Answers: Key Points

1. (a) Postulate 1 and 2 $(P_z)_{\text{operator}} = \frac{\hbar}{i}\frac{\partial}{\partial z}$
   (b) Ψ must be single-valued, finite, continuous
   (c) Ψ must be single-valued.
   You are given when the function is zero! use it.
   (d) Ψ must be single-valued.

2. superposition of states, that is, an arbitrary function can be written as a linear combination of a complete orthonormal set.
   The eigenfunctions of a Hermitian operator (S_z here) form a complete orthonormal set.
   Postulate 3. ($\langle S_x \rangle$ in this case)
   For a linear operator, $O_{op} c\psi = c\, O_{op}\psi$ if c = scalar constant
   Normalization (Here $c_1^2 + c_2^2 = 1$) and probability of each of the outcomes.

3. Postulate 3. ($\langle E_{SO} \rangle$ in this case)
   Vector addition $\vec{l} + \vec{s} = \vec{j}$
   Square of a sum of two vector operators
   $$\vec{j}_{op}^{\,2} = (\vec{l}_{op} + \vec{s}_{op})^2 = l_{op}^2 + s_{op}^2 + 2\,\vec{l}_{op}\cdot\vec{s}_{op}$$
   Properties of angular momentum: For example eigenvalues of square are $j(j+1)\hbar^2$

The rest is only algebra.

CHEMISTRY 542

First Exam Answers

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① a) $-\frac{\hbar^2}{2m}\frac{d^2\psi(z)}{dz^2} + mgz\,\psi(z) = E\,\psi(z)$

b) Boundary conditions: $\psi(z=0) = 0$ (single-valued since $\psi(z<0)$ must be zero)

also, $\psi(z=\infty) = 0$ (finite)

c) When $z = 0$, ψ must be zero

$$q = [2m^2g/\hbar^2]^{1/3}\Big[\underset{\uparrow}{0} - \frac{E}{mg}\Big]$$

set z to zero

∴ For these values of q, ψ must be zero

But we are given the values of q at which ψ is zero, therefore

$$\alpha_1 = [2m^2g/\hbar^2]^{1/3}\Big[0 - \frac{E}{mg}\Big]$$

or α_2

or α_3 etc. Once again, we find that single-valued criterion provides the values of E:

$$\alpha_n = [2m^2g/\hbar^2]^{1/3}\Big[0 - \frac{E_n}{mg}\Big]$$

Therefore the eigenvalues are

$$E_n = (-\alpha_n)\left(\frac{mg^2\hbar^2}{2}\right)^{1/3}$$

d) Once again, insist that the function be single-valued so that we need the condition that will make the function vanish at $z=0$:

$$\sin\Big\{\underbrace{\frac{2}{3}|q|^{3/2} + \frac{\pi}{4}}\Big\} = 0$$

Can only happen if this is $\pi, 2\pi, 3\pi, \cdots$

$$\therefore \frac{2}{3}\left|\frac{q}{\beta}\right|^{3/2} + \frac{\pi}{4} = \pi, 2\pi, 3\pi, \text{ or} \ldots n\pi \text{ in general}$$

where $n = 1, 2, 3, \ldots$

$$\left|\frac{q}{\beta}\right|^{3/2} = \frac{3\pi}{2}\left(n - \frac{1}{4}\right)$$ gives the values of q for which the soln vanishes

$$\therefore \alpha_n = -\left[\frac{3}{2}\pi\left(n-\frac{1}{4}\right)\right]^{2/3}$$

$$E_n = \left[\frac{3}{2}\pi\left(n-\frac{1}{4}\right)\right]^{2/3}\left(\frac{mg^2\hbar^2}{2}\right)^{1/3} = \frac{1}{2}\left(9\pi^2 mg^2\hbar^2\right)^{1/3}\left(n-\frac{1}{4}\right)^{2/3}$$

(2) Let ψ = eigenfunction of $S_x = c_1\alpha + c_2\beta$, that is, expand unknown ψ in the complete orthonormal set

$$S_x\psi = S_x(c_1\alpha + c_2\beta) = c_1\underbrace{S_x\alpha}_{\text{given } \frac{1}{2}\hbar\beta} + c_2\underbrace{S_x\beta}_{\text{given } \frac{1}{2}\hbar\alpha} = c_1\tfrac{1}{2}\hbar\beta + c_2\tfrac{1}{2}\hbar\alpha = \tfrac{1}{2}\hbar(c_1\beta + c_2\alpha),$$

We see that if $c_1 = c_2$, we would get the same function back and if $c_1 = -c_2$ we would get the same function back but only with a minus sign

$$\therefore S_x(\alpha+\beta) = \left(\tfrac{1}{2}\hbar\right)(\alpha+\beta) \quad \text{or} \quad S_x(\alpha-\beta) = \left(-\tfrac{1}{2}\hbar\right)(\alpha-\beta)$$

Now we have the eigenfunctions of S_x, except we need to normalize them: $\frac{\alpha+\beta}{\sqrt{2}}$ and $\frac{\alpha-\beta}{\sqrt{2}}$

And the eigenvalues have been found: $+\frac{1}{2}\hbar$ $\quad -\frac{1}{2}\hbar$

$\langle S_x \rangle$ for a state described by function α

is $\langle S_x\rangle = \int \alpha^* \underbrace{S_x\alpha}_{\frac{1}{2}\hbar\beta} d\tau = 0$ since $\int\alpha^*\beta = 0$. Get zero average value, means observe $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$ eigenvalues equally (50% each)

Answer equal intensities.

Another way to get 50% each from state α is to expand α in terms of the complete orthonormal set of S_x eigenfunctions

Let $\alpha = a_1\left[\frac{\alpha+\beta}{\sqrt{2}}\right) + a_2\left(\frac{\alpha-\beta}{\sqrt{2}}\right]$, find a_1 and a_2

Operate on both sides by $\int\left(\frac{\alpha+\beta}{\sqrt{2}}\right)^* d\tau$ to get

$$\int\left(\frac{\alpha+\beta}{\sqrt{2}}\right)^*\alpha\, d\tau = a_1 \cdot 1 + a_2 \cdot 0$$

1 ← normalized; 0 ← orthogonal

$$= \frac{1}{\sqrt{2}}\underbrace{\int \alpha^*\alpha\, d\tau}_{\substack{\text{normalized} \\ 1}} + \frac{1}{\sqrt{2}}\underbrace{\int \beta^*\alpha\, d\tau}_{\substack{\text{orthogonal} \\ 0}} \qquad \therefore a_1 = \frac{1}{\sqrt{2}}$$

Will also find $a_2 = \frac{1}{\sqrt{2}}$

$$\int\left(\frac{\alpha-\beta}{\sqrt{2}}\right)^*\alpha\, d\tau = a_1 \cdot 0 + a_2 \cdot 1$$

$$= \frac{1}{\sqrt{2}}\underbrace{\int \alpha^*\alpha\, d\tau}_{1} - \frac{1}{\sqrt{2}}\underbrace{\int \beta^*\alpha\, d\tau}_{0} \qquad \therefore a_2 = \frac{1}{\sqrt{2}}$$

$$\therefore \alpha = \frac{1}{\sqrt{2}}\underbrace{\left[\frac{\alpha+\beta}{\sqrt{2}}\right]}_{\substack{S_x \text{ eigenfunction} \\ \text{with eigenvalue} \\ +\frac{1}{2}\hbar}} + \frac{1}{\sqrt{2}}\underbrace{\left[\frac{\alpha-\beta}{\sqrt{2}}\right]}_{\substack{S_x \text{ eigenfunction} \\ \text{with eigenvalue} \\ -\frac{1}{2}\hbar}}$$

$$\langle S_x \rangle = \int \alpha^* S_x \alpha\, d\tau = \underbrace{\left(\frac{1}{\sqrt{2}}\right)^2}_{\substack{\frac{1}{2} \text{ of the time} \\ \text{get } +\frac{1}{2}\hbar}}\left(+\frac{1}{2}\hbar\right) + \underbrace{\left(\frac{1}{\sqrt{2}}\right)^2}_{\substack{\text{other } \frac{1}{2} \text{ of the time} \\ \text{get } -\frac{1}{2}\hbar}} \cdot \left(-\frac{1}{2}\hbar\right)$$

③ $E_{SO} = \int \Psi^*_{lsjm_j} \xi(r) \frac{\vec{l}\cdot\vec{s}}{\hbar^2} \Psi_{lsjm_j} \, d\tau$

$$= \underbrace{\alpha^2 Z \langle a_0^3/r^3 \rangle_{nl} \frac{e^2}{2a_0}}_{\text{given}} \langle ls;jm_j | \frac{\vec{l}\cdot\vec{s}}{\hbar^2} | ls;jm_j \rangle$$

To get $(\vec{l}\cdot\vec{s})_{op}$

$\vec{j}^2_{op} = (\vec{l}_{op} + \vec{s}_{op})^2 = l^2_{op} + s^2_{op} + 2(\vec{l}\cdot\vec{s})_{op}$

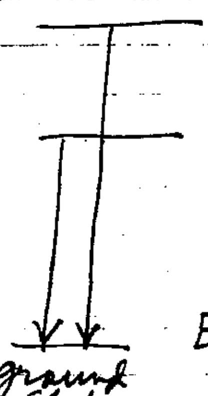
$\therefore (\vec{l}\cdot\vec{s})_{op} = (j^2_{op} - l^2_{op} - s^2_{op})/2$

$$E_{SO} = \alpha^2 Z \langle a_0^3/r^3 \rangle_{nl} \frac{e^2}{2a_0} \underbrace{\langle ls;jm_j | \frac{j^2_{op} - l^2_{op} - s^2_{op}}{2\hbar^2} | ls;jm_j \rangle}_{\frac{j(j+1) - l(l+1) - s(s+1)}{2}}$$

For the specific case of $s = \frac{1}{2}$, $l = l$, $\Rightarrow j = l + \frac{1}{2}$ or $j = l - \frac{1}{2}$

$j = l + \frac{1}{2}$: $\frac{(l+\frac{1}{2})(l+\frac{1}{2}+1) - l(l+1) - \frac{1}{2}(\frac{1}{2}+1)}{2} = \frac{l}{2}$

$j = l - \frac{1}{2}$: $\frac{(l-\frac{1}{2})(l-\frac{1}{2}+1) - l(l+1) - \frac{1}{2}(\frac{1}{2}+1)}{2} = \frac{-l-1}{2}$



Upper $^2P_{l+\frac{1}{2}}$ $\quad E = E^{(0)}_{2p} + E_{SO} = E^{(0)} + \alpha^2 Z \langle a_0^3/r^3 \rangle_{nl} \frac{e^2}{2a_0} \cdot \frac{l}{2}$

$^2P_{l-\frac{1}{2}}$ $\quad E = E^{(0)}_{2p} + E_{SO} = E^{(0)} + \alpha^2 Z \langle a_0^3/r^3 \rangle_{nl} \frac{e^2}{2a_0} \cdot \frac{(-l-1)}{2}$

difference is

$\Delta E_{SO} = \alpha^2 Z \langle a_0^3/r^3 \rangle_{nl} \frac{e^2}{2a_0} \frac{l-(-l-1)}{2}$

$= \alpha^2 Z \langle a_0^3/r^3 \rangle_{nl} \frac{e^2}{2a_0} (l + \frac{1}{2})$

$^2S_{1/2}$ ground state $\quad E = E^{(0)}_{2s}$

which is the equation of Barnes and Smith.

$1s^2 2s^2 2p^6 3s$

For Na it is $^2P_{3/2}$, $^2P_{1/2} \longrightarrow {}^2S_{1/2}$ which is the D line (a doublet)

the splitting is: use $Z_{eff} = 11 - 3 = 8$, $l = 1$

$\Delta E_{SO} = \left(\frac{1}{137}\right)^2 (8) \langle \frac{a_0^3}{r^3} \rangle_{3p} \; 13.6\,\text{eV} * \frac{8066.\,\text{cm}^{-1}}{1\,\text{eV}} (1 + \frac{1}{2}) = 17.\text{cm}^{-1}$

$\langle a_0^3/r^3 \rangle_{3p} = .245$ for Na

For Mg use $Z_{eff} = 12-3 = 9$, $l=1$

$$\Delta E_{SO} = \left(\frac{1}{137}\right)^2 (9) \left\langle a_0^3/r^3 \right\rangle_{3p} 13.6 \times 8066 \cdot \left(1+\tfrac{1}{2}\right) = 60.8$$

$$\left\langle a_0^3/r^3 \right\rangle_{3p} = 0.77 \quad \text{for Mg}$$

For Al use $Z_{eff} = 13-3 = 10$, $l=1$

$$\Delta E_{SO} = \left(\frac{1}{137}\right)^2 (10) \left\langle a_0^3/r^3 \right\rangle_{3p} 13.6 \times 8066 \left(1+\tfrac{1}{2}\right) = 112.0$$

$$\left\langle a_0^3/r^3 \right\rangle_{3p} = 1.28 \quad \text{for Al}$$

For Si use $Z_{eff} = 14-3 = 11$, $l=1$

$$\Delta E_{SO} = \left(\frac{1}{137}\right)^2 (11) \left\langle a_0^3/r^3 \right\rangle_{3p} 13.6 \times 8066 \left(1+\tfrac{1}{2}\right) = 223.3$$

$$\left\langle a_0^3/r^3 \right\rangle_{3p} = 2.315 \quad \text{for Si}$$

For S use $Z_{eff} = 16-3 = 13$, $l=1$

$$\Delta E_{SO} = \left(\frac{1}{137}\right)^2 (13) \left\langle a_0^3/r^3 \right\rangle_{3p} 13.6 \times 8066 \left(1+\tfrac{1}{2}\right) = 573.6$$

gives $\left\langle a_0^3/r^3 \right\rangle_{3p} = 5.03$ for S

For Cl $Z_{eff} = 17-3 = 14$ $l=1$

$$\Delta E_{SO} = \left(\frac{1}{137}\right)^2 (14) \left\langle a_0^3/r^3 \right\rangle_{3p} 13.6 \times 8066 \left(1+\tfrac{1}{2}\right) = 881.0$$

gives $\left\langle a_0^3/r^3 \right\rangle_{3p} = 7.18$ for Cl