

Thermodynamics and Statistical Mechanics of a Three-Level Maser*

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The three "spin" states of a maser are treated as individual chemical species. It is assumed that these three species are in thermal equilibrium with the lattice at temperature T but that they are not necessarily in chemical equilibrium with one another. The principle of minimum entropy production is used to derive an equation of reaction equilibrium from which the steady-state behavior of the system with a microwave pump may be completely described. In addition to the population distribution, which is in agreement in first order with the results obtained by solving the rate equations, explicit expressions are obtained for the internal energy, heat capacity, and entropy. The calculations are extended to include spontaneous emission and cross-relaxation as well as the usual thermal relaxation mechanisms.

I. INTRODUCTION

CONSIDER N paramagnetic impurity ions in a diamagnetic crystal placed in an external magnetic field. Let us suppose that the interaction between the spin magnetic moment of each ion and the combined magnetic and crystal field gives rise to three unequally spaced levels: E_i ($i=1,2,3$). Spin lattice relaxation mechanisms are "thermalizers." That is, they tend to bring the system to a Boltzmann distribution at the lattice temperature T . These are denoted in the customary way by the thermal transition probabilities w_{ij} ($i,j=1,2,3$) where $w_{ij}=w_{ji}\exp[(E_i-E_j)/kT]$. Time-varying magnetic fields of the proper frequencies are "equalizers." That is, they induce transitions between pairs of levels which tend to equalize (or saturate) the population distribution. The radiative induced transition probabilities are specified in the usual way by W_{ij} ($i,j=1,2,3$) where $W_{ij}=W_{ji}$. Competition between the thermal and radiative transition probabilities leads to a steady-state population distribution, denoted by n_i . The power output, gain-bandwidth product, noise-temperature, and other performance features of a three-level maser may be calculated once the n_i are known. The conventional method used to calculate the n_i is by solution of the rate equations and normalization condition:

$$\frac{dn_i}{dt} = \sum_j (n_j w_{ji} - n_i w_{ij}) + \sum_j W_{ij} (n_j - n_i) = 0, \quad (1)$$

$$N = \sum_{i=1}^3 n_i. \quad (2)$$

It is the purpose of this paper to analyze the problem of a three-level maser from the point of view of statistical mechanics and irreversible thermodynamics. This approach yields results which are consistent with those obtained by a solution of the rate equations. In addition it enables one to calculate related thermodynamic

quantities such as the internal energy, heat capacity, and entropy, and to describe in detail what happens to the "pump" power. The theory may be readily extended to include spontaneous emission and cross-relaxation.

II. STATISTICAL MECHANICS AND IRREVERSIBLE THERMODYNAMICS OF A THREE-LEVEL MASER

A. Statistical Mechanics

We divide the N paramagnetic ions into three chemical species corresponding to the three energy values, E_i . We assume that these three chemical species are in thermal equilibrium with the lattice at temperature T but they are not necessarily in chemical equilibrium with one another. The total partition function for a single ion with spin energy E_i may be written as the product of z_i and z_l , where $z_i = \exp(-E_i/kT)$ and z_l is a factor associated with all other contributions to the energy of the ion. We assume z_l is the same for all three chemical species and focus our attention on the partial partition function z_i . The corresponding partition function¹ for n_i identical ions of energy E_i is

$$Z_i = [\exp(-E_i/kT)]^{n_i}/n_i!. \quad (3)$$

The free energy F_i associated with the i th species is given by

$$F_i = -kn_i T \ln Z_i = -kn_i T \ln z_i + kT \ln n_i! \\ = n_i E_i + kT \ln n_i!. \quad (4)$$

The internal energy, entropy, and chemical potential for the i th species may be found from F_i as follows:

$$U_i = -T^2(\partial/\partial T)(F_i/T) = n_i E_i, \quad (5)$$

$$S_i = -(\partial F_i/\partial T)_{n_i} = -k \ln n_i!, \quad (6)$$

$$\mu_i = (\partial F_i/\partial n_i)_T = E_i + kT \ln n_i. \quad (7)$$

The expression for μ_i is obtained with the aid of Stirling's approximation,

$$\ln n_i! \simeq n_i \ln n_i - n_i. \quad (8)$$

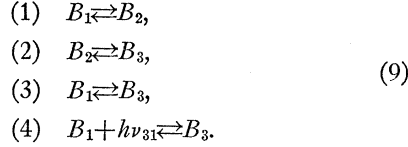
* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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¹ L. D. Landau and E. M. Lifschitz, *Statistical Physics* (Addison-Wesley Publishing Company, Reading, Massachusetts, 1958), p. 120.

B. Irreversible Thermodynamics

Let B_i denote the i th chemical species and consider the following "chemical" reactions among these species.



The first three reactions are thermal relaxation processes in which the lattice supplies or receives energy from the paramagnetic spin system. The last reaction represents a radiative transition induced by the presence of a time varying electromagnetic field of frequency $\nu_{31} = (E_3 - E_1)/h$.

We define the chemical affinities A_j ($j=1,2,3$) and the differential degrees of advancement $d\xi_k$ ($k=1,2,3,4$) as follows:

$$\begin{aligned} A_1 &\equiv \mu_2 - \mu_1, \\ A_2 &\equiv \mu_3 - \mu_2, \\ A_3 &\equiv \mu_3 - \mu_1, \end{aligned} \quad (10)$$

$$\begin{aligned} d\xi_1 &\equiv d_1 n_1 = -d_1 n_2, \\ d\xi_2 &\equiv d_2 n_2 = -d_2 n_3, \\ d\xi_3 &\equiv d_3 n_1 = -d_3 n_3, \\ d\xi_4 &\equiv d_4 n_1 = -d_4 n_3. \end{aligned} \quad (11)$$

In Eq. (11), $d_k n_i$ means the change in n_i due to the k th reaction,

$$dn_i \equiv \sum_{k=1}^4 d_k n_i. \quad (12)$$

We assume the validity of the Gibbs relation when the system is not necessarily in thermodynamic equilibrium:

$$TdS = dU - \sum_i \mu_i dn_i + dW. \quad (13)$$

We set $dW=0$ on the assumption that the sample volume and static magnetic field are held constant. With the aid of Eqs. (10)–(12), Eq. (13) may be rewritten as follows:

$$TdS = dU + \sum_{j=1}^3 A_j d\xi_j + A_3 d\xi_4. \quad (14)$$

The internal entropy production associated with the irreversible relaxation processes is

$$d_i S/dt = (1/T) A_j (d\xi_j/dt). \quad (15)$$

The $d\xi_j/dt$ and the A_j are related as follows:

$$\begin{aligned} d\xi_1/dt &= d_1 n_1/dt = n_2 w_{21} - n_1 w_{12} \simeq (N/3kT) w_{21} A_1, \\ d\xi_2/dt &= d_2 n_2/dt = n_3 w_{32} - n_2 w_{23} \simeq (N/3kT) w_{32} A_2, \\ d\xi_3/dt &= d_3 n_1/dt = n_3 w_{31} - n_1 w_{13} \simeq (N/3kT) w_{31} A_3, \\ d\xi_4/dt &= d_4 n_1/dt = (n_3 - n_1) W_{13} \simeq (N/3kT) W_{13} (A_3 - h\nu_{31}). \end{aligned} \quad (16)$$

Two approximations are made in obtaining the right-hand side of Eq. (16) from Eq. (10):

$$A_j \ll kT \quad \text{and} \quad h\nu_{ij} \ll kT. \quad (17)$$

Combining Eqs. (15) and (16), we have

$$\begin{aligned} d_i S/dt &\simeq (N/3kT^2) [w_{21} A_1^2 + w_{32} A_2^2 + w_{31} A_3^2] \\ &\simeq (N/3kT^2) [w_{21} A_1^2 + w_{32} (A_1^2 - 2A_1 A_3 + A_3^2) \\ &\quad + w_{31} A_3^2]. \end{aligned} \quad (18)$$

The second form for Eq. (18) follows from the fact that the A_j are not independent:

$$A_2 = A_3 - A_1. \quad (19)$$

In thermodynamic equilibrium $d_i S/dt=0$. It follows from Eqs. (18), (10) and (7) that $A_1=A_2=A_3=0$, $\mu_1=\mu_2=\mu_3$, and $n_i/n_j = \exp[(E_j - E_i)/kT]$, which is the normal Boltzmann distribution.

In the presence of a radiative "pumping" field, A_3 is held fixed at a nonzero value:

$$A_3 = s h\nu_{13}, \quad 0 \leq s \leq 1. \quad (20)$$

Equation (20) may be used as the defining equation for s , the saturation parameter. It may be readily interpreted with the help of Eqs. (7) and (10).

$$n_1/n_3 = \exp[h\nu_{31}(1-s)/kT]. \quad (21)$$

When $s=0$, there is no "pumping" field and we have the Boltzmann distribution. When $s=1$, the "pumping" field completely saturates levels 1 and 3 for which $n_1=n_3$. If Eq. (21) is expanded and only the linear term is retained, s is seen to be the same as the parameter defined by Overhauser²:

$$s = 1 - (n_1 - n_3)/(N_1 - N_3), \quad (22)$$

where the N_i 's represent the normalized Boltzmann population distribution. In the presence of the constraint on the system represented by $A_3 \neq 0$, the principle of minimum entropy production requires that

$$(\partial/\partial A_1)(d_i S/dt) = 0. \quad (23)$$

Carrying out the indicated differentiation on the second form of Eq. (18) leads to the condition

$$w_{21} A_1 = w_{32} A_2. \quad (24)$$

This is equivalent to the equation of reaction equilibrium

$$\mu_2 = f_1 \mu_1 + f_2 \mu_3, \quad (25)$$

where

$$f_1 \equiv w_{21}/(w_{21} + w_{32}) \quad \text{and} \quad f_2 \equiv w_{32}/(w_{21} + w_{32}). \quad (26)$$

This is one of the principal results of this paper. In conjunction with the normalization condition $\sum_i n_i = N$, it enables one to calculate the normalized population distribution of the three-level maser in terms of the saturation parameter, the relaxation rates, the energy

² A. W. Overhauser, Phys. Rev. **92**, 411 (1953).

level separations, and the lattice temperature. From Eqs. (7) and (24), it follows, for example that

$$n_3/n_2 = \exp[(f_1 s h \nu_{31} - h \nu_{32})/kT]. \quad (27)$$

If we take the linear term in the expansion of Eq. (27), the population difference is

$$n_3 - n_2 = \frac{Nh}{3kT} \left[\frac{s \nu_{31} w_{21} - \nu_{32} (w_{21} + w_{32})}{w_{21} + w_{32}} \right]. \quad (28)$$

In the limit of complete saturation, $s=1$, Eq. (28) yields a well-known consequence³ of the rate equations.

C. Internal Energy, Heat Capacity, and Entropy

It is now a simple matter to compute the internal energy, heat capacity, and entropy of a three-level maser.

$$U = \sum_{i=1}^3 U_i = \sum_{i=1}^3 n_i E_i, \quad (29)$$

$$C_H = (\partial U / \partial T)_H, \quad (30)$$

$$S = \sum_i k n_i (1 - \ln n_i) = Nk - k \sum_i n_i \ln n_i. \quad (31)$$

Thus

$$U(s=1) = \frac{N}{3} (\nu_{31} + \nu_{21}) - \frac{Nh^2}{9kT} (\nu_{21} - \nu_{32}) \left(\frac{\nu_{21} w_{21} - \nu_{32} w_{32}}{w_{21} + w_{32}} \right), \quad (32)$$

$$U(s=0) = \frac{N}{3} (\nu_{31} + \nu_{21}) - \frac{2Nh^2}{9kT} (\nu_{21}^2 + \nu_{21} \nu_{32} + \nu_{32}^2), \quad (33)$$

$$C_H(s=1) = \frac{Nh^2}{9kT^2} (\nu_{21} - \nu_{32}) \left(\frac{\nu_{21} w_{21} - \nu_{32} w_{32}}{w_{21} + w_{32}} \right) + \Phi(T), \quad (34)$$

$$C_H(s=0) = \frac{2Nh^2}{9kT^2} (\nu_{21}^2 + \nu_{21} \nu_{32} + \nu_{32}^2). \quad (35)$$

In Eq. (34), $\Phi(T)$ is added to take into account the temperature dependence of the thermal relaxation rates.

$$\Phi(T) = -\frac{Nh^2}{9kT} (\nu_{21} - \nu_{32}) \left(\nu_{21} \frac{\partial f_1}{\partial T} - \nu_{32} \frac{\partial f_2}{\partial T} \right). \quad (36)$$

If the thermal relaxation rates increase linearly with temperature, a not unreasonable assumption, then $\Phi(T)=0$.

From Eqs. (32) and (33), if $w_{21}=w_{32}$, we find that the internal energy of a fully saturated maser *exceeds* that of an unsaturated maser by $\frac{1}{6}N(h\nu_{31})^2/kT$.

³ See, for example, J. Weber's review article on masers, *Revs. Modern Phys.* **31**, 681 (1959).

From Eqs. (34) and (35), if $w_{21}=w_{32}$, we find that the heat capacity of a saturated maser is *less* than that of an unsaturated maser by $\frac{1}{6}Nk(h\nu_{31}/kT)^2$.

For the special case of $s=1$ and $w_{21}=w_{32}$,

$$S(s=1) - S(s=0) \simeq \frac{1}{6}Nk \ln \left[\frac{N}{3} \left(\frac{h\nu_{31}}{kT} \right)^2 \right]. \quad (37)$$

It is not surprising that the entropy of the paramagnetic spin system in thermodynamic equilibrium is less than that of the saturated system. The entropy is a maximum for the equilibrium state provided the energy is held constant, a condition which is clearly not met when a radiation field is pumping energy into the system.

D. Power Absorption

It is instructive to inquire what happens to the power P_{13} , absorbed by the maser system:

$$P_{13} = (n_1 - n_3)h\nu_{13}W_{13} \simeq \frac{N}{3} \left(\frac{h\nu_{13}}{kT} \right) (1-s)W_{13}. \quad (38)$$

A fraction s of this power increases the internal energy of the maser without an increase in temperature. This is represented by the last term on the right-hand side of Eq. (14):

$$-A_3 \frac{d\xi_4}{dt} = s(n_1 - n_3)h\nu_{13}W_{13} \simeq \frac{N}{3} \left(\frac{h\nu_{13}}{kT} \right) s(1-s)W_{13}. \quad (39)$$

The balance, $(1-s)P_{13}$, increases the temperature of the sample without an increase in the internal energy of the spin system. If the maser material is kept at constant temperature T , this power boils off some of the liquid helium or liquid nitrogen coolant. In the steady state the rate of increase in internal energy is exactly compensated by the power lost due to thermal relaxation. This latter is represented by

$$T \left(\frac{dS}{dt} \right)_{\min} = \frac{N}{3kT} (sh\nu_{13})^2 \left(w_{31} + \frac{w_{21}w_{32}}{w_{21} + w_{32}} \right). \quad (40)$$

By equating Eqs. (39) and (40) for the steady state, we find an explicit expression for the saturation parameter:

$$s = \frac{W_{13}(w_{32} + w_{21})}{W_{13}(w_{32} + w_{21}) + w_{31}w_{21} + w_{31}w_{32} + w_{21}w_{32}}. \quad (41)$$

This result may also be obtained by using Eq. (22) as the definition for s and solving the rate equations with the linear approximation to the Boltzmann factor.⁴ As the saturation is increased to higher levels, less of the power absorbed is used to increase the sample temperature (or boil the coolant) and more is used to increase

⁴ W. A. Barker, Argonne National Laboratory Report 6390, June, 1961 (unpublished).

the internal energy of the maser system. In the limit of $s=1$, when $W_{13} \gg w_{ij}$, we see from Eqs. (38)–(41) that

$$P_{13} = \frac{N}{3kT} (h\nu_{13})^2 \left(w_{31} + \frac{w_{32}w_{21}}{w_{32}+w_{21}} \right) = T \left(\frac{d_i S}{dt} \right)_{\min}. \quad (42)$$

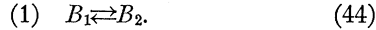
E. Spontaneous Emission and Cross Relaxation

In maser systems spontaneous emission⁵ and cross-relaxation⁶ processes may be important. The foregoing theory may be extended to take these mechanisms into account. In addition to the thermal relaxation probabilities w_{ij} let us consider a spontaneous emission probability A_{21} and a cross-relaxation probability w_{2123} . A_{21} tends to deplete the population of level 2 and increase the population of level 1 by emission of a photon. It is important to note that the relation

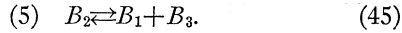
$$w_{21} + A_{21} = w_{12} \exp(h\nu_{21}/kT) \quad (43)$$

is now required to produce a Boltzmann distribution among the energy levels of the maser system in the absence of external constraints. w_{2123} tends to bring the populations of levels 1 and 2 into equilibrium with the populations of levels 2 and 3. It is important to bear in mind that w_{2123} is appreciable only if $\nu_{21} - \nu_{32}$ is small.

Spontaneous emission as well as nonradiative thermal relaxation is now understood to be included in the reaction



Cross-relaxation may be taken into account by adding a fifth "chemical" reaction to Eqs. (9):



And to Eqs. (10) and (11), we must therefore add another chemical affinity and differential degree of advancement:

$$A_5 \equiv (\mu_3 - \mu_2) + (\mu_1 - \mu_2), \quad (46)$$

$$d\xi_5 \equiv d_5 n_2 = -d_5 n_1 - d_5 n_3. \quad (47)$$

The relationship between the $d\xi_j/dt$ and the A_j is now more complicated than that specified by Eqs. (16). The first of Eqs. (16) now has an added term due to spontaneous emission:

$$\begin{aligned} d\xi_1/dt &= d_1 n_1/dt = n_2 w_{21} - n_1 w_{12} + n_2 A_{21} \\ &\simeq (N/3kT)(w_{21} + A_{21})A_1. \end{aligned} \quad (48)$$

An additional equation is required to describe the specified cross-relaxation effect.

$$\begin{aligned} d\xi_5/dt &= (w_{2123}/N)(n_1 n_3 - n_2^2) \\ &\simeq (N w_{2123}/9kT)[A_5 + h(\nu_{21} - \nu_{32})] \\ &\simeq N w_{2123} A_5 / 9kT. \end{aligned} \quad (49)$$

The right-hand sides of Eqs. (48) and (49) are obtained from Eq. (10) and the approximations of Eqs. (17) and in addition explicit use is made of Eq. (43) and of the fact that $\nu_{21} - \nu_{32}$ is small. The rate of internal entropy production now has two additional terms:

$$\begin{aligned} \frac{d_i S}{dt} &= \frac{N}{3kT^2} [(w_{21} + A_{21})A_1^2 + w_{32}A_2^2 + w_{31}A_3^2 + \frac{1}{3}w_{2123}A_5^2] \\ &\quad + \frac{N}{3kT^2} (w_{21} + A_{21})A_1^2 + w_{32}(A_1^2 - 2A_1A_3 + A_3^2) \\ &\quad + \frac{1}{3}w_{2123}(A_3^2 - 4A_1A_3 + 4A_1^2). \end{aligned} \quad (50)$$

The second form of Eq. (50) makes use of the inter-relationship among the chemical affinities:

$$A_5 = A_2 - A_1 = A_3 - 2A_1. \quad (51)$$

In thermodynamic equilibrium $d_i S/dt = 0$ again leads to the Boltzmann distribution. On the other hand if A_3 is held fixed at a nonzero value to represent the radiation "pump" field, then the principle of minimum entropy production requires that $(\partial/\partial A_1)(d_i S/dt) = 0$. This now leads to a more general condition:

$$(w_{21} + A_{21} + \frac{2}{3}w_{2123})A_1 = (w_{32} + \frac{2}{3}w_{2123})A_2, \quad (52)$$

which is equivalent to the equation of reaction equilibrium

$$\mu_2 = \mu_1 f_1' + \mu_3 f_2', \quad (53)$$

where

$$\begin{aligned} f_1' &= (w_{21} + A_{21} + \frac{2}{3}w_{2123}) / (w_{21} + A_{21} + w_{32} + \frac{4}{3}w_{2123}), \\ f_2' &= (w_{32} + \frac{2}{3}w_{2123}) / (w_{21} + A_{21} + w_{32} + \frac{4}{3}w_{2123}). \end{aligned} \quad (54)$$

Since Eq. (53) is precisely of the same form as Eq. (25), all the previous results derived for thermal relaxation mechanisms may now be extended to include spontaneous emission and cross relaxation by using the following simple prescription:

$$\begin{aligned} w_{21} &\rightarrow w_{21} + A_{21} + \frac{2}{3}w_{2123}, \\ w_{32} &\rightarrow w_{32} + \frac{2}{3}w_{2123}. \end{aligned} \quad (55)$$

III. CONCLUSION

It has been shown in this paper that the principle of minimum entropy production leads to an equation of reaction equilibrium which may be used in a statistical mechanical formulation to calculate the population distribution of a three-level maser. The mechanisms considered include thermal relaxation effects, spontaneous emission, and cross-relaxation. The approximations made are

$$\begin{aligned} (1) \quad & h\nu_{ij} \ll kT, \quad i \neq j = 1, 2, 3; \\ (2) \quad & sh\nu_{13} \ll kT \\ (3) \quad & f_2' sh\nu_{13} \ll kT \quad \left\{ \begin{array}{l} (A_j \ll kT), \\ (A_j \gg kT), \end{array} \right. \quad (56) \\ (4) \quad & \nu_{21} - \nu_{32} \simeq 0 \quad (\text{cross-relaxation}). \end{aligned}$$

⁵ T. Maiman, Nature **187**, 493 (1960) and Phys. Rev. Letters **4**, 564 (1960).

⁶ N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. **114**, 445 (1959).

Inasmuch as s and f_2' are less than or equal to unity, approximations (2) and (3) are less restrictive than (1). The results for the population distribution agree with those obtained from the rate equations in first order when approximation (1) is also made.

The new features of this paper include explicit calculations of the internal energy, heat capacity, entropy, saturation parameter, and minimum entropy production of a three-level maser. The spontaneous emission and cross relaxation mechanisms introduced tend to reduce the value of the saturation parameter from its value given in terms of w_{ij} and W_{13} alone. Since w_{2123} is appreciable when $\nu_{21} - \nu_{32}$ is small, this cross relaxation mechanism has an interesting effect

on the maser's internal energy and heat capacity as can be seen by an inspection of Eqs. (32)–(35) inclusive. As s goes from 0 to 1, the internal energy of a three level maser is increased by $(2N\hbar^2/9kT)(\nu_{21}^2 + \nu_{21}\nu_{32} + \nu_{32}^2)$ whereas the associated heat capacity is decreased from its equilibrium value of $(2N\hbar^2/9kT^2)(\nu_{21}^2 + \nu_{21}\nu_{32} + \nu_{32}^2)$ to zero.

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Energy Dissipation by Ions in the kev Region

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At low energies ionic collisions with atoms are largely elastic. Simple theoretical approximations to scattering cross sections, ranges and straggling are derived for power potentials, showing that the scattering is peaked in the forward direction rather than isotropic. Using an approximate universal potential of Thomas-Fermi type a natural measure of range, ρ , and of energy, ϵ , is obtained for all ions in all substances. The corresponding range-energy curve is computed.

At higher ion energies the electronic excitation becomes increasingly important. An approximate formula is given for the electronic stopping contribution, increasing proportional to ion velocity at low and moderate velocities. These results are applied in the interpretation of a few isotope effects, observed in range measurements.

FOR ions with velocity v comparable to or less than $v_0 = e^2/\hbar$, an interesting competition appears between loss of energy to electrons and loss of energy to atomic recoils, corresponding to stopping cross sections per atom S_e and S_r . Quantities of importance to this competition are S_e and S_r , combined with some averages over the differential cross section $d\sigma_r$ for scattering of the ion by a recoiling atom. The present discussion of the velocity region $v \lesssim v_0$ is intended as a step toward a quantitative treatment of the processes involved.

At first we shall disregard energy loss to electrons and discuss atomic recoils only. Bohr¹ introduced the assumption that S_r is nearly a constant in a considerable velocity interval at low velocities, and used arguments of the Thomas-Fermi type in order to give a comprehensive description. In fact, the Thomas-Fermi treatment gives an important simplification and a fair accuracy, at energies large compared to the Rydberg unit.

* Deceased.

¹ N. Bohr, Kgl. Danske Videnskab. Selskab, Mat.—fys. Medd. 18, No. 8 (1948).

The scattering problem in nearly elastic collisions between atoms and ions at low velocities can be treated by classical mechanics. It follows from dimensional arguments that the potential must behave as r^{-2} if S_r is independent of velocity. The scattering in this potential is very closely given by the useful formula

$$d\sigma_r = (S_r/2T_m^{\frac{1}{2}}) (dT/T^{\frac{3}{2}}), \quad (1)$$

where $T_m = 2M_1^2 M_2 v^2 / (M_1 + M_2)^2$ is the maximum value of the energy transfer T . The scattering cross section (1) has a large probability for small angular deflections, and is similar to the Rutherford scattering rather than to the isotropic scattering of hard-sphere collisions. Assume that the potential is $V = \xi_e Z_1 Z_2 e^2 a / 2r^2$, with the parameter a given by

$$a = (\hbar^2/m_e^2) \times 0.8853 (Z_1^{\frac{2}{3}} + Z_2^{\frac{2}{3}})^{-\frac{1}{2}}, \quad (2)$$

and therefore of similar type to the Thomas-Fermi unit of length. We then obtain the formula