

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
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CHEMICAL SCIENCES

CODE:01

2.5. Chemical applications of group theory

At a Glance

Symmetry elements, Group, Class, Group Multiplication Table, Reducible representation, Irreducible representation Standard Reduction Formula, The Great Orthogonal Theorem, Modes of vibration



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Key Statements

Basic Key Statements: Symmetry Elements (2.5.1), Symmetry Operation (2.5.2), Fundamental condition to be satisfy the well defined group (2.5.12), Abelian group (2.5.13), Non Abelian group (2.5.14), Cyclic groups (2.5.15), Order of a group (2.5.16), Sub group (2.5.17), Class (2.5.19), Definition of character/ Trace/ Spur (2.5.27), Mulliken's symbol of IRs (2.5.32), Dimensions of IR 2.5.36), Subscript and superscript (2.5.37), IR - selection rule (2.5.43), Raman selection rule (2.5.44), Normal modes of vibrations (2.5.45/46/47).

Standard Key Statements: Some important relationship (2.5.9), Deducing the implied presence of other symmetry elements (2.5.10), Point groups (2.5.21), Multiplication tables 2.5.22), Optical activity and point group (2.5.24), Matrices Representation of Symmetry elements (2.5.26), Construction of Character Table (2.5.30/31), Standard reduction formula (2.5.33/34), Direct product (2.5.35),

Advance Key Statements: Rearrangement theorem (2.5.23), Reducible and Irreducible representation (2.5.28/29), Great Orthogonal Theorem (GOT) (2.5.38), Spectral transition (2.5.39/40/41),

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2.5. Chemical applications of group theory

2.5.1. Symmetry Elements: A symmetry element is a geometrical entity such as a point, a line or a plane about which a symmetry operation is performed.

2.5.2. Symmetry Operation: An operation is the movement of a molecule about the symmetry element in such a manner that the resulting configuration of the molecule is indistinguishable from the original. The molecule may assume an equivalent configuration or an identical configuration.

There are 5 types of symmetry element: E , C_n , σ , S_n and i .

E is called the Identity.

C_n is the n -fold proper axis of rotation.

σ is the plane of symmetry.

S_n is the n -fold improper axis of rotation.

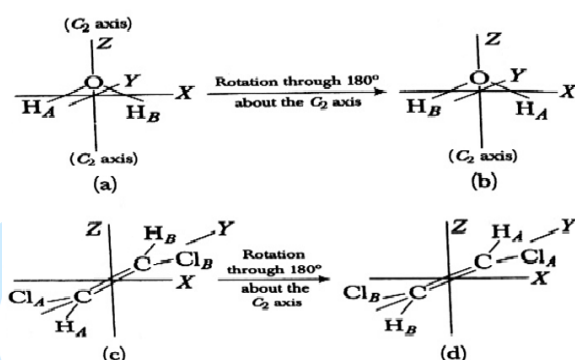
i is the centre of symmetry.

Symmetry Elements	Symmetry Operation
Identity (E)	The operation leaves the molecule unchanged.
Proper axis of rotation (C_n)	Rotation by an angle $\theta = \frac{2\pi}{n}$
Plane of symmetry (σ)	Reflection in the plane.
Improper axis of rotation (S_n)	Rotation about the axis followed by reflection in a plane perpendicular to the axis.
Centre of symmetry (i)	Inversion of all atoms in the molecule through the inversion centre.

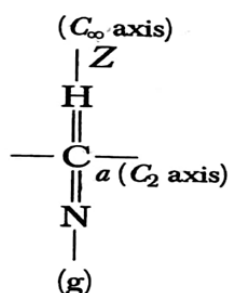
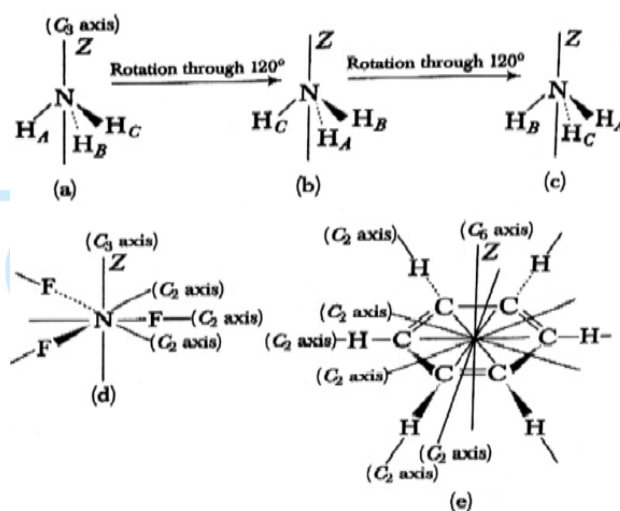
2.5.3. Proper axis of rotation (C_n): A molecule may have one more axes about which a rotation leads to a configuration that is indistinguishable from the original one. Such an axis is a symmetry element and is called a symmetry axis or a rotational axis.

There are in general two types of rotational axis:

- Principal rotational axes, C_n (n = highest). This is also called as the highest fold rotational axis.
- Simple or secondary rotational axes. This may be often C_2 axes and the number of such axes present is always equal to n , the order of principal axis, C_n .



Two molecules having a C_2 rotational axis (a) and (b). The water molecule. (c) and (d) *trans*-dichloroethylene. In both cases rotation through 180° about the Z axis leads to an indistinguishable configuration.



(a), (b) and (c) The non-planar ammonia molecule, having a C_3 axis. (d) The planar BF_3 molecule, which has a C_3 axis and three C_2 axes. (e) Benzene, having a C_6 axis and six C_2 axes. (f) The linear molecule HCN, having a C_∞ axis. (g) The linear molecule CO_2 , which has a C_∞ axis and an infinite number of C_2 axes.

2.5.4. Plane of symmetry (σ): For some molecules there is a plane such that if the molecule is reflected in the plane, it is indistinguishable from the original. Such a plane, which is another symmetry element, is called a plane of symmetry. It is also often called a mirror plane. This can be classified into:

- i) Vertical planes (σ_v)
- ii) Dihedral planes (σ_d): A dihedral plane is one which bisects the angle subtended between two similar consecutive C_2 axes.
- iii) Horizontal plane (σ_h)

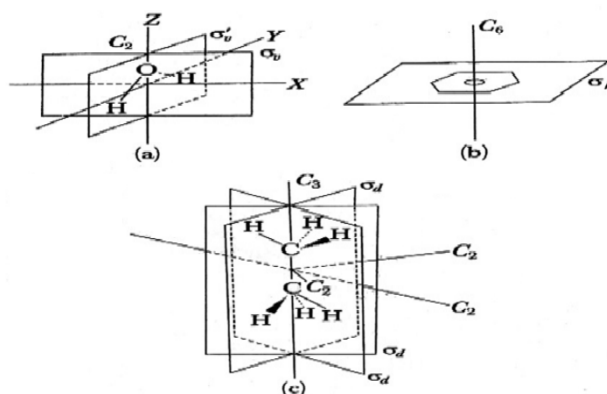


Fig. 19.4 Some molecules having planes of symmetry (a) H₂O : the σ_v plane is the plane of the molecule : the σ_v' plane is at right angles to the σ_v plane. (b) Benzene, C₆H₆, which has a σ_h plane. (c) Staggered ethane, which has three dihedral (σ_d) planes; these bisect the angles between the three C_2 axes.

2.5.5. Improper rotational axis: This is a product or a combination axis.

It is also called rotation reflection axis. This element is generated by rotating the molecule by an angle and then taking the reflection in a plane perpendicular to the rotational axis. If there is C_n axis along Z-axis then,

$$S_n(z) = C_n(z) \cdot \sigma_{xy}$$

σ_{xy} is a plane perpendicular to $C_n(z)$ -axis.

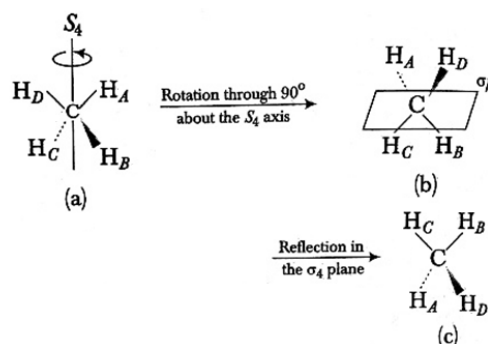


Fig. 19.5 Methane, which has an S_4 rotation reflection axis. (a) The original form. (b) After rotation through 90° (i.e., a C_4 rotation). (c) After reflection in the horizontal plane perpendicular to the S_4 axis.

2.5.6. Centre of symmetry (i): This is an element generated when all the atoms are inverted through the centre of the molecule. This operation requires that all the atoms or groups lying outside the centre of gravity of the molecule must always occur in identical pairs or twins and must be diagonally placed with each other.

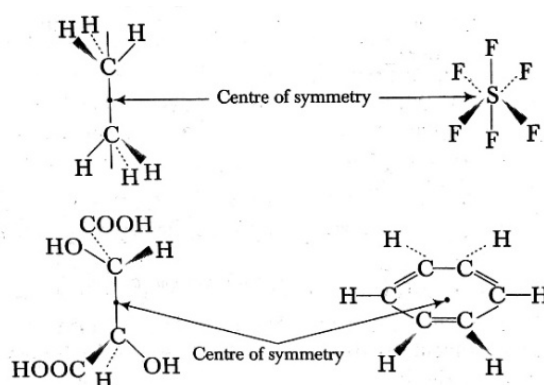
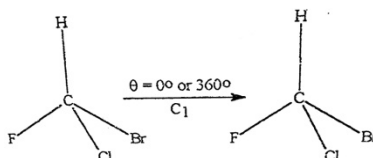


Fig. 19.3 Four molecules having a centre of symmetry. Heavy wedged lines represent bonds projecting toward the reader out of the plane of the paper. Dashed lines represent bonds projecting behind the plane of the paper.

2.5.7. Identity element: This element is obtained by an operation called 'identity operation'. This is a 'doing nothing' operation. After this operation, the molecule remains as such. This situation can be visualized by two ways. Either i) we do not do anything on the molecule or ii) we rotate the molecule by 360° . Consider the following molecule:



2.5.8. Note:

- $C_2^2(z) = C_2(z).C_2(z) = E$
- $C_2(z). \sigma_{xy} = i$
- $S_n(z) = C_n(z). \sigma_{xy}$
- $S_n(y) = C_n(y). \sigma_{xz}$
- $S_n(x) = C_n(x). \sigma_{yz}$

2.5.9. Some important relationship:

- $C_n^n = E$ ($n = \text{odd/even}$)
- $\sigma^n = E$ ($n = \text{even}$)
 $= \sigma(n = \text{odd})$
- $i^n = E$ ($n = \text{even}$)
 $= i(n = \text{odd})$
- $S_n^n = E$ ($n = \text{even}$)
 $= \sigma(n = \text{odd})$

2.5.10. Deducing the implied presence of other symmetry elements:

Sometimes the presence of certain symmetry elements necessitates the occurrence of the other elements in the group and they can be reduced by using the relationship above. Consider C_n and S_n axes for illustrative examples.

- i) **C_n (n = even/ odd):** The presence of a C_n axis in a molecule will always imply the presence of a total of n distinct symmetry elements.

$$C_n^1, C_n^2, C_n^3, \dots, C_n^m, \dots, C_n^{(n-1)}, C_n^n (=E)$$

This corresponds to a total of $(n-1) + E = n$ elements. If the series is to be extended to $C_n^{(n+1)}$, and onwards we have to check if any of the already listed elements is repeated. Thus

$$C_n^{(n+1)} = C_n^n \cdot C_n^1 = E \cdot C_n^1 = C_n^1 \text{ (repeated)}$$

When once the repeated element is encountered, the series should be terminated.

- A) **C_6 axis (n = even):**

$$C_6^1, C_6^2, C_6^3 = C_2^1, C_6^4 = C_3^2, C_6^5, C_6^6 = E$$

The 6 elements are $C_6^1, C_3^1, C_2, C_6^5, C_3^2, E$

- B) **C_9 axis (n = odd):**

$$C_9^1, C_9^2, C_9^3 = C_3^1, C_9^4, C_9^5, C_9^6 = C_3^2, C_9^7, C_9^8, C_9^9 = E$$

The 9 elements are, $C_9^1, C_9^2, C_3^1, C_9^4, C_9^5, C_3^2, C_9^7, C_9^8, E$

Thus in general of a C_n axis implies the presence of n-distinct symmetry elements.



- ii) **S_n^n (n = even):** The presence of this kind of axis necessitates the occurrence of n other distinct elements as in C_n (n = even or odd)

$$S_n^1, S_n^2, S_n^3, \dots, S_n^{(n-1)}, S_n^n = C_n^n \cdot \sigma^n = E \text{ (n elements)}$$

$$S_n^{(n+1)} = S_n^n \cdot S_n^1 = E \cdot S_n^1 = S_n^1 \text{ (repeated)}$$

S_6 axis (n = even):

$$S_6^1 = C_6^1 \cdot \sigma^1 = S_6^1$$

$$S_6^2 = C_6^2 \cdot \sigma^2 = C_3^1 \cdot \sigma^2 = C_3^1 \cdot E = C_3^1$$

$$S_6^3 = C_6^3 \cdot \sigma^3 = C_2^1 \cdot \sigma^2 \cdot \sigma = C_2^1 \cdot E \cdot \sigma = i = S_2^1$$

$$S_6^4 = C_6^4 \cdot \sigma^4 = C_3^2 \cdot \sigma^2 \cdot \sigma^2 = C_3^2 \cdot E \cdot E = C_3^2$$

$$S_6^5 = C_6^5 \cdot \sigma^5 = C_6^5 \cdot \sigma = S_6^5$$

$$S_6^6 = C_6^6 \cdot \sigma^6 = E \cdot E = E$$

$$S_6^7 = C_6^7 \cdot \sigma^7 = C_6^6 \cdot C_6^1 \cdot \sigma = C_6^1 \cdot \sigma = S_6^1 \text{ (repeated)}$$

The 6 elements are $C_3^1, C_3^2, E, S_6^1, S_6^3, i$

- iii) **S_n (n=odd):**

This type of axes will contain 2n distinct symmetry elements.

$$S_n^1, S_n^2, S_n^3, \dots, S_n^n = \sigma, S_n^{(n+1)}, S_n^{(n+2)}, \dots, S_n^{2n} = E$$

$$S_n^{(2n+1)} = S_n^{2n} \cdot S_n^1 = E \cdot S_n^1 = S_n^1 \text{ (repeated)}$$

S_3 axis (n=odd):

$$S_3^1 = C_3^1 \cdot \sigma^1 = S_3^1 \text{ with Technology}$$

$$S_3^2 = C_3^2 \cdot \sigma^2 = S_3^2$$

$$S_3^3 = C_3^3 \cdot \sigma^3 = E \cdot \sigma = \sigma$$

$$S_3^4 = C_3^4 \cdot \sigma^4 = S_3^4$$

$$S_3^5 = C_3^5 \cdot \sigma^5 = C_3^5 \cdot \sigma = S_3^5$$

$$S_3^6 = C_3^6 \cdot \sigma^6 = E \cdot E = E$$

$$S_3^7 = C_3^7 \cdot \sigma^7 = C_3^1 \cdot \sigma = S_3^1 \text{ (repeated)}$$

The 6 elements are $C_3^1, C_3^2, E, S_3^1, S_3^2, \sigma$

2.5.11. Group: A collection of symmetry operations or elements which obey certain mathematical conditions is called a group.



2.5.12. Fundamental condition to be satisfy the well defined group:

For a well defined group four condition to be satisfied:

Closure rule: “The product of any two elements and the square of any element in a group is also an element in the same group”.

Example: For $\text{H}_2\text{O} \rightarrow C_{2v} = E, C_2(z), \sigma_{xz}, \sigma_{yz}$

$$C_2(z) \cdot \sigma_{xz} = \sigma_{yz}; \sigma_{xz} \cdot C_2(z) = \sigma_{yz}$$

$$i^2 = E; \sigma^2 = E$$

Associative rule: “All the symmetry elements must obey the associative law of multiplication”.

$$A(BC) = (AB)C$$

Identity rule: “There should be at least one element in the group which when combined with all other elements must leave them unchanged”.

$$AE = EA = A$$

Inverse rule: “Each element has a reciprocal, which is also an element of the same group”.

$$AA^{-1} = A^{-1}A = E$$

$$i^{-1} = i$$

Examples: H_2O and NH_3 are well defined group.

2.5.13. Abelian group: An Abelian group is a group where the group elements are commute each other i.e., $AB = BA$. All cyclic groups are necessarily Abelian group.

For Abelian group:

h = order of the group = number of element of the group = number of class.

For $\text{H}_2\text{O} \rightarrow E, C_2(z), \sigma_{xz}, \sigma_{yz}$

$h = 4$ = number of class

2.5.14. Non Abelian group: A non-Abelian group is a group where all the symmetry elements do not commute with each other.

For non Abelian group;

h = order of the group; $h >$ number of class.

For $\text{NH}_3 \rightarrow E, 2C_3, 3\sigma_v$

$h >$ number of class = 3

2.5.15. Cyclic groups: A group is said to be cyclic if all its elements can be generated from one symmetry element. Thus A, A^2, A^3, \dots, A^n form the elements of a cyclic group, here, $A^n = E$, The Identity element. In general the roots of the equation $x^n - 1 = 0$ form a cyclic group. All cyclic groups are Abelian.

2.5.16. Order of a group: The number of elements in a group is known as its order (h). For a symmetry group the order is therefore the number of operations that leave the molecule unchanged.

2.5.17. Sub group: This is a group within a group. If one can find a set of elements from a bigger group so that this element constitutes a group under the same competition law as that the bigger group. Then the set of elements are called sub-group of the bigger group.

$\{E, H_1, H_2, \dots, H_n, \dots, G_1, G_2, G_3, \dots, G_n \in G\} \rightarrow$ bigger group

$\{E, H_1, H_2, \dots, H_n\} \rightarrow$ subgroup

$\{G_1, G_2, G_3, \dots, G_n\} \rightarrow$ subgroup

2.5.18. Coset of a sub group: From a bigger group if one can single out a subgroup and some other element say K_1, K_2, K_3, \dots . Which one outside of the subgroup then $K_1\{H\}, K_2\{H\}, K_3\{H\}$ are called left coset of the subgroup $\{H\}$ with respect to the element K_1, K_2, K_3, \dots and $\{H\}K_1, \{H\}K_2, \{H\}K_3, \dots$ are called the right coset of the subgroup with respect to the element K_1, K_2, K_3, \dots

$\{H_1, H_2, \dots, H_n, K_1, K_2, \dots, K_n \in G\}$

$\{H\} = \{H_1, H_2, H_3, \dots, H_n\}$ is a example of a subgroup.

2.5.19. Class: “A set of element which is conjugate to one another is called a class of group”.

$\begin{pmatrix} A \\ B \\ X \end{pmatrix}$ element of a group. There are three elements.

Such that $B = X^{-1}AX$, $A = X^{-1}BX$

B is the similarity transformation of A by X.

A is the similarity transformation of B by X.

So if this relation is achieved then A and B are said to be conjugate to each other. The complete list of element of a group which is interrelated to similarity transformations forms a well defined class.

Properties of class: The order of a class must be integral factors of order of a group. In most of the cases the number of class is less than the order of the group. But there are some group the class of the group = order of the group.

- In all Abelian point groups each element is in a class by itself i.e., the number of symmetry elements for the group is equal to the number of classes.
- In non Abelian group the number of classes is always less than the order of a group.
- No element of the group occurs in more than one class.

Identity element itself forms a class.

$C_{2v} \rightarrow E, C_2(z), \sigma_{xz}, \sigma_{yz}$

Order, $h = 4 = \text{number of class}$

$C_{3v} \rightarrow E, C_3^1, C_3^2, \sigma_v^1, \sigma_v^2, \sigma_v^3$
 $= E, 2C_3, 3\sigma_v$

Order = $h = 6 > \text{number of class} = 3$

2.5.20. Properties of conjugate elements:

- Every element is conjugate to itself (self conjugation)
- If A is conjugate with B then B must be conjugate with A (mutual conjugation).
- If A is conjugate with B and again A is conjugate with C then B and C are conjugate to each other (associative conjugation)
- No two class of a group can share a common element.

2.5.21. Point groups: All the symmetry operations in a molecule can be combined to form a molecular group. This group is called point group since all the symmetry elements of the molecule intersect at a common point which remains fixed under all the symmetry operations.

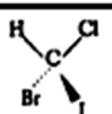
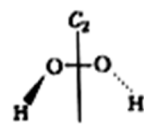
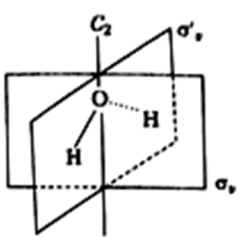
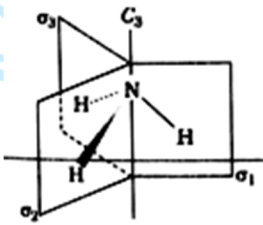


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Some Molecular Point Groups

Point group	Symmetry elements	Examples
C_1	E	CHFCIBr
C_2	E, C_2	H_2O_2
C_3	E, C_3	C_2H_6
C_∞	E, σ_v	NOCl
C_{2v}	$E, C_2, 2\sigma_v$	$\text{H}_2\text{O}, \text{CH}_2=\text{O}, \text{pyridine}$
C_{3v}	$E, C_3, 3\sigma_v$	$\text{NH}_3, \text{CHCl}_3, \text{PH}_3$
$C_{\infty v}$	$E, C_\infty, \infty\sigma_v$	$\text{HCl}, \text{NO}, \text{CO}$
C_{2h}	E, C_2, σ_h, i	<i>trans</i> $\text{CHCl}=\text{CHCl}$
D_{2h}	$E, 3C_2, 3\sigma, i$	$\text{CH}_2=\text{CH}_2, \text{naphthalene}$
D_{3h}	$E, 2C_3, 3C_2 (\perp \text{ to } C_3), 3\sigma_v, \sigma_h, 2S_6$	BF_3 (trigonal planar)
D_{4h}	$E, C_4, 4C_2 (\perp \text{ to } C_4), 2\sigma_v, 2\sigma_d, \sigma_h, C_2, S_4$ (coincident with C_4), i	$[\text{PtCl}_4]^{2-}$ (square planar)
D_{6h}	$E, 2C_6, 6C_2 (\perp \text{ to } C_6),$ $3\sigma_v, 3\sigma_d, \sigma_h, C_2,$ $2C_3, 2S_6, 2S_3, i$	C_6H_6
T_d	$E, 4C_3, 3C_2, 3S_4$ (coincident with C_2), $6\sigma_d$	CH_4
O_h	$E, 3C_4, 4C_3, 3S_4$ and $3C_2$ (both coincident with the C_4 axes), $6C_3, 4S_6, 3\sigma_6, 6\sigma_d$	SF_6

2.5.22. Multiplication tables: To write the group relation in group element a table is formed. This is called group multiplication table. The whole set of product relation of a group represent in a tabular form is known as group multiplication table.

Structure	Symmetry elements	Point group	Multiplication table																																																															
 <p>(a) CHClBrI</p>	E only (no symmetry)	C_1																																																																
 <p>(b) Hydrogen peroxide</p>	E, C_2	C_2	<table border="1"> <tr> <th rowspan="2">Second operation</th><th colspan="2">First operation</th></tr> <tr> <th>E</th><th>C_2</th></tr> <tr> <th>E</th><td>E</td><td>C_2</td></tr> <tr> <th>C_2</th><td>C_2</td><td>E</td></tr> </table>	Second operation	First operation		E	C_2	E	E	C_2	C_2	C_2	E																																																				
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 <p>(c) Water</p>	$E, C_2, \sigma_v, \sigma'_v$	C_{2v}	<table border="1"> <tr> <th rowspan="2">Second operation</th><th colspan="4">First operation</th></tr> <tr> <th>E</th><th>C_2</th><th>σ_v</th><th>σ'_v</th></tr> <tr> <th>E</th><td>E</td><td>C_2</td><td>σ_v</td><td>σ'_v</td></tr> <tr> <th>C_2</th><td>C_2</td><td>E</td><td>σ_v</td><td>σ'_v</td></tr> <tr> <th>σ_v</th><td>σ_v</td><td>σ'_v</td><td>E</td><td>C_2</td></tr> <tr> <th>σ'_v</th><td>σ'_v</td><td>σ_v</td><td>C_2</td><td>E</td></tr> </table>	Second operation	First operation				E	C_2	σ_v	σ'_v	E	E	C_2	σ_v	σ'_v	C_2	C_2	E	σ_v	σ'_v	σ_v	σ_v	σ'_v	E	C_2	σ'_v	σ'_v	σ_v	C_2	E																																		
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 <p>(d) Ammonia</p>	$E, C_3, \bar{C}_3 (= C_3^2), \sigma_1, \sigma_2, \sigma_3$	C_{3v}	<table border="1"> <tr> <th rowspan="2">Second operation</th><th colspan="7">First operation</th></tr> <tr> <th>E</th><th>C_3</th><th>\bar{C}_3</th><th>σ_1</th><th>σ_2</th><th>σ_3</th><th></th></tr> <tr> <th>E</th><td>E</td><td>C_3</td><td>\bar{C}_3</td><td>σ_1</td><td>σ_2</td><td>σ_3</td><td></td></tr> <tr> <th>C_3</th><td>C_3</td><td>\bar{C}_3</td><td>E</td><td>σ_3</td><td>σ_1</td><td>σ_2</td><td></td></tr> <tr> <th>\bar{C}_3</th><td>\bar{C}_3</td><td>E</td><td>C_3</td><td>σ_2</td><td>σ_3</td><td>σ_1</td><td></td></tr> <tr> <th>σ_1</th><td>σ_1</td><td>σ_2</td><td>σ_3</td><td>E</td><td>C_3</td><td>\bar{C}_3</td><td></td></tr> <tr> <th>σ_2</th><td>σ_2</td><td>σ_3</td><td>σ_1</td><td>\bar{C}_3</td><td>E</td><td>C_3</td><td></td></tr> <tr> <th>σ_3</th><td>σ_3</td><td>σ_1</td><td>σ_2</td><td>C_3</td><td>\bar{C}_3</td><td>E</td><td></td></tr> </table>	Second operation	First operation							E	C_3	\bar{C}_3	σ_1	σ_2	σ_3		E	E	C_3	\bar{C}_3	σ_1	σ_2	σ_3		C_3	C_3	\bar{C}_3	E	σ_3	σ_1	σ_2		\bar{C}_3	\bar{C}_3	E	C_3	σ_2	σ_3	σ_1		σ_1	σ_1	σ_2	σ_3	E	C_3	\bar{C}_3		σ_2	σ_2	σ_3	σ_1	\bar{C}_3	E	C_3		σ_3	σ_3	σ_1	σ_2	C_3	\bar{C}_3	E	
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σ_3	σ_3	σ_1	σ_2	C_3	\bar{C}_3	E																																																												

2.5.23. Rearrangement theorem: Important theorem which forms the group multiplication table is called rearrangement theorem.

Statement: Each row and column in the GMT (group multiplication table) lists each list of the group elements once and only once.

N.B: From this theorem it follows that neither any two rows may be identical nor may any two columns be identical. Thus each row and each column is rearranged list of the group element.

Theorem 1: Binary product of any two elements of a group (or a subgroup) will appear one and only once.

Theorem 2: Sub group $\{H\}$ and any of its coset i.e., $K_1\{H\}$ cannot have any element common.

Theorem 3: The cosets $K_1\{H\}$, $K_2\{H\}$ of a subgroup $\{H\}$ with respect to the elements K_1 , K_2 are either identical or completely different or having no element in common i.e., $K_1\{H\} \neq K_2\{H\}$

Theorem 4: The order of a group is an integral multiple of the order of its subgroup.

2.5.24. Optical activity and point group: If S_n is present in a molecule when the compound is optically active.

Molecules which contain an important axis of symmetry of order 'n' i.e., S_n are always super impossible on its mirror image. Hence in general molecule having S_n axis is optically active. Thus if a molecule belongs to C_n and D_n point group then the molecule will be optically active and it does not contain S_n operation.

If a molecule possesses a centre of inversion (i) it cannot have dipole moment. Since the dipole vector cannot lie on the centre. Similarly molecule with more than one non coincident axis of rotation cannot have dipole moment. Since the dipole moment vector cannot coincide the two distinct axes. Therefore **molecule belongs to C_i , C_{nh} , I_h , O_h , T_d , D_n , D_{nh} , D_{nd} will have zero dipole moment. Molecules belong to C_1 , C_3 , C_n , C_{nv} , C_∞ will have the dipole moment.**

2.5.25. Representation: The essential feature of group theory is that the symmetry operations are replaced by numbers or matrices that multiply in the same way as the operations themselves. These sets of numbers and matrices are known as representations or as symmetry species.

2.5.26. Matrix representation of symmetry elements:

E matrix:

$$\begin{array}{ccc}
 [x_1, y_1, z_1] & \xrightarrow[\text{operation}]{\text{identity}} & [x_2, y_2, z_2] \\
 \text{initial} & & \text{final} \\
 \text{(Before operation)} & & \text{(After operation)}
 \end{array}$$

Consider the transformation of general point defined by x, y, z coordinates.

$$x_2 = x_1 = 1.x_1 + 0.y_1 + 0.z_1$$

$$y_2 = y_1 = 0.x_1 + 1.y_1 + 0.z_1$$

$$z_2 = z_1 = 0.x_1 + 0.y_1 + 1.z_1$$

A matrix will be written by combining all the three equations. Thus,

$$\begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix}$$

The matrix of coefficient is a unit matrix in this case. Therefore, E matrix has the form:

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

σ -matrix:

$$\begin{array}{ccc}
 [x_1, y_1, z_1] & \xrightarrow[\text{say } \sigma_{xy} \text{ plane}]{\text{reflection}} & [x_2, y_2, z_2] \\
 \text{initial} & & \text{final}
 \end{array}$$

$$x_2 = x_1 = 1.x_1 + 0.y_1 + 0.z_1$$

$$y_2 = y_1 = 0.x_1 + 1.y_1 + 0.z_1$$

$$z_2 = -z_1 = 0.x_1 + 0.y_1 - 1.z_1$$

The matrix equation is

$$\begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix}$$

Therefore the σ_{xy} matrix is

$$\sigma_{xy} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Similarly, the matrix for σ_{yz} and σ_{zx} is

$$\sigma_{yz} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \text{ and } \sigma_{zx} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

i matrix:

$$[x_1, y_1, z_1] \xrightarrow{\text{i, inversion}} [x_2, y_2, z_2]$$

The changes can be represented as,

$$x_2 = -x_1 = -1.x_1 + 0.y_1 + 0.z_1$$

$$y_2 = -y_1 = 0.x_1 - 1.y_1 + 0.z_1$$

$$z_2 = -z_1 = 0.x_1 + 0.y_1 - 1.z_1$$

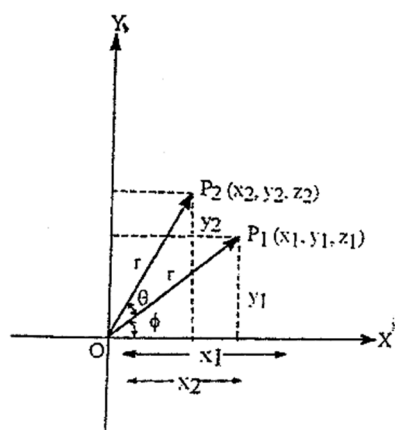
The matrix is

$$\begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix}$$

The *i* matrix is of the form,

$$i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

C_n matrix:



$$P_1[x_1, y_1, z_1] \xrightarrow[\text{clockwise}]{\text{rotation, } \theta} P_2[x_2, y_2, z_2]$$

The change can be represented as

$$x_2 = r \cos(\theta + \phi) = r \cos\theta \times \cos\phi - r \sin\theta \times \sin\phi = x_1 \cos\theta - y_1 \sin\theta$$

$$y_2 = r \sin(\theta + \phi) = r \sin\theta \times \cos\phi + r \cos\theta \times \sin\phi = x_1 \sin\theta + y_1 \cos\theta$$

$$z_2 = x_1 \cos\theta - y_1 \sin\theta + 0.z_1$$

$$y_2 = x_1 \sin \theta + y_1 \cos \theta + 0.z_1$$

$$z_2 = 0.x_1 + 0.y_1 + 1.z_1$$

The matrix is

$$\begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix}$$

Combining these equations to give a matrix equation, we get

The $C_n(z)$ matrix is that of coefficients:

$$C_n(z) = \begin{bmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

If the rotation made like clockwise then,

$$C_n(z) = \begin{bmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Similarly, it is possible to work out the matrices for $C_n(x)$ and $C_n(y)$:

$$C_n(x) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & \sin \theta \\ 0 & -\sin \theta & \cos \theta \end{bmatrix}$$

$$C_n(y) = \begin{bmatrix} \cos \theta & 0 & \sin \theta \\ 0 & 1 & 0 \\ -\sin \theta & 0 & \cos \theta \end{bmatrix}$$

S_n matrix: If the rotational axis, C_n is taken as Z axis then by definition-

$$S_n(z) = C_n(z) \times \sigma_{xy}$$

$$\begin{aligned} S_n(z) &= C_n(z) \times \sigma_{xy} = \begin{bmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \\ &= \begin{bmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & -1 \end{bmatrix} \end{aligned}$$

Similarly,

$$\begin{aligned}
 S_n(x) &= C_n(x) \times \sigma_{yz} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & \sin \theta \\ 0 & -\sin \theta & \cos \theta \end{bmatrix} \times \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \\
 &= \begin{bmatrix} -1 & 0 & 0 \\ 0 & \cos \theta & \sin \theta \\ 0 & -\sin \theta & \cos \theta \end{bmatrix} \\
 S_n(y) &= C_n(y) \times \sigma_{zx} = \begin{bmatrix} \cos \theta & 0 & \sin \theta \\ 0 & 1 & 0 \\ -\sin \theta & 0 & \cos \theta \end{bmatrix} \times \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \\
 &= \begin{bmatrix} \cos \theta & 0 & \sin \theta \\ 0 & -1 & 0 \\ -\sin \theta & 0 & \cos \theta \end{bmatrix}
 \end{aligned}$$

2.5.27. Definition of character/ Trace/ Spur: It is a number represented by the Greek symbol χ . It can be computed as a sum of the diagonal element of a square matrix.

χ_R = The number of orbitals or vector of a representation remains and changed their position and direction.

= Number of orbitals or vector remains unchanged, reverse their direction during operation.

= Number of atoms remains unchanged during operation into character corresponding to 3×3 matrix.

R = Operation

Character of the symmetry operations:

Symmetry operation (R)	Character of R, $\chi(R)$
E	$\chi(E) = 3$
C_n	$\chi(C_n) = 2 \cos \theta + 1$
σ	$\chi(\sigma) = 1$
S_n	$\chi(S_n) = 2 \cos \theta - 1$
i	$\chi(i) = -3$

2.5.28. Reducible and Irreducible representation: Symmetry operations i.e., rotations, reflections, inversions can be expressed in terms of orthogonal and other forms of matrices. The corresponding matrices obey the group multiplication table. Therefore, it follows that any symmetry group can be represented in terms of matrices. It is always possible to find it “similarity transformation matrix”, which would transform all the matrices of a group representation into “diagonal matrices” with identical block or sub matrices along the diagonal of all the matrices.

Let A, B, CE be the matrix representation of a group and P be the similarity transformation matrix. So we can write,

$$P^{-1}EP = E'$$

$$P^{-1}AP = A'$$

$$P^{-1}BP = B'$$

$$P^{-1}CP = C'$$

.....

.....

Just as A, B, C,....., E represent the symmetry group, the new set of diagonalized matrices, A', B', C',.....,E' also represent the full group.

These new diagonalised matrices are of the type;

$$[E'] = \begin{bmatrix} E'_1 & & & \\ & E'_2 & & \\ & & E'_3 & \\ & & & \ddots \end{bmatrix}; [A'] = \begin{bmatrix} A'_1 & & & \\ & A'_2 & & \\ & & A'_3 & \\ & & & \ddots \end{bmatrix}$$

The matrices A' , B' , C' ,....., E' are all identical block factor along the diagonal and if

$[A'] [B'] = [C']$ then,

$[A_1'] [B_1'] = [C_1']$ similarly,

$[A_2'] [B_2'] = [C_2']$

.....

.....

$$[B'] = \begin{bmatrix} B_1' & & \\ & B_2' & \\ & & B_3' \\ & & & \ddots \end{bmatrix}; [C'] = \begin{bmatrix} C_1' & & \\ & C_2' & \\ & & C_3' \\ & & & \ddots \end{bmatrix}$$

The sub matrices $[A_1']$, $[B_1']$, $[C_1']$,..... $[E_1']$ will have identical dimensions and so will be $[A_2']$, $[B_2']$, $[C_2']$,..... $[E_2']$ a full representation of the group can now be written as follows:

$E_1', A_1', B_1', C_1', \dots$

$E_2', A_2', B_2', C_2', \dots$

$E_3', A_3', B_3', C_3', \dots$

Each of the above rows of sub matrices is a representation by itself. If it is not further possible to reduce any of these rows of matrices by any similarity transformation matrix, then each of the row is said to be an irreducible representation (IR) can be one, two, three, four or five dimensional and this dimensionality correspond to the dimensionality of the sub-matrices it comprises of.

E , A , B , C or it's diagonalized matrices E' , A' , B' , C' ,..... are called Reducible Representation (RR). There is no limit to the dimensionality of these reducible representations (RRs).

Reducible Representation (RR)	Irreducible Representation (IR)
If the dimension of Representation can be reduced either using similarity transformation method or by block factoring method. Then they are referred as RR.	IR are those whose dimension can be reduced by any of the mathematical method like block factoring and similarity transformation method.
They can be expressed as a combination of various IR that are possible for a group.	They cannot be expressed as combination of any other representation.
RR derived for the product or for the combination of fundamental bases.	IR can we derived from fundamental bases.

2.5.29. Properties of IRs:

- Number of IRs: The number of non equivalent IR equal to the number of classes of a group. Let the IR be $\Gamma_1, \Gamma_2, \Gamma_3, \dots$
- Dimensionality of IRs: The sum of the squares of the dimensions of the IRs in a group to the order of the group.

Let dimensions be l_1, l_2, l_3, \dots

Such that, $l_1^2 + l_2^2 + l_3^2 + \dots = h = \text{order of the group.}$

$$\sum l_i^2 = 0$$

Since, the character under E class is also equals to the dimensions of the respective IR then we can you write-

$$\sum \chi_i^2(E) = h$$

$\chi_i(E)$ is the character of E class in any IR.

- Characters of IRs: The sum of the squares of the characters under any IR is equal to the order of the group.

$$\sum \chi_i^2(R) = h$$

$$\sum g(R) \chi_i^2(R) = h$$

Where, $g(R)$ is the coefficient of the class of the respective group.

- Orthogonality rule: The sum of the products of characters under any two IRs is equals to zero i.e.,

$$\sum g(R) \Gamma_i(R) \Gamma_j(R) = 0$$

Note:

$$\Gamma_i \Gamma_j = \sum g(R) \Gamma_i(R) \Gamma_j(R) = \delta_{ij}$$

Where, δ_{ij} called Kronecker delta.

$$\delta_{ij} = h \text{ (when } i = j)$$

$$= 0 \text{ (when } i \neq j)$$

2.5.30. Construction of Character Table of C_{2v} point group:

$$C_{2v} \rightarrow \text{number of IRs} = h = 4$$

Let they are $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4$

Let the dimensions are l_1, l_2, l_3, l_4 (where $\Gamma_1 = l_1, \Gamma_2 = l_2, \Gamma_3 = l_3, \Gamma_4 = l_4$)

Such that, $l_1^2 + l_2^2 + l_3^2 + l_4^2 = h = 4$

$$\Rightarrow 1^2 + 1^2 + 1^2 + 1^2 = 4$$

$$\Rightarrow l_1 = l_2 = l_3 = l_4 = 1$$

$$\Rightarrow 1.1^2 + 1.1^2 + 1.1^2 + 1.1^2 = 4$$

Comparing $\Gamma_1 \Gamma_2$,

$$1 \times 1 \times 1 + 1 \times 1 \times () + 1 \times 1 \times () + 1 \times 1 \times () = 0$$

$$\Rightarrow 1 \times 1 \times 1 + 1 \times 1 \times (1) + 1 \times 1 \times (-1) + 1 \times 1 \times (-1) = 0$$

Comparing $\Gamma_1 \Gamma_3$,

$$1 \times 1 \times 1 + 1 \times 1 \times () + 1 \times 1 \times () + 1 \times 1 \times () = 0$$

$$1 \times 1 \times 1 + 1 \times 1 \times (-1) + 1 \times 1 \times (1) + 1 \times 1 \times (-1) = 0$$

Comparing $\Gamma_1\Gamma_4$,

$$1 \times 1 \times 1 + 1 \times 1 \times () + 1 \times 1 \times () + 1 \times 1 \times () = 0$$

$$1 \times 1 \times 1 + 1 \times 1 \times (-1) + 1 \times 1 \times (-1) + 1 \times 1 \times (1) = 0$$

C_{2v}	E	$C_2(z)$	σ_{xz}	σ_{yz}
Γ_1	1	1	1	1
Γ_2	1	1	-1	-1
Γ_3	1	-1	1	-1
Γ_4	1	-1	-1	1

2.5.31. Construction of the character table of C_{3v} point group:

$$C_{3v} \rightarrow E, 2C_3, 3\sigma_v$$

Number of class = 3

Number of IRs = 3

Let they are $\Gamma_1, \Gamma_2, \Gamma_3$

The dimensions are l_1, l_2, l_3

$$\text{Such that, } l_1^2 + l_2^2 + l_3^2 = h = 6$$

$$\Rightarrow 1^2 + 1^2 + 2^2 = 6$$

$$\Rightarrow l_1 = l_2 = 1 \text{ and } l_3 = 2$$

Comparing $\Gamma_1\Gamma_2$,

$$1 \times 1 \times 1 + 2 \times 1 \times () + 3 \times 1 \times () = 0$$

$$1 \times 1 \times 1 + 2 \times 1 \times (1) + 3 \times 1 \times (-1) = 0$$

Comparing $\Gamma_1\Gamma_3$,

$$1 \times 1 \times 1 + 2 \times 1 \times (x) + 3 \times 1 \times (y) = 0$$

$$\Rightarrow 2 + 2x + 2y = 0$$

$$\Rightarrow 2x + 2y = -2$$

$$\Rightarrow x + y = -1 \dots \dots \dots (1)$$

Comparing $\Gamma_2\Gamma_3$,

$$1 \times 1 \times 2 + 2 \times 1 \times (x) + 3 \times (-1) \times (y) = 0$$

$$\Rightarrow 2 + 2x - 3y = 0$$

$$\Rightarrow 2x - 3y = -2 \dots \dots \dots (2)$$

Solving (1) and (2) we get

$$x = -1, y = 0$$

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0

2.5.32. Mulliken's symbol of IRs:

General: All one dimensional IRs are given in the label A and B where as two, three, four and five dimensional IRs are given E, T, G and H labels respectively.

The rules for one dimension representation: When the Representation is symmetric, it means the character under that class operation is +1, where as unsymmetric means, the character is -1 i.e.,

$$\begin{aligned}\chi_R = +1 &\rightarrow \text{symmetric} \\ &= -1 \rightarrow \text{unsymmetric}\end{aligned}$$

All those IRs which are symmetric with respect to the principal axis C_n are designated by A and those which are unsymmetric by B.

$$\begin{aligned}\chi_{C_n} = +1 &\rightarrow A \\ &= -1 \rightarrow B\end{aligned}$$

Superscript rule: Two types of superscript are involved for one dimensional representation. The representations which are symmetric with respect to secondary axis C_2 are given the subscript 1 and for those which are unsymmetric are given the subscript 2 i.e.,

$$\begin{aligned}\chi_{C_2} = +1 &\rightarrow 1 \\ &= -1 \rightarrow 2\end{aligned}$$

In such case secondary axis is lacking a subscript rule must be changed against the presence of simple plane of symmetry (σ_v). Thus,

$$\begin{aligned}\chi_{\sigma_v} = +1 &\rightarrow 1 \\ &= -1 \rightarrow 2\end{aligned}$$

Subscript higher than 2 do not occur often.

$\chi_i = +1 \rightarrow$ subscript 'g'

$= -1 \rightarrow$ subscript 'u'

$\chi_{\sigma_h} = +1 \rightarrow$ symmetric \rightarrow '

$= -1 \rightarrow$ unsymmetric \rightarrow ''

C_{2v}	E	$C_2(z)$	σ_{xz}	σ_{yz}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

2.5.33. Standard reduction formula:

$$a_i = \frac{1}{h} \left[\sum_R \chi(R) \chi_i(R) \right]$$

Here,

a_i = the number of times (frequency) K^{th} IR appear in a particular RR.

$\chi(R)$ = Character of symmetry operation R of RR and

$\chi_i(R)$ = The character of symmetry operation R of the IR.

h = order of the point group.

R = Operation

2.5.34.

C_{2v}	E	$C_2(z)$	σ_{xz}	σ_{yz}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1
$\Gamma_{RR}(1)$	21	-3	5	5
$\Gamma_{RR}(2)$	15	-1	3	3

Using standard reduction formula

$$a_{A_1} = \frac{1}{4} [(1 \times 1 \times 21) + \{1 \times 1 \times (-3)\} + (1 \times 1 \times 5) + (1 \times 1 \times 5)] = 7$$

$$a_{A_2} = \frac{1}{4} [21 - 3 - 5 - 5] = 2$$

$$a_{B_1} = 6$$

$$a_{B_2} = 6$$

$$\Gamma_{RR}(1) = 7A_1 + 2A_2 + 6B_1 + 6B_2$$

Similarly,

$$\Gamma_{RR}(2) = 5A_1 + 2A_2 + 4B_1 + 4B_2$$

2.5.35. Direct product:

$$\chi(AB) = \chi(A) \times \chi(B)$$

The direct product of any two representations especially IRs gives a representation of the same group. For each class of operation the product of the characters of two IR give the character of the product representation. This product representation is called the direct product, which is reducible into some combination of IR. There are two important statements concerning the characters of the direct product representation.

- i) If Γ_i is any IR in the group then,

$$\Gamma_i \times A_1 = \Gamma_i$$

Where Γ_i is the i^{th} IR and A_1 is totally symmetric IR.

- ii) The direct product of any one dimensional IR by itself gives a totally symmetric representation i.e.,

$$\Gamma_i \times \Gamma_i = A_1$$

If the IRs are multidimensional, the direct product obtained is a RR and contains necessarily a totally symmetric representation in its product, if both the IRs are identical i.e.,

$$\Gamma_i \times \Gamma_i = A_1 + \dots + \dots + \dots (\text{for multidimensional})$$

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	
A_2	1	1	-1	
E	2	-1	0	
$A_1.A_2$	1	1	-1	A_2
$A_1.E$	2	-1	0	E
$A_2.A_2$	1	1	1	A_1
$A_2.E$	2	-1	0	E
$E.E$	4	1	0	$A_1 + A_2 + E$
$\Gamma(RR)$	4	1	0	

$$\Gamma(RR) = A_1 + A_2 + E$$

2.5.36. Dimensions of IR:

$$A \times A = B \times B = A$$

$$A \times B = B \times A = B$$

$$A \times E = E \times A = E$$

$$A \times T = T \times A = T$$

$$B \times T = T \times B = T$$

$$E \times T = T \times E = T_1 + T_2$$

2.5.37. Subscript and superscript:

$$g \times g = g$$

$$g \times u = u$$

$$u \times g = u$$

$$u \times u = g$$

$$1 \times 1 = 1$$

$$1 \times 2 = 2$$

$$2 \times 2 = 1$$

$$2 \times 1 = 2$$

$$' \times ' = '$$

$$' \times " = "$$

$$" \times " = '$$

$$" \times ' = "$$

2.5.38. Great Orthogonal Theorem (GOT) :

$$\sum_R [\Gamma_i(R)_{mn}] [\Gamma_j(R)_{m'n'}]^* = \frac{h}{\sqrt{l_i l_j}} \delta_{ij} \delta_{mm'} \delta_{nn'}$$

h = order of the group

l_i and l_j are dimensions of i^{th} and j^{th} IRs

δ_{ij} = Kronecker delta

mm' = rows of the matrix

nn' = column of the matrix

R = operation

Γ_i = i^{th} IRs

Γ_j = j^{th} IRs

There are three corollaries:

- $\sum_R \Gamma_i(R)_{mn} \Gamma_j(R)_{mn} = 0$ when, $i \neq j$, $m = m'$, $n = n'$
- $\sum_R \Gamma_i(R)_{mn} \Gamma_i(R)_{m'n'} = 0$ when, $i = j$, but $m \neq m'$, $n \neq n'$
- $\sum_R \Gamma_i(R)_{mn} \Gamma_i(R)_{mn} = \frac{h}{l_i}$ when, $i = j$, $m = m'$, $n = n'$

2.5.39. Spectral transition:

The Intensity of transition I is defined by,

$$I \propto \int \psi_i \mu \psi_j d\tau$$

Where, I = intensity of transition

μ = transition dipole moment = $\mu_x + \mu_y + \mu_z$

Therefore we can write,

$$I_x \propto \int \psi_i x \psi_j dx$$

$$I_y \propto \int \psi_i y \psi_j dy$$

$$I_z \propto \int \psi_i z \psi_j dz$$

$$I = I_x + I_y + I_z$$

2.5.40. Condition for transition:

If $I \propto \int \psi_i \mu \psi_j d\tau \neq 0 \rightarrow$ allowed

If $I \propto \int \psi_i \mu \psi_j d\tau = 0 \rightarrow$ forbidden

Again,

$$I_x \propto \int \psi_i \mu \psi_j d\tau = \Gamma_i \times \Gamma_x \times \Gamma_j$$

2.5.41. Transition for C_{3v} point group:

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	Z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	(x,y) (R_x, R_y)	$(x^2 - y^2, xy)$ (xz, yz)
$A_1 \times E \times A_2$	2	-1	0		$E = 0$
$A_1 \times A_1 \times A_2$	1	1	-1		$A_2 = 0$
$A_1 \times E \times A_1$	2	-1	0		$E = 0$
$A_1 \times E \times E$	4	1	0		$A_1 + A_2 + E$
$A_1 \times A_1 \times A_1$	1	1	1		A_1

As the direct product of $A_1 \times A_1 \times A_1$ is totally symmetrical, so the transition $A_1 \rightarrow A_1$ along Z axis is allowed. But from the direct product of $A_1 \times E \times E$ we have $A_1 \times E \times A_2$. So the transition $A_1 \rightarrow E$ along xy plane is allowed. But the other direct products have the value zero. So the transition $A_1 \rightarrow A_2$ along xy plane, $A_1 \rightarrow A_2$ along z-axis, $A_1 \rightarrow A_2$ along xy plane are not allowed.

Note:

- $[\text{Mo}_2\text{Cl}_8]^{4-}$ have D_{4h} point group.
 $\delta \rightarrow \delta^*$ transition is allowed with Z polarized light.
 $\delta \rightarrow \delta^*$ is Forbidden for (x,y) polarised light.
- Formaldehyde have C_{2v} point group. The molecule contains σ , π , n, π and σ^* MO's.
 $n \rightarrow \pi^*$ transition is forbidden with x, y and z polarised light. So $n \rightarrow \pi^*$ transition in HCHO is totally forbidden.
 $\pi \rightarrow \pi^*$ transition in HCHO is allowed transition is radiation is z-polarized and is Forbidden is radiation is x,y polarised.

2.5.42. The integral of the product of two or more function over symmetric interval is non zero, if the direct product representation is totally symmetric.

If the direct product representation is irreducible representation over the integral of the product function has a non zero value when the product representation contains the totally symmetric representation. This rule can be applied to find out whether the vibrational modes are IR active or not.

2.5.43. IR – selection rule: A fundamental mode will be IR active if the normal mode which is excited belongs to the same representation as any one or several of the Cartesian coordinates.

Or,

Any electric dipole transition will be allowed with x, y or z polarization if the direct product of the representation of the two States concern is or contains the irreducible representations to which x, y, z respectively belong.

2.5.44. Raman selection rule: A fundamental transition will be Raman active in the normal mode is involved belongs to the same representation as one or more of the components of the polarizability tensor of the molecule.

Or,

A fundamental transition will be Raman active in normal mode belongs to the same representation of one or more of the binary product of the Cartesian coordinates of the linear combination.

2.5.45. Normal modes of vibrations:

Number of normal modes = $(3n - 6)$ for Non linear molecule.

= $(3n - 5)$ for linear molecule.

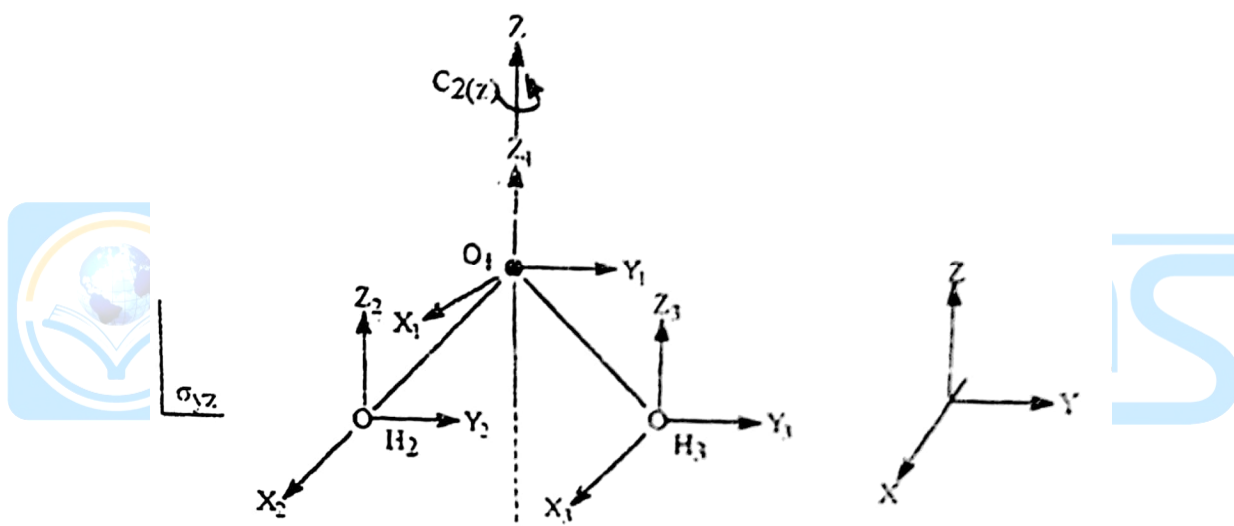
Total number of vibration = $3n$, where n = number of atom present.

$$\Gamma_{\text{total}} = \Gamma_{\text{translational}} + \Gamma_{\text{rotational}} + \Gamma_{\text{vibrational}}$$

$$\Gamma_{\text{vibrational}} = \Gamma_{\text{total}} - (\Gamma_{\text{translational}} + \Gamma_{\text{rotational}})$$

2.5.46. H₂O molecule: It has C_{2v} point group.

C_{2v}	E	$C_2(z)$	σ_{xz}	σ_{yz}		
A_1	1	1	1	1	Z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	X, R_y	xz
B_2	1	-1	-1	1	Y, R_x	yz

Cartesian co-ordinate method:

	E	$C_2(z)$	σ_{xz}	σ_{yz}
Number of unshifted atom	3	1	1	3
Character of (3×3) matrix	3	-1	1	1
$\Gamma_{\text{total}} = \Gamma_{\text{reducible}}$	9	-1	1	3

Using standard reduction method

$$a_{A_1} = 3$$

$$a_{A_2} = 1$$

$$a_{B_1} = 2$$

$$a_{B_2} = 3$$

$$\text{Therefore, } \Gamma_{\text{reducible}} = \Gamma_{\text{total}} = 3A_1 + A_2 + 2B_1 + 3B_2$$

$$\Gamma_{\text{translational}} = B_1 + B_2 + A_1$$

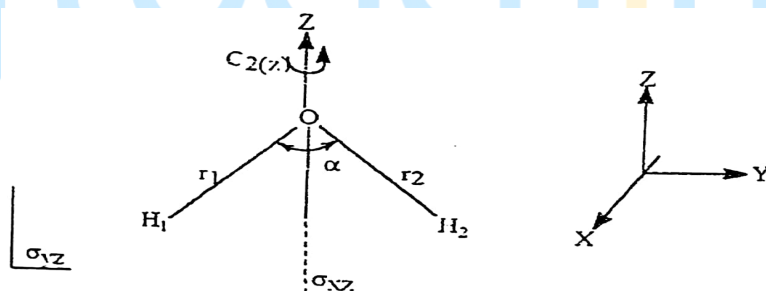
$$\Gamma_{\text{rotational}} = B_2 + B_1 + A_2$$

$$\Gamma_{\text{translational}} + \Gamma_{\text{rotational}} = A_1 + A_2 + 2B_1 + 2B_2$$

$$\Gamma_{\text{vibrational}} = 3A_1 + A_2 + 2B_1 + 3B_2 - A_1 - A_2 - 2B_1 - 2B_2 = 2A_1 + B_2$$

In order to find out the symmetry of translational motion, we have to follow that character table for this point group symmetry of translational motion, is same as x, y, z coordinates of a point group. For translational motion $A_1 \rightarrow Z$, $B_1 \rightarrow x$, $B_2 \rightarrow y$. For rotational motion $R_x \rightarrow B_2$, $R_y \rightarrow B_1$, $R_z \rightarrow A_2$. This method for determination of symmetric property of vibrational degree of freedom known as Cartesian co-ordinate method.

ICS (internal co-ordinate system):



Bond vectors and bond angles used as internal coordinates. There are two Bond vectors. Number of bond angle is one.

$$\text{Total ICS} = 3$$

C_{2v}	E	$C_2(z)$	σ_{xz}	σ_{yz}
$\Gamma_{r_1 r_2}$	2	0	0	0
Γ_{α}	1	1	1	1

Using standard reduction method,

$$\Gamma_{\text{vibrational}} = 2A_1 + B_2$$

The two results are same i.e., in both cases the total number of vibrational modes will be $2A_1 + B_2$.

In the IR active transition, the vibration in molecules in the ground state is symmetric in nature. Show a function corresponding to this ground level behaves as a base for totally symmetric representation. Now, IR active transition is electric dipole transition and for this reason the symmetry of μ is the same symmetry, as the x, y, z coordinates. Therefore, $I \neq 0$, only when x/y/z behaves as a bases which ψ e also behaves as a bases. So, this is also for attracting transition. For Raman active transition polarizability operator have same symmetry as corresponding to the symmetry of binary and quadrature cartesian coordinates such as x^2 , y^2 , x^2 or xy , yz , xz .

Symmetry of fundamental vibrations	IR	Raman
$2A_1$	Active	Active
B_2	Active	Active

2.5.47. HCHO molecule: C_{2v} point group

Cartesian method:

	E	$C_2(z)$	σ_{xz}	σ_{yz}
Number of unshifted atom	4	2	2	4
Character of (3×3) matrix	3	-1	1	1
$\Gamma_{\text{cartesian}}$	12	-2	2	4

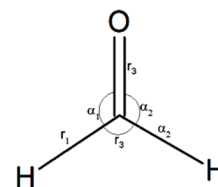
Using standard reduction method,

$$\Gamma_{\text{total}} = 4A_2 + A_2 + 3B_1 + 3B_2$$

$$\Gamma_{\text{translational}} = B_1 + B_2 + A_1$$

$$\Gamma_{\text{rotational}} = B_2 + B_1 + A_2$$

$$\Gamma_{\text{vibrational}} = 3A_1 + B_1 + 2B_2$$



ICS method:

C_{2v}	E	$C_2(z)$	σ_{xz}	σ_{yz}
Γ_{lr_3}	3	1	1	3
$\Gamma_{\alpha_1\alpha_3}$	3	1	1	3

Using standard reduction formula,

$$\Gamma_{\text{int}} = 4A_1 + 2B_2$$

By comparing with $\Gamma_{\text{vibrational}}$ of $\Gamma_{\text{cartesian}}$ and Γ_{internal} , we see that one A_1 mode is extra and hence reductant and B_1 mode is missing. Thus reducing the number of internal coordinating the missing mode can be identified as “out-of-plane” (OOP) which generally occurs in all planar molecules considering

C_{2v}	E	$C_2(z)$	σ_{xz}	σ_{yz}	
Γ_{OOP}	1	-1	1	-1	B_1

Symmetry of fundamental vibrations	IR	Raman
$3A_1$	Active	Active
B_1	Active	Active
$2B_2$	Active	Active

2.5.48. Applications of group theory:

- Construction of hybrid orbital.
- Construction of SALCs (symmetry adapted linear combination of atomic orbitals). SALCs are used in molecular orbital theory of chemical bonding.
- Determination of the irreducible representations to which the vibrational modes of molecules belong.
- Determining which spectral transition in infrared and Raman spectra are allowed or forbidden.
- Determining the selection rules for $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition in carbonyl compounds and other chromophores. It is found that the former transitions are forbidden whereas the latter are allowed.
- Determining optical activity of molecule.
- Determining which molecules are polar or nonpolar.
- Classification of elementary particles into Fermions and Bosons in quantum mechanics.



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Text with Technology

Previous Year Questions**NET JUNE 2014**

Q. The spatial part of the wave function of the atom in its ground state is $1s(1)1s(2)$. The spin part would be—

(a) $\alpha(1)\alpha(2)$

(b) $\beta(1)\beta(2)$

(c) $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$

(d) $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$

Ans. The four normalized two electrons spin eigen functions with correct exchange properties are—

$$\alpha(1)\alpha(2)$$

Symmetric: $\beta(1)\beta(2)$

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

Antisymmetric: $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$

Thus, $\psi^0 = 1s(1)1s(2) \cdot \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$

So, spin part = $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$

Spatial part = $1s(1)1s(2)$ [as $\psi^{total} = \psi^{spin} \times \psi^{spatial}$]

Correct option is (d).

Q. A particle in a one-dimensional box (potential zero between 0 to a and infinite outside) has the ground state energy $E_0 = \frac{0.125h^2}{ma^2}$. The expectation value of the above Hamiltonian with $\psi(x) = x(x - a)$ yields an energy E_1 . Using a linear combination of two even functions $x(x - a)$ and $x^2(x - a)^2$, we obtain variational minimum to the ground state energy as E_2 . Which of the following relations holds for E_0 , E_1 and E_2 ?

(A) $E_0 < E_1 < E_2$

(B) $E_0 < E_2 < E_1$

(C) $E_1 < E_0 < E_2$

(D) $E_2 < E_0 < E_1$

Ans.

$$E_0 = \frac{0.125h^2}{ma^2}$$

$$\psi(x) = x(x - a), E_1$$

linear combination of $x(x - a)$ and $x^2(x - a)^2$, E_2

Variational principle tells that ground state energy is always less than other higher level energies.

$$\text{So, } E_0 < (E_1, E_2)$$

Now, E_2 is obtained from even functions (two), it have high value than E_1

$$\text{Thus, } \boxed{E_0 < E_1 < E_2}$$

Correct option is (b).

Q. The ground state energy of hydrogen atom is -13.598 eV. The expectation values of kinetic energy, $\langle T \rangle$ and potential energy, $\langle V \rangle$, in units of eV, are—

- (a) $\langle T \rangle = 13.598$, $\langle V \rangle = -27.196$ (b) $\langle T \rangle = -27.196$, $\langle V \rangle = 13.598$
(c) $\langle T \rangle = -6.799$, $\langle V \rangle = -6.799$ (d) $\langle T \rangle = 6.799$, $\langle V \rangle = -20.397$

Ans. We know that for H-atom, energy, K.E. and P.E. holds following relation

$$\langle T \rangle = -\frac{1}{2}\langle V \rangle = -\langle E \rangle$$

Given that $\langle E \rangle = -13.598$

$$\therefore \langle T \rangle = -\langle E \rangle$$

$$\therefore \langle T \rangle = 13.598$$

and $\langle V \rangle = 2 \langle E \rangle$

$$= 2 \times (-13.598)$$

$$\langle V \rangle = -27.196$$

Correct option is (a).

Text with Technology

Q. If $\psi = 0.8 \phi_A + 0.4 \phi_B$ is a normalized molecular orbital of a diatomic molecule AB, constructed from ϕ_A and ϕ_B which are also normalized, the overlap between ϕ_A and ϕ_B is—

- (a) 0.11 (b) 0.31 (c) 0.51 (d) 0.71

Ans. $\psi = 0.8 \phi_A + 0.4 \phi_B$ – normalized M.O.

ϕ_A and ϕ_B are also normalized.

An overlap integral is a direct measure of the extent of the overlap of the orbitals centered on two different nuclei. We know that,

$$\begin{aligned}\psi &= a\phi_A + b\phi_B \\ a &= 0.8, b = 0.4\end{aligned}$$

Thus, overlap integral,



$$\begin{aligned}S_{AB} &= \int a\phi_A \cdot b\phi_B dt \\ &= ab = 0.8 \times 0.4 \\ &= 0.32\end{aligned}$$

Correct option is (b).

NET DEC 2014

Q. For a particle of mass m confined in a box of length L , assume $\Delta x = L$. Assume further that Δp (min) = $(p^2)^{1/2}$. Use the uncertainty principle to obtain an estimate of the energy of the particle. The value will be—

- (a) $\frac{h^2}{(8mL^2)}$ (b) $\frac{\hbar^2}{(8mL^2)}$ (c) $\frac{h^2}{(32mL^2)}$ (d) $\frac{h^2}{(2mL^2)}$

Ans. We know, $\Delta x \cdot \Delta p = \frac{\hbar}{2}$ i.e., $\Delta p = \frac{\hbar}{2L}$

$$\text{Energy of the particle} = \frac{(\Delta p)^2}{2m} = \left(\frac{\hbar}{2L}\right)^2 \frac{1}{2m} = \frac{\hbar^2}{(8mL^2)}$$

Correct option is (b).

Q. The angular momentum operator $L_z = -i\hbar \frac{\partial}{\partial \phi}$ has eigenfunctions of the form $\exp[iA\phi]$. The condition that a full rotation leaves such an eigen function unchanged is satisfied for all the values of A —

- (a) $0, \pm \frac{1}{3}, \pm \frac{2}{3}, \pm 1, \pm \frac{4}{3}, \dots$ (b) $0, \pm 1, \pm 2, \pm 3, \dots$
 (c) $0, \pm \frac{1}{2}, \pm 1, \pm \frac{3}{2}, \dots$ (d) $0, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$

Ans.

$$L_z = -i\hbar \frac{\partial}{\partial \phi}$$

The eigen function equation is

$$L_z Y_l^m = -i\hbar \frac{\partial}{\partial \phi} Y_l^m$$

$$Y_l^m = f_{(0)} e^{iA\phi}$$

f is arbitrary function ϕ must be periodic for Y is to be unchanged with period 2π . Thus, value of A should be $A = 0, \pm 1, \pm 2, \dots$

Correct option is (b).

Q. Wavelength (λ in nm) of the Lyman series for an one-electron ion is in the range $24 \leq \lambda \leq 30$. The ionization energy of the ion will be closest to ($1J = \frac{10^{19}}{1.6} \text{ eV}$) —

- (a) 32 eV (b) 42 eV (c) 52 eV (d) 62 eV

Ans. I.E. = $\frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8 \times 10^{19}}{24 \times 10^{-9} \times 1.6} = 52 \text{ eV}$

Ionization energy is the energy required to remove an electron from outermost orbital of gaseous system.

Correct option is (c).

Q. The probability of finding the harmonic oscillator in the energy level $n = 1$ is (neglect zero point energy and assume $h\nu = k_B T$).

- (A) e (B) e^2 (C) $1 - e^{-2}$ (D) $e^{-2}(e - 1)$

Ans. $E_n = \left(n + \frac{1}{2}\right) h\nu$

Probability, $P_{(E)} = \frac{e^{-E/k_B T}}{\sum_i e^{-E/k_B T}}$

$$= \frac{e^{-3/2}}{e^{-1/2} + e^{-3/2}} = \frac{e^{-1}}{1 + e^{-1}}$$

$$= \frac{e^{-1} \cdot e}{e + 1} \times \frac{(e - 1)}{(e - 1)} = \frac{e - 1}{e^2 - 1}$$

Assuming, $e^2 \gg 1$

$$= \frac{e - 1}{e^2}$$

Therefore, $P_{(E)} = e^{-2}(e - 1)$

Correct option is (d).

Q. A particle in a 1-dimensional box of length L is perturbed by a delta function potential, $\delta(x - \frac{L}{2})$, in the middle of the box. The first order energy correction to the ground state will be—

[Hint: $\int_{-\infty}^{+\infty} f(x)\delta(x - a)dx = f(a)$]

- (a) 0 (b) 1 (c) $\frac{L}{2}$ (d) $\frac{2}{L}$

Ans.

First order energy correction is—

$$E_n^{(1)} = \langle \psi_n^{(0)} | \bar{H} | \psi_n^{(0)*} \rangle$$

$$\psi_n^{(0)} = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

Thus, $E_n^{(1)} = \frac{2}{L} \int_{-L}^L \sin^2\left(\frac{n\pi x}{L}\right) \delta(x - \frac{L}{2}) dx$

Now, for ground state, $n=1$

$$E_n^{(1)} = \frac{2}{L} \int_{-L}^L \sin^2\left(\frac{\pi x}{L}\right) \delta(x - \frac{L}{2}) dx$$

$$\because \int_{-\infty}^{+\infty} \delta(x - a) dx = 1$$

Thus, $\boxed{E_n^{(1)} = \frac{2}{L}}$

Correct option is (d).

Q. The operators S_{\pm} are defined by $S_{\pm} = S_x \pm iS_y$, where S_x and S_y are components of the spin angular momentum operator. The commutator $[S_z, S_{\pm}]$ is—

- (A) $\hbar S_+$ (B) $\hbar S_-$ (C) $-\hbar S_+$ (D) $-\hbar S_-$

Ans. $[S_z, S_+] = [S_z, S_x] + i[S_z, S_y]$

$= i\hbar S_y + i(-i\hbar S_x) = \hbar(S_x + iS_y) = \hbar S_{\pm}$. **Correct option is (a).**

Q. The character table of C_{2v} point group is given below. In *cis*-butadiene molecule the vibrational modes belonging to A_2 irreducible representation are IR inactive. The remaining IR active modes are—

C_{2v}	E	C_2	σ_v	σ_v'	
A_1	1	1	1	1	z, x^2, y^2, z
A_2	1	1	-1	-1	R_z, xy
B_1	1	-1	1	-1	x, R_y, xz
B_2	1	-1	-1	1	y, R_x, yz

- (a) $7A_1 + 5B_1 + 8B_2$
 (b) $9A_1 + 4B_1 +$

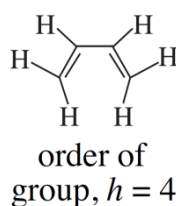
$7B_2$

- (c) $7A_1 + 3B_1 + 7B_2$

- (d) $9A_1 + 3B_1 + 8B_2$

Ans.

1	E	C_2	σ_v	σ_v'
no. of unshifted atoms	10	0	0	10
Character per atom	3	-1	1	1
	30	0	0	10



$A_1 = 10, A_2 = 5, B_1 = 5, B_2 = 10$ $l_{\text{trans}} = B_1 + B_2 + A_1, l_{\text{rot}} = B_2 + B_1 + A_2$. Thus, IR active model = $9A_1 + 3B_1 + 8B_2$

Correct option is (d).

Q. The product $\sigma_{xy}.S_z^4$ (S_z^4 is the four fold improper axis of rotation around the z axis, and σ_{xy} is the reflection in the xy plane) is—

- (a) C_z^4 (b) $C_z^4.i$ (c) C_y^4 (d) C_z^2

Ans. $\sigma_{xy}.S_z^4 = C_z^4$ (Rotational axis)

Correct option is (a).

Q. The configuration $[\text{Ne}] 2p^1 3p^1$ has a 3D term. Its levels are—

- (a) $^3D_{3/2}, ^3D_{1/2}$ (b) $^3D_{5/2}, ^3D_{3/2}, ^3D_{1/2}$
(c) $^3D_3, ^3D_2, ^3D_1$ (d) $^3D_3, ^3D_2, ^3D_1, ^3D_0$

Ans. $[\text{Ne}] 2p^1 3p^1$, Term = 3D , $S = n/2 = 1$, $L = 2(D)$ $J = (L - S)$ to $(L + S) = 1, 2, 3$, Thus, $^3D_3, ^3D_2, ^3D_1$,

Correct option is (c).

Q. For some one-electron system with $l = 0$ and $m = 0$, the functions $N_0 e^{-\sigma}$ and $N_1(2 - \sigma)e^{-\sigma/2}$ refer respectively to the ground (E_0) and first excited (E_1) energy levels. If a variational wave function $N_2(3 - \sigma)e^{-\sigma}$ yields an average energy \bar{E} , it will satisfy—

- (a) $\bar{E} \geq 0$ (b) $0 \leq \bar{E} \leq E_0$ (c) $\bar{E} \geq E_1$ (d) $E_0 \leq \bar{E} \leq E_1$

Ans. Ground state wave function: $N_0 e^{-\sigma}$

First excited wave function: $N_1(2 - \sigma)e^{-\sigma/2}$

Correct option is (c).

Q. The number of microstates that are possible, when two particles are distributed in four states such that the resulting wave functions are antisymmetric with respect to exchange of the particles, is—

- (a) 16 (b) 12 (c) 8 (d) 6

Ans. No. of microstates = $\frac{4!}{2!(4-2)!} = 6$

Correct option is (d).

Q. A Slater determinant corresponding to the ionic part of the ground state valence bond wave function of H₂ molecule is ($1s_a\alpha$, $1s_a\beta$, $1s_b\alpha$, $1s_b\beta$ are atomic spin orbitals of hydrogen atoms a and b of the hydrogen molecule)

- (a) $\begin{vmatrix} 1s_a\alpha(1) & 1s_a\beta(1) \\ 1s_a\alpha(2) & 1s_a\beta(2) \end{vmatrix}$ (b) $\begin{vmatrix} 1s_a\alpha(1) & 1s_b\beta(1) \\ 1s_a\alpha(2) & 1s_b\beta(2) \end{vmatrix}$
- (c) $\begin{vmatrix} 1s_a\alpha(1) & 1s_b\alpha(1) \\ 1s_a\alpha(2) & 1s_b\alpha(2) \end{vmatrix}$ (d) $\begin{vmatrix} 1s_a\alpha(1) & 1s_b\beta(1) \\ 1s_a\alpha(1) & 1s_b\beta(2) \end{vmatrix}$

Ans. $\begin{vmatrix} 1s_a\alpha(1) & 1s_a\beta(1) \\ 1s_a\alpha(2) & 1s_a\beta(2) \end{vmatrix} = 1s_a\alpha(1)1s_a\beta(2) - 1s_a\beta(1)1s_a\alpha(2)$

α and β are spin up and down

According to Pauli's principle, 2 electrons in 'a' atomic orbital with spin up and down.

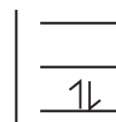
Correct option (a).

Q. According to Huckel theory, the π electron charge on the central carbon atom in propenyl cation $(\text{CH}_2\text{CHCH}_2)^+$ is (in units of electronic charge).

- (a) $\frac{1}{2}$ (b) $\frac{1}{\sqrt{2}}$ (c) 1 (d) 2

Ans. Wave function for central carbon in propenyl cation

$$\psi_2 = \frac{1}{\sqrt{2}}\phi_1 - \frac{1}{\sqrt{2}}\phi_3$$



π electron charge,

$$q_r = \sum \eta_i C_{ir}^2$$

$$q_2 = 2 \times \left(\frac{1}{\sqrt{2}}\right)^2 + 0 + 0 = 1$$

Correct option is (c).

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Q. A particle is in a one-dimensional box with a potential V_0 inside the box and infinite outside. An energy state corresponding to $n = 0$ (n : quantum number) is not allowed because—

- (a) the total energy becomes zero
 (b) the average momentum becomes zero
 (c) the wave function becomes zero everywhere
 (d) the potential $V_0 \neq 0$

Ans. As we know, $\Psi = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$ [$n \neq 0$]

then $\Psi = 0$ (*i.e.*, wavefunction become zero) and it is not possible. In I-D box for ground state $n = 1$. $n = 0$ exists only for Simple Harmonic Oscillator.

Correct option is (c).

Q. An eigenstate of energy satisfies $H\Psi_n = E_n \Psi_n$. In the presence of an extra constant potential V_0 —

- (a) both E_n and Ψ_n will change
- (b) both E_n and the average kinetic energy will change
- (c) only E_n will change, but not Ψ_n
- (d) only Ψ_n will change, but not E_n

Ans. When we add potential in the Hamiltonian the energy eigen value will shift but the eigen function will not change.

Correct option is (c).

Q. The product $C_2^x \cdot \sigma_{xy}$ (C_2^x is the two-fold rotation axis around the x-axis and σ_{xy} is the xy mirror plane) is—

- (a) σ_{xz}
- (b) σ_{yz}
- (c) C_2^y
- (d) C_2^z

Ans. $\begin{vmatrix} x \\ y \\ z \end{vmatrix} \xrightarrow{\sigma_{xy}} \begin{vmatrix} x \\ -y \\ z \end{vmatrix}; C_2^x \cdot \sigma_{xy} = \begin{vmatrix} x \\ y \\ z \end{vmatrix} \xrightarrow{C_2^x} \begin{vmatrix} x \\ -y \\ -z \end{vmatrix} \xrightarrow{\sigma_{xy}} \begin{vmatrix} x \\ -y \\ z \end{vmatrix};$ **Correct option is (a).**

Q. The simplest ground-state VB wave function of a diatomic molecule like HCl is written as $\Psi = \Psi_H(1s, 1) \Psi_{Cl}(3p_z, 2) + B$ where B stands for—

- (a) $\Psi_H(3p_z, 2) \Psi_{Cl}(1s, 1)$
- (b) $\Psi_H(1s, 2) \Psi_{Cl}(3p_z, 1)$
- (c) $\Psi_{Cl}(1s, 2) \Psi_{Cl}(3p_z, 1)$
- (d) $\Psi_{Cl}(1s, 2) \Psi_H(3p_z, 1)$

Ans. HCl is a covalent molecule. Thus, both the electrons cannot reside only in Cl atom. Thus, option (C) is wrong. In option (A) and (D) for H-atom, 3p orbital is not present ($H \rightarrow 1s$; $Cl = 3s^2 3p^5$).

Correct option is (b).

Q. A molecular orbital of a diatomic molecule changes sign when it is rotated by 180° around the molecular axis. This orbital is—

- (a) σ (b) π (c) δ (d) ϕ

Ans. In diatomic molecule only σ and π -bond is possible

σ (gerade) spherical $\xrightarrow{180^\circ}$ No change occur.

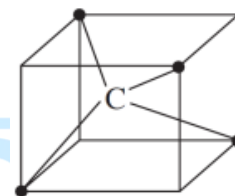
π (ungerade) $\xrightarrow{180^\circ}$ change in sign occur.

Correct option is (b).

Q. IR active normal modes of methane belong to the irreducible representation—



T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
A_1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1	
E	2	-1	2	0	0	$2z^2 - x^2 - y^2, x^2 - y^2$
T_1	3	0	-1	1	-1	R_x, R_y, R_z
T_2	3	0	-1	-1	1	x, y, z, xy, yz, zx



(A) $E + A_1$

(B) $E + A_2$

(C) T_1

(D) T_2

Ans.

$h = 24$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
No. of unshifted atom	5	2	1	1	3
Contribution per atom	3	0	-1	-1	1
Reducible representation	15	0	-1	-1	3

$$nA_1 = 1, nA_2 = 0, nE = 1, nT_1 = 1, nT_2 = 3.$$

So reducible representation: $A_1 + E + T_1 + 3T_2$

Translational: T_2

Rotational: T_1

Vibrational: $A_1 + E + 2T_2$

Since IR activity is count by x, y, z coordinate so T_2 mode is IR active by using character table.

Correct option is (d).

Q. Which of the following statements is INCORRECT?

- (a) A Slater determinant is an antisymmetrized wavefunction
- (b) Electronic wavefunction should be represented by Slater determinants
- (c) A Slater determinant always corresponds to a particular spin state
- (d) A Slater determinant obeys the Pauli Exclusion Principle

Ans. A Slater determinant always corresponds to a particular spin state. Slater determinate changes by changing sign upon exchange of 2 electrons.

Correct option is (c).

Q. Compare the difference of energies of the first excited and ground states of a particle confined in (i) a 1-d box (Δ_1), (ii) a 2-d square box (Δ_2) and (iii) a 3-d cubic box (Δ_3). Assume the length of each of the boxes is the same. The correct relation between the energy differences Δ_1 , Δ_2 and Δ_3 for the three cases is—

- (a) $\Delta_1 > \Delta_2 > \Delta_3$ (b) $\Delta_1 = \Delta_2 = \Delta_3$ (c) $\Delta_3 > \Delta_2 > \Delta_1$ (d) $\Delta_3 > \Delta_1 > \Delta_2$

Ans.

	1-D	2-D	3-D
Energy:	$\frac{n_x^2 h^2}{8ml_x^2}$	$\frac{h^2}{8m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} \right)$	$\frac{h^2}{8m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right)$
Ground State:	$n=1$	$n_x = 1, n_y = 1$	$n_x = 1, n_y = 1,$ $n_z = 1$
Excited State:	$n=2$	$n_x = 2, n_y = 1$	$n_x = 2, n_y = 1,$ $n_z = 1$
Energy difference:	$\frac{3h^2}{8ml_x^2}$	$\frac{3h^2}{8ml_x^2}$	$\frac{3h^2}{8ml_x^2}$

So, $\Delta_1 = \Delta_2 = \Delta_3$

Correct option is (b)

Q. The correct statement about both the average value of position ($\langle x \rangle$) and momentum ($\langle p \rangle$) of a 1-d harmonic oscillator wave function is—

- (a) $\langle x \rangle \neq 0$ and $\langle p \rangle \neq 0$ (b) $\langle x \rangle = 0$ but $\langle p \rangle \neq 0$
 (c) $\langle x \rangle = 0$ and $\langle p \rangle = 0$ (d) $\langle x \rangle \neq 0$ but $\langle p \rangle = 0$

Ans. For 1-d harmonic oscillator wave function,

$$\psi_{0(x)} = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2}$$

$$\begin{aligned}\langle x \rangle &= \int_{-\infty}^{+\infty} \psi^* x \psi dx = \int_{-\infty}^{+\infty} \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2} x \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2} dx \\ &= \left(\frac{\beta}{\pi}\right)^{1/2} \int_{-\infty}^{+\infty} x e^{-\beta x^2} dx \dots (i)\end{aligned}$$

Now for $\int_{-\infty}^{+\infty} x^n e^{-ax^2} dx$; if $n = \text{odd}$, integral will be 0,

In equation (i), $n=1$,

Therefore, $\langle x \rangle = 0$

$$\begin{aligned}\langle p_x \rangle &= \int_{-\infty}^{+\infty} \psi^* \langle p_x \rangle \psi dx = \int_{-\infty}^{+\infty} \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2} \left(-i\hbar \frac{\partial}{\partial x}\right) \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2} dx \\ &= \left(\frac{\beta}{\pi}\right)^{1/2} (-i\hbar) \int_{-\infty}^{+\infty} e^{-\beta x^2/2} \left\{ \frac{\partial}{\partial x} (e^{-\beta x^2/2}) \right\} dx \\ &= \left(\frac{\beta}{\pi}\right)^{1/2} (-i\hbar) \int_{-\infty}^{+\infty} e^{-\beta x^2/2} \left(\frac{-2\beta x}{2}\right) e^{-\beta x^2/2} dx \\ &= (-\beta) \left(\frac{\beta}{\pi}\right)^{1/2} (-i\hbar) \int_{-\infty}^{+\infty} x e^{-\beta x^2} dx \quad \left[\text{Now for, } \int_{-\infty}^{+\infty} x^n e^{-ax^2} dx; \right. \\ &\quad \left. \text{if } n = \text{odd, integral will be 0} \right] \\ &= (-\beta) \left(\frac{\beta}{\pi}\right)^{1/2} (-i\hbar) \times 0 = 0, \text{ Correct option is (c).}\end{aligned}$$

Q. The value of the commutator $[x, [x, p_x]]$ is—

- (a) $i\hbar x$ (b) $-i\hbar$ (c) $i\hbar$ (d) 0

Ans. Let the wave function is ψ .

$$\begin{aligned}\text{So, } [x, p_x]\psi &= xp_x\psi - p_x x\psi = x\left(-i\hbar \frac{\partial}{\partial x}\right)\psi - \left(-i\hbar \frac{\partial}{\partial x}\right)x\psi \\ &= -i\hbar x\left(\frac{\partial\psi}{\partial x}\right) + i\hbar\left[x\frac{\partial\psi}{\partial x} + \psi\right] \\ &= -xi\hbar \frac{\partial\psi}{\partial x} + i\hbar x \frac{\partial\psi}{\partial x} + i\hbar\psi = i\hbar\psi\end{aligned}$$

So, we have $[x, p_x] = i\hbar$

Now, $[x, [x, p_x]]\psi = 0$

Correct option is (d).

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Q. Two different non-zero operators \hat{A} and \hat{B} ($\hat{A} \neq \hat{B}$) satisfy the relation $(\hat{A} + \hat{B})(\hat{A} - \hat{B}) = \hat{A}^2 - \hat{B}^2$

- (a) $\hat{A}\hat{B} = \hat{A}^2$ and $\hat{B}\hat{A} = \hat{B}^2$ (b) $\hat{A}\hat{B} + \hat{B}\hat{A} = 0$
(c) \hat{A} and \hat{B} are arbitrary (d) $\hat{A}\hat{B} - \hat{B}\hat{A} = 0$

$$\begin{aligned}\text{Ans. } (\hat{A} + \hat{B})(\hat{A} - \hat{B}) &= \hat{A}(\hat{A} - \hat{B}) + \hat{B}(\hat{A} - \hat{B}) \\ &= \hat{A}^2 - \hat{A}\hat{B} + \hat{B}\hat{A} - \hat{B}^2 \\ &= \hat{A}^2 - \hat{B}^2 \text{ only if } \hat{A}\hat{B} = \hat{B}\hat{A}\end{aligned}$$

Correct option is (d).

Q. The degeneracy of an excited state of a particle in 3-dimensional cubic box with energy 3 times its ground state energy is

- (a) 3 (b) 2 (c) 1 (d) 4

Ans. Given, energy = $3 \times E_0 = 3 \times \frac{3h^2}{8ml^2} = \frac{9h^2}{8ml^2}$

So, possibility of energy states is (2,2,1), (2,1,2), (1,2,2)

Therefore, degeneracy = 3.

Correct option is (a).

Q. Possible term symbol(s) of the excited states of atom with the electronic configuration $[1s^2 2s^2 2p^6 3p^1]$ is/are

- (a) $^2S_{1/2}$ (b) $^2P_{3/2}$ and $^2P_{1/2}$ (c) 1S_0 and 1P_1 (d) 3P_0 and 3P_1

Ans. For $[1s^2 2s^2 2p^6 3p^1]$

$s = \frac{1}{2}$

$2s+1 = 2$



$J = |l+s| \dots \dots \dots |l-s|$

$= 3/2 \dots \dots \dots 1/2$

Term symbol is $^2P_{3/2}$ and $^2P_{1/2}$

Correct option is (b).

Q. A certain 2-level system has stationary state energies E_1 and E_2 ($E_1 < E_2$) with normalized wave functions ψ_1 and ψ_2 respectively. In the presence of a perturbation V , the second-order correction to the energy for the first state (ψ_1) will be

- (a) $\frac{\langle \psi_1 | V | \psi_2 \rangle}{E_1 - E_2}$ (b) $\frac{\langle \psi_1 | V | \psi_2 \rangle}{E_2 - E_1}$ (c) $\frac{|\langle \psi_1 | V | \psi_2 \rangle|^2}{E_1 - E_2}$ (d) $\frac{|\langle \psi_1 | V | \psi_2 \rangle|^2}{E_2 - E_1}$

Ans. The second order correction to n^{th} state

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \psi_m | V | \psi_n \rangle|^2}{E_n - E_m}$$

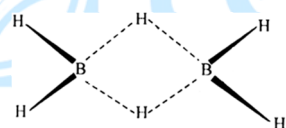
Hence, $E_1^{(2)} = \sum \frac{|\langle \psi_1 | V | \psi_2 \rangle|^2}{E_1 - E_2}$

Correct option is (c).

Q. The molecule diborane belongs to the symmetry point group

- (a) C_{2v} (b) C_{2h} (c) D_{2d} (d) D_{2h}

Ans.



$$C_2 + 2C_2 + 2\sigma_v + \sigma_h = D_{2h}$$

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Correct option is (c).

Q. The irreducible representations of C_{2h} are A_g , B_g , A_u and B_u . The Raman active modes of trans- 1,3-butadiene belong to the irreducible representations

- (a) A_g and B_g (b) A_g and A_u (c) A_u and B_g (d) B_g and B_u

Ans. Generally, Raman active modes of vibrations are the quadratic function of x , y , and z and which are may be possible for A_g and B_g .

Correct option is (a).

Q. The symmetry-allowed atomic transition among the following is

- (a) $^3F \rightarrow ^1D$ (b) $^3F \rightarrow ^3D$ (c) $^3F \rightarrow ^1P$ (d) $^3F \rightarrow ^3P$

Ans. As per selection rule we know that transition is allowed for which $\Delta S=0$, $\Delta L=0, \pm 1$

Only for $^3F \rightarrow ^3D$ transition the selection rules are been obeyed.

Correct option is (b).

Q. The radial part of a hydrogenic wave function is given as $r(\alpha - r)e^{-\beta r}$ (α and β are constants). This function is then identifiable as

- (a) 2s (b) 3p (c) 4d (d) 5f

Ans. In radial part of wave function highest power of r denote the value of l .

Correct option is (b).

Q. A normalized state Φ is constructed as a linear combination of the ground state (ψ_0) and the first excited state (ψ_1) of some harmonic oscillator with energies $1/2$ and $3/2$ units, respectively. If the average energy of the state Φ is $7/6$, the probability of finding ψ_0 in ψ_1 will be

- (a) $1/2$ (b) $1/3$ (c) $1/4$ (d) $1/5$

Ans. Let, $\Phi = c_1\psi_0 + c_2\psi_1$

Hence, $c_1^2 + c_2^2 = 1$(i) and $\frac{c_1^2}{2} + \frac{3c_2^2}{2} = \frac{7}{6}$(ii)

Multiplying $3/2$ to eqn. (i) we get

$$\frac{3c_1^2}{2} + \frac{3c_2^2}{2} = \frac{3}{2} \text{(iii)}$$

Comparing eqn. (ii) and (iii) we get

$$c_1^2 = \frac{1}{3}$$

Correct option is (b).

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Q. The simultaneous eigen functions of angular momentum operators L^2 and L_z are

- (a) all of $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals (b) only $2s$, $2p_x$ and $2p_y$ orbitals
 (c) only $2s$ and $2p_z$ orbitals (d) only $2p_z$ orbital

Ans. $2s$ and $2p_z$ orbitals are eigen functions of L^2 and L_z .

$$L_z 2s = L_z \psi_{200} = 0 \psi_{200}$$

$$L_z 2p_z = L_z \psi_{210} = 0 \psi_{210}$$

$$L^2 2s = L^2 \psi_{200} = 0 \psi_{200}$$

$$L^2 2p_z = L^2 \psi_{210} = 2\hbar^2 \psi_{210}$$

$$L^2 2p_x = L^2 R_{21} \sqrt{\frac{3}{4\pi}} \sin \theta \cos \Phi$$

$$L^2 2p_y = L^2 R_{21} \sqrt{\frac{3}{4\pi}} \sin \theta \sin \Phi$$

$$L^2 2p_y = L_z R_{21} \sqrt{\frac{3}{4\pi}} \sin \theta \cos \Phi \text{ Not eigen function}$$

As $L_z \rightarrow \frac{\partial}{\partial \Phi}$ will change $\cos \Phi$ to $-\sin \Phi$

$$L_z 2p_y = L_z R_{21} \sqrt{\frac{3}{4\pi}} \sin \theta \sin \Phi$$

Therefore not eigen functions,

$$= 2\hbar^2 R_{21} \sqrt{\frac{3}{4\pi}} \sin \theta \cos \Phi$$

$$= 2\hbar^2 R_{21} \sqrt{\frac{3}{4\pi}} \sin \theta \sin \Phi$$

Correct option is (c).

Q. The lowest energy term for the d^6 configuration is

- (a) 2D (b) 5D (c) 1P (d) 1D

Ans. $d^6 =$

$\uparrow\downarrow$	\uparrow	\uparrow	\uparrow	\uparrow
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$$L = \sum M_L = 2 = D$$

$$S = 2, 2S+1=5$$

Correct option is (b).

Q. The eigen functions of the Hamiltonian H ($H = T + V$) of a harmonic oscillator are (where T and V are kinetic energy and potential energy operators, respectively)

- (a) eigen functions of T as well as V (b) eigen functions of T , but not of V
 (c) eigen functions of V , but not of T (d) eigen functions of neither T nor V

Ans. We know if two operator commute this means that they have same sets of eigen functions.

$$\text{Now, } T = \frac{p^2}{2m} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}, V = \frac{1}{2} kx^2, H = T + V$$

$$\text{So, } [\hat{H}, \hat{T}] \neq 0 \text{ \& } [\hat{H}, \hat{V}] \neq 0$$

$$\text{Therefore, } [\hat{T}, \hat{V}] \neq 0$$

Correct option is (d).

Q. The point group obtained by adding symmetry operation σ_h to the point group C_4 is

- (a) S_4 (b) C_{4h} (c) D_{2h} (d) D_4

$$\text{Ans. } C_4 + \sigma_h = C_{4h}$$

Correct option is (b).

Q. For a particle of mass m confined in a rectangular box with sides $2a$ and a , the energy and degeneracy of the first excited state, respectively, are

- (a) $\frac{h^2}{8m} \left(\frac{2}{a^2} \right), 1$ (b) $\frac{h^2}{8m} \left(\frac{17}{4a^2} \right), 2$ (c) $\frac{h^2}{8m} \left(\frac{5}{4a^2} \right), 1$ (d) $\frac{h^2}{8m} \left(\frac{5}{a^2} \right), 2$

Ans.

$E = \frac{13h^2}{8ml^2}$	(2,3) (3,2)	$g=2$
$E = \frac{10h^2}{8ml^2}$	(1,3) (3,1)	$g=2$
$E = \frac{8h^2}{8ml^2}$	(2,2)	$g=1$
$E = \frac{5h^2}{8ml^2}$	(1,2) (2,1)	$g=2$
$E = \frac{2h^2}{8ml^2}$	(1,1)	$g=1$

Degeneracy in 2-D box

$$E = \frac{h^2}{8m} \left[\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} \right] = \frac{h^2}{8m} \left[\frac{n_x^2}{4a^2} + \frac{n_y^2}{a^2} \right] = \frac{h^2}{8m} \left[\frac{n_x^2 + 4n_y^2}{4a^2} \right]$$

Now, for first excited state, $n_x=2, n_y=1$

$$\text{Hence, } E = \frac{h^2}{8m} \left[\frac{4+4}{4a^2} \right] = \frac{h^2}{8m} \left(\frac{2}{a^2} \right)$$

Also for first excited state $n_x=1, n_y=2$

$$E = \frac{h^2}{8m} \left[\frac{n_x^2 + 4n_y^2}{4a^2} \right] = \frac{h^2}{8m} \left[\frac{1+16}{4a^2} \right] = \frac{h^2}{8m} \left(\frac{17}{4a^2} \right) = \frac{h^2}{8m} \left(\frac{4.25}{a^2} \right)$$

So, minimum energy $= \frac{h^2}{8m} \left(\frac{2}{a^2} \right), g = 1$.

Correct option is (a).

Q. The ionization energy of hydrogen atom in its ground state is approximately 13.6 eV. The potential energy of He^+ , in its ground state is approximately

- (a) -54.4 eV (b) -27.2 eV (c) -13.6 eV (d) -108.8 eV

Ans. $I. E_{\text{He}^+} = 13.6 \frac{Z^2}{n^2} = 13.6 \times 4$

As we know $\text{K.E} + \text{P.E} = -54.4\text{eV} \dots\dots\dots(\text{i})$

Now as per Virial Theorem,

$$2\langle T \rangle = -\langle V \rangle$$

Also, $\text{K.E} = -\frac{1}{2} \text{P.E}$

Thereafter, from eqn. (i) $-\frac{1}{2} \text{P.E} + \text{P.E} = -54.4$; $\text{P.E} = -108.8 \text{ eV}$

Correct option is (d).



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Q. The character table for the D_3 point group is provided below:

D_3	E	$2C_3$	$3C_2$		
A_1	1	1	1		$x^2 + y^2, z^2$
A_2	1	1	-1	z, R_z	
E	2	-1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

For this point group, the correct statement among the following is:

- (a) it is possible to have a totally symmetric normal mode of vibration which is IR-active
- (b) all IR-active normal modes are necessarily Raman inactive
- (c) all Raman-active normal modes are necessarily IR-active
- (d) it is possible to have a pair of IR-active normal modes that are degenerate.

Ans. In front of 'E' irreducible representation, it is clear that there is a pair of IR active mode which is degenerate.

Correct option is (d).

Q. Suppose $\psi_1, \psi_2, \psi_3, \dots$ are wavefunctions of an anharmonic oscillator and $\phi_0, \phi_1, \phi_2, \dots$ are wavefunctions of a harmonic oscillator with increasing order of energy. The subscripts denote vibrational quantum numbers in both the cases. Given

$$\psi_0 = a_1\phi_0 + a_2\phi_2 + a_3\phi_4$$

$$\psi_1 = b_1\phi_0 + b_2\phi_6 + b_3\phi_6$$

$$\psi_2 = c_1\phi_1 + c_2\phi_4$$

$$\psi_3 = d_1\phi_3 + d_2\phi_5$$

the FORBIDDEN electric dipole (assuming the dipole operator is linear in normal coordinates) transition among the following is

- (a) $\psi_0 \rightarrow \psi_1$ (b) $\psi_0 \rightarrow \psi_2$ (c) $\psi_0 \rightarrow \psi_3$ (d) $\psi_1 \rightarrow \psi_2$

Ans. $\phi_0, \phi_1, \phi_2, \dots$ are wavefunctions of a harmonic oscillator in ground state, first excited state, second excited state respectively.

We know that for a harmonic oscillator $\phi_0, \phi_2, \phi_4, \phi_6, \dots$ will have even parity and $\phi_1, \phi_3, \phi_5, \phi_7, \dots$ will have odd parity.

$$\text{So, } \psi_{0[\text{EVEN PARITY}]} = a_1\phi_{0[\text{EVEN PARITY}]} + a_2\phi_{2[\text{EVEN PARITY}]} + a_3\phi_{4[\text{EVEN PARITY}]}$$

$$\psi_{1[\text{EVEN PARITY}]} = b_1\phi_{0[\text{EVEN PARITY}]} + b_2\phi_{6[\text{EVEN PARITY}]} + b_3\phi_{6[\text{EVEN PARITY}]}$$

$$\psi_{2[\text{MIXED PARITY}]} = c_1\phi_{1[\text{ODD PARITY}]} + c_2\phi_{4[\text{EVEN PARITY}]}$$

$$\psi_{3[\text{ODD PARITY}]} = d_1\phi_{3[\text{ODD PARITY}]} + d_2\phi_{5[\text{ODD PARITY}]}$$

Since the dipole moment operator is linear, therefore electric dipole transition is forbidden if the initial and final states have same parity.

Since, ψ_0 and ψ_1 have same parity, so, the transition $\psi_0 \rightarrow \psi_1$ is forbidden.

Correct option is (a).

Q. The character table of C_{3v} point group is provided below, along with an additional reducible representation, Γ

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
Γ	6	0	2

Γ is given by

- (a) $A_1 + A_2 + 2E$ (b) $2A_1 + 2E$ (c) $2A_2 + 2E$ (d) $2A_1 + 2A_2 + E$

Ans. $n_{A_1} = 2, n_{A_2} = 2$

Correct option is (b).

Q. Average value of momentum for the ground state of a particle in a 1-d box is zero because

- (a) $[p, H] = 0$ (b) V (potential) = 0
 (c) H is hermitian (d) the state is bound and stationary

Ans. For any bound state particle has equal and opposite value of moment.

Correct option is (d).

Q. Choosing some Hamiltonian H and an orthonormal basis, a linear variation is carried out to get approximately energies \overline{E}_j . With 2 basis functions, one obtains $\overline{E}_1(2) \leq \overline{E}_2(2)$. Taking 3 basis functions, similarly three ordered energies $\overline{E}_1(3) \leq \overline{E}_2(3) \leq \overline{E}_3(3)$ are found. The relation which holds from the following is?

- (a) $\overline{E}_1(2) \leq \overline{E}_1(3)$; $\overline{E}_2(2) \leq \overline{E}_2(3)$
 (b) $\overline{E}_1(3) \leq \overline{E}_1(2)$; $\overline{E}_2(2) \leq \overline{E}_2(3)$
 (c) $\overline{E}_1(2) \leq \overline{E}_1(3)$; $\overline{E}_2(3) \leq \overline{E}_2(2)$
 (d) $\overline{E}_1(3) \leq \overline{E}_1(2)$; $\overline{E}_2(3) \leq \overline{E}_2(2)$

Ans. Correct option is (d).

Q. For a hermitian operator A , which does NOT commute with the Hamiltonian H , let ψ_1 be an eigenfunction of A and ψ_2 be an eigenfunction of H . The correct statement regarding the average value of the commutator of A with H ($[A, H]$) is

- (a) both $\langle \psi_1 | [A, H] | \psi_1 \rangle$ and $\langle \psi_2 | [A, H] | \psi_2 \rangle$ are non-zero
 (b) only $\langle \psi_1 | [A, H] | \psi_1 \rangle$ is zero, but $\langle \psi_2 | [A, H] | \psi_2 \rangle$ is non-zero
 (c) only $\langle \psi_2 | [A, H] | \psi_2 \rangle$ is zero, but $\langle \psi_1 | [A, H] | \psi_1 \rangle$ is non-zero
 (d) both $\langle \psi_1 | [A, H] | \psi_1 \rangle$ and $\langle \psi_2 | [A, H] | \psi_2 \rangle$ are zero

Ans. $A|\psi_1\rangle = a|\psi_1\rangle$ and $H|\psi_2\rangle = b|\psi_2\rangle$, $\langle \psi_2 | H = b \langle \psi_2 |$

Here, 'a' is eigen value.

$$\langle \psi_1 | A = A | \psi_1 \rangle^\dagger = a | \psi_1 \rangle^\dagger = a^* \langle \psi_1 | = a \langle \psi_1 | \text{ [as } a \text{ is real number]}$$

$$\begin{aligned} \text{Now, } \langle \psi_1 | [A, H] | \psi_1 \rangle &= \langle \psi_1 | AH - HA | \psi_1 \rangle = \langle \psi_1 | AH | \psi_1 \rangle - \langle \psi_1 | H | a \psi_1 \rangle \\ &= a [\langle \psi_1 | H | \psi_1 \rangle - \langle \psi_1 | H | \psi_1 \rangle] = 0 \end{aligned}$$

Similarly, $\langle \psi_2 | [A, H] | \psi_2 \rangle = 0$; **Correct option is (d).**

Q. In simple molecular orbital theory of hydrogen molecule, bonding σ_g and anti-bonding σ_u molecular orbitals are constructed as linear combinations of atomic orbitals of two hydrogen atoms. The spatial part of a purely covalent singlet wavefunction is obtained by

- (a) $\sigma_g^2 + \sigma_u^2$ (b) σ_g^2 (c) $\sigma_g^2 - \sigma_u^2$ (d) $\sigma_g^2 + \frac{1}{2}\sigma_u^2$

Ans. Correct option is (c).

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Q. Covariance is defined by the relation $\text{Cov}(x,y) = \langle xy \rangle - \langle x \rangle \langle y \rangle$. Given the arbitrary constants A, B and C, $\text{Cov}(x,y)$ will be zero only when

- (a) $y = Ax^2$ (b) $y = Ax^2 + B$ (c) $y = Ax + B$ (d) $y = Ax^2 + Bx + C$

Ans. Covariance has the tendency for the linear relationship between the variables

If $y = f(x) \propto x^n$ (where $n > 1$), then $\text{cov}(x, y) = +ve$

If $y = f(x) \propto x^n$ (where $n < 0$), then $\text{cov}(x, y) = -ve$

If $y = f(x) \propto x$, then $\text{cov}(x, y) = 0$

Correct option is (c).

Q. The correct normalized wavefunction for one of the sp^2 hybrid orbitals is

- (a) $\frac{1}{3}\psi_{2s} + \frac{1}{3}\psi_{2p_x} + \frac{1}{3}\psi_{2p_y}$ (b) $\frac{1}{\sqrt{3}}\psi_{2s} + \frac{2}{\sqrt{3}}\psi_{2p_x} + \frac{1}{\sqrt{6}}\psi_{2p_y}$
 (c) $\frac{1}{\sqrt{3}}\psi_{2s} + \frac{2}{\sqrt{3}}\psi_{2p_x} + \frac{1}{\sqrt{6}}\psi_{2p_y}$ (d) $\frac{1}{\sqrt{3}}\psi_{2s} + \frac{1}{2\sqrt{3}}\psi_{2p_x} + \frac{1}{\sqrt{6}}\psi_{2p_y}$

Ans. For normalized wave function, $c_1^2 + c_2^2 + c_3^2 = 1$

$$\frac{1}{3} + \frac{1}{2} + \frac{1}{6} = 1$$

Correct option is (c).

Q. The transition that belongs to the Lyman series in the hydrogen-atom spectrum is

- (a) $1s \leftarrow 4s$ (b) $1s \leftarrow 4p$ (c) $2s \leftarrow 4s$ (d) $2s \leftarrow 4p$

Ans. As we know for any allowed transition $\Delta l = \pm 1$ and for Lyman series transition is from the higher level to $n=1$.

Correct option is (b).

Q. Vibrations of diatomic molecules are usually modelled by a harmonic potential. If the potential is given by x^2 , the correct statement is

- (a) force is $2x$ and force constant is 2 (b) force is $-2x$ and force constant is 2
(c) force is $2x$ and force constant is -1 (d) force is $-2x$ and force constant is -1

Ans. Given, $V = x^2$

Now force, $-\frac{\partial V}{\partial x} = -\frac{\partial}{\partial x}(x^2) = -2x$

Now, $V = \frac{1}{2}kx^2 = x^2$ (given)

So, $k = 2$.

Correct option is (b).

Q. The orbital degeneracy of the level of a one-electron atomic system with $Z = 5$ and energy ≈ -13.6 eV, is

- (a) 1 (b) 5 (c) 25 (d) 36

Ans. We know that, $E_n = -13.6 \frac{Z^2}{n^2}$; $-13.6 \frac{25}{n^2} = -13.6$, $n=5$

Correct option is (b).

(a) \hat{A} is hermitian

(b) \hat{A} is anti-hermitian

(c) \hat{A} is unitary

(d) \hat{A} is any linear operator

$$\int (\hat{A}\phi)^\dagger (\hat{A}\phi) d\tau = 1$$

$$\text{i.e., } \int \phi^\dagger A^\dagger A \phi \, d\tau = 1, \text{ i.e., } \int \phi^\dagger \phi \, d\tau = 1$$

Therefore, ϕ will be normalized if $A^\dagger A = 1$ i.e., A is unitary.

Correct option is (c).

124. The ground state of a certain system with energy ϵ_0 is subjected to a perturbation V , yielding a first order correction ϵ_1 . If E_0 is the true ground-state energy of the perturbed system, the inequality that always holds is

(a) $\epsilon_1 \geq 0$

(b) $\epsilon_1 \geq E_0$

(c) $\epsilon_0 + \epsilon_1 \leq E_0$

(d) $\epsilon_0 + \epsilon_1 \geq E_0$

Ans. As per perturbation theory, “The energy of perturbed system is equal or greater than the standard system”.

Correct option is (d).

(a) only ionic parts (b) only covalent parts

(c) both ionic and covalent parts (d) neither ionic nor covalent parts

$$\begin{aligned}
&= \left[\left(\psi_{1s(H_a)}(1) + \psi_{1s(H_b)}(1) \right) \left(\psi_{1s(H_a)}(2) - \psi_{1s(H_b)}(2) \right) \right] \\
&= \left[\left(\psi_{1s(H_a)}(2) + \psi_{1s(H_b)}(2) \right) \left(\psi_{1s(H_a)}(1) - \psi_{1s(H_b)}(1) \right) \right] \\
&= 2 \left[\psi_{1s(H_a)}(2) \psi_{1s(H_b)}(1) - \psi_{1s(H_a)}(1) \psi_{1s(H_b)}(2) \right]
\end{aligned}$$

Q. The highest molecular orbitals for an excited electronic configuration of the oxygen molecule are $[1\pi_g]^1[3\sigma_u]^1$. A possible molecular term symbol for oxygen with this electronic configuration is

- (a) $^1\pi$ (b) $^3\Sigma$ (c) $^1\Delta$ (d) $^1\Sigma$

(I) $m_L \quad \frac{\uparrow}{0} \quad \sigma_u$

$\frac{\uparrow}{\pi_g} \quad \frac{\uparrow}{\pi_g}$

$m_L \quad +1 \quad -1$

$S = 1, 2S + 1 = 3$

$L = 1 \rightarrow \pi \text{ Term}$

Spectroscopic Term = $^3\pi$

(II) $m_L \quad \frac{\uparrow}{0} \quad \sigma_u$

$\frac{\uparrow}{\pi_g} \quad \frac{\uparrow}{\pi_g}$

$m_L \quad +1 \quad -1$

$L = 1 \rightarrow \pi \text{ Term}$

$S = 0, 2S + 1 = 1$

Spectroscopic Term $\rightarrow ^1\Sigma$

Correct option is (a).

C_{2v}	E	C_2	σ_v	σ_v'	
A_1	I	I	I	I	z, z^2, x^2, y^2
A_2	I	I	$-I$	$-I$	xy
B_1	I	$-I$	I	$-I$	x, xz
B_2	I	$-I$	$-I$	I	y, yz

- Ans.** We have $A_1 \times B_1 = 1 \quad -1 \quad 1 \quad -1$, i.e., X-polarised.

Q. The pair of symmetry points groups that are associated with only polar molecules is

- Ans.** The polar point groups are C_{nv} , C_n , C_l , C_s .

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Q. Two bound stationary states, 1 and 2, of a one-electron atom, with $E_2 > E_1$ (E is the total energy) obey the following statement about their kinetic energy (T) and potential energy (V)

(a) $T_2 > T_1$; $V_2 > V_1$

(b) $T_2 > T_1$; $V_2 < V_1$

(c) $T_2 < T_1$; $V_2 > V_1$

(d) $T_2 = T_1$; $V_2 > V_1$

Ans. $T_1 = \frac{1}{2} V_1$; $T_2 = -\frac{1}{2} V_2$

$E_2 > E_1$; $T_1 + T_2 < V_1 + V_2$

Correct option is (c).

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Q. Consider a particle in its ground state confined to a one-dimensional box in the interval $(0, 8)$. The probability of finding it between $4.0 - \frac{\delta}{2}$ and $4.0 + \frac{\delta}{2}$ is close to (δ is sufficiently small so that the wavefunction can be taken as a constant in this interval).

(a) $\frac{\delta}{4}$

(b) $\frac{\delta}{3}$

(c) $\frac{\delta}{2}$

(d) δ

Ans. Probability of finding electron is a particular region,

$$P_r = |\psi|^2 dx = \left[\sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \right] \delta$$

$$= \frac{1}{4} \sin^2 \left(\frac{\pi}{2} \right) \delta = \frac{\delta}{4}.$$

Correct option is (a)

Q. Which of the functions below is a common eigenfunction of $\frac{d}{dx}$ and $\frac{d^2}{dx^2}$ operators?

- (a) $\cos x$ (b) kx (c) e^{ix} (d) e^{-x^2}

Ans. $\frac{d}{dx} e^{ix} = i e^{ix}$; eigen function

$\frac{d^2}{dx^2} e^{ix} = i^2 e^{ix}$; eigen function

Correct option is (c).

Q. For the electronic configuration $1s^2 2s^2 2p^4$, two of the possible term symbols are 1S and 3P . The remaining term is

- (a) 1D (b) 1F (c) 3D (d) 3F

Ans. The number of possible microstate for $p^4 = \frac{6!}{4!(6-4)!} = 15$

$^1S = 1 \times 1 = 1$; $^3P = 3 \times 3 = 9$

Therefore the remaining microstates are 5 which comes from $^1D = 1 \times 5 = 5$

Correct option is (a)

Q. The correct relation involving symmetry operations

- (a) $S_4^2 = S_2$ (b) $\sigma(xz)\sigma(yz) = C_2(s)$
 (c) $S_4^3 = C_4^3$ (d) $S_6^3 = S_2$

Ans. $S_6^3 = C_6^3 \times \sigma^3 = C_2' \times a = S_2$

Correct option is (d)

Q. For a point group, an incomplete character table is given below with one irreducible representation missing

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
-	-	-	-
E	2	-1	0

The Mulliken symbol and characters of the missing representation are

(a) A'_1 1 -1 1

(b) B_1 1 -1 1

(c) A_2 1 1 -1

(d) B_2 1 -1 1

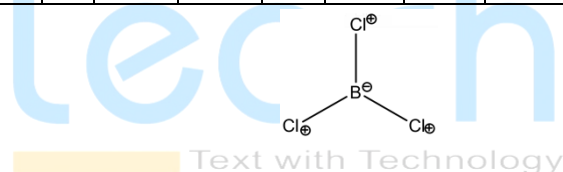
Ans. For a C_{3v} point group the complete character table is

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Correct option is (c).

Q. Given below is a specific vibrational mode of BCl_3 with \oplus and \ominus denoting movements of the respective atoms above and below the plane of the molecule respectively. The irreducible representation of the vibrational mode and its IR / Raman activity are

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1	1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	x, y	x^2-y^2, xy
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	R_x, R_y	xz, yz



- (a) A_2' ; neither IR nor Raman active (b) E' both IR and Raman active
 (c) A_1 ; Raman active (d) A_2' ; IR active

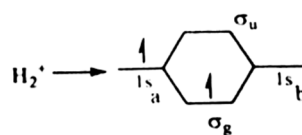
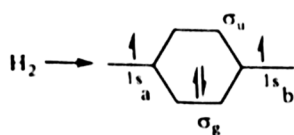
Ans. As per the given character table, the vibrational node is not symmetric with respect to σ_h .

Correct option is (d).

Q. The two limiting wavefunctions of the ground state of H_2^+ molecular ion, as the internuclear separation R goes to (i) (infinity) and (ii) 0 (zero) are ($1s_a, 1s_b$ are $1s$ -orbital wave functions of hydrogen atoms a and b in H_2^+ , and $He\ 1s$ is the wave function of the $1s$ orbital of He^+)

- (a) (i) $1s_a(r)$; (ii) $1s_b(r)$ (b) (i) $1s_b(r)$; (ii) $1s_a(r)$
 (c) (i) $1s_a(r_1)\ 1s_b(r_2)$; (ii) $1s_{He}(r_1)\ 1s_{He}(r_2)$ (d) (i) $1s_a(r)+1s_b(r)$; (ii) $1s_{He}(r)$

Ans.



$$2He = 1s^2;$$

$$He^+ = 1s^1$$

$$H_2^+ = r \rightarrow \infty = 1s_a(r) + 1s_b(r)$$

$$He^+ = r \rightarrow 0 = 1s_{He}(r);$$

Correct option is (d).

Q. The un-normalized radial wave function of a certain hydrogen atom eigenstate is $(6r-r^2)\exp(-r/3)$. A possible angular part of the eigenstate is

- (a) $5\cos^3\theta - 3\cos\theta$ (b) $3\cos^2\theta - 1$ (c) $\cos\theta$ (d) 1

Ans. In the given eigen state equation the maximum power of r is 1 i.e., $l=1$ i.e., possible angular part is $\cos\theta$.

Correct option is (c).

Q. Given a trial wave function $\psi_t = C_1\phi_1 + C_2\phi_2$, and the Hamiltonian matrix elements, $\int \phi_1^* H \phi_1 dv = 0$, $\int \phi_1^* H \phi_2 dv = 2.5$, $\int \phi_2^* H \phi_1 dv = 12.0$, the variationally determined ground state energy is

- (a) -0.52 (b) -0.50 (c) 12.50 (d) 12.52

Ans.
$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

$$\begin{vmatrix} 0 - E & 2.5 \\ 2.5 & 12 - E \end{vmatrix} = 0$$

$$E = -0.50$$

Correct option is (b).

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Q. The number of degenerate spatial orbital's of a hydrogen- like atom with principal quantum Number $n=6$ is

- (a) 12 (b) 6 (c) 72 (d) 36

Ans. As we know orbital degeneracy $= n^2 = 6^2 = 36$

Correct option is (d).

Q. If $[\hat{A}, \hat{B}] = 0$ and $[\hat{A}, \hat{C}] = 0$, then which of the following **necessarily** holds: $[\hat{A}, \hat{B}]$ & \hat{C} are operators]

- (a) $[\hat{B}, \hat{C}] = 0$ (b) $[\hat{A}, \widehat{BC}] = 0$ (c) $[\hat{B}, \widehat{AC}] = 0$ (d) $[\hat{C}, \widehat{AB}] = 0$

Ans.
$$[\hat{A}, \widehat{BC}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}] = 0$$

Correct option is (b).

Q. The correct statement among the following is (\hat{A} is a hermitian operator)

1. The eigenvalues of \hat{A}^2 can be negative.
2. The eigenvalues of \hat{A}^2 are always positive.
3. No eigenfunction of \hat{A} is an eigenfunction of \hat{A}^2 .
4. The eigenvalues of \hat{A}^2 can be complex.

Ans. Assuming $\hat{A} = \hat{p}_x$ and $\psi = e^{-ikx}$

Therefore, $\hat{A}\psi = \hat{A}e^{-ikx} = (-\hbar k)\psi$; $\hat{A}^2\psi = \hat{A}^2e^{-ikx} = (\hbar k)^2\psi$, i.e., +ve

Correct option is (b).

Q. The correct statement about the symmetry of the eigenfunctions of a quantum of 1-D harmonic oscillator is

- (a) All the eigenfunctions are only even functions, because the potential is an even function.
- (b) All the eigenfunctions are only odd functions, although the potential is an even function.
- (c) The eigenfunctions have no odd-even symmetry.
- (d) All the eigenfunction are either odd or even functions, because the potential is an even function.

Ans. Eigen functions are even for even values of vibrational quantum number and odd for odd values vibrational quantum number.

Correct option is (d)

Q. The correct statement about the difference of second and first excited state energies (ΔE) of a particle in 1-D, 2-D square and 3-D cubic boxes with same length for each, is

- (a) ΔE (1-D box) = ΔE (2-D box) = ΔE (3-D box)
- (b) ΔE (1-D box) > ΔE (2-D box) ΔE (3-D box)
- (c) ΔE (1-D box) > ΔE (2-D box) = ΔE (3-D box)
- (d) ΔE (1-D box) < ΔE (2-D box) < ΔE (3-D box)

Ans. In 1-D box, $\Delta E = 5 \left(\frac{h^2}{8ml^2} \right)$, for 2-D box, $\Delta E = 3 \left(\frac{h^2}{8ml^2} \right)$ and for 3-D box, $\Delta E = 3 \left(\frac{h^2}{8ml^2} \right)$.

Correct option is (c).

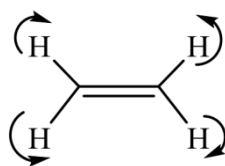
103. A one-dimensional quantum harmonic oscillator is perturbed by a potential λx^2 . The first order correction to the energy for the ground state [$\Delta E^{(1)}$] is,

- (a) $\Delta E^{(1)} > 0$ but < 1
- (b) $\Delta E^{(1)} < 0$
- (c) $\Delta E^{(1)} = 0$
- (d) $\Delta E^{(1)} > 2$

Ans. For odd power of perturbed potential, $\Delta E^{(1)} = 0$

Correct option is (c).

Q. The normal mode of ethylene represented, by the figure below, is



- (a) Only IR active
- (b) Only Raman active
- (c) Both IR and Raman active
- (d) Neither IR nor Raman active

Ans. Correct option is (b)

Q. A part of the character table of a point group (of order 4) is given below.

	E	X_1	X_2	X_3
Γ_1	I	I	I	I
Γ_2	I	$-I$	I	$-I$
Γ_3	I	$-I$	$-I$	I
Γ_4	$?$	$?$	$?$	$?$

The four characters of Γ_4 are, respectively

- (a) 1, 1, -1 , -1 (b) 2, -0 , 0, 1 (c) 1, i, i, 1 (d) 1, $-i$, i, -1

Ans. According to the Great Orthogonal Theorem, any two IR must be orthogonal to each other.

Correct option is (a).

Q. The electronic transition energy from $\pi_1 \rightarrow \pi_2$ in propenyl radical is 4.8 eV. Within the frame work of Huckel theory, the transitions energy from $\pi_1 \rightarrow \pi_3$ would be

- (a) 2.4 eV (b) 4.8 eV (c) 9.6 eV (d) 14.4 eV

Ans.
$$\begin{array}{l} \text{_____ } \pi_1 = \alpha - 2\sqrt{\beta} \\ \text{_____ } \pi_2 = \alpha \\ \text{_____ } \pi_3 = \alpha + 2\sqrt{\beta} \end{array} E_{\pi_1 \rightarrow \pi_3} = 2E_{\pi_1 \rightarrow \pi_2} = 2 \times 4.8 = 9.6$$

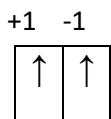
Correct option is (c).

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Q. The term symbol for the ground state of B_2 is

- (a) $^1\Sigma_g^+$ (b) $^1\Sigma_g^-$ (c) $^3\Sigma_g^-$ (d) $^3\Sigma_g^+$

Ans. For B_2 , $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_y^2 \pi_y^1 \pi_y^1 3\sigma_g^2$



$$S = \frac{1}{2} + \frac{1}{2} = 1$$

$$2S+1 = 3$$

$$\Delta\Lambda = 0, \pm 1$$

$$\Lambda = +1, -1, 0 \text{ i.e., } \Sigma$$

Thus, $^3\Sigma_g$

Correct option is (c).

Q. A Gaussian distribution has the functional form $f(x) = \frac{2}{\sqrt{2a^2\pi}} e^{-\frac{(x-b)^2}{2a^2}}$. The variance of such distribution is

- (a) a (b) a^2 (c) b (d) b^2

Ans. $f(x) = \frac{2}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-x_e)^2}{2a^2}}$ compare with $f(x) = \frac{2}{\sqrt{2a^2\pi}} e^{-\frac{(x-b)^2}{2a^2}}$

$$\text{Variance} = \sigma^2; \text{Variance} = a^2$$

Correct option is (b)

Q. The lowest energy state of a $1s^l 2s^l$ electronic configuration, according to Hund's rule, is

- (a) 3S_0 (b) 1S_0 (c) 3S_1 (d) 1S_1

Ans. $S = \frac{1}{2} + \frac{1}{2} = 1$

$2S+1 = 3$

i.e., $l=0$, S(term); 3S_1

Correct option is (c).

Q. The commutator of \hat{x} with the Hamiltonian, \hat{H} , $[\hat{x}, \hat{H}]$ is

- (a) 0 (b) $i\hbar$ (c) $-\frac{\hbar^2}{2m}\hat{p}_x$ (d) $\frac{i\hbar}{m}\hat{p}_x$

Ans. $[\hat{x}, \hat{H}] = [\hat{x}, \frac{p^2}{2m}] + [\hat{x}, V(x)] = \frac{1}{2m} [\hat{x}, \frac{p^2}{2m}] = \frac{i\hbar}{m} p$

Correct option is (d).

Q. Which of these is not a suitable unnormalized wave function for the excited $1s$ '2s' electron configuration of the helium atom?

- (a) $[1s(1)2s(2)-2s(1)1s(2)][\beta(1)\beta(2)]$
 (b) $[1s(1)2s(2)+2s(1)1s(2)][\alpha(1)\beta(2)-\beta(1)\alpha(2)]$
 (c) $[1s(1)2s(2)-2s(1)1s(2)][\alpha(1)\beta(2)+\beta(1)\alpha(2)]$
 (d) $[1s(1)2s(2)+2s(1)1s(2)][\alpha(1)\alpha(2)]$

Ans. $\psi_{total} = \psi_{space} \psi_{spin} = \frac{[1s(1)2s(2) + 1s(2)2s(1)]}{[1s(1)2s(2) - 1s(2)2s(1)]}$ spatial part

$\alpha(1) \alpha(2); \beta(1)\beta(2) =$ spin part

$\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \beta(1)\alpha(2))$ i.e., $\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))$ spin part

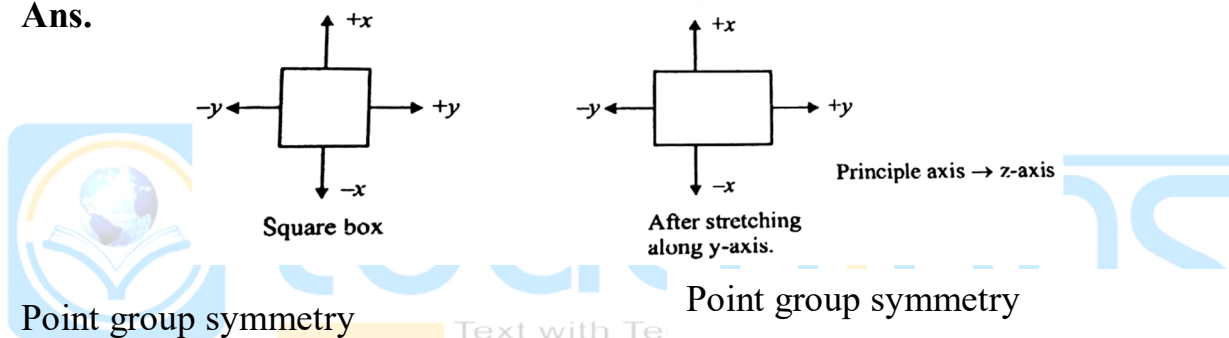
Correct option is (d).

Q. Two opposite sides (in the y – direction) of a square box of side L are slightly stretched. Consider the following four statements:

- A. The point group changes from D_{4h} to D_{2h} .
- B. The (1,2) and (2,1) energy levels remain doubly degenerate
- C. Both the energy levels are lowered and the energy of the (1,2) level higher than that of the (2,1) level.
- D. Both the energy levels are lowered and the energy of the (1,2) level lower than that of the (2,1) level. The two correct statements are:

- (a) A and B (b) A and C (c) B and C (d) A and D

Ans.



Point group symmetry

$C_4 \rightarrow$ along principle axis

$4C_2 \rightarrow$ perpendicular to principle axis

$\sigma_h \rightarrow$ along molecular plane

$C_4 \perp 4C_2 = D_4$

Hence D_{4h}

In above rectangle $L_y > L_x$

Energy of particle in rectangular box is given by

$$E_{xy} = \frac{h^2}{8m^2} \left[\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} \right]$$

Point group symmetry

$C_2 \rightarrow$ along principle axis

$2C_2 \rightarrow$ perpendicular to principle axis

$\sigma_h \rightarrow$ along molecular plane

$C_4 \perp 4C_2 = D_4$

Hence D_{4h}

$$\text{Hence, } E_{12} = \frac{h^2}{8m^2} \left[\frac{1}{l_x^2} + \frac{4}{l_y^2} \right] = \frac{h^2}{8m^2} \left[\frac{l_x^2 + 4l_y^2}{l_x^2 \cdot l_y^2} \right]$$

$$\text{and } E_{21} = \frac{h^2}{8m^2} \left[\frac{4}{l_x^2} + \frac{1}{l_y^2} \right] = \frac{h^2}{8m^2} \left[\frac{4l_x^2 + l_y^2}{l_x^2 \cdot l_y^2} \right]$$

As $L_y > L_x$

Hence $E_{21} > E_{12}$. **Correct option is (d).**

Q. Consider a model system of five non – interacting fermions in a single 3 – dimensional harmonic oscillator. The Hamiltonian of a single particle is

$$\hat{H} = \frac{1}{2m} (\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) + \frac{1}{2} m \omega^2 (x^2 + y^2 + z^2)$$

where m is the mass of the particle, ω is the angular frequency, \hat{p}_x , \hat{p}_y and \hat{p}_z are the momentum operators. The ground state energy of the system of non – interacting fermions is

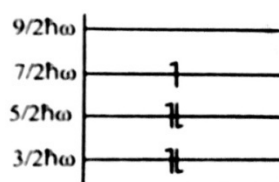
(a) $\frac{21}{2} \hbar \omega$

(b) $\frac{15}{2} \hbar \omega$

(c) $\frac{5}{2} \hbar \omega$

(d) $\frac{25}{2} \hbar \omega$

Ans. $E = \left(n_x + n_y + n_z + \frac{3}{2} \right) \hbar \omega$



Hence $E = \frac{21}{2} \hbar \omega$

Correct option is (a).

Q. A particle is in a state $\phi = \psi_1 + 3\psi_2$ where ψ_1 and ψ_2 are eigen functions of the Hamiltonian of the particle with eigen values E_1 and E_2 , respectively. The average energy of the particle in the state ϕ is

(a) $(E_1 + 9E_2)/10$

(b) $(E_1 + 3E_2)$

(c) $(E_1 + 9E_2)/4$

(d) $(E_1 + 3E_2)/10$

Ans. $\phi = \psi_1 + 3\psi_2$

So, $\hat{H}\psi_1 = E_1\psi_1$ and $\hat{H}\psi_2 = E_2\psi_2$

For average energy,

$$\begin{aligned}\langle E \rangle &= \frac{\langle \phi^* | \hat{H} | \phi \rangle}{\langle \phi^* | \phi \rangle} = \frac{\langle (\psi_1 + 3\psi_2) | \hat{H} | (\psi_1 + 3\psi_2) \rangle}{\langle (\psi_1 + 3\psi_2) | (\psi_1 + 3\psi_2) \rangle} \\&= \frac{\langle \psi_1 | \hat{H} | \psi_1 \rangle + 3\langle \psi_1 | \hat{H} | \psi_2 \rangle + 3\langle \psi_2 | \hat{H} | \psi_1 \rangle + 9\langle \psi_2 | \hat{H} | \psi_2 \rangle}{\langle \psi_1 | \psi_1 \rangle + 3\langle \psi_1 | \psi_2 \rangle + 3\langle \psi_2 | \psi_1 \rangle + 9\langle \psi_2 | \psi_2 \rangle} \\&= \frac{E_1\langle \psi_1 | \psi_1 \rangle + 3E_2\langle \psi_1 | \psi_2 \rangle + 3E_1\langle \psi_2 | \psi_1 \rangle + 9E_2\langle \psi_2 | \psi_2 \rangle}{\langle \psi_1 | \psi_1 \rangle + 3\langle \psi_1 | \psi_2 \rangle + 3\langle \psi_2 | \psi_1 \rangle + 9\langle \psi_2 | \psi_2 \rangle} \\&= \frac{E_1 + 9E_2}{1 + 9} = \frac{(E_1 + 9E_2)}{10}; \text{ Correct option is (a).}\end{aligned}$$

Q. Which of the following statements on ground state perturbation theory, involving the zeroth order energy $E_0^{(0)}$, first order energy correction $E_0^{(1)}$ and second order energy correction $E_0^{(2)}$, is false ?

- (a) $E_0^{(1)}$ is the average value of perturbation operator with respect to the ground state of the zeroth order Hamiltonian.
- (b) $E_0^{(1)}$ is necessarily negative.
- (c) $E_0^{(2)}$ is necessarily negative.
- (d) $E_0^{(0)} + E_0^{(1)}$ is an upper bound to the exact ground state energy.

Ans. First order energy correction is

$$E'_0 = \int_{-\infty}^{\infty} (\psi^0 | \hat{H}^0 + \hat{H}' | \psi^0) dy = E_0^0 + \Delta E$$

Hence, $E'_0 \geq E_0^0$

Correct option is (a).

Q. The allowed electronic transition in fluorine molecule is

- (a) $\Sigma_g^+ \rightarrow \Sigma_g^+$
- (b) $\Sigma_g^+ \rightarrow \Sigma_g^-$
- (c) $\Sigma_g^+ \rightarrow \Pi_u$
- (d) $\Sigma_g^+ \rightarrow \Delta_u$

Ans. As per selection rule, $\Delta\Lambda = 0, \pm 1$

And $g \rightarrow g$ forbidden

Correct option is (c).

Q. One of the correct normalized sp^2 hybrid orbitals is

- (a) $\frac{1}{3}\Phi_{2s} + \frac{1}{3}\Phi_{2p_x} + \frac{1}{3}\Phi_{2p_y}$ (b) $\frac{1}{2}\Phi_{2s} + \frac{\sqrt{3}}{\sqrt{8}}\Phi_{2p_x} + \frac{\sqrt{3}}{\sqrt{8}}\Phi_{2p_y}$
 (c) $\frac{1}{\sqrt{3}}\Phi_{2s} + \frac{\sqrt{2}}{\sqrt{3}}\Phi_{2p_x}$ (d) $\frac{1}{\sqrt{3}}\Phi_{2s} + \frac{2}{3}\Phi_{2p_x}$

Ans. For normalized molecular orbital must follow the total probability condition

$$\psi_{sp^2} = \frac{1}{\sqrt{3}}\Phi_{2s} + \frac{\sqrt{2}}{\sqrt{3}}\Phi_{2p_x}$$

$$\text{Now } \psi_{sp^2} = C_1\Phi_{2s} + C_2\Phi_{2p_x}$$

$$\text{Here, } C_1^2 + C_2^2 = 1$$

$$\left(\frac{1}{\sqrt{3}}\right)^2 + \left(\frac{\sqrt{2}}{\sqrt{3}}\right)^2 = 1$$

If we assume ψ_1 to point towards x-axis, then the contribution of p_y orbital will be zero i.e., $C_1 = 0$

Applying normalization condition for ψ_1 we get $a_1^2 + b_1^2 = 1$

$$\text{Hence } b_1 = \frac{\sqrt{2}}{\sqrt{3}} \text{ as } a_1 = \frac{1}{\sqrt{3}}$$

$$\text{So, } \psi_1 = \psi_{sp^2} = \frac{1}{\sqrt{3}}\Phi_{2s} + \frac{\sqrt{2}}{\sqrt{3}}\Phi_{2p_x}$$

Let us assume the three sp^2 orbitals are

$$\psi_1 = a_1\Phi_s + b_1\Phi_{2p_x} + c_1\Phi_{2p_y}$$

$$\psi_2 = a_2\Phi_s + b_2\Phi_{2p_x} + c_2\Phi_{2p_y}$$

$$\psi_3 = a_3\Phi_s + b_3\Phi_{2p_x} + c_3\Phi_{2p_y}$$

$$\text{For which } a_1^2 + a_2^2 + a_3^2 = 1$$

[As we know s – orbital is spherically symmetrical so $a_1 = a_2 = a_3$]

$$a_1 = a_2 = a_3 = \frac{1}{\sqrt{3}}$$

So, in sp^2 hybridization, the % of s character is 33.33%

Correct option is (c)