Statistical Theory of Electronic Energies*

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I. INTRODUCTION

IN 1927 L. H. Thomas[1] and in 1928 E. Fermi[2] independently proposed a simple theory for estimating certain properties of polyelectronic atoms. Their original theory dealt with the total binding energy of the electrons of a spherically symmetric atom, the electron density distribution, the resulting atomic field, and the angular momentum distribution of the electrons. By 1932 the theory was being applied to diatomic molecules by F. Hund,[3] and by 1935 it was being applied to metals by J. C. Slater and H. M. Krutter.[4] Thus, in a very short period of time, the Thomas-Fermi theory was applied to a wide range of electronic problems, the answers to which continue to be of considerable interest.

In spite of—or, perhaps, because of—the approximate nature of the Thomas-Fermi theory, it has received a great deal of attention, both with regard to applications to problems of physical interest and its theoretical foundations. Attesting to the great interest shown are the comprehensive works of L. Brillouin,[5] P. Gombas,[6] and N. H. March,[7] where the literature on the subject is covered thoroughly.

Perhaps the most intriguing aspect of the Thomas-Fermi theory—and this aspect may well be the basis for the interest which it has elicited—is the simplicity of the physical ideas underlying it. The electrons of a polyelectronic system are regarded as comprising a degenerate Fermi-Dirac gas, idealized to the extent that explicit interelectronic repulsions are disregarded and, in their stead, an effective, position-dependent potential is imposed. In semiclassical statistical-mechanical terms, such a gas is characterized by having each cell of phase-space either doubly occupied (because of electron spin) or empty. With the condition imposed that the electrons are bound, corresponding to a nonpositive total energy, one obtains an expression for the electron density directly in terms of the effective potential at each point of space. With such brevity, the statistical portion of the Thomas-Fermi theory is complete. There remains only the matter of determining the effective potential. Here, Poisson's equation of classical electrostatics is introduced as a means of obtaining a "self-consistent field." With an appropriate change of variables the equations of this theory, together with the conditions which must be satisfied by their solutions, can be rendered into a form of universal applicability to electrically neutral atomic systems.

This, is brief, is the Thomas-Fermi theory.

In spite of its remarkable simplicity, the results obtained with it are surprisingly good. Thus, the total electronic binding energy given by the Thomas-Fermi theory generally is greater than the observed values by 17–30%, closer agreement accompanying the atoms of larger atomic number. The electron density distribution of the Thomas-Fermi theory is a monotonic function of the distance from the nucleus and gives no evidence of "shell structure." It appears to resemble what might be expected if the shell structure were "smeared out"; the disagreement with quantum mechanical densities is with regard to detail.

As reasonable as the Thomas-Fermi results may appear to be, several important inadequacies should be noted: (1) The binding energies are *greater* than those observed, whereas quantum mechanical approximations based upon use of a variational principle give *lower* bounds to the binding energy. (2) Negative ions are not stable. (3) The monotonic variation of electron density with radial distance is in disagreement with quantum results, as a result of which the periodic system of the elements cannot be inferred from the Thomas-Fermi model. (4) The electron density in the vicinity of the nucleus diverges in the Thomas-Fermi model, whereas quantum mechanically it is finite. (5) The variation of electron density for large distances is also in disagreement with quantum results, decreasing as the inverse sixth power of the distance from the nucleus rather than decreasing exponentially.

In spite of these inadequacies, the Thomas-Fermi theory would appear to furnish a convenient first step in a more elaborate approximation scheme. This aspect has motivated many investigations into the foundations of the theory, as well as into modifications to improve it.

In 1930, P. A. M. Dirac[8] introduced the electronic exchange energy into the Thomas-Fermi theory. The means by which this was accomplished involved the expression of the Hartree-Fock equations in terms of Dirac's density matrix, with a semiclassical approximation being imposed upon the latter. By this means, a physically important term was introduced which (1) eliminated the electron self-interaction implicit in the Thomas-Fermi theory and (2) made stable negative

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[1] L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927).

[2] E. Fermi, Z. Physik **48**, 73 (1928).

[3] F. Hund, Z. Physik **77**, 12 (1932).

[4] J. C. Slater and H. M. Krutter, Phys. Rev. **47**, 559 (1935).

[5] L. Brillouin, *L'atome de Thomas-Fermi*, Actualites Sci. Industr., No. 160 (Hermann & Cie, Paris, 1934).

[6] P. Gombas, *Die Statistische Theorie des Atoms und Ihre Anwendungen* (Springer-Verlag, Vienna, 1949).

[7] N. H. March, *Advances in Physics* (Taylor and Francis, Ltd., London, 1957), Vol. 6, p. 1.

[8] P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930).

ions possible. These features were introduced explicitly, but somewhat more simply, into the theory of E. Fermi and E. Amaldi,[9] who in 1934 proposed that the Poisson's equation of the original Thomas-Fermi theory be modified to exclude one electron from the total electronic density. In both the Thomas-Fermi-Dirac and the Thomas-Fermi-Amaldi theories, a finite size is predicted for an atom, a result which is not in accord with quantum mechanical expectations. The results for the binding energies obtained with these theories are, however, in even poorer agreement with experimental values.[10] A further feature dealing with improvements related to electronic interactions was considered by P. Gombas[11] in 1943. He introduced the correlation energy, based upon the model of a free electron gas treated by E. Wigner.[12] Here, again, the effect is to increase the binding energy.

Recognizing that the Thomas-Fermi theory was based upon an analogy with the free electron-gas, C. F. v. Weizsacker[13] pointed out in 1935 that the kinetic energy density for free electron gases differs markedly from that expected quantum mechanically in regions where the potential gradient is large. Accordingly, he proposed an expression for the kinetic energy density which involves gradients of the density. This correction has the effect of radically modifying the equations of the Thomas-Fermi theory, particularly in the region surrounding the nucleus. It addresses itself, therefore, to one of the serious inadequacies of the original theory. The original introduction of this "inhomogeneity correction" was made on more-or-less *ad hoc* grounds and has been critically evaluated by R. A. Berg and L. Willets.[14] Nevertheless, it appears to be the first sort of correction applied to the original Thomas-Fermi theory that tends to *decrease* the binding energy[15] by presumably decreasing the electron density in the vicinity of the nucleus. This latter point has been more explicitly investigated by J. M. C. Scott[16] and N. H. March and J. S. Plaskett[16] to obtain remarkably good values of the (nonrelativistic) binding energies of atoms.

The present paper is primarily concerned with a general formulation of the statistical theory based upon the use of the density-matrix originally introduced by Dirac.[8] This viewpoint has recently been revived by W. R. Theis,[17] the present writer,[18] and N. H. March.[19]

[9] E. Fermi and E. Amaldi, Mem. accad. Italia **6**, 117 (1934).
[10] See, e.g., Table II.
[11] P. Gombas, Z. Physik **121**, 523 (1943).
[12] E. Wigner, Phys. Rev. **46**, 1002 (1934).
[13] C. F. v. Weizsacker, Z. Physik **96**, 431 (1935).
[14] R. A. Berg and L. Willets, Proc. Phys. Soc. (London) **A68**, 229 (1955).
[15] See, e.g., N. Sokolov, J. Exp. Theoret. Phys. (U.S.S.R.) **8**, 365 (1938).
[16] J. M. C. Scott, Phil. Mag. **43**, 859 (1952); N. H. March and J. S. Plaskett, Proc. Roy. Soc. (London) **A235**, 419 (1956); see also, R. A. Ballinger and N. H. March, Phil. Mag. **46**, 246 (1955).
[17] W. R. Theis, Z. Physik **142**, 503 (1955).
[18] S. Golden, Phys. Rev. **105**, 604 (1957); **107**, 1283 (1957).
[19] N. H. March, Proc. Phys. Soc. (London) **A70**, 839 (1957).

II. DENSITY-MATRIX

For a many-particle system, one may define a density matrix (representative)

$$\rho(x',x)=\sum_{n=1}^{M}\psi_n^*(x')\psi_n(x), \tag{2.1}$$

where $\{\psi_n(x)\}$ is a complete set of properly symmetrized orthonormal eigenfunctions of the Hamiltonian $\mathbf{H}$ of the system; x stands for the entire set of configurational and spin coordinates of the system; M is an integer not related to the number of particles. If E_n is the energy value corresponding to $\psi_n(x)$ and $E_n\leqslant E_{n+1}$, then Eq. (2.1) refers to the M lowest eigenstates of the system. This is emphasized by the normalization equation

$$\int dx\rho(x,x)=\sum_{n=1}^{M}\int dx|\psi_n(x)|^2=M. \tag{2.2}$$

For an arbitrary operator $\mathbf{O}$, it is evident that

$$\mathrm{Tr}\,\mathbf{O}\varrho=\sum_{n=1}^{M}\int dx\psi_n^*(x)\mathbf{O}\psi_n(x), \tag{2.3}$$

corresponding to the sum of the expectation values over the M lowest eigenstates of the system. As a consequence, if the density matrices are known for all values of M, one is able to determine all the properties of the system.

In order to accomplish this, one must solve Schroedinger's equation. However, as the basis of an approximation procedure, an important property of the density matrix (for fixed M) needs to be considered. For that purpose, note that

$$\rho(x',x)=\sum_{n=1}^{\infty}\psi_n^*(x')\theta(\lambda_M-\mathbf{H})\psi_n(x), \tag{2.4}$$

where

$$\left.\begin{aligned}\theta(\lambda_M-\mathbf{H})\psi_n=\theta(\lambda_M-E_n)\psi_n=\psi_n,\quad &\lambda_M>E_n,\\ =0,\quad &\lambda_M<E_n,\\ \mathbf{H}\psi_n=E_n\psi_n.&\end{aligned}\right\} \tag{2.5}$$

The effect of introducing the operator $\theta(\lambda_M-\mathbf{H})$ is to make Eq. (2.4) invariant to the basis of functions used. As a result, approximations to the density matrix may be related to those affecting $\theta(\lambda_M-\mathbf{H})$ and not at all to the wave functions. To effect this approximation, one may take advantage of the fact that $\theta(\lambda_M-\mathbf{H})$ is a step function in the space of the eigenvalues of $\mathbf{H}$. Then it is convenient to determine the Laplace transform of $\theta(\lambda_M-\mathbf{H})$, regarded as a function of λ_M. Thus,[20] in a

[20] Greater generality requires the use of the Mellin transform since λ is generally unrestricted in value. Use of the Laplace transform here tacitly supposes all the eigenvalues of H to be measured from a lowest value which is a formal convenience.

representation of eigenfunctions of $\mathbf{H}$,

$$\int_0^\infty d\lambda_M e^{-z\lambda_M}\rho(x',x)$$
$$=\sum_{n=1}^{\infty}\psi_n^*(x')\left\{\int_0^\infty d\lambda_M e^{-z\lambda_M}\theta(\lambda_M-E_n)\right\}\psi_n(x),$$
$$=\sum_{n=1}^{\infty}\psi_n^*(x')(e^{-zE_n}/z)\psi_n(x), \tag{2.6}$$

where $\mathrm{Re}\, z>0$. This last expression can be recognized as simply being related to the statistical[21] matrix and the partition function for complex "temperature." In formal terms, then,

$$\int_0^\infty d\lambda_M e^{-z\lambda_M}\theta(\lambda_M-\mathbf{H})=\exp(-z\mathbf{H})/z, \tag{2.7}$$

and employing the inversion formula[22] of Laplace transforms,

$$\theta(\lambda_M-\mathbf{H})=(2\pi i)^{-1}\mathcal{P}\int_{\gamma-i\infty}^{\gamma+i\infty}(dz/z)\exp[z(\lambda_M-\mathbf{H})],$$
$$\mathrm{Re}\,\gamma>0. \tag{2.8}$$

Equations (2.7) and (2.8) relate quantum mechanics with statistical mechanics and vice versa in a fundamental way.[23]

This relation may be emphasized by noting the significance of λ_M which originally appeared as a parameter affecting the normalization of the density matrix. When one takes $\mathbf{O}$ of Eq. (2.3) as the Hamiltonian, one obtains

$$\langle E\rangle_M\equiv\sum_{n=1}^{M}E_n=\sum_{n=1}^{\infty}\int dx\psi_n^*(x)\theta(\lambda_M-\mathbf{H})\mathbf{H}\psi_n(x),$$
$$=\sum_{n=1}^{\infty}(2\pi i)^{-1}\int dx\psi_n^*(x)\left\{\mathcal{P}\int_{\gamma-i\infty}^{\gamma+i\infty}(dz/z)\mathbf{H}\exp[z(\lambda_M-\mathbf{H})]\right\}\psi_n(x);$$
$$\partial\langle E\rangle_M/\partial\lambda_M=\sum_{n=1}^{\infty}(2\pi i)^{-1}\int dx\psi_n^*(x)\left\{\mathcal{P}\int_{-\gamma i\infty}^{\gamma+i\infty}dz\mathbf{H}\exp[z(\lambda_M-\mathbf{H})]\right\}\psi_n(x),$$
$$=\sum_{n=1}^{\infty}(2\pi i)^{-1}\int dx\psi_n^*(x)\left\{\mathcal{P}\int_{\gamma-i\infty}^{\gamma+i\infty}dz[\lambda_M-(\lambda_M-\mathbf{H})]\exp[z(\lambda_M-\mathbf{H})]\right\}\psi_n(x),$$
$$=\lambda_M\partial M/\partial\lambda_M-\sum_{n=1}^{\infty}(2\pi i)^{-1}\int dx\psi_n^*(x)\left\{\mathcal{P}\int_{\gamma-i\infty}^{\gamma+i\infty}dz(\partial/\partial z)\exp[z(\lambda_M-\mathbf{H})]\right\}\psi_n(x),$$
$$=\lambda_M\partial M/\partial\lambda_M,$$

since the last integral vanishes. This development is formal and assumes that $\langle E\rangle_M$ and M may be regarded as continuous functions of λ_M and have derivatives with respect to λ_M. Rearranging the last equation, one gets

$$\partial\langle E\rangle_M/\partial M=\lambda_M, \tag{2.9}$$

which reveals that λ_M is to be regarded as the "chemical potential per state" of the system. Equation (2.9) may be used to determine $\langle E\rangle_M$ when M is known as a function of λ_M.

III. QUASI-CLASSICAL APPROXIMATIONS

Equations (2.7) and (2.8) comprise a basis for approximating the density matrices of a many-particle system. Briefly, the method consists of approximating $\exp(z\mathbf{H})$ or, equivalently, the quantum statistical matrix and then applying the Laplace inversion formula to the approximation. For problems which deal only with energies, it is necessary to consider approximations only to the quantum mechanical partition function.

In this section, perhaps the simplest approximation that can be made to $\exp(z\mathbf{H})$ is discussed to illustrate the method. It is shown that it gives rise to the original Thomas-Fermi theory.

Now,

$$\mathbf{H}\equiv\mathbf{H}_0+V, \tag{3.1}$$

where, in the usual parlance, $\mathbf{H}_0$ may be regarded as an unperturbed Hamiltonian and V is a perturbation. Clearly, $\mathbf{H}_0$ and V do not generally commute. Nevertheless, and this is the essence of the approximation here termed "quasi-classical," one approximates

$$\exp(z\mathbf{H})\doteq\exp(zV)\exp(z\mathbf{H}_0), \tag{3.2}$$

a form which is certainly exact if they do commute. Equation (3.2) may be utilized in Eq. (2.7). Thus, in a basis of eigenfunctions of $\mathbf{H}_0$, $\{\phi_n\}$,

[21] The statistical matrix referred to here is that of an equilibrium distribution.

[22] See, e.g., *Tables of Integral Transforms* (McGraw-Hill Book Company, Inc., New York, 1954).

[23] This relation is well known. See, for example, E. Blade and G. E. Kimball, J. Chem. Phys. **18**, 626 (1950).

TABLE I. Results for heliumlike atoms, from quasi-classical approximation based upon independent particle model.

System	State	$-E$ calc	$-E$ obs
He	$1s$	2.9349 a.u.	2.9036 a.u.
Li^+	$1s$	7.2760	7.2797
	$3s$	5.1023	5.1107
	$1s$	5.0718	5.0468
Be^{++}	$1s$	13.624	13.655
	$3s$	9.2754	9.2972
	$1s$	0.2403	>9.175 ($^3P^0$)

$$\sum_{n=1}^{\infty}\phi_n^*(x')[\exp(-z\mathbf{H})/z]\phi_n(x)$$

$$\doteq\sum_{n=1}^{\infty}\phi_n^*(x')[e^{-zV}\exp(-z\mathbf{H}_0)/z]\phi_n(x),$$

$$=\sum_{n=1}^{\infty}\phi_n^*(x')[e^{-zV}\exp(-zE_n^0)/z]\phi_n(x), \quad (3.3)$$

and, using Eq. (2.8), one obtains

$$\sum_{n=1}^{\infty}\phi_n^*(x')\theta(\lambda_M-\mathbf{H})\phi_n(x)$$

$$\doteq\sum_{n=1}^{\infty}\phi_n^*(x')\phi_n(x)\theta(\lambda_M-V-E_n^0), \quad (3.4)$$

where V is a function of the configurational coordinates and spin. The effect of this approximation is to convert $\theta(\lambda_M-\mathbf{H})$ to a scalar operator. In the simpler situations, $\{\phi_n(x)\}$, $\{E_n^0\}$, and V may be presumed known. It is then necessary to solve the equations

$$M=\sum_{n=1}^{\infty}\int dx|\phi_n(x)|^2\theta(\lambda_M-V-E_n^0). \quad (3.5)$$

With the determined value of λ_M,

$$\langle E\rangle_M=\sum_{n=1}^{M}E_n\doteq\sum_{n=1}^{\infty}\int dx(E_n^0+V)|\phi_n(x)|^2\times\theta(\lambda_M-V-E_n^0). \quad (3.6)$$

These equations have been applied with good results to heliumlike atoms and ions.[24] H_0 was taken as the independent particle Hamiltonian in the field of the nucleus, V the interelectronic repulsion. The wave functions were taken to be antisymmetric with respect to electronic interchange. The results obtained are given in Table I.

Equations (3.5) and (3.6) also yield the Thomas-Fermi theory. To see this, an additional approximation must be stated. In order to eliminate explicit reference to interelectronic repulsions, one introduces a self-consistent field. Thereupon, one replaces the many-particle density matrix by a single-particle density matrix and, in accord with the Pauli principle, identifies M with the number of particles. It is inherent in the Thomas-Fermi theory to refer to the kinetic energy of the individual electrons, which prompts the identification of $\mathbf{H}_0$ with the kinetic energy and $\{\phi_n(x)\}$ as eigenfunctions of momentum. Taking these to be plane waves normalized in a large cubic box containing the atom, one is able to replace the sum of Eq. (3.4) by an integration over the classical components of momentum. One obtains for the density in a spherically symmetric potential

$$\rho(x,x)\doteq(2/h^3)\int d\mathbf{p}\theta(\lambda_M-V(x)-p^2/2m), \quad (3.7)$$

$$=(8\pi/h^3)\int_0^{\infty}dpp^2\theta(\lambda_M-V(x)-p^2/2m), \quad (3.8)$$

$$=(8\pi/3h^3)[2m(\lambda_M-V(x))]^{\frac{3}{2}}, \quad (3.9)$$

which is the Thomas-Fermi expression for the electron density. It remains to satisfy the self-consistency condition on $V(x)$, expressed by Poisson's equation and the normalization condition on $\rho(x,x)$. Then[25]

$$\nabla^2V=-4\pi e^2\rho(x,x) \quad (3.10)$$

and

$$\int dx\,\rho(x,x)=N. \quad (3.11)$$

There is a parallel between the two cases used to illustrate the quasi-classical approximation. Apart from differences identified with the respective choice of the unperturbed Hamiltonian, both cases restrict the system of regions of configuration space for which the total energy is less than some fixed value. This total energy is regarded as the sum of the unperturbed energy and the perturbation energy. In the heliumlike illustration, the latter is positive, so that electrons are unable to approach each other indefinitely closely and still comprise a stable system. In the Thomas-Fermi model the perturbation energy is negative, but the system is limited to individual particle kinetic energies which do not cause the total energy to exceed a fixed value.

IV. HIGHER APPROXIMATIONS

To improve the statistical theory beyond the quasi-classical approximation simply requires a better approximation for $\exp(z\mathbf{H})$ to be used in Eq. (2.8). This particular aspect has received considerable attention because of its relevance to quantum statistical mechanics.[26] There are several ways to proceed, but one

[24] S. Golden, Phys. Rev. **107**, 1283 (1957).

[25] In the Fermi-Amaldi theory, the right side of Eq. (3.10) is modified by a factor $(N-1)/(N)$.

[26] See, e.g., the first of footnote 18, where a list of references is given.

based upon the previous quasi-classical approximation is discussed here.

It can be shown[18] that

$$\exp(z\mathbf{H})=\exp(zV)\chi(z)\exp(z\mathbf{H}_0), \quad (4.1)$$

where $\chi(z)$ is an operator to be determined. Evidently,

$$\chi(z)=\exp(-zV)\exp(z\mathbf{H})\exp(-z\mathbf{H}_0) \quad (4.2)$$

and formally permits a series expansion in z,

$$\chi(z)=\sum_{k=0}^{\infty} z^k Q_k\cdot R_k, \quad (4.3)$$

where Q_k depends only upon configurational coordinates and R_k only upon momentum coordinates. The $Q_k\cdot R_k$ satisfy the relation

$$kQ_k\cdot R_k=[H_0, Q_{k-1}\cdot R_{k-1}]+[H_0,V]Q_{k-2}\cdot R_{k-2} +\tfrac{1}{2}[[H_0,V],V]Q_{k-3}\cdot R_{k-3}. \quad (4.4)$$

Since, when $\mathbf{H}_0$ and V commute, $\chi(z)=1$, $Q_0\cdot R_0=1$, and all the remaining $Q_k\cdot R_k$ are determined.

The case in which $\mathbf{H}_0$ is taken to be the kinetic energy operator corresponds to the Thomas-Fermi basis, and this has been examined.[18] By carrying out the evaluation of the $Q_k\cdot R_k$, but retaining terms only up to order $\hbar^2$, one is able to get the following expression for the density:

$$\rho(x,x)=[8\pi(2m)^{\frac{3}{2}}/3h^3][(\lambda_M-V)^{\frac{3}{2}} -(\hbar^2/16m)\nabla^2V(\lambda_M-V)^{-\frac{1}{2}} -(\hbar^2/64m)\nabla V\cdot\nabla V(\lambda_M-V)^{-\frac{3}{2}}]. \quad (4.5)$$

The first term can be recognized as the Thomas-Fermi result. This expression has limited validity, for it is possible for the density to assume negative values. Clearly this is not possible for an exact expression for $\rho(x,x)$. To use Eq. (4.5), it is necessary to restrict the particles to regions of nonnegative density, a procedure already inherent in the original Thomas-Fermi theory.

It is interesting to examine the normalization condition. Then

$$M=\frac{8\pi}{3}\left(\frac{2m}{h^2}\right)^{\frac{3}{2}}\int d\mathbf{x}(\lambda_M-V)^{\frac{3}{2}} -\frac{1}{12\pi}\left(\frac{2m}{h^2}\right)^{-\frac{1}{2}}\int d\mathbf{x}\nabla^2V(\lambda_M-V)^{-\frac{1}{2}} -\frac{1}{48\pi}\left(\frac{2m}{h^2}\right)^{-\frac{1}{2}}\int d\mathbf{x}\nabla V\cdot\nabla V(\lambda_M-V)^{-\frac{3}{2}}. \quad (4.6)$$

Equation (4.5) is the three-dimensional analog of the extension of the one-dimensional WKB formula for the number of eigenstates not exceeding a given value of the energy. Carrying out an integration by parts of the next-to-last integral of Eq. (4.6), one obtains

$$M=\frac{8\pi}{3}\left(\frac{2m}{h^2}\right)^{\frac{3}{2}}\int d\mathbf{x}(\lambda_M-V)^{\frac{3}{2}} +\frac{1}{48\pi}\left(\frac{2m}{h^2}\right)^{-\frac{1}{2}}\int d\mathbf{x}\nabla V\cdot\nabla V(\lambda_M-V)^{-\frac{3}{2}}. \quad (4.7)$$

This may be compared with the formula given by E. C. Titchmarsh[27] for the one-dimensional WKB case:

$$n+\tfrac{1}{2}=\left(\frac{2m}{h^2}\right)^{\frac{1}{2}}\int dx(E-V)^{\frac{1}{2}} -\frac{1}{128\pi^2}\left(\frac{2m}{h^2}\right)^{-\frac{1}{2}}\int dx\left(\frac{dV}{dx}\right)^2(E-V)^{-\frac{5}{2}}. \quad (4.8)$$

The connection between the WKB approximation and the Thomas-Fermi method has been discussed by March and Plaskett.[16]

It is of further interest to evaluate the energy of this extension of the Thomas-Fermi theory, but this is not displayed here. Some numerical results obtained with the Fermi-Amaldi modification are given in Table II and are compared with the Thomas-Fermi results as well as those of the Thomas-Fermi-Dirac theory obtained by R. D. Cowan and J. Ashkin.[28] However, simplification of the resulting energy expression with the retention of terms of order $\hbar^2$ and lower leads to the approximation

$$E\cong\int d\mathbf{x}\{\kappa_k\rho^{5/3}+\tfrac{1}{2}\rho(V+V_0) -(2/45)[(N-1)/N]\kappa_a\rho^{\frac{4}{3}} +(13/45)\kappa_i(\nabla\rho\cdot\nabla\rho/\rho)\}. \quad (4.9)$$

The constants are the usual quantities in this theory. The first term is the kinetic energy, the second the potential energy, as in the Thomas-Fermi theory. The third corresponds to exchange energy, while the last term corresponds to the inhomogeneity correction of

TABLE II. Results from modified Thomas-Fermi-Amaldi theory. Parentheses refer to calculations in which spinless Thomas-Fermi theory was employed. Asterisk values refer to the neutral carbon atom, which is only slightly greater in bonding energy (1.3 a.u.).

System	State	$-E_{TF}$	$-E_{TFD}$	$-E$ calc	$-E$ obs
H	$2s$	(0.484) a.u.	··· a.u.	0.501 a.u.	0.500 a.u.
He	$1s$	3.875	4.660	2.974	2.904
He	$3s$	(2.439)	···	2.048	2.175
C^{++}	$1s$	50.30*	54.94*	37.05	36.55
O	$1s$	98.43	105.9	73.28	74.96

[27] E. C. Titchmarsh, *Eigenfunction Expansions Associated with Second-Order Differential Equations* (Clarendon Press, Oxford, 1946), p. 136.

[28] R. D. Cowan and J. Ashkin, Phys. Rev. **105**, 144 (1957).

v. Weizsäcker.[13] In the usual *ad hoc* introduction of the last two quantities, the coefficients multiplying them are unity. With regard to the inhomogeneity correction term, the necessity for a smaller coefficient has been discussed by R. A. Berg and L. Willets.[14]

Table II shows that the energy value for the hydrogen atom is in remarkably good agreement with experiment. To determine if this is, in fact, fortuitous, calculations of $\langle E\rangle_M$ were made for the hydrogen atom. Since the theory is incapable of discriminating between degenerate states, the calculations were made for groups of degenerate states, i.e., $M=1$, 5, 14. These are given in Table III. The remarkable agreement with quantum mechanics is not entirely unexpected because of the relation this theory has to the WKB method. The latter gives exact results for the Coulomb field.

TABLE III. Results of modified Thomas-Fermi-Amaldi theory for excited states of hydrogen (in groups of degenerate states).

Number of states, M	$-\sum_{n=1}^{M} En$ (calc)	$-\sum_{n=1}^{M} En$ (obs)
1	0.501 a.u.	0.500 a.u.
5	0.998	1.000
14	1.503	1.500

V. PROSPECTUS[29]

From the foregoing results, it appears that the statistical theory of electronic energies, introduced originally as the Thomas-Fermi theory, is capable of approaching in accuracy the results of quantum mechanics. When formulated in terms of the density matrix, the problem reduces to one of determining good approximations to an exponential function of the Hamiltonian of a system. When the latter is simply approximated by a form which is valid for commuting kinetic energy and potential energy, the original Thomas-Fermi density results. Improvement can be had by using this approximation as the starting point for a more extended treatment. In mathematical terms, one may express

$$e^{zH}=e^{zV}\chi(z)e^{zH_0}, \tag{5.1}$$

and the problem may be stated as requiring a good approximation for $\chi(z)$.

This program is currently under investigation, and the progress to date holds out considerable promise for electron density functions derivable from approximations to the density matrix which manifest close agreement with quantum mechanical expectations. The corresponding energy values may be expected to be in much closer agreement with experimental values than has been obtained to date from the Thomas-Fermi theory and any of its modifications.

All of the improvements which can be envisaged have, however, the main shortcoming of making the beautifully simple theory of Thomas and Fermi not so simple. In view of the complexities of the quantum mechanical theories of atomic and molecular structure, such a shortcoming is perhaps to be expected from any theory which aims ultimately to approach them in providing a description of electronic systems.

[29] In the presentation of this paper, preliminary results obtained for the hydrogen molecule-ion were presented. These are not reproduced here because they are still incomplete. The full details will be published elsewhere. A preliminary value of the binding energy for the ground symmetric state of the hydrogen molecule-ion of 0.085 a.u. was obtained, with an equilibrium distance of 2.1 a.u. The accurate values are 0.104 a.u. and 2.0 a.u., respectively.