

Quantum-Corrected Statistical Method for Many-Particle Systems: The Density Matrix*

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Quantum corrections are obtained for the single-particle density matrix in a semiclassical ensemble where the distribution is unrestricted. A form for the density matrix containing explicitly a function of the wave-mechanical Hamiltonian operator is devised; a formalism is then developed to decompose this operator function into effectively classical and nonclassical parts. The classical part corresponds to the semiclassical density matrix and the quantum corrections are obtained from the nonclassical terms.

The quantum-corrected density matrix for a spherically symmetrical and a one-dimensional system have been evaluated. The densities for a linear harmonic oscillator and a Coulomb potential for a Fermi-Dirac distribution have also been examined in some detail.

1. INTRODUCTION

QUANTUM corrections depending on powers of \hbar can in principle be introduced into any basic physical model intermediate between the classical and the wave mechanical, to help convergence towards wave mechanics. Very satisfactory results may thus be obtained without resorting to a full-scale wave-mechanical treatment, by solving a problem first on an approximate physical model and then proceeding to the quantum-corrective stage. Quantum corrections have to satisfy three basic conditions, however, to be of any significance: (1) less labor should be involved in their evaluation than in the wave-mechanical treatment of the problem, (2) they should be obtained in a consistent way, and not be known wave-mechanical features inserted *ad hoc* in the approximate model, and (3) they should be of reasonable magnitude, so as to displace the approximate result significantly towards the wave-mechanical value. Two fairly general procedures for obtaining quantum corrections are (1) by applying a perturbation treatment on a wave-mechanical relation¹—starting the perturbation with the result of the approximate model, and (2) by breaking up or “processing” the wave-mechanical model, in such a way that it yields the approximate result along with corrective terms²—the approximate result appearing at the lower limit of approximation in \hbar .

The present investigation is mainly concerned with applying the method of the “processed wave-mechanical model,” to obtain corrections to the single-particle density matrix in a statistical model characterized essentially by a classical Hamiltonian and plane-wave functions. A form for the wave-mechanical density matrix containing explicitly a function of the wave-mechanical Hamiltonian operator will first be devised;

a formalism will then be developed to decompose this operator function for a plane-wave representation, into effectively classical and nonclassical parts. The terms of the representative corresponding to the classical Hamiltonian operator will lead to the density matrix of the basic model, and the other terms will give the quantum corrections.

The interest in the problem of quantum-correcting the semiclassical density matrix is tied up to a great extent with the well-known Thomas-Fermi (T.F.) statistical method.³ The T.F. model is a semiclassical system satisfying Fermi-Dirac statistics, it has the merits of simplicity and practicability, and it has been widely used in molecular and solid state work.³ Being an approximation, however, the T.F. model suffers from defects, and since its inception in 1928, several modifications have been suggested to correct these defects.⁴ Most of these modifications were introduced on an arbitrary basis, and the efforts of the more recent workers,^{2,5} have been aimed mainly at obtaining some of these corrections in a consistent way. The work which is of particular interest here, is that of Golden² and of Kirzhnits²: using the method of the “processed wave-mechanical model,” sketched above, they obtained an expression for the energy of the quantum-corrected system, with terms corresponding to the exchange energy correction of Dirac,⁴ and the Weizsäcker correction,⁴ which had been criticized as arbitrary corrections to the T.F. model.

In the present investigation, the method of Golden and of Kirzhnits is modified to give an effectively more compact form for the density matrix; in other words: the new density matrix converges faster to the wave-

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¹ L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw Hill Book Company, Inc., New York, 1935).

² S. Golden, *Phys. Rev.* **105**, 604 (1957); **107**, 1283 (1957).
D. A. Kirzhnits, *Soviet Phys.—JETP* **64**, 5 (1957).

³ P. Gombas, *Die Statistische Theorie des Atoms und Ihre Anwendungen* (Springer-Verlag, Vienna, 1949); N. H. March, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1957), Vol. 6, p. 21.

⁴ P. A. M. Dirac, *Proc. Cambridge Phil. Soc.* **26**, 376 (1930); C. F. Von Weizsäcker, *Z. Physik* **96**, 431 (1935); J. S. Plaskett, *Proc. Phys. Soc. (London)* **A66**, 178 (1953); Y. Tomishima, *Progr. Theoret. Phys. (Kyoto)* **22**, 1 (1959).

⁵ W. R. Theis, *Z. Physik* **142**, 503 (1955); W. Macke, *Phys. Rev.* **100**, 992 (1955); *Am. J. Phys.* **17**, 1 (1955); E. S. Fradkin, *Soviet Phys.—JETP* **64**, 5 (1957).

mechanical result. Some interesting features of this more accurate density matrix are illustrated by applications to the linear harmonic oscillator, and the Coulomb potential.

2. GENERAL CONSIDERATIONS ON THE DENSITY MATRIX

The single-particle density matrix of a many-electron system is defined here as

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \sum_1^M \psi_n^*(\mathbf{r}_1) \psi_n(\mathbf{r}_2), \quad (2.1)$$

where $\psi_n(\mathbf{r})$ is a normalized eigenfunction of the Hamiltonian of the system; \mathbf{r} stands for the position and spin coordinates of an electron; M is the number of states in the system, and need not correspond to the number of particles.

Equation (2.1) can be written

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \sum_1^{\infty} \psi_n^*(\mathbf{r}_1) \theta_M \psi_n(\mathbf{r}_2), \quad (2.2)$$

where θ_M is some function of the Hamiltonian operator \mathbf{H} , with the properties:

$$\begin{aligned} \theta_M \psi_n(\mathbf{r}) &= \psi_n(\mathbf{r}), & n \leq M; \\ \theta_M \psi_n(\mathbf{r}) &= 0, & n > M. \end{aligned}$$

Several forms for θ_M are possible—the representations of interest here involve the step function of Heaviside,⁶ which will be expressed in either of two forms: (1) as an inverse Laplace transform, or (2) as a Fourier sine transform. The corresponding representations for θ_M are then⁷:

$$\theta_M = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{dz}{z} \exp[z(\lambda_M - \mathbf{H})], \quad (2.3)$$

and

$$\theta_M = -\frac{2}{\pi} \int_0^{\infty} dy \frac{\sin(y\lambda_M) \cos(y\mathbf{H})}{y}, \quad (2.4)$$

where

$$\begin{aligned} \theta_M \psi_n &= \psi_n, & \lambda_M > E_n; \\ \theta_M \psi_n &= 0, & \lambda_M < E_n; \\ \mathbf{H} \psi_n &= E_n \psi_n; \end{aligned}$$

λ_M is a parameter which satisfies the condition

$$E_M < \lambda_M < E_{M+1},$$

and has been shown² to correspond to the chemical potential per state in the system.

⁶ E. J. Scott, *Transform Calculus* (Harper and Brothers, New York, 1955); G. Doetsch, *Theorie und Anwendung der Laplace Transformation* (Dover Publications, New York, 1943).

⁷ *Tables of Integral Transforms*, Bateman Manuscript Project (McGraw Hill Publishing Company, Inc., 1954), Vol. 1.

Using (2.3) and (2.4), (2.2) can be written explicitly as

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \sum_1^{\infty} \psi_n^*(\mathbf{r}_1) \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{dz}{z} \exp[z(\lambda_M - \mathbf{H})] \psi_n(\mathbf{r}_2), \quad (2.5a)$$

and

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \sum_1^{\infty} \psi_n^*(\mathbf{r}_1) \frac{2}{\pi} \int_0^{\infty} dy \frac{\sin(y\lambda_M) \cos(y\mathbf{H})}{y} \psi_n(\mathbf{r}_2). \quad (2.5b)$$

(2.5a) and (2.5b) are expressions for the density matrix involving the Hamiltonian operator \mathbf{H} in the form $\exp(\kappa\mathbf{H})$, where κ is in general complex. A formalism will now be developed to obtain the representative $\langle \mathbf{r} | \exp \kappa \mathbf{H} | \mathbf{p} \rangle$ for the evaluation of (2.5a) and (2.5b).

3. OPERATOR $\exp(\kappa\mathbf{H})$

The Hamiltonian operator \mathbf{H} can in general be written:

$$\mathbf{H} = \sum_1^m \mathbf{H}_i, \quad (3.1)$$

where the operators \mathbf{H}_i are not always commutable. If the \mathbf{H}_i are commutable, \mathbf{H} corresponds to a classical Hamiltonian operator \mathbf{H}_{cl} , and $\exp(\kappa\mathbf{H}_{cl})$ would simply lead to the basic semiclassical density matrix, when substituted in (2.5a) or (2.5b). If $\exp(\kappa\mathbf{H})$ were therefore decomposed into a series with $\exp(\kappa\mathbf{H}_{cl})$ as a first term, the other terms would have to arise as a consequence of the noncommutative property of the \mathbf{H}_i 's,⁸ and these additional terms substituted in (2.5a) and (2.5b), would correspond to quantum corrections to the semiclassical result obtained with the first term only.

For the system of interest here: a completely degenerate electron gas with no interaction and spin, \mathbf{H} can be taken as the sum of the kinetic energy operator \mathbf{T} , and the potential energy operator V , where

$$\mathbf{T} = -\hbar^2 \sum_1^N \frac{1}{2m_j} \nabla_j^2,$$

and

$$V = V(\mathbf{r}_1, \dots, \mathbf{r}_N),$$

N being the number of particles in the system; so that

$$\exp(\kappa\mathbf{H})\psi = \exp[\kappa(\mathbf{T} + V)]\psi.$$

Operators like $\exp[\kappa(\mathbf{T} + V)]$, or more generally of the form $\exp[\kappa(O_1 + O_2)]$, where O_1 and O_2 are non-commuting operators, have been studied extensively.⁹ The two more familiar methods of decomposing the double-operator exponent are given by Schwinger, and

⁸ R. Kubo, J. Chem. Phys. **20**, 770 (1952).

⁹ A. W. Saenz and R. C. O'Rourke, Revs. Modern Phys. **27**, 381 (1955); R. Peierls, Z. Physik **80**, 763 (1933); J. Schwinger, Phys. Rev. **82**, 664 (1951).

Saenz and O'Rourke, for operating on a general ψ . The basic method of expanding $\exp[\kappa(O_1+O_2)]$, has also been employed by Golden² for a plane-wave function, to derive the representative $\langle \mathbf{r} | \exp(\kappa \mathbf{H}) | \mathbf{p} \rangle$. In the present investigation, $\langle \mathbf{r} | \exp(\kappa \mathbf{H}) | \mathbf{p} \rangle$ is obtained by solving a nonlinear second order differential equation—this method is less laborious than the three previous ones, and it also leads to a much more compact and useful form for the representative.

4. FUNCTIONAL REPRESENTATIVE $\langle \mathbf{r} | \exp(\kappa \mathbf{H}) | \mathbf{p} \rangle$

The differential equation for $\langle \mathbf{r} | \exp(\kappa \mathbf{H}) | \mathbf{p} \rangle$ can be obtained as follows:

$$\begin{aligned} \frac{\partial \langle \mathbf{r} | \exp(\kappa \mathbf{H}) | \mathbf{p} \rangle}{\partial \kappa} &= \langle \mathbf{r} | \mathbf{H} \exp(\kappa \mathbf{H}) | \mathbf{p} \rangle \\ &= \left[\frac{p^2}{2m} + V + \frac{\hbar}{mi} (\mathbf{p} \cdot \nabla) - \frac{\hbar^2}{2m} \nabla^2 \right] \\ &\quad \times \langle \mathbf{r} | \exp(\kappa \mathbf{H}) | \mathbf{p} \rangle. \end{aligned} \quad (4.1)$$

If we put

$$\begin{aligned} \langle \mathbf{r} | \exp(\kappa \mathbf{H}) | \mathbf{p} \rangle &= \exp \left[\kappa \frac{p^2}{2m} + \Phi \right], \\ \alpha &= \hbar/mi, \quad \beta = -\hbar^2/2m, \end{aligned}$$

then (4.1) takes the form:

$$\partial \Phi / \partial \kappa = \alpha (\mathbf{p} \cdot \nabla) \Phi + \beta \nabla^2 \Phi + \beta \nabla \Phi \cdot \nabla \Phi + V. \quad (4.2)$$

This differential equation cannot be solved in closed form; it has to be solved by an iterative procedure. A tentative form of the differential equation for the iteration is

$$\partial \Phi_{n+1} / \partial \kappa = \alpha (\mathbf{p} \cdot \nabla) \Phi_{n+1} + \beta \nabla^2 \Phi_n + \beta \nabla \Phi_n \cdot \nabla \Phi_n + V, \quad (4.3)$$

where Φ_n is the solution at the n th stage of the iteration. The first approximation, Φ_1 , is obtained by neglecting the second and third terms on the right-hand side of (4.2), which amounts to taking $\Phi_0 = 0$.

The expression obtained for Φ is

$$\Phi = \xi_0 + \beta \xi_1 + \beta^2 \xi_2 + \dots, \quad (4.4)$$

where

$$\begin{aligned} \xi_0 &= \int_0^\kappa V(\mathbf{r} + \alpha \mathbf{p} u_1) du_1, \\ \xi_1 &= \int_0^\kappa du_1 u_1 \nabla^2 V(\mathbf{r} + \alpha \mathbf{p} u_1) \\ &\quad + (2!) \int_0^\kappa du_3 \int_0^{u_3} du_2 \int_0^{u_2} du_1 \nabla V(\mathbf{r} + \alpha \mathbf{p} u_1) \\ &\quad \quad \cdot \nabla V(\mathbf{r} + \alpha \mathbf{p} u_1) \\ &\quad + (3!) \int_0^\kappa du_4 \int_0^{u_4} du_3 \int_0^{u_3} du_2 \int_0^{u_2} du_1 \nabla V(\mathbf{r} + \alpha \mathbf{p} u_1) \\ &\quad \quad \cdot \nabla(\alpha \mathbf{p} \cdot \nabla) V(\mathbf{r} + \alpha \mathbf{p} u_1) \dots \end{aligned}$$

An alternative and more compact solution can be obtained by considering the differential equation:

$$\partial \Phi_{n+1} / \partial \kappa = \alpha (\mathbf{p} \cdot \nabla) \Phi_{n+1} + \beta \nabla^2 \Phi_{n+1} + \beta \nabla \Phi_n \cdot \nabla \Phi_n + V, \quad (4.5)$$

which gives for Φ the expression:

$$\begin{aligned} \Phi &= \int_0^\kappa du_1 \{ \exp u_1 [\alpha (\mathbf{p} \cdot \nabla) + \beta \nabla^2] \} V - \frac{\hbar^2 2!}{2m} \\ &\quad \times \int_0^\kappa du_3 \int_0^{u_3} du_2 \int_0^{u_2} du_1 \{ \exp u_1 [\alpha (\mathbf{p} \cdot \nabla) + \beta \nabla^2] \} \\ &\quad \times \nabla V \cdot \nabla V + \frac{\hbar^3 3! i}{2m^2} \int_0^\kappa du_4 \int_0^{u_4} du_3 \int_0^{u_3} du_2 \int_0^{u_2} du_1 \\ &\quad \times \{ \exp u_1 [\alpha (\mathbf{p} \cdot \nabla) + \beta \nabla^2] \} \nabla V \cdot \nabla (\mathbf{p} \cdot \nabla) V + \dots \end{aligned} \quad (4.6)$$

Using (4.6), the expression for the representative $\langle \mathbf{r} | \exp(\kappa \mathbf{H}) | \mathbf{p} \rangle$ is

$$\begin{aligned} \exp \left\{ \kappa \frac{p^2}{2m} + \int_0^\kappa du_1 \{ \exp u_1 [\alpha (\mathbf{p} \cdot \nabla) + \beta \nabla^2] \} V - \frac{\hbar^2 2!}{2m} \right. \\ \left. \times \int_0^\kappa du_3 \int_0^{u_3} du_2 \int_0^{u_2} du_1 \{ \exp u_1 [\alpha (\mathbf{p} \cdot \nabla) + \beta \nabla^2] \} \right. \\ \left. \times \nabla V \cdot \nabla V + \dots \right\}. \end{aligned} \quad (4.7)$$

It can be verified that (4.7) reproduces the series of Golden² on expansion, viz.

$$\begin{aligned} \langle \mathbf{r} | \exp(\kappa \mathbf{H}) | \mathbf{p} \rangle &= \left\{ \exp \left[\kappa \left(\frac{p^2}{2m} + V \right) \right] \right\} \\ &\quad \times \left\{ 1 + \kappa^2 \left(\frac{\hbar}{2mi} (\mathbf{p} \cdot \nabla) V - \frac{\hbar^2}{4m} \nabla^2 V \right) \right. \\ &\quad \left. + \kappa^3 \left[-\frac{\hbar^2}{6m^2} ((\mathbf{p} \cdot \nabla)^2 V + m \nabla V \cdot \nabla V) + \frac{i \hbar^3}{6m^2} (\mathbf{p} \cdot \nabla) \nabla^2 V \right. \right. \\ &\quad \left. \left. + \frac{\hbar^4}{24m^2} (\nabla \cdot \nabla)^2 V \right] + \dots \right\}. \end{aligned} \quad (4.8)$$

5. APPLICATIONS

The density matrix (2.5a) can be written as follows:

$$\begin{aligned} \rho(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{2\pi i} \oint_{\gamma-i\infty}^{\gamma+i\infty} dz \frac{e^{z\lambda}}{z} \langle \mathbf{r}_1 | \exp(-z\mathbf{H}) | \mathbf{r}_2 \rangle \\ &= \frac{1}{2\pi i} \oint_{\gamma-i\infty}^{\gamma+i\infty} dz \frac{e^{z\lambda}}{z} \sum_{\mathbf{p}} \langle \mathbf{r}_1 | \exp(-\frac{1}{2}z\mathbf{H}) | \mathbf{p} \rangle \\ &\quad \times \langle \mathbf{p} | \exp(-\frac{1}{2}z\mathbf{H}) | \mathbf{r}_2 \rangle \\ &= \frac{1}{2\pi i} \oint_{\gamma-i\infty}^{\gamma+i\infty} dz \frac{e^{z\lambda}}{z} \sum_{\mathbf{p}} \langle \mathbf{r}_1 | \exp(-\frac{1}{2}z\mathbf{H}) | \mathbf{p} \rangle \\ &\quad \times \langle \mathbf{r}_2 | \exp(-\frac{1}{2}z^*\mathbf{H}) | \mathbf{p} \rangle^\dagger, \end{aligned} \quad (5.1)$$

where λ_M has been replaced by λ . Substituting for $\langle \mathbf{r}_1 | \exp(-\frac{1}{2}z\mathbf{H}) | \mathbf{p} \rangle$ and $\langle \mathbf{r}_2 | \exp(-\frac{1}{2}z^*\mathbf{H}) | \mathbf{p} \rangle^\dagger$, from (4.7) in (5.1):

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{dz}{z} \left\{ \exp \left(z\lambda - \frac{z}{2} [V(\mathbf{r}_1) + V(\mathbf{r}_2)] - \frac{z^2 \hbar^2}{16m} [\nabla^2 V_{\mathbf{r}_1} + \nabla^2 V_{\mathbf{r}_2}] \cdots \right) \right. \\ \left. \times \int d\mathbf{p} \exp \left(-z \frac{p^2}{2m} + \frac{z^2 \hbar}{8mi} [\mathbf{p} \cdot (\nabla V)_{\mathbf{r}_1} - \mathbf{p} \cdot (\nabla V)_{\mathbf{r}_2}] + \frac{z^3 \hbar^2}{48m^2} [(\mathbf{p} \cdot \nabla)^2 V_{\mathbf{r}_1} + (\mathbf{p} \cdot \nabla)^2 V_{\mathbf{r}_2}] \cdots \right) \exp \left[\frac{i\mathbf{p}}{\hbar} \cdot (\mathbf{r}_1 - \mathbf{r}_2) \right] \right\}. \quad (5.2)$$

The exact evaluation of the density matrix (5.2) will be restricted to cases where the inverse transform and the integral over \mathbf{p} are both obtainable, and this will only be possible for certain potential functions. In most cases, (5.2) can be evaluated only after making approximations up to some order in \hbar in the exponents.

The integration over \mathbf{p} usually leads to some restrictions on the permissible values for the variable in the inverse transform, which means that the contour of integration has to be modified. It is in connection with this modification of contours that a judicious choice between a complex variable form and a real variable form for the θ_M operator of (2.2) is helpful. Only the complex variable forms for the density matrix and the density will be worked out in detail; the corre-

sponding expressions for the real variable form can be obtained on the same lines, they will only be indicated here whenever necessary.

A general form for the density matrix will now be evaluated using an approximation of (5.2) for two cases of interest: (1) a spherically symmetrical system and (2) a one-dimensional system. The densities for a one-dimensional harmonic oscillator and a Coulomb potential, derived from (5.2), will also be examined in some detail for a Fermi-Dirac distribution.

5a. DENSITY MATRIX

Neglecting terms in \hbar^2 in the exponents of (5.2), and integrating over \mathbf{p} ,

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \frac{(2m\pi)^{\frac{3}{2}}}{2\pi i} \int_C dz \frac{\exp\{z\lambda - \frac{1}{2}z[V(\mathbf{r}_1) + V(\mathbf{r}_2)]\}}{z^{\frac{3}{2}}} \exp \left\{ -\frac{1}{4} \left[\frac{2m}{\hbar^2} \frac{|\mathbf{r}_1 - \mathbf{r}_2|^2}{z} - \frac{z}{2} |\mathbf{r}_1 - \mathbf{r}_2| \right. \right. \\ \left. \left. \times \{ \nabla V_{\mathbf{r}_1} \cos(\mathbf{r}_1 | \mathbf{r}_1 - \mathbf{r}_2) - \nabla V_{\mathbf{r}_2} \cos(\mathbf{r}_2 | \mathbf{r}_1 - \mathbf{r}_2) \} + \frac{\hbar^2 z^3}{16m} \{ \nabla V_{\mathbf{r}_1} \cdot \nabla V_{\mathbf{r}_2} \cos(\mathbf{r}_1 | \mathbf{r}_2) + \frac{1}{2} (\nabla V_{\mathbf{r}_1})^2 + \frac{1}{2} (\nabla V_{\mathbf{r}_2})^2 \} \right] \right\}, \quad (5.3)$$

where \int_C denotes integration over the modified Bromwich contour. Neglecting terms in \hbar^2 again and integrating over z :

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \frac{4\pi}{3} (2m)^{\frac{3}{2}} \xi^{\frac{3}{2}} \frac{3[\sin \zeta - \zeta \cos \zeta]}{\zeta^3}; \quad (5.4)$$

where

$$\xi = \left\{ \lambda - \frac{1}{2} [V(\mathbf{r}_1) + V(\mathbf{r}_2)] + \frac{1}{8} |\mathbf{r}_1 - \mathbf{r}_2| [\nabla V_{\mathbf{r}_1} \cos \bar{\alpha} - \nabla V_{\mathbf{r}_2} \cos \bar{\beta}] \right\}; \\ \zeta = \xi^{\frac{1}{2}} |\mathbf{r}_1 - \mathbf{r}_2| (2m)^{\frac{1}{2}} / \hbar;$$

$\bar{\alpha}$ is the angle $(\mathbf{r}_1 | \mathbf{r}_1 - \mathbf{r}_2)$, and $\bar{\beta}$ the angle $(\mathbf{r}_2 | \mathbf{r}_1 - \mathbf{r}_2)$.

(5.4) has the form of the density matrix used by Froman¹⁰ for the T.F. model. They differ in that (5.4) is symmetrical in \mathbf{r}_1 and \mathbf{r}_2 , as the density matrix should be; (5.4) also involves the angles $\bar{\alpha}$ and $\bar{\beta}$, which appear in the wave-mechanical density matrix but do not in Froman's expression.

In the one-dimensional case, the form corresponding to (5.3) is

$$\rho(x_1, x_2) = \frac{(2m\pi)^{\frac{1}{2}}}{2\pi i} \int_C dz \frac{\exp\{z\lambda - \frac{1}{2}z[V(x_1) + V(x_2)]\}}{z^{\frac{3}{2}}} \exp \left\{ -\frac{1}{4} \left[\frac{2m}{\hbar^2} \frac{(x_1 - x_2)^2}{z} - \frac{z}{2} |x_1 - x_2| \left(\frac{\partial V(x_1)}{\partial x_1} - \frac{\partial V(x_2)}{\partial x_2} \right) \right. \right. \\ \left. \left. + \frac{\hbar^2 z^3}{32m} \left(\left(\frac{\partial V(x_1)}{\partial x_1} \right)^2 + \left(\frac{\partial V(x_2)}{\partial x_2} \right)^2 \right) \right] \right\}. \quad (5.5)$$

¹⁰ P. O. Froman, Arkiv Fysik 5, 135 (1952).

Neglecting the term in \hbar^2 , and integrating over z :

$$\rho(x_1, x_2) = \frac{2\hbar}{x_1 - x_2} \sin \left[\frac{(2m)^{\frac{1}{2}}}{\hbar} (x_1 - x_2) \eta^{\frac{1}{2}} \right], \quad (5.6)$$

where

$$\eta = \lambda - \frac{V(x_1) + V(x_2)}{2} + \frac{x_1 - x_2}{8} \left(\frac{\partial V(x_1)}{\partial x_1} - \frac{\partial V(x_2)}{\partial x_2} \right),$$

which differs from the density matrix in the one-dimensional T.F. model used by March,¹¹ by containing a third term in η .

5b. DENSITY

The density is given by (5.2) when $\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}$, so that

$$\rho(\mathbf{r}, \mathbf{r}) = \frac{1}{2\pi i} \oint_{\gamma-i\infty}^{\gamma+i\infty} \frac{dz}{z} \exp \left[z\lambda - zV - \frac{z^2 \hbar^2}{8m} \nabla^2 V + \frac{z^3 \hbar^2}{24m^2} (\nabla V)^2 \dots \right] \int d\mathbf{p} \exp \left[-z \frac{p^2}{2m} + \frac{z^3 \hbar^2}{24m^2} (\mathbf{p} \cdot \nabla)^2 V \dots \right]. \quad (5.7)$$

Keeping terms up to \hbar^2 in the exponent and integrating over p ,

$$\rho(\mathbf{r}, \mathbf{r}) = \frac{(2m\pi)^{\frac{3}{2}}}{2\pi i} \int_C dz \frac{\exp \left[z\lambda - zV - \frac{z^2 \hbar^2}{8m} \nabla^2 V + \frac{z^3 \hbar^2}{24m^2} (\nabla V)^2 \right]}{z^{\frac{3}{2}} \left(1 - \frac{z^2 \hbar^2}{12m} \frac{1}{r} \frac{\partial V}{\partial r} \right)^{\frac{1}{2}} \left(1 - \frac{z^2 \hbar^2}{12m} \frac{1}{r} \frac{\partial V}{\partial r} \right)^{\frac{1}{2}} \left(1 - \frac{z^2 \hbar^2}{12m} \frac{\partial^2 V}{\partial r^2} \right)^{\frac{1}{2}}}. \quad (5.8)$$

The corresponding expression in the one-dimensional case is

$$\rho(x, x) = \frac{(2m\pi)^{\frac{1}{2}}}{2\pi i} \int_C dz \frac{\exp \left[z\lambda - zV - \frac{z^2 \hbar^2}{8m} \frac{\partial^2 V}{\partial x^2} + \frac{z^3 \hbar^2}{24m^2} \left(\frac{\partial V}{\partial x} \right)^2 \right]}{z^{\frac{3}{2}} \left[1 - \frac{z^2 \hbar^2}{12m} \frac{\partial^2 V}{\partial x^2} \right]^{\frac{1}{2}}}. \quad (5.9)$$

(5.8) and (5.9) are general expressions for the density of states in a three-dimensional and one-dimensional system, respectively, in the form of contour integrals. It is not practical to perform these integrations at this stage for the general case; it is preferable to carry out separate integrations for each individual application, when available data on the potential will facilitate the operations and lead directly to a simplified form for the density.

At a lower limit of approximation in \hbar , (5.8) and (5.9) reduce to the less accurate expressions for the density obtainable by putting $\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}$ in (5.3), and $x_1 = x_2 = x$ in (5.5), respectively. It is also easy to verify that the T.F. densities, viz.:

$$\frac{8\pi}{3\hbar^3} (2m)^{\frac{3}{2}} [\lambda - V]^{\frac{3}{2}}, \quad \text{and} \quad \frac{2(2m)^{\frac{1}{2}}}{\hbar} [\lambda - V]^{\frac{1}{2}},$$

for a three-dimensional and a one-dimensional system, respectively, are recovered from (5.8) and (5.9), in the limit $\hbar^2 \rightarrow 0$, for a Fermi-Dirac distribution.

The expressions (5.8) and (5.9) will now be employed in the problems of the linear harmonic oscillator and of the Coulomb potential.

5c. THE LINEAR HARMONIC OSCILLATOR

The potential for the linear harmonic oscillator is¹ $V = \mu x^2$, where $\mu = 2\pi^2 m \nu_0^2$, ν_0 being the classical frequency of the oscillator. Substituting for V in (5.9) yields

$$\rho = \frac{(2m\pi)^{\frac{1}{2}}}{2\pi i} \int_C dz \frac{\exp [z\lambda - zV - z^2 \hbar^2 \mu / 4m + z^3 (\hbar^2 \mu^2 / 6m^2) x^2]}{z^{\frac{3}{2}} (1 - \mu \hbar^2 z^2 / 6m)^{\frac{1}{2}}}. \quad (5.10)$$

¹¹ N. H. March, Proc. Phys. Soc. (London) **70**, 839 (1957).

It is more convenient to use here the Fourier sine transform for the density, instead of the Laplace inverse transform. It can be easily verified that the expression corresponding to (5.10) as a Fourier sine transform is

$$\rho = \frac{2}{\pi} (2m\pi)^{\frac{1}{2}} \int_0^\infty dy \frac{\sin \lambda y}{y^{\frac{1}{2}}} \left\{ \frac{\cos(yV + y^3 \hbar^2 \mu^2 x^2 / 6m^2) - \sin(yV + y^3 \hbar^2 \mu^2 x^2 / 6m^2)}{(1 + \mu \hbar^2 y^2 / 6m)^{\frac{1}{2}}} \right\} \exp\left(\frac{y^2 \hbar^2 \mu}{4m}\right). \quad (5.11)$$

(5.11) will be evaluated as a first approximation, by neglecting terms in the numerator involving \hbar^2 . ρ is then given by the expressions:

$$\begin{aligned} \left(\frac{a_1 m}{\pi}\right)^{\frac{1}{2}} \left[-\left(\frac{\lambda+V}{a_1}\right)^{\frac{3}{2}} \left[K_{3/4}^2\left(\frac{\lambda+V}{2a_1}\right) - K_{1/4}^2\left(\frac{\lambda+V}{2a_1}\right) \right] + \left(\frac{\lambda-V}{a_1}\right)^{\frac{3}{2}} \left[K_{3/4}^2\left(\frac{\lambda-V}{2a_1}\right) - K_{1/4}^2\left(\frac{\lambda-V}{2a_1}\right) \right] \right. \\ \left. + \pi \sqrt{2} \left(\frac{\lambda-V}{a_1}\right)^{\frac{3}{2}} \left[K_{3/4}\left(\frac{\lambda-V}{2a_1}\right) I_{3/4}\left(\frac{\lambda-V}{2a_1}\right) + K_{1/4}\left(\frac{\lambda-V}{2a_1}\right) I_{-1/4}\left(\frac{\lambda-V}{2a_1}\right) \right] \right], \quad (5.12a) \end{aligned}$$

for $\lambda > V$; and

$$\left(\frac{a_1 m}{\pi}\right)^{\frac{1}{2}} \left[-\left(\frac{\lambda+V}{a_1}\right)^{\frac{3}{2}} \left[K_{3/4}^2\left(\frac{\lambda+V}{2a_1}\right) - K_{1/4}^2\left(\frac{\lambda+V}{2a_1}\right) \right] + \left(\frac{V-\lambda}{a_1}\right)^{\frac{3}{2}} \left[K_{3/4}^2\left(\frac{V-\lambda}{2a_1}\right) - K_{1/4}^2\left(\frac{V-\lambda}{2a_1}\right) \right] \right], \quad (5.12b)$$

for $\lambda < V$; where $K_s(v)$ is a modified Bessel function of the third kind, $I_s(v)$ is a modified Bessel function of the first kind, and $a_1 = \hbar \nu_0 / 2\sqrt{3}$.

If the terms in the numerator involving \hbar^2 are taken into account, ρ is then given approximately by the expressions:

$$\begin{aligned} \frac{\pi}{2} \left(\frac{a_2 m}{2}\right)^{\frac{1}{2}} \left[\left(\frac{\lambda+V}{a_2}\right)^{\frac{3}{2}} \left[J_{-1/4}^2\left(\frac{\lambda+V}{2a_2}\right) + J_{3/4}^2\left(\frac{\lambda+V}{2a_2}\right) - J_{-3/4}^2\left(\frac{\lambda+V}{2a_2}\right) - J_{1/4}^2\left(\frac{\lambda+V}{2a_2}\right) \right] \right. \\ \left. + \left(\frac{\lambda-V}{a_2}\right)^{\frac{3}{2}} \left[J_{-3/4}^2\left(\frac{\lambda-V}{2a_2}\right) + J_{1/4}^2\left(\frac{\lambda-V}{2a_2}\right) + J_{-1/4}^2\left(\frac{\lambda-V}{2a_2}\right) + J_{3/4}^2\left(\frac{\lambda-V}{2a_2}\right) \right] \right], \quad (5.13a) \end{aligned}$$

for $\lambda > V$; and

$$\begin{aligned} \frac{\pi}{2} \left(\frac{a_2 m}{2}\right)^{\frac{1}{2}} \left[\left(\frac{\lambda+V}{a_2}\right)^{\frac{3}{2}} \left[J_{-1/4}^2\left(\frac{\lambda+V}{2a_2}\right) + J_{3/4}^2\left(\frac{\lambda+V}{2a_2}\right) - J_{-3/4}^2\left(\frac{\lambda+V}{2a_2}\right) - J_{1/4}^2\left(\frac{\lambda+V}{2a_2}\right) \right] \right. \\ \left. - \left(\frac{V-\lambda}{a_2}\right)^{\frac{3}{2}} \left[J_{-1/4}^2\left(\frac{V-\lambda}{2a_2}\right) + J_{3/4}^2\left(\frac{V-\lambda}{2a_2}\right) - J_{-3/4}^2\left(\frac{V-\lambda}{2a_2}\right) - J_{1/4}^2\left(\frac{V-\lambda}{2a_2}\right) \right] \right], \quad (5.13b) \end{aligned}$$

for $\lambda < V$; where $J_s(v)$ is a Bessel function of the first kind, and $a_2 = \hbar \nu_0 / 2\sqrt{6}$. It can easily be checked that expressions (5.12a and b) and (5.13a and b) reduce to the T.F. density for the linear harmonic oscillator for a_1 and $a_2 \rightarrow 0$.

The expressions (5.12a and b) and (5.13a and b) were evaluated for the case $\lambda = 3\hbar \nu_0$, i.e., for two occupied energy levels, and in Fig. 1, the quantity ρ/α is plotted against αx , where $\alpha^2 = 4\pi^2 m \nu_0 / \hbar$. The corresponding curves for the wave mechanical and the T.F. oscillator are shown for comparison. It is clearly seen from the figure how each additional corrective term progressively brings more wave mechanical characteristics into the T.F. density.

5d. COULOMB POTENTIAL AND ISOLATED ATOM

For the Coulomb potential $V = -Q/r$, the density is given by (5.8) as

$$\rho = \frac{(2m\pi)^{\frac{1}{2}}}{2\pi i} \int_C dz \frac{\exp[z(\lambda - V) + (z^3 \hbar^2 / 24m^2)(Q^2/r^4)]}{z^{\frac{1}{2}} [1 - z^2(\hbar^2/12m)(Q/r^3)]^{\frac{1}{2}} [1 - z^2(\hbar^2/12m)(Q/r^3)]^{\frac{1}{2}} [1 + z^2(\hbar^2/6m)(Q/r^3)]^{\frac{1}{2}}}. \quad (5.14)$$

Neglecting the second term in the exponent, the integral has the value:

$$\rho = (2m\pi)^{\frac{3}{2}} \frac{a}{b^{\frac{3}{2}}} \times \int_0^{b(\lambda-V)} F(v) \sinh\left(\frac{a}{b}[b(\lambda-V)-v]\right) dv; \quad (5.15)$$

where

$$F(v) = \frac{1}{\sqrt{7/2}} v^{\frac{3}{2}} \left[{}_1F_2\left\{ \begin{matrix} 1 & 7 & 9 \\ 2 & 4 & 4 \end{matrix} ; -\frac{v^2}{4} \right\} \right],$$

$$a^2 = 12mr^3/\hbar^2 Q,$$

$$b^2 = 6mr^3/\hbar^2 Q,$$

and ${}_1F_2$ is a generalized hypergeometric function. It can be verified that (5.15) is finite at the origin, going to Q^3 as $r \rightarrow 0$, corresponding to the wave-mechanical behavior for the Coulomb potential at the origin, barring the numerical factor. For large values of r , $\rho \rightarrow (\lambda - V)^{\frac{3}{2}}$ as in the T.F. model.

For a proper self-consistent treatment of an isolated atom, Poisson's equation with a density given by (5.8) has to be solved subject to the appropriate conditions for V ; this calculation is now under way and the results will be reported in a subsequent publication. It is worth pointing out at this stage, however, that an estimate of the electron density for an isolated atom can be made perturbation-wise using Eq. (5.8) and taking for $(\lambda - V)$ the known values for the T.F. atom.¹² This approximate density for hydrogen is plotted in Fig. 2; the corresponding curve for the T.F., wave-mechanical, and

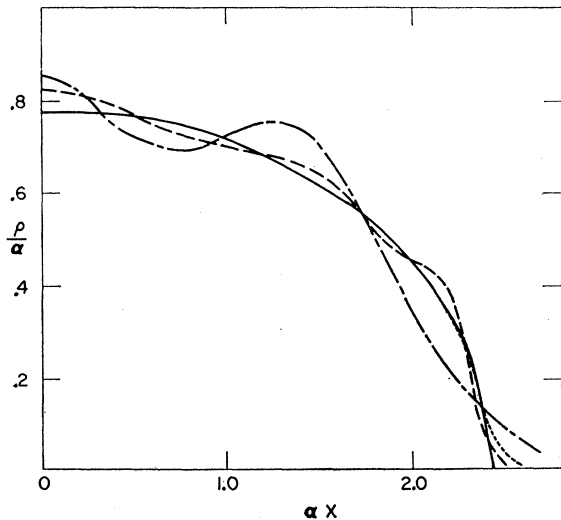


FIG. 1. Densities for linear harmonic oscillator. ——— Wave mechanics; ——— Thomas-Fermi; - - - - first approximation; ····· second approximation.

¹² V. Bush and S. H. Caldwell, Phys. Rev. 38, 1898 (1931).

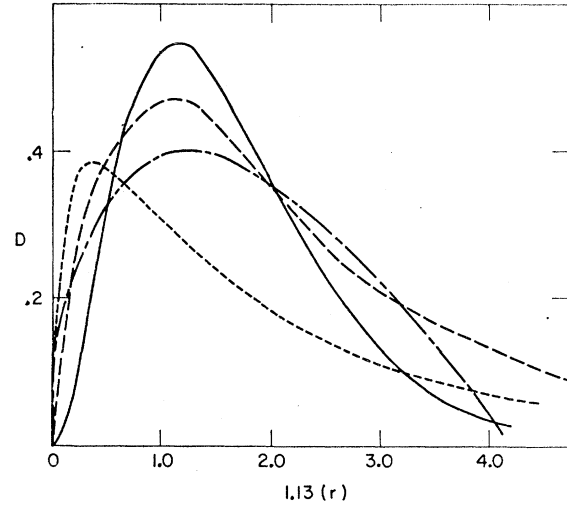


FIG. 2. Radial distribution of electrons for hydrogen, with r in atomic units. ——— Wave mechanics; - - - - Thomas-Fermi; ——— Fermi-Amaldi-Golden; ····· present calculations.

Fermi-Amaldi-Golden² models are shown for comparison.

6. DISCUSSION

It is found that even within the limits of fairly severe approximations, the more critical features of wave mechanics are brought out in the simple cases chosen for illustration here. In the harmonic oscillator problem, the crossover into the nonclassical region and the oscillation of curve 4 in Fig. 1, corresponding to the wave-mechanical behavior, are definite improvements over the T.F. results. Better agreement with wave-mechanical results should be expected as the number of occupied energy levels increases. It is also worth noting that the curve for the first approximation, has a close correspondence to the density curve of Ballinger and March¹³ for the T.F. oscillator with the Weizsäcker correction.

In the case of the Coulomb potential, the proper behavior at $r \rightarrow 0$ is a significant improvement over the T.F. method where the density is infinite. This overestimation of the density at a singularity in the T.F. model, is known to lead to low values in energy calculations; better results can, therefore, be expected with the present method.

The diagram for the electron density in the hydrogen atom indicates that the rough estimate made by employing the T.F. potential in the quantum-corrected density, is in better qualitative and quantitative agreement with wave mechanics than either the T.F. or the Fermi-Amaldi-Golden density, for the region $r < 2.5$ atomic units; for larger values of r , however, the density is overestimated and higher order corrections would probably have to be included.

¹³ R. A. Ballinger and N. H. March, Proc. Phys. Soc. (London) A67, 378 (1954).

The range of application of the method developed in the present investigation is determined by the possibility of carrying out the integration over \mathbf{p} , and the subsequent inverse transform. Approximations have to be made to permit this double integration, and these approximations curtail to a certain extent the great potentialities of the method. Applications to a wider range of problems would be possible if θ_M , the function of the Hamiltonian operator of (2.2), appeared in a simpler and more manageable form than as an inverse

transform. As the method stands, however, it is still applicable to a variety of interesting problems in quantum statistics.

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Effect of a Constant Electrical Field on Germanium Fast Surface States*

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The experimental evidence regarding the effect of electric fields on the fast states of germanium is, at present, contradictory: Litovchenko and Lyashenko explained their experimental results by assuming the fields only affect the density of states but not their energy, this would support the current view on charge transfer through the semiconductor oxide layer. Rzhano *et al.*, on the other hand, reported field-induced changes in energy as well as density. To resolve this question, careful measurements of surface recombination velocity and surface conductivity were performed before and after application of dc fields of about 2×10^6 volts/cm. Though the effect of the field on the surface state density was much smaller than that found by Litovchenko and Lyashenko, the experimental results indicated clearly that the energy and ratio of capture cross sections were indeed unaffected by the field. It was also found that in wet ambients an ac field shifted the unperturbed surface potential by more than $+5kT$.

1. INTRODUCTION

LITOVCHENKO and Lyashenko¹ reported that prolonged application (of over 10 minutes) of strong electric fields $\{ \geq [(0.5-1) \times 10^6 \text{ volts/cm}] \}$ affected the density of the fast germanium surface states. They investigated the field effect (change in surface conductivity $\Delta\sigma$ with applied pulsed field) on a *p*-type germanium specimen, dimensions of $1.5 \times 0.5 \times 0.03 \text{ cm}^3$, cut perpendicular to the 110 axis and of 20–30 ohm-cm resistivity. Their measurements were performed in a vacuum of 10^{-6} mm Hg and in a dry air atmosphere, the effect being present in both ambients. They found a considerable change in the $\Delta\sigma$ vs u_s curve (u_s being the surface potential; i.e., using the notation of Kingston and Neustadter² and of Many and Gerlich³: $u_s = q\varphi_s/kT$) after application of a dc field and explained their experimental results by assuming that the surface state energy ($E_t - E_i$) remains constant, whereas the

density N_t of the states does change. This assumption could not be verified experimentally by measuring only the change in surface conductivity, because for each $\Delta\sigma(u_s)$ plot ($E_t - E_i$) as well as N_t are unknown and one parameter can only be determined with a reasonable accuracy if the other is known. However, by performing combined measurements of surface recombination velocity s and changes in surface conductivity $\Delta\sigma$, the energy ($E_t - E_i$) of the recombination centers, the ratio c_p/c_n of the capture cross sections of holes c_p and electrons c_n , and the density of states can be measured and hence all surface state parameters be determined. Combined measurements were therefore performed on a germanium crystal, before and after application of a strong electric field, and the results are published in this paper.

2. EXPERIMENTAL METHOD

The germanium specimen investigated was *n* type, of 17 ohm-cm resistivity, of dimensions $1.45 \times 0.39 \times 0.038 \text{ cm}$, and cut parallel to the (111) plane. It had two soldered end contacts, one Ohmic and the other slightly injecting, and was etched in CP-4A for one minute at 35°C . After etching and rinsing, brass field plates were clamped to the crystal with mica sheets (of 0.004 cm thickness) sandwiched between them. The assembly was placed in a glass tube, subjected for two days to a

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¹ V. G. Litovchenko and V. I. Lyashenko, *Soviet Phys.-Solid State* **1**, 1470 (1960).

² R. H. Kingston and R. F. Neustadter, *J. Appl. Phys.* **26**, 718 (1955).

³ A. Many and D. Gerlich, *Phys. Rev.* **107**, 404 (1957).