and

$$\langle u_i|H_0|v_{n-i}\rangle + \langle u_i|H_1|v_{n-i-1}\rangle = \sum_{t=0}^{n-i} \epsilon_t \langle u_i|v_{n-i-t}\rangle \; ; \quad (30)$$

then subtracting (30) from (29), using the Hermitean properties of H_0 and H_1, and summing over i from 0 to n, we have

$$0 = \sum_{i=0}^{n} \sum_{S=0}^{i} E_S \langle v_{n-i}|u_{i-S}\rangle - \sum_{i=0}^{n} \sum_{t=0}^{n-i} \epsilon_t \langle u_i|v_{n-i-t}\rangle \, . \quad (31)$$

These finite double sums may be rewritten so that (31) becomes

$$0 = \sum_{S=0}^{n} (E_S - \epsilon_S) \sum_{i=0}^{n-S} \langle u_i|v_{n-S-i}\rangle \quad (32)$$

and (26) follows by induction.

This result is valid only for the *exact* solutions u_n, v_n of the perturbation equations; if the Eqs. (27) and (28) are solved by the variation technique u_n and v_n are not exact solutions and the orthogonality condition (26) may not be satisfied. Condition (26) then provides an additional criterion of the accuracy of the procedure and the resulting nth-order corrections to the eigenfunctions u, v.

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Statistical Theory of Atoms

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1. THE STATISTICAL FIELD EQUATION (T. F. EQUATION)

By 1925 some effective electric fields inside atoms had been calculated to fit observed data.[1] The Bohr–Sommerfeld theory[2] gave orbits in a spherically symmetrical field with definite energies for the series electron and for inner electrons. Pauli's equivalence principle[3] requiring that there are never two electrons in an atom with all their quantum numbers the same, coupled with the discovery of electron spin,[4] allowed just two electrons with opposite spins to occupy an orbit in the field. The field could then be adjusted to give, using Bohr's frequency condition, for outer normally unoccupied orbits, and for inner normally occupied orbits, respectively, approximations to the optical spectrum and to the x-ray spectrum.

The Bohr–Sommerfeld orbits correspond to successive discrete values of action variables, differing by Planck's constant h, which, with their conjugate phases, give a canonical mapping of the phase-space of the electron. Thus if each orbit is occupied by two electrons, these are distributed rather uniformly at two for each h^3 of six-dimensional configuration–momentum space. We need now suppose only that the electrons present fill the orbits of lowest energy in the effective field, so that if V is the potential in that field, measured from a suitable zero, electrons may have momentum up to $(2\,\mathrm{meV})^{\frac{1}{2}}$, where m and e are electron mass and charge, and may occupy volume $\frac{4}{3}\,\pi(2\,\mathrm{meV})^{\frac{3}{2}}$ of momentum space, to obtain the value for the charge density at a place with potential V,

$$\rho = -e\,\frac{2}{h^3}\,\frac{4}{3}\,\pi(2\,\mathrm{meV})^{\frac{3}{2}} \, .$$

Assuming also Poisson's equation, we have

$$\nabla^2 V = -4\pi\rho = 4\pi e\,\frac{2}{h^3}\,\frac{4}{3}\,\pi(2\,\mathrm{meV})^{\frac{3}{2}} \, ,$$

as an approximate equation for the potential of the effective electric field in an atom.[5] For a neutral atom we will expect $V \to 0$ as $r \to \infty$ and $Vr \to Z$, the nuclear charge, as $r \to 0$, as boundary conditions at infinite and zero radius r.

This field gives the structure of the periodic table, the total binding energies of atoms, their spectra, and atomic scattering cross sections—all in rough qualitative agreement with observation. Its advantage is its simplicity, one integration sufficing by scaling for all neutral atoms. Its disadvantage is its roughness.

In "atomic units," $h = 2\pi$, $e = 1$, $m = 1$, we have the T.F. equation

$$\nabla^2 V = \frac{8\sqrt{2}}{3\pi}\,V^{\frac{3}{2}} \, . \quad (1)$$

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[1] D. R. Hartree, Proc. Cambridge Phil. Soc. **21**, 615 (1924); E. Fues, Z. Physik **11**, 369 (1922).

[2] N. Bohr, Phil. Mag. **26**, 1 (1913); A. Sommerfeld, Ber. Akad. (München) 425 (1915).

[3] W. Pauli, Z. Physik **31**, 765 (1925).

[4] G. Uhlenbeck and S. Goudsmit, Naturwissenschaften, 957 (Nov. 1925).

[5] L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927); E. Fermi, Z. Physik **48**, 73 (1928).

2. THE QUANTUM-THEORY BACKGROUND

When it was discovered that a variational approach to the solution of the many-electron Schrödinger equation, by restricting the Schrödinger function to be an antisymmetrical sum of products of one-electron functions, leads directly to the Hartree–Fock approximate equations which can be regarded as the quantum-mechanical form of the Hartree–Fues picture of electrons moving separately in the average field of the other particles,[6] it was natural to attempt a similar approach to the simpler but rougher statistical field.

Dirac showed[7] that the Hartree–Fock equations could be expressed simply in terms of the density matrix $\rho(\mathbf{r}_1, \mathbf{r}_2)$ by the condition that

$$W = \int \{H(r)\rho(\mathbf{r},\mathbf{r}')\}_{r'=r}d\mathbf{r} + \tfrac{1}{2}\iint \{\rho(\mathbf{r}_1,\mathbf{r}_1)\rho(\mathbf{r}_2,\mathbf{r}_2) - \rho(\mathbf{r}_1,\mathbf{r}_2)\rho(\mathbf{r}_2,\mathbf{r}_1)\}V(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2 \tag{a}$$

should be stationary subject to the conditions

$$\int \rho(\mathbf{r}_1\mathbf{r}')\rho(\mathbf{r}',\mathbf{r}'')d\mathbf{r}' = \rho(\mathbf{r},\mathbf{r}'') \tag{b}$$

$$\int \rho(\mathbf{r},\mathbf{r})d\mathbf{r} = n\,. \tag{c}$$

Here $\rho(\mathbf{r},\mathbf{r}')$ is a Hermitian matrix, $H(\mathbf{r})$ is the Hamiltonian for a single electron in the given nuclear field, $V(\mathbf{r}_1\mathbf{r}_2)$ is the mutual potential energy of two electrons, and n is the total number of electrons. The integrations are to be interpreted as including summation over spin.

If each "self-consistent" equation is like a wave equation for a single particle, we may expect to be able to approximate near any position $\mathbf{r}$ by a set of plane waves, $\exp\,(2\pi i/h)(\mathbf{p}\cdot\mathbf{r})$, with values of the momentum $\mathbf{p}$ distributed uniformly within a sphere of radius say P at a rate 2, for the two directions of spin, for each h^3 of phase space. Replace the sum by an integral, and for definiteness take P a function of $\frac{1}{2}\,|\mathbf{r} + \mathbf{r}'|$, and after some integrations, using atomic units,

$$W = \frac{2}{5\pi}\int P^5r^2dr - Z\frac{4}{3\pi}\int P^3rdr - \frac{1}{\pi^2}\int P^4r^2dr + \frac{1}{18\pi^4}\iint P_1^3P_2^3\frac{1}{r_{12}}\,dr_1dr_2\,, \tag{d}$$

while condition (c) becomes

$$\frac{4}{3\pi}\int P^3r^2dr = n\,. \tag{e}$$

The successive terms of W correspond to kinetic energy; potential energy of the electrons in the nuclear field, exchange energy, arising from the second part of the second term in (a); and potential interaction energy. The problem of choosing a function $P(r)$ to make W a minimum[8] subject to (e) leads directly[9] to either $P > 5/4\pi$ or $P = 0$ (Jensen's condition) so that there is a finite boundary at which $P = 5/4\pi$.

Within the boundary P must satisfy the equation

$$\tfrac{1}{2}\,P_1^2 - \frac{1}{\pi}\,P_1 - \lambda = \frac{Z}{r_1} - \int\frac{\rho_2}{r_{12}}\,dr_2 = V_1,\ \text{say}\,,$$

where λ is a multiplier corresponding to condition (e). We find that the potential V satisfies the equation

$$\nabla^2V = 4\pi\rho = \frac{8\sqrt{2}}{3\pi}\,(V^{\frac{1}{2}} + \frac{1}{\sqrt{2}\pi})^3, \tag{2}$$

to which we add boundary conditions $Vr \rightarrow Z$ as $r \rightarrow 0$, and $V = (Z - n)/r = -(15/32\pi^2) - \lambda$, $(dV/dr) = -(Z - n)/r^2$ at the finite boundary. This gives the statistical field equation with Dirac's correction for exchange (the T.F.D. equation), and Jensen's boundary condition. Different choices of $P(\mathbf{r}_1,\mathbf{r}_2)$ lead to different fields,[10] and, in particular, can give the original statistical-field equation. The charge distributions for Cu$^+$ are compared with the Hartree–Fock theory in Fig. 1.

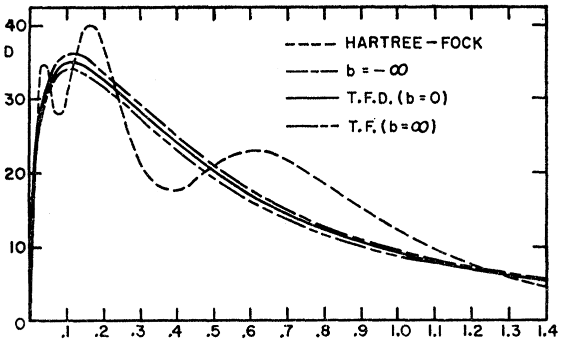

FIG. 1. The total radial charge densities D for Cu$^+$ for $b = -\infty$, 0, and ∞ are compared to the Hartree–Fock radial charge density. Density curves for $b > 0$ lie between the Thomas–Fermi–Dirac curve and the Thomas–Fermi curve.

3. CRITICISM AND IMPROVEMENTS

The statistical theories should not be expected to show the shell structure of the atom by maximum

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[6] J. C. Slater, Phys. Rev. **35**, 210 (1930); V. A. Fock, Z. Physik **61**, 126 (1930).

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

[8] H. Jensen, Z. Physik, **93**, 232 (1935).

[9] Consider a strong variation in which a continuous part of $P < 5/4\pi$ is replaced by $P = 5/4\pi$ over part of the range, 0 over part.

[10] K. M. King and L. H. Thomas, Phys. Rev. **124**, 785 (1961).

densities at K, L, M, $\cdots$ shell positions, since this is precisely what was averaged over. The original theory did not pretend to be accurate, where the field of an electron, itself, is of the same order of magnitude as the whole field, namely, near the outside of the atom; the modified theory, which should take care of this by the exchange term, leads to an unphysical boundary condition. Further, the fields are wrong near the nucleus, allowing density at very large negative potential energy,[11] and this is perhaps the principal reason for the large binding energies obtained for the whole field.

If we analyze the density matrix actually used, we find that we have not only given up the exact condition (b), which is equivalent to values 0 or 1 for the characteristic values of $\rho(\mathbf{r},\mathbf{r})$, corresponding to occupation numbers 0 or 1 for pure states, but have actually introduced completely unphysical negative characteristic values. If, perhaps, condition (b) could be replaced by a condition that the characteristic values of $\rho(\mathbf{r},\mathbf{r}')$ should be numbers between 0 and 1, which could correspond to an actual statistical state, the theory might well be improved.[12]

There have been many attempts to improve the theory while keeping it simple enough to be useful. The most successful seems to be the adaptation of March and Plaskett's[13] derivation of the statistical field equation using the W.K.B. approximation to Schrödinger's equation rather than plane waves, and using a more sophisticated approximation to the sum than an integral over the whole region, as adjusted by Scott[14] to fit a Coulomb field. In recent work by Barnes,[15] V in the expression for ρ on the right hand side of (1) or (2) is replaced by $V - (a^2/2r^2)$, where $a = l_{\min} + \frac{1}{2}$, $l_{\min}$ being a lowest allowed quantum number, so long as this is positive, otherwise $\rho = 0$. He obtains a great improvement in the total energy, for instance, for $Z = 8$, he obtains energy -2084 eV, as against the experimental value -2043 eV, while the T.F. field has energy -2678 eV and the T.F.D. field -2878 eV.

For many extensions to and improvements in the theory, reference is made to P. Gombas, *Die Statistische Theorie des Atoms und ihre Anwendungen* (Julius Springer-Verlag, Wien, 1949); and N. M. March, "The Thomas–Fermi Approximation in Quantum Mechanics," *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1957).

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[11] N. M. March and F J. Plaskett, Proc. Roy. Soc. (London) **A234**, 419 (1959).

[12] See discussion with A. J. Coleman below.

[13] N. M. March and F. J. Plaskett, (see reference 11).

[14] J. M. C. Scott, Phil. Mag. **43**, 859 (1952).

[15] J. F. Barnes, Los Alamos Scientific Laboratory, Report No. L. A. 2750 (1952) (unpublished).

Discussion on Statistical Theory of Atoms

R. McWeeny, *Chairman*

McWeeny: Recently there have been efforts, notably by Golden, to extend the method so as to introduce specifically quantal effects such as shell structure. These proceed roughly as follows: the one-body density matrix in Hartree–Fock approximations describes a degenerate Fermi–Dirac ensemble and may be written

$$\begin{aligned}\rho(x;x') &= \sum_{i=1}^{N} \psi_i(x)\psi_i^*(x') \\ &= \lim_{T\to 0} \sum_{i=1}^{\infty} \frac{1}{1+\exp\left[(E_i+\zeta)/kT\right]}\psi_i(x)\psi_i^*(x')\,,\end{aligned}$$

where ξ is determined by the normalization $\int \rho(x;x)dx = N$ and the sum is over *all* one-electron orbitals of the one-body problem. This may be written in operator form by putting the effective one-body Hamiltonian $\mathcal{H}$ in place of E_i ($\mathcal{H}$ working on the unprimed variables only) and an *arbitrary* complete set may then be introduced, since $\sum_i \psi_i(x)\psi_i^*(x')$ is merely the resolution of the identity. To obtain the Thomas–Fermi type of theory we choose a set of suitably normalized free-electron functions, $\{\phi_i\}$, and from

$$\rho(x;x') = \lim_{T\to 0} \sum_{i=1}^{\infty} \frac{1}{1+\exp\left[(\mathcal{H}+\zeta)/kT\right]}\,\phi_i(x)\phi_i^*(x')$$