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Memories of electrons in crystals

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As a student in Zurich, it was my good fortune to be present at the colloquium in which Schrödinger told the first time about his wave mechanics. When both he and Debye accepted positions in Germany I decided upon the latter's advice to continue my studies under Heisenberg in Leipzig, where I arrived in the autumn of 1927.

Already in Zurich my interests had turned from experimental to theoretical physics, and particularly towards quantum mechanics, and before coming to Leipzig I had started some calculations on the radiation-damping of wave-packets. As the first thing, Heisenberg encouraged me to complete this work, later published in the *Physikalische Zeitschrift*, whereupon he considered me ready to start on a topic for my Ph.D. thesis.

Although his famous preceding work had not dealt with problems of the solid state, Heisenberg felt by then – it was the beginning of 1928 – that quantum mechanics could be fruitfully applied to this field of research. Referring to his earlier paper on the *ortho*- and *para*-states of the helium atom, he casually remarked to me that ferromagnetism had to be explained by a changed sign of the exchange energy between electrons so as to energetically favour parallel orientation of their spins. I realized that Heisenberg saw already the crux of the matter and I felt that there would be nothing essentially new left for me to contribute. Indeed, he shortly afterwards wrote the paper that laid the groundwork for the modern theory of ferromagnetism. It was not until two years later that I somewhat embellished his treatment by the introduction of spin waves which, subsequently, led me to the recognition of domain walls.

There was more of a challenge in another suggestion of his: to look into the theory of metals. During my earlier studies I had read the classical book of H. A. Lorentz on the theory of electrons and it was obvious that his work, based on Boltzmann statistics, had to be modified. Pauli had already shown that the application of Fermi statistics led to the temperature-independent paramagnetism of conduction electrons, but the most important applications were made by Sommerfeld. He had solved an old puzzle by demonstrating the great reduction from the classical value in the specific heat of a degenerate Fermi gas and, further, had developed the new consequences for the ratio of the electric and thermal conductivity of metals. Except for the replacement of classical statistics and the inclusion of the spin, however, Pauli and Sommerfeld both accepted the old ideas of Drude and Lorentz, who treated the conduction electrons as an ideal gas of free particles. The high conductivity and reflectivity of metals of course strongly supported the assumption of very mobile electrons but I had never understood how anything like free motion could be even approximately true. After all, a metal wire with all its densely packed ions is far from being a hollow tube and as I started to think about it, I felt that the first thing to be done in my thesis was to face this striking paradox.

From the beginning I was convinced that the answer, if at all, could be found only in the wave nature of the electron, particularly since Heitler & London as well as Hund had shown before that the valency electrons in a molecule were not confined to stay on a single atom. The fact that the periodicity of a crystal would be essential was somehow suggested to me by remembering a demonstration in elementary physics where many equal and equally coupled pendula were hanging at constant spacing from a rod and the motion of one of them was seen to 'migrate' along the rod from pendulum to pendulum. Returning to my rented room one evening in early January, it was with such vague ideas in mind that I began to use pencil and paper and to treat the easiest case of a single electron in a one-dimensional periodic potential. By straight Fourier analysis I found to my delight that the solutions of the Schrödinger equation differed from the de Broglie wave of a free particle only by a modulation with the period of the potential. The generalization to three dimensions was obvious and while it certainly made me happy, the whole thing was so simple that I did not think it amounted to much of a discovery; indeed, I saw later that Wittmer and Rosenfeld had come before to the same conclusion and eventually I was even told by real scholars that something called 'Floquet's theorem' had been known for a long time. But my findings were news to Heisenberg, too, when I told him about them the next day and in his usual optimism he thought that the problem was now essentially in the bag. Actually, it took me a further half a year before my thesis was finished and submitted for publication in the *Zeitschrift für Physik*. The following remarks about my thoughts during that time might be of some historical interest.

In the first place, I considered my original proof for the modulated wavefunctions to be not sufficiently elegant and since the application of group theory to quantum mechanics had just become fashionable, I presented it in that form rather than by the use of the more primitive Fourier method.

Next and more important, I did not think of conduction bands in the sense in which they are now commonly understood, although they clearly appeared in my result for a periodic potential with deep minima. This must have been the cause of my misconception of the essential difference between insulators and conductors, later pointed out by A. H. Wilson. In retrospect it seems rather obvious that closed shells have their analogue in filled bands. Instead, I thought that the difference was merely quantitative in so far as the properties of an insulator would be the more pronounced the stronger the binding of the electrons. In that connection I want to mention the reasons for treating the conduction electrons as independent particles. Besides being the simplest assumption, it had led to good results in Sommerfeld's calculation of the specific heat and therefore appeared to be not unreasonable. Furthermore, their Coulomb interaction could be expected by conservation of momentum to have only a minor effect upon the resistance and was taken into account at least to the extent to which it led in a self-consistent way to neutralization of the positive ions. These soothing arguments did not succeed altogether in suppressing my uneasy feeling that the model of independent electrons might represent a rather poor approximation and would turn out in some respects to be entirely inadequate, but it nevertheless seemed advisable for me to carry it as far as I could.

The greatest effort in my thesis was spent on calculating the resistivity. Since a perfectly periodic lattice had been understood to present no impediment to the current, it was clear that a finite resistance could arise only from irregularities and that its temperature-dependence would have to be explained by the thermal motion of the ions. For the treatment of sound waves I borrowed from Debye's theory of the specific heat of crystals, and for their effect upon the electrons I followed as closely as possible the example of Lorentz in his discussion of the Boltzmann equation for the velocity distribution. There was an initial difficulty in trying to translate the acceleration by a weak electric field into the language of quantum-mechanical perturbation theory since the corresponding potential increases with increasing size of the crystal. Somewhat clumsily, I therefore went from plain modulated waves to Gaussian wave packets to prove that the rate of change of the wavenumber followed the same law as that of the momentum in classical mechanics. Peierls afterwards pointed out to me that, in fact, this was true irrespective of the shape of the wave-packet.

The essential difference from the classical Boltzmann equation, however, dealt with taking the exclusion principle into account, according to which the transition of an electron depends not only upon the probability of finding it in the initial state but also of finding the final state unoccupied. As a test for the correct formulation I verified that the stationary solution of the modified equation yielded in the absence of an external field the expression for the Fermi distribution and it gave me a good deal of pleasure to realize that the test actually amounted to a very simple derivation of that expression. It was not so simple, on the other hand, to solve the integral equation for the change in the stationary distribution caused by the electric field, to obtain the resulting current and, hence, the resistivity. While the linear temperature dependence and a reasonably good order of magnitude came out quite easily for temperatures well above the Debye temperature, I could not find the general solution and erroneously concluded upon a cubic dependence in the opposite case of low temperatures. The error was corrected in a later paper of mine where I deduced the proportionality to the fifth power of the temperature and then Grüneisen showed that this result and the linear dependence previously derived could be combined in a single formula which was found over a wide temperature range to agree well with the observed data.

The memories that I have presented so far are connected with my first and most important contribution to solid state theory. Rather than to extend them into my later work in this field, particularly that on ferromagnetism, I shall add an epilogue concerning my unsuccessful encounter with superconductivity. It started right after I had my Ph.D. and returned to Zurich as Pauli's assistant for the academic year 1928–9. Pauli thought that superconductivity was the only remaining matter of some interest in the theory of metals and that I should get on with it so as to be finally done with all these 'dirt-effects'. Actually, I had already started to think about the problem and had realized that the explanation of persistent currents required a consideration of the previously neglected interaction between electrons. The idea, independently expressed by Landau, was that it should thus be possible at low temperatures to obtain a minimum of the free energy in a state of the metal with finite current. My own confidence in the idea was supported by the analogy with ferromagnetism whereby I saw a parallelism between permanent magnetization below the Curie point and persistent current below the critical temperature. I therefore started industriously to consider various types of interaction, regardless of their possible origin, and to look whether the Schrödinger equation would allow stationary states of the electrons with non-vanishing current and a minimum of the energy. Once in a while I thought that I had indeed found such states but it never took Pauli long to point to some error in the calculations. While he did not object to my approach he became rather annoyed at my continued failure to come out with the desired answer to such a simple question. It finally turned out that there was a quite general reason for my lack of success. Assuming that a given state could be varied by letting the momentum of each electron increase by the same infinitesimal amount, I found that the corresponding differential change of the energy was proportional to the current with the consequence that an extremum of the former always led to a vanishing value of the latter. Now that one knows about the formation of Cooper pairs and the long-range order, so clearly manifested in flux quantization, it is easy to see that the assumption was unjustified. It took a far deeper insight into the nature of a superconductor than was available at that time, however, to understand why it is here essential not to treat the momentum in a system of macroscopic dimensions as a continuously variable quantity. Indeed, I was so discouraged by my negative result that I saw no further way to progress and for a considerable time there was for me only the dubious satisfaction to see that others, without noticing it, kept on falling into the same trap. This brought me to the facetious statement that all theories of superconductivity can be disproved, later quoted in the more radical form of 'Bloch's theorem': 'Superconductivity is impossible'!

After the fog, which so long enveloped the phenomenon, had begun to lift many years later, I could not resist reminding Pauli that the problem was not quite as easy to solve as he thought when he gave it to me. Since that time he had become more mellow – so much more, in fact, that he agreed.