

Quantum Mechanics

NAME:

Homework 5b: The Free Electron Gas Model and Statistical Mechanics

022 qmult 00100 1 1 3 easy memory: simplest quantum mechanical solid model

1. The simplest quantum mechanical solid model is arguably:
 - a) the hydrogen atom.
 - b) the helium atom.
 - c) the free electron gas model.
 - d) the infinite periodic potential model.
 - e) the finite periodic potential model.

SUGGESTED ANSWER: (c)

The free electron gas model of a solid was developed by Arnold Sommerfeld (1868–1951) starting in 1927 shortly after the discovery of quantum mechanics in 1926 or so. The free electron gas model was developed starting from Drude classical free electron gas model. Sommerfeld was getting on in years when he developed the free electron gas models. It's proof that older physicists/dogs can sometimes learn new tricks.

Wrong answers:

- a) A nonsense answer.

Redaction: Jeffery, 2008jan01

022 qmult 00110 1 1 1 easy memory: infinite square boundary conditions

2. For the free electron gas model of a solid, one common simple choice of boundary conditions is:
 - a) infinite square well boundary conditions.
 - b) finite square well boundary conditions.
 - c) Gaussian well boundary conditions.
 - d) hydrogen atom boundary conditions.
 - e) helium atom boundary conditions.

SUGGESTED ANSWER: (a)

Wrong answers:

- b) These can be used and must be used, I imagine, in some cases. But they are not a simple choice.

Redaction: Jeffery, 2008jan01

022 qmult 00130 1 4 4 easy deducto-memory: periodic boundary conditions

Extra keywords: mathematical physics

3. “Let’s play *Jeopardy!* For \$100, the answer is: These quantum mechanical boundary conditions for solids, also known as Born-von-Karman boundary conditions, are not realistic in most cases. They are realistic in some cases. For example, for the dimension of a solid that forms a closed loop: e.g., a solid that has donut shape can have an angular coordinate that must be periodic by symmetry over the range $[0^\circ, 360^\circ]$. But whether realistic or not, it can be shown that they lead to the same average behavior as realistic boundary conditions for macroscopically large solid samples.

Why are these boundary conditions used at all? Well for one thing they are an ideal kind of boundary conditions that are completely independent of what the surface behavior of solid is. Thus, they are neutral case. For another thing they are easy to use in developments in particular when dealing with periodic potentials in a solid.”

What are _____, Alex?

- | | |
|---|----------------------------------|
| a) infinite square well boundary conditions | b) aperiodic boundary conditions |
| c) Rabi-Schwinger-Baym-Sutherland boundary conditions | d) periodic boundary conditions |
| e) relaxed boundary conditions | |

SUGGESTED ANSWER: (d)

Wrong answers:

- a) Exactly wrong.
- b) Exactly wrong.
- c) I.I. Rabi (1898–1988), Julian Schwinger (1918–1994), Gordon Baym (circa 1935–), Peter Sutherland (circa 1945–) to well me: my Ph.D. pedigree.

Redaction: Jeffery, 2008jan01

022 qfull 00100 2 5 0 moderate thinking: free electron gas model of a solid

Extra keywords: (Ha-324:2.4)

4. The free electron gas model of a solid is arguably the simplest model of solid. The electrons are assumed to be non-interacting fermions confined to a potential well. The background of positive ions and the electrons's own Coulomb force combine to create the potential well. The potential inside the well is flat. The most obvious set of boundary conditions are infinite square well boundary conditions.

Periodic boundary conditions (AKA Born-Von-Karman boundary conditions) are also used. They give the same macroscopic results as infinite square well boundary conditions and are better suited for treating periodic potentials inside solids. Periodic boundary conditions actually means you imagine space looping back on itself for opposing ends of a rectangular box. If you go out one end, you come back in the opposing end. If we assume a 1-dimensional wave function along a box dimension (which we actually require in our development in this problem), then we demand that that wave function be single-valued as it loops around and around through looped space. We have no physical meaning for a multi-valued wave function. You could at first imagine that there could be a discontinuity in the wave function as it crosses a boundary. But the ordinary continuity conditions on a wave function at locations of finite potential require that the wave function and its 1st derivative must be continuous across the boundary. Thus, to loop back into itself, the wave function and its 1st derivative must have the same values at opposing boundaries.

Let us consider a free electron gas model of a solid in 1, 2, and 3 dimensions simultaneously. Use periodic boundary conditions in all three cases: a 1-dimensional rectangular box is a line segment, a 2-dimensional rectangular box is a rectangle, and a 3-dimensional rectangular box is what one ordinarily means by a rectangular box. Let L_i be the length of side i of the rectangular box and $V = \prod_i L_i$ be the rectangular box volume. Let ℓ be the number of dimensions.

- a) Solve the time-independent Schrödinger equation for the single-particle stationary states for all three dimension cases. These states can be called k states since they distinguished by their wavenumbers for the available dimensions. Normalize the solutions and give their quantization rules for wavenumber and energy. **HINT:** You must separate the multi-particle time-independent Schrödinger equation.
- b) Each single-particle stationary k state can be located in what is called k -space by a wavenumber vector $\vec{k} = (k_1, k_2, k_3)$, where we have used 1, 2, and 3 to label the dimensions. What is the volume V_k in k -space of the k -space rectangular boxes that are centered on the stationary state wavenumber vector tips and tile all k -space without gaps or overlaps and are all of the same size. The volume V_k is the k -space volume per state. What is the average density of spatial states in k -space ρ_k ?
- c) We now make the continuum approximation which is valid for samples that are macroscopic in all available dimensions. This means that we treat the average density of spatial states in k -space as if it were an uniform density. Find the expression for the differential number of states dN_k per unit space volume in a spherical shell in k -space. The shell radius is k and its thickness is dk . Include the spin degeneracy by a factor g which equals 2 for spin 1/2 electrons. But leave g unevaluated. By leaving g unevaluated, one can track how the spin degeneracy affects dN_k and expressions derived from dN_k .
- d) The Pauli exclusion principle for fermions requires that each single particle k state (where the states now thought of as distinguished by both wavenumber vector and spin state) have only one fermion at most. This statement must be qualified. What it really means is that the product wave function of single particle states can have each distinct single-particle state included once only. If there are N fermions, the overall symmetrized wave function contains $N!$ versions of the product wave function with the individual particle coordinate labels in all possible permutations. But we don't have to worry about product wave functions or symmetrized wave functions explicitly in the free electron gas model of solids. We simply make use of the Pauli exclusion principle to say that the single-particle states can only be used once in calculating results or to put this in common jargon only one electron can occupy at single particle state at most.

Now in the ground state of (which is the absolute zero temperature state) in our free electron gas model, the electrons occupy the lowest energy single-particle states consistent with the Pauli exclusion principle. This means in k -space, the electrons occupy a sphere of radius k_F where F where stands for Fermi. Since F stands for a name, not a variable it ought to be in Roman, not Italic, font, but convention seems to dictate Italic font (e.g., Gr-221, CT-1435). (I guess since

Fermi was Italian ...) The radius k_F is called the Fermi wavenumber. The sphere is called the Fermi surface. It's not called the Fermi sphere usually since the concept of Fermi surface applies to periodic potential cases, where in general the Fermi surface is not a sphere.

Using the results of the part (c) answer solve for k_F in general and explicitly for the 3 dimensional cases. Assume the electron density (in space space) is $n_e = N/V$.

- e) Now solve for the Fermi energy E_F in general and for the 3 dimensional cases.
- f) What is ρ_E : i.e., the density of states per unit space volume per unit energy in the continuum of states approximation. Write a general formula that is valid for all three dimension cases. **HINT:** One requires the same number of states between any corresponding limits: i.e.,

$$dN = \rho_{k \text{ shell}} dk = \rho_E dE ,$$

where $\rho_{k \text{ shell}}$ is the density of k states in the differential k space shell dk . The general expression for $\rho_{k \text{ shell}}$ must have turned up in the part (c) answer without so labeling it.

- g) Now solve for the total energy per unit space volume \mathcal{E} of the ground state for electron density n_e . Also find E_{ave} the average energy of the electrons. Don't bother to expand E_F using the expressions from the part (e) answer. The formulae for this answer are long enough as it is. Just do the general dimensional case for \mathcal{E} , but show all the dimensional cases explicitly for E_{ave} .

SUGGESTED ANSWER:

- a) The multi-particle time-independent Schrödinger equation for the free electron gas model is

$$H\psi = \sum_j H_j \psi = E\psi ,$$

where

$$H_j = -\frac{\hbar^2}{2m} \nabla_j^2$$

and the sum is over all particles. The equation is obviously separable. We let

$$\psi(\vec{r}_j) = \prod_j \psi_j(\vec{r}_j)$$

and we find

$$\sum_j \frac{H_j \psi_j}{\psi_j} = E .$$

If we take the derivative of the last equation with respect to general $x_{j'}$, where j' is one of the indexes j , all terms that do **NOT** depend on $x_{j'}$ are zero explicitly and the term that does depend on $x_{j'}$ must equal zero too since everything else in the derivative is zero. The same is true for y_j and z_j . We conclude that all terms in the last equation are constants with respect to the spatial coordinates. We can obviously define the constants of separation as the individual particle energies E_j .

The multi-particle Schrödinger equation now separates into single-particle Schrödinger equations. Since the particles are identical, all these equations are identical aside from particle label. These equations are

$$H_j \psi_j = E_j \psi_j .$$

We can separate the single-particle Schrödinger equation into single-dimension Schrödinger equations. The procedure is the same as that given above *mutatis mutandis*, and we get

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = E\psi ,$$

for the x dimension, where we have suppressed the particle label since it is no longer needed. All the other direction have the same single-dimension Schrödinger equations aside from the coordinate label. Thus, we only need to solve for the x dimension and the other dimension solutions are identical aside from coordinate label.

We rewrite the x dimension equation in the form

$$\frac{\partial^2 \psi}{\partial x^2} = \kappa^2 \psi ,$$

where we define

$$\kappa = \sqrt{\frac{2m(-E)}{\hbar^2}} .$$

The general solution for a given $E \neq 0$ is

$$\psi = Ae^{\kappa x} + Be^{-\kappa x} .$$

To satisfy the periodic boundary conditions, we demand that

$$A + B = Ae^{\kappa L_1} + Be^{-\kappa L_1} \quad \text{and} \quad A - B = Ae^{\kappa L_1} - Be^{-\kappa L_1} .$$

Adding and subtracting these expressions gives

$$A = Ae^{\kappa L_1} \quad \text{and} \quad B = Be^{-\kappa L_1} .$$

If $E < 0$, the boundary conditions cannot be satisfied, unless $A = B = 0$ which is an unnormalizable solution. So there are no physical solutions for $E < 0$. If $E > 0$, let $\kappa = ik$, where

$$k = \sqrt{\frac{2mE}{\hbar^2}} .$$

Now the boundary conditions imply

$$A = Ae^{ikL_1} \quad \text{and} \quad B = Be^{-ikL_1} .$$

These can only be satisfied if

$$kL_1 = 2\pi n ,$$

where $n = 1, 2, 3, \dots$. If $E = 0$, the general solution is

$$\psi = A + Bx .$$

The constant solution can match the periodic boundary solutions and is allowed, but the linear solution cannot and is not.

We can write all allowed solutions compactly if let k be positive or negative or zero and be quantized by

$$kL = 2\pi n \quad \text{or} \quad k = \frac{2\pi}{L}n ,$$

where $n = 0, \pm 1, \pm 2, \pm 3, \dots$ and

$$E = \frac{\hbar^2 k^2}{2m} .$$

The general k solution is then

$$\psi = Ae^{ikx} .$$

The general solution for a given energy E is

$$\psi = Ae^{i|k|x} + Be^{-i|k|x} .$$

The energy solutions are doubly degenerate. In fact, the general k solution is more useful form since it is the most elementary single-particle states that are useful in constructing or considering the overall symmetrized state. Also the two energy degenerate states are not degenerate for wavenumber and momentum (which are the same thing). They are different eigen-states of the wavenumber observable and momentum observable: i.e.,

$$\frac{1}{i} \frac{\partial}{\partial x} \quad \text{and} \quad \frac{\hbar}{i} \frac{\partial}{\partial x} .$$

These observables are actually the same observable aside from the coefficient \hbar . The eigenvalues are wavenumbers k and momenta $\hbar k$. Clearly, the states are not degenerate for k and $\hbar k$. So particle in a mixed state can be collapsed to one of them by a measurement of wavenumber or momentum.

Note that the periodic boundary conditions on the stationary states enforces quantization of k and therefore of E . Note also our solutions are infinitely differentiable everywhere, and thus everywhere satisfy the continuity conditions required of wave functions.

The normalization requirement determines A . We find

$$1 = |A|^2 \int_0^{L_1} |e^{ikx}|^2 dx = |A|^2 L_1 .$$

In general we could chose $A = e^{i\phi}/L^{1/2}$ where ϕ is some real number. The phase factor $e^{i\phi}$ is just a global phase factor. Global phase factors are physically irrelevant: wave functions that differ by different phases are **NOT** physically distinct.

Thus, the general wave function for 1-dimension is

$$\psi = \frac{1}{L_1^{1/2}} e^{ikx} .$$

The overall single-particle wave function is

$$\psi(\vec{r}) = \frac{1}{\sqrt{V}} e^{\sum_i ik_i x_i} = \frac{1}{\sqrt{V}} e^{i\vec{k}_i \cdot \vec{r}} ,$$

where V is the volume any number of dimensions of the rectangular box we used the subscripts 1, 2, and 3 to label the three dimensions, and \vec{k} is the wavenumber vector of the k state. The quantization rules for the k_i and energy are, respectively,

$$k_i L_i = 2\pi n_i \quad \text{or} \quad k_i = \frac{2\pi}{L_i} n_i$$

and

$$E = \frac{\hbar^2}{2m} (2\pi)^2 \sum_i \left(\frac{n_i}{L_i} \right)^2 ,$$

where

$$n_i = 0, \pm 1, \pm 2, \pm 3, \dots .$$

b) Well

$$\Delta k_i = \frac{2\pi}{L_i} \Delta n_i = \frac{2\pi}{L_i}$$

for $\Delta n_i = 1$. Thus, the volume per k state in k -space is

$$V_k = \frac{(2\pi)^\ell}{V} ,$$

where recall V is the rectangular box volume.

The average density of the k states in k space is

$$\rho_k = \frac{1}{V_k} = \frac{V}{(2\pi)^\ell} .$$

c) The number of states in differential shell of radius k and thickness dk is

$$dN_k = \frac{gf}{(2\pi)^\ell} k^{\ell-1} dk ,$$

where $g = 2$ is the spin degeneracy and where

$$f = \begin{cases} 2 & \text{for } \ell = 1; \\ 2\pi & \text{for } \ell = 2; \\ 4\pi & \text{for } \ell = 3. \end{cases}$$

d) Behold:

$$n_e = \int_0^{k_F} \frac{gf}{(2\pi)^\ell} k^{\ell-1} dk = \frac{gf}{(2\pi)^\ell} \frac{k_F^\ell}{\ell} .$$

Inverting, we find the Fermi wavenumber to be

$$k_F = \begin{cases} \left[\frac{(2\pi)^\ell \ell}{gf} \right]^{1/\ell} n_e^{1/\ell} & \text{in general;} \\ \left(\frac{2}{g} \right) \left(\frac{\pi}{2} \right) n_e & \text{for } \ell = 1; \\ \left[\left(\frac{2}{g} \right) (2\pi) \right]^{1/2} n_e^{1/2} & \text{for } \ell = 2; \\ \left[\left(\frac{2}{g} \right) (3\pi^2) \right]^{1/3} n_e^{1/3} & \text{for } \ell = 3. \end{cases}$$

e) Since

$$E_F = \frac{\hbar^2 k_F^2}{2m} ,$$

we find

$$E_F = \frac{\hbar^2}{2m} \begin{cases} \left[\frac{(2\pi)^\ell \ell}{gf} \right]^{1/\ell} n_e^{2/\ell} & \text{in general;} \\ \left[\left(\frac{2}{g} \right) \left(\frac{\pi}{2} \right) \right]^2 n_e^2 & \text{for } \ell = 1; \\ \left[\left(\frac{2}{g} \right) (2\pi) \right] n_e & \text{for } \ell = 2; \\ \left[\left(\frac{2}{g} \right) (3\pi^2) \right]^{2/3} n_e^{2/3} & \text{for } \ell = 3. \end{cases}$$

f) Well

$$\rho_E = \rho_{k \text{ shell}} \frac{dk}{dE} , \quad k = \sqrt{\frac{2mE}{\hbar^2}} , \quad \frac{dk}{dE} = \sqrt{\frac{2m}{\hbar^2}} \frac{1}{2\sqrt{E}} .$$

Thus

$$\rho_E = \left(\frac{2m}{\hbar^2} \right)^{\ell/2} \frac{gf}{(2\pi)^\ell} \frac{1}{2} E^{\ell/2-1} .$$

A curious point is that the density of states with respect to energy for $\ell = 1$ diverges as $E \rightarrow 0$. But there is no divergence for the $\rho_{k \text{ shell}}$ as $k \rightarrow 0$ for $\ell = 1$ and the integral of the density of states with respect to energy is finite. So it looks like we've skirted a bad event that would be a failure of the continuum approximation. The bad event being a divergence in the number of states integrated to finite energy.

g) Well

$$\begin{aligned} \mathcal{E} &= \int_0^{E_F} E \rho_E dE = \int_0^{E_F} E \left(\frac{2m}{\hbar^2} \right)^{\ell/2} \frac{gf}{(2\pi)^\ell} \frac{1}{2} E^{\ell/2-1} dE \\ &= \int_0^{E_F} \left(\frac{2m}{\hbar^2} \right)^{\ell/2} \frac{gf}{(2\pi)^\ell} \frac{1}{2} E^{\ell/2} dE \\ &= \left(\frac{2m}{\hbar^2} \right)^{\ell/2} \frac{gf}{(2\pi)^\ell} \frac{1}{2} \frac{1}{\ell/2+1} E^{\ell/2+1} . \end{aligned}$$

Now

$$n_e = \frac{gf}{(2\pi)^\ell} \frac{k_F^\ell}{\ell} = \frac{gf}{(2\pi)^\ell} \frac{1}{\ell} \left(\frac{2m}{\hbar^2} \right)^{\ell/2} E_F^{\ell/2} .$$

and thus

$$E_{\text{ave}} = \frac{\mathcal{E}}{n_e} = \begin{cases} \frac{\ell}{\ell+2} E_F & \text{in general;} \\ \frac{1}{3} E_F & \text{for } \ell = 1; \\ \frac{1}{2} E_F & \text{for } \ell = 2; \\ \frac{3}{5} E_F & \text{for } \ell = 3. \end{cases}$$

FINAL NOTE: In the part (a) answer we ruled out solutions with $E < 0$.

We can offer two proofs there. We can give another proof—which is overkill—but 2nd proof illustrate interesting aspects.

First, there is a simple proof in quantum mechanics that all eigen-energies and expectation value energies are greater than V_{\min} which is the minimum potential in the system. We will only do the proof for 1-dimensional systems with one particle since that gives the flavor, is hard enough, and all we need in this question.

We will consider the expectation value for energy for general state $|\Psi\rangle$ (which includes the time dependence in general) which is defined on the range $[a, b]$. At the endpoints continuity or normalization requires $\Psi(x, t) = 0$ unless periodic boundary conditions are imposed. Behold:

$$\begin{aligned} \langle \Psi | H | \Psi \rangle &= \int_a^b \Psi^* H \Psi \, dx = \int_a^b \Psi^* T \Psi \, dx + \int_a^b \Psi^* V \Psi \, dx \\ &\geq \int_a^b \Psi^* T \Psi \, dx + \int_a^b \Psi^* V_{\min} \Psi \, dx \\ &\geq \int_a^b \Psi^* T \Psi \, dx + V_{\min} \\ &\geq \int_a^b \Psi^* T \Psi \, dx + V_{\min} \\ &\geq -\frac{\hbar^2}{2m} \int_a^b \Psi^* \left(\frac{\partial^2}{\partial x^2} \right) \Psi \, dx + V_{\min} \\ &\geq -\frac{\hbar^2}{2m} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \int_a^b \frac{\partial \Psi^*}{\partial x} \frac{\partial \Psi}{\partial x} \, dx \right) + V_{\min} \\ &\geq \frac{\hbar^2}{2m} \int_a^b \frac{\partial \Psi^*}{\partial x} \frac{\partial \Psi}{\partial x} \, dx + V_{\min} , \end{aligned}$$

where the boundary terms vanish either because $\Psi(x, t) = 0$ there or because we impose periodic boundary conditions.

If we don't impose periodic boundary conditions, $\Psi(x, t)$ must have some curvature since it must be non-zero somewhere to be normalizable and zero at the boundaries. This means

$$\int_a^b \frac{\partial \Psi^*}{\partial x} \frac{\partial \Psi}{\partial x} \, dx > 0$$

which implies

$$\langle \Psi | H | \Psi \rangle > V_{\min} .$$

Since $|\Psi\rangle$ is general, it could be a stationary state. Thus,

$$E > V_{\min} ,$$

where E is a general eigen-energy.

If we do impose periodic boundary conditions, then a constant $\Psi(x, t)$ is allowed for which

$$\int_a^b \frac{\partial \Psi^*}{\partial x} \frac{\partial \Psi}{\partial x} \, dx = 0 .$$

So for periodic boundary conditions, we have only

$$\langle \Psi | H | \Psi \rangle \geq V_{\min} .$$

Since $|\Psi\rangle$ is general, it could be a stationary state. Thus,

$$E = V_{\min} ,$$

where E is a general eigen-energy.

Periodic boundary conditions really can occur for closed ring systems. But periodic boundary conditions are often chosen as ideal boundary conditions for large systems. A periodic system with a flat potential can have an $E = V_{\min}$ solution which is constant. A linear solution also exists for $E = V_{\min}$ from the Schrödinger equation, but it can't meet the periodic boundary conditions, and so is ruled out.

Redaction: Jeffery, 2001jan01

022 qfull 00110 1 3 0 easy math: free electron gas formulae and fiducial formulae

5. For a free electron gas (in 3 dimensions) at absolute zero temperature, the Fermi energy is given by

$$E_F = \frac{\hbar^2}{2m} \left[\left(\frac{2}{g} \right) (3\pi^2)n_e \right]^{2/3} ,$$

where \hbar is Planck constant divided by 2π , m is the electron mass, $g = 2$ is the spin 1/2 particle degeneracy, and

$$n_e = \frac{N}{V}$$

is the free electron density with N being the number of electrons and V being the sample volume. The average energy per electron E_{ave} is given by

$$E_{\text{ave}} = \frac{3}{5} E_F .$$

For this question, you will need the following constants,

$$\begin{aligned} e &= 1.602176487(40) \times 10^{-19} \text{ C} , \\ m &= 9.10938215(45) \times 10^{-31} \text{ kg} , \\ mc^2 &= 510998.910 \text{ eV} , \\ k_B &= 1.3806504(24) \times 10^{-23} \text{ J/K} , \\ \hbar &= 1.054571628(53) \times 10^{-34} \text{ J}\cdot\text{s} , \\ m_{\text{amu}} &= 1.660538782(83) \times 10^{-27} \text{ kg} . \end{aligned}$$

a) Free electron density can be expressed in terms of ordinary density (AKA mass density) ρ by

$$n_e = \frac{\rho}{m_{\text{amu}}} \sum_i \frac{X_i Z_i}{A_i} ,$$

where the sum is over all atoms in the sample, X_i is the mass fraction of atom i , Z_i is the number of free electrons per atom for atom i , and A_i is the atomic weight of atom i . Convince yourself that this formula makes sense. Actually the formula can be simplified by introducing the mean mass per electron μ_e defined by

$$\frac{1}{\mu_e} = \sum_i \frac{X_i Z_i}{A_i} .$$

Take 1000 kg/m^3 as a fiducial value for ρ (which is just like writing density in grams per cubic centimeter). Take 50 as a fiducial value for μ_e : this is like an element in the atomic weight vicinity

of iron with one valence electron delocalized. Now write n_e in terms of fiducial values: i.e., find the coefficient in the formula expression

$$n_e = \text{coefficient} \times \frac{\rho}{1000 \text{ kg/m}^3} \frac{50}{\mu_e},$$

The coefficient is a fiducial electron density.

- b) Now find the formula for E_F in terms of fiducial values both for joules and electronvolts: i.e., find the coefficient in the formula

$$E_F = \text{coefficient} \times \left[\left(\frac{2}{g} \right) \frac{\rho}{1000 \text{ kg/m}^3} \frac{50}{\mu_e} \right]^{2/3}.$$

The coefficient is a fiducial Fermi energy. Are solids in human environments relativistic?

- c) Now find the formula for the Fermi temperature $T_F = E_F/k_B$ in terms of fiducial values both for joules and electronvolts. The coefficient is a fiducial Fermi temperature. Are solids in human environments hot or cold in comparison to the Fermi temperature?
- d) Now find the formula for the Fermi velocity $v_F = \sqrt{2E_F/m}$ (which is the non-relativistic formula) in terms of fiducial values. The coefficient is a fiducial Fermi velocity.
- e) From classical thermodynamics, we know that pressure

$$P = - \left(\frac{\partial E}{\partial V} \right)_{S,N}$$

where E is the sample internal energy, V is the sample volume, S is the sample entropy, N is the sample particle number, and the subscript S, N indicates the partial derivative is taken with entropy and particle number held constant. Since a free electron gas is confined by a confining potential, it must exert a counter potential on entities that confine it. In fact, by the correspondence principle of quantum mechanics, this counter potential can be assumed at the macroscopic level to a free electron gas pressure. The energy of the free electron gas is identifiable with the classical internal energy. Thus, we expect that a free electron gas exhibits a pressure derivable from the classical expression. Observation shows that this expectation is fulfilled. The pressure is called the degeneracy pressure, and its equation of state (i.e., pressure formula) is quite unlike that for an ideal gas. Derive the zero-temperature free-electron-gas pressure formula as a function of n_e . Then find the pressure formula in terms of fiducial values. **HINT:** The total energy of a sample is NE_{ave} .

- f) The bulk modulus of a material is a measure of its incompressibility or stiffness. The definition is

$$B = -V \left(\frac{\partial P}{\partial V} \right)_X = \rho \left(\frac{\partial P}{\partial \rho} \right)_X$$

where one assumes a constant mass and X stands for the thermodynamic variable held constant, either temperature or entropy (which can be held constant by adiabatic conditions). For ordinary solids and liquids, the difference between constant temperature and constant entropy is usually negligible. For a free electron gas at zero temperature, there is no difference.

The bulk modulus is actually a characteristic pressure for significant volume or density change under a change pressure as can be seen by writing formula in the differential form

$$-\frac{dV}{V} = \frac{d\rho}{\rho} = \frac{dP}{B}.$$

If B were a constant (which it is not in any real case), then B would be the e -folding pressure: i.e., the pressure change required to change volume or density by a factor of e . The bigger the bulk modulus, the stiffer the substance.

Find the bulk modulus formula for the zero-temperature free electron gas. Then find the bulk modulus formula in terms of fiducial values.

SUGGESTED ANSWER:

a) Behold:

$$\begin{aligned} n_e &= \frac{\rho}{m_{\text{amu}}} \sum_i \frac{X_i Z_i}{A_i} , \\ &= 1.204 \dots \times 10^{28} \text{ m}^{-3} \times \frac{\rho}{1000 \text{ kg/m}^3} \frac{50}{\mu_e} . \end{aligned}$$

b) Behold—er Behold:

$$\begin{aligned} E_F &= \frac{\hbar^2}{2m} \left[\left(\frac{2}{g} \right) (3\pi^2) n_e \right]^{2/3} \\ &= 3.06973 \dots \times 10^{-19} \text{ J} \times \left[\left(\frac{2}{g} \right) \frac{\rho}{1000 \text{ kg/m}^3} \frac{50}{\mu_e} \right]^{2/3} \\ &= 1.91597958 \dots \text{ eV} \times \left[\left(\frac{2}{g} \right) \frac{\rho}{1000 \text{ kg/m}^3} \frac{50}{\mu_e} \right]^{2/3} . \end{aligned}$$

Since

$$\frac{E_F(\text{fiducial})}{mc^2} = 3.749 \times 10^{-6} ,$$

we can see that ordinary solids in the human environment are very non-relativistic.

c) Behold:

$$\begin{aligned} T_F &= \frac{\hbar^2}{2mk_B} \left[\left(\frac{2}{g} \right) (3\pi^2) n_e \right]^{2/3} \\ &= 2.223 \times 10^4 \text{ K} \times \left[\left(\frac{2}{g} \right) \frac{\rho}{1000 \text{ kg/m}^3} \frac{50}{\mu_e} \right]^{2/3} . \end{aligned}$$

Human environment temperatures are very cold compared to the Fermi temperature. This is a clue that the electrons in solids are at near absolute zero in a sense. The Maxwell-Boltzmann distribution of classical statistical mechanics and of quantum statistical mechanics for distinct particles suggests that excitations from a ground state should be of order $k_B T$. This also suggests that electrons in solids are at near absolute zero and that our $T = 0$ results approximately apply to them. But to know this for sure, one would need to do corrections finite temperature. Such corrections are small for human environment temperatures, and so confirm our guess that ordinary solids are nearly at absolute zero in a sense.

d) Behold:

$$\begin{aligned} v_F &= \sqrt{\frac{2E_F}{m}} \\ &= \sqrt{\frac{2}{m} \frac{\hbar^2}{2m} \left[\left(\frac{2}{g} \right) (3\pi^2) n_e \right]^{1/3}} \\ &= 8.20958 \dots \times 10^5 \text{ m/s} \times \left[\left(\frac{2}{g} \right) \frac{\rho}{1000 \text{ kg/m}^3} \frac{50}{\mu_e} \right]^{1/3} , \end{aligned}$$

Fermi velocities for ordinary solids at human environment temperatures are, in fact, of order 10^6 m/s. They are very high, but not relativistic since 10^6 m/s $\ll c$. The Fermi speed parameter $\beta_F = v_F/c \approx 3 \times 10^{-3}$. Relativistic corrections of order β or β^2 , and so we conclude again that ordinary solids in the human environment are very non-relativistic.

e) Since $n_e = M/V$, we have

$$V = \frac{M}{n_e} \quad \text{and} \quad dV = -\frac{M}{n_e^2} dn_e .$$

First note that since our electron gas formulae are all for $T = 0$, we can assume that any variation in their explicit parameters are with entropy held constant. We explicitly will hold N constant. Now

$$\begin{aligned} P &= - \left(\frac{\partial E}{\partial V} \right)_{S,N} = - \left(\frac{\partial N E_{ave}}{\partial V} \right)_{S,N} = - \frac{3}{5} N \left(\frac{\partial E_F}{\partial V} \right)_{S,N} = - \frac{3}{5} N \left(\frac{\partial E_F}{\partial n_e} \right)_{S,N} \left(\frac{\partial n_e}{\partial V} \right)_{S,N} \\ &= - \frac{3}{5} N \left(\frac{2 E_F}{3 n_e} \right) \left(- \frac{n_e}{V^2} \right) = \frac{2}{5} E_F n_e \\ &= \frac{\hbar^2}{2m} \left(\frac{2}{5} \right) \left[\left(\frac{2}{g} \right) (3\pi^2) \right]^{2/3} n_e^{5/3} \end{aligned}$$

Thus, we find

$$\begin{aligned} P &= \frac{\hbar^2}{2m} \left(\frac{2}{5} \right) \left[\left(\frac{2}{g} \right) (3\pi^2) \right]^{2/3} n_e^{5/3} \\ &= 1.47891 \dots \times 10^9 \text{ Pa} \times \left(\frac{2}{g} \right)^{2/3} \left(\frac{\rho}{1000 \text{ kg/m}^3} \frac{50}{\mu_e} \right)^{5/3} . \end{aligned}$$

f) Begorra:

$$B = \rho \left(\frac{\partial P}{\partial \rho} \right)_S = n_e \left(\frac{\partial P}{\partial n_e} \right)_S = \frac{5}{3} P .$$

Thus,

$$\begin{aligned} B &= \frac{\hbar^2}{2m} \left(\frac{2}{3} \right) \left[\left(\frac{2}{g} \right) (3\pi^2) \right]^{2/3} n_e^{5/3} \\ &= 2.46485 \times 10^9 \text{ Pa} \times \left(\frac{2}{g} \right)^{2/3} \left(\frac{\rho}{1000 \text{ kg/m}^3} \frac{50}{\mu_e} \right)^{5/3} . \end{aligned}$$

Fortran-95 Code

```

pi_con=acos(-1.d0)
emks=1.602176487d-19
xmemks=9.10938215d-31
xmeev=510998.910d0
hbarmks=1.054571628d-34
amumks=1.660538782d-27
xkmks=1.3806504d-23
xmuefid=50.d0
rhofid=1000.d0
ggfid=2.d0
con=hbarmks**2/(2.d0*xmemks)
rhoefid=rhofid/(amumks*xmuefid)
efid=con*( (2.d0/ggfid)*(3.d0*pi_con**2*rhofid) )**(2.d0/3.d0)
efidev=efid/emks
re=efidev/xmeev
tfid=efid/xkmks
vfid=sqrt(2*efid/xmemks)
pfid=.4d0*con*( (2.d0/ggfid)*(3.d0*pi_con**2) )**(2.d0/3.d0)
&
&      *rhoefid**(5.d0/3.d0)
bfid=(5.d0/3.d0)*pfid
print*, 'con,rhofid,efid'
print*,con,rhofid,efid
! 6.104263166643912E-039 1.204428358843353E+028 3.069737435446141E-019
print*, 'efidev,re,tfid'
print*,efidev,re,tfid

```

```

! 1.91597958174638      3.749478803675683E-006      22233.9951912964
  print*, 'vfid,pfid,bfid'
  print*, vfid,pfid,bfid
! 820958.402523807      1478911528.58177      2464852547.63628

```

Redaction: Jeffery, 2008jan01

022 qfull 00200 2 5 0 moderate thinking: Fermi energies for free electron gas metals

Extra keywords: (Ha-324:2.3) volumes per atom 39.3, 23.0, 16.6 in A**3

6. The metals Na, Mg, and Al have, respectively 1, 2, and 3 free electrons per atom, standard atomic masses 22.98976928, 24.3050, and 26.9815386, and, under ordinary pressure and temperature, densities 0.968 g/cm³, 1.738 g/cm³, and 2.70 g/cm³. What is the Fermi energy of these metals in electronvolts? Recall

$$\begin{aligned}
 E_F &= \frac{\hbar^2}{2m} \left[\left(\frac{2}{g} \right) (3\pi^2) n_e \right]^{2/3} \\
 &= 3.06973 \dots \times 10^{-19} \text{ J} \times \left[\left(\frac{2}{g} \right) \frac{\rho}{1000 \text{ kg/m}^3} \frac{50}{\mu_e} \right]^{2/3} \\
 &= 1.91597958 \dots \text{ eV} \times \left[\left(\frac{2}{g} \right) \frac{\rho}{1000 \text{ kg/m}^3} \frac{50}{\mu_e} \right]^{2/3},
 \end{aligned}$$

where density is in MKS units.

SUGGESTED ANSWER:

I did this the easy way. I just plugged the numbers into a short fortran code. I used CGS units in the code. For Na, Mg, and Al, I got respectively, 3.14 eV, 7.11 eV, and 11.7 eV.

Fortran 95 Code

```

  print*
!
  third=2.d0/3.d0
  pi=acos(-1.d0)
  amu=1.66053886d-24,
Atomic mass unit.
  boltzmann=1.3806505d-16,
Boltzmann's constant.
  boltzmannev=8.617343d-5 ,
Boltzmann's constant in eV.
  echarge=1.60217653d-19,
elementary charge in MKS.
  emass=9.1093826d-28,
Electron mass.
!
  con1=planckbar**2/(2.d0*emass)*(1.d0/amu)**third2
  con2=(pi**2*3.d0)**third2
  cone=con1*con2
  coneev=cone*(1.d0/(echarge*1.d7)) ! Fermi energy constant in ev
  cont=coneev/boltzmannev ! Fermi temperature constant in eV
  conp=cone*(1.d0/amu)*.4d0
  conpmks=conp*(1.d-5*1.d+4) ! But density still CGS
  conb=cone*(1.d0/amu)*third2
  conbmks=conb*(1.d-5*1.d+4) ! But density still CGS
  conw=2.d0*pi*(amu/(3.d0*pi**2))**third
  write(*,*) , ' cone, coneev, cont, conp, conpmks '
  write(*,936), cone, coneev, cont, conp, conpmks
  print*, ' conb, conbmks, conw '
  write(*,936), conb, conbmks, conw
  coneevcu=coneev*(8.94d0/(63.546d0/1.d0))**third2

```

```

contcu=cont*(8.94d0/(63.546d0/1.d0))**third2
conpcu=comp*(8.94d0/(63.546d0/1.d0))**(5.d0/3.d0)
conbcu=conb*(8.94d0/(63.546d0/1.d0))**(5.d0/3.d0)
conwcu=conw*((63.546d0/1.d0)/8.94d0)**third
print*, 'For copper'
print*, 'coneecv, contcu, conpcu, conbcu, conwcu'
write(*,936), coneecv, contcu, conpcu, conbcu, conwcu
! For Na, Mg, Al
ena=coneecv*(0.968d0/(22.98976928d0/1.d0))**third2
emg=coneecv*(1.738d0/(24.3050/2.d0))**third2
eal=coneecv*(2.70d0/(26.9815386/3.d0))**third2
print*, 'ena, emg, eal'
write(*,936) ena, emg, eal
936 format(5e15.6)

```

Redaction: Jeffery, 2001jan01

022 qfull 00210 1 3 0 easy math: free electron gas pressure

7. The pressure of a free electron gas (in three dimensions) is given by

$$P = \frac{2}{3} \mathcal{E} = \frac{\hbar^2}{2m} \left[3\pi^2 \left(\frac{2}{g} \right) \right]^{2/3} \frac{2}{5} \left(\frac{\rho}{\mu_e m_{\text{amu}}} \right)^{5/3},$$

where \mathcal{E} is the energy per unit volume and $g = 2$ for electron spin degeneracy. This result can be derived by using the classical 1st law of thermodynamics for $T = 0$ to relate P and \mathcal{E} interpreted as the classical internal energy per unit volume. But it can also be derived from kinematics argument.

First note that a standing wave free electron eigenstate for one dimension of a infinite square well of length ℓ and wave number k

$$\psi = \sqrt{\frac{2}{\ell}} \sin(kx)$$

can be written as a superposition of oppositely traveling traveling wave states

$$\psi = \frac{1}{\sqrt{2}} \left(\sqrt{\frac{1}{\ell}} e^{ikx} - \sqrt{\frac{1}{\ell}} e^{-ikx} \right),$$

where have used the complex number definition of the sine function and dropped the global phase factor $1/i$ since it is physically irrelevant. Following the paradigm of quantum mechanics, it seems plausible to treat the standing wave state as literally a superposition of traveling wave states. One can generalize this idea to three dimensions. The traveling wave states can be thought of as continuously bouncing elastically off the walls of a 3-dimensional infinite square well and having their momentum component normal to wall inverted in the bounce. During the bounce, some kinetic energy becomes potential energy for a brief time. Perhaps, in real metals wave packets that are strongly peaked about stationary state \vec{k} values are actually doing this. Textbooks grow coy on this point. But in any case, a classical interpretation of the traveling waves as particles bouncing off the walls of 3-dimensional infinite square well potential leads to the correct pressure result. One just says that the energy density of states per unit volume for $E \leq E_F$

$$\rho_E = \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{g}{2} \frac{1}{4\pi^2} E^{-1/2}$$

is the density of classical particles in energy space per unit volume up to E_F and uses that density to calculate the pressure the particles exert.

Let's do the calculation.

- a) If a (classical) particle of momentum magnitude p bounces elastically off a wall at an angle θ relative to the normal to the wall, what momentum is transferred to the wall in the normal direction? at angle
- b) If you have a density of particles per unit (kinetic) energy per unit volume of ρ_E and the particle distribution in angle is isotropic, what is the density of particles per unit energy per unit volume per unit solid angle?

- c) What is the flux of particles in per unit energy per unit area per unit solid angle?
- d) What is the momentum flux normal to the wall per unit area per unit energy per unit solid angle on the wall? Remember for a beam of particles coming in at angle to the wall of θ that cross-sectional area for the beam is $\cos\theta dA$, where dA is the area of wall the beam impinges on. For example, the cross-sectional area is $\theta = \pi/2$ is zero. A diagram might help you understand this cross-sectional area result.
- e) Integrate the result from the part (d) answer over 2π solid angle about the normal to the wall and over all energy up the Fermi energy E_F to get the formula for the free electron gas pressure. Express the formula in terms of \mathcal{E} .

SUGGESTED ANSWER:

- a) Well $2p \cos\theta$.
- b) Well $\rho_E/(4\pi)$.
- c) Well $v\rho_E/(4\pi)$, where v is the particle velocity.
- d) Well

$$2p \cos(\theta)v \frac{\rho_E}{4\pi} \cos\theta = 4E \cos^2 \frac{\rho_E}{4\pi} .$$

- e) Behold:

$$\begin{aligned} P &= 2\pi \int_0^{\pi/2} \int_0^{E_F} 4E \cos^2 \frac{\rho_E}{4\pi} dE \sin\theta d\theta = 2 \int_0^1 \mu^2 d\mu \int_0^{E_F} E \rho_E dE \\ &= \frac{2}{3} \mathcal{E} , \end{aligned}$$

where we have used the transformation $\mu = \cos\theta$. We find

$$P = \frac{2}{3} \mathcal{E}$$

which is exactly the pressure result we found using the 1st law of thermodynamics.

Redaction: Jeffery, 2008jan01

023 qfull 00140 1 3 0 easy math: the MB FD BE distributions derived

8. Consider a system consisting of quantized single-particle states and fixed total number of particles N and fixed total energy E . We make the approximation that particles can occupy only one single-particle state at time: i.e., they are not in superpositions of single-particle states. The overall microscopic state of the system is set by specifying arrangement of the particles in the single-particle states. Note that exchanging distinct particles changes the microscopic state and exchanging identical particles does not.

The set of single-particle states of the same energy E_i can be called an energy level—a term which is used in different ways in different contexts. The number of single-particle states in an energy level i is the energy level degeneracy g_i . A configuration is the set of occupation numbers $\{N_i\}$ for the energy levels of the system. The statistical weight W of a configuration is the number of distinct microscopic states that correspond to that configuration.

The fundamental axiom of statistical mechanics is that in thermodynamic equilibrium all the microscopic states are equally probable. Thermodynamic equilibrium for a system occurs when the system is not changing thermodynamically with time at the macroscopic level. In thermodynamic equilibrium, the initial conditions of the system no longer determine its macroscopic behavior and their signature in the system has been effectively erased.

The fundamental axiom implies that probability distribution for the configuration is just the normalized statistical weights and the most probable configuration is the one with the largest statistical weight. It turns out the probability distribution given by the statistical weights is extremely peaked around the most probable configuration for systems of macroscopically large numbers of particles. The macroscopic thermodynamic equilibrium state is essentially this most probable configuration. The natural logarithm the statistical weight times Boltzmann's constant k identified with the classical entropy which maximizes for thermodynamic equilibrium. Thus we have

$$S = k \ln(W) .$$

- a) The statistical weight for the configuration for a system with distinct particles is

$$W = N! \prod_i \frac{g_i^{N_i}}{N_i!}.$$

Solve for the set of N_i that maximize the statistical weight subject to the constraints

$$N = \sum_i N_i, \quad E = \sum_i N_i E_i, \quad N_i \geq 0.$$

For conventional reasons, the Lagrange multiplier for the particle number constraint should be label α and that for the energy constraint β . Use appropriate approximations to get a simple analytic formula for a maximizing N_i in which the degeneracy g_i occurs only as a leading coefficient. What is the function with the degeneracy factor suppressed and what is it called?

- b) The statistical weight for the configuration for a system with identical fermions is

$$W = \prod_i \binom{g_i}{N_i}.$$

Repeat the requirements from part (a) for this statistical weight.

- c) The statistical weight for the configuration for a system with identical bosons is

$$W = \prod_i \binom{g_i - 1 + N_i}{N_i}.$$

Repeat the requirements from part (a) for this statistical weight.

- d) The lagrange multiplier function has an unconstrained stationary point at the maximizing values of N_i . This fact along with the 1st law of classical thermodynamics

$$dE = T dS - \mu dN$$

for the case of fixed volume but variable entropy and particle number (T being temperature and μ being the chemical potential) and the identification of entropy allows α and β to be determined in terms of classical thermodynamics variables. Make the determinations.

SUGGESTED ANSWER:

- a) It is better and conventional to find maximizing N_i for the natural logarithm of W (i.e., for the entropy) rather than W itself. We define

$$h = \ln(W) + \alpha \left(\sum_i N_i - N \right) + \beta \left(\sum_i N_i E_i - E \right),$$

where α and β are Lagrange multipliers used handle the equality constraints. The inequality constraint cannot be built into the solution procedure, but can only be used to test the consistency of the result and help eliminate unphysical results. We make the approximation that the N_i are continuous variables in making use of Lagrange multipliers.

Stationary points of h with respect to N_j in the range $[N_j, N_{j-1}]$ determined by the requirement

$$0 = h(N_j) - h(N_j - 1).$$

In fact, we find only one finite, non-zero N_j value satisfying this requirement, and so all stationary points lie in the range. Since the N_i are actually integers there can be only one real stationary point in the range $[N_j, N_{j-1}]$, and there is no reason to believe the continuum approximation generates others. Even if there are multiple stationary points in the continuum approximation, they are all the same value to within our error. Our best estimate of the maximizing value in the continuum approximation is

$$N_j - \frac{1}{2}.$$

However the actual maximizing value must be an integer, and we judge our best estimate to be

$$\text{int}(N_j) ,$$

where int is the function that truncates a real number to the next lowest integer or the real number itself if it is an integer. Our N_j value turns out to be positive, and so the int function builds in the constraint that $N_i \geq 0$.

We prefer the just outlined procedure for finding the stationary point to using Stirling's approximation for the factorial functions since that approximation fails for factorial function arguments less than about 2. It's also simpler I think.

Now

$$\begin{aligned} 0 &= h(N_j) - h(N_j - 1) = 0 + \ln(g_j) - \ln(N_j) + \alpha + \beta E_j \\ N_j &= g_j e^{\alpha + \beta E_j} \\ N_{j,\text{stationary}} &= \text{int}(g_j e^{\alpha + \beta E_j}) . \end{aligned}$$

The formula for maximizing occupation numbers just displayed is useful in showing the good approximation when $g_j e^{\alpha + \beta E_j}$ is a small number of order a few or less. But the int function is analytically intractable and the improvement it gives is not needed for large $g_j e^{\alpha + \beta E_j}$ values which turn out to be the overwhelmingly important cases in most cases. Thus, the most useful formula for the maximizing occupation numbers is

$$N_i = g_i e^{\alpha + \beta E} ,$$

where for simplicity we use the index i and make no explicit indication that the N_i are the maximizing values: context tells us when they are maximizing.

If one suppresses the degeneracy factors which are system dependent and the index i which can be implicit for discrete states and is unneeded in the continuous states approximation, one obtains

$$f = e^{\alpha + \beta E_i}$$

which is called the Maxwell-Boltzmann distribution.

b) We do everything that we did in the part (a) answer, *mutatis mutandis*. Now

$$\begin{aligned} 0 &= h(N_j) - h(N_j - 1) = 0 - \{\ln[(g_j - N_j)!] - \ln[(g_j - (N_j - 1))!]\} \\ &\quad - \{\ln(N_j!) - \ln[(N_j - 1)!]\} + \alpha + \beta E_j \\ 0 &= \ln(g_j - N_j + 1) - \ln(N_j) + \alpha + \beta E_j \\ \ln\left(\frac{N_j}{g_j - N_j + 1}\right) &= \alpha + \beta E_j \\ \frac{N_j}{g_j - N_j + 1} &= e^{\alpha + \beta E_j} \\ N_j &= \frac{g_j + 1}{e^{-(\alpha + \beta E_j)} + 1} \\ N_{j,\text{stationary}} &= \text{int}\left(\frac{g_j + 1}{e^{-(\alpha + \beta E_j)} + 1}\right) . \end{aligned}$$

The formula for maximizing occupation numbers just displayed is useful in showing the good approximation when $g_j/[e^{-(\alpha + \beta E_j)} + 1]$ is a small number of order a few or less. But the int function is analytically intractable and the improvement it gives is not needed for large $g_j/[e^{-(\alpha + \beta E_j)} + 1]$ values which turn out to be the overwhelmingly important cases in most cases. Thus, the most useful formula for the maximizing occupation numbers is

$$N_i = \frac{g_i}{e^{-(\alpha + \beta E_i)} + 1} ,$$

where for simplicity we use the index i and make no explicit indication that the N_i are the maximizing values: context tells us when they are maximizing.

If one suppresses the degeneracy factors which are system dependent and the index i which can implicit for discrete states and is unneeded in the continuous states approximation, one obtains

$$f = \frac{g_i}{e^{-(\alpha+\beta E)} + 1}$$

which is called the Fermi-Dirac distribution. We note that in the limit that $e^{-(\alpha+\beta E_i)} \gg 1$ the Fermi-Dirac distribution approaches the Maxwell-Boltzmann distribution.

c) We do everything that we did in the part (a) answer, *mutatis mutandis*. Now

$$\begin{aligned} 0 &= h(N_j) - h(N_j - 1) = \{\ln[(g_j - 1 + N_j)!] - \ln[(g_j - 1 + (N_j - 1))!]\} \\ &\quad - \{\ln(N_j!) - \ln[(N_j - 1)!]\} + \alpha + \beta E_j \\ 0 &= \ln(g_j - 1 + N_j) - \ln(N_j) + \alpha + \beta E_j \\ \ln\left(\frac{N_j}{g_j - 1 + N_j}\right) &= \alpha + \beta E_j \\ \frac{N_j}{g_j - 1 + N_j} &= e^{\alpha + \beta E_j} \\ N_j &= \frac{g_j - 1}{e^{-(\alpha + \beta E_j)} - 1} \\ N_{j,\text{stationary}} &= \text{int}\left(\frac{g_j - 1}{e^{-(\alpha + \beta E_j)} - 1}\right). \end{aligned}$$

The formula for maximizing occupation numbers just displayed is useful in showing the good approximation when $g_j/[e^{-(\alpha + \beta E_j)} - 1]$ is a small number of order a few or less. But the int function is analytically intractable and the improvement it gives is not needed for large $g_j/[e^{-(\alpha + \beta E_j)} - 1]$ values which turn out to be the overwhelmingly important cases in most cases. Thus, the most useful formula for the maximizing occupation numbers is

$$N_i = \frac{g_i}{e^{-(\alpha + \beta E_i)} - 1},$$

where for simplicity we use the index i and make no explicit indication that the N_i are the maximizing values: context tells us when they are maximizing.

If one suppresses the degeneracy factors which are system dependent and the index i which can implicit for discrete states and is unneeded in the continuous states approximation, one obtains

$$f = \frac{g_i}{e^{-(\alpha + \beta E)} - 1}$$

which is called the Bose-Einstein distribution. We note that in the limit that $e^{-(\alpha + \beta E_i)} \gg 1$ the Bose-Einstein distribution approaches the Maxwell-Boltzmann distribution.

d) On general path in the space of the occupation numbers $N(t)$ (where t is a path parameter) through the constrained stationary point for $\ln(W)$, the h function has an unconstrained stationary point. Therefore,

$$0 = \frac{dh}{dt} = \frac{d \ln(W)}{dt} + \alpha \frac{dN}{dt} + \beta \frac{dE}{dt},$$

where for notational convenience N and E are now the unconstrained values of the total particle number and energy. The constrained total particle number N_{con} and E_{con} are constants and vanish in the differentiation with respect to t . By a usual convention of thermodynamics, we suppress the dt and write the last expression as a differential expression with it being implicit that the differentials stand for derivatives with respect to the path parameter of the general path. Thus, we have

$$0 = d \ln(W) + \alpha dN + \beta dE.$$

Using the entropy identification, this last expression becomes

$$0 = dS + k\alpha dN + k\beta dE$$

which rearranges to

$$dE = -\frac{1}{k\beta} dS - \frac{\alpha}{\beta} dN .$$

From the classical 1st law of thermodynamics, we now see that

$$T = -\frac{1}{k\beta} \quad \text{and} \quad \mu = kT\alpha ,$$

and thus that

$$\beta = -\frac{1}{kT} \quad \text{and} \quad \alpha = \frac{\mu}{kT} .$$

Redaction: Jeffery, 2008jan01

023 qfull 00440 1 3 0 easy math: photon gas the full story

9. Photons in thermodynamic equilibrium with some container or with some gas of massive particles can be thought as a photon gas obeying Bose-Einstein statistics. Photons are extreme relativistic particles, but nevertheless the simple formalism for the statistical mechanics of non-relativistic systems still applies with some modifications:

- 1) The energies of quantized single-particle states are related to the momentum, frequency, wavelength, and wavenumber of the state by

$$E = pc = h\nu = \frac{hc}{\lambda} = \hbar ck .$$

Note that above expression embodies the de Broglie formula $p = h/\lambda$ which de Broglie took from photons and applied to massive particles—but with the difference that massive particles in the non-relativistic limit relate kinetic energy to momentum by $E = p^2/(2m)$.

- 2) Photons are spin-1 bosons, but for some reason only the $m = \pm 1$ states are allowed. Thus, the each spatial quantized single state has a degeneracy of $g = 2$.
- 3) The number of photons is not conserved. The unspecified processes that transform one overall microscopic quantum state to another can create and destroy photons. Thus, photon gas will relax to a maximum entropy state with no constraint on total photon number. This means that the Lagrange multiplier $\alpha = \mu/kT$ is zero.
- a) Given that periodic boundary conditions for a 3-dimensional infinite well rectangular box and ℓ for the length of a general dimension, the wavenumber of single-particle states for this dimension is quantized according to the rule

$$k\ell = 2\pi n , \quad \text{where} \quad n = 0, \pm 1, \pm 2, \pm 3, \dots .$$

What is the density of states in phase space which is the product of k -space and space space? Do not forget the internal degeneracy factor g .

- b) Given the Bose-Einstein distribution

$$f = \frac{1}{e^{(E-\mu)/(kT)} - 1}$$

(where E is single-particle state energy, μ is chemical potential, and T is temperature), find the formula for the energy density per unit frequency \mathcal{E}_ν for the thermodynamic equilibrium photon gas. Note energy density per unit frequency, **NOT** photon number density per unit frequency.

- c) In radiative transfer it is customary to work with specific intensity B_ν rather than \mathcal{E}_ν . The specific intensity is the energy flux (energy per unit area perpendicular to the direction of motion per unit time) per unit frequency per unit solid angle. Find the formula for B_ν .
- d) Find the frequency integrated formula for B_ν : i.e., find B . Note that the factorial function is

$$z! = \int_0^\infty t^z e^{-t} dt = \begin{cases} z(z-1)! & \text{for general complex } z, \text{ except for } z \text{ a negative integer;} \\ \pm\infty & \text{for } z \text{ a negative integer;} \\ n! & \text{for } n \text{ an integer with } n \geq 0; \\ \sqrt{\pi} & \text{for } z = -1/2 \end{cases}$$

(Ar-453), that the Riemann zeta function defined as an infinite sum (convergent for $\text{Re}(z) > 1$) is

$$\zeta(z) = \sum_{\ell=1}^{\infty} \frac{1}{\ell^z} = \begin{cases} \frac{\pi^2}{6} & \text{for } z = 2; \\ \frac{\pi^4}{90} & \text{for } z = 4; \\ \frac{\pi^8}{945} & \text{for } z = 6, \end{cases}$$

(Ar-282, 285) and that the Stefan-Boltzmann constant is

$$\sigma = \frac{2\pi^5}{15} \frac{k^4}{h^3 c^2} = 5.670400(40) \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4} .$$

Also find the total energy per unit volume. Note that the radiation constant

$$a = \frac{4\sigma}{c} = 7.5657 \times 10^{-16} \text{ J m}^{-3} \text{ K}^{-4} .$$

- e) The energy flux from a surface emitting like an exact blackbody is given by

$$F = \int_{2\pi} B \cos \theta \, d\Omega ,$$

where the integral is over 2π solid angle and we have assumed the z direction is the outward normal direction from the surface. The $\cos \theta$ factor decrease in area perpendicular to a beam through an opening in the surface. For example, if $\theta = \pi/2$, there would be no emission through the opening. Evaluate the formula for F .

- f) What is the formula for B_λ : i.e., the specific intensity as a function of wavelength rather than μ . Note

$$B_\lambda \, d\lambda = B_\nu \, d\nu .$$

- g) The Wein approximation (derived 1896) is the approximate formula for B_λ in the limit of small wavelength. The Rayleigh-Jeans law (derived 1900–1905) is the approximate formula for B_λ in the limit of large wavelength. Derive these two approximate formulae from the exact formula for B_λ found in the part (f) answer.
- h) What is an iteration formula for the maximizing point of functions of the form

$$f(x) = \frac{x^p}{e^x - 1} ,$$

where $p > 1$? What is a good initial value x_0 for the iteration and is the iteration guaranteed to converge?

- i) Find the formulae for the maximizing ν and λ values for, respectively, B_ν and B_λ . You only need to find the coefficients of formulae approximately, but if you are ambitious a small computer code will allow you do find the coefficients to machine accuracy. Then give Wien's law (AKA Wien's displacement law).

SUGGESTED ANSWER:

- a) Well in k -space, the separation between state locations is

$$\Delta k = \frac{2\pi}{\ell}$$

Thus, the k -space cell volume surrounding each state is

$$V_k = \frac{(2\pi)^3}{V} ,$$

where V is the space volume of the rectangular box. This cell size result is actually true for any shape of container for large k , but the proof is suavely omitted by textbooks. The density of states in phase space is

$$\rho_k = \frac{g}{V_k V} = \frac{g}{(2\pi)^3} ,$$

where $g = 2$ is the spin degeneracy factor.

b) Note for photons that

$$E = h\nu , \quad \mu = 0 , \quad g = 2 , \quad k = \frac{2\pi\nu}{c} , \quad dk = \frac{2\pi}{c} d\nu .$$

Now

$$\begin{aligned} \mathcal{E}_\nu d\nu &= E \left(\frac{1}{e^{(E-\mu)/(kT)} - 1} \right) \frac{g}{(2\pi)^3} 4\pi k^2 dk \\ &= h\nu \left(\frac{1}{e^{h\nu/(kT)} - 1} \right) \frac{2}{(2\pi)^3} 4\pi \left(\frac{2\pi}{c} \right)^3 \nu^2 d\nu \\ &= \frac{2(4\pi)h\nu^3}{c^3} \frac{1}{e^{h\nu/(kT)} - 1} d\nu , \end{aligned}$$

and thus

$$\mathcal{E}_\nu = \frac{2(4\pi)h\nu^3}{c^3} \frac{1}{e^{h\nu/(kT)} - 1} .$$

c) Well the energy per unit frequency per unit volume moving in a direction per unit solid angle is

$$\frac{\mathcal{E}_\nu}{4\pi}$$

assuming isotropic distribution of directional motions. To convert the last quantity into a flux, we multiply by the speed of the particle which in the case of photons is c . Thus, we find.

$$B_\nu = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/(kT)} - 1} .$$

d) Behold:

$$\begin{aligned} B &= \int_0^\infty B_\nu d\nu = \int_0^\infty \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/(kT)} - 1} \nu^2 d\nu \\ &= \frac{2}{h^3 c^2} (kT)^4 \int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{2}{h^3 c^2} (kT)^4 \int_0^\infty x^3 e^{-x} \sum_{\ell=0}^\infty e^{-\ell x} dx \\ &= \frac{2}{h^3 c^2} (kT)^4 \sum_{\ell=0}^\infty \int_0^\infty x^3 e^{-(\ell+1)x} dx = \frac{2}{h^3 c^2} (kT)^4 \sum_{\ell=1}^\infty \int_0^\infty x^3 e^{-\ell x} dx \\ &= \frac{2}{h^3 c^2} (kT)^4 \sum_{\ell=1}^\infty \frac{1}{\ell} (3!) = \frac{2}{h^3 c^2} (kT)^4 \frac{\pi^4}{90} (3!) \\ &= \frac{2\pi^4}{15} \frac{k^4}{h^3 c^2} T^4 \\ &= \frac{\sigma T^4}{\pi} , \end{aligned}$$

where we have the geometric series expansion

$$\frac{1}{1-r} = \sum_{\ell=0}^\infty r^\ell ,$$

convergent for $|r| < 1$, (Ar-238) and the property of uniform convergence for infinite series in order to interchange summation and integration (Ar-258). Thus,

$$B = \frac{\sigma T^4}{\pi} \quad \text{and} \quad \mathcal{E} = \frac{4\pi}{c} B = \frac{4\sigma}{c} T^4 = aT^4 ,$$

where we have found \mathcal{E} by converting from a flux in a direction to a density.

e) Behold:

$$F = \int_{2\pi} B d\Omega = 2\pi \int_0^1 B \mu d\mu = \pi B = \sigma T^4 ,$$

where we have used the transformation $\mu = \cos\theta$. We can see now why the awkward π is conventionally left in the expression for B . So there is no awkward π in the expression for F .

f) Behold:

$$B_\lambda = B_\nu \frac{d\nu}{d\lambda} = B_\nu \frac{c}{\lambda^2} = \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/(\lambda kT)} - 1} ,$$

where we have suppressed the minus sign since it just indicates a reversal in the limits for integration.

g) Behold:

$$B_\lambda = \begin{cases} \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/(\lambda kT)} - 1} & \text{the exact Planck law;} \\ \frac{2hc^2}{\lambda^5} e^{-hc/(\lambda kT)} & \text{the small wavelength Wien approximation;} \\ \frac{2ckT}{\lambda^4} & \text{the large wavelength Rayleigh-Jeans law.} \end{cases}$$

For the Wien approximation, we have assumed $e^{hc/(\lambda kT)} \gg 1$. For the Rayleigh-Jeans law, we expanded $e^{hc/(\lambda kT)}$ to 1st order in $hc/(\lambda kT)$.

Wien's own version of his formula must have looked a little different since in 1896 there was no Planck's constant. Perhaps he had a fitted parameter.

The Rayleigh-Jeans law was derived finally fully derived in 1905 which was already 5 years after Planck's law was derived. Since Planck's law gave an exact fit within error to the blackbody spectra and gives the Rayleigh-Jeans law as the large wavelength limit, we may wonder why the Rayleigh-Jeans law has any special status. Well it's hard to know without an exact history of the developments, but I think it was a case of Planck's derivation (which is quite unlike modern textbook ones) was complicated and not fully accepted and perhaps not yet well known in 1905. The Rayleigh-Jeans derivation was purely classical—or at least seemed to be—and had no Planck's constant. As we see above, Planck's constant cancels out in the derivation. The Rayleigh-Jeans law had a problem though. Though it fits the long-wavelength part of a blackbody spectrum well, it diverges to infinity as $\lambda \rightarrow 0$ —which is not observed. This problem was called the ultraviolet catastrophe by Ehrenfest in 1911—Catwoman would have called it a Cat-astrophe. Of course, the solution was already available in Planck's law although getting the modern derivation may have taken some more time. The necessary symmetrization principle and Bose-Einstein statistics not being found until the 1920s.

h) First note that

$$f(x) = \frac{x^p}{e^x - 1} = \begin{cases} 0 & \text{for } x \rightarrow \infty; \\ x^{p-1} & \text{for } x \ll 1. \end{cases}$$

where $p > 1$. This shows that $f(x)$ goes to zero at $x = 0$ and $x = \infty$. Since $f(x) \geq 0$ for the range $[0, \infty]$, it is clear that it must have at least one maximum in this range. Now

$$\frac{df}{dx} = \frac{px^{p-1}}{e^x - 1} - \frac{x^p e^x}{(e^x - 1)^2} = \frac{x^{p-1} e^x}{(e^x - 1)^2} [p(1 - e^{-x}) - x] .$$

If we set this expression equal to zero, we obtain the stationary point iteration formula

$$x = p(1 - e^{-x}) .$$

We can say a few things about the iteration formula. First, an obvious exact solution is $x = 0$. But this is not a maximum since we know $f(0) = 0$. In fact, this point is a minimum for our case with $p > 1$. There is no other analytic solution.

Second, the function $g = p(1 - e^{-x})$ has slope $p > 1$ at $x = 0$ and then goes asymptotically to p as $x \rightarrow \infty$. Thus, there is clearly at least one intersection of g and the line $y = x$. In fact, there can be only one intersection since $dg/dx = pe^{-x}$ decreases monotonically with x . So there is only one stationary point for $f(x)$ between $x = 0$ and $x = \infty$. It must be a maximum since at $x = 0$ and $x = \infty$, $f(x)$ is zero.

Third, the exact solution for x must be less than p as we see from $g = p(1 - e^{-x})$ itself. On the other hand, as p goes to infinity, it is diagrammatically clear that the exact solution must go p asymptotically. Thus, it seems plausible to begin the iteration for x with initial $x_0 = p$.

Fourth, is convergence to the exact solution guaranteed starting from x_0 ? Well if x_{i-1} is too large, $e^{-x_{i-1}}$ is too small and $x_i = p(1 - e^{-x_{i-1}})$ will be too large. So if one starts the iteration with $x_0 = p > x$ (where x is the exact solution), then all the iterates will be too large for a finite number of iterations. Now the slope of $g = p(1 - e^{-x})$ is less than 1 at the intersection with $y = x$ (since it is the the intersection) and for all larger values of x . Thus, an iteration starting from $x_0 = p$ is always in the region where the slope of $g = p(1 - e^{-x})$ is less than 1, but greater than zero. The function g increases strictly in this region. This means that $x_i = g(x_{i-1}) < x_{i-1}$. Draw a diagram to see this clearly. Formally exact convergence only happens as the number of iterations goes to infinity, but after a finite number the iterates are unchanging to within machine accuracy. So the iteration is guaranteed to converge starting the iteration from $x_0 = p$. However, the convergence might be slow. It seems very likely that the convergence rate increases with p since the exact solution goes to p asymptotically in the limit that p goes to infinity.

i) For the maximizing points, we set

$$\frac{\partial B_\nu}{\partial d\nu} = \frac{\partial B_\nu}{\partial dx} \frac{\partial x}{\partial d\nu} = 0 \quad \text{and} \quad \frac{\partial B_\lambda}{\partial d\lambda} = \frac{\partial B_\lambda}{\partial dx} \frac{\partial x}{\partial d\lambda} = 0$$

which clearly lead to iteration formulae for the maximizing point

$$x = 3(1 - e^{-x}) \quad \text{and} \quad x = 5(1 - e^{-x}) ,$$

respectively.

Solving for the maximizing x values we should start the iteration with $x_0 = p$ as argued in the part (h) answer. For our two cases then we should start, respectively, with $x_0 = 3$ and $x_0 = 5$. It seems likely that the converged x solutions should be, respectively, of order 3 and 5. An actual iteration to machine accuracy convergence gives, respectively, 2.82143937212208 and 4.96511423174428.

The formulae for the maximizing ν and λ values are, respectively,

$$\nu_{\max} = x_{\max} \frac{kT}{h} = 2.821439372122 \dots \times \frac{kT}{h} \quad \text{and} \quad \lambda_{\max} = \frac{hc}{x_{\max} kT} = \frac{hc}{4.965114231744 \dots \times kT} .$$

From the latter expression, we find Wien's law (AKA Wien's displacement law)

$$\lambda_{\max} = \frac{0.28977684 \text{ cm K}}{T} = \frac{2897.7684 \mu\text{m K}}{T} .$$

Fortran-95 Code

```

print*
p=3.d0
x=p
do
  xold=x
  x=p*(1.d0-exp(-x))
  print*,xold,x
  if(x .eq. xold) exit
end do

```

```

      print*, 'x for p=3 is ', x
!   x for p=3 is    2.82143937212208
      print*
      p=5.d0
      x=p
      do
        xold=x
        x=p*(1.d0-exp(-x))
        print*, xold, x
        if(x .eq. xold) exit
      end do
      print*, 'x for p=5 is ', x
!   x for p=5 is    4.96511423174428
      print*, 'planck, clight, boltzmann'
      print*, planck, clight, boltzmann
!   6.626069300000000E-027  29979245800.0000  1.380650500000000E-016 in CGS
      wein=(planck*clight/boltzmann)/x
      print*, 'x, wein'
      print*, x, wein
!   4.96511423174428      0.289776843518791

```

Redaction: Jeffery, 2008jan01

Appendix 2 Quantum Mechanics Equation Sheet

Note: This equation sheet is intended for students writing tests or reviewing material. Therefore it neither intended to be complete nor completely explicit. There are fewer symbols than variables, and so some symbols must be used for different things.

1 Constants not to High Accuracy

Constant Name	Symbol	Derived from CODATA 1998
Bohr radius	$a_{\text{Bohr}} = \frac{\lambda_{\text{Compton}}}{2\pi\alpha}$	$= 0.529 \text{ \AA}$
Boltzmann's constant	k	$= 0.8617 \times 10^{-6} \text{ eV K}^{-1}$ $= 1.381 \times 10^{-16} \text{ erg K}^{-1}$
Compton wavelength	$\lambda_{\text{Compton}} = \frac{h}{m_e c}$	$= 0.0246 \text{ \AA}$
Electron rest energy	$m_e c^2$	$= 5.11 \times 10^5 \text{ eV}$
Elementary charge squared	e^2	$= 14.40 \text{ eV \AA}$
Fine Structure constant	$\alpha = \frac{e^2}{\hbar c}$	$= 1/137.036$
Kinetic energy coefficient	$\frac{\hbar^2}{2m_e}$	$= 3.81 \text{ eV \AA}^2$
	$\frac{\hbar^2}{m_e}$	$= 7.62 \text{ eV \AA}^2$
	h	$= 4.15 \times 10^{-15} \text{ eV}$
Planck's constant	h	$= 4.15 \times 10^{-15} \text{ eV}$
Planck's h-bar	\hbar	$= 6.58 \times 10^{-16} \text{ eV}$
Rydberg Energy	hc	$= 12398.42 \text{ eV \AA}$
	$\hbar c$	$= 1973.27 \text{ eV \AA}$
	$E_{\text{Ryd}} = \frac{1}{2} m_e c^2 \alpha^2$	$= 13.606 \text{ eV}$

2 Some Useful Formulae

Leibniz's formula
$$\frac{d^n(fg)}{dx^n} = \sum_{k=0}^n \binom{n}{k} \frac{d^k f}{dx^k} \frac{d^{n-k} g}{dx^{n-k}}$$

Normalized Gaussian
$$P = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x - \langle x \rangle)^2}{2\sigma^2}\right]$$

3 Schrödinger's Equation

$$H\Psi(x, t) = \left[\frac{p^2}{2m} + V(x) \right] \Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}$$

$$H\psi(x) = \left[\frac{p^2}{2m} + V(x) \right] \psi(x) = E\psi(x)$$

$$H\Psi(\vec{r}, t) = \left[\frac{p^2}{2m} + V(\vec{r}) \right] \Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} \quad H|\Psi\rangle = i\hbar \frac{\partial}{\partial t} |\Psi\rangle$$

$$H\psi(\vec{r}) = \left[\frac{p^2}{2m} + V(\vec{r}) \right] \psi(\vec{r}) = E\psi(\vec{r}) \quad H|\psi\rangle = E|\psi\rangle$$

4 Some Operators

$$p = \frac{\hbar}{i} \frac{\partial}{\partial x} \quad p^2 = -\hbar^2 \frac{\partial^2}{\partial x^2}$$

$$H = \frac{p^2}{2m} + V(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$

$$p = \frac{\hbar}{i} \nabla \quad p^2 = -\hbar^2 \nabla^2$$

$$H = \frac{p^2}{2m} + V(\vec{r}) = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r})$$

$$\nabla = \hat{x} \frac{\partial}{\partial x} + \hat{y} \frac{\partial}{\partial y} + \hat{z} \frac{\partial}{\partial z} = \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\phi} \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

5 Kronecker Delta and Levi-Civita Symbol

$$\delta_{ij} = \begin{cases} 1, & i = j; \\ 0, & \text{otherwise} \end{cases} \quad \varepsilon_{ijk} = \begin{cases} 1, & ijk \text{ cyclic}; \\ -1, & ijk \text{ anticyclic}; \\ 0, & \text{if two indices the same.} \end{cases}$$

$$\varepsilon_{ijk} \varepsilon_{ilm} = \delta_{jl} \delta_{km} - \delta_{jm} \delta_{kl} \quad (\text{Einstein summation on } i)$$

6 Time Evolution Formulae

$$\text{General} \quad \frac{d\langle A \rangle}{dt} = \left\langle \frac{\partial A}{\partial t} \right\rangle + \frac{1}{\hbar} \langle i[H(t), A] \rangle$$

$$\text{Ehrenfest's Theorem} \quad \frac{d\langle \vec{r} \rangle}{dt} = \frac{1}{m} \langle \vec{p} \rangle \quad \text{and} \quad \frac{d\langle \vec{p} \rangle}{dt} = -\langle \nabla V(\vec{r}) \rangle$$

$$|\Psi(t)\rangle = \sum_j c_j(0) e^{-iE_j t/\hbar} |\phi_j\rangle$$

7 Simple Harmonic Oscillator (SHO) Formulae

$$V(x) = \frac{1}{2} m \omega^2 x^2 \quad \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m \omega^2 x^2 \right) \psi = E \psi$$

$$\beta = \sqrt{\frac{m\omega}{\hbar}} \quad \psi_n(x) = \frac{\beta^{1/2}}{\pi^{1/4}} \frac{1}{\sqrt{2^n n!}} H_n(\beta x) e^{-\beta^2 x^2/2} \quad E_n = \left(n + \frac{1}{2} \right) \hbar \omega$$

$$H_0(\beta x) = H_0(\xi) = 1 \quad H_1(\beta x) = H_1(\xi) = 2\xi$$

$$H_2(\beta x) = H_2(\xi) = 4\xi^2 - 2 \quad H_3(\beta x) = H_3(\xi) = 8\xi^3 - 12\xi$$

8 Position, Momentum, and Wavenumber Representations

$$p = \hbar k \quad E_{\text{kinetic}} = E_T = \frac{\hbar^2 k^2}{2m}$$

$$|\Psi(p, t)|^2 dp = |\Psi(k, t)|^2 dk \quad \Psi(p, t) = \frac{\Psi(k, t)}{\sqrt{\hbar}}$$

$$x_{\text{op}} = x \quad p_{\text{op}} = \frac{\hbar}{i} \frac{\partial}{\partial x} \quad Q \left(x, \frac{\hbar}{i} \frac{\partial}{\partial x}, t \right) \quad \text{position representation}$$

$$x_{\text{op}} = -\frac{\hbar}{i} \frac{\partial}{\partial p} \quad p_{\text{op}} = p \quad Q \left(-\frac{\hbar}{i} \frac{\partial}{\partial p}, p, t \right) \quad \text{momentum representation}$$

$$\delta(x) = \int_{-\infty}^{\infty} \frac{e^{ipx/\hbar}}{2\pi\hbar} dp \quad \delta(x) = \int_{-\infty}^{\infty} \frac{e^{ikx}}{2\pi} dk$$

$$\Psi(x, t) = \int_{-\infty}^{\infty} \Psi(p, t) \frac{e^{ipx/\hbar}}{(2\pi\hbar)^{1/2}} dp \quad \Psi(x, t) = \int_{-\infty}^{\infty} \Psi(k, t) \frac{e^{ikx}}{(2\pi)^{1/2}} dk$$

$$\Psi(p, t) = \int_{-\infty}^{\infty} \Psi(x, t) \frac{e^{-ipx/\hbar}}{(2\pi\hbar)^{1/2}} dx \quad \Psi(k, t) = \int_{-\infty}^{\infty} \Psi(x, t) \frac{e^{-ikx}}{(2\pi)^{1/2}} dx$$

$$\Psi(\vec{r}, t) = \int_{\text{all space}} \Psi(\vec{p}, t) \frac{e^{i\vec{p}\cdot\vec{r}/\hbar}}{(2\pi\hbar)^{3/2}} d^3p \quad \Psi(\vec{r}, t) = \int_{\text{all space}} \Psi(\vec{k}, t) \frac{e^{i\vec{k}\cdot\vec{r}}}{(2\pi)^{3/2}} d^3k$$

$$\Psi(\vec{p}, t) = \int_{\text{all space}} \Psi(\vec{r}, t) \frac{e^{-i\vec{p}\cdot\vec{r}/\hbar}}{(2\pi\hbar)^{3/2}} d^3r \quad \Psi(\vec{k}, t) = \int_{\text{all space}} \Psi(\vec{r}, t) \frac{e^{-i\vec{k}\cdot\vec{r}}}{(2\pi)^{3/2}} d^3r$$

9 Commutator Formulae

$$[A, BC] = [A, B]C + B[A, C] \quad \left[\sum_i a_i A_i, \sum_j b_j B_j \right] = \sum_{i,j} a_i b_j [A_i, B_j]$$

$$\text{if } [B, [A, B]] = 0 \quad \text{then } [A, F(B)] = [A, B]F'(B)$$

$$[x, p] = i\hbar \quad [x, f(p)] = i\hbar f'(p) \quad [p, g(x)] = -i\hbar g'(x)$$

$$[a, a^\dagger] = 1 \quad [N, a] = -a \quad [N, a^\dagger] = a^\dagger$$

10 Uncertainty Relations and Inequalities

$$\sigma_x \sigma_p = \Delta x \Delta p \geq \frac{\hbar}{2} \quad \sigma_Q \sigma_Q = \Delta Q \Delta R \geq \frac{1}{2} |\langle i[Q, R] \rangle|$$

$$\sigma_H \Delta t_{\text{scale time}} = \Delta E \Delta t_{\text{scale time}} \geq \frac{\hbar}{2}$$

11 Probability Amplitudes and Probabilities

$$\Psi(x, t) = \langle x | \Psi(t) \rangle \quad P(dx) = |\Psi(x, t)|^2 dx \quad c_i(t) = \langle \phi_i | \Psi(t) \rangle \quad P(i) = |c_i(t)|^2$$

12 Spherical Harmonics

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}} \quad Y_{1,0} = \left(\frac{3}{4\pi}\right)^{1/2} \cos(\theta) \quad Y_{1,\pm 1} = \mp \left(\frac{3}{8\pi}\right)^{1/2} \sin(\theta) e^{\pm i\phi}$$

$$L^2 Y_{\ell m} = \ell(\ell+1) \hbar^2 Y_{\ell m} \quad L_z Y_{\ell m} = m \hbar Y_{\ell m} \quad |m| \leq \ell \quad m = -\ell, -\ell+1, \dots, \ell-1, \ell$$

0	1	2	3	4	5	6	...
<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>	...

13 Hydrogenic Atom

$$\psi_{n\ell m} = R_{n\ell}(r) Y_{\ell m}(\theta, \phi) \quad \ell \leq n-1 \quad \ell = 0, 1, 2, \dots, n-1$$

$$a_z = \frac{a}{Z} \left(\frac{m_e}{m_{\text{reduced}}} \right) \quad a_0 = \frac{\hbar}{m_e c \alpha} = \frac{\lambda_C}{2\pi\alpha} \quad \alpha = \frac{e^2}{\hbar c}$$

$$R_{10} = 2a_Z^{-3/2} e^{-r/a_Z} \quad R_{20} = \frac{1}{\sqrt{2}} a_Z^{-3/2} \left(1 - \frac{1}{2} \frac{r}{a_Z} \right) e^{-r/(2a_Z)}$$

$$R_{21} = \frac{1}{\sqrt{24}} a_Z^{-3/2} \frac{r}{a_Z} e^{-r/(2a_Z)}$$

$$R_{n\ell} = - \left\{ \left(\frac{2}{na_Z} \right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3} \right\}^{1/2} e^{-\rho/2} \rho^\ell L_{n+\ell}^{2\ell+1}(\rho) \quad \rho = \frac{2r}{nr_Z}$$

$$L_q(x) = e^x \left(\frac{d}{dx} \right)^q (e^{-x} x^q) \quad \text{Rodrigues's formula for the Laguerre polynomials}$$

$$L_q^j(x) = \left(\frac{d}{dx} \right)^j L_q(x) \quad \text{Associated Laguerre polynomials}$$

$$\langle r \rangle_{n\ell m} = \frac{a_Z}{2} [3n^2 - \ell(\ell+1)]$$

$$\text{Nodes} = (n-1) - \ell \quad \text{not counting zero or infinity}$$

$$E_n = -\frac{1}{2}m_e c^2 \alpha^2 \frac{Z^2}{n^2} \frac{m_{\text{reduced}}}{m_e} = -E_{\text{Ryd}} \frac{Z^2}{n^2} \frac{m_{\text{reduced}}}{m_e} = -13.606 \frac{Z^2}{n^2} \frac{m_{\text{reduced}}}{m_e} \text{ eV}$$

14 General Angular Momentum Formulae

$$[J_i, J_j] = i\hbar \varepsilon_{ijk} J_k \quad (\text{Einstein summation on } k) \quad [J^2, \vec{J}] = 0$$

$$J^2 |jm\rangle = j(j+1)\hbar^2 |jm\rangle \quad J_z |jm\rangle = m\hbar |jm\rangle$$

$$J_{\pm} = J_x \pm iJ_y \quad J_{\pm} |jm\rangle = \hbar \sqrt{j(j+1) - m(m \pm 1)} |jm \pm 1\rangle$$

$$J_{\left\{ \begin{smallmatrix} x \\ y \end{smallmatrix} \right\}} = \left\{ \begin{smallmatrix} \frac{1}{2} \\ \frac{1}{2i} \end{smallmatrix} \right\} (J_+ \pm J_-) \quad J_{\pm}^{\dagger} J_{\pm} = J_{\mp} J_{\pm} = J^2 - J_z (J_z \pm \hbar)$$

$$[J_{fi}, J_{gj}] = \delta_{fg} i\hbar \varepsilon_{ijk} J_k \quad \vec{J} = \vec{J}_1 + \vec{J}_2 \quad J^2 = J_1^2 + J_2^2 + J_{1+}J_{2-} + J_{1-}J_{2+} + 2J_{1z}J_{2z}$$

$$J_{\pm} = J_{1\pm} + J_{2\pm} \quad |j_1 j_2 j m\rangle = \sum_{m_1 m_2, m=m_1+m_2} |j_1 j_2 m_1 m_2\rangle \langle j_1 j_2 m_1 m_2 | j_1 j_2 j m \rangle |j_1 j_2 j m\rangle$$

$$|j_1 - j_2| \leq j \leq j_1 + j_2 \quad \sum_{|j_1 - j_2|}^{j_1 + j_2} (2j + 1) = (2j_1 + 1)(2j_2 + 1)$$

15 Spin 1/2 Formulae

$$S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$|\pm\rangle_x = \frac{1}{\sqrt{2}} (|+\rangle \pm |-\rangle) \quad |\pm\rangle_y = \frac{1}{\sqrt{2}} (|+\rangle \pm i|-\rangle) \quad |\pm\rangle_z = |\pm\rangle$$

$$|++\rangle = |1, +\rangle |2, +\rangle \quad |+-\rangle = \frac{1}{\sqrt{2}} (|1, +\rangle |2, -\rangle \pm |1, -\rangle |2, +\rangle) \quad |--\rangle = |1, -\rangle |2, -\rangle$$

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

$$\sigma_i \sigma_j = \delta_{ij} + i\varepsilon_{ijk} \sigma_k \quad [\sigma_i, \sigma_j] = 2i\varepsilon_{ijk} \sigma_k \quad \{\sigma_i, \sigma_j\} = 2\delta_{ij}$$

$$(\vec{A} \cdot \vec{\sigma})(\vec{B} \cdot \vec{\sigma}) = \vec{A} \cdot \vec{B} + i(\vec{A} \times \vec{B}) \cdot \vec{\sigma}$$

$$\frac{d(\vec{S} \cdot \hat{n})}{d\alpha} = -\frac{i}{\hbar} [\vec{S} \cdot \hat{\alpha}, \vec{S} \cdot \hat{n}] \quad \vec{S} \cdot \hat{n} = e^{-i\vec{S} \cdot \hat{\alpha}} \vec{S} \cdot \hat{n}_0 e^{i\vec{S} \cdot \hat{\alpha}} \quad |\hat{n}_{\pm}\rangle = e^{-i\vec{S} \cdot \hat{\alpha}} |\hat{z}_{\pm}\rangle$$

$$e^{ixA} = \mathbf{1} \cos(x) + iA \sin(x) \quad \text{if } A^2 = \mathbf{1} \quad e^{-i\vec{\sigma} \cdot \vec{\alpha}/2} = \mathbf{1} \cos(x) - i\vec{\sigma} \cdot \hat{\alpha} \sin(x)$$

$$\sigma_i f(\sigma_j) = f(\sigma_j) \sigma_i \delta_{ij} + f(-\sigma_j) \sigma_i (1 - \delta_{ij})$$

$$\mu_{\text{Bohr}} = \frac{e\hbar}{2m} = 0.927400915(23) \times 10^{-24} \text{ J/T} = 5.7883817555(79) \times 10^{-5} \text{ eV/T}$$

$$g = 2 \left(1 + \frac{\alpha}{2\pi} + \dots \right) = 2.0023193043622(15)$$

$$\vec{\mu}_{\text{orbital}} = -\mu_{\text{Bohr}} \frac{\vec{L}}{\hbar} \quad \vec{\mu}_{\text{spin}} = -g\mu_{\text{Bohr}} \frac{\vec{S}}{\hbar} \quad \vec{\mu}_{\text{total}} = \vec{\mu}_{\text{orbital}} + \vec{\mu}_{\text{spin}} = -\mu_{\text{Bohr}} \frac{(\vec{L} + g\vec{S})}{\hbar}$$

$$H_{\mu} = -\vec{\mu} \cdot \vec{B} \quad H_{\mu} = \mu_{\text{Bohr}} B_z \frac{(L_z + gS_z)}{\hbar}$$

16 Time-Independent Approximation Methods

$$H = H^{(0)} + \lambda H^{(1)} \quad |\psi\rangle = N(\lambda) \sum_{k=0}^{\infty} \lambda^k |\psi_n^{(k)}\rangle$$

$$H^{(1)} |\psi_n^{(m-1)}\rangle (1 - \delta_{m,0}) + H^{(0)} |\psi_n^{(m)}\rangle = \sum_{\ell=0}^m E^{(m-\ell)} |\psi_n^{(\ell)}\rangle \quad |\psi_n^{(\ell>0)}\rangle = \sum_{m=0, m \neq n}^{\infty} a_{nm} |\psi_n^{(0)}\rangle$$

$$|\psi_n^{1\text{st}}\rangle = |\psi_n^{(0)}\rangle + \lambda \sum_{\text{all } k, k \neq n} \frac{\langle \psi_k^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} |\psi_k^{(0)}\rangle$$

$$E_n^{1\text{st}} = E_n^{(0)} + \lambda \langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle$$

$$E_n^{2\text{nd}} = E_n^{(0)} + \lambda \langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle + \lambda^2 \sum_{\text{all } k, k \neq n} \frac{|\langle \psi_k^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_k^{(0)}}$$

$$E(\phi) = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} \quad \delta E(\phi) = 0$$

$$H_{kj} = \langle \phi_k | H | \phi_j \rangle \quad H\vec{c} = E\vec{c}$$

17 Time-Dependent Perturbation Theory

$$\pi = \int_{-\infty}^{\infty} \frac{\sin^2(x)}{x^2} dx$$

$$\Gamma_{0 \rightarrow n} = \frac{2\pi}{\hbar} |\langle n | H_{\text{perturbation}} | 0 \rangle|^2 \delta(E_n - E_0)$$

18 Interaction of Radiation and Matter

$$\vec{E}_{\text{op}} = -\frac{1}{c} \frac{\partial \vec{A}_{\text{op}}}{\partial t} \quad \vec{B}_{\text{op}} = \nabla \times \vec{A}_{\text{op}}$$

19 Box Quantization

$$kL = 2\pi n, \quad n = 0, \pm 1, \pm 2, \dots \quad k = \frac{2\pi n}{L} \quad \Delta k_{\text{cell}} = \frac{2\pi}{L} \quad \Delta k_{\text{cell}}^3 = \frac{(2\pi)^3}{V}$$

$$dN_{\text{states}} = g \frac{k^2 dk d\Omega}{(2\pi)^3 V}$$

20 Identical Particles

$$|a, b\rangle = \frac{1}{\sqrt{2}} (|1, a; 2, b\rangle \pm |1, b; 2, a\rangle)$$

$$\psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} (\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_b(\vec{r}_1)\psi_a(\vec{r}_2))$$

21 Second Quantization

$$[a_i, a_j^\dagger] = \delta_{ij} \quad [a_i, a_j] = 0 \quad [a_i^\dagger, a_j^\dagger] = 0 \quad |N_1, \dots, N_n\rangle = \frac{(a_n^\dagger)^{N_n}}{\sqrt{N_n!}} \dots \frac{(a_1^\dagger)^{N_1}}{\sqrt{N_1!}} |0\rangle$$

$$\{a_i, a_j^\dagger\} = \delta_{ij} \quad \{a_i, a_j\} = 0 \quad \{a_i^\dagger, a_j^\dagger\} = 0 \quad |N_1, \dots, N_n\rangle = (a_n^\dagger)^{N_n} \dots (a_1^\dagger)^{N_1} |0\rangle$$

$$\Psi_s(\vec{r})^\dagger = \sum_{\vec{p}} \frac{e^{-i\vec{p}\cdot\vec{r}}}{\sqrt{V}} a_{\vec{p}s}^\dagger \quad \Psi_s(\vec{r}) = \sum_{\vec{p}} \frac{e^{i\vec{p}\cdot\vec{r}}}{\sqrt{V}} a_{\vec{p}s}$$

$$[\Psi_s(\vec{r}), \Psi_{s'}(\vec{r}')]_{\mp} = 0 \quad [\Psi_s(\vec{r})^\dagger, \Psi_{s'}(\vec{r}')^\dagger]_{\mp} = 0 \quad [\Psi_s(\vec{r}), \Psi_{s'}(\vec{r}')^\dagger]_{\mp} = \delta(\vec{r} - \vec{r}') \delta_{ss'}$$

$$|\vec{r}_1 s_1, \dots, \vec{r}_n s_n\rangle = \frac{1}{\sqrt{n!}} \Psi_{s_n}(\vec{r}_n)^\dagger \dots \Psi_{s_1}(\vec{r}_1)^\dagger |0\rangle$$

$$\Psi_s(\vec{r})^\dagger |\vec{r}_1 s_1, \dots, \vec{r}_n s_n\rangle \sqrt{n+1} |\vec{r}_1 s_1, \dots, \vec{r}_n s_n, \vec{r}s\rangle$$

$$|\Phi\rangle = \int d\vec{r}_1 \dots d\vec{r}_n \Phi(\vec{r}_1, \dots, \vec{r}_n) |\vec{r}_1 s_1, \dots, \vec{r}_n s_n\rangle$$

$$1_n = \sum_{s_1 \dots s_n} \int d\vec{r}_1 \dots d\vec{r}_n |\vec{r}_1 s_1, \dots, \vec{r}_n s_n\rangle \langle \vec{r}_1 s_1, \dots, \vec{r}_n s_n| \quad 1 = |0\rangle \langle 0| + \sum_{n=1}^{\infty} 1_n$$

$$N = \sum_{\vec{p}s} a_{\vec{p}s}^\dagger a_{\vec{p}s} \quad T = \sum_{\vec{p}s} \frac{p^2}{2m} a_{\vec{p}s}^\dagger a_{\vec{p}s}$$

$$\rho_s(\vec{r}) = \Psi_s(\vec{r})^\dagger \Psi_s(\vec{r}) \quad N = \sum_s \int d\vec{r} \rho_s(\vec{r}) \quad T = \frac{1}{2m} \sum_s \int d\vec{r} \nabla \Psi_s(\vec{r})^\dagger \cdot \nabla \Psi_s(\vec{r})$$

$$\vec{j}_s(\vec{r}) = \frac{1}{2im} [\Psi_s(\vec{r})^\dagger \nabla \Psi_s(\vec{r}) - \Psi_s(\vec{r}) \nabla \Psi_s(\vec{r})^\dagger]$$

$$G_s(\vec{r} - \vec{r}') = \frac{3n \sin(x) - x \cos(x)}{2x^3} \quad g_{ss'}(\vec{r} - \vec{r}') = 1 - \delta_{ss'} \frac{G_s(\vec{r} - \vec{r}')^2}{(n/2)^2}$$

$$v_{2\text{nd}} = \frac{1}{2} \sum_{ss'} \int d\vec{r} d\vec{r}' v(\vec{r} - \vec{r}') \Psi_s(\vec{r})^\dagger \Psi_{s'}(\vec{r}')^\dagger \Psi_{s'}(\vec{r}') \Psi_s(\vec{r})$$

$$v_{2\text{nd}} = \frac{1}{2V} \sum_{pp'qq'} \sum_{ss'} v_{\vec{p}-\vec{p}'} \delta_{\vec{p}+\vec{q}, \vec{p}'+\vec{q}'} a_{\vec{p}s}^\dagger a_{\vec{q}s'}^\dagger a_{\vec{q}'s'} a_{\vec{p}'s} \quad v_{\vec{p}-\vec{p}'} = \int d\vec{r} e^{-i(\vec{p}-\vec{p}') \cdot \vec{r}} v(\vec{r})$$

22 Klein-Gordon Equation

$$E = \sqrt{p^2 c^2 + m^2 c^4} \quad \frac{1}{c^2} \left(i\hbar \frac{\partial}{\partial t} \right)^2 \Psi(\vec{r}, t) = \left[\left(\frac{\hbar}{i} \nabla \right)^2 + m^2 c^2 \right] \Psi(\vec{r}, t)$$

$$\left[\frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \nabla^2 + \left(\frac{mc}{\hbar} \right)^2 \right] \Psi(\vec{r}, t) = 0$$

$$\rho = \frac{i\hbar}{2mc^2} \left(\Psi^* \frac{\partial \Psi}{\partial t} - \Psi \frac{\partial \Psi^*}{\partial t} \right) \quad \vec{j} = \frac{\hbar}{2im} (\Psi^* \nabla \Psi - \Psi \nabla \Psi^*)$$

$$\frac{1}{c^2} \left(i\hbar \frac{\partial}{\partial t} - e\Phi \right)^2 \Psi(\vec{r}, t) = \left[\left(\frac{\hbar}{i} \nabla - \frac{e}{c} \vec{A} \right)^2 + m^2 c^2 \right] \Psi(\vec{r}, t)$$

$$\Psi_+(\vec{p}, E) = e^{i(\vec{p} \cdot \vec{r} - Et)/\hbar} \quad \Psi_-(\vec{p}, E) = e^{-i(\vec{p} \cdot \vec{r} - Et)/\hbar}$$