

Statistical Theory of Many-Electron Systems. Discrete Bases of Representation*

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The density matrix for a many-electron system has been examined. A formalism has been arrived at which facilitates its evaluation in terms of a basis corresponding to a discrete spectrum of eigenvalues. This allows a representation to be employed associated with a suitably chosen approximation to the Hamiltonian. Thereby, reasonably accurate estimates of the properties of many-electron systems may be anticipated for low orders of approximation.

In developing the formalism, attention was focused upon a means for approximating the quantity $\exp(z\mathbf{H})$, where \mathbf{H} is the many-particle Hamiltonian and z is a complex number. It was found possible to represent this quantity exactly as an infinite product of exponential factors, each of which depends upon a portion of the Hamiltonian alone. The relation of this result to statistical mechanical applications is indicated. An approximation procedure is described in terms of which various finite products of exponential factors approach the desired quantity in the limit of

indefinitely increasing numbers of factors; this limit is approached in a manner that permits any given approximation to contain all the terms of the previous approximation.

The first order of approximation was employed to approximate the many-particle density matrix. The resulting theory was applied to the helium-like systems: He, Li^+ , Be^{++} . The energies of the ground 1S state of helium and the three lowest states of Li^+ and Be^{++} were calculated. The agreement with experimental term values is reasonably satisfactory, the discrepancy between calculations and experiments not exceeding one percent. The triplet-singlet splitting for Li^+ was in the order observed; the magnitude calculated was about one-half that observed.

The relation between the present theory and the Thomas-Fermi theory is discussed. It is pointed out that the former is the analog of the latter when the density matrix is expressed in other than eigenfunctions of momentum. The quasi-classical character of the approximation is discussed.

1. INTRODUCTION

IN a previous paper,¹ the density matrix for a many-electron system was examined with a view toward extending the statistical theory of Thomas² and Fermi.³ This is also the purpose of the present paper.

To establish its connection with the Thomas-Fermi theory, the density matrix was evaluated in terms of a basis of eigenfunctions of momentum. Because the density matrix is invariant to changes in the basis of representation, no loss of generality was entailed thereby. In spite of some of the mathematical convenience which accompanies the use of a basis which corresponds to a continuous spectrum of eigenvalues,⁴ there is reason to suppose that for most problems of atomic and molecular structure such a basis is not the best suited one. Viewed in the sense of perturbation theory, the basis employed in (I) corresponds to an unperturbed problem in which the kinetic energy is diagonal, a rather poor approximation for atomic and molecular systems even if interelectronic repulsions are neglected. Accordingly, one of the present aims is to extend the formulation of (I) so as to facilitate the evaluation of the density matrix in terms of a basis of eigenfunctions of an arbitrary Hamiltonian. The attending flexibility introduced thereby allows one to anticipate that with a suitably chosen representation

(corresponding to a suitably chosen approximation to the Hamiltonian) reasonably accurate estimates of the properties of many-electron systems may be attained with no undue effort.

In Sec. 2 a formalism is presented suitable for a basis corresponding to a discrete spectrum of eigenvalues. A formally exact representation of $\exp(z\mathbf{H})$ is given, in terms of a decomposition of \mathbf{H} , where z is a complex number and \mathbf{H} is the many-particle Hamiltonian. This representation is utilized in Sec. 3 to arrive at an approximation for the many-particle density matrix. Expressions for the characteristic energy values of such a system are considered in Sec. 4. The theory is applied to helium-like atoms in Sec. 5, the results obtained being summarized in Sec. 6. Section 7 is devoted to a discussion of the method utilized, especially its relation to the original Thomas-Fermi theory.

2. DISCRETE FORMALISM

For the sake of brevity a familiarity with the results of (I) will be assumed. Then the present section relates in part to the determination of an expression for a function of the N -particle Hamiltonian,

$$f(\mathbf{H}) \equiv \sum_{n=0}^{\infty} \frac{f^{(n)}(0)}{n!} \mathbf{H}^n \quad (2.1)$$

in terms of which powers of an approximation to the Hamiltonian appear always on the right side of the expression. For an arbitrary power of the Hamiltonian, one has

$$\mathbf{H}^n = (\mathbf{H}_0 + V)^n = \mathbf{H}_0^n + \sum_{j=0}^{n-1} \mathbf{H}_0^{n-1-j} V \mathbf{H}_0^j \\ + \sum_{j,k=0}^{j+k=n-2} \mathbf{H}_0^{n-2-j-k} V \mathbf{H}_0^j V \mathbf{H}_0^k + \dots + V^n, \quad (2.2)$$

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¹ S. Golden, *Phys. Rev.* **105**, 604 (1957), hereinafter referred to as (I).

² L. H. Thomas, *Proc. Cambridge Phil. Soc.* **23**, 542 (1927).

³ E. Fermi, *Z. Physik* **48**, 73 (1928); see P. Gombas, *Die Statistische Theorie des Atoms und Ihre Anwendungen* (Springer-Verlag, Vienna, 1949) for extensive references to the original Thomas-Fermi theory and subsequent modifications; see also, N. H. March, *Advances in Physics* (Taylor and Francis, Ltd., London, 1957), Vol. 6, p. 1.

⁴ In particular, the summations over the eigenstates can be replaced by integrals.

where $\mathbf{H}_0 \equiv \mathbf{T} + V_0$, \mathbf{T} being the kinetic energy operator for the system and $V_0 + V$ being the total potential energy. In contrast to Eq. (2.2), one seeks to express [analogously to Eq. (2.7) of (I)]

$$\mathbf{H}^n \equiv \sum_{k=0}^{\infty} \sum_{j=1}^N \sum_i' \sum_{l=0}^{n-k} \frac{n!}{(n-k-l)!} \times V^{n-k-l} Q_{i,k}^{(j)} \cdot R_{i,k}^{(j)} \mathbf{H}_0^l, \quad (2.3)$$

where $Q_{i,k}^{(j)}$ and $R_{i,k}^{(j)}$ are vector functions of position and momentum operators alone, respectively, of the j th particle. The prime indicates that the summation over i extends over all necessary values.

The procedure employed in (I) may be utilized here and gives rise to a recursion relation among the $Q \cdot R$'s. Omitting the details and defining

$$Q_k \cdot R_k \equiv \sum_{j=1}^N \sum_i' Q_{i,k}^{(j)} \cdot R_{i,k}^{(j)}, \quad (2.4)$$

one obtains

$$kQ_k \cdot R_k = [H_0, Q_{k-1} \cdot R_{k-1}] + [H_0, V]Q_{k-2} \cdot R_{k-2} + \frac{1}{2}[[H_0, V], V]Q_{k-3} \cdot R_{k-3} \quad (2.5)$$

which differs from Eq. (2.16) of (I) in that H_0 replaces T (with a suitable modification in V). Since the present paper will have no need for the various $Q_k \cdot R_k$'s, explicit values will not be given.⁵ In terms of the $Q_k \cdot R_k$'s, with $H_0 \phi_m = E_m^0 \phi_m$, Eq. (2.1) leads to

$$f(\mathbf{H})\phi_m = \sum_{k=0}^{\infty} f^{(k)}(E_m^0 + V)Q_k \cdot R_k \phi_m. \quad (2.6)$$

For polynomials, or when $f(\mathbf{H})$ is adequately represented by a few terms of the series, Eq. (2.6) is relatively easy to apply. However, when such is not the case the procedure becomes cumbersome. To obviate this difficulty consider⁶

$$\exp z\mathbf{H} = e^{z(H_0+V)} = e^{zV}\chi(z)e^{zH_0}, \quad (2.7)$$

where, clearly,

$$\chi(z) = \sum_{k=0}^{\infty} z^k Q_k \cdot R_k. \quad (2.8)$$

A convenient way of determining the $Q_k \cdot R_k$ is provided by

$$\left. \frac{\partial^k \chi}{\partial z^k} \right|_{z=0} = k! Q_k \cdot R_k. \quad (2.9)$$

Now, inasmuch as $Q_0 \cdot R_0 = 1$ and $Q_1 \cdot R_1 = 0$ it is possible

⁵ It may be noted, however, that terms up to and including $k=2$ are identical with those of (I); for $k=3$, Eq. (2.5) gives the additional term $(\hbar^2/6m)\nabla V \cdot \nabla V_0$, the gradient being the $3N$ -dimensional quantity defined in (I).

⁶ The exponential function assumes a singular role because of its utility in both statistical thermodynamic theory and in applications of the present kind. This has been pointed out and utilized recently by A. W. Sáenz and R. C. O'Rourke, *Revs. Modern Phys.* **27**, 381 (1955).

to give a formally exact representation of Eq. (2.7) in terms of H_0 and V alone. Because

$$e^{2z\mathbf{H}} = e^{z\mathbf{H}}e^{z\mathbf{H}} = e^{zV}\chi(z)e^{zH_0}e^{zV}\chi(z)e^{zH_0} = e^{2zV}\chi(2z)e^{2zH_0}, \quad (2.10)$$

so that

$$\chi(z) = e^{-zV/2}\chi(z/2)e^{zH_0/2}e^{zV/2}\chi(z/2)e^{-zH_0/2}, \quad (2.11)$$

one obtains

$$e^{z\mathbf{H}} = e^{zV/2}\chi(z/2)e^{zH_0/2}e^{zV/2}\chi(z/2)e^{zH_0/2}. \quad (2.12)$$

Clearly,

$$e^{z\mathbf{H}} = [e^{zV/n}\chi(z/n)e^{zH_0/n}]^n.$$

If $\chi(z/n)$ were a scalar function (which it is not) it would be simple to demonstrate that, because $Q_0 \cdot R_0 = 1$ and $Q_1 \cdot R_1 = 0$,

$$\lim_{n \rightarrow \infty} \left[\chi\left(\frac{z}{n}\right) \right]^n = 1. \quad (2.13)$$

Presumably, this also will be the case for χ defined by Eq. (2.8) and suggests that

$$e^{z\mathbf{H}} = \lim_{n \rightarrow \infty} [e^{zV/n}e^{zH_0/n}]^n, \quad (2.14)$$

which may be verified directly. Consider

$$\lim_{n \rightarrow \infty} n \ln [e^{zV/n}e^{zH_0/n}] = \lim_{z \rightarrow 0} \frac{\ln [e^{zzV}e^{zzH_0}]}{z}.$$

Expanding the logarithm in a series, one has to examine

$$\lim_{z \rightarrow 0} \sum_{m=1}^{\infty} \frac{(-1)^m (1 - e^{zzV}e^{zzH_0})^m}{m z}.$$

Application of l'Hôpital's rule to each term leads to a vanishing quantity for $m > 1$. Evaluation of the remaining term yields

$$\lim_{n \rightarrow \infty} n \ln [e^{zV/n}e^{zH_0/n}] = z(H_0 + V), \quad (2.15)$$

and verifies Eq. (2.14).⁷

The form of Eq. (2.14) suggests that the exponential in \mathbf{H} may be approximated by some finite power of the product of exponentials indicated there. Associating the "order" of an approximation with the power of exponentials employed, one can obtain

First order:

$$e^{z\mathbf{H}} \doteq e^{zV}e^{zH_0}. \quad (2.16)$$

⁷ One may note that the representation of Eq. (2.14) is not unique. For instance, it is sufficient to employ other products of exponentials in H_0 and V of which the sum of the exponents is $z\mathbf{H}/n$. The ordering is also not unique. Furthermore, decompositions of \mathbf{H} other than the one considered may be employed. See note added in proof.

Second order:

$$e^{z\mathbf{H}} \doteq (e^{zV/2}e^{zH_0/2})^2 \\ = e^{zV}e^{zH_0} + e^{zV/2}[e^{zH_0/2}, e^{zV/2}]e^{zH_0/2}. \quad (2.17)$$

Fourth order:

$$e^{z\mathbf{H}} \doteq (e^{zV/4}e^{zH_0/4})^4 \\ = (e^{zV/2}e^{zH_0/2} + e^{zV/4}[e^{zH_0/4}, e^{zV/4}]e^{zH_0/4})^2 \\ = (e^{zV/2}e^{zH_0/2})^2 + e^{zV/4}[e^{zH_0/4}, e^{zV/4}]e^{zH_0/4}e^{zV/2}e^{zH_0/2} \\ + e^{zV/2}e^{zH_0/2}e^{zV/4}[e^{zH_0/4}, e^{zV/4}]e^{zH_0/4} \\ + e^{zV/4}[e^{zH_0/4}, e^{zV/4}]e^{zH_0/4}e^{zV/4}[e^{zH_0/4}, e^{zV/4}]e^{zH_0/4}. \quad (2.18)$$

From the method of construction employed, it is evident that the approximation corresponding to order 2^{p+1} will contain all terms of order 2^p (p integral). The remaining terms each contain commutators which vanish when H_0 and V commute and also appear to have a less sensitive dependence upon z than similar quantities which appear in approximations of lower order. Presumably, these factors should foster the convergence of a sequence of approximations of the sort indicated, but the convergence characteristics have not been examined and will not be discussed. In fact, the present paper will be concerned mainly with the first order of approximation.

It will be noted that no attempt has been made to symmetrize the product of exponentials. Because of the lack of uniqueness of the representation Eq. (2.14), no difficulty arises in doing so. For the purposes of the present paper, only the trace of Eq. (2.14) needs to be considered, so that such symmetrization is superfluous. When the Hamiltonian is decomposed into more than two noncommuting parts, attention will have to be given to this matter.⁸

3. QUASI-CLASSICAL APPROXIMATION TO THE DENSITY MATRIX

The density matrix recently has received considerable attention.⁹ As a consequence, its properties are relatively familiar.

For present purposes, the density matrix (representative) for a many-particle system will be taken as¹⁰

$$\rho(x', x) = \sum_{n=1}^M \psi_n^*(x') \psi_n(x), \quad (3.1)$$

⁸ See, for example, R. Kubo, *J. Chem. Phys.* **20**, 770 (1952). The first term of Kubo's expansion and the one given here, correspond to one another but differences in the higher order terms are to be noted. The essential difference is that higher order terms in Kubo's expansion involve exponentials of various sums of the partial Hamiltonians into which the total Hamiltonian is decomposed, while only exponentials of the individual partial Hamiltonians are involved in the present procedure.

⁹ See especially, P. O. Löwdin, *Phys. Rev.* **97**, 1474-1520 (1955); *Advances in Physics* (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 1; J. E. Mayer, *Phys. Rev.* **100**, 1579 (1955); R. McWeeny, *Proc. Roy. Soc. (London)* **235**, 496 (1956); R. H. Tredgold, *Phys. Rev.* **105**, 1421 (1957); U. Fano, *Revs. Modern Phys.* **29**, 74 (1957).

¹⁰ As used here, the term "density matrix" will refer to expressions of the form (3.1) in contrast to the term "statistical matrix"

where $\psi_n(x)$ is a member of the complete, orthonormal set of eigenfunctions of the Hamiltonian of the many-particle system and x stands for the entire set of configurational and spin coordinates; M is an integer not related to the number of particles. It is convenient to write

$$\rho(x', x) = \sum_{n=1}^{\infty} \psi_n^*(x') \theta(\lambda_M - \mathbf{H}) \psi_n(x), \quad (3.2)$$

where

$$\theta(\lambda_M - \mathbf{H}) \psi_n = \psi_n, \quad \lambda_M > E_n, \\ = \frac{1}{2} \psi_n, \quad \lambda_M = E_n, \\ = 0, \quad \lambda_M < E_n, \\ \mathbf{H} \psi_n = E_n \psi_n. \quad (3.3)$$

Then, with $E_M < \lambda_M < E_{M+1}$ Eqs. (3.1) and (3.2) become identical.¹¹ However, Eq. (3.2) is invariant to the basis of representation and has, therefore, greater utility than Eq. (3.1). The role of the θ operator, clearly, is to select out of an arbitrary function that portion corresponding to a linear combination of the ψ_n 's, corresponding to $E_n < E_{M+1}$. The normalization condition,

$$\int dx \rho(x, x) = M, \quad (3.4)$$

emphasizes this role. It also serves to fix the value of λ_M (within limits if necessary).

Now, if one has an expression for $\rho(x', x)$ with $M=1$, one is able to determine all the properties of the many-particle state for which $n=1$. If one has another expression for $\rho(x', x)$ with $M=2$, the difference between this density matrix and that just considered permits one to determine all the properties of the many-particle state for which $n=2$. This procedure may be extended, clearly, so that the problem at hand is to determine the ρ 's for all integral values of M . Lacking the eigenfunctions of the many-particle Hamiltonian, it is clear that approximations must be employed. The approximation considered here will be concerned with the θ operator.

A convenient representation for θ is⁶

$$\theta(\lambda_M - \mathbf{H}) = \frac{1}{2\pi i} \mathcal{P} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{dz}{z} - e^{z(\lambda_M - \mathbf{H})}, \quad (3.5)$$

in which \mathcal{P} refers to the principal part of the integral, $\gamma > 0$ and z is a complex variable. Introducing, now, an approximation considered in the previous section for the exponential of the Hamiltonian one obtains a

for which each term of Eq. (3.1) contains a statistical weight factor W_n . It should be emphasized that the density matrices used here correspond to a summation of the usual many-particle density matrix over various many-particle states.

¹¹ The procedure followed here is that of reference 6. It is tacitly assumed that the eigenfunctions are ordered in terms of increasing values of E_n : $E_n \geq E_{n'}$ if $n > n'$.

convenient approximation for θ . Let $\{\phi_n\}$ be a set of complete, orthonormal eigenfunctions of H_0 . Then, using Eq. (2.16), one further obtains

$$\begin{aligned} \theta(\lambda_M - \mathbf{H}) &\doteq \frac{1}{2\pi i} \mathcal{P} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{dz}{z} \exp[z(\lambda_M - V - E_n^0)] \phi_n, \\ &= \theta(\lambda_M - V - E_n^0) \phi_n, \end{aligned} \quad (3.6)$$

where θ is now scalar operator. To this first order of

$$\begin{aligned} \rho^{(2)}(x', x) &= \sum_{n=1}^{\infty} \phi_n^*(x') \theta(\lambda_M - V(x) - E_n^0) \phi_n(x) + \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \phi_n^*(x') \phi_m(x) \left\langle \phi_m(x') \left| \theta \left(\lambda_M - \frac{V(x) + V(x') + E_m^0 + E_n^0}{2} \right) \right. \right. \\ &\quad \left. \left. - \theta \left(\lambda_M - \frac{V(x) + V(x') + 2E_n^0}{2} \right) \right| \phi_n(x') \right\rangle. \end{aligned} \quad (3.8)$$

In using the equations of this section, one may require that the basis of representation satisfies certain restrictions (e.g., Fermi-Dirac or Bose-Einstein statistics) with no alteration in their form.

4. ENERGY

While an approximate expression for the density matrix permits one to estimate the quantum-mechanical expectation value of any observable, considerable

$$\begin{aligned} \langle E \rangle_2 &= \sum_{n=1}^{\infty} E_n^0 \langle \phi_n | \theta(\lambda_M - V - E_n^0) | \phi_n \rangle + \sum_{n=1}^{\infty} \langle \phi_n | V \theta(\lambda_M - V - E_n^0) | \phi_n \rangle \\ &\quad + \frac{1}{2} \sum_{m, n=1}^{\infty} (E_m^0 + E_n^0) \left\langle \phi_m(x) \phi_n(y) \left| \theta \left(\lambda_M - \frac{V(x) + V(y) + E_m^0 + E_n^0}{2} \right) \right. \right. \\ &\quad \left. \left. - \theta \left(\lambda_M - \frac{V(x) + V(y) + 2E_n^0}{2} \right) \right| \phi_n(x) \phi_m(y) \right\rangle \\ &\quad + \frac{1}{2} \sum_{m, n=1}^{\infty} \left\langle \phi_m(x) \phi_n(y) \left| \{V(x) + V(y)\} \left\{ \theta \left(\lambda_M - \frac{V(x) + V(y) + E_m^0 + E_n^0}{2} \right) \right. \right. \right. \\ &\quad \left. \left. \left. - \theta \left(\lambda_M - \frac{V(x) + V(y) + 2E_n^0}{2} \right) \right\} \right| \phi_n(x) \phi_m(y) \right\rangle, \end{aligned} \quad (4.2)$$

the first two series corresponding to the first-order approximation $\langle E \rangle_1$. It may be noted that the last two series of Eq. (4.2) have a structure similar to that of *exchange integrals* in the many-particle configuration space.

The calculation of $\langle E \rangle$ is facilitated if M is known as a function of λ_M . For, from Eq. (4.1) and (3.5), one obtains

$$\begin{aligned} \langle E \rangle &= \text{Tr} \left\{ \frac{1}{2\pi i} \mathcal{P} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{dz}{z} \mathbf{H} e^{z(\lambda_M - \mathbf{H})} \right\}, \\ &= \lambda_M M - \text{Tr} \left\{ \frac{1}{2\pi i} \mathcal{P} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{dz}{z^2} e^{z(\lambda_M - \mathbf{H})} \right\}, \end{aligned}$$

approximation,

$$\rho^{(1)}(x', x) = \sum_{n=1}^{\infty} \phi_n^*(x') \theta(\lambda_M - V(x) - E_n^0) \phi_n(x). \quad (3.7)$$

This equation is the "quasi-classical" approximation referred to in the section heading and will be discussed in Sec. 7. It will serve as the basis for the computations considered in Sec. 5.

One obtains, using Eq. (2.17), the second-order approximation

interest is attached to the characteristic energy values of a system. Accordingly, approximate expressions for these quantities will be given in this section.

It is evident that

$$\langle E \rangle = \sum_{n=1}^M E_n = \text{Tr}(\mathbf{H}\rho), \quad (4.1)$$

where E_n are the eigenvalues of \mathbf{H} . Using Eq. (3.8) and the Hermitian property of \mathbf{H} , one obtains

when one carries out an integration by parts. Differentiating with respect to λ_M , one finally obtains

$$\partial \langle E \rangle / \partial \lambda_M = \lambda_M \partial M / \partial \lambda_M. \quad (4.3)$$

This equation reveals the role of λ_M to be that of a "chemical potential" (per state). Since $\langle E \rangle = 0$ for $M = 0$, one obtains the equation

$$\langle E \rangle = \int_0^M \lambda dM. \quad (4.4)$$

When M has discontinuities (as a function of λ_M), Eq. (4.4) may be utilized in the sense of a Steiltjes integral.¹²

¹² The form of Eq. (4.4) suggests that the procedure employed here may readily be adapted for constructing approximations for

In order to provide an internal check upon the adequacy of the approximations which may be employed, it is useful to compute the quantity

$$\langle E^2 \rangle = \sum_{n=1}^M E_n^2 = \text{Tr}(\mathbf{H}^2 \rho). \quad (4.5)$$

Following the procedure leading to Eq. (4.4), one obtains

$$\langle E^2 \rangle = \int_0^M \lambda^2 dM. \quad (4.6)$$

Considering, then, only the first order of approximation, one readily obtains

$$\begin{aligned} \langle E^2 \rangle_1 = \sum_{n=1}^{\infty} [& (E_n^0)^2 \langle \phi_n | \theta(\lambda_M - V - E_n^0) | \phi_n \rangle \\ & + 2E_n^0 \langle \phi_n | V \theta(\lambda_M - V - E_n^0) | \phi_n \rangle \\ & + \langle \phi_n | V^2 \theta(\lambda_M - V - E_n^0) | \phi_n \rangle]. \quad (4.7) \end{aligned}$$

5. APPLICATION TO HELIUM-LIKE ATOMS AND IONS

The usefulness of the approximations which have been discussed in the previous sections depends, first, upon their yielding relatively precise results in the very first order of approximation and, second, upon a rapid convergence (but small influence) of the higher order terms. The latter, which would require an analytical investigation of the quantities in Eqs. (2.16)–(2.18) and others, poses a formidable mathematical task and will not be attempted. The former can be tested empirically for various systems, but the calculations reported here will be confined to certain two-electron systems which are isoelectronic with the helium atom.

The helium atom, as well as isoelectronic atomic systems, continues to be the subject of many investigations¹³ in spite of the extremely precise results which have been obtained from variational treatments applied to this system.¹⁴ Because of its simplicity, and because it has all of the essential interactions which need to be considered in more complex electronic systems, it comprises a good system for testing the performance of any theory designed to cope with more complex atomic and molecular systems.

To apply the first-order approximation of the previous sections it is necessary to specify H_0 . For simplicity, although it is not necessarily capable of yielding the best results, H_0 will be taken as the two-electron

Hamiltonian in which the interelectronic repulsion has been neglected. Thus, let (in atomic units)

$$\mathbf{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - Z(1/r_1 + 1/r_2) + 1/r_{12}, \quad (5.1)$$

where the subscripts 1, 2 refer to the separate electrons; r_1, r_2 are distances of the indicated electrons from the fixed nucleus, and r_{12} is the distance between them; Z is the nuclear charge, measured in terms of the magnitude of the electronic charge; ∇_1^2, ∇_2^2 are Laplacians with respect to the position of the indicated electrons. Then

$$H_0 = \mathbf{H} - 1/r_{12}. \quad (5.2)$$

The eigenfunctions of this Hamiltonian are certain linear combinations of hydrogen-like wave functions. The symmetry restrictions imposed upon the eigenfunctions have been discussed fully^{9,13} and will not be considered here in detail.

For the present purposes, only states of zero angular momentum, the S -states, will be treated. Then, as is well known, the separation of spin and configurational coordinates of the electrons leads to the so-called singlet states, symmetric with respect to interchange of the configurational coordinates of the electrons, and to the so-called triplet states, antisymmetric with respect to this interchange. Arranging the properly symmetrized eigenfunctions of H_0 which have been utilized here in order of increasing value of their eigenvalues, one obtains (with suppression of the normalized spin factors):

$$\begin{aligned} E_{1^0} &= -Z^2; & \phi_{1^0} &= \zeta_{1s}(r_1)\zeta_{1s}(r_2); \\ E_{2,\pm^0} &= -5Z^2/8; & \phi_{2,\pm} &= \frac{1}{\sqrt{2}}(\zeta_{1s}(r_1)\zeta_{2s}(r_2) \\ & & & \pm \zeta_{1s}(r_2)\zeta_{2s}(r_1)); \quad (5.3) \\ E_{3,\pm^0} &= -5Z^2/9; & \phi_{3,\pm} &= \frac{1}{\sqrt{2}}(\zeta_{1s}(r_1)\zeta_{3s}(r_2) \\ & & & \pm \zeta_{1s}(r_2)\zeta_{3s}(r_1)). \end{aligned}$$

The plus sign refers to the singlet states, the minus sign to the triplet states. Here, in atomic units, the orthogonal hydrogen-like wave functions are¹⁵

$$\begin{aligned} \zeta_{1s}(r) &= \frac{Z^{3/2}}{\sqrt{\pi}} \exp(-Zr), \\ \zeta_{2s}(r) &= \frac{Z^{3/2}}{4(2\pi)^{1/2}} (2 - Zr) \exp(-\frac{1}{2}Zr), \\ \zeta_{3s}(r) &= \frac{Z^{3/2}}{81(3\pi)^{1/2}} (27 - 18Zr + 2Z^2r^2) \exp(-\frac{1}{3}Zr). \end{aligned} \quad (5.4)$$

These quantities have been employed to evaluate Eqs. (3.4), (3.7), the first two series of Eq. (4.2), and

¹⁵ See, for example, L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1925), p. 138.

the *resolution of identity* belonging to an Hermitian operator. See J. V. Neumann, *Mathematische Grundlagen der Quantenmechanik* (Dover Publications, New York, 1943), pp. 56–62.

¹³ For investigations related to the present one see, for example, P. O. Löwdin and H. Shull, *Phys. Rev.* **101**, 1730 (1956); H. Shull and P. O. Löwdin, *J. Chem. Phys.* **25**, 1035 (1956).

¹⁴ The classic work is by E. Hylleraas, *Z. Physik* **54**, 347 (1929); **65**, 209 (1930); see, also, S. Chandrasekhar and G. Herzberg, *Phys. Rev.* **98**, 1050 (1955); H. S. Schwartz, *Phys. Rev.* **103**, 110 (1956); L. Wilets and I. J. Cherry, *Phys. Rev.* **103**, 112 (1956); T. Kinoshita, *Phys. Rev.* **105**, 1490 (1957).

TABLE I. A summary of results.^a

System	M	State	$-E_{\text{obs}}$	$-⟨E⟩$	$-⟨E^2⟩^{\frac{1}{2}}$	$w(1s1s)$	$w(1s2s)$	$w(1s3s)$
He	1	1S	2.9036	2.9349	2.9652	0.83129	0.16871	...
Li ⁺	1	1S	7.2797	7.2760	7.3270	0.92772	0.07228	...
	2	1S	5.1107	5.1023	5.1715	...	0.85542	0.14458
Be ⁺⁺	1	1S	13.655	13.624	13.690	0.96398	0.03602	...
	1	3S	9.2972	9.2754	9.4404	...	0.93469	0.06531
	2	1S	>9.175 ^b	9.2403	9.4168	0.01169	0.85576	0.13255

^a Energy units are in modified atomic units, $2R_zhc(\mu/m)$, where R_z is the Rydberg constant for a nucleus of charge z and infinite mass; m and μ are, respectively, the mass and reduced mass of an electron in the system considered. See Sec. 6 for comments on results.

^b Energy value corresponds to $^3P^0$ -state; excited 1S -states not observed.

Eq. (4.7). The integrals which arise are evaluated most conveniently in terms of Hylleraas' coordinates.¹⁶ They differ from the usual integrals encountered in problems of this sort. Because of the presence of the θ functions, they do not include the entire configuration space of the system. Three kinds of integrals arise:

$$\begin{aligned}
 I(ab; cd; \gamma) & \equiv \langle \zeta_a(r_1)\zeta_b(r_2) | \theta(1/r_{12} - 1/\gamma) | \zeta_c(r_1)\zeta_d(r_2) \rangle, \\
 J(ab; cd; \gamma) & \equiv \langle \zeta_a(r_1)\zeta_b(r_2) | \theta(1/r_{12} - 1/\gamma)/r_{12} | \zeta_c(r_1)\zeta_d(r_2) \rangle, \quad (5.5) \\
 K(ab; cd; \gamma) & \equiv \langle \zeta_a(r_1)\zeta_b(r_2) | \theta(1/r_{12} - 1/\gamma)/r_{12}^2 | \zeta_c(r_1)\zeta_d(r_2) \rangle.
 \end{aligned}$$

For simplicity, explicit expressions for these integrals in terms of Eqs. (5.4) will be given in the Appendix. The I -integrals were combined in accordance with Eqs. (5.3). Equation (3.4) was solved numerically for λ_M , $M=1, 2$. The determined values of λ_M then were employed to evaluate the appropriate combination of J - and K -integrals. Computations were carried out for He, Li⁺, and Be⁺⁺.

The radial probability distribution for the ground state of helium was determined by computing $\text{Tr}\{\delta(\mathbf{r}-\mathbf{r}_2)\rho\}$. Since the integrals which arise are specific to this computation, as well as complicated, they will not be displayed.

6. RESULTS

The results obtained are summarized in Tables I and II and in Figs. 1 and 2. All numerical work was checked to within at least six significant figures. (The

TABLE II. Comparison of energy of excited states and normalization parameters.

System	M	Excited state	$-E_{\text{obs}}$	$-\lambda_M$
He	1	1S	2.1460	2.2658
Li ⁺	1	1S	5.0468	5.3271
	2	1S	4.7337	4.8264
	1	3S	4.7520	4.8378

¹⁶ See, for example, H. Hellmann, *Einführung in die Quantenchemie* (Edwards Brothers, Inc., Ann Arbor, 1944), p. 333.

coefficients of the integrals in the Appendix were checked to eight significant figures.)

The values reported in Table I for the singlet excited states represent the differences between the values for $M=2$ and $M=1$. The w 's correspond to the appropriate combination of I -integrals of Eqs. (5.5) and represent the fractional contribution of the indicated hydrogen-like states to the indicated state of the system. Their nonzero values illustrate the removal of "orbital degeneracy."^{18,17} The value of $\langle E^2 \rangle^{\frac{1}{2}}$ gives some measure of the adequacy of the approximation employed here. While the disparities between E_{obs} , $\langle E \rangle$, and $\langle E^2 \rangle^{\frac{1}{2}}$ are small, considerable improvement in the theory is necessary to approach the results of variational treatments.¹⁴ The observed values are taken from Moore.¹⁸

It is to be noted that the singlet-triplet order for Li⁺ (the only one for which data were available) is in agreement with experiment and the splitting (which amounts to approximately one percent of the term values) is within a factor of two of the observed value.

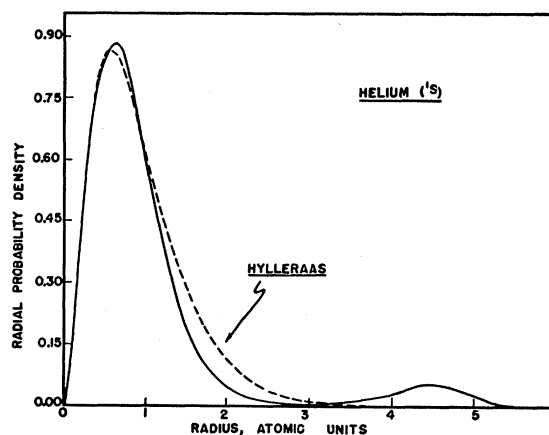


FIG. 1. Radial probability density for ground state of helium.

In the case of helium the computations for the first 3S state and second 1S state were attempted with the integrals on hand but it was impossible to satisfy Eq. (3.4), additional excited states of the unperturbed system being required. Similarly, the computations for the ground state of H⁻ could not be carried through.

In Table II the various values of λ_M are compared with the energy values of the *next* excited state of the same symmetry. Inasmuch as the λ 's are bounded between successive characteristic energy values they serve as lower bounds to the energy of the following excited state. The agreement is reasonably satisfactory.

Figure 1 is a plot of the radial probability distribution for the ground 1S state of helium. It is compared with the distribution obtained from the 3-parameter vari-

¹⁷ See also Green, Chandler, and Rush, *Phys. Rev.* **104**, 1593 (1956).

¹⁸ C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949).

ational function obtained by Hylleraas.¹⁴ While the latter has an exponential term which corresponds to a screening of the nucleus by one of the electrons, the result obtained from the present investigation allows both electrons to "see" the bare nucleus. Nevertheless, the initial radial distribution compares quite well with that obtained from a variational treatment. Small differences in probability density are obtained in this region and are presented in Fig. 2, where a comparison is made also with the density obtained from the simple variational function of Kellner.¹⁹ The "orbital-splitting" noted previously is emphasized by the appearance of a pseudoshell at large distances from the nucleus.

In order to assess the reliability of the radial distributions in Fig. 1, the mean-square-radius was evaluated by graphical integration. From the values obtained, the diamagnetic susceptibilities were estimated.²⁰ The Hylleraas density yielded a molar susceptibility of -1.85×10^{-6} cm³ mole⁻¹, in substantial agreement with experimental results. The "quasi-classical" density

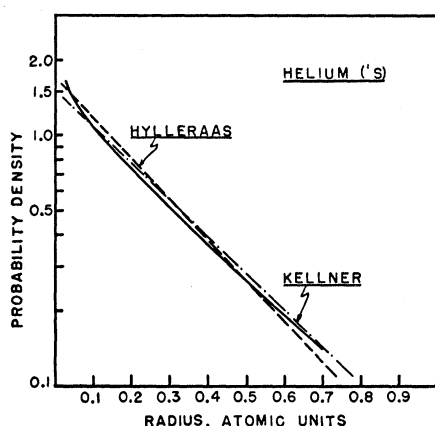


FIG. 2. Probability density for ground state of helium.

yielded a value of -3.30×10^{-6} cm³ mole⁻¹, clearly in poor agreement with experiment. The reliability of the "quasi-classical" density which has been obtained is, therefore, questionable. Presumably, higher order approximations are necessary to yield results in closer agreement with experiment.

7. DISCUSSION

In spite of the reasonableness of the results which have been obtained, their limitations are emphasized when one examines the properties of the θ operator. In the exact case, the θ operator is an Hermitian, idempotent operator (i.e., projection operator). This property is not duplicated by the approximation employed here. As can be verified from Eq. (3.6), the approximate θ is an idempotent operator but is not Hermitian.

¹⁹ G. W. Kellner, Z. Physik 44, 91 (1927).

²⁰ See, for example, J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1948), pp. 206-208.

Presumably, the latter property may be related to the lower energy values obtained for the ground state of He and the first excited singlet state of Li⁺. Since an idempotent operator generally consists of the sum of a projection operator and a nilpotent operator,²¹ it should be possible to separate out the former quantity as an improved approximation to θ . The approximation which has been examined numerically in this paper has been referred to as a "quasi-classical" approximation. The reason for this appellation is the following. Consider that the effect of the approximation is first to ascribe an "energy" to the system which is the sum of an unperturbed energy (corresponding to the energy possessed by the system in the absence of interelectronic repulsions) and the interelectronic repulsive energy. This "energy" is presumed, then, to depend upon the configuration of the system. The second effect of the approximation, and its most significant one, is to restrict the system to configurations for which its ascribed "energy" is less than some specific value. This value is the λ_M of Eq. (3.2). Since λ_M is bounded between successive characteristic energy values of the system the approximation effectively excludes those configurations which correspond to "energies" exceeding that of the next excited state of the system.

Now, this is precisely the sort of physical description involved in the original Thomas-Fermi theory in which case the unperturbed energy simply is the kinetic energy. Then, the "energy" of the system in the Thomas-Fermi theory is restricted to negative values (i.e., $\lambda=0$) which corresponds, in turn, to bound configurations of the system. Because the unperturbed basis there is an unbound one, the existence of excited bound states of the system is not in evidence, as in the approximation considered here. When one recognizes this difference as due to the difference in bases, the "quasi-classical" approximation simply assumes the role of the Thomas-Fermi theory in a different basis of representation.

As a result of the imposition of a somewhat classical behavior upon the quantum mechanics, an important shortcoming may be noted. Whenever the perturbation $V(x)$ has negative poles, θ is equal to unity. Then, if x_0 is the location of such a pole, $\rho^{(1)}(x', x_0) = \delta(x' - x_0)$, so that infinite densities in configuration-space are manifest to this order of approximation. This situation, clearly, does not arise where $V(x)$ has positive poles. In such cases, in fact, θ vanishes and zero densities occur, corresponding to classical expectations. The numerical illustrations considered in this paper correspond to the latter case. Applications of this method to other systems should arrange that the perturbation avoids the complication mentioned. Thus, in molecular problems atomic orbitals will usually introduce such a complication; molecular orbitals which take fully into account the influence of the bare nuclei will not.

²¹ S. Golden, Nuovo cimento (to be published).

A result which may have some important utilization in statistical thermodynamics is embodied in Eqs. (2.14) and (2.16)–(2.18). When $z \equiv -1/kT$, the quantity involved is germane to estimating the partition function. It resembles the results obtained by others,^{22†} but differs from these in providing an explicit expansion procedure solely in terms of exponentials of H_0 and V . (Clearly, other decompositions of the total Hamiltonian are possible.) Since, then, only terms in $\exp(-V/kT)$ and $\exp(-H_0/kT)$ and fractional powers of these quantities are involved, and approximations of order greater than the first involve commutators of these quantities, good estimates of the partition function at both small and large temperatures seem likely. This appears reasonable, since the commutators vanish under

these circumstances (providing V and H_0 are measured from their minimum values). Moreover, as indicated in Eqs. (2.16)–(2.18), a given order of approximation to the partition function will automatically contain the approximations of lower order. One may also show that the trace of the Bloch equation²³ (i.e., Bloch's equation for the partition function) is satisfied for any order of approximation (even for different decompositions of the Hamiltonian). Higher moments, which correspond to higher derivatives of the partition function, only approximate those obtainable from Bloch's equation.

8. ACKNOWLEDGMENT

I wish to express my appreciation to Mrs. Dorothy Hallé for the numerical computations reported here.

APPENDIX

The integrals defined by Eqs. (5.4) and (5.5) are listed here:

$$I(1s1s; 1s1s; x) = (1 + 2x + 2x^2 + 7x^3/6 + x^4/3)e^{-2x}.$$

$$I(1s2s; 1s2s; x) = -(128/81 + 128x/81 - 88x^2/27 + 8x^3/9 - 2x^4/9)e^{-x} + (209/81 + 418x/81 + 10x^2/9)e^{-2x}.$$

$$I(1s2s; 2s1s; x) = -x^3(4/243 + 2x/81 + 4x^2/405 - x^3/270)e^{-3x/2}.$$

$$I(1s3s; 1s3s; x) = (0.46224976 + 0.30816650x + 0.92358398x^2 - 0.35937500x^3 + 0.13281250x^4 - 0.019675926x^5 + 0.0015432099x^6)e^{-2x/3} + (0.53775024 + 1.0755005x + 0.25463867x^2)e^{-2x}.$$

$$I(1s3s; 3s1s; x) = -x^3(0.47200521 + 0.62934028x + 0.16203704x^2 - 0.15689300x^3 + 0.020086224x^4 - 0.00065321053x^5)e^{-4x/3} \times 10^{-2}.$$

$$J(1s1s; 1s1s; x) = Z(5/8 + 5x/4 + x^2 + x^3/3)e^{-2x}.$$

$$J(1s2s; 1s2s; x) = -Z(356/81 - 100x/27 + 10x^2/9 - 2x^3/9)e^{-x} + Z(373/81 + 10x/9)e^{-2x}.$$

$$J(1s2s; 2s1s; x) = Z(16/729 + 8x/243 - 2x^3/81 - x^4/81 + x^5/270)e^{-3x/2}.$$

$$J(1s3s; 1s3s; x) = Z(0.84869385 + 1.0759277x - 0.48828125x^2 + 0.14843750x^3 - 0.021990741x^4 + 0.0015432099x^5)e^{-2x/3} + Z(0.94818115 + 0.25463867x)e^{-2x}.$$

$$J(1s3s; 3s1s; x) = Z(0.57678223 + 0.76904297x - 0.19531250x^2 - 0.71614583x^3 - 0.23148148x^4 + 0.16975309x^5 - 0.020576132x^6 + 0.00065321053x^7)e^{-4x/3} \times 10^{-2}.$$

$$K(1s1s; 1s1s; x) = Z^2(2/3 + 5x/6 + x^2/3)e^{-2x}.$$

$$K(1s2s; 1s2s; x) = Z^2(124/27 - 4x/3 + 2x^2/9)e^{-x} + (10Z^2/9)e^{-2x} + (656Z^2/81)[\text{Ei}(-x) - \text{Ei}(-2x)].$$

$$K(1s2s; 2s1s; x) = Z^2(512/10935 + 76x/3645 - 26x^2/1215 - 2x^3/135 + x^4/270)e^{-3x/2}.$$

$$K(1s3s; 1s3s; x) = Z^2(1.5759277 - 0.64322917x + 0.17100695x^2 - 0.024305556x^3 + 0.0015432099x^4)e^{-2x/3} + 0.25463867Z^2e^{-2x} - 1.6417236Z^2[\text{Ei}(-2x/3) - \text{Ei}(-2x)].$$

$$K(1s3s; 3s1s; x) = Z^2(1.2946429 + 0.31017485x - 0.73722718x^2 - 0.31801146x^3 + 0.18334803x^4 - 0.021066040x^5 + 0.00065321053x^6)e^{-4x/3} \times 10^{-2}.$$

²² See, for example, R. P. Feynman, Phys. Rev. **84**, 108 (1951). (See also note added in proof.)

[†] Note added in proof.—The expression of $\exp(z\mathbf{H})$ as an infinite product seems first to have been employed by S. T. Butler and M. H. Friedman, Phys. Rev. **98**, 287 (1955), whose paper was called to the author's attention after the present paper had been accepted for publication. The present development differs from that cited in considering the unperturbed Hamiltonian to be different from the kinetic energy operator.

²³ See, for example, K. Husimi, Proc. Phys.-Math. Soc. Japan **22**, 264 (1940).