CHEMISTRY 273
PROBLEMS

13. In problem 7 you found that for $S_{AB} = \langle \chi_A^{uo} | \chi_B^{uo} \rangle$, where χ_N^{uo} is an atomic orbital completely on atom N

$$\underline{\underline{\mathbf{S}}}^{\mathbf{uo}} = \begin{pmatrix} \mathbf{1} & \mathbf{.25} \\ \mathbf{.25} & \mathbf{1} \end{pmatrix}$$

and

$$\underline{\underline{\mathbf{S}}}^{-1/2} = \begin{pmatrix} \mathbf{1.0246} & \mathbf{-.1301} \\ \mathbf{-.1301} & \mathbf{1.0246} \end{pmatrix} \qquad \underline{\underline{\mathbf{S}}}^{-1/2}\underline{\underline{\mathbf{S}}}\,\underline{\underline{\mathbf{S}}}^{-1/2} = \underline{\underline{\mathbf{1}}}$$

Since $\quad \underline{\underline{\mathbf{S}}}^{-1/2} = \left(\tilde{\underline{\underline{\mathbf{S}}}}^{-1/2}\right)^*$

$\underline{\underline{\mathbf{S}}}^{-1/2}$ provides a change of basis set from $\{\chi_A^{uo}, \chi_B^{uo}\} \Rightarrow \{\chi_A, \chi_B\}$; and for a general matrix $\underline{\underline{\mathbf{M}}}'$: $\quad \underline{\underline{\mathbf{S}}}^{-1/2}\, \underline{\underline{\mathbf{M}}}'\, \underline{\underline{\mathbf{S}}}^{-1/2} = \underline{\underline{\mathbf{M}}}$ would transform the matrix $\underline{\underline{\mathbf{M}}}'$ in the uo basis to $\underline{\underline{\mathbf{M}}}$ in the new basis.

(a) Are $\{\chi_A^{uo}, \chi_B^{uo}\}$ orthogonal?

(b) Explicitly write the new basis set $\{\chi_A, \chi_B\}$ in terms of the old.

(c) Explicitly calculate $\langle \chi_A | \chi_B \rangle$?

(d) What can be said about $\{\chi_A, \chi_B\}$?

14. In the group multiplication table each row and column must contain *every operation once and only once.*

Given that the set of elements {E, A, B} form a group of order 3, illustrate the above rule by explicitly showing how the following multiplication table would be inconsistent with the properties of a group.

	E	A	B
E	E	A	B
A	A	E	B
B	B	A	E

15. Carter, p. 65, Problem 2.4.

16. Carter, p. 64, Problem 2.1
plus (c) Do the same for the bilinear operators x^2, y^2, z^2, xy, xz, yz.

17. Carter, p. 64-65, Problem 2.3.

18. Carter, p. 64, Problem 2.2.

19. For the group O show that the sets of functions (x, y, z) and (xy, xz, yz) correspond to the irreducible representations T_1 and T_2, respectively (Cotton, ex 4.4).

20. Consider the hydrogen atoms in NH_3 with a basis set $\{1s_A, 1s_B, 1s_C\}$.

(a) Write the matrices, with respect to this basis set, for the operators in C_{3V}: $\underline{\underline{E}}$, $\underline{\underline{C}}_3$, $\underline{\underline{C}}_3^2$, $\underline{\underline{\sigma}}'_v$, $\underline{\underline{\sigma}}''_v$, $\underline{\underline{\sigma}}'''_v$.

(b) Show that the similarity transform

$$\underline{\underline{V}} = \begin{pmatrix} \sqrt{\frac{1}{3}} & 0 & \sqrt{\frac{2}{3}} \\ \sqrt{\frac{1}{3}} & \sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{6}} \\ \sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{6}} \end{pmatrix} \quad \text{with} \quad \underline{\underline{V}}^{-1} = \tilde{\underline{\underline{V}}}$$

block diagonalizes all of the operator matrices into a form

$$\left(\begin{array}{c|cc} x & 0 & 0 \\ \hline 0 & x & x \\ 0 & x & x \end{array}\right)$$

(c) Write explicitly the new basis functions, $\{SALC_1, SALC_2, SALC_3\}$ which arise from $\underline{\underline{V}}$, in forms of the old $\{1s_A, 1s_B, 1s_C\}$ basis.