Physics 607 Exam 1

Please show all significant steps clearly in all problems.

1. We treated a diatomic molecule as a rigid rotor, but it actually stretches as it rotates faster. If the rotations are treated classically, we can write

\[ \varepsilon = aL^2 - bL^4 + ... \]  

where

\[ a = \frac{\hbar^2}{2I} \]  

and \( I \) is the unperturbed moment of inertia. If the rotations are treated quantum-mechanically, this becomes

\[ \varepsilon_J = a\ell(\ell + 1) - b\ell^2(\ell + 1)^2 + ... \]  

where

\[ \ell = 0, 1, 2, ... \]  

is the angular momentum quantum number, with a degeneracy of \( (2\ell + 1) \) since

\[ m_\ell = -\ell, -\ell + 1, ..., -1, 0, 1, ..., \ell - 1, \ell . \]

You may treat the term involving \( b \) as very small (since enormous values of \( L \) are not regarded as physically relevant) and you may also ignore the higher-order terms.

(a) (4) Write down the quantum partition function \( z_{rot} \) for the rotations of the molecule when \( b = 0 \). In the following this partition function will be called \( z^0_{rot} \).

(b) (4) Obtain a simple expression for \( z^0_{rot} \) at high temperatures by replacing the sum over \( \ell \) by an integral.

(c) (4) Use the result of (b) to calculate the average rotational energy \( \overline{\varepsilon} \) of the molecule at temperature \( T \).

(d) (4) Finally, calculate the rotational contribution to \( C_V \), the heat capacity at constant volume, for a gas of \( N \) diatomic molecules at high temperature. You should get a very simple answer in terms of \( N \) and \( k_B \) – the same answer we got in class.

(e) (5) Now we need to include centrifugal stretching of the molecule in high angular-momentum states. Write down the quantum partition function \( z_{rot} \) again in an approximate form, this time with \( b \neq 0 \) but \( b \) regarded as small. You want to get a fairly simple result of the form \( z_{rot} = z^0_{rot}(1 + \text{correction}) \).

(f) (5) Obtain a simple result for \( z_{rot} \) at high temperature, including the leading correction involving \( b \).

(g) (4) Use the result of (f) to find the average rotational energy \( \overline{\varepsilon} \) and the heat capacity \( C_V \) for a gas of \( N \) diatomic molecules (with \( b \neq 0 \)).
2. (20) A neutral atom $A$ has two unoccupied one-electron states of the same energy. (These correspond to the same orbital, but opposite spin orientations.) When neither state is occupied (so that there is no extra electron), the energy of the atom is taken to be zero.

When either state is occupied by a single electron (so that the atom has one extra electron with either spin up or spin down), the energy is equal to $\varepsilon$.

On the other hand, the Coulomb repulsion between two electrons in the same orbital is so large that we take the energy of the atom with two extra electrons to be infinite.

In other words, the energy of the neutral atom $A$ with “zero electrons” is 0; the energy of the $A^+$ ion with one electron in either the spin up or the spin down state is $\varepsilon$; and the energy of the $A^{++}$ ion is $\infty$.

If $\mu$ is the chemical potential of an electron, what is the average number $\pi$ of extra electrons residing on an $A$ atom in a gas of such atoms? Give your answer in terms of $\mu$, $\varepsilon$, and the temperature $T$. 
3. We made the thermodynamic connection for the grand canonical ensemble by showing that \( \Omega = -k_B T \log \mathcal{Z} \), where \( \mathcal{Z} \) is the grand partition function and \( \Omega \equiv E - TS - \mu N \).

(a) (5) Using Euler’s theorem, relate \( \Omega \) to \( PV \), where \( P \) is the pressure and \( V \) is the volume.

(b) (20) Using the above expressions, and interpreting \( E \) and \( N \) as the statistical averages \( \overline{E} \) and \( \overline{N} \) within the grand canonical ensemble, show that

\[
S = -k_B \sum_{Nj} p_{Nj} \log p_{Nj} \tag{6}
\]

where \( p_{Nj} \) is the probability that the system has \( N \) particles and is in state \( j \).