Thomas-Fermi Calculation of Potential Between Atoms

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ABSTRACT

A Thomas-Fermi model calculation of the potential
energy for the collision of two neutral, identical atoms
is developed. The classical scattering distribution
for this potential is compared to Rutherford scattering.

I. INTRODUCTION

In a collision between two atoms in which the
atomic velocities are somewhat lower than the atomic
electron velocities, one may expect the Thomas-Fermi
model to give a fairly reasonable estimate of the
interatomic force. Non-adiabatic effects such as
the excitation of excited states and ionization will,
of course, not come out of the calculation. Molecu-
lar binding effects will also not show up, for as we
shall see, the Thomas-Fermi method can only give
rise to a potential which is everywhere repulsive.
The range of validity of such a calculation is
therefore for atomic kinetic energies somewhat
greater than, say, 10 eV and for atomic velocities
somewhat less than, say, 10^8 cm/sec.

In Sec. II, some general theorems concerning
the Thomas-Fermi model are discussed. In Sec. III,
a calculation of the potential energy for the
collision of two neutral, identical atoms is de-
scribed, and in Sec. IV, the classical scattering
distribution for this potential is given.

II. GENERAL THEOREMS CONCERNING THE THOMAS-FERMI MODEL

We imagine that the ion (nuclear) charge
distribution ρ_+ is held fixed by suitable external
forces. The distribution ρ_+ is a series of δ-func-
tions, but we need not specify it in detail at
present, nor do we need to restrict our consideration
to any specific number of nuclei. The Thomas-Fermi

method then consists of solving the Poisson equation
for the electrostatic potential ϕ,

$$\nabla^2 \phi = -4\pi\rho_+ - 4\pi\rho_- \qquad (1)$$

where ρ_-, the electron charge density, is given by

$$\rho_- = -A\phi^{3/2} . \qquad (2)$$

The constant A is given by

$$A = \frac{2e}{(2\pi\hbar)^3} \frac{4\pi}{3} (2me)^{3/2} . \qquad (3)$$

Here the symbols have their usual meanings, and e is
taken positive. According to the model, the kinetic
energy T_- of the electrons is

$$T_- = \frac{3}{5} A \int \phi^{5/2} d^3x . \qquad (4)$$

We shall discuss three simple but interesting
theorems that apply to the problem posed here. The
first of these is the virial theorem, which is
rather well known.[*] The virial V is defined as usual
as the integral of $\vec{r} \cdot \vec{F}$ ($\vec{r}$ = position, $\vec{F}$ = force) over
the electron distribution,

$$V = -\int \rho_- \vec{r} \cdot \nabla\phi \, d^3x . \qquad (5)$$

[*]See P. Gombas, Die Statistische Theorie des Atoms
und ihre Anwendungen, Wien, Springer-Verlag, 1949.

If the Thomas-Fermi expression (2) is used for ρ_- here, one finds, after integration by parts, that

$$V = -\frac{6}{5} A \int \phi^{5/2} d^3x = -2T_- \quad . \qquad (6)$$

On the other hand, if one replaces $\nabla\phi$ in Eq. (5) by

$$-\nabla\phi = \int \frac{(\vec{r} - \vec{r}')}{|\vec{r} - \vec{r}'|^3} \rho(\vec{r}') d^3x;$$

one finds that

$$V = V - \sum_{\text{ions}} Ze \, \vec{r} \cdot \vec{E} \quad . \qquad (7)$$

Here V is the total electrostatic potential energy of electrons and ions, and $\vec{E}$ is the electric field at position of the ion (excluding its self-field). The sum is extended over all ions. Comparison of Eqs. (6) and (7) yields the viral theorem

$$V = -2T_- + \sum_{\text{ions}} Ze \, \vec{r} \cdot \vec{E} \quad . \qquad (8)$$

The second theorem says that in any displacement of the ions, the work done against the electric fields which they see goes into increasing $T_- + V$ -- that is to say, $T_- + V$ is the potential energy for the motion of the ions. This theorem therefore amounts to the conservation of energy for the system of ions and electrons. To prove the theorem, we make a variation $\delta\rho_+$ in the ion charge density. Through Eqs. (1) and (2), this will induce variations $\delta\phi$ and $\delta\rho_-$, which will satisfy

$$\nabla^2\delta\phi = -4\pi\delta\rho_+ - 4\pi\delta\rho_- \qquad (9)$$

and

$$\delta\rho_- = -\frac{3}{2} A\phi^{1/2}\delta\phi \quad . \qquad (10)$$

Multiplying Eq. (1) by $\delta\phi$, Eq. (9) by ϕ, subtracting and integrating over space yields ($\rho = \rho_+ + \rho_-$)

$$\int \phi\delta\rho_+ = \int \rho\delta\phi - \int \phi\delta\rho_- \quad . \qquad (11)$$

Now $\int \phi\delta\rho_+$ is the work done by the ions against the electric fields which they see, and $\int \rho\delta\phi$ is the change in the electrostatic potential energy of ions and electrons. Furthermore, $-\int \phi\delta\rho_-$ is the work done by the electric field on the electrons, and this ought to equal the change in kinetic energy of

the electrons. In fact, using Eq. (10),

$$-\int \phi\delta\rho_- = \frac{3}{2} A \int \phi^{3/2} \delta\phi = \delta T_-$$

according to Eq. (4), and the theorem is proven.

The third theorem relates the electric forces on the ions to the electron pressure. According to the Maxwell stress theory, the electric force on the charges in a volume V is related to the electric stresses on the surface S of the volume,

$$\int_V \rho E_i d^3x = \int_S n_j T_{ij} d^2x \quad . \qquad (12)$$

Here E_i is the i'th component of the electric field, the vector n_j is the inward normal to the surface, and T_{ij} is the electric stress tensor

$$T_{ij} = \frac{1}{8\pi} \delta_{ij} E^2 - \frac{1}{4\pi} E_i E_j \qquad (13)$$

in Cartesian coordinates. Separating ρ into ρ_+ and ρ_-, we find that the force on the ions in any volume is

$$\int_V \rho_+ E_i d^3x = -\int_V \rho_- E_i d^3x + \int_S n_j T_{ij} d^2x \quad . \qquad (14)$$

Now the electric force on the electrons is, according to Eq. (2)

$$\int_V \rho_- E_i d^3x = A \int_V \phi^{3/2} \frac{\partial}{\partial x_i} \phi \, d^3x = -\int_S p n_i d^2x \qquad (15)$$

where we have introduced the electron pressure

$$p = \frac{2}{5} A\phi^{5/2} \quad . \qquad (16)$$

(Note that the pressure is two-thirds of the kinetic energy density, appropriate for an ideal gas.) Thus we may rewrite the electric force on the ions as

$$\int_V \rho_+ E_i d^3x = \int_S \left[p n_i + n_j T_{ij} \right] d^2x \quad . \qquad (17)$$

This is the general form of the theorem. The utility of the theorem can be seen by applying it to a simple case where there are only two nuclei, which are identical. If we choose the surface S to be the plane which is the perpendicular bisector of the line joining the two nuclei, we find that the force on one nucleus is in a direction away from the other nucleus, and has magnitude

$$ZeE = \int_S \left(p + \frac{E^2}{8\pi}\right) d^2x \quad \cdot \qquad (18)$$

Since the integrand here is always positive, the force between the two nuclei is always repulsive. Reduction to the simple form (18) depended on the fact that $\vec{E}$ has no component normal to the plane S, which is a result of symmetry in this case. In the general case, with several non-identical nuclei, a similar simple form with positive total pressure holds for the surfaces which nowhere have any normal component of $\vec{E}$. It is therefore intuitively evident that no system of nuclei can be bound in this model.

III. CALCULATION OF THE POTENTIAL FOR TWO IDENTICAL NEUTRAL ATOMS

For two identical atoms, Eqs. (1) and (2) can be reduced to a universal set of equations independent of the nuclear charge Z by using the unit of length

$$\lambda = (4\pi A)^{-2/3}\, e^{-1/3}\, Z^{-1/3} = 0.885\ a_0/Z^{1/3} \qquad (19)$$

where a_0 is the Bohr radius, and the unit of energy

$$\epsilon = Z^2 e^2/\lambda \quad . \qquad (20)$$

The potential function ϕ is replaced by

$$\chi = Ze\phi/\epsilon \quad . \qquad (21)$$

With these units, Eqs. (1) and (2) become

$$\nabla^2\chi = \chi^{3/2} \qquad (22)$$

with the boundary condition that

$$\chi \sim |\vec{r} - \vec{r}_n|^{-1} \qquad (23)$$

near the position of each nucleus $\vec{r}_n$.

Equation (22) has been solved numerically on the IBM-704 for various distances between the two nuclei. Use was made of the solutions χ_1 and χ_2 for the two atoms separately; we let

$$\chi = \chi_1 + \chi_2 + \psi \qquad (24)$$

so that

$$\nabla^2\psi = (\chi_1 + \chi_2 + \psi)^{3/2} - \chi_1^{3/2} - \chi_2^{3/2} \quad . \quad (25)$$

This transformation removes the singularities from ψ at the positions of the nuclei, and probably improves the accuracy of the calculation when the nuclei are far apart. Instead of using Cartesian coordinates, we used the coordinates

$$2\xi = |\vec{r} - \vec{r}_1| + |\vec{r} - \vec{r}_2|$$

$$2\eta = |\vec{r} - \vec{r}_1| - |\vec{r} - \vec{r}_2| \quad .$$

In the differencing, equal intervals of η were used, and equal intervals of $\sqrt{\xi}$, the latter to reduce the number of points at large distances from the nuclei where χ is small. For distances ξ larger than about 12 times the separation of the nuclei, the solution was joined on to the Thomas-Fermi solution for an atom with nuclear charge 2Z.

The second-order Richardson relaxation scheme was used to arrive at the solution of Eq. (25). The kinetic and potential energy integrals $T_- + V$ were then calculated, and the energies of the separated atoms $2U_0$ subtracted, giving the potential U for the collision of the two atoms,

$$U = T_- + V - 2U_0 \quad . \qquad (26)$$

The virial theorem was used as a check on the accuracy. The third theorem of Sec. II, unfortunately, was not used as a check. The virial check was such that we estimate that the calculated potential U is accurate to about five percent. The results are given in Table I.

The asymptotic form of U for close distances can be calculated. This asymptotic form is the potential energy of the two interacting nuclei, $Z^2 e^2/d$, plus the difference in the binding energies of an atom with nuclear charge 2Z and two atoms with nuclear charge Z. The Thomas-Fermi binding energy is[*] -0.681ϵ, which is proportional to $Z^{7/3}$. The asymptotic form of U is therefore, in our units

$$U \rightarrow 1/r - 0.681(2^{7/3} - 2) \qquad (27)$$
$$\rightarrow 1/r - 2.07$$

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[*]P. Gombas, loc cit, p. 60

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TABLE I

POTENTIAL ENERGY AS A FUNCTION OF THE DISTANCE BE-
TWEEN NUCLEI, IN UNITS GIVEN BY EQS. (19) AND (20).

Distance	Energy
1/16	14.4
1/8	6.54
1/4	**2.77**
1/2	1.04
1	0.318
2	0.089
4	0.0103

At a separation of 1/16, this would give $U = 13.97$,
which disagrees with the entry in Table I by three
percent.

We were unable to determine the asymptotic form
for large nuclear separation, but estimate from the
pressure theorem of Sec. II that $U \sim r^{-7}$ in this
limit, using the known asymptotic form of the single
atom function. The numerical integrations obviously
do not go this far out.

IV. CLASSICAL SCATTERING OF TWO IDENTICAL NEUTRAL ATOMS

The classical scattering theory becomes valid
in general when the product of the wave number k of
the particle with the radius of the scattering po-
tential -- the unit of length λ in our case -- is
very large compared to unity. Making the approxima-
tion that the mass number of an atom is twice its Z,
we find that the condition for the validity of
classical scattering is

$$k\lambda \approx 2 \times 10^5 \, Z^{2/3} \left(\frac{v}{c}\right) \gg 1 \qquad (28)$$

where v is the relative velocity of the atoms and c
is the velocity of light. For oxygen atoms, for
example, $k\lambda$ is equal to thirty at an energy of about
ten electron-volts, and the classical approximation
should be quite good.

According to classical mechanics, for scattering
in a central potential $U(r)$, a particle with impact
parameter S is scattered through an angle θ, in the
center-of-mass system, given by

$$\theta(S) = \pi - 2 \int_{r_1}^{\infty} \frac{S \, dr}{r^2 \sqrt{1 - \frac{S^2}{r^2} - \frac{U}{W}}} \qquad (29)$$

where W is the center-of-mass energy, and r_1 is the
value of r at which the radical vanishes. Since
only dimensionless ratios occur in Eq. (29), we may
regard the units of length and energy to be the
Thomas-Fermi units λ and ϵ. The differential scat-
tering cross section (per unit solid angle) in the
center-of-mass system is

$$\sigma(\theta) = \lambda^2 S / \sin \theta \, \frac{d\theta}{dS} \, cm^2 \text{ per steradian} . \quad (30)$$

Equations (29) and (30) may be used to obtain $\sigma(\theta)$
for various values of the energy parameter W. The
result is naturally valid for all Z provided the
length and energy units λ and ϵ are employed. Fig-
ure (1) shows $\sigma(\theta)/\lambda^2$ for various energies. It is
seen that for small energies, where the potential
looks "hard," the scattering is more isotropic than
at high energies, where it tends towards the Ruther-
ford shape. It should be noted that if the incident
and struck particles are not distinguished, the
effective scattering cross section is the sum of
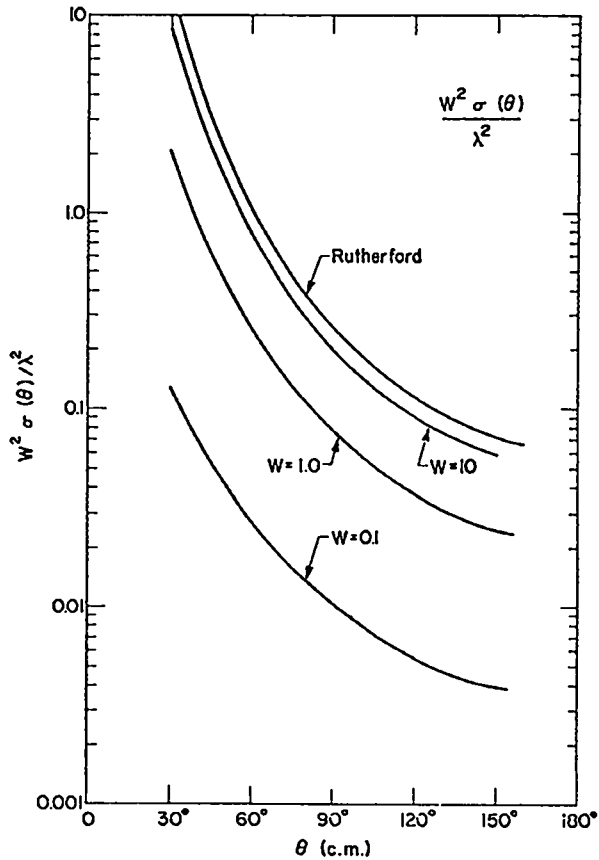$\sigma(\theta)$ and $\sigma(\pi - \theta)$.

Figure 1

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