

## PH.D. QUALIFYING EXAM 2004

MATT THIESSE

MODERN

**Problem 1.** *The radial part of the Schroedinger equation for an arbitrary central potential can be cast into the form*

$$-\frac{\hbar^2}{2\mu} \frac{d^2 U(r)}{dr^2} + \left[ V(r) + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} \right] U(r) = EU(r)$$

where  $U(r)$  is the radial wave function. Consider the special case of the hydrogen atom.

- (a) *For a state with zero angular momentum, an uncritical look at the shape of the Coulomb potential energy suggests that the most energetically favorable state (i.e. the state of lowest potential energy) would correspond to the electron coming as close as possible to the proton. How does quantum mechanics prevent this collapse?*

The answer lies completely in the fact that the total energy cannot be zero. Since there has to be *some* energy, that energy manifests mainly in the form of rotational kinetic energy. In QM, the energy is quantized and the lowest amount of energy an electron in the Hydrogen atom can have is the ground state energy

$$E(n, \ell) = -\frac{1}{2} mc^2 \alpha^2 \frac{Z^2}{N^2} = -13.6 \text{eV}, \quad N = n + \ell + 1$$

- (b) *Consider now the general case of non-zero angular momentum. With the help of the above radial equation, provide a convincing argument (no calculations needed) in support of the existence of a range of energy values for which bound stationary states can be found.*

Orbital angular momentum has quantum number  $\ell$ . This value is an integer, by definition, so the angular momentum is quantized. By solving the Schroedinger equation, one finds that the allowed energy values are dependent on  $\ell(\ell+1)$  so there are discrete energy levels in which bound states can be found.

- (c) *Again with the help of the above radial equation, argue for the existence of unbound states of the hydrogen atom corresponding to a continuous spectrum of energies.*

The eigenvalues of the Schrodinger equation are negative. Thus, these states correspond to bound states  $E < 0$ . However, if external reasons cause  $E > 0$  than the normal eigenvalues are not satisfied. When this happens, the energy can take on any continuous value and the state is unbounded.

**Problem 2.**

- (a) *What is the ground state electronic configuration of a lithium atom ( $Z = 3$ )?*

$$1s^2 2s^1$$

- (b) *Give a rough estimate of the energy of the 2p state of lithium.*

From the energy equation given in problem 1,

$$E(n, \ell) = -13.6 \text{ eV} \left( \frac{Z}{n + \ell + 1} \right)^2$$

Normally,  $Z = 3$  since there are three protons in the nucleus. However, the two inner electrons are shielding the outer one, so  $Z_{\text{eff}} = 1$ . Therefore,

$$E_2 = -13.6 \text{ eV} \left( \frac{1}{2} \right)^2 = \boxed{-3.4 \text{ eV}}$$

**Problem 3.** *3 particles are confined to a cubical box with sides of length  $a$ , centered at  $x = y = z = 0$ .*

- (a) *What is the ground state energy if they are 3 bosons?*

The energy of a given bound state in 3 dimensions is

$$E_n = \frac{\pi^2 \hbar^2}{2m} \left( \frac{n_x^2}{x^2} + \frac{n_y^2}{y^2} + \frac{n_z^2}{z^2} \right)$$

Since bosons do not follow the Pauli exclusion principle, all three particles can be in the exact same state. For a particle in a box, the ground state has  $n = 1$  so in 3 dimensions, the ground state is

$$E_1 = \frac{\pi^2 \hbar^2}{2ma^2} [1^2 + 1^2 + 1^2] \times 3 \text{ particles}$$

$$\boxed{E_1 = \frac{9\pi^2 \hbar^2}{2ma^2}}$$

- (b) *What is the ground state energy if they are 3 fermions?*

*Hint: write down the eigenfunctions and energy levels of the 1D box, generalize to 3D, then populate the energy levels in a way that obeys the exclusion principle, where appropriate.*

The (normalized) eigenfunction of a particle in a 1D box is

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

and the energy levels are

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

And one particle in a 3D box has

$$\psi_{\mathbf{n}}(x, y, z) = \left( \frac{2}{a} \right)^{3/2} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right)$$

and

$$E_n = \frac{\pi^2 \hbar^2}{2ma^2} (n_x^2 + n_y^2 + n_z^2)$$

The wavefunction for 3 particles in a 3D box is (simplified)

$$\psi_{\mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3}(\mathbf{r}_1; \mathbf{r}_2; \mathbf{r}_3) = N \begin{vmatrix} \psi_{\mathbf{n}_1}(\mathbf{r}_1) & \psi_{\mathbf{n}_2}(\mathbf{r}_1) & \psi_{\mathbf{n}_3}(\mathbf{r}_1) \\ \psi_{\mathbf{n}_1}(\mathbf{r}_2) & \psi_{\mathbf{n}_2}(\mathbf{r}_2) & \psi_{\mathbf{n}_3}(\mathbf{r}_2) \\ \psi_{\mathbf{n}_1}(\mathbf{r}_3) & \psi_{\mathbf{n}_2}(\mathbf{r}_3) & \psi_{\mathbf{n}_3}(\mathbf{r}_3) \end{vmatrix}$$

Basically, it is the sum of all the permutations of the three particle wavefunctions with half of them subtracted since we are dealing with fermions. By definition, the construction of the wavefunction is done by using the [Slater] determinant.

Anyway, to find the ground state energy of 3 fermions in a box, we look at each particle separately. The first has energy

$$E_n = \frac{\pi^2 \hbar^2}{2ma^2} (1^2 + 1^2 + 1^2) = \frac{3\pi^2 \hbar^2}{2ma^2}$$

The second particle cannot be in the same state as the first particle. For spin  $\frac{1}{2}$  particles, two particles with the same  $n$ ,  $\ell$  can occupy the same state if their spins are opposite. So, the second particle in our box will have the same energy but opposite spin. The third particle must have a different  $n$  value since there are only two spin states for the spin  $\frac{1}{2}$  particles. The ground state of all three particles in the box is given by

$$E_n = \frac{3\pi^2 \hbar^2}{2ma^2} + \frac{3\pi^2 \hbar^2}{2ma^2} + \frac{\pi^2 \hbar^2}{2ma^2} (1^2 + 1^2 + 2^2) = \boxed{\frac{6\pi^2 \hbar^2}{ma^2}}$$

**Problem 4.** For a spin  $\frac{1}{2}$  particle, suppose we measure the sum of the  $x$  and  $z$  components of the spin  $\mathbf{S}$ . The Pauli matrices are:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

(a) What are the possible results of this measurement of  $S_x + S_z$ ?

$$\begin{aligned} S_x + S_z &= \frac{\hbar}{2} \sigma_x + \frac{\hbar}{2} \sigma_z \\ &= \frac{\hbar}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \end{aligned}$$

The eigenvalues of this operator will be the possible measurements:

$$\begin{aligned} \det [(S_x + S_z) - \lambda I] &= 0 \\ \left(\frac{\hbar}{2} - \lambda\right)\left(-\frac{\hbar}{2} - \lambda\right) - \frac{\hbar^2}{4} &= 0 \\ -\frac{\hbar^2}{2} + \lambda^2 &= 0 \end{aligned}$$

So, the possible measurements of  $S_x + S_z$  are

$$\boxed{\lambda = \pm \frac{\hbar}{\sqrt{2}}}$$

(b) Suppose that the measurement yielded the largest possible eigenvalue. Find a spin wave function that describes the state of the system immediately after measuring the sum of the  $x$  and  $z$  components.

Given  $\lambda = \frac{\hbar}{\sqrt{2}}$ ,

$$\frac{\hbar}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \psi = \frac{\sqrt{2}}{2} \hbar \psi$$

$$\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \sqrt{2} \begin{pmatrix} a \\ b \end{pmatrix}$$

Solving the system of linear equations, we find that  $a = 1$  and  $b = \sqrt{2} - 1$ . Thus,

$$\psi = A \begin{pmatrix} 1 \\ \sqrt{2} - 1 \end{pmatrix}$$

Normalizing  $\psi$ , we find that

$$\psi = (4 - 2\sqrt{2})^{-1/2} \begin{pmatrix} 1 \\ \sqrt{2} - 1 \end{pmatrix}$$

**Problem 5.** *Brrrrr! It is KKCCCCOOOOOOOOLLLLLDDDD outside!! In running from 30th St. Station to Drexel at 8:10 in the morning, you remember that you have the Physics Department's most notorious professor for the most boring class in the world. If you don't stop along the way for a hot cup of coffee you will surely fall asleep even before you sit down in your seat. Soooooo, you stop at one of the trucks and ask for a hot cup of half ℰ half (half hot coffee, half cold milk). The proprietor/ress asks you if you want to take the two halves with you, and mix them once you get to class, or if you want them mixed there, and then run to class with the whole. What do you answer, in the interests of having the hottest drink after you arrive? Explain.*

The most direct way to solve this problem is to use Newton's Law of Cooling which states that the rate of change of temperature is proportional to the difference between the ambient temperature and the temperature of the substance:

$$\frac{dT}{dt} = -k(T - T_a)$$

Solving the differential equation reveals the equation for the final temperature after a time  $t$ :

$$T_f(t) = T_a + (T_i - T_a) e^{-kt}$$

where  $T_a$  is the ambient temperature,  $T_i$  is the initial temperature, and  $k$  is some constant which is characteristic to the given substance. We assume, for simplicity, that the coffee and milk have the same density, specific heat, etc. In addition, the final temperature of a mixture is given by

$$T_f = \frac{T_1 m_1 + T_2 m_2}{m_1 + m_2}$$

Since there is equal amounts of coffee and milk the final mixture temperature is just the average of the two initial temps.

So, let's mix the coffee and milk and then walk to class:

$$T_i = \frac{T_c + T_m}{2}$$

$$T_f(t) = T_a + \left( \frac{T_c + T_m}{2} - T_a \right) e^{-kt}$$

Now, if we walk to class with the coffee and milk separate, then mix, we get

$$T_{f_c}(t) = T_a + (T_c - T_a) e^{-kt}$$

$$T_{f_m}(t) = T_a + (T_m - T_a) e^{-kt}$$

$$T_f(t) = \frac{T_a + (T_c - T_a)e^{-kt} + T_a + (T_m - T_a)e^{-kt}}{2} = T_a + \left(\frac{T_c + T_m}{2} - T_a\right)e^{-kt}$$

Apparently, it doesn't matter when you mix the coffee and milk.

Prof. Gilmore's solution is somewhat different. Apparently, he took into account the exposed surface area of the two liquids in their respective vessels. The half cup of coffee has a smaller surface area than the mixture if we assume a conical cup shape. The question is how much heat escapes out of each surface area. More heat would escape out of the fuller cup so mix later.

The change in temperature is proportional to the difference between the temperature of the liquid and that of the air and the surface area.

If you mix inside,  $\Delta T_c = A(T_c - T_o)$  and  $\Delta T_m = A(T_m - T_o)$ , where  $T_c$  is the temperature of the coffee,  $T_m$  is the temperature of the milk,  $T_o$  is the temperature of the outside air, and  $A$  is the exposed surface area of the milk / coffee. The final temperature will then be

$$T_f = \frac{(T_c - \Delta T_c) + (T_m - \Delta T_m)}{2}$$

$$T_f = \frac{1}{2}((1 - A)(T_c + T_m) + 2AT_o)$$

If you mix inside,  $\Delta T' = A' \left(\frac{T_c + T_m}{2} - T_o\right) = \frac{1}{2}A'(T_c + T_m - 2T_o)$ , where  $A'$  is the exposed area of the combined liquids in the conical-shaped cup. The final temperature is then

$$T'_f = \frac{T_c + T_m}{2} - \Delta T'$$

$$T'_f = \frac{1}{2}((1 - A')(T_c + T_m) + 2A'T_o)$$

After doing lots of crazy algebra to combine the volumes of the two liquids into one cup, you should find that  $A' = 2^{2/3}A$ . Therefore,

$$T'_f = \frac{1}{2} \left( (1 - 2^{2/3}A)(T_c + T_m) + 2^{5/3}AT_o \right)$$

If you assume a conical shaped cup, and work through all the nitty-gritty math with the exposed surface areas and temperatures, you should find that when the difference between the coffee and milk is greater than twice the outside temperature, the drink will be warmest when mixed before going to class. Otherwise, it is better to wait until you reach class to mix them.

**Problem 6.** Give a physical interpretation of chemical potential. What roles does chemical potential play in diffusive motions, chemical reactions, and phase transitions?

Chemical potential,  $\mu$ , is found in the equation for Gibbs free energy,

$$dG = -SdT + VdP + \mu dN$$

and Helmholtz free energy,

$$dA = -SdT - PdV + \mu dN$$

and internal energy,

$$dU = TdS - PdV + \mu dN$$

Also,

$$\mu = -T \left( \frac{\partial S}{\partial N} \right)_{U,V}$$

Chemical potential is defined as the slope of the free energy with respect to the total number of particles. It is an intrinsic property of a system. Think of chemical potential as a form of potential energy in the sense that particles tend to move from high chemical potential to low. For example, at  $T > 0^\circ\text{C}$ ,  $\mu_{\text{ice}} > \mu_{\text{liquid water}}$  so particles move from the solid phase to the liquid phase and the ice melts. In general, two phases are in equilibrium when the chemical potentials are equal. In

diffusion, the particles with higher  $\mu$  move to places in the volume of lower  $\mu$ . The speed at which this happens depends on the difference between the chemical potentials.

The chemical potential is the total ground state energy of a system at  $T = 0$  K. It is a form of potential energy that can be emitted or absorbed during a chemical reaction. The total sum of all the chemical potentials must equal 0 during a phase transition, since the energy is at a minimum. When two systems of different chemical potentials are brought together, the particles in the systems will redistribute themselves so that there is no longer an energy gradient.

**Problem 7.** A system has two energy levels with an energy gap of  $0.50\text{eV}$ . The upper level is degenerate with 3 states, while the ground state is non-degenerate. What is the probability that any of the excited states is occupied at  $25^\circ\text{C}$ ?

The first state is at energy  $\varepsilon_0$  and the higher state is at energy  $\varepsilon_0 + 0.5\text{eV}$ . The probability of occupation is given by

$$P_i = \frac{g_i e^{-\beta E_i}}{\sum g_i e^{-\beta E_i}}$$

where  $g_i$  is the degeneracy of the energy level. We have

$$P = \frac{3e^{\frac{-(\varepsilon_0 + 0.5\text{eV})}{kT}}}{1 + 3e^{\frac{-(\varepsilon_0 + 0.5\text{eV})}{kT}}}$$

where  $T = 298\text{K}$ , or a probability  $P_{\varepsilon_1} = 1.049 \times 10^{-8}$

**Problem A1.** A particle of mass  $M$  is fixed at one end of a rigid rod of negligible mass and length  $\rho$ . The other end of the rod holds the mass, and the system is free to rotate about the origin about the  $z$ -axis. The angle between the  $x$ -axis and the rod is  $\phi$ .

- (a) Write an expression for the total energy of the system in terms of its angular momentum  $L$  and moment of inertia  $I$ , and write the time-independent Schrodinger equation using polar coordinates  $(\rho, \phi)$ .

The total energy of the rotor is only the rotational kinetic energy,

$$E = \frac{1}{2} I \dot{\phi}^2$$

The angular momentum is  $L = I \dot{\phi}$  so the energy simplifies to

$$E = \frac{L^2}{2I}$$

The hamiltonian is written as

$$\begin{aligned} \mathcal{H} &= \frac{-\hbar^2}{2M} \nabla^2 \\ &= \frac{-\hbar^2}{2M} \left[ \frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} \right] \\ &= \frac{-\hbar^2}{2I} \left[ \frac{\partial^2}{\partial \phi^2} \right] \end{aligned}$$

So, Schrodinger's equation is

$$\frac{-\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2} \psi(\phi) = E \psi(\phi)$$

- (b) Find the normalized solution,  $\psi(\phi)$ , of the Schrodinger equation. Is there any degeneracy?  
The solution is clearly of the form

$$\psi(\phi) = Ne^{i\sqrt{2IE}\phi/\hbar}$$

Now, to normalize it,

$$1 = N^2 \int_0^{2\pi} e^{i\sqrt{2IE}\phi/\hbar} e^{-i\sqrt{2IE}\phi/\hbar} d\phi$$

$$N = \frac{1}{\sqrt{2\pi}}$$

The normalized solution is, therefore,

$$\psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{i\sqrt{2IE}\phi/\hbar}$$

There is rotational degeneracy, or at least the quantum mechanical model says there should be. The wavefunction should repeat itself for every interval of  $2\pi$ :

$$\psi(\phi + 2\pi) = \psi(\phi)$$

This introduces quantization of the states. So, the value  $\frac{\sqrt{2IE}}{\hbar}$  must be an integer for this rotational symmetry to be satisfied.

- (c) Find the allowed energies for the two-dimensional rotator.

Since,

$$\frac{\sqrt{2IE}}{\hbar} = n, \quad n = 0, \pm 1, \pm 2, \dots$$

then

$$E = \frac{n^2 \hbar^2}{2I}, \quad n = 0, \pm 1, \pm 2, \dots$$

- (d) Using the old quantum theory (Wilson-Sommerfeld rules), what are the allowed energies of the two-dimensional rotator? Compare this result to (c).

The old quantum theory states that

$$\int p dq = nh$$

where  $p$  is the generalized momentum and  $q$  is the generalized coordinate. The integral is calculated over one rotation. The momentum is angular,

$$L = I\dot{\phi}$$

so

$$\int_0^{2\pi} I\dot{\phi} d\phi = 2\pi L = nh$$

More clearly,

$$L = n\hbar$$

Therefore, the energy is

$$E = \frac{L^2}{2I} = \frac{n^2 \hbar^2}{2I}$$

exactly the same as using the ‘new’ quantum theory.

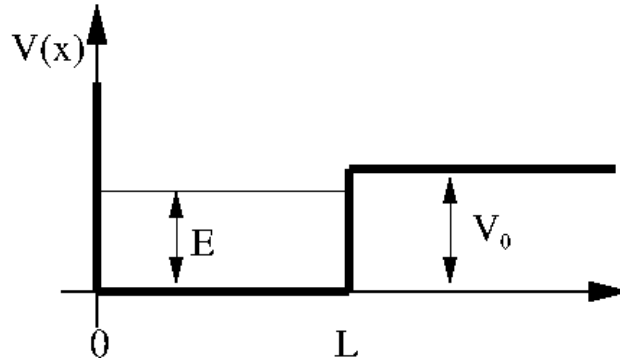
- (e) Consider a particle of mass  $M$  fixed at one end of a rigid rod of negligible mass and length  $\rho$ , but this time the mass is free to move about the origin in three dimensions. Without proof, what are the allowed energies of this system, and compare this set of values to the two-dimensional rotator. Can this more general case reduce to the simpler case?

The 3D rotor has energies

$$E = \frac{\hbar^2 \ell(\ell + 1)}{2I}$$

where  $\ell$  is the orbital angular momentum quantum number. The energy in the 3D case only depends on  $\ell$ , however the energy levels are  $2\ell + 1$  degenerate with  $m = -\ell, -\ell + 1, \dots, \ell - 1, \ell$ .

**Problem A2.** A particle of mass  $m$  is located in a one dimensional potential field  $V(x)$  whose shape is shown below, where  $V(0) = +\infty$



- (a) Find the transcendental equation defining the possible bound state energies of the particle.

Given that  $E < V_0$ , the wavefunction is described by the following:

$$\psi(x) = \begin{cases} Ae^{i\sqrt{2mE}x/\hbar} + Be^{-i\sqrt{2mE}x/\hbar}, & 0 < x \leq L \\ Ce^{-\sqrt{2m(V_0-E)}x/\hbar}, & x \geq L \end{cases}$$

Between 0 and  $L$ , the wave function is sinusoidal but since the potential is infinity at  $x = 0$ , the wave function must be zero there, which leads to the first boundary condition. Simply,

$$A + B = 0$$

The second condition is the continuity at  $x = L$ . So, including the first condition,

$$Ae^{i\sqrt{2mE}L/\hbar} - Ae^{-i\sqrt{2mE}L/\hbar} = Ce^{-\sqrt{2m(V_0-E)}L/\hbar}$$

The final condition is the continuity of the first derivative of the wave function at  $L$ :

$$\frac{i\sqrt{2mE}}{\hbar}e^{i\sqrt{2mE}L/\hbar} + \frac{i\sqrt{2mE}}{\hbar}Ae^{-i\sqrt{2mE}L/\hbar} = \frac{-\sqrt{2m(V_0-E)}}{\hbar}Ce^{-i\sqrt{2m(V_0-E)}L/\hbar}$$

Dividing the two equations gives

$$\frac{-\sqrt{2m(V_0-E)}}{\hbar} = \frac{i\sqrt{2mE}}{\hbar} \left( \frac{e^{i\sqrt{2mE}L/\hbar} + e^{-i\sqrt{2mE}L/\hbar}}{e^{i\sqrt{2mE}L/\hbar} - e^{-i\sqrt{2mE}L/\hbar}} \right)$$

or

$$-\sqrt{\frac{V_0-E}{E}} = \cot \left( \frac{\sqrt{2mE}}{\hbar} L \right)$$



To simplify, square and solve for  $V_0$ :

$$V_0 = E \csc^2 \left( \frac{\sqrt{2mE}}{\hbar} L \right)$$

which is the transcendental equation that defines the possible bound state energies of the particle.

For completeness' sake, if  $E > V_0$ , the wave function changes only slightly:

$$\psi(x) = \begin{cases} Ae^{i\sqrt{2mE}x/\hbar} + Be^{-i\sqrt{2mE}x/\hbar}, & 0 < x \leq L \\ Ce^{i\sqrt{2m(E-V_0)}x/\hbar}, & x \geq L \end{cases}$$

Nothing really changes from the  $E < V_0$  case except the transcendental equation loses the negative and gains an  $i$ . So, working it out, we get

$$\sqrt{\frac{E - V_0}{E}} = \coth \left( \frac{\sqrt{2mE}}{\hbar} L \right)$$

- (b) Sketch a graphical solution of this equation and identify (of course only qualitatively) the values of the discrete energy spectrum
- (c) Find the minimum value of the quantity  $L^2 V_0$  for which the first bound state energy appears for  $E < V_0$ .

Start with

$$\sin^2 \sqrt{\frac{2mEL^2}{\hbar^2}} = \frac{E}{V_0}$$

Let  $m = 1$  and let  $x = \frac{E}{V_0}$ . Then

$$\sin^2 \sqrt{\frac{2}{\hbar^2} V_0 L^2 x} = x$$

Solving for  $V_0 L^2$ , we find that

$$V_0 L^2 = \frac{\hbar^2}{2x} (\sin^{-1} \sqrt{x})^2$$

For  $x = 1$  (for the minimum value), we then see that

$$V_0 L^2 = \frac{\hbar^2 \pi^2}{8}$$

**Problem A3.** A particle of mass  $m$  moves under the action of a two-dimensional field of force whose potential energy is given by

$$V(X, Y) = \frac{1}{2} m \omega^2 [(1+k)^2 X^2 + (2-2k)^2 Y^2]$$

where  $\omega > 0$  and  $k$  is a parameter whose range of variation is  $0 \leq k \leq 1$ .

- (a) Write the Hamiltonian of this system in terms of the creation and annihilation operators  $a_x^\dagger$ ,  $a_y^\dagger$ ,  $a_x$ , and  $a_y$ . Also, write down the eigenstates and the corresponding eigenvalues.

The Hamiltonian is

$$\mathcal{H} = \frac{P_x^2}{2m} + \frac{P_y^2}{2m} + \frac{1}{2} m \omega^2 [(1+k)^2 X^2 + (2-2k)^2 Y^2]$$

Letting  $\omega_x = \omega(1 + k)$  and  $\omega_y = \omega(2 - 2k)$ , we can rewrite the Hamiltonian as

$$\begin{aligned}\mathcal{H} &= \frac{1}{2m}(p_x^2 + p_y^2) + \frac{m}{2}(\omega_x^2 x^2 + \omega_y^2 y^2) \\ \mathcal{H} &= \left[ \frac{p_x^2}{2m} + \frac{1}{2}m\omega_x^2 x^2 \right] + \left[ \frac{p_y^2}{2m} + \frac{1}{2}m\omega_y^2 y^2 \right]\end{aligned}$$

There is a clear symmetry in the  $x$  and  $y$  directions, so we will just look at the  $x$  component of the Hamiltonian. By rewriting the position and momentum operators as

$$\begin{aligned}x &= \sqrt{\frac{\hbar}{2m\omega_x}} (a_x^\dagger + a_x) & y &= \sqrt{\frac{\hbar}{2m\omega_y}} (a_y^\dagger + a_y) \\ p_x &= i\sqrt{\frac{m\hbar\omega_x}{2}} (a_x^\dagger - a_x) & p_y &= i\sqrt{\frac{m\hbar\omega_y}{2}} (a_y^\dagger - a_y)\end{aligned}$$

we can transform the Hamiltonian into a function of the creation and annihilation operators.

$$\begin{aligned}\mathcal{H} &= \frac{p_x^2}{2m} + \frac{1}{2}m\omega_x^2 x^2 \\ &= -\frac{1}{2m} \frac{m\hbar\omega_x}{2} (a_x^\dagger - a_x)^2 + \frac{1}{2}m\omega_x^2 \frac{\hbar}{2m\omega_x} (a_x^\dagger + a_x)^2 \\ &= -\frac{\hbar\omega_x}{4} (a_x^\dagger a_x^\dagger - a_x^\dagger a_x - a_x a_x^\dagger + a_x a_x) + \frac{\hbar\omega_x}{4} (a_x^\dagger a_x^\dagger + a_x^\dagger a_x + a_x a_x^\dagger + a_x a_x) \\ \mathcal{H} &= \frac{\hbar\omega_x}{2} (a_x^\dagger a_x + a_x a_x^\dagger)\end{aligned}$$

Therefore, the total Hamiltonian is

$$\boxed{\mathcal{H} = \frac{\hbar\omega(1+k)}{2} (a_x^\dagger a_x + a_x a_x^\dagger) + \hbar\omega(1-k) (a_y^\dagger a_y + a_y a_y^\dagger)}$$

Since  $\mathcal{H}\psi_n = E_n\psi_n$ , the corresponding energy eigenvalues are

$$\begin{aligned}E_n &= E_{nx} + E_{ny} = \hbar\omega_x \left( n_x + \frac{1}{2} \right) + \hbar\omega_y \left( n_y + \frac{1}{2} \right) \\ &= \hbar\omega \left[ (1+k) \left( n_x + \frac{1}{2} \right) + 2(1-k) \left( n_y + \frac{1}{2} \right) \right]\end{aligned}$$

$$\boxed{E_n = \hbar\omega \left[ (1+k)n_x + 2(1-k)n_y + \frac{1}{2}(3-k) \right]}$$

By solving for  $a$  and  $a^\dagger$  in terms of the position and momentum operators, we can solve for the ground eigenstate. With  $a_x d = \frac{1}{2} \sqrt{\frac{2}{m\hbar\omega_x}} (m\omega_x x + \hbar \frac{\partial}{\partial x})$ ,

$$a\psi_0 = 0$$

$$\frac{1}{2} \sqrt{\frac{2}{m\hbar\omega_x}} \left( m\omega_x x + \hbar \frac{\partial}{\partial x} \right) \psi_0 =$$

$$\hbar \frac{\partial}{\partial x} \psi_0 = -m\omega_x x \psi_0$$

$$\frac{\partial \psi_0}{\partial x} = -\frac{m\omega_x}{\hbar} x \psi_0$$

$$\int \frac{1}{\psi_0} d\psi_0 = -\frac{m\omega_x}{\hbar} \int x dx$$

$$\ln \psi_0 = -\frac{m\omega_x}{2\hbar} x^2$$

$$\psi_0 = A e^{-\frac{m\omega_x x^2}{2\hbar}}$$

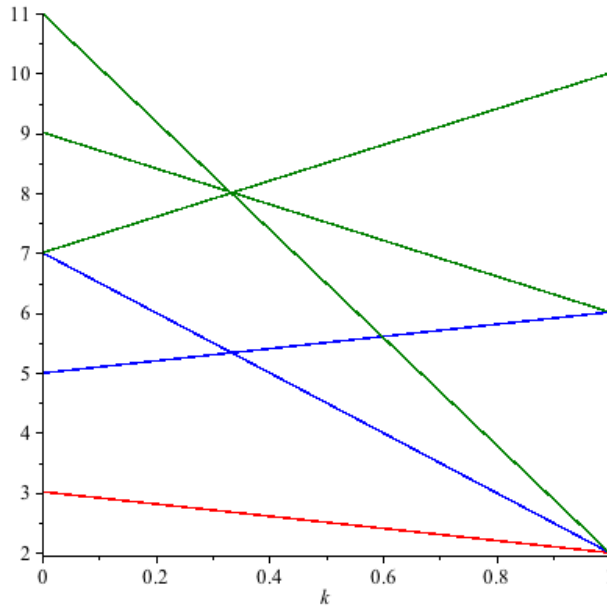
By normalizing  $\psi_0$ , we find that  $A^2 = \sqrt{\frac{m\omega_x}{\pi\hbar}}$ . The complete ground state is then

$$\psi_0(x, y) = \sqrt{\frac{m\omega(1-k)}{\pi\hbar}} (2)^{1/4} e^{-\frac{m\omega}{2\hbar} ((1+k)x^2 + 2(1-k)y^2)}$$

All eigenstates are then

$$\psi_n(x, y) = \frac{(a_x^\dagger)^{n_x}}{\sqrt{n_x!}} \frac{(a_y^\dagger)^{n_y}}{\sqrt{n_y!}} \psi_0(x, y)$$

- (b) Plot the ground state energy and the energies of the lowest three excited states as functions of the parameter  $k$ . Discuss the possible degeneracies.



The ground state energy corresponds to  $n_x = n_y = 0$ . As a function of  $k$ , the energy is

$$E_0(k) = \frac{1}{2} \hbar \omega (3 - k)$$

It is difficult to determine which energy is the lowest excited state. For example, comparing the state  $n_x = 1$  and  $n_y = 0$  with the state  $n_x = 0$  and  $n_y = 1$ , there are certain ranges of  $k$  for which each state could have a higher energy. In this case, for  $k$  less than  $\frac{1}{3}$ , the state  $n_x = 0$ ,  $n_y = 1$  has a lower energy than the state  $n_x = 1$ ,  $n_y = 0$ . For two different states, there could either be zero or one degeneracies in  $k$ .

- (c) When  $k = 0$ , the angular momentum operator  $L_z = XP_y - YP_x$ , expressed in terms of creation and annihilation operators, takes the form

$$L_z = i\hbar (a_x a_y^\dagger - a_x^\dagger a_y)$$

If the oscillator is prepared in the state

$$|\psi\rangle = \frac{1}{\sqrt{2}} (|1, 0\rangle + i|0, 1\rangle)$$

what is the expectation value of its angular momentum along the  $z$ -axis?

*Hint:*

$$X = \sqrt{\frac{\hbar}{2m\omega}} (a_x^\dagger + a_x), \quad P_x = i\sqrt{\frac{m\hbar\omega}{2}} (a_x^\dagger - a_x)$$

The expectation value for angular momentum is

$$\begin{aligned} \langle\psi|L_z|\psi\rangle &= \left( \frac{1}{\sqrt{2}}\langle 1, 0| - \frac{i}{\sqrt{2}}\langle 0, 1| \right) i\hbar (a_x a_y^\dagger - a_x^\dagger a_y) \left( \frac{1}{\sqrt{2}}|1, 0\rangle + \frac{i}{\sqrt{2}}|0, 1\rangle \right) \\ &= \left( \frac{1}{\sqrt{2}}\langle 1, 0| - \frac{i}{\sqrt{2}}\langle 0, 1| \right) \frac{i\hbar}{\sqrt{2}} (a_x a_y^\dagger |1, 0\rangle + i a_x a_y^\dagger |0, 1\rangle - a_x^\dagger a_y |1, 0\rangle - i a_x^\dagger a_y |0, 1\rangle) \end{aligned}$$

Since we can't lower the zero state, two of the terms drop out and we are left with

$$\begin{aligned} \langle\psi|L_z|\psi\rangle &= \left( \frac{1}{\sqrt{2}}\langle 1, 0| - \frac{i}{\sqrt{2}}\langle 0, 1| \right) \frac{i\hbar}{\sqrt{2}} (a_x a_y^\dagger |1, 0\rangle - i a_x^\dagger a_y |0, 1\rangle) \\ &= \left( \frac{1}{\sqrt{2}}\langle 1, 0| - \frac{i}{\sqrt{2}}\langle 0, 1| \right) \frac{i\hbar}{\sqrt{2}} (|0, 1\rangle - i|1, 0\rangle) \\ &= \frac{\hbar}{2} + \frac{\hbar}{2} \\ \boxed{\langle\psi|L_z|\psi\rangle} &= \hbar \end{aligned}$$

**Problem B1.**  $N$  atoms are arranged to lie on a simple cubic crystal lattice. Then  $M$  of these atoms are moved from their lattice sites to lie at the interstices of the lattice, that is, points which lie centrally between the lattice sites (i.e., centers of the unit cells). Assume that the atoms are placed in the interstices in a way which is completely independent of the positions of the vacancies; therefore a lattice atom does not necessarily go to one of the nearest interstitial sites. Assume also that no two atoms may be placed at the same interstitial site and  $N$  and  $M$  are much larger than 1.

- (a) Show that the number of ways of taking  $M$  atoms from the lattice sites and placing them on interstices is

$$W = \left[ \frac{N!}{M!(N-M)!} \right]^2$$

if there are  $N$  interstitial sites where displaced atoms can sit.

If there are  $N$  places for an atom to sit and  $M$  atoms to be removed, there are

$$W_{remove} = \binom{N}{M} = \frac{N!}{M!(N-M)!}$$

ways of removing  $M$  atoms from the lattice sites. Additionally, once those atoms are removed, there are

$$W_{place} = \frac{N!}{M!(N-M)!}$$

ways of placing those  $M$  atoms once removed. So, there are total

$$W = \left[ \frac{N!}{M!(N-M)!} \right]^2$$

ways of removing and placing  $M$  atoms.

- (b) Suppose that the energy required to move an atom off its lattice site into an interstitial site is  $\varepsilon$ . The energy is  $U = M\varepsilon$ , if there are  $M$  interstitial atoms. Show that the fraction of interstitial atoms over the total number of atoms at temperature  $T$  is given by

$$\frac{M}{N} = \frac{1}{e^{\frac{\varepsilon}{2k_B T}} + 1}$$

Begin by writing the entropy:

$$\begin{aligned} S &= k \ln W \\ &= 2k \ln N! - 2k \ln M! - 2k \ln(N-M)! \\ &= 2kN \ln N - 2kN - 2kM \ln M + 2kM - 2k(N-M) \ln(N-M) + 2k(N-M) \\ &= 2kN \ln N - 2kM \ln M - 2k(N-M) \ln(N-M) \end{aligned}$$

We can plug in  $M = \frac{U}{\varepsilon}$  and use the equation

$$\frac{\partial S}{\partial U} = \frac{1}{T}$$

to solve for  $N$ :

$$\begin{aligned} \frac{1}{T} &= \frac{\partial}{\partial U} \left[ 2kN \ln N - 2k \frac{U}{\varepsilon} \ln \frac{U}{\varepsilon} - 2k \left( N - \frac{U}{\varepsilon} \right) \ln \left( N - \frac{U}{\varepsilon} \right) \right] \\ &= -2k \frac{U}{\varepsilon} \frac{1}{U} - 2k \frac{1}{\varepsilon} \ln \frac{U}{\varepsilon} - 2kN \frac{1}{N - \frac{U}{\varepsilon}} \left( -\frac{1}{\varepsilon} \right) + 2k \frac{U}{\varepsilon} \frac{1}{N - \frac{U}{\varepsilon}} \left( -\frac{1}{\varepsilon} \right) + 2k \frac{1}{\varepsilon} \ln \left( N - \frac{U}{\varepsilon} \right) \\ &= \frac{-2k}{\varepsilon} + \frac{2k}{\varepsilon} \ln \left( \frac{N - \frac{U}{\varepsilon}}{\frac{U}{\varepsilon}} \right) + \frac{2k}{\varepsilon} \left( \frac{1}{N - \frac{U}{\varepsilon}} \right) \left( N - \frac{U}{\varepsilon} \right) \\ &= \frac{2k}{\varepsilon} \ln \left( \frac{N\varepsilon}{U} - 1 \right) \\ \frac{\varepsilon}{2kT} &= \ln \left( \frac{N\varepsilon}{U} - 1 \right) \\ e^{\frac{\varepsilon}{2kT}} &= \frac{N\varepsilon}{U} - 1 \end{aligned}$$

So, we find that

$$N = \frac{U}{\varepsilon} \left( 1 + e^{\frac{\varepsilon}{2kT}} \right) = M \left( 1 + e^{\frac{\varepsilon}{2kT}} \right)$$

Finally, we get

$$\frac{M}{N} = \frac{1}{1 + e^{\frac{\epsilon}{2kT}}}$$

**Problem B2.** Consider an ideal gas made of a uniform suspension of non-interacting, randomly oriented electric dipoles, of mass  $m$  and dipole moment  $\mu$  in a uniform electric field of magnitude  $E$ .

(a) Write the classical Hamiltonian for each dipole.

$$\mathcal{H} = \vec{\mu} \cdot \vec{E} + \frac{5}{2}kT$$

(b) Write the canonical partition function for an ideal gas consisting of an ensemble of  $N$  such dipoles in a volume  $V$  at a temperature  $T$ .

$$Z_N = \frac{1}{N!} Z_1^N$$

$$Z_N = \frac{1}{N!} e^{-(\mu NE + \frac{5}{2}NkT)/kT}$$

(c) Derive an expression for the Helmholtz free energy of the ensemble as a function of field  $E$ .

$$\begin{aligned} A &= -kT \ln Z_N \\ &= -kT \left[ - \left( \mu NE + \frac{5}{2}NkT \right) \frac{1}{kT} - N \ln N + N \right] \\ &= \mu NE + \frac{5}{2}NkT + NkT \ln N - NkT \\ A &= \mu NE + NkT \left( \frac{3}{2} + \ln N \right) \end{aligned}$$

(d) What happens to the entropy  $S$  as the field increases?

$$\begin{aligned} S &= k \ln Z_N \\ &= k \left[ - \left( \beta \mu E + \frac{5}{2} \right) N - N \ln N + N \right] \\ S &= k \left( -\beta \mu NE - \frac{3}{2}N - N \ln N \right) \end{aligned}$$

As the electric field increases, the entropy decreases.

(e) Explain qualitatively why your answer to part (d) makes sense.

The entropy is a measure of how ordered a system is: the more chaos and randomness, the greater the entropy. As the strength of the electric field increases, more of the electric dipoles

will align themselves with the field. This reduces the randomness, causing the entropy to decrease.