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Hartree and Thomas: the forefathers of density functional theory

Andrew Zangwill

Abstract Douglas Hartree and Hilleth Thomas were graduate students together at Cambridge University in the mid-1920s. Each developed an important approximation method to calculate the electronic structure of atoms. Each went on to make significant contributions to numerical analysis and to the development of scientific computing. Their early efforts were fused in the mid-1960s with the development of an approach to the many-particle problem in quantum mechanics called *density functional theory*. This paper discusses the experiences which led Hartree and Thomas to their approximations, outlines the similarities in their subsequent careers, and highlights the essential role their work played in the foundational papers of modern density functional theory.

1 Introduction

The year 1924 was quite hectic for Ralph Fowler's research group at Cambridge University.[1] His most senior Ph.D. student, Douglas Hartree, published three papers in a continuing series that reported the results of Bohr–Sommerfeld calculations designed to reveal the electron orbits responsible for the observed spectra of one-electron-like atoms. Another Ph.D. student, Paul Dirac, submitted five papers for publication, beginning with a study of molecular dissociation in a temperature gradient and ending with an analysis of the adiabatic invariance of action integrals. Fowler's most junior Ph.D. student, Hilleth Thomas, wrote a paper that discussed adiabatic invariants from

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[1] For students interested to do a theoretical PhD, Fowler was the only potential supervisor at Cambridge with an interest in quantum theory (Mehra and Rechenberg 1982, Volume 4).

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a statistical point of view and began classical calculations relevant to the passage of charged particles through matter.

It is not surprising that old quantum theory topics figured prominently in the activities of these students. By 1924, the spectacular successes of the Bohr–Sommerfeld theory for hydrogen and hydrogen-like atoms could be studied from the latest (fourth) edition of Arnold Sommerfeld's *Atombau und Spektrallinien*. Max Born's book devoted to the same subject, *Vorlesungen über Atommechanik*, was published early in 1925. On the other hand, calculations performed by rising stars like James Franck, Hendrik Kramers, Werner Heisenberg, and John Van Vleck were unable to reproduce those successes for helium and other non-hydrogen-like multi-electron atoms (Mehra and Rechenberg 1982, Volume 4; Darrigol 1992). For that reason (Kragh 2012),

> Among many physicists in the period 1923–1925 there was a mounting feeling that the existing quantum theory of the atom had come to a dead end and that further search for substantial progress within the framework of the Bohr–Sommerfeld theory was futile. The old framework had to be replaced by a new one.

The new framework was supplied by Heisenberg, who sent a proof copy of his paper "Quantum-theoretical re-interpretation of kinematic and mechanical relations" to Fowler in August of 1925. Fowler passed the paper on to Dirac and the story of how Dirac quickly grasped the essentials and went on to create his unique and profound approach to quantum mechanics (beginning with a paper submitted only two months later) has been told many times (Jammer 1966, Chapter 5; Mehra and Rechenberg 1982, Volume 4).

In this paper, I examine the activities of Dirac's classmates, Hartree and Thomas, during this period of rapid transition from the old quantum theory of Bohr and Sommerfeld to the new quantum theory of Heisenberg, Dirac, and Schrödinger. Sections 2 and 3 review the experiences that led each to develop an approximation method to compute the properties of many-electron atoms and the subsequent contributions each made to numerical analysis and scientific computing. The approximation schemes invented by Thomas and Hartree have historical importance because their generalizations and application to other many-electron systems have enjoyed many years of quantitative success. Equally important, each stands out as an essential intellectual precursor to a very successful approach to many-particle quantum mechanics developed in the 1960s called density functional theory (Parr and Yang 1989). Section 4 outlines the foundations of modern density functional theory and highlights the debt this theory owes to the Hartree and Thomas methodologies.

2 Douglas Hartree and the self-consistent atom

The life of Douglas Rayner Hartree is recounted admirably in a biography written by his final Ph.D. student, Charlotte Froese Fischer (2003). Her book rightly draws attention to Hartree's career-long interest and ability to find numerical solutions to scientific problems. This talent appeared early when he was recruited from his first year of graduate studies at Cambridge to join a group of more senior

Cambridge-trained men (including his future Ph.D. advisor Ralph Fowler) studying anti-aircraft gunnery in support of the British Ministry of Munitions during World War I (van der Kloot 2011). The differential equations that determine the trajectory of artillery shells are not solvable analytically when frictional drag and wind effects are treated realistically. The 20-year-old Hartree introduced several innovations which made the numerical integration of these equations fast and efficient (Darwin 1958).

Douglas Rayner Hartree (ca. 1939).
Courtesy of the AIP Emilio Segrè Visual Archive, Hartree Collection.

After his return to graduate school, Hartree discovered that he had no aptitude for experimental work and initially contented himself to assist a fellow graduate student from Ernest Rutherford's laboratory who recruited him to analyze the trajectories of electrons in an inhomogeneous magnetic field (Hartree 1923a). Hartree's true research career was launched by a set of lectures on quantum theory given at Cambridge by Niels Bohr in 1922. Bohr's articles and lectures were famously qualitative and Hartree was interested to obtain quantitative results from Bohr's theory of the spectra of atoms. Fowler was well aware that this choice leveraged Hartree's unusual background because "such an application must involve much numerical computation" and "he is to be judged as a computing and classifying physicist".[2] This opinion must not have been limited to Fowler because, 50 years later, the American physicist John Slater took umbrage with any characterization of Hartree as a "mere computer" and preferred to describe him as a "matter-of-fact sort who indicates the argument behind what he does and tries to write or speak in the most comprehensible manner possible" (Slater 1975, Section 7).

Hartree's first Bohr-inspired paper on atomic spectra adopted the prevailing view that the electrons in an atom move in planar elliptical orbits in a force field produced by the nucleus and the electrons themselves (Hartree 1923b). For simplicity, he assumed a *central* field of force so the associated potential function, $v(\rho)$, depended only on the variable $\rho = r/a_B$, the electron–nucleus distance scaled by the Bohr radius. He also

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[2] From Fowler's unpublished report on Hartree's Ph.D. dissertation quoted in Jeffreys (1987).

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accepted Bohr's re-purposing of Sommerfeld's quantization conditions to explain the structure of the periodic table and wrote

$$n - k = \frac{1}{\pi} \int\limits_{\rho_0}^{\rho_1} d\rho \left[2v - \epsilon - \frac{k^2}{\rho^2} \right]^{1/2}. \tag{1}$$

In this expression, the integer n is the principal quantum number, the azimuthal quantum number k quantizes the total angular momentum, and ϵ is the orbit energy.[3] The largest and smallest values of the scaled orbit radii, ρ_1 and ρ_0, are the roots of the quantity in the square brackets in Eq. (1). Hartree introduced an "effective nuclear charge" $Z(\rho)$, using the electrostatic formula,

$$v(\rho) = \int\limits_{\rho}^{\infty} ds \frac{Z(s)}{s^2}, \tag{2}$$

and set his task as

> the determination of $Z(\rho)$ such that for given n and k the values of ϵ calculated from Eq. (1) and Eq. (2) become as nearly as possible those of the terms of the [measured] optical and X-ray spectra... The assignment of quantum numbers to the different terms is taken from Bohr's theory.

In other words, his goal was to work backwards from each atom's observed ionization energies and the quantum numbers assigned to that energy level to find an empirical potential function $v(\rho)$ characteristic of that atom.

In a section of his paper labeled "Sketch of Practical Work", Hartree explained that it was desirable to replace $v(\rho)$ by $Z(\rho)$ for numerical work [despite the extra numerical integration implied by Eq. (2)] because the latter was a slower varying function with a smaller total range of variation. As a result, it was possible to "arrange the computational part of the work in such a way that no apparatus is required beyond a 10-inch slide rule and a table of squares". Hartree made a point to contrast his explicitly numerical calculations with similar work published earlier by Erwin Fues (a former student of Sommerfeld) who had used a piece-wise analytic approximation for $v(\rho)$ to avoid numerical integrations (Fues 1922a,b, 1923). This procedure introduced features into the results which Hartree believed made them "appear doubtful".

Hartree achieved some measure of success with this paper and with several related papers published soon thereafter. He received his Ph.D. in 1926. Dirac also earned his Ph.D. in 1926 and Hartree's biographer informs us that Hartree was "a great admirer of Dirac" (Fischer 2003). That being said, there is no evidence that the quantum mechanical work of his classmate had a direct effect on him. By contrast, the publication of Schrödinger's four papers on the foundations of wave mechanics in the first half of 1926 had a profound effect (Schrödinger 1926a,b,c,d). This becomes clear from the first two parts of the seminal paper which Hartree read to the Cambridge Philosophical Society on November 21, 1927 (Hartree 1923a,b).

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[3] The energies ϵ and $v(\rho)$ in Eq. (1) are scaled by the Rydberg constant to have dimensions of inverse length.

In Part I of this paper, Hartree wrote out the Schrödinger equation for a typical electron in a multi-electron atom and outlined the practical steps needed to solve it. He adopted the Schrödinger perspective that $|\psi|^2$ gives the volume density of charge for an electron in a quantum state described by the wave function ψ. Moreover, he knew from a theorem proved by Sommerfeld student Albrecht Unsöld that a closed shell of electrons produces a spherically symmetric distribution of charge (Unsöld 1927). This suggested to him that a wave mechanical calculation with "the assumption of a central field may give results more satisfactory in detail than could be expected [from] the older form of quantum theory." Accordingly, he used the known spherical harmonic of order l, $S_l(\theta, \phi)$, to make the wave function *ansatz*,

$$\psi(\rho, \theta, \phi) = \frac{P(\rho)}{\rho} S_l(\theta, \phi). \tag{3}$$

This form separates the one-particle Schrödinger partial differential equation into an ordinary differential equation for $P(\rho)$ and a partial differential equation for which $S_\ell(\theta, \phi)$ is a solution. If $v(\rho)$ and ϵ have the same meanings as in Eq. (1), he concluded that the radial function must be a solution of

$$\frac{d^2 P}{d\rho^2} + \left[2v(\rho) - \epsilon - \frac{l(l+1)}{\rho^2} \right] P = 0. \tag{4}$$

Comparing Eq. (4) with Eq. (1) shows that $k = \sqrt{l(l+1)}$ is the dimensionless angular momentum of an electron described by the wave function in Eq. (3).

Characteristically, Hartree first pointed out the conceptual advantages of using the function $P(\rho)$ and then described in detail the method he had devised to solve Eq. (4). He applied the method of "central differences" described in Whittaker and Robinson's textbook *The Calculus of Observations*[4] and proposed to

> integrate the equation outward from $P = 0$ at $\rho = 0$, and inward from $P = 0$ at $\rho = \infty$, and by trial find a value of ϵ for which these solutions meet at some convenient intermediate radius ρ ...

All the work was done by hand, but he reported that

> only one calculation in each interval requires a slide rule (or logs), namely, that of P'' from the differential equation; the rest involves only additions and subtractions, largely of numbers with one or two significant figures, and multiplications by 2, $\frac{1}{2}$, $\frac{1}{6}$, $\frac{1}{12}$, $\frac{1}{24}$, which can be done mentally.

Part II of Hartree's 1928 paper applied the methods of Part I to calculate the effective nuclear charge $Z(\rho) = P^2(\rho)/\rho^2$ and spectral term energy ϵ associated with each electron for a variety of atoms. Hartree's key innovation was to use solutions of the *one-particle* Schrödinger equation (4) to approximate the charge density and potential for a system properly described using a *many-particle* Schrödinger equation. Proceeding entirely intuitively to define the potential $v(\rho)$ in Eq. (4), he decided that

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[4] Whittaker and Robinson (1924) was probably the first textbook devoted entirely to numerical analysis. The authors intended it to be used by "astronomers, meteorologists, physicists, engineers, naval architects, actuaries, biometricians, and statisticians."

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each of the N electrons of an atom should experience the spherical average of the electrostatic potential in Eq. (2) produced by the nucleus and the $N − 1$ other electrons. A crucial feature is that each electron wave function is determined from a potential field which depends, in part, on the wave functions of all the other electrons. To deal with this, Hartree began with a guess for the central potential to be used in the Schrödinger equation for each electron. From the calculated wave functions, he found the charge density associated with each electron and the electrostatic potential produced by all the other electrons. The spherical average of the latter generally did not agree with the initial guess potential. On the other hand, he could use this output potential in place of the initial potential for a repetition of the entire process. After three repetitions or so, Hartree found that his results were *self-consistent* in the sense that the output potential equaled the input potential to within his desired numerical accuracy.[5] Specifically,

> In the numerical work, two places of decimals have usually been kept in $Z(\rho)$ in the initial and final fields, and the successive approximations towards a self-consistent field have been continued until the maximum difference in $Z(\rho)$ between the initial and final fields became less than 0.1.

Hartree presented quantitative results for four atomic systems: He, Rb, Na^+, and $Cl^−$. In each case, the initial guess potential was taken from a statistical treatment of atoms published one year earlier by his classmate Hilleth Thomas (see the next section). For helium, Hartree's calculated energy of 24.85 eV to remove the least well-bound electron from the atom agreed very well with the observed value of 24.6 eV. For rubidium, he judged "the general agreement of X-ray and optical term values calculated by the methods here given with those observed very satisfactory." Moreover, a detailed study of the effective potential felt by the various electrons in the Rb atom allowed him to make contact with Bohr's idea of penetrating versus non-penetrating orbits (Kragh 2012). Finally, he used his calculated charge distributions for Na^+ and $Cl^−$ to evaluate Bragg's formula for the scattering power of x-rays from rocksalt and announced that the comparison with experiment was "very satisfactory indeed".[6]

Very soon, papers by John Slater and Vladimir Fock provided firm mathematical support for Hartree's intuition (Slater 1930; Fock 1930). An orbital variational calculation based on the simplest guess for a many-electron wave function as a product of one-electron orbitals reproduced Hartree's equations (except for his extra approximation to spherically average the potential). A similar variational calculation based on the simplest guess for a many-electron wave function which builds in the Pauli exclusion principle generates what are called the Hartree–Fock equations. The latter are generally acknowledged as foundational to many parts of atomic physics and much of quantum chemistry (Cowan 1981; Pople 1999; Park 1999).

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[5] Hartree cited self-consistent Bohr–Sommerfeld calculations using Eq. (1) by the American physicist Robert Bruce Lindsay as precedent for the view that one should "find a field of force such that the distribution of charge given by the wave functions for the core electrons shall reproduce the field." See pp. 29–31 and p. 45 of Froese (2003) for more on Lindsay.

[6] The complete comparison was published later by James, Waller and Hartree (1928).

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As a professor at the University of Manchester, and later back at Cambridge University, Hartree continued to perform various kinds of self-consistent atomic structure calculations for many years. His 1957 monograph, *The Calculation of Atomic Structures*, summarized 30 years of work by himself, his students, and his collaborators. The titles of two earlier books, *Calculating Instruments and Machines* (1949) and *Numerical Analysis* (1952), reveal two other passions of his mature scientific life. Particularly notable are the many contributions he made to the design, construction, and application of an analog device designed to integrate differential equations mechanically called a *differential analyzer*. He was also one of the first (scientific) users of the ENIAC (Electronic Numerical Integrator and Computer), the first electronic, general-purpose programmable digital computer. The last decade of his life was spent promoting and popularizing the use of computers in all areas of science and engineering.

3 Hilleth Thomas and the statistical atom

London native Llewellyn Hilleth Thomas was told that as a small child he "could say at once what day of the week it would be on any date in the next few years" (Thomas 1975). He recalled reading a popular account of the Bohr atom around the age of 10 years and went up to Trinity College, Cambridge at age 18. As an undergraduate, Thomas attended lectures given by a galaxy of scientific stars including Charles G. Darwin, Thomas J. Bromwich, John E. Littlewood, Geoffrey I. Taylor, Arthur S. Eddington, E. Arthur Milne, and Joseph Larmor (Jackson 2009). In his final term (Easter 1924), he followed his usual practice and took careful notes of Ralph Fowler's lectures on "The Quantum Theory of Spectra".[7]

Llewellyn Hilleth Thomas (ca. 1961)
Courtesy of the AIP Emilio Segrè Visual Archive.

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[7] Thomas' lecture notes for his Cambridge courses (1922–1925) are available at the Archive for Sources for History of Quantum Physics, American Philosophical Society Memoir 68, 1967, Microfilm 5.

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In the fall of 1924, Thomas began graduate studies with Fowler just as the latter left to begin an academic year-long visit to Bohr's institute in Copenhagen. The main thrust of Thomas' thesis work was to be classical calculations relevant to the passage of charged particles through matter.[8] However, in Fowler's absence, Thomas worked on an old quantum theory problem which became the subject of his first published paper, "An extended form of Kronecker's theorem with an application which shows that Burgers' theorem on adiabatic invariants is statistically true for an assembly" (Thomas 1925). We discuss this little-known and awkwardly-titled paper—which won him the coveted Smith Prize for 1925—because its content bears directly on Thomas' later invention of the statistical atom.

As early as 1918, Bohr used ideas developed by his Leiden colleague Paul Ehrenfest to justify the quantization rules which elevated certain classical electron orbits to the status of "stationary states" (Darrigol 1992; Kragh 2012). These stationary orbits needed to maintain their integrity in the presence of modest perturbations like the application of external electric and magnetic fields. This implied that the phase integral in Eq. (1) had to remain the same ("invariant") when very slow ("adiabatic") changes were made to the Hamiltonian that defined the orbits. For his Ph.D. work, Ehrenfest's student Johannes Martinus Burgers proved that this was true for multiply periodic systems (like many-electron atoms) as long as the various frequencies present in the Fourier decomposition of the orbital motions were not related to one another in a simple way (Burgers 1917). Unfortunately, there was good reason to believe that the unwanted relations between frequencies could not be avoided in practice. Early in 1925, this motivated Dirac and Max von Laue to independently publish generalizations of Burgers' theorem that removed this assumption (Dirac 1925; von Laue 1925). Thomas was aware of the work of Dirac and von Laue and took a rather different approach to the problem.[9] His paper asserts that

> The quantum conditions must be such that they are, statistically, adiabatic invariants, but need not necessarily be so for single systems. ...it is clear that the average changes in [the invariant] can be made as small as we like in an assembly of similar systems sufficient in number for the state of the assembly to be represented sufficiently by a continuous density in its phase space.

The remark about "a continuous density in its phase space" speaks to Thomas' aim to prove Burgers' theorem as a statistical result using his own generalization of a theorem proved by the mathematician Leopold Kronecker (Kronecker 1884). One starts with the points $(nx_1, nx_2, \ldots, nx_k)$ in a k-dimensional space where $n = 1, 2, \ldots$ and the x_k are independent irrational numbers. If one retains only the decimal part of each nx_m, Kronecker's theorem states that the points are densely distributed in a k-dimensional unit cube. The connection between this result and the dense filling of phase space needed to compute statistical averages was by then well established by scientists working to apply the methods of probability theory to physics problems

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[8] This was a favorite subject of Fowler at the time. See Sect. 4 of the Bibliography of Milne (1945).

[9] Dirac (1925) thanks Fowler "for suggesting this investigation and for his help during its progress. Thomas (1925) thanks "J.E. Littlewood for his criticism and encouragement" and Fowler "for his help". It is not clear if Fowler actually suggested this topic to Thomas.

(von Plato 1994). A statistical proof of the Burgers' theorem followed by applying this idea to the orbits used to compute the Bohr–Sommerfeld phase integrals.

Fowler arranged for Thomas to spend his second academic year in graduate school (1925–1926) at Bohr's institute in Copenhagen. This turned out to be his *annus mirabilis*. Most famously, he exploited his knowledge of relativity learned at Cambridge from Arthur Eddington and applied Willem De Sittter's relativistic corrections to the moon's motion to the motion of an electron with spin angular momentum (Thomas 1975). This work, done "over a weekend at Christmas time" produced the "Thomas precession factor of 1/2" that reconciled the magnitude of the atomic fine structure in hydrogen with the anomalous Zeeman effect (Thomas 1926a). Apart from this, and despite meeting Kramers, Heisenberg and Wolfgang Pauli, the remainder of Thomas' activity in Copenhagen had nothing to do with the exciting work being done by these physicists (or his classmate Dirac) to invent the new quantum mechanics. As he later put it, "I was always slow in accepting new ideas and understood nothing of this for four or five years" (Jackson 2009).

Our interest here is the work Thomas did at Bohr's institute motivated by his familiarity with his classmate Hartree's Bohr–Sommerfeld calculations. Specifically (Thomas 1962),

> it was a great deal of work to carry this through for any one atom, and the question was whether one couldn't get by [with] a simple averaging assumption, something which would be an approximation which would apply to all atoms.

The paper Thomas published on this subject, "The calculation of atomic fields", is very terse (Thomas 1926b). A three-sentence introduction gives way quickly to "Assumptions and the deduction from them of an equation". The explicitly stated assumptions are (i) neglect relativity; (ii) the electrons possess an effective radial potential energy $V(r)$ which approaches zero as $r \to \infty$ and $-Ze^2/r$ as $r \to 0$ for an atom with nuclear charge Z; (iii) the electrons are distributed uniformly in the phase space at a rate of two for each phase space volume h^3; and (iv) $V(r)$ is determined by the nuclear charge and the distribution of electrons as specified in (iii). The first two assumptions were made by Hartree (1923b). The other two assumptions are more interesting.

Thomas later recalled that the crucial assumption (iii) followed from his "old business of Kronecker's theorem and Burgers' theorem" which told him that "the Bohr orbits filled up phase space uniformly. It was only a short step to saying that if you have two electrons per orbit you just distribute them in the phase space and you have naturally defined them up to a definite energy" (Thomas 1962). In other words, since each differential element of phase space has volume $d^3p\, d^3r$, a spherical approximation to the total volume of phase space occupied by all the electrons in a unit volume of coordinate space at a radial distance r from the nucleus is $(4\pi/3)p_0^3(r)$, where $p_0(r)$ is the momentum of the most energetic electron. Now, the statistical physics of the time had established that each particle of even a classical system occupies a phase space volume of h^3 (Desalvo 1992). Therefore, using the recently deduced fact that each Bohr orbit could accommodate two electrons (spin degeneracy), Thomas concluded that the number density of electrons at each point in his statistical atom was

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$$n(r) = \frac{2}{h^3} \frac{4}{3} \pi p_0^3(r). \tag{5}$$

This formula is true only for a system with uniform density; Thomas *assumed* it could be used *locally* for an atom with a spatially varying number density. Therefore, if E_0 is the total energy of the most energetic electron so $E_0 = p_0^2(r)/2m + V(r)$, the effective potential determines the electron density from

$$n(r) = \frac{8\pi}{3h^3} \{2m[E - V(r)]\}^{3/2}. \tag{6}$$

Thomas' assumption (iv) makes the approximation that the electron density determines the effective potential energy entirely through the Poisson equation of classical electrostatics,

$$\nabla^2 V(r) = -4\pi e^2 n(r). \tag{7}$$

Substituting Eq. (6) into Eq. (7) amounts to a requirement of *self-consistency* entirely analogous to (albeit much simpler than) the later use of this concept by Hartree. Thomas used a dimensionless radial distance $\rho = r/a_B$ and a dimensionless effective potential $\phi(\rho)$ to write the one-dimensional, non-linear differential equation that results from this substitution as

$$\frac{1}{\rho^2} \frac{\mathrm{d}}{\mathrm{d}\rho} \left(\rho^2 \frac{\mathrm{d}\phi}{\mathrm{d}\rho} \right) = \phi^{3/2}. \tag{8}$$

Today, Eq. (8) is called the *Thomas–Fermi equation* because Enrico Fermi independently derived Eqs. (5)–(8) about a year after Thomas' paper (Fermi 1927). For Fermi, this was a natural application of the new statistics he had derived for particles that obey the Pauli exclusion principle.[10] We have seen that Thomas' line of reasoning was quite different. Indeed, Thomas' derivation of Eq. (8) in Copenhagen *preceded* the publication of the 1926 papers by both Fermi and Dirac where they announced what we today call "Fermi–Dirac" statistics.[11]

The majority of Thomas' paper concerns the integration of Eq. (8). He only needed to do this once because, with $\phi(\rho)$ in hand, a simple return to the original variables (including the atomic number) made the results applicable to any atom. Thomas later reported that the solution "took considerable time to do since it involved numerical integration. I didn't know how to do numerical integration. I had to learn" (Thomas 1962). Using logarithmic tables and the textbook by Whittaker and Robinson (1924), he computed the effective nuclear charge from Eq. (2) and compared his results with unpublished Bohr–Sommerfeld results for this quantity for cesium he had obtained from Hartree. The agreement was quite satisfactory. Indeed, Hartree's first paper on

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[10] See the commentary by Franco Rasetti on papers 43-38 of Fermi (1962).

[11] It is very unlikely Thomas would have seen the February 1926 Italian version of Fermi's paper on quantum statistics. The easily accessible German version did not appear until April, one month after Thomas completed his numerical integration of Eq. (8). Dirac's paper appeared in August.

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his self-consistent method (discussed in Sect. 2) remarks that "the [charge] distribution given by Thomas' method is a good smoothed-out approximation to the distribution giving the self-consistent field" (Hartree 1928a).

Dirac (1930) soon generalized the Thomas–Fermi atom to include quantum mechanical exchange and Wilhelm Lenz (1932) showed that the Thomas–Fermi equation follows naturally from a variational principle if the energy is chosen as a specific functional of the density alone. An important advance was made when Carl Friedrich von Weizsäcker (1935) introduced a density gradient $\nabla \rho(\mathbf{r})$ into the Lenz energy functional to provide a better description of density inhomogeneities. The theory has been used extensively over the years in atomic physics, plasma physics, astrophysics, nuclear physics, and condensed matter physics whenever the need to discover broad trends was greater than the need for great accuracy. Indeed, a commentator mused in 1991 that (Spruch 1991)

> it would be interesting to contemplate how profitable it might have been for Thomas and Fermi...to have formed a Thomas–Fermi Model Company. It would certainly have been a growth industry, for there have been literally thousands of published articles based on the model.

By the time he returned to Cambridge in the fall of 1926, Thomas had completed (or nearly completed) the work for seven research papers.[12] He received his Ph.D. in 1927 and took an assistant professor position at Ohio State University in 1929. During 17 years at Ohio State, Thomas published papers on diverse topics ranging from the quantum theory of optical reflection from metallic surfaces to non-linearities in the ro-vibrational spectrum of polyatomic molecules to the introduction of the "sector focusing" method for charged particles in cyclotrons. He spent 3 years during World War II at the Aberdeen Proving Ground where, like Hartree during World War I, he was attached to a Ballistics Research Laboratory (Price 1994). A 1946 move to the new IBM Watson Scientific Computing Laboratory at Columbia University began a new phase of his research career. Again like Hartree, Thomas contributed significantly to both the design of computer hardware and to the development of numerical methods designed to exploit the newly available computing power. Historians of computing credit Thomas with the first variable-step-size algorithm for the efficient numerical integration of differential equations (Gear and Skeel 1990).

At the Watson Lab (Brennan 1971),

> Thomas pioneered in the development of an iterative computer method of approximating wave functions for three-particle problems and in adapting for computer solution problems in hydrodynamics, elasticity theory and electron distributions in atoms... As far back as 1946, he had considered the possibility of using tiny pieces of various kinds of steels to store information magnetically and perform logic—work which anticipated the subsequent development of magnetic core memory.

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[12] One of these (Thomas 1927), reports a *tour-de-force* classical calculation of electron capture by double scattering which has withstood the test of time and subsequent quantum mechanical calculations (Shakeshaft and Spruch 1979).

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An article entitled "The use of large scale computing in physics" was intended to alert physicists to both the hardware and numerical methods then available to solve a variety of problems they might encounter in their work (Sheldon and Thomas 1953). Thomas moved to North Carolina State University in 1968 where he "continued his role as encyclopedic scholar" until his retirement in 1976 (Jackson 2009).

4 Density functional theory

Essential features of Thomas' statistical atom and Hartree's self-consistent atom were combined and generalized in the mid-1960s by an approach to the electronic structure of many-electron systems called *density functional theory* (DFT). In its many variations, DFT is arguably the most popular method used by contemporary physicists, chemists, and material scientists who are interested to calculate (albeit approximately) the electronic, mechanical, and thermal properties of atoms, molecules, and condensed phases (Koch and Holthausen 2000; Louie and Cohen 2006). Several of the most highly cited papers in the entire physics literature pertain to DFT (Redner 2005) and one-half of the 1998 Nobel Prize for Chemistry was awarded for the development of the theory.

Density functional theory was born in 1964 when physics professor Walter Kohn (then at the University of California at San Diego) and post-doctoral fellow Pierre Hohenberg published a paper with the innocuous title "Inhomogeneous electron gas" (Hohenberg and Kohn 1964). The paper's abstract establishes the authors' interest in "the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$." A typical example of the latter is the Coulomb potential produced by one or more positively charged atomic nuclei fixed in space. In their introduction, Hohenberg and Kohn (HK) single out the usefulness of the Thomas–Fermi method for its "simple though crude descriptions of inhomogeneous systems like atoms and impurities in metals".[13] They alert the reader that the Thomas–Fermi method had seen "some important advances... in the last decade" and announce that "the present paper represents a contribution in the same area." In this way, they prepare the reader to engage with a work where "the electronic density $n(\mathbf{r})$ plays a central role."

The first result HK report is a four-line *reductio ad absurdum* proof that the exact ground state energy of a many-electron system is a functional of the ground-state electron density, *i.e.*, $E = E[n(\mathbf{r})]$. This was quite unexpected because, up to that point, it was widely believed that any calculation of the ground state energy required knowledge of either the many-particle wave function or the two-particle density matrix (Löwdin 1960; Pople 1999). HK then cite the long range of the Coulomb interaction as motivation to "separate out the classical Coulomb energy" and write the total energy functional in the form,

$$E[n] = \int \mathrm{d}^3 r \, v(\mathbf{r}) n(\mathbf{r}) + \frac{e^2}{2} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + G[n]. \tag{9}$$

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[13] HK do not refer to the original papers of either Thomas or Fermi. Instead, they direct the reader to a review paper (March 1957).

The first term on the right side of Eq. (9) is the interaction energy of the electrons with the external potential $v(\mathbf{r})$. The second term is the classical Coulomb self-energy of the electrons. The functional $G[n]$ in Eq. (9) includes the exact kinetic energy of the electron system, as well as all the energy associated with electron–electron Coulomb repulsions *not* already counted by the classical electrostatic energy. Specifically, the classical term does not account for quantum mechanical *exchange* effects which tend to keep electrons with the same spin apart and short-range *correlation* effects which tend to keep electrons with opposite spin apart.

A major interest of HK was to study approximations to $G[n]$ for electron systems with nearly constant density or with a slowly varying density. In both cases, they used information that was known at the time about the *homogeneous electron gas*. This is a model system of quantum mechanical electrons with uniform density n and infinite volume. For example, if the sum of the kinetic, exchange, and correlation energy per particle for this gas is

$$g_0(n) = t_0(n) + \epsilon_{\text{exchange}} + \epsilon_{\text{correlation}}(n), \tag{10}$$

one simple approximation to $G[n]$ for an *inhomogeneous* gas is to evaluate Eq. (10) using the local electron density at every point in the system, weight this energy/particle by the local density itself, and integrate over all of space to get[14]

$$G[n] \approx \int \mathrm{d}^3 r \, n(\mathbf{r}) \, g_0(n(\mathbf{r})). \tag{11}$$

In a section designed to make contact with Thomas–Fermi theory, HK make a drastic approximation to Eq. (10). They neglect the exchange and correlation energies altogether and approximate the exact kinetic energy per particle $t_0(n)$ by the kinetic energy per particle of a *non-interacting* electron gas with uniform density n. The latter is the kinetic energy per particle the electrons would have if they had no electric charge. Using this approximation for $g_0(n)$ to evaluate Eq. (11) gives

$$G[n] \approx \frac{3h^2}{10m} \left(\frac{3}{8\pi}\right)^{2/3} \int \mathrm{d}^3 r \, [n(\mathbf{r})]^{5/3}. \tag{12}$$

Substituting Eq. (12) and the potential energy $v(\mathbf{r}) = -Ze^2/r$ into Eq. (9) produces exactly the energy functional used by Lenz (1932) to derive the Thomas–Fermi equation (8) by varying the density function. HK thereby demonstrated that the Thomas–Fermi method is the simplest possible version—and therefore the natural intellectual precursor—of their more general density functional theory. Most of the remainder of the HK paper examines systematic improvements to Eq. (11) from a formal point of view. Among other insights, their analysis provided a way to explain (Hohenberg and Kohn 1964)

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[14] HK actually define g_0 as the energy per unit volume rather than the energy per particle. We use the latter here to simplify comparison with Kohn and Sham (1965) discussed later.

why neither the original Thomas–Fermi method...nor its generalizations by the addition of gradient terms, have correctly yielded wave-mechanical density oscillations, such as the density oscillations in atoms which correspond to shell structure, or the Friedel oscillations in alloys which are of the same general origin.

One year later, Kohn and another post-doctoral fellow, Lu Jeu Sham, published a paper (Kohn and Sham 1965) which they suggested would "offer the hope of new progress" for the "theory of cohesive energies, elastic constants, etc. of real (i.e., inhomogeneous) metals and alloys." In the introduction to this paper, Kohn and Sham (KS) remind the reader that the Thomas–Fermi method uses the properties of a homogeneous electron system to study the properties of inhomogeneous electron systems. They then announce their goal to

> use the formalism of HK to carry this approach further... [to] obtain a set of self-consistent equations which include, in an approximate way, exchange and correlation... [and] which are analogous to the conventional Hartree equations.[15]

The key insight used by KS was to partition the energy functional $E[n]$ in a different way than HK had done in Eq. (9). Specifically, they wrote

$$E[n] = T_N[n] + \int \mathrm{d}^3r\, v(\mathbf{r})n(\mathbf{r}) + \frac{1}{2} \int \mathrm{d}^3r \int \mathrm{d}^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n]. \qquad (13)$$

The first term on the right side of Eq. (13) is the exact kinetic energy of a collection of *non-interacting* electrons with charge density $n(\mathbf{r})$.[16] The second and third terms are the same as those in Eq. (9). The final "exchange-correlation" term $E_{xc}[n]$ is similar to $G[n]$ in Eq. (9) in the sense that it accounts for all the energy associated with the electron–electron Coulomb repulsions *not* already counted by the classical Coulomb self-energy. However, where $G[n]$ had also to account for the total kinetic energy of the real electron system, $E_{xc}[n]$ has only to account for the *difference* in kinetic energy between the real electron system and the non-interacting electron system. In this way, Eq. (13) sweeps the most difficult part of the many-body problem into the exact and universal (but generally unknown) functional $E_{xc}[n]$.

Kohn and Sham proceeded to vary their expression for $E[n]$ with respect to the density. However, their familiarity with the variational approach to Hartree theory[17] informed them that the very same variational principle results if one considers a set of N one-electron orbital functions $\phi_k(\mathbf{r})$, writes the electron number density as $n(\mathbf{r}) = \sum_{k=1}^{N} |\phi_k(\mathbf{r})|^2$, and use the exact quantum mechanical expression for the kinetic energy of N non-interacting electrons assumed to occupy these orbitals:

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[15] KS do not cite either the original paper by Hartree or any general review of his method. Presumably, they assumed that the Hartree equations were "conventional" and well-known to their readers. This is plausible, because their readers were mostly solid-state physicists and the standard solid-state textbook at that time by Seitz (1940) discusses the Hartee equations thoroughly.

[16] This differs from the approximation to the kinetic energy discussed above Eq. (12) which uses the kinetic energy of non-interacting electrons with *uniform* density to evaluate Eq. (11).

[17] Kohn had previously taught a class using the textbook by Seitz (1940), which reproduces the variational derivation of Hartree's equation in its Appendix. See Kohn (1998).

$$T_N = \sum_{k=1}^{N} \int d^3r \, \phi_k^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \phi_k(\mathbf{r}). \tag{14}$$

By varying the orbitals rather than the density (just as Slater and Fock had done in 1930), KS found that the orbitals satisfy *exactly* the self-consistent Hartree equations except that the potential $v(\rho)$ in the one-particle Schrödinger equation (4) contains an extra term besides the external and classical Coulomb potentials. This new term comes from the variational derivative of the exchange-correlation energy and is explicitly a *local* function of position,

$$v_{xc}(n(\mathbf{r})) = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}. \tag{15}$$

This analysis permitted KS to establish an important point of principle. If $E_{xc}[n(\mathbf{r})]$ is known, the exact solution of the many-body problem has the same form as (and is no more difficult to solve numerically than) Hartree's self-consistent equations. Of course, $E_{xc}[n]$ is not known in general (this would imply that the problem of interest was already solved) and KS proposed to use a *local density approximation* (LDA) based on $\epsilon_{xc}(n)$, the exchange-correlation energy per particle of a homogeneous electron gas:[18]

$$v_{xc}(n(\mathbf{r})) \approx \frac{d(n\epsilon_{xc}(n))}{dn}. \tag{16}$$

This suggestion could be used immediately for practical calculations because good approximations for $\epsilon_{xc}[n]$ had recently been summarized by Pines (1963). KS did not report calculations of this kind themselves. Instead, they studied gradient corrections to Eq. (16), considered a Hartree–Fock-like version of their theory, and compared an explicit version of Eq. (16) with a local potential that had been proposed years earlier by Slater (1951) to approximate the non-local exchange potential. Six months later, Sham and one of Kohn's Ph.D. students, Bok Yin Tong, published numerical results for the energies and charge densities of a series of atoms using the local density approximation (Tong and Sham 1966). The results reported for the ionization energies of a sequence of oxygen ions were judged by the authors to be "in good shape" compared to experiment. LDA calculations became a growth industry soon thereafter.

5 Conclusion

This paper has chronicled how two Cambridge classmates in the 1920s, Douglas Hartree and Hilleth Thomas, used largely heuristic arguments to propose complementary approximate theories for the electronic structure of many-electron atoms. Both went on to have successful scientific careers and both made significant contributions

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[18] In the main body of their paper, KS propose Eq. (16) at the same time that they derive their Hartree-like equations. A note added in proof points out that the definition of $v_{xc}(\mathbf{r})$ in Eq. (15) makes the Hartree-like equations formally exact.

to numerical analysis and to computer hardware. 40 years later, Hohenberg, Kohn, and Sham fused and generalized the work of Hartree and Thomas to produce a formally exact theory applicable to any system of electrons subject to a fixed external potential. The circumstances that motivated Kohn and his collaborators to develop density functional theory when they did, the subsequent history that attended the basic theory, the responses to their proposed local density approximation, and the evolving reactions of different segments of the physics and chemistry communities to DFT, are issues to be explored in future publications.

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