S U = λ U.
The eigenvalues, λ, of this overlap matrix are:
[0.807436 0.999424 1.193139],
and the corresponding eigenvectors, U, are:

$$\begin{bmatrix} 0.596540 & -0.537104 & -0.596372 \\ -0.707634 & -0.001394 & 0.706578 \\ 0.378675 & 0.843515 & -0.380905 \end{bmatrix} \tag{22.2.5.1}$$

The $\lambda^{-\frac{1}{2}}$ matrix becomes:

$$\lambda^{-\frac{1}{2}} = \begin{bmatrix} 1.112874 & 0.000000 & 0.000000 \\ 0.000000 & 1.000288 & 0.000000 \\ 0.000000 & 0.000000 & 0.915492 \end{bmatrix}.$$

Back transforming into the original eigenbasis gives $S^{-\frac{1}{2}}$, e.g.

$$S^{-\frac{1}{2}} = U\lambda^{-\frac{1}{2}}U^T$$

$$S^{-\frac{1}{2}} = \begin{bmatrix} 1.010194 & & \\ -0.083258 & 1.014330 & \\ 0.006170 & -0.052991 & 1.004129 \end{bmatrix}$$

The old ao matrix can be written as:

$$C=\begin{bmatrix} 1.000000 & 0.000000 & 0.000000 \\ 0.000000 & 1.000000 & 0.000000 \\ 0.000000 & 0.000000 & 1.000000 \end{bmatrix}$$

The new ao matrix (which now gives each ao as a linear combination of the original aos) then becomes:

$$C'=S^{-\frac{1}{2}}C=\begin{bmatrix} 1.010194 & -0.083258 & 0.006170 \\ -0.083258 & 1.014330 & -0.052991 \\ 0.006170 & -0.052991 & 1.004129 \end{bmatrix}$$

These new aos have been constructed to meet the orthonormalization requirement $C'^{T}SC'=1$ since:

$$\left(S^{-\frac{1}{2}}C\right)^{T}SS^{-\frac{1}{2}}C=C^{T}S^{-\frac{1}{2}}SS^{-\frac{1}{2}}C=C^{T}C=1.$$

But, it is always good to check our result and indeed:

$$C'^{T}SC'=\begin{bmatrix} 1.000000 & 0.000000 & 0.000000 \\ 0.000000 & 1.000000 & 0.000000 \\ 0.000000 & 0.000000 & 1.000000 \end{bmatrix}$$

2. The least time consuming route here is to evaluate each of the needed integrals first. These are evaluated analogous to exercise 1, letting χ_i denote each of the individual Slater Type Orbitals.

$$\int_0^\infty \chi_i r \chi_j r^2 dr = \langle r\rangle_{ij} \tag{22.2.5.2}$$

$$= \left(\frac{2\xi_i}{a_0}\right)^{n_i+\frac{1}{2}}\sqrt{\frac{1}{(2n_i)!}}\left(\frac{2\xi_j}{a_0}\right)^{n_j+\frac{1}{2}}\sqrt{\frac{1}{(2n_j)!}}\int_0^\infty r^{(n_i+n_j+1)}e^{\left(-\frac{(\xi_i+\xi_j)r}{a_0}\right)}dr \tag{22.2.5.3}$$

Once again using integral equation (4) the integral recduces to:

$$= \left(\frac{2\xi_i}{a_0}\right)^{n_i+\frac{1}{2}}\sqrt{\frac{1}{(2n_i)!}}\left(\frac{2\xi_j}{a_0}\right)^{n_j+\frac{1}{2}}\sqrt{\frac{1}{(2n_j)!}}\int_0^\infty r^{(n_i+n_j+1)}e^{\left(-\frac{(\xi_i+\xi_j)r}{a_0}\right)}dr$$

Again, upon substituting in the values for each of these constants, evaluation of these expectation values yields:

$$\langle r\rangle_{11} = (12.482992)(0.707107)(12.482992)(0.707107)(6.00)(0.001193) = 0.557496$$

$$\langle r\rangle_{21} = \langle r\rangle_{12}(1.850743)(0.204124)(12.482992)(0.707107)(24.00)(0.002441) = 0.195391$$

$$\langle r\rangle_{22} = (1.850743)(0.204124)(1.850743)(0.204124)(120.00)(0.228228) = 3.908693$$

$$\langle r\rangle_{31} = \langle r\rangle_{13} = (0.014892)(0.0337268)(12.482292)(0.707107)(120.00)(0.001902) = 0.001118$$

$$\langle r\rangle_{32} = \langle r\rangle_{23} = (0.014892)(0.037268)(1.850743)(0.204124)(720.00)(5.211889) = 0.786798$$

$$\langle r\rangle_{33} = (0.014892)(0.037268)(0.014892)(0.037268)(5040.00)(14999.893999) = 23.286760$$

$$\int_0^\infty \chi_i r \chi_j r^2 dr = \langle r\rangle_{ij} \begin{bmatrix} 0.557496 & & \\ 0.195391 & 3.908693 & \\ 0.001118 & 0.786798 & 23.286760 \end{bmatrix}$$

Using these integrals one then proceeds to evaluate the expectation values of each of the orthogonalized aos, χ'_n, as:

$$\int_0^\infty \chi'_n r \chi'_n r^2 dr = \sum_{i=1}^{3}\sum_{j=1}^{3} C'_{ni} C'_{nj} \langle r\rangle_{ij}.$$

This results in the following expectation values (in atomic units):

$$\int_0^\infty \chi'_{1s} r \chi'_{1s} r^2 dr = \quad 0.563240 \text{ bohr} \tag{22.2.5.4}$$

$$\int_0^\infty \chi'_{2s} r \chi'_{2s} r^2 dr = \quad 3.973199 \text{ bohr} \tag{22.2.5.5}$$

$$\int_0^\infty \chi'_{3s} r \chi'_{3s} r^2 dr = \quad 23.406622 \text{ bohr} \tag{22.2.5.6}$$

3. The radial density for each orthogonalized orbital, χ'_n, assuming integrations over θ and ϕ have already been performed can be written as:

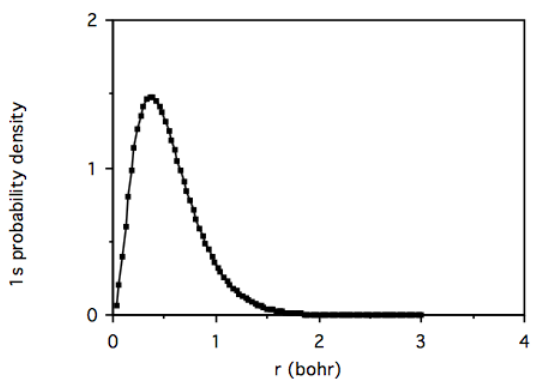
$$\int_0^\infty \chi'_n \chi'_n r^2 dr = \sum_{i=1}^{3} \sum_{j=1}^{3} C'_{ni} C'_{nj}$$

$\int_0^\infty R_i R_j r^2 dr$, where R_i and R_j are the radial portions of the individual Slater Type Orbitals, e.g.,

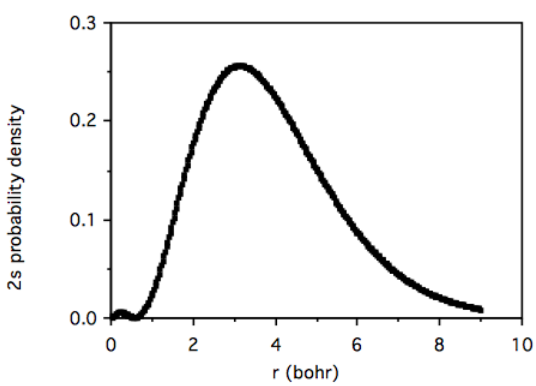
$$R_i R_j r^2 = \left(\frac{2\xi_i}{a_0}\right)^{n_i+\frac{1}{2}} \sqrt{\frac{1}{(2n_i)!}} \left(\frac{2\xi_j}{a_0}\right)^{n_j+\frac{1}{2}} \sqrt{\frac{1}{(2n_j)!}} r^{(n_i+n_j)} e^{\left(-\frac{(\xi_i+\xi_j)r}{a_0}\right)}$$

Therefore a plot of the radial probability for a given orthogonalized atomic orbital, n, will be: $\sum_{i=1}^{3} \sum_{j=1}^{3} C'_{ni} C'_{nj} R_i R_j r^2$ vs. r.

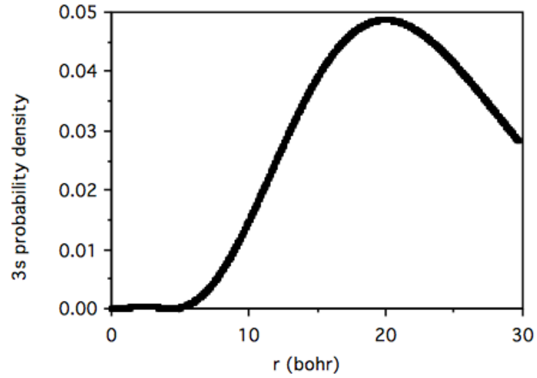
Plot the orthogonalized 1s orbital probability density vs r; note there are no nodes.

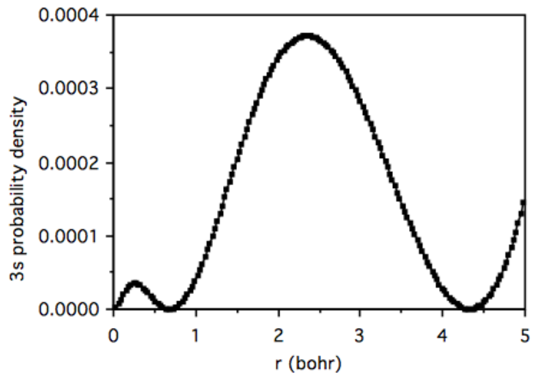


Plot of the orthogonalized 2s orbital probability density vs r; note there is one node.



Plot of the orthogonalized 3s orbital probability density vs r; note there are two nodes in the 0-5 bohr region but they are not distinguishable as such. A duplicate plot with this nodal region expanded follows.


3s probability density
0.05
0.04
0.03
0.02
0.01
0.00
0
10
20
30
r (bohr)


3s probability density
0.0004
0.0003
0.0002
0.0001
0.0000
0
1
2
3
4
5
r (bohr)