CHEMISTRY 542

ANSWERS to Exam II

November 8, 2004

In applying the principles of Quantum Mechanics in answering each question, be sure to <u>state the principle you are using at each step</u>.

1. Given the complete orthonormal set of functions $\{\alpha, \beta, \gamma\}$ which are eigenfunctions of the z component of angular momentum I_z with eigenvalues $\hbar$, $-\hbar$, and 0 respectively. The operators I_- and I_+ have the following properties:

$I_-\alpha = \sqrt{2}\,\hbar\,\gamma \qquad I_+\alpha = 0$

$I_-\gamma = \sqrt{2}\,\hbar\,\beta \qquad I_+\gamma = \sqrt{2}\,\hbar\,\alpha$

$I_-\beta = 0 \qquad I_+\beta = \sqrt{2}\,\hbar\,\gamma$

$I_x = (I_+ + I_-)/2 \qquad I_y = (I_+ - I_-)/2i$

(a) Find the matrix representation of the operators I_+, I_-, I_z, I_x, and I_y in this basis set.

ANSWER

$I_+ \quad = \quad \sqrt{2}\,\hbar$

	β	γ	α
β	0	0	0
γ	1	0	0
α	0	1	0

$I_- \quad = \sqrt{2}\,\hbar$

	β	γ	α
β	0	1	0
γ	0	0	1
α	0	0	0

$I_z \quad = \hbar$

	β	γ	α
β	-1	0	0
γ	0	0	0
α	0	0	1

$I_x \quad = \frac{1}{2}(I_+ + I_-) = \frac{1}{2}\sqrt{2}\,\hbar$

	β	γ	α
β	0	1	0
γ	1	0	1
α	0	1	0

$I_y \quad = \frac{1}{2}(I_+ - I_-) = \sqrt{2}\hbar/2i$

	β	γ	α
β	0	-1	0
γ	1	0	-1
α	0	1	0

(b) Find the eigenvalues of the I_x operator.

ANSWER

In units of ½√2 $\hbar$

$I_x \, \Psi = \lambda\Psi$

Use the matrix representation

$$\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \begin{vmatrix} c_1 \\ c_2 \\ c_3 \end{vmatrix} = \lambda \begin{vmatrix} c_1 \\ c_2 \\ c_3 \end{vmatrix}$$

Do matrix multiplication:

row 1 $0c_1+1c_2+0c_3 = \lambda\, c_1$

row 2 $0c_1+1c_2+0c_3 = \lambda\, c_2$

row 3 $0c_1+1c_2+0c_3 = \lambda\, c_3$

Rearrange:

$(0-\lambda)c_1 + 1c_2 + 0c_3 = 0$

$1c_1 + (0-\lambda)c_2 + 1c_3 = 0$

$0c_1 + 1c_2 + (0-\lambda)c_3 = 0$

Simultaneous equations will have a non-trivial solution (that is, other than $c_1=c_2=c_3=0$) if and only if the determinant of the coefficients of the unknowns equals zero.

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

Expanding in terms of row 1:

$$-\lambda \det \begin{bmatrix} 0-\lambda & 1 \\ 1 & 0-\lambda \end{bmatrix} \qquad -1 \det \begin{bmatrix} 1 & 1 \\ 1 & 0-\lambda \end{bmatrix} = 0$$

leads to

$-\lambda(\lambda^2-1) - 1(-\lambda) = 0$; or $-\lambda^3 + 2\lambda = 0$; or $\lambda\,(\lambda^2-1) = 0 \rightarrow$ roots are $\lambda=0$, $\lambda=\pm\sqrt{2}$ in units of ½√2 $\hbar$. Therefore the eigenvalues are 0, $\hbar$, and $-\hbar$.

(c) Find the eigenfunctions of the I_x operator.

ANSWER

The simultaneous equations are: where the coefficients c_1, c_2, c_3 are the coefficients of β, γ, α, respectively

$(0-\lambda)c_1 + (1)c_2 + (0)c_3 = 0$ (1)

$(1)c_1 + (0-\lambda)c_2 + (1)c_3 = 0$ (2)

$(0)c_1 + (1)c_2 + (0-\lambda)c_3 = 0$ (3)

Normalization is $c_1^2 + c_2^2 + c_3^2 = 1$

Into these, substitute the first $\lambda=0$ to find its corresponding eigenfunction.

(1) $0 \cdot c_1 + c_2 = 0$ which gives $c_2 = 0$

(2) $c_1 + 0 \cdot c_2 + c_3 = 0$ which gives $c_1 + c_3 = 0$ or $c_1 = -c_3$

Normalization gives $c_1^2 + 0 + (-c_1)^2 = 1$. which gives $c_1 = \pm 1/\sqrt{2}$.

These give $c_2 = 0$, $c_3 = 1/\sqrt{2}$ and $c_1 = -1/\sqrt{2}$; $\Psi = (1/\sqrt{2}) \cdot \{\alpha - \beta\}$ for eigenvalue 0

Next substitute $\lambda = \sqrt{2}$ into the equations to find its corresponding eigenfunction.

(1) $-\sqrt{2}c_1 + c_2 = 0$ from which, $\sqrt{2}c_1 = c_2$ (2) $c_1 - \sqrt{2}c_2 + c_3 = 0$ from which $c_3 = c_1$

Normalization $c_1^2 + c_2^2 + c_3^2 = 1$ gives $4c_1^2 = 1$, so that $c_1 = c_3 = ½$; $c_2 = 1/\sqrt{2}$

$\Psi = \{ ½(\beta + \alpha) + (1/\sqrt{2})\gamma \}$ for eigenvalue $\hbar$

Finally, substitute $\lambda = -\sqrt{2}$ into the equations to find its corresponding eigenfunction.

(1) $\sqrt{2}c_1 + c_2 = 0$ which gives $c_2 = -\sqrt{2}c_1$ and (3) gives $c_2 + \sqrt{2}c_3 = 0$ which gives

$c_3 = c_1$ and normalization gives $c_1^2 + 2c_1^2 + c_1^2 = 1$ so that $c_1 = ½$

Thus, $c_3 = ½$, $c_2 = -1/\sqrt{2}$. $\Psi = \{ ½(\beta + \alpha) - (1/\sqrt{2})\gamma \}$ for eigenvalue $-\hbar$.

(d) Suppose it is found that the system is described by the state function:

$$\Psi = 2^{-1/2}\alpha + \tfrac{1}{2}\gamma + \tfrac{1}{2}\beta$$

What values would result from a measurement of I_z on this system?

ANSWER

Since the eigenfunctions $\{\alpha, \beta, \gamma\}$ are all represented in this state, then values that would result from a measurement of I_z on this system are $\hbar$, $-\hbar$, and 0 with probabilities ½ for $\hbar$, ¼ for $-\hbar$, and ¼ for 0 (Since we can see that the function is normalized.).

What is the expected average of a series of measurements of I_x on a system described by Ψ ?

ANSWER

Using the postulate on expectation values, $\langle I_x \rangle = \int \Psi^* I_x \Psi \, d\tau$, where Ψ is normalized.

$\langle I_x \rangle = \int (2^{-1/2}\alpha + \tfrac{1}{2}\gamma + \tfrac{1}{2}\beta)^* I_x \ (2^{-1/2}\alpha + \tfrac{1}{2}\gamma + \tfrac{1}{2}\beta) \, d\tau$

$= \int (2^{-1/2}\alpha + \tfrac{1}{2}\gamma + \tfrac{1}{2}\beta)^* (I_+ + I_-)/2 \ (2^{-1/2}\alpha + \tfrac{1}{2}\gamma + \tfrac{1}{2}\beta) \, d\tau$

From the given relations on page 1, we get

$\langle I_x \rangle = \tfrac{1}{2} \int (2^{-1/2}\alpha + \tfrac{1}{2}\gamma + \tfrac{1}{2}\beta)^* \ (2^{-1/2}0 + \tfrac{1}{2}\sqrt{2}\,\hbar\,\alpha + \tfrac{1}{2}\sqrt{2}\,\hbar\,\gamma) \, d\tau$

$+ \tfrac{1}{2} \int (2^{-1/2}\alpha + \tfrac{1}{2}\gamma + \tfrac{1}{2}\beta)^* \ (2^{-1/2}\sqrt{2}\,\hbar\,\gamma + \tfrac{1}{2}\sqrt{2}\,\hbar\,\beta + \tfrac{1}{2}0) \, d\tau$

$= \tfrac{1}{2}\{\tfrac{1}{2}\hbar + \tfrac{1}{4}\sqrt{2}\,\hbar\} + \tfrac{1}{2}\{\tfrac{1}{4}\sqrt{2}\,\hbar + \tfrac{1}{2}\hbar\} = \tfrac{1}{4}\sqrt{2}\,\hbar + \tfrac{1}{2}\hbar$

2. The matrix representations of χ, χ^2 and χ^4 in the basis of the complete orthonormal set of harmonic oscillator eigenfunctions $\{\varphi_0, \varphi_1, \varphi_2, \varphi_3, \ldots\}$ are given by: (where $a = \hbar/4\pi\nu_e\mu$), and the corresponding energy eigenvalues are $(v+½)\hbar\nu_e$

$\chi = a^{½}$

0	$\sqrt{1}$	0	0	0	...
$\sqrt{1}$	0	$\sqrt{2}$	0	0	...
0	$\sqrt{2}$	0	$\sqrt{3}$	0	...
0	0	$\sqrt{3}$	0	$\sqrt{4}$	...
...	...	...	...	...	...

$\chi^2 = a$

1	0	$\sqrt{2}$	0	0	0	0	0	...
0	3	0	$\sqrt{6}$	0	0	0	0	...
$\sqrt{2}$	0	5	0	$\sqrt{12}$	0	0	0	...
0	$\sqrt{6}$	0	7	0	$\sqrt{20}$	0	0	...
0	0	$\sqrt{12}$	0	9	0	$\sqrt{30}$	0	...
...	...	...	...	...	...	...	...	...

$\chi^4 = a^2$

3	0	$6\sqrt{2}$	0	$\sqrt{24}$	0	0	0	...
0	15	0	$10\sqrt{6}$	0	$\sqrt{120}$	0	0	...
$6\sqrt{2}$	0	39	0	$14\sqrt{12}$	0	$\sqrt{360}$	0	...
0	$10\sqrt{6}$	0	75	0	$18\sqrt{20}$	0	$\sqrt{840}$	...
$\sqrt{24}$	0	$14\sqrt{12}$	0	123	0	$\sqrt{1680}$	0	...
...	...	...	...	...	...	...	...	...

Suppose a harmonic oscillator is placed in an electric field, i.e., perturbed by $\hbar = c\,\chi$ where c is a constant,
what is the energy of the v=2 level in the presence of the perturbation? Provide an answer that is correct to second order.

ANSWER

$\mathcal{H} = \mathcal{H}^{(0)} + \boldsymbol{h}$ given $E_v^{(0)} = (v+½)\hbar\nu_e$ and $\Psi_v^{(0)}$ = harmonic oscillator

$E = E^{(0)} + E^{(1)} + E^{(2)}$

Use v quantum number as the index to indicate member of basis set:

$E_2^{(0)} = (2+½)\hbar\nu_e$ (given)

Since non-degenerate, $E_2^{(1)} = \boldsymbol{h}_{22} = 0$ (read from the first matrix)

Summing up over all v≠2, $E_2^{(2)} = \sum_v - |\boldsymbol{h}_{2v}|^2/[\varepsilon_v - \varepsilon_2]$

There are only two non-zero matrix elements of $\boldsymbol{h}$ matrix for each level.

For v=2 there are only v=1 and v=3 that have $\boldsymbol{h}$ matrix elements that are non-zero: $\boldsymbol{h}_{21} = \sqrt{2}\, c\boldsymbol{a}^{½}$, and $\boldsymbol{h}_{23} = \sqrt{3}\, c\boldsymbol{a}^{½}$. And $\varepsilon_v = (v+½)\hbar\nu_e$

$$E_2^{(2)} = \frac{-|\boldsymbol{h}_{21}|^2}{[(3/2)-(5/2)]\,\hbar\nu_e} \quad \frac{-|\boldsymbol{h}_{23}|^2}{[(7/2)-(5/2)]\,\hbar\nu_e} \quad = -c^2\boldsymbol{a}\{-2+3\}/\hbar\nu_e = -c^2\boldsymbol{a}/\hbar\nu_e$$

$$E_2 = (2+½)\hbar\nu_e + 0 \;- c^2\boldsymbol{a}/\hbar\nu_e$$

What is the wavefunction for this level, correct to first order?

ANSWER

$\Psi_2 = \Psi_2^{(0)} + \Psi_2^{(1)}$

where $\Psi_2^{(0)} = \varphi_2$

$$\text{and } \Psi_2^{(1)} = \frac{-\boldsymbol{h}_{21}}{[(3/2)-(5/2)]\,\hbar\nu_e}\varphi_1 \quad \frac{-\boldsymbol{h}_{23}}{[(7/2)-(5/2)]\,\hbar\nu_e}\varphi_3 \quad = \frac{\{\sqrt{2}\varphi_1 - \sqrt{3}\varphi_3\}\times c\boldsymbol{a}^{½}}{\hbar\nu_e}$$

$$\Psi_2 = \varphi_2 + \frac{\{\sqrt{2}\varphi_1 - \sqrt{3}\varphi_3\}\times c\boldsymbol{a}^{½}}{\hbar\nu_e}$$

3. Using the complete orthonormal basis set $\{\varphi_1, \varphi_2, \varphi_3, \varphi_4\}$, the **H** matrix for a physical system is given by:

H =

-7	-3	0	0
-3	-9	0	0
0	0	-7	-7
0	0	-7	-9

Find the energy eigenvalues and the eigenfunctions of this system.

ANSWER

Solve the problem **H** Ψ=E Ψ in matrix representation.
Write out the results of matrix multiplication:

$$H_{11}c_1+H_{12}c_2+H_{13}c_3+H_{14}c_4=Ec_4$$
$$H_{21}c_1+H_{22}c_2+H_{23}c_3+H_{24}c_4=Ec_4 \qquad \text{etc.}$$

These form a set of simultaneous linear equations in the unknowns c_1, c_2, c_3, c_4:

$$(H_{11}-E)c_1+H_{12}c_2 \quad +H_{13}c_3+H_{14}c_4=0$$
$$H_{21}c_1 \quad +(H_{22}-E)c_2+H_{23}c_3+H_{24}c_4=0 \qquad \text{etc.}$$

which have non-trivial solutions <u>if and only if</u> the determinant of the coefficients of the unknowns equals zero.
We see that we can do the 2x2 blocks separately.

$$\det \begin{vmatrix} -7-E & -3 \\ -3 & -9-E \end{vmatrix} =0$$

Solve for E: $(-7-E)(-9-E) = 9$; $E = ½\{-16\pm[16^2-4(54)]^{1/2}\}$
$E = -8\pm(10)^{1/2} = -4.838$ and -11.162

$$\det \begin{vmatrix} -7-E & -7 \\ -7 & -9-E \end{vmatrix} =0$$

Solve for E: $(-7-E)(-9-E) = 49$; $E = ½\{-16\pm[16^2-4(14)]^{1/2}\}$
$E = -8\pm(50)^{1/2} = -0.929$ and -15.071

To find the eigenfunctions, substitute each root into the equations:
$(-7-E)c_1 -3c_2 = 0$ (1)
$-3c_1 + (-9-E)c_2 = 0$ (2) and use $c_1^2 + c_2^2 = 1$ (Normalization)
To find the other set, substitute each root into the equations:
$(-7-E)c_3 -7c_4 = 0$ (3)
$-7c_3 + (-9-E)c_4 = 0$ (4) and use $c_3^2 + c_4^2 = 1$

$E_a = -11.162$: From (1): $(-7-E)c_1 = 3c_2$, $c_2 = c_1[(-7+ 11.162)/3] = 1.387c_1$
$c_1^2 + c_1^2[1.387]^2 = 1$; $c_1 = 0.585$; $c_2 = 0.811$
$E_b = -4.838$: From (1): $(-7-E)c_1 = 3c_2$, $c_2 = c_1[(-7+ 4.838)/3] = -0.72067c_1$
$c_1^2 + c_1^2[0.72067]^2 = 1$; $c_1 = 0.811$; $c_2 = -0.585$
$E_c = -15.071$: From (3): $(-7-E)c_3 = 7c_4$, $c_4 = c_3[(-7+ 15.071)/7] = 1.153c_3$
$c_3^2 + c_3^2[1.153]^2 = 1$; $c_3 = 0.655$; $c_4 = 0.755$
$E_d = -0.929$: From (3): $(-7-E)c_3 = 7c_4$, $c_4 = c_3[(-7+ 0.929)/7] = -0.8673c_3$
$c_3^2 + c_3^2[0.8673]^2 = 1$; $c_3 = 0.755$; $c_4 = -0.655$

summary:

Eigenvalues	Eigenfunctions
$E_a = -11.162$	$\Psi_a = 0.585\varphi_1 + 0.811\varphi_2$
$E_b = -4.838$	$\Psi_b = 0.811\varphi_1 - 0.585\varphi_2$
$E_c = -15.071$	$\Psi_c = 0.655\varphi_3 + 0.755\varphi_4$
$E_d = -0.929$	$\Psi_d = 0.755\varphi_3 - 0.655\varphi_4$