

# 15 Molecular symmetry

## Solutions to exercises

### Discussion questions

**E15.1(b)**

Symmetry operations	Symmetry elements
1. Identity, $E$	1. The entire object
2. $n$ -fold rotation	2. $n$ -fold axis of symmetry, $C_n$
3. Reflection	3. Mirror plane, $\sigma$
4. Inversion	4. Centre of symmetry, $i$
5. $n$ -fold improper rotation	5. $n$ -fold improper rotation axis, $S_n$

**E15.2(b)** A molecule may be chiral, and therefore optically active, only if it does not possess an axis of improper rotation,  $S_n$ . An improper rotation is a rotation followed by a reflection and this combination of operations always converts a right-handed object into a left-handed object and *vice-versa*; hence an  $S_n$  axis guarantees that a molecule cannot exist in chiral forms.

**E15.3(b)** See Sections 15.4(a) and (b).

**E15.4(b)** The direct sum is the decomposition of the direct product. The procedure for the decomposition is the set of steps outlined in Section 15.5(a) on p. 471 and demonstrated in *Illustration 15.1*.

### Numerical exercises

**E15.5(b)**  $\text{CCl}_4$  has  $4 C_3$  axes (each C–Cl axis),  $3 C_2$  axes (bisecting Cl–C–Cl angles),  $3 S_4$  axes (the same as the  $C_2$  axes), and  $6$  dihedral mirror planes (each Cl–C–Cl plane).

**E15.6(b)** Only molecules belonging to  $C_s$ ,  $C_n$ , and  $C_{nv}$  groups may be polar, so . . .

(a)  $\text{CH}_3\text{Cl}$  ( $C_{3v}$ ) may be polar along the C–Cl bond;

(b)  $\text{HW}_2(\text{CO})_{10}$  ( $D_{4h}$ ) may not be polar

(c)  $\text{SnCl}_4$  ( $T_d$ ) may not be polar

**E15.7(b)** The factors of the integrand have the following characters under the operations of  $D_{6h}$

	$E$	$2C_6$	$2C_3$	$C_2$	$3C_2'$	$3C_2''$	$i$	$2S_3$	$2S_6$	$\sigma_h$	$3\sigma_d$	$3\sigma_v$
$p_x$	2	1	-1	-2	0	0	-2	-1	1	2	0	0
$z$	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1
$p_z$	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1
Integrand	2	1	-1	-2	0	0	-2	-1	1	2	0	0

The integrand has the same set of characters as species  $E_{1u}$ , so it does not include  $A_{1g}$ ; therefore the integral vanishes

**E15.8(b)** We need to evaluate the character sets for the product  $A_{1g}E_{2u}q$ , where  $q = x, y, \text{ or } z$

	$E$	$2C_6$	$2C_3$	$C_2$	$3C_2'$	$3C_2''$	$i$	$2S_3$	$2S_6$	$\sigma_h$	$3\sigma_d$	$3\sigma_v$
$A_{1g}$	1	1	1	1	1	1	1	1	1	1	1	1
$E_{2u}$	2	-1	-1	2	0	0	-2	1	1	-2	0	0
$(x, y)$	2	1	-1	-2	0	0	-2	-1	1	2	0	0
Integrand	4	-1	1	-4	0	0	4	-1	1	-4	0	0

To see whether the totally symmetric species  $A_{1g}$  is present, we form the sum over classes of the number of operations times the character of the integrand

$$c(A_{1g}) = (4) + 2(-1) + 2(1) + (-4) + 3(0) + 3(0) + (4) \\ + 2(-1) + 2(1) + (-4) + 3(0) + 3(0) = 0$$

Since the species  $A_{1g}$  is absent, the transition is **forbidden** for  $x$ - or  $y$ -polarized light. A similar analysis leads to the conclusion that  $A_{1g}$  is absent from the product  $A_{1g}E_{2u}z$ ; therefore the transition is forbidden.

**E15.9(b)** The classes of operations for  $D_2$  are:  $E$ ,  $C_2(x)$ ,  $C_2(y)$ , and  $C_2(z)$ . How does the function  $xyz$  behave under each kind of operation?  $E$  leaves it unchanged.  $C_2(x)$  leaves  $x$  unchanged and takes  $y$  to  $-y$  and  $z$  to  $-z$ , leaving the product  $xyz$  unchanged.  $C_2(y)$  and  $C_2(z)$  have similar effects, leaving one axis unchanged and taking the other two into their negatives. These observations are summarized as follows

	$E$	$C_2(x)$	$C_2(y)$	$C_2(z)$
$xyz$	1	1	1	1

A look at the character table shows that this set of characters belong to symmetry species  **$A_1$**

**E15.10(b)** A molecule cannot be chiral if it has an axis of improper rotation. The point group  $T_d$  has  **$S_4$  axes** and **mirror planes ( $= S_1$ )**, which preclude chirality. The  $T_h$  group has, in addition, a **centre of inversion ( $= S_2$ )**.

**E15.11(b)** The group multiplication table of group  $C_{4v}$  is

	$E$	$C_4^+$	$C_4^-$	$C_2$	$\sigma_v(x)$	$\sigma_v(y)$	$\sigma_d(xy)$	$\sigma_d(-xy)$
$E$	$E$	$C_4^+$	$C_4^-$	$C_2$	$\sigma_v(x)$	$\sigma_v(y)$	$\sigma_d(xy)$	$\sigma_d(-xy)$
$C_4^+$	$C_4^+$	$C_2$	$E$	$C_4^-$	$\sigma_d(xy)$	$\sigma(-xy)$	$\sigma_v(y)$	$\sigma_v(x)$
$C_4^-$	$C_4^-$	$E$	$C_2$	$C_4^+$	$\sigma_d(-xy)$	$\sigma(xy)$	$\sigma_v(x)$	$\sigma_v(y)$
$C_2$	$C_2$	$C_4^-$	$C_4^+$	$E$	$\sigma_v(y)$	$\sigma_v(x)$	$\sigma_d(-xy)$	$\sigma_d(xy)$
$\sigma_v(x)$	$\sigma_v(x)$	$\sigma_d(-xy)$	$\sigma_d(xy)$	$\sigma_v(y)$	$E$	$C_2$	$C_4^-$	$C_4^+$
$\sigma_v(y)$	$\sigma_v(y)$	$\sigma_d(xy)$	$\sigma_d(-xy)$	$\sigma_v(x)$	$C_2$	$E$	$C_4^+$	$C_4^-$
$\sigma_d(xy)$	$\sigma_d(xy)$	$\sigma_v(x)$	$\sigma_v(y)$	$\sigma_d(-xy)$	$C_4^+$	$C_4^-$	$E$	$C_2$
$\sigma_d(-xy)$	$\sigma_d(-xy)$	$\sigma_v(y)$	$\sigma_v(x)$	$\sigma_d(xy)$	$C_4^-$	$C_4^+$	$C_2$	$E$

**E15.12(b)** See Fig. 15.1.

- (a) Sharpened pencil:  $E$ ,  $C_\infty$ ,  $\sigma_v$ ; therefore  **$C_\infty v$**   
 (b) Propellor:  $E$ ,  $C_3$ ,  $3C_2$ ; therefore  **$D_3$**   
 (c) Square table:  $E$ ,  $C_4$ ,  $4\sigma_v$ ; therefore  **$C_{4v}$** ; Rectangular table:  $E$ ,  $C_2$ ,  $2\sigma_v$ ; therefore  **$C_{2v}$**   
 (d) Person:  $E$ ,  $\sigma_v$  (approximately); therefore  **$C_s$**

**E15.13(b)** We follow the flow chart in the text (Fig. 15.14). The symmetry elements found in order as we proceed down the chart and the point groups are

- (a) Naphthalene:  $E$ ,  $C_2$ ,  $C_2'$ ,  $C_2''$ ,  $3\sigma_h$ ,  $i$ ;  **$D_{2h}$**   
 (b) Anthracene:  $E$ ,  $C_2$ ,  $C_2'$ ,  $C_2''$ ,  $3\sigma_h$ ,  $i$ ;  **$D_{2h}$**

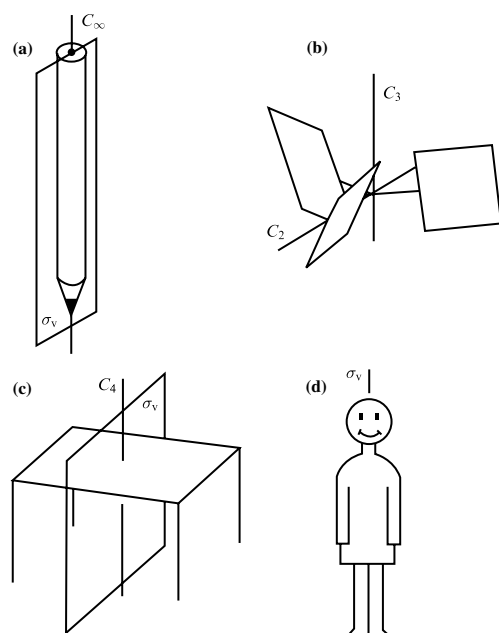


Figure 15.1

(c) Dichlorobenzenes:

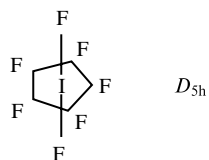
(i) 1,2-dichlorobenzene:  $E, C_2, \sigma_v, \sigma'_v$ ;  $C_{2v}$

(ii) 1,3-dichlorobenzene:  $E, C_2, \sigma_v, \sigma'_v$ ;  $C_{2v}$

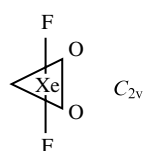
(iii) 1,4-dichlorobenzene:  $E, C_2, C'_2, C''_2, 3\sigma_h, i$ ;  $D_{2h}$

**E15.14(b)** (a) H-F  $C_{\infty v}$

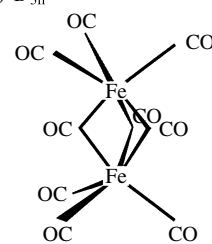
(b)



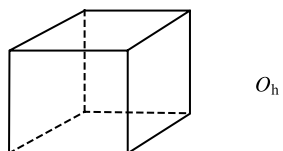
(c)



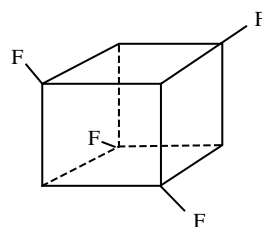
(d)  $D_{3h}$



(e)



(f)  $T_d$



The following responses refer to the text flow chart (Fig. 15.14) for assigning point groups.

(a) HF: linear, no  $i$ , so  $C_{\infty v}$

(b) IF<sub>7</sub>: nonlinear, fewer than  $2C_n$  with  $n > 2$ ,  $C_5, 5C'_2$  perpendicular to  $C_5$ ,  $\sigma_h$ , so  $D_{5h}$

- (c)  $\text{XeO}_2\text{F}_2$ : nonlinear, fewer than  $2C_n$  with  $n > 2$ ,  $C_2$ , no  $C'_2$  perpendicular to  $C_2$ , no  $\sigma_h$ ,  $2\sigma_v$ , so  $C_{2v}$
- (d)  $\text{Fe}_2(\text{CO})_9$ : nonlinear, fewer than  $2C_n$  with  $n > 2$ ,  $C_3$ ,  $3C_2$  perpendicular to  $C_3$ ,  $\sigma_h$ , so  $D_{3h}$
- (e) cubane ( $\text{C}_8\text{H}_8$ ): nonlinear, more than  $2C_n$  with  $n > 2$ ,  $i$ , no  $C_5$ , so  $O_h$
- (f) tetrafluorocubane (**23**): nonlinear, more than  $2C_n$  with  $n > 2$ , no  $i$ , so  $T_d$

- E15.15(b)** (a) Only molecules belonging to  $C_s$ ,  $C_n$ , and  $C_{nv}$  groups may be polar. In Exercise 15.13b  $ortho$ -dichlorobenzene and  $meta$ -dichlorobenzene belong to  $C_{2v}$  and so may be polar; in Exercise 15.10b, HF and  $\text{XeO}_2\text{F}_2$  belong to  $C_{nv}$  groups, so they may be polar.
- (b) A molecule cannot be chiral if it has an axis of improper rotation—including disguised or degenerate axes such as an inversion centre ( $S_2$ ) or a mirror plane ( $S_1$ ). In Exercises 15.9b and 15.10b, all the molecules have mirror planes, so none can be chiral.

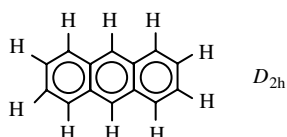
- E15.16(b)** In order to have nonzero overlap with a combination of orbitals that spans E, an orbital on the central atom must itself have some E character, for only E can multiply E to give an overlap integral with a totally symmetric part. A glance at the character table shows that  $p_x$  and  $p_y$  orbitals available to a bonding N atom have the proper symmetry. If  $d$  orbitals are available (as in  $\text{SO}_3$ ), all  $d$  orbitals except  $d_z^2$  could have nonzero overlap.

- E15.17(b)** The product  $\Gamma_f \times \Gamma(\mu) \times \Gamma_i$  must contain  $A_1$  (Example 15.7). Then, since  $\Gamma_i = B_1$ ,  $\Gamma(\mu) = \Gamma(y) = B_2$  ( $C_{2v}$  character table), we can draw up the following table of characters

	$E$	$C_2$	$\sigma_v$	$\sigma'_v$	
$B_2$	1	-1	-1	1	
$B_1$	1	-1	1	-1	
$B_1B_2$	1	1	-1	-1	= $A_2$

Hence, the upper state is  $A_2$ , because  $A_2 \times A_2 = A_1$ .

- E15.18(b)** (a) Anthracene



The components of  $\mu$  span  $B_{3u}(x)$ ,  $B_{2u}(y)$ , and  $B_{1u}(z)$ . The totally symmetric ground state is  $A_g$ .

Since  $A_g \times \Gamma = \Gamma$  in this group, the accessible upper terms are  $B_{3u}$  ( $x$ -polarized),  $B_{2u}$  ( $y$ -polarized), and  $B_{1u}$  ( $z$ -polarized).

- (b) Coronene, like benzene, belongs to the  $D_{6h}$  group. The integrand of the transition dipole moment must be or contain the  $A_{1g}$  symmetry species. That integrand for transitions from the ground state is  $A_{1g}qf$ , where  $q$  is  $x$ ,  $y$ , or  $z$  and  $f$  is the symmetry species of the upper state. Since the ground state is already totally symmetric, the product  $qf$  must also have  $A_{1g}$  symmetry for the entire integrand to have  $A_{1g}$  symmetry. Since the different symmetry species are orthogonal, the only way  $qf$  can have  $A_{1g}$  symmetry is if  $q$  and  $f$  have the same symmetry. Such combinations include  $zA_{2u}$ ,  $xE_{1u}$ , and  $yE_{1u}$ . Therefore, we conclude that transitions are allowed to states with  $A_{2u}$  or  $E_{1u}$  symmetry.

**E15.19(b)**

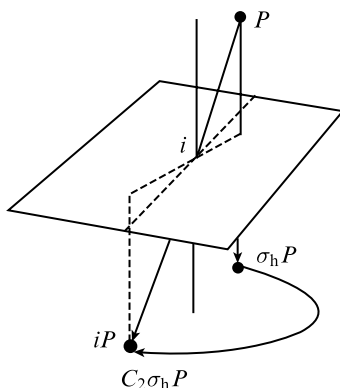
	$E$	$2C_3$	$3\sigma_v$
$A_1$	1	1	1
$A_2$	1	1	-1
$E$	2	-1	0
$\sin \theta$	1	Linear combinations of $\sin \theta$ and $\cos \theta$	1
$\cos \theta$	1		-1
Product	1	1	-1

The product does not contain  $A_1$ , so  the integral vanishes.

## Solutions to problems

**P15.3**

Consider Fig. 15.2. The effect of  $\sigma_h$  on a point  $P$  is to generate  $\sigma_h P$ , and the effect of  $C_2$  on  $\sigma_h P$  is to generate the point  $C_2\sigma_h P$ . The same point is generated from  $P$  by the inversion  $i$ , so  $C_2\sigma_h P = iP$  for all points  $P$ . Hence,   $C_2\sigma_h = i$ , and  $i$  must be a member of the group.



**Figure 15.2**

**P15.6**

*Representation 1*

$$\mathbf{D}(C_3)\mathbf{D}(C_2) = 1 \times 1 = 1 = \mathbf{D}(C_6)$$

and from the character table is either  $A_1$  or  $A_2$ . Hence, either  $\mathbf{D}(\sigma_v) = \mathbf{D}(\sigma_d) = \text{ +1 or -1}$  respectively.

*Representation 2*

$$\mathbf{D}(C_3)\mathbf{D}(C_2) = 1 \times (-1) = -1 = \mathbf{D}(C_6)$$

and from the character table is either  $B_1$  or  $B_2$ . Hence, either  $\mathbf{D}(\sigma_v) = -\mathbf{D}(\sigma_d) = \text{ 1}$  or  $\mathbf{D}(\sigma_v) = -\mathbf{D}(\sigma_d) = \text{ -1}$  respectively.

**P15.8**

A quick rule for determining the character without first having to set up the matrix representation is to count 1 each time a basis function is left unchanged by the operation, because only these functions give a nonzero entry on the diagonal of the matrix representative. In some cases there is a sign change,  $(\dots -f \dots) \leftarrow (\dots f \dots)$ ; then  $-1$  occurs on the diagonal, and so count  $-1$ . The character of the identity is always equal to the dimension of the basis since each function contributes 1 to the trace.

- $E$ : all four orbitals are left unchanged; hence  $\chi = 4$   
 $C_3$ : One orbital is left unchanged; hence  $\chi = 1$   
 $C_2$ : No orbitals are left unchanged; hence  $\chi = 0$   
 $S_4$ : No orbitals are left unchanged; hence  $\chi = 0$   
 $\sigma_d$ : Two orbitals are left unchanged; hence  $\chi = 2$

The character set 4, 1, 0, 0, 2 spans  $A_1 + T_2$ . Inspection of the character table of the group  $T_d$  shows that  $s$  spans  $A_1$  and that the three  $p$  orbitals on the C atom span  $T_2$ . Hence, the  $s$  and  $p$  orbitals of the C atom may form molecular orbitals with the four  $H1s$  orbitals. In  $T_d$ , the  $d$  orbitals of the central atom span  $E + T_2$  (character table, final column), and so only the  $T_2$  set ( $d_{xy}, d_{yz}, d_{zx}$ ) may contribute to molecular orbital formation with the H orbitals.

- P15.9** (a) In  $C_{3v}$  symmetry the  $H1s$  orbitals span the same irreducible representations as in  $NH_3$ , which is  $A_1 + A_1 + E$ . There is an additional  $A_1$  orbital because a fourth H atom lies on the  $C_3$  axis. In  $C_{3v}$ , the  $d$  orbitals span  $A_1 + E + E$  [see the final column of the  $C_{3v}$  character table]. Therefore, all five  $d$  orbitals may contribute to the bonding.
- (b) In  $C_{2v}$  symmetry the  $H1s$  orbitals span the same irreducible representations as in  $H_2O$ , but one " $H_2O$ " fragment is rotated by  $90^\circ$  with respect to the other. Therefore, whereas in  $H_2O$  the  $H1s$  orbitals span  $A_1 + B_2$  [ $H_1 + H_2, H_1 - H_2$ ], in the distorted  $CH_4$  molecule they span  $A_1 + B_2 + A_1 + B_1$  [ $H_1 + H_2, H_1 - H_2, H_3 + H_4, H_3 - H_4$ ]. In  $C_{2v}$  the  $d$  orbitals span  $2A_1 + B_1 + B_2 + A_2$  [ $C_{2v}$  character table]; therefore, all except  $A_2(d_{xy})$  may participate in bonding.
- P15.10** The most distinctive symmetry operation is the  $S_4$  axis through the central atom and aromatic nitrogens on both ligands. That axis is also a  $C_2$  axis. The group is  $S_4$ .
- P15.12** (a) Working through the flow diagram (Fig. 15.14) in the text, we note that there are no  $C_n$  axes with  $n > 2$  (for the  $C_3$  axes present in a tetrahedron are not symmetry axes any longer), but it does have  $C_2$  axes; in fact it has  $2C_2$  axes perpendicular to whichever  $C_2$  we call principal; it has no  $\sigma_h$ , but it has  $2\sigma_d$ . So the point group is  $D_{2d}$ .
- (b) Within this point group, the distortion belongs to the fully symmetric species  $A_1$ , for its motion is unchanged by the  $S_4$  operation, either class of  $C_2$ , or  $\sigma_d$ .
- (c) The resulting structure is a square bipyramid, but with one pyramid's apex farther from the base than the other's. Working through the flow diagram in Fig. 15.14, we note that there is only one  $C_n$  axis with  $n > 2$ , namely a  $C_4$  axis; it has no  $C_2$  axes perpendicular to the  $C_4$ , and it has no  $\sigma_h$ , but it has  $4\sigma_v$ . So the point group is  $C_{4v}$ .
- (d) Within this point group, the distortion belongs to the fully symmetric species  $A_1$ . The translation of atoms along the given axis is unchanged by any symmetry operation for the motion is contained within each of the group's symmetry elements.
- P15.14** (a)  $xyz$  changes sign under the inversion operation (one of the symmetry elements of a cube); hence it does not span  $A_{1g}$  and its integral must be zero
- (b)  $xyz$  spans  $A_1$  in  $T_d$  [Problem 15.13] and so its integral need not be zero
- (c)  $xyz \rightarrow -xyz$  under  $z \rightarrow -z$  (the  $\sigma_h$  operation in  $D_{6h}$ ), and so its integral must be zero

**P15.16** We shall adapt the simpler subgroup  $C_{6v}$  of the full  $D_{6h}$  point group. The six  $\pi$ -orbitals span  $A_1 + B_1 + E_1 + E_2$ , and are

$$a_1 = \frac{1}{\sqrt{6}}(\pi_1 + \pi_2 + \pi_3 + \pi_4 + \pi_5 + \pi_6)$$

$$b_1 = \frac{1}{\sqrt{6}}(\pi_1 - \pi_2 + \pi_3 - \pi_4 + \pi_5 - \pi_6)$$

$$e_2 = \begin{cases} \frac{1}{\sqrt{12}}(2\pi_1 - \pi_2 - \pi_3 + 2\pi_4 - \pi_5 - \pi_6) \\ \frac{1}{2}(\pi_2 - \pi_3 + \pi_5 - \pi_6) \end{cases}$$

$$e_1 = \begin{cases} \frac{1}{\sqrt{12}}(2\pi_1 + \pi_2 - \pi_3 - 2\pi_4 - \pi_5 + \pi_6) \\ \frac{1}{2}(\pi_2 + \pi_3 - \pi_5 - \pi_6) \end{cases}$$

The hamiltonian transforms as  $A_1$ ; therefore all integrals of the form  $\int \psi' H \psi \, d\tau$  vanish unless  $\psi'$  and  $\psi$  belong to the same symmetry species. It follows that the secular determinant factorizes into four determinants

$$A_1: \quad H_{a_1 a_1} = \frac{1}{6} \int (\pi_1 + \dots + \pi_6) H (\pi_1 + \dots + \pi_6) \, d\tau = \alpha + 2\beta$$

$$B_1: \quad H_{b_1 b_1} = \frac{1}{6} \int (\pi_1 - \pi_2 + \dots) H (\pi_1 - \pi_2 + \dots) \, d\tau = \alpha - 2\beta$$

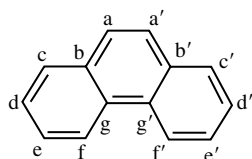
$$E_1: \quad H_{e_1(a)e_1(a)} = \alpha - \beta, \quad H_{e_1(b)e_1(b)} = \alpha - \beta, \quad H_{e_1(a)e_1(b)} = 0$$

$$\text{Hence } \begin{vmatrix} \alpha - \beta - \varepsilon & 0 \\ 0 & \alpha - \beta - \varepsilon \end{vmatrix} = 0 \text{ solves to } \varepsilon = \alpha - \beta \text{ (twice)}$$

$$E_2: \quad H_{e_2(a)e_2(a)} = \alpha + \beta, \quad H_{e_2(b)e_2(b)} = \alpha + \beta, \quad H_{e_2(a)e_2(b)} = 0$$

$$\text{Hence } \begin{vmatrix} \alpha + \beta - \varepsilon & 0 \\ 0 & \alpha + \beta - \varepsilon \end{vmatrix} = 0 \text{ solves to } \varepsilon = \alpha + \beta \text{ (twice)}$$

**P15.17** Consider phenanthrene with carbon atoms as labeled in the figure below



(a) The  $2p$  orbitals involved in the  $\pi$  system are the basis we are interested in. To find the irreducible representations spanned by this basis, consider how each basis is transformed under the symmetry operations of the  $C_{2v}$  group. To find the character of an operation in this basis, sum the coefficients of the basis terms that are unchanged by the operation.

	a	a'	b	b'	c	c'	d	d'	e	e'	f	f'	g	g'	$\chi$
$E$	a	a'	b	b'	c	c'	d	d'	e	e'	f	f'	g	g'	14
$C_2$	-a'	-a	-b'	-b	-c'	-c	-d'	-d	-e'	-e	-f'	-f	-g'	-g	0
$\sigma_v$	a'	a	b'	b	c'	c	d'	d	e'	e	f'	f	g'	g	0
$\sigma_v'$	-a	-a'	-b	-b'	-c	-c'	-d	-d'	-e	-e'	-f	-f'	-g	-g'	-14

To find the irreducible representations that these orbitals span, multiply the characters in the representation of the orbitals by the characters of the irreducible representations, sum those products, and divide the sum by the order  $h$  of the group (as in Section 15.5(a)). The table below illustrates the procedure, beginning at left with the  $C_{2v}$  character table.

	$E$	$C_2$	$\sigma_v$	$\sigma'_v$	product	$E$	$C_2$	$\sigma_v$	$\sigma'_v$	sum/ $h$
$A_1$	1	1	1	1		14	0	0	-14	0
$A_2$	1	1	-1	-1		14	0	0	14	7
$B_1$	1	-1	1	-1		14	0	0	14	7
$B_2$	1	-1	-1	1		14	0	0	-14	0

The orbitals span  $7A_2 + B_2$ .

To find symmetry-adapted linear combinations (SALCs), follow the procedure described in Section 15.5(c). Refer to the table above that displays the transformations of the original basis orbitals. To find SALCs of a given symmetry species, take a column of the table, multiply each entry by the character of the species' irreducible representation, sum the terms in the column, and divide by the order of the group. For example, the characters of species  $A_1$  are 1, 1, 1, 1, so the columns to be summed are identical to the columns in the table above. Each column sums to zero, so we conclude that there are no SALCs of  $A_1$  symmetry. (No surprise here: the orbitals span only  $A_2$  and  $B_1$ .) An  $A_2$  SALC is obtained by multiplying the characters 1, 1, -1, -1 by the first column:

$$\frac{1}{4}(a - a' - a' + a) = \frac{1}{2}(a - a').$$

The  $A_2$  combination from the second column is the same. There are seven distinct  $A_2$  combinations in all:  $1/2(a - a')$ ,  $1/2(b - b')$ ,  $\dots$ ,  $1/2(g - g')$ . The  $B_1$  combination from the first column is:

$$\frac{1}{4}(a + a' + a' + a) = \frac{1}{2}(a + a').$$

The  $B_1$  combination from the second column is the same. There are seven distinct  $B_1$  combinations in all:  $1/2(a + a')$ ,  $1/2(b + b')$ ,  $\dots$ ,  $1/2(g + g')$ . There are no  $B_2$  combinations, as the columns sum to zero.

- (b) The structure is labeled to match the row and column numbers shown in the determinant. The Hückel secular determinant of phenanthrene is:

a	$\alpha - E$	$\beta$	0	0	0	0	0	0	0	0	0	0	0	$\beta$
b	$\beta$	$\alpha - E$	$\beta$	0	0	0	$\beta$	0	0	0	0	0	0	0
c	0	$\beta$	$\alpha - E$	$\beta$	0	0	0	0	0	0	0	0	0	0
d	0	0	$\beta$	$\alpha - E$	$\beta$	0	0	0	0	0	0	0	0	0
e	0	0	0	$\beta$	$\alpha - E$	$\beta$	0	0	0	0	0	0	0	0
f	0	0	0	0	$\beta$	$\alpha - E$	$\beta$	0	0	0	0	0	0	0
g	0	$\beta$	0	0	0	$\beta$	$\alpha - E$	$\beta$	0	0	0	0	0	0
g'	0	0	0	0	0	0	$\beta$	$\alpha - E$	$\beta$	0	0	0	$\beta$	0
f'	0	0	0	0	0	0	0	$\beta$	$\alpha - E$	$\beta$	0	0	0	0
e'	0	0	0	0	0	0	0	0	$\beta$	$\alpha - E$	$\beta$	0	0	0
d'	0	0	0	0	0	0	0	0	0	$\beta$	$\alpha - E$	$\beta$	0	0
c'	0	0	0	0	0	0	0	0	0	0	$\beta$	$\alpha - E$	$\beta$	0
b'	0	0	0	0	0	0	0	$\beta$	0	0	0	$\beta$	$\alpha - E$	$\beta$
a'	$\beta$	0	0	0	0	0	0	0	0	0	0	0	$\beta$	$\alpha - E$

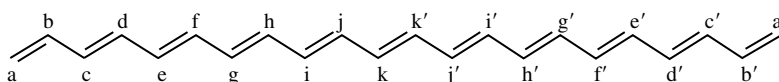
This determinant has the same eigenvalues as as in exercise 14.16(b)b.



- (c) The ground state of the molecule has  $A_1$  symmetry by virtue of the fact that its wavefunction is the product of doubly occupied orbitals, and the product of any two orbitals of the same symmetry has  $A_1$  character. If a transition is to be allowed, the transition dipole must be non-zero, which in turn can only happen if the representation of the product  $\Psi_f^* \mu \Psi_i$  includes the totally symmetric species  $A_1$ . Consider first transitions to another  $A_1$  wavefunction, in which case we need the product  $A_1 \mu A_1$ . Now  $A_1 A_1 = A_1$ , and the only character that returns  $A_1$  when multiplied by  $A_1$  is  $A_1$  itself. The  $z$  component of the dipole operator belongs to species  $A_1$ , so  $z$ -polarized  $A_1 \leftarrow A_1$  transitions are allowed. (Note: transitions from the  $A_1$  ground state to an  $A_1$  excited state are transitions from an orbital occupied in the ground state to an excited-state orbital of the same symmetry.) The other possibility is a transition from an orbital of one symmetry ( $A_2$  or  $B_1$ ) to the other; in that case, the excited-state wavefunction will have symmetry of  $A_1 B_1 = B_2$  from the two singly occupied orbitals in the excited state. The symmetry of the transition dipole, then, is  $A_1 \mu B_2 = \mu B_2$ , and the only species that yields  $A_1$  when multiplied by  $B_2$  is  $B_2$  itself. Now the  $y$  component of the dipole operator belongs to species  $B_2$ , so these transitions are also allowed ( $y$ -polarized).

**P15.21**

- (a) Following the flow chart in Fig. 15.14, note that the molecule is not linear (at least not in the mathematical sense); there is only one  $C_n$  axis (a  $C_2$ ), and there is a  $\sigma_h$ . The point group, then, is  $C_{2h}$ .



- (b) The  $2p_z$  orbitals are transformed under the symmetry operations of the  $C_{2h}$  group as follows.

	a	a'	b	b'	c	c'	...	j	j'	k	k'	$\chi$
$E$	a	a'	b	b'	c	c'	...	j	j'	k	k'	22
$C_2$	a'	a	b'	b	c'	c	...	j'	j	k'	k	0
$i$	-a'	-a	-b'	-b	-c'	-c	...	-j'	-j	-k'	-k	0
$\sigma_h$	-a	-a'	-b	-b'	-c	-c'	...	-j	-j'	-k	-k'	-22

To find the irreducible representations that these orbitals span, we multiply the characters of orbitals by the characters of the irreducible representations, sum those products, and divide the sum by the order  $h$  of the group (as in Section 15.5(a)). The table below illustrates the procedure, beginning at left with the  $C_{2h}$  character table.

	$E$	$C_2$	$i$	$\sigma_h$	product	$E$	$C_2$	$i$	$\sigma_h$	sum/ $h$
$A_g$	1	1	1	1		22	0	0	-22	0
$A_u$	1	1	-1	-1		22	0	0	22	11
$B_g$	1	-1	1	-1		22	0	0	22	11
$B_u$	1	-1	-1	1		22	0	0	-22	0

The orbitals span  $11A_u + 11B_g$ .

To find symmetry-adapted linear combinations (SALCs), follow the procedure described in Section 15.5(c). Refer to the above that displays the transformations of the original basis orbitals. To find SALCs of a given symmetry species, take a column of the table, multiply each entry by the character of the species' irreducible representation, sum the terms in the column, and divide by the order of the group. For example, the characters of species  $A_u$  are 1, 1, 1, 1, so the

columns to be summed are identical to the columns in the table above. Each column sums to zero, so we conclude that there are no SALCs of  $A_g$  symmetry. (No surprise: the orbitals span only  $A_u$  and  $B_g$ ). An  $A_u$  SALC is obtained by multiplying the characters 1, 1,  $-1$ ,  $-1$  by the first column:

$$\frac{1}{4}(a + a' + a' + a) = \frac{1}{2}(a + a').$$

The  $A_u$  combination from the second column is the same. There are 11 distinct  $A_u$  combinations in all:  $\frac{1}{2}(a + a')$ ,  $\frac{1}{2}(b + b')$ ,  $\dots$ ,  $\frac{1}{2}(k + k')$ . The  $B_g$  combination from the first column is:

$$\frac{1}{4}(a - a' - a' + a) = \frac{1}{2}(a - a').$$

The  $B_g$  combination from the second column is the same. There are 11 distinct  $B_g$  combinations in all:  $\frac{1}{2}(a - a')$ ,  $\frac{1}{2}(b - b')$ ,  $\dots$ ,  $\frac{1}{2}(k - k')$ . There are no  $B_u$  combinations, as the columns sum to zero.

- (c) The structure is labeled to match the row and column numbers shown in the determinant. The Hückel secular determinant is:

	a	b	c	...	i	j	k	k'	j'	i'	...	c'	b'	a'
a	$\alpha - E$	$\beta$	0	...	0	0	0	0	0	0	...	0	0	0
b	$\beta$	$\alpha - E$	$\beta$	...	0	0	0	0	0	0	...	0	0	0
c	0	$\beta$	$\alpha - E$	...	0	0	0	0	0	0	...	0	0	0
...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
i	0	0	0	...	$\alpha - E$	$\beta$	0	0	0	0	...	0	0	0
j	0	0	0	...	$\beta$	$\alpha - E$	$\beta$	0	0	0	...	0	0	0
k	0	0	0	...	0	$\beta$	$\alpha - E$	$\beta$	0	0	...	0	0	0
k'	0	0	0	...	0	0	$\beta$	$\alpha - E$	$\beta$	0	...	0	0	0
j'	0	0	0	...	0	0	0	$\beta$	$\alpha - E$	$\beta$	...	0	0	0
i'	0	0	0	...	0	0	0	0	$\beta$	$\alpha - E$	...	0	0	0
...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
c'	0	0	0	...	0	0	0	0	0	0	...	$\alpha - E$	$\beta$	0
b'	0	0	0	...	0	0	0	0	0	0	...	$\beta$	$\alpha - E$	$\beta$
a'	0	0	0	...	0	0	0	0	0	0	...	0	$\beta$	$\alpha - E$

The energies of the filled orbitals are  $\alpha + 1.98137\beta$ ,  $\alpha + 1.92583\beta$ ,  $\alpha + 1.83442\beta$ ,  $\alpha + 1.70884\beta$ ,  $\alpha + 1.55142\beta$ ,  $\alpha + 1.36511\beta$ ,  $\alpha + 1.15336\beta$ ,  $\alpha + 0.92013\beta$ ,  $\alpha + 0.66976\beta$ ,  $\alpha + 0.40691\beta$ , and  $\alpha + 0.13648\beta$ . The  $\pi$  energy is  $27.30729\beta$ .

- (d) The ground state of the molecule has  $A_g$  symmetry by virtue of the fact that its wavefunction is the product of doubly occupied orbitals, and the product of any two orbitals of the same symmetry has  $A_g$  character. If a transition is to be allowed, the transition dipole must be non-zero, which in turn can only happen if the representation of the product  $\Psi_f^* \mu \Psi_i$  includes the totally symmetric species  $A_g$ . Consider first transitions to another  $A_g$  wavefunction, in which case we need the product  $A_g \mu A_g$ . Now  $A_g \mu A_g = A_g$ , and the only character that returns  $A_g$  when multiplied by  $A_g$  is  $A_g$  itself. No component of the dipole operator belongs to species  $A_g$ , so no  $A_g \leftarrow A_g$  transitions are allowed. (Note: such transitions are transitions from an orbital occupied in the ground state to an excited-state orbital of the same symmetry.) The other possibility is a transition from an orbital of one symmetry ( $A_u$  or  $B_g$ ) to the other; in that case, the excited-state wavefunction will have symmetry of  $A_u B_g = B_u$  from the two singly occupied orbitals in the excited state. The symmetry of the transition dipole, then, is  $A_g \mu B_u = \mu B_u$ , and the only species that yields  $A_g$  when multiplied by  $B_u$  is  $B_u$  itself. The  $x$  and  $y$  components of the dipole operator belongs to species  $B_u$ , so these transitions are allowed.