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March 25 2017
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Answer: Inorganic Chemistry Cumulative Exam  
March 25, 2017

1 (20)  (A, 15) What is the point symmetry group of a cube when a line is drawn across each of its faces in the manner shown on right? (B, 5) Suppose that the line on each face is rotated by 45° in the clockwise direction as viewed from outside, what is the point group? Key symmetry elements must be marked to justify your assignment.

A: \( T_h \); B: \( T_d \)

2. (20) For the group \( T_d \) find to which irreducible representations the sets of functions \((x, y, z)\) and \((R_x, R_y, R_z)\) belong to, respectively. (No guesswork – **must show transformation matrices**)

<table>
<thead>
<tr>
<th>(T_d)</th>
<th>8C(_3)</th>
<th>3C(_2)</th>
<th>6S(_4)</th>
<th>6(\sigma_d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(A_2)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>(E)</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>(T_1)</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>(T_2)</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

\(T_1\): \((R_x, R_y, R_z)\); \(T_2\): \((x, y, z)\)

3. (40 pt) Recently, cyclo-(N\(_2\))\(^3\) was prepared and structurally characterized (Science, 2017, 355, 374-6). Inspired by this report, let us consider hypothetical molecule cyclo-N\(_4\) that is a perfect square. Please (i) reduce the \(\Gamma\)s formed by all \(N-p\)\(_\pi\) orbitals; (ii) construct the SALCs; (iii) deriving its π-MOs, energies, delocalization energy and bond order (between N1 and N2) using symmetry-based Hückel calculation (using \(\beta_{\text{H}}\) as the unit of \(E_{\text{H}}\)).

\[
\begin{align*}
\Gamma &= A_{2u} + B_{1u} + E_g \\
A_{2u} (A) &= \frac{(\phi_1 + \phi_2 + \phi_3 + \phi_4)}{2} = \Psi_1 \\
B_{1u} (B) &= \frac{(\phi_1 - \phi_2 + \phi_3 - \phi_4)}{2} = \Psi_2 \\
E &= \frac{(\phi_1 + \phi_2 - \phi_3 - \phi_4)}{2} \quad \rightarrow \frac{(\phi_1 - \phi_3)}{2} = \Psi_3 \\
&\quad \frac{(\phi_1 - \phi_2 + \phi_3 + \phi_4)}{2} \quad \rightarrow \frac{(\phi_2 - \phi_4)}{2} = \Psi_4 \\
E_{1} &= H_{33} = \alpha_N + 2\beta_{\text{H}} \\
E_{2} &= H_{23} = \alpha_N - 2\beta_{\text{H}} \\
E_{3} &= E_{4} = H_{33} = \alpha_N \\
E_{\pi} &= 4\beta_{\text{H}} \quad \Rightarrow \ E_{\text{delocalization}} = 0; \quad \text{BO (N-N) = 0.5}
\end{align*}
\]

4. (20) Consider a six coordinated V\(^{3+}\) complex of an effective \(D_3\) symmetry. (i) Derive the free ion ground state term symbol (5 pt). (ii) Determine the ligand field term symbols originated from the ground state free ion term (15 pt).

\(V^{3+}, d^2 \rightarrow ^3F\) ground state term; Using \(\chi(\alpha) = \sin(L+1/2)\alpha/\sin(1/2\alpha), \quad ^3F \rightarrow ^3(A_1 + 2A_2 + 2E)\)
Physical Chemistry CUME
March 25th 2017

Topic: Quantum Mechanics

1. (70 points) The following questions pertain to a quantum harmonic oscillator.

(a) (15 points) $\psi_0$ and $\psi_1$ are normalized eigenfunctions for the $n = 0$ and $n = 1$ eigenstate.
Verify that $\psi_0$ and $\psi_1$ are orthogonal to each other.

(b) (10 points) Evaluate expectation values of momentum and position, $<p>$ and $<x>$, for the $n = 0$
state.

(c) (15 points) Evaluate $\sigma_x \sigma_p$ for $n = 0$ state.

(d) (10 points) A particle is described by a wavefunction that is a linear combination of the $n = 0$
and $n = 1$ eigenfunctions has the form $\Psi = \frac{1}{\sqrt{2}} (2\psi_0 + \psi_1)$. Please calculate the expectation
value of energy $<E>$ for this particle.

(e) (20 points) Determine whether or not the transition from $n = 0$ to $n = 1$ eigenstate is optically
allowed.

Useful Information:

$$\sigma_A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}, \quad \langle A \rangle = \langle n \mid \hat{A} \mid n \rangle = \int \Psi_n^* \hat{A} \Psi_n \, dx$$
if $V(x) = ax^n$, then $\frac{\langle V \rangle}{\langle K \rangle} = \frac{2}{n}$

$$\psi_0 = N_0 e^{-\frac{x^2}{2\sigma^2}} \quad \psi_1 = N_0 \sqrt{2} \left(\frac{x}{\sigma}\right) e^{-\frac{x^2}{2\sigma^2}} \quad N_0 = \left(\frac{m\omega}{\pi \hbar}\right)^{1/4} \quad \sigma = \sqrt{\frac{\hbar}{m\omega}} \quad E_n = \hbar\omega(n + \frac{1}{2})$$

$$\hat{p} = -i\hbar \frac{d}{dx} \quad \hat{a} = \frac{m\omega \hat{x} + i\hbar \hat{p}}{\sqrt{2m\hbar\omega}} \quad \hat{a}^\dagger = \frac{m\omega \hat{x} - i\hbar \hat{p}}{\sqrt{2m\hbar\omega}} \quad \int_0^\infty e^{-ax^2} \, dx = \frac{\sqrt{\pi}}{a} \quad \int_0^\infty xe^{-ax^2} \, dx = \frac{1}{2a^2} \quad \mu_{fi} = \langle f \mid \hat{\mu} \mid i \rangle = \langle f \mid e\hat{x} \mid i \rangle$$

$$\int_0^\infty x^4 e^{-ax^2} \, dx = \frac{3}{8} \sqrt{\frac{\pi}{a^5}} \quad \int_0^\infty x^2 e^{-ax^2} \, dx = \frac{1}{4} \sqrt{\frac{\pi}{a^3}} \quad \int_0^\infty x^3 e^{-ax^2} \, dx = \frac{1}{2a^2} \quad \mu_{fi} = \langle f \mid \hat{\mu} \mid i \rangle = \langle f \mid e\hat{x} \mid i \rangle$$

2. (30 points) The following questions pertain to a hydrogen atom whose electron is in the 3d excited
state.

(a) (10 points) What are all the possible values of the quantum numbers $n$, $l$, $m_n$ and $m_l$ for such
an excited H atom?

(b) (10 points) What is the root-mean-squared magnitude of the orbital angular momentum $\sqrt{< L^2 >}$
for the electron? Please express in terms of $\hbar$.

(c) (10 points) What are the possible values for the projection of the orbital angular
momentum on the z axis, also known as $L_z$? Please express in terms of $\hbar$.

$$\langle L^2 \rangle = l(l+1) \hbar^2 \quad \langle L_z \rangle = m_e \hbar$$
1. (a) \[ \int_{-\infty}^{\infty} \psi_0^* \psi_1 \, dx \]

\[ = N_0^2 \int_{-\infty}^{\infty} \left( e^{-\frac{x^2}{2\sigma^2}} \right) \left[ \frac{x^2}{\sigma^2} e^{-\frac{x^2}{2\sigma^2}} \right] \, dx \]

\[ = N_0^2 \int_{-\infty}^{\infty} \text{odd function} \, dx \]

\[ = 0 \]

\( \psi_0 \) and \( \psi_1 \) are orthogonal to each other.

(b) \[ \langle \rho \rangle = \int_{-\infty}^{\infty} \psi_0^* \left( -i \hbar \frac{2}{dx} \right) \psi_0 \, dx \]

\[ = i \hbar N_0^2 \int_{-\infty}^{\infty} e^{-\frac{x^2}{2\sigma^2}} \left[ \frac{x}{\sigma^2} e^{-\frac{x^2}{2\sigma^2}} \right] \, dx \]

\[ = 0 \]

\[ \langle \chi \rangle = \int_{-\infty}^{\infty} \psi_0^* \chi \psi_0 \, dx \]

\[ \text{even odd even} \]

\[ = 0 \]

('alternatively, you can also use \( \hat{a}^\dagger, \hat{a} \)')
(c) Virial theorem \( \langle V \rangle = \langle k \rangle = \frac{\langle \mathcal{E} \rangle}{2} \)

for \( n = 0 \) \( \langle V \rangle = \langle k \rangle = \frac{1}{4} \hbar \omega \)

\[
\langle k \rangle = \frac{\langle p^2 \rangle}{2m} = \frac{\hbar \omega}{4}, \quad \langle p^2 \rangle = \frac{1}{2} m \hbar \omega
\]

\[
\langle V \rangle = \frac{1}{2} m \omega^2 \langle x^2 \rangle = \frac{\hbar \omega}{4}
\]

\[
\langle x^2 \rangle = \frac{\hbar}{2m \omega}
\]

\[6p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \sqrt{\frac{m \hbar \omega}{2}}\]

\[6x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\frac{\hbar}{2m \omega}}\]

\[6p \cdot 6x = \frac{\hbar}{2}\]

(d) \( \langle E \rangle = \langle \Psi | \hat{H} | \Psi \rangle \)

\[= \langle \begin{pmatrix} \frac{1}{5} \left( 2 \mathcal{E}_0 + \mathcal{E} \right) \\ \mathcal{E}_0 \mathcal{E}_0 \end{pmatrix} | \hat{H} | \begin{pmatrix} \frac{1}{5} \left( 2 \mathcal{E}_0 + \mathcal{E} \right) \\ \mathcal{E}_0 \mathcal{E}_0 \end{pmatrix} \rangle\]

\[= \frac{1}{5} \langle \begin{pmatrix} \mathcal{E}_0 \mathcal{E}_0 \mathcal{E}_0 \mathcal{E}_0 \mathcal{E} \end{pmatrix} | \begin{pmatrix} \mathcal{E}_0 \mathcal{E}_0 \mathcal{E}_0 \mathcal{E}_0 \mathcal{E} \end{pmatrix} \rangle\]

\[= \frac{1}{5} \left( 4 \mathcal{E}_0 \mathcal{E}_0 \mathcal{E}_0 + 2 \mathcal{E}_0 \mathcal{E}_0 \mathcal{E}_0 \mathcal{E}_0 \mathcal{E}_0 \right) + \frac{3}{5} \frac{\hbar \omega}{2}\]

\[= \frac{1}{5} \left( 4 \mathcal{E}_0 + \mathcal{E}_0 \right) = \frac{1}{5} \left( \frac{4 \mathcal{E}_0 \omega}{2} + \frac{3}{2} \hbar \omega \right) = \frac{7}{10} \hbar \omega\]
\[ M_{01} = e \int_{-\infty}^{\infty} \psi_0^* \cdot \hat{L} \cdot \psi_1 \, dx \]
\[ = e \int_{-\infty}^{\infty} \psi_0^* \cdot \mathbf{r} \cdot \psi_1 \, dx \]
\[ = e \int_{-\infty}^{\infty} \text{even function} \, dx \]
\[ \neq 0 \quad \text{transition is allowed.} \]

2. (a) H atom in 3d orbital

- \( n = 3 \)
- \( l = 2 \)
- \( m_l = 0, \pm 1, \pm 2 \)
- \( m_s = \pm \frac{1}{2} \)

(b) \[ \sqrt{2l^2} = \sqrt{2 \times 2 + 1} = \sqrt{6} \, h = \sqrt{\frac{3}{2} \times (2 + 1)} = \sqrt{6} \, h \]

(C) \[ L_z = 2h, \, h, \, 0, \, -h, \, -2h \]