HW #4 Solution

Problem 1

To show V_1, V_2 are eigenvectors of $[A]$ we need to show
$[A]V_1 = \lambda_1 V_1$, $[A]V_2 = \lambda_2 V_2$.

$$[A]V_1 = \begin{bmatrix} \cos\theta & \sin\theta\, e^{-i\varphi} \\ \sin\theta\, e^{+i\varphi} & -\cos\theta \end{bmatrix} \begin{Bmatrix} \cos(\frac{\theta}{2})\, e^{-i\varphi/2} \\ \sin(\frac{\theta}{2})\, e^{+i\varphi/2} \end{Bmatrix}$$

$$= \begin{Bmatrix} \left(\cos\theta \cos(\frac{\theta}{2}) + \sin\theta \sin(\frac{\theta}{2})\right) e^{-i\varphi/2} \\ \left(\sin\theta \cos(\frac{\theta}{2}) - \cos\theta \sin(\frac{\theta}{2})\right) e^{+i\varphi/2} \end{Bmatrix}$$

$$= \begin{Bmatrix} \cos(\theta - \frac{\theta}{2})\, e^{-i\varphi/2} \\ \sin(\theta - \frac{\theta}{2})\, e^{+i\varphi/2} \end{Bmatrix} = 1 \times V_1$$

$$[A]V_2 = \begin{bmatrix} \cos\theta & \sin\theta\, e^{-i\varphi} \\ \sin\theta\, e^{+i\varphi} & -\cos\theta \end{bmatrix} \begin{Bmatrix} -\sin(\frac{\theta}{2})\, e^{-i\varphi/2} \\ \cos(\frac{\theta}{2})\, e^{+i\varphi/2} \end{Bmatrix}$$

$$= \begin{Bmatrix} -\left(\cos\theta \sin(\frac{\theta}{2}) - \sin\theta \cos(\frac{\theta}{2})\right) e^{-i\varphi/2} \\ -\left(\sin\theta \sin(\frac{\theta}{2}) + \cos\theta \cos(\frac{\theta}{2})\right) e^{+i\varphi/2} \end{Bmatrix}$$

$$= (-1) \times \begin{Bmatrix} -\sin(\theta - \frac{\theta}{2})\, e^{-i\varphi/2} \\ \cos(\theta - \frac{\theta}{2})\, e^{+i\varphi/2} \end{Bmatrix} = (-1) \times V_2$$

$\therefore$ V_1 & V_2 are eigenvectors of $[A]$ and their eigenvalues are 1 & -1 respectively.

Orthogonality

$$V_1^{\dagger} V_2 = \left\{ \cos\left(\frac{\theta}{2}\right) e^{+i\varphi/2} \quad \sin\left(\frac{\theta}{2}\right) e^{-i\varphi/2} \right\} \begin{Bmatrix} -\sin\left(\frac{\theta}{2}\right) e^{-i\varphi/2} \\ \cos\left(\frac{\theta}{2}\right) e^{+i\varphi/2} \end{Bmatrix}$$

$$= -\cos\left(\frac{\theta}{2}\right)\sin\left(\frac{\theta}{2}\right) + \cos\left(\frac{\theta}{2}\right)\sin\left(\frac{\theta}{2}\right) = 0.$$

Problem 2,

We will apply basis transformation such that with this specific basis set, [A] will be diagonalized.

$$[B] = [V]^{\dagger}[A][V]$$

$$= \begin{bmatrix} - V_1^* - \\ - V_2^* - \end{bmatrix} \begin{bmatrix} A \end{bmatrix} \begin{bmatrix} | & | \\ V_1 & V_2 \\ | & | \end{bmatrix}$$

$$= \begin{bmatrix} - V_1^* - \\ - V_2^* - \end{bmatrix} \begin{bmatrix} | & | \\ 1\cdot V_1 & (-1)\cdot V_2 \\ | & | \end{bmatrix} \quad \left(\text{using } V_1, V_2 \text{ are eigenvectors}\right)$$

$$= \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (\text{using orthonormality})$$

Matlab $\quad \theta = \frac{\pi}{2},\ \varphi = 0 \quad [A] = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$

[V, B] = eig[A]

$$V = \begin{bmatrix} -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix} \quad B = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}$$

Problem 3

As discussed in class or textbook, Hamiltonian is given like this.

$$\begin{array}{c} \\ \\ [H] = \end{array}\begin{array}{c} \begin{array}{ccccc} 1s & 2s & 2p_x & 2p_y & 2p_z \end{array} \\ \begin{bmatrix} E_1 & 0 & A & 0 & 0 \\ 0 & E_2 & B & 0 & 0 \\ A & B & E_2 & 0 & 0 \\ 0 & 0 & 0 & E_2 & 0 \\ 0 & 0 & 0 & 0 & E_2 \end{bmatrix} \end{array}$$

(g F x)

Non-zero off diagonal terms will be given by the argument of symmetric / anti-symmetric wavefunctions.

Following the given information in the problem, let's ignore 1s.

$$\begin{array}{c} \\ [H] = \end{array}\begin{array}{c} \begin{array}{cccc} 2s & 2p_x & 2p_y & 2p_z \end{array} \\ \begin{bmatrix} E_2 & B & & \\ B & E_2 & & \\ & & E_2 & \\ & & & E_2 \end{bmatrix} \end{array}$$

Block diagonal!

By inspection, eigenvectors & eigenvalues are give like these.

$$\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\\0\\0\end{pmatrix} \quad \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\\0\\0\end{pmatrix} \quad \begin{pmatrix}0\\0\\1\\0\end{pmatrix} \quad \begin{pmatrix}0\\0\\0\\1\end{pmatrix}$$

$$\downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow$$

$$E_2+B \qquad E_2-B \qquad E_2 \qquad E_2$$

Problem 4

Energy of system

$E_{00} = 0$, $E_{10} = \varepsilon_1$, $E_{01} = \varepsilon_2$, $E_{11} = \varepsilon_1 + \varepsilon_2$

$N_{00} = 0$, $N_{10} = 1$, $N_{01} = 1$, $N_{11} = 2$

Using law of equilibrium,

$$P_{00} = \frac{1}{Z} \exp\left(-\frac{0-0}{kT}\right)$$

$$P_{01} = \frac{1}{Z} \exp\left(-\frac{(\varepsilon_2 - \mu)}{kT}\right)$$

$$P_{10} = \frac{1}{Z} \exp\left(-\frac{(\varepsilon_1 - \mu)}{kT}\right)$$

$$P_{11} = \frac{1}{Z} \exp\left(-\frac{(\varepsilon_1 + \varepsilon_2 - 2\mu)}{kT}\right)$$

$$f_1 = \frac{1}{1 + \exp\left(\frac{\varepsilon_1 - \mu}{kT}\right)}$$

$$f_2 = \frac{1}{1 + \exp\left(\frac{\varepsilon_2 - \mu}{kT}\right)}$$

$$P_{00} + P_{10} + P_{01} + P_{11} = 1$$

$$Z = 1 + \exp\left(-\frac{(\varepsilon_1 - \mu)}{kT}\right) + \exp\left(-\frac{(\varepsilon_2 - \mu)}{kT}\right) + \exp\left(-\frac{(\varepsilon_1 + \varepsilon_2 - 2\mu)}{kT}\right)$$

$$= \left(1 + \exp\left(-\frac{(\varepsilon_1 - \mu)}{kT}\right)\right)\left(1 + \exp\left(-\frac{(\varepsilon_2 - \mu)}{kT}\right)\right)$$

$$= \frac{1}{(1-f_1)(1-f_2)}$$

$$\therefore P_{00} = (1-f_1)(1-f_2)$$

$$P_{01} = f_2(1-f_1)$$

$$P_{10} = f_1(1-f_2)$$

$$P_{11} = f_1 f_2$$

Problem # 5,

$(U_0 = 0.1)$

N_α	$U_{ee} = \frac{U_0 N(N-1)}{2}$	E_α	$E_\alpha - \mu N_\alpha$
0	0	0	0
1	0	$\varepsilon = 0$	$\varepsilon - \mu = -\mu$
2	$U_0 = 0.1$	$2\varepsilon + U_0 = 0.1$	$2\varepsilon + U_0 - 2\mu = 0.1 - 2\mu$
3	$3U_0 = 0.3$	$3\varepsilon + 3U_0 = 0.3$	$3\varepsilon + 3U_0 - 3\mu = 0.3 - 3\mu$
4	$6U_0$ 0.6	$4\varepsilon + 6U_0 = 0.6$	$4\varepsilon + 6U_0 - 4\mu = 0.6 - 4\mu$

$$P_\alpha = \frac{1}{Z} \exp\left(-\frac{(E_\alpha - N_\alpha \mu)}{kT}\right)$$

Regardless of any finite # of degeneracy, In the zero temperature limit, A system with the smallest $(E - \mu N)$ will dominate. (exponential factor dominates)

By comparing $E_\alpha - \mu N_\alpha$ for various state (equating them to see when the transition occurs)