Chapter 5
Answers to Problems

5.1 $P(E)\sigma_2$

O	E	C_3	C_3	C_3	C_3	C_3^2	C_3^2	C_3^2	C_3^2	C_2	C_2	C_2
label		*aa*	*bb*	*cc*	*dd*	*aa*	*bb*	*cc*	*dd*	*12*	*34*	*56*
$R_j\sigma_2$	σ_2	σ_6	σ_4	σ_5	σ_3	σ_4	σ_5	σ_3	σ_6	σ_2	σ_1	σ_1
E	2	-1	-1	-1	-1	-1	-1	-1	-1	2	2	2
$\chi_i^R R_j\sigma_2$	$2\sigma_2$	$-\sigma_6$	$-\sigma_4$	$-\sigma_5$	$-\sigma_3$	$-\sigma_4$	$-\sigma_5$	$-\sigma_3$	$-\sigma_6$	$2\sigma_2$	$2\sigma_1$	$2\sigma_1$

$$P(E)\sigma_2 \propto 4\sigma_1 + 4\sigma_2 - 2\sigma_3 - 2\sigma_4 - 2\sigma_5 - 2\sigma_6 \propto 2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6$$

This is the same result as $P(E)\sigma_1$, and therefore the companion function can be found in the same way as shown in the text, either by another projection or a transformation by a symmetry operation.

$P(E)\sigma_4$

O	E	C_3	C_3	C_3	C_3	C_3^2	C_3^2	C_3^2	C_3^2	C_2	C_2	C_2
label		*aa*	*bb*	*cc*	*dd*	*aa*	*bb*	*cc*	*dd*	*12*	*34*	*56*
$R_j\sigma_4$	σ_4	σ_6	σ_5	σ_1	σ_5	σ_2	σ_2	σ_6	σ_1	σ_3	σ_4	σ_3
E	2	-1	-1	-1	-1	-1	-1	-1	-1	2	2	2
$\chi_i^R R_j\sigma_4$	$2\sigma_4$	$-\sigma_6$	$-\sigma_5$	$-\sigma_1$	$-\sigma_5$	$-\sigma_2$	$-\sigma_2$	$-\sigma_6$	$-\sigma_1$	$2\sigma_3$	$2\sigma_4$	$2\sigma_3$

$$P(E)\sigma_4 \propto -2\sigma_1 - 2\sigma_2 + 4\sigma_3 + 4\sigma_4 - 2\sigma_5 - 2\sigma_6 \propto -\sigma_1 - \sigma_2 + 2\sigma_3 + 2\sigma_4 - \sigma_5 - \sigma_6$$

This is the same result as $P(E)\sigma_3$, and the companion function can be obtained by the identical addition shown in the text (p. 145).

$P(E)\sigma_5$

O	E	C_3	C_3	C_3	C_3	C_3^2	C_3^2	C_3^2	C_3^2	C_2	C_2	C_2
label		*aa*	*bb*	*cc*	*dd*	*aa*	*bb*	*cc*	*dd*	*12*	*34*	*56*
$R_j\sigma_5$	σ_5	σ_3	σ_2	σ_3	σ_1	σ_1	σ_4	σ_2	σ_4	σ_6	σ_6	σ_5
E	2	-1	-1	-1	-1	-1	-1	-1	-1	2	2	2
$\chi_i^R R_j\sigma_5$	$2\sigma_5$	-σ3	$-\sigma_2$	$-\sigma_3$	$-\sigma_1$	$-\sigma_1$	$-\sigma_4$	$-\sigma_2$	$-\sigma_4$	$2\sigma_6$	$2\sigma_6$	$2\sigma_5$

$$P(E)\sigma_5 \propto -2\sigma_1 - 2\sigma_2 - 2\sigma_3 - 2\sigma_4 + 4\sigma_5 + 4\sigma_6 \propto -\sigma_1 - \sigma_2 - \sigma_3 - \sigma_4 + 2\sigma_5 + 2\sigma_6$$

To get the partner add $P(E)\sigma_1 + 2P(E)\sigma_5$:

$$P(E)\sigma_1 \propto 2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6$$
$$2P(E)\sigma_5 \propto -2\sigma_1 - 2\sigma_2 - 2\sigma_3 - 2\sigma_4 + 4\sigma_5 + 4\sigma_6$$

$$- 3\sigma_3 - 3\sigma_4 + 3\sigma_5 + 3\sigma_6 \propto -\sigma_3 - \sigma_4 + \sigma_5 + \sigma_6$$

This is the negative of the same function as previously obtained in the text.

5.2 Effect of $C_4(56)$ on $\Sigma_2(E) \propto P(E)\sigma_1$

$C_4(56)$ transforms the initial functions as follows:

Before	σ_1	σ_2	σ_3	σ_4	σ_5	σ_6
After	σ_4	σ_3	σ_1	σ_2	σ_5	σ_6

$$2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6 \rightarrow 2\sigma_4 + 2\sigma_3 - \sigma_1 - \sigma_2 - \sigma_5 - \sigma_6$$
$$= \sigma_1 - \sigma_2 + 2o_3 + 2\sigma_4 - \sigma_5 - \sigma_6 \propto P(E)\sigma_3 = P(E)\sigma_4$$

The partner function can be generated from this as shown in the text.

Effect of $C_4(34)$ on $\Sigma_2(E) \propto P(E)\sigma_1$

$C_4(34)$ transforms the initial functions as follows:

Before	σ_1	σ_2	σ_3	σ_4	σ_5	σ_6
After	σ_5	σ_6	σ_3	σ_4	σ_2	σ_1

$$2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6 \rightarrow 2\sigma_5 + 2\sigma_6 - \sigma_3 - \sigma_4 - \sigma_2 - \sigma_1$$
$$= -\sigma_1 - \sigma_2 - o_3 - \sigma_4 + 2\sigma_5 + 2\sigma_6 \propto P(E)\sigma_5 = P(E)\sigma_6$$

This can be used to obtain the partner by the addition shown in the answer to 5.1 given above.

Effect of $C_4(12)$ on $\Sigma_2(E) \propto P(E)\sigma_1$

$C_4(12)$ transforms the initial functions as follows:

Before	σ_1	σ_2	σ_3	σ_4	σ_5	σ_6
After	σ_1	σ_2	σ_6	σ_5	σ_3	σ_4

$$2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6 \rightarrow 2\sigma_1 + 2\sigma_2 - \sigma_6 - \sigma_5 - \sigma_3 - \sigma_4$$
$$2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6 \propto P(E)\sigma_1 = P(E)\sigma_2$$

This just gives back the initial function.

5.3 $\int \Sigma_4\Sigma_5 d\tau = \int (\sigma_1 - \sigma_2)(\sigma_3 - \sigma_4) d\tau = 0$ Clearly, the other two combinations $\Sigma_4\Sigma_6$ and $\Sigma_5\Sigma_6$ will give 0.

$\int \Sigma_4\Sigma_1 d\tau = \int (\sigma_1 - \sigma_2)(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6) d\tau = 0$ Other combinations with Σ_1 will have the same result.

$\int \Sigma_4\Sigma_2 d\tau = \int (\sigma_1 - \sigma_2)(2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6) d\tau = 2 - 2 = 0$
$\int \Sigma_5\Sigma_2 d\tau = \int (\sigma_3 - \sigma_4)(2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6) d\tau = -1 + 1 = 0$
$\int \Sigma_6\Sigma_2 d\tau = \int (\sigma_5 - \sigma_6)(2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6) d\tau = -1 + 1 = 0$

$\int \Sigma_4\Sigma_3 d\tau = \int (\sigma_1 - \sigma_2)(\sigma_3 + \sigma_4 - \sigma_5 - \sigma_6) d\tau = 0$
$\int \Sigma_5\Sigma_3 d\tau = \int (\sigma_3 - \sigma_4)(\sigma_3 + \sigma_4 - \sigma_5 - \sigma_6) d\tau = 1 - 1 = 0$
$\int \Sigma_6\Sigma_3 d\tau = \int (\sigma_5 - \sigma_6)(\sigma_3 + \sigma_4 - \sigma_5 - \sigma_6) d\tau = -1 + 1 = 0$

5.4 The terms of the full $P(T_2)s_A$ operator are shown below. The $8C_3$ operations have zero characters and can be skipped.

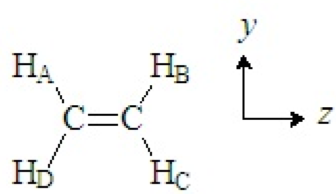
T_d	E	...	C_2	C_2	C_2	S_4	S_4	S_4	S_4^3	S_4^3	S_4^3	σ_d	σ_d	σ_d	σ_d	σ_d	σ_d
Label			x	y	z	x	y	z	x	y	z	bd	ac	bc	ad	ab	cd
$R_j s_A$	s_A		s_C	s_D	s_B	s_B	s_C	s_C	s_D	s_B	s_D	s_C	s_A	s_D	s_A	s_A	s_B
T_2	3		-1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1
$\chi_i R_j s_A$	$3s_A$		$-s_C$	$-s_D$	$-s_B$	$-s_B$	$-s_C$	$-s_C$	$-s_D$	$-s_B$	$-s_D$	s_C	s_A	s_D	s_A	s_A	s_B

Gathering the terms:

$$P(T_2)s_A \propto 6s_A - 2s_B - 2s_C - 2s_D \propto 3s_A - s_B - s_C - s_D$$

This is the result obtained from the $P(T)s_A$ operator in the subgroup T.

5.5 (a)



D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ_H	4	0	0	0	0	0	0	4

$$\Gamma_H = A_g + B_{3g} + B_{1u} + B_{2u}$$

By inspection

$$P(A_g) \propto s_A + s_B + s_C + s_D$$
$$\Phi_1(A_g) = ½(s_A + s_B + s_C + s_D)$$

Projection for B_{3g}:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
R_js_A	s_A	s_D	s_B	s_C	s_C	s_B	s_D	s_A
B_{3g}	1	-1	-1	1	1	-1	-1	1
$\chi_i R_js_A$	s_A	$-s_D$	$-s_B$	s_C	s_C	$-s_B$	$-s_D$	s_A

$$P(B_{3g})s_A \propto s_A - s_B + s_C - s_D \Rightarrow \Phi_2(B_{3g}) = ½(s_A - s_B + s_C - s_D)$$

This is clearly orthogonal to $\Phi_1(A_g)$.

Projection for B_{1u}:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
R_js_A	s_A	s_D	s_B	s_C	s_C	s_B	s_D	s_A
B_{1u}	1	1	-1	-1	-1	-1	1	1
$\chi_i R_js_A$	s_A	s_D	$-s_B$	$-s_C$	$-s_C$	$-s_B$	s_D	s_A

$$P(B_{1u})s_A \propto s_A - s_B - s_C + s_D \Rightarrow \Phi_3(B_{1u}) = ½(s_A - \mathrm{s_B} - s_C + s_D)$$

This is clearly orthogonal to both $\Phi_1(A_g)$ and $\Phi_2(B_{3g})$.

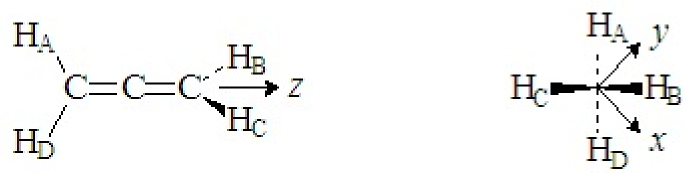
Projection for B_{2u}:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
R_js_A	s_A	s_D	s_B	s_C	s_C	s_B	s_D	s_A
B_{2u}	1	-1	1	-1	-1	1	-1	1
$\chi_i R_js_A$	s_A	$-s_D$	s_B	$-s_C$	$-s_C$	s_B	$-s_D$	s_A

$$P(B_{2u})s_A \propto s_A + s_B - s_C - s_D \Rightarrow \Phi_3(B_{2u}) = ½(s_A + \mathrm{s_B} - s_C - s_D)$$

This is clearly orthogonal to both $\Phi_1(A_g)$, $\Phi_2(B_{3g})$, and $\Phi_3(B_{1u})$.

5.5 (b)



D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$
Γ_H	4	0	0	0	2

$$\Gamma_H = A_1 + B_2 + E$$

If we do the work in the subgroup D_2, we will not only reduce the number of terms, but more importantly we will lift the E degeneracy, allowing separate projections for the two degenerate SALCs. In the descent from D_{2d} to D_2, $A_1 \rightarrow A$, $B_2 \rightarrow B_1$, and $E \rightarrow B_2 + B_3$.

The totally symmetric SALC is clearly $\Phi_1(A) = ½(s_A + s_B + s_C + s_D)$. In D_2, the $P(B_1)s_A$ projection is found as follows:

D_2	E	$C_2(z)$	$C_2(y)$	$C_2(x)$
$R_j s_A$	s_A	s_D	s_B	s_C
B_1	1	1	-1	-1
$\chi_i R_j s_A$	s_A	s_D	$-s_B$	$-s_C$

$$\Phi_2(B_1) = ½(s_A - s_B - s_C + s_D) \Rightarrow \Phi_2(B_2) = ½(s_A - s_B - s_C + s_D) \text{ in } D_{2d}$$

The first of the degenerate functions is found as the projection $P(B_2)s_A$ in D_2:

D_2	E	$C_2(z)$	$C_2(y)$	$C_2(x)$
$R_j s_A$	s_A	s_D	s_B	s_C
B_2	1	-1	1	-1
$\chi_i R_j s_A$	s_A	$-s_D$	s_B	$-s_C$

$$\Phi_3(B_2) = ½(s_A + s_B - s_C - s_D) \Rightarrow \Phi_3(E^a) = ½(s_A + s_B - s_C - s_D) \text{ in } D_{2d}$$

The second of the degenerate functions is found as the projection $P(B_3)s_A$ in D_2:

D_2	E	$C_2(z)$	$C_2(y)$	$C_2(x)$
$R_j s_A$	s_A	s_D	s_B	s_C
B_3	1	-1	-1	1
$\chi_i R_j s_A$	s_A	$-s_D$	$-s_B$	s_C

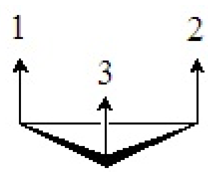
$$\Phi_4(B_3) = ½(s_A - s_B + s_C - s_D) \Rightarrow \Phi_4(E^b) = ½(s_A - s_B + s_C - s_D) \text{ in } D_{2d}$$

The orthogonality of all four functions is easily shown.

If the doubly degenerate projection is carried out in D_{2d} on s_A, we obtain an initial projection $P(E) \propto s_A - s_D$, because only the operations E and C_2 have nonzero characters. The normalized function $\Phi_3'(E^a) = 1/\sqrt{2}\,(s_A - s_D)$ is orthogonal to our previously obtained Φ_1 and Φ_2 expressions, which are the same functions generated by $P(A_1)s_A$ and $P(B_2)s_A$ in D_{2d}. The companion can be generated by applying the operation S_4^3 (for example) to $\Phi_3'(E^a)$ to obtain $\Phi_4'(E^b) = 1/\sqrt{2}\,(s_B - s_C)$. Both $\Phi_3'(E^a)$ and $\Phi_4'(E^b)$ are orthogonal to each other and to $\Phi_1(A_1)$ and $\Phi_2(B_2)$. They are related to the previously obtained functions as $\Phi_3(E^a) \propto \Phi_3'(E^a) + \Phi_4'(E^b)$ and $\Phi_4(E^b) \propto \Phi_3'(E^a) - \Phi_4'(E^b)$. The distinction is a matter of definition, with neither pair of degenerate SALCs being "right" and the other "wrong".

5.6 For all of these planar cyclic systems, the projections can be read off from the characters for the appropriate representations in the C_n subgroup of the molecule's true D_{nh} point group (n = 3, 4, 5).

(a) C_3H_3



$$\Gamma = A' + E' \text{ in } D_{3h} \Rightarrow \Gamma = A + E \text{ in } C_3$$

The A projection and resulting normalized wave function are

$$P(A)p_1 \propto p_1 + p_2 + p_3 \;\Rightarrow\; \Pi_1\ 1/\sqrt{3}\,(p_1 + p_2 + p_3)$$

From the complex conjugate pair of E representations we obtain the following two projections:

$$P(E^a)p_1 \propto p_1 + \epsilon p_2 + \epsilon^* p_3$$

$$P(E^a)p_1 \propto p_1 + \epsilon^* p_2 + \epsilon p_3$$

We can add and subtract these two to obtain real functions, realizing that

$$\epsilon + \epsilon^* = 2 \cos 2\pi/3 = 2(-½) = -1$$
$$\epsilon - \epsilon^* = 2i \sin 2\pi/3 \quad \text{and} \quad \epsilon^* - \epsilon = -2i \sin 2\pi/3$$

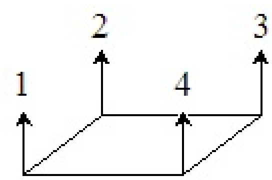
The imaginary constant $2i \sin 2\pi/3$ can be factored out of the subtractive combination prior to normalization. Thus, we obtain the following real SALCs:

$$P(E^a)p_1 + P(E^b)p_1 \propto 2p_1 - p_2 - p_3$$
$$P(E^a)p_1 - P(E^b)p_1 \propto p_2 - p_3$$

These give the normalized functions

$$\Pi_2 = 1/\sqrt{6}\ (2p_1 - p_2 - p_3)$$
$$\Pi_3 = 1/2\ (p_2 - p_3)$$

(b) C_4H_4



$$\Gamma = E_g + A_{2u} + B_{2u} \text{ in } D_{4h} \Rightarrow \Gamma_\perp = A + B + E \text{ in } C_4$$

By inspection of the C_4 character table, the A and B functions are

$$\Pi_1(A) = 1/2\ (p_1 + p_2 + p_3 + p_4)$$
$$\Pi_4(B) = 1/2\ (p_1 - p_2 + p_3 - p_4)$$

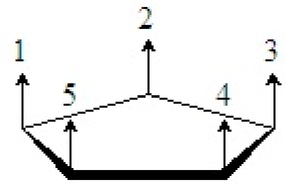
The two E projections are

$$P(E^a)p_1 \propto (p_1 + ip_2 - p_3 - ip_4)$$
$$P(E^b)p_1 \propto (p_1 - ip_2 - p_3 + ip_4)$$

By addition and subtraction, these give the two normalized functions

$$\Pi_2(E^\alpha) = 1/\sqrt{2}\ (p_1 - p_3)$$
$$\Pi_3(E^\beta) = 1/\sqrt{2}\ (p_2 - p_4)$$

(c) C_5H_5



$$\Gamma = A_2'' + E_1'' + E_2'' \text{ in } D_{5h} \Rightarrow \Gamma = A + E_1 + E_2 \text{ in } C_5$$

By inspection, $\Pi_1(A) = 1/\sqrt{5}\,(p_1 + p_2 + p_3 + p_4 + p_5)$. From the C_5 character table we can read off the two E_1 projections and the two E_2 projections. The following relationships will be useful in transforming these into real functions:

Let $\omega = 2\pi/5 = 72^\circ$ and $2\omega = 4\pi/5 = 144^\circ$

$$\epsilon + \epsilon^* = 2\cos\omega = 2\,(0.3090)$$
$$\epsilon - \epsilon^* = -2i\sin\omega = -2i\,(0.9511)$$

$$\epsilon^2 + \epsilon^{2*} = 2\cos 2\omega = 2\,(-0.8090)$$
$$\epsilon^2 - \epsilon^{2*} = -2i\sin 2\omega = -2i\,(0.5878)$$

The two E_1 projections are

$$Pp_1(E_1^a) \propto (p_1 + \epsilon p_2 + \epsilon^2 p_3 + \epsilon^{2*} p_4 + \epsilon^* p_5)$$

$$Pp_1(E_1^b) \propto (p_1 + \epsilon^* p_2 + \epsilon^{2*} p_3 + \epsilon^2 p_4 + \epsilon p_5)$$

Adding:

$$Pp_1(E_1^a) + Pp_1(E_1^b) \propto 2p_1 + 2p_2\cos\omega + 2p_3\cos 2\omega + 2p_4\cos 2\omega + 2p_5\cos\omega$$

$$\propto p_1 + p_2\cos\omega + p_3\cos 2\omega + p_4\cos 2\omega + p_5\cos\omega$$

$$\propto p_1 + 0.3090p_2 - 0.8090p_3 - 0.8090p_4 + 0.3090p_5 \propto \Pi_2(E_1)$$

Normalizing:

$$N^2\int \Pi_2^2 d\tau = 1 + 0.0955 + 0.6545 + 0.6545 + 0.0955 = 2.5$$

$$N = (1/2.5)^{1/2} = (2/5)^{1/2}$$

Normalized function:

$$\Pi_2(E_1) = (2/5)^{1/2}\{p_1 + p_2\cos\omega + p_3\cos 2\omega + p_4\cos 2\omega + p_5\cos\omega\}$$

Subtracting:

$$Pp_1(E_1{}^a) - Pp_1(E_1{}^b) \propto -2ip_2 \sin\omega - 2ip_3 \sin 2\omega + 2ip_4 \sin 2\omega + 2ip_5 \sin\omega$$

$$\propto p_2 \sin\omega + p_3 \sin 2\omega - p_4 \sin 2\omega - p_5 \sin\omega$$

$$\propto 0.9511p_2 + 0.5878p_3 - 0.5878p_4 - 0.9511p_5 \propto \Pi_3(E_1)$$

Normalizing:

$$N^2 \int \Pi_3{}^2 d\tau = 0.9045 + 0.3455 + 0.3455 + 0.9045 = 2.5$$

$$N = (1/2.5)^{1/2} = (2/5)^{1/2}$$

Normalized function:

$$\Pi_3(E_1) = (2/5)^{1/2}\{p_2 \sin\omega + p_3 \sin 2\omega - p_4 \sin 2\omega - p_5 \sin\omega\}$$

The two E_2 projections are

$$Pp_1(E_2{}^a) \propto (p_1 + \epsilon p_2 + \epsilon^2 p_3 + \epsilon^{2*} p_4 + \epsilon^* p_5)$$

$$Pp_1(E_2{}^b) \propto (p_1 + \epsilon^* p_2 + \epsilon^{2*} p_3 + \epsilon^2 p_4 + \epsilon p_5)$$

Adding:

$$Pp_1(E_2{}^a) + Pp_2(E_2{}^b) \propto 2p_1 + 2p_2 \cos 2\omega + 2p_3 \cos\omega + 2p_4 \cos\omega + 2p_5 \cos 2\omega$$

$$\propto p_1 + p_2 \cos 2\omega + p_3 \cos\omega + p_4 \cos\omega + p_5 \cos 2\omega$$

$$\propto p_1 - 0.8090p_2 + 0.3090p_3 + 0.3090p_4 - 0.8090p_5 \propto \Pi_4(E_2)$$

Normalizing:

$$N^2 \int \Pi_4{}^2 d\tau = 1 + 0.6545 + 0.0955 + 0.0955 + 0.6545 = 2.5$$

$$N = (1/2.5)^{1/2} = (2/5)^{1/2}$$

Normalized function:

$$\Pi_4(E_2) = (2/5)^{1/2}\{p_1 + p_2 \cos 2\omega + p_3 \cos\omega + p_4 \cos\omega + p_5 \cos 2\omega\}$$

Subtracting:

$$Pp_1(E_2{}^a) - Pp_1(E_2{}^b) \propto -2ip_2 \sin 2\omega - 2ip_3 \sin\omega + 2ip_4 \sin\omega + 2ip_5 \sin 2\omega$$

$$\propto p_2 \sin 2\omega + p_3 \sin \omega - p_4 \sin \omega - p_5 \sin 2\omega$$

$$\propto 0.5878p_2 + 0.9511p_3 - 0.9511p_4 - 0.5878p_5 \propto \Pi_5(E_2)$$

Normalizing:

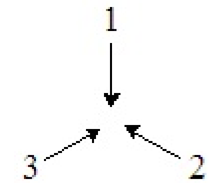
$$N^2 \int \Pi_5^{\,2} d\tau = 0.34555 + 0.9045 + 0.9045 + 0.3455 = 2.5$$

$$N = (1/2.5)^{1/2} = (2/5)^{1/2}$$

Normalized function:

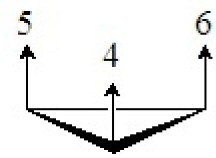
$$\Pi_5(E_2) = (2/5)^{1/2}\{p_2 \sin 2\omega + p_3 \sin \omega - p_4 \sin \omega - p_5 \sin 2\omega\}$$

5.7 The three basis sets, their reducible representations in D_{3h}, and the species of which they are composed are shown below.



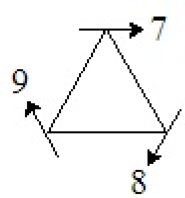
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_σ	3	0	1	3	0	1

$$\Gamma_\sigma = A_1' + E'$$



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_\perp$	3	0	-1	-3	0	1

$$\Gamma_\perp = A_2'' + E'$$



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_\parallel$	3	0	-1	-3	0	1

$$\Gamma_\parallel = A_2' + E'$$

If we carry out the projections in the subgroup C_3, all three reducible representations will be $\Gamma = A + E$. Therefore, once we find the forms of the SALCs for one case, the other two cases will have the same forms. In addition, working in C_3 lifts the double degeneracy, allowing us to read off the pair of projections from the characters for each species. Taking the sigma case as the model, the A projection and resulting normalized wave function are

$$P(A)\phi_1 \propto \phi_1 + \phi_2 + \phi_3 \;\Rightarrow\; \Phi_1(\sigma) = 1/\sqrt{3}\,(\phi_1 + \phi_2 + \phi_3)$$

From the complex conjugate pair of *E* representations we obtain the following two projections:

$$P(E^a)\phi_1 \propto \phi_1 + \epsilon\phi_2 + \epsilon^*\phi_3$$
$$P(E^a)\phi_1 \propto \phi_1 + \epsilon^*\phi_2 + \epsilon\phi_3$$

We can add and subtract these two to obtain real functions, realizing that

$$\epsilon + \epsilon^* = 2\cos 2\pi/3 = 2(-\tfrac{1}{2}) = -1$$
$$\epsilon - \epsilon^* = 2i\sin 2\pi/3 \;\text{ and }\; \epsilon^* - \epsilon = -2i\sin 2\pi/3$$

The imaginary constant $2i \sin 2\pi/3$ can be factored out of the subtractive combination prior to normalization. Thus, we obtain the following real SALCs:

$$P(E^a)\phi_1 + P(E^b)\phi_1 \propto 2\phi_1 - \phi_2 - \phi_3$$
$$P(E^a)\phi_1 - P(E^b)\phi_1 \propto \phi_2 - \phi_3$$

These give the normalized functions

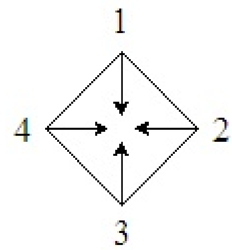
$$\Phi_2(\sigma) = 1/\sqrt{6}\,(2\phi_1 - \phi_2 - \phi_3)$$
$$\Phi_3(\sigma) = 1/2\,(\phi_2 - \phi_3)$$

It follows that the other two sets have SALCs with the same forms:

$$\Phi_4(\perp) = 1/\sqrt{3}\,(\phi_4 + \phi_5 + \phi_6)$$
$$\Phi_5(\perp) = 1/\sqrt{6}\,(2\phi_4 - \phi_5 - \phi_6)$$
$$\Phi_6(\perp) = 1/2\,(\phi_5 - \phi_6)$$

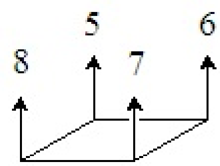
$$\Phi_7(\parallel) = 1/\sqrt{3}\,(\phi_7 + \phi_8 + \phi_9)$$
$$\Phi_8(\parallel) = 1/\sqrt{6}\,(2\phi_7 - \phi_8 - \phi_9)$$
$$\Phi_7(\parallel) = 1/2\,(\phi_8 - \phi_9)$$

5.8 The four basis sets, their reducible representations in D_{4h}, and the species of which they are composed are shown below.



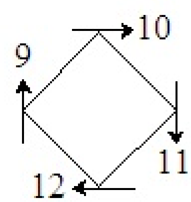
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_σ	4	0	0	2	0	0	0	4	2	0

$$\Gamma_\sigma = A_{1g} + B_{1g} + E_u$$



D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\Gamma_\perp$	4	0	0	-2	0	0	0	-4	2	0

$$\Gamma_\perp = A_{2u} + B_{2u} + E_g$$



D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\Gamma_\parallel$	4	0	0	-2	0	0	0	4	-2	0

$$\Gamma_\parallel = A_{2g} + B_{2g} + E_u$$

If we carry out the projections in the subgroup C_4, all three reducible representations will be $\Gamma = A + B + E$. Therefore, once we find the forms of the SALCs for one case, the other two cases will have the same forms. In addition, working in C_4 lifts the double degeneracy, allowing us to read off the pair of projections from the characters for each species. Taking the sigma case as a model, the A projection and resulting normalized wave function are

$$P(A)\phi_1 \propto \phi_1 + \phi_2 + \phi_3 + \phi_4 \Rightarrow \Phi_1(A) = 1/2\,(\phi_1 + \phi_2 + \phi_3 + \phi_4)$$

Likewise, for the B projection and resulting normalized wave function we have

$$P(B)\phi_1 \propto \phi_1 - \phi_2 + \phi_3 - \phi_4 \Rightarrow \Phi_2(B) = 1/2\,(\phi_1 - \phi_2 + \phi_3 - \phi_4)$$

The two E projections are

$$P(E^a)\phi_1 \propto \phi_1 + i\phi_2 - \phi_3 + i\phi_4$$
$$P(E^b)\phi_1 \propto \phi_1 - i\phi_2 - \phi_3 - i\phi_4$$

By adding and subtracting we obtain the following two normalized functions

$$\Phi_3(E) = 1/\sqrt{2}\,(\phi_1 - \phi_3) \quad \text{and} \quad \Phi_4(E) = 1/\sqrt{2}\,(\phi_2 - \phi_4)$$

5.9 (a) For trigonal planar sp^2 hybrids, $\Gamma = A_1' + E$ in D_{3h}. Use the rotational subgroup C_3 to read off the projections for the $s = A$ and $(p_x, p_y) = E$ AOs as SALCs of the hybrids. From the A projection we obtain the normalized function

$$s = 1/\sqrt{3}\,(\Psi_1 + \Psi_2 \;\; \Psi_3)$$

For the two complex conjugate E projections we have

$$P(E^a) \propto \Psi_1 + \epsilon\Psi_2 + \epsilon^*\Psi_3$$
$$P(E^b) \propto \Psi_1 + \epsilon^*\Psi_2 + \epsilon\Psi_3$$

Add and subtract these two imaginary functions to obtain real functions, realizing that

$$\epsilon + \epsilon^* = 2\cos 2\pi/3 = 2(-½) = -1$$
$$\epsilon - \epsilon^* = 2i\cos 2\pi/3 \;\text{ and }\; \epsilon^* - \epsilon = -2i\cos 2\pi/3$$

The real functions, then, are

$$P(E^a) + P(E^b) \propto 2\Psi_1 - \Psi_2 - \Psi_3$$
$$P(E^a) - P(E^b) \propto \Psi_2 - \Psi_3$$

The normalized expressions for the AOs are

$$p_x = 1/\sqrt{6}\,(2\Psi_1 - \Psi_2 - \Psi_3)$$
$$p_y = 1/2\,(\Psi_2 - \Psi_3)$$

In matrix form the three AO expressions become

$$\begin{bmatrix} s \\ p_x \\ p_y \end{bmatrix} = \begin{bmatrix} 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \\ 2/\sqrt{6} & -1/\sqrt{6} & -1/\sqrt{6} \\ 0 & 1/2 & -1/2 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{bmatrix}$$

Taking the transpose of the 3 x 3 matrix **A** to obtain the **B** matrix, we obtain an expression for the hybrids as functions of the AOs:

$$\begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{bmatrix} = \begin{bmatrix} 1/\sqrt{3} & 2/\sqrt{6} & 0 \\ 1/\sqrt{3} & -1/\sqrt{6} & 1/2 \\ 1/\sqrt{3} & -1/\sqrt{6} & -1/2 \end{bmatrix} \begin{bmatrix} s \\ p_x \\ p_y \end{bmatrix}$$

The three individual sp^2 functions are

$$\Psi_1 = 1/\sqrt{3}\, s + 2/\sqrt{6}\, p_x$$
$$\Psi_2 = 1/\sqrt{3}\, s - 1/\sqrt{6}\, p_x + 1/2\, p_y$$
$$\Psi_3 = 1/\sqrt{3}\, s - 1/\sqrt{6}\, p_x - 1/2\, p_y$$

(b) For square planar dsp^2 hybrids, $\Gamma = A_{1g} + B_{1g} + E_u$. Use the rotational subgroup C_4 to read off the projections for the $s = A$, $(p_x, p_y) = E$, and $d_{x^2\text{-}y^2} = B$ AOs as SALCs of the hybrids. From the A and B projections we obtain the normalized functions

$$s = 1/2\,(\Psi_1 + \Psi_2 + \Psi_3 + \Psi_4)$$
$$d_{x^2\text{-}y^2} = 1/2\,(\Psi_1 - \Psi_2 + \Psi_3 - \Psi_4)$$

For the E projections we obtain

$$P(E^a) \propto \Psi_1 + i\Psi_2 - \Psi_3 - i\Psi_4$$
$$P(E^a) \propto \Psi_1 - i\Psi_2 - \Psi_3 + i\Psi_4$$

Adding and subtracting these give the following two normalized functions:

$$p_x = 1/\sqrt{2}\,(\Psi_1 - \Psi_3)$$
$$p_y = 1/\sqrt{2}\,(\Psi_2 - \Psi_4)$$

Gathering all four equations into matrix form gives

$$\begin{bmatrix} s \\ p_x \\ p_y \\ d_{x^2-y^2} \end{bmatrix} = \begin{bmatrix} 1/2 & 1/2 & 1/2 & 1/2 \\ 1/\sqrt{2} & 0 & -1/\sqrt{2} & 0 \\ 0 & 1/\sqrt{2} & 0 & -1/\sqrt{2} \\ 1/2 & -1/2 & 1/2 & -1/2 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix}$$

Using the transpose of the 4 x 4 **A** matrix to obtain the **B** matrix, we obtain

$$\begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} = \begin{bmatrix} 1/2 & 1/\sqrt{2} & 0 & 1/2 \\ 1/2 & 0 & 1/\sqrt{2} & -1/2 \\ 1/2 & -1/\sqrt{2} & 0 & 1/2 \\ 1/2 & 0 & -1/\sqrt{2} & -1/2 \end{bmatrix} \begin{bmatrix} s \\ p_x \\ p_y \\ d_{x^2-y^2} \end{bmatrix}$$

The four dsp^2 function are

$$\Psi_1 = 1/2\, s + 1/\sqrt{2}\, p_x + 1/2\, d_{x^2-y^2}$$
$$\Psi_2 = 1/2\, s + 1/\sqrt{2}\, p_y - 1/2\, d_{x^2-y^2}$$
$$\Psi_3 = 1/2\, s - 1/\sqrt{2}\, p_x + 1/2\, d_{x^2-y^2}$$
$$\Psi_4 = 1/2\, s - 1/\sqrt{2}\, p_y - 1/2\, d_{x^2-y^2}$$

(c) For octahedral d^2sp^3 hybrids, $\Gamma = A_{1g} + E + T_{1u}$. We can use the previously obtained expressions for σ-SALCs developed in section 5.1 to write equations for the AOs as functions of the hybrids.

$$s(A) = 1/\sqrt{6}\,(\Psi_1 + \Psi_2 + \Psi_3 + \Psi_4 + \Psi_5 + \Psi_6)$$
$$p_x(T) = 1/\sqrt{2}\,(\Psi_5 - \Psi_6)$$
$$p_y(T) = 1/\sqrt{2}\,(\Psi_3 - \Psi_4)$$
$$p_z(T) = 1/\sqrt{2}\,(\Psi_1 - \Psi_2)$$
$$d_{z^2}(E) = 1/\sqrt{12}\,(2\Psi_1 + 2\Psi_2 - \Psi_3 - \Psi_4 - \Psi_5 - \Psi_6)$$
$$d_{x^2-y^2}(E) = 1/2\,(\Psi_3 + \Psi_4 - \Psi_5 - \Psi_6)$$

In matrix form these are

$$
\begin{bmatrix} s \\ p_x \\ p_y \\ p_z \\ d_{z^2} \\ d_{x^2-y^2} \end{bmatrix} = \begin{bmatrix} 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} \\ 0 & 0 & 0 & 0 & 1/\sqrt{2} & -1/\sqrt{2} \\ 0 & 0 & 1/\sqrt{2} & -1/\sqrt{2} & 0 & 0 \\ 1/\sqrt{2} & -1/\sqrt{2} & 0 & 0 & 0 & 0 \\ 1/\sqrt{3} & 1/\sqrt{3} & -1/\sqrt{12} & -1/\sqrt{12} & -1/\sqrt{12} & -1/\sqrt{12} \\ 0 & 0 & 1/2 & 1/2 & -1/2 & -1/2 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \\ \psi_5 \\ \psi_6 \end{bmatrix}
$$

Using the transpose of the 6 x 6 **A** matrix to obtain the **B** matrix, we obtain

$$
\begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \\ \psi_5 \\ \psi_6 \end{bmatrix} = \begin{bmatrix} 1/\sqrt{6} & 0 & 0 & 1/\sqrt{2} & 1/\sqrt{3} & 0 \\ 1/\sqrt{6} & 0 & 0 & -1/\sqrt{2} & 1/\sqrt{3} & 0 \\ 1/\sqrt{6} & 0 & 1/\sqrt{2} & 0 & -1/\sqrt{12} & 1/2 \\ 1/\sqrt{6} & 0 & -1/\sqrt{2} & 0 & -1/\sqrt{12} & 1/2 \\ 1/\sqrt{6} & 1/\sqrt{2} & 0 & 0 & -1/\sqrt{12} & -1/2 \\ 1/\sqrt{6} & -1/\sqrt{2} & 0 & 0 & -1/\sqrt{12} & -1/2 \end{bmatrix} \begin{bmatrix} s \\ p_x \\ p_y \\ p_z \\ d_{z^2} \\ d_{x^2-y^2} \end{bmatrix}
$$

The six hybrid functions are

$$\Psi_1 = 1/\sqrt{6}\, s + 1/\sqrt{2}\, p_z + 1/\sqrt{3}\, d_{z^2}$$
$$\Psi_2 = 1/\sqrt{6}\, s - 1/\sqrt{2}\, p_z + 1/\sqrt{3}\, d_{z^2}$$
$$\Psi_3 = 1/\sqrt{6}\, s + 1/\sqrt{2}\, p_y - 1/\sqrt{12}\, d_{z^2} + 1/2\, d_{x^2-y^2}$$
$$\Psi_4 = 1/\sqrt{6}\, s - 1/\sqrt{2}\, p_y - 1/\sqrt{12}\, d_{z^2} + 1/2\, d_{x^2-y^2}$$
$$\Psi_5 = 1/\sqrt{6}\, s + 1/\sqrt{2}\, p_x - 1/\sqrt{12}\, d_{z^2} - 1/2\, d_{x^2-y^2}$$
$$\Psi_6 = 1/\sqrt{6}\, s - 1/\sqrt{2}\, p_x - 1/\sqrt{12}\, d_{z^2} - 1/2\, d_{x^2-y^2}$$

5.10 The matrix equation for the AOs as functions of the hybrids is

$$\begin{bmatrix} s \\ p_x \\ p_y \\ p_z \\ d_{z^2} \end{bmatrix} = \begin{bmatrix} 1/\sqrt{5} & 1/\sqrt{5} & 1/\sqrt{5} & 1/\sqrt{5} & 1/\sqrt{5} & \\ 2/\sqrt{6} & -1/\sqrt{6} & -1/\sqrt{6} & 0 & 0 & \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/\sqrt{2} & -1/\sqrt{2} & \\ -2/\sqrt{30} & -2/\sqrt{30} & -2/\sqrt{30} & 3/\sqrt{30} & 3/\sqrt{30} & \end{bmatrix} \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \\ \Psi_5 \end{bmatrix}$$

Taking the transpose of the **A** matrix to obtain the **B** matrix gives the following matrix equation for the hybrids as functions of the AOs:

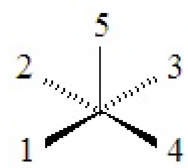
$$\begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \\ \Psi_5 \end{bmatrix} = \begin{bmatrix} 1/\sqrt{5} & 2/\sqrt{6} & 0 & 0 & -2/\sqrt{30} \\ 1/\sqrt{5} & -1/\sqrt{6} & 1/\sqrt{2} & 0 & -2/\sqrt{30} \\ 1/\sqrt{5} & -1/\sqrt{6} & -1/\sqrt{2} & 0 & -2/\sqrt{30} \\ 1/\sqrt{5} & 0 & 0 & 1/\sqrt{2} & 3/\sqrt{30} \\ 1/\sqrt{5} & 0 & 0 & -1/\sqrt{2} & 3/\sqrt{30} \end{bmatrix} \begin{bmatrix} s \\ p_x \\ p_y \\ p_z \\ d_{z^2} \end{bmatrix}$$

The resulting individual functions are

$$\Psi_1 = 1/\sqrt{5}\, s + 2/\sqrt{6}\, p_x - 2/\sqrt{30}\, d_{z^2}$$
$$\Psi_2 = 1/\sqrt{5}\, s - 1/\sqrt{6}\, p_x + 1/\sqrt{2}\, p_y - 2/\sqrt{30}\, d_{z^2}$$
$$\Psi_3 = 1/\sqrt{5}\, s - 1/\sqrt{6}\, p_x - 1/\sqrt{2}\, p_y - 2/\sqrt{30}\, d_{z^2}$$
$$\Psi_4 = 1/\sqrt{5}\, s + 1/\sqrt{2}\, p_z + 3/\sqrt{30}\, d_{z^2}$$
$$\Psi_5 = 1/\sqrt{5}\, s - 1/\sqrt{2}\, p_z + 3/\sqrt{30}\, d_{z^2}$$

These hybrids might be used to describe bonding in a transition metal *tbp* complex in which the axial and equatorial positions made equal contributions to the bonding. The involvement of the d_{z^2} orbital in the hybrid set makes this mode of hybridization, in general, inappropriate for describing the bonding in *tbp* structures in which the central atom is a *p*-block element.

5.11 The representation for the σ-SALCs is based on the following vector model:



The reducible representation and its component species are

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
Γ	5	1	1	3	1

$$\Gamma = 2A_1 + B_1 + E$$

If we apply projection operators to any reference function, we will project LCAOs that are expressions only of the members of the same set, basal or axial. The basal functions are σ_1, σ_2, σ_3, σ_4, and the axial function is simply σ_5. The axial function σ_5 clearly has A_1 symmetry, so the symmetries of the SALCs that can be formed from the basal set are the remaining species in Γ. The symmetries of the two sets, then, are

$$\Gamma_{\text{basal}} = A_1 + B_1 + E \quad \text{and} \quad \Gamma_{\text{axial}} = A_1$$

We can carry out the basal projections in the subgroup C_4, from which it is immediately apparent that nondegenerate functions are

$$\Phi_1(A_1) = 1/2\ (\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$$
$$\Phi_2\ (B_1) = 1/2\ (\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$$

The two E projections take advantage of the complex conjugate representations in C_4:

$$P(E^a)\sigma_1 \propto \sigma_1 + i\sigma_2 - \sigma_3 - i\sigma_4$$
$$P(E^b)\sigma_1 \propto \sigma_1 - i\sigma_2 - \sigma_3 + i\sigma_4$$

By addition and subtraction, we obtain the following two real functions:

$$\Phi_3(E) = 1/\sqrt{2}\ (\sigma_1 - \sigma_3)$$
$$\Phi_4(E) = 1/\sqrt{2}\ (\sigma_2 - \sigma_4)$$

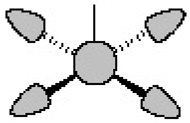
For the axial position, the SALC is simply σ_5:

$$\Phi_5(A_1) = \sigma_5$$

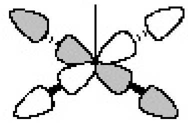
The AOs on a central atom that would match with these SALCs are

$$A_1 = s, p_z, d_{z^2} \quad B_1 = d_{x^2-y^2} \quad E = (p_x, p_y)$$

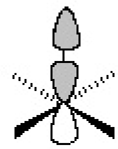
We will ignore the d_{z^2} initially, because we are assuming $d_{x^2-y^2}sp^3$ hybrids on the central atom. If we accept the SALCs we obtained from the projection operator approach, we would make the following matches between SALCs and central-atom AOs:



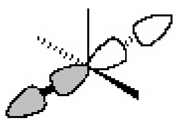
$s + \Phi_1(A_1)$



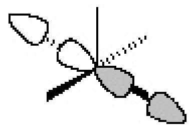
$d_{x^2-y^2} + \Phi_2(B_1)$



$p_z + \Phi_5(A_1)$

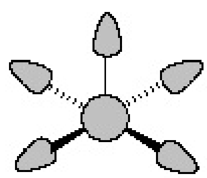


$p_x + \Phi_3(E)$



$p_y + \Phi_4(E)$

Looking at the matches between AOs and SALCs, it appears that the B_1 and E SALCs are correctly formulated, despite the basal-axial segregation inherent in our approach. However, the two A_1 SALCs are artificially exclusive with regard to the two kinds of positions. The $\Phi_1(A_1)$ SALC would be improved by including the σ_5 function, which would in no way change its A_1 symmetry. This results in the following match:



$s + \Phi'_1(A_1)$

If the axial and equatorial positions made equal contributions to the bonding (not a typical result) the redefined SALC would be

$$\Phi'_1(A_1) = 1/\sqrt{5}\ (\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5)$$

More generally, this would be

$$\Phi'_1(A_1) = c_{\text{basal}}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) + c_{\text{axial}}\sigma_5$$

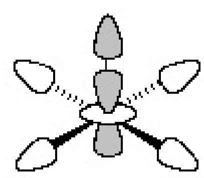
If the angle between axial and basal positions were exactly 90°, there would be no possibility of basal participation in $\Phi_5(A_1)$, because the four basal functions would fall on a nodal plane of the matching p_z orbital. In most real examples of square pyramidal geometry, the central atom is not coplanar with the basal positions. Such departures from perfect $\theta = 90°$ geometry would allow some measure of constructive overlap between the basal functions. The modified function to include such minor basal participation would be

$$\Phi'_5(A_1) = c'_{\text{axial}}\sigma_5 \pm c'_{\text{basal}}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$$

where the negative sign would be appropriate for $\theta > 90°$, and the positive sign would be appropriate for $\theta < 90°$. If the d_{z^2} orbital were to replace the p_z orbital as the major axial AO on the central atom, the basal positions would make a significant contribution and the SALC would be

$$\Phi''_5(A_1) = c''_{\text{axial}}\sigma_5 - c''_{\text{basal}}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$$

The match between d_{z^2} and this modified SALC would be as follows:



$d_{z^2} + \Phi''_5(A_1)$

Overlap between the annular part of the d_{z^2} orbital and the basal functions of the SALC would be most effective at $\theta = 90°$.

5.12 The purpose of this question is to explore an alternative approach to constructing SALCs and hybrids in general, and for the *tbp* case in specific. In the Dahr method, an expression for each SALC that would match with the various central-atom AOs is written down as the sum of the projections of each pendant atom function, ϕ_i, on the reference axes of the central atom AO, with proper adjustment of the mathematical signs of the orbital. Each projection is given by $\phi_i \cos \theta_i$, where θ_i is the angle between the AB_i bond of each pendant atom and the reference axis of the central AO. The *d* orbital functions require combining projections. In the case of the SALC to match with d_{z^2}, this approach yields a function with unequal contributions in the equatorial plane, which is intuitively incorrect. Recognizing this, Dahr corrects the function empirically to maintain C_3 symmetry. Beyond addressing the C_3 dissymmetry, Dahr's correction implicitly gives equal weight to the equatorial and axial positions, although this is not explicitly stated in the paper. The final set of functions is comparable to Eqs. (5.26a - 5.26e), shown on page 161 of the text. As such, SALCs represent a special case in which axial and equatorial positions are made equivalent. Dahr does not note the lack of generality in these results. The advantages and disadvantages of each approach are primarily a matter of personal preference.