CH 3203 End-Semester Examination, 30th April 2019, 14:00 h, 2.5 hrs. Total Marks: 50

1. Let $\{\psi_i, i = 1, M\}$ form a complete set of orthonormal set of functions. Let ***P*** and ***Q*** be two operators such that

$$P = \sum_{i=1}^{k} |\psi_i\rangle\langle\psi_i| \quad \text{and} \quad Q = \sum_{i=k+1}^{M} |\psi_i\rangle\langle\psi_i| \quad ; \quad k < M$$

State if the following statements are True or False, and add a small proof in defense of your answer. **(5)**

Note: An idempotent operator is one whose square is equal to itself. ***I*** *is the identity operator. [No negative marks, but without a correct proof, marks will not be given]*

(a) $P^2 = P$ (Idempotent operator)
(b) (***P***+***Q***) is an Idempotent operator
(c) (***P***+***Q***)(***P***+***Q***) = 2***I***
(d) $P^2 = Q^2 = I$
(e) (***PQ***) = 0

2. Let a square matrix ***A*** commute with a diagonal square matrix ***D*** of the same dimension.

(a) If each of the diagonal elements of ***D*** are distinct, that is, $D_{mm} \neq D_{nn}$ for m ≠ n. Then, show that all off-diagonal matrix elements of ***A*** must vanish. **(2)**
(b) If none of the off-diagonal matrix elements of ***A*** are required to vanish, ***D*** must be a constant matrix. **(2)**

3. (a) Show that if ***P*** is an idempotent operator so is ***I***–***P***. **(1)**

(b) Show that for any orthogonal projector ***P*** and a normalized state with wave function Ψ, **(2)**

$$0 \leq \langle P \rangle \leq 1, \text{ where } \langle P \rangle = \int \Psi^* P \Psi \partial\tau$$

4. (a) List all the elements of D_4 point group. **(1)**

(b) How many classes are there? **(1)**

(c) Using the consequences of Great Orthogonality Theorem, derive the character table for the above group. **(2)**

5. Reduce the following representation into its component irreducible representations. **(5)**

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ	10	4	2	6	0	6

Character table of D_{3h} group:

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)

6. Consider a five-pointed star as follows: **(3)**

(a) What is the principal axis of rotation? How many other C_n axes are there?

(b) How many reflection planes perpendicular to the principal C_n axis?

(c) Is there any center of inversion?

(d) Identify improper rotations, if any?

(e) Identify the point group.

7. Write the group multiplication table of a cyclic group of order 4 with elements E, A, B, C. **(2)**

8. Prove that the order of any subgroup g within a group of order h must be a divisor of h. **(2)**

9. Show that for a heteronuclear diatomic molecule, total kinetic energy can be expressed as sum of kinetic energy terms for its translational and internal motions. **(2)**

10. If Ψ_0, Ψ_1 and Ψ_2 are the vibrational wavefunctions of a molecule, such that $\Psi_0 = c_{00}\phi_0 + c_{01}\phi_1$, $\Psi_1 = c_{10}\phi_0 + c_{11}\phi_1$ and $\Psi_2 = c_{20}\phi_0 + c_{21}\phi_1$, where ϕ_0 and ϕ_1 are harmonic oscillator wavefunctions for $v = 0$ and $v = 1$, respectively. Show that both $\Psi_0 \rightarrow \Psi_1$ and $\Psi_0 \rightarrow \Psi_2$ transitions can in principle be optically allowed. Get an expression for the ratio of two transition probabilities. **(2+1)**

11. Derive the relation between Einstein A and B coefficients for a 2-level system interacting with light. Why is the steady state population ratio (N_1/N_0) independent of light intensity? **(3+1)**

12. Spectral width of both gaseous and solid samples decreases at low temperature. In which case is the decrease expected to be more significant? Explain. **(2)**

13. Cyclopentadienyl anion ($C_5H_5^-$) belongs to D_{5h} point group.

(a) Determine the irreducible representations (IRREPs) of its vibrational modes. **(4)**

(b) How many vibrational modes are IR active? Identify their symmetry (IRREPs). **(1)**

(c) Identify the modes that involve C–H bond stretching. **(2)**

(d) Identify the modes that involve a change in C–C–C bond angle. **(1)**

(e) Do you expect to see C–H and C–C stretching bands in the IR spectrum? **(1)**

(f) Which modes will result in the loss of molecular planarity? Are these modes IR active? **(2)**

Character table of D_{5h}:

D_{5h}	E	$2C_5$	$2(C_5)^2$	$5C'_2$	σ_h	$2S_5$	$2(S_5)^3$	$5\sigma_v$	linear functions, rotations
A'_1	+1	+1	+1	+1	+1	+1	+1	+1	-
A'_2	+1	+1	+1	-1	+1	+1	+1	-1	R_z
E'_1	+2	$+2\cos(2\pi/5)$	$+2\cos(4\pi/5)$	0	+2	$+2\cos(2\pi/5)$	$+2\cos(4\pi/5)$	0	(x, y)
E'_2	+2	$+2\cos(4\pi/5)$	$+2\cos(2\pi/5)$	0	+2	$+2\cos(4\pi/5)$	$+2\cos(2\pi/5)$	0	-
A''_1	+1	+1	+1	+1	-1	-1	-1	-1	-
A''_2	+1	+1	+1	-1	-1	-1	-1	+1	z
E''_1	+2	$+2\cos(2\pi/5)$	$+2\cos(4\pi/5)$	0	-2	$-2\cos(2\pi/5)$	$-2\cos(4\pi/5)$	0	(R_x, R_y)
E''_2	+2	$+2\cos(4\pi/5)$	$+2\cos(2\pi/5)$	0	-2	$-2\cos(4\pi/5)$	$-2\cos(2\pi/5)$	0	-