Christian Joas

Statement

and

Readings

New Perspectives on the Birth of Quantum Mechanics from the Perspective of Solid-State Physics *or* Why Dirt Matters

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Abstract

When quantum mechanics emerged in 1925–1926, the behavior of solids and molecules apparently was the least of concerns for the physicists involved in its development. Yet, almost immediately after the advent of quantum mechanics, its fathers started pondering its extension to many-particle systems. In 1927–1935, many long-open questions were settled on the basis of quantum mechanics, e.g., the structure and stability of molecules, the nature of ferromagnetism, or the thermal and electrical conductivity of metals. Max Jammer has referred to this phase in the history of quantum physics as the "validation of quantum mechanics." While viewed as crucial cornerstones for the history of the emerging fields of solid-state physics or quantum chemistry, these early "applications" of quantum mechanics are usually portrayed as subsequent and subordinate events when it comes to the history of quantum mechanics itself. Based on collaborative work conducted together with Jeremiah James, I will challenge this view by showing (a) that the techniques for addressing the many-body problem in quantum mechanics had important roots in attempts to extend old quantum theory to many-body systems, which greatly facilitated their appropriation, and (b) that the “applications” of quantum mechanics altered central aspects of how physicists conceived of and used quantum mechanics, by introducing and integrating new concepts (such as exchange interactions, resonance, tunneling, spin) that are now taken to be integral parts of the formalism.

Reading reference:
Hoddeson, L. H., Baym, G. (1980). The development of the quantum mechanical electron theory of metals,1900–28. In: Mott, N. F. (Ed.). *The beginnings of solid state physics*. London: The Royal Society (Cambridge University Press) (p. 8–23).

Proc. R. Soc. Lond. A **371**, 8–23 (1980)
Printed in Great Britain

The development of the quantum mechanical electron theory of metals: 1900–28

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Introduction

The development of the electron theory of metals from Drude's free electron picture to Bloch's quantum mechanical treatment of electrons in crystal lattices reflects in structure the evolution of quantum mechanics itself. As in that development, the steps leading to the quantum theory of metals may be divided into three periods: classical, 1900–26; semi-classical, 1926–8; and modern, late 1928 onwards. The classical period was dominated by the model of Drude and Lorentz in which a metal contained an ideal gas of conduction electrons governed by kinetic theory. Although the failures and contradictions of the model were strikingly apparent by World War I, few useful new concepts were added until Pauli's crucial application in 1926 of Fermi–Dirac statistics to metals opened up the semi-classical period. In the following two years Sommerfeld, and others in his circle, by further application of the new statistics within the framework of the classical Drude–Lorentz theory, were able to resolve most of that theory's outstanding difficulties. But it was not until Bloch's paper in August 1928 that the full machinery of quantum mechanics, developed in 1925–6, was brought to bear on solids, thereby spearheading the creation between 1928 and 1933, by the first generation of theoretical solid-state physicists including Peierls, Wilson, Mott and others, of the modern quantum theory of solids.

Our principal aim in this communication[1] is to survey the issues and events in the transition from the classical to the modern period, a transition that one might call the 'old quantum theory of metals'. To provide the background and setting of the events in these years we begin with a brief review of the electron theory of solids, in the earlier period 1900–26.[2]

The classical period, 1900–26: inadequacies of the Drude-Lorentz theory

While pre-twentieth century science includes many examples of attempts to answer basic questions about the properties and behaviour of metals,[3] the first solid state theory capable of computing observed quantities from microscopic concepts was that of P. Drude (1900).[4] Drude pictured metals as an overall electrically neutral gas of positive and negative mobile particles characterized by their charges e_i, masses m_i, densities n_i, mean free paths l_i, and mean velocities u_i,

which were given according to Boltzmann by $(3k_{\mathrm{B}}T/m_i)^{\frac{1}{2}}$, where T is the absolute temperature and k_{B} is Boltzmann's constant.

The major triumph of Drude's theory was a derivation of the empirical Wiedemann–Franz law for the ratio of the thermal and electrical conductivities of metals. To derive this he computed, by simple kinetic theory, a thermal conductivity

$$K = \sum_i (\tfrac{3}{2}k_{\mathrm{B}}n_i)(\tfrac{1}{3}u_i l_i)$$

and an electrical conductivity

$$\sigma = \sum_i \tfrac{1}{2}n_i^2 e_i^2 l_i/m_i u_i,$$

and thus derived, for the case that all e_i are equal in magnitude to the charge e of the electron, the Wiedemann–Franz ratio

$$K/\sigma = 3(k_{\mathrm{B}}/e)^2 T,$$

a result he showed to be in remarkably good agreement with the experiments of Jaeger & Diesselhorst. (Modern kinetic theory[5] gives a coefficient $\frac{1}{3}\pi^2 = 3.29$ in place of the 3; however, had Drude used a consistent definition of l_i in calculating K and σ he would not have found the $\frac{1}{2}$ in σ and thus would have obtained the much less agreeable coefficient, $\frac{3}{2}$.)

Within the next five years, H. A. Lorentz[6] refined the Drude model by assuming: first, that the mobile negative carriers were a single species of electron, the same in all metals;[7] second, that the electrons were described by a Maxwellian velocity distribution in equilibrium; and third, that the positively charged particles remained fixed in the matter. Except in so far as they caused a finite electron mean free path, the presence of the atoms was neglected. His expression for the Wiedemann–Franz law, $2(k_{\mathrm{B}}/e)^2 T$, derived more rigorously than Drude's, was 'somewhat less satisfactory'; Lorentz nevertheless considered the results 'a fair start ... towards the understanding of the electric and thermal properties of metals'. Furthermore, his results for thermoelectric phenomena and emissivity and absorptivity of low frequency 'heat rays' (black-body radiation) agreed, as a consequence of his use of a thermal distribution of electron velocities, with Kelvin's and Planck's thermodynamic theories.[8] These successes strongly confirmed the free electron picture of metals.

Despite its successes, however, the Drude–Lorentz theory could not determine K or σ separately, since these involved the unknown electron density and mean free path. The most reasonable assumptions, that there was about one conduction electron per atom and that l was of the order of the interatomic spacing, could not be reconciled with the temperature dependence or (often larger) magnitudes of the observed conductivities.[9]

But the most glaring failure of the classical theory was its inability to explain why the electrons, while participating in thermal motion according to the Lorentz theory, did not appear to contribute to the measured specific heats.[10] Classically one would expect a specific heat per unit volume $3k_{\mathrm{B}}n_i + \frac{3}{2}k_{\mathrm{B}}n_{\mathrm{e}}$, where n_i is the

number density of bound oscillating atoms and n_e the number density of free electrons; rather a value approximately $3k_B n_i$ was observed at high temperatures for both metals and insulators. The thermal properties of the electrons were further clouded by the observation that specific heats decreased with decreasing temperature, and the explanation of this decrease by Einstein,[11] entirely in terms of quantized thermal vibrations of the atoms, with no contribution from the electrons. Einstein, searching for further applications of his and Planck's quantum hypothesis, assumed in his calculation a single oscillation frequency ν_0 for the atoms, thus neglecting the effects of the lattice on the vibrational spectrum; he obtained an expression for the specific heat in reasonable agreement with experiment for $T \gtrsim 0.1h\nu_0/k_B$, where h is Planck's constant, but far too small below that.

A more rigorous explanation of the specific heat in terms of vibrations of a lattice of bound atoms in a solid (without consideration of electrons), which brought the theory into agreement with experiment, was given independently by Debye and Born & von Karman.[12] While Born & von Karman did a detailed computation of the vibrational spectrum, assuming nearest neighbour interactions only, Debye realized[13] that to derive the structure of the specific heat he needed, for high temperatures, to know only the number of degrees of freedom, and for low temperatures he could find the low frequency oscillation spectrum directly from macroscopic elasticity theory. Both theories correctly predicted that the low-temperature specific heat should be proportional to T^3, rather than proportional to $T^{-2}\exp(-h\nu_0/k_B T)$ as in Einstein's theory.

One should note that the idea of the periodic lattice was fairly well accepted by 1912 when von Laue, Friedericks and Knipping, working in Munich, first demonstrated its existence experimentally by diffracting X-rays by crystals, and showed that the lattice spacing was of the order of 10^{-8} cm.[14, 15] As Born relates, 'We regarded the existence of lattices as evident not only because we knew the group theory of lattices as given by Schoenflies and Fedorov which explained the geometrical features of crystals, but also because a short time before, Erwin Madelung in Göttingen had derived the first dynamical inference from lattice theory, a relation between the infra-red vibration frequency of a crystal and its elastic properties.'[16] Indeed, the first Born–von Karman paper was published before von Laue's discovery; the fact that the second also contains no reference to von Laue suggests that the experiments were regarded as a confirmation of an accepted idea.

While Einstein, Debye, and Born and von Karman were undermining the Drude–Lorentz theory by explaining the specific heats in terms of the ions alone, Niels Bohr was uncovering other fundamental failures. His 1911 doctoral thesis[8] aimed to develop an electron theory of metals allowing more general assumptions than Lorentz had made. Retaining the free electron model, he replaced Lorentz's 'hard elastic sphere' scattering law with the assumption that the atoms attract or repel electrons with an inverse nth power of distance force. Within this more general framework he was able to improve on Lorentz's calculations of transport phenomena, and confirm the derivation from electron theory of thermoelectric properties and

the law of black-body emission of heat. While many observed properties, such as Hall coefficients of the wrong sign, could not be explained, the most crucial failing was that since, as he showed, free electrons can exhibit neither diamagnetism nor paramagnetism (a result independently derived by van Leeuwen in 1919), the free electron theory could not explain the magnetic properties of metals. Unfortunately, Bohr was unable to publish a translation of his thesis (written in Danish), and thus its impact on the development of the theory of metals was to be negligible.

We may summarize the difficulties of the Drude–Lorentz theory in 1915 by noting the fundamental incompatibility between the Drude–Lorentz and Einstein–Debye–Born–von Karman pictures: the Drude–Lorentz theory, based on the electron motion alone, with only minimal account taken of the presence of the ions (to provide scattering of electrons consistent with the assumption of a mean free path), gave a satisfying account of the transport properties, as reflected in the Wiedemann–Franz Law, and an excellent account of the heat radiation properties, but it could not explain a series of phenomena including the specific heat and magnetic susceptibility of metals. On the other hand, the Einstein–Debye–Born–von Karman theory, which was based on a picture of solids containing only ions with thermal motion of the electrons neglected, gave a good account of the specific heat but could not explain large electron mean free paths in terms of interactions with the ions. The resolution of these inconsistencies awaited the application over a decade later of the Pauli exclusion principle and quantum mechanics itself.

Fermi–Dirac statistics: 1926

The first step towards the creation of the semi-classical theory of metals was the development, independently by Fermi and Dirac in 1926, of a quantum statistics applicable to a gas of particles that obeyed the exclusion principle, the principle proposed by Pauli in early 1925 to explain the closure of atomic shells in atoms.[17] Fermi, then in Florence, was disturbed by the fact that the classical ideal gas specific heat, $\frac{3}{2}k_B$ per particle, did not vanish at very low temperatures, as required by the Nernst theorem. 'It is therefore necessary to assume', Fermi wrote in his paper, submitted in March 1926, 'that the motion of the molecules of an ideal gas are quantized, and that this quantization manifests itself at low temperatures through certain degeneracy phenomena ....'[18] He continues, 'Since this Pauli rule has shown itself to be extraordinarily fruitful in the interpretation of spectroscopic phenomena, we want to examine whether it is not also useful for the problem of the quantization an ideal gas.' Fermi is considering here an ordinary gas of atoms or molecules, rather than an electron gas in a metal.

The explicit model he studied was that of an ideal gas in an external three-dimensional harmonic oscillator potential (of frequency ν), whose individual energy levels would be quantized, according to Einstein, by

$$E = h\nu(s_1 + s_2 + s_3),$$

where s_i is the number of quanta associated with oscillations in the ith direction. The Pauli principle for this case becomes the condition that at most one molecule can be in a state specified by a given s_1, s_2 and s_3. After computing the degeneracy Q_s of the energy levels he proceeds to derive, by maximizing the entropy *à la* Boltzmann, the mean number of particles per energy level,

$$N_s = Q_s[\alpha^{-1} e^{\beta s} + 1]^{-1},$$

where $s = s_1 + s_2 + s_3$. He then goes on to calculate, by a semi-classical approach that we now identify as the Fermi–Thomas method, the equation of state of the gas, which is simply that of a free Fermi–Dirac gas at each point in space, and he notes particularly the presence of a zero point pressure and energy, and that the low temperature specific heat varies linearly with T, thus obeying the Nernst theorem.

Heisenberg learned of the new statistics directly from Fermi in the spring of 1926, shortly before the paper appeared in print.[19] He had stopped off to see Fermi on the way back from a tour through Italy and later recalled Fermi's explanation of the relation between the Bose–Einstein statistics[20, 21] and his new statistics as a 'kind of complement ... something like plus and minus'. Heisenberg developed some of his ideas about the two statistics in June 1926 in his paper on 'The many-body problem and resonance',[22] the first paper to deal with the quantum mechanics of more than one particle. Applying quantum mechanics to systems composed of many identical particles, he found two groups of stationary state solutions, one symmetric and the other antisymmetric, which neither combine with one another nor in any way transform into the other; only the antisymmetrical group – the one observed empirically – obeys the Pauli principle.

Dirac's derivation of the new statistics, in his classic paper, 'On the theory of quantum mechanics',[23] submitted in August 1926, independently considers the connection between the antisymmetry of the many-particle wave function, and the Pauli principle, noting that non-interacting electrons are described by a determinantal wave function. After introducing the quantization condition through boundary conditions on the single particle wave functions, he derives the statistics and equation of state, again through maximation of the entropy. He also points out that had one begun from a completely symmetric wave function, Bose–Einstein statistics would result.

Dirac does not refer to Fermi's prior work, and on 25 October 1926, Fermi wrote to Dirac somewhat crisply:[24] 'In your interesting paper ... you have put forward a theory of the Ideal Gas based on Pauli's exclusion Principle. Now a theory of the ideal gas that is practically identical to yours was published by me at the beginning of 1926 ... Since I suppose that you have not seen my paper, I beg to attract your attention on it.' Pauli recalled in 1956[25] that 'Dirac was in Copenhagen in the autumn of 1926 and I wrote to him there, whether he knows how a spin of the atoms (or electrons) would modify the results. I also mentioned Fermi's paper. He answered me, that he never considered this question and that Fermi's paper was

entirely new to him. Immediately after that I started to work on this question myself (autumn 1926), and I found very quickly all answers.'

As Pauli set to work to apply the new statistics to metals, and thus begin the semi-classical period of the theory, R. H. Fowler began application to the equation of state of matter in white dwarf stars. His paper, published in December 1926[26] (which included an argument that the presence of the zero point energy of matter obeying Fermi–Dirac statistics would resolve the paradox raised by Eddington concerning the limiting zero temperature state of white dwarfs), proved to be the root of modern theories of dense matter in astrophysics.

Let us turn now to Pauli's pivotal contribution.

Pauli's application of the Fermi–Dirac statistics to metals: late 1926

With the work of Fermi and Dirac, there were now two different quantum statistics: Bose–Einstein, for which the mean number of particles in a simple particle state of energy E was of the form

$$n_{\mathrm{B.E.}} = (\alpha^{-1} e^{E/k_B T} - 1)^{-1},$$

and which applied to photons for $\alpha = 1$; and Fermi–Dirac, for which the mean number was given by

$$n_{\mathrm{B.E.}} = (\alpha^{-1} e^{E/k_B T} + 1)^{-1}.$$

Both reduced in the limit of very high temperatures to the classical Maxwell–Boltzmann distribution,

$$n_{\mathrm{B.E.}} = \alpha e^{-E/k_B T}.$$

One of the central questions was which of these statistics applies to matter.[27]

Dirac discussed this question at several points in his 1926 paper, stating that 'the symmetrical eigenfunctions alone or the antisymmetrical eigenfunctions alone give a complete solution of the problem. The theory at present is incapable of deciding which solution is the correct one.' But he pointed out that since the symmetrical solution 'allows any number of electrons to be in the same orbit ... this solution cannot be the correct one for the problem of electrons in an atom'. He later speculated that 'The solution with antisymmetrical eigenfunctions ... is probably the correct one for gas molecules, since it is known to be the correct one for electrons in an atom, and one would expect molecules to resemble electrons more closely than light quanta.'

Pauli discussed the issue of the two alternate quantum statistics with Heisenberg in a detailed, almost daily, technical correspondence.[28] On 19 October 1926, Pauli wrote: 'On the question of degeneracy of gases [i.e. when the probability of occupation of the low energy states is near unity], I am now thinking considerably more mildly about the Fermi–Dirac statistics, and it seems to me now that there are many arguments that speak for it.' He had come to believe that 'there does after all exist a difference between crystal lattices and radiation', and this difference

might be attributable to the difference between Bose–Einstein and Fermi–Dirac statistics; since solids have a zero point energy, $\frac{1}{2}h\nu$, unlike radiation, and since 'such an energy can be supported by the Einstein–Bose statistics only artificially ... this speaks right from the beginning against this theory and for the Fermi–Dirac'.

By December, Pauli was convinced that Fermi–Dirac and not Bose–Einstein statistics applied to the degenerate electron gas. To prove this required deriving a physical consequence of Fermi–Dirac statistics that could be experimentally verified, and he chose to try to explain why there is such weak paramagnetism in metals. Heisenberg had employed[22] the exclusion principle in showing that there is no paramagnetism in the ground state of helium, and Pauli now considered making a similar argument for metals, approximating them as a degenerate electron gas obeying Fermi–Dirac statistics.[29]

Pauli's arguments soon appeared in his famous paper on paramagnetism,[30] submitted to the *Zeitschrift für Physik* on 16 December 1926. Most of the paper is devoted to a close examination of the thermodynamical basis and fluctuation properties of the Fermi statistics; by calculating the partition function in the grand canonical ensemble, Pauli rederives the properties of the Fermi–Dirac as well as Bose–Einstein gases. He goes on, in the last section, to calculate in a now familiar way the paramagnetic susceptibility of a gas of atoms obeying Fermi statistics and having a quantized spin of magnitude j and a magnetic moment

$$\mu = \sqrt{\{j(j+1)\}}\, g\mu_0,$$

where μ_0 is the Bohr magneton and g the Landé factor. His crucial result is that at low temperatures – the appropriate limit, as Pauli observes, for electrons in a metal – the spin susceptibility χ approaches a constant value $\frac{3}{10}n\mu^2/\epsilon_0$ (where n is the particle density and ϵ_0 is the mean zero point energy per particle); in contrast, the Langevin theory, applicable when there is no exclusion of states, would give a Curie law spin susceptibility greater by a factor $\frac{10}{9}(2j+1)\epsilon_0/k_{\mathrm{B}}T$, about 10^2 at room temperature. Not only did the Pauli result give the correct magnitude of the observed magnetic susceptibilities of metals, it also explained its temperature independence, and provided direct confirmation that the electrons in a metal form a degenerate gas. The basic argument for the reduction of the susceptibility was that, even though a magnetic field would want to align all the spins along the field, for this to happen would require more than one electron to occupy each of the low energy states, in violation of the exclusion principle. Only electrons in a thin shell of relative size *ca.* $k_{\mathrm{B}}T/\epsilon_0$ around the Fermi surface are capable of being aligned by the magnetic field, and the susceptibility is reduced by this factor from the Langevin result.

Thus, analogously to the way in which Heisenberg showed that the Pauli principle implies that there is no magnetic moment in the normal state of a helium atom, Pauli demonstrated that Fermi–Dirac statistics – which he regarded as the generalization of his exclusion principle – implies a suppression of the magnetic susceptibility in metals. Pauli recalled 30 years later in a letter[25] that 'I was so glad that

I had eventually an answer to the question "If it is true, that the electron has a spin, why then is there not a strong paramagnetism in metals according to the Curie law?"'

Through carrying out this physical example, which showed the correctness of applying Fermi–Dirac rather than Bose–Einstein statistics to electrons in a metal, Pauli opened up the development of modern solid state physics, a field which Pauli himself was often critical of as messy and applied – 'I don't like this solid state physics ... though I initiated it'[31] – and a field in which the Pauli principle plays an all-important role, including answering the fundamental question of why matter is stable against collapse. As Ehrenfest wrote to his 'Dear Awesome Pauli' on 24 January 1926, 'I have for a long time had the feeling that it is your prohibiting condition that above all prevents the atoms and through them the crystal from falling together. I suggested this some months ago in a popular lecture on "What makes solid bodies solid?" In the attempt rationally, at long last, to consider an ideal gas, to quantize the impenetrability of the molecules, I noticed for the first time the peculiar running about of this idea ....'[32]

Sommerfeld's semi-classical electron theory of metals: 1927–8

The next steps, to extend and apply the technique Pauli had demonstrated for paramagnetism to other phenomena and to enlist additional workers in the field, were carried out in 1927–8 by A. Sommerfeld, Pauli's former mentor in Munich. Sommerfeld passed through Hamburg in the spring of 1927 and saw the proofs of Pauli's paper; as Pauli recalls: 'The next day he said to me, that he was very much impressed by it and that one should make further application to other parts of metal theory like the Wiedemann–Franz law, thermoelectric effects, etc. As I was not eager to do that he made then this further application himself.'[25] Deeply interested in the Drude–Lorentz theory for more than two decades,[33] Sommerfeld realized that some of the worst failures of the theory could be overcome by using the new statistics, and when he returned to Munich he set seriously to work.

He soon began obtaining interesting results; Peierls recollects that 'Sommerfeld ... was going around with a little book by Baedeker[34] which was then the reference book about the properties of metals and definitions of the various coefficients and seeing how far things could be made to agree with the theory and how far they couldn't.'[35] The new theory was for a time the main subject in his research seminar – whose participants included Peierls, Bethe, Eckart, Houston and Pauling – as well as in a lecture course in the summer of 1927.[36]

Sommerfeld's pedagogical skill with graduate research students contributed substantially in this phase of the development of solid state theory. As Eckart recalls, 'he got all of us involved in ... the big project for the year ... to rework the Lorentz theory of electrons using the Fermi statistics ... He was, of course, a very great teacher. His principal technique was to appear dumber than any of us, and

this of course spurred everyone on "to explain to the Herr Geheimrat". He certainly was not as dumb as he pretended to be, but he had no inhibitions about appearing dumb. Sometimes it seemed that he went out of his way to misunderstand and thus force you to become clearer.'[38] On occasion he would, as Peierls recalls, 'grab a student' to talk with him about a problem that happened to interest him; other times he would take his whole department on skiing trips, thus bringing them closer together.[35]

Sommerfeld announced his results on the free electron gas in September 1927, at the Volta Congress at Como, attended by Bohr, Born, Lorentz and other leading physicists of the period.[38] Soon afterwards, he published an outline of his theory in *Die Naturwissenschaften*,[37] with a full treatment appearing in two parts in the *Zeitschrift für Physik*.[40] Theory and experiment had for the first time come together for a wide variety of phenomena in metals. Starting from Pauli's observation that the electrons in metals are essentially completely degenerate, and thus described by the low temperature limits of the thermodynamic formulae, he evaluates Fermi's linear specific heat expression; since the result for the electron specific heat is *ca.* $k_B T/\epsilon_f$, about $\frac{1}{100}$ of the classical value, the specific heat dilemma of the Drude–Lorentz theory was resolved. Calculating the electrical and thermal conductivities by using the Boltzmann kinetic equation with a relaxation time, he derives the Wiedemann–Franz ratio $\frac{1}{3}\pi^2(k_B/e)^2 T$, which agreed with experiment much better than Lorentz's, or even Drude's, original expression (cf. ref. 5). Other phenomena studied included thermionic emission and thermoelectric, galvanomagnetic and thermomagnetic effects. As he concluded in the *Naturwissenschaften* paper: 'The overall impression that this work provides is without any doubt that through the new statistics the contradictions of the older theory are lifted and the observational facts are, in part quantitatively, in part qualitatively reproduced.' [41,42]

Response to Sommerfeld's paper were, by and large, extremely favourable. Bohr wrote to Hume–Rothery in February 1928, answering an inquiry regarding his 1911 thesis, 'Nowadays the old theories based on the classical mechanics can hardly make claim of actual physical interest. Indeed they are left quite behind by the recent fundamental work of Sommerfeld which has just been published in *Zeitschrift für Physik*. Although not yet complete, Sommerfeld's work surely means a decisive step as regards the adequate quantum theoretical treatment of the metallic problem.' [43]

By reworking the classical electron theory of metals so as to resolve many earlier failures and give better agreement with experiments, and by casting the theory into an easily understood form, Sommerfeld brought the new theory within reach of the larger scientific community. Not only did he involve theorists of his immediate circle at Munich, and through Heisenberg and Pauli at Leipzig and Zurich, he involved theorists and experimentalists abroad. For example, L. Nordheim became interested in the theory of metals through reading Sommerfeld's papers during his year with R. H. Fowler in Cambridge.[44] In another example, in 1931, W. Brattain,

a Bell Labs experimentalist, attended Sommerfeld's course on the electron theory of metals at the Michigan summer symposium in theoretical physics[45] to better understand thermionic emission, and after the summer communicated the new theory to his co-researchers in a series of lectures.[46]

But Sommerfeld's theory was not without failings. Its predictions did not always agree with experiment. It could not, for example, account for variations of the Hall coefficient (describing the transverse voltage generated by a current flow in a transverse magnetic field) with temperature or magnetic field, or explain why it sometimes even had the wrong sign. Nor could it account for the temperature dependence of the electrical resistance, since it had no explanation of the electron mean free path.[47] While Sommerfeld estimated the mean free path in Ag at room temperature to be about 100 atomic separations, he did not inquire how the electrons managed to avoid the ions so successfully. More generally, he did not seem to have asked why the ions did not influence the electrons between collisions, or why the effects due to motion of the ions could be neglected. As Bethe recalls, 'he didn't even care terribly much why the electrons were free, which I thought was a very important thing to know ...'.[48] The neglect of the ions disturbed a number of other physicists including Heisenberg[49] and Frenkel;[50] Schottky wrote to Sommerfeld that 'to assume a field free condition inside a metal appears to me to be too specialized for the problem ...'.[51]

To solve the mystery of why Sommerfeld's free electron theory worked so well would require developing a fully quantum mechanical treatment of electrons in metals. Bethe reflects, 'I believed the whole theory only when the Bloch paper appeared.'[48] Sommerfeld had used just enough quantum mechanics, via the Pauli principle, to enumerate the states and their energies correctly, but he did not avail himself of the full theoretical machinery already developed by Heisenberg, Schrödinger, Dirac and others, such as wave functions and transition probabilities. Indeed Sommerfeld's theory can be construed, as F. Bopp remarks, as a 'successful revival of Paul Drude's theory of conductivity'.[52] For while Sommerfeld had one foot in the new modern quantum school, many of whose leading practitioners he had himself trained at Munich, his other foot was still caught in the classical theory in which he had invested some three decades of his professional career. Rather than as the beginnings of a *new* theory, he saw the Pauli paper as raising the question 'whether the well known difficulties in the *old* theory of metallic conduction could be lifted by the new statistics'.[53] (Italics added.) The transition to a quantum mechanical theory of metals was carried out by Heisenberg's first student, F. Bloch, whose important contribution we now examine.

Bloch's quantum mechanics of electrons in crystals: 1928

Several months after Bloch came to Leipzig as a student in the fall of 1927, Heisenberg suggested to him two possible research problems: to study either the theory of metals, or the origins of ferromagnetism, within the framework of quan-

tum mechanics.[54, 55] Bloch chose the metal problem, and so Heisenberg worked on the ferromagnetism question himself.[56]

When Bloch started to think about metals, he felt, as he recalled, 'that the main problem was to explain how the electrons could sneak by all the ions in a metal so as to avoid a mean free path of the order of atomic distances. Such a distance was much too short to explain the observed resistances, which even demanded that the mean free path become longer and longer with decreasing temperature.'[55] Bearing in mind Heitler & London's recent explanation of the covalent bond in terms of electrons hopping between atoms,[57] he began to work out the wave function of an electron in a one-dimensional periodic potential. 'By straight Fourier analysis I found to my delight that the wave differed from the plane wave of free electrons only by a periodic modulation. This was so simple that I didn't think it could be much of a discovery, but when I showed it to Heisenberg he said right away: "That's it!"'[55]

Bloch had discovered the one-dimensional version of the important theorem bearing his name, that the wave function of an electron energy eigenstate in a perfect periodic lattice has the form (now known as a 'Bloch state')

$$\psi(\boldsymbol{r}) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}u(\boldsymbol{r}),$$

where $\boldsymbol{r}$ is the electron coordinate, $\boldsymbol{k}$ its 'crystal wave vector' and $u(\boldsymbol{r})$ is a periodic function with the periods of the lattice.[58] This theorem, by implying that electrons would move freely through a perfect lattice, as in free space, provided at once the conceptual basis for Sommerfeld's semi-classical model. Furthermore, it implied that the electrical conductivity of a perfect lattice of identical atoms would be infinite, and therefore that finite conductivity would be caused only by lattice imperfections or ionic motion.

In August 1928, Bloch submitted the work of his thesis for publication in the *Zeitschrift für Physik*.[59] The paper lays out the foundations, and many basic principles and techniques of the quantum theory of electrons in lattices. He begins by deriving the 'Bloch theorem' and the expression for the electrical current carried by an electron in a Bloch state; he then goes on to derive, in the 'tight binding' approximation, the wave functions and energies of the 'ground state band'. To calculate the specific heat, he introduces essentially the motion of an effective mass at the Fermi surface, and finds, by the Fermi–Dirac formulae, that the specific heat is proportional at low temperature to T and to the effective mass.

Turning then to the dynamics of electrons, he shows first how a (Gaussian) wave packet is accelerated by a uniform electric field, and then considers the interaction of electrons with elastic waves of the lattice. To do this he assumes the ionic motion to be described by a (continuous) elastic displacement vector $\boldsymbol{u}(\boldsymbol{r}, t)$, which is a sum of quantized harmonic normal modes (the same modes entering the Debye–Born–von Karman specific heat calculation), and assumes that the displacement of the lattice changes the regular periodic potential $V(\boldsymbol{r})$ felt by the electrons to

$V(\boldsymbol{r}-\boldsymbol{u}(\boldsymbol{r})) = V(\boldsymbol{r})-\boldsymbol{u}(\boldsymbol{r})\cdot\nabla V(\boldsymbol{r})+\ldots$. The extra term, $-\boldsymbol{u}\cdot\nabla V$, causes scattering of the electrons, whose rate Bloch calculates by lowest order perturbation theory.

Having at this point the rates of emission and absorption of lattice vibrational quanta by electrons, he shows that the electrons and lattice vibrations are in equilibrium if and only if the electron Fermi distribution is one of equilibrium, at rest with respect to the lattice, and having the same temperature as that describing the lattice vibrations. Thus any lingering doubts as to whether the electrons partook in the thermal motion of a solid could be laid to rest.

Finally, he calculates the electric conductivity by solving the Boltzmann kinetic equation, with the full electron–lattice vibration collision term, and with a simple drifting Fermi sea approximation for the electron distribution function. Unlike in previous theories, the resistivity emerges with a well defined and experimentally verifiable temperature dependence, linear in T for temperatures large compared with the 'Debye temperature' of the lattice, and, as Bloch showed in a later paper[60] (correcting an error in solving the Boltzmann equation in the first paper), proportional to T^5 at low temperatures. Bloch's paper was followed by a cluster of rapid developments in the 'modern' theory of solids between 1928 and 1933, in which one after another of the basic phenomena were explained. As Peierls reviewed the state of the theory of metals in his 1932 article:[61] '... one gains the impression that its problem, to explain the typical conditions of metals from molecular properties, and to derive the quantitative laws that exist, is, with exceptions ... solved'.[62]

Summary and conclusion

The transition from Drude's classical to Bloch's quantum mechanical electron theory of metals passed, as we have seen, from a classical, through a semi-classical and then into a modern period. In the classical period, the basic model of a metal as formulated by Drude and Lorentz – an ideal gas of free electrons obeying kinetic theory – enabled computation of certain thermal, electrical and magnetic quantities and relations including the experimentally established Wiedemann–Franz ratio. However, basic problems remained unsolved, for example, explanation of the lack of an observable electron contribution to the specific heat. With the Einstein, Debye and Born & von Karman explanations of the specific heat solely in terms of the ions, the classical theory entered a crisis, underlined by the experimental discovery of the lattice. The difficulties were in part removed by Sommerfeld's semi-classical theory, based on Fermi's and Dirac's application of the exclusion principle to the quantum mechanical ideal gas and Pauli's introduction of Fermi–Dirac statistics into the theory of solids. But this new theory still suffered from the inability to explain why the free electron assumption worked, and it remained essentially classical, with quantization and the Pauli exclusion principle tacked on. Only after Bloch's application of the newly developed wave mechanics to the problem of electrons in a lattice was the theory put on a firm basis.

This development replayed the stages that the theory of the atom passed through:

a classical period in severe crisis shortly after the turn of the century, a semi-classical period – the old quantum theory – during which non-classical assumptions, such as the Bohr–Sommerfeld quantization condition, were included *ad hoc* in the classical framework, and the revolutionary modern period, heralded by Heisenberg's first paper on quantum mechanics.[63] One may indeed characterize the development of the electron theory of metals as a 'secondary scientific revolution'.

Since it was clear by 1926 that quantum mechanics was *the* approach to physical phenomena, and since the basic concepts needed for a modern theory of solids were already available by late 1926, one may ask why the development of the quantum theory of solids passed through a semi-classical stage at all? Part of the answer lies in the character of Sommerfeld himself. For the younger physicists of the period, the Drude–Lorentz theory was not a pressing issue,[64] and thus for them Pauli's paramagnetism paper had little immediate significance. But Sommerfeld, on the other hand, with his longstanding commitment to the classical theory of metals, was well aware of and deeply interested in solving the problems that were marring the Drude–Lorentz picture. By immersing himself in the semi-classical electron theory and eloquently presenting it to his colleagues and students,[65] he attracted to its research frontier a nucleus of highly talented young theoretical physicists, and thus acted as the link between the old theory and the new. Sommerfeld, curiously, played much the same role in the semi-classical periods of the developments of both quantum mechanics and the quantum theory of solids. In both, Sommerfeld's research seminar students – including Pauli and Heisenberg in the development of quantum mechanics, and Peierls, Bethe, Eckart and Houston in the development of the quantum theory of solids – had, as members of the next generation, no binding commitment to Sommerfeld's conservative framework, and could therefore freely and imaginatively break ground towards a new theory.[66]

The generous assistance in researching archival material, by Joan Warnow and Spencer Weart of the Center for History of Physics of the American Institute of Physics, and Fru S. Hellmann of the Niels Bohr Institute, is most gratefully acknowledged.

References and notes

(1) The present paper is based on a more complete history of the development of the quantum theory of metals, to be published in the literature on the history of science.

(2) Useful reviews of this period are given by A. H. Wilson, *Theory of metals* (Cambridge, 1936), pp. 1–21; and R. E. Peierls, 'Quantum theory of solids,' in *Theoretical physics in the twentieth century: a memorial volume to Wolfgang Pauli* (ed. M. Fierz & V. F. Weisskopf) (New York: Interscience, 1960), pp. 140–160.

(3) An interesting account of very early solid state physics is contained in C. S. Smith's 'The prehistory of solid-state physics,' *Physics Today* (December 1964), p. 18.

(4) Drude, P. 1900 Zur Electronentheorie der Metalle. *Annln Phys.* **1**, 566; **3**, 369.

(5) In such a calculation of the thermal conductivity, as done originally by Sommerfeld (ref. 40), the electron specific heat, $\frac{3}{2}k_{\mathrm{B}}n$ in Drude's calculation, is decreased by a factor $\frac{1}{2}\pi^2(T/T_{\mathrm{f}})$, while the diffusion constant, $\frac{1}{3}ul$, is, for a given scattering time, l/u enhanced by a compensating factor T_{f}/T, where $k_{\mathrm{B}}T_{\mathrm{f}}$ is the electron Fermi energy. See, for example, N. Ashcroft & N. D. Mermin, *Solid State Physics* (New York: Holt, Rinehart & Winston, 1976) for a fuller discussion.

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(9) Bohr, N. (ref. 8), pp. 336–345, reviews attempts to fit the Lorentz–Drude expressions to experiment.

(10) Lorentz pointed out this outstanding difficulty in a footnote added to his *Theory of electrons* (see note 2, p. 67) in 1915.

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(15) For a detailed discussion of the status of the lattice *circa* 1911 see Forman, P. 1970 The discovery of the diffraction of X-rays by crystals; a critique of the myths. *Archs Hist. exact Sci.* **6**, 38. See also P. P. Ewald, *Fifty years of X-ray diffraction* (Utrecht, 1962), especially 'the Beginnings,' pp. 6–80, and interview with P. Debye, A. Einstein, P. P. Ewald and W. Friedrich in *A.Q.P.*

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(19) Interview with Heisenberg by T. S. Kuhn in *A.Q.P.*, pp. 12–13.

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(21) Einstein, A. 1924 Quantentheorie des Einatomigen Idealen Gases. *Sber. preuss. Akad. Wiss*, p. 261; 1925, pp. 3, 18.

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(24) *A.Q.P.*, reel 59.

(25) W. Pauli to F. Rasetti, October 1956, *A.Q.P.*, reel 66.

(26) Fowler, R. H. 1926 On dense matter. *Mon. Not. R. astr. Soc.* **87**, 114.

(27) Page 138 of H. B. G. Casimir, 'Pauli and the theory of the solid state', in *Theoretical physics in the twentieth century: a memorial volume to Wolfgang Pauli* (ed. M. Fierz & V. F. Weisskopf) (New York: Interscience, 1960), pp. 137–139.

(28) Formerly in the Pauli Letter Collection, Zollikon, Switzerland. The author (L.H.) is grateful to Mrs Pauli for making selected letters in this collection available to her. They are now published by A. Hermann and K. von Maijenn, as *Wolfgang Pauli, Scientific Correspondence*, 1919–29 (New York: Springer-Verlag, 1979); hereafter cited as *W.P.*

(29) Pauli to Weintzel, 5 December 1926, *W.P.*
(30) Pauli, W. 1927 Über Gasentartung und Paramagnetismus. *Z. Phys.* **41**, 91.
(31) Quoted by Casimir, ref. 27. In his recollection it runs 'Der Pauli liebt die Metallphysik nicht', and then regretfully, 'Ich hab' zwar den Anfang gemacht.'
(32) P. Ehrenfest to Pauli, 24 January 1927 from Leiden, *W.P.*
(33) In 1899–1903 Sommerfeld corresponded in detail about the electron theory and particularly heat conduction with both Lorentz and Drude, and subsequently in 1904–5, wrote a series of papers on electron theory which impressed Lorentz. He also regularly taught courses in the classical theory of metals at Munich. Nine letters between Lorentz and Sommerfeld on *A.Q.P.*, reel 32; four letters between Lorentz and Sommerfeld on *A.Q.P.*, reel 30; notes by Sommerfeld on *A.Q.P.*, reel 23; and T. S. Kuhn *et al.*, *Sources for history of quantum physics: an inventory and report* (Philadelphia: American Philosophical Society, Philadelphia, 1967) (hereafter cited as *S.H.Q.P.*), pp. 140, 231–238.
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(37) Interview with C. Eckart by J. Heilbron, *A.Q.P.*, p. 10.
(38) *S.H.Q.P.*, p. 144.
(39) Sommerfeld, A. 1927 Zur Elektronentheorie der Metalle. *Naturwissenschaften* **15**, 825.
(40) Sommerfeld, A. 1928 Zur Elektronentheorie der Metalle auf Grund der Fermischen Statistik. *Z. Phys.* **47** (1), 43.
(41) Page 831 of ref. (37).
(42) While it was now certain that electrons in a metal obeyed Fermi–Dirac statistics, the question of the statistics obeyed by a gas of atoms or ions remained open. Sommerfeld commented that '[these statistics] would hold for a possible "proton gas." It appears doubtful that the extension suggested by Fermi of his statistics to the ordinary electrically neutral gas is legitimate...'[40]; but he did point out that ^{4}He gas would become degenerate at about 5 K if it obeys Fermi statistics.[37] The full experimental and theoretical resolutions of this question did not take place until at least the establishment of the connection between spin and statistics over a decade later.
(43) Bohr to Hume-Rothery, 28 Feb. 1928, *A.Q.P.* Bohr Scientific Correspondence, reel 12.
(44) Interview with Nordheim, *A.Q.P.*, pp. 17–19.
(45) S. Goudsmit, 'The Michigan Symposium in theoretical physics', *Michigan Alumnus Quarterly Review*, 20 May 1961, pp. 181–182.
(46) Memo, J. A. Becker to N. H. Williams, University of Michigan, 15 May 1931, and memo, Becker to Bell superiors 15 October 1931 in Brattain papers; interviews with W. Brattain by A. Holden and C. Weiner, A.I.P. Center for History of Physics and letters from Brattain to author (L.H.), January 1979.
(47) For a more complete survey of the failures of the free electron theory see Ashcroft & Mermin, ref. 5, ch. 3.
(48) Interview with Bethe by T. S. Kuhn, *A.Q.P.*, p. 21.
(49) Interview with Bloch, *A.Q.P.*, p. 21.
(50) J. Frenkel to Sommerfeld, 13 March 1928, *A.Q.P.*, reel 14.
(51) W. Schottky to Sommerfeld, 11 May 1928, *A.Q.P.*, reel 34.
(52) Page 91 in Sommerfeld, A. & Bopp, F. 1951 Fifty years of quantum theory. *Science, N.Y.* **113**, 85.
(53) Ref. 40, p. 1.
(54) Interview with Bloch, *A.Q.P.*, pp. 20–22.
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(57) Heitler, W. & London, F. 1927 Wechselwirkung neutraler Atome und homöopolare Bindung nach der Quantenmechanik. *Z. Phys.* **44**, 455.
(58) This form of the wave function was derived independently by E. Witmer and L. Rosenfeld (1928 Über die Beugung von de Broglieschen Wellen an Kristallgittern. *Z. Phys.* **48**, 530) in a description of the photo-effect, and submitted for publication five months before Bloch's paper (ref. 59). They realized that electrons in such states carried momentum, but they did not seem to have appreciated the significance of the result for the problem of conduction.

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(60) Bloch, F. 1930 Zum elektrischen Widerstandsgesetz bei tiefen Temperaturen. *Z. Phys.* **59**, 208.
(61) Peierls, R. 1932 Elektronen theorie der Metalle. *Ergebn. exakt. Naturw.* **11**, 264–322. Peierls's article was only one of an impressively large number of review articles in the subject that appeared between 1932 and 1934, including the influential Bethe–Sommerfeld *Handbuch* article, 'Elektronentheorie der Metalle', *Handb. Phys.* **24** (2), 333–622 (1933), which helped make the new quantum theory of solids accessible to broad numbers of students. Other review articles on metals in this period were Bloch, F., 'Elektronentheorie der Metalle', *Handbuch der Radiologie*, VI/1, 2te Aufl., Leipzig, pp. 226–275 (1933); Borelius, G., 'Physikalische Eigenschaften der Metalle', *Handbuch der Metallphysik*, i, Berlin, pp. 181–520 (1934); Nordheim, L. W., 'Kinetische Theorie des metallischen Zustendes' in Müller-Pouillet's *Lehrbuch der Physik*, **1**, Braunschweig, pp. 243–876 (1934); and Slater, J. C., 'Electronic structure of metals', *Rev. mod. Phys.* **6**, 208–280 (1934).
(62) The major exception listed was the lack of a theory of superconductivity. It was in general not understood in 1932 how to apply the quantum theory to other than 'ideal' solids.
(63) For a penetrating discussion of this structure in relation to the general problem of the development of scientific theory see T. S. Kuhn, *The structure of scientific revolutions* (University of Chicago, 1962).
(64) A. H. Wilson, private communication, May 1979.
(65) Sommerfeld sailed around the world in 1928, giving many lectures on his work. During part of this period he was a visiting professor at Caltech and lectured in Japan and India. *S.H.Q.P.* p. 145.
(66) When Pauli moved on to Zurich and Heisenberg to Leipzig, in 1927, they took over and to a degree continued Sommerfeld's role by involving research students, including Bloch, Peierls, Slater and Landau, in the fundamental problems of solid state physics. Interviews with P. Debye, W. Heisenberg and J. Slater, by T. S. Kuhn; Houston to Sommerfeld, 30 May 1928 and 6 July 1928 in *A.Q.P.*, reel 31; and Heisenberg to Pauli in a letter no. 0017-057r, *ca.* 1928, in *W.P.*