WAVE FUNCTIONS OF ELECTRONS IN A HIGHLY COMPRESSED GAS

by

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ABSTRACT

Quantum mechanical treatments of problems which deal with gases inside the stars have thus far been carried out by using the wave function of an electron moving in the field of a single atom. This simplified picture is no longer valid when the pressure of the gaseous medium is very high. This anomalous situation may give rise to two special phenomena. The bound electrons may be squeezed out of the atoms completely, or if any bound level does exist, its ionization potential is lowered. It is the purpose of the present study to find the wave function of electrons for both cases. Only hydrogen gas will be considered here; however, the method developed may be extended to other elements.

By using the method of self-consistent fields, developed by Hartree and Fock, calculations are first carried out for electrons that are completely squeezed out of their bound levels. Those free electrons form a highly degenerate gas about the ions. The problem can be considered as spherically symmetric and the Schrödinger equation of the electron is solved by using an assumed potential. The charge distribution can then be determined by the solutions and from the charge distribution, a potential can be calculated. A new method is used in obtaining a self-consistency between the calculated and the assumed potential. This is done by adjusting a parameter which determines the density of the gas and the Fermi energy. The correction due to the exchange potential is also taken into account by assuming the electrons are perfectly free.

For the case that a bound level with very low ionization potential exists, the problem is treated by methods which have been developed for the theory of solids. The situation differs in the fact that there is no periodicity in the arrangement of the gaseous atoms. The single electron wave function is assumed to be of the Bloch type. The width of the energy band is determined as a function of the interatomic distance. A self-consistent calculation is then carried out for cases which have different ionization potentials.

Using the wave functions obtained, the opacity of a compressed hydrogen gas is determined as a function of temperature and density. The absorption of radiation is mainly caused by absorption by the bound electrons as well as that of the free electrons in the presence of the field. The coefficients of the absorption are calculated for both cases and the results are compared with that obtained by Kramers from a semi-classical treatment. Ratios between the two, called the Gaunt's factors, are determined for various densities and frequencies. From these are computed the opacities of the gas for various densities and temperatures.

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INTRODUCTION

Following the development of quantum mechanics, many astrophysical problems such as photoelectric absorption, recombination, and problems concerning the stellar models have been explored by means of the new method. So far, however, most of the calculations have been made under the assumptions of oversimplified models of the stellar material concerned; since more rigorous treatments, if not unsolvable, usually involve a great deal of mathematical difficulties. It is known that very high pressures usually exist inside the stars. The pressure can be so high that the electrons are squeezed out of their quantized levels. This phenomenon is usually called "pressure ionization". Under such anomalous conditions, it is not justifiable to use the same wave functions for the electrons as those that are used in problems concerning only a single atom. In the present study, an attempt will be made to find the wave function of electrons which are applicable to very high density gaseous media.

As the interatomic distance decreases on account of the high density, the field exerted on an electron is not only that due to the single nucleus and the electrons belonging to the same atom; that caused by the other nuclei and electrons of the other atoms must also be taken into account. Therefore, the high pressure gaseous media give rise to manybody problems, the satisfactory solutions of which cannot be obtained without certain approximations and simplifications. It is hoped to reduce the complexities of the problem, and yet present a valid description of the physical phenomena. Although the stellar material consists of hydrogen, helium, and many other elements, it is generally believed that hydrogen is the predominating element in many stars. In the present study, calculations will only be made to find the wave functions of electrons for a hydrogen gas, but it is hoped that the method developed may be extended to other elements, as well as to gases which are mixtures of various elements.

Among the various methods which are employed in solving complex quantum mechanical problems, the Hartree(1) method of self consistent field is generally used in dealing with the many electrons problem. Hartree has shown that it is plausible to replace the mutual interaction of the electrons and of the electron with the nuclei by a "representative" or "self consistent" potential field. The method has been widely used in finding the wave function for electrons of complex atoms. To carry out the self-consistent calculations, one has to assume an averaged potential field and solve the one electron wave equation. From the solution one can then determine the charge distribution and the potential in which the electron is moving. The purpose of the method is to make the potential assumed agree with that calculated; this is usually done by means of successive revisions of the former. Although Hartree's method yields satisfactory results for many purposes, yet it still has the defect of not having taken into account the Pauli exclusion principle. If one starts out with an antisymmetric wave function of all the electrons and then varies the one electron wave function so as to make the energy an extreme, the result shows that the electron moves in the field of all the nuclei and all the electrons other than itself. The equation resulting from the variational principle is called the Hartree Fock(2) equation. It contains an extra term in addition to the potential energy of the Hartree equation. This is called the "exchange term", the physical meaning of which will be mentioned in greater detail in the further discussions.

For the present problem the principle of the self consistent calculations is to be employed. As the gas atoms or ions do not have any preferred relative orientations, the averaged effect from all the other nuclei and electrons on a particular one may be considered as approximately spherical. Therefore it is justifiable to assume that the averaged field acting on an electron has spherical symmetry and this is going to be used as the starting point of the self consistent calculations.

Discussions and calculations will be first carried out for pressures so high that the gas is completely ionized. The electrons, although freed from the atoms, remain in the gas, so that the whole medium is electrically neutral. It is known that electrons obey the Fermi-Dirac statistics and it is degenerate at sufficiently low temperatures. The energy distribution depends on a parameter which is the maximum energy of the electrons in the distribution. This maximum energy, which is called Fermi energy, is a function of density at the absolute zero of temperature. It is of the order of the ionization potentials and increases as the density increases. Consequently the Fermi energy is much higher than kT, and is even more so as the pressure increases. Therefore under very high pressure, the maximum energy of the electron at any temperature does not differ much from the Fermi energy at zero temperature. The high density gas medium can be considered as consisting of ions embedded in a highly degenerate Fermi-Dirac electron gas. The electrons form an energy band with all the energy states filled up to the Fermi energy. Since all the ions are surrounded by the same kind of electron bands, one can simplify the problem by considering a box with the ion at the center surrounded by enough electrons so as to make the whole volume electrically neutral. The assumed potential is such that the electrons are almost free except when they are near to the nucleus. The free electron wave functions can be joined smoothly to those of the neighboring boxes by means of periodic boundary conditions. The problem is therefore reduced to solving a one electron problem with an assumed potential field. The electron density is then determined from the solutions averaged over all the occupied states in the energy band. The potential which is obtained from the charge distribution must be consistent with the one assumed. The self-consistency between the two is reached by varying the Fermi energy, or in other words, quantities which determine the density of the electrons are used as the adjustable parameters in the self-consistent calculations. Since the wave functions remain unaltered as the density is varied, the calculation is much easier to perform than the usual Hartree procedure. The correction due to the exchange potential is also introduced by considering the electrons as perfectly free. This is not a bad approximation, since the wave functions considered are not too much different from those of the perfectly free case. The detailed discussions of this method and the physical significance of the parameters involved will be discussed in Chapter I.

As the density of the gas decreases, the former situation changes into one where bound levels of very low ionization potential begin to appear. The electrons, instead of forming a free, degenerate, Fermi gas, are loosely bound to the respective nuclei. If the atoms are still sufficiently close to each other so that the interatomic distances are not too much greater than the magnitude of the electron orbits of an individual atom, the loosely bound electron does not remain around one atom, but the electron wave can be considered as travelling from one atom to the other. The situation bears a certain similarity to that of electrons in a metal. The electrons behave either like bound ones or like free ones depending on their positions with respect to the nuclei. Consequently, the present problem can be treated by using the method developed in the theory of solids. The one electron wave functions suggested by Bloch[3] are to be used in building up the antisymmetric wave function of all the electrons in the medium. The effect on the electron energy due to the presence of other atoms and a self-consistent calculation of the potential field is to be carried out.

Although it is quite appropriate to apply methods similar to that used in solids, the situation differ in the fact that there is no periodicity in the arrangement of the gas atoms. The effect of various possible orientations is taken into consideration and an averaged result obtained. As a consequence of the close approach of the atoms, the bound energy level instead of being a discrete one, is spread into a band. The width of the band is a function of the mean interatomic distance. The self-consistent calculation of the potential is performed by the adjustment of the parameters which are connected with atomic volume and potentials. The method is similar to that used for the case described in the first chapter; the difference lies in the fact that for the bound case there is no Fermi band. The charge density is obtained by averaging over the occupied states in the energy band. A detailed description of the method and the comparison with that for the free electrons are given in Chapter II.

Using the wave functions obtained for both the "pressure ionized" and the atomic hydrogen gas, calculations of opacity for a hydrogen gas will be made. Phenomena such as photoelectric absorption of radiation by the bound electron, absorption of radiation by the free electrons in the presence of an atomic field, are both dominating factors in determining the opacity of stars. The problems of the continuous absorption have been solved by Kramers(4) using a semi-classical method. Quantum mechanical calculations using hydrogen wave functions have been carried out by many authors.(5)-(8) With the wave functions obtained in the present treatment, absorption cross-sections are to be calculated as functions of gas density and frequency. Both bound-free and free-free transitions are to be considered. The opacity is then obtained by evaluating the Rosseland mean which is a weighted average of the absorption coefficient over the distributions in frequency. The result can be expressed as a function of the density and temperature and is to be compared with Kramers' result and those using the simple hydrogenic wave functions. It is hoped that the result obtained may have some significance for solving problems concerning stellar interiors.

CHAPTER I

SELF-CONSISTENT CALCULATIONS FOR A COMPLETELY IONIZED GAS

The gas medium to be discussed in the present chapter is so dense that there are no bound levels. The electrons are moving in the field of all the bare nuclei and the electrons that are present in the medium. This many electron problem is to be solved by using the principle of the self-consistent field developed by Hartree and Fock. A new method is developed so as to take the place of the hitherto tedious computations involved in such problems. The calculations will be started with an assumed spherical potential and then the charge density determined, from which the process of self-consistent calculations can be pursued. A model of the ionized gas medium is to be obtained whose charge distribution is in satisfactory conformity with that of the potential field.

1.1. Potential Field Assumed

As it has been pointed our previously, the electron is to be considered as moving in a spherical potential field. The problem is further simplified by considering a single nucleus, embedded in a degenerate electron gas, enclosed in a big box. When the electron is near the nucleus, the dominating force that is exerted on the electron is that due to the nucleus and is of the ordinary Coulombian type. However, this field may be reduced by the presence of other electrons. This repulsive force becomes more prominent as the electron is further away from the nucleus, As a first approximation, it is possible to use an averaged potential field of the following type:

$$V = -\left(\frac{e}{r} - \frac{e}{a}\right) \qquad r \leqq a$$

$$V = 0 \qquad r \geqq a \qquad (1.1)$$

Physically, such a field is due to the presence of a nucleus and a spherical shell of electrons with radius "a" carrying the same total amount of charge as that of the nucleus. This field caused by the spherical shell of electrons is introduced so as to represent the field due to all the other electrons. Therefore one can regard "a" as some kind of averaged distance between the nucleus and the nearest electrons present. It is rather presumptive to assume that the electrons are localized in such a predescribed manner; however, since a self-consistent calculation is going to be carried out, an improved model may be obtained from this seemingly crude approximation.

The kind of potential given by (1.1) has been used by Guth and Sexl(9) to study the emission of alpha-particles by radioactive nuclei and by Allis and Morse(10) in computing the scattering cross-section of electrons in rare gas atoms and sodium atoms. Putting (1.1) in the Schrödinger equation:

$$\nabla^2\psi + \left[E + 2\left(\frac{1}{r} - \frac{1}{a}\right)\right]\psi = 0 \qquad r \leqq a$$

$$\nabla^2\psi + E\psi = 0 \qquad r \geqq a\ . \qquad (1.2)$$

Atomic units will be used throughout the calculations, their values in terms of the C.G.S. unit are given in Appendix (IA). Solutions of (1.2) can be obtained separately for electrons of negative and positive energy. Only the positive energy solutions will be considered in the present chapter. In finding the solution, the usual process of determining the wave functions for regions $r < a$ and $r > a$ separately are used; the values and slopes of the wave functions are equated at $r = a$. The solution for the region $r > a$ is that of a free electron with the phase distorted due to the presence of the nucleus. The amount of distortion is called the phase shift η_ℓ . The value of η_ℓ depends on the angular momentum of the electron; it is also a function of the energy of the electron as well as the range of the potential. If one lets $k = \sqrt{E}$, η_ℓ can be most conveniently expressed as a function of ka, where "a" is the range of our potential field. The product ka gives a measure for the scattering strength of the potential field. The wave functions are normalized in such a manner that the radial wave functions have the asymptotic form

$$R(r) \xrightarrow[r\to\infty]{} \frac{\sin(kr - \frac{1}{2}\ell\pi + \eta_\ell)}{kr} . \qquad (1.3)$$

The solutions of (1.2) for both regions $r < a$ and $r > a$ are given in Appendix (IIB). The relation of η_ℓ and ka are also obtained for various values of cut-off radius "a". The values of phase shifts expressed as functions of ka and that of $\sqrt{a/2}$ are given in Figs. (1.1) - (1.4). Similar curves have been shown by Morse$^{(11)}$ in the review article.

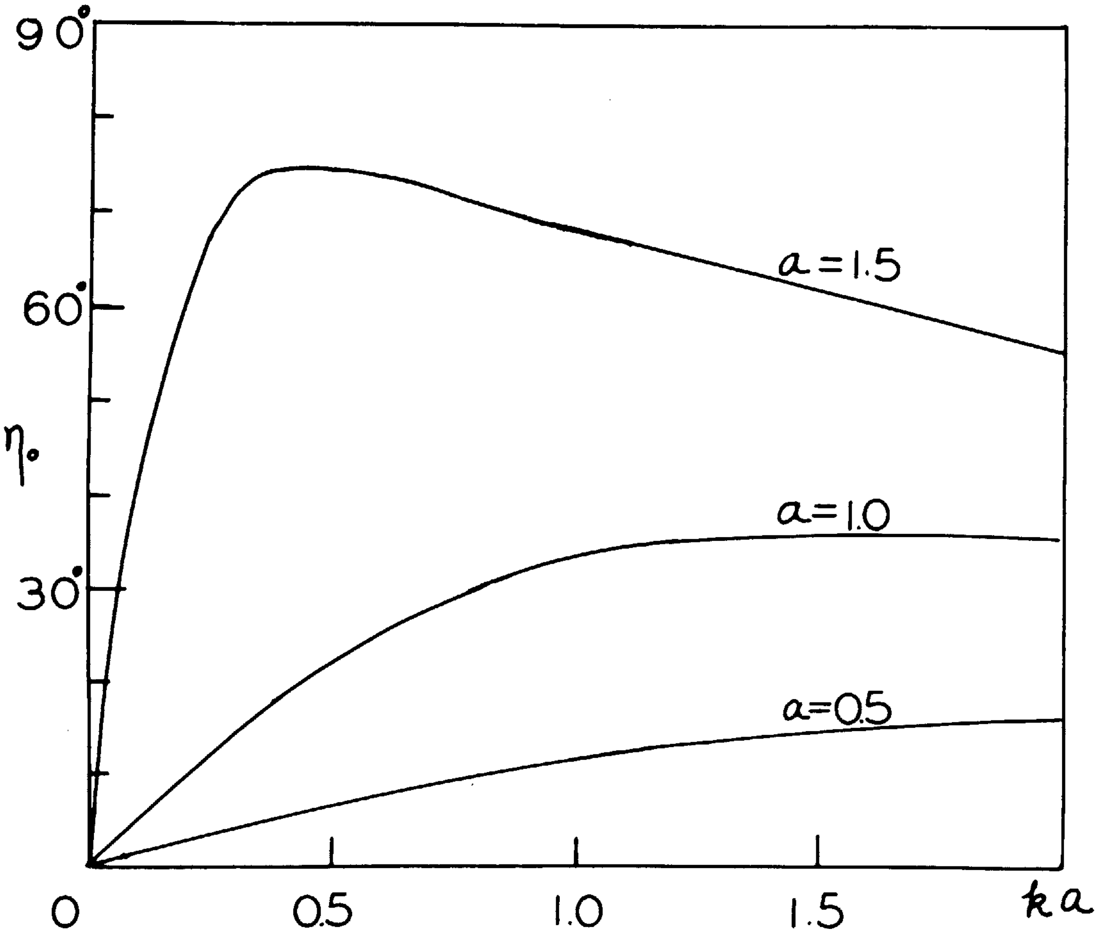


Fig. 1.1 PHASE SHIFTS η_o AS FUNCTIONS OF ka

$k = \sqrt{E}$

"a" satisfies the conditions $V = -(\frac{e}{r} - \frac{e}{a})$ $\quad r \leqq a$

$V = 0$ $\quad r \geqq a$

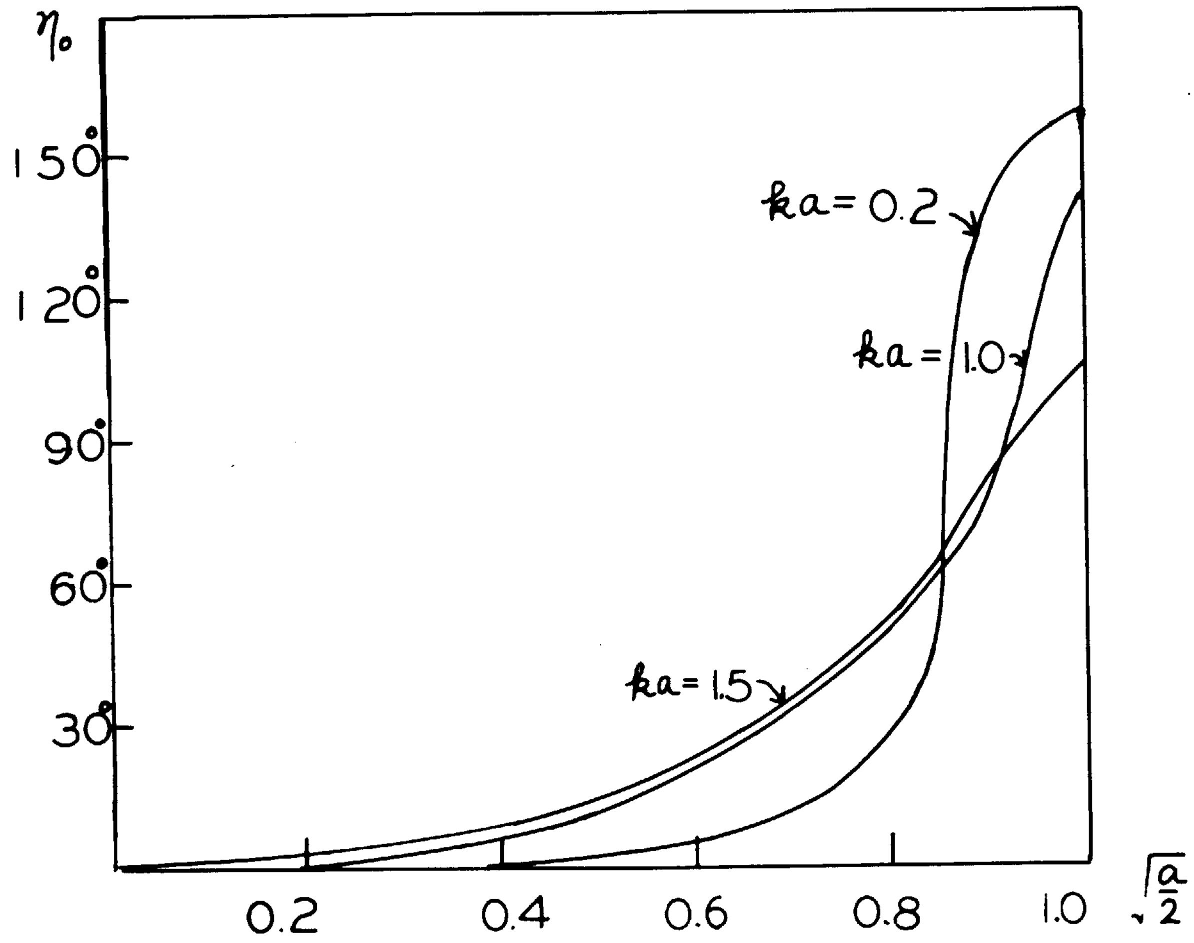


Fig. 1.2 PHASE SHIFTS η_0 AS FUNCTIONS OF $\sqrt{a/2}$ FOR CONSTANT ka

$k = \sqrt{E}$

"a" satisfies the conditions $V = -(\frac{e}{r} - \frac{e}{a}) \qquad r \leqq a$

$V = 0 \qquad r \geqq a$

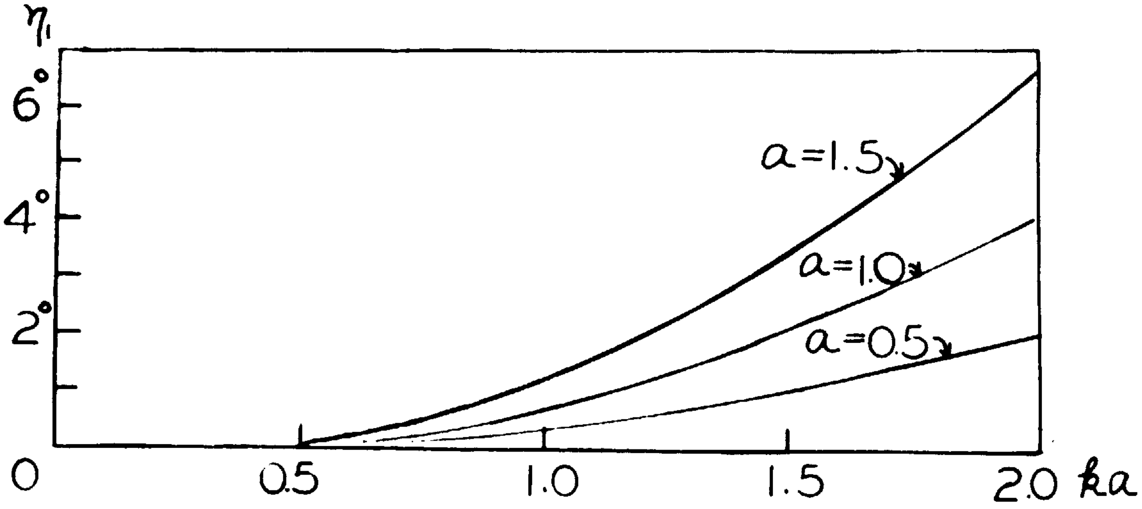


Fig. 1.3 PHASE SHIFTS η_1 AS FUNCTIONS OF ka

$k = \sqrt{E}$

"a" satisfies the conditions $V = -(\frac{e}{r} - \frac{e}{a}) \quad r \leqq a$

$V = 0 \quad r \geqq a$

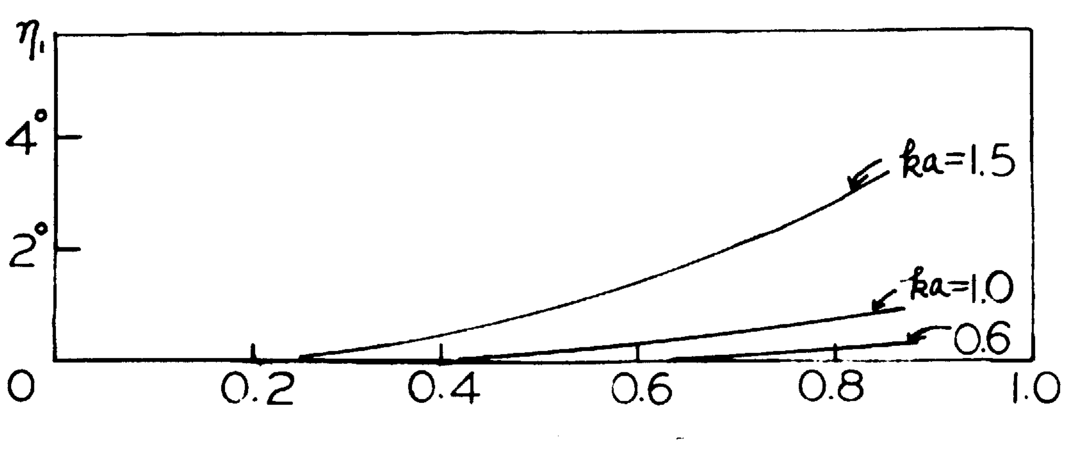


Fig. 1.4 PHASE SHIFTS η_1 AS FUNCTIONS OF $\sqrt{a/2}$

From Figs. (1.1) and (1.3), it can be seen that the phase shifts for $\ell = 0$ wave is greater than that for the $\ell = 1$ wave, while that of the $\ell = 2$ wave can be regarded as zero for most of the present purposes. This is to be expected, since it is quite unlikely for electrons of higher angular momentum to get close to the nucleus. In Fig. (1.2) and (1.4), the phase shifts η_ℓ are given as functions of $\sqrt{a/2}$; it can be seen that η_0 behaves like a step function which has a sudden rise at $\sqrt{a/2} = 0.87$ $(a = 1.75)$. If one considers the relation between the solution of Schrödinger equations and the cut-off radius "a", it can be shown that a bound level will begin to appear as "a" increases; there exists a critical value of "a" such that the bound level appears at zero energy. Correspondingly, at this value of "a", one would expect a sudden change of phase shift. Since only the completely ionized cases are considered here, values of "a" are chosen to be smaller than the critical value.

1.2 Determination of the Charge Density

In order to carry out the self-consistent calculations, the charge distribution is to be calculated from the solution of the Schrodinger equations obtained in Appendix B. Since the positive energy electron has a continuous spectrum, the charge density should be obtained from electrons of all states. For a Fermi-Dirac gas, the number of states for electrons of energy between E and E + dE is

$$dN = \frac{VE^{1/2}}{2\pi^2} \frac{1}{e^{\frac{E - E_F}{T_a}} + 1} \qquad (1.4)$$

where E_F is the Fermi energy and T_a is the energy kT of the electron in the atomic unit. Consider first the case where the temperature is at absolute zero, then from (1.4) it follows that

$$E_{Fo} = (3\pi^2 n_o)^{2/3} \tag{1.5}$$

where E_{Fo} is the maximum energy of the electron at the absolute zero and n_o is the density of electrons. For the density of interest at present, E_{Fo} is higher than 15.6 e.v. Consequently, this is much higher than the thermal energy of the electron. The relation between E_F and E_{Fo} is given approximately by

$$E_F = E_{Fo}\left[1 - \frac{\pi^2}{12}\left(\frac{T_a}{E_{Fo}}\right)^2\right]. \tag{1.6}$$

Therefore for high densities $E_{Fo} >> T_a$, $E_F = E_{Fo}$. One can consider the free electron gas as completely degenerate with all the states filled up to E_{Fo} which will be called Fermi energy. For the present problem, the potential given by Eq. (1.1) corresponds to a charge of one electron distributed uniformly over a spherical surface of radius a. One can substitute in (1.5) for $n_o = 3/4\pi a^3$ or any smaller quantity, as any sphere of radius larger than "a" also contains one electron. Using the limiting value E_{Fo} is given as a function of "a" by:

$$E_{Fo} = 3.68 \frac{1}{a^2}. \tag{1.7}$$

The charge density of electrons with energy E at any position (r,θ,ϕ) is given by $|\psi_E(r,\theta,\phi)|^2$. To obtain the total charge density, the value of $|\psi_E(r,\theta,\phi)|^2$ is to be averaged over all the possible states in the Fermi band. Since for each energy there is a $(2\ell+1)$ fold degeneracy of the angular momentum, the electron density at a position (r,θ,ϕ) is

$$n(r,\theta,\phi) = \sum_{\ell} (2\ell+1) \int_0^{E_{Fo}} |\psi_{E.\ell}(r,\theta,\phi)|^2 \frac{E^{1/2}dE}{2\pi^2} . \qquad (1.8)$$

As a result of the spherical symmetry of the problem (1.8) can also be written as

$$n(r) = \sum_{\ell} \frac{(2\ell+1)}{2\pi^2} \int_0^{E_{Fo}} |R_{E\ell}(r)|^2 E^{1/2} dE \qquad (1.9)$$

where $R_{E,\ell}(r)$ is the radial wave function of the electron. For the case of a free electron gas without the presence of any potential field, the solution is $R_{E,\ell}(r) = j_\ell(kr)$. As to be expected, (1.9) then gives a uniform distribution throughout the medium, since $\sum(2\ell+1)j_\ell^2(kr) = 1$.

The charge densities for various cut-off radii are shown in Fig. (1.5). The ordinate is the ratio $n(r)/n_o$, where n_o is the uniform charge distribution given by $n_o = 3/4\pi a^3$. Figure (1.5) shows that the electrons tend to stay inside the radius "a". This effect is extremely prominent for the case of $a = 1.5$, becoming less so for smaller values of cut-off and finally approaching a uniform distribution as $a = 0$ which is the same as saying that the electron is completely free. As it has been shown at the end of the last section the bound level begins to appear at a cut-off of $a = 1.75$. When $a = 1.5$, the quantized level is just about to appear, consequently the electron

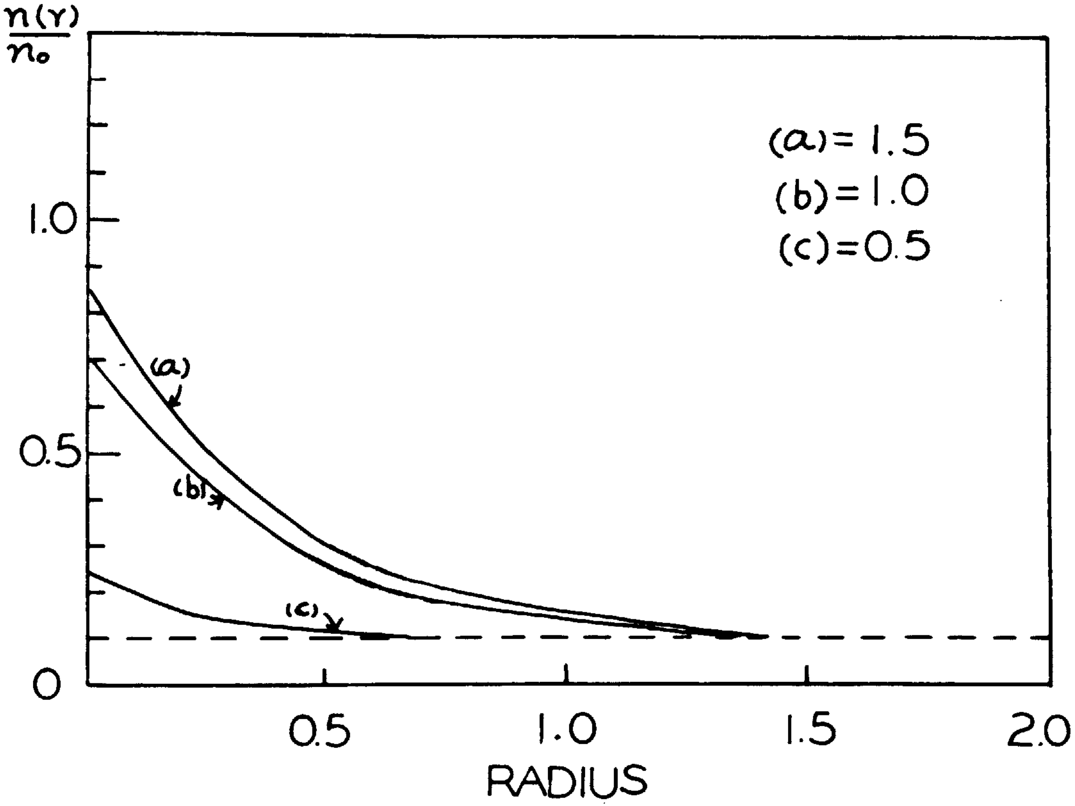


Fig. 1.5 NORMALIZED CHARGE DISTRIBUTIONS FOR VARIOUS CUT-OFF RADII

$n_o(r) = 3/4\pi a^3$

has a tendency to become partially bound by the nucleus and there is a higher probability for the electron to stay inside the cut-off radius.

1.3 Self-Consistent Calculation of the Potential

Having solved the wave equation with the assumed potential field and determined the charge density, the next step is to calculate the potential function.

Let $n_j(r)$ be the charge density at r due to the j^{th} electron, then the potential of the i^{th} electron at a position r_1 can be written as

$$eV_i(r_1) = \sum_n -\frac{e^2}{r_{in}} + e^2 \sum_j \int \frac{n_j(r_2)d\tau_2}{r_{12}} \, . \qquad (1.10)$$

The first term is the potential energy due to all the hydrogen nuclei and the second term is that caused by all the electrons except for the one considered, since the electron does not act on itself. However, (1.10) is not a satisfactory expression for the potential energy since it has not taken into account the antisymmetric property of the electron wave function.

Let u_i be the normalized one electron wave function of both coordinate and spin, then the antisymmetric wave function of the N electrons can be written as

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(x_1) & u_1(x_2) \ldots\ldots\ldots\ldots u_1(x_n) \\ u_2(x_1) & u_2(x_2) \ldots\ldots\ldots\ldots u_2(x_n) \\ & \\ u_n(x_1) & u_n(x_2) \ldots\ldots\ldots\ldots u_n(x_n) \end{vmatrix} \qquad (1.11)$$

where $x_1, x_2, \ldots . x_n$ are the coordinates of the respective electrons, and Ψ satisfies the equation $H\Psi = E\Psi$. It has been shown by many authors that the Hartree Fock equation, which is obtained by varying the one electron wave function so as to make the energy an extreme, gives the best set of one electron wave functions for self-consistent calculations. The equation is of the following form(13):

$$Hu_i(x_1) + \left\{ \sum_{k=1}^{n} \int u_k^*(x_2) u_k(x_2) \frac{2}{r_{12}} \, dx_2 \right] u_i(x_1)$$

$$- \sum_{k=1}^{n} \left[\int u_k^*(x_2) u_i(x_2) \frac{2}{r_{12}} \, dx_2 \right] u_k(x_1) = E_i u_i(x_1). \qquad (1.12)$$

The integration of dx_2 includes also the summing of the spin. The second term at the left of Eq. (1.12) represents the potential due to the charge of all the electrons including the i^{th} one concerned. The last term can be shown to represent the exchange potential. The exchange charge density represents a charge equal to that of one electron caused by all the electrons having the same spin as the one considered. The explanation given here was first carried out by Wigner and Seitz(14) and extended by Slater(15). Although in both (1.12) and the potential energy given by (1.10), the electrons are moving in the field of all the nuclei and N-1 electrons, yet they differ in the fact that in (1.12) the effect of this removed electron is localized at the position x_1 of the i^{th} electron; whereas in (1.10) the similar effect being spread out, it can be considered as equivalent to the reduction of the nuclear charge by an amount of 1/N of the removed charge. This effect is consequently much smaller than that given by (1.12).

Although (1.12) gives a good description of the averaged field in which the electrons are moving, unfortunately its applicability is greatly hindered by the difficulties involved in the evaluation of the exchange term. The unit charge that has to be removed can be considered as being localized around the i^{th} electron with a spherical symmetry and the dimensions of the exchange hole depend primarily on the electron density at the point concerned. Slater(15) has suggested that the exchange potential can be obtained by using that for a free electron gas. This simplified exchange potential energy at a certain position r has the form

$$eV(r) = -6\left[\frac{3n(r)}{8\pi}\right]^{1/3} \qquad (1.13)$$

where n(r) is the charge density at the point r concerned. Therefore by combining (1.12) and (1.13), the potential energy of the i^{th} electron is

$$eV(r_1) = \sum_n -\frac{2}{r_{1n}} + \sum_j \int \frac{n_j(r_2)d\tau_2}{r_{12}} - 6\left\{\frac{3n(r_1)}{8\pi}\right\}^{1/3}. \qquad (1.14)$$

(1.14) can be further simplified by considering the model used in the present treatment. Here it is essentially an electron band surrounding the nucleus. The electron band and the nucleus form a neutral unit with a radius δ. So far in the discussions, the cut-off radius "a" has been used as that of a neutral unit. Inside this neutral unit, an averaged potential field of spherical symmetry is assumed; therefore, the existence of the other ions outside the unit considered does not play an explicit role in the determination of the wave function. One can then venture to carry out the self-consistent calculations just within one neutral unit. Similar measures can be taken for all the neutral units around each nucleus and attain a self-consistent result throughout the medium. The assumption makes it possible to reduce (1.14) into simpler form:

$$eV(r) = -\frac{2}{r} + \frac{2}{r}\int_0^r 4\pi r'^2 n(r')dr' + 2\int_r^\delta 4\pi r' n(r')dr' - 6\left[\frac{3n(r)}{8\pi}\right]^{1/3} \quad (1.15)$$

where δ is determined by the relation

$$\int_0^\delta 4\pi r'^2 n(r')dr' = 1 \ . \quad (1.16)$$

The first term in the right side of (1.15) does not involve a summation anymore, since only the field due to one nucleus has to be concerned. The second term is the field due to the electrons inside the radius r, while the third term is that due to those lying between r and δ. The integration does not have to be extended to the region beyond $r = \delta$. Equation (1.15) can be calculated with the use of n(r) given in Sec. 1.2. As a first trial, it is simpler not to take into account the correction due to the exchange. By evaluating (1.16), it is found that the value of δ so determined is smaller than "a", consequently the potential calculated by (1.15) approaches zero at $r = \delta$ instead of $r = a$. Moreover, a comparison of the calculated potential with that assumed does not give satisfactory agreement. The discrepancy might have been expected, however, since the calculation has been started out with a rather crude assumption. For further improvement, if the method developed by Hartree is to be followed, then a new potential has to be assumed and a numerical integration of the Schrödinger equation carried out. In order to avoid this cumbersome calculation, a simplified procedure is developed.

As has been shown previously the cut-off radius "a" can be considered as an averaged distance between the nearest electrons and the nucleus. It has also been assumed that the Fermi energy is determined by an electron density corresponding to unit charge in a volume of $4\pi a^3/3$. By doing so, it is automatically assumed that this averaged radius is at the edge of the neutral unit. In order to increase the value of δ, one has to reduce the charge density n(r) inside the radius δ. This can be done by decreasing the Fermi energy, which is the same as saying that the density n_o is reduced. Let us define a sphere of radius β such that there is, in the average, one electron inside it:

$$\frac{3}{4\pi\beta^3} = n_o \ .$$

There are now two parameters β and δ at our disposal, the adjustment of which will be carried out in such a way as to obtain good agreement with the assumed potential. The agreement is satisfactory if the following criteria can be satisfied:

$$\text{(i)} \quad \int_0^{\delta} n_o(r)4\pi r^2 dr = 1 \qquad (1.17a)$$

$$\text{(ii)} \quad V(\delta) = 0 \qquad (1.17b)$$

$$\text{(iii)} \quad V_{\text{assumed}}(r = 0) = V_{\text{cal.}}(r = 0) \qquad (1.17c)$$

Calculations have shown that the second condition $V(\delta) = 0$ cannot be satisfied unless an extra constant is added to the potential energy term

$$eV = -\frac{2}{r} + \frac{2}{r}\int_0^r n(r')4\pi r'^2 dr' + 2\int_r^{\delta} n(r')4\pi r' dr' + V_{\text{exchange}}(r) + \overline{V'}. \qquad (1.18)$$

With the insertion of $\overline{V'}$, the three criteria can be fulfilled and the self-consistent calculation accomplished. The physical significance of $\overline{V'}$ can be considered as the average potential of the electrons and nuclei in the medium. The situation can be understood from the fact that the net electric field due to all the electrons and nuclei does not vanish at any position of the space. Since this is a mean value of the field produced by all the particles, it should have a constant value. At radius δ the value of the potential will vanish only if this averaged potential $\overline{V'}$ is chosen as the point of reference.

Self-consistent calculations are carried out for a = 0.5, 1.0 and 1.5. The results are shown in Fig. (1.6). The agreement between the calculated potential and the assumed one is quite satisfactory. Better results seem to favor the case of small cut-off; this

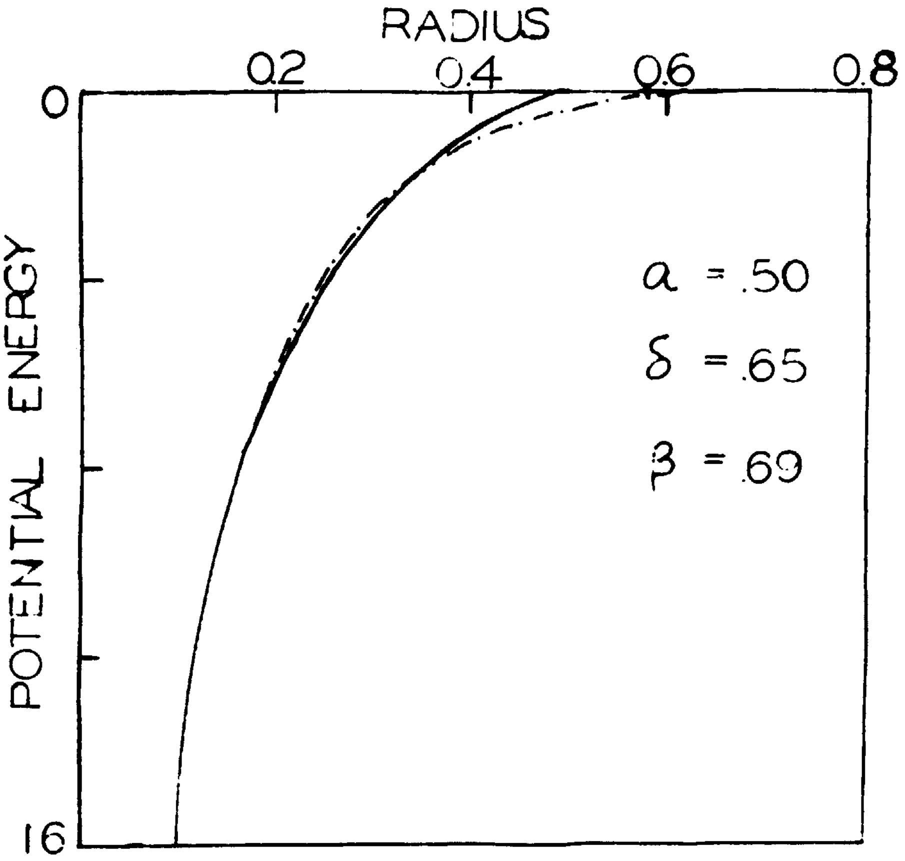


Fig. 1.6a COMPARISON OF THE ASSUMED POTENTIAL AND THE RESULT OF THE SELF-CONSISTENT CALCULATION FOR "a" = 0.50

_____Assumed potential

-.-.-Potential determined by the self-consistent calculation

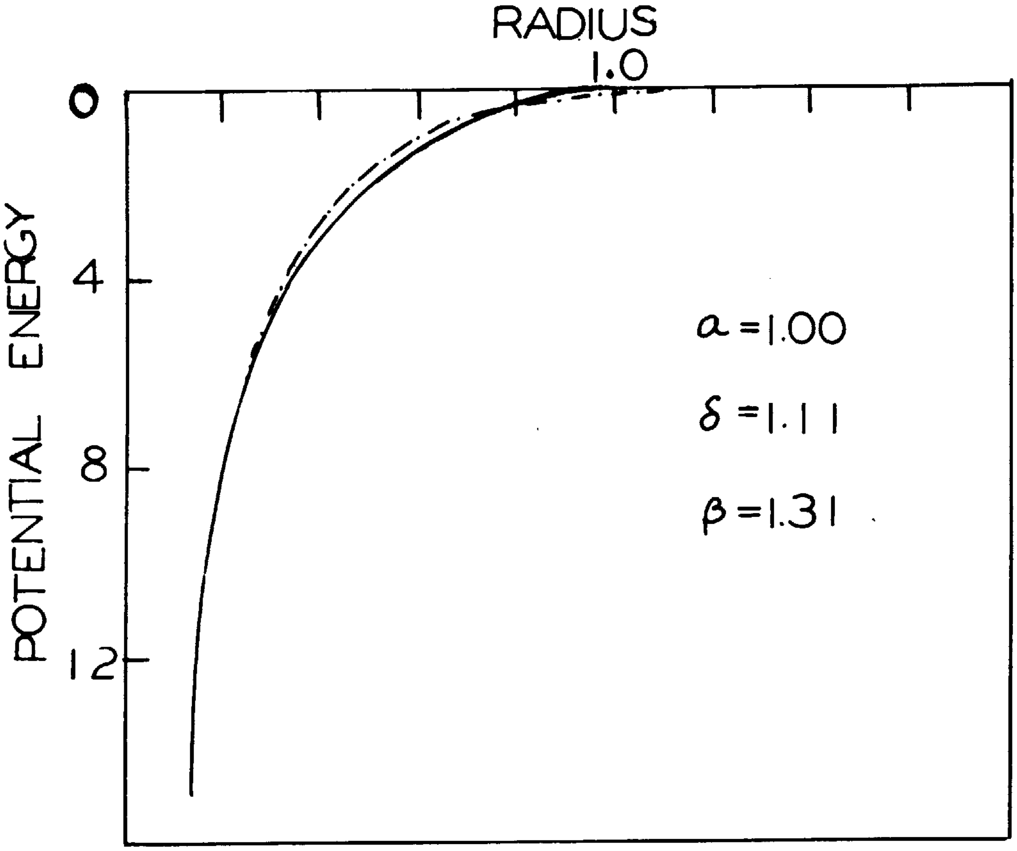


Fig. 1.6b COMPARISON OF THE ASSUMED POTENTIAL AND THE RESULT OF THE SELF-CONSISTENT CALCULATION FOR "a" = 1.00

_____Assumed potential

-.-.-Potential determined by the self-consistent calculation

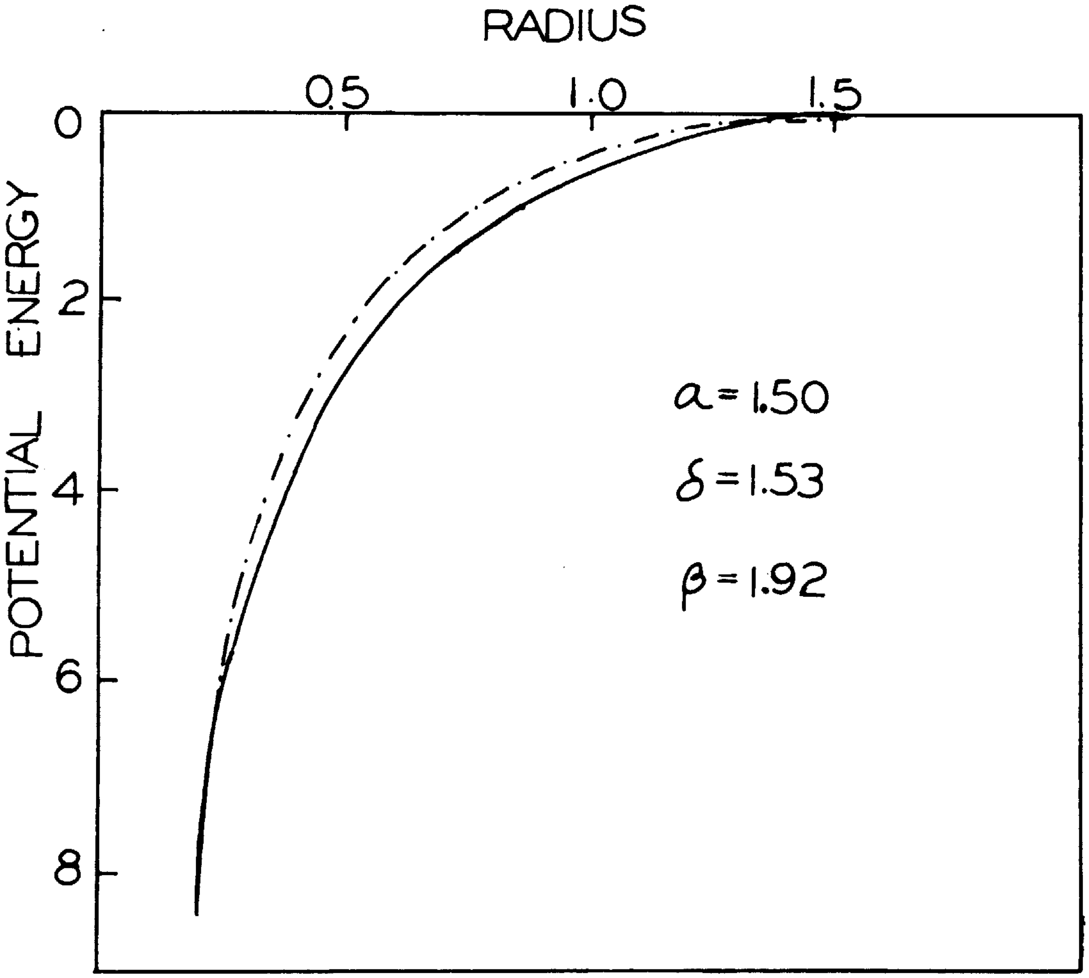


Fig. 1.6c COMPARISON OF THE ASSUMED POTENTIAL AND THE RESULT OF THE SELF-CONSISTENT CALCULATION FOR "a" = 1.50

_____Assumed Potential

-.-.-Potential determined by the self-consistent calculation

fact may imply that the approach used is more suitable for very high density cases.

The parameters a, β and δ bear the following relation in their relative magnitude

$$a < \delta < \beta. \tag{1.19}$$

Since δ satisfies the condition given by (1.17a), it is the radius of the sphere inside which the net charge is zero. The distance between each electron and the nucleus ranges from 0 to δ. To get a representation of their average effect, their presence has been replaced by a spherical shell of the same amount of charge located at certain average radius. Consequently, "a" must be smaller than "δ".

So far the problem has been regarded as a spherically symmetric one; as a result of this justifiable assumption, the volume of the sphere is equal to that of a sphere of radius δ. However, one cannot join them smoothly from one unit to the other, since it is impossible to divide the space into equal volume spheres without having some gaps existing between the spheres. This discrepancy is remedied by the introduction of β. β can be considered as an effective radius for a volume including the gaps. This effective volume may be of certain geometric dimensions which will allow smooth joining from one unit to the other. Since the "effect volume" is larger than $4\pi\delta^3/3$, it is not surprising that β is greater than δ as shown by the result. With the initial assumption that the nuclei are embedded in the free electron gas, the electron band surrounding one nucleus should join smoothly to that around the neighboring nuclei. It is to be expected

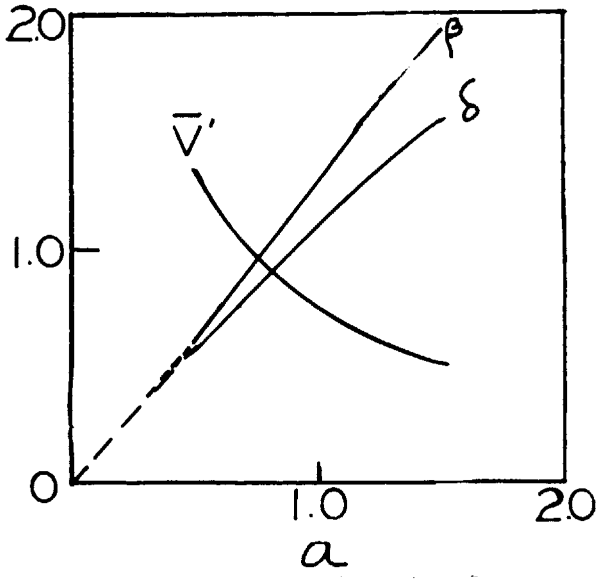


Fig. 1.7 VALUES OF β, δ, and $\overline{V'}$ AS A FUNCTION OF THE CUT-OFF RADII

β Effective radius of the atom

δ Radius of the sphere inside which the net charge is zero

$\overline{V'}$ Average potential

that the Fermi energy should also be determined by the density corresponding to unit charge in the effective volume $4\pi\beta^3/3$. The values of β, δ, and $\bar{V}$ as functions of "a" are shown in Fig. (1.7).

CHAPTER II

DETERMINATION OF SELF-CONSISTENT POTENTIAL FOR BOUND ELECTRONS IN THE HIGH DENSITY HYDROGEN GAS

In the previous chapter, the method of self-consistent field has been used to determine wave functions of electrons in a completely ionized gas medium. In order to get a further understanding of electrons in gases of various densities, it is necessary to extend the method to the case of a high pressure atomic hydrogen gas. Starting with an assumed average potential given by Eq. (1.1), the wave equation will be solved for electrons of negative energies and the discrete energy levels determined. As a consequence of the close approach of the atoms, it is possible for a bound electron of atom A to get to the vicinity of the nuclei of its neighboring atoms. The fact that an electron can no longer be considered as being bound by a particular nucleus, suggests the possibility of using wave functions of the Bloch type for a single electron wave function. The electron wave is considered as a modulated wave travelling in the medium with various possible energies; consequently the discrete energy levels will spread into bands whose widths are functions of the interatomic distance. In this chapter, the energy bands of electrons in gases of various densities will be determined and self-consistent calculations of the potential field will be carried out.

2.1 Solutions of Wave Equations for Negative Energy Electrons

The wave equations to be solved are

$$\nabla^2\psi + \left[E + 2\left(\frac{1}{r} - \frac{1}{a}\right)\right]\psi = 0 \qquad r \leqq a \tag{2.1}$$

$$\nabla^2\psi + E\psi = 0 \qquad r \geqq a \tag{2.2}$$

Since only a high pressure gas is of primary interest, discussions will be limited to atoms that possess only the ground level. The density is so high that no bound excited levels can exist. Consequently only solutions corresponding to $\ell = 0$ have to be found. The detailed solutions of Eqs. (2.1) and (2.2) are given in Appendix IIA.

In previous discussions, it has been shown that the phase shift of a positive energy electron in a potential field depends strongly on both the energy of the electrons and the range of the force. Similarly, the energy of a bound level is primarily governed by the range and depth of the force field under consideration. To determine the discrete energy levels, it is convenient to introduce two dimensionless quantities ξ and η given by:

$$\xi = \sqrt{\left|E - \frac{2}{a}\right|}\,a \tag{2.3}$$

$$\eta = \sqrt{|E|}\;a \tag{2.4}$$

ξ and η being the variables upon which the position of the energy levels depend. From (2.3) and (2.4), it follows that

$$\zeta^2 - \eta^2 = 2a \ . \tag{25}$$

Another relation between ζ and η can be obtained by the continuity conditions of the values and slopes of wave functions at the cut-off radius a. It is shown in Appendix IIA Eqs.(5) that ζ and η satisfy the relation

$$\zeta \left[1 - (1-\lambda)\, \frac{{}_1F_1(2-\lambda,3,2\ )}{{}_1F_1(1-\lambda,2,2\ )}\right] = \eta + 1 \tag{2.6}$$

where λ satisfies the condition $E' = -\frac{1}{\lambda^2}$. (2.7)

The energy levels can be determined by a graphical solution of the two simultaneous equations (2.5) and (2.6). The values of ζ and η are given by the points of intersection of the two families of curves shown in Fig. 2.1. The energy level determined is plotted as a function of the cut-off radius in Fig. 2.2. The first excited level which corresponds to $\ell = 0$ and sets in at $a = 6.48a_o$ is also shown in Fig. 2.2. Since only the high density case is of interest, calculations will only be made for cases that have cut-off radii smaller than a = 6.48.

In general, the energy of the first bound level E can be written as:

$$E = -\frac{1}{\lambda^2} + \frac{2}{a} \ . \tag{2.8}$$

As the range of the potential field increases, the electrons become more

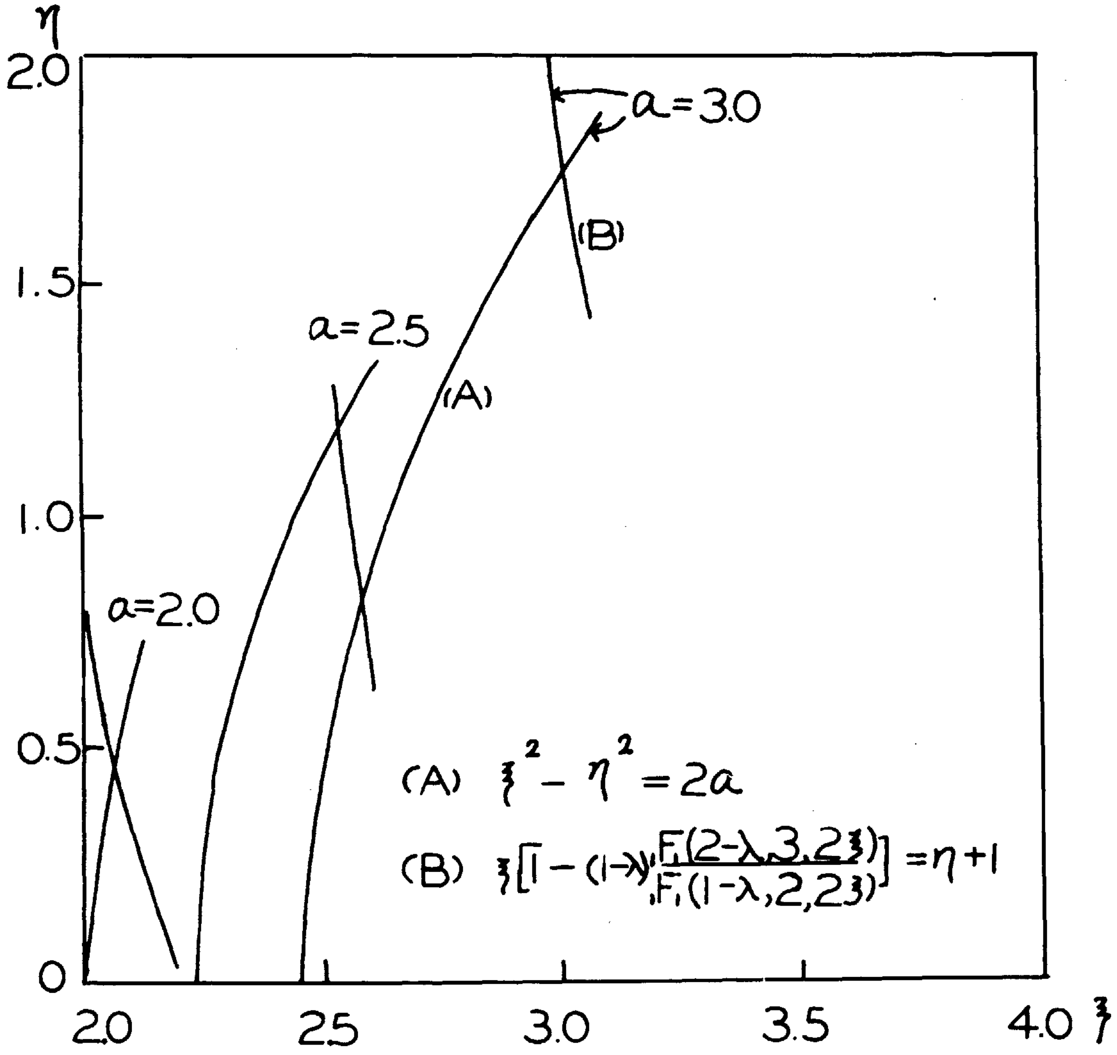


Fig. 2.1 DETERMINATION OF THE BOUND ENERGY LEVELS FOR VARIOUS CUT-OFF RADII

$$\xi = \sqrt{\left|E - \frac{2}{a}\right|}\, a\,, \qquad \eta = \sqrt{|E|}\, a$$

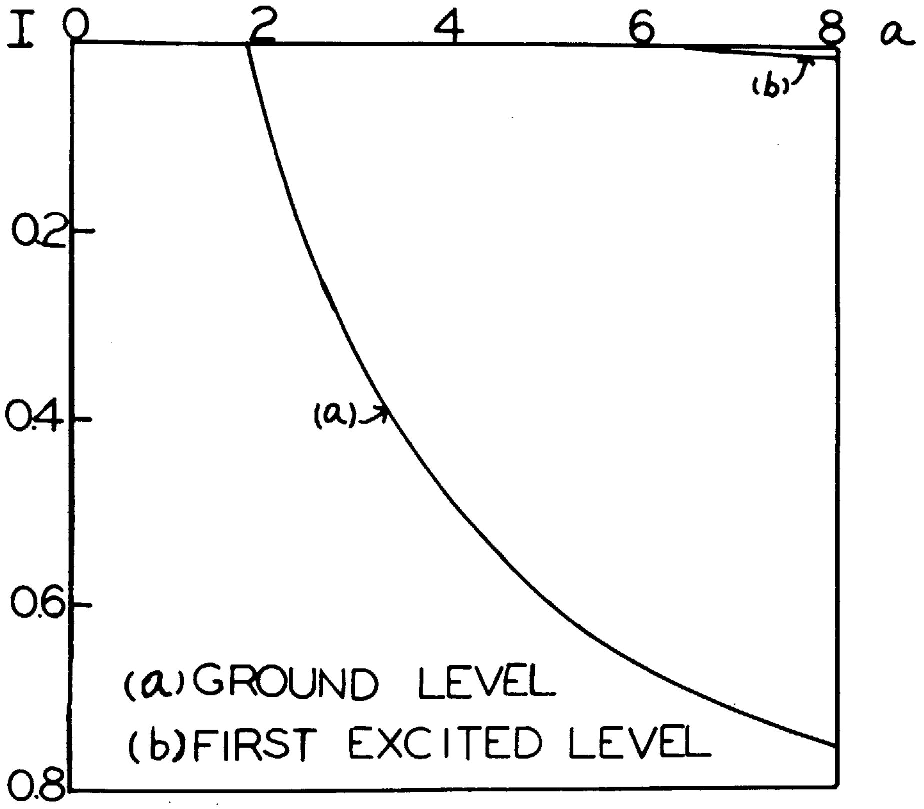


Fig. 2.2 IONIZATION POTENTIALS AS FUNCTIONS OF CUT-OFF RADII FOR ELECTRONS IN THE FIELD

$V = -(\frac{e}{r} - \frac{e}{a}) \qquad r \leqq a$

$V = 0 \qquad r \geqq a$

tightly bound and the energy approaches the value of the ground level of a normal hydrogen atom as "a" goes to infinity.

2.2 Determination of the Energy Band

The solution obtained in the last section is that for an electron of a single atom in an assumed potential field. As the atoms are close to each other, the solution of the Schrödinger equation must be some linear combination of the wave functions for single atoms. It has been shown by Bloch$^{(3)}$ that the wave function of an electron in a periodic potential field can be written as:

$$\psi(r) = \frac{1}{\sqrt{N'}} \sum_j \phi(|\vec{r} - \vec{r}_j|) e^{i\vec{k}\cdot\vec{r}_j} \qquad (2.9)$$

where $\phi(|\vec{r} - \vec{r}_j|)$ is the wave function of an electron surrounding the j^{th} nucleus. $\vec{r}_j$ is the radius vector of the j^{th} nucleus. N' is the normalizing factor. For cases where overlapping of wave functions is negligible, N' is just equal to the number of atoms in the medium. The wave function given by (2.9) gives a good description for electrons in the medium concerned. At points near a nucleus, save for a constant factor, it behaves similar to an electron bound to a single atom; whereas it is more like a plane wave with wave number $|k|$ in the interatomic space.

In determining the energy of an electron described by the Bloch wave function, the single electron wave function $\phi(|\vec{r} - \vec{r}_j|)$, which satisfies Eqs. (2.1) and (2.2), is calculated by using a potential of the form:

$$U = -\left(\frac{1}{|\vec{r} - \vec{r}_j|} - \frac{1}{a}\right) \qquad |\vec{r} - \vec{r}_j| \leqq a \tag{2.10}$$

$$U = 0 \qquad |\vec{r} - \vec{r}_j| \geqq a$$

There is a potential of the same type about each nucleus; hence the potential of the whole gas medium is

$$V(r) = \sum_j U(|\vec{r} - \vec{r}_j|) \qquad |\vec{r} - \vec{r}_j| \leqq a \tag{2.11}$$

Both $U(|\vec{r} - \vec{r}_j|)$ and $V(r)$ are shown in Fig. 2.3. The Bloch wave function ψ satisfies the equation

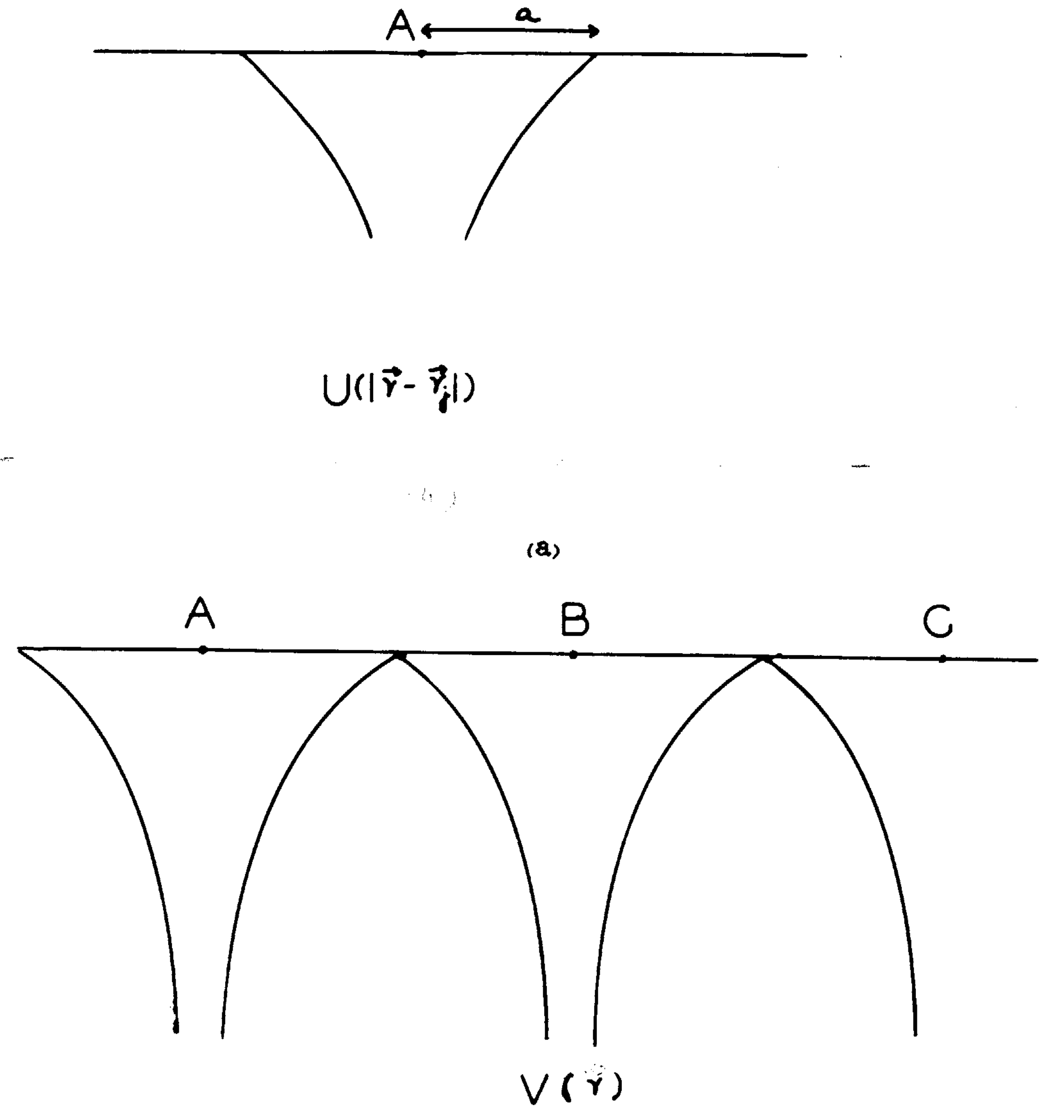
$$\nabla^2\psi + (E - 2V)\psi = 0, \tag{2.12}$$

from which one obtains

$$E = \frac{\int \psi^* [-\nabla^2 + 2V(r)]\psi \, d\tau}{\int |\psi|^2 d\tau} . \tag{2.13}$$

Since the unperturbed wave function $\phi(|\vec{r} - \vec{r}_j|)$ satisfies Eqs. (2.1) and (2.2) and the potential is given by (2.10), therefore in order to carry out the integration, it is more convenient to write the potential function as

$$V(r) = V(r) + U(|\vec{r} - \vec{r}_j|) - U(|\vec{r} - \vec{r}_j|) \tag{2.14}$$



(a)

(b)

Fig. 2.3 ASSUMED POTENTIALS $U(|\vec{r} - \vec{r}_j|)$ AND $V(\vec{r})$

a $U(|\vec{r} - \vec{r}_j|)$ Assumed potential around the j^{th} nucleus

b $V(\vec{r})$ Assumed potential in the gas medium

(Atoms A, B, C may have arbitrary positions)

By using (2.14), it is shown in Appendix IIB that (2.13) can be written as:

$$E = E_o + \frac{A + C}{1 + D} \tag{2.15}$$

where E_o is the energy of an electron of a single atom. The values of C, A, and D are given as follows:

(i) $$C = \int \phi^*(|\vec{r} - \vec{r}_j|)\left[V(r) - U(|\vec{r} - \vec{r}_j|)\right]\phi(|\vec{r} - \vec{r}_j|)\,d\tau \tag{2.16}$$

The difference of $V(r)$ and $U(|\vec{r} - \vec{r}_j|)$ represents the field due to all the atoms other than the one at the position $\vec{r}_j$. Therefore C is the average value of the potential given rise to by all the neighboring atoms. Since $V(r) - U(|\vec{r} - \vec{r}_j|)$ is always negative, the effect of its presence is to make the energy E more negative than that of E_o. This is to be expected, since when the atoms are nearer to each other, the Coulombian energy of the electron increases in absolute value.

(ii) $$A = \sum_{\rho_i \neq 0} e^{-i\vec{k}\cdot\vec{\rho}_i} \int \phi^*(|\vec{r} - \vec{\rho}_i|)\left[V(r) - U(r)\right]\phi(r)\,d\tau \tag{2.17}$$

where ρ_i is the inter-nuclear distance. This represents the effect of the potential of the neighboring atoms averaged over the overlapping wave functions. A is a function of both the propagation vector $\vec{k}$ and inter-atomic distance. It gives the major contribution in determining the width of the energy band.

$$\text{(iii)} \qquad D = \sum_{\rho_i \neq 0} e^{-i\vec{k}.\vec{\rho}_i} \int \phi^*(|\vec{r} - \vec{\rho}_i|)\phi(r)\,d\tau \qquad (2.18)$$

Since the $\phi(r)$'s are normalized wave functions, D is the term which gives the modification of the normalizing factor. The magnitude of D depends on the amount of overlapping between the neighboring wave functions.

To evaluate the integrals C, A and D, solutions of Eqs. (2.1) and (2.2) are used for $\phi(r)$

$$\phi(r) = \frac{N_1}{\sqrt{4\pi}}\, e^{-\alpha r}F(-\lambda + 1,2,2\alpha r) \qquad r \leqq a \qquad (2.19a)$$

$$\phi(r) = \frac{N_1}{\sqrt{4\pi}}\, e^{-\sigma r}/\sigma r \qquad r \geqq a \qquad (2.19b)$$

where N_1 and N_2, normalizing factors, satisfy the condition of continuity at the cut-off radius a.

$$\alpha = \sqrt{-(E_o - \tfrac{2}{a})}\,, \qquad \sigma = \sqrt{|E_o|} \qquad \text{and} \qquad E_o = -\frac{1}{\lambda^2} + \frac{2}{a}\,.$$

As calculations show that both α and λ differ very slightly from unity, Eq. (2.19a) can be reduced to

$$\phi(r) = \frac{N_1}{\sqrt{4\pi}}\, e^{-\alpha r}. \qquad (2.20)$$

For $\alpha = 1$, (2.20) is the same wave function as that of a normal hydrogen atom except for the difference of the normalizing factor. When electrons are near to the nucleus, the Coulombian force provides the major effect in determining the electron wave function. The cut-off potential affects chiefly the part of the wave function outside the cut-off radius. (2.20) can be used in evaluating A, C, and D. Although the wave function deviates somewhat from that of the exact form, the energy determined can still be fairly accurate, for the exact wave function gives a minimum of the energy and therefore the mean of the energy over a poor wave function is nearly correct. Evaluations of A, C, and D involve wave functions having different points on their origins. The integrations can be carried out by using the expansions given by Coulson(16).

For calculating A and C, integrals of the following form have to be evaluated:

$$\sum_{\rho_i \neq 0} e^{-i\vec{k}\cdot\vec{\rho}_i} \frac{N_1 N_2}{4\pi} \int \phi(r)\phi(|\vec{r}-\vec{\rho}_i|) \sum_{\rho_j \neq i} U(|\vec{r}-\vec{\rho}_j|)\, d\tau \qquad (2.21)$$

This involves wave functions belonging to two different origins and a potential function with a third point as the origin. The evaluation can be simplified considerably if the actual potential $U(|\vec{r}-\vec{\rho}_j|)$ of the third atom is replaced by an averaged potential which is defined as:

$$\bar{V} = \frac{1}{\Omega} \int_0^{2\pi} \int_0^{\pi} \int_0^{x} \left(-\frac{1}{r} + \frac{1}{a}\right) r^2 \sin\theta \, dr\, d\theta\, d\phi \qquad (2.22)$$

where Ω is the volume of a single atom and x is the radius of the atom. Similarly to the case of determining the Fermi energy for the ionized gas, the cut-off radius "a" can be considered as that of an average radius of the atom. If for the first approximation $\Omega = \frac{4\pi}{3} a^3$, it follows from (2.22) that

$$\bar{V} = -\frac{1}{2a} \, . \tag{2.23}$$

As $U(|\vec{r} - \vec{\rho}_j|)$ has a non-vanishing value only inside the sphere of radius "a" with $\vec{\rho}_j$ as the center; and the values of both wave functions $\phi(r)$ and $\phi(|\vec{r} - \vec{\rho}_i|)$ are of the form $\frac{e^{-\sigma|\vec{r}|}}{\sigma|\vec{r}|}$ and $e^{-\sigma|\vec{r} - \vec{\rho}_i|}/\sigma|\vec{r} - \vec{\rho}_i|$ which decrease slowly as $|\vec{r}|$ and $|\vec{r} - \vec{\rho}_i|$ increase, consequently, it is justifiable to replace $U(|\vec{r} - \vec{\rho}_j|)$ by the averaged value in evaluating the integral. The potentials with and without approximations are shown in Fig. 2.4. The atoms are drawn in such a way that they are contiguous, since only under such a relative configuration do the wave functions give appreciable contribution to the value of the integral.

With this approximation, all the integrals can be readily evaluated. The detailed evaluations are given in Appendix IIC and the results are as follows:

$$C = \sum_{\rho_j \neq 0} \frac{N_2^2}{\rho_j} \frac{e^{-2\sigma\rho_j}}{(2\sigma\rho_j)^2} \sum_{\ell} \frac{1}{\rho_j^{\ell}} \left[-B_\ell + \frac{C_{\ell+1}}{a}\right] \sum_{p=0}^{\ell} \frac{(\ell+p)!}{p!(\ell-p)!(4\sigma\rho_j)^p} \tag{2.24a}$$

$$A = \sum_{\rho_i \neq 0} e^{-i\vec{k}\cdot\vec{\rho}_i} \left\{ \frac{e^{-\sigma\rho_i}}{\sigma\rho_i} \left[h(\sigma,\alpha,a) - \frac{N_1 N_2}{\sigma^2} a\bar{V} \right] + \bar{V} \frac{N_1 N_2}{2\sigma^3} e^{-\sigma\rho_i} \right\} \tag{2.24b}$$

$$D = \sum_{\rho_i \neq 0} e^{-i\vec{k}\cdot\vec{\rho}_i} \left\{ \frac{e^{-\sigma\rho_i}}{\sigma\rho_i} F(\alpha,\sigma,a) + e^{-\sigma\rho_i} p(\alpha,\sigma,a) \right\} \tag{2.24c}$$

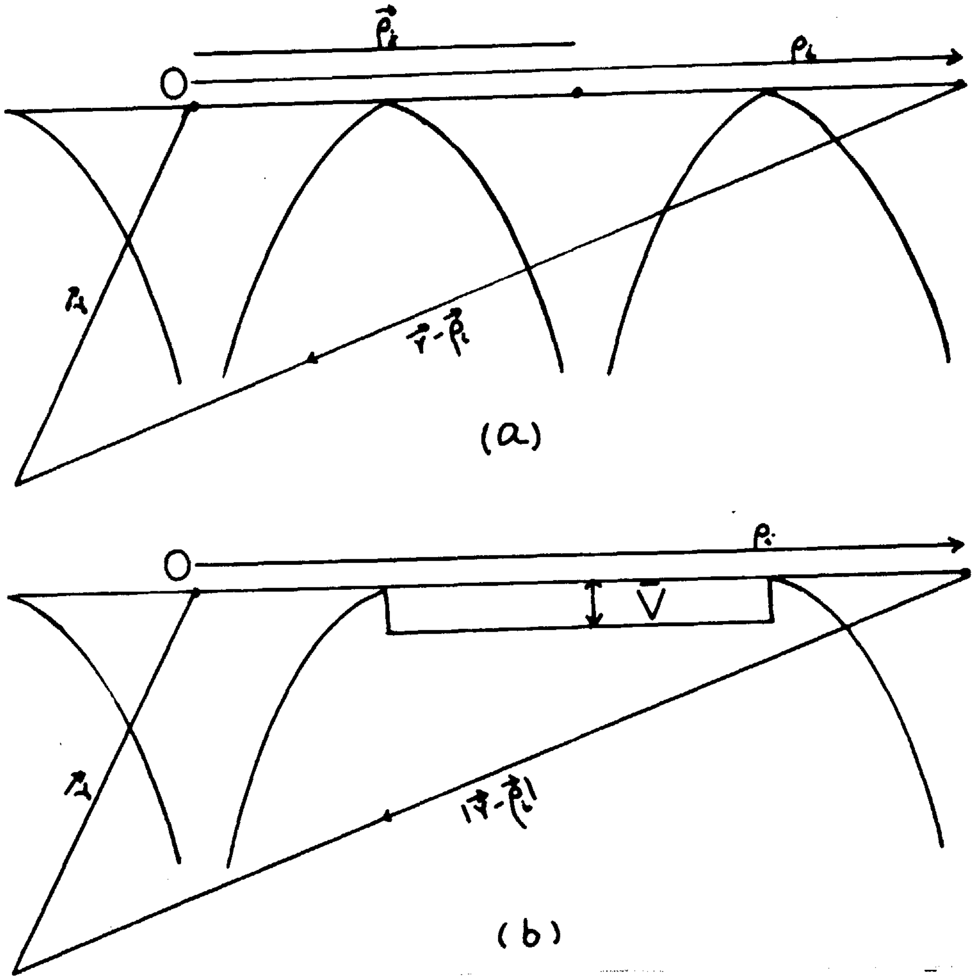


Fig. 2.4 APPROXIMATED POTENTIAL FOR THE EVALUATION OF THE EXCHANGE INTEGRAL A

a No approximation

b With approximation

where the constants B_ℓ, C_ℓ and functions $h(\sigma,\alpha,a)$, $F(\alpha,\sigma,a)$ and $p(\alpha,\sigma,a)$ are defined in Appendix IIC.

In order to determine the energy, the summation over $\vec{\rho}_i$ in (2.24) must be carried out. For atoms in a metal, the relation between vector $\vec{k}$ and $\vec{\rho}_i$ is definite once the direction of $\vec{k}$ is specified. In the present problem $\vec{k}$ only represents an arbitrary direction of propagation and the angle between $\vec{k}$ and $\vec{\rho}_i$ varies at random; therefore, an average over all possible directions of $\vec{\rho}_i$ should be made. This can be fulfilled by replacing the summation in (2.24) by an integral. For example (2.24c) becomes:

$$D = \frac{1}{\Omega} \int_0^{2\pi} \int_0^{\pi} \int_{2x}^{\infty} e^{-i\vec{k}\cdot\rho} \left[\frac{e^{-\sigma\rho}}{\sigma\rho} F(\alpha,\sigma,a) + e^{-\sigma\rho} p(\sigma,\alpha,a) \right] \rho^2 d\rho \sin\theta \, d\theta \, d\phi \qquad (2.25)$$

where, as shown previously, Ω is the volume of each atom and the lower limit of integration is the minimum interatomic distance.

With the values of A, C and D, energy bands corresponding to cut-off radii equal to 2.5, 3 and 4 atomic units are calculated. Figure 2.5 gives the energy as a function of wave number k and Fig. 2.6 shows the variation of the bandwidth produced by the change of cut-off radius "a". Calculation for a = 2 is not shown, since for this case the electron is not very tightly bound and there is a great deal of overlapping between wave functions of electrons of the neighboring atoms; this is a situation for which the Bloch scheme is no more applicable. The bottom of each energy band is lower than the corresponding discrete level; this is the consequence of the increase of the Coulombian energy. It can also be seen in Fig. 2.6 that the band, becoming narrower as the cut-off radius increases, approaches the ground level of a normal hydrogen atom at the limit.

2.3 Self-Consistent Calculation of the Potential Field

If the gas medium is considered as an entity, wave functions of all the electrons should be an antisymmetric combination of all the single electron wave functions. It is shown in the last section that the wave function of an electron is:

$$\psi_n(r_m) = \frac{1}{\sqrt{N'}} \sum_j e^{i\vec{k}_n \cdot \vec{r}_j} \phi(\vec{r}_m - \vec{r}_j) \chi(\sigma_1) \qquad (2.26)$$

where r_m is the radius vector of the mth electron, N' is the normalizing factor and $\chi(\sigma_1)$ is the spin function. $\psi_n(r_m)$ represents the wave function of the mth electron with an energy of propagation corresponding to wave number k_n. The wave function for all the electrons is of the form

$$\sum \psi_1(r_1)\psi_2(r_2)\ldots\ldots\psi_n(r_n)$$

with all the possible permutations of all the r_n's. It can be shown that the ψ's are orthogonal for functions corresponding to different propagation energies(17). The antisymmetric wave function of the medium is of the form

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(r_1) & \psi_1(r_2) \ldots\ldots\ldots\ldots \psi_1(r_n) \\ \psi_2(r_1) & \psi_2(r_2) \ldots\ldots\ldots\ldots \psi_2(r_n) \\ & \\ \psi_n(r_1) & \psi_n(r_2) \ldots\ldots\ldots\ldots \psi_n(r_n) \end{vmatrix} \qquad (2.27)$$

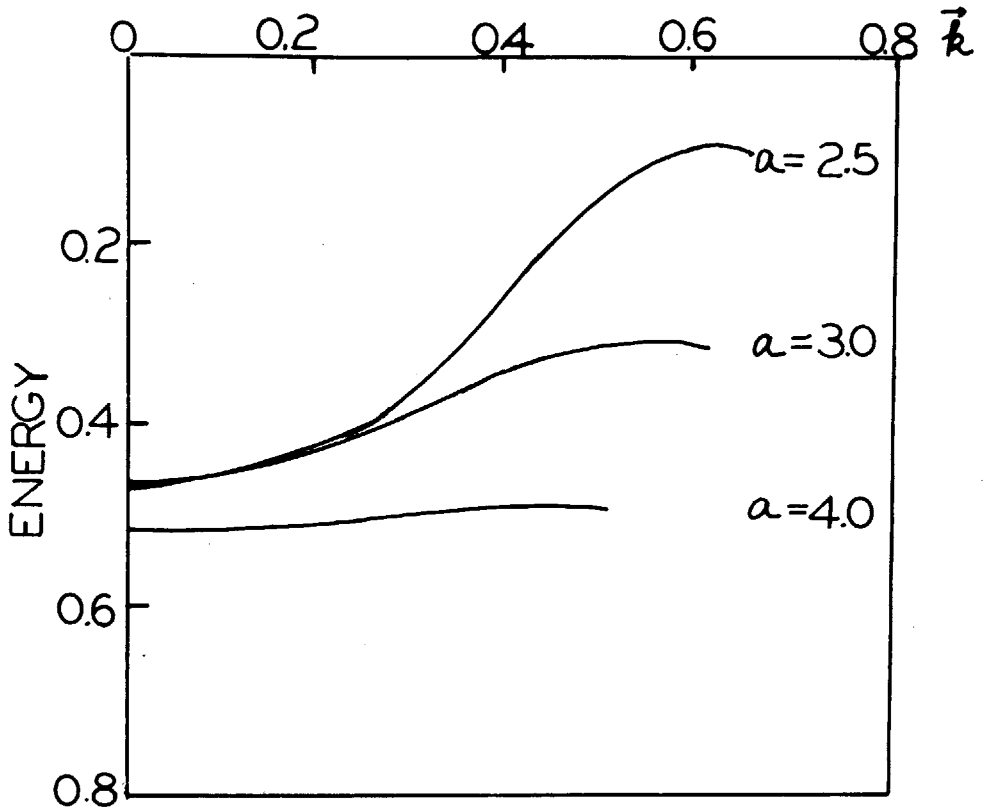


Fig. 2.5 ENERGY BANDS AS FUNCTIONS OF $\vec{k}$ FOR VARIOUS CUT-OFF RADII

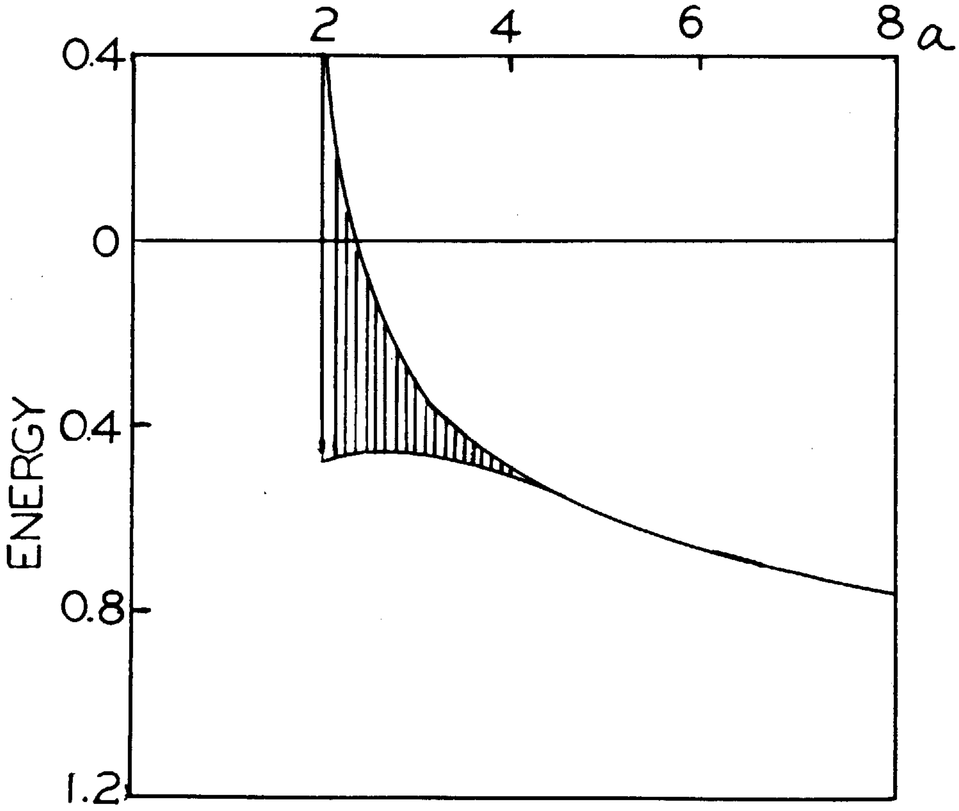


Fig. 2.6 ENERGY BANDS AS FUNCTIONS OF CUT-OFF RADIUS "a"

where N is the number of electrons.

The probability that an electron with coordinate $\vec{r}_1$ is at the volume element $d\tau_1$ is

$$n_1 = \iiint \cdots |\Psi|^2 d\tau_2 d\tau_3 \ldots\ldots d\tau_n \qquad (2.28)$$

The integration is carried out over all coordinates other than $\vec{r}_1$. Substituting the value of Ψ given by (2.28) and making use of the orthonormal properties of ψ's; it can be shown that the total charge density at r_1 is

$$n_1(r_1) = \sum_n |\psi_n(r_1)|^2 \qquad (2.29)$$

where the summation is to be carried over electrons of all energies.

In problems on metals where atoms form a regular periodic array, it is usually more convenient to discuss energies and densities in the reciprocal lattice space; the structure of which is based on the periodic and symmetric properties of the propagational vectors $(\vec{k})$. The space is filled with cells of equal volumes. It can be proved(18) that the volume of the unit cell in the reciprocal lattice space is such that there are the right number of states in each cell to accommodate two electrons per atom. For alkali metals that have only one valence electron, the valence bands are only half filled. For the present problem, the direction of $\vec{k}$ is chosen at random; therefore, it is justifiable to assume that the cells in the k space must have spherical symmetry. However, the unit cell cannot be a sphere on account of the fact that it is impossible to fill up the space with spheres.

The number of electrons in a volume Ω in configuration space and in a volume of $\vec{dk}_x\vec{dk}_y\vec{dk}_z$ can be written as

$$dN = \frac{2\Omega}{8\pi^3}\vec{dk}_x\vec{dk}_y\vec{dk}_z \qquad (2.30)$$

For problems of spherical symmetry (2.30) becomes

$$dN = \frac{\Omega}{\pi^2}k^2 dk \qquad (2.31)$$

From the Fig. 2.5 of the energy as a function of k, it can be shown that the value of k corresponding to the maximum energy satisfies approximately the relation

$$k = \frac{\pi}{2a} . \qquad (2.32)$$

This resembles the relation in the theory of solids between the translational vector $\vec{k}$ in the reciprocal lattice space and the primitive translation of the lattice $\vec{\tau}_i$ which is given as

$$N_i\vec{k}.\vec{\tau}_i = 2\pi n_i \qquad (2.33)$$

where $n_i = 0, \pm 1, \pm 2, \pm \ldots$.. The difference lies in the fact that there is no translational periodicity in the present case. If (2.32) is taken to be the maximum radius for the integration of (2.31) and if Ω is assumed to be $4\pi a^3/3$ for the first approximation, the integration shows that the densities of states cannot accommodate even one electron. The situation can be improved, however, by redefining an effective volume for the atom. If Eq. (2.32) determines the boundaries of a cubic cell with the nucleus at the center, it can be shown that this volume Ω_c for N = 2 is $8a^3$. This will lead to a half filled band for a monovalent element. In order to take into account the empty gaps between the spheres, one can assume that Ω_c is the effective volume of the atom. By substituting Ω_c into Eq. (2.31) for the volume Ω, the maximum value of k for N = 1 can be determined. By using the wave functions for electrons of all energies, the total charge density can then be calculated by summing the densities over all the possible states up to the maximum value of k thus determined.

In Chapter I, the self-consistent calculations are performed by adjusting a parameter β which determines the Fermi energy of the free electron band and is also the radius of an effective volume in which the net charge is zero. The exchange potential is determined by using the free electron approximation. Due to the complicated form of the exchange integral, it can only be evaluated for cases either of free electrons or those of tightly bound ones. Figure 2.6 shows that for cut-off radius $3a_o$ or $4a_o$, the energy bands are not very broad; therefore the electrons resemble more of the tightly bound case; whereas for the broader bands, the free electron approximation previously used can be applied.

When the electrons are more tightly bound by the nuclei, the overlapping of the wave functions belonging to the neighboring atoms is small and the band is narrow. The exchange correction for the electrons with wave functions of the Bloch type has been worked out(19) for the case of narrow band. It can be shown that the effect of the exchange integral reduces the potential due to the electrons by one half of its original value; since only electrons of the same kind of spin give a non-vanishing exchange integral.

Self-consistent calculations are made for a = 3 and a = 4. Although the calculated potential can be altered by changing the size of the effective volume, calculations show that better agreement can be achieved by readjusting the cut-off potential. The assumed potential about each atom is of the form given in Fig. 2.3, and it has also been seen that in order to evaluate the exchange integral A, an approximation illustrated in Fig. 2.4 is used. Consequently, one is led to test the possibility of obtaining self-consistency by making a less sharp transition between the two types of potential in Fig. 2.4. This can be done by letting

$$\begin{aligned} V &= -\left(\frac{e}{r} - \frac{e}{a}\right) & r &\leqq \frac{2}{3}a \\ V &= -\bar{V} = -\frac{1}{2a} & r &\geqq \frac{2}{3}a \end{aligned} \qquad (2.34)$$

Schrödinger equations with potentials given by (2.34) can be solved analytically by the method given in Appendix IIA. By using the solutions corresponding to the new potential, the self-consistent calculation is performed and the results are shown in Figs. 2.7a and 2.7b. The agreement between the assumed and calculated potentials is quite satisfactory. Greater deviations occur in the region near r = 2a/3, since this is the position corresponding to a discontinuity of slope of

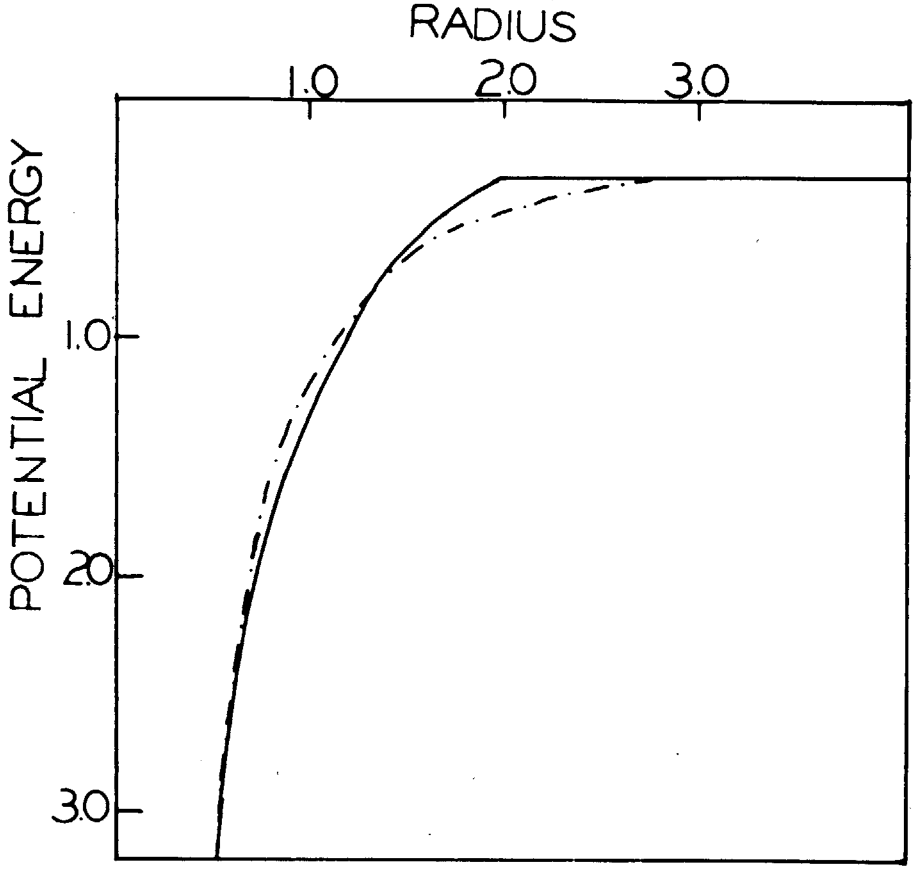


Fig. 2.7a COMPARISON OF THE ASSUMED POTENTIAL AND THE RESULT OF THE SELF-CONSISTENT CALCULATION FOR a = $3a_0$

_____Assumed potential

-.-.-Potential determined by the self-consistent calculation

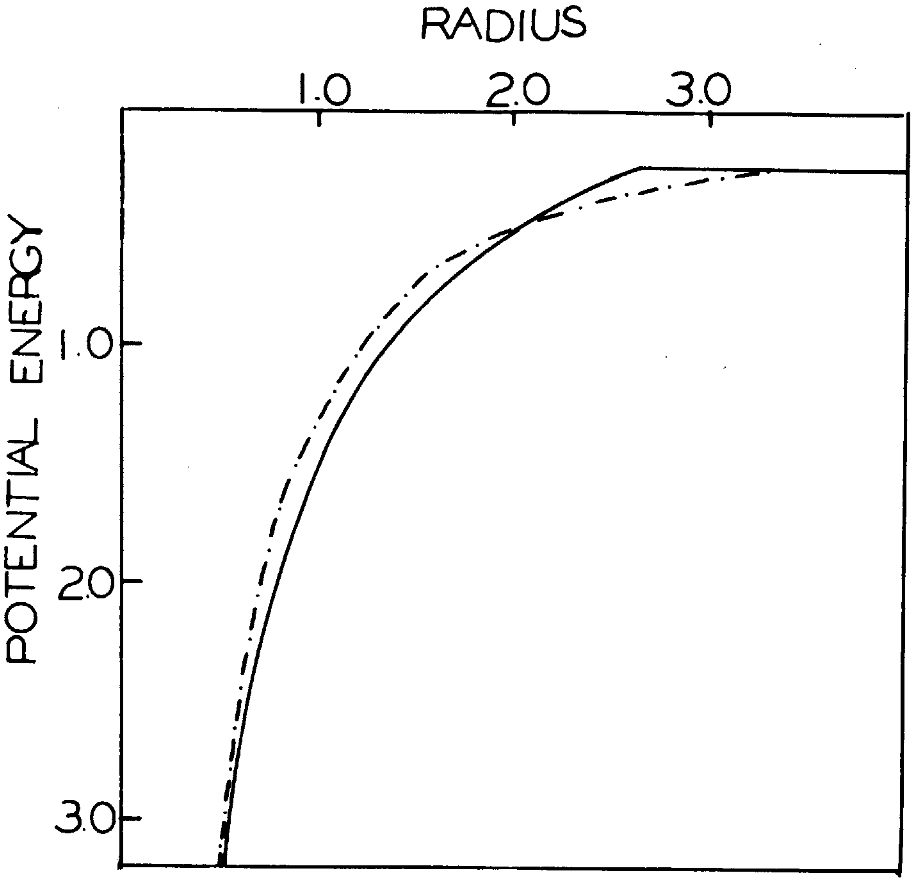


Fig. 2.7b COMPARISON OF THE ASSUMED POTENTIAL AND THE RESULT OF THE SELF-CONSISTENT CALCULATION FOR a = $4a_0$

_____Assumed potential

-.-.-Potential determined by the self-consistent calculation

the assumed potential, it is natural that poor results occur at the position where the assumption made on the shape of the potential is not satisfactory.

This method of obtaining self-consistency is different from that previously used, yet a closer comparison shows that the results obtained are in good conformity with each other. In the method used in Chapter I, in addition to the adjustment of the parameter β, it is necessary to introduce an average potential $\overline{V'}$. The charge density is given by $3/4\pi\beta^3$ and the cut-off radius "a" is smaller than "β". In the present calculations, $\bar{\bar{V}}$ is an average potential, the charge density is determined by the effective volume Ω_c, the equivalent radius of which is larger than the radius of the spherical shell of charge in the assumed potential.

CHAPTER III

CALCULATIONS OF THE OPACITY OF A HIGH DENSITY HYDROGEN GAS

In the previous discussions, the wave functions of electrons in a hydrogen gas are determined for the case that the electrons are completely squeezed out of the bound levels as well as for the case that they remain being bound with their ionization potentials lowered. The results are to be used in the study of the opacity of a dense hydrogen gas. In order to make further discussions easier, we shall distinguish the two cases by considering the first case as a "pressure-ionized" hydrogen gas and the latter case, atomic hydrogen gas.

In the temperature range that is to be covered by the present study, the opacity due to scattering which occurs at high temperature will not be considered. The photoelectric absorption of the bound electrons and the absorption of the free electrons in the presence of the nuclear fields give the major contributions to the opacity of the gas. The reduction of the total intensity of radiation in passing through a certain thickness of medium depends both on the number of electrons in the medium and the intensity distribution of the radiation. According to Planck's law, the distribution of the intensity of radiation in atomic units is

$$I(\omega) = \frac{8\pi}{h^2 c^3} \frac{\omega^3}{e^{\frac{\omega}{T_a}} - 1} \qquad (3.1)$$

where ω, T_a are defined in Appendix IA.

An absorption coefficient per electron a_ω for a given frequency is defined in such a way that the intensity of radiation of frequency ω is reduced by a factor e^{-Na_ω} in passing through 1 cm length of a gas containing N electrons per cc. a_ω is given in the unit of cm^2. In the study of opacity, an absorption coefficient k_ω is defined such that the intensity of radiation is reduced by a factor $e^{-\kappa k_\omega}$ in passing through 1 cm length of a gas of density κ. k_ω is obtained by multiplying a_ω by the number of electrons per unit mass of material. In studying the opacity, there are two quantities that are of interest. One can either study the "straight mean" of the atomic absorption coefficient which is defined as

$$K = \frac{\int_0^\infty k_\omega I(\omega)\,d\omega}{\int_0^\infty I(\omega)\,d\omega} \qquad (3.2)$$

or express the opacity by the "Rosseland mean"(21) which is given by:

$$\frac{1}{K} = \frac{\int_0^\infty \frac{1}{k'_\omega}\frac{\partial I(\omega)}{\partial T_a}\,d\omega}{\int_0^\infty \frac{\partial I(\omega)}{\partial T_a}\,d\omega} \qquad (3.3)$$

where $k'_\omega = k_\omega(1 - e^{-\frac{\omega}{T_a}})$. The Rosseland mean is an energy-transparency mean, which also takes into consideration the temperature dependence of the radiation intensity. The extra factor $(1 - e^{-\omega/T_a})$ is introduced by Rosseland to eliminate the stimulated emission from the absorption. Radiation incident in a given direction stimulates emission in a direction exactly parallel to itself. However, the absorption followed by stimulated emission has no influence on the net flux of energy and therefore k'_ω is used instead of k_ω.

The coefficient of opacity of the stellar material has been calculated by Eddington using Kramers' formula for the absorption coefficient.(22) Strömgren(7) has applied the quantum mechanical calculation of the absorption coefficient to evaluate the opacity of certain gas mixtures. Evaluation of the opacity for high density gas mixtures has been carried out by Marshak(23) and Morse(24), using the Fermi Thomas potential for the gas atoms. In general, the opacity can be expressed as a function of temperature, gas density, and the constituents of the gas. For the present problem, the dependence on the constituents is not considered. In the following calculation of the opacity of hydrogen gas, a general description of the methods used in the determination of the absorption coefficient and the opacity will be made. This is to be followed by the results of calculation and a discussion of these results.

3.1 Opacity of a "Pressure-Ionized" Hydrogen Gas

For the very high density case where no bound states exist, the free-free transitions give the only contribution to the absorption of radiation. The absorption coefficient a_ω of an electron with energy ε_i absorbing a radiation of frequency ω is given by the quantum theory of radiation as:

$$a_\omega(\varepsilon_i) = \frac{256\pi^2}{3}\left(\frac{e^2}{\hbar c}\right)(a_o)^5 \frac{\sqrt{\varepsilon_f}}{\omega^3}\sum_{\ell=1}^{\infty}\ell\left\{\left|\left(\ell-1,\varepsilon_i\left|\frac{1}{r^2}\right|\quad,\varepsilon_f\right)\right|^2 + \left|\left(\ell,\varepsilon_i\left|\frac{1}{r^2}\right|\quad -1,\varepsilon_f\right)\right|^2\right\} \quad \text{cm}^5 \tag{3.4}$$

where the matrix element corresponds to the acceleration, ε_i and ε_f are the energies of the initial and final states, a_o is the Bohr's radius, ω is the frequency of absorption, and ℓ is the orbital angular momentum quantum number of the final state.

For the sake of convenience, the absorption coefficient is usually expressed in terms of Kramers' formula multiplied by a factor "$g(\omega,\varepsilon_i)$" which is called Gaunt's factor. Using Kramers' formula, the absorption coefficient for the free-free transition can be written as

$$a_\omega = \frac{4}{3\sqrt{3}\pi^2}\left(\frac{\hbar c}{e^2}\right)^4\left(\frac{h}{mc}\right)^5 \frac{1}{\sqrt{\varepsilon_i}\,\omega^3}\, g(\omega,\varepsilon_i) \qquad \text{cm}^5 \tag{3.5}$$

To calculate the absorption coefficient as a function of frequency, one has to sum over all the electrons in the initial states; moreover, the transition can only take place when the upper state is vacant. Using the Fermi-Dirac statistics, the number of electrons per unit volume having energy between ε and $\varepsilon + d\varepsilon$ is

$$\left(\frac{1}{a_o^3}\right)\frac{\varepsilon}{2\pi^2}\frac{d\varepsilon}{1 + e^{\frac{\varepsilon - \varepsilon_F}{T_a}}} = \frac{\varepsilon\ d\varepsilon}{2\pi^2\left[1 + e^{\varepsilon/T_a}/A\right]}\left(\frac{1}{a_o^3}\right) \tag{3.6}$$

where $A = e^{\varepsilon_F/T_a}$ and ε_F is the Fermi energy. The value of A is determined by the number of free electrons N_e per unit volume

$$N_e = \frac{T_a^{3/2}}{2\pi^2} \int_0^\infty \frac{x^{1/2}dx}{1 + \frac{1}{A}e^x} \left(\frac{1}{a_o^3}\right) \qquad (3.7)$$

where $x = \varepsilon/T_a$.

At high temperature such that $kT >> \varepsilon_F$, the distribution is Maxwellian and it can be shown that A is given by

$$A = 4N_e\left(\frac{\pi}{T_a}\right)^{3/2}(a_o)^3. \qquad (3.8)$$

For the general case, A is determined by Eq. (3.7) and its value corresponding to various electron densities is given by Morse.(24) The probability that the upper state is vacant is

$$1 - \frac{1}{\frac{1}{A}e^{\frac{\varepsilon_i + \omega}{T_a}} + 1} = \frac{\frac{1}{A}e^{\frac{\varepsilon_i + \omega}{T_a}}}{\frac{1}{A}e^{\frac{\varepsilon_i + \omega}{T_a}} + 1}. \qquad (3.9)$$

By using Eqs. (3.5), (3.6) and (3.9), the absorption coefficient per gram for the free-free transition can be written as:

$$k(\omega) = \frac{4.[illegible]7 \times 10^6}{\omega^3} \int_0^\infty \frac{\frac{1}{A}e^{\frac{\varepsilon_i + \omega}{T_a}}}{\left(1 + \frac{1}{A}e^{\frac{\varepsilon_i}{T_a}}\right)\left(1 + \frac{1}{A}e^{\frac{\varepsilon_i + \omega}{T_a}}\right)} g(\omega,\varepsilon_i)d\varepsilon_i \quad cm^2/g \qquad (3.10)$$

If the g factor is independent of the initial energy, then (3.10) can be integrated. The absorption coefficient becomes

$$k(\omega) = \frac{4.87 \times 10^6 T_a e^{\frac{\omega}{T_a}}}{\omega^3 (e^{\frac{\omega}{T_a}} - 1)} g(\omega) \ln \frac{e^{\frac{\omega}{T_a}} (A + 1)}{e^{\frac{\omega}{T_a}} + A} \qquad \mathrm{cm}^2/\mathrm{g} \qquad (3.11)$$

It can be shown that for a non degenerate case (3.11) reduces to

$$k_\omega = \frac{1.565 \times 10^{-17}}{\omega^3} \frac{N_e}{T_a^{1/2}} g(\omega) \qquad \mathrm{cm}^2/\mathrm{g} \qquad (3.12)$$

For most cases in the present calculation, $g(\omega, \varepsilon_i)$ is not slowly varying and Eq. (3.10) must be evaluated by a numerical integration. It has been shown in the first chapter that the free electrons form a Fermi band with all the energy states filled up to the Fermi energy. The only transition that can occur is between a state in the Fermi band and any one above the band. Since the electron gas has been considered as highly degenerate, Eq. (3.10) can be written as:

$$k_\omega = \frac{4.87 \times 10^6}{\omega^3} \int_{\varepsilon_F - \omega}^{\varepsilon_F} g(\omega, \varepsilon_i) d\varepsilon_i \qquad \mathrm{cm}^2/\mathrm{g} \qquad (3.13)$$

Having determined the absorption coefficient, the opacity is then calculated by finding the "Rosseland mean". Substituting (3.13) into (3.3) and using the dimensionless variable $u = \omega/T_a$, one can show that the opacity κ is given by:

$$\frac{1}{\kappa} = \frac{15}{4\pi^4}\int_0^\infty \frac{1}{k_\omega} u^4 e^{2u}(e^u - 1)^3 du \quad . \tag{3.14}$$

A discussion on the evaluation of the Rosseland mean is given in Appendix III.

3.2 Opacity of a High Density Atomic Hydrogen Gas

Through the process of photoelectric ionization, the bound electron becomes free after the absorption of radiation. For gases of high density such as that shown in the second chapter, only the K level exists; therefore, to calculate the opacity of such an atomic hydrogen gas, only the absorption by the K electron and that of the free electron have to be considered. The absorption coefficient of a K electron can be written as:

$$a_\omega = \frac{4\pi}{3}\frac{e^2}{\hbar c}(a_o)^2(\omega)(\varepsilon_f)^{1/2}\left|(\ell=0,\varepsilon_i|r|\ell=1,\ \varepsilon_f)\right|^2 \quad \mathrm{cm}^2 \tag{3.15}$$

where ω is the frequency of absorption and ε_f is the energy of the final state. The matrix element is that of dipole radiations. As in the case of a free-free transition, it is convenient to express the absorption coefficient in terms of Kramers' formula multiplied by a Gaunt factor. The g factor for the bound free transition of a hydrogen atom has been evaluated by Menzel and Pekeris$^{(8)}$ and many others. It is a slowly varying function of frequency and differs not much from unity over a certain range of frequency. The absorption coefficient per gram can then be written as

$$k_\omega = \frac{1}{M_H}\,\frac{16}{3\sqrt{3}}\,\frac{e^2}{mc}\left(\frac{1}{Ry}\right)\frac{1}{\omega^3}\,g(\omega) \qquad cm^2/g \tag{3.16}$$

where Ry is the Rydberg constant and M_H is the mass of the hydrogen atom.

The number of electrons having a negative energy -I is

$$\frac{2}{1+\frac{1}{A}e^{-\frac{I}{T_a}}} \tag{3.17}$$

and the probability that the final state is vacant is

$$\frac{\frac{1}{A}e^{-\frac{I+\omega}{T_a}}}{\frac{1}{A}e^{-\frac{I+\omega}{T_a}}+1} \tag{3.18}$$

The absorption coefficient for the bound free transition is then obtained by multiplying (3.16) by (3.17) and (3.18). To calculate the opacity, the total absorption coefficient due to both the bound free and free-free transition must be considered. For frequencies lower than the ionization potential, the contribution to the absorption is given by the free-free transition alone. In the high temperature region when $e^{\varepsilon_F/T_a} \ll 1$, the electron gas is non degenerate, the absorption coefficient is given by:

$$k_\omega = \frac{9.484 \times 10^6}{u^3} \frac{n}{T_a^{3.5}} \quad \mathrm{cm}^2/\mathrm{g} \qquad \omega < I$$

$$k_\omega = \frac{9.484 \times 10^6}{u^3} \frac{n}{T_a^{3.5}} \left[1 + \frac{1.99e^{I/T_a}}{T_a} g(\omega)\right] \qquad \omega > I \tag{3.19}$$

where n is the density of the gas and the g factor for the free-free transition is taken as unity. This approximation is justifiable if the gas is non degenerate, since it can be shown that for a non degenerate gas the bound free transition is more important. The opacity can then be calculated by substituting (3.19) in (3.3). The result is usually expressed in the form:

$$\kappa = 9.484 \times 10^6 \frac{n}{T_a^{3.5}} \frac{1}{\tau} \quad \mathrm{cm}^2/\mathrm{g} \tag{3.20}$$

where τ is called the "guillotine factor". For temperatures such that the Maxwellian distribution is no more valid, the exact form of the absorption coefficient has to be used. This is given as:

$$k_\omega = \frac{4.87 \times 10^6}{u^3 T_a^2} g'(\omega) \frac{e^u}{e^u - 1} \ln \frac{e^u(A + 1)}{e^u + A} \quad \mathrm{cm}^2/\mathrm{g} \qquad (\omega < I)$$

$$k_\omega = \frac{1}{u^3 T_a^3} \Bigg\{ 4.87 \times 10^6 T_a g'(\omega) \frac{e^u}{e^u - 1} \ln \frac{e^u(A + 1)}{e^u + A} \tag{3.21}$$

$$+ 4.76 \times 10^6 g(\omega) \frac{1}{1 + e^{-I/T_a}/A} \frac{\frac{1}{A}e^{-I/T_a + u}}{\frac{1}{A}e^{-I/T_a + u} + 1} \Bigg\} \quad \mathrm{cm}^2/\mathrm{g} \qquad (\omega > I)$$

$g'(\omega)$ is the g factor for the free-free transition and $g(\omega)$ is that of the bound free transition.

3.3 Results of Calculations and Discussions

Calculations for the "pressure ionized" gas are carried out by using the wave functions computed in the first chapter. Absorption coefficient is then determined by means of Eq. (3.4). The matrix element is that corresponding to the acceleration. This is preferred to the usually used one of the dipole radiation on account of better convergence. Since the acceleration is proportional to grad V, therefore the matrix element vanishes in the region where the potential is either zero or a constant. This simplifies considerably the procedure in the evaluation of the matrix element, since the integration only has to be carried out radially up to the cut-off radius. The method used is given in Appendix III.

The absorption coefficient for electrons of a given energy is obtained by summing over all the possible values of the angular momentum. For low energy electrons, only those that have zero angular momentum give the major contribution to the absorption coefficient since the "closest approach" of those with large angular momentum is greater than the cut-off radius. For higher energy electrons, absorption caused by those with higher angular momentum must be taken into account. The maximum energy of the absorbing electron is determined by the density; it can be shown by means of the classical analogy that there is an upper limit for the angular momentum such that the closest approach is within the cut-off radius. Calculations were made for cut-off radii $a = 0.5\ a_o$ and $a = 1.0\ a_o$. As shown in Chapter I, the density of the electron gas is determined by the effective radius β. The corresponding values of β are found to be $0.69\ a_o$ and $1.31\ a_o$, respectively. The values of densities are 8.29 g/c.c. and 1.21 g/c.c. for the two cases.

For the high density region, the g factor varies with the initial energy of the electron. Their values are shown in Fig. 3.1. For a cut-off radius as large as $a = a_o$, however, g is only a function of frequency. The absorption coefficient and the opacity are determined by Eqs. (3.13) and (3.14). The density does not appear explicitly in these equations. This is characteristic of a strongly degenerate gas. The increase of electron concentrations does not alter the distribution of electrons in the Fermi band. The change of concentration results only in the addition of electrons with energies greater than the original Fermi energy; consequently, the absorption coefficient does not vary explicitly with the density.

Except for the g factor, the integral in the determination of the Rosseland mean is of the form:

$$\int_0^\infty \frac{u^7 e^{2u}}{(e^u - 1)^3}\, du$$

where $u = \omega/T_a$.

The integrand has a maximum value near $u = 7$; it decreases rather fast and becomes negligible as $u > 20$. The temperature T_a chosen for the present calculation satisfies the condition $T_a \ll \varepsilon_F$. Consequently for small values of T_a, only the low frequency absorptions

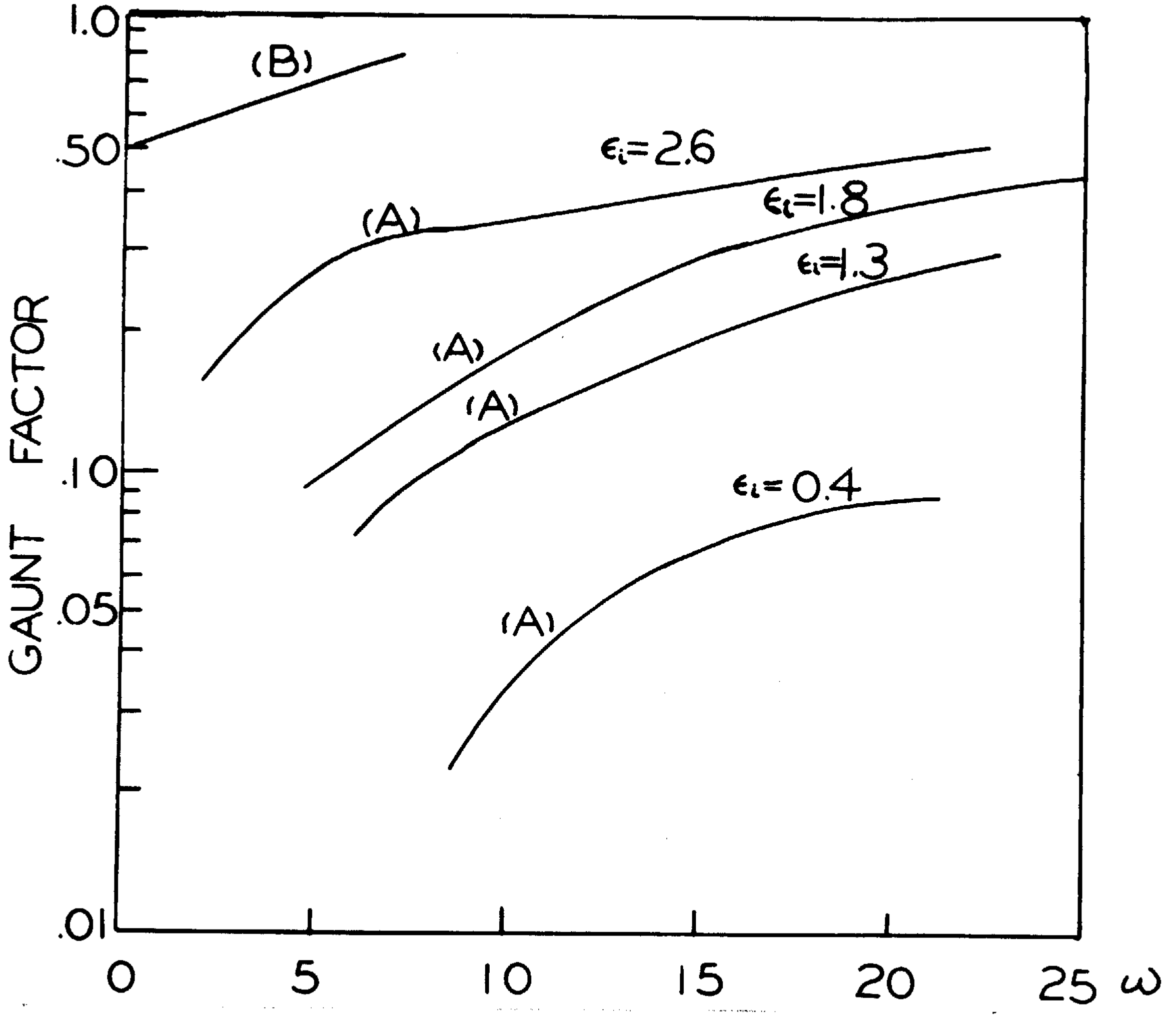


Fig. 3.1 GAUNT FACTORS g AS FUNCTIONS OF FREQUENCY FOR THE FREE-FREE TRANSITION

(the definition of the gaunt factor is given on p. 58)

(A) Gaunt factor for a = 0.5

(B) Gaunt factor for a = 1.0

are important in the evaluation of the Rosseland mean. In other words, only the electrons near the top of the Fermi band take an important part in the absorption process.

Absorption coefficients for the bound free transition are calculated by using the wave functions obtained in Chapter III. Their values corresponding to various cut-off radii are given in Fig. 3.2. They are compared with the absorption coefficient of a K electron for a normal hydrogen atom. The essential difference lies in the shift of the absorption edge with changes of density. At high frequencies the effect of the cut-off potential is not important and the absorption coefficients for all densities approach asymptotically that of a normal hydrogen atom.

The opacity is calculated as a function of temperature for $a = 4a_o$ and $6a_o$ which correspond to densities of 0.0225 and 0.0065 g/c.c. respectively. The calculations are made for a temperature range which lies between $T_a = 0.1$ to $T_a = 4$. The results are shown together with that for a completely ionized gas in Fig. 3.3. The values of the g factors and the absorption coefficients are given in Tables IA, IB, IIA and IIB. It can be seen that the opacity varies with temperature and density. The dependence on the two factors is discussed as follows:

a) The Temperature Dependence

For the non-degenerate case, the opacity varies approximately as $T_a^{-3.5}$. This is clearly seen in Eq. (3.19). When T_a is very high, the opacity decreases faster than the $T_a^{-3.5}$ factor. However, for very

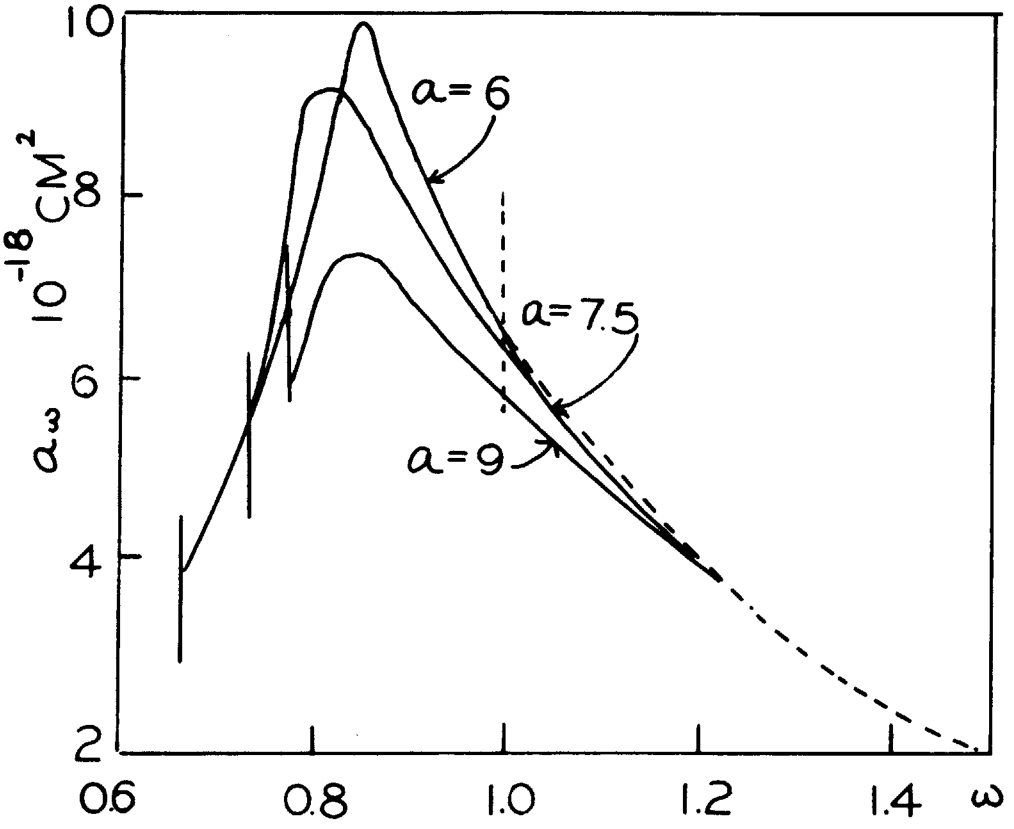


Fig. 3.2a ABSORPTION COEFFICIENTS a_ω AS FUNCTIONS OF FREQUENCIES FOR THE BOUND FREE TRANSITIONS FOR a = 6, 7.5 and 9

--- a_ω for the normal hydrogen atoms

Vertical lines indicate the absorption edges

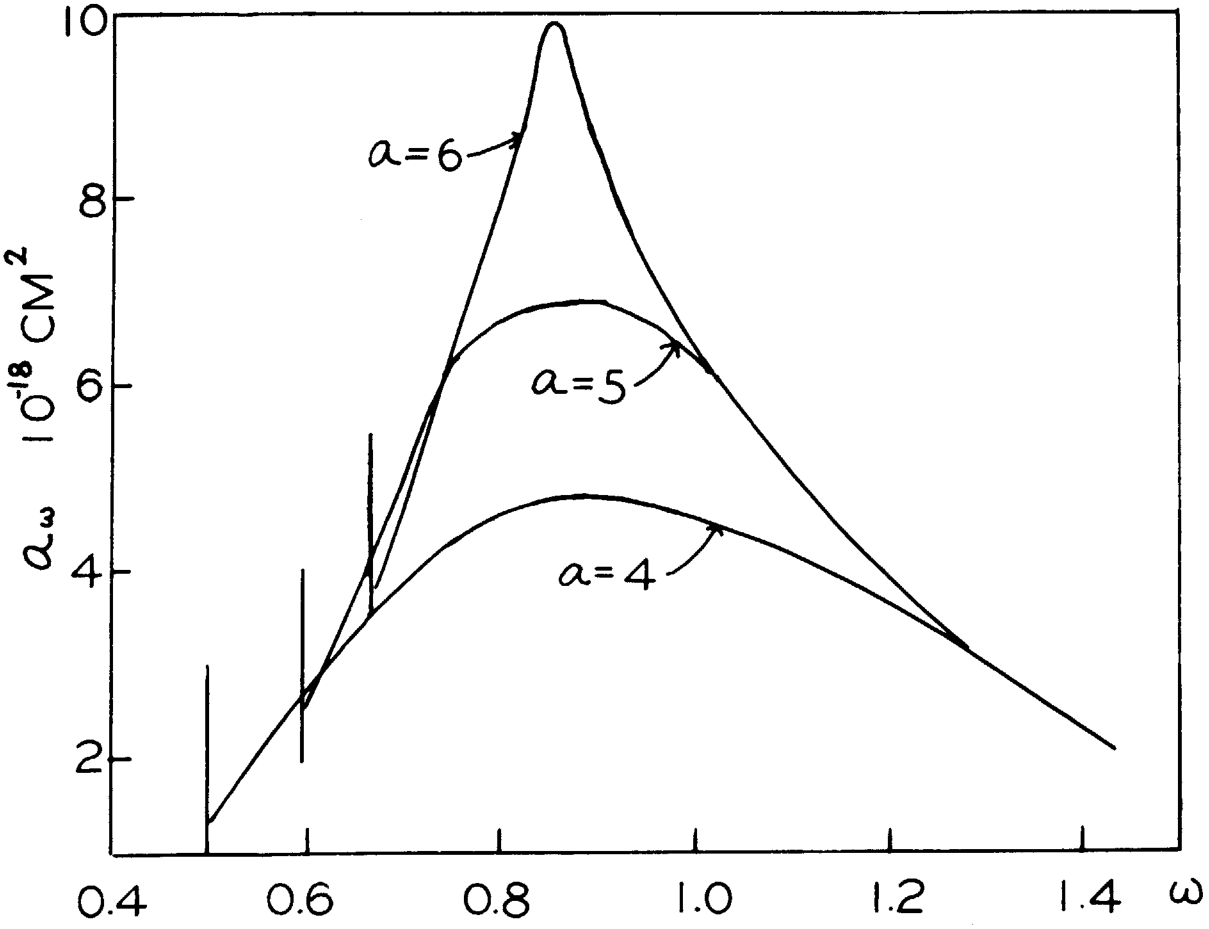


Fig. 3.2b ABSORPTION COEFFICIENTS a_ω AS FUNCTIONS OF FREQUENCIES FOR THE BOUND FREE TRANSITIONS FOR $a = 4$, 5 and 6

Vertical lines indicate the absorption edges

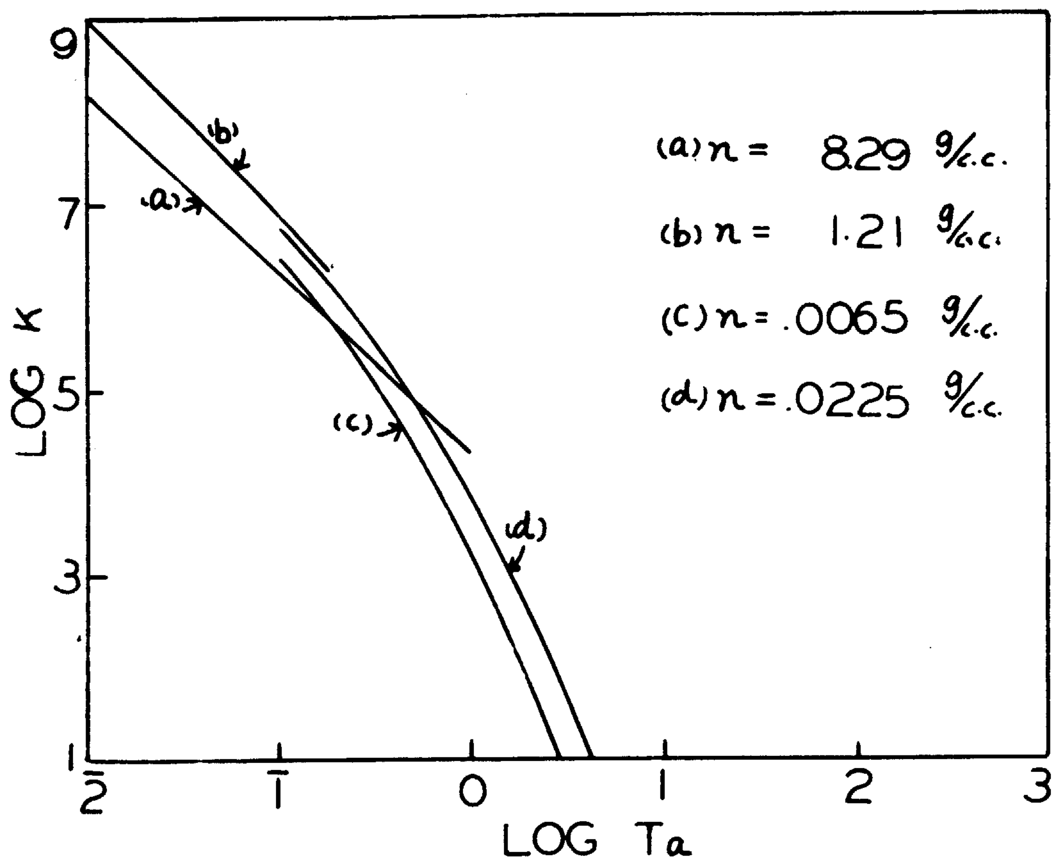


Fig. 3.3 COEFFICIENTS OF THE OPACITY AS FUNCTIONS OF TEMPERATURE FOR VARIOUS DENSITIES

TABLE IA

g FACTORS FOR THE FREE-FREE TRANSITION ($a = 0.5a_o$)

Initial Energy ε_i	Frequency ω	g
0.40	8.84	3.27×10^{-2}
	12.8	5.52×10^{-2}
	30.0	1.26×10^{-1}
1.3	7.31	9.24×10^{-2}
	11.2	1.55×10^{-1}
	14.3	1.98×10^{-1}
	18.5	2.27×10^{-1}
	28.5	3.52×10^{-1}
1.8	5.76	1.11×10^{-1}
	9.72	1.87×10^{-1}
	12.7	2.36×10^{-1}
	27.0	4.74×10^{-1}
2.6	2.08	1.44×10^{-1}
	6.20	3.07×10^{-1}
	9.24	3.49×10^{-1}
	13.5	3.96×10^{-1}
	23.5	5.49×10^{-1}

TABLE IB

g FACTORS FOR THE FREE-FREE TRANSITION ($a = a_o$)

Frequency ω	g
1.76	5.88×10^{-1}
3.80	6.59×10^{-1}
5.33	7.04×10^{-1}
6.93	7.82×10^{-1}

TABLE IIA

ABSORPTION COEFFICIENT FOR $a = 4a_o$

Frequency ω (in atomic unit)	Absorption coefficient $a_\omega (10^{-18} cm^2)$
0.553	2.08
0.656	3.46
0.812	4.63
0.870	4.75
0.930	4.70
0.962	4.63
1.06	4.31
1.13	4.06
1.27	3.21

TABLE IIB

ABSORPTION COEFFICIENT FOR $a = 6a_o$

Frequency ω (in atomic unit)	Absorption coefficient $a_\omega (10^{-18} cm^2)$
0.706	4.78
0.826	8.53
0.859	9.89
0.916	8.21
0.955	7.19
1.14	4.65
1.35	2.78
1.50	1.91

high temperature, scattering sets in and the present discussion is no more adequate. As the temperature decreases, the opacity increases more slowly than that determined by $T_a^{-3.5}$. This can be explained by considering the effect of T_a on the value of $A = e^{\varepsilon_F/T_a}$. The value of "A" for the non-degenerate case given by Eq. (3.8) is

$$4N_e\left(\frac{\pi}{T_a}\right)^{3/2}(a_o)^3 .$$

For a given density, "A" increases with the decrease of temperature. The probability that the upper state is vacant decreases as "A" increases; this means a corresponding reduction of absorption processes. Consequently, it results in a smaller value of opacity.

In the determination of the Rosseland mean, the reciprocal of the opacity is averaged over the temperature variation of the intensity of radiation for all frequencies. The integrand in the Rosseland mean is a function of the variable $u = \omega/T_a$. For small values of T_a, the absorption of the frequency immediately below the absorbing edge gives the major contribution to the integral for the Rosseland mean. Therefore, the free-free transition is more important for lower temperatures. This fact has been pointed out by Chandransekhar.(25) He has shown that for a highly degenerate gas, the opacity varies essentially according to T_a^{-2}. This effect is brought out likewise by the present calculation. A change of slope is noticeable in a log K versus log T_a plot as that given by Fig. 3.3.

For the "pressure-ionized" gas, no calculation is made for temperature T_a greater than unity. Since the self-consistent determination of the potential is carried out under the assumption that the electron gas is strongly degenerate, the temperature dependence of opacity for this case comes mainly from the temperature variation of the distribution of the radiation intensity. The Fermi energy ε_{Fo} is that for a gas at absolute zero of temperature. This is no longer valid when the condition $T_a/\varepsilon_{Fo} \ll 1$ is not satisfied. The actual Fermi energy ε_F will be displaced and there will be some non-occupied states and some occupied ones below and above the Fermi energy. As it has been pointed out previously that the electrons near the top of the Fermi band give the major contribution to the absorption; the change of ε_F as a consequence of temperature will affect the value of the opacity. To get a better determination of opacity for such cases requires a recalculation of the self-consistency of the potential.

b) <u>The Density Dependence</u>

For a non-degenerate gas, the opacity increases with the density at a given temperature. This is shown in the Fig. 3.3 for $T_a = 1$. As the density keeps increasing, the gas gradually approaches the state of degeneracy; the opacity no longer depends on the density explicitly. In the lower temperature range, the opacity decreases with respect to the density on account of the low values of the "g" factors for the high density gas. The opacity increases at first with the density and then decreases as the gas becomes degenerate. This is usually considered as a "saturation effect" and it is shown for $T_a = .1$.

In pointing out the importance of the free-free transition for a degenerate gas, Chandrasekhar$^{(25)}$ has considered the free-free transition as analegous to that of a bound free case. Since absorption can only occur under the condition $\omega > \varepsilon_F - \varepsilon_i$, this is as if the electron with energy ε_i is bound with an ionization potential $\varepsilon_F - \varepsilon_i$. In the present calculations, by using the self-consistent potentials and the model of ions embedded in a highly degenerate Fermi gas, the analogy is automatically fulfilled. The opacities for densities corresponding to $a = 2a_o$ and $3a_o$ are not included, since, from the results given by Fig. 3.3, the variation of opacity with density is not very rapid for the range of temperature studied. As the density becomes very high, the problem of electronic conductivity has to be considered; this is beyond the scope of the present study.

3.4 Comparison with Previous Work and Further Suggestions

In the discussion of opacity, the coefficient is usually given as (3.20)

$$K = 9.48 \times 10^6 \frac{n}{T_a^{3.5}} \frac{1}{\tau} \quad cm^2/g$$

Without the factor $1/\tau$, this is just Kramers' formula. The results of the present calculations show that τ is much greater than unity. Therefore the actual opacity for a high density hydrogen gas given by the present study is less than that given by Kramers' formula. For $T_a = 1$, the "guillotine factor" for various densities are given as:

n(g/c.c.)	τ(T = 156,000°C)	τ^*(T = 400,000°C)
8.29	3.14×10^3	8.3×10^2
2.22×10^{-2}	4.15×10	2.26
6.59×10^{-3}	4.04×10	1.35

The values are compared with the corresponding factor τ^* which is given by Morse(24) for a certain mixture of Fe, K, Ca, Na, Mg, O and H with a density of similar order of magnitude. The temperatures are not the same though they are also of similar order of magnitude. The opacity of a pure hydrogen gas is considerably less than that of a mixture. For an electron in an ordinary Coulombian field of a nucleus with charge Ze, the energy level is given by

$$E_n = \frac{Z^2}{n^2}$$

if the shielding of the other electrons are neglected. The K shell of the heavier element has a higher ionization potential. Although this is reduced as a result of high pressure, it is still considerably higher than that for an electron of a hydrogen atom. From Eq. (3.19), it can be seen that for a non-degenerate case a high value of ionization potential will favor the increase of the opacity. At a density when hydrogen is completely ionized, the K shells of the heavier elements still exist, the bound free transition causes the increase of the opacity.

Although hydrogen gas is the chief constituent of the stellar matter, yet the study of the opacity of the star cannot be considered as satisfactory without including the other elements. This can be carried out by further study.

APPENDIX IA

Table of units used

Energy	E	$\frac{e^2}{2a_o} = 15.53$ e.v.
Length	r	$r_o = 0.528 \times 10^{-8}$ cm
Temperature	T_a	$\frac{e^2}{2a_o k} = 157{,}000^\circ C$
Frequency	ω	$\frac{e^2}{2a_o h}$ = Rydberg constant $= 3.29 \times 10^{15} \text{sec}^{-1}$

APPENDIX IB

Solutions of the wave equations for positive energy states with the assumed potential

$$V = -\left(\frac{e}{r} - \frac{e}{a}\right) \qquad r \leqq a$$

$$V = 0 \qquad r \geqq a$$

The Schrodinger equations are

$$\nabla^2\psi + \left[E + 2\left(\frac{1}{r} - \frac{1}{a}\right)\right]\psi = 0 \qquad r \leqq a \tag{1}$$

$$\nabla^2\psi + E\psi = 0 \qquad r \geqq a \tag{2}$$

$$\text{Let} \quad E - \frac{2}{a} = E'$$

Solutions of (1) have different forms according to whether $E' > 0$ or $E' < 0$. They are to be considered separately.

(i) $E' < 0$. i.e. $E < \frac{2}{a}$

$r < a$

Let $\psi = \sum A_\ell P_\ell(\cos \theta) L(r)$ for equation (1) where $L(r)$ satisfies the equation

$$\frac{d^2L}{dr^2} + \frac{2}{r}\frac{dL}{dr} + \left[E' + \frac{2}{r} - \frac{\ell(\ell+1)}{r^2}\right]L = 0$$

Let $\chi = rL$

$$\frac{d^2\chi}{dr^2} + \left(E' + \frac{2}{r}\right)\chi - \frac{\ell(\ell+1)}{r^2}\chi = 0 \qquad (3)$$

Let $\lambda = \sqrt{-\frac{1}{E'}}$ or $E' = -\frac{1}{\lambda^2}$

$\rho = 2\alpha r$ where $\alpha = -E' = \frac{1}{\lambda}$

Equation (3) becomes

$$\frac{d^2\chi}{d\rho^2} + \left[-\frac{1}{4} + \frac{\lambda}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right]\chi = 0 \qquad (4)$$

The solution of (4) is in the form

$$\chi = e^{-\rho/2}\rho^{\ell+1}{}_1F_1(-\lambda + \ell + 1, 2\ell + 2, \rho)$$

${}_1F_1$ is the confluent hypergeometric function.

The solution for the region $r < a$ is

$$\psi_i = \sum A_\ell P_\ell(\cos\theta)\frac{1}{r}(2\alpha r)^{\ell+1}e^{-\alpha r}{}_1F_1(-\lambda + \ell + 1, 2\ell + 2, 2\alpha r) \tag{5}$$

For the region $r > a$, the radial equation has the form

$$\frac{d^2R_o}{d\rho^2} + \frac{2dR_o}{\rho d\rho} + \left[1 - \frac{\ell(\ell+1)}{\rho^2}\right]R_o = 0$$

where $\rho = kr$ $\quad k^2 = E$; the solution of which is of the form

$$R_o(r) = B_\ell\left[j_\ell(kr)\cos\eta_\ell - n_\ell(kr)\sin\eta_\ell\right]$$

$$\xrightarrow[r\to\infty]{} (kr)^{-1}B_\ell\sin(kr - \frac{\ell\pi}{2} + \eta_\ell) \tag{6}$$

η_ℓ is the phase shift of the ℓ^{th} partial wave and can be determined by means of the continuity relation

$$\frac{1}{R_i}\frac{dR_i}{dr}\Big]_{r = a} = \frac{1}{R_o}\frac{dR_o}{dr}\Big]_{r = a}$$

If $$\frac{1}{R_i}\frac{dR_i}{dr}\Big]_{r\,=\,a} = \gamma_\ell$$

$$\gamma_\ell = \frac{k\left[j_\ell'(ka)\cos\eta_\ell - n_\ell'(ka)\sin\eta_\ell\right]}{j_\ell(ka)\cos\eta_\ell - n_\ell(ka)\sin\eta_\ell}$$

or $$\tan\eta_\ell = \frac{kj_\ell'(ka) - \gamma_\ell\, j_\ell(ka)}{kn_\ell'(ka) - \gamma_\ell\, n_\ell(ka)}$$

Having determined η_ℓ, the normalization is determined so that the wave function has the asymptotic form given by (6)

(ii) $E' > 0$

Solution of Eq. (1) can be obtained by letting

$$k' = \sqrt{E'} \qquad n = -\frac{i}{k'}$$

$$\rho = 2ik'r$$

The solution is of the form

$$L = (-i\rho)^\ell \frac{C_\ell}{(2\ell+1)!}e^{-\rho/2}\,{}_1F_1\left(\ell + 1 + \frac{i}{k'},\ 2\ell + 2,\ 2ik'r\right) \tag{7}$$

which has the same asymptotic form as that given by (6).

A series expansion of L can be obtained in the form

$$L = \frac{C_\ell}{(2\ell+1)!}\,(2k'r)^\ell \sum_0^\infty c_m \frac{(k'r)^m}{m!} \tag{8}$$

where the C_m's follow the recurrence relation:

$$(2\ell + 2 + m)C_{m+1} + \frac{2}{k'} C_m + mC_{m-1} = 0 \tag{9}$$

with $C_0 = 1$

$$C_1 = -\frac{1}{k'(\ell + 1)}$$

has the following form

$$\left.\frac{1}{L}\frac{dL}{dr}\right]_{r = a} = \gamma_\ell = \frac{\ell}{a} + k' \frac{\sum_m C_m \frac{(k'r)^{m-1}}{(m-1)!}}{\sum_m C_m \frac{(k'r)^m}{m!}} \tag{10}$$

The normalization factor can be determined by the same method as that given for $E' < 0$.

APPENDIX IIA

DETERMINATION OF THE NEGATIVE ENERGY STATE

Equations to be solved are:

$$\nabla^2\psi + \left[E + 2\left(\frac{1}{r} - \frac{1}{a}\right)\right]\psi = 0 \qquad r \leqq a \tag{1}$$

$$\nabla^2\psi + E\psi = 0 \qquad r \geqq a \tag{2}$$

Solution for (1) is the same as that given by Appendix IB

$$\psi_i = \sum_{\ell} A_\ell P_\ell(\cos\theta)\frac{1}{r}(2\alpha r)^{\ell+1} e^{-\alpha r}\, {}_1F_1(-\lambda + \ell + 1,\ 2\ell + 2,\ 2\alpha r) \qquad (3)$$

where

$$\alpha = \sqrt{\left|E - \frac{2}{a}\right|}$$

$$E = -\frac{1}{\lambda^2}$$

For $r > a$

Let

$$\sigma^2 = |E|$$

$$\rho = i\sigma r$$

The radial wave equation has the form

$$\frac{d^2R}{d\rho^2} + \frac{2dR}{\rho d\rho} + \left[1 - \frac{\ell(\ell+1)}{\rho^2}\right] R = 0 \qquad (3)$$

the solution of which can be given by the spherical Hankel function

$$R = B_\ell \, h_\ell^{(1)}(i\sigma r)$$

If R_i and R_o are solutions of the radial wave equation for $r < a$ and $r > a$ respectively, then the continuity condition gives

$$\left.\frac{1}{R_i}\frac{dR_i}{dr}\right]_{r = a} = \left.\frac{1}{R_o}\frac{dR_o}{dr}\right]_{r = a} \tag{4}$$

For the case of $\ell = 0$, Eq. (4) gives

$$\xi \left[1 - (1-\lambda)\, \frac{{}_1F_1(2-\lambda,3,2\xi)}{{}_1F_1(1-\lambda,2,2\xi)}\right] = \eta + 1 \tag{5}$$

where
$$\xi = \alpha a$$
$$\eta = \sigma a$$

Equation (5) together with the relation

$$\xi^2 - \eta^2 = 2a \tag{6}$$

are used to determine graphically the values of ξ and η, from which the bound level is determined.

APPENDIX IIB

CALCULATIONS OF THE ENERGY BAND

To evaluate Eq. (2.13)

$$E = \frac{\int \psi^{*}\left[-\nabla^{2} + 2V(r)\right]\psi \, d\tau}{\int |\psi|^{2} d\tau} \qquad (1)$$

Let

$$V(r) = V(r) + U(|\vec{r} - \vec{r}_j|) - U(|\vec{r} - \vec{r}_j|) \qquad (2)$$

The numerator of (1) becomes

$$\int \sum_i e^{-i\vec{k}.\vec{r}_i} \phi^{*}(|\vec{r} - \vec{r}_i|) \{ -\nabla^{2}$$

$$+ 2\left[V(r) + U(|\vec{r} - \vec{r}_j|) - U(|\vec{r} - \vec{r}_j|)\right] \quad \sum_j e^{i\vec{k}.\vec{r}_j} \phi(|\vec{r} - \vec{r}_j|) d\tau$$

$$= \int \psi^{*} E_o \psi \, d\tau + \int \sum_i e^{-i\vec{k}.\vec{r}_i} \phi^{*}(|\vec{r} - \vec{r}_i|) 2\left[V(r) - U(|\vec{r} - \vec{r}_j|)\right]$$

$$\sum_j e^{i\vec{k}.\vec{r}_j} \phi(|\vec{r} - \vec{r}_j|) d\tau \qquad (3)$$

Let $|\vec{r}_i - \vec{r}_j| = \rho_i$

then

$$\vec{r} - \vec{r}_j \rightarrow \vec{r}$$

$$\vec{r} - \vec{r}_i \rightarrow \vec{r} - \vec{\rho}_i$$

The second term in (3) becomes

$$N \sum_i e^{-i\vec{k}\cdot\vec{\rho}_i} \int \phi(|\vec{r} - \vec{\rho}_i|) 2\left[V(r) - U(r)\right] \phi(r) d\tau \tag{4}$$

Similarly the denominator of (1) becomes

$$\int |\psi|^2 d\tau = \int \sum_i e^{-i\vec{k}\cdot\vec{r}_i} \phi^*(|\vec{r} - \vec{r}_i|) \sum_j e^{i\vec{k}\cdot\vec{r}_j} \phi(|\vec{r} - \vec{r}_j|) d\tau$$

$$= N \sum_i e^{-i\vec{k}\cdot\vec{\rho}_i} \int \phi^*(|\vec{r} - \vec{\rho}_i|) \phi(r) d\tau$$

$$= N\Big[1 + \sum_{\rho_i \neq 0} e^{-i\vec{k}\cdot\vec{\rho}_i} \int \phi^*(|\vec{r} - \vec{\rho}_i|) \phi(r) d\tau \tag{5}$$

Substituting (3), (4) and (5) into (1)

$$E = E_o + \frac{2 \sum_i e^{-i\vec{k}\cdot\vec{\rho}_i} \int \phi^*(|\vec{r} - \vec{\rho}_i|)\left[V(r) - U(r)\right] \phi(r) d\tau}{1 + \sum_{\rho_i \neq 0} e^{-i\vec{k}\cdot\vec{\rho}_i} \int \phi^*(|\vec{r} - \vec{\rho}_i|) \phi(r) d\tau}$$

$$= E_o + \frac{2\int \phi^*(r)\left[V(r)-U(r)\right]\phi(r)d\tau + \sum e^{-i\vec{k}.\vec{\rho}_i}\int \phi^*(|\vec{r}-\vec{\rho}_i|)\left[V(r)-U(r)\right]\phi(r)d\tau}{1 + \sum\limits_{\rho_i \neq 0} e^{-i\vec{k}.\vec{\rho}_i}\int \phi^*(|\vec{r}-\vec{\rho}_i|)\phi(r)d\tau}$$

$$= E_o + \frac{A + C}{1 + D} \qquad (6)$$

where

$$A = 2\sum_{\rho_i \neq 0} e^{-i\vec{k}.\vec{\rho}_i}\int \phi^*(|\vec{r}-\vec{\rho}_i|)\left[V(r) - U(r)\right]\phi(r)d\tau \qquad (7)$$

$$C = 2\sum_{\rho_j \neq 0}\int \phi^*(r)\sum_{\rho_j} U(|\vec{r}-\vec{\rho}_j|)\,\phi(r)d\tau \qquad (8)$$

since

$$V(r) = U(r) + \sum_{\rho_j \neq 0} U(|\vec{r}-\vec{\rho}_j|)$$

$$D = \sum_{\rho_i \neq 0} e^{-i\vec{k}.\vec{\rho}_i}\int \phi^*(|\vec{r}-\vec{\rho}_i|)\phi(r)d\tau \qquad (9)$$

APPENDIX IIC

EVALUATIONS OF THE INTEGRALS A, C, AND D

$$\phi(r) = \frac{N_1}{\sqrt{4\pi}} e^{-\alpha r} \qquad r < a$$

$$\phi(r) = \frac{N_2}{\sqrt{4\pi}} \frac{e^{-\sigma r}}{\sigma r} \qquad r > a$$

The integrals A, C, and D can be simplified by using the expansion of $\frac{e^{-\alpha|\vec{r}-\vec{\rho}|}}{|\vec{r}-\vec{\rho}|}$ and $e^{-\alpha|\vec{r}-\vec{\rho}|}$ given by Coulson(16):

$$\frac{e^{-\alpha|\vec{r}-\vec{\rho}|}}{|\vec{r}-\vec{\rho}|} = \sum_{\ell} \frac{(2\ell+1)}{(r\rho)^{1/2}} P_\ell(\cos\theta)\, \gamma_\ell(\alpha,r,\rho) \tag{1}$$

$$\begin{aligned} \gamma_\ell(\alpha,r,\rho) &= I_{\ell+1/2}(\alpha\rho)K_{\ell+1/2}(\alpha r) \qquad r > \rho \\ &= I_{\ell+1/2}(\alpha r)K_{\ell+1/2}(\alpha\rho) \qquad r < \rho \end{aligned} \tag{2}$$

$$e^{-\alpha|\vec{r}-\vec{\rho}|} = \sum_{\ell} \frac{(2\ell+1)}{(r\rho)^{1/2}} P_\ell(\cos\theta)\, p_\ell(\alpha,r,\rho) \tag{3}$$

$$\begin{aligned} (\alpha,r,\ ) &= rI_{\ell+1/2}(\alpha\rho)K_{\ell+1/2}(\alpha r)-\rho I_{\ell-1/2}(\alpha\rho)K_{\ell+1/2}(\alpha r) \qquad r > \rho \\ &= \rho I_{\ell+1/2}(\alpha r)K_{\ell+3/2}(\alpha\rho)-rI_{\ell-1/2}(\alpha r)K_{\ell+1/2}(\alpha\rho) \qquad r < \rho \end{aligned} \tag{4}$$

where I_m and K_m are Bessel functions of the imaginary arguments defined by Watson(20).

a) Evaluation of D

$$D = \sum_{\rho_i \neq 0} e^{-i\vec{k}\cdot\vec{\rho}_i} \int \phi^*(|\vec{r} - \vec{\rho}_i|)\phi(r)\,d\tau$$

where

$$\int \phi^*(|\vec{r} - \vec{\rho}_i|)\phi(r)\,d\tau = \frac{N_1N_2}{4\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{a} e^{-\alpha r}\,\frac{e^{-\sigma|\vec{r} - \vec{\rho}_i|}}{\sigma|\vec{r} - \vec{\rho}_i|}\,r^2\sin\theta\,d\theta\,d\phi\,dr$$

$$+\frac{N_2^2}{4\pi}\int_0^{2\pi}\int_0^{\pi}\int_a^{\rho-a} \frac{e^{-\sigma r}}{\sigma r}\,\frac{e^{-\sigma|\vec{r} - \vec{\rho}_i|}}{\sigma|\vec{r} - \vec{\rho}_i|}\,r^2\sin\theta\,d\theta\,d\phi\,dr$$

$$+\frac{N_1N_2}{4\pi}\int_0^{2\pi}\int_0^{\pi}\int_{\rho-a}^{\rho} \frac{e^{-\sigma r}}{\sigma r}\,e^{-\alpha|\vec{r} - \vec{\rho}_i|}\,r^2\sin\theta\,d\theta\,d\phi\,dr$$

$$+\frac{N_1N_2}{4\pi}\int_0^{2\pi}\int_0^{\pi}\int_{\rho}^{\rho+a} \frac{e^{-\sigma r}}{\sigma r}\,e^{-\alpha|\vec{r} - \vec{\rho}_i|}\,r^2\sin\theta\,d\theta\,d\phi\,dr$$

$$+\frac{N_2^2}{4\pi}\int_0^{2\pi}\int_0^{\pi}\int_{\rho+a}^{\infty} \frac{e^{-\sigma r}}{\sigma r}\,\frac{e^{-\sigma|\vec{r} - \vec{\rho}_i|}}{\sigma|\vec{r} - \vec{\rho}_i|}\,r^2\sin\theta\,d\theta\,d\phi\,dr$$

$$= \frac{N_1N_2}{2\sigma}\left\{\frac{e^{-\sigma\rho_i}}{\sigma\rho_i} - \frac{ae^{-(\alpha-\sigma)a}}{(\alpha-\sigma)} + \frac{1 - e^{-(\alpha-\sigma)a}}{(\alpha-\sigma)^2} + \frac{ae^{-(\alpha+\sigma)a}}{(\alpha+\sigma)} - \frac{1 - e^{-a(\alpha+\sigma)}}{(\alpha+\sigma)^2}\right\}$$

$$+ \frac{N_2^2}{2\sigma^2}\frac{e^{-\sigma\rho_i}}{\sigma\rho_i}\left\{\rho_i - 2a + \frac{e^{-2\sigma(\rho_i-a)} - e^{-2\sigma a}}{2\sigma}\right\}$$

$$+ \frac{N_1N_2}{2\alpha}\frac{e^{-\sigma\rho_i}}{\sigma\rho_i}\left\{-\frac{a}{(\alpha-\sigma)}e^{-a(\alpha-\sigma)} + \frac{2\left[\left(e^{-2\alpha\rho_i} - e^{-2\alpha\rho_i + a(\alpha+\sigma)}\right)\right] + \frac{a}{\rho_i}e^{-2\alpha\rho_i + a(\alpha+\sigma)}}{(\alpha+\sigma)}\right.$$

$$+ \frac{1 - e^{-a(\alpha-\sigma)}}{\alpha-\sigma}\left[\frac{1}{\alpha} + \frac{1}{\alpha-\sigma}\right]$$

$$\left. + \frac{e^{-2\alpha\rho_i}(1 - e^{a(\alpha+\sigma)})}{(\alpha+\sigma)}\left(\frac{1}{\alpha} + \frac{1}{\alpha+\sigma}\right)\right\}$$

$$+ \frac{N_1N_2}{2\alpha}\frac{e^{-\sigma\rho_i}}{\sigma\rho_i}\left\{-\frac{ae^{-a(\alpha+\sigma)}}{\alpha+\sigma} + \frac{2\left[e^{-2\alpha\rho_i - a(\alpha+\sigma)} - e^{-2\alpha\rho_i}\right] + \frac{a}{\rho_i}e^{-2\alpha\,{}_i-a(\alpha+\sigma)}}{(\alpha+\sigma)}\right\}$$

$$+ \frac{N_1N_2}{2\alpha}\frac{e^{-\sigma\rho_i}}{\sigma\rho_i}\left\{\frac{e^{-a(\alpha+\sigma)}}{(\alpha+\sigma)}\left(-\frac{1}{\alpha+\sigma} - \frac{1}{\alpha}\right) - \frac{e^{-2\alpha\rho_i - a(\alpha+\sigma)} - e^{-2\alpha\rho_i}}{\alpha+\sigma}\left(-\frac{1}{\alpha+\sigma} - \frac{1}{\alpha}\right)\right\}$$

$$+ \frac{N_2^2}{2\sigma^3}\frac{e^{-\sigma\rho_i}}{\sigma\rho_i}\left[\sigma\rho_i - 2\sigma a\right]$$

Neglecting terms of small order of magnitude, D can be simplified as:

$$\begin{aligned}
D = \sum_{\rho_i} e^{-i\vec{k}\cdot\vec{\rho}_i} \Bigg\{ \frac{e^{-\sigma\rho_i}}{\sigma\rho_i} \Bigg[\frac{N_1N_2}{2\sigma} \Big(& - \frac{ae^{-(\alpha-\sigma)a}}{(\alpha-\sigma)} + \frac{1 - e^{-(\alpha-\sigma)}}{(\alpha-\sigma)^2} + \frac{ae^{-a(\alpha+\sigma)}}{(\alpha+\sigma)} - \\
& - \frac{1 - e^{-a(\alpha+\sigma)}}{(\alpha+\sigma)^2} \Bigg] + \frac{N_1N_2}{2\alpha} \Bigg[- \frac{a}{(\alpha-\sigma)} e^{-a(\alpha-\sigma)} + \frac{1 - e^{-a(\alpha-\sigma)}}{\alpha-\sigma} \left(\frac{1}{\alpha} + \frac{1}{\alpha-\sigma}\right) \\
& - \frac{a}{(\alpha-\sigma)} e^{-a(\alpha-\sigma)} + \frac{1 - e^{-a(\alpha-\sigma)}}{\alpha-\sigma} \left(\frac{1}{\alpha} + \frac{1}{\alpha-\sigma}\right) \\
& - \frac{a}{(\alpha+\sigma)} e^{-a(\alpha+\sigma)} + \left(\frac{1}{(\alpha+\sigma)^2} + \frac{1}{a(\alpha+\sigma)}\right) \left(1 - e^{-a(\alpha+\sigma)}\right) \Bigg] \Bigg\}
\end{aligned}$$

$$+ \sum_{\rho_i} e^{-i\vec{k}\cdot\vec{\rho}_i} \left\{ \frac{e^{-\sigma\rho_i}}{\sigma\rho_i} (\sigma \; - 2\sigma a) \right\}$$

$$= \sum_{\rho_i} e^{-i\vec{k}\cdot\vec{\rho}_i} \left\{ \frac{e^{-\sigma\rho_i}}{\sigma\rho_i} F(\alpha,\sigma,a) + e^{-\sigma\rho_i} p(\alpha,\sigma,a) \right\} \qquad (5)$$

b) Evaluation of C

$$C = 2 \sum_{\rho_j \neq 0} \int \phi^*(r) \left[\sum_{\rho_j \neq 0} U(|\vec{r} - \vec{\rho}_j|) \right] \phi(r) d\tau$$

To evaluate C, it is convenient to define the following quantities(16)

$$P_{mn}(a) = \int_0^a r^m I_n(2\sigma r) dr \qquad (6)$$

$$P_{mn}[a] = a^{m}I_{n}(2\sigma a) \qquad (7)$$

$$A_{n} = \sqrt{4\pi\sigma}\, P_{n + 1/2, n + 1/2}[a] \qquad (8)$$

$$B_{n} = \sqrt{4\pi\sigma}\, P_{n + 1/2, n + 1/2} \qquad (9)$$

$$C_{n} = \sqrt{4\pi\sigma}\, P_{n + 1/2, n + 1/2} \qquad (10)$$

$$A_{-1} = \frac{e^{2\sigma a} + e^{2\sigma a}}{a}$$

$$A_{0} = e^{2\sigma a} - e^{-2\sigma a}$$

$$B_{0} = \frac{e^{2\sigma a} + e^{-2\sigma a} - 2}{2\sigma}$$

$$A_{1} = a^{2}A_{-1} - \frac{A_{0}}{2\sigma}$$

$$B_{1} = \frac{aA_{0} - 2B_{0}}{2\sigma}$$

$$C_{1} = \frac{A_{1}}{2\sigma}$$

The general recurrence formulas for A_n, B_n, and C_n are

$$A_{n} = a^{2}A_{n-2} - \frac{(2n-1)A_{1}}{2\sigma} \qquad (11)$$

$$B_{n} = \frac{aA_{n-1} - 2nB_{n-1}}{2\sigma} \qquad (12)$$

$$C_{n} = \frac{A_{n}}{2\sigma} \qquad (13)$$

Since $U(|\vec{r} - \vec{\rho}_j|)$ vanishes except inside a sphere of radius a around the j^{th} nucleus, the integration of C can be carried out by moving the origin to the j^{th} nucleus

$$C = 2 \sum_{\rho_j \neq 0} \int \phi^2(|\vec{r} - \vec{\rho}_j|)\left[-\left(\frac{1}{r} - \frac{1}{a}\right)\right] d\tau$$

$$\phi^2(|\vec{r} - \vec{\rho}_j|) = \frac{N_2^2}{4\pi}\left[\frac{e^{-\sigma|\vec{r} - \vec{\rho}_j|}}{\sigma|\vec{r} - \vec{\rho}_j|}\right]^2$$

$$= \frac{N_2^2}{4\pi\sigma^2} \sum_{\ell'} \frac{2\ell'+1}{(r\rho_j)^{1/2}} I_{\ell'+1/2}(2\sigma r) K_{\ell'+1/2}(2\sigma\rho_j) P_{\ell'}(\cos\theta)$$

$$\sum_{\ell} P_{\ell}(\cos\theta)\left(\frac{r}{\rho_j}\right)^{\ell} \frac{1}{\rho_j}$$

After integrating over the angles, all terms drop out except for those with $\ell = \ell'$

$$C = 2 \sum_{\rho_j \neq 0} \frac{N_2^2}{\sigma^2} \int_0^a \frac{I_{\ell+1/2}(2\sigma r)}{(r\rho_j)^{1/2}} K_{\ell+1/2}(2\sigma\rho_j)\left(\frac{r}{\rho_j}\right)^{\ell} \frac{1}{\rho_j}\left(-\frac{1}{r} + \frac{1}{a}\right) r^2 dr$$

$$C = 2 \sum_{\rho_j \neq 0\ j} \frac{N_2^2\, e^{-2\sigma\rho_j}}{(2\sigma\rho_j)^2} \frac{1}{\rho_j}\left[-B_{\ell} + \frac{C_{\ell+1}}{a}\right] \sum_{p=0} \frac{(\ell+p)!}{p!(\ell-p)!(4\sigma\rho_j)^p} \qquad (14)$$

The series converges rather fast; for most cases, terms of $\ell = 2$ can be neglected.

c) Evaluation of A

$$A = 2 \sum_{\rho_i \neq 0} e^{-i\vec{k}\cdot\vec{\rho}_i} \int \phi(r)\Big[\sum_{\rho_j} U(|\vec{r} - \vec{\rho}_j|) - U(r)\Big] \phi(|\vec{r} - \vec{\rho}_j|)\, d\tau$$

The integral can be carried out for two different cases

(i) $\rho_j = \rho_i$

(ii) $\rho_i \neq \rho_j$

(i) $\rho_j = \rho_i$

$$A = 2 \sum_{\rho_i \neq 0} e^{-i\vec{k}\cdot\vec{\rho}_i} \frac{N_1 N_2}{4\pi} \int \frac{e^{-\sigma r}}{\sigma r} e^{-\alpha|\vec{r} - \vec{\rho}_i|}\left[- \frac{1}{|\vec{r} - \vec{\rho}_i|} + \frac{1}{a}\right] d\tau \qquad (15)$$

Since $- \dfrac{1}{|\vec{r} - \vec{\rho}_i|} + \dfrac{1}{a}$ has ~~a~~ non-vanishing value within the sphere of radius a around the nucleus, (15) is equivalent to

$$A = 2 \sum_{\rho_i \neq 0} e^{-i\vec{k}\cdot\vec{\rho}_i} \frac{N_1 N_2}{4\pi} \int_0^{2\pi}\int_0^{\pi}\int_0^{a} \frac{e^{-\sigma|\vec{r} - \vec{\rho}_i|}}{\sigma|\vec{r} - \vec{\rho}_i|} e^{-\alpha r}\left[- \frac{1}{r} + \frac{1}{a}\right] r^2 dr \sin\theta\, d\theta\, d\phi$$

$$= 2 \sum_{\rho_i \neq 0} e^{-i\vec{k}\cdot\vec{\rho}_i} \frac{e^{-\sigma\rho_i}}{\sigma\rho_i} \frac{N_1 N_2}{2\sigma}\left[- \frac{1}{\alpha-\sigma}\left(1 - \frac{1-e^{-a(\alpha-\sigma)}}{a(\alpha-\sigma)}\right) + \frac{1}{\alpha+\sigma}\left(1- \frac{1-e^{-a(\alpha+\sigma)}}{a(\alpha+\sigma)}\right)\right]$$

$$= \sum_{\rho_i \neq 0} e^{-i\vec{k}\cdot\vec{\rho}_i} \frac{e^{-\sigma\rho_i}}{\sigma\rho_i} h(\alpha,\sigma,a) \qquad (16)$$

(ii) $\rho_i \neq \rho_j$

$$A = 2 \sum_{\rho_i \neq 0} e^{-i\vec{k}\cdot\vec{\rho}_i} \frac{N_1N_2}{4\pi} \int \frac{e^{-\sigma r}}{\sigma r} e^{-\alpha|\vec{r} - \vec{\rho}_i|} \sum_{\rho_j} \left[- \frac{1}{|\vec{r} - \vec{\rho}_j|} + \frac{1}{a} \right] d\tau \quad (17)$$

This integral can be simplified by using the approximation discussed on Page ( ); (17) can be evaluated as

$$A = 2 \sum_{\rho_i} e^{-i\vec{k}\cdot\vec{\rho}_i} \left(\bar{V} \frac{N_1N_2}{2\sigma^3}\right) \left(e^{-\sigma\rho_i} - \frac{e^{-\sigma\rho_i}}{\sigma\rho_i} 2\sigma a\right) \qquad (18)$$

Combining (16) and (18)

$$A = \sum_{\rho_i} e^{-i\vec{k}\cdot\vec{\rho}_i} \left\{ \frac{e^{-\sigma\rho_i}}{\sigma\rho_i} \left[h(\alpha,\sigma,a) - \frac{N_1N_2}{\sigma^2} a\bar{V} \right] + \bar{V} \frac{N_1N_2}{2\sigma^3} e^{-\sigma\rho_i} \right\} \qquad (19)$$

To replace the summation over ρ_i by an integration

$$A = \frac{h(\alpha,\sigma,a) - \frac{N_1N_2}{\sigma^2} a\bar{V}}{\Omega} \int_{2x}^{\infty} \frac{e^{-\sigma\rho}}{\sigma\rho} \frac{\sin k\rho}{k\rho} \rho^2 d\rho$$

$$+ \bar{V} \frac{N_1N_2}{\sigma^3} 2\pi \int_{2x}^{\infty} e^{-\sigma\rho} \frac{\sin k\rho}{k\rho} \rho^2 d\rho$$

APPENDIX III

A Calculation of the Absorption Coefficient

a) Absorption coefficient for the free-free transition

$$a_\omega(\varepsilon_i) = \frac{256\pi^2}{3}\left(\frac{e^2}{\hbar c}\right)(a_o)^5 \frac{\sqrt{\varepsilon_f}}{\omega^3} \sum_{\ell=1}^{\infty} \ell \left\{ \left|(\ell-1,\varepsilon_i|\frac{1}{r^2}|\ell,\varepsilon_f)\right|^2 + \left|(\ell,\varepsilon_i|\frac{1}{r^2}|\ell-1,\varepsilon_f)\right|^2 \right\} \quad \text{cm}^5 \tag{1}$$

The matrix is to be evaluated only inside the cut-off radius. The radial wave functions as given by Appendix IB are different depending on whether $E - \frac{2}{a} < 0$ or $E - \frac{2}{a} > 0$

(i) $E - \frac{2}{a} < 0$

$$R = Ne^{-\alpha r}\,{}_1F_1(1 - \lambda + \ell, 2\ell + 2, 2\alpha r)(2\alpha r)^{\ell} \tag{2}$$

(ii) $E - \frac{2}{a} > 0$

$$R = N\frac{(2k'r)^{\ell}}{(2\ell + 1)!} \sum_0^{\infty} C_m \frac{(k'r)^m}{m!} . \tag{3}$$

For the high density gas which corresponds to the small cut-off radius of the potential, the matrix element can be evaluated by means of the series expansion. The integration can then be performed term by term. If the integration involves the product of wave functions given by Eqs. (2) and (3), integral of the following form is involved:

$$\gamma(\mu,b) = \int_0^b e^{-t} e^{\mu-1} dt \tag{4}$$

This is an incomplete gamma function and can be evaluated by the following formula

$$\gamma(\mu,b) = \int_0^b e^{-t} e^{\mu-1} dt = \Gamma(\mu)\left\{ 1 - e^{-b} b^{\mu-1} \sum_{s=0}^{\mu-1} \frac{b^{-s}}{\Gamma(\mu-s)} \right\} \tag{5}$$

b) Absorption coefficient for the bound free transition

$$a_\omega = \frac{4\pi}{3} \frac{e^2}{\hbar c} (a_o)^2 (\omega) (\varepsilon_f)^{1/2} \left\{ |\ell=0,\varepsilon_i|r|\ell=1,\varepsilon_f)| \;^2 \right\} \text{cm}^2 \tag{6}$$

The radial wave functions for the matrix element are the solutions of the self-consistent potential given by Eq. (2.34)

$$\begin{aligned} V &= -\left(\frac{e}{r} - \frac{e}{a}\right) && r \leqq \frac{2}{3}\,a \\ V &= -\frac{1}{2a} = \overline{V} && r \geqq \frac{2}{3}\,a \end{aligned} \tag{7}$$

The solution for the K electrons is

$$\begin{aligned} R &= N_1 e^{-\alpha r}\, {}_1F_1(1-\lambda,2,2\alpha r) && r \leqq \frac{2}{3}\,a \\ &= N_2\, \frac{e^{-\sigma r}}{\sigma r} && r \geqq \frac{2}{3}\,a \end{aligned} \tag{8}$$

For the final state which corresponds to $\ell = 1$

$$\begin{aligned} R_f &= N_1'(2\alpha' r)e^{-\alpha' r}\,{}_1F_1(2-\lambda', 2\ell + 2, 2\alpha' r) && r \leqq \tfrac{2}{3}a \\ &= j_1(k'r)\cos\eta_1 - n_1(k'r)\sin\eta_1 && r \geqq \tfrac{2}{3}a \end{aligned} \tag{9}$$

where the quantities λ, α and σ are those defined in Appendix IIA. The evaluation of the matrix element involves essentially the integral given by Eq. (5). Integrations are carried out separately for the regions $r \leqq \frac{2}{3}a$ and $r \geqq \frac{2}{3}a$.

B <u>Evaluation of the Rosseland Mean</u>

As shown by Eq. (3.3), the Rosseland mean is given by

$$\frac{1}{K} = \frac{\displaystyle\int_0^\infty \frac{1}{k_\omega}\,\frac{1}{(1 - e^{-\omega/T_a})}\,\frac{\partial I(\omega)}{\partial T_a}\,d\omega}{\displaystyle\int_0^\infty \frac{\partial I(\omega)}{\partial T_a}\,d\omega} \tag{10}$$

Let $u = \omega/T_a$

$$I = \frac{8\pi}{h^2c^3}\,\frac{\omega^3}{e^{\omega/T_a} - 1}$$

Equation (10) becomes

$$\frac{1}{K} = \frac{\displaystyle\int_0^\infty \frac{1}{k_\omega} \frac{u^4 e^{-u}}{(1 - e^{-u})^3}\, du}{\displaystyle\int_0^\infty \frac{u^4 e^{-u}}{(1 - e^{-u})^2}\, du}$$

Since k_ω can be written as $f(u) \frac{1}{u^3}$

$$\frac{1}{K} = \frac{\displaystyle\int_0^\infty \frac{1}{f(u)} \frac{u^7 e^{2u}}{(e^u - 1)^3}\, du}{\displaystyle\int_0^\infty \frac{u^4 e^u}{(e^u - 1)^2}\, du}$$

$$\int_0^\infty \frac{u^4 e^u}{(e^u - 1)^2}\, du = \frac{4\pi^4}{15}$$

Therefore

$$\frac{1}{K} = \frac{15}{4\pi^4} \int_0^\infty \frac{1}{f(u)} \frac{u^7 e^{2u}}{(e^u - 1)^3}\, du$$

The integral $S(x) = \frac{15}{4\pi^4} \int_0^x \frac{u^7 e^{2u}}{(e^u - 1)^3}\, du$ has been evaluated by Strömgren(7) for values of x from 0 to ∞. A more accurate table is given by Morse.(24) If f(u) is a function of u, then a numerical integration has to be carried out.

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BIOGRAPHICAL NOTE

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