

Quantum Mechanics

NAME:

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

- The simplest quantum mechanical solid model is arguably:
 - the hydrogen atom.
 - the helium atom.
 - the free electron gas model.
 - the infinite periodic potential model.
 - the finite periodic potential model.
- For the free electron gas model of a solid, one common simple choice of boundary conditions is:
 - infinite square well boundary conditions.
 - finite square well boundary conditions.
 - Gaussian well boundary conditions.
 - hydrogen atom boundary conditions.
 - helium atom boundary conditions.
- “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?

- infinite square well boundary conditions
 - aperiodic boundary conditions
 - Rabi-Schwinger-Baym-Sutherland boundary conditions
 - periodic boundary conditions
 - relaxed boundary conditions
- 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.

- 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.
- 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} .
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.

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.

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} .

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.

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).

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	$\frac{\hbar^2}{2m_e}$	$= 3.81 \text{ eV \AA}^2$
	$\frac{\hbar^2}{m_e}$	$= 7.62 \text{ eV \AA}^2$
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

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

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

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

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

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

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

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

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