

**Problem 1.** (15 points) Answer the following five conceptual questions. Please be brief and straight to the point in your answers. A single sentence or equation will suffice.

**A.** Assume a quantum-mechanical system is in a state defined by the wave function  $\Psi$ . Write the general equation for the average outcome of many measurements of a physical observable  $A$ , each performed once on identically prepared such systems. (Remember the name of the equation?)

The expectation value equation:  $\langle A \rangle = \frac{\int \Psi^* \hat{A} \Psi dx}{\int \Psi^* \Psi dx}$  where  $\hat{A}$  is the corresponding QM operator

**B.** What is the *fundamental philosophical* basis for the Pauli Exclusion Principle that states that no two electrons can be in the same quantum state within the same quantum system (atom) simultaneously? (This question is about the philosophical basis, not about the principle itself! Do not recite the Exclusion Principle.)

Indistinguishability of particles of the same kind

**C.** What is the physical meaning of the value of the molecular partition function? In other words what does the numerical value of a partition function represent?

It represents the number of thermally accessible states for a molecule/particle

**D.** The table below lists expressions for the energy of a stationary state for various types of quantum-mechanical models of motion you studied in this course. Identify the type of motion and motion model each of these energies corresponds to.

Energy	Type of motion	Quantum-mechanical motion model
$\frac{\hbar^2}{2\mu r^2} l(l+1)$	Rotational	3D rigid rotor or particle on a sphere
$h\nu(n + \frac{1}{2})$	Vibrational	Harmonic oscillator
$\frac{h^2 n^2}{8ma^2}$	Translational	Particle in a 1D box

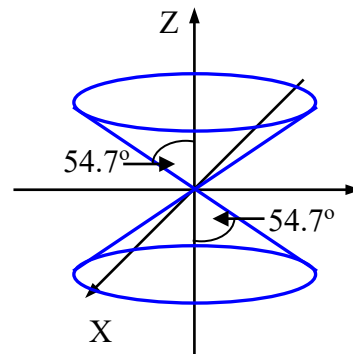
**Problem 2.** (45 points) Consider electron in the hydrogen atom. Assume it is in a 3d orbital with  $m_l = 0$ . Answer the following five questions (continued on the next page). You don't need to provide fully numerical answers – they can be expressed via a combination of numerical factors and physical constants, like  $e$ ,  $\hbar$ ,  $a_0$ , etc.

A. (5 points) Write the expression for the wave function of the electron in this state.

$$\Psi_{3,2,0} = R_{3,2}(r) \times Y_{2,0}(\theta, \varphi) = \frac{1}{81\sqrt{6\pi}} \frac{1}{a_0^{3/2}} \left(\frac{r}{a_0}\right)^2 e^{-r/3a_0} (3\cos^2\theta - 1)$$

B. (10 points) In which point(s) in the 3D space you are unlikely to find the electron? *Explain your reasoning.*

We need to find points in space where the probability density  $P = |\Psi_{320}|^2 = 0$ . You can write the equation for the probability density, but it is perhaps simpler to realize that  $|\Psi_{320}|^2 = \Psi_{320}^2$  equals zero when the wave function  $\Psi_{320}$  itself equals zero. Because the wave function is a product of the radial function ( $R_{3,2}(r)$ ) and angular function ( $Y_{2,0}(\theta, \phi)$ ), it equals zero when either its radial or angular part or both are zero. The radial part  $P_{\text{rad}}$  is zero only at  $r = 0$ , while the angular part is zero when  $\cos^2\theta = 1/3$ , i.e.  $\cos\theta = \pm 1/\sqrt{3}$ , which gives  $\theta = 54.7^\circ$  and  $\theta = 180^\circ - 54.7^\circ = 125.3^\circ$  (independent of the angle  $\phi$ ). This defines two nodal cones, both along the z axis, with the semiangles of  $\theta = 54.7^\circ$  and  $\theta = 125.3^\circ$  (naturally, these cones also contain the origin, i.e.  $r = 0$ ) as the points in the 3D space where the electron cannot be found.



C. (10 points) In which point(s) in the 3D space you are most likely to find the electron? *Explain your reasoning.*

We need to find points in space where the probability density is at maximum. Because  $P = \Psi_{320}^2 = [R_{3,2}(r)]^2 \times [Y_{2,0}(\theta, \phi)]^2$  is a product, it's at maximum where *both* the radial  $[R_{3,2}(r)]^2$  and the angular  $[Y_{2,0}(\theta, \phi)]^2$  terms of  $P$  are at maximum. The angular part as a function of  $\theta$  has the main maximum when  $\theta = 0^\circ$  or  $180^\circ$  ( $(3\cos^2\theta - 1)^2 = 4$ ) and a subsidiary maximum when  $\theta = 90^\circ$  ( $(3\cos^2\theta - 1)^2 = 1$ ). The maximum of the radial part can be found by solving for zeros of the derivative of the radial term of  $P$ . However, because  $R_{3,2}(r)$  is non-negative, and the square function  $f(x) = x^2$  is a monotonic function of  $x$ , we can search for maxima of  $R_{3,2}(r)$ , which means solving a simpler

equation:  $\frac{d}{dr} R_{3,2}(r) = 0$ . Defining a new variable:  $u = \frac{r}{a_0}$ , we get

$$\frac{d}{dr} R_{3,2}(r) \Rightarrow \frac{d}{du} [u^2 e^{-u/3}] = 2u e^{-u/3} - \frac{1}{3} u^2 e^{-u/3} = \frac{1}{3} e^{-u/3} u(6 - u) = 0. \text{ This gives } u = 6, \text{ i.e. } r = 6a_0 \text{ as}$$

the value of  $r$  at which  $R_{3,2}(r)$  and hence  $P(r)$  has a maximum. Bringing together the angular and radial maxima, we can conclude that the electron is most likely to be found along the z-axis at the

following points:  $x = 0, y = 0, z = 6a_0$  and  $x = 0, y = 0, z = -6a_0$ . Subsidiary maxima points are located on the circle of radius  $6a_0$  in the  $x$ - $y$  plane, i.e. along the equator.

Note after grading this problem: the question was about points in 3D space, not about distance from the nucleus. You needed to use the probability density, not the radial distribution function. Obviously, using the latter resulted in wrong answers.

**D. (10 points)** Determine the average distance of the electron from the nucleus. *Show your calculation.*

You can simply plug  $r$  into the expectation value equation from the 4<sup>th</sup> postulate and evaluate the corresponding integrals. Because  $r$  does not depend on the angles, the integrals over the angular parts of the wave function in the numerator and denominator cancel each other, and so do the numerical factors.

$$\langle r \rangle = \frac{\int \Psi^* r \Psi d\mathbf{v}}{\int \Psi^* \Psi d\mathbf{v}} = \frac{\int_0^\infty [R_{3,2}(r)]^2 r^3 dr}{\int_0^\infty [R_{3,2}(r)]^2 r^2 dr} = \frac{\int_0^\infty r^7 e^{-2r/3a_0} dr}{\int_0^\infty r^6 e^{-2r/3a_0} dr} = \frac{7! a^7}{6! a^8} = \frac{7}{a} = \frac{21}{2} a_0 = 10.5 a_0. \text{ Here I used the table}$$

integral  $\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$  where  $n=7$  in the numerator and  $n=6$  in the denominator, and  $a=2/(3a_0)$ .

An alternative way to get the answer is to use the expression for the radial distribution function  $W(r)$  (which gives the probability to find the electron at a given distance  $r$  from the nucleus) and calculate the average distance as the following integral (make sure you use the correct normalization factor):

$$\langle r \rangle = \int_0^\infty r W(r) dr = \int_0^\infty r [R_{3,2}(r)]^2 r^2 dr = \frac{4^2}{81^2 30} \frac{1}{a_0^7} \int_0^\infty r^7 e^{-2r/3a_0} dr = \frac{8}{81^2 15 a_0^5} \left[ \frac{7!}{(2/3a_0)^8} \right] = 10.5 a_0$$

**E. (10 points)** Calculate the possible angles between the vector of the spin angular momentum of the electron and the  $z$  axis.

Electron's spin is  $S=1/2$ . The length of the spin angular momentum vector

is  $|\vec{S}| = \sqrt{S(S+1)} \hbar = \sqrt{3/4} \hbar$ ; and although its  $z$ -projection is not specified, we know that there are

only two possibilities:  $S_z = m_S \hbar = \pm \hbar/2$ . Thus the tilt angle from the  $z$ -axis is defined by the

following equation:  $\cos \theta = \frac{m_S}{\sqrt{S(S+1)}} = \pm \frac{1}{\sqrt{3}}$ . Therefore the  $\theta$  angle is  $54.7^\circ$  (for  $m_S = 1/2$ ) or

$180^\circ - 54.7^\circ = 125.3^\circ$  (for  $m_S = -1/2$ ).

Note after grading this problem: this problem is similar to the problems on the practice exam, except that it's about electron spin rather than orbital angular momentum. The relevant equations for electron spin were included in the equations sheets. Only three students realized that the question was about the spin angular momentum. In fact, this problem was assigned as the end-of-chapter homework problem Pr. 10.3.

**Problem 3.** (40 points) Consider a gas of nitric oxide (NO) molecules at standard temperature and pressure (0°C and 1 atm (101.325 kPa)). The bond length in nitric oxide is 1.15Å, the force constant is 527 N/m. Answer the following four questions (continued on the next page).

A. (10 points) Calculate the molecular partition function for rotations of nitric oxide at these conditions. *Explain your assumptions and support with calculations if needed.*

Assume that rotations of the nitric oxide molecule can be described using the 3-D rigid rotor model (particle on a sphere). Also assume high-temperature approximation ( $k_B T \gg hcB$ ), where

$T = 273.15$  K. The latter assumption is justifiable because  $\frac{k_B T}{hcB} = \frac{2\mu r^2 k_B T}{\hbar^2} = 111.12 \gg 1$ .  $\leftarrow$  this should be part of the reasoning explanation and has to be checked...

Then the rotational molecular partition function is  $q_{rot} = \frac{1}{hcB\beta} = \frac{k_B T}{hcB} = \frac{2\mu r^2 k_B T}{\hbar^2}$ . (No need to use the symmetry number for a heteronuclear diatomic molecule.) Substituting the above result into this equation gives:  $q_{rot} = 111.12$ .

Here I list a few intermediate results/steps in the above calculations:  $\mu = 14 \times 16 / 30$  a.m.u. =

$$1.24 \times 10^{-26} \text{ kg}; B = \frac{\hbar^2}{2\mu r^2 hc} = 170.65 \text{ m}^{-1}; hcB = 3.38 \times 10^{-23} \text{ J}; \text{ and } k_B T = 3.77 \times 10^{-21} \text{ J}.$$

Note after grading: Some students forgot my warning that a.m.u. has a value ( $1.66 \times 10^{-27}$  kg), and as the result obtained answers that differed from the correct ones by many orders of magnitude.

B. (10 points) What fraction of nitric oxide molecules on average occupy the second excited rotational energy level at this temperature? *Explain your assumptions.*

The second excited rotational level corresponds to  $l = 2$ , its energy is

$\epsilon_{l=5} = \frac{\hbar^2 l(l+1)}{2\mu r^2} = \frac{6\hbar^2}{2\mu r^2} = \frac{3\hbar^2}{\mu r^2}$  and its degeneracy is  $2l+1 = 5$ . Therefore the fractional population of this level is

$$p_l = (2l+1) \exp\left(-\frac{\hbar^2 l(l+1)}{2\mu r^2 k_B T}\right) / q_{rot} = 5 \exp\left(-\frac{6\hbar^2}{2\mu r^2 k_B T}\right) / q_{rot} = 5 \exp\left(-\frac{6}{111.12}\right) / 111.12 = 0.0426 = 4.26\%$$

C. (10 points) Calculate the contribution from rotational motion to the entropy of 1 mole of nitric oxide molecules at these conditions.

The general equation relating the entropy in question to the rotational partition function is

$$S = \frac{E}{T} + Nk_B \ln q_{rot} = -N \frac{\partial}{\partial \beta} \ln q_{rot} + Nk_B \ln q_{rot}.$$

Using the expression for the molecular partition function from Question A and taking into account that we have 1 mole of molecules, i.e.  $N_A \times k_B = R$ ,

$$\text{we get } S = N_A k_B + N_A k_B \ln\left(\frac{k_B T}{hcB}\right) = R + R \ln\left(\frac{k_B T}{hcB}\right) = R \left[1 + \ln\left(\frac{k_B T}{hcB}\right)\right] = R \left[1 + \ln\left(\frac{2\mu r^2 k_B T}{\hbar^2}\right)\right]$$

$$= 8.308 \times (1 + \ln(111.12)) \text{ J} = 8.308 \text{ J} + 39.134 \text{ J} = 47.442 \text{ J}$$

Note that because the high-T approximation is valid, and rotation of a di-atomic molecule is characterized by 2 degrees of freedom, you can save time by simply replacing  $E$  here with

$2 \times \frac{1}{2} k_B T \times N_A = RT$  without calculating the derivative of  $\ln q_{rot}$ . Remember, we already obtained this in class?

**D.** (10 points) Calculate the molecular partition function for translational motion of nitric oxide at these conditions. *Explain your assumptions.* (Because this question is about the molecular partition function, you can treat the molecules as distinguishable.)

The molecular partition function for translational motion is  $q_{transl} = \frac{V}{\Lambda^3}$ , where  $V = 22.4 \text{ L} =$

$22.4 \times 10^{-3} \text{ m}^3$  is the volume of 1 mole of ideal gas at standard conditions, and  $\Lambda = \frac{h}{\sqrt{2\pi m_{NO} k_B T}}$  is

the thermal de Broglie wavelength for the nitric oxide molecule:  $\Lambda = 1.93 \times 10^{-11} \text{ m} = 0.193 \text{ \AA}$  at these conditions. (Note that  $m_{NO} = (14+16) \text{ a.m.u.} = 4.98 \times 10^{-26} \text{ kg}$ )

Thus,  $q_{transl} = 3.1 \times 10^{30}$ . *Note:* as you might realize, the value of  $q_{transl}$  is huge compared to  $q_{rot}$ .

**If you are done with the rest of the problems, you might want to solve one of the following two problems for an extra credit. Note that only one problem per person will count – choose your problem wisely!**

**Bonus Problem 1.** (10 points) According to the Big Bang theory (the cosmological model not the once popular TV sitcom), at the beginning (13.8 billion years ago), the universe was so hot that atoms could not exist because the average thermal energy was sufficient to destroy them. Atoms started forming only when the Universe cooled down sufficiently -- this happened about 400,000 years after the Big Bang. Estimate the temperature of the Universe at which hydrogen atoms started to form. *Explain your reasoning.*

If the thermal energy is too high, electron absorbing this energy will be ejected from the atom. As the temperature goes down, at some point the thermal energy won't be sufficient for this, hence stabilization of the atom. The highest temperature at which H-atom can still exist can be estimated by equating the average thermal energy to the minimal quantum of energy required for the (ground-state) 1s electron to leave the H-atom:

$$\Delta E = 0 - E_{n=1} = \frac{m_e e^4}{8 \epsilon_0^2 h^2} = x \frac{1}{2} k_B T$$

or  $\Delta E = \frac{\hbar^2}{2 m_e a_0^2} = x \frac{1}{2} k_B T$  if I use the expression for the energy of electron in terms of  $a_0$ .

Here  $x$  (=1, 2, or 3) represents the number of degrees of freedom associated with the thermal

motion. Solving for  $T$  gives:  $T = \frac{m_e e^4}{4 \epsilon_0^2 h^2 k_B x}$  (or  $T = \frac{\hbar^2}{m_e a_0^2 k_B x}$  if I use an alternative expression for  $E_{n=1}$ ).

This gives the temperature of  $3.156 \times 10^5$  K when  $x=1$ ;  $1.578 \times 10^5$  K when  $x=2$ ; and  $1.052 \times 10^5$  K for  $x=3$ .

So, if we simply use  $k_B T$  as the average thermal energy, the estimated temperature at which H atoms will start forming is approximately 157,800 K

Note after grading: Only two students did this problem correctly.

**Bonus Problem 2.** (15 points) Consider rotational levels of the nitric oxide molecule from Problem 3. Determine the rotational energy level (find the corresponding quantum number  $l$ ) that is most populated at that temperature. *Show your calculation.*

The fractional population of a rotational energy level corresponding to quantum number  $l$  is:

$p_l = (2l+1) \exp\left(-\frac{\hbar^2 l(l+1)}{2I k_B T}\right) / q_{rot}$ . The  $l$  value at which  $p_l$  is at maximum can be obtained by equating the derivative over  $l$  to 0:

$$\frac{d}{dl} p_l = 2 \exp\left(-\frac{\hbar^2}{2I k_B T} l(l+1)\right) - (2l+1)^2 \frac{\hbar^2}{2I k_B T} \exp\left(-\frac{\hbar^2}{2I k_B T} l(l+1)\right) = 0 \rightarrow$$

$2 - (2l+1)^2 \frac{\hbar^2}{2I k_B T} = 0$ . From here we get the following relationship between the temperature and the  $l$  value (let's call it  $l_{max}$ ) corresponding to the most populated energy level:

$$(2l_{max} + 1)^2 = \frac{4I k_B T}{\hbar^2}. \text{ This gives } l_{max} = \left[ \sqrt{\frac{4I k_B T}{\hbar^2}} - 1 \right] / 2 = \sqrt{\frac{I k_B T}{\hbar^2}} - \frac{1}{2} = \sqrt{\frac{\mu r^2 k_B T}{\hbar^2}} - \frac{1}{2}. \text{ For the}$$

reduced mass and the bond length of nitric oxide and  $T=273.15\text{K}$  the right-hand side of this equation is: 6.95, and rounding it to the nearest whole number we obtain  $l_{max} = 7$ .

Intermediate steps/results in the above calculations:  $\mu = 14 \times 16 / 30 \text{ a.m.u.} = 1.24 \times 10^{-26} \text{ kg}$ ;

$$\frac{\hbar^2}{2\mu r^2 k_B T} = 0.009; \quad \frac{\mu r^2 k_B T}{\hbar^2} = 55.56.$$

Note after grading: Only a few students attempted to solve this problem and only one student did this problem correctly.

**Some equations and formulae that might or might not be useful:**

$$\Delta E = h\nu; \nu = \frac{c}{\lambda}; \lambda = \frac{h}{p}; \tilde{\nu} = \frac{1}{\lambda}$$

$$E_{kinet} = K = \frac{p^2}{2m}; \hat{p}_x = -i\hbar \frac{\partial}{\partial x}; \Delta p_x \cdot \Delta x \geq \frac{\hbar}{2}$$

$$E_n = \frac{h^2 n^2}{8ma^2}; \Psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right)$$

$$E_n = \left(n + \frac{1}{2}\right) h\nu; \Psi_n(x) = A_n H_n e^{-\alpha x^2/2}$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}; \alpha = \frac{\sqrt{k\mu}}{\hbar}; A_n = \frac{1}{\sqrt{2^n n!}} \left(\frac{\alpha}{\pi}\right)^{1/4}$$

$$E_{m_l} = \frac{\hbar^2}{2I} m_l^2; \Psi_{m_l}(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_l\phi}$$

$$E_l = \frac{l(l+1)\hbar^2}{2I}; \Psi_{l,m_l} = Y_{l,m_l}(\theta, \phi);$$

$$|\vec{l}|^2 = l(l+1)\hbar^2; l_z = m_l \hbar$$

$$E_J = \frac{J(J+1)\hbar^2}{2I} = hcBJ(J+1); B = \frac{\hbar^2}{2hcI}$$

$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 \hbar^2 n^2} = -\frac{\hbar^2}{2m_e a_0^2 n^2};$$

$$\Psi_{n,l,m_l} = R_{n,l}(r) Y_{l,m_l}(\theta, \varphi);$$

$$a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2}; V = -\frac{e^2}{4\pi\varepsilon_0 r}$$

$$e = 1.6 \times 10^{-19} \text{ C};$$

$$\varepsilon_0 = 8.85 \times 10^{-12} \text{ m}^{-3} \text{ kg}^{-1} \text{ s}^4 \text{ A}^2$$

$$4\pi\varepsilon_0 = 1.11 \times 10^{-10} \text{ m}^{-3} \text{ kg}^{-1} \text{ s}^4 \text{ A}^2$$

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}; \Delta A \times \Delta B \geq \frac{1}{2} \left| \langle [\hat{A}, \hat{B}] \rangle \right|$$

$$\text{For spin S: } |\vec{S}|^2 = S(S+1)\hbar^2; S_z = m_s \hbar$$

$$h = 6.62 \times 10^{-34} \text{ J s}; \hbar = h/(2\pi); c = 3 \times 10^8 \text{ m/s}$$

$$k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}; N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$R = N_A \times k_B = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$m_e = 9.1 \times 10^{-31} \text{ kg}; m_p = 1.67 \times 10^{-27} \text{ kg}$$

$$1 \text{ a.m.u.} = 1.66 \times 10^{-27} \text{ kg}$$

$$H_0 = 1; H_1 = 2\sqrt{\alpha x}; H_2 = 2(2\alpha x^2 - 1)$$

$$H_3 = 4\sqrt{\alpha x}(2\alpha x^2 - 3)$$

$$\mu = m_1 m_2 / (m_1 + m_2)$$

$$\hat{l}_z = -i\hbar \frac{\partial}{\partial \phi}; l_z = m_l \hbar; I = \mu r^2$$

$$Y_{0,0}(\theta, \phi) = 1/\sqrt{4\pi}; Y_{1,0}(\theta, \phi) = (3/4\pi)^{1/2} \cos\theta$$

$$Y_{1,\pm 1}(\theta, \phi) = \mp (3/8\pi)^{1/2} \sin\theta e^{\pm i\phi}$$

$$Y_{2,0}(\theta, \phi) = (5/16\pi)^{1/2} (3\cos^2\theta - 1)$$

$$Y_{2,\pm 1}(\theta, \phi) = \mp (15/8\pi)^{1/2} \cos\theta \sin\theta e^{\pm i\phi}$$

$$Y_{2,\pm 2}(\theta, \phi) = (15/32\pi)^{1/2} \sin^2\theta e^{\pm 2i\phi}$$

$$R_{1,0} = 2(1/a_0)^{3/2} e^{-r/a_0}$$

$$R_{2,0} = \frac{1}{\sqrt{8}} (1/a_0)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

$$R_{2,1} = \frac{1}{2\sqrt{6}} (1/a_0)^{3/2} \frac{r}{a_0} e^{-r/2a_0}$$

$$R_{3,0} = \frac{2}{81\sqrt{3}} (1/a_0)^{3/2} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$$

$$R_{3,1} = \frac{4}{81\sqrt{6}} (1/a_0)^{3/2} \left(6\frac{r}{a_0} - \frac{r^2}{a_0^2}\right) e^{-r/3a_0}$$

$$R_{3,2} = \frac{4}{81\sqrt{30}} (1/a_0)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0}$$

$$\Delta p_x \cdot \Delta x \geq \frac{\hbar}{2}$$

For  $S = 1/2$ :

$$\hat{S}_z \alpha = \frac{\hbar}{2} \alpha; \quad \hat{S}_z \beta = -\frac{\hbar}{2} \beta; \quad [\hat{S}_x, \hat{S}_y] = i\hbar \hat{S}_z; \quad \hat{S}_x \alpha = \frac{\hbar}{2} \beta; \quad \hat{S}_x \beta = \frac{\hbar}{2} \alpha; \quad \hat{S}_y \alpha = i\frac{\hbar}{2} \beta; \quad \hat{S}_y \beta = -i\frac{\hbar}{2} \alpha$$

$$\hat{S}^2 \alpha = \frac{3\hbar^2}{4} \alpha; \quad \hat{S}^2 \beta = \frac{3\hbar^2}{4} \beta; \quad \int \alpha^* \alpha d\sigma = 1; \quad \int \beta^* \beta d\sigma = 1; \quad \int \beta^* \alpha d\sigma = 0; \quad \int \alpha^* \beta d\sigma = 0$$

$$p_i = \frac{a_i}{N} = \frac{g_i e^{-\epsilon_i \beta}}{q}; \quad q = \sum_i g_i e^{-\epsilon_i \beta}$$

$$\beta = \frac{1}{k_B T}$$

$$q_{transl} = \frac{V}{\Lambda^3}; \quad \Lambda = h \left( \frac{\beta}{2\pi m} \right)^{1/2} = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$W = \frac{N!}{a_0! a_1! a_2! \dots}$$

$$n! \approx \sqrt{2\pi} n^{n+1/2} e^{-n}; \quad \ln n! \approx n \ln n - n \quad (\text{for } n \gg 1)$$

$$q_{rot} = \frac{1}{(\sigma) h c B \beta} \quad (\text{assuming } k_B T \gg h c B)$$

$$q_{vibr} = \frac{1}{1 - e^{-h\nu\beta}}; \quad q_{vibr} \approx \frac{1}{h\nu\beta} \quad (\text{when } k_B T \gg h\nu)$$

$$E = -N \frac{\partial}{\partial \beta} \ln q = N k_B T^2 \frac{\partial}{\partial T} \ln q$$

$$S = k_B \ln W; \quad S = \frac{E}{T} + k_B N \ln q$$

$$e^{i\alpha} = \cos \alpha + i \sin \alpha$$

$$\cos \alpha = (e^{i\alpha} + e^{-i\alpha})/2$$

$$\sin \alpha = (e^{i\alpha} - e^{-i\alpha})/2i$$

$$\sin \alpha \sin \beta = [\cos(\alpha - \beta) - \cos(\alpha + \beta)]/2$$

$$\sin \alpha \cos \beta = [\sin(\alpha - \beta) + \sin(\alpha + \beta)]/2$$

$$\sin 2\alpha = 2 \sin \alpha \cos \alpha$$

$$\cos 2\alpha = \cos^2 \alpha - \sin^2 \alpha$$

$$2 \sin^2 \alpha = 1 - \cos 2\alpha$$

$$2 \cos^2 \alpha = 1 + \cos 2\alpha$$

$$\cos \alpha \cos \beta = [\cos(\alpha - \beta) + \cos(\alpha + \beta)]/2$$

$$\int_0^a \sin^2 \left( \frac{\pi n}{a} x \right) dx = \frac{a}{2}$$

$$\int_0^\infty e^{-ax^2} x^{2n} dx = \sqrt{\frac{\pi}{a}} \frac{1 \cdot 3 \cdot 5 \cdot \dots \cdot (2n-1)}{2^{n+1} a^n}, \quad (\text{for } n \geq 1); \quad \int_0^\infty e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}}; \quad \int_0^\infty e^{-ax^2} x^2 dx = \frac{1}{4a} \sqrt{\frac{\pi}{a}}$$

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}; \quad n! = 1 \cdot 2 \cdot \dots \cdot n$$