

## Thomas-Fermi Theory of Excited Atomic States\*

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The usual Thomas-Fermi theory of the atom applies only to ground states. The present paper outlines the general method of extending the theory to excited states and carries out this program in the case of a one-dimensional atom. The treatment is completely self-consistent and yields a nonlinear differential equation which must be solved simultaneously with other equations expressing Bohr-Sommerfeld quantization conditions. Numerical computations show the magnitude of core polarization effects arising from the self-consistent field.

### 1. INTRODUCTION

THE Thomas-Fermi (TF) theory of the atom was originally conceived to describe the ground state of complex atoms. No attempt has been made to extend this theory for the characterization of excited states of the atom in a similar self-consistent manner. (We mean here, of course, the excited states of the whole atom and not the excited energy states of the electrons in the ground state of the atom.) The customary approach treats the nucleus with part of the electron cloud as an ionic core with a fixed potential while distributing the rest of the electrons independently over the different energy levels of the core.<sup>1</sup> This, naturally, is not a self-consistent treatment since the core will, in general, be polarized by the rest of the electrons, and the remaining electrons will also interact with each other.

In this paper we develop a very simple generalization of the original TF theory which is capable of describing excited atomic states in a self-consistent fashion. We restrict, for the moment, our interest to one-dimensional atoms, composed of charged sheets. Although this is physically unrealistic, it has several advantages. First, everything can be immediately visualized because the phase space of an electron is two dimensional. Second, the extension to three dimensions is immediate for states with zero angular momentum, and very simple for the others. Third, the mathematical analysis is simplified, since the ground-state problem can be solved analytically, without the use of numerical methods. And fourth, at this point the one-dimensional self-consistent treatment can be compared with the more approximate ion-core treatment.

### 2. ONE-DIMENSIONAL ATOM

A one-dimensional atom consists of  $N$ -charged sheets (the  $N$  electrons) moving in the presence of a field generated by a  $Z$ -charged sheet located at the origin (the nucleus). The sheets can freely pass through each other and through the nucleus. The potential energy between two charged sheets of unit area will be  $\pm 2\pi q^2|s|$ , where  $s$  is the separation between the sheets. The plus sign refers to attraction (opposite charges), the minus sign to

repulsion. The  $2\pi$  factor comes about because of the  $4\pi$  lines of force emanating from a sheet, half go to the right, and half to the left. The potential is linear in  $s$  in one dimension because the lines of force are everywhere parallel to each other; hence the electric force, the derivative of the potential, must be a constant, and the absolute value arises because the potential must be symmetric in its argument.

An additional constant is free in the potential energy. In three dimensions the added constant is fixed by the agreement that the potential is zero at infinity. Here the electric field is never zero, thus this simple rule is of no use. The only preferred point in space is at the nucleus, and so we let the potential equal zero there. Then, if  $m$ ,  $-e$ ,  $P_i$ ,  $Q_i$  are the mass, charge, momentum, and coordinate of the  $i$ th electron sheet, the Hamiltonian of the whole system is given by

$$H = \frac{1}{2m} \sum_{1 \leq i \leq N} P_i^2 + \sum_{1 \leq i \leq N} U_Z(Q_i) + \sum_{1 \leq i < j \leq N} U_e(Q_i - Q_j),$$

where

$$U_Z(Q_i) = 2\pi Z e^2 |Q_i|; \quad U_e(Q_i - Q_j) = -2\pi e^2 |Q_i - Q_j|.$$

### 3. THOMAS-FERMI MODEL

The purpose of the present paper is to extend the usual Thomas-Fermi theory to excited states, but without attempting to include all known higher order corrections. The usual theory rests on several assumptions which we now list explicitly.

*Assumption 1.* The theory is semiclassical. Each electron is characterized by its position  $Q$ , and momentum  $P$ . The set of  $N$  electrons are described in the  $2N$ -dimensional phase space by the distribution function  $F_N(P_1, Q_1, \dots, P_N, Q_N)$  such that  $F_N(P_1, Q_1, \dots, P_N, Q_N) \times dP_1 \cdots dQ_N / h^N$  gives the probability that  $N$  elements of volume in the neighborhood of  $Q_1, P_1, \dots, Q_N, P_N$  are each occupied by a single electron. In the customary way we may introduce the reduced probability densities  $F_s(P_1, Q_1, \dots, P_s, Q_s)$  by

$$F_s = \int F_N(P_1, Q_1, \dots, P_s, Q_s, P_{s+1}, Q_{s+1}, \dots, P_N, Q_N) dP_{s+1} \cdots dQ_N / h^{N-s}.$$

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<sup>1</sup> P. Gombas, *Die Statistische Theorie des Atoms* (Springer-Verlag, Vienna, 1949).

The function  $F_s dP_1 \cdots dQ_s / h^s$  tell us the probability that  $s$  elements of volume are occupied by one electron each, irrespective of the other  $N-s$  electrons. If  $F_N$  is normalized to unity,  $F_1$  is normalized to  $N$ ,  $F_2$  is normalized to  $N(N-1)$ , and  $F_s$  to  $N!/(N-s)!$

*Assumption 2.* Any approximate theory has as its aim to determine (approximately) the first few members as  $F_1, F_2$ , etc., of the hierarchy of functions  $F_s$ . This is accomplished by an assumption of closure, expressing the higher order functions in terms of the lower order ones. If we close the problem by assuming  $F_2$  to be a functional of  $F_1$ , then only the determination of  $F_1$  is needed, and thus we speak of an independent particle or self-consistent model. If the closure proceeds by expressing  $F_3$  in terms of  $F_2$  and  $F_1$ , we speak of a model in which the pair correlations are also taken into account, but not the higher correlations, and so forth. (It is worthwhile to emphasize this definition, since even in the independent-particle picture some correlation is already taken into account through the self-consistent field, and thus a definition is needed to sharpen the meaning of correlation in these cases.) Assumption 2 states that in the TF theory  $F_2$  is a functional of  $F_1$ , thus giving an independent particle model. The form of this functional depends on further assumptions.

*Assumption 3.* The exclusion principle shall be taken into account in the same way as for noninteracting electrons. This stipulates that the functional form of  $F_1$  and  $F_2$  shall be the same as for a free-electron gas. Hence,  $F_1$  must be zero or one for an electron of a given spin. (We shall assume for simplicity that only electrons with one kind of spin are present to save us a factor of two here and there.)  $F_2$  in turn must be of the form  $F_2(P_1, Q_1; P_2, Q_2) = \text{const}[F_1(P_1, Q_1)F_1(P_2, Q_2)] + \text{additional term}$ , where the additional terms come from the exclusion principle and would lead to the appearance of exchange forces. However, we shall omit the exchange forces in the spirit of the original TF theory.

If these terms are omitted, the constant in the above expression is  $(N-1)/N$  to satisfy the normalization condition on  $F_2$ . This factor is missing in the usual TF theory, except when it appears as the so-called Fermi-Amaldi correction. However, we see that it is necessary to include at a very elementary level.

*Assumption 4.* Finally, we stipulate that the atom is in a stationary state, and so  $F_1$  can only be a function of the constants of motion referring to a particle. Thus, in one dimension  $F_1$  is a function of the energy only.

Assumptions 3 and 4 together tell us that  $F_1$  is piecewise constant, zero or one, and that the boundary surfaces, here simple boundary curves, separating the zero and one regions from each other must be energy constant surfaces with equations given by  $H(P, Q) = E_0$  or  $E_1$ , or  $E_2$ , etc. (Fig. 1). If we knew these surfaces, and a rule by which we could fill in the areas between these surfaces with  $F_1$  equal to one or zero (i.e., one or zero electrons per phase cell), the problem would be solved. To know the surfaces we must determine  $U$ ; to know

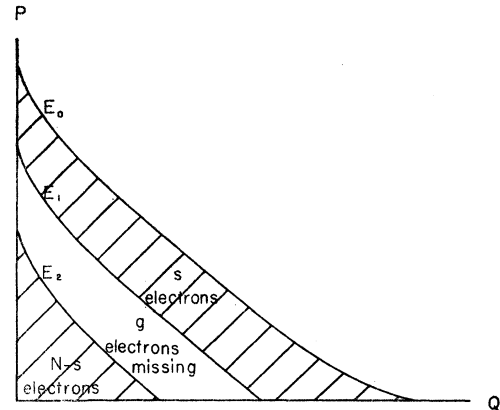


FIG. 1. Electron distribution in  $\mu$  space.

which regions to fill in, we must know whether we are to determine the ground state or an excited state of an atom.

If the atom is to be in its ground state, its energy must be as small as possible. Thus, there must be no holes in the  $\mu$  space distribution. In an excited state there are unfilled layers, gaps, sandwiched among filled ones, where the boundaries are energy constant surfaces (Fig. 1 shows a single-gap excited state, where the shaded areas are filled in). Once we agree which regions to fill in, and which regions to leave out, we proceed as follows.

According to its definition, the potential  $U(Q)$  consists of two parts;  $U_z(Q)$ , the potential of an electron at  $Q$  due to the nucleus at the origin, and  $U_{N-1}(Q)$ , the potential of an electron at  $Q$  due to the  $N-1$  other electrons. If  $U_e(Q-Q')$  is the potential between two electrons at a separation  $|Q-Q'|$ ,  $U_{N-1}(Q)$  is given by

$$U_{N-1}(Q) = \int U_e(Q-Q') \nu(Q, Q') dQ'$$

where

$$\nu(Q, Q') = \int F_2(P, Q; P', Q') \frac{dP dP'}{h} / \int F_1(P, Q) dP.$$

With

$$F_2 = [(N-1)/N] F_1(P, Q) F_1(P', Q'),$$

we get

$$\nu(Q, Q') = \frac{N-1}{N} \int F_1(P', Q') dP' / h.$$

Thus,  $U$  is a solution of the integral equation

$$U(Q) = U_z(Q) + \frac{N-1}{N} \int U_e(Q-Q') n(Q') dQ'; \quad (3.1)$$

where

$$n(Q') = \int F_1(P, Q') dP' / h.$$

To determine  $n(Q')$ , the density at the point  $Q'$ , we observe that  $n(Q')dQ'$  is the area of a strip of width  $dQ'$  at  $Q'$  parallel to the  $P$  axis, not counting those segments of the strip which lie in the unfilled regions or gaps. If we define momenta  $P_0, P_1, P_2$ , etc., by the equations

$$\begin{aligned} P_0^2/2m+U=E_0, \quad P_1^2/2m+U=E_1, \\ P_2^2/2m+U=E_2 \end{aligned} \quad (3.2)$$

(the equations of the boundaries of the different regions), and if the phase space is filled in up to the energy  $E_0$ , leaving the region between the two energy constant surfaces unfilled, then  $n(Q)$  is simply given by the expression

$$n(Q) = (2/\hbar)[P_0 - (P_1 - P_2)]. \quad (3.3)$$

If the space distribution has more empty layers, we get additional terms on the right-hand side of (3.3). For the ground state, there are no holes in the distribution, and the right-hand side contains only the  $P_0$  term. [In three dimensions we would get a sum of terms like  $(4\pi/3)P_0^3/\hbar^3$ , this being now the volume of the different cross sections of the six-dimension phase space at  $Q$  bounded by the constant energy surfaces.]

For simplicity we shall discuss the case where there is only one gap in the phase-space distribution since the extension to more than one gap is obvious. We determine the values of  $E_0, E_1, E_2$  with the Bohr-Sommerfeld quantization conditions. Let us suppose that there are a total of  $N$  electrons, where  $N-s$  of these are accommodated below  $E_2$ . Let the gap between  $E_2$  and  $E_1$  accommodate  $g$  electron holes ( $s \leq N, g \geq 0$ ). Then, according to the quantization conditions,

$$\begin{aligned} \oint P_0(E_0, Q) dQ &= (N+g)\hbar, \\ \oint P_1(E_1, Q) dQ &= (N-s+g)\hbar, \\ \oint P_2(E_2, Q) dQ &= (N-s)\hbar. \end{aligned} \quad (3.4)$$

In one dimension these equations have a very simple geometrical meaning. The left-hand side of each gives the area in  $P, Q$  space within the corresponding energy constant curve; and the right-hand side is the number of phase cells within this area, occupied or unoccupied.

Thus, we are to solve the set of coupled equations (3.1), (3.2), (3.3), (3.4).

$$U(Q) = U_z(Q) + \frac{N-1}{N} \int U_e(Q-Q') n(Q') dQ',$$

$$n(Q) = (2/\hbar)[P_0 - P_1 + P_2],$$

$$P_0^2/2m+U=E_0, \quad P_1^2/2m+U=E_1, \quad P_2^2/2m+U=E_2,$$

$$\oint P_0(E_0, Q) dQ = (N+g)\hbar, \quad (3.5)$$

$$\oint P_1(E_1, Q) dQ = (N-s+g)\hbar,$$

$$\oint P_2(E_2, Q) dQ = (N-s)\hbar.$$

With  $U_z, U_e, N, g$ , and  $s$  given,  $U(Q), n(Q), P_0, P_1, P_2, E_0, E_1, E_2$  are 8 unknowns together with 8 equations. By successive eliminations, we can reduce the number of unknowns and equations.

Eliminating  $n, P_0, P_1, P_2$ , we retain four equations. These are the integral equation for  $U(Q)$ , with  $n$  expressed in terms of  $U$  and  $E_0, E_1, E_2$ , plus the three quantization conditions, with the  $P$ 's expressed in terms of  $U$  and the corresponding  $E$ 's. Solve the integral equation. This determines  $U(Q, E_0, E_1, E_2)$ , the self-consistent potential, which depends parametrically on  $E_0, E_1, E_2$ . Substitute this in the three quantization conditions, and these, in turn, give three coupled equations for the determination of  $E_0, E_1, E_2$ . If there are more gaps, there are more equations. With each new gap we have to add two more  $E$ 's for the description of the two boundaries of the gap. In turn we have two more quantization conditions with two more quantum numbers, the latter determining the relative location of the new gap.

Thus the equation system remains determined. According to this scheme, an excited state is characterized by (1) a number of separate layers, each occupied by a specified number of electrons, and by (2) a number of gaps sandwiched between the layers, each with a specified number of missing electrons. It is by no means clear in advance what the relationship is between a state specified in this way and the total energy of the atom. One would expect that if there are many gaps, the atom would have a large energy because so many electrons are excited. However, because of this the electrons are further apart, and so the self-consistent field is diminished, thereby depressing the value of the total energy. There is even the possibility that the two opposing effects will militate against each other in such a way as to produce an energy reversal as one increases the gap widths. For this reason a detailed calculation is needed in each case to determine the energy of a specified state.

#### 4. DIFFERENTIAL EQUATIONS

If the intersection is electrostatic, we can convert the first integral equation of (3.5) into a differential one. Let the potentials be given by  $U_e = 2\pi Z e^2 |Q|$ , and  $U_e(Q-Q') = -2\pi e^2 |Q-Q'|$ , and differentiate the inte-

gral equation twice with respect to  $Q$  using the identity  $d^2|Q|/dQ^2=2\delta(Q)$ . We obtain

$$d^2U/dQ^2=4\pi Ze^2\delta(Q)-4\pi v^2[(N-1)/N]n(Q). \quad (4.1)$$

Since  $U(Q)$  is symmetrical, we may confine our interest to  $Q>0$ , and extend the solution to negative  $Q$ 's as an even function. Then the  $\delta$ -function term can be treated as a boundary condition, asserting that  $U'(+0)=2\pi Ze^2$  and dropping the  $\delta$ -function term. Integrating (4.1) from 0 to infinity then gives

$$\begin{aligned} U'(+\infty) &= U'(+0) - 4\pi e^2[(N-1)/N]N/2 \\ &= 2\pi e^2[Z - (N-1)]. \end{aligned}$$

This is the boundary condition at infinity. Physically it implies that the electric force on an electron at infinity is  $-2\pi e^2[Z - (N-1)]$ , thus if  $Z > (N-1)$  it is a restoring force coming from the unshielded part of the nuclear charge, where the shielding is caused by the  $(N-1)$  other electrons. The  $-1$  is the well-known Fermi-Amaldi (FA) correction; and, as we have seen, it is a natural consequence of a properly normalized closure condition. For this reason, no additional assumption is necessary to obtain it, and thus the objections raised in this regard seem to be invalid.<sup>2</sup>

We now introduce new dimensionless variables  $v_k$ ,  $p_k$ ,  $e_k$ , and  $q$  by  $\tilde{V}v_k = E_k - U$ ;  $\tilde{P}p_k = P_k$ ,  $E_k = \tilde{V}e_k$ , and  $\tilde{Q}q = Q$ , where the quantities marked with a tilde carry the dimensions and  $k=0, 1, 2$ . They are solutions of the three algebraic relations

$$\tilde{P}\tilde{Q} = Nh, \quad \tilde{Q}/\tilde{V} = 9/16\pi Ze^2, \quad \tilde{P} = (N-1)(m\tilde{V})^{1/2}/Z.$$

The Hamiltonian then acquires the form

$$H/\tilde{V} = [(N-1)/Z]^{1/2}p^2 + u.$$

In terms of these variables, the differential equation reads

$$v_k'' = (9/\sqrt{2})[v_0^{1/2} - v_1^{1/2} + v_2^{1/2}] \quad \text{for } g > 0, v_k \geq 0 \quad (4.1)$$

and with

$$v_k'(+0) = -9/8, \quad v'(\infty) = -(9/8)(Z - N + 1)/Z, \quad v \text{ (even)}.$$

In addition, the quantization conditions are

$$\sqrt{2} \oint v_0^{1/2} dq = A_0, \quad \sqrt{2} \oint v_1^{1/2} dq = A_1, \quad \sqrt{2} \oint v_2^{1/2} dq = A_2$$

with

$$\begin{aligned} A_0 &= [(N-1)/Z][1 + (g/N)], \\ A_1 &= [(N-1)/Z][1 - (s-g)/N], \\ A_2 &= [(N-1)/Z][1 - (s/N)]. \end{aligned} \quad (4.2)$$

The first-order differential equation obtained from (4.1) is

$$(v')^2 = 12/\sqrt{2}[v_0^{3/2} - v_1^{3/2} + v_2^{3/2}] + (9/8Z)^2(Z - N + 1)^2. \quad (4.3)$$

<sup>2</sup> P. Gombas, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1949), Vol. 36, p. 109.

## 5. GROUND-STATE SOLUTIONS

In the ground state there are no gaps. Hence  $v_1$  and  $v_2$  are equal and  $A_0 = (N-1)Z^{-1}$ . The simplest solution is obtained if  $Z = N-1$ , for a singly charged negative ion, because then the boundary condition (b.c.) at  $+\infty$  becomes simplified. If  $Z = N$ , this solution also represents the potential for a neutral atom but without the FA correction. In this case,  $A_0 = 1$ .

The solution is given by  $v = (9/32)(1 - |q|)^4$  for  $|q| \leq 1$ , and  $v = 0$  for  $q \geq 1$ . Thus, in this case the ion has the radius  $\tilde{Q}$ . It is easy to verify that this solution satisfies both the differential equation, the boundary conditions, and the quantum condition with  $A_0 = 1$ . Actually, the quantization condition is redundant (but compatible) in this case. In the ground state this condition states that the area within the  $H = E_0$  surface contains  $N$  electrons (and no holes); hence it is equivalent to the normalization condition on the density which, however, is *already* incorporated in the boundary condition. Since the initial slope  $v'(0)$  is known, the initial value  $v(0)$  is found through (4.3), thereby determining all initial conditions so that the differential equation need only continue the curve. Thus, a solution of the differential equation, which satisfies the b.c. automatically satisfies the quantization condition. The value of  $E_0$  is determined by the requirement that  $v(0) = E_0/\tilde{V}$ .

The total energy can be obtained by simple integration.

$$\begin{aligned} \mathcal{E} &= \oint_{H \leq E_0} \frac{dP dQ}{h} \left( \frac{1}{2m} P^2 + U \right) \\ &= NE_0 - \frac{4}{3} \oint \frac{P_0^3}{2m} \frac{dQ}{h}. \end{aligned} \quad (5.1)$$

Substituting  $U$  in terms of  $P_0$  and  $E_0$  and integrating over  $P$  gives for this special case

$$\mathcal{E} = NE_0 - (9/112)\tilde{V}N, \quad (5.2)$$

where  $E_0 = 9\tilde{V}/32$ . The phase space for this state (in reduced units) will appear like Fig. 1 without the gap. It will be a single shaded area filled in under the curve  $p_0 = [2(e_0 - u)]^{1/2} = (2v)^{1/2} = \frac{3}{4}(1 - |q|)^2$ .

If  $v'(\infty)$  is not zero any longer, though it is still small and negative, a perturbation calculation leads to a good approximate solution. This pertains to the case in which  $Z > N-1$  including the FA correction. Since the perturbation is in the boundary condition, we begin with the first-order differential equation (4.3), which, for this case, is

$$(v')^2 = (12/\sqrt{2})v^{3/2} + (9/8)^2\beta^2, \quad v'(+0) = -9/8, \quad (5.3)$$

where  $\beta = (Z - N + 1)/Z$  is the small quantity.

Assume that the solution can be written as  $v = F - \frac{2}{3}\beta^2 f$ , where  $F$  is the solution obtained before. Substitute this into Eq. (5.3), and neglect powers of  $\beta^4$ . We get

$$\frac{4}{3}f'F' = (12/\sqrt{2})F^{1/2}f - (9/8)^2,$$

with  $f'(0)=0$ ;  $f$  is even. This has the solution

$$f = (27/160)[(1-|q|)^{-2} + \frac{2}{3}(1-|q|)^3] \quad \text{for } q < q_b.$$

The boundary is now found to be  $q_b = 1 - (\frac{2}{3})^{1/6}\beta^{1/3}$ , hence the atom shrinks in response to the additional binding force that has been introduced. Because of this, the singularity in  $f$  is outside the physically meaningful range and causes no difficulties in the approximation. At the boundary the correction is of the order  $0.15\beta^{4/3}$ , small already for  $\beta \sim \frac{1}{10}$ . The energy correction up to  $\beta^2$  due to the change in boundary conditions is given as  $(21/40)\bar{V}N\beta^2$ .

## 6. EXCITED STATES

In the case of excited states, neither a general analytic solution nor a first-order approximation have been found. For these reasons, it is necessary to resort to numerical methods to evaluate the energy of any given excited state. A few low-lying states have been evaluated for the one-dimensional neutral atom  $Z=25$ . Also, it is shown below that there is a definite core polarization effect due to the outer electron of this atom.

The necessary integrations were done on a 1620 computer using the reduced variables of (4.1) and (4.2). Functions  $v_0$ ,  $v_1$ , and  $v_2$  are symmetric as stated above, and behave topologically like the boundaries of constant energy  $E_0$ ,  $E_1$ , and  $E_2$  shown in Fig. 1. If one arbitrarily chooses initial values  $v_1(0)$  and  $v_2(0)$ , then  $v_0(0)$  is determined by (4.3), since the initial slope is known to be  $v_0'(0) = -9/8$ . The computer can then be employed to continue the curves  $v_0$ ,  $v_1$ , and  $v_2$  until each cuts off at the  $q$  axis, and to calculate the areas  $A_0$ ,  $A_1$ , and  $A_2$ .

From a knowledge of any two of the  $A$ 's in Eq. (4.2),  $s$  and  $g$  are determined, and the remaining  $A$  can be used to check the accuracy of the calculation. (Here again is the redundancy referred to in Sec. 5.) Thus  $s$  and  $g$  are fixed by the original arbitrary choice of  $v_1(0)$  and  $v_2(0)$ . A grid of initial values must therefore be used to investigate any given integers  $s$  and  $g$ .

As in (5.1), the energy associated with a region of phase space is given by

$$\mathcal{E} = \frac{1}{\bar{V}} \oint \frac{dP dQ}{h} \left( \frac{P^2}{2m} + U \right),$$

where the units are now more conveniently chosen. The total energy of an atom having a single vacancy of  $g$  electrons, and a single band of  $s$  excited electrons is found to be

$$\mathcal{E}_T = (N+g)v_0(0) - (N-s+g)v_1(0) + (N-s)v_2(0) - \frac{8\sqrt{2}}{3} \left( \frac{NZ}{N-1} \right) \int [v_0^{3/2} - v_1^{3/2} + v_2^{3/2}] dq, \quad (6.2)$$

where the integral conditions (4.2) are used. Similarly,

the energy associated with the  $s$  excited electrons is

$$\mathcal{E}_s = (N+g)v_0(0) - (N-s+g)v_1(0) - \frac{8\sqrt{2}}{3} \left( \frac{NZ}{N-1} \right) \int [v_0^{3/2} - v_1^{3/2}] dq; \quad (6.3)$$

and the energy  $\mathcal{E}_g$  associated with the gap is

$$\mathcal{E}_g = (N-s+g)v_1(0) - (N-s)v_2(0) - \frac{8\sqrt{2}}{3} \left( \frac{NZ}{N-1} \right) \int [v_1^{3/2} - v_2^{3/2}] dq. \quad (6.4)$$

For a one-dimensional atom, the energy differences between neighboring states are very small, and so an accuracy to four and five significant figures is sometimes necessary to distinguish them. The computational requirement is hindered by the need to use a grid of initial values for  $v_1$  and  $v_2$ , as well as the nonanalytic character of the continuation when  $v_1$  and  $v_2$  meet the  $q$  axis. Our estimate of these limitations is the basis of the error in the figures reported below, which we set uniformly to be within  $\pm 0.0001$ .

## 7. COMPUTATIONAL RESULTS

The ground state for the neutral atom  $Z=N=25$  corresponds to the case in which  $g=0$  and is found to have an energy in reduced units equal to  $\mathcal{E}_T = 4.9420$ . The lowest excited state is found by letting the outer electron jump up one level, thereby making  $s=g=1$ . The total energy of this state is found to be 4.9452.

The next pair of low-lying states would be degenerate on a linear scale. The first of these is found by letting the outer electron move up another notch, and the other is found by letting the second outer electron move up a level adjacent to the first (excited) electron. That is, the configurations  $(s=1, g=2)$  and  $(s=2, g=1)$  for  $N=Z=25$ . Computation shows the state  $(s=1, g=2)$  to be energetically preferred. We have

$$\begin{array}{ll} \text{state } s=1, g=2 & \mathcal{E}_T = 4.9481 \\ \text{state } s=2, g=1 & \mathcal{E}_T = 4.9492. \end{array}$$

It was mentioned at the end of Sec. 4 that as a gap width increases, the total atomic energy is also likely to increase, but there is another opposing effect due to the further separation of the electrons, and a consequent diminishing of the self-consistent field. Actually, the second effect will be noticeable only to the extent that the excited electrons penetrate the core of a one-dimensional atom, because of the complete shielding of electric lines of force in this case.

A series of points were computed in the  $s-g$  plane to see if there is such an effect. For the series chosen, the value of  $s$  stayed fairly close to one, while  $g$  increased from 1.17 to 13.2. The results show no sign of energy reversal. The series was generated by keeping the

initial value  $v_2(0)$  constant at 0.279 and by varying the difference  $v_1(0) - v_2(0)$  from 0.003 to 0.010 in steps of 0.001, and from 0.010 to 0.030 in steps of 0.002. The first member of the series gave  $s=0.84$ ,  $g=1.17$ ,  $\mathcal{E}_T=4.9450$ , and the last member gave  $s=1.08$ ,  $g=13.24$ ,  $\mathcal{E}_T=4.9775$ . A plot of the points show an increase in energy with gap width which is quite linear after the first few points.

As stated in the introduction, the customary approach to Thomas-Fermi theory adds outer electrons to a hard ionic core, and therefore does not take core polarization into account. It is a matter of interest to see if the present theory does include a polarization effect, and if this effect goes in the expected direction. For this purpose, we compare (a) the total energy of the ground state of the atom  $Z=N=25$  with (b) the total energy of the ground state of the positive ion  $Z=25$ ,  $N=24$ , plus the energy associated with a one-electron gap immediately above the ionic core. That is, in the latter case we find the sum  $\mathcal{E}_T + \mathcal{E}_g$  of the state  $Z=25$ ,  $N=24$ ,  $s=0$ ,  $g=1$ . The ionic-core energy was found to be  $\mathcal{E}_T=4.6668$ , and the energy associated with the one missing electron in the gap was found to be  $\mathcal{E}_g=0.2816$ . Their sum 4.9484 is greater than the ground-state energy 4.9421 of the atom  $Z=N=25$ . This means that when the outer electron is actually present in the gap it produces an additional binding or attractive force.

The energy difference cannot be due to a decrease in the potential energy at the nuclear origin in the presence of the added electron's field, since all energies are measured relative to the potential energy at the origin in the present one-dimensional case. The measured effect must therefore be a sum of the change in the potential energy of the core electrons in the field of the added electron, which effect is repulsive, plus an attractive polarization effect. Since an attractive effect predominates, it is concluded that a significant degree of polarization is present.

Perhaps a better measure of the polarization can be had by comparing (a) the energy associated with just the outer electron in the neutral atom  $Z=N=25$ , with (b) the energy associated with the empty gap above the ionic core  $Z=25$ ,  $N=24$ . The latter energy has already been given above to be  $\mathcal{E}_g=0.2816$ , and to find the

former energy, one need only investigate the state  $Z=N=25$ ,  $s=1$ ,  $g=0$  for the value of  $\mathcal{E}_s$ . Computation shows to be  $\mathcal{E}_s=0.2797$ . Again, the energy associated with the outer level is greater when it is vacant than when it is occupied, indicating a greater binding when an electron is actually present. In this case, however, the energy difference can only be due to a changed configuration of the ion core in response to the added electron, and hence it is purely a polarization effect.

## 7. CONCLUSION

We have shown how the original Thomas-Fermi method can be extended to the computation of the energies of atomic excited states. In these cases the  $\mu$ -space distribution has gaps, bounded by energy constant surfaces. The location of these surfaces are co-determined with the density and the self-consistent potential through the Bohr-Sommerfeld quantization conditions.

While this method is self-consistent, its quantitative value is not clear. The heuristic correction terms added to the original TF theory (exchange correction, Weitzsacker correction, correlation correction) are usually small relative to the ground-state energy; however, for excited states these corrections may be of the same order as the difference in energies between adjacent excited states. If this be the case, the best we can strive for is a qualitative understanding. There is, however, hope for more. In the three-dimensional situation, the exchange and Weitzsacker corrections for the average energy of an electron in the ground state of an atom are of the order  $N^{-2/3}$ .<sup>3</sup> The order of magnitude of the difference between low-lying excited states will be the mean energy of an electron in the ground state times the number of excited electrons. Thus, as long as this number is much less than  $N^{+2/3}$ , the correction terms will not overwhelm the effect.

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<sup>3</sup> N. L. Balazs, Phys. Rev. **134**, A841 (1964).