5500 Problem Set 3

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Question I.

Consider the chemical reaction $nA + mB \iff A_nB_m$. As the double arrow indicates, chemical reactions go both ways. Suppose this reaction happens at a fixed temperature and pressure. Show that the equilibrium conditions is $n\mu(A) + m\mu(B) = \mu(A_nB_m)$.

Since G is at a minimum at equilibrium

$$\begin{aligned} \mathrm{d}G &= n\mu(A)\,\mathrm{d}N_A + m\mu(B)\,\mathrm{d}N_B + \mu(A_nB_m)\,\mathrm{d}N_{AB} \\ 0 &= n\mu(A) + m\mu(B) + \mu(A_nB_m) \end{aligned}$$

Combining these give the desired $n\mu(A) + m\mu(B) = \mu(A_nB_m)$.

Question II.

A variation of the infamous lattice gas. Suppose we have a big volume V divided into cells of volume v. Each cell can accommodate at most one diatomic molecule. There are N ($N >> 1, N << V/v$) molecules, and by assumption there are no other degrees of freedom for a molecule except that it is in one of the cells. However, if supplied the dissociation energy D, a molecule will break up into two atoms, each of which can similarly occupy one of the cells. There are no constraints for an atom and a molecule occupying the same cell.

(a) Find the free energy (can't say if it is Helmholtz or Gibbs, as there are no volume/pressure type thermodynamic parameters in this problem) at temperature T, assuming that the gas is either all atoms, or all molecules.

We can find the number of microstates as

$$\begin{aligned} g &= \binom{V/v}{N} \\ S &= k\ln g \\ &= k[\ln n! - \ln N! - \ln{(n-N)!}] \\ &= k[\frac{V}{v}\ln\frac{V}{v} - N\ln N - (\frac{V}{v} - N)\ln{(\frac{V}{v} - N)}] \end{aligned}$$

We want this as

$$\begin{aligned}
\frac{\mathrm{d}S}{\mathrm{d}U} &= \frac{1}{T} \\
E &= N\epsilon \\
&= U \\
S(U) &= k[\frac{V}{v}\ln\frac{V}{v} - \frac{U}{\epsilon}\ln\frac{U}{\epsilon} - (\frac{V}{v} - \frac{U}{\epsilon})\ln(\frac{V}{v} - \frac{U}{\epsilon})] \\
\frac{\mathrm{d}S}{\mathrm{d}U} &= \frac{k}{\epsilon}[\ln\frac{n\epsilon}{U} - 1] \\
&= \frac{1}{T} \\
U &= \frac{n\epsilon}{e^{\frac{\epsilon}{kT}} + 1}
\end{aligned}$$

(b) Take it as given that there is a phase transition in which the molecules dissociate. What is the transition temperature?

From the first question of this homework we can say

$$\begin{aligned}
\mu(A) + D &= \mu(B) \\
\mu(A) &= kT\ln\frac{N_A}{n-(N_A+N_B)} \\
\mu(B) &= kT\ln\frac{N_B}{n-(N_A+N_B)} \\
kT\ln\frac{N_A}{n-(N_A+N_B)} + D &= 2kT\ln\frac{N_B}{n-(N_A+N_B)}
\end{aligned}$$

The temperature follows.

Question III.

Take it as given that two hermitian operators may be diagonalized simultaneously if and only if they commute.

(a) As already noted, every operator A may be decomposed trivially in the form $A = A_1 + iA_2$, where A_1 and A_2 are hermitian. Suppose we have a normal operator N with the corresponding components N_1 and N_2. Verify the following items: (i) $[N_1, N_2] = 0$. (ii) N may be diagonalized.

(i) For a normal operator N

$$\begin{aligned}
N &= N_1 + iN_2 \\
\left[N, N^\dagger\right] &= 0 \\
NN^\dagger &= (N_1 + iN_2)(N_1 - iN_2) \\
&= N_1N_1 + iN_2N_1 - iN_1N_2 + N_2N_2 \\
N^\dagger N &= N_1N_1 + iN_2N_1 - iN_1N_2 + N_2N_2 \\
[N_1, N_2] &= NN^\dagger - N^\dagger N \\
&= 0
\end{aligned}$$

(ii) If we suppose N is diagonalizable, we can act with N on $|\psi\rangle$ as follows:

$$\begin{aligned}
N|\psi\rangle &= N\mathbb{I}|\psi\rangle \\
&= N\left(\sum_n |n\rangle\langle n|\right)|\psi\rangle \\
&= N\sum_n |n\rangle\langle n|\,|\psi\rangle \\
&= \left(\sum_n c_n |n\rangle\langle n|\right)|\psi\rangle
\end{aligned}$$

Thus we know that N is diagonalizable since an operator with a spectral representation is diagonalizable.

(b) Conversely, suppose that an operator N can be diagonalized, with the eigenvalues c_n (not necessarily real) and the orthonormal eigenvectors u_n. Verify the following items: (i) $(u_n, N^\dagger u_m) = c_n^* \delta_{nm}$. (ii) $N^\dagger u_m = c_m^* u_m$. Therefore, $N^\dagger$ can also be diagonalized, eigenvalues and eigenvectors c_n^* and u_n. (iii) N is normal.

(i)

$$\begin{aligned}
\langle u_n|N^\dagger|u_m\rangle &= (\,\langle u_m|N|u_n\rangle)^* \\
&= \langle u_m|c_n^*|u_n\rangle \\
&= c_n^* \langle u_m|u_n\rangle \\
&= c_n^* \delta_{nm}
\end{aligned}$$

(ii)

$$\begin{aligned}
Nu_m &= \sum_n c_n |u_n\rangle\langle u_n|\,|u_m\rangle \\
N^\dagger u_m &= \sum_n c_n^* |u_n\rangle\langle u_n|\,|u_m\rangle \\
&= c_m^* u_m
\end{aligned}$$

(iii)

$$
\begin{aligned}
NN^\dagger &= \sum_n c_n |n\rangle\langle n| \sum_m c_m^* |m\rangle\langle m| \\
&= \sum_{nm} c_n c_m^* |n\rangle \langle n|m\rangle \langle m| \\
&= \sum_n c_n^* c_n^* |n\rangle\langle n| \\
&= N^\dagger N
\end{aligned}
$$

Thus N is normal.

We have, again, the result that normal, and only normal, operators can be diagonalized.

Question IV.

(a) Show that all eigenvalues of a unitary operator have unit modulus.

$$
\begin{aligned}
U |u_i\rangle &= u_i |u_i\rangle \\
U |u_j\rangle &= u_j |u_j\rangle
\end{aligned}
$$

We can then take

$$
\begin{aligned}
\langle u_j|U^\dagger U|u_i\rangle &= u_i u_j^* \langle u_j|u_i\rangle \\
(1 - u_i u_j^*) \langle u_j|u_i\rangle &= 0 \\
\therefore \langle u_j|u_i\rangle &= \delta_{nm}
\end{aligned}
$$

(b) Show that an operator U is unitary if and only if there is a Hermitian operator A such that $U = e^{iA}$.

$$
\begin{aligned}
U &= e^{iA} \\
&= \sum_{m=0}^{\infty} \frac{(iA)^m}{m!} \\
U^\dagger &= (e^{iA})^\dagger \\
&= \sum_{m=0}^{\infty} \frac{[(iA)^m]^\dagger}{m!} \\
&= \sum_{m=0}^{\infty} \frac{(-iA^\dagger)^m}{m!} \\
&= \sum_{m=0}^{\infty} \frac{(-iA)^m}{m!} \\
&= e^{-iA} \\
U^\dagger U &= e^{-iA} e^{iA} \\
&= 1
\end{aligned}
$$

Thus U is unitary.

In the other direction, assume U is unitary and find some A for which $U = e^{iA}$ is Hermitian. We know that for some diagonal operator D we can say $U = VDV^\dagger$. We can then say that for some set of real numbers $\{\theta_i\}$ that

$$
D = \begin{bmatrix} e^{i\theta_1} & & \\ & \ddots & \\ & & e^{i\theta_1} \end{bmatrix}
$$

We can then let

$$
\begin{aligned}
H &= V \begin{bmatrix} \theta_1 & & \\ & \ddots & \\ & & \theta_1 \end{bmatrix} V^\dagger \\
e^{iH} &= V \begin{bmatrix} e^{i\theta_1} & & \\ & \ddots & \\ & & e^{i\theta_1} \end{bmatrix} V^\dagger \\
&= U \\
H &= H^\dagger \ \because \{\theta_i\} \in \mathbb{R}
\end{aligned}
$$

So H is a Hermitian operator.